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

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Presentation Outline

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Advanced Exploration Systems (AES)
Nuclear Cryogenic Propulsion Stage (NCPS)
Task 4: NCPS Fuel Design and Fabrication

- **Fuel Element Materials Overview & Background**
    - 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

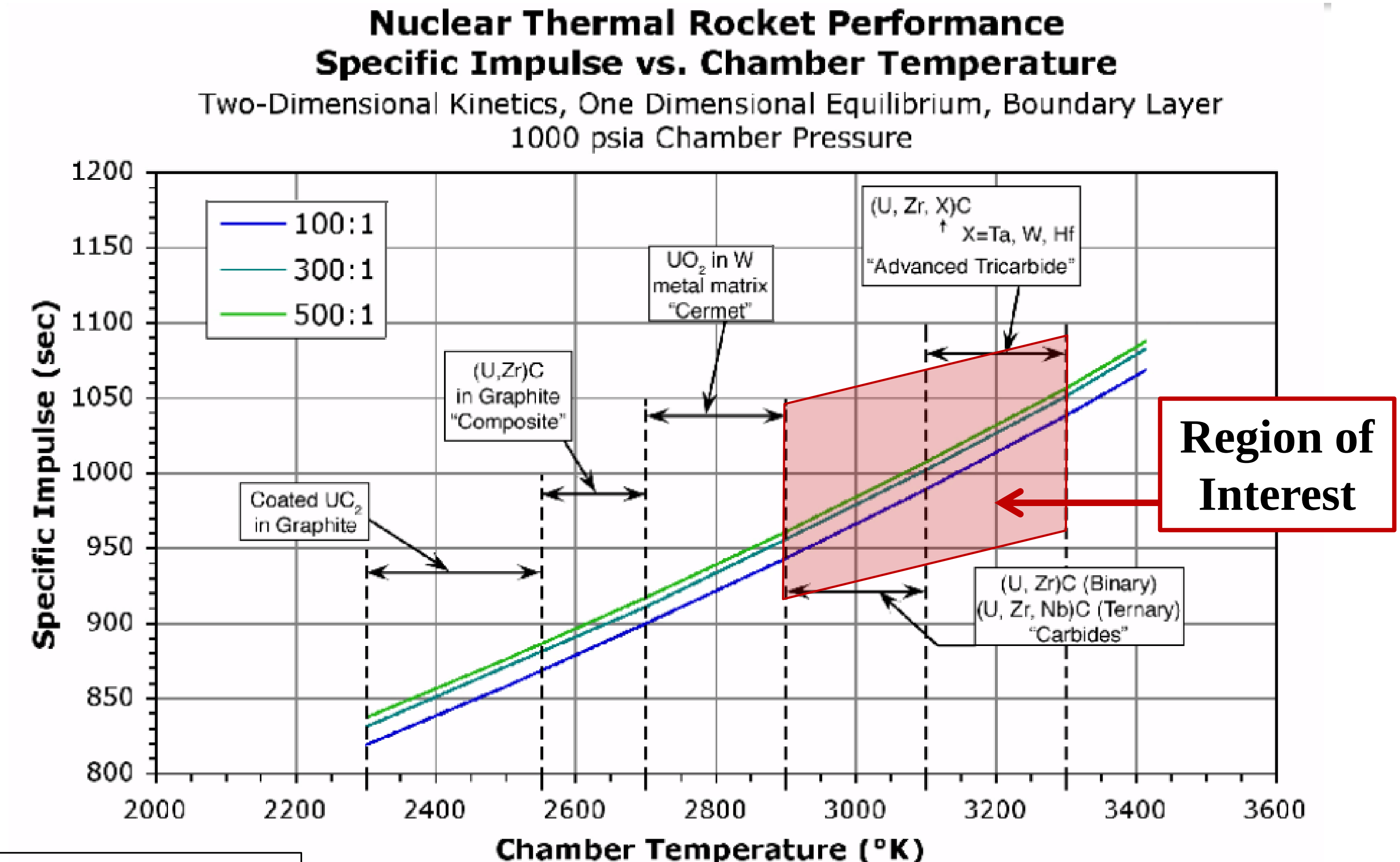
3 Classes of NTP Fuel Elements Under Consideration:

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}.**



Modified version of S. Borowski chart.

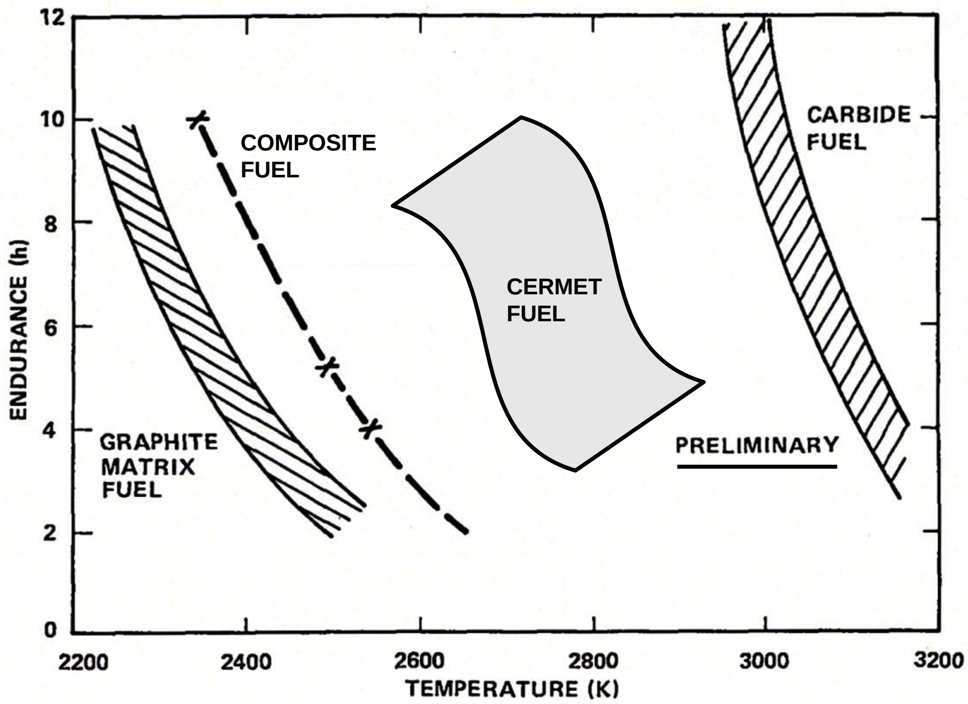
Benefits of Advanced Ceramics

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

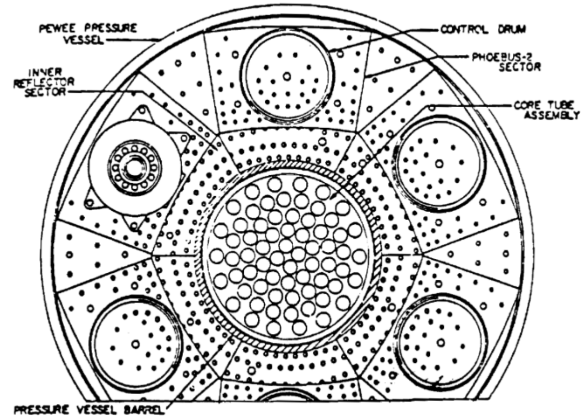
To Operate:
- At extremely high temperatures (3200K, or above),
- For "long" lifetimes (at least 10 hrs.),
- In a very reactive environment (hot H_2 propellant),
- With little or no degradation.



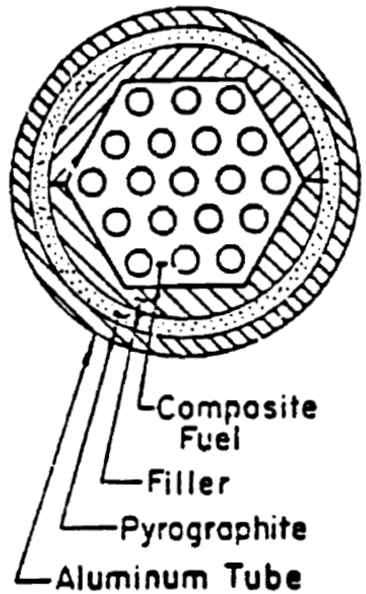
Modification of chart from D.R. Koenig, LA-10062-H, 1986

Past Efforts with All-Ceramic Fuels

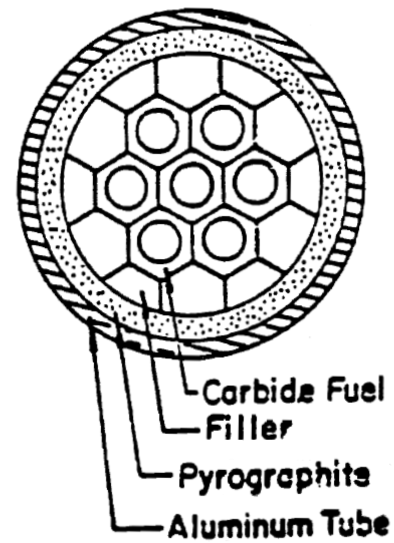
- **AEC/NASA: Rover/NERVA – NF-1 (1972)**
  - (UC-ZrC)C "Composite"
    - 47 of 49 cells in furnace
  - (U, Zr)C (0%, 3%, 8% Zr impregnation)
    - 2 of 49 cells in furnace
    - 8% Zr elements demonstrated minimum fracture behavior
- **Russia**
  - 1970-1986 (RD-0410 Engine)
    - (U, Zr)C
    - (U, Zr, Nb)C – "twisted ribbon" fuel element
  - 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



Nuclear Furnace (NF-1) Transverse View



NF-1 Reactor Cell Containing (U,Zr)C-Graphite Composite Fuel Elements



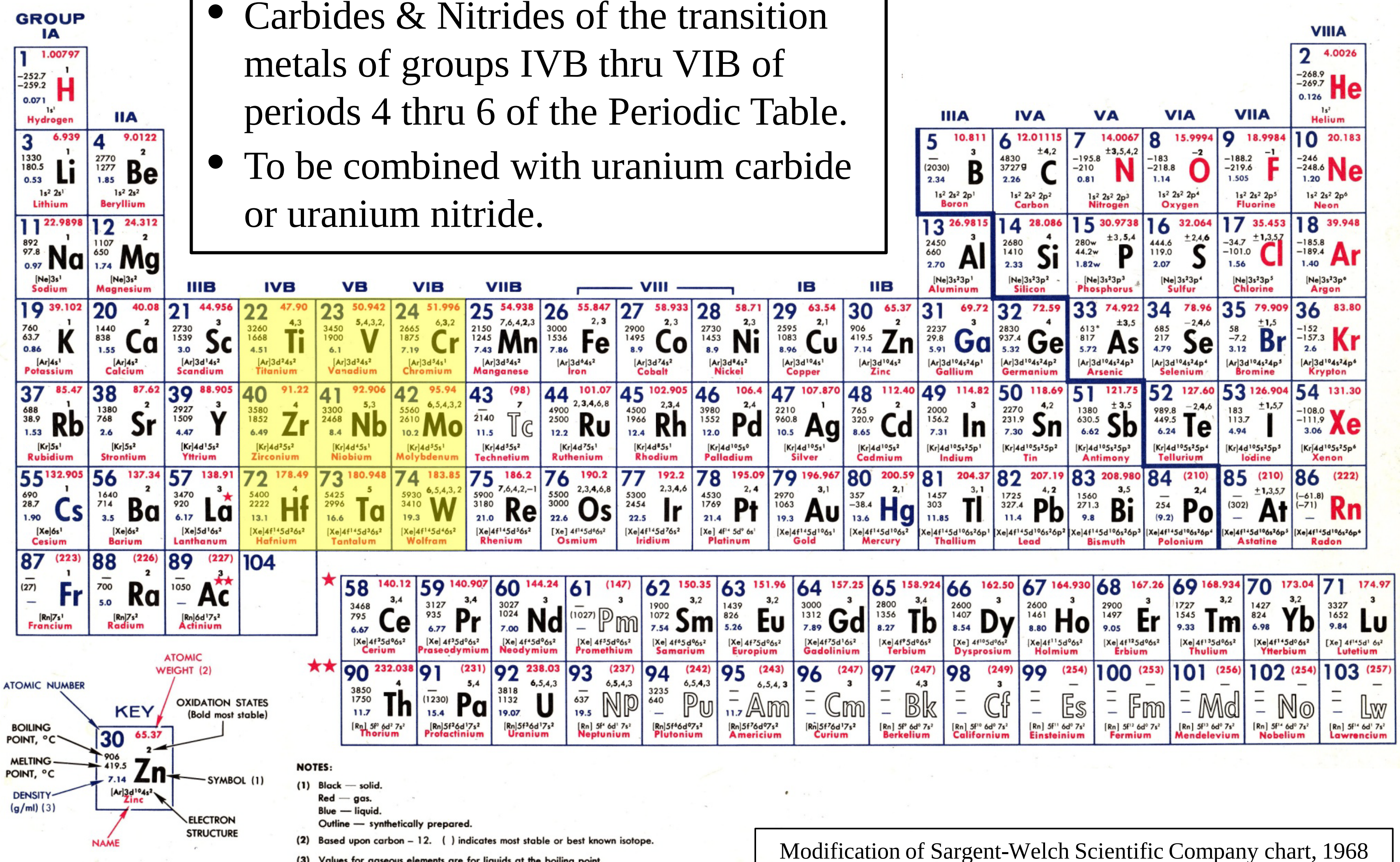
NF-1 Reactor Cell Containing (U,Zr)C Fuel Elements

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^0 Cross-Sections

Compound	Melting Point (K)
$Cr_{23}C_6$	1850
Cr_3C_2	2080
HfC	4220
$HfC_{0.88}$	4200
Mo_2C	2795
MoC	2870
NbC	3890
$NbC_{0.85}$	3871
NbC_2	3353
TaC	4260
$TaC_{0.88}$	4273
TaC_2	3600

Compound (continued)	Melting Point (K)
TiC	3340
UC	2800
$UC_{0.98}$	2798
UC_2	2860
V_2C	2440
VC	3083
$VC_{0.75}$	2920
W_2C	3050
WC	3050
ZrC	3690
$ZrC_{0.81}$	3693

Element	Thermal Neutron Absorption Cross Section (barns)
C	0.0035
N	1.9
Cr	3.05
Hf	104.1
Mo	2.48
Nb	1.15
Ta	20.6
Ti	6.09
V	5.08
W	18.3
Zr	0.185

Rating Scale: Worst → Best

Conductivities, CTE's, Vapor Pressures

Compound	Thermal Cond. (W/m·K)	CTE (10^6/K)
Cr_3C_2	19	10.2
HfC	22	6.8
MoC	8	6
Mo_2C	N/A	5.6
NbC	30	6.9
TaC	22	6.6
TiC	50	7.9
WC	29	5
W_2C	29	4
UC	25	**12**
UC_2	33	10
$VC_{0.75}$	39	8.4
ZrC	20	7.3

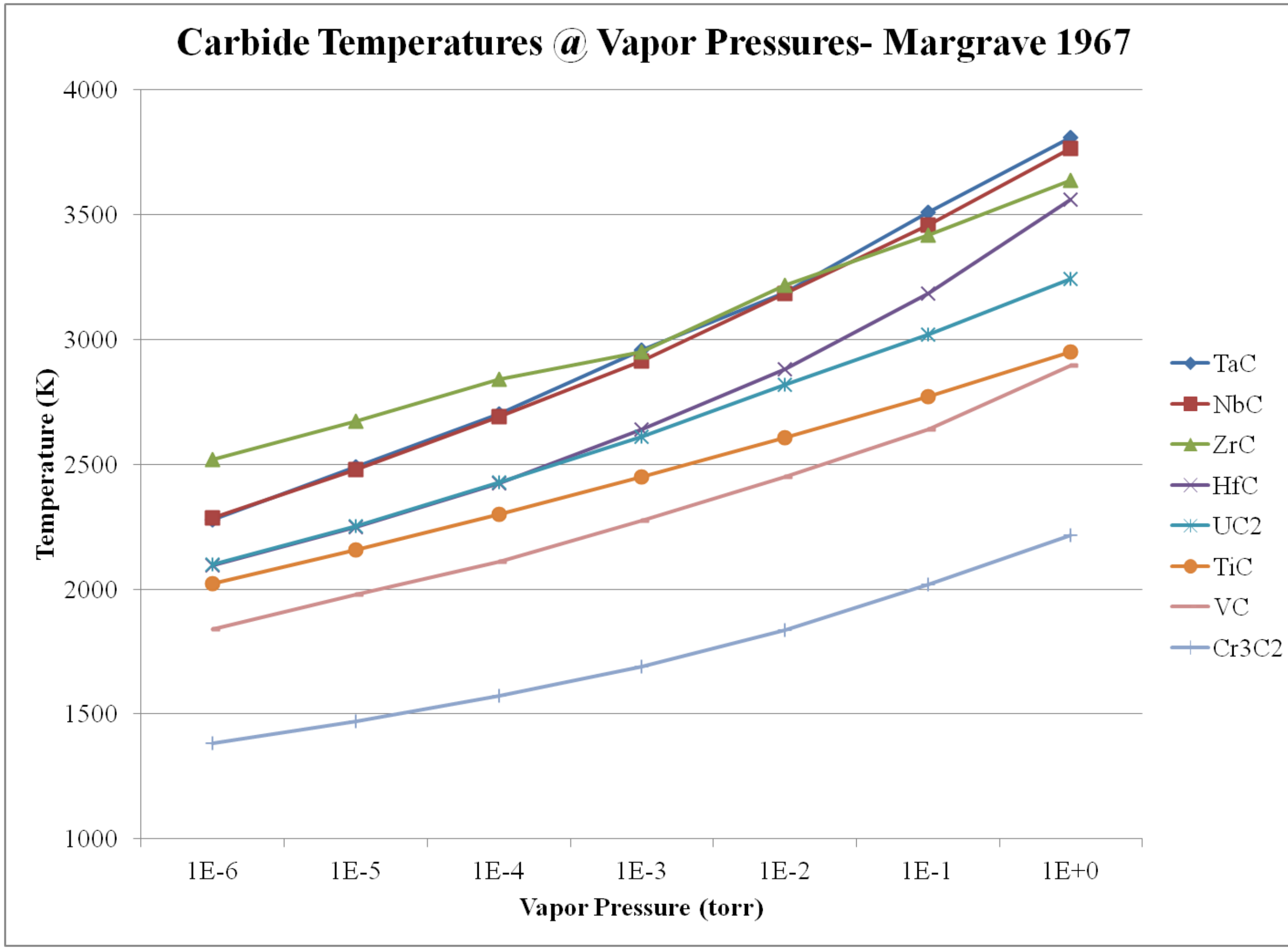


Table Rating Scale: Worst → Best

Fabrication Processes To Be Investigated

- **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

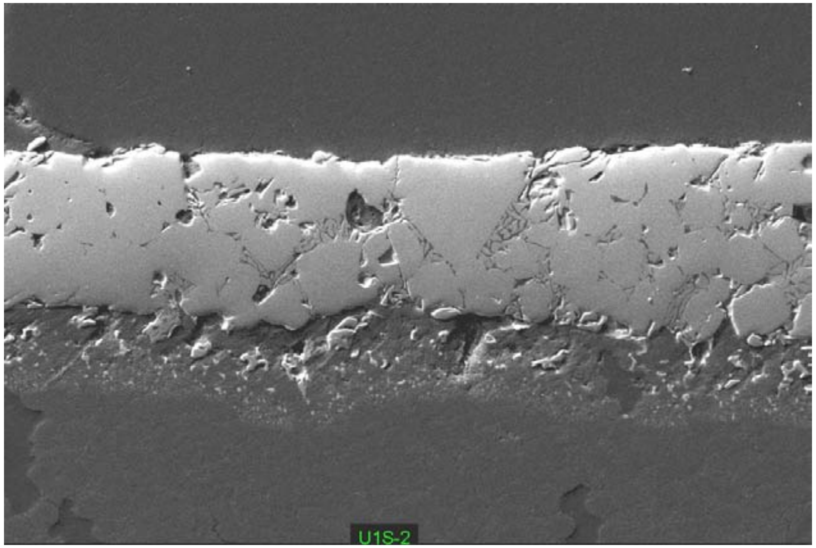
- **Development and Fabrication of Prototype Fuel Elements**
  - Fabricate test pieces with more fuel-element-like geometries:
    - Increased diameters and lengths; addition of through-holes
  - Assess path forward for fabricating all-ceramic 3200K fuel elements

Coatings for Graphite Composites

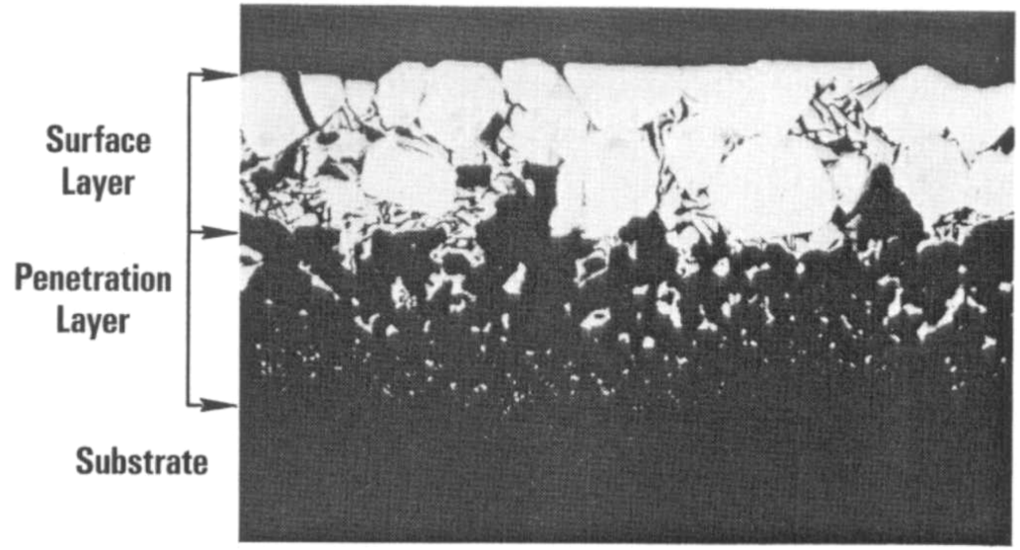
Development of Ceramic Reaction-Sintered Coatings (CRSC's) for graphite-based fuel elements being pursued to allow additional options.

- **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
    - Precursor coating material reacts with outer portion of substrate (~ 50 μm)
    - Two-layer type coating microstructure, with graded interaction with substrate
  - Hard, adherent coatings formed that can withstand very high temperatures
    - 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
    - As boron is undesirable, mixtures of carbides and nitrides will be investigated

Typical Coating Microstructures



100 µm
(0.004 in.)



50 µm
(0.002 in.)

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

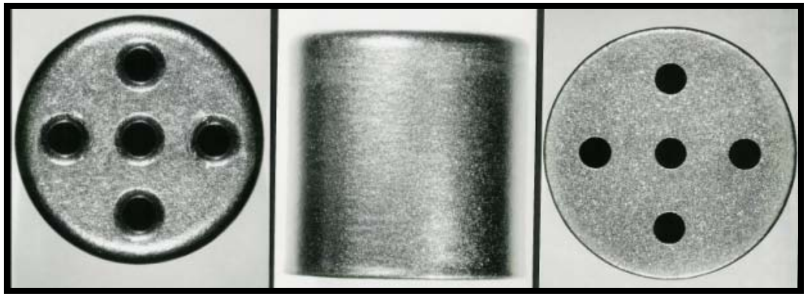
Prior CRSC Development Efforts:

- 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.

ISUS (Integrated Solar Upper Stage) Development Components



Top | Side | Bottom

Solid-Fuel Pintle and Pintle Seat

Summary

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