Microstructure of Matrix in UHTC Composites

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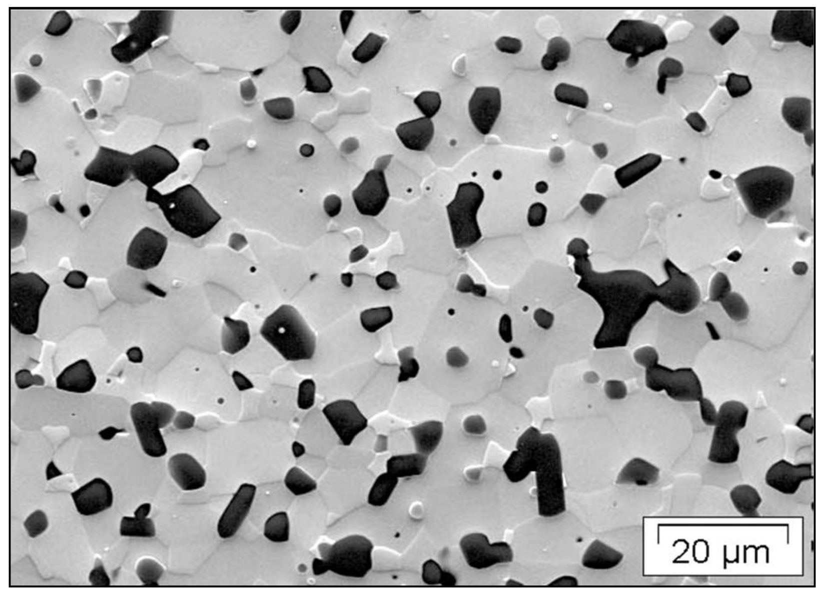
Outline

- 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

- 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_2/SiC material

Where are we going?

- 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' = σk/(αE)**
  - 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?

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!**

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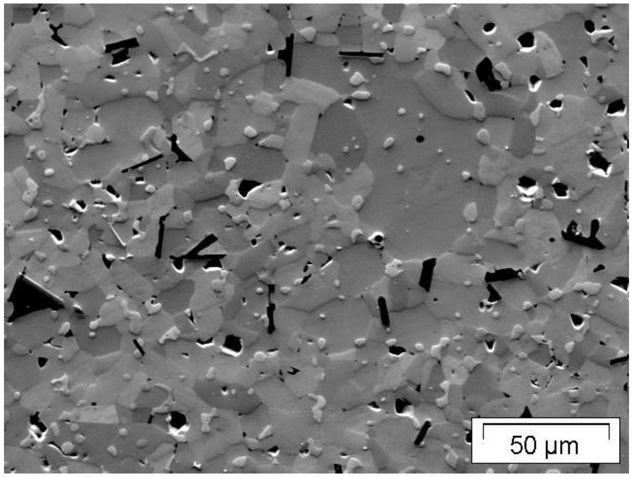
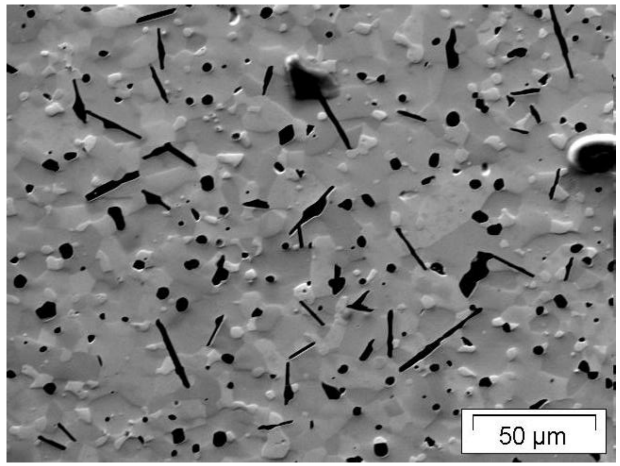
Preceramic Polymers Can Control Grain Shape

- 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 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.

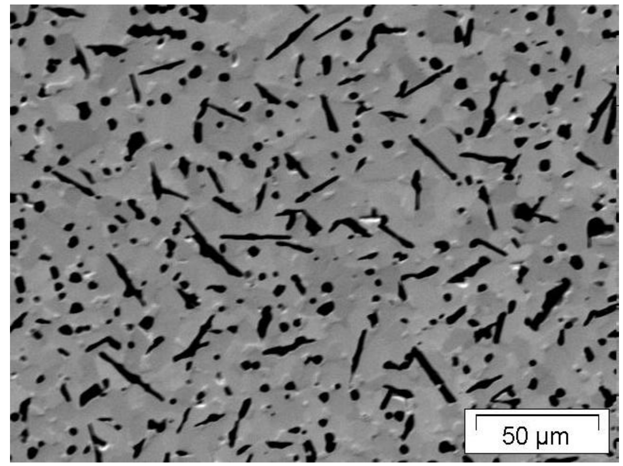
Growth of Elongated SiC Grains



5%* SiC



10%* SiC — Rod diameter ~2µm



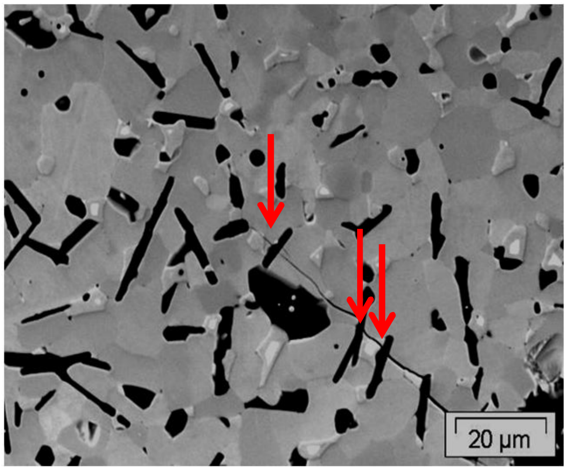
15%* SiC — Rod diameter ~5µm

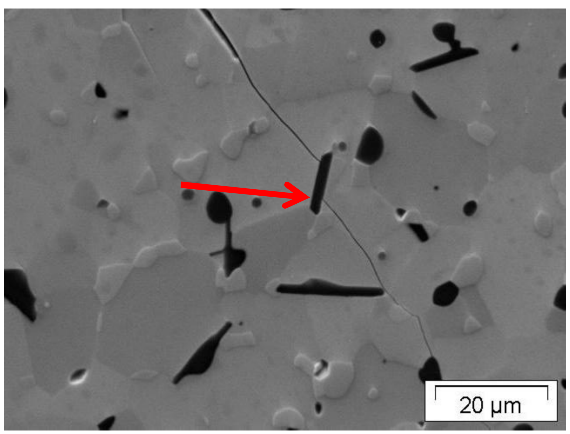
SiC Preceramic Polymer Promotes Growth of Acicular Grains

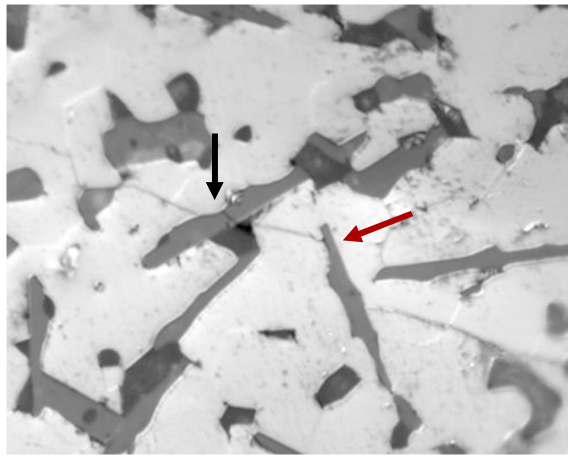
- Samples processed with 5 to >20 volume % SiC
- Can adjust volume of SiC in the UHTC without losing the high l/d architecture
- Amount of SiC affects number and thickness (but not length) of rods — length constant (~20–30µm)
- Possible to obtain dense samples with high-aspect-ratio phase
- Hardness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

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

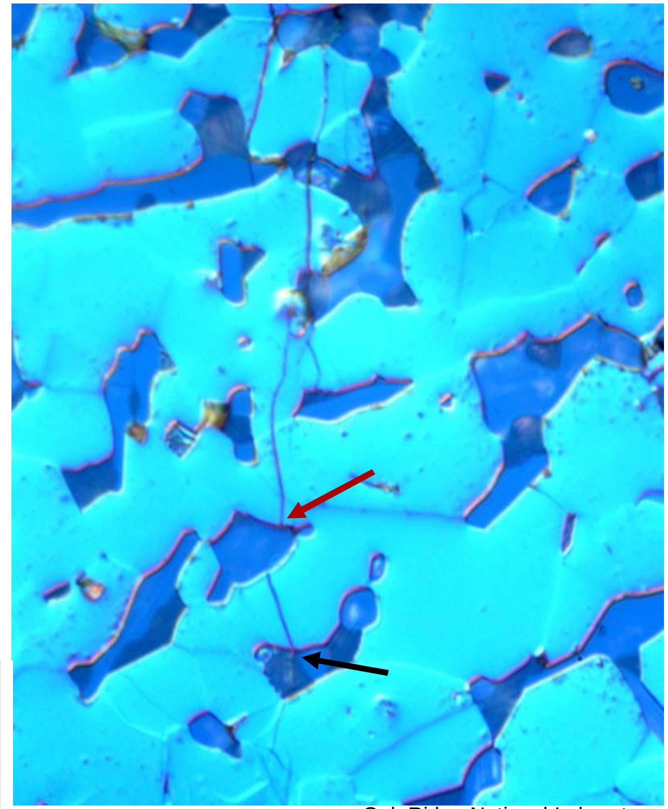
In Situ Composite for Improved Fracture Toughness







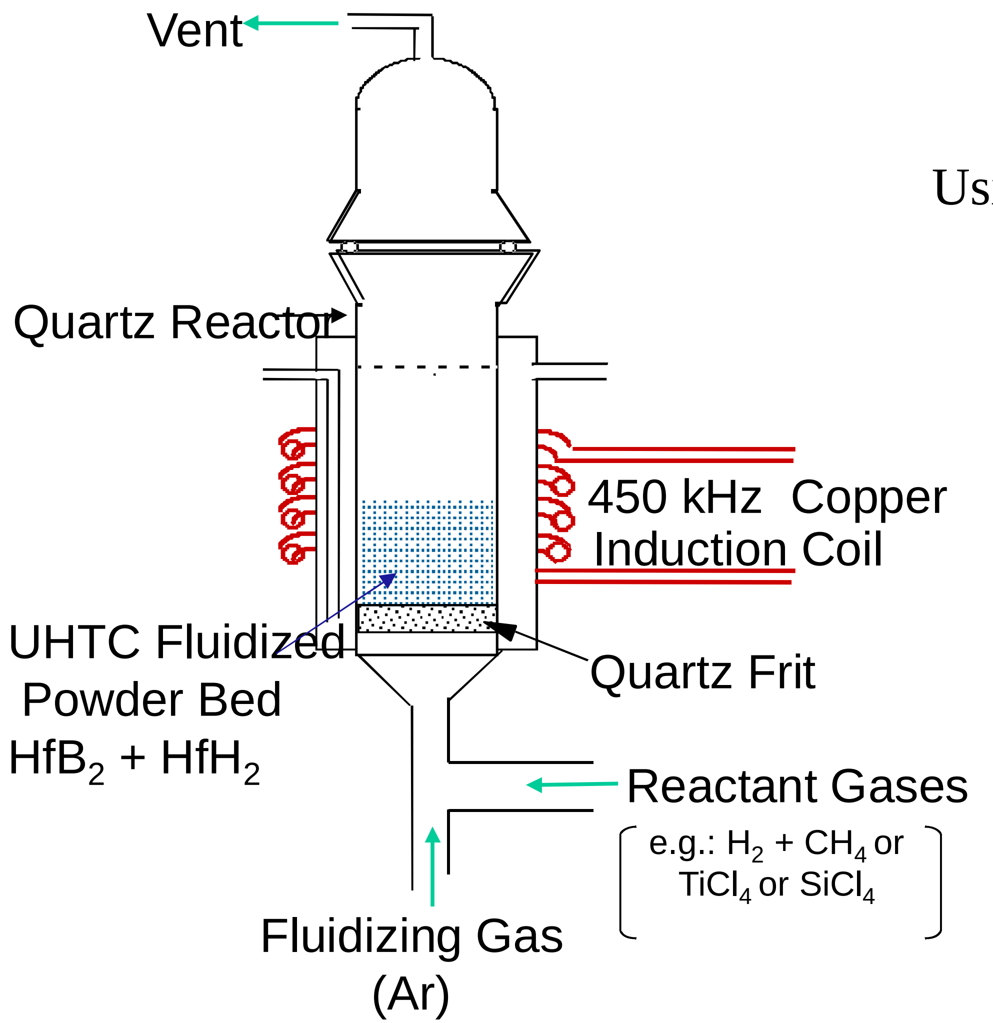
SiC Content	Fracture Toughness (MPam$^{1/2}$)
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33



Oak Ridge National Laboratory

Evidence of crack growth along HfB_2-SiC interface, with possible SiC grain bridging

When Additives for UHTCs Are Added as Coatings

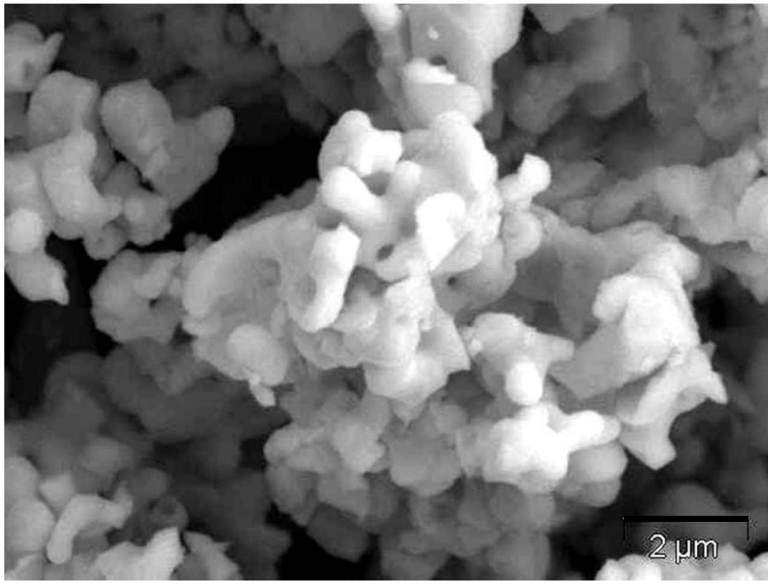


Fluidized Bed Reactor - Chemical Vapor Deposition Technique (FBR-CVD)

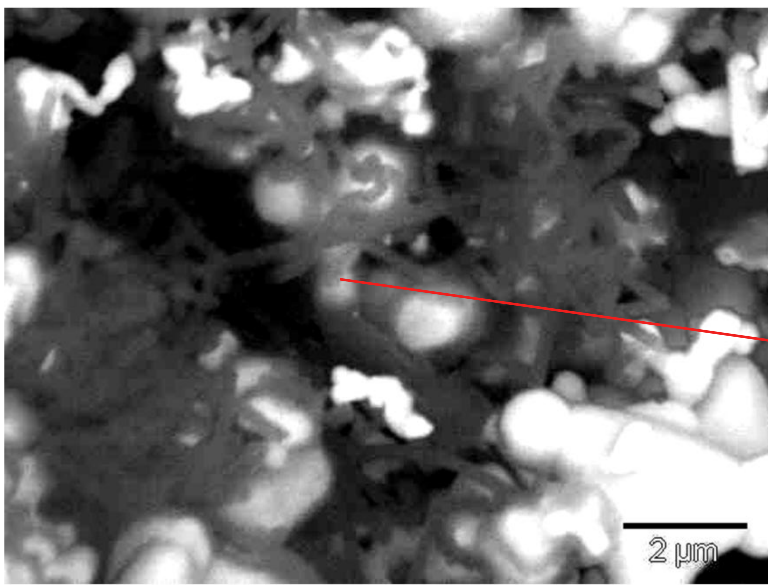
Using coatings, instead of particles, to introduce additives, offers several advantages:

- Uniform distribution and control of coating composition
- Bypasses traditional sources of processing contamination
- May lead to improved oxidation and creep resistance (less O_2 contamination)
- Amount of additive can be controlled
- Reductions in hot-press temperature, pressure, and time

SiC Coating Appearance on Powders



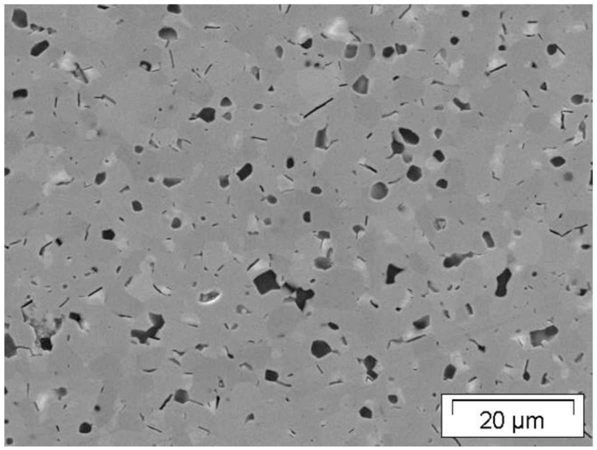
Uncoated Powder

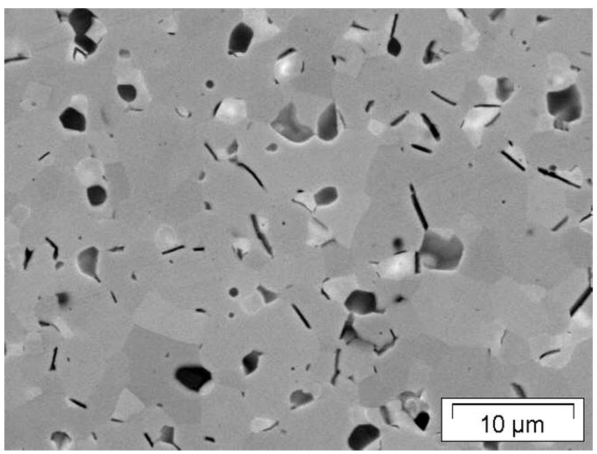


SiC Coated Powder

Gray filamentous material is SiC

Addition of SiC as “Coating”





HfB_2- 5 vol-%SiC (SPS)

- Alternative route to growing acicular grains
- HfB_2 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

Processing of Composites

Objectives:

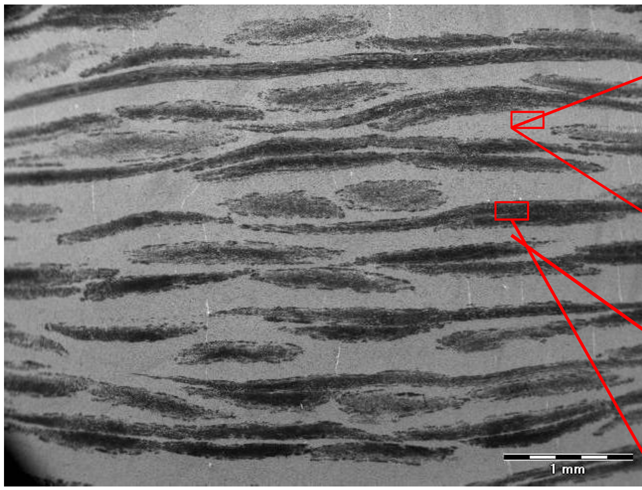
- Can we use knowledge gained form controlling microstructures in “monolithic” UHTCs to make matrices for fiber reinforced composites?
- Can both 2D and 3D weaves be infiltrated?
- Caveats
  - Using available carbon fiber structures
  - No fiber coating

Processing of 2D Weave

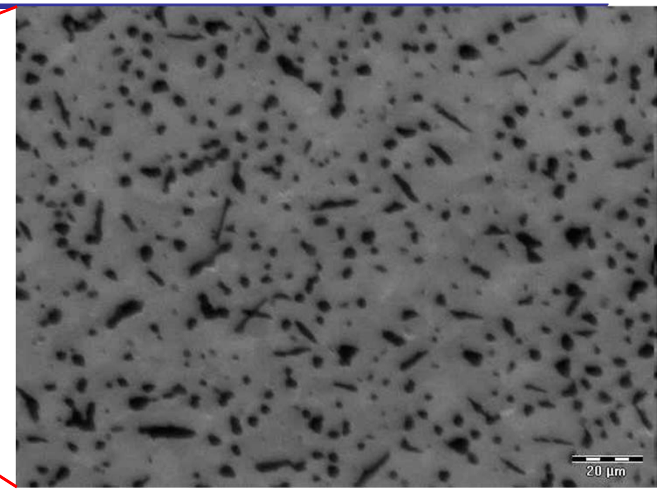
Composites from 2D weaves

- Carbon fiber cloth (PAN-based)
- Impregnated with preceramic polymer/HfB_2 powder mixture—one infiltration per layer
- Layers stacked and hot pressed (~15 layers)

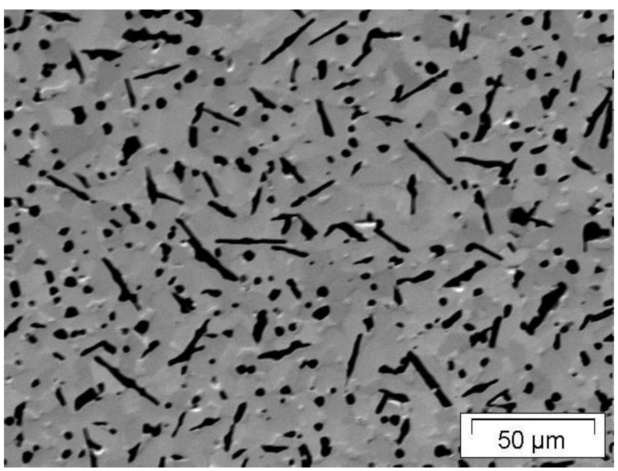
Ultra High Temperature Continuous Fiber Composites



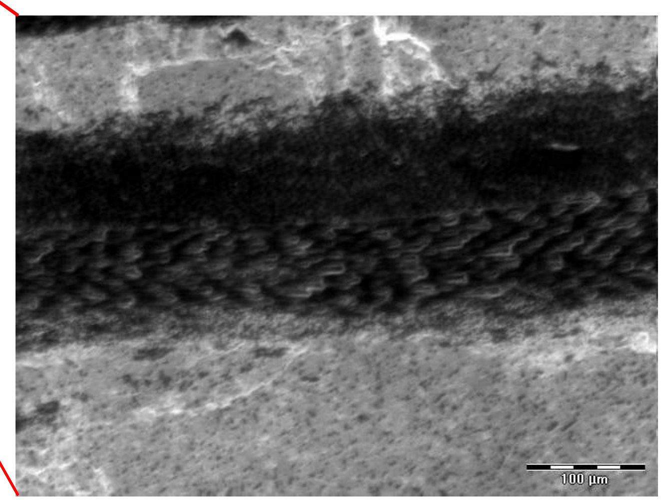
2D Composite microstructure



Dense UHTC matrix with acicular SiC.



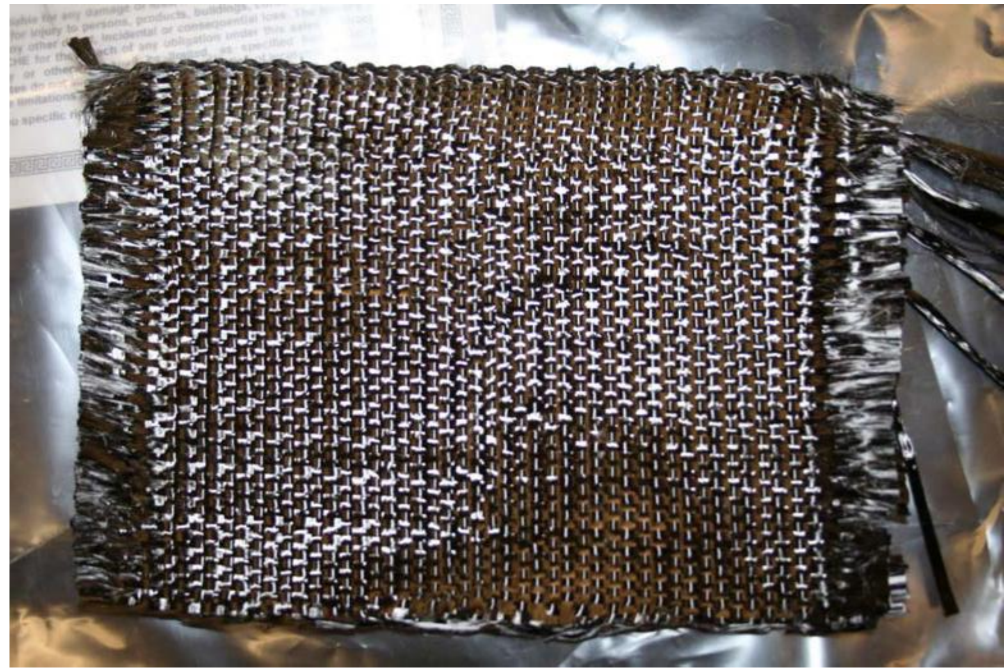
Monolithic microstructure

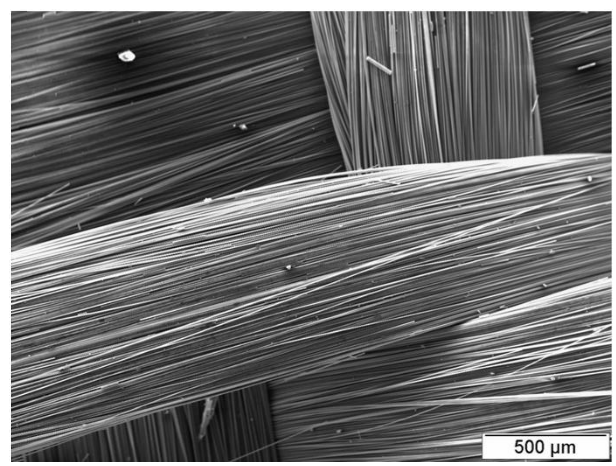


C fibers present after processing.

Woven 3-D Carbon Fabric

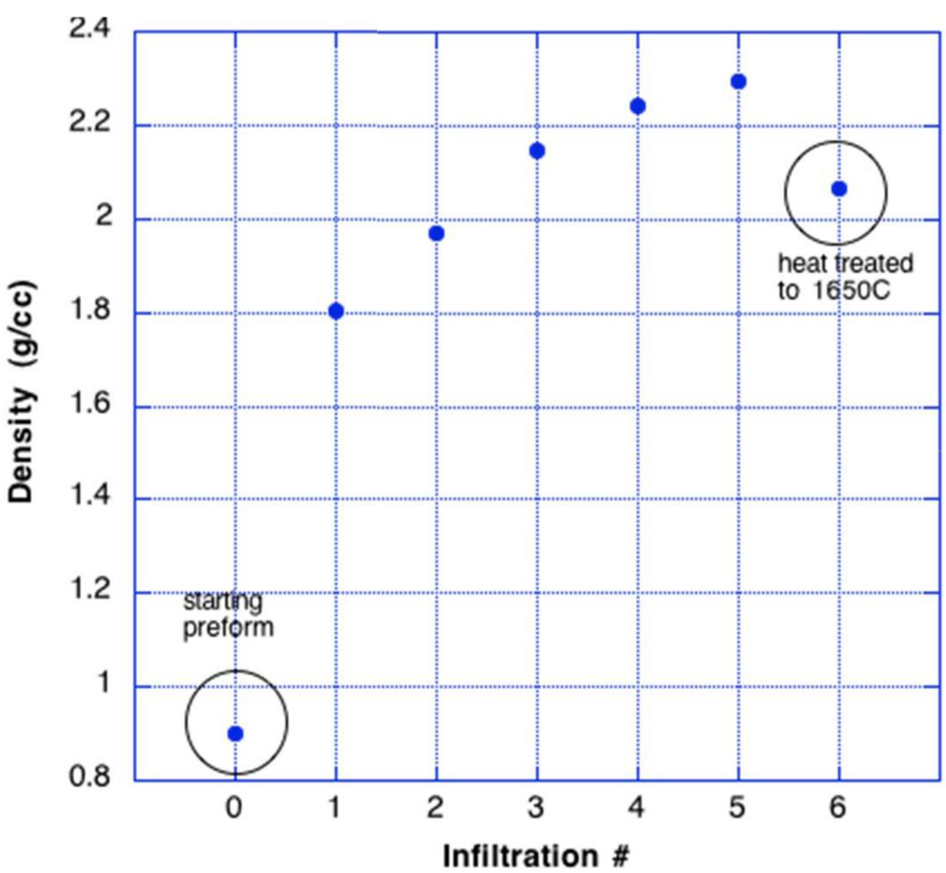
- 3D carbon preform
- PAN based fibers
- V_f ~ 55%
- Density ~ 0.85 g/cc



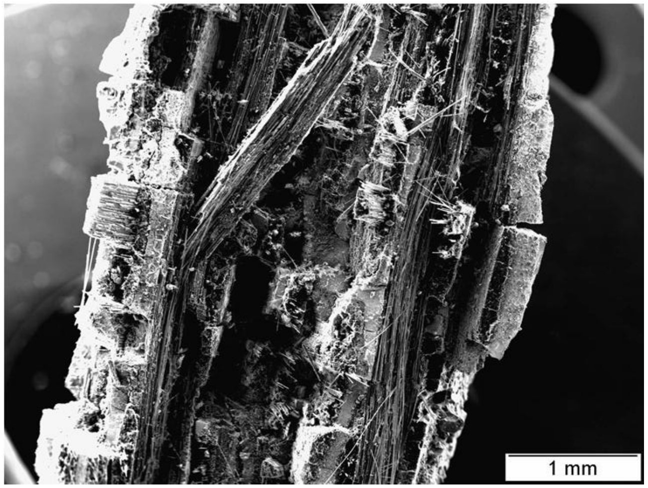


3D Woven Composite Infiltration

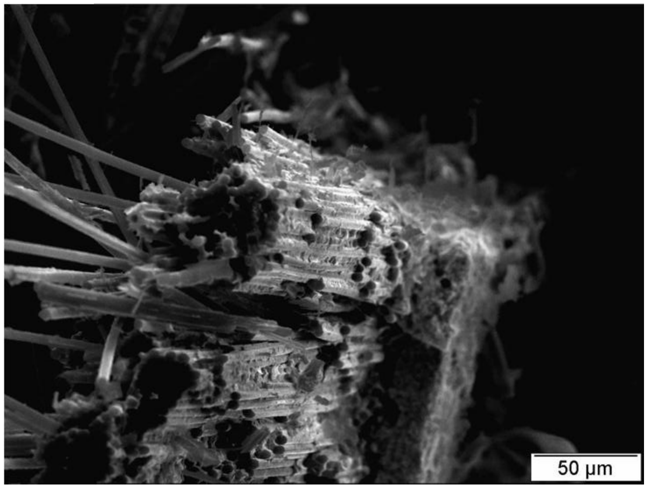
- Sample infiltrated with milled HfB_2 powder followed by repeated infiltrations with preceramic polymer
  - SiC precursor
- Sample heat treated to > 600°C between infiltrations to convert the polymer and remove organics
- Final heat treatment to 1650°C
- Initial density~0.9g/cc
- Final density ~2.1g/cc

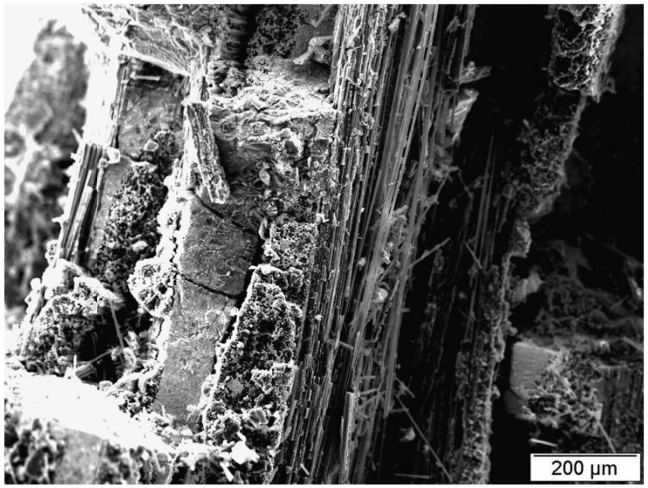


Fracture Surface of 3D Composite



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

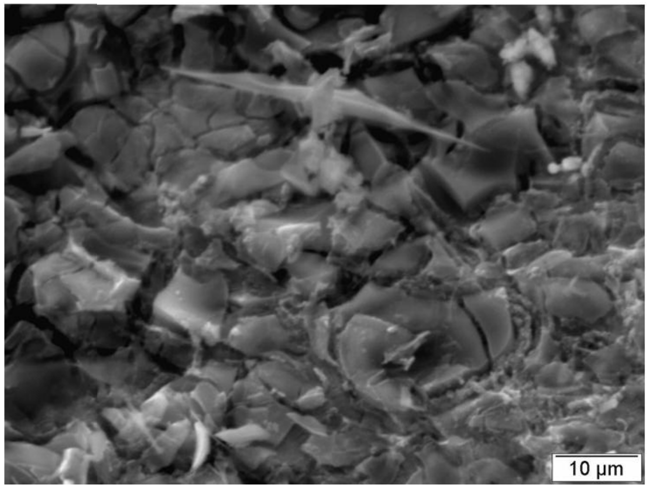


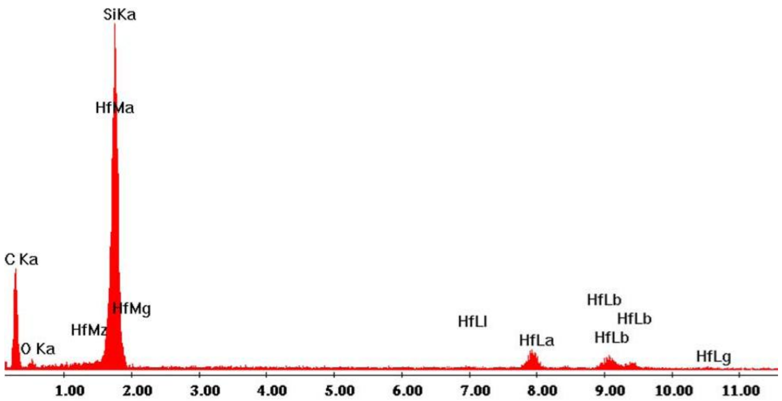


Infiltrated fiber bundle

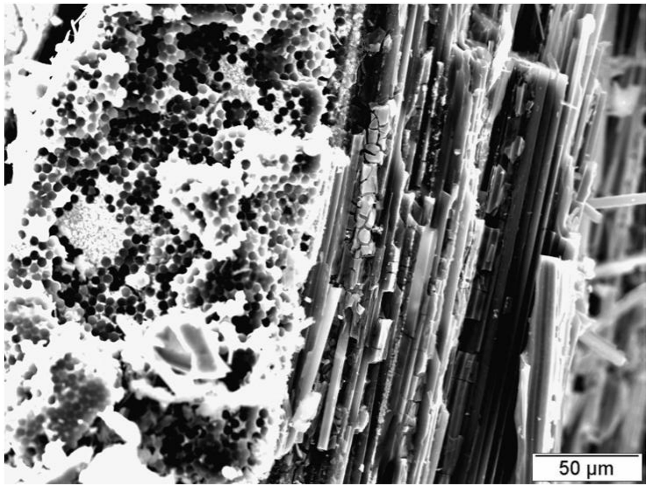
Polymer-Rich Matrix

- Matrix is generally a mix of HfB_2 powder and polymer
- Matrix infiltrates densely in some areas; poorly in others



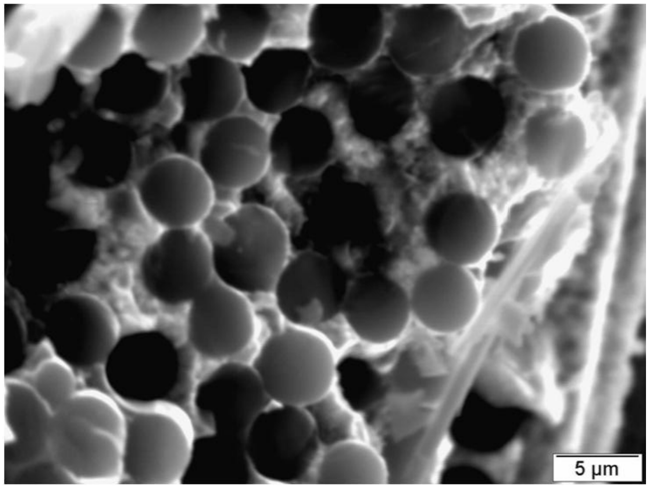


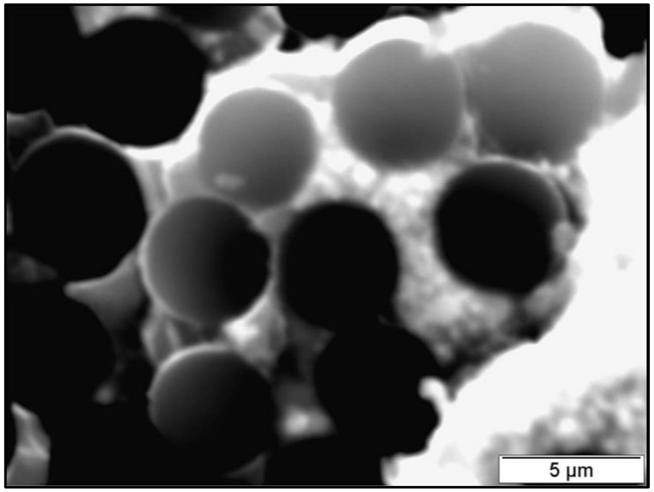
Infiltration of Powder and Polymer into Fiber Bundles



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

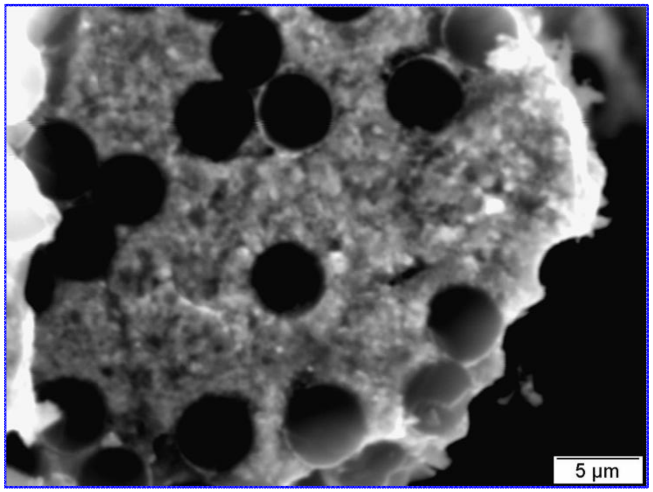
HfB_2 powder

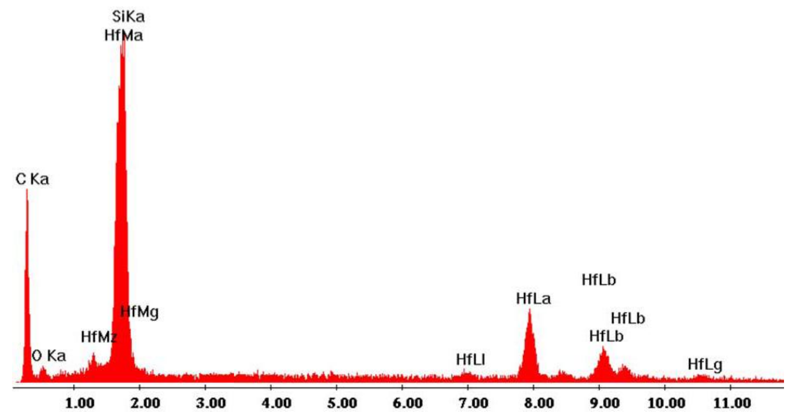


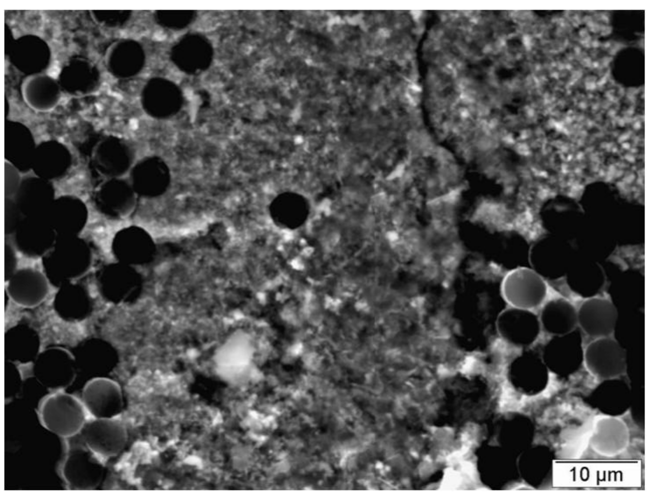


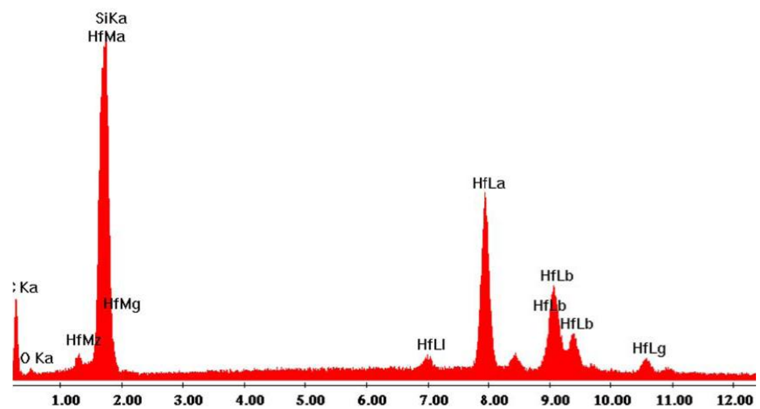
Infiltration of Fiber Bundles

Both powder and polymer infiltrate fiber bundles

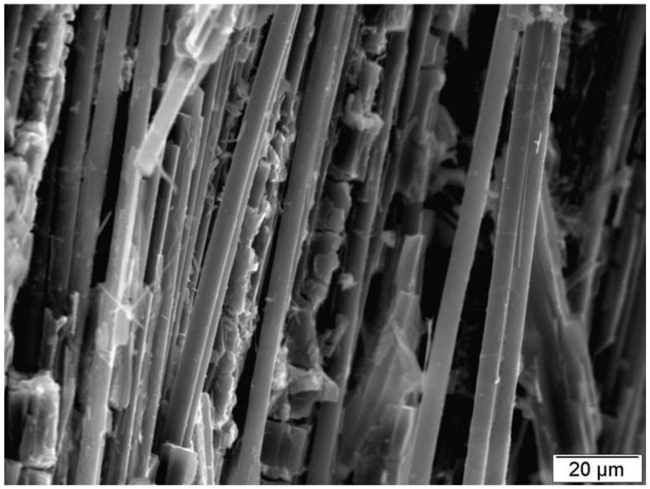


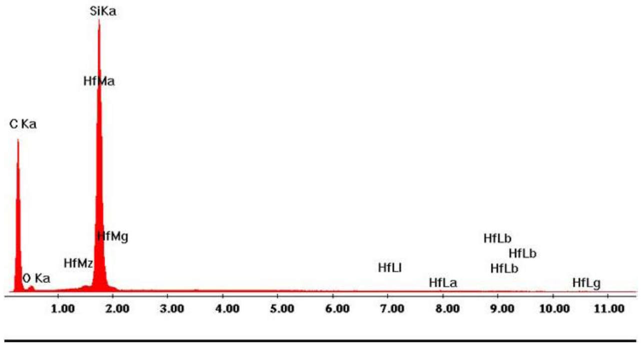






Infiltration into 3D weave

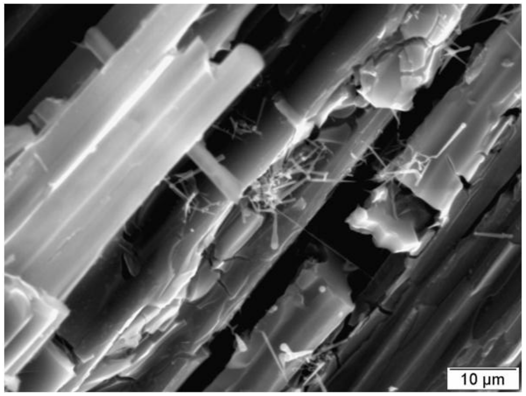


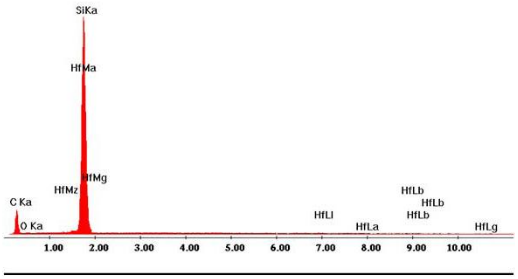


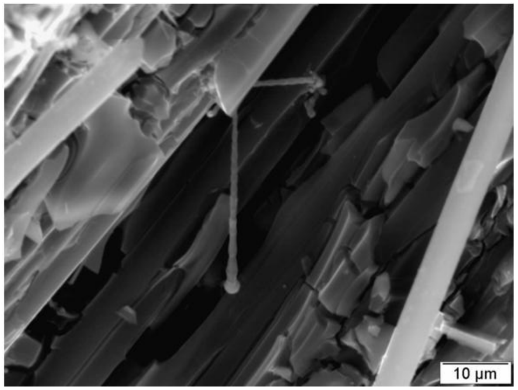
Preceramic polymer infiltrates throughout the sample

Powders infiltrate non-uniformly

Whiskers Growing on Fibers

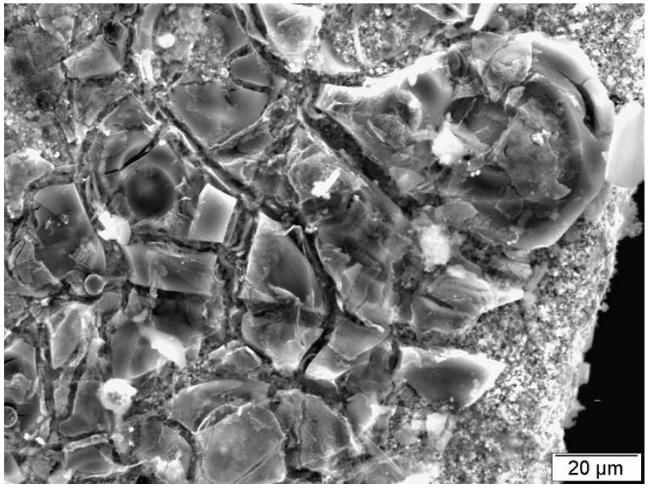


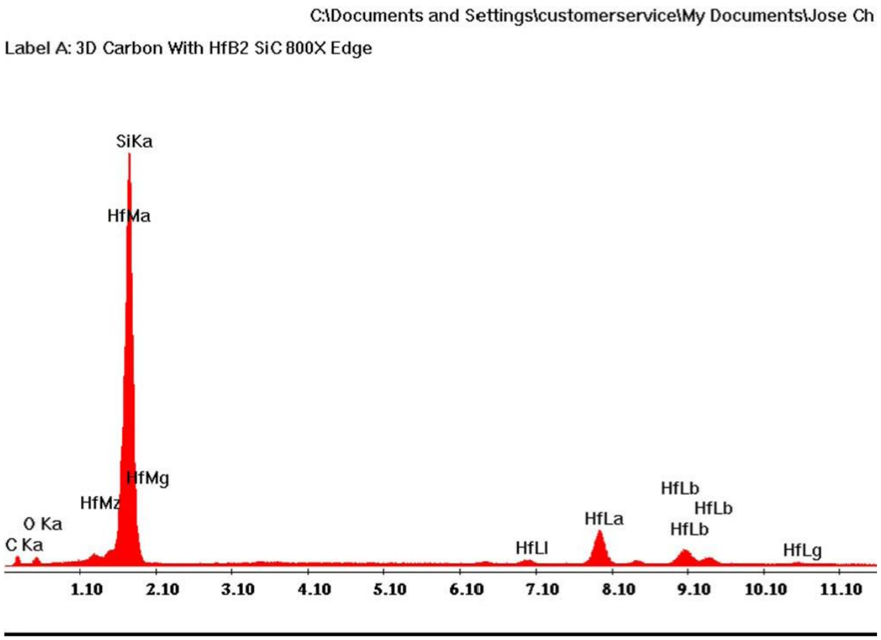




SiC whiskers grow in poorly-infiltrated areas.

Edge





Powder and polymer build up on edge of weave

Summary

- Have two approaches to *in-situ* reinforcement of 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

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