

Production of β -Silicon Carbide Nanofibers using the Forcespinning[®] Method

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received November 11, 2015; received in revised form May 24, 2016; accepted June 1, 2016

Abstract

Silicon carbide (SiC) nanofibers were produced on a large scale using the Forcespinning[®] method. Non-oxide ceramics such as SiC are known for their low density, oxidation resistance, thermal stability, and wear resistance. The nanofibers were prepared using a solution-based method with polystyrene and polycarbomethylsilane as the precursor materials. Fiber spinning was performed under different parameters to obtain high yield, fiber homogeneity, and small diameters. The fibers were spun under a controlled nitrogen environment to prevent fiber oxidation. The resultant nonwoven nanofiber mats were then subjected to different heat treatments to evaluate the effect of these on the crystalline structure. Characterization was conducted using scanning electron microscopy, x-ray diffraction, and thermogravimetric analysis. The results show high yield, semi-continuous bead-free nanofibers with diameters ranging from 280 nm to 2 micron depending on the selected processing parameters. The sintered precursors show formation of SiC nanofibers with a beta phase crystalline structure and oxygen content below 15 %.

Keywords: Silicon carbide, high-temperature materials, ceramic nanofibers, Forcespinning[®]

I. Introduction

In the past three to four decades a vast number of studies have been conducted on the synthesis and development of nanostructures in response to numerous potential applications. These structures include nanoparticles, nanofibers, nanowires, nanotubes, and nanoribbons¹. The development of these structures has been accomplished by a variety of methods such as: chemical vapor deposition, electrospinning, liquid vapor grown, carbothermal reduction, arc discharge, laser ablation, and plasma torch just to mention some²⁻⁷. As a nano-structure, β -silicon carbide (SiC) has been intensively studied, especially for ultra-high-temperature applications, given its unique properties such as high mechanical strength, high thermal conductivity, low thermal expansion coefficient, chemical inertness, and excellent thermal shock resistance⁸.

Many studies have focused on the development of β -SiC nanofibers and nanowires due to their large surface-to-volume ratio. The lab-scale results show promising applications^{1,2,8-11}. Therefore, scientists are researching new and easier methods to increase the production yield of β -SiC structures. Electrospinning, considered a low-cost and easy set-up to develop laboratory-scale samples, has been included in most of the reported literature to obtain SiC precursor nanofibers². For example, Jiayan *et al.* electrospun a solution of polyvinylpyrrolidone/tetraethyl orthosilicate (PVP/TEOS) and were able to obtain single-crystalline β -SiC nanowires by carbothermal reduction of the electrospun nanofibers. In the carbothermal reduc-

tion, they used carbon at high temperatures, 1700 °C, in order to reduce the PVP/TEOS nanofibers to β -SiC⁹. Balkus *et al.* used a preceramic polymer in order to decrease the heat treatment temperature; SiC nanofibers were electrospun from a blend of high-molecular-weight polystyrene (PS) and polycarbosilane (PCS). They obtained fibers with diameters as small as 1 to 2 nm, the smallest reported to date. Eick *et al.* also obtained β -SiC fibers (avg. diameter of 20 nm), they utilized UV light to crosslink the precursor fibers to promote fiber integrity during the heat treatment process. Chen *et al.* synthesized polymolybdenocarbosilane (PMoCS) from a reaction of polycarbosilane (PSCS) with molybdenum (V) chloride (MoCl₅) in an argon atmosphere utilizing a lab-scale melt spinning apparatus equipped with a single 200-nm capillary tube. The extruded filament was stretched and collected in a rotating spool and subsequently pyrolyzed¹. Oya *et al.* performed a similar study, although they added a stabilization step (heating the fibers in air at 200 °C for 7 h before pyrolyzing) with the goal of separating fibers from each other. Their XRD spectra showed an amorphous silicon oxycarbide. In order to obtain a β -SiC crystalline structure, the heat treatment temperature was increased to 1500 °C¹¹.

The above-mentioned studies are far from being realized in a real world application given that the yield of the utilized methods is too low. For example, in electrospinning the yield is about 0.3 g/h¹²⁻²¹, furthermore the nanofibers have to go through a pyrolysis process where the material loss is close to 50 wt% depending on the polymer being used. Therefore, the yield being produced is on-

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ly about 0.15 g/h. In the case of the melt blown process, even though proven highly reliable and cost effective for micron-size fibers, for nanofibers, the process would consume a large amount of heated gas, rendering it not feasible for scale-up. For example, to prepare fibers of about 3 μm of polypropylene (density 0.900 g/cm³), with a polymer flow rate of 0.2 gr/min per hole, the spinning speed is calculated to be 516.6 m/sec (about Mach 1.5) and most of this energy is wasted. Reduction of fiber diameter would considerably increase the needed speed²².

Commercial SiC fibers on micron scale have been produced successfully over the last 30 years. The most common method for producing ceramic fibers is melt spinning of a pre-ceramic polymer followed by heat treatment. SiC-based fibers are spun from organo-metallic polymer precursors followed by cross-linking and different heat treatment steps to convert the precursors into ceramic materials. Commercial SiC fibers have also been developed by means of chemical vapor deposition. Nicalon SiC fiber produced by Nippon Carbon from Japan was the first commercially available fiber. Here they used a production method where the pre-ceramic polymer, PCS is synthesized from dimethyldichlorosilane. PCS is spun, followed by crosslinking, and sintering. The fibers had an average diameter in the range of 10–20 μm ²⁵.

In 1987, Ube Industries publicized the development of their own SiC fiber “Tyranno” which was derived from polytitanocarbo-silane (PTC) precursors. Ube Industries reported that their fibers had better thermal and chemical stability when compared to the other SiC fibers at that time²³. Sylramic™ is another commercial SiC fiber produced by COI Ceramics with a similar process as that used for the Tyranno fibers. Glenn Research Center developed Sylramic™-iBN, a new type of SiC small-diameter (10- μm) fiber and was given an R&D 100 award in 2001. The development of Super Sylramic™ consists of subjecting Sylramic™ fibers to a sintering process at high temperatures using boron sintering aids. The resultant fibers possess a strength of > 3 GPa, are dense, oxygen-free, and nearly stoichiometric (Si/C = 1)²⁵.

In the development of SiC fibers, the oxygen content plays a crucial role. For example, at temperatures above 1200 °C, SiC fibers with high oxygen content decompose²⁶. Oxygen content also degrades interfacial properties and promotes fiber-fiber bonding, therefore negatively affecting strength and toughness of the ceramic matrix composites (CMCs). In order for SiC to be used in high-temperature applications (1200–1300 °C) the oxygen content ideally should be less than 10 wt%²⁵.

This work presents the development of β -SiC nanofibers utilizing the Forcespinning® (FS) method. The ultimate goal is to analyze the potential to scale up the production of fine SiC fibers. FS uses centrifugal forces to overcome shear forces to promote fiber elongation. On lab scale, a yield of more than 1 g/min is usually obtained. Several polymeric and metallic oxide nanofibers have been developed utilizing FS^{12–21}. For this study, the green SiC nanofibers were developed utilizing a solution of polystyrene (PS) and polycarbomethylsilane (PCmS).

Production parameters were evaluated as well as the path to obtain fibers with optimum oxygen content.

II. Experimental

(1) Materials

Polystyrene (PS, $M_w = 280\,000$ g/mol) and polycarbomethylsilane (PCmS, $M_w = 800$ g/mol) were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used as received. Toluene was purchased from Fisher Scientific (Waltham, MA, USA) and used as received. The PS/PCmS/Toluene (15, 20, 25 wt% of PS with a 2:1 ratio of PS:PCmS) solutions were prepared inside a MBRAUN (Stratham, NH) glovebox under nitrogen atmosphere in order to prevent oxidation. The solutions were prepared in 20-mL scintillation vials and sealed with parafilm, to prevent solvent evaporation. These were magnetically stirred for a period of 4 h.

(2) Nanofiber development

An FS system was placed inside a glovebox under nitrogen environment. Approximately 2 mL solution was deposited into a cylindrical-type spinneret using a 10-mL syringe. The spinneret was outfitted with capillary tubes having an inner diameter of 133 μm and length of 12.7 mm. The angular velocity at which the fibers were spun was varied from 5000 rpm to 9000 rpm. The angular velocity applied to the spinneret causes a centrifugal force on the solution, which forces the solution through the nozzles. The centrifugal force varies with angular velocity and design of the spinneret. Studies have been conducted by Padron *et al.*²⁶ and Taghavi *et al.*²⁷ to better understand the force applied to the tailoring jet of the solution according to spinneret design and its ultimate effect on the diameter of the fibers.

After spinning, the fibers were collected on a circular collector having 16 equally spaced polytetrafluoroethylene (PTFE) bars. The produced fibers were stored in a glovebox to prevent fiber oxidation.

(3) Cross-linking

The collected fibers were placed under a 254-nm wavelength UV light source for a period of 24 h. The cross-linking was performed in a glovebox under nitrogen environment. The fibers had to be cross-linked because PS reaches the glass transition temperature before the preceramic polymer (PCmS) changes from amorphous to a crystalline β -phase.

(4) Heat Treatment

Heat treatment of the produced fibers was performed in a CM tube furnace (Bloomfield, NJ, USA) under a controlled atmosphere of either nitrogen (1200 °C with a flow of 30 ml/min) or argon (1100 °C, 1300 °C, and 1500 °C with a flow rate of 144 ml/min). Under nitrogen, the fibers were sintered to a temperature of 1200 °C with a ramping rate of 10 K/min and a dwell cycle of 2 h. The fibers were heat treated under argon at 1100 °C, 1300 °C, 1400 °C and 1500 °C with a heating rate of 2.5 K/min and 1 h dwell times.

(5) Fiber Characterization

Fiber morphology was analyzed using a Carl Zeiss Sigma VP Scanning Electron Microscope. Fiber diameters were measured with Carl Zeiss AxioVision software. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 from room temperature to 1200 °C at a rate of 10 °C/min under nitrogen flow of 30 mL/min. X-ray diffraction analysis (Bruker AXS D8 diffractometer) was utilized, fibers were scanned from 20–80° 2 θ angles using a 2D-detector.

III. Results and Discussion

To optimize the development of homogeneous, high-yield, bead-free continuous green SiC fibers, several parameters were altered throughout the study such as the concentration of polystyrene in the polymer solution. Three polymer solutions were developed and analyzed (15 wt%, 20 wt% and 25 wt%). The angular velocity of the spinneret was also varied (5000, 7000, and 9000 rpm) for each one of the different concentrations as well as the heat treatment process, which was varied for the precursor systems.

After the spinning process, morphological analysis using SEM was performed to evaluate processing effects on fiber diameter and overall fiber structure. Statistical analysis was performed based on over one hundred measurements from each angular velocity and concentration, diameter distribution graphs are shown in Figs. 1, 2, and 3. The lowest obtained average diameter was 270 nm and it was obtained using a concentration of 15 wt% with an angular velocity of 5000 rpm. The highest average diameter was 2090 nm, and was obtained using the 25-wt% concentration solution with an angular velocity of 7000 rpm. It is important to note that even though the fibers undergo shrinkage during pyrolysis, it was still desirable to select the lower fiber diameter, although yield was a serious consideration as well. Therefore, it was decided to select the concentration of 20 wt% with an angular velocity of 7000 rpm to proceed with the characterization. These parameters offered an optimum compromise between fiber diameter and yield (even though yield was observed to be much larger in the 25-wt% sample). Fig. 4 displays an SEM image of the SiC precursor fibers 20 wt% spun at 7000 rpm. Fig. 5 displays an SEM image of heat-treated fibers.

The fibers were exposed to UV light (frequency of 254 nm for 24 h) before the heat treatment process in order to promote cross-linking. The main purpose of the cross-linking is to maintain the fiber shape during the heat treatment process; thus, high-temperature pyrolysis can be achieved while maintaining fiber integrity.

In order to convert the SiC precursor fibers to SiC, the developed fibers were subjected to a heat treatment process. The preceramic polymer in this case, PCmS, undergoes a change from an amorphous to crystalline structure at high temperatures. A heat treatment method was designed based on TGA analysis. The TGA curve showed a weight loss starting at 350 °C, the samples became stable at 800 °C with a total weight loss of 27 wt%. Samples were then subjected to heat treatment in an oven for a period of

2 h. Different temperatures with an increment of 100 °C were analyzed. XRD analysis was conducted with samples exposed to the different temperatures to analyze the effect on the development of crystallinity. Diffraction peaks were not observed until samples were treated at ≥ 1200 °C. At this temperature, SiC diffraction peaks at 35.2°, 60.2°, and 71.7° corresponding to the β -SiC face-centered cubic structure were observed.

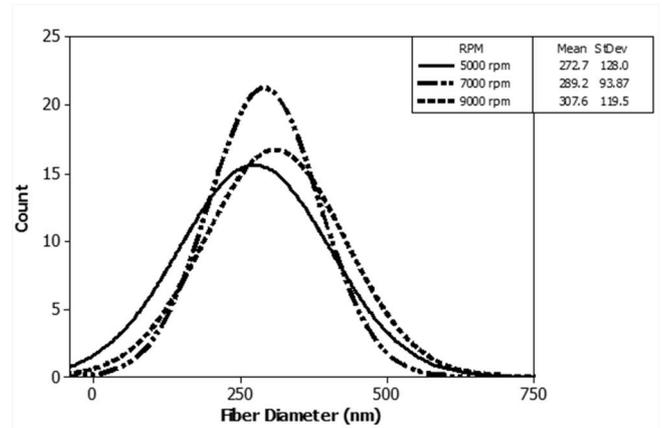


Fig. 1: Diameter distribution histogram of 15 wt% PS/PCmS solution spun at 5000, 7000, and 9000 rpm for 30 sec.

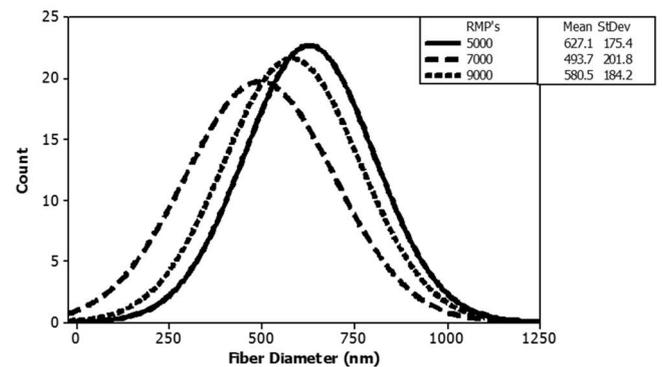


Fig. 2: Diameter distribution histogram of 20 wt% of PS/PCmS solution spun at 5000, 7000, and 9000 rpm for 30 sec.

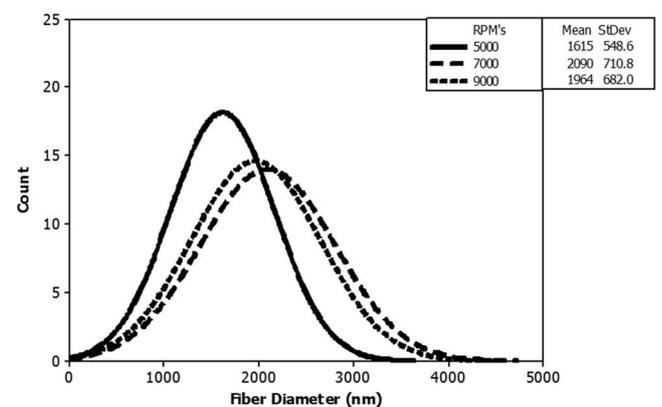


Fig. 3: Diameter distribution histogram of 25 wt% PS/PCmS solution spun at 5000, 7000, and 9000 rpm for 30 sec.

As discussed, the percentage of oxygen present in the fiber has to be less than or equal to 10 wt% otherwise it is considered silicon oxycarbide (SiOC). Energy dispersive spectroscopy was used to measure the chemical composition of the fibers. Table 1 shows the EDS spectra

of the SiC fibers sintered at 1200 °C. EDS spectra show the oxygen content in the fibers to be 42.59 wt%. This O content is too high when compared to the commercially available SiC fibers and therefore considered unacceptable for high-temperature applications. The developed process was reevaluated at every step of the experiment with a corresponding EDS study.

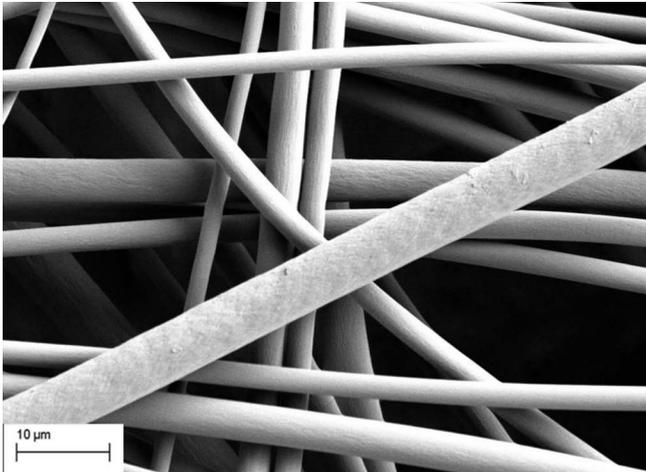


Fig. 4: Scanning electron micrograph of SiC fibers precursor spun at 7000 rpm.

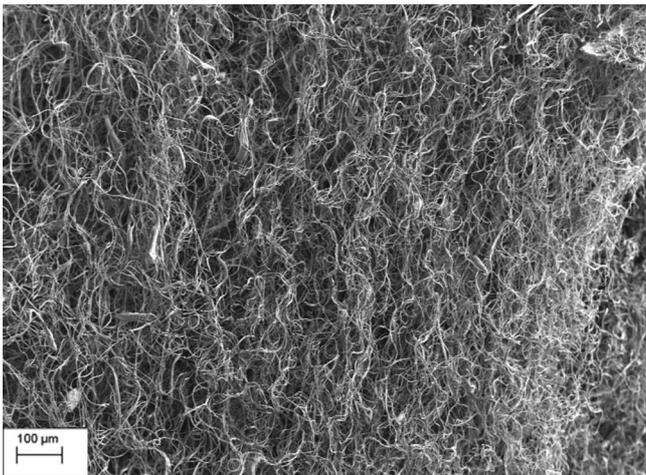


Fig. 5: Scanning electron micrograph of SiC fibers.

The first step to be evaluated was the polymer solution. A drop of the polymer solution was placed in an SEM stub and dried inside an environmental chamber overnight; Table 2 shows the EDS results where an oxygen content of 25.4 wt% is present. Results also show 3.76 wt% aluminum that corresponds to the SEM sample holder.

Table 1: Element composition of NFs sintered at 1200 °C.

Element	Sintered at 1200 °C
C	23.09
Si	42.59
O	34.31

The second step in the experiment was the development of the green SiC fibers with the FS method. Table 2 shows

the EDS results for the SiC precursor fibers. The results show that the oxygen content is 13.38 wt%. From the solution to the green SiC fiber, the oxygen content decreased by 12 wt%. This is due to evaporation of the solvent during spinning.

The final step in the experiment is the sintering process at 1200 °C. Table 2 shows the EDS results for the sintered fibers. After sintering, the percentage of oxygen was 48.58 wt%, the oxygen content in the fibers increased from 13.38 wt% to 48.58 wt%, an increment of 35.2 wt%. Carbon powder was then used to cover the SiC precursor fibers before and during sintering to prevent fiber oxidation. Table 2 shows the results obtained from the EDS. The oxygen content decreased from 48.58 wt% to 4.33 wt%.

Different sintering temperatures (1100 °C, 1200 °C, 1300 °C, 1400 °C, and 1500 °C) were studied to observe the change from an amorphous to a crystalline nanofiber. Fig. 6, shows the XRD results of the five different sintering temperatures. It can be observed that the crystallinity increased as the sintering temperature was increased. TGA analysis was performed on the SiC nanofibers before and after heat treatment. The temperature range for this instrument is limited to 1200 °C. Fig. 7 confirms stability of the sintered fibers after heat treatment. Table 3 shows the EDS results from the five different sintering temperatures. It can be observed that as temperature increased the wt% oxygen decreased.

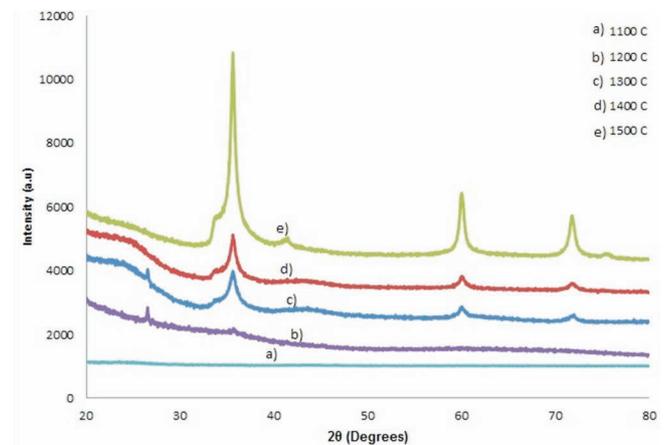


Fig. 6: XRD spectra of SiC fibers sintered at various temperatures.

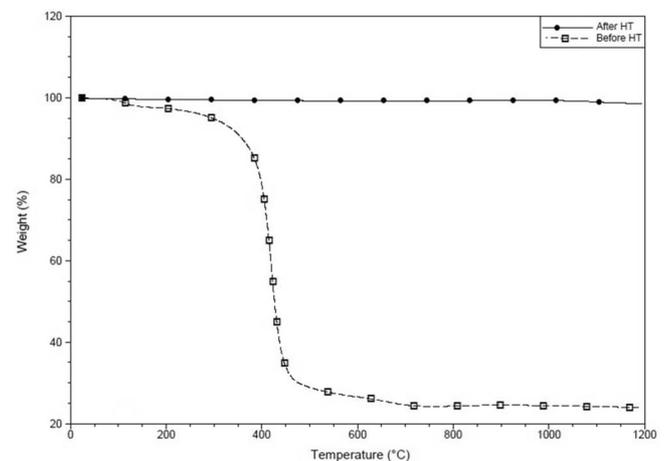


Fig. 7: TGA of SiC NFs before and after sintering (1200 °C). Test was conducted under nitrogen environment.

Table 2: Element composition of solution, NF precursor, NFs sintered at 1200 °C, and NFs sintered in the presence of carbon powder at 1200 °C.

Element	Solution	NF Precursor	Sintered at 1200 °C	Sintered with carbon powder at 1200 °C
C	70.84	68.99	1.46	54.48
Si	0	17.63	48.58	41.39
O	25.4	13.38	49.96	4.33
Al	3.76	0	0	0

Table 3: Elemental composition after sintering at 1100 °C, 1200 °C, 1300 °C, 1400 °C, and 1500 °C with carbon powder.

Element	Sintering Temperature				
	1100 °C	1200 °C	1300 °C	1400 °C	1500 °C
Si	27.09	41.19	37.46	35.85	51.48
C	57.72	54.48	59.08	62.59	48.52
O	15.19	4.33	3.46	1.56	0

IV. Conclusions

We have successfully synthesized non-woven continuous β -SiC nanofibers with average diameter of 677 nm. The Forcespinning[®] technology was utilized to develop small-diameter, semi-continuous, bead-free SiC fibers. The precursor SiC nanofibers were developed from a polymeric solution consisting of a blend of PS/PCmS dissolved in toluene. The developed nonwoven nanofiber mats were then sintered and β -SiC fibers with an oxygen content of < 5 wt% were obtained. Crystallinity was observed to increase as sintering temperature increased.

Acknowledgment

The authors gratefully acknowledge financial support received from the National Science Foundation under DMR grant No. 1523577 (PREM- UTRGV-UMN Partnership for Fostering Innovation by Bridging Excellence in Research and Student Success). We are also grateful to the Biology Department at the University of Texas Rio Grande Valley for allowing use of the EDS instrument.

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