Thermal conductivity and bending strength of SiC composites reinforced by pitch-based carbon fibers

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Abstract: In this work, pitch-based carbon fibers were utilized to reinforce silicon carbide (SiC) composites via reaction melting infiltration (RMI) method by controlling the reaction temperature and resin carbon content. Thermal conductivities and bending strengths of composites obtained under different preparation conditions were characterized by various analytical methods. Results showed the formation of SiC whiskers (SiC_w) during RMI process according to vapor–solid (VS) mechanism. SiC_w played an important role in toughening the C_{pf}/SiC composites due to crack bridging, crack deflection, and SiC_w pull-out. Increase in reaction temperature during RMI process led to an initial increase in thermal conductivity along in-plane and thickness directions of composites, followed by a decline. At reaction temperature of 1600 °C, thermal conductivities along the in-plane and thickness directions were estimated to be 203.00 and 39.59 W/(m·K), respectively. Under these conditions, bending strength was recorded as 186.15±3.95 MPa. Increase in resin carbon content before RMI process led to the generation of more SiC matrix. Thermal conductivities along in-plane and thickness directions remained stable with desirable values of 175.79 and 38.86 W/(m·K), respectively. By comparison, optimal bending strength improved to 244.62±3.07 MPa. In sum, these findings look promising for future application of pitch-based carbon fibers for reinforcement of SiC ceramic composites.

Keywords: pitch-based carbon fiber; continuous carbon fiber reinforced silicon carbide matrix composites (C/SiC); thermal conductivity; bending strength

1 Introduction

Continuous carbon fiber reinforced silicon carbide matrix composites (C/SiC) are promising thermal structural

materials with low density, high specific strength, superior specific modulus, elevated temperature resistance, good wear resistance, and relevant chemical resistance [1–3], which make them useful for applications in aerospace-related fields. As a result, comprehensive research investigations have been focused on the preparation technologies, such as chemical vapor infiltration (CVI), reaction melting infiltration (RMI), and polymer infiltration

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pyrolysis (PIP), as well as the mechanical properties of obtained C/SiC composites to satisfy the increasingly stringent demands for new types of aerospace vehicles and advanced engines [4,5].

However, the poor heat conduction of C/SiC composites along the in-plane and thickness directions has limited their wider applications. In recent years, numerous research investigations have been devoted to improving the thermal conductivity of C/SiC composites [6–11]. One of the most widely used approaches is the incorporation of materials with high thermal conductivity into ceramic materials. For instance, Chen *et al.* [9] utilized PIP method to produce C/SiC composites with vertically aligned carbon nanotubes (CNTs) on carbon fiber preform. The thermal conductivity in through-thickness direction of the resulting materials reached 16.8 W/(m·K). Yang *et al.* [10] successfully improved the thermal conductivity of C/SiCN composites to 5.6 W/(m·K) by embedding CNTs into inter-bundle spaces of two adjacent carbon fiber sheets by the vacuum infiltration method. Feng *et al.* [11] introduced bucky-papers (CNT film) into SiC fiber preform to prepare SiC_f-CNTs/SiC composites with layered matrix structures. The thermal conductivity of the as-obtained material was found to be 23.9 W/(m·K), which was 2.9-fold higher than that of the traditional SiC/SiC composites. Besides, we previously developed a novel approach based on the introduction of heat transfer channels into C/SiC composites to yield better thermal conductivities [8,12]. Cao *et al.* [8] employed laser assisted-chemical vapor infiltration (LA-CVI) method to fabricate CNT/SiC micro-pillars in C/SiC composites as heat transfer channels to yield improved thermal conductivity of 20.69 W/(m·K). Zhang *et al.* [12] inserted pitch-based carbon fiber along the thickness direction of C/SiC composites to construct heat conductive micro-pipelines with the highest thermal conductivity of 32.70 W/(m·K). However, the above studies are based on the use of CNTs or other materials to modify the composites or construction of heat conduction channels inside the composites, which still lack control and stability due to the uncontrollable behaviors of CNTs or other nanomaterials at the nanoscale, as well as the difficulties encountered with various preparation techniques [8,12].

Polyacrylonitrile (PAN)-based carbon fibers, such as T300 and T700, are preferred fiber reinforcement materials used in C/SiC composites for aerospace applications due to their excellent mechanical properties

[13,14]. However, the thermal conductivity of PAN-based carbon fibers along the radial direction is only about 4.9 W/(m·K) [15], resulting in limited improvement of thermal conductivity of C/SiC composites. Pitch-based carbon fibers derived from mesophase pitch have superior modulus and high thermal conductivity that may reach hundreds of folds that of PAN carbon fibers. Hence, pitch-based carbon fibers have great potential in aerospace, medical treatment, construction, sports equipment, and many other application fields [16–18]. Recently, pitch-based carbon fibers have mainly been used in carbon matrix composites, while few research studies have been reported on the use of pitch-based carbon fibers to reinforce ceramic matrix composites. For example, Odeshi *et al.* [16] compared C/C–SiC composites reinforced by PAN-based carbon fiber and pitch-based carbon fiber. They found that C/C–SiC composites prepared by pitch-based carbon fiber possessed higher flexural strength (152 MPa) than PAN-based carbon fiber (133 MPa), which can be attributed to the longer load transfer length of the pitch-based fiber compared to PAN-based fiber. Servadei *et al.* [19] fabricated C/ZrB₂–SiC composites reinforced by ultra-high modulus pitch-based carbon fiber via PIP process. The bending strengths of carbon preform constituted by 0°, 0°/90°, and 2D were found to be 500, 370, and 190 MPa, respectively. Mainzer *et al.* [20] used pitch-based fibers to produce C/SiCN composites via PIP method with a tensile strength of 288 MPa. Therefore, pitch-based carbon fiber reinforced ceramic matrix composites are promising but their potential in the engineering field is still untapped.

The RMI process is effective for the rapid fabrication of ceramic matrix composites with high density [21]. The phase composition and microstructure caused by factors such as reaction rate, melt viscosity, behavior of silicon during phase transition, and wetting of reinforcement, are critical for successful composites. Li *et al.* [22] studied the effects of different diamond concentrations on thermal conductivities of diamond–C/SiC produced by RMI method. They found that higher diamond concentrations led to improved density (2.18 g/cm³), bending strength (309.01 MPa), and thermophysical properties (thermal conductivity: 14.68 W/(m·K), thermal expansion coefficient: $2.69 \times 10^{-6} \text{ K}^{-1}$) of the resulting composites. Zhong *et al.* [23] fabricated novel hierarchically porous carbon structures in fiber preform with a median pore size of 1.8 μm. The as-formed

C/SiC composites exhibited tensile strength of 159 ± 5 MPa, a value of 46% higher than that of normal C/SiC composites.

In this work, pitch-based carbon fiber reinforced SiC composites were obtained by CVI combined with RMI process. The effects of reaction temperature and resin carbon content during RMI process on the microstructures and phase compositions of the composites were investigated. The bending strengths and thermal conductivities of C_{pf}/SiC composites were thoroughly studied. SiC_w samples were also constructed, and both growth and action mechanisms were investigated. The results indicated that C_{pf}/SiC composites possessed good bending strength and excellent thermal conductivity.

2 Experimental

2.1 Materials

Mesophase pitch-based carbon fibers TC-HC-500 (Shaanxi Tiance New Materials Technology Co., Ltd., China) were used as reinforcement for C/SiC composites. Phenolic resin (Henan Hengtong Chemical Co., Ltd., China) was utilized as a carbon source for the reaction with molten Si (thermosetting resin).

2.2 Preparation of C_{pf}/SiC composites

Pitch-based carbon fiber was abbreviated as PB-fiber. Basic property of T300 and PB-fibers are listed in Table 1. SiC composites reinforced by pitch-based carbon fibers in this work were named as C_{pf}/SiC . As depicted in Fig. 1, the PB-fibers were woven into unidirectional fiber sheets and stacked by needle-punching along the $0^\circ/90^\circ$ direction to fabricate fiber preform.

The fiber volume content of the composites was 43%.

The combined CVI–RMI process mainly consisted of two steps. The first step was the preparation of porous C_{pf}/SiC composites by CVI. To this end, PyC interphase (150 nm in thickness) was deposited on the preform, and then treated at 1800°C for 2 h under vacuum to eliminate residual thermal stress. Thereafter, SiC matrix was infiltrated into the porous preform via CVI for 280 h at 1100°C . During the CVI process, methyltrichlorosilane (MTS, CH_3SiCl_3) was used as a precursor, and the process was carried out by bubbling hydrogen. Argon was employed as the diluent gas to slow down the reaction rate, and the pressure of the whole system was controlled at 5 kPa. After 3–4 CVI cycles in the furnace, the density of C_{pf}/SiC composites reached 1.6 g/cm^3 .

The second step consisted of the densification process by RMI. To this end, phenolic resin powder and absolute ethanol were mixed at the mass ratio of 1:3 to obtain a phenolic resin solution. After infiltration by resin solution in vacuum pot for 30 min, C_{pf}/SiC composites with resin were pyrolyzed under argon (purity $\geq 99.999\%$) at 950°C for 2 h to transform the polymer carbon into amorphous carbon, representing the end of one cycle of impregnation. After pyrolysis, the change in mass of the samples was recorded, and samples were embedded with superfluous Si powders followed by wrapping with graphite papers. Next, the samples were placed in a Si-infiltration furnace for 30 min under vacuum to yield C_{pf}/SiC composites.

Siliconization samples prepared at 1500, 1600, 1700, and 1800°C were denoted as T15#, T16#, T17#, and T18#, respectively. Porous samples were infiltrated with resin and pyrolyzed for 2, 4, 6, and 8 times to yield composites 2C#, 4C#, 6C#, and 8C#, respectively.

Fig. 1 Schematic diagram showing the pitch-based carbon fiber sheet, fiber preform, and composites.

Table 1 Properties of T300 and PB-fibers [15]

Carbon fiber	Thermal conductivity (W/(m·K))	Strength (MPa)	Modulus (GPa)	Linear density (g/cm ³)
T300	4.9	3530	230	0.06
PB-fibers	480	2078	806	0.46

2.3 Characterization

The density and open porosity of the composites were measured by the Archimedes method, and the results are gathered in Table 2. The crystal phases of the samples were identified by X-ray diffraction (XRD; Rigaku D/max-2400, Japan). Raman spectrum was conducted by a Raman spectroscopy (confocal Raman microscope, Renishaw, Beijing, China). Three-point bending tests were carried out by an electro-mechanical universal testing system (Instron 5567, UK) at room temperature and a loading rate of 0.5 mm/min. To this end, the prepared composites were processed into 40 mm × 5 mm × 3 mm specimens for use in each test. The microstructures of the composites were characterized by the scanning electron microscope (SEM; FEI, Helios G4 CX, USA) equipped with the energy dispersive spectrometer (EDS) and the back-scattered electron (BSE) detector. The thermodynamic properties were calculated by the FactSage software (Thermfact/CRCT, Canada and GTT-Technologies, Germany). The thermal diffusivity (α) and heat capacity (C_p) of each sample were measured by the laser flash method (LFA 427, NETZSCH, Germany) at a heating rate of 2 °C/min. The thermal conductivity (λ) of each composite was calculated according to the equation: $\lambda = \alpha \times C_p \times \rho$, where ρ is the specimen density and C_p is the specific heat capacity. The sample sizes in through-thickness and in-plane directions were Φ 12.7 mm × 3 mm and 10 mm × 5 mm × 3 mm, respectively.

Table 2 Properties of C_{pr}/SiC composites at different siliconization temperatures

Sample	Density (g/cm ³)	Porosity (%)	Thermal conductivity (W/(m·K))	
			In-plane	Through-thickness
RMI C/SiC	2.18	8.67	15.62	7.55
T15#	2.31	11.64	174.03	35.44
T16#	2.35	9.96	203.00	39.59
T17#	2.22	13.26	151.96	28.16
T18#	2.17	15.10	145.31	16.98

3 Results and discussion

3.1 Microstructures and morphologies of pitch-based carbon fibers

The crystal structures of the two types of carbon fibers were analyzed by XRD, and the results are shown in Fig. 2(a). The interplanar spacing (d_{002}) and half-peak width of (002) peak can reveal the graphitization degree of carbon fibers [24]. Smaller d_{002} values and narrower (002) peak indicated more integrated crystallinity and higher degree of graphitization [25]. Additionally, the half-peak width of (002) peak in the equatorial scanning patterns of the fibers (Fig. 2) was used to calculate the graphite microcrystalline stacking thickness (L_C). Smaller half-peak widths demonstrated larger stack thicknesses and more stacked graphite layers. The d_{002} values were obtained by the Bragg equation (Eq. (1)) [26], where λ is the wavelength of the X-ray (Cu K α_1 , 1.54060 nm) and θ represents the half-peak width (in radian). The L_C values were calculated by the Scherrer formula (Eq. (2)) [27], where K is the Scherrer factor (also known as the shape factor or $K = 0.92$), and β is the full width at half maximum of the diffraction peak. The XRD structural parameters of the two types of fibers are listed in Table 3.

$$d_{002} = \frac{\lambda}{2 \sin \theta} \quad (1)$$

$$L_C = \frac{K \lambda}{\beta \cos \theta} \quad (2)$$

As depicted in Fig. 2(a) and Table 3, the two types of carbon fibers showed a radiating peak at about $2\theta = 25^\circ$ with significantly different features. Compared to T300, PB-fibers displayed a strong and sharp (002) peak, as well as smaller interplanar spacing and thicker stacked sizes. These features indicated larger microcrystal dimension, higher degree of graphitization, and more complete stacking of graphite microcrystals.

The as-obtained composites were further analyzed by the Raman spectroscopy [25,28]. As shown in Fig. 2(b), the two types of carbon fibers exhibited typical Raman bands identified as D peak and G peak. The intensity of G peak was used to characterize the integrity of sp² hybridized structure in graphite, while

Table 3 XRD structural parameters of T300 and PB-fibers

Fiber	Diffraction angle (°)	Interplanar spacing d_{002} (nm)	FWHM	Stack thickness L_C (nm)
T300	26.23	0.361	6.63	1.22
PB-fibers	26.56	0.339	0.77	14.62

Fig. 2 XRD patterns and Raman spectra of T300 and PB-fibers.

D peak was employed to study the degree of orientation and structural defects in graphite. The 2D peak (2700 cm^{-1}) in Raman spectrum was also utilized to identify the monolayer and multilayer of graphene [29], which verified the layered graphite structure of PB-fibers. The intensity ratio (R) of D to G peak was used to estimate the degree of graphitization, where a lower R -value represents a higher degree of graphitization. In Fig. 2(b), the larger strength of D peak in T300 yielded broad and overlapped D peak and G peak, suggesting incomplete graphite structures and disordered lamellars of T300. Tuinstra and Koenig [30] observed a linear relationship between R and reciprocal value of grain size in crystal plane (L_a) according to the empirical formula shown by Eq. (3). The Raman structural parameters of the two fibers are compiled in Table 4.

$$L_a = \frac{4.4}{R} \quad (3)$$

The cross-sectional SEM images of the two types of fibers are presented in Fig. 3. Both fibers displayed significant differences in the order of graphite structures. The structures of carbon fibers were made of disorderly lamellar graphite structures. Bennet *et al.* [31] proposed a skin-core model to describe the microstructure of

carbon fibers. They found high modulus carbon fiber to possess layers of graphite microcrystals arranged orderly along the fiber axis in the cortex. The cores showed a slightly disordered shape of folds with intricate pore structures between the layers of graphite. The skin-core model could accurately describe the microstructures of PB-fibers. Compared to PB-fibers, the graphite microcrystals of T300 were tightly stacked but in a disordered manner. These data were consistent with the XRD and Raman analyses.

3.2 Growth mechanism of SiC whiskers

As shown in Fig. 4, large amounts of SiC whiskers (SiC_w , diameter: $\sim 0.8\text{ }\mu\text{m}$) were formed during RMI process. Note that SiC_w was characterized by a single crystal with a high orientation (diameter from nanometer to micrometer). Besides, SiC_w possessed few chemical impurities, no grain boundaries, few crystal defects, and uniform crystalline phase composition. These features

Table 4 Raman structural parameters of T300 and PB-fibers

Fiber	$R = I_D/I_G$	L_a (nm)
T300	2.96	1.49
PB-fibers	0.14	31.43

Fig. 3 Microstructures of cross-sections: (a) T300 and (b) PB-fibers.

provided SiC_w with good specific strength, high specific elastic modulus, and high thermal conductivity. In the following sections, $\text{C}_{\text{pf}}/\text{SiC}$ composites are produced at different siliconization temperatures; therefore, the different growth mechanisms of SiC_w at various siliconization temperatures should be discussed first.

According to the studies [32–34], SiC_w can be synthesized without the assistance of a catalyst. In other words, C and Si can directly react to form SiC_w . Wei *et al.* [34] studied the growth mechanism of SiC nanowires prepared by ball-milled activated carbon and vaporized silicon at 1600 °C without a catalyst. Their results identified vapor–solid (VS) interaction as the dominant mechanism. Li *et al.* [33] synthesized SiC_w using reactive graphite as a template and found that graphite with a higher density of defects could accelerate the formation of SiC_w . The studies of Dai *et al.* [32] and Chen *et al.* [35] indicated that the formation of SiC_w was achieved by three main stages, which included the generation of intermediate products, the formation of SiC nuclei, and the growth of SiC_w . The related reactions (several intermediate reactions included) are shown as Reactions (4)–(10). To further understand the growth mechanism of SiC whiskers in this work, the Gibbs free energy of the reaction at various temperatures (1500–1800 °C) was calculated by FactSage software. The reaction can happen spontaneously when the Gibbs free energy is less than 0. The standard Gibbs free energy of each reaction is shown in Fig. 5.

First, the intermediate products SiO and CO were produced via Reactions (4)–(6). As depicted in Fig. 5(a), Reaction (5) had positive Gibbs free energy at 1500–1800 °C, and Reaction (6) had negative Gibbs free energy, which demonstrated that generation of SiO and CO was mainly due to Reactions (4) and (6) (greater than around 1650 °C). Second, the Gibbs free energy in Fig. 5(b) had negative value, which illustrated that the formation of SiC nuclei could happen completely spontaneously and mainly contributed by Reaction (7) (lower Gibbs free energy). Finally, as shown in Fig. 5(c), the growth of SiC_w was basically dominated by Reactions (8) and (9). When the temperature exceeded around 1740 °C, Reaction (8) was the only reaction for SiC_w growth.

Based on the above analysis, the growth mechanism of SiC_w in the present work can be concluded as follows: VS mechanism governed the whole process. At 1500 and 1600 °C, the dominant reactions were Reactions (6)–(9). At 1700 °C, the dominant reactions were Reactions (4) and (6)–(9). At 1800 °C, the

Fig. 4 Microstructures and EDS analyses of SiC_w .

Fig. 5 Gibbs free energy change of Reactions (4)–(10) calculated by FactSage software: (a) formation of intermediate products, (b) formation of SiC nuclei, and (c) growth of SiC_w.

dominant reactions were Reactions (4) and (6)–(8). Si, carbon, and porous C_{pf}/SiC composites provided a good environment for SiC_w growth. In Fig. 4(a), SiC_w grew on the outside of the layered CVI SiC matrix, suggesting that SiC_w was formed during RMI instead of CVI process. The O-element involved in the reaction processes originated from SiO₂ in commercial Si powder. The schematic diagram of the growth of

SiC_w is depicted in Fig. 6. First, SiO and CO were generated by Reactions (4)–(6). Then, the superfluous Si vapor and SiO vapor were adsorbed on the residual carbon (activated carbon atoms) surface during RMI process and reacted to form SiC nucleus. Later, SiC_w grew along (111) direction [32,34,35] of SiC nucleus to form long and randomly oriented SiC_w following Reactions (8) and (9), according to the literature.

3.3 Thermal conductivity of C_{pf}/SiC composites

3.3.1 Effects of different siliconization temperatures

The melt infiltration process can use almost any reinforced geometry to yield high-density and low-porosity matrices. Different reaction temperatures (beyond the melting point of silicon, 1415 °C) of RMI can lead to various phase compositions and microstructures, thereby affecting the properties of C_{pf}/SiC composites. Table 2 summarizes the properties of C_{pf}/SiC composites prepared at different siliconization temperatures. The thermal conductivities in this work were measured at 35 °C. Note that the densities were repeatedly measured, and the obtained thermal conductivities were averaged to yield the values shown in Table 2. The data of traditional RMI C/SiC were collected from our database and were compared with the composites in this work. Apparently, composites in this work possessed excellent thermal conductivity. As can be seen, the densities of composites increased first with the reaction temperature and then decreased, and maximum density was recorded at 1600 °C. As shown in Fig. 7, the microstructures of the composites were consistent with the changing trend of density. The reaction between Si and C was theoretically more efficient at high temperatures. However, the exothermic reaction between Si and C resulted in excess local temperature and vaporization of large amounts of Si [36,37]. At reaction temperatures of 1500 and 1600 °C (Fig. 8), the reactants Si and C displayed weaker peaks, while the product SiC illustrated stronger peaks. At temperatures of 1600 and 1700 °C, the C peaks became extremely strong but the Si peaks weakened or even vanished. Hence, large amounts of Si vaporized while the graphitized resin carbon remained in the composites. The incomplete reaction between Si and C resulted in porous microstructures of T17# and T18#, while larger-sized pores remained. On the other hand, the reaction rate of Si and C was too fast and was much higher than the flow rate of liquid Si at high

Fig. 6 Schematic diagram showing the formation of SiC_w.

Fig. 7 Microstructures of C_{pf}/SiC composites prepared at different siliconization temperatures: (a) 1500 °C, (b) 1600 °C, (c) 1700 °C, and (d) 1800 °C.

Fig. 8 XRD patterns of C_{pf}/SiC composites prepared at different siliconization temperatures.

temperature, which blocked the permeability channels for molten Si.

The thermal conductivity of the as-prepared composites showed the same trend as the density, suggesting the crucial impact of densification on heat transfer properties. Compared to C/SiC composite prepared by T300, the C_{pf}/SiC composites possessed much better thermal conductivities in both the thickness and in-plane directions. In particular, the thermal conductivity in the in-plane direction was more than a dozen-fold higher than that of RMI C/SiC. As mentioned in Section 3.1, graphite crystallites with high orientation along the fiber axis direction greatly reduced the scattering of phonons, thereby improving the transfer efficiency. Compared to the preform prepared by plain weave in

axial and radial directions, the preform fabricated by unidirectional fibers possessed more fibers per unit volume along specific directions. The heat transfer modes along different directions are presented in Fig. 9. Obviously, the heat flow was faster along the fiber direction with less loss. Along the thickness direction, the heat transfer efficiency greatly reduced due to the elevated interfacial thermal resistance (top right corner of Fig. 9).

In this work, because of the evaporation of large amounts of Si under high temperature, SiC_w tended to grow at lower reaction temperatures (1500, 1600, and 1700 °C). As a result, SiC_w did not only improve the densification of the composites but also filled some pores (Fig. 7(c)).

3.3.2 Effect of different contents of resin carbon

All samples were fabricated by the same RMI process at 1600 °C but at various resin carbon contents. The densities and thermal conductivities of composites obtained at different resin carbon contents are displayed in Table 5. In Section 3.3.1, 1600 °C was identified as the appropriate preparation temperature of C_{pf}/SiC composites. As a result, the increase in resin carbon content did not significantly affect the density and porosity, as seen from the microstructures of the composites. In Fig. 10, no obvious pores were observed, and the microstructures were relatively dense. Compared to thermal conductivities along the thickness direction

Fig. 9 Schematic diagram of heat transfer in different directions of the composites.

Fig. 10 Microstructures of C_{pf}/SiC composites obtained with different resin carbon contents: (a) 2C#, (b) 4C#, (c) 6C#, and (d) 8C#.

Table 5 Properties of C_{pr}/SiC composites prepared with different resin carbon contents

Sample	Density (g/cm ³)	Porosity (%)	Thermal conductivity (W/(m·K))	
			In-plane	Through-thickness
2C#	2.29	10.85	170.03	27.67
4C#	2.31	11.63	175.79	34.66
6C#	2.28	13.26	170.19	38.86
8C#	2.21	13.88	162.50	18.45

Fig. 11 XRD patterns of C_{pr}/SiC composites prepared with different resin carbon contents.

(Table 5), the variation trend of the thermal conductivity along the in-plane direction was not obvious. Hence, the thermal conductivities along the in-plane direction were not significantly affected by the change in composite

structures. Various resin carbon contents induced different phase compositions, thereby significantly affecting the thermal conductivities along the thickness direction of the composites. The phase constitution of the composites was analyzed by the XRD patterns (shown in Fig. 11), where the composites showed stronger SiC peaks compared to Fig. 8. Note that the amorphous type of resin carbon is more difficult to detect by XRD. However, the resin carbon remaining in the matrix would be graphitized at high temperature (1600 °C) [38]. Consequently, the C peak in XRD became sharper and stronger. Additionally, BSE images of samples 4C#, 6C#, and 8C# in Fig. 12 revealed the local content and distribution of carbon. In the magnified image of Fig. 12(c), massive and agglomerated carbon particles were surrounded by SiC matrix and some Si, generating many grain boundaries.

As shown in Table 5, the thermal conductivities increased with carbon content and maximum value reached 38.86 W/(m·K). This could be attributed to the compact microstructure and high thermal conductivity of graphitized resin carbon. However, the thermal conductivity of 8C# reduced to 18.45 W/(m·K) due to the interface thermal resistance generated by excess graphitized resin carbon and other phases (SiC and Si). On the other hand, the thermal conductivities along the in-plane direction were mainly generated by the pitch-based fibers, which were less impacted by the composite structures (Section 3.3.1). As a result, the thermal conductivities remained relatively stable.

Fig. 12 BSE images of C_{pr}/SiC composites prepared with different resin carbon contents: (a) 4C#, (b) 6C#, and (c) 8C#.

Table 6 Bending strengths of C_{pf}/SiC composites prepared at different siliconization temperatures

Sample	T15#	T16#	T17#	T18#
Bending strength (MPa)	178.54±6.88	186.15±3.95	178.26±6.74	139.34±1.77
Bending modulus (GPa)	27.05±0.83	28.71±3.13	40.09±5.69	11.76±4.22

3.4 Bending strengths of C_{pf}/SiC composites

3.4.1 Effect of different siliconization temperatures

The bending strengths and bending moduli of C_{pf}/SiC composites obtained at different reaction temperatures are listed in Table 6. The bending strength of the composites at various siliconization temperatures was about 170 MPa, and composites with higher densities possessed better bending strengths. Compared to the bending strengths of traditional C/SiC composites prepared by CVI process, C_{pf}/SiC composites showed lower but acceptable values. This could first be attributed to pitch-based carbon fibers. Microcrystalline graphite highly orientated along the fiber axis could provide elevated heat transfer properties but poor bending and compressive strengths since the graphite sheets were spaced far apart (Fig. 3). Second, the unidirectional fibers preform significantly affected the transverse bending strengths of the composites. For transverse strength of 0°/0° composites, the fibers could not effectively bear the load transferred from the matrix in this direction [39]. Finally, the reactive melt of RMI process might damage the fibers, and the presence of residual Si and C would also reduce the mechanical properties of the composite due to cracks generated at the interface between the residual phase and matrix [22].

Photographs and microstructures of the fractured

surfaces of samples T15# and T18# are depicted in Fig. 13. The fractured areas of the composites were large with layered failure mode, indicating the formation of composites with good toughness. The microstructures of the fractured samples showed that long fiber bundles were pulled out (Fig. 13). A pull-out effect [40] of the fibers can also be observed in Fig. 14(a). As mentioned above, pitch-based carbon fibers had distinct and highly orientated layered structures (Figs. 14(a) and 14(b)). Large amounts of fiber fragments were observed in Fig. 14(a), especially at high magnifications where the fractured surface of the fiber was not only flat but similar to a layered structure. Hence, the graphite layers of the fibers were pulled out from the inside through layer by layer mode under tensile and shear loads. This type of internal layered pull-out phenomenon is typical for pitch carbon fibers.

On the other hand, SiC_w played an important role in strengthening and toughening of composites, especially in terms of toughening [41,42]. Here, the main toughening mechanisms of SiC_w were based on crack deflection, crack bridging, and whisker pull-out. First, the crack propagating in the matrix was deflected upon contact with SiC_w due to the mismatch in the elastic modulus between SiC_w and SiC matrix [43]. In turn, crack deflection could change the propagation path of the crack or make the crack branched, thereby absorbing the fracture energy and resulting in cracks no longer

Fig. 13 Photographs and microstructures of the fractured surfaces of samples T15# and T18#.

Fig. 14 Microstructures of fractured fibers and SiC_w .

perpendicular to the stress. Hence, the crack can further be expanded by only increasing the strength of the stress at the crack tip. In turn, this process released stress concentration at the crack tip, inhibiting the crack propagation in the composites [43]. Second, crack bridging occurred behind the crack front where the bridging ligaments were connected to the crack faces. By adding extra pressure during the crack opening, SiC_w decreased the stress intensity near the crack tip, thereby toughening the composites [44]. As shown in Figs. 14(c) and 14(d), large amounts of SiC_w were distributed on both sides of the crack. Lastly, plenty of pulled-out SiC_w covered by SiC matrix and holes left after pull-out were clearly observed in Figs. 14(e)–14(g). Due to the high tensile strength of whiskers, they are difficult to break. When the

load was transferred from the matrix to the whiskers, and the shear stress generated on the interface between them reached the shear strength of the interface, the whiskers pulled out from the matrix [45]. Extra energy would be consumed when whiskers are pulled out.

3.4.2 Effect of different contents of resin carbon

The bending strengths and moduli of C_{pf}/SiC composites prepared with different resin carbon contents are listed in Table 7. The average bending strength improved by 25% compared to the values listed in Table 6, and the optimal value reached 244.62 ± 3.07 MPa. During RMI process, residual Si remaining in the SiC matrix reduced the mechanical properties due to the unequal stress generated by different coefficients of thermal expansion.

Table 7 Bending strengths of C_{pf}/SiC composites prepared with different resin carbon contents

Sample	2C#	4C#	6C#	8C#
Bending strength (MPa)	176.15±13.62	195.03±7.98	244.62±3.07	233.57±10.33
Bending modulus (GPa)	34.39±1.33	36.66±5.95	40.32±3.21	38.09±5.91

Hence, sufficient carbon sources were beneficial to the RMI process with less residual Si.

Photographs and microstructures of C_{pf}/SiC composites prepared with different resin carbon contents are presented in Fig. 15. The holes are left after fiber pull-out and abundant SiC_w can be clearly observed in Figs. 15(a) and 15(b), respectively. This indicated the ductile fracture of the composites. Note that the same fracture behavior and the toughening mechanism by SiC_w were discussed in Section 3.4.1.

The thermal conductivities and bending strengths of recently reported fiber-reinforced ceramic matrix composites in comparison with materials prepared in this study are summarized in Table 8. Composites prepared herein showed excellent heat transfer performance and favorable bending strengths. At present, there is limited research on pitch-based fiber reinforced ceramic matrix composites, but this comparison shows great potential of these materials, which deserve to be studied further.

Fig. 15 Photographs and microstructures of fractured surfaces of samples 4C# and 8C#.**Table 8** Thermal conductivities and bending strengths of recently reported fiber-reinforced ceramic matrix composites in comparison with the materials prepared in this study

Ref.	Composite	Method	Thermal conductivity (W/(m·K))	Bending strength (MPa)
[8]	C/SiC–CNT	CVI	22.36±	395.92±19.01
[12]	C/SiC–CNT	CVI	32.70±0.72±	—
[46]	C/SiC–SiC _{nw}	PIP	3.30±, 8.18 //	336±16
[22]	Diamond–C/SiC	RMI	14.68±	309.01
[47]	Diamond–C/SiC	RMI	9–10±	365
[9]	C/SiC–CNT	PIP	16.8±	248.62
[48]	C/SiC–Ti ₃ SiC ₂	RMI	12.6±	539±39
[16]	C/SiC (pitch-based fibers)	PIP	—	150
[40]	C/SiC	PIP	35±, 150 //	285
This work	C/SiC	RMI	39.59±, 203.00 //	244.62±3.07
[6]	SiC/SiC	CVI	26.7±	482.00±36
[49]	SiC/SiC	PIP	14.3±	468.16±16
[39]	C/ZrB ₂ –SiC (pitch-based fibers)	PIP	—	260±20
[50]	C/ZrB ₂ –SiC (short pitch-based fibers)	Hot-press	48.3–104.7±	—
[51]	C/HfB ₂ –SiC (short pitch-based fibers)	Hot-press	93.8±	—

4 Conclusions

C_{pf}/SiC composites were successfully fabricated by RMI method by controlling the reaction temperature and resin carbon content. The thermal conductivities and bending strengths of the as-obtained composites under different preparation conditions were studied and results were discussed. The following conclusions can be drawn:

SiC whiskers were formed during RMI process through a VS mechanism. Growth mechanism at different siliconization temperatures was investigated by the Gibbs free energy of the reactions. The presence of SiC_w played an important role in toughening of C_{pf}/SiC composites.

The increase in reaction temperature of RMI process first led to a rising trend of the thermal conductivity along the in-plane and thickness directions, followed by a decline. At 1600 °C, the thermal conductivities along the in-plane and thickness directions were recorded as 203.00 and 39.59 W/(m·K), respectively. The bending strength was 186.15±3.95 MPa.

The increase in resin carbon content before RMI process led to the formation of more SiC matrix. The thermal conductivities along the in-plane and thickness directions remained stable at 175.79 and 38.86 W/(m·K), respectively. Also, the optimal bending strength improved to 244.62±3.07 MPa.

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References

- [1] Krenkel W. Carbon fiber reinforced CMC for high-performance structures. *Int J Appl Ceram Technol* 2004, **1**: 188–200.
- [2] Krenkel W, Berndt F. C/C–SiC composites for space applications and advanced friction systems. *Mater Sci Eng A: Struct* 2005, **412**: 177–181.
- [3] Kumar S, Kumar A, Sampath K, *et al.* Fabrication and erosion studies of C–SiC composite Jet Vanes in solid rocket motor exhaust. *J Eur Ceram Soc* 2011, **31**: 2425–2431.
- [4] Lamouroux F, Bertrand S, Pailler R, *et al.* Oxidation-resistant carbon-fiber-reinforced ceramic-matrix composites. *Compos Sci Technol* 1999, **59**: 1073–1085.
- [5] Dong Y, Ren K, Lu YH, *et al.* High-entropy environmental barrier coating for the ceramic matrix composites. *J Eur Ceram Soc* 2019, **39**: 2574–2579.
- [6] Tao PF, Wang YG. Improved thermal conductivity of silicon carbide fibers-reinforced silicon carbide matrix composites by chemical vapor infiltration method. *Ceram Int* 2019, **45**: 2207–2212.
- [7] Zhao ZF, Liu YS, Feng W, *et al.* Improvement on the thermal conductivity of diamond/CVI–SiC composites using large diamond particles. *Diam Relat Mater* 2017, **74**: 1–8.
- [8] Cao LY, Liu YS, Zhang YH, *et al.* Enhancing thermal conductivity of C/SiC composites containing heat transfer channels. *J Eur Ceram Soc* 2020, **40**: 3520–3527.
- [9] Chen SC, Feng YY, Qin MM, *et al.* Improving thermal conductivity in the through-thickness direction of carbon fibre/SiC composites by growing vertically aligned carbon nanotubes. *Carbon* 2017, **116**: 84–93.
- [10] Yang JS, Sprengard J, Ju LC, *et al.* Three-dimensional-linked carbon fiber-carbon nanotube hybrid structure for enhancing thermal conductivity of silicon carbonitride matrix composites. *Carbon* 2016, **108**: 38–46.
- [11] Feng W, Zhang LT, Liu YS, *et al.* Fabrication of SiC_f–CNTs/SiC composites with high thermal conductivity by vacuum filtration combined with CVI. *Mater Sci Eng: A* 2016, **662**: 506–510.
- [12] Zhang YH, Liu YS, Cao YJ, *et al.* Effect of initial density on thermal conductivity of new micro-pipeline heat conduction C/SiC composites. *J Am Ceram Soc* 2021, **104**: 645–653.
- [13] Rahaman MSA, Ismail AF, Mustafa A. A review of heat treatment on polyacrylonitrile fiber. *Polym Degrad Stab* 2007, **92**: 1421–1432.
- [14] Huang XS. Fabrication and properties of carbon fibers. *Materials* 2009, **2**: 2369–2403.
- [15] El-Hage Y, Hind S, Robitaille F. Thermal conductivity of textile reinforcements for composites. *J Text Fibrous Mater* 2018, **1**, <https://doi.org/10.1177/2515221117751154>.
- [16] Odeshi AG, Mucha H, Wielage B. Manufacture and characterisation of a low cost carbon fibre reinforced C/SiC dual matrix composite. *Carbon* 2006, **44**: 1994–2001.
- [17] Liu JC, Chen XJ, Liang DC, *et al.* Development of pitch-based carbon fibers: A review. *Energy Sources A: Recovery Util Environ Eff* 2020, <https://doi.org/10.1080/15567036.2020.1806952>.
- [18] Nysten B, Piriaux L, Issi JP. Thermal conductivity of pitch-derived fibres. *J Phys D: Appl Phys* 1985, **18**: 1307–1310.
- [19] Servadei F, Zoli L, Galizia P, *et al.* Development of UHTCMCs via water based ZrB₂ powder slurry infiltration

- and polymer infiltration and pyrolysis. *J Eur Ceram Soc* 2020, **40**: 5076–5084.
- [20] Mainzer B, Lin CR, Jemmali R, *et al.* Characterization and application of a novel low viscosity polysilazane for the manufacture of C- and SiC-fiber reinforced SiCN ceramic matrix composites by PIP process. *J Eur Ceram Soc* 2019, **39**: 212–221.
- [21] Patel M, Saurabh K, Prasad VVB, *et al.* High temperature C/C–SiC composite by liquid silicon infiltration: A literature review. *Bull Mater Sci* 2012, **35**: 63–73.
- [22] Li JX, Liu YS, Chen C, *et al.* Effect of diamond content on microstructure and properties of C/SiC–diamond composites. *Diam Relat Mater* 2020, **107**: 107902.
- [23] Zhong Q, Zhang XY, Dong SM, *et al.* Reactive melt infiltrated C_f/SiC composites with robust matrix derived from novel engineered pyrolytic carbon structure. *Ceram Int* 2017, **43**: 5832–5836.
- [24] Iwashita N, Park CR, Fujimoto H, *et al.* Specification for a standard procedure of X-ray diffraction measurements on carbon materials. *Carbon* 2004, **42**: 701–714.
- [25] Zickler GA, Smarsly B, Gierlinger N, *et al.* A reconsideration of the relationship between the crystallite size L_a of carbons determined by X-ray diffraction and Raman spectroscopy. *Carbon* 2006, **44**: 3239–3246.
- [26] Pradere C, Batsale JC, Goyhnche JM, *et al.* Thermal properties of carbon fibers at very high temperature. *Carbon* 2009, **47**: 737–743.
- [27] Patterson AL. The Scherrer formula for X-ray particle size determination. *Phys Rev* 1939, **56**: 978–982.
- [28] Cuesta A, Dhamelincourt P, Laureyns J, *et al.* Raman microprobe studies on carbon materials. *Carbon* 1994, **32**: 1523–1532.
- [29] Ferrari AC, Meyer JC, Scardaci V, *et al.* Raman spectrum of graphene and graphene layers. *Phys Rev Lett* 2006, **97**: 187401.
- [30] Tuinstra F, Koenig JL. Raman spectrum of graphite. *J Chem Phys* 1970, **53**: 1126–1130.
- [31] Bennett SC, Johnson DJ, Murray R. Structural characterisation of a high-modulus carbon fibre by high-resolution electron microscopy and electron diffraction. *Carbon* 1976, **14**: 117–122.
- [32] Dai JX, Sha JJ, Zhang ZF, *et al.* Synthesis of high crystalline beta SiC nanowires on a large scale without catalyst. *Ceram Int* 2015, **41**: 9637–9641.
- [33] Li YW, Wang QH, Fan HB, *et al.* Synthesis of silicon carbide whiskers using reactive graphite as template. *Ceram Int* 2014, **40**: 1481–1488.
- [34] Wei J, Li KZ, Li HJ, *et al.* Large-scale synthesis and photoluminescence properties of hexagonal-shaped SiC nanowires. *J Alloys Compd* 2008, **462**: 271–274.
- [35] Chen JP, Song G, Liu Z, *et al.* Preparation of SiC whiskers using graphene and rice husk ash and its photocatalytic property. *J Alloys Compd* 2020, **833**: 155072.
- [36] Larpiattaworn S, Ngerchnuklin P, Khongwong W, *et al.* The influence of reaction parameters on the free Si and C contents in the synthesis of nano-sized SiC. *Ceram Int* 2006, **32**: 899–904.
- [37] Chiang YM, Messner RP, Terwilliger CD, *et al.* Reaction-formed silicon carbide. *Mater Sci Eng: A* 1991, **144**: 63–74.
- [38] Tzeng SS, Chr YG. Evolution of microstructure and properties of phenolic resin-based carbon/carbon composites during pyrolysis. *Mater Chem Phys* 2002, **73**: 162–169.
- [39] Sciti D, Zoli L, Vinci A, *et al.* Effect of PAN-based and pitch-based carbon fibres on microstructure and properties of continuous C_f/ZrB₂–SiC UHTCMCs. *J Eur Ceram Soc* 2021, **41**: 3045–3050.
- [40] Reimer T, Petkov I, Koch D, *et al.* Fabrication and characterization of C/C–SiC material made with pitch-based carbon fibers. In: *Processing and Properties of Advanced Ceramics and Composites VII*. Mahmoud MM, Bhalla A, Bansal NP, *et al.* Eds. John Wiley & Sons, Inc., 2015: 277–293.
- [41] Mei H, Wang HW, Ding H, *et al.* Strength and toughness improvement in a C/SiC composite reinforced with slurry-prone SiC whiskers. *Ceram Int* 2014, **40**: 14099–14104.
- [42] Oh BJ, Lee YJ, Choi DJ, *et al.* Fabrication of carbon/silicon carbide composites by isothermal chemical vapor infiltration, using the in situ whisker-growing and matrix-filling process. *J Am Ceram Soc* 2001, **84**: 245–247.
- [43] Jiang X, Chen Y, Sun XW, *et al.* Mechanical property improvement and microstructure observation of SiC_w–AlN composites. *J Eur Ceram Soc* 1999, **19**: 2033–2038.
- [44] Qin QH. 1—Introduction to the composite and its toughening mechanisms. In: *Toughening Mechanisms in Composite Materials*. Amsterdam (the Netherlands): Elsevier, 2015: 1–32.
- [45] Deng JX. Effect of thermal residual stress on the high temperature toughening behaviour of TiB₂/SiC_w composites. *J Mater Process Technol* 2000, **98**: 292–298.
- [46] Hu JB, Dong SM, Wu B, *et al.* Mechanical and thermal properties of C_f/SiC composites reinforced with carbon nanotube grown *in situ*. *Ceram Int* 2013, **39**: 3387–3391.
- [47] Li JX, Liu YS, Nan BY, *et al.* Microstructure and properties of C/SiC–diamond composites prepared by the combination of CVI and RMI. *Adv Eng Mater* 2019, **21**: 1800765.
- [48] Fan XM, Yin XW, Cao XY, *et al.* Improvement of the mechanical and thermophysical properties of C/SiC composites fabricated by liquid silicon infiltration. *Compos Sci Technol* 2015, **115**: 21–27.
- [49] Feng W, Zhang LT, Liu YS, *et al.* Thermal and mechanical properties of SiC/SiC–CNTs composites fabricated by CVI combined with electrophoretic deposition. *Mater Sci Eng: A* 2015, **626**: 500–504.
- [50] Guo SQ. Thermal and electrical properties of hot-pressed short pitch-based carbon fiber-reinforced ZrB₂–SiC matrix composites. *Ceram Int* 2013, **39**: 5733–5740.
- [51] Guo SQ, Naito K, Kagawa Y. Mechanical and physical behaviors of short pitch-based carbon fiber-reinforced HfB₂–SiC matrix composites. *Ceram Int* 2013, **39**: 1567–1574.

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