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ARTICLE

Structure and Thermal Properties of Layered Ti-clad Diamond/Cu Composites Prepared by SPS and HP

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Abstract: Layered Ti-clad diamond/Cu composites used in electronic packaging were prepared by spark plasma sintering (SPS) and hot pressing (HP) separately. The structure was determined by Scanning Electron Microscopy (SEM) and the thermal properties, including the thermal conductivity (TC) and the coefficient of thermal expansion (CTE) were analyzed. The theoretical TC of the layered composites 446.66 W·(m·K)$^{-1}$ was calculated by the modified Hasselman and Johnson (HJ) model considering the influence of the TiC interface and the CTE was determined by dilatometer. The results show that the sample of SPS has fewer defects than that of HP and the interfacial bonding affects the TC of the composites significantly. A schematic graph of the interface influences is proposed and the TC decreases with the increase of carbide layer thickness and the appearance of pores. In this regard, the composites with a thin carbide layer and no pores should be processed to achieve a high TC.

Key words: Ti-clad diamond/Cu composites; hot pressing; spark plasma sintering; thermal properties

In recent years, diamond/Cu composites have received much attention because of their high thermal conductivity and moderate thermal expansion coefficient (4~6)×10^{-6} K^{-1} [1-8]. However, a major obstacle for promoting the TC of the diamond/Cu composites is the poor wettability of the copper and diamond at the interface [9-11]. Several approaches have been adopted to solve this problem, including adding different active elements (Zr, B, Co) into the matrix and coating strong carbide-forming elements (Ti, Zr, Cr, W) on the surfaces of the diamond particles [12-16]. Researches show that these elements play an effective role in improving the bonding strength and the thermal properties [17].

In this paper, a new kind of layered Ti-clad diamond/Cu composites was fabricated by SPS and HP[18-20] separately. To modify the interfacial bonding, strong carbide-forming element Ti was coated on the surfaces of the diamond particles. Then Cu is deposited on the Ti film as a transition layer. The unique three-layer structure of Cu/Ti-clad diamond and Cu/Cu could improve the weldability and machinability of the composites.

1 Experiment

Cu powder (99.99% purity) with the mean size of 40 μm was used as the matrix and MBD10-type synthetic diamond with an average diameter of 120 μm was used as the reinforcement. To improve the wettability between diamond and Cu, vacuum vapor deposition was used to coat Ti on the surfaces of diamond particles and the thickness of Ti coating can range from several nanometers to ten microns. Due to the vacuum vapor deposition and diffusion which were carried out in the reaction temperature range of the diamond and Ti, TiC may form[21,22].

The Ti-clad diamond particles were mixed homogeneously with the pure Cu powder by mechanical mixing. And then the mixture was compressed at room temperature to obtain the disk-shape sample with Φ30 mm. The volume fraction of diamond in the mixture was about 55%. To improve the weldability and machinability, the disk-shape sample was compressed again with a layer of Cu powder on both upper and lower surfaces. Then the layered composites were

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compressed by SPS and HP.

In SPS method, the disk-shape specimen was fabricated by sintering at 930 °C under 30 MPa for 10 min. In HP method, the mixture of diamond and Cu was prepared by hot-pressing sintering at 930 °C, 30 MPa in Ar atmosphere for 1 h. During the sintering, the die was covered with a layer of graphite felt to prevent powders from sticking to the inner wall. After sintering, the graphite felt was removed. To investigate the influence of the cold compression on the layered composites, sintered samples were compressed into different thickness under 100 MPa and then machined to a particular size via laser cutting. Finally, the disk-shape samples were prepared: *Φ*12.7 mm in diameter and 1.3 mm in thickness. Samples after compression were ground and polished to obtain a mirror-like surface.

The characteristics of the diamond particles were investigated by SEM (Zeiss EVO18). According to the ASTM standard, the cold compression was conducted on the SPS sample by Gleeble-3500 and the stress-strain curve was obtained at room temperature. The CTE was determined by a dilatometer (Netzsch DIL 402C) with a heating rate of 5 °C/min from room temperature to 175 °C.

2 Results and Discussion

2.1 Microstructure of layered diamond/Cu composites

The morphologies of the diamond particles are shown in Fig.1 and Fig.2 shows the fracture surfaces of the layered diamond/Cu composites prepared by SPS and HP.

The diamond particles are distributed homogeneously in the copper matrix in Fig.2a and 2c. Compared with Fig.2b and 2d, defects such as pores can be observed in both samples. In general, the increasing fluidity of the metal fills more pores in the composite at a higher pressure. Therefore, the composite with a high relative density and few pores should be prepared at a high pressure.

2.2 Thermal and mechanical properties of layered diamond/Cu composites

The morphologies of the three-layer composites and the schematic graph are shown in Fig.3.

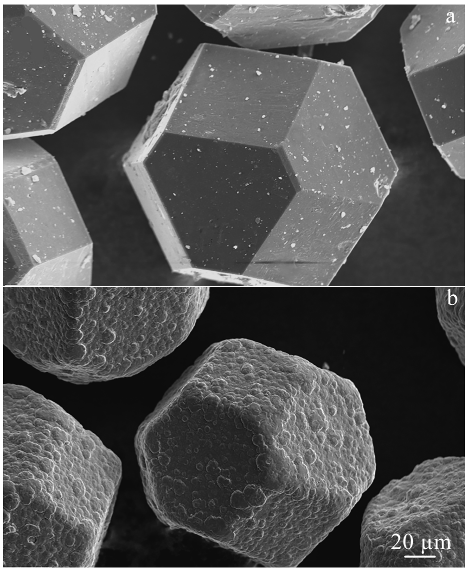

Fig.1 SEM images of the MBD10-type diamond particles (a) and the Ti clad diamond particles (b)

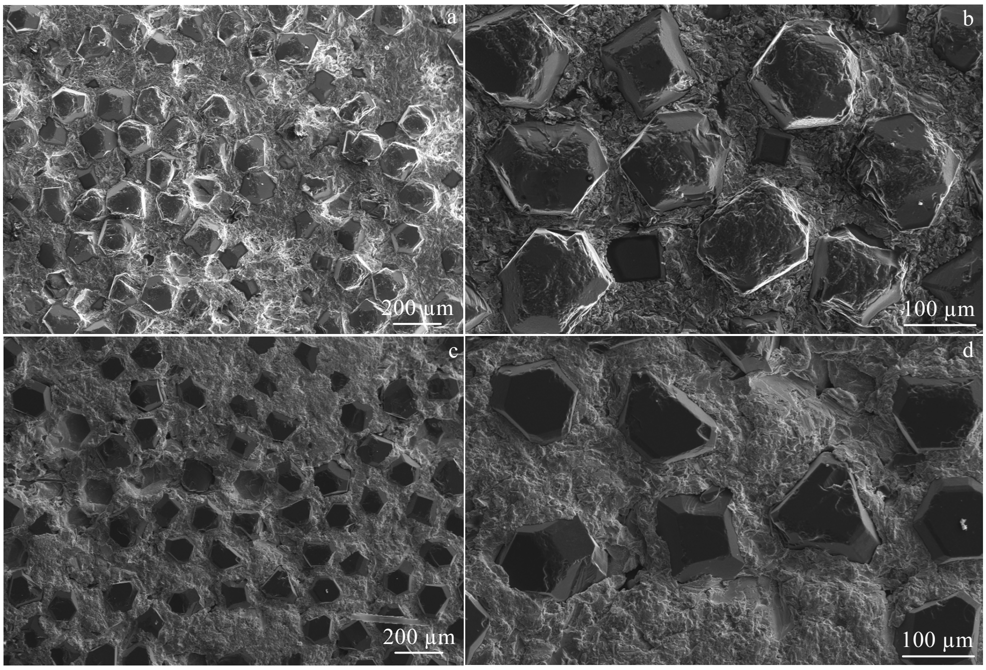

Fig.2 Fracture surface SEM images of diamond/Cu composites fabricated by SPS (a, b) and HPC (c, d)

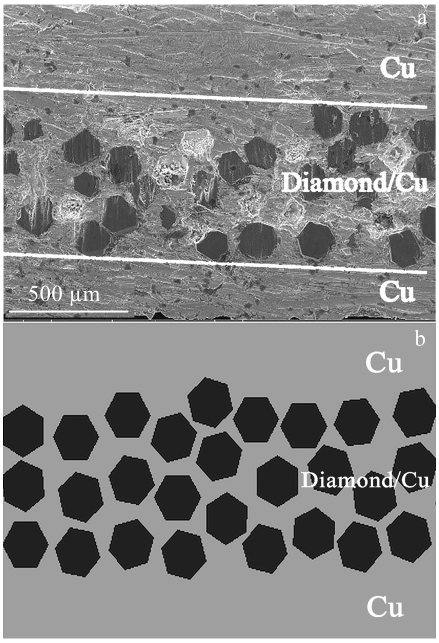

Fig.3 SEM images of the layered composites: (a) three-layer structure and (b) schematic graph

From Fig.3a, the composites can be classified into three layers: the upper copper layer, the middle mixture of diamond/Cu layer and the bottom copper layer. Fig.3b represents the schematic illustration of the layered composite. It can be seen that no obvious boundary appears between the mixture layer and copper layers. The lines shown in Fig.3a are used to approximately distinguish the different layers of composites. In general, two mechanisms act in the densification process of the layered composite. First, diffusion process is active at the pressure of the composite, and micro-cracks in the matrix could be welded. Second, the plastic deformation of the matrix leads to the expelling of the lager pores. Higher sintering temperatures result in a faster diffusion and fluidity of the metals; therefore a higher relative density can be achieved.

Fig.4 shows the CTE evolution of the composites at different testing temperatures. It can be seen that the CTE increases with the increasing temperature both in SPS and HP samples with an approximately linear relationship. For a particular temperature, layered composite prepared by SPS route presents a higher CTE. The above phenomenon may be explained by the appearance of micro-pores and micro-cracks which offset the expansion of the material to a certain degree. Fig.5 shows the stress vs. strain curve of the sample with 1.3 mm in thickness. The compressive stress and strain are plotted by their absolute values. The maximum compression stress reaches 500 MPa and is enough for the mechanical support.

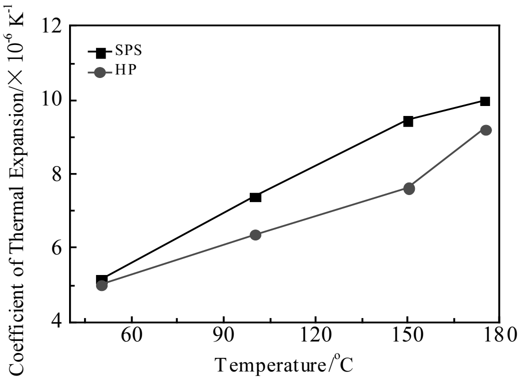

Fig.4 Evolution of CTE with temperature of layered diamond/Cu composite prepared by SPS and HP

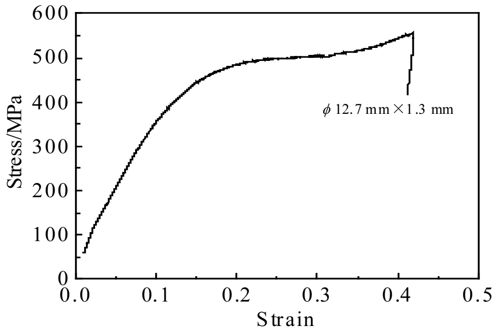

Fig.5 Compressive stress and strain curve of the sample by SPS

2.3 Heat resistance model of layered diamond/Cu composites

The TC of the SPS sample is predicted by the modified heat resistance model in this section. The schematic diagram of the interfacial thermal resistance of layered composite is shown in Fig.6, which explains the heat transfer process in the layered diamond/Cu composite. The thermal resistance of the Cu matrix and the diamond particles is relatively low compared with that of the interface. In this regard, the interface is one of key factors for the TC of the composite. In order to analyze the thermal conduction characterization of the composites, it is important to establish a heat diffusion model based on the Hasselman and Johnson (H-J) model. For the calculation of the whole composite, the rule of mixture (ROM) should be considered.

In the H-J model, Kapitza resistance effect and particle size are considered as follows [23-25]:

$$K_{\mathrm{mix}}=\frac{K_{\mathrm{m}}[2K_{\mathrm{m}}+K_{\mathrm{p}}^{\mathrm{eff}}+2(K_{\mathrm{p}}^{\mathrm{eff}}-K_{\mathrm{m}})V_{\mathrm{p}}]}{2K_{\mathrm{m}}+K_{\mathrm{p}}^{\mathrm{eff}}-(K_{\mathrm{p}}^{\mathrm{eff}}-K_{\mathrm{m}})V_{\mathrm{p}}} \quad (1)$$

where K is the TC, V is the volume fraction of reinforcements and the subscripts mix, m and p refer to mixture, matrix and reinforcement particles in the mixture layer, respectively. The effective thermal conductivity of the reinforcement particles $K_{\mathrm{p}}^{\mathrm{eff}}$ is defined as:

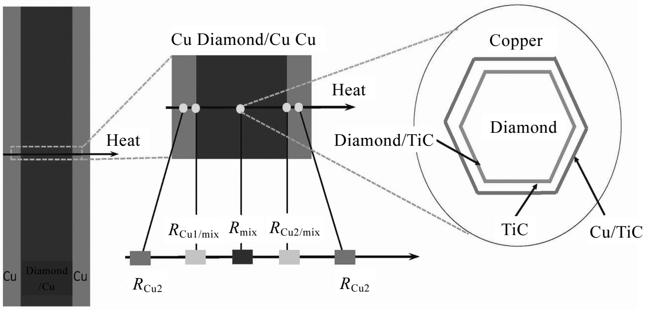

Fig.6 Schematic diagram of the interfacial thermal resistance of the layered diamond/copper composite

$$K_{p}^{eff} = \frac{K_{p}}{1 + 2R_{K}K_{p}/d} \tag{2}$$

where d is the average diameter of the reinforcements and R_K is the interfacial resistance (Kapitza resistance). However, the H-J model is under the assumption that the interfaces between the matrix and the reinforcements are perfect and sharp. In this paper, the thermal resistance of the interphase TiC should be considered. As shown in Fig.6, in order to simplify the calculation, the TiC is assumed to be the only layer between the diamond and the Cu. The interfacial thermal resistance is expressed by [26]:

$$R_{mix} = R_{k} = R_{Cu/TiC} + R_{TiC} + R_{TiC/diamond} \tag{3}$$

where R_{mix}, $R_{Cu/TiC}$, R_{TiC} and $R_{TiC/diamond}$ are the thermal resistance of mixture layer, Cu/TiC, TiC and TiC/diamond interface, respectively. In Eq.(3), R_{TiC} can be calculated as follows:

$$R_{TiC} = \Delta TiC / K_{TiC} \tag{4}$$

where ΔTiC is the thickness of the TiC interface.

The $R_{Cu/TiC}$ and $R_{TiC/diamond}$ are described by diffuse mismatch model (DMM) which assumes that all the phonons are diffusely scattered at the interface. The relationship between thermal resistance R, absolute temperature T and phonon velocities v can be expressed by [27]:

$$R_{i/3-i} = [1.02 \times 10^{10} \frac{(\Sigma_{j} v_{i,j}^{-2})(\Sigma_{j} v_{3-i,j}^{-2})}{\Sigma_{i,j} v_{i,j}^{-2}}]^{-1} T^{-3} \tag{5}$$

where the subscripts i and 3-i refer to the two adjacent phases on each side of the interface. The subscript j represents the mode of the phonon velocity (longitudinal or transverse). Through Eq.(1)~(5), the K_{mix} can be obtained and the parameters used in above equations are listed in Table 1[27-29]. The TC of the whole composite is considered by the ROM as follows:

$$K_{c} = K_{Cu1}V_{Cu1} + K_{Cu2}V_{Cu2} + K_{mix}V_{mix} \tag{6}$$

where K_c is the TC of the composite, K_{Cu1} and K_{Cu2} are the TCs of the Cu layers on the upper and bottom of the composites. No obvious boundary can be seen at the interface of the Cu layer and the mixture layer, so the $R_{Cu/mix}$ can be neglected. Considering the pores in the composite, the final TC can be expressed as:

$$K_{c\text{-}p} = K_{c}V_{c} + K_{air}V_{pores} \tag{7}$$

In this model, the pores are considered by adding an effective thermal conductivity to the composite. All the thermal resistance and TCs calculated in this paper are listed in Table 2.

Fig.7 describes the heat transfer process in the layered diamond/Cu composites. From the schematic illustration we can see that the loss of the heat occurs mainly at the interfaces. Although the TC of the TiC layer is remarkably lower than that of Cu and diamond, the formation of carbide strengthens the interfacial bonding and thus reduces the thermal resistance by decreasing pores[30]. In Fig.7, it can be revealed that the TC is significantly influenced by the thickness of the TiC layer. When the interface is fully coated by the TiC layer with no pore (shown in Fig.7a), the loss of heat is relatively low. However, when the Ti content is not enough and TiC can hardly fill the interface (shown in Fig.7b), pores can be found due to the poor wettability. Correspondingly, the TC of the composite declines significantly. Fig.7c represents the condition that an air layer forms without Ti. As the TC of air is only 0.026 W·(m·K)$^{-1}$, the TC of the composite is poor. Fig.7d shows a partial formation of carbide at the interface between the diamond and the Cu. According to the H-J model and the ROM, the seamless combination between the diamond and the Cu is optimal but difficult to achieve. High temperature and high pressure method (HPHT) may be conducive to eliminate pores and reduce the TiC layer. It is favorable for preparing the high thermal conductive diamond/Cu composite and the homogeneous carbide layer is not needed for obtaining a high TC.

Table 1 Parameters of the composite in the calculation[27-29]

Materials	Thermal conductivity/ W·(m·K)$^{-1}$	Phonon velocity longitudinal/m·s^{-1}	Phonon velocity transverse/m·s^{-1}
Cu	398	4800	2300
Diamond	1750	17500	12800
TiC	19	10100	7300

Table 2 Interfacial resistance and theoretical TC

$R_{TiC/Diamond}$/ (m^2·K)·W^{-1}	R_{TiC}/ (m^2·K)·W^{-1}	$R_{Cu/TiC}$/ (m^2·K)·W^{-1}	R_K/ (m^2·K)·W^{-1}	K^{eff}_{p}/ W·(m·K)$^{-1}$	K_{mix}/ W·(m·K)$^{-1}$	K_c/ W·(m·K)$^{-1}$	$K_{c\text{-}p}$/ W·(m·K)$^{-1}$
5.15×10^{-10}	6.05×10^{-8}	1.43×10^{-10}	6.12×10^{-8}	628.36	514.41	460.47	446.66

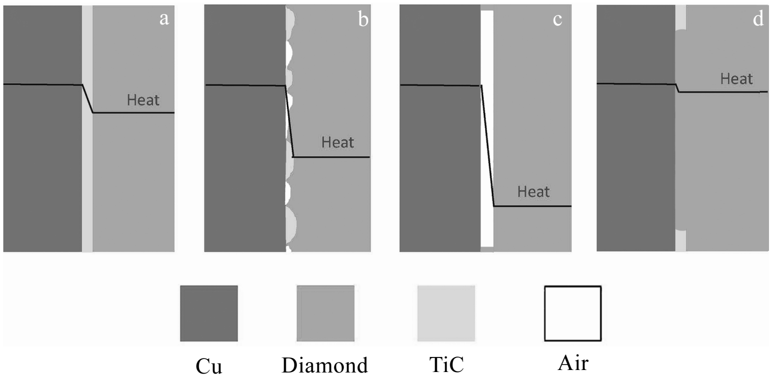

Fig.7 Schematic graph of the interfaces with different TiC contents: (a) full TiC layer, (b) partial TiC layer, (c) air layer, and (d) carbide at the interface

In Table 2, it can be found that R_{TiC} is noticeably larger than $R_{\mathrm{TiC/diamond}}$ and $R_{\mathrm{TiC/Cu}}$. The interfacial thermal resistance is expressed by Eq.(3) and the thickness of TiC directly affects R_{TiC} according to Eq.(4). Thus the thickness of TiC is one of the main factors affecting the interfacial thermal resistance. The excess thin layer may not coat on the surface of the diamond particles perfectly, but the increasing thickness of the carbide formation layer leads to the sharp reduction in TC because of the low TC of TiC (19 W·(m·K)$^{-1}$). In this way, the proper processing should be used to control the thickness of the TiC layer to obtain a maximum TC.

3 Conclusions

1) SPS and HP methods are used to prepare the diamond/Cu composites. The unique three layer structure could be obtained but the defects such as pores can be seen in both samples.

2) The CTE of the composites increases with the increasing temperature. It is below 8×10^{-6} K^{-1} at 100 °C and meets the requirement of electronic packaging. The theoretical thermal conductivity of the layered composite is about 446.66 W·(m·K)$^{-1}$ considering the TiC layer and pores.

3) The interface between the diamond and the Cu is one of the most important factors affecting the thermal conductivity of the composite. The TC decreases with the increasing thickness of carbide layer and air pores. In this regard, eliminating air pores and reducing TiC layer can help to obtain the diamond/Cu composites with a high TC.

References

1 Zhang Chun, Wang Richu, Peng Chaoqun *et al. Rare Metal Materials and Engineering*[J], 2016, 45(10): 2692 (in Chinese)
2 Cui W, Xu H, Chen J H *et al. International Journal of Minerals, Metallurgy and Materials*[J], 2016, 23(6): 716
3 Deng Jiali, Zhang Hongdi, Fan Tongxiang *et al. Materials Review*[J], 2016, 30(2): 19 (in Chinese)
4 Mizuuchi K, Inoue K, Agari Y *et al. Materials Science Forum*[J], 2010, 638-642: 2115
5 Zhang X M, Guo H, Yin F Z *et al. Rare Metals*[J], 2011, 30(1): 94
6 He J S, Wang X T, Zhang Y *et al. Composites: Part B*[J], 2015, 68: 22
7 Zhao C, Wang J. *Materials Science & Engineering A*[J], 2013, 588: 221
8 Liu X Z, Wei Q P, Zhai H *et al. Transactions of Nonferrous Metals Society of China*[J], 2013, 23(3): 667
9 Yoshida K, Morigami H. *Microelectronics Reliability*[J], 2004, 44(2): 303
10 Chen G Q, Yang W S, Dong R H *et al. Materials & Design*[J], 2014, 63: 109
11 Hu H B, Kong J. *Journal of Materials Engineering and Performance*[J], 2014, 23(2): 651
12 Mizuuchi K, Inoue K, Agari Y *et al. Journal of Materials Science and Chemical Engineering*[J], 2016, 4(9): 1
13 Zhang Ximin, Guo Hong, Yin Fazhang *et al. Chinese Journal of Rare Metals*[J], 2013, 37(2): 335 (in Chinese)
14 Li Jianwei, Zhang Hailong, Zhang Shaoming *et al. Journal of Functional Materials*[J], 2016, 47(1): 1034 (in Chinese)
15 Edtmaier C, Weber L, Tavangar R. *Advanced Materials Research*[J], 2009, 59: 125
16 Ren Xuetang, Dong Yinghu, Zhang Ruiqing *et al. Transactions of Materials and Heat Treatment*[J], 2017, 38(1): 1 (in Chinese)
17 Ciupinski L, Siemiaszko D, Rosinsk M *et al. Advanced Materials Research*[J], 2009, 59: 120
18 Zhang C, Wang R C, Cai Z Y *et al. Journal of Materials Science*[J], 2015, 26(1): 185
19 Guyot P, Antou G, Pradeilles N *et al. Scripta Materialia*[J], 2014, 84-85: 35
20 Chen H, Jia C C, Li S J. *Journal of Materials Science*[J], 2012, 47(7): 3367

21 Raza K, Khalid F. *Journal of Alloys and Compounds*[J], 2014, 615: 111

22 Zhu C X, Zhu X L, Zhao H X *et al*. *Journal of Wuhan University of Technology*[J], 2015, 30(2): 315

23 Ma Shuangyan, Wang Enze, Lu Weiyuan *et al*. *Material & Heat Treatment*[J], 2007, 36(20): 24 (in Chinese)

24 Zhang Yujun, Tong Zhensong, Shen Zhuoshen. *Electronic Components and Materials*[J], 2009, 28(10): 37 (in Chinese)

25 Fang Ming, Wang Aiqin , Xie Jingpei *et al*. *Material & Heat Treatment*[J], 2011, 40(4): 84 (in Chinese)

26 Chu K, Jia C C, Guo H *et al*. *Mater & Design*[J], 2013, 45: 36

27 Chung C, Lee M, Tsai M *et al*. *Applied Thermal Engineering*[J], 2014, 69(1-2): 208

28 Klein B, Frage N, Zaretsky E *et al*. *AIP Conference Proceedings*[C]. New York: American Institute of Physics, 2002

29 Swartz E T, Pohl R O. *Reviews of Modern Physics*[J], 1989, 61(3): 605

30 Xia Yang, Song Yueqing, Lin Chenguang *et al*. *Transactions of Nonferrous Metals Society of China*[J], 2009, 19(5): 1161 (in Chinese)

放电等离子烧结法和热压法制备的镀钛金刚石/铜多层复合材料的结构和热性能

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摘　要：采用放电等离子烧结技术（SPS）和热压法（HP）分别制备用于电子封装领域的多层镀钛金刚石/铜复合材料获得。借助扫描电子显微镜（SEM）分析了复合材料的显微组织，同时对热导率（TC）和热膨胀系数（CTE）等热性能参数进行了分析。层状复合材料的热导率理论值参考改良的哈塞尔曼-约翰逊（HJ）模型，同时考虑 TiC 界面的影响计算，结果为 446.66 $W\cdot(m\cdot K)^{-1}$，而热膨胀系数则通过热膨胀仪测试确定。结果显示，经放电等离子烧结的试样与经热压制备的试样相比，缺陷相对较少，界面的结合对于复合材料热导率的影响十分明显。提出了一个界面影响的模型示意图，热导率随着碳化物层厚度的增加和气孔的出现而减小。由此可见，实现高热导率的条件是复合材料中的碳化物层较薄、同时没有气孔的出现。

关键词：镀钛金刚石/铜复合材料；热压法；放电等离子烧结法；热性能

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