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Ultrahigh thermal conductivity copper/graphite membrane composites prepared by tape casting with hot-pressing sintering

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ABSTRACT

Ultrahigh thermal conductivity Cu/graphite membrane composite with continuous well-packed laminate structure is prepared by tape casting with hot-pressing sintering. As-prepared composite material has anisotropic thermal properties with ultrahigh in-plane thermal conductivity and low in-plane coefficient of thermal expansion because of its extraordinary packed laminate structure. Thermal properties of Cu/graphite membrane composite can be designed according to requirements by adjusting volume fraction of graphite membrane in the composite. The maximum value of Cu/graphite membrane composite (50 vol% graphite membrane) in-plane thermal conductivity is 1005 $W \cdot m^{-1} K^{-1}$, while the minimum value of the in-plane coefficient of thermal expansion is $7 \times 10^{-6} K^{-1}$. This meets the high requirements for thermal management materials.

1. Introduction

With the increasing demand of electronic products for higher thermal efficiency, electronic packaging thermal management materials with excellent heat transfer performance have become increasingly important in aerospace and integrated circuit industries [1]. In recent years, metal matrix composites (MMCs) have received significant attention because of their outstanding combination of high thermal conductivity (TC) and adjustable coefficient of thermal expansion (CTE), as well as excellent mechanical properties [2–5]. Copper is a promising matrix material due to its high TC and excellent formability, as well as good corrosion resistance [6]. Graphite membrane (GM) with ultrahigh in-plane TC of 1100–1600 $W \cdot m^{-1} K^{-1}$ and low in-plane CTE is a promising thermal management material, which has been widely used in dissipating heat from electronic products and can be made into large area of continuous uniform films [7–9]. Therefore, GM-reinforced Cu matrix composite may be a good candidate to meet the requirements of numerous thermal management applications.

In this study, the ultrahigh TC Cu/GM composite with well-packed laminate structure was successfully fabricated by tape casting with hot-pressing sintering without other additives into the raw materials. The aim of the current study was to obtain suitable composition and structure for optimal composite performance. The effects of composite microstructure and GM volume fraction on composite properties were investigated. This work demonstrates a new type of MMCs with ultrahigh TC along with the suitable preparation method.

2. Experimental

Electrolytic copper powder (99.9%, <10 μm) with TC of 400 $W \cdot m^{-1} K^{-1}$ and CTE of $16.8 \times 10^{-6} K^{-1}$ and GM (25 μm average thickness) with in-plane TC of 1500 $W \cdot m^{-1} K^{-1}$ and out-plane TC of 20 $W \cdot m^{-1} K^{-1}$, and in-plane CTE of $-1.5 \times 10^{-6} K^{-1}$ were used as raw materials. The slurry for tape casting process was made by adding solvent, binder, plasticizer and defoamer to the copper powder. Subsequently, slurry was cast into thin films on the GM with a doctor blade, and film thickness was adjusted by the height of the doctor blade [10,11]. After composite film was dried in the vacuum drying oven at 313 K for 1 h, debonding and reduction process of the film proceeded simultaneously at 673 K for 2 h in hydrogen atmosphere. Subsequently, the composites were sintered by hot-pressing sintering at 1273 K under 10 MPa pressure.

Cu/GM composite microstructure was observed by field emission scanning electron microscope (FE-SEM, QUANTAFEG450, USA). The crystal orientation of the composite was analyzed by X-ray diffraction (XRD, RIGAKU TTR3, Japan). λ $(W \cdot m^{-1} K^{-1})$ is

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thermal conductivity of the composite, which was calculated using the following formula:

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

Here, α ($m^2 \cdot s^{-1}$) is the thermal diffusion coefficient of the composite measured at room temperature by laser flash method (NETZSCH LFA447, Germany) in radial direction of GM with the sample size of $10 \times 10 \times 4$ mm; C_p ($J \cdot g^{-1}\ K^{-1}$) is specific heat of the composite, which was calculated according to rule of mixture:

$$C_p = C_{Cu}V_{Cu} + C_{GM}V_{GM} \tag{2}$$

Here, C_{Cu}, C_{GM} is specific heat and V_{Cu}, V_{GM} is volume fraction of copper and GM, respectively. Composite density was measured using the Archimedes principle. Coefficient of thermal expansion of the composite was measured in the 293–473 K range by the thermal dilatometer (NETZSCH DIL 402PC, Germany) in the axial direction of GM.

3. Results and discussion

Fig. 1a shows the FE-SEM image of GM, while the image in the top right corner shows oblique section of GM. GM consists of multiple thin films with many wrinkles, which evidently indicates that GM has excellent flexibility and certain strength. Fig. 1b shows the XRD pattern of ground GM and the in-plane of GM. The two diffraction peaks at 26.52° and 54.72° of both XRD patterns correspond to the diffraction of the (003) and (006) planes of in-plane of GM, respectively. This XRD result indicates that GM grains are neatly arranged. Fig. 1c is an FE-SEM image of typical local structure. Composite has a dual component structure of copper and GM, arranged alternatively in the form of lamellae, which reveals that GMs in the composite are uniform and continuous. XRD pattern of the x-axis of Cu/GM composite is shown in Fig. 1d, where the three peaks at 43.40°, 50.50° and 74.54° correspond to the (111), (200) and (220) diffraction planes of copper. Diffraction peak intensity of (003) GM plane is decreased significantly, while the intensity of (006) crystal plane is almost invisible, which proves that the as-prepared Cu/GM composite with laminate structure is anisotropic. Thus, composite properties are also anisotropic.

Cu/GM composite was prepared with volume fraction of GM ranging from 10% to 50%. It should be noted that GM is an anisotropic material with in-plane TC of 1500 $W \cdot m^{-1}\ K^{-1}$ and out-plane TC of 20 $W \cdot m^{-1}\ K^{-1}$. Fig. 2a and b show that the x-y plane TC of the composite increases approximately linearly from 585 $W \cdot m^{-1}\ K^{-1}$ to 1005 $W \cdot m^{-1}\ K^{-1}$ with the increasing GM volume fraction. The z-axis TC decreases from 40 $W \cdot m^{-1}\ K^{-1}$ to 12 $W \cdot m^{-1}\ K^{-1}$ at the same time, which proves that GM has significant impact on the composite TC. Compared with the highest known thermal conductivity of carbon/Cu matrix composite at 930 $W \cdot m^{-1}\ K^{-1}$ [12], we prepared composite with higher thermal conductivity.

To better understand the thermal conductivity of the Cu/GM composite, series-parallel connection models were used to predict TC of Cu/GM composites without considering interface thermal resistance (ITR), which can be expressed by the following equations:

$$\lambda_c = V_{Cu}\lambda_{Cu} + V_{GM}\lambda_{GM} \tag{3}$$

$$\lambda_c^{-1} = V_{Cu}\lambda_{Cu}^{-1} + V_{GM}\lambda_{GM}^{-1} \tag{4}$$

Here, λ_c is TC of the Cu/GM composite, V_{Cu} and V_{GM} is the volume fraction of copper and GM, λ_{Cu} and λ_{GM} is TC of copper and GM, respectively. Eq. (3) represents the parallel connection model, which is suitable for predicting TC of the x-y plane, while Eq. (4) is the series connection model, which is suitable for predicting TC of the z-axis. It can be observed that the experimental values of the x-y plane fit well with the predicted values in Fig. 2a, while predicted values of the z-axis have relatively large difference with the experimental values in Fig. 2b. This proves that the series-parallel connection models can predict TC of material relatively accurately

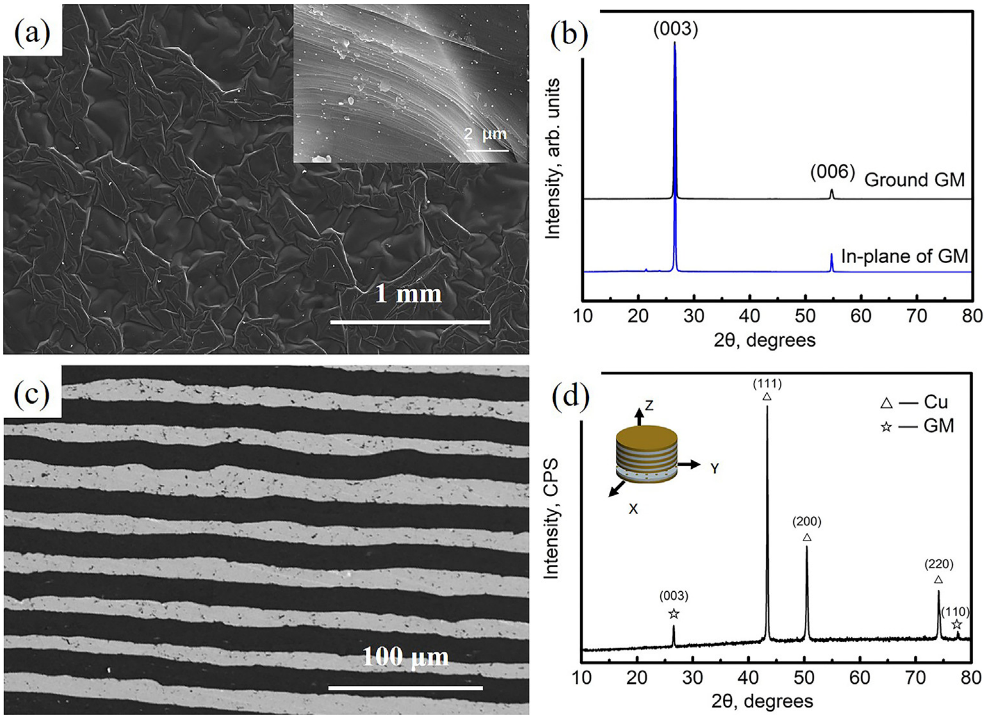

Fig. 1. (a) FE-SEM images of surface and interlayer GM morphology; (b) XRD patterns of ground GM and in-plane of GM; (c) FE-SEM image of local structure and (d) XRD pattern of x-axis of Cu/GM composite. Thumbnail in (a) is oblique image of GM.

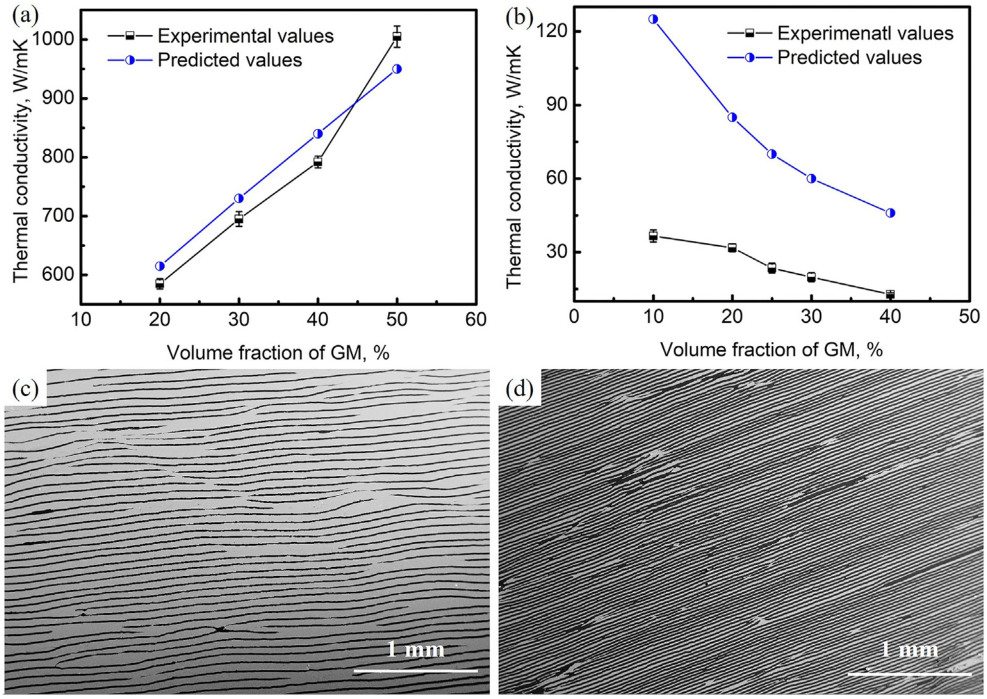

Fig. 2. Experimental values and predicted values of TC of (a) the x-y plane and (b) the z-axis of Cu/GM composite; complete FE-SEM images of Cu/GM composites with (c) 20 vol% and 50 vol% GM.

when ITR is not considered. This also indicted that ITR has a negative impact on TC of the composite and it is necessary to reduce ITR as much as possible with other conditions unchanged. Furthermore, it is worth noting that the TC value of the composite with 50 vol% of GM is much higher than the predicted value. For comparison, Fig. 2c and d show complete FE-SEM images of the composites with 20 vol % and 50 vol% GM. The latter has better continuous laminate structure, which demonstrates that better reinforcement continuity results in higher TC of as-prepared composites.

Fig. 3 shows that the in-plane CTE values of Cu/GM composites decrease from 13.5×10^{-6} K^{-1} to 7×10^{-6} K^{-1} with volume fraction of GM ranging from 20% to 50%. This indicates that reinforcements in as-prepared composite can greatly affect the CTE of the composite. In general, Cu/GM composite has a Si-matched CTE, which makes it a promising thermal management material.

The fabricated Cu/GM composite has excellent thermal properties. However, graphite membrane with lower strength has negative effects on the mechanical properties of the composite, which requires further experiments.

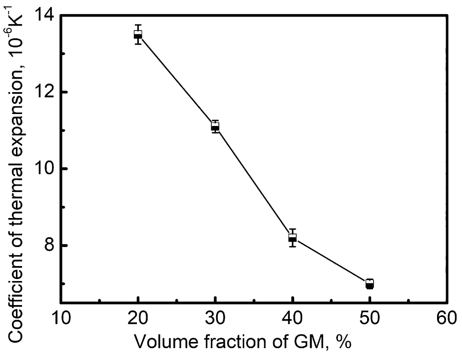

Fig. 3. Coefficient of thermal expansion values of the x-y plane of the Cu/GM composite.

4. Conclusion

Cu/GM composite with well-packed laminate structure is successfully prepared by tape casting with hot-pressing. Tape casting makes the macrostructure of as-prepared composite organized into alternating stacks of uniform and integrated copper layers and GM layers. Properties of the Cu/GM composite exhibit strong anisotropy because of its special structure. The Cu/GM composite shows in-plane CTE of 7×10^{-6} K^{-1} and promising in-plane thermal conductivity of 1005 W $\cdot$ m^{-1} K^{-1} with 50 vol% of GM, which is 2.5 times higher than the thermal conductivity of pure copper. The addition of ultrahigh thermal conductivity GM greatly improves thermal management of the Cu/GM composite. Optimized overall performance material can be prepared with the addition of suitable volume fraction of GM.

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