The background of the slide is a composite image of space. In the foreground, the blue and white horizon of Earth is visible. In the middle ground, the grey, cratered surface of the Moon is prominent. In the background, the reddish-orange planet Mars is visible. A satellite with solar panels is seen in the lower right. The NASA logo is in the top right corner. The title text is in a yellow, italicized font.

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

**P.G. Valentine,
L.R. Allen,
A.P. Shapiro**

**NASA Marshall Space
Flight Center**

*NETS 2012
March 23, 2012*



Presentation Outline

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**
 - 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

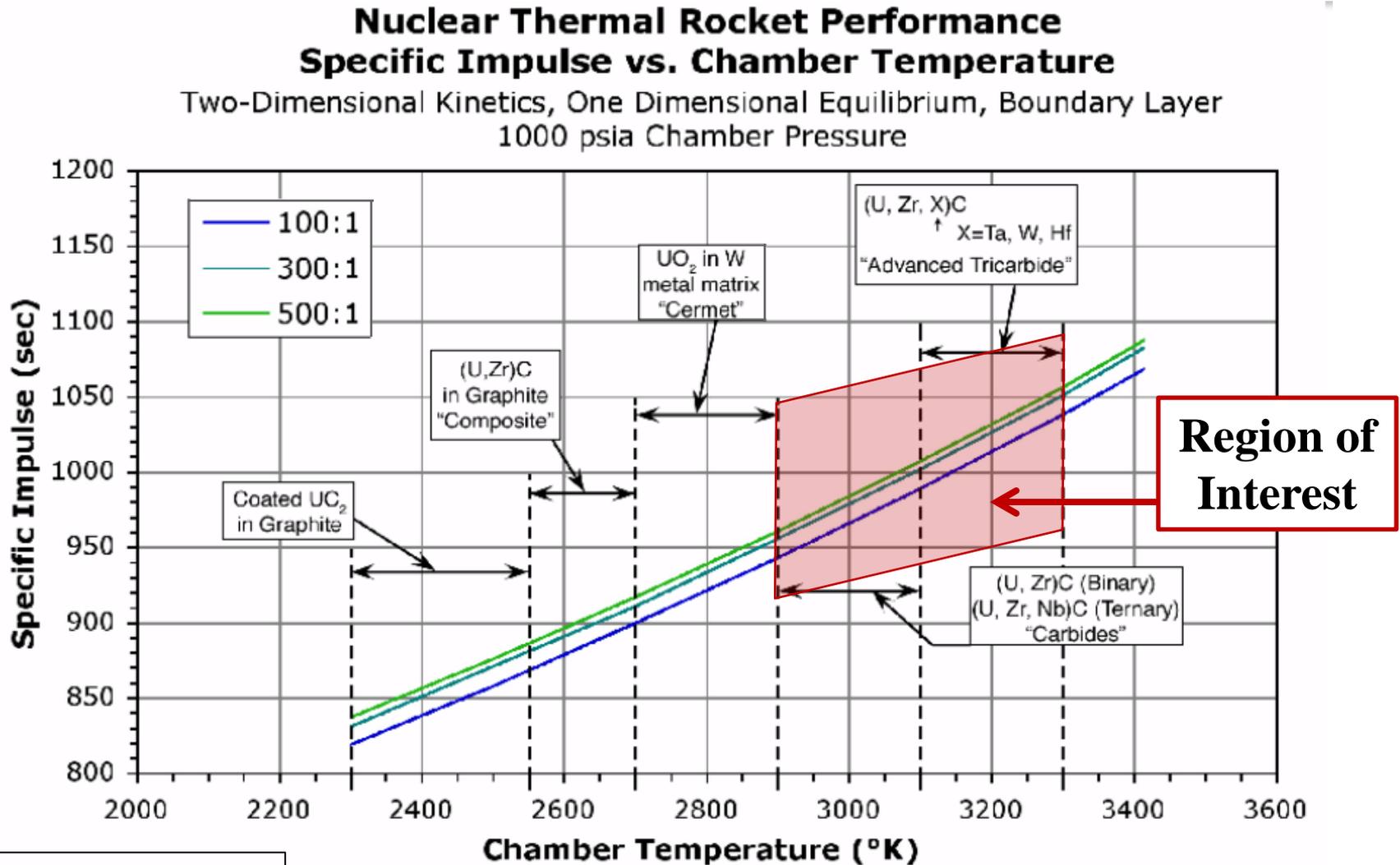
- Lowest TRL approach, but with greatest performance potential
- All-ceramic fuel elements – investigating carbides and nitrides**

** 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

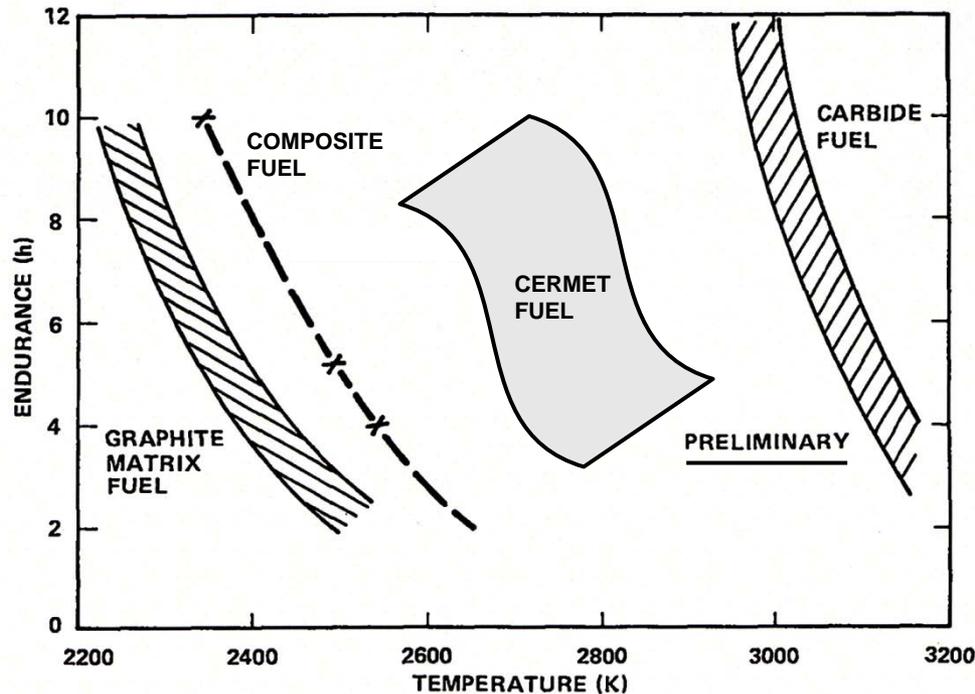
Carbide and/or nitride fuel elements have the potential to enable the highest performance class of fuel elements being considered for NTP.

- 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 UC₂)



Program Goal for NTP Fuel Elements

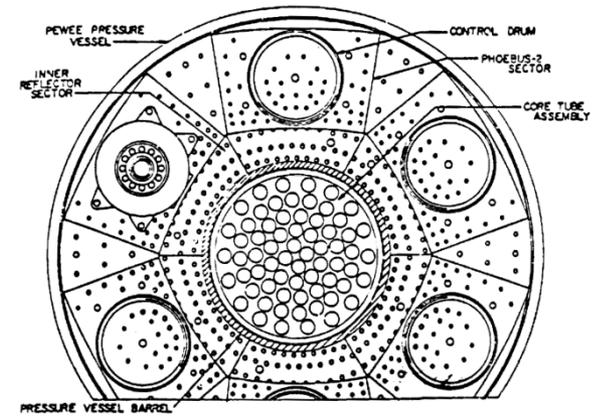
- To Operate:
- At extremely high temperatures (3200K, or above),
 - For “long” lifetimes (at least 10 hrs.),
 - In a very reactive environment (hot H₂ propellant),
 - With little or no degradation.



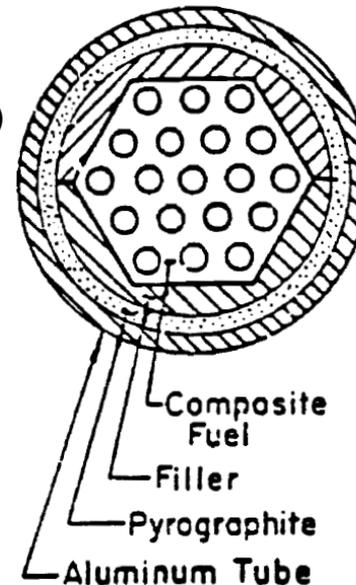


Past Efforts with All-Ceramic Fuels

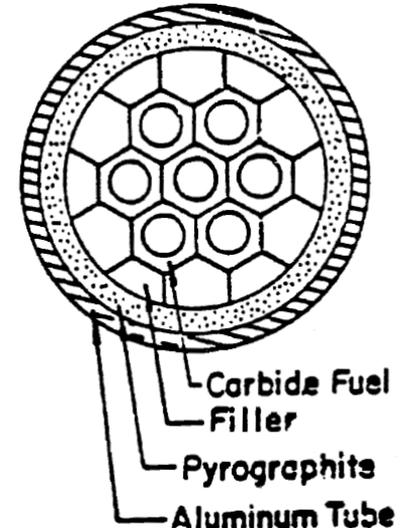
- **AEC/NASA: Rover/NERVA – NF-1 (1972)**
 - (UC-ZrC)C “Composite”
 - 47 of 49 cells in furnace
 - (U, Zr)C (0%, 3%, 8% Zr impregnation)
 - 2 of 49 cells in furnace
 - 8% Zr elements demonstrated minimum fracture behavior
- **Russia**
 - 1970-1986 (RD-0410 Engine)
 - (U, Zr)C
 - (U, Zr, Nb)C – “twisted 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**
 - DUO₂-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.

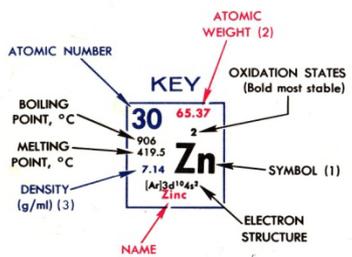
- **Secondary Goals:** Besides fully characterizing the constituent powder materials used and defining all fabrication processing steps and procedures, the following will be accomplished:
 - Assess resistance to thermal environment – melting point, vaporization losses, phase stability, overall durability, 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.

GROUP IA										GROUP IIA										GROUP IIIA										GROUP IVA										GROUP VA										GROUP VIA										GROUP VIIA										GROUP VIIIA																																																																																																													
1 1.00797 -252.7 -259.2 0.071 H Hydrogen										3 6.939 1330 180.5 0.53 Li Lithium										4 9.0122 2770 1277 1.85 Be Beryllium										5 10.811 -2030 3727.9 2.34 B Boron										6 12.01115 4830 3727.9 2.26 C Carbon										7 14.0067 -195.8 -210 0.81 N Nitrogen										8 15.9994 -188.2 -218 1.14 O Oxygen										9 18.9984 -188.2 -219.6 1.505 F Fluorine										10 20.183 -246 -248.6 1.20 Ne Neon																																																																																																			
11 22.9898 892 97.8 0.97 Na Sodium										12 24.312 1107 650 1.74 Mg Magnesium										13 26.9815 2450 660 2.70 Al Aluminum										14 28.086 3680 1410 2.33 Si Silicon										15 30.9738 2800 1410 2.33 P Phosphorus										16 32.064 4444 44.2 2.07 S Sulfur										17 35.453 -34.7 -101.0 1.56 Cl Chlorine										18 39.948 -185.8 -189.4 1.40 Ar Argon																																																																																																													
19 39.102 760 63.7 0.86 K Potassium										20 40.08 1440 1.55 Ca Calcium										21 44.956 2730 1539 4.51 Sc Scandium										22 47.90 3260 1668 4.51 Ti Titanium										23 50.942 3450 1900 6.1 V Vanadium										24 51.996 3450 1875 7.19 Cr Chromium										25 54.938 2150 1245 7.43 Mn Manganese										26 55.847 3000 1536 7.86 Fe Iron										27 58.933 2900 1495 8.9 Co Cobalt										28 58.71 2730 1453 8.9 Ni Nickel										29 63.54 2595 1086 8.96 Cu Copper										30 65.37 906 419.5 7.14 Zn Zinc										31 69.72 2237 29.8 5.91 Ga Gallium										32 72.59 2830 937.4 5.32 Ge Germanium										33 74.922 613 817 5.72 As Arsenic										34 78.96 2800 444.5 2.19 Se Selenium										35 79.909 58 217 3.12 Br Bromine										36 83.80 -152 -157.3 2.6 Kr Krypton									
37 85.47 688 38.9 1.53 Rb Rubidium										38 87.62 1380 768 2.6 Sr Strontium										39 88.905 2927 1509 4.47 Y Yttrium										40 91.22 3580 1852 6.49 Zr Zirconium										41 92.906 3400 2368 8.4 Nb Niobium										42 95.94 5560 2610 10.2 Mo Molybdenum										43 (98) 2140 11.5 Tc Technetium										44 101.07 4900 2500 12.2 Ru Ruthenium										45 102.905 4500 1966 12.4 Rh Rhodium										46 106.4 3982 1966 12.0 Pd Palladium										47 107.870 2210 960.8 10.5 Ag Silver										48 112.40 765 320.9 8.65 Cd Cadmium										49 114.82 2000 7.31 In Indium										50 118.69 2270 231.9 7.30 Sn Tin										51 121.75 613 630.5 6.62 Sb Antimony										52 127.60 1380 449.5 6.24 Te Tellurium										53 126.904 183 113.7 4.94 I Iodine										54 131.30 -108.0 -111.9 3.06 Xe Xenon									
55 132.905 690 28.7 1.90 Cs Cesium										56 137.34 1640 714 3.5 Ba Barium										57 138.91 3470 2222 6.17 La Lanthanum										58 140.12 3468 795 6.77 Ce Cerium										59 140.907 3127 935 6.77 Pr Praseodymium										60 144.24 3027 1024 7.02 Nd Neodymium										61 (147) 1900 1072 7.54 Pm Promethium										62 150.35 1900 1072 7.54 Sm Samarium										63 151.96 1439 826 7.89 Eu Europium										64 157.25 3000 1312 8.27 Gd Gadolinium										65 158.924 2800 1356 8.27 Tb Terbium										66 162.50 2600 1407 8.54 Dy Dysprosium										67 164.930 2600 1461 8.54 Ho Holmium										68 167.26 2900 1497 9.05 Er Erbium										69 168.934 1727 1543 9.33 Tm Thulium										70 173.04 1427 824 6.98 Yb Ytterbium										71 174.97 3327 1652 9.84 Lu Lutetium																			
87 (223) -27 7.0 Fr Francium										88 (226) 500 7.14 Ra Radium										89 (227) 1050 6.17 Ac Actinium										90 232.038 3850 1750 11.7 Th Thorium										91 (231) 3127 935 6.77 Pa Protactinium										92 238.03 3818 1132 19.07 U Uranium										93 (237) 637 19.5 Np Neptunium										94 (242) 3235 640 Pu Plutonium										95 (243) 6.5, 4, 3 11.7 Am Americium										96 (247) 3 Cm Curium										97 (247) 4, 3 Bk Berkelium										98 (249) 3 Cf Californium										99 (254) 3 Es Einsteinium										100 (253) 3 Fm Fermium										101 (256) 3 Md Mendelevium										102 (254) 3 No Nobelium										103 (257) 3 Lw Lawrencium																			



- NOTES:**
- (1) Black — solid.
Red — gas.
Blue — liquid.
Outline — synthetically prepared.
 - (2) Based upon carbon - 12. () indicates most stable or best known isotope.
 - (3) Values for gaseous elements are for liquids at the boiling point.

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 ₃ C ₂	2080
HfC	4220
HfC _{0.88}	4200
Mo ₂ C	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 ₂ C	2440
VC	3083
VC _{0.75}	2920
W ₂ C	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:





Conductivities, CTE's, Vapor Pressures

Compound	Thermal Cond. (W/m·K)	CTE (10 ⁶ /K)
Cr ₃ C ₂	19	10.2
HfC	22	6.8
MoC	8	6
Mo ₂ C	N/A	5.6
NbC	30	6.9
TaC	22	6.6
TiC	50	7.9
WC	29	5
W ₂ C	29	4
UC	25	12
UC ₂	33	10
VC _{0.75}	39	8.4
ZrC	20	7.3

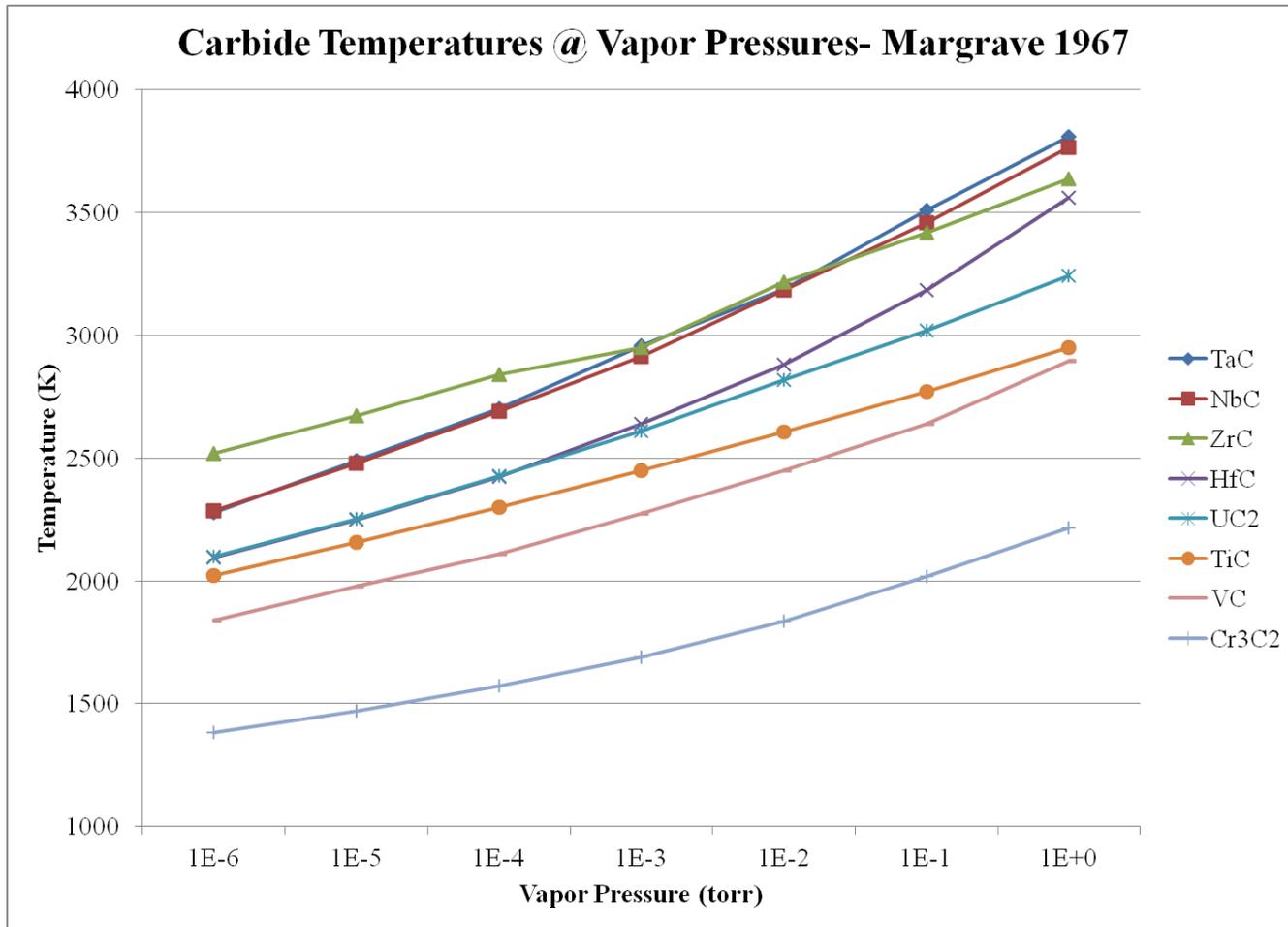


Table Rating Scale:





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:**

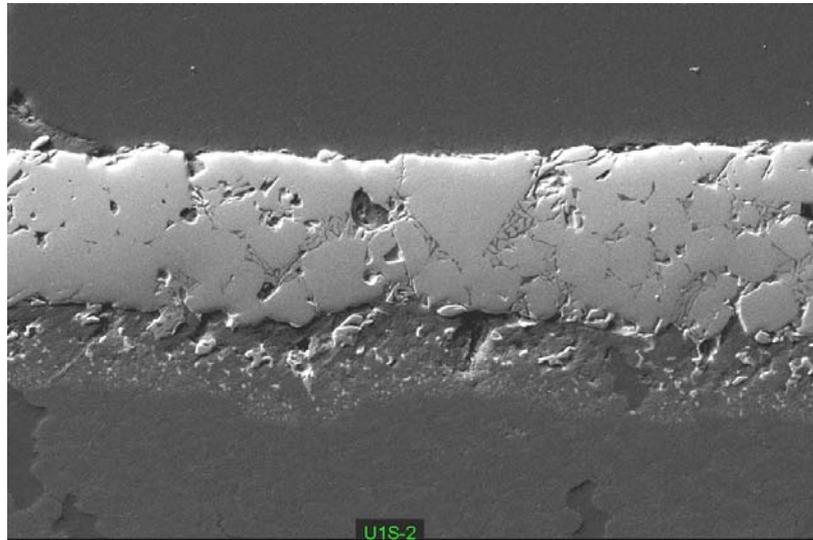
- Coating process involves simultaneous eutectic melting and powder particle sintering
 - Precursor coating material reacts with outer portion of substrate (~ 50 μm)
 - Two-layer type coating microstructure, with graded interaction with substrate
- Hard, adherent coatings formed that can withstand very 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:**

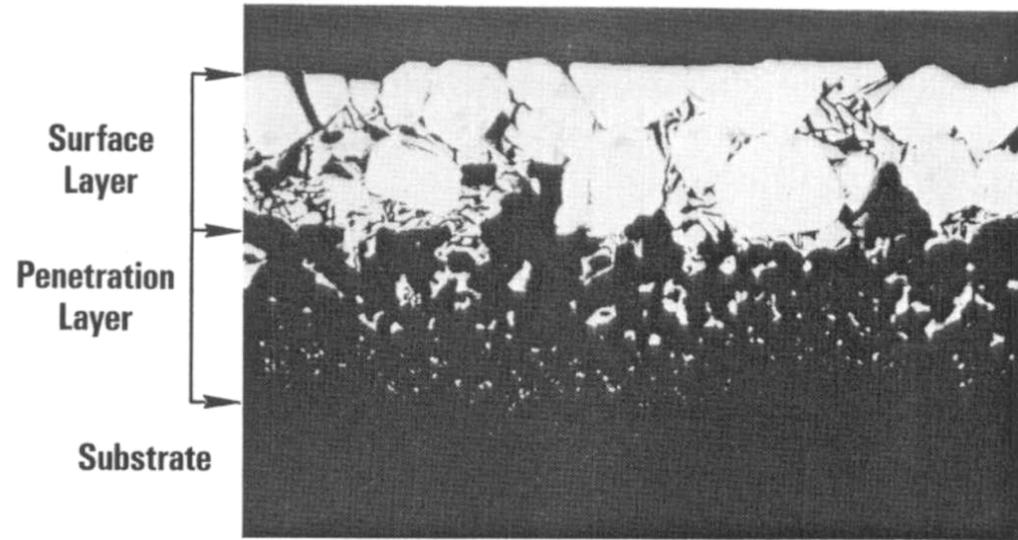
- Supports Oak Ridge National Laboratory led graphite composites effort
- Based upon prior work with CRSC's fabricated with carbide/boride mixtures
 - As boron is undesirable, mixtures of carbides and nitrides will be investigated



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.

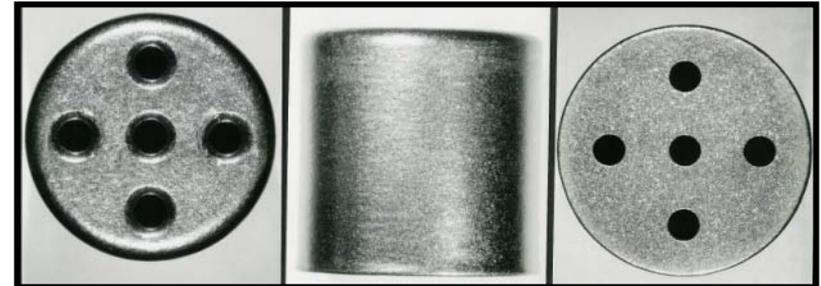


Coatings Applications Investigated

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

ISUS (Integrated Solar Upper Stage) Development Components



Top

Side

Bottom

Solid-Fuel Pintle and Pintle Seat



For both applications depicted at right:

HfB₂-HfC Coatings on Poco Graphite, Grade AXF-5Q.



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