Effect of degree of crystallinity on elastic properties of silicon carbide fabricated using polymer pyrolysis

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Abstract

In this study, silicon carbide (SiC) is fabricated using polymer infiltration and pyrolysis (PIP). Allylhydridoploycarbosilane (AHPCS) is used as the preceramic polymer. Final processing temperatures are varied to observe the change in microstructure as well as physical and mechanical properties. Density, porosity and thermal conductivity are determined as a function of processing temperatures. Microstructural characterization, done using atomic force microscopy (AFM) and x-ray diffraction (XRD), has revealed the presence of nanocrystalline domains with grain sizes in the range of 5–20 nm. The degree of crystallinity is determined using non-contact mode atomic force microscopy. The degree of crystallinity follows an increasing trend with processing temperature. Hardness and modulus are determined using nanoindentation, and are found to be influenced by the degree of crystallinity.

Keywords: SiC, Elastic modulus, PIP, Nanoindentation, Atomic force microscopy

1. Introduction

Due to its superior qualities and ease of processibility, AHPCS has been extensively used as a matrix source for polymer precursor derived silicon carbide (SiC) composites. It has also been used for fabricating SiC coatings and for joining ceramic parts [1]. However, for determining the feasibility of using precursor derived SiC for various applications, extensive mechanical characterization is required, especially as a function of processing conditions.

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Although AHPCS has been used for number of applications, limited mechanical property data for AHPCS derived SiC has been available through open literature till date [1, 2, 3, 4].

Polymer to ceramic conversion is accompanied by large amount of volume shrinkage that results in cracks and pores in bulk samples. Since cracks and pores highly influence bulk properties, to get true local property for AHPCS derived SiC, their nano-scale characterization is important. As mechanical properties such as elastic modulus, and hardness depend on microstructure, evaluation of changes in microstructure with processing conditions is also of great importance.

There have been very few studies on bulk mechanical characterization of AHPCS derived SiC [1, 2, 3, 4, 5]. One of the reasons could be that volume shrinkage during polymer to ceramic conversion makes it difficult to fabricate monolithic specimen for bulk characterization. However, mechanical properties, if available, would be of great value for designing ceramic parts and designing composites using AHPCS derived SiC as matrix. Interrante *et al.* fabricated SiC/SiC composites using AHPCS and determined the average fracture stress to be ~ 378 MPa which was 80 MPa higher than other reported values [2]. Moraes *et al.* reported the effect of heat treatment for a range of temperature on fracture toughness and Vickers hardness for AHPCS derived SiC using PIP technique [1]. A non-linear relationship was found for both fracture toughness and Vickers hardness with heat treatment. Recently, Zunjarrao *et al.* have reported elastic modulus and hardness of AHPCS derived SiC after one cycle of PIP processing [3]. The highest modulus and hardness values were observed for SiC processed at 1150°C , and were found to be 218 GPa and 30 GPa, respectively.

Since AHPCS derived SiC has been evaluated as a potential candidate for structural applications as well as matrix for nuclear fuel [6], physical properties like thermal conductivity and density are also of great concern for increase in thermal efficiency. Moraes *et al.* reported increase in density with increasing processing temperature for SiC derived from AHPCS [1]. Dong *et al.* studied mechanical behavior of SiC/SiC which has AHPCS derived matrix and found that higher strength of SiC/SiC composite could be obtained with higher density [4].

The average strength for the composite from a three point bend test was found to be 400 MPa. According to Kotani *et al.* oxidation resistance of AHPCS derived SiC/SiC composite was better as compared to polycarbosilane (PCS) derived SiC/SiC composites [5]. Lee *et al.* evaluated thermal conductivity of SiC particulate reinforced AHPCS derived SiC composites [7]. Higher crystallization temperature resulted in improved thermal conductivity by removing carbon impurities and increasing crystallite sizes.

For any given ceramic, properties are governed by underlying microstructure. For understanding the property dependence on microstructure, it is important to follow microstructural evolution of AHPCS derived SiC. Nonetheless, only limited microstructural characterization data for AHPCS derived SiC exists in literature. Interrante *et al.* have studied conversion of AHPCS to amorphous SiC in a temperature range of 800–1000°C using a combination of differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), x-ray diffraction (XRD), transmission electron microscopy (TEM), raman spectroscopy and solid state nuclear magnetic resonance (NMR) [8]. Very small amount of mass loss was detected using DSC/TGA analysis and oxygen in the form of SiO_xC_y in amorphous SiC was detected using elemental analysis. Microstructure of polymer derived SiC has been found to vary with different processing temperatures. For example, at lower processing temperature up to 1000°C polymer-to-ceramic conversion results in amorphous SiC. Nano-crystalline domains of SiC start to form as the processing temperature is increased beyond 1100°C [9]. Zunjarrao *et al.* have used XRD for determining the crystal size for AHPCS derived SiC processed at different temperatures [3]. Average crystallite size of 11 nm was observed for material processed at 1650°C. Hardness and modulus were greatly influenced by microstructural change. However, the effect of nanocrystalline domain in amorphous matrix on the mechanical properties has not been probed from the degree of crystallinity perspective.

In this investigation, non-contact mode atomic force microscopy image analysis is used for determining the degree of crystallinity in polymer derived SiC as a function of processing conditions. In addition, the effect of nanocrystalline domains in an amorphous matrix on

mechanical properties is investigated using a particulate composite model.

2. Experimental Procedure

2.1. Bulk sample fabrication

Allylhydriodopolycarbosilane has a nominal structure of $[\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2\text{CH}_2]_{0.1}[\text{SiH}_2\text{CH}_2]_{0.9}$ [1]. The polymer is designated as SMP-10 by the manufacturer (Starfire Systems Co., Malta, New York, USA) and is in the form of a clear amber colored viscous liquid at room temperature. Fabrication of SiC as a bulk sample purely from AHPCS is tricky and lengthy since shrinkage occurs as the precursor converts to ceramic SiC. The shrinkage is due to removal of oligomers and gaseous by-products during polymer-to-ceramic conversion. Using reinforcing agents such as SiC whiskers or fibers helps in minimizing the overall volume shrinkage. These fillers can be added in a considerable volume fraction in the composites and do not undergo a volumetric change during processing. However, the current investigation is focused only on the characterization of SiC derived from AHPCS. So, reinforcing agents such SiC fibers or whiskers were not used. Instead, SiC powder produced by AHPCS was itself used as filler.

Figure 1. Flow diagram of bulk SiC sample fabrication using polymer infiltration and pyrolysis.

Figure 1 shows the flow diagram of complete PIP processing steps. This process requires

heating of the polymer precursor to a temperature above 800°C under controlled atmosphere for polymer to ceramic conversion. An inert atmosphere was maintained using a constant flow of ultra high purity argon (99.999%) to prevent oxidation of SiC at higher temperatures.

The fabrication process was started by heating the liquid polymer precursor (AHPCS) to 650°C with a heating rate of 1°C/min and holding at that temperature for 10 minutes. This started the cross-linking of the polymer precursor. For complete conversion to SiC ceramic, the heating was continued till the desired final temperatures i.e. 900°C, 1150°C, and 1400°C with a heating rate of 3°C/min. All specimens were held at the final temperature for 1 hour to ensure thermal equilibrium and complete processing. Finally, the specimens were cooled down to room temperature at a cooling rate of 5°C/min.

Due to the release of hydrogen gas and oligomers during the process, the acquired materials contained large voids. To produce a bulk sample with minimal porosity, these were ground using a hand grinder till the particles passed through a colander of mesh size 12. Subsequently, the particles were ground into a fine powder using a planetary ball mill (PM-100, Retsch GmbH, Haan, Germany) in a tungsten carbide (WC) bowl with 10 mm WC balls for 12 min at 300 rpm. These powders were used as reinforcing fillers in the next step of the fabrication process.

The powders were mixed with a small amount of polymer precursor (3% by weight of the milled powder) to prepare a semi-dry paste. A steel ram-cylinder setup was used to compact the semi-dry paste to a cylindrical preform. Hand compaction was used to apply a maximum load of ~450 N. The resulting plugs were then heated to the final temperature (900°C, 1150°C, or 1400°C) using the heating cycle described earlier. Although the resulting samples had a good dispersion of SiC particles in an amorphous silicon carbide matrix; pores were present in the plugs due to the release of the hydrogen gas and oligomers during polymer pyrolysis. Multiple PIP cycles were then carried out to minimize porosity and to increase the material density. The infiltration with the liquid preceramic polymer was carried out under vacuum with a repeated 1 hour cycle for 4 hours and 1 minute purge in between of

each cycle.

The plugs were cut into 1 mm thick discs using a precision sectioning saw (Isomet 1000, Buehler, 202 Lake Bluff, Illinois, USA) after the 3rd PIP cycle. Since, 8 infiltration cycles are sufficient to obtain the maximum achievable density [10], the discs were subjected to infiltration and pyrolysis till the 8th cycle. Slicing the plugs into discs allows for more efficient reinfiltration process.

2.2. Physical and thermal characterization

Density and porosity of the silicon carbide samples were determined after the 8th cycle of infiltration and pyrolysis as a function of different processing temperatures . The buoyancy method was used for determining bulk density and open porosity of the samples using a density measurement kit along with a high-resolution analytical balance [11]. Then, the samples were crushed and a helium pycnometer (Ultrapycnometer 1000, Quantachrome Instruments, Pittsburgh, PA, USA) was used for measuring solid density. The closed porosity was calculated from the measurement of bulk and solid densities.

Thermal conductivity was measured for cylindrical samples of $\phi 25 \times 5$ mm, using a steady state axial flow setup [12]. The sample was placed between two 25 mm diameter copper rods of length 140 mm each. Eight T-type high precision copper-constantan thermocouples were used to measure the heat flow of eight equi-spaced points on two copper rods. Thick cylindrical polytetrafluoroethylene (PTFE) insulation was used to prevent heat loss through radial conduction from the setup. The temperatures on the hot and cold sides were controlled using a temperature/process controller (Omega CN132, Omega engineering, Stamford, CT, USA) and an analog controlled chiller (Cole Palmer, model:12750-00, Vernon Hills, IL, USA), respectively. A thin layer of high thermal conductivity paste (Omegatherm 201, Omega engineering, Stamford, CT, USA) was used to minimize the thermal resistance between the copper rods and the SiC samples. After ~ 24 hours, steady state conditions were achieved and a digital storage thermometer (Fluke 53 series II) was used to record the temperature at eight different points. The data points on both hot and cold side followed a linear trend.

Linear curves on hot and cold sides were extrapolated to determine the temperatures at the sample interfaces. These temperatures were considered as T_{hot} and T_{cold} (Eqn 2). Heat flow at the sample interfaces were calculated using equation 1 and represented as Q_{hot} and Q_{cold} . Finally, the thermal conductivity (λ_{sample}) of the sample with a surface area of A_{sample} was determined using the Fourier law of heat conduction (Eqn. 2).

$$Q = -\lambda A \left(\frac{\Delta T}{\Delta Z} \right) \quad (1)$$

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

For Eqn 1, λ is the thermal conductivity of the copper rod, A is the surface area of the circular copper rod through which heat flow occurs, ΔT is the temperature difference between the two surfaces of the copper rod and ΔZ is the thickness of the copper rod.

2.3. Mechanical characterization of hardness and modulus

Nanoindentation was performed on silicon carbide samples derived from AHPCS pyrolyzed to 900, 1150, and 1400°C to characterize local mechanical properties in terms of hardness and modulus. Discs of SiC, processed at different temperatures, were mounted in epoxy and polished using a metallographic polisher (Ecomet 3, Buehler, Lake Bluff, IL, USA) to a mirror finish. Nanoindentation was done using a Berkovich tip with a peak load of 25 mN in an instrumented indenter (Nano Indenter XP system, MTS, Eden Prairie, MN, USA).

2.4. Microstructure characterization of grain size and the degree of crystallinity

Non-contact mode atomic force microscopy was used to image the chemically etched specimen surface. Microstructural features revealed in these images were analyzed to determine grain size and degree of crystallinity of the samples.

Figure 2 shows the steps that were followed to prepare the sample for AFM scanning. AHPCS derived SiC discs were mounted in epoxy and polished to a mirror finish using a

metallographic polisher (Ecomet 3, Buehler, Lake Bluff, Illinois, USA) to prepare sample for atomic force microscopy (AFM). However, a thin layer of epoxy was found on the surface of the sample using nano-lithography which indicated a need for further sample preparation. Subsequently, unmounted cylindrical samples of $\phi 25 \times 5$ mm were polished to a mirror finish. Since, the samples had micro-pores, after polishing with $0.05 \mu\text{m}$ Al_2O_3 particles some of these were left in the pores. Ultrasonic cleaning was carried out using de-ionized water to remove residual Al_2O_3 particles. Even after cleaning the samples with ultrasonic cleaner, AFM image revealed existence of organic contaminant on the surface of the sample. For ceramics samples the best way to remove organic contaminants is to use a UV-Ozone cleaner. Therefore, the PSD UV3 (Novascan Technologies, Inc. Ames, IA 50010) UV-Ozone cleaner was used to remove organic contaminants from the surface of the sample. On polished surface, grain boundaries and other microstructural features are not apparent. Etching, a selective corrosion technique for enhancement of microstructure, can be used to reveal and delineate grain boundaries. Chemical etching was performed using hydrofluoric (HF) acid.

Figure 2. Steps followed for preparing samples for atomic force microscopy.

Several concentrations of HF acid along with different etching time were employed to determine the required time for HF etching. Finally, 4% HF concentration (by volume) was determined to be sufficient concentration for successful etching. For AHPACS derived SiC processed at 1150°C , 65s of etching time revealed the crystalline structure. For sample processed at 1400°C the required etching time was 80s.

For non-contact mode imaging a stand alone atomic force microscope (MFP3D, SA, Asylum Research, Santa Barbara, CA, USA) was used. The AFM tip used for non-contact mode imaging should be sharp enough to reveal surface morphology precisely and be thin

with a proper tip angle to allow observation of narrower parts in the sample. For the current study, a silicon probe (AC240TS, Olympus) with a reflective coating of aluminum was used. The probe has a spring constant (k) of 2 N/m and resonance frequency (f_0) of ~ 70 kHz. Igor Pro was used for data acquisition and image processing. Particle analysis was used for determining degree of crystallinity. For every sample, 5 different areas were scanned and an average value was considered as degree of crystallinity for all the samples.

For comparison with the AFM based technique, phase analysis of the samples was performed using x-ray diffraction (Philips Norelco diffractometer) with Cu K α ($\lambda = 1.54178$ Å) radiation at 45 kV and 40 mA. The diffraction angle (2θ) was varied between 10° and 90° at a step increment of 0.02° with a count time of 1 s.

3. Results and discussion

3.1. Densification

Density and porosity of silicon carbide as functions of processing temperatures are listed in Table 1. It is evident that the bulk densities were lower compared to the solid material density. This is because of the residual porosity of these materials. The ceramic yield was about 72-74% for the samples.

Processing Temperature (°C)	Density (g/cc)		Porosity (%)	
	Bulk	Solid	Open	Closed
900	2.26 ± 0.01	2.43 ± 0.02	3.0	3.9
1150	2.34 ± 0.02	2.50 ± 0.02	4.1	2.3
1400	2.43 ± 0.01	2.73 ± 0.02	9.7	1.4

Table 1. Density and porosity of AHPCS derived SiC as functions of processing temperature

Table 1 also shows that the material density increased with increase in processing temperature. This is due to two factors. First, for material processed at lower temperature (800 – 900°C), polymer derived SiC contains bonds between Si and residual H in addition to Si-C bonds [9]. This results in reduced density as compared to monolithic SiC. The amount

of residual hydrogen reduced with increase in processing temperature and thereby leads to increase in density. Yu *et al.* have reported release of H_2 and SiH_4 gases between 300–700°C, and that of CH_4 , C_3H_8 , C_4H_{10} between 400–800°C [13]. Moreover, FTIR analysis revealed presence of SiH_4 even at sample pyrolyzed at 900°C in a prior study [9]. This SiH_4 is released at higher pyrolysis temperature and the peak for SiH_4 completely disappeared for sample pyrolyzed at 1150 °C. Therefore, as the pyrolysis temperature is increased release of these gases results in reduction of impurities and increase in density. Second, polymer to ceramic conversion at lower processing temperature leads to amorphous SiC. As the density of amorphous SiC (typically 2.0 – 2.8 g/cc) is lower than that of crystalline SiC [14], material processed at lower temperature has low density. Amorphous to crystalline conversion occurs with increase in processing temperature leading to higher volume fraction of crystalline phase in the processed material. This results in higher density of SiC processed at higher temperature.

Although SiC processed at 1400°C had the highest observed solid density (~ 2.7 g/cc), this value is still lower than the theoretical density of SiC (~ 3.16 g/cc). This could be the results of several factors. First, material processed at 1400°C were not completely crystalline, and contained amorphous SiC which has a lower density. Second, the presence of excess amorphous carbon could also lower the effective material density, as amorphous carbon is significantly less dense than SiC [14].

Moraes *et al.* [1] have reported density of AHPCS derived SiC for a range of processing temperatures and for different processing times. They reported that density increased with increase in temperature and a density of 2.6 g/cc was observed for SiC processed at 1400°C. For our investigation, the solid density of materials processed to 1400°C is 2.7 g/cc, which is slightly higher in comparison. This is possibly the result of multiple reinfiltration cycles that result in the material being processed at the maximum temperature for a longer effective duration.

Table 1 also shows decrease in closed porosity with increase in processing temperature.

This is because at higher processing temperature higher amount of hydrogen evolution occurs from AHPCS which could lead to removal of higher amount of hydrogen at the first heating cycle. Consequently, after compaction when the specimen is subjected to another cycle of heat treatment, the evolution of hydrogen was lower for higher processing temperature specimen which led to decrease in closed porosity at higher processing temperature.

Open porosity increased with increase in processing temperature. Open porosity observed for SiC processed at 1400°C was ~10% by volume which is due to the decomposition of the oxycarbide phase at higher processing temperature [15]. The presence of oxygen in the form of SiO_xC_y has been reported by Moraes *et al.* They have determined the amount of oxygen content to be ~9 wt% through elemental analysis [1]. Open porosity determined by Moraes *et al.* for AHPCS derived SiC also showed a nonlinear trend with higher heat treatment temperature. In their study, for SiC heat treated at 1400°C the open porosity was ~2% by volume and increased to ~9% by volume at 1600°C.

Density and porosity have significant effect on multiple properties of ceramics, including flexural strength, hardness, and fracture toughness. Generally, minimal porosity is desired in ceramics for higher mechanical properties to be used for structural applications. However, for certain applications, a certain percentage of residual porosity is desired. For example, nuclear fuels require residual porosity to accommodate irradiation swelling and redistribution [16]. So, the pores present in AHPCS derived SiC could be beneficial for such applications. Control of processing conditions could be used to produce specific levels of porosity for particular applications.

3.2. Thermal conductivity

Thermal conductivities of silicon carbide as a function of processing temperatures were 2.4, 3.8, and 12.0 $\text{W.m}^{-1}.\text{K}^{-1}$ for samples processed at 900, 1150, and 1400°C, respectively. Samples processed at higher temperature showed higher thermal conductivity which is due to two factors. The first factor is the reduction of amorphous content in the processed material with increase in temperature. Polymer derived silicon carbide processed at 900°C is

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2
3 amorphous in nature. Increasing the processing temperature to 1150 or 1400 °C results in
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5 crystallization of the amorphous structure that leads to an increase in the thermal conduc-
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7 tivity. This phenomenon can be explained using the phonon scattering theory of thermal
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9 conductivity [17]. According to the phonon scattering theory, the thermal conductivity of
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11 most solids with perfect crystals is controlled by the transfer of thermal elastic waves known
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13 as phonons. For materials with imperfections, thermal conductivity depends on the mean
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15 free path of phonon. If the mean free path is reduced, thermal conductivity will decrease.
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17 Imperfections like grain boundaries, pores or impurities cause phonon scattering and result
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19 in reduced mean free path. Therefore, decrease in amorphous content will decrease phonon
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21 scattering and thereby increase thermal conductivity. The second factor is the reduction of
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23 impurities such as hydrogen and carbon in the amorphous phase with increase in processing
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25 temperature. Reduction of impurities at higher processing temperature will lead to decrease
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27 in phonon scattering and increase thermal conductivity of polymer derived SiC.
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31 Lee *et al.* have observed an increase in thermal conductivity in SiC particulate reinforced
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33 AHPCS derived SiC matrix composite with increasing crystallization temperature [7]. A
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35 thermal conductivity of $\sim 10 \text{ W.m}^{-1}.\text{K}^{-1}$ was observed for crystallization temperature of
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37 1300°C which is close to the value ($\sim 12 \text{ W.m}^{-1}.\text{K}^{-1}$) found for material processed to 1400°C
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39 in the current study. Increase in crystallite size and removal of impurity i.e. carbon were
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41 attributed to the increase in thermal conductivity. Thermal conductivity for β -SiC is in the
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43 range of $35\text{--}121 \text{ W.m}^{-1}.\text{K}^{-1}$, thus, complete crystallization of the SiC derived from AHPCS
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45 could lead to further improvements in thermal conductivity [18, 19].
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48 49 3.3. Mechanical behavior

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51 Instrumented nanoindentation was performed on AHPCS derived samples processed at
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53 900, 1150, and 1400°C to obtain the local mechanical properties in terms of hardness and
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55 modulus. It was determined in a previous work that a 25 mN peak load produces repeatable
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57 displacements for polymer derived silicon carbide [3]. Therefore, a 25mN peak load was
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59 used for indentation and the results were consistent over multiple tests.
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Pyrolysis Temperature (°C)	Modulus E (GPa)	Hardness H (GPa)
900	183±2	22±0.4
1150	227±12	23±0.6
1400	250±8	25±0.3

Table 2. Modulus and hardness of AHPCS derived SiC as a function of processing temperature.

Modulus and hardness of SiC samples as a function of processing temperature were determined as shown in Table 2. For statistical distribution of data, 10 indentations were performed on AHPCS derived SiC. The Oliver-Pharr method was used to analyze load-displacement data to determine hardness and modulus value [20]. Lowest values of hardness (~ 22 GPa) and modulus (~ 183 GPa) were observed for SiC processed at 900°C, which are close to typical values of amorphous SiC with residual hydrogen content [21]. Material processed at 1400°C had the highest modulus (~ 250 GPa) and hardness (~ 25 GPa) value compared to materials processed at 900°C and 1150°C.

Elastic modulus depends on the ability of a material to recover elastically. Since, at higher processing temperature the degree of crystallinity as well as Si-C bond content increases, the ability of elastic recovery of SiC processed at higher temperature increases. This is the governing factor for increase in elastic modulus at higher processing temperature. Nominal changes in hardness were observed with increase in processing temperature. This is due to the fact that hardness is the resistance against permanent deformation and permanent deformation is primarily governed by flaws present in the structure. Since, even at higher processing temperature, there was amorphous content present in the SiC having disordered structure compared to crystalline SiC, hardness of the material did not change much at higher processing temperature.

Zunjarrao *et al.* [3] found the highest hardness of 30 GPa and modulus of 218 GPa for AHPCS derived SiC processed at 1150°C for hold time of 1 hour using a different heat treatment cycle. Hardness and modulus values were lower at higher processing temperature. However,

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3 indentation was performed on samples prepared using only one cycle of heat treatment. The
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5 variation in hardness and modulus was attributed to classical Hall-Petch effect. The results
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7 obtained in the current study is different than observed by Zunjarrao *et al.* [3]. However,
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9 material used for the current study had undergone eight cycle of heat treatment. This could
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11 have reduced the impurities i.e. carbon present in the grain boundaries leading to higher
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13 hardness and modulus at higher processing temperature.
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16 17 *3.4. Microstructural variation* 18

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20 Non-contact AC mode imaging was used to study the microstructure of chemically etched
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22 samples processed at 900, 1150, and 1400°C temperatures to determine the average grain size
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24 and the degree of crystallinity. Scanning was conducted using a closed loop technique. In this
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26 technique, the AFM tip was vibrated at its resonant frequency. Using a feedback loop the
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28 amplitude was kept constant at a set value. The voltage sent through the feedback loop was
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30 recorded to determine the topography of the surface. Changes in amplitude and phase of the
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32 tip vibration were also recorded simultaneously. Etching using hydrofluoric acid selectively
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34 removes more of the amorphous phase from the surface. Therefore, spherical protrusions on
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36 the surface would indicate crystalline grains of SiC. Five different locations were scanned for
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38 each sample and an average value is reported here.
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42 Figure 3 shows a typical topography and line profile for SiC processed at 900°C. The
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44 average RMS value of roughness was calculated to be 106 pm. From the topography and
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46 the line profile, it is difficult to distinguish the amorphous and crystalline region. If any
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48 crystalline domain exists, then they would be in the range of 1–2 nm. This is at the resolution
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50 limit of the AFM. Due to this reason, the degree of crystallinity and average grain size for
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52 materials processed at 900°C could not be determined.

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54 Figure 4 shows a typical representation of topography and line profile for material pro-
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56 cessed at 1150°C. In this case, the average RMS value of roughness was determined to be
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58 182 pm. Unlike the material processed at 900°C, topography of material processed at 1150°C
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60 shows formation of crystalline domains. In order to estimate the area of the crystals, grains
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(a)

(b)

Figure 3. Topography (a) and line profile (b) of SiC processed at 900°C.

were masked using particle analysis software. Three different masking techniques were used, namely iterative, fuzzy, and a custom method. The masking method uses a threshold operation to convert gray scale image to binary image. In case of iterative masking, this threshold value is determined using an iterative scheme based on maximum correlation between the original image and the converted image. For fuzzy masking, the image is considered as a fuzzy set of background and object pixels. A threshold value is obtained by minimizing the fuzziness that is calculated based on Shannon's entropy function [22]. Using iterative and fuzzy masking, the average area of crystalline grains was determined to be 41% and 46%, respectively. For the case of custom masking a threshold value of -17.3 pm and a minimum detect area of 20 pixel² were selected. For these parameters the custom masking resulted in an average 49% area of crystalline grains. Based on these three measurements, an average value of 45% was considered as the degree of crystallinity of the material.

To determine the average grain size, the number of particles were counted in the image. By considering the particles to be circular, the average diameter of the grains was determined as,

$$\frac{\pi D^2}{4} \times N = A_t \times A_g, \quad (3)$$

where D is the average diameter of the grains, N is the number of particles, A_t is the total area of the scan, and A_g is the percentage of crystalline phase present in the total scan. The average grain size was estimated to be 10–11 nm for material processed at 1150°C.

A similar procedure was followed for SiC processed at 1400°C. Figure 5 shows a typical topographic image and line profile for material processed at 1400°C. In this case, the average RMS value of roughness was determined to be 423 pm. From Fig. 5, it was evident that crystal size was bigger for SiC processed at 1400°C as compared to SiC processed at 1150°C. Using iterative and fuzzy masking method, average area of crystalline grains was determined to be 52% and 58%, respectively. For custom masking a threshold value of -1.2 pm and a minimum detect area of 20 pixel² were selected. For these parameters the custom masking resulted in an average 53% area of crystalline grains. Based on these three measurements,

(a)

(b)

Figure 4. Topography (a) and line profile (b) of SiC processed at 1150°C.

an average value of 54% was considered as the degree of crystallinity for the material. The average grain size and degree of crystallinity for SiC processed at 1400°C were 14–16 nm and 54% respectively. There was a ~20% increase in degree of crystallinity for materials processed at 1400°C.

Figure 5. Topography (a) and line profile (b) of SiC processed at 1400°C.

For comparison with the AFM based technique, X-ray diffraction (XRD) analysis was performed to determine the average grain size of the pyrolyzed samples. Figure 6 shows XRD patterns for samples prepared using PIP technique. All these samples exhibited characteristic broad halo peak with diffused intensity that refers to amorphous/nanocrystalline structure. At 900°C only a peak at 36° corresponding to (111) plane of β -SiC (ICCD: 29–1129) is visible. This indicates the evolution of a nanocrystalline structure in the sample. At 1150

and 1400°C peaks at 60 and 72° corresponding to (220) and (311) planes of β -SiC (ICCD: 29–1129) further confirmed the conversion of amorphous structure to nanocrystalline domains. XFIT program was used to perform full pattern analysis utilizing fundamental parameters (FP) approach [23]. **XFIT is a free software for analyzing x-ray diffraction data developed at the University of Sydney. This can be used to fit the experimental x-ray data using different models for determining full width at half maximum (FWHM), peak position, crystallite size, etc. For FP approach, the line-profile is developed by using information regarding the Cu $K\alpha$ emission profile, and the geometry of the diffractometer. As the developed line-profile is fitted to the experimental line profile corresponding grain size is estimated.** Estimated average crystallite sizes were 6, 14, and 22 nm for materials processed at 900, 1150, and 1400°C PIP samples, respectively. With increase in pyrolysis temperature from 900°C to 1400°C crystallite size increased from 6 nm to 22 nm. The grain sizes estimated from XRD pattern showed a similar trend as compared to grain sizes estimated from AFM images.

Figure 6. XRD patterns from SiC compacts processed using PIP technique at various temperatures.

In the past, Zunjarrao *et al.* [24] had used x-ray diffraction (XRD) to determine the average crystallite size of AHPCS derived SiC to be ~ 4 nm and 5–7 nm for materials processed at 1150°C and 1400°C, respectively. Grain sizes determined by Zunjarrao *et al.* are smaller than grain sizes estimated in the current study. This difference is possibly due to the fact that SiC powder used for XRD by Zunjarrao *et al.* went through one pyrolysis cycle as opposed to 8 cycle used in the current study that can lead to grain growth due to longer duration exposure to higher temperature.

3.5. Effect of Degree of Crystallinity on Elastic Modulus

For the case of ceramics mechanical properties are strongly influenced by the microstructure of the material. Since, there was a change in the microstructure at different processing temperatures, to understand the effect of this change on mechanical properties it is desirable to establish a relationship between change in mechanical properties with increased volume of crystalline phase in amorphous SiC. It should be noted that even though Zunjarrao *et al.* were able to determine the average grain size for AHPCS derived SiC as a function of processing temperature, they were not able to measure the degree of crystallinity [24]. As a result these past studies have not been able to investigate the influence of the microstructure on mechanical properties. The current study shows a way to determine the degree of crystallinity for samples processed at different final temperatures and its influence on elastic modulus of the samples.

A particulate composite model, considering the SiC crystals as particulates and amorphous SiC as matrix phase, was used to determine the effect of degree of crystallinity on the mechanical properties of these materials. Halpin-Tsai equations for spherical particulate reinforced composites were used for this model. Predictions of these equations are quite accurate as long as filler volume fraction does not approach 1. The following equations were used [25]:

$$\frac{E_c}{E_m} = \frac{1 + \zeta\eta V_f}{1 - \eta V_f}, \quad (4)$$

where,

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta}, \quad (5)$$

where, E_c is the effective modulus of the composite, E_m is the modulus of the matrix phase, E_f is the modulus of the particulate phase, ζ is a measure of reinforcement geometry, packing geometry, and loading conditions, and V_f is the volume fraction of reinforcements. For spherical reinforcement ζ could be calculated using the following equation:

$$\zeta = 2 + 40V_f^{10} \quad (6)$$

Combining equations 4 and 5, effective modulus of the composite, E_c was expressed as a function of filler volume fraction V_f , E_f , and E_m in the following form:

$$E_c = \frac{(E_f + \zeta V_f E_f) + E_m(\zeta - \zeta V_f)}{\left(\frac{E_f - V_f E_f}{E_m} + \zeta + V_f\right)} \quad (7)$$

Two separate equations as a function of E_f and E_m were obtained by substituting the values of E_c and V_f for samples processed at 1150 and 1400 °C in equation 7 (Table 3). These two equations were solved using an iterative scheme to determine the elastic moduli of the crystalline phase (E_f) and the amorphous phase (E_m). The elastic moduli determined using this approach were 404 GPa and 139 GPa for the crystalline phase and amorphous phase, respectively.

Material	Degree of Crystallinity (%)	Effective Modulus (GPa)
	V_f	E_c
SiC-900	-	183
SiC-1150	45	227
SiC-1400	54	250

Table 3. Degree of crystallinity and Elastic modulus values used to determine E_f and E_m

Elastic modulus of stoichiometric β -SiC has been reported to be ~ 400 GPa [26], which is similar to the elastic modulus of crystalline phase determined above. However, the elastic

modulus of amorphous phase (139 GPa) is lower as compared to stoichiometric amorphous silicon carbide (200 – 230 GPa) [21]. Khakani *et al.* have reported elastic modulus of hydrogenated amorphous $\text{Si}_x\text{C}_{1-x}:\text{H}$ to be dependent on the composition [21]. In their study, the elastic modulus of hydrogenated amorphous $\text{Si}_x\text{C}_{1-x}:\text{H}$ varied between 154 to 88 GPa for $x = 0.4\text{--}0.67$. Therefore, the lower value of elastic modulus of the amorphous phase determined in the current study could be attributed to the presence of impurities such as hydrogen and carbon within the amorphous phase.

Now, considering the elastic moduli of the crystalline and amorphous phases to be $E_f = 404$ GPa, and $E_m = 139$ GPa respectively, the volume fraction of crystalline phase (V_f) in sample processed at 900°C was estimated using $E_c = 183$ GPa in equation 7. The degree of crystallinity for material processed at 900°C was estimated to be $\sim 11\%$. This indicates that material processed at 900°C possibly had some nanocrystalline grain formed within the amorphous phase. However, the size of crystals was too small to be detected using the current technique.

4. Conclusions

Conventional sintering requires high temperature and pressure for fabrication of dense silicon carbide. Polymer infiltration and pyrolysis (PIP), an alternative to sintering, requires low temperature and minimal pressure for fabrication of silicon carbide. A major advantage of PIP technique over sintering process is the ability to control microstructure of the fabricated sample. However, only limited microstructural characterization data exists in literature till date for AHPCS derived SiC materials containing a mixture of amorphous and crystalline phase. The current study employed PIP to fabricate SiC from allylhydridopolycarbosilane (AHPCS) at different temperatures. These materials were characterized for physical, mechanical, and microstructural properties. Based on the experimental investigation, the following conclusions are drawn:

1. For AHPCS derived SiC, there was an increase in density with increasing processing

temperature. A 12% increase in density was observed for material processed at 900°C to material processed at 1400°C. This was due to the partial conversion of amorphous SiC to crystalline SiC. Thermal conductivity of AHPCS derived SiC followed an increasing trend with increase in processing temperature and a 400% increase in thermal conductivity for sample processed at 1400°C as compared to sample processed at 900°C was observed. This indicates that significant improvement in thermal conductivity can be obtained by complete nano-crystallization of α -SiC to β -SiC.

2. From nanoindentation it was observed that mechanical properties were influenced by increase in processing temperature for AHPCS derived SiC. Increase in processing temperature resulted in nano-crystalline SiC formation in the amorphous SiC matrix. As nano-crystalline SiC is expected to have superior properties, hence this increase in hardness and modulus. The highest value of hardness was observed to be ~ 25 GPa for material processed at 1400°C. There was a 12% increase in hardness and 37% increase in modulus for material processed at 1400°C from 900°C. This was a result of reduction of impurities and increase in crystalline phase in material processed at 1400°C as compared to SiC processed at 900°C.
3. Microstructural characterization using AFM and XRD confirmed presence of nanocrystalline domains with grain sizes in the range of 5–20 nm in the PIP samples. Increasing pyrolysis temperature from 1150°C to 1400°C increased degree of crystallinity in the corresponding samples from 45% to 54% and thereby affected elastic modulus of the samples. Using a particulate composite model, elastic moduli were estimated for crystalline phase and amorphous phase to be 404 GPa and 139 GPa, respectively. The estimated elastic modulus of the crystalline phase corresponds well with the elastic modulus of β -crystalline SiC. However, the estimated elastic modulus of amorphous phase was lower as compared to stoichiometric amorphous silicon carbide due to presence of impurities such as hydrogen and carbon.

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