Innovative procedure for 3D printing of hybrid silicon carbide/carbon fiber nanocomposites

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Abstract
A novel route to fabricating hybrid ceramic matrix composites has been developed. The fabrication is based on the unique combination of additive manufacturing (AM), a preceramic polymer, and a chopped carbon fiber precursor. After introducing the photoinitiator to the preceramic polymer formulation, a photosensitive resin was introduced. The resulting resin was loaded with distinct weight percentages of stabilized polyacrylonitrile nanofiber—the carbon fiber precursor. These formulations were 3D printed, cured, and converted to ceramic phases using a pyrolysis cycle. The end objective of the pyrolysis cycle is the conversion of the polycarbosilane resin into a silicon carbide matrix and the transformation of the PAN polymer into reinforcing carbon nanofibers within one cycle. The results of this work showed that ceramic matrix composite components can be successfully fabricated using a suitable combination of 3D printing, resin formulation, and processing cycle. The pyrolyzed ceramic hybrid composite was fully dense with nearly linear shrinkage and a shiny, smooth surface. Approximately 60% retained weight after pyrolysis to 1350°C was confirmed by thermogravimetric analysis. In terms of crystallography, the ceramic matrix composite displayed three coexisting phases including silicon carbide, silicon oxy carbide, and turbostratic carbon. The results showed this combination of material and processes has a high potential for fabricating hybrid composites with high-temperature performance and improved mechanical properties combined with complex geometries.

KEYWORDS
additive manufacturing, composite materials, microstructural characterization, preceramic polymer, silicon carbide

1 | INTRODUCTION

Silicon Carbide/Carbon Fiber (SiC/C) composites possess very promising features such as high strength to weight ratio, excellent oxidation resistance, and improved thermostructural stability.\(^{[1,2]}\) Such qualities have made SiC/C composites leading candidates for many demanding applications such as nozzles for rocket engines, combustion
chambers, turbine rotors, and thruster components.\textsuperscript{[3–5]} Currently, the main fabrication techniques used to process SiC/C composites consist of precursor infiltration and pyrolysis,\textsuperscript{[6]} slurry infiltration and pyrolysis,\textsuperscript{[7]} chemical vapor infiltration/deposition,\textsuperscript{[8,9]} sol-gel,\textsuperscript{[10]} and additive manufacturing (AM).\textsuperscript{[11]} Among these techniques, AM has a major advantage over the conventional SiC/C processing methods because it can produce final complex structures without the need for further machining. However, at present, very limited studies have been published about the use of additive manufacturing in the fabrication of SiC/C composites.

Lu et al.\textsuperscript{[12]} utilized a combination of stereolithography–gel casting–reaction infiltration to fabricate SiC/C ceramic matrix composite turbine blades. Zhu et al.\textsuperscript{[11]} fabricated near-net-shaped SiC/C composites with complex geometries by combining the 3D printing technique of selective laser sintering with liquid silicon infiltration. Phenolic resin-coated carbon fiber powder was utilized to fabricate 3D printed green parts. After the carbonization of the green material, the part was subjected to vacuum infiltration with a low viscosity phenolic resin which produced a carbon/carbon (C/C) composite after the second carbonization. To obtain SiC/C composites, the C/C composite was infiltrated with liquid silicon at elevated temperatures. Although the resulting composite showed outstanding mechanical and thermal properties, the prolonged fabrication procedure and the residual Si in the composite were major issues for this process. Liquid silicon infiltration (LSI) to convert C/C composite to SiC/C, could be eliminated by replacing the carbon-based polymers with Si-based preceramic polymers. Franchin et al.\textsuperscript{[13,14]} used a direct ink writing technique to print a mixture consisting of a preceramic polymer, poly(methylsilsesquioxane), SiC fillers, and chopped carbon fibers for the potential fabrication of ceramic matrix composite structures. 3D printing of Ceramic Matrix Composites (CMCs), using preceramic polymer/fibers mixture, has not been investigated so far; however, a few studies about additive manufacturing of preceramic polymers for the potential fabrication of complex monolithic ceramic parts have been presented in the literature. Wang et al.\textsuperscript{[15]} proposed three preceramic polymers, namely, methylvinylhydrogen polysiloxane, allylhydroxypolycarbosilane, (SMP-10), and methylvinylhydrogen polycarbosilazane for the production of high-performance ceramics.

Eckel et al.\textsuperscript{[16]} utilized the stereolithography (SLA) technique to produce complex honeycomb structures from UV curable preceramic polymers. The printed ceramic parts possessed high quality, fully dense products with minimal defects. Min et al.\textsuperscript{[17]} employed digital light processing (DLP) to produce dense silicon nitride ceramics which revealed outstanding structural and mechanical properties. Hazan et al.\textsuperscript{[18]} developed a photocurable preceramic polymer system involving allyl hydrido polycarbosilane and multifunctional acrylates for use in STL 3D printing technique. They successfully printed relatively sophisticated geometries which, eventually, after heat treatment, converted to SiC-rich ceramic.

In this study, an innovative AM method—a DLP technique—was developed to fabricate hybrid SiC/C composites from a carbon nanofibers precursor and UV-curable preceramic polymer formulations. Unlike conventional SiC/C fabrication techniques in which the matrix and carbon fibers are prepared separately and then mixed and shaped, the proposed process showed a quick route whereby the 3D printed polymeric based parts convert to SiC/C composite by utilizing one pyrolysis cycle. In such a cycle the preceramic polymer evolves as a ceramic phase and stabilized PAN fibers transform to carbon fibers simultaneously. Near-final complex SiC/C parts can be produced in such a procedure without subsequent machining. An extensive microstructural analysis of the resulting composites was performed in this investigation.

## 2 | EXPERIMENTAL PROCEDURE

### 2.1 | Materials and method

A commercially available preceramic polymer, allylhydrido polycarbosilane, SMP-10 (Starfire Systems, Glenville, NY) and a commercially available acrylate, 1,6-hexanediol diacrylate (HDDA) (Sigma-Aldrich, St. Louis, Missouri) were mixed in a 1:1 weight ratio to produce the preceramic polymer. A curing agent, phenyl bis (2,4,6-trimethylbenzoyl) phosphine oxide (Sigma-Aldrich), was added to the mixture to make them UV-curable. To complete the resin formulation, polyacrylonitrile PAN co-polymer, has 6% methyl acrylate copolymer, with a molecular weight of about 100,000 (Scientific Polymer Products Inc, Ontario, NY) was utilized to spin the PAN nanofibers. The PAN was dissolved in 10 ml N,N-Dimethylformamide (DMF) with 10PAN:90DMF, wt%wt%. Following the solution mixing and stirring, the mixture was loaded in an electrospinning apparatus to fabricate the nanofibers. The machine consists of a pump (New Era pump systems, Inc. NE-300), a voltage regulator (Stanford Research Systems, Inc), a rotating collector (Dayton DC Motor, 4Z145), a syringe, and a needle. Electrospinning parameters consisted of an applied voltage of around 15 kV, the feeding rate of 20 µm min\textsuperscript{−1}, the distance between the syringe tip and the collector close to 16 cm.

To produce high-quality carbon fibers during the pyrolysis cycle, the PAN fibers were stabilized in flowing air at 225°C with a 1°C min\textsuperscript{−1} heating rate and a 1 hour soaking
time at the final temperature. To use the stabilized PAN fibers (SPFs) in the later additive manufacturing process, the fibers were chopped in two steps, specifically, coarse cutting using a kitchen-like chopper and final fine chopping using a probe ultrasonic (Cole-Parmer 500-Watt Ultrasonic Homogenizer) (Figure 1). After final chopping, milled fibers with average diameter of around 1 µm and average length of 20 µm were obtained.

Additive manufacturing was performed in an ANYCUBIC Photon S 3D printer with a UV-LED light source (50 W, \( \lambda = 405 \) nm). The printing solution was prepared by initially mixing the components with a stir bar for specific times (Table 1). Subsequently, all the samples were mixed for 1 hour after adding the photoinitiator (2% Irgacure 819) relative to the total resin (SMP-10 and HDDA) mass.

A cure cycle was used in the printer that consisted of 1 minute UV exposure to each printed layer of a nominal 50 µm thickness. The cured parts were then subjected to a multi-step pyrolysis processing cycle in which the printed preceramic polymer/SPFs hybrid materials are converted to ceramic/carbon fiber composites. The process starts with placing the cured printed part in a tube furnace and purging with argon for 10 minutes to remove air. This is followed by heating the part to 1350°C using the following steps:

- Heat the specimens in argon from room temperature to 350°C at 1°C/min. Hold the temperature at 350°C for 30 minutes
- Heat the specimens in argon from 350°C to 550°C at 0.5°C/min. Hold the temperature at 550°C for 30 minutes
- Heat the specimens in argon from 550°C to 850°C at 0.5°C/min. Hold the temperature at 850°C for 30 minutes
- Heat the specimens in argon from 850°C to 1350°C at 1°C/min. Hold the temperature at 1350°C for 1 hour.

### Table 1 Polymeric mixture ratios

| Sample ID | Resin percentages (wt%) | Mixing time |
|-----------|-------------------------|-------------|
| 0% SPFs   | 50%SMP-10:50%HDDA       | 1 h         |
| 2% SPFs   | 50%SMP-10:50%HDDA-2%SPFs| 12 h        |
| 5% SPFs   | 50%SMP-10:50%HDDA-5%SPFs| 12 h        |

The thermal and structural properties of the cured/pyrolyzed and printed samples were characterized by utilizing several experimental tools. A Simultaneous Thermal Analysis (SDT, 650, TA Instruments, New Castle, DE), an analysis in which both the heat flow (DSC) and weight change (TGA) of material are measured simultaneously, was employed to track polymer to the ceramic conversion of the printed materials. The analysis done using
flowing nitrogen with the heating program was set to ramp to 1350°C at 10°C min⁻¹. The microstructure of pyrolyzed composites was investigated using X-ray diffraction (XRD, RIGAKU, JAPAN) with a voltage of 40 kV, a current of 44 mA, CuKα radiation (λ = 1.541 Å) with a scan rate of 1° C min⁻¹, a high-resolution scanning electron microscopy (HR-SEM,) and transmission electron microscopy (TEM; Talos F200X, FEI). Small lamellae containing CF and SiC matrix for TEM characterization were extracted using a focused ion beam (FIB; Helios Nanolab 660/G3, FEI). For quick TEM sample preparation, a small piece from 3D printed/pyrolyzed SiC/C was crushed to a fine powder, suspended in isopropanol and ultrasonicated, then a drop deposited on the lacey carbon TEM grid. The implemented TEM technique was combined with annular dark-field (ADF) imaging, energy dispersive x-ray spectroscopy (EDS), and selected area electron diffraction (SAED) to analyze the structural features. A nanoindenter, Nano Indenter XP from the Materials and Manufacturing Directorate, Air Force Research Lab, WPAFB, Ohio, was applied to measure the mechanical properties of materials. In a typical indentation test, a hard tip whose mechanical properties are known is pressed into a sample whose properties are unknown. Using the load applied and indentation area, mechanical properties such as modulus and hardness can be measured. The used samples were polished through the build direction.

3 RESULTS AND DISCUSSION

3.1 TGA results

The polymer to the ceramic conversion of all formulations was investigated using TGA analysis. A major weight loss between 350°C and 450°C has been attributed to small moieties separating from the acrylate and preceramic polymer main chain at this temperature range. Figure 2 compared the weight retentions of the cured SMP-10/HDDA with that loaded with several weight percentages of stabilized PAN fibers. The residual weight was in the range of 55-60% which is typical for this class of polymeric formulations.

SPFs additions showed a shift in the weight loss onset temperature by 50°C toward higher temperatures. The maximum retained weight was recorded for 2% SPF samples which were slightly higher than the other two variants. As shown in Figure 1, SPFs have a brown color, and loading more than 2 wt% has a slight negative impact on UV transmittance which reduces the curability of samples loaded more with fibers. The insufficient cross-linking means less mass retention during the pyrolysis cycle due to low molecules loss at lower temperatures.

3.2 XRD results

XRD of pyrolyzed samples, Figure 3, revealed characteristics SiC peaks at 35.6°, 60.2°, and 71.9° which correspond to (111), (220), and (311) planes, respectively. The interatomic spacing for such planes, calculated using Bragg’s law, coincides with SAED interplanar distancing. From the same figure, with increasing carbon content, the turbostratic carbon peaks around 24° and 43.1° increased slightly. In addition, the lattice parameters of the cubic-SiC matrix were calculated according to XRD results and by utilizing the d-spacing and Miller indices values. The resulted value
Figure 4  SEM images of a SiC/C composite after pyrolysis of the 2% SPF sample, (A) low magnification image showing printed layers, (B) high-resolution SEM image

Figure 5  HRTEM image showing (A) CF lattice fringes and picture inset showing SEAD, with [1]: 0.35 nm, d_{(002)}; [2]: 0.21 nm, d_{(100)}; [3]: 0.12 nm, d_{(110)}, (B) CF/interface, the sample extracted, using FIB, from pyrolyzed 2% SPF hybrid material

of lattice constant, \( a = b = c = 4.35 \text{ Å} \), was very similar to reported estimations of lattice parameters of cubic-SiC.\[19–22\]

3.3 Microstructure examinations

SEM and TEM analyses were employed to characterize the microstructural features and defects after pyrolysis. A dense, hybrid matrix SiC/C composite with nanoporosity was confirmed from SEM and TEM images. Figures 4–7 show results for a pyrolyzed SiC/C composite that contained 2% SPF in the polymer formulations before pyrolysis. Figure 4A shows a piece of the sample’s cross-section, specifically, at the gage section of the tensile coupon. SEM imaging of such a section showed that the layered structure of the 3D printed part has random fibers distributed in a relatively dense matrix. The fiber diameter is around 700 nm, which is smaller than that of as-spun PAN fibers, as shown in Figure 4B (right inset). A reduction in the cross-sectional area is typical when PAN is converted into carbon fibers.

TEM lattice fringes imaging and SEAD, of the cross-section of pyrolyzed carbon fibers, Figure 5A, confirmed the formation of turbostratic carbon structure with interatomic spacing between carbon layers of approximately 0.34 nm. The goal was to produce carbon fibers from the SPF precursor which was 3D printed as part of the polymer formulation. The microscopy confirmed these fibers to be of similar quality to the ones pyrolyzed individually.\[9\] This finding demonstrated a shortened and potentially cost-effective route to fabricating SiC/C materials in which all constituents are pyrolyzed concurrently. In addition, the potential exists for enhancing the interphase SiC/C adhesion because of the fibers and SiC phases forming in the same pyrolysis cycle. This is confirmed in Figure 5B where a continuous fiber/matrix interface was observed for the hybrid composite. The interface region consisted mainly of amorphous phases.

The HRTEM image, Figure 6, confirms highly crystallized SiC/C materials. SiC grains with a size of approximately 10 nm were detected from lattice fringes. Well-defined diffraction patterns were illustrated by SEAD images which they were corresponding to (111), (220),
and (311) planes of cubic SiC. Figure 6 displays the lattice ordering of SiC particles within (111) planes, which also shows a highly ordered atomic plane with an interatomic distance of 0.25 nm.

The matrix showed a turbostratic carbon surrounding SiC grains (Figure 6) as it was originated from carbon side groups in SMP-10 and the main chain carbon in HDDA. The formation of turbostratic carbon from preceramic polymers was reported in the literature.\[2,23\] Furthermore, SAED image showed C and SiC diffraction rings.

The elemental analysis using TEM-EDS showed the coexistence of C, Si, and O elements (Figure 7) which indicates that the matrix consisted mainly of nanocrystalline SiC in addition to amorphous SiOC. The presence of O within the matrix is connected with the chemical composition of the HDDA (oxygen side groups) and the possible oxidation of SMP-10 during the printing process in ambient air.\[15\]

### 3.4 Nanoindentation results

Nanoindentation is a versatile technique that has been widely used for the characterization of the mechanical properties of materials. In this research, a nanoindenter was used to measure the hardness and tensile modulus of the three ceramic samples with different carbon fiber loadings (0%, 2%, and 5% wt%/wt%). The preliminary mechanical data of these samples were obtained and analyzed. Figure 8 shows that the hardness was improved when carbon fibers were added to the 3D printed hybrid composites. Similarly, tensile modulus data shows the reinforcement effect of the addition of carbon fiber. Further, the hardness and tensile modulus increase with higher carbon fiber loading (Figure 8). These preliminary hardness and tensile modulus data indicated the desirable goal of a strengthening effect of carbon fibers in the 3D printed hybrid ceramic composite is achievable. However, these are preliminary results and further investigation of mechanical
An innovative additive manufacturing procedure for fabricating high-performance SiC/C hybrid composites was developed. The process offers the potential to rapidly and economically fabricate CMCs as compared with traditional fabrication processes for such composites. The process uses a formulation of a preceramic polymer (SMP-10 and HDDA) and a stabilized carbon fiber precursor (PAN fibers). A UV-type AM process was used to produce and cure the preceramic composites. A step-wise pyrolysis cycle was used to convert the preceramic composite to the final ceramic matrix/carbon fiber composite. After processing, the composite exhibited excellent physical and mechanical properties. Microstructure characterization using TEM lattice fringes imaging and XRD analysis showed well-defined SiC and turbostratic carbon features. Nanoindentation tests showed a positive impact of increasing carbon fiber content on the mechanical properties of the composites.

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CONFLICT OF INTEREST
The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT
Research data are not shared.

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