UHTC Research at NASA Ames

Sylvia M. Johnson
Sylvia.m.johnson@nasa.gov
Sharp Leading Edge Technology

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

UHTCs are candidate materials
Some UHTC Development History

- Hf and ZrB₂ materials investigated in early 1950s as nuclear reactor material
- Extensive work in 1960s & 1970s (by ManLabs for Air Force) showed potential for HfB₂ and ZrB₂ 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 HfB₂/SiC, ZrB₂/SiC ceramics for sharp leading edges
- Ballistic flight experiments: Ames teamed with Sandia National Laboratories, New Mexico, Air Force Space Command, and TRW
- 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 Aero thermodynamic 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, then retracted into protective housing.

• Material recovered. Led to new effort in UHTCs / decision to bring development in-house and improve processing.
Recovered UHTC Strakes

• Post-flight recovery showed that all four HfB$_2$-SiC aft-strake segments suffered similar, multiple fractures.
• No evidence of severe heating damage (for example, ablation, spallation, or burning) was observed.
• Defects inherent in material lot are present on fracture surfaces.
• Actual material properties exhibit wider scatter and greater temperature dependence than those assumed in design.
Processing Defects on Fracture Surface of Aft-Segment, Strake 2

HfB₂ agglomerate

SiC agglomerate
Processing Defects in HfB$_2$-SiC Flexure Specimens
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.
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.

Thermal Conductivity Comparison

- 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.

HfB$_2$/SiC materials have relatively high thermal conductivity.
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$^3$
UHTC Material Properties

Sharp leading edges require:
- High thermal conductivity (directional)
- High fracture toughness/mechanical strength/hardness
- Oxidation resistance (in reentry conditions)

<table>
<thead>
<tr>
<th>Property</th>
<th>HfB$_2$/20vol%SiC</th>
<th>ZrB$_2$/20vol%SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>9.57</td>
<td>5.57</td>
</tr>
<tr>
<td>Strength (MPa) 21°C</td>
<td>356±97*</td>
<td>552±73*</td>
</tr>
<tr>
<td></td>
<td>1400°C</td>
<td>137±15*</td>
</tr>
<tr>
<td>Modulus (GPa) 21°C</td>
<td>524±45</td>
<td>518±20</td>
</tr>
<tr>
<td></td>
<td>1400°C</td>
<td>178±22</td>
</tr>
<tr>
<td>Coefficient of Thermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expansion (x10$^{-6}$/K) RT</td>
<td>5.9</td>
<td>7.6</td>
</tr>
<tr>
<td>Thermal Conductivity (W/mK)$^#$</td>
<td>80</td>
<td>99</td>
</tr>
</tbody>
</table>

Source: ManLabs and Southern Research Institute

* Flexible Strength

Improving Processing and Microstructure

- Initial focus on improving material microstructure and strength
- HfB$_2$/20vol%SiC selected as baseline material for project constraints
- Major issue was poor mixing/processing of powders with different densities

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

Granulated HfB$_2$/SiC Powder
Early Progress in Processing of HfB₂ - 20% SiC Materials

- Early and SHARP materials made by an outside vendor
- Improvements in powder handling provide a more uniform microstructure
Weibull Modulus of Ames HfB$_2$/SiC Improved Compared to Previous Materials

Weibull Modulus SHARP B2 Materials ~4

Increased Weibull Modulus to ~15 with processing improvements
Need for Arc Jet Testing

• Arc jet testing is the best ground-based method of evaluating a 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 SiO₂ layer is removed as SiO
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

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

Runs 4 and 5 lasted ~ 2 min. each

HSp-45
Pretest

Run 1
Post-Test

Run 2
Post-Test

Run 3
Post-Test

Run 6
Post-Test

Run 7
Post-Test

Run 8
Post-Test

Run 9
Post-Test

Increasing heat flux

300 sec
% Δwt = 0
$T_{ss} = 1280°C$

600 sec
% Δwt = 0
$T_{ss} = 1220°C$

600 sec
% Δwt = 0
$T_{ss} = 1325°C$

600 sec
% Δwt = -0.06
$T_{ss} = 1970°C$

1200 sec
% Δwt = -0.2
$T_{ss} >2000°C$

1200 sec
% Δwt = -0.32
$T_{ss} >2000°C$

600 sec
% Δwt = -1.24
$T_{ss} >2000°C$

2.54 cm
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

*qCw = 350 W/cm², Pstag = 0.07 atm

*Arc jet test data from Space Launch Initiative program
Controlling Microstructure & Composition

• Goal for UHTCs for TPS has been to improve:
  – Fracture toughness
  – Strength
  – Thermal conductivity
  – Oxidation resistance — arcjet performance

• Properties controlled by processing, microstructure, and composition
  – Grain Size
    • Additives (Ir additions)
    • Processing by field-assisted sintering (FAS)
  – Grain Shape
    • Addition of preceramic polymers
    • Particle coatings (Fluidized Bed CVD)
  – Purity (grain boundaries)
    • Addition of preceramic polymers
    • Processing (FB CVD)
    • Self-propagating reactions
  – Oxide formation
    • Increase oxide stability / emissivity (additives)
    • Reduce amount of SiC
Control of Grain Size

HfB₂/20v%SiC
Hot Pressed
(long process)

HfB₂/20v%SiC
Hot Pressed
(short process)

HfB₂/20v%SiC
Spark Plasma Sintered
Third-Phase Additions

• Explore effect of additional refractory phases (Ir and TaSi$_2$) on microstructure and oxidation behavior of baseline material (HfB$_2$-20 vol% SiC)

HfB$_2$-SiC

HfB$_2$-SiC-TaSi$_2$

HfB$_2$/SiC/TaSi$_2$ clearly has a higher post-test emissivity than HfB$_2$/SiC and demonstrated lower surface temperatures

Effect of Additives on Microstructure

Addition of Ir (short process)

HfB$_2$-SiC (hot press, short process)

Addition of Ir and TaSi$_2$ (short process)

HfB$_2$-SiC-TaSi$_2$-Ir (hot press, short process)

Samples processed with additional phases show less grain growth

HfB$_2$-SiC (SPS)

Similar microstructure

Similar microstructure

HfB$_2$-SiC-Ir (hot press, short process)
Physical Characterization: Microstructure

**Hot Pressed**

- **HfB$_2$-SiC Baseline**
  - Grain Size 7.7µm
- **HfB$_2$-SiC-TaSi$_2$**
  - Grain Size 8.5µm
- **HfB$_2$-SiC-TaSi$_2$-Ir**
  - Grain Size 5.1µm

**Spark Plasma Sintered (SPS)**

- Grain Size 4.1µm
- Grain Size 2.3µm
- Grain Size 1.6µm
Arc Jet Characterization: Additives & Influence of Microstructure

Both oxide scale and depletion zone can be reduced.
Preceramic Polymers Can Control Grain Shape

- Conventional source of SiC is powder.
- SiC from a preceramic polymer source:
  - Will affect densification and morphology.
  - May achieve better distribution of SiC source through HfB$_2$.
  - Previous work shows that preceramic polymers can enhance growth of acicular particles (for fracture toughness).

- Potential to improve mechanical properties with reduced amount of SiC and also potentially improve oxidation behavior.
Growth of Elongated SiC Grains

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

SiC Preceramic Polymer Promotes Growth of Acicular Grains

- Precursor added in amounts sufficient to yield nominal amounts of SiC
In Situ Composite for Improved Fracture Toughness

Evidence of crack growth along HfB$_2$-SiC interface, with possible SiC grain bridging

<table>
<thead>
<tr>
<th>SiC Content</th>
<th>Fracture Toughness (MPam$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>3.61</td>
</tr>
<tr>
<td>10%</td>
<td>4.06</td>
</tr>
<tr>
<td>15%</td>
<td>4.47</td>
</tr>
<tr>
<td>Baseline UHTC (20%)</td>
<td>4.33</td>
</tr>
</tbody>
</table>
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.
UHTC Challenges

1. Fracture toughness

   Composite approach is required

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

2. Oxidation resistance in reentry environments

   Promising approaches but challenge is active oxidation of materials containing SiC

3. Modeling is critical

   Shorten development time, improve properties, design
Some Recent Research Efforts in UHTCs:
Materials and Properties

<table>
<thead>
<tr>
<th>ZrB₂ Based Ceramics</th>
<th>Catalytic Properties of UHTCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Missouri University of Science &amp; Technology</td>
<td>PROMES-CNRS Laboratory, France</td>
</tr>
<tr>
<td>US Air Force Research Lab (AFRL)</td>
<td>CNR-ISTEC</td>
</tr>
<tr>
<td>NASA Ames &amp; NASA Glenn Research Centers</td>
<td>CIRA, Capua, Italy</td>
</tr>
<tr>
<td>University of Illinois at Urbana-Champaign</td>
<td>SRI International, California</td>
</tr>
<tr>
<td>Harbin Institute of Technology, China</td>
<td></td>
</tr>
<tr>
<td>Naval Surface Warfare Center (NSWC)</td>
<td>University of Connecticut</td>
</tr>
<tr>
<td>NIMS, Tsukuba, Japan</td>
<td>AFRL</td>
</tr>
<tr>
<td>Imperial College, London, UK</td>
<td>NASA Ames Research Center</td>
</tr>
<tr>
<td>Korea Institute of Materials Science</td>
<td>Teledyne (NHSC-Materials and Structures)</td>
</tr>
<tr>
<td>CNR-ISTEC</td>
<td></td>
</tr>
<tr>
<td><strong>HfB₂ Based Ceramics</strong></td>
<td><strong>Imaging and Analysis (Modeling)</strong></td>
</tr>
<tr>
<td>NASA Ames Research Center</td>
<td></td>
</tr>
<tr>
<td>NSWC—Carderock Division</td>
<td></td>
</tr>
<tr>
<td>Universidad de Extremadura, Badajoz, Spain</td>
<td></td>
</tr>
<tr>
<td>CNR-ISTEC, Italy</td>
<td></td>
</tr>
<tr>
<td><strong>Fiber Reinforced UHTCs</strong></td>
<td><strong>Oxidation of UHTCs</strong></td>
</tr>
<tr>
<td>Chinese Academy of Sciences, Shenyang</td>
<td>AFRL</td>
</tr>
<tr>
<td>University of Arizona</td>
<td>NASA Glenn Research Center</td>
</tr>
<tr>
<td>MATECH/GSM Inc., California</td>
<td>Georgia Institute of Technology</td>
</tr>
<tr>
<td>AFRL</td>
<td>Missouri University of Science &amp; Technology</td>
</tr>
<tr>
<td></td>
<td>Texas A &amp; M University</td>
</tr>
<tr>
<td></td>
<td>CNR-ISTEC, Italy</td>
</tr>
</tbody>
</table>
Some Recent Research Efforts in UHTCs: Processing

<table>
<thead>
<tr>
<th>Field Assisted Sintering</th>
<th>UHTC Polymeric Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>University of California, Davis</td>
<td>SRI International, California</td>
</tr>
<tr>
<td>Air Force Research Laboratory (AFRL)</td>
<td>University of Pennsylvania</td>
</tr>
<tr>
<td>CNR-ISTEC, Italy</td>
<td>Missouri University of Science &amp; Technology</td>
</tr>
<tr>
<td>Stockholm University, Sweden</td>
<td>MATECH/GSM Inc., California</td>
</tr>
<tr>
<td>NIMS, Tsukuba, Japan</td>
<td>Teledyne (NHSC)</td>
</tr>
<tr>
<td><strong>Pressureless Sintering</strong></td>
<td><strong>Nano &amp; Sol Gel Synthesis of UHTCs</strong></td>
</tr>
<tr>
<td>Missouri University of Science &amp; Technology</td>
<td>Loughborough University, U.K.</td>
</tr>
<tr>
<td>Politecnico di Torino, Italy</td>
<td>IGIC, Russian Academy of Science</td>
</tr>
<tr>
<td><strong>Reactive Hot-Pressing</strong></td>
<td>University of Erlangen-Nürnberg, Germany</td>
</tr>
<tr>
<td>Shanghai Institute of Ceramics, China</td>
<td>Korea Institute of Materials Science</td>
</tr>
<tr>
<td>NASA Ames Research Center</td>
<td>Iran University of Science and Technology</td>
</tr>
<tr>
<td>National Aerospace Laboratories, India</td>
<td></td>
</tr>
<tr>
<td>Sandia National Laboratories, New Mexico</td>
<td></td>
</tr>
<tr>
<td>McGill University, Montreal, Canada</td>
<td></td>
</tr>
<tr>
<td>University of Erlangen-Nürnberg, Germany</td>
<td></td>
</tr>
</tbody>
</table>