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Effect of silicon addition on the microstructure, mechanical and thermal properties of C_f/SiC composite prepared via selective laser sintering

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Abstract

Carbon fiber reinforced silicon carbide (C_f/SiC) composite was fabricated by infiltrating liquid silicon (Si) into the carbon preform, which was built by selective laser sintering (SLS) additive manufacturing process from the phenolic resin coated carbon fiber powder with addition of submicron Si. The effect of Si addition on the microstructures of the laser-sintered green part, carbon preform and derived C_f/SiC composite was investigated. The results show that the introduced submicron Si plays an important role in reducing porosity and average pore size of the carbon preform, and contributes to improving the microstructure homogeneity of C_f/SiC composite by reducing the size of continuous bulk carbon in the **preforms**. The maximum density, flexural strength and fracture toughness of the C_f/SiC composite are 2.89±0.01 g/cm³, 237±9.6 MPa and 3.56±0.24 MPa·m^{1/2}, respectively. The coefficient of thermal expansion (CTE) of the C_f/SiC composite is approximately 5.5×10⁻⁶/K from 25 to 900°C, and the thermal conductivity is in the range of 74-84 W/m·K at room temperature, while decreases to 35-40 W/m·K at 900 °C.

Keywords: Carbon fiber reinforced SiC ceramics, additive manufacturing, selective laser sintering, liquid silicon infiltration, mechanical and thermal properties

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1 Introduction

SiC has been regarded as one of the most promising structural ceramics owing to its high strength-to-weight ratio, high thermal conductivity coupled with low thermal expansion, excellent resistance to abrasion and corrosion, and most importantly high strength retention at high temperatures (approaching 1600°C) [1-5]. All these characteristics have led to a wide range of applications, such as abrasive and cutting tools, high-temperature kilns, composite armor and gas turbines engines [6-8]. Meanwhile, these intrinsic features conversely make it very difficult to process by use of conventional manufacturing techniques, such as pressureless sintering, hot pressing or hot isostatic pressing, which normally need high temperature, additional pressure or sintering aids [9-11]. Furthermore, shaping of a SiC component is only possible with expensive diamond tooling and quite time-consuming. Alternatively, reactive sintering through liquid silicon infiltration (LSI) process is an attractive approach to produce SiC ceramics due to their low processing temperature, short reaction time and near-net shape fabrication capability [12]. One of the primary way is reaction-bonded SiC (RBSC), in which a porous preform consisting of α -SiC and carbon (C) is infiltrated with molten Si, resulting in the formation of secondary SiC (β -SiC) particles to bond existing α -SiC grains through the occurrence of chemical reaction between Si and C [13-14]. In the other modified approach, named reaction-formed SiC (RFSC), shaped monolithic carbonaceous materials such as resin-derived carbon, biomorphic carbon or carbon fiber are used as raw materials and infiltrated by molten Si to form SiC ceramics directly [15]. It has been demonstrated that infiltration of porous carbon preforms with molten Si can achieve high density, fine SiC grains and even high mechanical strength at significantly reduced cost.

The desired shape of a reaction-formed SiC part is derived from the geometry of a porous carbon preform, which is conventionally produced by slip casting, injection molding or uniaxial pressing, etc [16-21]. However, these methods usually require molds and tools, which are more suitable for mass production of SiC parts with simple shapes. In recent years, additive manufacturing (AM) of SiC ceramics is

increasingly under development owing to its unparalleled flexibility of manufacturing 3D structures over traditional shaping processes [22-26]. Among the various AM technologies, SLS is one of the most promising powder bed fusion AM techniques capable of producing near-net-shape SiC parts with complex geometries due to its versatility in processing polymeric, metallic, ceramic and composite materials [12, 27-28]. Stierlen et al. [29] utilized SLS for the first time to fabricate pre-designed preforms with the mixture of SiC powder and polymer binder, and subsequently removed the sacrificed polymer by debinding process to obtain a porous preform, which is then infiltrated with liquid Si to form SiC ceramics. Sebastian et al. [30] proposed a direct SLS method to construct preforms using Si-SiC powder blends, in which Si powder served as a non-sacrificed binder to unify SiC particles during the SLS process. After impregnating of carbon-yielding resin, pyrolysing and infiltrating of liquid Si, nearly full dense SiC ceramic parts were obtained.

In contrast, our previous work reported a novel method to fabricate SiC materials from a starting material of phenolic resin coated carbon fiber (PF/C_f) composite powder [31]. SLS technology was used to process the carbon fiber green parts, which were impregnated with phenolic resin and then pyrolyzed to generate carbon fiber/carbon (C_f/C) preforms with increased density. The preforms were finally converted to C_f/SiC composite parts through LSI process. The used carbon fibers served not only as dimension stabilization element as well as carbon source to increase SiC content, and the remaining carbon fiber can also contribute to the improvement of the fracture toughness of the SiC ceramic matrix. However, the derived microstructure of the C_f/SiC composite was appreciably nonhomogeneous due to the wide pore size distribution and existence of large-dimension bulk carbon in the preforms. This could lead to residual Si with varying sizes and even appearance of residual pyrolytic carbon in final products, which was detrimental to their mechanical properties [32].

In this work, we aim to improve the microstructure homogeneity and properties of the C_f/SiC composite by optimizing the composition of the starting PF/C_f composite powder. More specifically, submicron Si particles are introduced into the

feedstock with the purpose of reducing the size of the continuous bulk carbon in the carbon preforms. The effect of Si addition on the microstructure evolution of the laser-sintered green part, carbon preform and derived C_f/SiC composite is investigated. The mechanical and thermal properties of the fabricated C_f/SiC composite parts are also evaluated.

2 Experimental and characterization

2.1 Preparation of samples

The composite powder used for SLS process was prepared by a solvent evaporation method. Firstly, the soluble phenol resin (PF) powder (PF2123, Wuxi Mingyang Bonding Material Co., Ltd., China) was completely dissolved in absolute ethanol and then carbon fibers and pure Si powder (Hunyuan Fuhong Mineral Products Co., Ltd.) were sequentially added to the above solution and stirred. Subsequently, the mixture was uniformly dispersed by means of ball-milling for 1h, which was dried in air-circulating oven at 60 °C. Finally, the mixture was crushed and sieved to obtain the PF/C_f-Si composite powder. The volume ratio of PF and C_f is fixed at 3:7. Four groups of composite powders with different volume fraction of Si (0%, 5%, 15% and 30%) were prepared, which were labeled as PF/C_f-0%Si, PF/C_f-5%Si, PF/C_f-15%Si and PF/C_f-30%Si. The compositions of the composite powders are shown in [Table 1](#).

Table 1 Compositions of the PF/C_f-Si composite powders

Composite powders	Materials compositions (vol. %)		
	Si	C _f	PF
PF/C _f -0%Si	0	70	30
PF/C _f -5%Si	5	66.5	28.5
PF/C _f -15%Si	15	59.5	25.5
PF/C _f -30%Si	30	49	21

The PF/C_f-Si composite powders were shaped into green parts through SLS technique (HK P320™, Wuhan Huake 3D Technology Co., Ltd., China). The processing parameters were optimized as follows: the laser power was 8 W, scanning speed was 2000 mm/s, powder layer thickness was 0.1 mm, scanning spacing was

0.15 mm and part bed temperature was set as 60 °C.

In order to improve strength of the green parts, post-curing and carbonizing process were performed in a tube furnace with protection of flowing argon. Then, the carbonized parts were further densified to achieve proper porosity by impregnating, curing and carbonizing of boron-modified phenolic resin (THC-400, Shaanxi Taihang Impedefire Polymer Co. Ltd., China). The impregnating process was conducted by immersing the samples into the phenolic resin solution under vacuum condition. The impregnated samples were then gradually cured at 120°C for 1h, 150°C for 1h and 180°C for 3h to avoid residual stress and shrinkage distortion. Afterwards, they were carbonized at 900 °C for 1h to obtain the C_f/C preforms, which are denoted as CP0, CP5, CP15 and CP30 corresponding to different Si contents in the starting composite powders.

In the Si infiltration process, the C_f/C preforms were placed in a graphic crucible coated with boron nitride (BN) layer. Granulated Si with an average size of 1~3 mm was placed around the samples to be infiltrated. The crucible was put into a vacuum furnace. The infiltration temperature and time were 1550 °C and 1 h, respectively. **The derived C_f/SiC composites** are labeled as SC0, SC5, SC15 and SC30, respectively. The C_f/SiC composite samples were cut by wire electrical discharge machining and grinded by diamond grinding wheel prior to characterization.

2.2 Characterization

The apparent porosity of the green parts, porous C_f/C preforms and bulk density of the C_f/SiC composites were determined according to the Archimedes principle. The pore size distributions of the C_f/C preforms were measured with a mercury porosimeter (Autopore IV 9500, Micromeritics Instrument Corp., USA). The surface morphology of the powders, **microstructure of the C_f/C preforms and C_f/SiC composites** were observed by field scanning electron microscope (JSM-7600F JEOL, Japan; Quanta 650 FEI, USA). All samples were coated with platinum to avoid discharge before observation. The phase composition of the specimens was analyzed by X-ray diffractometer (XRD-7000, SHIMADZU Corporation, Japan), using Cu K α radiation in the 2 θ range between 10° and 80° **at a scan speed of 10 °/min.**

High-resolution transmission electron microscopy (HRTEM) analysis was carried out on a FEI Tecnai G2 F30 transmission electron microscope. The TEM samples were first mechanically grinded and polished by using the Leica EM TXP (Leica, Germany) target surfacing system, and further ion-beam thinning was performed on a precise ion polishing system (Model 691, Gatan, USA) at 5 kV at an angle of 5° ensured electron transparency. The HRTEM micrographs were analyzed using Digital Micrograph software. Three point bending testing was performed in accordance with ISO 14704-2008, using a universal testing machine (Zwick/Roell Z010, Ulm, Germany) at a crosshead speed of 0.5 mm/min. The sample size was 40 mm×4 mm×3 mm. Fracture toughness was evaluated using a single edge notched beam (SENB) with the crosshead speed of 0.05 mm/min, and the sample size was 20 mm×4 mm×3 mm.

The coefficient of thermal expansion (CTE, α) of the SiC specimens was measured by a thermal dilatometer (DIL402C, NETZSCH, Germany) at 25-900 °C at a heating rate of 10 °C/ min. The dimension of the testing samples is 20 mm×4 mm×3 mm. The instantaneous CTE at temperature T can be calculated through the following equation [33]:

$$\alpha = \frac{1}{L_0} \cdot \frac{\Delta L}{\Delta T} \quad (1)$$

where L_0 is the nominal length at the room temperature (RT), ΔL is the length change of the samples, and ΔT is the change of temperature. The length change at each temperature during the heating procedure was recorded by the software of Netzsch. The thermal conductivity λ of the C_f/SiC specimens within 25-900°C can be calculated by the following formula:

$$\lambda = \alpha \cdot \rho \cdot C_p \quad (2)$$

where α , ρ and C_p represent thermal diffusivity, density and specific heat capacity, respectively. The thermal diffusivity was measured by laser flash apparatus (LFA 427 MicroFlash, NETZSCH, Germany). The dimension of the testing samples is 10 mm×10 mm×1 mm. The specific heat capacity was characterized by differential scanning calorimetry (DSC) analyzer (STA449F3, NETZSCH, Germany).

3 Result and discussion

3.1 Morphologies of the PF/C_f-Si composite powder and laser-sintered green part

Fig.1 shows the SEM micrographs of the carbon fibers, PF/C_f-Si composite powders and the corresponding green parts formed by SLS. As shown in Fig.1a, the carbon fibers exhibit smooth surfaces and uniform lengths. The length of fibers can be measured by image processing software (Image J). The results show that the carbon fibers have an average length and diameter of 47.5 μm and 7.0 μm , respectively. The energy dispersive X-ray spectrometry (EDX) pattern of the fiber shows that it contains 95.23 wt% of carbon and 4.77 wt% of oxygen, indicating the existence of some oxygen-containing groups, which could be beneficial to improve the interfacial bonding strength between the carbon fiber and PF resin. As seen in Fig.1b, the surfaces of carbon fibers are rough due to the coating of PF resin. The insert picture in Fig.1b shows the microstructure of laser-sintered green parts, the PF resin is melted and flows to bond the carbon fibers into a porous and self-supported structure. With addition of Si powder, less PF resin is coated onto the carbon fibers due to the competing effect of Si particles (Fig.1c). When the percentage of Si powder increases to 30 vol.%, the field of view bristles with single Si particles, and the surfaces of carbon fibers become further smoother due to the increased surface area of Si particles (Fig.1d). The insert pictures in Fig.1c and d show that Si particles are uniformly dispersed and connect to carbon fibers through the viscous flow of PF resin. It also shows that porosity in the green parts decreases with increasing of Si particles.

Figure 1 (a) Morphology and EDX pattern of raw carbon fibers. Morphologies of (b) PF/C_f-0% Si, (c) PF/C_f-15%Si and (d) PF/C_f-30%Si composite powders, and the inset pictures are microstructures of the corresponding green parts built by SLS.

3.2 Microstructure of the C_f/C preforms

The C_f/C preforms were obtained after impregnating the green parts with PF resin solution and sequentially curing and carbonizing. The surface morphologies of the preforms were observed with SEM in the backscattered electron (BSE) imaging mode. Fig.2a shows the typical microstructures of the C_f/C preforms without addition of Si powder (CP0). The bonding between carbon fibers (gray color) is realized by the residual carbon ligaments after carbonizing of PF resin. Pores (dark color) can be easily identified. The microstructures of the C_f/C preforms are diverse with addition of Si powder. As shown in Fig.2b, Si particles (bright color) are well distributed in the porous CP5 sample. The pyrolytic carbon (PyC) becomes a continuous phase filled in the gaps between carbon fibers. Cracks between carbon fibers and pyrolytic carbon are observed because of the shrinkage during curing and carbonization process. The density of CP5 sample seems to increase and the pore size decrease compared with CP0 sample. With the increase of Si content, the Si particles are prone to agglomerate

(Fig.2c and d), and the pore size in the preforms is further deceased.

Figure 2 SEM micrographs of the porous C_f/C preforms. (a) CP0, (b) CP5, (c) CP15 and (d) CP30.

In order to reveal the microstructure evolution of C_f/C preforms quantitatively, characterizations of porosity and pore size distribution were carried out. As illustrated in Fig. 3a, the apparent porosity of the green parts formed by SLS fluctuates around 70.0 %, and slightly increases with the Si content. After impregnating and carbonizing of PF resin, the porosity of C_f/C preforms is significantly reduced to the range of 50.4%-56.8%, which is inversely decreased with the Si content in the starting materials. This result coincides with the obtained microstructures from SEM analysis (Fig.2). It is demonstrated that there is an approximately 58% volume expansion when one mole of amorphous carbon reacts with liquid Si to form one mole SiC [34]. Therefore, the porosity of carbon preform should not below a critical value of 38 % to ensure the complete infiltration of liquid Si and avoid the “choking-off” phenomenon [35]. In this work, the porosity of the preforms is in an appropriate range.

The pore size distribution is also critical and can be measured by mercury

porosimetry, the results are presented in Fig. 3b. All the C_f/C preforms show a broad spectrum of pore size distribution from several microns to $\sim 30\ \mu\text{m}$. As for the C_f/C preform without addition of Si, the pore size distribution curve is multimodal with shoulders towards smaller pore, which indicates nonhomogeneous pore channels inside. Moreover, the average pore size is calculated to be $20.3\ \mu\text{m}$. With increasing of Si content in the starting materials, the average pore size of C_f/C preforms gradually decrease to $19.0\ \mu\text{m}$, $16.7\ \mu\text{m}$, and $12.1\ \mu\text{m}$, respectively. This is mainly because that during the impregnation stage, the distributed Si particles in the green parts contributes to intercept more resin as they reduced the diameters of the capillary, which is subsequently transferred to pyrolytic carbon and takes over the previous space.

Figure 3 (a) Apparent porosity of green parts and (b) pore size distribution of C_f/C preforms.

3.3 Microstructure and phase composition of the C_f/SiC composites

Fig. 4 illustrates the SEM micrographs of polished cross-sections of the C_f/SiC composites. All C_f/SiC composites show a three-phase microstructure consisting of reaction-formed SiC (dark gray), residual Si (light gray) and unconverted C (black) resulting from the C_f/C preforms. The SC0 sample shows a relatively nonhomogeneous phase distribution and a large amount of unreacted carbon wrapped in the SiC matrix (Fig. 4a). As aforementioned, the corresponding C_f/C preforms has a nonhomogeneous microstructure with a multimodal distribution of pore channel, which subsequently leads to an identical nonhomogeneous microstructure in the SC0 sample. With addition of Si powder in the starting materials, the microstructure homogeneity of the resulting C_f/SiC composites is improved, as shown in Fig. 4 b-d.

The phase volume fractions of the C_f/SiC composites are calculated from several SEM micrographs and listed in Table 2. As is seen, the SC0 sample has high residual carbon as well as low SiC contents (~ 62 vol.%). In contrast to that, the SC5 sample shows a increased SiC content (~71.3 vol.%) and a marginally lower residual carbon content. However, with further increase of Si powder content in the starting materials, the residual carbon in the resulting C_f/SiC composites nearly vanish, while the content of residual Si increases greatly (Fig.4 c, d).

Figure 4 SEM micrographs of the polished cross-sections of the C_f/SiC composites. (a) SC0, (b) SC5, (c) SC15 and (d) SC30.

Table 1 Bulk density and phase volume fraction of the C_f/SiC composites

Samples	Bulk density (g/cm ³)	Phase volume fraction (vol. %)		
		SiC	Si	C and pores
SC0	2.82±0.04	62.0	29.0	9.0
SC5	2.89±0.01	71.3	22.1	6.6
SC15	2.84±0.03	65.8	30.4	3.8
SC30	2.84±0.03	63.9	35.3	0.8

The reaction during the LSI process is proceed by infiltrating of liquid Si into the

C_f/C preform and dissolving of carbon in liquid Si. The Poiseuille capillary flow equation can be used to estimated the time t required to achieve a certain infiltration height h [36],

$$t = h^2 \left[\frac{\gamma r (r^3 / r_0^2 R) \cos \theta}{2\eta} \right]^{-1} \quad (3)$$

where γ and η are the surface tension and viscosity of liquid Si, respectively. θ is the contact angle, R is the effective capillary radius which drives the infiltration, r_0 is the mean geometrical capillary radius, and r is the effective fluid radius which provide rapid access to the penetrating liquid Si driven by capillarity ($r < R < r_0$). Taking an infiltration height h of 10 mm as a reasonable order of magnitude in this study and using literature data for the infiltration properties of liquid Si at around 1550 °C ($\gamma = 0.82$ N/m, $\eta = 0.7$ mPa·s, $\theta = 50^\circ$ for glassy carbon and $\theta = 10^\circ$ for highly oriented pyrolytic graphite, $r \approx 20$ μm) [36-38]. Assuming $r^3 / r_0^2 R = 1$, the infiltration time is expected to be about 0.01 s, which means that the liquid Si penetrates into the pore channels immediately after melting.

The reaction between liquid Si and solid carbon is dominated by a solution-precipitation mechanism at the early and intermediate stages. The newly formed SiC acts as a barrier to further reaction. The time t required for dissolving a carbon layer with thickness of τ can be calculated using the following equation [37-39]

$$\tau = \sqrt{D_e t} \quad (4)$$

where D_e is the effective diffusion coefficient of carbon through SiC layer, which is expressed by the Arrhenius equation

$$D_e = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (5)$$

where D_0 is the pre-exponential factor (2×10^{-6} cm²/s), Q is the activation energy (132

kJ/mol), R is the gas constant (8.314 J/(mol·K)), T is the processing temperature (1550 °C or 1823 K), D_e is calculated to be 3.301×10^{-10} cm²/s [39]. Therefore, the time for converting, for example, a carbon fiber with diameter of 7 μm into SiC is estimated as approximately 24 min. It should be noted that the reaction time is proportional to square of the thickness of carbon, which means that the bulk carbon with large thickness can not be fully transformed into SiC within a certain time, thus resulting in the remaining of carbon.

Through the analysis of reaction kinetic, it can be known that the obtained **microstructures** of C_f/SiC composites are correlated to the characteristics of the corresponding initial C_f/C preforms, such as volume fraction and thickness of carbon as well as porosity [38]. The addition of Si powder in the C_f/C preform separates the continuous bulk carbon into small pieces, which can shorten the reaction time thus reduce the size of residual carbon. Another effect governing the formation of SiC grain is the reactivity of carbon source, which is determined by their crystal structures. The carbon fibers formed from polyacrylonitrile (PAN) precursor at a temperature of 1200 to 1500°C are better crystallized and thus relatively less reactive than the pyrolytic carbon derived from the phenolic resin at a lower temperature [9]. The liquid Si firstly **reacts with** the pyrolytic carbon that coated on the carbon fiber, which provides a protective effect for carbon fiber against siliconization by prolonging the reaction time. For this reason, **the residual carbon consists of mostly strip-like carbon fibers suffering from different degree of siliconization**, as can be seen from Fig.4b. It has been reported in our previous work that the residual carbon fiber have a positive effect on **improving** the toughness of the C_f/SiC composite [27].

SiC has many different variant types in crystalline structure, of which α-SiC and β-SiC are the major variant types. The α-SiC is a stable structure in high temperature, while β-SiC is usually formed at temperatures below 1700 °C. The phase compositions of C_f/SiC composite parts were analyzed through XRD patterns, as shown in Fig.5. It can be seen that the C_f/SiC composite is mainly composed of β-SiC and Si, while carbon phase is hardly detected except for a very small peak at about 2θ=26.5° [17] for SC0 sample. This may be related to the less content of carbon phase

in the samples. It has been reported that exothermic reaction of Si and C will leads to localized temperature increase and some newly-formed β -SiC will transform into α -SiC when the temperature is above 2100 °C [34]. However, in this study α -SiC is also undetected, which is mainly because of the low infiltration temperature (1550 °C) and micron-sized pore channels of the C_f/C preforms.

Figure 5 X-ray diffractogram of the C_f/SiC composite parts.

To further investigate the mechanism of SiC formation during siliconization, the representative sample was characterized using TEM. Precipitates with two different sizes were observed. Fig.6a shows the bright field TEM image of polygonal micron-scale precipitates, which grows outwards as parallel faceted plates. The EDX results in Fig. 6b, c indicates that the polygonal precipitate is SiC and the matrix is Si. As shown in Fig. 6d, the selected area electron diffraction (SAED) patterns taken from different spots (A and B) further reveals the precipitate is β -SiC. Fig. 6f shows the bright filed image of the nanocrystals region with size of approximately 100 nm. To determine the composition of the nanocrystals, HRTEM was performed at the interface between a nanocrystal and matrix (Fig. 6g). The corresponding Fast-Fourier-Transformed (FFT) images showing in the insets suggest that both areas feature the face centered cubic (FCC) structure. The lattice parameters of this two regions were calculated to be $d(111)=0.315$ nm (Si), $d(111)=0.258$ nm (β -SiC), which

perfectly matches the standard XRD JCPDS cards (No.27-1402, No. 65-0360). Therefore, it is concluded that the nano-scale precipitates also correspond to β -SiC grains. Fischedick et al [40] and Zollfrank et al [41] have observed separately the same nano-SiC grains in processing C/C-SiC composites and biomorphous Si/SiC ceramics using LSI method. As proposed by [40-43], the nano-SiC grains are generally formed at the C-SiC interface during the initial stage of LSI, where liquid Si rapidly wets the carbon surface resulting in a spontaneous chemical reaction. These nano-SiC grains usually have a high density of stacking faults, which are the driving force for the formation of coarse SiC grains by dissolution and re-crystallization mechanism [42]. It is noted that α -SiC is still not detected in this case, although some researchers have found the existence of α -SiC nanocrystals in the reaction-formed SiC composites owing to the $\beta \rightarrow \alpha$ transformation occurred at high temperature [40].

Figure 6 (a) Bright field image of the micron-scale SiC grain. SAED patterns obtained from (b) spot A and (c) spot B. EDX patterns collected from from (d) spot A and (e) spot B. (f) Bright field image of the nanoscale SiC grain. (g) HRTEM image of the Si-SiC

interface, and the inserts are the FFT patterns of the corresponding phases.

3.4 Mechanical and thermal properties of the C_f/SiC composite

As listed in Table 2, all the C_f/SiC composites show similar bulk density, among which the SC5 sample has the maximum value of $2.89 \pm 0.01 \text{ g/cm}^3$. The mechanical properties of C_f/SiC composite parts are shown in Fig. 7. The flexural strength and fracture toughness of the SC0 sample are $191 \pm 8.2 \text{ MPa}$ and $3.26 \pm 0.06 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. Both flexural strength and fracture toughness of the SiC composites first increase with the Si content in the starting materials up to a maximum and then decrease. The variation in the mechanical properties is attributed to the change in microstructure of the samples, especially the SiC content and phase homogeneity [44]. The maximum flexural strength of $237 \pm 9.6 \text{ MPa}$ and fracture toughness of $3.56 \pm 0.24 \text{ MPa}\cdot\text{m}^{1/2}$ are simultaneously attained for SC5 sample, which contains the most quantity of SiC phase. Compared without addition of Si, the flexural strength and fracture toughness increase by 24.1%, 9.5% respectively.

Figure 7 Mechanical properties of C_f/SiC composite parts. (a) Flexural strength and (b) fracture toughness.

Thermal properties including CTE and thermal conductivity are two key factors for the application of SiC ceramics at high temperatures. Fig.8a is the CTE curve of C_f/SiC composites as a function of temperature. The thermal expansion of all materials shows nearly the same non-linear tendency and increases over the entire temperature range, which resembles most polycrystalline materials [45]. In the range between RT to 300 °C, the CTE increases rapidly up to approximately $4.51 \times 10^{-6}/\text{K}$. In the range of 300-900 °C, however, the increase of CTE becomes slower. The CTE of

SC0 sample from RT to 900 °C is around $5.56 \times 10^{-6}/\text{K}$, which is slightly higher than that of β -SiC from RT to 1000 °C ($4.45 \times 10^{-6}/\text{K}$) [46]. Fig.8b shows the inverse temperature dependence of thermal conductivity of the C_f/SiC composites. The RT thermal conductivity of the C_f/SiC composites in this study is in the range of 74-84 W/m·K, and the values of SC5 and SC15 is slightly higher than that of SC0 and SC30 samples. As the temperature increase to 900 °C, the thermal conductivity monotonously decreases to 35-40 W/m·K. The RT thermal conductivity of the C_f/SiC composites is relatively lower than the reported value of liquid phase sintered SiC (110 W/m·K) [47] and hot-pressed SiC (120 W/m·K) ceramics [48], but better than that of the biomorphic Si/SiC (70 W/m·K) ceramic composite from wood [49]. In contrast to metals, in which free electrons carry heat, most ceramics transport heat primarily by lattice vibrations (phonons). Thermal conductivity is subjected to variations as the temperature changes, often decreasing as the temperature increases. There are three major reasons for the low thermal conductivity behavior of the C_f/SiC composites. Firstly, the presence of pyrolytic carbon (~ 3 W/m·K) [50], in which submicroscopic voids exist, acts as poor thermal conductors in the matrix. Secondly, the C_f/SiC composites are composed of three different phases, the interfaces of the two different materials are likely hindering the phonon movement, thus lead to low thermal conductivity. Besides, the existing of small pores in the composites, which can also act as a barrier for thermal conductivity.

Figure 8 Thermal properties of the C_f/SiC composite parts. (a) CTE and (b) thermal conductivity.

4 Conclusions

C_f/SiC composites have been fabricated by infiltrating liquid Si into the carbon preforms, which were built by SLS process from the PF resin coated carbon fiber powder with addition of Si particles. The introduced submicron Si particles play an important role in reducing porosity (from 56.8 to 50.4%) and average pore size (from 20.3 to 12.1 μm) of the C_f/C preforms. The C_f/SiC composites consist of typical β -SiC, residual Si and a small fraction of unconverted carbon, which is mostly the partially siliconized carbon fibers. With addition of Si particles in the starting materials, the microstructure homogeneity of the C_f/SiC composites is improved because that the continuous bulk carbon in the C_f/C preforms is separated into small pieces, thus reducing the amount of unreacted carbon and meanwhile increasing the SiC content. When further increasing the Si content, the residual Si increases accordingly. The maximum density of $2.89\pm0.01\text{ g/cm}^3$, flexural strength of $237\pm9.6\text{ MPa}$ and fracture toughness of $3.56\pm0.24\text{ MPa}\cdot\text{m}^{1/2}$ are simultaneously achieved for the C_f/SiC sample with addition of 5 vol.% Si. The CTE of the C_f/SiC composites is approximately $5.5\times10^{-6}/\text{K}$ from RT to 900°C, and the thermal conductivity at RT is in the range of 74-84 W/m·K, while decreases to 35-40 W/m·K at 900 °C.

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Highlights

- The introduced submicron Si improves the microstructure homogeneity of the C_f/SiC composites.
- The mechanism of SiC formation is explained in terms of solution and precipitation.
- The CTE and thermal conductivity of the C_f/SiC composites from RT to 900 °C are evaluated.