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

Ceramic Matrix Composites for H_2 Combustion

(FE003228)

Christopher Varela, *Yiting Wang, Michael Tonarely, Kareem Ahmed, Jihua Gou*

University of Central Florida, Orlando, FL

David Barnhard, Qingda Yang
University of Miami, Miami, FL

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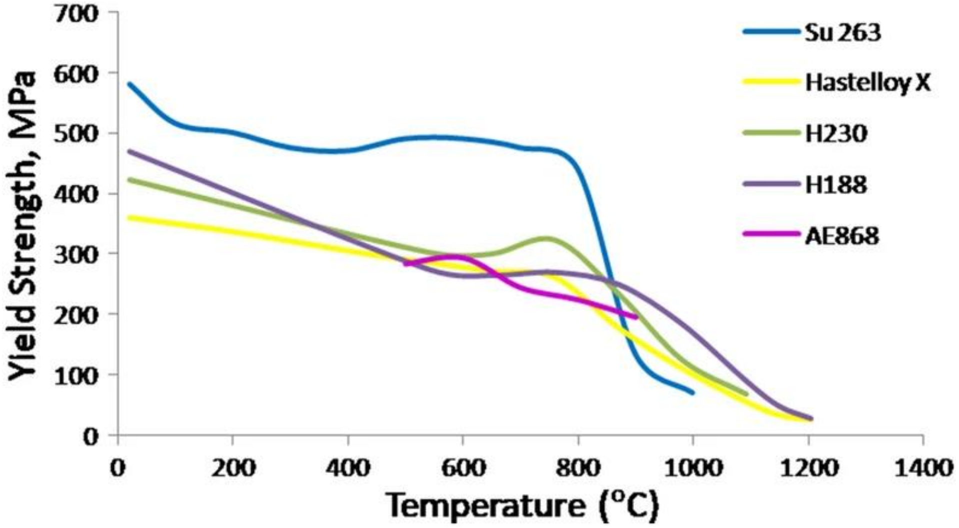
Background

- 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.

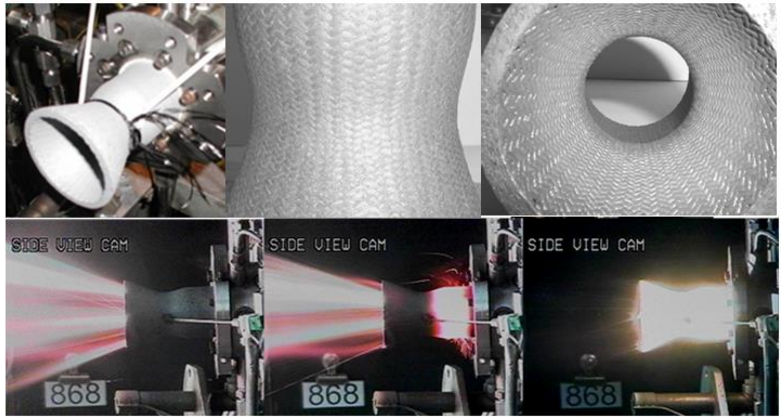


Strength of various superalloys in combustor and afterburner application.
*(*https://doi.org/10.1007/s41745-022-00295-z*)*

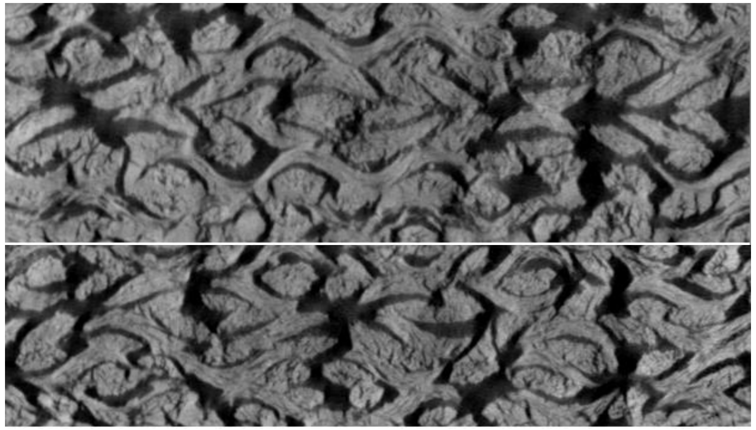
Ceramic Matrix Composites (CMCs)

- 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.

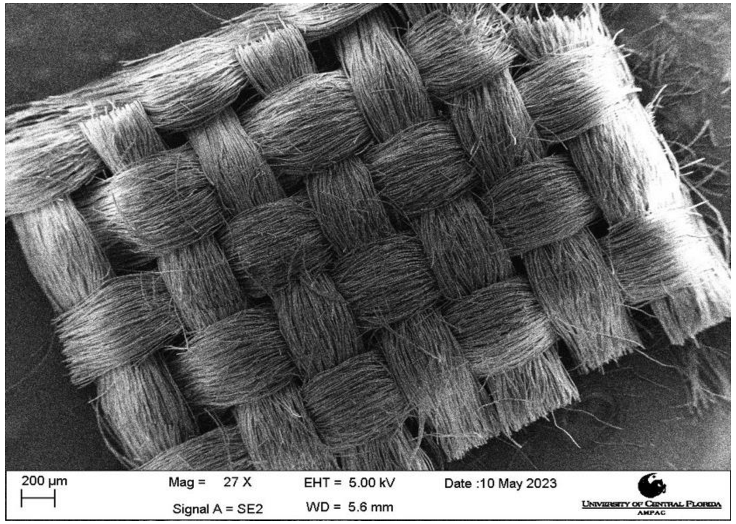


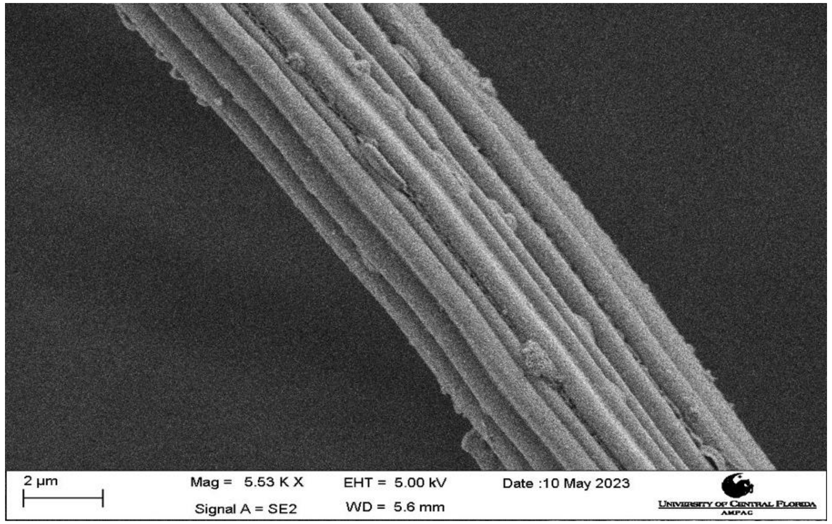
Cf/ZrC CMC combustion chamber undergoing oxygen-hydrogen hot fire testing.
(https://ultramet.com/ceramic-matrix-composites/ceramic-matrix-composites-performance/)



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

Material Selection: YSZ Fiber



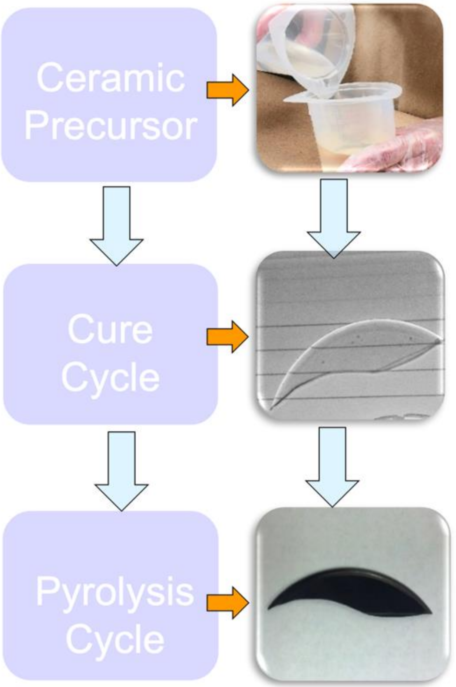


- **Yttria-Stabilized Zirconia (YSZ) is the ceramic fiber used in the CMCs**
  - Currently used in thermal barrier coatings.
  - Melting point of 2,590ºC with continuous use limit of 2,200ºC.
  - Excellent performance in corrosive & oxidizing environments.
  - High porosity of woven YSZ results in effective wetting and solution retention.
  - Phase-stabilized with Yttria eliminates disruptive phase transitions.

- **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.

Material Selection: Ceramic Matrices

- When selecting ceramic precursor, factors such as ceramic yield, processing ability, and thermal performance should be considered.



Ceramic Precursor

Cure Cycle

Pyrolysis Cycle

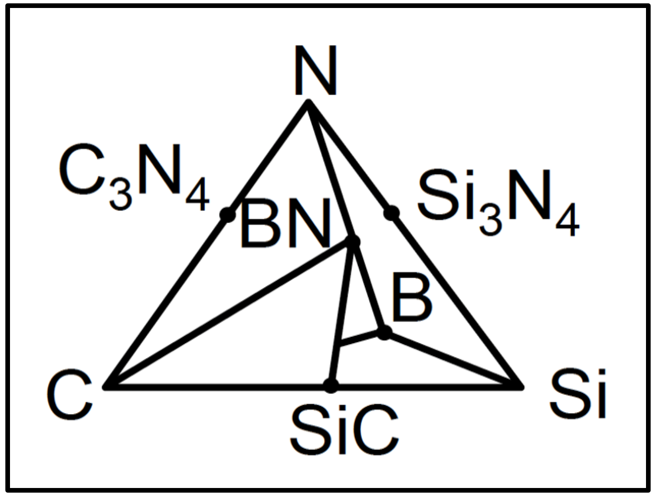
Polymer to Ceramics:

- Low cost
- Near net shape manufacturing
- Outstanding thermo-chemical stability

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%

Commercially available preceramic polymers

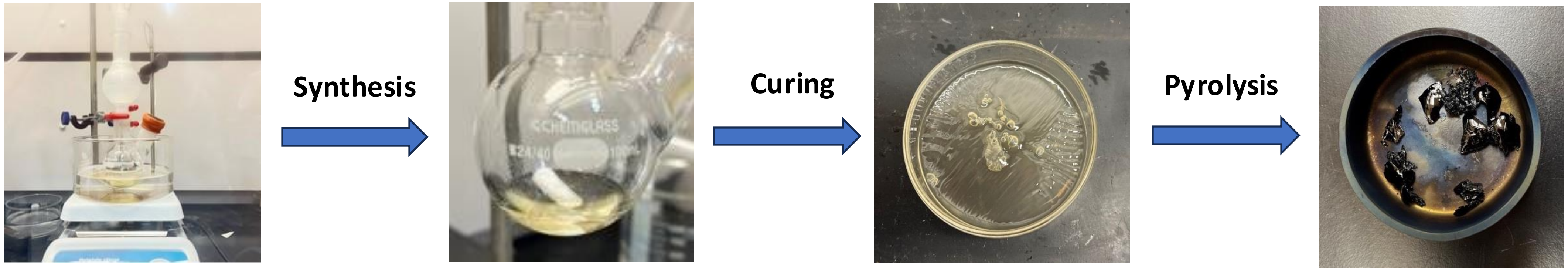
Ceramic Matrix Design: Adding Boron to Preceramic Precursor

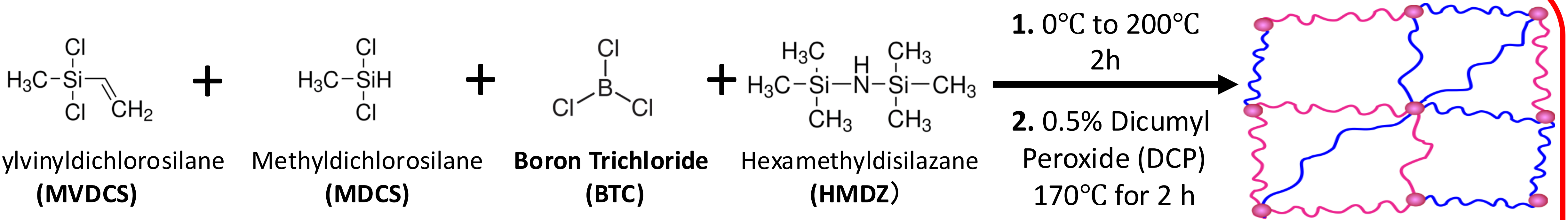


Amorphous Ceramic Si(B)CN

- **Boron** significantly enhances the **high-temperature stability**.
- The presence of **boron delays** the onset of **crystallization**, enabling the material to maintain its amorphous structure at higher temperatures and maintaining **structural integrity** of the CMC.
- By forming protective borosilicate glass layer, enhancing **resistance to oxidation**.
- The incorporation of boron leads to the formation of stronger bonds, providing Si(B)CN ceramics with **high flexural strength**, even at elevated temperatures.

Synthesis, Curing and Pyrolysis of Si(B)CN Ceramic





Methylvinyldichlorosilane **(MVDCS)** + Methyldichlorosilane **(MDCS)** + **Boron Trichloride (BTC)** + Hexamethyldisilazane **(HMDZ)**

1. 0℃ to 200℃ 2h

2. 0.5% Dicumyl Peroxide (DCP) 170℃ for 2 h

Crosslinked Si(B)CN preceramic polymer **(PSNB)**

Ratio of reactants: MVDCS:MDCS:BTC:HMDZ = 1:1:1:6

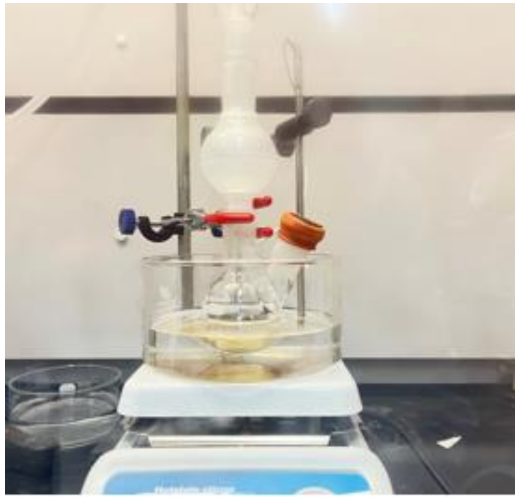
- Synthesis procedures of the Si(B)CN preceramic polymer precursor in the
- Curing was conducted in presence of 0.5% Dicumyl Peroxide (DCP) at 170℃ for 2 hours.
- Pyrolysis was conducted at 850℃ for 2 hours.

Synthesis, Curing and Pyrolysis of Si(B)CN Ceramic

PSNB : A liquid polyborosilazane precursor for Si–B–C–N ceramic by co-condensation reaction

Synthesis (Nitrogen)

- Boron Trichloride (BTC)
- Methylvinyldichlorosilane (MVDCS)
- Methyldichlorosilane (MDCS)
- Hexamethyldisilazane (HMDZ)

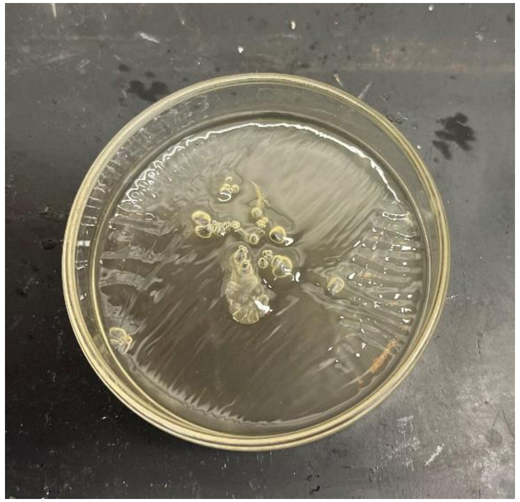


Drying (Nitrogen)

- At 200 ℃ for 1 h in vacuum
- PSNB was obtained as a light yellow viscous liquid

Curing (Nitrogen)

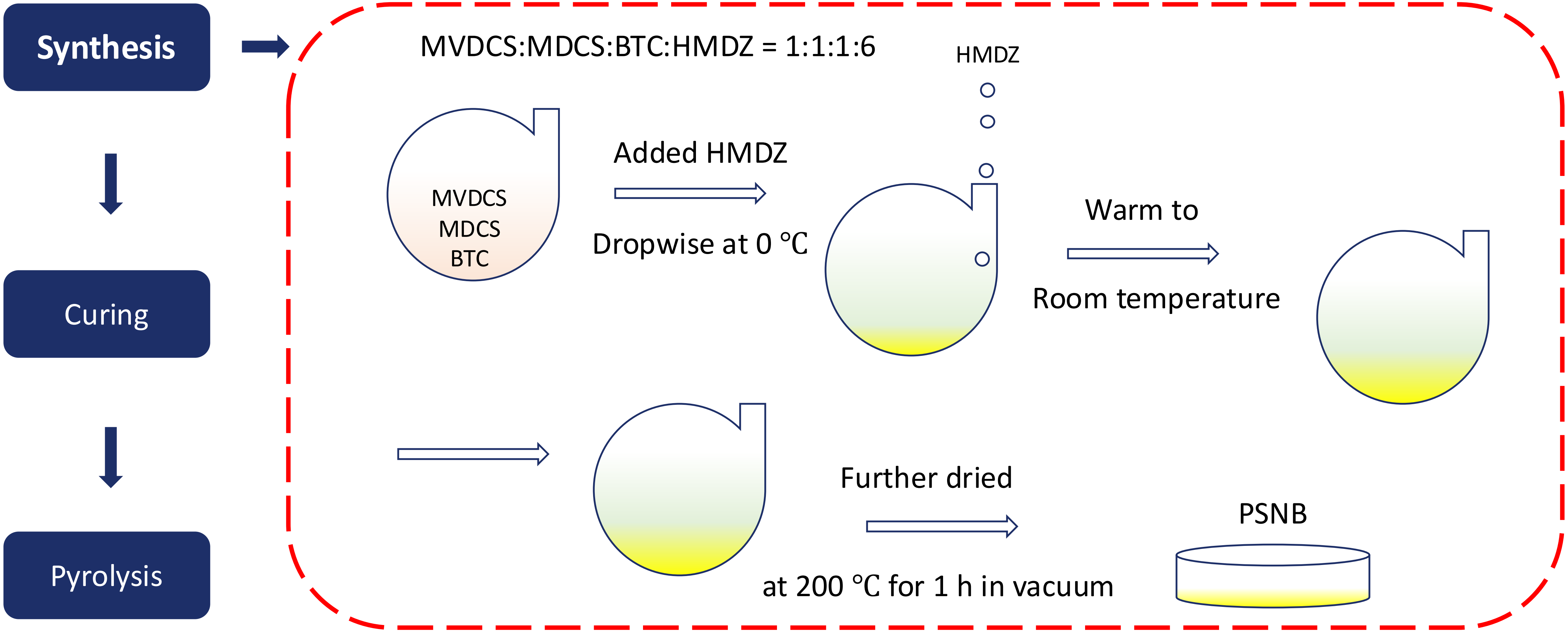
- Dicumyl Peroxide (DCP) of 0.5 wt% was added
- Obtained a hard bulk cured PSNB with light yellow color



Pyrolysis (Argon)

- At a heating rate of 5 ℃/min
- 850 ℃ for 2 h
- Got black and glassy sample

Synthesis of Si(B)CN Preceramic Polymer



Synthesis

Curing

Pyrolysis

MVDCS:MDCS:BTC:HMDZ = 1:1:1:6

HMDZ

MVDCS
MDCS
BTC

Added HMDZ

Dropwise at 0 ℃

Warm to

Room temperature

Further dried

at 200 ℃ for 1 h in vacuum

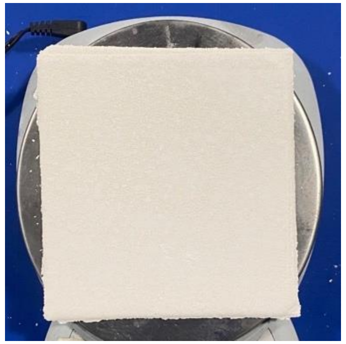
PSNB

Synthesis of Si(B)CN preceramic polymer using the Schlenk Line technique

Manufacturing of CMCs through the PIP Process

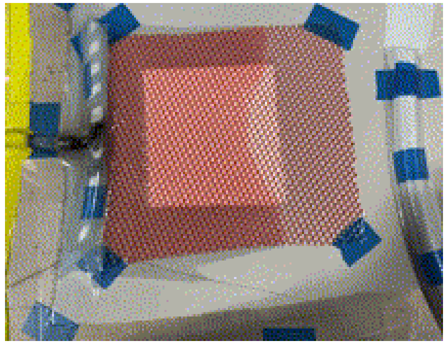
- Polymer Infiltration and Pyrolysis (PIP) is the manufacturing method used in this study
  - Relative ease and low cost of manufacturing make PIP an attractive option compared to other CMC manufacturing methods
  - Volatilization of organic compounds in ceramic precursors result in very high initial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



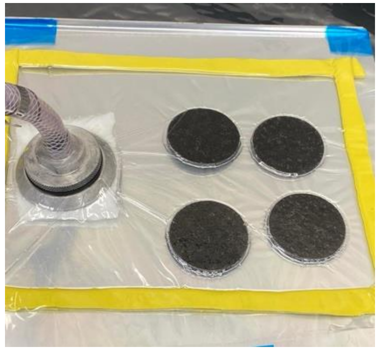
The polymer-infused laminate is cured in autoclave for 1 hour at 180ºC then 2 hours at 200ºC

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

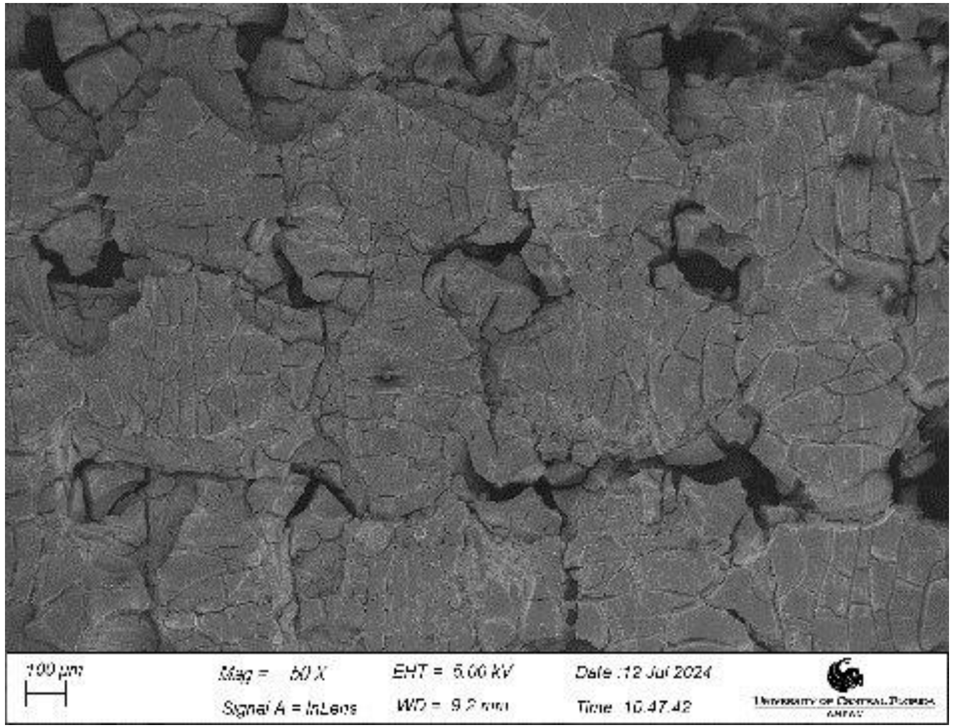
CMCs are reinfiltrated with more pre-ceramic polymer and cured in autoclave again



This ‘densifies’ the composite and reduces porosity

Reinfiltrated samples are pyrolyzed again under same conditions

SEM & EDS Characterization



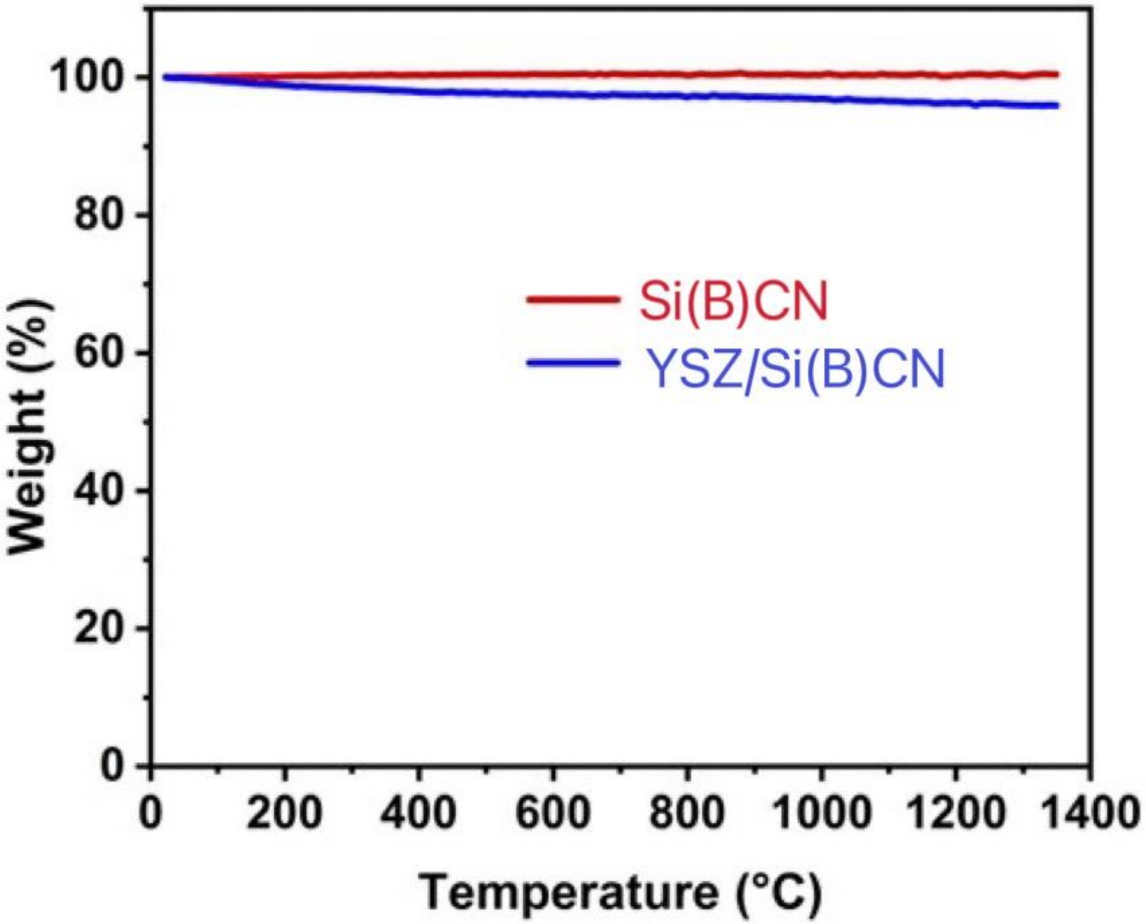
Element Line	*Weight %*	*Weight % Error*	*Atom %*	*Atom % Error*
B K	2.1	± 0.1	5.4	± 0.4
C K	9.3	± 0.2	21.4	± 0.4
N K	2.9	± 0.3	5.8	± 0.6
O K	22.2	± 0.2	38.3	± 0.4
Si K	14.6	± 0.2	14.4	± 0.2
Zr L	48.8	± 0.9	14.7	± 0.3
Zr M	---	---	---	---
Total	100.0		100.0	

- The SEM and EDS analysis has confirmed the presence of elemental Zr, **B**, Si, C, and N.
- The fabrication of YSZ/Si(B)CN ceramic matrix composites was successful.

Thermogravimetric Analysis (TGA)

Thermal Stability of Ceramic Matrix and CMC

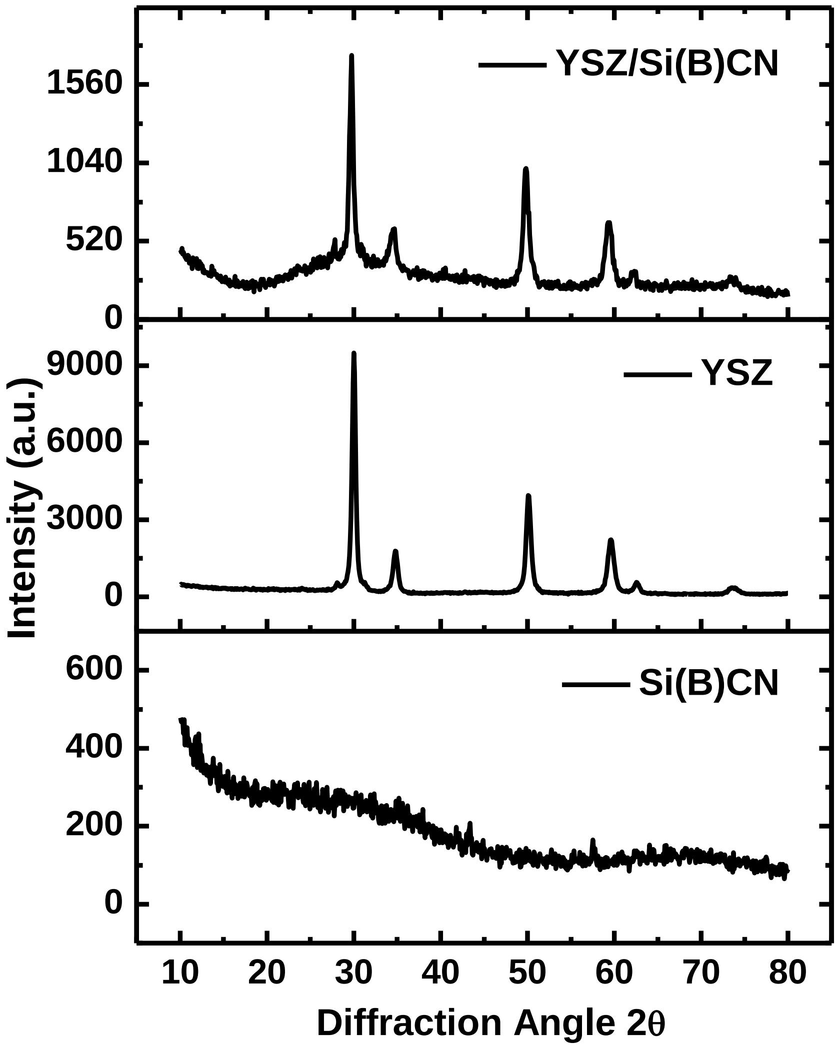
- Si(B)CN: almost no weight loss was observed at1,350℃.
- YSZ/Si(B)CN: ~4% weight loss was measured at1,350℃.



X-Ray Diffraction (XRD) Analysis

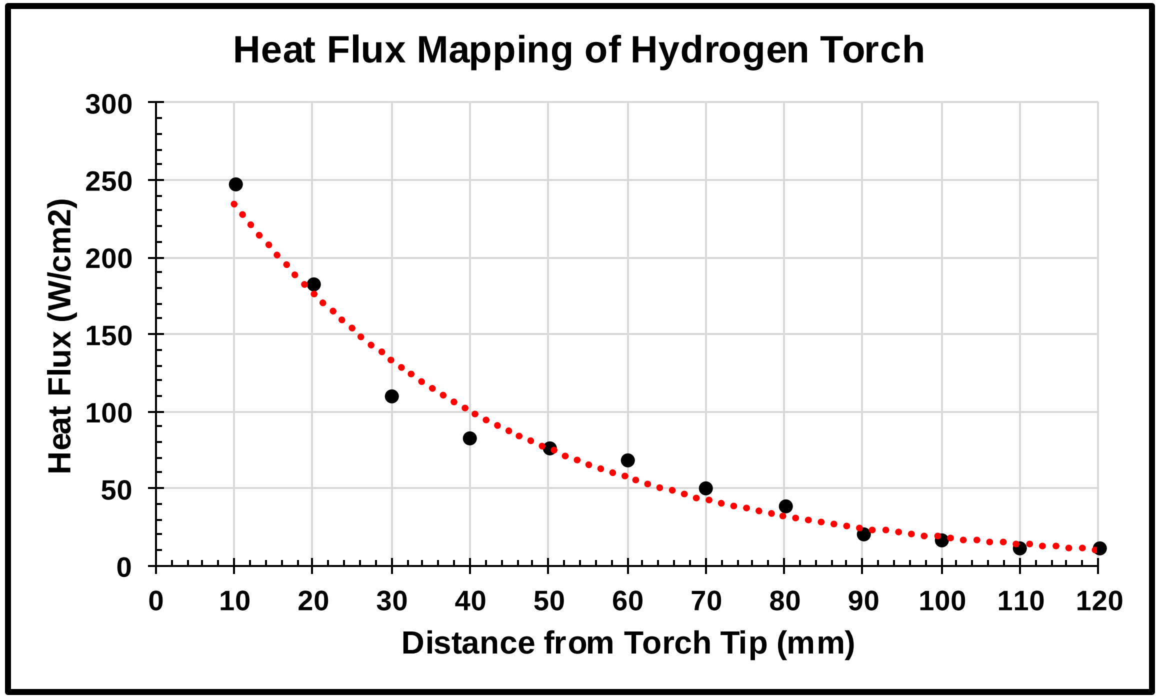
Phase Analysis of Ceramic Matrix and CMC

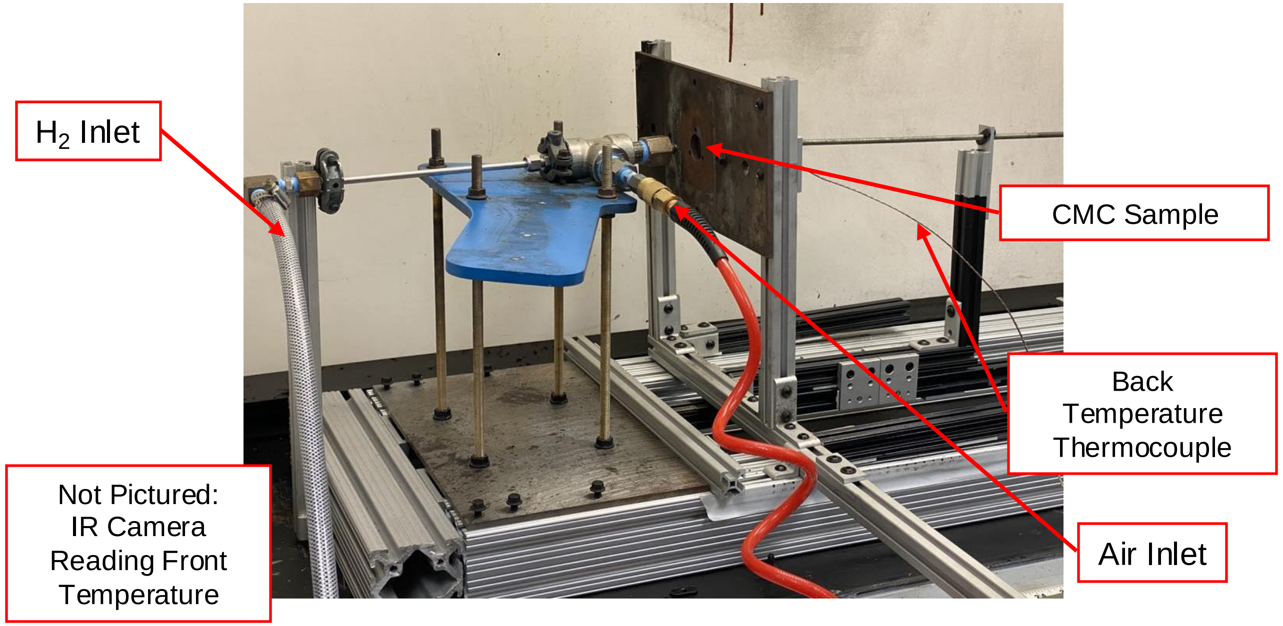
- ☐ The XRD analysis suggested the Si(B)CN matrix after the pyrolysis remained in an amorphous state
- ☐ The crystallinity in the YSZ/Si(B)CN composite arose from the presence of the YSZ fiber.



Hydrogen-Air Torch Test for Material Screening

- 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

CMC Sample

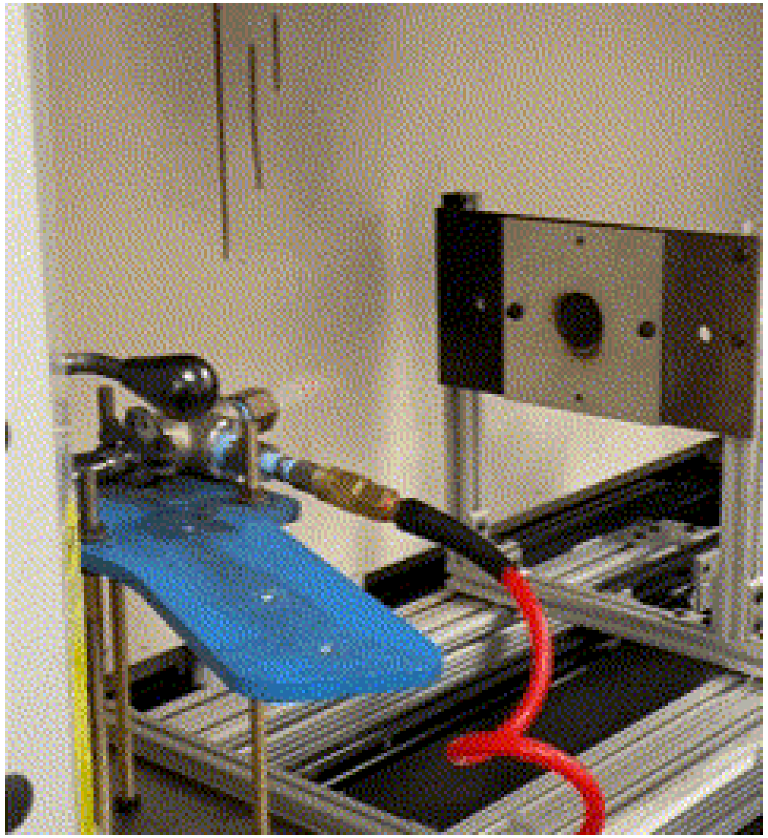
Back Temperature Thermocouple

Air Inlet

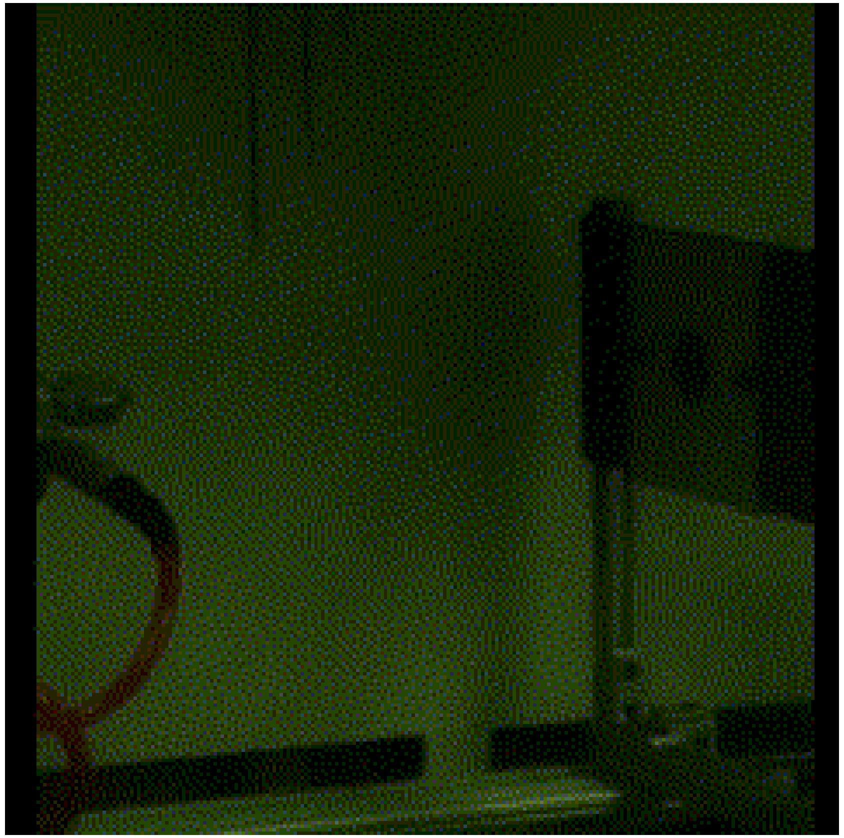
Not Pictured:
IR Camera Reading Front Temperature

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

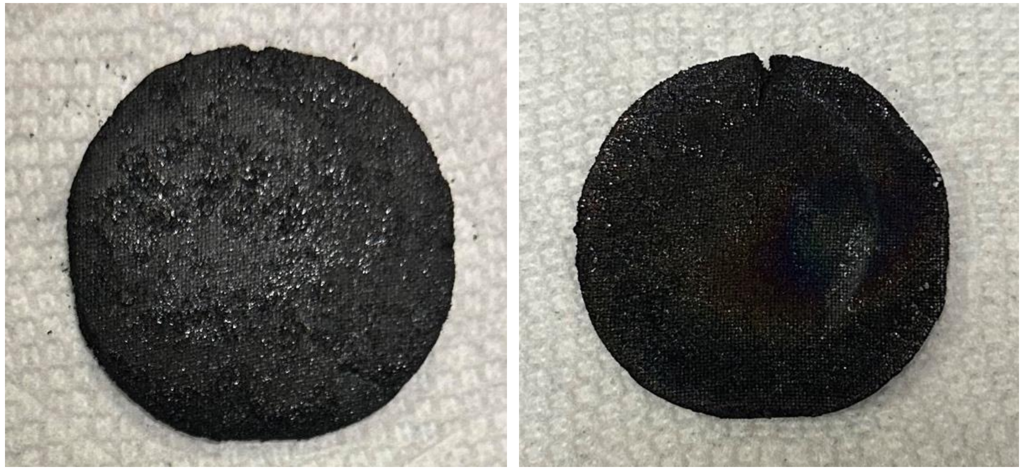


Oxyacetylene Torch Test

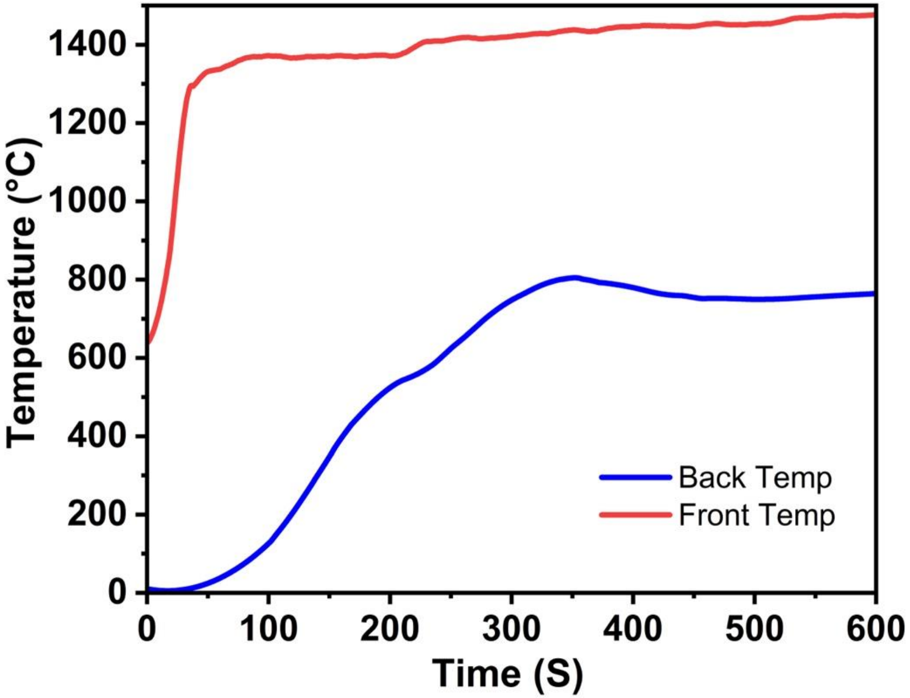


H2/Air Torch Test

Hydrogen-Air Torch Test Results



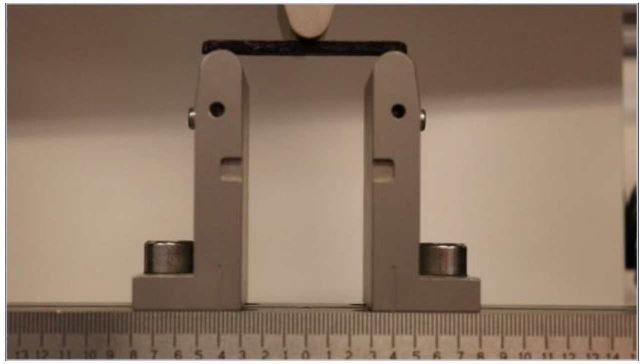
The CMC sample before and after the 10-minute H2/Air torch test.



The front and back temperature plots of the CMC during 10-minute H_2/Air torch test.

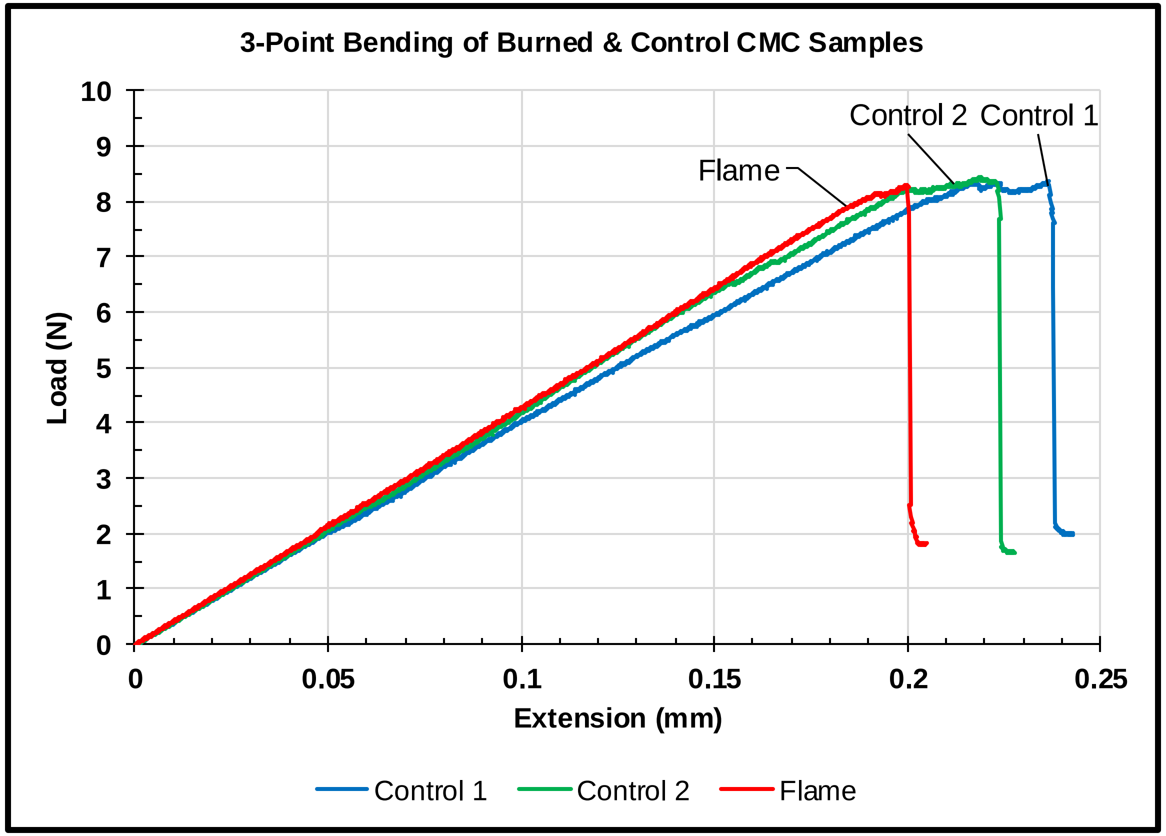
- The YSZ/Si(B)CN ceramic matrix composites withstood 10 minutes of continuous hydrogen combustion for multiple trials without visible damage.

Post-Torch Test: Mechanical Property Characterization

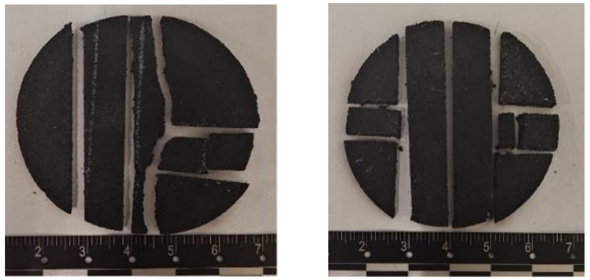


$$E_f = \frac{L^3}{4bh^3}\left(\frac{dP}{dw}\right) \qquad \sigma_f = \frac{3PL}{2bh^2}$$

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



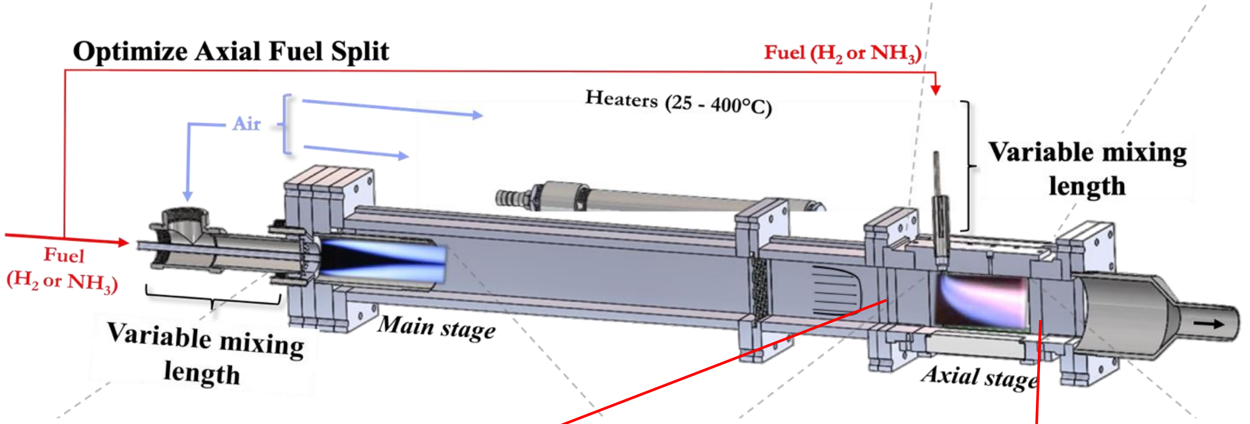
Sample	ΔP/Δw (N/mm)	P_{max} (N)	$w(P_{max})$ (mm)	σ_f (MPa)	E_f (GPa)
Control 1	40.819	8.363	0.168	7.73	3.78
Control 2	43.909	8.433	0.170	8.01	4.19
Flame	43.419	8.288	0.153	7.88	4.17



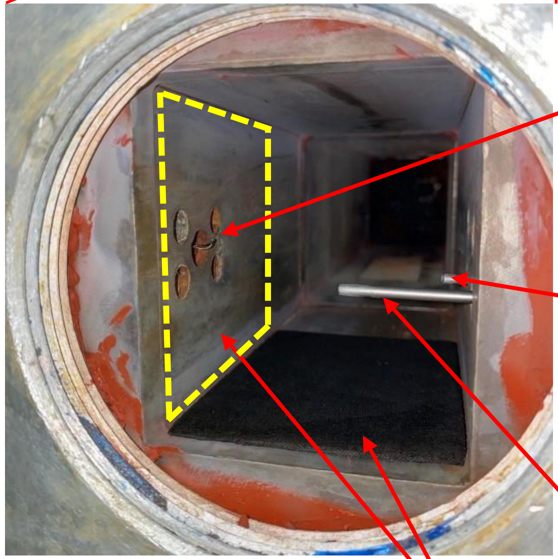
- Hydrogen flame damage had minimal effect on mechanical strength
- Matrix enhanced fracture strength (YSZ Tow $\sigma_f = 1.5\ MPa$)
- Average Values
  - $\sigma_f = 7.87 \pm 0.16$ MPa
  - $E_f = 4.05 \pm 0.26$ GPa
  - $P_{max} = 8.36 \pm 0.08$ N

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

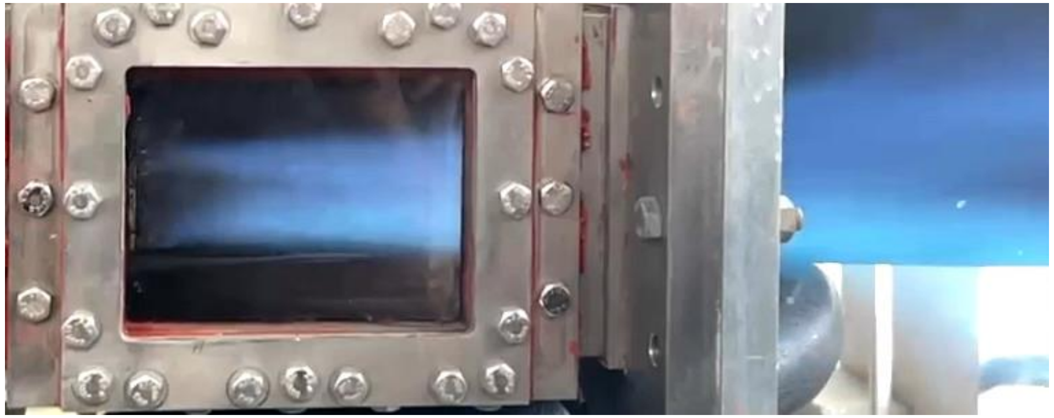


CMC Back Temperature Thermocouple

Inside Wall Temperature Thermocouple

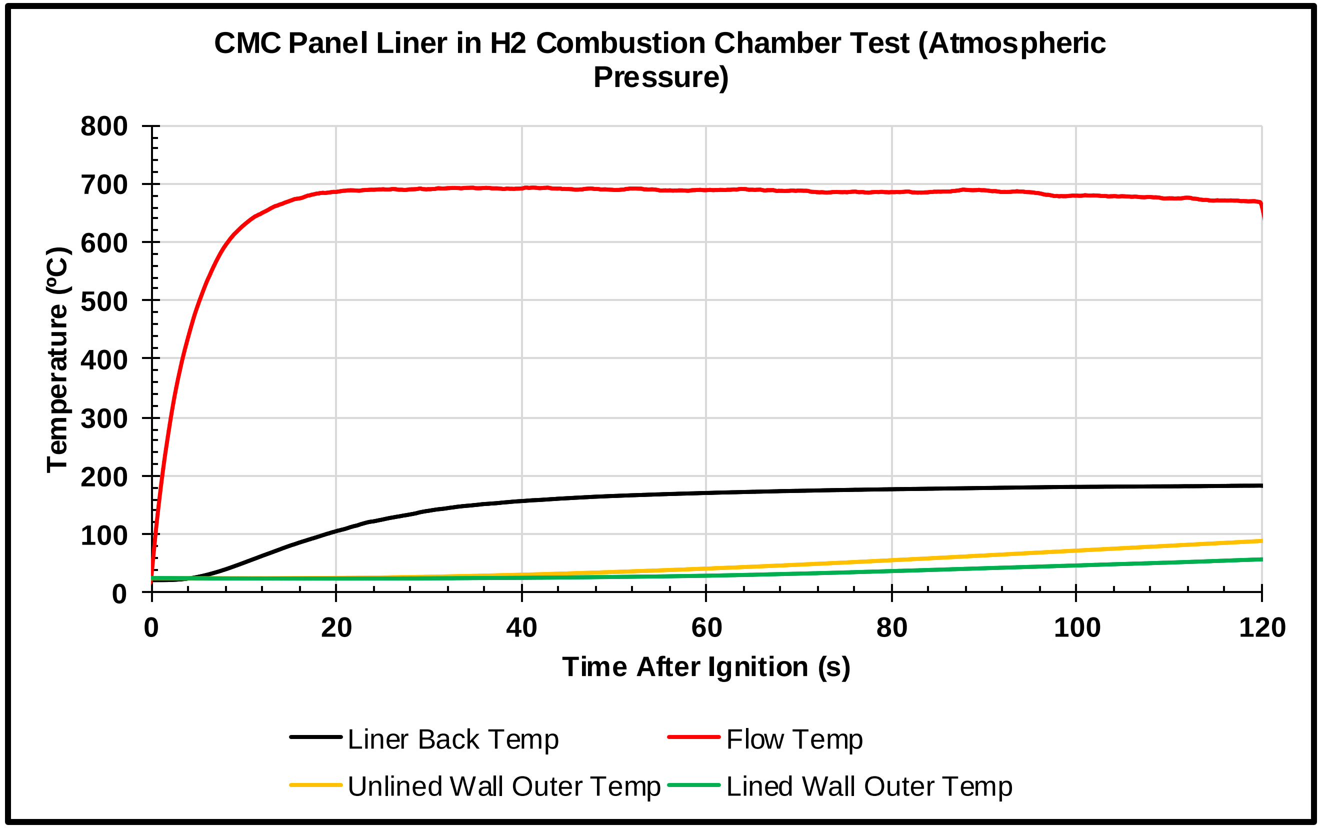
Flow Temperature Thermocouple

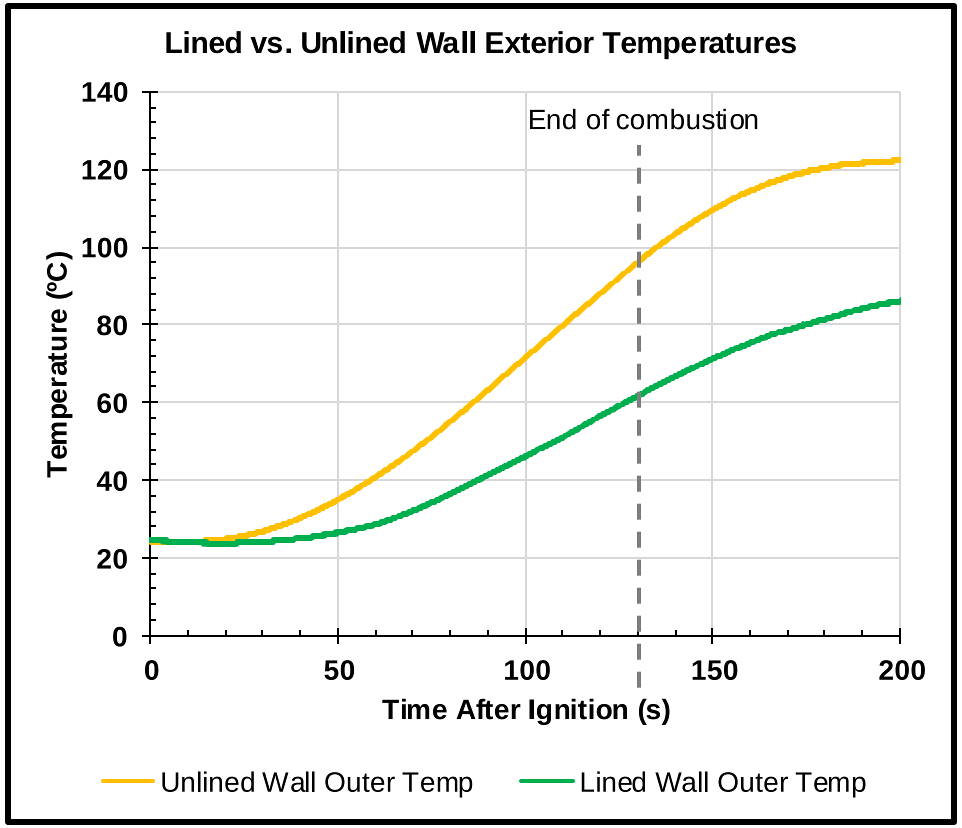
CMC Panel Liners



- 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.

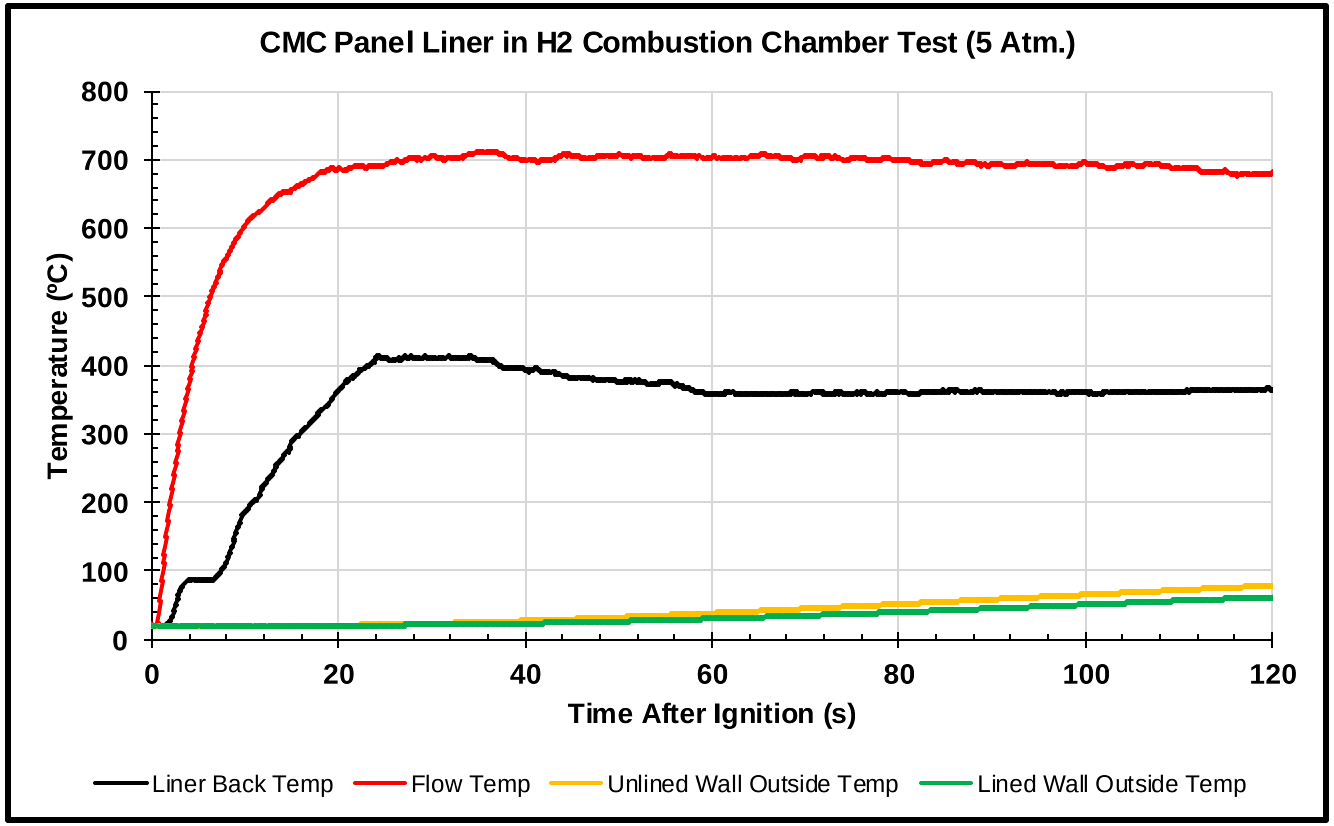
Hydrogen Combustion Chamber Test Results (1 Atm.)

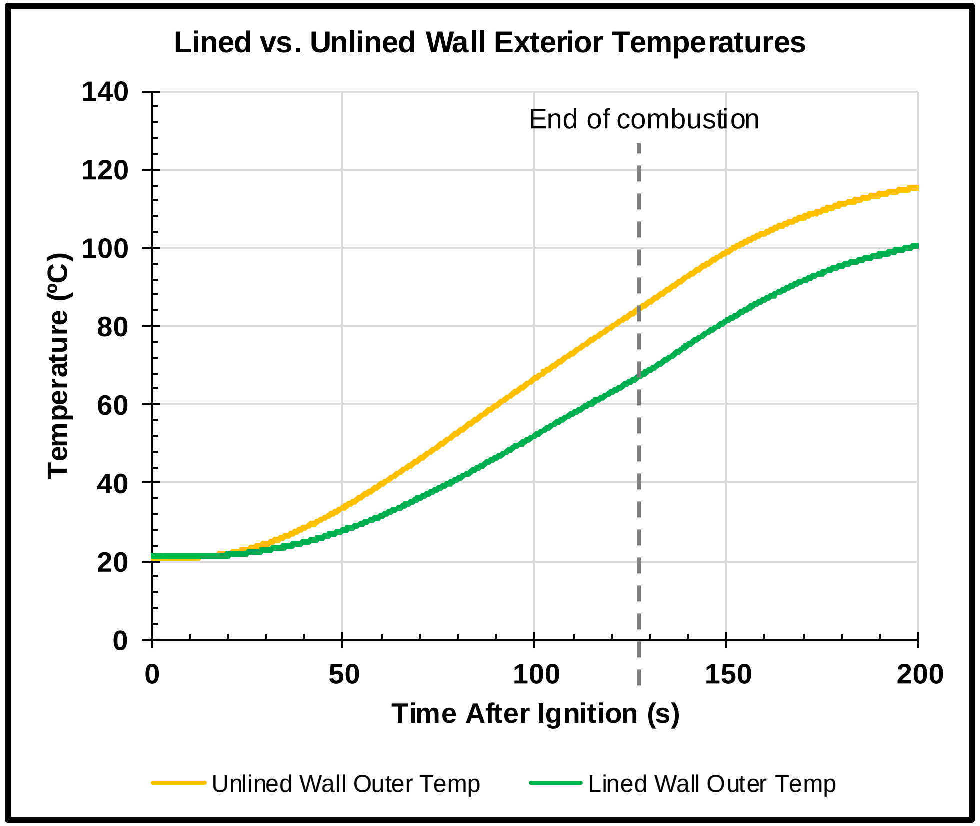




- The CMC liner withstood 2 minutes of continuous hydrogen combustion for multiple trials with no visible damage
- Flow temperature stabilized at ~680ºC while liner back face temperature did not increase past 185ºC
- Successfully protected the stainless-steel walls of the combustion chamber facility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

Ongoing Work:
Fabrication of the CMC Liner for Long Duration Testing

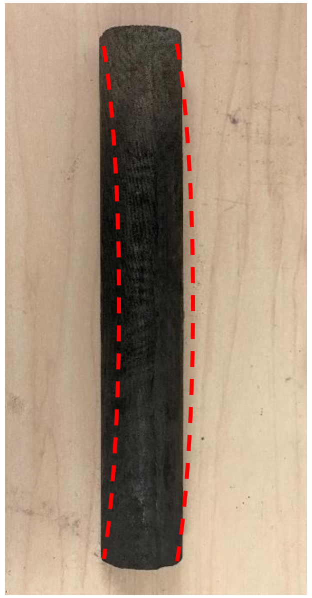
Aluminum mandrel /
YSZ Preform

2 sheets of YSZ fiber
(18” x 44” total) saturated with
rigidizer and wrapped around
mandrel to create cylindrical
porous preform

Resin infiltration and curing
of the green body

Air-tight PVC infiltration chamber
was designed to accommodate large
part geometry

Pyrolysis



OD: 48.51 mm
The CMC line had a slight warping
after pyrolysis

Curvature of liner caused stress
fracture when fitting inside
chamber

Liner length reduced to 11”, combustion
chamber length can be adjusted

Ongoing Work:
Calibration of the Test Rig for Long Duration Testing

☐ Combustor firing - Pressure validation

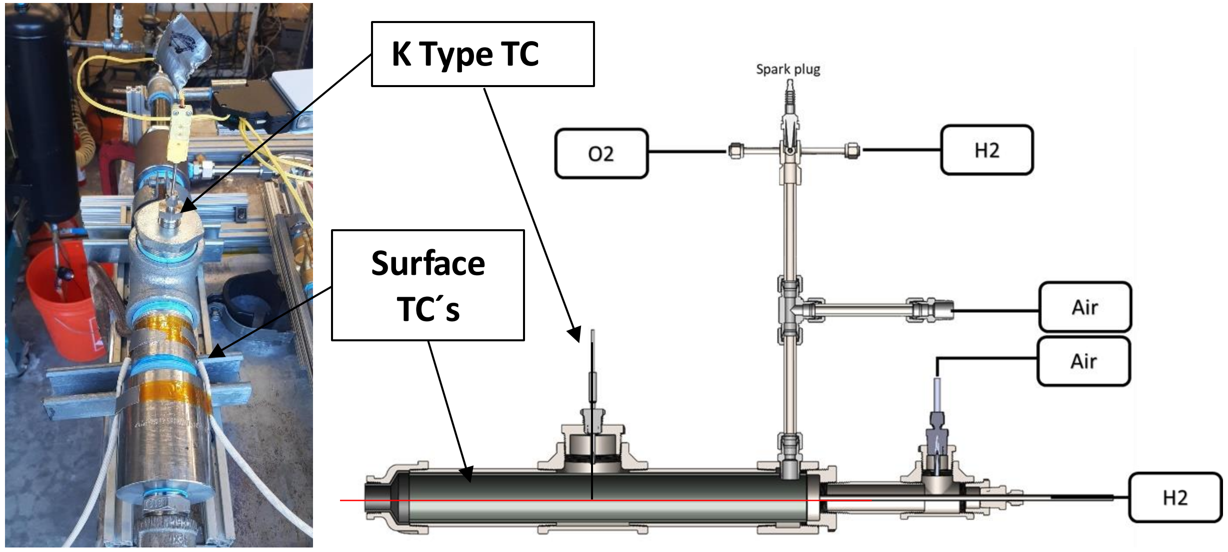
- Ran H2-air mixture at a set equivalence ratio of 0.34 resulting in a calculated crossflow temperature of 1000°C
  - The current condition at 5 atm pressure would have a flow velocity of about 24 m/s

Results

- The facility was pressurized up to 70 psi (4.7 atm)

☐ Combustor firing - Temperature validation

- Set 2 surface thermocouples outside the combustor
- Set 1 K type thermocouple in the crossflow.
- The K Type thermocouple was located a the centerline of the combustor



Conclusions & Future Work

- The Si(B)CN preceramic polymer formulation and its CMC processing technique show a promise for H_2 combustion environments.
- Direct H_2 flame exposure at high heat flux resulted in minimal damage to the CMC.
- 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 long-duration testing will be conducted to investigate long-term H_2 combustion effects and survivability.

Acknowledgements

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Christopher Varela, MS Student/UCF
Michael Tonarely, PhD Student/UCF
Yiting Wang, PhD Student/UCF
David Barnhard, PhD Student/UM

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