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The Next Steps for Ultra-High Temperature Ceramics

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The Next Steps for UHTC Materials

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Ultra-High Temperature Ceramics for Extreme Environment Applications II

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Hernstein, Austria

Outline

Background

- Why UHTCs?
- Current research & development focus

Systems Needs/Designers Phobias – are UHTCs getting a bad reputation?

- How to integrate into structure?
- Catastrophic Failure
- Long-term applications - oxidation

What needs to be done?

- New Processing Technologies
- Testing in Relevant Environments

Why UHTCs?

What does a UHTC need to do:

- Carry engineering load at RT - √
- Carry load at high use temperature
- Respond to thermally generated stresses (coatings)
- Survive thermochemical environment - √

High Melting Temperature is a major criteria, but not the only one

Melting temperature of oxide phases formed

Potential eutectic formation

Thermal Stress – $\mathbf{R' = \sigma k/(\alpha E)}$

Increasing strength helps, but only to certain extent

Applications are not just function of temperature

- **Materials needs for long flight time reusable vehicles are different that those for expendable weapons systems**

Random Thoughts

In many aerospace systems, designers will add weight and complexity by using metals and active fuel cooling to avoid using advanced ceramics and composites.

- Direct function of the conservatism engrained in industry and the system integrator being contracted to build a system and not demonstrate a materials technology
- Unfamiliarity with designing with brittle materials - safety factor.
- Advantages of weight savings and uncooled temperature capability not high enough to overcome risk aversion

Using monolithic ceramics and CMC requires a different design approach, not just dropping in a ceramic part to replace a metallic component

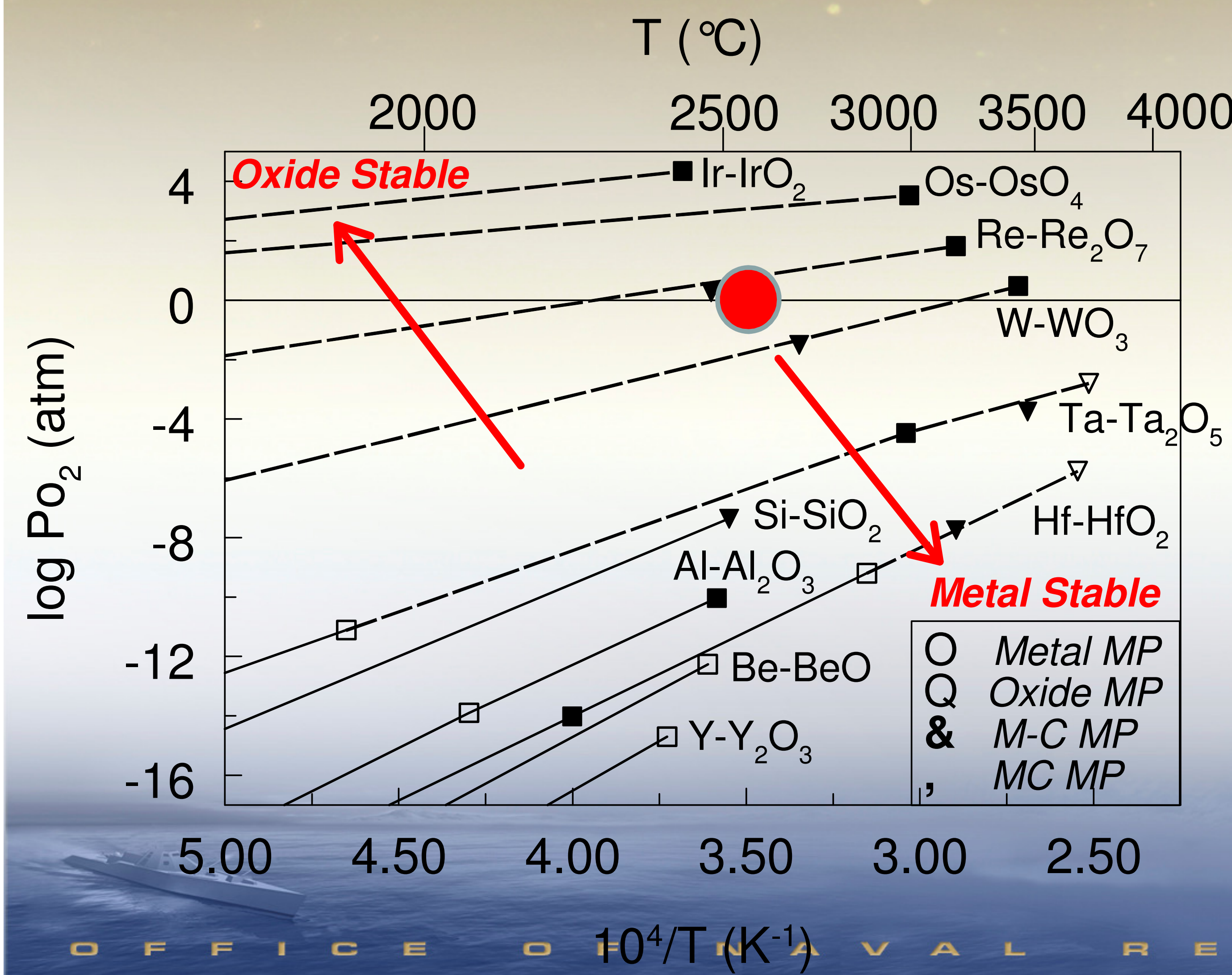
- Rocket nozzle examples – learning how to use a brittle material in a highly transient heating environment

Need for subscale materials/component testing in realistic environments is imperative

Onus is on US to develop materials that will be used by designers

High Temp Materials Selection

Thermochemistry is Driver



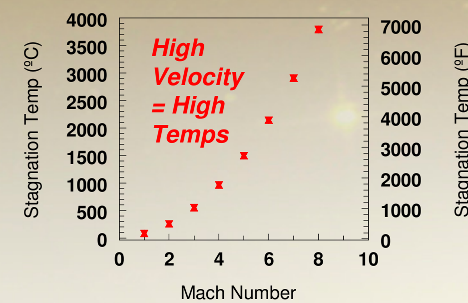
- Metallurgical Thermo tools employed
- Lines divide stability regions of metal vs condensed metal oxide
- Each element shown is best representative of Group (eg., Ta-Nb-V)
- Each element is also representative of compounds (HfC, HfN, HfB_2, HfO_2, etc.)
- So what ????
How is this useful ????

Current research vs future directions

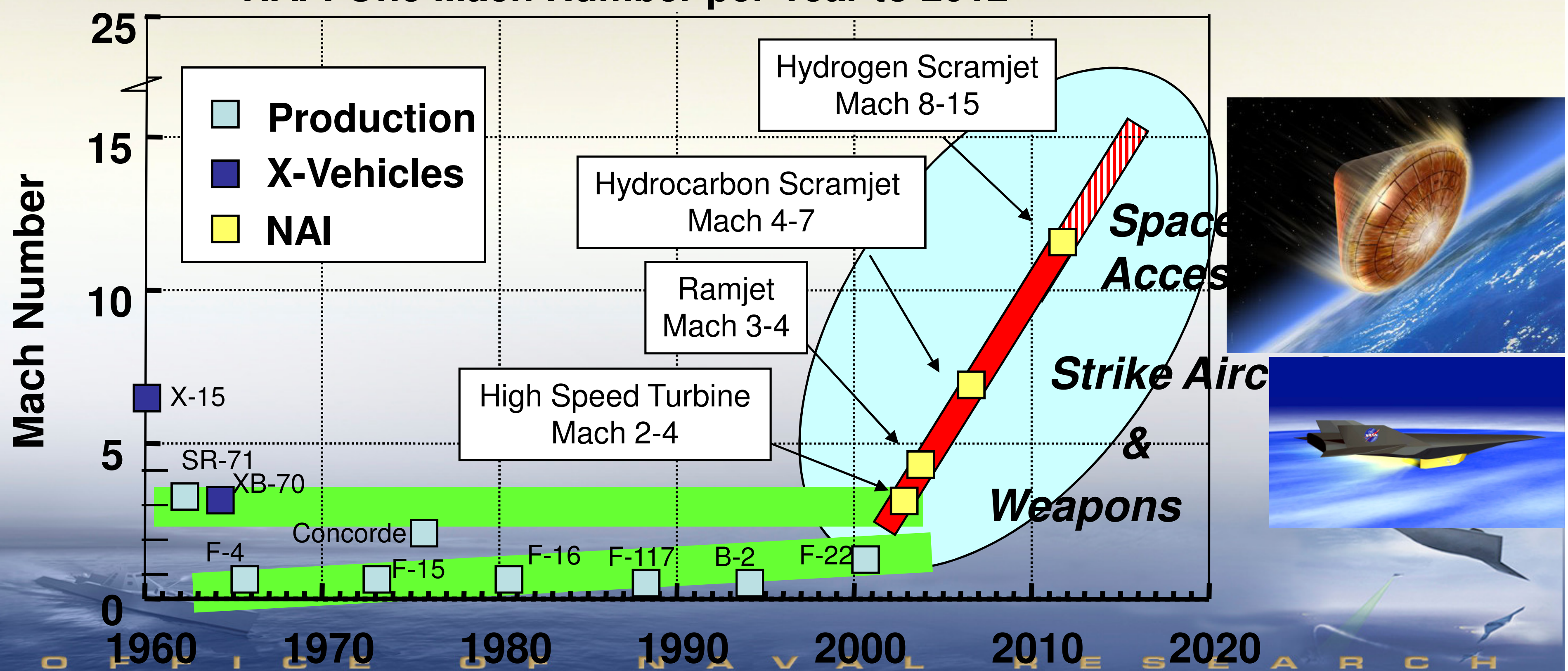
- Increase strength - SPS (engineers don't like lack of toughness)
- Increase thermal conductivity (HfB_2 is already very high)
- Decrease modulus (graphite second phases, but eutectic issue)
- Decrease thermal expansion (intrinsic property)
- Design around thermal stresses – rocket nozzles (ONR & AFRL)
- **Understand and improve oxidation behavior – why SiC?**
- **Develop UHTC-matrix composites – hot pressing, SPS, HIP, all produce bulk monolithic materials.**
  - Modulus/CTE mismatch w/ C fibers a problem
  - Current polymeric precursors - expensive and air sensitive
  - Organnometallics
  - Melt infiltration – refractory alloys reactive with fibers
  - Densification/conversion of matrix
  - Alternative Processing routes (CVC, in-situ reinforcement, cermets)

Hypersonics

High Operational Velocities
⇒ High Temps & Heating Rates



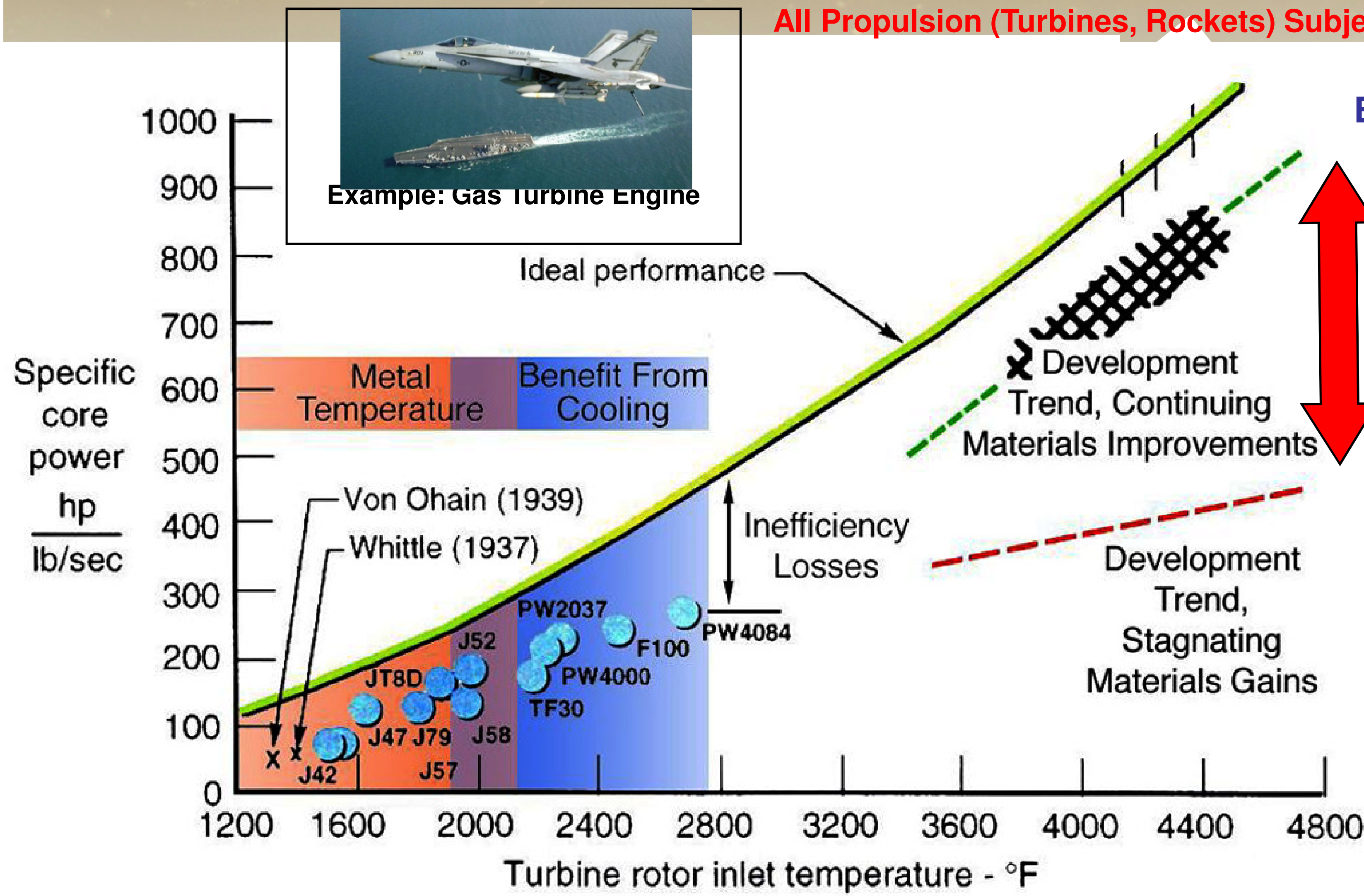
NAI : One Mach Number per Year to 2012



Thermodynamics

Higher Operating Temps Yield Higher Engine Performance

All Propulsion (Turbines, Rockets) Subject to 2nd Law



Breakthrough Materials Technology

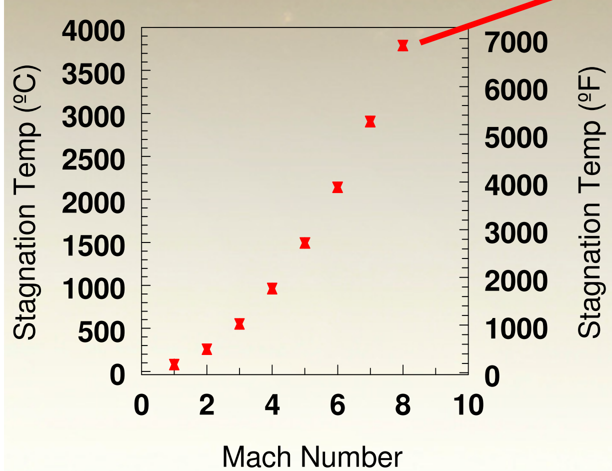
Loss If No Matls Devt

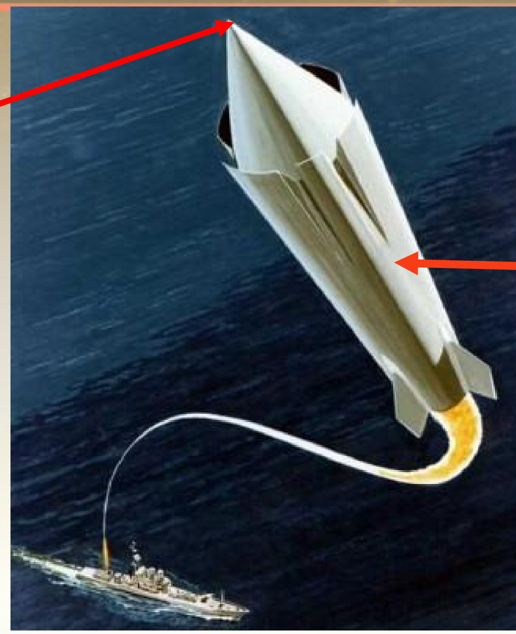
Data from Dr. B. L. Koff, Pratt& Whitney, 1996

Scramjet Propulsion

High Operational Velocities → High Temps & Heat Rates

High speed = High T





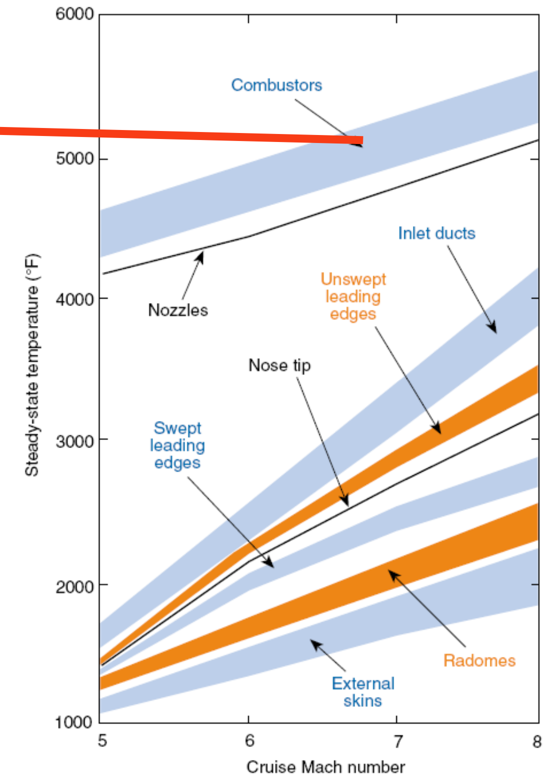
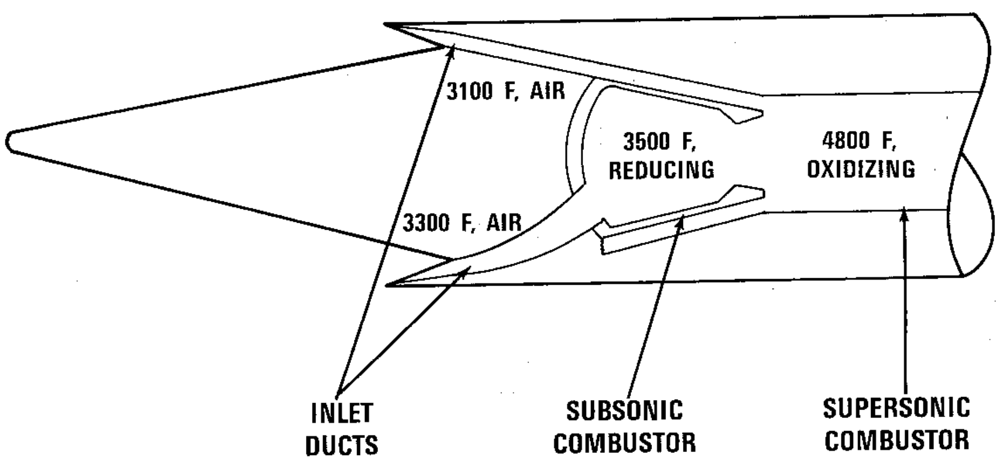
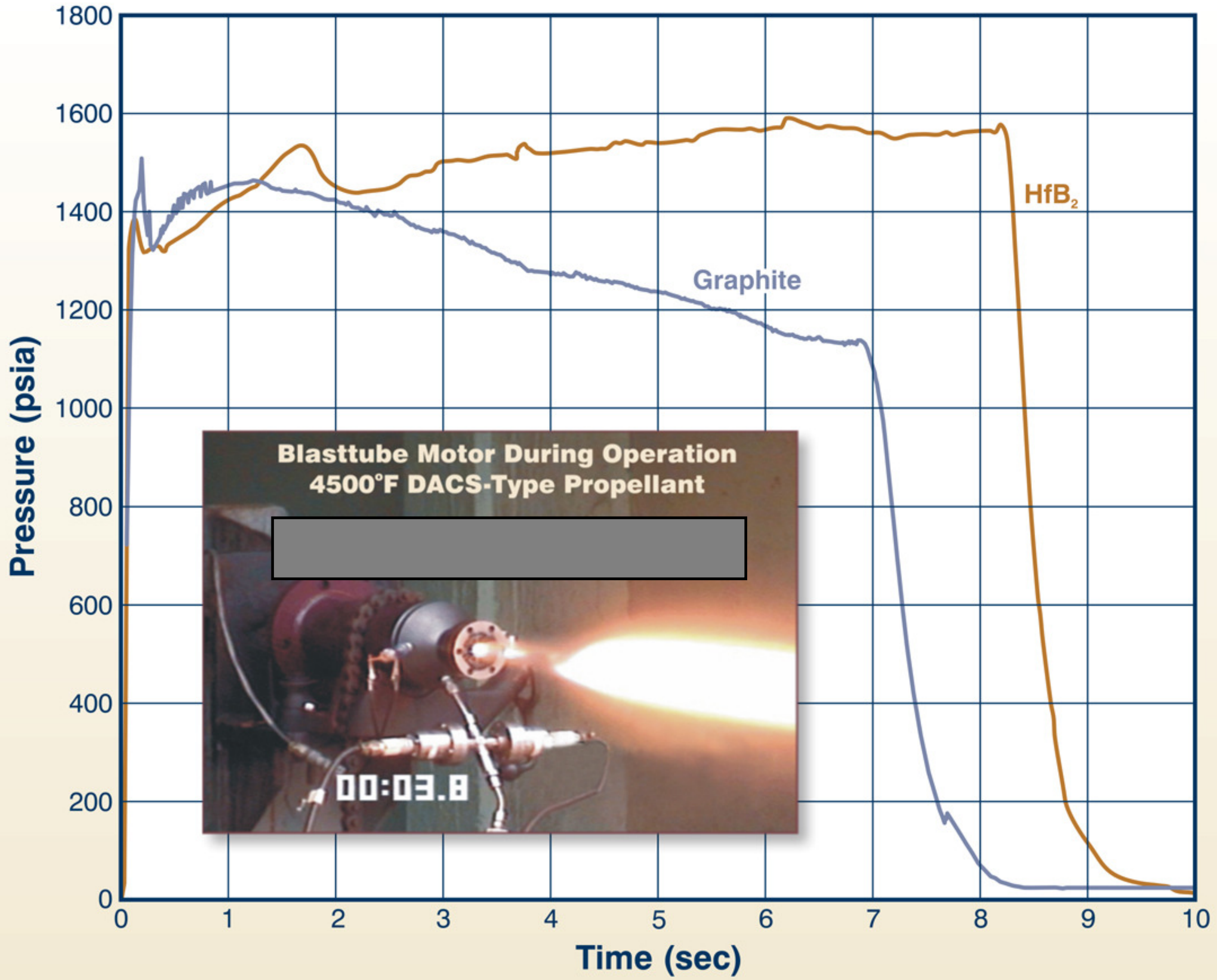


Figure 5. Steady-state temperature versus cruise Mach number for critical components at an 80,000-ft altitude.

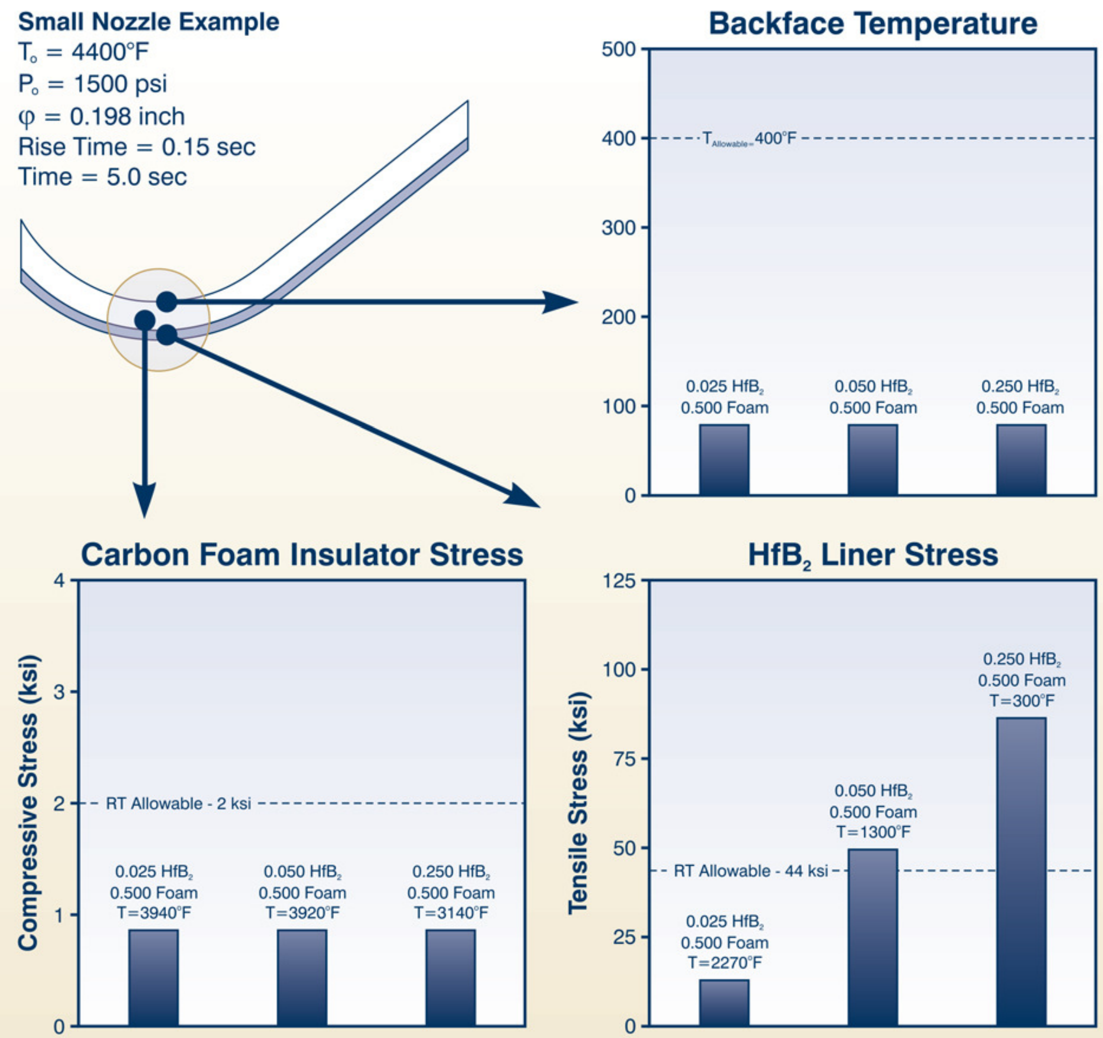


Pressure-Time Traces of Graphite & HfB_2 Throats Showing Non-eroding Behavior of Ceramic Nozzle



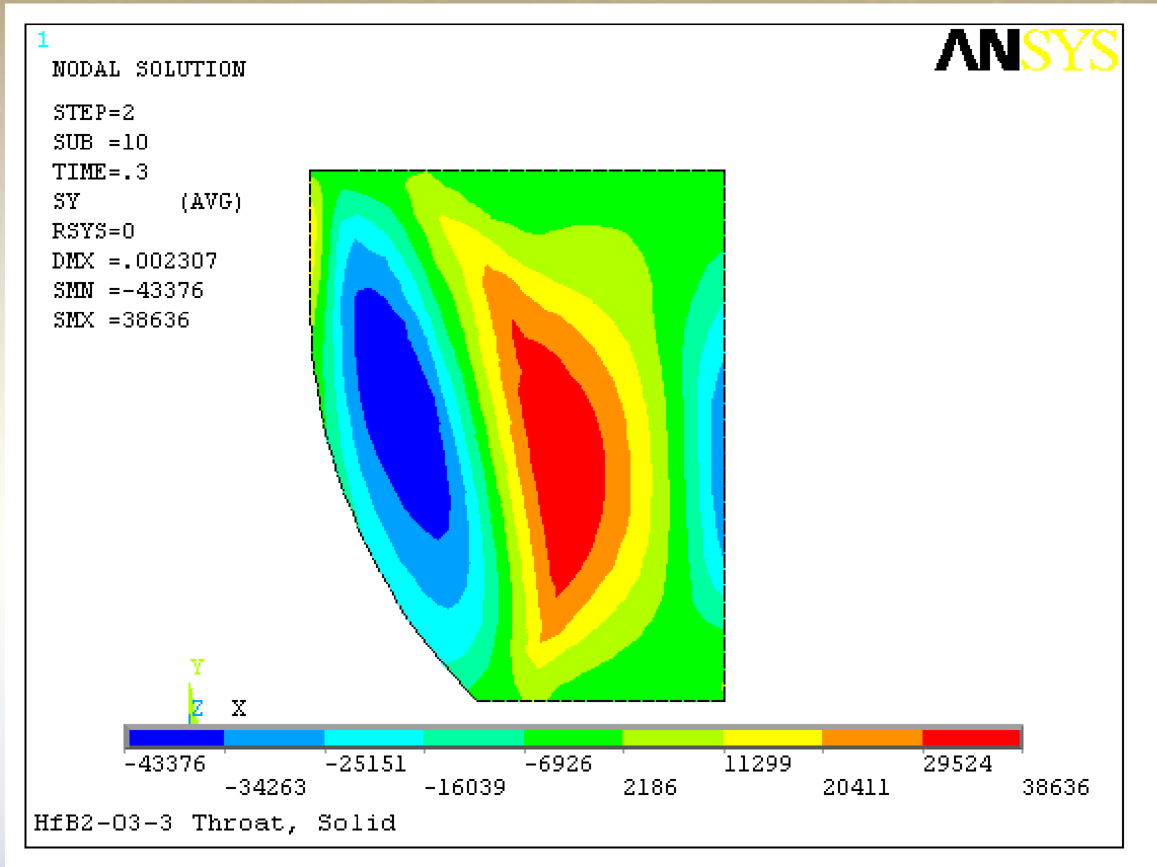
Thermal Stress-Based Failure Mode:

Thinner Liners - Lower Thermally Generated Stresses



C-foam provides insulation and allows expansion of liner

THERMALLY GENERATED STRESSES
Solid HfB_2 Throat



Similar Axial Stress Fields Have Been Observed In Previous Analysis Efforts

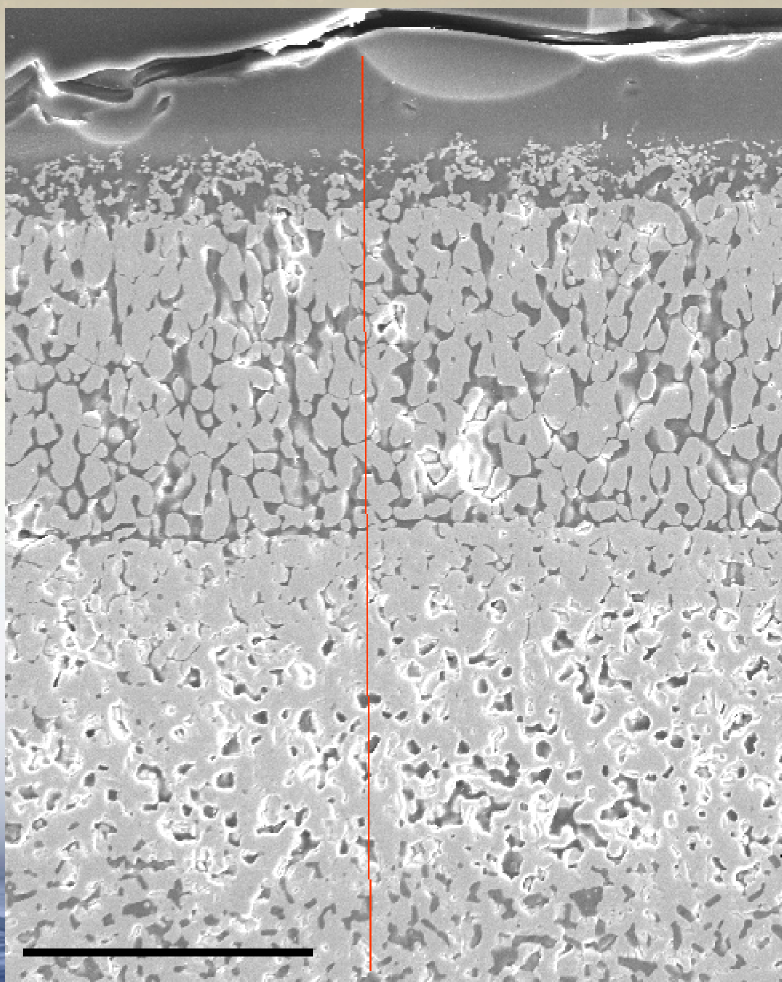
Maybe the models are too conservative in predicting thermal stress failures?

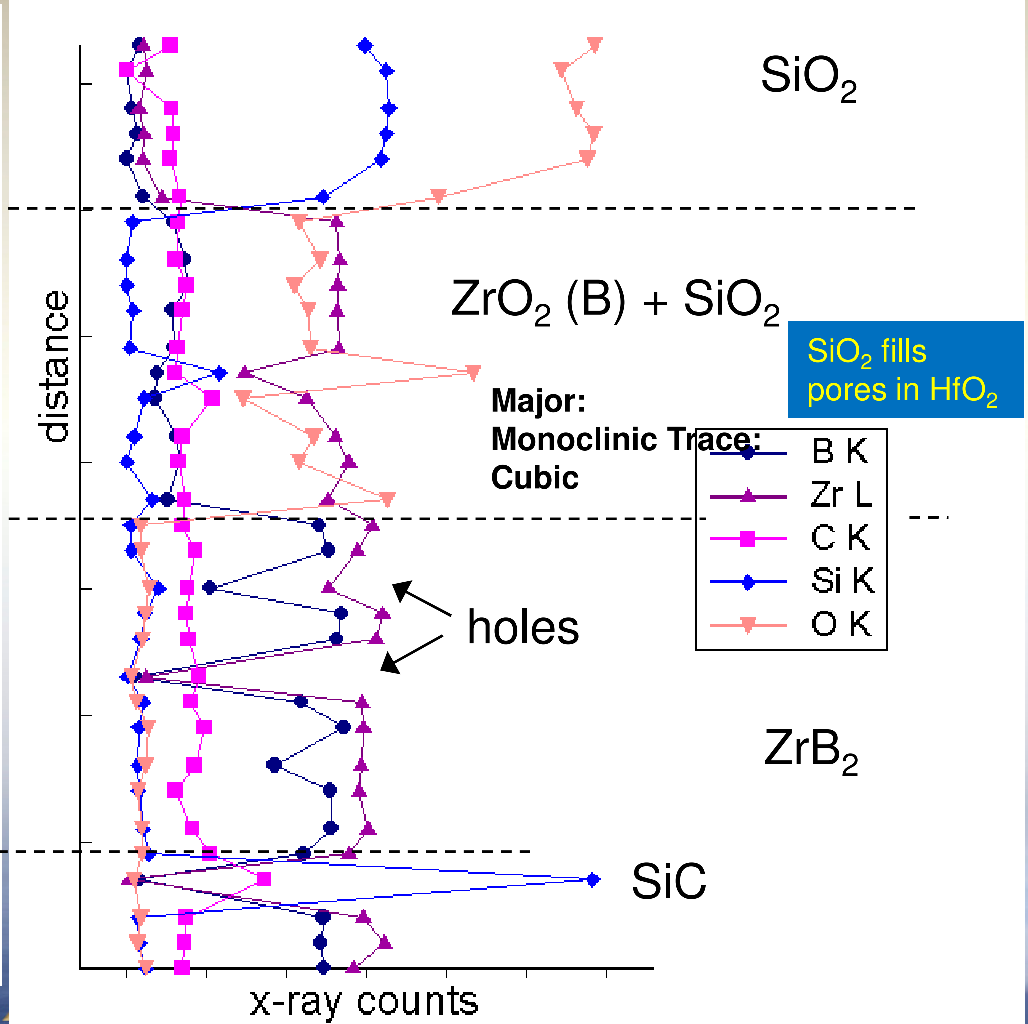
Understanding of Oxidation at Relevant Temperatures

(1627C not high enough!)

Ref: Evaluation of Ultra High Temperature Ceramics for Propulsion Application

S.R. Levine, et al., NASA Glenn Res. Ctr, ACerS PacRim Conf., Seattle, WA, 01 Nov 2002



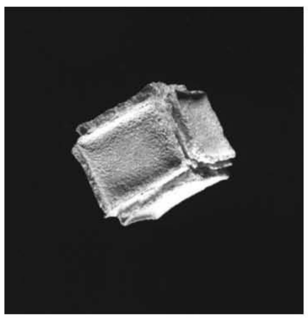


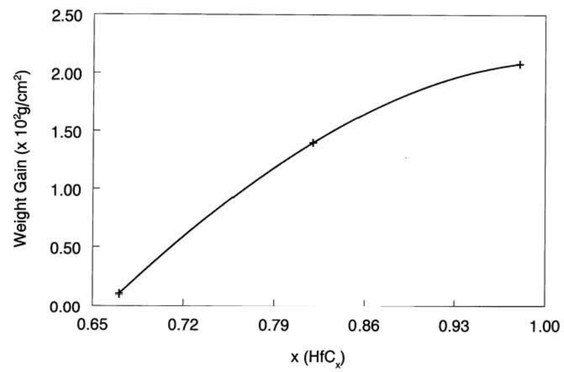
Borides are not the only UHTC Materials

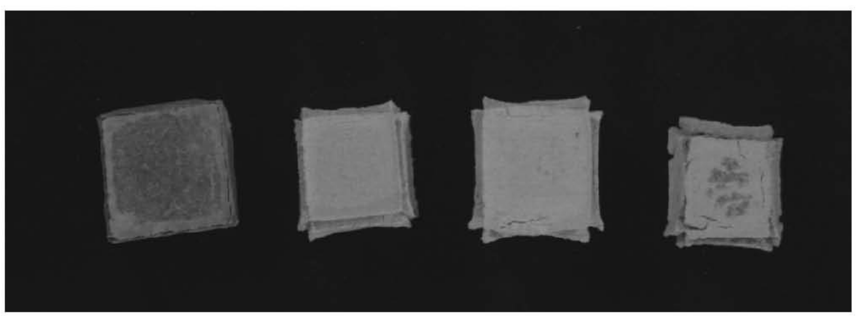
Boria has high Pv, SiC active oxidation, and HfO_2 does not sinter below 1800℃, so oxidation behavior **improves** with temperature

Furnace Testing of HfC – 1500°C

Pesting Issues at Low T – Sinterability of HfO_2





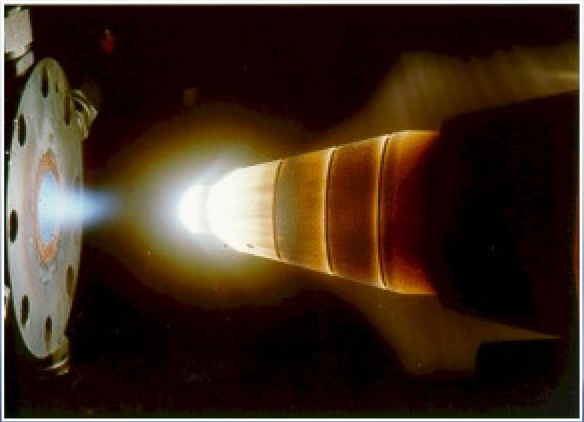


Arc-jet tests help understanding thermochemical environment

$HfN_{.75}$

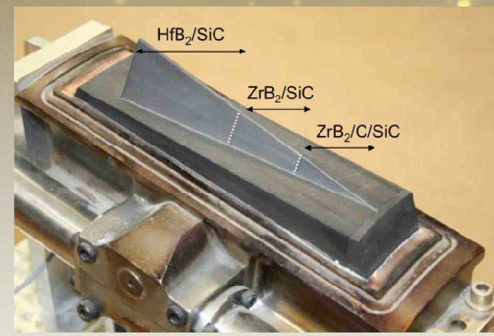
$HfN_{.95}$

But sample geometry (radius of curvature), enthalpy, catalycity, and pressure all affect performance



Relevant Testing Can be Enlightening – and Scary

- **SHARP-B2 UHTC flight test [Sannes, 9 and Johnson, 10]**
  - Very progressive & expensive
  - Failure attributed to UHTC processing



Pre-test


Post-test

Slide from D. Glass, NASA-Langley

- **ZrB_2-SiC nose tip during arc-jet test [Marino, 11].**
  - Failure attributed to titanium screw [12].

Second assembly withstood two test at 3 MW/m^2 for 108 sec. Non-critical damage observed at base of UHTC tip. [Scatteia, 12]

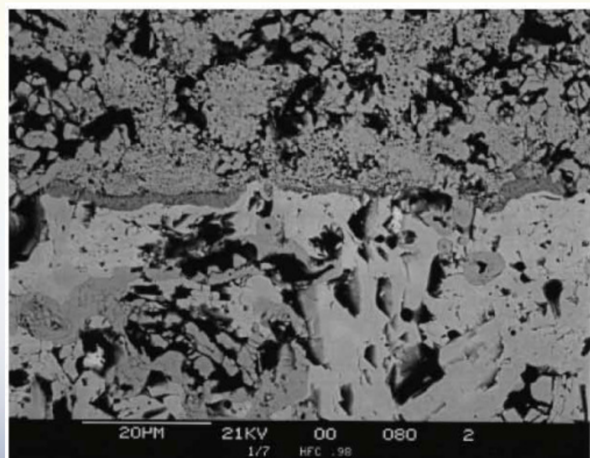
Affecting future of Italian UHTC work?

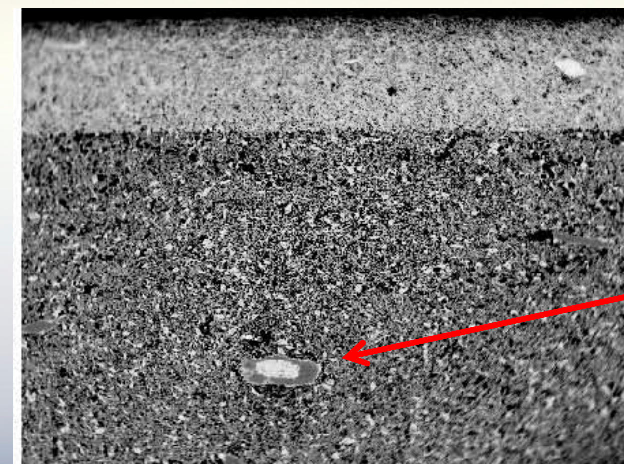
Even in constrained 1-D heating environment for oxidation testing, **low thermal shock resistance** and **low fracture toughness** of **monolithic ceramics** can result in catastrophic failure

Improve oxidation behavior

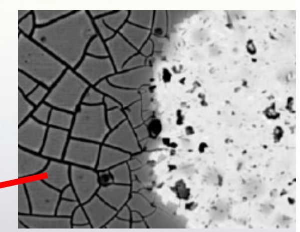
- Eliminate presence of Si - detrimental above 1700℃
- Test in relevant environments
- Dopants to control oxygen diffusion through oxide scale
- Decrease porosity of scale
  - Substoichiometry & Doping – Wuchina & Opeka
  - Liquid phase sintering – Fahrenholtz & Hilmas

HfCxOy Interphase





WO_3 formation



Careful on effects on high-temperature strength

Current NSWCCD Research

Oxidation and Mechanical Properties in the Hf-Ta-N System

Hf, Ta: *Linear Oxidation Kinetics at High Temperature (HT)*

Hf-20Ta: *Parabolic Kinetics to 2000°C with strongly adherent scale (Marnoch, 1965)*

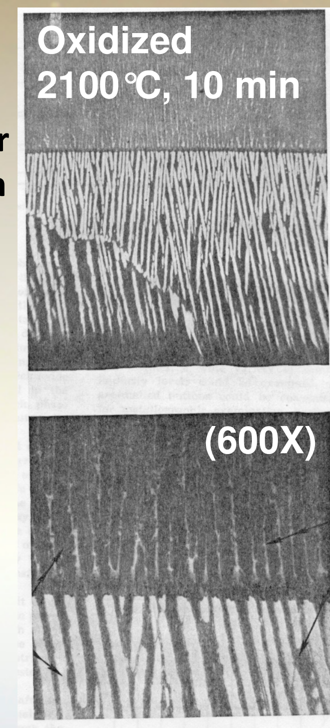
HfC-25TaC: *Linear Kinetics at HT (Holcomb, 1988)*

HfB_2-20TaB_2: *Linear Kinetics at HT (Talmy, unpublished)*

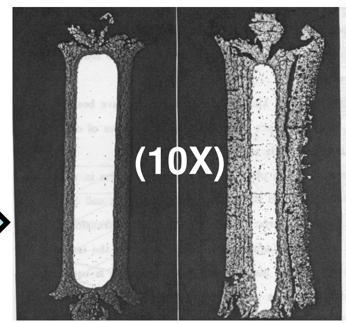
(Hf,Ta)N_x Ceramics: *Not Investigated To-Date; Initial Navy Expts Conducted with HfTa alloys*

Hf20Ta:

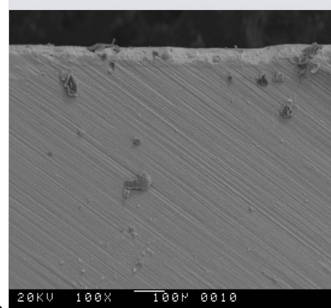
HfO_2 columnar morphology in alloy & oxide

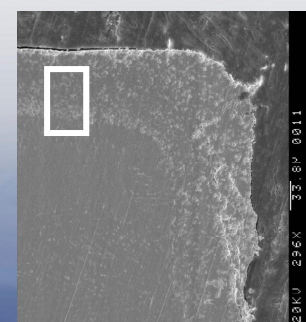


HfC, HfC-25TaC



Oxidized at 2000°C

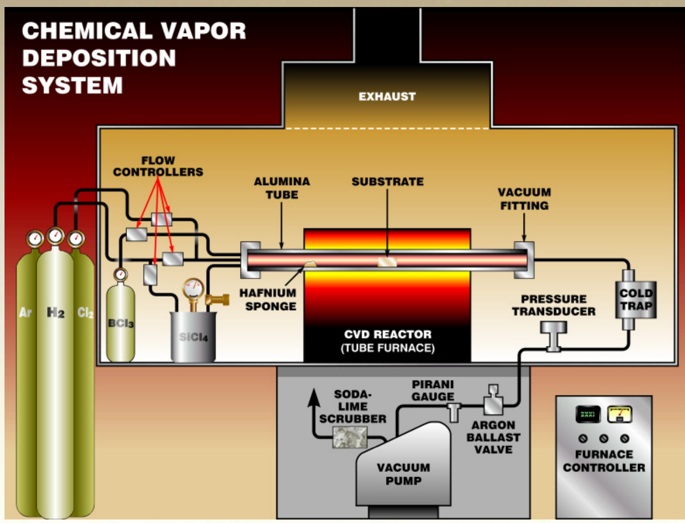


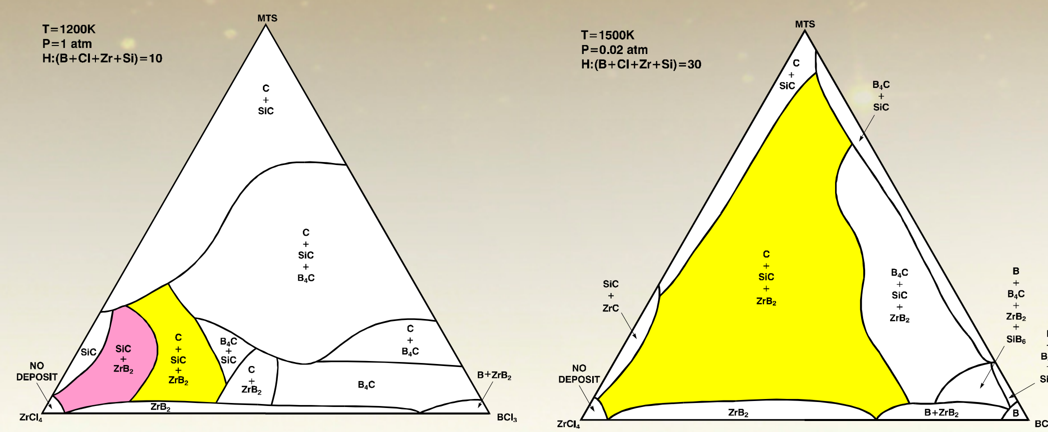


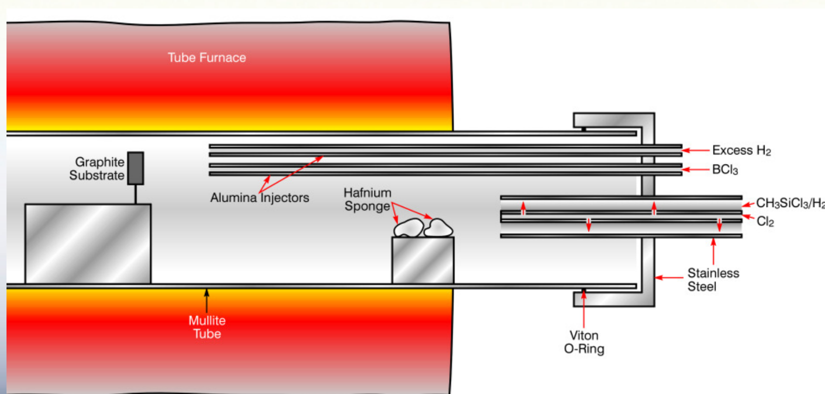
Hf27Ta:

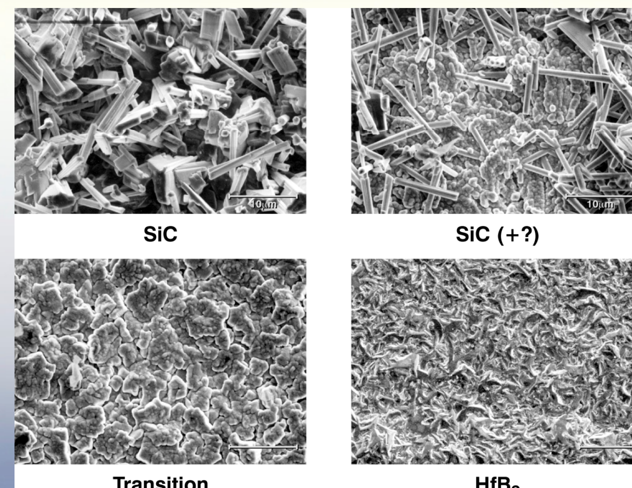
Oxidized at 1500C, 15 minutes; Oxide scale thickness ≈ 50 µm

Alternative Processing Techniques





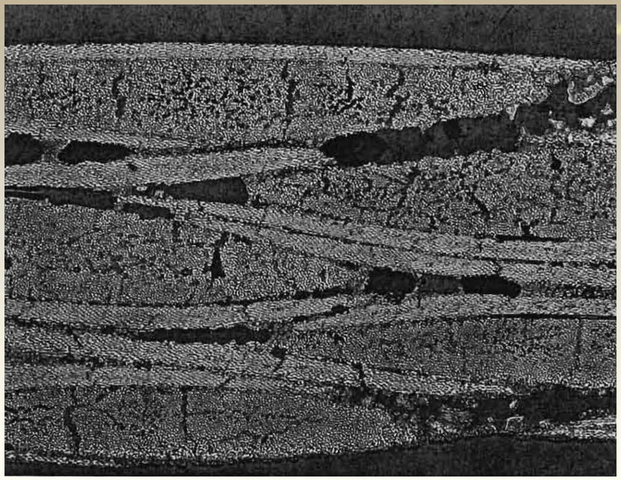


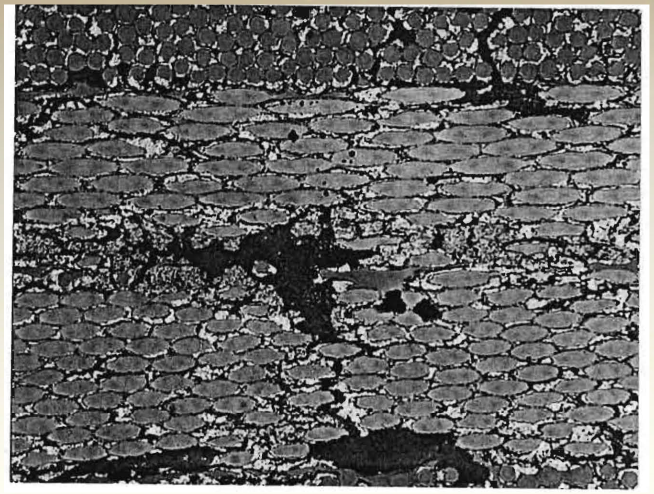


CVD not a panacea, but shows possibilities

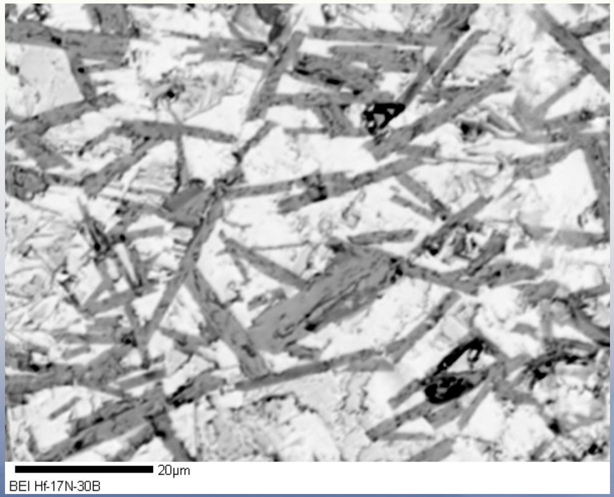
UHTC-matrix composite – ca 1997 and Hf-HfN-HfB_2 cermet

Hf acetate + C, CVI, C/C late stage PIP or gas infiltration, nano HfC





X-51 Inlet leading edge was follow-on to work initiated in late 1990s through SBIR



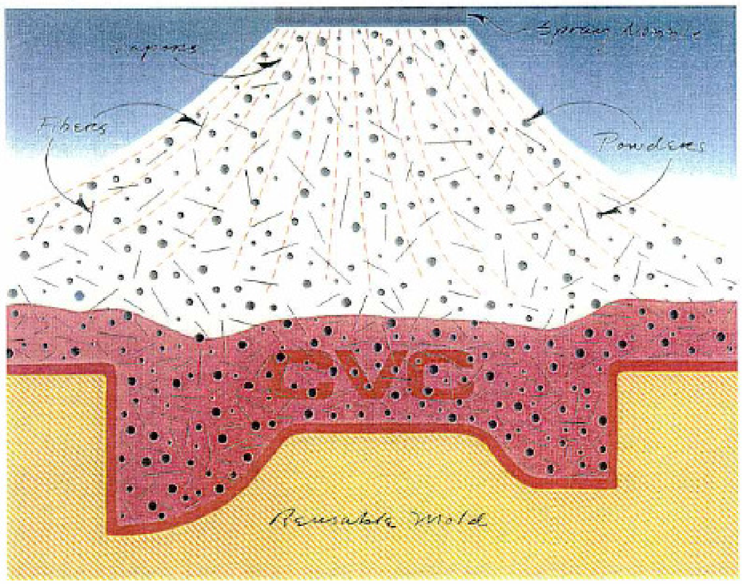
Chemical Vapor Composites

CVD with Particulate or fiber reinforcement

TTC

Chemical Vapor Composites

Powders and fibers are mixed with reactant vapors and deposited on a reusable mold, producing a composite in the exact shape of the component



LOW COST
- Single step
- High deposition rate
- Net shape

HIGH QUALITY
- Strong – tough
- Lightweight
- High temperature

VERSATILE
- Metal composites
- Ceramic composites
- Transition joints

4025-V/8-1

The Intersection of Basic Science and Engineering

Ab-initio calculations for discovery of new materials and correlation of chemical & physical models with materials by design approach for improving properties

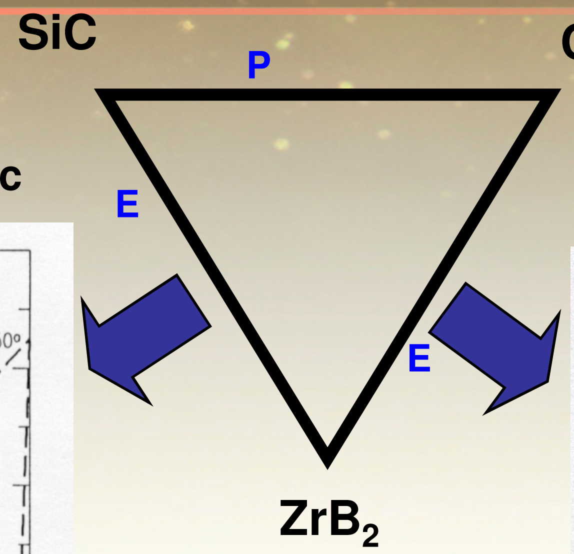
High-fidelity analysis to understand multi-scale effects on macroscopic properties

Chemical Vapor Infiltration
- Organnometallic Precursors
- Mean Free Path
- Modulus Mismatch – fiber breakage

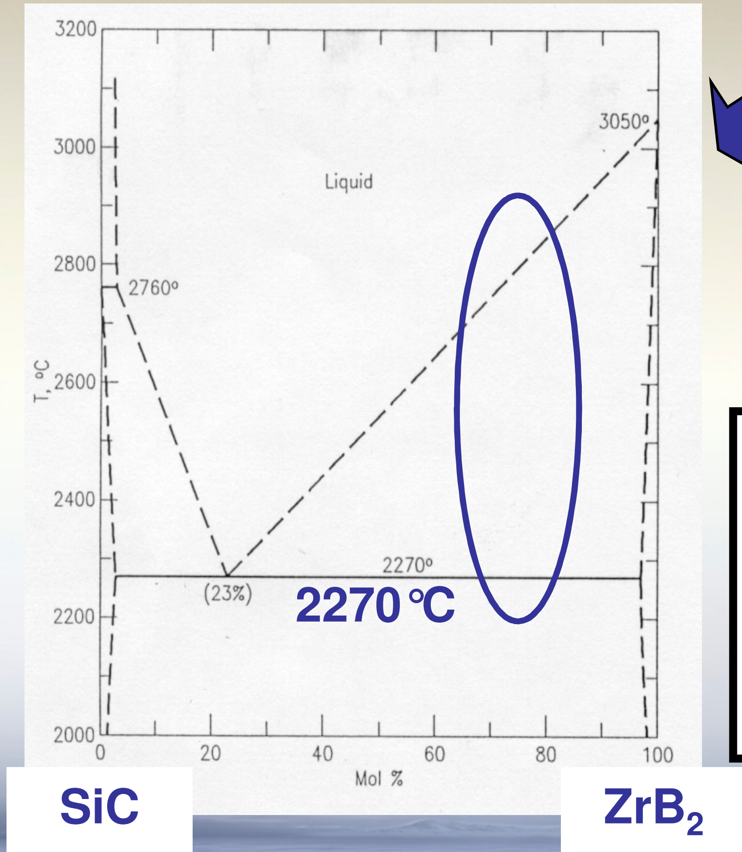
PIP Processing
- Preceramic Polymer Development
- Particulate Additions – filtration
- Increase Yield & Reduce Cycles

Other Techniques
- Vapor Phase Conversion
- UHTC fibers

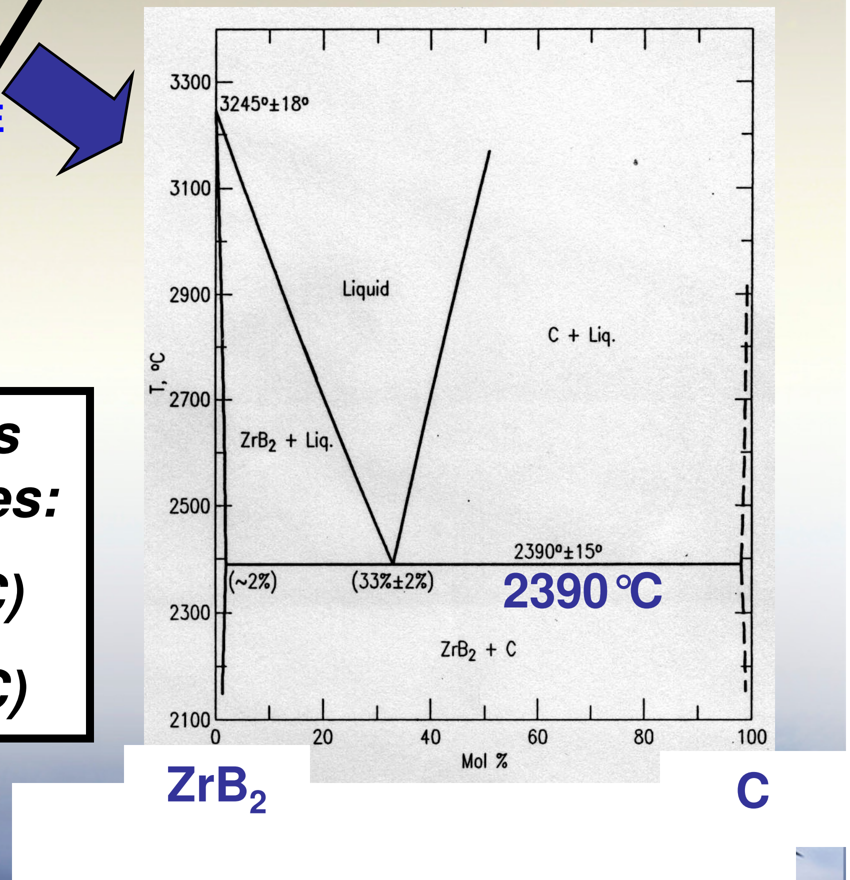
New Materials for Hypersonic Vehicles Include Eutectics



Hard-Hard Ceramic Eutectic



Hard-Soft Ceramic Eutectic



Hypersonics Aerosurfaces:

ZrB_2-SiC (-C)

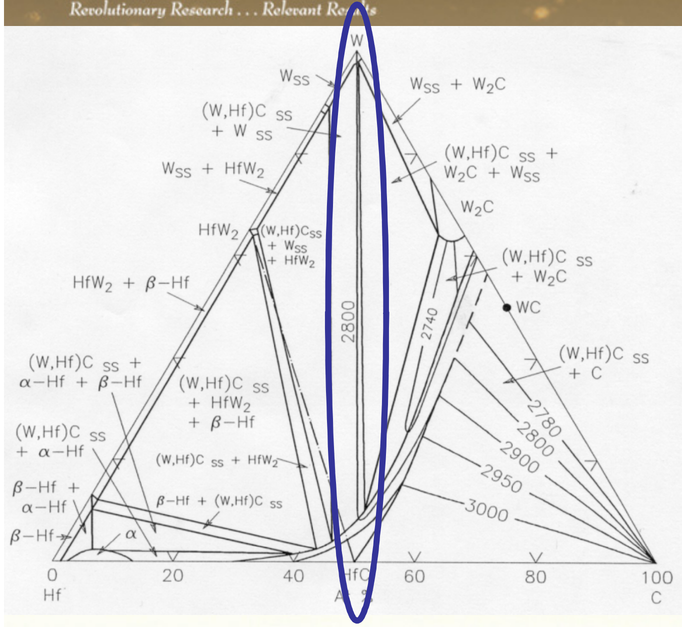
HfB_2-SiC (-C)

Microstructure and Property Differences Between Hard-Hard and Hard-Soft Ceramic Eutectics?

Revolutionary Research . . . Relevant Results

New Materials for Propulsion Systems Include Eutectics

NAVSEA
WARFARE CENTERS
Carderock Division



Microstructure and Properties of Ceramic-Metal Eutectics?

Eutectic Temps & Intersolubilities Vary Significantly:

- **HfC-W: 2890 ℃,**
- **HfN-W: 2800 ℃ (P_{N2}-Dependent),**
- **HfB_2-W: 2280 ℃**

- **HfC-Ta: 2550 ℃ (large intersolubilities)**
- **HfN-Ta: 2800 ℃ (some intersolubility)**
- **HfB_2-Ta: Reaction to (TaHf)B**

Composition Control and Properties of “Metal” Phase a Major Issue for Cermet Eutectics

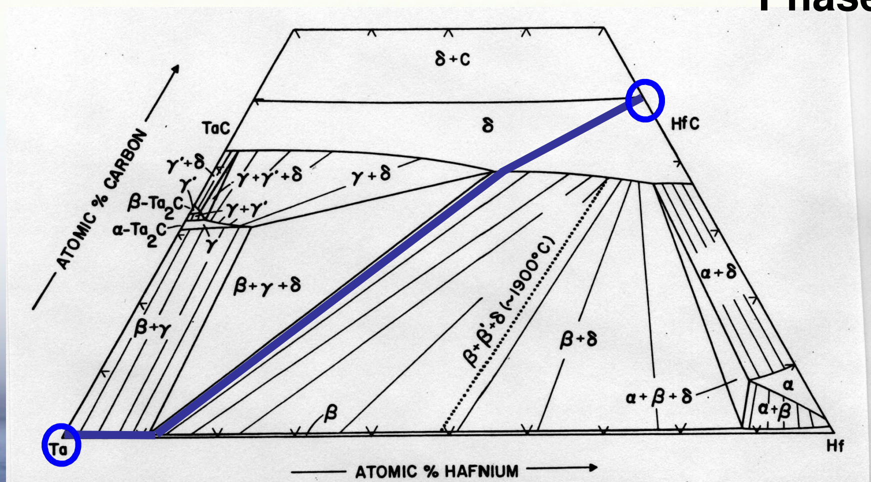


Figure III.E.9.10. Isothermal Section of the Ta-Hf-C System at 2000° C

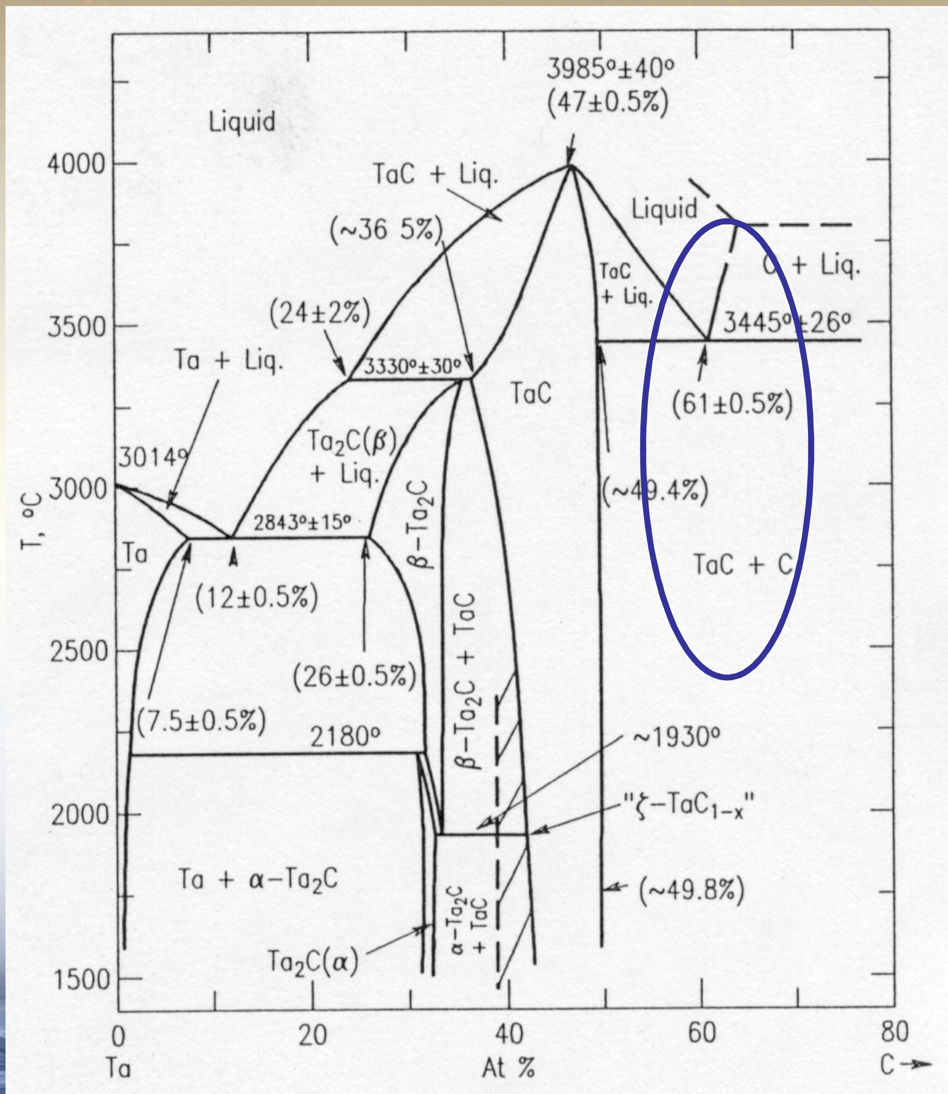
Non-Aluminized Propulsion:

HfC-W	***HfN-W***
HfC-Ta	***HfN-Ta***

(and ZrC, ZrN compositions)

NAVAL RESEARCH

New Materials for Propulsion Systems Include Eutectics



Aluminized Boost Propulsion:

TaC-C

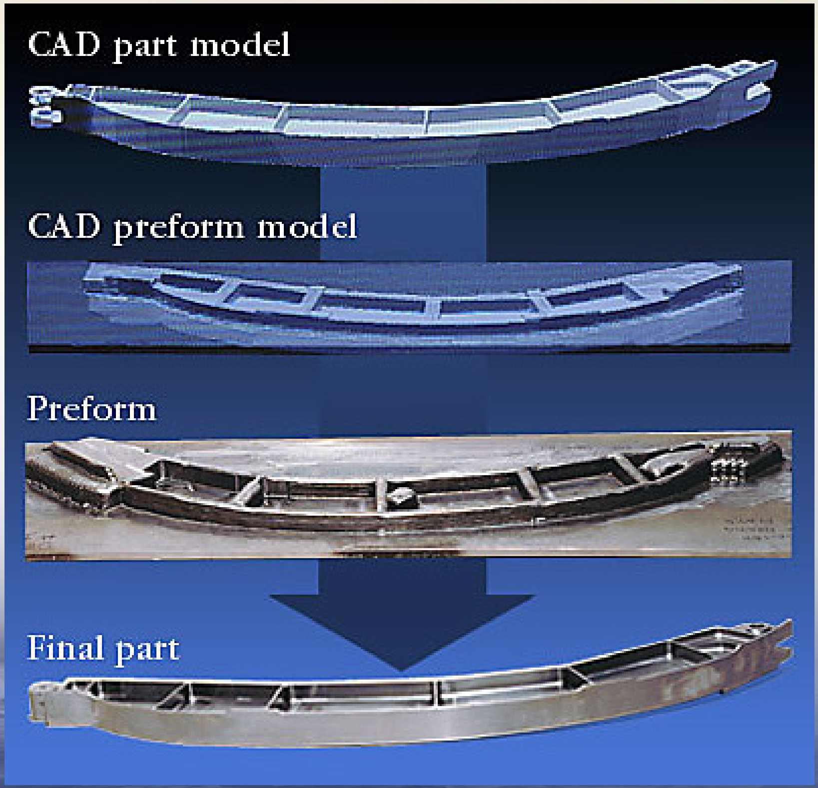
Non-Aluminized Boost Propulsion:

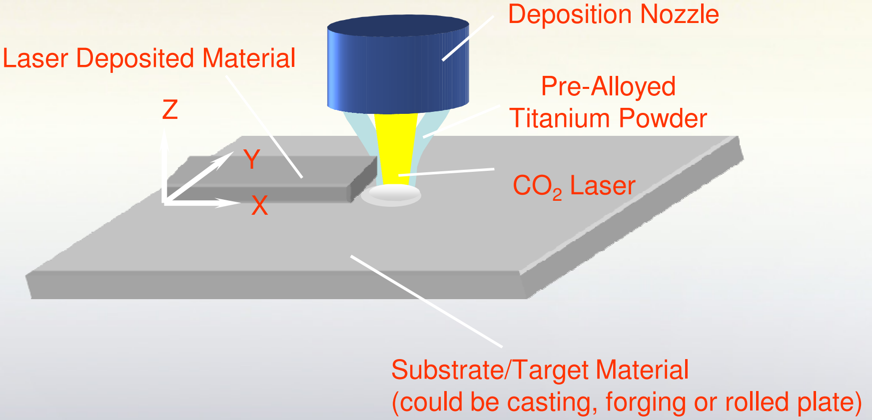
HfC-C
HfN-BN
HfB_2-BN

Notional Eutectic Production via Additive Manufacturing

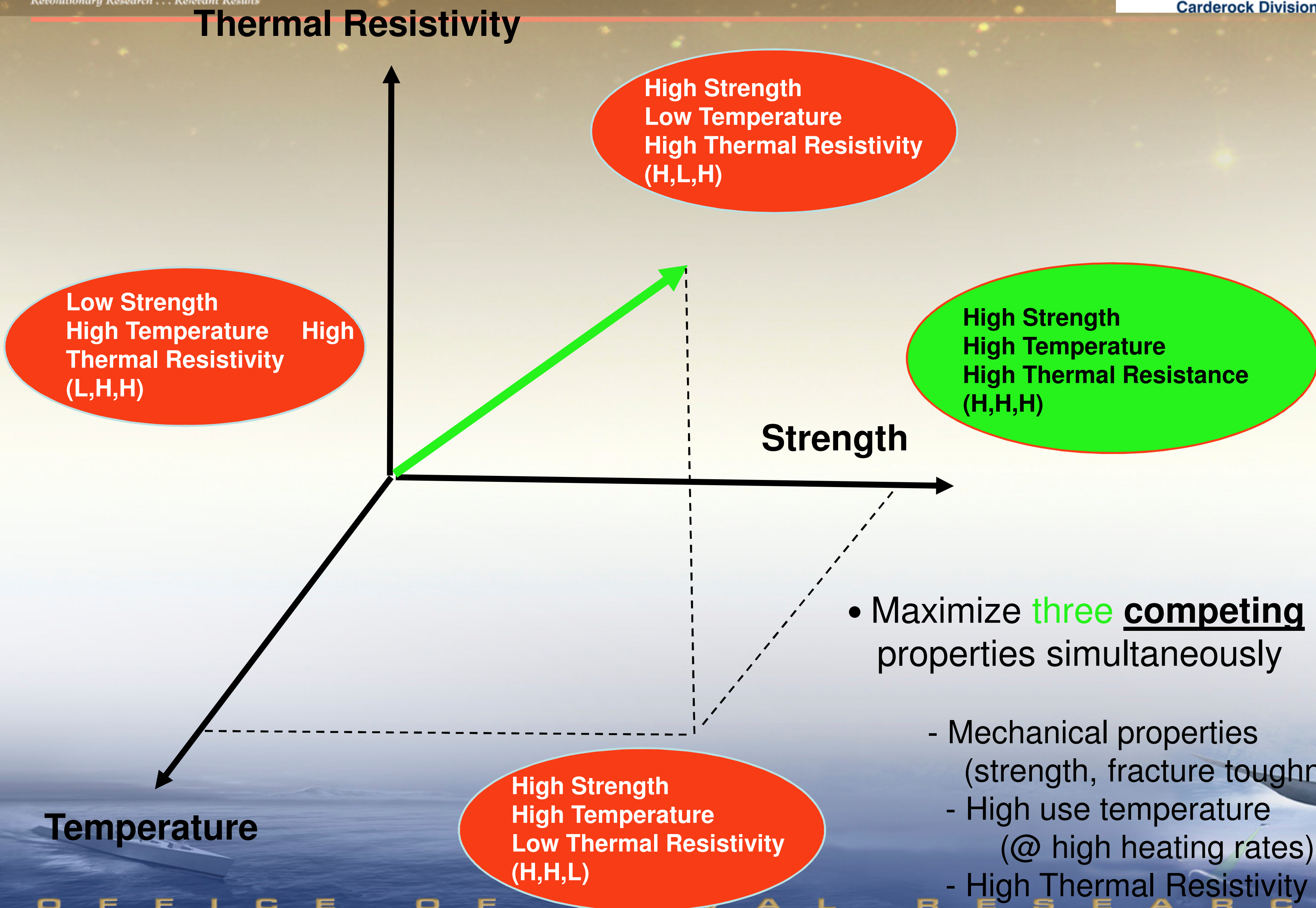
From CAD to part using laser or e-beam(?) metal deposition:

Metals were low-hanging fruit – Refractory Eutectic Ceramics and/or Coatings are a bit tougher





Structural Insulators: A Materials Challenge



- Maximize three **competing** properties simultaneously
  - Mechanical properties (strength, fracture toughness)
  - High use temperature (@ high heating rates)
  - High Thermal Resistivity

Conclusions

UHTCs are necessary for future hypersonic flight/propulsion systems due to higher use temperatures

Oxidation must be understood and controlled

Monolithic Ceramics will not likely be used in flight hardware

- Flaw Sensitivity (Attachment issues)
- Thermal Shock failure

Current work – joining and reinforced UHTCs

Do good research, but think like an engineer, not a scientist!