Production Of Bulk Ceramic Shapes From Polymer Derived Ceramics

2008

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PRODUCTION OF BULK CERAMIC SHAPES FROM POLYMER DERIVED CERAMICS

by

ARNOLD HILL
B.S. University of Central Florida, 2005

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering in the department of Mechanical, Materials and Aerospace Engineering in the college of Engineering and Computer Science at the University of Central Florida
Orlando, Florida

Spring Term
2008
ABSTRACT

A method has been developed to produce bulk ceramic components from a class of ceramics known as polymer derived ceramics. In the past polymer derived ceramics have been limited to thin film applications or in the fabrication of MEMS devices. The reason being that when the polymer is into a ceramic, large quantities of gas are generated which produce internal pressure that fractures the ceramic components. The method developed here solves that issue by casting into the polymer a 3 dimensional network of polymer fibers in the form of a foam which, during pyrolysis, burns out and leaves a network of open channels that allows decomposition gases to escape thus preventing pressure from building up. The inclusion of the polymer foam allows for the formation of strong plastic like green bodies which can be machined into any shape. The green bodies are then pyrolized into ceramic components. This process allows for the simple and inexpensive fabrication of complex ceramic components that have the potential to replace current components that are made with traditional methods.
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INTRODUCTION

Ceramics are an important class of materials used by engineers in the design of many of today’s high tech products ranging from dental fillings to rocket engine combustion chamber liners. In general ceramics offer high strength, high temperature stability and resistance to chemical attack. It is these properties that are sought after by engineers when designing products to be used in environments where the properties of metals are insufficient. There are many different ceramics for engineers to choose from and the ceramic chosen will depend on the application requirements. Ceramics can be of either oxide or non-oxide chemistry and may have either a crystalline or non-crystalline structure. The type of ceramic will depend on the precursors used and the production processes used.

Ceramics are produced in several forms by several different processes. Thin film ceramics can be produced by a dip coating or spray-on process where a liquid suspension of ceramic particles is applied to a surface and then baked on to produce a thin ceramic coating that provides thermal and oxidation resistance. Large single piece ceramic components are also produced. To produce bulk ceramic objects, i.e. lab ware, combustion liners or Space Shuttle thermal protection tiles, any of several different manufacturing processes can be used. Generally, as in the case of the oxide ceramics, the process begins with a wet mixture of metal oxide powders and casting agents which are extruded, pressed or slip cast into the desired shape and then placed in a high temperature furnace to fuse the components together. The process is similar for the non-oxide ceramics except the non-oxygen containing metal powders are mixed with carbon, boron
etc. and fired in a high temperature furnace with an inert atmosphere to sinter the powder particles together.

There is however, a class of ceramics, called polymer derived ceramics that are produced in an entirely different way. Polymer derived ceramics (PDC’s) are a relatively new class of ceramics that are synthesized by the thermal decomposition of polymeric precursors. The polymeric precursors are generally organometallic polymer based liquids that can theoretically be cast into virtually any shape and then cured to a “green body” (solid) with the aid of cross linking agents and the application of heat or radiation (UV, microwave, laser etc.). After the polymer precursor is formed into the desired green body shape it is converted to a ceramic through high temperature firing in a furnace under an inert atmosphere such as argon or nitrogen. A wide range of ceramics can be produced in this way from the polymer precursors:

\[(\text{R})(\text{R'})\text{SiX}]_n \rightarrow \text{SiC, Si-O-C, Si-C-N, Si}_3\text{N}_4, \text{etc.}\]

and

\[(\text{R})\text{SiX}1.5]_n\]

where X = O: poly(siloxanes); (NH): poly(silazanes), (CH2): poly(carbosilanes), and R, R' = H, alkyl, aryl, arenyl, etc. groups. With increasing temperature amorphous as well as nanocrystalline inorganic materials are formed upon release of the organic constituents (R,R'). Table 1 gives a list of several different polymer precursors and the resulting ceramic yielded by thermal decomposition.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (ºC)</th>
<th>Ceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-Si-Si-]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylsilane</td>
<td>950/Ar</td>
<td>SiC</td>
</tr>
<tr>
<td>Methylvinylsilane</td>
<td>1000/Ar</td>
<td>SiC</td>
</tr>
<tr>
<td>[-Si-O-]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylsiloxane</td>
<td>1000/He</td>
<td>SiOxCy</td>
</tr>
<tr>
<td>Methylborosiloxane</td>
<td>1000/NH₃</td>
<td>SiBO₁.₃N₁.₄</td>
</tr>
<tr>
<td>[-Si-C-]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silaethylene</td>
<td>1200/N₂</td>
<td>SiC</td>
</tr>
<tr>
<td>Titanocarbosilane</td>
<td>1300/N₂</td>
<td>SiCₙOᵧTiᵢ₂</td>
</tr>
<tr>
<td>[-Si-N-]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydridosilazane</td>
<td>1200/N₂</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>Hydridomethylsilazane</td>
<td>1000/Ar</td>
<td>Si₁.₇CN₁.₅</td>
</tr>
<tr>
<td>Methylsilazane</td>
<td>800/NH₃</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>Vinylsilazane</td>
<td>1200/N₂</td>
<td>SiCₙNᵧ/C</td>
</tr>
<tr>
<td>Vinylphenylsilazane</td>
<td>1000/N₂</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>Cyclemethylsilazane</td>
<td>1000/Ar</td>
<td>Si₃N₄/SiC</td>
</tr>
<tr>
<td>[-Si-N-B-]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Borosilazane</td>
<td>1000/Ar</td>
<td>BN/Si₃N₄</td>
</tr>
<tr>
<td>Borosiliciumimide</td>
<td>1250/N₂</td>
<td>Si₃B₃N₇</td>
</tr>
<tr>
<td>Borosilazane</td>
<td>1650/Ar</td>
<td>SiBN₃C</td>
</tr>
</tbody>
</table>

PDC processing includes the following basic steps as shown in Figure 1:[2]

1. Synthesis/modification of the polymer precursors.
2. Solidification, shaping and de-molding.
3. Cross-linking to form infusible polymer components.
4. Conversion of the polymer component to a ceramic by pyrolysis at ~ 1000ºC.

The materials thus obtained using the polymer precursors in this work are predominantly amorphous silicon carbonitride (SiCN).[3] Other elements such as boron and aluminum can also be incorporated for modifying and improving the materials properties.[4][5] These polymer-derived ceramics properties are superior even to other more traditional ceramics.
The SiCN PDC’s used here have the following properties:

(I) **Excellent thermo-mechanical properties:** Table 2 compares some of the physical and mechanical properties of polymer-derived SiCN ceramics with other ceramics.

- **Low thermal conductivity:** Owing to its amorphous structure, the SiCN has a much lower thermal conductivity (1.5 W/m·K) than other ceramics and metals. The low thermal conductivity is critical in designing heat shielding or combustion chamber liners.

- **High strength:** The high strength of SiCN allows it to withstand high stresses and maintain adequate rigidity in high temperature applications.

- **Excellent thermal shock resistance:** SiCN ceramics shows much better thermal shock resistance than other ceramics. Thermal shock is one of the most critical issues that determine the lifetime and reliability of system components when ceramics are used.
• **Excellent thermal and environmental stability and creep resistance:** SiCN ceramics shows excellent high temperature properties: (1) it resists thermal decomposition and crystallization up to 1400°C, (2) it has high resistance to oxidation and corrosion, and (3) its creep resistance is comparable to that of state-of-the-art polycrystalline SiC and Si₃N₄⁸⁹ and is much higher than that of oxide-based ceramics.

• **High heat capacity:** The heat capacity of SiCN is approximately 50% higher than the stainless steel alloys. The heat capacity of SiCN is similar to SiC at approximately 0.67 J/g-°C whereas the heat capacity of stainless steel is approximately 0.46 J/g-°C.

### Table 2: Properties of polymer derived SiCN and other ceramics.

<table>
<thead>
<tr>
<th>Properties</th>
<th>SiCN</th>
<th>SiC</th>
<th>Si₃N₄</th>
<th>Alumina</th>
<th>LTCC**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.0</td>
<td>3.17</td>
<td>3.19</td>
<td>3.95</td>
<td>3.1</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>90-150</td>
<td>400</td>
<td>320</td>
<td>400</td>
<td>152</td>
</tr>
<tr>
<td>CTE (x10⁻⁶/K)</td>
<td>1.8</td>
<td>3.8</td>
<td>2.5</td>
<td>8.4</td>
<td>5.8</td>
</tr>
<tr>
<td>Thermal conductivity (W/Km)</td>
<td>1.5</td>
<td>40-90</td>
<td>20-40</td>
<td>30-40</td>
<td>3.0</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>~1000</td>
<td>420</td>
<td>700</td>
<td>400</td>
<td>320</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>20</td>
<td>30</td>
<td>28</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Thermal Shock *</td>
<td>~3000</td>
<td>350</td>
<td>880</td>
<td>120</td>
<td>360</td>
</tr>
</tbody>
</table>

**LTCC, low temperature co-fired ceramics, data based on Dupont® 951.  
*Thermal shock formula = strength/ (E-modulus·CTE), Ceramics data vary because of various sintering methods.

(II) **Ease of fabrication:** The chemical-to-ceramic processing described in Figure 1 enables the utilization of many well-developed fabrication techniques for making ceramic components using this material. The desired components can be cast in a mold and then cured by UV radiation or heat application. The cured polymer shape is then converted to a ceramic in a furnace. Recently, micro-fabrication techniques, such as injection molding, micro-casting, precision machining and lithography, have been
developed for the fabrication of SiCN MEMS by Professor An (University of Central Florida) and co-workers under a DARPA funded program.\cite{8,9,10,11} Figure 2 shows several typical SiCN ceramic MEMS structures.

![Figure 2](image)

**Figure 2**: SEM micrographs showing typical MEMS structures made from SiCN: (a) micro-gear made by micro-casting, (b) micro-channel heat exchanger made by lithography (single-layer structure), and (c) atomizer made by lithography (two-layer structure).

As promising as PDC’s appeared to be when they were first developed, it quickly became apparent that producing bulk ceramic components, \textit{i.e.} components with thick cross sections, was going to be difficult. The problem arose when large green bodies were placed in a furnace to be pyrolyzed. During pyrolysis thermal decomposition of the polymer precursors takes place which generates large volumes of gaseous decomposition products.\cite{1} If the diffusion length for the gases is larger than \(\sim 500 \, \mu \text{m}\), the gasses can’t escape from the green body fast enough and the internal pressure will build until the green body fractures into granules with linear dimensions \(< 1\text{mm}\). In addition to the gas pressure issue there is a marked shrinkage of the green body during pyrolysis that can also contribute to fracturing problem. Due to these problems, PDC’s have been restricted in the past to thin film coatings and MEMS devices as described above. There has been some success recently in making bulk ceramic components from PDC’s by crushing the green bodies into fine powders and then compacting the powders into molds followed by
de-molding and pyrolysis. Additionally, active powder fillers have been added to the polymer precursors which then can be molded into bulk shapes or cast into blocks for machining before being. These methods have been somewhat successful in producing bulk PDC components but they are complex, requiring many fabrication steps and multiple precursor ingredients.

This paper reports a novel method for dealing with the gas pressure and shrinkage cracking issues encountered during the production of bulk PDC components.
MATERIALS SELECTION

The approach taken here was to provide a gas escape channel network in the green body to allow the gaseous decomposition products to escape during pyrolysis thus preventing the destructive pressure build up. In order to maintain sufficient strength of the ceramic components it was necessary to have a uniformly distributed channel network and keep the channel diameter to a minimum so as to achieve the highest density ceramic as possible. Since the ceramic precursors are liquids it was decided to identify an interconnected three dimensional open network of thin fibers which could be infiltrated with the liquid precursors and then solidified to form a green body. During pyrolysis of the green body the fiber network would be burned out in the early stages thus providing hollow channels for the decomposition gasses to escape as they were formed during the later stages of pyrolysis. The ideal fiber network would form open cells with diameters no larger than two times the maximum allowable diffusion length of the decomposition gasses. A maximum allowable diffusion length of ~500µm was chosen based on experimental observation of the size of the surviving solid pieces of ceramic that were obtained when large (10’s of mm) solid green bodies with no gas channels were pyrolized. Other criteria for the fiber network were that when it was burned out, it had to leave little residue behind so as not to clog the gas channels and more importantly, it had to burn out at a temperature less than ~400 °C. The reason being that at ~400 °C the polymer precursor chosen, in this case, Ceraset polysilazane resin (Ceraset®, Kion Corp., USA), begins to decompose and release large volumes of gas that need to escape through the gas channels. Figure 3 shows a Thermogravimetric Analysis (TGA) diagram of
Ceraset obtained using a SETARAM, Mettler TC11 thermogravimetric analyzer under an N2 atmosphere with a heating rate of 10 °C per min.

Figure 3: TGA graph of Ceraset in an N2 atmosphere with heating rate of 10 °C/min.

It was decided that a polymer material would be the best candidate to form the fiber network and a review of the properties of several polymers was undertaken to identify the best polymer. Table 3 shows a list of several polymers and their thermal decomposition temperatures.\textsuperscript{[13]}
Table 3: Various polymers and their thermal decomposition data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_d^a$ (ºK)</th>
<th>$T_{1%}^b$ (ºK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetal</td>
<td>503</td>
<td>548</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>528</td>
<td>555</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>531</td>
<td>588</td>
</tr>
<tr>
<td>Polyethylene (LDPE)</td>
<td>490</td>
<td>591</td>
</tr>
<tr>
<td>Polyethylene (HDPE)</td>
<td>506</td>
<td>548</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>436</td>
<td>603</td>
</tr>
<tr>
<td>ABS copolymer</td>
<td>440</td>
<td>557</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>482</td>
<td>507</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>460</td>
<td>513</td>
</tr>
<tr>
<td>Cotton</td>
<td>379</td>
<td>488</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>337</td>
<td>379</td>
</tr>
<tr>
<td>Wool</td>
<td>413</td>
<td>463</td>
</tr>
<tr>
<td>Nylon-6</td>
<td>583</td>
<td>n/a</td>
</tr>
<tr>
<td>Silicone oil</td>
<td>418</td>
<td>450</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>628</td>
<td>683</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>356</td>
<td>457</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>746</td>
<td>775</td>
</tr>
</tbody>
</table>

$aT_d$: Minimum thermal decomposition temperature from TGA (10-mg sample, 10-K/min heating rate, nitrogen atmosphere)

$bT_{1\%}$: Temperature for 1% thermal decomposition, conditions as above

It can be seen from the data in Table 3 that the polymer with the lowest thermal decomposition temperature is Poly(vinyl alcohol)(PVA). In addition to having a low thermal decomposition temperature, when decomposed in air, PVA leaves no residue behind.\[^{[13]}\] For these reasons PVA was chosen as the polymer to be used to form the gas channels the ceramic precursor green bodies. In addition to having a low thermal decomposition temperature, PVA foam is inexpensive and commercially available. Also it doesn’t produce lint and has no production residues that would have to be removed prior to use. Another important feature of PVA foam is its fine pore structure. Figure 4 is
an electron micrograph showing the pore structure of commercially available PVA foam.

It can be seen that the pore size is ~50µm and the PVA fiber size is ~10-20µm.

Figure 4: An electron micrograph showing the pore structure of commercially available PVA foam.

If the pore size is kept small the diffusion length for the gaseous by products of pyrolysis will be small and therefore the pyrolysis can be performed at a faster rate and the final product can be realized sooner. Additionally, the finer the PVA fiber size is, the higher the density of the final ceramic piece will be and will therefore have higher strength.
MATERIALS PREPARATION

The PVA foam used was from a commercial source (McMaster- Carr Industrial Supply, Atlanta, Georgia) and the as received foam is packaged wet to maintain softness. To remove the moisture the foam was placed in an oven at 120 °C for ~4 hours. After drying the foam was cut into pieces ~1 cm³ and the pieces were placed back into the oven until needed. It is necessary to keep the PVA above 100 °C prior to use because PVA is highly hydrophilic and will rapidly absorb moisture from the air. If the moisture was not removed it would undergo a decomposition reaction with the resin which would produce copious amounts of bubbles which would then force the resin back out of the PVA foam. To avoid this problem the PVA was kept above 120 °C prior to placing it in the resin. Figure 5 is a diagram showing the TGA results for several samples of PVA foam including a sample that had been kept in the oven continuously. The other samples had been stored at room temperature in are and had absorbed some moisture. It can be seen that the thermal decomposition temperature of the dry sample is markedly lower than the other samples.
Figure 5: TGA graph of various samples of PVA foam in an N₂ atmosphere at a heating rate of 10 °C/min.

The main difficulty in producing large bulk ceramic components is controlling the gas evolved during pyrolysis. This problem can be reduced if the amount of gas evolved can be reduced. Initial attempts to fabricate green bodies kept failing when the PVA foam was placed in the resin while in a vacuum, which will be discussed further in the next section, due to the formation of bubbles. This was attributed to impurities on the internal surfaces of the PVA fibers nucleating bubbles of low molecular weight molecules such as NH₃, CO and CO₂ that are dissolved in the resin. These molecules were also a problem because during the early stages of pyrolysis, they would diffuse out of the green body thus generating high internal stresses due to gas build up which would then lead to cracks. The small molecules played no role in the chemical reactions that form the final ceramic products during pyrolysis and were thus deemed unnecessary. To remove them
the resin was placed under vacuum for ~10 hours while being heated at ~120 °C. After many trials these parameters seemed to give the best results. This would result in an increase in viscosity and a mass reduction of ~8% which was used as the measure of treatment. Once the vacuum cycle was complete the resin was covered to prevent moisture absorption and allowed to cool to room temperature. In this un-catalyzed state the resin had a shelf life of several weeks. Prior to using the resin, it was catalyzed with ~1-5% (Dicumyl peroxide, (Aldrich Chemical, Milwaukee WI, USA) while being heated under constant stirring at 120 °C for ~10 min. The amount of catalyst used only had a marginal effect on the curing time of the resin. In the early stages of the research, attempts were made to cure the resin using UV radiation however due to the thickness of the samples and the effects of the internal foam structure the curing was incomplete. The heating of the resin resulted in a decrease in viscosity which facilitated the infiltration of the PVA foam material.
GREEN BODY PREPARATION/PROCESSING

Once the PVA foam and the pre-ceramic resin are prepared green bodies can be formed. During initial attempt to make green bodies warmed, freshly catalyzed resin was poured into a shallow dish and pieces of PVA foam were taken out of the oven and while they were still hot they were placed in the resin. Capillary action would quickly draw the resin up into the foam. Once the infiltration was complete the wet green bodies were placed in an oven and cured for ~4 hrs at 120 °C. However, when the cured green bodies were cut open areas of incomplete infiltration were found. This was attributed to trapped air in the foam cells preventing the resin from fully penetrating the cell network. To alleviate this problem a vacuum oven was set up to remotely drop the PVA foam into the resin once all of the air was removed. When the foam initially hits the resin there was some rapid boiling that quickly tapered off and the foam would then sink down into the resin. This technique allowed full penetration of the resin into the foam structure and it had the added benefit of assisting in moisture removal from the foam. Once vacuum infiltration was complete the green bodies could be cured. The curing parameters mentioned above were determined after a long systematic study of the process. Early attempts showed that if the curing temperature was too high, the green body would cure too fast and the result would be randomly oriented planar cracks that resembled delamination. These cracks may also result from a thermal expansion mismatch between the cured resin and the PVA foam inside but it is not certain at this time. On the other hand, if the curing temperature was too low, fine bubbles would start to form in the green body. Interestingly, these bubbles could be seen forming in real time with the naked eye. What’s more, they could be seen forming in a solidified body. This was attributed to the
resin, while essentially solid, was in a somewhat plastic state and gasses being generated, presumably by the curing process, would collect in weak zones in the solid and plastically deform the solid in those areas. Once the ideal temperature was found it was only a matter of determining how long it would take to cure the resin. As expected, green bodies with larger cross sections required more time to cure. Once successfully cured the green bodies are in the form of a tough, hard plastic that can be easily machined into any shape that is obtainable by standard industrial machining techniques. The amount of time the green body was in the curing oven dictated it’s final hardness and thus the machinability of the piece. Green body blocks of sizes ranging from a few millimeters to a few centimeters were fabricated and then machined into various shapes. Figure 6 shows a complex machined green body that may serve as a light weight telescope mirror. If the green body was cured for a longer time it would become harder and could then be polished to a shine. This would give the final ceramic components a very smooth finish. This was much easier than polishing the component after it was converted to a ceramic. If desirable the PVA foam can be preformed into the desired shape by machining prior to infiltration with the resin however during the curing process the green body undergoes a linear shrinkage of ~4% which must be taken into account to obtain the desired shape and geometry of the cured green body. This shrinkage would also cause the geometry of the foam to distort. If the desired ceramic component has a lot of open pockets such as the shape shown in Figure 6, it may be desirable to pre-machine the PVA foam into the general desired shape and then infiltrate it with the resin. After the curing process the green body would require a final machining to restore the shape and obtain the desired
dimensions. This would allow a savings on the amount of wasted resin and reduce the curing time of the component.

Figure 6: A complex machined green body that may serve as a light weight telescope mirror.
PYROLYSIS

Once the green body is machined into the desired shape it is ready to be pyrolyzed. For the experiments performed during this research the green bodies were placed in a tube furnace under flowing \( \text{GN}_2 \). Pyrolysis under \( \text{GN}_2 \) will result in the conversion of the polymer resin to SiCN and pyrolysis under an ammonia containing atmosphere will result in a silicon nitride ceramic. The pyrolizing process also required a long, systematic investigation to obtain the correct scheme to obtain successful ceramic components. If the green bodies were simply pure resin with maximum characteristic lengths of < 500µ, the furnace temperature could be quickly brought up to the final target temperature which, in this research, was 1000 ºC. However, since the green bodies made here contained a polymer network that needed to be burned out, the temperature had to be brought up in stages. The resin doesn’t start to decompose into ceramic until the temperature reaches ~400 ºC. Once that temperature is reached the resin starts to decompose and generate large volumes of gas that will cause the component to fracture into many pieces. The key is to bring the furnace temperature up to a temperature < 400 ºC and hold it there until the PVA foam decomposes and creates gas paths for the resin decomposition products. This temperature turns out not to be simply less than 400 ºC however. If for example the temperature is brought up to 390 ºC the PVA foam will start to decompose and the resin won’t. However, at this temperature, the PVA foam will decompose so fast that the rate of gas evolution will be too high and the result will be the same, \( i.e. \) a fractured final product. The problem was to find a temperature that was high enough to decompose the PVA foam but at a rate slow enough so that the gas can diffuse out of the green body fast enough to prevent pressure build up. Finding the ideal temperature was somewhat of a
challenge. The TGA results obtained earlier weren’t much help because in TGA the PVA is decomposed in a \( \text{GN}_2 \) atmosphere where as the PVA in a green body is decomposing while deeply embedded in a polymer resin and the atmosphere would be composed of the PVA’s own decomposition gasses. TGA results for a sample of the resin with PVA foam inside as shown in Figure 7 were obtained however since the PVA only makes up \( \sim 10\% \) of the mass of the sample, there wasn’t enough resolution in the data to obtain any useful information.

![TGA for PVA&Ceraset resin vs. Pure Ceraset](image)

**Figure 7:** Showing the similarity in the TGA results between pure Ceraset resin and Ceraset with PVA foam embedded.

An additional issue is that as the furnace temperature is decreased, the time it takes for the PVA to decompose increases exponentially. It was found experimentally that if the temperature was too low, it would take many days for the PVA to decompose. This would make the whole process impractical for commercial use. After much trial and
error, a set of pyrolyzing schemes were identified that allowed for the successful fabrication of many different ceramic components. The final temperature in the pyrolyzing schemes was chosen to be 1000 °C which was held for 1 hour followed by a furnace cool to room temperature. **Figure 8** shows the complex ceramic component obtained from the green body.

![Figure 8: Shows the complex ceramic component obtained from the green body.](image)
CERAMIC CHARACTERIZATION

The ceramic material that results from the above described process is a porous solid that consists of an amorphous SiCN ceramic matrix with a microscopic network of interconnected open channels running throughout. Figure 9 is an electron micrograph of the surface of a polished sample of the ceramic material. The open channels are clearly visible however they are partially blocked with amorphous carbon that is left over from the decomposition of the PVA fibers. Normally PVA leaves little residue during thermal decomposition however because the pyrolysis is performed under GN₂ the PVA leaves behind carbon residue. This residue can be removed by heating the ceramic to ~1000 °C in air for ~1 hour to burn out the carbon.

Figure 9: Shows the final ceramic structure including the open channel network.
In addition to the ceramic shapes that were fabricated for demonstration purposes, ceramic discs were also fabricated to measure some of the properties of the resulting ceramic material. Ceramic discs were produced 25mm in diameter and ranged from 1.5 to 2 mm in thickness. Measurements of the discs before pyrolysis reveal a ~25% linear shrinkage during pyrolysis which is due to the mass lost during decomposition of the resin and the PVA foam. The density of the test samples was measured to be ~2.1 g/cm³ however previous experiments show that the final density can be tailored by adjusting the pyrolysis temperature and by the amount of preprocessing done on the PVA foam.

The samples were polished to a 1µ finish on one side and then the mechanical fracture strength, \( f_c \), of the ceramic material was measured using a biaxial testing method\cite{14} and calculated from the beam equation:

\[
 f_c = -(3P/(4\pi t^2))(X-Y)
\]

where

\[
 P = \text{load at fracture;}
 t = \text{Sample thickness;}
 X = (1+v)\ln(R_L/R)^2+(1-v/2)(R_L/R)^2;
 Y = (1+v)(1+\ln(R_S/R)^2)-(1-v)(R_S/R)^2;
 R_L = \text{Radius of the uniform loading area} = (1.6z^2+t^2)^{1/2}-.675t
\]

Where \( z = \text{Contact radius of the loading flat} \)

\( R_S = \text{Radius of the support circle} \)

\( R = \text{Radius of the specimen} \)

\( v = \text{Poisson’s ratio} \)

Figure 10 is a diagram of the loading fixture used for determining the fracture strength of the material. The load at fracture, \( P \), was measured for several samples using a universal testing machine (Model 1350, Instron Corp.). Figure 11 is a typical graph of the stress-strain behavior of the samples.
Figure 10: Diagram of the loading fixture used for determining the fracture strength of the material.

Figure 11: Graph of the stress-strain behavior of the samples.
It can be seen from the stress-strain curve of the samples that the material shows linear elastic behavior right up to fracture which is typical of brittle materials such as ceramics. The calculated fracture strength ranged from 130-170 Mpa with an average around 150 Mpa. It was found that the fracture strength was proportional to the density which is determined by the pre-processing of the PVA foam. This fact allows for the tailoring of the properties of the obtained ceramic material.
POTENTIAL APPLICATIONS

The potential applications for this material are huge. Due to the simplicity of the manufacturing process and the relatively low cost of the precursor materials the ceramics obtainable in this way may be able to replace some of the higher cost ceramic materials used in many areas of industry. An initial area of applications may be in the high temperature lab ware industry where objects such as crucibles and ceramic substrates are used in large quantities. The process described above is fast and can be scaled up to industrial levels which would make the products made in this way cost effective. Additionally, the properties of the SiCN ceramic which include high purity, high thermal shock resistance and high temperature tolerance make these potential products very attractive. Another area of potential use is in the power generation industry where turbine engines are used to generate electricity. The components used in the high temperature areas of turbine engines, typically nickel based superalloys, are expensive and difficult to make. They are also susceptible to high temperature corrosion which means they need to be replaced frequently. Using the material described here components such as combustion liners and flow dividers can be quickly and cheaply manufactured. Also, because SiCN has excellent oxidation resistance, the components could stay in service longer.
FUTURE WORK

Work that needs to be performed in the further development of this material will include determining more of the fundamental properties. Some of the key properties that need to be determined are Young’s modulus, thermal conductivity and coefficient of thermal expansion (CTE). These properties need to be known before the material can be used in more advanced applications. Also further work needs to be done in the area of strengthening the material. A possible method of strengthening would be the addition of nanoscale second phases such as carbon nanotubes, nanosize alumina particles or nanosize metallic particles. Not only would this increase the strength but it could, depending on the nano particles used, be used to tailor other properties such as CTE, thermal conductivity, and electrical conductivity. Another important area of future work will be to find a way to shorten the required sintering time of the green bodies. The reason for the long sintering time is due to the length of time required to decompose the PVA foam. Research needs to be done using other polymer foams which can be pretreated to decompose faster. Also the pore structure of the polymer foam needs to be addressed. If the foam has a smaller pore size and a smaller fiber size the foam may decompose faster. A smaller foam structure will also lead to a finer channel network in the final ceramic which should improve strength.
CONCLUSIONS

This research has identified a process that allows bulk ceramic components to be fabricated from polymer derived ceramics. The concept is simple but the route to its development was not. Since the field of polymer derived ceramics is relatively new, there is very little prior research to build upon. Most of the developments were made through trial and error and many of the details are proprietary and have been left out of this document pending the issue of a patent. The polymer derived ceramic obtained in this research is SiCN however other ceramics such as silicon carbide or silicon nitride can be obtained from this resin depending on the processing conditions such as pyrolyzing atmosphere and the addition of seeding particles. There are several other polymer systems in existence which can be used to derived exotic rare earth ceramics and new polymer systems are currently being developed. These other polymer derived ceramic materials should also benefit from this research.
REFERENCES


