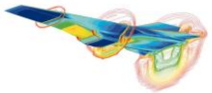

Overview of Environmental Durability Coatings and Test Capabilities

Craig Robinson

GRC Materials Division

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Hypersonic Propulsion Materials and Structures Workshop

NASA Glenn Research Center

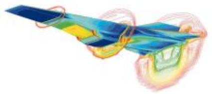
May 1-3, 2019

Outline

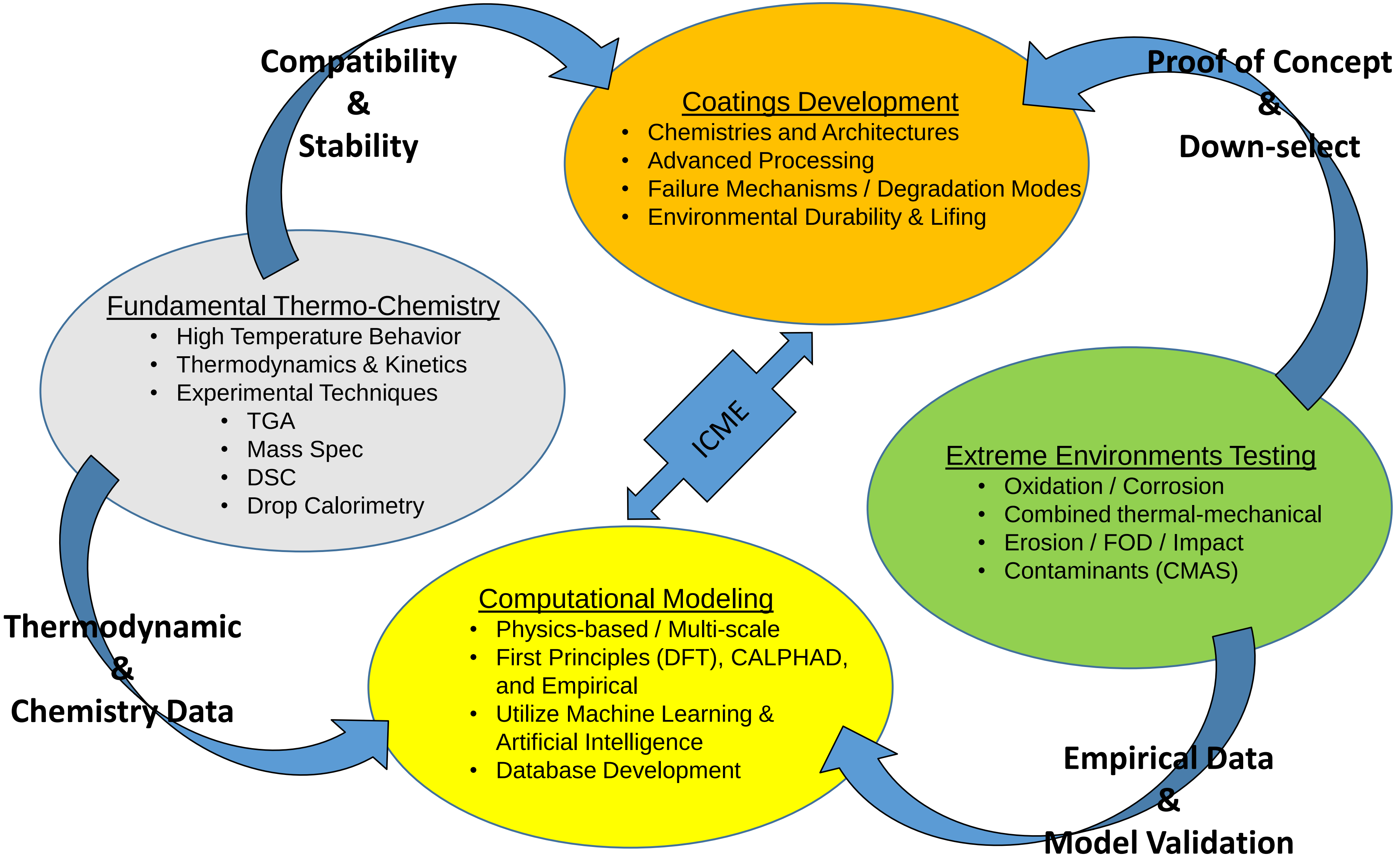
- Environmental Effects and Coatings Branch (LME)
  - Analytical and experimental capabilities
  - Much more than just coatings

- Case Studies - Past Hypersonics related work
  - Space Shuttle RCC Consultant
  - 3000°F Coating for C/SiC Leading Edge

- Current capabilities relevant for future Hypersonics work
  - Multi-layer Coatings Concept
  - Unique Testing Capabilities



NASA Environmental Effects & Coatings



Compatibility & Stability

Coatings Development
- Chemistries and Architectures
- Advanced Processing
- Failure Mechanisms / Degradation Modes
- Environmental Durability & Lifing

Proof of Concept & Down-select

Fundamental Thermo-Chemistry
- High Temperature Behavior
- Thermodynamics & Kinetics
- Experimental Techniques
  - TGA
  - Mass Spec
  - DSC
  - Drop Calorimetry

ICME

Extreme Environments Testing
- Oxidation / Corrosion
- Combined thermal-mechanical
- Erosion / FOD / Impact
- Contaminants (CMAS)

Thermodynamic & Chemistry Data

Computational Modeling
- Physics-based / Multi-scale
- First Principles (DFT), CALPHAD, and Empirical
- Utilize Machine Learning & Artificial Intelligence
- Database Development

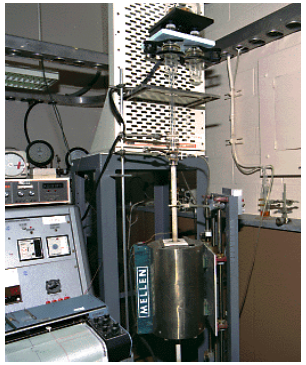
Empirical Data & Model Validation

High Temperature Thermo-Chemistry

- Degradation modes, kinetic rates, and thermodynamic data measurements
- World Class Mass Spectroscopy
  - (2) Knudsen Effusion Mass Spectrometers
  - High Pressure Mass Spectrometer
- Thermogravimetric Analysis, Differential Scanning and Drop Solution Calorimetry
- Hi Temp X-ray Diffraction, Energy Dispersion and Raman Spectroscopy
  - Soup-to-nuts characterization

Instrument	Measurements
Mass Spec (2000°C)	Products, activities, vapor pressure, enthalpy of vaporization
TGA (1650°C air, 3000°C vacuum)	Wt. change, oxidation, reduction, vaporization
DSC (2400°C)	Enthalpy of fusion, heat capacity
Drop Calorimeter	Enthalpy of formation, reaction, and mixing
XRD, EDS, Raman (1600°C)	Crystal structure, phase, composition, bonding

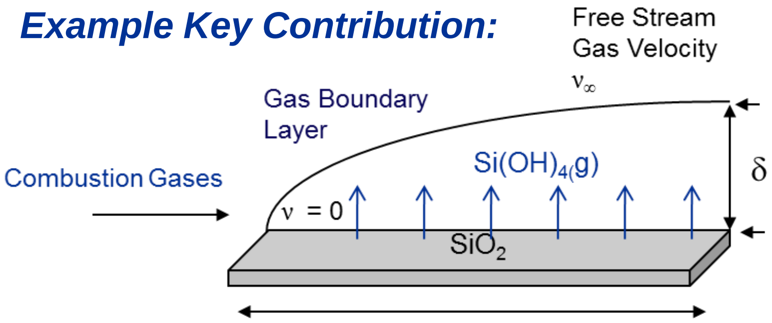
KEMS



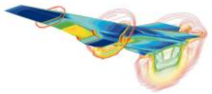
***Thermo-gravimetric Analysis** (air/water/vacuum)*

Calorimeter

Example Key Contribution:



*GRC identified Si(OH)$_4$ product for reaction of SiC with moisture – **reaction is life limiting to SiC/SiC durability in turbine engines***

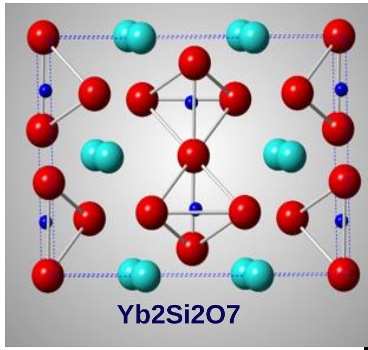


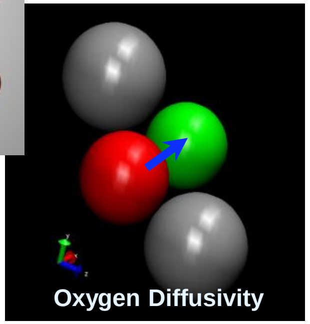
Computational Modeling

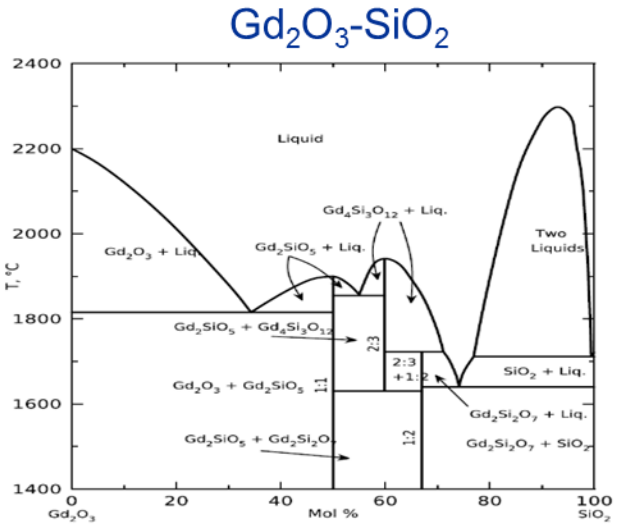
Thermodynamic codes and ab initio (First Principles) calculations

Ab inito (First Principles) atomistic materials modeling

- Density Function Theory (DFT) using VASP
  - Migration barrier energies, geometry optimization
  - Eqn. of State calculations (bulk modulus, density, equilibrium)
  - Phonon calculations (free energy, ΔH, S, Cp, k)
- Kinetic Monte Carlo and Molecular Dynamics analyses
  - O2/H2O diffusivity
- DFT-derived data augments experimental data and imported into thermodynamic codes and CALPHAD models





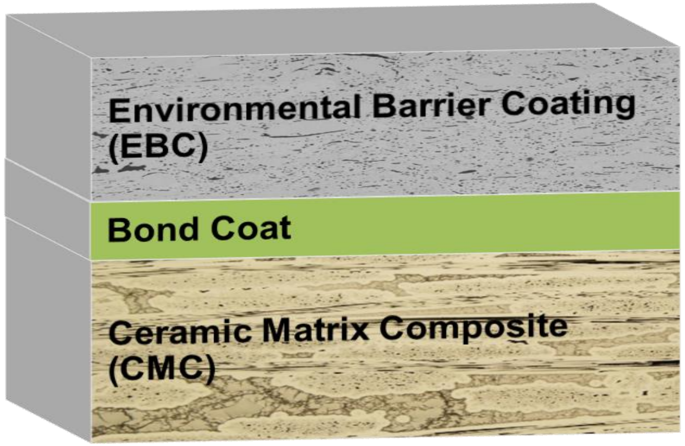


Gd_2O_3-SiO_2

CALPHAD - CALculation of PHAse Diagrams

- Computer Coupling of Phase Diagrams and Thermochemistry
- Phase Diagram optimization for Rapid Materials Discovery
  - Thermodynamic logic infers between compounds
  - Databases needed containing boundaries & thermodynamic data from GRC's experimental measurements & ab initio calculations
- Factsage, Thermo-Calc (includes Dictra & Prism), and Pandat
- Examples: phase diagrams/databases for Rare Earth oxides & silicates, diffusion studies, phase and chemistry stability

NASA EBC History

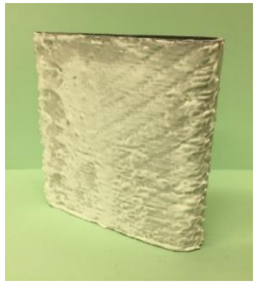


- EBC Topcoat provides barrier from turbine environment (H2O/CMAS)
- Bond Coat provides bonding / oxidation resistance
- Intrinsic Material Selection Criteria
  - CTE match
  - Phase stability throughout thermal cycle
  - Chemical compatibility
  - Crack resistance
  - Low modulus & sintering
  - Erosion & impact toughness

Hypersonics coatings will have different and unique requirements, but approach to materials properties and selection are the same.

- 1990's: Gen 1 (w/ GE & PW)
  - Silicon Bond coat
  - Mullite / Mullite + BSAS interlayers
  - BSAS top coat
- 2000's: Gen 2.0
  - Silicon bond coat
  - Rare earth (RE) silicate top coat
    - improves H_2O resistance
- Si bond coat limits CMC/EBC interface temperature (T_{melt} = 2400°F / 1416°C)
- 2010's: Next Generation EBCs
  - 2700°F bond coat, CMAS resistance, novel processing
    - CMAS: calcium-magnesium-aluminum-silicon oxides
  - Slurry: non line-of-sight, material & chemistry flexible
  - PS-PVD: non line-of-sight, hybrid , microstructure flexible

Slurry

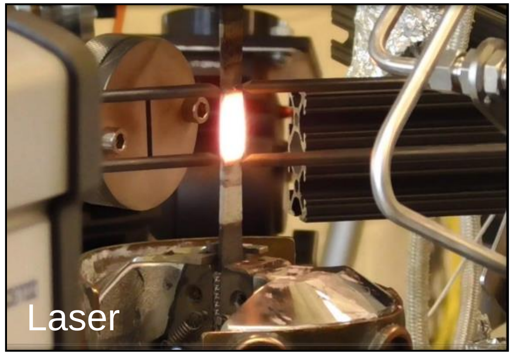


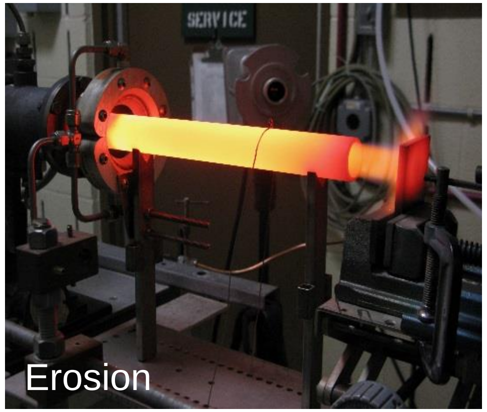
PS-PVD

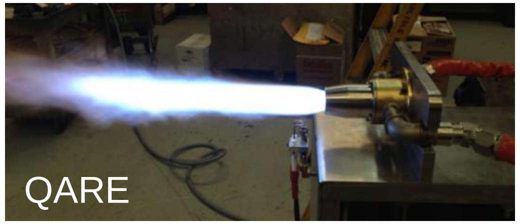
Extreme Environments Testing

Materials evaluated in relevant conditions for various failure modes

Facility	Failure Modes
High Heat Flux Lasers 3500-4000W Combined thermal-mechanical stress	Thermo-mechanical Erosion/FOD
Mach 0.3 Burner Rigs Tgas ~ 3000°F (1648°C) Tsrf ~ 2700°F (1482°C)	Recession Oxidation Thermo-mechanical Erosion/FOD CMAS
Dedicated Erosion Burner Rigs Adapted for CMAS compositions	Erosion/FOD CMAS
Steam Cyclic Oxidation Testing 90% H2O, 2700°F (1482 C)	Recession Oxidation CMAS
Quick Access Rocket Exhaust (QARE) Rig High temp, heat flux, velocity Also incorporates recession	Recession Oxidation Thermo-mechanical Erosion/FOD CMAS

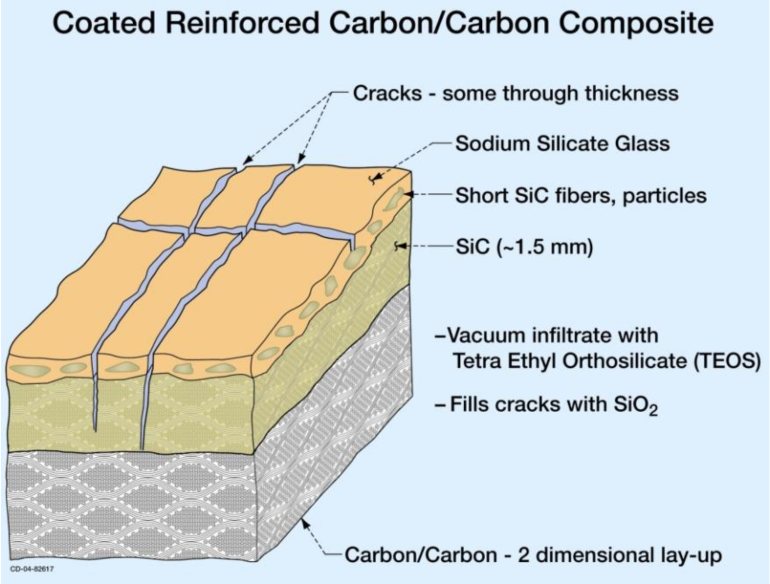


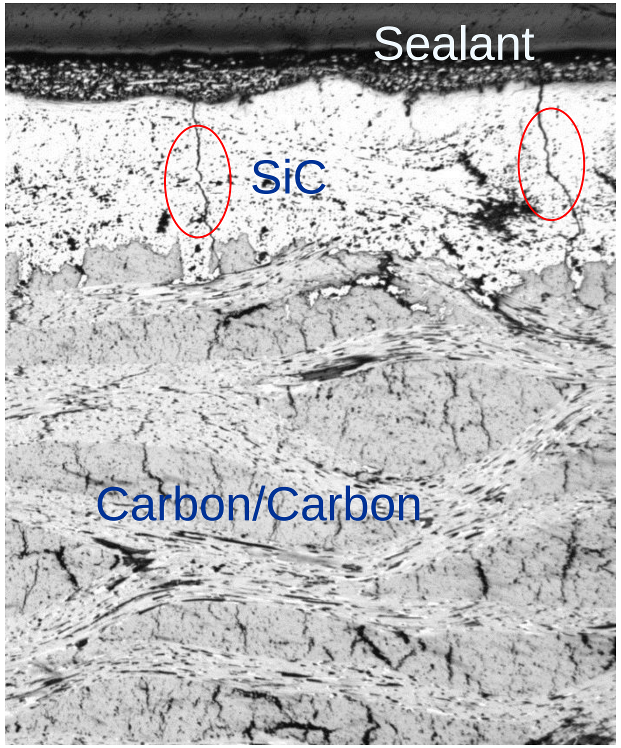




Need combination of rigs to investigate synergies between failure modes.

Consultants on RCC for Shuttle Orbiter 1995-2011



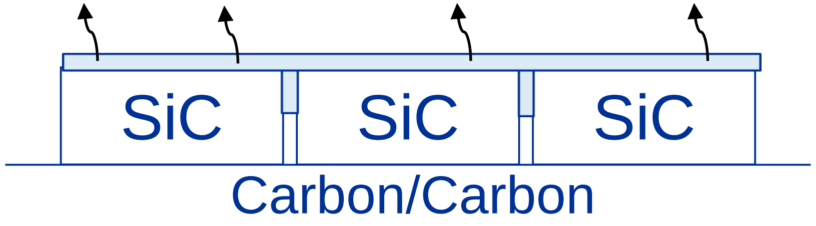


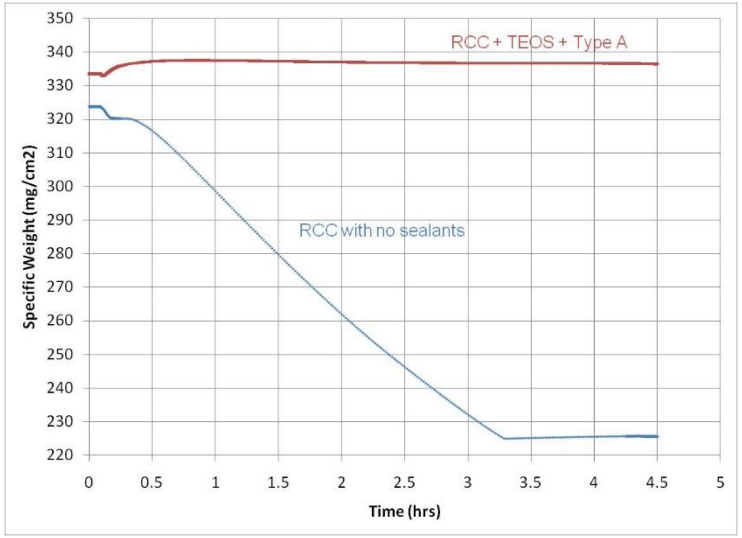
Tasks:

- RCC Durability
  - Developed model for oxidation through coating cracks
  - Understand behavior of sealants
- Developed characterization techniques with GRC’s ASG Group
- Understand processing issues and coating adherence (Tiger Team)
- Studies on repair materials (Tiger Team)
- Contributions to accident investigation
  - Establish RCC breach location, sequence, timeline

Shuttle Orbiter Contributions

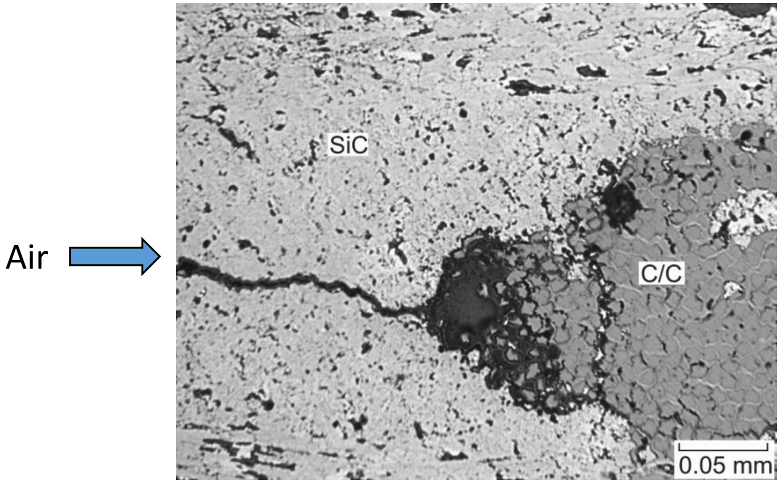
Coating Sealant behavior





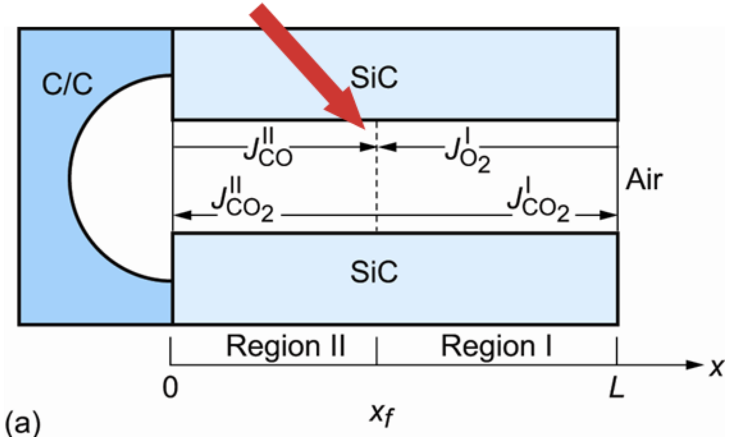
- Understand effectiveness of sealant
  - Viscosity and velocity effects
- Model sealant loss
  - Expressions for vaporization

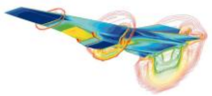
Modeling of Oxidation through coating cracks



$CO_2 + C = 2\,CO$ **$2CO + O_2 = 2CO_2$**

Expressions for CO and CO_2 fluxes developed to describe cavity growth





2010 C/SiC Work - Challenge

NASA Fundamental Aero Pgm / Hypersonics Project C/SiC 3000°F Leading Edge Coating Task

Oxidation protection for various regimes

- Protect carbon fibers from oxidation at low temps when cracks are open
    - Seal cracks in SiC seal coat
- Protect SiC from active oxidation at high temps and low pressures

Coating Concept: Leading Edge EBC

- Sealant Glass over C/SiC
    - Viscosity to seal cracks in coating over temp range
- Primary oxygen barrier topcoat
    - Low oxygen diffusivity to limit active oxidation of SiC
- Model oxygen diffusivity in coating

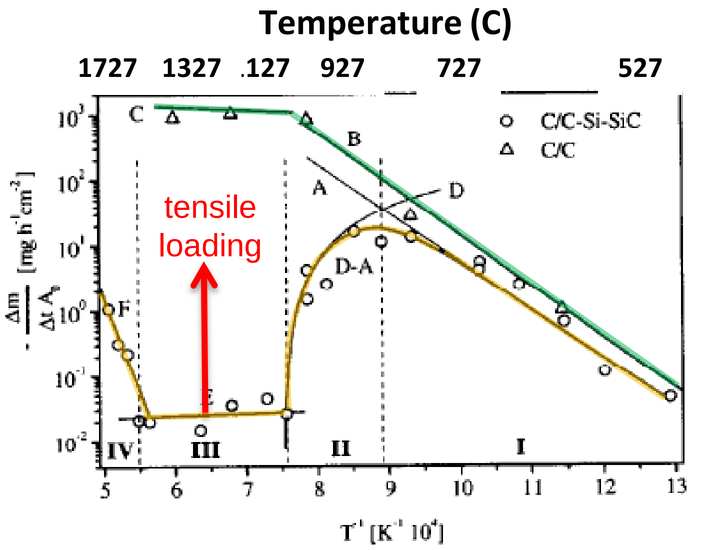
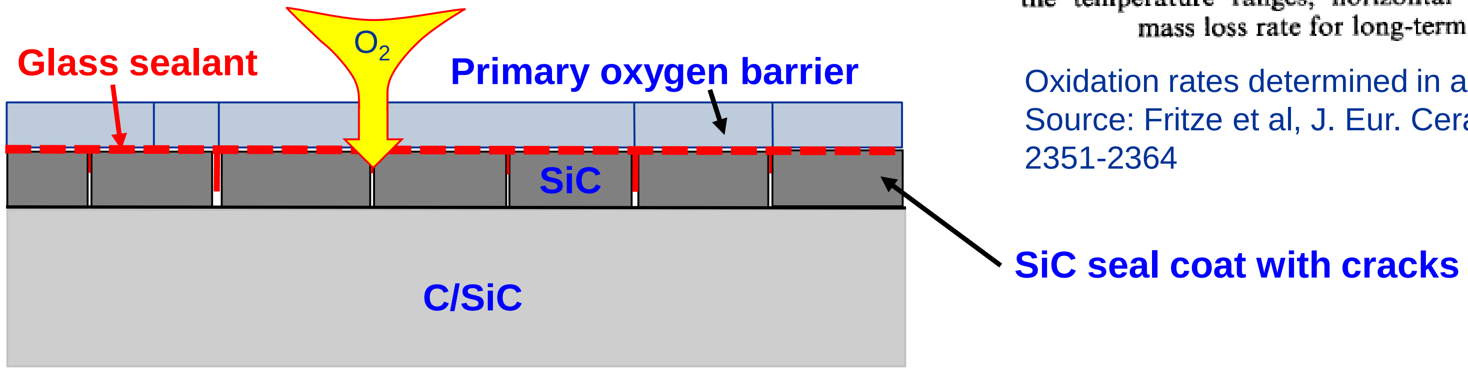


Fig. 10. Temperature dependence of the oxidation rates for silicon/silicon carbide coated C/C material and uncoated C/C material (solid curves: see text, vertical dashed lines: limits of the temperature ranges, horizontal dashed line: maximum mass loss rate for long-term applications).

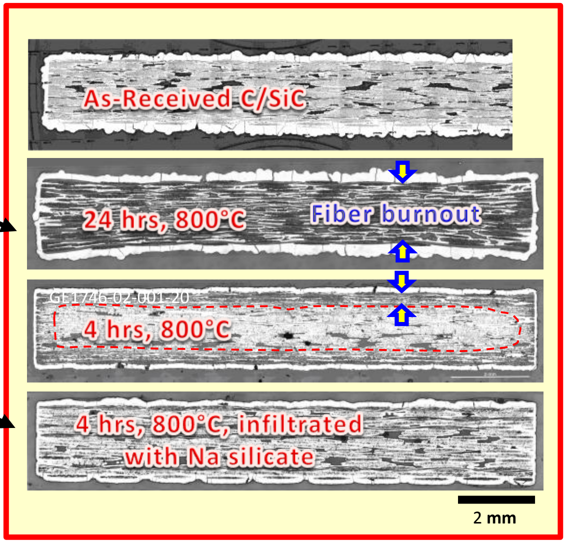
Oxidation rates determined in air
Source: Fritze et al, J. Eur. Ceram. Soc. 18 (1998) 2351-2364



2010 C/SiC Work - Accomplishments

Coating Development

- Degradation mechanisms identified: C fiber burnout (<1000°C) and active oxidation of SiC (>1500°C, low PO_2)
- Potential sealants identified: Na-silicate, CAS, MAS, evaluated for both mechanisms
- Stable oxygen barriers ($HfSiO_4$, $Y_2Si_2O_7$) identified
  - Negligible wt. change & sealcoat / topcoat compatibility
- SiO_2 scale investigated as a barrier to active oxidation
  - Delayed onset of active oxidation from 2-16 hours



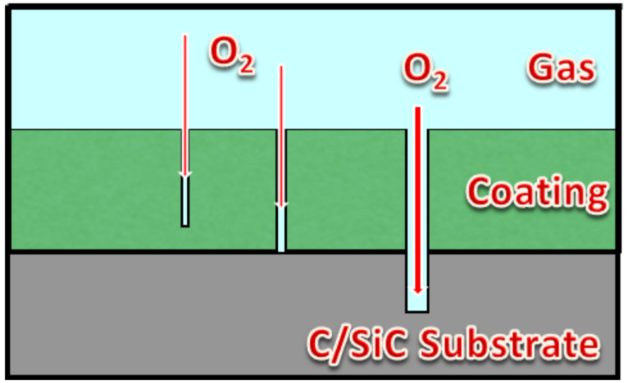
Fundamental Understanding

- Passive-to-active oxidation investigated for SiC, C/SiC, and C-rich SiC

Modeling

- A 2-D oxygen diffusion model for coatings with cracks developed.
  - Effect of crack width on transport
  - Effect of relative diffusivity in crack vs bulk

Schematic of the Diffusion Model



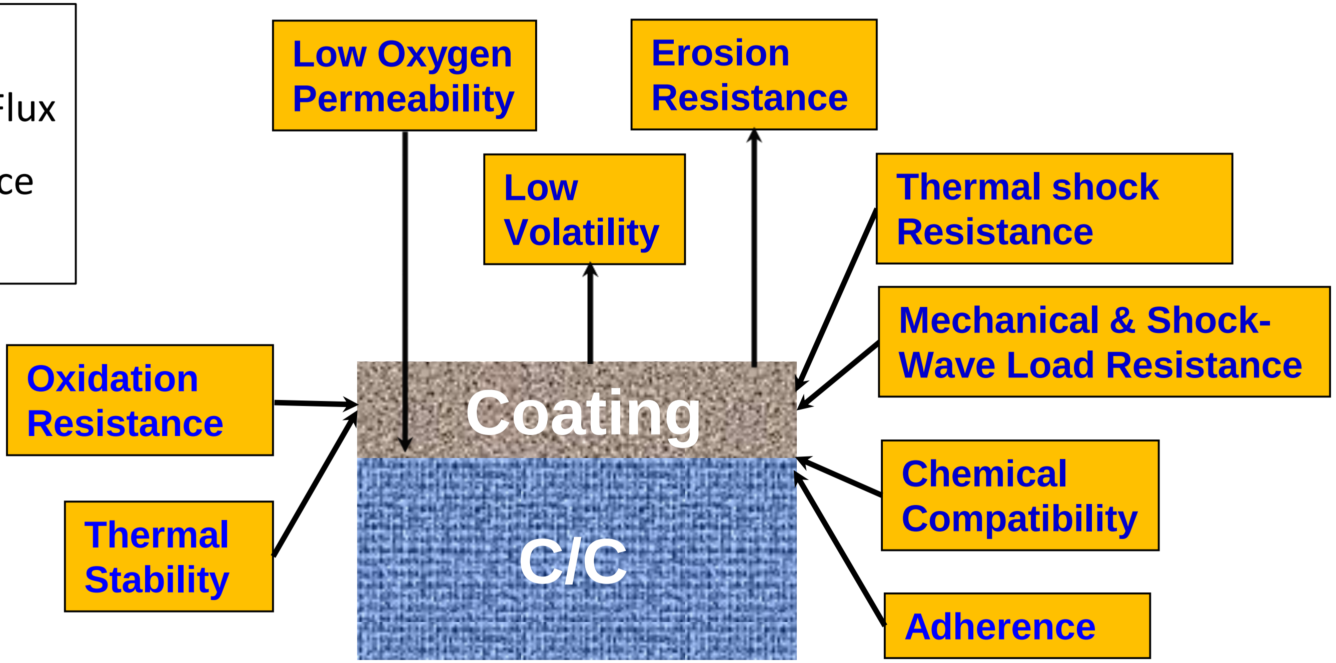
Next Steps: create multi-layers systems to evaluate; fundamental understanding of crystallinity, impurities, O_2/Ar transition points; combine diffusion & oxidation models, 3D.

Hypersonics LE Coatings Requirements

Very different than traditional EBCs

Requirements:

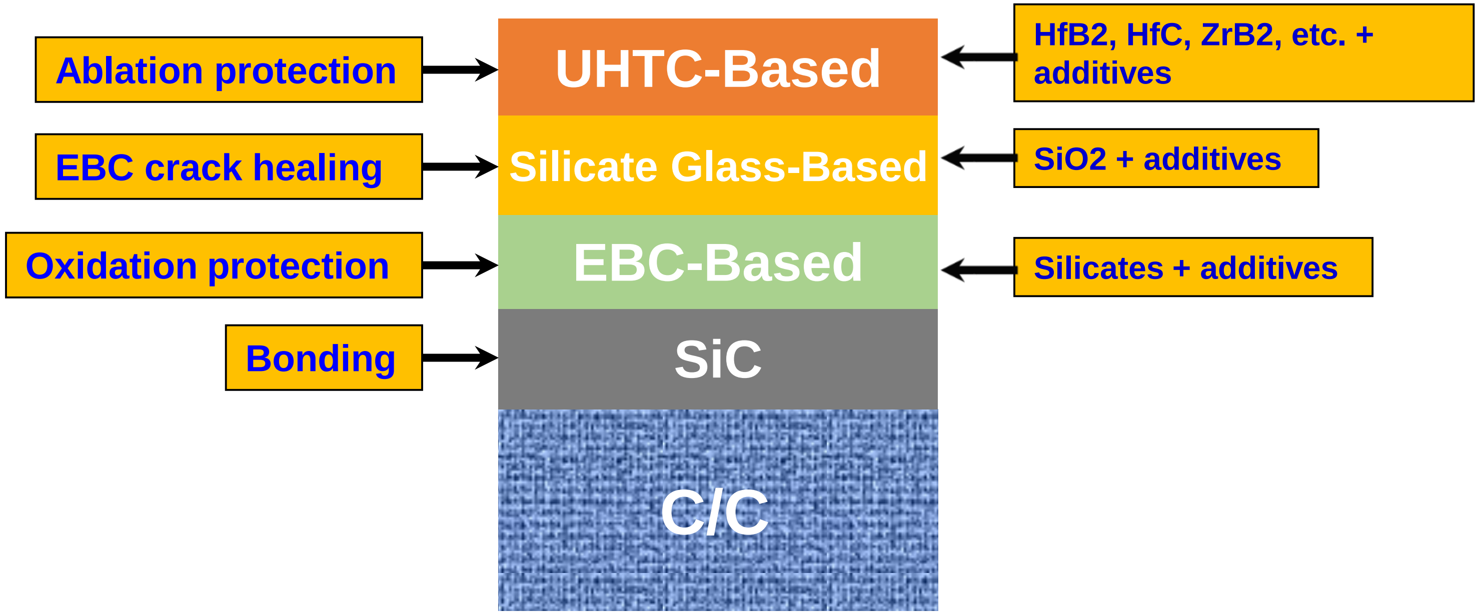
- High Temp / Heat Flux
- Oxidation Resistance
- Shape Retention



- Like EBCs, no single material can meet all the requirements
- Multilayer coatings are a promising approach / architecture
  - Multilayer coatings have shown success for EBCs
  - Bond layer + oxygen layer + seal-healing layer + ablation-resistant layer
  - Key is to define & evaluate failure modes for each layer then integrate

Multi-layer Coatings Concept

UTHCs, Silicate glasses, and SiC technologies all part of SOA. Key is to successfully integrate the various layers and add EBCs for oxidation.



Ablation protection → **UHTC-Based** ← **HfB2, HfC, ZrB2, etc. + additives**

EBC crack healing → **Silicate Glass-Based** ← **SiO2 + additives**

Oxidation protection → **EBC-Based** ← **Silicates + additives**

Bonding → **SiC**

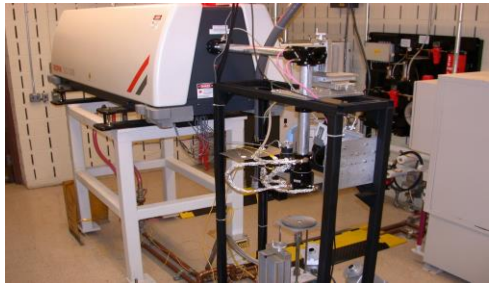
C/C

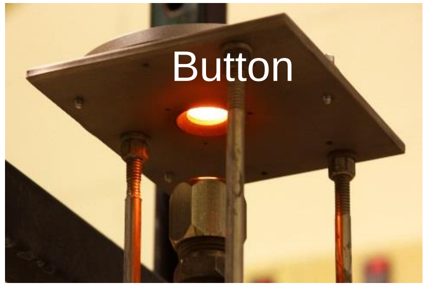
- Multilayer coatings approach to individually address all coating requirements
- Technology for each layer exists, but no coatings technology combining all four technologies exist
- Leverages NASA’s expertise in EBCs, slurry process, high temperature materials chemistry, and environmental testing

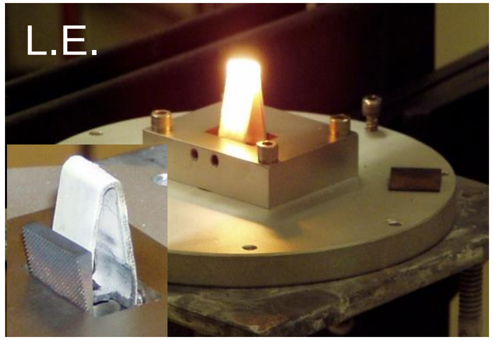
High Heat Flux Laser Facility – Suite of (3) Lasers

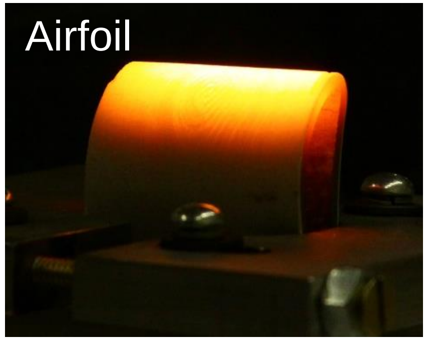
Specifications

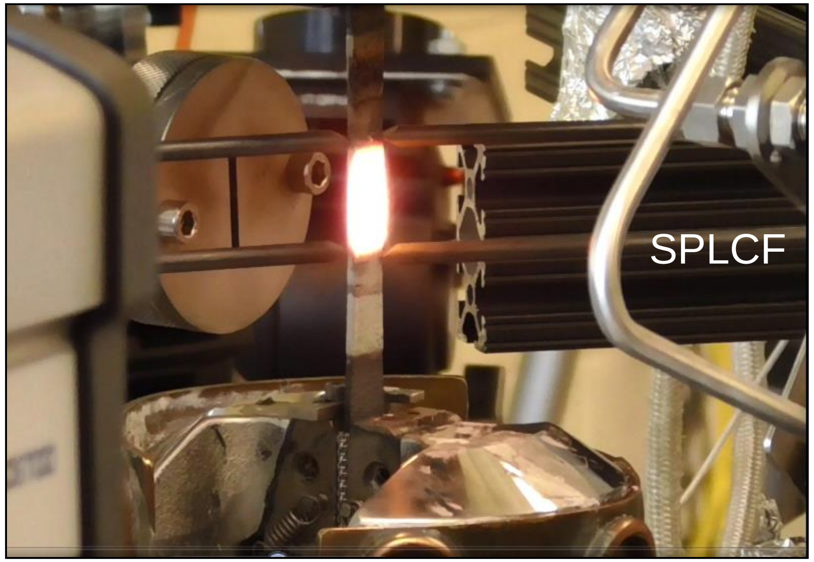
- Laser Heating (3500-4000W)
  - Heat fluxes ~ 300-500 W/cm^2 (265-440 Btu/ft^2-sec)
  - 1650W max w/ focused spot size
- Backside air cooling ⟶ thermal stresses
- Surface Temperature:
  - Multi-λ pyrometers and IR Camera
  - Surface Temperatures over 3100°F (1700°C) are material dependent
- Combined thermal-mechanical load
  - Multi-axis loading
  - In-plane and thru thickness strains





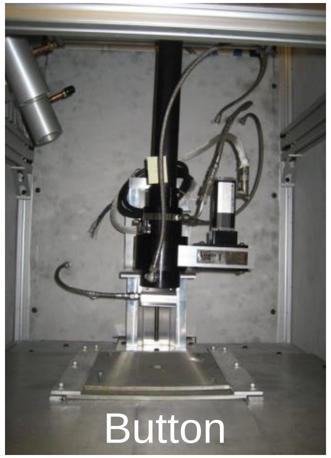






Configurations

- Button, dog-bone, leading edge or airfoil geometries
  - CMC, EBC, SiC, Si_3N_4
- Isothermal, thermal gradient, steady-state, cyclic capability
- Tensile, flexural, fatigue, creep, thermal conductivity

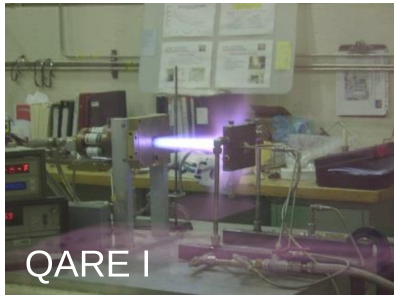


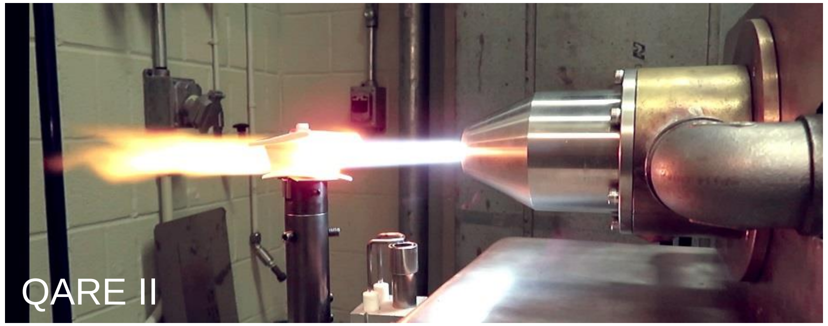
Quick Access Rocket Exposure (QARE) Rig

Atmospheric rig for testing in high heat flux oxidation environments for evaluating combined thermal-mechanical-environmental failure modes

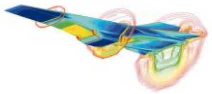
Specifications:

- QARE I recently replaced w/ QARE II
- Continuous supply of natural gas & 93% Oxygen
  - 1-1.5” dia. flame (3 nozzle sizes)
  - Estimated 4200°F (2325°C) T_{flame}
  - 3100°F (1700°C) $T_{surface}$
  - HF ~230 W/cm^2 (200 Btu/ft^2-sec) for ¼” cylinder
- Also provides ~58% H_2O for recession
  - Higher volatility than Jet A burner rigs and Lasers
- Pre-Arc Jet Test Screening
- Over $1M investment to date





- **Configurations:**
- Coupon, airfoil, leading edge geometries
  - RCC, GRCop84, NiAl, various coatings
- Surface Temperature:
  - Pyrometers and IR Camera
- Active cooling available
  - Cooled heat flux sensors, GRCop84 panels
- Static load frame available



Summary

- Recap LME’s Capabilities:
  - We understand the environments & degradation modes
    - Fundamental high temperature thermo-chemistry
  - In-house processing of coatings
    - Slurry & PS-PVD
  - We have extensive experience developing & testing materials under extreme conditons

- Past related contributions can serve as jump-off point
  - Oxidation modeling & sealants
  - 30+ yrs SiC and EBC expertise
  - Characterization

- Ready for immediate contributions
  - Multilayer coating architectures
  - Unique test capabilities
    - QARE Rig
    - Lasers
    - *Please join our tours this afternoon interested*