Ultra High Temperature (UHT) SiC Fiber (Phase I)

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PURPOSE OF PROJECT

The primary objective of this project in Phase I was to initiate innovative theoretical and experimental studies which seek to demonstrate an Ultra High Temperature (UHT) SiC (silicon carbide) fiber with high structural capability up to 3000°F. Key is the development of process approaches that, when applied to low-cost commercially available SiC-based precursor fibers in multi-fiber architectural forms, will optimize such fiber microstructural factors as fiber stoichiometry, grain size, grain aspect ratio, grain boundary chemistry, and surface roughness. These microstructural factors control fiber as-produced tensile strength and fiber creep-rupture resistance, which in turn control fiber load-carry ability at high temperatures. A second key objective of this project in Phase II will be to seek production methods for the UHT fiber that will be cost-effective when compared to the acquisition costs of current high performance SiC fibers.

BACKGROUND

As reinforcement for silicon carbide (SiC) ceramic matrix composites (CMC), continuous-length, high-performance, small-diameter (~10 μm) SiC fibers are considered enabling materials for a variety of advanced aeronautics applications where lightweight re-usable structural materials are required to operate within extreme environments at temperatures well above the upper use temperatures for metals (~2100°F). Today the first generation of SiC/SiC CMC with a temperature capability of 2200-2400°F are on the verge of being introduced into the hot-section components of commercial and military gas turbine engines. In comparison to metallic components, these CMC components will not only reduce engine weight, but also reduce component cooling air requirements. Reduction in cooling air would then have the additional engine benefits of reduced fuel burn and reduced harmful exhaust emissions. Although CMC with higher temperature capability are highly desired by NASA, the AF, and the U.S. aero-engine industry for further improving engine performance, the 2400°F upper use temperature of current CMC is limited by the temperature capability of today's best SiC fiber, the NASA-developed Sylramic-iBN fiber. Under a previous Glenn IR&D task **[1]**, a research team led by the PI demonstrated and patented (US-7687016-B1) the basic process for producing this fiber by thermally treating the commercial Sylramic fiber to improve its creep and rupture resistance. The Sylramic-iBN fiber is recognized as the world's best SiC fiber because of its excellent long-term load-carrying ability at temperatures as high as 2500°F. However, as demonstrated in a recent NASA report **[2]**, an even more advanced Ultra High Temperature (UHT) SiC fiber with structural capability up to 3000°F will be needed to enable such future NASA aeronautics applications as un-cooled gas turbine engine and re-usable hypersonic components. This advanced fiber should also be available at lower cost than the Sylramic-iBN fiber since current estimates put the acquisition cost of high-performance SiC/SiC components at from 5 to 10 times higher than similar high-performance metallic components.

The general UHT SiC fiber production approach selected for this project is innovative in multiple ways in that

- It begins with a low-cost low-grade precursor fiber and converts it by judiciously selected high-temperature chemical processes into a state-of-the-art high-performance SiC fiber with temperature and structural capability at least 300°F higher than the Sylramic-iBN fiber.
- It can be applied to precursor fibers within a variety of textile-formed architectures, which can range from continuous lengths of multi-fiber tows to the complex-shaped architectural preforms needed for reinforcement of multi-directionally stressed CMC components.
- It can be used for a wide range of commercial precursor fiber types with different additives that may provide extra beneficial properties to the final UHT fiber.
- It can be stream-lined with less process steps than currently employed for the best SiC fibers, and thus be more cost-effective.

The UHT fiber approach is also expected to produce high performance fibers with important properties other than greater temperature capability, such as, high thermal conductivity, and with surface coatings that are not only environmentally protective, but also compliant enough to provide the weak matrix bonding needed for tough CMC.

APPROACH

Polycrystalline SiC fibers are thermally stable to well over 3000°F, but under stress will rupture with time at much lower temperatures due to creep and creation of flaws as grains slide over each other. Creep and rupture resistance can be improved by increasing grain size, grain size uniformity, and viscosity of the grain boundary phases. Currently the state-of-the-art SiC fiber is the NASA-developed "Sylramic-iBN", but is limited in temperature capability to ~2500°F due to a variety of microstructural issues. Key amongst these is the fact that the iBN fiber and its precursor Sylramic fiber typically display a center core region where the SiC grains are smaller in size than the larger grains near the fiber surface, thereby creating a shell and core morphology within the fiber cross-section as shown in Fig. 1. Associated with this center core is excess carbon and a high density of small voids that remain after final processing. Since creep-resistance (and temperature capability) increases with grain size, the shell region provides the primary fiber structural capability at high temperatures. Thus as one aspect of the UHT Fiber development, process conditions will be sought that result in little if any excess creep-prone carbon or volume fraction of voids in the fiber core and a nearly uniform grain size across the fiber diameter so that the whole cross-section will be load bearing at high temperatures. Likewise another objective will be to develop process conditions that increase the average grain size without significantly debiting fiber strength since the grains are effectively flaws in the fiber. Increased grain size will not only increase fiber creep resistance, but also increase fiber thermal conductivity, which is important in reducing thermal stresses in SiC/SiC CMC components.

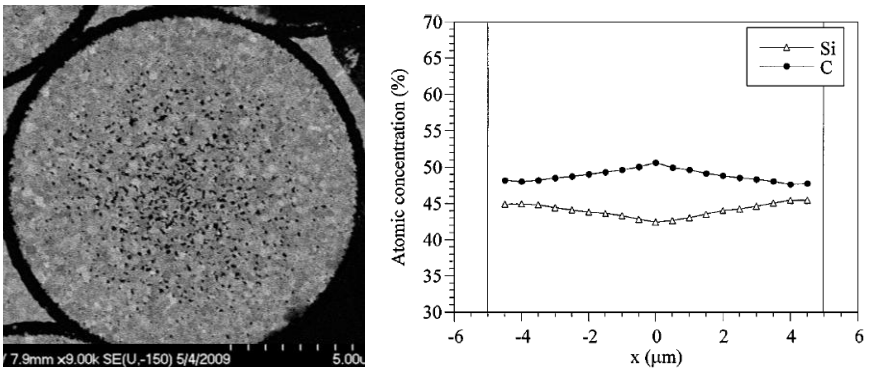


Figure 1. Sylramic-iBN SiC fiber: (a) core-shell morphology with voids and more creep-prone grains in the core, and (b) carbon-rich composition in core.

The technical approach initially selected for Phase I of this project is to follow process steps similar to those of Sylramic-iBN fiber, but apply innovative thermo-chemical treatments at various process stages that result in a UHT fiber with larger grain sizes that are more uniformly distributed in the cross-section, with reduced pores, and with higher viscosity phases in the grain boundaries. The general approach selected for the UHT fiber is shown in Fig. 2.

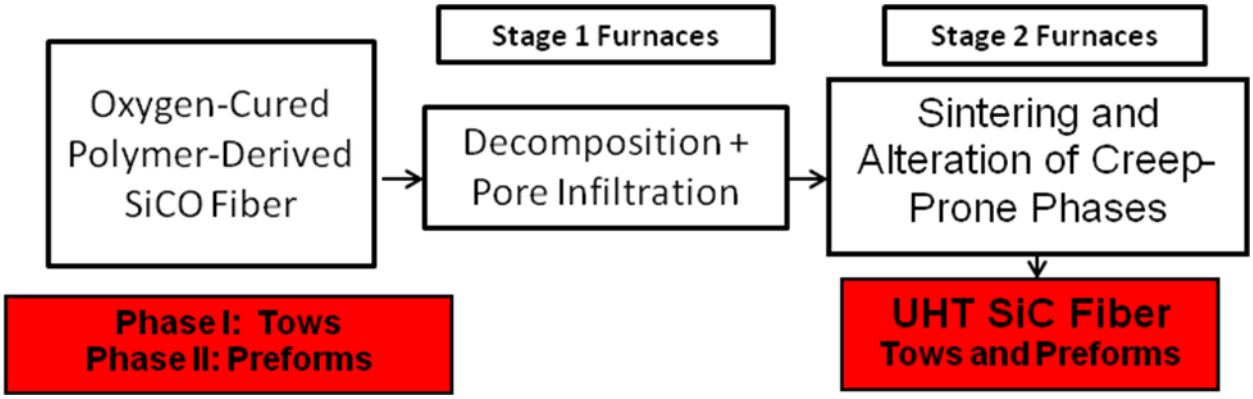


Figure 2. The general processes selected for the UHT SiC fiber.

First, oxygen- and carbon-rich polycrystalline precursor SiCO fibers in multi-fiber tow form (Phase I) or in a 3D preform (Phase II) are heat-treated in a Stage 1 furnace to allow decomposition of the oxide phases leaving pores behind. The porous fibers are then infiltrated with a specially-selected gas to form a solid phase within the fiber pores that could also act as a sintering aid. Then in a Stage 2 furnace, the fiber is heat-treated at higher temperatures where the infused phase acts to grow the fiber grains uniformly across the fiber diameter, resulting in the dense and nearly-stoichiometric SiC fiber with high temperature capability. Since the infused phase may inhibit fiber creep resistance, the fiber in the Stage 2 furnace will also be exposed to a gas that improves creep-prone phases in the fiber, thereby further increasing the fiber temperature capability. In Phase I, emphasis was placed on primarily using boron-containing gases to form boron-containing phases within the fibers. Here the objective was to follow similar steps as in the examples of the expired Dow Corning patent US5279780 in order to assure that all the GRC process facilities were performing properly for producing a high-performance SiC fiber. In Phase II, alternate gas compositions are planned that will better achieve the goal microstructure for the UHT fiber after scale-up of Stage 2 processing. A key metric for the UHT fiber is shown in Fig. 3 in that, in comparison to the iBN fiber, it should display a higher rupture strength and better time retention of this strength as measured under constant stress in air at 2550^{o}F. Actual upper use temperature for the UHT fiber would depend on the life requirements and stresses within a UHT-reinforced CMC component.

For Phase II of this project, technical efforts will also be aimed at developing and demonstrating the UHT SiC fiber in multiple 3D architectural preforms that display thermo-structural capability similar to that of the fiber. These 3D preforms will be needed as reinforcement for multi-directionally stressed components such as cooled CMC vanes and blades, but are not easily obtainable with current high-performance high-modulus SiC fibers due to their tendency to fracture when sharply bent to form the complex architecture. A final scale-up objective in Phase II will be to seek ways for streamlining the UHT processes and for making them as cost-effective as possible. Beyond the technical approaches described above, Phase II will also seek to demonstrate industry-adaptable production methods for the UHT SiC fiber both as continuous multifilament tows and as final preforms of CMC components. These efforts will involve collaboration and transfer of the developed UHT fiber technologies to select

fiber vendors and to CMC end-users to verify their enhanced performance in commercially produced SiC/SiC components that are of high interest to them, NASA, and others. For transfer of production methods for UHT fiber tows, the infusion process will be faster since we are improving the properties of an existing precursor fiber and thus the implementation will not require establishment of a new fiber production line. However, it may be more significant and more cost-effective to transfer the processes for UHT fiber preforms directly to select CMC vendors, where they perform the UHT preform conversion before infiltrating the preforms with matrix material to form the final CMC component.

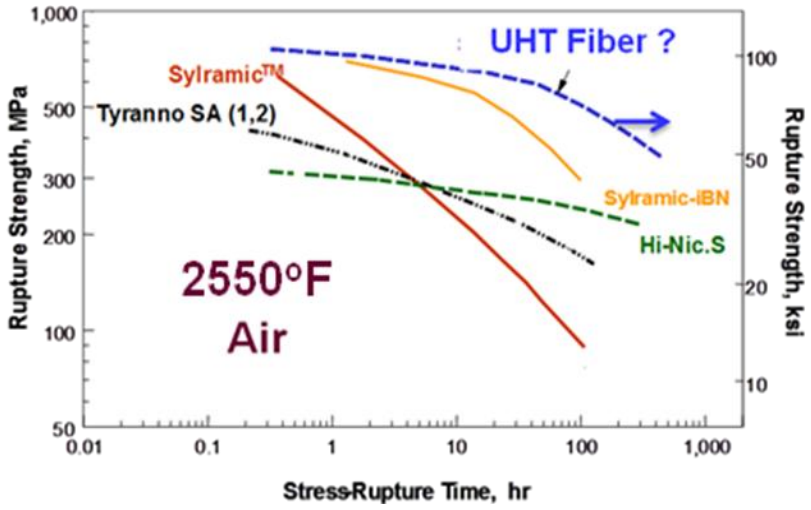


Figure 3. Metric goal for the UHT SiC fiber: better rupture strength and strength retention in air at 2550°F than the state-of-the-art Sylramic-iBN fiber.

SUMMARY OF PHASE I RESEARCH

The primary objective of the Phase I efforts was aimed at establishing facilities and characterization methods that are needed for developing and demonstrating processes for an Ultra High Temperature (UHT) SiC fiber. Although progress has been unexpectedly limited by acquisition of the required process facilities and their safety permits, significant progress toward achieving the Phase I milestones has been made as described in the following.

Milestone 1A: Down-select UHT fiber process approach

After conceiving of multiple approaches for producing the UHT fiber based on starting with low-cost commercial precursor fibers and converting them into high-temperature high-performance SiC fibers, the UHT Fiber Team down-selected the initial in-house approach as described in Fig. 2 in order to establish the required facilities and characterization methods.

Milestone 1B: Purchase precursor SiC fibers.

To initiate the Phase I work efforts, continuous lengths of one type of commercial low-cost precursor SiCO fibers were acquired from two sources: (1) recently fabricated fibers in the form of multiple spools of multi-fiber tow and a 4 m^2 piece of 2D woven fabric, and (2) long lengths of older precursor tows, which may possess slightly different quantities of chemical impurities that arise during production of this fiber type. Since impurities in the precursor fibers can adversely affect the final UHT fiber strength properties, chemical analysis has been performed at GRC to down-select fiber tows

from these initial acquisitions (see Table 1). Typically the starting C/Si atom ratio of the precursor fiber tows is ~ 1.3, but needs to be decreased to ~1.0 during processing for a high performance UHT SiC fiber. The precursor tows should also have low metallic content to avoid exaggerated grain growth during processing that will then cause fiber strength degradation. To understand the robustness of the UHT processes, other types of low-cost precursor SiC fibers will be purchased in Phase II. Once the UHT processes have been established on a down-selected precursor type, its tows will be woven into complex 3D shapes that NASA is currently considering for reinforcement of SiC/SiC vanes and blades.

Table 1. Chemical analysis of Initial Precursor Fibers

Element	Lot 1	Lot 2	Lot 3	Lot 4	Lot 5
Si, wt%	53.211	52.736	52.692	53.593	52.720
C, wt%	33.82	33.45	34.145	33.82	33.42
O, wt%	10.885	11.660	11.105	10.505	11.715
Fe, ppm	110	260	70	80	50
Ca,ppm	ND	44	ND	ND	ND
Na,ppm	ND	10	5	ND	2
Fe, ppm	110	260	70	80	50
N, wt%	0.115	0.125	0.129	0.132	0.146

ND-Not Detected

Milestone 2: Up-grade GRC fiber process and test facilities for UHT fiber.

During Phase I, extensive time was required to assemble, set up, and up-grade all the facilities and safety permits required for the UHT fiber processes. They are now all in place in two buildings at GRC and include (see Appendix A): (1) One controlled-atmosphere Stage 1 research furnace and one Stage 1 production furnace with gas composition detectors for the precursor decomposition and doping processes; (2) Three controlled-atmosphere Stage 2 furnaces (small, medium, large) that will accommodate various fiber specimens ranging from short tows to complex preforms for the sintering and boron removal processes; and (3) One Mini-hip for the larger fiber specimens where pressures much higher than one atmosphere can be applied in Stage 2. For fiber characterization and mechanical testing, GRC already has the multiple required capabilities, such as SEM, TEM, microprobe, chemical analysis, TGA, RGA, Also during Phase I, draw contracts were set up for Auger surface analysis and alternate high-pressure treatment processing at, respectively, Case Western Reserve University in Cleveland and Avure Inc. in Columbus. Rigs and methods are also available at GRC for measuring such fiber properties as Bend Strength and Bend Stress-Relaxation for short single fibers up to 3000^{o}F in argon, and Tensile Strength, Creep, and Rupture for longer single fibers, multi-fiber tows, and fabric up to 2550^{o}F in air. In Phase I, research emphasis was placed on achieving the proper fiber microstructures before mechanical testing, which will be carried out in Phase II.

Milestone 3: Deliver written technical status report 6 months after award.

A Phase I semi-annual report was submitted on January 17, 2012 to ARMD Seedling Fund.

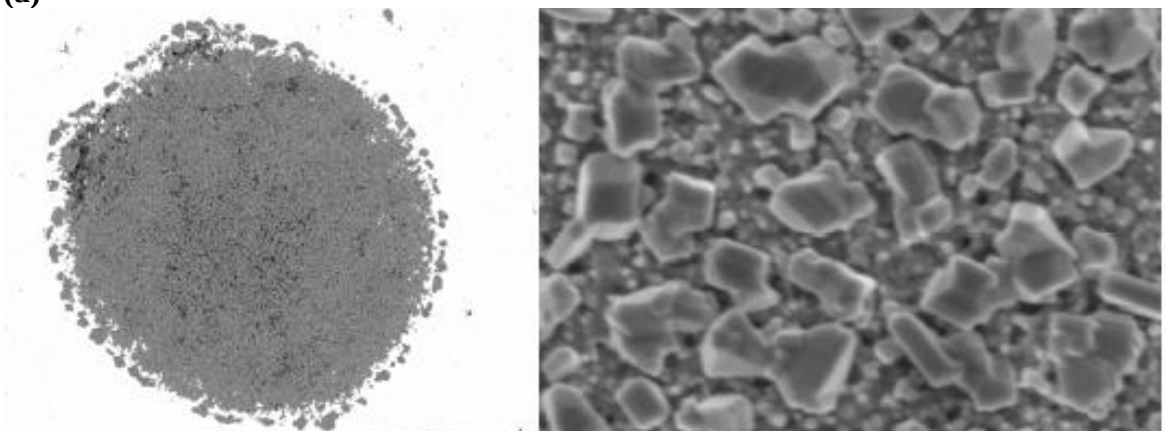
Milestone 4: Demo feasibility for UHT fibers in multi-fiber tow forms.

For convenience and better understanding of Phase I progress, this **Milestone 4** is broken down into four sub-milestones according to the two key process steps in Stage 1 and the two key process steps in Stage 2. Note that actual process conditions are not revealed because of Export Control restrictions.

<u>Milestone 4A</u>: **Down-select temperature, time, and gas conditions in Stage 1 furnace to allow oxide phase in precursor fiber tows to decompose and volatilize, leaving fine size pores and grains uniformly distributed across each fiber cross-section.**

This process step is considered the most crucial in that it sets up the fiber with the optimum chemistry and morphology for the succeeding steps. Initial decomposition studies were performed in the small Stage 1 research furnace. These were successful in understanding the basic aspects of decomposition of the precursor fiber in terms determining the optimum time, temperature, and gas conditions for complete decomposition**.** However, it was also determined that the gas flow conditions in this furnace were not completely optimum for the goal of leaving fine size pores and grains uniformly distributed in the fiber cross-section and on the surface (Fig. 4a). Nevertheless, when these studies recently shifted to the newly constructed Stage 1 production furnace where gas flow could be better controlled, excellent microstructures were produced in the fiber cross-sections and on the fiber surfaces as shown in Fig. 4b. In addition, the individual fibers in the precursor tow could be easily separated and they retained enough strength to be handle-able, even though highly porous. As such, subsequent studies in Phase I turned to primarily using the Stage 1 production furnace for UHT fiber development.

(a)



(b)

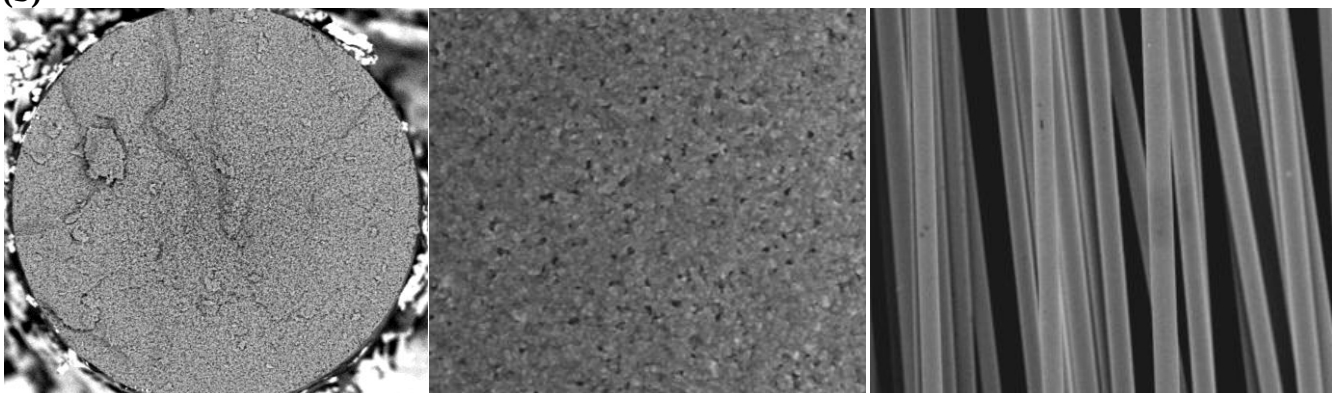


Figure 4. Precursor fiber after decomposition step in (a) **small Stage 1 research furnace** and (b) **Stage 1 production furnace**.

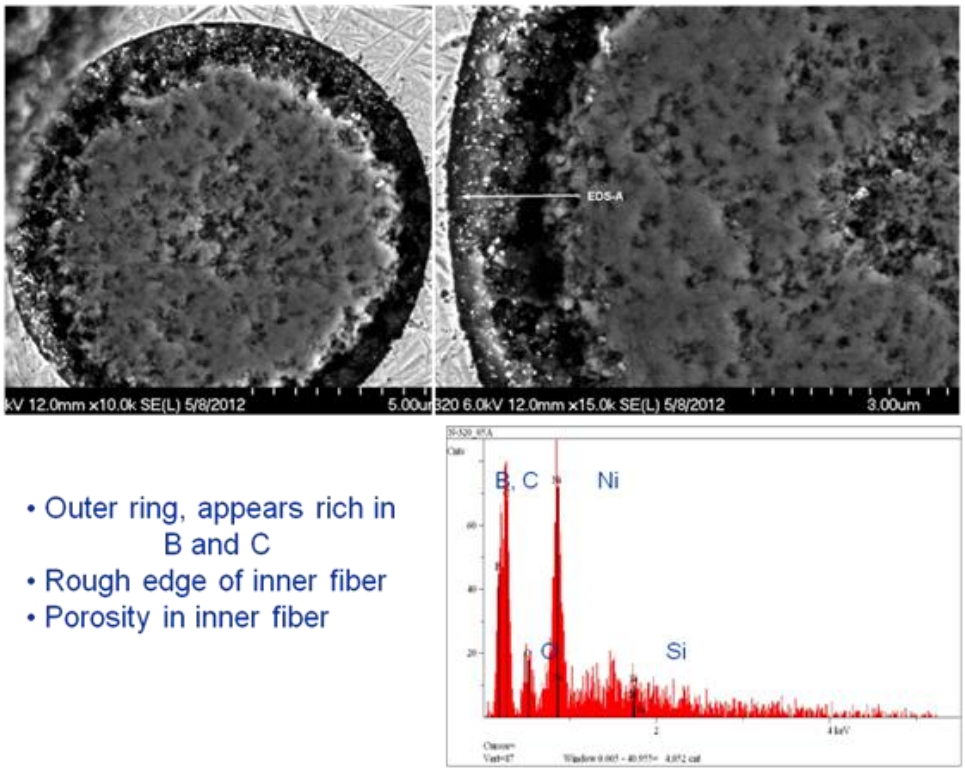


Figure 5. Typical fiber microstructure after boron infiltration in **Small Stage 1 Research Furnace**.

<u>Milestone 4B</u>: **Down-select temperature, time, and gas conditions in Stage 1 furnace to infiltrate boron into the fine pores of the precursor fiber tows, leaving a boron-containing sintering aid uniformly distributed across fiber cross-section with no carbon-rich core.**

Despite the non-optimized microstructure of the decomposed fiber (Fig.4a), initial boron infiltration studies were conducted in the small Stage 1 research furnace. As expected, a uniform boron distribution was not achieved for the fibers decomposed within this furnace, as indicated in Fig. 5. However, when the doping studies were conducted recently in the Stage 1 production furnace, excellent microstructures were obtained as well as a uniform boron distribution as shown in Fig. 6. These results have provided new insight on the proper gas conditions both for decomposition and boron doping.

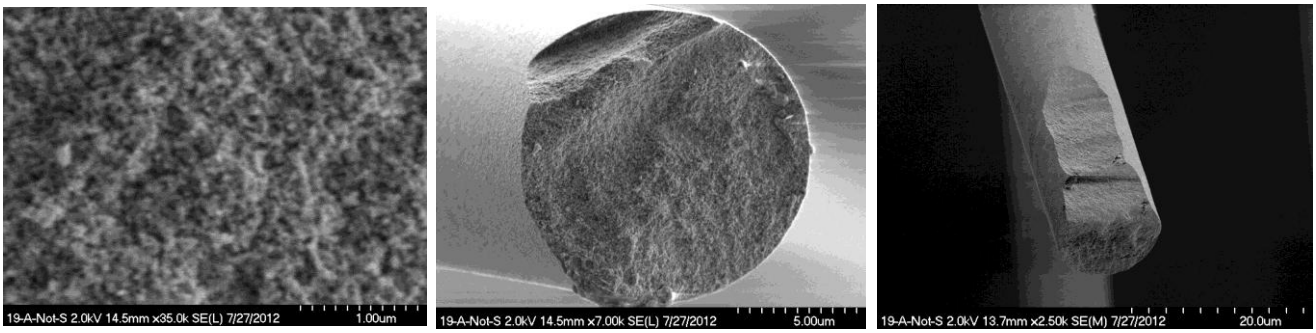


Figure 6. Typical fiber microstructures after boron infiltration in **Stage 1 Production Furnace**

<u>Milestone 4C</u>: Down-select temperature, time, and gas conditions in Stage 2 furnace to allow boron-sintering aids to remove all pores and grow grains into a uniform distribution across each precursor fiber cross-section with as large a size as possible.

A typical microstructure is shown in Fig. 7 for the Fig. 5 fibers that were infiltrated in the small Stage 1 research furnace and then sintered in the small Stage 2 sintering furnace. Despite non-uniform microstructures, good fiber densification was achieved, but with a boron-rich shell region. Studies are on-going to understand whether this result has any practical advantages.

Recently, when the precursor fibers that were decomposed and doped in the small Stage 1 production furnace and then sintered in the large Stage 2 furnace, excellent results were obtained in that the fibers were loose and handle-able, with very uniform microstructures as shown in Fig. 8. Physical and mechanical properties for these sintered fibers will be obtained in Phase II. Thus by using boron as the intial infiltrant in Phase I, this project was able to demonstrate the process capability of the Stage 1 Production Furnace as well as two of our in-house Stage 2 sintering furnaces. In Phase II, infiltrants other than boron will be employed since it is believed that the high reactivity of boron will be detrimental in the final scale-up of the UHT SiC fiber.

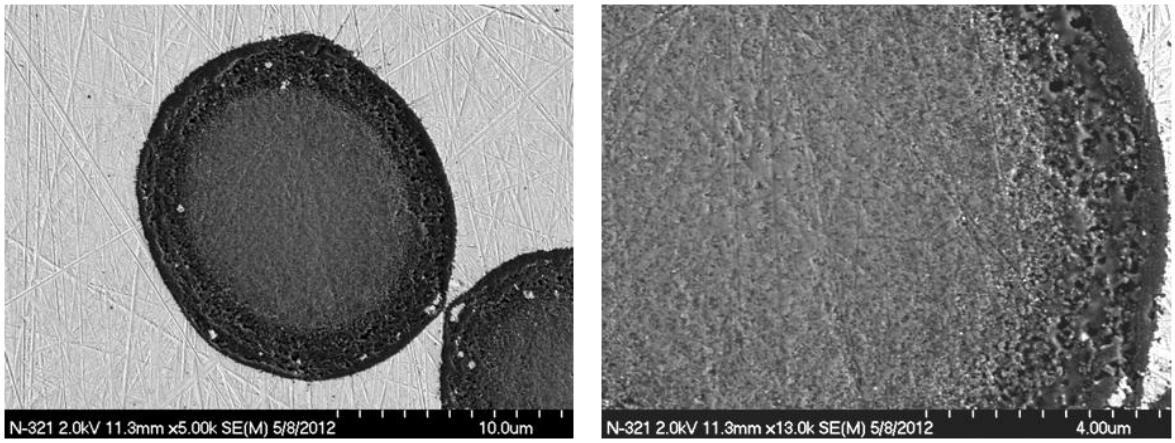


Figure 7. Typical microstructure for a sintered boron-infiltrated fiber from the **small Stage 1 research furnace** indicating that although the fiber core is dense, an outer B-rich ring remains.

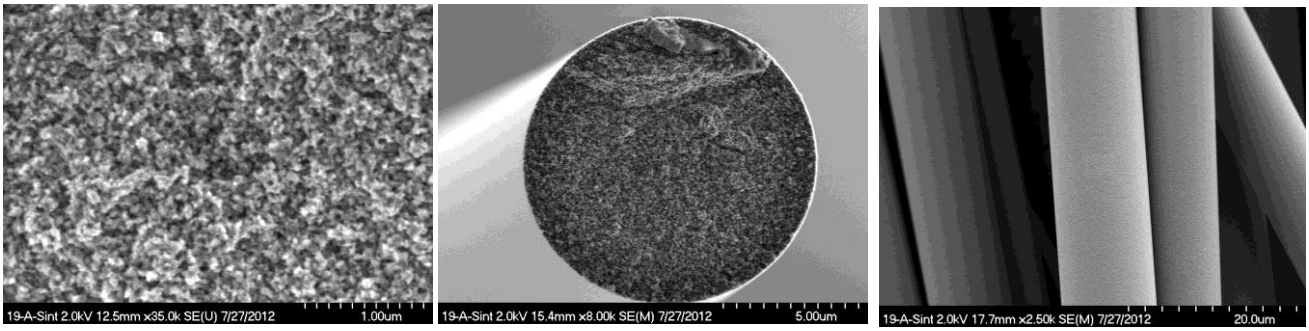


Figure 8. Typical results for a sintered boron-infiltrated fiber from the **Stage 1 production furnace** indicating excellent grain distribution in fiber and on fiber surface, plus good handle-ability.

<u>Milestone 4D</u>: Down-select temperature, time, and gas conditions in Stage 2 furnace to allow a nitrogen atmosphere to remove boron from the precursor fiber tows, infusing creep-resistant silicon-nitride into grain boundaries of each fiber, and forming a thin protective BN coating on each fiber surface.

Although this Stage 2 process step has not been utilized in Phase I, the Fiber Team has significant prior experience that this process is indeed feasible and will significantly enhance the performance of the final UHT fiber and its composites. For example, working with commercial boron-doped Sylramic fibers from Dow Corning and COIC, Figure 9 shows an Auger depth analysis of the final fiber surface after high-pressure treatment in nitrogen. Here one can see the formation of a thin environmentally protective BN layer and the infusion of nitrogen atoms into the fiber depth.

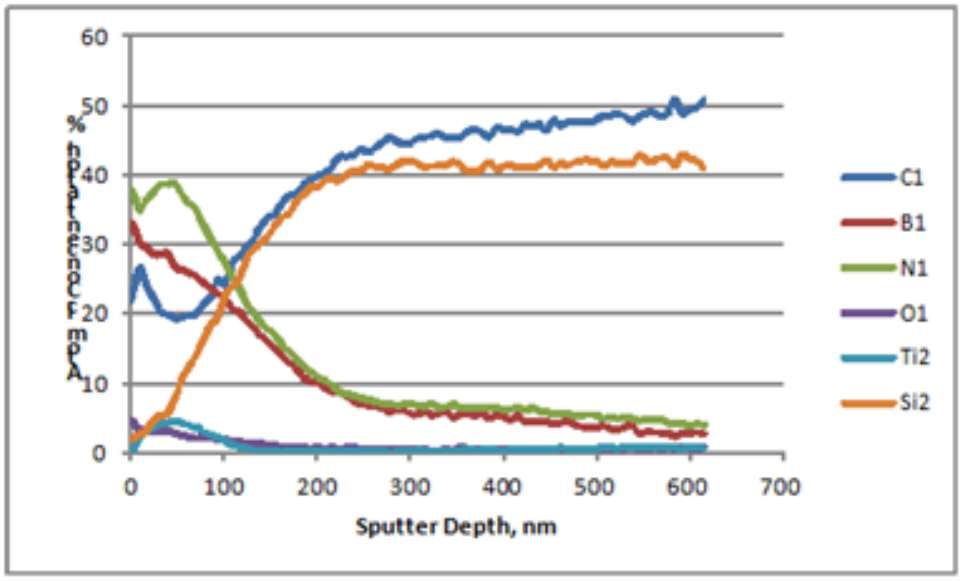


Figure 9. Auger depth analysis of a precursor Sylramic fiber showing the effects of a NASA-developed treatment in high-pressure nitrogen.

<u>Milestone 5:</u> Demo feasibility for UHT fibers in 2D fabric form

2D fabric pieces have also been subjected to the decomposition and boron doping processes within the Stage 1 production furnace. Just as shown in Fig. 5b, excellent microstructures were obtained after the decomposition and infiltration steps. In addition, although woven into a 2D fabric, the individual fibers in the precursor tows could be easily separated and they retained enough strength to be handle-able, even though highly porous. The question as to whether these tightly contacting fibers and tows will remain un-bonded during the sintering step will be answered in Phase II of this project.

ACCOMPLISHMENTS

- All the equipment and safety permits required for the initial UHT fiber processes have been assembled, set up, and up-graded, and are now in place in two GRC buildings.
- Low-cost precursor fiber was acquired in tow and fabric forms, and chemically characterized for major and impurity elements.
- Fiber microstructural characterization methods have been established and up-graded in terms of turn-around time and analysis across the fiber cross-section.
- Processing conditions were determined for achieving good precursor microstructures after decomposition, doping, and sintering

- Feasibility was demonstrated that the Stage 1 decomposition process can be successfully conducted on 2D fabric containing tightly woven precursor tows.

NEXT STEPS

- Finalize time-temperature-gas conditions in Stage 1 production furnace for pore infiltration and optimum cross-sectional microstructures.
- Optimize Stage 2 furnace conditions for fully densifying fiber and increasing its grain size and creep resistance without debiting fiber strength below ~3 GPa.
- Perform tests to demonstrate that the thermal and mechanical properties of single UHT fibers are enhanced in comparison to current SOA Sylramic-iBN SiC fibers.
- Demonstrate optimized process conditions that can be practiced on tightly contacting fibers in simple and complex-shaped 3D preforms for CMC components
- Determine feasibility of enhancing all processes in terms of increased fiber performance, streamlined process steps, and reduced process costs.
- Report all successful results to the NASA ARMD, Air Force, and other interested government agencies to determine the best path forward
- Work with outside ceramic processors to determine feasibility of technology transfer for eventual commercialization of the UHT fiber and processes.

CURRENT TRL

Innovation has moved from basic principles (TRL1) to formulated concept (TRL 2).

APPLICABLE NASA PROGRAMS/PROJECTS

In terms of NASA significance, the UHT fiber addresses aeronautics challenges within the Fundamental Aero program, such as minimally and un-cooled SiC/SiC propulsion components that will require temperatures on the order of 2700 to 3000^{o}F, and re-usable hypersonic components that will require operation near 3000^{o}F. Similar goals also exist for the new Air Force multi-million dollar program aimed at developing 2700^{o}F SiC/SiC engine materials.

PUBLICATIONS AND PATENT APPLICATIONS

If project is successful, patents applications are expected concerning the processing of SiC fibers with state-of-the-art thermal-structural capability and also concerning the low-cost processing of these fibers in the complex architectural preforms needed for aerospace components.

AWARDS & HONORS RELATED TO SEEDLING RESEARCH: To be determined

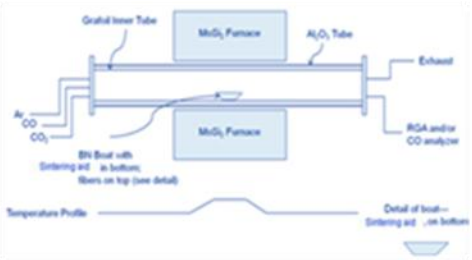
REFERENCES

1. NASA Glenn Research IR&D -FY2005 Annual Report: Improved SiC Fibers and Composites, Project Number: IRD 04-11

2. J.A. DiCarlo and R.T. Bhatt: "Modeling SiC/SiC Creep-Rupture Behavior from 2400 to 3000^{o}F", *Proceedings of the 35st Annual Conference on Ceramics, Metal & Carbon Composites, Materials and Structures*, Cape Canaveral, Florida, January 2011.

APPENDIX A: Current UHT Fiber Process Facilities established at GRC

Stage 1 Facilities for Decomposition and Boron Doping



Graphite tube inside alumina tube with BN spacers

Small Research Furnace

Small Production Furnace

Stage 2 Facilities for Sintering and Creep Modification

Small, 1 atm.

Medium,1 atm.

Large, high atm.

Large,1 atm.