Article

Improvement in Mechanical and Thermal Properties of Graphite Flake/Cu Composites by Introducing TiC Coating on Graphite Flake Surface

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Abstract: In this work, TiC coating was successfully deposited on a graphite flake surface via molten salt technique, for the purpose of promoting the interfacial connection between Cu and graphite flake. Vacuum hot pressing was then employed to prepare TiC-coated graphite flake/Cu composite. The results indicate that introducing TiC coating on graphite flake surface can evidently reduce the pores and gaps at the interface, resulting in a significant improvement on the bending strength. When the TiC-coated graphite flake content is 60 vol%, the bending strength is increased by 58% compared with the uncoated one. The coefficient of thermal expansion dropped from 6.0 ppm·K−1 to 4.4 ppm·K−1, with the corresponding thermal conductivity as high as 571 W·m−1·K−1. The outstanding thermal conductivity, apposite coefficient of thermal expansion, as well as superior processability, make TiC-coated graphite flake/Cu composite a satisfactory electronic packaging material with vast prospect utilized in microelectronic industry.

Keywords: graphite flake; composites; interface; thermal properties

1. Introduction

Heat removal has become even more important for electronic device due to the constantly advancing power density, as well as the sustained miniaturization of circuits and chips in modern electronic industry. In order to guarantee the performance and maintain the reliability of electronic devices, thermal management materials, serving as heat transfer mediums, should possess high thermal conductivity (TC). This ensures these mediums efficiently dispel heat, which is generated from the electron device, and applicable coefficient of thermal expansion (CTE), commensurate with the silicon substrate for minimizing thermal stress. The metal matrix composite, incorporating high TC filler, can fulfill the requirements in thermal management. Cu has a relatively high TC among metals, and an acceptable price, which can make it a preferred choice for the matrix [1–4]. Among Cu matrix composites, the traditional thermal management materials such as SiC/Cu and W/Cu are no longer to fulfill the increasing requirements in the electronics industry, due to their TC lower than 300 W·m−1·K−1 [5,6]. Recently, diamond has been widely investigated as a filler, introduced into Cu matrix, because of its outstanding TC and relatively low CTE [7–11]. Indeed, the resulting diamond/Cu composites exhibit extraordinary TC and suitable CTE, but the poor machinability, especially in composites with a high-volume fraction and large diamond size, have been obstacles for a wide range of commercial applications. Thus, there is an urgent requirement for filler, with high TC, low CTE, and ease of processing.
Graphite flake (GF), an allotrope of carbon, which has remarkable TC and negative CTE in the basal plane, good machining property, as well as a reasonable cost, has drawn much recent attentions for thermal management [12–16]. However, an inevitable problem for the fabrication of graphite flake/Cu (GF/Cu) composites, is that there is no chemical reactivity or atom diffusion between Cu and graphite, rendering poor interface connection. Several efforts have been invested to solve this troublesome problem, and the results show that depositing carbide coating on the GF surface can significantly promote the interfacial combination [17,18]. The reported coating techniques, such as sol-gel technique, high speed impact treatment technique, or chemical vapor deposition more or less suffer from several defects, including expensive equipment, high synthesis temperature, as well as difficulty in controlling thickness. By contrast, molten salt synthesis technique offers a facile way of synthesizing high quality and low-cost carbides coating on GF [19,20]. Bai et al. have synthesized boron carbide-boron coating on the GF surface, through molten salt technique, and found that the interface connection between GF and Cu matrix were markedly enhanced by this coating [17]. Zhu et al. also found the same effects of the SiC coating [18]. In summary, these studies mentioned above mainly concentrate on the influence of carbide coating on the TC, while the effect on bending strength and CTE, is rarely investigated. Besides, adding large size fillers can reduce the thermal resistance, but the diameter of GF, used in the aforementioned research, were all lower than 600 μm because of the difficulty in deposits uniform carbide coating on the large GF surface. Thus, it is vital significance to explore the method of depositing carbide coating on the large size GF and investigate the corresponding influence on microstructure and properties of graphite flake/Cu composites.

In this study, TiC coating was selected to improve the interfacial bonding between GF and Cu, since it has a higher TC than other carbides, such ZrC, Cr2C3 and Cr3C2. A uniform and continuous TiC coating was prepared on the GF surface via molten salt approach under flowing Ar atmosphere, followed by the TiC-coated graphite flake/Cu composites, with well aligned GF orientation were manufactured using vacuum hot-pressing method. The microstructure and phase composition of the TiC-coated GF were well studied, and the effects of TiC coating on the interface structure, bending strength, TC, and CTE of the resultant TiC-coated graphite flake/Cu (TiC-GF/Cu) composites were systematically investigated.

2. Experimental Procedure

2.1. Raw Materials

Natural GF (purity 99.9%), with a mean diameter of 1000 μm, was provided by Alfa Aesar Chemical Co., Ltd. (Shanghai, China). Figure 1a shows the SEM image of raw GF, which presented a neat plate-like morphology. Cu powders (purity 99.9%), with an average particle size of 5 μm, and Ti powders (purity 99%), an average particle size of around 40 μm was acquired from Beijing Xin Rong Yuan Technology Co., Ltd. (Beijing, China). As displayed in Figure 1b,c, the Cu particles are near elliptical, while the Ti particles are irregular. NaCl and KCl were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

![Figure 1. Cont.](image-url)
2.2. Synthesizing TiC Coating on GF

TiC coating was deposited on GF surface through molten salt approach. First, NaCl and KCl were homogeneously blended by a ceramic mortar, according to the molar ratio of 1:1, after which the mixed salt, GF and Ti powder, according to the mass ratio of 30:10:1, were mixed by a rolling mixer machine. Then, the mixed powders were heated to 950 °C and held for 1 h under flowing argon in a tube furnace. After sintering, the cooled and solidified product was decanted in hot deionized water and sieved, which was repeated several times to eliminate residual Ti powders and salt. Finally, the resulting product was oven-dried at 60 °C for 4 h and kept in a desiccator.

2.3. Fabrication of Composites

The composites, containing various GF content, were fabricated by the following procedures. First, a desired proportion (30, 40, 50, and 60 vol%) of GF and TiC-coated GF were mechanically mixed with Cu powders, and a certain amount of alcohol, respectively. Subsequently, the mixed powders were decanted in a graphite mold and sintering at 980 °C for 0.5 h in vacuum atmosphere. In the sintering process, a unidirectional pressure of 40 MPa was employed to guarantee densification when the temperature reached 980 °C and held until the temperature dropped to 400 °C.

2.4. Characterization

XRD patterns were obtained by X-ray diffraction spectrometer (XRD, Rigaku Ultima IV for powder samples and Rigaku SmartLab for bulk samples, Tokyo, Japan) using Cu Kα radiation. The surface coating compositions of TiC-coated GF were determined by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, Waltham, MA, USA) using Al Kα radiation. The microstructure and element distribution of the interface were characterized by field emission environmental scanning electron microscopy (SEM, Quanta FEG 450, Hillsboro, OR, USA). The high-resolution lattice fringe images at the interface were obtained by spherical aberration corrected transmission electron microscope (TEM, Titan Cubed Themis G2 300, Hillsboro, OR, USA). Three-point bending tests were performed on the electromechanical universal testing machine (SANS CMT 6104, Shanghai, China). The dimension of bending test sample is 3.5 mm × 3.5 mm × 25 mm. Limited by the sample size, only the bending strength of the X-Y plane was measured. The specimens, with a size of Φ 10 mm × 3.5 mm, were carried out on laser flash instrument (Netzsch LFA 427, Selb, Germany) to measure room temperature thermal diffusivity (α). The sample density (ρ) was calculated according to Archimedes’ theorem. The specific heat capacity (C_p) was obtained according to the linear rule of mixtures, by using the C_p of respective components. Thus, the TC of the composites can be derived from the formula: K = αρC_p. The CTE values were measured using the sample dimension of Φ 12 mm × 6 mm in the temperature, ranging from 25 °C to 150 °C, by a dilatometer (Netzsch DIL 402 C, Selb, Germany). Before CTE measuring, the sample was heated to 250 °C for stress relief annealing.
3. Results and Discussion

3.1. Observation and Characterization of TiC-Coated Graphite Flake

The representative morphologies of the pristine GF and TiC-coated GF are presented in Figure 2. As shown in Figure 2c,d, the coating layer was uniformly and compactly overlaid on the GF, and the TiC-coated GF still maintains the original shape. The magnification image of the coating surface (Figure 2e) reveals that the coating layer is constituent of numerous sub-micro-sized granules. In order to identify the composition of the coating layer, the XRD pattern of the TiC-coated GF is displayed in Figure 2f. As seen, apart from graphite diffraction peaks, two peaks at 2θ value of 35.88° and 41.66° appear, confirming the formation of TiC on the GF surface. Although the carburizing reaction, between metal and carbon materials in the molten salt, has not yet been thoroughly understood, the dominant reaction mechanism considers that the metals, particularly the transition metal, which has vacant electron orbitals, would dissociate delocalized electrons in the molten salt and simultaneously generate mobile cation, a state which can be regarded as intermediate between metallic and ionic [21]. Thereby, the carbide formed through the migration of Ti cations from Ti powders surface to the GF surface with subsequent reaction in the molten salt. The chemical reaction between GF and Ti in the molten salt can be represented as [22]:

$$\text{Ti} + \text{C} \text{ (graphite)} \rightarrow \text{TiC}, \Delta G = (-184,116.4 + 10.60445 \times T) \text{ J·mol}^{-1}$$  \hspace{1cm} (1)

$\Delta G$ for the formation of TiC at 950°C is calculated to be $-171,146$ J·mol$^{-1}$. Therefore, it demonstrates TiC can be thermodynamically formed at this temperature.
The corresponding XPS spectra of the TiC-coated GF is shown in Figure 3, indicating the chemical bond on GF surface. Figure 3b represents the binding energy of C 1s, the observed main peak (284.79 eV) represents the C-C bonding of the crystal graphite, while the peaks at 281.94 eV and 285.59 eV are corresponding to the C-Ti and C-O bonding [23]. Figure 2c reveals the Ti 2p spectrum, which can be divided into six peaks. The peaks at 455.26 eV, 455.88 eV, and 461.43 eV originate from Ti-C bond, indicating the existence of TiC [24]. The other three peaks at 457.00 eV, 459.00 eV, and 464.53 eV belong to the Ti-O bond, manifesting the presence of titanium oxide, which is due to the peculiarity of easily absorbing oxygen of Ti. Figure 3d shows the O 1s core level spectrum, the peaks at 531.90 eV and 530.41 eV are assigned to O-C and O-Ti bond, corresponding to the C-O and Ti-O bond in Figure 3b,c [25]. The XPS results further confirm that the GF surface is coated by TiC.

Figure 3. XPS spectra of TiC-coated GF: (a) full spectra, (b) C1s, (c) Ti2p, (d) O1s.

3.2. Microstructure and Phase Composition of TiC-Coated Graphite Flake/Cu Composites

The representative SEM images of GF distribution, within the TiC-coated graphite flake/Cu composites, in a Z direction (parallel to the pressing direction) are depicted in Figure 4. The GF are evenly embedded in the Cu matrix and mainly oriented consistently, separated from each other and stacked in parallel. These well GF alignments will contribute to achieving superior in-plane TC along the preferred orientation. Since the TiC coating is too thin, no carbide is observed at the current magnification.
The XRD results in the direction perpendicular to the pressing direction (X-Y plane) and parallel to the pressing direction (Z direction) of the composites are displayed in Figure 5. In the X-Y plane, apart from the strong diffraction signals of graphite and Cu, two weak diffraction peaks, which are only observed at the 2θ angles of 35.90° and 41.74° in the TiC-coated graphite flake/Cu composite, are identified as the (111) and (200) crystal plane of TiC, demonstrating the coating layer still exist after sintering. As described in Figure 5b, the diffraction peaks in Z direction are nearly the same as that in X-Y plane except the diffraction peaks intensity of graphite. Obviously, the intensity of (002) crystal plane of graphite is ultra-low in the Z direction and the (004) crystal plane peak of graphite even disappears. Furthermore, two weak diffraction peaks belonging to (100) and (101) crystal plane of graphite appear. This discrepancy is relevant to the particular two-dimensional layered structure of graphite, and generally its appearance indicates that the GF exhibits preferred orientation inside the graphite flake/Cu composite [26].
flakes compared to the uncoated one. As a result, an intimate interface, without obvious pores and fissures, is obtained in the TiC-coated graphite flake/Cu composites [27,28]. The elemental mapping clearly shows the enrichment of Ti element as well as plenty of C element at the interfacial layer. No obvious signal of Ti element was detected in the Cu matrix, except the region adjacent to the interfacial layer, indicating only a weak inter-infiltration, between the Cu matrix and TiC coating, during the sintering process. Figure 7 shows the detailed characteristic of the interfacial layer explored by TEM. The result clearly indicates that the interfacial layer is composed of polycrystalline structure of TiC, which sufficiently prove that the carbide is still covered on GF surface after vacuum hot processing sintering.

Figure 6. (a) Interfacial morphology of graphite flake/Cu composite, (b) Interfacial morphology of TiC-coated graphite flake/Cu composite; and (c) the element distribution in (b).

Figure 7. TEM image with the corresponding selected area electron diffraction pattern and HRTEM lattice image of the TiC interfacial layer.
Figures 8 and 9 show the high resolution TEM (HRTEM) photos of the composites interface. Figure 8a reveals the interface characteristic of graphite flake/Cu composite, which can be divided into three regions. The corresponding morphologies of the interface zones labeled 1, 2, and 3 are shown in Figure 8b–d, respectively. Evidently, the result reveals that a discontinuous amorphous layer exists between the Cu matrix and crystalline graphite, which may be attributed to the imperfection of the raw GF surface itself.

![HRTEM photos of the composites interface](image_url)

**Figure 8.** TEM observation of uncoated graphite flake/Cu composite: (a) typical Cu/GF interface photo, (b–d) HRTEM lattice image of position 1–3 in (a).

Figure 9 discloses the detailed characteristic of GF/TiC/Cu interface in TiC-coated graphite flake/Cu composite. Figure 9a delineates the representative HRTEM interface photograph of TiC/Cu interface. An obvious lattice distortion appears between TiC (200) plane and Cu (111) plane, which can be principally attributed to the slight dissolution of TiC into Cu matrix. Commonly, such lattice distortion is greatly conducive to promoting interface combination but is slightly adverse to phonon transmission. Figure 9b shows the HRTEM image of the interface between the TiC interfacial layer and GF. Obviously, the GF and TiC interfacial layer is separated by a transition layer rather than directly connected. The corresponding HRTEM images of the interface between the transition layer and TiC (numbered 1), as well as the interface between the transition layer and GF (numbered 2) are shown in Figure 9c,d, respectively. Combining Figure 9c,d, the transition layer is identified as an amorphous phase, according to the corresponding Fast Fourier Transform. The thickness of amorphous layer is about 60–90 nm, which is significantly larger than that in the uncoated graphite flake/Cu composite (seen in Figure 8a), indicating that it may be formed in the molten salt process instead of the imperfection coming from the raw GF itself. In the molten salt process, the C atoms from the GF surface firstly reacted with activated Ti cation to produce TiC layer. Subsequently, the intimal C atoms gradually diffused through the newly formed TiC layer to participate in the carbonization reaction because C atoms have a much higher speed of traversing TiC than that of Ti atoms crossing TiC [29]. Due to the absence of chemical bond between every adjacent graphene in the crystalline graphite,
the long-range order carbon atoms close to the GF surface easily transform into short-range order once part of the C-C $sp^2$ bonding break. Besides, not all these short-range order C atoms can diffuse through the ever-thickening TiC layer, to generate carbide in the molten salt process. Thus, part of short-range order C atoms remained between the TiC layer and crystalline graphite after the molten salt process, leaving an amorphous layer.

![Figure 9](image-url)

**Figure 9.** Interface characteristic of TiC-coated graphite flake/Cu composite: (a) HRTEM lattice image of Cu/TiC interface, (b) typical HRTEM image of TiC/GF interface, (c) HRTEM photo of interface 1 in (b), (d) HRTEM photo of interface 2 in (b).

### 3.3. Bending Strength

The X-Y plane bending strengths of the composites are described in Figure 10. Clearly, the value is inversely proportional to the GF content, due to the low bending strength of GF (34.2 MPa) [30] with respect to Cu (170 MPa) [31]. Meanwhile, the bending strength of TiC-coated graphite flake/Cu composite is notably higher than the uncoated one. Especially for 60 vol% TiC-coated graphite flake/Cu composite, the bending strength rises to 53 MPa, a 58% increase of the uncoated one. The improvement can ascribe to the following factors. Firstly, the TiC interfacial layer tightly connects the Cu matrix and the GF, giving rise to an intimate interface, thereby inhibiting the sliding of GF to a certain extent. Secondly, the carbide possesses a fairly high strength and its break needs to consume more energy.
hereby resists the micro-cracks propagating along the GF surface. As a result, the fracture occurred inside the GF instead of GF surface, seen in Figure 11a. Differently, in TiC-coated graphite flake/Cu composite, the TiC coating reduces the interfacial defects and thereby resists the micro-cracks propagating along the GF surface. As a result, the fracture occurred inside the GF instead of GF surface, seen in Figure 11b.

![Graph showing bending strength versus GF content](image)

**Figure 10.** The X-Y plane bending strength of the graphite flake/Cu and TiC-coated graphite flake/Cu composite.

Figure 11 exhibits the SEM fractographs of the obtained composites after the bending test in X-Y plane. In graphite flake/Cu composite, cracks will preferentially germinate in the interfacial defects, such as pores and gaps, and subsequently spread along the poorly connected interface as the load gradually increases, finally resulting in the GF extracted out from the matrix, as shown in Figure 11a. Differently, in TiC-coated graphite flake/Cu composite, the TiC coating reduces the interfacial defects and thereby resists the micro-cracks propagating along the GF surface. As a result, the fracture occurred inside the GF instead of GF surface, seen in Figure 11b.

![SEM images of fracture morphologies of composites](image)

**Figure 11.** Typical SEM images of fracture morphologies of composites after bending test in X-Y plane of (a) uncoated and (b) TiC coated graphite flake/Cu composites.

### 3.4. Thermal Conductivity

Figure 12 depicts the TC along X-Y plane and Z direction of graphite flake/Cu and TiC-coated graphite flake/Cu composites. The TC, in the two directions, show a converse tendency with an increase in GF content, and apparently the composites exhibit obviously anisotropic characteristics. It is easy to understand of this converse tendency, since the GF possesses a higher intrinsic TC than Cu matrix in the X-Y plane, but a lower intrinsic TC than Cu matrix in the Z direction [32,33]. However, the TiC-coated graphite flake/Cu composites exhibit lower TC than the uncoated one, which can be attributed to two reasons. On one hand, the solid solution deriving from inter-diffusion between the TiC coating and Cu matrix can trigger a growth of phonon scattering thus deteriorates the heat transfer ability [17,18]. On the other hand, the formation of amorphous layer between the GF and TiC interfacial layer not
only can induce the phonon scattering but also possess extremely low TC, resulting in a reduction in the interfacial thermal conductance [34,35]. Although the introduction of TiC coating reduces the TC, whereas the TiC-coated graphite flake/Cu composites still exhibit a very high value. The highest TC of TiC coated graphite flake/Cu composites reaches 571 W m\(^{-1}\) K\(^{-1}\), which is acquired at the volume fraction of 60%.

To better comprehend the influence of TiC coating on the TC of the composites, the effective medium approach (EMA) model was employed to investigate the TC behavior. In the EMA model, the intrinsic TC, content, orientation, and geometrical shape of the graphite flakes have all been taken into account to evaluate TC of the composites, which can be represented as [36]:

\[
K_c^{X-Y} = \frac{2 + f[\beta^{X-Y}(1 - S^{X-Y})(1 + \cos^2\theta) + \beta^Z(1 - S^Z)(1 - \cos^2\theta)]}{2 - f[\beta^{X-Y}S^{X-Y}(1 + \cos^2\theta) + \beta^ZS^Z(1 - \cos^2\theta)]}
\]

(2)

\[
K_c^Z = \frac{1 + f[\beta^{X-Y}(1 - S^{X-Y})(1 - \cos^2\theta) + \beta^Z(1 - S^Z)(\cos^2\theta)]}{1 - f[\beta^{X-Y}S^{X-Y}(1 - \cos^2\theta) + \beta^ZS^Z(\cos^2\theta)]}
\]

(3)

With

\[
\beta^{X-Y} = \frac{K_{re}^{X-Y} - K_m}{K_m + S^{X-Y}(K_{re}^{X-Y} - K_m)}
\]

(4)

\[
\beta^Z = \frac{K_{re}^Z - K_m}{K_m + S^Z(K_{re}^Z - K_m)}
\]

(5)

where \(K\) is the TC, \(f\) is the volume fraction of graphite flakes, \(S\) is the shape factor which is related to the diameter (\(D\)) and thickness (\(t\)) of graphite flakes: \(S^{X-Y} = \pi t/4D\) and \(S^Z = 1 - \pi t/2D\), \(\cos^2\theta\) is the orientation function which depends on the angle (\(\theta\)) between the basal plane of graphite flakes and the X-Y plane of the composites. The superscripts X-Y and Z represent the X-Y plane and Z direction, and the subscripts c, m and re denote the composites, matrix and reinforcement, respectively.

In this research, since almost all the graphite flakes are parallel to X-Y plane, then \(\cos^2\theta \rightarrow 1\). Thus, Equations (2) and (3) can be simplified as following:

\[
K_c^{X-Y} = K_m \left[1 + \frac{f}{S^{X-Y}(1 - f) + \frac{K_m}{K_{re}^{X-Y} - K_m}}\right]
\]

(6)

\[
K_c^Z = K_m \left[1 + \frac{f}{S^Z(1 - f) + \frac{K_m}{K_{re}^Z - K_m}}\right]
\]

(7)

![Figure 12. TC of the composites in X-Y plane (a), and Z direction (b).](image)
In order to take into account of the influence of interfacial thermal resistance ($R$) on the TC, the graphite flakes can be considered to be covered by a very thin interfacial thermal barrier. Thus, an effective TC is employed to replace the intrinsic TC of GF, and can be expressed as:

$$K_{re}^{eff}(X-Y) = \frac{K_X - Y}{1 + \frac{2K_X - Y}{D}}$$  \hspace{1cm} (8)

$$K_{re}^{eff}(Z) = \frac{K_Z}{1 + \frac{2K_Z}{t}}$$  \hspace{1cm} (9)

Generally, the interfacial thermal resistance between two different phases can be theoretically calculated by the acoustic mismatch model (AMM) [12]:

$$R = \frac{2(\rho_m v_m + \rho_{re} v_{re})^2}{C_m \cdot \rho_{re} v_{re} \rho_m v_m^2 \cdot \nu_m}$$  \hspace{1cm} (10)

where $\rho$ is the density, $v$ represents the Debye phonon velocity, $C$ denotes the specific heat. Besides, the interfacial thermal resistance of the interfacial layer itself can be estimated by the following relationship:

$$R = \frac{d_{layer}}{K_{layer}}$$  \hspace{1cm} (11)

where $K_{layer}$ and $d_{layer}$ is the TC and thickness of the interfacial layer, respectively. Thus, the total interfacial thermal resistance ($R_i$) for the TiC coated graphite flake/Cu interface can be expressed as:

$$R_i = R_{Cu/TiC} + R_{TiC} + R_{TiC/a-C} + R_{a-C} + R_{a-C/GF}$$  \hspace{1cm} (12)

Some previous studies have shown that the phonon velocity and specific heat of amorphous carbon (a-C) mainly depend on the content of C-C $sp^2$ and C-C $sp^3$ bonding [37–39]. Thus, we suppose the a-C layer in this work could have a phonon velocity and specific heat approximate to the crystalline graphite, since it is derived from the crystalline graphite that could have a high proportion of C-C $sp^2$ bonding and can be essentially regarded as the graphite in the short range. Consequently, we approximatively take the TiC/a-C interface as TiC/GF interface and neglect the interfacial thermal resistance between the a-C and GF. As a result, the total interfacial thermal resistance can be roughly calculated as:

$$R_i = R_{Cu/TiC} + R_{TiC} + R_{TiC/graphite} + R_{a-C}$$  \hspace{1cm} (13)

Table 1 presents the parameters for theoretical calculation. The TC and the thickness of TiC is 36.4 W·m⁻¹·K⁻¹ and 600 nm. For the a-C layer, the thickness is taken an average value about 75 nm while its TC is related to the ordering and the amount of $sp^2$ ($sp^3$) phase [40]. It is difficult to provide the accurate TC of the a-C layer in this TiC-coated graphite flake/Cu composite, and thereby a value of 0.75 W·m⁻¹·K⁻¹ stemming from the literature is roughly taken as the TC of the a-C layer [41]. Submitting the relevant parameters into Equations (10) and (11), $R_{Cu/TiC}$, $R_{TiC}$, $R_{TiC/GF}$ and $R_{a-C}$ are calculated to be $0.45 \times 10^{-8}$ m²·K·W⁻¹, $1.65 \times 10^{-8}$ m²·K·W⁻¹, $0.2 \times 10^{-8}$ m²·K·W⁻¹ and $10 \times 10^{-8}$ m²·K·W⁻¹, Therefore, the total interfacial thermal resistance of the TiC-coated graphite flake/Cu composite is $12.3 \times 10^{-8}$ m²·K·W⁻¹. Taking $K_{TiC}^{eff} = 1000$ W·m⁻¹·K⁻¹, $K_{GF}^{eff} = 38$ W·m⁻¹·K⁻¹, $D = 1000$ µm and $t = 50$ µm, we obtain $K_{GF}^{eff}(X-Y) = 803$ W·m⁻¹·K⁻¹ and $K_{GF}^{eff}(Z) = 32$ W·m⁻¹·K⁻¹. As a contrast, the interfacial thermal resistance of the ideal TiC-coated graphite flake/Cu composite, which has the same thickness TiC layer but without no a-C layer at the interface, is calculated to be $2.3 \times 10^{-8}$ m²·K·W⁻¹. Accordingly, the resulting effective TC of the graphite flake within this ideal TiC-coated graphite flake/Cu composite is 956 W·m⁻¹·K⁻¹ in the X-Y plane and 36.7 W·m⁻¹·K⁻¹ in Z
direction, respectively. The calculation results indicate that the a-C layers contribute the most to the total interfacial thermal resistance and give rise to a dramatic reduction on effective TC of graphite flake.

Table 1. Material parameters for theoretical calculation.

| Material | Specific Heat (J kg\(^{-1}\) K\(^{-1}\)) | Density (kg m\(^{-3}\)) | Phonon Velocity (m s\(^{-1}\)) | Ref |
|----------|----------------------------------------|--------------------------|-------------------------------|-----|
| Cu       | 385                                    | 8960                     | 2881                          | [42]|
| Graphite | 710                                    | 2260                     | 14,800                        | [12]|
| TiC      | 562                                    | 4930                     | 6777                          | [8,43]|

Submitting the above parameters into Equations (6) and (7), the theoretical TC of the TiC-coated graphite flake/Cu composites was calculated, as shown in Figure 12. The variation trend of experimental TC is consistent with the EMA model and its values are close to the theoretical value (red dash line). The discrepancy between the experimental value and theoretical one can be explained as the following reason. The theoretical model is based on the assumption that the interface is straight, however, the actual interface is accidented, which results in the actual interface thermal resistance being greater than that calculated according to the AMM model. Besides, we can find that the theoretical TC, which neglects the a-C layer, is higher than the a-C layer. Thus, the TC of the composites will be improved if we decrease the thickness of a-C layer, which will be studied in our further work by optimizing the technological parameters of molten salt method.

3.5. Coefficient of Thermal Expansion

In order to fully grasp the thermal expansion behavior of graphite flake/Cu composites, two classic models are applied to describe the CTE. The simplest one is the rule of mixture (ROM) model, which only considers the CTE and content of each component:

\[
\alpha_c = \alpha_{Cu}(1-f) + \alpha_{GF}f
\]  

(14)

where \(\alpha_{Cu}\) and \(\alpha_{GF}\) is the CTE of Cu (17 ppm K\(^{-1}\)) and graphite flake (~1 ppm K\(^{-1}\) in X-Y plane and 28 ppm K\(^{-1}\) in Z direction), \(f\) is the volume fraction of graphite flake. The other is Turner model [44], in which the elastic interaction of each component is also taken into account:

\[
\alpha_c = \frac{\alpha_{Cu}B_{Cu}(1-f) + \alpha_{GF}B_{GF}f}{B_{Cu}(1-f) + B_{GF}f}
\]  

(15)

where \(B_{Cu}\) and \(B_{GF}\) represent the bulk modulus of Cu and graphite flake.

Figure 13 delineates the CTE values of the composites. In X-Y plane, the CTE values decrease slowly with the increasing GF content. The variation trend is consistent with the above two models, but the Turner model is more agreement with the experimental value than ROM model, indicating that the elastic interaction between the Cu matrix and GFs cannot be neglected when we predict the CTE of these graphite flake/Cu composites. Meanwhile, the CTE of TiC-coated graphite flake/Cu composites is slightly lower than the uncoated one. This is because introducing TiC coating leads to a tighter interface bonding, which makes GF, better restrains the expansion of Cu along X-Y plane.
When it is heated. Combining the above inference and ROM model, they calculated the theoretical CTE where the transfer ability at the GF as the TiC-coated graphite flake flake.

\[ \alpha_{\text{TiC-Cu}} = \frac{\Delta \alpha_{\text{Cu}}}{1 + \nu_{\text{Cu}}} \]

\[ \alpha_{\text{GF}} = \alpha_{\text{GF}} - \alpha_{\text{Cu}} \]

\[ \alpha_{\text{TOT}} = \alpha_{\text{GF}} - \alpha_{\text{Cu}} + \frac{\Delta \alpha_{\text{Cu}}}{1 + \nu_{\text{Cu}}} \]

This is because introducing TiC coating leads to a larger CTE than Cu in the Cu matrix is calculated to be 24 ppm. Accordingly, they derived a formula to estimate the c-direction CTE of GF within graphite flake/Cu composites, which is given as:

\[ \alpha_{33} = \alpha_{\text{gr,3}} + v_{2D}\Delta \alpha_x - \frac{d\nu_{2D}}{dT} \epsilon_{11} \]

where \( \alpha_{\text{gr,3}} \) denotes the intrinsic c-direction CTE of graphite, \( v_{2D} \) stands for the two dimensional equivalent of Poisson ratio of GF. \( \Delta \alpha_x \) is the temperature derivative of in-plane strain. \( \frac{d\nu_{2D}}{dT} \) represents the temperature derivative of \( v_{2D} \), \( \epsilon_{11} \) is the residual in-plane strain. As a result, they calculated the c-direction CTE of GF within the composite (50 vol% GF) to be -26 ppm-K\(^{-1}\). Accordingly, the CTE of Cu matrix is calculated to be 24 ppm-K\(^{-1}\). Although this result was derived from an idealized model, it demonstrates that the GF within the composite exhibits negative expansion behavior in Z direction when it is heated. Combining the above inference and ROM model, they calculated the theoretical CTE of graphite flake/Cu composite (50 vol%) to be -1 ppm-K\(^{-1}\) in Z direction. Further, they considered that the CTE value varies linearly between 17 ppm-K\(^{-1}\) and -1 ppm-K\(^{-1}\) as the graphite flake content increases from 0 to 50 vol\%. Based on the above theory, they finally developed a theoretical model, namely laminar model, to predict the CTE of graphite flake/Cu composites in Z direction.

At present, the laminar model has been accepted by many scholars because it can well explain this abnormal Z direction thermal expansion behavior of graphite flake/metal composites, such as graphite flake/Cu composites and graphene/Cu composites [17,46]. As shown in Figure 13b, although there is a certain difference between the experimental value and the theoretical value predicted by the laminar model, their trend is consistent, which gradually decreases with the increase in GF content. In addition, as the TiC-coated graphite flake/Cu composites possess a more intimate interface between Cu and GF, the GF can more efficiently inhibit the expanding of Cu in Z direction because of the superior stress transfer ability at the GF/Cu interface [31]. Therefore, a lower CTE can be acquired in Z direction by introducing TiC layer on GF surface.

\[ \alpha_{\text{CTE}} = \alpha_{\text{GF}} - \alpha_{\text{Cu}} + \frac{\Delta \alpha_{\text{Cu}}}{1 + \nu_{\text{Cu}}} \]

\[ \alpha_{\text{TOT}} = \alpha_{\text{GF}} - \alpha_{\text{Cu}} + \frac{\Delta \alpha_{\text{Cu}}}{1 + \nu_{\text{Cu}}} \]

\[ \alpha_{\text{CTE}} = \alpha_{\text{GF}} - \alpha_{\text{Cu}} \]

\[ \alpha_{\text{TOT}} = \alpha_{\text{GF}} - \alpha_{\text{Cu}} + \frac{\Delta \alpha_{\text{Cu}}}{1 + \nu_{\text{Cu}}} \]
4. Conclusions

TiC coating was synthesized on graphite flake surface through molten salt method to promote the interfacial bonding between Cu and graphite flake. The TiC-coated graphite flake/Cu composites were subsequently prepared through vacuum hot pressing. The results reveal that the TiC coating remarkably reduces the interfacial pores and gaps, resulting in a firmly contacted interface. The bending strength was significantly improved as a result. When the TiC-coated graphite flake content is 60 vol%, the bending strength is increased by 58% compared with the uncoated one. The coefficient of thermal expansion dropped from 6.0 ppm·K\(^{-1}\) to 4.4 ppm·K\(^{-1}\), with the corresponding thermal conductivity as high as 571 W·m\(^{-1}\)·K\(^{-1}\). These TiC-coated graphite flake/Cu composites with the outstanding TC and CTE values, together with superior mechanical properties, can be an ideal heat sink material with a wide range of potential applications.

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