National Energy Technology Laboratory (NETL)
Office of Fossil Energy and Carbonization Management (FECM)

Ceramic Matrix Composites for H_2 Combustion

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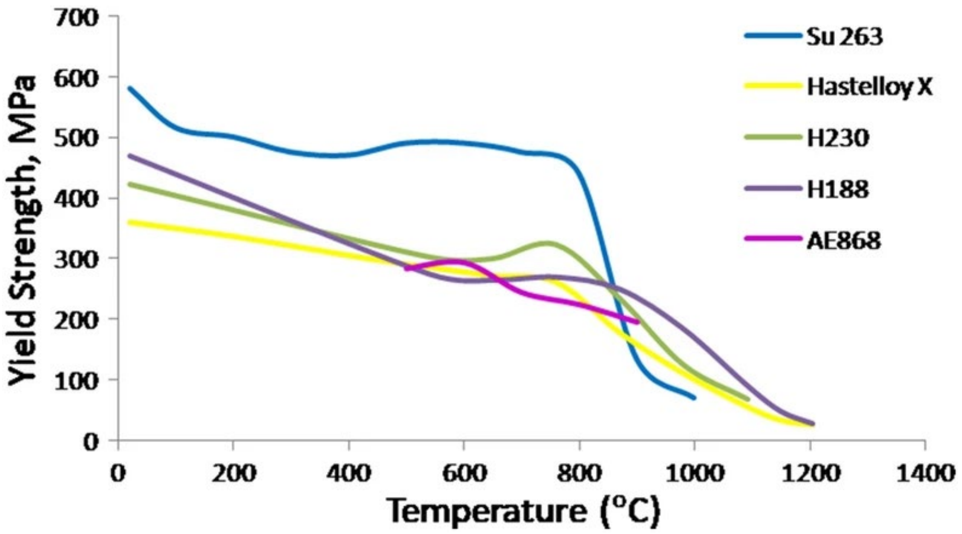
Motivation

- Gas turbine engines for power generation are under transition to hydrogen-based combustion systems to achieve net-zero or net-negative carbon emissions.
- A transition to hydrogen-based fuel combustion systems heavily relies on advancements in materials technology:
  - Hydrogen burns ~250ºC hotter than natural gas.
  - Current metal-based components are often operated very close to their melting points (within 100ºC)
  - Large amounts of water vapor production oxidizes current metal materials.
  - Small molecular size of hydrogen interacts metals to hydrogen embrittlement and can cause dangerous fuel leaks.

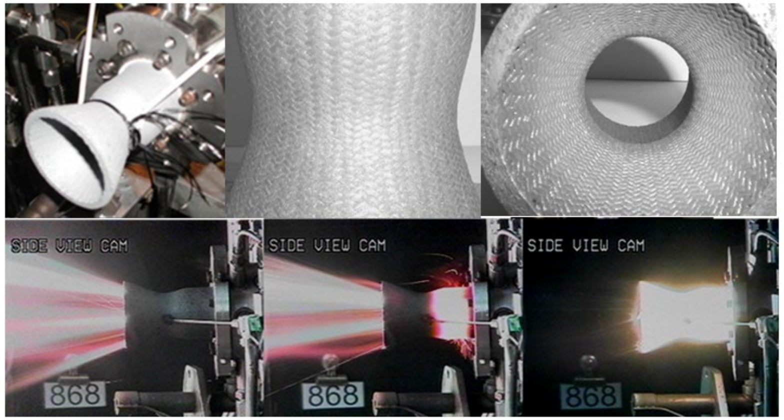


Strength of various superalloys in combustor and afterburner application. [1]

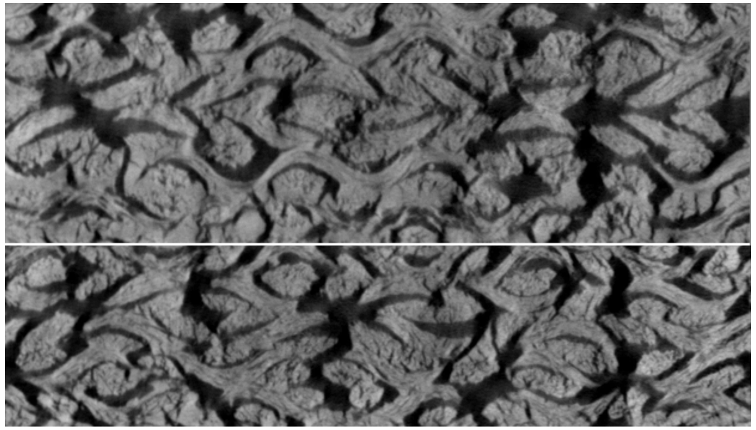
Hydrogen-induced cracking in metal. Photo by CEphoto, Uwe Aranas.

Ceramic Matrix Composites (CMCs)

- CMCs are investigated as a possible alternative to metal alloy components in H_2 gas turbine engines for their thermal and chemical resistivity as well as high customizability.
    - Modular nature of composites allow for selection of fiber, matrix, and additives that tailor the material to the intended application.
    - Have seen success in use as refractory materials in gas turbine engines using traditional fuels – must be adapted to address unique challenges posed by H_2 combustion.
- CMC production does not come without its own set of challenges:
    - High processing temperatures during pyrolysis result in shrinking and thermal warping that impacts final part geometry.
    - Outgassing of volatiles during pyrolysis result in highly porous matrix (densification via multiple re-infiltrations is necessary).
    - Brittleness of CMC materials make them difficult to machine after manufacturing.



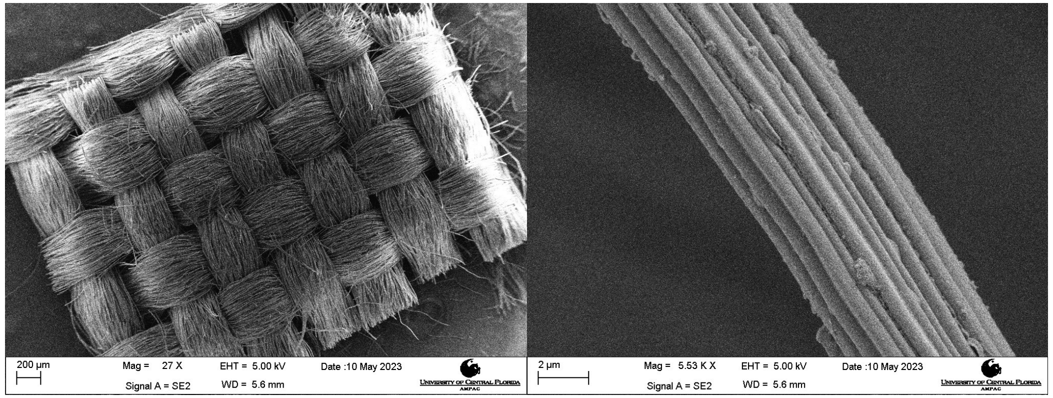
Cf/ZrC CMC combustion chamber undergoing oxygen-hydrogen hot fire testing. [2]



Micro-CT image of porous CMC cross section before densification.

Material Selection

- Yttria-Stabilized Zirconia is the ceramic fiber used in the presented CMCs
  - Currently used in thermal barrier coatings
  - Melting point of 2590ºC with continuous use limit of 2200ºC
  - Excellent performance in corrosive & oxidizing environments
  - High porosity of woven YSZ results in effective wetting and solution retention
  - Phase-stabilized with Yttria eliminates disruptive phase transitions



SEM images of YSZ plain weave (left) and close-up of individual YSZ fiber (right).

- Zirconium Oxide Rigidizer contains sub-micron particles of YSZ in a zirconium acetate aqueous solution
  - Used in fabrication to provide dimensional stability and mechanical strength to laminates while increasing YSZ content

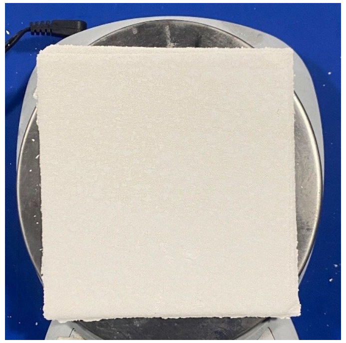
- When selecting ceramic precursor, factors such as ceramic yield, workability, and thermal performance were considered
  - Durazane 1800 was selected as the pre-ceramic polymer in this study for its higher ceramic yield and lower viscosity while maintaining comparable thermal performance

Ceramic Precursor	Resulting Ceramic	Ceramic Yield (Literature)	Ceramic Yield of Precursor (Experimental)
SPR-688	SiOC	65-85%	79.08%
SMP-10	SiC	72-78%	73.02%
Durazane 1800	**SiCN**	**80-90%**	**82.45%**

Manufacturing of CMC Parts through PIP

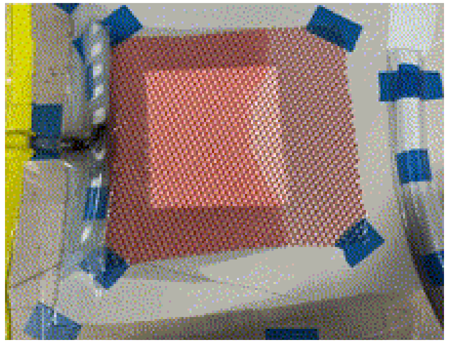
- Polymer Infiltration and Pyrolysis (PIP) is the manufacturing method used in this study
  - Relative ease and low cost of manufacturing make PIP an attractive option compared to other CMC manufacturing methods
  - Volatilization of organic compounds in ceramic precursors result in very high initial porosity: multiple reinfiltrations required for dense samples
  - Initial samples underwent 2 cycles of PIP

Hand layup of YSZ ‘preform’ consisting of 8 layers of YSZ fiber saturated in YSZ rigidizer



The ‘preform’ is dried in autoclave for 2 hours at 180ºC

The preform is then saturated with pre-ceramic polymer via vacuum infusion



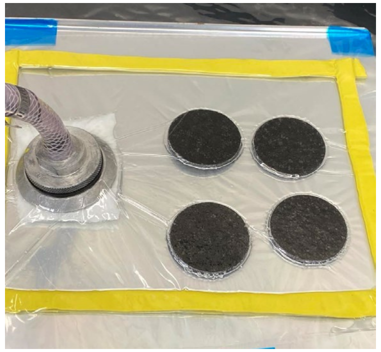
The polymer-infused laminate is cured in autoclave for 1 hour at 180ºC then 2 hours at 200ºC

The ‘green body’ material is waterjet cut into desired geometry before undergoing pyrolysis

Samples undergo pyrolysis at 950ºC for 2 hours in N_2 atmosphere

Resulting matrix phase is amorphous

CMCs are reinfiltrated with more pre-ceramic polymer and cured in autoclave again

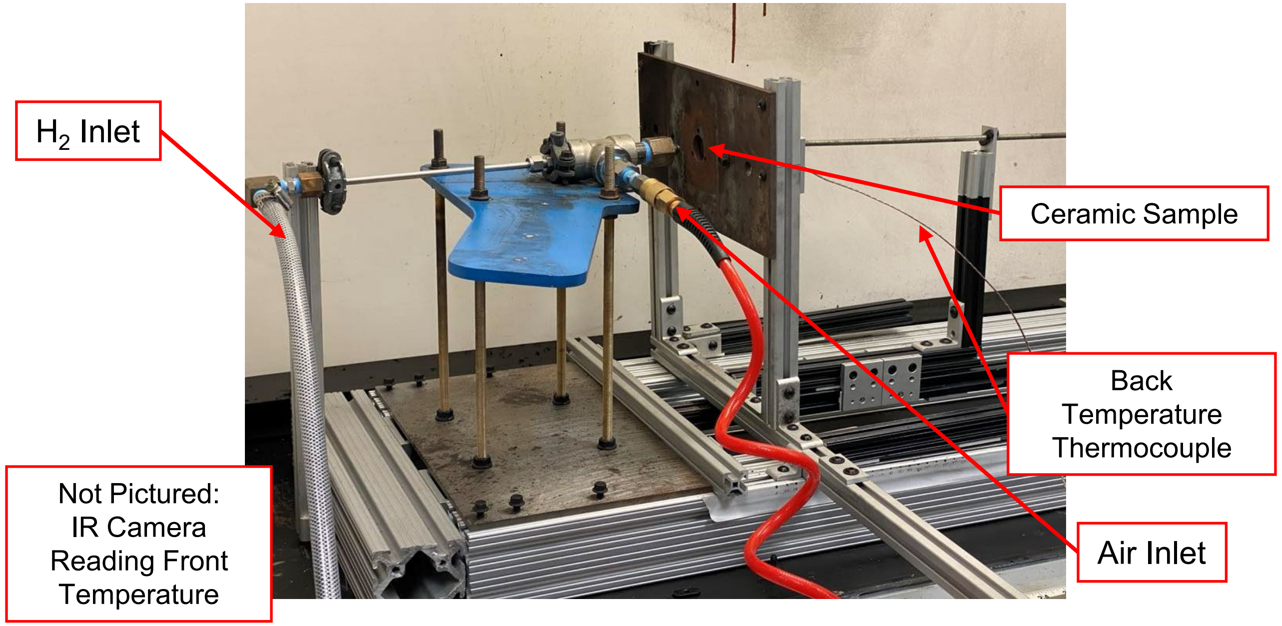


This ‘densifies’ the composite and reduces porosity

Reinfiltrated samples are pyrolyzed again under same conditions

Hydrogen-Air Torch Test Setup

- Air and fuel flow rates measured with control orifices and upstream pressure regulators
- Heat flux is mapped at various distances from the torch tip
- Hydrogen torch gives us insight on how material behaves in hydrogen- and water vapor-rich erosion environment

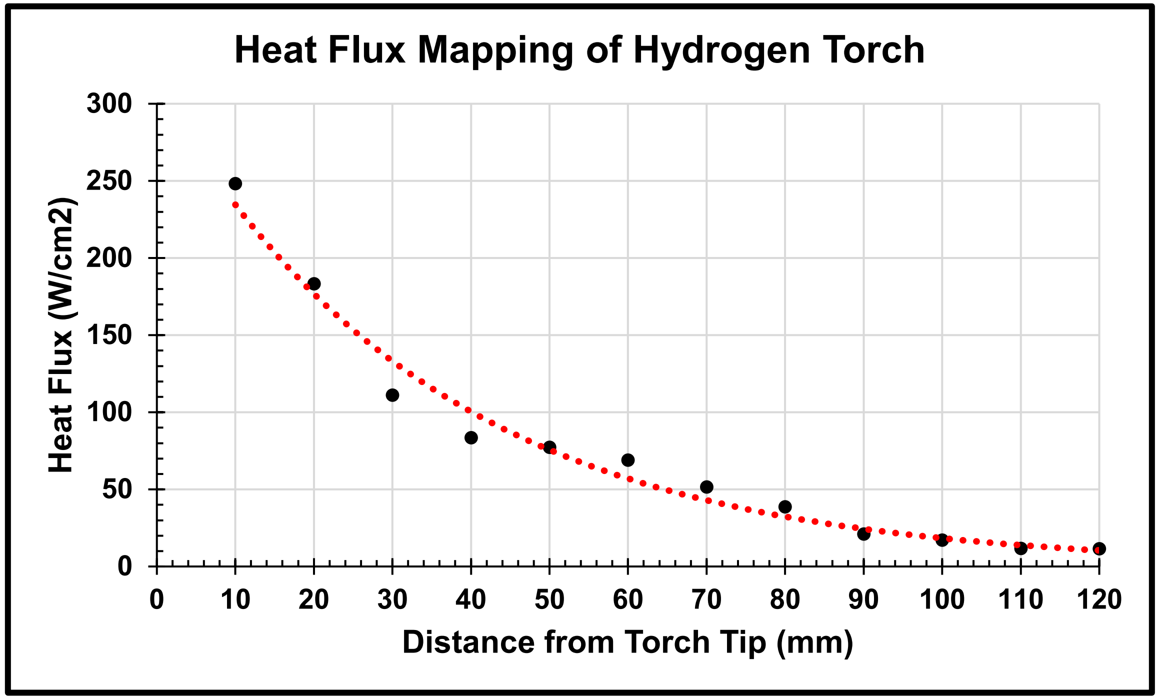

H_2 Inlet

Ceramic Sample

Back Temperature Thermocouple

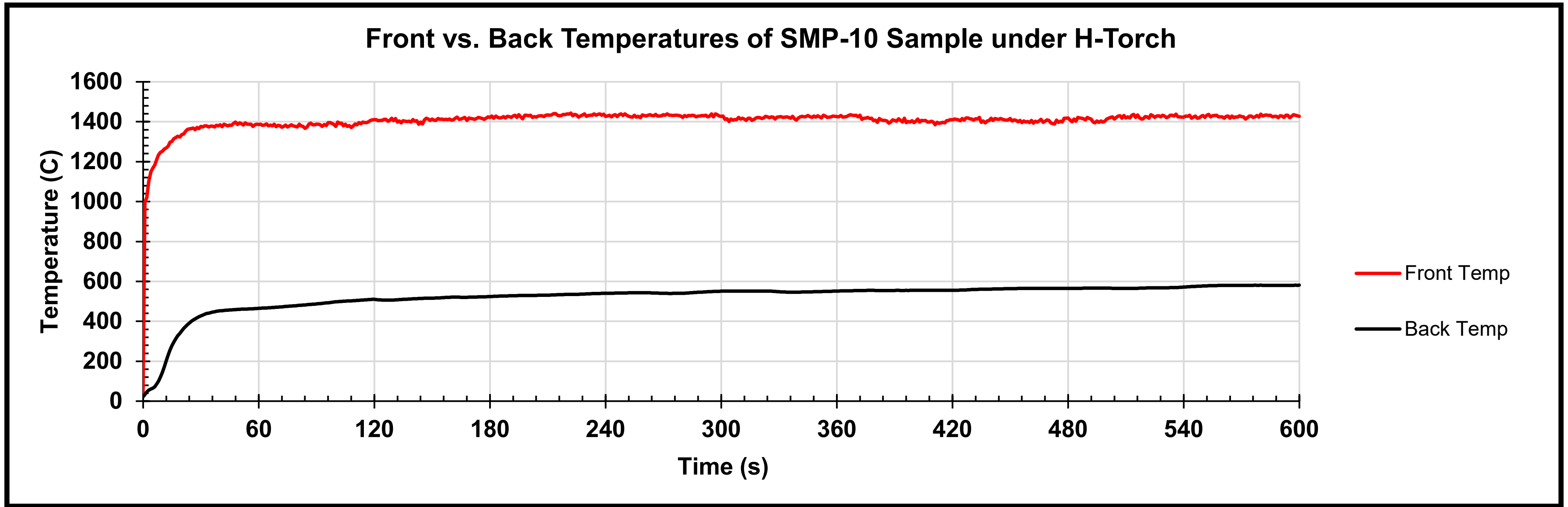
Air Inlet

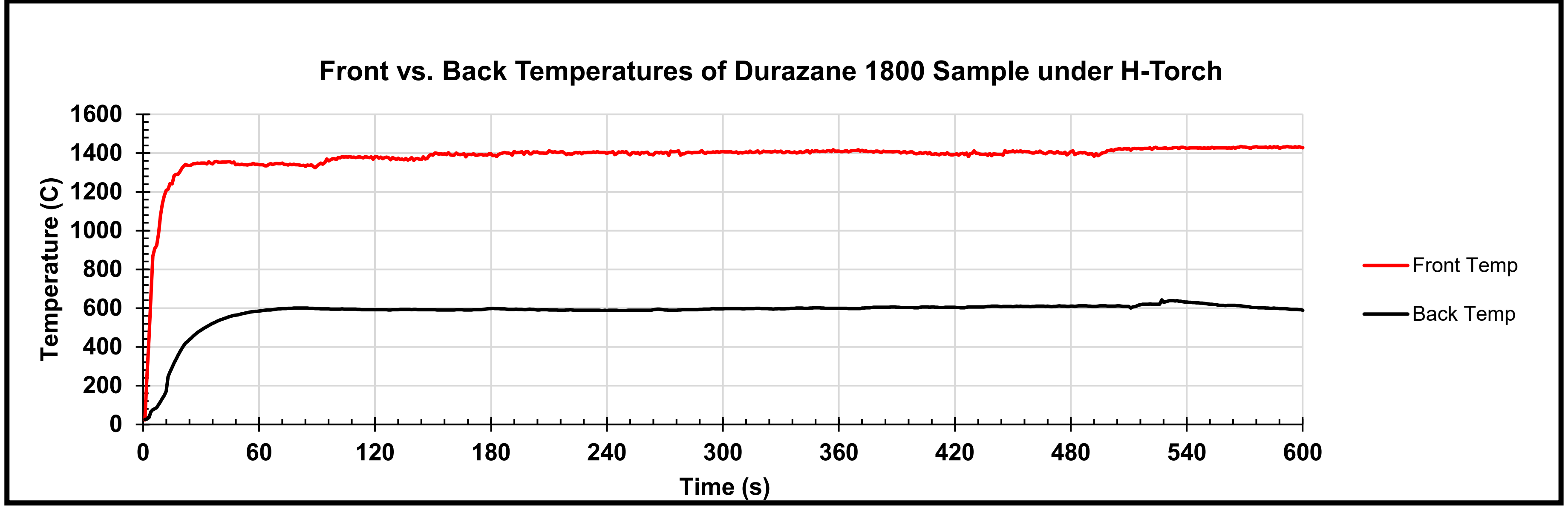
Not Pictured:
IR Camera Reading Front Temperature

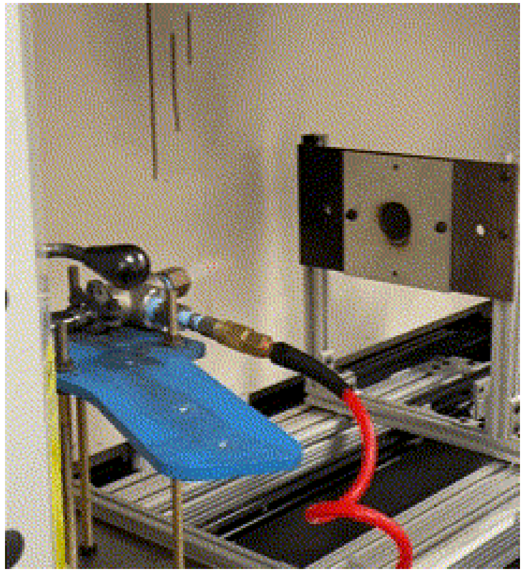

Heat Flux Mapping of Hydrogen Torch

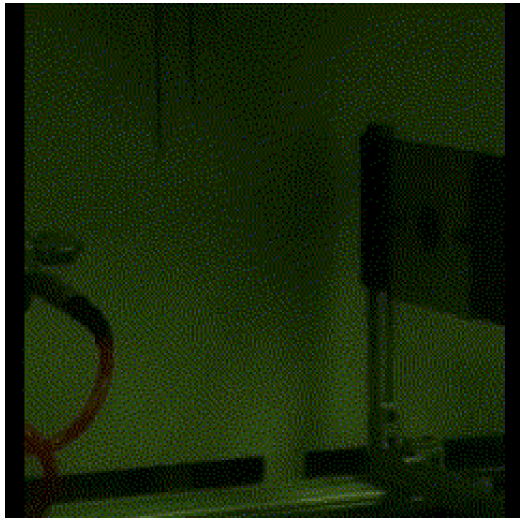
Test Conditions	
Heat Flux (W/cm2)	183.3
Flame Temperature (ºC)	2,000
Exit Velocity (m/s)	30
Equivalence Ratio	>1
Exposure Duration (s)	600

Hydrogen-Air Torch Test Results


Front vs. Back Temperatures of SMP-10 Sample under H-Torch

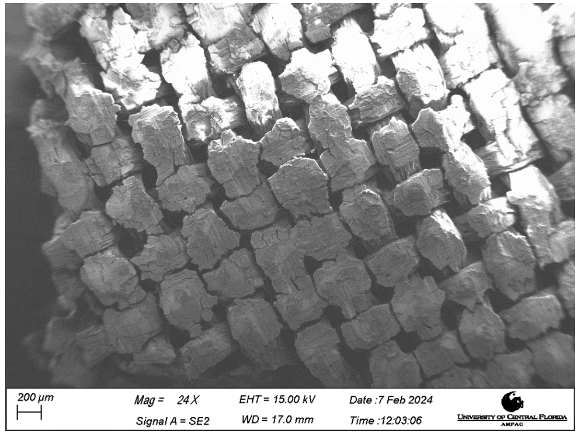

Front vs. Back Temperatures of Durazane 1800 Sample under H-Torch





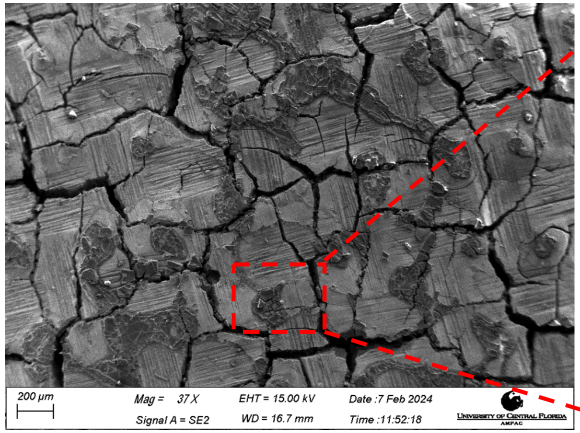
Post-Torch Test: Material Characterization

Intact Front Face

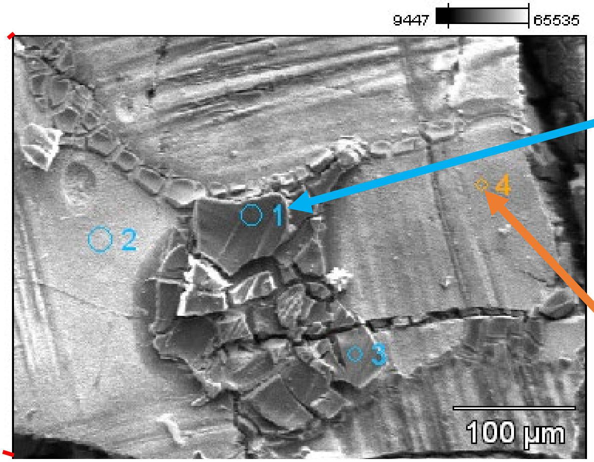


Element	Weight %	Atom %
C K	14.8	28.1
N K	0.0	0.0
O K	29.6	42.2
Si K	27.1	22.0
Zr L	27.8	7.0

Burned Front Face



Element	Weight %	Atom %
C K	8.1	15.5
N K	0.0	0.0
O K	41.5	59.5
Si K	21.8	17.8
Zr L	28.6	7.0



Passive oxidation of SiC:

$$2\,\mathrm{SiC}(s) + 3\,\mathrm{O}_2(g) \rightarrow 2\,\mathrm{SiO}_2(s) + 2\,\mathrm{CO}(g)$$

Occurs at oxygen pressures close to 1 bar and starts around 600ºC

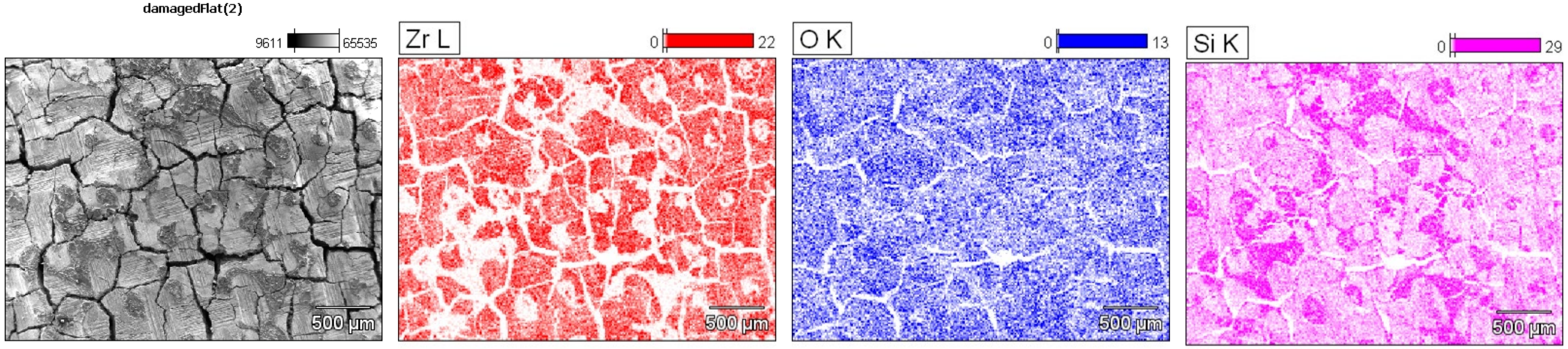
Point 1

Element	Weight %	Atom %
C K	4.8	8.6
N K	4.6	6.9
O K	32.0	42.4
Si K	55.1	41.7
Zr L	0	0

Point 4

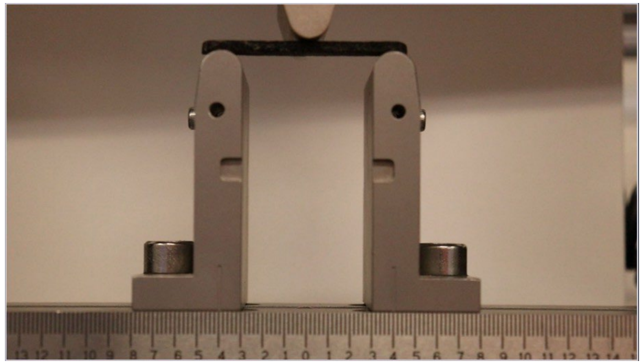
Element	Weight %	Atom %
C K	6.4	16.4
N K	2.7	5.8
O K	27.4	52.5
Si K	5.4	5.9
Zr L	58.0	19.4

- Pores in the matrix are filled after the torch exposure
- Formation of protective oxide plaques (SiO_2)
- Large increase in oxygen content post-damage



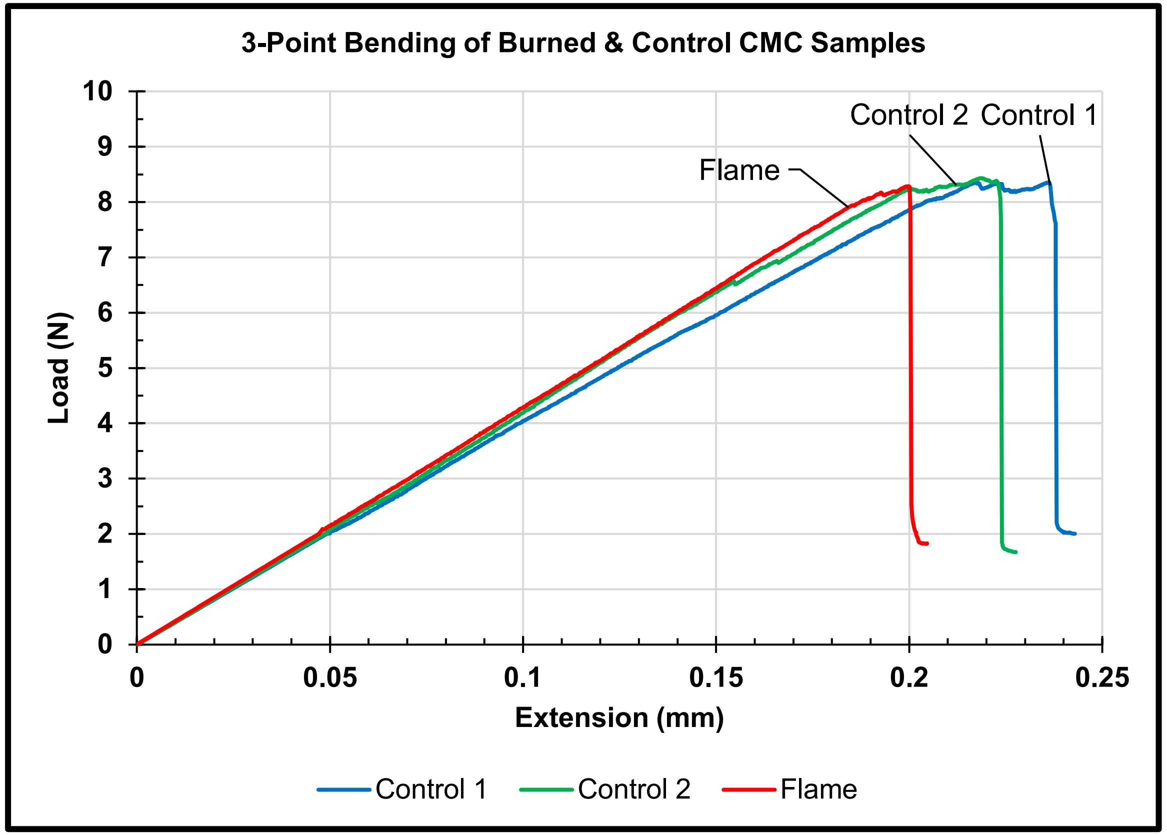
Spectral Mapping – distribution of elements on damaged surface

Post-Torch Test: Mechanical Property Characterization

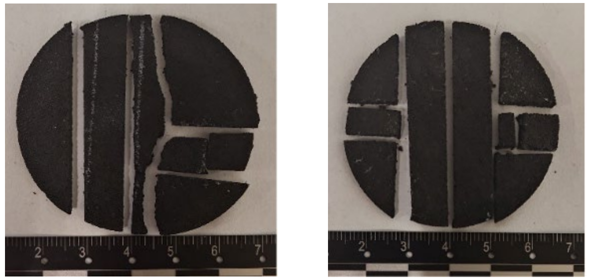


$$E_f = \frac{L^3}{4bh^3}\left(\frac{dP}{dw}\right) \qquad \sigma_f = \frac{3PL}{2bh^2}$$

σ_f	Stress required to fracture the sample
E_f	Flexural modulus of elasticity
L	Support span
b	Width of specimen
h	Thickness of specimen
P	Force
w	Cross head displacement
ΔP/Δw	Initial stiffness
Δw/Δt	Deflection rate
ΔP/Δt	Initial loading rate
P_{max}	Max load
$w(P_{max})$	Deflection at max load



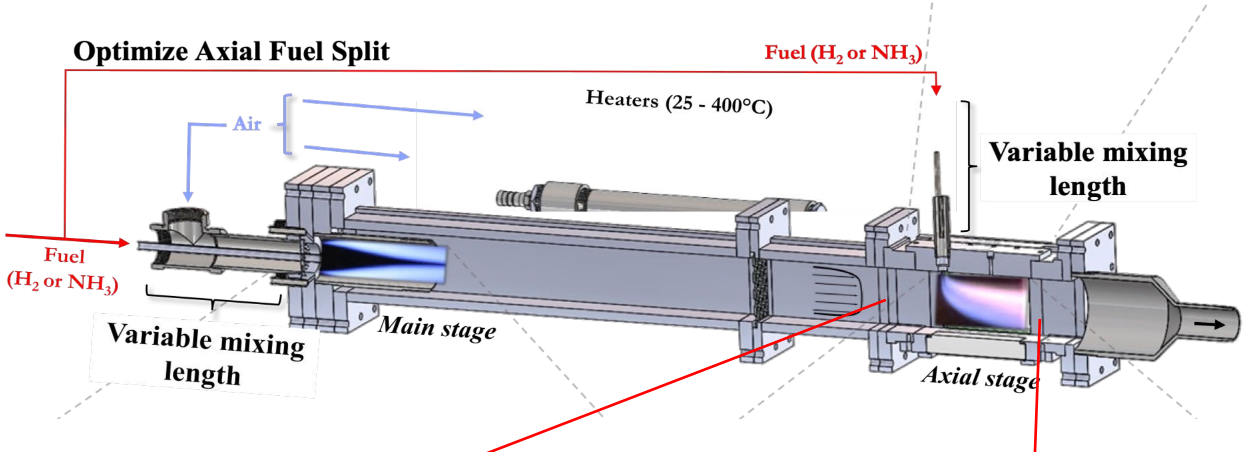
Sample	ΔP/Δw (N/mm)	P_{max} (N)	$w(P_{max})$ (mm)	σ_f (MPa)	E_f (GPa)
Control 1	40.819	8.363	0.168	7.73	3.78
Control 2	43.909	8.433	0.170	8.01	4.19
Flame	43.419	8.288	0.153	7.88	4.17



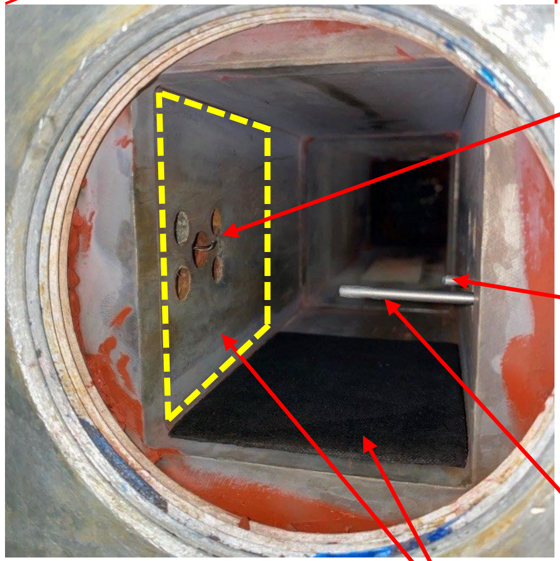
- Hydrogen flame damage had minimal effect on mechanical strength
- Matrix enhanced fracture strength (YSZ Tow $\sigma_f = 1.5\ MPa$)
- Average Values
  - σ_f = 7.87 ± 0.16 MPa
  - E_f = 4.05 ± 0.26 GPa
  - P_{max} = 8.36 ± 0.08 N

3-point bending test of flame-damaged and control samples were compared to understand effect of H_2 flame exposure on mechanical strength.

Hydrogen Combustion Engine Test Rig



Not Pictured: Thermocouples Measuring Outside Wall Temperatures



CMC Back Temperature Thermocouple

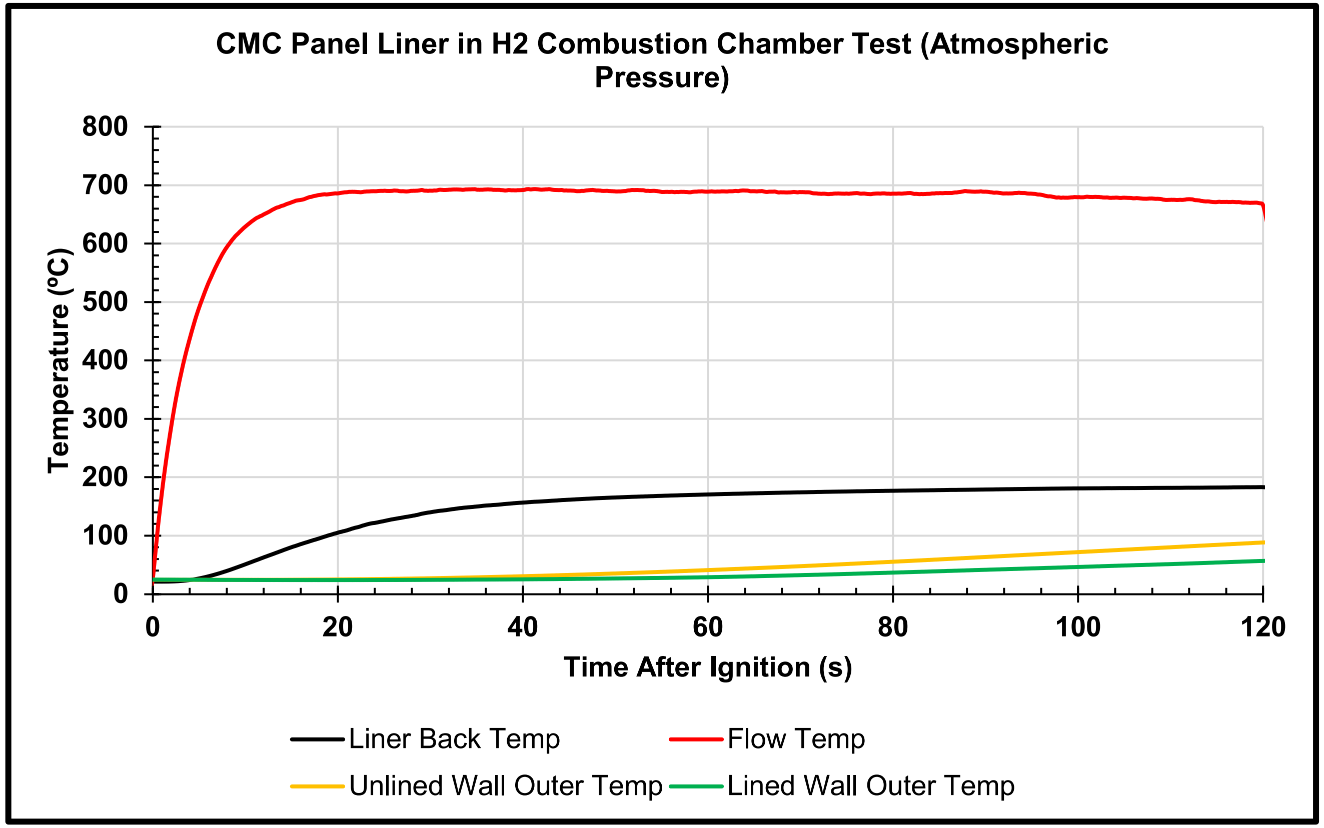
Inside Wall Temperature Thermocouple

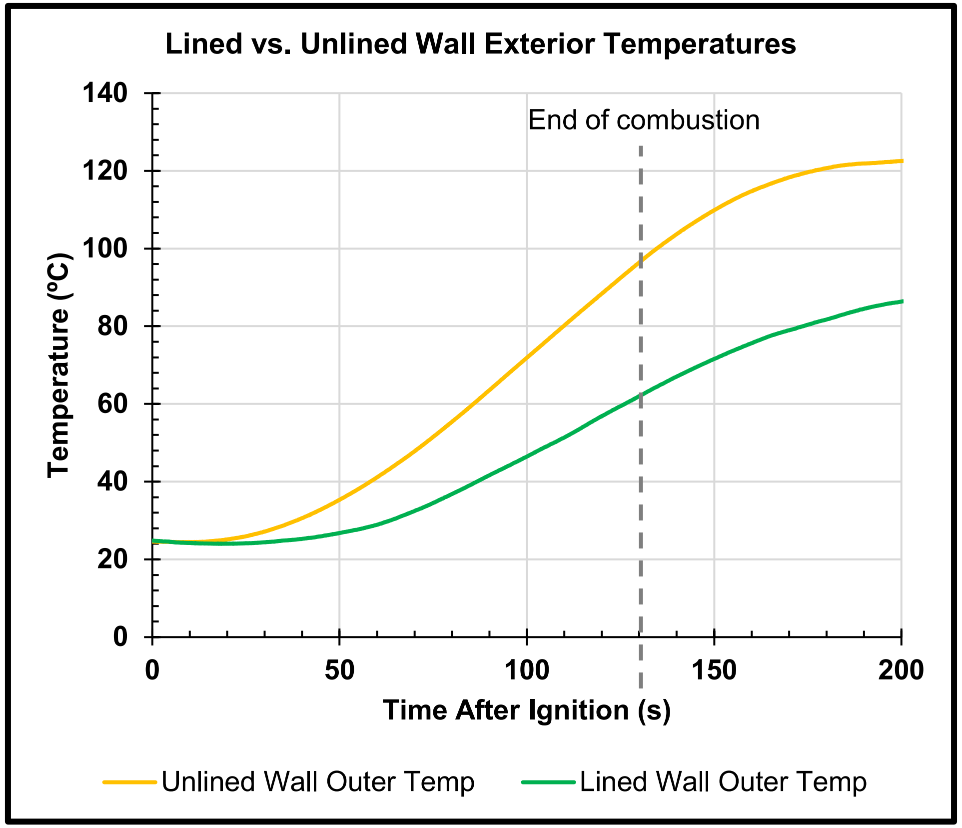
Flow Temperature Thermocouple

CMC Panel Liners

- Preliminary testing, targeting low temperatures (~700ºC) at atmospheric and pressurized conditions.
- Investigating effects of hydrogen flame traveling parallel to CMC (as opposed to through-thickness as in the torch test).
- Combustion testing duration of 2 minutes.

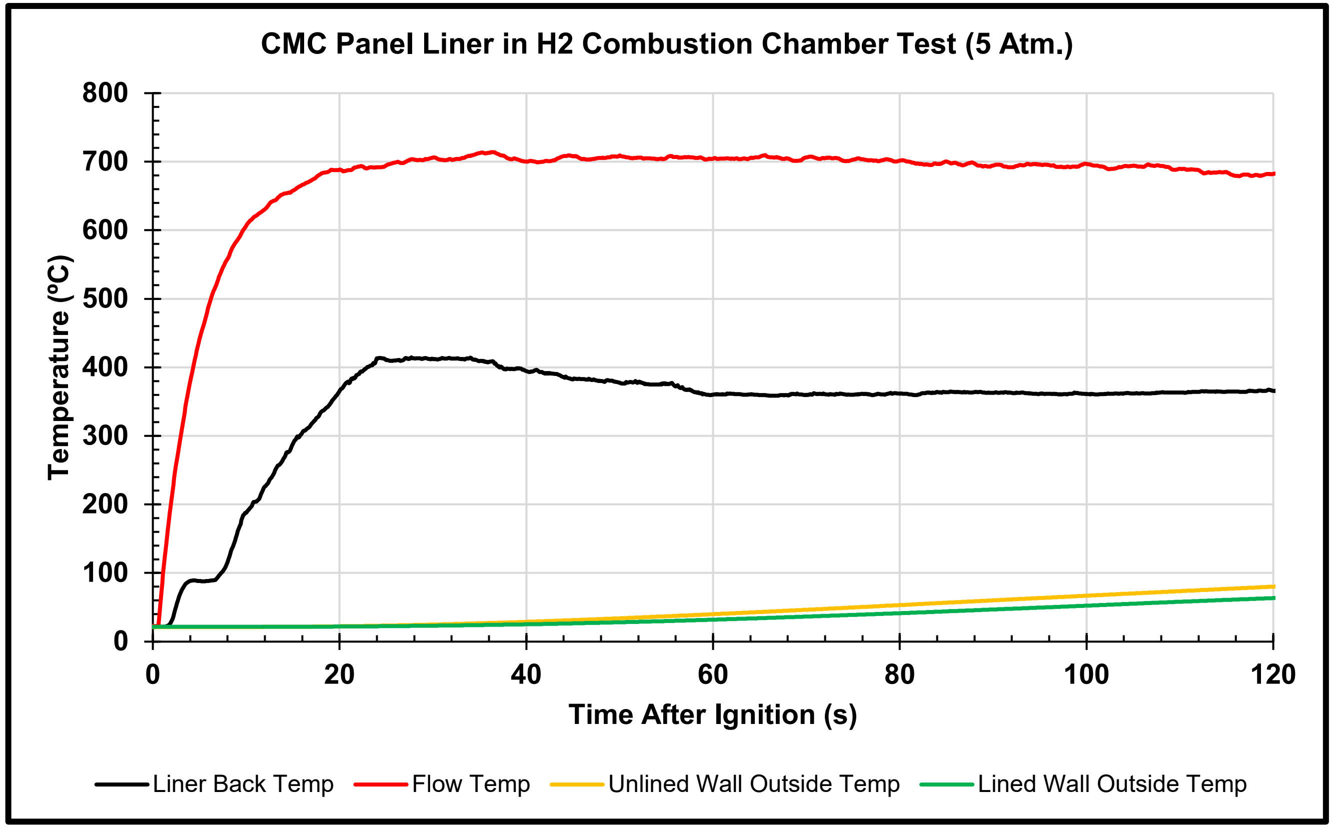
Hydrogen Combustion Chamber Test Results (1 Atm.)

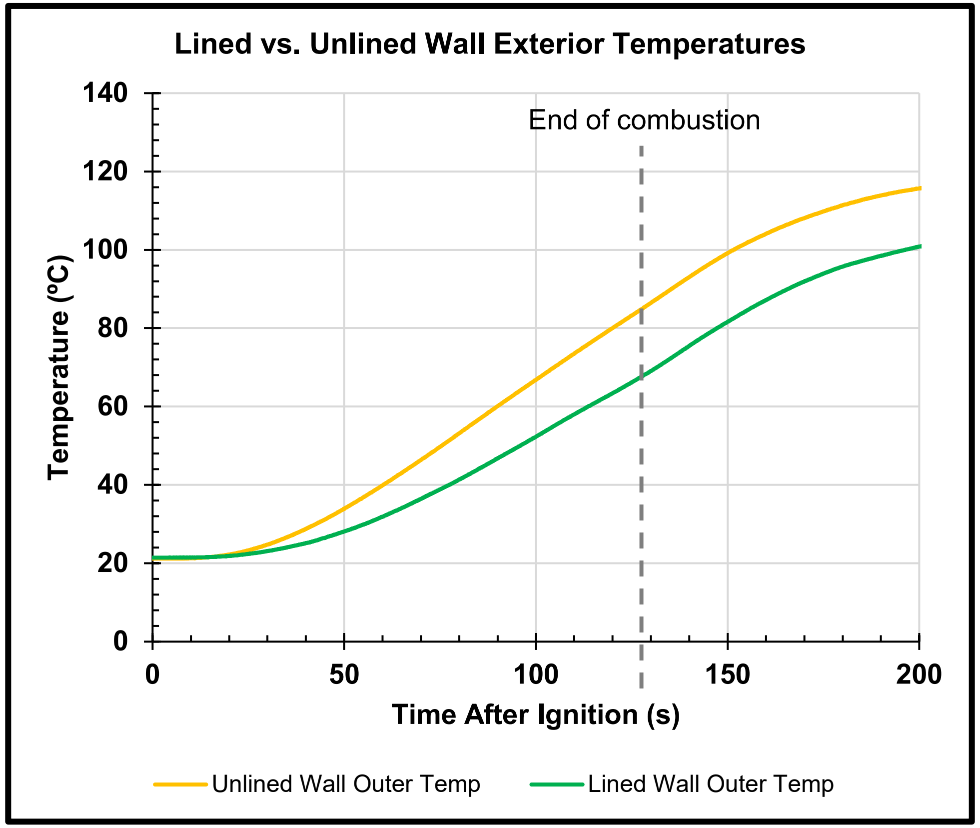




- The CMC liner withstood 2 minutes of continuous hydrogen combustion for multiple trials with no visible damage
- Flow temperature stabilized at ~680ºC while liner back face temperature did not increase past 185ºC
- Successfully protected the stainless-steel walls of the combustion chamber facility
  - Lined wall was ~32ºC cooler than unlined wall by end of combustion

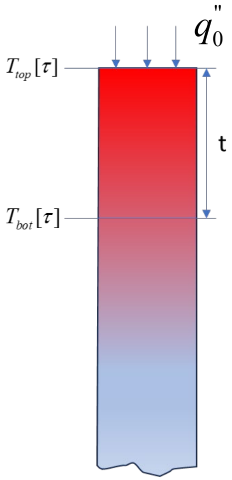
Hydrogen Combustion Chamber Test Results (5 Atm.)





- ○ While CMC liner still did not experience acute or visible damage, temperature profile was very different from atmospheric test
- ○ Flow temperature stabilized at ~700ºC and liner back face temperature rose beyond 400ºC before lowering and stabilizing ~360ºC
- ○ CMC still protected stainless-steel walls of the combustion chamber, however to a much lesser degree
  - Lined wall was only ~17ºC cooler than unlined wall by end of combustion
  - Could be explained by porosity in composite allowing pressurized hot gas to travel through voids and heat up backside of CMC

Numerical Modeling



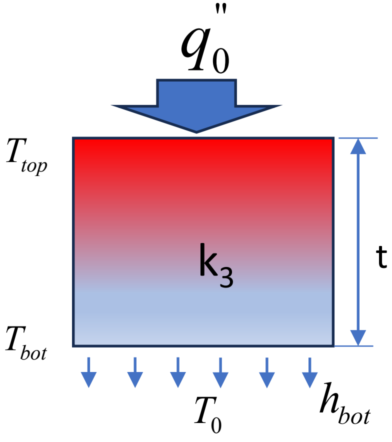
1D Transient analytical solution for given heat flux

$$T(t,\tau)-T_0=\frac{q_0''t}{k}\left(\frac{1}{\sqrt{\pi}}\frac{1}{t/(2\sqrt{\alpha\tau})}e^{-\frac{t^2}{4\alpha\tau}}-\left(1-erf\left[\frac{t}{2\sqrt{\alpha\tau}}\right]\right)\right)$$

$\alpha = k_3/\rho\gamma \quad (\mathrm{m}^2/s)$

t – –specimen thickness

τ – –time elapsed

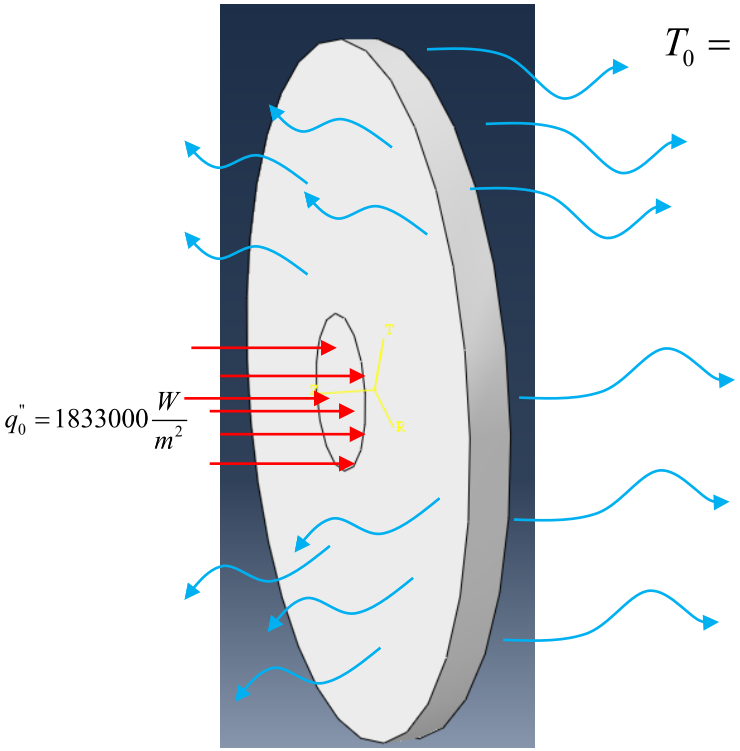


1D Steady-state analytical solution for given heat flux $\dot{q}$

$$T_{bot}=\frac{q_0''}{h_{bot}}+T_0$$

$$T_{top}=\frac{q_0''}{k_3/t}+\frac{q_0''}{h_{bot}}+T_0$$

$$T_{top}-T_{bot}=\frac{q_0''}{k_3/t}$$



$T_0=T_\infty=22^oC$

Convective cooling

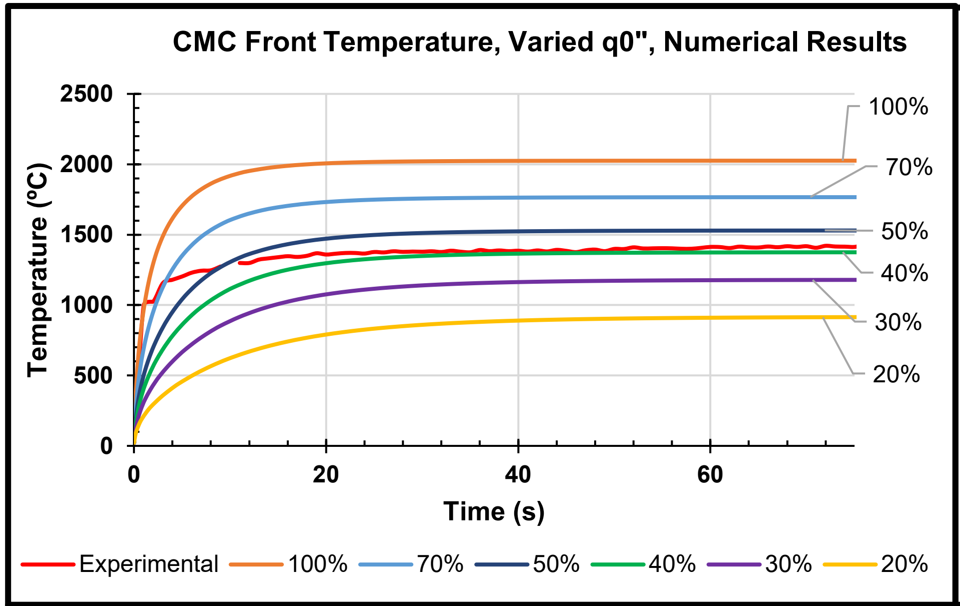
$h = 200 - 400\,\frac{W}{m^2K}$

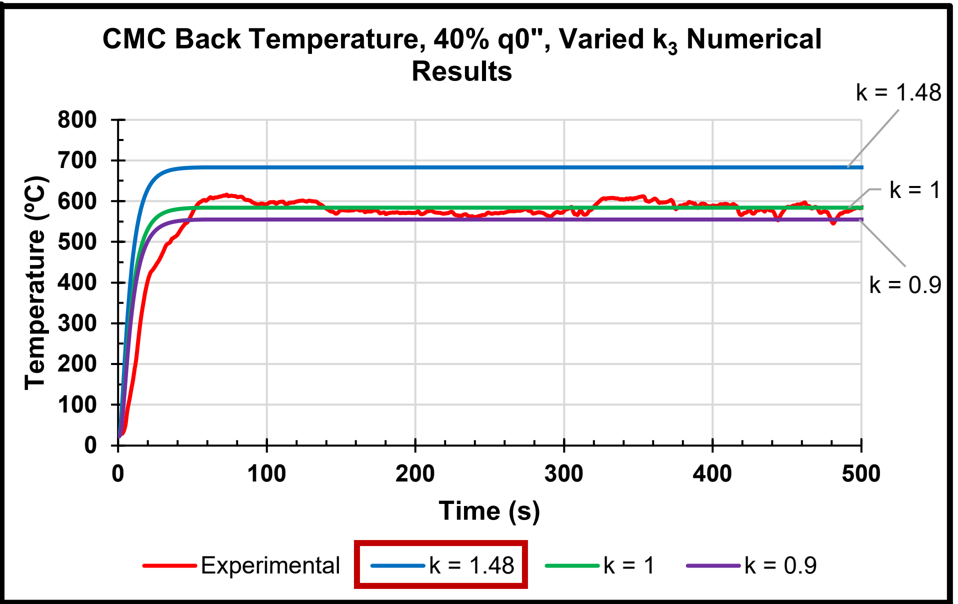
and

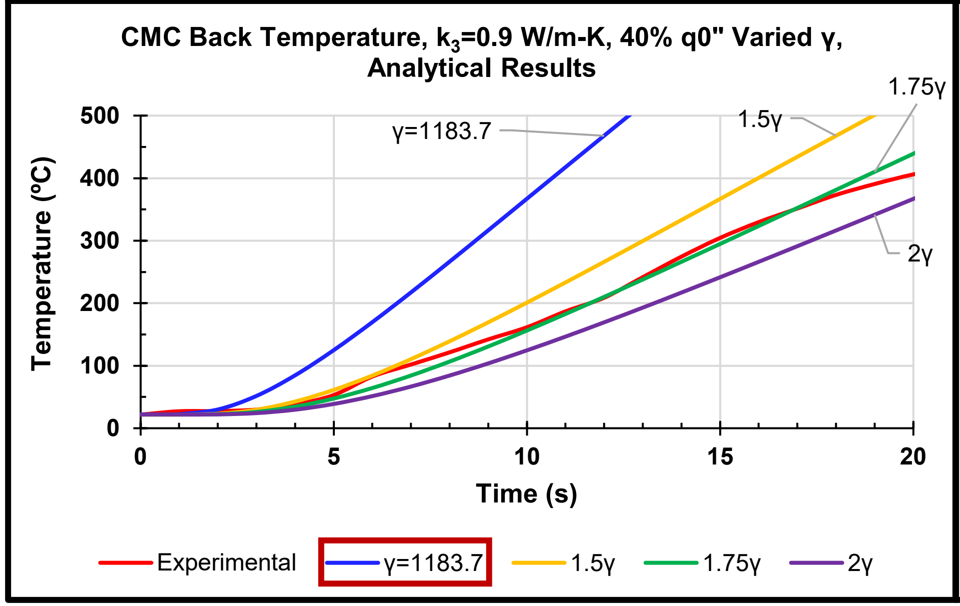
radiation

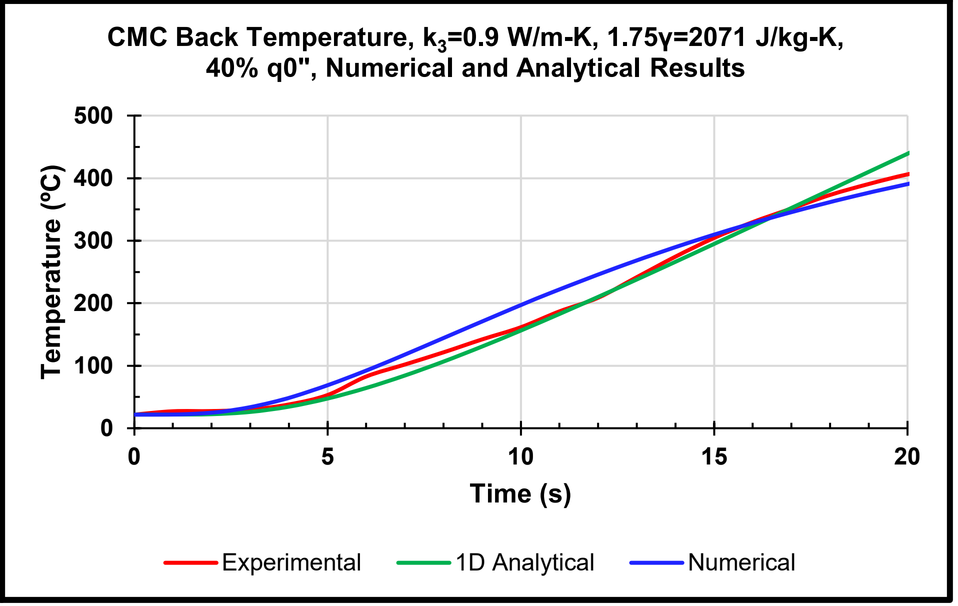
Numerical modeling of torch test data used to match experimentally measured T_{top} and T_{bot} to determine absorbed heat flux q_0'', through-thickness conduction coefficient k_3, and specific heat $\boldsymbol{\gamma}$

Numerical Modeling


CMC Front Temperature, Varied q0", Numerical Results


CMC Back Temperature, 40% q0", Varied k_3 Numerical Results

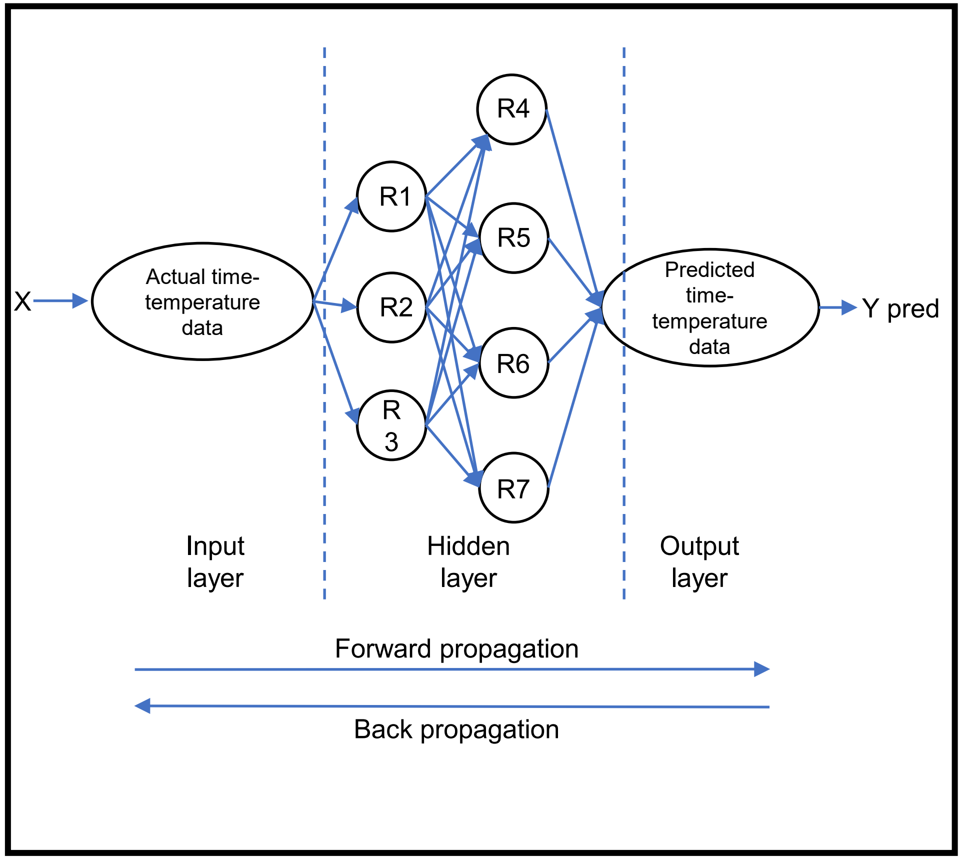

CMC Back Temperature, k_3=0.9 W/m-K, 40% q0" Varied γ, Analytical Results

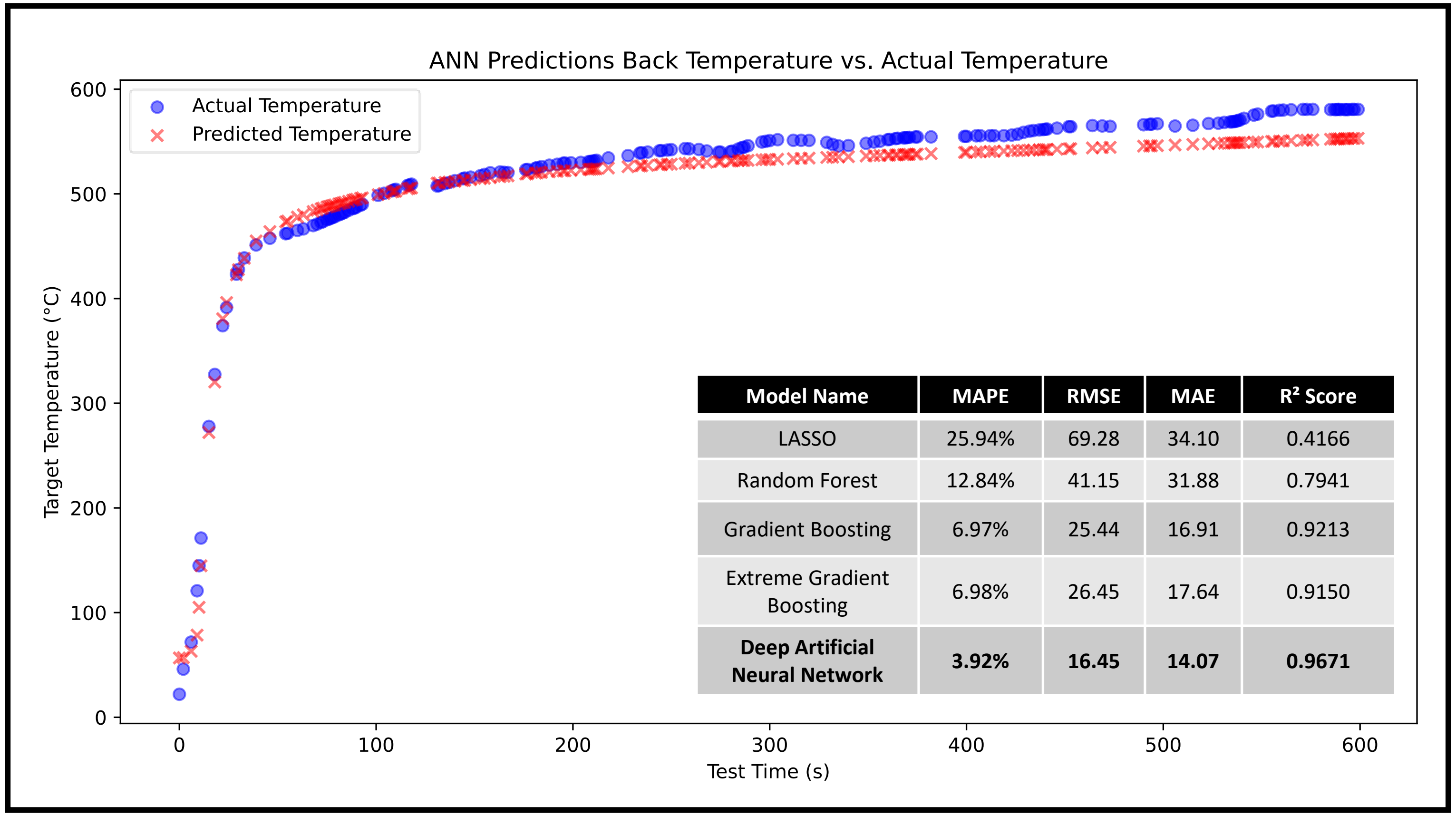

CMC Back Temperature, k_3=0.9 W/m-K, 1.75γ=2071 J/kg-K, 40% q0", Numerical and Analytical Results

Boxed values are theoretical based on fiber volume fraction

- Sample absorbed heat flux lower than what applied by torch
  - Heat reflection is a characteristic of YSZ
- Through thickness conduction coefficient lower than theoretical value
  - Caused by voids in matrix
- Specific heat higher than theoretical value
  - Likely from water vapor in voids in matrix

Deep Artificial Neural Network Modeling

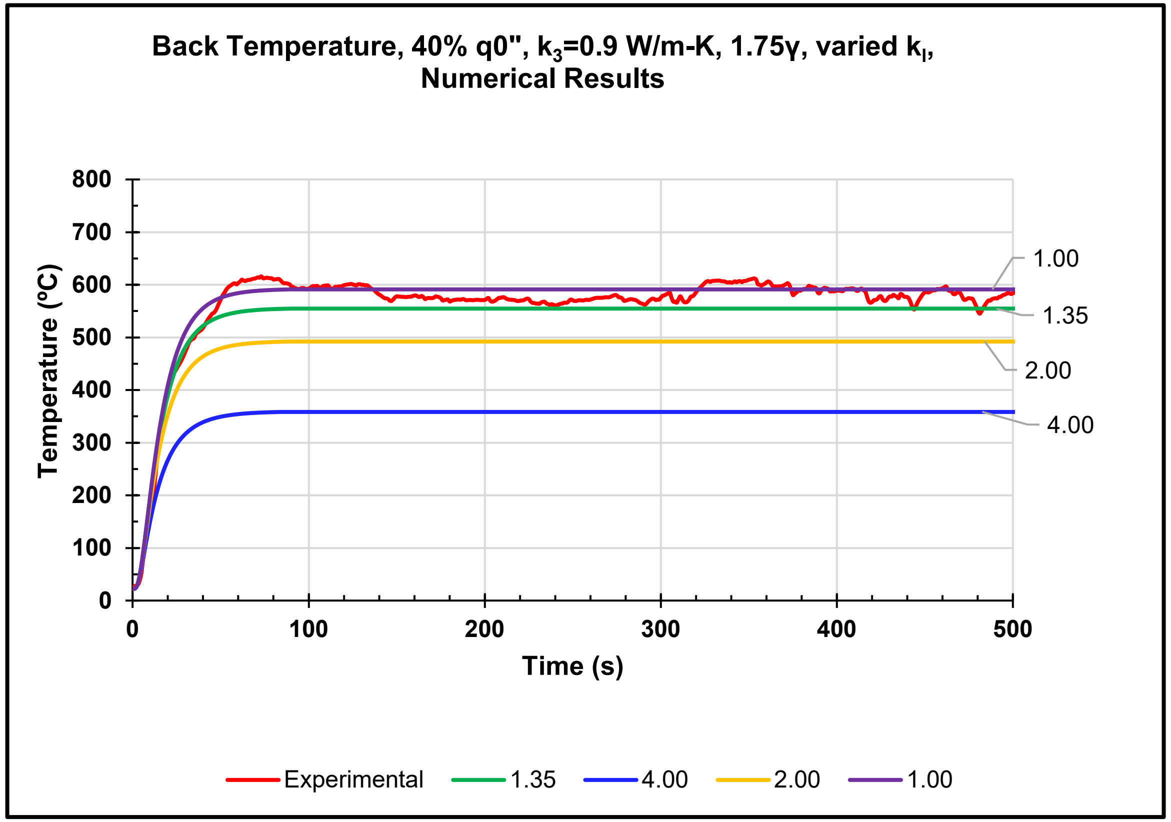




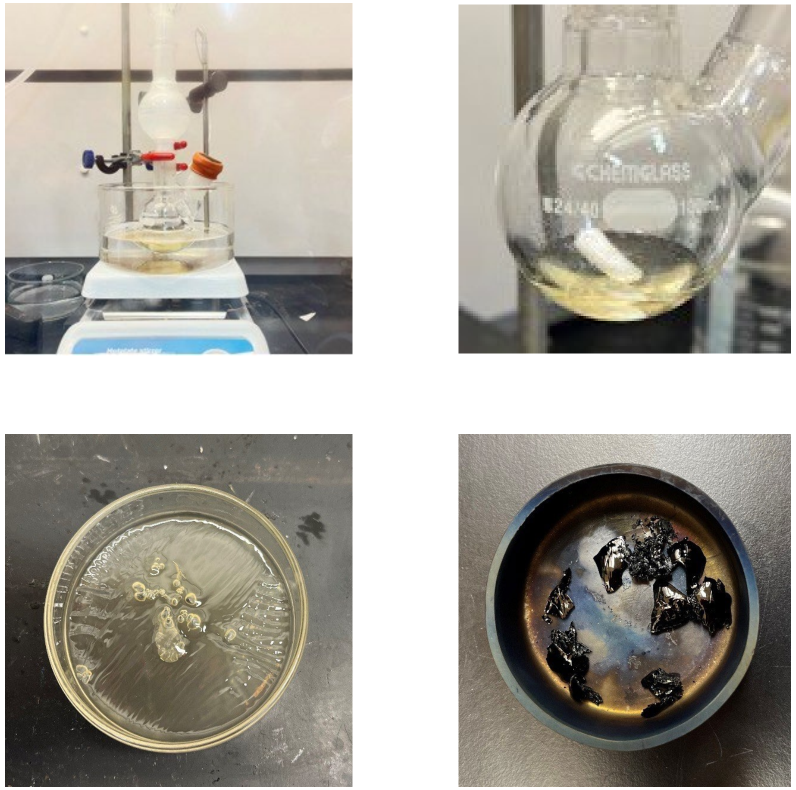
Model Name	MAPE	RMSE	MAE	R^2 Score
LASSO	25.94%	69.28	34.10	0.4166
Random Forest	12.84%	41.15	31.88	0.7941
Gradient Boosting	6.97%	25.44	16.91	0.9213
Extreme Gradient Boosting	6.98%	26.45	17.64	0.9150
Deep Artificial Neural Network	**3.92%**	**16.45**	**14.07**	**0.9671**

- Machine learning techniques are being explored to predict the ablation performance of the CMCs during the H2/Air torch test.
- ML models to predict long-term ablation performance will be developed based on material formulations, manufacturing parameters, and H2 combustion testing parameters.

Synthesized Si(B)CN Pre-Ceramic for Surface Treatment



Back Temperature, 40% q0", k_3=0.9 W/m-K, 1.75γ, varied k_l, Numerical Results



- Numerical analysis of CMC behavior shows that a higher in-plane conduction coefficient, kl, would result in significant decrease in back-face temperature during hydrogen flame exposure.
- As such, a Si(B)CN pre-ceramic polymer is being synthesized at UCF Composites Laboratory for potential use as a matrix or surface coating of CMC to increase in-plane heat dissipation, reducing thermal shock, hot spots, and back-face temperature.

Conclusions & Future Work

- The proposed CMC formulation and processing technique show promise for use in H_2 combustion environments.

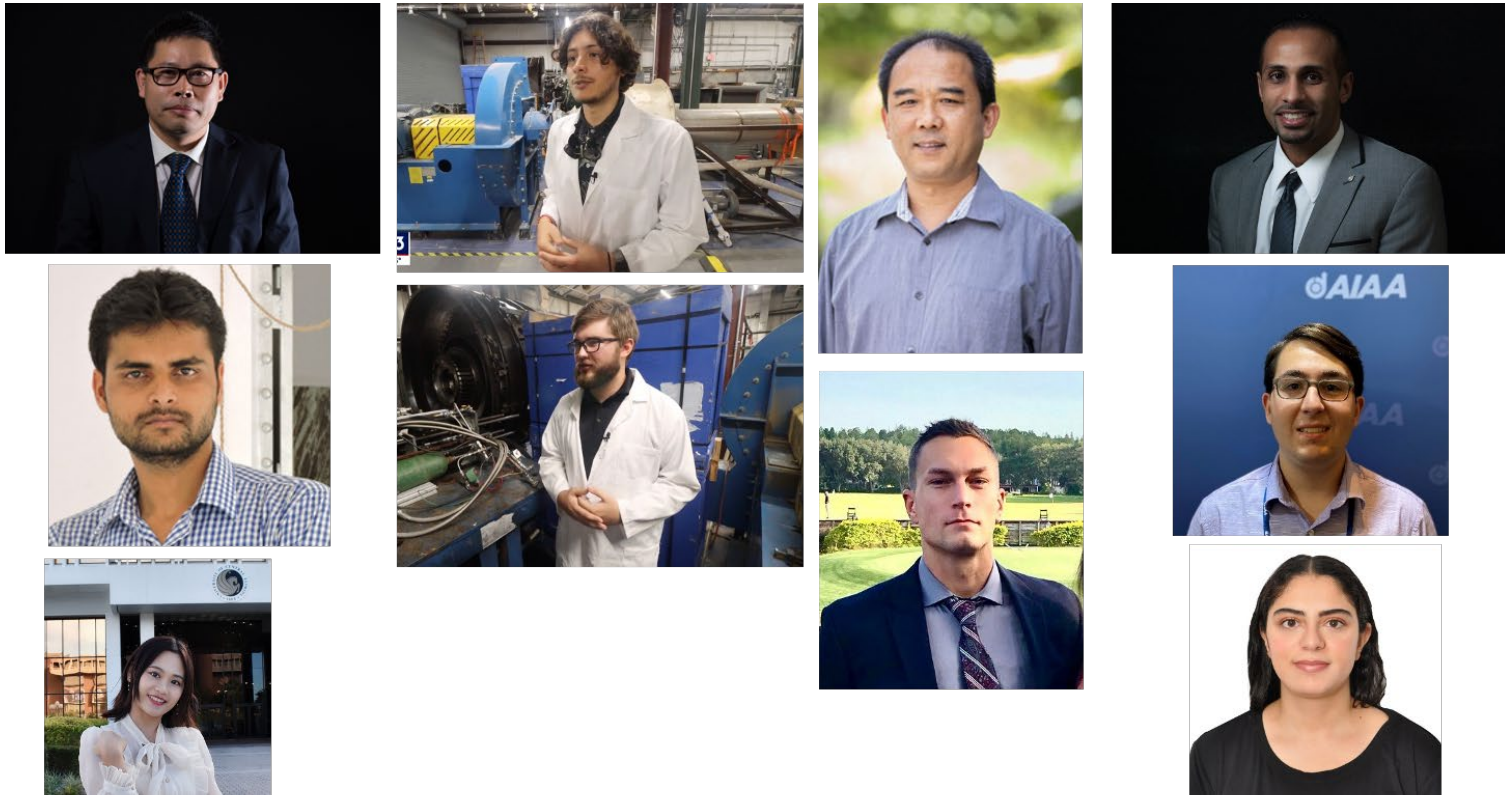
- Direct H_2 flame exposure at high heat flux resulted in minimal damage to the CMCs, and post-damage characterization shows favorable behavior by way of silica (SiO_2) formation.

- The reduced insulation effectiveness of the CMCs at higher pressures suggest the need to further densify the material through more PIP cycles, reducing porosity and increasing thermal performance.

- A densification study will be carried out to identify optimal number of PIP cycles by measuring mass gained per subsequent cycle and using Micro-CT to assess porosity at each step.

- A full-sized CMC combustion liner will be manufactured using the material formulation presented, and larger time scale testing will be conducted to investigate long-term H_2 combustion effects and survivability.

Acknowledgements



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