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Project Summary

Materials Processing

Advances in nuclear reactor technology and the use of gas-cooled fast reactors require the development of new materials that can operate at the higher temperatures expected in these systems. These include refractory alloys based on Nb, Zr, Ta, Mo, W, and Re; ceramics and composites such as those based on silicon carbide ($\text{SiC}_f\text{-SiC}$); carbon-carbon composites; and advanced coatings. Besides the ability to handle higher expected temperatures, effective heat transfer between reactor components is necessary for improved efficiency. Improving thermal conductivity of the materials used in nuclear fuels and other temperature critical components can lower the center-line fuel temperature and thereby enhance durability and reduce the risk of premature failure.

Silicon carbide (SiC) is an important ceramic, most commonly used because of its excellent properties such as high strength, high modulus, excellent creep resistance and its high temperature stability. Moreover, crystalline silicon carbide is attracting wide attention as a promising candidate for several applications in nuclear reactors owing to its high thermal conductivity, high melting temperature, good chemical stability, and resistance to swelling under heavy ion bombardment. There have been many efforts to develop SiC based composites in various forms for use in advanced energy systems. However, fabricating SiC based composites by traditional powder processing route generally requires very high temperatures for pressureless sintering. In recent years, with the development of high yield preceramic precursors, the polymer infiltration and pyrolysis (PIP) method has aroused interest for the fabrication of ceramic based materials. Polymer derived ceramic materials offer unique advantages such as ability to fabricate net shaped components, incorporate reinforcements, along with lower processing temperatures, and perhaps most importantly relatively easy control over the microstructure. The raw materials are element-organic polymers whose composition and architecture can be tailored and varied.

The primary focus of this work is to use a pyrolysis-based process to fabricate a host of novel silicon carbide-metal carbide/oxide composites, and to synthesize new materials based on mixed-metal (metal/silicon) carbides that cannot be processed using conventional techniques. These mixed-carbide material systems are expected to offer improved material properties for higher-temperature applications. Our fabrication technique resulted in both amorphous and nano-grained SiC matrix composites by controlled pyrolysis of allylhydridopolycarbosilane (AHPCS), the precursor for SiC for our study, under inert argon atmosphere.

Cylindrical pellets, $\phi 25 \times 25$ mm, were fabricated for bulk scale characterization. These samples were analyzed in terms of density and porosity, thermal conductivity, and flexural strength under multiaxial loading conditions. The final composition in the fabricated composite was studied using X-ray diffraction (XRD). This was useful in understanding the relative stability of the starting material with AHPCS during high temperature pyrolysis. An extremely favorable conversion of U_3O_8 to UO_2 was observed during our fabrication. Furthermore, a novel technique for processing UC based composites and Nb/Zr/U-based mixed-carbides was developed. Typically, the bulk samples were fabricated by pyrolysis to 1150°C . Hence, complete crystallization of SiC was not yet achieved. This resulted in low thermal conductivity and biaxial strength in most cases. However, higher strength and conductivity were observed after pyrolysis to higher temperatures and the feasibility of our process was established.

We also investigated the processing-property-structure relationship for our matrix material, polymer-derived silicon carbide. Final processing temperatures and hold times at final temperatures were varied to study the influence of processing parameters on the microstructure and resulting properties. Chemical changes, phase transformations, and microstructural changes occurring

during the pyrolysis process were studied as a function of the processing temperatures. Polymer cross-linking and polymer to ceramic conversion was studied using infrared spectroscopy (FTIR). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed to monitor the mass loss and phase change as a function of temperature. X-ray diffraction studies were done to study the intermediate phases and microstructural changes. Variation in density was monitored as a function of processing temperature. Finally, hardness and modulus measurements were carried out using instrumented nanoindentation to establish processing–property–structure relationship for polymer precursor derived SiC. It was seen that the presence of nanocrystalline domains in amorphous SiC significantly influences the modulus and hardness. A non-linear relationship was observed in these properties with optimal mechanical properties for SiC that was processed to 1150 °C for 1 hour hold duration, having average grain size around 3 nm. In addition, a comparison was conducted between properties of polymer precursor derived silicon carbide and commercially available sintered silicon carbide (Hexoloy®).

Nanoindentation tests showed that the mechanical properties were influenced by increasing processing temperature for AHPCS derived SiC. The highest values of hardness were observed to be around 25 GPa for material processed at 1400°C. However, there was about 12% increase in hardness and about 37% increase in modulus values for material processed at 1400°C compared to those processed at 900°C. Similarly, density and thermal conductivity of AHPCS derived SiC followed an increasing trend with increasing processing temperature and further improvement in thermal conductivity could be obtained by complete nano-crystallization of α -SiC to β -SiC.

Process Modeling

For this task, researchers developed a macroscale global model that described polymer pyrolysis and uranium/ hafnium/zirconium ceramic material processing. The model included heat transfer, polymer pyrolysis, silicon carbide crystallization, chemical reactions, and species transport of a porous mixture of preceramic polymer and filler particles such as uranium oxide. The model was capable of accurately predicting the polymer pyrolysis and chemical reactions of the source material and the effects of transport processes such as heat-up, polymer decomposition, and volatiles escape. In addition, the model could obtain the yields of multiple different components. The model was capable of simulating pyrolysis and sintering of a sample with any geometry according to fuel pellet design requirements. The team also investigated the effects of heating rate, particle size, and volume ratio of metal and polymer on reaction rates.

In addition, the group developed a microscale “local process model”. The microscale model was based on the smoothed particle hydrodynamics (SPH) method and focused on the interaction between SiC matrix and filler particles, U₃O₈, or UC. First, the researchers investigated the uncertainty associated with the random distribution of the filler particles in the microscale model, taking advantage of the mesh-free nature of SPH. The uncertainty was characterized by comparing the composition change of the filler for filler particles with the same particle size and volume ratio, but different random distribution. The reaction rates, heat and mass transfer, and composition changes of different components were also simulated, along with the effects of filler particle size on the microstructure and material properties of the final product. It was concluded that the production rate of both UO₂ and UC, as well as the microstructure of the product, were strongly dependent on the filler particle size. Also, the production rate of UC increased as the filler particle size increased. The effect of heating rate applied to the furnace on the composition evolution was also investigated, and it was concluded that the production rate of both UO and UC increased as the heat flux increased.

Nuclear Transport

The researchers developed a simplified model for a fuel pin and its associated coolant volume. The maximum pin temperature was estimated assuming the implied power density and standard values for material conductivities as a function of coolant velocity. The pressure drop across the core could then be estimated for each value of coolant velocity. These initial estimates were sufficiently accurate to indicate whether or not it was necessary to re-configure the core. In order to determine the proper coolant velocity, researchers performed a more detailed analysis of the core using the Monte Carlo code MCNP. In this analysis, they determined heat generated in individual pins. Using this information, they assembled a computer drafted version of the core using Star Design, which forms input for use in the commercial CFD code STAR CCM+. The team also used parameters from previous and current MCNP calculations to estimate the temperature distributions in the core. Using this CFD code provided them with better insight into the benefit of increasing the clad surface roughening and by how much the roughening should be increased. In addition, they investigated the type of surface roughening. This study was based on previous work carried out in connection with the Gas Cooled Fast Breeder Reactor (GCFBR) program. In this task, the team determined that increased surface roughening would increase heat transfer coefficient. However, the core pressure drop also increased simultaneously.

In addition, this effort focused on reactor design modifications for UC–SiC based fuels and initiated efforts for understanding the effects of other elements on the nuclear reactivity. Initially, researchers continued their investigation on the core configuration that contained 271 pins per fuel assembly. This effort focused on the estimation of the requirements for fuel loading and the establishment of targets for the fuel development work. It was found that a UC/SiC combination of 0.45/0.55 resulted in an acceptable beginning of life multiplication factor, a U density of 4.60 gm/cc, and an acceptably long core life to be practical. Later, the core configuration was further modified by increasing the number of pins per fuel assembly from 271 to 331. This change decreased the fuel power density from approximately 100 W/cc to 84 W/cc. This value is consistent with gas-cooled reactors; thus, heat removal under normal operating conditions and scrammed accident conditions should present no problems. The investigation then studied the sensitivity of the magnitude of the multiplication factor to various versions of the evaluated nuclear data files, as well as the size of significant feedback coefficients.

Finally, researchers investigated the reactivity effects of using fuel compositions based on NbC–UC–SiC, using the original core configuration. It was found that the multiplication factors showed a significant drop when Nb was used in the core. This drop was due to the significant amount of resonance absorption that takes place in Nb. Furthermore, adding U to the composition did not have the desired effect of significantly increasing the multiplication factor, since the Nb content was increased at the same rate. To alleviate this condition, two alternatives were investigated: varying the level of enrichment and using Zr instead of Nb.

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1 Introduction

This study investigated the feasibility of a novel processing approach for the fabrication of silicon carbide (SiC) based composite fuels and in-core materials for ultra high temperature applications such as the Generation IV (Gen IV) Gas-Cooled Fast Reactor (GFR).

Current nuclear power generation technology is based on Gen II and Gen III reactors. Advances in reactor technology and the use of gas-cooled fast reactors requires the development of new materials that can operate at the higher temperatures expected in these systems. Such materials include refractory alloys based on Nb, Zr, Ta, Mo, W, and Re; ceramics and ceramic-matrix composites such as SiC–SiC_f; carbon–carbon composites; and advanced coatings. Besides the ability to handle higher expected temperatures, effective heat transfer between reactor components is necessary for improved efficiency. Improving thermal conductivity of the fuel can lower the center-line temperature and thereby enhance durability and reduce the risk of fuel pellet failure due to cracking and premature degradations. This also leads to increased power production and lower waste generation because of the less temperature buildup and longer fuel service life. Finally, the materials must be suitable for applications in a nuclear environment.

For this investigation, the focus is on crystalline silicon carbide, which has superior characteristics as a structural material from the viewpoint of its thermal and mechanical properties, thermal shock resistance, chemical stability, and low radioactivation [1,2]. There has been much effort to develop SiC based composites in various forms for use in advanced energy systems [3,4].

1.1 Motivation

World’s primary energy need has increased by more than 50 times since the pre-industrial level. However, the biggest energy challenge of today is not running out of resources but the increase in greenhouse gas emissions, such as CO₂ levels in the atmosphere. Global warming remains a controversial issue, but according to the Intergovernmental Panel on Climatic Change (IPCC), the observed increase in overall global temperature is most likely due to high greenhouse gas concentration [5]. This report predicts a temperature increase of 1.8–4.0 °C in the next century, and it is theorized that such changes can cause irreversible damage to life on earth [6].

In recent years there has been renewed interest in nuclear energy as a viable, long term, and economic power source, that is free of geo-political supply disruption risks, and also free of carbon emission problems. While, proliferation, reactor safety, and nuclear waste management continue to be issues, it has been recognized that nuclear power continues to have significant potential as a non-greenhouse gas producing source of energy. At the current usage rate, the existing nuclear resources are sufficient for over 85 years of operation [7]. Furthermore, wider use of breeder reactors and fuel reprocessing would significantly improve the fuel availability. In that case, it is estimated that the total conventional resources of uranium could suffice for 16000–19000 years [8].

The current nuclear reactors are considered second generation (Gen II). The Department of Energy’s Generation IV Initiative is focussed to develop reactors that will offer significant advances in sustainability, economics, safety and reliability, and proliferation resistance [9]. The new reactor technologies have stringent requirements to achieve higher efficiencies. Therefore, specifically tailored materials are now required to handle high temperature functionality.

Gas-Cooled Fast Reactors (GFR) are one of the six identified systems under focus for the Gen IV reactors [10]. For the GFR the in-core temperatures in the gas-cooled reactors can be as high as 1200 °C during normal reactor operation and may exceed 1700 °C in case of an accident [11]. In general, fuel elements should have high mechanical strength to endure various external mechanical loads, irradiation, and thermal stresses, while maintaining their integrity [12]. This is even more

so for the GFR and other high temperature reactors, as a result ceramic materials are being investigated as candidates for both advanced nuclear fuels and in-core materials.

Refractory-based ceramics (carbides: SiC, ZrC, TiC, NbC; nitrides ZrN, TiN; and oxides: MgO, Zr(Y)O₂) display a number of unique properties, including extremely high melting points and hardness, as well as high thermal and electrical conductivity, and solid-state phase stability [10, 13, 14]. This combination of properties makes these “refractory carbides” potential candidates for high-temperature nuclear reactor components, including shielding, fuel, control elements, and structural components. Refractory carbides are also excellent candidates for a variety of other high-temperature structural applications, including zero-erosion rocket nozzle throats, hypersonic leading edge materials, combustion liners, engines, plasma arc electrodes, cutting tools, furnace elements, and high temperature shielding [15, 16].

In recent years, with the development of high yield preceramic precursors, the polymer infiltration and pyrolysis (PIP) method has aroused interest for net-shape fabrication of ceramic based materials, for various applications ranging from disc brakes to nuclear reactor fuels [17]. The pyrolysis of preceramic polymers allows a wide variety of ceramic materials to be processed at relatively low temperatures. The raw materials are element-organic polymers whose composition and architecture can be tailored and varied. At first, during the pyrolysis of these precursors, amorphous materials are formed which have an atomically homogenous element distribution and, in this state, represent a new class of materials with very interesting properties. Additionally, these amorphous states can be crystallized to stable or metastable phases by a second annealing, where, under certain conditions, and with surprising ease, nanocrystalline materials are formed, whose microstructures are stable at very high temperatures. These technological characteristics of precursor pyrolysis processing, and the fact that the preceramic stage can be processed relatively easily using standard techniques of polymer processing technology to various material forms (fibers, films, infiltrates, etc.) and components, means that this method has a high application relevance.

The pyrolysis-based process also provides numerous advantages in comparison with other techniques used to manufacture advanced ceramic materials and composites, including chemical vapor deposition (CVD), and chemical vapor infiltration (CVI), and high-temperature sintering. The pyrolysis process requires only a controlled atmosphere oven for material fabrication. The liquid polymer precursor is easy to handle and can be stored for long periods of time under appropriate conditions. The PIP process is environmentally friendly, does not require hazardous acid scrubs, as for CVD/CVI, and produces only simple gaseous byproducts. The liquid and dust-free nature of the process makes it especially attractive for remote processing of highly radioactive species, such as plutonium (²³⁹Pu, ²⁴⁴Pu) and americium (²⁴¹Am, ²⁴³Am).

Finally, the preceramic stage can be processed relatively easily using standard techniques of polymer processing technology to generate various material forms and components (fiber reinforced and graded structures, thin films, complex shaped bulk materials, etc.), with no inherent limitations with regard to component size. If needed, appropriately designed gradations and microstructures can be used to minimize residual, thermal, and irradiation induced swelling stresses, provide multifunctional characteristics, and optimize nuclear characteristics.

The primary focus of this effort is to use a pyrolysis based process to fabricate a host of novel silicon carbide-metal carbide/oxide composites, and to synthesize new materials based on mixed-metal (metal/silicon) carbides that cannot be processed using conventional techniques. It is expected that these mixed-carbide material systems will offer improved material properties at higher-temperature applications. In addition to material processing, mechanical property characterization of precursor-derived ceramic matrix composites, in terms of biaxial strength, is carried out using equibiaxial ‘ring-on-ring’ test. Room temperature thermal conductivity of these composites are measured and the effect of various constituents in the composite on mechanical strength are characterized. This

has led to a better understanding of the manufacturing process. Solid state reactions that take place during the pyrolysis are determined from X-ray diffraction and thermogravimetric analysis. Finally, factors affecting the fabrication of precursor-derived SiC matrix composites for nuclear applications are characterized and the feasibility of the current process is analyzed.

1.2 Classification of Nuclear Materials

Nuclear materials can be broadly classified into in-core and out-of-core components. The in-core component materials include fuel assemblies and the neighboring coolant channels for water reactors, clad (cylindrical tubes that house the fuel pellets) for the fuel, and wrapper (a container that houses fuel elements, in between which the coolant flows) for subassemblies of fast reactors. The out-of-core materials form the rest of the nuclear reactor system. Typical issues of concern for all nuclear materials are radiation resistance, high-temperature mechanical performance, compatibility with the fuel and the coolant, and manufacturability [8].

In a nuclear reactor core, generally all materials are subjected to demanding temperature, stress, and neutron irradiation conditions. Depending on the design of the reactor, the service exposure conditions including temperature, temperature gradient, irradiation dose, and stresses vary from component to component within the same reactor. Ceramic materials offer the advantage of a much higher temperature and environmental stability in comparison to conventional polymers or metals without large change in the physical properties. These properties associated with ceramic materials make them highly attractive for their use as nuclear materials. Table 1 represents the screening requirements for GFR material selection based on Generation IV goals [18].

Requirement	Reference Value
Melting/decomposition temperature	$> 2000^{\circ}\text{C}$
Radiation induced swelling	$< 2\%$ over service life
Fracture toughness	$> 12 \text{ MPa}\cdot\text{m}^{1/2}$
Thermal conductivity	$> 10 \text{ W/m}\cdot\text{K}$

Table 1: GFR fuel matrix and structural material reference requirements.

1.3 Conventional Oxide-based Nuclear Fuels

Only one fissile nuclide, ^{235}U , is found in nature, where it occurs with an isotopic abundance of 0.72%. The remainder of natural uranium is ^{238}U and ^{234}U with 99.2745% and 0.0055% natural abundance respectively. Despite this low concentration of the fissile isotope, it is possible to fuel certain types of critical reactors with natural uranium, and all the early reactors were of this type.

Natural uranium obtained from the ore exists in the form of a number of complex oxides. These are first converted to U_3O_8 , which is then converted to uranium hexafluoride, UF_6 , for enrichment. The enrichment process increases the concentration of ^{235}U , following which UF_6 is converted to UO_2 [19]. Finally, UO_2 is fabricated into fuel assemblies and loaded into the reactor. The fuel pellets are formed using compaction followed by sintering to remove voids. The presence of voids can lead to decreased thermal conductivity. Most present-day nuclear power reactors employ uranium dioxide based fuel.

The wide-spread use of uranium dioxide fuel is primarily due to the many desirable characteristics of the uranium dioxide material, such as a high density of uranium atoms necessary for initiating and sustaining a nuclear reaction, inertness and insolubility of the uranium dioxide in

high temperature water, and the ease of fabricating fuel pellets by sintering. Additionally, UO_2 has a high melting point and does not contain neutron poisons which could affect reactor performance. In fact, UO_2 is the only stable oxide of uranium at higher temperatures above 1500°C [20] till its melting point of 2800°C [21]. However, UC and UN were chosen as the reference fuel for GFRs, instead of UO_2 , due to their higher thermal conductivity, higher heavy metal density, and minimal impact on neutron spectrum [18].

1.3.1 Fabrication of oxide based fuels

Powder metallurgical routes have been used successfully in the industry for the production of both UO_2 and mixed oxide (MOX, mixed U-Pu oxide) fuel pellets. Powder based processes involve large number of mechanical steps [22] and the fabricated pellets have to meet stringent dimensional quality control requirements. The typical fast reactor fuel pellets are about 5 mm in diameter and 8–10 mm in height. The tolerance on the diameter of these pellets is less than $50\ \mu\text{m}$ [23]. Each fuel pin holds around 100 such pellets and there are several thousands of fuel pins in a typical fast reactor core. The precise dimensional requirements along with surface defects are very difficult to be met in a shielded cell fabrication facility. This results in a high percent of rejects and lower throughput.

Amongst other efforts to fabricate fuel, sol–gel processes provide one possible solution for the fabrication of ceramic nuclear fuels [23]. With the sol–gel process, handling of radioactive toxic powder is eliminated. However, this process has not been studied to improve the existing thermal behavior of the fuels. Sol–gel processing generally has lower yields, and porosity issues due to greater shrinkage, and produces in–situ particles that must be sintered. Another non–powder based method of preparing ceramics, and which is potentially promising, is pyrolysis based processing of polymer–derived ceramics.

1.3.2 Thermal conductivity enhancement in oxide based fuels

The low thermal conductivity of the oxide based uranium fuel, which further decreases with increasing temperature [21,24], is one of its biggest shortcoming. This can limit the operating temperature of a reactor and thereby the efficiency and gas outlet temperature. Furthermore, low thermal conductivity also results in higher center-line temperatures leading to faster fuel degradation and thermo-mechanical cracking. A few critical properties of UO_2 and other alternative uranium based fuels are given in Table 2 [25–28]. Increasing the thermal conductivity by as little as 5% or 10% would provide significant benefits in terms of lowered volume-averaged fuel temperature, fission gas release, and fuel rod internal pressure [29]. The nuclear industry has made attempts to increase the thermal conductivity of uranium dioxide fuel, but none of the attempts have been successful so far. Apart from this, uranium dioxide based fuels are supported by a well-established technology and currently remains the dominant fuel for nuclear power reactors [30].

Polymer infiltration and pyrolysis was used recently by Sarma *et al.* [31] to fabricate enhanced thermal conductivity oxide (ECO) fuels. They used SiC and BeO as a non-fissile, high-conductivity phase in the uranium dioxide based fuels. The choice of these materials was based on its sufficient chemical compatibility with UO_2 , stability in aqueous environments, compatibility with zircaloy, neutronic properties, and irradiation performance. They compared upon the improvement of thermal conductivities using these high-conductivity phases (SiC and BeO). In general, SiC is known to react with UO_2 at relatively low temperatures in open systems at 1370°C [32], and at 1800°C in closed isothermal systems [33]. Due to these restrictions, sintering could not be used as SiC is very difficult to sinter below 2000°C without using large volume fractions of sintering aids [34].

Property	UO ₂	UC	UN	U metal
Theoretical density (g/cm ³ at 25 °C)	10.96	13.63	14.32	18.95
Heavy metal atom density (g/cm ³)	9.67	12.97	13.52	18.95
Melting point (°C)	~2800	~2400	~2700	1132
Thermal conductivity (W/m-K)				
200 °C	7.19	22.49	4	30
1000 °C	3.35	7.58	20	50.2
Static modulus of elasticity (GPa at 25 °C)	190	87.3	–	

Table 2: Critical properties of Uranium based fuels.

Therefore, they used the polymer infiltration technique to incorporate precursor derived SiC as the secondary phase in pre-sintered UO₂ pellets. However, unacceptable thermal conductivities were observed, possibly due to limited infiltration of the polymer precursor. Their alternative approach was to try BeO, which is stable with UO₂ up to its eutectic points of 2160 °C [35]. Also, it can be sintered at typical fuel fabrication temperatures as well.

For ECO fuels, Solomon *et. al.* [36] found that 10 vol.% of continuous phase BeO in UO₂ increases the thermal conductivity of the composite by 50% over standard UO₂ fuel. Furthermore, a 25% increase in thermal conductivity of UO₂ can be obtained at 1100 °K with an almost continuous 4.2 vol.% of BeO phase at the grain boundaries [37]. But to achieve this, it has to be processed above 2433 °K, the eutectic temperature. However, dispersed BeO in UO₂, processed at lower temperatures did not result in the same improvements [29].

The presence of BeO in the ECO fuel necessarily displaces some uranium and therefore decreases the uranium loading of a fuel assembly. Although it might be expected that a significant increase in ²³⁵U enrichment would be required to offset the loss of uranium, neutronic calculations showed that the required increase in enrichment is only about 0.007%. Because of this insignificant change, McCoy *et. al.* [29] claim a possibility of significant reductions in uranium costs. However, hexagonal structure of BeO raises the concern for anisotropic radiation growth at high damage doses. This still remains to be addressed for particular applications.

1.4 Carbide-based Nuclear Fuels

Carbide based fuels are the primary candidates for gas-cooled fast reactors (GFR) [10]. The high thermal conductivity and density of carbide based fuels allows for a superior specific power operation compared to conventional oxide based fuels [38]. Also, carbide based fuels have higher melting point and higher thermal conductivity compared to similar oxide- or nitride-based fuels [39]. For example, the thermal conductivity of uranium monocarbide (UC) is about five times higher than UO₂ (as shown in Table 2). This is of extreme importance for high temperature applications. For this reason, uranium carbide based fuels in a silicon carbide clad are being considered for the GFR systems where, under nominal full power operation, the peak fuel and clad temperature limits are 1500 °C and 1100 °C, respectively [18].

The reactivity of uranium carbide with metals poses a restriction on materials for cladding and coolant. However, niobium and its alloys are compatible with UC up to very high temperatures. Moreover, the solubility of zirconium, niobium, tantalum, and vanadium in uranium monocarbide can be used to develop cermets with enhanced mechanical properties and corrosion resistance. For example, UC alloyed with 50 mole% of ZrC shows significant improvement in resistance against water corrosion. Furthermore, stoichiometric monocarbide is stable in sodium up to at least 900 °C.

Thus, sodium is an attractive coolant for systems with (U, Pu)C fuels [21].

The U.S. and the former Soviet Union developed solid solutions of uranium carbide and carbides of refractory metals in support of high temperature nuclear fuel development for space nuclear propulsion systems. Owing to this growing interest, several fuel forms and microstructures were tested earlier in the U.S.'s NERVA/Rover program including dispersed fuels with UO_2 or UC_2 particles in graphite and a composite solid-solution (U, Zr)C and graphite [40]. Tosdale [41] predicted similar improved performances in a study of UC–ZrC–NbC systems. While UC–ZrC and ZrC–NbC–UC based composite fuels have exhibited melting temperatures in excess of 2927°C , the rather involved sintering-based material processing procedures have restricted their widespread adoption.

1.5 Mixed-metal Carbides

Mixed-metal carbide and metallic silicocarbide systems are even more of an exciting development in refractory carbides. Mixed-metal carbide systems rely upon the ability of refractory metals such as hafnium and zirconium to form alloys with niobium, tantalum, titanium, and other transition metals. While research in this area has been limited by processing issues, the evidence is highly promising. For example, the alloy tantalum hafnium carbide (Ta_4HfC_5), with a melting point of 4215°C , is one of the most refractory substances known to mankind. Also, the high-temperature hardness of $(\text{Ta}_{0.8}\text{Hf}_{0.2})\text{C}_{1+x}$ exceeds that of both pure-metal carbides TaC_{1-x} and HfC_{1+x} . The melting points of the mixed-metal carbides outperform those of the pure-metal carbides, as well. For example, 8TaC –ZrC and 4TaC –HfC exhibit melting points of 3890°C and 3990°C , respectively, somewhat higher than those of the pure-metal carbides (measured at 3470 , 3750 , and 3840°C for ZrC, HfC and TaC, respectively) [42].

Mixed carbide fuels, (U, Zr, Nb)C, are being currently studied for their applicability in Gen IV reactors. Their high thermal conductivity make them a more desirable form of fuel over the conventional UO_2 based nuclear fuels. High thermal conductivity aids in lowering centerline fuel temperatures, thus increase safety and fuel efficiency. Moreover, their longer life expectancy and stability at higher temperatures, high thermal conductivity, and resistance to hot hydrogen corrosion make them a candidate fuel for nuclear thermal propulsion (NTP) [43].

Fuel performances such as melting temperature and corrosion resistance due to hydrogen (critical for NTP), varies with its microstructure [43]. Czechowicz *et al.* [44] observed the formation of a second phase, carbon, in equilibrium with the solid-solution (U, Zr) C_x during their stoichiometric studies of (U, Zr)C. The melting temperature of these eutectic compositions, (U, Zr) C_x +C, was also affected by the uranium content in the compound.

The evolution toward an uncoated all carbide, solid-solution (U, Zr)C fuel was motivated by unacceptable mass losses from earlier designs due to the high reactivity of free carbon with the flowing hot hydrogen propellant and the mismatch in coefficient of thermal expansion between the graphite matrix and NbC or ZrC coatings. Furthermore, Butt *et al.* [45], in a thermochemical analysis of the binary carbide systems (U, Zr)C and (U, Nb)C, suggested that an optimized composition of (U, Zr, Nb)C, might exhibit the longest operating lifetime.

Due to the stringent requirements associated with fabricating these materials using powder metallurgy techniques it is apparent that the development of novel processing techniques, that permit the formation of mixed-metal carbides and allow for direct control over the ceramic composite microstructure, is highly desirable to fully harness the ultra-high temperature potential of refractory mixed-metal carbides.

1.6 SiC-based Materials in Nuclear Applications

Irradiation induced creep and void swelling are two major material issues in fast reactors. The tendency of a material for swelling and irradiation creep is characterized in terms of its change in dimensions with increasing irradiation dose or increasing stress measured at a constant temperature and dose, respectively [8]. Of the various advanced ceramics, silicon carbide has superior characteristics as a structural material from the viewpoint of its thermal and mechanical properties, thermal shock resistance, an excellent hermeticity with respect to gases (cooling gas fluids or gaseous species formed by nuclear reactions), and low radioactivation [1, 2].

Several other favorable attributes of silicon carbide includes a very high disassociation temperature of 2830 °C [46], oxidation resistance up to about 1600 °C, excellent thermal conductivity, 31 W/m °C, and a very low coefficient of thermal expansion, $4.7 \times 10^{-6}/^{\circ}\text{C}$ at 1200 °C [47]. Moreover, Munro reported extremely high stiffness, 387 GPa, even at elevated temperatures of 1200 °C [47]. The combination of high thermal conductivity and low thermal expansion provide exceptional thermal shock resistance [48]. Such properties make SiC an extremely attractive ceramic material. However, the same characteristics make SiC a very difficult material to fabricate.

The effect of high temperature irradiation on swelling and mechanical properties of high purity SiC has been evaluated by various researchers. Raffrey *et al.* [49] found that high cycle efficiency and safety considerations make SiC/SiC materials attractive for use as high performance blankets with LiPb. While the irradiation stability of SiC has always been of concern, it has been established that acceptable properties are expected when the composition of silicon carbide is close to stoichiometric and the microstructure is crystalline [2, 50–55]. In a recent study, Hinoki *et al.* found excellent high temperature irradiation resistance for high purity SiC/SiC composites irradiated up to 1600 °C [2]. Moreover, Newsome *et al.* [54] reported insignificant degradation in mechanical properties for high purity silicon carbide after irradiation. They found that the magnitude of volumetric swelling depended on the irradiation temperature and material, and was nearly independent of the irradiation fluence. Such properties make crystalline SiC a promising candidate for use in nuclear applications.

There have been many efforts to develop SiC based composites in various forms for use in advanced energy systems. Alkan *et al.* [3] proposed a joining technique of SiC parts so that the fissile material could be encapsulated in SiC capsules. Lee *et al.* [4] studied the effect of cyclic thermal shock on the mechanical and thermal properties of various ceramics being considered as candidates for nuclear fuel matrices. They observed that the silicon carbide based material exhibited superior mechanical and thermal shock performance at higher temperatures, as compared to those based on zirconia or magnesia aluminate.

However, there are several requirements for the successful application of these materials. First, the fabrication process must allow control over microstructure and material purity to ensure performance under high temperature and irradiation environments. Second, the processing technique should allow for facile incorporation of reinforcements and net shape manufacturing. Finally, a non-powder based method would be preferable for processing techniques that involve the handling of highly radiotoxic and pyrophoric materials.

2 SiC Fabrication Using Polymer Infiltration and Pyrolysis

Typical manufacturing of ceramic products is based on shaping and consolidation of fine ceramic powders. Large sintering shrinkage of 15–20% limits geometrical accuracy; therefore, machining is often needed to achieve precision and intricacy. Very high temperatures or pressures, required during sintering, magnify the energy requirements for these techniques. This also inhibits the incorporation of reinforcements such as silicon carbide fibers, which degrade at temperatures above 1200 °C [56].

Polymer infiltration and pyrolysis (PIP) is an alternative approach for the fabrication of ceramic materials and composites. It offers direct control of the microstructure and composition; allows for incorporation of fibrous and particulate reinforcements; and, perhaps most importantly, offers the possibility of net shape manufacturing at temperatures as low as 500–1500 °C [57–59]. In this manner, the PIP process can be used for consolidation of several compatible species due to its adaptability. Therefore, fabrication of ceramic components through PIP is a flexible and a potentially cost efficient approach. Also, ceramic yield is much higher in polymer derived processing as compared to other non-powder chemical routes. In some cases, ceramic yield as high as 85% has been reported [60]. It is advisable to use slow heating (usually ~ 1 °C/min) below 650 °C for better yield. Slow heating favors the lower temperature (~ 400 °C) curing of the polymer that involves the competitive processes of gas evolution by decomposition of the lighter molecules releasing H_2 and polymerization. This stage is critical in filling the porosity [36]. Finally, this process offers the unique possibility of modifying the structure and composition, and thereby the properties of ceramics, by designing the chemistry of the polymer precursor [61].

Polymer infiltration and pyrolysis has been identified as a viable alternative for fabricating SiC based materials [31, 57–59, 62–65]. However, the use of PIP for fabricating materials targeted for nuclear applications is limited. Very recently, Sarma *et al.* [31] fabricated UO_2 based fuel pellets using a combination of sintering and polymer infiltration and pyrolysis. However, unacceptable improvements were observed, and has been explained earlier. Sarma *et al.* [31] also showed that PIP can be used for consolidating other dispersed phases like Tristructural-isotropic (TRISO) fuel particles with compatible SiC outer layers. They used relatively low processing temperature for PIP based pyrolysis to avoid reactions with UO_2 which impaired the composite’s thermal conductivity. However, they postulated that UC or PuC would be more preferable as the fissile phase in SiC ceramics.

The current study investigates the use of the PIP technique to fabricate silicon carbide and uranium oxide/carbide, and metal carbide based nuclear materials. Materials are fabricated by directly incorporating the compound of interest to the preceramic polymer, and then converting the latter to SiC by pyrolysis. In this manner, the subject process does not involve pre-sintering and can be used with any uranium or non-uranium additive [66].

2.1 Allylhydridopolycarbosilane (AHPCS), as a precursor for SiC

Allylhydridopolycarbosilane (AHPCS) was chosen as the preceramic polymer precursor for this study. Selection of this particular preceramic polymer was favored due to the fact that it is claimed to be a high purity precursor and provides high ceramic yields of near stoichiometric SiC. Additional benefits include reduced cycle times, ease of use, and relatively low shrinkage. It is now widely used as precursor to SiC fibers. The polymer, designated as SMP-10, was acquired from Starfire Systems Incorporation (Malta, New York, USA). It is a clear, amber-colored, and viscous liquid and with relevant properties listed in Table 3.

AHPCS is an olefin-modified polymer that undergoes pyrolysis when heated under an inert

Property	Allylhydridopolycarbosilane (AHPCS)
Density	0.998 g/cc
Appearance	Clear, amber liquid
Viscosity	80 to 100 cps
Solubility	Hexane, THF, acetone, toluene, insoluble in water
Flash Point	89 °C (192 °F)
Moisture Absorbtion	< 0.1% in 24 hrs at room temperature
Nominal Cure Temperature	250 to 400 °C
Surface Tension	30 dynes/sq.cm

Table 3: Properties of allylhydridopolycarbosilane (AHPCS).

atmosphere to yield near-stoichiometric SiC. Upon heating, the polymer precursor yields a dry and partially cross-linked solid at about 300 °C. Further heating results in more cross-linking accompanied by the loss of low molecular weight oligomers and hydrogen gas until amorphous silicon carbide (α -SiC) is obtained at about 900 °C [67]. According to manufacturer's specifications [68], a fully-ceramic, amorphous SiC forms at 850–1200 °C with minimal shrinkage, 80–82% ceramic yield and nano-crystalline β -SiC forms at 1250–1700 °C with a 75–80% yield. Figure 1 shows the images of the cured precursor, pyrolyzed to different temperatures.

Figure 1: Color changes observed during the pyrolysis of AHPCS.

2.2 UO_2 -SiC based Nuclear Fuels

The feasibility of our novel technique was initiated by fabricating a uranium oxide based fuel composite. A complete description of the fabrication for our first sample case, U_3O_8 - UO_2 conversion, is presented here. For later works, the procedure essentially remains the same and minor deviations are stated as necessary.

Depleted uranium (DU) was used as the material for fabricating fuel composites. A byproduct of the gaseous diffusion enrichment cycle, DU is artificially depleted in the lighter isotopes and

contains 0.2% ^{235}U by weight. This depletion process effectively eliminates nuclear criticality concerns. Four type of depleted uranium materials were acquired from International Bio-Analytical Industries (Boca Raton, Florida, USA) including a block of solid depleted uranium metal, powders of uranium oxide (U_3O_8) and uranium dioxide (UO_2), and 4–20 mm sized irregular pieces of uranium carbide (UC).

Inherent radioactivity, pyrophoricity in powdered form, and perhaps most importantly, heavy metal toxicity associated with these materials poses additional handling requirements. Therefore, all the process involving these powders were performed in Unilab-2000 (MBraun Inc., Statham, NH, USA) glove box where an inert environment was maintained using argon flow. The glove box is equipped with an oxygen sensor module and all materials were handled at oxygen concentrations below 50 ppm. Some of the preliminary work for this study was conducted in another smaller glove box, which lacked the capability of an oxygen sensor or an active purge system. Figure 2 shows Unilab-2000 glove box used for all current material handling.

Figure 2: Unilab-2000 glove box equipped with oxygen sensor for handling pyrophoric powders.

2.2.1 Pellet fabrication

Pellet fabrication using the proposed technique involves mixing of the desired powder with a small amount of polymer precursor, net shape compaction in a mold to make a green body pellet that can be handled, and finally pyrolysis of the fabricated pellet. Due to large shrinkage during pyrolysis of the polymer, high porosity remains in the fabricated samples. Several infiltration and pyrolysis steps (typically 8 or more) are therefore required to fill these pores and aid densification. The complete fabrication process is schematically shown in Fig. 3.

To fabricate U_3O_8 based pellets, first a slurry was prepared by mixing 92 wt.% of U_3O_8 particles (International Bio-Analytical Industries, Boca Raton, Florida, USA) and 8 wt.% of the liquid AHPCS polymer precursor in a planetary ball mill (PM-100, Retsch GmbH, Haan, Germany). The

Figure 3: Schematic representation of the PIP based fabrication process.

composition of the initial slurry was selected so that the final material would contain $\sim 4.99 \text{ g/cm}^3$ solid density of elemental uranium at the end of processing. This requirement was established by criticality calculations, carried out at Brookhaven National Laboratory, and was based on fissile loading used in the GCFBR design for the pin fuel concept [69]. An intermittent, on-off cycle of 3 min. each, at 300 rpm, for 6 hours was used to prepare the slurry. Such a cycle was chosen to provide adequate grinding and mixing while avoiding excessive heating. As-received U_3O_8 particles were irregular in shape ($5\text{--}10 \mu\text{m}$ chunks), as shown in Fig. 4(a). The ball milling process reduced the size of the U_3O_8 particles and facilitated the coating of the polymer precursor.

Figure 4: Uranium particles after initial processing.

The liquid slurry, obtained after ball milling, was pyrolyzed in a covered alumina crucible in a box furnace. This furnace was fitted with a retort that allowed for a continuous flow of an inert gas such as nitrogen or argon. In this case, the pyrolysis was carried out under ultra high purity (UHP) argon. The slurry was heated to 900°C at a rate of $60^\circ\text{C}/\text{hour}$, and was held at the peak temperature for 90 minutes to ensure thermal equilibrium. The pyrolysis of this slurry resulted in a solid that contained uranium oxide particles dispersed in an $\alpha\text{-SiC}$ matrix. However, due to the amount of polymer precursor used for this initial cycle, this solid acquired the shape of the crucible and contained large voids that were generated by the release of hydrogen gas.

In order to make cylindrical samples from this material, which could be tested for mechanical properties, the solid obtained after the above pyrolysis was crushed into powder by ball milling for 12 min. at 300 rpm. The powder thus obtained was then mixed with a small amount of polymer precursor ($\sim 3\%$ by weight of the milled powder) and compacted into short cylinders, $\phi 25.4 \times 15$ mm, using a hydraulic press. A nominal compaction pressure of about 26 MPa was sufficient for producing green-body plugs that could be handled for further processing. These pre-compacted plugs, in the form of short cylinders, were pyrolyzed up to 900°C at a rate of $60^\circ\text{C}/\text{hour}$ under argon atmosphere. A set of compacted pellets for this work are shown in Fig. 5.

Figure 5: Compacted pellets, with a little use of polymer precursor with the powders.

As is customary in PIP processing, the samples were subjected to multiple polymer reinfiltration cycles. The reinfiltration of the cylindrical pellets was carried out under vacuum, with repeated 1 hour cycles for 3 hours with intermediate 1 min. purges. In addition, pressurized argon was used during each purge. This enhanced the reinfiltration while minimizing contamination [70]. A reinfiltration chamber acquired from Abbess Instruments (Holliston, Massachusetts, USA) was fitted with timed automated purge controller. However, before pouring the polymer onto the pellet for the first time, the chamber was vacuumed for 15 min. This aids in removing any trapped air in the pellet and reducing polymer's viscosity for better infiltration. Figure 6 shows the reinfiltration chamber designed to assist during impregnation cycles of PIP.

In the case of uranium oxide bearing samples, two types of composites were fabricated using different reinfiltration schemes. The first type of material, designated as $\alpha\text{-SiC-U}_3\text{O}_8\text{-A}$, was prepared by using a mixture of polymer precursor and uranium powder (obtained after first pyrolysis and specifically ball milled for 9 hours to reduce its particle size) as the reinfiltrating liquid. The second type of material, designated as $(\alpha\text{-SiC})\text{-U}_3\text{O}_8\text{-B}$, was infiltrated using neat polymer precursor. In the first case, the use of uranium oxide particles in the infiltrating media to promote uranium loading, was stopped after the 5th reinfiltration cycle. Beyond five reinfiltrations, the pore size becomes small and the presence of uranium oxide particles in the liquid polymer precursor could impede material densification. Subsequent reinfiltrations were continued using neat polymer precursor. In the second case, all reinfiltrations were done using neat polymer precursor.

The cylindrical specimens were sliced after the 3rd reinfiltration cycle to obtain discs of 1 mm thickness using a precision sectioning saw (Isomet 1000, Buehler, Lake Bluff, Illinois, USA). Prior work with polymer derived ceramic composites, using this polymer system, has showed that $\sim 6\text{--}$

Figure 6: Reinfiltration chamber

8 reinfiltration cycles are sufficient to obtain the maximum achievable density [64]. Therefore reinfiltration of the discs was continued for a total of eight cycles.

To avoid oxidation of the components at any stage, all the handling and processing was carried out in an argon atmosphere. Also, control samples that contained only amorphous silicon carbide (α -SiC) were fabricated using the same procedure, but without the addition of any uranium oxide.

2.3 Metal-Carbide based Composites and Fuel

Uranium carbide and refractory metal carbides were used to fabricate SiC based composites. Fine powders, -325 mesh, of niobium carbide (NbC), and zirconium carbide (ZrC) were acquired from Alfa Aesar (Ward Hill, Massachusetts, USA) to fabricate carbide-carbide composites. Various combination of these materials were studied for investigating their reaction kinetics with AHPCS during pyrolysis.

No.	Material	Composition	Volume Ratio	Compaction
1	SiC-PP-9010-H	SiC and PP	90:10	Hand
2	SiC-PP-9010-M	SiC and PP	90:10	Machine
3	NbC-PP-9010-H	NbC and PP	90:10	Hand
4	NbC-PP-9010-M	NbC and PP	90:10	Machine
5	ZrC-PP-9010-H	ZrC and PP	90:10	Hand
6	ZrC-PP-9010-M	ZrC and PP	90:10	Machine
7	NbC-SiC-PP-454510-H	NbC, SiC, and PP	45:45:10	Hand
8	ZrC-SiC-PP-454510-H	ZrC, SiC, and PP	45:45:10	Hand
9	ZrC-NbC-PP-454510-H	ZrC, NbC, and P	45:45:10	Hand
10	UC-PP-H	UC, and AHPCS	n/a	Machine

Table 4: Fabrication scheme and composition of carbide based materials

Table 4 provides a list of metal carbide based materials fabricated during this investigation. Composites were fabricated using both *hand*- and *machine*-compaction technique to study carbide-

carbide based systems. Both these schemes were essentially identical except for the compaction pressure employed during green-body preparation. The fabrication of these materials was to provide a basis for the mechanical, physical, and thermal property variations as functions of NbC, ZrC, and UC content. Salient features of the fabrication process and the compositional variations were as follows,

- Materials were fabricated using both low and high compaction pressures, corresponding to *hand* and *machine* compaction, respectively. The examination of physical properties, however, did not reveal significant differences between materials fabricated using the two schemes. Furthermore, the use of lower pressure compaction leads to a nominally simpler fabrication process. Thus, later materials were fabricated using only hand compaction.
- SiC–PP materials were the control samples fabricated using commercially acquired β -SiC.
- The ‘PP’ designation refers to ‘polymer precursor’ and specifically to allylhydridopolycarbosilane (AHPCS), which is used to generate the amorphous/nanocrystalline silicon carbide, α -SiC or n -SiC, matrix for our materials.
- The nominal volume ratios represent the initial mixtures and not the final volume fractions. The latter can be determined only by gravimetric analysis after all the re-infiltrations have been completed.
- The uranium carbide based material, UC–PP–H, was fabricated by a procedure that involved slurry-pyrolysis followed by crushing and compaction. Therefore, the concept of a nominal volume ratio does not apply. As for all other cases, the final constituent distribution can be determined only by gravimetry.

2.3.1 Uranium carbide based fabrication

To fabricate uranium carbide based materials, the as-received uranium carbide was directly mixed into the preceramic polymer. This processes was expected to yield a UC–SiC based fuel element. The process was similar to that explained in the previous section. However, it was observed that all UC compacted samples fell apart during the first run but were intact upon re-compaction. Figures 7(a) and 7(b) show the plugs processed after first and second compaction cycles, respectively.

This required us to refine the fabrication process. It was found that either excessive ball milling may lead to very fine crushing or insufficient ball milling may lead to coarse metal particles. Both these conditions lead to the disintegration of the pellets as shown in Fig. 8. Therefore an iterative process was adopted to optimize the ball milling parameters.

In addition, it was suspected that these materials were oxidizing, which was confirmed later by XRD analysis (see Fig. 15(a) on page 22). During the first cycle UC oxidized to UO_2 and was therefore unstable due to the resulting volume change. Upon re-compaction no further compositional change occurred and the material was stable.

Further investigation showed that environmental control in the box oven was limited and allowed oxidation to occur over long durations, especially when highly reactive species, such as UC, were present. This oxidation was not observed when SiC or other more stable species were processed. Furthermore, we were restricted to 900 °C for pyrolysis because of the furnace limitations. Additionally, since evidence of crystallization for AHPCS was reported near 1100 °C by Zunjarrao *et. al.* [71](presented in greater detail in section 6.4.2 on page 54), it was decided to upgrade the furnace. We acquired a new tube furnace after moving to Oklahoma State University (OSU) in

(a) Resulting plugs after first compaction using UC (b) Resulting plug after second compaction using UC

Figure 7: Fabrication attempt using UC as the base material. Pellets were pyrolyzed to 900 °C.

(a) Excessive milling of slurry lead to instability in the pellet.

(b) Coarse metal reinforcement lead to cracking of the pellet.

Figure 8: Disintegration of pellets due to incompatible reinforcement filler size obtained after ball milling.

Figure 9: Setup used for inert gas pyrolysis up to 1150 °C. The furnace is capable of controlled heating to the maximum of 1650 °C

2006. The new tube furnace is shown in Fig. 9. At the inlet, an ultra high purity argon gas is passed through a combination of moisture and oxygen traps to ensure zero-oxidation due to impurities that may be present in the tanked gas. Also, steel tubing is used at the inlet to avoid contamination by air diffusion into the tubes. This tube furnace is capable of pyrolysis up to 1650 °C. Moreover, fast curing is possible with the current furnace. This capability was used to pyrolyze materials at 1 °C/min up to 650 °C, and at 3 °C/min up to 1150 °C for samples fabricated later.

2.4 Mixed-metal Carbide and Silicocarbide Composites

The final focus of this investigation was to fabricate mixed-metal carbides (U/Nb/Zr)C using the proposed technique. It was based on pyrolysis of a mixture of a metal with metal/metal-carbide and the polymer. The concept here is to form mixed-metal carbide or silicocarbide compositions contained within an SiC matrix, where the metal carbide or silicocarbide is generated by direct solid state reactions between the metal of interest (U, Nb, Zr, or combination) and the preceramic polymer.

Powders for metallic Nb, –325 mesh, and Zr, 50 mesh, were acquired from Alfa Aesar (Ward Hill, Massachusetts, USA), and Atlantic Equipment Engineers (Bergenfield, New Jersey, USA), respectively. However, since the availability of uranium powder is limited, a hydriding procedure was adopted to generate UH_3 flakes from a block of depleted uranium metal block. And then this UH_3 was used as the source for uranium. UH_3 is highly pyrophoric, but, it is an interesting substance, since it is the intermediate in the preparation for most uranium compounds for which uranium is the starting material. UH_3 starts dissociating at 400 °C, and later disintegrates easily with rising temperature [21]. This makes it an extremely interesting for the current fabrication process due to the possible solid state reactions with a combination of other metals and the current precursor during pyrolysis.

We used UH_3 and the polymer precursor to prepare UC in the final composition. Typically, there are several ways of fabricating UC: (i) by direct reaction of elements during electric arc processing, (ii) by reaction of uranium with hydrocarbon gases (usually methane), (iii) by reaction between UO_2 and carbon [21]. The powders produced by any of the above mentioned method are

highly reactive and must be stored in an inert environment. However, in our technique, uranium carbide is obtained in the final composite due to a reaction that takes place during the regular pyrolysis cycle. The innovation of this procedure is in the use of polymer infiltration and pyrolysis to directly achieve UC in the composite. The schematic of the proposed technique is shown in Fig. 10.

Figure 10: The schematic of the proposed technique to produce nuclear fuel.

A hydriding setup, shown in Fig. 11, was setup inside the glove box under a sealed inert environment to avoid any oxidation during preparation. The use of a sealed inert environment also prevents oxidation after hydriding has taken place. Typically, hydriding involves heating the uranium block to about 200 °C under constant hydrogen flow. Uranium metal reacts rapidly with hydrogen to form uranium hydride. This results in complete disintegration of the metallic structure due to volumetric expansion during the chemical conversion. A gas mix of 5% hydrogen and 95% argon was used to obtain the hydrogen flow over the uranium block. The amount of gas flow was monitored by a bubbler in the exhaust outlet. The glass flask containing an uranium block was heated by an analog controlled mantle heater. Metal tubing was used for both gas inlet and exhaust. A subsequent de-hydriding step, to acquire uranium, is not required as that would occur during the pyrolysis procedure. Figure 11 show a photograph of the uranium block undergoing the hydriding process. Initially about 200 g of UH_3 was produced using the hydriding process for material fabrication.

Outline of the processing steps and optional variations for fabricating nuclear fuel are given as follows:

1. Start with a mixture of polymer precursor for silicon carbide (or another ceramic) and a uranium containing powder (metal, hydride, oxide, etc.). Other refractory metals or compounds may be added (e.g. Zr, Nb, or Hf based). The process can be used with other fuels compositions of interest including those based on transuranics.
2. Mechanically mix initial constituents using a ball mill or another scheme.

Figure 11: Hydriding of uranium to produce UH_3

3. (Optional) Remove volatile species from the mixture. These could be from the polymer precursor, or could be mixing aids added in previous step.
4. (Optional) Add catalyst to start precuring of the mixture.
5. For the first cycle only, pyrolyze the slurry in an inert gas oven. This will lead to a foamy solid mass. The uranium (or other metals) would convert to a carbide, silicide or silico-carbide through solid state reactions. The polymer precursor would convert to silicon carbide (or other ceramic based on selection of the precursor).
6. For the first cycle only, crush the foamy mass and bind the resulting powder with small amount of polymer precursor. Mold in a press to form a green body.
7. Conduct single or multiple polymer infiltration and pyrolysis cycles.
8. (Optional) Subject the formed shaped to higher temperatures to nanocrystallize the silicon carbide (or other ceramic) matrix.

A list of materials fabricated to study mixed-metal carbides/silicides are listed in Table 5.

No.	Material	Composition	Form
1	UH_3 -PP	UH_3 and PP	Powder & Pellet
2	UH_3 -Nb-PP	UH_3 , Nb and PP	Powder
3	UH_3 -Zr-PP	UH_3 , Zr and PP	Powder
4	Nb-PP	Nb and PP	Powder
5	Zr-PP	Zr and PP	Powder
6	UC-Nb-PP	UC, Nb and PP	Pellet

Table 5: Fabrication scheme and composition of mixed-metal carbide based materials

3 Physical, Analytical, and Mechanical Characterization

3.1 Analytical characterization

3.1.1 Oxide materials

The starting material for our oxide based composites was either U_3O_8 or UO_2 . The ceramic composite fabricated using U_3O_8 showed a color change. After the first pyrolysis, the pellet came out as a brown cinnamon colored solid. Figure 12 shows the as-received U_3O_8 and the pyrolyzed powder obtained after the first heating cycle. This change in color indicated a chemical conversion. Therefore, in order to investigate the microstructure and formation of new chemical species, due to *in situ* reactions, the fabricated materials were studied using powder x-ray diffraction (XRD). These measurements were performed on a Phillips PW1729/APD3520 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) operating at 40 kV and 30 mA. Peaks in the XRD patterns were identified using the JCPDS-ICDD database.

Figure 12: Color change of parent uranium powder after first pyrolysis.

Figure 13 shows the diffraction patterns obtained for as-received U_3O_8 powder and ball milled slurry powder after one cycle of pyrolysis. The diffraction peaks in the pyrolyzed slurry pattern were mostly dominated by the presence of UO_2 providing evidence of the conversion of U_3O_8 to UO_2 during the first pyrolysis cycle. This conversion has been widely studied [72–74]. Since the pyrolysis was carried out in an inert environment, it is highly likely that the reduction took place due to the presence of hydrogen gas that evolves during the pyrolysis of the precursor. In the presence of hydrogen this reduction can take place in the temperature range of 400–600 °C [73, 74]. However, this process is highly affected by the powder properties such as BET surface area and size. A more detailed understanding of these conversion is needed. Nonetheless, the conversion of U_3O_8 to UO_2 is favorable given the stability of the latter at higher temperatures.

Scanning electron microscopy (SEM) was performed on $a\text{-SiC-U}_3\text{O}_8\text{-A}$ and $a\text{-SiC-U}_3\text{O}_8\text{-B}$ after three and eight reinfiltrations. It can be observed from these microscopy images, shown in Fig. 14, that the distribution of U_3O_8 (actually UO_2) was highly uniform and pores were not visible even after the third reinfiltration at this scale.

3.1.2 Carbide materials

In order to investigate niobium, zirconium, or uranium based metal carbides it is essential to first understand the stability of these carbides during pyrolysis in the presence of AHPCS, the precursor for SiC. This was done by adding a small amount of the metal carbide of interest to sufficient

Figure 13: X-ray diffraction pattern for as-received U_3O_8 and after first temperature cycle to 900°C .

liquid polymer precursor and then extensively ball-milling this to produce a slurry. The slurry was pyrolyzed and the resulting materials were characterized using XRD. Table 6 lists the carbide based materials prepared during this study for X-ray diffraction characterization.

Constituents	Pyrolysis Temperature	Final Composition (from XRD)
UC, PP	900°C	UO_2 , α -SiC
UC, NbC, PP	1150°C	UC_2 , UO_2 , NbC, α -SiC
NbC, ZrC, PP	1150°C	ZrC, NbH_2 , NbC, α -SiC
ZrC, PP	1650°C	ZrC, SiC

Table 6: Compositions prepared for stability analysis of the metal carbides with AHPCS during pyrolysis. All starting constituents include the AHPCS polymer precursor (PP).

Figure 15(a) shows the diffraction pattern of the crushed powder after two pyrolysis cycles to 900°C during uranium carbide based pellet fabrication. It was observed in the diffraction pattern that the uranium carbide was completely converted to UO_2 . This also explained the failing pellet fabrications observed in Fig. 7. There is an approximate 30% increase in volume for the UC to UO_2 conversion. Once the conversion was complete, we were able to fabricate solid pellets with ease.

Separate slurries of 50% v/v mix ratio of UC and NbC with AHPCS, NbC and ZrC with AHPCS, and ZrC with AHPCS, were pyrolyzed. The slurry with ZrC was pyrolyzed up to 1650°C . Figures 15(b) and 16 show diffraction patterns obtained from the pyrolysis of these compositions. It should be noted that SiC is also formed, but is not detected by XRD due to the amorphous microstructure.

Figure 15(b) shows XRD data from a region that has excess carbon and thus exhibits the formation of UC_2 from UC. However, the conversion to UO_2 is also prominent. An unidentified

(a) (a -SiC- U_3O_8 -A) After 3rd reinfiltration

(b) (a -SiC- U_3O_8 -A) After 8th reinfiltration

(c) (a -SiC- U_3O_8 -B) After 8th reinfiltration

Figure 14: Uranium ceramic composite after 3rd and 8th reinfiltrations. The bright portion of the micrograph represents UO_2 and the dark regions represent SiC matrix phase.

(a) X-ray diffraction pattern for as-received UC and after second temperature cycle to 900 °C, showing its complete conversion to UO_2 .

(b) X-ray diffraction pattern for UC and niobium carbide-AHPCS pyrolysis to 1150 °C, showing presence of UC_2 , UO_2 , and NbC.

Figure 15: X-ray diffraction data for pyrolyzed zirconium carbide-AHPCS slurry.

(a) XRD data for zirconium carbide and niobium carbide-AHPCS pyrolysis to 1150 °C, showing presence of ZrC, NbH₂, and NbC

(b) XRD data for zirconium carbide-AHPCS pyrolysis to 1650 °C, showing presence of ZrC and cubic SiC

Figure 16: X-ray diffraction data for pyrolyzed zirconium carbide-AHPCS slurry. Zirconium carbide does not react with either niobium carbide or the polymer precursor even at higher temperatures. The slurry pyrolyzed to 1650 °C shows the presence of crystalline SiC.

peak at $2\theta \approx 31.3^\circ$ is also observed.

Figure 16(a) shows the pattern for ZrC–NbC pyrolysis with AHPCS. Zirconium carbide did not react with AHPCS or NbC, however, niobium carbide reacted with AHPCS to form NbH₂. In another x-ray diffraction pattern of zirconium carbide pyrolyzed to 1650 °C, silicon carbide is apparent now in crystalline form and zirconium carbide stays as a stable component (shown in Fig. 16(b)). This snapshot of the zirconium carbide’s behavior could be instrumental in explaining the lowest biaxial strength observation amongst the various refractory metal carbide plug combinations fabricated in the current study.

3.1.3 Mixed-metal carbides and silicocarbides

Separate slurries were prepared with either niobium, zirconium or uranium hydride (equivalent to using uranium metal) with AHPCS. The slurry was pyrolyzed and the resulting material was characterized using XRD. The objective was to investigate stability and possible in-situ solid-state reactions. Table 7 is a list of materials fabricated for this analysis. Figure 17 shows diffraction patterns obtained from two regions of pyrolyzed Nb-AHPCS. These regions correspond to AHPCS-rich and niobium-rich regions, respectively, and represent different local compositions of Nb:Si:C leading to potentially different solid-state reactions. Figure 17(a) shows XRD data from a region that has excess carbon and thus exhibits the formation of NbC with no free Nb. Again, SiC is also formed, but is not detected by XRD due to the amorphous microstructure. Figure 17(b) is generated from a region that has excess niobium and thus exhibits the formation of NbC along with excess free Nb. This figure also shows some peaks that could not be identified in the currently available 2004 JCPDS database. These do not correspond to any carbides or silicides of niobium. Nor do they correspond to possible contaminants from the tungsten carbide ball mill or the alumina crucibles. It is suspected that these correspond to ternary carbides/silicides that are formed due to *in situ* solid-state reactions.

Constituents	Pyrolysis Temperature	Final Composition (from XRD)
Nb, PP	1150 °C	Nb, NbC, <i>a</i> -SiC
Zr, PP	1150 °C	ZrC, Zr ₂ Si, <i>a</i> -SiC
UH ₃ , PP	1150 °C	UC, <i>a</i> -SiC
UH ₃ , Nb, PP	1150 °C	UC, Nb, NbC, <i>a</i> -SiC
UH ₃ , Zr, PP	1150 °C	UC, ZrC, <i>a</i> -SiC

Table 7: Compositions prepared for stability analysis and solid-state kinetics of the mixed-metal carbides/silicides with AHPCS during pyrolysis. All starting constituents include the AHPCS polymer precursor (PP). The final composition also includes unidentified materials.

Similarly, a slurry of Zr with AHPCS was also pyrolyzed. The diffraction pattern of zirconium pyrolyzed with AHPCS results in the formation of zirconium silicide, Zr₂Si, and zirconium carbide as shown in Fig. 18. This figure also shows some peaks that could not be identified in the currently available 2004 JCPDS database. It was confirmed that these do not correspond to any possible contaminants from the tungsten carbide ball mill or the alumina crucibles. It is suspected that these correspond to ternary carbides/silicides that are formed due to *in situ* solid-state reactions. However, the presence of quartz, SiO₂, is suspected.

UH₃ was used as the source for uranium metal for our mixed-metal carbide and silicocarbide studies. Slurries were prepared by mixing UH₃ with AHPCS, UH₃ and niobium powder with

(a) XRD data for AHPCS-rich region showing presence of NbC and no free Nb

(b) XRD data for niobium-rich region showing presence of NbC, free Nb, and some unidentified material(s)

Figure 17: X-ray diffraction data for pyrolyzed niobium-AHPCS slurry showing evidence of *in situ* solid-state reactions

Figure 18: XRD data for zirconium-AHPCS pyrolysis, showing presence of ZrC, Zr₂Si

AHPCS, or UH_3 and zirconium powder with AHPCS. The formation of uranium carbide in the final composite was confirmed in all of these compositions by performing x-ray diffraction studies on the crushed powder after first pyrolysis. Figure 19 shows the diffraction patterns, which show the presence of uranium carbide and unidentified materials in all cases. The unidentified peaks could be due to the presence of an unknown silicides or silico-carbides and therefore are possibly favorable for our process.

3.2 Density and porosity measurements

The density and porosity of the fabricated materials was determined after the 8th reinfiltration using the buoyancy method. First the specimen was dried at 120 °C for 12 hours, until it reached a constant mass, and then cooled to room temperature in a desiccator. The dry mass of the sample, m_1 , was recorded. Subsequently, the dried sample was saturated using ultra-high purity water to fill all the open pores. A few drops of Photo-Flo[®] (Kodak Corporation, Rochester, New York, USA) were added to reduce the surface tension of water and aid in saturation. A four-hour evacuation cycle was employed with intermittent purges at every thirty minutes to release trapped air. The apparent mass of the saturated sample, m_2 , was then determined using a density determination kit. The temperature of the saturation liquid was also recorded to correct for variations in the density of water, ρ_{fl} , as a function of temperature. Finally, the mass of the saturated sample, m_3 , was determined by weighing in air. Any liquid that remained on the surface of the sample was removed with a damp sponge and the operation was performed quickly, to avoid loss of mass due to evaporation. Subsequently, the bulk density, ρ_b , was calculated as,

$$\rho_b = \frac{m_1}{m_3 - m_2} \rho_{fl}, \quad (1)$$

and the open porosity, π_a , in vol. % was calculated as,

$$\pi_a = \frac{m_3 - m_1}{m_3 - m_2} \times 100. \quad (2)$$

Bulk densities and open porosities of the oxide based pellets after the 8th reinfiltration are listed in Table 8. The PIP processing generated closed pores in the consolidated pellets and therefore the bulk densities of the composites obtained were lower than the solid material densities. The solid material densities of polymer derived SiC have been found to vary from 2.7 g/cm³ at 900 °C to 3.2 g/cm³ at 1650 °C [71]. The bulk density and porosity values for both α -SiC- U_3O_8 -A and α -SiC- U_3O_8 -B were found to be close. It is possible that the modified reinfiltration process, as for α -SiC- U_3O_8 -A, impeded the densification leading to lower bulk density and higher open porosity, as indicated in Table 8. Given the scatter in data, however, it is not possible to make this claim unambiguously.

Material	Bulk density ρ_b (g/cm ³)	Open Porosity π_a (%)
(α -SiC)	2.21±0.01	3.39±1.14
(α -SiC)- U_3O_8 -A	4.58±0.06	2.77±1.14
(α -SiC)- U_3O_8 -B	4.70±0.06	1.94±0.56

Table 8: Density and porosity of the samples after 8th reinfiltration.

(a)

(b)

(c)

Figure 19: X-ray diffraction pattern observed on the powder obtained after one heating cycle of the slurry of AHPs and (a) UH_3 powder, (b) UH_3 and Nb powder, and (c) UH_3 and Zr powder.

During fuel fabrication using sintering, the fuel pellets are produced to $\sim 90\%$ of the theoretical density. The deliberate introduction of residual porosity is desired in fresh fuel to accommodate fission product swelling and redistribution [75]. Similarly, it is hypothesized that the presence of pores, in the current fabrication process, is beneficial and may decrease the effect of irradiation swelling of SiC.

For carbide materials, the bulk density after the 8th reinfiltration was measured using buoyancy method as well as using helium pycnometry (Ultrapycnometer 1000 (Quantachrome Instruments, Pittsburgh, PA, USA)). Helium was used as the purge gas for the instrument. The sample, after dry mass measurement, was placed in the measurement cell of the pycnometer. The pycnometer was purged with helium for 5 minutes, and then it was programmed to average 3, out of maximum 6, readings with standard deviation less than 0.01%. The pycnometer measures the volume of the material placed in the cell and using the dry mass, m_1 , the bulk density can be calculated. Bulk density values, as determined using helium pycnometry, are listed in Table 9, and are in good agreement with those determined using the buoyancy procedure.

No.	Material	Buoyancy Method		Pycnometry
		Bulk Density (g/cc)	Open Porosity (%)	Bulk Density (g/cc)
1	SiC-PP-9010-H	2.69	7.54	2.57
2	SiC-PP-9010-M	2.68	7.47	2.64
3	NbC-PP-9010-H	4.77	10.48	4.47
4	NbC-PP-9010-M	5.07	7.52	4.88
5	ZrC-PP-9010-H	4.16	7.20	3.93
6	ZrC-PP-9010-M	4.39	10.47	4.27
7	NbC-SiC-PP-454510-H	3.75	7.79	3.71
8	ZrC-SiC-PP-454510-H	4.53	13.33	4.44
9	ZrC-NbC-PP-454510-H	3.57	2.84	3.45
10	UC-PP-H	4.20	8.49	4.07

Table 9: Physical characteristics of carbide based materials

3.3 Thermal characterization

Thermal conductivity (λ) is an intrinsic property of a material and is extremely important in advanced designs and modern material fabrications. It has a critical role in material selection for nuclear fuels [76]. Fundamentally, thermal conductivity is a measure of the heat flux that flows through the material for a certain temperature gradient over the material. Thermal conductivity of a material depends on various factors including its microstructure and the temperature. For example, pure crystalline substances may exhibit different thermal conductivities along different crystal planes due to differences in phonon coupling along a given crystal axis. Also, the thermal transport in nanomaterials is different from that in bulk materials due to the strong boundary scattering of energy carriers (phonons or free electrons).

Measurement of thermal conductivity involves two processes: heating and sensing. In general, there are several techniques to achieve these. Each of them suitable for only a limited range of materials, depending on the thermal properties, geometry and the surrounding temperature. These can be broadly classified into steady-state and non-steady-state techniques [77].

Steady-state techniques perform a measurement when the material, that is analyzed, is in thermal equilibrium. This provides a more precise measurement (theoretically) but it can take a long time to reach the required thermal equilibrium. For such measurements, the ends of the sample are maintained at different temperatures, and after steady state is achieved, the temperature variation across the sample length is measured.

In the current study, the room temperature thermal conductivity, λ , was measured using a steady state axial flow setup [86], shown in Fig. 20, using cylindrical samples of $\phi 25 \times 5$ mm. The heat flow was measured using eight T-type, high precision, copper-constantan thermocouples, located in the hot and cold side of the sample on pure copper rods. Heat loss from the setup through conduction in the radial direction was prevented by thick teflon cylinder insulation. The hot side temperature was controlled using Omega CN132 temperature/process controller and the cold side using an analog controlled Cole Palmer chiller, model:12750-00. The heat source and heat sink were located far apart so that the measured temperature represented the temperature of the whole cross-section at that location. A thin layer of high thermal conductivity paste, Omegatherm 201, was used to minimize the thermal resistance between the copper rods and the sample. Data was recorded using a Fluke 53 series II digital storage thermometer, after steady state conditions had been achieved in ≈ 20 hours. Figure 21 shows a typical data set that was recorded. The hot and cold side linear curves were extrapolated to determine the temperatures, T_{hot} and T_{cold} , at the specimen interfaces. Equation 3 is used to calculate the heat flow, Q , on both sides of the specimen, which are represented as Q_{hot} and Q_{cold} . Subsequently, the thermal conductivity, of the sample was determined using the Fourier law of heat conduction, as given in Eqn. 4.

Figure 20: Axial heat flow setup for measuring room temperature thermal conductivity

$$Q = -\lambda A \left(\frac{\Delta T}{\Delta Z} \right) \quad (3)$$

$$\lambda_{sample} = \frac{(Q_{hot} + Q_{cold})L_{sample}}{2A_{sample}(T_{hot} - T_{cold})} \quad (4)$$

The results obtained for room temperature thermal conductivity measurements are listed in Table 10. It should be noted that the values of thermal conductivity listed in Table 10 were rather low, especially from the perspective of a nuclear fuel. Although the thermal conductivities shown by the carbide materials were higher than oxide materials, they were still not as high as required for a nuclear fuel. Normally, this would be a cause for concern as low values of thermal conductivity

Figure 21: Typical thermocouple data at steady state heat conduction stage.

can lead to greater center-line temperatures and reduced thermal shock performance. In this case, however, the low values of thermal conductivity was almost entirely due to the presence of the amorphous silicon carbide matrix, α -SiC. In fact a heat-treatment for nano-crystallization led to a *significant* increase in the thermal conductivity, as illustrated in Table 11.

In the current study, room temperature measurements were carried out using an in-house axial flow meter. However, since it is essential to perform such measurements at higher temperatures to analyze in-service performance these fuels, it would be worth measuring thermal conductivity using a laser based technique with high temperature capabilities. Variation of thermal conductivity due to the changes in the porosity levels must also be studied since the porosity in such fabrication affects the density as well as the convection based heat transport.

3.4 Mechanical Testing

The strength of ceramic materials depends on the stressed area and the statistical distribution of strength-controlling three dimensional flaws [87]. The test must be designed such that the maximum area is tested to minimize sampling error. Therefore, mechanical characterization of the samples was carried out using biaxial flexural strength tests. Such test methods, including ring-on-ring (RoR) and ball-on-three-ball (Bo3B), are preferred over uniaxial testing (in tension or in bending) [88,89]. Both the RoR and Bo3B tests include the examination of a large surface area that is free from edge finishing defects, ease of test piece preparation, and are applicable to thin sheets. In uniaxial tests, failure takes place only if the stress reaches maximum in the direction normal to the plane of crack. This may result in improper judgement of the material strength and behavior. This makes the biaxial stress distribution, where the stress is maximum in a plane, more discriminate of material defects than a uniaxial distribution. Finally, in the biaxial flexure test method the maximum tensile stress occurs within the central loading area, and spurious edge failures are eliminated [90].

Material	Thermal Conductivity (W/m-K)
SiC-PP-9010-H	7.05
(<i>a</i> -SiC)-U ₃ O ₈ -A*	1.55
(<i>a</i> -SiC)-U ₃ O ₈ -B*	1.08
NbC-PP-9010-H	4.14
NbC-PP-9010-M	4.09
ZrC-PP-9010-H	4.00
ZrC-PP-9010-M	6.52
NbC-SiC-PP-454510-H	6.67
ZrC-SiC-PP-454510-H	5.29
ZrC-NbC-PP-454510-H	5.28
UC-PP-H*	1.78

Table 10: Room temperature thermal conductivity of the carbide based materials processed to 1150 °C, determined using the axial heat flow setup. Note that the SiC-PP materials were the control samples fabricated using commercial acquired β -SiC and uranium carbide was converted to UO₂ during its pyrolysis as seen in Fig. 15(a). (*represents materials pyrolyzed to 900 °C.)

Material	Processing Temperature	Thermal Conductivity (W/m-K)
SiC-PP-9010-H	1150 °C	7.05
SiC-PP-9010-H	1600 °C	192.72

Table 11: Heat treatment at 1600 °C for four hours leads to an $\sim 2600\%$ increase in the thermal conductivity due to amorphous-to-nanocrystalline conversion.

Ring-on-ring (RoR) biaxial tests were carried out in the current investigation. The ring-on-ring (RoR) configuration is one of the biaxial tests that exposes the maximum area and volume under a constant maximum stress. The RoR is an axisymmetric test, where the disc is supported by a ring and loaded from the opposite side by another smaller concentric ring, as shown in Fig. 22. This configuration subjects a greater portion of the specimen to an equibiaxial stress state and distributes the applied contact load over a larger area compared to any other biaxial test methods. The concentric support ring in RoR configuration is also preferable over finite number of balls at fixed intervals because of the undesirable stress concentration at the contact locations. This reduces the likelihood of fixture-induced specimen failure leading to invalid test data. On the other hand, there is an approximate 20% increase in the stress under the loading ring [87, 89]. A standard for biaxial tests, ASTM F394-02 [91], is not active anymore and is going through major revision. However, ASTM C1499-05 [92] is the current standardized test method for the ring-on-ring tests. In general, there is no strict shape requirement for the test sample as long as the outer perimeter is known. The shape of overhang area does not influence the stress distribution within the support ring. Stress magnification is reported under the loading ring in the cases where the deflection of the center of the disc exceeds half the disc thickness. Also, theories of elastic bending of rigid plates are valid if the thickness of the disc is less than 0.2 times the diameter of the support ring and the center deflection is less than half of its thickness [87].

Figure 22: RoR, flexure fixture schematic.

For a ring-on-ring test, the radial (σ_r) and the tangential (σ_t) stresses within the smaller ring are equal and is given by Eqn. 5 [87],

$$\sigma_{\text{RoR}} = \frac{3P}{4\pi t^2} \left[\frac{(1-\nu)(a^2-b^2)}{a^2} \frac{a^2}{R^2} + 2(1+\nu) \ln \frac{a}{b} \right] \quad (5)$$

where P is the applied load, ν is the Poisson ratio of the specimen and was assumed to be 0.20 for SiC, a is the radius of the support ring, b is the radius of the load ring, and R and t are the radius and thickness of the disc specimen, respectively. A correction factor, a^2/R^2 , is used for the stiffening effect due to the overhang. The radial (σ_r) and the tangential (σ_t) stresses outside the inner ring, $b \leq r \leq a$, are given by the expressions given below [87]:

$$\sigma_r = \frac{3P}{4\pi t^2} \left[2(1+\nu) \ln \frac{a}{r} + \frac{(1-\nu)b^2(a^2-r^2)}{a^2 r^2} \frac{a^2}{R^2} \right] \quad (6)$$

$$\sigma_t = \frac{3P}{4\pi t^2} \left[2(1+\nu) \ln \frac{a}{r} - \frac{(1-\nu)b^2(a^2-r^2)}{a^2 r^2} \frac{a^2}{R^2} + 2(1-\nu) \frac{a^2}{R^2} \right]. \quad (7)$$

Care is needed to select the diameters of the loading and support rings, relative to the specimen thickness, in order to promote a valid failure event. Also, clean loading conditions and plane-parallel disk shaped specimens are required for the RoR configuration. Lack of these conditions

may result in a 3-point contact between ring and specimen. The concentric rings in the current setup were made up of stainless steel and had bullnose edges with a radius of 0.3125 mm towards the loading side. This configuration employed a support ring diameter of 19.05 mm and the loading ring diameter of 6.35 mm.

Figure 23: Photograph of the RoR fixture.

The specimens were loaded in the RoR fixture using a table-top test frame (Instron® 5567, Instron Corporation, Norwood, Massachusetts, USA) as shown in Fig. 23. Adhesive tape was applied as per ASTM C1499-05 [92] on the compressive side of the sample which reduced stress concentration and helped in retaining the disc fragments together after the failure. Displacement controlled loading at a rate of 0.5 mm/min. was used and the load versus load-point displacement was recorded till the point of failure. Then the flexural strength was calculated from the peak load sustained by the specimen. A minimum of five samples were tested for each material. The flexure strength was then determined as per Eqn. 5 [87], using the peak load at failure.

The stress calculated using Eqn. 5 is the maximum stress achieved by the sample with $\sigma_{\text{RoR}} = \sigma_r = \sigma_t$. This also defines the validity of the test where the failure must initiate from the central loaded region. The validity of ring-on-ring results was examined by testing commercially obtained alumina discs (AD-90, CoorsTek, Golden, Colorado, USA). Figure 24 illustrates valid tests in which the failure initiates from the central region of the discs [93]. Uniaxial flexure test and RoR tests were compared by Wereszczak *et al.* [93], on 99.5% pure alumina samples purchased from CoorsTek. They reported that the RoR values were $\sim 20\%$ less than their uniaxial flexural strength. However, the biaxial strength obtained for alumina (AD-90, 90% purity) in our test was $\sim 35\%$ lower than the uniaxial strength reported by CoorsTek. However, a valid failure pattern was obtained, as suggested by Wereszczak *et al.* [93], for both alumina and uranium-ceramic samples, as shown in Fig. 24.

The flexural strength results are shown in Table 12. Note that the samples named SiC-PP were fabricated using commercially obtained silicon carbide as the initial powder. Figure 25 shows the typical loading curve obtained for the RoR biaxial tests done on the prepared discs.

Figure 24: Typical RoR failure.

Material	Biaxial Strength (MPa)	Pyrolysis Temp. (°C)
SiC-900	42±2	900
SiC-1150-H	80±8	1150
SiC-1400-H	85±5	1400
SiC-PP-9010-H	128±14	1150
SiC-PP-9010-M	118±7	1150
(a-SiC)-U ₃ O ₈ -A	54±3	900
(a-SiC)-U ₃ O ₈ -B	49±5	900
UO ₂ -PP-9010-H	55±2	1150
NbC-PP-9010-H	178±16	1150
NbC-PP-9010-M	151±9	1150
NbC-SiC-PP-454510-H	154±17	1150
ZrC-PP-9010-H	117±17	1150
ZrC-PP-9010-M	136±10	1150
ZrC-SiC-PP-454510-H	109±11	1150
ZrC-NbC-PP-454510-H	124±12	1150
UC-PP-H	72±9	900
UH ₃ -PP-H	72±6	1150
UC-Nb-PP-H	103±6	1150
Alumina	222±17	—

Table 12: Biaxial strength of the fabricated ceramic composite and alumina using the RoR test

Figure 25: Typical load-deflection curve of ceramic composites test under RoR.

3.5 Discussion

Silicon carbide based ceramic matrix composites were fabricated using the polymer-derived process. The fabrication incorporated a wide variety of powders including commercially obtained crystalline silicon carbide, niobium carbide, zirconium carbide, uranium carbide and uranium oxides (U_3O_8 and UO_2). The fabrications can be categorized as oxide-, carbide-, and mixed-metal carbide and silicocarbide materials. The objective was to fabricate solid composite pellets with these composites at low temperatures having silicon carbide in the matrix that could act as the high conductivity phase as well as improved thermal properties in case of solid-state reactions.

In case of oxide based fuel fabrication, composite ceramic samples containing uranium oxide powder and α -SiC were manufactured using the PIP technique. The starting material, U_3O_8 , was converted to UO_2 , as indicated by a color change and confirmed using x-ray diffraction. This conversion is advantageous as U_3O_8 is readily available and UO_2 shows better stability at higher temperatures.

Bulk densities of the composites, fabricated with our methodology, were $4.52\text{--}4.76\text{ g/cm}^3$. The open porosity values were very low and highlight the efficiency of the pressure-assisted vacuum purge method. Even better densification could be obtained using pressure assisted curing of the initially compacted cylinder, as reported by Shah *et al.* [60] for pressure cast SiCN samples. Fairly uniform distribution of uranium particles in the specimens was observed by scanning electron microscopy.

Equibiaxial flexure strengths of samples with uranium oxide as the filler materials were higher than that of composites containing only α -SiC. Furthermore, it was observed that reinfiltration of the discs using a mixture of filler particles and polymer precursor led to composites with a higher load carrying capacity than those infiltrated with neat polymer precursor. This indicates the filler, with α -SiC matrix can provide strengthening mechanisms.

The biaxial strength as well as thermal conductivity obtained with carbide based fabrication were higher than the oxide-based pellets. This is partially due to the fact that the base material used

in these composites had higher thermal conductivities. In addition, the biaxial strength for these materials were better than the oxide counterparts. Furthermore, niobium carbide and zirconium carbide inclusion helped in mechanical performance. Note that the the composite fabricate using uranium carbide as the starting material showed a conversion of uranium carbide to uranium oxide (UO_2) and therefore showed lower mechanical strength and thermal conductivity. Also, the fabrication was not successful in the first attempt because of the large volume change involved ($\approx 30\%$) in such a conversion. However, a novel method to fabricate UC based pellets was developed. This involved preparation of UH_3 that acts as a source of uranium metal and finally converts to UC during pyrolysis with AHPCS.

This composite fabrication technique holds promise for nuclear fuel preparation. However, since the pyrolysis temperature used in this study was limited to 1500°C , crystallization of SiC was not achieved. It is generally agreed that α -SiC, undergoes swelling under neutron irradiation, which may not be insignificant even at lower temperatures, making it unsuitable for nuclear applications. In a parallel study by Zunjarrao *et al.* [67], it was observed that pyrolysis to $1150\text{--}1650^\circ\text{C}$ produces β -crystalline silicon carbide from AHPCS, which would be more suitable for nuclear applications [53, 54, 94]. Finally it should be noted that allylhydridopolycarbosilane, the precursor used in this study, is known for its ultra high purity and ability to form near-stoichiometric SiC, which are favorable attributes for nuclear applications of SiC. In that manner, the composite prepared in this investigation could be subjected to further thermal treatment to reduce the effects of neutron irradiation.

Given the fact that porosity may be a desirable feature, the achievable strength will be lower than those for near theoretically-dense sintered ceramics. Surprisingly, there is a lack of published data on mechanical strength requirement for fuel pellets aimed towards GFR applications. Brittle fracture stress of approximately 1400 MPa , was reported for UO_2 based sintered fuel pellets [75]. However, this may not represent the actual physical requirement for next generation fuel pellets. To understand creep behavior, compressive stress magnitude of 41.4 MPa is typically used in literature for temperatures below 1350°C [95]. Furthermore, the strength requirement should be studied as a function of irradiation damage, temperature and exposure time. Nonetheless, here we report the biaxial failure strength, determined at room temperature, as a means of comparing the effects of inclusions in the PIP densified SiC matrix. Moreover, Weibull distribution was not studied in the current analysis because the large number of tests required for such analysis. This was not feasible in the current analysis due to a small number of samples fabricated.

Solid-state reactions were observed in several mixed-metal fabrications. The powders obtained after the pyrolysis of UH_3 mixed with niobium or zirconium and AHPCS showed the formation of UC and NbC or ZrC respectively. These observations are extremely promising and thus demands for further attention. Similarly, niobium and zirconium mixed with AHPCS showed interesting unidentified peaks.

4 Nuclear Transport Analyses and Characterization

4.1 Basic Fuel Calculations

The core configurations and the two fuel types described previously were used as a starting point in the determination of beginning of cycle (BOC) multiplication factor, and subsequent burn-up calculations. The burn-up calculations were carried out using the Monte Carlo code MONTE-BURNS (combination of MCNP and ORIGEN). At first a simple burn-up calculation was carried out, assuming no fuel element shuffling, no burnable poison, and no addition of fresh fuel elements.

The core configuration had has a uranium density in the fuel of 4.98 gm/cc . The BOC value of

the multiplication factor was found to be 1.0382, and assuming the reactor generated a constant 600 MW, the core life was determined to be 290 days (time after which point the multiplication factor is below unity). The sensitivity of these values to uranium loading was determined by arbitrary varying the above uranium density by $\pm 15\%$. The results are shown in Table 13, and in Fig. 26.

Case	Uranium density (gm/cc)	BOC Multiplication factor	Core life (days)
1	4.23	1.0053	30
2	4.98	1.0382	290
3	5.73	1.0653	>520

Table 13: Summary of uranium loading sensitivity calculations.

Figure 26 shows the variation of multiplication factor with time as a function of uranium loading. It should be pointed out that the power level of 600 MW implies an average power density of ~ 400 W/cc, which is high for a gas cooled reactor using pin type fuel. A heat transfer and fluid dynamics analysis is necessary to confirm the validity of this mechanical configuration. It is clear that for this particular design uranium loadings of ~ 5 gm/cc is necessary. The build up of higher actinides

Figure 26: Variation of multiplication factor with burn-up and uranium loading

(Np, Pu, Am, etc.) due to neutron capture in U-238 is also of interest, since these could change the chemical and metallurgical behavior of the fuel pellets. Fig. 27 shows the variation of total plutonium and Pu-239 with time for case 3. It is seen that the plutonium is primarily Pu-239 with minor contributions from the higher isotopes. The maximum plutonium density is ~ 0.1 gm/cc, which is a relatively low value, but may be sufficient to affect the pellet performance. Finally, the build up of americium, primarily from decay of Pu-241, is expected to be quite small, since the quantity of Pu-241 is expected to be low.

Figure 27: Pu-239 and total Pu mass as function of burn-up

4.2 Reactor Cooling Calculations

In the previous progress report the sensitivity of core life to uranium loading was investigated. It was found that a uranium density of approximately 5 gm/cc is necessary to achieve an acceptable core life (~ 300 days), for the assumed core configuration (109 fuel elements). Furthermore, the implied average power density in this core is 400 W/cc, for a total power output of 600 MW. The next step in the design process will be to determine the feasibility of removing this amount of heat from the core using pressurized helium. If no acceptable solution can be reached following this step, the core configuration must be modified to allow for any mechanical incompatibilities.

In order to address the above question, a simplified model for a fuel pin (271 per fuel element) and its associated coolant volume was analyzed. The maximum temperature in the fuel pin was estimated assuming the implied power density (400 W/cc), pin dimensions discussed previously, and standard values for material conductivities as a function of coolant velocity. The pressure drop across the core could then be estimated for each value of coolant velocity. Although these estimates were approximate at this stage, they were sufficiently accurate to indicate whether or not it was necessary to re-configure the core.

The results of this analysis indicated that at acceptable coolant velocities (40–60 m/s) the fuel centerline temperature was unacceptably high, or for acceptable fuel temperatures the pressure drop across the core would be too high. The following two methods of modifying the core configuration were investigated:

- The number of fuel elements could be increased in order to decrease the power density. A reduction of approximately a factor of four would result in an acceptable fuel temperature.
- Using appropriate surface roughening could increase the fuel pin surface heat transfer coefficient. This would also increase the pressure drop across the core, and a compromise must be found between increased heat transfer and core pressure drop.

4.3 Reactor Design Modifications

In order to reduce the average power density in the core, the core volume was increased by adding additional fuel elements to the core periphery. The fuel element configuration was not changed from the previous design (271 fuel pins on a pitch of 22.9 cm), thus the overall core diameter increased to 440 cm. The core height was maintained at 140 cm, thus pressure drop should not be affected by longer flow paths through the core.

It was found that this core arrangement required a lower fissile density to achieve an acceptable value of the multiplication factor, thus putting a lower requirement on the fuel development goals. The current loading is approximately 4.1 gm/cc of uranium (20 % enriched) in the carbide mixture.

Assuming a power of 600 MW the power density in the core dropped to 150 W/cc from a previous value of 400 W/cc. In addition, a burn-up calculation of the core indicated that at this power density it should last well beyond 500 days with an acceptable value of the multiplication factor, and relatively low burn-up (~ 25 GWD/MTU). This result indicates that the core should be able to operate at a higher power and for a longer time in order to achieve a burnup several times that determined for the lower power assumed in this case.

4.4 Further Reactor Design Modifications

The core configuration proposed earlier was further modified by increasing the number of pins per fuel assembly from 271 to 331. This change decreases the fuel power density from approximately 100 W/cc to 84 W/cc. This value is consistent with gas-cooled reactors, and thus heat removal under normal operating conditions, and scrammed accident conditions should present no problems. During this reporting period an attempt was made to determine the sensitivity of the magnitude of the multiplication factor to various versions of the evaluated nuclear data files, and the size of significant feedback coefficients.

A comparison of the multiplication factor was made between that determined using the Evaluated Nuclear Data File/B-V (ENDF/B-V) and ENDF/B-VI. In both these cases it was assumed that the fuel was at room temperature (300 K), and the coolant density corresponded to operating density. The results are given in table 14 below.

Multiplication Factor	Nuclear Data File
1.05471 ± 0.00083	ENDF/B-V
1.07114 ± 0.00085	ENDF/B-VI

Table 14: Comparison of Multiplication Factor.

It is seen that the value determined using ENDF/B-V is lower by $\sim 1.6\%$. This change will change depending on the burnup of the core and its changing isotopic composition. This value corresponds to a Beginning of Life (BOL) case with no transuranic isotopes present, and thus reflects sensitivity to uranium isotopes only.

An estimate was made of the Doppler coefficient by estimating the variation of multiplication factor with fuel temperature. A series of multiplication factor determinations were carried out for various temperatures. Based on the data an estimate of dk_e/dT was made, and found to be approximately $3.62E-05$.

In addition, an estimate was made of the change in multiplication factor implied by voiding the core of all the coolant. Voiding the coolant will results in a harder neutron energy spectrum, and

thus increases the U-238 fission rate. However, it also increases the neutron mean free path, thus enhancing the neutron leakage. These two compensating phenomena tend to increase and decrease the magnitude of the multiplication factor respectively. Their relative magnitudes, and thus the sign and size of the change in multiplication factor is dependent on the neutron energy spectrum. In order to estimate the overall sensitivity two cases are considered. First, coolant voiding is assumed to take place from operating conditions (fuel temperature = 1200 K, coolant pressure = 7 MPa, coolant temperature = 900 K), and second the voiding takes place from cold conditions. The results are given in Table 15 below.

Multiplication Factor	Coolant State
1.03849 $\pm$ 0.00081	Operating Condition
1.03884 $\pm$ 0.00083	Voided
1.07114 $\pm$ 0.00085	Cold Condition
1.07084 $\pm$ 0.00088	Voided

Table 15: Multiplication Factor Change due to Coolant Voiding.

It is seen that the change in multiplication factor is very slight, being positive at operating conditions, and negative at cold conditions. However, the changes are small and correspond to significantly less than a dollar of reactivity.

Once a more mature design has been developed both these feedback effects should be studied in more detail, including the effects of changing isotopic content brought about by reactor operation.

4.5 Reactivity Effects of Mixed Fuel Compositions

The reactivity effects of using fuel compositions based on NbC–UC–SiC was investigated. The core configuration proposed in first annual report (Annual Report 2006) was used in the comparative analyses. In addition, the multiplication factor obtained using the original UC–SiC based fuel was used as a comparison. Finally, suggestions were made to ameliorate any deviations from the multiplication factor corresponding to the original configuration and composition.

The fuel compositions were chosen in such a manner that the uranium and niobium atomic number density per unit volume was the same. Thus, regardless of the carbide form of the uranium (UC or UC₂) the uranium and niobium content will be approximately equal, the remainder of the fuel will be assumed to be silicon carbide. Initially, it will be assumed that the uranium is enriched to 20%, which is the maximum acceptable value from a proliferation point of view. As a starting point for this study it was assumed that the uranium content was the same as that used in the previous study based on a UC–SiC compound.

The fuel compositions, and corresponding multiplication factors are shown in Table 16. For comparison the results for the original fuel composition are also shown. The fuel compositions are shown in atoms/barn-cm.

The multiplication factors in the above table shows a significant drop when niobium is used in the core. This drop is due to the significant amount of resonance absorption that takes place in niobium. The resonance integral for niobium is approximately an order of magnitude greater than that for zirconium. Furthermore, adding uranium to the composition did not have the desired effect of significantly increasing the multiplication factor, since the niobium content is increased at the same rate. There are two ways in which this situation can be corrected; first increase the enrichment of the uranium, keeping the same amount, thus not changing the niobium content,

Case Number	1	2	3	4
Uranium – 235	1.555568(-3)	1.555568(-3)	1.866681(-3)	2.177795(-3)
Uranium 238	6.222272(-3)	6.222272(-3)	7.466726(-3)	8.711180(-3)
Niobium	-	7.777840(-3)	9.333408(-3)	1.088897(-2)
Silicon	3.382342(-2)	2.520811(-2)	2.043901(-2)	1.596514(-2)
Carbon	4.937910(-2)	4.854163(-2)	4.843923(-2)	4.863206(-2)
Multiplication factor	1.07084 (± 0.00088)	0.89311 (± 0.00079)	0.91312 (± 0.00074)	0.92938 (± 0.00104)

Table 16: Compositions and corresponding multiplication factors (Case no. 1: Original case; Case no. 2: Original uranium; Case no. 3: Uranium increase by 20%; and Case no. 4: Uranium increase by 40%)

second remove the niobium and use a lower absorbing substitute. The first correction would violate the non-proliferation limit on the fuel, and the second correction would require a substitute that would be chemically compatible with the fuel and the manufacturing process.

In order to determine the sensitivity of the multiplication factor to the above two suggestions a series of calculations was carried out in which the enrichment was varied, and zirconium used instead of niobium. The results are shown in Table 17.

Case Number	1	2	3	4
Uranium-235	2.177795(-3)	2.177795(-3)	4.355588(-3)	2.800022(-3)
Uranium-238	8.711180(-3)	8.711180(-3)	6.533382(-3)	8.088954(-3)
Niobium	1.088897(-2)		1.088897(-2)	1.088897(-2)
Zirconium	-	1.088897(-2)	-	-
Silicon	1.596514(-2)	1.596514(-2)	1.596514(-2)	1.596514(-2)
Carbon	4.863206(-2)	4.863206(-2)	4.863206(-2)	4.863206(-2)
Multiplication factor	0.92938 (± 0.00104)	1.09774 (± 0.00112)	1.23290 (± 0.00119)	1.03560 (± 0.00108)

Table 17: Sensitivity of multiplication factor to enrichment and material choice (Case no. 1: Same as Case no. 1 for Table 16 (uranium increased by 40%); Case no. 2: Niobium replaced by zirconium; Case no. 3: Enrichment increased from 20% to 40%; and Case no. 4: Enrichment increased from 20% to 25.71%)

4.6 Reactor Analysis

A series of calculations was carried out in which the metal in the SiC–UC–metalC fuel composite was varied to include several possible candidates. Included in the list of candidate metals are Zr, Nb, Fe, Cr, and Y. In all cases the atom fractions and fissile material atom density were kept constant, thus the mass fractions varied from cases to cases. The results are given in Tables 18 and 19 below.

These preliminary results indicate that four of the five possible candidate metal additions to the carbide composite result in multiplication factors of acceptable magnitude. It should be possible

Isotope	at/b-cm	Atom fraction
Uranium-235	2.1778(-3)	0.0252132
Uranium-238	8.7112(-3)	0.100853
Metal	1.0889(-2)	0.126066
Silicon	1.5965(-2)	0.184835
Carbon	4.8632(-2)	0.563033

Table 18: Atom fractions in fuel.

Metal	Zr	Nb	Fe	Cr	Y
Uranium-235	0.111002	0.110563	0.121120	0.122334	0.111613
Uranium-238	0.449688	0.447909	0.490677	0.495594	0.452163
Metal	0.215407	0.218512	0.143891	0.135312	0.211089
Silicon	0.097234	0.096850	0.106097	0.107161	0.097770
Carbon	0.126668	0.126167	0.138214	0.139599	0.127365
k_e	1.0977	0.9294	1.1071	1.1045	1.1114
Density	7.658	7.688	7.018	6.848	7.616

Table 19: Mass fractions and Multiplication factors

for all four of them to form an acceptable fuel forms, either individually, or in combination with each other if it is desirable for metallurgical reasons. Future studies should be conducted that that recognize the exact mixtures of silicon, uranium and metal carbide combinations based on experimentally verification.

5 Process Modeling

5.1 Macroscopic Model

A macroscopic process model is developed describing polymer pyrolysis and uranium, hafnium, or zirconium ceramic material processing. The model includes heat transfer, polymer pyrolysis, silicon carbide crystallization, chemical reactions, and species transport of a porous mixture of preceramic polymers and submicron or nano-sized metal particles of uranium, zirconium, niobium, and hafnium. The model is capable of accurately predicting the polymer pyrolysis and chemical reactions of the source material. It describes the process via conservation equations of mass, species and energy for the entire domain. Included in the model formulation are the effects of transport processes such as heat-up, polymer decomposition, and volatiles escape. In addition, the model considers multi-size particles by grouping the granules to multi categories such that yields of all groups of particles can be obtained.

According to the requirement of fuel pellet, pyrolysis and sintering of a sample with certain geometry were simulated. The effects of heating rate, particle size and volume ratio of metal and polymer on reaction rate were investigated. The results indicated that the SiC production rate can be increased by increasing the heat flux. In addition, polymer pyrolysis rate and SiC production rate decreased when the metal volume increased. Moreover, polymer pyrolysis rate and SiC production rate could be increased as the size of metal particles increased. Once the process chemistry of

metal and polymer interaction has been established experimentally, the relevant parameters will serve as inputs into the process model. The production of both metal carbide and SiC can then be investigated, and numerical simulations used to guide and optimize the fabrication processes.

A pore level model based on the smoothed particle hydrodynamics (SPH) method was also developed. The method aims to provide the correct global behavior of the flow enabling the possibility to include more fine-grained porous structures. It is used to study the effects of filler particle materials, sizes, concentrations, and distributions on the microstructures and material properties of the final product. Fluid flow and solute transport in a complex pore structure is being explored. Pressure drops through reaction porous media and permeability variation is also being investigated.

In the macroscopic model, Darcys law and convection-diffusion equations apply to resolve flow and solute transport in porous media. At the mesoscopic level, the SPH method applies to repetitive units (pore level) in the porous structure and describes transport phenomena of both solids and fluids. Therefore, the integrated model will allow calculating the densification and grain growth behavior of ceramic samples as a function of the temperature and time of the material sintering process. At the next step, mesoscale uncertainties with stochastic characteristics of macroscale permeability will be related using SPH method. Integration of pore-level mesoscopic and system-level macroscopic models will be further improved. Efficient integration of the two methods without losing information on porous structure, physics, chemistry, and variation were investigated as well.

5.2 Reaction Kinetics of U_3O_8

During this quarter, the effects of U_3O_8 in the polymer pyrolysis and uranium ceramic material processing is investigated with the global model weve already developed. The issues investigated mainly include uniformity of the product and reaction rate. The model is based on heat transfer, species transport and reactions in porous media consisting of binary particles. The chemical reaction mechanisms of the process are simplified through apparent kinetic parameters, and reaction kinetics is established. The effect of sample geometry on the uniformity of product is studied. The results show that reaction rate for polymer pyrolysis decreases and product uniformity reduces as the sample radius increases. Volatiles transport is driven by a driving force induced from both natural and forced convection. Forced convection can be operated and vary in a wide range in experiments. The effect of different forced convection on the growth rate is investigated. The results indicate that reaction zone and rate, together with the uniformity of product increase as the driving force induced by forced convection increases. There is a critical forced driving force, above which the polymer can decompose in the entire mixed powder. The influence of particles sizes on the reaction rate and product uniformity is also investigated. The results indicate that polymer pyrolysis rate and product uniformity can be increased as the size of U_3O_8 increases. The effects of initial volume ratio of two different components on the process are also investigated. The results indicate that polymer pyrolysis rate and product uniformity increase when U_3O_8 volume increases if U_3O_8 particles are bigger than SiC particles; polymer pyrolysis rate decreases and product uniformity increase as U_3O_8 volume increases if U_3O_8 particles are smaller than SiC particles.

A pore level local model based on the smoothed particle hydrodynamics (SPH) method was also developed. The local model focuses on the interaction between SiC matrix and U_3O_8 . In the interaction process, filler particles U_3O_8 are converted to UO_2 when temperature is above 900 oC, followed by reaction between SiC and UO_2 , UC will be finally produced and mixed with SiC, and the uniformity of the composite depends mainly on the wetting behavior between SiC and UC. This is a multiphase system, including solid phases (U_3O_8 and UO_2) and liquid phases (UC and SiC). Wetting behavior at solid boundaries (filler particles) and miscible behavior of the wetting fluids

(UC and SiC) are both investigated with particle-particle interactions approach. The strength of the wetting was determined by the strength of the fluid-solid particle-particle interactions and the strength of the fluid-fluid particle-particle interactions.

In the macroscopic model, Darcys law and convection-diffusion equations apply to resolve flow and solute transport in porous media. At the mesoscopic level, the SPH method applies to repetitive units (pore level) in the porous structure and describes transport phenomena of both solids and fluids. Therefore, the integrated model will allow calculating the densification and grain growth behavior of ceramic samples as a function of the temperature and time of the material sintering process. At the next step, mesoscale uncertainties with stochastic characteristics of macroscale permeability will be related using SPH method. Integration of pore-level mesoscopic and system-level macroscopic models will be further improved in future studies. Efficient integration of the two methods without losing information on porous structure, physics, chemistry, and variation will be investigated as well.

5.3 Development of Local Process Model

The microscale model based on the smoothed particle hydrodynamics (SPH) method is further improved and it has been used to study the interaction between SiC matrix and filler particles, U_3O_8 . Reaction between SiC matrix and filler particles, composition changes, uniformity of the product, shrinkage and bulk motion of filler particles in the SiC are investigated. The microstructure and composition of the produced composite are evolved due to heat fluxes. Since the process temperature plays an important role in material quality, the effects of heating rate on species uniformity and microstructure are investigated. The reaction rates, heat and mass transfer, and composition changes of different components are simulated using the microscale model. The effect of heat flux q'' applied to the global computational domain on the composition evolution is studied. Figure 28 shows the history of the ratio of UO_2 (a) and UC (b) particles for three different heat fluxes: $0.025W/m^2$, $0.05W/m^2$ and $0.1W/m^2$. The filler particle diameter is 0.062 mm for three cases. It is indicated that the production rate of both UO_2 and UC increases as the heat flux increases.

Figure 28: Composition evolution of filler particles with heat fluxes.

Due to the increasing density and decreasing mass of the filler particles (U_3O_8 or other components produced) during the synthesis process, the shrinkage of the filler particles needs to be

considered. It is assumed that $\text{U}_3\text{O}_8/\text{UO}_2$ particles shrink once they are converted to UO_2/UC particles. Gaps between the filler particles and SiC matrix are formed. The filler particles move translational in the gap due to the pressure of the gases generated. We characterize this motion by plotting the positions of the centers of filler particles. Figure 29 show the velocity vectors of filler particles in the baseline case. By choosing the initial position of the filler particle, we compute the relative position of the filler particle. In addition, the relative position is normalized to the dimension of the unit. Figure 30 shows the normalized relative position of a filler particle with different diameters. It is seen that the translational velocity in x-direction is higher than that in y-direction. This is because the heat flux is higher in x-direction, thus, $\text{UO}_2\text{--UC}$ conversion is faster in this direction. Therefore, more gases are produced and filler particles move faster in x-direction.

Figure 29: Velocity vectors of filler particles in baseline case for reaction times of 10 hours and 11.5 hours.

The integration of the microscale and macroscale models is being established. Integration of pore-level mesoscopic and system-level macroscopic models will be further improved. Efficient integration of the two methods without losing information on porous structure, physics, chemistry, and variation will be investigated as well. The models will then be integrated for comparison with experimental measurements. Then the model can be used to guide the design of the system and process of experiments. For instance, during the composite material fabrication, micro-cracks with various orientations/sizes may form. The optimal operating conditions to avoid such micro-cracks and shorten the fabrication need to be obtained from the integrated model.

5.4 Refinement of Process Models

The local particle level model was further improved to study multiple particle types in an SiC matrix. For the UC+SiC system, numerical simulations were performed for different sample sizes based on the experimental conditions. The results show that the reaction rate for polymer pyrolysis decreases and product uniformity reduces as the sample radius increases. Simulation results also show that the particle size uniformity is important for the reaction rate and species distribution. Uniform size of filler particles should be used. It will need to take a longer time for a larger particle to complete the reactions. On the other hand, the effect of particle distribution has only a minor influence on the reaction process since high thermal conductivity of the SiC matrix. It means that the process developed for 10% volume fraction can be applied for 25% volume fraction if the particle sizes are the same. Numerical simulations have also performed to investigate the effect of volume fraction on reaction process up to 25% UC. The evolution of species is very similar for the volume fraction up to 25%. It is also due to the reason of high thermal conductivity of SiC

Figure 30: Normalized relative position of a filler particle for two different particle diameters.

matrix. The situation varies from 25% since the particle phase will start to play some important roles in heat transfer. The mass transfer and reaction rate will be affected. The study of NbC+SiC and UC+NbC+SiC systems is on going since reaction kinetics are being determined from the experiments.

The integration of the local particle level and system level models will continue to be developed. The efficient integration between two methods without losing information on porous structure, physics, chemistry, and variation will be investigated in ongoing and future studies. The models will be used to study the maximum stress possible during process. This will be helpful for preventing the cracking of the material.

6 Characterization of the SiC Matrix

Polymer precursor derived silicon carbide is the base matrix for all nuclear materials investigated in this effort. This section reports on a fundamental characterization of the silicon carbide matrix and its comparisons with conventionally processed silicon carbide.

6.1 Powder-free Techniques for Processing of Ceramics

In the last two decades, there has been considerable research interest in the development of alternative, powder-free, chemical methods for the preparation of ceramics. Non-powder based ceramic processing and coating methods that have been developed include melt casting, chemical vapor deposition, sol-gel processing, and polymer pyrolysis [96]. The development of these fabrication techniques has been driven by several requirements such as homogenous dispersion of phases, denser ceramics, and incorporation of fillers such as fibers and whiskers.

6.1.1 Conventional powder-free processing

For melt casting, arc melting using graphite electrodes is employed and parts are cast in graphite molds. Melt casting yields much larger grains and more porosity as compared to sintering. Further, grain sizes are nonuniform during different cooling rates on surface and interiors.

Chemical vapor deposition (CVD) involves the deposition of a solid material on to an activated or heated surface by reaction with a gaseous phase. Besides being used for making ceramic coat-

ings, CVD can also be used to produce ceramic powders and free standing parts [97]. Usually, inorganic precursors in form of halides and metal carbonyls are used as a source of vapor [98–100]. Advantages of this technique include lower costs, good densification, and the fabrication of ceramics without additives [101]. Control over the processing temperature is critical for CVD as this regulates the process thermodynamics and kinetics [102]. Challenges include gas phase nucleation and homogenous reaction occurring due to supersaturation of the reactive species in the gaseous phase. Also, CVD is an undesirable process for producing dense ceramics. Finally, control of microstructure and residual stresses is a matter of concern. CVD results in substantial grain sizes; large grains result in weaker mechanical properties.

A variant of CVD is the chemical vapor infiltration (CVI) process. In CVI, inorganic vapors are used to infiltrate porous structures or preforms where they deposit, react and form part of the composite. It is a very effective technique for forming composites such as fiber reinforced ceramic composites and other unique structure that are difficult or impossible to form by using CVD alone. CVI is widely used for fabrication of silicon carbide matrix composites reinforced by continuous silicon carbide fibers. However, the CVI processing is usually very slow due to low diffusion rates.

Sol-gel processing involves precipitation of ceramic particles from aqueous media. The precursors are in form of inorganic salts or metal alkoxide solutions that are processed to form hydrous metal oxides or hydroxides. The sol-gel method is generally confined to hydrolysable metal-ion species that produce aqueous sols, such as SiO_2 , Al_2O_3 , ZrO_2 , TiO_2 , CeO_2 , etc [103]. Advantages of the sol-gel technique are lowering sintering temperature, lower energy cost and higher purity of resulting material. Although more commonly used for making ceramic coatings, this technique can produce bulk pieces of limited sizes [104, 105]. This technique can also be adopted to produce ceramic composites by dispersion of powders, fibers or whiskers as reinforcement phase into sols [106, 107]. However, control over porosity and low densities are the major challenges in sol-gel technique.

6.1.2 Polymer-precursor derived ceramics

Another non-powder based method of preparing ceramics, and which is potentially promising, is polymer pyrolysis based processing of polymer-derived ceramics. This method is considerably simple and involves condensation of organometallic compounds into inorganic materials by proper thermal treatment under controlled atmosphere.

Polymer precursors (also known as preceramic polymers) are organo-element polymers that undergo a polymer-to-ceramic conversion when heated at temperatures above 800 °C. They generally contain silicon, and in some cases boron, and are typically used to obtain non-oxide ceramics such as SiC, SiNC, Si_3N_4 , and BN [108]. Preceramic polymers can be envisioned as long chain molecules with the chain composed of main-group inorganic elements and with organic branches. Upon heating to a sufficient temperature, the organic branches are shed, leaving behind an amorphous network of inorganic elements which crystallizes on further heating [109]. A typical flow diagram of the overall process of formation of polymer-derived ceramics is shown in Fig. 31 [57].

Fabrication of ceramics by pyrolysis of preceramic polymers has several clear advantages. Preceramic polymers can be processed and shaped using conventional polymer forming techniques such as polymer infiltration and pyrolysis (PIP), injection molding, coating from solvent, extrusion, or resin transfer molding (RTM) [17]. This allows for fabrication of highly three-dimensional covalent refractory components (fibers, films, membranes, foams monolithic bodies, ceramic matrix composites) that are difficult to fabricate via the traditional powder-processing route [110], and also allows for the incorporation of reinforcements. Fabrication by pyrolysis also provides the ease of processibility familiar to polymer and sol-gel science and relatively low processing temperatures

Figure 31: Schematic representation of molecular and microstructural transitions during ceramic manufacturing from preceramic polymers.

(<1200 °C) [111–113]. Lowered processing temperatures reduce fiber damage in reinforced ceramic matrix composites, and as a result the pyrolysis route has been touted as being suitable for fabrication of continuous fiber-reinforced ceramic composites (CFCCs) [114]. In this manner polymer precursor processing can offer several of the advantages for carbide- or nitride-based ceramics that are manifested for oxide-based ceramics fabricated using sol-gel processing.

Typically, the ceramic yield is much higher in polymer derived processing as compared to other non-powder chemical routes. In some cases, ceramic yield as high as 85% has been reported [60]. Nonetheless, the main challenge of polymer precursor based methods is the increase in density observed upon conversion from the polymer (mass density of ~ 1 g/cc) to ceramic (mass density of ~ 3 g/cc). This results in volumetric shrinkage, which coupled with <100 % ceramic yield, leads to the formation of porosity in the form of open pores and cracks. Accordingly, several polymer infiltration and pyrolysis (PIP) cycles are required to densify the ceramic component.

6.2 Fabricating Nanocrystalline Ceramics Using PIP

Polymer pyrolysis route allows for a greater control over the reaction kinetics and microstructure evolution that can be tailored to yield a rich amorphous/nanocrystalline ceramic material [115–117]. Such nano-crystalline ceramics are the focus of intense research as they have the potential for unique properties such as “super hardness” and significantly high toughness [118–121].

Nanocrystalline SiC has been pursued for its mechanical properties, and also for its superior electrical and optical properties [122]. Vassen *et al.* [123] reported hardness of up to 27 GPa for bulk-sintered SiC materials with grain sizes as small as 70 nm. Tymiak *et al.* [124] have reported hardness value of about 37 GPa with grain sizes around 20 nm, for SiC films deposited by hypersonic plasma particle deposition. Recently, Liao *et al.* [121] have reported hardness as high as 50 GPa for nanocrystalline SiC films with grain sizes of 10–20 nm, deposited by thermal plasma CVD.

The superior properties of nanocrystalline ceramics are governed primarily by the crystal structure [119, 121, 125]. There have been attempts to simulate the atomic structure and understand the materials properties of PDCs at fundamental level by modeling and computational studies [126–129], but these studies have not addressed the unique properties that are sometimes observed in these materials. Besides the effect of grain size, other factors, such as the presence of

hydrogen as in the case of SiC, can also contribute to the hardness [127]. Currently, the effect of grain size on the mechanical properties of nanocrystalline ceramics is not as well characterized or understood as that for metals.

In contrast to metals, a fundamental mechanistic understanding of hardness in nano-crystalline ceramics is lacking. Veprek *et al.* [130] attempted to explain superior properties of nanocrystalline ceramics based on conventional fracture mechanics. They ascribe the extremely high values of fracture toughness observed to a low concentration of flaws. Liao *et al.* [121] experimentally investigated hardness, crystal size, and crystallinity as a function of the substrate temperature for nanocrystalline β -SiC films deposited by thermal plasma chemical vapor decomposition, and observed increase in all three, with increase in the substrate temperature. Recently, Szlufarska *et al.* [118] studied atomistic processes occurring during nanoindentation of amorphous silicon carbide (a -SiC) by molecular dynamic simulations and found onset of plasticity at different indentation depths. They observed that load drops occurred during the simulated indentation of a -SiC, similar to the case of single crystal SiC. According to the authors, their observations point towards a crossover from inter-granular continuous deformation to intra-granular discrete deformation which is governed by indentation depth.

Since polymer-derived ceramics allow for the fabrication of microstructures with significant control over the grain size, they offer an ideal system for understanding the effect of crystallinity on the yield strength and other mechanical properties. There have been recent efforts to characterize the overall structure of polymer-derived ceramics by means of molecular dynamic simulations [126, 128, 131–133]. Kroll [126] studied the structure, energy and bulk modulus of amorphous silicon nitride and its ternary derivatives using molecular dynamic (MD) simulations and found that the hydrogen plays a vital role in kinetic and thermodynamic stability of these materials. Bulk modulus was found to scale with the density. Atomic models by Amkreutz *et al.* [128] predict phase separation to occur between amorphous phases of SiC, Si₃N₄ and carbon which is also observed experimentally. These MD simulations focus mainly on understanding the structure of the polymer derived ceramics at the atomic scale and look at the mechanical properties influenced by atomistic phenomena. These models do not consider the mesoscale phenomena that seem to govern the bulk mechanical properties that can, and are being, experimentally investigated.

6.3 Prior Studies on AHPCS-Derived Silicon Carbide

The high temperature ceramic of our interest is silicon carbide. And, of the several available SiC polymer precursors, allylhydridopolycarbosilane (AHPCS) is the polymer of our choice. It is an ultra high purity precursor that yields a near stoichiometric ratio on complete pyrolysis [59]. Its high ceramic yield, relatively low shrinkage and ability to be handled and processed in ambient conditions have attracted wide attention, especially as precursor to SiC fibers and more recently as matrix material [48, 58, 134, 135].

Whitmarsh *et al.* [136, 137] first reported the synthesis of allylhydridopolycarbosilane (AHPCS) by Grignard coupling of (chloromethyl)trichlorosilane, followed by reduction with lithium aluminum hydride. AHPCS has a nominal structure of $[\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2\text{CH}_2]_{0.1}[\text{SiH}_2\text{CH}_2]_{0.9}$ [48, 136–138], diagrammatically described as show in Fig. 32 [139]. Thus it has a Si:C ratio that is close to 1:1 and yields a near stoichiometric SiC upon pyrolysis. AHPCS is commercially available through Starfire Systems Co. (Malta, New York, USA) and is being researched as a binder for ceramic powders and matrix source for polymer-derived ceramic matrix composites [58, 59, 134]. It has also been used to produce SiC coatings and join monolithic and composite ceramic parts [62, 140]. Furthermore, Solomon *et al.* [70] have used AHPCS in developing a light water reactor (LWR) fuel by impregnation of uranium oxide matrix with AHPCS as a SiC precursor. Previously, Singh

Figure 32: Diagrammatic representation of AHPCS structure.

and coworkers have researched ceramic foams based on AHPCS-derived SiC and hollow alumino-silicate spheres [64], and currently are pursuing AHPCS-derived SiC as a potential matrix material for the fabrication of ceramic composite fuels for gas cooled fast reactors (GCFR) [65].

6.3.1 Mechanical properties

Ceramics derived from preceramic polymers are often prone to develop cracks and porosity, especially at higher processing temperatures, due to volume shrinkage and evolution of hydrogen gas during pyrolysis [48, 62, 134, 140]. Such inherent porosity influences the bulk properties of these composites and measurement of “true” or mesoscale properties becomes difficult by bulk measurement techniques. Since AHPCS is largely used as a source of SiC matrix in SiC/SiC composites, its fracture toughness is particularly important. Fracture toughness of the matrix would have a significant effect on the fracture toughness of the overall composite since the cracks could initiate and propagate in the ceramic matrix which will inherently contain pores. Another property of great interest when it comes to AHPCS-derived SiC is the hardness. For applications such as ceramic brakes, the hardness would determine the wear rate.

There are very limited measurement of mechanical properties of SiC carbide derived from any polymer precursor, perhaps partly due to the difficulty in fabrication of monolithic specimens. Bulk characterization of AHPCS-derived SiC sample, prepared by PIP process, has been reported by Mores *et al.* [48]. The materials were characterized in terms of density (by immersion method), fracture toughness (by bulk V-notched beam method) and hardness (by bulk Vickers indentation test). The highest values for fracture toughness and hardness were found to be about $167 \text{ MPa}\cdot\text{m}^{1/2}$ and 13 GPa, respectively. Porosity was found to adversely affect the properties. Thus, there arises the need to characterize the properties of these materials in the monolithic domain. In this context, nanoindentation, which is widely used to characterize the mechanical properties at the nano-scale [141], is particularly helpful in determining the true or mesoscale properties of ceramics that have inherent micro-pores. In a recent study, Liao *et al.* [121] successfully used nanoindentation to

determine hardness of super-hard SiC films deposited by thermal plasma chemical vapor deposition. They found higher hydrogen flow rate during the deposition process resulted in greater crystallinity, bigger crystals sizes (27 nm) and lower hardness (30 GPa). Conversely, at lower hydrogen flow rates, the crystalline fractions and grain sizes were smaller and the hardness was higher. With an average grain size of 10–20 nm and crystalline fractions of 80–85% they got film hardness of up to 50 GPa.

The processing parameters such as temperature and time have a bearing on the microstructure of ceramic formed. For example, silicon carbide formed from polymer precursor generally forms amorphous structure at 1000 °C and crystalline beyond 1600 °C. The mechanical properties can be expected to vary greatly between these temperatures. Hence, information on how the mechanical properties change with processing parameters will be of great value, and aid not only in design of parts using these ceramics but also in optimization of processing parameters and constituents (in composites) to fabricate materials with desired mechanical properties. Furthermore, crystallization is also important for controlling thermal conductivity and radiation stability.

6.3.2 Microstructure characterization

Material microstructure largely governs the final properties in ceramics, and hence microstructure characterization, as well as, the study of nucleation and crystallization are vital to understanding the structure–property relationships. While very limited literature, if any, exists on microstructural characterization of AHPCS–derived SiC there is some data on Si–C systems derived by other chemical methods. Mitchell *et al.* [117] examined the nucleation and crystallization process in Si–C and Si–N–C systems produced by pyrolysis of granulated polymethylsilane and found processing temperature and time to influence the crystal sizes. Nanocrystalline β -SiC derived from chlorine containing polysilanes/polycarbosilane prepared from poly(chloromethylsilane-co-styrene) was characterized by DTA, TGA, XRD, TEM, mass spectroscopy and infrared spectroscopy by Mitchell *et al.* [117]. Grain sizes were calculated to be 5–20 nm. Nechanicky *et al.* [142] reported TGA, FTIR, TEM and XRD studies on alpha-SiC/beta-SiC particulate reinforced composites prepared by PIP using a hyper-branched polymethylsilane (mPMS). Kerdiles *et al.* [143] used FTIR and HREM to study nano-crystalline SiC in SiC thin films grown by reactive magnetron co-sputtering of SiC and C targets. Hongtao Zhang *et al.* [144] characterized crystal structure of nanocrystalline SiC by TEM and Raman Spectroscopy in SiC thin films deposited by a plasma-enhanced CVD process. Yongcheng Ying *et al.* [145] used XRD, TEM and SAED to study the microstructure of nanocrystalline SiC prepared by reacting magnesium silicide (Mg₂Si) and carbon tetra fluoride (CCl₄) in an autoclave and reported crystal sizes of 30–80 nm.

All these studies demonstrate that a very fine-grained microstructure can be developed in precursor derived ceramics.

6.3.3 Structure–property relationships

Currently AHPCS is preferred more as a matrix source for SiC-fiber/SiC-matrix or particulate-SiC composites than as a source of monolithic unreinforced SiC components. Perhaps this is the reason why reports of property-structure characterization are limited to AHPCS derived composites. While characterizing C/SiC composites fabricated by infiltrating a woven carbon fiber fabric with a slurry of SiC powder and AHPCS, Berbon *et al.* [134] found improved thermal conductivity and diffusivity with crystallization in polymer derived phase. Dong *et al.* [135] studied microstructural evolution and mechanical performance of SiC/SiC composites fabricated by polymer infiltration process (PIP). They used AHPCS–derived SiC as a matrix along with uncoated and carbon coated Tyranno SA fibers and pyrolysis was performed using microwave radiations. Mechanical strength

results showed improved flexural strength, with a strong dependence on the quality of matrix–fiber interface. Jing Zheng *et al.* [140] examined the thermal decomposition behavior of AHPCS (Nippon Carbon Co, Tokyo, Japan) while developing a method of joining SiC ceramics in green state without applied pressure. Using XRD, they observed the formation of amorphous SiC (a-SiC) at about 850 °C, which completely crystallized at 1600 °C. A mixture of SiC particles and AHPCS, used as a joining paste was found to produce good crack-free joints. Kotani *et al.* [63] studied the effect of filler dispersion on the mechanical properties of unidirectional composites with SiC fibers and SiC matrix prepared using PIP technique. The polymer precursors they investigated included polyvinylsilane (PVS) and polycarbosilane (PCS). In another study involving AHPCS, Lewinsohn *et al.* [62] found that, when using AHPCS-derived SiC in joining SiC composites, increasing processing temperatures increased the strength of joints, possibly due to extensive crystallization. But there is still a need to realize the processing–microstructure–property–application relationships for this organic polycarbosilane which will aid in the characterization of composites derived from AHPCS.

6.4 Investigation of the Processing-Microstructure-Property Relationship in AHPCS Derived SiC

6.4.1 Processing and sample preparation

The preceramic polymer precursor chosen for this study is allylhydridopolycarbosilane (AHPCS). This polymer, designated as SMP-10, is an ultra high purity precursor, yields a near stoichiometric Si:C ratio on complete pyrolysis, has a high ceramic yield, exhibits relatively low shrinkage and is widely used as precursor to SiC fibers. At room temperature, it is in form of a clear amber colored viscous liquid and has properties as listed in Table 3. The polymer was stored under 0 °C at all times and handled in air at room temperature. All processing during pyrolysis was done under inert atmosphere, as specified.

One of the main advantages of precursor polymer route to ceramics is the ease of fabrication. Preparing SiC from AHPCS simply requires heating the polymer to temperature of above 900 °C in a oxygen free atmosphere. When the precursor is heated from room temperature, cross-linking starts at about 100 °C and a cured green body is formed. To track the polymer-to-ceramic conversion as a function of temperature, carefully weighed quantities of liquid AHPCS were heated, under argon atmosphere, from room temperature up to 300 °, 500 °, 700 ° and 900 °C, respectively. Samples were held at final temperatures for 30 min to ensure thermal equilibrium. Figure 33 shows the setup of the box furnace, fitted with a retort and modified for inert gas pyrolysis up to 900 °C. Pyrolysis beyond 900 °C was performed in a specially modified high temperature furnace (Model no. F46248, Barnstead International, Dubuque, Iowa, USA). During the initial stages of heating, cross-linking in the polymer is accompanied by loss of volatile components in the precursor which were observed to form yellowish-white deposits on the inner walls of the furnace up to about 700 °C. Hence, the heating was controlled at the slow rate of 5 °C/min, for samples heated up to 700 °C, to ensure minimal loss of polymer due to volatilization prior to cross-linking. There is no fear of losing the volatile components beyond this temperature and hence higher heating rates can be safely employed beyond 700 °C. Small quantities of amorphous SiC derived from AHPCS pyrolyzed at 900 °C were loaded in alumina crucibles and heated to different temperatures of 1150 °, 1400 ° and 1650 °C starting from room temperature at 5 °C/min and held at final temperature for 30 min, in the high temperature oven under a constant flow of argon.

Since moving to Oklahoma State University in 2006, a new setup consisting of argon purged tube furnace was setup as shown in Fig. 9. At the inlet, an ultra high purity argon gas is passed through a combination of moisture and oxygen traps to ensure zero-oxidation due to impurities that

Figure 33: Setup used for inert gas pyrolysis up to 900 °C

may be present in the tanked gas. Also, steel tubing is used at the inlet to avoid contamination by air diffusion into the tubes. After initial runs of the tube furnace with the polymer precursor yielding slightly oxidized silicon carbide, traps were set up for purifying the argon gas fed to the tube furnace. The traps used were a high capacity gas purification system (Agilent Technologies) that consisted of three cartridges: one cartridge removing moisture and organics, second cartridge removing oxygen and third indicator cartridge to warn of system saturation; and an indicating moisture removal trap. The setup of these traps is shown in Fig. 34.

To study the effect of processing parameters on the structure of SiC formed and its mechanical properties, SiC samples were made by pyrolysis of precursor, starting with the liquid form, heated to 900 °, 1150 °, 1400 ° and 1650 °C in a single runs at 4 °C/min. To study the effect of holding the material at the final temperature for different durations, the aforementioned materials being processed were held at the final temperatures (i.e. 900 °, 1150 °, 1400 ° and 1650 °C) for time durations of 2 minutes, 60 minutes and 4 hours in different experiments. The resulting material was in the form of chunks of SiC. Samples for nanoindentation were prepared by embedding part of the chunk in epoxy and polished. Samples for X-ray diffraction and TEM were prepared by crushing part of the chunk; by hand using mortar and pestle for XRD, and using a ball-mill for TEM.

Other than mesoscale characterization using nanoindentation, bulk characterization was done using ring-on-ring (ROR) biaxial flexure test. Due to the severe shrinkage in the precursor during transition from polymer liquid to ceramic SiC, fabricating a bulk sample purely of SiC derived from AHPCS is a tricky and lengthy process. The use of reinforcing agents in the form of SiC powders, fibers or whiskers, which is common in the use of AHPCS, greatly helps since it substitutes a considerable volume of the composites with these fillers that do not change in volume significantly. Thus the shrinkage occurs only in the matrix phase which is formed by pyrolysis of the precursor. Since the aim of this investigation is to characterize the SiC derived from AHPCS alone, use of reinforcing agents such as SiC fibers or whiskers was avoided. However, a similar fabrication approach of polymer infiltration and pyrolysis (PIP) used for fabrication polymer derived ceramic

Figure 34: Setup of traps to purify argon fed to the tube furnace. These include: a cartridge removing moisture and organics, a cartridge removing oxygen and a third indicator cartridge to warn of system saturation. Finally there is an indicating moisture removal trap.

composites was adopted.

First, SiC powder was prepared by pyrolysis of AHPCS to 900° , 1150° , 1400° and 1650°C in a single runs at $4^{\circ}\text{C}/\text{min}$. The samples were held at the final temperature for 60 minutes to ensure thermal equilibrium. The resulting material acquired the shape of the crucible and contained large voids generated by the release of hydrogen gas. These were crushed into powder by planetary ball mill (PM-100, Retsch GmbH, Haan, Germany) in a tungsten carbide bowl (WC) with 10 mm WC balls for 12 min at 300 rpm. These powders in turn form the reinforcing fillers in the next step of fabricating composites using PIP process. Thus by using SiC powder derived from AHPCS, we could make bulk samples made of SiC purely derived from AHPCS alone. The powders obtained from the initial pyrolysis of the precursor were then mixed with a small amounts of polymer precursor (3% by weight of the milled powder). These mixtures were compacted into short cylinders using the procedure explained earlier and the complete pyrolysis scheme was followed.

6.4.2 Physical & analytical characterization

Fourier transform infrared spectroscopy (FTIR) analysis performed on polymer precursor material heated from room temperature to final temperatures of 300° , 500° , 700° , 900° , 1150° , 1400° and 1650° using a Nicolet Model Magna 760 FTIR spectrometer with ZnSe ATR crystal with 4cm^{-1} resolution and average over 256 scans. The crushed powders were used as-is and analyzed in microscope using reflectance mode. Figure 35 shows the IR spectra obtained for products at different temperatures; data is offset to aid comparison. Peaks attributed to C–H (stretching), Si–H (stretching) and Si–C (rocking) bonds were clearly observed in the ranges of $2800\text{--}3000\text{ cm}^{-1}$, $2000\text{--}2140\text{ cm}^{-1}$ and $870\text{--}1070\text{ cm}^{-1}$ [59, 146, 147], respectively.

It can be seen that relative intensity of all the peaks initially increases with increasing temperature, which is a result of increase in cross-link density as the polymer cures forming a network

Figure 35: IR Spectra for AHPCS heated to 300 °C (i), 500 °C (ii), 700 °C (iii), 900 °C (iv) and 1150 °C (v).

structure. A gradual shift in the Si-H peak towards lower wave numbers, with increasing temperatures, suggests conversion of silicon-hydrogen bonding from Si-H₃ to Si-H₂ to Si-H, as hydrogen is expelled in the form of gas. The broad peak attributed to several C-H bonds reduces, and eventually disappears, along with the Si-H peak at 1150 °C as hydrogen is completely removed. Small peaks resulting from the presence of mono-substituted alkenes in the polymer appear around 900 cm⁻¹ (d) at 300 ° and 500 °C and soon disappear at higher temperatures. Peaks attributed to CH₃ (bending) (a and b) and SiCH₂Si bonding (c) are also identified in the IR spectra. A small amount of hydrogen appears to be present in the system even at 900 °C, whereas at 1150 °C only a SiC peak shows complete conversion of polymer into SiC.

To determine the mass loss during polymer-to-ceramic conversion as a function of temperature, samples prepared, as described earlier by heating polymer precursor to temperature of 300 °, 500 °, 700 °, 900 °, 1150 °, 1400 ° and 1650 °C were carefully weighed before and after pyrolysis. All weights were measured using high-resolution analytical balance (Model BP-301S, Sartorius, Edgewood, NY). Bulk density and porosity of the ceramic composite discs fabricated by PIP process using AHPCS-derived SiC powder and AHPCS-SiC matrix were determined using the buoyancy method [148] using a density determination kit in conjunction with the high-resolution analytical balance. Figure 36 shows the ceramic yield obtained as a function of decomposition temperature.

The loss in weight is attributed to the loss of low-molecular weight oligomers and hydrogen gas [59]. It should be noted that in our case, volatilization driven mass loss was not limited even with very slow heating rates. Marginal loss in mass was observed beyond 700 °C and about 72–74% ceramic yield in the form of amorphous SiC was obtained in the range 900 °–1650 °C. In a separate study [149] on reaction kinetics during the pyrolysis of AHPCS, the polymer pyrolysis was characterized as a three-step process consisting of volatilization, cross-linking and crystallization; and activation energies for the volatilization and cross-linking were determined as 83.1 kJ/mol and 149.7 kJ/mol, respectively, using the mass loss data discussed above.

Conversion of polymer precursor into ceramic material was also tracked in terms of density (shown in Fig. 36 along with sample mass variation) of pyrolysis products at different stages of

Figure 36: Mass loss and density variation as a function of temperature for AHPCS pyrolyzed to different temperatures.

heating. Density measurements were performed using helium pycnometry (Ultrapycnometer 1000, Quantachrome, Boynton Beach, FL) on finely crushed powders, dried for 2–3 h at 60 °C in a drying oven. This method yields true density of inherently porous materials, which cannot be accessed by bulk density measurements. Starting with a liquid AHPCS having a density of 0.997 g/cc (as mentioned by Starfire Systems Inc., USA), a dry and partially cross-linked solid with density about 1.07 g/cc is obtained at 300 °C. Further heating results in more cross-linking accompanied by the loss of low molecular weight oligomers and hydrogen gas. As the processing temperatures increase, density is observed to increase steadily until it reaches values that are close to theoretical density for SiC at 1150 °C. It is worthwhile to note that SiC obtained at 900 °C measured a density of 2.67 g/cc, which could be due the presence of hydrogen as was observed during FTIR analysis.

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) was performed to study the conversion of amorphous SiC to nanocrystalline SiC. A small amount of SiC derived from polymer precursor pyrolyzed at 900 °C was heated to 1300 °C at a rate of 5 °C/min under nitrogen atmosphere (STA 449 C Jupiter, NETZSCH, Selb/Bavaria, Germany). Evidence of crystallization in our SiC samples derived from AHPCS was first seen in these experiments. Figure 37 shows the DTA and TG curves obtained. A distinct peak is seen in the DTA curve around 1100 °C which is attributed to crystallization in the material. The occurrence of this peak coincides with the change in slope in the TG curve. Further evidence of on-set of crystallization at this temperature was seen in the X-ray diffraction (XRD) and electron diffraction patterns obtained for the pyrolyzed products.

X-ray diffraction studies were performed on SiC powders pyrolyzed at 900 °, 1150 °, 1400 °, and 1650 °C. Powder samples were prepared by wet milling in a planetary ball mill (PM-100, Retsch GmbH, Haan, Germany) for 4h in ethanol and then mounted on glass slide. Powder diffraction patterns were collected using Scintag PAD-X automated diffractometer with a $\text{CuK}\alpha$ radiation ($\lambda = 0.1540$ nm) using a scanning rate of 0.5 ° per min and operating at 45 kV and 25 mA. Figure 38 shows the XRD patterns obtained for various samples; data is offset to aid comparison.

Amorphous SiC formed at 900 °C shows a greatly diffused peak whereas the peak intensity increases as the processing temperatures increase. Gradual growth of SiC peaks at 2θ values of 35.7°, 60.2° and 72.0° suggests increasing ordering as nano-crystalline domains form and grow

Figure 37: DTA and TG curves for AHPCS heated to 1300 °C at a rate of 5 °C/min.

Figure 38: Powder diffraction patterns of SiC derived from AHPCS heated to 900 °, 1150 °, 1400 ° and 1650 °C.

Figure 39: Powder diffraction patterns of SiC derived from AHPCS heated to 900 °, 1150 °, 1400 ° and 1650 °C, from a professional laboratory (XRD.US).

in amorphous SiC. It is noted that small peaks for residual tungsten carbide (WC), from the grinding media, are seen in the patterns. Also, even though a peak for WC lies very close to the SiC peak at 35.7°, the prominent peaks at his 2 θ are attributed to SiC since the WC peak at 35.6° and 48.3° are expected to be of same intensity according to JCPDS (ICCD 29–1131). An estimate of the crystallite size was obtained from the peak broadening using the Debye–Scherrer equation [150]. Peak broadening, in terms of full width at half–maximum (FWHM), was determined by fitting the obtained pattern using XFIT program, which uses the pseudo Voigt (PV) and split Pearson (PVII) functions along with a fundamental parameters (FP) convolution approach [151]. Instrument broadening, determined by using NIST–traceable line–width standard LaB₆ sample (SRM 696), was accounted for, while determining the crystallite sizes at different temperatures. The crystallite sizes were found to be about 3.65 nm, 5.02 nm and 11.03 nm at 1150 °, 1400 ° and 1650 °C, respectively. Samples sent to professional laboratory (XRD.US) for determination of crystal sizes gave similar results of 3.83 nm, 6.50 nm and 11.07 nm for SiC fabricated at 1150 °, 1400 °, 1650 °, respectively. Figure 39 shows the powder diffraction plots obtained by them. The sharp peaks near 2 theta values of 28°, 47°, and 56° are from pure Si powder that was added to the SiC sample powders. Similar observations, for this material system, have been reported in literature [134].

Further evidence on the presence of amorphous SiC at 900 °C and its polycrystalline nature at higher temperature was seen from transmission electron microscopy (TEM). TEM studies were performed using JEOL JEM-2100 Scanning Transmission Electron Microscope System with an EDAX Genesis 2000 EDS system. Figures 40(a)–40(d) shows the TEM micrographs obtained for SiC processed at 900 °, 1150 °, 1400 °, and 1650 °C, and held at the final temperature for 4h. While at 900 °C, SiC is mostly seen in amorphous form, small domains of ordered regions are seen at some places. This is due to the long hold duration at this temperature. A lot of small crystalline regions are seen in SiC processed to 1150 °C. Similar, but larger domains are seen at 1400 °C. These domains appear to be surrounded by amorphous phase as the one seen at 900 °C. TEM micrograph for 1650 °C clearly show large domains of well ordered material. All these domains are showing the nanocrystalline SiC. A rough estimate of the size from TEM micrographs supports the crystal sizes

determined by powder diffraction.

Further, selected area electron diffraction (SAED) patterns were obtained during transmission electron microscopy (TEM) studies on these SiC samples and are shown in Fig. 41. As seen in the figure, greatly diffused concentric rings for SiC processed at 900 °C (a) suggests a largely amorphous structure. These rings are seen to gradually become distinct and sharp for SiC processed at higher temperatures (b–d), which is suggestive of growing crystallite size. SAED patterns obtained for SiC processed at 1650 °C (d) shows tiny bright specks intermittently along the rings. These are typically seen for nano-sized polycrystalline materials [152].

6.4.3 Characterization of mesoscale mechanical properties

Chunks of SiC derived from AHPCS pyrolyzed to 900 °, 1150 °, 1400 °, and 1650 °C and held at the final temperature of 2 min, 60 min and 4h were mounted in epoxy (Epoxicure, Buehler, Lake Bluff, Illinois, USA) and polished to a mirror finish using Ecomet 3 polisher (Buehler, USA). Samples were then indented using a sharp Berkovich diamond indenter (NanoTest System, Micro Materials, Wrexham, UK) to a peak load of 10, 25, 50, 75 and 100 mN for each material. A total of 10 indentations were performed for every sample. Nanoindentation was performed in the Polymer Mechanics Lab in the mechanical and aerospace engineering department at the Oklahoma State University, which is directed by Dr. Hongbing Lu.

Indentations with multiple loads was performed to determine the loads required to obtain sufficient displacements, so as to obtain reliable results. Very low indentation loads could result in insufficient displacements that are influenced by surface effects and indenter tip radius, which lead to inconsistent results. At the same time, very high loads could lead to large depths and results could be affected by porosity or substrate effects. Figure 42 shows the values of hardness obtained for SiC processed at 900 °C along with the error bars showing the standard variation. Large variation in data was observed at low load of 10mN. At 25mN, data was consistent over multiple tests and a good nanoindentation depth of 250–300 nm was observed. Hence indentation data being discussed further is from experiments performed with peak indentation load of 25 mN.

Figures 43 and 44 show load-displacement plots typically obtained for these materials. A quick comparison of those obtained for materials processed at different temperatures with the same hold time of 1h (Fig. 43) suggests that the SiC obtained at 900 °C is the most compliant amongst all, showing the highest deformation, and the materials processed to higher temperatures are less compliant. It is interesting to note that the depth of indentation does not decrease directly with increasing processing temperature. Material processed at 1150 °C typically shows the lowest indentation depth followed by material processed at 1400 °C and then that processed at 1650 °C. This suggests that during the processing of SiC, the materials undergoes change in mechanical properties, becoming harder at 1150 °C and then softening when processed beyond this temperature. Similarly, a comparison of load-displacement plots for SiC processed to the same final temperature (1150 °C) and different hold times, as shown in fig 44, suggest a softer SiC when processed for 2 min hold time becoming hard when processed to 1h hold time and then softening again when processed further to 4h hold time. These trends differ greatly for different combinations of processing temperatures and hold times and can be better tracked in terms of the modulus and hardness.

Figures 50(a) and 50(b) show the hardness and modulus as a function of processing temperature. Error bars show standard deviation. Nominal values of hardness and modulus were obtained for SiC that was pyrolyzed at 900 °C with a hold time of 1h and 4h. For 25 mN peak load, these values were about 160 GPa for modulus and about 23 GPa for hardness, which are typical for a-SiC. Material processed at 900 °C with a hold time of 4h showed higher values of about 197 GPa for modulus and about 25 GPa for hardness. There is considerable variation seen in hardness

(a) While the microstructure is mostly amorphous, some areas of crystalline regions are seen. (b) Large number of crystalline area with average size of 2-3 nm can be seen.

(c) Crystalline regions of average size of 5-6 nm are seen. (d) Large and distinct crystalline regions of 10-15 nm are seen.

Figure 40: TEM micrographs for SiC derived from AHPCS heated to (a) 900 °C, (b) 1150 °C, (c) 1400 °C, and (d) 1650 °C and hold duration of 4h.

Figure 41: SAED patterns for SiC derived from AHPCS heated to (a) 900 °C, (b) 1150 °C, (c) 1400 °C and (d) 1650 °C.

Figure 42: Modulus obtained with different indentation loads for SiC processed to 900 °C. Large error bar shows that lower load of 10 mN gave inconsistent results due to surface effects and low indentation depth.

Figure 43: Load displacement plots obtained during indentation of SiC processed at different temperatures and for a hold time of 1h. Peak indentation load of 25 mN.

Figure 44: Load displacement plots obtained during indentation of SiC processed at 1150 °C and for different hold times. Peak indentation load of 25 mN.

and modulus as a function of temperature and these variations are also dependent on the hold time at final temperatures. Figure 50(a) shows three curves for three different trends seen in the hardness values, as a function of processing temperature, for materials held for three different time durations at the final temperature. Materials held for 2 min and 1 h hold durations show a similar trend of an initial increase in the hardness values for materials processed at 1150 °C and then a drop in hardness progressively as material was processed to higher temperatures of 1400 °C and 1650 °C. Whereas material held for 4h shows a progressive drop in hardness with increasing processing temperatures. It is also interesting to note that the hardness values are very close for materials held for 2 min and 1 h hold durations at the lowest and highest processing temperatures being considered, i.e. at 900 °C and 1650 °C. The highest values for hardness of around 30 GPa were seen for the material processed at 1150 °C for a hold time of 1 h. This is about 52% higher than the lowest value, which is seen for material processed at 1650 °C and a hold time of 4 h. Similarly, Fig. 50(b) shows three curves for three different trends seen in the modulus values, as a function of processing temperature, for materials held for three different time durations at the final temperature. While values for modulus were very close for material processed for 2 min and 1h hold durations at temperatures of 900 °C and 1650 °C, the values peaked at 1150 °C for 1h hold samples and at 1400 °C for those held for 2 min. In both these cases, higher modulus values were seen at intermediate processing temperatures of 1150 °C and 1450 °C as compared to 900 °C and 1650 °C. Samples held for 4h at the final temperature show lowest values of about 197 GPa, which increases with processing temperature to about 205 GPa at 1650 °C. Just like in the case of hardness, highest values of modulus were observed for materials processed at 1150 °C for a hold time of 1 h. Highest modulus values were about 218 GPa, which is 37% higher than the lowest value which is seen for material processed with 2 min hold time at 900 °C.

Figures 47 and 48 show the hardness and modulus as a function of the hold durations at final temperature for SiC processed to different temperatures. In general, for both hardness and modulus, progressive increase is seen for SiC processed to final temperature of 900 °C as the hold time at 900 °C is increased. On the other hand, SiC processed to 1650 °C shows continuous drop in hardness as the hold time is increased from 2 min to 4h. The values of modulus do not change significantly

Figure 45: Hardness determined by nanoindentation for SiC derived from AHPCS heated to 900 °C, 1150 °C, 1400 °C and 1650 °C, as a function of processing temperature.

Figure 46: Modulus determined by nanoindentation for SiC derived from AHPCS heated to 900 °C, 1150 °C, 1400 °C and 1650 °C, as a function of processing temperature.

Figure 47: Hardness determined by nanoindentation for SiC derived from AHPCS heated to 900 °C, 1150 °C, 1400 °C and 1650 °C, as a function of hold duration at final temperature.

as a function of hold time for SiC processed to 1650 °C. For both, hardness and modulus, material processed to intermediate temperatures of 1150 °C and 1400 °C shows slightly higher values for hold time of 1h as compared to other hold times.

These results, in conjunction with the microstructural information at different temperatures, make for interesting observations. Amorphous SiC is formed at 900 °C with 2 min hold time and increasing the hold time further densifies the material resulting in improvements in its mechanical properties. With a hold time of 4h, the microstructure remains mostly amorphous at 900 °C, but there are some crystalline regions formed which explain the small increase in mechanical properties observed for SiC processed at 900 °C for 4h. Nanocrystalline SiC with average crystal size of about 3 nm is formed at 1150 °C and this greatly influences its mechanical properties. SiC formed at higher processing temperatures of 1400 °C and 1650 °C had larger grain sizes but lower mechanical properties. This could be due to the classical Hall-Petch effect which ascribes increasing mechanical properties for smaller grains sizes to dislocation pile-up on grain boundaries. Varying the hold duration at final temperature has a limited effect on the mechanical properties. While hardness and modulus increases for amorphous SiC processed to 900 °C with increasing hold duration, for SiC processed to higher temperatures, these properties generally increased only marginally for 1h hold and generally dropped for 4h hold durations. Thus, there appears to be an optimum processing temperature (about 1150 °C) that results in just the right grain size to achieve higher mechanical properties. Similarly, an optimum hold time of 1h results in better properties as compared to 2 min and 4h hold durations.

Discs of SiC processed at different temperatures, 900°C, 1150°C, and 1400°C, with a hold time of 1 hour were also characterized in terms of hardness and modulus using nanoindentation. The discs were also used to calculate their performance under biaxial stress using RoR tests. For nanoindentation, the discs were mounted in epoxy and polished using a Ecomet 3 polisher (Buehler,

Figure 48: Hardness determined by nanoindentation for SiC derived from AHPCS heated to 900 °C, 1150 °C, 1400 °C and 1650 °C, as a function of hold duration at final temperature.

Lake Bluff, Illinois, USA) to a mirror finish. Nanoindentation was done using a berkovich tip with a peak load of 25 mN.

Figure 49 shows load-displacement curve for 25 mN peak load for samples processed at different temperatures with a hold time of 1 hour. From figure 49, it was interesting to observe that material processed at 900°C had the highest indentation depth and indentation depth decreased for samples processed at higher temperature. From this it can be interpreted that as processing temperature increases, mechanical properties of SiC improve and the hardness increases.

Figures 50(a) and 50(b) show hardness and modulus of SiC samples as a function of processing temperature. Error bars show standard deviation. Figure 50(a) shows three points of hardness values as a function of processing temperature. Similarly, figure 50(b) shows three points of modulus values as a function of processing temperature. Material processed at 1400°C had the highest hardness as well as modulus value compared to materials processed at 900°C and 1150°C. From this it can be interpreted that increase in processing temperature results in better hardness and modulus value when it is held for 1 hour at final temperature.

6.4.4 Comparison of AHPCS Derived SiC with Hexoloy®

The physical, mechanical and thermal properties of silicon carbide samples prepared using our technique was compared with the commercially obtained Hexoloy® SA silicon carbide (Saint-Gobain Ceramics, 23 Acheson Drive, NY) sintered specimens. Both mesoscale and bulk properties were compared using nanoindentation and ring-on-ring tests respectively. The comparison of Hexoloy® SiC and AHPCS-derived SiC is presented in Table 20.

Table 20 compares the biaxial strength, hardness, modulus, thermal conductivity, density and closed porosity for the commercial obtained SiC with AHPCS derived SiC. Hexoloy samples showed better mechanical strength and higher thermal conductivity as compared to polymer derived SiC.

Figure 49: Load displacement plots obtained during indentation of SiC discs processed at different temperatures for a hold time of 1h. Peak indentation load of 25 mN.

Figure 50: Hardness and modulus determined by nanoindentation for SiC discs derived from AH-PCS heated to 900°C, 1150°C, and 1400°C, as a function of processing temperature.

Property	Hexoloy® SiC	AHPCS derived SiC		
		900°C	1150°C	1400°C
Biaxial Strength (MPa)	263±75.7	55.3±2.0	79.6±8.1	85.3±5.3
Hardness (GPa)	28.57*, 35.1±4.6	22.036	23.24	24.66
Modulus (GPa)	410*, 466±38	183.039	226.691	249.49
Density (gm/cc)	3.15	2.43	2.5	2.73
Open Porosity (%)	0.58	2.98	4.08	10.12
Closed Porosity (%)	1.93	4.15	1.84	1.05
Thermal Conductivity (W/m-K)	65.60	2.44	3.86	12.03
Average Grain Size (nm)	4000-10000*	—	3.65	5.02

Table 20: Comparison of different properties of AHPCS derived SiC using PIP technique and Hexoloy® SA SiC, Saint-Gobain Ceramics Structural Ceramics, NY. (* These specifications were obtained from manufacturer's website)

However, both hardness and modulus values obtained for AHPCS derived silicon carbide samples show an improvement with increasing pyrolysis temperature.

From ring-on-ring test on AHPCS derived samples as well as Hexoloy® SA samples, it was observed that Hexoloy sample showed better strength, however, for the former there was ~44% and ~54% increase in biaxial strength from SiC processed at 900°C to 1150°C and 1400°C, respectively. From nanoindentation, it was observed that mechanical properties were influenced by increasing processing temperature for AHPCS derived SiC. The highest values of hardness were observed to be around 25 GPa for material processed at 1400°C. Hardness value of Hexoloy sample was higher than AHPCS derived SiC, however, there was 12% increase in hardness value for material processed at 1400°C from 900°C. There was a 37% increase in modulus from material processed at 900°C to 1400°C. Though modulus of AHPCS derived SiC was lower than Hexoloy sample, improvement was achieved with increasing processing temperature. Density and thermal conductivity of AHPCS derived SiC followed an increasing trend with increasing processing temperature and great improvement in thermal conductivity can be obtained by complete nano-crystallization of α -SiC to β -SiC [34, 70]. These properties were higher for Hexoloy sample as it is formed from α -SiC. From x-ray diffraction, it was observed that with increasing processing temperature crystallite sizes increases. Average grain size for Hexoloy sample was in the range of 4-10 micron whereas grain size for AHPCS derived SiC were in range of 3-12 nm. Thus, changes in properties of SiC derived from AHPCS with increasing processing temperatures were studied and compared with Hexoloy® SA SiC.

6.5 Finite Element Modeling

The goal of this task is to develop a better understanding of the processing - microstructure - property relationships for AHPCS-derived SiC. In order to optimize the overall mechanical properties of composite materials fabricated using AHPCS-derived SiC, it is necessary to systematically examine the influence of material morphology and constituent properties. As the mechanical properties of a material are governed by its microstructure, this implies one needs to be able to model the microstructure and deformation mechanisms that govern the resulting properties.

According to Meyers *et al.* [153], classical analytical solution methods are inadequate to obtain closed form solutions for polycrystalline materials and necessitates the use of numerical modelling. They provide a comprehensive account of numerical models in literature targeted towards studying

polycrystalline materials. Finite element methods (FEM) and molecular dynamics (MD) are the two numerical methods that are most commonly used to model these and nanocrystalline materials. Further, irrespective of the method, most work in literature at this scale has focused on nanocrystalline metals, particularly Ni and Cu, and work on modeling of nanocrystalline ceramics has been extremely limited.

Using FEM, Fu *et al.* [154] studied the phenomena of grain boundary strengthening in polycrystalline materials, by idealizing the material as a two-dimensional composite of grain and grain boundaries. Material systems they studied included nanocrystalline iron and copper. They modeled the grain interiors using crystal plasticity and grain boundary region using isotropic plasticity in an attempt to capture the increase in strength with decreasing grain size, which has been established experimentally. While working on FEM modeling of nanocrystalline Ni, Anand *et al.* [155] coupled a crystal-plasticity model for grain interiors with a elastic - plastic grain-boundary interface model. They introduced cohesive elements along the grain boundaries to model grain-boundary slip which account for reversible elastic, as well as irreversible inelastic sliding-separation deformations. According to them, a competition between grain-boundary deformation and grain interior deformation governs the observed macroscopic mechanical response in the nanocrystalline materials.

Finite Element Modeling (FEM) has been well established in simulation of structural behaviors of composites owing to its capability to deal with multiple material constituents and flexibility of variation in materials properties parameters and morphology. However, FEM method is continuum based and has no intrinsic length scale associated. At the nanocrystalline level, the validation of a continuum model is a primary issue due to the length scales. The dimensions of grains in nanocrystalline materials are so small that classical continuum based theories may not be applicable. Length scale effects must be introduced through the material models in the finite element calculation, while molecular dynamics is better equipped to handle such small length scale models since it directly models the atoms and thus incorporates the atomic length scales of the crystal directly into the computation. While phenomena such as grain slipping can be easily handled by MD, development of specialized models is required to include these effects in finite element models. For phenomena that exist only at the length scales being investigated, obtaining the material constants and verifying the accuracy of the model independently from the systems being investigated is a major challenge [153].

As compared to FEM, more work has been done in modeling of nanocrystalline materials using MD simulations because of the advantages mentioned above. Extensive MD modeling of nanocrystalline metals has been done by Van Swygenhoven and coworkers [156–159]. They have studied the role of grain-boundary structure using models of polycrystalline nickel and copper with average grain sizes between 5–12 nm. For uniaxial stress they found that there was no damage accumulation during deformation and there was a change in deformation mechanism which was governed by the grain size. While all deformations were accommodated in the grain boundaries and grain boundary sliding at smallest grain sizes (~ 3 nm), a combination of sliding and intra-grain dislocation activity was observed for large grain sizes (10–12 nm).

While most of the simulations of nanocrystalline materials involve uniaxial deformations, other dynamic phenomena have been studied as well. While studying nanoindentation, modeled by defining a moving repulsive potential on gold, Swygenhoven *et al.* [160] found that, for an indenter smaller than the grain, dislocation absorption and emission took place at the grain boundaries. In their study, the MD model contained 15 grains with a mean diameter of 12 nm and was indented with a spherical indenter with a radius of 40 Å. Molecular dynamic simulations has thus helped understand the deformation processes at the length scales of the nanocrystalline grain size. A summary of the general things learnt from MD simulations is presented in Derlet *et al.* [159].

However MD modeling has several limitations, as pointed out by Meyer *et al.* [153], associated

with time scales, length scales and computational costs. Molecular dynamics calculations occur at extremely high strain rates that cannot be reproduced experimentally. The length scales of MD models has a direct bearing on the computational cost and this has limited the sample size to a great extent. As a result of this, direct comparisons to results of macroscopic experiments is not possible.

Other than FEM and MD models, there have been efforts to describe deformation in nanocrystalline materials using simple mixture based models. Kim *et al.* [161] modeled the plastic deformation of nanocrystalline materials with a constitutive equation based on the evolution of the dislocation density. In their model, the mechanical properties of the crystalline phase were modeled using unified viscoplastic constitutive relations and the deformation mechanism for the grain-boundary phase modeled as a diffusional flow of matter through the grain boundary. They analyzed the overall plastic deformation of the composites as function of grain size by using a simple rule of mixtures approach. According to the authors, their model is able to interpret the breakdown of the Hall Petch relation with decreasing grain size and the rate dependence of the deformation behavior. In another mixture based model, Zhou *et al.* [162] investigated the effect of grain size and porosity on the elastic modulus and strength of porous and multi-phase nanocrystalline ceramics. The authors developed a mixtures-based model to describe the mechanical behavior of constituent phases and further applied Budiansky's self-consistent method [163] to determine the effective mechanical properties of the composites. However, their model does not look at the deformation mechanisms governing the mechanical properties at small scales and hence the model fails to show any decrease in mechanical properties as a function of grain size that would occur due to grain-boundary activity.

A method that couples atomistic MD approach and continuum approach is the quasicontinuum method (QC) developed by Tadmor *et al.* [164–167]. In this method, MD approach is applied to the areas where critical phenomena occur while the surrounding areas are modeled using FEM. This approach has been successfully applied to look at problems such as interactions of cracks with grain boundaries [166] and dislocation generation at grain boundaries [168].

Another numerical modeling approach which has great potential and gaining attention for modeling deformation in nanocrystalline materials is the generalized interpolation material point method (GIMP) [169–171]. GIMP is an improvement over the material point method (MPM), overcoming its limitations with handling large scale deformations. Further, GIMP can deal with the multi-scale modeling approach and has the potential to bridge the gap between the atomic level modeling methods (MD) and continuum based methods (FEM). Moreover, there have been successful efforts to couple MD with MPM [170, 172, 173].

However, in the current work, effort is directed towards modeling the polycrystalline material using the simplest approach. Finite element modeling was adopted simply due to the ease of use, relatively short learning curve and availability of user-friendly commercial code such as Abaqus.

6.5.1 Procedure

A two dimensional diagram consisting of randomly distributed crystals was created using a centroidal voronoi tessellation (also called Dirichlet or Thiessen tessellation). Voronoi tessellation divides a given space into a set of disjoint and convex voronoi polytopes. Given a number of seed points, N , to divide a space R_d into N voronoi polytopes, N nuclei points are randomly generated in the space and the set of points closer to a nucleus P , than the neighbouring nuclei, is assigned to the nucleus P . The points that are equidistant from a pair of seeds lie on the boundary between two adjacent polygons and those equidistant from three points form the vertex of three adjacent polygons. This is typically achieved by introducing planar cell walls as perpendicular bisectors of line connecting neighboring points (seeds). The resulting polygons form a contiguous, space-exhaustive

tessellation that is unique for any given distribution of points [174]. A centroidal Voronoi tessellation (CVT) is a Voronoi tessellation of a given set such that the associated generating points are centroids of the corresponding Voronoi regions. Voronoi tessellation has been extensively used in materials science for modeling microstructure of randomly distributed grains in polycrystalline materials [154, 155, 175–177].

From a material science perspective, the Voronoi tessellation can be interpreted in terms of a simple homogenous crystal growth process with the following assumptions [174, 178]:

- all nuclei appear simultaneously,
- all nuclei remain fixed in location throughout the growth process,
- all nuclei are weighted equally,
- for each nucleus growth occurs at the same rate in all directions,
- the linear growth rate is the same for each cell associated with a nucleus,
- growth ceases for each cell whenever and wherever it comes into contact with a neighboring cell.

To incorporate a grain boundary phase around each grain, a small isotropic in-plane compression is applied to each Voronoi grain. When grains are compressed in this fashion, an inter-granular space is created which form the grain boundary phase. The compression is achieved by drawing a vector from each coordinate on the edges of the grain to the centroid and translating the points on the edges towards the centroids by a certain translation factor, r . Area fraction occupied by grains and grain boundary is calculated. The value of r can be set to obtain a desired grain-grain boundary area fraction. Since the model is two dimensional, this area fraction covered by grains becomes the volume fraction of crystalline material in the polycrystalline model. This approach has been used by Zhang *et al.* [177] to create grain boundary phase in finite element modeling of polycrystalline silicon carbide.

Finite element modeling was done using Abaqus Standard where a single part was formed by drawing grains onto a unit square using the coordinates, obtained after compression of Voronoi grains, as the input vertices for the grain edges. After all the grains were drawn, the section was partitioned using the edges formed by grains. This resulted in a two dimensional model, as shown in Fig. 51, containing grains as obtained from compression of Voronoi polytopes embedded in a unit square domain. The area between the grains forms a continuous two dimensional network of inter-granular region which is assigned the properties of grain boundary phase. The dimension of the square domain was assumed to be 100 x 100 nm, unless otherwise noted.

6.5.2 Polycrystalline Models

The polycrystalline model can be considered to be a composite with purely crystalline grains surrounded by a purely amorphous grain boundary matrix. For all the models described here, the grain and grain boundary material are considered purely elastic with elastic modulus for grains assumed to be equal to that of pure crystalline β -SiC (262 GPa) [179] and that for the grain boundary phase assumed to be equal to that of amorphous SiC (159 GPa) [67]. The assumption of purely elastic property for grain and grain boundary is a simplified approximation and is justified in this case by the purpose of these model, which is to simply determine the effective elastic modulus of the composite polycrystalline materials.

Figure 51: A typical two dimensional model generated by drawing and sectioning Voronoi grains on a unit square.

The approach chosen for this analysis allows for control over three variables in the models: the number of grains, the average size of grains and the volume fraction occupied by grains. For a given unit square model, only two of these variables could be changed while the third was determined. Using the procedure described in the earlier section, three different sets of models with different morphologies were studied. In each set, one of the variables was kept constant while changing other parameters.

The global mesh size for all models was set to 0.01. This mesh size optimizes accuracy and computational cost and was selected after a comparison of modulus values obtained using different mesh sizes. Primarily, Abaqus linear, quadrilateral, plain stress, continuum elements with reduced integration (CPS4R) were used, along with 3-node, linear, plane stress triangular continuum elements (CPS3), wherever required. The total number elements varied between 11500 and 11800.

Since the experimental data in this work was generated by nano-indentation, the boundary conditions and loading conditions were set to simulate loading under an indenter. Although ideally, a three-dimensional model is required to accurately determine the complex stress state under the indenter, a greatly simplified approach of uniform compression on the top surface of the model is used in this work. Motion of a corner node on the bottom edge was constrained in both X and Y directions ($u_1 = u_2 = 0$) and all nodes on bottom edge were constrained in Y direction ($u_2 = 0$). A uniform strain of 0.05 in the negative Y direction was applied to all nodes on the top surface ($u_2 = -0.05$). Stress-strain curves were plotted using the reaction forces, resulting from the given strain, summed over all the nodes on the top surface. The elastic modulus was determined from the slope of these stress-strains plots.

Multiple models were generated starting with the Voronoi polycrystals and varying the number of grains, grain sizes and the crystalline volume fraction. These models were elastic-elastic with grain and grain boundaries treated as purely elastic. Elastic modulus of amorphous SiC, determined from experiments, was prescribed to the intergranular regions, while the elastic modulus of β -SiC was prescribed to all the grains. The first set of models contained 100-grains in each case with volume fractions of the crystalline phase between 80–20%. The deformed models after applying a uniform strain (of -0.05) on the top surface are shown in Fig. 52 (a–d). It is important to note that, the modulus here is not simply a function of the crystalline volume fraction but also depends on the grain sizes. A comparison of the deformed models shows that the higher stresses were generated

in the model with higher crystalline volume fraction as compared to those with higher amorphous fractions. This is expected since higher volume fraction of amorphous phase, which has a lower elastic modulus, makes the models more compliant. For the same reason the stresses within the grain were higher compared to those in the intergranular regions.

Figure 52: Deformed models with 100 grains and varying crystal size and crystalline volume fractions; (a) 80%, (b) 60%, (c) 40% and (d) 20%.

The second set of deformed models with average grain size of 10 nm in each and crystalline fraction of 20, 40, 60 and 80% is shown in Fig. 53. These models were intended to capture the influence of crystalline volume fraction on the effective elastic modulus, independent of the grain sizes. Figure 54 show the effective elastic modulus obtained from these models as a function of crystalline volume fraction. Unlike in the earlier case, here the elastic modulus is truly a function of crystalline volume fraction alone since the grain size in all models was the same. The polycrystalline material can also be considered as a composite with the amorphous region analogous to the matrix and grains being the reinforcing media. In the light of this, a simple estimate of variation of modulus can be determined using rule of mixtures. These estimates typically mark the upper and lower bound for the modulus. The modulus determined by ROF and IROF are also shown in Figure 54. The effective modulus estimated from the simple FEM models developed here lie within these bounds. Thus these models can capture the effective elastic modulus of a polycrystalline material purely as a function of crystalline volume fraction.

The third set of models was aimed at investigating the effect of grain size alone on the effective modulus of the polycrystalline composite. The deformed models with 80% crystalline volume fraction in each and containing grains of average sizes of 5, 10 and 15 nm is shown in Fig. 55. The

Figure 53: Deformed models with grain size of 10 nm in all cases and with different crystalline volume fractions; (a) 80%, (b) 60%, (c) 40% and (d) 20%.

Figure 54: Elastic modulus determined for the models with 10 nm, as a function of the crystalline volume fraction.

No. of grains	Avg. grain size	Crystalline vol (%)	E (GPa)
100	5 nm	80	235.17
25	10 nm	80	234.91
10	15 nm	80	235.83

Table 21: Elastic modulus obtained for models with the same crystalline volume fraction of 80% and having different grain sizes.

global size of the square was set to 50 nm x 50 nm in order to achieve 5 nm grains with 100 grains. Table 21 lists the effective modulus obtained from these models as a function of grain size.

From the values listed in Table 21 it is clear that such a simple finite element models fails to capture any effect of grain size on the mechanical properties. Several phenomena such as grain strengthening at smaller grain sizes due to dislocation movement and pile-up, intragranular plasticity, grain boundary slipping, etc need to be accounted for in order to capture any effect of grain size on the mechanical properties. Nevertheless, the simple FEM model developed here provides a frame work and first step towards such a model.

Figure 55: Deformed Models, with 80% crystalline volume fractions in each case, and average grain size varying from 5 nm to 15 nm.

7 Publications

Journal Publications

1. Singh, A. K., Zunjarrao, S. C., and Singh, R. P., 2008, "Processing of Uranium Oxide and Silicon Carbide based Fuel using Polymer Infiltration and Pyrolysis", *Journal of Nuclear Materials*, **378**(3), pp 238–243.
2. Wang, X., S. C. Zunjarrao, H. Zhang, and R. P. Singh, 2006, "A Binary Particle Model for Polymer Pyrolysis and Uranium Ceramic Material Processing", *Journal of Analytical and Applied Pyrolysis* accepted, 2008.
3. Singh, A. K., Apblett, A., and Singh, R. P., "Novel Fabrication of Uranium Carbide and Silicon Carbide based Fuel using Polymer Infiltration and Pyrolysis", (*under preparation*).
4. Singh, A. K., Pandey, G., and Singh, R. P., "Finite Element Modeling of Porous Ceramics under Ring-on-Ring Biaxial Testing", (*under preparation*).

Patent Disclosures

1. Singh, R. P., Singh, A. K., Metzger, J. D., Apblett, A., 2008, "Preparation of Uranium Carbide and Other Ceramic Matrix Nuclear Fuels using Polymer Infiltration and Pyrolysis".

Conference Proceedings and Presentations

1. Zunjarrao, S. C., A. K. Singh and R. P. Singh, "Structure–Property Relationships In Polymer Derived Amorphous/Nano–Crystalline Silicon Carbide For Nuclear Application", *Proceedings of ICONE14, 14th International Conference On Nuclear Engineering*, Miami, USA, July 17 – 20, 2006.
2. Singh, A. K., S. C. Zunjarrao and R. P. Singh, "Novel Processing and Characterization of Uranium–Ceramic Nuclear Material", *Proceedings of ICONE14, 14th International Conference On Nuclear Engineering*, Miami, USA, July 17 – 20, 2006.
3. Wang Xiaolin, S. C. Zunjarrao, Hui Zhang and R. P. Singh, "Advanced Process Model for Polymer Pyrolysis and Uranium–Ceramic Nuclear Material Processing", *Proceedings of ICONE14, 14th International Conference On Nuclear Engineering*, Miami, USA, July 17 – 20, 2006.
4. Wang, X., S. C. Zunjarrao, H. Zhang, and R. P. Singh, 2006, "Advanced Process Model for Polymer Derived Ceramic Processing", *Proceedings of IMECE2006, ASME International Mechanical Engineering Congress and Exposition*, Chicago, Illinois, USA, Nov. 5 – 10, 2006.
5. Singh, A. K., and R. P. Singh, "Fabrication of NbC, ZrC and UC based Silicon Carbide Matrix Composites for Nuclear Applications Using Polymer Infiltration and Pyrolysis", *Proceedings of Material Science & Technology 2007 Conference and Exhibition*, Detroit, Michigan, USA, September 16 – 20, 2007.
6. Singh, A. K., and R. P. Singh, "Synergistic Effects of Mechanical Loading and Environmental Degradation on Carbon Fiber Reinforced Composites", *XXVII Oklahoma AIAA/ASME Symposium*, Tulsa, Oklahoma, USA, March 3, 2007.

7. Singh, A. K., and R. P. Singh, "Silicon Carbide and Uranium Oxide based Composite Fuel Preparation using Polymer Infiltration and Pyrolysis", *18th Annual Research Symposium*, Stillwater, Oklahoma, USA, February 21 – 23, 2007.
8. Singh, A. K., S. C. Zunjarrao and R. P. Singh, "Preparation of Silicon Carbide and Uranium Oxide/Carbide based Composite Fuels using Polymer Infiltration and Pyrolysis", *Proceedings of American Nuclear Society Annual Meeting*, Boston, Massachusetts, USA, June 24 – 28, 2007.
9. Zunjarrao, S. C., A. K. Singh and R. P. Singh, "Modulus and Hardness of Nanocrystalline Silicon Carbide as Functions of Grain Size", *Proceedings of 31st International Cocoa Beach Conference and Exposition on Advanced Ceramics and Composites*, Daytona Beach, Florida, USA, Jan 21 – 26, 2007.
10. Singh, A. K., and R. P. Singh, "Fabrication of Silicon Carbide and Refractory Metal based Composites for Nuclear Applications using Polymer Infiltration and Pyrolysis", *SAMPE, Fall Technical Conference, 2008*, Memphis, Tennessee, USA, September 8 – 11, 2008.
11. Singh, A. K., and R. P. Singh, "Novel Technique for Fabrication of Silicon Carbide Matrix Composites using Polymer Infiltration and Pyrolysis for Nuclear Applications", *2008 American Nuclear Society Student Conference*, College Station, Texas, USA, February 28 – March 1, 2008.

Thesis/Dissertation

1. Zunjarrao, S. C., 2008, "Polymer Derived Ceramics: Processing-Structure-Property Relationships", Ph.D. dissertation, *Oklahoma State University*.
2. Singh, A. K., (expected 2009), "Novel Fabrication of SiC based Ceramics For Nuclear Applications", Ph.D. dissertation, *Oklahoma State University*.

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