Thermal Protection Materials

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  - NASA project support

Outline

- Classes of Thermal Protection Systems (TPS)
  - Reusable materials
  - Ablative materials
  - Ultra high temperature ceramics (UHTCs)
- Characterization of TPS for Performance and design
  - Ablators
  - UHTCs
- UHTCS
  - 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

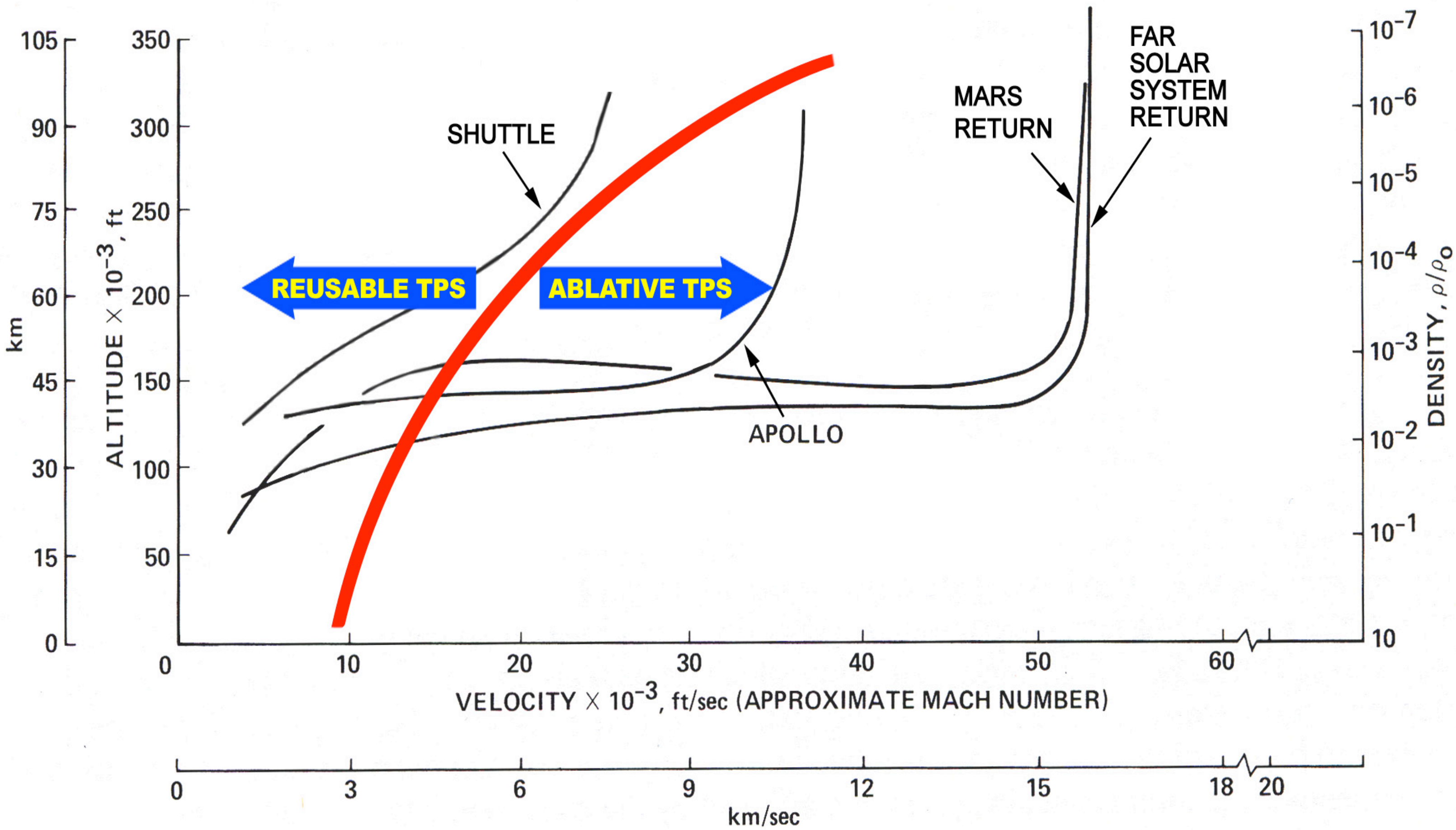
Introduction

- NASA Ames focused on:
  - Qualifying and certifying TPS for current missions
  - Developing new TPS for upcoming missions
- Approaches to TPS development differ with risk — crewed vs. robotic missions:
  - Crewed
    - Loss of life must be avoided
    - What must be done to qualify and certify TPS?
  - Robotic missions
    - Can take more risk
    - But scientific knowledge can be lost too
- *Goal for all TPS is efficient and reliable performance!*

Heritage vs. New Materials

- Historical approach:
  - Use heritage materials: “*It’s worked before…*”
  - Risk-reduction strategy
  - Limited number of flight-qualified materials
    - Several low density (< 0.3 g/cm^3) and high density (> 1 g/cm^3) ablative TPS solutions have flight heritage.
  - Different vehicle configurations and reentry conditions (need to qualify materials in relevant environments)
- As missions become more demanding, we need higher capability materials — necessary to have a robust research and development program, *both reusable and ablative materials*
- Must test materials in relevant environments
- Provide path for insertion/use of new materials

Reusable vs. Ablative TPS



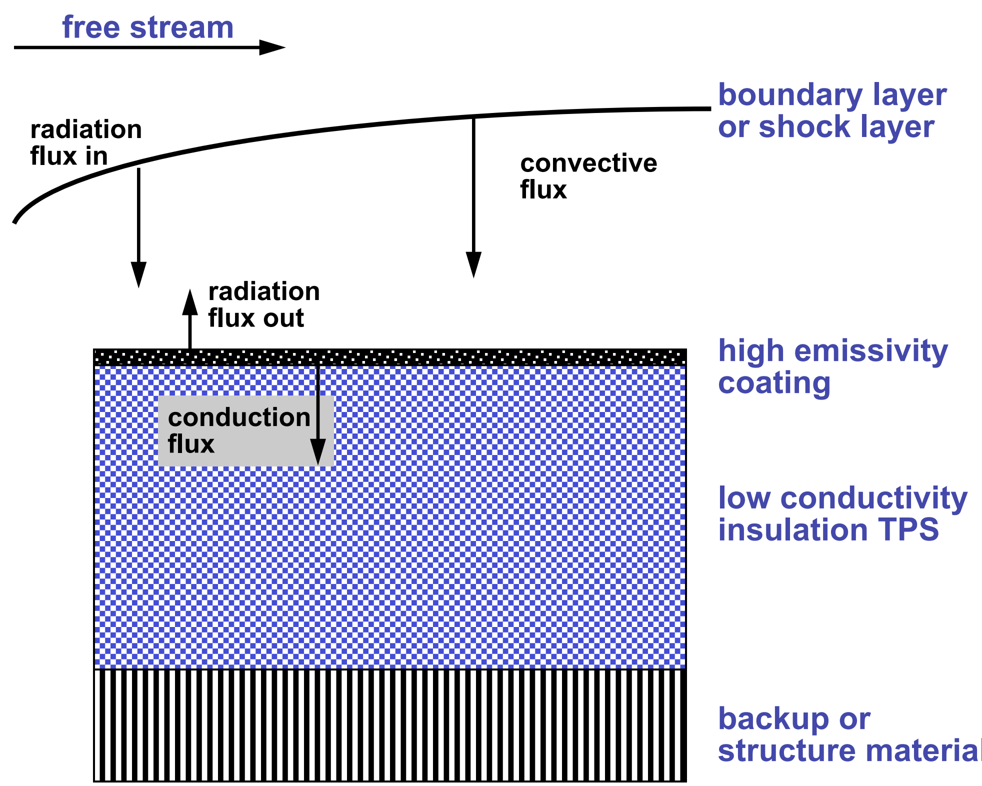
Insulative TPS Processes

Energy management through storage and re-radiation — material unchanged

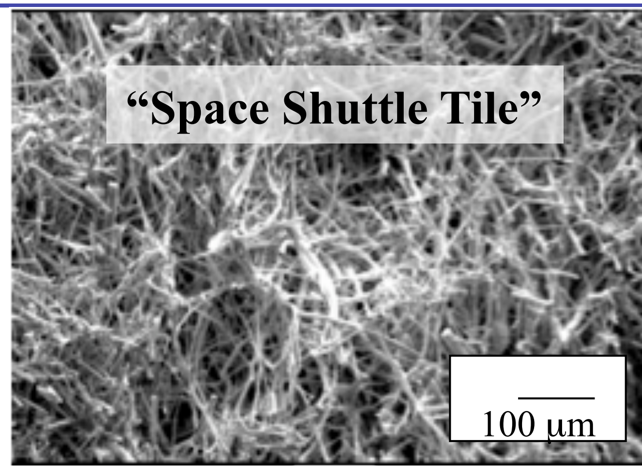
When exposed to atmospheric entry heating conditions, surface material will heat up and reject heat in the following ways:

•Re-radiation from the surface and internal storage during high heating condition

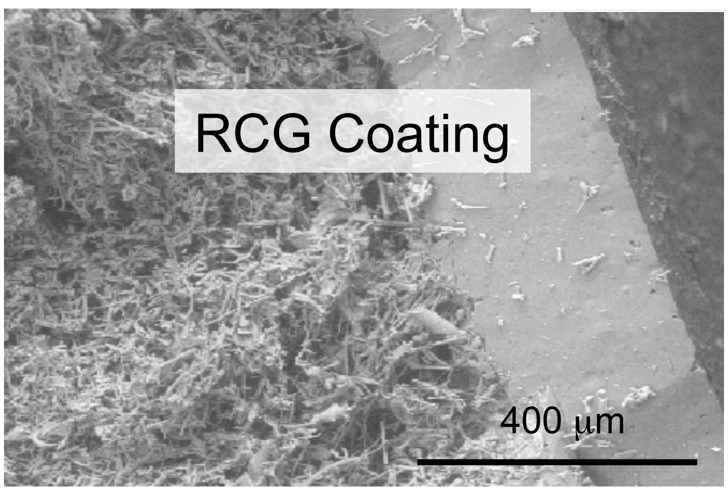
•Re-radiation and convective cooling under post-flight conditions

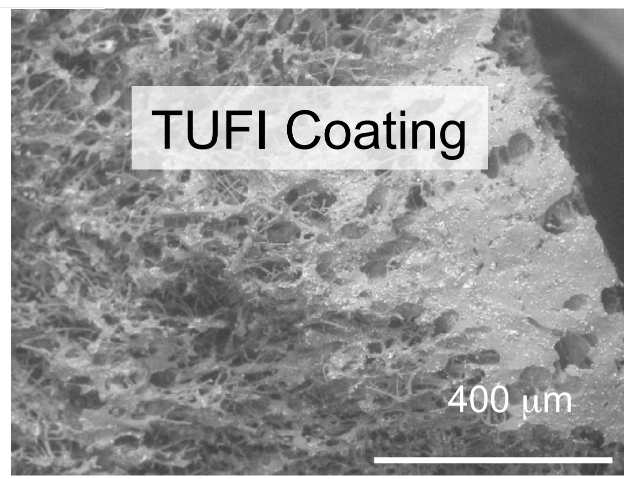


Reusable TPS: Tiles and Coatings



•Silica-based fibers
•Mostly empty space- >90%porosity



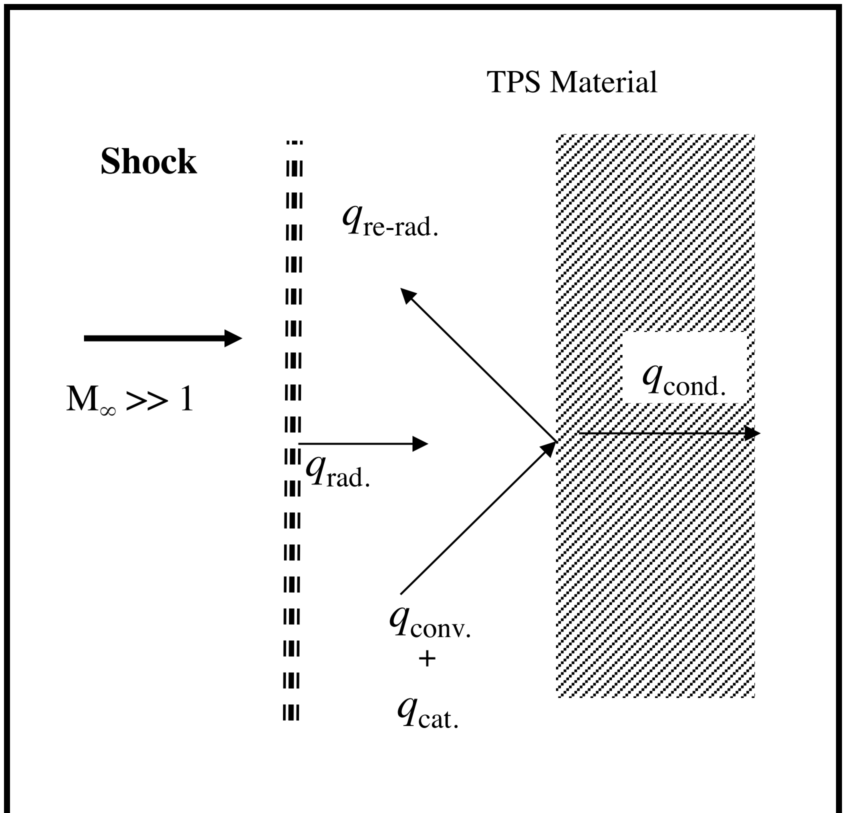


- RCG is a thin dense high emittance glass coating on the surface of shuttle tiles
- Poor impact resistance

•TUFI coatings penetrate into the sample
• Porous but much more impact resistant system

Reusable TPS

Reusable TPS systems are designed to reject as much heat as possible and conduct as little heat as possible in order to meet the bond-line temperature requirements with minimal heat-shield mass. Low catalytic efficiency, high emissivity and low thermal diffusivity are desired in designing a TPS system.



- High emissivity coatings increase the re-radiated heat-flux and thereby reduce the heat-flux to which the material must respond:

$$q_{\text{re-rad.}} = \varepsilon_w \sigma T_w^4, \; \textit{where } \varepsilon_w = \textit{emissivity}$$

- Coatings with low catalytic efficiency reduce the release of chemical energy near the surface, thereby reducing the heat-flux at the wall
- Conduction within the TPS material depends on material properties: thermal diffusivity (***K***), density(ρ), thermal conductivity(***k***) and specific heat (***Cp***)

$$\textit{Thermal Diffusivity}, K = {}^{k}\!/_{\rho C_p}$$

Ablative TPS Processes

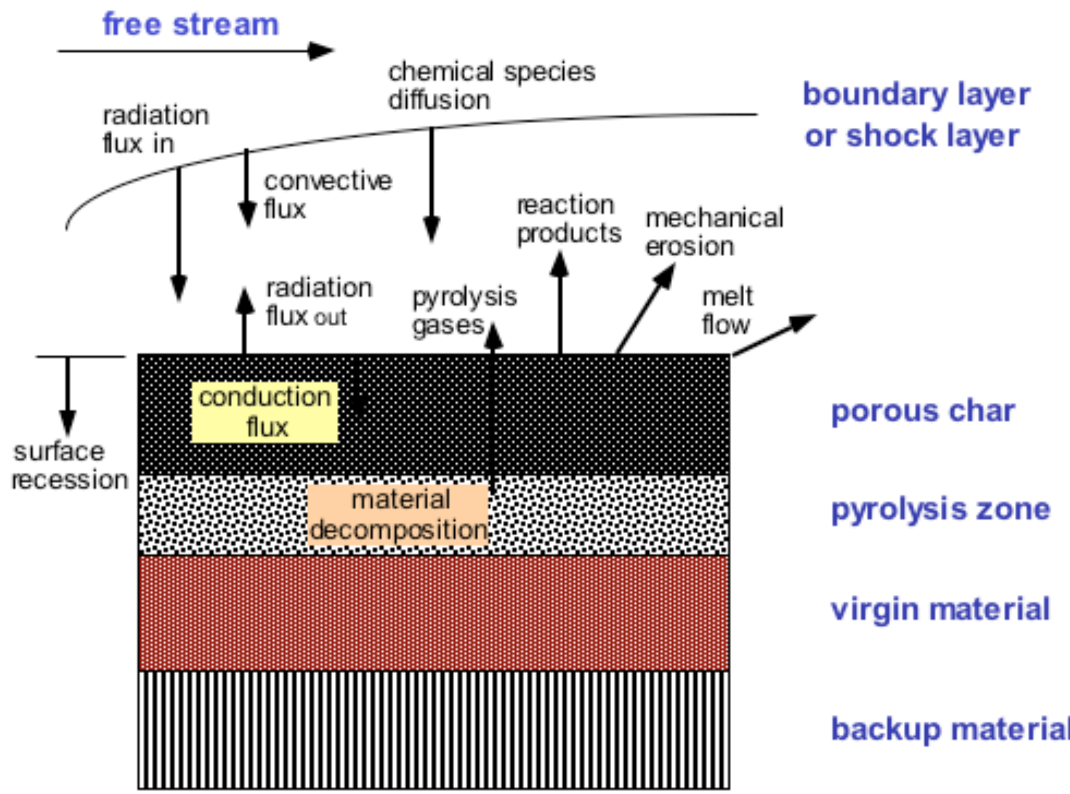
Energy management through material consumption

When exposed to atmospheric entry heating conditions, material will pyrolyze (char), and reject heat in the following ways:

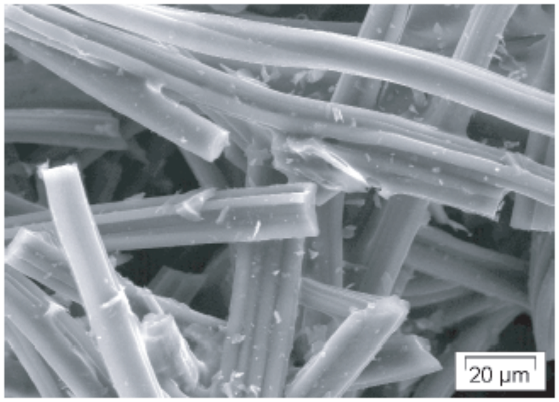
•Pyrolysis of polymer

•Blocking in boundary layer

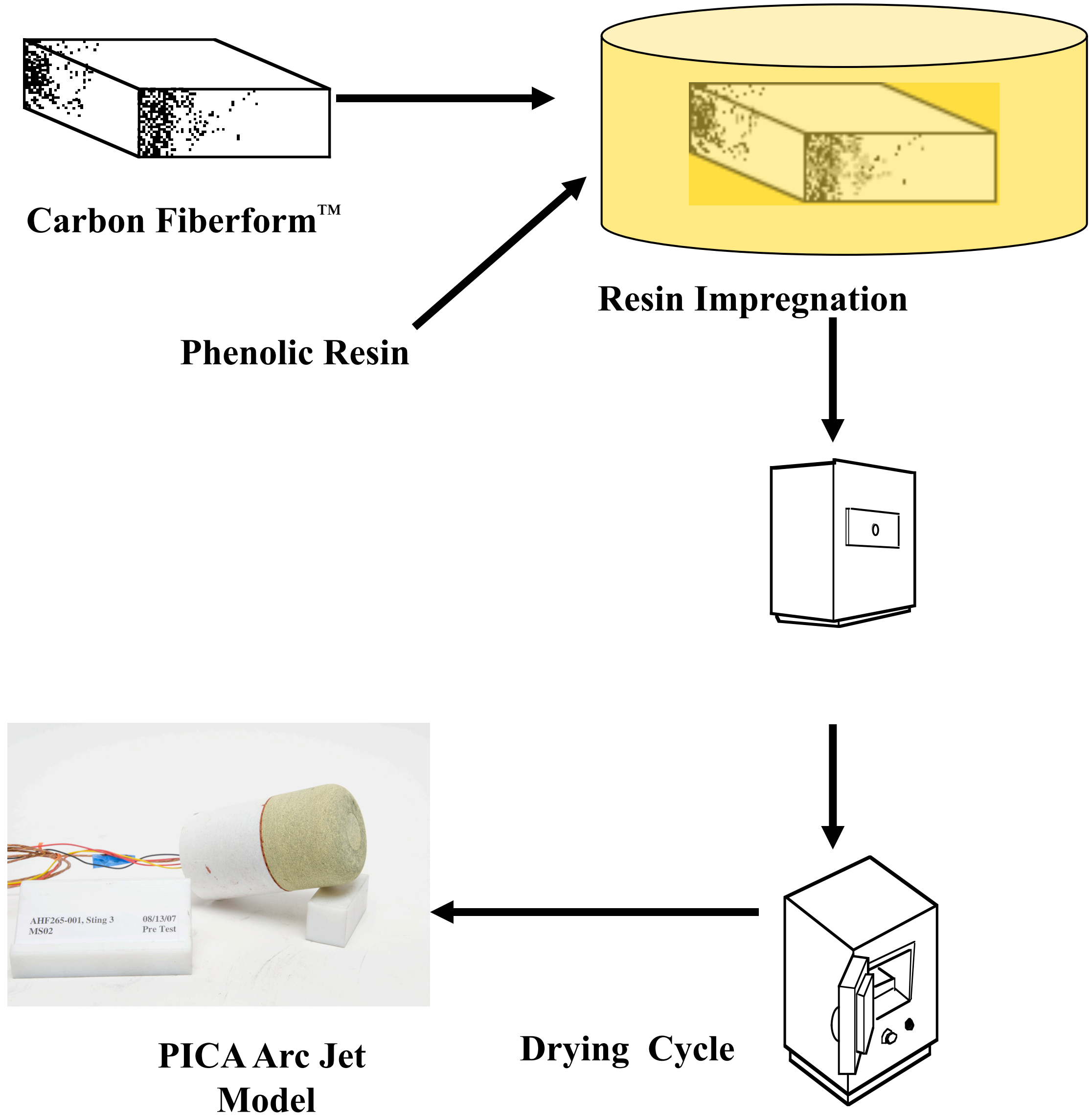
•Formation of char layer and re-radiation

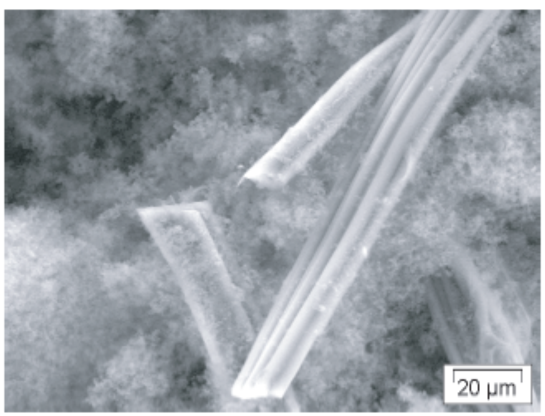


PICA Processing Detail



Fiberform™ before impregnation

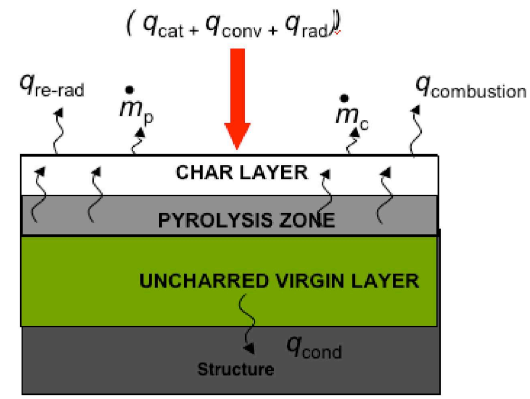




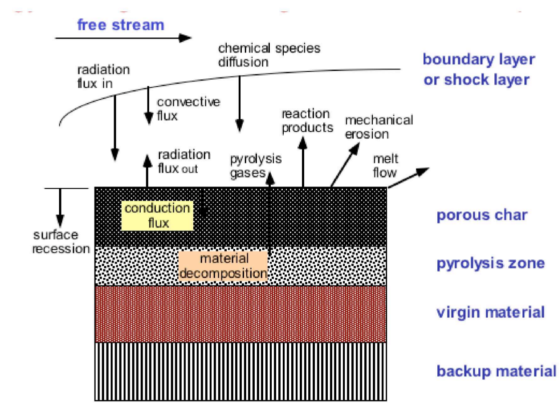
PICA: Fiberform™
with phenolic resin

Ablators Overview

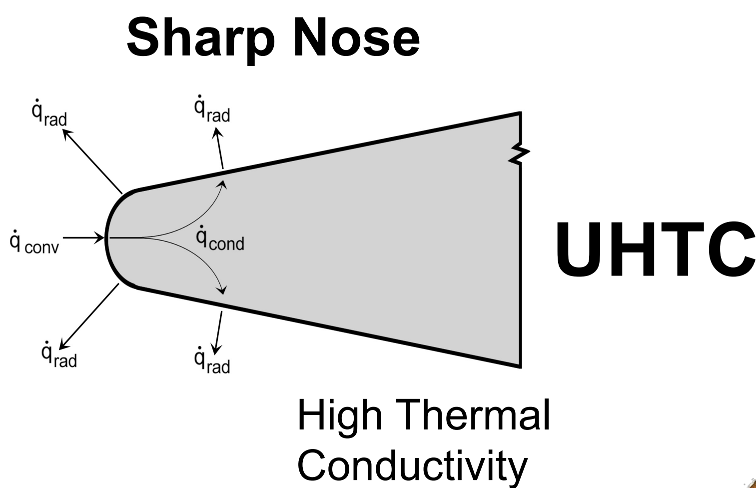
- Evaluating different density classes for:
  - Virgin/char strength
  - Recession rate
  - Thermal conductivity
- Evaluating the interconnection between properties
  - Tradeoffs
  - Greater density = greater strength, but generally increase thermal conductivity
- Tailoring for specific applications by examining different density ranges and material composition



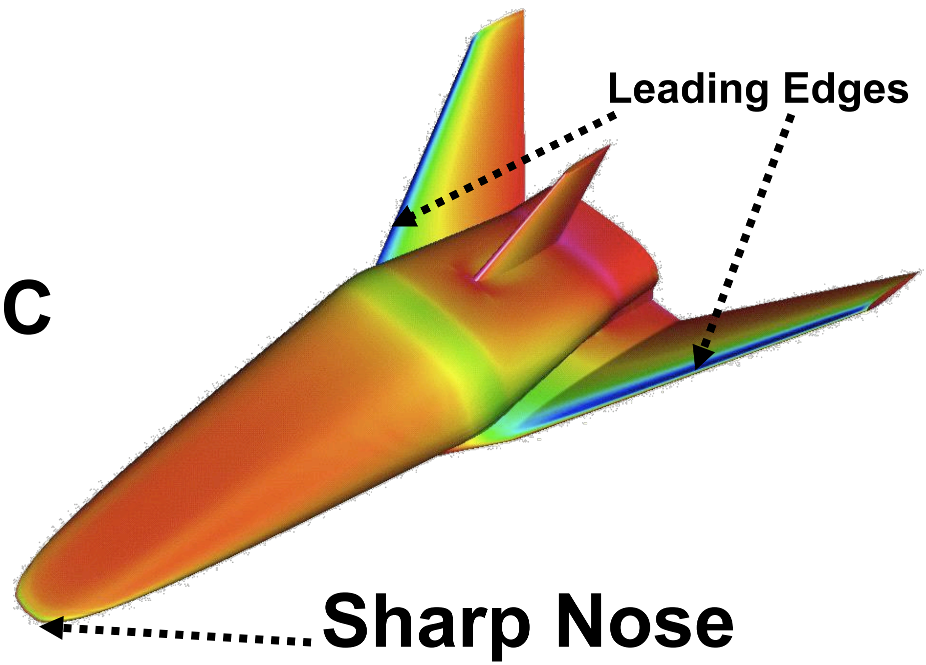
Single use (ablative) TPS



Sharp Leading Edge Energy Balance



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



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

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

Characterization of TPS

- Characterize thermal protection materials and systems: efficiency and reliability
  - Evaluate performance
  - Select materials
  - Verify reliability of manufacture
  - Enable modeling of behavior
  - Design of system/heatshield
  - Correlate processing/properties—improvement of materials

General Property Requirements

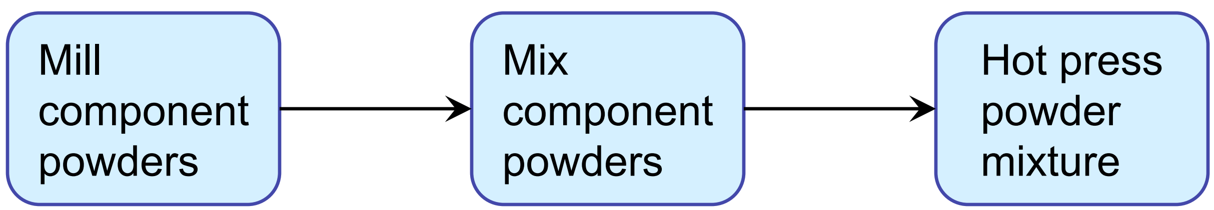
- In addition to specific material properties, designers and analysts require certain general material information.
- This category of information is not directly used in analyses, but can be used to evaluate analyses, determine dispersions design parameters, and assess the viability of designs.

Other General Information

- Directionally dependent properties
  - Many real materials exhibit directional dependence of thermal and mechanical properties.
- Property measurement uncertainties
  - Critical to document property measurement techniques and define the nature of the distribution of data.
  - Material property uncertainties drive the analysis dispersions and ultimately affect the design.
  - Tests to measure material properties should be performed under recognized standards, such as ASTM.
- Limitations in material application
  - Manufacturer-derived limitations to material use are valuable data for designers.

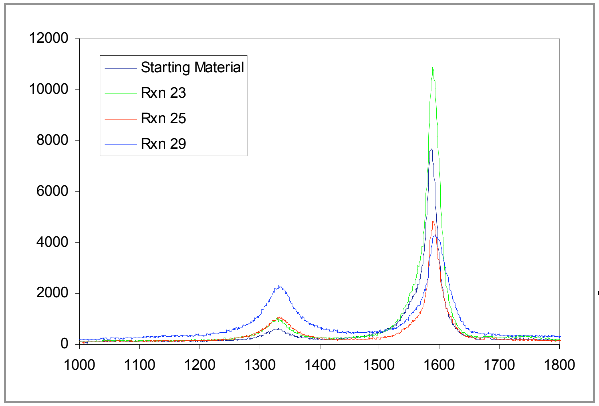
Manufacturing Variability

- Real-world manufacturing processes have inherent variability.
  - These variabilities can lead to variations in the material properties.
- Necessary to quantify allowable lot-to-lot and in-lot variability of properties.
  - This may also include acceptable flaw and inclusion size.

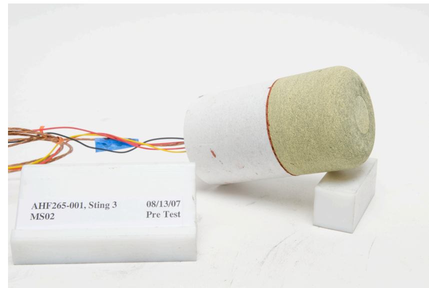


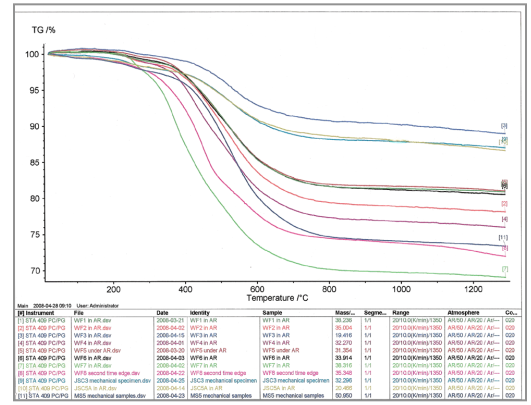
UHTC Processing Example

Characterization of Ablative Materials

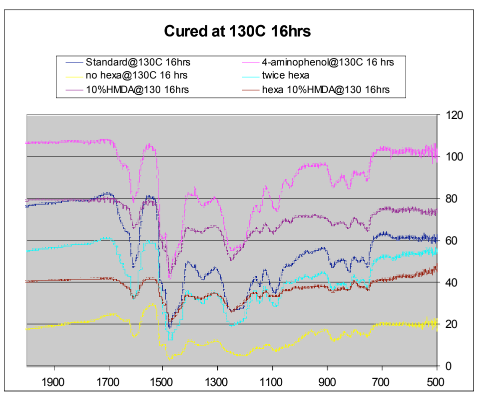


Raman — atomic

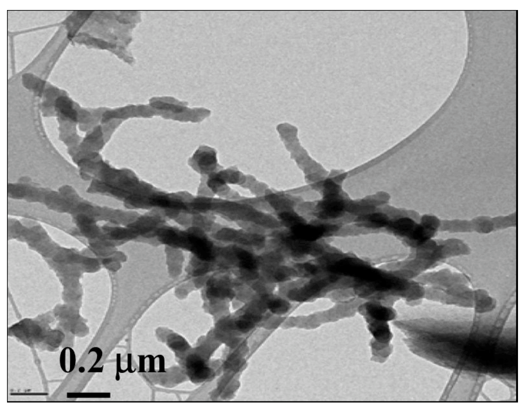




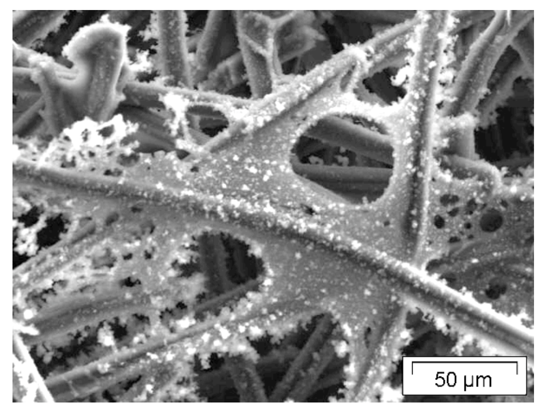
Thermogravimetric analysis — thermal stability



Infrared — molecular



TEM — nanoscopic



SEM — morphology

Properties for Design

Thermal Response Model
Density (virgin/char)
Thermal Conductivity (virgin/char)
Specific Heat (virgin/char)
Emissivity & Solar Absorptivity (virgin/char)
Elemental Composition (virgin/char)
Thermal Gravimetric Analysis
Porosity & Gas Permeability
Heat of Combustion (virgin/char)
Heat of Pyrolysis

Thermal Structural Analysis
Tensile: strength, modulus, strain to failure
Compressive: strength, modulus, strain to failure
Shear: strength, modulus, strain to failure
Poisson’s Ratio
Thermal Expansion (virgin/char)
TPS/Carrier System Tests Tensile strength Shear strength

Process for Characterizing Ablators

Produce Material

Flight-like production, not model material

Consider mission environments

Evaluate Material's Variability

NDE recommended

Insight into construction is critical to determine likely challenges

Determine Appropriate Techniques

May depend on material's density and construction

4 cm honeycomb not represented by a 1 cm coupon

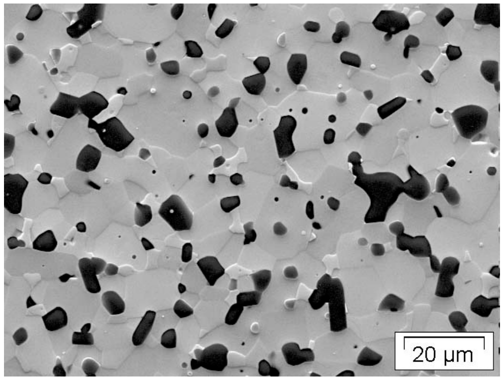
Determine Quantity and Sampling Scheme

Influenced by material variability & project scope

Execute Testing & Evaluate Data

Material Morphology

- In the aerospace design and analysis field, UHTCs are often referred to, and treated as, “monolithic.”
- The microstructure of UHTCs clearly shows their composite nature.
  - Distribution of material phases
  - Flaw size and distribution



- This information can be useful in interpreting the macroscopic performance of the material — for example, mechanical failure modes.

Ultra High Temperature Ceramics

- UHTCS
  - What are UHTCs?
    - Background and features
  - Aerospace applications
    - Sharp leading edges
  - Properties
  - Thoughts on materials development and testing
  - Specific issues with UHTCS and approaches
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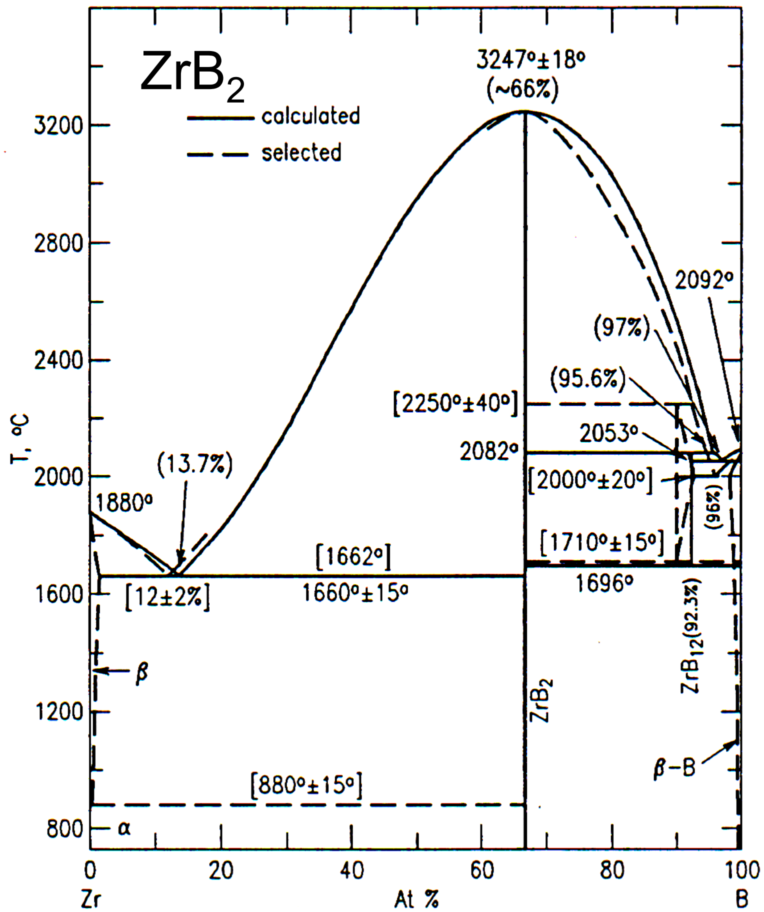
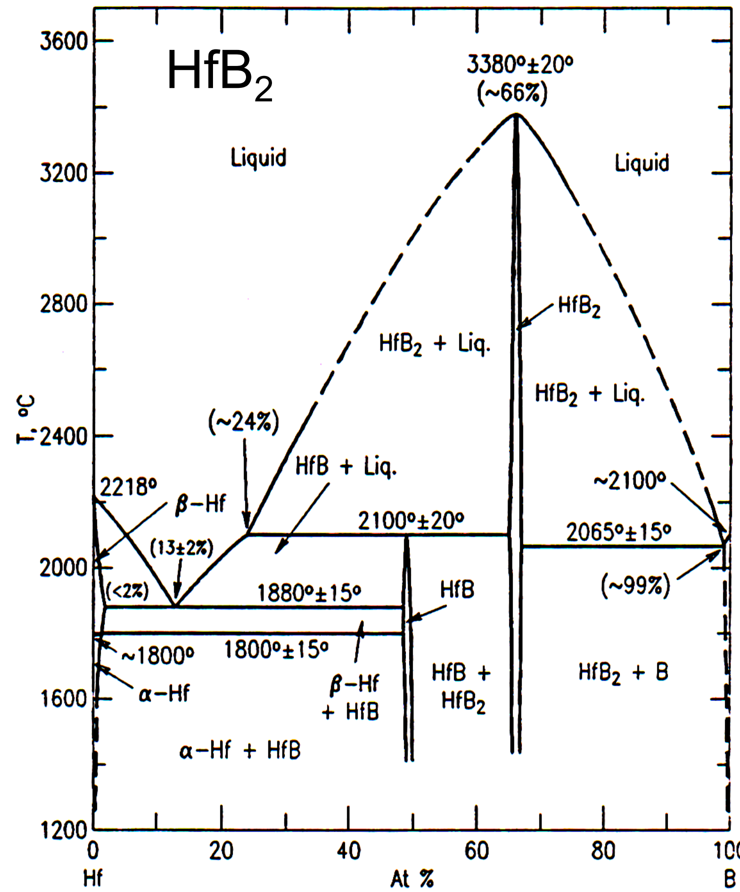
Diborides Have Very High Melting Temperatures





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.

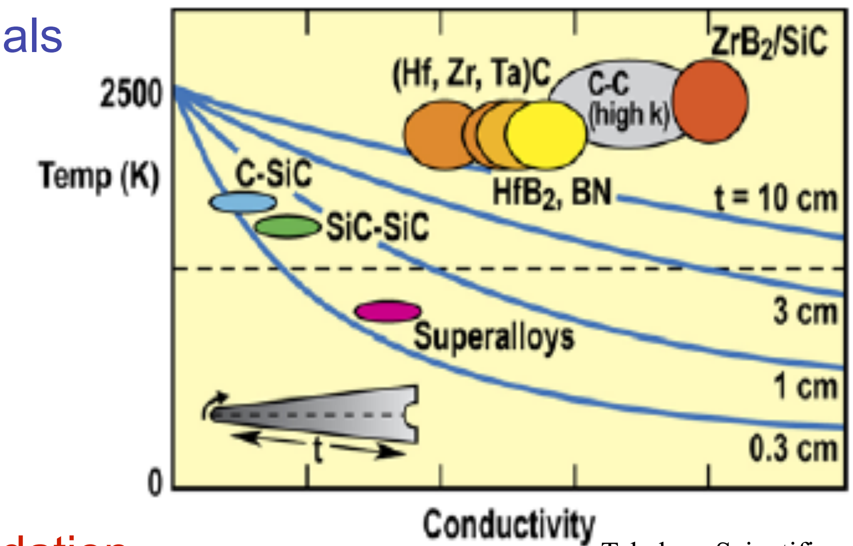
UHTC billets, quarter for scale

Courtesy: AFRL

Materials for Sharp Leading Edges

Sustained Hypersonic Flight Limited by Materials

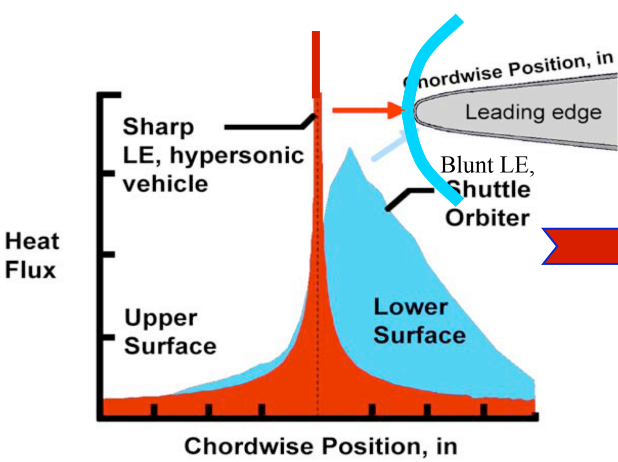
- High heat flux over small area
- High temperature, oxidation, erosion
- Very high temperature gradients

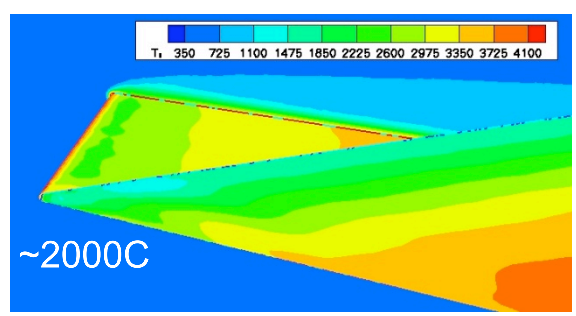


Teledyne Scientific

UHTCs (ZrB_2/HfB_2-based composites)

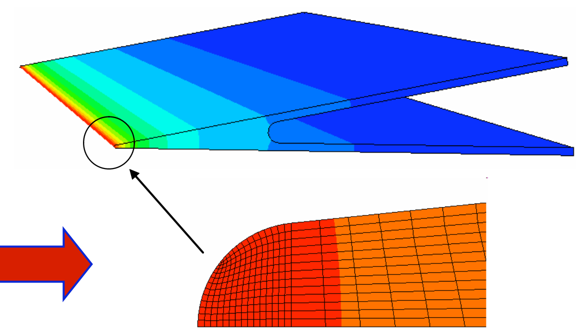
- High temperature capability and high thermal conductivity
- Poor oxidation resistance → Modeling/Validation
- Low fracture toughness → Fiber Reinforcement





Cowl Leading Edge

Free-Stream at Mach 8



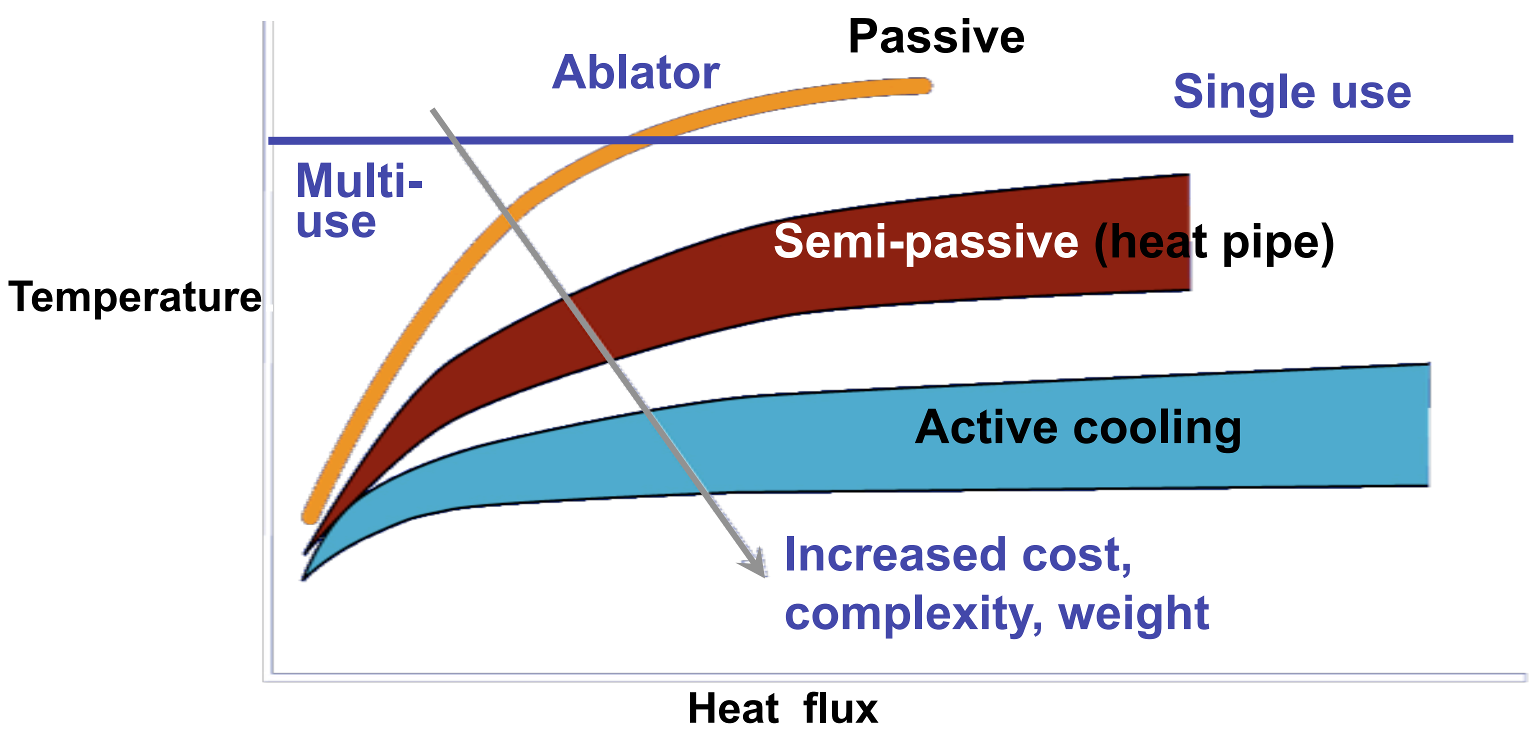
High Temperature at Tip

Steep Temperature Gradient

Sharp Leading Edge Technology / Review

- Sharp leading edge technology
  - Enhances 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 RCC leading edge materials: T~1650 °C
  - Sharp leading edged vehicles will require: T>2000 °C
- Ultra High Temperature Ceramics (UHTCs) are candidates for use in sharp leading edge applications.

Leading-Edge Thermal Management Options



- There are multiple options to manage the intense heating on sharp leading edges.
- Simplest option is passive cooling.

Courtesy: D. Glass

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

Processing of HfB_2-SiC

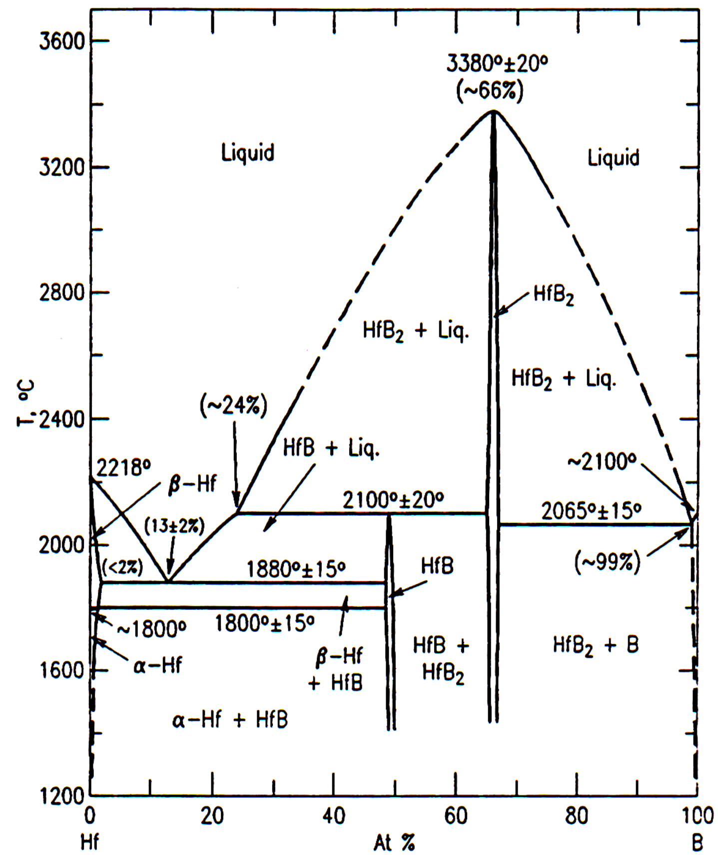
- **HfB_2** has a narrow range of stoichiometry with a melting temperature of 3380°C

  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



Role of SiC in UHTCs

•Silicon carbide is added to boride powders

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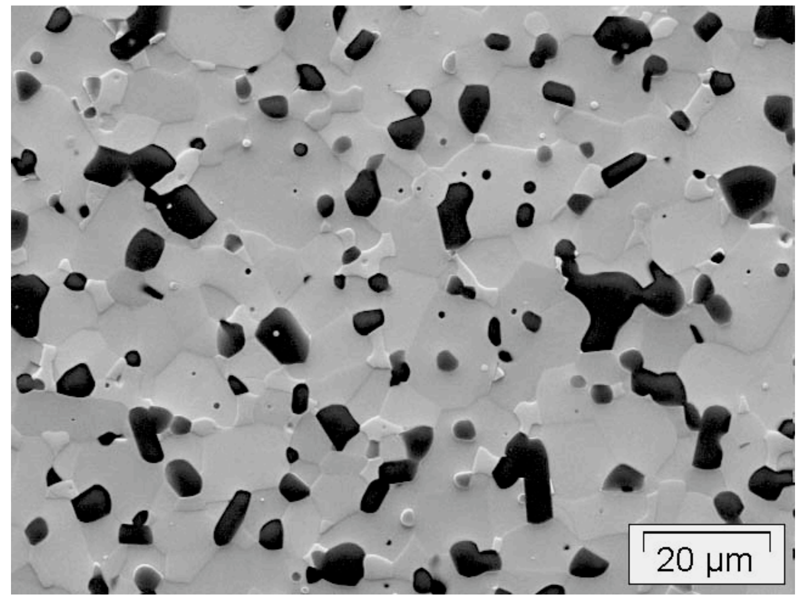


Baseline hot pressed UHTC microstructure
Dark phase is SiC

UHTC Material Properties

Sharp leading edges require :

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

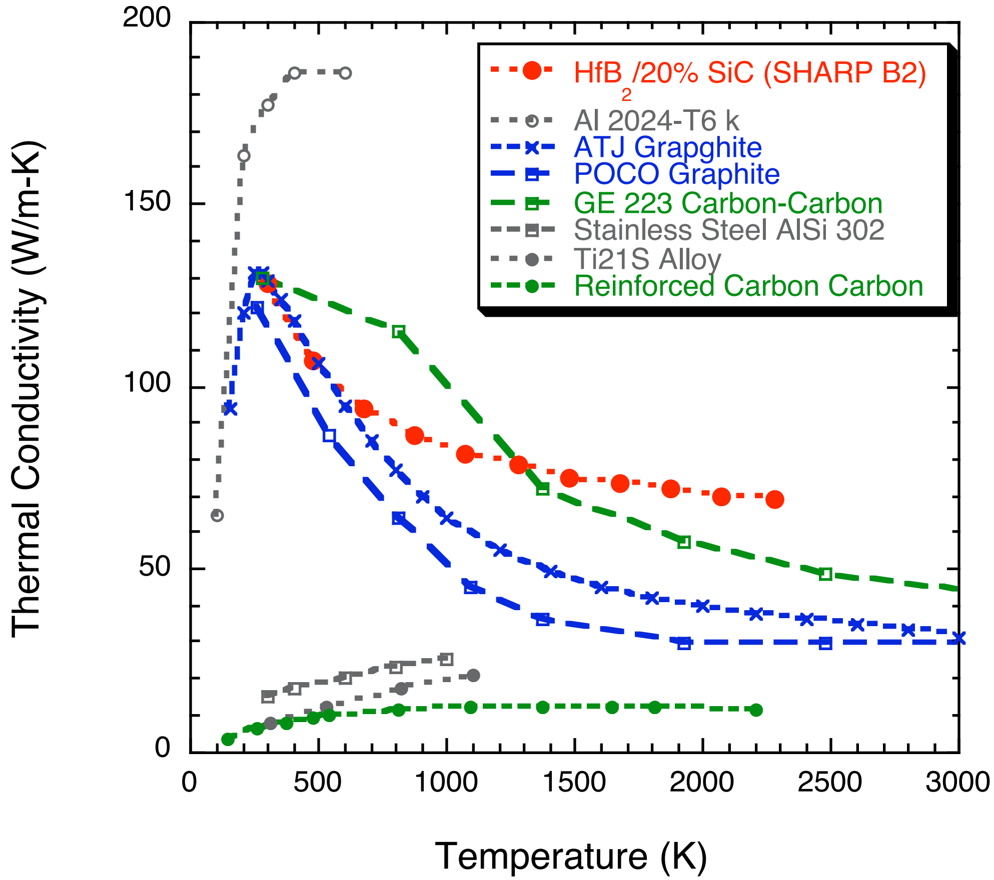
Property		HfB_2/20vol%SiC	ZrB_2/20vol%SiC
Density (g/cc)		9.57	5.57
Strength (MPa)	21°C	356±97*	552±73*
	1400°C	137±15*	240±79*
Modulus (GPa)	21°C	524±45	518±20
	1400°C	178±22	280±33
Coefficient of Thermal Expansion ($x10^{-6}$/K) RT		5.9	7.6
Thermal Conductivity (W/mK)# RT		80	99

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

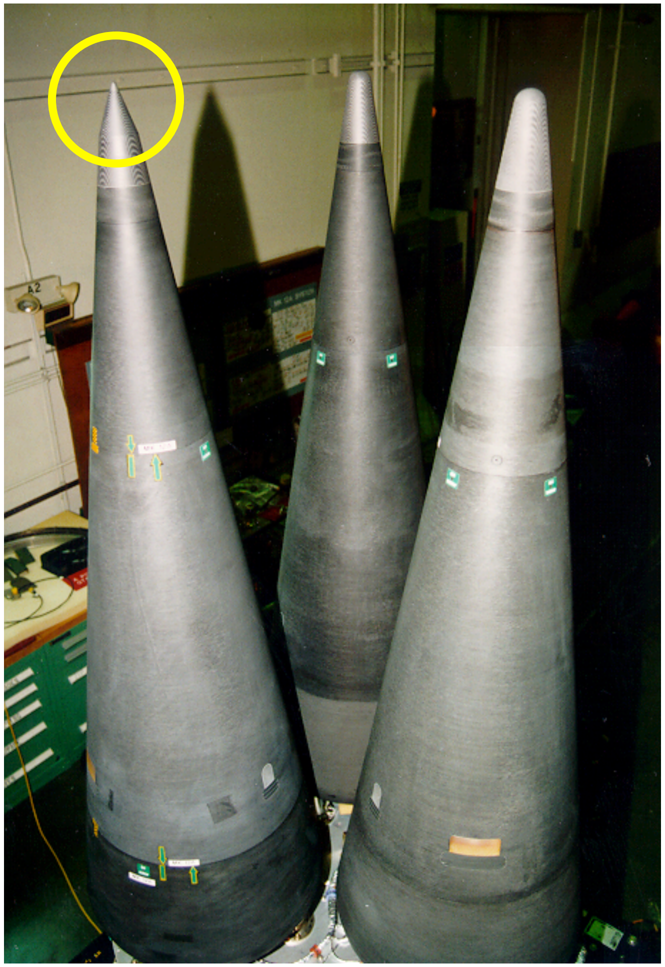
- HfB_2/SiC thermal conductivity was measured on material from the SHARP-B2 program.
- Thermal Diffusivity and Heat Capacity of HfB_2/SiC were measured using Laser Flash.

Some UHTC Development History

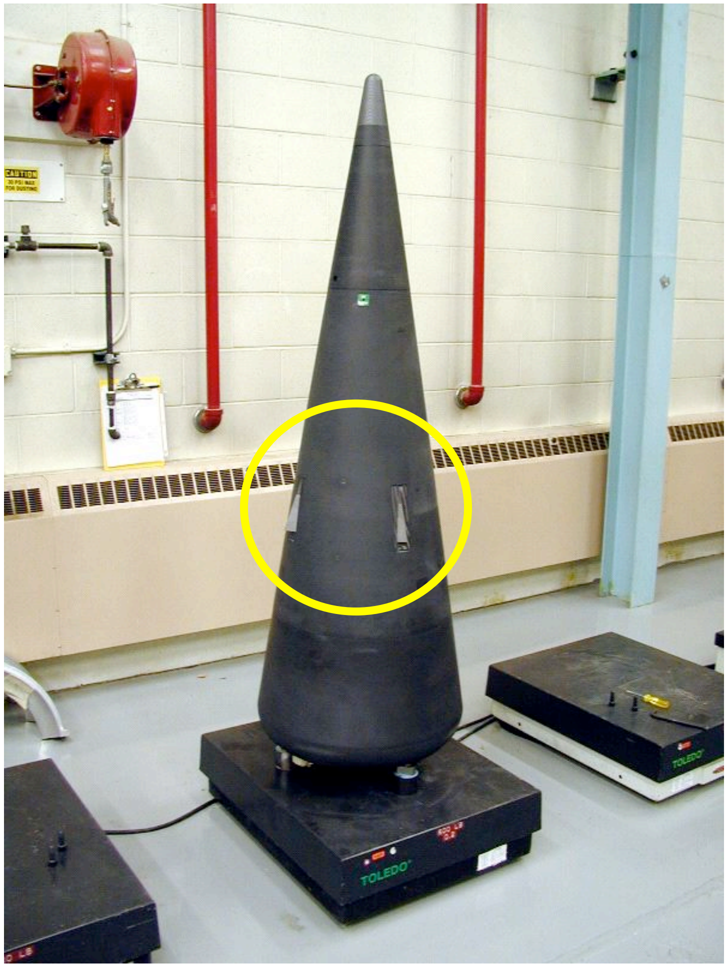
- Hf and ZrB_2 materials investigated in early 1950s as nuclear reactor material
- Extensive work in 1960s & 1970s (by ManLabs for Air Force) showed potential for HfB_2 and ZrB_2 for use as nosecones and leading edge materials (Clougherty, Kaufman, Kalish, Hill, Peters, Rhodes et al.)
- Gap in sustained 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

Flight Hardware



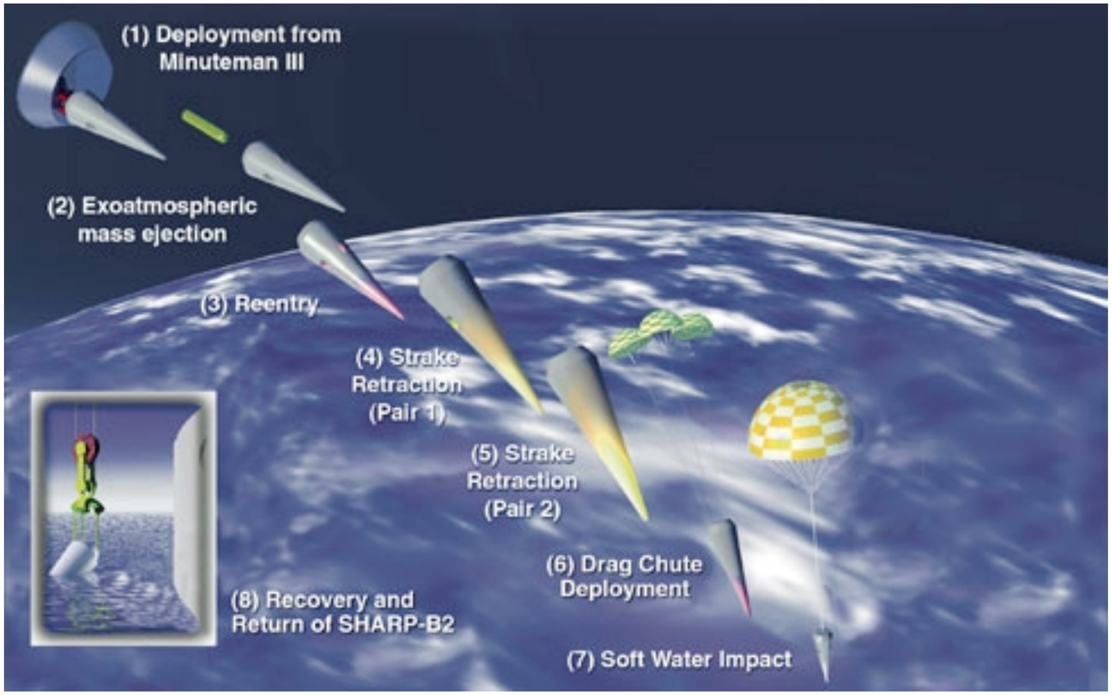
SHARP-B1 May 21, 1997



SHARP-B2 Sept. 28, 2000

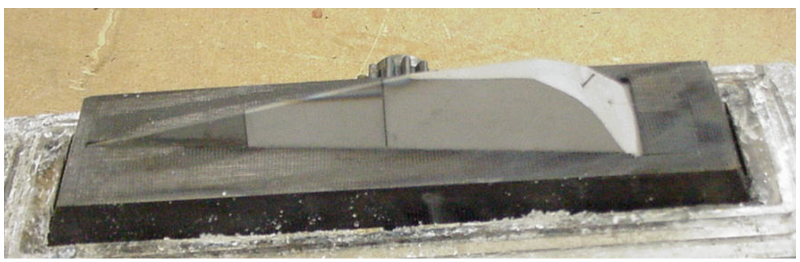
SHARP-B2

- 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.***

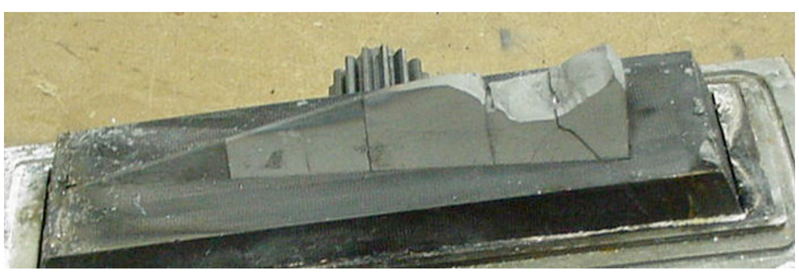


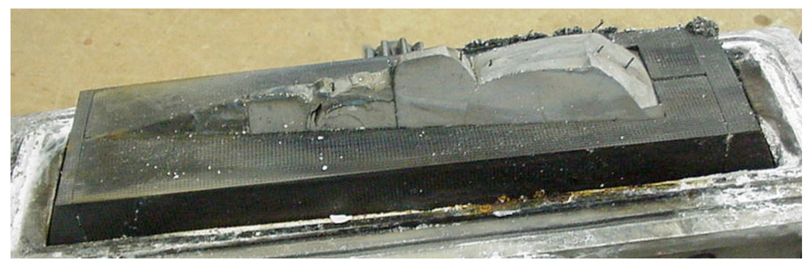
Recovered Strakes

- 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.

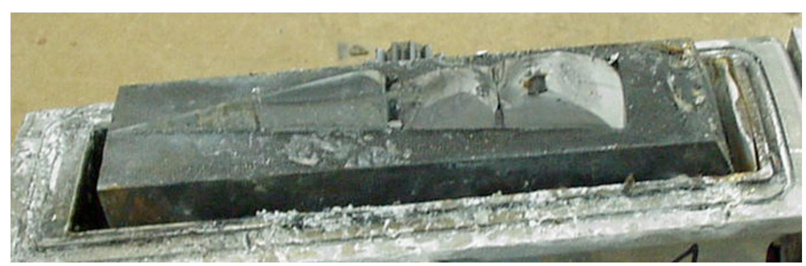


Pair 1 (47.9 km)



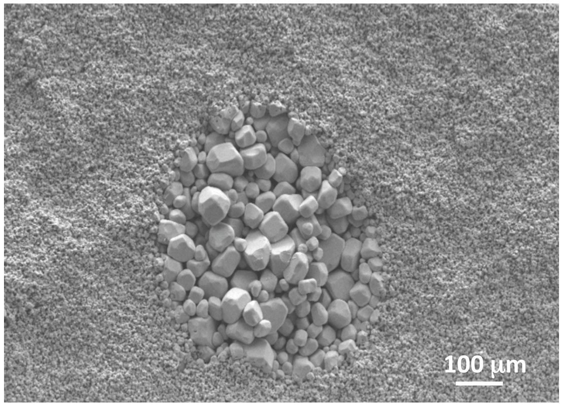


Pair 2 (43.3 km)



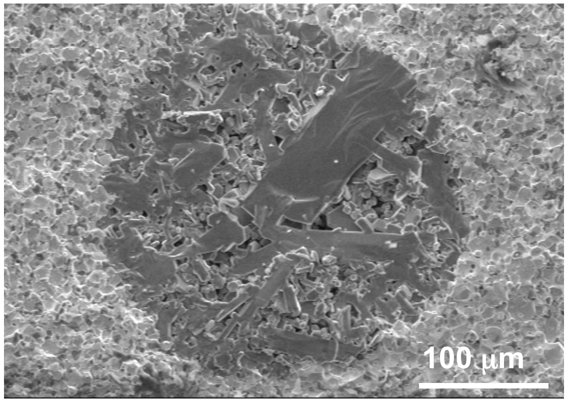
A Cautionary Tale

- 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

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 – $R' = \sigma k/(\alpha E)$
  - 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**

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

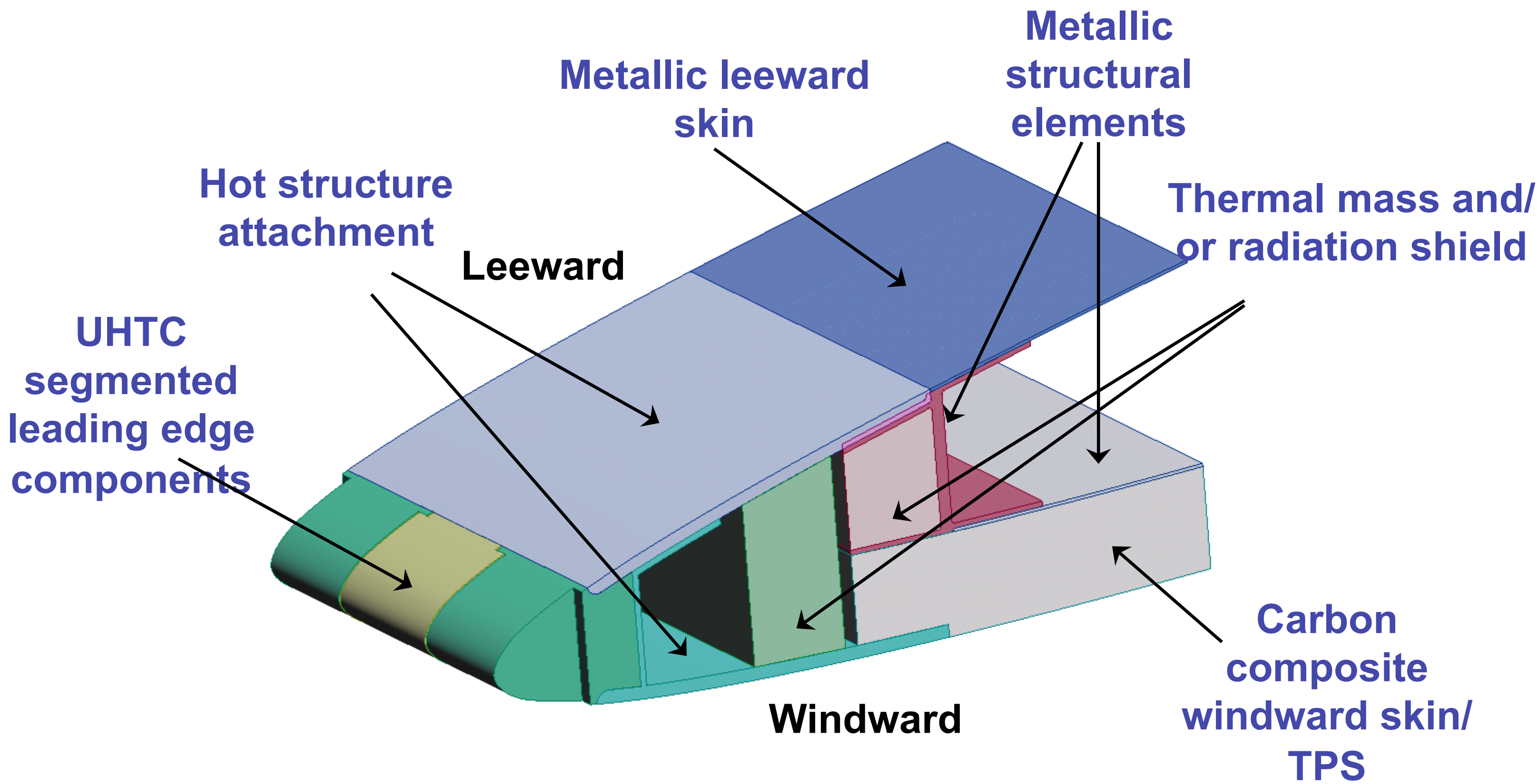
Design Challenges for UHTC Flight Components

- 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

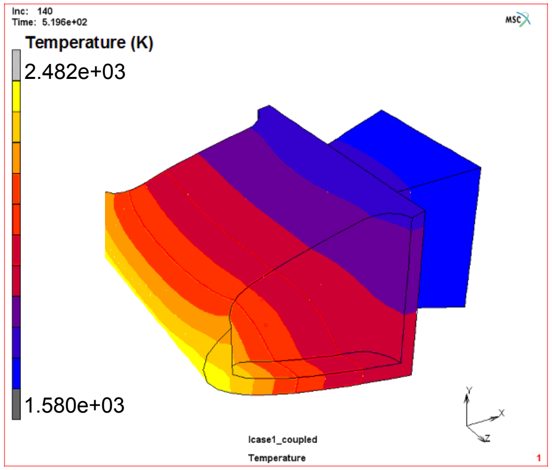
UHTC wing leading edge (WLE) concept for a hypersonic aircraft:

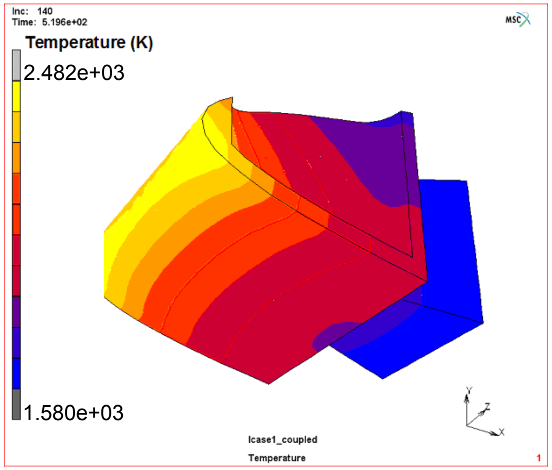
- UHTC segmented leading edge attached to carbon-based hot structure
- Nose radius ~1cm

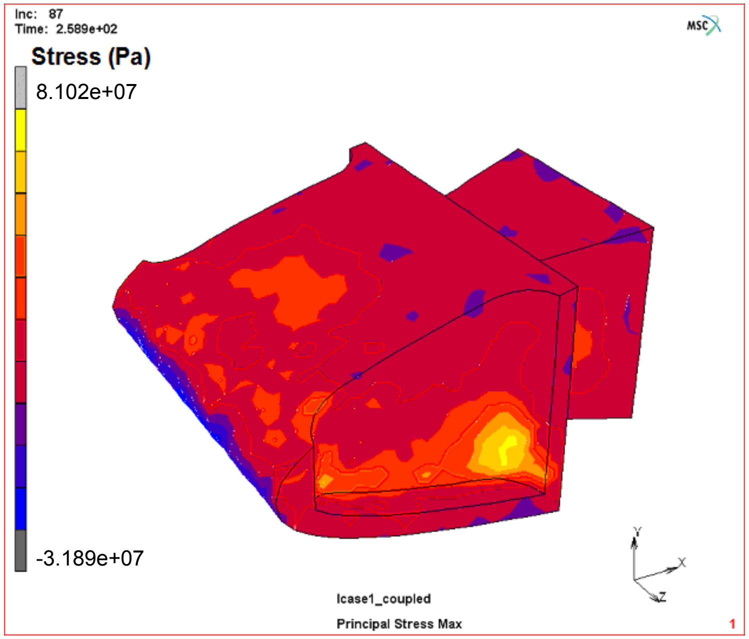


Example of Predicted UHTC WLE Component Performance

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

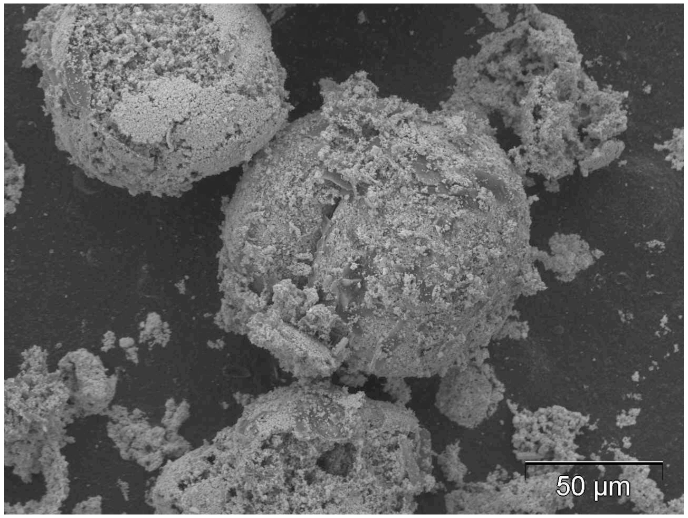






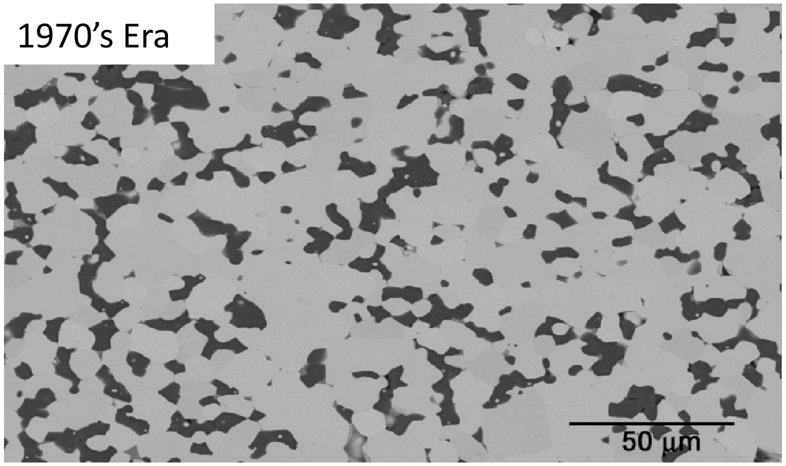
Improving Processing and Microstructure

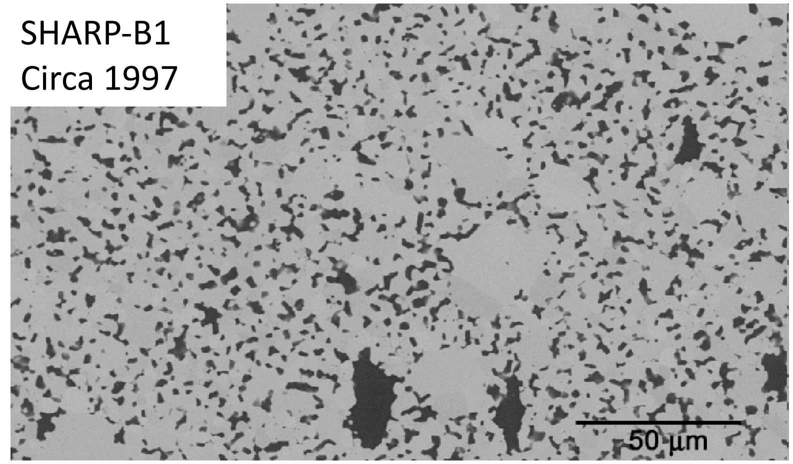
- Initial focus on improving material microstructure and strength
- HfB_2/20vol%SiC selected as baseline material for project constraints
- Major issue was poor mixing/processing of powders with different densities
  - Used freeze-drying to make homogenous powder granules
  - Developed appropriate hot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

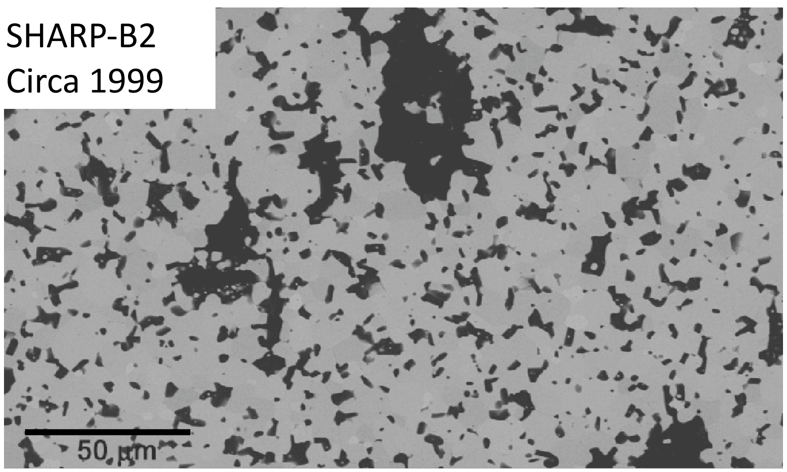


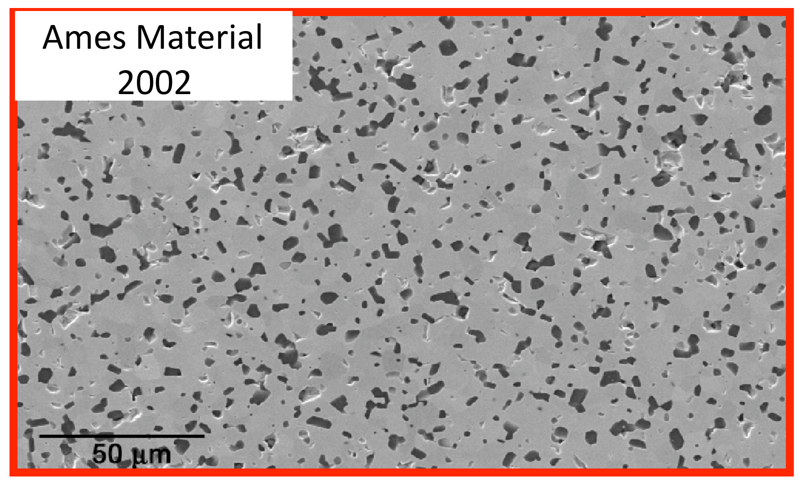
Granulated HfB_2/SiC Powder

Early HfB_2 - 20% SiC Materials









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

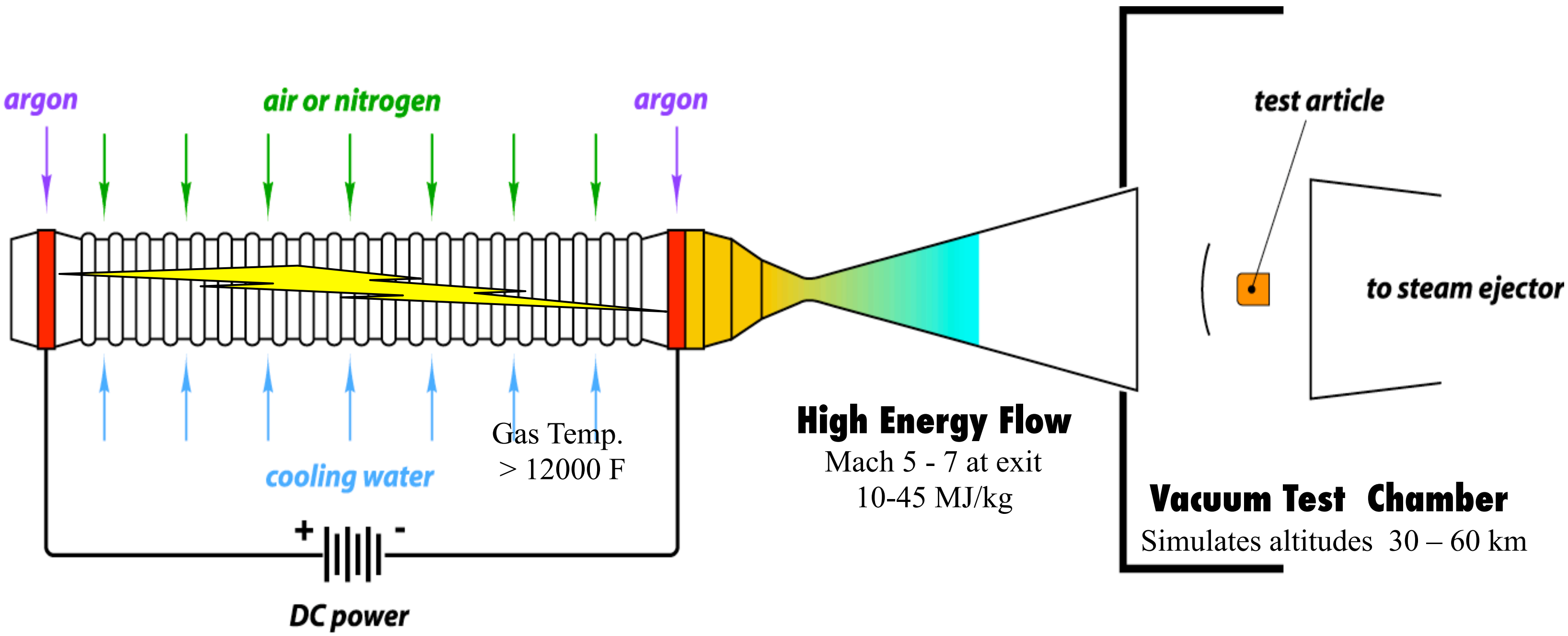
Understand what you are testing!

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



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

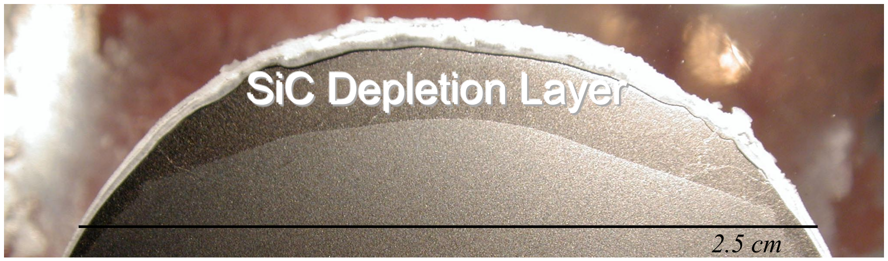
Run 6 Post-Test | Run 7 Post-Test | Run 8 Post-Test | Run 9 Post-Test

HSp-45 Pretest | Run 1 Post-Test | Run 2 Post-Test | Run 3 Post-Test

Run 1	Run 2	Run 3	Run 6	Run 7	Run 8	Run 9
300 sec	600 sec	600 sec	600 sec	1200 sec	1200 sec	600 sec
% Δwt = 0	% Δwt = 0	% Δwt = 0	%Δwt = -0.06	%Δwt = -0.2	%Δwt = -0.32	%Δwt = -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

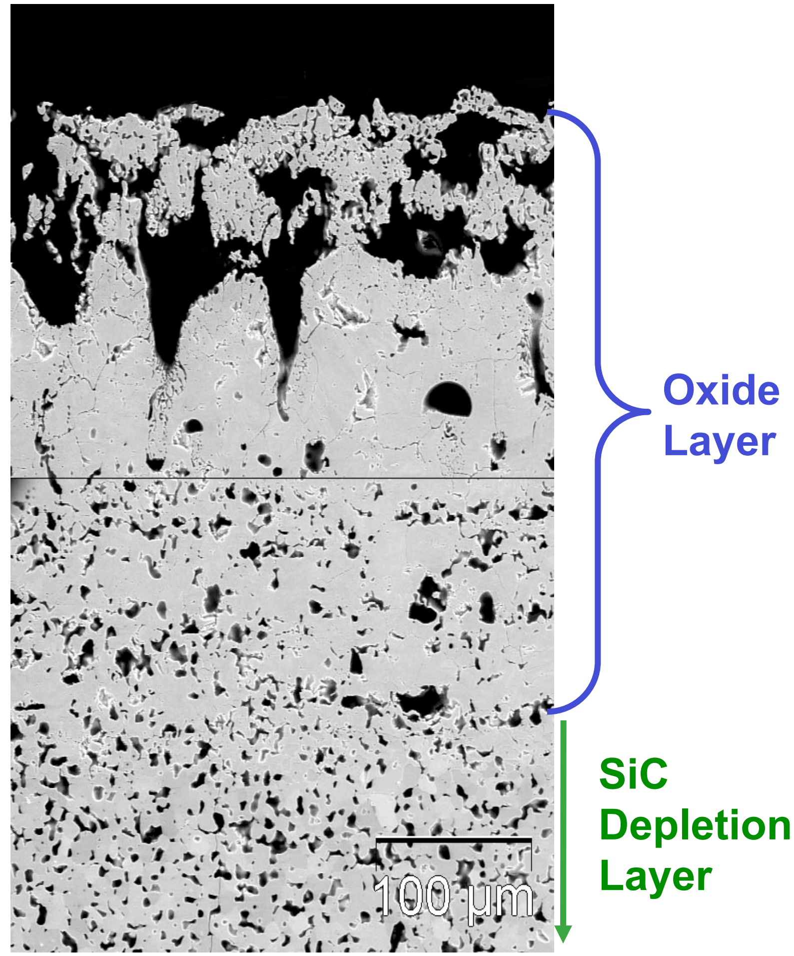
Increasing heat flux →

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/cm²

- 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



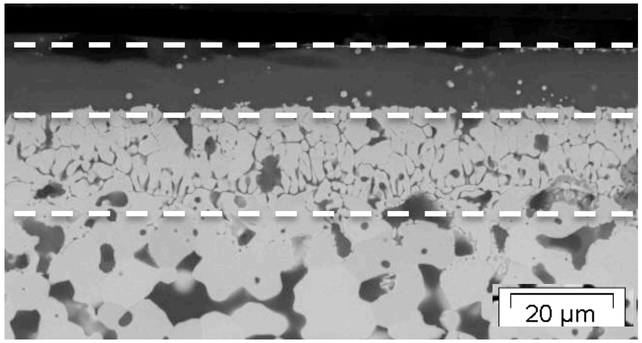
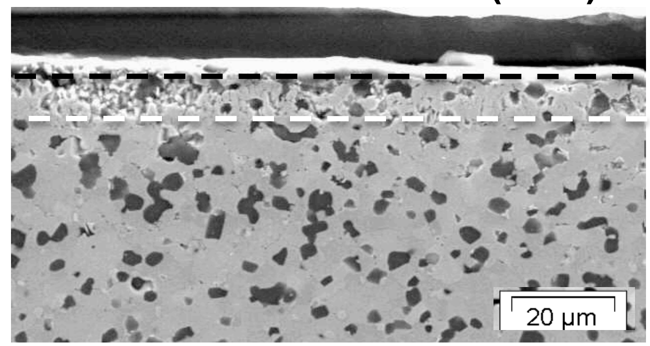
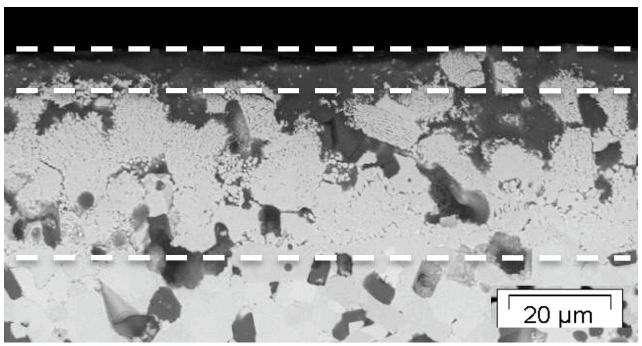
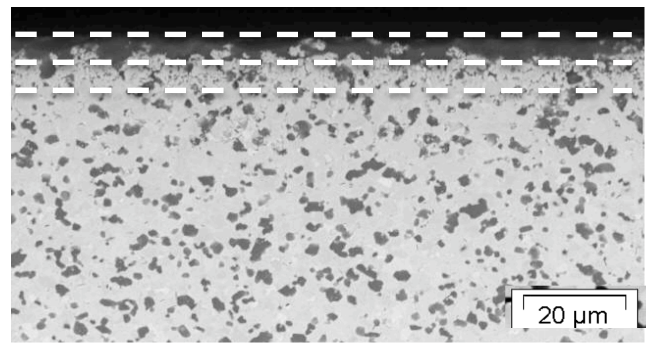
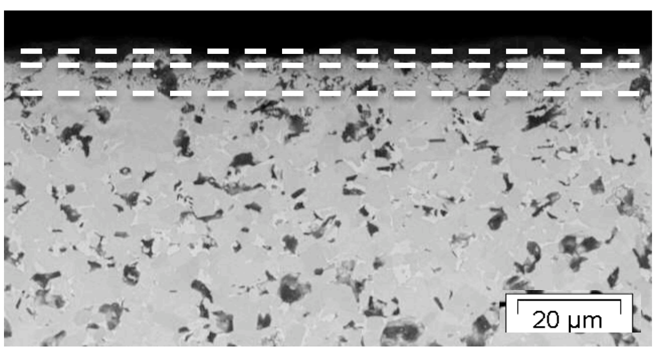
$q_{CW} = 350\ W/cm^2$, $P_{stag} = 0.07$ atm

*Arc jet test data from Space Launch Initiative program

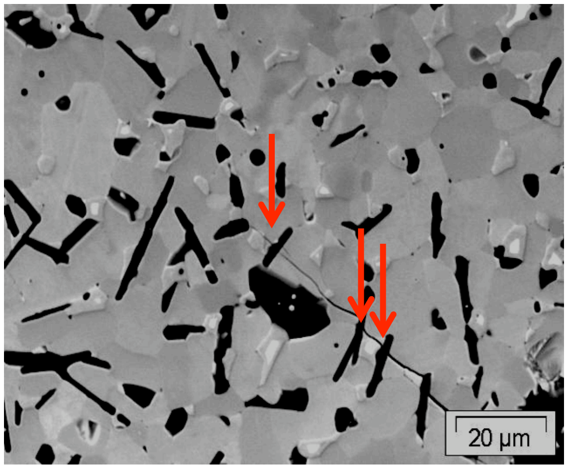
What About Active Oxidation?

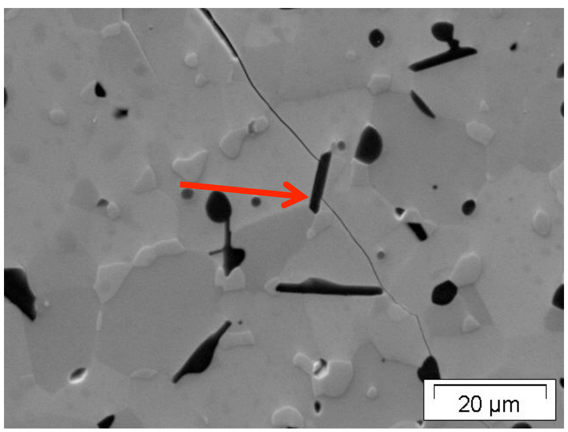
- Silicon-containing materials will actively oxidize under high temperature, low pressure conditions, forming SiO as gas
- Most problematic during re-entry (not during cruise)
- Mitigation approaches:
  - Reduce volume of SiC
    - Reduce overall oxidation
    - Below percolation threshold
  - Reduce 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

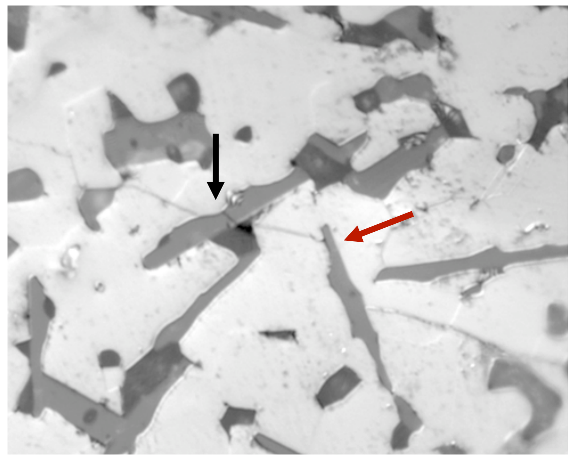
Arcjet Characterization: Additives & Influence of Microstructure

	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.

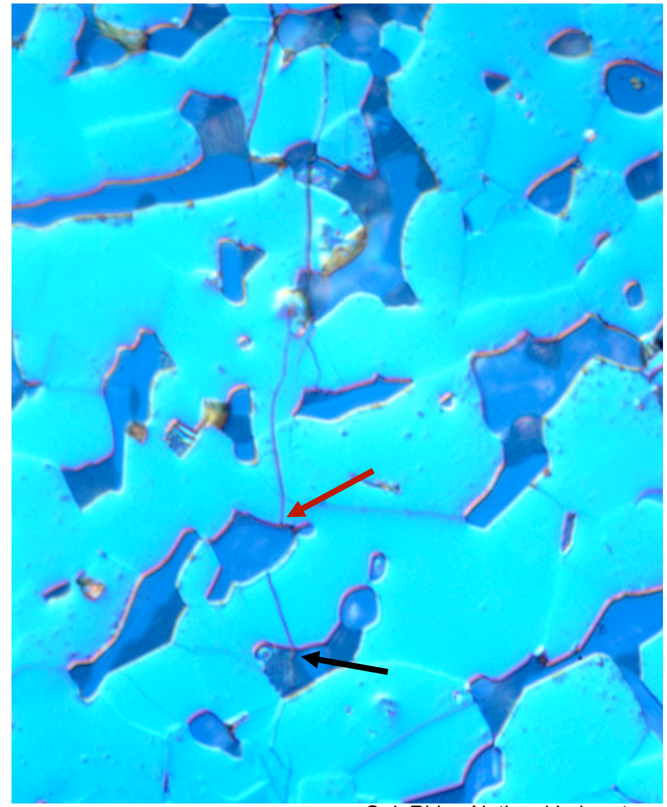
In Situ Composite for Improved Fracture Toughness







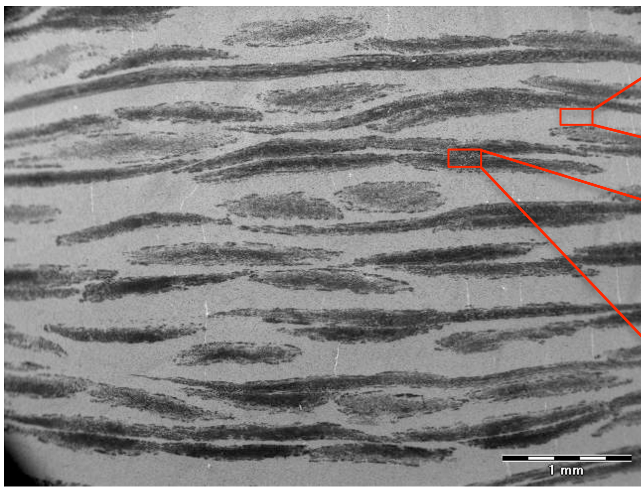
SiC Content	Fracture Toughness (MPam$^{1/2}$)
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33

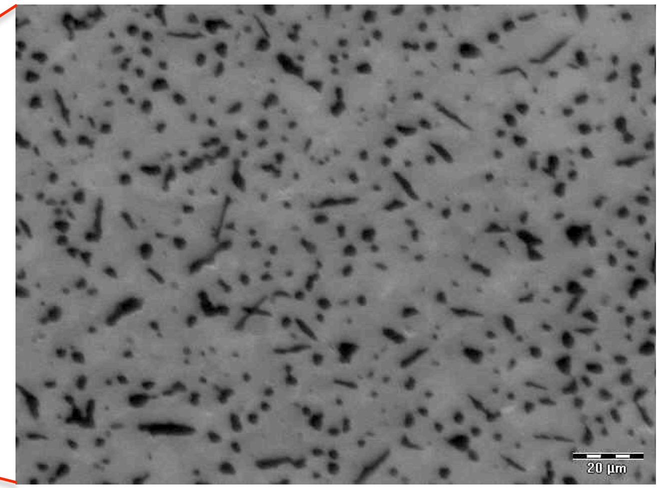


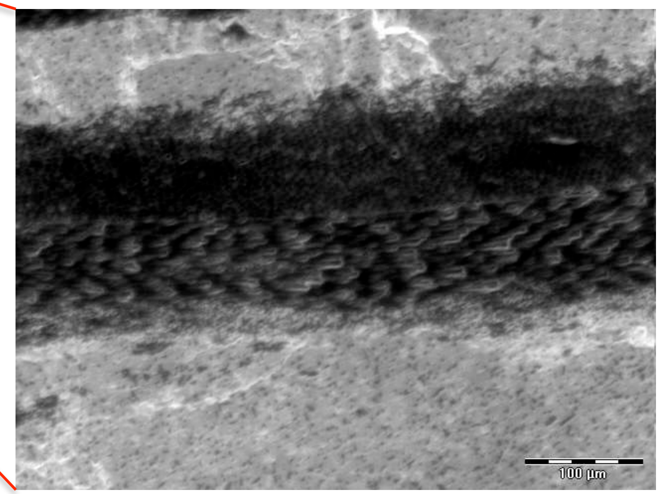
Oak Ridge National Laboratory

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.

Computational Modeling of UHTCs Will Enhance Development

Goals

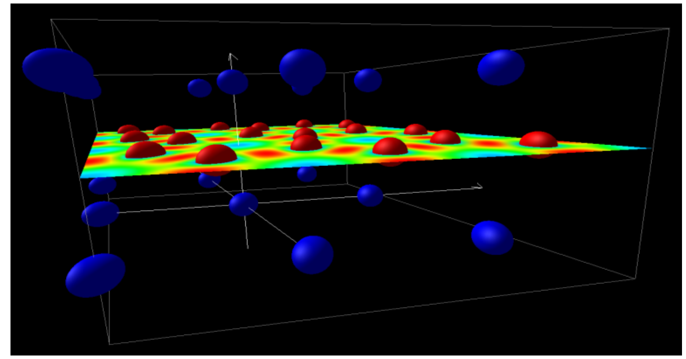
- Reduce materials development time
- Optimize material properties/tailor materials
- Guide processing of materials
- Develop design approaches

Approach

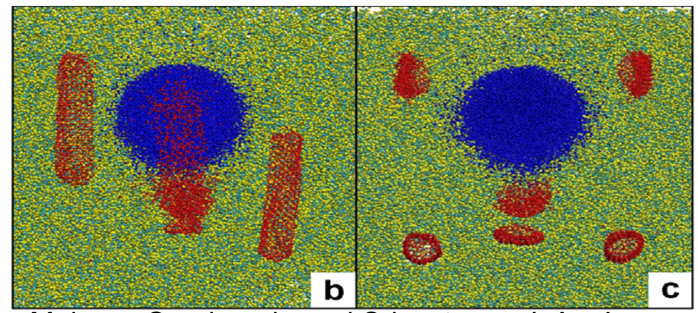
- Develop models integrated across various length scales
- Correlate models with experiment whenever possible

Multiscale Modeling of Materials

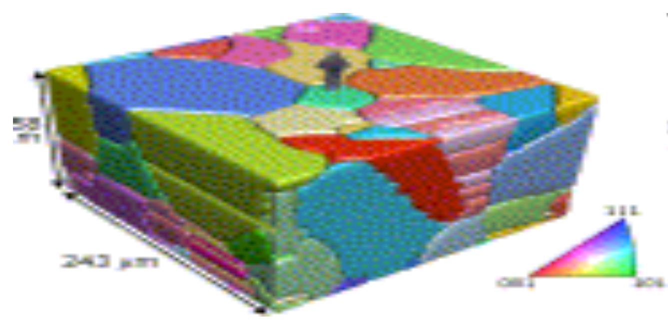
- **Ab initio calculations** — intrinsic material properties
  - *Enables*: structure, bonding, optical and vibrational spectra, chemical reactions, etc
  - *Challenges*: computationally very demanding (very small systems only — 10^2 atoms)
- **Atomistic simulations** — localized interfaces, defects, transport, and so forth
  - *Enables*: thermal transport, mechanical properties, interface (for example, grain boundary) adhesion, impurities effects
  - *Challenges*: requires difficult interatomic potential development (except for C, Si, and so forth) (small systems and short time scales — 10^8 atoms and 10^{-9} sec)
- **Image-based FEM — microstructural modeling**
  - *Enables:* thermal, mechanical, fracture analysis based on microstructure
  - *Challenges*: requires large database of materials parameters (from experiment or modeling). Nonlinear problems (fracture, plasticity) are very challenging. Macroscopic limit may be difficult.



Lawson, publication in preparation (2010)



Makeev, Sundaresh, and Srivastava, J. Appl. Phys. 106, 014311 (2009)



Lewis and Geltmacher, Scripta Materialia 55 (2006)

Modeling UHTCs – What's Next?

- **Accomplishments**
  - *Ab initio* calculations of lattice structure, bonding characteristics, elastic constants, phonon spectra and thermal properties of ZrB_2 and HfB_2
  - *Ab initio* calculations of formation and migration energies for simple defects (vacancies)
  - Development of interatomic potentials for ZrB_2 and HfB_2 for atomistic simulations
- **Opportunities**
  - *Ab initio* calculations of simple/ideal grain boundary structures with and without chemical impurities
  - *No UHTC atomistic simulations exist in the literature. New potentials mean the field is wide open!*
  - FEM modeling of microstructure to relate processing and properties

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!**

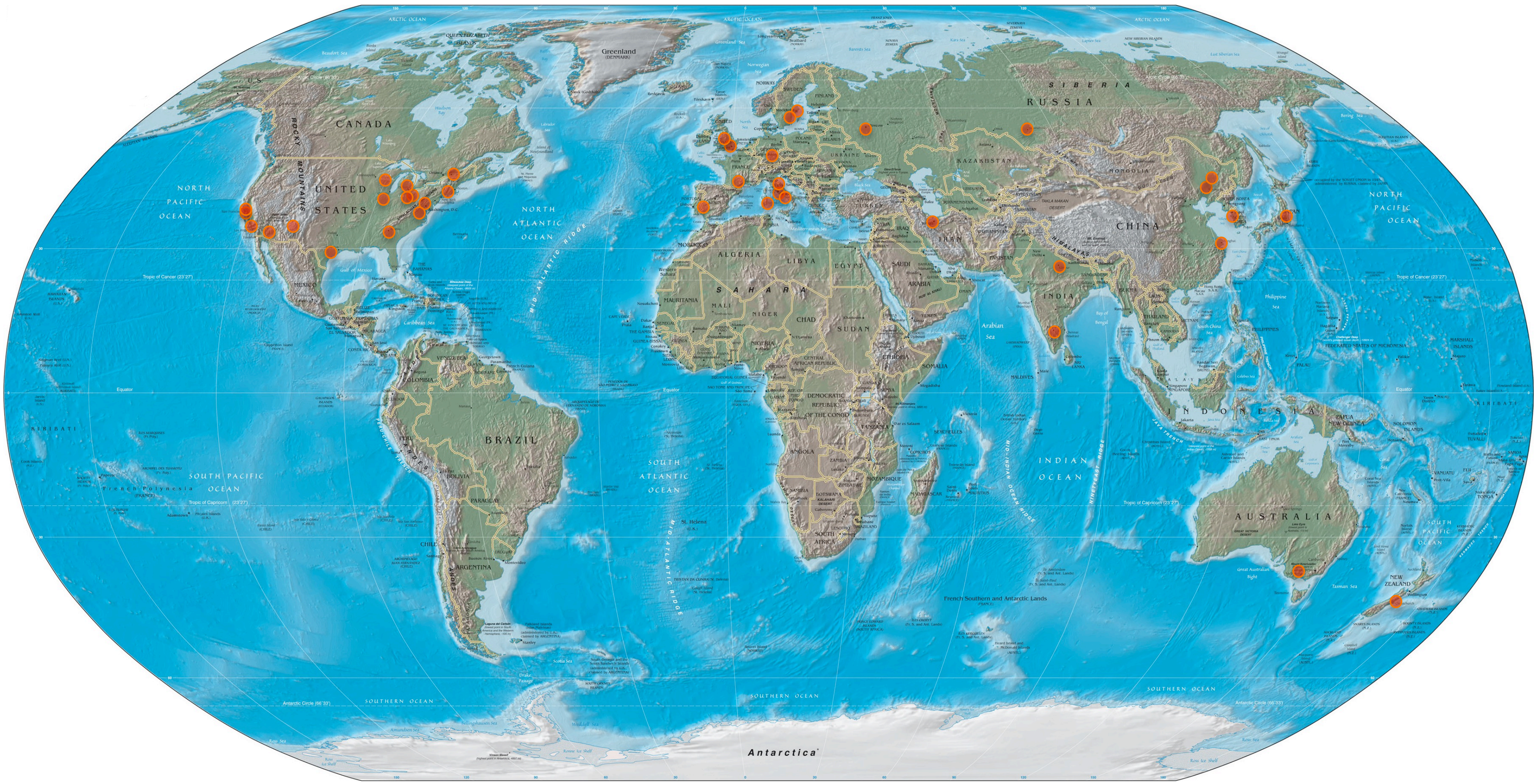
Some Recent Research Efforts in UHTCs: Materials and Properties

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 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!

Back up

Research Needs and Directions

Strength : proven approaches to improve strength; high enough?
Reliability : improved; designers would like to be higher
Thermal conductivity: (HfB_2 is already very high); modeling and characterization to understand role of grain boundaries and composition
Decrease modulus: (graphite second phases, but eutectic issue)
Design around thermal stresses: – rocket nozzles (ONR & AFRL)
Understand and improve oxidation behavior : approaches to reduce SiC
Develop UHTC-matrix composites – hot pressing, SPS, HIP, all produce bulk monolithic materials.

- Modulus/CTE mismatch w/ C fibers a problem
- Need high temperature/compatible fibers
- Current polymeric precursors - expensive and air sensitive
- Melt infiltration – refractory alloys reactive with fibers
- Densification/conversion of matrix
- Alternative Processing routes (CVC, in-situ reinforcement, cermets)

Summary

•UHTCs are necessary for future hypersonic flight/propulsion systems due to higher use temperatures

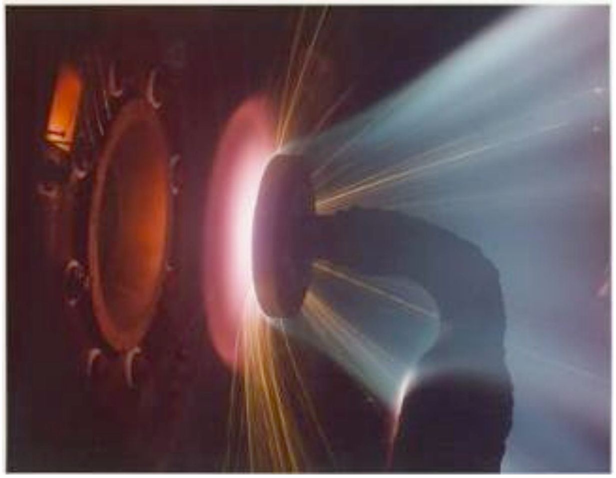
•Oxidation must be understood and controlled

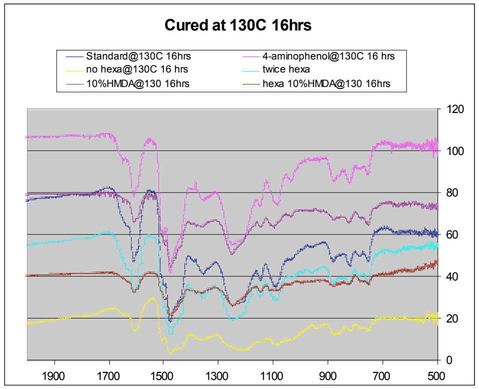
•Monolithic Ceramics will not likely be used in flight hardware
- Flaw Sensitivity (Attachment issues)
- Thermal Shock failure

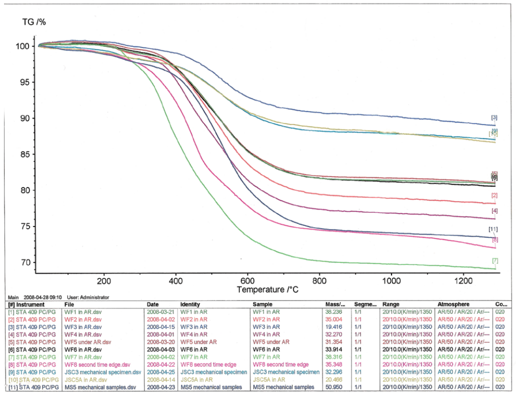
•Current focus :
  - joining
  - reinforced UHTCs
  - oxidation behavior
  - modeling of material properties

Introduction

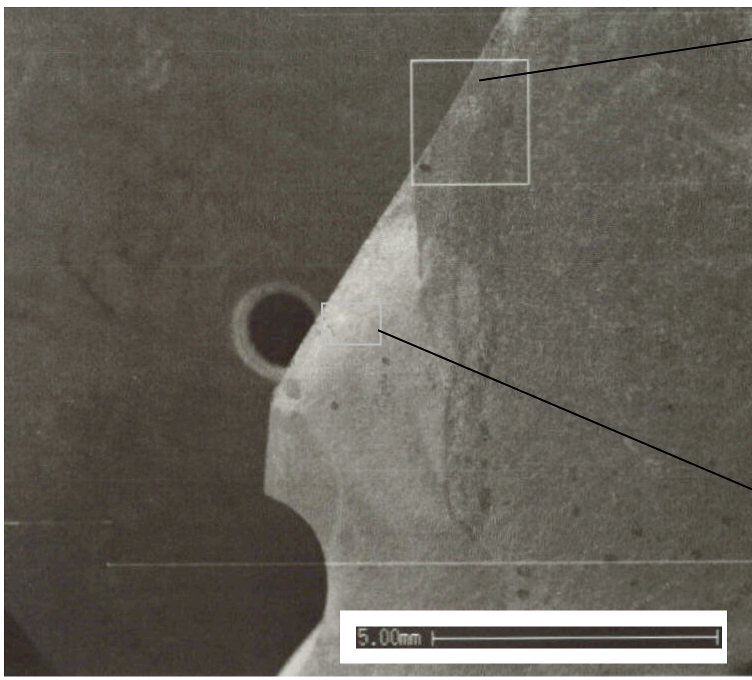
- **Goal of all TPS is *efficient* and *reliable* performance**
- Efforts in ablative and reusable TPS
  - Experimental
    - Processing
    - Characterization
    - Testing
  - Analysis and modeling
    - Thermal-structural
    - Materials response
    - TPS sizing

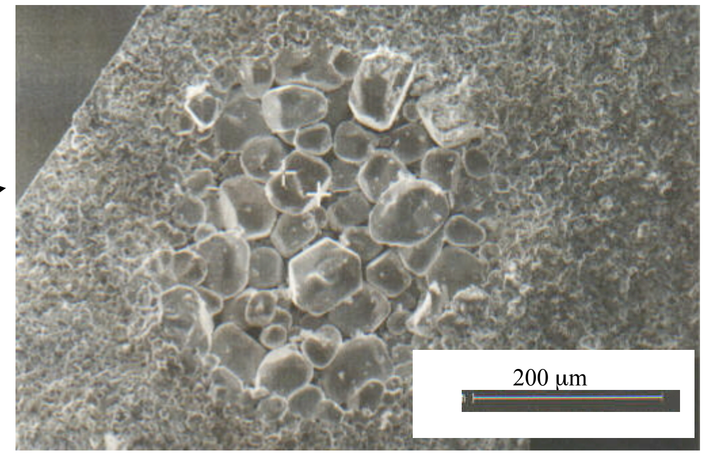




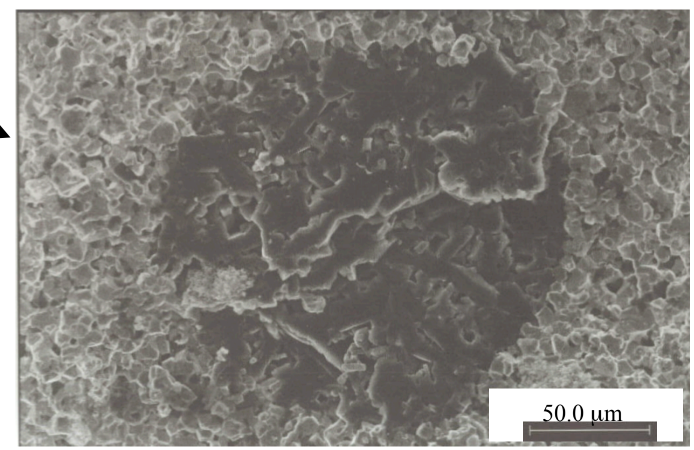


Processing Defects on Fracture Surface of Aft-Segment, Strake 2



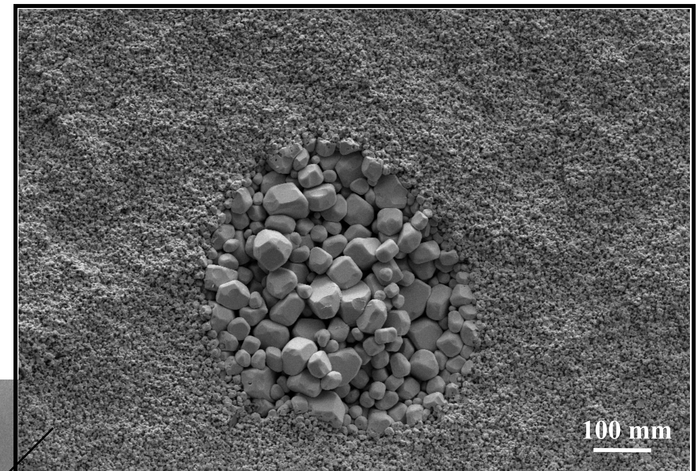


HfB_2 agglomerate

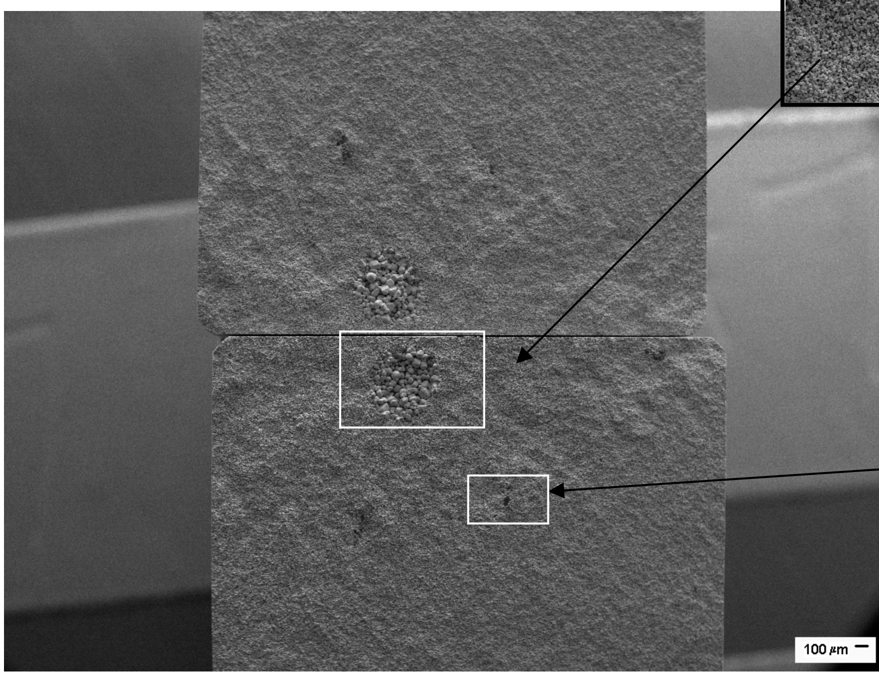


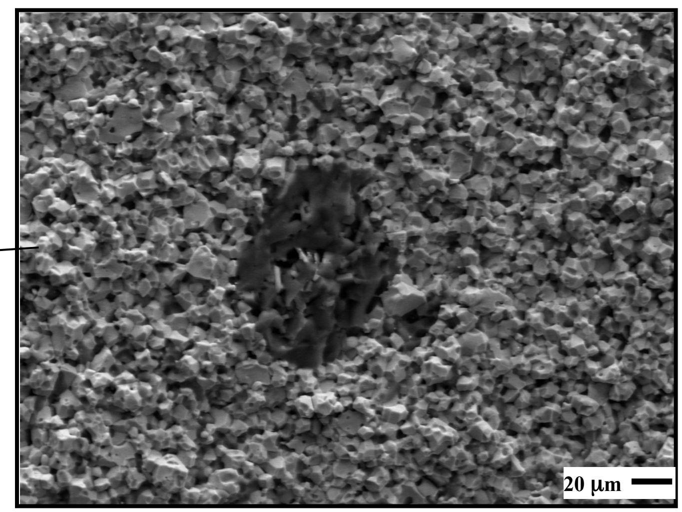
SiC agglomerate

Processing Defects in HfB_2-SiC Flexure Specimens



HfB_2 agglomerate





Grafoil™ agglomerate

Why Continue to Develop UHTCs *Now*?

Given that …

- *Sharp leading edges require refractory materials.*
- *UHTCs have required temperature capability.*

And history tells us …

- Material development is a time-consuming process — 20 years is typical.
- Improvements in ceramic materials and design approaches over time have enabled many advanced applications.

We need to develop UHTCs now if we want materials to be available for applications.

Example of Material Development Success – Silicon Nitride

- Intensive research over the past 50 years
- 1950s–1970s: early and substantial research
- 1980s: programs to use material in engines
  - — US (turbocharger rotors, cylinder liners)
  - — Japan (government and industry). Substantial progress made but applications failed (rotating)
  - — Estimated costs of ceramic engine programs: "several thousand million dollars" (ca 2000, F.L. Riley)
- Recent research: substantial improvements in properties leading to significant applications

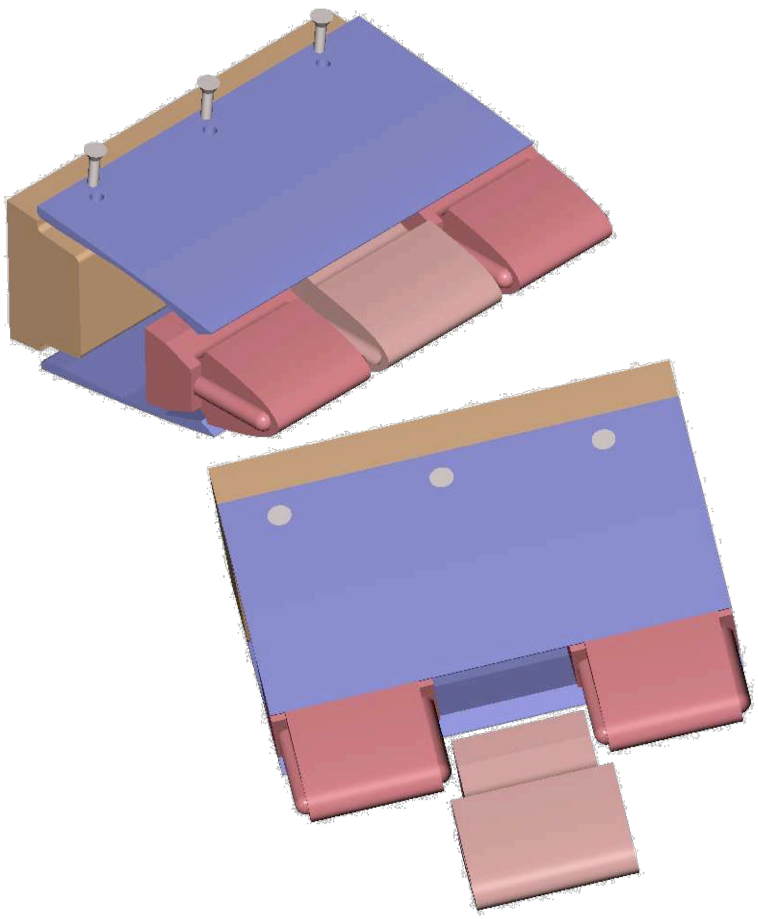
SiC/SiC and C/SiC Development

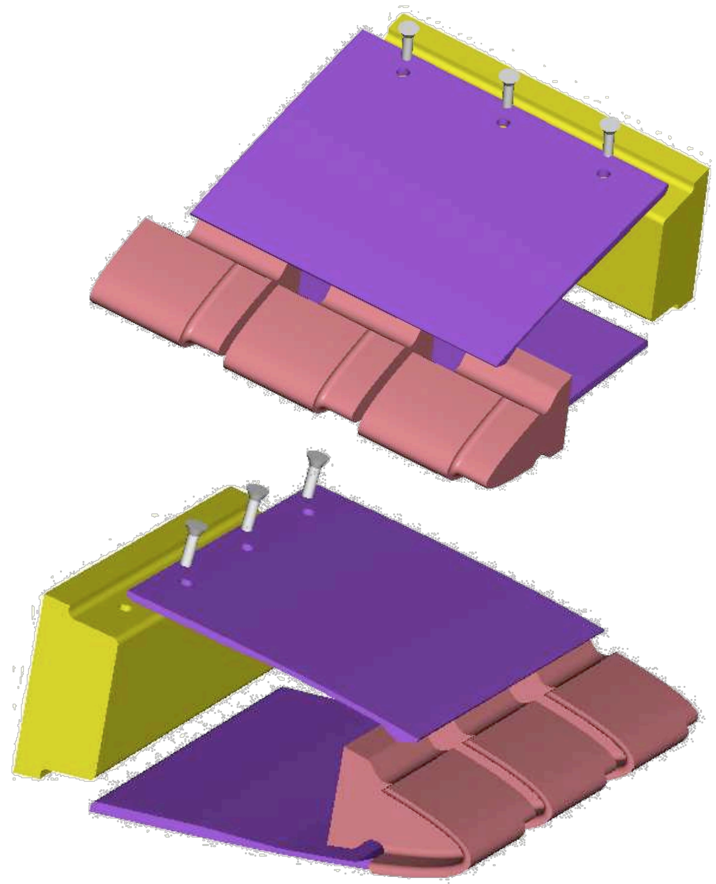
- Started with fiber technology — fibers still an issue
- Numerous tech driven projects performed over the past 2+decades in Europe, Japan, and the US
- SiC/SiC and C/SiC extensively studied since discovery in the mid 70s (French pat. 77/26979 Sept. 1977)
- NASA Enabling Propulsion Materials (EPM) Program: identifying proper CMC constituent materials and processes
  - EPM program terminated in 1999
  - Subsequent Ultra Efficient Engine Technologies (UEET) program built on EPM success
  - US Air Force has built on EPM success
- Hot structures of NASA X38 as example of combined efforts (nose cap, 2 leading edge segments manufactured and ground tested by German consortium, as examples)

DARPA/Air Force Falcon HTV-2 C/C aeroshell

UHTC WLE Concept

UHTC wing leading edge component concepts — intersegment faces with interlocking geometric features — would aid in assembly and mitigate hot gas flow through the gap from the windward side to leeward side.





Modeling Oxidation Kinetics

Model MB_2 (isothermal)

Adequate literature data available on ZrB_2, HfB_2 (but scattered)

Model MB_2-SiC (isothermal)

Limited data (none @ T >1650C) on ZrB_2-SiC, HfB_2-SiC

Model MB_2-SiC high velocity air

No data under well-controlled conditions

Model MB_2-SiC high velocity air in temperature gradient

No data under "well-controlled" conditions; some arc-jet data on ZrB_2-SiC, HfB_2-SiC

Parthasarathy et al., Acta Mater., 2007
Parthasarathy et al., Mater. Sci. Forums, 2008
Parthasarathy et al., J. Am. Ceram. Soc., 2009
Parthasarathy et al., J. Am. Ceram. Soc., in review

Courtesy AFRL