

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Service Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.					
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 11/16/2004-05/15/2008	
4. TITLE AND SUBTITLE Ceramic Nanofibers by Electrospinning of Precursor Polymers				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA-9550-05-1-0023	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Jeffrey P Youngblood				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Purdue University				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2016-0602	
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution Statement A: Approved for Public Release. Distribution is Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Elelctrospinning of preceramic polymers offers the ability to produce oxide and non-oxide ceramic fibers with diameters several orders of magnitude smaller than those available by comercial methods enabling composite materials with new and unique properties. In this project fibers were produced at scales smaller than currently available by commercial processes. Ceramic precursor polymers were combined with polystyrene to prepare electrospun fibers that are subsequently pyrolyzed into SiC nanofibers. Sol-gel precursors were pyrolyzed into transition metal carbides and nitrides by applying the carbothermal reduction (CTR) process using pitch as a carbon source. Elelctron and X-ray diffractions, electron microscopy, and electron energy loss spectroscopy show crystalline fibers were produced with average diameters as small as 50nm. A variety of carbide and nitride nanofibers were produced based on silicon, titinium, zirconium, hafnium, vanadium, niobium, and tantalum. The CTR process was expanded to examine a wide range of metal-oxide powders to aid in predicting success or failure of more expensive sol-gel materials and pitch was found to be a better carbon source for CTR than graphite or amorphous carbon.					
15. SUBJECT TERMS Ceramic Nanofibers					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Jeffrey P. Youngblood
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) 765-496-2294

CERAMIC NANOFIBERS BY ELECTROSPINNING OF PRECURSOR POLYMERS

AFOSR # FA9550-05-1-0023

Jeffrey P. Youngblood
School of Materials Engineering
Purdue University

Executive Summary

Electrospinning of preceramic polymers offers the ability to produce oxide and non-oxide ceramic fibers with diameters several orders of magnitude smaller than those available by commercial methods enabling composite materials with new and unique properties. In this project fibers were produced at scales smaller than currently available by commercial processes. Ceramic precursor polymers were combined with polystyrene to prepare electrospun fibers that are subsequently pyrolyzed into SiC nanofibers. Sol-gel precursors were pyrolyzed into transition metal carbides and nitrides by applying the carbothermal reduction (CTR) process using pitch as a carbon source. Electron and X-ray diffractions, electron microscopy, and electron energy loss spectroscopy show crystalline fibers were produced with average diameters as small as 50 nm. A variety of carbide and nitride nanofibers were produced based on silicon, titanium, zirconium, hafnium, vanadium, niobium, and tantalum. The CTR process was expanded to examine a wide range of metal-oxide powders to aid in predicting success or failure of more expensive sol-gel materials and pitch was found to be a better carbon source for CTR than graphite or amorphous carbon. This project resulted in 1 PhD dissertation, 9 technical presentations, 2 publications currently in submission (1 planned), 1 interaction leading to a funded proposal, and 1 travel award to present the results of this work.

Research Objective

The goal of this AFOSR sponsored project is to produce high quality non-oxide ceramic nanofibers by electrospinning ceramic precursors. The technical objectives are: 1) produce silicon carbide fibers by a new process involving electrospinning of polymer preceramics with subsequent thermalization to ceramic, 2) investigate factors involved in these electrospinning systems so as to attain control over the process, 3) reduce the size of these fibers to the ultimate limit allowable, with 50nm being our specific goal, 4) characterize and quantify the resultant ceramics for ceramic content, graphite content, oxygen content, crystallinity (SiC), and density, and 5) improve ceramic density and purity to the limit allowable to obtain the best possible properties.

We report here on the production of carbide and nitride ceramic fibers at scales smaller than currently available by commercial processes. Ceramic precursors are combined with polystyrene (PS) to prepare electrospun fibers that are thermally processed into ceramic fibers. With these methods a variety of carbides and nitrides of silicon, titanium, zirconium, hafnium, niobium, tantalum, and vanadium were created.

Status of Effort

Highlights of the project were:

1. Optimized processes for electrospinning of preceramic polymers such that we produced SiC fibers with an average diameter as low as 50 nm – 2 ½ orders of magnitude smaller than commercially available. This satisfies Objectives 1-3.
2. Performed optimization of the materials and characterization of the fibers confirming that they are polycrystalline beta-phase SiC with nanoscale unoriented phases. Orientation and phase

does not change with size of the fibers. We also found that a silicon native oxide layer varies from 15-50 nm on the surface of the fibers and is dependant on the pyrolysis conditions. This satisfies Objectives 4 and 5 (and, therefore, all objectives of the project).

3. Developed a general method to metal nitride and carbide nanofibers based on in situ carbothermal reduction of electrospun sol-gel oxide/pitch blend fibers. A variety of materials were studied such as carbides and nitrides of titanium, zirconium, hafnium, niobium, tantalum, and vanadium.
4. Performed an exploration of carbothermal reduction using pitch as a carbon source on metal oxide powders as a less expensive alternative to sol-gel materials to elucidate the utility of the process across materials types. We found that in most instances pitch is a superior carbon source to graphite and both were always superior to amorphous carbon.
5. A new method for the near net-shape production of metal carbide monoliths by using metal powders and mesophase pitch as a reactive binder and carbon source was developed.
6. Performed preliminary work on the production of nanofibers of electroactive materials such as superconducting YBCO and semi-conducting Ge, InN, and CdS.

RESULTS

Ceramic Nanofibers by Electrospinning of Precursor Polymers. The production of SiC fibers was established with polycarbomethyl silane (PCmS) as the precursor because it can easily be formed into silicon carbide. It was dissolved with polystyrene (PS) into toluene with added tetrabutyl ammonium bromide (TBAB). PS has a dual role in fiber formation. The addition of high molecular weight PS (2,000,000 g/mol) to the short chain precursor polymers increases the viscosity of the solution providing for lower overall polymer loading and smaller fibers. Prior to ceramization, the as-spun fibers are susceptible to flow during pyrolysis. A cure step is performed on the as-spun fibers to “set” the PS, providing for infusible fibers for pyrolysis. The fibers are placed under a shortwave UV lamp for 24 hours until the PS crosslinks. During subsequent pyrolysis, the PS is degraded and volatilized leaving only ceramic behind. A benefit of UV-curing over thermal oxidative crosslinking is the low amount of oxygen incorporation into the ceramic material during the cure. The incorporation of a second polymer into the solution reduces the solvent design space such that typical polar solvents amenable to electrospinning are unavailable. An alternate choice is a non-polar solvent with added soluble salt to provide the polarity needed for charge conduction. Toluene with 5% w/w TBAB was chosen as this provides for the most uniform fibers.

Electrospun polymer fibers are typically a mass of randomly oriented fibers with several branches and overlap points, although oriented fibers are possible. **Figure 1** shows SiC nanofibers at different magnifications in optical photography (1a) and field emission scanning electron microscopy (FE-SEM) (1b and 1c). As shown, bulk electrospun SiC nanofibers synthesis is possible (1a). FE-SEM and transmission electron microscopy (TEM) (**Figure 2**) determined average fiber diameters can be obtained as low as 50 nm with selected fibers down to 20 nm. TEM (**Figure 2**) and FESEM demonstrate that in most cases the fibers the fibers are long, smooth, and kink-free with internal structure.

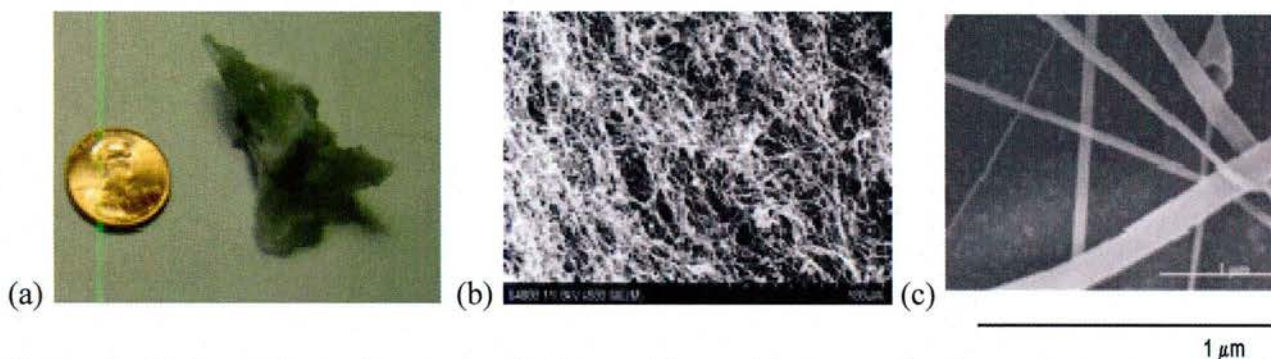


Figure 1. Different size scale images of SiC nanofibers: (a) macroscale picture showing a mass of fibers, (b) field emission scanning electron micrograph of random mat of SiC fibers, and (c) FE-SEM showing fiber diameters of 50 nm to 200 nm.

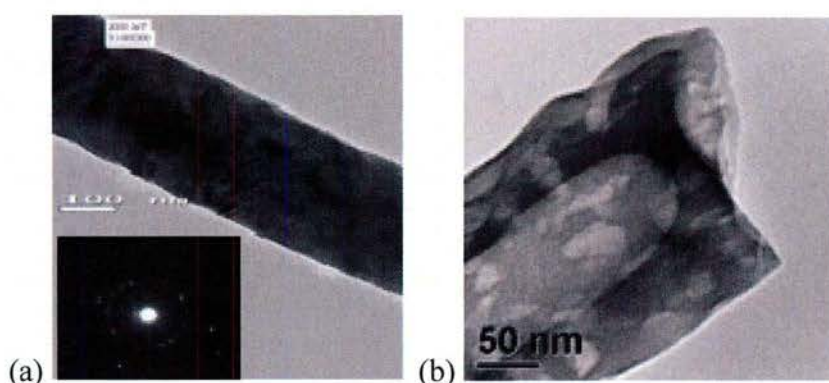


Figure 2. TEM images of polycarbomethyl silane co-spun with polystyrene after eight hour pyrolysis, showing (a) structure of fiber and electron diffraction of a SiC fiber and (b) an internal fiber diameter of 70 nm with a 50 nm silica shell.

Transmission electron microscopy (TEM) of the fibers reinforces the diameter measurements from the FESEM, as shown in **Figure 2**. There is little evidence for large-scale voiding in the fibers, however, structure is apparent. The lack of voids can be attributed to the low percentage of PS in the electrospinning solution. While it is possible that the fine structure is carbon inclusions and/or grains, measurements do not allow determination of the fine structure. Also apparent are line-like structures at an angle to the fiber in the center of the fiber near the bottom edge that resemble shear bands. Twinning is ruled out as the cause of these structures due to a nanocrystalline grain morphology being smaller than the lines and angles not corresponding to published twin angles of SiC.

X-ray diffraction (XRD) spectra of the fibers show broad peaks that are indicative of SiC, and does not show a peak indicative of graphite or non-graphitic carbon at 26.6° . The lack of sharp peaks makes it difficult to verify the phase and polytype or polytypes of SiC and is due to the nanocrystallinity of the SiC fibers. The nanocrystallinity is not surprising due to the size scale of those fibers as the crystallites must be the same or smaller than the fibers. Electron diffraction was performed and confirms the presence of both crystalline silicon carbide and crystalline silica and shows that the fibers are polycrystalline. Once again the XRD spectra do not show the presence of graphitic carbon in the nanofibers although amorphous carbon may be present.

Silicon carbide is especially difficult to determine the polytype because there are some angles where up to five polytypes share a peak. The peaks and rings are most closely associated with α -SiC, 4H polytype as verified by the d-spacing given in JCPDS files. Due to the similarities in polytypes, it is possible that multiple polytypes may be represented by some of the fainter peaks. The polymeric precursor used here, PCmS, is used in the production of NicalonTM fibers. Studies conducted on NicalonTM fibers show that the grains are β -phase SiC, 3C polytype.

As determined by XRD, the material resulting from the preceramic solution, that was not electrospun, was α -phase SiC, 15R polytype. Also, the peaks were sharp and distinguishable, compared to peaks from fibers and must therefore have much larger crystallites than in the fibers. The results of this experiment are just as surprising as that of the fibers. It is possible that the electrospinning process, the thermal processing or the PS/PCmS system that was used changes the polytype from the expected 3C of the commercial fibers. However, the differences in polytype between electrospun nanofibers and bulk material show that there are effects due to the electrospinning process or the nanofiber morphology that can affect polytype. In all cases, electron diffraction (ED) was used to confirm the results.

Further inspection of pyrolyzed fibers in the TEM shows that there is a core-shell structure on the fibers, as seen in **Figure 2**. An oxide shell is known to grow on all silicon carbide fibers due to various sources of oxygen such as the room atmosphere, furnace atmosphere, and impurities in the furnace tube. **Figure 2** shows the core-shell structure of the electrospun silicon carbide fibers. These fibers were shown to be silica and SiC by electron diffraction and it is expected that the outer layer is silica. While great care was taken to remove oxygen from the furnace system, even the smallest amount of oxygen would contribute to the formation of a crystalline silica shell. This behavior was not unexpected due to the fast diffusion of oxygen at the nano scale. In the case of the process here, our fibers had oxide layers with the thinnest attained being 30 nm. By comparison, commercial SiC nanoparticles have a native oxide layer of at least 100 nm. Thus, there is a lower limit to the fiber diameters produced by this process because of the native oxide layer that forms during processing. If the fiber diameters are smaller than 30 nm, it is likely that the fiber will consist of entirely "shell" with no core. The thickness of the native oxide shell is process parameter dependant and can be adjusted to control the growth of such oxide as presented in **Figure 2**. Generally, higher temperatures and/or longer temperature treatments result in thicker oxide layers. In **Figure 2**, the SiC core is around 50 nm in diameter and the silica shell is approximately 40 nm thick.

Transition Metal Carbides and Nitrides from Sol-gel Materials. We have developed a method to prepare arbitrary metal carbide and metal nitride nanofibers using a novel method where mesophase synthetic pitch is added to a solution of sol-gel precursor as a carbon source. After water hydrolysis to the gel phase, and an oxidative thermalization a graphite/metal oxide nanocomposite nanofibers is formed that can be pyrolyzed via carbothermal reduction by the in-situ carbon source to the metal nitride or metal carbide nanofibers.

We screened possible ceramic nanofibers formulations by pyrolyzing metal oxide powder and pitch mixtures as described in the next section. Based on these observations, we prepared nanofibers of sol-gel precursors and pitch to prepare metal carbide and metal nitride ceramic nanofibers. Specifically, the following ceramic nanofibers were prepared: titanium nitride (TiN), titanium carbide (TiC) hafnium nitride (HfN), hafnium carbide (HfC), zirconium nitride (ZrN), zirconium carbide (ZrC), tantalum nitride (TaN), tantalum carbide (TaC), niobium nitride (NbN), niobium

carbide (NbC), vanadium carbide (VN), and vanadium carbide (VC). The fibers were electrospun both with and without pitch inside the fiber and were pyrolyzed at various temperatures in dinitrogen, 5%hydrogen balance argon, and ammonia gases.

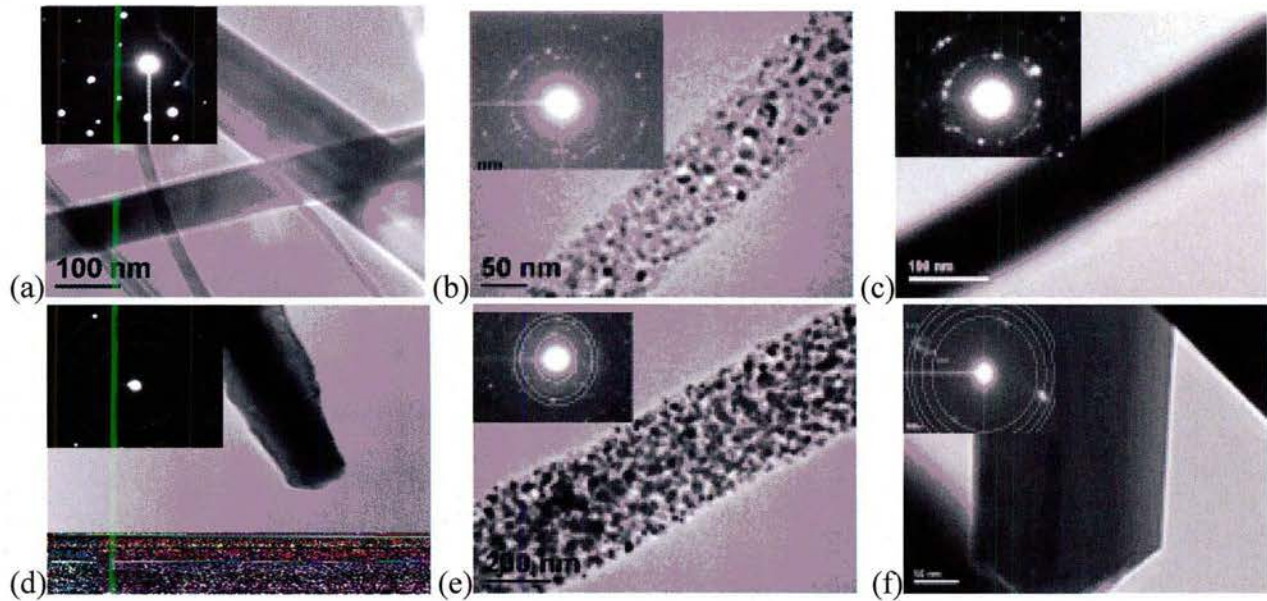
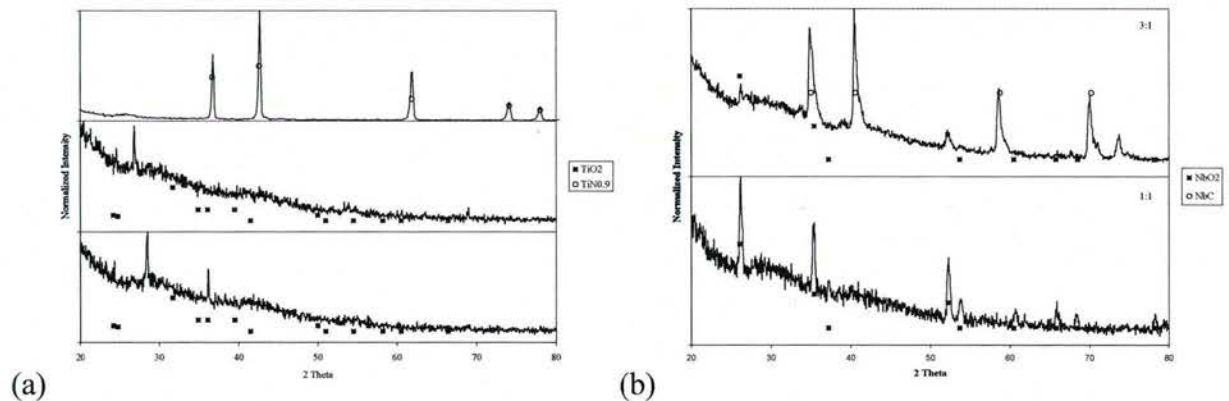


Figure 3. TEM micrographs of selected materials: (a) Titanium nitride, (b) niobium carbide, (c) zirconium nitride (d) tantalum carbide, (e) vanadium nitride, and (f) niobium nitride nanofibers produced from sol-gel precursor materials.

The fibers produced were in almost all cases smooth and most were straight, cylindrical, and free of beads. The TEM micrographs in **Figure 3** show various fibers produced from the in-situ pitch carbothermal reduction of sol-gel nanofibers method. They are crystalline in nature as shown by selected area electron diffraction (SAED) and confirmed by XRD. The granules are nanocrystalline domains as evidenced by spots both lighter and darker than the background electron density.



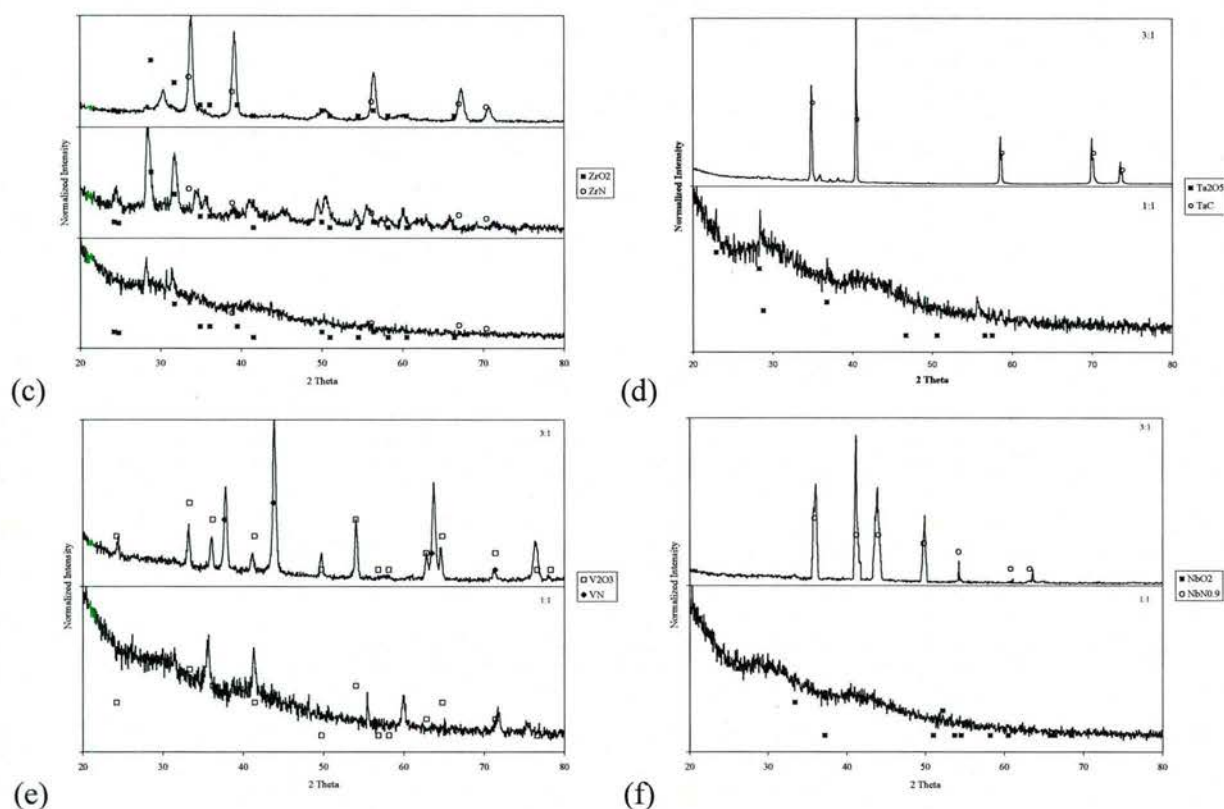


Figure 4. X-ray diffraction of selected fibers (above) for both 3:1 (top graph) and 1:1 (bottom graph) pitch loading: (a) Titanium nitride, (b) niobium carbide, (c) zirconium nitride (d) tantalum carbide, (e) vanadium nitride, and (f) niobium nitride nanofibers.

The CTR of metal oxide powder experiments demonstrated that CTR was much less likely to occur at 900°C than at 1500°C, so the sol-gel experiments were only pyrolyzed at 1500°C. This decision, combining with the knowledge that the smallest fiber were produced in our system when electrospun at 40 kV with a PP tip on the solution reservoir, allowed for more flexibility in the formulation of the solutions used in the electrospinning process. It was shown that there was no conversion from metal oxide in the fibers produced without pitch or with a 1:1 pitch to sol-gel ratio. However, it was also shown that there was conversion in all the gases tested for all solutions prepared with a 3:1 pitch to sol-gel ratio.

The granular structure shown in many of the fibers is not uncommon in electrospun sol-gel fibers. Several research groups have reported on the production of nanoscale oxide fibers with the same granular structure as seen in **Figure 4**. The reason is unclear for the morphological differences between the granular and smooth fibers, however, one hypothesis is that the volumetric change between carbide, oxide, and nitride account for the morphology differences after pyrolysis. The fibers produced were in almost all cases were straight, cylindrical, and free of beads. The TEM micrographs show that nearly every single one of the solutions was able to produce fibers that were in the nanoscale (< 100nm diameter). However, each individual material solution electrospin conditions were not optimized so that there is a large dispersion of size-scales. Also, the sol-gel based solutions were especially susceptible to a range of sizes because the solutions were mixed quickly to prevent the sol from gelling before electrospinning. There were fibers produced that were smaller than the fibers presented in the images, and there were fibers produced at sizes up to

one micrometer in diameter. Overall, the micrographs do show, however, that production of ceramic nanofibers by this method is possible.

Fibers did always achieve 100% conversion as evidenced by the oxide present in some XRD spectra. Some materials such as titanium, tantalum and niobium always showed total conversion to non-oxide ceramic. Others, such as vanadium were problematic in that it was difficult to attain total conversion. This may be due to relative reactivities and/or a lack of optimization in carbon content. For convenience we chose to perform the experiments at 1:1 and 3:1 weight ratios of pitch to sol-gel precursor. Due to relative densities and reactivities, this is likely not optimal for all conversions. However, pyrolysis in ammonia produced 100% conversion from metal oxide fibers to metal nitride fibers. This development was interesting because in the experiments with the metal oxide powders, the experiments were not 100% successful in converting metal oxides to metal nitrides, some of the oxides still converted to metal carbides. The most likely explanation for the conversion in the fibers that did not occur in the powders was the shorter diffusion lengths needed due to the nanoscale of the fibers and the intimate contact between the sol-gel material and the pitch that were dissolved in the electrospinning solutions.

Table I shows a summary of the in-situ pitch carbothermal reduction of sol-gel nanofibers results of the six metal oxide precursors investigated. A breakdown is given as to whether the metal oxide fiber produced carbide or nitride ceramic in the process gas given at 1500 °C.

Table I. Summary of In-Situ Carbothermal Reduction of Sol-Gel Metal Oxide Nanofibers.

Gas	Sol-gel					
	Hafnium	Niobium	Tantalum	Titanium	Vanadium	Zirconium
Ar/H ₂	C	C	C	C	C	C
N ₂	C	C	C	N	N	N
NH ₃	N	N	N	N	N	N

Carbothermal Reduction of Metal-Oxide Powders. Due to the expense of the sol-gel materials used to create nanofibers, an alternative method of testing carbothermal reduction techniques was developed using relatively inexpensive metal-oxides combined with the pitch used in the fiber experiments. Identical thermal processing was employed to transform the metal oxides to metal carbides and nitrides, utilizing different process gases to screen possible non-oxide ceramic production with pitch and lower the design space for the nanofibers production in a cost-efficient manner.

In this study, a variety of metal oxides were heated at various temperatures in 5% hydrogen in argon and the results compared to find which carbon source is superior. As the pyrolysis gas influences the final product of the carbothermal reduction, nitrogen and ammonia gases were explored as nitrogen sources to perform the study on nitride ceramic formation. Each of the thirteen metal-oxides that were used in the experiments were pyrolyzed at 900°C, 1100°C, 1300°C, and 1500°C in each of the process gases: dinitrogen, ammonia, and 5% hydrogen balance argon. The metal-oxides were combined with either graphite, synthetic pitch, or no carbon sources in each of the experiments. In most cases, comparing the results between the pitch experiments and the graphite experiments shows that there were not many differences. In the experiments under flowing 5 wt. % hydrogen balance argon, all of the tests with pitch had equal or more complete transformation to

metal carbide as the graphite tests. In the experiments carried out under flowing nitrogen and ammonia, there was more conversion to ceramic phases as well as more instances of conversion to metal nitrides (as opposed to carbides or metal) when pitch was present than when graphite was present. In certain extreme cases, conversion of oxide was apparent with synthetic pitch where none was shown in graphite: magnesium oxide and silicon oxide showing conversion to carbides in 5% hydrogen in argon, manganese oxide showing conversion to carbide in nitrogen, magnesium oxide showing conversion to mixed carbide/nitride in nitrogen, silicon oxide showing conversion to carbide in ammonia, and zirconium oxide showing conversion to nitride in ammonia. Additionally, for 5% hydrogen in argon, nitrogen, and ammonia experiments, general results indicate that the onset of conversion in carbothermal reduction occurs at a lower temperature when synthetic pitch is the carbon source than with graphite. Synthetic pitch has shown itself to be more reactive in reductive processes, and these results were summarized in **Table II**.

Table II. Summary of Carbothermal Reduction and Nitridation Experiments.

Gas	Carbon Source	Metal oxide powders								
		Co ₃ O ₄	Fe ₂ O ₃	ZrO ₂	SiO ₂	V ₂ O ₅	Ta ₂ O ₅	WO ₃	Cr ₂ O ₃	TiO ₂
ArH ₂	Pitch	C,M 1100	C,M 1300	-	C 1500	C 1300	C 1300	C 1300	C 1100	C 1300
	Graphite	C 1500	C,M 1500	-	-	C 1300	C 1300	C 1100	C,M 1300	C 1300
N ₂	Pitch	C,M 1500	C,O 900	-	C,N 1500	C 1100	C 1300	C,N 1100	C 1100	N 1300
	Graphite	C 1500	M 900	-	C 1500	C 1100	C 1300	C,N 1100	C,O,M 1300	N 1100
NH ₃	Pitch	C,N,M 1500	N 900	O,N 1500	C 1500	C,N 1100	C,N 1300	N 900	C 1100	N 1100
	Graphite	N 1500	N 1100	-	-	C,N 1100	C,N 1300	N 900	C 1100	C,N 1500

* The numbers represent the lowest temperature of conversion (°C)

O=oxide, C=carbide, and M=reduced to metal, the phases are reported for 1500°C tests

** Fe₂O₃ and V₂O₅ converted to Nitride without adding carbon to the system.

***Shaded regions are experiments where pitch performed better than graphite in onset temperature or conversion.

While synthetic pitch has proven to be a better carbon source than graphite or charcoal, the explanation for this effect is at present unknown, but one of two explanations are probable. Pitch is an organic semi-solid tar-like material that is used in the manufacture of high tensile graphitic carbon fiber. Even after air-oxidation, as used in this study, the pitch is liquid at elevated temperatures so as it begins to melt, it will obtain relatively low viscosity and flow. The low surface energy of the pitch will drive the wetting of the pitch across the relatively high energy oxide surface to create more contact area with the metal oxide powders. As the temperature is increased further, the pitch “sets” and forms a graphitic coating on the oxide. The increased contact area and intimacy over graphite particles where point contact is dominant greatly improves interfacial and gaseous diffusion of reductive species. We believe that this surface contact is the dominant mechanism for the improved ability and kinetics of synthetic pitch for carbothermal reduction over graphite. An alternate possibility is that the synthetic pitch is inherently more reactive. Synthetic pitch does have a large amount of chemical reactions occurring as it sets into a carbonaceous phase that requires significant bond breaking and bond forming. These events show that synthetic pitch is in a more reactive state and this may lead to a higher reactivity towards metal oxides. Additionally, residual aluminum chloride catalyst may increase the reactivity. In the gas phase, the carbonizing process of synthetic pitch evolves significant quantities of hydrogen, carbon monoxide, and lower alkanes such as methane. The gas evolution may also increase reduction by placing the oxides in a more reducing atmosphere. Regardless of mechanism, synthetic pitch has shown itself to be more

reactive in reductive processes and thus is useful as a soluble carbon source for electrospinning non-oxide ceramic nanofibers.

Net-Shape Processing of Ceramic Parts through In-Situ Carbothermal Reduction with Mesophase Pitch. A method for reducing the polymer content for pressureless sintering and creating near net shape parts is gel casting. In this method, a slurry made from a ceramic powder and a monomer is molded and polymerized in-situ. The crosslinked gel provides stability to the green body after removal from the mold and drying. After drying, the part can be machined to add more complexity. Gel casting is able to increase the green density of the parts but still suffers from the inherent limitations of residual porosity after binder burnout and difficulty in pressureless sintering of non-oxides.

Our work combined gel-casting of sol-gel precursors and in-situ carbothermal reduction to convert complex shaped precursors directly to metal carbide or nitride parts. This method allows for polymer processing techniques, such as injection molding, to form green bodies, thus lowering costs. In our process, a mixture of polymer, pitch, and oxide precursor (no water) were die-cast with the polymer providing cohesion of the green-body. Exposing the molded part to humidified air caused the precursor to form a gel within the part. The part was then heat treated by the same process as the nanofibers.

We have used the proposed methods to prepare shaped parts of TiN by the in-situ carbothermal reduction/nitridation of TiO₂ gel. Titanium n-butoxide sol-gel precursor was dissolved along with mesophase pitch in a common solvent and were cast into molds. After curing, the moldings were fired at 1500°C in nitrogen to form the ceramic parts. We have also found that TiN can be formed by the sol-gel/pitch process at temperatures as low as 900°C. Additionally, we have shown that in-situ sol-gel carbothermal reduction with pitch can be used to form ZrN, Al₃N₄, HfC, TaC and NbC with > 95% yield at 1500°C, although lower temperatures may be achievable.

Electrospinning of Electroactive Fibers. Another avenue being explored is the possibility of producing semiconducting nanofibers and this has been demonstrated by the production of germanium based nanofibers. Other semiconducting nanofibers are envisioned by combining sol-gel precursors to form semiconductors, currently in the possession of our lab, such as tetraethyl orthosilicate and tetraethoxygermane to form silicon germanide, aluminum n-butoxide and antimony n-butoxide to form aluminum antimonide, and indium methoxyethoxide and antimony n-butoxide to form indium antimonide and a variety of nitride semiconductors such as indium nitride.

Fibers with semiconductor chemistry have been produced but not tested for electronic behavior. The following fibers have been created that have the same chemistry of known semiconductor materials: germanium, silicon carbide, and titanium oxide (anatase phase).[14] However, producing fibers with chemical make-up matching known semiconductors does not mean that the fibers will be semiconductors. Producing electrospun semiconducting nanofibers would be attractive to the microelectronics industry and be used in the ever expanding world of nano-machines.

Additionally, microfibers of conducting and superconducting materials such as indium-tin oxide (ITO) and yttrium-barium-copper oxide (YBCO) have been produced by electrospinning.

Acknowledgement/Disclaimer

This work was sponsored (in part) by the Air Force Office of Scientific Research, USAF, under grant/contract number F49620-04-NA-153. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.

Personnel Supported

Katherine Frank	Undergraduate Student, Purdue University
Lachlan Badger	Undergraduate Student, Purdue University
Brian Ginn	Undergraduate Student, Purdue University
Benjamin M. Eick	Graduate Student, Purdue University
Jeffrey P. Youngblood	Professor, Purdue University

Technical Presentations and Posters

1. "Electrospinning of Carbide and Nitride Ceramic Nanofibers" Jeffrey P Youngblood, Benjamin Eick *European Ceramic Society Meeting (Berlin, Germany)* June, **2007**.
2. "Electrospinning of Non-oxide Transition Metal Nanofibers and Conducting Ceramic Nanofibers" Benjamin M. Eick, Jeffrey P. Youngblood. *American Chemical Society (Chicago, IL)* March, **2007**.
3. "Ceramic Fibers by Electrospinning of Precursor Polymers" Benjamin M. Eick, Jeffrey P Youngblood. *Air Force Office of Scientific Research Metallic and Non-metallic Materials Program Review (Washington, DC)*, November **2006**.
4. "Electrospinning of Conducting Nanofibers and Transition Metal Carbides and Nitrides" Benjamin M. Eick, Jeffrey P Youngblood. *Purdue Materials Engineering Graduate Student Poster Symposium (West Lafayette, IN)*, October, **2006**.
5. "Electrospinning Polymer Precursors to Produce Ceramic Fibers" Benjamin M. Eick, Jeffrey P. Youngblood. *Gordon Research Conference, Solid State Studies in Ceramics (Andover, NH)*, August, **2006**.
6. "Electrospinning of Ceramic Nanofibers from Pre ceramic Polymer Precursors" Benjamin M. Eick, Jeffrey P Youngblood. *Purdue Materials Engineering Graduate Student Poster Symposium (West Lafayette, IN)*, November, **2005**.
7. "Electrospinning of Ceramic Nanofibers from Pre ceramic Polymer Precursors" Benjamin M. Eick, Jeffrey P Youngblood. *The American Chemical Society, Fall Meeting (Washington, DC)*, August, **2005**.
8. "Electrospinning of Ceramic Nanofibers from Polymer Precursors" Benjamin M. Eick, Jeffrey P Youngblood. *ASM, The Materials Information Society (Indianapolis, IN)*, March, **2005**.
9. "Advanced Materials from Rational Design" Jeffrey P Youngblood, John Howarter, Benjamin M. Eick, Philippe H. Sellenet, Bruce M. Applegate, Thomas Webster. *National Institute of Standards and Technology (Gaithersburg, MD)*, April, **2005**.
9. "It Came from the Swamp" Jeffrey P Youngblood, Benjamin M. Eick, John Howarter, Philippe H. Sellenet, Bruce M. Applegate. *Louisiana State University (Baton Rouge, LA)*, October, **2004**.

Interactions/Transitions

1. Proposal funded by NSF: National Science Foundation "Design and Manufacture of Ultra-High Temperature Ceramics with Oriented Strengthening and Toughening Phases" with Rod Trice 09/07-08/10, \$287,974 (50%)

2. Awarded an National Science Foundation Travel Fellowship to present this research at the 2007 European Ceramics Society Meeting in Berlin, Germany.

Publications

1. "Carbothermal Reduction of Metal-Oxide Powders by Synthetic Pitch to Carbide and Nitride Ceramics" Benjamin M. Eick, Jeffrey P Youngblood Journal of Materials Science, *submitted*.
2. "SiC Nanofibers by Pyrolysis of Electrospun Preceramic Polymers" Benjamin M Eick, Jeffrey P Youngblood Journal of Materials Science, *submitted*.
3. "Electrospinning of Ceramic Nanofibers" Benjamin M. Eick, PhD Dissertation, Purdue University, 2008.