PURDUE UNIVERSITY

Additive Manufacturing of Boron Carbide via Robocasting of Aqueous Ceramic Suspensions

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Army Educational Outreach Program
Undergraduate Research Apprenticeship Program (URAP)
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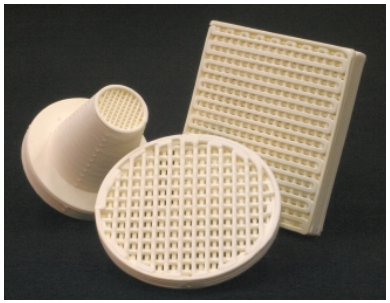
Program Managers: Dr. Michael Bakas and Dr. David Stepp

Boron Carbide Properties, Armor Applications and Processing Limitation

- Possesses a low density: 2.52 g/cm^3
- High melting point ~ 2450°C
- High hardness
- Applications
  - Light weight armor
- Conventional processing methods
  - Hot pressing
  - Hot isostatic pressing

How do we make cost effective complex shapes?

- Additive manufacturing
- Sintering without pressure



P. Dünner, H.-J. Heuvel, M. Hörle, J. Nucl. Mater. 124 (1984) 185–194.
F. Thévenot, J. Eur. Ceram. Soc. 6 (1990) 205–225.

Additive Manufacturing Methods for Ceramics

- Additive manufacturing
  - No expensive tooling or dies

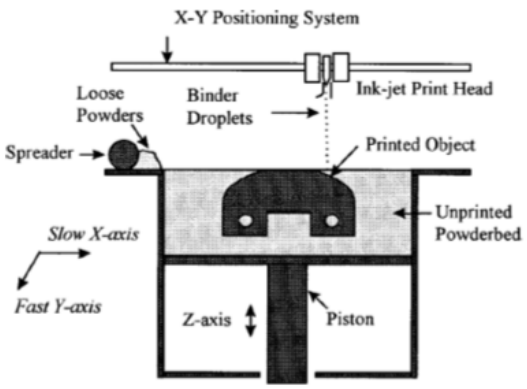
Methods

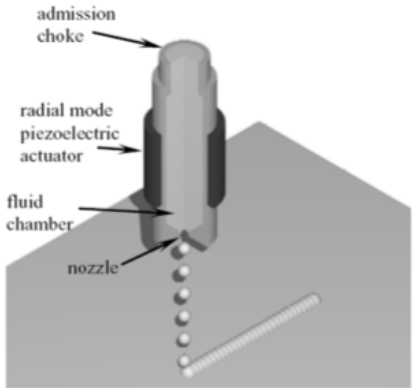
Droplet-based

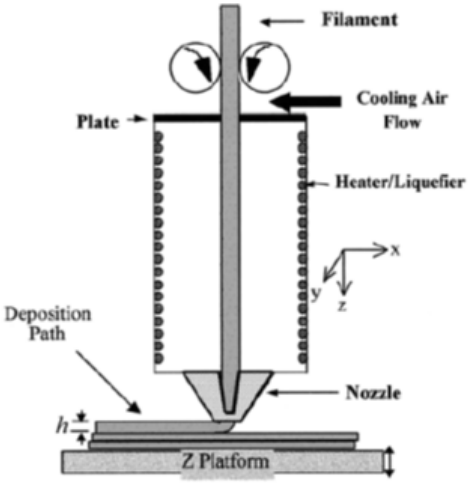
- 3D printing (powder bed)
- Direct ink-jet printing

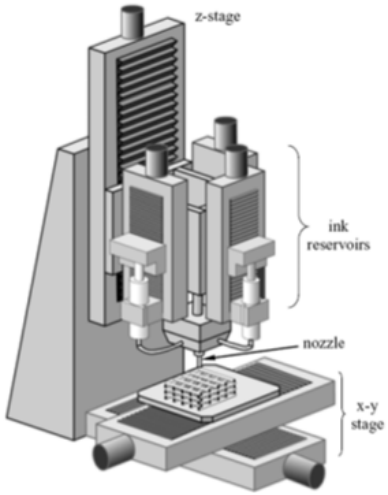
Filament-based

- Fused deposition
- Robocasting





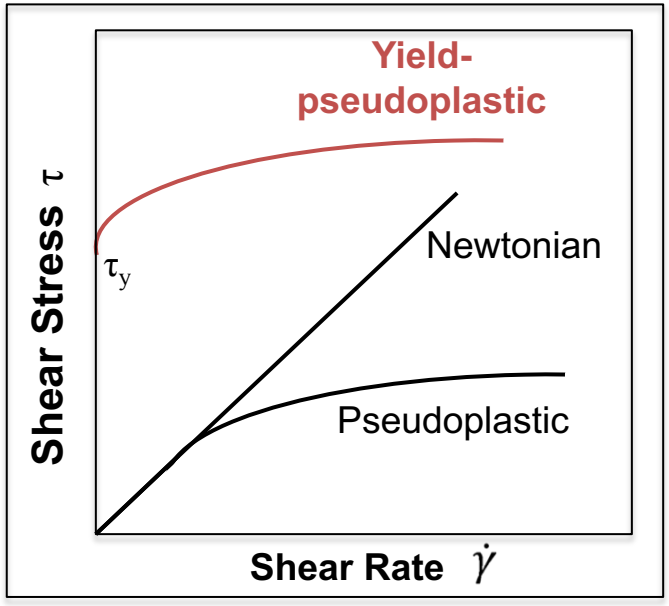




J.A. Lewis, Curr. Opin. Solid State Mater. Sci., 6 [3] 245–250 (2002).

Colloidal Ceramic 'Inks' Required for Robocasting

- Colloidal ceramic "ink" or suspension
  - Ceramic powders
  - Water soluble polymer dispersant
  - Water
- Must behave in a yield-pseudoplastic manner
  - Flow at yield stress (σ_y)
  - σ_y keeps supension from free-flowing
  - Layer shape retention
  - Must have strength to support additional layers
- Stable suspensions lead to more uniform mechanical properties



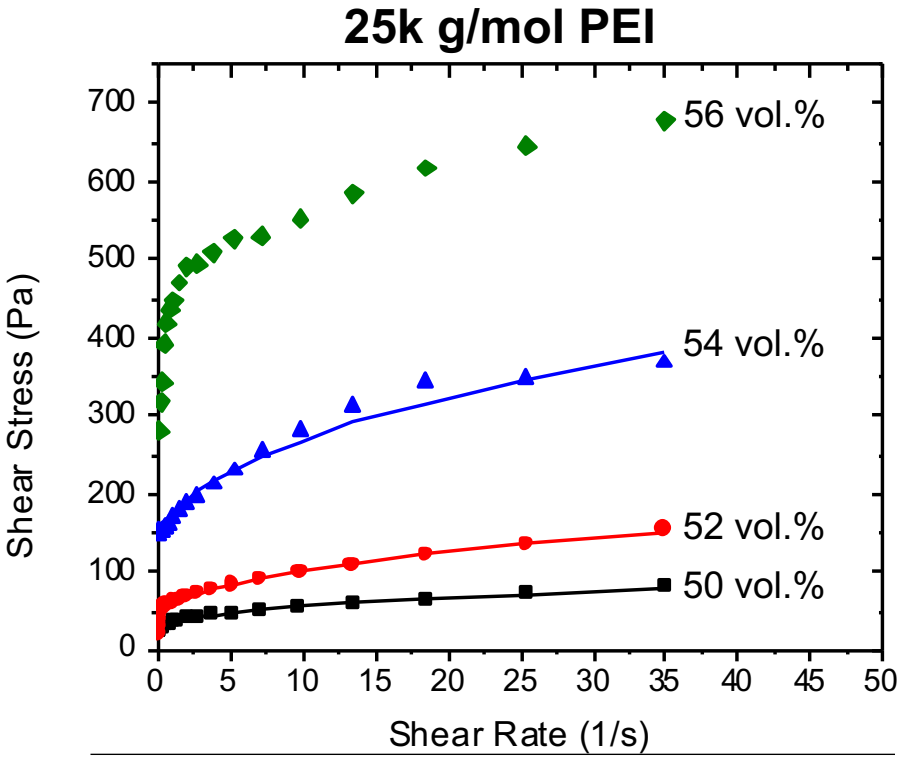
J. Cesarano, MRS Proc. 542 (1998).
S. Leo, C. Tallon, G. V. Franks, J. Am. Ceram. Soc. 97 (2014) 3807–3817.

Boron Carbide Suspension Preparation for Robocasting in Air

- H.C. Starck Grade HS boron carbide attrition milled for 2hrs. with tungsten carbide (WC) media
  - B_4C particle size: 1.7 µm
  - 12 wt.% residual WC
- Polyethlenimine (PEI)
  - M_w = 25,000 g/mol
  - M_w = 750,000 g/mol
- Hydrochloric acid (HCl)
- Water
- Flacktek Mixer
- All suspensions
  - 5 vol.% PEI
  - 5 vol.% HCl

PEI Molecular Weight [g/mol]	B_4C [vol.%]	Water[vol.%]
25,000	50	40
25,000	52	38
25,000	54	36
25,000	56	34
750,000	48	42
750,000	50	40
750,000	52	38
750,000	54	36

Rheological Properties of Yield-pseudoplastic Boron Carbide Suspensions for Robocasting



B_4C [vol.%]	σ_y[Pa]	k[Pa·s^n]	n
50	24	11.6	0.44
52	37	22.3	0.46
54	122	51.3	0.46
56	359*	66.5*	0.47*

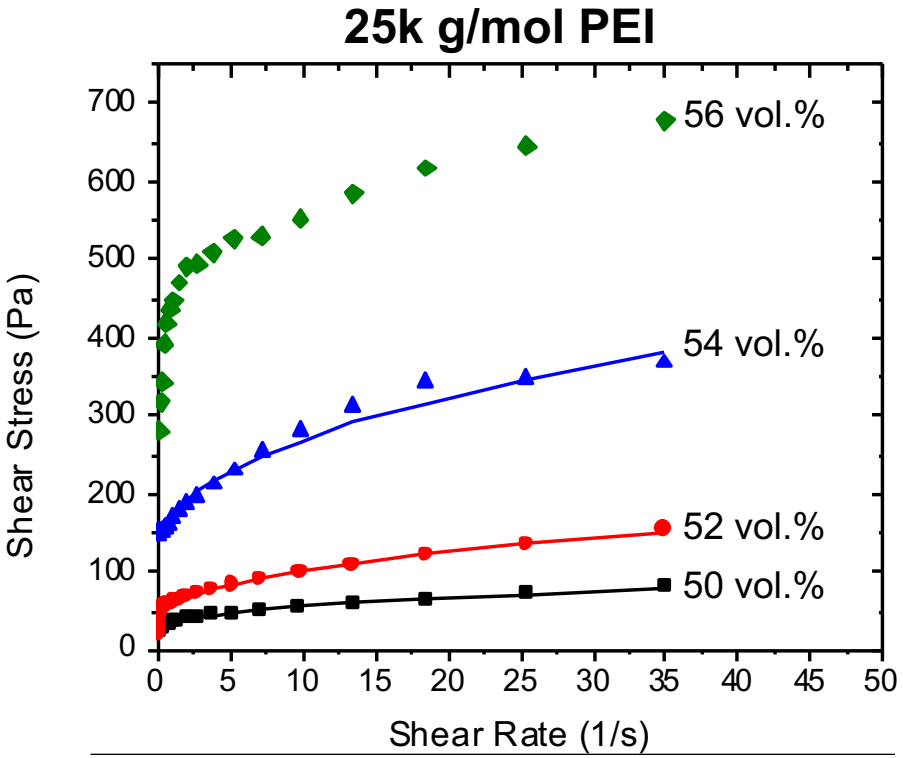
- Malvern Instruments rheometer
  - Cup and Bob rheometer set up
  - Measured shear stresses for controlled shear rates from (0.01-35) s^{-1}
- Flow curves fit to **Herschel-Bulkley model** for yield-pseudoplastic fluids:

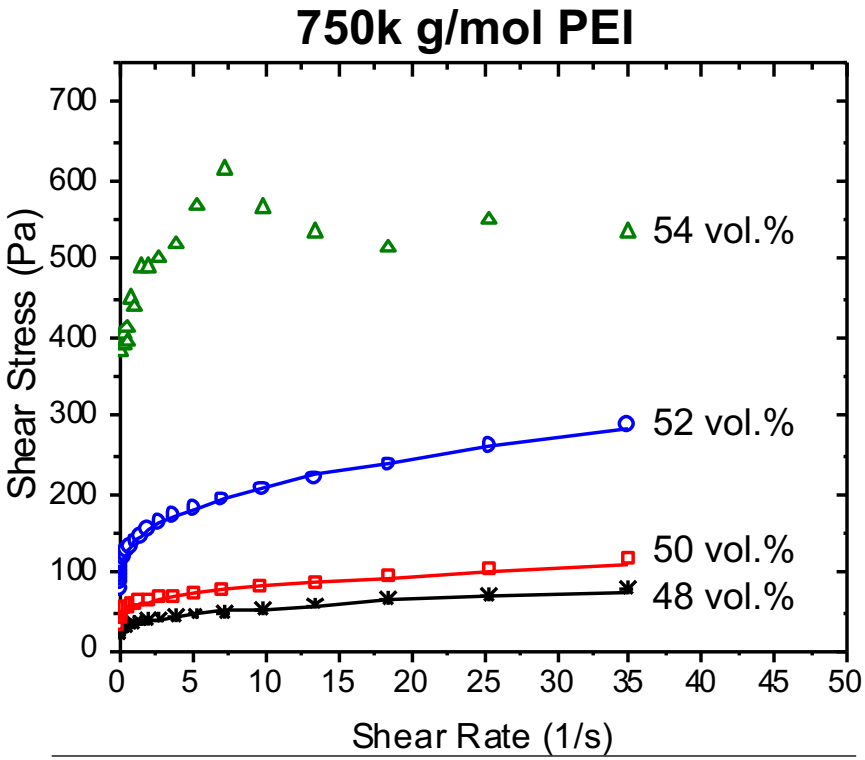
$$\sigma = \sigma_y + k\dot{\gamma}^n$$

- Increase in solids loading lead to an increase in the yield point
  - Uniform behavior after yield point

W.H. Herschel, R. Bulkley, Proc ASTM Part II. 26 (1926) 621–629.
* Unreliable data

Rheological Properties of Yield-pseudoplastic Boron Carbide Suspensions for Robocasting





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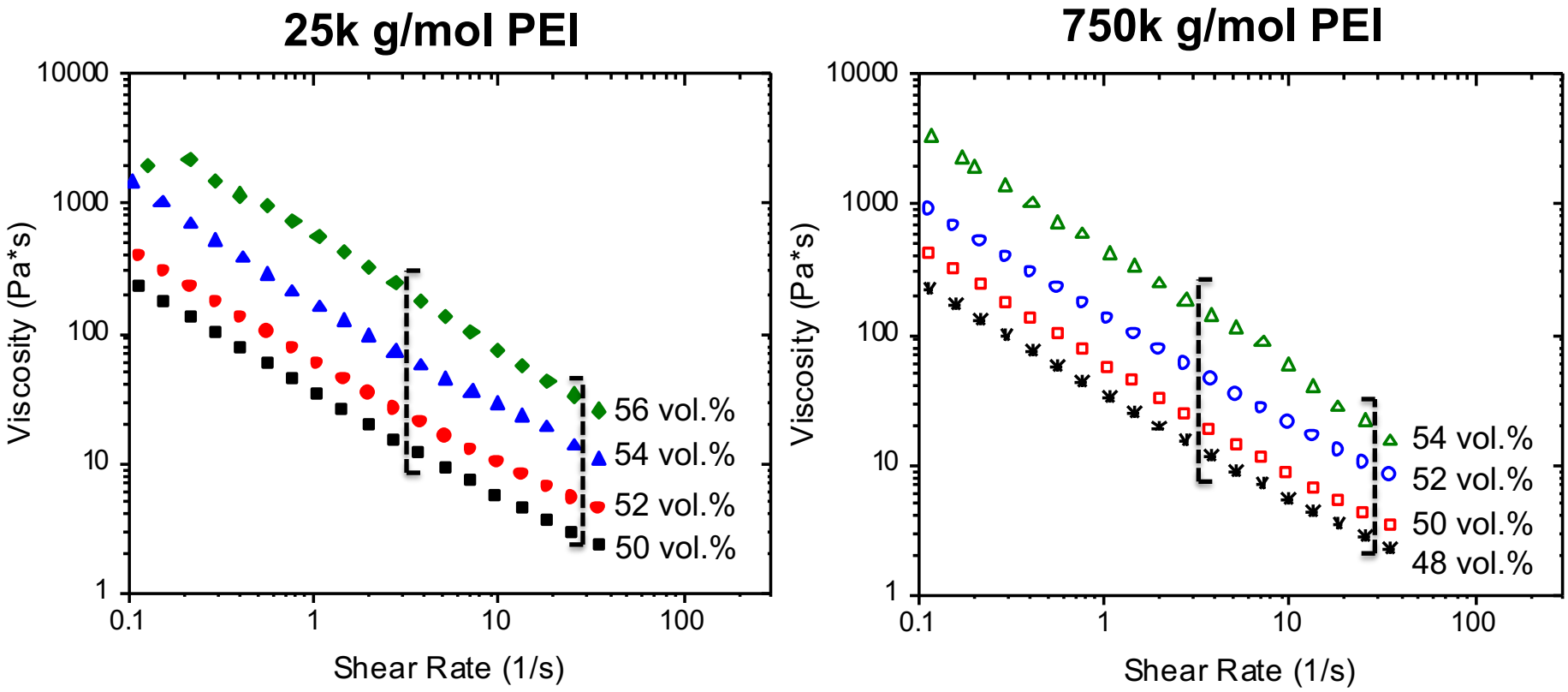
B_4C [vol.%]	σ_y[Pa]	k[Pa·s^n]	n
48	20	14.6	0.38
50	43	15.3	0.42
52	83	55.4	0.36
54	352*	108.9*	0.25*

- Increase in PEI molecular weight lead to an increase in yield point for a constant solids loading.

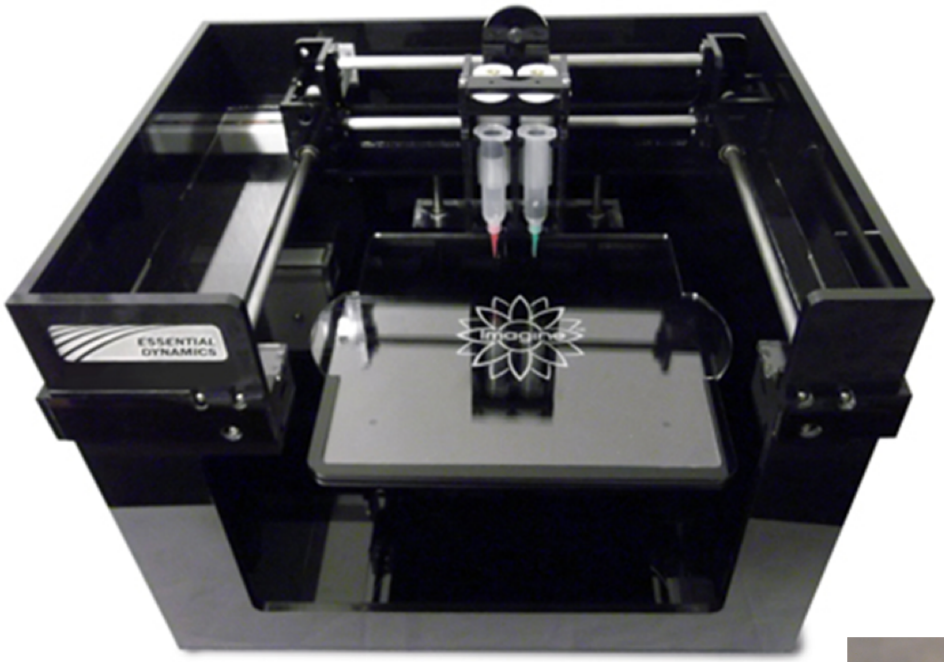
Viscosity Behavior of Boron Carbide Suspensions for Robocasting

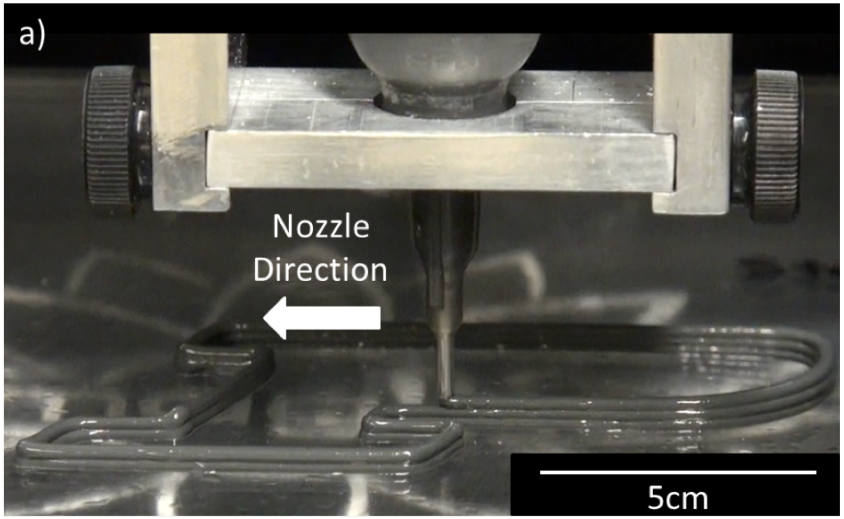


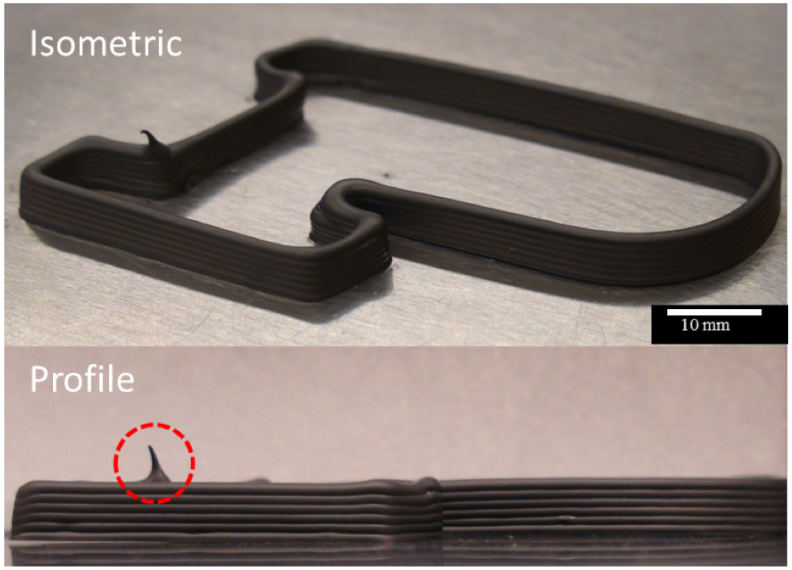
- Uniform shear-thinning behavior in forming range
- Increase in solids loading lead to an increase in viscosity
  - Increase in the inter-particle interactions and inter-particle collisions
- Increasing PEI Mw increased viscosity
  - Increase in average polymer chain length

J. Cesarano, Solid Free. Addit. Fabr. a Mater. 542 (1999) 133–139.

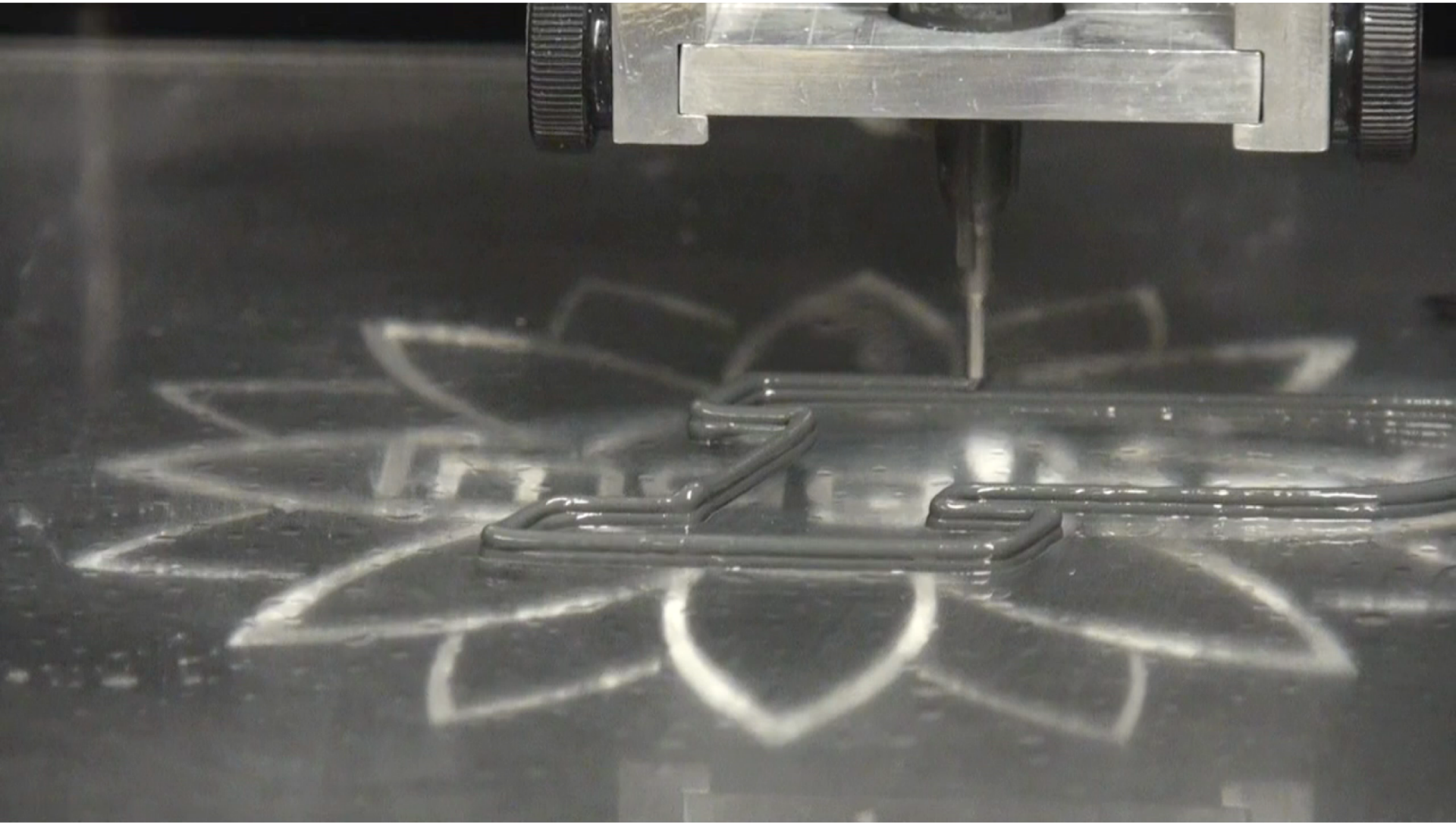
Modified Simple Syringe-style Robocasting Setup



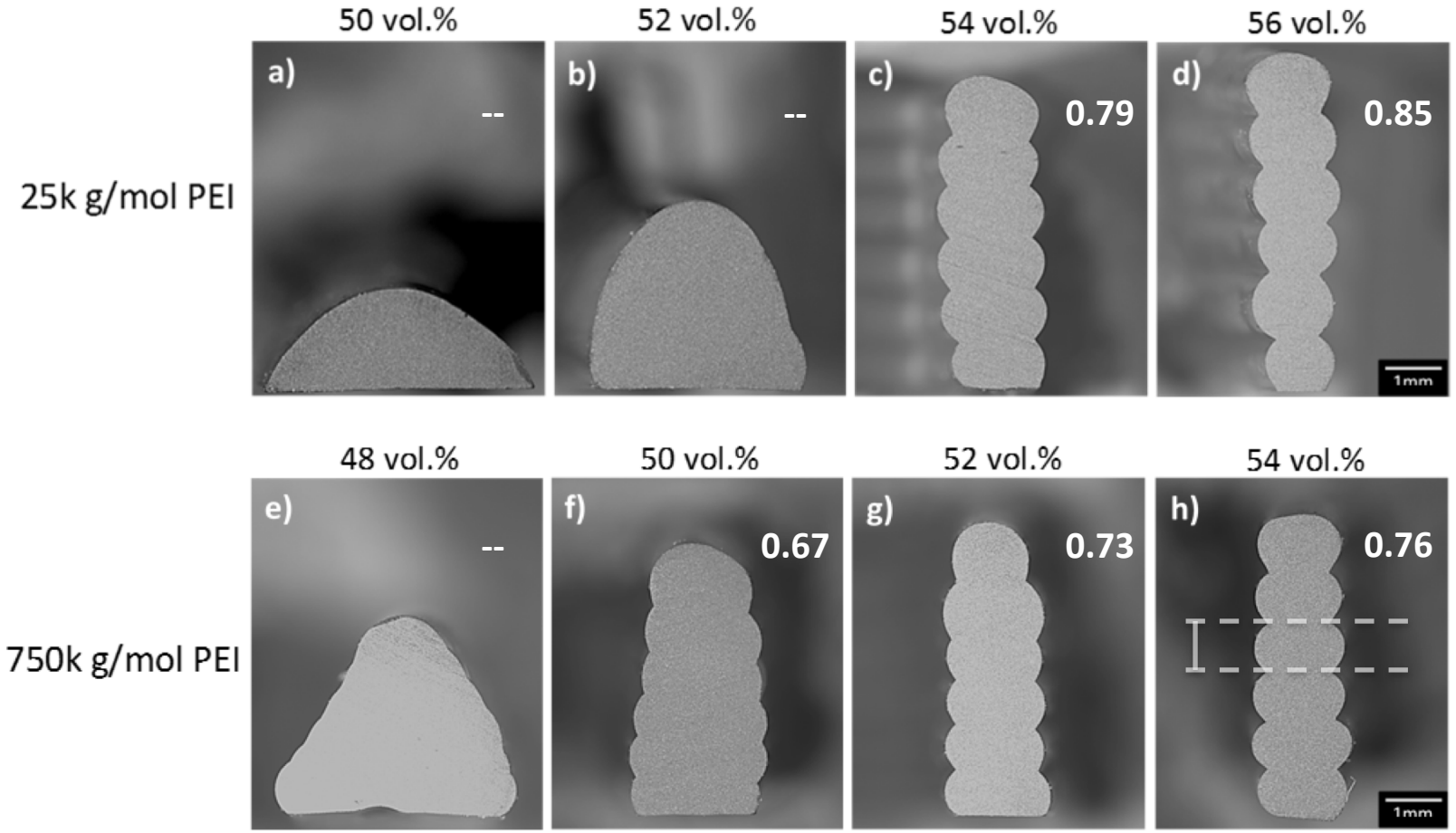




Robocasting Test Shape of 54 vol.% Boron Carbide Suspension with 25k g/mol PEI

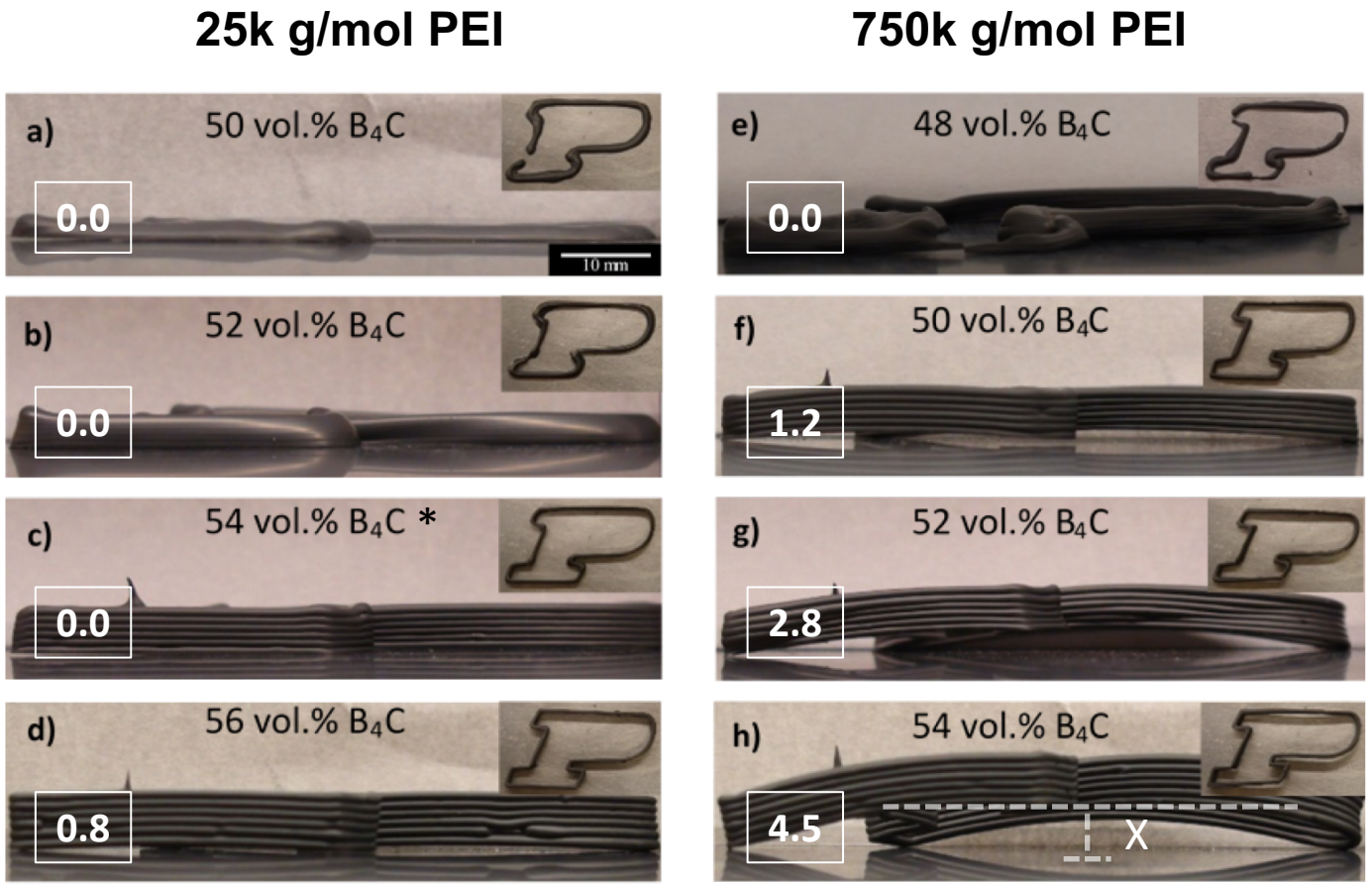


Cross Sectional Comparison of Green Body Filament Layer Shape Retention in Relation to Yield Point



- Shape retention
  - Average filament layer height (mm)
  - Shape retention increases with solids loading
  - Yield point increases with solids loading

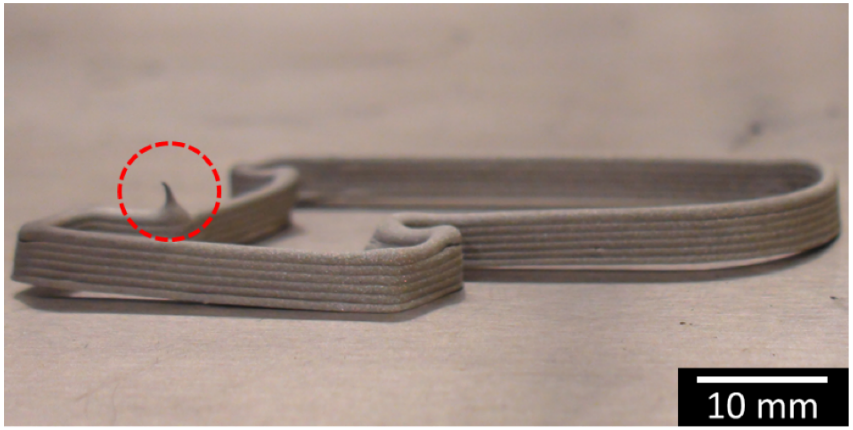
Comparison of Final Specimen Warpage in Relation to Solids Loading and PEI Molecular Weight

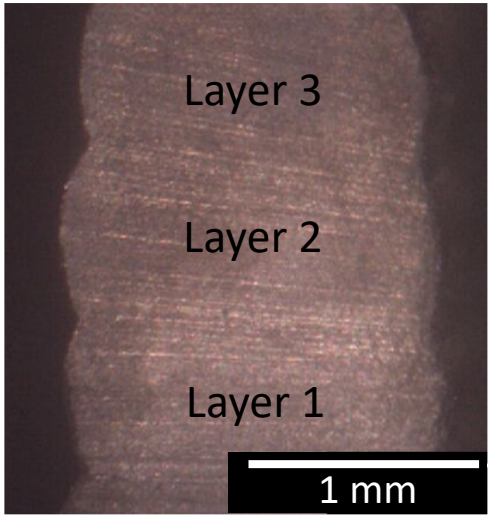


- Specimen warpage (X)
  - Measurement from a flat surface to the bottom of the B_4C specimen
  - An increase in solids loading lead to an increase in the amount of warpage
    - Entropic relaxation of elongated PEI polymer chains
  - An increase in PEI molecular weight lead to an increase in the amount of warpage

Binder Burnout and Sintering Parameters for 54 vol.% Boron Carbide 25k g/mol PEI Specimens

- Binder Burnout
  - Argon atmosphere
  - At 500°C for 25 hrs
- Sintering without external pressure
  - Argon atmosphere
  - 2000°C for 1 hour
- Layer adhesion
  - No systematic residual porosity

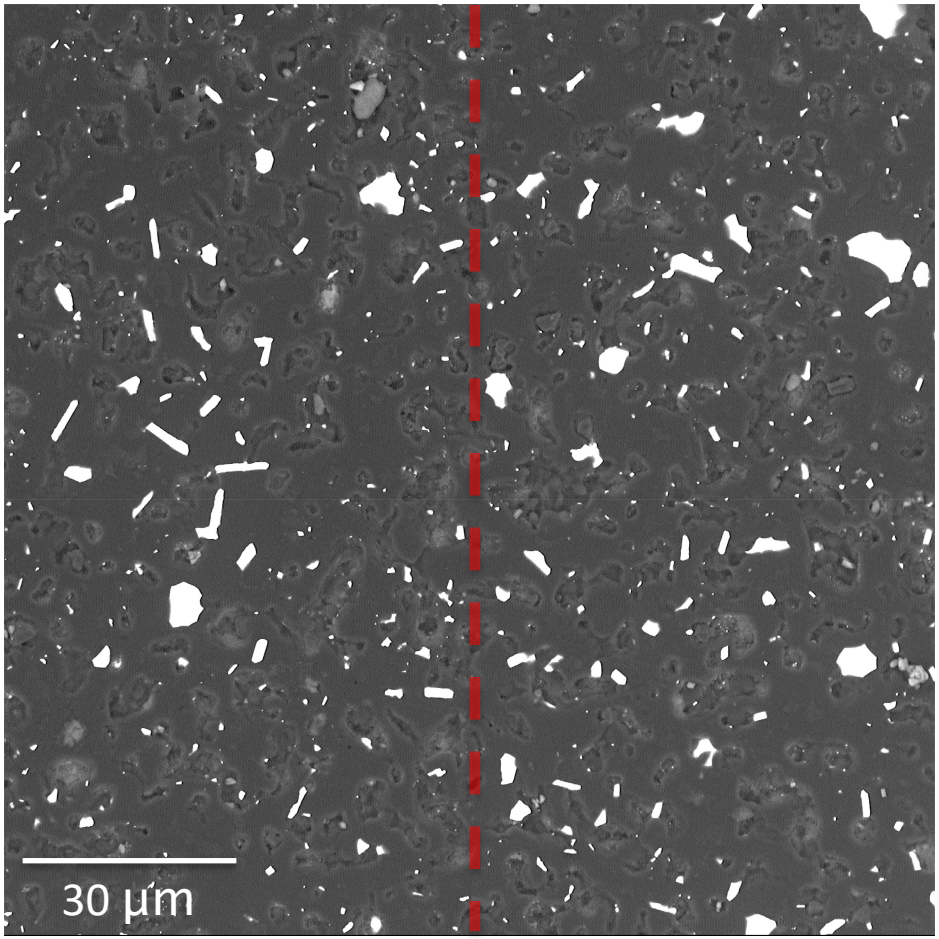




SEM Analysis of sintered specimen

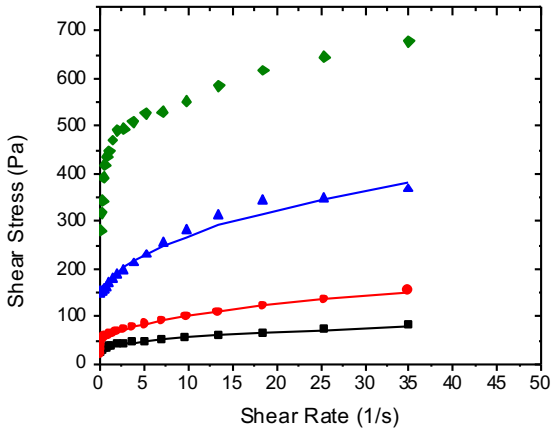
- No macroscopic porosity or cracking between layers
- Microscopic porosity due to incomplete sintering

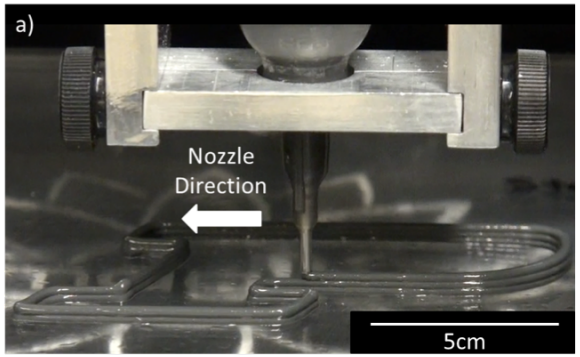
- Density (54 vol.% B_4C)
  - Archimedes testing
  - Average density: 82% TD
- Chemical analysis of sintered specimens*
  - 0.33 wt% oxygen remained
  - Effectively eliminated polymer solution



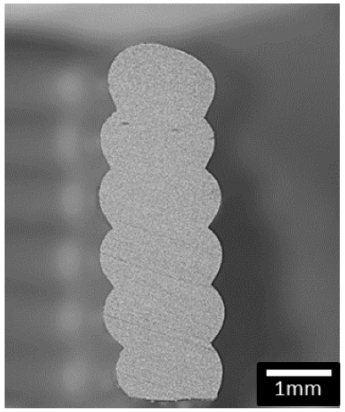
Z. Zakhariev, D. Radev, in: Adv. Hard Mater. Prod., London; UK, 1988: pp. 3.1–33.7.
L. Sigl, H. Thaler, K.-A. Schwetz, 5,505,899, 1996.
*NSL Analytical Services, Inc. (Clevelandprocess a, OH)

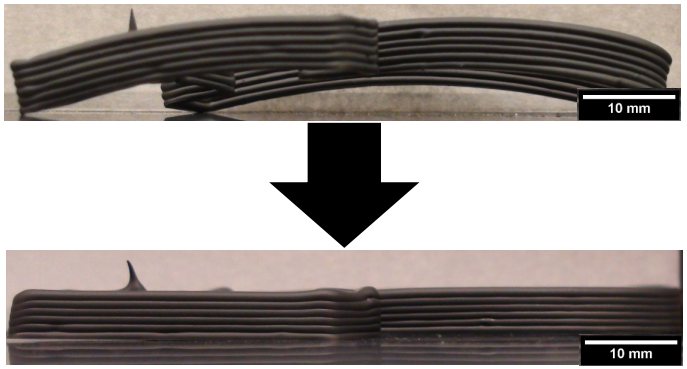
Summary



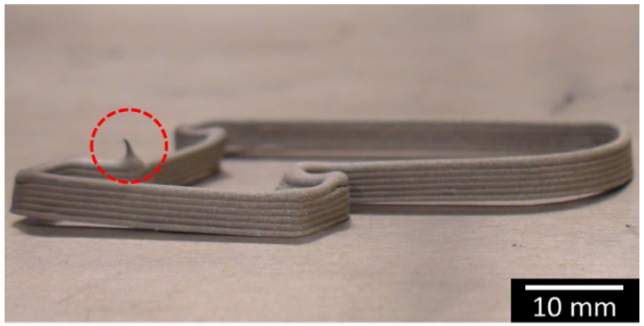


Stable aqueous colloidal processing of B_4C with PEI can be tailored for robocasting

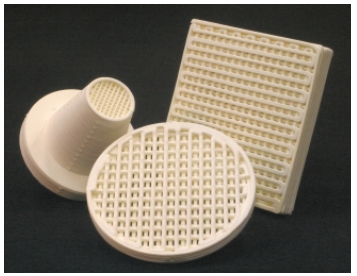




Careful control of the rheological properties (solids loading and PEI Mw) can effect the quality of the final specimens



- Chemical analysis of sintered specimens showed minimal oxygen remained



Robocasting will be used to produce cost-effective complex-shapes out of B_4C

Acknowledgements

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Questions?