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Ultra-High Temperature Ceramics: Historic Perspectives and Recent Progress

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Ultra-High Temperature Ceramics

Historic Perspective and Recent Progress

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Historic Context

- Boride and carbide synthesis noted as far back as mid 1800s
- Moisson studied transition metal carbides in the late 1800s
  - Developed specialized electric arc furnace
  - Pioneer in SiC research (artificial diamond)
- Reactive processing of ZrB_2
  - Tucker and Moody, Proc. Chem. Soc. 17, 129 (1901).

"Although many of the refractory materials displayed capabilities for leading-edge and nose applications, some development efforts would be required to produce satisfactory components from these materials"

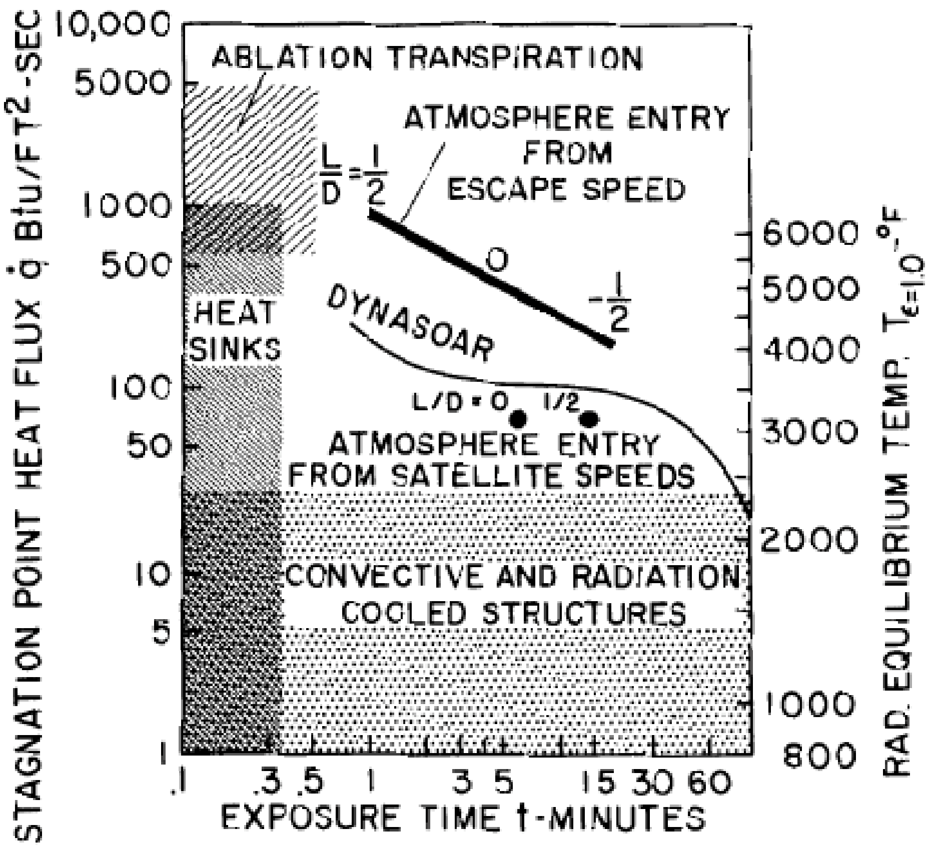
E.B. Mathauser, "Materials for Application to Manned Reentry Vehicles," pp. 559-570 in U.S. Air Force and NASA Joint Conference on Lifting Hypervelocity and Reentry Vehicles, April 11-14, 1960.

UHTC is a Recent Term

- Terms from literature of the 1960s and 70s
  - Refractory transition metal borides
  - Oxidation resistant diboride materials
  - Hard metals
  - Ceramals

Recommendation 12: “Studies on materials at extreme temperatures and establishment of thermal and other pertinent material properties”

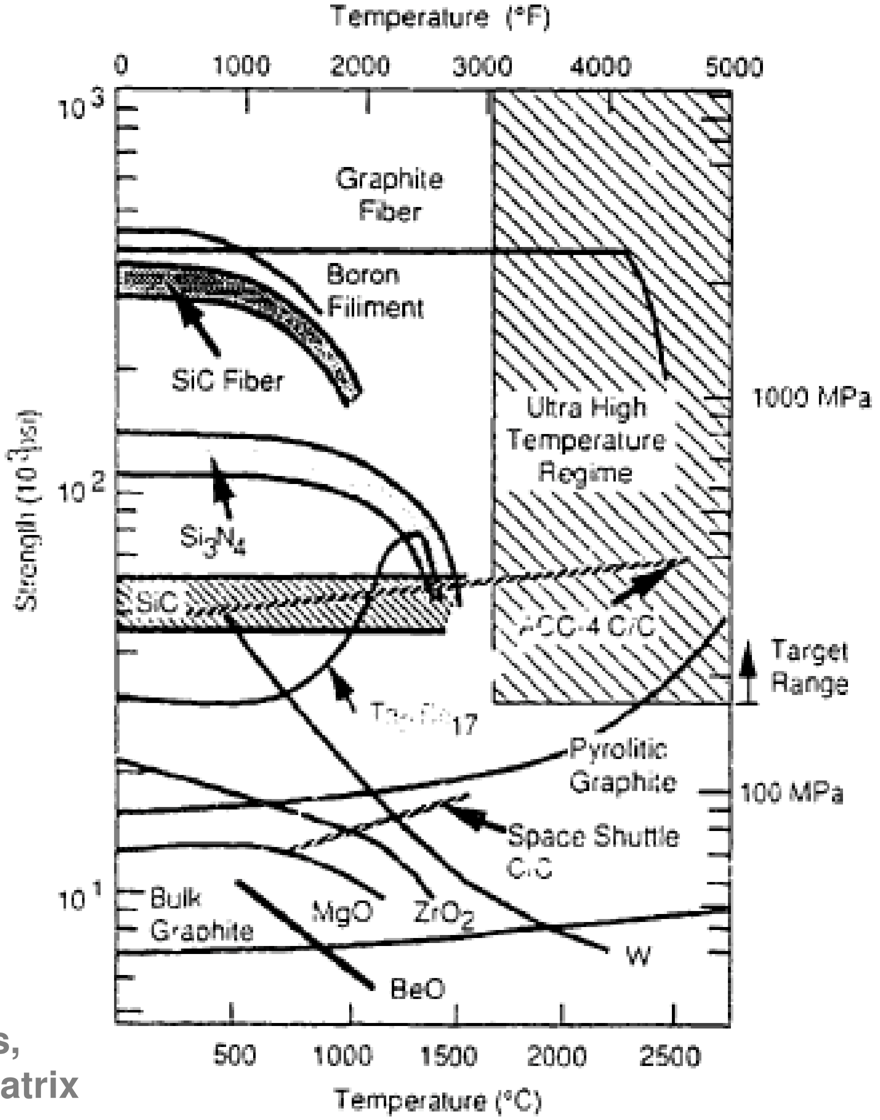
“Thermal Protection Systems: Report on the Aspects of Thermal Protection of Interest to NASA and the Related R&D Requirements” NASA Technical Memorandum X-650, 1962.



NOTE: AREAS OF APPLICABILITY OF VARIOUS TPS BY DR. W. STEURER

UHTC is a Recent Term

- Term first used in the open literature in the late 1980s and early 90s
  - 1989: AFRL report “Ultra-High Temperature Ceramic Composites by K. Vedula from CWRU
  - 1991: AFRL report “Ultra-High Temperature Applications” by Mehrotra from Wright State Univ.
  - 1993: “Ultra-High Temperature Assessment Study” by Katz, Kerans, et al.
  - 1994: NASA report “Ultra-High Temperature Ceramics” by D.J. Rasky and J.D. Bull
  - NSWC CrB_2-NbB_2 from NSWC 1997



E.L. Courtright, H.C. Graham, A.P. Katz, and R.J. Kerans, “Ultra-High Temperature Assessment Study-Ceramic Matrix Composites,” WL-TR-91-4061, September 1992.

Historic Studies

- Projects sponsored by Air Force Materials Lab
  - Avco and Arthur Little examined thermodynamics and kinetics
  - ManLabs et al. studied thermomechanical properties
    Kaufman, Clougherty, Rhodes, Kalish, Tye, et al.
  - Aerojet focused on phase equilibria
    Rudy with Nowotny as a consultant
- NASA
  - Nozzle materials in the 1950s
  - TPS materials
- Russia
  - All aspects of borides and carbides
  - >2000 of publications by Samsonov

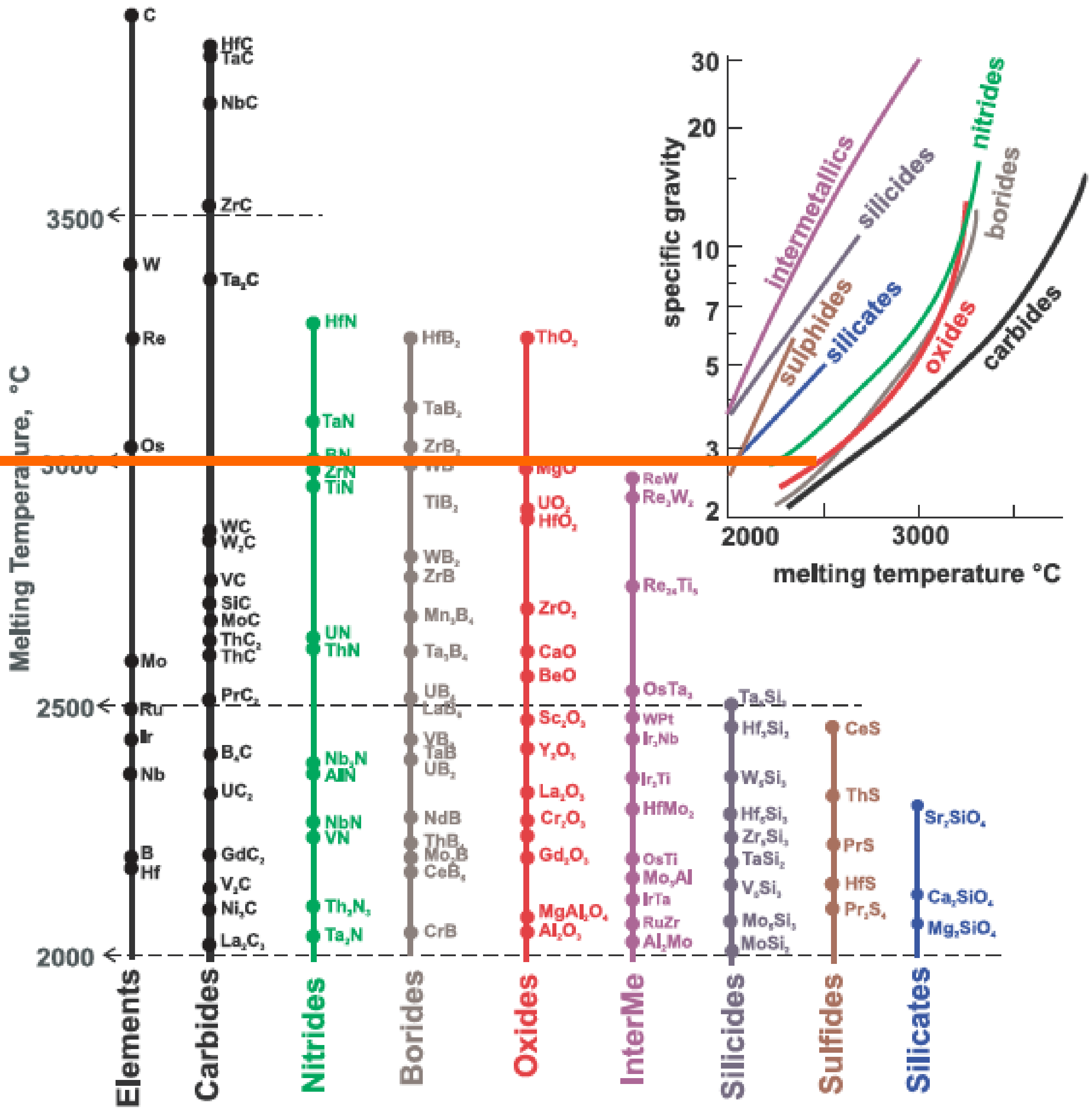
Image from G.S. Upadhaya, "Professor Grigorii Valentinovich Samsonov: The Complete Materials Scientist," Science of Sintering, 40, 99-103 (2008).

How Do We Define UHTCs?

- Melting temperature
  - Melting temperature above some threshold
  - 3000° C is commonly cited
- Use temperature
  - Can be used for extended times above some temperature
  - Extended use vs. short duration
  - SiC can be used up to 1650° C for short times
- Chemistry
  - Strong covalent bonds, but mixed bond character
  - Brittle at room temperature

Melting Temperature

S.V. Ushakov and A. Navrotsky, “Experimental Approaches to Thermodynamics above 1500° C,” Journal of the American Ceramic Society in press, DOI: 10.1111/j.1551-2916.2012.05102.x



Use Temperature

Today

Subsonic / Supersonic Flight Vehicles →

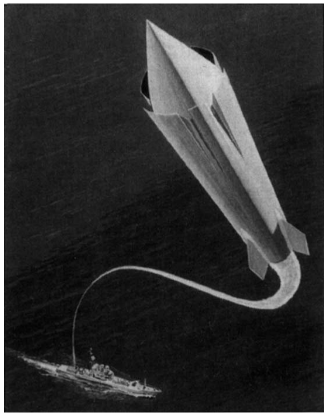
Future

Hypersonic Flight (Mach 4-5+)

- **Access to Space**
- **Global Reach**

Solid Propulsion Missiles →

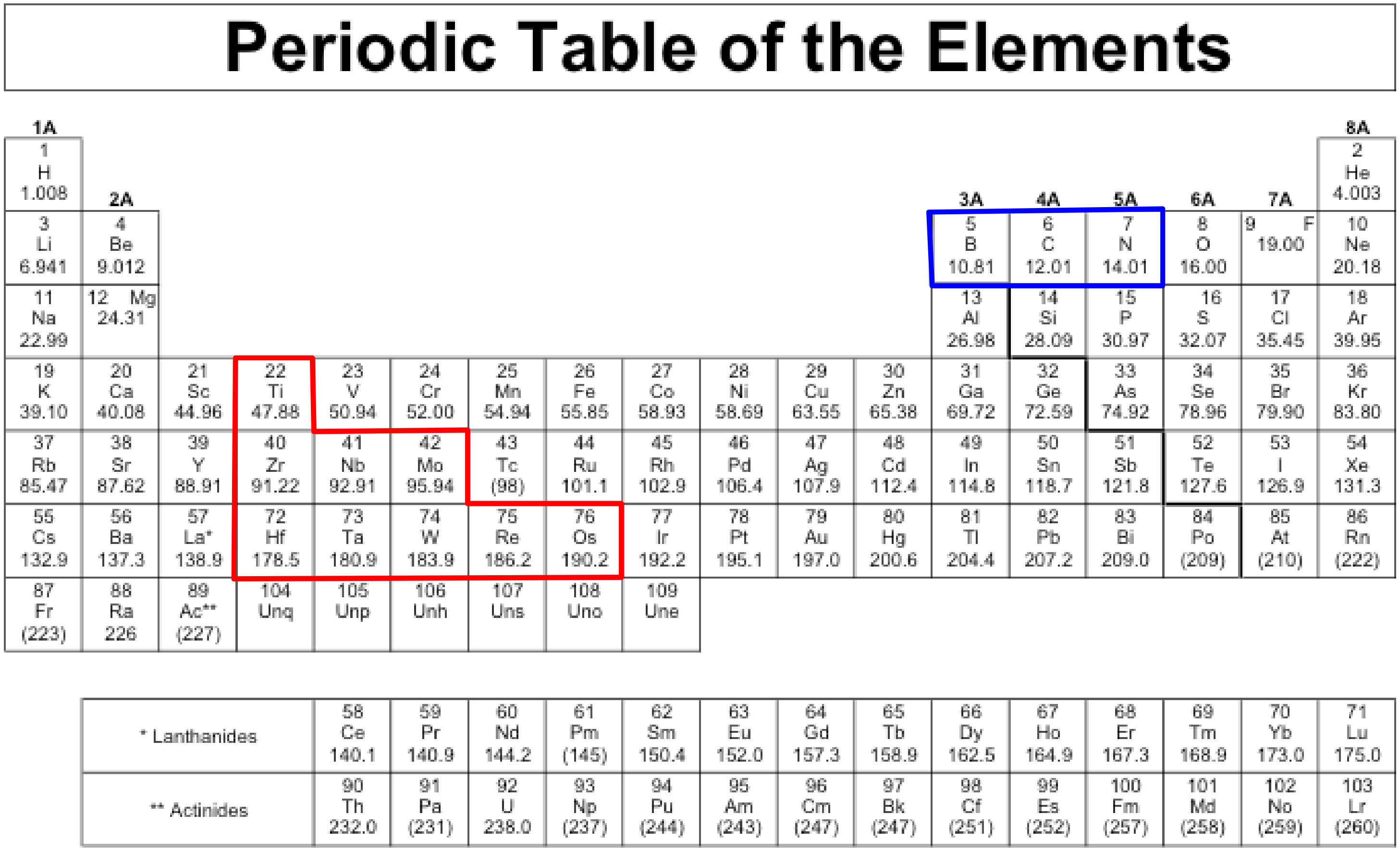
Hypersonic Airbreathers



Requires new materials with >2000° C capability

Based on slides by M. Opeka, U.S. Naval Surface Warfare Center

Chemistry



Periodic Table of the Elements

1A	2A											3A	4A	5A	6A	7A	8A
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac** (227)	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

* Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
** Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Research from the 1960s

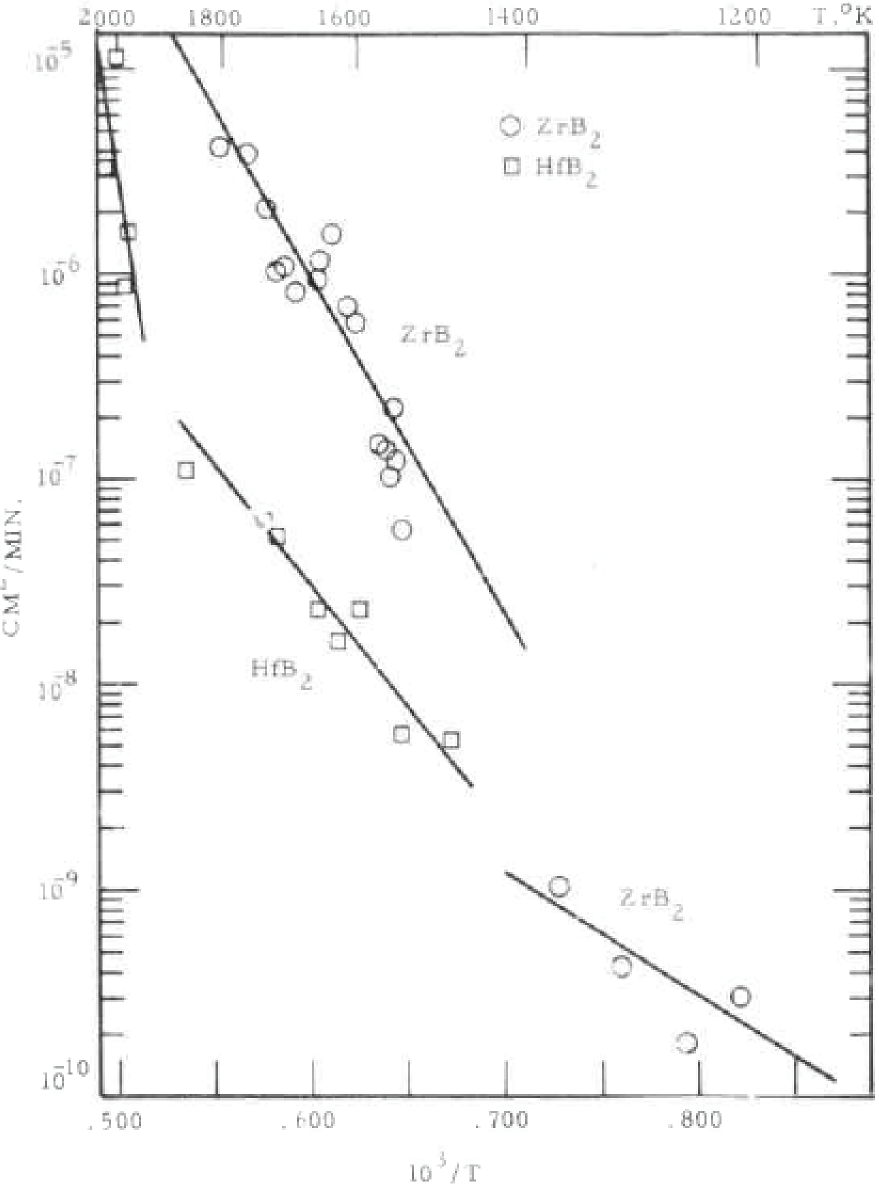
- Why diborides and carbides?
- How were Zr and Hf compounds identified?
- What was studied?
  - Thermochemical properties
  - Mechanical properties
  - Thermal properties
  - Oxidation and environmental studies
  - Phase equilibria
- Summary

Why Diborides and Carbides?

- Oxides found to be unsuitable for these temperatures
  - Melting temperatures are lower than borides and carbides
  - Creep is an issue
  - Resistance to thermal shock is poor
  - Thermal conductivity is too low
- Borides and carbides
  - Thermodynamically stable
  - Strong covalent bonding leads to higher strength
  - Strength is maintained at elevated temperatures
  - Bonding has metallic character
  - Thermal shock and creep resistance is higher

Why Diborides?

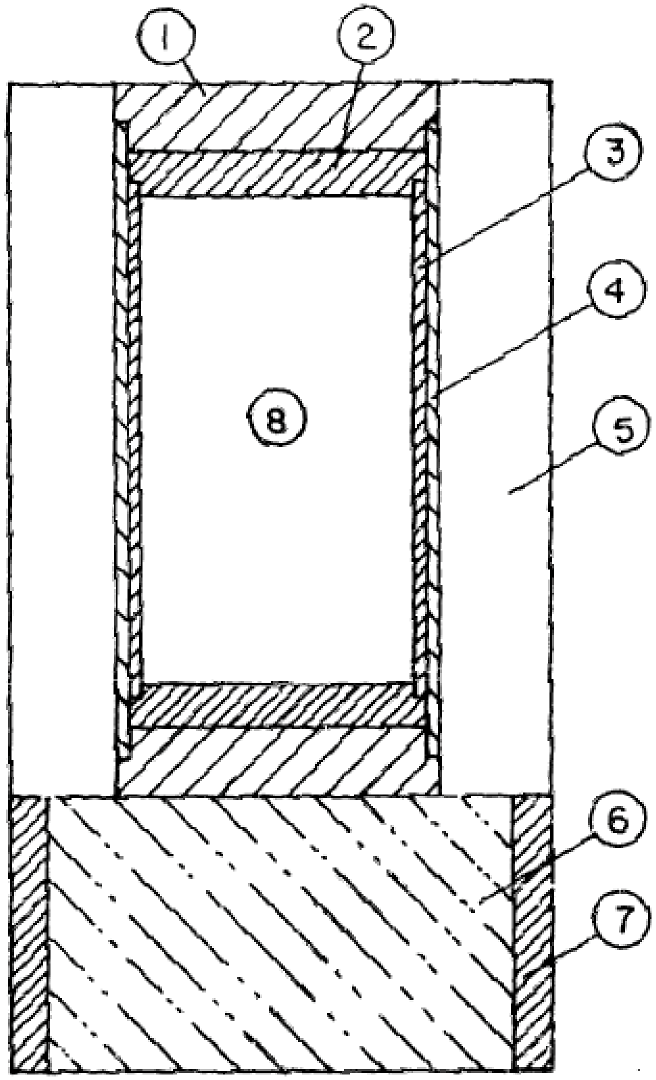
- **Thermodynamically stable**
  - **AFRL research focused on commercial materials that were further processed**
  - **Melted or zone refined using induction heating apparatus**
- **Oxidation behavior**
  - **Carbides showed linear kinetics over wide temperature range**
  - **Borides had parabolic kinetics at some temperatures and were deemed more promising**



L.A. McClaine, "Thermodynamic and Kinetic Studies for a Refractory Materials Program" ASD-TDR-62-204

Densification Behavior

- Army funded densification studies of B_4C, SiC, TiC, and TiN
  - Pressures up to 120 ksi or 850 MPa
  - Reactive hot pressing
  - Specimens were 1 inch in diameter
- Reported microstructures, strength and hardness

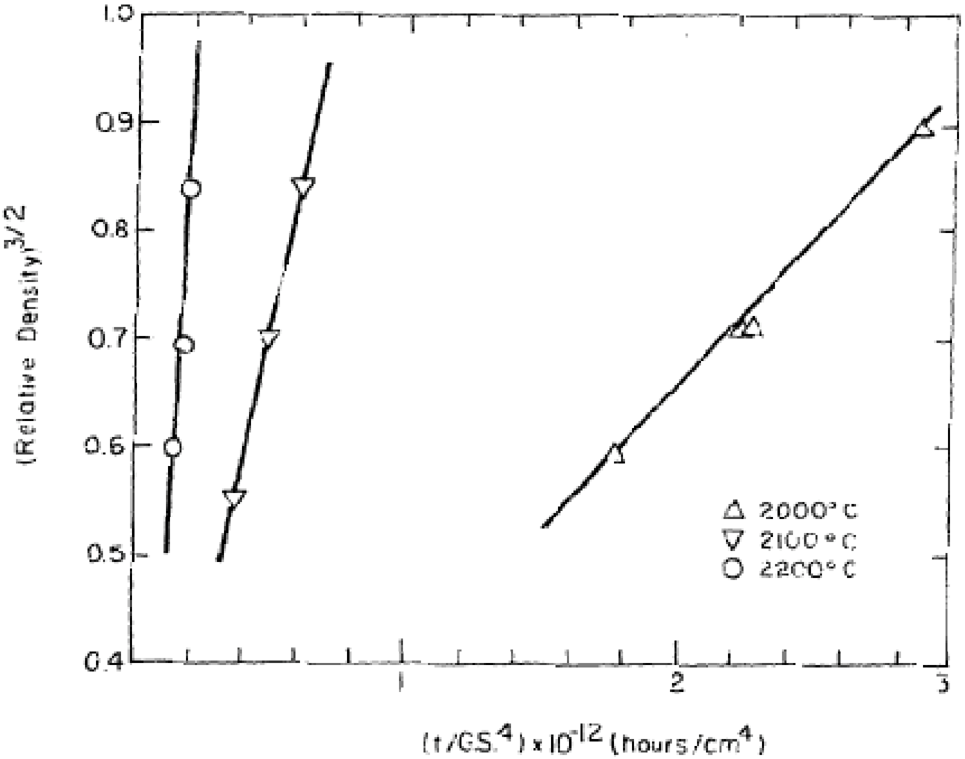


1. Furnace Contact Pad(Carbon)
2. Elec. Insulating Pad (BN)
3. Elec. Insulating Liner (BN)
4. Graphite Furnace
5. Thermal Insulator (Lava)
6. OL. FM. Closure
7. Closure Electrical Insulator (Lava)
8. Compact Chamber (1.0 inch diam. x 2.5 inches long)

D. Kalish, E.V. Clougherty, and J. Ryan, "Fabrication of Dense Fine Grained Ceramic Materials" AMRA CR 6 7-04(F)

Why Zr and Hf Diborides?

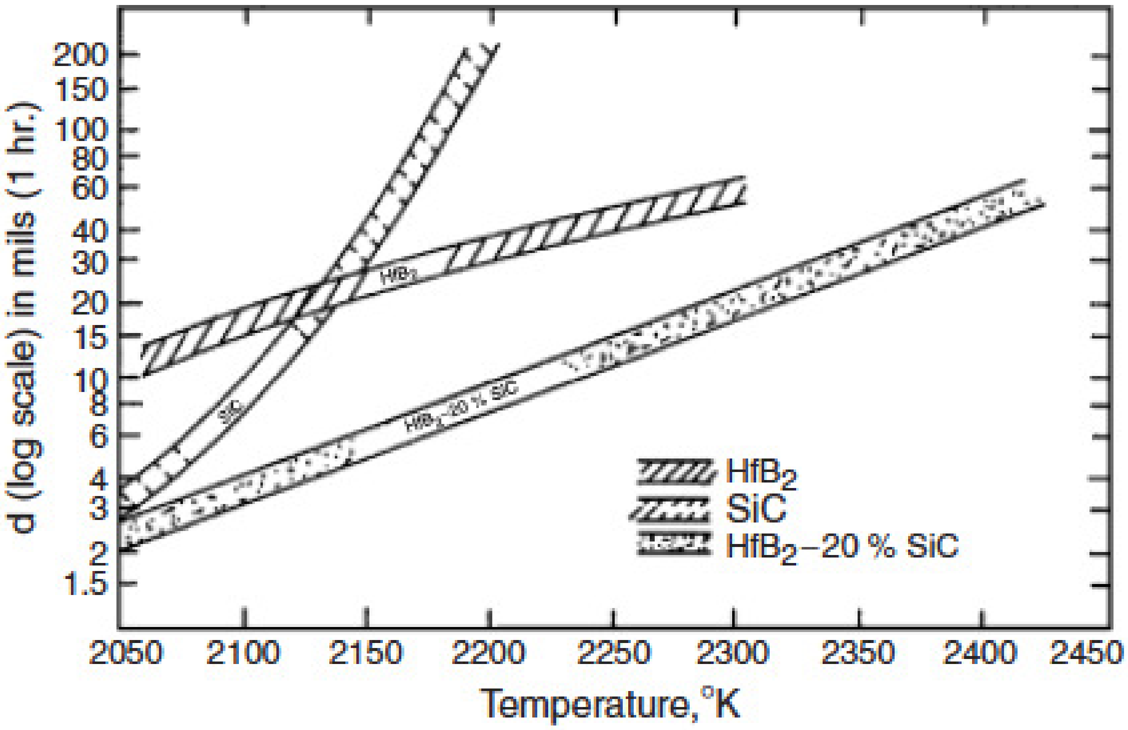
- Initial study focused on comparing borides and other materials
- Part II compared different borides
- Ranked oxidation behavior
  - HfB_2 and ZrB_2 best
  - Ta, Ti, and Nb compounds were inferior
- Examined impact of metal to boron ratio on densification, oxidation, and physical properties
- Temperatures up to 2300° C were needed for densification



L. Kaufman and E.V. Clougherty, “Investigation of Boride Compounds for Very High Temperature Applications” AFML-TR-68-190

Oxidation Behavior

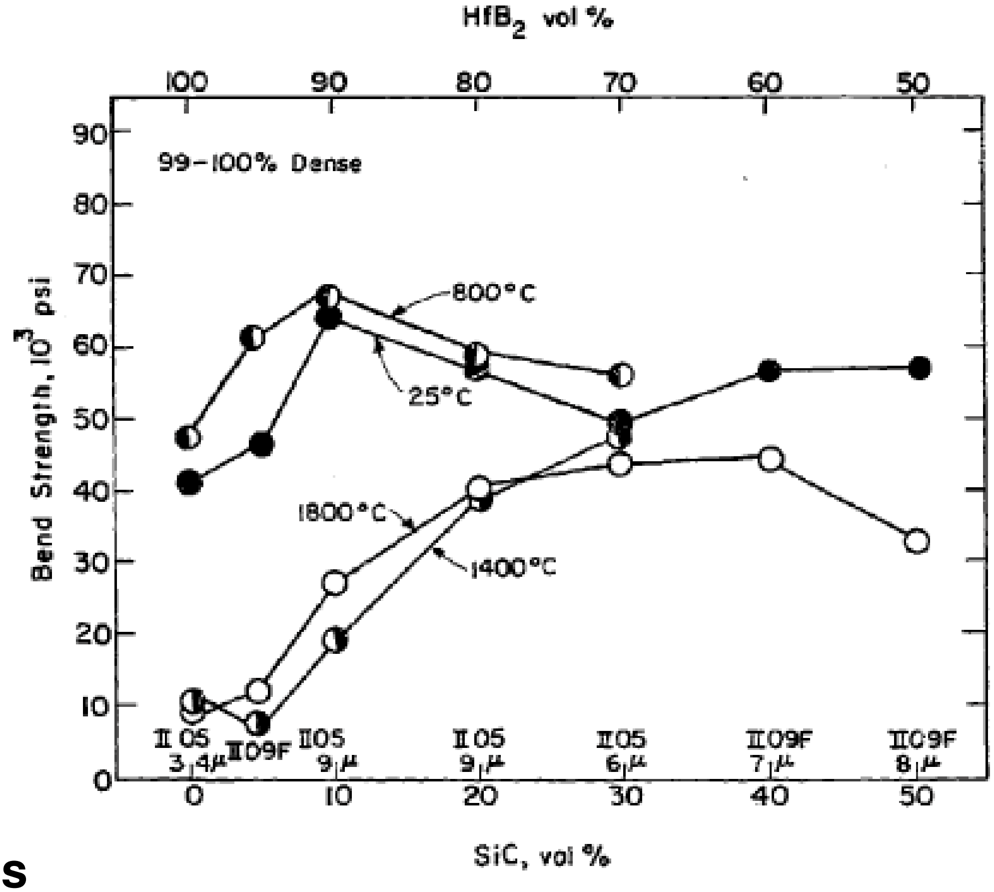
- Zr and Hf diborides were identified as the most promising
  - Lowest oxidation rates
- SiC additions improved oxidation rate at intermediate temperatures
  - Protective SiO_2 scale
- HfB_2 was better than ZrB_2



E.V. Clougherty, R.L. Pober, and L. Kaufman, “Synthesis of Oxidation Resistant Metal Diboride Composites,” Transactions of the Metallurgical Society of AIME, 242(6) 1077-1082 (1968).

Mechanical Properties

- Strength tested up to 1800° C
- Range of relative density values
- ZrB_2 and HfB_2
  - Nominally pure
  - SiC additions
  - Carbon additions
- Porosity reduces strength despite a decrease in grain size
- SiC reduces grain growth
- Carbon improves resistance to crack propagation and reduces elastic modulus



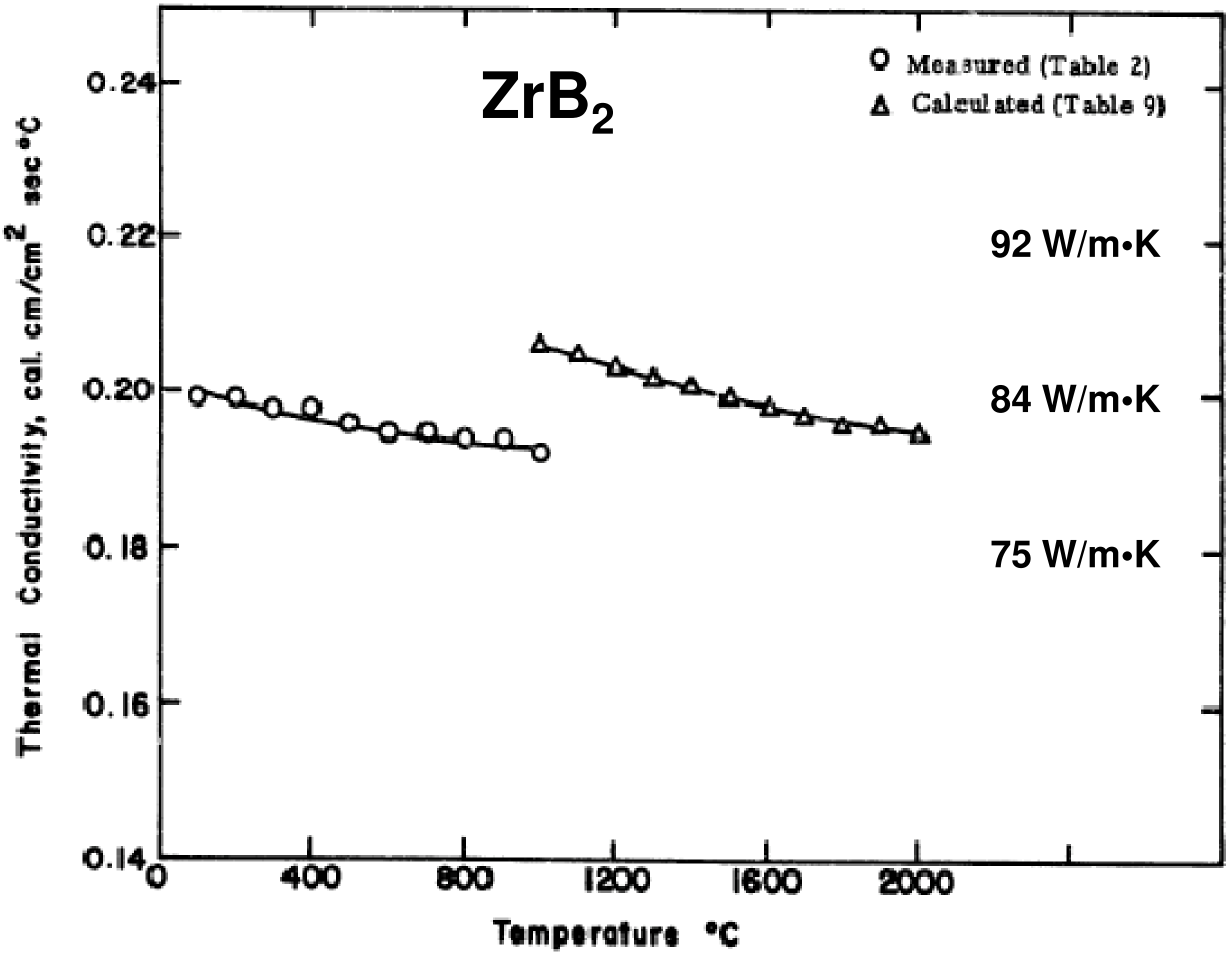
50 ksi ≈ 350 MPa

W.H. Rhodes, E.V. Clougherty, and D. Kalish "Research and Development of Oxidation-Resistant Diborides: Mechanical Properties" AFML-TR-68-190 Part II, Vol IV.

Thermal Properties

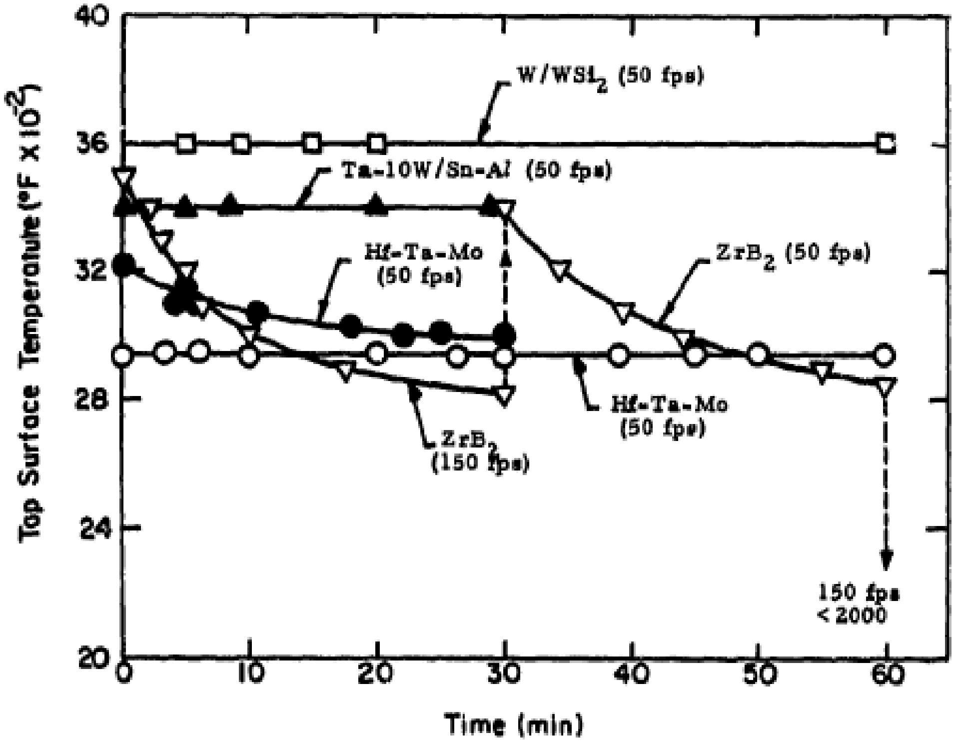
- Thermal conductivity measured 100° C to 1000° C by cut bar method
- Thermal diffusivity measured 1000° C to 2000° C by laser flash
- Also measured:
  - – CTE
  - – Total emittance
  - – C_P
  - – ΔS and ΔH
- Built unique equipment for their studies

E.V. Clougherty, K.E. Wilkes, and R.P. Tye, "Research and Development of Oxidation-Resistant Diborides: Thermal, Physical, Electrical, and Optical Properties" AFML-TR-68-190 Part II, Vol V.



High Velocity Testing

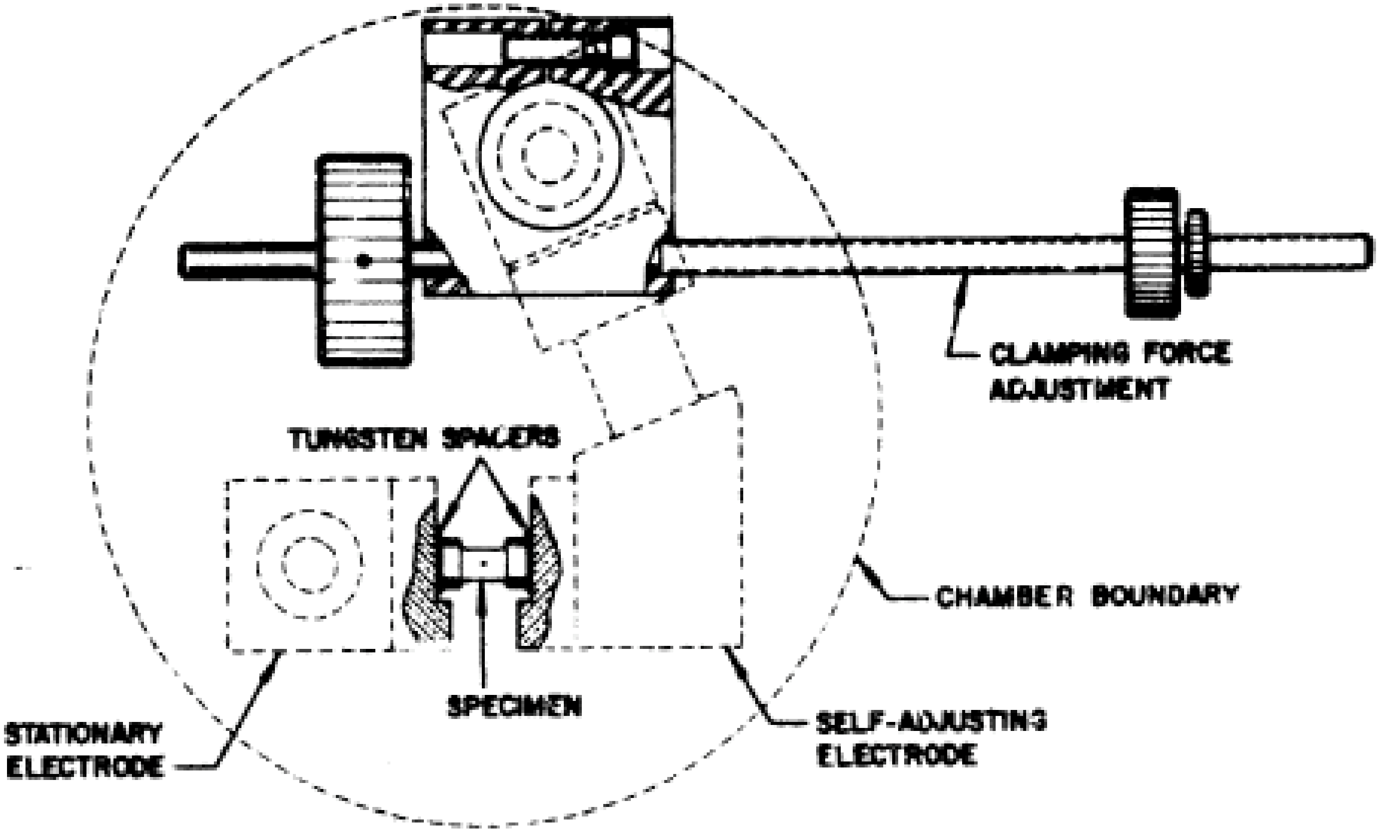
- Inductively heated furnaces (cold gas, hot wall)
  - Low velocity: 1 cm/sec, pO_2 range 0.013 atm to 0.2 atm, 1 atm total pressure.
  - High velocity: 100 m/sec, air
- Goal was to "bridge the gap" between furnace and arc heater testing
- Temperature gradients impacted results
  - Induction heating
  - Inverse T gradient due to insulating oxide scale



L. Kaufman and H. Nesor "Stability Characterization of Refractory Materials Under High Velocity Atmospheric Flight Conditions" AFML-TR-69-84 Part II, Vol II.

Phase Equilibria

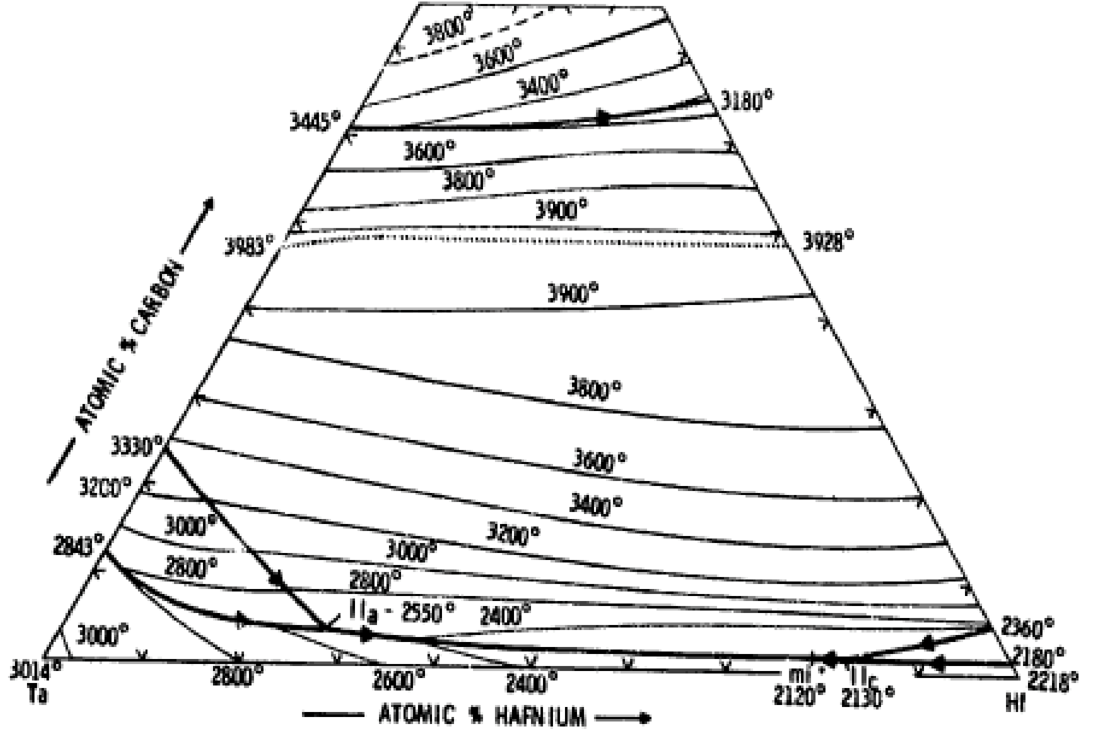
- Rudy designed equipment for ultra-high temperature studies
  - Pirani furnace for melting of refractory materials
  - Melting points, solidus studies

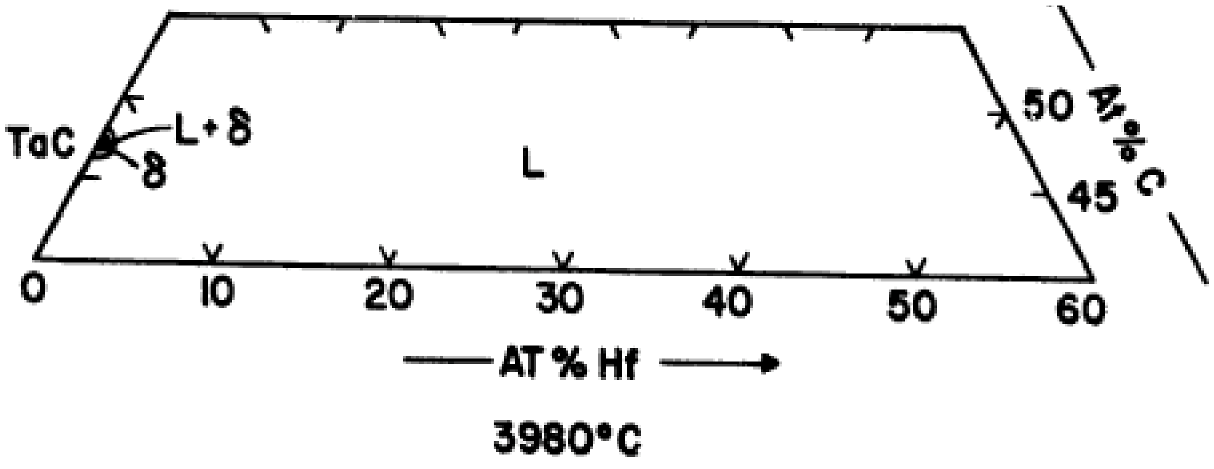


E. Rudy and G. Progulski, “Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems: Part III, Vol II. Special Test Procedures” AFRL-TR-65-2

Phase Equilibria

- Ta-Hf-C ternary system
- No maximum in melting temperature between HfC and TaC!





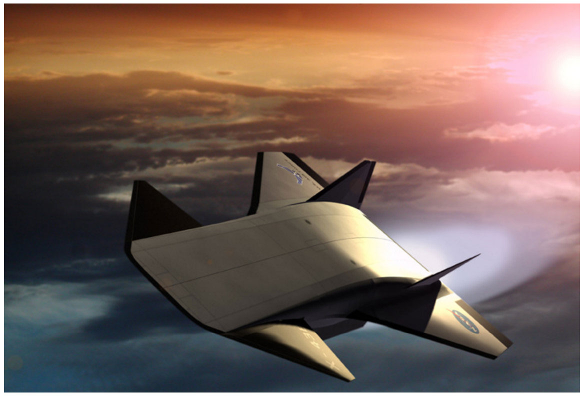
E. Rudy, "Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems: Part II, Vol I. Ta-Hf-C System" AFRL-TR-65-2

Summary of Historic Studies

- Detailed fundamental studies were conducted in the 1960s and 70s
  - AFRL-sponsored research in the U.S.
  - Samsonov and others in in the U.S.S.R.
- Unique equipment was designed and built
- Significant advances in fundamental science
  - Processing and densification
  - Oxidation
  - Mechanical behavior
  - Thermal properties
  - Phase equilibria and thermochemical properties

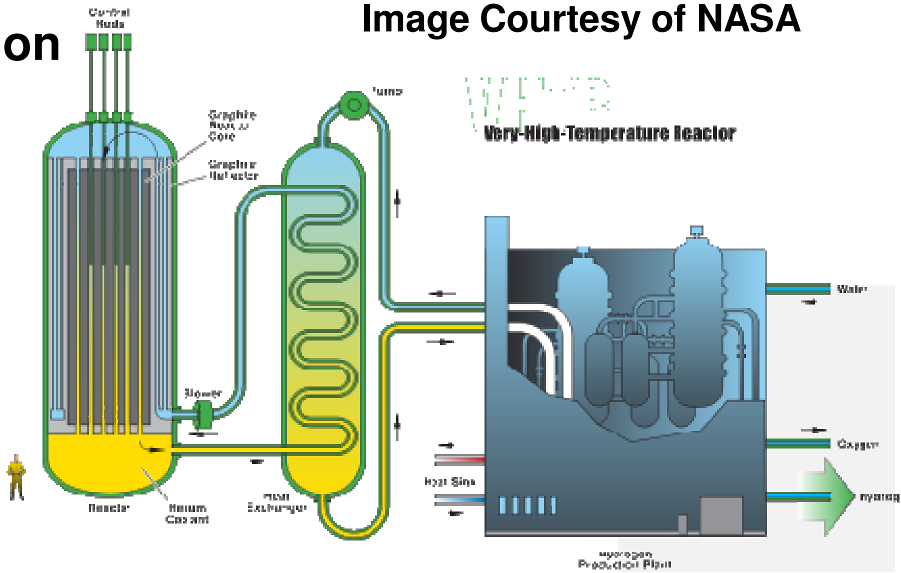
What Drove The Resurgence?

- Advanced aerospace vehicle concepts
  - Hypersonic aviation
  - Reusable atmospheric re-entry vehicles
  - Air-breathing hypersonic missile systems
- Nuclear renaissance
  - Advanced reactor designs
  - Fuel cycles to minimize proliferation
- Other niche applications
  - High temperature electrodes
  - Microelectronics
  - Molten metal handling



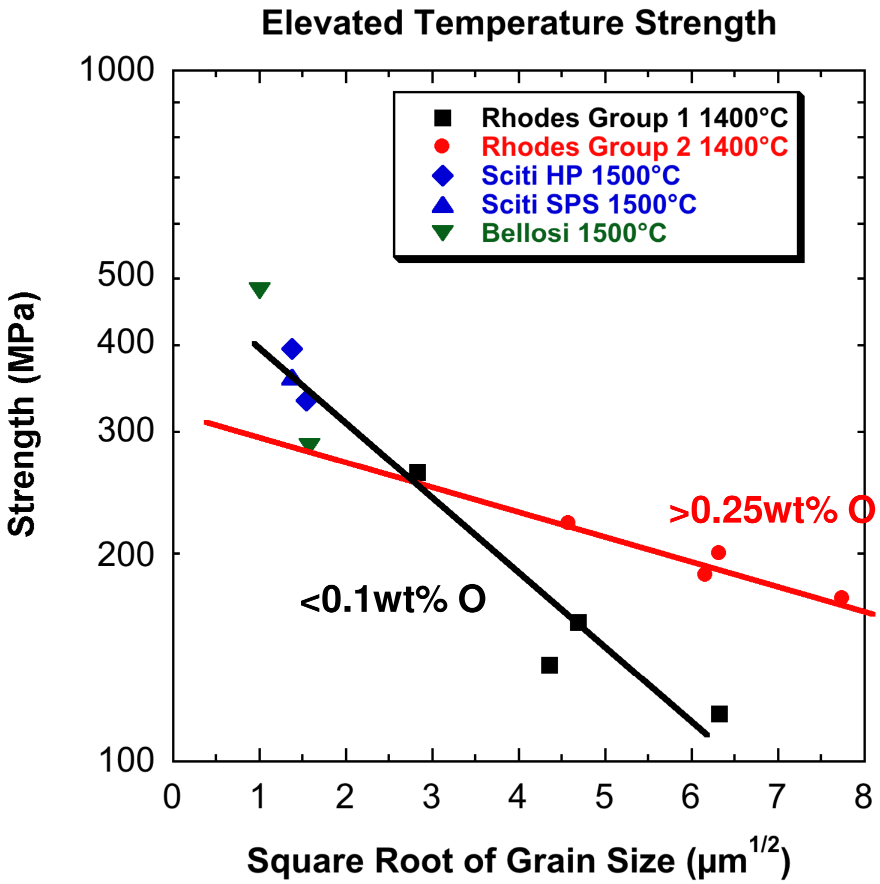
X-43B Hypersonic Concept

Image Courtesy of NASA



Strength

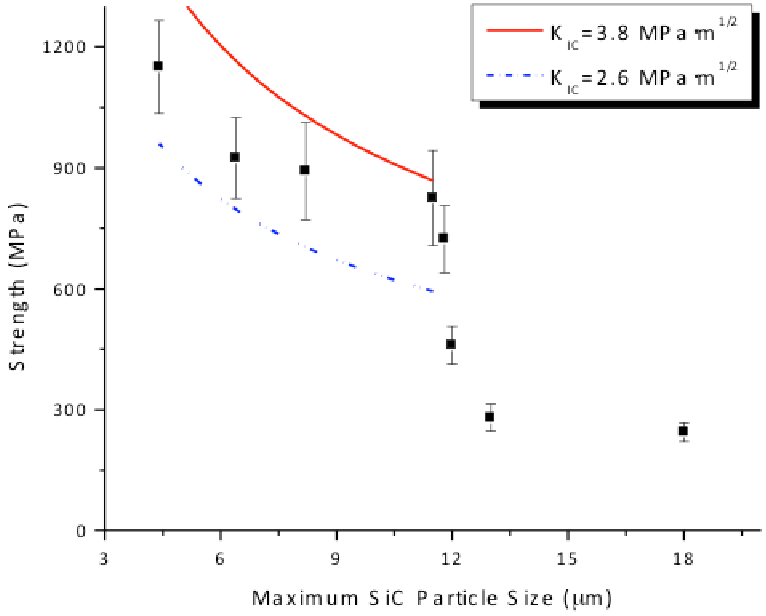
- Strengths have improved due to the ability to produce fine grained, dense ceramics
  - Historically 300-500 MPa
- Monteverde, Sciti, et al. have used silicides as sintering aids
  - Hot pressing ~800 MPa
  - Sintering >500 MPa
- Chamberlain used attrition milling to reduce particle size
  - >1000 MPa at room temperature

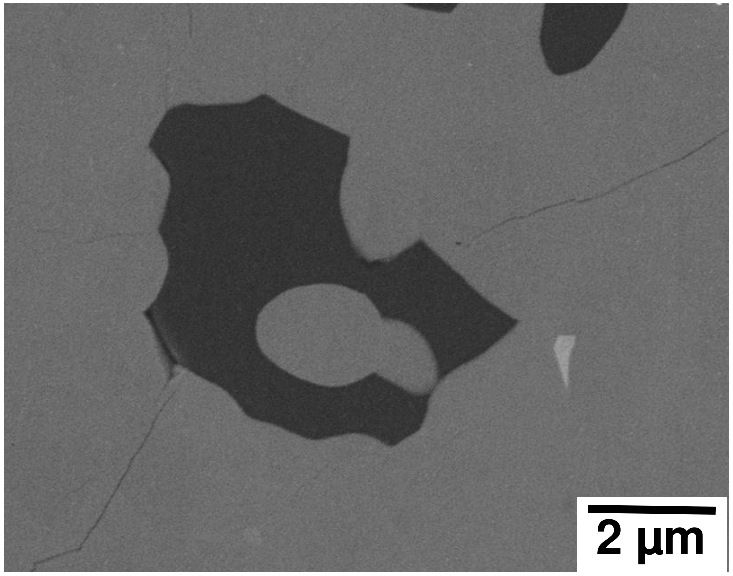


W.H. Rhodes, E.V. Clougherty, and D. Kalish “Research and Development of Oxidation-Resistant Diborides: Mechanical Properties” AFML-TR-68-190 Part II, Vol IV.
A. Balbo and D. Sciti, Mater. Sci. and Eng. A, 475 108-112 (2008)
A. Bellosi, F. Monteverde, and D. Sciti, Int. J. Applied Ceram. Technol., 3(1) 32-40 (2006).

Mechanical Behavior

- Nominally pure ZrB_2
  - Strength proportional to inverse square root of grain size for dense ceramics
- ZrB_2-SiC ceramics
  - Thermal expansion mismatch results in residual stresses
  - ZrB_2 in tension
  - SiC particle size controls strength
  - Microcracking threshold for SiC particle sizes around 12 µm

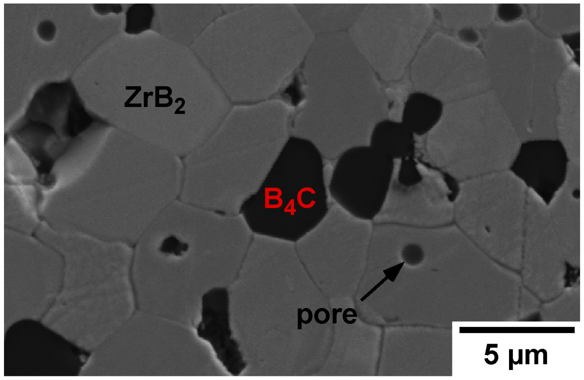


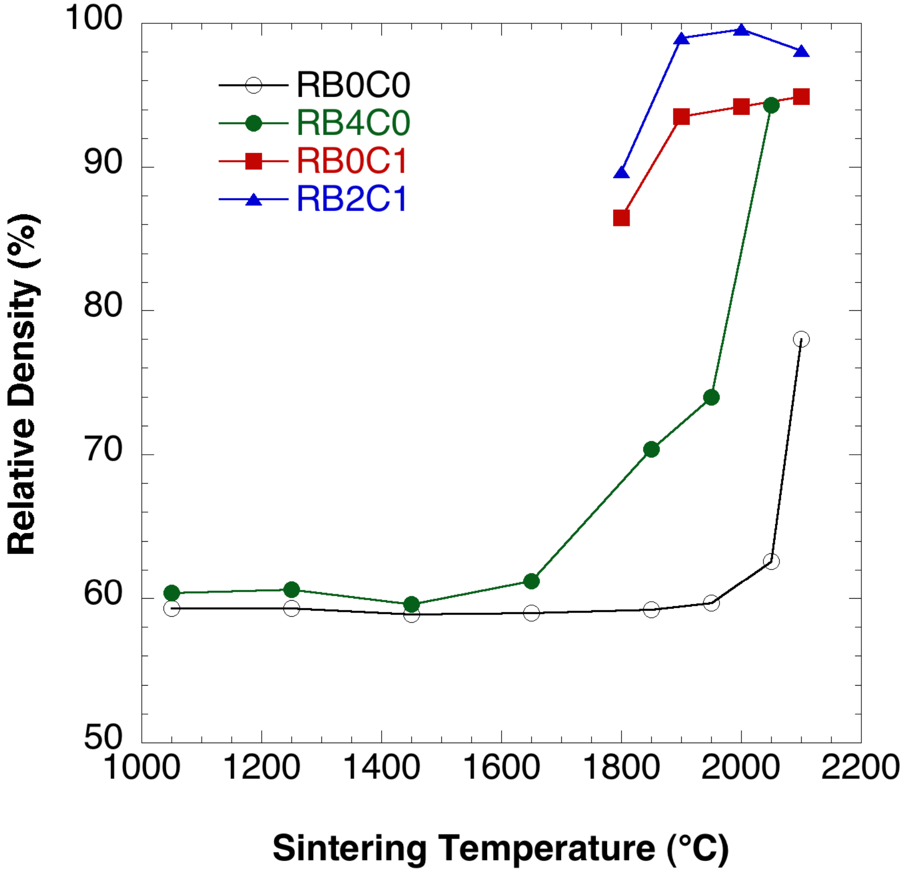


J. Watts et al., J. Am. Ceram. Soc., 94(12) 4410-4418 (2011).

Densification

- Nominally pure ZrB_2
  - Historically, relative density >98% not possible with grain size <50 µm
  - O impurities are critical
  - Pressureless sintering
- ZrB_2-SiC compositions
  - Historically, 2100° C or higher
  - PS or HP at 1900° C
  - SPS at 1750° C or higher
  - Additives and particle size

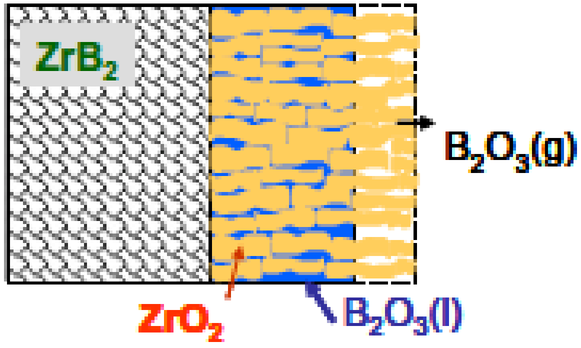




W.G. Fahrenholtz et al., J. Am. Ceram. Soc., 91(5) 1398-1404 (2008).

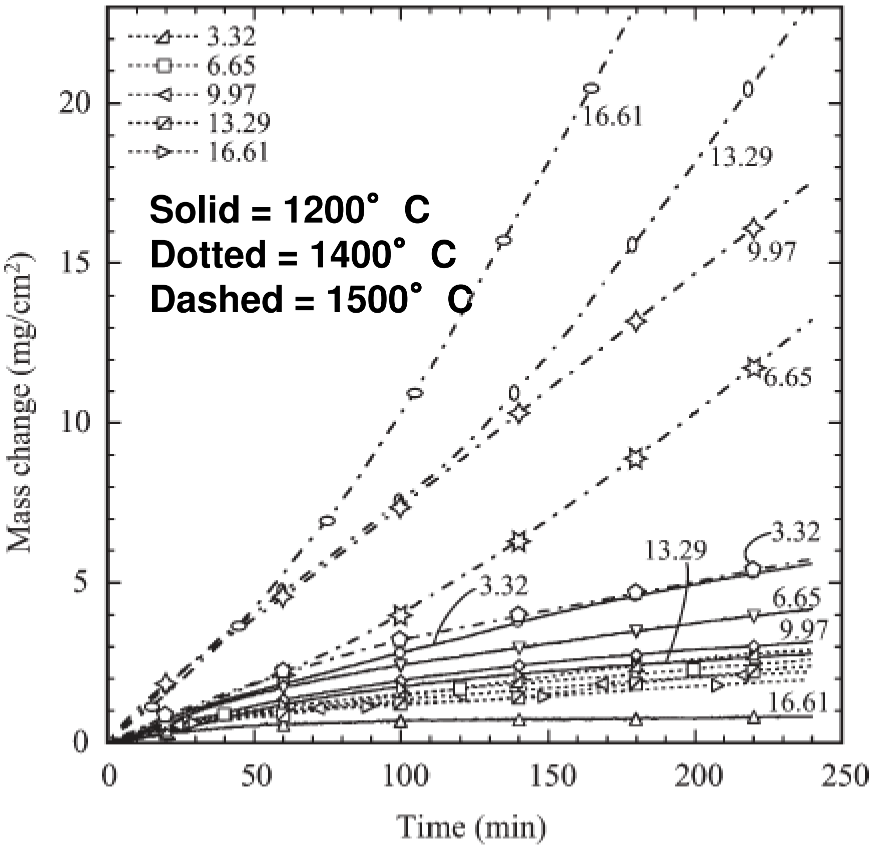
Oxidation

- Historic studies
  - Compared oxygen uptake, mass gain, and scale thickness
- Modern studies
  - Mainly TGA studies and furnace oxidation at ≤1600° C
  - Modeling to understand mechanisms
  - Best performance with silica scale formers plus modifying additives



Intermediate Temp (~1000 to ~1800 °C)

ZrB_2-SiC with TaB_2

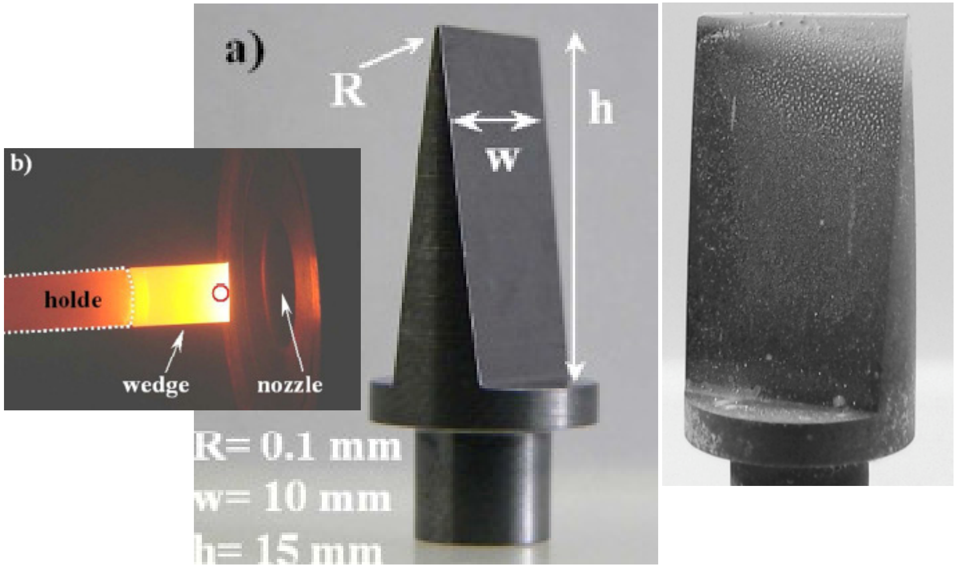


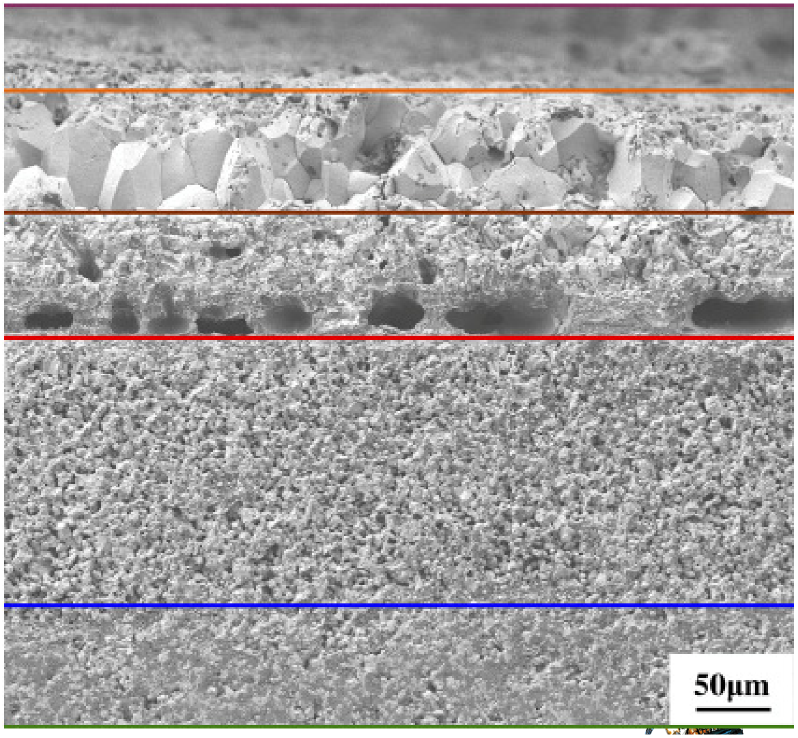
Solid = 1200° C
Dotted = 1400° C
Dashed = 1500° C

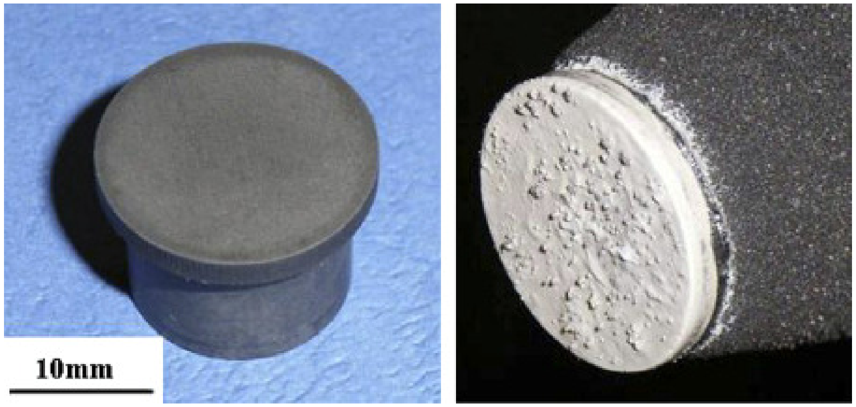
Peng et al., J. Mater. Res. 24(5) 1855-1867 (2009)
Parthasarathay et al., Acta Mater, 55, 5999-6010 (2007)

Testing

- **Historic studies**
  - **Compared oxygen uptake, mass gain, and scale thickness**
- **Modern studies**
  - **Arc heater testing**
  - **Plasma wind tunnel reports by ISTEC**
  - **Torch tests and extreme temperatures from Harbin group**
  - **Laser melting by Imperial**







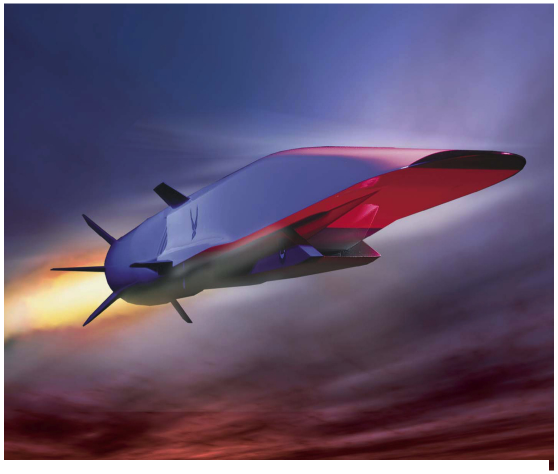
Monteverde and Savino, J. Am. Ceram. Soc., in press
J. Han, Compos. Sci. Technol., 68, 799-806 (2008)

Summary of Recent Progress

- Interest in UHTCs grew in the 1990s
  - Hypersonics, re-entry, and propulsion
- Mechanical behavior has been studied
  - Improved strength due to finer grain sizes
  - Strength-limiting features were identified
- Densification behavior was improved
  - Control of surface oxide impurities and starting powder size
- Oxidation and testing have continued
  - Modeling and additive studies
  - Relevant environment testing

Key Issues for Implementation

- **Fabrication technologies**
  Can parts be made to near net shape at reasonable cost?
- **Properties**
  Is behavior representative of inherent properties?
- **Performance**
  Improvements needed in resistance to oxidation, thermal shock, thermal cycling, and creep



X-51 Concept
Image Courtesy of NASA

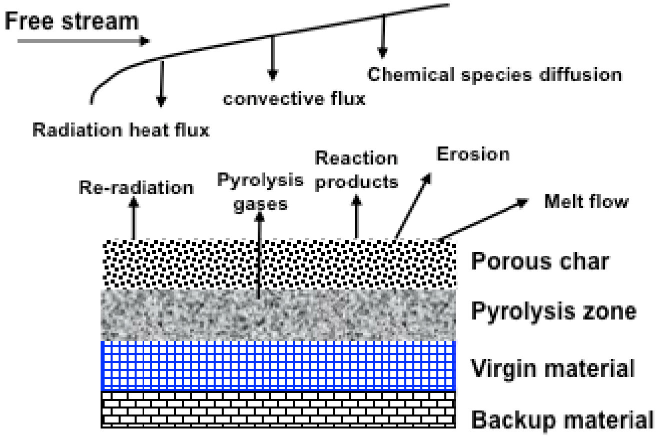
Can we move from concept to an operational hypersonic flight vehicle?

X-51 Test Vehicle
Image Courtesy of NASA

Thank you!

TPS Types

Ablative


Free stream

Chemical species diffusion

convective flux

Radiation heat flux

Re-radiation

Pyrolysis gases

Reaction products

Erosion

Melt flow

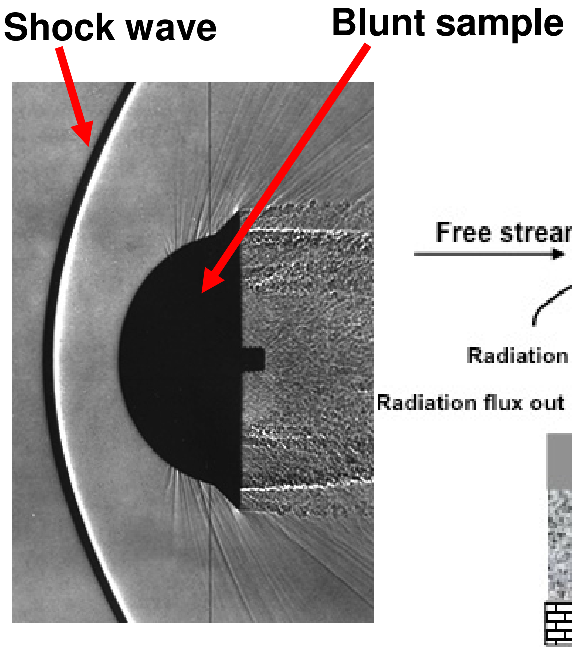
Porous char

Pyrolysis zone

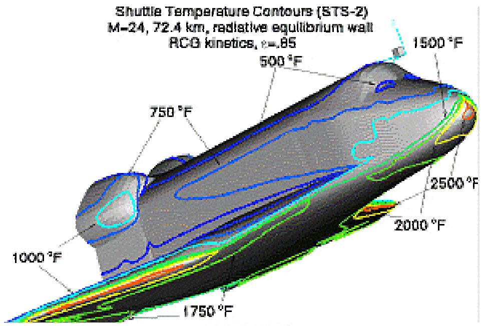
Virgin material

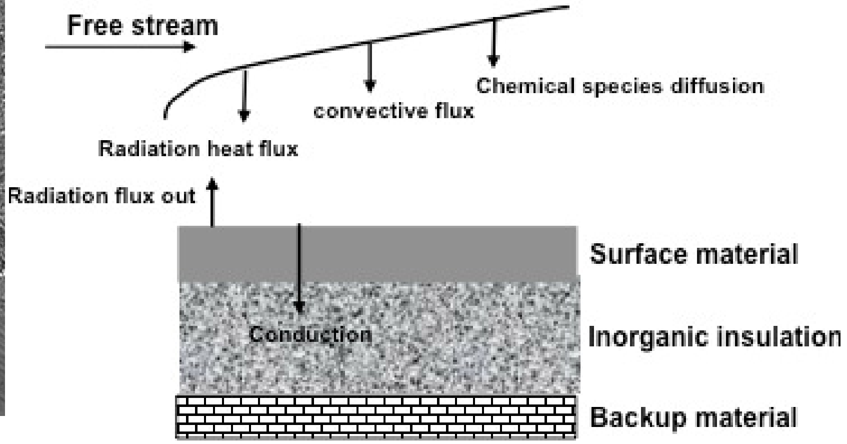
Backup material

Reusable Insulation


Shock wave

Blunt sample


Shuttle Temperature Contours (STS-2)
M=24, 72.4 km, radiative equilibrium wall
RCG kinetics, ε=.85


Free stream

Chemical species diffusion

convective flux

Radiation heat flux

Radiation flux out

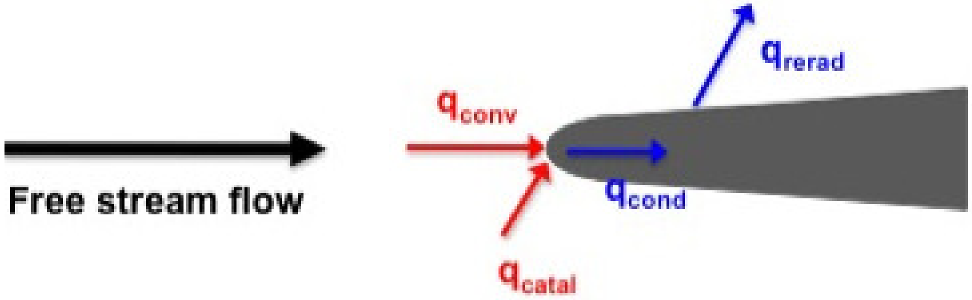
Conduction

Surface material

Inorganic insulation

Backup material

Sharp Leading Edge


Free stream flow

q_{rerad}

q_{conv}

q_{cond}

q_{catal}