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*Properties of SiC-Si made via Binder Jet 3D Printing of SiC Powder, Carbon addition, and Silicon Melt Infiltration*

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**Abstract**

We report the physical and mechanical properties of ceramic composite materials fabricated by binder jet 3D printing with silicon carbide (SiC) powders, followed by phenolic resin infiltration and pyrolysis (IP) to generate carbon, and a final reactive silicon melt infiltration step. After two phenolic resin infiltration and pyrolysis cycles; porosity was less than 2%, Young's modulus was close to 300 GPa, and the flexural strength was  $517.6 \pm 24.8$  MPa. However, diminishing returns were obtained after more than 2 phenolic resin infiltration and pyrolysis cycles as surface pores in carbon were closed upon the formation of SiC, resulting in reaction choking and residual

free carbon and porosity. The instantaneous coefficient of thermal expansion of the composite was found to be independent of the number of phenolic IP cycles and had values of between 4.2 and 5.0 ppm/°C between 300°C and 1,000°C, while the thermal conductivity was found to have a weak dependence on the number of phenolic IP cycles. While the manufacturing procedures described here yielded highly dense, gas impermeable, siliconized SiC composites with properties comparable to those of bulk siliconized silicon carbide processed according to conventional techniques, binder jet 3D printing (BJ3DP) enables the manufacture of objects with complex shape, unlike conventional techniques.

**Key Words:** Binder Jet 3D Printing, SiC, Phenolic Impregnation and Pyrolysis, Reactive Melt Infiltration

## **Introduction**

Because of its unique combination of physical, thermal, and mechanical properties silicon carbide (SiC) remains the material of choice for many industrial and energy applications at high temperatures, including heat exchangers [1]. Relative to other structural materials, SiC has low density, high elastic modulus, high thermal conductivity [2], low thermal expansion [3], high resistance to creep deformation, and retains its mechanical strength at high temperatures [4]. In air, SiC forms a silica scale that is durable and protective [5]–[8].

Traditionally, monolithic SiC is made by powder processing techniques, which in most cases is restricted to the fabrication of objects with simple shapes. However, additive manufacturing (AM) has demonstrated the potential of revolutionizing the manufacturing of ceramics, including SiC by the ability of manufacturing objects with complex shapes, without having to involve expensive machining operations. Among the various AM methods currently available for

shaping monolithic ceramics, binder jet 3D printing (BJ3DP)[9], [10] is particularly promising because it can achieve high volume throughput (i.e. fast relative to other AM methods) while maintaining high spatial resolution. BJ3DP is scalable, and can produce objects with large overhangs and geometric complexity due to its reliance on a powder bed [11]. Although BJ3DP is ideal for manufacturing preforms with complex geometries, it uses relatively large (>5 micrometer) powders and the preforms need to be post-processed to achieve full density using methods such as polymer impregnation and pyrolysis using a ceramic polymer precursor (PIP), chemical vapor infiltration (CVI), or reactive melt infiltration (RMI).

Several researchers have used BJ3DP to make preforms with SiC powder and fibers that were subsequently densified by PIP [12], [13]. However, the densities obtained were low (85-95% TD). Terrani et al. fabricated high purity SiC components through a combination of BJ3DP using SiC powders and CVI post-processing step [14]. However, this fabrication method is time-intensive and expensive, and objects manufactured by this method still had a residual porosity of 8%.

Reactive melt infiltration of a carbon-containing preform using silicon has been successfully used to achieve greater densification, because some of the silicon can react with carbon available in the preform to form SiC, while excess silicon can fill open pores through capillary forces and through the volumetric expansion experienced by silicon during solidification [15]. Furthermore, there is a positive volumetric change associated with the conversion of carbon into SiC upon reacting with molten silicon, which will vary depending on the skeletal density of the carbon precursor [16]–[18]. Moon et al. fabricated SiC-Si composites via BJ3DP using glassy carbon powders of 45–105  $\mu\text{m}$  sizes followed by reactive infiltration with liquid silicon [19]. They obtained relatively complex-shaped carbon preforms with overhang, undercut, and inner channel

structures but due to the presence of large glassy carbon particles, some entrapped residual carbon was left after reaction. Fleisher et al. investigated the fabrication of siliconized SiC objects by a combination of BJ3DP with phenolic binder, followed by multiple infiltration and pyrolysis cycles of the phenolic binder and a final reactive melt infiltration step with silicon [20]. They designed their process so that each phenolic binder infiltration and pyrolysis cycle contributed  $\sim 3\%$  of carbon, which fills preform pores and becomes available for producing SiC upon reaction with molten silicon, thus significantly reducing the residual silicon content. They also found that more than 3 infiltration and pyrolysis cycles could cause clogging of pores, which would impede liquid silicon infiltration increase residual porosity. In contrast to chemical vapor infiltration, which can yield stoichiometric compositions, such as SiC, reactive melt infiltration can result in unreacted excess silicon, which will limit the operation of these materials to  $1350^{\circ}\text{C}$ , when the material loses its creep resistance and strength [21], [22].

Here, we present results from the fabrication and characterization of objects fabricated by BJ3DP using SiC powders and commercial phenolic binder, followed by multiple impregnation and pyrolysis (IP) cycles using a phenolic resin, and by a final reactive melt infiltration step with silicon. The effect of the number of phenolic resin impregnation and pyrolysis (IP) cycles on microstructure, physical, thermal, and mechanical properties is reported. To date, none of the publications on the fabrication of siliconized SiC composites by the reactive melt infiltration of BJ3DP preforms has reported values of gas permeability of the final product, except for objects manufactured by BJ3DP of SiC powder followed by preceramic PIP [23], which despite being dense, were permeable to air. Here, we demonstrate that it is possible to obtain air impermeable materials with thermal and mechanical properties comparable to traditionally-manufactured SiC monoliths but with significantly more design flexibility because of the use of BJ3DP.

## Materials and Methods

### *Materials*

F500 Green SiC (6H phase) powders (Panadyne, Montgomeryville, PA) with loose packing density of 0.95 g/cm<sup>3</sup>, purity of 99.6%, were used to make preforms via BJ3DP. Figure 1 shows a scanning electron micrograph of the particles, illustrating their morphology, which is characterized by sharp and jagged irregular shapes. The particle size distribution is also presented in Figure 1, for which  $D_{50} = 11.32$  micrometers. The binder used for BJ3DP was a phenolic-based binder (FB101 Phenolic Binder, ExOne, North Huntingdon, PA). The resin used for subsequent IP cycles was APS-100 phenol formaldehyde (EEMS, Saratoga Springs, NY), which was thinned with ethanol in a 2:1 by mass ratio of resin to ethanol. Silicon powder (US Nanomaterial, Inc.) with purity of 99.9% and 20 micrometer particle size was used for reactive melt infiltration.

**Figure 1:** SEM image (left) and plot of the size distribution (right) of the 6H SiC powder used for BJ3DP.

### *Printing*

An Innovent+ (ExOne, North Huntingdon, PA) printer was used to form preforms using the SiC powders. Powder dispensing speed was 25 mm/s with an oscillator speed of 2700 rpm. The powder surface was leveled to a 50-micron layer height with a counter-rotating 31.75 mm diameter steel roller rotating at 300 rpm and traveling at 25 mm/s across the powder bed. A binder saturation of 80% was used. Following binder deposition, no set time was used before the heater passed over the surface at a speed of 22 mm/s. The powder bed surface temperature was kept at 50°C. Disks of 57.15 mm diameter and 5 mm thickness as well as  $15 \times 15 \times 5$  mm<sup>3</sup>

parallelepipeds were printed and post-processed. For voxel calculations, the X-spacing was 63.5 micrometers, Y-spacing was 75.5 micrometers, and Z-spacing was 50.0 micrometers (or the same as the layer thickness). An 80  $\mu\text{L}$  nozzle was used for jetting the binder onto the powder bed. After printing, the specimens were cured at 200°C in air for 2 h. Before further processing, the samples were pyrolyzed to convert the phenolic binder to carbon by heating in  $\text{N}_2$  gas at 1°C/min to 850°C and holding at that temperature for 30 min.

#### *Phenolic Resin Impregnation and Pyrolysis (IP)*

Phenolic resin impregnation and pyrolysis adds carbon to the surface of the SiC particles and forms bridges between SiC particles. Then, the final reactive melt infiltration step with silicon results in the conversion of that carbon into SiC. Control samples (denoted as 0 IP) were melt-infiltrated with silicon after printing, binder curing, and a single pyrolysis cycle to convert the binder to carbon char. The remaining samples underwent additional phenolic resin IP cycles with the phenol formaldehyde resin from EEMS. The phenolic IP process consisted in dripping into the preforms ethanol-thinned phenolic resin (2:1 ratio of resin to ethanol), followed by the application of vacuum to ensure uniform infiltration, curing, and pyrolysis. Ethanol was used to improve infiltration and impregnation by reducing the viscosity of the phenolic resin and therefore avoid damaging the printed structure when forcing the flow of the resin through the preform. The cycle for curing was 190°C for 30 min with a heating rate of 2°C/min, while the subsequent pyrolysis cycle was conducted at 850°C for 30 min at a heating rate of 2°C/min. All samples were processed through 1 IP cycle to build up carbon into the preform. Subsequent cycles are denoted as conditions 2\*, 2, and 3 IP, where conditions 2 and 3 IP consisted of full saturation of the phenolic resin during impregnation, while the 2\* IP cycle represents a second cycle of phenolic resin treatment but using only half of the amount used in the second cycle of

the sample processed according to the 2 IP. It should be noted that the amount of phenolic resin that can be absorbed by the preform to achieve saturation during infiltration decreases with increasing number of IP cycles because the volume available for infiltration decreases as a result of the buildup of carbon during previous IP cycles. Even though the samples processed with 2\* IP cycles were not fully saturated during impregnation, the phenolic resin is assumed to be uniformly distributed throughout the entire sample. Therefore, condition 2\* IP has more carbon compared to the condition 0 IP, but less carbon than condition 2 IP. The rationale for investigating the behavior of the 2\* IP condition was to determine the conditions that might optimize the amount of carbon that is converted into SiC before the reaction can be choked when silicon infiltration is blocked by the formation of SiC on the surface pores of carbon. Figure SFig. 1 shows a flow chart illustrating the processes used for fabricating all the samples in this investigation. Once the desired carbon content was reached for each condition, the samples were subjected to a final silicon reactive melt infiltration step.

#### *Silicon reactive melt infiltration*

Pressureless, reactive melt infiltration of silicon was performed on samples after the phenolic IP cycles. The amount of silicon used for each sample was determined as that needed to react all the carbon added to the preform to form SiC, and to fill the rest of the open pores in the preform with silicon. The predetermined amount of powdered silicon was placed onto BN plates in a graphite crucible, and the printed preforms containing SiC particles and carbon were placed on top of the silicon powder so that when heated above silicon's melting temperature, it would infiltrate the preform through capillary action [21]. The heating schedule associated with the reactive melt infiltration of silicon was done in a two-step furnace cycle. The first step consisted in heating to 1450°C at 10°C/min holding for 30 min under vacuum of ~0.1 Pa, followed by the



second step, in which the chamber is filled with Ar to a total pressure of  $\sim 1,000$  Pa to minimize silicon volatilization, and temperature increased to  $1670^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$  followed by holding for 4 h. The purpose of the second step at  $1,670^{\circ}\text{C}$  was to reduce the viscosity of silicon to maximize infiltration and increase the SiC content from reaction [24].

### *Characterization and Mechanical Properties*

Thermogravimetric analysis (TGA) was used to determine the decomposition, mass loss, and char yield of the binder and phenolic resin during a thermal schedule similar to that used for an IP cycle. The binder and resin were heated in a TA Q50 (TA Instruments, New Castle, DE, USA) at a  $10^{\circ}\text{C}/\text{min}$  heating rate from room temperature to  $800^{\circ}\text{C}$  (temperature limitation of this system) in flowing nitrogen at rates between 40 ml/min and 60 mL/min for the balance and the furnace, respectively.

Optical microscopy of specimen cross sections was performed with a Keyence VHX-1000 system. Scanning electron microscopy (SEM) (Hitachi S4800) in backscatter electron imaging mode was used to characterize microstructures. Densities were measured geometrically and by Archimedes principle. X-ray diffraction (XRD) was used to characterize and identify materials and crystallographic phase composition using a PANalytical X'pert diffractometer with Mo K- $\alpha$  radiation ( $\lambda = 0.709319 \text{ \AA}$ ). The system used 40 kV, 40 mA,  $2\theta$  step size of 0.02, and MDI Jade 2010 software database.

For measurements of flexural strength, Young's modulus and thermal expansion behavior, parallelepiped test specimens were obtained by slicing and grinding from the 55-mm diameter disks with their longitudinal orientation orthogonal to the axis of the disks. Four-point bending tests were performed on samples with dimensions of  $50 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$  to measure the

flexural strength following the procedure outlined in ASTM C1161 using an electro-mechanical test frame (Instru-Met, 1210AF-300-B) and a silicon carbide fixture. Samples were tested in air at room temperature, 600°C, and 1000°C. Young's modulus was measured in air as a function of temperature between ambient temperature and 800°C following the procedures outlined in ASTM standard C1259 -15 and Radovic et al., [25], [26] using a Buzz-o-sonic (BuzzMac International, Glendale, WI, USA) impulse excitation system. Thermal expansion measurements were performed on sample bars of 20 mm× 5 mm× 4 mm between room temperature and 1,000°C in air using thermomechanical analysis (TMA) with a system from (TA Instruments Mod. Q400) at a heating/cooling rate of 3°C/min. Permeability tests were performed on flat disk-shaped specimens according to the procedure outlined in [23], which quantify the amount of air that permeates through the material when subjected to a pressure differential across the thickness of the disk.

Thermal conductivity ( $\kappa = \alpha \rho C_p$ ) was determined from separate measurements of thermal diffusivity ( $\alpha$ ) using the laser flash method (Netzsch LFA 457) according to ASTM 1461-13 and specific heat ( $C_p$ ) from differential scanning calorimetry (DSC) using a Netzsch Pegasus 404 system according to ASTM E1269-11. Thermal diffusivity was measured between 25°C and 900°C in argon flowing at a constant rate of 100 mL/min. The thermal diffusivity values were calculated based on the sample thickness and the temperature rise curve after each laser pulse using the Cowan method with pulse width correction [27], [28]. Specific heat capacity was measured in the temperature range between 25°C and 600°C at 10°C/min using platinum pans and lids, and the results were extrapolated to 900°C. This extrapolation is an acceptable assumption because the Dulong-Petit law does not have an effect on SiC-Si composites until temperatures higher than 1200°C, so the trends are linear in the current research test range [29].

Sapphire was used as a standard reference material in the DSC runs. Prior to the experiments, the DSC furnace was evacuated and purged with argon three times. The DSC runs were conducted with titanium oxygen getters under flowing argon to prevent oxidation.

Raman spectroscopy was used to identify the various phases present in the materials, in particular SiC, carbon, and silicon. Raman spectra were obtained with a Renishaw Invia Raman microprobe using a Nd-YAG laser operating at 532 nm and a spot size of  $\sim 1\ \mu\text{m}$ . Phase identification was conducted using the principal component analysis within the vendor's Wire 5.2 software. Chemical analysis was done with a LECO RC412 instrument using ISO210682-2, in particular to quantify the amount of free carbon in BJ3DP samples that had been cured and pyrolyzed. This information was essential for determining the correct amount of silicon to be used during the reactive melt infiltration step. The measured amount of carbon was compared to a predicted amount based on voxel size and printhead size.

## **Results and Discussion**

Figure 2 shows TGA data for the phenolic binder and resin used in this study. The char yield of the as received ExOne phenolic binder was 24.1 wt.%. This phenolic binder contains isopropyl alcohol as solvent in roughly 50 wt.%, which allows it to have low surface tension for jetting but at the expense of carbon yield. The EEMS resin, which was thinned with ethanol (2:1 resin to ethanol ratio), had higher yield of 34.3 wt.%. These values were used to estimate the total amount of carbon deposited from printing and by the various phenolic IP cycles. Because the EEMS resin had higher char yield per unit volume, it was used for the phenolic IP cycles. To that point, both the phenolic binder from ExOne and the phenolic resin from EEMS have approximately the same char yield after curing, 63.8 wt.%. This is due to the fact that the

chemical composition of the two resins is similar once their carrier fluids were removed during curing.

**Figure 2:** TGA data of ExOne binder as received and cured, and TGA of the EEMS resin that is thinned (2:1 resin to ethanol) for impregnations as well as cured.

To quantify the amount of carbon present in samples printed with phenolic binder after curing and pyrolyzing the printed SiC parts, the masses of SiC and liquid phenolic binder were calculated in Eq. (1) for an individual voxel (i.e., 3D pixel), where M is mass,  $\rho$  is density, V is volume, PF is the packing factor of the SiC powder, and CF is the conversion factor of the as received ExOne phenolic binder from the TGA results. The volume of the printed voxel was taken from the printing parameters and was approximated as the volume of powder that one inkjet droplet binds. The volume and density of the drop were measured by weighing the mass of a number of droplets deposited by the printhead in a common calibration process called “drop mass measurement.” Using Eq. (1) and the measured parameters (packing factor of 0.36 and 80 pL nozzle), the amount of carbon added to SiC preforms from printing with phenolic binder was calculated as 6.3 wt.% as shown in Table 1. The chemical analysis showed that there was 7.4 wt.% free carbon in prints after curing and pyrolyzing (the as received powder had 0.1 wt.% free carbon), so the calculation based on voxel size was very close to the measured value. This initial amount of carbon deposited on the surface of SiC particles in printed parts was used to estimate successive amounts of carbon from phenolic IP cycles and ultimately determine the final SiC content.

$$\text{SiC:C ratio after print} = \frac{M_{\text{SiCvoxel}}}{M_{\text{Carbon after pyrovoxel}}} = \frac{\rho_{\text{SiC}} \cdot V_{\text{Printvoxel}} \cdot \text{PF}_{\text{SiC}}}{(V_{\text{droplet}} \cdot \rho \cdot \text{CF})_{\text{phenolic binder}}} \quad (1)$$

Following curing, the samples were pyrolyzed, and the mass gained from each phenolic IP cycle was recorded to quantify the total amount of carbon in the samples as well as brown (i.e. after burnout) geometric densities as shown in Table 1. These calculated carbon amounts were used to determine the amount of silicon needed for infiltration to both react with carbon to form silicon carbide as well as to fill the rest of the part volume with silicon (residual silicon). The amount of SiC in the final composition was estimated using Eq. (2) and has been presented in Table 1, which considers the initial printed SiC and carbon content from the binder, carbon from subsequent phenolic IP cycles, and silicon added during reactive melt infiltration. The derivation of this equation assumes that all of the carbon is consumed and converted to SiC, which is discussed later in the results section. The predictions for final composition when increasing the number of phenolic IP cycles are shown in Table 1.

$$\begin{aligned} \text{Vol.\% SiC after RMI} &= \frac{V_{\text{SiCPrinted}} + V_{\text{SiCReacted}}}{V_{\text{PartBouding}}} \\ &= \frac{\frac{M_{\text{SiCPrinted}}}{\rho_{\text{SiC}}} + (M_{\text{SiCPrinted}} - M_{\text{PartAfter IP}}) * \frac{1 + 2.33}{\rho_{\text{SiC}}}}{\frac{M_{\text{SiCPrinted}} * \text{PF}}{\rho_{\text{SiC}}}} \end{aligned} \quad (2)$$

**Table 1:** Information on preforms, predictions on SiC amount, and final compositions (where wt. = weight, cc = cubic centimeters, TD = theoretical density, vol. = volume, and L = liter).

Figure 3 shows Raman spectroscopy analysis after the pyrolysis of SiC preforms with 1 phenolic IP cycle. Figure 3A is an optical image of the local microstructure, Figure 3B shows the Raman maps from the spectra of the principal components detected in that area, and Figure 3C-E are the Raman spectra for the principal components for different frequency ranges in order to see differences in SiC phases more clearly. It can be seen in Figure 3A that four phases are present in samples after phenolic IP treatment: 6H (primary printing powder), 4H (small amounts in the printing powder), 15R (small amounts in the printing powder), and the Raman signal of the

carbon shows that it was an amorphous carbon (from pyrolysis of the phenolic). The rest of the material is the epoxy mount. The preforms were thus a porous SiC-C composite of crystalline SiC from the powder and amorphous carbon from the phenolic resin pyrolysis. SFig.2 shows photographs of printed preforms, preforms after impregnation, and preforms after curing.

**Figure 3:** Raman spectroscopy analysis of SiC-C preforms after 1 phenolic IP cycle. Optical image (A), Raman spectra principal component mapping (B) and the principal component spectra (C)-(E) with different frequency ranges. 6H (white); 4H (yellow); 15R (green); epoxy (cyan). The grey shade around SiC particles in the optical image is amorphous carbon.

The SiC-C preforms with prescribed values of free carbon content were then subjected to reactive melt infiltration with silicon. Figure 4 shows cross sections with optical images as well as insets of SEM images of the samples processed with 0, 2\*, 2, and 3 phenolic IP cycles followed by silicon reactive melt infiltration. These images revealed that the sample processed with 0 IP cycles had larger pores compared with the other samples and that rows of pores were aligned along printed layers. The amount of porosity of each sample was determined by quantitative image analysis using the ImageJ software and porosity values are listed in Table 1, along with the estimated SiC content, which were consistent with estimated values except for the samples processed with 3 IP cycles. The samples with 0 IP cycles were comprised of only three constituents: SiC (grey shade), silicon (light shade), and pores (black shade). For samples processed with 0 and 2\* IP cycles, most of the carbon was found to be consumed to form SiC, and no material was found in the pores according to EDS and Raman spectroscopy. Similar results were obtained with the sample processed with 2\* IP cycles (Figure 4B), except that the clusters of SiC particles were more interconnected, which is likely due to an increase of SiC content from the reaction bonding of the additional carbon to newly formed SiC, and the

increasing SiC content is noted in Table 1. The optical micrograph of the reaction bonded sample processed with 2 IP cycles in Figure 4C shows that there are no large pores, and that the layered structure becomes evident from the concentration of silicon between deposited layers. The SEM image of the sample processed with 2 IP cycles showed connectivity of SiC, residual silicon, and some small clusters of unreacted carbon as identified from EDS. After 3 IP cycles (Figure 4D) samples show larger and higher quantities of clusters of unreacted carbon than the sample with 2 IP cycles, most likely because the pathways for molten silicon infiltration were closed off after 2 IP cycles, leaving these areas of unreacted carbon. This happens because the kinetics of SiC formation is fast and competes with the infiltration kinetics in samples with higher carbon content or more pore closure [16], [24]. Also, it should be noted that there was no evidence of growth of the original SiC particles, but there was evidence of particles being joined by new links or necks to form SiC clusters as evidence in Figure 4 where the SEM images with higher magnification show some areas of reaction zones around the primary 6H SiC particles from the printing process.

Values of air permeability as a number of phenolic IP cycles are listed Table 1. There are engineering applications, such as heat exchangers, which require the material used for their fabrication to be impermeable to the working fluids. The experimental conditions used to evaluate the air permeability of the materials fabricated are described in the supplementary material section. It was found that the permeability of samples processed with 0 and 2\* IP cycles was greater than those of samples processed with 2 and 3 IP cycles. These results are consistent with the porosity characteristics of the material as described in Figures 3 and 6 and listed in Table 1. For the samples processed with 2 and 3 IP cycles, the values of permeability decreased and were equal to the intrinsic leak rate of the testing system. Therefore, samples processed with

2 and 3 phenolic IP cycles followed by silicon reactive melt infiltration, are sufficiently sealed for applications such as heat exchangers.

**Figure 4:** Optical, backscatter SEM images, and high magnification secondary electron SEM of cross-sections of parallelepiped samples of microstructures from samples processed with a) 0 IP cycles, b) 2\* IP cycles, c) 2 IP cycles, and d) 3 IP cycles.

Figure 5 shows the XRD patterns of the samples processed with 0, 2\*, 2, and 3 phenolic IP cycles. For all samples, the patterns correspond to silicon and alpha-SiC peaks. Carbon was not detected because most of it was consumed to form silicon carbide during silicon reactive melt infiltration, and because the remaining unreacted carbon from the pyrolysis of phenolic is amorphous. Higher order silicon peaks were detected in all samples, which means there is some preferred orientation belonging to the (422) and (511) planes of the small amounts of silicon. These findings were unexpected and are being investigated in more detail. Analysis of the XRD patterns for the samples prepared in this investigation did not reveal the presence of beta-SiC most likely because of the small volume fraction. Pampuch et al. reported the reaction between PAN-derived carbon fibers and molten silicon at 1,500°C resulted in the formation of beta-SiC and that SiC crystals are precipitated from the carbon solution in liquid silicon during the soaking period at elevated temperatures and not after the cooling down [30]. Thus, to detect beta-SiC, a detailed analysis of these samples by Raman spectroscopy was performed.

**Figure 5:** XRD data for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

Figure 6A shows a micrograph of a sample processed with 3 IP cycles followed by silicon reactive melt infiltration, whereas Figure 6B shows the results of a principal component analysis



of the Raman spectral map of the region identified in Figure 6A. The analysis showed the presence of several polytypes of SiC in particular 6H (white), 3C (red), 15R (blue). 4H was detected in small amounts, and silicon is shown in cyan. Polytypes 4H, 15R, and 6H are associated with the starting silicon carbide particles whereas the beta phase (3C) correspond to SiC formed from the reaction between carbon and molten silicon [31]. The analysis of the Raman spectrum associated with unreacted carbon revealed the presence of two broad peaks centered at around  $1358\text{ cm}^{-1}$  and  $1603\text{ cm}^{-1}$ , with the latter having greater intensity (Figure 6C). These features are characteristic of poorly ordered carbons [32], consistent with the formation of amorphous carbon from the pyrolysis of the phenolic resin. A comparison of the Raman spectra for carbon in Figures 3 and 6, suggest that unreacted carbon in the pores became more ordered when the material was exposed to high temperature (e.g.,  $1670^{\circ}\text{C}$ ) during reactive silicon melt infiltration.

**Figure 6:** Raman spectroscopy principal component analysis of SiC-Si composite. (A) Optical micrograph of sample processed with 3 IP cycles followed by reactive melt infiltration. (B) Principal component analysis of the inset in Figure 5A revealing the various phases present. 6H (white); 3C (red); 15R (green); Si (cyan). Unreacted carbon is in the pores as shown in the optical image.

Figure 7 shows representative flexural stress versus displacement curves from 4-pt. bend testing of samples processed with 0, 2\*, 2, and 3 IP cycles followed by reactive silicon melt infiltration. Only one print orientation was tested i.e., the x-y plane orientation as shown in Figure 7. The flexural strength of the samples processed with 0 and 2\* IP cycles have the lowest flexural strength with  $244.8 \pm 10.5\text{ MPa}$  and  $170.3 \pm 19.6\text{ MPa}$ , respectively. The samples processed with zero and one IP cycle also had lower displacement to failure compared to the samples processed

with 2 and 3 IP cycles, which is consistent with the differences in density between the samples. The strength of the samples processed with 2 IP cycles had the highest strength ( $517.6 \pm 24.8$  MPa) and displacement to failure of all the samples, even higher than the samples processed with 3 IP cycles. It is believed that this is the result of lower porosity in the samples processed with 2 phenolic IP cycles compared to the others. These strength values are lower than those reported for traditional hot-pressed SiC ( $\sim 650$  MPa) [33] but greater than those reported for siliconized silicon carbide ( $\sim 385 \text{ MPa} \pm 42 \text{ MPa}$ ) [34]. Among the limited mechanical property data reported for SiC processed by AM techniques, Xu et al. reported flexural strength data between 203.7 and 234.9 MPa from tests performed between 800°C and 1,000°C for materials processed by selective laser sintering and preceramic polymer IP [35]. The lower values obtained in that study, compared to the results reported here, could be explained by the relatively low densities obtained by the IP of polymeric precursors for silicon carbide [35].

**Figure 7:** Typical 4-pt bending flexural stress versus crosshead displacement curves for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

Figure 8 shows values of Young's modulus as a function of temperature for the different processing conditions. The sample processed with 0 IP cycles had the lowest stiffness, consistent with the high level of porosity. Samples processed with 2 IP cycles had the highest values of Young's modulus because among all conditions, these samples had both the highest SiC content and the lowest porosity. All samples exhibited decreasing stiffness with increasing temperature consistent with the temperature dependence of Young's modulus of SiC and silicon. Using the volume fractions of SiC, Si and porosity listed in Table I, and a decrease of 3.9% in Young's modulus of polycrystalline SiC between room temperature 800°C [36] and a decrease of 6.1% in the Young's modulus of polycrystalline silicon in the same temperature interval, decreases of

4.5% and 4.3% are predicted, which compare well with experimentally determined values of 3.1% and 3.9% for samples 0 IP and 2 IP, respectively.

**Figure 8:** Young's modulus versus temperature for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

Figure 9 shows values of flexural strength as a function of temperature for the 0, 2\*, 2, and 3 IP cycles followed by reactive melt infiltration with silicon. All samples experienced a decrease in strength at higher temperatures. The samples processed with 0 IP cycles had a higher strength at 1000°C compared to 600°C. The decrease in strength at 600°C is anomalous because the decrease in strength of siliconized SiC typically does not occur until residual silicon softens, which is usually greater than 1200°C [37], and it remains the subject of continuing investigation.

**Figure 9:** 4-pt bending flexural strength vs. temperature for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

Figure 10 shows optical and scanning electron micrographs of the fracture surfaces of samples from flexural strength testing at room temperature where the SEM/EDS images are in secondary electron emission mode. Figure 10A corresponds to a sample processed with 3 IP cycles, and it is representative of the fracture surface of all the samples tested at room temperature, where failure occurred on the tensile side of the sample. The micrograph also shows the occurrence of a compression lip, which was common to most specimens. Also, different features were observed including microcracks and surface flaws from machining or pores. Figure 10B shows the fracture surface of a sample processed with 2\* IP cycles; and there are large pores ( $\geq 20$  micrometer), and Wallner lines in the silicon from crack propagation. Figure 10C shows fracture of a sample processed with 2 IP cycles, suggesting the occurrence of both transgranular and intergranular

fracture, similar to the observations of others from the evaluation of this class of materials [38], [39]. Figure 10D shows fracture of a sample processed with 3 IP cycles where large carbon-filled areas and pores were present in the fracture surface.

**Figure 10:** SEM images in secondary electron emission mode of fracture surfaces from room temperature flexural strength testing where a) was performed on a sample that was processed with 3 IP, and b)-d) are higher magnification images and EDS maps of samples processed with 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration, respectively.

Figure 11 shows plots of thermal expansion as a function of temperature for samples processed after 0, 2\*, 2, and 3 IP cycles followed by reactive silicon melt infiltration. The thermal strain was mostly linear between 300°C and 1,000° and there was no difference in behavior between the different samples. The values of the linear coefficient of thermal expansion were between 4.2 and 5 ppm/°C range, which is consistent with values published for siliconized silicon carbide [40].

**Figure 11:** Thermal expansion measurements between room temperature and 1,000°C using a thermomechanical analyzer.

Figure 12 shows the thermal conductivity values as a function of temperature for samples processed with 0, 2\*, 2, and 3 IP cycles plus the final silicon reactive melt infiltration step. The thermal conductivity was determined from the product of separate measurements of heat capacity, thermal diffusivity, and mass density. The thermal conductivity was lowest for the samples processed with 0 IP, which is consistent with the large amount of porosity of these samples. For the samples processed with 2 IP cycles, the amount of open porosity was lower, so

the values of thermal conductivity were higher. Values of thermal conductivity are comparable among the samples with varying phenolic IP with numbers close to bulk sintered SiC.

**Figure 12:** Thermal conductivity as a function of temperature for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

## **Conclusion**

The physical and mechanical properties of binder jet 3D printing with SiC powders, followed by multiple phenolic infiltration and pyrolysis cycles and a final silicon reactive melt infiltration step have been reported. It was found that optimum values of density, Young's modulus, flexural strength and thermal conductivity were obtained after 2 phenolic infiltration and pyrolysis cycles, and that diminishing returns were obtained for more than 2 phenolic infiltration and pyrolysis cycles as surface pores in carbon are closed upon the formation of SiC, resulting in reaction choking, and consequently residual porosity and residual unreacted carbon. The final product is a composite material comprised of the starting silicon carbide powders, silicon carbide from the reaction between carbon and molten silicon, a silicon matrix and in some cases small fraction of unreacted carbon from the pyrolysis of phenolic resin. The results from this investigation have provided insights for microstructural control in order to further improve the mechanical and physical properties of these materials.

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**Figure 3:** Raman spectroscopy analysis of SiC-C preforms after 1 phenolic IP cycle. Optical image (A), Raman spectra principal component mapping (B) and the principal component spectra (C)-(E) with different frequency ranges. 6H (white); 4H (yellow); 15R (green); epoxy (cyan). The grey shade around SiC particles in the optical image is amorphous carbon.

**Figure 4:** Optical, backscatter SEM images, and high magnification secondary electron SEM of cross-sections of parallelepiped samples of microstructures from samples processed with a) 0 IP cycles, b) 2\* IP cycles, c) 2 IP cycles, and d) 3 IP cycles.

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**Figure 6:** Raman spectroscopy principal component analysis of SiC-Si composite. (A) Optical micrograph of sample processed with 3 IP cycles followed by reactive melt infiltration. (B) Principal component analysis of the inset in Figure 5A revealing the various phases present. 6H (white); 3C (red); 15R (green); Si (cyan). Unreacted carbon is in the pores as shown in the optical image.

**Figure 7:** Typical 4-pt bending flexural stress versus crosshead displacement curves for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

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**Figure 9:** 4-pt bending flexural strength vs. temperature for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

**Figure 10:** SEM images in secondary electron emission mode of fracture surfaces from room temperature flexural strength testing where a) was performed on a sample that was processed with 3 IP, and b)-d) are higher magnification images and EDS maps of samples processed with 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration, respectively.

**Figure 11:** Thermal expansion measurements between room temperature and 1,000°C using a thermomechanical analyzer.

**Figure 12:** Thermal conductivity as a function of temperature for samples processed with 0, 2\*, 2, and 3 phenolic IP cycles and the final silicon infiltration.

**Table 1:** Information on preforms, predictions on SiC amount, and final compositions (where wt. = weight, cc = cubic centimeters, TD = theoretical density, vol. = volume, and L = liter).