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Ceramic Matrix Composites: An Investigation into Methods to Improve Environmental, Thermal, and Mechanical Properties

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Ceramic Matrix Composites: An Investigation into Methods to Improve Environmental, Thermal, and Mechanical Properties

Timothy P. Coons, Ph.D.
University of Connecticut, 2013

ABSTRACT

The overall goal of this dissertation was to develop and understand ceramic material systems in order to improve the environmental, thermal, and mechanical properties of Continuous Fiber Reinforced Ceramic Matrix Composites (CFR-CMC). Ceramic materials provide alternatives to metals for use in high-temperature applications (>800 °C) because of their melting points and thermo-mechanical behavior. Since mankind’s realization of the properties associated with ceramics, their efforts to exploit those attributes for structural applications have been limited by the inherent brittleness of ceramics. Incorporating reinforcing materials into ceramic materials has allowed significant progress in improving their toughness over monolithic counterparts. This allows for their use in structural applications. Moreover, the improved thermo-mechanical sta-
bility of reinforced ceramic materials has prompted extensive research of these composite materials. As the requirements for reinforced ceramic materials increase, the fabrication of multicomponent material systems, which attempt to enhance the environmental, thermal, and mechanical properties of ceramics, needs to be investigated.

A CFR-CMC is composed of continuous ceramic fibers, an interfacial coating on the fibers (if applicable), and a matrix to embed the fibers. The three components essentially operate together to provide toughening mechanisms that increase mechanical strength. Although CFR-CMCs can achieve the same or even surpass the mechanical strengths obtained by metal systems, environmental attack on CFR-CMC components at elevated temperatures significantly compromises their thermo-mechanical properties.

This dissertation addresses several different ceramic material systems used to improve mechanical properties after exposure to high-temperature oxidation. The first area of research discusses the synthesis of silicon based inorganic polymers to be used as matrix materials in CFR-CMCs. The focus of silicon based inorganic polymers is to create ceramic materials after pyrolysis and investigate their thermal stability. The inorganic polymer synthesized was modified through the doping of the backbone or the addition of reactive fillers to develop advanced material systems for high-temperature oxidative environments.
The second area investigated is gas phase deposition of non-oxide and oxide materials for advanced matrices and interface systems. Multilayered matrix materials were employed to mitigate oxidative degradation to the CFR-CMC components. Non-oxide and oxide interfaces were also investigated as possible protection from environmental degradation. The collected research developed and discussed throughout this dissertation provides information on concepts that individually improved the environmental, thermal and mechanical properties of CFR-CMCs. The manipulation of these material systems to provide the desired properties will ultimately be determined by the application.
Ceramic Matrix Composites: An Investigation into Methods to Improve Environmental, Thermal, and Mechanical Properties

Timothy P. Coons

B.S.E. Biomedical Engineering, University of Connecticut, 2008
Ceramic Matrix Composites: An Investigation into Methods to Improve Environmental, Thermal, and Mechanical Properties

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To my parents, Phil, Liz, Dave, and Deb
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2.3.30 Tensile strength as a function of coated thin film or films on Hi-Nicalon™ Type S fibers using parameters previously described. . 170
Continuous Fiber Reinforced Ceramic Matrix Composites (CFR-CMC) are receiving greater attention in high temperature (>800 °C) structural applications due to their ability to maintain their strength and toughness at these high temperatures. CFR-CMCs allow for an increase in efficiency due to the lower specific weight of the materials as compared to metals. [1] The mechanical strength and toughness of a CFR-CMC at high temperatures is dependent on the interactions between the matrix and the reinforcement fiber, as well as the interface between the two. [2] For a CFR-CMC to obtain high mechanical strength, the fiber/matrix interface needs to provide the correct amount of bonding/debonding between the fiber and the matrix. [3] There are stresses between each contact site that dominate the design and consistency of the structure. The overall objective of CFR-CMC development is to effectively redistribute concentrated stresses throughout the entire structure utilizing the components described above.

Inherently, each component is a variable requiring extensive testing to provide empirical data to optimize the final product. Figures 0.0.1 and 0.0.2 are
representations of toughening mechanisms for CFR-CMCs in which inelastic strains are created through matrix cracking and fiber failure. Fiber pull-out and matrix crack dispersion provide the fundamental principles to increase mechanical strength for a continuous fiber reinforced ceramic body.

![Diagram of toughening mechanisms](image)

Figure 0.0.1: Fundamental toughening mechanisms for a propagating crack in a CFR-CMC. [4]

The mechanisms that provide a CFR-CMC with increased mechanical strength depend on the loading technique as well as the design. Tensile loading and shear behavior are the damage mechanisms that are typically addressed when analyzing mechanical data. For this dissertation, only tensile or compressive loading will be discussed. The failure progression of a CFR-CMC under tensile loading is shown in Figure 0.0.3. This representation is specific
Figure 0.0.2: Representation of mechanical stresses applied to a 2D CFR-CMC. [4]
for the given system but the failure progression stages can be generalized for many CFR-CMC systems. Stage 1 shows a linear elastic region in which no micro-structural damage is observed in the CFR-CMC. Fabricated CFR-CMCs inherently have flaws, which are represented in the image associated with stage 1. As the load increases above the matrix strength, cracks are formed throughout the CFR-CMC structure. This region continues to increase in strength but a plateau is observed as matrix cracking is distributed throughout the entire structure. At this point, information pertaining to the design of a CFR-CMC can be obtained where the region first becomes nonlinear. This is referred to as the proportional limit stress. The proportional limit stress describes the region where the transition from elastic to plastic deformation occurs. [6]

Stage 3 represents the load transfer from the matrix to the reinforcing fibers. This occurs when there is complete saturation of cracks in the matrix. The cracks will stop at the interface of the fiber if there is an interface that has a lower fracture toughness than the matrix that is allowing the debonding to occur. If the interface does not exhibit this property, embrittlement will occur. Depending on the design of the CFR-CMC, stage 3 will produce a linear increase as the load completely transfers to the fibers. The mechanical stress will continue to increase at a similar rate until fiber failure -- stage 4 -- which will yield the ultimate tensile strength (UTS) of the system.

To visually understand the complexity of investigating the mechanical
strengths of CFR-CMCs, different CFR-CMC systems are shown in Figure 0.0.4. The systems represented are SiC/SiC, C/C and SiC/C. The denotation A/B refers to the reinforcing fiber material (A) and the matrix material (B). The dotted line refers to the CFR-CMC utilizing a carbon interface where the solid line refers to no interface used. The difference in stress vs. strain curves as well as the interface component will be discussed later. Analysis of failure mechanisms in CFR-CMCs are not limited to stress vs. strain curves, but include 6 independent parameters that are measured separately. These are: interfacial sliding stress, debonding energy, fiber properties, fiber/matrix misfit strain, matrix fracture energy, and elastic properties. [6] Mechanical data are reported as stress vs.
displacement curves, which are sufficient to determine the UTS and toughening mechanisms (i.e., fiber pull-out) throughout this dissertation.

![Graph showing tensile stress vs. strain for different CFR-CMCs](image)

Figure 0.0.4: Reported tensile stress vs. strain curves for different CFR-CMCs.

A ceramic body can utilize discontinuous and continuous reinforcing materials from whiskers to ceramic fibers. Continuous fiber reinforced ceramics have gained in popularity because of the increased mechanical performance that is observed. Continuous ceramic fiber development has advanced significantly from utilizing Chemical Vapor Deposition (CVD) to deposit on a tungsten core to the development of pre-ceramic polymers to draw into micron-sized filaments. Primarily, pre-ceramic polymers are of interest to develop continuous ceramic fibers because of the stability in oxidative or corrosive environments, the ease of processing, and the uniformity of distribution of
high-purity ceramic materials that can be achieved between temperatures of 1000 °C and 1600 °C. Information on the advancements of commercially available fibers can be found in several books and articles. [7–15] A drawback of this method of fiber forming is the incorporation of impurities, which can cause severe loss of mechanical strength. Impurities ranging from oxygen to carbon can cause spallations of the interfacial coating to microstructure changes. Currently, these drawbacks limit the availability of commercial fibers, however this creates opportunities in research to develop inorganic polymer systems that minimize these effects. Table 0.0.1 shows selected properties of commercially available continuous non-oxide and oxide fibers. There are several factors in choosing a ceramic fiber as the reinforcing material in a CFR-CMC but one of the main determining factors is cost. The cost depends on the complexity and availability of the ceramic fiber, and ranges from $1,300/kg to $25,000/kg.

As the requirements for materials to possess high temperature mechanical properties and to be able to resist environmental attack increases, research for more stable and stronger ceramic fibers will continue. As ceramic fibers obtain these enhanced requirements, interface and matrix components within the CFR-CMC will also need to be tailored for such conditions. The interface plays a crucial role in dissipating energy to increase mechanical strength in a CFR-CMC. Figure 0.0.5 shows a representation of the interaction of the interface with the matrix and the fiber. As stress is applied and matrix cracks are formed,
<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Fiber type</th>
<th>Composition (wt.%)</th>
<th>Tensile strength (GPa)</th>
<th>Strain to failure (%)</th>
<th>Specific gravity (µm)</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nippon Carbon</td>
<td>CG-Nicalon™</td>
<td>57 Si, 32 C, 12 O</td>
<td>3</td>
<td>1.4</td>
<td>2.55</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Hi-Nicalon™</td>
<td>62 Si, 37 C, 0.5 O</td>
<td>2.8</td>
<td>2.74</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hi-Nicalon™ Type S</td>
<td>69 Si, 31 C, 0.2 O</td>
<td>2.6</td>
<td>3.1</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Ube Chemicals</td>
<td>Tyranno®</td>
<td>Si, C, O, Ti &lt;5</td>
<td>3</td>
<td>1.5</td>
<td>2.4</td>
<td>9</td>
</tr>
<tr>
<td>Dow Corning</td>
<td>HPZ</td>
<td>59 Si, 10 C, 28 N</td>
<td>2.2</td>
<td>1.5</td>
<td>2.35</td>
<td>10</td>
</tr>
<tr>
<td>3M</td>
<td>Nextel™ 312</td>
<td>Al₂O₃, SiO₂, B₂O₃</td>
<td>1.75</td>
<td>1.1</td>
<td>2.7</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Nextel™ 440</td>
<td>Al₂O₃, SiO₂, B₂O₃</td>
<td>2.1</td>
<td>1.1</td>
<td>3.05</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Nextel™ 480</td>
<td>Al₂O₃, SiO₂, B₂O₃</td>
<td>2.3</td>
<td>1</td>
<td>3.05</td>
<td>11</td>
</tr>
</tbody>
</table>
the interface on the fiber debonds, allowing the crack to propagate around the surface of the fiber and absorb energy. Examples of toughening mechanisms and energy dissipation are shown in Figures 0.0.6 and 0.0.7. These figures are stereo-micrographs, which provide visual depth to aid in understanding the interactions between the ceramic fiber, interface, and matrix. Note 3-dimensional glasses are need to view the figures.

![Diagram of interface debonding](image)

**Figure 0.0.5:** Representation of the interface debonding from the fiber.

There are several methods of depositing an interface onto a fiber that include, but are not limited to, dip coating (e.g., sol-gel, slurry) and gas phase chemistries, one of which is CVD. The method of choice for this dissertation was CVD. This provided benefits of a non-line-of-sight coating, uniform thick-
ness, and limited impurities incorporated within the layer. The drawbacks of this method are that precise conditions must be maintained to obtain the desired coating. Figure 0.0.8 shows the different morphologies of coatings that can be deposited as a function of temperature and supersaturation. The deposition of powders occurs when supersaturation is increased and temperature is decreased. The condensation of atoms that occurs through nucleation is kinetically controlled and powders are produced. Thermodynamics play a greater role when temperature is increased and supersaturation is decreased. With increasing temperature, the surface energies are decreased for both the thin film and the substrate, promoting an epitaxial film to be deposited. The morphology of choice for an interface in a CFR-CMC range between amorphous
Figure 0.0.7: A stereo-micrograph showing a ceramic fiber protruding from the surrounding interface and matrix. (Note 3D glasses are needed)
and columnar growths. This range of morphologies has proven crucial to the bonding/debonding that provides toughening mechanisms in a CFR-CMC.

Currently, there are only a limited number of ceramic materials that can provide this bonding/debonding interaction. These materials include, but are not limited to, pyrolytic carbon (PyC), [5, 17] boron doped carbon, [18] boron nitride, [19–22] silicon doped boron nitride, [23, 24] multi-layered coatings of boron nitride with either silicon carbide or silicon nitride, [25,26] and zinc oxide and lanthanum phosphate. [2] PyC was one of the first materials investigated as an interfacial material for use in high temperature composites. Although the use of carbon as an interfacial material provided both strength and toughness in a composite, the carbon interface suffered from high temperature oxidation. [27] This environmental effect is observed for many non-oxide materials when exposed to long-term oxidation. The main objective of investigation for this dissertation will be to develop material systems to inhibit oxidation and corrosion for the interface and matrix in a CFR-CMC. The CVD process will be the method used throughout this research for all of the interfacial and matrix coatings.

Depending on the material deposited, the CVD process provides several benefits, but a drawback occurs when a material needs elevated temperatures to be formed. This can create thermal expansion mismatches and undesirable stresses within the material system. [28, 29] Understanding this principle is
Figure 0.0.8: Morphology of coatings as a function of temperature and supersaturation. [16]
critical to developing new interfaces and matrices. Efforts were made to choose material systems that minimize the differences between the substrate and the coating layer. This research examined non-oxide and oxide coatings for use as interfaces and matrices in CFR-CMCs.

CFR-CMCs are fabricated by consolidating a matrix around continuous ceramic fibers (coated or uncoated). This can be achieved by hot-pressing, [30] Chemical Vapor Infiltration (CVI), [31, 32] Melt Infiltration (MI), [33] or by Polymer Impregnation and Pyrolysis (PIP). [34–36] Commonly, woven fabric or continuously spun fibers are used as reinforcing materials to provide support in the X and Y axis directions. Multiple plies (layers) of fabric are combined using consolidation techniques to increase support. Recently, the PIP process has gained popularity due to the ease of fabrication and the ability to use conventional manufacturing techniques. Multiple impregnations of a pre-ceramic polymer (sometimes referred to as an inorganic polymer or resin) are used to form a dense matrix around the reinforcing material (Figure 0.0.8) through a process called pyrolysis. Pyrolysis is the decomposition of an organic, or in this research inorganic, material at elevated temperatures to irreversibly change the chemical and physical composition of the material. This conversion is conducted under non-oxygen containing environments. The benefits of the PIP process are that complex shapes can be fabricated and fabrication time is decreased. There are drawbacks to this process, which include a lim-
ited number of available pre-ceramic polymers and interfacial degradation (if applicable) when the inorganic material is converted into its final form.

Figure 0.0.9: Diagram of the PIP process fabricating a CFR-CMC.

Pre-ceramic polymers are the primary component to fabricating a matrix for a PIP CFR-CMC. These materials have a distinct advantage in the PIP fabrication process because some inorganic polymers have the ability to cross-link at low temperatures (≈200 - 300°C). At these temperatures, complex shapes can be modeled more easily as compared to using the CVI or MI. Complex shapes are formed using “tooling,” which refers to a material system of interest taking the shape of a pre-designed substrate. Curing at low temperatures
allows for more economical pre-designed substrates to be used (e.g., stainless steel). The main disadvantages to using CVI and MI to fabricate a CFR-CMC are time and elevated temperatures. Similar to the PIP process, the fabric needs to be laid up and compressed in tooling to form the multiple plies into a rigid structure. The CVI and MI processes have to use expensive and intricate materials for the tooling because of elevated temperatures observed during these processes. After the multiple plies of fabric for a CFR-CMC have been impregnated with the inorganic polymer and laid up in the tooling, a curing process to rigidify the inorganic polymer is performed by heating the tooling to 300 °C at 5 °C/min. At this point the fabric is bound together by a disordered polymer network. To convert the disordered network to a crystalline ceramic material, additional thermal treatments are needed. The polymer-to-ceramic conversion takes place through the pyrolysis cycle, in which the amorphous polymer network is heated to temperatures between 900 °C and 1800 °C to create an ordered ceramic structure. Table 0.0.2 describes the pyrolysis cycle from a polymer to an ordered ceramic material.

For decades, the primary outlook of pre-ceramic polymers has been to control the properties and structure of ceramic materials on an atomic level. This potential for developing ceramic materials on an atomic level was not recognized until the 1960s with the work developed by Yajima et al. and Veerbeck and Winter. [37,38] Since then, many different methods for the development of
Table 0.0.2: A temperature profile of the polymer-to-ceramic transition.

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-200 °C</td>
<td>Loss of organic solvents (e.g., toluene, THF). Typically at this stage the precursor (polysilane/carbosilane) is still a monomer (i.e. no cross-linking has occurred)</td>
</tr>
<tr>
<td>200-400 °C</td>
<td>Loss of volatilities (e.g., low molecular weight oligomers). At this stage cross-linking occurs through condensation forming the basic polymer skeleton.</td>
</tr>
<tr>
<td>400-500 °C</td>
<td>Loss of hydrocarbons (e.g., CH₄, C₂H₄, etc.) and hydrogen. Polymer-to-ceramic transformation starts to occur at this stage.</td>
</tr>
<tr>
<td>900-1200 °C</td>
<td>Depending on the pre-ceramic polymers backbone varying degrees of crystallization develop.</td>
</tr>
<tr>
<td>1200-1700 °C</td>
<td>Highly crystalline ceramic materials form.</td>
</tr>
</tbody>
</table>

non-oxide based ceramics have been reported. [39–41] The objectives for developing pre-ceramic polymers include the ability to use inexpensive materials, stability (shelf-life), and the potential for doping elements while producing a ceramic material with high ceramic yields (>80%). A ceramic yield is the percent mass that is retained after pyrolysis (Equation 1).

\[
\text{Ceramic yield} = \frac{\text{Matrix mass after pyrolysis}}{\text{Matrix mass after cure}} \times 100 \tag{1}
\]

Commercially available polymers such as Ceraset® Polysilazane 20 and S200 polymer distributed by COI Ceramics, Inc., are reliable for several years but lack the ceramic yield or are hard to manufacture. [42, 43] For these reasons, research in silicon-based inorganic polymers has not subsided. The current research progression is shown in Figure 0.0.9. The routes to fabri-
cate silicon-based inorganic polymers from a single precursor are extensive. [37–41, 44–49] Introducing multiple silicon precursors to develop complex inorganic polymer systems have also been fabricated, but an emerging area of interest is the modification of the polymer backbone to tailor the ceramic material after pyrolysis. [41,54,55] Recently, the incorporation of dopant precursors (e.g., B, Ti, etc.) have shown promise in fabricating ceramic materials suitable for enhanced chemical and physical properties of a CFR-CMC. [59,60] Furthermore, the potential applications of inorganic polymers for use in CFR-CMCs are not limited to matrix materials, but can also be derived into reinforcing materials (e.g., continuous fibers). There are challenges with using inorganic polymers to fabricate continuous ceramic fibers as well as matrices. Despite the challenges, this area of research continues to develop promising material systems for advancements in CFR-CMCs.

The scope of current research for a CFR-CMC is not limited to tailoring the chemical and physical properties of inorganic polymers but also the development of interfacial coatings to improve environmental, thermal, and mechanical properties. Non-oxide and oxide interfacial coatings are key to advancing the operational range of CFR-CMCs. The interfacial coatings discussed in this dissertation consist of individual or combinations of materials to control the stability of the coating under oxidation and corrosion attack. Over time, ceramic materials can form micro-cracks that further expose the ceramic
Figure 0.0.10: Methods to fabricate silicon-based inorganic polymers. [16]
material to oxygen or other corrosive elements, which form undesirable phases to the detriment of the properties of the CFR-CMC components. Creating materials that can mitigate the damage caused from oxidation or corrosion by reacting with the source prior to reaching crucial components is vital to advancing this science. Examples of materials that exhibit qualities appropriate for CFR-CMCs include metals, borides, carbides, nitrides, and silicides (e.g., W, TiB$_2$, HfB$_2$, ZrB$_2$, MoB$_2$, HfC, TaC, ZrC, SiC, HfN, TaN, TiN, ZrN, TaSi, Zr$_2$Si, WSi$_2$, MoSi$_2$, etc). The material systems developed herein are those focused on inhibiting the damage caused by environmental attack.

This dissertation will discuss the modification of silicon-based inorganic polymers either through the backbone or using reactive fillers, shelf-healing matrix systems, and non-oxide and oxide interfaces for CFR-CMCs. The approach to develop a new material system was to first understand the chemical and physical properties of the material of interest, propose a mechanism to fabricate the desired material system, construct an experimental setup, and characterize the material system. The ceramic material systems presented show significant advancements in the current science and introduce different avenues to improve the environmental, thermal, and mechanical properties. In addition to improving the environmental, thermal, and mechanical properties, it was desired that a silicon-based inorganic polymer be developed using simple low-cost precursors to show an understanding of the demands and
potential utilization of this technology. The construction of ceramic materials after pyrolysis from silicon-based inorganic polymers by means of doping or reacting with the polymer backbone also provides valuable insight into inorganic polymer research. Gas phase deposition of a “self-healing” matrix system and non-oxide and oxide interfaces complement the overall goal of increasing the environmental protection of CFR-CMCs while maintaining thermal and mechanical properties. Additionally, the impact of these new material systems will not be limited to its individual uses but provide a basis for which different combinations of these materials can be employed. Table 0.0.3 presents materials that have attractive properties for the applications discussed throughout the dissertation.

Table 0.0.3: Materials deposited by CVD at the University of Connecticut

<table>
<thead>
<tr>
<th>Carbides</th>
<th>Nitrides</th>
<th>Oxides</th>
<th>Borides</th>
<th>Metals</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>Si$_3$N$_4$</td>
<td>Al$_2$O$_3$</td>
<td>TiB$_2$</td>
<td>Fe</td>
<td>C</td>
</tr>
<tr>
<td>TiC</td>
<td>TiN</td>
<td>TiO$_2$</td>
<td>Si</td>
<td>MoSi$_2$</td>
<td></td>
</tr>
<tr>
<td>B$_4$C</td>
<td>ZrN</td>
<td>SiO$_2$</td>
<td>B</td>
<td>TiSi$_2$</td>
<td></td>
</tr>
<tr>
<td>BC$_x$</td>
<td>AlN</td>
<td>ZnO</td>
<td>Zn</td>
<td>ZnSe</td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>Y$_2$O$_3$</td>
<td>ZrO$_2$</td>
<td>YSZ</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

YSZ = Yttria stabilized Zirconia
Chapter 1

Polymeric Matrix Systems for PIP CFR-CMCs

1.1 Polymer Synthesis

Polysilazane-based pre-ceramic polymers have received increasing attention due to their ability to produce SiC and Si$_3$N$_4$ based ceramic materials. [37–41,44–49] SiC and Si$_3$N$_4$ have attractive properties for high-temperature applications, which include thermal stability in oxidizing environments, chemical inertness, and strength. [50–52] Along with these properties, extensive research into inorganic polymers was conducted because of their ability to convert from a viscous liquid to a solid network. Developing a CFR-CMC through the PIP process requires a viscous inorganic polymer to wet the reinforcing material and the material to polymerize to form a rigid body and finally convert to a ceramic material after pyrolysis.

Previous research into polymer synthesis utilized vinyltrichlorosilane (VTS) as the starting precursor. [40,41] Vinyltrichlorosilane proved to be an interesting precursor that, after ammonolysis and pyrolysis, had the ability to tailor the ceramic material depending on the pyrolyzing environment. The
VTS precursor also provided a vinyl group, which aided in cross-linking. The first thought was that the vinyl group could prematurely induce cross-linking due to its reactivity [44] in the presence of moisture; however evidence also pointed to the vinyl groups not providing protection against hydrolysis and/or condensation to the SiN bond. [53] This presented a shelf-life problem because the polymer was limited to less than three days before cross-linking occurred. For industrial applications, this is an undesirable outcome that resulted in diluting the polymer with more solvent to provide a longer shelf-life, which reduced the overall polymer-to-ceramic yield. Synthesis and characterization of a silicon-based inorganic polymer that preserves the ability to tailor the final ceramic material increases the shelf-life and provides functional groups that act as addition sites for modifying precursors are addressed in this section.

A polysilazane-based pre-ceramic polymer was synthesized via co-ammonolysis of vinyltrichlorosilane and dichloromethylsilane (DCMS). The co-ammonolysis developed polymers with varying branched and unbranched structures. The vinyl moiety created a branched structure due to its reactive nature while the methyl moiety provided an unbranched structure. [54] Lücke et al. provided insight into this co-ammonolysis process between the VTS and DCMS precursors. [54] Although the research studied many different combinations of silicon-containing precursors, for the VTS and DCMS precursor combination, the research only analyzed a molar ratio of 1:1. The results
showed a $\beta$-SiC ceramic after a pyrolysis to 1800 °C in an argon atmosphere. This section will provide analysis of the as-synthesized polysilazane-based pre-ceramic polymer with VTS to DCMS molar ratios of 1:1 to 1:0.6, and 1:0.4 and provide a starting pre-ceramic polymer for doping metals to the backbone in Section 1.2.

This reaction follows the general equation described in the literature for the ammonolysis of other similar silane precursors. [37] The proposed reaction is described below (Figure 1.1.1) and results in a linear polymethylvinylsilazane (PMVSZ) network.

![Figure 1.1.1: Proposed linear structure of the as-synthesized PMVSZ polymer.]

1.1.1 Experimental Procedure

A polymethylvinylsilazane polymer with Si-Vinyl, Si-CH$_3$, Si-H, and N-H groups was synthesized by the ammonolysis of vinyltrichlorosilane (Gelest,
Inc.) and dichloromethylsilane (Gelest, Inc.) dissolved in reagent grade toluene (Alfa Aesar®) and reagent grade tetrahydrofuran (THF) (Alfa Aesar®). To synthesize the polymer, THF and toluene were first added to a 5000 mL three-neck round bottom flask equipped with a 9 mm silica injector rod, a mechanical stirrer, and a reflux condenser (Figure 1.1.2).

Ultra High Purity (UHP) nitrogen was first introduced into the flask in order to purge any residual air from the reactor. THF and toluene were then added to the flask under anhydrous conditions, followed by the addition of an appropriate amount of VTS and DCMS (1:1, 1:0.6, and 1:0.4 molar ratios). Anhydrous ammonia gas was then bubbled into the solution via the silica tube accompanied by mechanical stirring. A separate flow of nitrogen was used to dilute the ammonia and prevent the exhaust from becoming clogged with ammonium chloride. The resulting mixture was filtered to remove any by-products formed from the reaction. The by-product (NH₄Cl) was removed via a vacuum filtration system, which consisted of a 1 L Erlenmeyer vacuum flask and a 600 mL Büchner funnel equipped with a 4 - 5 µm ceramic frit. Prior to the filtration, the funnel was rinsed several times with toluene to remove any adsorbed moisture in the frit. If the filter became clogged, this meant that the reaction did not go to completion and the mixture had to be placed back into the reactor to be further ammonolyzed. Once the solid ammonium chloride was separated from the polymer/THF/toluene solution, the solvent was removed.
Figure 1.1.2: Reaction vessel designed and built to synthesize the PMVSZ polymer from chlorosilane precursors.
via a rotary evaporator to yield a pale yellow, viscous liquid. The density of the polymer was determined using a 10 mL pycnometer. The shelf-life of the PMVSZ polymer was around three months but can be extended if kept under a nitrogen atmosphere and stored below 0°C.

1.1.2 Characterization Techniques

Attenuated Total Reflectance (ATR) characterization of the liquid PVSZ and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers was performed using a Nicolet iD3 ATR with a resolution of 4 cm\(^{-1}\). Raman spectroscopy was used to study structural changes of the different polymers during the curing process between room temperature and 300 °C. These temperatures are in a typical range where inorganic polymers cross-link, forming a solid network. The molecular weights of the polymers were determined using a GPC Viscotek MAX TDA 302 tetra-detector. The ceramic powders produced for Thermogravimetric Analysis (TGA) and X-ray Powder Diffraction (XRD) analysis were obtained by pouring liquid PMVSZ polymer into a 50 mL beaker and cured to 300 °C at 2 °C/min under house nitrogen. TGA characterization was performed utilizing a SDT Q600. The TGA experiments were carried out by placing the cured PVSZ and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers in an Al\(_2\)O\(_3\) boat and heated to 1400 °C at 2 °C/min and held at temperature for five minutes. Fourier Transform Infrared (FT-IR) spectroscopy was conducted on a Nicolet 8700 with a resolution of 4 cm\(^{-1}\). Samples of the PVSZ polymer and PMVSZ polymers were heat treated
to 500 °C, 700 °C, 900 °C, and 1100 °C in five different atmospheres (UHP Ar, UHP N₂, UHP H₂, UHP He, and anhydrous NH₃) and pellets were fabricated with KBr. For XRD analysis, the cured polymers were put into an alumina combustion boat and pyrolyzed in five different atmospheres (Ar, H₂, He, N₂, and NH₃) at a heating rate of 2 °C/min to 1600 °C and held at the final temperature for two hours. Caution should be taken in using gases such as hydrogen and ammonia. The XRD patterns were obtained using a Scintag 2000 XDS instrument with a Cu Kα X-ray source with a beam voltage of 45 kV and 40 mA beam current. The scan was 5 - 90° with a scan rate of 0.1°/min. X-ray diffraction patterns were verified by JCPDS cards and Jade™ X-ray software. Elemental analysis of carbon, nitrogen, and hydrogen on pyrolyzed PVSZ and PMVSZ ceramic materials were conducted using an Elementar vario Micro cube model CHNS.

1.1.3 Attenuated Total Reflectance Spectroscopy

ATR spectroscopy was used to analyze the structure of the liquid PVSZ and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers shown in Figure 1.1.3. For the labs capabilities, the ATR spectroscopic technique provided clearer spectra for liquid polymers vs. the FT-IR spectrometer. The structural groups of the liquid PVSZ and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers share similar stretches and bands, which are summarized in Table 1.1.4.

The spectrum in Figure 1.1.3 shows a broad absorption band at 3380
Figure 1.1.3: ATR of PVSZ and PMVSZ polymers. The insert shows an overlay of the varying Si-H stretch due to the different ratios of VTS to DCMS precursor.

Table 1.1.4: Similar frequencies and structural groups for typical PVSZ and PMVSZ polymers.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Structural Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3380</td>
<td>N-H</td>
</tr>
<tr>
<td>3480 and 3200</td>
<td>NH(_2)</td>
</tr>
<tr>
<td>3048</td>
<td>CH (vinyl)</td>
</tr>
<tr>
<td>2952 and 2896</td>
<td>CH (aliphatic)</td>
</tr>
<tr>
<td>2078</td>
<td>Si-H</td>
</tr>
<tr>
<td>1397 and 1246</td>
<td>CH(_3)-Si</td>
</tr>
<tr>
<td>1180</td>
<td>C-O-C</td>
</tr>
</tbody>
</table>
cm$^{-1}$, which is attributed to N-H bonds. The shoulders at 3480 cm$^{-1}$ and 3200 cm$^{-1}$ indicate stretches corresponding to NH$_2$. The two nitrogen bonding environments support the presence of the linear structure seen in Figure 1.1.1. The presence of Si-CH=CH$_2$ is seen at 3050, 1920, 1590, and 1400 cm$^{-1}$, meaning that there is no degradation of the vinyl group during the ammonolysis process. Residual bands at 2980, 2870, 1450, 1180, 1070, and 1010 cm$^{-1}$ are attributed to THF and toluene.

1.1.4 Raman Spectroscopy

Figures 1.1.4 - 1.1.7 show Raman spectra for PMVSZ 1:1, PMVSZ 1:0.6, PMVSZ 1:0.4, and PVSZ polymers, respectively. The polymer was heated to 300 °C at a rate of 2 °C/min under flowing nitrogen. The polymer was removed from the furnace at intervals of 50 °C and Raman spectroscopy was performed on the material. Raman shifts for N-H bonds (3380 cm$^{-1}$), Si-H bonds (2078 cm$^{-1}$), and Si-CH=CH$_2$ bonds (3050, 1920, 1590, and 1400 cm$^{-1}$) can be observed in all spectra (no Si-H in the PVSZ polymer). The Raman spectra showed a significant trend for all of the polymers. As temperature increased there was a decrease in the vinyl moiety (3048 cm$^{-1}$) and an increase in the aliphatic C-H moiety (2896 and 2952 cm$^{-1}$) while little to no change was observed to the Si-H bonds. This suggested a cross-linking mechanism through a polyaddition (Figure 1.1.8) reaction rather than hydrosilylation (Figure 1.1.9) for the characterized polymers.
Figure 1.1.4: Raman compilation of the thermal treatment from 50 °C to 300 °C for the PMVSZ 1:1 polymer.

Figure 1.1.5: Raman compilation of the thermal treatment from 50 °C to 300 °C for the PMVSZ 1:0.6 polymer.
Figure 1.1.6: Raman compilation of the thermal treatment from 50 °C to 300 °C for the PMVSZ 1:0.4 polymer.

Figure 1.1.7: Raman compilation of the thermal treatment from 50 °C to 300 °C for the PVSZ polymer.

Figure 1.1.8: Polymer cross-linking through the polyaddition reaction.
1.1.5 Thermogravimetric Analysis

The results of the TGA are shown in Figure 1.1.10. From the analysis, the resulting ceramic yields were 87%, 86.9%, 85.5%, and 85% for the PVSZ polymer, the PMVSZ 1:0.4 polymer, the PMVSZ 1:0.6 polymer, and the PMVSZ 1:1 polymer, respectively. The decrease in ceramic yield from the PVSZ polymer to the PMVSZ 1:1 polymer can be attributed to the decrease in cross-linking reactivity from a branched polymer to a more unbranched polymer. As a result, it was determined that low molecular weight oligomers evaporate before the polymer-to-ceramic conversion. [59]
Figure 1.1.10: TGA of PVSZ polymer and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers heated to 1400 °C under Ar.

1.1.6 Gel Permeation Chromatography

The average molecular weight of the PVSZ and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers are reported in Table 1.1.5. The instrument used to determine the molecular weight of the polymer has a lower limit of detection at around 1,000 g mol$^{-1}$. Therefore, the molecular weight is an average and will have a higher standard deviation of around 50 g mol$^{-1}$. These molecular weights are close in comparison to other commercially available polymer resins. [42, 43]
Table 1.1.5: Molecular weights of as-synthesized PMVSZ and PVSZ polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular weight (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMVSZ 1:1</td>
<td>721</td>
</tr>
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</tr>
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<td>PVSZ [40]</td>
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**1.1.7 Fourier Transform Infrared Spectroscopy**

FT-IR spectroscopy was used to observe the polymer-to-ceramic transition of the PVSZ and PMVSZ 1:1 polymers. Figures 1.1.11 to 1.1.15 show the compilation of FT-IR spectra for the PMVSZ 1:1 polymer heat treated to 500 °C, 700 °C, 900 °C, and 1100 °C in Ar, N\(_2\), H\(_2\), He, and NH\(_3\), respectively. The other polymer systems showed the same trends as the PMVSZ 1:1 polymer, and this is the rationale for only reporting one compilation. Figures 1.1.16 and 1.1.17 show the polymer-to-ceramic transition for the PVSZ polymer heat treated to 500 °C, 700 °C, 900 °C, and 1100 °C in Ar and He atmospheres, respectively.
Figure 1.1.11: FT-IR compilation of the PMVSZ 1:1 polymer thermal treatment under an Ar environment from 500 °C to 1100 °C.

Figure 1.1.12: FT-IR compilation of the PMVSZ 1:1 polymer thermal treatment under an N₂ environment from 500 °C to 1100 °C.
Figure 1.1.13: FT-IR compilation of the PMVSZ 1:1 polymer thermal treatment under an H\textsubscript{2} environment from 500 °C to 1100 °C.

Figure 1.1.14: FT-IR compilation of the PMVSZ 1:1 polymer thermal treatment under an He environment from 500 °C to 1100 °C.
Figure 1.1.15: FT-IR compilation of the PMVSZ 1:1 polymer thermal treatment under an NH$_3$ environment from 500 °C to 1100 °C.

Figure 1.1.16: FT-IR compilation of the PVSZ polymer thermal treatment under an Ar environment from 500 °C to 1100 °C.
Figure 1.1.17: FT-IR compilation of the PVSZ polymer thermal treatment under an He environment from 500 °C to 1100 °C.
1.1.8 X-ray Powder Diffraction

Figures 1.1.18 - 1.1.22 show XRD patterns for the PMVSZ (1:1, 1:0.6, and 1:0.4) polymers and the PVSZ polymer pyrolyzed under argon, helium, hydrogen, nitrogen, and ammonia atmospheres, respectively. Each pattern is subsequently followed by Tables 1.1.6 - 1.1.10 specifically relating the observed reflections to ASTM standards. Note that reflections with low intensities are not indexed.

Figure 1.1.18: XRD patterns for PVSZ polymer and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers pyrolyzed to 1600 °C under Ar (\(\alpha\)-SiC, \(\beta\)-SiC, \(\alpha\_3\)N\(_4\)).
Table 1.1.6: JCPDS vs. experimental reflections for the PMVSZ polymers and PVSZ polymer pyrolyzed to 1600 °C under Ar.

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<th>I/I₀</th>
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<td>72.05</td>
<td>100</td>
<td>72.13</td>
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α-Si₃N₄:

| 1 0 1 | 20.59 | 78 | – | – | – | – | 20.69 | 20 | 20.82 | 10 | 20.52 | 24 |
| 1 1 0 | 22.92 | 41 | – | – | – | – | 23.12 | 12 | 23.45 | 5 | 22.99 | 29 |
| 2 0 1 | 30.99 | 100 | – | – | 30.98 | 4 | 31.21 | 99 | 30.84 | 29 |
| 1 0 2 | 34.56 | 85 | – | – | – | – | – | – | 34.4 | 24 |
| 2 1 0 | 35.33 | 99 | – | – | 35.9 | 100 | 35.62 | 70 | 35.69 | 100 |
| 2 1 1 | 38.9 | 54 | – | – | 38.1 | 40 | – | – | 38.96 | 40 |
| 3 0 1 | 43.48 | 44 | – | – | 43.6 | 5 | 43.62 | 22 | 43.62 | 29 |

* = Not observed
"*" = ASTM Card No.: 22-1319
β = ASTM Card No.: 29-1129
\(^\wedge\) = ASTM Card No.: 41-360
Figure 1.1.19: XRD patterns for PVSZ polymer and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers pyrolyzed to 1600 °C under He (* = α-SiC, β = β-SiC).
Table 1.1.7: JCPDS vs. experimental reflections for the PMVSZ polymers and PVSZ polymer pyrolyzed to 1600 °C under He.

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– = Not observed
*=ASTM Card No. : 22-1319
β=ASTM Card No. : 29-1129
Figure 1.1.20: XRD patterns for PVSZ polymer and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers pyrolyzed to 1600 °C under H₂ (* = α-SiC, β = β-SiC, ^ = α₃SiN₄, # = Silicon).
Table 1.1.8: JCPDS vs. experimental reflections for the PMVSZ polymers and PVSZ polymer pyrolyzed to 1600 °C under H₂.

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- = Not observed
* = ASTM Card No.: 22-1319
β = ASTM Card No.: 29-1129
^ = ASTM Card No.: 41-360
# = ASTM Card No.: 27-1402

45
Figure 1.1.21: XRD patterns for PVSZ polymer and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers pyrolyzed to 1600 \(^\circ\)C under N\(_2\) (* = \(\alpha\)-SiC, \(\beta\) = \(\beta\)-SiC, ^ = \(\alpha\)-Si\(_3\)N\(_4\)).
Table 1.1.9: JCPDS vs. experimental reflections for the PMVSZ polymers and PVSZ polymer pyrolyzed to 1600 °C under N₂.

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<th>I/I₀</th>
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= Not observed
*=ASTM Card No. : 22-1319
β=ASTM Card No. : 29-1129
^=ASTM Card No. : 41-360
Figure 1.1.22: XRD patterns for PVSZ polymer and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers pyrolyzed to 1600°C under NH₃ (\(\alpha\)-Si₃N₄).
Table 1.1.10: JCPDS vs. experimental reflections for the PMVSZ polymers and PVSZ polymer pyrolyzed to 1600 °C under NH₃.

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=ASTM Card No.: 41-360
1.1.9 Elemental Analysis

Table 1.1.11 shows data from the elemental analysis of carbon, nitrogen, and hydrogen on pyrolyzed PMVSZ polymers and PVSZ polymer to 1600°C under different atmospheres. The remaining concentration calculated by difference was attributed to SiOₓ. This oxygen inclusion is attributed to the vulnerability of the Si-NH₂ and/or Si-NH-Si groups to hydrolysis in the presence of moisture. Previously reported oxygen concentrations between 1 - 10 at.% are consistent with other reported values. [40, 44] Due to limitations, the oxygen concentration for the PMVSZ ceramic materials and PVSZ ceramic material were estimated to be between 1 - 6 at.%. Ceramic yields are also presented as a function of atmosphere and polymer blend.
Table 1.1.11: Elemental analysis of pyrolyzed PMVSZ polymers and PVSZ polymer to 1600 °C in different atmospheres.

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<th>Ceramic yield (%)</th>
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<tr>
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<tr>
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<td>PMVSZ 1:0.6</td>
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</tr>
<tr>
<td></td>
<td>PVSZ</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Where, 0.01 ≤ x ≤ 0.06
*Note: % SiOₓ was calculated by difference
1.1.10 Discussion

Prior to the introduction of ammonia gas into the THF/toluene/VTS/DCMS solution, the solution was a faint yellow color. Once the ammonia gas was introduced, the color changed to milky white due to the formation of the by-product ammonium chloride (NH$_4$Cl). During the first half of the synthesis process, the reaction vessel showed little to no variation in temperature. Throughout this process, the first and second chlorine atoms on the vinyltrichlorosilane and dichloromethylsilane were lost, as reported by Matsumoto et al. [42] During the last half of the reaction, the reaction underwent an exothermic process causing an increase in temperature. This has been attributed to the removal of the third chlorine atom. Due to this exothermic process, a reflux condenser was added to the setup in order to retain the reaction solution. The addition of the stirrer motor broke up the agglomerated NH$_4$Cl solid to ensure that the chlorosilanes completely reacted. The reaction was considered completed when the by-product (NH$_4$Cl) had the resemblance of “cottage cheese”. The PMVSZ polymers ranged in color from a pale yellow to a cloudy solution depending on the ratios used. The polymers had a density of approximately 1.0 g/cm$^3$.

As expected, the ATR, GPC, and TGA data all confirmed the structure and thermal stability of the polymers. The ATR data showed the decreasing absorbance of the Si-H stretch from the PMVSZ 1:1 polymer to the PVSZ polymer.
The GPC data denoted a small difference between the four polymer systems which is comparable to other polymer systems. [42,43,54]

Prior to the polymers’ exposure to elevated temperatures, Raman spectroscopy provided a possible understanding into the cross-linking mechanism. The Raman data suggested a polyaddition reaction through the vinyl moieties. The TGA data showed a decrease in ceramic yield with increasing DCMS precursor. Previous research has shown that a higher degree of cross-linking is one of many mechanisms that decrease decomposition during pyrolysis and thus increase ceramic yield and reduce volume contraction. [46,60–62] The thermogram presented in Figure 1.1.10 shows a mass loss event between 500 °C and 600 °C, which is attributed to the mineralization of the polymer to a ceramic. At these temperatures hydrogen bonds in the polymer (C-H, N-H, and Si-H) become unstable, thus releasing hydrogen and resulting in a solid SiNC network. Previous research reported residual gas analysis in combination with the TGA data from liquid polymer samples that exhibited three mass loss events. These were attributed to the evolution of the solvent at 200 °C, NH₃ and CH₄ between 250 °C and 425 °C, and H₂ beginning at 500 °C. Due to the use of cross-linked solid samples for the TGA, only one mass loss event was observed.

The polymer-to-ceramic transitions as a function of atmosphere for the PVSZ and PMVSZ (1:1, 1:0.6, and 1:0.4) polymers were studied using FT-IR. Similar trends were observed for the PVSZ and PMVSZ polymers where
transmittance bands for Si-H, C-H, and N-H strongly decrease with increasing temperatures. At temperatures above 900°C, almost all observed bands for Si-H, C-H, and N-H are gone except for a broad band between 700 and 1100 cm\(^{-1}\), which was attributed to Si-N or Si-C bonds. Unfortunately these results do not provide insight into the mechanism for which these polymers can be tailored as a function of atmosphere.

X-ray diffraction was used to characterize the ceramic material produced from the four polymer systems in different pyrolyzation atmospheres. This characterization technique is limited to only crystalline materials and can only provide information on the final product. Crystallization temperatures for pre-ceramic polymers can vary depending on a variety of conditions so 1600°C was selected to provide a high degree of crystallization in the resulting ceramic material. The results showed that depending on the pyrolyzing atmosphere of the polymer-to-ceramic conversion, a tailored material of different combinations of silicon, nitrogen, and/or carbon can result. This is seen in an argon atmosphere where \(\alpha\)-SiC and \(\beta\)-SiC are predominant species but decreasing the DCMS precursor increased the \(\alpha\)-Si\(_3\)N\(_4\) phase in the ceramic material. Helium, unlike argon, produced only the \(\alpha\)-SiC and \(\beta\)-SiC ceramic material, which is believed to be due to the significantly higher thermal conductivity, which aided in the carbothermal reduction and/or decomposition of the Si\(_3\)N\(_4\) phase. To further understand this interesting result between two noble gases, FT-IR and
elemental analysis was utilized and showed no distinctive differences. FT-IR spectra in Figures 1.1.16 and 1.1.17 show similar polymer-to-ceramic transitions in argon and helium, and elemental analysis (Table 1.1.11) showed similar nitrogen and carbon concentrations for the polymers pyrolyzed in argon and helium. The mixed phases of $\alpha$-SiC and $\alpha$-Si$_3$N$_4$ were observed under an argon atmosphere for the PVSZ polymer. [40]

The reducing atmosphere of hydrogen produced $\alpha$-SiC, $\beta$-SiC, $\alpha$-Si$_3$N$_4$, and free silicon materials. Free silicon is an unusual observation because during the polymer-to-ceramic conversion elements of carbon, nitrogen, and oxygen are present, which would lead to the formation of only the carbide, nitride, and/or oxide phases. A possible reason for the formation of free silicon is the higher degree of branching for the PVSZ polymer vs. lower branching in the PMVSZ (1:1, 1:0.6, and 1:0.4) polymers. The atmosphere of hydrogen also plays a role in reducing the carbide, nitride, and/or oxide phase of silicon. Free silicon can be observed in all polymer systems with the concentration of free silicon increasing with the increase in the methyl concentration. With high concentrations of vinyl groups branching together, the decomposition of the organic groups, to yield free silicon, does not occur as readily as with lower concentrations of vinyl groups. Elemental analysis confirmed the decrease in nitrogen and carbon species as a function of methyl concentrations. For nitrogen, mixed phases of $\alpha$-SiC, $\beta$-SiC, and $\alpha$-Si$_3$N$_4$ materials were observed. For the PVSZ
system a micro-crystalline phase of $\alpha$-Si$_3$N$_4$ is observed while the presence of the $\alpha$-SiC or $\beta$-SiC phases are absent. This potentially indicates the presence of amorphous carbon from the highly branched polymer, inhibiting crystallization of the $\alpha$-Si$_3$N$_4$ phase while excess nitrogen in the atmosphere prevented the carbothermal reduction of the Si-N backbone. Elemental analysis confirmed the increase of carbon for the PVSZ polymer as compared to the PMVSZ polymers. For the PMVSZ polymers, the more unbranched structure allowed for higher crystallization of the $\alpha$-Si$_3$N$_4$ phase as well as the formation of $\alpha$-SiC and $\beta$-SiC. The ammonia atmosphere produced the $\alpha$-Si$_3$N$_4$ phase indicating the hydrogenation of the carbon groups occurred rather than carbothermal reduction of the backbone.

1.1.11 Conclusion

The ability to tailor polysilazane polymers by (1) varying precursors and/or (2) pyrolyzation atmosphere was investigated. Previously, the PVSZ polymer was synthesized by the ammonolysis of a single silane precursor: vinyltrichlorosilane. This polymer had the ability to be tailored into different combinations of SiC and Si$_3$N$_4$ phases by changing the pyrolyzing atmosphere. The problem with this polymer was its lack of stability. Introducing a second silane precursor, dichloromethylsilane, into the synthesis provided stability by inserting methyl groups to space apart the reactive vinyl groups in the polymer as well as decreasing hydrolysis and/or condensation. XRD characterization
showed the effect of atmosphere on ceramic materials produced after pyrolyzation. Varying the DCMS precursor produced ceramic materials with different combinations of silicon, nitrogen, and/or carbon allowing for the final ceramic material to be tailored to user specifications. The addition of the Si-H bonds to the backbone of the PMVSZ 1:0.6 polymer allowed for investigation into the modification of the backbone with different precursors. The PMVSZ 1:0.6 polymer was engineered to provide potential dopant sites to the backbone. Investigation into the doping of the polymer backbone could not occur until extensive characterization was completed to understand the innate properties associated with the as-fabricated polymer.

1.2 Polymer Doping

The as-synthesized pre-ceramic polymer from Section 1.1 was tailored for the purpose of increasing shelf-life and doping of the backbone. Due to the limited pre-ceramic polymers available and harsh operating conditions that are required of certain ceramic materials, alternative materials needed to be investigated. [63–65] The products produced from the polymer in the previous section range from SiC and Si₃N₄ ceramic materials to mixtures of those phases. This limits the application of the current polymer system. To enhance the properties of inorganic polymers for use as matrix materials in CFR-CMCs, research was focused on using dopant precursors to procure tailored ceramic
material after pyrolysis from 1000 °C to 1600 °C. For example, a dopant introduced to the backbone of a polysilane or polysilazane polymer may be used to decrease the overall crystallization temperature of the ceramic formed. This is advantageous for matrix materials in a CFR-CMC because if atoms are rearranging after fabrication (i.e., grain growth), internal stresses could develop and compromise properties of the structure.

Dopant materials are also used to inhibit oxidation by forming scales that retard oxygen migration into the system. A material that exhibits this characteristic is SiC, which forms an SiO₂ layer at elevated temperatures under oxidative environments. The SiC layer reacts with oxygen to form the SiO₂ layer, hindering the migration of remaining oxygen that is present. The diffusion of oxygen is low for SiO₂, which makes SiC an attractive material for high-temperature oxidative environments.

The goal of doping the as-synthesized PMVSZ 1:0.6 polymer was to introduce two dopant precursors to create a completely new ceramic material. The dopant materials of choice were titanium and boron. These elements were chosen because the proposed co-doped polymer, after pyrolysis, would yield a TiB₂ ceramic material. Due to the proximity of the elements attached to the backbone of the polymer, a refractory material might be formed. TiB₂ is classified as a refractory material, which by definition retains its strength at elevated temperatures -- a property desirable for CFR-CMCs. After con-
siderable thought, the dopant precursors were chosen based on the proposed mechanisms for the desired attachment sites on the polymer backbone of the two elements. The advantages of this approach include dispersement of the elements on an atomic level, limited “settling-out” of material because of density differences, and the ability to investigate other elements (e.g., Zr, Hf).

The precursors that were chosen for doping the PMVSZ 1:0.6 polymer backbone were metal alkoxides. The use of metal alkoxides provided an ideal reaction with the backbone of the PMVSZ polymer so that the precursor was dispersed on an atomic level rather than in a bulk suspension (i.e., powders). Titanium isopropoxide and triethyl borate were used in this research because they are both liquids that are miscible with the solvent used for the reaction. In comparison to other titanium- and boron-containing precursors, these are more air-stable and cost-effective. The drawback to using alkoxides as dopant precursors is the inherent oxygen and carbon incorporation. These impurities may cause degradation or other undesirable ceramic materials to form, which will need to be addressed in future studies. The alkoxide precursors provide a route to understanding the proposed mechanism and showing proof of concept to tailor the ceramic material after pyrolysis.

The intended refractory material chosen for this study was TiB$_2$ due to its high melting point, low coefficient of thermal expansion, and high erosion and oxidation resistance. Titanium diboride ceramic bodies have existed for many
years in the nuclear industry due to their high hardness, wear resistance, and nuclear properties. As with any ceramic material the inherent brittleness limits its use in structural applications. Discussed earlier, reinforcing materials incorporated within the ceramic monolith provide increased mechanical strength. A common fabrication technique for TiB$_2$ ceramics involves hot-pressing titanium and boron powders to extremely high-temperatures (>2300 °C). The formation of ceramic monoliths at extreme temperatures limits the reinforcing materials that can be used to enhance mechanical properties. For the TiB$_2$ ceramic monolith, continuous ceramic fiber additions would supply the needed support, ultimately forming a CFR-CMC with TiB$_2$ as the matrix material. Current fiber reinforcements limit this development because the upper use temperature of any ceramic fiber is 1600 °C, which is well below the formation temperature of TiB$_2$ and other borides through hot-pressing. Currently, to obtain the potential benefits of TiB$_2$ in a matrix material for a CFR-CMC, powders have to be mixed with the desired matrix material. Powders are undesirable because of density differences, causing settling of the material and uneven distribution throughout the final material. The ability to develop a matrix material that incorporates TiB$_2$ without the use of powders or extreme temperatures (>2300 °C) is the focus of this section.

The PMVSZ 1:0.6 polymer was synthesized to provide options for different doping routes. Figure 1.2.1 shows the proposed mechanism for the at-
attachment of a boron precursor to the backbone of the polymer. The mechanism shows a borate molecule reacting with the N-H moiety. This was proposed because the borate molecule is a Lewis acid and the N-H moiety is a Lewis base. In this fashion the reaction between the borate molecule and the NH\textsubscript{2} moiety would follow a Lewis acid/base reaction. Figure 1.2.2 shows the reaction between titanium isopropoxide and the Si-H moiety to form the Si-O-Ti bond. The reduction of primary amines also occurred with titanium isopropoxide, which restricted the doping procedure. By reducing the Si-H and N-H moieties on the backbone of the PMVSZ 1:0.6 polymer, the titanium isopropoxide precursor limited the ability of other precursors to interact and dope the polymer backbone. Spectroscopic characterization confirmed the reactivity of the titanium precursor to the backbone and led to the decision to dope the backbone with the boron precursor first. The objective of this preliminary investigation for co-doping the PMVSZ 1:0.6 polymer was to dope two precursors to the backbone on an atomic level and propose reaction mechanisms. Proposed linear structures of the bonds formed after reactions were generated. The applications of the co-doped PMVSZ 1:0.6 polymer will only be realized after pyrolysis.

The proposed reactions to the backbone do not convey the mechanisms associated with the polymer-to-ceramic conversion of the co-doped PMVSZ 1:0.6 polymer. Prior to pyrolysis, the titanium and boron molecules are not
Figure 1.2.1: Proposed linear structure of the as-synthesized boron-doped PMVSZ 1:0.6 polymer.
Figure 1.2.2: Proposed linear structure of the as-synthesized titanium- and boron-doped PMVSZ 1:0.6 polymer.
bound together, merely in proximity to each other. During the polymer-to-ceramic conversion, low molecular weight oligomers (hydrocarbons and/or NH₃) are evaporated from the backbone, subsequently decreasing the amount of material that surrounds each atom. This allows for reactions to occur between the elements that are in proximity to each other. Moreover, the chance of the doped heteroatoms evaporating during the polymer-to-ceramic conversion is decreased by their bonding directly to the backbone. Experimental trials involving the reaction between titanium isopropoxide and triethyl borate revealed the formation of TiO₂ after pyrolysis to 1600 °C. The lack of B₂O₃ formed in the final material is due to its sublimation temperature at 1500 °C causing evaporation of the material after pyrolysis to 1600 °C. To form the desired TiB₂ phase using these precursors, a carbon source had to be included to carbothermically reduce each ceramic material. Equations 1 - 6 show carbothermic reductions of different titanium- and boron-containing compounds.

\[
\begin{align*}
\text{TiO}_2(s) + 3C(s) & \xrightarrow{\text{Ar(g)}} \geq 1400^\circ C \rightarrow \text{TiC}(s) + 3\text{CO}(g) \\
\text{TiO}_2(s) + 2C(s) + 0.5N_2(g) & \xrightarrow{\text{N}_2(g)} \geq 1400^\circ C \rightarrow \text{TiN}(s) + 2\text{CO}(g) \\
2\text{TiO}_2(s) + \text{B}_2\text{O}_3(s) + 8C(s) & \xrightarrow{\text{Ar(g)}} 1900–2500^\circ C \rightarrow \text{TiB}_2(s) + \text{TiC}(s) + 7\text{CO}(g) \\
2\text{TiO}_2(s) + \text{B}_2\text{O}_3(s) + 7C(s) + 0.5N_2(g) & \xrightarrow{\text{N}_2(g)} 1900–2500^\circ C \rightarrow \text{TiB}_2(s) + \text{TiN}(s) + 7\text{CO}(g) \\
\text{TiC}(s) + \text{B}_2\text{O}_3(s) + 2C(s) & \xrightarrow{\text{Ar(g)}} 1900–2500^\circ C \rightarrow \text{TiB}_2(s) + 3\text{CO}(g) \\
\text{TiO}_2(s) + 0.5\text{B}_4\text{C}(s) + 1.5C(s) & \xrightarrow{\text{Ar(g)}} 1900–2500^\circ C \rightarrow \text{TiB}_2(s) + 2\text{CO}(g)
\end{align*}
\]
As the disordered polymer network is converted into an ordered ceramic material, traditional solid state reactions take place. Equations 1 - 6 offer limited explanations of the effect the decomposition of the PMVSZ 1:0.6 polymer has on the observed TiB₂ and TiCN ceramic materials formed after pyrolysis. Equations 7 - 15 provide reaction equations that attempt to justify the formation of the TiB₂ and TiCN materials.

\[
\begin{align*}
\text{Ti(O-\text{iC}_3\text{H}_7)_{4(l)}} & \xrightarrow{350^\circ\text{C}} \text{TiO}_{2(s)} + 4\text{C}_3\text{H}_6(g) + 2\text{H}_2\text{O}(g) \\
2\text{B(OC}_2\text{H}_5)_{3(l)} & \xrightarrow{\leq100^\circ\text{C}} \text{B}_2\text{O}_3(s) + 6\text{C}_2\text{H}_4(g) + 3\text{H}_2\text{O}(g) \\
\text{B}_2\text{O}_3(s) & \xrightarrow{400^\circ\text{C}} \text{B}_2\text{O}_3(l) \\
\text{SiC}_{(s)} + \frac{1}{2}\text{O}_{2(g)} & \xrightarrow{800^\circ\text{C}} \text{SiO}_2(s) + \text{CO}(g) \\
\text{Si}_3\text{N}_4(s) + 3\text{O}_{2(g)} & \xrightarrow{1300-1500^\circ\text{C}} 3\text{SiO}_2(s) + 2\text{N}_2(g) \\
\text{SiO}_{2(l,s)} + \text{B}_2\text{O}_3(l) & \xrightarrow{1000^\circ\text{C}} \text{B}_2\text{O}_3 \cdot x\text{SiO}_2(l) \\
\text{SiO}_{2(l,s)} + \text{C}_{(g,s)} & \xrightarrow{1500^\circ\text{C}} \text{SiO}(g) + \text{CO}(g) \\
\text{TiO}_{2(s)} + \text{B}_2\text{O}_3(l) + 7\text{C}_{(s)} + \frac{1}{2}\text{N}_2(g) & \xrightarrow{1600^\circ\text{C}} \text{TiB}_2(s) + \text{TiCN}(s) + 6\text{CO}(g)
\end{align*}
\]

1.2.1 Experimental Procedure

As-synthesized PMVSZ 1:0.6 polymer was dissolved in reagent grade toluene (Alfa Aesar®). A 1:5 ratio of PMVSZ 1:0.6 polymer to solvent was
used. To synthesize the co-doped PMVSZ 1:0.6 polymer, toluene was first added to a 500 mL three-neck round bottom flask equipped with a nitrogen purge, magnetic stirrer, and a reflux condenser. After the solvent was allowed to purge, 10 grams of PMVSZ 1:0.6 polymer was added to the flask. The polymer was allowed to dissolve completely into the solvent before the dopant solution was added. 5.4 mL of triethyl borate was injected into the flask and allowed to mix. No reaction was observed. The hot plate was heated to around 100°C and monitored until the solution began refluxing. The solution was refluxed for 12 hours. A gold color change was observed after the reflux. The solution was allowed to cool to room temperature before the titanium precursor was added. 9.7 mL of titanium isopropoxide was injected into the flask and allowed to mix. The solution was refluxed for an additional 12 hours. The final observed color change was dark green (Figure 1.2.3).

The excess solvent was removed via a rotary evaporator to yield a viscous polymer. To synthesize only boron- or only titanium-doped PMVSZ 1:0.6 polymer, the same experimental procedure was followed except only the desired dopant solution was added to the flask and refluxed for 12 hours. The as-synthesized PMVSZ 1:0.6 polymers were characterized using ATR, Scanning Auger Microscopy (SAM), and XRD to determine the structure of the backbone, the atomic concentration, and the crystalline ceramic material after pyrolysis. For X-ray and SAM analysis the polymer samples were placed in an alumina
boat and pyrolyzed to 1600 °C at 2 °C/min under an argon atmosphere. The ATR and XRD instruments are described in Section 1.1.2 and SAM was performed on a Perkin-Elmer PHI 610 scanning Auger microscope.

Figure 1.2.3: Reaction vessel designed to synthesize the doped PMVSZ 1:0.6 polymer.
1.2.2 Attenuated Total Reflectance Spectroscopy

ATR spectroscopy was used to analyze the structure of the liquid PMVSZ polymers after reflux. The structure of the neat polymer and the doped polymers share similar stretches and bands, which are summarized in Table 1.2.12. ATR spectra are shown for the neat PMVSZ 1:0.6 polymer (Figure 1.2.4), the boron-doped PMVSZ 1:0.6 polymer (Figure 1.2.5), the titanium-doped PMVSZ 1:0.6 polymer (Figure 1.2.6), and the co-doped boron and titanium PMVSZ 1:0.6 polymer (Figure 1.2.7). Visual changes to structural groups on the backbone can be observed in the ATR spectra. Ideally, to understand if the proposed mechanisms are correct, the NH$_2$ and Si-H regions are of interest. Also regions pertaining to vibrations that are inherent to the precursors will indicate the potential addition of that molecule.

Table 1.2.12: Frequency and structural groups for the proposed doping site in the PMVSZ 1:0.6 polymer.

<table>
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<tr>
<th>Boron-doped PMVSZ</th>
<th>Titanium-doped PMVSZ</th>
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<tr>
<td>Frequency (cm$^{-1}$)</td>
<td>Structural group</td>
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<tr>
<td>1300 - 1540</td>
<td>B-O, B-N</td>
</tr>
<tr>
<td>2952 and 2896</td>
<td>CH (aliphatic)</td>
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Figure 1.2.4: ATR spectrum of neat PMVSZ 1:0.6 polymer.
Figure 1.2.5: ATR spectrum of the PMVSZ 1:0.6 polymer refluxed with triethyl borate compared to the neat PMVSZ 1:0.6 polymer.
Figure 1.2.6: ATR spectrum of the PMVSZ 1:0.6 polymer refluxed with titanium isopropoxide compared to the neat PMVSZ 1:0.6 polymer.
Figure 1.2.7: ATR spectrum of the PMVSZ 1:0.6 polymer refluxed with titanium isopropoxide and triethyl borate compared to the neat PMVSZ 1:0.6 polymer.
1.2.3 X-ray Powder Diffraction

Figures 1.2.8 - 1.2.10 show XRD patterns for the boron-doped PMVSZ 1:0.6 ceramic material (Figure 1.2.8), the titanium-doped PMVSZ 1:0.6 ceramic material (Figure 1.2.9), and the co-doped PMVSZ 1:0.6 ceramic material (Figure 1.2.10) pyrolyzed to 1600°C at 2°C/min in an argon atmosphere. An argon atmosphere was used to eliminate any potential reactions of the polymer-to-ceramic conversion with the atmosphere. Exploration into other pyrolyzing atmospheres such as H₂, He, N₂, and NH₃ will need to be conducted in order to understand the scope of the final tailored ceramic material.

The XRD patterns presented in this section show the effect of modifying the backbone of the polymer with single and multiple dopant precursors. The XRD patterns for the boron-doped PMVSZ 1:0.6 ceramic material and the titanium-doped PMVSZ 1:0.6 ceramic material show a micro-crystalline phase of β-SiC and crystalline phases of titanium carbide nitride and cristobalite, respectively. For the boron and titanium co-doped PMVSZ 1:0.6 ceramic material, crystalline phases of titanium diboride and titanium carbide nitride are present.
Figure 1.2.8: XRD pattern of the boron-doped PMVSZ 1:0.6 polymer pyrolyzed to 1600 °C under an Ar environment ($\beta = \beta$-SiC).
Table 1.2.13: JCPDS vs. experimental reflections for the boron-doped PMVSZ 1:0.6 ceramic material.

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ASTM Card No. : 29-1129
Figure 1.2.9: XRD pattern of the titanium-doped PMVSZ 1:0.6 polymer pyrolyzed to 1600 °C under an Ar environment (\(^\circ\) = TiCN, \(\zeta\) = cristobalite).
Table 1.2.14: JCPDS vs. experimental reflections for the titanium-doped PMVSZ 1:0.6 ceramic material.

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<th>^TiCN</th>
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^=ASTM Card No.: 42-1488
Figure 1.2.10: XRD pattern of the boron- and titanium-doped PMVSZ 1:0.6 polymer pyrolyzed to 1600 °C under an Ar environment (♯ = TiB₂, ^ = TiCN).
Table 1.2.15: JCPDS vs. experimental reflections for the boron- and titanium-doped PMVSZ 1:0.6 ceramic material.

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#:ASTM Card No. : 35-741

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<td>2 2 2</td>
<td>77.46</td>
<td>12</td>
<td>77.56</td>
<td>14</td>
</tr>
</tbody>
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^#:ASTM Card No. : 42-1488
1.2.4 Scanning Auger Microscopy

Figure 1.2.11 shows atomic concentrations of the resulting ceramic material for the boron and titanium co-doped PMVSZ 1:0.6 polymer after pyrolysis. The Auger data complemented the XRD data by confirming that no silicon was present, in either a crystalline or an amorphous phase. Atomic concentrations of a TiB$_2$ standard are presented in Figure 1.2.12.

In this case, the Auger data that complement the XRD data are represented in the peak shapes of the spectrum and not with respect to the atomic concentrations. The energies associated with bonds between elemental boron and elemental titanium differ from the bond energy between boron and titanium. When the peak shapes for the Auger data in Figure 1.2.11 are compared with the peak shapes in Figure 1.2.12 there are similar trends observed. This indicates the presence of a TiB$_2$ material rather than elemental boron and titanium.
Figure 1.2.11: Atomic concentration of the as-synthesized co-doped PMVSZ ceramic material analyzed by SAM.

Figure 1.2.12: Atomic concentration of a TiB$_2$ standard analyzed by SAM.
1.2.5 Discussion

This section focuses on the modification of a silicon-based inorganic polymer (from Section 1.1). ATR of the as-synthesized modified polymer showed evidence for the proposed mechanisms. First, triethyl borate and the PMVSZ 1:0.6 polymer were refluxed in toluene to obtain the resulting polymer shown in Figure 1.2.5. In this reaction, triethyl borate acted as a Lewis acid and the Si-NH$_2$ moiety acted as a Lewis base. ATR of the neat PMVSZ 1:0.6 polymer was used as a baseline to observe any changes after reflux. Figure 1.2.5 showed an increase in absorbance and broadening in the region between 1300 - 1540 cm$^{-1}$, indicating the presence of B-O stretching. The B-O stretching is characteristic to the precursor, so this is not conclusive evidence for determining the bonding site or mechanism. The absorbance changes of interest are around the 3400 cm$^{-1}$ region. This region is attributed to the NH$_2$ and N-H moieties, which observed an overall decrease in absorbance relative to the neat PMVSZ 1:0.6 polymer. Inherently, the backbone of the PMVSZ 1:0.6 polymer has a larger quantity of N-H moieties as compared to NH$_2$ moieties, which results in only a slight decrease in absorbance for this region after modification.

Second, titanium isopropoxide and the PMVSZ 1:0.6 polymer were refluxed in toluene (Figure 1.2.6). ATR spectra showed decreases in the Si-H and the N-H regions attributed to the titanium isopropoxide precursor reacting with both of these moieties. Significant absorbance changes in the 1000 -
1100 cm$^{-1}$ region indicated the presence of the titanium precursor after reflux and rotary evaporation. These changes concluded the successful incorporation of the titanium species. The reduction in both the N-H and Si-H regions confirmed the reactivity of the titanium isopropoxide precursor, limiting the experimental procedure to perform the boron doping first. The ATR characterization provided preliminary data that suggested significant changes to the backbone of the polymer. This research limited the spectroscopic studies of the doped polymer; however this allows for future research opportunities to investigate the polymers properties using $^1$H, $^{13}$C, $^{29}$Si, $^{11}$B, and $^{47/49}$Ti nuclear magnetic resonance, GPC, and rheological characterization techniques.

XRD analysis of the doped PMVSZ 1:0.6 ceramic materials after pyrolysis provided insight into the crystalline material formed. XRD patterns were obtained of the crystalline material after pyrolysis to 1600 $^\circ$C under an Ar environment for the boron-doped PMVSZ 1:0.6 ceramic material, the titanium-doped PMVSZ 1:0.6 ceramic material, and the co-doped PMVSZ 1:0.6 ceramic material. An XRD pattern shown in Section 1.1.3 of neat PMVSZ 1:0.6 ceramic material was used for comparison. XRD analysis of boron-doped PMVSZ 1:0.6 ceramic material resulted in micro-crystalline $\beta$-SiC and the titanium-doped PMVSZ 1:0.6 ceramic material resulted in TiCN and cristobalite phases. The micro-crystalline $\beta$-SiC phase may be explained by the incorporation of amorphous phases such as borosilicate glass, which is formed through the reaction
between SiO$_2$(l) and B$_2$O$_3$(l) at a temperature of 1000 $^\circ$C (Equation 13). A broad region observed in the XRD pattern around 25 2-$\theta$ suggested such incorporations. XRD patterns for the titanium modification, showed crystalline cristobalite was formed indicating the oxygen present from the dopant precursor remained bonded to the silicon during pyrolysis. Crystalline cristobalite rather than an amorphous phase appeared because there was no boron-containing material present to react and form a borosilicate glass.

The characterization techniques presented up to this point, are limited in understanding the solid state interactions between the elements of the doped PMVSZ 1:0.6 polymer during the polymer-to-ceramic conversion. Several different material phases can be formed throughout the pyrolysis cycle and the explanations of the formed crystalline materials are theorized. Equations 1, 2, 7, 8, 11, and 12 show the possible reactions that take place to explain the resulting TiCN and cristobalite phases. Equation 8 shows that at 350 $^\circ$C the alkoxide precursors will form an oxide phase. At temperatures above 1400 $^\circ$C and in the presence of a carbon or nitrogen source, carbothermic reduction occurs to form TiC or TiN phases, respectively, and CO$_2$ (Equations 1 and 2). Equations 7, 11, and 12 show reactions that form the possible sources of carbon and nitrogen to form the TiCN ceramic material. The Si-O-Ti bond that is formed on the backbone explains the possible formation of SiO$_2$ during pyrolysis. Although Si-N-O-B bonds were proposed for the boron-doped PMVSZ
1:0.6 polymer, the XRD patterns for the ceramic material after pyrolysis showed no crystalline SiO$_2$ material and an amorphous borosilicate glass was formed that also decreased the crystallinity of the $\beta$-SiC phase.

The XRD analysis of the boron and titanium co-doped PMVSZ 1:0.6 ceramic material showed crystalline TiB$_2$ and TiCN phases. Equations 7 - 15 show possible reactions during the polymer-to-ceramic conversion to form the TiB$_2$ and TiCN ceramic phases. Equation 9 shows the decomposition of the boron alkoxide precursor into B$_2$O$_3$($s$) at temperatures below 100 °C. B$_2$O$_3$($s$) has a melting point around 400 °C and a sublimation temperature of around 1500 °C. Again SiO$_2$($s$) is assumed to form during the polymer-to-ceramic conversion because of the Si-N-O-B and Si-O-Ti bonding. At temperatures of around 1000 °C, B$_2$O$_3$($l$) will react with SiO$_2$($l,s$) to form borosilicate glass (Equation 13). The TiO$_2$($s$) formed will convert from an anatase phase to a rutilite phase during the pyrolysis but until temperatures exceed 1400 °C, carbothermic reduction will not occur. Equation 15 shows a reaction between the hypothesized ceramic materials going through carbothermic reduction at 1600 °C to form TiB$_2$($s$), TiCN($s$), and CO($g$). At temperatures greater than 1500 °C, SiO$_2$($g$) is thought to evaporate resulting in the boride, carbide, and nitride phases formed. Equation 14 shows that at temperatures above 1500 °C and in the presence of carbon, SiO$_2$($s$) reduces to SiO($g$). The evolution of SiO($g$) is the current hypothesis for the significant decrease in the silicon concentration. Auger atomic concentrations also
showed no presence of silicon in the co-doped PMVSZ 1:0.6 ceramic material. The Auger spectrum confirmed the presence of the titanium, boron, nitrogen, carbon, and oxygen in the ceramic material after pyrolysis. The as-synthesized TiB$_2$ material is confirmed by comparing the peak shape of boron and titanium to a TiB$_2$ standard. This discussion presents a detailed hypothesis into the potential reactions that occur during the polymer-to-ceramic conversion of a co-doped silicon-based inorganic polymer. Continued characterization and thought are required for the reactions that occur during the polymer-to-ceramic conversion. Nevertheless, the results herein represent an advancement in inorganic polymers that allows for a novel pathway to develop complex material systems.

1.2.6 Conclusion

A silicon-based inorganic polymer was synthesized to have the ability to modify the backbone with multiple heteroatoms. The heteroatoms used were boron and titanium in the attempt to create a boride ceramic material after pyrolysis to 1600°C. Liquid alkoxide precursors allowed for the dispersion of the heteroatoms to occur at an atomic level. ATR provided insight into the reaction mechanisms of the polymer backbone. XRD and SAM analyzed the ceramic material after pyrolysis of the polymers. XRD showed the formation of TiB$_2$ and TiCN phases for the co-doped PMVSZ 1:0.6 ceramic material. Auger atomic concentrations showed the loss of silicon within the final ceramic
material for the co-doped PMVSZ 1:0.6 ceramic material. Equations 1 - 15 began the discussion into the reaction mechanisms that occurred during the polymer-to-ceramic conversion.

1.3 Reactive Filler Additions

The ability of an inorganic polymer to be modified at an atomic level relies on precursors that are able to be dissolved in solvents and/or react with the backbone. These types of precursors are limited by availability, cost, and reactivity with the backbone. So far this chapter has created different ceramic materials after pyrolysis through the reaction of precursors with the backbone of an inorganic polymer. This section will discuss the modification of an inorganic polymer with reactive fillers. Reactive fillers (powders) can play an important role in creating new materials for matrices used for CFR-CMCs that otherwise may not be formed through the reaction between a precursor and the backbone of an inorganic polymer. Recently, silicon has been shown to be an excellent reactive filler to form CFR-CMCs. [62] Silicon has its drawbacks, which include but are not limited to the high processing temperature (well above the melting temperature of 1415 °C for silicon) and a large volume change resulting from the liquid to solid phase transformation. [63–66] This limits the reinforcing fibers of a CFR-CMC. [67] A good alternative to silicon would be to use aluminum fillers. Al fillers have promise due to a low melting point
and high reactivity. Previously, Al fillers have been melted with particles such as B$_4$C to form materials like AlBC. [68] The AlBC material formed offered a combination of high hardness and toughness. Following this information, varying amounts of Al fillers were introduced into an inorganic polymer prior to pyrolysis to try to obtain enhanced properties. Although this system has the potential for material to “settle out” because of different densities, the low melting point and high reactivity of the metal filler should create a uniform material after pyrolysis. Al fillers also have the ability to react with elements in the inorganic polymer to form new phases that may enhance the materials properties.

This system was chosen to be used as a matrix material in a PIP fabricated CFR-CMC. The previous sections provided insight into the inorganic polymer field but due to the current stage of the research, the PMVSZ polymer was not selected for any matrix materials used in the fabrication of a CFR-CMC. The inorganic polymer selected for the PIP fabrication was a commercially available SiCN-based inorganic polymer that is similar in structure to the PMVSZ polymer and resulting ceramic material after pyrolysis. This allowed for future research to transition from a commercially available inorganic polymer to the as-synthesized PMVSZ polymer with limited differences. Currently, the commercially available SiCN-based inorganic polymer provides a route for concepts to be investigated.
Depending on the filler used within the matrix material of a CFR-CMC, not only is the inorganic polymer subject to interactions, but the reinforcing materials and interfacial coatings (if applicable) are as well. This section will first investigate the new material formed as a result of the Al filler addition to the inorganic polymer after pyrolysis to 1000 °C and 1600 °C. Second, an interfacial coating that has been examined extensively, BN/Si$_3$N$_4$, [25, 26, 78] will be employed in PIP fabricated CFR-CMCs. Briefly, the microstructure of BN has shown to have properties that exhibit weak fiber/matrix bonding as well as good oxidative resistance. [19, 20, 82] BN inherently adsorbs moisture, which is reduced via a duplex coating of Si$_3$N$_4$ (BN/Si$_3$N$_4$ as an interfacial coating is discussed in Section 2.2). [78] Presently, the BN/Si$_3$N$_4$ coating is one of the advanced interfacial systems commercially used today and the above stated reason is why it is employed in the CFR-CMCs.

A major problem with using Al as a filler material and BN/Si$_3$N$_4$ as an interfacial coating is the reaction between Al and Si$_3$N$_4$ at temperatures above 800 °C. Degradation to the Si$_3$N$_4$ coating would cause vulnerability to the BN layer, which could affect the mechanical properties of the CFR-CMC. A solution to this problem is to increase the thickness of the Si$_3$N$_4$ layer to provide a layer that proactively protects the reinforcing material and BN layer from attack. This research will investigate different Si$_3$N$_4$ thicknesses to retard Al attack. The BN/Si$_3$N$_4$ interfacial coating has been investigated extensively to
determine the optimal thickness for both layers and increasing the Si$_3$N$_4$ layer will have an effect not only on the mechanical properties but on the work-ability of the fabric. Work-ability is defined as the ease of ability for a substrate to take a desired shape without damaging the properties associated with that substrate. The increase of the Si$_3$N$_4$ layer was a result of the reactivity of Al at elevated temperatures. The overall goal of this research was to modify and understand the ceramic material formed after pyrolysis.

1.3.1 Optimal Weight Percent of Filler Addition

For a matrix material to be acceptable for the use in a CFR-CMC, properties such as strength and the ability to form a solid monolith are required. To determine the optimal amount of filler to add to an inorganic polymer, different wt.% of filler were selected and pyrolyzed under similar conditions for a CFR-CMC. The optimal amount was determined by the structure of the ceramic material after pyrolysis. The desired structure would form a solid monolith. The reactive filler used was Al particles (Alfa Aesar 10576, Ward Hill, MA) with an average particle size of 13-17 $\mu$m. The polysilazane polymer used in this study was a hydridopolysilazane (HPZ) polymer distributed by COI Ceramic, Inc. The polymer decomposed to $\beta$-SiC and $\alpha$-Si$_3$N$_4$ after pyrolysis to 1600 °C in a nitrogen atmosphere. To obtain the optimal wt.%, Al particles were added to the HPZ polymer in 10 wt.% increments. The increments started with 10 wt.% and increased to 50 wt.%. The Al particles were added to the HPZ polymer and
stirred until completely dispersed in the mixture. The heterogeneous mixture was slowly heated to approximately 180°C on a hot plate to form a solid network. To keep the Al particle well dispersed, it was necessary to continuously stir the mixture of Al particles and polymer on the hot plate while heating. When the mixture solidified, the beaker was removed from the hot plate and allowed to cool. Separately, the solid Al/polymer network was pyrolyzed to 900°C at 2°C/min under flowing UHP N₂ and held at temperature for two hours. The optimal wt.% was determined to be 20 wt.% because this ceramic material remand as a solid monolith after pyrolysis to 900°C.

### 1.3.2 X-ray Powder Diffraction

Figure 1.3.1 presents the results of the XRD study that were performed in order to determine the crystalline phases after pyrolysis of the 20 wt.% Al filler additions to the HPZ polymer. The major phases identified were AlN, β-SiC, and Si. Equations 17 and 18 show the products of the decomposition of the HPZ polymer pyrolyzed to 900°C at 2°C/min under a nitrogen atmosphere and the Al and Si₃N₄ reaction at 1600°C. Figure 1.3.6(a) shows the XRD pattern for the 20 wt.% addition to the HPZ polymer pyrolyzed to 900°C at 2°C/min under a nitrogen atmosphere. The spectrum contains weak reflections for AlN, SiC, and Si. To increase the intensity of the observed reflections, the sample was pyrolyzed to 1600°C 2°C/min under a nitrogen atmosphere. After the pyrolyzation to 1600°C, the intensities for the AlN, β-SiC, and Si reflections
became more pronounced (Figure 1.3.1[b]). Although $\alpha$-Si$_3$N$_4$ is a product of the decomposition of the HPZ polymer (Equation 13), the reflections for $\alpha$-Si$_3$N$_4$ were not observed in either Figure 1.3.1(a,b).

Although the crystallization temperature for $\beta$-Si$_3$N$_4$ was reached for the sample pyrolyzed to 1600 °C, the Al particles must have reacted with all the Si-N species formed during the polymer-to-ceramic conversion of the HPZ polymer. Kawai et al. investigated the reaction between Al and $\beta$-Si$_3$N$_4$ materials. [71] They concluded that AlN and Si are formed when Al particles react with a Si$_3$N$_4$ network (Equation 17). The results also showed that the AlN and Si were formed in the regions around the interface of the $\beta$-Si$_3$N$_4$ ceramic. The reaction products shown in the Kawai et al. research between Al and Si$_3$N$_4$ provide confirmation for the resulting products that were obtained after the polymer-to-ceramic conversion for this research. Gibbs free energy calculations in Equations 17 and 18 provide an explanation for the $\beta$-SiC phase to be maintained. A spontaneous reaction occurs between Al and Si$_3$N$_4$, while a non-spontaneous reaction is shown for the Al and SiC reaction at 1600 °C. The XRD patterns confirmed the presence of no Al$_4$C$_3$ reflections.

\[
\begin{align*}
\left[ \text{HN-Si-NH} \right]_{(s)} & \xrightarrow{900 \degree C} \text{N}_2(g) \\
\text{CH}_3 & \\
\text{CH}_3 &
\end{align*}
\]

\[
\begin{align*}
900 \degree C & \quad \beta\text{-SiC}_{(s)} + \alpha\text{-Si}_3\text{N}_4(s)
\end{align*}
\]  

\[
\begin{align*}
4\text{Al}_{(s)} + \text{Si}_3\text{N}_4(s) & \xrightarrow{1600 \degree C} 4\text{AlN}_{(s)} + 3\text{Si}_{(s)} \\
\Delta G & = -94.56 \text{ kcal}
\end{align*}
\]  

\[
\begin{align*}
4\text{Al}_{(s)} + 3\text{SiC}_{(s)} & \xrightarrow{1600 \degree C} \text{Al}_4\text{C}_3(s) + 3\text{Si}_{(s)} \\
\Delta G & = 13.39 \text{ kcal}
\end{align*}
\]
Figure 1.3.1: XRD patterns of (a) 20 wt.% Al filler additions to HPZ polymer pyrolyzed to 900 °C and (b) 1600 °C under an N₂ atmosphere (*=ASTM Card No. : 29-1129 [β-SiC], ^=ASTM Card No. : 25-1133 [AlN], #=ASTM Card No. : 27-1402 [Silicon]).
1.3.3 PIP Composite Fabrication

Three CFR-CMCs were fabricated using the PIP process. First, the BN/Si₃N₄ interfacial coating was deposited on Ceramic Grade (CG) Nicalon™ woven fabric. The detailed experimental procedure and setup for the deposition are in Section 2.2. Varying thicknesses of the Si₃N₄ layer were employed and Table 1.3.16 shows the deposition parameters. The designations 1X, 2X, and 3X relates to the deposition time and the different Si₃N₄ coating thickness. Eight individual 10.16 cm by 10.16 cm plies were cut from the coated woven fabric and impregnated with the 20 wt.% Al filler and HPZ polymer slurry to form a CFR-CMC. Prior to impregnation, the slurry was allowed to mix in a beaker until the Al particles were dispersed evenly. The impregnated plies were laid up in a warp-aligned symmetric fashion. The wetted plies were then sandwiched between two stainless steel plates and compressed to the desired thickness using Equation 19.

The desired thickness for a CFR-CMC can be determined by knowing the number of plies, ariel weight and density of the woven fabric, and the desired fiber volume ratio. Typically, a fiber volume ratio of around 40% provides the optimal amount of matrix material to reinforcing fiber to obtain maximum strength for a CFR-CMC. All CFR-CMCs fabricated in this dissertation have fiber volume ratios of 40%. After the stainless steel plates were compressed to the desired thickness, the plates were placed into an oven vacuum and heated.
to around 150 °C to form a cured green body. The green body consists of a disordered polymer network consolidated around the coated fabric. The green body was pyrolyzed by placing the CFR-CMC in a furnace and heated to 900 °C at a rate of 2 °C/min under flowing UHP N₂ with a soak time of one hour at temperature. This cyclic process was repeated, with as-received HPZ polymer, multiple times until the CFR-CMC had a density of around 2.1 g/cm³. The PIP fabrication process is represented in Figure 0.0.7. Labels of 1X, 2X, and 3X were used to denote the coating thickness of the Si₃N₄ layer as well as the three corresponding CFR-CMCs fabricated with the differing Si₃N₄ thickness.

\[
\text{Thickness} = \frac{(\text{Plies})(\text{Ariel Weight})}{(\text{Density})(\text{Fiber Volume Ratio})} \tag{19}
\]

| Table 1.3.16: Deposition parameters used to deposited BN and Si₃N₄ layers. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sample          | Time (BN) (min) | Time (Si₃N₄) (min) | Temperature (°C) | Pressure (Torr) | NH₃ (BN) (sccm) | NH₃ (Si₃N₄) (sccm) | N₂ (sccm) | BCl₃ (sccm) | SiCl₄ (sccm) |
| 1X 60 0 800 0.954 500 0 400 125 0 | 1X 0 60 800 0.956 0 400 400 0 100 | 2X 60 0 800 0.954 500 0 400 125 0 | 2X 0 120 800 0.956 0 400 400 0 100 | 3X 60 0 800 0.954 500 0 400 125 0 | 3X 0 180 800 0.956 0 400 400 0 100 |
1.3.4 CFR-CMC Testing and Characterization

Test samples were cut from the three CFR-CMCs for four-point bend tests with a support span and load span of 10.6 cm and 2.54 cm, respectively. The gauge length and the crosshead speed were 8.1 cm and 0.38 cm/min, respectively. The flexural strengths were measured on an Instron® model 4202 universal testing machine. Thickness measurements of the duplex coating were measured using a Zeiss DSM 982 Gemini FE-SEM with a Schottky Emitter at an accelerating voltage range from 2 to 4 kV and a beam current of about 1 mA. Density measurements were also taken at various stages during the fabrication process.

The densities vs. impregnation cycles for the as-fabricated CFR-CMCs are shown in Fig. 1.3.2. Although the processing conditions were kept constant, a discrepancy between the CFR-CMCs was noted. This discrepancy has not yet been resolved, however the impregnation cycles were terminated once the densities of the CFR-CMC started to show a minimal gain. The first PIP cycle for each CFR-CMC showed a large increase in density due to the large concentration of voids in the preforms. The subsequent PIP cycles showed increases in density that were attributed to the polymer infiltrating into the voids of the CFR-CMC. The final bulk densities for the CFR-CMCs labeled as 1X, 2X, and 3X were 1.82 g/cm³, 1.57 g/cm³, and 1.77 g/cm³, respectively.
Figure 1.3.2: Panel density vs. impregnation cycles for CFR-CMCs 1X, 2X, and 3X.

1.3.5 Field Emission Scanning Electron Microscopy

FE-SEM analysis was performed on several fibers taken from the three different deposition runs presented in Table 1.3.16. FE-SEM was used to confirm the Si$_3$N$_4$ thickness change as a function of deposition time. The Si$_3$N$_4$ coating thickness for the 1X, 2X, and 3X coating was 75 nm, 150 nm, and 225 nm, respectively. The variation in thickness of the Si$_3$N$_4$ layer was around 15 nm. A typical micrograph of the fracture surface of a duplex-coated fiber is presented in Figure 1.3.3. This micrograph is from one of the fibers removed from the fabric that was coated in the run designated as 2X. The micrograph shows the BN coating as the first layer next to the fiber. The Si$_3$N$_4$ coating appears as the thinner layer over the BN layer. The results from the FE-SEM analysis showed
that the thicknesses of the BN coatings vary from 250 nm to 300 nm.

![Image](image.png)

**Figure 1.3.3: FE-SEM micrograph of the duplex BN/Si₃N₄ (2X) coating.**

FE-SEM micrographs of the polished surface of the CFR-CMC labeled 3X are shown in Figure 1.3.4. The thicknesses of the coatings in the CFR-CMC labeled 3X were found to be around 250 nm thick for the BN layer and around 225 nm for the Si₃N₄ layer. The BN/Si₃N₄ interfacial coating appears to have bonded homogeneously to the surface of the CG-Nicalon™ fibers. Some pitting is observed on the surface of the matrix and the fibers which may have occurred during the polishing process. In Figure 1.3.4(b), there appears to be a reaction zone around the outer Si₃N₄ layer. This may have been the result of the molten Al attacking the Si₃N₄ to form AlN and Si during the first pyrolysis cycle. Figure 1.3.5 shows an FE-SEM micrograph of a fracture surface of the CFR-CMC labeled as 1X. This micrograph shows multiple reaction zones. The first zone depicts the reaction between Al particles and the Si₃N₄ interface. The
second reaction zone shown in Figure 1.3.5 consists of a large grain that was formed by the reaction between the Al particles and the HPZ polymer forming AlN.

Figure 1.3.4: FE-SEM micrographs of (a) the polished 3X CFR-CMC and (b) a higher magnification of the polished 3X CFR-CMC.

![Figure 1.3.4](image)

The primary reason for increasing the Si₃N₄ layer was to limit degradation to the BN layer and the reinforcing fibers due to the reactivity of Al at
elevated temperatures. FE-SEM analysis confirmed that the Si$_3$N$_4$ layer in the CFR-CMCs 1X, 2X, and 3X were not completely degraded by the reaction with the Al particles. However reaction zones were observed near the interface indicating possible degradation to the Si$_3$N$_4$ layer. These zones pointed to areas in which the Si$_3$N$_4$ layer was compromised and Al was allowed to attack the BN layer and/or reinforcing fibers. Also as the Si$_3$N$_4$ layer is reduced to AlN and Si, the silicon that is formed has the potential to migrate to the BN interface. If the Si migrates to the BN interface, microstructural changes will occur because silicon is known to react with BN to form Si$_3$N$_4$ and B. [72] By increasing the thickness of the Si$_3$N$_4$ layer, these degradation mechanisms will be mitigated.

1.3.6 CFR-CMC Mechanical Testing

Four-point bend tests were conducted on the CFR-CMCs denoted as 1X, 2X, and 3X and the results of the ultimate bend strengths are shown in
Figure 1.3.6. The ultimate bend strengths of the CFR-CMCs increased as a function of Si$_3$N$_4$ thickness. There was a three-fold increase in strength for the CFR-CMC labeled 3X as compared to 1X. The mechanical strength for the CFR-CMCs labeled 1X, 2X, and 3X were 61.5 MPa, 104.6 MPa, and 176.8 MPa, respectively. To obtain optimal mechanical strengths, stress vs. displacement curves that display minimal displacement after the ultimate bend strengths are desirable. The CFR-CMC labeled 3X exhibited this characteristic and observed the greatest mechanical strength. The CFR-CMCs labeled 2X and 1X showed longer displacements and subsequently lower mechanical strengths. The strength loss is attributed to the ability of the BN layer and/or fiber to resist attack from Al or Si and is diminished as the thickness of the Si$_3$N$_4$ layer is decreased.

1.3.7 CFR-CMC Fractograph Analysis

FE-SEM fractographs are micrographs obtained after mechanical testing that provide information pertaining to failure mechanisms within a CFR-CMC. Figure 1.3.7(a,b,c) shows fractographs for CFR-CMCs labeled 1X, 2X, and 3X, respectively. The fractographs confirm that the CFR-CMCs labeled 2X and 3X possessed toughening mechanisms such as fiber pull-out. The CFR-CMC labeled 1X displayed significant fiber pull-out, which occurs when load transfer between the matrix and fiber is compromised. By degrading the BN layer, voids are created and this limits the ability to transfer the load from the matrix to the
fibers. The thin Si₃N₄ layer for CFR-CMC labeled 1X could not protect the BN layer from being exposed to Al or Si and degrading the coating. Excess fiber pull-out is the result of a degraded interface and is shown in Figure 1.3.7(a). Fiber debonding and fiber holes in Figure 1.3.7(b,c) are evidence of toughing mechanisms that aid in dissipating stresses and supporting the load throughout the failure progression.

1.3.8 Conclusion

Reactive materials, such as Al and Si, allow for new phases of matrices to be formed for CFR-CMCs but cause degradation to reinforcing materials and limit their operating conditions. Al particles were used to react with a SiCN-based inorganic polymer to create new phases for matrix materials. XRD showed the formation of AlN, β-SiC, and Si after pyrolysis. This synthesis presented a simple and quick way to potentially tailor the matrix material properties for CFR-CMCs.

CFR-CMCs were fabricated with the modified matrix material. An SiCN-based inorganic polymer and 20 wt.% addition of Al particles were used as the matrix material. The interface of choice was BN/Si₃N₄. Recognizing that Al reacts with BN and Si₃N₄ led to an improved coating with increasing layers of Si₃N₄. The main goal of using different thicknesses of Si₃N₄ was to mitigate any free elements from degrading the BN coating. The effects of increasing the Si₃N₄ layer can be seen in the stress vs. displacement curves shown in
Figure 1.3.6: Stress vs. displacement curves for 1X, 2X, and 3X CFR-CMCs.
Figure 1.3.7: FE-SEM fractographs of (a) the 1X CFR-CMC, (b) the 2X CFR-CMC, and (c) the 3X CFR-CMC.
Figure 1.3.6. The results showed that there was a direct relationship between the thickness of the Si$_3$N$_4$ layer and the mechanical strengths of the CFR-CMCs. FE-SEM was used to confirm the toughening mechanisms for the CFR-CMCs with the highest mechanical strength. The CFR-CMC with the thinnest Si$_3$N$_4$ layer proved to be inadequate in its ability to transfer load between the matrix and the reinforcing fiber.
2.1 Self-Healing Matrix Systems

The previous chapter focused on the development of ceramic materials to consolidate around reinforcing fibers using inorganic polymers. The pyrolysis of silicon-based inorganic polymers led to the formation of SiC and Si₃N₄ ceramic materials that possess desirable features, making them good materials for use in CFR-CMCs. The use of the polymer impregnation and pyrolysis process to fabricate CFR-CMCs have gained popularity and inorganic polymers provide the desired polymer-to-ceramic material to consolidate a matrix around reinforcing fibers. Tailoring the ceramic material after pyrolysis by modifying the backbone of the inorganic polymer or the addition of reactive fillers produced materials that showed promise to enhance the thermal, mechanical, and environmental properties for the matrix component of a CFR-CMC. However, these enhancements are limited to the availability and cost of the reinforcing ceramic fibers. Currently, one of the mass produced fibers easily available are carbon-based fibers.
Carbon-based fibers are produced using polymer precursors such as polyacrylonitrile (PAN) or petroleum derived pitch. The availability has increased and the cost of these fibers has decreased, making them favorable for use in this research due to their high mechanical strengths and corrosion resistance at low temperatures (<300 °C). The high mechanical strength, stability at high-temperatures (>2000 °C), and abundance of the product make carbon fibers an attractive reinforcing material for CFR-CMCs. The major drawback to the use of carbon fibers as the reinforcement in $C_{fiber}/SiC_{matrix}$ CFR-CMCs is the susceptibility of the fibers to oxidation at elevated temperatures (>400 °C).

Using SiC as a matrix material results in a thermal expansion mismatch that causes micro-cracks to form in the matrix. Whether forming an SiC matrix through pyrolysis of an inorganic polymer, CVD, CVI, and/or other techniques, micro-cracks are inherently formed. Exposing the $C_{fiber}/SiC_{matrix}$ system to high-temperature oxidation allows oxygen to penetrate through the micro-cracks, thus oxidizing the carbon fibers to CO$_2(g)$ or CO$_2(g)$. Although SiC and Si$_3$N$_4$ ceramic materials produce passive SiO$_2$ layers that mitigate oxygen diffusion, the micro-cracks are not completely sealed through this process and allow the oxygen to migrate and degrade the components.

One way to prevent the oxidation of carbon fibers is to incorporate material systems that can “self-seal” or “self-heal” the micro-cracks and/or react with the migrating oxygen prior to the oxygen interacting with the fiber.
or interface (if applicable). A material system that has shown promise is the in situ formation of borosilicate glass. Borosilicate glass as a matrix alone is not desirable because of its softening point at 820 °C. However, its use as a material formed within the micro-cracks can lead to protection of the fibers and interface during environmental attack by hindering further oxidation. This approach was used for this research.

The fabrication of borosilicate glass has been around for more than a century, and different methods of producing this material have been investigated. For use as a matrix material in CFR-CMCs, a more complex approach had to be engineered because the borosilicate material must be homogeneous, uniform, and stoichiometric materials needs to be deposited onto to substrates rather than reacting compounds together. The approach seen in this section utilizes multiple layers of a boron-containing material and a silicon-containing material. As oxygen migrates through the micro-cracks in the silicon-containing layer (SiC) in high-temperature oxidative environments, the boron-containing layer (i.e., B₄C), will oxidize to B₂O₃. At a temperature of 600 °C, B₄C will react with oxygen to form B₂O₃, which in this state does not provide the desired effect of self-healing, rather it acts as an oxygen “getter.” As temperatures increase to 1000 °C, the B₂O₃ will react with the SiO₂ to form a borosilicate glass. The glass acts as a viscous liquid to fill in the micro-cracks. Equations 20 - 25 show the desired reaction sequence to forming the self-healing matrix material.
\[ 2 \text{SiC}(s) + 3 \text{O}_2(g) \xrightarrow{800 \degree C} 2 \text{SiO}_2(l,s) + 2 \text{CO}(g) \] (20)

\[ \text{B}_4\text{C}(s) + 4 \text{O}_2(g) \xrightarrow{600 \degree C} 2 \text{B}_2\text{O}_3(l) + \text{CO}_2(g) \] (21)

\[ \text{B}_2\text{O}_3(l) \xrightarrow{600-1000 \degree C} \text{B}_2\text{O}_3(g) \] (22)

\[ \text{SiO}_2(l,s) + \text{B}_2\text{O}_3(l) \xrightarrow{1000 \degree C} \text{B}_2\text{O}_3 \cdot x\text{SiO}_2(l) \] (23)

\[ \text{B}_2\text{O}_3 \cdot x\text{SiO}_2(l) \xrightarrow{\geq 1000 \degree C} \text{B}_2\text{O}_3(g) + x\text{SiO}_2(s) \] (24)

\[ 2 \text{C}(s) + \text{O}_2(g) \xrightarrow{400 \degree C} 2 \text{CO}(g) \] (25)

This approach was successful in preventing oxidation in C\text{fiber}/C\text{interface} and C\text{fiber}/SiC\text{matrix} CFR-CMCs. [73–76] Although the engineering of this self-healing matrix is most suitable for carbon fiber reinforced CMCs, this section used a SiC-based fiber (Nicalon\textsuperscript{TM}) to analyze mechanical and oxidative properties of the multilayered matrix system. Nicalon\textsuperscript{TM} fibers enabled two interfacial coatings, PyC and BN/Si\textsubscript{3}N\textsubscript{4}, to be used for this study. For reasons not explained in this dissertation, the BN/Si\textsubscript{3}N\textsubscript{4} interface does not deposit uniformly on carbon fibers, but both interfaces are deposited homogeneously on Nicalon\textsuperscript{TM} fibers.

Single strand unidirectional mini-composites, which are classified as CFR-CMCs, were fabricated to investigate the mechanical properties for both interfacial coatings. To perform initial studies on the multilayered matrix material, single strand unidirectional mini-composites were fabricated. This method provided information in a short time frame as compared to the PIP
process, which provided critical data to determine whether the system was suitable for larger fabrication techniques. Rather than using large woven plies of fabric, a single continuous fiber (tow) was infiltrated with matrix material. Commonly, the CVI process is used to infiltrate the tow to form the single strand unidirectional mini-composite. Similar to the CVD process, the CVI process uses gaseous precursors that are allowed to decompose or react and infiltrate the substrate. The architecture of the substrate mainly denotes the difference between the two processes.

The following research shows a multilayered matrix system deposited on two interfacial coatings. The two systems will be labeled as SiC$_{fiber}$/X/SiC/(B$_4$C/SiC)$_x$, where SiC$_{fiber}$ is CG-Nicalon™ fiber, X is either the PyC or the BN/Si$_3$N$_4$ interface and SiC/(B$_4$C/SiC)$_x$ is the self-healing matrix material. After the SiC/(B$_4$C/SiC)$_x$ matrix material was deposited, the CVI process was used to infiltrate a final SiC matrix to form the single strand unidirectional mini-composites.

2.1.1 B$_4$C Deposition Parameters

Deposition parameters for B$_4$C had to be determined prior to the fabrication of the multilayered matrix. The precursors used for the deposition needed to be precisely controlled otherwise different phases of boron carbide could have been formed. Reagent grade BCl$_3$ and reagent grade propylene (C$_3$H$_6$) were used as the precursors to deposit the boron-containing layer. A
similar hot-wall tube furnace shown in Figure 2.1.1 was used to deposit a crystalline B$_4$C material. Swagelok™ compression fittings were used to seal the reactor and MKS™ Mass Flo Controllers (MFCs) were used to deliver the gasses. Table 2.1.17 shows the experimental parameters used to determine the optimal precursor flow rates to deposit crystalline B$_4$C. The lowest temperature in which crystalline B$_4$C could be deposited was determined to be 1150°C. Temperatures below 1150°C produced amorphous materials. To begin deposition, the furnace and mixing chamber were flushed with Ar in order to remove any residual air from the system. The furnace was then brought to a deposition temperature of 1150°C under flowing H$_2$. Once the furnace reached equilibrium and was under flowing H$_2$, BCl$_3$ and C$_3$H$_6$ were allowed to flow.

2.1.2 X-ray Powder Diffraction

For each of the conditions presented in Table 2.1.17, the material deposited on the silica tube was collected from four zones, separated by 7.62 cm. The position of the four zones can be seen in Figure 2.1.1. Each zone was carefully cut to remove the deposited material and analyzed by XRD. Of the multiple parameters investigated, Run # 3 was the only combination that produced the desired crystalline B$_4$C phase. All other combinations produced amorphous materials. Figure 2.1.2 shows the crystalline phases in the four zones obtained from Run # 3. Although Run # 3 produced an amorphous material in the first zone, zones two - four produce varying crystalline ma-
Figure 2.1.1: Diagram of the atmospheric CVD rig used to deposit the various thin films.
Table 2.1.17: Flow rate variations of the boron precursor (BCl$_3$) and carbon precursor (C$_3$H$_6$) used to determine the conditions needed to deposit crystalline boron carbide.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>BCl$_3$ (sccm)</th>
<th>C$_3$H$_6$ (sccm)</th>
<th>H$_2$ (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>1150</td>
<td>30</td>
<td>2</td>
<td>155</td>
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</tr>
<tr>
<td>3</td>
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<td>7</td>
<td>30</td>
<td>1150</td>
<td>50</td>
<td>3</td>
<td>155</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>1150</td>
<td>50</td>
<td>4</td>
<td>155</td>
</tr>
</tbody>
</table>
terial. The forth zone of the furnace produced the desired crystalline B$_4$C phase. Precise concentration of the precursors and position within the furnace demonstrate the complexity of depositing crystalline B$_4$C at a temperature of 1150 °C.

2.1.3 Multilayered Matrix Deposition Parameters

After the parameters for depositing crystalline B$_4$C were acquired, a new furnace configuration was developed to allow for the deposition of two materials. Reagent grade BCl$_3$ and reagent grade propylene (C$_3$H$_6$) were used as the precursors to deposit the boron-containing layer. The silicon-containing layer was formed through the decomposition of methyltrichlorosilane (MTS). The furnace configuration shown in Figure 2.1.1 was used to deposit crystalline B$_4$C- and SiC-layered matrices on coated CG-Nicalon™ fibers. Commercially available PyC-coated CG-Nicalon™ and BN/Si$_3$N$_4$-coated CG-Nicalon™ (described in Section 2.2.1) were used as the interfaces.

To begin depositing on the coated fibers, the reactor and the mixing chamber were flushed with Ar to remove any residual air from the system. The reactor was then brought to a deposition temperature of 1150 °C under flowing H$_2$. Once the reactor reached equilibrium and with flowing H$_2$, either BCl$_3$ and C$_3$H$_6$ or CH$_3$SiCl$_3$ were allowed to flow, depending on which layer was being deposited. This process was varied several times to produce a multilayer matrix material. Table 2.1.19 shows the deposition parameters that
Figure 2.1.2: XRD patterns of the deposition zone dependency on the crystallinity of boron carbide material formed (* = $\text{B}_4\text{C}$).
Table 2.1.18: JCPDS vs. experimental reflections of the deposited material from the forth zone using Run # 3 parameters.

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>2θ</th>
<th>I/I₀</th>
<th>2θ</th>
<th>I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td>22.02</td>
<td>21</td>
<td>21.72</td>
<td>54.87</td>
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<tr>
<td>0</td>
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<td>2</td>
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<td>49</td>
<td>23.72</td>
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<td>34.66</td>
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<td>100</td>
<td>37.38</td>
<td>100</td>
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<td>13</td>
<td>63.82</td>
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<td>0</td>
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<td>12</td>
<td>66.08</td>
<td>23.39</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>70.36</td>
<td>8</td>
<td>70.9</td>
<td>23.48</td>
</tr>
</tbody>
</table>

*=ASTM Card No. : 35-798
were run consecutively for each multilayer matrix formed.

2.1.4 Field Emission Scanning Electron Microscopy

FE-SEM micrographs showed the multilayered \((B_4C/\text{SiC})_x\) matrix deposited uniformly around the CG-Nicalon\textsuperscript{TM} fibers shown in Figures 2.1.3 and 2.1.4. The darker rings are attributed to the B\(_4\)C layer and the lighter, metallic rings are the SiC layers. The thickness of the B\(_4\)C and SiC layers ranged between 2 - 5 \(\mu\)m. The PyC (Figure 2.1.4) and BN/\(\text{Si}_3\text{N}_4\) (Figure 2.1.3) interfaces cannot be observed in their respective micrographs because of the low magnification. The reported thickness for the commercially available PyC coated CG-Nicalon\textsuperscript{TM} is around 10 nm. Previous examination of the BN/\(\text{Si}_3\text{N}_4\) interface showed the BN layer had a thickness range of 250 - 350 \(\mu\)m and the \(\text{Si}_3\text{N}_4\) layer ranged from 75 to 100 \(\mu\)m. The FE-SEM instrument used for this characterization is described in Section 1.3.4.

2.1.5 Single Strand Unidirectional Mini-Composite Mechanical Testing

To understand the multilayered matrix properties, single strand unidirectional mini-composites were fabricated. Single continuous fibers with the \((B_4C/\text{SiC})_x\) multilayered matrix and either the PyC or BN/\(\text{Si}_3\text{N}_4\) interface were placed in a 2.54 cm diameter silica tube. The silica tube was positioned in a hot-walled reactor and UHP argon was allowed to flow through the setup. The reactor was brought to a temperature of 1050 °C and allowed to equilibrate.
Table 2.1.19: Deposition parameters for the multilayered (B$_4$C/SiC)$_x$ interface.

<table>
<thead>
<tr>
<th>Film</th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>BCl$_3$ (sccm)</th>
<th>C$_3$H$_6$ (sccm)</th>
<th>H$_2$ (sccm)</th>
<th>H$_2$ through MTS (sccm)</th>
<th>Ar (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>20</td>
<td>1050</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>150</td>
<td>20</td>
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<td>B$_4$C</td>
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<td>1150</td>
<td>50</td>
<td>2</td>
<td>155</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiC</td>
<td>20</td>
<td>1050</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>B$_4$C</td>
<td>30</td>
<td>1150</td>
<td>50</td>
<td>2</td>
<td>155</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiC</td>
<td>20</td>
<td>1050</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>B$_4$C</td>
<td>30</td>
<td>1150</td>
<td>50</td>
<td>2</td>
<td>155</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiC</td>
<td>20</td>
<td>1050</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>150</td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 2.1.3: FE-SEM micrograph of a polished SiC\textsubscript{fiber}/BN/Si\textsubscript{3}N\textsubscript{4}/SiC/(B\textsubscript{4}C/SiC)\textsubscript{x} system.
Figure 2.1.4: FE-SEM fractograph of a SiC<sub>fiber</sub>/PyC/SiC/(B<sub>4</sub>C/SiC)<sub>3</sub> system.
After 15 minutes, UHP hydrogen was bubbled through methyltrichlorosilane (Gelest, Inc.) at a rate of 150 sccm for three to five hours. This procedure was used to fabricate all single strand unidirectional mini-composites discussed throughout this dissertation.

Tensile testing was conducted on the as-fabricated mini-composites. The standard practice for tensile testing a mini-composite is to mount the single strand fiber in a cardboard holder with a gauge window of 2.54 cm by 1.27 cm. The ends of the continuous fiber not within the gauge window were secured to the cardboard using epoxy. The cardboard holder provides support for the mini-composite during processing. An Instron™ 1011 machine was used to provide the mechanical data of the mini-composites. The cardboard and mini-composite setup was placed between an upper and lower grip and secured using pneumatic pressure. Prior to exerting tension, all cardboard support was detached so the load was entirely concentrated on the mini-composite. The crosshead speed used was 0.254 mm/min. The information obtained from this instrument was stress vs. displacement curves. The stress values were reported in pounds for this instrument. In order to convert to MPa, the cross-sectional areas of the mini-composites were measured. FE-SEM provided micrographs that showed the cross-sectional area for each mini-composite. Using ASTM standard equations, the stress value in pounds was converted to MPa. The curves for the as-fabricated mini-composites with the PyC interface and
multilayered matrix are shown in Figure 2.1.5.

An average tensile strength of 192.2 MPa with a standard deviation of 34.8 MPa was attained. The curves for the as-fabricated mini-composites with the BN/Si$_3$N$_4$ interface and multilayered matrix are shown in Figure 2.1.6. An average tensile strength of 229 MPa with a standard deviation of 78.5 MPa was attained. Table 2.1.20 shows the tensile strengths for each mini-composite fabricated.

**2.1.6 Fractograph of the Single Strand Unidirectional Mini-Composite**

After tension was applied to the mini-composites and the stress vs. displacements curves were generated, FE-SEM fractographs were obtained. Figure 2.1.7 shows the mini-composite denoted as SiC$_{\text{fiber}}$/PyC/SiC/(B$_4$C/SiC)$_3$. The multilayered matrix surrounds the individual fibers while the CVI SiC fills in the voids, creating a denser mini-composite. The fractograph shows toughening mechanisms of fiber pull-out and crack deflection, which correspond to the non-linearity or dips in the stress vs. displacement curves.

**2.1.7 Environmental Testing**

To continue the concept for improving environmental resistance by using a multilayered matrix approach, TGA analysis under air was conducted. The SiC$_{\text{fiber}}$/PyC/SiC/(B$_4$C/SiC)$_3$ mini-composite and an SiC$_{\text{fiber}}$/PyC/SiC mini-composite were compared for oxidation resistance. The SiC$_{\text{fiber}}$/PyC/SiC mini-
Figure 2.1.5: Stress vs. displacement curves for the (1 - 4) as-fabricated single strand unidirectional mini-composites using the PyC interface as reported in Table 2.1.16.
Figure 2.1.6: Stress vs. displacement curves for the (5 - 7) as-fabricated single strand unidirectional mini-composites using the BN/Si$_3$N$_4$ interface as reported in Table 2.1.16.
Table 2.1.20: Tensile strength comparison between PyC and BN/Si$_3$N$_4$ interfaces for as-fabricated multilayered (B$_4$C/SiC)$_3$ single strand unidirectional mini-composites.

<table>
<thead>
<tr>
<th>Single strand unidirectional mini-composites</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) SiC$_{fiber}$/PyC/SiC/(B$_4$C/SiC)$_3$</td>
<td>209.1</td>
</tr>
<tr>
<td>(2) SiC$_{fiber}$/PyC/SiC/(B$_4$C/SiC)$_3$</td>
<td>174.2</td>
</tr>
<tr>
<td>(3) SiC$_{fiber}$/PyC/SiC/(B$_4$C/SiC)$_3$</td>
<td>153.9</td>
</tr>
<tr>
<td>(4) SiC$_{fiber}$/PyC/SiC/(B$_4$C/SiC)$_3$</td>
<td>231.7</td>
</tr>
<tr>
<td>(5) SiC$_{fiber}$/BN/Si$_3$N$_4$/SiC/(B$_4$C/SiC)$_3$</td>
<td>317.2</td>
</tr>
<tr>
<td>(6) SiC$_{fiber}$/BN/Si$_3$N$_4$/SiC/(B$_4$C/SiC)$_3$</td>
<td>167.1</td>
</tr>
<tr>
<td>(7) SiC$_{fiber}$/BN/Si$_3$N$_4$/SiC/(B$_4$C/SiC)$_3$</td>
<td>202.4</td>
</tr>
</tbody>
</table>
Figure 2.1.7: FE-SEM fractograph of a SiC<sub>fiber</sub>/PyC/SiC/(B<sub>4</sub>C/SiC)<sub>3</sub> system.
composite was fabricated using the same conditions provide in Section 2.1.5. Figure 2.1.8 shows the effect of the multilayered matrix (solid line) compared to a matrix containing only SiC (dotted line). Oxidation of B₄C occurs at 600 °C initiating the percentage mass gain for the multilayered matrix system. At around 800 °C, the SiC_fiber/PyC/SiC mini-composite showed a decrease in percent mass indicating the limits of the SiC matrix protection of the PyC interface. The oxidation of the PyC interface for the SiC_fiber/PyC/SiC mini-composite continued to occur, suggested by the percentage mass decrease up to 1000 °C. The SiC_fiber/PyC/SiC/(B₄C/SiC)₃ mini-composite plateaued around a temperature of 1000 °C, suggesting the decrease in oxidation of matrix materials and possible sealing of the micro-cracks. A protective mechanism is shown in Figure 2.1.9 where the B₄C layer has a change in morphology after environmental testing. As oxygen migrates, the B₄C layer reacts with oxygen and diffuses into the micro-cracked SiC layer, hindering oxygen from reaching the reinforcing fiber and the interface. The diffusion of the B₄C layer is shown for the outermost layers, while the core showed limited change representing a multilayered protection.

2.1.8 Discussion

Investigation of multilayered matrix materials for CFR-CMCs shows the importance of arresting environmental attack of the fiber and interface. Providing multiple layers to inhibit oxygen migration through the matrix decreases
Figure 2.1.8: Air TGA analysis comparison of $\text{SiC}_{\text{fiber}}/\text{PyC}/\text{SiC}/(\text{B}_4\text{C}/\text{SiC})_3$ and $\text{SiC}_{\text{fiber}}/\text{PyC}/\text{SiC}$ single strand unidirectional mini-composites.
Figure 2.1.9: FE-SEM micrograph of a polished SiC$_{fiber}$/PyC/SiC/(B$_4$C/SiC)$_x$ system after partial oxidation.
the probability of catastrophic degradation to a CFR-CMC. An interesting area to investigate regarding improved environmental resistance is to explore materials that actively react with oxygen and form barriers so subsequent attack does not occur. Equations 8 - 13 show desired reactions to impede oxidation in a ceramic body. A multilayered system was developed using repeating $B_4C$ and SiC layers. In order to deposit crystalline material, careful attention was given to the $B_4C$ layer. Crystalline vs. amorphous deposited materials decrease the chance of microstructural changes to the coating. Commonly, operating temperatures for ceramic materials deposited using CVD are above the processing temperatures, facilitating the need for crystalline material. Microscopy characterization of the multilayered matrix material revealed concentric rings of repeating $B_4C$ and SiC layers. Mini composites obtained average tensile strengths of 192.2 and 229 MPa that used a PyC or BN/$Si_3N_4$ interface, respectively, with the multilayered matrix. This range represented acceptable strengths using CG-Nicalon™ as the reinforcing fiber. [77] While the multilayered matrix material provided properties of protection for the mini-composites using CG-Nicalon™ fibers, the overall application will be realized with the use of carbon-based reinforcing fibers.

2.2 Non-Oxide Interfaces for CFR-CMCs

To complement the work in the previous section, a similar approach
was taken to developing non-oxide interfaces for CFR-CMCs. A multilayered system of BN/Si₃N₄/BN was investigated for both mechanical and environmental applications. Boron nitride was chosen as the interface on CG-Nicalon™ fibers due to its softness, the turbostratic crystal structure, and inertness. These are desired properties for an interface to exhibit toughening mechanisms in CFR-CMCs. [19, 20, 82] One of the main disadvantages of using BN as an interfacial material is the inherent oxygen pick-up that occurs when exposed to the atmosphere. This drawback was solved by depositing an Si₃N₄ overcoat on the BN layer. The BN/Si₃N₄ duplex coating was proven to be beneficial in increasing mechanical strength of CFR-CMCs. [78]

A drawback of using Si₃N₄ as an overcoat layer is that it is a highly stressed material. [83] This can potentially hinder the environmental resistance of the BN/Si₃N₄ duplex coating by creating micro-cracks, which cause oxidation to the interface. A boron-containing outer layer, boron nitride, was employed to protect the original BN/Si₃N₄ interfacial coating. The BN/Si₃N₄/BN interfacial coating offers a more economical approach to the development of a multilayered system. Previously, the B₄C/SiC system was repeated three times over the course of several hours on a single continuous fiber. Depositing this system on woven fabric or 3D structures will be a long and complex process. Although the previous section investigated the properties for a multilayered matrix material and the reason for the lengthy deposition time, this research focused on
applying the self-healing mechanism to the interfacial coating.

A CVI SiC matrix was used on coated CG-Nicalon™ fibers to form single strand unidirectional mini-composites to initially observe the mechanical and environmental behavior of the BN/Si₃N₄/BN triplex interfacial coating as compared to the BN/Si₃N₄ duplex interfacial coating. Then, 15.24 cm by 22.86 cm CFR-CMC panels with the duplex and triplex interfacial coating were fabricated using the PIP process. Larger CFR-CMC panels were developed to validate the feasibility of the triplex coating for industrial purposes. Mechanical tests of the PIP CFR-CMC panels with the duplex and triplex interfaces were performed before and after environmental exposure. The use of the PIP process to produce CFR-CMCs as compared to the CVI process has gained popularity due to the ease of fabrication and the ability to use conventional manufacturing techniques. A unique problem with the use of the PIP process to fabricate CFR-CMCs is the formation of “eyebrows”. [80, 81] This terminology, known as “eyebrowing” or “earing,” arises from the appearance of the interface coating after composite processing (Figure 2.2.1). During the several infiltration and pyrolysis cycles in which the polymer is converted from an amorphous network to a crystalline network, gases are evolved [40, 41] and the matrix shrinks, potentially causing damage to the interface. This investigation will also examine micro-structural evidence of the triplex BN/Si₃N₄/BN coating to understand whether the outer BN layer can eliminate or reduce the
eyebrowing effect. BN was chosen for the outer layer due to its ease of de-
position and mechanical properties. The CVI process was used to fabricate
mini-composites to show proof of the concept, and the PIP process was used
secondly to fabricate larger CFR-CMCs for industrial applications.

![Image](image_url)

Figure 2.2.1: Optical image of a CFR-CMC fabricated using the PIP process
showing “eyebrowing” of the interface.

### 2.2.1 Deposition Parameters for Interfacial Coatings

The BN/Si$_3$N$_4$ duplex and BN/Si$_3$N$_4$/BN triplex interface coatings were
deposited on 8 harness satin CG-Nicalon$^{\text{TM}}$ fabric using a hot-walled low-
pressure (LP) CVD reactor (Figure 2.2.2). The reactor consisted of a 21 cm
inner diameter silica tube with an 18.4 cm inner diameter graphite sleeve. The
graphite sleeve was used to protect the silica tube from the deposition of the
BN and Si$_3$N$_4$. Elastomer seals were used to maintain a vacuum. A Lindberg Blue tube furnace provided the heat. MKS$^\text{TM}$ mass flow controllers were used to deliver the gases along with an MKS$^\text{TM}$ throttling valve and MKS$^\text{TM}$ absolute pressure manometers, which maintained the pressure. A liquid nitrogen trap was used to collect by-products and a Trivac$^\text{TM}$ D30A vacuum pump was used to evacuate the system.

In a typical experiment, a 1 meter long by 0.4 meter wide section of woven CG-Nicalon$^\text{TM}$ fabric was wrapped around a graphite mandrel and loaded into the furnace. The furnace was evacuated three times and backfilled with UHP nitrogen to remove any oxygen. The reactor was then brought up to the deposition temperature under flowing anhydrous NH$_3$ and UHP N$_2$. The anhydrous ammonia was used to remove the sizing on the fabric. After the reactor reached an equilibrium temperature, flows were set and either chemically pure BCl$_3$ (99.9%, Airgas) or research grade SiCl$_4$ (99.9%, Sigma Aldrich) were allowed to flow. A liquid nitrogen trap was filled prior to the flowing of any of the reactive gases. Experimental parameters for the deposition of BN and Si$_3$N$_4$ are given in Table 2.2.21. Note for the triplex coating the BN parameters were rerun following the Si$_3$N$_4$ deposition.

2.2.2 PIP CFR-CMC Fabrication

CFR-CMCs were fabricated with eight plies of BN/Si$_3$N$_4$ or BN/Si$_3$N$_4$/BN coated CG-Nicalon$^\text{TM}$ fabric and impregnated with a hydridopolysilazane poly-
mer (COI Ceramics, Inc.) containing less than 15% of 30 µm α-silicon nitride (Alfa Aesar, 95%) filler. The plies of fabric were laid up in a warped aligned symmetric orientation and were impregnated using standard vacuum bag processing techniques. The eight plies were heated to around 250 °C to form a cured disordered polymer network around the reinforcing fibers (referred to as a green body). The green body was then pyrolyzed by placing the CFR-CMC in a hot-wall reactor and heated to 1200 °C at a rate of 2 °C/min under flowing UHP N₂ with a soak time of one hour at temperature. This cyclic process was repeated with as-received HPZ polymer nine times until the CFR-CMC had a density of around 2.1 g/cm³. A fiber volume of 40% was achieved for both CFR-CMCs. The HPZ polymer was converted into a SiCN matrix material during the pyrolysis to 1200 °C (shown in Equation 16). The fabrication of the single strand unidirectional mini-composite followed the procedure in Section 2.1.5.
2.2.3 Environmental Testing

As-fabricated single strand unidirectional mini-composites and CFR-CMCs were exposed to environmental testing. For the single strand unidirectional mini-composites, this consisted of high-temperature cyclic oxidation. The mini-composites were placed in a box furnace under flowing air and brought to a temperature of 816 °C and held for three hours. The mini-composites were allowed to cool to room temperature and then brought back up to 816 °C. The cycle was repeated a total of three times. The procedure for the CFR-CMCs introduced exposure to humidity at room temperature followed by high-temperature oxidation. The procedure for the CFR-CMCs’ environmental testing is outlined below:

(1) The composites were sprayed with de-ionized water.
(2) The composites were placed in a humidity chamber for 24 hours at 32 °C in 90% humidity.

(3) The composites were placed in a drying oven for two hours at around 127 °C.

(4) The composites were placed into an air furnace at 816 °C held for three hours.

(5) This cycle was repeated three times.

2.2.4 Testing and Characterization

Thickness measurements were taken of the triplex coating before and after composite fabrication using the FE-SEM described in Section 1.3.4. Four-point bend tests and tensile tests were measured on an Instron™ model 4202 and an Instron™ model 1011 universal testing machines, respectively. For the four-point bend tests, samples were cut from the PIP fabricated CFR-CMCs with average dimensions of 12.7 cm by 1 cm by 0.30 cm with a support span and load span of 10.6 cm and 2.54 cm, respectively and a crosshead speed of 0.38 cm/min. For the tensile tests, single strand unidirectional mini-composites were mounted in a cardboard holder with a gauge window of 2.54 cm by 1.27 cm. The crosshead speed used was 0.254 mm/min.
2.2.5 Results

Visual examination of the coated fiber revealed that the fabric had a translucent blue-green coating that was fairly even throughout the fabric. Figure 2.2.3 shows an FE-SEM micrograph of the triplex interface coated on a CG-Nicalon™ fiber. A uniform Si₃N₄ layer can clearly be seen sandwiched between two BN layers. The surface morphology appeared to be smooth indicating the layers adhered well to the fiber. As described in Table 2.2.22, the average thickness obtained for the BN layer closest to the fiber, the middle Si₃N₄ layer, and the outermost BN layer were 70 nm ± 10 nm, 40 nm ± 10 nm, and 70 nm ± 10 nm, respectively. Room temperature mechanical testing was performed on the as-fabricated and environmentally exposed single strand unidirectional mini-composites. The average UTS of the single strand unidirectional mini-composites with the triplex and the duplex interfaces were 186 MPa and 234 MPa, respectively. The single strand unidirectional mini-composites fabricated with the triplex interface after environmental exposure observed an average mechanical strength of 137.8 MPa. This was a 26% decrease from the unexposed mini-composites with the triplex interface. The mini-composites fabricated with the duplex interface were degraded after environmental exposure to the extent that tensile tests could not be conducted.

Figure 2.2.4 shows FE-SEM fractographs of single strand unidirectional mini-composites fabricated with the BN/Si₃N₄/BN triplex interface and the
BN/Si$_3$N$_4$ duplex interface. To confirm the significance of the outer BN layer prior to environmental exposure, micro-structural evaluation of the triplex interface is shown in Figure 2.2.5. These fractographs show toughening mechanisms (e.g., fiber pullout and crack deflection) and three distinctive interfacial layers with no interactions between the outermost BN layer and the SiC matrix. FE-SEM fractographs of a single strand unidirectional mini-composite after exposure to high-temperature oxidation are presented in Figure 2.2.6. Figure 2.2.6(a) shows interaction zones within the SiC matrix, which are indicated by the darker regions of the matrix closest to the interface. This region is compared to the lighter regions of the matrix furthest from the interface.

To test the validity of the triplex interface on an industrial level, PIP CMC panels were fabricated and tested under similar conditions for the mini-composites. Tables 2.2.23 - 2.2.25 present results for the four-point bend tests performed on the composites made with the duplex and triplex interfaces before and after environmental exposure. The average mechanical strength for the PIP fabricated CFR-CMC using the duplex interface was 239 MPa. After environmental exposure, the CFR-CMC using the duplex interface had an average mechanical strength of 90.5 MPa, a decrease of 62%. The average mechanical strength for the composite fabricated with the triplex interface prior to environmental exposure was 191 MPa. After environmental exposure, the CFR-CMC using the triplex interface had an average mechanical strength of
129 MPa, a decrease of 32%. Figure 2.2.7 presents a FE-SEM micrograph of a polished surface of a CFR-CMC with the BN/Si$_3$N$_4$/BN triplex interface. The Si$_3$N$_4$ layer appears as the lighter color material in between the two darker BN layers. The overall thickness is consistent with measurements observed before composite fabrication. FE-SEM analysis also showed the absence of eyebrows. Figure 2.2.8 shows a fractograph of a PIP fabricated CFR-CMC panel with the triplex interface prior to environmental exposure showing debonding between the interface and matrix.

![FE-SEM micrograph of the triplex coated CG-Nicalon™](image)

Figure 2.2.3: FE-SEM micrograph of the triplex coated CG-Nicalon™.
Table 2.2.22: Coating thickness of the BN/Si$_3$N$_4$/BN interface from four different areas using FE-SEM micrographs.

<table>
<thead>
<tr>
<th>Position of coating</th>
<th>Area #1 (nm)</th>
<th>Area #2 (nm)</th>
<th>Area #3 (nm)</th>
<th>Area #4 (nm)</th>
<th>Average (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner BN layer</td>
<td>70</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>Middle Si$_3$N$_4$ layer</td>
<td>50</td>
<td>40</td>
<td>30</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Outer BN layer</td>
<td>80</td>
<td>60</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 2.2.23: Strengths for a PIP fabricated CFR-CMC using the triplex interface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Width (cm)</th>
<th>Thickness (cm)</th>
<th>Load (lbs)</th>
<th>Support span (cm)</th>
<th>Load span (cm)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.3</td>
<td>34.2</td>
<td>10.6</td>
<td>2.54</td>
<td>195.1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.3</td>
<td>35.2</td>
<td>10.6</td>
<td>2.54</td>
<td>199</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.3</td>
<td>37.1</td>
<td>10.6</td>
<td>2.54</td>
<td>195.7</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.3</td>
<td>28.5</td>
<td>10.6</td>
<td>2.54</td>
<td>161.3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>33.8 ± 3.7</td>
<td>191 ± 20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2.24: Strengths for a PIP fabricated CFR-CMC using the duplex interface after environmental testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Width (cm)</th>
<th>Thickness (cm)</th>
<th>Load (lbs)</th>
<th>Support span (cm)</th>
<th>Load span (cm)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.26</td>
<td>12.9</td>
<td>10.6</td>
<td>2.54</td>
<td>96.7</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.26</td>
<td>13.8</td>
<td>10.6</td>
<td>2.54</td>
<td>94.2</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.28</td>
<td>13.7</td>
<td>10.6</td>
<td>2.54</td>
<td>93.3</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.28</td>
<td>11.4</td>
<td>10.6</td>
<td>2.54</td>
<td>77.6</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>12.9 ± 1.1</td>
<td>90.5 ± 9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.2.4: FE-SEM fractographs of single strand unidirectional mini-composites with (a) BN/Si₃N₄/BN triplex interface and (b) BN/Si₃N₄ duplex interface. [78]
Figure 2.2.5: FE-SEM fractographs of a single strand unidirectional mini-composite not exposed to environmental testing with magnification of (a) 10000x and (b) 100000x.
Figure 2.2.6: FE-SEM fractographs of a single strand unidirectional mini-composite exposed to environmental testing with magnification of (a) 10000x and (b) 100000x.
Figure 2.2.7: FE-SEM micrograph of the polish surface of a PIP CFR-CMC with a triplex interface.

Table 2.2.25: Strengths for a PIP fabricated CFR-CMC using the triplex interface after environmental testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Width (cm)</th>
<th>Thickness (cm)</th>
<th>Load (lbs)</th>
<th>Support span (cm)</th>
<th>Load span (cm)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.3</td>
<td>34.2</td>
<td>10.6</td>
<td>2.54</td>
<td>111.3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.3</td>
<td>35.2</td>
<td>10.6</td>
<td>2.54</td>
<td>120.5</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.3</td>
<td>37.1</td>
<td>10.6</td>
<td>2.54</td>
<td>121.1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.3</td>
<td>28.5</td>
<td>10.6</td>
<td>2.54</td>
<td>163.4</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>23.9 ± 4.4</td>
<td></td>
<td></td>
<td>129 ± 23</td>
</tr>
</tbody>
</table>
Figure 2.2.8: FE-SEM fractograph of the PIP fabricated CFR-CMC with a triplex interface prior to environmental exposure.
2.2.6 CVI Fabricated Single Strand Unidirectional Mini-Composites Discussion

In recent years, there has been an increase in the amount of research that deals with material systems based on self-healing matrices. The premise is that micro-cracks in the matrix of a CFR-CMC, which are formed through various methods, are filled in due to the viscous borosilicate material formed under high-temperature oxidation conditions. [85] As shown in the previous section, multilayered matrix materials were fabricated and showed promise for hindering oxidation. This research investigated the use of a multilayered interface to obtain similar mechanisms observed for the matrix system. The BN/Si$_3$N$_4$/BN triplex interface showed this self-healing protection. The fractographs of the CVI fabricated mini-composites with the duplex and triplex interface showed drastically different results. Total embrittlement was observed for the mini-composites using the duplex interface after environmental exposure while a decrease of 26% was shown with the triplex interface.

Microstructural evaluation of the environmentally exposed mini-composites using the triplex interface showed reaction zones within the CVI SiC matrix indicating that a potential protective barrier was formed. The mechanism that is believed to be occurring is the formation of a glassy borosilicate material. The fractographs of the exposed single strand unidirectional mini-composite using the triplex interface showed dark areas representing a change in the
morphology of the matrix. Examination of this zone using Energy Dispersive X-ray Spectroscopy (EDS) showed the presence of boron in the SiC matrix. For this research, EDS only provides qualitative information because of the detection limits inherent to the technique but further investigation in the chemical composition of this area will need to be performed.

FE-SEM analysis of the exposed single strand unidirectional mini-composite with the duplex interfacial coating showed no morphological changes to the SiC matrix. This confirmed that the dark regions shown in Figure 2.2.6(a,b) represented more than just the oxidation of the SiC matrix but diffusion of boron material into the matrix.

2.2.7 PIP Fabricated CFR-CMCs Discussion

By adding an outer layer of BN to the duplex BN/Si₃N₄ interface, the properties associated with this material might be able to be manipulated to be advantageous in PIP CFR-CMC fabrication. Prior to environmental exposure the duplex and triplex interfaces were compared using PIP fabricated CFR-CMCs. The average four-point bend strengths for the as-fabricated CFR-CMCs with the triplex interface were 20% lower than the average observed for the CFR-CMCs having the traditional duplex interface. This decrease is potentially due to the outer BN layer inefficiently transferring the load between the matrix, the interface, and the fiber. Another reason for this decrease is the potential interaction between the outermost BN layer and the polymer used to form the
matrix prior to the pyrolysis cycle. Boron nitride is known to pick up oxygen and the polymer may contain trace amounts of oxygen in various forms, which could react readily with that layer causing degradation to the interface. Figure 2.2.8 shows good debonding between the interface and matrix which might indicate that there is little reaction between the outer BN layer and the polymer resin.

However, after environmental exposure, the PIP CFR-CMC panel with the triplex interface had an average mechanical strength 30% higher than the PIP CFR-CMC panel with the duplex interface. The mechanical strengths suggest the triplex interface is more applicable in high-temperature (>800 °C) oxidative applications. FE-SEM fractographs obtained for the PIP fabricated CFR-CMC with the triplex interface showed no indication of boron material diffusing into the matrix. Although FE-SEM analysis showed no mechanism for the oxidation retardation, future work will need to focus on understanding the mechanism in a PIP fabricated CFR-CMC. Lastly, a problem called eyebrowning associated with the PIP process also promoted the investigation of the outer BN. If eyebrowing was eliminated using the triplex interface, the corresponding mechanical data would show an increase in the mechanical strength, but this was not observed. Nevertheless, microstructural evaluation of the PIP CFR-CMC panel with the triplex interface showed no eyebrowing. The decrease in mechanical properties indicated a load transfer limitation of the triplex
interfacial coating. Overall the triplex coating showed promise as an interfacial material with potential increased oxidation resistance.

2.2.8 Conclusion

Single strand unidirectional mini-composites and CFR-CMCs were fabricated using CVI SiC and standard PIP processing, respectively. For each technique, the BN/Si$_3$N$_4$ duplex interface and BN/Si$_3$N$_4$/BN triplex interface were employed. FE-SEM analysis of the triplex coating showed that the thicknesses of the BN layers were 70 nm and the thickness of the Si$_3$N$_4$ layer was 40 nm. Mechanical testing of the single strand unidirectional mini-composites showed that the composites using the triplex interface had better mechanical properties than the mini-composite fabricated with the duplex interface after environmental testing. Fractographs of the as-fabricated mini-composites showed toughening mechanisms using both the duplex and triplex as interfaces.

After environmental exposure, FE-SEM analysis showed interaction zones in the triplex interface between the outer BN and the CVI SiC matrix. EDS characterization showed the presence of boron in the dark regions of the SiC matrix indicating the diffusion of the outer BN layer. The current mechanism for oxidation resistance in a multilayered system with a boron-containing layer and a silicon-containing layer, is the potential to form borosilicate glass. The characterization techniques used in this research are limited in the detection
of borosilicate glass. However, the mechanical data showed promise for the triplex interface after environmental exposure.

A decrease of 26% was observed for the mini-composite using the triplex interface after environmental exposure, where the mini-composite with the duplex coating saw complete degradation. Finally, the duplex and triplex interfaces were fabricated using a different matrix consolidation process that allowed for larger CFR-CMCs to be developed. The PIP fabricated CFR-CMC with the triplex interface saw a decrease of 20% as compared to the PIP CFR-CMC using the duplex interface prior to environmental exposure. After environmental expose the CFR-CMC with the duplex interface had an overall decrease of 62% while the CFR-CMC with the triplex interface had a decrease of 32%. The interfacial coating addressed in this section provided corresponding evidence of the oxidation resistance observed for other multilayered material systems.

2.3 Oxide Interfaces for CFR-CMCs

Metal Organic Chemical Vapor Deposition (MOCVD) was used to deposit a zinc oxide (ZnO) coating on ceramic fibers as an interfacial system for CFR-CMCs. ZnO coatings were deposited on CG-Nicalon™, Hi-Nicalon™, and Hi-Nicalon™ Type S fabric by the thermal decomposition of zinc acetate dihydrate in a low-pressure hot-wall CVD reactor. A duplex SiO₂ coating was
also deposited to protect the ZnO layer from the reducing conditions during composite fabrication. Mechanical testing was used to evaluate the effect of the ZnO coating on the strength retention of the ceramic fabrics. Single strand unidirectional mini-composites were fabricated by infiltrating SiC into the ZnO/SiO$_2$ duplex-coated fibers to understand the interfacial properties of the ZnO coating.

One solution to developing an interfacial coating for high-temperature oxidative environments would be to use interfaces that are already oxides. Examples of such interfaces are monazite (LaPO$_4$) and scheelite (CaWO$_4$), which have been extensively investigated. [86–90] Both of these coatings demonstrated properties that are attractive for an interfacial coating in a CFR-CMC but due to the micro-cracked structures and difficulties in maintaining the correct stoichiometry, other materials need to be investigated. Tin oxide (SnO$_2$) and zirconia (ZrO$_2$) coatings have also been investigated for their oxidation resistance and chemical compatibility with alumina. However, their ability to act as interfaces was limited to only porous coatings. [87, 91] An alternative approach to oxide composite fabrication is the development of porous matrices. Pores create toughening mechanisms by allowing cracks to arrive at fibers with less stress concentration than a dense matrix. This allows the fiber to remain intact until higher stresses are imposed. [92, 93] However, this process is limited by the matrix porosity and stability.
Zinc oxide was selected to be explored as an interfacial coating for CFR-CMCs. ZnO was expected to be a good interfacial material because of its softness, which is needed to allow for appropriate compliancy in CFR-CMCs and due to its high melting point (1977 °C). Zinc oxide has a hardness of 4.0 on the Mohs scale, which ranges from a hardness of 1.0 (talc) to a harness of 10 (diamond). For comparison, interfaces such as PyC and h-BN have a Mohs hardness of 1 - 2 and 1.65, respectively. [82] Zinc oxide was deposited from a zinc acetate precursor as shown in Equations 26 and 27. An advantage of using MOCVD to deposit the ZnO coating was that the processing parameters were at an optimal temperature when compared to other processing temperatures for interfaces such as PyC and BN, which are deposited at 650 - 1100 °C and 600 - 900 °C, [95] respectively. ZnO can uniformly be deposited at temperatures of 400 °C. This allows for lower operating costs and the potential interactions between the fiber and the coating can be minimized. One of the disadvantages of MOCVD is the incorporation of impurities such as carbon and oxygen. For oxide coatings, the incorporation of carbon in the coating can lead to the formation of CO_{(g)} or CO_{2(g)} at elevated temperatures (~400 °C) which creates spallations, in turn weakening the composite.

\[
4 \text{[Zn(CH}_3\text{CO}_2\text{)]}_2 \cdot 2\text{H}_2\text{O}}_{(s)} \xrightarrow{\Delta} \text{Zn}_4\text{O(}\text{CH}_3\text{CO}_2\text{)}_{6(s)} + 7\text{H}_2\text{O}}_{(g)} + (\text{CH}_3\text{CO})_2\text{O}}_{(g)} \tag{26}
\]

\[
\text{Zn}_4\text{O(}\text{CH}_3\text{CO}_2\text{)}_{6(s)} \xrightarrow{\Delta} 4\text{ZnO}}_{(s)} + 3(\text{CH}_3\text{CO})_2\text{O}}_{(g)} \tag{27}
\]

To protect the ZnO coating from the harsh by-products that are formed...
during composite fabrication, a SiO$_2$ duplex coating was employed. Overall, this allowed for the duplex coating to be categorized as an oxide coating. SiO$_2$ thin films also have other attractive properties, which include a close matching thermal expansion coefficient to ZnO, no reactivity with ZnO until 1300 °C, [96] and low oxygen diffusion as compared to other oxide materials. [97] Previous research has attempted to use SiO$_2$ as an interfacial material on SiC-based fibers but results showed complete degradation to the substrate. [26] This section presents the results of a new ZnO interfacial coating for applications in non-oxide systems.

### 2.3.1 Deposition Reactor Setup

Zinc oxide coatings were deposited using a hot-walled isothermal CVD furnace (main reactor) and a hot-walled vaporizing furnace shown in Figure 2.3.1. The reactor consists of a silica tube with an inner diameter of 7.62 cm and a mullite insert that was 6.35 cm in diameter. The mullite insert was used to protect the silica tube from the deposited ZnO. Stainless steel end caps with fluoroelastomer (Viton®) O-rings and Swagelok™ compression fitting were used to seal off the reactor. MKS™ MFCs were used to control the flow of UHP nitrogen and UHP oxygen gasses into the system. Two MKS™ absolute pressure transducers were used to monitor the pressure inside the reactor. A liquid nitrogen trap and a particulate trap were used to collect the by-products. A Welch Duo-seal™ (model 1402) vacuum pump provided the vacuum.
2.3.2 Deposition Parameters

In a typical experiment, a 15.2 cm by 20.3 cm section of CG-Nicalon\textsuperscript{TM}, Hi-Nicalon\textsuperscript{TM}, or Hi-Nicalon\textsuperscript{TM} Type S fabric was rolled and secured with spool CG-Nicalon\textsuperscript{TM}. The substrate was placed into the mullite tube and measured to the correct distance. Prior to adding the mullite tube into the main silica tube, an aluminum foil precursor boat (10 cm in length) was filled with the appropriate amount of zinc acetate dihydrate (98\%\%, Sigma-Aldrich\textsuperscript{TM}) precursor (around 35 g). The precursor boat was then loaded into the mullite tube and measured to the correct distance. The mullite tube containing the Nicalon\textsuperscript{TM} fabric and zinc precursor was placed inside the silica tube and measured to the correct distance. After the setup was evacuated down to less than one torr, the main reactor and vaporizer furnaces were then brought up to the desired temperatures. For this experiment, the main reactor was allowed to equilibrate at temperature (400 °C) before the vaporizing furnace was turned on and allowed to equilibrate (around 220 °C). The reaction was considered started when the UHP nitrogen was allowed to flow over the precursor boat. Table 2.3.26 provides certain parameters that were used on Nicalon\textsuperscript{TM} fabric.

2.3.3 Mechanical Testing

To test the tensile strength of the coated fiber, single tows were pulled from the coated fabric. These tows were mounted on a 3.8 cm by 12.7 cm piece of cardboard, centered in a 2.54 cm by 1.27 cm gauge window cut out
of the center of the cardboard mount. The fiber was placed lengthwise across the gauge window and held in place with an epoxy glue. An acrylic binder was placed on the fiber in the gauge window to ensure a uniform load was transferred between the fibers. Samples were tested using an Instron™ 1011 machine with a crosshead speed of 0.05 cm/min. Tables 2.3.28 - 2.3.30 show tensile data for as-received, ZnO-coated and ZnO/SiO₂-coated Nicalon™ fabric.

2.3.4 Duplex Coating Deposition

The thermal decomposition of tetraethyloorthosilicate (TEOS) (Gelest, Inc.) was employed to deposit SiO₂ on ZnO-coated Nicalon™ fabric. UHP nitrogen was bubbled through TEOS and flowed into a 2.54 cm diameter silica tube in a hot-walled CVD reactor. Single strand ZnO-coated Nicalon™ tows were placed on graphite tooling and set into the silica tube. The fibers were positioned 7.62 cm into a 39.37 cm long furnace. Deposition parameters are
presented in Table 2.3.26. Using the thickness measurements obtained from the FE-SEM, a deposition rate for SiO$_2$ was determined to be 50 nm per hour.

### 2.3.5 Single Strand Unidirectional Mini-Composite Fabrication

To test the ability of the coating to act as an interface, single strand unidirectional mini-composites were fabricated. SiC was used as an infiltrating matrix material to develop a SiC$_{fiber}$/ZnO/SiO$_2$/SiC$_{matrix}$ system. Deposition parameters are presented in Table 2.3.26 and discussed in Section 2.1.5.

| Table 2.3.26: Experimental parameters for ZnO, SiO$_2$, and SiC depositions. |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Thin film | Vaporizer temp (°C) | Reactor temp (°C) | N$_2$ flow rate (sccm) | N$_2$ flow rate through TEOS (sccm) | O$_2$ flow rate (sccm) | H$_2$ flow rate through MTS (sccm) | Pressure (Torr) | Time (hrs) | Deposition rate (nm/hr) |
| ZnO  | 210-220 | 400 | 70 | 0 | 30 | 0 | 2.3-3.4 | 1-2 | * |
| SiO$_2$  | N/A | 600 | 0 | 400 | 0 | 0 | 760 | 7 | 50 |
| SiC  | N/A | 1050 | 0 | 0 | 0 | 150 | 760 | 3-5 | 1.4 |

*Dependant on zinc acetate dihydrate precursor amount (35 g of precursor = 450 nm of ZnO coating)

### 2.3.6 Scanning Electron Microscopy

Figure 3.2.3 shows an FE-SEM micrograph of a ZnO-coated CG-Nicalon™ fiber. The ZnO coating appears as a smooth coating with no visible spallations. Figure 2.3.9 shows a uniform ZnO/SiO$_2$ coating on CG-Nicalon™. The thickness of the ZnO layer is around 500 nm and the SiO$_2$ layer is 350 nm. A fractograph at 200x magnification of a Hi-Nicalon™ Type S coated ZnO/SiO$_2$/SiC
system is presented in Figure 2.3.11. Fiber debonding and fiber pullout are clearly seen in the fractograph. A higher magnification (30000x) fractograph of a SiC\textsubscript{fiber}/ZnO/SiO\textsubscript{2}/SiC\textsubscript{matrix} system is shown in Figure 2.3.12. ZnO that has bonded to the surface of the fiber can be seen flaking off of the surface indicating fiber/interface debonding. Note the thinner SiO\textsubscript{2} coating attributed to the slow infiltration of the TEOS system.

2.3.7 X-ray Powder Diffraction

XRD was used to determine the crystallinity of the ZnO coating on the ceramic fiber (Figure 2.3.3). Comparison of the XRD pattern with the ASTM standard (Table 2.3.27) show a good comparison of experimental values vs. established values. The corresponding difference in the intensity of the reflections indicates that some preferred orientation may have occurred during the coating process.

2.3.8 Scanning Auger Microscopy

Auger was used to determine the chemical composition of the coating and to see if there were any interactions between the coating and the fibers. Figure 2.3.4 presents the results of the SAM analysis after an argon etch to remove any adventitious carbon and oxygen. From the spectrum, the ZnO coating did not contain any appreciable amount of carbon but appears to have a higher zinc concentration. The concentration difference between zinc and oxygen is
attributed to ZnO having oxygen deficiencies. The higher concentration of zinc could contribute to the fabric having a black color after coating. Figure 2.3.5 shows the results of the SAM depth profile performed on the ZnO-coated CG-Nicalon™ fabric. CG-Nicalon™ fabric is reported to have around 12 wt.% oxygen and a C/Si ratio of 1.31, which is consistent with the data after 450 nm in the SAM depth profile. Figures 2.3.6 - 2.3.8 show SAM depth profiles for ZnO/SiO₂-coated CG-Nicalon™, Hi-Nicalon™ and Hi-Nicalon™ Type S fabric, respectively, performed under the same conditions as Figure 2.3.5.

2.3.9 Mechanical Testing

The results of tensile testing are presented in Tables 2.3.28 - 2.3.30. The data show UTS of as-received, ZnO-coated and ZnO/SiO₂ duplex coating on CG-Nicalon™, Hi-Nicalon™, and Hi-Nicalon™ Type S fibers, respectively. For a reference, as-received fibers of CG-Nicalon™, Hi-Nicalon™, and Hi-Nicalon™ Type S were tested. The UTS observed for the as-received fibers were 2.3 GPa, 2.4 GPa, and 1.75 GPa, respectively. For the as-received Hi-Nicalon™ Type S fiber, a significant decrease (>30%) from the reported values was observed. The other two fibers had tensile strengths within acceptable ranges of reported values. The average UTS values for ZnO-coated CG-Nicalon™, Hi-Nicalon™, and Hi-Nicalon™ Type S fibers were found to be 1.7 GPa, 2.3 GPa, and 1.6 GPa, respectively, an average decrease from as-received fibers of 26%, 4%, and 8%, respectively. For the ZnO/SiO₂-coated CG-Nicalon™, Hi-
Nicalon™, and Hi-Nicalon™ Type S fiber, the average UTS was 0.6 GPa, 1.0 GPa, and 1.6 GPa, respectively, an average decrease from as-received fibers of 74%, 58%, and 8%, respectively. Figure 2.3.10 shows stress vs. displacement curve for a single strand unidirectional mini-composite of Hi-Nicalon™ Type S fiber coated ZnO/SiO₂/SiC. FE-SEM micrographs provided the cross-sectional area data needed to convert pounds into MPa. The UTS of this mini-composite was 330 MPa.

![Image](image.png)

Figure 2.3.2: FE-SEM micrograph of ZnO-coated CG-Nicalon™ fiber.

### 2.3.10 Discussion

This section focuses on the deposition of a ZnO and ZnO/SiO₂ coating on CG-Nicalon™, Hi-Nicalon™, and Hi-Nicalon™ Type S fabric. Utilizing low temperature (400 °C) MOCVD to deposit ZnO and a deposition temperature of
Figure 2.3.3: XRD pattern of ZnO coating on CG-Nicalon™ fabric (* = ZnO).

Table 2.3.27: JCPDS vs. experimental reflections of ZnO-coated CG-Nicalon™ fabric.

<table>
<thead>
<tr>
<th>*ZnO</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>h k l</td>
<td>2θ</td>
</tr>
<tr>
<td>1 0 0</td>
<td>31.769</td>
</tr>
<tr>
<td>0 0 2</td>
<td>34.421</td>
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<tr>
<td>1 1 2</td>
<td>67.961</td>
</tr>
<tr>
<td>2 0 1</td>
<td>69.098</td>
</tr>
</tbody>
</table>

* = ASTM Card No. : 36-1451
Figure 2.3.4: Atomic concentration of ZnO-coated CG-Nicalon™ fabric analyzed by SAM.

Atomic Concentration:
Zn: 60.3%
O: 39.7%
Figure 2.3.5: Depth profile of ZnO-coated CG-Nicalon\textsuperscript{TM} fabric analyzed by SAM.
Figure 2.3.6: Depth profile of ZnO/SiO$_2$ coated CG-Nicalon$^\text{TM}$ fabric analyzed by SAM.
Figure 2.3.7: Depth profile of ZnO/SiO$_2$-coated Hi-Nicalon$^\text{TM}$ fabric analyzed by SAM.
Figure 2.3.8: Depth profile of ZnO/SiO$_2$-coated Hi-Nicalon$^{TM}$ Type S fabric analyzed by SAM.
Figure 2.3.9: FE-SEM micrograph of ZnO/SiO₂-coated CG-Nicalon™ fiber.
Table 2.3.28: Tensile strength as a function of coated thin film or films on CG-Nicalon™ fibers using parameters previously described.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CG-Nicalon™ Tensile Strength (GPa)</th>
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<tr>
<td></td>
<td>As-received</td>
<td>ZnO coated</td>
</tr>
<tr>
<td>1</td>
<td>2.4</td>
<td>1.9</td>
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<tr>
<td>Avg nm</td>
<td>2.3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

% decrease from as-received fibers: 26% 74%
Table 2.3.29: Tensile strength as a function of coated thin film or films on Hi-Nicalon™ fibers using parameters previously described.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hi-Nicalon™ Tensile Strength (GPa)</th>
<th>As-received</th>
<th>ZnO coated</th>
<th>ZnO/SiO₂ coated</th>
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<tbody>
<tr>
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<td></td>
<td>2.3</td>
<td>2.3</td>
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<tr>
<td>3</td>
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<td>4</td>
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<td>1</td>
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<tr>
<td>5</td>
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<td>2.5</td>
<td>2.2</td>
<td>0.9</td>
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<tr>
<td>Avg nm</td>
<td></td>
<td>2.4</td>
<td>2.3</td>
<td>1</td>
</tr>
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</table>

% decrease from as-received fibers

4% 58%
Table 2.3.30: Tensile strength as a function of coated thin film or films on Hi-Nicalon™ Type S fibers using parameters previously described.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hi-Nicalon™ Type S Tensile Strength (GPa)</th>
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</tr>
</thead>
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<tr>
<td></td>
<td>As-received</td>
<td>ZnO coated</td>
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<tr>
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<td>1.75</td>
<td>1.6</td>
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<td>1.8</td>
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<td>1.7</td>
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<tr>
<td>5</td>
<td>1.75</td>
<td>1.6</td>
</tr>
<tr>
<td>Avg nm</td>
<td>1.75</td>
<td>1.6</td>
</tr>
</tbody>
</table>

% decrease from as-received fibers | 8% | 8% |
Figure 2.3.10: Stress vs. displacement curve of Hi-Nicalon\textsuperscript{TM} Type S fiber coated ZnO/SiO\textsubscript{2}/SiC single strand unidirectional mini-composite.
600 °C for SiO$_2$, an original interface system has been deposited on Nicalon$^{TM}$ fabric (Figure 2.3.9). Depositing ZnO and ZnO/SiO$_2$ on CG-Nicalon$^{TM}$ fabric yielded the largest decrease of tensile strength as compared to the as-received fabric of 26% and 74%, respectively. Initially, SAM was used to characterize the composition of the ZnO coating but more importantly depth profiles acquired through SAM allowed for a detailed understanding of the interactions at the interfaces of the coating and fibers.

Figure 2.3.5 shows a depth profile of ZnO-coated CG-Nicalon$^{TM}$ with the appearance of sharp profiles at the interface between the coating and the fiber but after further investigation the oxygen appears to diffuse noticeably into the fiber. This indicates a potential reaction zone that would lead to degradation of the fiber. This observation is in agreement with the reported tensile strength data where a 26% decrease in strength was observed. To further understand this coating system a depth profile was obtained for ZnO/SiO$_2$-coated CG-Nicalon$^{TM}$ (Figure 2.3.6).

The depth profile showed a significant diffusion of silicon into the ZnO coating and oxygen diffusion at the interface between the ZnO coating and the CG-Nicalon$^{TM}$ fiber. This reaction zone is the potential mechanism for the catastrophic degradation observed using CG-Nicalon$^{TM}$. Figure 2.3.7 shows a depth profile of ZnO/SiO$_2$ coating on a Hi-Nicalon$^{TM}$ fiber with silicon and oxygen diffusion and a corresponding degradation in tensile strength (58%).
Figure 2.3.8 shows a depth profile of ZnO/SiO₂ coating on a Hi-Nicalon™ Type S fiber that shows limited silicon and oxygen diffusion at the interfaces of the coating and the fiber. This indicates that the degradation mechanism at the interface of the coating and fiber is attributed to the silicon diffusion into the ZnO coating and oxygen diffusion into the fiber.

The oxygen from the coating and/or the fiber might have reacted with the excess carbon in the fiber forming structural defects due to the formation of \( \text{CO}_2(g) \) or \( \text{CO}_2(g) \). This observation corresponds to the fibers with non-stoichiometric C/Si ratios (CG-Nicalon™ and Hi-Nicalon™), which have decreases in mechanical strengths of over 50% when coated with ZnO/SiO₂. The stoichiometric C/Si ratio of 1.05 and minimal oxygen concentration inherent to the Hi-Nicalon™ Type S fabric allowed for minimal silicon and oxygen diffusion that showed the best tensile strengths for the ZnO/SiO₂ duplex coating. To understand the interfacial properties of the ZnO/SiO₂ duplex coating, single strand unidirectional mini-composites were fabricated using Hi-Nicalon™ Type S as the reinforcing material and silicon carbide as the matrix. Figure 2.3.10 shows a stress vs. displacement curve for the system described above with an ultimate tensile strength of 330 MPa. Load transfers between the matrix and the fiber at 144.8 MPa and 186.2 MPa can be seen in the stress vs. displacement curve indicating composite-like properties. FE-SEM fractographs confirm the composite-like properties in the single strand unidirectional mini-composite.
with fiber pullout and crack deflection (Figures 2.3.11 and 2.3.12).

2.3.11 Conclusion

A process for depositing a ZnO and ZnO/SiO$_2$ coating on CG-Nicalon$^{TM}$, Hi-Nicalon$^{TM}$, and Hi-Nicalon$^{TM}$ Type S fabric has been established via MOCVD. The SiO$_2$ coating was used to protect the ZnO coating from degradation during composite fabrication. XRD analysis showed that crystalline ZnO was deposited at 400 $^\circ$C on CG-Nicalon$^{TM}$. Auger was performed to understand the interactions between the interfacial coating and the fiber and determine the composition of the ZnO coating. Depth profiles of the ZnO/SiO$_2$ duplex coating on CG-Nicalon$^{TM}$, Hi-Nicalon$^{TM}$, and Hi-Nicalon$^{TM}$ Type S fibers acquired through SAM showed silicon and oxygen diffusion as a potential degradation mechanism for Nicalon$^{TM}$ fabrics with non-stoichiometric C/Si ratios. FE-SEM micrographs of the ZnO coating and ZnO/SiO$_2$ duplex coating on CG-Nicalon$^{TM}$ fibers show uniform morphologies with coating thickness of roughly 400-500 nm and 350 nm, respectively. Single strand unidirectional mini-composite were fabricated using Hi-Nicalon$^{TM}$ Type S fibers because they had the highest strength retention after ZnO/SiO$_2$ was deposited. An FE-SEM fractograph of the SiC$_{fiber}$/ZnO/SiO$_2$/SiC$_{matrix}$ confirmed the ZnO/SiO$_2$ duplex coating to have interfacial properties suitable for CFR-CMCs. A stress vs. displacement curve also confirmed composite-like properties.
Figure 2.3.11: FE-SEM fractograph of Hi-Nicalon™ Type S fiber coated ZnO/SiO₂/SiC single strand unidirectional mini-composite.
Figure 2.3.12: FE-SEM fractograph of a SiC$_{\text{fiber}}$/ZnO/SiO$_2$/SiC$_{\text{matrix}}$ single strand unidirectional mini-composite.
Chapter 3

Conclusions and Future Work

The research discussed in this dissertation described various methods to produce material systems for use in PIP fabricated CFR-CMCs. Non-oxide and oxide materials were investigated for use in high-temperature oxidizing applications. Silicon-based inorganic polymers and CVD deposited ceramic materials provided routes to enhancing the environmental, thermal, and mechanical properties of a CFR-CMC.

First, synthesizing the PMVSZ 1:0.6 polymer allowed for the attachment of heteroatoms to backbone. After pyrolysis, the heteroatom modification produced a novel TiB$_2$ ceramic material. Modifications of an inorganic polymer by adding reactive metal fillers also showed promise in tailoring the ceramic material after pyrolysis for a desired application. The research progressed from inorganic polymer synthesis to using CVD to fabricate new matrices and interfacial coatings that would ultimately hinder environmental attack. Novel non-oxide multilayered B$_4$C/SiC matrices and BN/Si$_3$N$_4$/BN interfaces were developed and tested under oxidative conditions.

This research showed the ability of the multilayered material system
to be multifaceted by increasing the thermo-mechanical properties under oxidizing environments for matrix and interfacial coatings. Finally, ZnO was employed as an oxide interface and stabilized with SiO$_2$. The oxide interfacial research represents significant progress and understanding in this science. The systems presented show the complexity needed to develop a new ceramic material for advanced CFR-CMCs as well as the direction in which research will need to progress in order to satisfy the ever-increasing requirements of environmental, thermal, and mechanical properties. The following presents future research for this field.

- Continue to modify the backbone of silicon-based inorganic polymers. This can be done using different precursors such as zirconium butoxide and aluminum sec-butoxide; combination with a boron precursor may create other boride ceramic materials after pyrolysis. Using titanium and boron precursors with no oxygen bound to the molecule such as titanium tetrakis(dimethylamide) may reduce the incorporation of oxygen into the final ceramic material.

- Investigate other transition metal powders to understand the reactivity between the inorganic polymer and powder during pyrolysis as well as the final ceramic material observed.

- Develop a polycarbosilane (PCS)-based inorganic polymer that yields a stoichiometric silicon to carbon ratio after pyrolysis. Current syntheses
of PCS-based inorganic polymers produce varying silicon to carbon ratios after pyrolysis, which facilitates degradation to the ceramic material under oxidizing environments through the reaction between carbon and oxygen to form CO$_2$(g).

- Modify the PCS polymer with heteroatoms to observe the environmental, thermal, and mechanical property differences for matrix and ceramic fiber applications.

- Combine the boron- and silicon-containing layers to form a SiBC deposited material. Using the precursors and experimental setup presented for the B$_4$C/SiC work, blend BCl$_3$ and MTS together to obtain a SiBC layer. This might alleviate the multiple layers needed to increase oxidation resistance.

- Deposit Al$_2$O$_3$ as a duplex coating for the ZnO interface. The phase diagram for ZnO and Al$_2$O$_3$ show no interactions until 1700°C while the phase diagram for ZnO and SiO$_2$ indicate possible interactions as low as 1300°C. The Al$_2$O$_3$ coating would provide higher temperature capabilities for the oxide interface.
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