

Exceptional long-duration ablation tolerance over 2500 °C of C/ZrC–SiC–Cu₃Si–Cu interpenetrating composites

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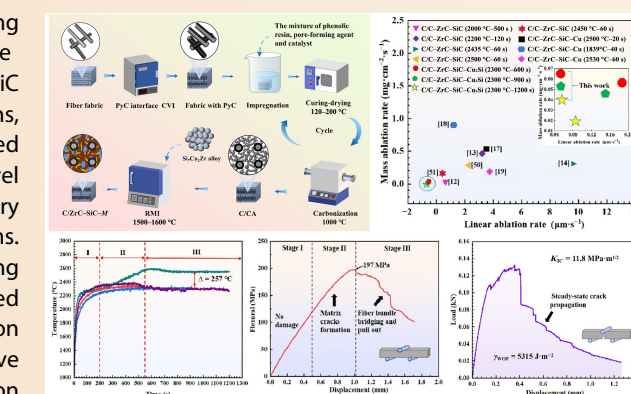
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ABSTRACT: The development of materials capable of withstanding long-term ablation above 2500 °C in an oxidizing atmosphere remains a critical challenge. Although conventional C/ZrC–SiC composites show promise for ultrahigh-temperature applications, they typically suffer from high ablation rates under prolonged exposure. To address this limitation, we fabricated novel C/ZrC–SiC–Cu₃Si–Cu composites by infiltrating a Zr–Si–Cu ternary melt into carbon fiber-reinforced carbon aerogel (C/CA) preforms. This process resulted in the formation of a uniform, interpenetrating metal-ceramic matrix through the ceramization of CA accompanied by precipitation of Cu-containing phases from the melt. Relying on sweat gland-like channel migration heat dissipation and evaporative heat removal of metallic phases as well as mechanical denudation resistance and inhibition of oxygen diffusion by the Zr–Si–O layer, the composite exhibited exceptional long-term ablation resistance. After 1200 s of oxyacetylene ablation at a surface temperature of 2557–2600 °C, the composite exhibited ultralow mass and linear ablation rates of 0.0604 mg·cm⁻²·s⁻¹ and 0.1808 μm·s⁻¹, respectively, surpassing the benchmark performance of conventional C/ZrC–SiC as well as other reported ceramic matrix and ceramic-metal matrix composites under similar test conditions. Moreover, the composite demonstrated excellent mechanical properties, with a flexural strength of 194±7 MPa, a fracture toughness of 11.8±1.2 MPa·m^{1/2}, and a work of fracture of 5315±1232 J·m⁻², exceeding those of most reaction-melt-infiltration-derived C/ZrC–SiC. This favorable combination of ablation resistance and mechanical performance makes the composite a promising candidate for structural applications in extreme thermal-mechanical environments.

KEYWORDS: ceramic-metal matrix composites; C/ZrC–SiC–Cu₃Si–Cu; carbon aerogels; transpiration cooling; ablation behavior

1 Introduction

Carbon fiber-reinforced ultrahigh-temperature ceramic composites (C/UHTCs) have emerged as leading candidates in thermal protection systems in spacecraft or engines owing to their low density, high strength, and excellent ablation resistance [1–5]. In the design of the ceramic matrix, ZrC–SiC is particularly noteworthy, offering a favorable combination of low cost and superior anti-ablation performance derived from its oxidation products [6–10]. Upon oxidation, ZrC transforms into ZrO₂, which is stable at ultrahigh temperatures with a melting point of ~2700 °C [11], while SiC yields a low-permeability SiO₂ glass that infiltrates and seals the pores of the evolving ZrO₂ skeleton. This synergistic process results in a dense, coherent Zr–Si–O surface layer, which is responsible for the superior anti-ablation performance of C/ZrC–SiC composites.



Owing to these advantages, C/ZrC–SiC composites have garnered significant interest in recent years. For instance, Zhao *et al.* [12] prepared C/ZrC–SiC via precursor impregnation and pyrolysis (PIP), reporting a linear ablation rate of 0.37 μm·s⁻¹ after exposure to an oxyacetylene flame at 2000 °C for 200 s. In contrast, Wen *et al.* utilized reactive melt infiltration to fabricate C/ZrC–SiC, which demonstrated a linear ablation rate of 3.2 μm·s⁻¹ under a higher ablation temperature (2200 °C for 120 s) [13]. A further escalation was reported by Zang *et al.*, where the linear ablation rate of PIP-derived C/ZrC–SiC reached 9.7 μm·s⁻¹ after ablation at 2435 °C for 60 s [14]. These data clearly indicate a sharp increase in the ablation rate with rising surface temperature and prolonged ablation time. This deterioration in performance is primarily attributed to the accelerated volatilization of the protective Zr–Si–O or SiO₂ layer and the ensuing rapid mechanical denudation of the underlying ZrO₂ framework.

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Consequently, developing materials capable of withstanding prolonged ablation at temperatures exceeding 2500 °C in an oxidizing atmosphere remains a critical challenge.

Transpiration cooling is recognized as an effective strategy for reducing surface temperatures in passive thermal protection materials, particularly in ceramic matrix composites [15,16]. Among phase-change cooling media, copper stands out due to its exceptional thermal properties, featuring a high latent heat of fusion (208.67 kJ·kg⁻¹) and evaporation (4730 kJ·kg⁻¹) [16]. The phase transition of copper dissipates substantial heat, thereby lowering surface temperatures and suppressing ablation rates of thermal protection materials. For instance, Weng *et al.* [17] fabricated C/ZrC–SiC–Cu via high-pressure infiltration (10 MPa) of Cu into a porous PIP-derived C/ZrC–SiC preform, achieving a linear ablation rate of 3.5 μm·s⁻¹ at 2500 °C for 20 s. Similarly, Huang *et al.* [18] incorporated Zr₂Cu into a porous C/C–SiC preform, producing a composite where the synergistic evaporation of Cu and SiO₂ effectively reduced ablation surface temperatures. Further advances by Weng *et al.* [19] involved Zr₂Cu infiltration into a porous PIP-derived C/C–SiC preform, yielding C/ZrC–SiC–Cu_xZr_y with a linear ablation rate of 3.8 μm·s⁻¹ after exposure at 2530 °C for 60 s. At the same time, the process of preparing composites with two-step RMI, PIP, and CVI is complex, the preparation period is long, and the cost is high [17–19].

However, the fabrication of composites mentioned above suffers from complex procedures, long preparation cycles and high cost. Limited by the complexity of the preparation process and its own characteristics, the C/ZrC–SiC–*M* composites (*M* represents metallic phases) reported are limited by nonuniform copper distribution and high carbon matrix content, which disrupts continuous transpiration cooling and degrades performance [17,18,20]. To overcome this issue, our team previously fabricated novel C/SiC–*M* composites via ceramization of carbon fiber-reinforced carbon aerogel (C/CA) preforms using a Cu–Si alloy according to reactive melting infiltration (RMI) mechanisms. The resulting interpenetrating metal-ceramic microstructure endowed the composites with excellent ablation resistance: under test conditions where conventional C/SiC reached 2200 °C, the modified composites maintained a surface temperature of 1750 °C for 1160 s and exhibited a very low mass ablation rate of 0.489 mg·cm⁻²·s⁻¹ and a linear ablation rate of 0.349 μm·s⁻¹ [21]. The marked reduction in surface temperature and low long-term ablation rates underscore the potential of this approach for ultrahigh temperature thermal protection systems. This breakthrough demonstrates the viability of microstructure-engineered composites in applications demanding prolonged thermal stability at extreme temperatures. Nevertheless, the applicability of C/SiC–*M* interpenetrating composites becomes limited above 2500 °C due to the vigorous evaporation of the formed SiO₂ glass layer and the transformation from passive to active oxidation of the SiC matrix at low oxygen pressures over 1700 °C [22].

Building upon previous work, in this study, we developed novel C/ZrC–SiC–Cu₃Si–Cu interpenetrating composites via ceramization of C/CA preforms using a Si–Zr–Cu ternary alloy. The composites exhibited exceptional long-term ultrahigh-temperature ablation resistance, with extremely low mass and linear ablation rates of 0.0604 mg·cm⁻²·s⁻¹ and 0.1808 μm·s⁻¹ under prolonged 1200 s oxyacetylene ablation, respectively, under test conditions where conventional C/ZrC–SiC reached 2600 °C, surpassing the benchmark performance of reported ceramic matrix and ceramic-metal matrix composites under similar test conditions (Table S1 in the Electronic Supplementary Material (ESM)). Meanwhile, the composites exhibited good mechanical

performance with a flexural strength of 194±7 MPa, fracture toughness of 11.8±1.2 MPa·m^{1/2}, and work of fracture of 5315±1232 J·m⁻², exceeding those of most reaction-melt infiltration-derived C/ZrC–SiC. The favorable combination of ablation and mechanical properties makes the material promising for structural applications in extreme thermal-mechanical environments.

2 Experimental

2.1 Material preparation

Needle-punched fabrics of polyacrylonitrile-based carbon fibers (T700, Toray Industries, Japan) with fiber contents of approximately 28 vol% were used as reinforcements for fabrication of the C/ZrC–SiC–*M* composites. The fabrics were fabricated by alternatively stacking carbon fiber weftless layers composed of 12k bundles and short-cut webs and then pierced with carbon fiber bundles in the Z direction. The successive weftless layers were oriented at an angle of 90° to each other. Figure 1 illustrates the preparation process for the C/ZrC–SiC–*M* composites. First, a pyrolytic carbon (PyC) interface with a thickness of ~900 nm was prepared by pyrolysis of C₃H₆ at 1100 °C in an isothermal chemical vapor infiltration device. Second, a mixture of phenolic resin, pore-forming agent and catalyst with a proportion of (5–15) : (8–20) : 1 was infiltrated into the C/PyC preform with a pressure of 1–6 MPa. Numerous experimental results demonstrated that the preform fabricated with the above proportion achieves optimal alloy wettability during melt infiltration while exhibiting superior process repeatability. Through subsequent curing at 80–200 °C, ambient pressure drying, and carbonization in an argon atmosphere at 800–1000 °C, C/CA preforms were obtained. After several impregnation, curing, ambient pressure drying and carbonization cycles, their densities were increased to 1.1–1.4 g·cm⁻³. Finally, an appropriate amount of Si–Zr–Cu ternary alloyed powder (with a nominal composition of Si₇Zr₂Cu 200#, ≥ 99.5% purity, Jinzhou Jinrui New Materials Co., Ltd., China), which was mainly composed of Cu₄Si₆Zr₃, Cu₃Si, ZrSi₂, and Si according to the X-ray diffraction (XRD) pattern (Fig. S1(b) in the ESM), was infiltrated into the C/CA preforms at 1500–1600 °C under vacuum to fabricate the C/ZrC–SiC–*M* composites. As shown in Fig. S2 in the ESM, the selection of Si–Zr–Cu ternary alloys in this paper is based on phase diagrams. First, fine adjustments were made to the composition design, and three low-melting-point alloys were developed. Combined with infiltration exploratory experiments, DSC analysis and wettability tests between the three alloys and carbon materials, the Si₇Cu₂Zr alloy was finally selected. Normalized volume fractions of various components in the composites are shown in Table S2 in the ESM.

2.2 Mechanical tests

The flexural strength and fracture toughness of the materials were evaluated using an electronic universal testing machine (Alliance RF/100, MTS, USA). Three-point bending tests were performed on specimens measuring 80 mm (length) × 7 mm (width) × 5 mm (height), with a span of 70 mm and a loading rate of 1 mm·min⁻¹. Fracture toughness (*K_{IC}*) was measured by a single-edge notched beam (SENB) method at room temperature, employing a loading rate of 0.05 mm·min⁻¹ and a span of 20 mm. The SENB specimens measured had dimensions of 36 mm × 3 mm × 4 mm, with a notch depth of approximately 2 mm and a notch width of approximately 0.2 mm. Both bending and SENB specimens were precisely contoured and notched via wire electrical discharge machining, effectively avoiding surface damage

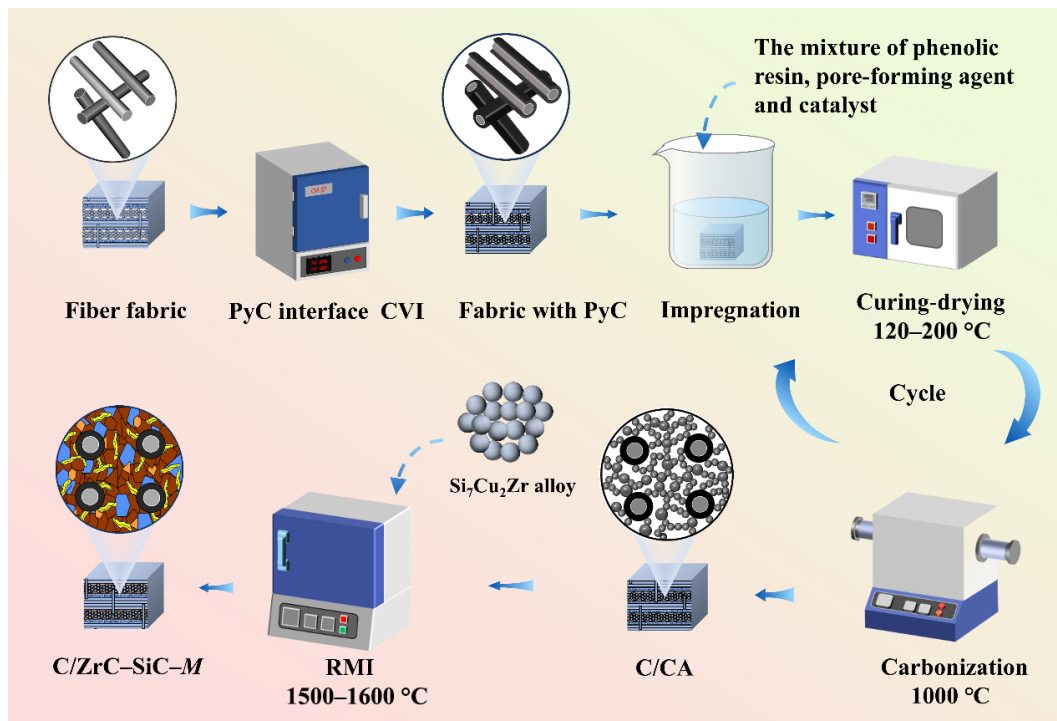


Fig. 1 Schematic of the preparation process of the C/ZrC–SiC–M composites.

and microcrack initiation induced by conventional mechanical cutting. After cutting, all specimens were wet-polished to scratch-free, axially oriented mirror surfaces and ultrasonically cleaned with acetone. All specimens were machined within ± 0.02 mm dimensional and geometrical tolerances. The SENB specimens were fabricated with a notch depth ratio of 0.45–0.55 and a root radius ≤ 0.02 mm to guarantee accurate and repeatable bending and fracture testing. Based on the load–displacement curves obtained from the fracture toughness tests, the work of fracture (γ_{WOF}) for the C/ZrC–SiC–M composites was calculated. The parameters γ_{WOF} and K_{IC} were calculated according to the methods in Ref. [23]. All the given values were the average of at least five measured values.

A Vickers indenter (Qness 60 EVO, QATM, the Netherlands) was employed to introduce cracks for the analysis of crack propagation behavior. At least five indentations were made on the composite surface under a load of 19.6 N (2 kg). The resulting indentations exhibited diameters of approximately 50 μm , with center-to-center spacing exceeding 300 μm between adjacent impressions.

Single-fiber push-out tests were conducted using an advanced in situ nanotesting system (TI950, Hysitron, USA) to evaluate the fiber–matrix interfacial shear strength (ISS) [24]. The test specimens were prepared by first sectioning the composite into 1 mm thick slices with a diamond saw blade, followed by thinning both surfaces using diamond abrasive paper. The final thickness of each push-out specimen was determined via optical microscopy. A specialized fixture featuring an approximately 80 μm wide groove was employed to support the sample during testing. Selected individual fibers were displaced using a Berkovich indenter at a constant loading rate of 20 $\text{nm}\cdot\text{s}^{-1}$. The maximum indentation depth was set to less than 1.2 μm to prevent contact with the surrounding matrix.

Residual stress in the composites was evaluated using Raman spectroscopy (LabRam HR800, Horiba Jobin-Yvon, France). The underlying principle of the residual stress analysis has been detailed in a previous study [25]. The G-band of carbon and the

TO-band of SiC were selected for stress analysis. Their respective unstressed reference positions were determined as 1579.4 cm^{-1} (measured from carbon fibers in C/CA) and 790.0 cm^{-1} (obtained from finely polished SiC). The piezo-spectroscopic coefficients (C_{ps}) were taken as 0.3058 for SiC and 0.1038 for carbon, based on an established Ref. [26].

2.3 Ablation tests

An oxyacetylene flame with a heat flow density of 3.18 $\text{MW}\cdot\text{m}^{-2}$ was used to evaluate the anti-ablation properties of the C/ZrC–SiC–M composites. The distance between the sample ($\Phi 30$ mm $\times$ 10 mm²) and the nozzle tip ($\Phi 2$ mm) was 10 mm. The surface temperatures were observed using an infrared thermometer. Mass and linear ablation rates (R_{m} and R_{l}) were calculated according to the changes in sample mass and central thickness before and after ablation, respectively [27]. Three parallel specimens were used for ablation tests. The details of the ablation parameters are shown in Table S3 in the ESM.

2.4 Characterization

The bulk density and open porosity of the C/ZrC–SiC–M composites were measured through an Archimedes method. Phase compositions were identified by X-ray diffraction (XRD; D/Max-2500PC, Rigaku, Japan). 3D macroscopic morphologies of the composites after ablation were obtained by digital optical microscopy (VHX-900F, Keyence Co., Ltd., Japan). Microstructure and composition were characterized using transmission electron microscopy (FEI Tecnai G2 F20, TEM, USA) equipped with energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM; Verios G4 UC, ThermoScientific, USA) equipped with EDS. The TEM bulk specimens were sliced by wire electrical discharge machining, ground, punched into 3 mm discs, dimpled, and finally thinned via ion milling to achieve electron-transparent areas. TEM powder samples were ultrasonically dispersed in ethanol, dropped onto carbon-coated copper grids and air-dried. All specimens were plasma cleaned before TEM characterization.

3 Results and discussion

3.1 Microstructure of the C/ZrC–SiC–M composite and its formation mechanism

Figure 2 presents the cross-sectional morphology of the C/ZrC–SiC–M composite, along with magnified views of the fiber and matrix regions. The composite is composed of three distinct alternating layers: 0° weftless layers, short-cut fiber webs, and 90° weftless layers, each exhibiting different carbon fiber and matrix contents (Fig. 2(a)). The composite has a dense structure with no visibly large pores. Accordingly, it achieves a high bulk density of $3.0 \text{ g}\cdot\text{cm}^{-3}$ and a low open porosity of 3%. In comparison, previously reported C/ZrC–SiC–M composites fabricated by other methods exhibit higher porosity, ranging from 4.4% to 12.5% [17–20], as shown in Table 1. Enlarged images clearly show that the carbon fibers remain intact, with a well-preserved PyC interfacial layer approximately 700 nm thick (Fig. 2(b)), indicating effective protection of the fibers against alloy corrosion by the interface phase. After ceramization of C/CA, the CA matrix has almost fully transformed into a multiphase ceramic–metal matrix, as hardly any CA residue remains (Fig. 2(c)), which is attributed

to the fact that CA exhibits a far higher chemical reactivity toward the $\text{Si}_2\text{–Zr–Cu}$ melt than PyC [4]. EDS mappings (Fig. 2(d)) combined with XRD results (Fig. 2(e)) indicate that the dark gray phase corresponds to SiC, while the white regions mainly consist of ZrC, Cu_3Si , Cu, with a small amount of $\text{Cu}_4\text{Si}_6\text{Zr}_3$ phase. The dark gray and light areas are uniformly distributed and nearly fully interconnected (Fig. 2(c)). Therefore, a C/ZrC–SiC– $\text{Cu}_3\text{Si–Cu}$ composite is obtained with a uniform, interpenetrating network architecture, which is crucial for enabling high-efficiency active-passive hybrid cooling during ablation.

To further verify the phase compositions of the C/ZrC–SiC–M composite, TEM analysis was performed. As shown in Fig. 3(a), combined with the EDS results (Fig. 3(b)), the dark particles are identified as SiC based on the interplanar spacing of 0.25 nm corresponding to the (110) plane (Fig. 3(c)). Similarly, the gray phase is determined to be ZrC, with a measured d-spacing of 0.27 nm matching the (111) plane (Fig. 3(d)). Area scan analysis at the junction of SiC, ZrC, and Cu reveals a phase with an interplanar spacing of 0.37 nm, corresponding to the (101) plane (Fig. 3(e)), which matches well with $\text{Cu}_4\text{Si}_6\text{Zr}_3$ [19]. Additionally, an interface (Fig. 3(b)) between the red regions (SiC) and yellow regions (Cu) was observed, where the measured interplanar

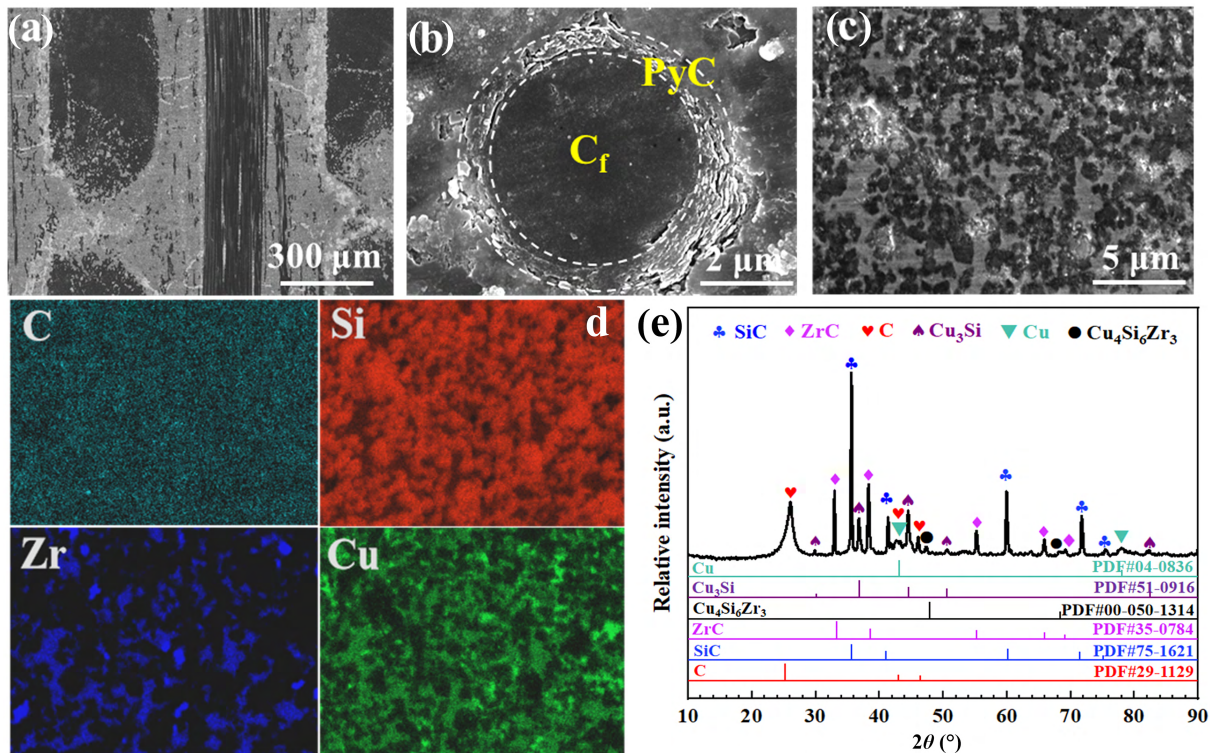


Fig. 2 Morphologies and compositions of the C/ZrC–SiC– $\text{Cu}_3\text{Si–Cu}$ composites. (a–c) SEM images for the polished cross-section, (d) EDS mappings for the matrix in (c), and (e) XRD pattern.

Table 1 Fabrication methods, infiltrating phases, and open porosities of reported C/ZrC–SiC–M composites

Composite	Preform	Fabrication method	Infiltrating phase	Open porosity	Ref.
C/ZrC–SiC– $\text{Cu}_3\text{Si–Cu}$	C/CA	one-step RMI	$\text{Si}_2\text{Zr}_2\text{Cu}$	3%	This work
C/C–SiC–ZrC–Cu	C/C	CVI + PIP + VPI	SiC + ZrC–SiC	12.5%	[17]
C/C–SiC–ZrC–Cu	C/C	two-step RMI	Si + Zr/Cu	5%	[18]
C/C–SiC–ZrC– Cu_xSi_y	C/C–SiC	PIP + PRI	Zr_2Cu	4.4%	[19]
C/C–SiC–ZrC–Cu	C/C	two-step RMI	Si/Zr + Cu/Ti	4.77%	[20]

Note: VPI—vacuum-pressure infiltration; PRI—pressure-assisted reactive melt infiltration.

spacing of 0.39 nm suggests the presence of Cu₃Si [28] (Fig. 3(f)). The light-gray phase (Fig. 3(f)) exhibited low crystallinity due to the coexistence of amorphous regions and crystalline nuclei. These nuclei, exhibiting lattice spacings of 0.39 and 0.22 nm, were attributed to Cu₃Si and Cu, respectively, indicating that a reaction had occurred between the excess Si at the Cu/SiC interface and Cu, leading to the formation of Cu₃Si.

The microstructure characteristics are closely related to the ceramization process of the C/CA preform. The formation mechanism of the C/ZrC–SiC–Cu₃Si–Cu composites can be schematically illustrated in Fig. 4. As mentioned above, the Si–Zr–Cu ternary alloy was mainly composed of Cu₄Si₆Zr₃, Cu₃Si, ZrSi₂, and Si (Fig. S1 in the ESM). Based on the DSC curve of the Zr–Si–Cu alloy (Fig. S2 in the ESM) and relevant phase diagrams (Fig. S3 in the ESM), the phase evolution during heating can be stated below. An endothermic reaction occurs at 802 °C, corresponding to the reverse eutectic reaction: Cu₃Si + Si → Liquid, which results in the melting of Cu₃Si and a portion of Si.

At 927 °C, the melting of the alloy proceeds via another reverse eutectic reaction: CuZr + CuZr₂ → Liquid, leading to the liquidation of Zr–Cu constituents. Subsequently, the solid-phase derived Cu₈Zr₃ undergoes a reverse peritectic reaction at 973 °C: Cu₈Zr₃ → Liquid + Cu₅₁Zr₁₄. Finally, the Cu₅₁Zr₁₄ phase melts at 1115 °C. However, due to the poor wettability, the melt cannot infiltrate into the C/CA preform to react with the CA matrix at low temperatures. Despite the continuous increase of silicon within the melt, the wettability between the melt and the carbon matrix is only achieved upon heating to 1300 °C. The wettability characteristics were evaluated through a designed experiment in which Si–Zr–Cu alloys placed on C/CA preforms were maintained for 3 min at temperatures ranging from 1000 to 1550 °C (specifically at 1000, 1100, 1200, 1300, 1420, and 1550 °C) (Fig. S4 in the ESM). When the temperature is over 1420 °C (Fig. 4), the Si–Cu–Zr melt can infiltrate into the porous CA matrix and subsequently react with the carbon walls.

Reactions (1)–(4) may occur as follows:

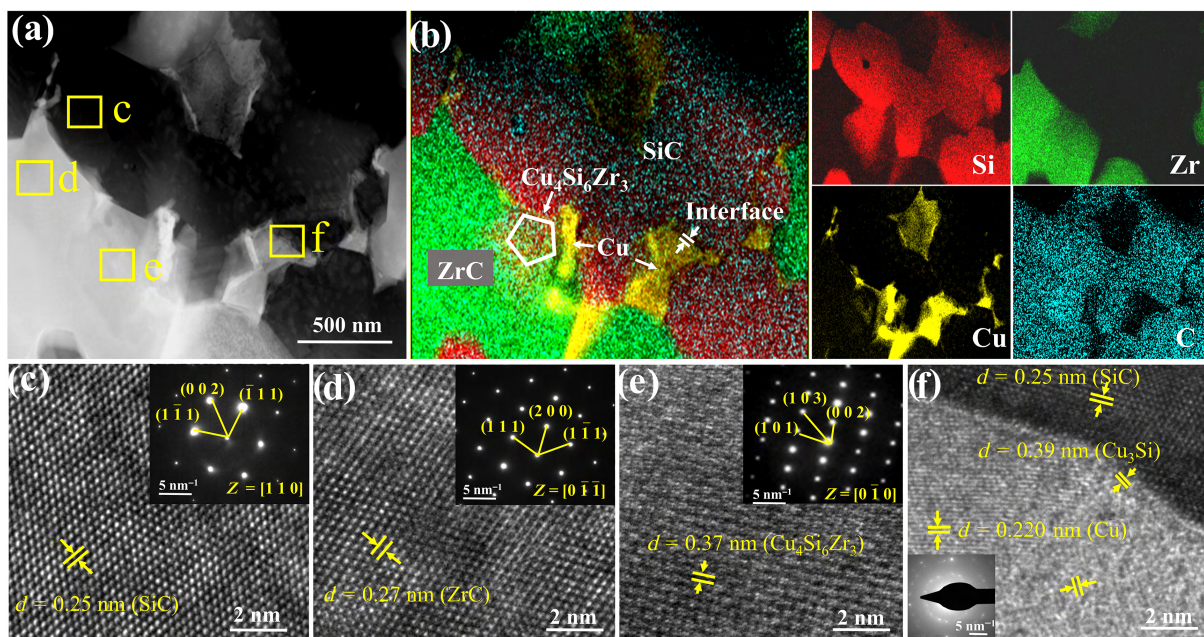


Fig. 3 TEM images of the matrix: (a) bright-field image; (b) elements distribution of C, Zr, Si and Cu in (a); (c–f) enlarged images of the corresponding areas in (a) and their respective selected area electron diffraction (SAED) patterns.

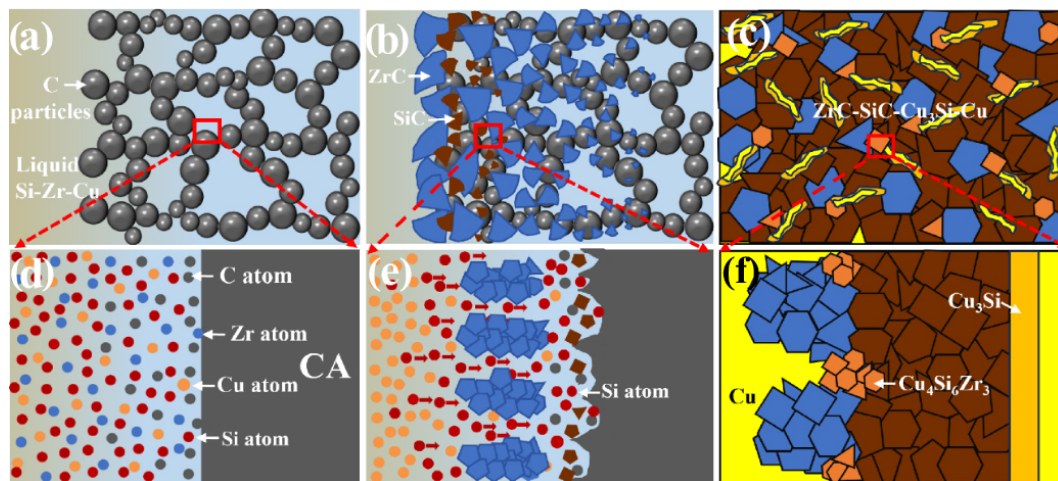
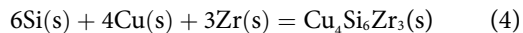
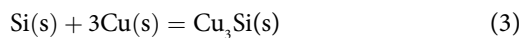


Fig. 4 Schematic diagram of the formation process of C/ZrC–SiC–Cu₃Si–Cu. (a) infiltration of Si–Zr–Cu melt into the CA matrix, (b) partial ceramization of CA and initial precipitation of Cu-containing phases, (c) formation of the C/ZrC–SiC–Cu₃Si–Cu, (d) dissolution of carbon atoms into melt, (e) precipitation of SiC and ZrC, (f) formation of the ZrC–SiC–Cu matrix.



Although the Gibbs free energy for the formation of Cu_3Si is lower than those for the formation of ZrC and SiC [29] at high temperatures above 1450 °C, Cu, Zr, and Si exist in a highly active, intermixed atomic state due to the liquid state, while ZrC and SiC possess superior thermodynamic stability [30,31]. Consequently, the formation of SiC and ZrC is kinetically and thermodynamically favored. Furthermore, since the Gibbs free energy of Reaction (1) is lower than that of Reaction (2), as is shown in Fig. S5 in the ESM, ZrC forms prior to SiC . Once the metal infiltrate in C/CA, carbon atoms in the carbon walls rapidly dissolve into the metal to form a Si-Zr-Cu-C solution with a carbon concentration gradient (Figs. 4(a) and 4(d)). Subsequently, fine ZrC crystals preferentially precipitate from the supersaturated solution near the carbon walls. Concurrently, Zr atoms in the melt continuously diffuse toward the Cu-Si-Zr/CA interface, leading to the epitaxial growth of ZrC on the initially formed crystals until the Zr supply is depleted. Following this, Si atoms undergo a similar process, resulting in the epitaxial growth of SiC . Consequently, the epitaxial growth of these carbides led to the formation of a new, uniformly distributed SiC and ZrC framework based on the original carbon skeleton of the CA matrix. Due to the nonreactive nature of Cu with carbon, Cu atoms continuously precipitated from the C-Zr-Si-Cu solution in regions distant from the Cu-Si-Zr/CA interface. As the process proceeds, the carbon particles are gradually consumed and eventually exhausted (Figs. 4(b) and 4(e)). During cooling, the high cooling rate inhibited the crystallization of the precipitated Cu, resulting in the formation of amorphous Cu [32]. Meanwhile, excess Si atoms at the Cu-SiC interface bonded with Cu, leading to the formation of Cu_3Si (Reaction (3)). Additionally, at the junction of SiC , ZrC , and Cu, surplus Si, Zr, and Cu atoms bonded to form the $\text{Cu}_4\text{Si}_6\text{Zr}_3$ phase (Reaction (4)). As a result, the highly reactive nanocarbon particles are completely reacted to form SiC and ZrC , and the Cu-containing metal remained in the original pores (Figs. 4(c) and 4(f)). Due to the volume expansion of carbon into SiC , ZrC , and Cu-containing phases [33], pore closure occurs simultaneously, resulting in the formation of a highly dense composite. Overall, the unique morphology of C/CA, its high reactivity, and the protective effect of the PyC interface jointly promoted the selective ceramization of C/CA, leading to the formation of an interconnected network composed of uniformly dispersed SiC and ZrC ceramics and copper-containing phases, as well as intact carbon fibers.

3.2 Mechanical behaviors of the C/ZrC-SiC-Cu₃Si-Cu composite

Figure 5(a) presents the flexural stress-strain curves of the C/ZrC-SiC-Cu₃Si-Cu composite. In the initial stage (stage I), the response is linearly elastic, reflecting simultaneous elastic deformation of the fibers and matrix under load. As loading exceeds the matrix fracture strain, the curve deviates from linearity due to the onset of matrix cracking (stage II). Multiple matrix cracks form but are deflected at the fiber-matrix interface,

preventing unstable crack propagation. Upon reaching peak load, stress concentration at matrix crack tips induces controlled interfacial debonding, load does not drop abruptly but is maintained through frictional pull-out of the bridging fibers, producing a distinct plateau in stage III. Final failure occurs via progressive fracture of the load-bearing fibers, followed by fiber pull-out. This process allows the fibers to slide relative to the matrix and achieve crack bridging, and Consequently, channels form within the matrix. This mechanism dissipates considerable energy, leading to a gradual load decrease rather than a sudden drop. In contrast, conventional ceramic composites fabricated by RMI typically fail in a brittle manner, characterized by a sharp load drop after the maximum, only limited fiber bridging maintains a low residual load [12]. This behavior is attributed to strong interfacial bonding caused by reactions between carbon fibers and the melt, which significantly degrades mechanical properties. The pseudoplastic fracture behavior exhibited by the present composite results from optimized fiber-matrix interfacial bonding and crack-tip blunting induced by the metallic phases, as discussed below. The composite shows high flexural strength of 194 ± 7 MPa, despite the low fiber content, which exceeds most of the RMI-derived C/ZrC-SiC and C/ZrC-SiC-M composites, as shown in Table 2 ([24,34–46]).

Fracture toughness and work of fracture were evaluated using a SENB method to assess crack-growth resistance and total energy absorption up to failure. The composite shows a fracture toughness of 11.8 ± 1.2 MPa·m^{1/2}, higher than that of the RMI-derived C/C-Cu and C/ZrC-SiC listed in Table 2, indicating an improved ability to suppress unstable crack propagation. Moreover, this composite achieves high work of fracture with a value of 5315 ± 1232 J·m⁻². This parameter correlates positively with the area under the load-displacement curve (Fig. 5(b)) [47], further confirming the composite's excellent toughness and damage tolerance [48]. Compared to the C/SiC-Cu composites with a similar interface thickness previously reported by our team [23], the flexural strength, fracture toughness, and work of fracture of C/ZrC-SiC-Cu₃Si-Cu are significantly higher by 32.8%, 144.8%, and 161.1%, respectively.

To further clarify the fracture behavior, representative flexural fracture morphologies of the C/ZrC-SiC-Cu₃Si-Cu composites are shown in Figs. 5(c)–5(h). The fracture surfaces exhibit extensive fiber and bundle pull-out (Fig. 5(c)). Notably, the carbon fibers remain intact without obvious corrosion, while many ceramic-metal matrix fragments adhere to the pulled-out fibers (Fig. 5(d)). Interfacial debonding occurs primarily within the PyC interlayer and at the interface between fibers and PyC (Fig. 5(e)). These observations suggest that the carbon fibers were effectively protected during RMI, with slight ceramization at the periphery of the PyC interface enhancing matrix-interface bonding. The interfacial shear strength (ISS) between fibers and matrix was measured via a single-fiber push-out test. To minimize interference from adjacent fibers and ensure consistent interfacial properties, single fibers in fiber-sparse regions were selected. The calculated ISS is 137 ± 2.6 MPa, which is moderate relative to conventional ceramic-matrix composites [49]. This moderate interfacial strength induces interfacial crack deflection and suppresses brittle fracture of fibers. Meanwhile, it facilitates appropriate interfacial debonding, which promotes fiber pull-out and dissipates fracture energy efficiently. These coupled microscopic behaviors establish the intrinsic microtoughening mechanism, thereby endowing the composite with integrated superior strength and toughness. Consequently, pronounced crack deflection and branching can be observed during crack

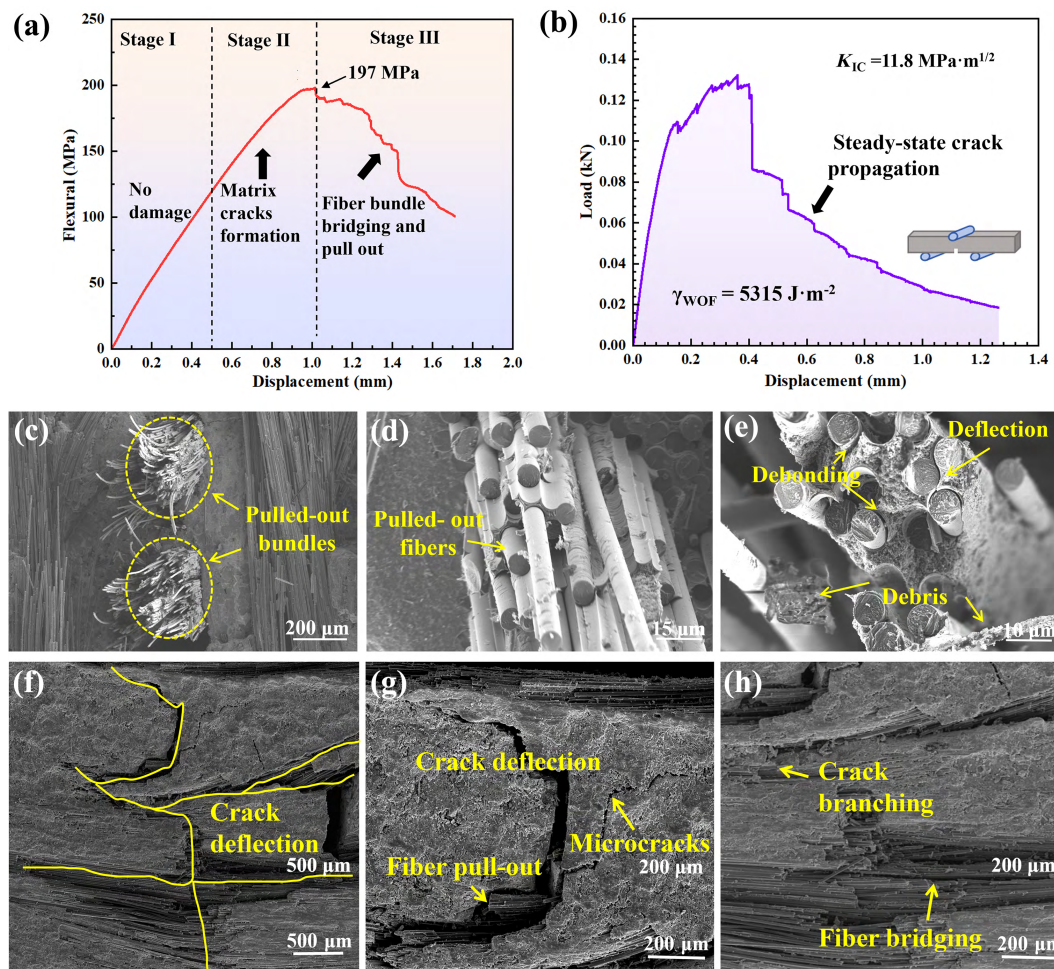


Fig. 5 (a) Flexural stress–strain curve of C/ZrC–SiC–Cu₃Si–Cu; (b) curve of load–displacement during the SENB tests; (c–e) SEM images of the typical flexural fracture morphologies; (f–h) SEM images of crack propagation profiles after the SENB tests.

Table 2 Flexural strengths, work of fracture and fracture toughnesses of the C/(C–)SiC–M, C/(C–)SiC–ZrC, and C/ZrC–SiC–Cu₃Si–Cu composites

Composite	Preform/ fiber content	Fabrication method	Flexural strength (MPa)	Work of fracture (J·m ⁻²)	Fracture toughness (MPa·m ^{1/2})	Ref.
C/ZrC–SiC–Cu ₃ Si–Cu	3D needle-punched/28%	RMI	194±7	5315±1232	11.8±1.2	This work
C/SiC–Cu	3D needle-punched/28%	RMI	145±23	2171±487	4.5±1.1	[23]
C/C–SiC–Cu ₃ Si	3D needle-punched/28%	RMI	186±17	7288±536	—	[34]
C/C–SiC–Cu	3D needle-punched/—	RMI	151±16	—	—	[35]
C/C–ZrC–Cu	3D needle-punched/30%	RMI	99±3	—	5.5±0.5	[36]
C/C–Cu	3D needle-punched/30%	RMI	189±10	—	4.5±0.3	[37]
C/C–Cu	3D needle-punched/30.6%	PIP + RMI	113	—	—	[35]
C/SiC–ZrC	3D needle-punched/36%	RMI	224±5	—	—	[38]
C/SiC–ZrC	3D needle-punched/28%	RMI	126±3	—	4.8±0.5	[39]
C/C–ZrC–SiC	3D needle-punched/45%	RMI	117±5	—	—	[40]
C/SiC–ZrC	3D needle-punched/45%	PIP + GSI	182.9±11.9	—	8.1±2.9	[41]
C/SiC–ZrC	3D needle-punched/45%	PIP + RMI	102±8	—	—	[42]
C/C–ZrC–SiC	3D needle-punched/—	PIP	163±24	—	—	[43]
C/C–ZrC–SiC	3D needle-punched/—	SI + VI	177±8	951±12	5.4±0.3	[44]
C/C–ZrC–SiC	2.5D needle-punched/25%	PIP	172	—	—	[45]
C/C–ZrC–SiC	3D needle-punched/25%	CVI + PIP	137±17	—	—	[46]

Note: GSI—gaseous silicon infiltration; VI—slurry injection and vacuum impregnation; —means not tested.

propagation, accompanied by much fiber-bundle bridging and pull-out (Figs. 5(f)–5(h)). Specifically, when a crack penetrates through the 0° nonwoven layers, cracks tend to deflect within the 90° nonwoven layers, propagating further along the interfaces

between the nonwoven and web fiber layers. This results in a complex crack profile, with cracks advancing both in-plane and out-of-plane, thereby dissipating substantial fracture energy.

To better understand crack-propagation mechanisms, Fig. 6

illustrates crack paths in C/ZrC–SiC–Cu₃Si–Cu induced by Vickers indentation. When cracks encounter carbon fibers, the weaker PyC interface splits preferentially, leading to interfacial debonding. Consequently, a multiarch-shaped crack profile forms as the crack deflects along fiber edges (Fig. 6(a)). Within the ceramic-metal matrix, cracks deflect around SiC, ZrC, and Cu-containing metallic phase grains, propagating along grain boundaries; occasional grain pull-out is also observed (Figs. 6(b) and 6(c)). When the cracks encounter the metal matrix, crack bridging occurs, dissipating energy through plastic deformation while blunting crack tips to reduce stress concentration and inhibit further propagation (Figs. 6(d) and 6(e)). This crack behavior results from the combined presence of hard (SiC, ZrC) and soft (Cu-containing) phases. The metallic phases provide alternative crack paths, promoting bifurcation and diversifying deflection modes, especially through metal bridging and crack blunting, compared to conventional ceramic matrix composites. In addition, residual stress also plays a significant role in crack propagation. Raman spectroscopy was used to analyze residual stresses in carbon fibers and SiC matrix since ZrC is Raman-inactive. The compressive stresses in carbon fibers and SiC matrix were calculated as -0.519 and -1.259 GPa, respectively (Figs. 6(g) and 6(h)). These compressive residual stresses counteract external tensile stresses, inhibiting crack initiation and propagation by

effectively “clamping” microcracks, thereby improving damage tolerance against impacts.

Overall, the composite's superior mechanical properties originate from four synergistic mechanisms: (1) The high reactivity of the CA matrix coupled with the protective PyC interface effectively preserves carbon fiber integrity, sustaining their load-bearing capacity; (2) Optimized interfacial debonding energy maximizes fiber reinforcement and toughening effects; (3) Multiple crack deflection mechanisms, including metal bridging and crack blunting, significantly enhance fracture energy dissipation; and (4) Beneficial compressive residual stresses effectively inhibit crack initiation and propagation under tensile loading conditions.

3.3 Ablation behaviors of the C/ZrC–SiC–Cu₃Si–Cu composites

Figures 7(a) and 7(b) exhibit the ablation temperature curves and ablation rates of the C/ZrC–SiC–Cu₃Si–Cu composites, respectively. In the long-term ablation process, the surface temperatures rapidly increase to approximately 2300°C within 200 s and remained stabilized at this level until the cessation of the ablation process. Compared to the reference C/ZrC–SiC, which exhibits an ablation surface temperature up to $2557\text{--}2600^{\circ}\text{C}$, the

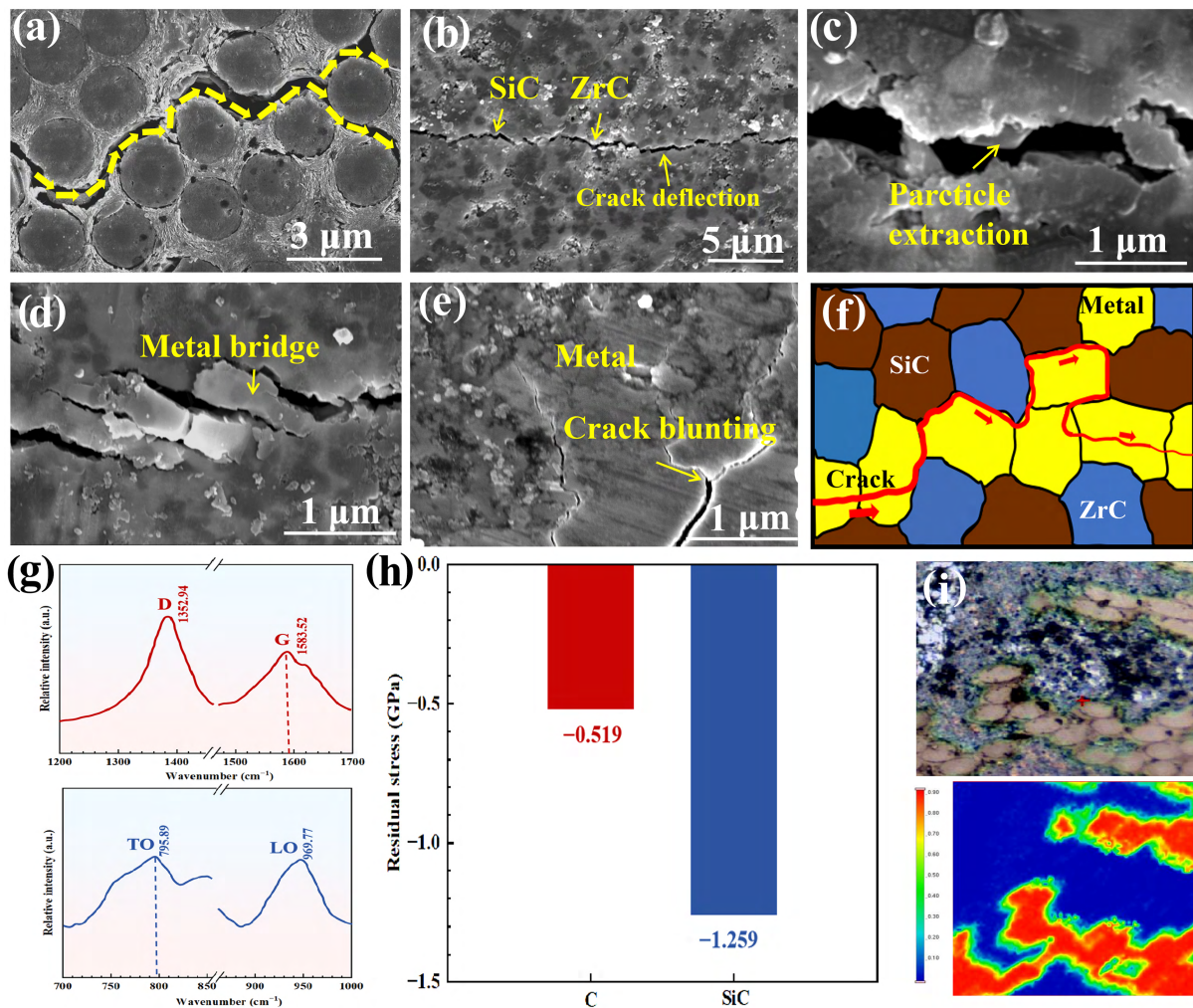


Fig. 6 SEM images of the polished surface morphologies showing Vickers-indentation-induced crack propagation in the case of encounter of: (a) the fibers with PyC interfaces; (b–e) the matrix; (f) schematic crack propagation in the matrix; (g) Raman spectra of the fibers and SiC matrix; (h) their residual stresses, (i) Raman face scanning of the cross-section.

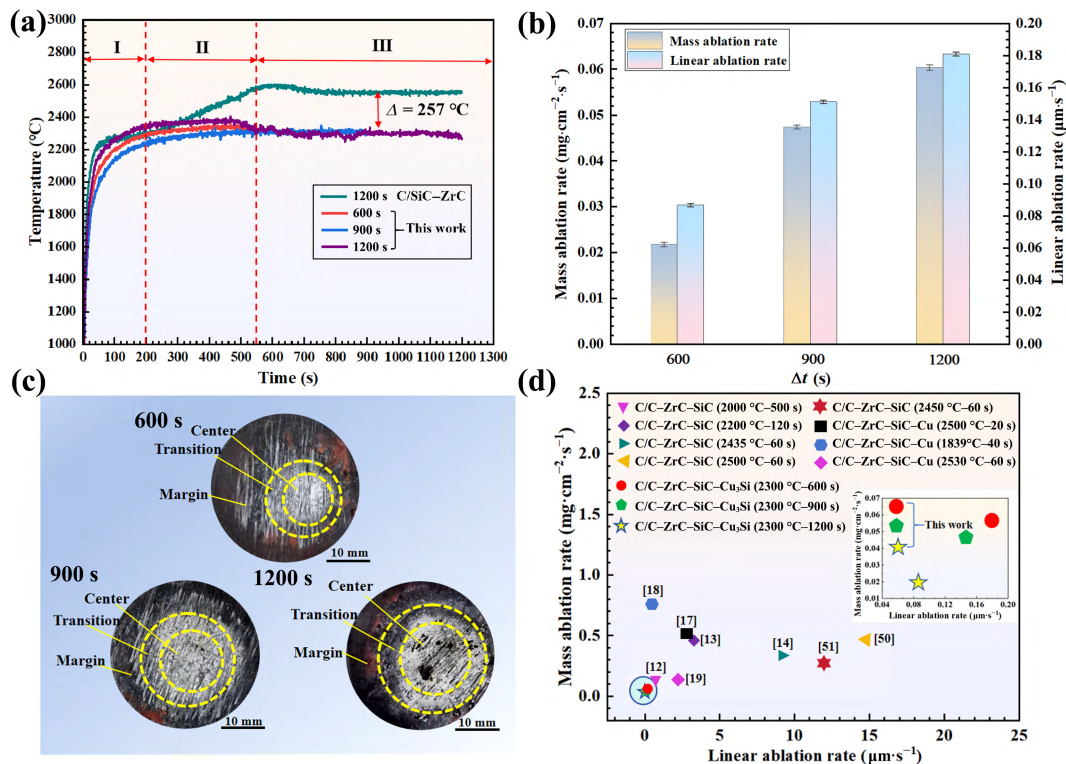


Fig. 7 (a) Surface temperature of the C/ZrC–SiC–Cu₃Si–Cu composites during long-term ablation; (b) ablation rates for different times; (c) macroscopic features after 600, 900, and 1200 s ablation; (d) comparisons of the ablation rates of the composites and other reported material [12–14,17–19,50–51].

C/ZrC–SiC–Cu₃Si–Cu composite demonstrates a significantly lower surface temperature with a reduction of over 250 °C. The R_m and R_l values are $0.0218 \pm 0.0011 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ and $0.0867 \pm 0.0010 \text{ }\mu\text{m}\cdot\text{s}^{-1}$ for 600 s, $0.0476 \pm 0.0024 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ and $0.1511 \pm 0.0010 \text{ }\mu\text{m}\cdot\text{s}^{-1}$ for 900 s, and $0.0604 \pm 0.0030 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ and $0.1808 \pm 0.0012 \text{ }\mu\text{m}\cdot\text{s}^{-1}$ for 1200 s ablation tests, respectively. The ablation rates are closely related to the ablation morphologies. As shown in Fig. 7(c), all ablation surfaces can be divided into three regions: center, transition and outer regions. As the ablation time increases from 600 to 1200 s, both the central and transitional regions significantly increase, with the diameter of the central area expanding from an initial 10.2 to 15.6 mm, and the diameter of the transitional zone growing from 3.5 to 6.3 mm. In addition, many abundant red-hued oxides, presumably identified as Cu₂O, were all observed in the outer region of the ablated surface in the different ablation times.

To further understand the evolution process with ablation time, the ablated morphologies in the center regions for 600, 900, and 1200 s are shown in Fig. 8. After 600 s, an oxide layer composed of a porous solid skeleton filled with a glass phase formed on the surface (Figs. 8(a) and 8(d)). The analyses of HRTEM and SAED indicate that the solid phase is ZrO₂ due to its interplanar spacing of 0.32 nm assigned to (111) plane (Figs. 9(a) and 9(c)). The EDS result also shows that the atomic ratio of Zr and O is 33.4 : 66.6 (Fig. 9(f)). The interplanar spacing of Cu₂O is 0.25 nm, corresponding to its (111) plane (Figs. 9(a) and 9(d)). Similarly, the EDS result shows that the atomic ratio of Cu and O is 67.2 : 32.8 (Fig. 9(g)). The glass can be verified to be SiO₂ with an amorphous structure with an atomic ratio of Si and O of 32.3 : 67.7 (Figs. 9(b) and 9(e)). With prolonged ablation time, the SiO₂ glass phase on the ablated surface gradually decreases. A SiO₂-sporadic zirconia layer remains after 900 s ablation with an atomic ratio of Si–Zr–O of 7.5 : 23.4 : 69.1 (Figs. 8(b), 8(c), and 8(h)), whereas the SiO₂ oxide is almost depleted after 1200 s ablation and a completely

ZrO₂-dominant structure is formed with an atomic ratio of Zr–O of 33.4 : 66.6 (Figs. 8(c), 8(f), and 8(i)). Similarly to the central zone, the glass phases in the transition region of the ablated surface exhibit a reduction with prolonged ablation time and the structure gradually transforms from a relatively dense form into a porous one (Fig. S6 in the ESM).

The ablation behavior in the central region of the ablated surface predominantly determines the ablation rate of the composite. Consequently, detailed examinations were performed on the cross-sectional morphology of oxides in the central region. The affected zones for the specimens ablated for 600, 900, and 1200 s gradually increase with a respective oxide layer thickness of 70, 110, and 220 μm (Figs. 10(a), 10(c), and 10(e)). The Zr–Si–O layers were formed on the ablated surfaces for 600 and 900 s from the EDS mapping (Figs. 10(b) and 10(d)). However, with the ablation time further prolonging to 1200 s, a double-layer oxide structure composed of an upper ZrO₂ layer and a lower Zr–Si–O layer (Fig. 10(f)) is present.

It is particularly worth mentioning that current evaluations of ultrahigh-temperature ablation performance of ceramic matrix or ceramic-metal matrix composites above 2500 °C are typically limited to 30–300 s and are characterized by a drastic increase in ablation rate with time. This is the first report in open literatures of a material demonstrating near-zero ablation after an even 1200 s prolonged exposure to such extreme conditions at temperatures exceeding 2500 °C. The ablation rate under prolonged ultrahigh-temperature exposure is significantly lower than even the short-term ablation rates reported in the literatures [17–19]. This performance also significantly surpasses that of our previously reported C/SiC–Cu composites, which can withstand ablation for 600 s at 2500 °C [23].

The exceptional long-term ultrahigh-temperature ablation resistance of C/ZrC–SiC–Cu₃Si–Cu is closely related to the ablation mechanisms. Based on the morphological and

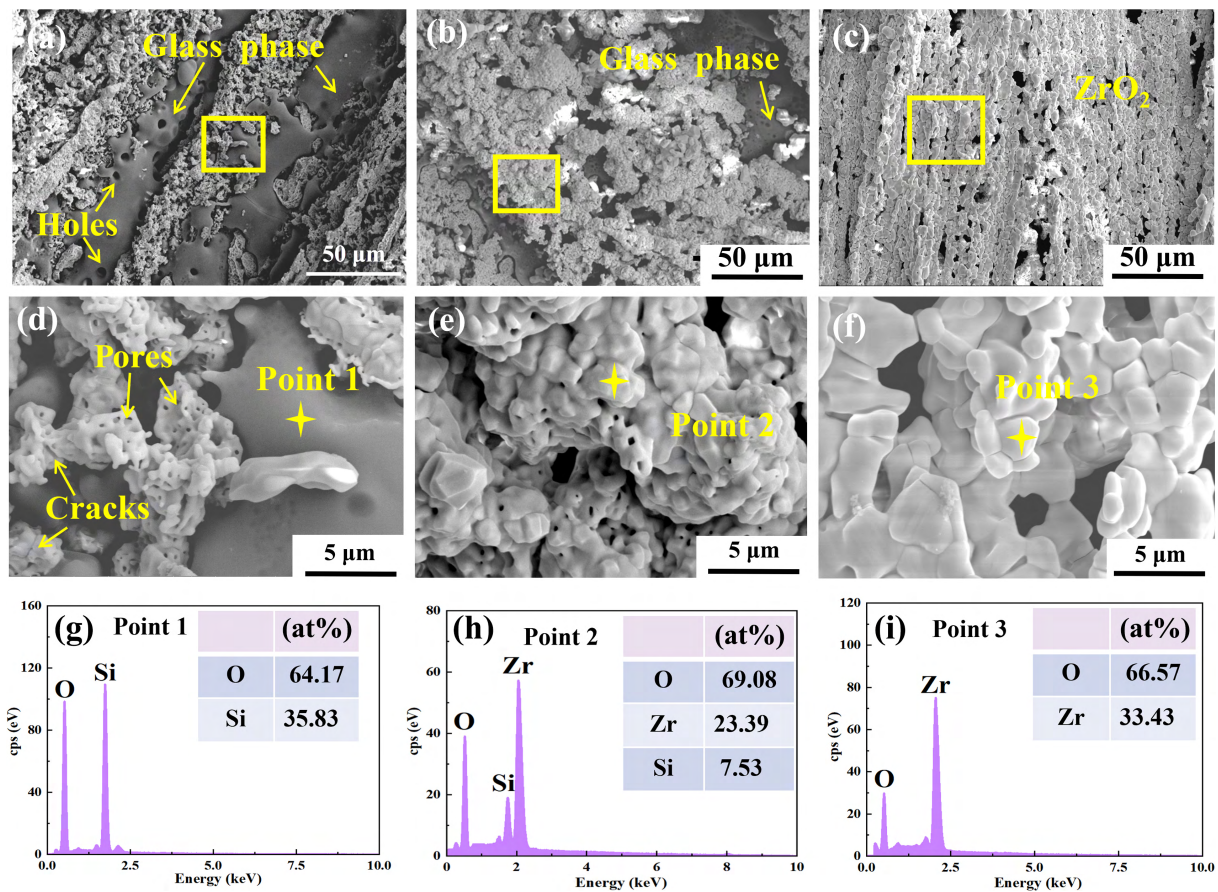


Fig. 8 Morphology of C/ZrC-SiC-Cu₃Si-Cu in the central region after ablation for (a, d) 600 s, (b, e) 900 s, and (c, f) 1200 s, and the corresponding EDS for different points marked in (g, h, i).

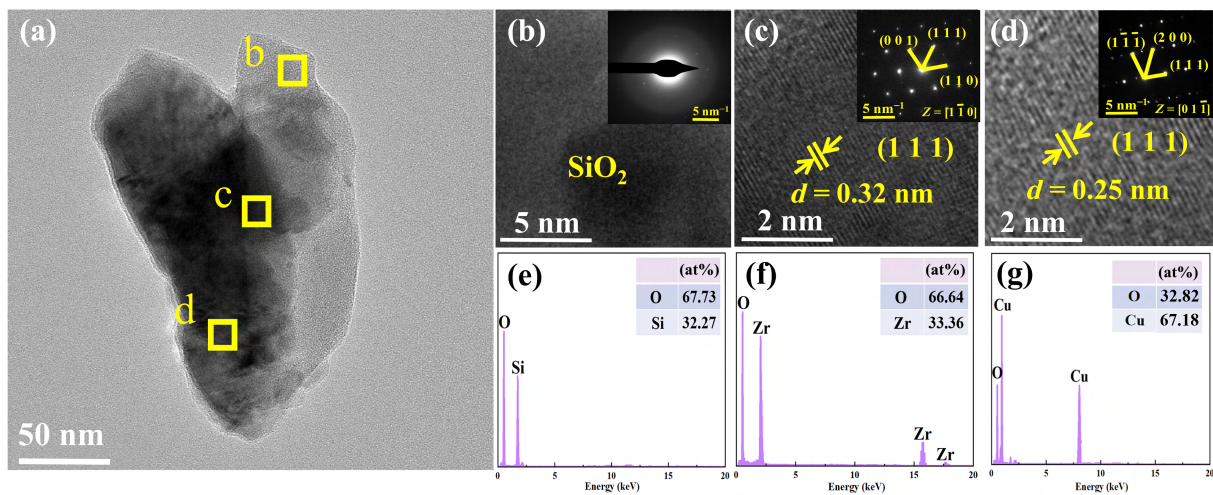
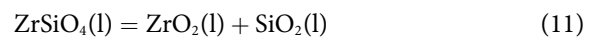
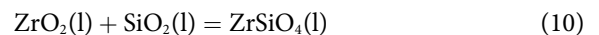
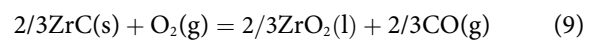
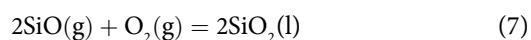
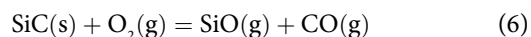
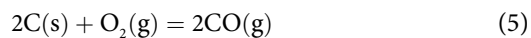


Fig. 9 TEM images of the oxide after ablation: (a) dark field image; and distribution of O, Zr, Si, and Cu elements, (b–d) enlarged TEM images of partitions in the oxide, and (e–g) the corresponding EDS mapping for different areas marked in (a).

thermodynamic analyses, the ablation mechanism can be illustrated in Fig. 11. In the ablation process, Reactions (5)–(18) may occur.



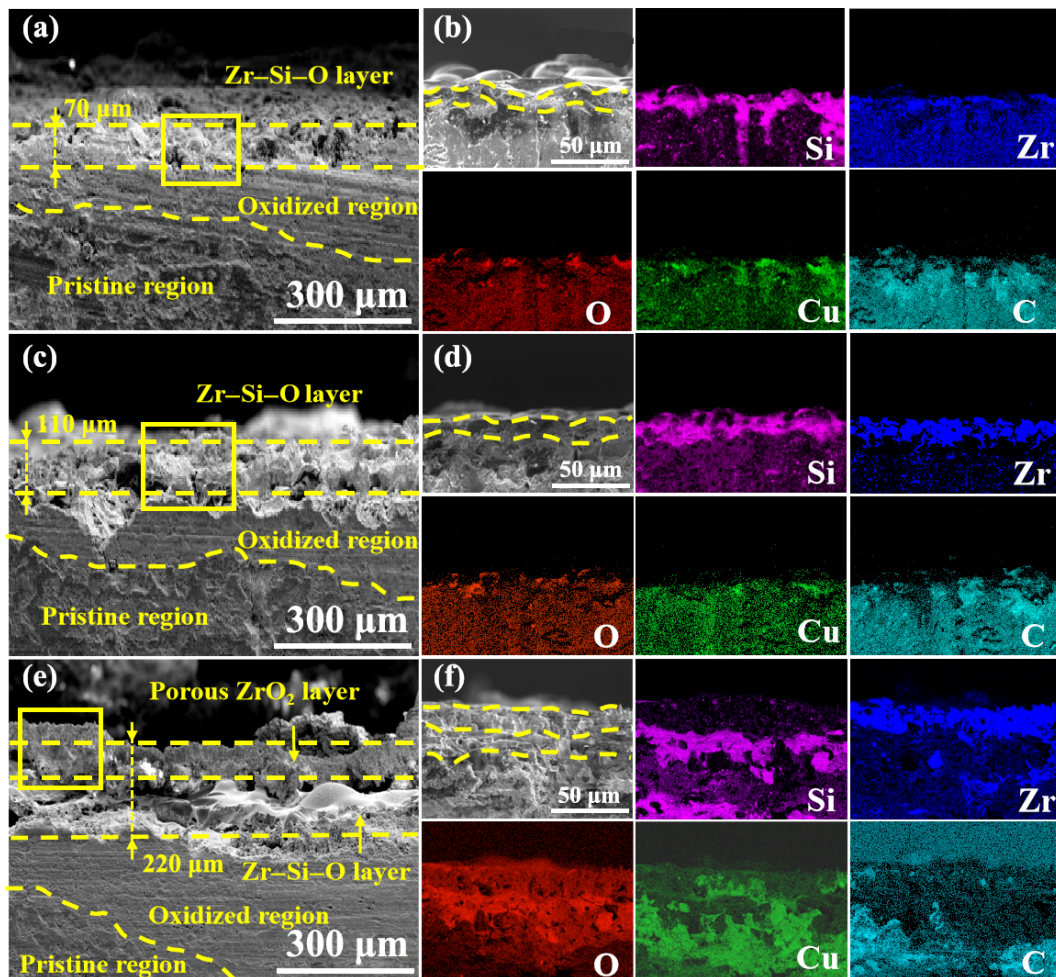


Fig. 10 Cross-sectional oxide morphology of C/ZrC–SiC–Cu₃Si–Cu after ablation at 3.18 MW·m^{−2} for (a, b) 600 s, (c, d) 900 s, and (e, f) 1200 s.

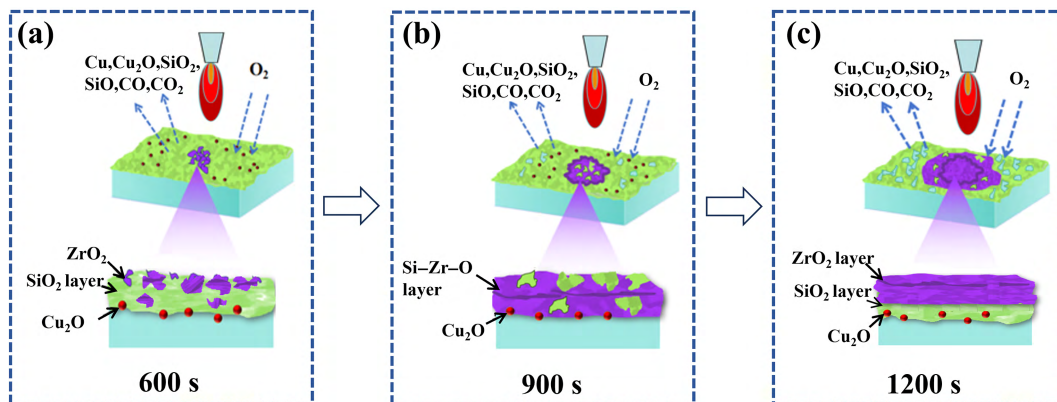
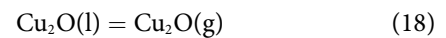
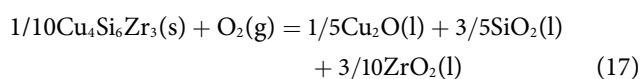
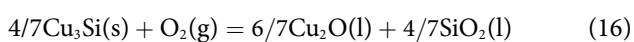
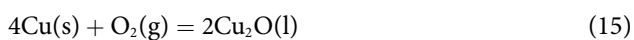
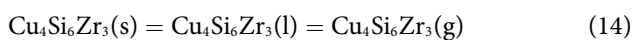
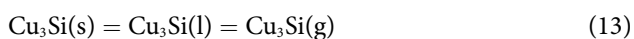


Fig. 11 Schematic diagram of ablation mechanisms of C/ZrC–SiC–Cu₃Si–Cu for: (a) 600 s, (b) 900 s, and (c) 1200 s.



As is shown in Fig. S7 in the ESM, thermodynamic analysis based on Gibbs free energy demonstrates that the ablation-oxidation reactions and product formation of C/SiC–ZrC–Cu composites exhibit obvious temperature-dependent sequential characteristics.

At low temperatures, preferential oxidation of matrix carbon and melting oxidation of copper phases take place to produce CO, CO₂ and copper oxides (Reactions (5), (12), and (14)–(15)). Meanwhile, Cu₃Si undergoes melting and decomposition (Reaction (13)), laying a foundation for subsequent high-

temperature oxidation reactions. In the medium-to-high temperature range, SiC is oxidized stepwise to form intermediate SiO, which further transforms into stable SiO₂. Synchronously, ZrC is preferentially oxidized to generate ZrO₂ particles accompanied by the formation of ZrSiO₄ (Reactions (6)–(11) and (16)–(17)). In addition, the oxidation of Cu, Cu₃Si, and Cu₄Si₆Zr₃ yields Cu₂O phase with superior high-temperature thermal stability (Reactions (15)–(17), and (18)). Fig. S8 in the ESM presents the XRD patterns of the C/ZrC–SiC–Cu₃Si–Cu composite surface after ablation for 600, 900, and 1200 s, which identifies the oxide compositions formed during ablation. With increasing ablation time, the diffraction peak intensity of ZrO₂ increases while that of SiO₂ decreases, indicating a gradual rise in the relative content of ZrO₂. The introduction of Zr plays a critical role in the ablation process. On one hand, ZrO₂, with its high melting point of 2700 °C, acts as a solid skeleton. On the other hand, with the introduction of Zr, Zr atoms are more inclined to diffuse into the SiO₂ lattice and occupy its intergap regions or replace Si atoms, moreover, intergap Zr atoms can better increase the interinterface binding energy of Zr-doped SiO₂ (110)/SiO₂ (001) [52]. This structural integration enhances the chemical stability and high-temperature resistance of the SiO₂ glass, thereby inhibiting its evaporation under ultrahigh temperatures [53]. Additionally, trace amount of copper oxide can dissolve into the ZrO₂ lattice to form a solid solution, which lowers the melting point of ZrO₂ [54]. Consequently, a Cu-doped Zr–Si–O glass is formed, exhibiting more moderate viscosity and lower oxygen diffusivity compared to a pure SiO₂ glass [55,56], can effectively fill pores and cracks. Together, the ZrO₂ solid skeleton and the Cu-doped Zr–Si–O glass filler jointly resist mechanical denudation and suppress oxygen diffusion during ultrahigh temperature ablation. Meanwhile, surface species such as Cu, Cu₃Si, and Cu₄Si₆Zr₃ with respective low melting points of 1083, 850, and 1130–1310 °C undergo melting and then vaporize (Reactions (12)–(14)). The process can absorb a large amount of heat due to the solid-liquid-gas phase transition; for instance, Cu has a high latent heat of fusion (208.67 kJ·kg⁻¹) and evaporation (4730 kJ·kg⁻¹). Additionally, the resulting Cu₂O from partial metal-phase oxidation with a melting point of 1235 °C and a boiling point of 1800 °C, melts and eventually vaporizes (Reaction (18)), accompanied heat absorption. Consequently, the metal-containing phases and their oxides collectively mitigate the surface thermal response through substantial heat dissipation via phase change. This collective effect is evidenced by a significantly lower surface temperature compared to the C/ZrC–SiC composite. As the ablation continues, although the ablation temperature exceeds the melting and boiling points of cuprous oxide, the synergistic effects of temperature gradient, *in situ* phase formation, oxide layer protection, and rapid quenching enable its metastable retention, whereas SiO₂ evaporation is moderated by the stabilizing effect of ZrO₂. After 600 s of ablation, a mixed SiO₂–ZrO₂ layer is formed at the center due to the stabilizing effect of ZrO₂ on SiO₂ as well as the reduced ablation surface temperature, which suppresses matrix ablation by acting as a physical barrier. By 900 s, the SiO₂ content in the SiO₂–ZrO₂ layer decreases markedly, resulting in a porous scale as SiO₂ substantially evaporates. At the same time, ZrO₂ particles sinter to form a continuous skeleton. The ablation behavior is jointly dominated by liquid-phase volatilization and ceramic particle sintering. After 1200 s, SiO₂ at the center is nearly completely volatilized, while ZrO₂ particles sinter into a relatively dense oxide layer overlying the residual SiO₂, forming a distinct double-layer structure. According to classic and recent studies, ZrO₂ sintering above 2000 °C is dominated by lattice diffusion of Zr⁴⁺ and O²⁻, following three stages: rapid densification, intensive

grain coarsening, and steady-state grain growth with isolated pores; meanwhile, t→c phase transformation and surface melting/ablation equilibrium occur with prolonged time [57–59]. What more as demonstrated in prior analyses, molten ZrO₂ formed during ablation significantly reduces surface oxide layer porosity, thereby suppressing oxygen diffusion rates through the oxide layer [60]. This mechanism effectively enhances the material's ablation resistance.

Meanwhile, as illustrated in Fig. S9 in the ESM, the as-prepared composite possesses higher thermal conductivity than conventional C/ZrC–SiC materials, which effectively reduces the surface ablation temperature. The ablation temperature is also strongly influenced by the infrared emissivity of ablation-generated oxides. ZrO₂ exhibits moderate-to-low high-temperature emissivity with weak radiative cooling performance, and Cu₂O suffers from severe high-temperature volatilization. In comparison, molten SiO₂ with excellent high infrared emissivity efficiently dissipates interfacial heat through thermal radiation, lowering the ablation temperature and mitigating substrate thermal ablation damage [61–63].

In summary, the ablation resistance of C/ZrC–SiC–Cu₃Si–Cu originates from the synergistic effects of multiple mechanisms: the evaporation of the Cu-containing phase, the volatilization of formed glassy phases, and the development of protective oxide layers including solid ZrO₂ and liquid Zr–Si–O. The architecture serves as effective thermal and oxygen diffusion barriers, which suppress oxidative degradation of the matrix by blocking oxygen and resisting mechanical denudation. Combined with the heat-absorbing and cooling effects provided by the Cu, Cu₃Si, and Cu₄Si₆Zr₃ and their oxide product Cu₂O, the C/ZrC–SiC–Cu₃Si–Cu composite exhibits outstanding ablation resistance.

4 Conclusions

In this study, a novel C/ZrC–SiC–Cu₃Si–Cu composite with a density of 3.0 g·cm⁻³ and an open porosity of 3% was fabricated by infiltrating a Zr–Si–Cu melt into a carbon fiber-reinforced CA preform. A uniform, interpenetrating metal-ceramic matrix was obtained through ceramization of the CA matrix and *in situ* precipitation of Cu-containing phases. Due to the continuous evaporation of the uniformly dispersed Cu-containing phases during oxyacetylene ablation, the composite exhibits a pronounced transpiration-cooling effect, which maintains a surface temperature approximately 2300 °C under a heat flux of 3.18 MW·m⁻² for 1200 s, significantly lower than that of the C/ZrC–SiC reference material (2557–2600 °C). Concurrently, a protective solid skeleton infiltrated with glassy phases forms on the surface, effectively resisting mechanical denudation and hindering oxygen diffusion. The synergy of these mechanisms endows the composite with exceptional long-term ablation resistance, delivering ultralow mass and linear ablation rates of 0.0604 mg·cm⁻²·s⁻¹ and 0.1808 μm·s⁻¹, respectively. Relying on the sweat gland-like channel migration heat dissipation and evaporative cooling of the metallic phases, the composite achieves active cooling, while the ceramic skeleton provides passive protection; the interpenetrated biphasic structure endows the material with outstanding ablation resistance via active-passive synergistic cooling effect. To our knowledge, compared with the reported works under similar conditions, this is the first reported material under similar test conditions that demonstrates near-zero ablation after 1200 s of exposure to temperatures exceeding 2500 °C under such extreme thermo-oxidative conditions. Moreover, the composite displays outstanding mechanical properties, including a flexural strength of 194±7 MPa, a fracture

toughness of 11.8 ± 1.2 MPa·m^{1/2}, and a work of fracture of 5315 ± 1232 J·m⁻². These superior characteristics arise from four key mechanisms: the highly reactive CA matrix and protective PyC interface, preserving fiber integrity; optimized interfacial debonding energy for enhanced toughening; multifaceted crack deflection (e.g., metal bridging, crack blunting); and compressive residual stresses suppressing crack propagation. This work establishes a novel fabrication strategy for high-performance metal-ceramic matrix composites with excellent ablation resistance and mechanical robustness.

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Author contributions

Guoliang Jin: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing—original draft, Writing—review & editing, Funding acquisition. Bin Liang: Data curation, Formal analysis, Investigation, Methodology, Writing—review & editing. Rida Zhao: Data curation, Formal analysis, Investigation, Methodology, Writing—review & editing, Funding acquisition. Keyue Bao: Data curation, Formal analysis, Investigation, Methodology. Shengyang Pang: Data curation, Formal analysis, Investigation, Methodology. Chenglong Hu: Data curation, Formal analysis, Investigation, Methodology. Jian Li: Data curation, Formal analysis, Investigation, Methodology, Funding acquisition. Meng Yan: Data curation, Formal analysis, Investigation, Methodology. Sufang Tang: Conceptualization, Data curation, Formal analysis, Methodology, Writing—review & editing, Funding acquisition, Supervision, Project administration.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

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

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.26599/JAC.2026.9221334>.

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