Microstructure and thermal conductivity of graphite flake/Cu composites with a TiC or Cu coating on graphite flake

Qian Liu 1,2,3,4, Siwen Tang 1, Junchen Huang 2, Yun Ou 1, Juanjuan Cheng 1,3, Youming Chen 1, Fang Wang 1 and Zheng Lv 1

1 Hunan Provincial Key Laboratory of Health Maintenance for Mechanical Equipment, Hunan University of Science and Technology, Xiangtan 411201, Hunan, People’s Republic of China
2 School of Materials Science and Engineering, Hunan University of Science and Technology, Xiangtan 411201, Hunan, People’s Republic of China
3 Hunan Provincial Key Laboratory of Advanced Materials for New Energy Storage and Conversion, Xiangtan 411201, People’s Republic of China
4 Author to whom any correspondence should be addressed.
E-mail: 8180001@hnust.edu.cn

Keywords: Cu matrix composites, graphite flake, interfacial structure, thermal conductivity

Supplementary material for this article is available online

Abstract
Graphite flake/Cu composites with Cu or TiC coatings on the graphite surface were fabricated via a powder metallurgy method. The effect of the flake’s surface coating on the microstructure and thermal conductivities of the graphite flake/Cu composites was studied. The results show that a good contact interfacial structure is established when the TiC or Cu coating is introduced. The thermal conductivity of the TiC- and Cu-coated composites with a 60 vol% flake reached 668 W m\(^{-1}\) K\(^{-1}\) and 612 W m\(^{-1}\) K\(^{-1}\), respectively. A modified Diffuse Mismatch Model for anisotropic graphite was established to estimate the interfacial thermal resistance, and the Effective Medium Approach was used to analyze the thermal conductivity behavior of composites. The results show that both coated composites exhibit low interfacial thermal resistance, resulting in high thermal conductivity in the X-Y plane. The thermal conductivity may be further enhanced if a preferable alignment control is used.

1. Introduction

With increasing power density and continuing miniaturization in semiconductor devices, heat removal has become a crucial issue for continuing progress in the electronic industry. Thermal management of the next generation of integrated circuits requires a heat sink material with high thermal conductivity (TC) [1–3]. Current high-TC materials mainly used for heat spreaders and heat sinks are composed of metal matrix composites reinforced with appropriate reinforcement, such as SiC, diamond, and graphite [4–9]. Among various candidate reinforcements, graphite flakes (GFs) exhibit good comprehensive properties, with a theoretical TC above 2000 W m\(^{-1}\) K\(^{-1}\) in the (002) crystal plane (basal plane), low mass, affordability and ease of machinability. Graphite flakes combined with copper, which is a widely used heat-spreading material matrix, are considered an ideal composite for heat sink applications [7, 10].

When considering the fabrication of graphite flake-copper composites, there are two main problems. First, in the uniaxial pressing process, the flakes are easily made to lie on top of each other, making it difficult for the metal matrix to fully fill the pores. This problem has been recently solved by the addition of a third phase, which acts as a separator between flakes [9, 11], or by using powder metallurgy with a delicate mixing process [12–14]. The other problem is poor interfacial bonding between the graphite flake and copper. Similar to diamond–Cu composites, copper is non-wetting with graphite due to chemical incompatibility. As a result, the TCs of composites are not fully exploited due to their high interfacial thermal resistance [15, 16]. There are two effective ways to modify the interface structure: matrix alloying and reinforcement surface coating. Compared with matrix alloying, reinforcement surface modification more easily forms a continuous and homogeneous interface and is thus
widely used to improve the interfacial bonding between carbon materials and copper. One example of this is from SB Ren et al who fabricated GF/copper composites with Ni coating on the surface of GF. The TC of composites with 20 vol%–60 vol% GF ranged from 466–532 W m^{-1} K^{-1} [1]. Bai et al prepared GF/copper composites with a Si coating on GF to improve the mechanical properties. However, the TC decreased from 676 to 610 W m^{-1} K^{-1} after the Si coating was introduced [17]. In our previous study, graphite flake/copper composites were fabricated by electroless copper coating. The composite containing 70 vol% graphite flakes with diameters from 20 μm to 70 μm has a TC of 565 W m^{-1} K^{-1} and CTE of 5 × 10^{-6} K^{-1}. It has been suggested that the TC performance could be improved via better interface control [18]. In recent years, strong carbide-forming elements, such as Ti, Cr, Mo or W, were coated on the surface of diamond and carbon fibers to form carbide layers, which act as inter-layers that strengthen the interface and decrease interfacial thermal resistance. The results show that with a carbide layer on the reinforcement surface, the composites with diamond exhibit a 150%–300% increase in TC [19–21], and those with graphite fibers show a 25%–45% increase [22, 23]. Zhang et al coated Ti on the surface of diamond particles and reported a thermal conductivity of 716 W m K^{-1} for the composites due to the formation of a TiC layer between the diamond and the Cu matrix [19]. These studies indicate that the interface structure design could significantly improve the thermo-physical properties of the composites. However, graphite is soft and highly anisotropic. To fully exploit the high TC of GF in the basal plane, it is important to keep the graphite morphology unspoiled in the design of the interface structure for graphite reinforcement. To this date, the effect of the carbide interlayer structure on the TC performance of copper-graphite composites has rarely been reported on. The influence of the anisotropy on the TC of the composite is not fully understood.

This work aims to study the effect of different interface structures on the TC performance of GF–Cu composites. To maintain the configuration of the GF, the TiC and Cu coatings are applied on the surface of GF in vapor and liquid phase environments, respectively. The coated or uncoated GF reinforced Cu-based composites are fabricated via a powder metallurgical method. The effect of flake surface coating on the microstructure and thermal conductivities of GF–Cu composites is studied. Furthermore, efforts are devoted to determining predictive models for anisotropic graphite to estimate the interfacial thermal resistance and analyze the TC behavior of GF/Cu composites.

2. Experimental procedure

Electrolytic copper powders (purity >99.9%, mesh −3000, purchased from General Research Institute for Nonferrous Metals, Beijing, China) were used as the matrix powders. The graphite flakes (purity >99.9%, mesh −10, purchased from Alfa Aesar Co., Ltd, Tianjin, China) were sieved through a −30 mesh screen prior to use (25/+30). The SEM image of the sieved GF is shown in figure 1(a). The diameter of the GF ranges from 450 μm to 550 μm with a thickness of approximately 20 μm. The XRD pattern of the as-received GFs is given in figure 1(b). As shown, the sharp peak at θ = 26.45° corresponds to the 002 crystal plane of the graphite phase. According to the Bragg equation, the (002) d-spacing of GF is 3.366 Å, indicating that the as-received material is highly graphitized.

The Cu coating process for the graphite flakes was carried out using an electroless coating technique. More details on this process can be found in [18]. The TiC coating on the graphite flakes was obtained via a chemical reaction between the graphite flakes and chemically vapor-deposited Ti on the surface. During the chemical vapor deposition process, TiCl₃ powders and TiH₂ powders were chosen as the titanium source and reducing agent, respectively. The TiCl₃ was gasified and reduced to Ti atoms by reacting with TiH₂ at a pressure of ~10⁻² Pa and a temperature of 953 K. These generated reactive gaseous Ti atoms were deposited on the surface of graphite flakes. More details on this process can be found in our previous work in [24]. Then, graphite flakes were heated at 973 K in an argon atmosphere for 6 h to form TiC. The reaction of the Ti with graphite over the range from 298–1200 K is given by [25]:

![Figure 1. SEM images (a) and (b) and XRD pattern (c) of the as-received graphite flakes.](image-url)
Figure 2 shows the morphology of the graphite flakes after the Cu (a) and TiC (b) coating processes. The surface of the graphite shows a copper luster (inset image in figure 2(a)). A continuous and homogeneous coating is obtained. The mass fraction of the graphite flakes is approximately 30%. Figure 2(b) shows the morphology of the graphite flakes after the TiC coating process. Compared with the uncoated ones, the graphite flakes after the TiC coating process exhibit a metallic luster, but the presence of the coating is not immediately obvious. When examined at a high magnification, a thin and comparatively homogeneous coating is observed on the surface of the GF, as shown in figure 3(a). The EDS and XRD results are also presented in figure 3(b). The EDS result shows that only the C and Ti elements are detected on the surface of the GF. In the XRD patterns, three sharp peaks at 2θ = 35.91°, 41.70° and 60.45° correspond to diffraction from the 111, 200 and 220 crystal planes of a face centered cubic TiC phase, respectively. From the EDS and XRD results, we conclude that a TiC coating was formed on the surface of the GF after the coating process. The peak of the Ti element in the EDS and the peaks of the TiC phase in the XRD are extremely low, indicating that the coating is very thin. The mass fraction of the TiC-coated graphite flakes is approximately 2%.

During the fabrication process, coated or uncoated flakes at a designed volume fraction were mixed with copper powders and a certain amount of ethyl alcohol and filled into a graphite die in batches. A pressure of 2 MPa was applied to each filling to better align the orientation. Then, the graphite die containing the GF/Cu mixture was placed into a vacuum hot pressing sintering system. Finally, the GF/Cu composites with various fractions (40–70 vol%) of GF were fabricated by hot press sintering at a sintering pressure of 40 MPa and a sintering temperature of 1253 K. The pressure in the filling and the unidirectional pressed sintering process orient the flakes in the direction perpendicular to the pressing direction.

The TCs in perpendicular (X-Y plane) and parallel (Z plane) pressing directions were determined by a laser flash method. The TC of composites could be calculated by the equation: $K = \alpha \rho C_p$, where $\alpha$, $\rho$ and $C_p$ were the thermal diffusivity, density and specific heat, respectively. Thermal diffusivity $\alpha$ was tested by IR-3 thermal physical testing instrument (Changsha Yin Shen Research Instrument, China) at room temperature. The sample size for the thermal diffusivity measurement was 3.8 mm $\times$ 3.8 mm $\times$ 10 mm. An oxygen-free high purity copper (99.999%) with a TC of 400 W m$^{-1}$ K$^{-1}$ was used as reference. The density $\rho$ was measured by an Archimedes’ principle. The specific heat $C_p$ was calculated by rule mixture based on the weight ratio.
3. Results and discussion

3.1. Microstructure and interface of the GF/Cu composites

Figure 4 shows the microstructures of the cross-sections of uncoated-GF/Cu composites with a graphite percentage ranging from 40% to 70%. The graphite (black gray) is homogeneously dispersed to a moderate degree in the copper matrix (light gray). In all the samples, the GFs are basically oriented to the plane perpendicular to the pressing direction. We note that the preferred dispersion and orientation of the GF are observed in all the samples independent of the coating condition. As the GFs increased, the amount of GF overlap increased. However, no obvious macro pores are observed in the samples, as shown in figures 4(a)–(d).

The interfacial structures of the obtained composites with uncoated and coated GF are investigated by FE-SEM. Figure 5(a) shows the FE-SEM micrograph of the interface area of the Cu composite with 50 vol% uncoated GF. Interfacial gaps are observed between the flakes and the matrix due to the poor wettability between the copper and graphite (indicated by the red arrow). However, for the Cu-coated composites (figure 5(b)), good interfacial bonding with no gaps is obtained. The Cu coating enables the Cu atoms to better cover the surface of the graphite and infiltrate into the graphite micropores. Thus, the contact area of the copper and graphite increases significantly compared to a simple mixture of copper and graphite flakes [26]. In the TiC coated composites, the continuous TiC interlayer (dark gray) is in good contact with the GF (black gray) and Cu matrix.
Table 1. The density and relative density of the obtained GF-Cu composites.

| Samples V_{GF} (vol%) | Uncoated           | Cu-coated          | TiC-coated         |
|----------------------|--------------------|--------------------|--------------------|
|                      | Density (g / cm$^3$) | Relative density   | Density (g / cm$^3$) | Relative density | Density (g / cm$^3$) | Relative density |
| 40                   | 6.21               | 99.2%              | 6.24               | 99.6%           | 6.27               | 99.8%           |
| 50                   | 5.54               | 99.2%              | 5.58               | 99.8%           | 5.60               | 99.8%           |
| 60                   | 4.84               | 98.6%              | 4.88               | 99.2%           | 4.86               | 98.4%           |
| 70                   | 4.10               | 96.6%              | 4.20               | 99.1%           | 4.18               | 97.9%           |

(light gray). The thickness of the TiC interlayer is approximately 200 nm. The distribution of the composite elements was examined by EDS line-scanning and was shown to have an overlapping area between the Cu and Ti(C) signals at the interface, suggesting that the copper, to some extent, is diffused into the interlayer and that a strong diffusion bond is formed.

More detailed observations of the interface were performed by TEM on the coated composites. As shown in figure 6(a), the Cu-coated composites have a clear and high-quality contact interface with no microvoids along the interface. In the TiC-coated composites, there is an interlayer of approximately 200 nm between the Cu and the graphite. Excellent contact at the Gr–TiC and TiC–Cu interfaces is formed, and no pores are observed along the interface. A typical high-resolution TEM (HRTEM) image of the TiC-GF interface is shown in figure 6(c). The surface of the GF in contact with the TiC layer was observed to be amorphous. This was confirmed by the corresponding FFT pattern. Such amorphization of the graphitic structure is frequently observed when the carbon source reacts with titanium. It has been reported that the thickness of this amorphous layer can reach as much as 430 nm [27]. This extensive transformation of the graphitic structure to an amorphous state results in a reduction in the TC. However, in this study, the amorphous layer is approximately 5 nm thick, and its negative impact on the TC is limited [28].

### 3.2. Thermo-physical properties of GF/Cu composites

Table 1 shows the thermo-physical properties of the composites with GF volume fractions ranging from 40%–70%. Figure 7 shows the flexural strength of obtained composites. In general, the density and flexural strength of the composites decrease as the amount of graphite flakes increases. Compared with the uncoated composites, the density and strength of the coated composites are higher due to the electroless copper plating improving the interfacial bonding between the copper and the graphite [29]. As shown in figure 5, after the Cu-coating, the number of pores at the interface is greatly reduced. As a consequence, higher density and flexural strength are obtained. For the TiC coated composites, the strong diffusion bonding in the Cu-TiC-C interface results in better strength performance than for the Cu coated ones. Similar results were found in diamond or carbon (graphite) copper matrix composites, which have shown that strong carbide-forming elements (e.g., Ti, Cr, Mo or W) and their carbides can act as middle layers to strengthen the interface [23, 30–32].

Figure 8 shows the measured TCs of the GF/Cu composites. Due to the high TC in the a-axis and the oriented alignment of the flakes, the TC in the X-Y plane is one order of magnitude larger than in the Z direction. As the amount of graphite flakes increases, the TC in the X-Y plane increases, and the TC in the Z plane decreases. An improvement to the TC in the X-Y plane is shown for the coated composites. When the flake volume fraction is 40%, there is a small difference (24 W m$^{-1}$ K$^{-1}$) in the TC. As the volume fraction increases, the difference between the uncoated and coated composites becomes obvious. The TC of the uncoated GF/Cu with 60% GF is approximately 70 W m$^{-1}$ K$^{-1}$ lower than that of the Cu-coated GF/Cu and is 125 W m$^{-1}$ K$^{-1}$ lower than that of the TiC-coated composites. As the graphite content increases, the copper content is further...
reduced. Pores, which are harmful to the TC, form more easily in composites with a high graphite content. This phenomenon is more evident in uncoated composites with poor interfacial bonding, which results in a lower TC.

Comparing Cu-coated composites with TiC-coated composites, the difference is not obvious. In research on diamond-copper composites for electronic packaging applications, the TC varies significantly for different interfacial structures. Composites with a TiC, WC or Mo₂C interlayer between the diamond and copper exhibit a much better TC performance than composites without an interlayer. The TC of coated diamond-Cu composites is 2–3 times higher than for uncoated ones. Zhang [31] reported that when using 60 vol% TiC-

---

**Figure 7.** The flexural strength of the GF/Cu composites as a function of the flake volume fraction.

**Figure 8.** The thermal conductivity of the GF/Cu composites as a function of the flake volume fraction.
coated diamond, the TC of the diamond/Cu composites is enhanced by 170% compared to uncoated samples. The C-TiC-Cu interfacial structure in this study is very similar to the diamond–TiC–Cu in Zhang’s report, but the difference between the un-coated and coated flake composites is only 30–125 W m\(^{-1}\) K\(^{-1}\) (5%–23%). There were no significant differences in the coated composites with different interfacial structures. To further understand the TC behavior of the GF/Cu composites, we modified the Diffuse Mismatch Model (DMM) for anisotropic graphite to estimate the interfacial thermal resistance and used an Effective Medium Approach (EMA) to calculate the TC of the composites.

### 3.3. Modeling

The TC theoretical predictions are made within the framework of the effective medium approximation (EMA) model developed by Nan [33]. This model considers the effect of geometry (the geometrical factors \(L_{11}\) and \(L_{33}\)) and the orientation of the reinforcement (the factor \(\langle \cos^2 \theta \rangle\)), as well as the interface (Kapitza resistance effect \(R\)), and is given as:

\[
K_x = K_y = K_m \frac{2 + f [\beta_1 (1 - L_{11}) (1 + \langle \cos^2 \theta \rangle) + \beta_3 (1 - L_{33}) (1 - \langle \cos^2 \theta \rangle)]}{2 - f [\beta_1 L_{11} (1 + \langle \cos^2 \theta \rangle) + \beta_3 L_{33} (1 - \langle \cos^2 \theta \rangle)]},
\]

\[
K_z = K_m \frac{1 + f [\beta_1 (1 - L_{11}) (1 - \langle \cos^2 \theta \rangle) + \beta_3 (1 - L_{33}) \langle \cos^2 \theta \rangle]}{1 - f [\beta_1 L_{11} (1 - \langle \cos^2 \theta \rangle) + \beta_3 L_{33} \langle \cos^2 \theta \rangle]},
\]

where, \(\beta_i = \frac{k_i - k_m}{k_m + L_{11} (k_i - k_m)} (i = 1, 3)\), \(K_m\) is the TC of the matrix, \(f\) is the volume fraction of the inclusion phase (i.e., flakes).

The geometrical factors \(L_{11}\) and \(L_{33}\) depend on the length-to-diameter ratio \(p\). In the calculation, the mean diameter and thickness of the flakes are 500 \(\mu\)m and 20 \(\mu\)m. Thus, \(p = 0.04\). Then, the geometrical factors are given as:

\[
L_{11} = \frac{p^2}{2(p^2 - 1)} - \frac{p}{2(1 - p^2)^{3/2}} \cosh^{-1} p,
\]

\[
L_{33} = 1 - 2L_{11},
\]

The factor \(\langle \cos^2 \theta \rangle\) describes the orientation of the reinforcement, which is given as:

\[
\langle \cos^2 \theta \rangle = \frac{\int \rho(\theta) \cos^2 \theta \sin \theta d\theta}{\int \rho(\theta) \sin \theta d\theta},
\]

where \(\rho(\theta)\) is a distribution function describing the inclusion phase orientation and \(\theta\) is the tilting angle between the X-Y plane of the composite and the basal plane of the flake. If the tilting angles \(\theta\) of all flakes in the composite are \(0^\circ\), the \(\langle \cos^2 \theta \rangle = 1\). This presents an ideal preferential orientation. If the angles of all flakes are between \(0^\circ\) and \(90^\circ\), and have an uniform distributed, i.e. \(\rho(\theta) = 1\). This indicates that the number of flakes at each angle is equal. The composite is an isotropic and the \(\langle \cos^2 \theta \rangle = 1/3\). In reality, \(\langle \cos^2 \theta \rangle\) ranges from 1/3 to 1. For a highly oriented alignment, \(\langle \cos^2 \theta \rangle\) may be closer to 1.

The terms \(K_{11}^e\) and \(K_{33}^e\) are the TCs of the GF in the basal plane and the c-axis direction, respectively, with consideration to the interfacial thermal resistance. Here, the effective TC can be obtained from the rule of mixtures via a simple series model of the interface-barrier/flake/interface-barrier:

\[
K_{11}^e = \frac{K_{11}}{1 + \frac{2R_{11}K_{11}}{d}},
\]

\[
K_{33}^e = \frac{K_{33}}{1 + \frac{2R_{33}K_{33}}{t}},
\]

where \(R_{11}\) and \(R_{33}\) are the interfacial thermal resistance along the a-axis (basal plane) and the c-axis of the graphite, respectively. The variables \(d\) and \(t\) are the diameter and thickness of the graphite flake. The interfacial thermal resistance \(R\) can be theoretically estimated by the diffuse mismatch model (DMM), which is one of the most widely implemented models for predicting interfacial thermal resistance.

In the DMM, we assume that all the incident phonons scatter diffusely and elastically at the interface between the two materials. The interfacial thermal resistance \(R\) can be expressed as [34]:

\[
R = \left[\frac{1}{4} \sum_n \int_0^{\omega_n} \xi^{1/2} \hbar \omega v_1 D(\omega, v_1) \frac{\partial}{\partial T} f \omega d\omega \right]^{-1},
\]

where \(j\) is an acoustic polarization (one longitudinal and two transverse), \(\omega_p\) is the phonon frequency, \(\omega_c\) is the cutoff frequency, \(v\) is the phonon group velocity, \(D\) is the density of the states, \(\xi^{1/2}\) is the phonon transmissivity from material 1 (the matrix) to material 2 (the reinforcement), and \(f\) is Bose–Einstein occupation function. The
phonon transmissivity from material 1 to material 2, which describes the probability of a phonon diffusely scattering across the interface, is given by

\[
\xi_{1 \rightarrow 2} = \frac{\sum_j \int_0^{\omega_{D,j}} h\omega \nu_{2,j} D_{\text{eff}}(\omega, \nu_{1,j}) f(\omega) d\omega}{\sum_j \int_0^{\omega_{D,j}} h\omega \nu_{1,j} D_{\text{eff}}(\omega, \nu_{1,j}) f(\omega) + \sum_j \int_0^{\omega_{D,j}} h\omega \nu_{2,j} D_{\text{eff}}(\omega, \nu_{2,j}) f(\omega)}.
\]

(9)

For three-dimensional isotropic solids, the Debye density of states is given by

\[
D(\omega, \nu) = \frac{\omega^2}{2\pi^2\nu^3},
\]

(10)

\[
\omega_{D,j} = v_{1,j} \sqrt{6\pi^2 N_a / V_{\text{mol}}},
\]

(11)

where \(N_a\) is Avogadro’s number and \(V_{\text{mol}}\) is the molar volume. For graphite with highly anisotropic properties, an effective two dimensional density of states proposed by Duda [35] is used to describe the \(D(\omega, \nu)\) of graphite flakes:

\[
D_{\text{eff}}(\omega, \nu) = \frac{\omega}{2\pi\nu^2} \cdot \frac{1}{l},
\]

(12)

where \(l\) is the interlayer spacing for the graphite. When calculating the interfacial thermal resistance between the copper and the graphite, we assume that the copper is the matrix (material 1) and graphite is the reinforcement (material 2). Note that only the in-plane phonon velocities are used when calculating the effective two-dimensional state of the density. The accuracy of the model is evaluated by comparing the calculated value with the measured one. The calculated \(R\) is in good agreement with the experimental value in [36] in which the interfacial thermal conductance (the reciprocal of \(R\)) between the graphite and several metals (Al, Au, Ti and Cr) is measured. For example, the interfacial thermal conductivities of metallic Cr and the graphite are about 4.3 × 10^7 W m^{-2} K^{-1} and 4.7 × 10^7 W m^{-2} K^{-1}, respectively [36]. In this model, the corresponding calculated values are 4.7 × 10^7 W m^{-2} K^{-1} and 4.9 × 10^7 W m^{-2} K^{-1}, respectively.

For TiC coated composites, \(R\) includes two interfaces (GF/TiC and TiC/Cu) and the TiC coating itself, i.e.,

\[
R_{\text{coated}} = R_{\text{GF/TiC}} + R_{\text{TiC}}.
\]

The longitudinal and transversal phonon velocities of the TiC can be calculated using the following equations:

\[
\nu_l = \left[\left(B + \frac{4}{3}G\right)/\rho\right]^{1/2},
\]

(13)

\[
\nu_t = \left(G/\rho\right)^{1/2},
\]

(14)

where \(G\), \(B\) and \(\rho\) are the shear moduli, bulk modulus and density, respectively. The value of the carbide coating \(R_{\text{TiC}}\) is given by \(R = b/K\), where \(b\) is the thickness of the carbide layer (200 nm in this calculation) and \(K\) is the TC of the carbide. The related parameters are listed in table 2.

Table 2. Material parameters for calculating the interfacial thermal resistance.

| Parameters | Graphite | Cu [31] | TiC [31] |
|------------|----------|---------|---------|
| TC (W m^{-1} K^{-1}) | \(a\)-Axis: 1000 [8] | \(c\)-Axis: 27 [11] | 345 |
| Density (kg m^{-3}) | 2250 | 8960 | 4930 |
| Specific heat (J kg^{-1} K^{-1}) | 711 | 385 | 568 |
| Phonon velocity (km s^{-1}) | \(a\)-Axis [37]: | \(c\)-Axis [38]: | |
| | T: 23.6 | L: 1.96 | L: 4.91 |
| | L: 15.9 | T: 0.7 | T: 2.5 |
| Bulk modulus (GPa) | — | — | 242 [39] |
| Shear modulus (GPa) | — | — | 186 [39] |
| Calculated results \(R\) (m^2 K W^{-1}): | | | |
| GF/Cu | \(a\)-Axis: \(2.90 \times 10^{-9}\) | \(c\)-Axis: \(4.05 \times 10^{-9}\) |
| GF/TiC/Cu | \(a\)-Axis: \(6.71 \times 10^{-9}\) | \(c\)-Axis: \(2.03 \times 10^{-9}\) |

* TC of pure copper fabricated by hot pressing.
Figure 9 shows the comparison between the TC obtained from the experimental data and the estimated values via the EMA. In an ideal condition where all the flakes are parallel to the X-Y plane, the orientation function is defined as $\langle \cos^2 \theta \rangle = 1$. The blue dotted line, denoted as 'Estimated Cu coated (0.937)', shows the best fit curves for our data. The corresponding value of $\langle \cos^2 \theta \rangle$ is 0.937 corresponds to a maximum $\theta$ of approximately 21°. In other words, the orientations of all the flakes range from 0°–21° and have the same proportions. This seems reasonable when we examine the orientation angle in figure 4. Compared to the TiC coated composites, the curve fit variance is larger. We note that 60% Ti-coated composite has a relative high TC of 668 W m$^{-1}$ K$^{-1}$. According to the Image Statistics Analysis of GF orientation (in supplementary material is available online at stacks.iop.org/MRX/6/125632/mmedia), we found that tilting angles ($\theta$) of 80% flakes are less than 12°. The number of angles that greater than 12° has dropped significantly. When maximum $\theta$ is 12°, the corresponding estimated TC of 60% TiC-coated composite is 658 W m$^{-1}$ K$^{-1}$. The experiment agrees with the theoretical results. Thus, we believe that the reason for large curve fit variance is not the different interfacial structure but the difference in the orientation degree for each sample. During manufacturing, the mixing and loading of the powder mixtures require detailed experience and extreme care. A single disordered flake could impact the alignment of the flakes around it, resulting in a noticeable decrease in the TC.

In order to study the effect of flake orientation on TC, the 60 vol% flake/Cu composites with Cu-graphite interface is analyzed (set $R_{ij} = 2.90 \times 10^{-9}$ m$^2$ K W$^{-1}$, maximum tilting angle is variable). Figure 10 shows the effect of GF orientation on the theoretical TC values, where $\theta_{\text{max}}$ is the maximum angle between the flake basal plane and the X-Y plane existing in the matrix. For example, $\theta_{\text{max}} = 45^\circ$ means that the orientations of all the flakes are in the range from 0°–45° and have the same proportions. As shown in figure 10, the TC in the X-Y plane is sensitive to variations in flake orientation. For example, when $\theta_{\text{max}} = 30^\circ$, the TC decreases by 33.7% compared with the perfect orientation. This indicates that the imperfect orientation leads to a decrease in the TC.
in the X-Y plane. Thus, variations in the TC in the X-Y plane are reasonable and unavoidable. For the Z plane, the orientation has little impact due to the low TC in the c direction. The experimental data basically ranges within the forecast interval. When we consider measurement errors, this result is reasonable.

We note that the estimated value of the TiC coated composites is not much different from the Cu coated one. It is known that when heat passes through the composites, great losses occur at the interface. The ability to transmit heat, i.e., TC, shows a negative correlation with the interfacial thermal resistances for other fixed conditions. Theoretical analyses and experiments indicate that the interfacial thermal resistance of the diamond/copper is approximately $10^{-7}$ m² K W⁻¹. Zhang et al calculated the interfacial thermal resistances for Ti-coated diamond/Cu composites. The interfacial thermal resistances of Diamond/285 nm thickness TiC/Cu is $1.4 \times 10^{-8}$ m² K W⁻¹ [21]. The TCs of coated diamond/Cu composites are 2–3 times those of the uncoated ones. When compared with diamond reinforced copper composites, the interfacial thermal resistances of the graphite in the c-axis ($R_{13}$) are within the same order of magnitude ($\sim 10^{-8}$ m² K W⁻¹), whereas the graphite in the a-axis ($R_{31}$) exhibit a lower interfacial thermal resistance ($\sim 10^{-9}$ m² K W⁻¹). In order to further analyze the influence of interfacial thermal resistance, we set the orientation factor ($\cos^2 \theta$) to 0 in the equation (1). Then, we can obtain the theoretical estimates for the TC in the X-Y plane of the composites with 60 vol% GF as a function of the interfacial thermal resistance, as is shown in figure 11. Increasing the interfacial thermal resistance causes the TC of the composites to first decrease slightly and then rapidly. Compared with the perfect interface when the TCs of the composites decease by 20%, the corresponding interfacial thermal resistance is approximately $8 \times 10^{-8}$ m² K W⁻¹. When the interfacial thermal resistance is lower than $8 \times 10^{-8}$ m² K W⁻¹, the TC remains at a good level. In particular, for the interval marked with a short red dashed line, the fluctuations of the interfacial thermal resistance have a limited impact on the TC. According to the previous calculation, the composites with both Cu–C and Cu–TiC–C interfacial structures exhibit a low interfacial thermal resistance for graphite in the a-axis over the marked interval. Meanwhile, graphite flakes have an excellent TC in the a-axis. Thus, the composites with graphite reinforcement show good and similar TC performances in the X-Y plane.

Figure 11 also shows a schematic diagram of different interface structures and their corresponding interfacial thermal resistance. According to the theoretical calculation of interfacial thermal resistance, the values of TCs with different interfacial structures are indicated by arrows. For purposes of comparison, the unknown interfacial thermal resistance of uncoated composites (Cu–voids–graphite interface structure) is inversely determined by submitting the experimental TC data and ($\cos^2 \theta$) = 0.937 into equation (1). Its average value of estimated interfacial thermal resistance is also shown in figure 11. It is suggested that the excellent TC behavior of the GF/Cu composites depends on (1) a well-contacted interface with no microvoids; and (2) based on rule (1), establishment of a clean interface while avoiding interfacial products or reducing the thickness of interlayer as much as possible. By considering that a Cu–C direct bonding is poor, the risk of interfacial cracking upon thermal cycling in a thermal management application may turn the Cu-C structure into a Cu-voids-C structure. In that case, the TCs will decrease significantly.

In summary, we established an EMA with a modified Diffuse Mismatch Model for anisotropic reinforcement and compared the model with the experimental data. This prediction approach is not completely precise due to the lack of information on the flake orientations. However, it is still appealing due to its simplicity and ease of application. By using this approach, the effect of the interfacial thermal resistance on the TC of
composites is discussed, which is valuable for scientists seeking to design new devices and materials using graphite flakes. From the aspect of improving the TC, it is favorable to establish a simple, clean and well-contacted Cu-graphite interface. Different from diamond-Cu composites, the multiple layer interfacial structure in the Cu-graphite composites could increase the interfacial thermal resistance in most cases. However, the high-quality multiple layer structure, such as Cu-TiC-graphite with a thin TiC interlayer, is more favorable, as it could strengthen the interface bonding and if appropriately controlled maintain the TC at a high level. More detailed studies could focus on the effect of the interface structure on the mechanical properties to improve the comprehensive performance of the materials and control of the orientation of the graphite flakes. These topics are currently being studied in our lab.

4. Conclusions

(1) Graphite flake/Cu composites with a Cu or TiC coating on the graphite surface were fabricated by the vacuum hot pressing method. Observations of the composite’s microstructures reveal pores at the interface of the GF/Cu composites from the direct combination of GF and Cu. Good contacting Cu-graphite and Cu-TiC-graphite structures are established, respectively, when Cu and TiC interlayers are introduced.

(2) The coated composites exhibit better TC and flexural strength. The X-Y plane TC of the TiC- and Cu-coated composites with 60 vol% graphite flakes reaches as much as 668 W m$^{-1}$ K$^{-1}$ and 612 W m$^{-1}$ K$^{-1}$, respectively. The flexural strengths for this addition are 48 MPa and 42 MPa, respectively, which can be used for heat dissipation applications.

(3) A modified Diffuse Mismatch Model (DMM) for anisotropic graphite was established to estimate the interfacial thermal resistance, and the Effective Medium Approach (EMA) was used to analyze the TC behavior of the GF/Cu composites. The results show that compared with diamond-Cu composites, the interfacial thermal resistance of graphite in the a-axis is one order of magnitude lower.

(4) The calculation results indicate that the interfacial thermal resistance in the interval less than $1 \times 10^{-8}$ m$^2$ K W$^{-1}$ has a limited impact on the TC in the X-Y plane. The TC could be further enhanced if preferable alignment control is obtained.

Acknowledgments

This research was financially supported by the Natural Science Foundation of China (No. 51704113), Hunan Provincial Natural Science Foundation of China (No. 2018JJ3172) and the Scientific Research Fund of Hunan Provincial Education Department (No. 17C0621 and No. 18B230).

Author contributions:

Q Liu and S Tang conceived of and designed the experiments. Q Liu and J Cheng performed the experiments and analyzed the data. Y Chen and Y Ou contributed to the materials processing. Q Liu wrote the paper. F Wang, J Huang and Z Lv revised the paper. All authors have discussed the results and read and approved the final manuscript.

Conflicts of interest

The authors declare no conflict of interest.

ORCID iDs

Qian Liu https://orcid.org/0000-0003-0794-7005

References

[1] Chen J, Ren S, He X and Qu X 2017 Properties and microstructure of nickel-coated graphite flakes/copper composites fabricated by spark plasma sintering Carbon 121 25–34

[2] Subramaniam C, Yasuda Y, Takeya S, Ata S, Nishizawa A, Futaba D, Yamada T and Hata K 2014 Carbon nanotube-copper exhibiting metal-like thermal conductivity and silicon-like thermal expansion for efficient cooling of electronics Nanoscale 6 2669–74
Zhang Y, Zhang H L, Wu J H and Wang X T 2011 Enhanced thermal conductivity in copper matrix composites reinforced with
Zhang C, Wang R, Cai Z, Peng C, Feng Y and Zhang L 2015 Effects of dual-layer coatings on microstructure and thermal conductivity
Moustafa S, El-Badry S, Sanad A and Kieback B 2002 Friction and wear of copper
Xie G, Ju Z, Zhou K, Wei X, Guo Z, Cai Y and Gang Z 2018 Ultra-low thermal conductivity of two-dimensional phononic crystals in the
Zhang C, He X, Liu Q, Ren S and Qu X 2015 Fabrication and thermo-physical properties of graphite flake/Al composite with a SiC nano-layer on graphite surface Mater. Des. 108 250–8
Ren S, Hong Q, Chen J, He X and Qu X 2015 The influence of matrix alloy on the microstructure and properties of (flake graphite + diamond)/Cu composites by hot pressing J. Alloys Compd. 652 351–7
Zhou C, Huang W, Chen Z, Ji G, Wang M L, Chen D and Wang H W 2015 In-plane thermal enhancement behaviors of Al matrix composites with oriented graphite flake alignment Composites Part B 78 256–62
Priezo R, Molina J M, Narciso J and Louis E 2011 Thermal conductivity of graphite
Li J, Zhang H, Zhang Y, Che Z and Wang X 2015 Microstructure and thermal conductivity of Cu
Kang Q, He X, Ren S, Zhang L, Wu M, Liu T, Liu Q, Guo C and Qu X 2013 Preparation of high thermal conductivity copper–diamond composites using molybdenum carbide–coated diamond particles J. Mater. Sci. 48 6133–40
Chu K, Jia CC, Guo H and Li W S 2013 On the thermal conductivity of Cu–Zr/diamond composites Mater. Des. 45 36–42
Liu Q, He X B, Ren S B, Liu T T, Kang Q P and Qu X H 2013 Effect of titanium carbide coating on the microstructure and thermal conductivity of short graphite fiber/copper composites J. Mater. Sci. 48 5810–7
Liu Q, He X B, Ren S B, Liu T T, Kang Q P and Qu X H 2013 Fabrication and thermal conductivity of copper matrix composites reinforced with Mo2C or TiC coated graphite fibers Mater. Res. Bull. 48 6811–7
Zhang H-M, He X-B, Qu X-H, Liu Q and Shen X-Y 2013 Microstructure and thermal properties of copper matrix composites reinforced with titanium-coated graphite fibers Rare Met. 11 1–6
Li X, Dong Z, Westwood A, Brown A, Zhang S, Brydson R, Li N and Rand B 2008 Preparation of a titanium carbide coating on carbon fibre using a molten salt method Carbon 46 696–703
Xie G, Ju Z, Zhou K, Wei X, Guo Z, Cai Y and Gang Z 2018 Ultra-low thermal conductivity of two-dimensional phononic crystals in the incoherent regime NPI Comput. Mater. 4 21
Xie G, Ding D and Zhang G 2018 Phonon coherence and its effect on thermal conductivity of nanostructures Adv. Phys. X 3 719–754.
Zhu Y, Bai H, Xue C, Zhou R, Xu Q, Tao P, Wang C, Wang J and Jiang N 2016 Thermal conductivity and mechanical properties of a flake graphite/Cu composite with a silicon nano-layer on a graphite surface RSC Adv. 6 98190–6
Liu Q, He X B, Ren S B, Zhang C, Liu T T and Qu X H 2014 Thermophysical properties and microstructure of graphite flake/copper composites processed by electrolysis copper coating J. Alloys Compd. 587 255–9
Li J, Zhang H, Zhang Y, Che Z, and Wang X 2015 Microstructure and thermal conductivity of Cu/diamond composites with Ti-coated diamond particles produced by gas pressure infiltration J. Alloys Compd. 647 941–6
Kang Q, He X, Ren S, Zhang L, Wu M, Liu T, Liu Q, Guo C and Qu X 2013 Preparation of high thermal conductivity copper–diamond composites using molybdenum carbide–coated diamond particles J. Mater. Sci. 48 6133–40
Chu K, Jia CC, Guo H and Li W S 2013 On the thermal conductivity of Cu–Zr/diamond composites Mater. Des. 45 36–42
Liu Q, He X B, Ren S B, Liu T T, Kang Q P and Qu X H 2013 Effect of titanium carbide coating on the microstructure and thermal conductivity of short graphite fiber/copper composites J. Mater. Sci. 48 5810–7
Liu Q, He X B, Ren S B, Liu T T, Kang Q P and Qu X H 2013 Fabrication and thermal conductivity of copper matrix composites reinforced with Mo2C or TiC coated graphite fibers Mater. Res. Bull. 48 6811–7
Zhang H-M, He X-B, Qu X-H, Liu Q and Shen X-Y 2013 Microstructure and thermal properties of copper matrix composites reinforced with titanium-coated graphite fibers Rare Met. 11 1–6
Li X, Dong Z, Westwood A, Brown A, Zhang S, Brydson R, Li N and Rand B 2008 Preparation of a titanium carbide coating on carbon fibre using a molten salt method Carbon 46 696–703
Kovačič J and Emmer S 2011 Thermal expansion of Cu/graphite composites: effect of copper coating Krovove Mater. 49 411–6
Lloyd J C, Neubauer E, Barcena J and Clegg W J 2010 Effect of titanium on copper–titanium/carbon nanofibre composite materials Compos. Sci. Technol. 70 2284–9
Zhou C, Ji G, Chen Z, Wang M, Addad A, Schyvers D and Wang H 2014 Fabrication, interface characterization and modeling of oriented graphite flake/Si/Al composites for thermal management applications Mater. Des. 63 719–28
Moustafa S, El-Badry S, Sanad A and Kieback B 2002 Friction and wear of copper–graphite composites made with Cu-coated and uncoated graphite powders Wear 253 699–710
Ren S B, Shen X Y, Guo C Y, Liu N, Zang J B, He X B and Qu X H 2011 Effect of coating on the microstructure and thermal conductivities of diamond–Cu composites prepared by powder metallurgy Compos. Sci. Technol. 71 1550–5
Zhang Y, Zhang H L, Wu J H and Wang X T 2011 Enhanced thermal conductivity in copper matrix composites reinforced with titanium-coated diamond slicesScr. Mater. 65 1097–100
Zhang C, Wang R, Cai Z, Peng C, Feng Y and Zhang J 2015 Effects of dual-layer coatings on microstructure and thermal conductivity of diamond/Cu composites prepared by vacuum hot pressing Surf. Coat. Technol. 277 299–307
Nan C W, Birringer R, Clark D R and Gleiter H 1997 Effective thermal conductivity of particulate composites with interfacial thermal resistance J. Appl. Phys. 81 6692–9
Szwartz E and Pohl R 1989 Thermal boundary resistance Rev. Mod. Phys. 61 605–68
Duda J C, Smoyer J L, Norris P M and Hopkins P E 2009 Extension of the diffuse mismatch model for thermal boundary conductance between isotropic and anisotropic materials Appl. Phys. Lett. 95 031912
Schmidt A J, Collins K C, Minnich A J and Chen G 2010 Thermal conductance and phonon transmissivity of metal–graphite interfaces J. Appl. Phys. 107 104907
Sun K, Stroscio M A and Dutta M 2009 Graphite c-axis thermal conductivity Superlattices Microstruct. 45 60–4
Duda J C, Hopkins P E, Beechem T E, Smoyer J L and Norris P M 2010 Inelastic phonon interactions at solid–graphite interfaces Superlattices Microstruct. 47 550–5
Medvedeva N, Enayashin A and Ivanovskii A 2011 Modeling of the electronic structure, chemical bonding, and properties of ternary silicon carbide TiSiC2 J. Struct. Chem. 52 785–802