James I. Mueller

1917 - 1986

James I. Mueller

- Professor of Ceramic Engineering at the University of Washington
- Led team of scientists that helped develop insulating ceramic tiles used to protect the Space Shuttle
- Inspired future generations of materials scientists and engineers – one of whom, Bonnie Dunbar, became a NASA astronaut

Ultra High Temperature Ceramics
A Journey

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Daytona Beach, January 24, 2011

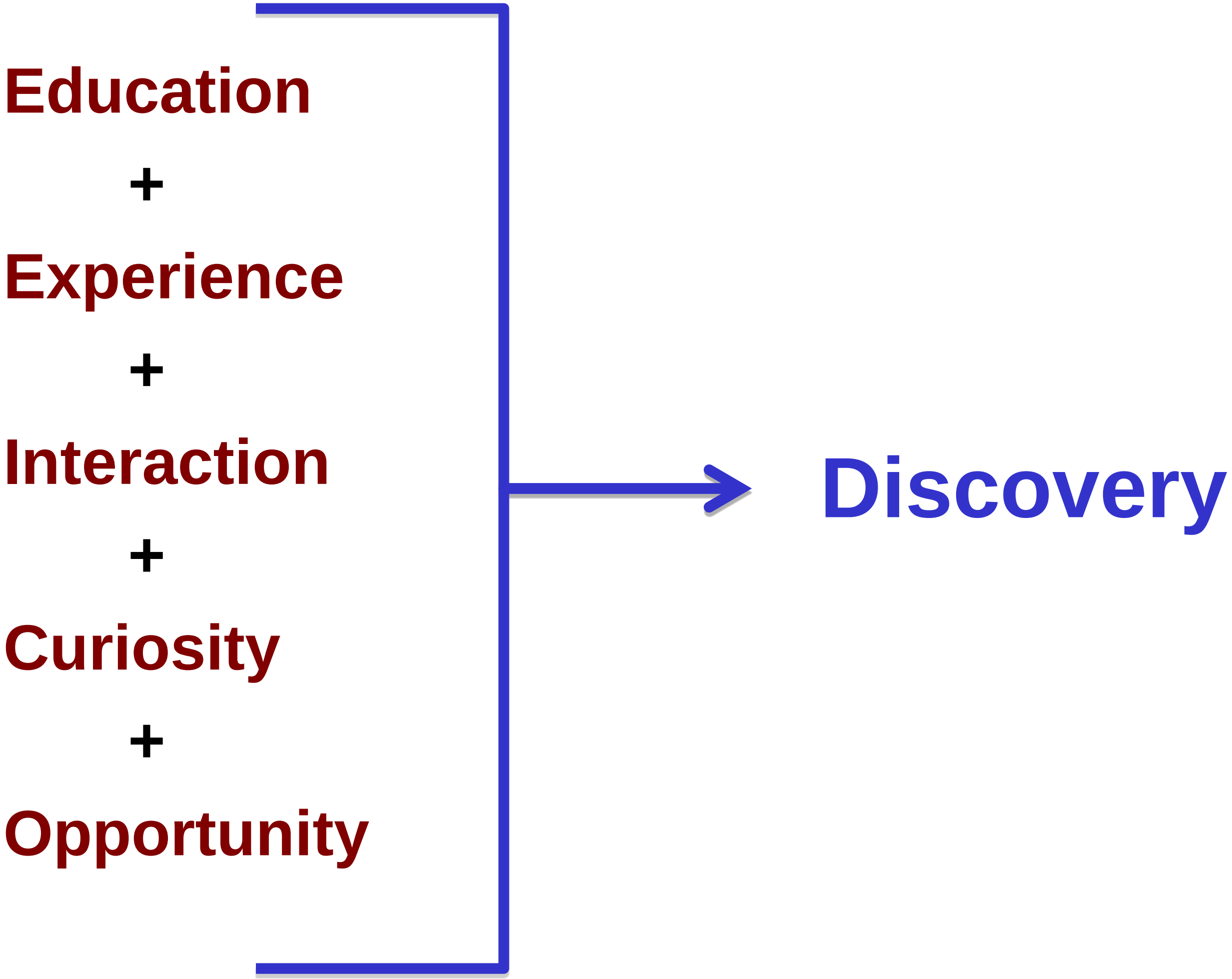
Acknowledgements

- NASA Ames Research Center
  - Don Ellerby, Matthew Gasch, Michael Olson, Sarah Beckman, Tom Squire, John Lawson
- ELORET at NASA Ames Research Center
  - Mairead Stackpoole, Michael Gusman
- Glenn Research Center
- SRI International
- University of California at Berkeley
- Many colleagues throughout the world
- My family

Outline

- The Process of Discovery
- Education
- Experience
- Curiosity
- Opportunity
- Discovery
- New Frontiers
- Conclusion

Process of Discovery



Education

+

Experience

+

Interaction

+

Curiosity

+

Opportunity

Discovery

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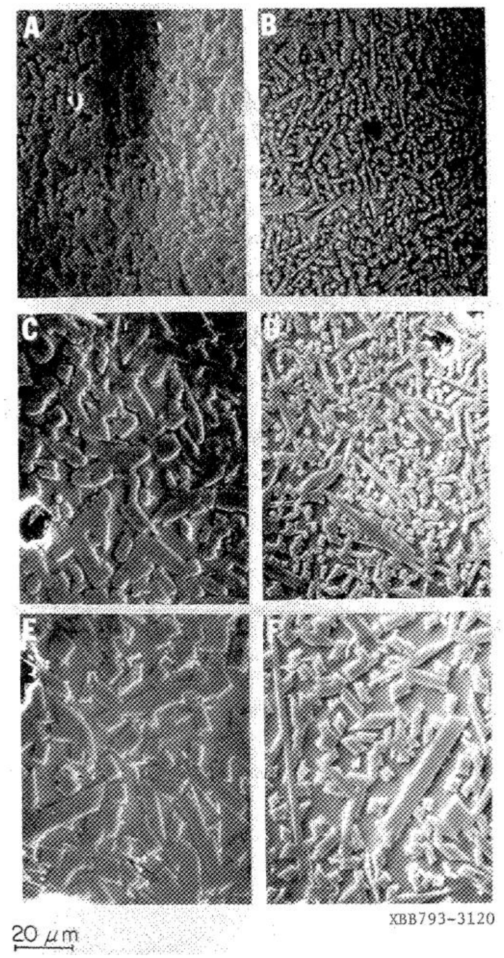
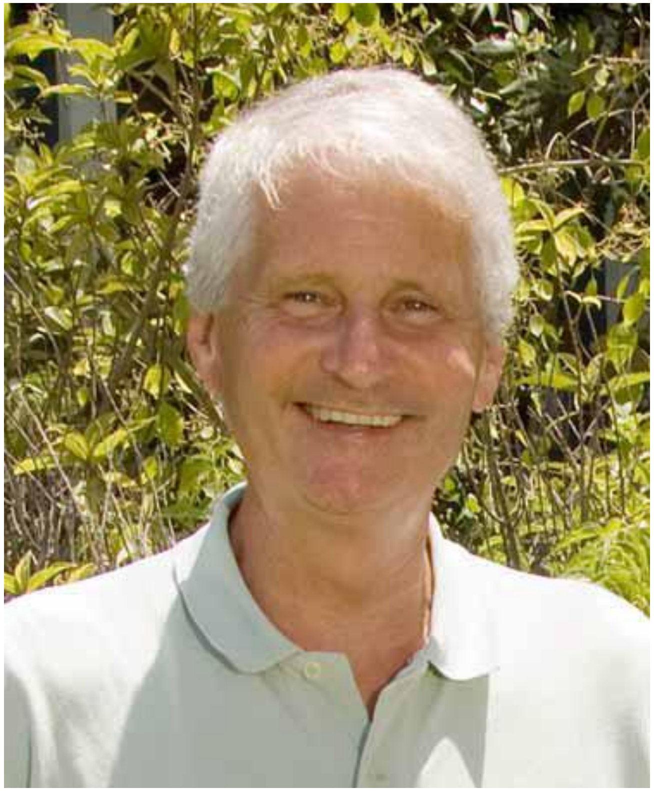
UC Berkeley

Joseph A. Pask

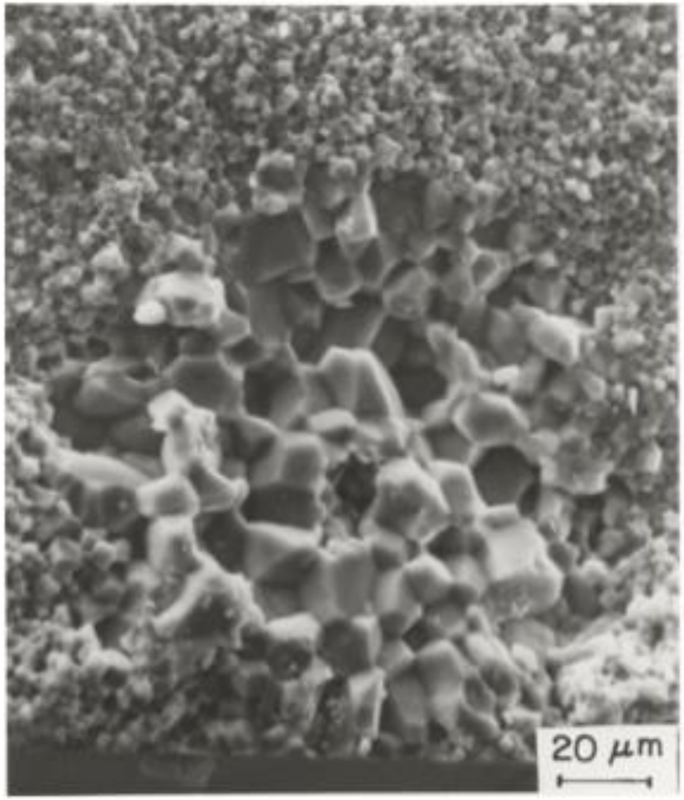


Effect of CaO on grain growth in Al_2O_3 and kaolinite

UC Berkeley



Tony Evans



Effect of defects/large grains on creep of Al_2O_3

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Experience at SRI International

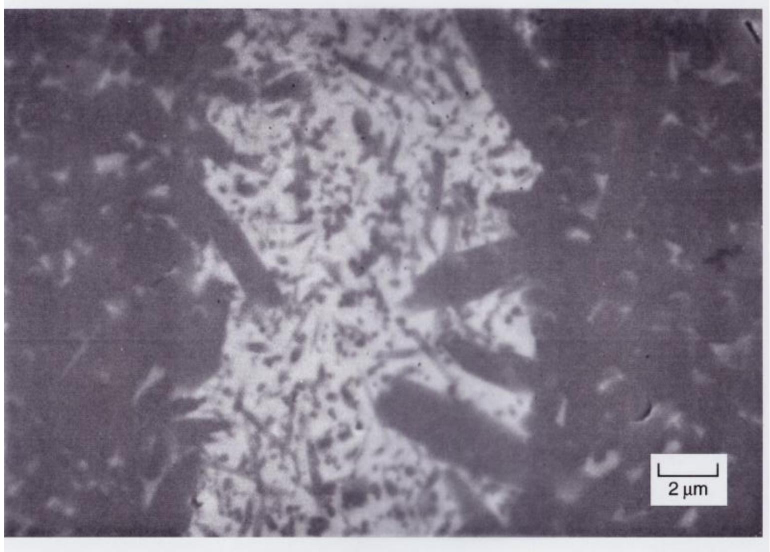
- Contract research: opportunities to solve problems and develop materials for many clients and applications

- Silicon nitride, powder synthesis, preceramic polymers, high temperature superconductors, oxide composites

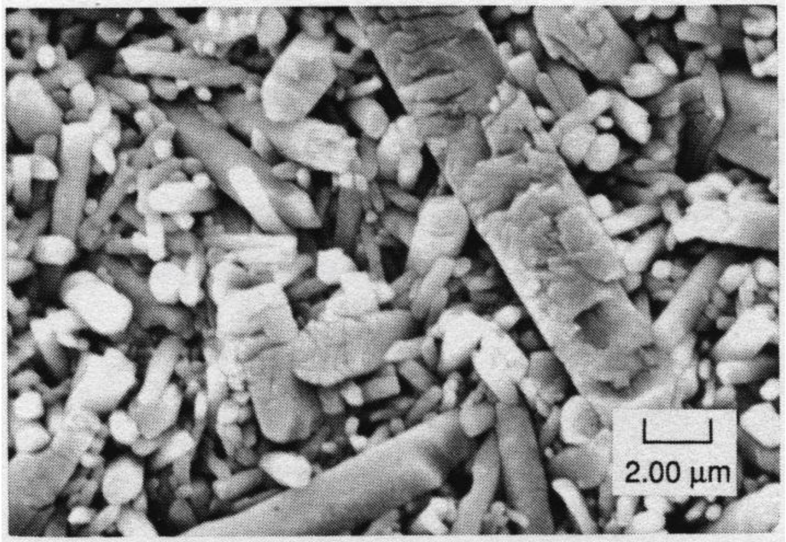
- David Rowcliffe, Yigal Blum, Michael Gusman, Bob Lamoureaux, Don Hildenbrand

Grain Growth in Si_3N_4 Preceramic Polymer Mixtures

Silicon nitride joined with a preceramic polymer

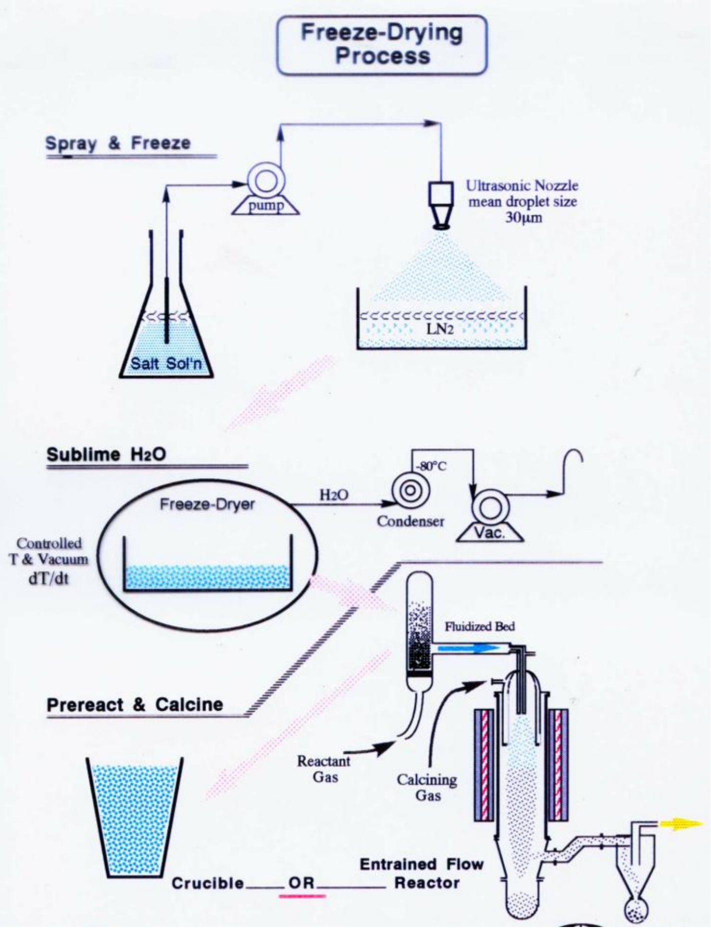


Elongated grains in sintered silicon nitride /preceramic polymer powder

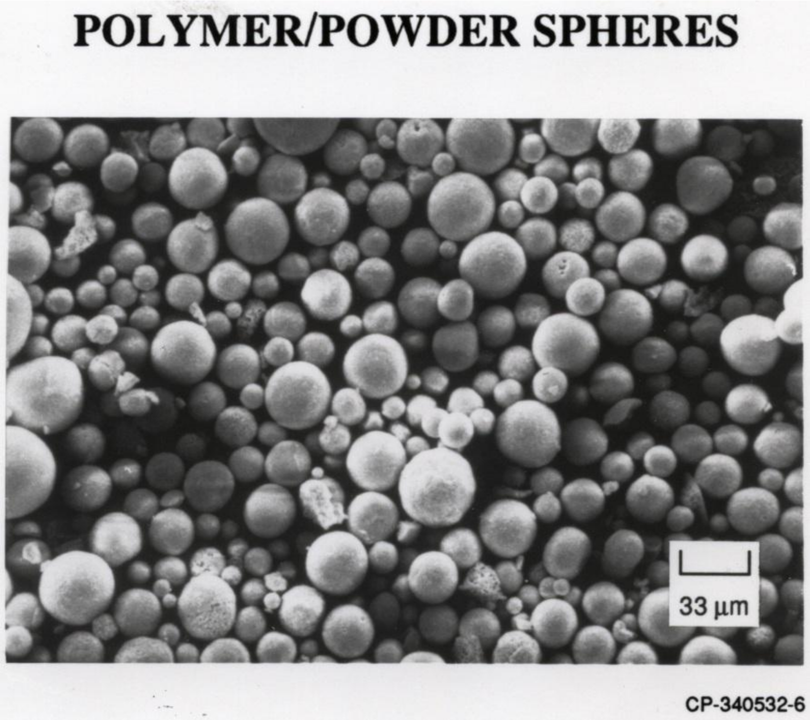


Images from work done at SRI International in 1980s/90s

Powder Preparation by Freeze-Drying



Patent: Cryochemical Method of Preparing Ultrafine Particles of High-Purity Superconducting Oxides - M. I. Gusman and S. M. Johnson. U.S. Patent 4,975,415

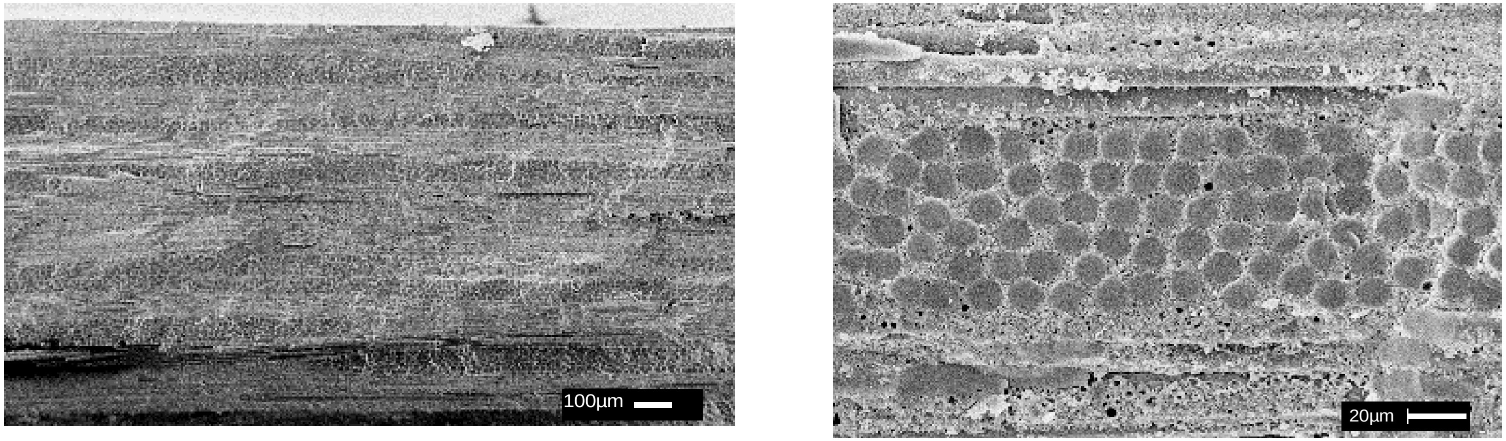


Si_3N_4/preceramic polymer powders

Images from work done at SRI International in 1990s

Oxide Composite Fabrication

- Consortium funded by DARPA
- SRI made matrix from Al/Al_2O_3/polymer slurry
- Rockwell demonstrated RTM
- 3M made large components by prepregging and by winding
- Large oxide-matrix structures made by winding



Al/Al_2O_3/polymer slurry (SRI matrix) infiltrates well into and between weaves in prepregged composite

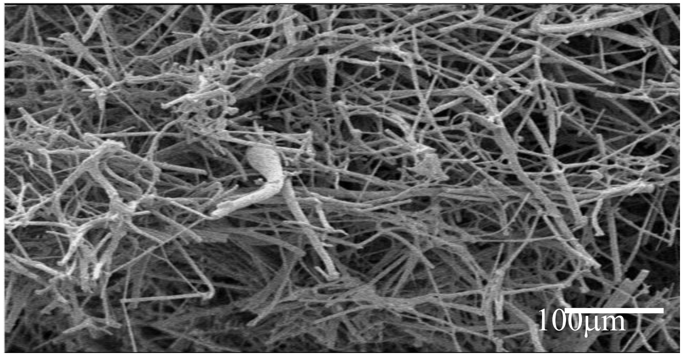
Images from work done at SRI International in mid 1990s

Thermal Protection Materials at NASA Ames

Two Types of Thermal Protection Systems (TPS)

Reusable systems reject as much heat as possible and conduct as little heat as possible

- Low thermal conductivity
- High emissivity



Microstructure of an alumino-silicate tile (AETB)

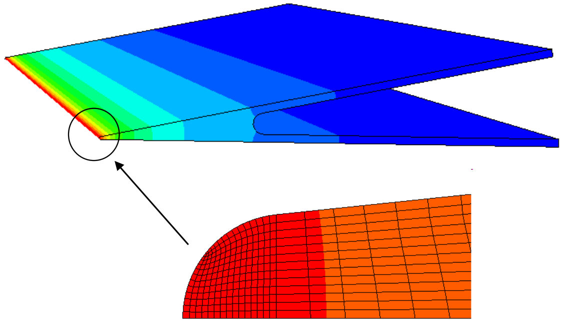
Ablative systems reject heat by material consumption

- Charring/pyrolyzing materials

Charred ablator

Sharp Leading Edge Technology

- For enhanced aerodynamic performance
- Materials for sharp leading edges can be reusable but need different properties because of geometry and very high temperatures
- Require materials with significantly higher temperature capabilities, but for short duration
  - Current shuttle RCC leading edge materials: T~1650°C
  - Materials for vehicles with sharp leading edges: T>2000°C



High Temperature at Tip

Steep Temperature Gradient

Passive cooling is simplest option to manage the intense heating on sharp leading edges.

UHTCs are candidate materials

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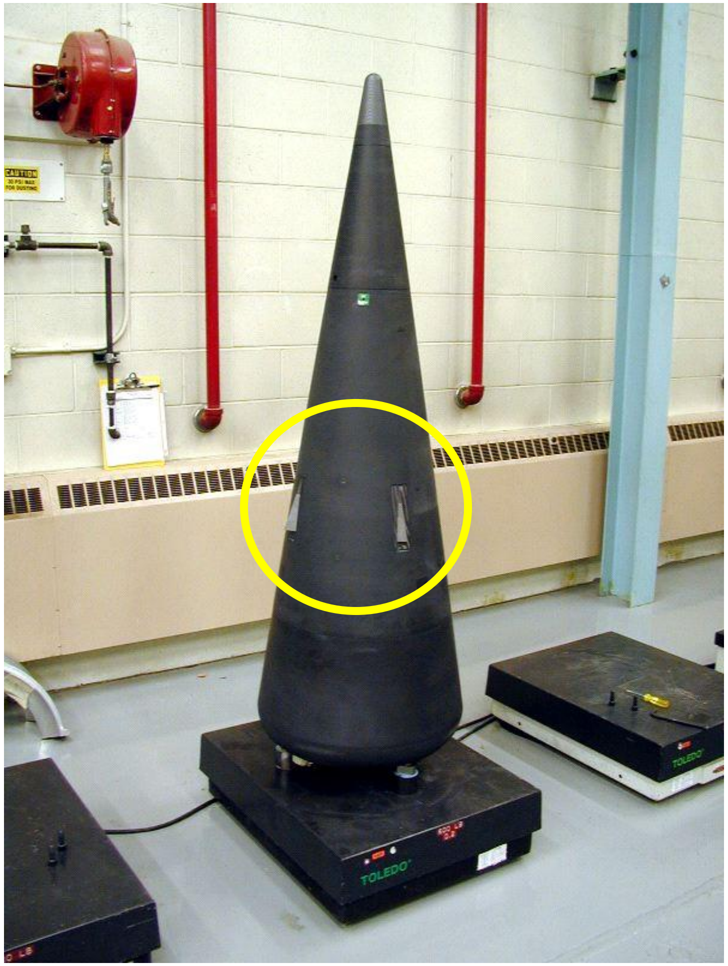
Flight Hardware

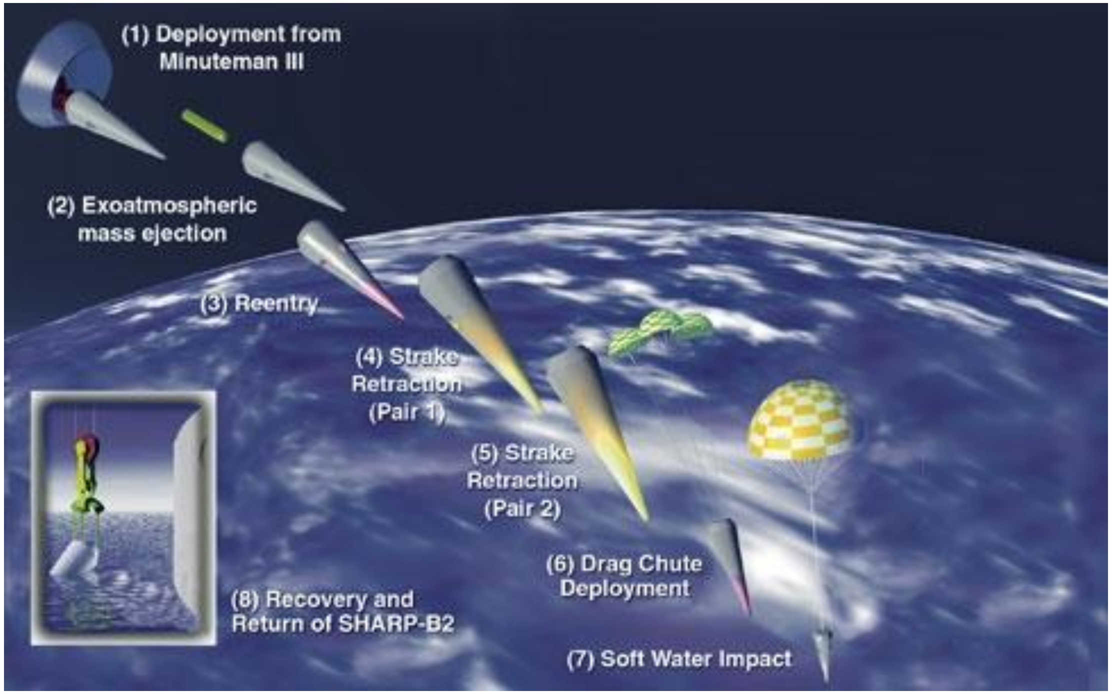
SHARP-B1 May 21, 1997



SHARP-B2 Sept. 28, 2000

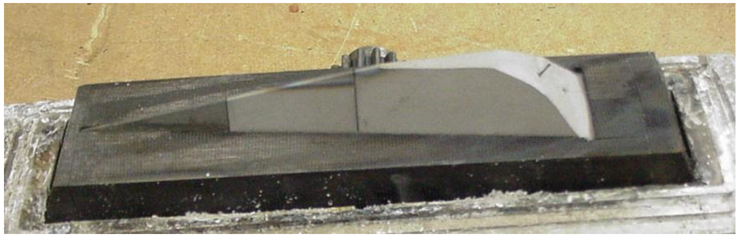
SHARP-B2

- Flight test designed to evaluate three different compositions of UHTCs in strake (fin) configuration exposed to ballistic reentry environment.
- Strakes exposed as vehicle reentered atmosphere, then retracted into protective housing.
- ***Material recovered. Led to new effort in UHTCs / decision to bring development in-house and improve processing.***

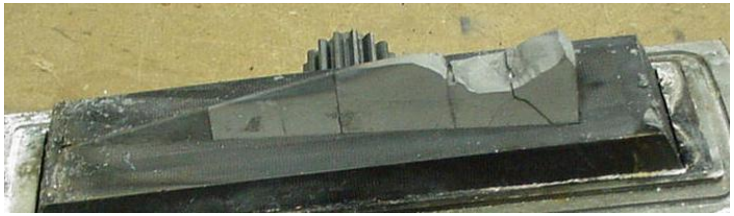


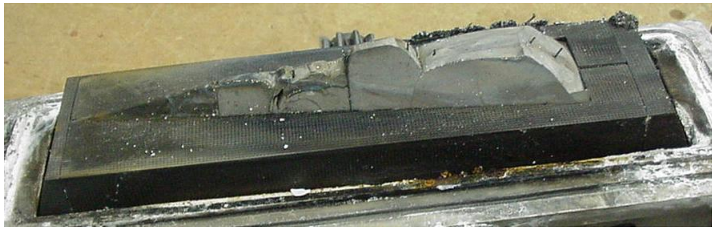
Recovered UHTC Strakes

- Post-flight recovery showed that all four HfB_2-SiC aft-strake segments suffered similar, multiple fractures.
- No evidence of severe heating damage (for example, ablation, spallation, or burning) was observed.
- Defects inherent in material lot are present on fracture surfaces.
- Actual material properties exhibit wider scatter and greater temperature dependence than those assumed in design.

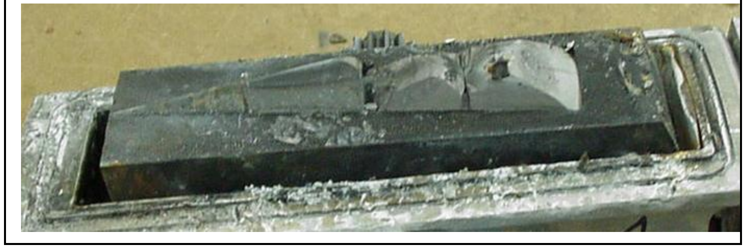


Pair 1 (47.9 km)

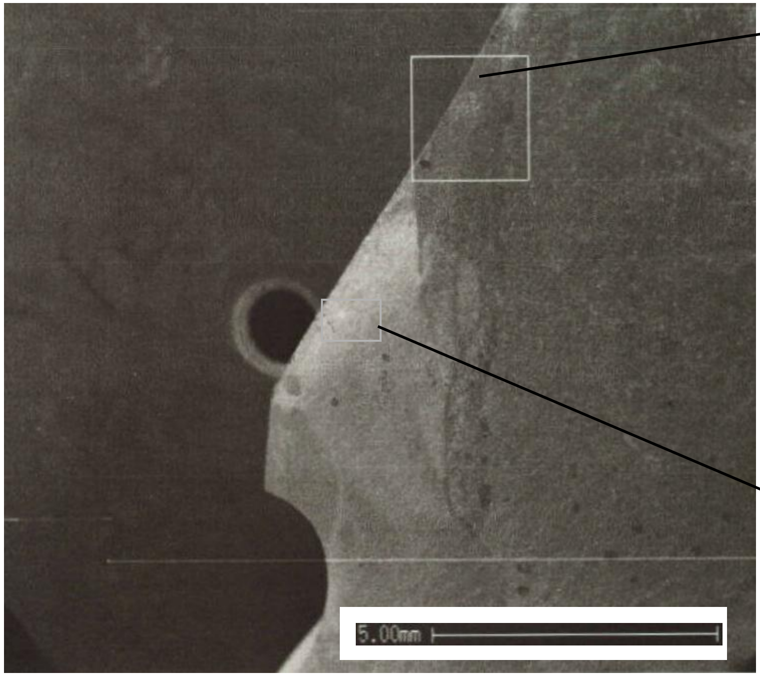


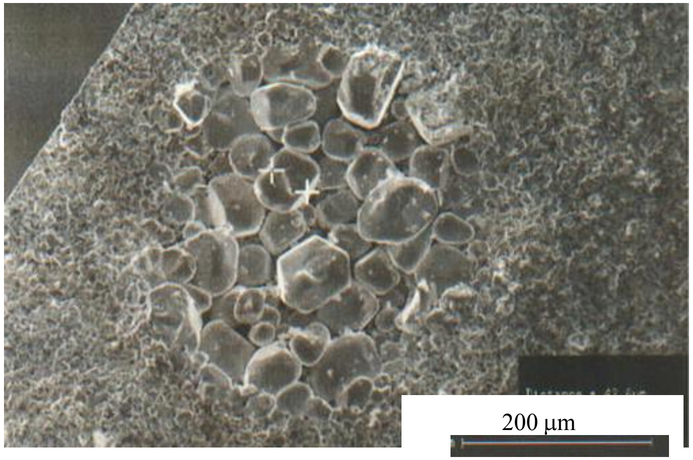


Pair 2 (43.3 km)

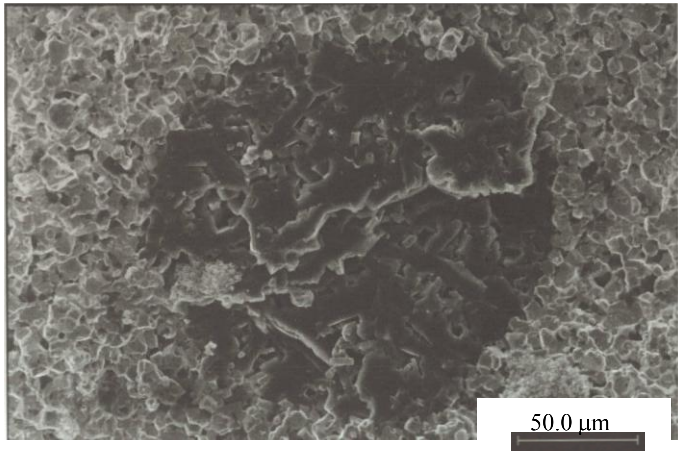


Processing Defects on Fracture Surface of Aft-Segment, Strake 2



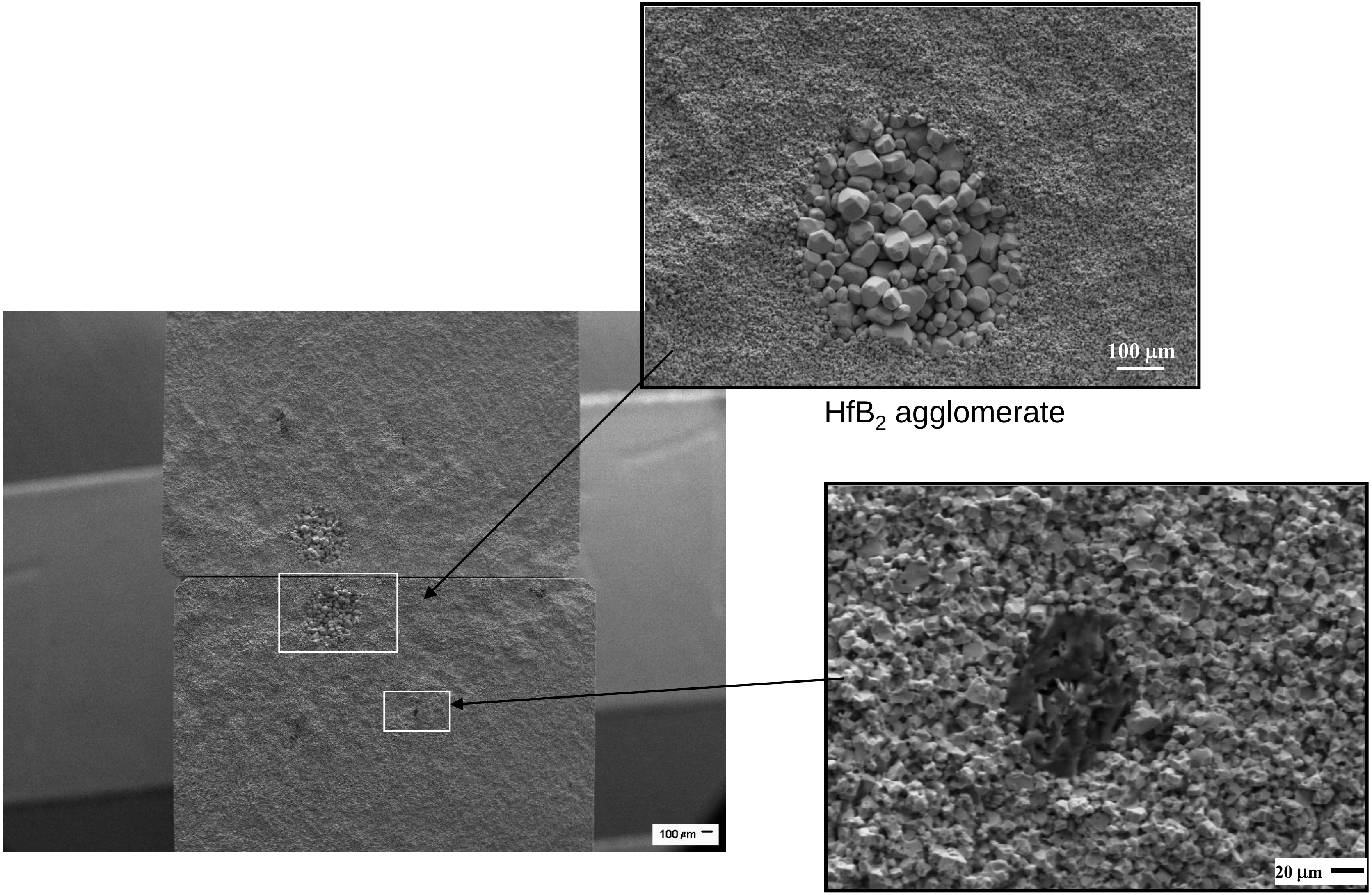


HfB_2 agglomerate



SiC agglomerate

Processing Defects in HfB_2-SiC Flexure Specimens

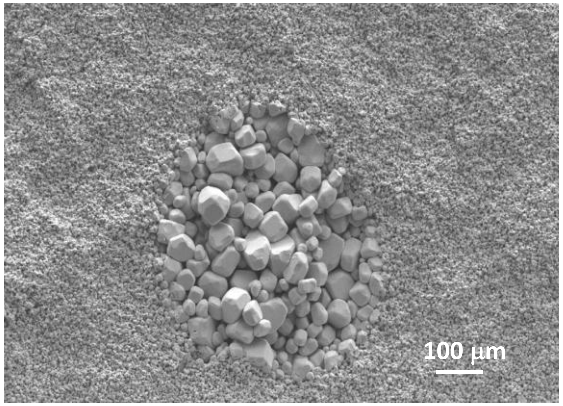


HfB_2 agglomerate

Grafoil™ agglomerate

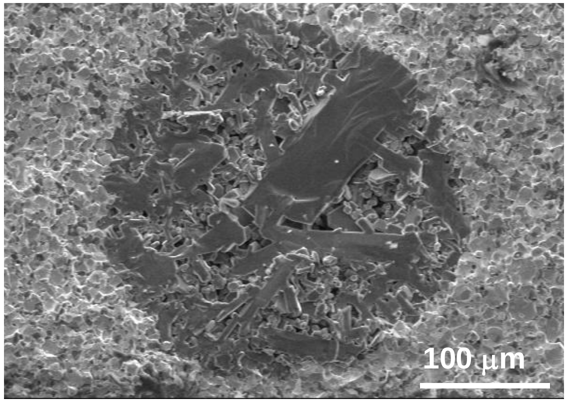
A Cautionary Tale

- Materials did not have expected fracture toughness, strength, or reliability (Weibull modulus).
- Unexpected fractures were due to poor materials processing by external vendor.
- SHARP B-2 underlined importance of controlling materials development, processing methodologies, and resulting material properties if we are to get the maximum value from an experiment.



Large HfB_2 agglomerate

Poorly processed $HfB_2$20v%SiC



Large SiC-rich agglomerate

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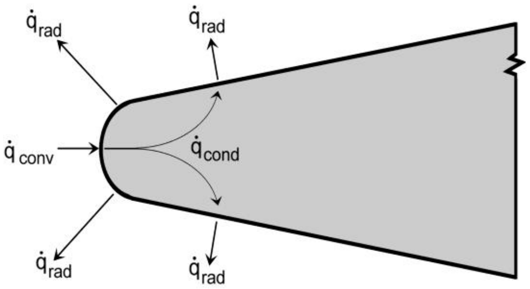
Sharp Leading Edge Energy Balance

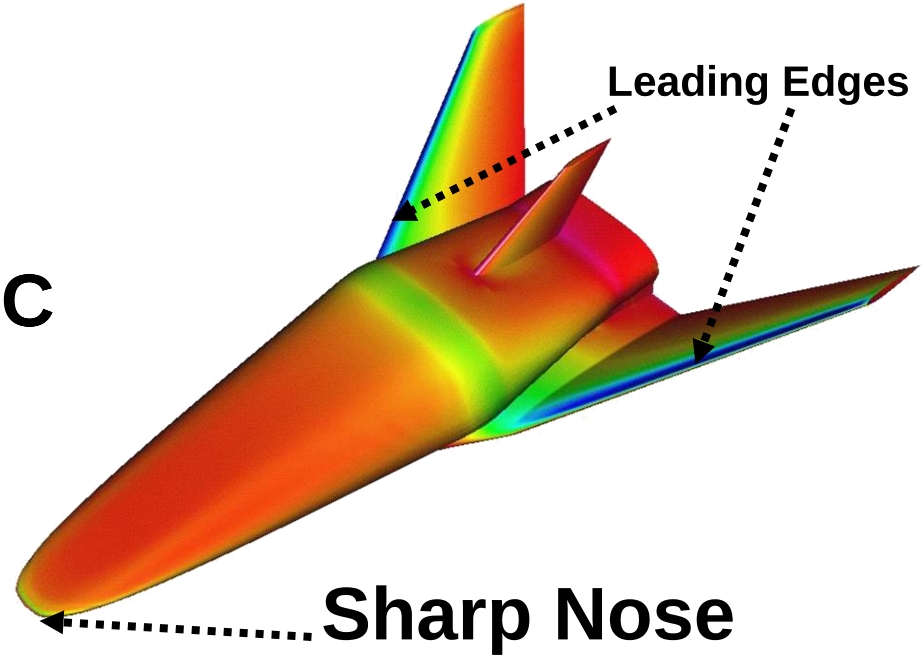
Sharp Nose



UHTC

High Thermal Conductivity

$$\dot{q}_{conv} = \dot{q}_{rad} + \dot{q}_{cond}$$



Leading Edges

Sharp Nose

Insulators and UHTCs manage energy in different ways:

- Insulators store energy until it can be eliminated in the same way as it entered
- UHTCs conduct energy through the material and reradiate it through cooler surfaces

Dean Kontinos, Ken Gee and Dinesh Prabhu. “Temperature Constraints at the Sharp Leading Edge of a Crew Transfer Vehicle.” AIAA 2001-2886 35th AIAA Thermophysics Conference, 11-14 June 2001, Anaheim CA

High Temperature Passive Material Options

- SiC-based coatings, as on Shuttle Orbiter leading edges, are applicable to ~1650 °C (3000 °F).
- Above ~1650 °C (3000 °F), different class of materials required:
  - Carbides, oxides, and diborides of Hf and Zr
  - Refractory metals such as iridium and rhenium
- Some of these materials can be used as a monolith or matrix; some are more appropriate as a coating.
- Thermal properties have a significant impact on surface temperatures.
- HfB_2 has highest melting temperature of borides
  - HfB_2 T_m ~ 3380°C ; ZrB_2 T_m ~ 3250°C

UHTC billets, US quarter for scale

HfB_2-SiC

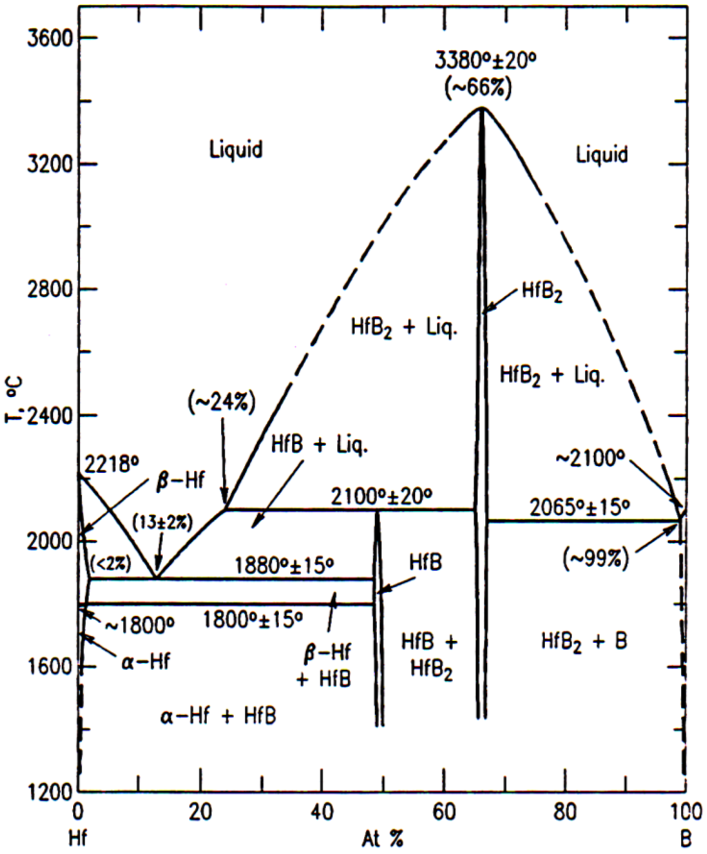
- **HfB_2** has a narrow range of stoichiometry with a melting temperature of 3380°C

Density = 11.2 g/cm^3

- **Silicon carbide** is added to boride powders
  - Promotes refinement of microstructure
  - Decreases thermal conductivity of HfB_2
  - 20v% may not be optimal but is common amount added
  - SiC will oxidize either passively or actively, depending upon the environment

Density = 3.2 g/cm^3

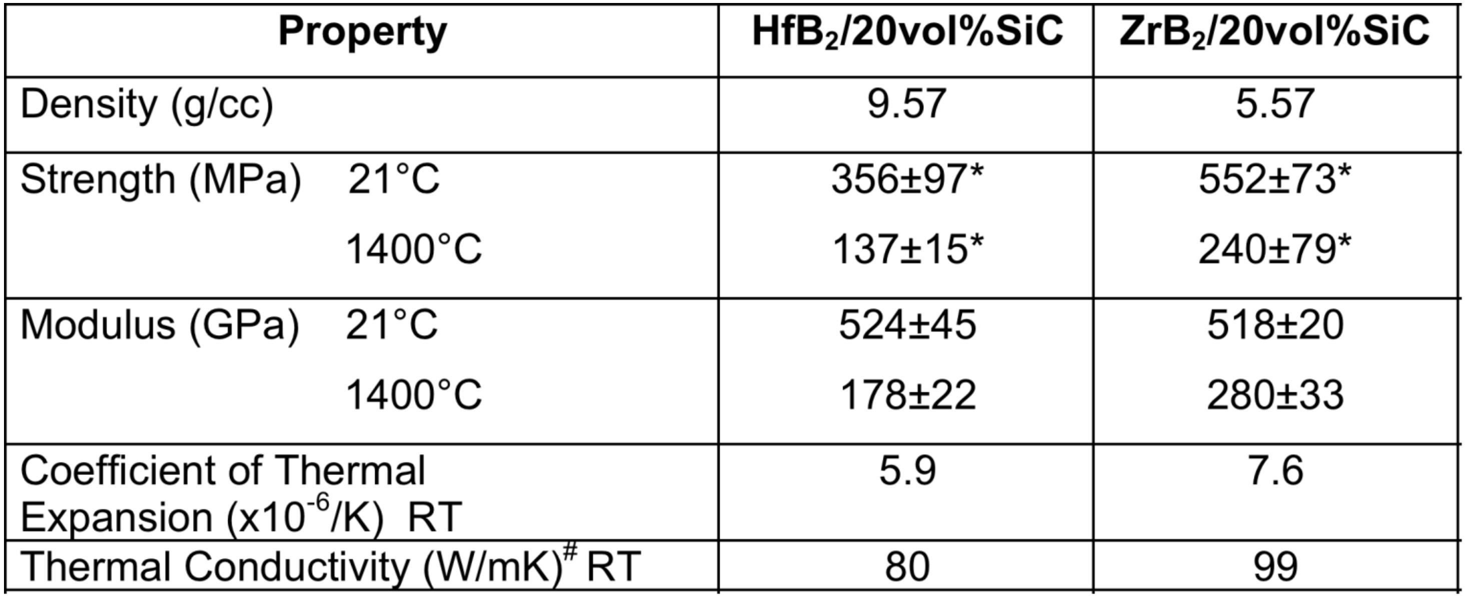
HfB_2



UHTC Material Properties

Sharp leading edges require :

- High thermal conductivity (directional)
- High fracture toughness/mechanical strength/hardness
- Oxidation resistance (in reentry conditions)



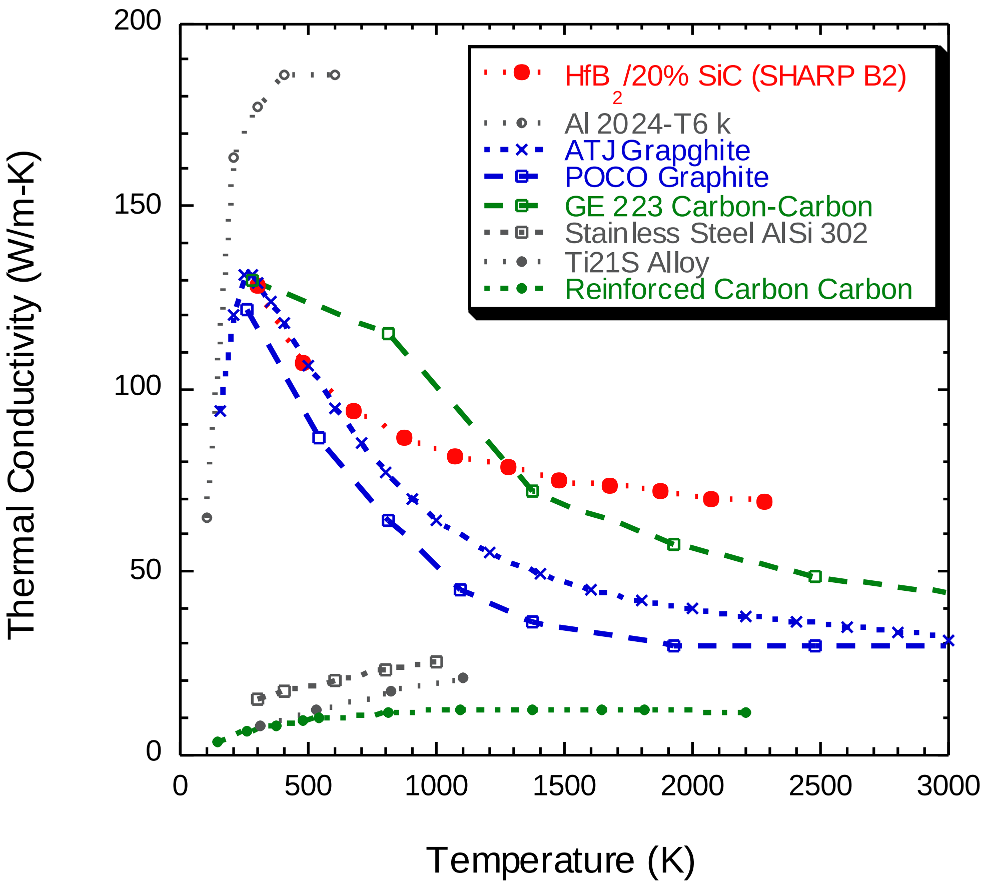
Property		**HfB_2/20vol%SiC**	**ZrB_2/20vol%SiC**
Density (g/cc)		9.57	5.57
Strength (MPa)	21°C	356±97*	552±73*
	1400°C	137±15*	240±79*
Modulus (GPa)	21°C	524±45	518±20
	1400°C	178±22	280±33
Coefficient of Thermal Expansion ($\times10^{-6}$/K)	RT	5.9	7.6
Thermal Conductivity (W/mK)#	RT	80	99

Source: ManLabs and Southern Research Institute

* Flexural Strength

R. P. Tye and E. V. Clougherty, “The Thermal and Electrical Conductivities of Some Electrically Conducting Compounds.” Proceedings of the Fifth Symposium on Thermophysical Properties, The American Society of Mechanical Engineers, Sept 30 – Oct 2 1970. Editor C. F. Bonilla, pp 396-401.

Thermal Conductivity Comparison



HfB_2/SiC materials have relatively high thermal conductivity

- HfB2/SiC material was measured on material from the SHARP B2 program.
- Thermal Diffusivity and Heat Capacity of HfB_2/SiC were measured using Laser Flash.

Some UHTC Development History

- Hf and ZrB_2 materials investigated in early 1950s as nuclear reactor material
- Extensive work in 1960s & 1970s (by ManLabs for Air Force) showed potential for HfB_2 and ZrB_2 for use as nosecones and leading edge materials (Clougherty, Kaufman, Kalish, Hill, Peters, Rhodes et al.)
- Gap in sustained development during 1980s and most of 1990s
  - AFRL considered UHTCs for long-life, man-rated turbine engines
- During late 1990s, NASA Ames revived interest in HfB_2/SiC, ZrB_2/SiC ceramics for sharp leading edges
- Ballistic flight experiments: Ames teamed with Sandia National Laboratories New Mexico, Air Force Space Command, and TRW
  - SHARP*-B1 (1997) UHTC nosetip & SHARP-B2 (2000) UHTC strake assembly
- Space Launch Initiative (SLI) ,NGLT, UEET programs: 2001-5
- NASA’s Fundamental Aeronautics Program funded research until 2009
- Substantial current ongoing effort at universities, government agencies, & international laboratories

* Slender Hypervelocity Aerothermodynamic Research Probes

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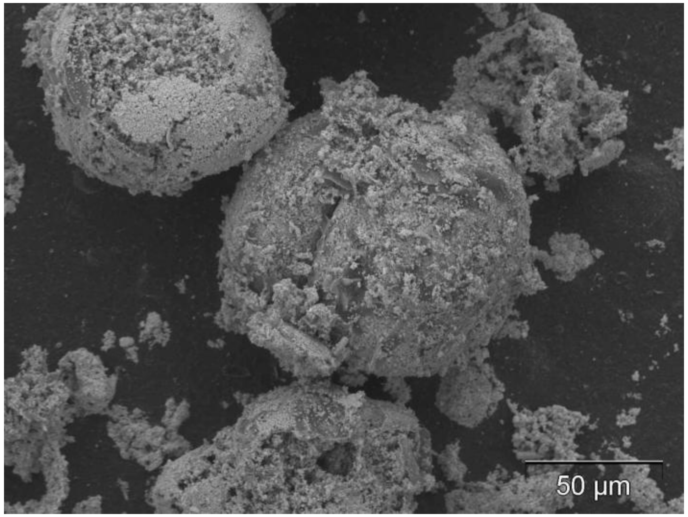
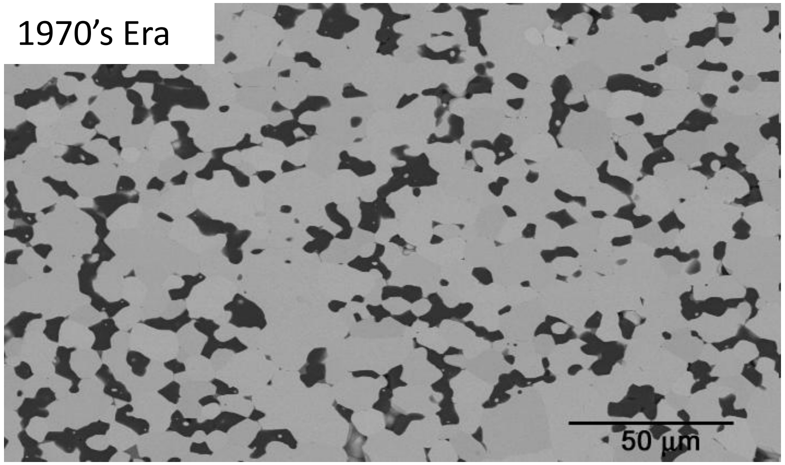
Improving Processing and Microstructure

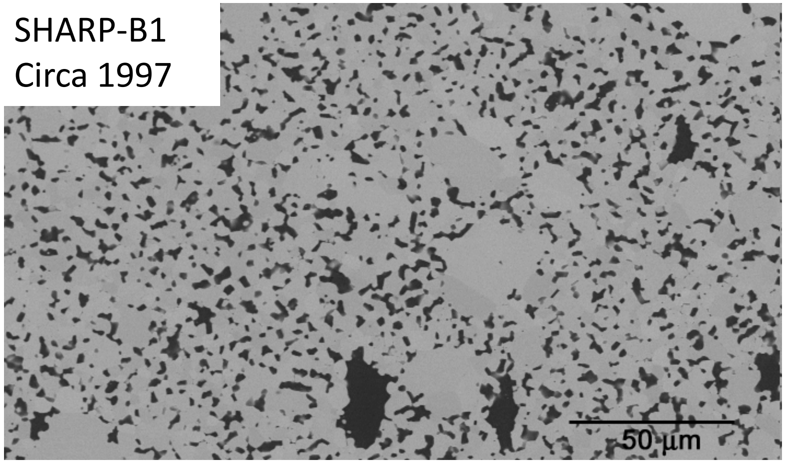
- Initial focus on improving material microstructure and strength
- $HfB_2/20vol\%SiC$ selected as baseline material for project constraints
- Major issue was poor mixing/processing of powders with different densities
  - Used freeze-drying to make homogenous powder granules
  - Developed appropriate hot pressing schedules

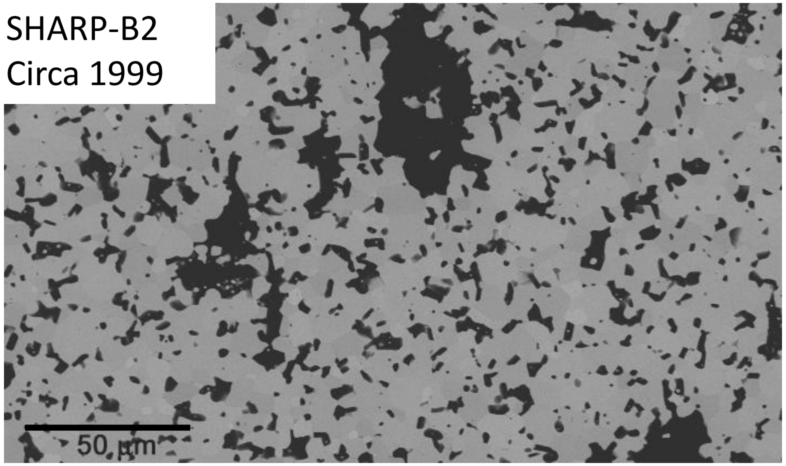


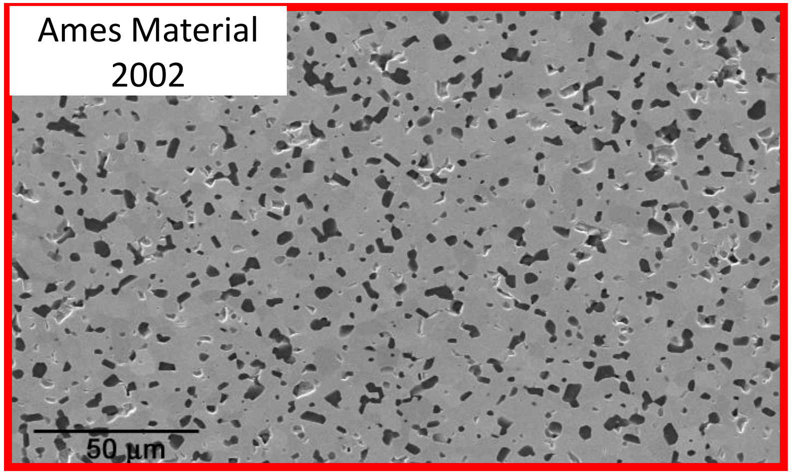
Granulated HfB_2/SiC Powder

Early Progress in Processing of HfB_2 - 20% SiC Materials


1970’s Era

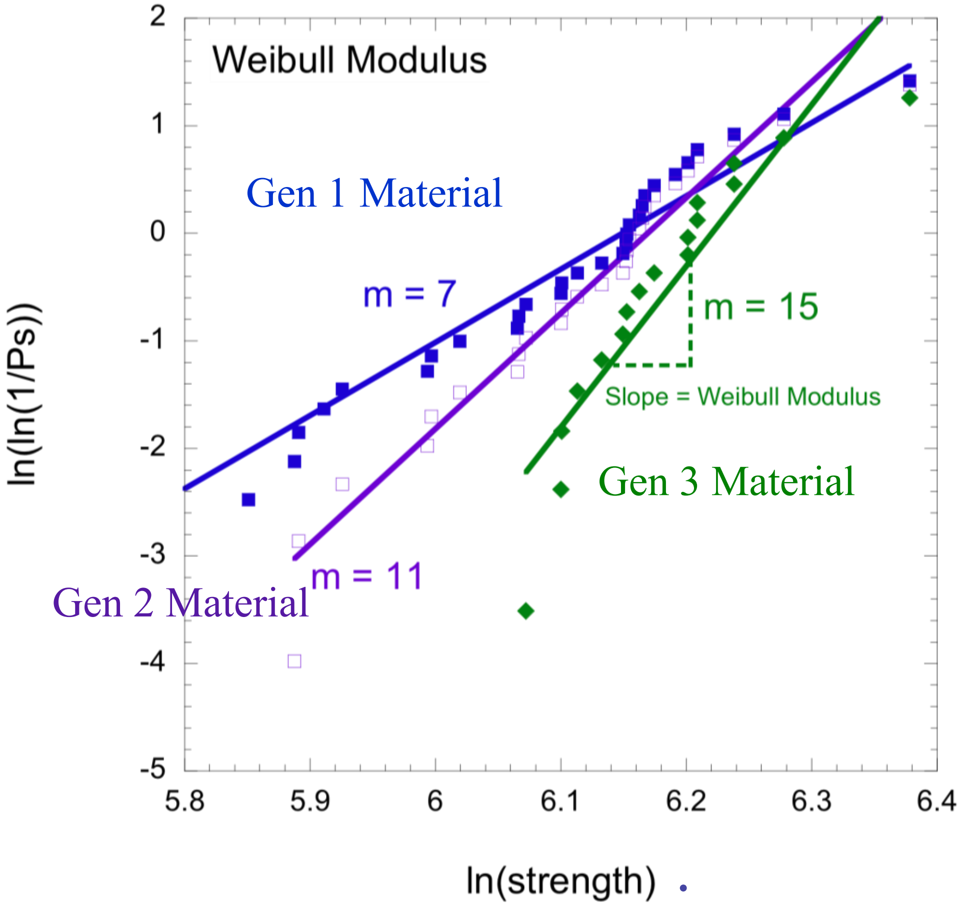

SHARP-B1
Circa 1997


SHARP-B2
Circa 1999


Ames Material
2002

- Early and SHARP materials made by an outside vendor
- Improvements in powder handling provide a more uniform microstructure

Weibull Modulus of ARC HfB_2/SiC Improved Compared to Previous Materials



Weibull Modulus SHARP B2 Materials ~4

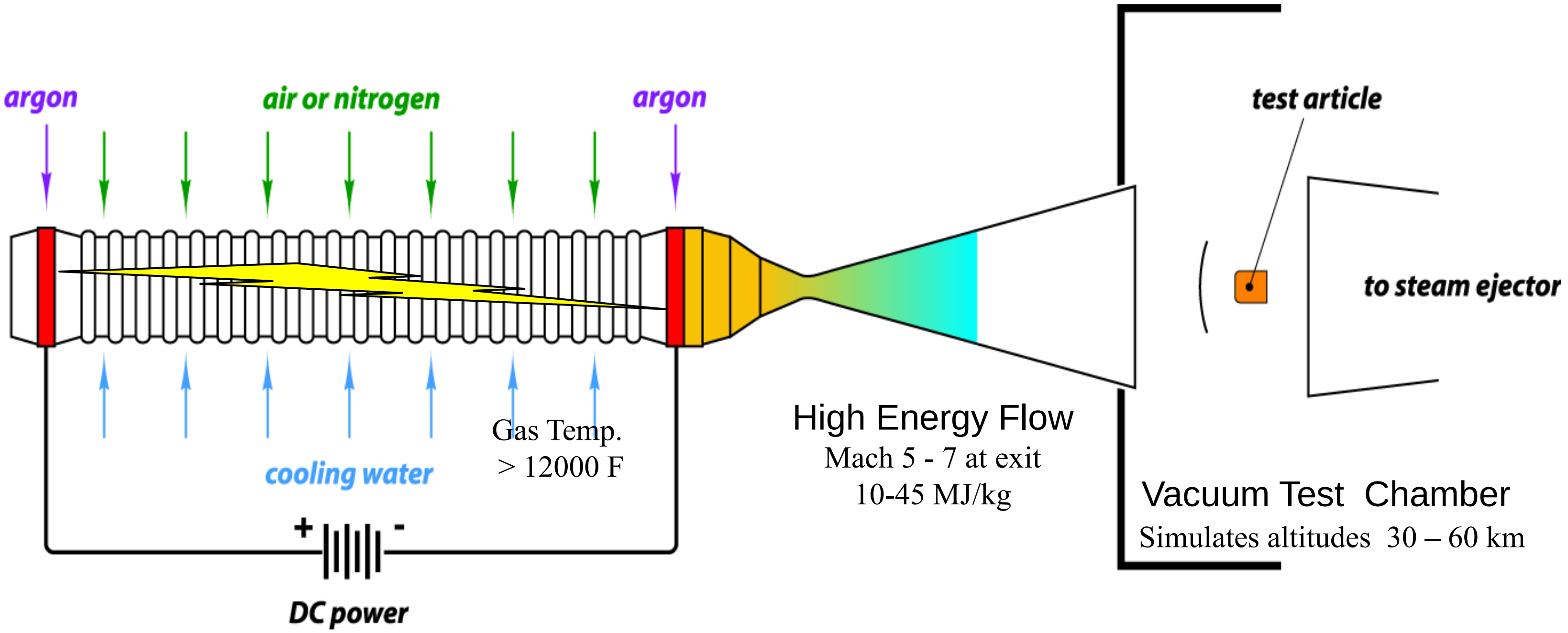
Increased Weibull Modulus to ~15 with processing improvements

Need for Arc Jet Testing

- Arc jet testing is the best **ground-based method** of evaluating a materials oxidation/ablation response in re-entry environments
- A material's oxidation behavior when heated in static or flowing air at ambient pressures is likely to be significantly different than in a re-entry environment.
- In a re-entry environment:
  - Oxygen and nitrogen may be dissociated
    - Catalycity of the material plays an important role
    - Recombination of O and N atoms adds to surface heating
  - Stagnation pressures may be less than 1 atm.
    - Influence of active to passive transitions in oxidation behavior of materials
      - SiC materials show such a transition when the protective SiO_2 layer is removed as SiO

Arc Jet Schematic

Simulates reentry conditions in a ground-based facility



Gas Temp.
> 12000 F

High Energy Flow
Mach 5 - 7 at exit
10-45 MJ/kg

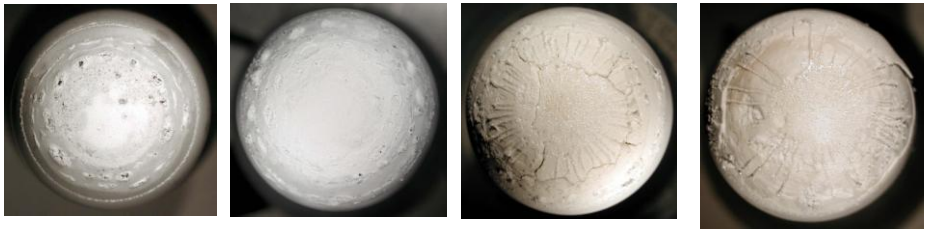
Vacuum Test Chamber
Simulates altitudes 30 – 60 km

Method: Heat a test gas (air) to plasma temperatures by an electric arc, then accelerate into a vacuum chamber and onto a stationary test article

Stine, H.A.; Sheppard, C.E.; Watson, V.R. Electric Arc Apparatus. U.S. Patent 3,360,988, January 2, 1968.

UHTC Cone After 9 Arc Jet Exposures (89 minutes total run time)

Runs 4 and 5 lasted ~ 2 min. each



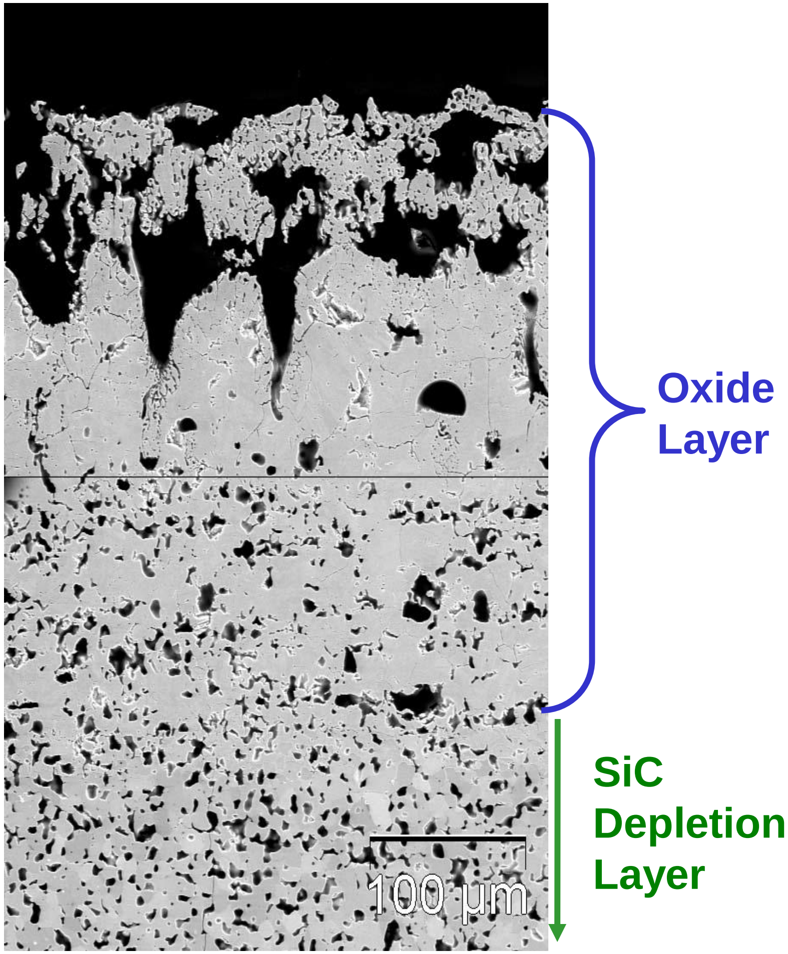
HSp-45 Pretest	Run 1 Post-Test	Run 2 Post-Test	Run 3 Post-Test	Run 6 Post-Test	Run 7 Post-Test	Run 8 Post-Test	Run 9 Post-Test
	300 sec	600 sec	600 sec	600 sec	1200 sec	1200 sec	600 sec
	% □wt = 0	% □wt = 0	% □wt = 0	%□wt = -0.06	%□wt = -0.2	%□wt = -0.32	%□wt = -1.24
	T_{ss} = 1280°C	T_{ss} = 1220°C	T_{ss} = 1325°C	T_{ss} =1970°C	T_{ss} >2000°C	T_{ss} >2000°C	T_{ss} >2000°C

Increasing heat flux

Reducing Oxide Formation

* Post-test arc jet nosecone model after a total of 80 minutes of exposure. Total exposure the sum of multiple 5 and 10 minute exposures at heat fluxes from 200W/cm^2

- In baseline material:
  - SiC depleted during arc jet testing
  - Surface oxide is porous
- Potential solution: Reduce amount of SiC below the percolation threshold while maintaining mechanical performance



$q_{CW} = 350\ \mathrm{W/cm^2},\ P_{stag} = 0.07\ \mathrm{atm}$

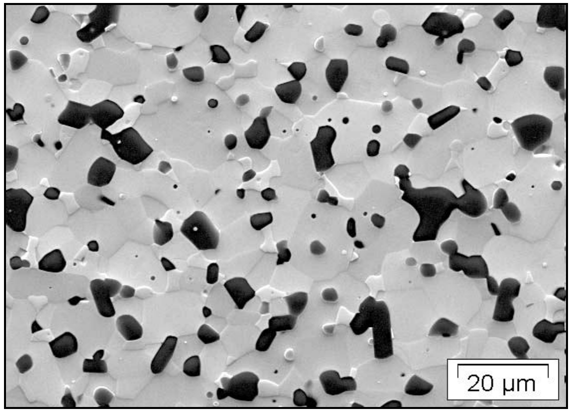
*Arc jet test data from Space Launch Initiative program

Controlling Microstructure & Composition

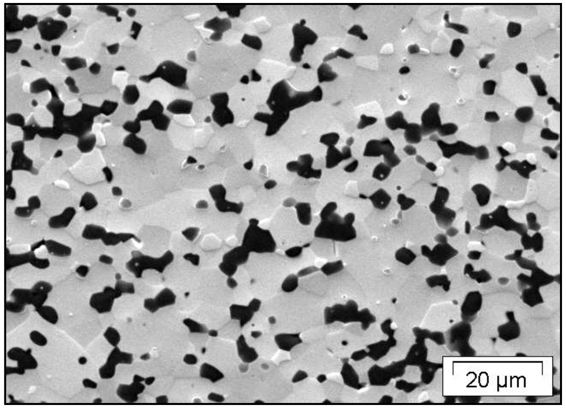
- Goal for UHTCs for TPS has been to improve:
  - **Fracture toughness**
  - Strength
  - Thermal conductivity
  - **Oxidation resistance — arcjet performance**
- Properties controlled by processing, microstructure, and composition
  - **Grain Size**
    - **Additives (Ir additions)**
    - **Processing by field-assisted sintering (FAS)**
  - **Grain Shape**
    - **Addition of preceramic polymers**
    - Particle coatings (Fluidized Bed CVD)
  - Purity (grain boundaries)
    - Addition of preceramic polymers
    - Processing (FB CVD)
    - Self-propagating reactions
  - **Oxide formation**
    - **Increase oxide stability / emissivity (additives)**
    - Reduce amount of SiC

Control of Grain Size

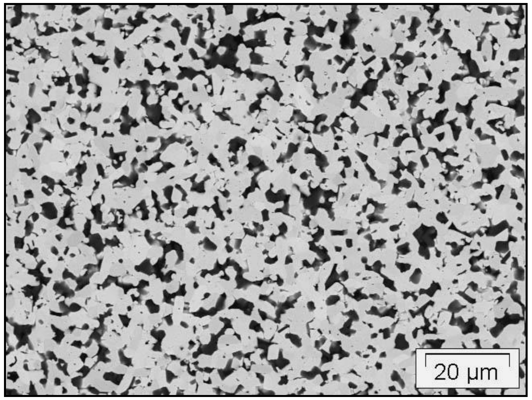
HfB_2/20v%SiC
Hot Pressed
(long process)



HfB_2/20v%SiC
Hot Pressed
(short process)



HfB_2/20v%SiC
Spark Plasma Sintered

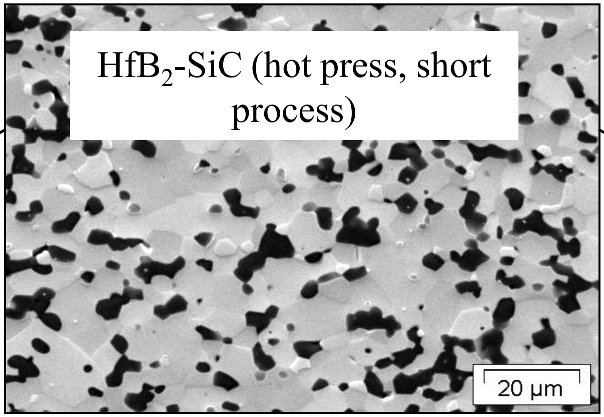


Third-Phase Additions

Explore effect of additional refractory phases on oxidation resistance / fracture toughness (ductile-phase toughening)

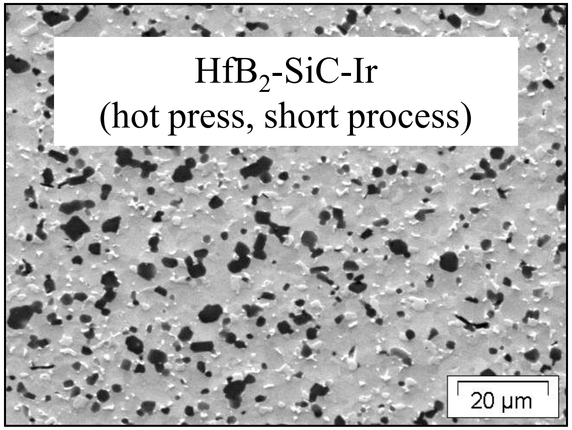
- Effect of additives on microstructure of baseline material (HfB_2-20 v% SiC):
  - Ir
  - Ir with $TaSi_2$
- Evaluation of thermal conductivity
- Evaluation of mechanical properties

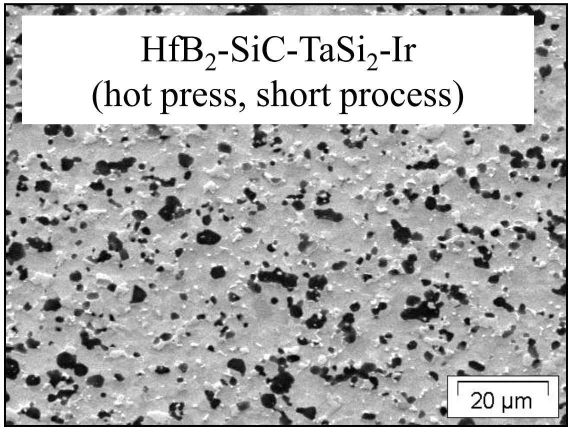
Effect of Additives on Microstructure



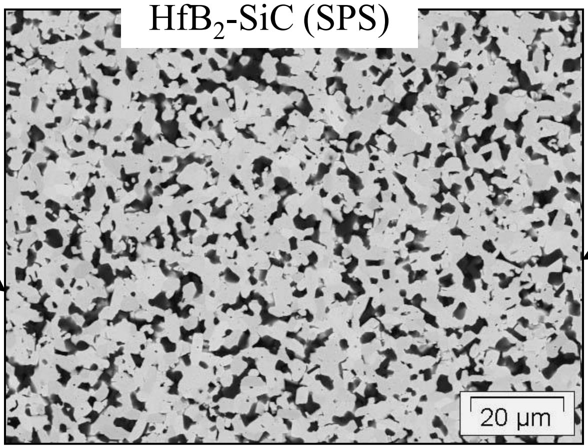
Addition of Ir
(short process)

Addition of Ir and $TaSi_2$
(short process)





Samples processed with additional phases show less grain growth

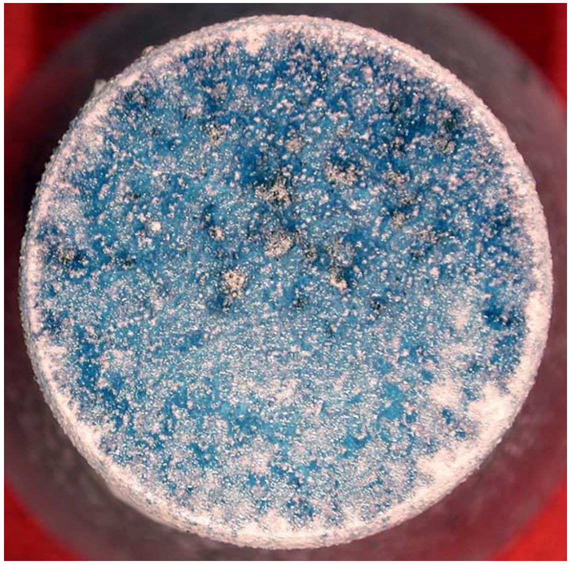


Similar microstructure

Similar microstructure

Increasing Oxide Emissivity

HfB_2-SiC



HfB_2-SiC-$TaSi_2$

- Arcjet test: Performance of HfB_2/SiC/$TaSi_2$ **comparable** to HfB_2/SiC after testing for 5 minutes at Q_{cw}~300 W/cm^2
- HfB_2/SiC/$TaSi_2$ clearly has a higher post-test emissivity than HfB_2/SiC and demonstrated lower surface temperatures

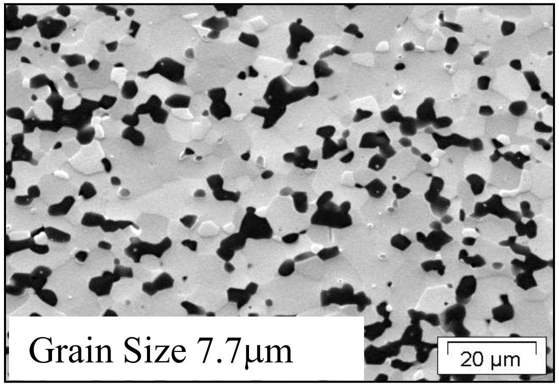
Opila, E. and Levine, S., “Oxidation of ZrB_2- and HfB_2-based ultra-high temperature ceramics: Effect of Ta additions,” *Journal of Materials Science* 39 (2004) 5969–5977

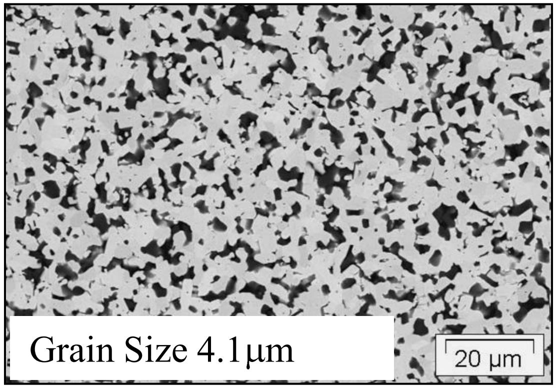
Physical Characterization: Microstructure

Hot Pressed

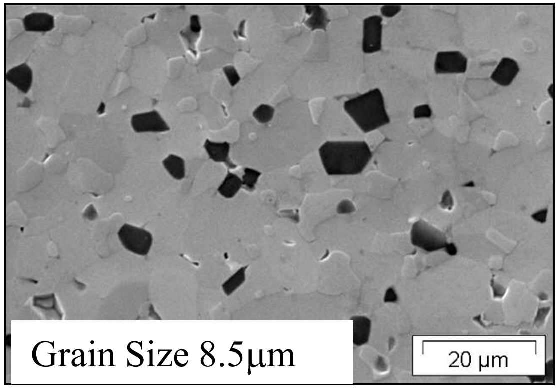
Spark Plasma Sintered (SPS)

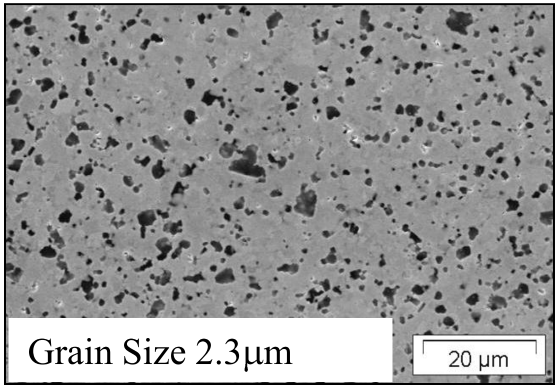
HfB_2-SiC Baseline


Grain Size 7.7µm

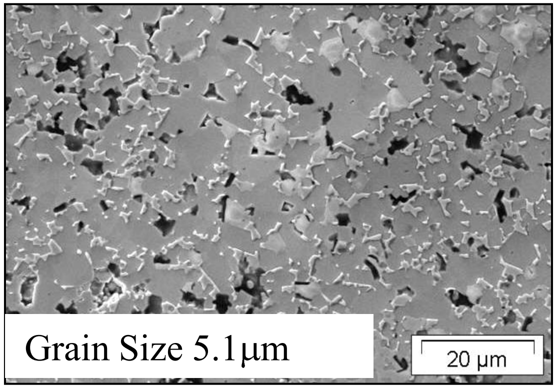

Grain Size 4.1µm

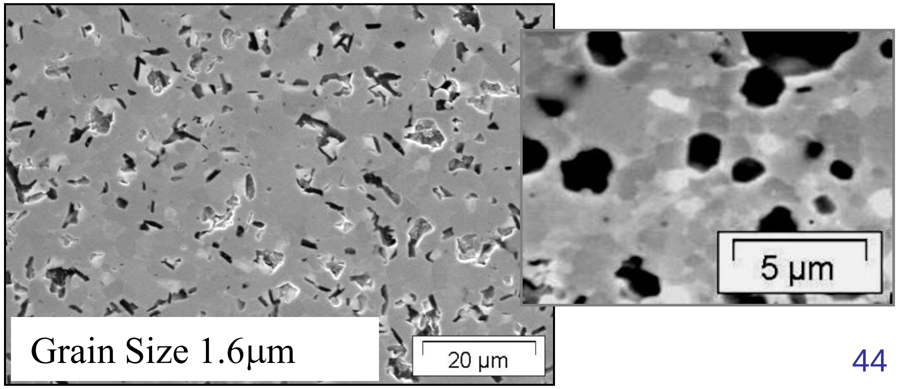
HfB_2-SiC-$TaSi_2$


Grain Size 8.5µm

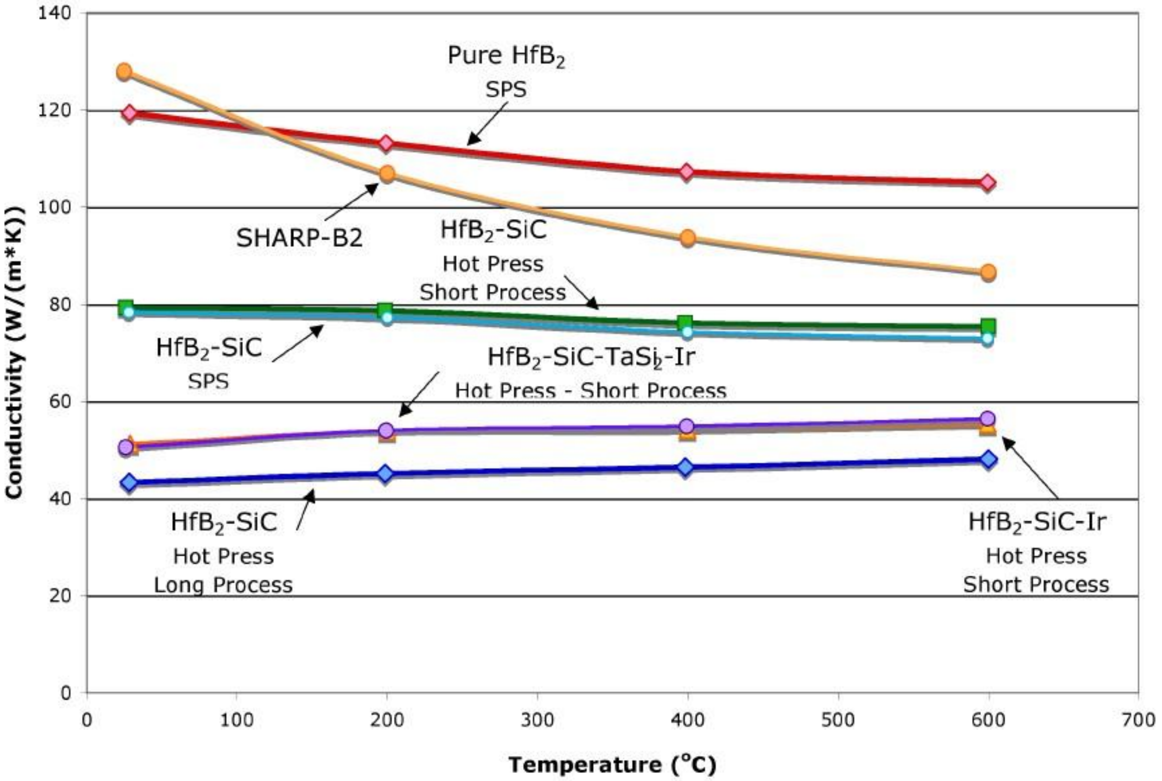

Grain Size 2.3µm

HfB_2-SiC-$TaSi_2$-Ir


Grain Size 5.1µm


Grain Size 1.6µm

Thermal Conductivity



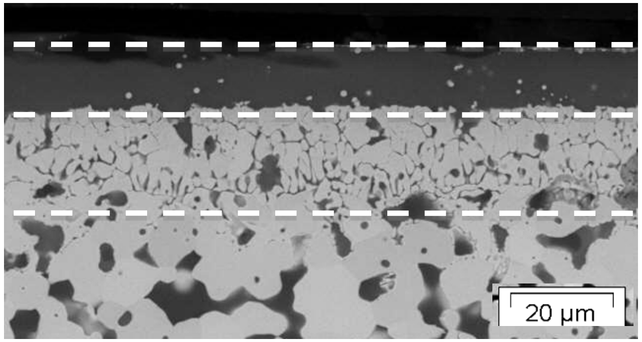
- Long process, hot pressing — lowest thermal conductivity
- Short process, hot pressing — significant increase in thermal conductivity
- SPS — similar increase in thermal conductivity to short process
- Addition of Ir or Ir and $TaSi_2$ to HfB_2/SiC (modified HP) — lowers thermal conductivity

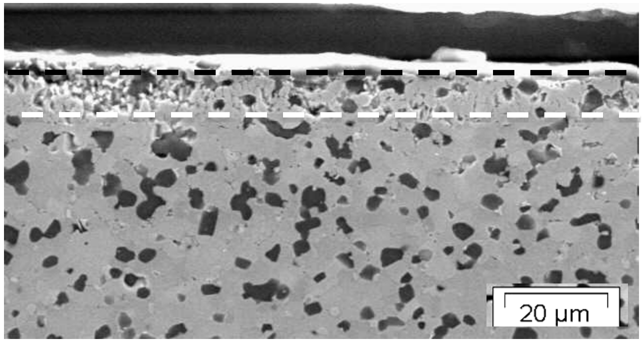
Arc Jet Characterization:
Additives & Influence of Microstructure

Hot Pressed

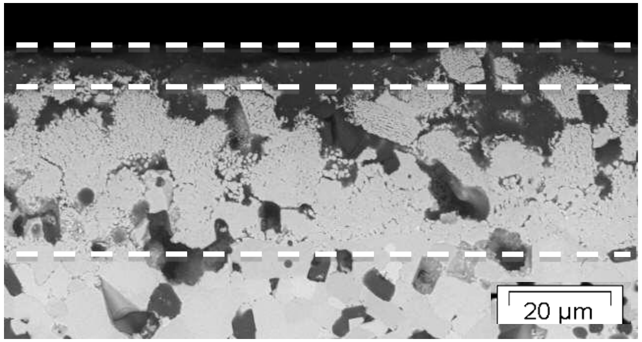
Spark Plasma Sintered

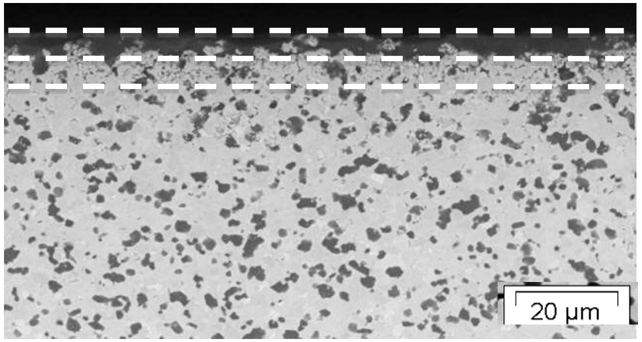
HfB_2-SiC Baseline



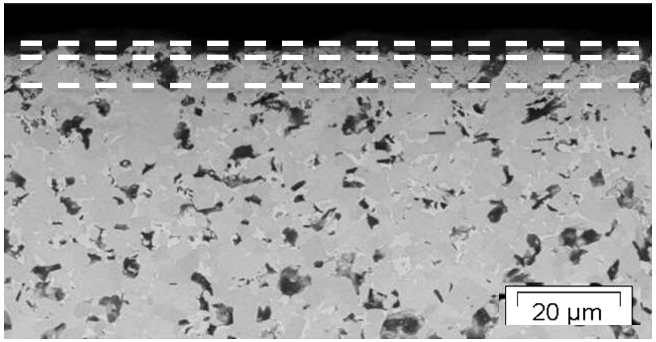


HfB_2-SiC-$TaSi_2$





HfB_2-SiC-$TaSi_2$-Ir

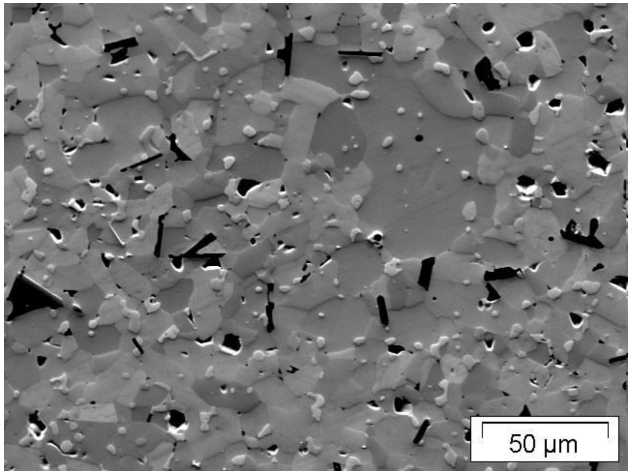


Both oxide scale and depletion zone can be reduced.

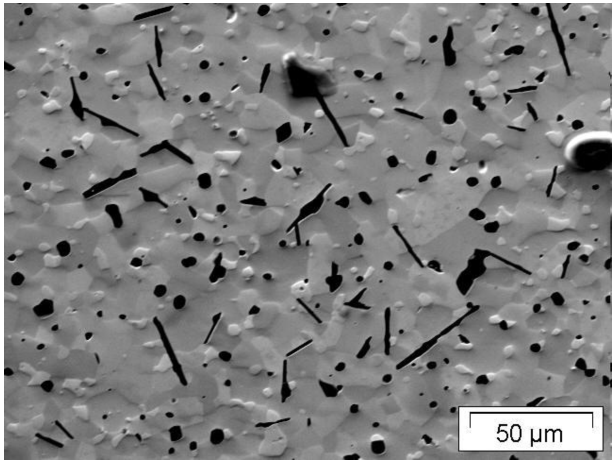
Controlling Grain Shape Role of SiC Source

- Conventional source of SiC is powder.
- Preceramic polymer source:
  - Preceramic polymer 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.

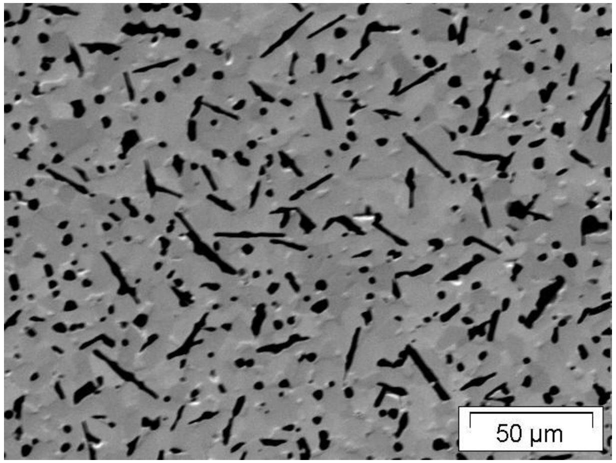
Growth of Elongated SiC Grains



5%* SiC



10%* SiC — Rod diameter ~2μm



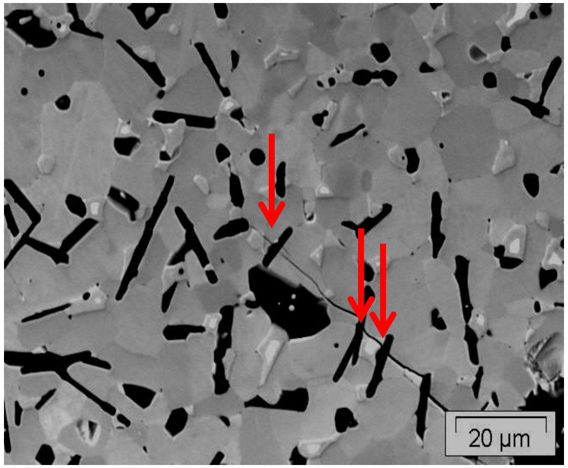
15%* SiC — Rod diameter ~5μm

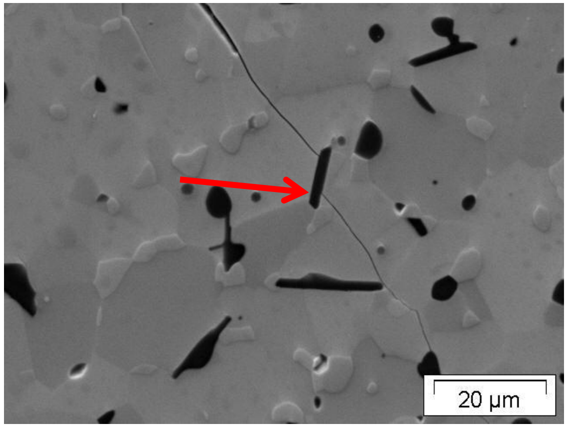
SiC Preceramic Polymer Promotes Growth of Acicular Grains

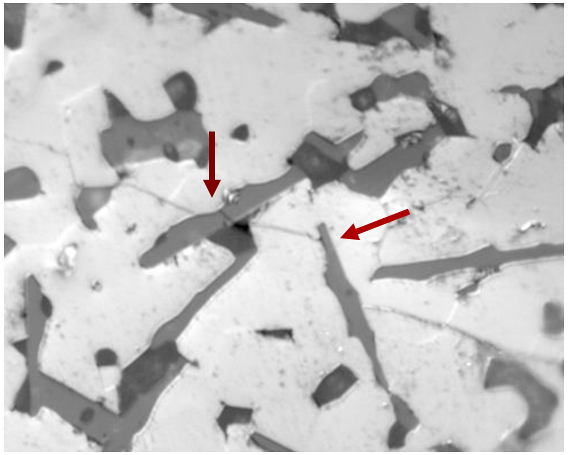
- Samples processed with 5 to >20 volume % SiC
- Can adjust volume of SiC in the UHTC without losing the high l/d architecture
- Amount of SiC affects number and thickness (but not length) of rods — length constant (~20–30μm)
- Possible to obtain dense samples with high-aspect-ratio phase
- Hardness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

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

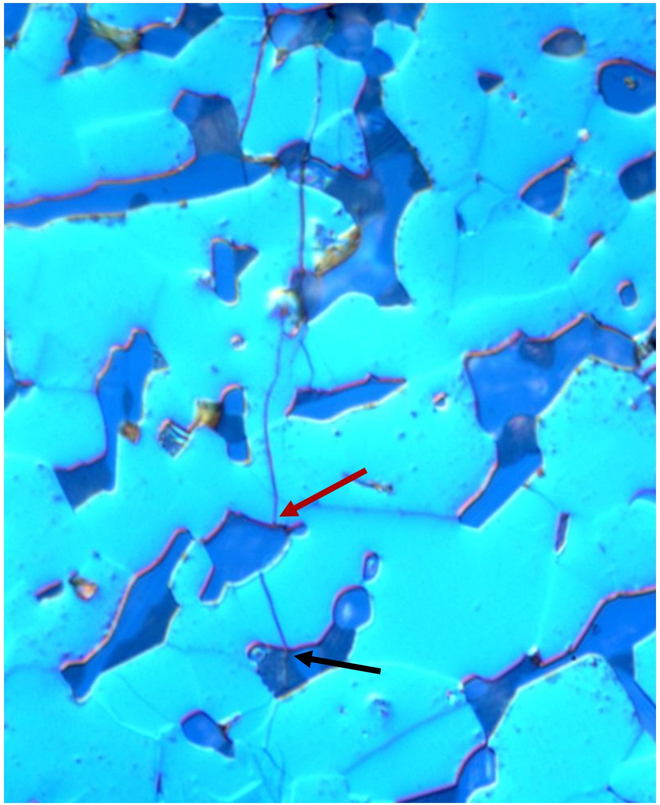
In Situ Composite for Improved Fracture Toughness







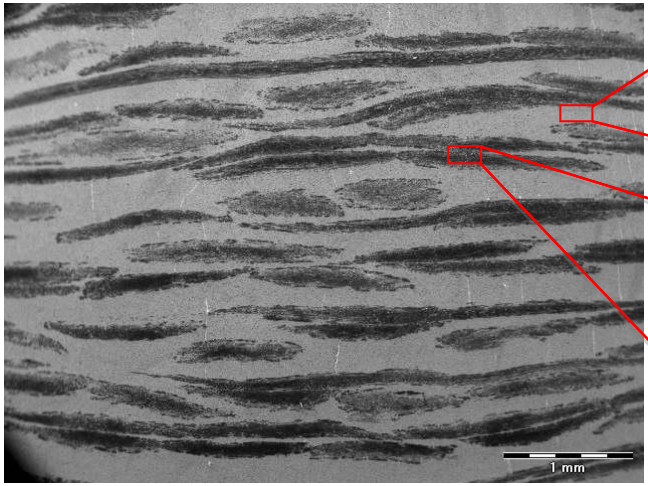
SiC Content	Fracture Toughness (MPam$^{1/2}$)
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33

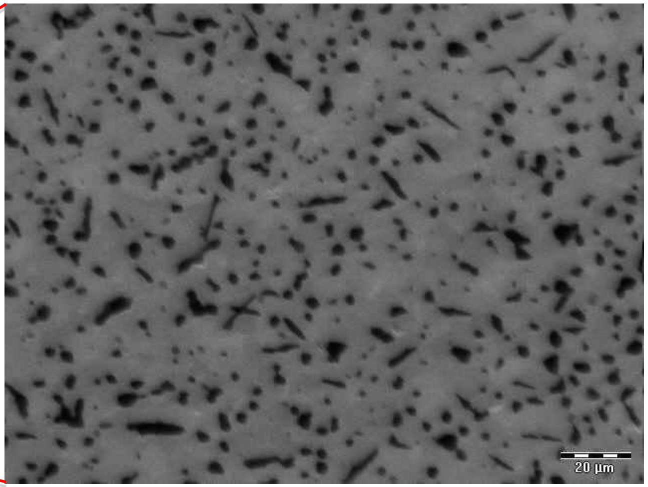


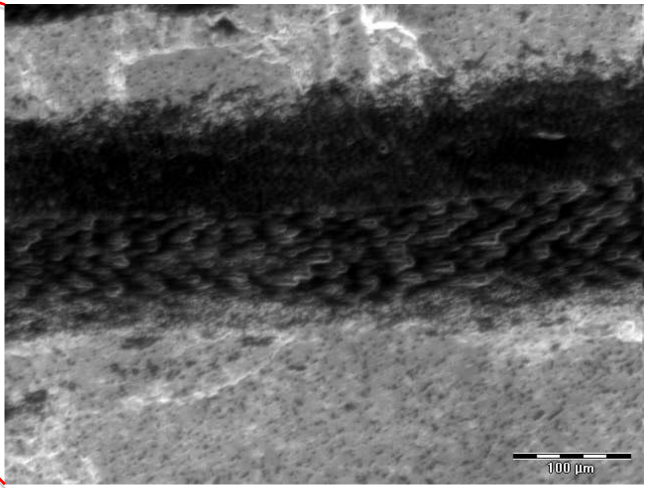
Oak Ridge National Laboratory

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

Ultra High Temperature Continuous Fiber Composites







- Image at top right shows dense UHTC matrix with indications of high aspect ratio SiC.
- Image at bottom right shows the presence of C fibers after processing.

Outline

- The Process of Discovery
- Education
- Experience
- Curiosity
- Opportunity
- Discovery
- **New Frontiers**
- Conclusion

UHTC Challenges

1. **Fracture toughness**

   Composite approach is required

   - Integrate understanding gained from monolithic materials
   - Need high temperature fibers

2. **Oxidation resistance in reentry environments/ hypersonic flight**

   Promising approaches but challenge is active oxidation of materials containing SiC

3. **Modeling is critical**

   Shorten development time, improve properties, design

Outline

- The Process of Discovery
- Education
- Experience
- Curiosity
- Opportunity
- Discovery
- New Frontiers
- **Conclusion**

Some Recent Research Efforts in UHTCs: Materials and Properties

ZrB_2 Based Ceramics	**Catalytic Properties of UHTCs**
Missouri University of Science & Technology	PROMES-CNRS Laboratory, France
US Air Force Research Lab (AFRL)	CNR-ISTEC
NASA Glenn Research Center	CIRA, Capua, Italy
University of Illinois at Urbana-Champaign	SRI International, California
Harbin Institute of Technology, China	**Imaging and Analysis (Modeling)**
Naval Surface Warfare Center (NSWC)	University of Connecticut
NIMS, Tsukuba, Japan	AFRL
Imperial College, London, UK	NASA Ames Research Center
NASA Ames Research Center	Teledyne (NHSC-Materials and Structures)
CNR-ISTEC	**Oxidation of UHTCs**
HfB_2 Based Ceramics	AFRL
NASA Ames Research Center	NASA Glenn Research Center
NSWC—Carderock Division	Georgia Institute of Technology
Universidad de Extramdura, Badajoz, Spain	Missouri University of Science & Technology
CNR-ISTEC, Italy	Texas A & M University
Fiber Reinforced UHTCs	CNR-ISTEC, Italy
Chinese Academy of Sciences, Shenyang	University of Michigan, Ann Arbor, Michigan
University of Arizona	NSWC—Carderock
MATECH/GSM Inc., California	Harbin Institute of Technology, China
AFRL	University of Illinois at Urbana-Champaign

Some Recent Research Efforts in UHTCs: Processing

Field Assisted Sintering	**UHTC Polymeric Precursors**
University of California, Davis	SRI International, California
Air Force Research Laboratory (AFRL)	University of Pennsylvania
CNR-ISTEC, Italy	Missouri University of Science & Technology
Stockholm University, Sweden	MATECH/GSM Inc., California
NIMS, Tsukuba, Japan	Teledyne (NHSC)
Pressureless Sintering	
Missouri University of Science & Technology	
Reactive Hot-Pressing	
Shanghai Institute of Ceramics, China	
NASA Ames Research Center	
National Aerospace Laboratories, India	
Sandia National Laboratories, New Mexico	
McGill University, Montreal, Canada	

UHTC Researchers Throughout the World

Another Perspective………