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Properties and microstructure of Cu/diamond composites prepared by spark plasma sintering method

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Abstract: Cu/diamond composites have been considered as the next generation of thermal management material for electronic packages and heat sinks applications. Cu/diamond composites with different volume fractions of diamond were successfully prepared by spark plasma sintering (SPS) method. The sintering temperatures and volume fractions (50%, 60% and 70%) of diamond were changed to investigate their effects on the relative density, homogeneity of the microstructure and thermal conductivity of the composites. The results show that the relative density, homogeneity of the microstructure and thermal conductivity of the composites increase with decreasing the diamond volume fraction; the relative density and thermal conductivity of the composites increase with increasing the sintering temperature. The thermal conductivity of the composites is a result of the combined effect of the volume fraction of diamond, the homogeneity and relative density of the composites.

Key words: Cu/diamond composites; spark plasma sintering; relative density; thermal conductivity

1 Introduction

With the rapid development of microelectronic technology and semiconductor technology, thermal stress and warping arise from the difference of coefficient of thermal expansion (CTE) due to the fact that high heat generated becomes significant in advanced electronic devices, which will lead to instability of the device. Therefore, thermal aspects become more important for the reliability of the electronic components [1−3]. However, pursuing the miniaturization and large function of the device at the same time will inevitably lead to the increase of heat, and consequently the temperature of the device will increase faster. Therefore, new type of electronic packaging materials with high thermal conductivity and low CTE for maximizing heat dissipation and minimizing thermal stress and warping will become a key and hot research direction in the future [1,4−6]. To ensure ideal or desired performance and adequate life of these electronic devices, it is necessary to decrease the junction temperature between two components. Currently, the material with the highest thermal conductivity is good quality diamond which has a high thermal conductivity of 2000 W/(m·K) and a low CTE of 2.3×10^{-6} K^{-1} [7,8]. Compared with traditional electronic packaging materials, Cu/diamond composite is a new kind of composite which has high thermal conductivity and low CTE, and changing the composition of the composite can adjust its CTE to match with the matrix. However, copper is known to be not naturally wet with diamond, and de-bonding can occur upon thermal cycling [9], so the major problem in the development of Cu/diamond composites is to obtain a well bonded interface between the copper and the diamond [3,9].

Spark plasma sintering (SPS) is a relatively new sintering method [10,11], and has recently attracted considerable attention in the development of high performance diamond-based metal matrix composites (MMCs) [7,12]. The advantages of SPS, such as lower temperatures and shorter holding time, have made it possible to sinter nano-metric powders to near theoretical density values with little grain growth [13−16]. Therefore, the use of SPS to fabricate Cu/diamond composites is a very promising method to attain expected thermal properties.

In this work, SPS was used to prepare the Cu/diamond composites, and the influences of sintering temperature and volume fraction of diamond on the

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relative density, homogeneity of the microstructure and thermal conductivity of the composites were analyzed.

2 Experimental

Copper powder (particle size of 40 μm, 99.9% in purity) was used as the composite matrix. The reinforcements were synthetic diamonds with an average diameter of 40 μm. The copper powders with different volume fractions (50%, 60%, and 70%) of diamond particles were dry mixed evenly at room temperature. SPS system (DR.SINTER−SPS−3.20) was used to synthesize Cu/diamond composites. The powder mixture was put into a cylindrical graphite die with an inner diameter of 15 mm. Before sintering, the chamber was pumped to low vacuum (<5 Pa). The sample was heated by passing alternating DC current through the die and punches from room temperature to 700−950 °C and hold for 5 min. A pressure of 50 MPa was applied from the start to the end of the sintering.

The density of the composites was measured by Archimedes principle, and the theoretical densities of pure copper (8.96 g/cm^3) and diamond (3.52 g/cm^3) were used to calculate the relative density of the samples. The microstructure of the composites was observed and investigated by scanning electronic microscopy (SEM, XL30ESEM-TMP). The laser flash method was used to measure the thermal diffusivity of the composites at room temperature. The thermal diffusivity and specific heat measurement were performed on a NETZSCH LFA 447 thermal physical testing instrument, and the thermal conductivity of composites could be calculated by

$$K=\alpha \cdot c_p \cdot \rho \quad (1)$$

where K, α, c_p and ρ are the thermal conductivity, thermal diffusivity, specific heat capacity and density of the composites, respectively.

3 Results and discussion

3.1 Effect of diamond volume fraction on property and microstructure of Cu/diamond composites

In order to investigate the influence of diamond volume fraction on the density, the homogeneity of microstructure and the thermal conductivity of the composites, the evenly mixed powders with different volume fractions of diamond (50%, 60% and 70%, respectively) were sintered at 750 °C.

Figure 1 shows the change of relative density of the composites with the different volume fractions of diamond sintered at 750 °C. As shown in Fig. 1, with the increase of diamond volume fraction, the relative density of the composites decreases after sintering. In the Cu/diamond composites, copper will be the main support to connect the whole sintered compact, and the addition of larger content of diamonds will increase the interfacial area between the two phases. Due to the poor wettability between copper and diamond, the increase of interfacial area will make it more difficult to obtain a good interfacial bonding between copper and diamond because there is no sufficient matrix which can fill up the gaps left by the adjacent diamond particles, and then the relative density of the composites will decrease with increasing of diamond volume fraction.

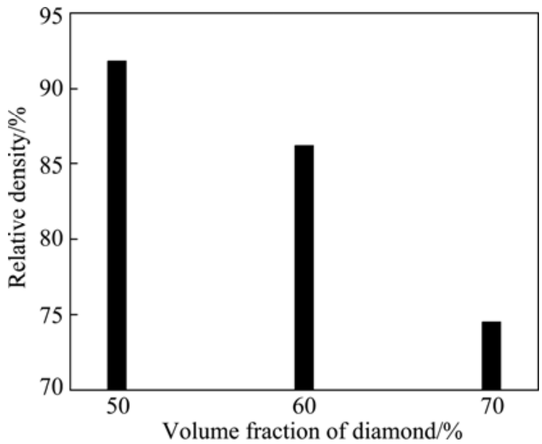

Fig. 1 Relative density of composites versus volume fraction of diamond

Figure 2 shows the morphologies of fracture surface of the composites with different diamond volume fractions sintered at 750 °C. Figure 2(a) shows the composite with 70% of diamond, and it can be clearly seen that there are obvious cracks in the surrounding of diamond particles, which demonstrates that the interfacial bonding between copper and diamonds is poor, and the corresponding relative density of the composite is only 74.5%. Figures 2(b) and (c) show the composites with the diamond volume fractions of 60% and 50%, respectively. With the decease of diamond volume fraction, the interfacial bonding between copper and diamond gets much better, and the number of cracks between the two phases also drops off. At the same time, the relative density increases to 86.2% and 91.8% when the diamond volume fractions decrease to 60% and 50%, respectively.

Figure 3 shows the change of thermal conductivity of the composites with different diamond volume fractions after being sintered at 750 °C. With the decrease of diamond volume fraction, the interfacial area between copper and diamond particles also decreases, which is beneficial to the heat conduction within the matrix. As shown in Fig. 3, the thermal conductivity of the composites has the same variation trend with the relative density, which increases from 44 W/(m·K) to 149 W/(m·K) when the volume fraction of diamond decreases from 70% to 50%. Relative density is one of

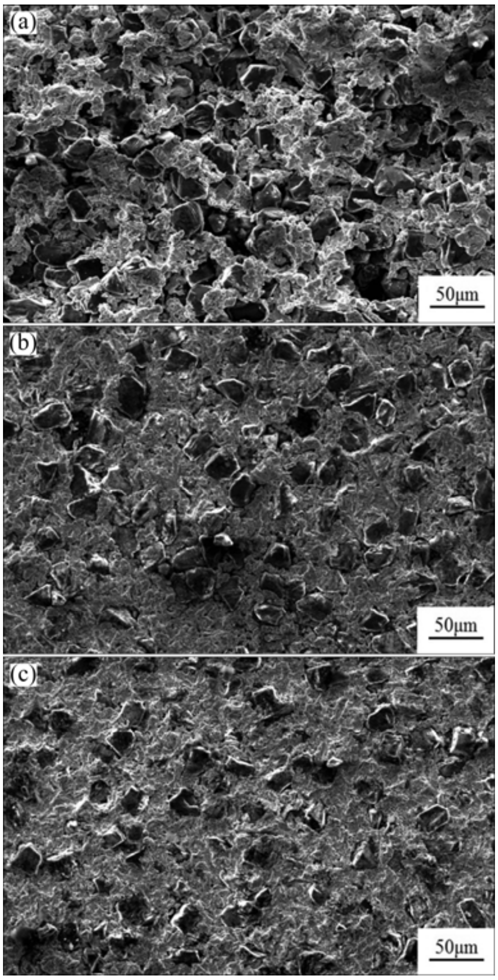

Fig. 2 SEM images of Cu/diamond composites with different volume fractions of diamond sintered at 750 °C: (a) 70%; (b) 60%; (c) 50%

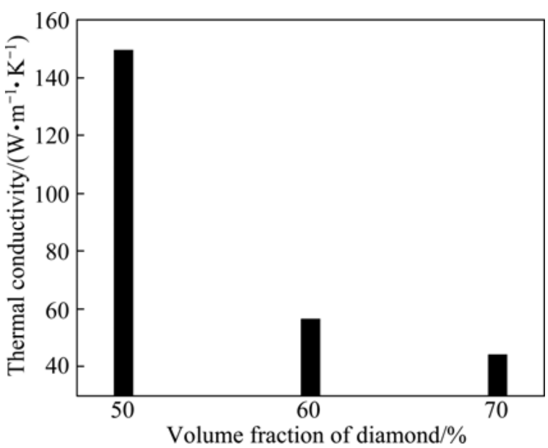

Fig. 3 Thermal conductivity of composites versus volume fraction of diamond

the key factors which will influence the thermal conductivity of the materials, especially for the sintered compact prepared by powder metallurgy [17].

The above analysis indicates that at the same sintering temperature, with the decrease of diamond volume fraction, the relative density of the composites increases and the interfacial bonding between copper and diamond gets better, which will significantly improve the thermal conductivity of the composites.

3.2 Effect of sintering temperature on property and microstructure of Cu/diamond composites

In order to investigate the influence of sintering temperature on the relative density and thermal conductivity of the composites, the evenly mixed powder with the same diamond volume fraction of 50% was sintered at 700, 750, 850 and 950 °C, respectively.

Figure 4 shows the change of relative density of the Cu/diamond composites with the sintering temperature. As shown in Fig. 4, when the sintering temperature is as low as 700 °C, owing to the poor flowability of copper, the gaps between diamond particles could not be filled very well and the relative density of the composites is lower than 90%. When the sintering temperature is higher than 750 °C, the relative density of the composites after sintering is improved significantly. The relative density of the composites sintered at 750 °C has reached 91.8%, while the relative density of the composites sintered at 950 °C reaches 94%. It can also be seen that when sintering temperature is higher than 750 °C, the relative density of the composites does not improve drastically and tends to be stable. The flowability of the copper gets better when the sintering temperature is improved, therefore, copper could fill the gaps between diamond particles by better flowing deformation, which will greatly improve the relative density of the composites after sintering.

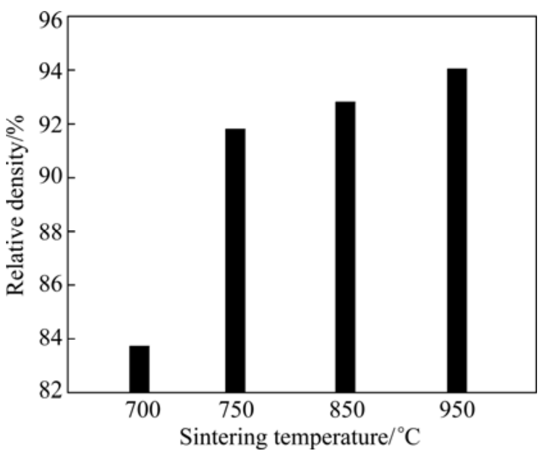

Fig. 4 Relative density of composites versus sintering temperature

Figure 5 shows the morphologies of fracture surface of Cu/diamond composites sintered at different temperatures. As shown in Fig. 5(a), the composite sintered at 700 °C exhibits the feature of poor interfacial bonding with the obvious cracks between the copper and

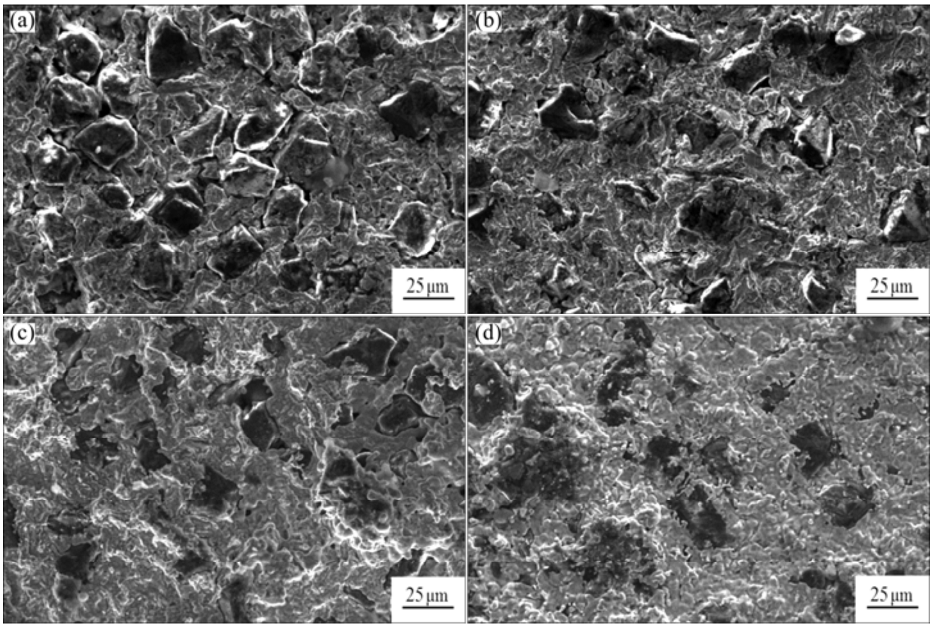

Fig. 5 SEM images of Cu/diamond composites sintered at different temperatures: (a) 700 °C; (b) 750 °C; (c) 850 °C; (d) 950 °C

diamond particles. It is clearly seen in Figs. 5(b)−(d), with the improvement of sintering temperature, owing to the better flowability of copper, the porosity between copper and diamond particles decreases obviously. The interface morphology of the composite sintered at 950 °C shows the marked difference compared with that sintered at 700 °C, showing a noticeable improvement of interfacial adherence.

Figure 6 shows the change of thermal conductivity of the composites at different sintering temperatures. As shown in Fig. 6, with the improvement of sintering temperature, the thermal conductivity of the composites keeps increasing, and has the same change trend with the relative density. The thermal conductivity of the composite sintered at 700 °C is only 71.8 W/(m·K), while it increases drastically to 190.5 W/(m·K) after being sintered at 950 °C.

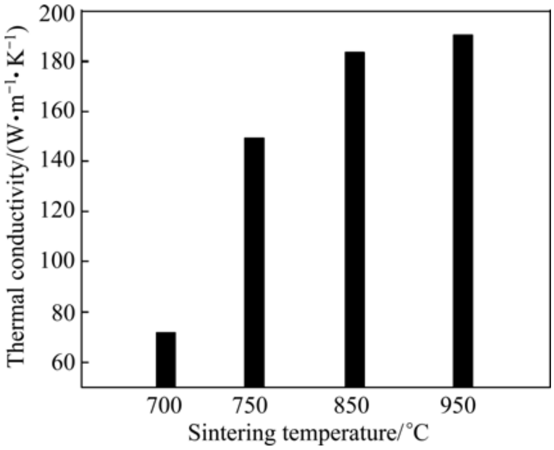

Fig. 6 Thermal conductivity of composites versus sintering temperature

The maximum relative density of the Cu/diamond composites in this work is 94%, therefore, there is still a small portion of pores in the composites. Interfacial microstructure observation indicates that most of these pores exist in Cu/diamond interface, which can introduce additional thermal barriers to the composite, and hence reduce the overall thermal conductivity. Increasing the relative density is a key factor to further increase the thermal conductivity of the composites, so it needs to decrease the residue pores in the interface. Improvement of technical parameters of SPS combined with subsequent processing, such as hot extrusion or hot isostatic pressing, seems to be the effective way to increase the relative density of the composites, which will increase the thermal conductivity.

4 Conclusions

1) Cu/diamond composites were prepared by SPS method at sintering temperature of 700−950 °C with holding pressure of 50 MPa and holding time of 5 min, and their relative density, thermal conductivity and interfacial microstructure were investigated.

2) With the decrease of diamond volume fraction, the relative density, homogeneity of the microstructure and thermal conductivity of the composites all increase.

3) When sintering temperature is as low as 700 °C, the interfacial bonding between copper and diamond particles is poor, and obvious cracks exhibit between the copper and diamond particles.

4) With the increase of sintering temperature, the flowability of copper gets better and the gaps between copper and diamond particles can be filled by better

flowing deformation, which can greatly improve the relative density and thermal conductivity of the composites after sintering.

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放电等离子烧结法制备 Cu/金刚石复合材料的性能与显微组织

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摘 要：由于具备较高的热导率，铜/金刚石复合材料已成为应用于电子封装领域的新一代热管理材料。采用放电等离子烧结工艺(SPS)成功制备含不同金刚石体积分数的 Cu/金刚石复合材料，研究复合材料的相对密度、微观结构均匀性和热导率(TC)随金刚石体积分数（50%、60%和 70%）和烧结温度的变化规律。结果表明：随着金刚石体积分数的降低，复合材料的相对密度、微观结构均匀性和热导率均升高；随着烧结温度的提高，复合材料的相对密度和热导率不断提高。复合材料的热导率受到金刚石体积分数、微观结构均匀性和复合材料相对密度的综合影响。

关键词：Cu/金刚石复合材料；放电等离子烧结；相对密度；热导率

(Edited by Chao WANG)