Overview of Environmental Durability Coatings and Test Capabilities

Craig Robinson
GRC Materials Division
raymond.robinson-1@nasa.gov; (216)433-5590

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

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

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

Compatibility & Stability

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

ICME

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

Empirical Data & Model Validation

Proof of Concept & Down-select
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

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

Example Key Contribution:

KEMS
Thermo-gravimetric Analysis (air/water/vacuum)
Calorimeter

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 initio (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, \( \Delta H \), S, \( C_p \), 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

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
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 H₂O resistance

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

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

Si bond coat limits CMC/EBC interface temperature ($T_{melt} = 2400°F / 1416°C$)

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

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

*Materials evaluated in relevant conditions for various failure modes*

<table>
<thead>
<tr>
<th>Facility</th>
<th>Failure Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Heat Flux Lasers</strong></td>
<td>Thermo-mechanical Erosion/FOD</td>
</tr>
<tr>
<td>3500-4000W</td>
<td></td>
</tr>
<tr>
<td>Combined thermal-mechanical stress</td>
<td></td>
</tr>
<tr>
<td><strong>Mach 0.3 Burner Rigs</strong></td>
<td>Recession</td>
</tr>
<tr>
<td>T_{gas} ~ 3000°F (1648°C)</td>
<td>Oxidation</td>
</tr>
<tr>
<td>T_{surf} ~ 2700°F (1482°C)</td>
<td>Thermo-mechanical Erosion/FOD</td>
</tr>
<tr>
<td></td>
<td>CMAS</td>
</tr>
<tr>
<td><strong>Dedicated Erosion Burner Rigs</strong></td>
<td>Erosion/FOD</td>
</tr>
<tr>
<td>Adapted for CMAS compositions</td>
<td>CMAS</td>
</tr>
<tr>
<td><strong>Steam Cyclic Oxidation Testing</strong></td>
<td>Recession</td>
</tr>
<tr>
<td>90% H_{2}O, 2700°F (1482 C)</td>
<td>Oxidation</td>
</tr>
<tr>
<td></td>
<td>CMAS</td>
</tr>
<tr>
<td><strong>Quick Access Rocket Exhaust (QARE) Rig</strong></td>
<td>Recession</td>
</tr>
<tr>
<td>High temp, heat flux, velocity</td>
<td>Oxidation</td>
</tr>
<tr>
<td>Also incorporates recession</td>
<td>Thermo-mechanical Erosion/FOD</td>
</tr>
<tr>
<td></td>
<td>CMAS</td>
</tr>
</tbody>
</table>

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
Coating Sealant behavior

SiC  SiC  SiC
Carbon/Carbon

Modeling of Oxidation through coating cracks

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

Expressions for CO and CO₂ fluxes developed to describe cavity growth

CO₂ + C = 2 CO
2CO + O₂ = 2CO₂
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
2010 C/SiC Work - Accomplishments

Coating Development
- Degradation mechanisms identified: C fiber burnout (<1000°C) and active oxidation of SiC (>1500°C, low PO₂)
- Potential sealants identified: Na-silicate, CAS, MAS, evaluated for both mechanisms
- Stable oxygen barriers (HfSiO₄, Y₂Si₂O₇) identified
  - Negligible wt. change & sealcoat / topcoat compatibility
- SiO₂ 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

Next Steps: create multi-layers systems to evaluate; fundamental understanding of crystallinity, impurities, O₂/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

- Low Oxygen Permeability
- Erosion Resistance
- Low Volatility
- Thermal shock Resistance
- Mechanical & Shock-Wave Load Resistance
- Chemical Compatibility
- Adherence

- Oxidation Resistance
- Thermal Stability

• 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.

- 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
Specifications

- Laser Heating (3500-4000W)
  - Heat fluxes ~ 300-500 W/cm² (265-440 Btu/ft²-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, Si₃N₄
- 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) $T_{\text{flame}}$
  - 3100°F (1700°C) $T_{\text{surface}}$
  - HF ~230 W/cm² (200 Btu/ft²·sec) for ¼” cylinder
- Also provides ~58% H₂O 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
• 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 conditions

• 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