Advanced Ceramics for Use as Fuel Element Materials in Nuclear Thermal Propulsion Systems

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Note: Funded through the NASA Human Exploration and Operations Directorate’s Advanced Exploration Systems (AES) Nuclear Cryogenic Propulsion Stage (NCPS) Task 4: NCPS Fuel Design and Fabrication

• Fuel Element Materials Overview & Background
  o Emphasis on Benefits of Advanced Ceramic Fuel Elements

• Goals & Materials to Be Considered

• Material Selection Considerations

• Fabrication Processes & Approach Being Considered

• Development of Carbide/Nitride Coatings for Graphite Composites

• Summary
NCPS Fuel Element Materials Overview

3 Classes of NTP Fuel Elements Under Consideration:

1. Coated Graphite Composites – led by DOE (ORNL)
   - Highest TRL approach – based upon Rover/NERVA work
   - Coatings effort at MSFC to investigate ceramic coatings**

2. Cermets – led by NASA w/ significant DOE support (INL, ORNL)
   - Intermediate TRL approach
   - Discussed in other NETS presentations

3. Advanced Ceramics – led by NASA
   - Lowest TRL approach, but with greatest performance potential
   - All-ceramic fuel elements – investigating carbides and nitrides**

** Discussed in this presentation.
Why Interest in Advanced Ceramics?

- Advanced ceramics enable highest operating temperatures, and highest $I_{sp}$. 

![Graph showing Nuclear Thermal Rocket Performance: Specific Impulse vs. Chamber Temperature.](chart)

Region of Interest

Modified version of S. Borowski chart.
Benefits of Advanced Ceramics

Carbide and/or nitride fuel elements have the potential to enable the highest performance class of fuel elements being considered for NTP.

- Many refractory carbides and nitrides have extremely high melting points, thus enabling very high operating temperatures (and high $I_{sp}$)
  - Allows $I_{sp}$ improvements of roughly 200 s over Rover/NERVA-type materials
  - Enables increases in operating temperatures of roughly 600 to 800 K

- More stable (resistant to hot hydrogen attack) than graphite or graphite composite fuel elements fabricated with uranium oxide or carbide particles

- Solid solution (single-phase) elements more resistant to degradation via carbon diffusion and CTE-mismatch induced stresses

- Advanced bi- and tri-carbide single-phase solid solutions have the potential to operate at temperatures well above the melting point of uranium carbide (2800K for UC, 2860K for UC$_2$)
Program Goal for NTP Fuel Elements

To Operate:
• At extremely high temperatures (3200K, or above),
• For “long” lifetimes (at least 10 hrs.),
• In a very reactive environment (hot H₂ propellant),
• With little or no degradation.

Modification of chart from D.R. Koenig, LA-10062-H, 1986
Past Efforts with All-Ceramic Fuels

• **AEC/NASA: Rover/NERVA – NF-1 (1972)**
  - (UC-ZrC)C “Composite”
    - 47 of 49 cells in furnace
  - (U, Zr)C (0%, 3%, 8% Zr impregnation)
    - 2 of 49 cells in furnace
    - 8% Zr elements demonstrated minimum fracture behavior

• **Russia**
    - (U, Zr)C
  - 1993 – 1996 (LUTCH / Univ. of Florida Collaboration)
    - (U,Zr,Nb)C
    - (U, Zr, Ta)C
    - (U,Zr)CN
    - (U,Zr)CN / W

• **NASA Space Exploration Initiative (1989-1993)**
  - (U, Zr)C

• **Los Alamos National Lab (2006) – NASA funded**
  - DUO$_2$-ZrC

• **University of Florida (2000’s; 2005-2008)**
  - Research performed for DOE
  - TaC
  - WC
  - ZrC
  - (U, Zr, Ta)C
  - (U, Zr, Nb)C – explored several different mole fractions in Hot Hydrogen samples
Goals for All-Ceramic Fuel Element Effort

- **Primary:** Demonstrate the feasibility of using carbide and/or nitride ceramic powders for fabricating all-ceramic nuclear fuel element components.
  - Determine two candidate ceramic fuel element fabrications approaches.
  - Each “approach” is defined by both the constituent materials employed and the fabrication methods and processes used.
  - Binary and/or ternary carbide material compositions are of greatest interest.

- **Secondary Goals:** Besides fully characterizing the constituent powder materials used and defining all fabrication processing steps and procedures, the following will be accomplished:
  - Assess resistance to thermal environment – melting point, vaporization losses, phase stability, overall durability, projected useful lifetime
  - Assess resistance to hot hydrogen attack
  - Assess resistance to nuclear reactor radiation environment – will require DOE support
  - Characterize microstructural morphology and crystallographic phases present
  - Determine critical material properties and physical characteristics – fracture toughness, porosity content/distribution, other TBD
Materials To Be Considered

- Carbides & Nitrides of the transition metals of groups IVB thru VIB of periods 4 thru 6 of the Periodic Table.
- To be combined with uranium carbide or uranium nitride.

Modification of Sargent-Welch Scientific Company chart, 1968
Material Selection Considerations

- **Primary Material Properties and/or Issues:**
  - **Melting Point** --- generally, the higher, the better
  - **Nuclear Absorption Cross-Section** --- both material choice and neutron energy level
  - **Vaporization Rate** --- including any dissociation issues
  - **Hydrogen Compatibility / Reactivity** --- testing to be performed at MSFC
  - **Phase Stability** --- equilibrium vs. metastable, stoichiometric vs. non-stoichiometric
  - **Coefficient of Thermal Expansion (CTE)** --- esp. important for multi-phase materials
  - **Thermal Conductivity** --- also important for multi-phase materials
  - **Crystallographic Phase Relationships** --- volume change transformations
  - **Diffusion Rates** --- both self-diffusion and uranium transport issues
  - **Thermal Shock Characteristics** --- includes fracture toughness assessments
  - **Cost / Availability** --- are any desired materials difficult to obtain?

- **Initial efforts will concentrate on determining candidate materials, and how to fabricate viable material compositions and microstructures. How to fabricate prototype geometrically-accurate fuel element components will occur later.**
## Melting Points, n° Cross-Sections

<table>
<thead>
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<th>Compound</th>
<th>Melting Point (K)</th>
<th>Compound (continued)</th>
<th>Melting Point (K)</th>
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<td>Cr&lt;sub&gt;23&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;</td>
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<table>
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<th>Element</th>
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<td>W</td>
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<tr>
<td>Zr</td>
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**Rating Scale:**

- **Worst**
- **Best**
### Conductivities, CTE’s, Vapor Pressures

#### Table Rating Scale:

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<thead>
<tr>
<th>Compound</th>
<th>Thermal Cond. (W/m·K)</th>
<th>CTE (10^6/K)</th>
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<tr>
<td>Cr₃C₂</td>
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<tr>
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</tbody>
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#### Carbide Temperatures @ Vapor Pressures - Margrave 1967

![Graph of Carbide Temperatures @ Vapor Pressures - Margrave 1967](image)

**Legend:**
- TaC
- NbC
- ZrC
- HfC
- MoC
- Mo₂C
- NbC
- TiC
- WC
- W₂C
- UC
- UC₂
- VC₀.₇₅
- Cr₃C₂
Initially, efforts will focus on fabricating coupons for material performance and microstructure evaluations. Towards the end of the current project, increasing emphasis will be given to fuel element geometrical manufacturing concerns.

**Precursor Component / Coupon Preparation Methods:**

- Uniaxial Pressing
- Cold Isostatic Pressing (CIP) --- wet bag process ★
- Slip Casting
- Tape Casting

**Component / Coupon Fabrication Methods:**

[Most will include a final high temperature heat treatment.]

- Extrusion
- Sintering ★
- Hot Pressing ★
- Hot Isostatic Pressing (HIP) ★
- Reaction Pressing ★

★ Primary processes to be investigated.
All-Ceramic Fuel Element Approach

Advanced ceramics development effort consists of three primary phases:

- **Materials and Processes Analysis and Development**
  - Conduct investigations aimed at determining compositions and thermal process cycles that yield ceramic microstructures and phases appropriate for NTP fuels
    - Solid solutions of interest to avoid “low-melting” uranium carbide phase
  - Small solid cylindrical coupons made via pressing and sintering
    - Thermal processing up to 3273 K (3000 °C)

- **Fabrication and Characterization of Advanced Ceramics**
  - Evaluate additional processing methods: hot pressing and hot isostatic pressing
  - Goal: dense (low porosity) materials with appropriate microstructural morphologies
    - Conduct material characterization and hot hydrogen testing

- **Development and Fabrication of Prototype Fuel Elements**
  - Fabricate test pieces with more fuel-element-like geometries:
    - Increased diameters and lengths; addition of through-holes
  - Assess path forward for fabricating all-ceramic 3200K fuel elements
Coatings for Graphite Composites

Development of Ceramic Reaction-Sintered Coatings (CRSC’s) for graphite-based fuel elements being pursued to allow additional options.

➢ Coatings for graphite composite fuel elements needed to:
  • Prevent hydrogen attack
  • Prevent fuel vaporization

➢ Overview of Ceramic Reaction-Sintered Coatings:
  • Coating process involves simultaneous eutectic melting and powder particle sintering
    o Precursor coating material reacts with outer portion of substrate (~ 50 μm)
    o Two-layer type coating microstructure, with graded interaction with substrate
  • Hard, adherent coatings formed that can withstand very high temperatures
    o Adherence through thermal cycling best when coating/substrate CTE’s are similar
  • Prior efforts conducted with both graphite and carbon-carbon substrates

➢ MSFC Coatings Effort for Graphite Composite Fuel Elements:
  • Supports Oak Ridge National Laboratory led graphite composites effort
  • Based upon prior work with CRSC’s fabricated with carbide/boride mixtures
    o As boron is undesirable, mixtures of carbides and nitrides will be investigated
Two examples of CRSC’s on 2D Carbon-Carbon Composites:

• Left: Coating made from HfB$_2$, HfC, and SiC powders; Hitco Carbon Composites, Inc. substrate provided by NASA-LaRC (Hyper-X Program). Secondary electron image.

• Right: Coating made from HfB$_2$ and HfC powders; Hitco Carbon Composites, Inc. substrate. Back-scattered electron image.

• In both images, note two-layer coatings with graded penetration layers, which promote adherence.
Coatings Applications Investigated

Prior CRSC Development Efforts:

- Propulsion
  - Nozzles, thrust chambers
  - Hot gas valve components

- Thermal Management
  - Sharp leading edges
  - Heat shields

- Fusion Energy Tokamak
  - First wall tiles

- DoD Spacecraft Shielding
  - X-ray, laser irradiation
  - Particle-, electron-beams

For both applications depicted at right:
HfB$_2$-HfC Coatings on Poco Graphite, Grade AXF-5Q.
1. Advanced ceramics offer the greatest benefits for NCPS fuels
   • Highest $I_{sp}$ through highest operating temperature
   • More stable than graphite, or graphite composites
   • Investigated off & on over past 40+ years, but TRL is still very low

2. Current effort aimed primarily at bi- & tri-carbide materials
   • Nitride materials also of interest
   • Carbides & nitrides of Group IVB-VIB / Period 4-6 transition metals
   • Various material properties & fabrication approaches being investigated

3. Development approach initially emphasizing material microstructure
   • Latter phases will stress fabrication methods and fuel element geometries

4. Ceramics coatings for graphite composites also being developed
   • Coatings will make use of reaction-sintering process