ARL-TR-10118 ● JUNE 2025

Investigation of Fiber-Reinforced Ultra-High Temperature Ceramic Matrix Composites

by Anindya Ghoshal, Nesredin Kedir, Christina Hoffman, Robert Slapikas, and Michael Ammendola

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REPORT DOCUMENTATION PAGE

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED	
		START DATE	END DATE
June 2025	Technical Report	1 October 2021	30 November 2024

4. TITLE AND SUBTITLE
Investigation of Fiber-Reinforced Ultra-High Temperature Ceramic Matrix Composites

5a. CONTRACT NUMBER	5b. GRANT NUMBER	5c. PROGRAM ELEMENT NUMBER
5d. PROJECT NUMBER A2110-097-057-016094	**5e. TASK NUMBER**	**5f. WORK UNIT NUMBER**

6. AUTHOR(S)
Anindya Ghoshal, Nesredin Kedir, Christina Hoffman, Robert Slapikas, and Michael Ammendola

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
DEVCOM Army Research Laboratory ATTN: FCDD-RLA-VA Aberdeen Proving Ground, MD 21005	ARL-TR-10118

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
Office of the Under Secretary of Defense		

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
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14. ABSTRACT
Ultra-high temperature ceramic matrix composites (UHTCMCs) have been a recent topic of interest as candidate materials for aerospace applications. The ultra-high temperature ceramic matrix can provide appreciable thermochemical protection at temperatures beyond 2000 °C, while the ceramic matrix composite architecture enables graceful mechanical failure through enhanced toughening mechanisms. Development of UHTCMCs is ongoing, with current research focused on addressing the manufacturing challenges of densifying weave reinforcement architectures without undesirable fiber-matrix reactions. This work investigates UHTCMC samples fabricated by particulate slurry infiltration (SI) and chemical vapor infiltration (CVI). 2D and 3D C_f/ZrB_2-SiC samples are fabricated by SI while 3D C_f/HfC-SiC samples are synthesized of CVI. SI samples did not see matrix infiltration through the thickness of the sample, and the slurry instead densified as a coating on the surface of the carbon fiber preform. Slurry-coated surfaces still demonstrated good ablation resistance under an oxyacetylene torch environment up to 2000 °C. By comparison, CVI samples experienced matrix inflation through the thickness of the preform, but they failed under ablation testing at 1300 °C because the matrix-to-fiber ratio was low.

15. SUBJECT TERMS
Mechanical Sciences, Sciences of Extreme Materials, ultra-high temperature ceramics, ceramic matrix composites, slurry infiltration, chemical vapor infiltration, carbon fiber, oxidation, ablation testing

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
a. REPORT	b. ABSTRACT	C. THIS PAGE		
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UU	20

19a. NAME OF RESPONSIBLE PERSON	19b. PHONE NUMBER *(Include area code)*
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STANDARD FORM 298 (REV. 5/2020)
Prescribed by ANSI Std. Z39.18

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1. Introduction

Ultra-high temperature ceramic matrix composites (UHTCMCs) comprised an important area of materials research and development in the last decade. The attraction of this class of materials stems from combining the desired mechanical, thermal, and oxidation properties of ultra-high temperature ceramics (UHTCs) with the superior damage and failure tolerance that can be achieved by ceramic matrix composite (CMC) architectures.[1–3] As it is, monolithic ceramics see limited implementation in industrial and commercial applications because they are susceptible to brittle failure, whereas the reinforcement phase in CMCs can enable greater deflections and enhanced toughening mechanisms (crack bowing, crack deflection, material pullout, etc.).[4,5]

UHTC materials have been thoroughly investigated for applications in thermal protection systems. These materials are defined as the carbides, borides, and nitrides of Group IV and V transition metals—typically zirconium, hafnium, titanium, niobium, and tantalum. The strong covalent and ionic bonding in these ceramics facilitates high thermal conductivities, good chemical stability (i.e., oxidation resistance), and ultra-high melting temperatures (typically near or above 3000 °C).[6–8] The Zr- and Hf- systems are especially interesting, as their respective oxides (ZrO_2 and HfO_2) also exhibit very high melting temperatures (greater than 2500 °C).[9] These properties demonstrate that UHTCs are exceptional candidates for the matrix phase in composite material, which has encouraged the recent research and development efforts for UHTCMCs.

CMC reinforcement phases have been engineered in various forms. These architectures can include particulates, whiskers, nanotubes, short fibers, and continuous fibers. Many recent studies focused on continuous fiber reinforcements,[10–17] as the multidimensional (2D and 3D) fiber network tends to provide superior strain tolerance over the discontinuous reinforcements. Carbon fiber weaves have seen the most exploration in literature, given their high temperature stability, high flexibility, and low relative cost.

A host of manufacturing processes have been applied toward the synthesis of continuous fiber-reinforced UHTCMCs. These processes include slurry infiltration (SI), precursor infiltration and pyrolysis, reactive melt infiltration, chemical vapor infiltration (CVI), pressure-assisted sintering (PAS), and pressureless sintering (PLS). Each of these processes come with unique advantages and drawbacks. For example, CVI can uniformly infiltrate continuous fiber weaves, but large-scale depositions are extremely costly and time-consuming, and certain chemistries are not easily accessed by the technique. By contrast, SI is a quicker and more cost-

effective approach, although the technique struggles to fully infiltrate densely packed fiber bundles, especially in the case of complex weave architectures.[18] As such, the most successful UHTCMC processing is often achieved through some hybridization of the various techniques.

Despite the wide array of manufacturing methodologies that have been approached, significant challenges remain in the manufacturing of continuous fiber-reinforced UHTCMCs. The underlying issue is the difficulty in achieving a dense UHTC matrix phase that fully penetrates around individual fibers, while mitigating fiber degradation and reaction during processing. A dense matrix phase promotes the desired thermal properties and oxidation resistance of the UHTC material, but fiber damage must be avoided to retain the flexibility of the reinforcement phase. This issue has proven to be especially detrimental for PAS, as the high-temperature, high-pressure environment of these processes often results in reactions between the matrix and fiber phases.[19,20] Strong interactions generate strong interfaces, which can critically undermine toughening mechanisms like fiber pullout under high stress and strain conditions. In this manner, the fiber–matrix interface becomes a dominating microstructural feature in determining the mechanical failure performance of the composite.

2. Methods

2.1 Fabrication of C_f/ZrB_2–SiC Composites by SI

UHTCMC samples were processed by the SI method using the U.S. Army Combat Capabilities Development Command Army Research Laboratory facilities. Ceramic powders of ZrB_2 (abcr GmbH) and SiC (US Research Nanomaterials, Inc.) were infiltrated into 2D and 3D T300 carbon fiber weaves (Composite Envisions) using a variety of different aqueous and ethanolic mixtures as the liquid transport medium. Post-synthesis observations suggested that the slurry-based technique with solid ceramic particles struggled to achieve infiltration through the thickness of the fiber preforms. The solid ceramic powders tend to aggregate and clog at the surface of the carbon fiber where the slurry is first applied, curing as more of a surface coating than an infiltrated matrix.

For slurry development, various mixtures of deionized water, ethyl alcohol, and various dispersants and binders were explored. Aqueous slurries with polyethyleneimine as dispersant showed good particle suspension but intermediate viscosity with a 45 vol% solid loading. Ethanol-based slurries showed similarly good particle suspensions when combined with peracetic acid as binder and polymeric phosphoric acid ester (BYK110) as dispersant. This ethanolic slurry also

showed lower viscosity with a 35 vol% solid loading, making it preferable for infiltration trials.

The SI process was executed as follows. First, fiber sheets were placed into a slurry bath in a vacuum environment. Vacuum was pulled in the chamber to motivate particle deposition from the slurry in between fiber tows. After impregnation, samples were removed from the vacuum chamber and allowed to dry in air. The infiltrated sheets were then stacked in a hand-layup fashion with the desired number of layers. For the 2D fiber preforms, stacks of two layers and four layers were made. Layups were then sealed in vacuum bags and introduced into an autoclave environment, where they undergo curing at a temperature of 177 °C and a pressure of 1379 kPa. Following the autoclave exposure, the cured samples underwent a sintering step for final densification of the ceramic matrix. The PLS was carried out in a graphite furnace environment at 2100 °C for 1 h. Figure 1 illustrates this process workflow.

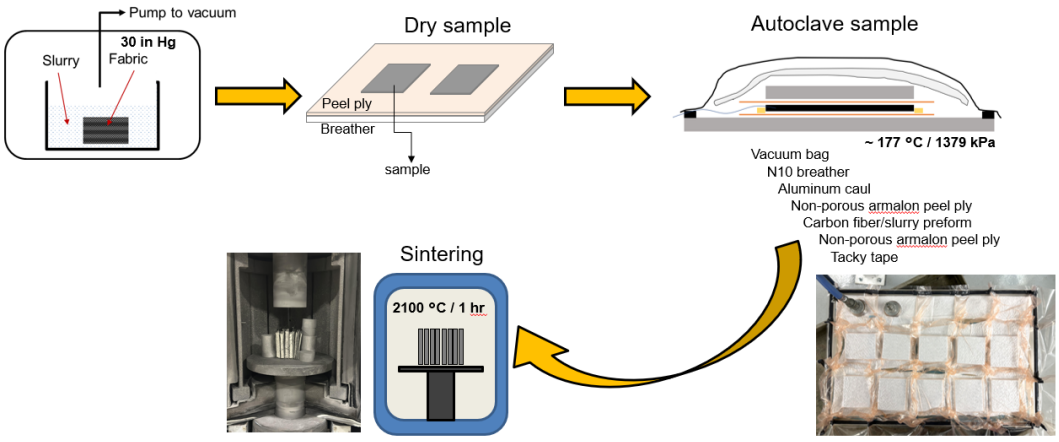

Figure 1. Slurry infiltration process map carried out for the fabrication of UHTCMC materials at DEVCOM Army Research Laboratory. 2D and 3D carbon fiber preforms were infiltrated with ethanolic slurries containing ZrB_2 and SiC powders followed by curing and sintering of the final composite samples.

Observations of the post-sintered samples showed varying degrees of success (Figures 2–3). It was clear that many samples experienced nonuniform coverage of the ceramic phase on preform surfaces, and in the worst cases, large cracking was observed in the ceramic matrix. Some samples showed good adhesion of the ceramic phase to the carbon fiber preform, although the results were inconsistent between samples.

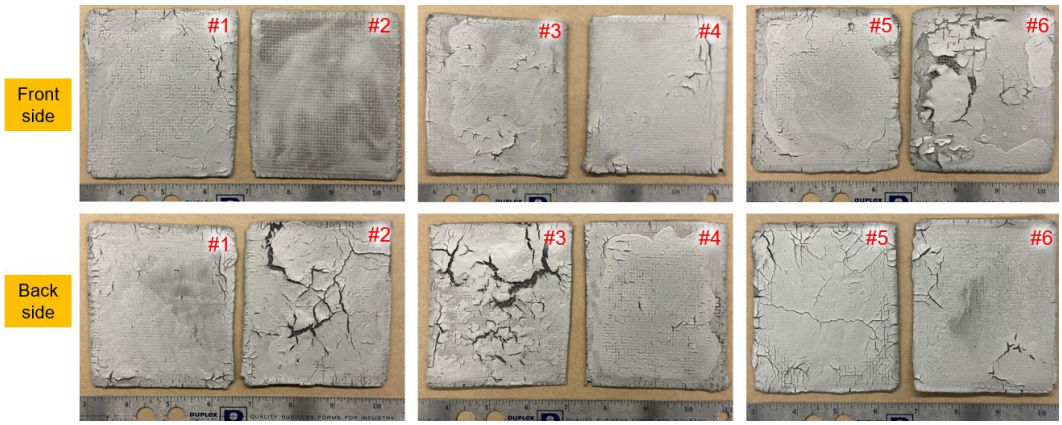

Figure 2. 2D C_f/ZrB_2–SiC composite samples fabrication at ARL by SI and PLS.

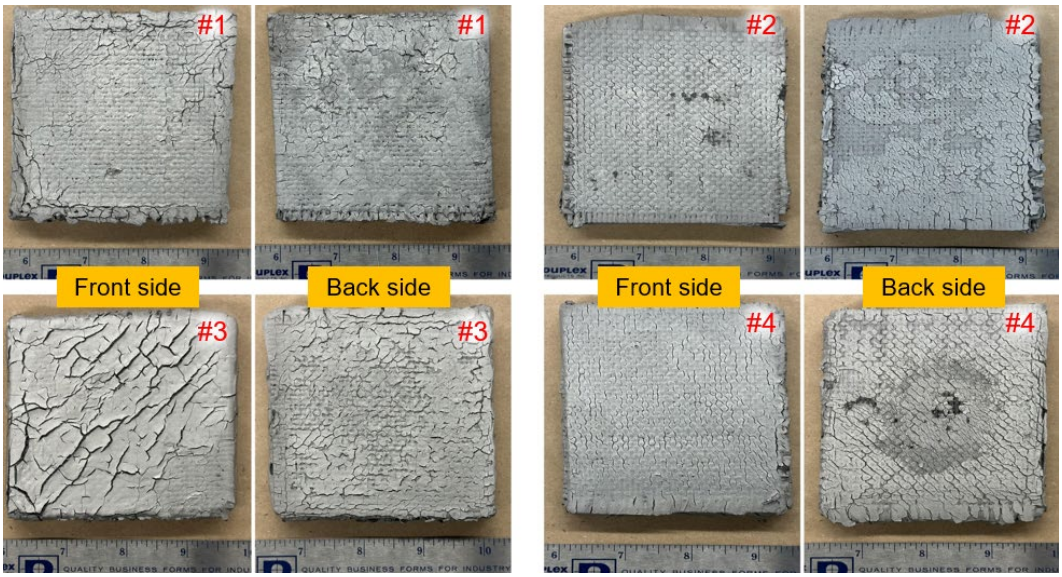

Figure 3. 3D C_f/ZrB_2–SiC composite samples fabrication at ARL by SI and PLS.

Future work in this space should be devoted toward improving the robustness and efficacy of the process. Individual steps should be streamlined and refined to avoid inconsistencies between samples. Slurries can be more quantitatively characterized by particle size distribution measurements to correlate to the effectiveness of matrix phase infiltration into the carbon fiber preform. Additional attention should be paid to the heating profile during sintering to identify the cause of macro-cracks on composite surfaces.

2.2 Fabrication of C_f/HfC–SiC Composites by CVI

Another fabrication method investigated for UHTCMCs was CVI. CVI trials were carried out by Technology Assessment and Transfer under SINTX Technologies. 3D carbon fiber panels (Bally Ribbon Mills) were first coated with a pyrolytic carbon (PyC) interphase, which served to protect the underlying fiber preform from degradation during subsequent deposition steps. Following this, layers of SiC and HfC were introduced to form the ceramic matrix of the composite material.

The presence of the HfC chemistry and crystallinity was confirmed via X-ray diffraction (XRD) in Figure 4. Scanning electron microscopy (SEM) was used to characterize the microstructure of the composite surface after infiltration. A highly textured fine-grained microstructure is observed in the SEM micrographs, which is to be expected from the CVI deposition process, although defects were also apparent in the HfC microstructure. Cracking, pores, and pinholes were observed (Figure 5). While microcracking can be beneficial to maintain structural flexibility of the underlying preform, these defect features enable pathways of oxygen ingress in an oxidizing environment, suggesting that the microstructure is nonideal for such conditions. Furthermore, there is a tangible nonuniformity in the microstructure, where the two surfaces of the same composite panel have differences. On one surface, the microstructure is largely coherent despite the presence of cracking; by contrast, the opposite surface is dominated by pinholes and pores throughout the HfC matrix, undermining the intended protection to be provided by the ceramic phase.

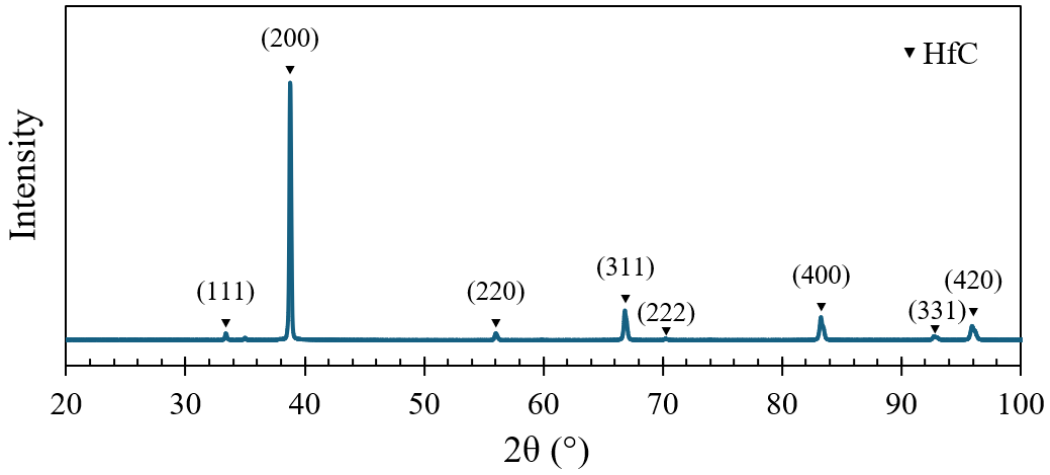

Figure 4. XRD pattern with labeled diffraction peaks shown for 3D C_f/HfC–SiC composite samples fabricated by CVI.

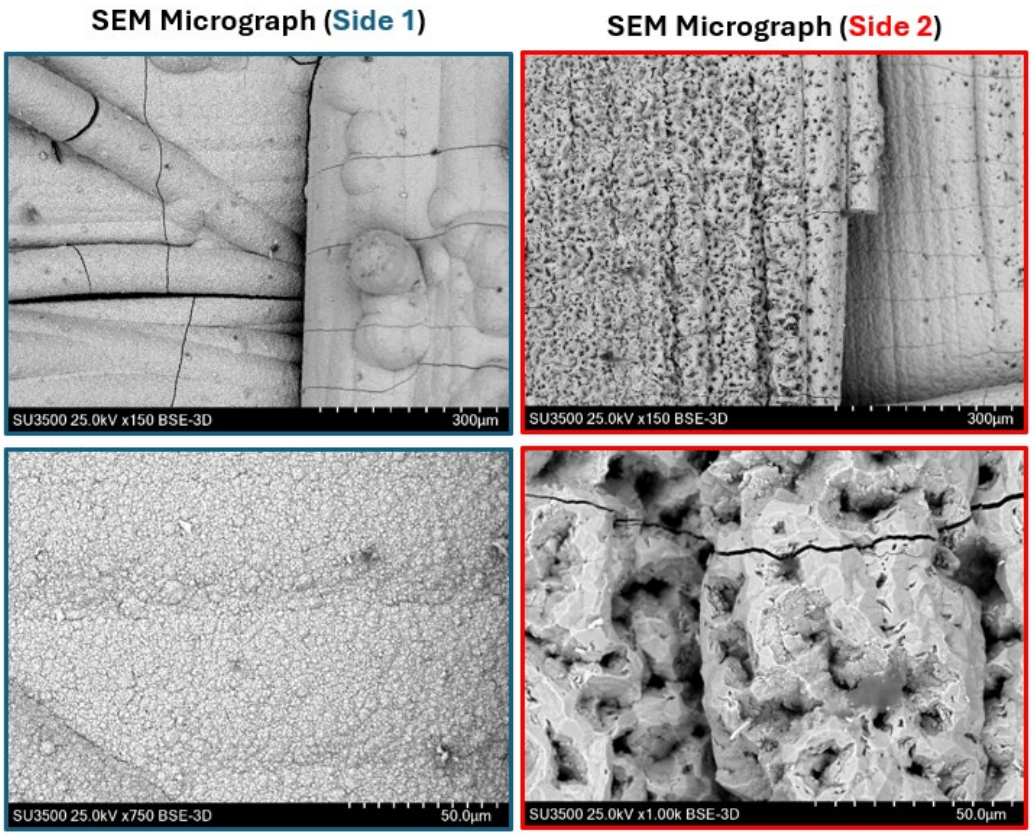

Figure 5. Surface SEM micrographs of a 3D C_f/HfC–SiC composite fabricated by CVI. The nonuniformity of the coating deposition is demonstrated by microstructural differences between the two sides of the sample.

Further efforts should be made to improve the uniformity of the CVI deposition quality. A coherent and consistent ceramic matrix is necessary to ensure proper protection of the underlying carbon preform. Additionally, given that the CVI process cannot efficiently fill void space in fiber preforms, this technique should be hybridized with a refined slurry approach as introduced in Section 2.1. A CVI process can be performed initially to coat between individual carbon fiber tows, followed by refined SI and sintering steps to densify the larger void space. This combined processing approach can enable greater UHTC matrix infiltration, and tailoring of the individual processing steps will ensure greater control over the matrix phase content in the fiber preform. In this manner, greater control over material properties like flexibility and ablation resistance will be enabled.

2.3 Testing and Evaluation

High-temperature oxidation testing was performed for slurry- and vapor-infiltrated UHTCMC samples using ARL's Sand-Modified Ablation Rig Test (SMART) setup (Figure 6). The SMART setup exposes samples to an oxyacetylene torch

environment, where the flow ratios of oxygen to acetylene can be modified to achieve oxidizing, carburizing, or neutral test environments. In these environments, samples can be exposed to heat fluxes greater than 1000 W/cm^2 and temperatures more than 3000 °C. Heat flux measurements were performed using a water-cooled sensor from Vatell Corporation. Temperature measurements are taken during ablation testing using single and dual wavelength pyrometers. Figure 7 shows select SI and CVI samples positioned in the rig, with images of the samples before, during, and after exposure to the oxyacetylene flame.

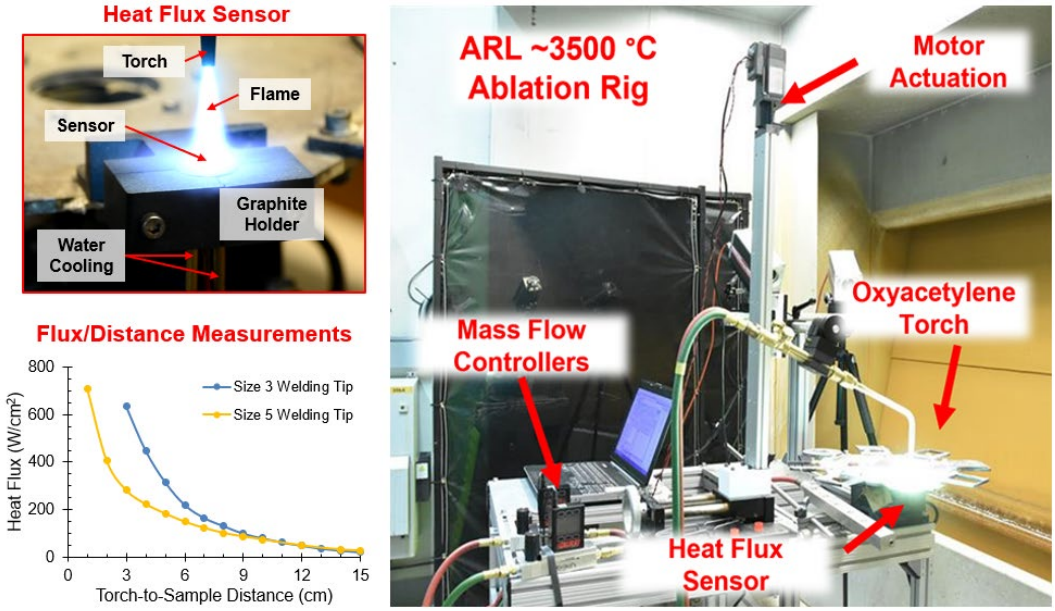

Figure 6. SMART setup at ARL's high-temperature testing laboratory. The right image shows an overview of the testing rig. On the left, an enhanced image of the water-cooled heat flux sensor is shown, along with recorded measurements of heat flux with respect to distance in a 20% excess oxygen environment.

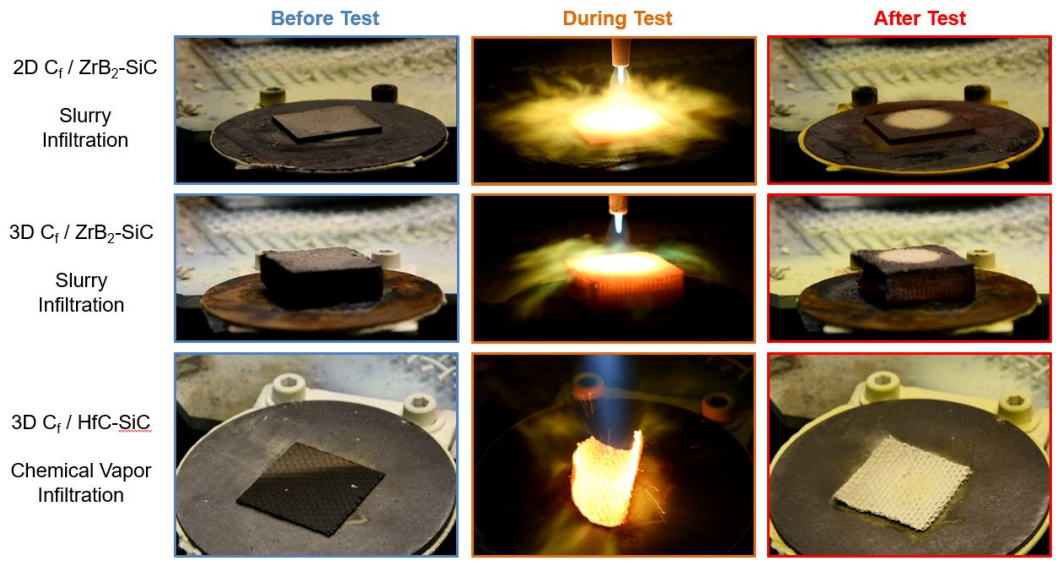

Figure 7. Digital images of slurry infiltrated and chemical vapor infiltrated UHTCMCs before, during, and after ablation testing with the ARL SMART setup. As imaged, SI samples were tested at 2000 °C, while the CVI sample was tested at 1300 °C.

2D and 3D slurry infiltrated samples were tested in a 20% excess oxidizing environment for 10 min. Oxidation resistance was characterized at 1500 and 2000 °C. For both temperatures, the slurry samples showed good oxidation resistance with the formation of a protective ZrO_2/SiO_2 oxide scale as observed with SEM and XRD. Although the ceramic phase struggled to fully penetrate the through-thickness of the preforms, the ZrB_2/SiC instead functioned as more of a coating on the preform surface, which protected the underlying carbon from degradation when exposed to the oxyacetylene flame. The micrographs in Figure 8 depict the cross-section microstructure after exposure at 1500 °C. Three distinct regions are observed in the postmortem microstructure including 1) the formed oxide scale, 2) the reacted ZrB_2-SiC matrix affected by oxygen ingress and large heat fluxes, and 3) the mostly pristine ZrB_2-SiC matrix that was protected from appreciable reaction. The matrix phase reaction from flame exposure was limited to approximately 100 µm, indicating reasonable ablation protection at this temperature–time condition. Figure 9 further highlights the postmortem cross section with compositional mapping, showing the presence of oxygen in the microstructure.

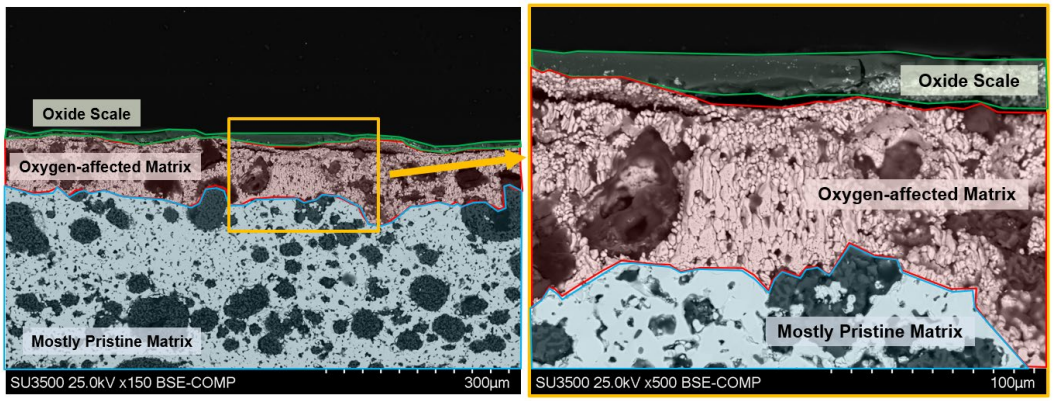

Figure 8. Cross-section electron micrographs of slurry infiltrated 2D C_f/ZrB_2-SiC composite samples after oxyacetylene torch testing at 1500 °C. The three distinct regions of the oxidized microstructure are identified: the unaffected pristine matrix, the oxygen-affected matrix, and the oxide scale.

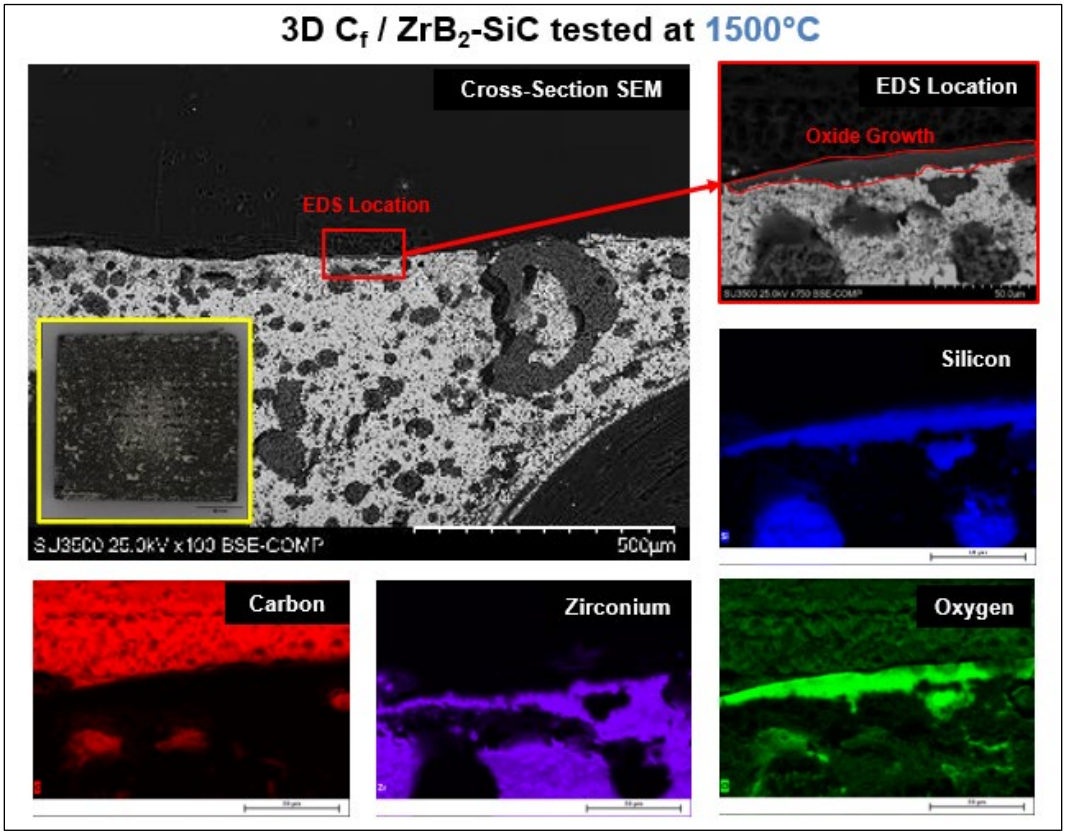

Figure 9. Cross-section electron micrographs of slurry infiltrated 3D C_f/ZrB_2-SiC samples with compositional mapping by energy dispersive spectroscopy. Oxyacetylene torch testing was conducted at 1500 °C for 10 min.

Despite exhibiting good ablation protection, more effective infiltration of the ceramic phase is still highly desirable. Additional tailoring is also needed to retain the flexibility of the carbon fibers, as the slurry infiltrated samples were rigid in the as-fabricated state.

3D CVI samples were characterized under similar testing conditions, but the maximum temperature investigated for these samples was only 1300 °C. It was apparent that the CVI samples did not survive the ablation test at this relatively low temperature, with the samples turning into a chalky white material after complete oxidation. Although CVI processes are effective at penetrating through the thickness of fiber preforms, the content of matrix incorporation was low, such that the HfC–SiC was very rapidly oxidized. While the large void space allowed CVI samples to maintain their flexibility in the as-fabricated state, the large amounts of porosity served to undermine the effective oxidation and ablation resistance of the UHTCMCs. Since the CVI samples were embrittled and deteriorated after testing, cross-section metallography and SEM analysis could not be performed with fidelity.

3. Conclusions

The results of the ablation testing further reinforce the potential advantages of a hybridized approach. While the CVI technique enabled infiltration of the ceramic phase through the thickness of the preform, without significantly reducing its flexibility, the low overall incorporation of UHTC matrix material made these composites vulnerable to oxidation in the oxyacetylene test environment. By contrast, the slurry infiltrated samples survived up to 2000 °C because the ceramic slurry had cured as a coating-like feature on the preform surface, which served to protect the underlying fibers from oxidation. However, slurry infiltrated samples were rigid and did not maintain their flexibility, indicating that further refinements are needed to the processing space.

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List of Symbols, Abbreviations, and Acronyms

2D/3D	two-/three-dimensional
ARL	Army Research Laboratory
CMC	ceramic matrix composite
CVI	chemical vapor infiltration
DEVCOM	U.S. Army Combat Capabilities Development Command
PAS	pressure-assisted sintering
PLS	pressureless sintering
PyC	pyrolytic carbon
SEM	scanning electron microscopy
SI	slurry infiltration
SMART	Sand-Modified Ablation Rig Test
UHTCMC	ultra-high temperature ceramic matrix composite
UHTC	ultra-high temperature ceramic
XRD	X-ray diffraction

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