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Enhancing CMC Temperature Performance in High-Hydrogen Environments Using Field Assisted Sintering Technology



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Cost Share Partner: Bobby Noble, Electric Power Research Institute (EPRI)



MECHANICAL ENGINEERING



PennState Applied Research Laboratory This presentation covers the project management and technical task details for our work on developing novel CMC manufacturing processes to enable high hydrogen operation



Background, motivation, and technical advancement being pursued



Developments of baseline CMC formulations using Field Assisted Sintering Technology (FAST)



Developments in a realistic combustion exposure test facility



Increasing the blend of hydrogen in natural gas can result in 1 point increase in gas turbine cycle efficiency for the same firing temperature, due to the higher water vapor content







3

By enabling even higher temperatures, ceramic matrix composite (CMC) parts could generate another 4 pt increase in efficiency, but are highly susceptible to water vapor degradation



More, et al., J. Am. Ceram Soc., 2000



Klocke, et al., CIRP Annals, 2014

The advancement here is development of CMCs with higher oxidation resistance and integrated environmental barrier coatings using Field Assisted Sintering Technology (FAST)



Benefits of FAST:

- Near theoretical density (~100%)
- Short sintering times
- Can retain sub-grained structure
- Compositional graded structures
- Solid state joining of dissimilar materials (metal and ceramics)
- Compatible with metals, ceramics, polymers, and composites

SiC/SiC composite with varying fiber lay-up orientation



Direct incorporation of rare-earth EBCs into CMC



Fibers

The full task list for the project is shown; we will be discussing Tasks 2 and 3 today

- Task 1: Project Management and Planning
 - 1.1: Project management plan
 - 1.2: Technology maturation plan
 - 1.3: Environmental justice questionnaire
 - 1.4: Revitalization of job creation questionnaire
- Task 2: CMC Development with Field Assisted Sintering Technology (FAST)
 - 2.1: Fabricate baseline CMC formulations
 - 2.2: Fabricate improved CMC compositions and build methods
- Task 3: Experimental Facility Development and Build
 - 3.1: Design and build new exposure test facility
 - 3.2: Startup and shakedown exposure test facility
- Task 4: Experimental Testing of CMC Samples
 - 4.1: Perform exposure tests at different operating conditions and fuel compositions
 - 4.2: Perform exposure tests in high water vapor environments
- Task 5: Post-Test Analysis of CMC Samples
 - 5.1: Perform microstructural inspection and failure analysis
 - 5.2: Perform mechanical property testing





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Task 2.1 – Baseline CMC Silicon Carbide (SiC) Cloth Applied Research Laboratory **Development**



- Characterization of woven SiC NicalonTM cloth (1mm tow, 22 epi) for baseline CMC-EBC FAST processing provided direct insights into fiber architecture and matrix particle size requirements for pore/interstitial infiltration
- Insights have been applied to powder processing and green body developments \rightarrow Targeting max densities



Task 2.1 – Baseline CMC Carbon Fiber (C_f) Analog Applied Research Laboratory **Cloth Development**



- Analog carbon fiber cloth/chopped fibers (similar weave, tows, filaments) for efficient CMC testing has been developed with custom cut shapes using tape lamination/solvent-debinding methods and organic binder coatings
- As-received SiC particles on chopped fibers demonstrate promising coverage \rightarrow Fiber/matrix developments



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Task 2.1 – Baseline FAST Processing of SiC Matrix Applied Research Laboratory



Preliminary FAST processing of SiC powder matrix across various soak conditions provided baseline insights ٠

New critical SiC densification, pressed dimensions, tolerances, & carbide layer thicknesses were obtained ٠



Task 2.1 - Characterization of Baseline FAST Applied Research Laboratory **Processed SiC Matrix**



- Characterization of SiC crystallinity via XRD demonstrates high apparent reproducibility between baseline test coupons •
- Preliminary NDE insights of pre-combustion SiC test coupons were obtained \rightarrow Available for first burn tests ٠

PennState Applied Research Laboratory Task 2.1 – Baseline Powder Processing of SiC Matrix



• Applying PEG to SiC was found to be an effective dispersant/binder for robust infiltration & green bodies



PennState Tas Applied Research Laboratory via

Task 2.1 – Baseline Powder Processing of Reactive SiCboratoryvia Elemental Si/C Precursors



- Baseline powder processing of new reactive SiC via elemental nanopowder blends were developed via ball milling
- Substantial potential for in-situ CMC molten infiltration and densification through reactive FAST



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Task 2.1 – Baseline CMC-EBC Green Body Processing Applied Research Laboratory



- Baseline CMC-EBC green body processing is currently being explored across various methods, such as conventional cold-pressing of thin layers, vat photopolymerization, and direct graphite die cavity fillings for FAST
- Thus far, binding, pulverizing, sieving, thin layer cold-pressing, stacked-layer pressing, thermal annealing, and debinding appears to yield the most tailorable/uniform green CMC-EBC architectures → Still more to develop





- Slurry/melt infiltration of SiC-PEG mixture into fiber cloth sheets are stacked/fused into green CMCs with silicone molds
- The green CMCs are aqueously debinded, dried, & loaded into the graphite FAST die assembly for sintering \rightarrow Scalable Process

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Applied Research LaboratoryTask 2.1 – Baseline FAST CMC Processing Results



- C_f/SiC Fairly low sinterability between carbon fiber & SiC particles, useful analog for processing developments
- SiC_f/SiC High sinterability observed in porous fabric, balancing between max density & fiber/matrix interfaces is critical
 → Optimize FAST parameters for sufficient activated diffusion to densify with minimal composite changes



2.

3.

- Optimize SiC/SiC FAST sintering conditions
- Compare between matrix, chopped fibers, & fabric sheets

Prototype CMC-EBC candidate development with initial testing
Compare between different coatings, interface grading, & doping

- Improved CMCs with layering, slurry, reactive, & PIP methods
- Baseline testing/characterization using best EBC integration method

Task 3.1: Specific design goals were identified for the test facility that led to selection of a trapped vortex combustor design

Design goals:

- Fuel flexible 100% H2 to 100% natural gas
- Highly instrumented be able to measure temperatures, heat flux (total and radiative), and H2O concentration
- Ability to place samples in two different flow regimes (low and high velocities) to change H2O residence time above the samples
- Long term stable combustion for long duration test times without combustion dynamics issues

Trapped vortex combustor design





Zhao, Gutmark, de Goey, 2018, Progress in Aerospace Sciences





Task 3.1: The test section was designed to hold 1" diameter coupons in two important regions, and have a high degree of instrumentation for sample temperature and gas composition



IR transmissive windows: Wall and sample temperatures

0

Tunable Diode Laser Absorption Spectroscopy (TDLAS): Gas temperature, H2O concentration



Task 3.1: The heat flux block will be used to mount the CMC samples and measure the steady state total heat flux in the test facility.



Task 3.1: To validate the heat flux block measurements, tests were taken by using an element heater connected to a power supply to create a known heat flux.









Task 3.1: Heat loss through insulation was estimated using thermal resistance circuits.



Task 3.1: The block temperature measurements and cooling flow calculations agreed well with delivered heat flux indicating accuracy of the block measurement technique.



Task 3.1: The heat flux block was tested over a natural gas flame to test the method in combustion, and indicated that heat flux was correlated to adiabatic flame temperature







Task 3.1: Next steps include validation of heat flux block with SiC sample disks, and assembly of test rig once parts are received

Trial SiC disks are being tested for adhesive attachment and validation of the total heat flux block

The testing facility is currently being manufactured, and shakedown testing will be conducted in the coming months.



SiC disk







In conclusion, we are developing the CMC manufacturing processes and fabricating the exposure testing facility with a goal to be testing CMC samples by summer 2024



We are establishing SiC matrix processing parameters and have established fiber layup/matrix infiltration processes



A highly instrumented combustion exposure test facility has been designed and will be online this summer



Future testing will establish degradation rates and microstructural changes in untreated SiC/SiC, and efficacy of integrated EBC coatings



Appendix



We expect gas temperatures between 1800 – 2200 K and H₂O concentrations up to 30% in the combustion products. Experimental design will incorporate several GT-relevant flow features

- Task 4: Expose CMC samples to relevant environment
 - 4.1: Exposure at various relevant operating conditions
 - Evaluate different fuel compositions (hydrogen/natural gas blends), fuel air ratios, exposure times; measure concentration and thermal conditions for all cases
 - 4.2: Exposure to high water vapor conditions
 - Repeat selected cases from 4.1 but with additional water vapor added to reactants (steam dilution)



The significant measurement capabilities at Penn State's Materials Characterization Lab and at **ARL-Penn State will be used to analyze the CMC samples**

- Task 5: Perform post-exposure analysis of CMC samples
 - 5.1: Microstructural inspection and failure analysis
 - SEM, EDS, X-ray CT to analyze density, homogeneity, EBC bond
 - 5.2: Mechanical property testing
 - Shear, flexural, hardness, in-plane tensile strength characterization after exposure

Scanning electron microscope



High temperature Instron





Progress Summary:

- 1. ✓ Procured majority of raw CMC FAST materials (i.e. powders, graphite dies, fiber cloths, etc.) and enrolled participating personnel [1-8/23]
 - Includes SiC powder, EBC powders, SiC fiber cloth, binders, carbon fiber cloth/chopped fiber analog, Si/C nanoparticles, and 1"OD graphite dies
- 2.
 Performed baseline characterization of raw components (i.e. powders, fiber cloths) before processing [8-10/23]
 - XRD, SEM-EDS, OM, planimetric measurements, Laser PSD, and effect of milling conditions/surfactants
- 3. **√** Performed baseline SiC matrix FAST processing, optimization, and characterization [9-10/23]
 - Evaluated effects of sintering soak temperature & time on density, dimensions/tolerances, and crystallinity (XRD)
- 4. **√** Investigated viable & scalable fiber cloth processing methods for FAST CMCs [9-10/23]
 - Compared/evaluated cloth processing between taped lamination (single/dual) & infiltrated organic binder matrices (esp. PEG)
- 5. ✓ Explored various slurry infiltration methods for producing FAST CMC green bodies [10/23]
 - Investigated conventional gravity infiltration and centrifugal-accelerated infiltration of slurries into fiber preforms
- 6. **✓** Evaluated cold-pressing methods for producing FAST CMC green bodies [10/23-2/24]
 - Investigated effect of pressure, binder content, binder type (esp. stearic acid vs. PEG), fiber treatment, trimming, & layup



Progress Summary:

- ✓ Explored Vat photopolymerization as an AM technique for PIP-based FAST CMCs [10/23-3/24] 7.
 - Evaluated viability of direct resin printing on fibers; developed preliminary SiC-based precursor/photoinitiator prints ٠
- ✓ Explored reactive Si/C nanopowder processing for in-situ SiC formation via FAST in CMCs [11-12/23] 8.
 - Developed ball milling process from small to large-scale nanopowder blends and evaluated post-milled particle • morphology/crystallinity
- ✓ Improved cold-pressed green CMCs with miniaturization & mold-assisted fusing for robust stacking [12/23] 9.
 - Developed thin layers with pressing of sieved fines & thermal fusing of fiber/matrix layer stacks with silicone molds ٠
- 10. **V** Optimized slurry composition for ideal particle infiltration/retention, green body robustness/machinability, and scalable processing [1-2/24]
 - Investigated effects of solvent type, solvent concentration, binder content, particle loadings, viscosity, & duration
- 11. **V** Optimized solvent debinding processes for preparing binderless green CMCs before subsequent FAST processing [1-2/24]
 - Investigated effects of green body diffusion barriers/containment, submersion duration, & debinding cycles
- 12. V Performed initial baseline FAST CMC fabrication from cumulative developments (i.e. slurry infiltrating, cutting, stacking, debinding) [3/24]
 - Obtained post-fired shrinkages, average layer thicknesses, dimensions, and preliminary CMC microstructural insights (surface/X-section)



PennStateTask 5.0.Perform Post-Test Analysis of CMC SamplesApplied Research LaboratoryOverview of Microstructural & Mechanical Analysis (subtasks 5.1-5.2)



Project team leads

- PI: Prof. Steve Lynch
 - Associate Professor, Mechanical Engineering, Penn State
 - Expertise in cooling and durability for gas turbine hot section components
- Co-PI: Prof. Jackie O'Connor
 - Professor, Mechanical Engineering, Penn State
 - Expertise in combustion and renewable fuels
- Co-PI: Dr. Doug Wolfe
 - Associate Vice President for Research, and Prof of Mat'l Science & Engineering and Engr Sci & Mechanics, Penn State
 - Expertise in high temperature materials and coatings including development, processing, and evaluation
- Industry partner: EPRI
 - Technical contact: Bobby Noble, Program Manager: Gas Turbine Life Cycle Management (P216) and Gas Turbine Advanced Components & Technologies (217)









Project milestones were updated with a revision of the PMP in July due to personnel delays but Milestones 1, 2, and 4 are completed

Task/ Subtask	Milestone Title & Description	Original Completion	Revised Completion	Actual Completion	Comments
1.1	M1: Deliver PMP to NETL	1/31/2023		01/03/2023	Revision provided 7/2023
1.2	M2: Deliver TMP to NETL	3/31/2023		04/13/2023	
2.1	M3: Fabrication of baseline CMC formulation complete	9/30/2023	3/30/2024	4/30/2024	
3.1	M4: Experimental facility detail design review	6/30/2023	12/30/2023	10/4/2023	Review completed with EPRI
3.1	M5: Experimental facility fabrication complete	9/30/2023	3/30/2024		Delayed due to procurement of materials
3.2	M6: Standard operating procedures and operability map for experimental facility	12/31/2023	6/30/2024		
4.1	M7: Testing results for baseline CMC in experimental facility	3/31/2024	8/30/2024		
5.1	M8: Detailed characterization for baseline CMC complete	6/30/2024	9/30/2024		
2.2	M9: Fabrication of improved CMC formulation	6/30/2024	8/30/2024		
4.1	M10: Testing results for improved formulation CMC	9/30/2024	11/30/2024		
5.1	M11: Detailed characterization for improved formulation CMC complete	12/31/2024	12/31/2024		



The full project schedule is shown below with some shift of task completions due to the aforementioned delays

	2023			2024			
Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q 8
Task 1 - Project Management and Planning							
M	1						
M	2						
Task 2 – CMC Development with Field Assisted Sintering Technology							
					3		
						M9	
Task 3 – Experimental Facility Development and Build							
		M 4			15		
						6	
Task 4 – Experimental Testing of CMC Samples							
						M7	M10
Task 5 – Post-Test Analysis of CMC samples							
						М	8
							N
	Q1	 Q1 Q2 M1 M2 	2023 Q1 Q2 Q3 M1 M2 M2 M4 M3 M4 M4 M4 M3 M4 M4 M4 M3 M4 M3 M4 M3 M4 M4 M4 <td>2023 Q1 Q2 Q3 Q4 M1 </td> <td>2023 Q1 Q2 Q3 Q4 Q5 M1 M1 M2 M1 M1</td> <td>2023 2 Q1 Q2 Q3 Q4 Q5 Q6 M1 M2 M M M M M2 M4 M M M M M1 M2 M M M M M2 M4 M M M M M4 M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M</td> <td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td>	2023 Q1 Q2 Q3 Q4 M1	2023 Q1 Q2 Q3 Q4 Q5 M1 M1 M2 M1 M1	2023 2 Q1 Q2 Q3 Q4 Q5 Q6 M1 M2 M M M M M2 M4 M M M M M1 M2 M M M M M2 M4 M M M M M4 M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M M	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$



There are significant manufacturing and cost challenges with CMC materials; one recent development is the use of Field Assisted Sintering Technology (FAST)

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Challenges:

- Scalable manufacturing of net-shape, continuous fiber structures via CVD, infiltration, and pyrolysis-based techniques
- High internal surface area for oxidation and sensitivity to embrittlement

Approaches/Solutions:

- FAST processing Rapid/enhanced consolidation, joining, adhesion, and minimal thermal degradation of CMCs
- EBC coatings Deposit environmental barrier coatings for protection

Benefits of FAST:

- Near theoretical density (~100%)
- Short sintering times
- Can retain sub-grained structure
- Compositional graded structures
- Solid state joining of dissimilar materials (metal and ceramics)
- Compatible with metals, ceramics, polymers, and composites



We will develop a baseline CMC against which to evaluate improved formulations including integrated EBC Powder Processing and Slurry Preparation

- Task 2: Develop new CMC compositions using FAST method
 - 2.1: Perform baseline CMC fabrication
 - Procure SiC cloths and powders, infiltrate cloths with slurry, determine FAST processing parameters, evaluate pre-exposure microstructure and properties
 - 2.2: Fabricate improved CMC compositions and build methods
 - Improve cloth formulation (fiber coatings), slurry formulation (add YbDS, YbMS), and integrated EBC coatings, revisions to FAST processing parameters, evaluate pre-exposure microstructure and properties



Initial design of the test facility has begun in collaboration with Bobby Noble at EPRI. Facility is designed to vary H₂ concentration and gas temperature for a range of material samples

- Task 3: Design, build, and shakedown a hydrogen combustion test facility for CMC samples
 - 3.1: Design and build facility
 - Mechanical & thermal design for long term operation; novel instrumentation for diagnostics of flame/products composition and thermal environment; capability to increase water vapor content
 - 3.2: Shakedown of facility
 - Evaluate safe and stable operating ranges, temperatures, achievable water vapor levels



Test section will rest above this table, which will have all the optics/ diagnostics.



Task success criteria review

- Task 2 CMC Development with Field Assisted Sintering Technology (FAST): this task will be deemed successful if the project team can fabricate SiC/SiC CMCs with integrated EBC coating using the FAST process.
- Task 3 Experimental Facility Development and Build: this task will be deemed successful if the experimental facility can operate with up to 100% hydrogen at repeatable conditions.
- Task 4 Experimental Testing of CMC Samples: this task will be deemed successful if the project team
 can expose the CMC samples to a range of hydrogen blend levels and measure the accompanying
 combustion gas conditions.
- Task 5 Post-Test Analysis of CMC Samples: this task will be deemed successful if the project team is able to observe quantitative differences in microstructural effects and degradation of uncoated and EBC coated SiC/SiC composites after several run cycles.



We are tracking success criteria that will be evaluated for each major task

Task/ Subtask	Milestone Title & Description	Status	Comments
2	CMC Development with Field Assisted Sintering Technology (FAST): this task will be deemed successful if the project team can fabricate SiC/SiC CMCs with integrated EBC coating using the FAST process.	In progress	
3	Experimental Facility Development and Build: this task will be deemed successful if the experimental facility can operate with up to 100% hydrogen at repeatable conditions.	In progress	
4	Experimental Testing of CMC Samples: this task will be deemed successful if the project team can expose the CMC samples to a range of hydrogen blend levels and measure the accompanying combustion gas conditions.		
5	Post-Test Analysis of CMC Samples: this task will be deemed successful if the project team is able to observe quantitative differences in microstructural effects and degradation of uncoated and EBC coated SiC/SiC composites after several run cycles.		



Task 3.1: The heat flux block is the method that will be used to mount the CMC samples and measure the steady state total heat flux through the samples in the test facility.

