

# Fabrication, Microstructural Characterization, and Ablation Behavior of a Novel 3D Orthogonal Woven C/C-SiC-ZrB<sub>2</sub> Composite Through I-CVI, SI, and LSI Combined Processes

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**Abstract:** This paper presents the novel fabrication method of a three-dimensional orthogonally woven (3DW) C/C-SiC-ZrB<sub>2</sub> composite and the effects of ZrB<sub>2</sub> and SiC particles on microstructure and the ablation behavior of the C/C-SiC-ZrB<sub>2</sub> composite are studied. C/C-SiC-ZrB<sub>2</sub> composite was prepared by isothermal-chemical vapor infiltration (I-CVI), slurry infiltration (SI), and liquid silicon infiltration (LSI) combined process. Pyrolytic carbon (PyC) was first infused into the 3DW preform by I-CVI at 1050°C using CH<sub>4</sub> as a precursor in order to form a C/C preform with porous media. The next step was graphitization at 2400°C for 1hr. Then ZrB<sub>2</sub> was introduced into 3DW C/C preform with a void percentage of 48 by impregnating the mixture of ZrB<sub>2</sub> and phenolic resin, followed by a pyrolysis step at 1050°C. A liquid Si alloy was infiltrated, at 1650 °C, into the 3DW C/C composites porous media containing the ZrB<sub>2</sub> particles to form a SiC-ZrB<sub>2</sub> matrix. An oxyacetylene torch flame was utilized to investigate The ablation behavior. ZrB<sub>2</sub> particles, along with the SiC matrix situated between carbon fiber bundles, form a compact ZrO<sub>2</sub>-SiO<sub>2</sub> layer. This layer acts as a barrier, restricting oxygen infiltration into the composite and reducing the erosion of carbon fibers. The findings were supported by FESEM imaging and further confirmed through x-ray diffraction and EDS analysis. The addition of ZrB<sub>2</sub> to the C/C-SiC composite resulted in a lower mass and linear ablation rate; 2.20 mg/s and 1.4 μm/s respectively while those for C/C-SiC composite were 4.8 mg/s and 6.75 μm/s after ablation under an oxyacetylene flame (2500°C) for 120 s.

**Keywords:** three-dimensional orthogonal woven preform; liquid silicon infiltration; ceramic-matrix composite; C/C–SiC–ZrB<sub>2</sub> composite; ablation resistance

**Introduction:** Continuous carbon fiber-reinforced (CFC) SiC–ZrB<sub>2</sub> matrix composites have attracted considerable attention for Ultrahigh-temperature application due to their superior characteristics, such as low density, low thermal expansion coefficient, high-temperature mechanical strength, excellent thermal shock resistance, high thermal conductivity and high modules [1–3]. CFC preform structures, which encompass both two-dimensional (2D) laminated forms and three-dimensional (3D) composites, can be produced using techniques like stitching, weaving, braiding, knitting, and needle punching. [4–6]. Three-dimensional orthogonal woven (3DW) preform possess a simple fabrication method and relatively good mechanical properties, but has a high production cost.

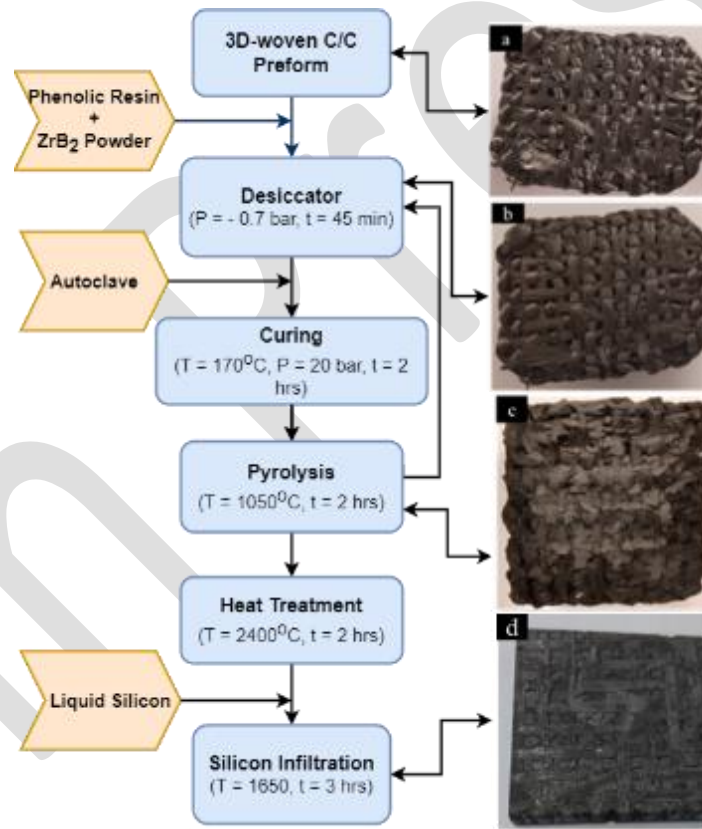
Several techniques have been explored to incorporate SiC–ZrB<sub>2</sub> ceramics into CFC composites, including chemical vapor infiltration (CVI) [7], polymer infiltration and pyrolysis (PIP) [8], liquid silicon infiltration (LSI) [9], and slurry infiltration (SI) [10]. Among these, the LSI method is known for being fast, straightforward, and cost-effective while achieving high densification, which has drawn significant attention from researchers [11–13]. Wang et al. [11] produced a Cf/C–SiC–ZrC composite using a combination of CVI and LSI with a Si–Zr alloy, and studied its ablation characteristics. The results showed no significant reduction in linear ablation rates when compared to C/C–ZrC composites. Kong et al. [14] created a Cf/SiC–ZrB<sub>2</sub> composite via the SI and LSI processes and evaluated its ablation performance, finding a notable decrease in both mass and linear ablation rates due to the formation of a protective ZrO<sub>2</sub> layer on the surface. ZrB<sub>2</sub> is recognized as a highly promising ultra-high temperature ceramic (UHTC), with properties such as low density (6.085 g/cm<sup>3</sup>), a high melting point (~3000°C), an elastic modulus of ~440–460 GPa, and a hardness of ~20–25 GPa [15]. Boride ceramics exhibit greater thermal conductivity compared to carbide ceramics, which is vital for effective heat dissipation in regions with concentrated heat [16]. While most studies focus on the mechanical properties of C/C composites [17–19], only a few have

addressed the ablation behavior of 3D needle-punched C/C-SiC composites [20–22]. Additionally, there remains a gap in research on the ablation behavior of C/C-SiC-ZrB<sub>2</sub> composites utilizing 3DW preforms. Therefore, in this work, a newly fabricated three-dimensional orthogonal woven carbon fiber preform was selected. The C/C-SiC-ZrB<sub>2</sub> composites were produced through a combination of I-CVI, SI, and LSI methods, making it one of the most recent and cost-effective approaches for manufacturing these composites. The porous C/C-ZrB<sub>2</sub> preforms were created via SI and then infiltrated with a Si alloy at 1650°C to form C/C-SiC-ZrB<sub>2</sub> composites. The SiC matrix was generated by the reaction between carbon and silicon during the LSI process, while the ZrB<sub>2</sub> matrix was introduced directly through slurry impregnation. The study also explored the microstructure and ablation performance of the C/C-SiC-ZrB<sub>2</sub> composites.

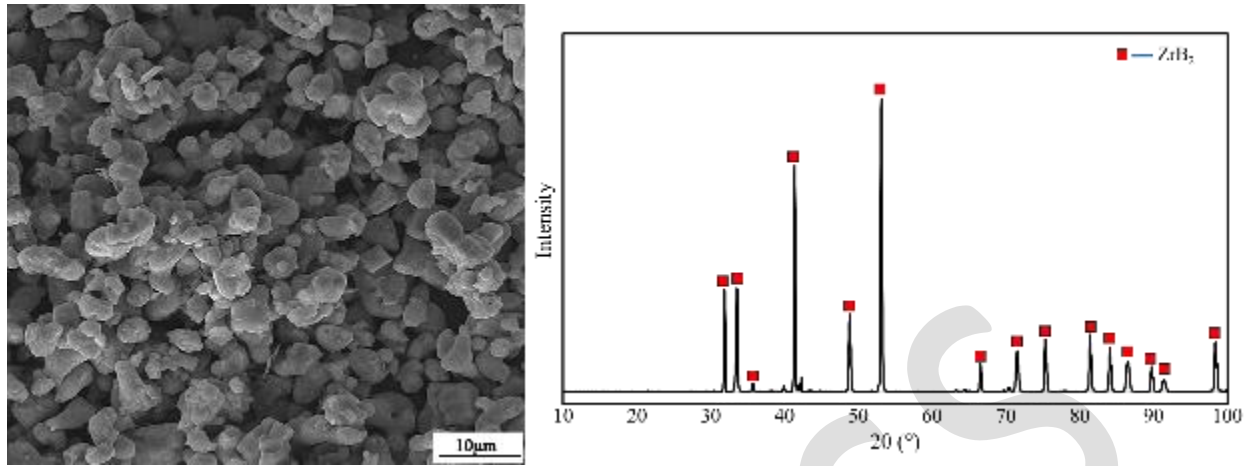
## Material and Methods

Fig 1 illustrates the process of fabricating C/C-SiC-ZrB<sub>2</sub> composites using a combination of I-CVI, SI, and LSI methods. In this study, a 3DW fabric made from T-300 (6K) carbon fiber, with a density of 0.48 g/cm<sup>3</sup>, was used as the preform. A carbon matrix was deposited into the 3DW preform via I-CVI at 1050°C using methane (CH<sub>4</sub>) as the precursor, creating a porous C/C structure. This was followed by a graphitization process at 2400°C with a heating rate of 5°C/min for one hour in a vacuum furnace with a 10<sup>-2</sup> vacuum level. The temperature was then decreased to 1000°C by a -5°C/min and then furnace cooled to room temperature. The preform's density reached 0.83 g/cm<sup>3</sup> with 48% open porosity. ZrB<sub>2</sub> powder with 99.99% purity and size distribution of 1-5 μm (Naiou Nano Technology Co., Ltd., Shanghai, China) made up 40 wt% of the mixed slurry. Ethanol solution was used to prepare a high-solid-content ZrB<sub>2</sub> mixture via planetary ball milling with ZrO<sub>2</sub> balls for six hours. THC-800 phenolic resin with 95.0% purity (Shaanxi Taihang Fire Retardant Polymer Co., Ltd., Xi'an, China) was also added and acted as the carbon source of the matrix and also the binder for the ZrB<sub>2</sub>. Fig 2 displays the morphology and XRD pattern of ZrB<sub>2</sub> particles. The slurry was then impregnated into the 3DW carbon fabric in a desiccator at a pressure of -0.7 bar for 45 minutes. Following this, the preform was treated in an autoclave under vacuum at 170°C for

two hours, followed by pyrolysis and thermal treatment at 1050°C and 2400°C for two hours each. By repeating the impregnation-pyrolysis cycle three times, a C/C-ZrB<sub>2</sub> composite with a density of 1.54 g/cm<sup>3</sup> was obtained. The 3DW preform was then placed in a graphite crucible along with Si powder and heated to 1650°C for three hours in a vacuum environment at a constant pressure of 10<sup>-2</sup> bar for the LSI process. Once the temperature surpassed the melting point of silicon (T<sub>m</sub> = 1415°C), the liquid silicon became more fluid, allowing it to penetrate the micro-cracks formed during carbonization. The molten Si infiltrated the preform through capillary action along the carbon fibers, where it reacted with the carbon to create the SiC matrix.



**Fig. 1.** Flow chart for the process of fabricating C/C-SiC-ZrB<sub>2</sub> composites by the combined process of I-CVI, SI and LSI, and Photographs of (a) 3DW, (b) 3DW + I-CVI, (c) 3DW + I-CVI + SI and (d) 3DW + I-CVI + SI + LSI preform.



**Fig. 2.** The morphology and X-ray diffraction pattern of ZrB<sub>2</sub> powder.

The phase composition of the C/C-SiC-ZrB<sub>2</sub> composite was determined using an X-ray diffractometer (XRD; GNR, Italy) with CuKα1 radiation at room temperature. The density and open porosity of the specimens were measured using Archimedes' method, with values averaged from five tests. The ablation characteristics of the samples were evaluated with an oxyacetylene torch. The pressure and flow rate for C<sub>2</sub>H<sub>2</sub> were set at 0.095 MPa and 0.31 L/s, while for O<sub>2</sub>, they were 0.4 MPa and 0.42 L/s. The specimens were exposed to the flame for 120 seconds. The nozzle tip had an internal diameter of 2.0 mm, and the distance between the samples and the nozzle was set at 10 mm. Using an optical pyrometer, the surface temperature at the center of the samples reached 2500°C.

The linear and mass ablation rates of the samples were calculated using Equations (1) and (2), respectively:

$$R_l = (d_0 - d_1) / t \quad (1)$$

$$R_m = (m_0 - m_1) / t \quad (2)$$

Where  $R_l$  is the linear ablation rate;  $d_0$  and  $d_1$  are the thickness values of samples in the center region before

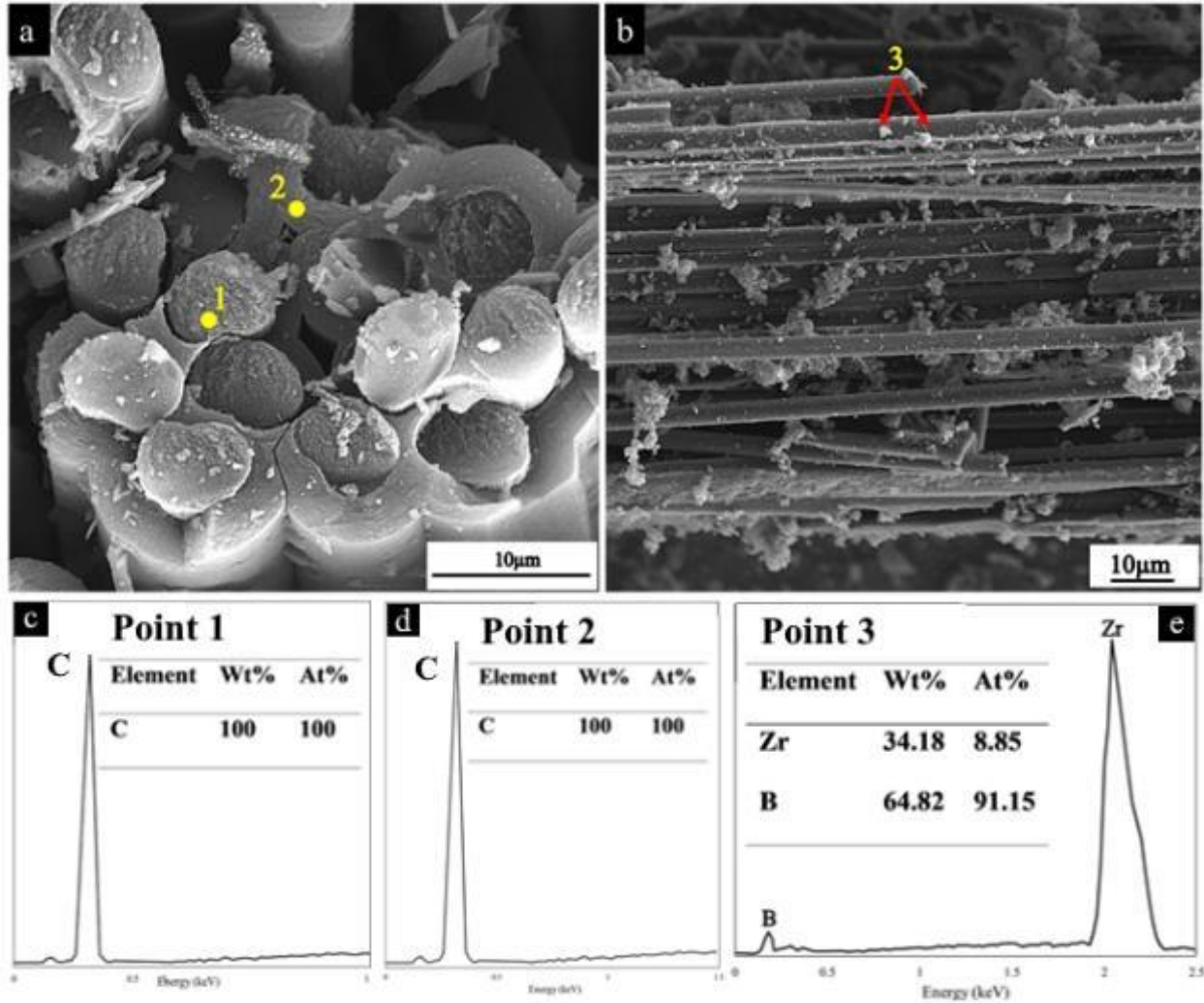
And after ablation, respectively;  $R_m$  is the mass ablation rate;  $m_0$  and  $m_1$  are the masses of the samples before and after ablation, respectively;  $t$  is the ablation time. The microstructure and elemental distribution

of the composites were examined using a field emission scanning electron microscope (FESEM) and an energy dispersive spectroscope (EDS) (MIRA3, TESCAN, Czech).

## Results and Discussion

**Microstructure of as-built C/C–ZrB<sub>2</sub>–SiC composite:** The density and porosity of the C/C, C/C–SiC, and C/C–SiC–ZrB<sub>2</sub> composites are displayed in Table 1. When compared with C–C (1.81 g/cm<sup>3</sup>), C–C–SiC (1.92 g/cm<sup>3</sup>), 2D C<sub>f</sub>/SiC–ZrB<sub>2</sub> (2.36 g/cm<sup>3</sup>) [20], 2D C<sub>f</sub>/SiC–ZrB<sub>2</sub> (2.1 g/cm<sup>3</sup>) [28], 2D C/SiC–ZrB<sub>2</sub>–ZrC (2.23 g/cm<sup>3</sup>) [18] and 2D C/SiC–ZrB<sub>2</sub>–TaC (2.35 g/cm<sup>3</sup>) [29] composites, the C/C–SiC–ZrB<sub>2</sub> (2.38 g/cm<sup>3</sup>) composite has a relatively higher density and lower porosity due to the high-solid content (ZrB<sub>2</sub> particles) of the added slurry and lower viscosity and flow resistance into the loose and porous 3DW preform. Additionally, the molten silicon reacts with the carbon fibers in the 3DW preform (point 1 in Fig 5c) at 1650°C, leading to the formation of SiC. This reaction enhances the density and reduces the porosity of the C/C–SiC–ZrB<sub>2</sub> composite by filling the pores within the porous 3DW C/C–ZrB<sub>2</sub> structure. The LSI process offers a cost-effective, rapid, and efficient technique for producing composites with high density and low porosity [20].

Fig 3 presents the microstructures and EDS analysis of porous C/C and C/C–ZrB<sub>2</sub> composites which are not yet introduced to the silicon infiltration. The gaps in the densely packed fiber bundle areas are filled with pyrolytic carbon layers, approximately 2.5 μm thick (Fig 3a). As shown in Fig. 3b, ZrB<sub>2</sub> powders are distributed almost uniformly, coating the carbon fibers. The porous 3DW C/C–ZrB<sub>2</sub> composite contains voids of varying sizes, providing infiltration paths for molten Si alloy during the LSI process. The even distribution and stability of ZrB<sub>2</sub> particles help form a nearly uniform microstructure after the LSI process, which enhances the ablation resistance of the C/C–SiC–ZrB<sub>2</sub> composite. EDS analysis was conducted on different areas of the cross-sections of the C/C and C/C–ZrB<sub>2</sub> composites, as shown in Fig. 3c, d, and e.

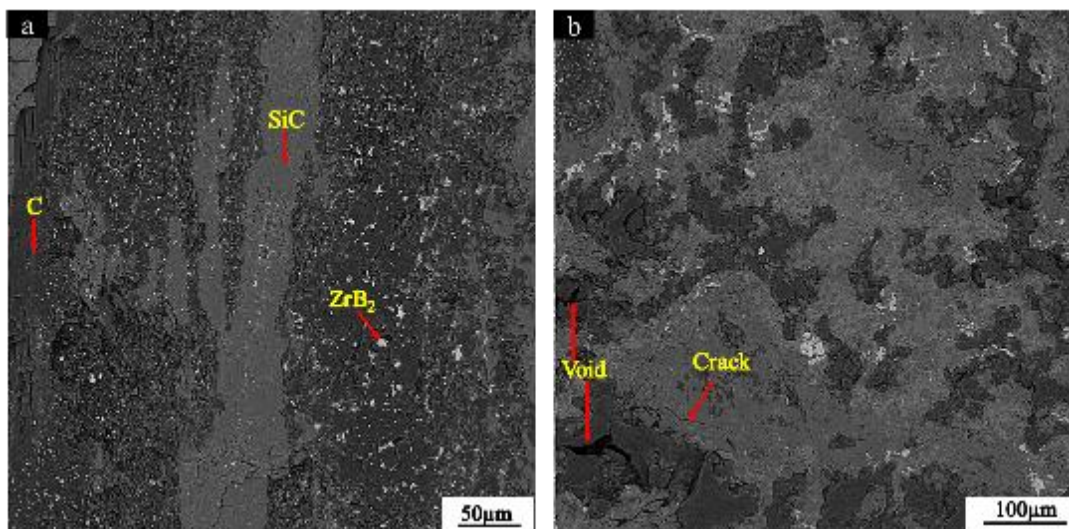


**Fig. 3.** (a and b) SEM images of the microstructure of C/C and C/C-ZrB<sub>2</sub> composites (before the LSI process) and (c, d and e) EDS analyses of the indicated points.

Fig. 4 shows the polished cross-sectional microstructures of the C/C-SiC-ZrB<sub>2</sub> composite following the I-CVI, SI, and LSI processes. The scattered voids within the fiber bundles are filled with carbon, SiC, and ZrB<sub>2</sub>. The voids between the pyrolytic carbon layers and ZrB<sub>2</sub> particles (as shown in Fig. 3b) are mostly occupied by the newly formed SiC ceramic. In Fig. 4a, the ZrB<sub>2</sub> particles exhibit a nearly uniform distribution across the matrix. Additionally, micro-cracks observed in the C/C-SiC-ZrB<sub>2</sub> composite likely result from the infiltration of the Si alloy into the channels of the 3DW preform. The SiC matrix formation, driven by the reaction between molten Si, pyrolytic carbon, and carbon fibers, is highly exothermic. The



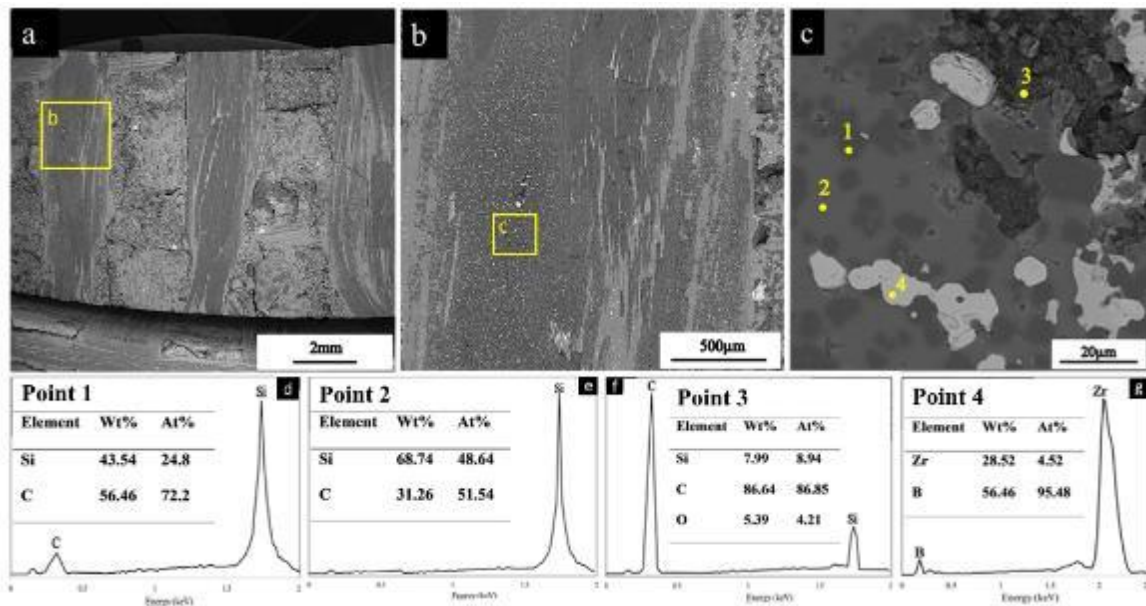
difference in thermal expansion coefficients between SiC ( $4 \times 10^{-6} \text{ K}^{-1}$ ) and carbon ( $2\text{--}4 \times 10^{-6} \text{ K}^{-1}$ ) is the primary cause of these micro-cracks, as seen in Fig. 4b [30, 31].



**Fig. 4.** cross-sectional microstructures of the C/C–SiC–ZrB<sub>2</sub> composite: (a) micro-cracks and (b) scatter voids.

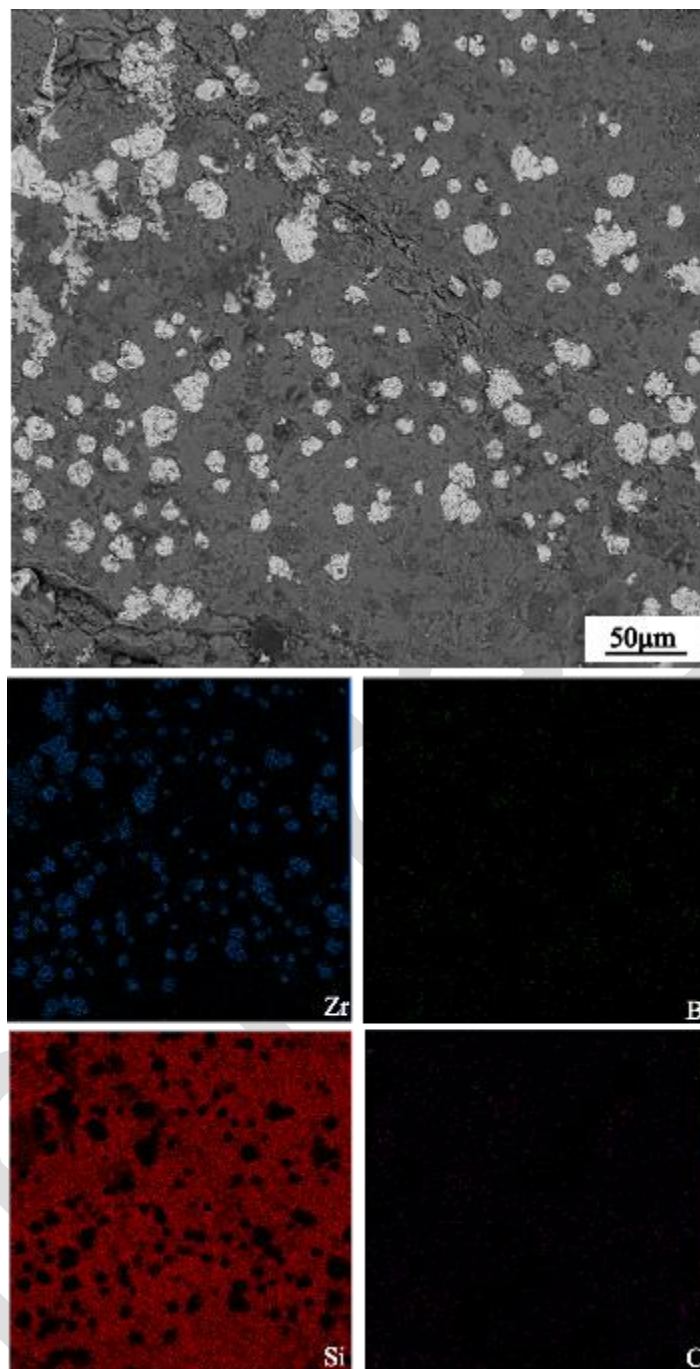
Fig. 5a, b, c, and d show the C/C–SiC–ZrB<sub>2</sub> composite's intricate microstructure. The four contrasted zones that fill the inter-bundles are as follows: dark gray, white, medium gray, and light gray, which represent C, ZrB<sub>2</sub>, SiC, and Si, respectively. With a few tiny voids, the resulting matrix is dense. The C/C–SiC–ZrB<sub>2</sub> composite was subjected to the EDS examination at various locations (Fig. 5e–h). At point 1, adjacent to the carbon source and fiber bundle, only SiC is present. Further from this point, silicon starts to appear in the matrix, with higher concentrations nearer the center of the matrix (as shown in Fig. 5f, point 2). Although the infiltrated silicon is expected to react fully with the carbon source and fibers, some residual silicon was found between the SiC matrices. Point 3 identifies the carbon source resulting from the phenolic resin pyrolysis. Point 4 highlights the presence of ZrB<sub>2</sub> particles located in the center of the C/C–SiC–ZrB<sub>2</sub> composite (Fig. 5e).





**Fig. 5.** (a-c) Back-scattered electron images of the cross sections of C/C-SiC-ZrB<sub>2</sub> composite, and (e-h) EDS analyses of different spots.

Fig. 6 displays an SEM image and EDS mapping of the C/C-SiC-ZrB<sub>2</sub> composite. It clearly comprises an interpenetrating microstructure consisting of four phases: C, Si, SiC, and ZrB<sub>2</sub>. Based on the EDS maps, the C/C-SiC-ZrB<sub>2</sub> composite surface contains Zr, B, Si, and C. From these data, combined with XRD findings (Fig. 7), it is concluded that the composite surface regions include four main phases: C, Si, SiC, and ZrB<sub>2</sub>. Additionally, the relatively uniform distribution of ZrB<sub>2</sub> particles in the microstructure is clearly evident from the SEM image. This uniform distribution of ZrB<sub>2</sub> particles creates a completely uniform protective ZrO<sub>2</sub> oxide layer on the C/C-SiC-ZrB<sub>2</sub> composite surface after the oxyacetylene test, which ultimately prevents the penetration of oxygen into underlying layers and the oxidation of the C/C-SiC-ZrB<sub>2</sub> composite.



**Fig. 6.** SEM image and EDS mapping of a representative area of C/C-SiC-ZrB<sub>2</sub> composite.

Fig. 7 displays the crystalline phases present in the C/C-SiC-ZrB<sub>2</sub> composite after fabrication. The primary phases identified in the composite are ZrB<sub>2</sub>, SiC, and carbon. XRD also reveals a minor presence of ZrSi<sub>2</sub>, which is probably the result of a reaction between remnant molten silicon and the ZrB<sub>2</sub>. While the LSI

process is an efficient, cost-effective method for producing high-density C/C-SiC-ZrB<sub>2</sub> composites, the presence of residual silicon reduces the composite's ablation resistance. Analysis from XRD and EDS (shown in Figs. 5 and 6) confirms that the majority of the infiltrated silicon has reacted with the carbon to form the SiC matrix.

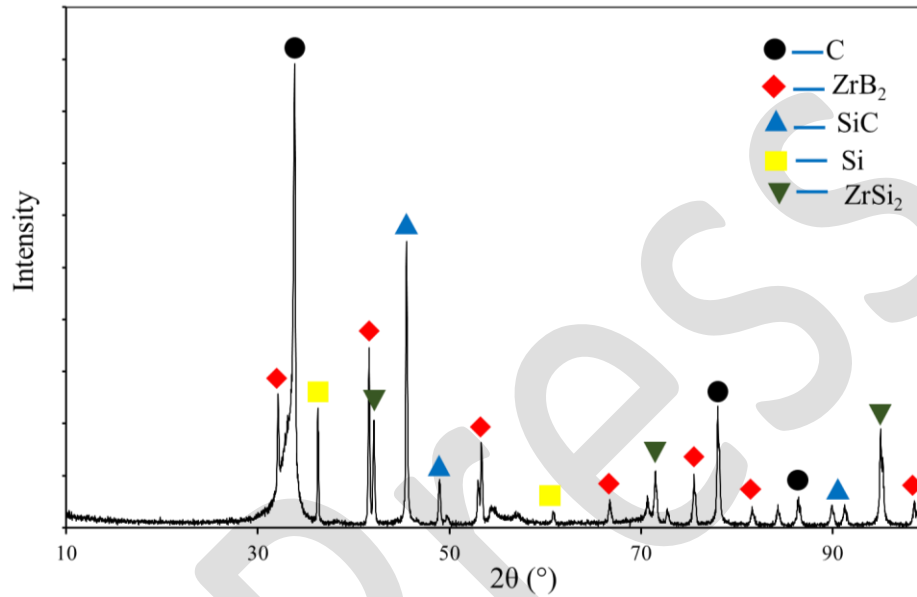
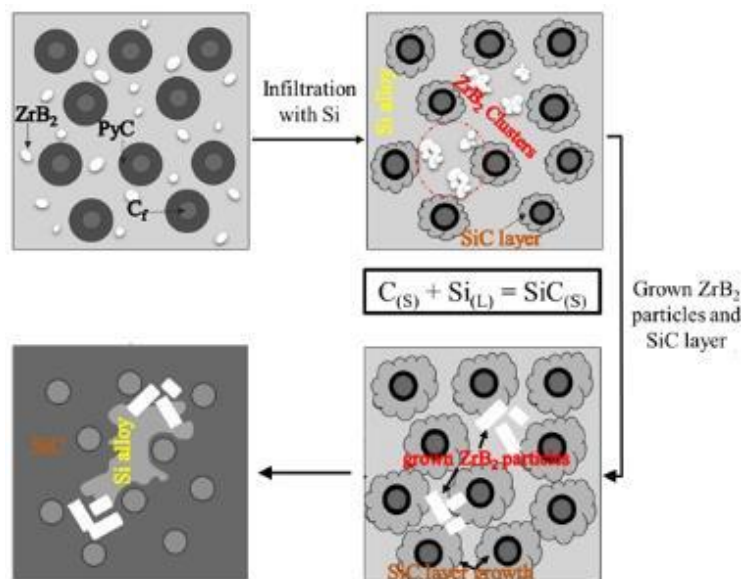


Fig. 7. X-ray diffraction patterns of different C/C-SiC-ZrB<sub>2</sub> composite.

**Formation mechanism of the C/C-SiC-ZrB<sub>2</sub> composite:** Fig. 8 illustrates the structural evolution of the C/C-SiC-ZrB<sub>2</sub> composite through the innovative combined process of I-CVI, SI, and LSI. Initially, when the molten silicon alloy is introduced into the porous C/C-ZrB<sub>2</sub> preform, carbon atoms dissolve and react with silicon to form a continuous and substantial SiC layer. Subsequently, ZrB<sub>2</sub> particles, which are not fixed by carbon resin, are rearranged due to the surface tension of the molten silicon, resulting in the formation of large, integrated clusters. Research has shown that the presence of the liquid alloy among ZrB<sub>2</sub> particles of varying sizes can enhance mass transfer and facilitate the migration of grain boundaries. Smaller particles dissolve within the ZrB<sub>2</sub> clusters, penetrate the melt, and crystallize onto larger particles, creating irregular spaces between the growing ZrB<sub>2</sub> particles. In summary, while the ZrB<sub>2</sub> particles' penetration does not significantly impact the C and Si reaction process, the melt promotes the growth of ZrB<sub>2</sub> particles, which can affect the uniformity of ZrB<sub>2</sub> distribution within the C/C-SiC-ZrB<sub>2</sub> composite.



**Fig. 8.** Depiction of the changes in microstructure and the formation process of C/C–SiC–ZrB<sub>2</sub> composites during the LSI process.

**Ablation resistance behavior of C/C–SiC–ZrB<sub>2</sub> composite:** Fig. 9 displays macroscopic photographs of the C/C–SiC–ZrB<sub>2</sub> composite before and after the ablation test at a temperature of 2500°C for 120 seconds. The LSI-processed sample, measuring 40 mm × 40 mm and shown in Fig. 9a, was subjected to an oxyacetylene torch test for 120 seconds. Post-ablation, the coating surface was categorized into three distinct areas: the outer edge ©, the transition zone near the center (B), and the central area (A) (Fig. 9b). The ablated surface of the C/C–SiC–ZrB<sub>2</sub> composites shows a white, loose layer. As illustrated in Fig. 9, this white layer becomes more prominent with extended ablation times, reaching up to 120 seconds. This layer likely consists of oxidation products from the composite’s primary components. The most intense ablation is observed at the flame’s center. Given that the oxyacetylene torch flame reaches temperatures of 2500°C, the ZrB<sub>2</sub>–SiC in the composite reacts with oxygen, forming ZrO<sub>2</sub> and SiO<sub>2</sub> phases rapidly on the surface.

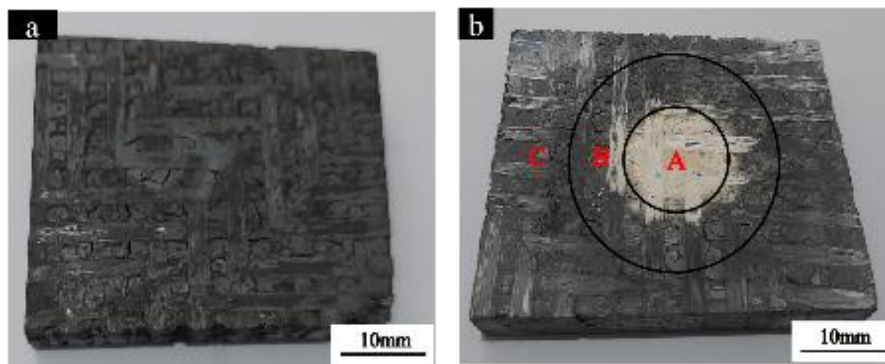
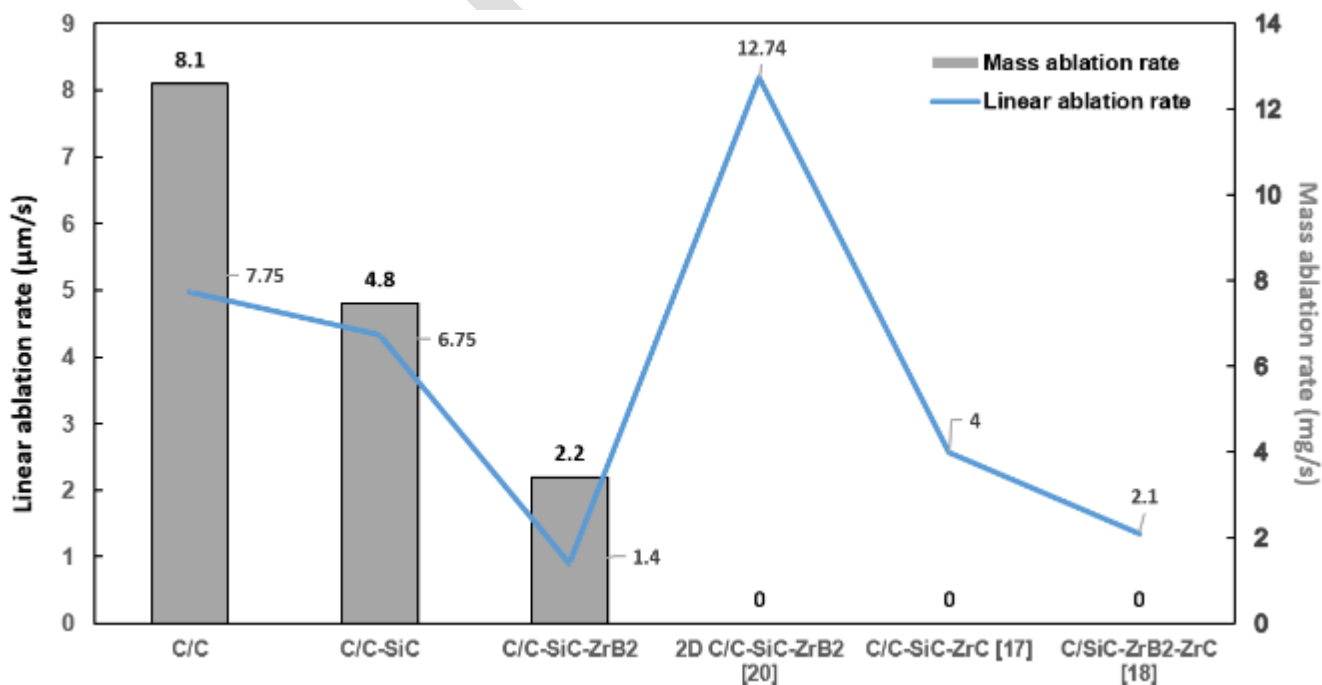


Fig. 9. Macroscopic images of the C/C-SiC-ZrB<sub>2</sub> composite (a) before and (b) after the oxyacetylene torch test.

To determine the linear and mass ablation rates, the dimensions and mass of the samples were measured before and after the ablation test. Fig. 10 (a and b) presents the linear and mass ablation rates for the C/C-SiC-ZrB<sub>2</sub> composite. For comparison, the ablation rates of C/C, C/C-SiC, and C/C-SiC-ZrB<sub>2</sub> are also displayed in Fig. 10 (a and b). Of these composites, C/C-SiC-ZrB<sub>2</sub> demonstrates the highest ablation resistance in oxyacetylene torch tests.



**Fig. 10.** Mass and linear ablation rates of variable composites.

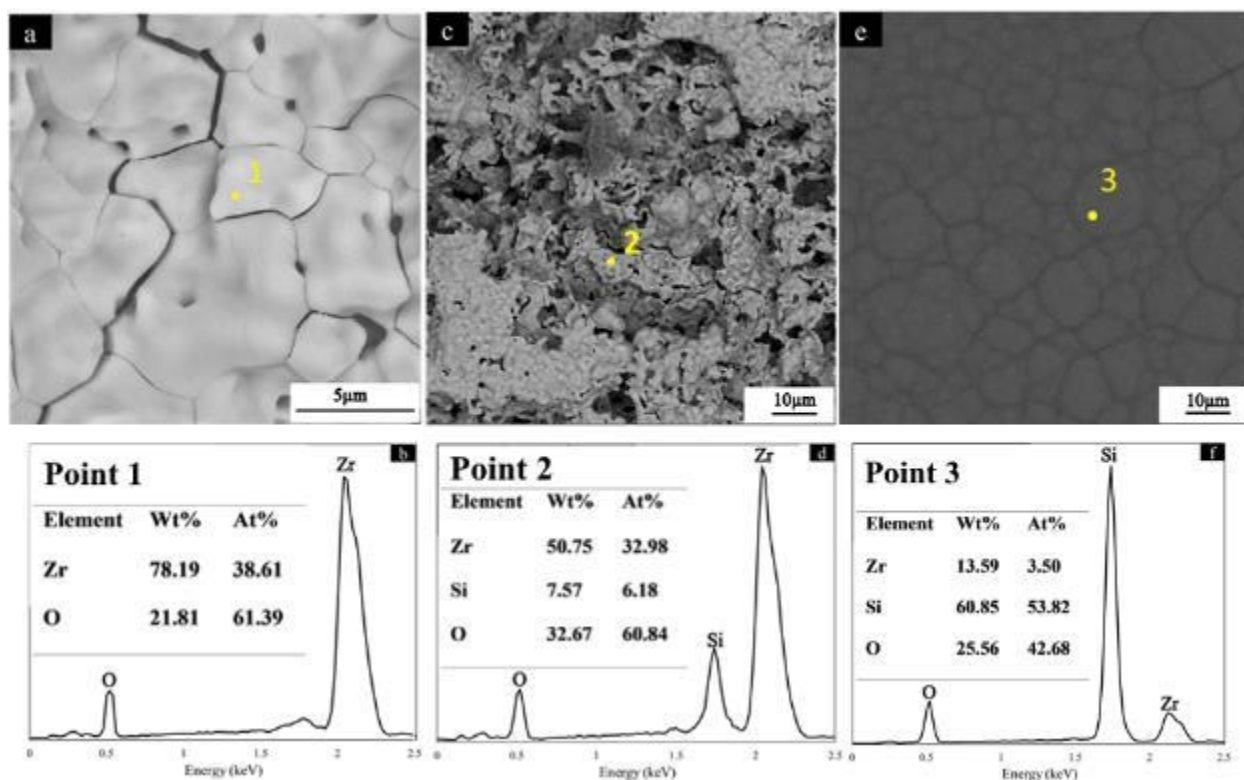
Fig. 10 provides a comparison of the linear and mass ablation rates for 2D C/C-SiC-ZrB<sub>2</sub> [20], 3D C/C-SiC-ZrC [17], 2D C/SiC-ZrB<sub>2</sub>-ZrC [18], and C/C-SiC-ZrB<sub>2</sub>. Among these materials, C/C-SiC-ZrB<sub>2</sub> exhibits the highest linear ablation resistance when exposed to oxyacetylene torch conditions.

According to Fig. 10, the linear and mass ablation rates of the C/C-SiC-ZrB<sub>2</sub> composite are 1.4  $\mu\text{m/s}$  and 2.2 mg/s at 120 seconds, respectively. This indicates that the weight of the C/C-SiC-ZrB<sub>2</sub> composite has decreased after the ablation due to the generation and evaporation of oxide products. This is due to the C/C-SiC-ZrB<sub>2</sub> composite withstanding high-temperature exposure for 120 seconds during the ablation test. Under these conditions, some oxide products such as CO, CO<sub>2</sub>, SiO, SiO<sub>2</sub>, and B<sub>2</sub>O<sub>3</sub> evaporate and exit from the surface. Among these composites, C/C-SiC-ZrB<sub>2</sub> exhibits the highest ablation resistance in the oxyacetylene torch environment, attributed to the high ZrB<sub>2</sub> particle loading achieved through slurry impregnation and as can be seen, the present C/C-SiC-ZrB<sub>2</sub> composite with a 3DW preform has a higher resistance to ablation compared to the composites investigated in [17], [18], and [20] due to the higher density of carbon fibers in all dimensions, increase in the amount of ZrB<sub>2</sub> particles trapped in the preform, and reducing the overall porosity. Additionally, the XRD pattern (Fig. 12), along with the microstructural and EDS analysis (Fig. 11a) of the ablated sample's surface, reveals that the white layer is composed of ZrO<sub>2</sub>. This ZrO<sub>2</sub> layer acts as a barrier, restricting further oxygen diffusion into the composite and thereby reducing additional ablation.

Fig. 11 (a–f) shows the BSE images and EDS analysis of the microstructures from the center, transition, and edge regions of the C/C-SiC-ZrB<sub>2</sub> composite after 120 seconds of ablation. At the center of the sample, where temperatures reach approximately 2500°C, the rapid oxidation of ZrB<sub>2</sub> and SiC forms a dense layer of ZrO<sub>2</sub> and SiO<sub>2</sub>. This oxidation causes a significant loss of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>, which contributes to an increased mass ablation rate and the formation of voids. The EDS analysis confirms that the white particles

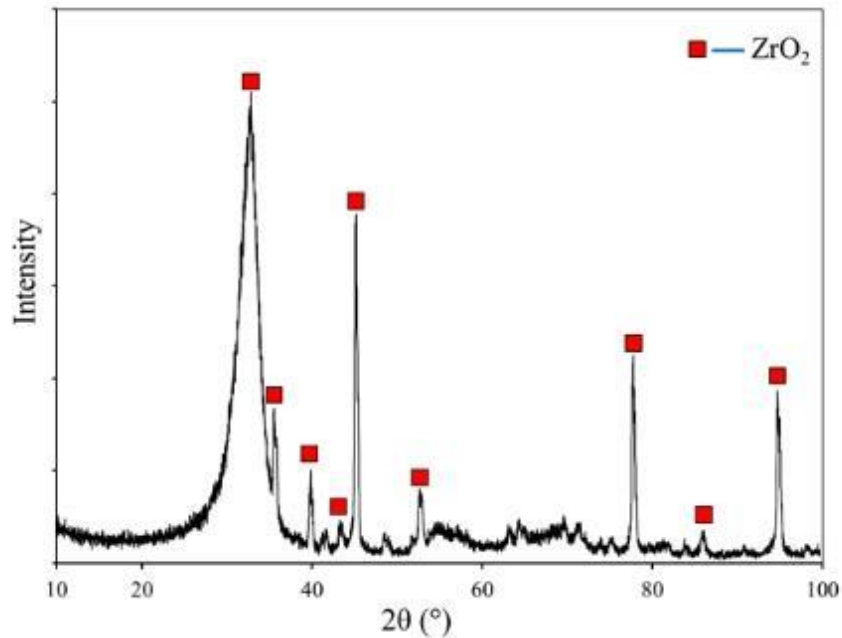
are  $\text{ZrO}_2$  (Fig. 11b). Fig. 11c illustrates the microtopography of the transition area (B), showing a surface covered with rough, porous white and gray glass phases. According to Fig. 11d, EDS analysis of area B reveals that the layer consists of a mixture of  $\text{SiO}_2$  and  $\text{ZrO}_2$ , which helps prevent further ablation. In the transition oxidation region, where temperatures are lower than at the center, only a small amount of  $\text{ZrO}_2$  forms, while most of the silicon oxides and evaporated  $\text{B}_2\text{O}_3$  create numerous voids. The edge oxidation region is covered by a gray coating (Fig. 11e). The EDS results (Fig. 11f) indicate that the ablation products are primarily Si–Zr–O phases, with silicon as the dominant element. Few  $\text{ZrB}_2$  particles are oxidized in this region due to the lower temperature compared to the transition zone. The matrix morphology in Figure 11e is representative of a chemical product, and the composition of the point 3 matches with  $\text{ZrSiO}_4$  which is brought in the references. Sun et al. [32] demonstrated that  $\text{ZrSiO}_4$  phase forms after the ablation test of a C/C–SiC– $\text{ZrB}_2$  composite produced by the same method used in the current study. The Zr–Si–O phase has a higher melting point than  $\text{SiO}_2$  and resists being blown away by gas flow, thus protecting the underlying fibers from oxidation.





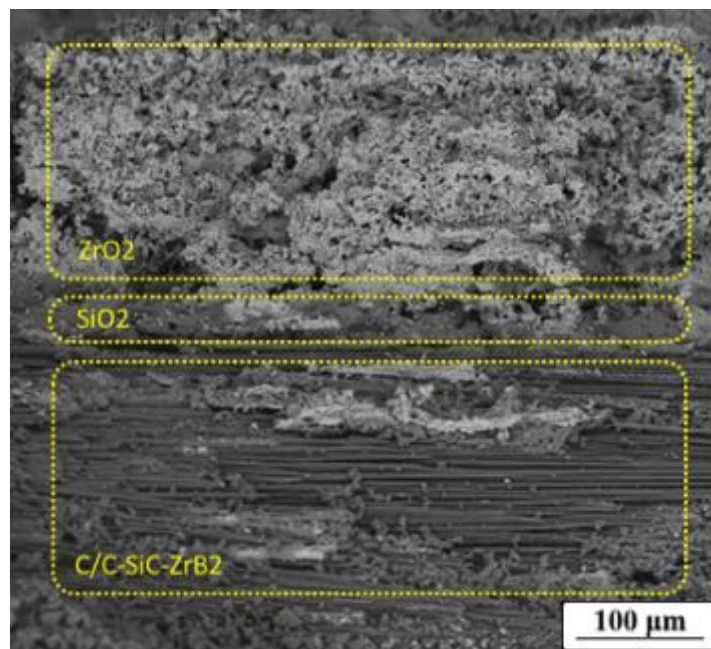
**Fig. 11.** Back-scattered electron images and EDS analyses of the C/C-SiC-ZrB<sub>2</sub> composite ablated surface in oxyacetylene flame: (a) center, (b) transition and (c) border regions.

Fig. 12 shows the crystalline phases present in the sample after the oxyacetylene torch test. The ablated surface of the C/C-SiC-ZrB<sub>2</sub> composites (Fig. 11a) features a white layer. The XRD pattern of this surface reveals that this white molten layer is composed solely of ZrO<sub>2</sub>, formed from the oxidation of ZrB<sub>2</sub> ceramics. ZrO<sub>2</sub> remains stable at temperatures up to 2500°C due to its high melting point (2715°C), despite other potential reaction products. In contrast, SiO<sub>2</sub> rapidly evaporates at temperatures approaching 2500°C and is carried away by the fast-moving oxyacetylene torch in the central ablation zone. Similarly, B<sub>2</sub>O<sub>3</sub>, which has a low melting point of 450°C and a high vapor pressure that leads to its quick vaporization above 1100°C, also evaporates swiftly. The instability of SiC and B<sub>2</sub>O<sub>3</sub> oxidation products at the flame tip explains the lack of SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> peaks in the XRD pattern [23].



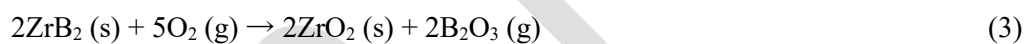
**Fig. 12.** X-ray diffraction pattern of C/C-SiC-ZrB<sub>2</sub> composites after being exposed to the oxyacetylene torch.

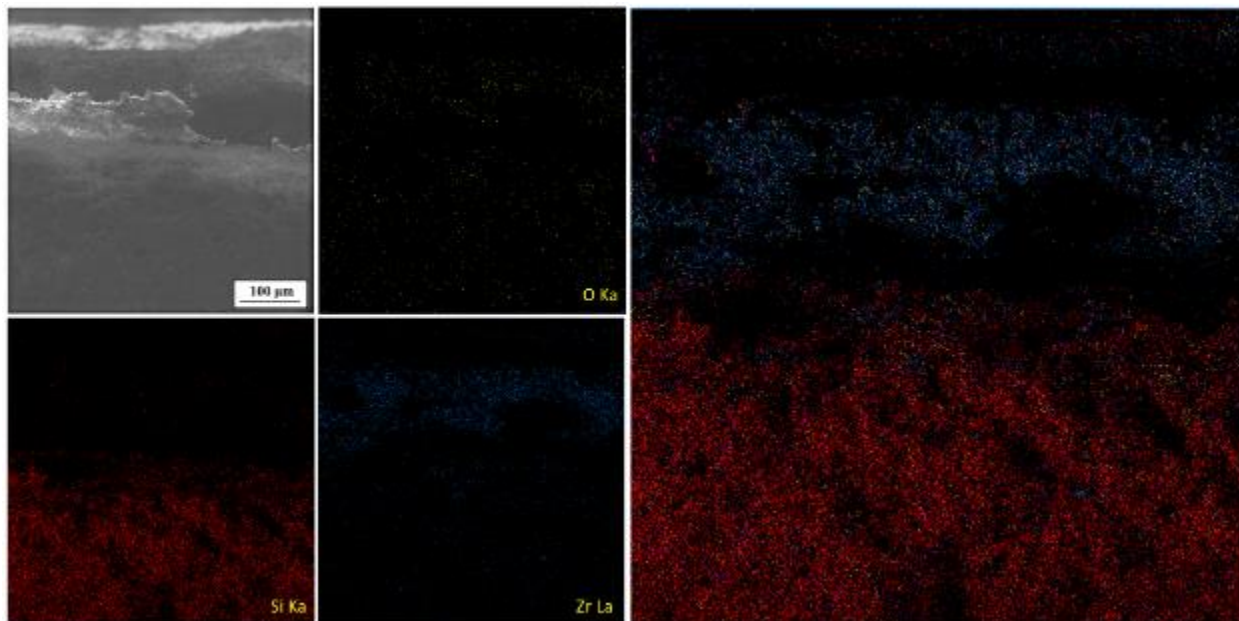
Fig. 13 presents the cross-sectional image of the C/C-SiC-ZrB<sub>2</sub> composite after undergoing the ablation test. The thickness of the surface oxide layer, primarily composed of ZrO<sub>2</sub>, as approved by the map scanning presented in Fig. 14, measures 330 μm. During the oxyacetylene flame test, the surface layer of the composite is damaged and subsequently transformed into a protective oxide phase of ZrO<sub>2</sub>. The oxide layer near the surface, consisting of ZrO<sub>2</sub>, and the subsequent SiO<sub>2</sub> layer have a combined thickness of 42 μm. The lower layers of the composite, being in contact with the surface layer and exposed to lower temperatures, undergo a transformation of the continuous SiC phase into a protective SiO<sub>2</sub> oxide layer. This SiO<sub>2</sub> layer serves to inhibit oxygen penetration into the deeper layers of the composite.



**Fig. 13.** Cross section of C/C-SiC-ZrB<sub>2</sub> composite after being exposed to the oxyacetylene torch.

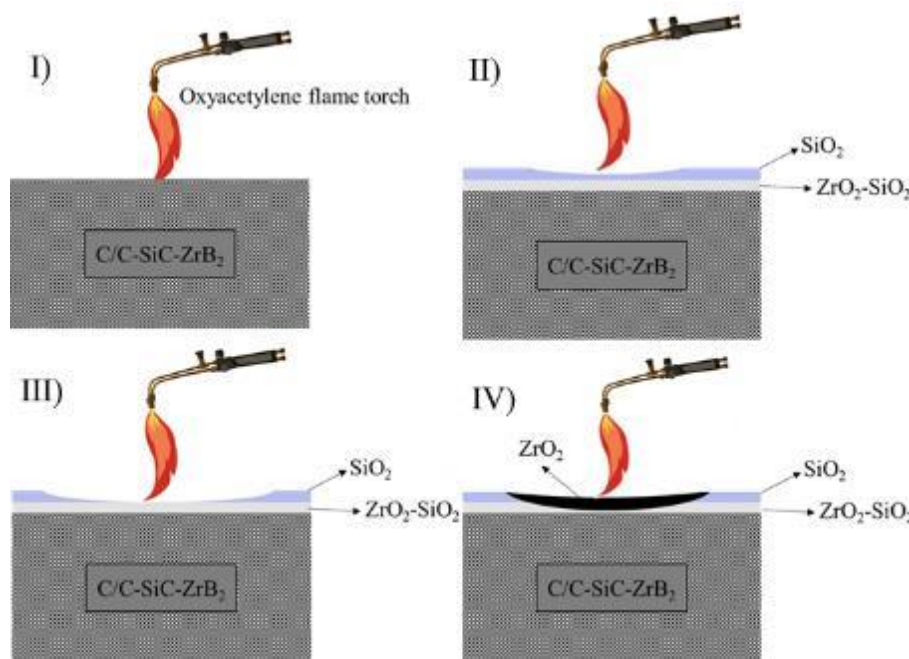
**Ablation mechanism:** The reactions below might occur in the central region during the oxyacetylene torch ablation test [24, 25]





**Fig. 14.** Elemental map of the cross section of C/C-SiC-ZrB<sub>2</sub> composite after the oxyacetylene torch test.

Fig. 15 illustrates the ablation process of the C/C-ZrB<sub>2</sub>-SiC composite. At the start of ablation, the surface temperature of the composite rises quickly, and oxidative gases interact with the carbon fibers, carbon matrix, SiC, and ZrB<sub>2</sub> (Eqs. (1)–(8)). The initial contact with the oxyacetylene torch flame leads to rapid oxidation of the carbon fibers (Eqs. 1 and 2). As the flame temperature increases, SiC and ZrB<sub>2</sub> react with oxygen, forming ZrO<sub>2</sub> and SiO<sub>2</sub> on the surface through reactions 3-5 at temperatures of 1100°C and 1500°C, respectively. These oxide phases help shield the carbon structure from further oxidation. Once the temperature exceeds 1415°C, Si and SiO<sub>2</sub> start to melt and evaporate due to the high-pressure combustion gases (Eqs. 6-8). Furthermore, ZrB<sub>2</sub> particles near the surface produce a ZrO<sub>2</sub> layer with a high melting point (2850°C), resulting in a thick, viscous ZrO<sub>2</sub>-SiO<sub>2</sub> layer. This robust ZrO<sub>2</sub> layer, formed and densified at high temperatures, effectively blocks additional oxygen from penetrating the composite and thus prevents further ablation. At temperatures around 2500°C, intense oxidation from reaction 4 may damage the SiC matrix [26, 27]. However, the dense ZrO<sub>2</sub> layer helps alleviate this oxidation, thereby preserving the SiC matrix.



**Fig. 15.** surface ablation phenomena of 3DW C/C-SiC-ZrB<sub>2</sub> composite.

**Conclusion:** The innovative 3D orthogonal woven C/C-SiC-ZrB<sub>2</sub> composite was produced using a combined technique of I-CVI, SI, and LSI, involving Si alloy infiltration and chemical reactions at 1650°C. The composite's mass and linear ablation rates were evaluated using an oxyacetylene torch test. Compared to the bare C/C and C/C-SiC composites, the C/C-SiC-ZrB<sub>2</sub> composite demonstrated superior ablation resistance. Specifically, the mass and linear ablation rates of the C/C-SiC-ZrB<sub>2</sub> composite were 1.4 μm/s and 2.2 mg/s, respectively, at 120 seconds. At high temperatures, residual Si in the composite melted to form a protective SiO<sub>2</sub> layer on the surface. However, the SiC matrix was susceptible to oxidation and evaporation from the high-speed torch flame, failing to fully shield the carbon fibers. The incorporation of ZrB<sub>2</sub> into the C/C-SiC composite, achieved through the LSI process, markedly reduced both the linear and mass ablation rates by creating a dense ZrO<sub>2</sub> layer with low open porosity. This high-temperature-sintered ZrO<sub>2</sub> layer effectively blocked further oxygen penetration into the composite and mitigated additional ablation. Adequate ZrB<sub>2</sub> content enhanced the composite's ablation and oxidation resistance by continuously generating ZrO<sub>2</sub> to safeguard the surface.

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#### References:

- [1] Su-fang, T., Jing-yi, D., Shi-jun, W., Wen-chuan, L., “*Comparison of thermal and ablation behaviors of C/SiC composites and C/ZrB<sub>2</sub>-SiC composites.*” *Corr. Sci.*, 2009, 51, 54–61

- [2] He-jun, L., Xi-yuan, Y., Yu-lei, Z., Ke-zhi, L., Ling-jun, G., Lei, L., “*Effect of heat flux on ablation behaviour and mechanism of C/C–ZrB<sub>2</sub>–SiC composite under oxyacetylene torch flame.*” *Corr. Sci.*, 2013, 74, 265–270.
- [3] Li-ping, R., Fei, R., Ke, P., Huan, Y., Mao-zhong, Y., “*Preparation and properties of C/C–ZrB<sub>2</sub>–SiC composites by high-solid-loading slurry impregnation and polymer infiltration and pyrolysis (PIP).*” *Trans. Nonferrous Met. Soc. China*, 2019, 29, 2141–2150.
- [4] Ping, T., Liyong, T., G.P., S., Takashi, I., “*Behavior of 3D orthogonal woven CFRP composites. Part I. Experimental investigation.*” *Compos. Part A*, 2000, 31, 259–271.
- [5] Xue, H., Zhang, L., Cheng, L., “*The effect of Z-yarn density on the in-plane shear property of three-dimensional stitched carbon fiber reinforced silicon carbide composites.*” *Comp. Sci. Technol.*, 2015, 106, 120–126.
- [6] Mei, H., Liang, C., Zhang, D., Chen, C., Cheng, L., “*Controlled deposition of density defects for understanding mechanical reduction on 2D C/SiC composites.*” *Comp. Part B*, 2019, 161, 241–251.
- [7] Tang, S.F., Deng, J.Y., Wang, S.J., Liu, W.C., “*Fabrication and characterization of an ultra-high temperature carbon fiber-reinforced ZrB<sub>2</sub>–SiC matrix composite.*” *J. Am. Ceram. Soc.*, 2007, 90, 3320–3322.
- [8] Li, Q.G., Dong, S.M., Wang, Z., He, P., Zhou, H.J., Yang, J.S., Wu, B., Hu, J.B., “*Fabrication and properties of 3D Cf/SiC–ZrC composites, using ZrC precursor and polycarbosilane.*” *J. Am. Ceram. Soc.*, 2012, 95, 1216–1219.
- [9] Tulbez, S., Esen, Z., Dericioglu, A.F., “*Effect of CNT impregnation on the mechanical and thermal properties of C/C–SiC composites.*” *Adv. Comp. Hybrid Mater.*, 2020, 3, 177–186.



- [10] Zhou, H.J., Ni, D.W., He, P., Yang, J.S., Hu, J.B., Dong, S.M., “Ablation behavior of C/C-ZrC and C/SiC-ZrC composites fabricated by a joint process of slurry impregnation and chemical vapor infiltration.” *Ceram. Int.*, 2018, 44, 4777–4782.
- [11] Yiguang, W., Xiaojuan, Z., Litong, Z., Laifei, C., “C/C–SiC–ZrC composites fabricated by reactive melt infiltration with Si<sub>0.87</sub>Zr<sub>0.13</sub> alloy.” *Ceram. Int.*, 2012, 38, 4337–4343.
- [12] Mei, H., Cheng, L., “Comparison of the mechanical hysteresis of carbon/ceramic-matrix composites with different fiber preforms.” *Carbon*, 2009, 47, 1034–1042.
- [13] Seyoung, K., In Sub, H., Young-Hoon, S., Do Kyung, K., “Mechanical properties of C–SiC composite materials fabricated by the Si–Cr alloy melt-infiltration method.” *J. Comp. Mater.*, 2015, 49, 3057–3066.
- [14] Jung Hoon, K., Seung Yong, L., Young Il, S., Do Kyung, K., “Synergistic reinforcement effects of ZrB<sub>2</sub> on the ultra-high temperature stability of Cf/SiC composite fabricated by liquid silicon infiltration.” *J. Eur. Ceram. Soc.*, 2023, 43, 3062–3069.
- [15] Mrumun David, T., Anejo, I., “Effects of surface modification (surface treatment) on friction and surface abrasion of ceramic composites.” *Adv. Ceram. Mater.*, 2023, 91–114.
- [16] Jin, X., Fan, X., Lu, C., Wang, T., “Advances in oxidation and ablation resistance of high and ultra high temperature ceramics modified or coated carbon/carbon composites.” *J. Eur. Ceram. Soc.*, 2018, 38, 1–28.
- [17] Wang, Y.G., Zhu, X.J., Zhang, L.T., “C/C–SiC–ZrC composites fabricated by reactive melt infiltration with Si<sub>0.87</sub>Zr<sub>0.13</sub> alloy.” *Ceram. Int.*, 2012, 38, 4337–4343.
- [18] Huilong, P., Shangwu, F., Yiguang, W., “C/SiC–ZrB<sub>2</sub>–ZrC composites fabricated by reactive melt infiltration with ZrSi<sub>2</sub> alloy.” *Ceram. Int.*, 2012, 38, 6541–6548.

- [19] Du, X.B., Li, D.S., Wei, Q.H., Jiang, L., “*High temperature bending properties and failure mechanism of 3D needled C/SiC composites up to 2000°C.*” J. Eur. Ceram. Soc., 2022, 42, 3036–3043.
- [20] Fan, X., Dang, X., Ma, Y., Yin, X., Zhang, L., Cheng, L., “*Microstructure, mechanical and ablation behaviour of C/SiC–Si with different preforms.*” Ceram. Int., 2019, 45, 23104–23110.
- [21] Li, W., Xiang, Y., Wang, S., Ma, Y., Chen, Z., “*Ablation behavior of three-dimensional braided C/SiC composites by oxyacetylene torch under different environments.*” Ceram. Int., 2013, 39, 463–468.
- [22] Lei, L., He-jun, L., Kui, H., Xiao-hong, S., Ke-zhi, L., Chang, N., “*Effect of SiC location on the ablation of C/C–SiC composites in two heat fluxes.*” J. Mater. Sci. Technol., 2015, 31, 345–354.
- [23] Yue, L., Qian-gang, F., Bei-bei, W., Tian-yu, L., Jia, S., “*The ablation behavior and mechanical property of C/C–SiC–ZrB<sub>2</sub> composites fabricated by reactive melt infiltration.*” Ceram. Int., 2017, 43, 6138–6147.
- [24] Han, J.C., Hu, P., Zhang, X.H., Meng, S.H., Han, W.B., “*Oxidation-resistant ZrB<sub>2</sub>–SiC composites at 2200°C.*” Comp. Sci. Technol., 2008, 68, 799–806.
- [25] Ping, H., Wang, G.L., Wang, Z., “*Oxidation mechanism and resistance of ZrB<sub>2</sub> – SiC composites.*” Corr. Sci., 2009, 51, 2724–2732.
- [26] Lee, S.J., Kim, D.K., “*Effect of TaB<sub>2</sub> addition on the oxidation behaviors of ZrB<sub>2</sub>–SiC based ultra-high temperature ceramics.*” Korean J. Mater. Res., 2010, 20, 217–222.
- [27] Balat-Pichelin, M., Charpentier, L., Panerai, F., Chazot, O., Helber, B., Nickel, K., “*Passive/active oxidation transition for CMC structural materials designed for the IXV vehicle re-entry phase.*” J. Eur. Ceram. Soc., 2015, 35, 487–502.
- [28] Wang, Y.G., Liu, W., Cheng, L.F., Zhang, L.T., “*Preparation and properties of 2D C/ZrB<sub>2</sub>–SiC ultra-high temperature ceramic composites.*” J. Appl. Ceram. Technol., 2009, 524, 129–133.

[29] Li, L.L., Wang, Y.G., Cheng, L.F., Zhang L.T., “*Preparation and properties of 2D C/SiC–ZrB<sub>2</sub>–TaC composites.*” *Ceram. Int.*, 2011, 34, 891–896.

[30] Baxter, R.I., Rawlings, R.D., Iwashita, N., Sawada, Y., “*Effect of chemical vapor infiltration on erosion and thermal properties of porous carbon/carbon composite thermal insulation.*” *Carbon*, 2000, 38, 441–449.

[31] Fahrenholtz, W.G., Hilmas, G.E., Talmy, I.G., Zaykoski, J.A., “*Refractory diborides of zirconium and hafnium.*” *J. Am. Ceram. Soc.*, 2007, 90, 1347–1364.

[32] Sun, Q., Zhang, H., Huang, C., Zhang, W., “*Fabrication of C/C–SiC–ZrB<sub>2</sub> ultra-high temperature composites through liquid–solid chemical reaction.*” *Crystals*, 2021, 11, 1352.

**Table 1.** Open porosity and density in the C/C, C/C–SiC and C/C–SiC–ZrB<sub>2</sub> composites.

Samples	Density (gr/cm <sup>3</sup> )	Open porosity (%)
C/C	1.71	22.7
C/C–SiC	1.92	10.5
C/C–SiC–ZrB <sub>2</sub>	2.38	9.3
2D C <sub>f</sub> /SiC–ZrB <sub>2</sub> [20]	2.36	10.7
2D C <sub>f</sub> /SiC–ZrB <sub>2</sub> [28]	2.10	-
2D C/SiC–ZrB <sub>2</sub> –ZrC [18]	2.23	10
2D C/SiC– ZrB <sub>2</sub> –TaC [29]	2.35	11.5