Continuous SiC skeleton reinforced highly oriented graphite flake composites with high strength and specific thermal conductivity

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Abstract: Highly oriented graphite-based composites have attracted great attention because of their high thermal conductivity (TC), but the low mechanical properties caused by the inhomogeneous distribution and discontinuity of reinforcements restrict the wide applications. Herein, continuous SiC ceramic skeleton reinforced highly oriented graphite flake (SiC/GF) composites were successfully prepared by combining vacuum filtration and spark plasma sintering. The effect of SiC concentration on the microstructure, flexural strength, and thermophysical properties of the composites was investigated. The GF grains in the composites exhibited high orientation with a Lotgering factor of > 88% when the SiC concentration was ≤ 30 wt%, and the SiC skeleton became continuous with the SiC concentration reaching 20 wt%. The formation of continuous SiC skeleton improved the flexural strength of the composites effectively while keeping the TC in a high level. Especially, the composites with 30 wt% SiC exhibited the flexural strength up to 105 MPa, and the specific TC reaching $0.118 \text{ W}\cdot\text{m}^2\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$. The composites with excellent flexural strength and thermophysical properties showed significant promise for thermal management applications.

Keywords: ceramics; composite materials; high orientation; flexural strength; heat conduction

1 Introduction

Nowadays, the intelligent electronic devices have been developed towards high power density and miniaturization direction, which arouses urgent requirement for the thermal management materials (TMMs) with excellent performance [1–4]. The advanced TMMs should have the characteristics of low density, high strength, and high thermal conductivity (TC) perpendicular to the

electronic/TMM interface for effective heat dissipation. Besides, similar coefficient of thermal expansion (CTE) with those of semiconductor chips (4×10^{-6} – $7 \times 10^{-6} \text{ K}^{-1}$) along the interface direction is necessary to minimize the thermal strain during operation [5–8].

Graphite materials as promising TMMs have attracted great attention because of the high TC in basal plane, light weight, and low cost. To take full advantage of outstanding in-plane TC of graphite, it is an efficient way to make graphite flake (GF) alignment to obtain highly oriented graphite blocks. By this means, the graphite blocks with high crystal orientation display ultrahigh TC (550 – $700 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [9,10]. Nevertheless,

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inferior mechanical properties and high CTE in out-plane direction of the highly oriented graphite blocks lead to the failure under harsh service environments [11]. In order to overcome the obstacles, some studies attempted to promote the mechanical properties of the graphite-based composites by using metal and ceramic powers (such as Cu, AlN, and SiC) as reinforcements [12–14]. However, the huge differences between metal/ceramic powders and GF particles in size, shape, and dimension lead to the inhomogeneous distribution of metal/ceramic reinforcements in GF matrix [15], which makes the flexural strength improvement rather limited. For instance, Ren *et al.* [16] reported that the flexural strength of the Cu/GF composites was only ~50 MPa when the volume fraction of Cu was 50%. On account of this, the rational design and fabrication of the inorganic substance reinforced highly oriented GF composites are actively pursued.

Generally, highly oriented GF-based materials are consolidated by spark plasma sintering (SPS) or hot-pressing because the thin GF particles with platelet geometry (large length to thickness ratio) can be deflected and aligned by the sintering pressure [17]. Based on the finite element simulation and experimental results, the mechanical and thermophysical properties of highly oriented graphite-based materials can be optimized by constructing three-dimensional (3D) topological and continuous skeleton as reinforcement in the composites [18–21]. Therefore, various 3D continuous networks including metals (such as Cu and Al) [14,22] and ceramics (AlN, WC) [23,24] have been used to promote the mechanical properties of highly oriented graphite-based composites. Among them, the Cu skeleton with high density results in low specific TC, i.e., TC divided by density, which is unsatisfied with the light weight requirement for advanced TMMs. For the Al reinforced GF composites, it is widely accepted that the formation of Al_4C_3 at the GF/Al interface during high temperature sintering would degrade the TC and chemical stability of the composites [4]. For the ceramic reinforcements, the SiC skeleton stands out because it possesses low density ($3.21 \text{ g}\cdot\text{cm}^{-3}$), high flexural strength (550 MPa), and high TC ($490 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for single crystalline, $270 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for polycrystalline) [25]. Moreover, its CTE of about $4 \times 10^{-6} \text{ K}^{-1}$ [26,27], much lower than that of GF in through-plane direction ($28 \times 10^{-6} \text{ K}^{-1}$), can introduce tensile stress in GF along this direction and hence reduce the CTE of the composites [17]. This improves the reliability of SiC

reinforced GF composites as TMMs for electronic devices after repetitive thermal cycles. Therefore, preparing 3D continuous SiC skeleton reinforced highly oriented GF composites is an appealing approach to synergistically optimize the mechanical and thermophysical properties of highly oriented graphite-based composites.

Herein, we demonstrated a method combining vacuum filtration and SPS to realize the 3D continuous SiC skeleton reinforced highly oriented GF-matrix (SiC/GF) composites. Vacuum filtration is a universal technique to fabricate well aligned GFs on account of the flow-directed assembly of two-dimensional (2D) carbon/graphite particles (i.e., graphene or GF) with good orientation [28,29]. SPS is an efficient process not only for preparing high performance ceramics and composites in a short sintering time at relatively low temperature [30,31], but also for promoting the orientation of anisotropic particles by sintering pressure [32]. Thereby, the 3D continuous SiC skeleton can be successfully introduced in the highly oriented GF matrix, and the anisotropic SiC/GF composites with high strength and specific TC in plane direction were achieved. The effect of SiC weight fraction on the microstructure, flexural strength, and thermophysical properties of the composites were systematically investigated.

2 Experimental

2.1 Sample preparation

The raw materials were GF particles (purity 99.8%, Alfa Aesar, USA) and α -SiC powders (purity 99.9%, Shanghai St-nano Science and Technology Co., Ltd., China). Figure 1 shows the micrographs of GFs and α -SiC powders. The averaged lateral size and thickness of GFs are about 15 and 1 μm , respectively, and α -SiC powders exhibit irregular morphology with an average size of 0.5 μm . 5 wt% of Al_2O_3 (purity 99%, Sinopharm Chemical Reagent Co., Ltd., China) and Y_2O_3 (purity 99%, Sinopharm Chemical Reagent Co., Ltd., China)

Fig. 1 Morphologies of (a) GF and (b) SiC powders.

powders with a weight ratio of 2:1 were added as sintering aids. To explore the influence of SiC concentration on the microstructure and properties of the composites, the amounts of SiC powders were set as 15 wt%, 20 wt%, 25 wt%, 30 wt%, and 50 wt%, and SiC15/GF, SiC20/GF, SiC25/GF, SiC30/GF, and SiC50/GF were named for the resultant composites in the following discussion, respectively.

The SiC/GF composites were fabricated by vacuum filtration followed by SPS, and the schematic illustration of the fabrication process is shown in Fig. 2. All the powders were weighted and ball-milled for 5 h in a polyethylene bottle using ethanol as the mixing media. Then the wet bodies were prepared by vacuum filtration of the as-received slurries. The micrographs of powders after ball milling and vacuum filtration are exhibited in Fig. S1 in the Electronic Supplementary Material (ESM). The size of GF remains unchanged (Fig. S1(a) in the ESM) and the GFs are aligned roughly at atmospheric pressure during vacuum filtration (Fig. S1(b) in the ESM). After removing the ethanol of the wet body at 80 °C for 24 h, the obtained green body was put into a graphite die and sintered at 1800 °C for 5 min, applying 50 MPa uniaxial pressure and under the vacuum (5 Pa) using a SPS furnace (Ed-PASIII, Elenix Ltd., Japan). The sintered samples were machined by wire-electrode cutting, then ground by 2000# sandpapers, and polished in different orientations to achieve the required dimensions for the following flexural strength, electrical conductivity, and thermophysical properties tests.

2.2 Characterization

The bulk density (ρ) and relative density (ρ_{RD}) were

Fig. 2 Schematic illustration of the fabrication process of SiC/GF composites.

measured by Archimedes method (the detailed procedure shown in Section S2 in the ESM), using deionized water as immersion medium. Phase identification was performed by X-ray diffraction (XRD; X-Pert Pro, the Netherlands) with Cu K α radiation. The Lotgering factor f of (00 l) of graphite phase, obtained from XRD patterns, was calculated by Eq. (1) [33]:

$$f_{(00l)} = (P_{(00l)} - P_0)/(1 - P_0) \quad (1)$$

where

$$P_{(00l)} = (\sum I_{(00l)})/(\sum I_{(hkl)}) \quad (2)$$

$$P_0 = (\sum I_{0(00l)})/(\sum I_{0(hkl)}) \quad (3)$$

In Eq. (2), $\sum I_{(00l)}$ and $\sum I_{(hkl)}$ are the integrated intensities of the (00 l) peaks of graphite and all the (hkl) peaks of graphite in the oriented sample pattern, respectively. In Eq. (3), $\sum I_{0(00l)}$ and $\sum I_{0(hkl)}$ are the summation of the (00 l) peaks of graphite and all the (hkl) reflections of graphite in random crystallographic orientation sample, respectively. The f value is between 0 and 1, and higher value demonstrates the higher degree of orientation. All the micrographs of the samples were observed through a tungsten filament scanning electron microscope (SEM; SU3500, Hitachi, Japan). The polished and fractured surfaces of the SiC/GF composites were examined by backscattered electron image (BEI) mode and secondary electron image (SEI) mode, respectively. The interfacial configuration was observed using the high-resolution transmission electron microscope (HRTEM; JEM-2100F, Japan). Raman spectra were characterized by a spectrometer (Nanofinder FLEXG, Tokyo Instruments Inc., Japan) with a 633 nm laser as the excitation light source.

The flexural strength, electrical conductivity, and thermophysical properties were measured in both perpendicular (x - y plane) and parallel (z axis) to the sintering pressure directions. The sizes of sintered samples and schematics of specimens cut for the different tests and orientations are shown in Fig. S2 in the ESM. The flexural strength (σ_f) of the sample with a dimension of 3 mm $\times$ 4 mm $\times$ 16 mm was tested by three-point bending method with a crossed speed of 0.5 mm $\cdot$ min $^{-1}$ at room temperature. The thermal diffusivity (α) was measured by the light flash method (Netzsch LFA447 NanoFlash, Germany) at room temperature. For the thermal diffusivity measurements in z axis and x - y plane directions, the dimensions of specimens were $\varnothing$ 12.7 mm $\times$ 3 mm and 10 mm $\times$ 10 mm $\times$ 3 mm, respectively. Two alloy holders were used for the TC

tests (Fig. S3 in the ESM). The specific heat capacity (C_p) of the SiC/GF composites was obtained by the linear rule of mixtures. The TC value (λ) was calculated by multiplying α , C_p , and ρ . Then, the λ divided by ρ equals the specific TC. Surface temperature distribution of the composites on a homiothermal Cu block was tested by an infrared thermal imager (Fotric 280, USA). The thermal expansion behavior was studied via a dilatometer (Netzsch DIL 402C, Germany) in the temperature range of 20–350 °C with a constant heating rate of 5 °C·min⁻¹. The expansion was conducted on the sample with a dimension of 5 mm × 5 mm × 10 mm. The electricity conductivity (EC) with the size of 3 mm × 4 mm × 10 mm was measured by the four probe method (Linseis LSR-3, Germany) in a helium atmosphere.

3 Results and discussion

3.1 Phase composition and microstructure

Figure 3(a) shows the XRD patterns of the SiC30/GF composite in x - y plane and z axis directions. The diffraction peaks of α -SiC and graphite phases in the composite can be detected. Besides, AlYO_3 phase is also found, which was probably derived from the eutectic reaction of Al_2O_3 and Y_2O_3 to facilitate the sintering process [34,35]. Significant differences are shown in two principle directions of the composite. The intensity of (002) diffraction peak of graphite in x - y plane at $2\theta = 26.5^\circ$ is about 200 times higher than that in z axis direction, indicating the strong orientation of GF in the composites. Lotgering factor f values calculated from the XRD patterns of the SiC/GF composites with different SiC concentrations (Fig. S4 in the ESM) are higher than 88% when the SiC concentration is ≤ 30 wt%. This indicates that most

of the GFs are aligned along the direction perpendicular to the sintering pressure. When the SiC concentration reaches 50 wt%, the f value declines sharply to 52%, indicating that the introduction of SiC disturbs the arrangement of GFs. The intensity ratios of the D and G peaks (I_D/I_G) of graphite characterized by the Raman spectra (Fig. S5 in the ESM) are used to investigate the crystalline quality of GF after sintering. The smaller I_D/I_G value expresses the higher crystalline quality of GF [36]. With the increase of SiC concentration, the I_D/I_G value of the graphite increases from 0.32 to 0.66 (Fig. 3(b)), which can be ascribed to the fracture and deformation of the GFs during the ball milling and SPS processes. The disorder of GF crystals will lead to the reduction of the phonon mean free path and be inferior to the phonon vibration as well as the heat conductivity [10].

The BEIs of polished surfaces parallel to z axis direction of the composites with different SiC concentrations are shown in Figs. 4(a)–4(e). The bright areas are identified as SiC and dark regions refer to GF. A small number of pores can be observed in the SiC/GF composites when the SiC concentration is lower than 50 wt%. As the concentration of SiC increases, the number of pores gradually reduces and the pores finally disappear in the SiC50/GF composite, which demonstrates that the increase of SiC concentration is beneficial to the densification of the composites. The patterns of SiC phase are approximately parallel to each other, indicating the composites possess good orientation. It also can be seen that the SiC particles disperse discretely in GF matrix when the fraction of SiC is 15 wt%. With the SiC concentration increasing to 20 wt%, the SiC reinforcement begins to be continuous in the composite (the inset in Fig. 4(b)) and bridges to form a network architecture. After decarburizing of the SiC20/GF composite at 700 °C for 5 h, the oriented porous SiC skeleton can be obtained (Fig. 4(f)), which

Fig. 3 (a) XRD patterns of SiC30/GF composite in two principle directions. (b) Lotgering factor f values of (002) plane and the intensity ratios of D to G peaks (I_D/I_G) of graphite in SiC/GF composites.

Fig. 4 BEIs of polished surfaces (parallel to z axis direction) of (a) SiC15/GF, (b) SiC20/GF, (c) SiC25/GF, (d) SiC30/GF, and (e) SiC50/GF composites, where the insets in (a–e) are the magnified images corresponding to the polished surfaces. (f) Microstructure of the decarbonized SiC20/GF composite.

further verifies the 3D continuity of the skeleton. The holes in the SiC skeleton shown in Fig. 4(f) (noted by the yellow dotted lines) have a length of $\sim 15 \mu\text{m}$ and the thickness of $3\text{--}5 \mu\text{m}$, illustrating that a structural unit of the “cell-like” composite contains several stacked GFs. With further increase of the SiC concentration to 50 wt%, almost all the GFs are surrounded by the integrated SiC skeleton and isolated as islands in the composite (Fig. 4(e)).

In order to clarify the connectivity of SiC in the SiC/GF composites, the EC tests were conducted and the results are shown in Fig. 5. With the increase of SiC concentration, the z axial EC decreases one order of magnitude from $0.06 \text{ MS}\cdot\text{m}^{-1}$ for SiC15/GF to $0.005 \text{ MS}\cdot\text{m}^{-1}$ for SiC20/GF and then remains basically unchanged, indicating that the SiC reinforcement in the interlayer of GFs begins to be continuous with the SiC concentration achieving 20 wt%. The x – y plane EC increases first from 0.07 to $0.11 \text{ MS}\cdot\text{m}^{-1}$ as the SiC

concentration increases from 15 to 30 wt% and then drops to $0.03 \text{ MS}\cdot\text{m}^{-1}$ when the SiC concentration reaches 50 wt%. The increase of EC with the SiC concentration is mainly ascribed to the increase of relative density, which makes the GFs connected tightly. However, when the SiC concentration achieves 50 wt%, the significant reduction of EC demonstrates that the integral 3D SiC skeleton is formed, which separates the GF grains thoroughly.

3.2 Density and flexural strength

Figure 6(a) shows the densities and relative densities of the composites with different SiC concentrations. It can be seen that the density increases gradually from $2.26 \text{ g}\cdot\text{cm}^{-3}$ for SiC15/GF to $2.61 \text{ g}\cdot\text{cm}^{-3}$ for SiC50/GF, and the relative density increases correspondingly from 93.3% to 95.7%, which indicates that the SiC is beneficial to the densification of the GF-based composites. This is also consistent with the microstructure of the SiC/GF composites (Figs. 4(a)–4(e)). It is supposed that not only the densification of SiC reinforcements but also the growth of SiC grains contributes to the fill of the gaps between the GF grains during SPS, leading to the densification of the SiC/GF composites.

The flexural strengths of the composites in two principle directions are exhibited in Fig. 6(b). It can be seen that the flexural strength in two principle directions almost grows linearly as the SiC concentration increases. The flexural strength rises from 67 MPa for SiC15/GF to 100 MPa for SiC30/GF when the loading direction

Fig. 5 EC of SiC/GF composites in x – y plane and z axis directions.

Fig. 6 (a) Densities and relative densities of SiC/GF composites with different SiC concentrations. (b) Flexural strengths of the composites in two principle directions.

is along z axis, and the corresponding flexural strength tested along x axis increases from 79 to 105 MPa. When the SiC skeleton becomes completely continuous in SiC50/GF, the flexural strengths with loading directions along z and x axes achieve 152 and 156 MPa, respectively, which are about 7.5 times higher than that of the oriented graphite blocks fabricated by hot-pressing of GFs at 3000 °C (21.1 MPa) [11]. For the SiC/GF composites, the graphite is the weak phase and the SiC acts as the reinforcement for the flexural strength. With the increase of SiC concentration, the relative density of the composites also increases (Fig. 6(a)), which means that the porosity of the composites decreases. Hence, the increased SiC content contributes to the increment of flexural strength of the composites. It also can be seen that the flexural strength in x - y plane is close to z axis direction. The graphite has much lower flexural strength than that of SiC, and thus it can be served as crack in the SiC/graphite composites and determines the scale of the maximum flaw size [37,38]. For the SiC/GF composites, when the crack propagates to the weak SiC/GF interface or the GF grain, the cracks with similar size to the averaged lateral size of GF are formed by the stress fields at crack tips. Therefore, the flexural strengths of the SiC/GF composites in two principle directions are comparable. Furthermore, the flexural strength of composites is also closely connected with their microstructures of fracture surfaces. From the fracture surfaces of the SiC50/GF composite (Figs. 7(a)–7(d)), similar tortuous fracture surfaces can be observed, which contain the intergranular fracture of SiC and transgranular fracture of GFs, resulting in the similar flexural strengths in two principle directions.

3.3 Thermal conductivity

Figure 8(a) shows the TC of the sintered samples in

Fig. 7 Fracture surfaces of SiC50/GF composite obtained along (a) z axis and (b) x axis. (c, d) Enlarged images corresponding to (a) and (b), respectively.

two principle directions. The TC in x - y plane is much higher than that in z axis direction, indicating that the composites are highly anisotropic. The TC in z axis direction increases slowly from 18 to 26 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ with the increase of SiC concentration, which is ascribed to not only the elevated density of the composites, but also the higher TC of SiC skeleton ($\sim 60 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) than that of GF matrix in z axis direction ($15 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [39]. The TC of $60 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for SiC skeleton was measured by sintering of the SiC bulk with the same components as the reinforcement. Hence, the heat conduction mainly spreads along the SiC skeleton (Fig. 8(b)). The TC of the composites in x - y plane first increases from 253 to $289 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ as the SiC concentration increases from 15 to 20 wt%, then slightly decreases to $285 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when the SiC concentration reaches 30 wt%, and finally falls to $247 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ as the SiC concentration increases to 50 wt%. It was reported that the TC was related with the phonon scattering resulted from pores, defects, and

Fig. 8 (a) TC, (b) conductive paths, and (c) thermal diffusivity of the composites in two principal directions.

interfaces in ceramic composites [40,41]. For the anisotropic composites, the orientation degree is also a determining factor for TC [42]. Therefore, the TC should decrease theoretically with the increase of SiC concentration when defects/interfaces increase and orientation factor f reduces. Nevertheless, the TC first increases as SiC concentration increases from 15 to 20 wt%, and remains stable at $\sim 285 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ until SiC concentration reaches 30 wt%. This phenomenon can be explained by two reasons. Firstly, the SiC particles are sintered to be a continuous reinforcement, which facilitates the densification of SiC/GF composites and reduces the phonon scattering resulting from the pores in the composites. Secondly, the GFs with conspicuous directional alignment form a chain structure at high concentrations, which provide the conductive paths (Fig. 8(b)). Hence, GF particles can be considered as continuum in the SiC20/GF composite, and this structure remains until the SiC concentration reaches 30 wt%. Further increasing the SiC concentration to 50 wt%, the integral SiC skeleton separates the GF grains, which reduces the heat conduction paths in x-y plane of GFs.

Although it is reported that the TC of GF in x-y plane is $1000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [43], the maximum TC of SiC/GF composite only reaches $289 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, much lower than the theoretical value of GF. To better understand the effect of SiC reinforcement on the TC of the SiC/GF composites, we used the model developed by Nan *et al.* [39] within the effective-medium approximation (EMA) to estimate the variation of TC, and then compared with the experimental values. The EMA formulations in two directions are illustrated as Eqs. (4) and (5):

$$K_{c(xy)} = K_m \frac{2 + v[\beta_{xy}(1 - S_{xy})(1 + \langle \cos^2 \theta \rangle) + \beta_z(1 - S_z)(1 - \langle \cos^2 \theta \rangle)]}{2 - v[\beta_{xy}S_{xy}(1 + \langle \cos^2 \theta \rangle) + \beta_zS_z(1 - \langle \cos^2 \theta \rangle)]} \quad (4)$$

$$K_{c(z)} = K_m \frac{1 + v[\beta_{xy}(1 - S_{xy})(1 - \langle \cos^2 \theta \rangle) + \beta_z(1 - S_z)\langle \cos^2 \theta \rangle]}{1 - v[\beta_{xy}S_{xy}(1 - \langle \cos^2 \theta \rangle) + \beta_zS_z\langle \cos^2 \theta \rangle]} \quad (5)$$

with

$$\beta_i = \frac{K_i - K_m}{K_m + S_i(K_i - K_m)} \quad (i = xy, z) \quad (6)$$

$$\langle \cos^2 \theta \rangle = \frac{\int \rho(\theta) \cos^2 \theta \sin \theta d\theta}{\int \rho(\theta) \sin \theta d\theta} \quad (7)$$

where K_c , K_i , and K_m are the TC of composites, GF, and SiC, respectively; the subscripts xy and z denote the x-y plane and z axis directions, respectively; v refers to the volume fraction of GF; and $\langle \cos^2 \theta \rangle$ reflects the statistical orientation of the GFs. S represents the geometrical factor of GF described as $S_{xy} = \pi t/4D$ and $S_z = 1 - \pi t/2D$, where t and D are the thickness and diameter of the GF, respectively. The $\langle \cos^2 \theta \rangle$ nearly to 1 is simplified for the general EMA model because almost all the GFs are aligned vertically to the z axis direction. The TCs of GF in x-y plane and z axis directions are taken as 1000 and $15 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [43] to calculate the theoretical TC values of the composites. Meanwhile, the TC of $60 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for SiC is used to carry out the theoretical calculations. It can be seen from Fig. 8(a) that the calculated TC values in z axis direction fit well with the measured values. However, the calculated TCs in x-y plane are obviously higher than those of experiments. The reason is that the introduction of SiC reinforcement leads to a lot of defects in GFs, including the curve, wrinkle, fold, and fracture of GF grains (Figs. 9(a)–9(d)), which largely intensifies the phonon scattering along x-y plane of GF. From Fig. 9(e), it can be observed many disordered areas of graphite lattice (yellow dashed circle) near the SiC/GF interface, which further results in the reduction

Fig. 9 GF with different defects in SiC/GF composites: (a) curve, (b) wrinkle, (c) fold, and (d) fracture. (e) HRTEM image of SiC/GF interface.

Fig. 10 (a) Schematic diagram of the heat dissipation experiments. (b) Side surface temperature–time curves of the samples. (c) Changes of infrared thermal images over time. (d) Specific TC of SiC30/GF composite compared with several key TMMs [8,17,21,23].

of TC of the SiC/GF composites. Taking the factors above into consideration, the actual TC of GF is much lower than $1000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. We used the TC value of $400 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to replace the original TC of $1000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to modulate the EMA model, and then the experimental TCs of the composites in x - y plane agree well with the modulated EMA model. Thus, the nominal TC of GF would be $400 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ in x - y plane. Similar tendency is observed between the thermal diffusivity (Fig. 8(c)) and TC of the composites, which indicates that thermal diffusivity is the dominating factor for the heat conductivity compared with heat capacity and density [10].

In order to demonstrate the heat conduction performance of SiC/GF composites in x - y plane direction, the commercial Al6061 (TC of $180 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and SiC30/GF samples with the same dimension of $10 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$ were placed on a homothermal Cu block (100°C), and their side surface temperatures

were tested by an infrared thermal imager, as shown in Fig. 10(a). The center temperature–time curves of the samples are plotted in Fig. 10(b). It is observed that the SiC30/GF composite displays a higher raising rate than Al6061. As time goes on, the surface temperatures of the SiC30/GF composite and Al6061 sample finally reach 90 and 65°C , respectively, which should be ascribed to the higher TC of the SiC30/GF composite compared with Al6061. This can be further verified by the infrared thermal images (Fig. 10(c)), where the SiC30/GF composite with higher TC shows more shallow color (at higher temperatures) over time.

The specific TC is also a significant parameter to evaluate the performance of advanced TMMs. It can be seen from Fig. 10(d) that the specific TC ($0.118 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$) of SiC30/GF composite is 2.5 times higher than that of Cu ($0.045 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$) [17] and nearly 1.5 times as high as that of Al ($0.088 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$) [21]. The relative low TC of SiC/GF

composite is greatly compensated by the low density compared with Cu/GF composite [17]. Only Al2024/GF composite can be comparable to our study [8], but its poor tensile strength (22 MPa) limits the further application in advanced TMMs. Compared with metal/alloy reinforced highly oriented GF composites, it is more complex and expensive to prepare the SiC/GF composites. However, the high flexural strength and specific TC of SiC/GF composites can not only ensure the serviceability, but also remove heat effectively, which could be applied in the field of aerospace and other extreme conditions in the future.

3.4 Thermal expansion

The measured and calculated CTE values of the composites in two principle directions are displayed in Fig. 11. Obvious discrepancy of CTE in x - y plane and z axis directions indicates good anisotropy of SiC/GF composites. The CTE in x - y plane increases slightly from 1.17×10^{-6} to $2.91 \times 10^{-6} \text{ K}^{-1}$ with the SiC concentration increasing from 15 to 50 wt% (Fig. 11(a)). The CTE in z axis drops significantly from $14.8 \times 10^{-6} \text{ K}^{-1}$ for SiC15/GF to $5.32 \times 10^{-6} \text{ K}^{-1}$ for SiC50/GF (Fig. 11(b)). The measured CTE values in z axis are much lower than those of the highly oriented graphite blocks, demonstrating that the SiC skeleton constrains the thermal expansion of the graphite matrix effectively.

To understand the effect of SiC concentration on the thermal expansion behavior of SiC/GF composites, Turner model was used to estimate the theoretical CTE values [44]. The weight fraction is converted to volume fraction for the CTE calculation. Turner model assumes only uniform hydrostatic stresses which exist in the phases of the composite. The thermal expansion of each phase changes at the same rate with the composites should be well described by the Turner model [45,46].

Because the CTE of SiC ($4.7 \times 10^{-6} \text{ K}^{-1}$) is close with that of graphite in basal plane ($-1.5 \times 10^{-6} \text{ K}^{-1}$), the internal stress of composites in this direction is low. Therefore, the experimental CTE of composites in x - y plane direction is consistent with the values calculated by Turner model.

From Fig. 11(b), it is noted that the measured CTE in z axis of the composites is lower than that of the predicted CTE by Turner model, which demonstrates that there exists a thermal stress between SiC and GF in z axis direction. The thermal stress is introduced by the large difference in thermal expansion between SiC and GF in z axis direction. When the SiC concentration reaches 20 wt%, the incompact SiC skeleton is formed in the composite and the GF grains cannot be separated by the skeleton completely. Therefore, the thermal expansion of GF in z axis direction cannot be constrained by the SiC skeleton effectively in the SiC20/GF composite. This structure is remained until the SiC weight fraction increases to 30%. Thus, the CTE values of SiC/GF composites are higher than those of SiC but much lower than those of GF in z axis direction with the SiC concentration in the range of 20–30 wt%. According to the elastic theory, thermal expansion and stress can be connected. Hence, we can calculate the CTE in z axis of GF to be $20.3 \times 10^{-6} \text{ K}^{-1}$ (see the detailed calculation process in Section S7 in the ESM) and replace the theoretical CTE ($28 \times 10^{-6} \text{ K}^{-1}$) of GF to modulate Turner models. As can be seen from Fig. 11(b), the measured data agrees with the modulated Turner model when the SiC concentration changes in the range of 20–30 wt%. Meantime, the lower relative density indicates more residual pores in the composites, which facilitates the absorption of thermal stress. When the SiC concentration reaches 50 wt%, the SiC forms an integral continuous skeleton, which plays a

Fig. 11 Measured and calculated CTE values of the composites in (a) x - y plane and (b) z axis directions. The curves are the modeling predictions.

rigid constraint for the GF expansion. Thus, the CTE of composites is close to that of SiC.

4 Conclusions

Continuous SiC skeleton reinforced highly oriented GF composites with excellent flexural strength and high specific TC were successfully fabricated via vacuum filtration and SPS route. The densification and flexural strength of the SiC/GF composites increased with the increase of SiC concentration. The SiC/GF composites possessed high orientation with Lotgering factor higher than 88% when the SiC concentration was ≤ 30 wt%, which endowed the composites with obviously anisotropic properties. Oriented GFs with chain conductive structure in the SiC/GF composites promoted the formation of effective thermal conductive networks, which ensured the high TC of the composites. With the SiC concentration ≥ 20 wt%, the SiC skeleton became continuous in the composites. The continuous SiC skeleton not only improved the flexural strength but also restrained the CTE in z axis effectively by introducing the thermal stress. Compared with most of the existent TMMs, the SiC30/GF composites exhibited the optimal comprehensive properties with the flexural strength of 105 MPa and specific TC of $0.118 \text{ W}\cdot\text{m}^2\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$.

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Electronic Supplementary Material

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