Ultra High Temperature Ceramics UHTCs

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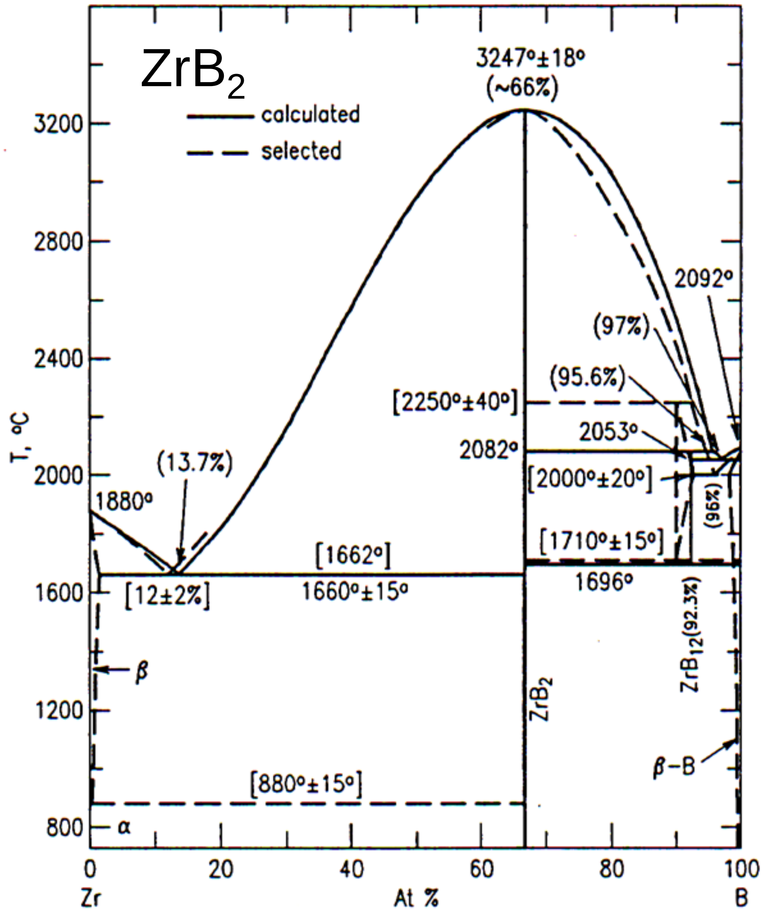
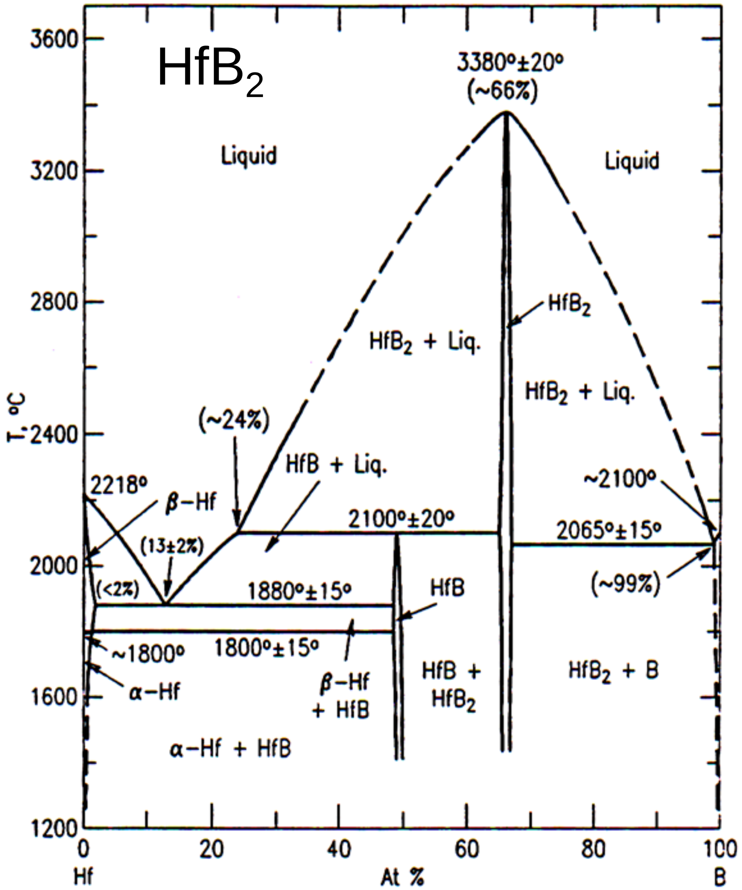
Outline

- What are UHTCs?
- Some early history and rationale
- History of development at Ames

What are UHTCs?

UHTCs include carbides and borides of transitional metals, e.g. Zr, Hf, Ta





Diborides have very high melting temperatures and high thermal conductivity

From American Ceramic Society Phase Diagrams

Some UHTC Development History

- HfB_2 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

UHTC Suitability for TPS

- UHTCs are only for specialized TPS applications for which other material systems are not as capable or straightforward or their capabilities are required when active cooling is not feasible.
- Choice of materials driven by design, environment, and material properties.
  - Feasible simple nose-cone and passive-leading-edge designs have been developed. (UHTC leading edge designs use small volumes of material.)
  - UHTCs have high temperature capabilities (> 2000 °C / 3600 °F)
- Material selection should be based on appropriate testing of matured material in relevant environment.
- Concerns about monolithic UHTC properties are being addressed by processing and engineering improvements (ceramic matrix composites [CMCs])
- Use will depend upon level of maturity relevant to specific application

Sharp Leading Edge Technology

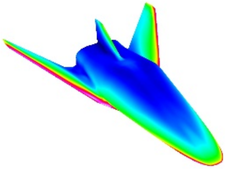
Benefits of sharp leading edge technology.

- Enhanced vehicle performance
- Leads to improvements in safety
  - Increased vehicle cross range
  - Greater launch window with safe abort to ground

Sharp leading edges place significantly higher temperature requirements on the materials:

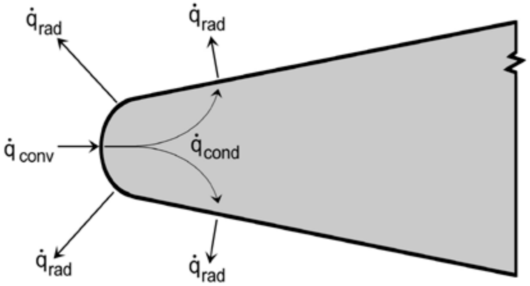
- Current shuttle reinforced carbon-carbon (RCC) leading edge materials: T~1650°C
- Sharp leading edged vehicles will require: T>2000°C

Ultra High Temperature Ceramic compositions are one candidate for use in sharp leading edge applications.



Sharp Leading Edge Energy Balance

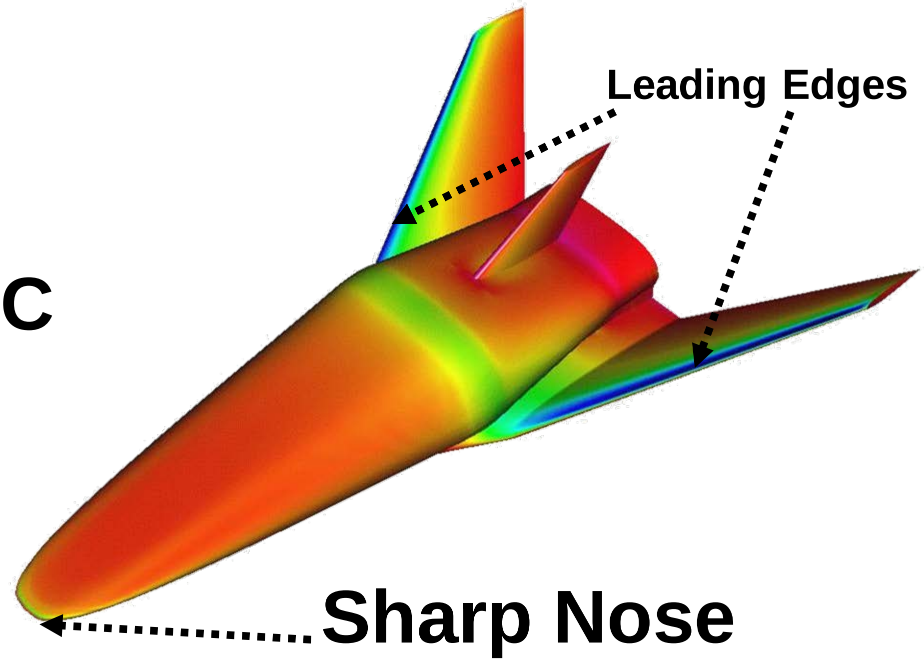
Sharp Nose



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:

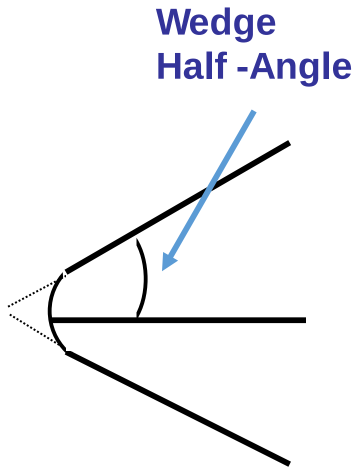
- Insulators store energy until it can be eliminated in the same way as it entered
- UHTCs conduct energy through the material and reradiate it through cooler surfaces

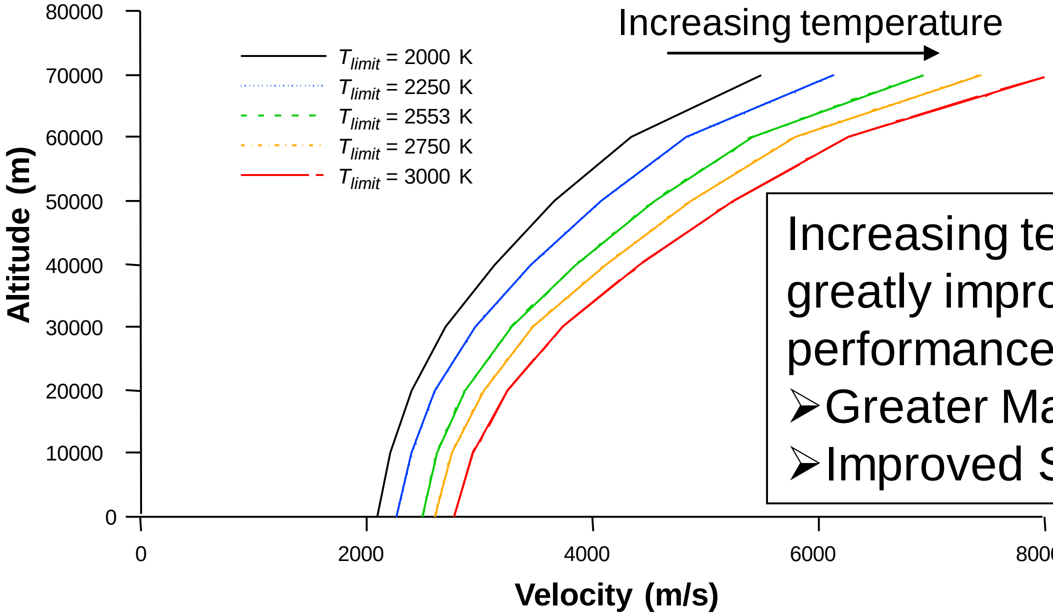
Dean Kontinos, Ken Gee and Dinesh Prabhu. “Temperature Constraints at the Sharp Leading Edge of a Crew Transfer Vehicle.” AIAA 2001-2886 35th AIAA Thermophysics Conference, 11-14 June 2001, Anaheim CA

Rationale for Sharp Leading Edges

Temperature Limit Sensitivity

AIAA 2001-2886 Dean Kontinos, (650) 604-4283 dkontinos@mail.arc.nasa.gov



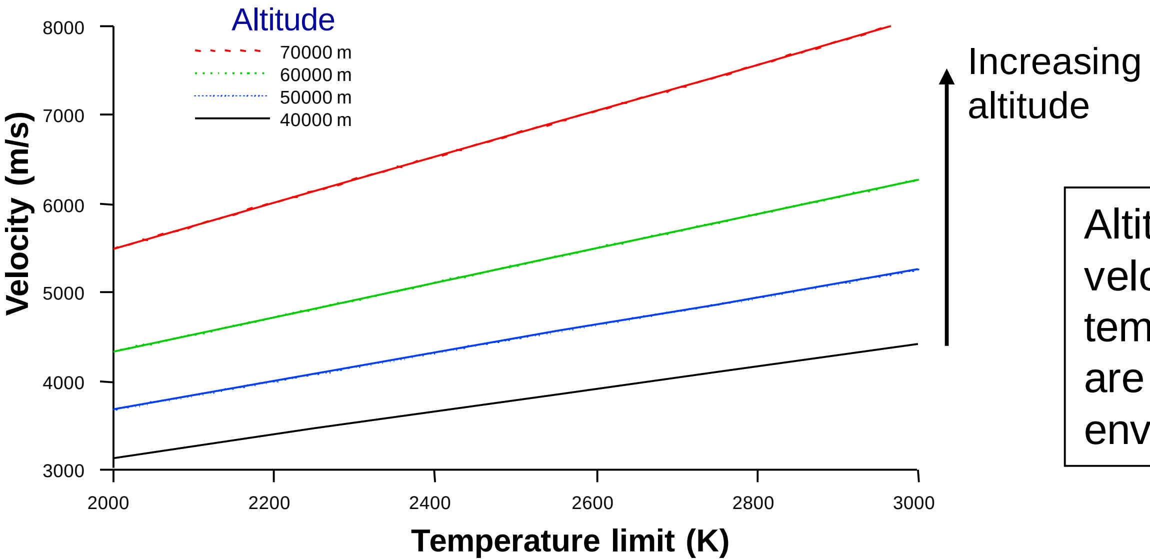


Increasing temperature limit greatly improves aerothermal performance constraint

- ➢Greater Maneuverability
- ➢Improved Safety

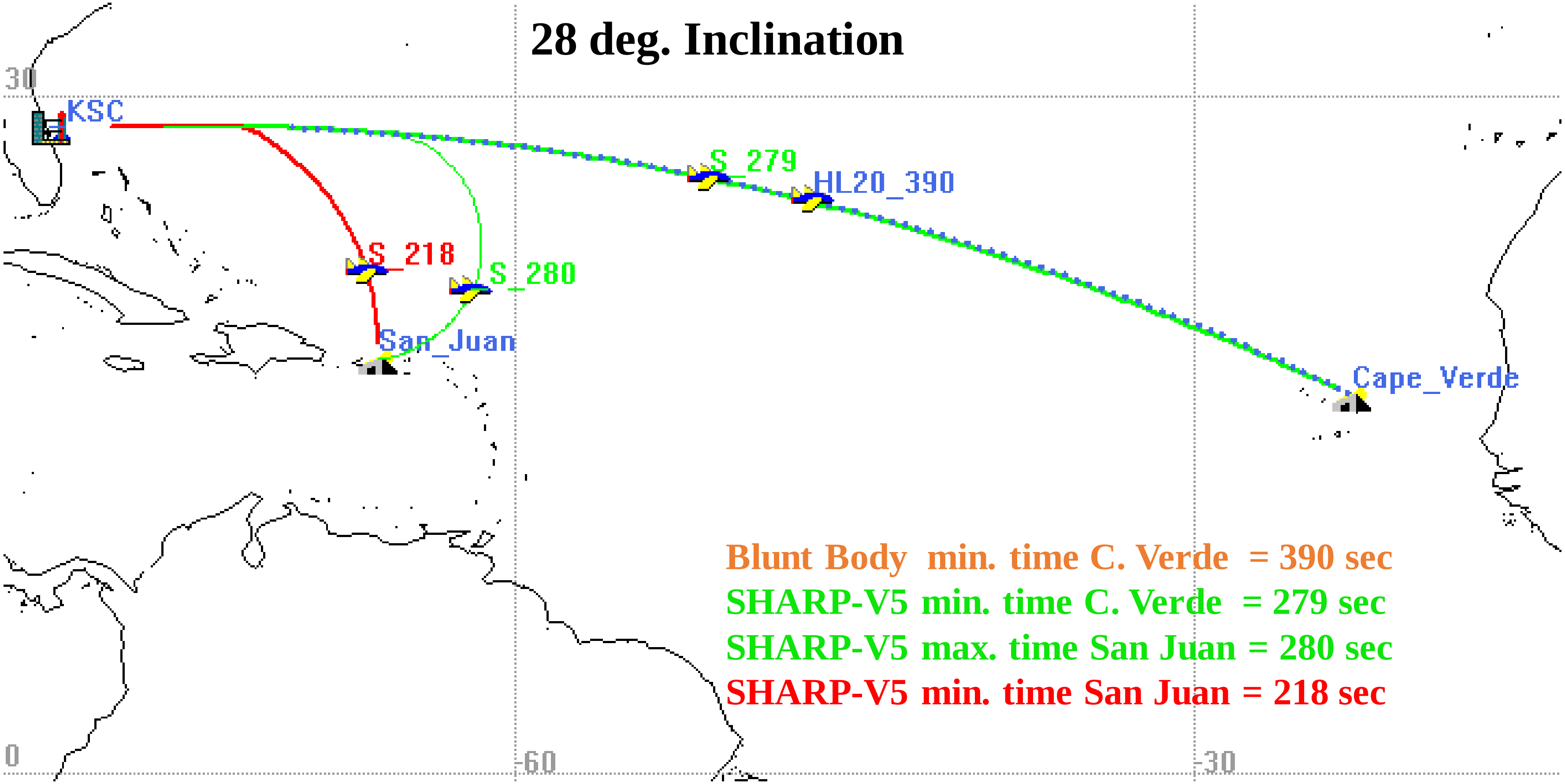
Nose Radius:
R_n = 0.005 m

Wedge
Half Angle
θ_c = 15°



Altitudes, velocities and temperatures are for reentry environments.

Potential Benefit – Impact On Crew Safety



Blunt Body min. time C. Verde = 390 sec

SHARP-V5 min. time C. Verde = 279 sec

SHARP-V5 max. time San Juan = 280 sec

SHARP-V5 min. time San Juan = 218 sec

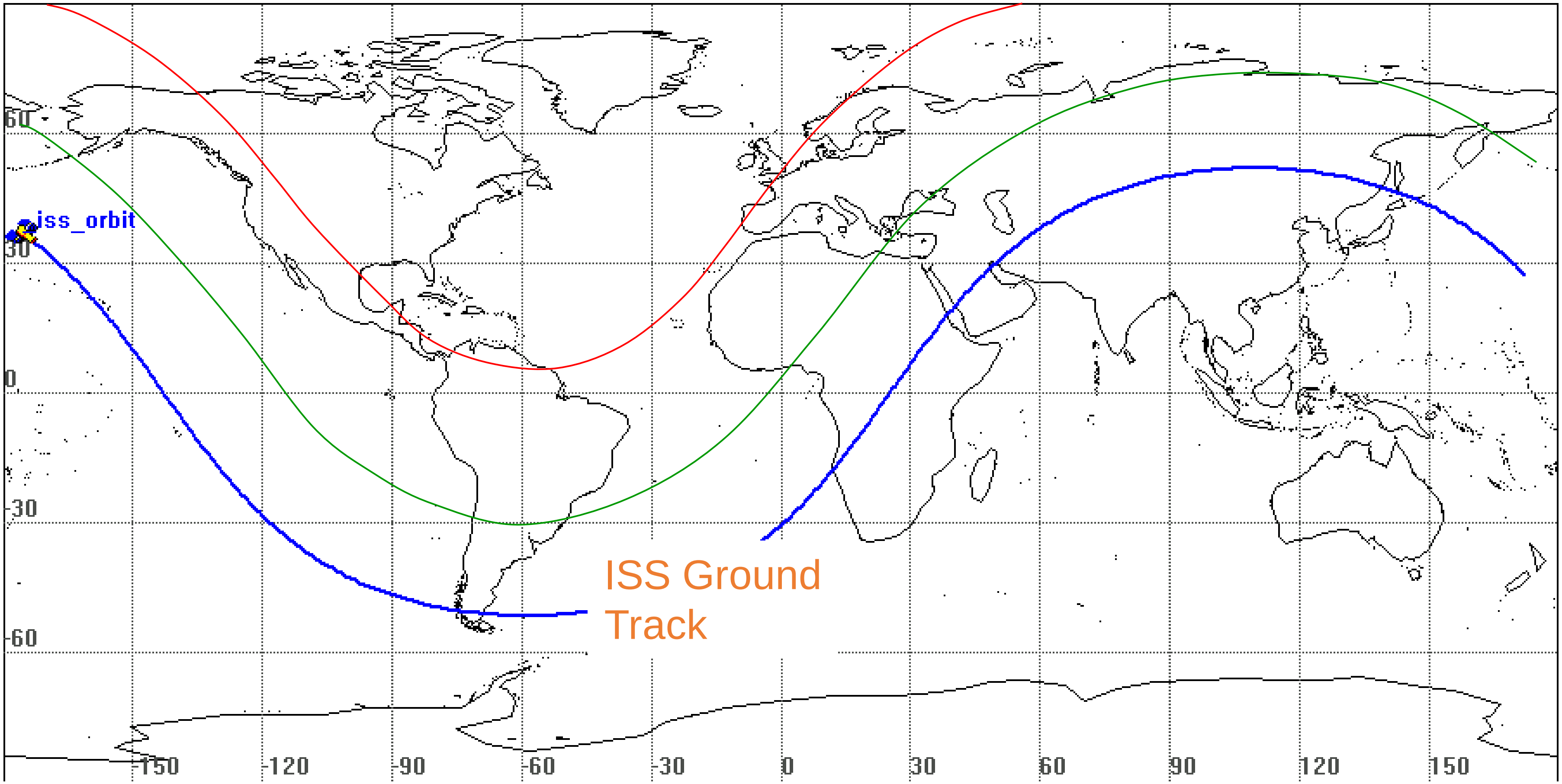
Results of the SHARP CTV study show the potential of minimizing the need to abort into the ocean by increasing the capability of landing on a runway in the event of a failure during launch. 390 - 218 = 172 seconds improvement.

ISS Ground Track vs. Cross Range

International Space Station Ground Track

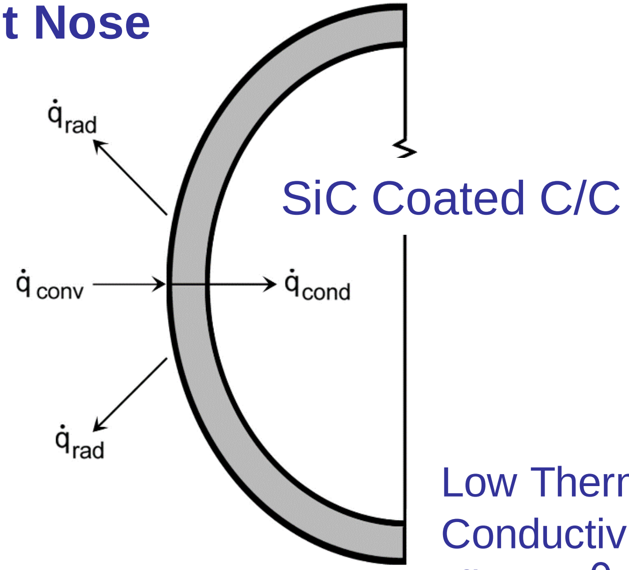
Blunt Range Max Cross-Range 1360 nautical miles

Sharp Body Max Cross-Range 3500 nautical miles



Surface Energy Balance

Blunt Nose

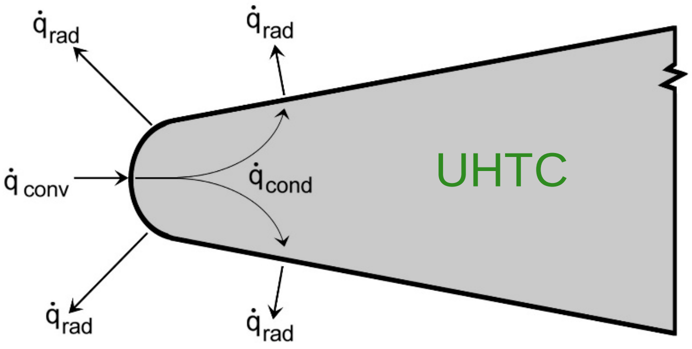


Low Thermal Conductivity

$q_{cond} \approx 0$

$$\dot{q}_{conv} \approx \dot{q}_{rad}$$

Sharp Nose



High Thermal Conductivity

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

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

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35th AIAA Thermophysics Conference, 11-14 June 2001, Anaheim CA. Dean Kontinos, (650) 604-4283 dkontinos@mail.arc.nasa.gov

Aerospace Application

- The diborides of hafnium and zirconium are of particular interest to the aerospace industry for sharp leading edge applications which require chemical and structural stability at extremely high operating temperatures.

- Some can be used as a monolith or matrix; some are more appropriate as a coating.
- Thermal properties have a significant impact on the surface temperatures.

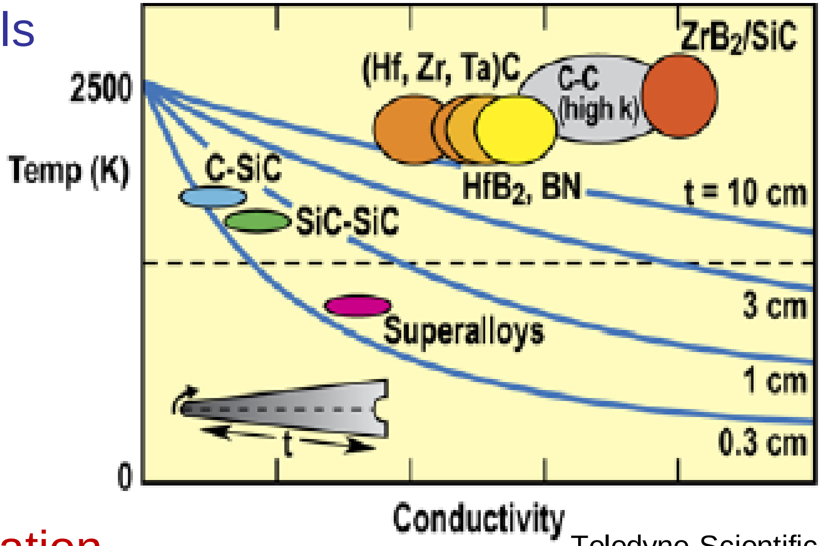
UHTC billets, quarter for scale

Materials for Sharp Leading Edges

Courtesy: AFRL

Sustained Hypersonic Flight Limited by Materials

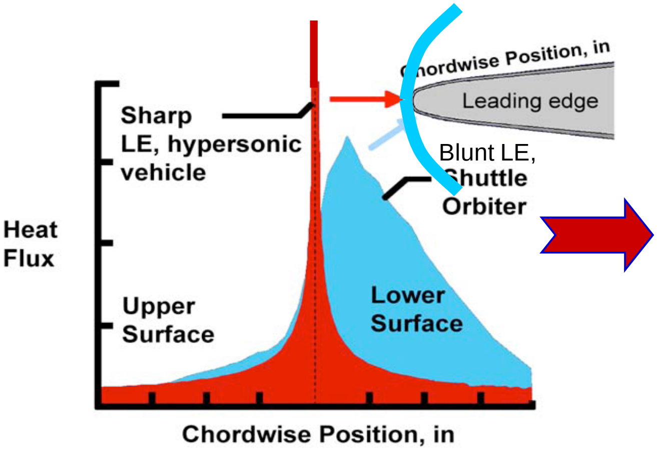
- High heat flux over small area
- High temperature, oxidation, erosion
- Very high temperature gradients



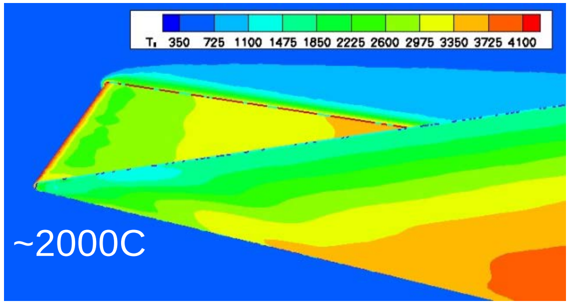
Teledyne Scientific

UHTCs (ZrB_2/HfB_2-based composites)

- High temperature capability and high thermal conductivity
- Poor oxidation resistance → Modeling/Validation
- Low fracture toughness → Fiber Reinforcement

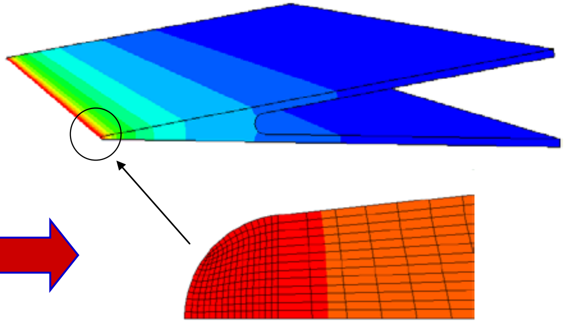


From D. Glass, NASA



Cowl Leading Edge

Free-Stream at Mach 8



High Temperature at Tip

Steep Temperature Gradient

Interest in UHTCs for Aerospace Applications Initiated Over Thirty Years Ago

- Initial work performed by ManLabs Inc. in the 1960's and 1970's for the Air Force on materials capable of withstanding extreme temperatures
- In the early 1990's NASA-Ames began investigating HfB_2 and ZrB_2 based materials for sharp leading edge applications.
  - Ground based research: initial materials development by external vendors, Arc Jet testing, computer modeling, etc.
  - SHARP-B1(1997) and SHARP-B2 (2000) ballistic flight experiments
- NASA-Ames was mostly interested in HfB_2-SiC composites
  - For a monolithic ceramic HfB_2-SiC has a relatively good thermal shock resistance
  - Retains shape at elevated temperatures

Processing of HfB_2-SiC

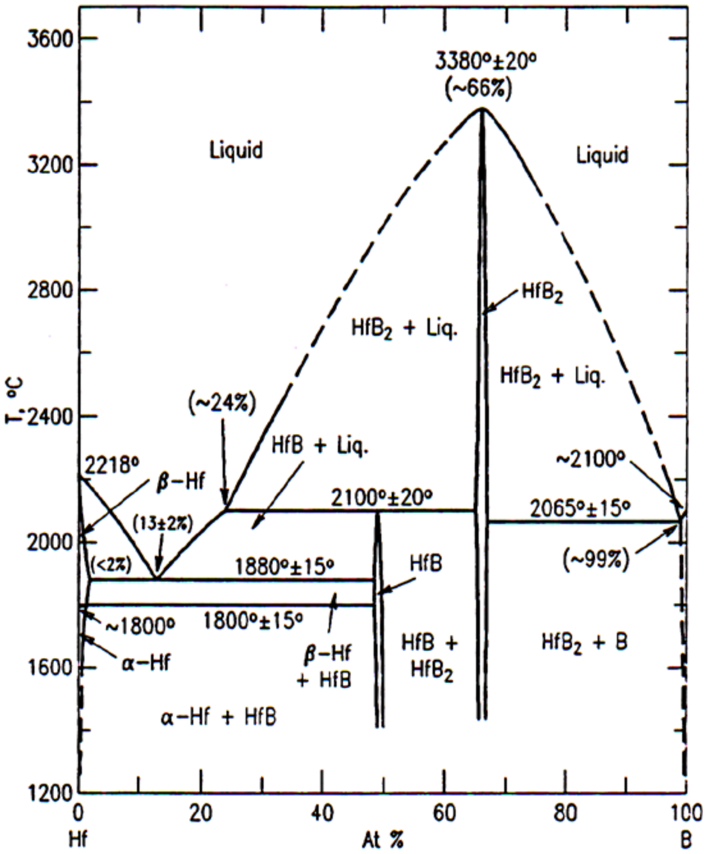
- **HfB_2** has a narrow range of stoichiometry with a melting temperature of 3380°C

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

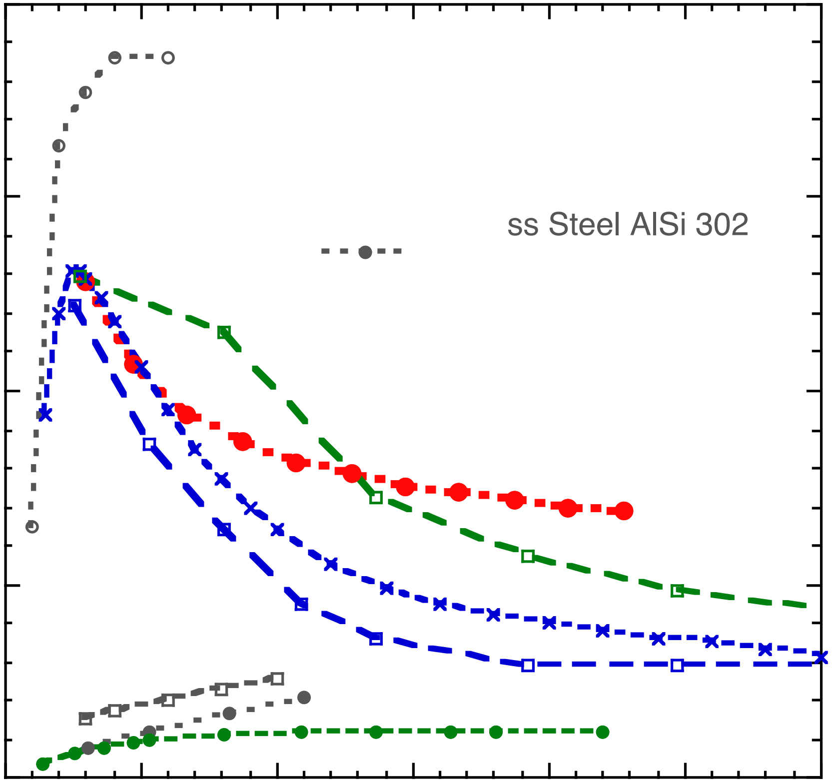
Density = 3.2 g/cm^3

HfB_2



Phase diagram from American Ceramic Society Phase diagrams

HfB_2/SiC Materials Have Relatively High Thermal Conductivities

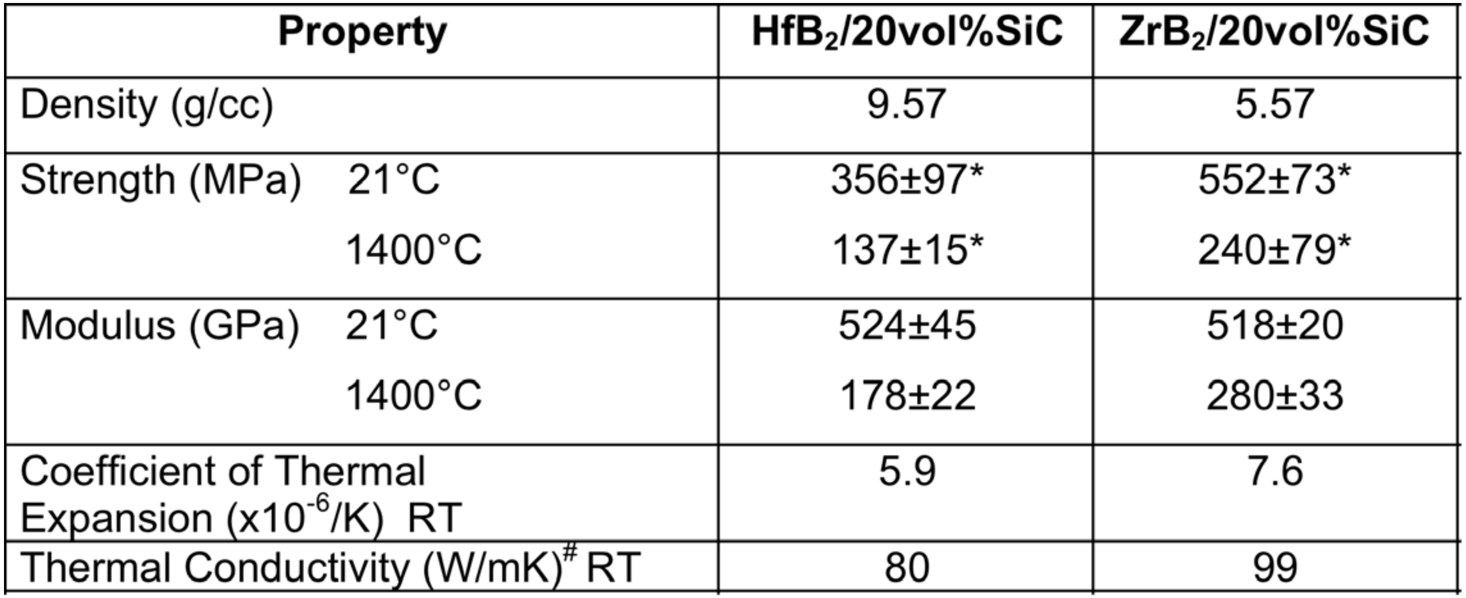


- HfB_2/SiC material was measured from 1999 era materials manufactured by an outside vendor.
- Thermal Diffusivity and Heat Capacity of HfB_2/SiC was measured using Laser Flash.

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

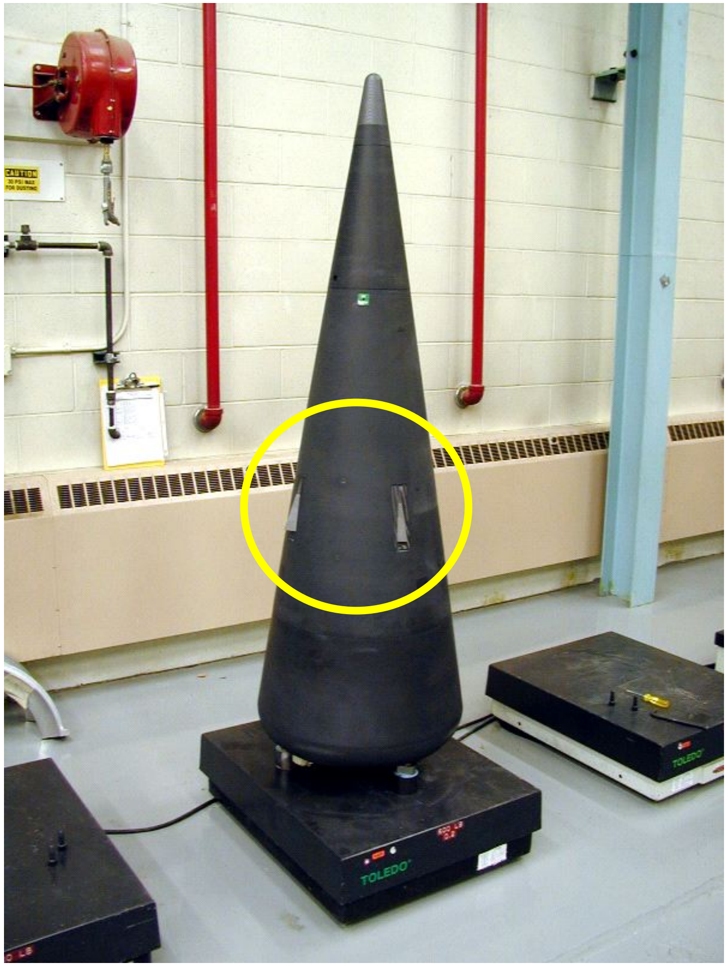
\# R. P. Tye and E. V. Clougherty, “The Thermal and Electrical Conductivities of Some Electrically Conducting Compounds.” Proceedings of the Fifth Symposium on Thermophysical Properties, The American Society of Mechanical Engineers, Sept 30 – Oct 2 1970. Editor C. F. Bonilla, pp 396-401.

UHTC Flight Experiments

- 2 flight experiments on U.S. Air Force Minuteman III missile carrying a modified Mk 12A reentry vehicle (RV)
  - SHARP B1: 1997
  - SHARP B2: 2000
- Purpose was to test materials
- Materials were made by 2 different outside vendors
- Materials were not recovered in SHARP B1
  - Sharp nosetip on RV
- Materials were recovered from SHARP B2
  - 4 strakes on body of RV
  - 3 different materials: HfB_2/SiC, ZrB_2/SiC, $ZrB_2/SiC/C$
  - One pair retracted before ablation predicted
  - One pair retracted after ablation predicted

Flight Hardware

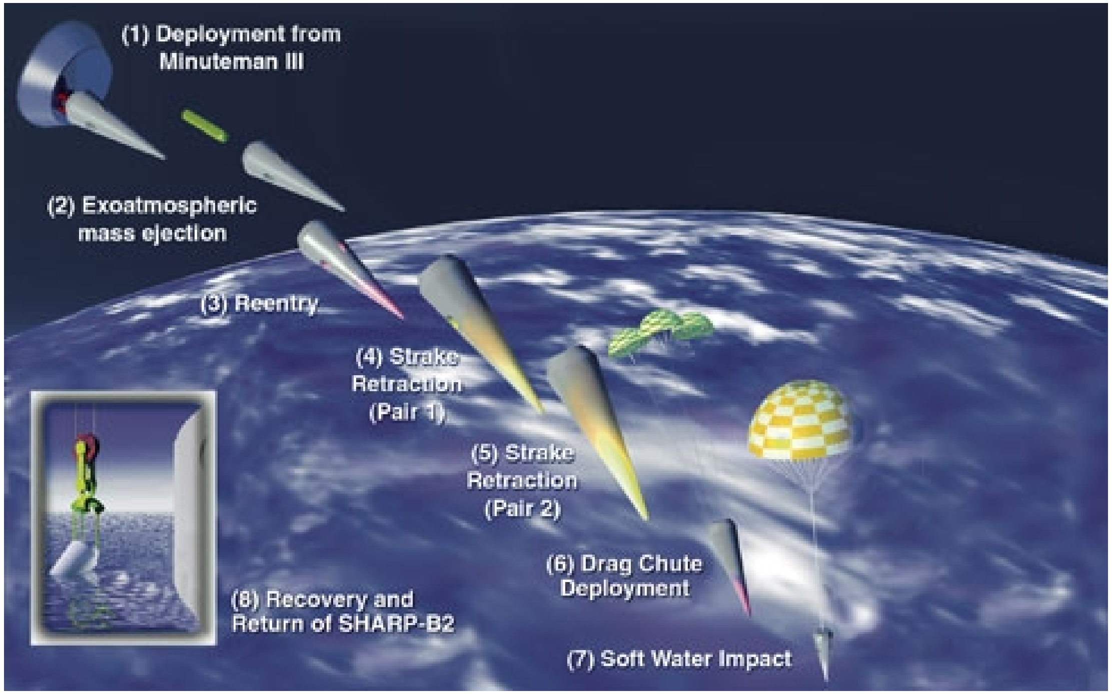
SHARP-B1 May 21, 1997



SHARP-B2 Sept. 28, 2000

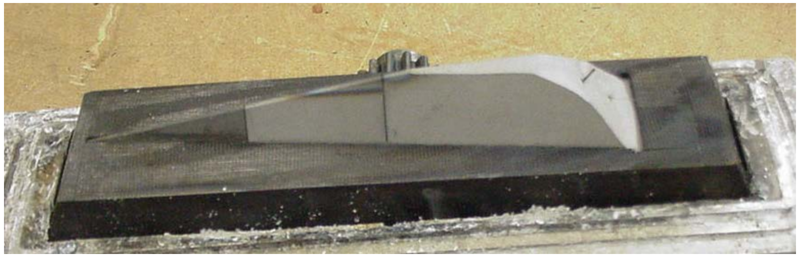
SHARP-B2

- 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 and then retracted into protective housing.
- ***Material recovered. Led to new effort in UHTCs / decision to bring development in-house and improve processing.***

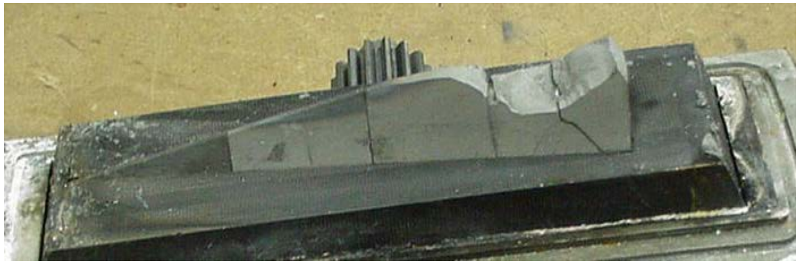


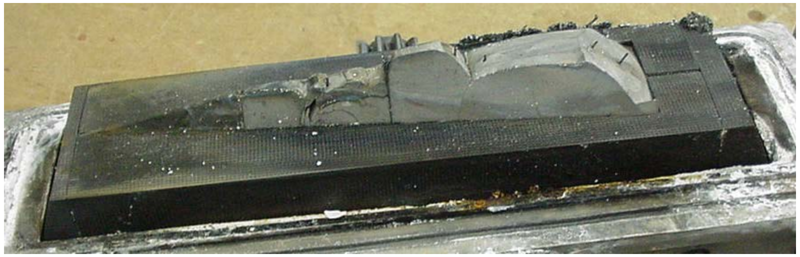
Recovered Strakes

- 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.

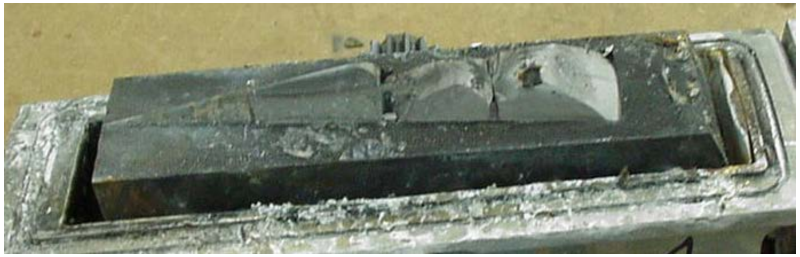


Pair 1 (47.9 km)

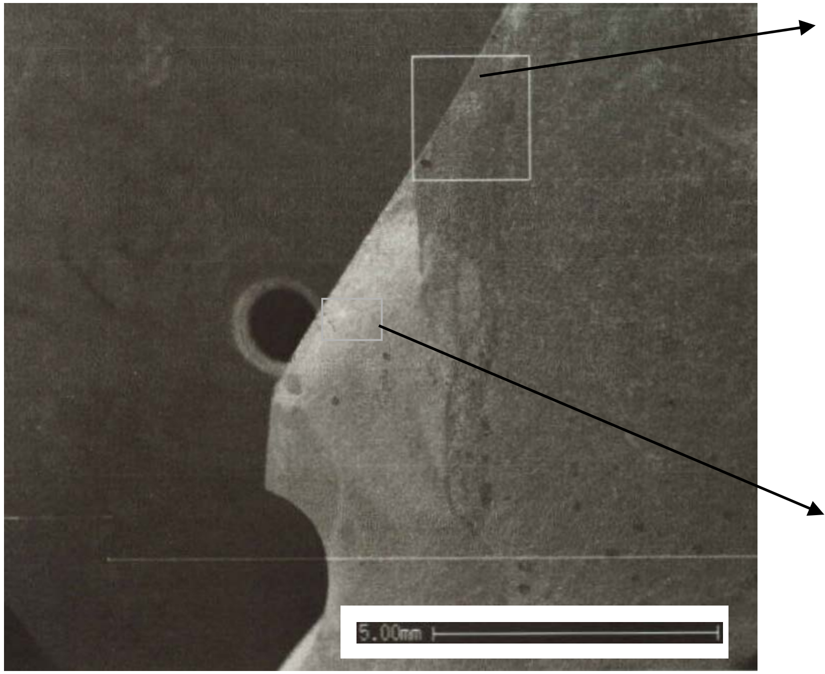


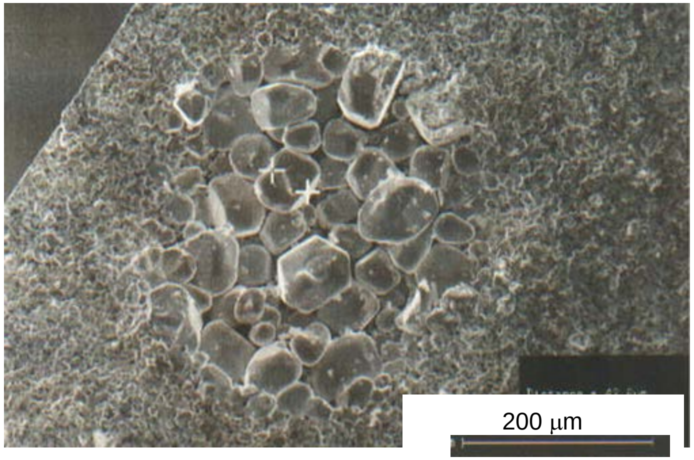


Pair 2 (43.3 km)

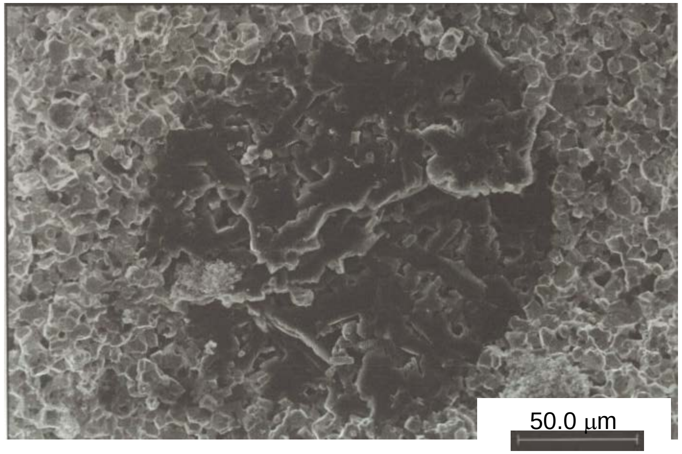


Processing Defects on Fracture Surface



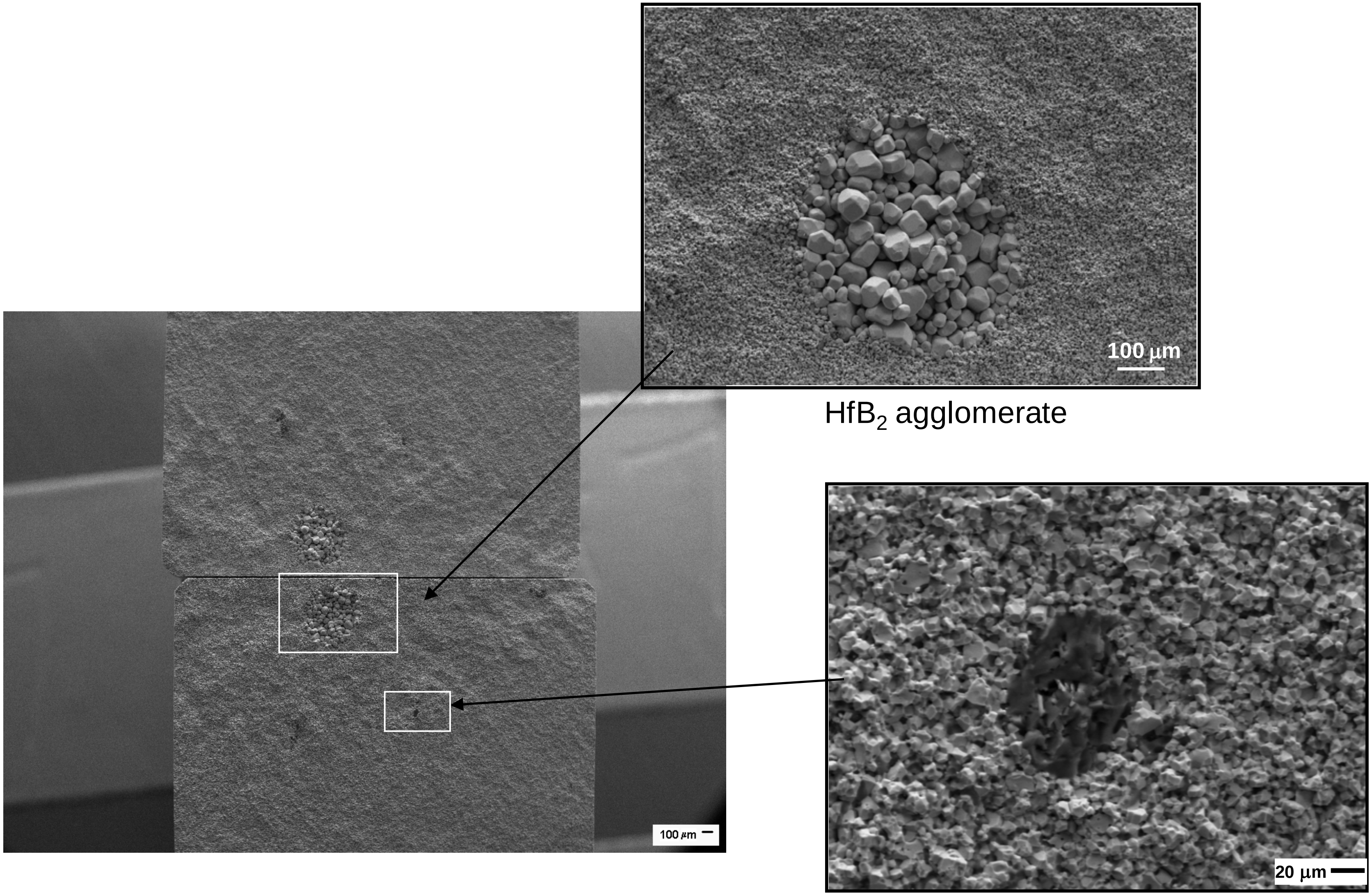


HfB_2 agglomerate



SiC agglomerate

Processing Defects in HfB_2-SiC



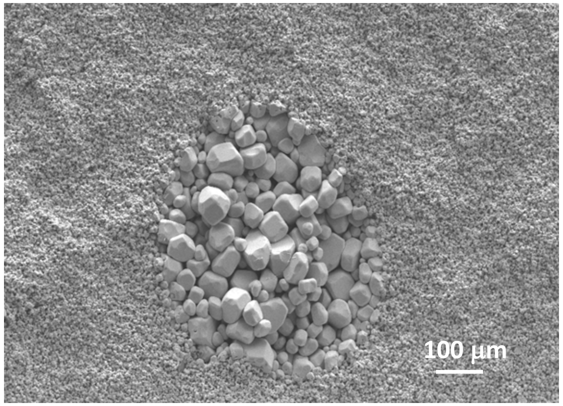
HfB_2 agglomerate

Grafoil™ agglomerate

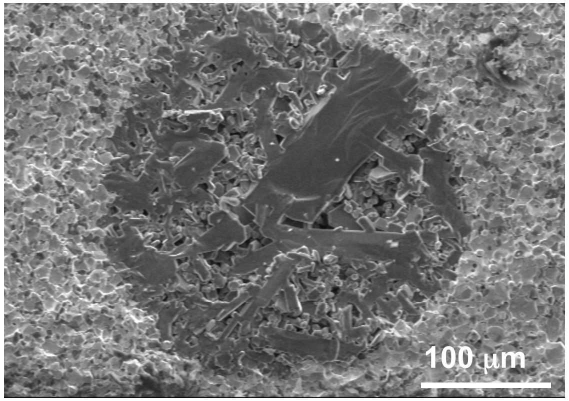
A Cautionary Tale

- 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.

Poorly processed $HfB_2 20v\%SiC$

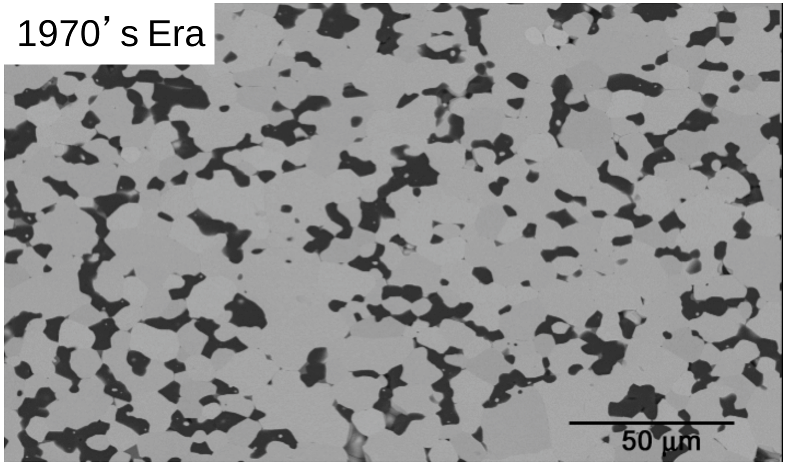


Large HfB_2 agglomerate

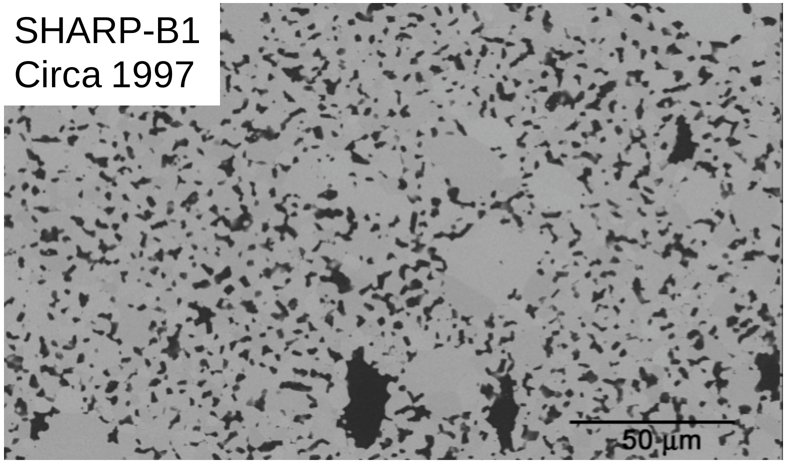


Large SiC-rich agglomerate

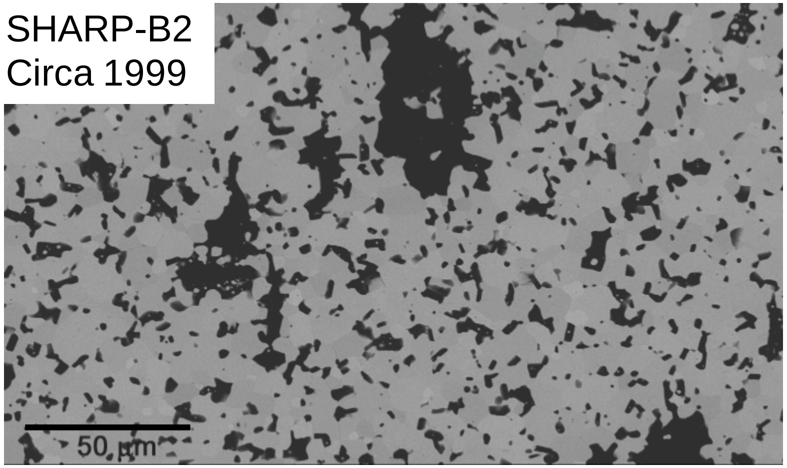
Typical Microstructures of Previous HfB_2 - 20% SiC Materials



1970’s Era



SHARP-B1
Circa 1997



SHARP-B2
Circa 1999

Coarse, poorly sintered microstructures and/or large agglomerates of SiC and HfB_2 were common in previous materials.

HfB_2: $\rho = 11.2$ g/cc
SiC: $\rho = 3.2$ g/cc

- Improved processing techniques are required to produce homogeneous, fine grained materials

Motivation for In-House UHTC Processing at Ames

- Until 2000 there was no consistent effort to develop the UHTC family of materials at NASA.
  - Development work was primarily part of flight experiment programs such as the SHARP-B1 and SHARP-B2 flight experiments
- Different vendors supplied materials for the SHARP-B1 and SHARP-B2 flight experiments.
  - NASA did not retain the knowledge on how to process these materials.
    - Therefore, each time we have had to start at the beginning, evaluating material properties, etc…
- Resulted in inconsistent materials
  - Significant differences in microstructure leads to significant variability in material properties.
- Bringing the UHTC processing in-house allowed the government to retain the knowledge of how to process the materials and then transfer the technology to industry for production.
  - Precedent was set at ARC with development of tile coatings.

General UHTC Processing Route

Characterize Starting Powders

SEM micrographs

Particle size distribution

X-ray diffraction

Oxide content

Milling / Mixing

Particle size reduction

Additives: dispersants, binders & solvents

Duration

Controlled Drying

Milled powders dried

No hard agglomerates

Controlled atmosphere

Characterize Dried Powders

SEM micrographs

Particle size distribution

X-ray diffraction

Oxide content

Pack Hot Press Die

Die coating

Die liner

Packing method

Hot Press

Time

Temperature

Pressure

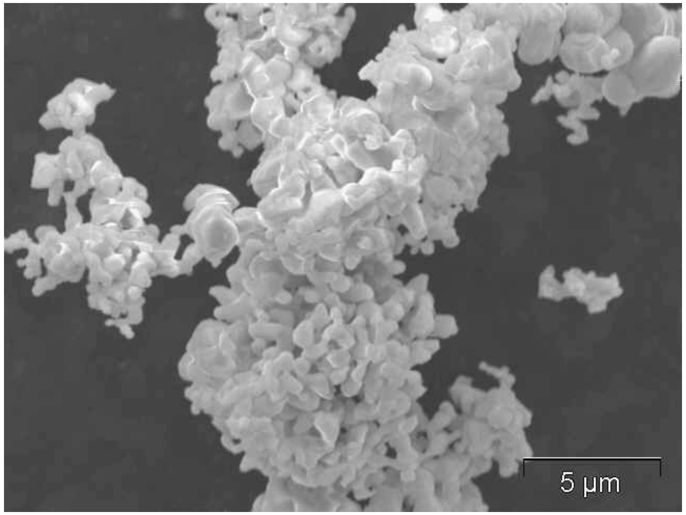
Ramp rates (pres. & temp.)

Atmosphere

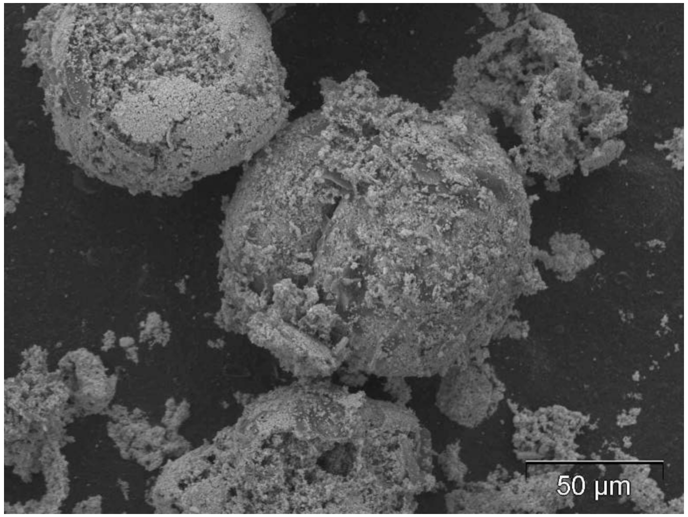
Powder Granulation

- Large density difference between HfB_2 (ρ = 11.2 g/cc) and SiC (ρ = 3.2 g/cc) make these constituents susceptible to phase segregation
- Powders are granulated by freeze-drying to prevent phase segregation
- Granulation improves powder handling
  - Prevents post-milling phase segregation
  - Granulated powders flow better aiding die filling
    - Reduces density gradients within the green and sintered parts
- Continually improving the granulation process

As received HfB_2 Powder



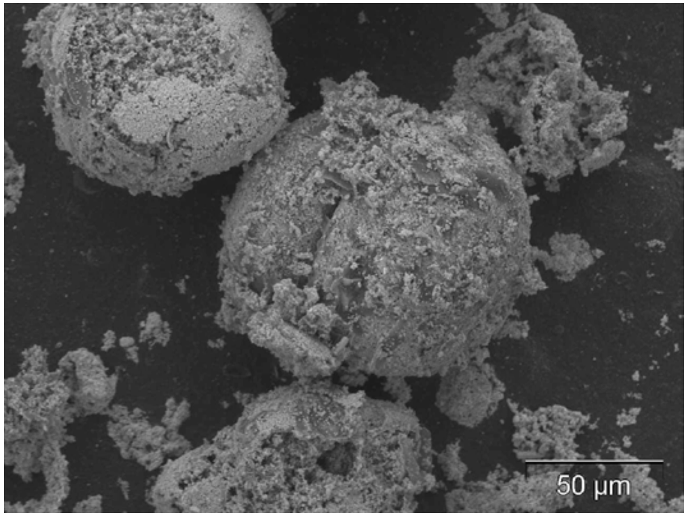
Granulated freeze-dried HfB_2/SiC Powder



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

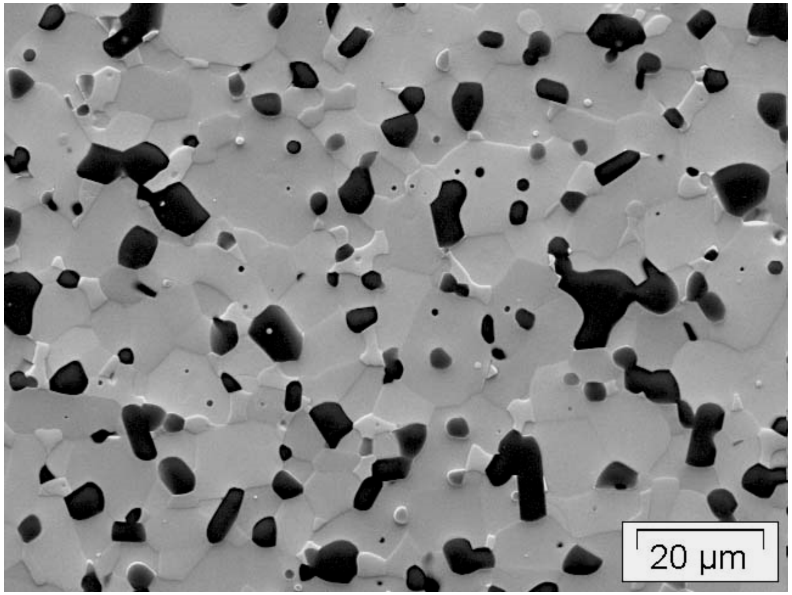
  - Used freeze-drying to make homogenous powder granules
  - Developed appropriate hot pressing schedules



Granulated HfB_2/SiC Powder

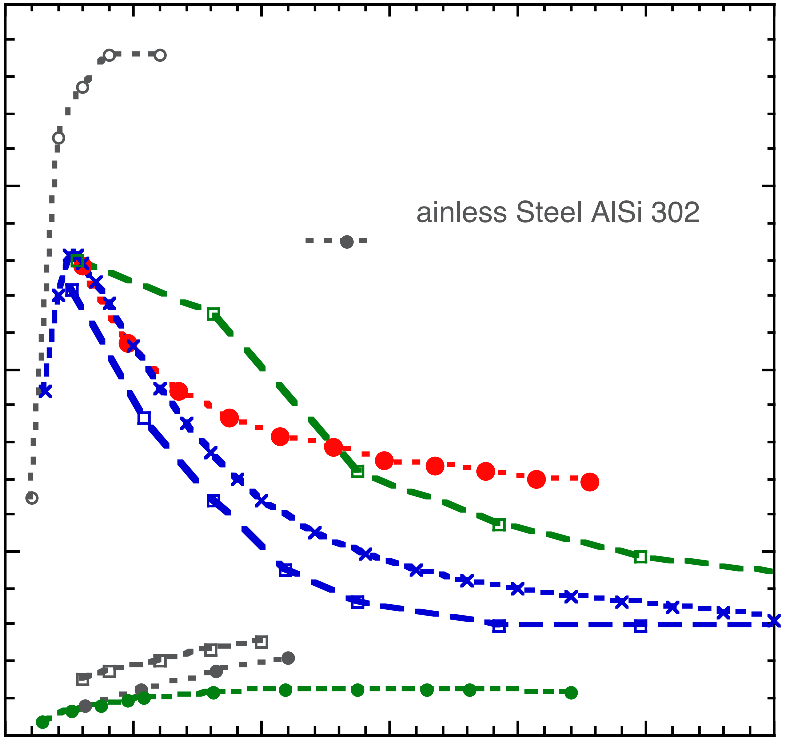
Role of SiC in UHTCs

- 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



Baseline hot pressed UHTC microstructure
Dark phase is SiC

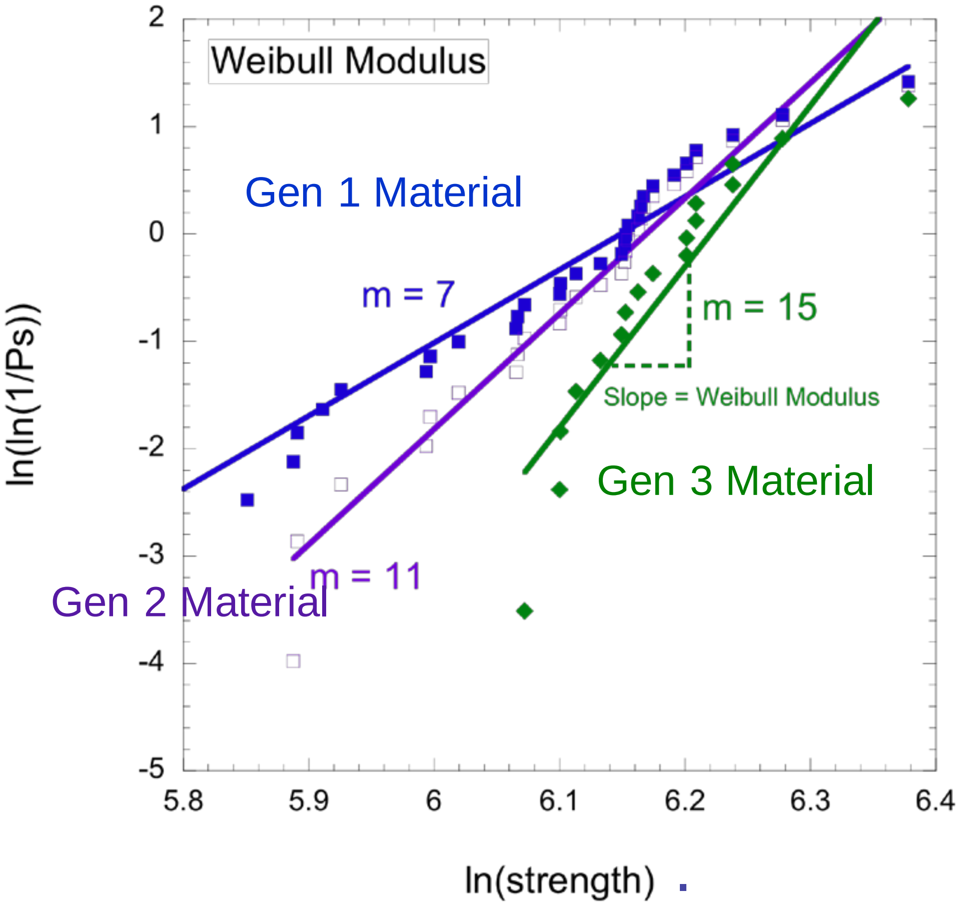
Thermal Conductivity



HfB$_2$/SiC materials have relatively high thermal conductivity

- HfB$_2$/SiC thermal conductivity was measured on material from the SHARP-B2 program.
- Thermal Diffusivity and Heat Capacity of HfB$_2$/SiC were measured using Laser Flash.

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

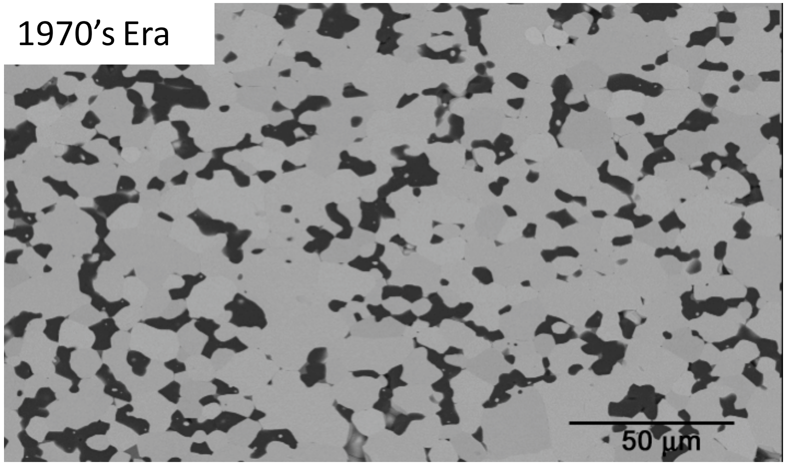


Room temperature data

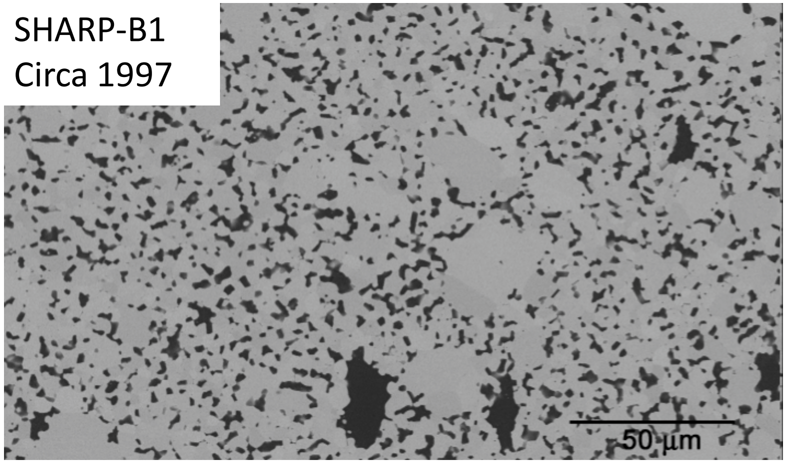
Weibull Modulus SHARP B2 Materials ~4

Increased Weibull Modulus to ~15 with processing improvements

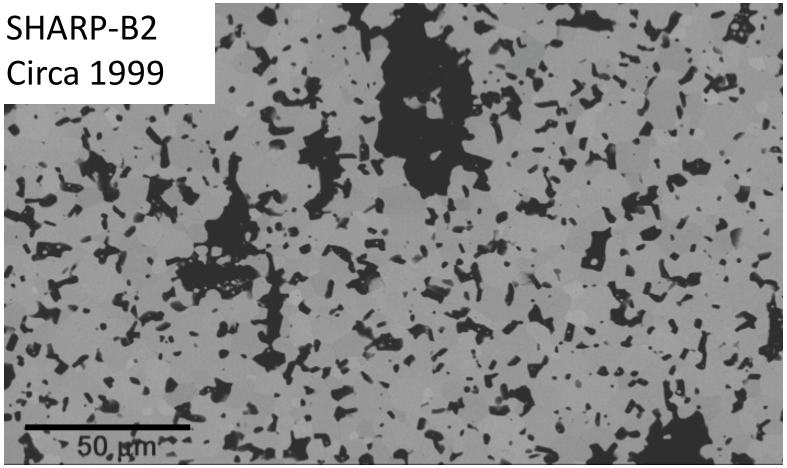
Early HfB_2 - 20% SiC Materials



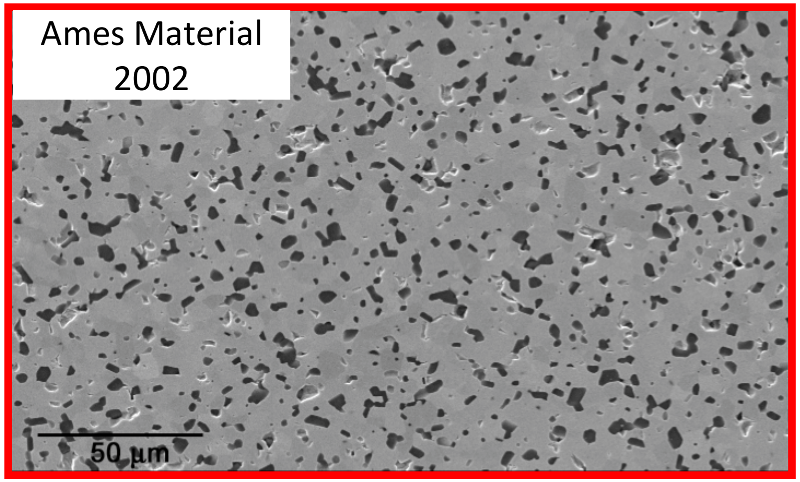
1970’s Era



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

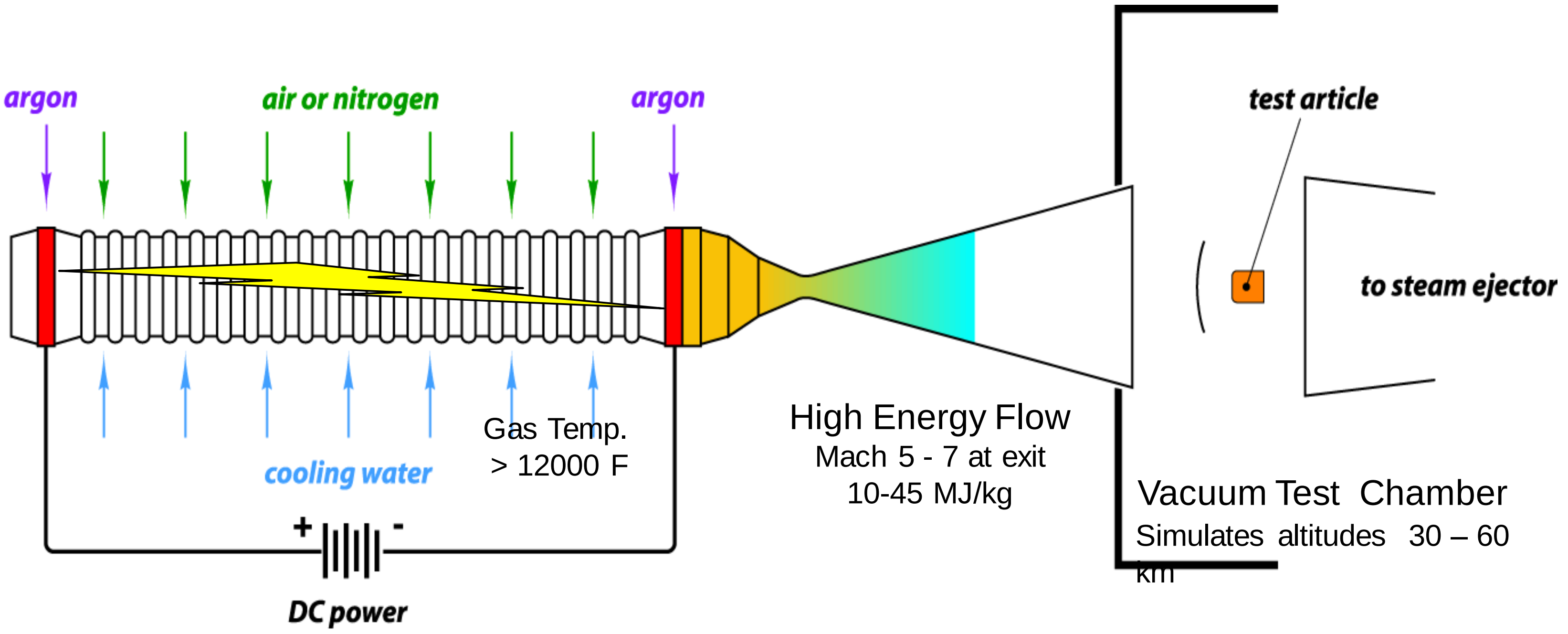
Understand what you are testing!

Need for Arc Jet Testing

- Arc jet testing is the best **ground-based method** of evaluating a material's 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

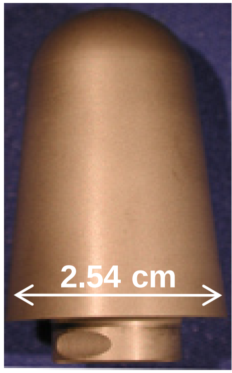
Stine, H.A.; Sheppard, C.E.; Watson, V.R. Electric Arc Apparatus. U.S. Patent 3,360,988, January 2, 1968.

UHTC Cones After 9 Arc Jet Exposures

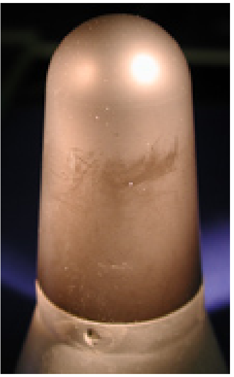
(89 minutes total run time)

Runs 4 and 5 lasted ~ 2 min. each

HSp-45
Pretest



Run 1
Post-Test



300 sec
% Δwt = 0
T_{ss} = 1280°C

Run 2
Post-Test

600 sec
% Δwt = 0
T_{ss} = 1220°C

Run 3
Post-Test

600 sec
% Δwt = 0
T_{ss} = 1325°C

Run 6
Post-Test

600 sec
%Δwt = -0.06
T_{ss} =1970°C

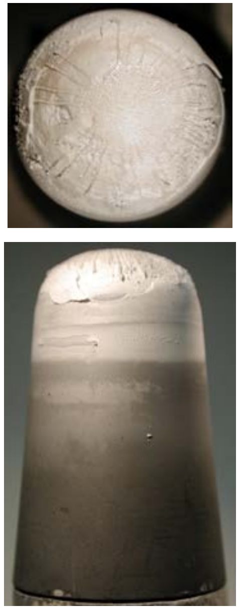
Run 7
Post-Test

1200 sec
%Δwt = -0.2
T_{ss} >2000°C

Run 8
Post-Test

1200 sec
%Δwt = -0.32
T_{ss} >2000°C

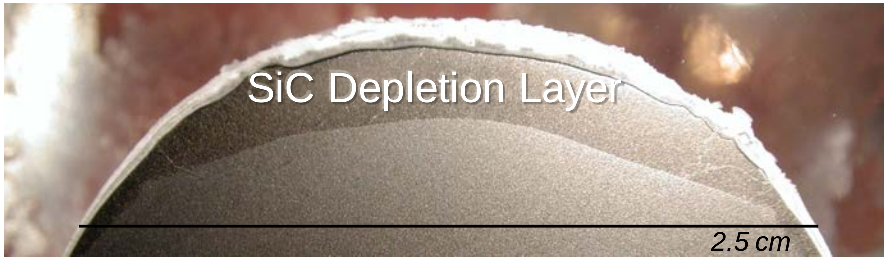
Run 9
Post-Test



600 sec
%Δwt = -1.24
T_{ss} >2000°C

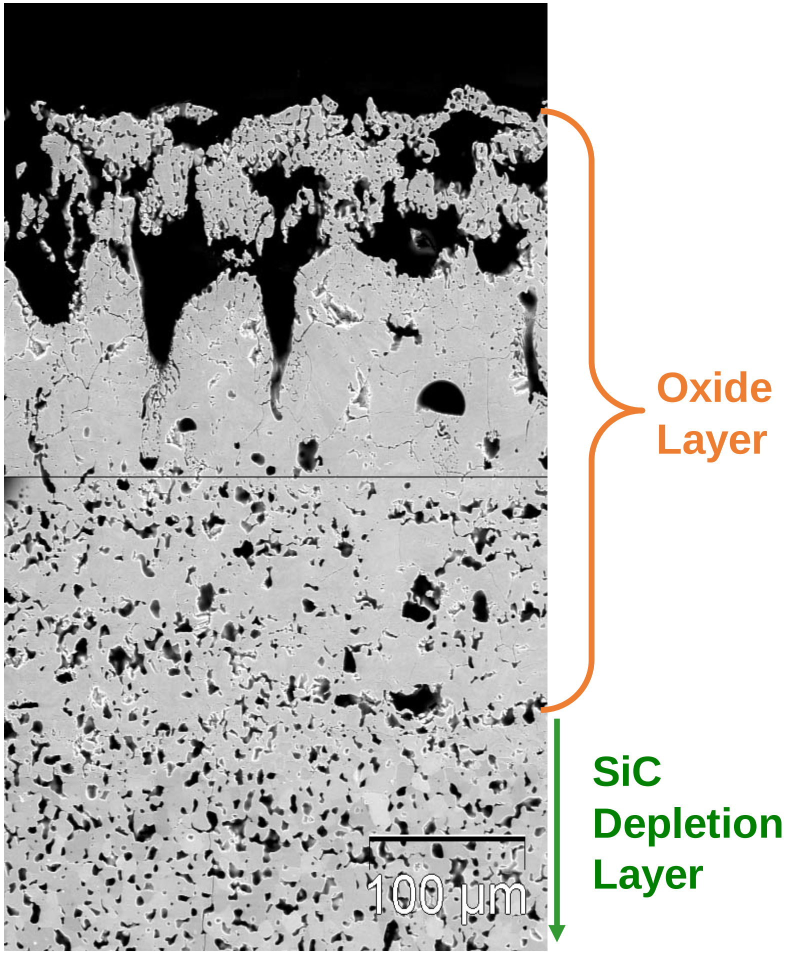
Increasing heat flux →

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 W/cm^2, P_{stag} = 0.07 atm

*Arc jet test data from Space Launch Initiative program

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 – $\mathbf{R' = \sigma k/(\alpha E)}$
  - 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**

Adapted from E. Wuchina, NSWC

Outline

- What are UHTCs?
  - Background and features
- Aerospace applications
  - Sharp leading edges
- Properties
- Thoughts on materials development
- Specific issues with UHTCS and approaches
  - Design issues
  - Material issues
  - Modeling
- Thoughts on future directions
  - Technical
  - Application
- Concluding remarks

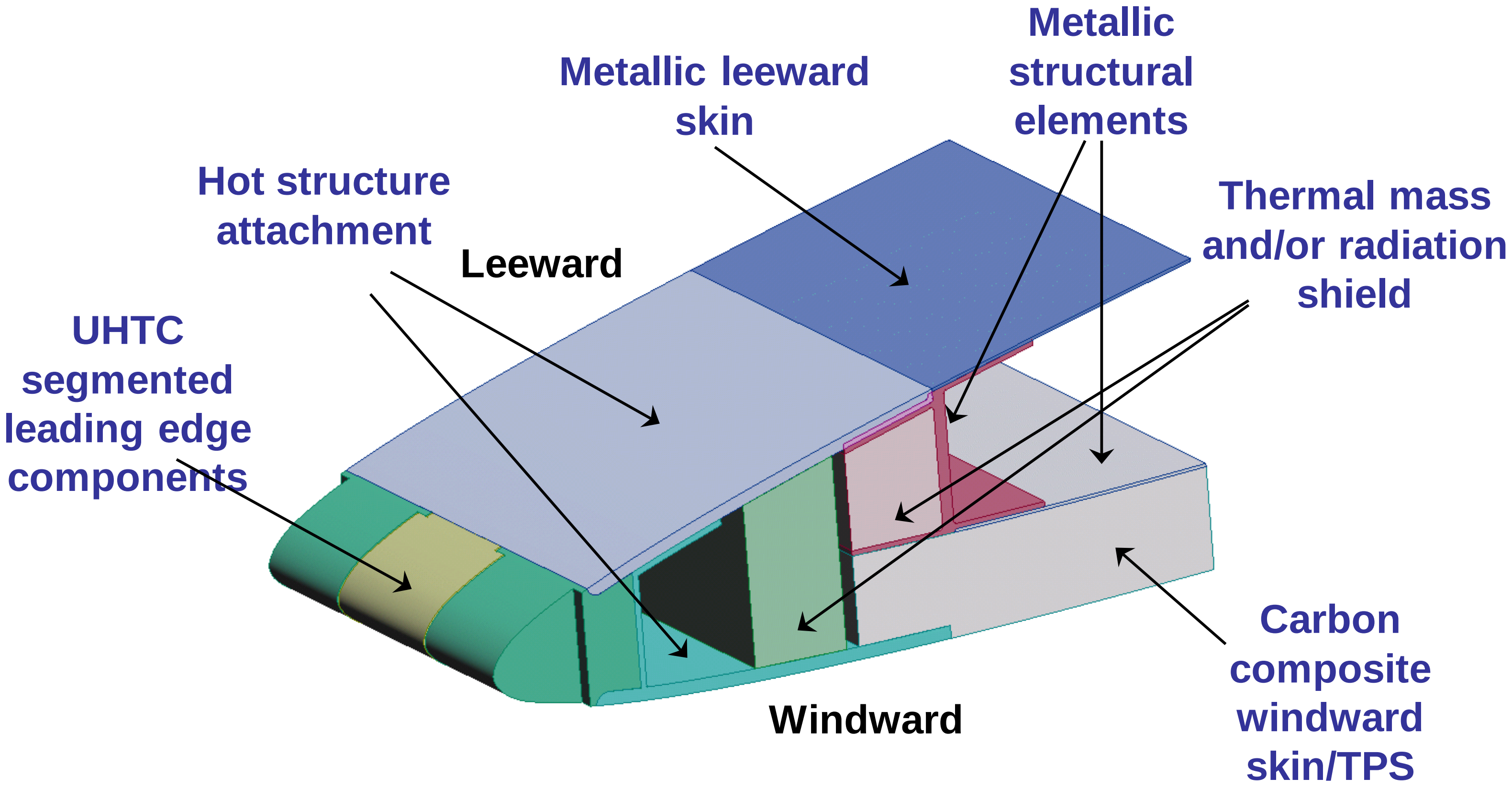
Design Challenges for UHTC Flight

- Integrated approach that combines:
  - Mission requirements
  - Aerothermal and aerodynamic environments
  - Structural material selection
  - Component serviceability requirements
  - Safety requirements
- Size of UHTC billets limited to several centimeters — wing leading edges and nosetips must be *segmented*
  - The design of interfaces between segments is critical
- The mechanical loads on small UHTC components during flight are primarily result of differential thermal expansion within material
- High temperature UHTC components must be attached to vehicle structure (with lower operating temperature limits)
  - *Design issue, not materials issue*
  - Design concepts developed showed feasibility

UHTC Wing Leading Edge Concept

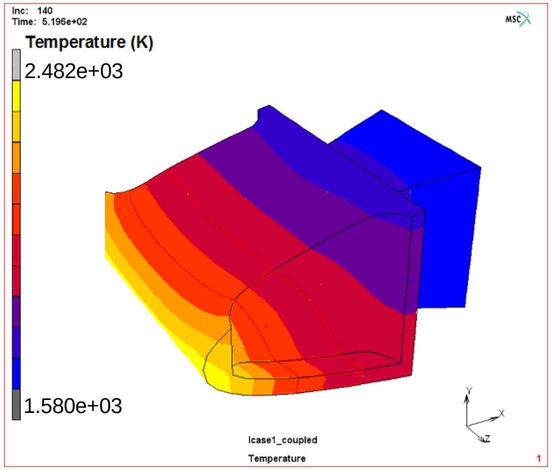
UHTC wing leading edge (WLE) concept for a hypersonic aircraft:

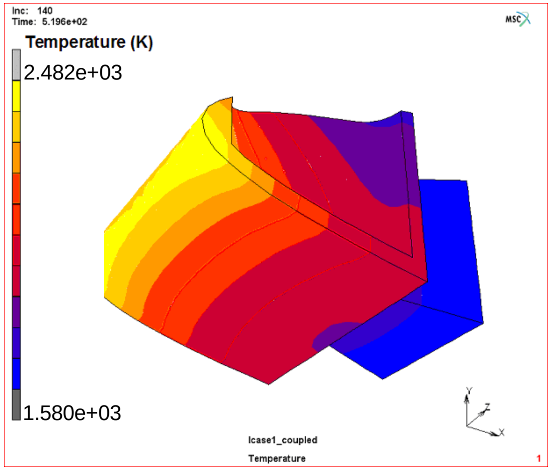
- UHTC segmented leading edge attached to carbon-based hot structure
- Nose radius ~1cm

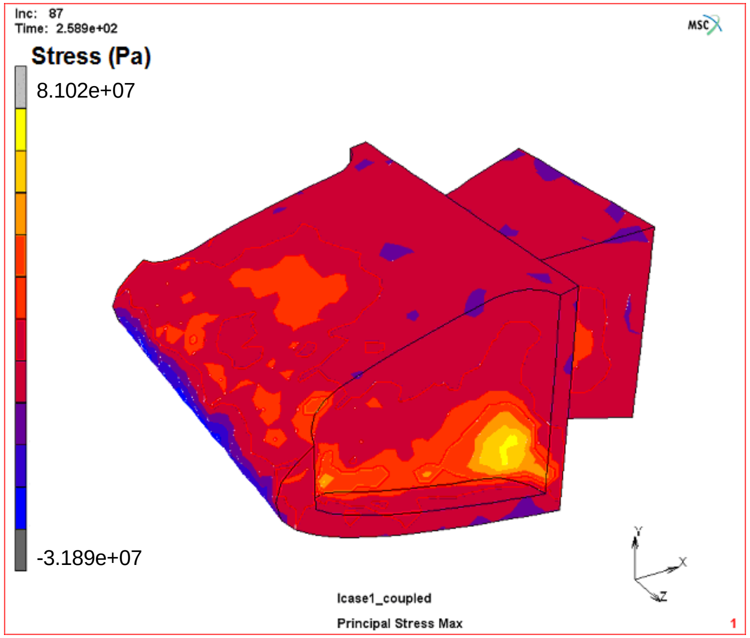


Example of Predicted UHTC WLE Component Performance

- UHTC WLE under reentry heating conditions
- Peak predicted thermal stress of 80 MPa was well below demonstrated UHTC strengths between 300 to 400 MPa







What About Active Oxidation?

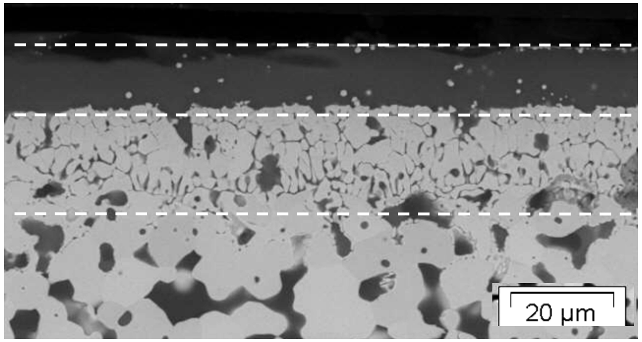
- Silicon-containing materials will actively oxidize under high temperature, low pressure conditions, forming SiO as gas
- Most problematic during re-entry (not during cruise)
- Mitigation approaches:
  - Reduce volume of SiC
    - Reduce overall oxidation
    - Below percolation threshold
  - Reduce scale of SiC particles
    - Allows formation of protective oxide sooner
    - Increase tortuosity of diffusion path
    - Balance between control of grain size and limit of oxidation
  - Additives
    - To change viscosity of the oxide
      - Change emissivity (lower surface temperature)
      - Change diffusivity of species through the oxide
    - To form a physical barrier
    - To change sintering behavior of UHTC with consequent reduction in SiC

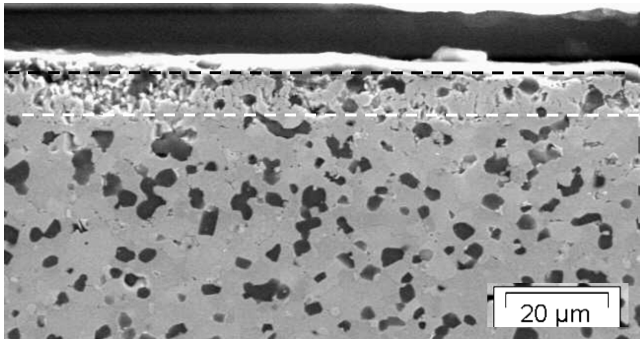
Arcjet Characterization:

Hot Pressed

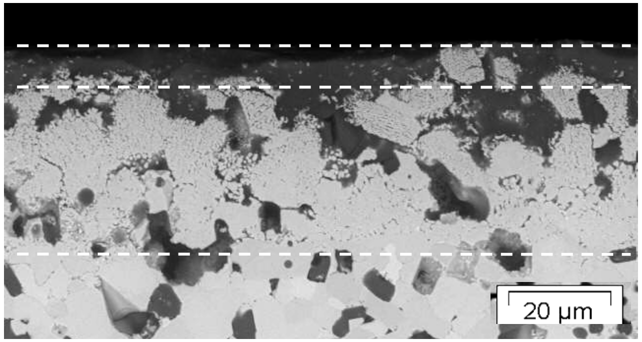
Field Assist Sintered (FAS)

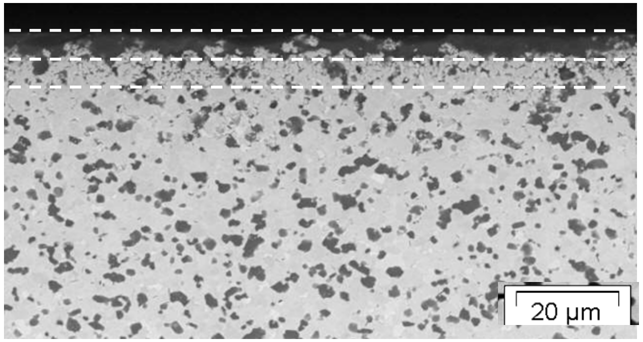
HfB_2-SiC
Baseline



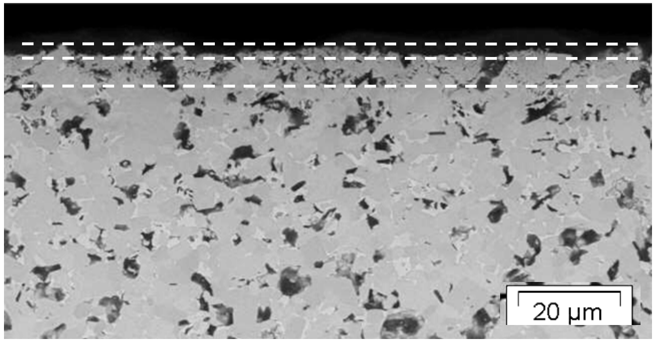


HfB_2-SiC-$TaSi_2$



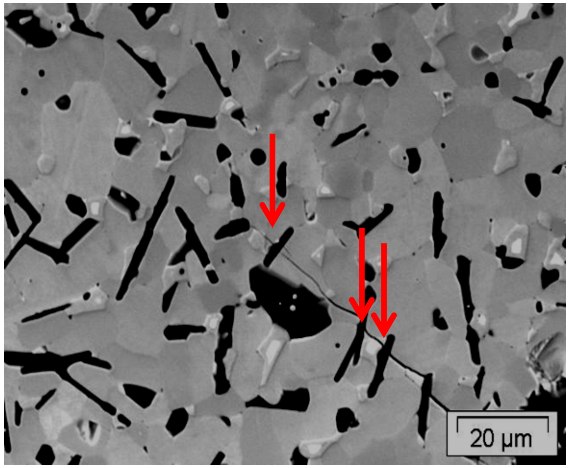


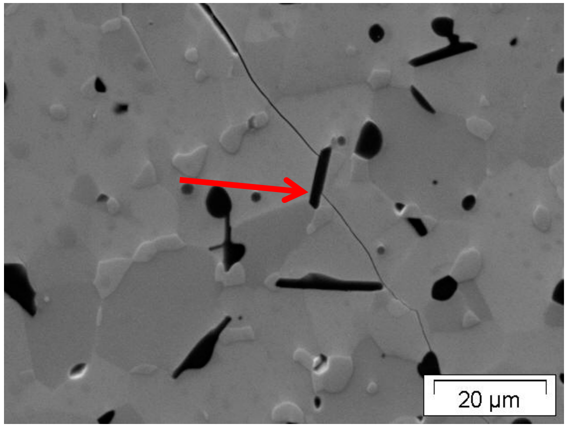
HfB_2-SiC-
$TaSi_2$-Ir

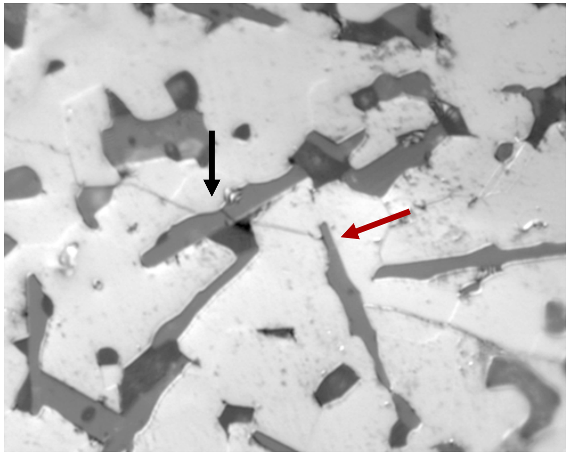


Both oxide scale and depletion zone can be reduced.

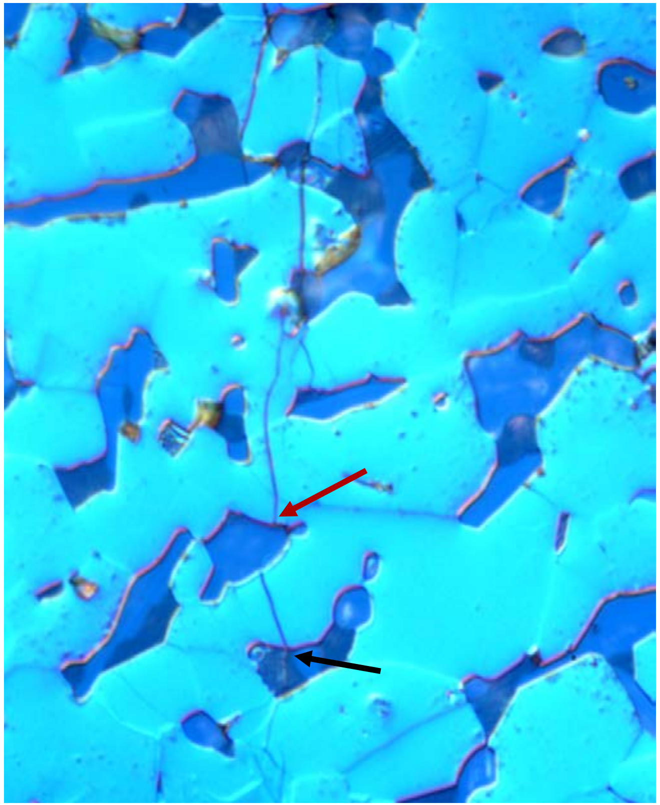
In-Situ Composite for Improved Fracture Toughness







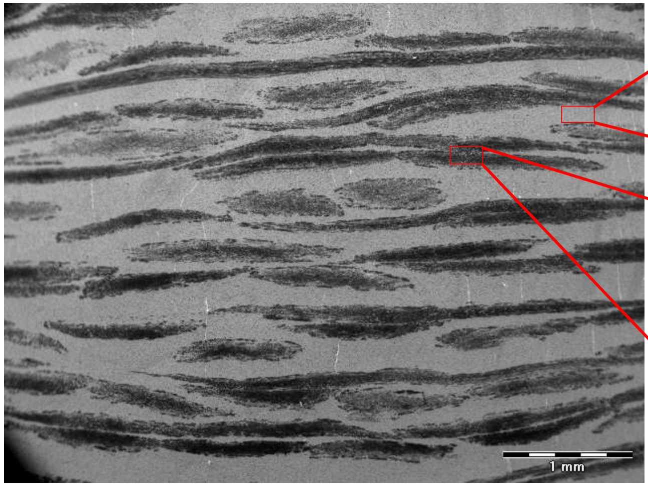
SiC Content	Fracture Toughness ($MPam^{1/2}$)
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33

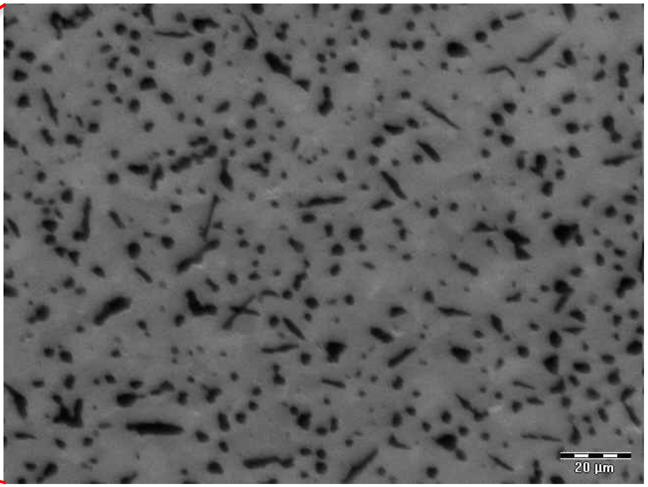


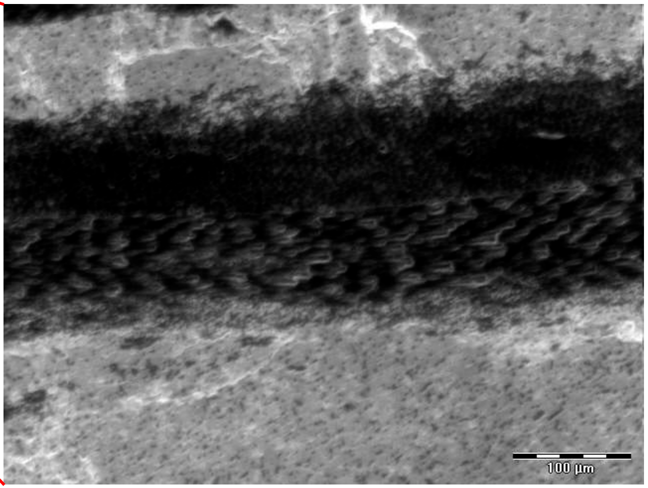
Oak Ridge National Laboratory

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.

Current researchers/areas

- NASA no longer involved in UHTC research
- Major research efforts include
  - AFRL
  - Missouri University of Science and Technology
  - University of Arizona (Erica Corral) (Hilmas/Fahrenholtz)
  - UK consortium: University of Birmingham/Imperial College/Ministry of Defence)
  - Italy: Faenza
  - AFOSR-NASA National Hypersonics Science Center for Materials & Structures (Teledyne Scientific)(completed)

  - Many others

  - Emphasis is on processing, properties, behavior in relevant conditions, and composites.

Computational Modeling of UHTCs

Goals

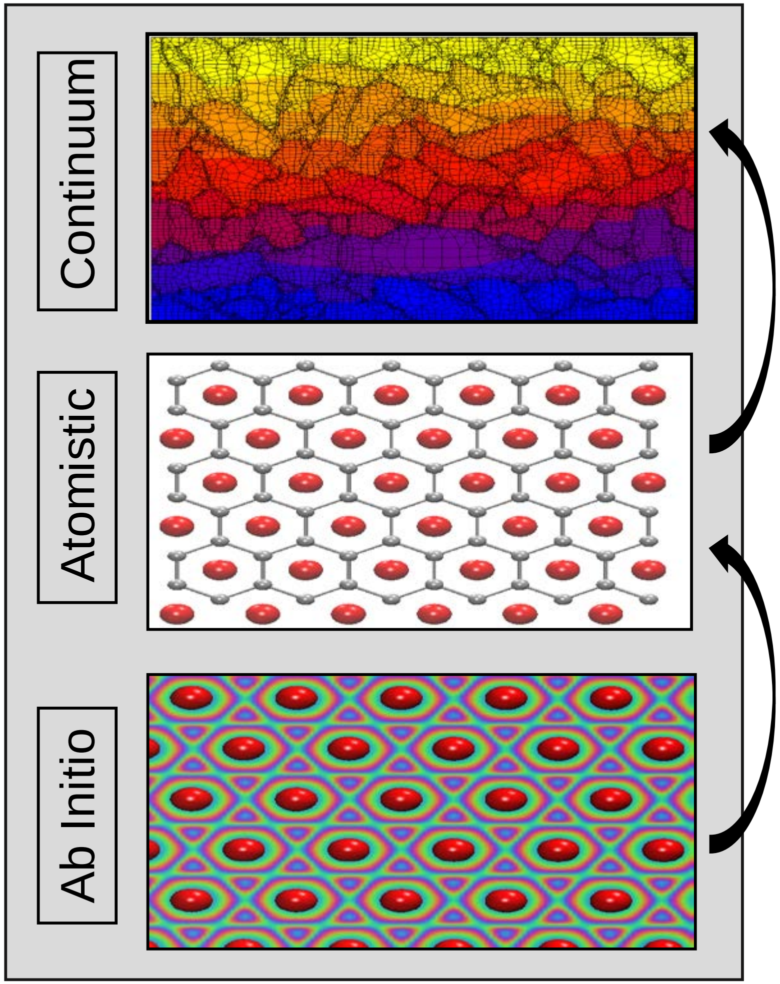
- Reduce materials development time
- Optimize material properties/tailor materials
- Guide processing of materials
- Develop design approaches

Approach

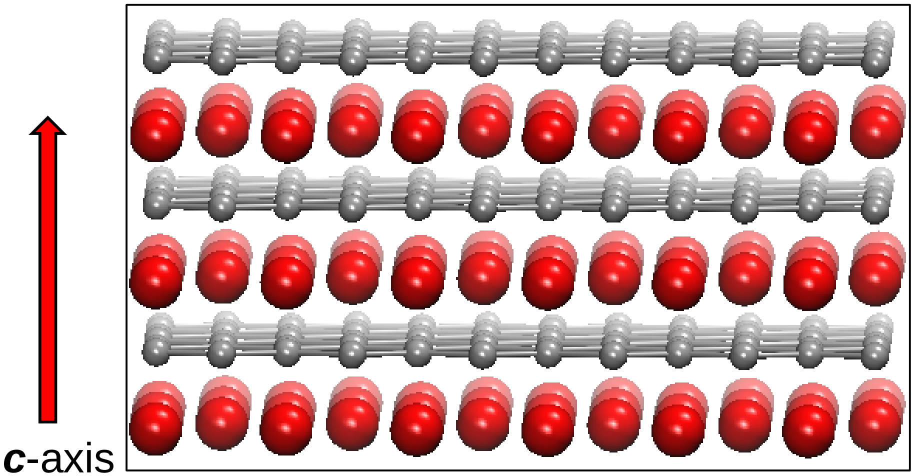
- Develop models integrated across various length scales
- Correlate models with experiment whenever possible

Multiscale Modeling of UHTCs

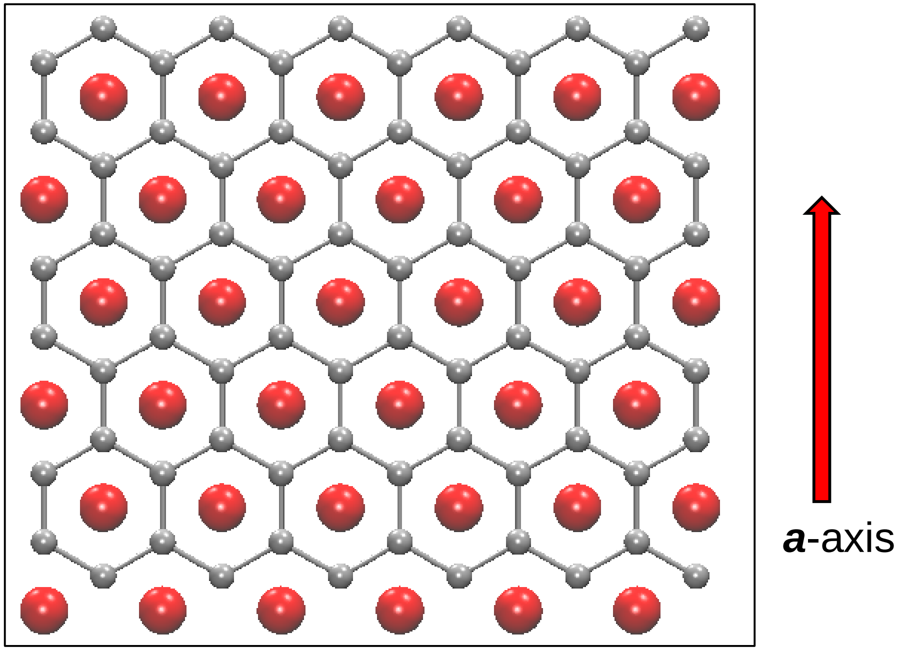
- **Framework integrates three methods**
- **Multiscale framework for ZrB_2 and HfB_2:**
  - *Ab initio* – fundamental chemistry, electronic properties
  - *Atomistic* – thermal/mechanical properties, thermal resistance
  - *Continuum* – macro properties, thermal/mechanical analysis of microstructure
- **This talk will focus on thermal conductivity:**
  - Atomic structure and bonding
  - Interatomic potentials
  - Lattice thermal conductivity
  - Grain boundary structures
  - Interfacial thermal resistance
  - FEM thermal analysis of microstructures



Atomic Structure: ZrB_2

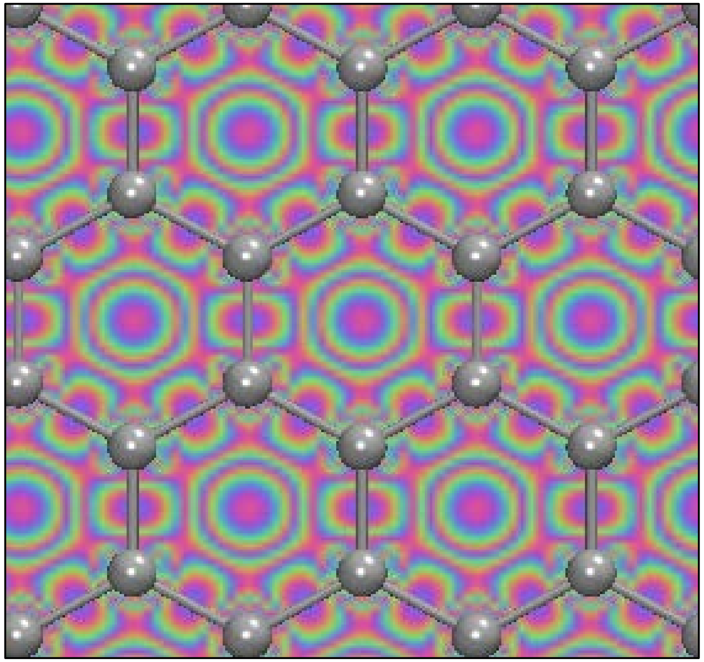


Alternating layers of
Zr (red) and Boron (gray)

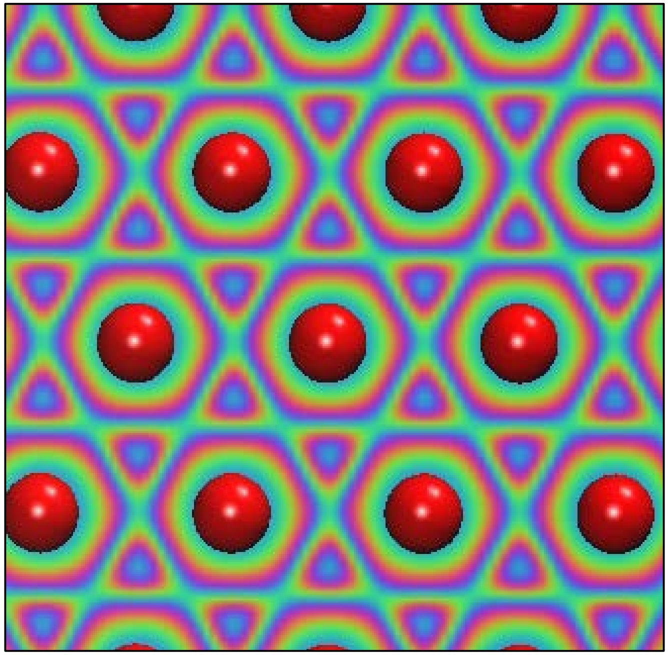


Graphitic Boron layers
with Zr over each ring

Bonding: Electron Localization Fnt (ELF)



Boron plane: **covalent**



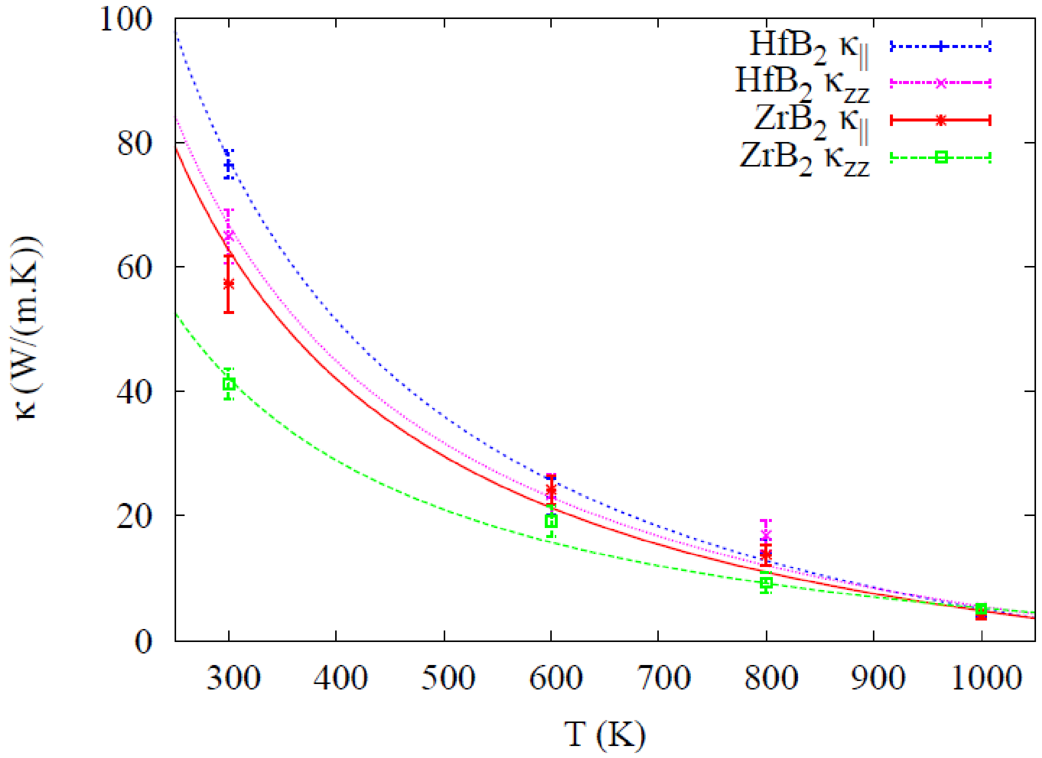
Zirconium plane: **metallic**

Interlayer: **ionic**

Blue = High
Red = Low

JWL, Bauschlicher, and Daw, J. Am. Ceram. Soc, (2011)

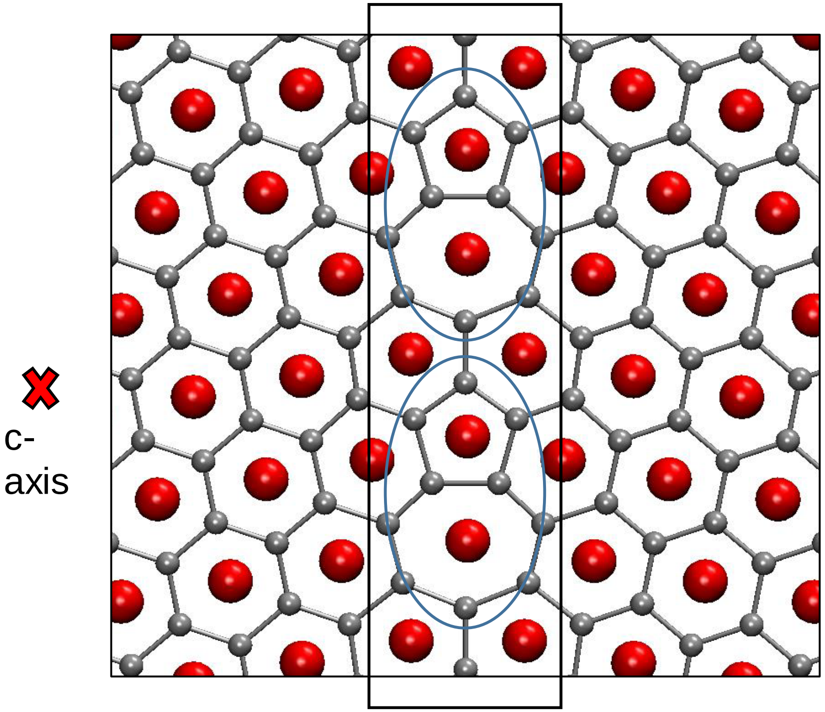
Lattice Lattice Thermal Conductivity Simulation



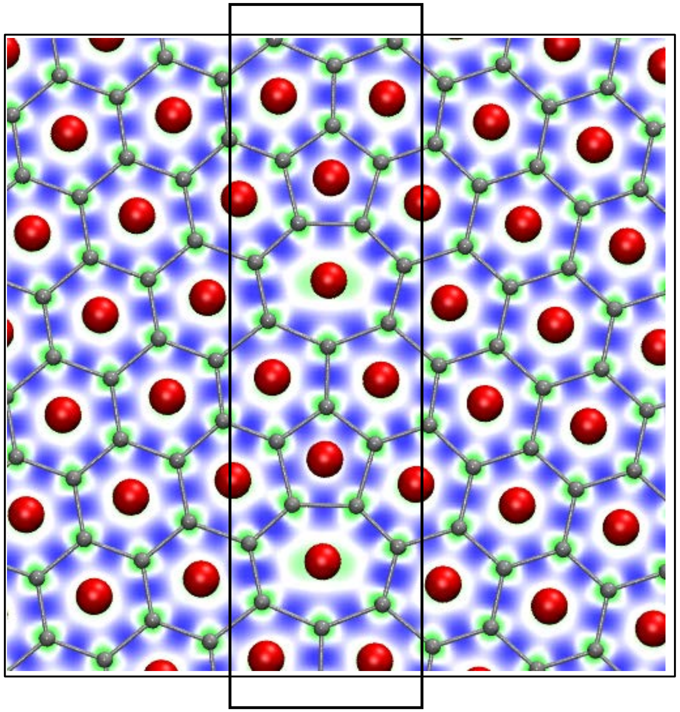
- Reasonable values at 300K
- High T values are probably too low

Lawson, Daw and Bauschlicher, J. App. Phys, (2011)

Symmetric Σ7 *C*-axis *Tilt*



Graphene GB structure: 7-5 pairs

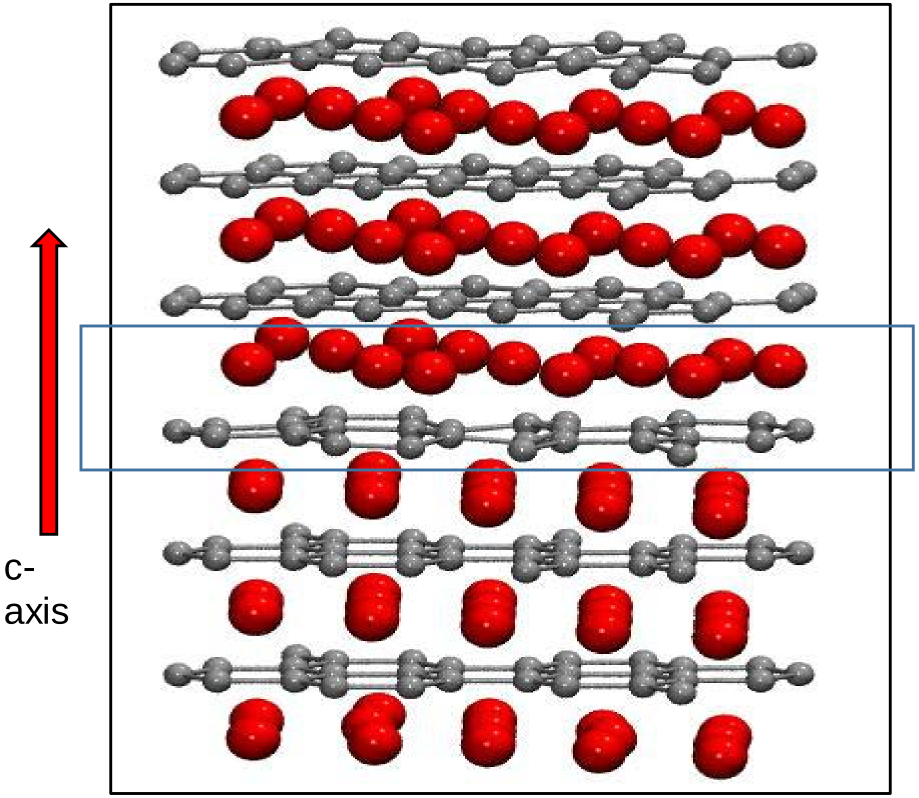


Electron localization function (ELF):
strong covalent bonding

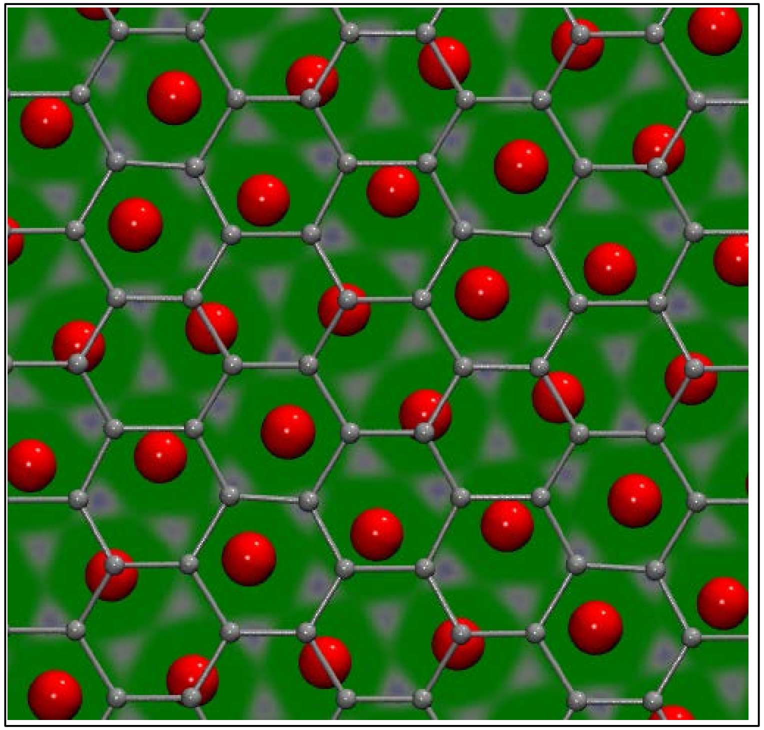
Lawson, Daw, Squire and Bauschlicher, J. Am. Ceram. Soc., (2012)

Blue = High; Green = Low

Symmetric Σ7 *C*-axis ***Twist***



Misalignment of atomic layers

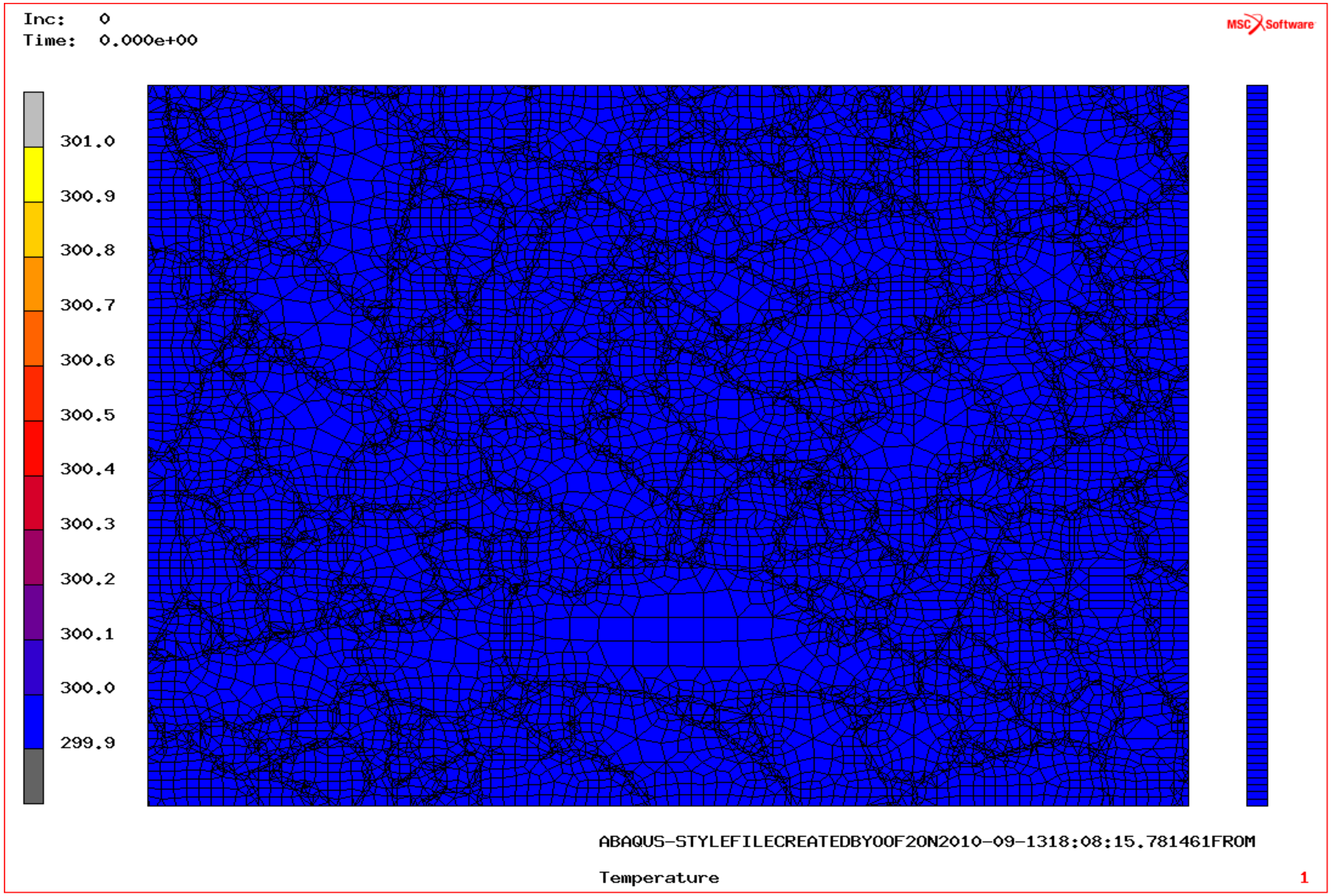


ELF: shifted planes, ring distortion

Weakened ionic bonding: inert plane vs inert plane

Blue = High
Green = Low

Development of Steady State Thermal Gradient



Uniform thermal gradient (UTG) applied vertically across structure

Effective Thermal Conductivity

	Vertical	Horizontal	Avg
Intrinsic - κ_0			**<u>50</u>**
Brick Layer Model (BLM)			10
Rule of Mixtures (ROM)			44
FEM/UTG	17.48	16.24	**<u>16.8</u>**
FEM/UHF	16.72	15.93	**<u>16.3</u>**
Experiment			**<u>22</u>**[1]

Experimental interfacial resistance

- BLM is **series** resistor model (lower bound)
- ROM is **paralle**l resistor model (upper bound)
- *FEM has* ***<u>series</u>*** *and* ***<u>parallel</u>*** *contributions*
- **Thus***:* ***realistic microstructure and interfaces needed***

[1] Zimmermann, Hilmas, Fahrenholtz, Dinwiddie, Porter, Wang , J. Am. Ceram. Soc., (2008)

Modeling Summary

- **Multiscale framework for UHTC:**
  - *Ab Initio* – bonding, electronic & vibrational spectra
  - Atomistic simulation – bulk and interfacial thermal conductivity
  - Continuum – microstructural modeling and effective properties
  - Iteration with experiment needed to “close” loop
- **Modeling unanswered questions**:
  - Interatomic potential fidelity
  - Lattice TC without potentials (*ab initio*, Boltzmann, etc.)
  - Conducting versus resistive phonons
  - Isotope and defect effects
  - Complex grain boundary structural models and properties
- **Experimental unanswered questions**:
  - Single crystal thermal conductivity
  - Electronic versus lattice conductivity
  - Grain boundary atomic structures and properties
  - Improved grain boundaries from improved processing

What are the issues with use of UHTCs?

- Similar to the risk aversion in many industries in using structural ceramics!
- Designers prefer to use metals or complex systems to avoid using advanced ceramics and composites.
  - Industry Is conservative
  - Building a system, not developing materials
  - Unfamiliarity with designing with brittle materials - safety factor.
  - Advantages of weight savings and uncooled temperature capability not high enough to overcome risk aversion
- Using monolithic ceramics and CMCs requires a different design approach, not straight replacement of a metal part
- Need for subscale materials/component testing in realistic environments is imperative
- **Must develop materials and test them such that designers can increase their comfort level**
  - **Must do in advance of need!**
- **Must have ways of moving materials from research and development (low technology readiness level) to demonstration of applications through testing in realistic environments**

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!**

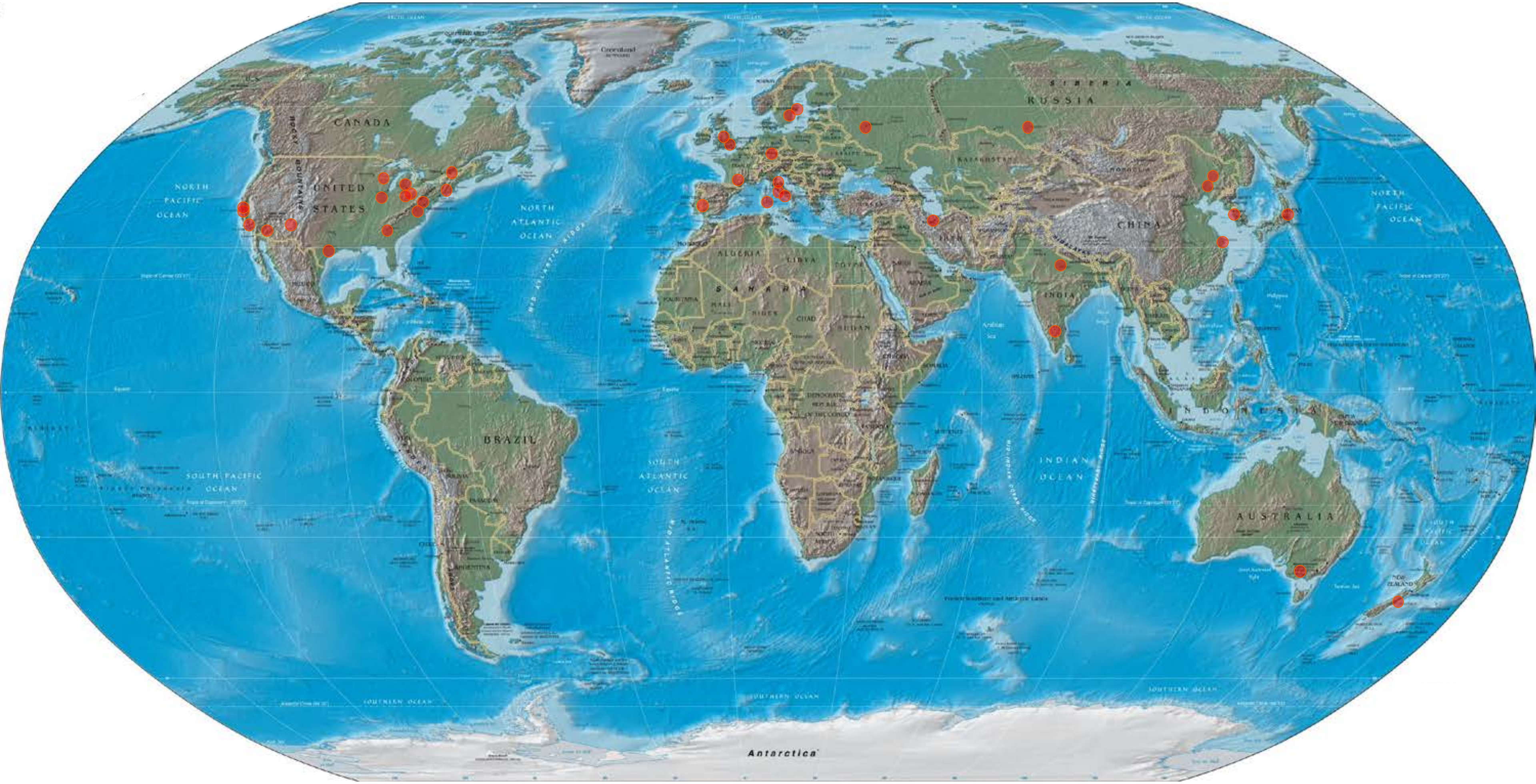
Some Recent Research Efforts in UHTCs: Materials and Properties

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 Ames & NASA Glenn Research Centers	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
Korea Institute of Materials Science	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	Technische Universität Darmstadt, Germany
Missouri University of Science & Technology	**Nano & Sol Gel Synthesis of UHTCs**
Politecnico di Torino, Italy	Loughborough University, U.K.
Reactive Hot-Pressing	IGIC, Russian Academy of Science
Shanghai Institute of Ceramics, China	University of Erlangen-Nürnberg, Germany
NASA Ames Research Center	Korea Institute of Materials Science
National Aerospace Laboratories, India	Iran University of Science and Technology
Sandia National Laboratories, New Mexico	
McGill University, Montreal, Canada	
University of Erlangen-Nürnberg, Germany	

UHTC Researchers Throughout the World



Thermal Protection Materials Summary

- Thermal protection materials must be efficient and reliable: specific to application
- Should develop materials in anticipation of need— "heritage" can be a trap
- Must develop materials to meet needs of application
- Must characterize appropriately and sufficiently
- Must test known material in relevant environment

UHTC Summary

- Work on UHTC-type compositions decades in development, but non-continuous.
- Significant expansion of interest in UHTCs in past 10-15 years — multinational research.
- Considerable improvements have been made in processing and properties.
- Must develop materials to meet needs of application
- Must test in relevant environment
- Must characterize appropriately
- UHTCs may not find application by themselves but as parts of systems, and thus continued research is critical to the success of future applications.

Long and winding road to applications!

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