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Fabrication and thermo-physical properties of TiB_{2p}/Cu composites for electronic packaging applications

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Abstract: TiB_{2p}/Cu composites with high reinforcement content (φ_p=50%, 58% and 65%) for electronic packaging applications were fabricated by squeeze casting technology. The microstructures and thermo-physical properties of the TiB_{2p}/Cu composites were investigated. The results show that TiB_2 particles are homogeneous and distribute uniformly, and the TiB_2-Cu interfaces are clean and free-from interfacial reaction products and amorphous layers, the densifications of the TiB_{2p}/Cu composites are higher than 98.2%. The mean linear coefficients of thermal expansion at 20−100 ℃ for TiB_{2p}/Cu composites range from 8.3×10^{-6} to 10.8×10^{-6}/K and decrease with increasing volume fraction of TiB_2. The experimental coefficients of thermal expansion agree well with the predicted values based on Turner's model. The thermal conductivities of TiB_{2p}/Cu composites range from 167.3 to 215.4 W/(m·K), decreasing with increasing volume fraction TiB_2.

Key words: TiB_{2p}/Cu composites; densification; coefficient of thermal expansion; thermal conductivity

1 Introduction

The development of packaging technology has resulted in need for new materials with superior properties[1]. Firstly, packaging materials should have coefficient of thermal expansion(CTE) matching the ceramic substrates such as alumina, beryllia or aluminum nitride or semiconductors such as silicon or gallium arsenide to avoid thermally induced stresses that often cause eventual device failure. Additionally, since the reliability of semiconductors drops dramatically as temperature rises, higher thermal conductivity is demanded to remove excess heat and keep operating temperature low. Further, large mechanical properties and low density are desirable in applications that require maximal performance at low mass[2−3].

Particulate reinforced copper matrix composite combines the benefits of compatible and tailorable CTE, high thermal conductivity, lightmass, enhanced specific strength and stiffness[4−5]. So, it has been identified as an ideal candidate material for power module baseplates, printed wiring board cores, microprocessor lids and heat spreaders. Titanium diboride (TiB_2) is well known for its high thermal and electrical conductivities, good chemical stability and good thermal shock stability[6−7]. Thus, the addition of TiB_2 to copper matrix greatly decreases its coefficient of thermal expansion, while reducing the electrical and thermal conductivities much less than the addition of most other ceramic reinforcements[8−9]. Therefore, TiB_2 reinforced metal matrix composites have received a great attention recently. The previous researches about the TiB_{2p}/Cu composites were mostly focused on the thermal shock resistance properties and fabrication methods[10−12].

In the present study, high particle content TiB_{2p}/Cu

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composites with particle volume fraction of 50%, 58% and 65% were fabricated by the patent squeeze casting technology, the densification of which was higher than 98.2%, with their microstructures, thermo-physical properties were tested and analyzed.

2 Experimental

The reinforcements used in this work were titanium diboride, TiB_2, particles with nominal diameters of 2−3 μm, and the reinforcements volume fraction were 50%−65%. The copper matrix was commercially available pure copper (w(Cu)≥99.7%). This pure copper was chosen for the purpose of high thermal conductivity and low cost. Table1 lists the typical parameters of TiB_2.

Table 1 Typical parameters of TiB_2 particle reinforcements

Parameter	Value
Density/(g·cm^{-3})	4.4
Melting point/℃	2 930
Hardness/GPa	30
Elastic modulus/GPa	574
Poisson's ratio	0.11
CTE/10^{-6}K^{-1}	6.9
Thermal conductivity/(W·m^{-1}·K^{-1})	96

The TiB_{2p}/Cu composites were fabricated by squeeze casting technology. The TiB_2 preform was first fabricated and preheated. At the same time, copper alloy was melted, after which the molten copper was infiltrated into TiB_2 preform under the pressure and held for some time. And then, TiB_{2p}/Cu composite was solidified. A flow chart of the above process is shown in Fig.1. The composites were annealed in vacuum at 700 ℃ for 1.5 h and furnace cooled in order to release residual stress within the composites.

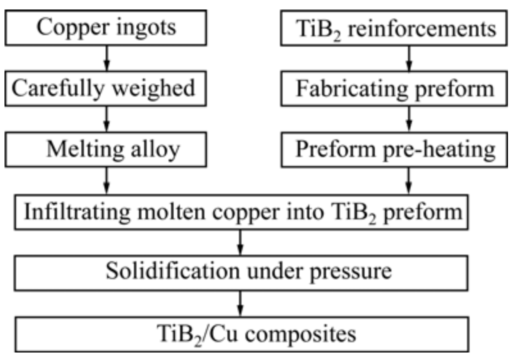

Fig.1 Flow chart of squeeze casting technology used for fabricating TiB_{2p}/Cu composites

An S-570 scanning electron microscope(SEM) was used to examine the microstructure of as-fabricated TiB_{2p}/Cu composites. The measured density was obtained using the Archimedes method and compared with the theoretical density to obtain various degree of densification. The CTE was measured on a DIL 402C (NETZSCH Corp.) with a heating rate of 5 ℃/min. The thermal conductivity was measured by the laser flash method with the NETZSCH LFA427 thermal constant measuring equipment. The testing sample was cylindrical, 12.7 mm in diameter and 3 mm in thickness.

3 Results and discussion

3.1 Densification

The effect of TiB_2 volume fraction on the densification for TiB_{2p}/Cu composites is shown in Fig.2. The densification of the TiB_{2p}/Cu composites decreases with increasing TiB_{2p} volume fraction under the same processing conditions. The densification of three composites is in the range of 98.2%−99.3%, which can completely meet the high dense requests for the electronic package materials.

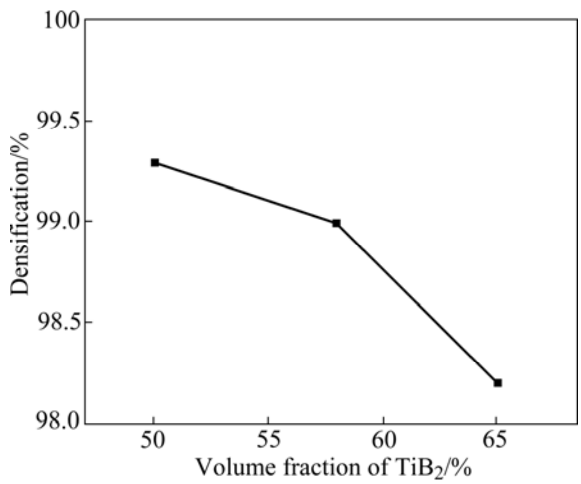

Fig.2 Dependence of TiB_2 volume fraction on densification for TiB_{2p}/Cu composites

3.2 Microstructure observation

Fig.3 reveals the microstructure of as-cast TiB_{2p}/Cu composites. The TiB_2 particles are observed to be homogeneously distributed in the copper matrix. And the composites are free from common cast defects such as porosity and shrinking cavities because pressure was applied during the solidification of TiB_{2p}/Cu composite.

The interface and the existing of interface effect are the important factors which can affect the properties of the composite. Fig.4 illustrates the typical TEM micrographs of the interfaces in TiB_{2p}/Cu composites. A large a mount of observations indicate that the TiB_2-Cu interfaces are clean, smooth and free from interfacial reaction products and amorphous layers, and no TiB_2 particles dissolved are observed.

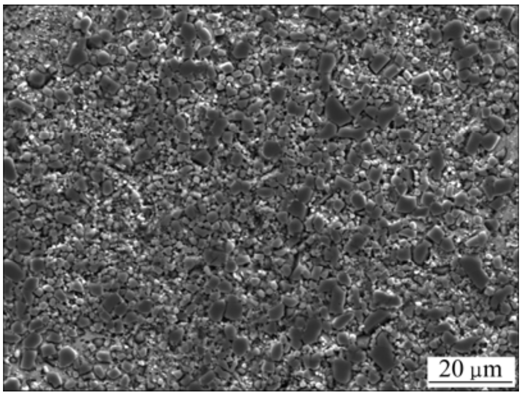

Fig.3 Microstructure of TiB_{2p}/Cu composite

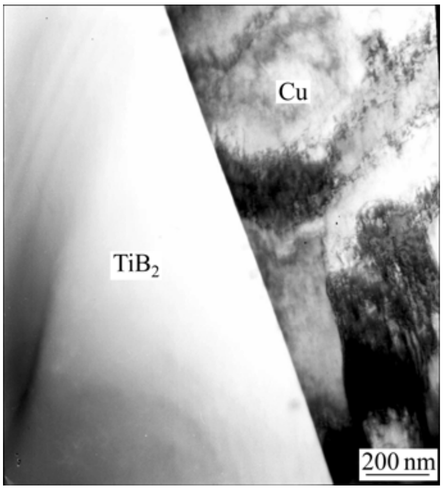

Fig.4 TEM micrographs of TiB_2-Cu interfaces

3.3 Thermal expansion analysis

The measured CTEs of TiB_{2p}/Cu composites are 8.9×10^{-6}, 9.5×10^{-6} and 10.4×10^{-6} K^{-1} for the composites with volume fraction of TiB_2 of 65%, 58% and 50%, respectively. The CTEs reduce with increasing volume fraction of TiB_2. In a TiB_{2p}/Cu composite, the thermal expansion behavior is influenced by the thermal expansion of copper matrix and the tightened restriction of TiB_2 particles. Several theoretical models were proposed to predict the CTE of particulate composite [13−14]. If the matrix modulus is much smaller than that of reinforcement, the CTE of a composite is expressed as rule-of-mixture(Rom):

$$\alpha_c=\alpha_m\varphi_m+\alpha_p\varphi_p \tag{1}$$

where α is the CTE, φ is the volume fraction; and subscripts c, m, p refer to the composite, matrix and particle, respectively.

Turner's model considers the uniform hydrostatic stresses and gives the CTE of a composite as

$$\alpha_c=\frac{\alpha_m K_m\varphi_m+\alpha_p K_p\varphi_p}{K_m\varphi_m+K_p\varphi_p} \tag{2}$$

where K is the bulk modulus.

Both the normal and shear stress are taken into account in Kerner's model, and the CTE of a composite is expressed as

$$\alpha_c=\alpha_m\varphi_m+\alpha_p\varphi_p+\varphi_p\varphi_m(\alpha_p-\alpha_m)\times\frac{K_p-K_m}{\varphi_m K_m+\varphi_p K_p+(3K_pK_m/4G_m)} \tag{3}$$

where G is shear modulus.

Fig.5 shows the comparison between the above theoretical predictions and experimental data. It can be seen that the experimental data are in good agreement with the predicted values based on Turner's model, but deviate from ROM and Kerner's model. This may be attributed to the fact that the uniform hydrostatic stresses are included in Turner's.

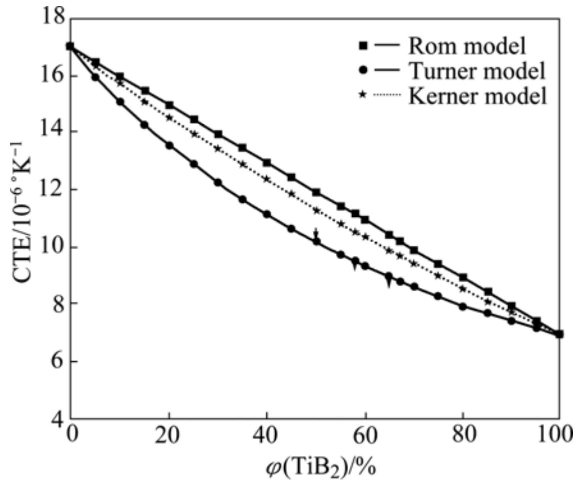

Fig.5 Comparison between theoretical predictions and experimental CTEs

3.4 Thermal conductivity

The measured thermal conductivities of TiB_{2p}/Cu composites are 215.4, 180.5 and 167.3 W/(m·K) for the 50%, 58% and 65% composites, respectively, which are enough to satisfy the high thermal conductivity requests for electronic package materials. The thermal conductivities of TiB_{2p}/Cu composites increased with increasing volume fraction of Cu. It is attributed to the thermal conductivity of TiB_2 which is lower so far than that of copper.

Although the thermal conductivity of PMMCs is mainly decided by the thermal conductivity and content of constituent components, it connects with the densification of materials, interface condition, the figures and distribution of particles[15−17]. There are two ways for heat transfer in TiB_{2p}/Cu composites: free electron in Cu matrix and phonon in TiB_2 particles. Both the movement would be scattered by interface. Therefore, heat conduction in TiB_{2p}/Cu composite depends on the Cu matrix, TiB_2 particles and their interface. Fortunately, the interface between Cu and TiB_2 particles are smooth without any reactant (see Fig.4), which is beneficial to heat transfer.

Accurate prediction of the composite properties is one important goal for researchers on materials, and two widely used models for prediction of PMMCs thermal conductivity are as the following[18−19]:

1) For Rom model

$$\lambda_c=\lambda_m\varphi_m+\lambda_p\varphi_p \tag{3}$$

2) For Maxwell model

According to the conductance and the thermal conductivity property of biphase and multiphase, the expression of the thermal conductivity is deduced:

$$\lambda_c=\lambda_m\frac{1+2x-2\varphi_p(x-1)}{1+2x+\varphi_p(x-1)} \tag{4}$$

where λ is thermal conductivity; φ is volume fraction; x equals λ_m/λ_p; and subscripts c, p and m refer to composite, reinforcement particle and matrix, respectively.

Generally, the thermal conductivity of matrix Cu is 398 W/(m·K), the thermal conductivity of TiB_2 is 96 W/(m·K). The calculated thermal conductivity is obtained from the above models, and the comparison between predictions and experimental data is listed in Table 2.

Table 2 Predicted and experimental thermal conductivities of TiB_{2p}/Cu composite

Composite	Thermal conductivity/($W\cdot m^{-1}\cdot K^{-1}$)		
	Rom	Maxwell	Experimental
50% TiB_{2p}/Cu	244.0	221.2	215.4
58% TiB_{2p}/Cu	219.4	197.6	180.5
65% TiB_{2p}/Cu	197.8	177.9	167.3

The comparison of those with experimental data indicates that the calculated thermal conductivity of Maxwell models is close to that of TiB_{2p}/Cu composites. The achievement of higher thermal conduction is attributed the high dense composite fabricated by the patent squeeze casting technology, and the TiB_2-Cu interfaces are clean, smooth and free-from interfacial reaction products and amorphous layers.

4 Conclusions

1) The full densities of the TiB_{2p}/Cu composites with volume fractions of TiB_2 of 50%−65% were fabricated. The composites are full dense and porosity-free macroscopically. TEM observations indicate the TiB_2-Cu interfaces are clean, smooth and free from interfacial reaction products and amorphous layers.

2) The linear CTEs of TiB_{2p}/Cu composites range from 8.9×10^{-6} to 10.4×10^{-6}/K, depending on the volume fraction of TiB_2. The experimental CTEs are in good agreement with the predicted values based on Turner's model.

3) The thermal conductivities of TiB_{2p}/Cu composites at ambient temperature range from 167.3 to 215.4 W/(m·K) and decrease with increasing volume fraction of TiB_2, which agrees with the calculated values of Maxwell model.

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