

## Development of Matrix Microstructures in UHTC Composites

Sylvia M. Johnson, NASA-Ames Research Center  
Margaret Stackpoole and Michael Gusman, ERC Corporation

One of the major issues hindering the use of ultra high temperature ceramics for aerospace applications is low fracture toughness. There is considerable interest in developing fiber-reinforced composites to improve fracture toughness.

Considerable knowledge has been gained in controlling and improving the microstructure of monolithic UHTCs, and this paper address the question of transferring that knowledge to composites. Some model composites have been made and the microstructures of the matrix developed has been explored and compared to the microstructure of monolithic materials in the hafnium diboride/silicon carbide family. Both 2D and 3D weaves have been impregnated and processed.



# Development of Matrix Microstructures in UHTC Composites

Sylvia M. Johnson, NASA -ARC

Margaret Stackpoole, Michael Gusman, Jose  
Chavez-Garcia ERC Corp.

[Sylvia.m.johnson@nasa.gov](mailto:Sylvia.m.johnson@nasa.gov)



# Outline

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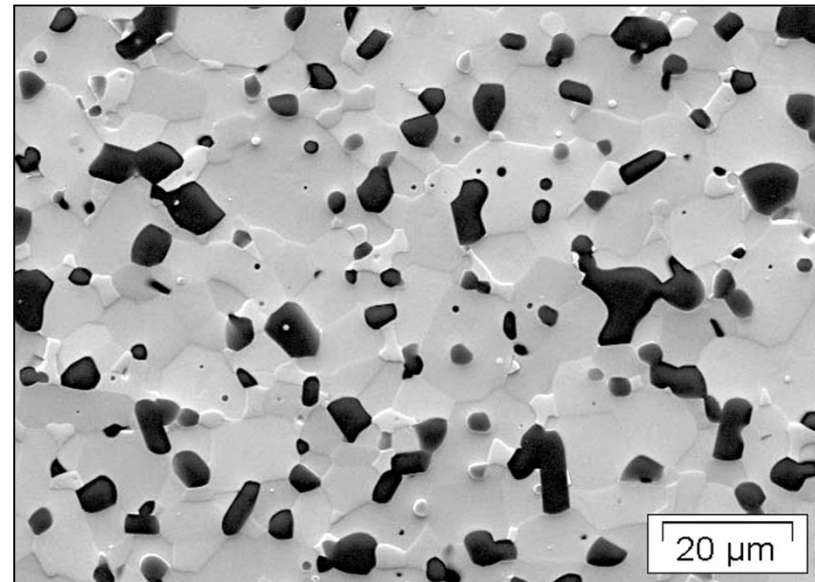
- Issues with UHTCS
- Approaches to improve fracture toughness
  - In -situ reinforcement
    - Preceramic polymer route
    - “Coating” route
  - Fiber reinforcement
    - 2D weaves
    - 3D weaves



# Ultra High Temperature Ceramics (UHTCs) : A Family of Materials

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- Borides, carbides and nitrides of transition elements such as hafnium, zirconium, tantalum and titanium.
- Some of highest known melting points
- High hardness, good wear resistance, good mechanical strength
- Good chemical and thermal stability under certain conditions
- High thermal conductivity (diborides).
  - good thermal shock resistance



Typical microstructure of a "monolithic" HfB<sub>2</sub>/SiC material



# Where are we going?

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- What does a UHTC need to do?
  - Carry engineering load at RT
  - Carry load at high use temperature
  - Respond to thermally generated stresses (coatings)
  - Survive thermochemical environment
- High Melting Temperature is a major criterion, but not the only one
  - Melting temperature of oxide phases formed
  - Potential eutectic formation
- Thermal Stress –  $R' = \sigma k / (\alpha E)$ 
  - Increasing strength helps, but only to certain extent
- Applications are not just function of temperature
- **Materials needs for long flight time reusable vehicles are different to those for expendable weapons systems**



# UHTC Challenges: What will make designers use these materials?

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- 1. Fracture toughness: Composite approach is required**
  - Integrate understanding gained from monolithic materials
  - Need high temperature fibers
  - Need processing methods/coatings
- 2. Oxidation resistance in reentry environments**

reduce/replace SiC
- 3. Modeling is critical to shorten development time, improve properties and reduce testing**
- 4. Joining/integration into a system**
- 5. Test in relevant environment—test data!**



# Outline

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    - Preceramic polymer route
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# Preceramic Polymers Can Control Grain Shape

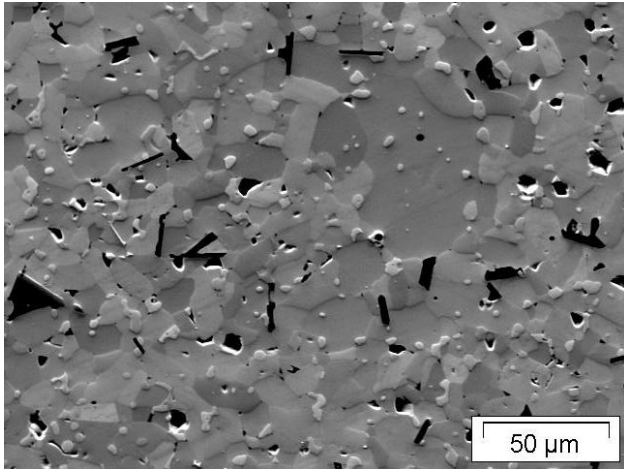
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- Conventional source of SiC is powder.
- SiC from a preceramic polymer source:
  - Will affect densification and morphology.
  - May achieve better distribution of SiC source through  $\text{HfB}_2$ .
  - Previous work shows that preceramic polymers can enhance growth of acicular particles (for fracture toughness).
- Potential to improve mechanical properties with reduced amount of SiC and also potentially improve oxidation behavior.

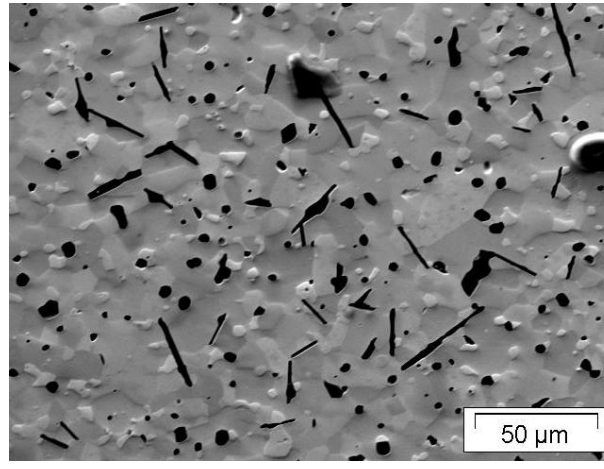




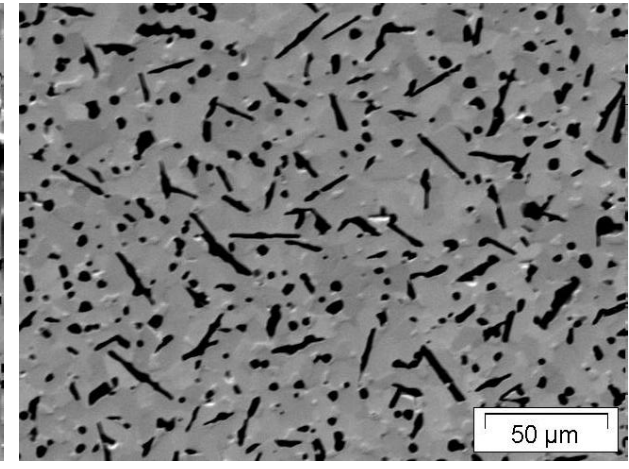
# Growth of Elongated SiC Grains



5%\* SiC



10%\* SiC — Rod diameter  $\sim 2\mu\text{m}$



15%\* SiC — Rod diameter  $\sim 5\mu\text{m}$

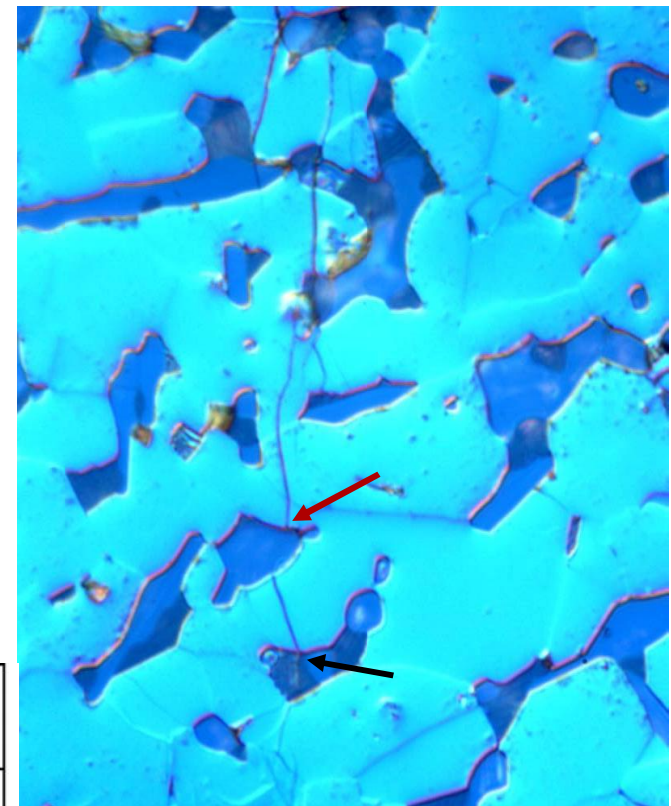
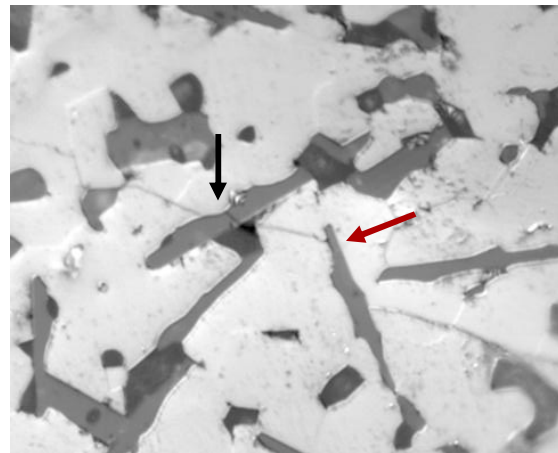
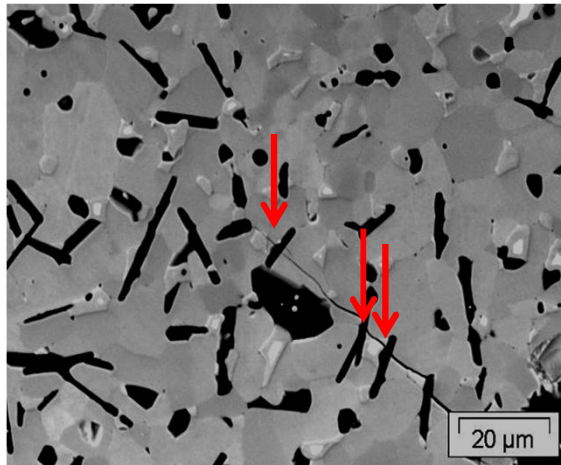
## SiC Preceramic Polymer Promotes Growth of Acicular Grains

- Samples processed with 5 to  $>20$  volume % SiC
- Can adjust volume of SiC in the UHTC without losing the high l/d architecture
- Amount of SiC affects number and thickness (but not length) of rods — length constant ( $\sim 20\text{--}30\mu\text{m}$ )
- Possible to obtain dense samples with high-aspect-ratio phase
- Hardness of high-aspect-ratio materials comparable to baseline material

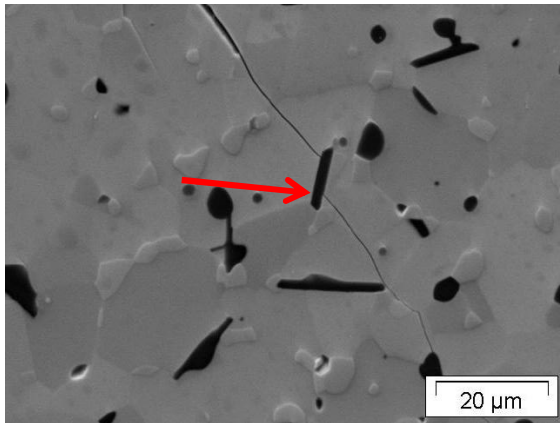
\* Precursor added in amounts sufficient to yield nominal amounts of SiC



# In Situ Composite for Improved Fracture Toughness



Oak Ridge National Laboratory

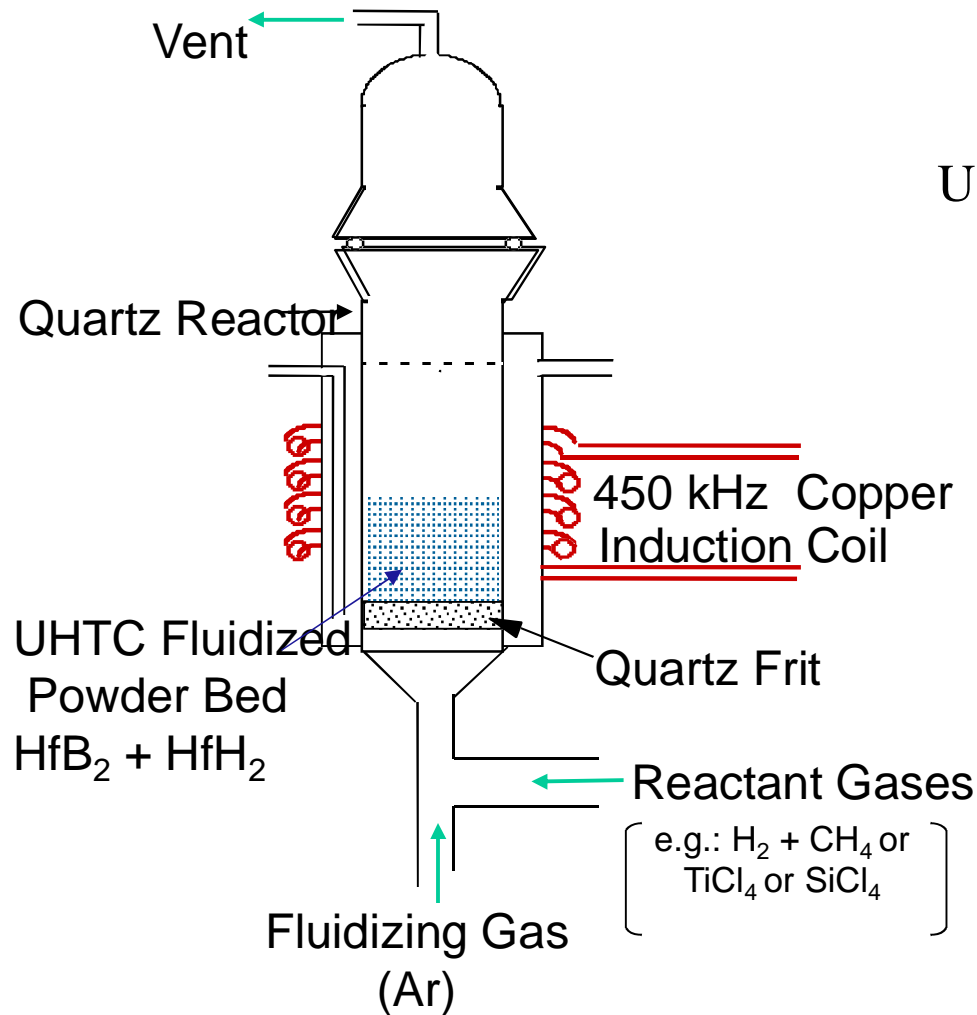


SiC Content	Fracture Toughness (MPam <sup>1/2</sup> )
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33

Evidence of crack growth along HfB<sub>2</sub>-SiC interface, with possible SiC grain bridging



# When Additives for UHTCs Are Added as Coatings



## Fluidized Bed Reactor - Chemical Vapor Deposition Technique (FBR-CVD)

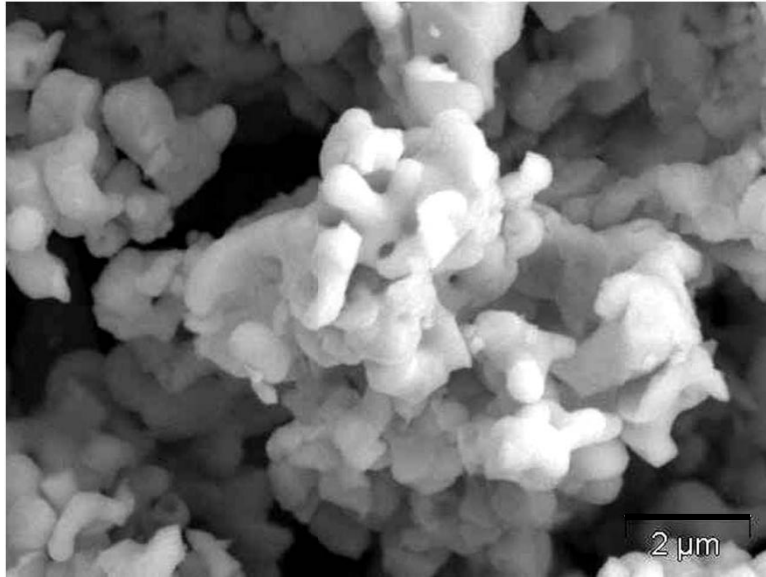
Using coatings, instead of particles, to introduce additives, offers several advantages:

- Uniform distribution and control of coating composition
- Bypasses traditional sources of processing contamination
- May lead to improved oxidation and creep resistance (less  $\text{O}_2$  contamination)
- Amount of additive can be controlled
- Reductions in hot-press temperature, pressure, and time

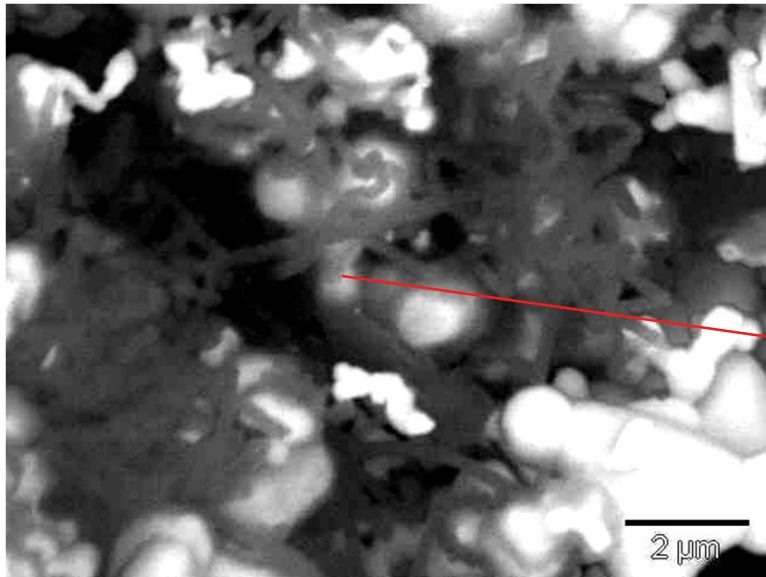


# SiC Coating Appearance on Powders

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**Uncoated Powder**

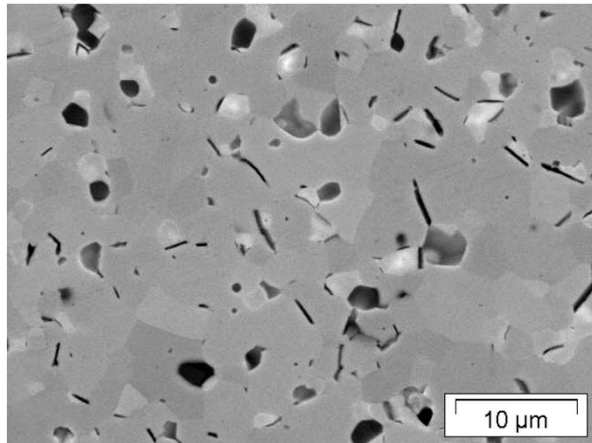
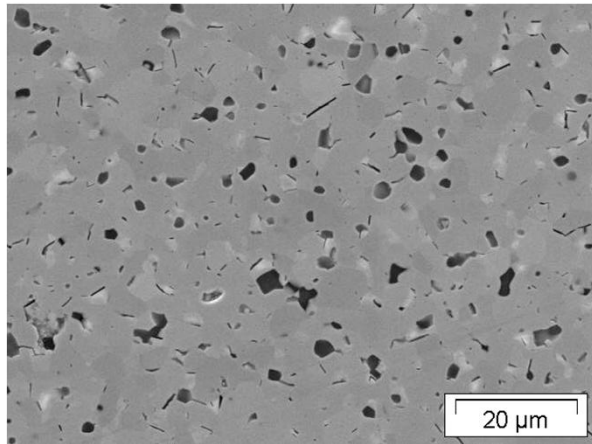


**SiC Coated Powder**

Gray filamentous material is SiC



# Addition of SiC as “Coating”



- Alternative route to growing acicular grains
- HfB<sub>2</sub> powders “coated” with Si/C in fluidized bed
- Spark plasma sintered
  - Not fully dense
  - Growth of acicular SiC grains
- Grain boundaries should be very clean, leading to potential improvements in thermal conductivity

HfB<sub>2</sub>- 5 vol-%SiC (SPS)



# Processing of Composites

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## Objectives:

- Can we use knowledge gained from controlling microstructures in “monolithic” UHTCs to make matrices for fiber reinforced composites?
- Can both 2D and 3D weaves be infiltrated?
- Caveats
  - Using available carbon fiber structures
  - No fiber coating



# Processing of 2D Weave

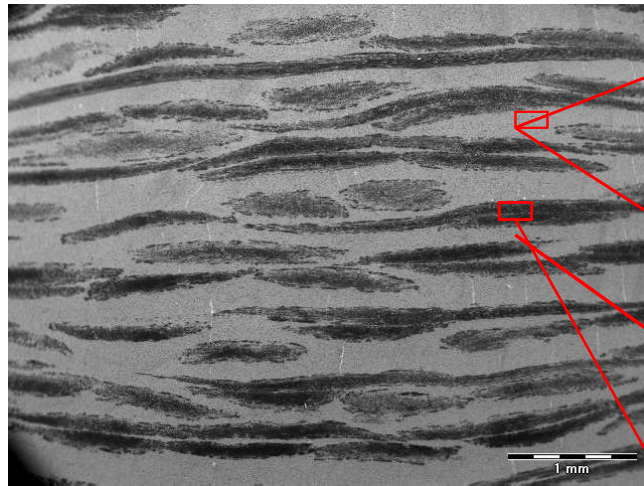
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## Composites from 2D weaves

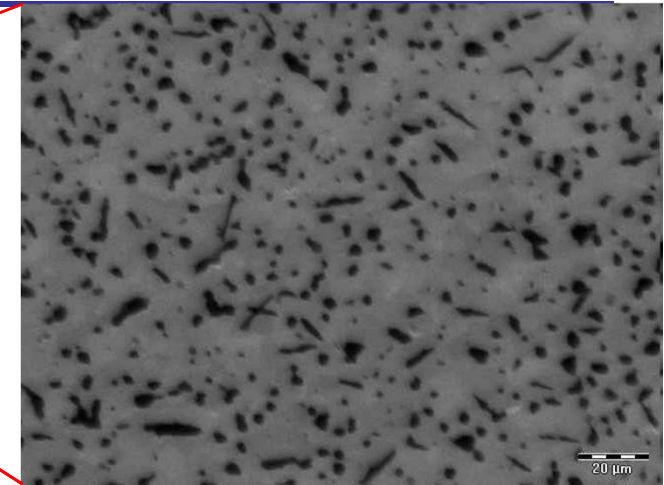
- Carbon fiber cloth (PAN-based)
- Impregnated with preceramic polymer/ $\text{HfB}_2$  powder mixture—one infiltration per layer
- Layers stacked and hot pressed (~15 layers)



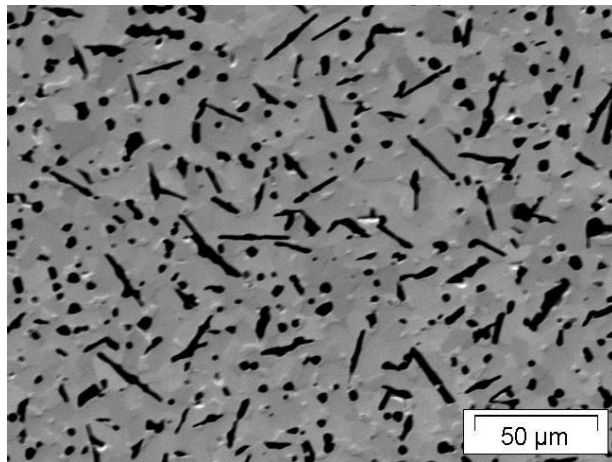
# Ultra High Temperature Continuous Fiber Composites



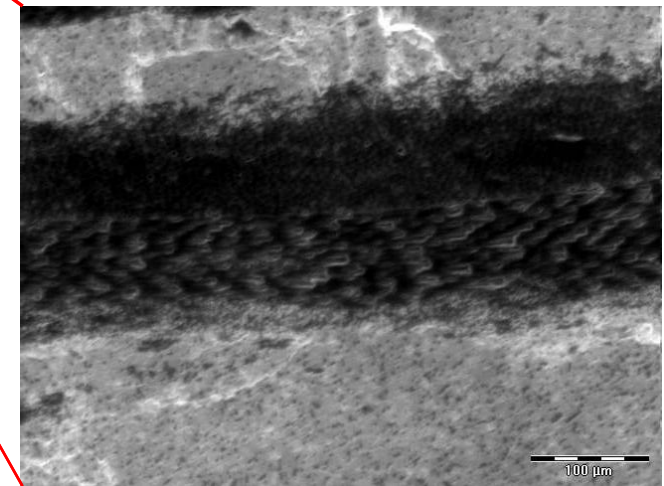
2D Composite microstructure



Dense UHTC matrix with acicular SiC.



Monolithic microstructure



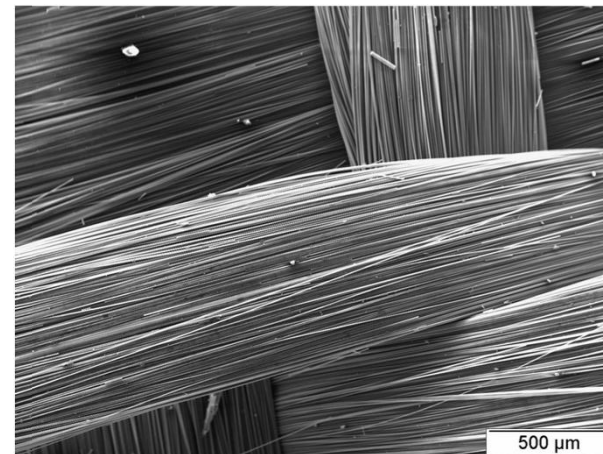
C fibers present after processing.<sup>15</sup>





# Woven 3-D Carbon Fabric

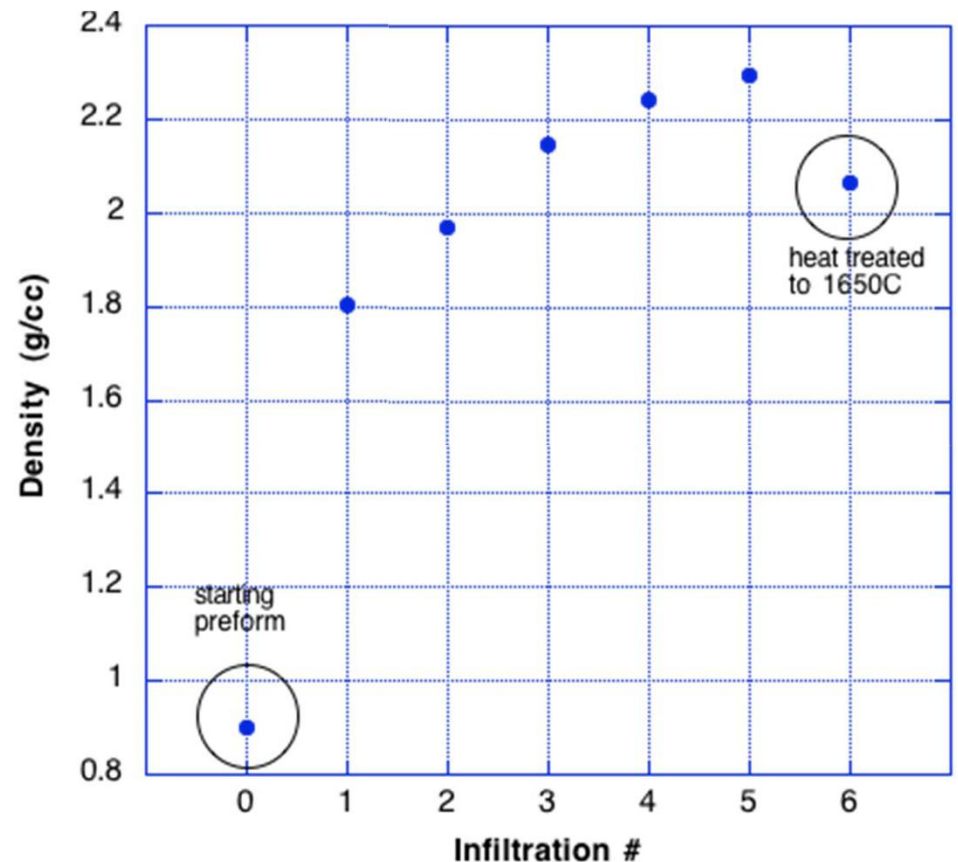
- 3D carbon preform
- PAN based fibers
- $V_f \sim 55\%$
- Density  $\sim 0.85$  g/cc





# 3D Woven Composite Infiltration

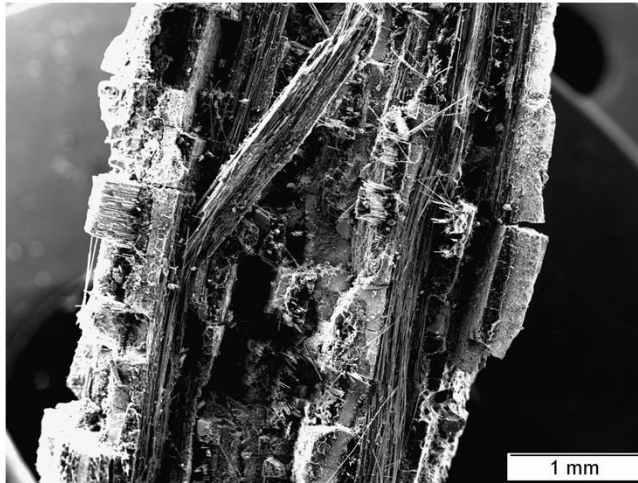
- Sample infiltrated with milled  $\text{HfB}_2$  powder followed by repeated infiltrations with preceramic polymer
  - SiC precursor
- Sample heat treated to  $> 600^\circ\text{C}$  between infiltrations to convert the polymer and remove organics
- Final heat treatment to  $1650^\circ\text{C}$
- Initial density  $\sim 0.9\text{g/cc}$
- Final density  $\sim 2.1\text{g/cc}$



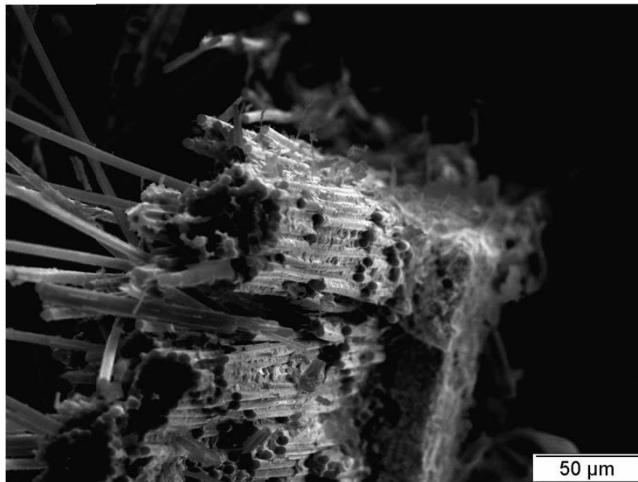


# Fracture Surface of 3D Composite

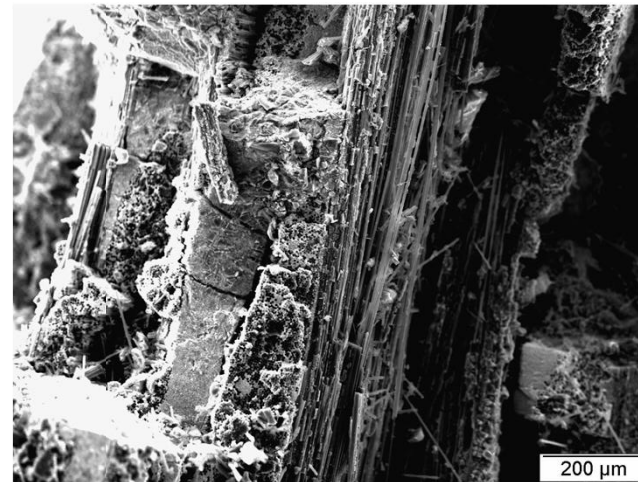
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- Non-uniform infiltration
- Accumulation on surface
- Infiltration throughout the thickness
- Infiltration into fiber bundles
- Brittle fracture



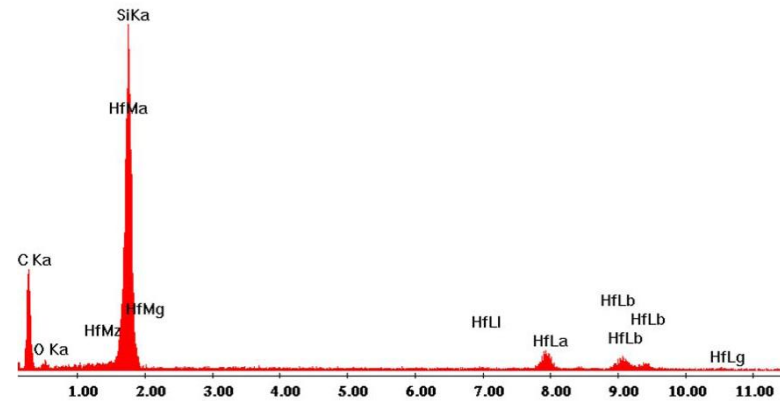
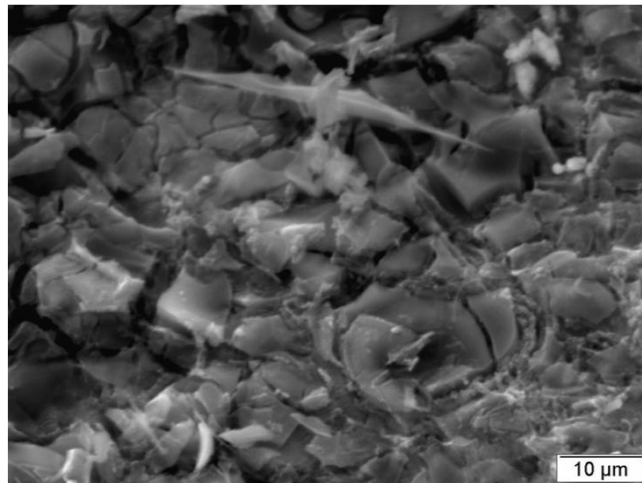
Infiltrated fiber bundle





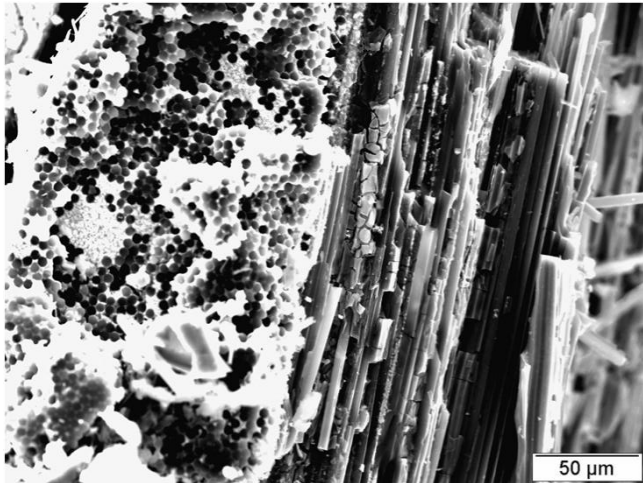
# Polymer-Rich Matrix

- Matrix is generally a mix of  $\text{HfB}_2$  powder and polymer
- Matrix infiltrates densely in some areas; poorly in others



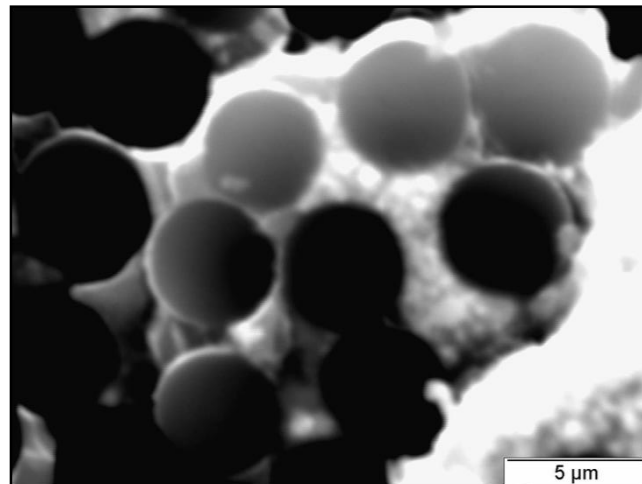
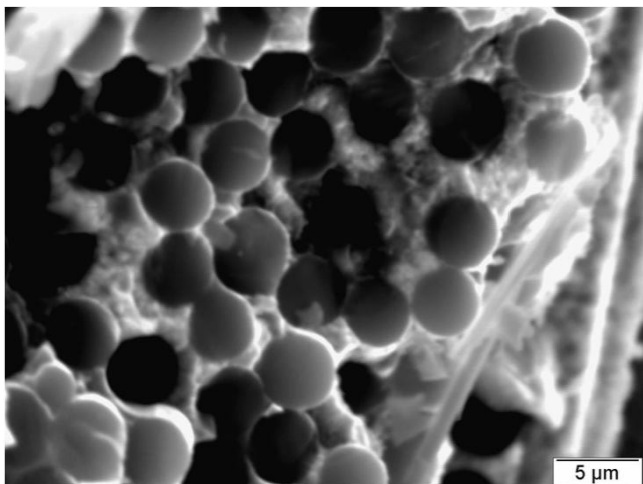


# Infiltration of Powder and Polymer into Fiber Bundles



- Non-uniform
- Both polymer and powder infiltrate between fibers

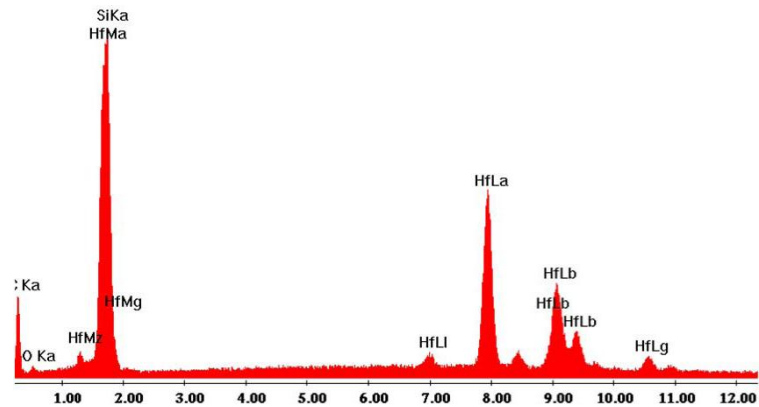
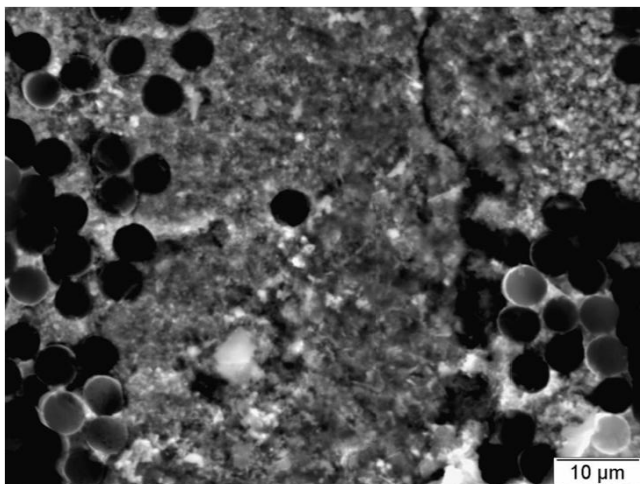
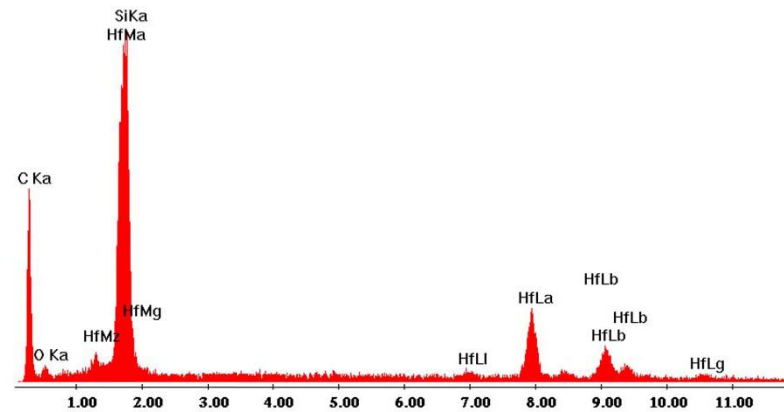
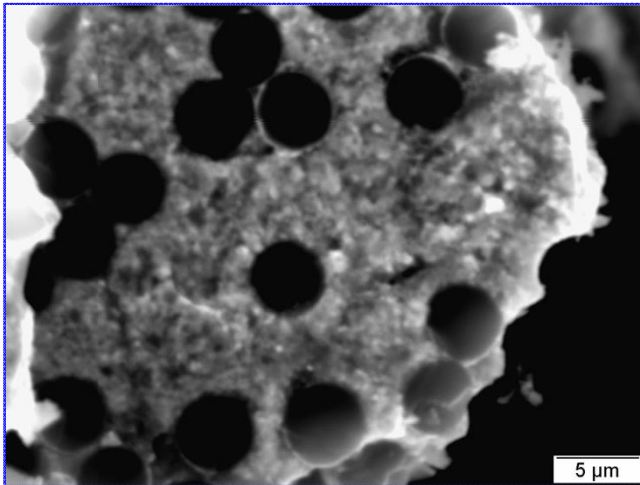
HfB<sub>2</sub> powder





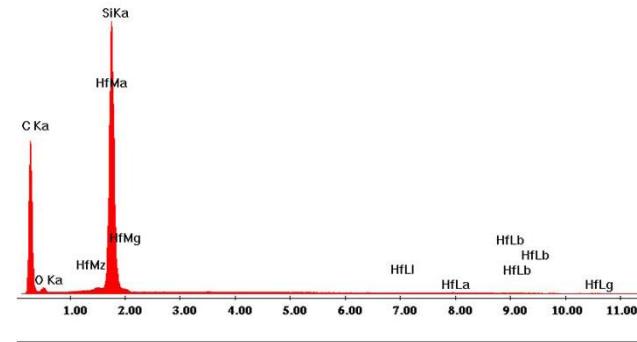
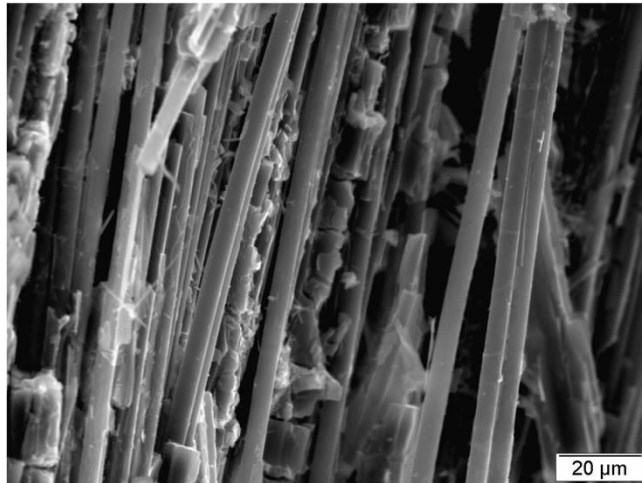
# Infiltration of Fiber Bundles

Both powder and polymer infiltrate fiber bundles





# Infiltration into 3D weave

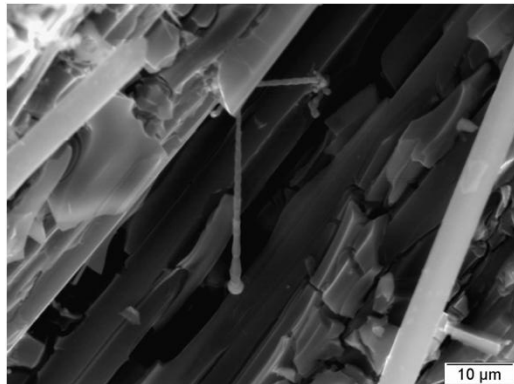
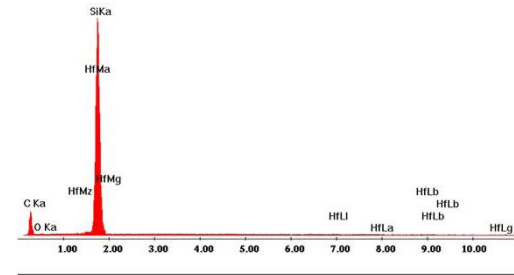
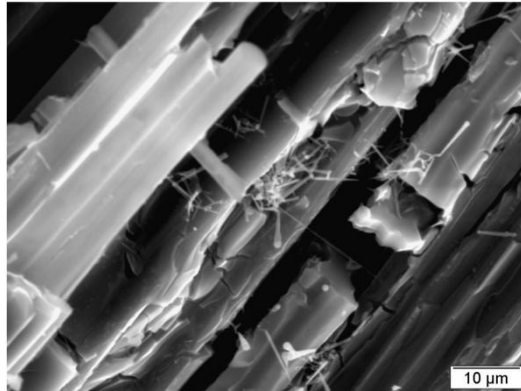


Preceramic polymer infiltrates throughout the sample

Powders infiltrate non-uniformly



# Whiskers Growing on Fibers



SiC whiskers grow in poorly-infiltrated areas.

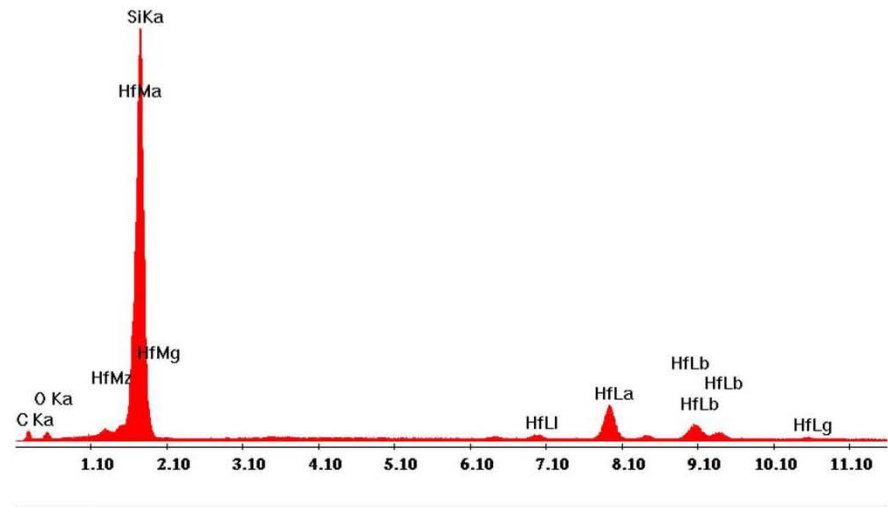
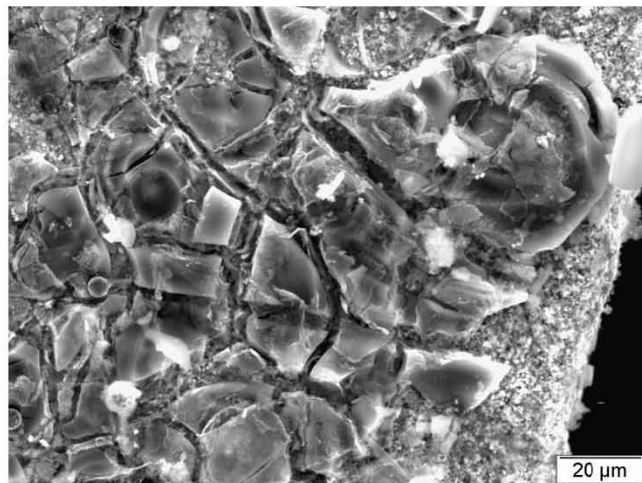




# Edge

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Label A: 3D Carbon With HfB2 SIC 800X Edge



Powder and polymer build up on edge of weave



# Summary

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- Have two approaches to *in-situ* reinforcement of  $\text{HfB}_2$ 
  - Preceramic polymers
  - Fluidized bed process for “coating”
- Can infiltrate 2D C fiber weave and achieve desired matrix microstructure
- Can infiltrate 3D C fiber weave
  - Non-uniform infiltration
    - Powder and polymer both penetrate
  - Significant amount of infiltration
  - Growth of SiC whiskers in poorly-infiltrated areas
- Final microstructure unknown



# Future Work

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- Refine infiltration process
- Complete high temperature treatments of infiltrated composites
- Characterize microstructure