Report (LEARN), Phase I

Solicitation # NNH11ZEA001N-LEARN, E.2 Leading Edge Aeronautics Research For NASA

Title: Advanced Manufacturing of Ceramic Matrix Composites (CMC) By Innovative Field Assisted Sintering Technology (FAST)

Principal Investigator: Jogender Singh / Penn State University (PSU)

Team Member: R. T. Bhatt / OAI-GRC-RXC

Technical Monitor: James DiCarlo

Period Covered: 11/15/2012-11/14/2014

Grant # NNX13AB79A

Background: Light-weight silicon carbide fiber reinforced silicon carbide ceramic matrix composites (SiC/SiC CMC) have recently gained interest for a wide range of applications, especially for extreme environmental conditions such as gas turbine engine and leading edge of hypersonic vehicles. For optimum composite performance, the matrix material should be as dense as possible with little or no porosity. Currently, the only process that can lead to very low porosity in SiC/SiC matrix is the high temperature liquid infiltration of silicon that would be converted into SiC by chemical reaction between the infiltrated molten silicon and the carbon precursor. The serious draw backs associated with this process includes poor creep resistance due to the presence of residual Si in the matrix that also limits its application to below 2400°F. So far, conventional processing techniques, such as polymer impregnation and pyrolysis (PIP) and chemical vapor infiltration (CVI) that can provide silicon-free matrices with temperature capability well above 2400°F, have failed to achieve matrix porosities below 10%. Globally, efforts are underway to combine CVI and PIP process to reduce the porosity below 10%. Dual processes, in spite of significantly raising the manufacturing cost, are not guaranteed to reduce the porosity in the resulting CMC as these porosities are not interconnected. This calls for an exploration of an alternative approach based on novel concept and technology such as Field Assisted Sintering Technology (FAST) under the LEARN Phase-I effort. The new technology must be economically viable and demonstrate high flexibility in fabrication of CMC components with superior mechanical properties.

Objective of LEARN Phase-I: The primary objectives of this research was to demonstrate fabrication of fully dense SiC- SiC composite (CMC) flat panels using slurry infiltrated nano SiC powder followed by rapid compaction and sintering via emerging Field Assisted Sintering Technique (FAST) that is expected to have lower the porosity (<5%) without sacrificing its elevated temperature properties including thermal conductivity and mechanical properties.

What is Field Assisted Sintering Technique (FAST): FAST is an emerging manufacturing technology that is capable of compacting and sintering powder materials (metal, ceramic and composite) in a very short time to near theoretical density, thereby retaining nano/submicron grained structure in the component.

The schematic diagram of a FAST system is shown in Figure 1. The powder material to be sintered is contained in the graphite die through which pressure is applied via an upper and lower punch. The continuous DC current flows through the punches, the die, and the powder housed within the die (depending on powder properties). The high density current flow through the die provides radiative heat to the powder, while current flowing through the powder causes direct resistive (Joule) heating that is instantaneous. Current that normally flows through the least resistant path upon encountering resistance leads to melting and vaporization of native oxides due to the extreme localized heating phenomenon. Combined effect of pressure, temperature, heating rate (associated with localized heating at the grain boundaries), sintering-time results in dense product with sub-grained microstructure. Benefits of FAST are illustrated in Figure 1 - inset.

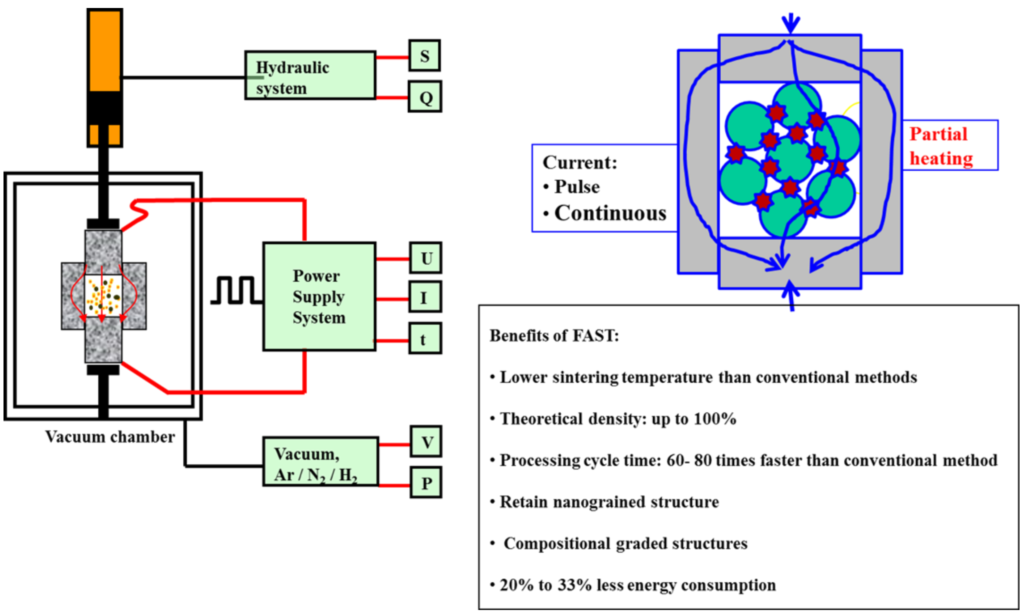

Figure 1: Schematic diagram of the FAST and its benefits

Due to the rapid heating rate (up to 500 ^{0}C/min), high temperature (up to 2400 ^{0}C), high pressure (75 MPa) and high density current (10,000 amps), particles deform and fuse together by the concurrent volumetric (Joule), and radiant heating that results in lower sintering temperature, activation energy (30-40% lower) and sintered product with near theoretical density. Since the processing cycle takes few minutes (~2-10 minutes, rather than hours in conventional method) to sinter the product with theoretical density, it is possible to retain sub grained microstructure in the sintered products that will offer superior mechanical properties under extreme operating environments. This cannot be achieved using conventional compaction and sintering methods in a cost effective manner.

Pennsylvania State University is the only academic institution in the country having two fully computer controlled FCT Systems with maximum operating chamber temperature of 2400 °C, load capacity of 25 and 250 tons and up to 10,000 amps of DC pulsed power capable of producing plates up to 16 inches in diameter and height up to 4" (Figure 2). The system has an optical pyrometer capable of precisely measuring the temperature from 400°C to 3000°C, provision for measuring the specimen linear displacement (during shrinkage), a pressure control unit and a gas flow controller. The die system is water cooled and contained in a vacuum system to eliminate oxidation and contamination. The system is capable of sintering materials in various environments that include nitrogen, argon and hydrogen.

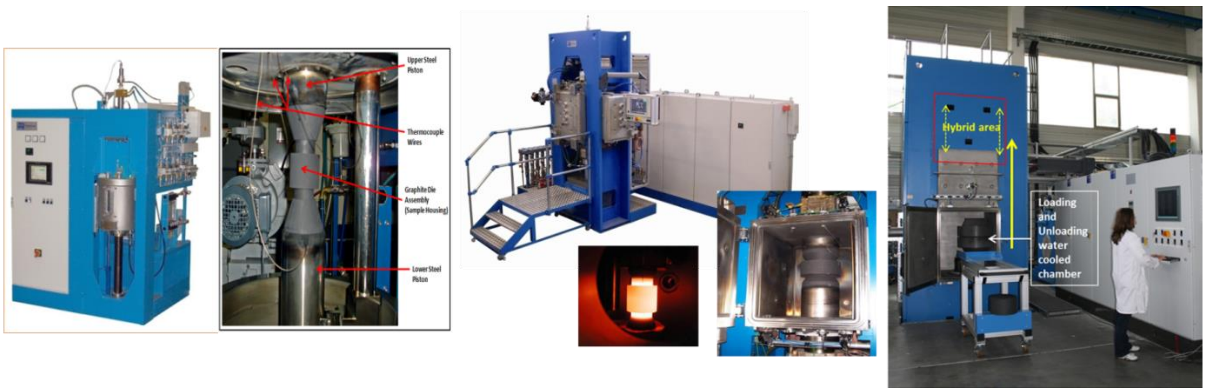

Figure 2: (a) R&D unit with 25 ton capacity, (b) 250 ton capacity, with as inset showing - sintering chamber with graphite die; (c) Hybrid unit with 400 ton capacity.

Experimental Procedure-Nanostructured Sylramic SiC fiber developed by NASA was used in the present study. Three types of sample configuration were considered for the fabrication of CMC (a) uncoated Sylramic SiC fabric; (b) graphite coated Sylramic SiC fabric and (3) modified graphite coated Sylramic SiC fabric with infiltrated nano-SiC.

To begin with, stack of Sylramic SiC fabric cloth was placed in the graphite cavity as shown in Figure 3b. Sacrificial Graphite foil liner was placed between the graphite die and the stack of Sylramic SiC fabric to minimize the chemical reactivity between the die and CMC and to prevent graphite die damage. The loaded graphite die was placed in the sintering chamber as shown in Figure 3d.

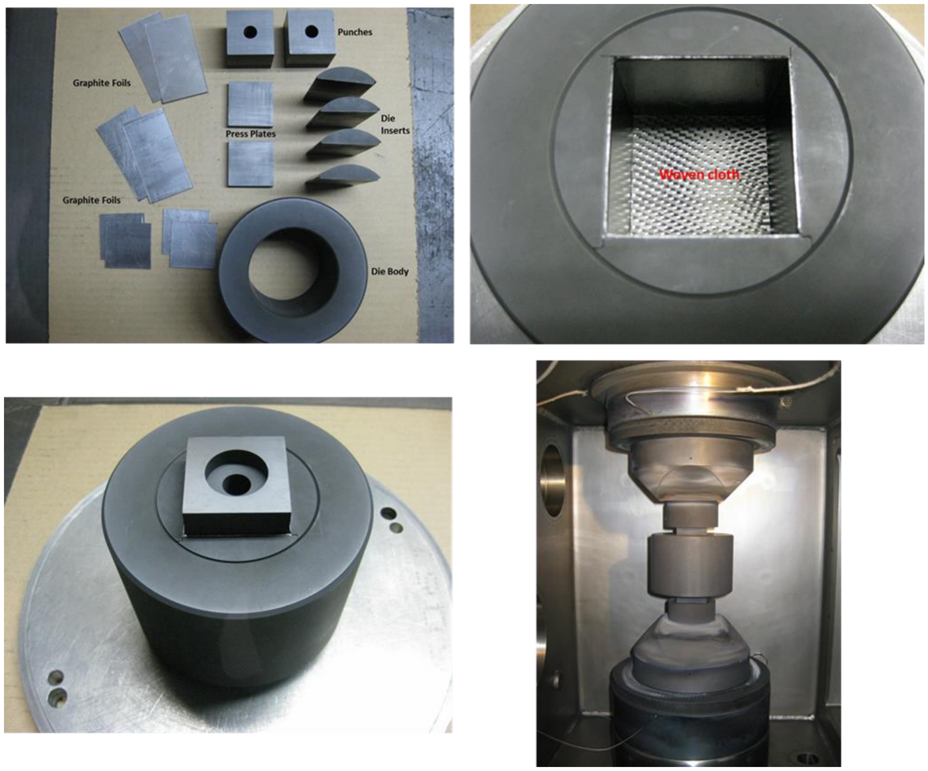

Figure 3: Assembly of graphite die used for making CMC panels (a) various pieces of graphite mold, (b) Sylramic woven fabric placed with the graphite die mold, (c) assembly of graphite mold with top and bottom press plates, die body and (d) die assembly placed within the vacuum chamber of FAST system.

Sintering was carried out in the temperature range of 1800 to 2000 ^{0}C with pressure of 50-55MPa applied for about 2-20 minutes. A typical sintering plot and the photograph of the fabricated SiC-SiC composite (CMC) coupon are shown in Figure 4.

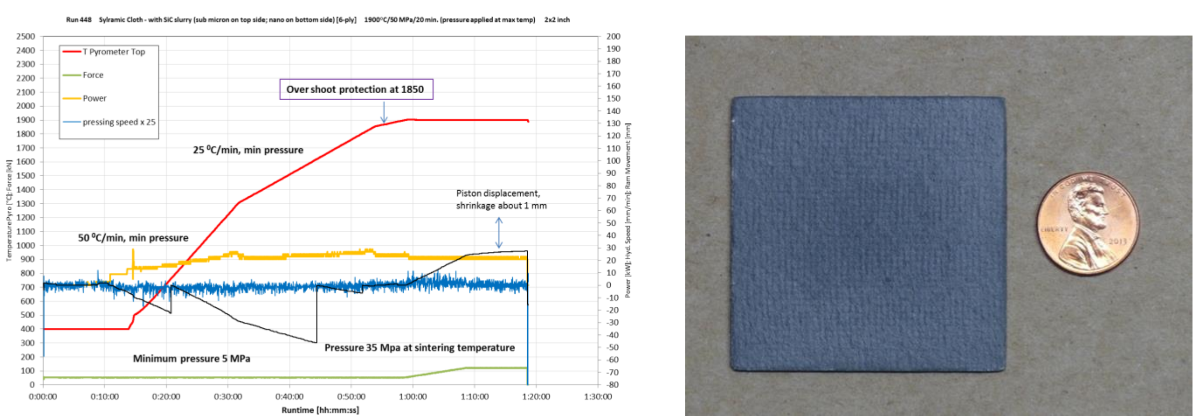

Figure 4: (a) Compaction and sintering plot of the fabrication of CMC using FAST; (b) Typical photograph of the sintered SiC-SiC composite (CMC)- after compaction and sintering.

Highlights of the LEARN Phase-I effort:

Following are the highlights of LEARN Phase-I efforts:

*Fabrication of SiC-SiC composite (CMC) coupons***:** The primary focus of this effort was to define the process window for the sintering of stacked Sylramic woven fabric without a fiber coating. It was observed that sintering of SiC fabric starts at about 1800 ^{0}C. As sintering temperature increased, density of the stacked Sylramic fabric stack also increased. At the same time, stack of fabric appeared to be fused and behaved like monolithic SiC material (Figure 5a). In order to minimize the chemical reaction between the fabric layers, SiC fabric was coated with thin layer of pyrolitic carbon (with a thickness of coating about <1 **µ**m). Coated fabric was sintered under the identical process conditions as the uncoated fabric (Figure 5b).

It was established that applying thin layer of carbon coating (about <1 **µ**m) on Sylramic woven fabric alone did not prevent the chemical reaction between the SiC fibers during compaction and sintering (Figure 5b). It appeared that thin carbon coating was consumed by residual oxygen during the sintering process. Fibers fused together and sintered products appeared more like monolithic SiC material with some porosity that is due to the spacing or gap between the woven fabrics.

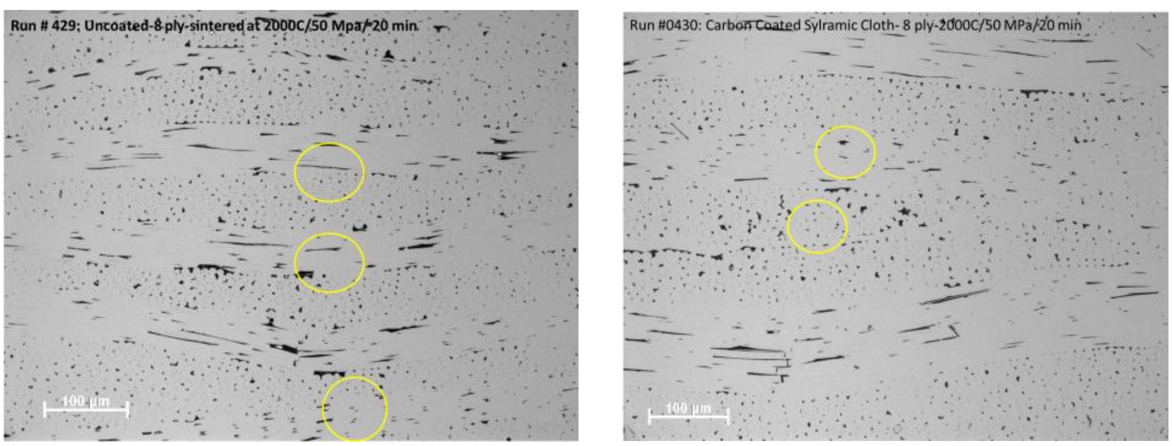

Figure 5: SEM micrographs showing the microstructure of sintered (a) uncoated 8ply Sylramic SiC woven fabric; and (b) pyrolitic carbon coated 8ply Sylramic SiC woven fabric. Fiber bonded together during compaction and sintering at 2000 ^{0}C/50MPa/20min.

The above mentioned challenges were addressed by infiltrating nano-sized SiC particulate into the coated fabric. Extra thick layer of infiltrated particulate was maintained on both sides of each fabric ply that would act as a matrix. Eight infiltrated plies were stacked on each other and subjected to compaction and sintering by FAST under various sintering conditions with temperature ranging from 1700 to 2000 ^{0}C (Figure 6). It was observed that porosity of the compacts was reduced with the increase in the sintering temperature. On the other hand, higher sintering temperatures lead to increased chemical reactivity between the fiber and SiC matrix.

This indicated that the graphite coating thickness was not sufficient to act as a barrier layer and was probably consumed by oxygen as shown in Figure 6(C).

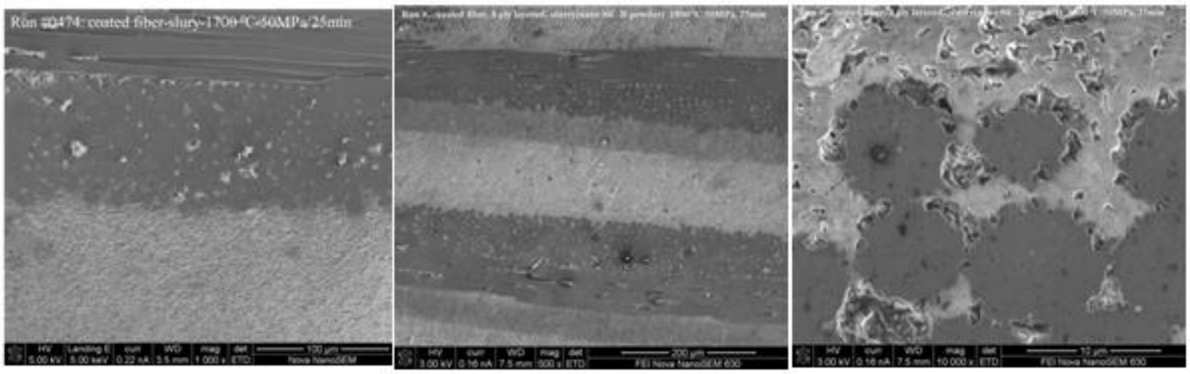

Figure 6: Scanning electron micrograph showing microstructure of sintered pyrolitic carbon coated 8ply Sylramic SiC woven cloth with infiltrated SiC powder. Fiber was fused together during the compaction and sintering at (a) 1700 ^{0}C, (b) 1800 ^{0}C (d) 2000 ^{0}C/50MPa/20min.

In order to improve the fabrication process of CMC coupons, a new approach was e developed involving tape casting with bimodal SiC particle distribution that will serve as matrix (Figure 7a). Starfire SiC-yielding polymer and nano sized B_4C particulates as a sintering aid were infiltrated within each coated Sylramic SiC fabric. Before infiltration, the fibers were coated with an interphase coating consisting of a thin layer of silicon nitride on top of BN (Mod-1 coating produced by Synterials Inc.). A total of 9 stacked alternate layers of tape cast nano SiC and infiltrated Sylramic SiC fabric were used to fabricate the CMC coupons as illustrated in Figure 7c. Sintering was carried out using the identical processing conditions as mentioned above.

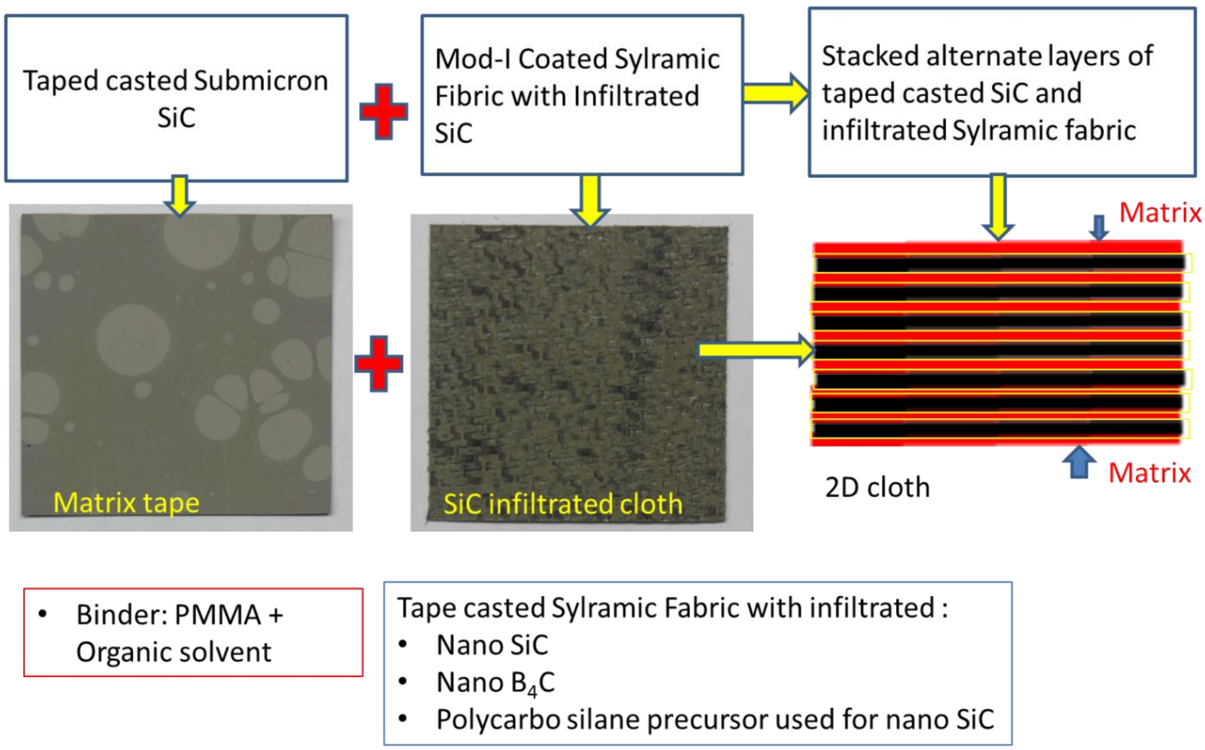

Figure 7: Flow Chart showing the details of the fabrication of SiC-SiC composite (CMC) prior to sintering.

Images of the sintered coupons are shown in Figure 8. From Figure 8 it can be seen that the density of the CMC increases with the sintering temperature.

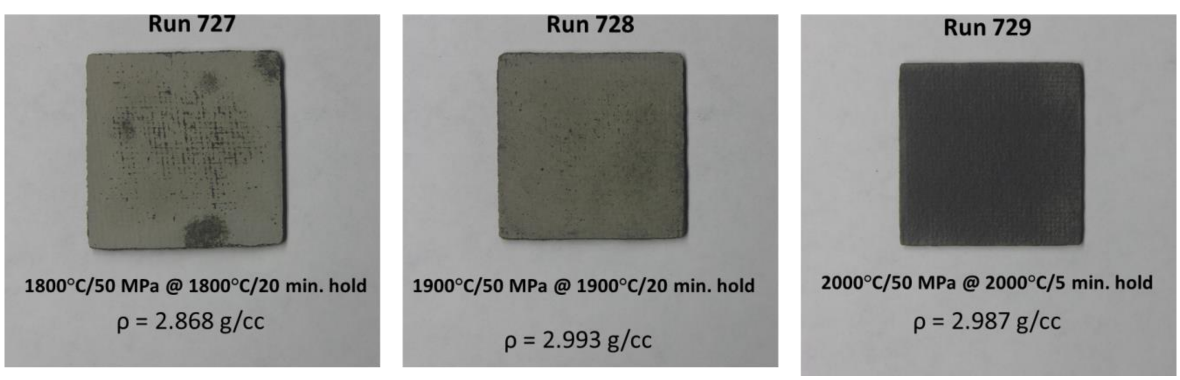

Figure 8: Images of the sintered SiC/SiC coupons sintered at (a) 1800 ^{0}C/50MPa/20 min, (b) 1900 ^{0}C/50MPa/20 min, (c) 2000 ^{0}C/50MPa/5 min.

Microstructures of the sintered SiC-SiC composite (CMC) products was examined using optical and scanning electron microscope (SEM) and are shown in Figure 9. These microstructures indicate that the integrity of the fiber was maintained at all sintering conditions. In addition, fiber did not break during sintering process.

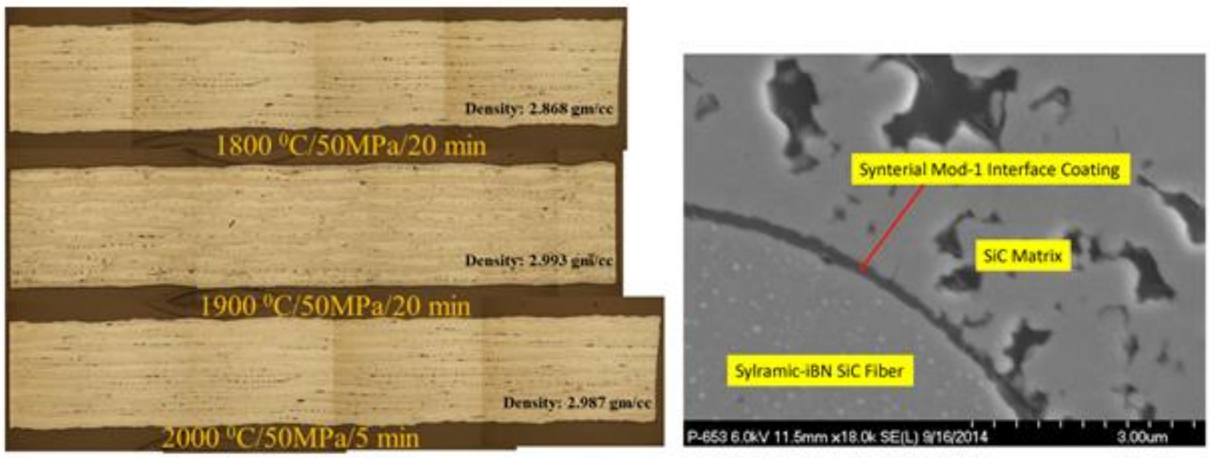

Figure 9: (a) Optical micrographs and (b) SEM of the SiC-SiC composite panel fabricated using slurry approach followed by FAST.

Bend tests were performed on the sintered Mod-I SiC-SiC composite (CMC) at room temperature and at 1315 ^{0}C. From the stress-strain plots, it appeared the CMC sintered at 1800 ^{0}C exhibited higher strain than the CMC samples sintered at higher temperatures 1900 ^{0}C and 2000 ^{0}C (Figure 10). The lower strain is probably due to the grain growth within the fiber structure and disintegration of fiber.

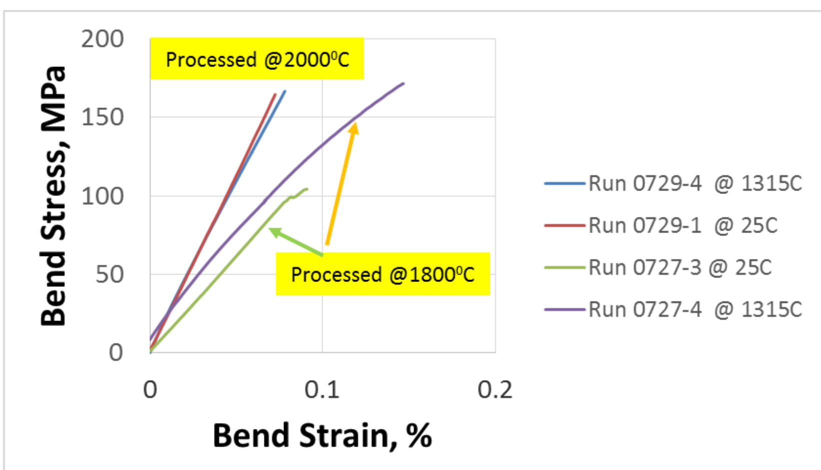

Figure 10: Flexural Stress-Strain Behaviors of SiC/SiC Composites Fabricated by FAST Process.

Table I: Bend Properties of SiC/SiC Composites Fabricated by FAST

Fabric	Basic lay-up	FAST processing conditions	Bend Properties			
			Test temperature ^{0}C	Average Ultimate Bend Strength Mpa	Average Bend Strain %	Average Tangent Modulus Gpa
Mod1 coated Sylramic/8ply	PCS+B4C infiltrated fabric and matrix tape with submicron SiC powder	1800^{0}C/50MPa/20min/w/o cooling	25	102	0.085	115
Mod1 coated Sylramic/8ply	PCS+B4C infiltrated fabric and matrix tape with submicron SiC powder	1800^{0}C/50MPa/20min/w/o cooling	1315	172	0.15	140
Mod1 coated Sylramic/8ply	PCS+B4C infiltrated fabric and matrix tape with submicron SiC powder	1900^{0}C/50MPa/20min/w/o cooling	25	142	0.08	176
Mod1 coated Sylramic/8ply	PCS+B4C infiltrated fabric and matrix tape with submicron SiC powder	1900^{0}C/50MPa/20min/w/o cooling	1315	120	0.07	120
Mod1 coated Sylramic/8ply	PCS+B4C infiltrated fabric and matrix tape with submicron SiC powder	2000^{0}C/50MPa/5min/w/o cooling	25	148	0.06	230
Mod1 coated Sylramic/8ply	PCS+B4C infiltrated fabric and matrix tape with submicron SiC powder	2000^{0}C/50MPa/5min/w/o cooling	1315	167	0.07	167

Based on the finding reported above, it can be concluded that tough CMC could be fabricated by a novel approach with the density ranging from 2.86 to 2.97gram/cc that is close to the density of SiC (3.21 gram/cc). The next step in Phase II is to improve the mechanical properties of the composite by optimizing the composition and thickness (pyrolitic carbon/SiC or BN/Si_3N_4) of the fiber coating and using lower sintering temperature (1800-1850 ^{0}C) and high pressure (60-70 MPa) to maintain the structural stability of the fiber and to make the CMC pore free.

Summary:

Following are the major conclusions/findings of the LEARN Phase – I Efforts:

- Successfully produced SiC-SiC composites (CMC) with 93% theoretical density using infiltrated SiC particulate and Mod-1 interphase coatings. Mechanical properties need further evaluation.
- Compacting and sintering cycles is very short few minutes (10-20 minutes) as compared to other manufacturing processes (CVI and PIP) that take hours and days.
- FAST is a cost effective manufacturing process with energy saving 30-40% as compared to other manufacturing processes (CVI and PIP).
- FAST is more environmentally friendly manufacturing process than other manufacturing processes (CVI and PIP).

LEARN Phase-II: Proposed efforts are aimed at:

(1) Establishing processing conditions for fabrication of fully dense SiC-SiC composites (CMC) with enhanced strength and toughness.
(2) Fabricating large sample coupons with the size ranging from 101 x101 mm^2 to 200X200 mm^2 with varying thicknesses for evaluation of thermo-mechanical properties including tensile and fatigue strength at elevated temperatures.
(3) Fabricating components with more complex configuration such as turbine airfoils and leading edges of hypersonic vehicles.