

# Microstructural tailoring, mechanical and thermal properties of SiC composites fabricated by selective laser sintering and reactive melt infiltration

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**Abstract:** Poor flowability of printable powders and long preparation cycles are the main challenges in the selective laser sintering (SLS) of chopped carbon fiber ( $C_f$ ) reinforced silicon carbide (SiC) composites with complex structures. In this study, we develop an efficient and novel processing route in the fabrication of lightweight SiC composites via the SLS of phenolic resin (PR) and  $C_f$  powders with the addition of  $\alpha$ -SiC particles combined with the one-step reactive melt infiltration (RMI). The effects of  $\alpha$ -SiC addition on the microstructural evolution of the  $C_f$ /SiC/PR printed bodies,  $C_f$ /SiC/C green bodies, and derived SiC composites were investigated. The results indicate that the added  $\alpha$ -SiC particles play an important role in enhancing the flowability of raw powders, reducing the porosity, increasing the reliability of the  $C_f$ /SiC/C green bodies, and contributing to improving the microstructure homogeneity and mechanical properties of the SiC composites. The maximum density, flexural strength, and fracture toughness ( $K_{IC}$ ) of the SiC composites are  $2.749 \pm 0.006 \text{ g} \cdot \text{cm}^{-3}$ ,  $266 \pm 5 \text{ MPa}$ , and  $3.30 \pm 0.06 \text{ MPa} \cdot \text{m}^{1/2}$ , respectively. The coefficient of thermal expansion (CTE,  $\alpha$ ) of the SiC composites is approximately  $4.29 \times 10^{-6} \text{ K}^{-1}$  from room temperature (RT) to  $900 \text{ }^\circ\text{C}$ , and the thermal conductivity ( $\kappa$ ) is in the range of  $80.15\text{--}92.48 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at RT. The high-temperature strength of the SiC composites increase to  $287 \pm 18 \text{ MPa}$  up to  $1200 \text{ }^\circ\text{C}$ . This study provides a novel as well as feasible tactic for the preparation of high-quality printable powders as well as lightweight, high-strength, and high- $\kappa$  SiC composites with complex structures by the SLS and RMI.

**Keywords:** chopped carbon fiber ( $C_f$ ); microstructural tailoring; selective laser sintering (SLS); mechanical properties; thermal properties

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## 1 Introduction

With the rapid development of space technology, large-scale and lightweight space optical components have become the important components of space-based observation systems, LIDAR systems, and space astronomical telescopes. Different from the traditional optical component materials including glass–ceramic, ultra-low expansion glass, and beryllium (Be), chopped carbon fiber ( $C_f$ ) reinforced silicon carbide (SiC) composite is gradually becoming the main candidate material for a new generation of space optical components due to its excellent properties such as high specific strength, high reliability, and excellent isotropy [1–3].

Generally, the SiC composites are fabricated by hot pressing (HP), spark plasma sintering (SPS), chemical vapor infiltration (CVI), polymer infiltration pyrolysis (PIP), and reactive melt infiltration (RMI) [4,5]. Among them, the RMI characterized by a low sintering temperature, rapid reaction time, and near-net shaping has been widely applied to the fabrication of the SiC composites. Wang *et al.* [6] fabricated the SiC composites from the carbon cloth by infiltrating phenolic resin (PR), pure carbon slurry, or C/SiC slurry combined with the RMI. Reference [6] indicated that both the flexural strength and fracture toughness ( $K_{IC}$ ) increased after adding SiC particles from 74.81 to 82.32 MPa and 4.72 to 9.82 MPa·m<sup>1/2</sup>, respectively. Compared with that of the pure carbon preform, the incorporation of SiC particles into the C/SiC preform plays a critical role, acting not only as an inert filler to inhibit the formation of cracks in the pyrolysis process but also as rigid skeleton particles to improve the reliability of the porous bodies [7]. Furthermore, the presence of SiC particles in the initial material recipe can provide seeding sites, favoring the formation of  $\beta$ -SiC during the subsequent RMI process [8].

The desired shape of the SiC composites fabricated by the RMI method depends on the modeling process, including slip casting, dry pressing, and tape casting [9]. However, it is difficult or even impossible to fabricate components with large-scale and complex structures, such as lattice, honeycomb, and topological structures via conventional methods ascribed to the limitation of models. Recently, selective laser sintering (SLS), a promising and moldless three-dimensional (3D)-printing technology, has been applied to near-net shaping SiC

composites due to its high efficiency, non-obligatory-additional support structure, high raw material utilization, and flexibility for large-scale and complex-shaped components [10–13]. Especially, the indirect SLS method involving a low-melting-point binder phase has been widely used in the SiC ceramics and their composites [14,15]. Xu *et al.* [16] used the epoxy resin–SiC mixed powders to construct preforms via the SLS, in which epoxy resin acted as a sacrificed binder and was removed during the debinding process. The SiC ceramics were obtained by polycarbosilane (PCS) infiltration and pyrolysis for 9 times and exhibited an excellent high-temperature flexural strength (220 MPa at room temperature (RT) and 203.7 MPa at 1600 °C) retention. Zhu *et al.* [17] fabricated the SiC composites via the SLS, PR infiltration and pyrolysis, and RMI of the PR-coated  $C_f$  composite powders. Reference [18] reported an efficient and novel approach to fabricate SiC composites from the starting materials of  $C_f$  and PR mechanical mixing powders. The SLS was used to fabricate  $C_f$ /PR printed bodies, which were converted into pure carbon ( $C_f/C$ ) green bodies in the subsequent debinding process. The dense SiC composites were obtained through an *in-situ* reaction of carbon and silicon in the one-step RMI process. However, the SiC composites exhibited inhomogeneous microstructures due to the poor flowability of printable powders, high open porosity ( $O$ ), and large pore size distribution of pure  $C_f/C$  green body. These could cause the formation of large-scale residual silicon in final products, which could deteriorate the mechanical properties.

In this study, we aim to enhance the flowability of printable powders, improve the reliability of porous green bodies, and regulate the microstructures and comprehensive properties of the SiC composites by compositional tailoring of initially raw composite powders, as well as establishing an efficient, cost-effective, and near-net-shape technique, which is promising to fabricate lightweight, large-scale, and complex-shaped SiC composites. More specifically,  $\alpha$ -SiC particles were introduced into the feedstocks for tailoring the microstructures and hence improving the properties. The effects of SiC addition on the flowability of raw powders, microstructural tailoring, and properties of green bodies as well as sintered composites were investigated. Simultaneously, the mechanical property, toughening mechanism, thermal property, and high-temperature flexural strength were also investigated comprehensively.

## 2 Experimental

### 2.1 Materials

Commercially available 6H-SiC (H represents hexagonal;  $3.2 \text{ g}\cdot\text{cm}^{-3}$ ,  $D_{50} = 38.9 \text{ }\mu\text{m}$ , purity = 99.5 wt%; Shanghai Shangmo Electromechanical Co., Ltd., China) and chopped  $C_f$  powders ( $1.76 \text{ g}\cdot\text{cm}^{-3}$ , 200 mesh; Shanghai Lishuo Composite Material Technology Co., Ltd., China) were used as the raw materials. The thermoplastic PR ( $1.22 \text{ g}\cdot\text{cm}^{-3}$ ,  $D_{50} = 19.5 \text{ }\mu\text{m}$ , with a residual carbon yield of 27.9 wt% after binder removal; Shanghai Qi'nan Adhesive Material Factory, China) mixed with the methenamine hardener (10 wt%) was used as the low-melting-point binder in the SLS. The molecular formula of PR is as in Fig. 1.

### 2.2 Preparation of samples

The  $C_f$ , SiC, and PR powders were ball-milled at  $66 \text{ r}\cdot\text{min}^{-1}$  for 1 h using the SiC milling media. The volume fraction ( $V$ ) of PR was fixed at 25%. Six groups of composite powders with different  $V$  of SiC (0%, 15%, 25%, 40%, 50%, and 75%) were prepared, which were labeled as  $C_f/\text{PR}-0 \text{ vol}\% \text{ SiC}$ ,  $C_f/\text{PR}-15 \text{ vol}\% \text{ SiC}$ ,  $C_f/\text{PR}-25 \text{ vol}\% \text{ SiC}$ ,  $C_f/\text{PR}-40 \text{ vol}\% \text{ SiC}$ ,  $C_f/\text{PR}-50 \text{ vol}\% \text{ SiC}$ , and  $C_f/\text{PR}-75 \text{ vol}\% \text{ SiC}$ , respectively. The compositions of the  $C_f/\text{PR}-\text{SiC}$  composite powders are shown in Table 1.

The  $C_f/\text{PR}-\text{SiC}$  composite powders with different SiC contents were applied to the SLS of  $C_f/\text{SiC}/\text{PR}$  printed body through the laser printing equipment

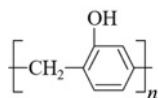


Fig. 1 Molecular structure of PR.

Table 1 Compositions of  $C_f/\text{PR}-\text{SiC}$  composite powders

Composite powders	Material composition (vol%)			Ratio of SiC to inorganic matter (IM), SiC:IM ( $V_{\text{SiC}}:(V_{\text{SiC}}+V_{C_f})$ )
	SiC	$C_f$	PR	
$C_f/\text{PR}-0 \text{ vol}\% \text{ SiC}$	0	75	25	0
$C_f/\text{PR}-15 \text{ vol}\% \text{ SiC}$	15	60	25	0.20
$C_f/\text{PR}-25 \text{ vol}\% \text{ SiC}$	25	50	25	0.33
$C_f/\text{PR}-40 \text{ vol}\% \text{ SiC}$	40	35	25	0.53
$C_f/\text{PR}-50 \text{ vol}\% \text{ SiC}$	50	25	25	0.67
$C_f/\text{PR}-75 \text{ vol}\% \text{ SiC}$	75	0	25	1

Note:  $V_{\text{SiC}}$  and  $V_{C_f}$  represent the volume fractions of SiC and  $C_f$ , respectively.

(Hunan Farsoon High-Technology Co., Ltd., China). The optimized printing parameters are as follows: The laser power, scanning velocity, and hatch distance were  $45 \text{ W}$ ,  $7620 \text{ mm}\cdot\text{s}^{-1}$ , and  $80 \text{ }\mu\text{m}$ , respectively. The movement direction of the roller was  $X$ -axis, the direction of print layer thickness was  $Z$ -axis, and  $Y$ -axis was perpendicular to the  $Z-X$  plane.

### 2.3 Fabrication of SiC composites

The  $C_f/\text{SiC}/\text{PR}$  printed bodies were heat-treated at  $1100 \text{ }^\circ\text{C}$  to remove PR binders and obtain porous  $C_f/\text{SiC}/\text{C}$  green bodies under vacuum. After that, Si ( $2.33 \text{ g}\cdot\text{cm}^{-3}$ , average size: 1–3 mm) was melted and infiltrated into the porous  $C_f/\text{SiC}/\text{C}$  green body under vacuum at  $1550 \text{ }^\circ\text{C}$ . Finally, the SiC composites were obtained. The schematic of the fabrication procedures is shown in Fig. 2.

### 2.4 Characterization

The angle of repose (AOR), apparent density ( $\rho_0$ ), and tap density ( $\rho_1$ ) of the composite powders were measured according to the American Society for Testing Material (ASTM) D6393-99, GB/T 16913.3-2008, and GB/T 5162-2006 standards, respectively. The flowability can be characterized according to Carr index and Hausner ratio by Eqs. (1) and (2), respectively:

$$\text{Carr index} = [(\rho_1 - \rho_0) / \rho_1] \times 100\% \quad (1)$$

$$\text{Hausner ratio} = \rho_1 / \rho_0 \quad (2)$$

The contents of impurity elements were tested using an inductively coupled plasma mass spectrometer (ICP-MS; iCAP RQ, Thermo Fisher Scientific, USA). The powder size distribution was measured using a laser-diffraction-based particle size analyzer (Malvern Panalytical, UK). The length distribution of  $C_f$  was manually measured by the Nano Measurer software, and the number of measurements was  $\geq 100$ . The morphologies and microstructures of raw powders,  $C_f/\text{SiC}/\text{PR}$  printed bodies,  $C_f/\text{SiC}/\text{C}$  green bodies, and SiC composites with different SiC contents were observed using a scanning electron microscope (SEM; SU8220, Hitachi, Japan) along with an energy dispersive spectrometer for the elemental analysis. The bulk densities ( $\rho$ ) and  $O$  of printed bodies, green bodies, and composites were determined based on the Archimedes principle. The  $\rho$  and  $O$  can be calculated by Eqs. (3) and (4), respectively:

$$\rho = W_d \rho_w / (W_w - W_s) \quad (3)$$

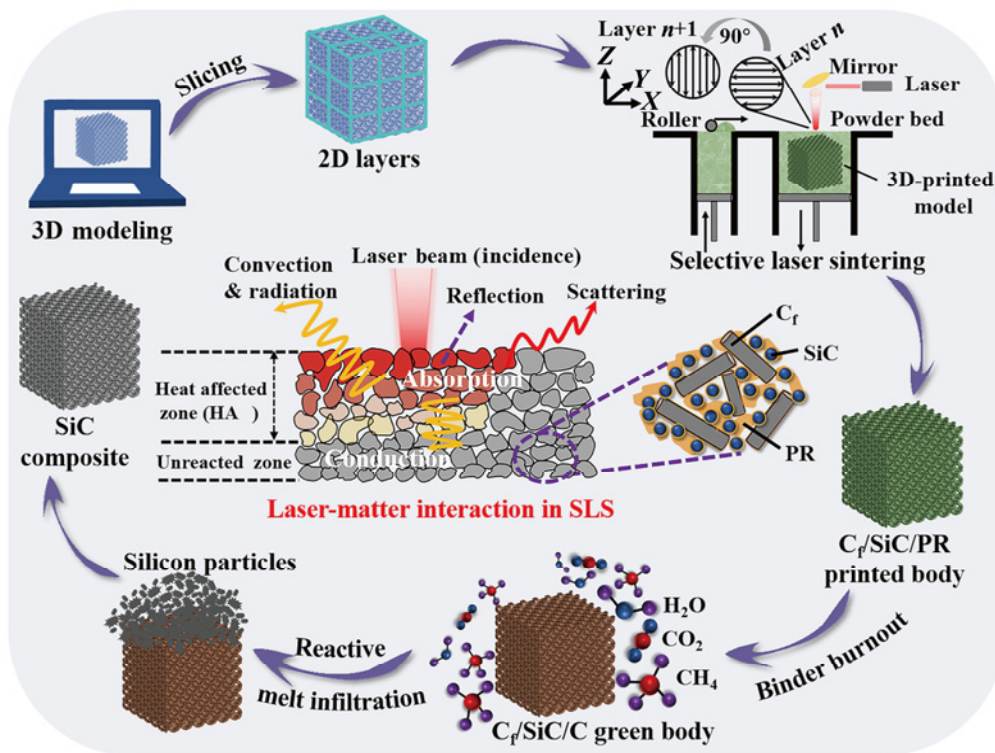


Fig. 2 Schematic diagram of the fabrication of SiC composites.

$$O = [(W_w - W_d) / (W_w - W_s)] \times 100\% \quad (4)$$

where  $\rho_w$ ,  $W_w$ ,  $W_d$ , and  $W_s$  represent the density of deionized water, the wet weight of the sample saturated with water in air, the dry weight of the sample, and the floating weight of the sample in water, respectively.

The volume fraction of residual silicon ( $V_{Si}$ ) was calculated by Eq. (5):

$$V_{Si} = [(m_1 - m_2)\rho_{SiC}] / (2.33m_1) \quad (5)$$

where  $\rho_{SiC}$  is the density of the SiC composite, and  $m_1$  and  $m_2$  are the mass of the SiC composites before and after etching in the 1HF:5HNO<sub>3</sub> mixture for 72 h, respectively. 2.33 in Eq. (5) represents the density of Si.

The orientation distribution and ‘‘Hermans’’ orientation parameter ( $f_p$ ) of the C<sub>f</sub> in the C<sub>f</sub>/SiC/C green body were determined by Eqs. (6) and (7), respectively [19]:

$$\langle \cos^2 \phi \rangle = \int_{-\pi/2}^{\pi/2} \cos^2 \phi n(\phi) d\phi \quad (6)$$

$$f_p = 2 \langle \cos^2 \phi \rangle - 1 \quad (7)$$

where  $\phi$  is the orientation angle,  $n(\phi)$  is the fraction of fibers within the angular range ( $d\phi$ ). The  $f_p$  ranges from

0 (random distribution) to 1 (perfect orientation).

A digital caliper with 0.01 mm accuracy was used to measure the dimensional deviation ratio (DDR) of printed bodies and green bodies by Eq. (8):

$$DDR = [(L - L_0) / L_0] \times 100\% \quad (8)$$

where  $L_0$  is the dimension of the STL model, and  $L$  is the measured dimension. Rectangular bars with the dimension of 40 mm ( $X$ )  $\times$  8 mm ( $Y$ )  $\times$  6 mm ( $Z$ ) were used to measure the DDR and subsequent mechanical properties. At least five samples were tested to obtain the average data.

The pore size distributions of the green bodies and the SiC composites after acid corrosion were obtained by a mercury porosimeter (Poremaster60, Micromeritics Instrument Corp., USA). The phase analyses of the SiC composites were performed using an X-ray diffractometer (40 kV, 40 mA; D/max 2550V, Rigaku, Japan) with Cu K $\alpha$  radiation ranging from 10° to 80°. The oxygen contents of the SiC composites were measured by an oxygen–nitrogen tester (TC600C, Leco Instrument LD, USA).

The flexural strength was measured by a three-point bending test instrument (Instron-1195, Instron, USA) at a crosshead speed of 0.5 mm·min<sup>-1</sup>, according to the GB/T 6569-2006 and GB/T 10700-2006 standards. The



sample size was 4 mm × 3 mm × 36 mm. The  $K_{IC}$  was measured by a single-edge notched beam (SENB) method according to the ASTM C1421-16 standard with a crosshead speed of 0.05 mm·min<sup>-1</sup>, notch depth of 2.5 mm, and the sample size of 2.5 mm × 5 mm × 36 mm. The high-temperature three-point flexural strengths of the SiC composites were measured at 600, 800, 1000, and 1200 °C under an Ar atmosphere using an ultra-high-temperature strength testing machine (AG-X Plus, Shimadzu, Japan). The sample size and crosshead speed were 4 mm × 3 mm × 36 mm and 0.5 mm·min<sup>-1</sup>, respectively. The heating rate was 33 °C·min<sup>-1</sup>. The measurements were performed using a semi-articulating fixture according to the ASTM C1161-13 and ASTM C1211-13 standards.

The coefficient of thermal expansion (CTE,  $\alpha$ ) values were measured by a thermal dilatometer (DIL402 E, NETZSCH, Germany) from 25 to 900 °C at a heating rate of 10 °C·min<sup>-1</sup> under an Ar atmosphere. The sample size was 4 mm × 4 mm × 20 mm. The thermal diffusivity ( $a$ ) was tested from 25 to 900 °C under an Ar atmosphere using a laser-flash technique (DLF2800, TA, USA) based on the ASTM E1461 standard. The specific heat capacity ( $c_p$ ) at RT was measured using a differential scanning calorimeter (DSC; STA 449 F1 Jupiter, NETZSCH, Germany). The sample size was  $\phi$ 5.5 mm × 0.5 mm. The  $c_p$  at the elevated temperatures were measured based on the ASTM E1269 standard from 25 to 900 °C under an

Ar atmosphere using a high-temperature  $c_p$  analyzer (MHTC96, Setaram, France). The sample size was  $\phi$ 4.9 mm × 18 mm. The thermal conductivity ( $\kappa$ ) at 25 °C can be calculated by Eq. (9) [20]:

$$\kappa = a\rho c_p \quad (9)$$

The density decreases with the increasing temperature, as calculated by Eq. (10) [21]:

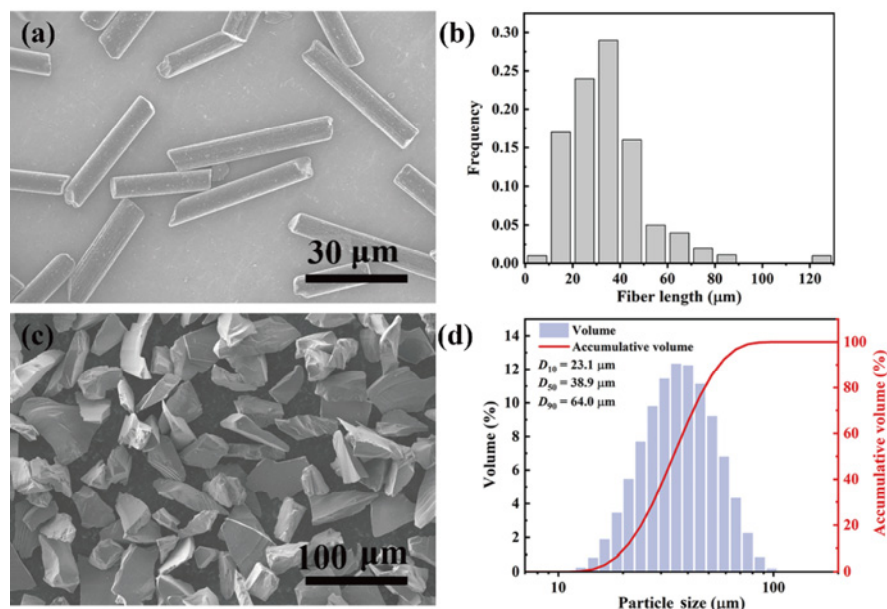
$$\rho = \rho_0 [1 + 3(\Delta l / l_0) + 3(\Delta l / l_0)^2 + (\Delta l / l_0)^3]^{-1} \quad (10)$$

where  $\rho$ ,  $\rho_0$ , and  $\Delta l / l_0$  represent the density at a specific temperature, the density at RT, and the linear  $\alpha$ , respectively.

### 3 Results and discussion

#### 3.1 Powder characteristics

The printable powders with good flowability are critical for successive layer deposition in the SLS. The morphology and granulometry have effects on the flowability. As shown in Figs. 3(a) and 3(b), the  $C_f$  is cylindrical with an aspect ratio of 1–30 [22]. The morphology and size distribution of SiC powders are shown in Figs. 3(c) and 3(d), respectively. As shown in Fig. 3(c), the SiC powders are irregular with sharp edges and smooth surfaces. The particles with the relatively small aspect ratios can improve the packing density and flowability [23]. The SiC powders have the



**Fig. 3** (a) SEM image of  $C_f$  powders; (b) length distribution of  $C_f$  powders [22]; (c) SEM image of SiC powders; and (d) PSD of SiC powders.

unimodal and wide size distribution from 11.2 to 98.1 μm, as shown in Fig. 3(d). The particle size distribution (PSD) values of SiC are  $D_{10} = 23.1 \mu\text{m}$ ,  $D_{50} = 38.9 \mu\text{m}$ , and  $D_{90} = 64.0 \mu\text{m}$ . The corresponding PSD span (PSD S) is 1.05, which is smaller than 1.5, indicating that the SiC powders exhibit good flowability [24]. The PSD S of PR is 2.61, which is larger than that of SiC particles, leading to more cohesive flowability.

Figure 4 shows the AOR,  $\rho_0$ ,  $\rho_1$ , Carr index, and Hausner ratio results of  $C_f$ /PR–SiC composite powders with different SiC contents. As shown in Fig. 4(a), the AOR decreases with the increase of SiC content. And when the SiC:IM  $\geq 0.67$ , the AOR only slightly changes. Generally, a smaller AOR indicates better flowability. According to Table 2, the SiC raw powders

**Table 2 Flowability of raw powders**

Sample of raw powders	PSD S (( $D_{90} - D_{10}$ ) / $D_{50}$ )	AOR (°)	$\rho_0$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\rho_1$ ( $\text{g}\cdot\text{cm}^{-3}$ )	Carr index (%)	Hausner ratio
$C_f$	—	51	0.512	0.769	33.44	1.50
SiC	1.05	37	1.413	1.702	16.95	1.20

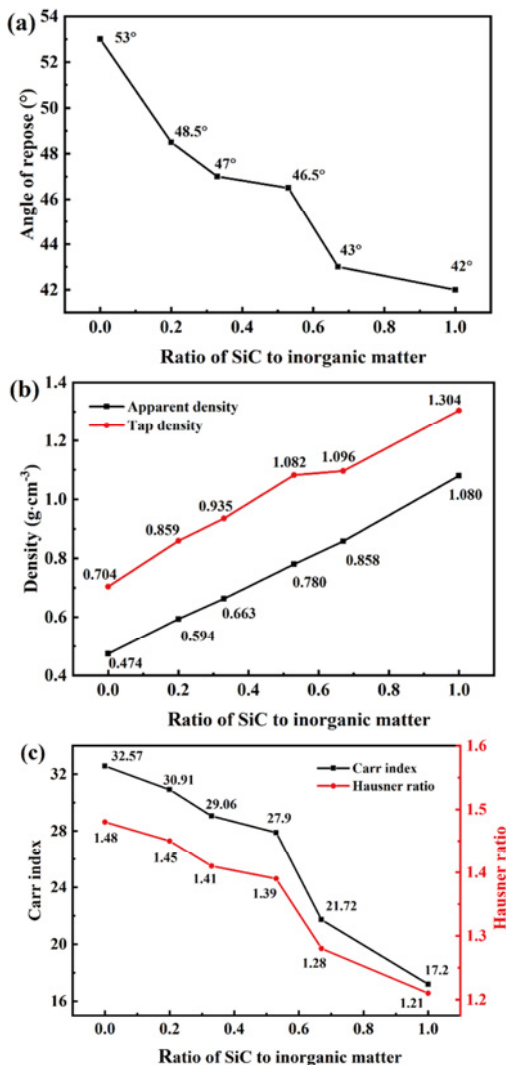
exhibit relatively good flowability due to its irregular shapes and large particle size ( $D_{50} = 38.9 \mu\text{m}$ ) compared with the cylindrical  $C_f$ . For the PR, the long molecular chain structure, small particle size ( $D_{50} = 19.5 \mu\text{m}$ ), large PSD (PSD S = 2.61), and strong inter-particle attractive force (van der Waals force) lead to poor flowability. Therefore, the AOR of SiC:IM = 0 is larger than that of the  $C_f$  powders. When the SiC:IM = 0.20, the AOR intensively decreases by 8.5%. As the content of SiC increases further, the AOR of composite powders gradually decreases ascribed to the good flowability of SiC powders.

The  $\rho_0$  and  $\rho_1$ , as shown in Fig. 4(b), increase evidently with the increasing SiC content. The  $\rho_0$  is mainly influenced by particle morphology. The higher the sphericity of the particles, the higher the  $\rho$  of the powders is. The SiC powders are irregular, so it is easier to achieve dense packing than cylindrical  $C_f$  with an aspect ratio of 1–30. Therefore, with the increase of SiC content, the  $\rho_0$  of the composite powders increase significantly and continuously. In the  $C_f$ /PR–0 vol% SiC (SiC:IM = 0) composite powders without SiC particles, the  $\rho_0$  is the lowest of  $0.474 \text{ g}\cdot\text{cm}^{-3}$ . In the  $C_f$ /PR–75 vol% SiC (SiC:IM = 1) composite powders without  $C_f$ , the  $\rho_0$  is the highest of  $1.080 \text{ g}\cdot\text{cm}^{-3}$ . As shown in Fig. 4(b), as the  $\rho_0$  increases, the  $\rho_1$  also increases. The highest  $\rho_1$  is  $1.304 \text{ g}\cdot\text{cm}^{-3}$  when SiC:IM = 1. It can be noted from Fig. 4(b) that the addition of the SiC has a clear effect on the  $\rho_0$  and the  $\rho_1$ .

To further characterize the flowability of the  $C_f$ /PR–SiC composite powders with different contents of SiC, the Carr index and Hausner ratio are shown in Fig. 4(c). Both the Carr index and Hausner ratio decrease with the rise of the SiC content. The smaller the Carr index and Hausner ratio, the better the flowability is. The results indicate that the added SiC particles can act as the “lubricant” to improve the flowability of the composite powders.

### 3.2 Microstructural evolution and properties of $C_f$ /SiC/C green bodies

The microstructures of  $C_f$ /SiC/PR printed bodies with

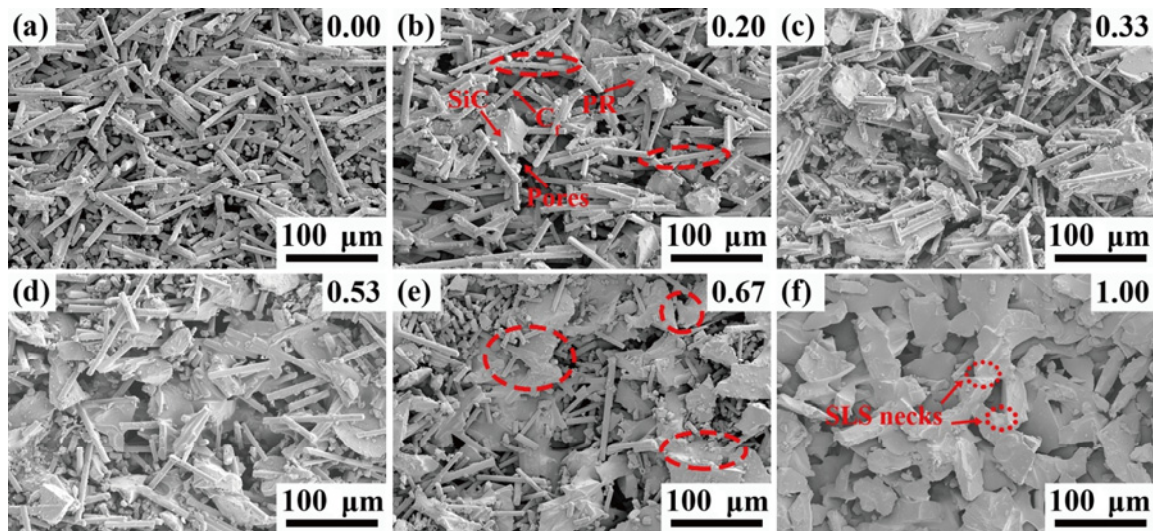


**Fig. 4** (a) AOR; (b)  $\rho_0$  and  $\rho_1$ ; and (c) Carr indexes and Hausner ratios of  $C_f$ /PR–SiC composite powders with different SiC contents.

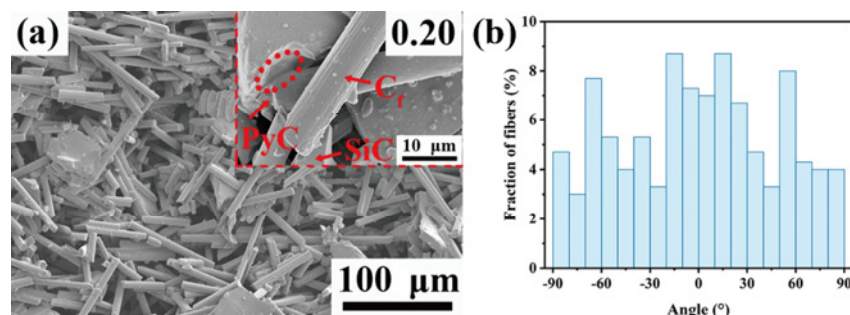
different SiC contents are shown in Fig. 5. The  $C_f$ /SiC/PR printed bodies show the porous structures with connected pores, and the melted PR is coated on the surfaces of the  $C_f$  and SiC particles, forming “SLS necks” to bond powders together, as shown in Figs. 5(e) and 5(f). With the addition of SiC powders, since the surface of SiC enriches numerous reactive  $-Si-OH$  oxygen-containing functional groups with higher surface free energy than the inert surface of  $C_f$  [25], the competing effect leads to more and more PR coated onto the SiC surface, and then the sharp edges of SiC particles become blur and rounded. Therefore, the surface of SiC becomes further rougher due to coating with PR. Figure 5(b) shows that SiC particles are uniformly dispersed and connected to  $C_f$  through the viscous flow of PR. When the SiC:IM increases to 0.67, the PR-coated SiC particles are bonded together forming aggregates, as shown in the red circles in Fig. 5(e). Moreover, based on the microstructural control, since SiC particles fill into the pores of the  $C_f$  skeleton, therefore, the porosity

decreases gradually with the increase of SiC content, as shown in Fig. 5.

Figure 6 shows the representative microstructure and orientation distribution of the  $C_f$ /SiC/C (SiC:IM = 0.2) green body. After pyrolysis, PR was converted into pyrolytic carbon (PyC) and pores. Simultaneously, the  $C_f$  and SiC surfaces become smoother than those of the printed bodies due to the chemical bond reorganization [17], as shown in Fig. 6(a). The PyC bonds the  $C_f$  and SiC particles together, as shown in the inset of Fig. 6(a). Combined with the aforementioned analysis, the PR-coated  $C_f$  and SiC printed bodies are converted into PyC-coated  $C_f$  and SiC porous green bodies after pyrolysis; therefore, there is an obvious color change from green to black after pyrolysis for the sample of SiC:IM = 1 without  $C_f$  addition. Figure 6(b) shows the orientation distribution of  $C_f$  along the  $X$ -axis, which shows that the fibers are evenly distributed between all angles. The  $f_p$  calculated by Eqs. (6) and (7) is 0.12, which further confirms that the fibers are distributed isotropically and randomly in this study.



**Fig. 5** Morphologies of  $C_f$ /SiC/PR printed bodies with different SiC contents: (a) SiC:IM = 0; (b) SiC:IM = 0.20; (c) SiC:IM = 0.33; (d) SiC:IM = 0.53; (e) SiC:IM = 0.67; and (f) SiC:IM = 1.



**Fig. 6** (a) Representative morphology of  $C_f$ /SiC/C green body (SiC:IM = 0.20); (b)  $C_f$  orientation distribution corresponding to (a).



The SiC content has an effect on the physical properties of  $C_f$ /SiC/C green bodies, including dimensional accuracy, microstructure, and mechanical property. Figure 7 shows the DDR results of the  $C_f$ /SiC/C green bodies in length ( $X$ ), width ( $Y$ ), and height ( $Z$ ) directions. When the SiC:IM = 0, the DDR shows a positive deviation in both  $X$  and  $Y$  directions. The reason for the positive deviation is that the residual heat of the laser bonds the neighboring excess powders together, resulting in excessive densification during the SLS process. However, when the SiC:IM = 0.2, the dimension deviations in  $X$  and  $Y$  directions gradually convert into negative deviations and continue to decrease with the increasing SiC content. With the increase of SiC content, on the one hand, the multiple

reflections of the powders on the laser are weakened, resulting in the decrease of the laser absorption of the composite powders. Under the same laser energy density, the depth and width of the molten pool decrease, and the diffusion of the heat-affected zone decreases [26]. On the other hand, the “connective” effects of  $C_f$  gradually weaken. Therefore, the DDR decreases. Thus, the SiC:IM = 1 sample without  $C_f$  powders exhibits the highest DDRs of  $-0.58\%$  and  $-2.86\%$  in the  $X$  and  $Y$  directions, respectively. Because the  $X$  direction is the paving powder direction, the powders have a tendency to self-compact along with the  $X$  direction; therefore, the DDRs in the  $X$  direction exhibit lower than those in the  $Y$  direction. Additionally, the DDRs in the  $Z$  direction are relatively higher than those in the  $X$  and  $Y$  directions. This is mainly due to the laser penetration effect induced by the temperature variation of the thermal conduction gradient along the  $Z$  direction between the printing layer and as-printed layer. Moreover, heat penetration along the  $Z$  direction would result in the excess binding of adjacent as well as sub-adjacent unprinted layers, which is different from  $X$  and  $Y$  directions. It should also be noted that the printed green bodies experienced further shrinkage after subsequent pyrolysis process. According to Ref. [27], the RMI has been known as a near-net-shape forming method with less line shrinkage ( $\leq 1\%$ ).

The pore diameters of porous  $C_f$ /SiC/C green bodies are important for the subsequent RMI. Figure 8 shows the pore size distributions of the  $C_f$ /SiC/C green bodies varying with the SiC content. All the  $C_f$ /SiC/C green bodies show the broad and unimodal pore size distributions from 10 to 35  $\mu\text{m}$ , which indicate that the green bodies possess homogeneous pore channels. The median pore diameter (MPD) varies from 18.77 to 28.72  $\mu\text{m}$ , while the average pore diameter (APD) varies from 468.4 nm to 12.2  $\mu\text{m}$ . With the increasing SiC content, the pore size distribution narrows down initially before widening up, and the MPD first decreases, and then increases. When the SiC:IM increases to 0.33, the MPD achieves a minimum of 18.77  $\mu\text{m}$ , and the corresponding APD is 504.3 nm. In this study, the pores are produced by the stacking of  $C_f$  and SiC particles as well as debinding of PR. Under the fixed PR content, it can be considered that the pore size distributions of the porous  $C_f$ /SiC/C green bodies are mainly affected by the particle stacking pore. When the SiC:IM  $\leq 0.33$ , the  $C_f$  acts as a skeleton phase

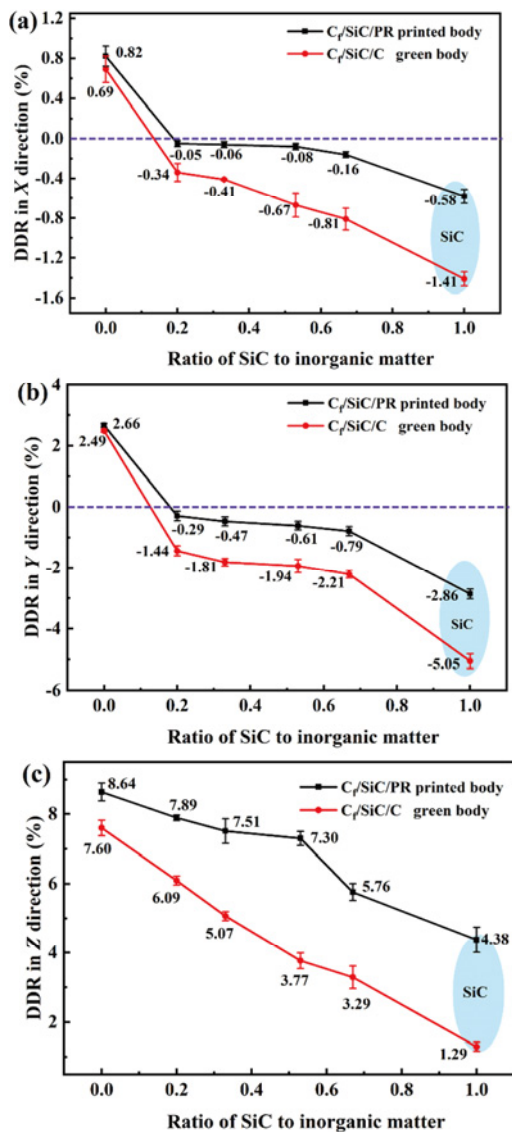


Fig. 7 (a) DDRs in  $X$  direction; (b) DDRs in  $Y$  direction; and (c) DDRs in  $Z$  direction.



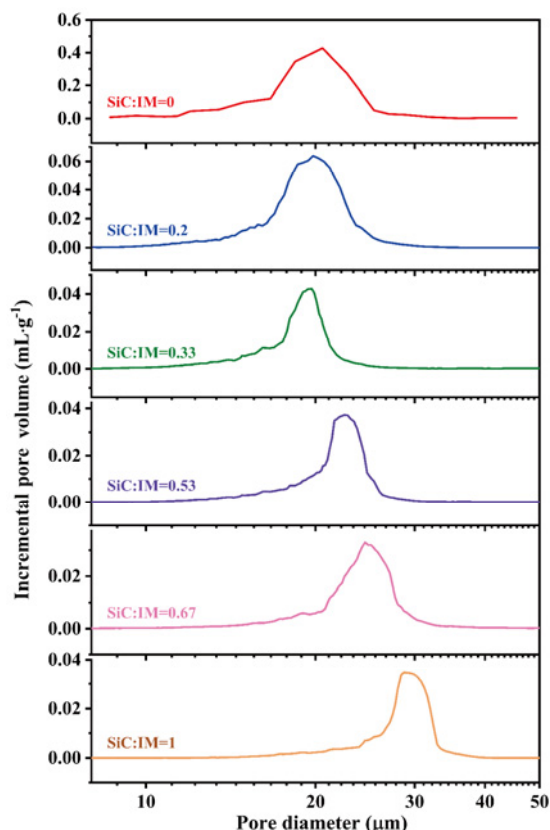


Fig. 8 Pore size distributions of  $C_f/SiC/C$  green bodies.

that can encapsulate SiC particles and fill the voids between the particles, resulting in the decrease of MPD. When the SiC:IM further increases to 1, the “connective” effects of  $C_f$  gradually weaken due to the decrease of  $C_f$  content, resulting in the gradual increase of MPD.

Combined with Ref. [18], the thermodynamical parameters including the capillary force and infiltration depth in the RMI process can be calculated. The penetration depth increases with the increasing pore size, while the corresponding capillary driving force decreases. The maximum capillary force is  $6.09 \times 10^6$  N,

and the corresponding infiltration depth in one second reaches a minimum of 13.13 mm for the SiC:IM = 1 green body, indicating that the RMI is a very rapid process.

Figure 9 shows the porosity,  $\rho$ , and flexural strengths of  $C_f/SiC/C$  green bodies with different SiC contents. As shown in Fig. 9(a), the  $O$  of the  $C_f/SiC/C$  green bodies decreases with the increase of SiC content, while the  $\rho$  shows the opposite trend. Notably, the  $\rho$  of  $C_f/SiC/C$  green body is very close to the  $\rho_0$ , but lower than the  $\rho_1$  of corresponding  $C_f/PR-SiC$  composite powders. The static and dynamical wall effects cause a large number of pores in the powder layer during the powder-spreading process [28]. As a powder-spreading additive manufacturing technique, the  $O$  of printed  $C_f/SiC/C$  green body is related to the flowability of the  $C_f/PR-SiC$  composite powders. With the increase of SiC content, the flowability of composite powders increases gradually, and thus the  $O$  of  $C_f/SiC/C$  green body decreases. Simultaneously, since the  $C_f$  is cylindrical with an aspect ratio of 1–30, it is difficult to achieve dense packing, so the SiC:IM = 0 sample without any SiC particles shows the highest  $O$  and lowest  $\rho$  of  $74.89\% \pm 0.1\%$  and  $0.449 \pm 0.003 \text{ g} \cdot \text{cm}^{-3}$  [18], respectively. The added irregular SiC particles can fill in the pores forming from the  $C_f$  skeletons; therefore, the porosity of  $C_f/SiC/C$  green bodies is significantly reduced from 74.89% to 67.29%. The abundant porosity provides the infiltrative channels for the subsequent RMI.

Figure 9(b) shows the flexural strengths of the  $C_f/SiC/C$  green bodies. As shown in Fig. 9(b), the flexural strengths of green bodies first increase by 22.21% and 7.65% when the SiC:IM increases to 0.20 and 0.33, respectively. When the SiC:IM increases to 0.20, the  $C_f$  can dissipate the energy of crack propagation and deflect the crack [29];

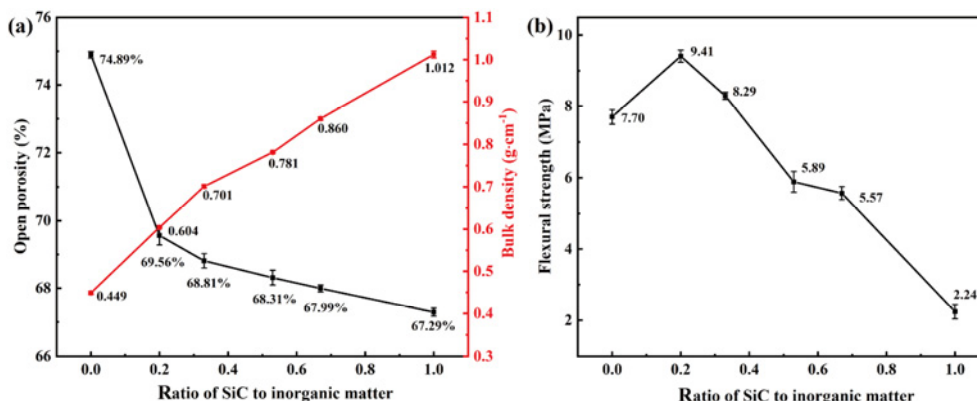


Fig. 9 (a)  $O$  and  $\rho$  and (b) flexural strengths of  $C_f/SiC/C$  green bodies with different SiC contents.

meanwhile, the  $C_f$  acts as a skeleton phase that can encapsulate the SiC particles and fill the voids between the particles, that is, the  $C_f$  and SiC particles synergistically improve the flexural strength. Additionally, according to the Ryskewitch–Duckworth relationship ( $\sigma \propto e^{-bP}$ ) [30], the strengths of porous materials have the negative exponential relationships with porosity, and the decrease in the  $O$  of  $C_f$ /SiC/C green bodies also contributes to the increase in the strength ( $SiC:IM \leq 0.2$ ). When the SiC:IM further increases from 0.53 to 1, although the  $O$  of  $C_f$ /SiC/C green bodies decreases continuously, the strength of  $C_f$ /SiC/C green bodies is lower than that of the sample of SiC:IM = 0 without SiC particles due to the loose microstructure, large pore size, and weak “connective” effect of  $C_f$ . The maximum flexural strength of  $9.41 \pm 0.17$  MPa is finally achieved for the SiC:IM = 0.2 green bodies. These flexural strength results coincide with the obtained microstructures from the SEM analysis (Fig. 5) and the pore diameter distributions of  $C_f$ /SiC/C green bodies (Fig. 8).

### 3.3 Microstructural evolution and phase compositions of SiC composites

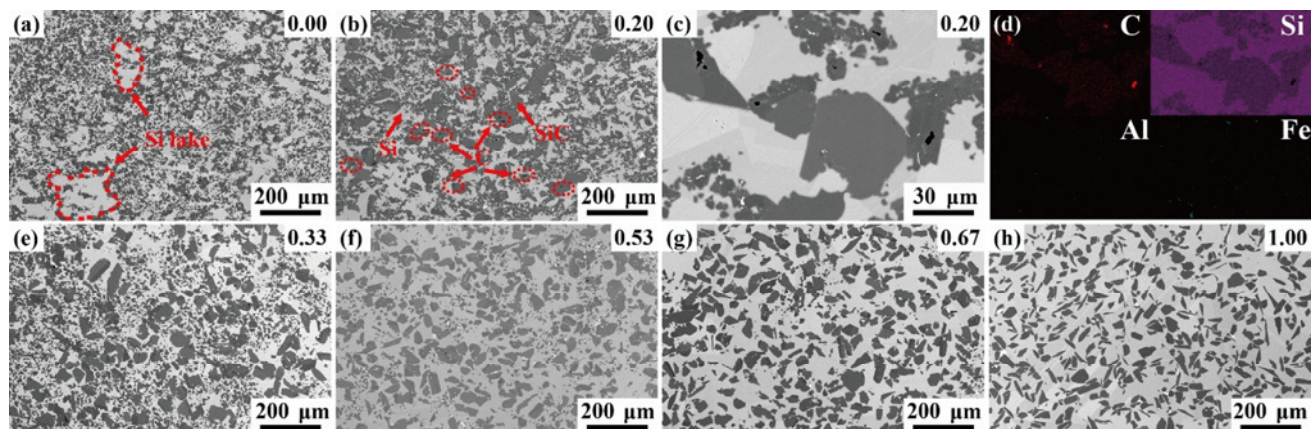
The microstructures and element distributions of the SiC composites are shown in Fig. 10. All the SiC composites consist of SiC (dark-gray), residual silicon (light-gray), and carbon (black). The SiC:IM = 0 sample shows a relatively heterogeneous element distribution with a large amount of “Si lake”, as shown in Fig. 10(a). As mentioned in Section 3.2, the corresponding green body (SiC:IM = 0) has a high

porosity ( $74.89\% \pm 0.1\%$ ) and large pore diameter (MPD =  $21.04 \mu m$ ), which subsequently lead to a heterogeneous microstructure in the SiC:IM = 0 sample. With the increase of SiC content in the starting materials, the microstructure homogeneity of the SiC composites is improved, as shown in Figs. 10(b)–10(h). Figures 10(c) and 10(d) show the high-magnification SEM micrograph and energy dispersive spectroscopy (EDS) mapping of the SiC:IM = 0.2 sample, respectively; in addition to SiC, residual Si, and C, a small amount of bright-white region is also observed, which is analyzed by the EDS as Al–Fe alloys originating from impurities in the raw materials, as shown in Table 3.

During the RMI process, the liquid silicon infiltrates into the porous  $C_f$ /SiC/C green bodies driven by capillary forces and reacts with the carbon *in-situ* to form SiC based on Reaction (11).



The initial addition of SiC particles can act as grain seeds to induce the formation of  $\beta$ -SiC [8]. Moreover, the reaction-formed SiC shows a fine PSD of 0.5–10  $\mu m$  in the SiC:IM = 0 sample without  $\alpha$ -SiC addition, as shown in Fig. 10(a). Thus, with the increase of SiC content, the amount of large-sized  $\alpha$ -SiC particles ( $D_{50} = 38.9 \mu m$ ) increases, since the grain size of SiC obtained by the RMI was merely 0.5–10  $\mu m$ . Additionally, it should be noted that with the increasing SiC content, the amount of residual silicon first decreases ( $SiC:IM \leq 0.33$ ), and then increases ( $SiC:IM > 0.33$ ), which coincides with the pore diameter distributions of  $C_f$ /SiC/C green bodies.



**Fig. 10** Polished surface morphologies of SiC composites (back-scattered electron SEM): (a) SiC:IM = 0; (b) SiC:IM = 0.20; (c) SiC:IM = 0.33; (f) SiC:IM = 0.53; (g) SiC:IM = 0.67; and (h) SiC:IM = 1. (c) High-magnification SEM micrograph of SiC:IM = 0.20. (d) EDS mappings of SiC:IM = 0.20.

**Table 3 Properties of raw powders**

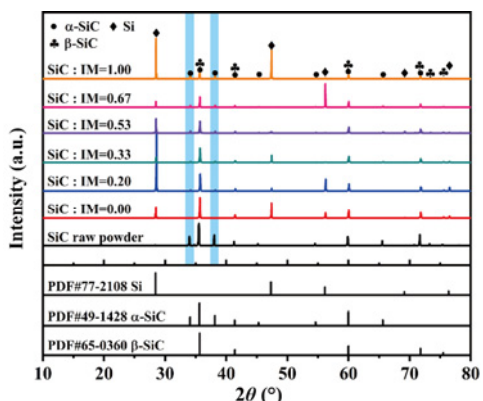
Impurity	C <sub>r</sub>	SiC	PR	Si
Fe (wt%)	0.15 [18]	0.19	0.01 [18]	0.44
Al (wt%)	< 0.001 [18]	0.019	< 0.001 [18]	0.13
Si (wt%)	< 0.005	—	< 0.005	—

The X-ray diffraction (XRD) patterns show the phase compositions of the obtained SiC composites, as shown in Fig. 11. The SiC raw powders have a hexagonal cell ( $\alpha$ -SiC, 6H) with a lattice parameter of 3.079 Å × 3.079 Å × 15.109 Å. The SiC composite fabricated by the SiC:IM = 0 sample without initial SiC addition is mainly composed of  $\beta$ -SiC (3C) and residual Si. The characteristic diffraction peaks of  $\alpha$ -SiC at about  $2\theta = 34.13^\circ$  and  $38.16^\circ$  are detected in the SiC composites after adding SiC particles. Furthermore, the residual carbon and Al-Fe alloy impurities observed in the SEM images are not detected in the XRD patterns, indicating that their contents are less than 5 wt%.

To quantitatively analyze the phase volume percentage of the SiC composite, we used the acid mixture (1HF:5HNO<sub>3</sub>) to etch residual silicon for 72 h at RT, as shown in Reaction (12).



The SiC has the high-temperature-stable  $\alpha$ -SiC (2H, 4H, and 6H) phase and low-temperature-stable  $\beta$ -SiC (3C, where C represents cubic) phase polymorphy, and a remarkable phase transition from  $\beta$ -SiC to  $\alpha$ -SiC occurs when the temperature exceeds 2000 °C [31]. Based on Ref. [18], the theoretical phase volume percentage can be obtained by combining the volume expansion of the infiltration process without considering the phase transition and residual pores. The quantitative phase volume percentage of the SiC composites based on the theoretical calculation and experimental measurement are listed in Table 4.



**Fig. 11** XRD patterns of SiC composites.

**Table 4 Phase compositions of SiC composites**

Sample	Theoretical parameter		Experimental parameter
	Total SiC (vol%)	Residual Si* (vol%)	Residual Si (vol%)
SiC:IM = 0	47	53	56.72±0.78
SiC:IM = 0.20	49.84 <sup>a</sup>	50.03	50.31±0.26
SiC:IM = 0.33	50.15	49.85	52.40±0.39
SiC:IM = 0.53	45.06	54.94	60.48±0.76
SiC:IM = 0.67	43.02	56.98	61.68±0.81
SiC:IM = 1	35.08	64.92	—

Note: <sup>a</sup>The residual carbon content is 0.13 vol% measured by the image method in the representative SiC composite (SiC:IM = 0.20).

As shown in Table 4, the content of theoretical residual Si first decreases (SiC:IM ≤ 0.33), and then increases (SiC:IM ≥ 0.53) with the increasing addition amounts of SiC powders, which is consistent with the changing trend of pore diameters of C<sub>r</sub>/SiC/C porous green bodies. When the SiC:IM increases to 0.33, the experimentally measured residual Si content is very close to the theoretically calculated values, and the deviation is ≤ ±3%. However, when the SiC:IM further increases from 0.53 to 1.0, the measured Si content is much higher than the calculated ones. The reason can be explained as follows: During the RMI, the silicon reacts with carbon to obtain SiC, resulting in volume expansion. The excess pores are filled with liquid silicon. The HF-HNO<sub>3</sub> mixture can etch free silicon and only retain SiC and residual carbon. As the pore size of the C<sub>r</sub>/SiC/C porous green bodies increases, the size of free silicon also increases. For SiC:IM ≥ 0.53 samples, it is difficult to maintain the bulk form for the porous SiC skeleton after corrosion due to the large pore size distribution of the corresponding C<sub>r</sub>/SiC/C green bodies, resulting in that some SiC particles are precipitated in the etching solution, so the measured residual Si content is much higher than the theoretical parameters. Additionally, for the SiC:IM = 1 sample, the residual silicon content could not be determined by etching due to the large pore size of the corresponding green body. Meanwhile, the residual carbon contents in representative SiC composites (SiC:IM = 0.20) before and after the RMI have been tested by the image method, which are 25.42 and 0.13 vol%, respectively, as shown in Table 4. The amount of C<sub>r</sub> decreases after the RMI due to corrosion of C<sub>r</sub> by liquid silicon, resulting in the not quite high K<sub>IC</sub>. Based on the differed applications, superior K<sub>IC</sub> is not critically required, such as for space optical and nuclear usages. However, it is difficult to deposit SiC



or BN coating on the surface of the chopped  $C_f$  by the CVI technique like the continuous  $C_f$  woven into blocks. Therefore, the chopped  $C_f$  is corroded during the RMI process (with the purpose of reducing the fabrication cost as well). Further systematic investigation is currently conducted by adopting CVI technique to fabricate SiC, BN, or PyC-coated  $C_f$  to prevent corrosion of  $C_f$  during the RMI.

Additionally, we analyzed the mean grain size (MGS) of  $\beta$ -SiC after acid corrosion, the MGS of  $\beta$ -SiC in the SiC:IM = 0.20 sample decreases compared with that of the SiC:IM = 0 sample, and the MGSs of  $\beta$ -SiC are 4.0 and 5.54  $\mu\text{m}$ , which indicate that the addition of  $\alpha$ -SiC can inhibit the growth of  $\beta$ -SiC grain. According to Ref. [32], the Zener pinning effect at grain boundaries could exert a pinning pressure to counteract the driving force of grain boundary movement, and thus inhibit grain boundary migration, indicating that the added  $\alpha$ -SiC suppresses the grain boundary migration and the growth of  $\beta$ -SiC by pinning the grain boundaries.

### 3.4 Mechanical and thermal properties of SiC composites

Figure 12 shows the RT mechanical properties (i.e.,  $O$ ,  $\rho$ , flexural strength, and  $K_{IC}$ ) parallel to the printing layer of the SiC composites. As shown in Fig. 12(a), all the SiC composites show the similar  $O$  within 1%, indicating complete densification. Since the density of composites conforms to the mixing rule, the  $\rho$  of the SiC composites initially increases, and then decreases with the increasing SiC, coinciding with the experimentally measured residual Si content, as shown in Table 4, among which the SiC:IM = 0.20 sample has the maximum value of  $2.749 \pm 0.006 \text{ g}\cdot\text{cm}^{-3}$ . As shown in Fig. 12(b), the flexural strength and  $K_{IC}$  of the SiC:IM = 0 sample are  $266 \pm 5 \text{ MPa}$  and  $2.87 \pm$

$0.07 \text{ MPa}\cdot\text{m}^{1/2}$  [18], respectively. The flexural strength gradually decreases with the increase of SiC content. The flexural strength of the SiC composites fabricated by the RMI is related to the grain sizes of SiC and residual Si content. According to the Hall–Petch relationship ( $\sigma \propto d^{-1/2}$ ) [33], when the SiC:IM increases to 0.33, although the residual Si content decreases, the flexural strength decreases because the particle size of the initially added SiC ( $D_{50} = 38.9 \mu\text{m}$ ) is much larger than that of reaction-formed SiC ( $0.5\text{--}10 \mu\text{m}$ ). With further increase of SiC:IM to 1, the flexural strength decreases further under the effect of the gradual increase of the residual Si content and the gradual increase of the SiC grain size. The  $K_{IC}$  of the SiC composites first increases with the SiC content in the starting materials, and then decreases. The SiC:IM = 0.20 sample has the highest  $K_{IC}$  of  $3.30 \pm 0.06 \text{ MPa}\cdot\text{m}^{1/2}$  and high flexural strength of  $250 \pm 11 \text{ MPa}$ . Compared with that of the SiC:IM = 0 sample (without the introduction of SiC raw powders), its  $K_{IC}$  increases by 15%. By analyzing the pores of the SiC composites after acid corrosion, the grain size of the residual Si in SiC:IM = 0.20 specimen is found to decrease significantly in comparison with that of SiC:IM = 0 counterpart, with the corresponding APDs to be 52.93 nm and 4.43  $\mu\text{m}$ , respectively, which are consistent with the aforementioned SEM results. The addition of SiC raw powders can effectively avoid the formation of large-sized “Si lakes” and further improve the microstructural homogeneity, thus leading to enhanced  $K_{IC}$ . Furthermore, we tested the mechanical properties perpendicular to the printing layer. The  $\rho$ , flexural strength, and  $K_{IC}$  of the SiC:IM = 0.20 sample are  $2.774 \pm 0.003 \text{ g}\cdot\text{cm}^{-3}$ ,  $241 \pm 9 \text{ MPa}$ , and  $3.49 \pm 0.08 \text{ MPa}\cdot\text{m}^{1/2}$ , respectively. Although the SLS is a layer-by-layer stacking method along the Z direction, there is

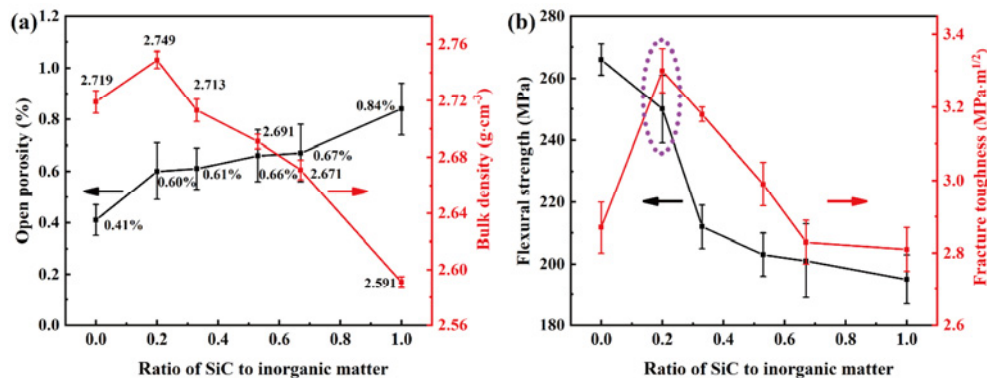


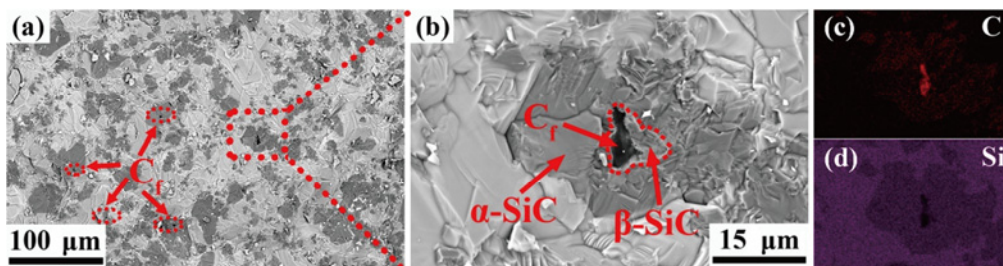
Fig. 12 RT mechanical properties of SiC composites: (a)  $O$  and  $\rho$  and (b) flexural strength and  $K_{IC}$ .

a slight difference in mechanical properties in different directions. Compared with other SiC-based composites fabricated by additive manufacturing [17,18,34,35], this study shows a higher flexural strength and  $K_{IC}$ .

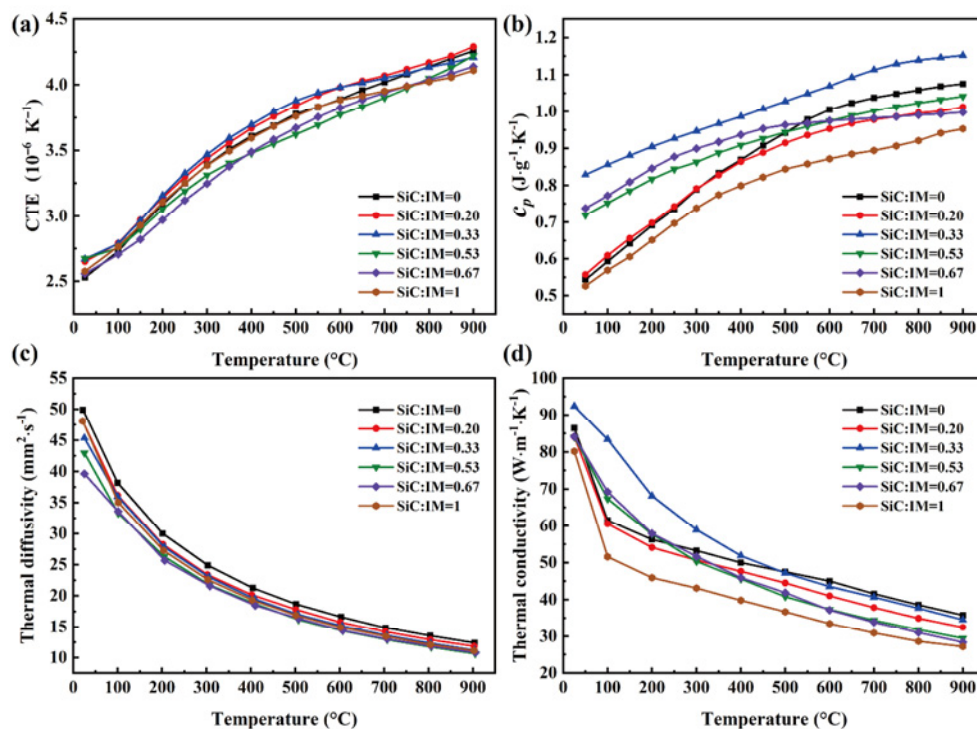
The fracture-surface morphologies of the SiC composite are used to elucidate the fracture mechanism of the SiC composites. Figure 13 shows the typical fractured surfaces of the SiC:IM = 0.20 composite after the bending tests. As shown in the red circles in Fig. 13(a), residual  $C_f$  embedded within the  $\beta$ -SiC grains can be observed. The thermodynamic calculation by HSC Chemistry version 6.0 (Outokumpu Research Oy, Finland) shows that the Gibbs free energy change ( $\Delta G$ ) of the silicon–carbon reaction, as shown in Reaction (11), is about  $-12.641$  kcal at  $1550$  °C, indicating that the reaction between carbon and silicon is spontaneous. It is worth noting that the activity of

the carbon source also affects the formation of  $\beta$ -SiC. During the RMI, the liquid Si preferentially reacts with the PyC, and then reacts with the surficial layer of  $C_f$  to form the  $\beta$ -SiC layer, which can act as a barrier against the diffusion of liquid silicon and further siliconization of  $C_f$ . For this reason, the residual  $C_f$  is embedded within the  $\beta$ -SiC grains, as shown in Fig. 13(b). Simultaneously, the  $\beta$ -SiC layer of the  $C_f$  surface and the  $\alpha$ -SiC layer of the matrix form the strong interface bonding, and the crack perpendicular to the fiber will penetrate into the fiber, releasing the elastic strain energy [29]; therefore, obvious fiber breakages are detected. Moreover, the SiC matrix shows typical transgranular fractures.

The  $\kappa$  and  $\alpha$  are the key thermal properties of the SiC composites as important components in space optical systems. Figure 14 shows the thermal properties



**Fig. 13** Fractured morphologies of SiC composite with SiC:IM = 0.20: (a) back-scattered electron SEM; (b) high-magnification SEM micrograph; and (c, d) EDS mappings.



**Fig. 14** Thermal properties of SiC composites: (a)  $\alpha$ ; (b)  $c_p$ ; (c)  $\alpha$ ; and (d)  $\kappa$ .

of the SiC composites parallel to the printing layer. As shown in Fig. 14(a), the  $\alpha$  value increases over the entire temperature range, which is lower than  $4.3 \times 10^{-6} \text{ K}^{-1}$  (average linear  $\alpha$  of the SiC composites, RT–900 °C). According to Refs. [36,37], the  $\alpha$  of Si and SiC are  $2.6 \times 10^{-6}$  and  $3.3 \times 10^{-6} \text{ K}^{-1}$  at RT, respectively. Thus, the  $\alpha$  of the SiC composites increase slightly with the increasing SiC fraction. Although the SiC:IM = 0.20 sample has relatively the highest  $\alpha$  of  $4.29 \times 10^{-6} \text{ K}^{-1}$  due to its highest total SiC fraction among all samples (Table 4), its  $\alpha$  is still in low level. Furthermore, for the sample with the recipe of SiC:IM = 0.20, its  $\alpha$  measured perpendicular to the printing layer is  $4.39 \times 10^{-6} \text{ K}^{-1}$ , which is also comparable with that measured parallel to the printing layer direction.

The  $c_p$ ,  $a$ , and  $\kappa$  of the SiC composites were measured from RT to 900 °C, as shown in Figs. 14(b)–14(d). The  $c_p$  increases with temperature for the SiC composites, which coincides with the Debye theory [20]. While the  $a$  shows the inverse temperature dependence, indicating that the phonon conduction behavior dominates in the SiC composites. And the  $a$  of SiC:IM = 0 sample is in the range of  $12.39\text{--}48.97 \text{ mm}^2 \cdot \text{s}^{-1}$  from RT to 900 °C, the highest among all the SiC composites reported in this study. The RT  $\kappa$  of the SiC composites in this study is in the range of  $80.15\text{--}92.48 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , and the SiC:IM = 0.33 sample has the highest  $\kappa$  of

$92.48 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . As the temperature increases to 900 °C, the  $\kappa$  monotonously decreases to  $27.21\text{--}35.81 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . As the temperature increases, the vibration frequency of the phonon increases, and the scattering effect increases, so the free path decreases, and the  $\kappa$  decreases. The RT  $\kappa$  of the SiC composites is relatively lower than those of the reported values of pressureless sintered SiC ( $160\text{--}180 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) [38] and hot-pressed SiC ( $120 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) ceramics [39], but better than those of the wood-derived Si/SiC composite ( $70 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) from wood [20] and the SiC composite ( $74\text{--}84 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) fabricated by the SLS-PIP-RMI hybrid route due to the homogeneous microstructure [34]. There are three main reasons for the low  $\kappa$  of the SiC composites in this study. The first reason is the presence of PyC (about  $3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , RT) as a poor thermal conductor [40]. And then, according to the aforementioned phase composition and microstructure analysis, the SiC composites are mainly composed of three-phase SiC, residual silicon, and residual carbon. The phase interface can cause the phonon scattering and low  $\kappa$ . Additionally, the defects including pores and impurities (Al-Fe alloys) induce phonon scattering, resulting in the decrease of mean free path and  $\kappa$ .

The high-temperature flexural strengths of the SiC composite (SiC:IM = 0.20) were measured at 600, 800,

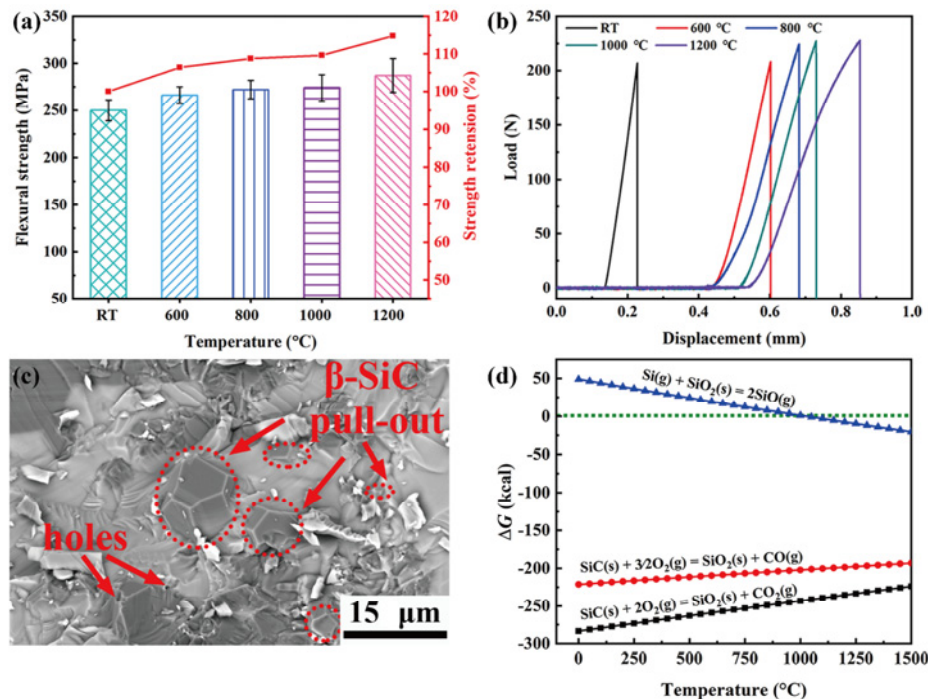


Fig. 15 (a) Flexural strengths of SiC composite (SiC:IM = 0.20) at RT, 600, 800, 1000, and 1200 °C; (b) load–displacement curves of SiC composite (SiC:IM = 0.20) in (a); (c) fracture surfaces at 1200 °C; and (d)  $\Delta G$  of Reactions (13)–(15).

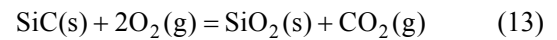


1000, and 1200 °C under an Ar atmosphere (Fig. 15). As shown in Fig. 15(a), the flexural strengths of the SiC composites at RT, 600, 800, 1000, and 1200 °C are 250±11, 266±9, 272±10, 274±11, and 287±18 MPa, respectively. As the temperature increases, the flexural strength increases and reaches the maximum at 1200 °C. The strength retention is 114.8% at 1200 °C. The increase in strength at elevated temperatures might be due to the crack healing effect [41]. Compared with the other SiC-based composites fabricated by laser additive manufacturing [16], the present material shows a higher high-temperature strength and retention due to the homogeneous microstructure and low porosity (0.6% vs. 19.1%).

Figure 15(b) shows the load–displacement curves of the flexural strength tests at different temperatures. It can be seen that the curves for different conditions of RT, 600, 800, and 1000 °C samples are almost linear up to the maximum load, and then followed by sharp load decrease, exhibiting brittle fracture due to the strong interface bonding between the  $\alpha$ -SiC and  $\beta$ -SiC layers of the  $C_f$  surface. However, the load–displacement curve for 1200 °C sample exhibits significant non-linear tendency up to the maximum load, indicating the creep behavior of Si. Moreover, the displacement to the failure of the RT sample is less than 0.3 mm, while the 1200 °C sample shows the increased displacement to the failure up to 0.85 mm ascribed to the plastic deformation of residual Si.

The fractured surface of the 1200 °C sample is shown in Fig. 15(c). The  $\beta$ -SiC grains and holes can be observed clearly due to the pullout of SiC. Therefore, the SiC matrix is the intergranular failure at 1200 °C. The transition of fracture mode might be related to the weakening of the bonding strength between the Si and SiC interface at elevated temperatures [41]. Meanwhile, the oxygen contents in the samples after high-temperature strength testing first slightly increase from

2.64 to 2.73 wt% from RT to 800 °C, and then decrease to 1.92 wt% at 1200 °C. Notably, when the temperature is below 1200 °C, the SiC will undergo passive oxidation to form solid SiO<sub>2</sub> [42]. The relevant reactions involved in the high-temperature bending tests are shown in Reactions (13)–(15).



To further investigate the oxidation mechanism in this study, the  $\Delta G$  of the reactions at various temperatures (0–1500 °C) was calculated by the HSC Chemistry software, as shown in Fig. 15(d). Generally, a negative  $\Delta G$  indicates that the reaction is spontaneous. As shown in Fig. 15(d), the  $\Delta G$  of Reactions (13) and (14) are negative within 0–1500 °C, while the  $\Delta G$  of Reaction (15) is positive at 0–1000 °C. As the temperature exceeds 1000 °C,  $\Delta G$  of Reaction (15) changes to negative. Therefore, the increase in oxygen content is mainly due to the passive oxidation of SiC to form SiO<sub>2</sub>; and when the temperature exceeds 1000 °C, Reaction (15) is spontaneous, and the formation of SiO vapor leads to a decrease in oxygen content. Additionally, the study by Ness and Page [43] showed that impurity elements including K, Ca, Al, and Fe tend to form amorphous phases at the Si/SiC interface. At high temperatures, the softening of the amorphous phase leads to the weakening of the interface bond strength. At this time, the crack can propagate along the Si/SiC interface, forming the intergranular failure. The formation of SiO<sub>2</sub> as well as the mismatch of  $\alpha$  [44] between Si- and SiC-induced crack healing effects and the change of the fracture mode is beneficial to the improvement of high-temperature strength.

As shown in Table 5, compared with the SiC composites fabricated by different additive manufacturing methods, enhanced mechanical and thermal properties

**Table 5 Comparison of mechanical and thermal properties by different additive manufacturing techniques**

Method	Composition	Density (g·cm <sup>-3</sup> )	Flexural strength (MPa)	$K_{IC}$ (MPa·m <sup>1/2</sup> )	$\kappa$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )	Ref.
SLS+RMI	SiC composites	2.749	266	3.30	92.48	This work
SLS+PIP+RMI	C <sub>f</sub> /SiC	2.83	249	3.48	—	[17]
SLS+PIP+RMI	C <sub>f</sub> /SiC	2.89	237	3.56	84	[34]
SLA+RMI	C <sub>f</sub> /SiC	2.75	262	1.80	—	[35]
SLA+RMI	C <sub>f</sub> /SiC	2.69	250	3.46	—	[46]
DIW+RMI	SiC	2.94	224	—	112	[45]
DIW+CVI+RMI	C <sub>f</sub> /SiC	—	274	5.82	—	[47]

Note: SLA is the abbreviation of stereolithography, and DIW is the abbreviation of direct ink writing.

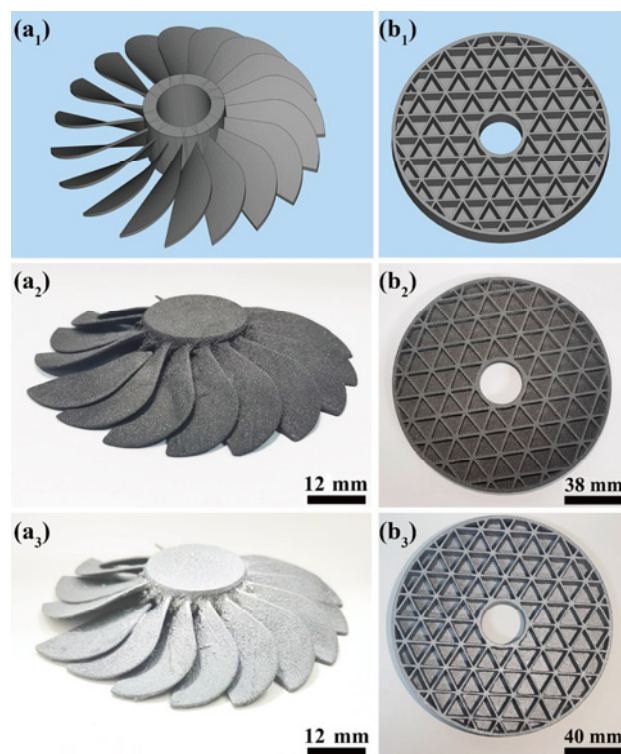
in combination with the relatively lower density are measured for our SiC composites compared with Ref. [34], such as SiC composites fabricated by using SLS+PIP+RMI method or SiC ceramics fabricated by direct ink writing (DIW)+RMI technique [45]. The reason is mainly due to the homogeneous microstructure and lower sintered porosity (0.6% vs. 2.1%).

The STL models and sintered components of turbine blades and mirrors with complex structures are shown in Fig. 16. These results indicate the flexibility of SLS in fabricating the larger size and lightweight SiC components.

## 4 Conclusions

The SiC composites have been fabricated by RMI of the porous  $C_f$ /SiC/C green bodies, which were obtained by the SLS process from the  $C_f$  and PR mixture with the addition of  $\alpha$ -SiC particles. The initially introduced  $\alpha$ -SiC particles play an important role in improving the flowability (AOR from  $53^\circ$  to  $42^\circ$ ), reducing the porosity (from 74.89% to 67.29%),

pore size (from 21.04 to 18.77  $\mu\text{m}$ ), and flexural strength (from 7.70 to 9.41 MPa) of the  $C_f$ /SiC/C green bodies. The SiC composites are mainly composed of typical SiC, residual Si, and residual  $C_f$  from partially siliconized  $C_f$ . Furthermore, the results indicate that the initial addition of SiC particles can not only avoid the formation of large-sized “silicon lakes” and improve the microstructural homogeneity, but also reduce the contents of residual silicon. More importantly, the  $\beta$ -SiC layer formed by RMI can act as a diffusion barrier to prevent the fibers from siliconization, and the residual  $C_f$  could improve the  $K_{IC}$  by fiber breakage. The maximum density of  $2.749\pm 0.006\text{ g}\cdot\text{cm}^{-3}$  and  $K_{IC}$  of  $3.30\pm 0.06\text{ MPa}\cdot\text{m}^{1/2}$  are simultaneously achieved, and the medium flexural strength only possesses  $250\pm 11\text{ MPa}$  for the SiC composite sample with the addition of 15 vol%  $\alpha$ -SiC particles. In addition, the  $\alpha$  of the SiC composites is approximately  $4.29\times 10^{-6}\text{ K}^{-1}$  from RT to  $900^\circ\text{C}$ , and the  $\kappa$  at RT is in the range of  $80.15\text{--}92.48\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , whose values decrease to  $27.21\text{--}35.81\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $900^\circ\text{C}$ . Additionally, we reported the high-temperature mechanical properties of laser additive manufacturing SiC composites. The high-temperature strength ( $1200^\circ\text{C}$ ) of the SiC:IM = 0.20 sample increases to 287 MPa, which is 15% higher than the strength at RT. The fracture mode transition and crack healing contribute to strength improvement. Although the versatile performance still need to be further optimized, this study provides a new opportunity to fabricate the SiC composites.



**Fig. 16**  $C_f$ /SiC/C green bodies and sintered SiC composites with complex structures fabricated via SLS: (a<sub>1</sub>–a<sub>3</sub>) turbine blade; (b<sub>1</sub>–b<sub>3</sub>) flat mirror (the subscripts 1, 2, and 3 represent the STL models, printed  $C_f$ /SiC/C green bodies, and sintered SiC composites, respectively).

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## Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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