Direct Ink Write of Porous Carbon Fiber-Loaded Silicon Nitride CMC

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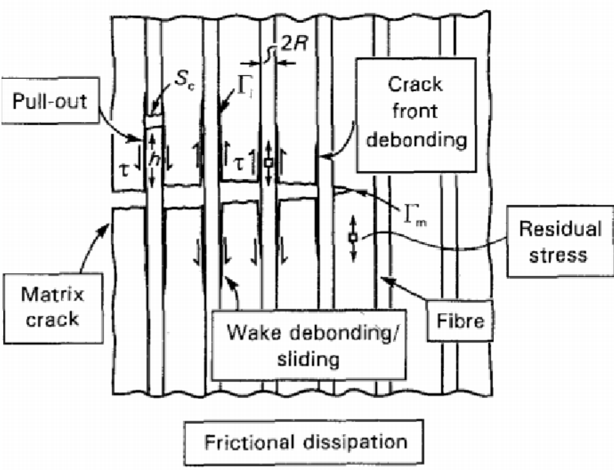
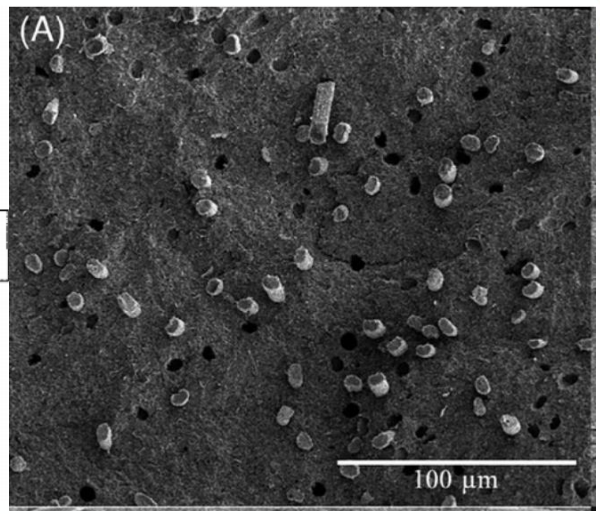
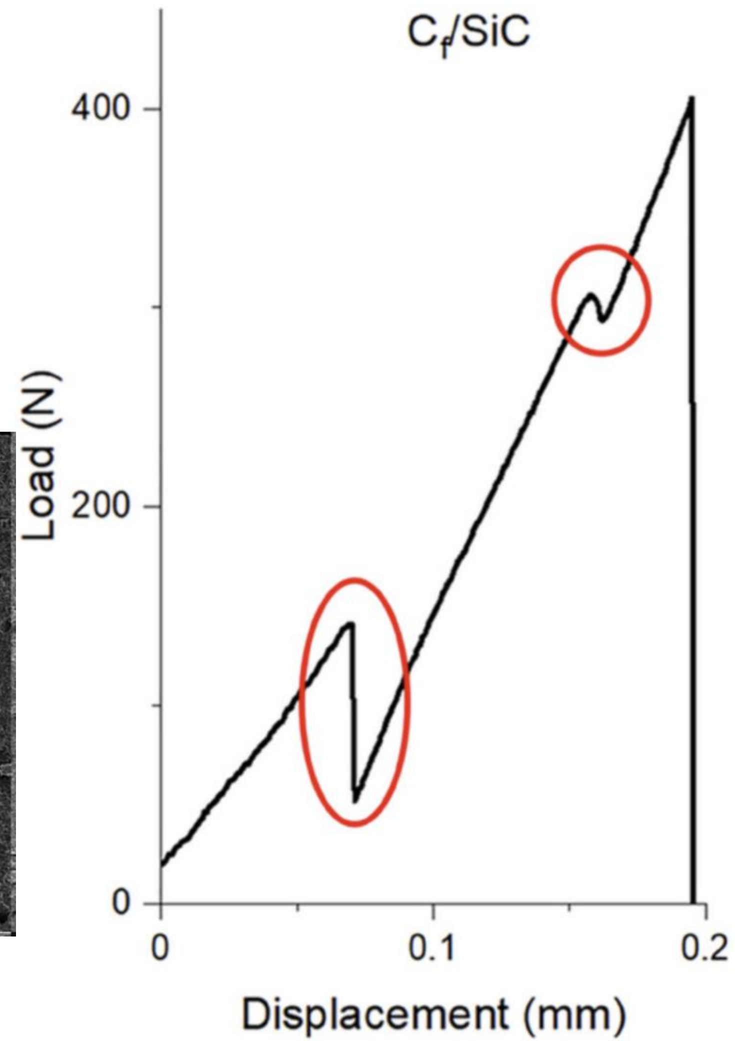
Benefits of Ceramic Matrix Composite(CMC)

- Fibers in a ceramic composite
  - Carbon/Carbon, Carbon/Silicon Carbide, SiC/SiC
- Ceramics generally exhibit brittle fracture
- Introduction of fibers can toughen ceramics
- Enable non-brittle behavior in CMCs
  - Fiber pullout, Debond sliding, etc.







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Densification of CMCs

Current methods of producing CMCs:

- Chemical Vapor Infiltration: Ceramic matrix is deposited using gaseous precursor into fiber preform
  - Long, expensive process, multiple steps, start with preform and gas
- Polymer Infiltration and Pyrolysis: Using a liquid or gel, material is deposited onto the part and sintered
  - Multiple steps, start with preform
- Melt Infiltration: Carbon Fiber preform is infiltrated with silicon to form SiC
  - High temperature applications limited by residual Si
- **Direct Ink Write(DIW) was investigated as a potential method of producing CMCs**

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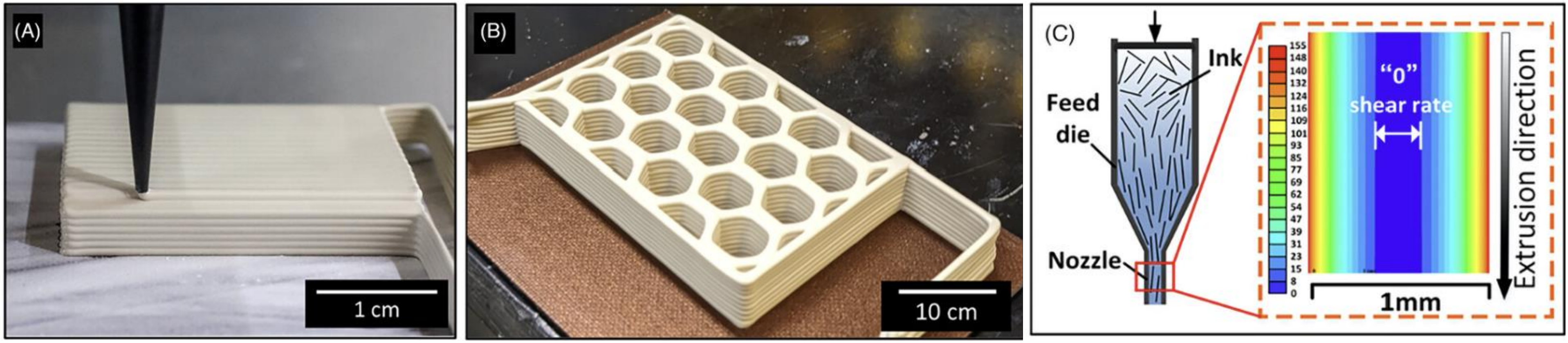
Advantages of Direct Ink Write (DIW)

- Can start with powders and fibers
- CMC densified in one sintering step
    - Powder and fiber mixed and sintered in one step vs preform made and multiple steps in CVI or PIP
- Fibers can be aligned due to shear stresses near nozzle walls and elongational flow



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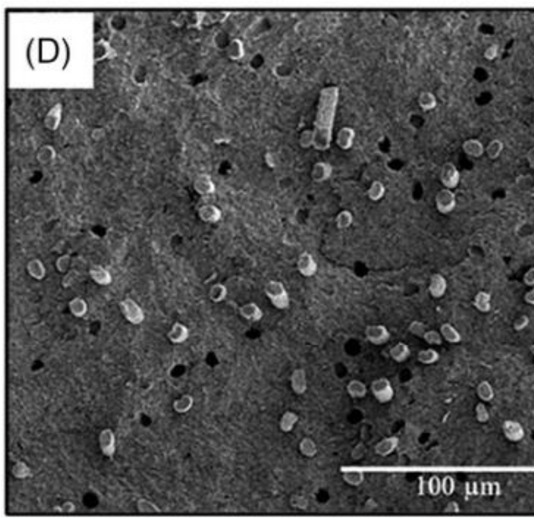
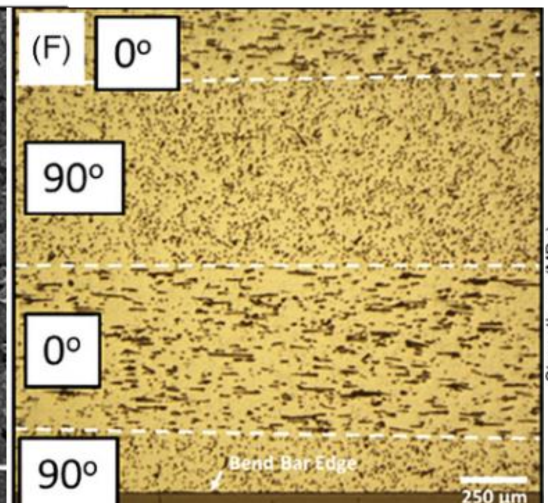
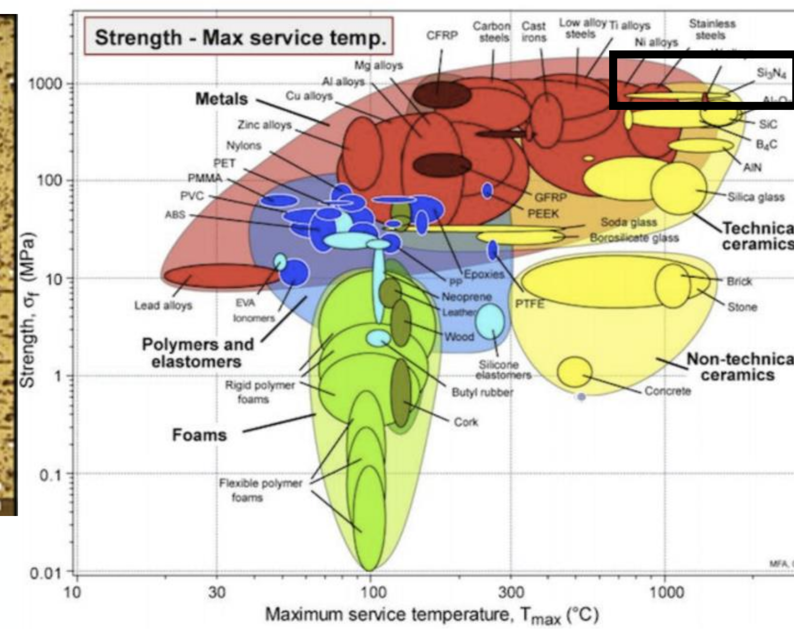
Advantages of Silicon Nitride

- Silicon Nitride as one of the toughest ceramics
- Flexural Strength: ~900 MPa (Fully densified)
- Fracture Toughness (K_{IC}): ~6.0 to ~6.5 $MPa*m^{1/2}$
- Introducing carbon fiber will improve this fracture toughness, a property important to maximize for many applications of silicon nitride







1) Becher, Paul F., Ellen Y. Sun, Kevin P. Plucknett, Kathleen B. Alexander, Chun-Hway Hsueh, Hua-Tay Lin, Shirley B. Waters, et al. 1998. "Microstructural Design of Silicon Nitride with Improved Fracture Toughness: I, Effects of Grain Shape and Size." *Journal of the American Ceramic Society* 81 (11): 2821–30. https://doi.org/10.1111/j.1151-2916.1998.tb02702.x.
2) Trice, Rodney W., and John W. Halloran. 1999. "Mode I Fracture Toughness of a Small-Grained Silicon Nitride: Orientation, Temperature, and Crack Length Effects." *Journal of the American Ceramic Society* 82 (10): 2633–40. https://doi.org/10.1111/j.1151-2916.1999.tb02134.x.

Development of Silicon Nitride Inks for DIW

Aqueous base

Water + Glenium 7500 + PVP

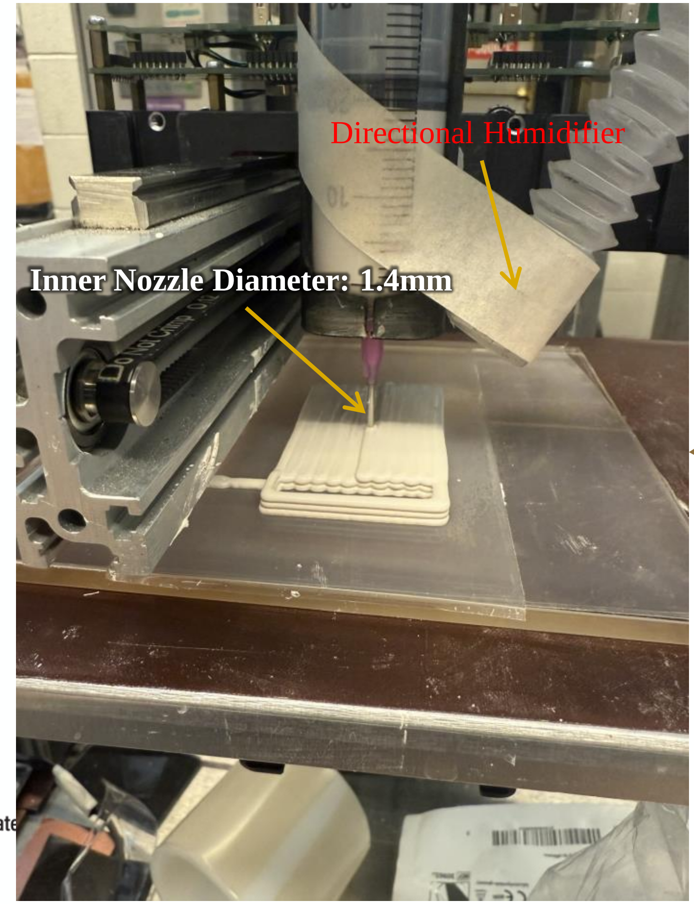
Alumina +Yttria

Sintering Aids: Depending on the ink

Ytterbia

Silicon Nitride
Or
Silicon Nitride
plus
Milled Carbon Fiber

Print



Water: 43V% to 53V%
Glenium 7500: 5V% to 6V%
PVP: 4V% to 5V%
Alumina: 5w%
Yttria: 5w%
or
Ytterbia: 5w%

Print Velocity: 4mm/s
Fibers aligned uniaxially
Directional Humidifier to slow rate of drying

Post Printing: Binder Burn Out and Sintering

- The green body samples are dried in a humidity oven and transferred to a furnace for burn out in flowing nitrogen gas
- The brown body samples are transferred to Carbolite Graphite Furnace for pressure less sintering in a slight nitrogen overpressure

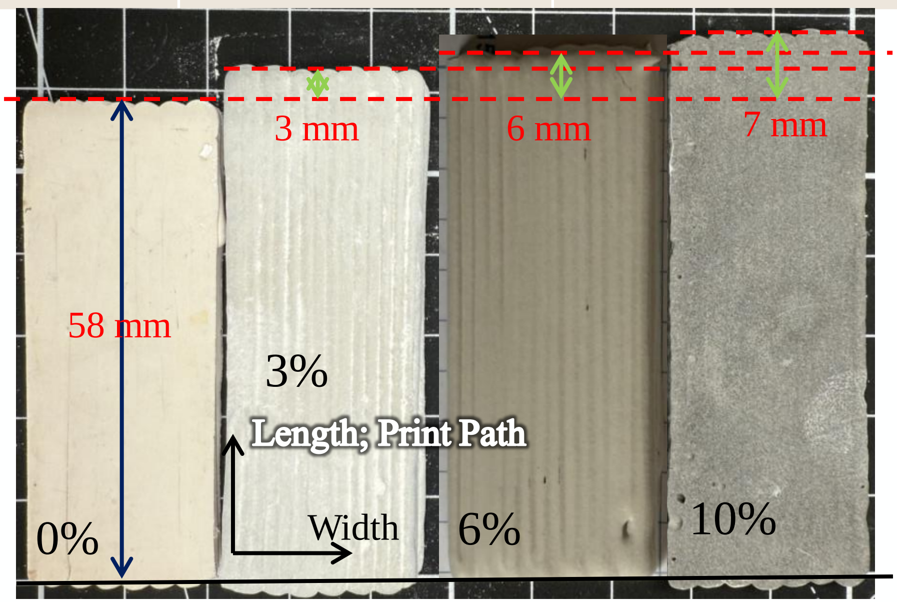
Burn Out Scheme	
Target Temperature	525 C
Rate	1 C/min
Dwell	6 hours
Cool	Uncontrolled

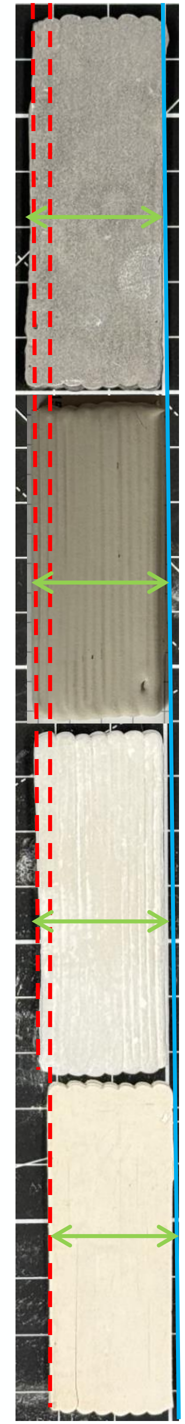
Sintering Scheme	
Target Temperature	1750 C
Rate	16.6 C/min
Dwell	1 hour
Cool	Uncontrolled

Density of CF-loaded SiN CMC

Inks using Alumina and Yttria as Sintering Aids			
Ink Types	*Relative Density*	*Shrinkage for Printed to Sintered (Length) %*	*Shrinkage for Printed to Sintered (Width) %*
0%CFAY	72 ± 0.06	13.1	16.2
3%CFAY	69 ± 0.09	7.9	13.1
6%CFAY	59 ± 0.19	5.4	6.9
10%CFAY	53 ± 0.25	2.7	4.9

5w% Alumina
5w% Yttria



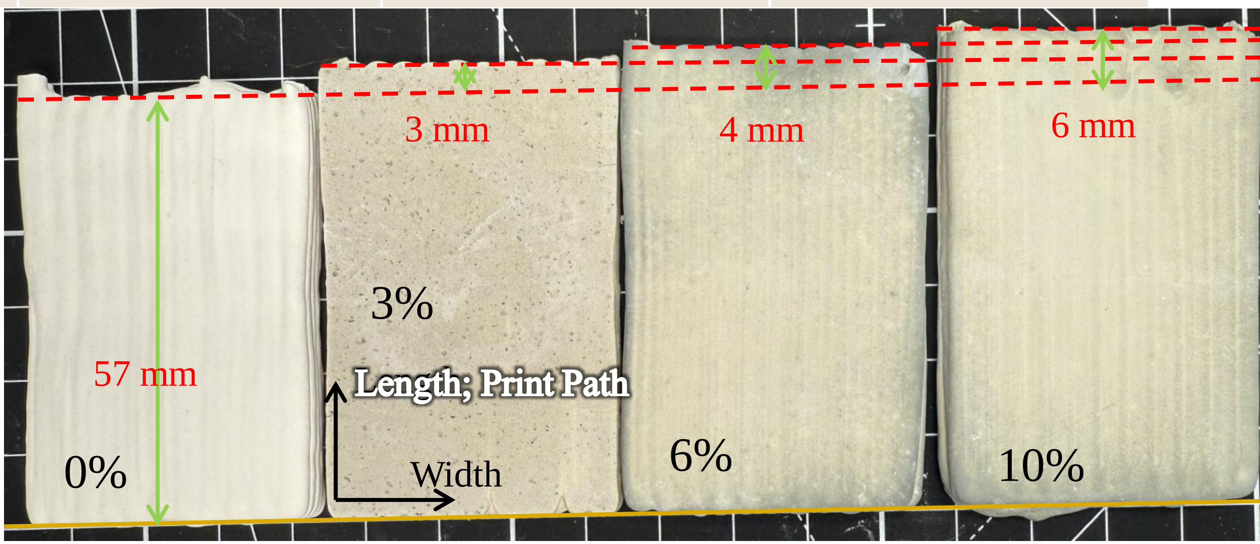


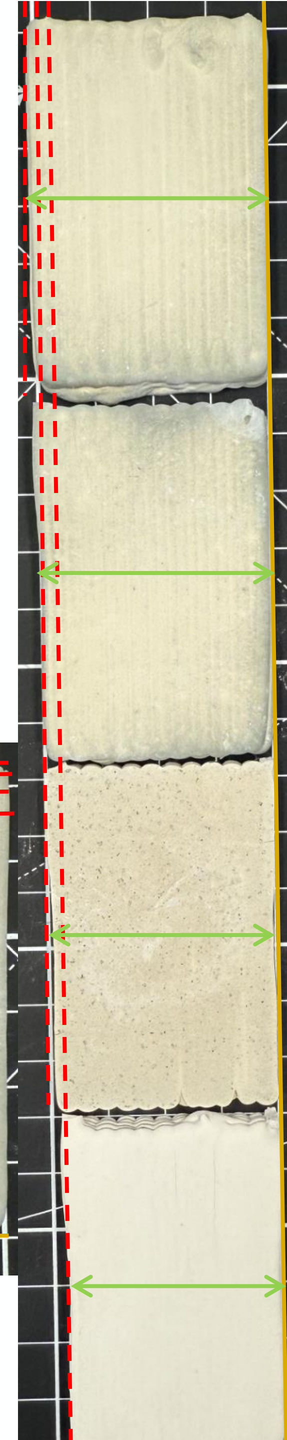
Carbon fiber reduces shrinkage along the orientation axis

Density of CF-loaded SiN CMC

Inks using Ytterbia as Sintering Aid			
Ink Types	*Relative Density*	*Shrinkage for Printed to Sintered (Length) %*	*Shrinkage for Printed to Sintered (Width) %*
0%CFYB	54 ± 0.16	6	6.2
3%CFYB	46 ± 0.13	2.4	3.7
6%CFYB	49 ± 0.13	2	4.7
10%CFYB	46 ± 0.14	1.5	4.6

5w% Ytterbia





Carbon fiber inhibits shrinkage along the orientation axis

Four Point Bend Test

4 point bend performed according to ASTM C1161-18

- Specimen size B (4mm by 3mm by 45mm to 50mm) bend bars were used

Number of Samples Tested	
Ink Type:	Number of Bend Bars:
0CFAY	4
3CFAY	3
6CFAY	8
10CFAY	8
0CFYb	6
3CFYb	7
6CFYb	7
10CFYb	7

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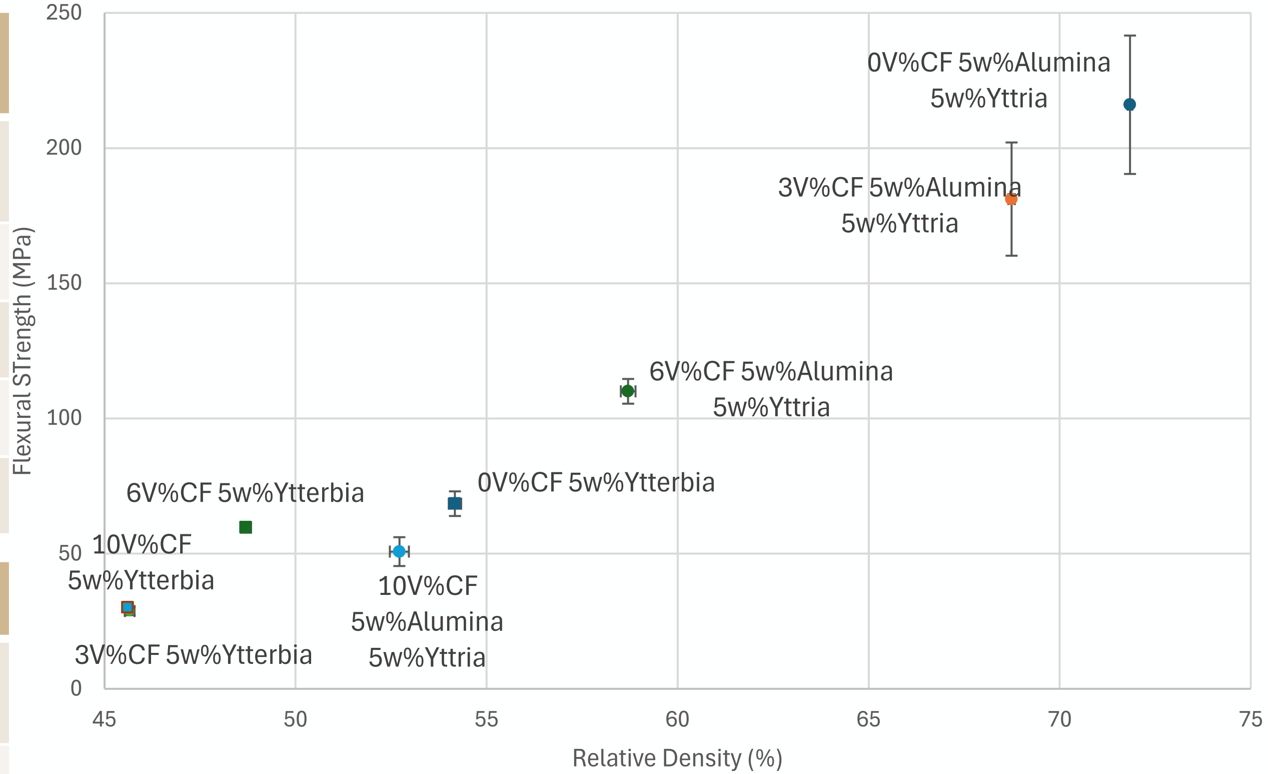
One billet each ink

Average Flexural Strength of CF-loaded SiN CMC

Inks using Alumina and Yttria as Sintering Aids	
Ink Types	***Flexural Strength (MPa)***
0%CFAY	216 ± 26
3%CFAY	181 ± 21
6%CFAY	110 ± 5
10%CFAY	51 ± 5

Inks using Ytterbia as Sintering Aid	
Ink Types	***Flexural Strength (MPa)***
0%CFYb	68 ± 5
3%CFYb	29 ± 2
6%CFYb	60 ± 2
10%CFYb	30 ± 1



- **Flexural strength is proportional to density**
- **Standard error is also proportional to density**

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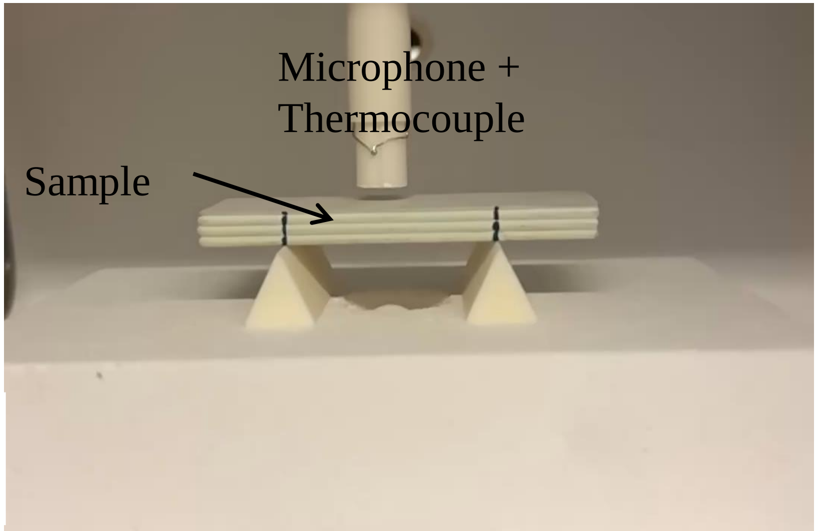
Grindosonic HT1600

- Non-Destructive Evaluation (NDE) technique that measures resonant frequencies to determine elastic properties
  - "Excites" sample by striking
  - Record induced vibrations with microphone
    - Converts vibrations to frequency

- Outputs (up to 1600C)
  - Elastic Modulus
  - Shear Modulus
  - Poisson's Ratio
  - Internal Friction/Damping



Elastic Modulus

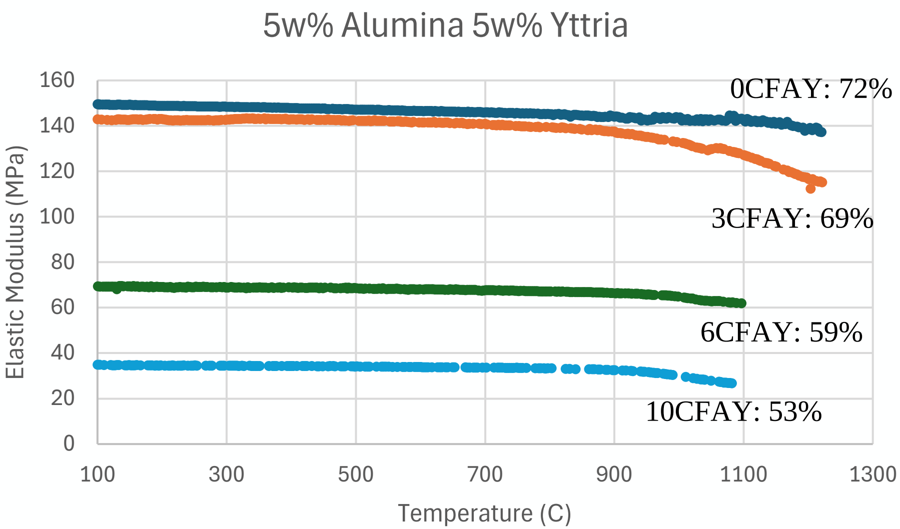
Inks using Alumina and Yttria as Sintering Aids				
Ink Types	*Relative Density (%):*	*Elastic Modulus 23C: (GPa)*	*Elastic Modulus 600C: (GPa)*	*Elastic Modulus 1100C: (GPa)*
0V%CFAY	72%	150	147	141
3V%CFAY	69%	143	141	127
6V%CFAY	59%	70	68	62
10V%CFAY	53%	35	34	27

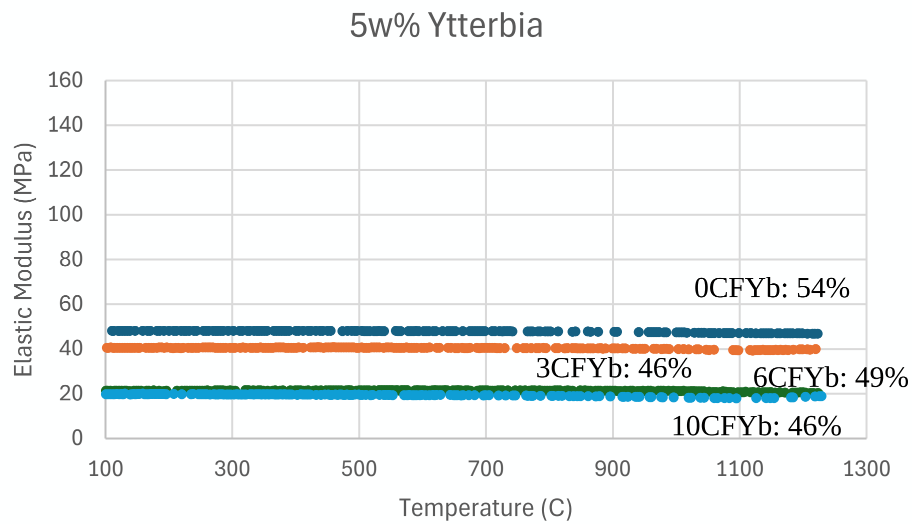
5w%Alumina
5w%Yttria

Inks using Ytterbia as Sintering Aid				
Ink Types	*Relative Density (%):*	*Elastic Modulus 23C: (GPa)*	*Elastic Modulus 600C: (GPa)*	*Elastic Modulus 1100C: (GPa)*
0V%CFYb	54%	48	48	47
3V%CFYb	46%	41	40	39
6V%CFYb	49%	21	21	20
10V%CFYb	46%	20	19	18

5w%Ytterbia

Elastic Modulus: Comparison between Two Systems





- **Elastic Modulus is proportional to density**
- **Carbon fiber may be delaying the decrease in elastic modulus due to higher temperature**
- **That decrease is higher once it does start**

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Preliminary Conclusions:

Inks using Alumina and Yttria as Sintering Aids			
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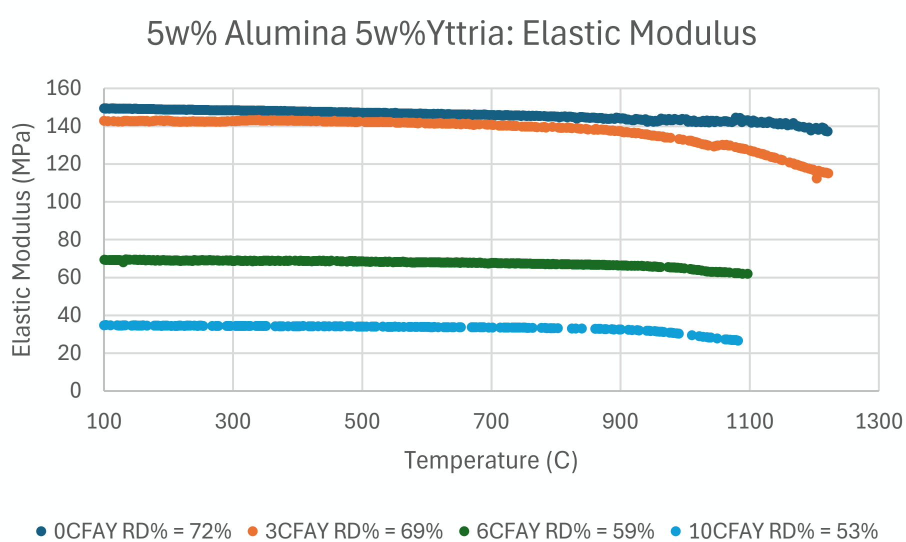

Carbon fiber causes the silicon nitride matrix around it to shrink less along its length

Introducing carbon fiber into silicon nitride reduces the densification of the sintering step

Elastic modulus decreases as density decreases

- Carbon fiber may delay the decrease in elastic modulus due to increased temperatures
- This decease appears to occur at a greater rate

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https://engineering.purdue.edu/PMRI

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Thank You

Questions?

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