LME –Environmental Effects & Coatings Branch

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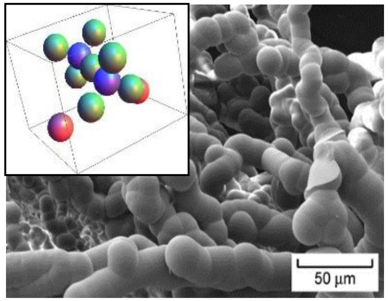
March 28, 2017

LME Coatings Activities



Fundamental High Temperature Behavior of Materials – Thermo-chemistry, Physics, and Modeling

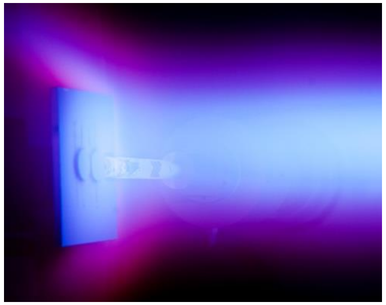
- Oxidation/corrosion, compatibility & diffusion, experimental & computational methods
- Experimental thermodynamics and kinetics testing for identification and quantification of degradation/failure modes
- Computational thermodynamics and computational models

Durability testing in Extreme Environments

- Exposure to relevant conditions (thermal + mechanical + environmental)
- High temp, high heat flux, isothermal & cyclic, combustion, oxidation & corrosion, steam & water vapor, CMAS, erosion, impact

Advanced Coatings Development: Concepts and Processing

- TBCs, EBCs, multi-layer engineered coatings
- Develop coating compositions to mitigate environmental degradation
- Characterize and develop new coating processing methods



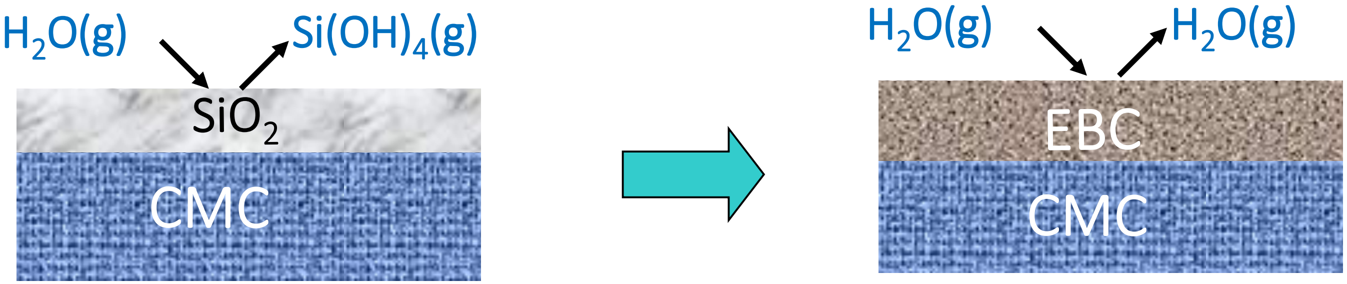
Outline

- EBCs
    - Thermo-chemistry & Modeling efforts
    - Environmental Durability testing capabilities and current efforts
    - Processing
- TBCs
- Challenges & Potential Collaborations

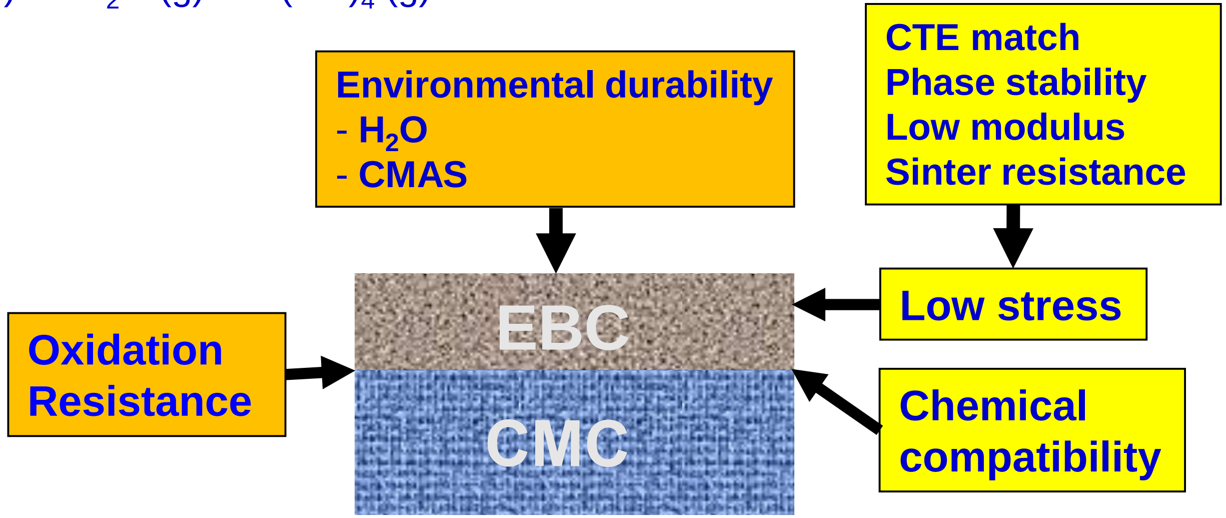
EBCs

Environmental Barrier Coating (EBC)

An external coating to protect CMC from water vapor



SiO_2 (s) + $2H_2O$ (g) = Si(OH)$_4$ (g)



Environmental durability
- H_2O
- CMAS

CTE match
Phase stability
Low modulus
Sinter resistance

Low stress

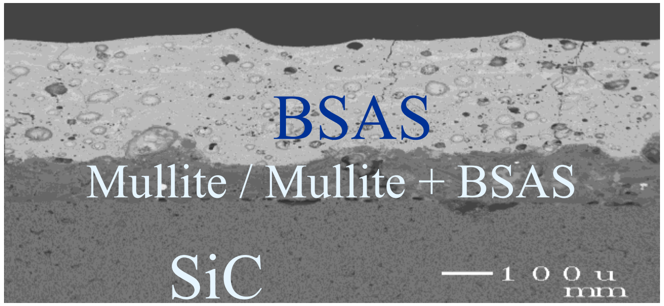
Oxidation Resistance

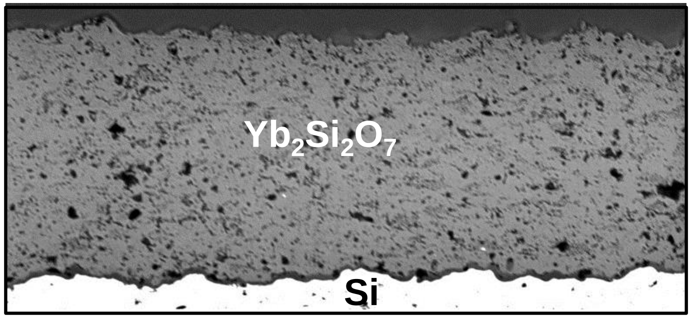
Chemical compatibility

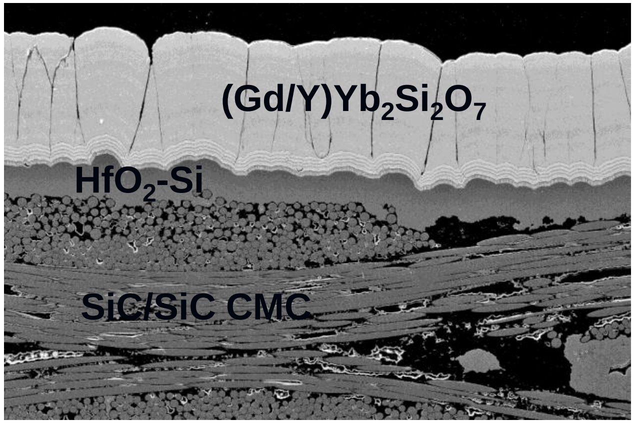
EBC is essential for CMC operation. Uncoated CMC suffers rapid recession.

NASA EBC History

- 1990’s: Gen 1.0
  - Silicon Bond coat
  - Mullite (3Al2O3-2SiO2) / Mullite + BSAS intermediate layer
  - BSAS (BaO/SrO/Al2O3/SiO2) Topcoat
- 2000’s: Gen 2.0
  - Silicon Bondcoat
  - Rare earth (RE) silicate topcoat (e.g. Yb2Si2O7)
  - RE silicates improve H2O resistance
- 2010’s: Next Generation EBCs
  - 2700ºF capable bond coat
    - HfO2+Si & RESi Bond coat
    - Oxide-based bond coat
  - CMAS mitigation
  - Novel EBC processes
    - DVD
    - PS-PVD
    - Slurry







Thermo-chem & Modeling

Thermo-chemistry & Modeling

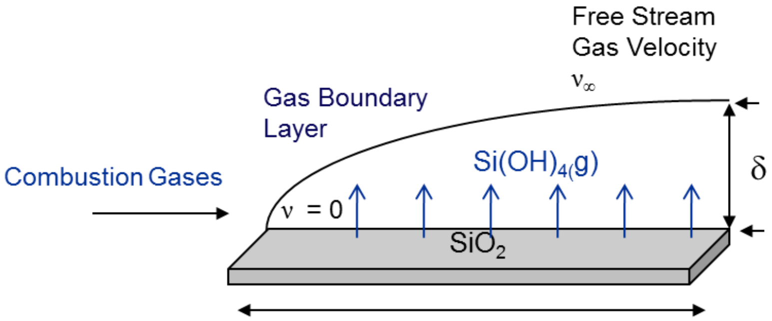
Experimental Thermodynamics & Kinetics Capabilities:

- Identify gaseous reaction products
- Determine kinetic rates

SiO_2 (s) + $2H_2O$ (g) = $Si(OH)_4$ (g)

Knudsen Effusion Mass Spectrometer

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

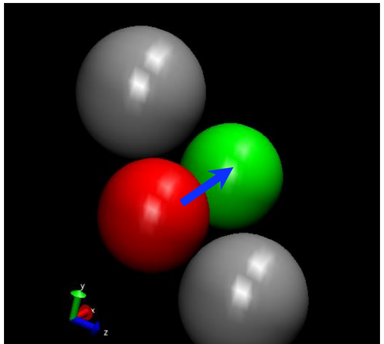


*GRC identified $Si(OH)_4$ product for reaction of SiC with moisture – **reaction is life limiting to SiC/SiC durability in turbine engines***

Boundary Layer Vapor Flux α $a(SiO_2)\cdot K_p$

Computational Thermodynamics & Computational Models:

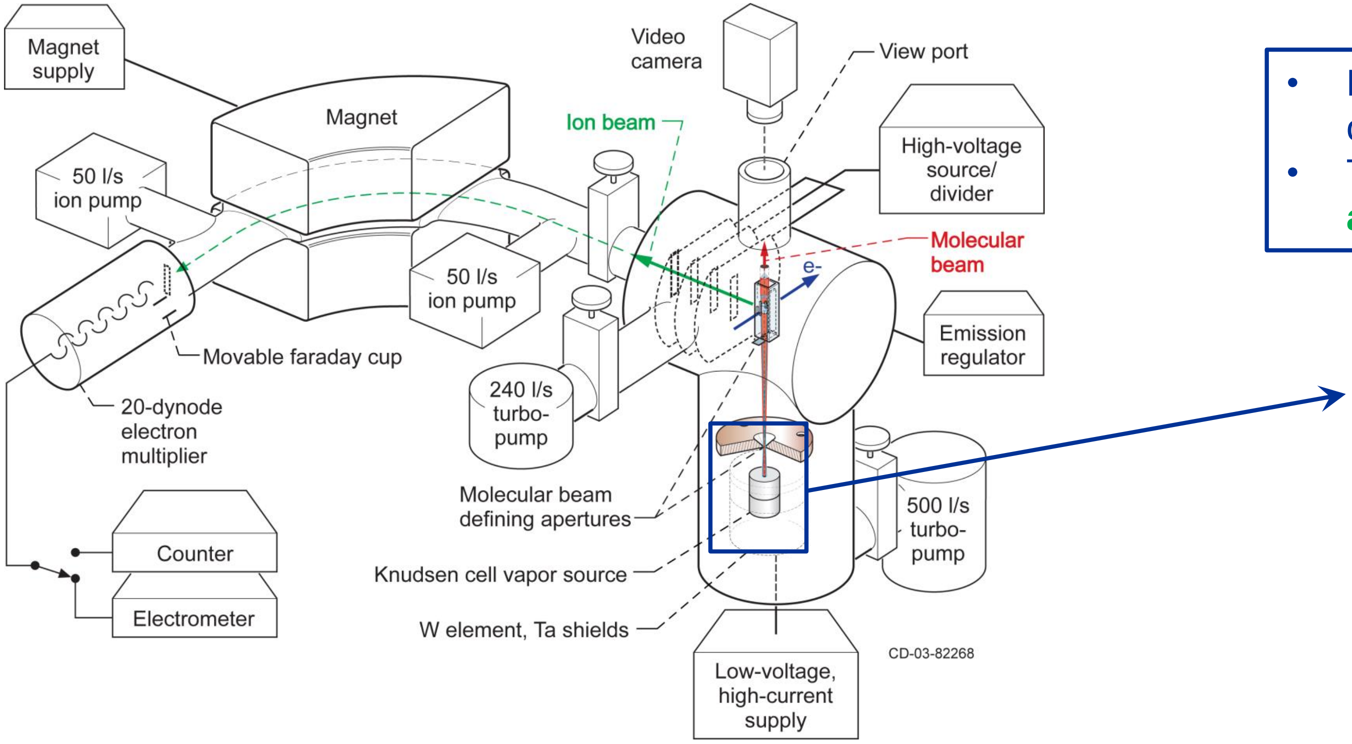
- Thermodynamics & kinetic approach
  - Identify degradation modes due to adverse reactions w/ adjoining materials and environment constituents
  - Code generated phase diagrams (FactSage / ThermoCalc / Dictra)
  - Modeling efforts complimented with in-house experimental capabilities
- Atomistic, nanoscale, and continuum DFT materials modeling
  - Molecular dynamics, Metropolis/Kinetic Monte Carlo, and particle statics/dynamics



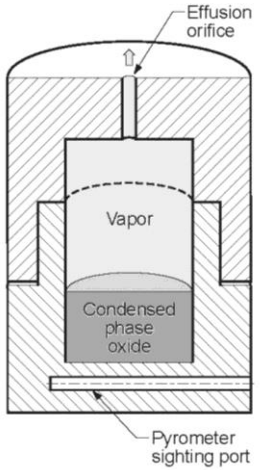
Oxygen Diffusivity in ZrO_2

Solid Phase Thermodynamics

- Measured thermodynamic activity of SiO_2, a(SiO_2) in
  - Y_2O_3-SiO_2, Yb_2O_3-SiO_2, Lu_2O_3-SiO_2 (in progress)…looking for trends
  - Use Knudsen Effusion Mass Spectrometry (KEMS)



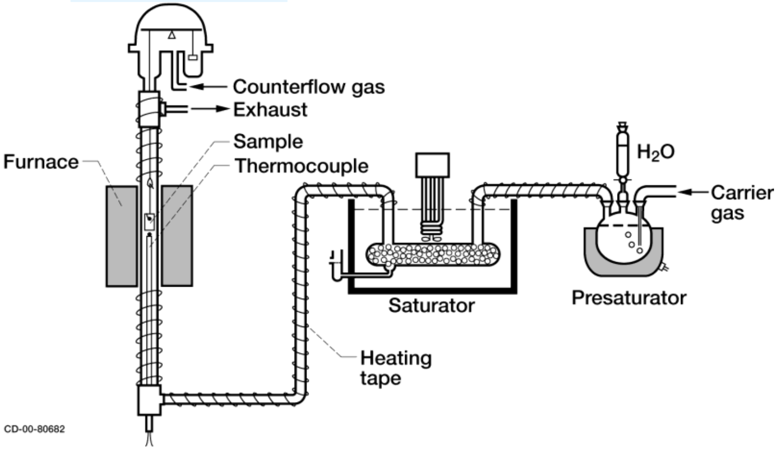
- Measure ion intensity of species in vapor
- These relate to **activity in the solid**

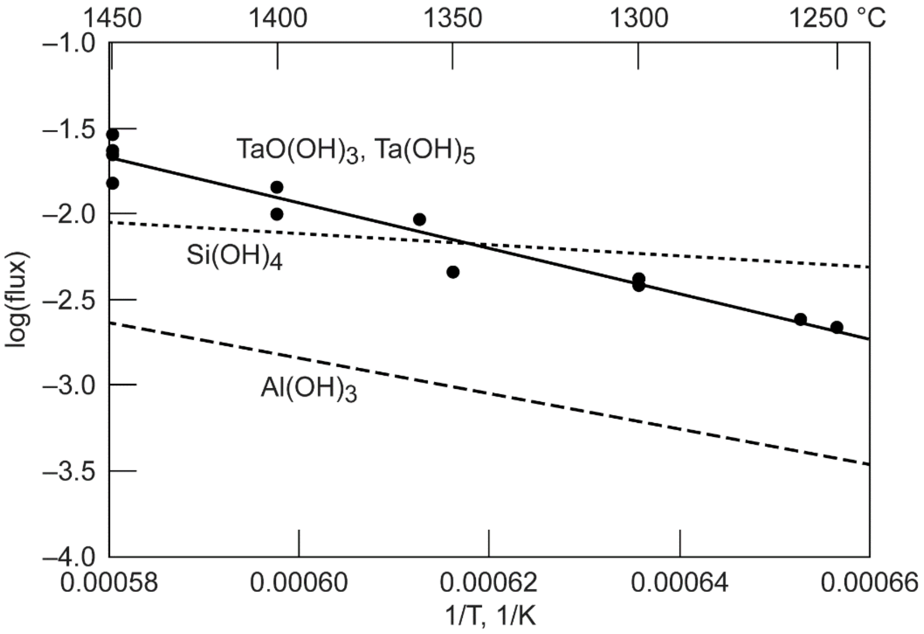


Vapor Pressures and Fluxes

- Measure vapor pressures and vapor fluxes via several methods, primarily TGA (thermogravimetric analysis)
- Test both free-standing coatings and individual coating constituents (SiO_2, Al_2O_3, Ta_2O_5, etc.)

Setaram Balance

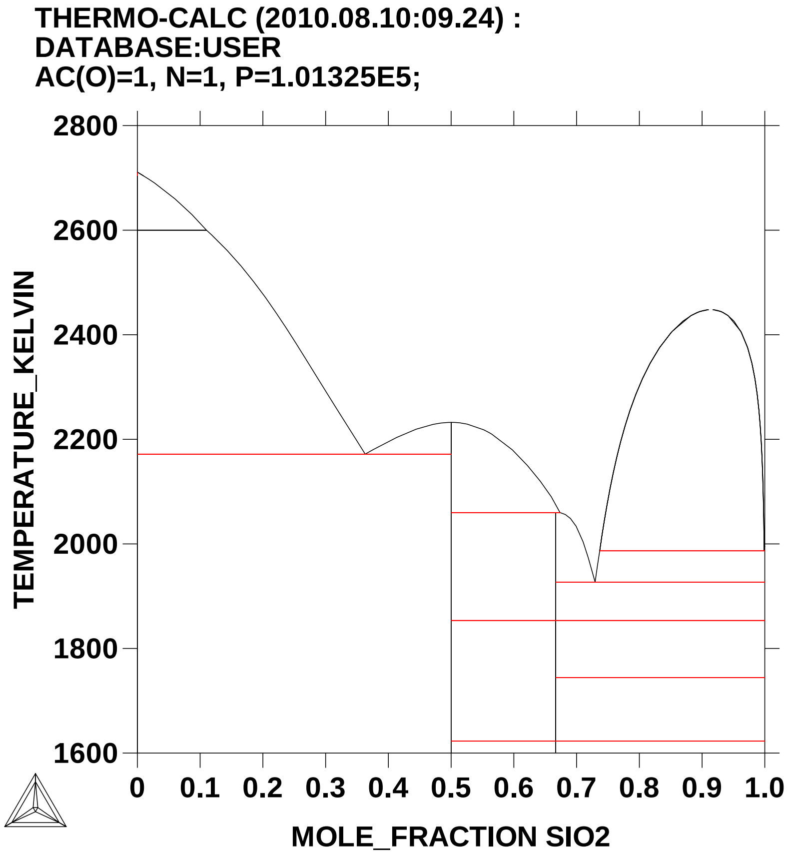




D. Myers, M. Kulis, et al., J. Am. Ceram. Soc., in press

Calculation of EBC Phase Diagrams (M. Kulis)

Literature: Y_2O_3-SiO_2



- Developing databases for other RE_2O_3-SiO_2 Systems
- Based on Free Energy Expressions for each phase (Calphad method)
- $G = G^{ref} + G^{id\ mix} + G^{excess}$
  $= x_1G^{ref,\,1} + x_2G^{ref,\,2} -$
  $RT\,[\,x_1 \ln x_1 + x_2 \ln x_2] + G^{excess}$

  G^{excess} from solution models

Atomistic Modeling

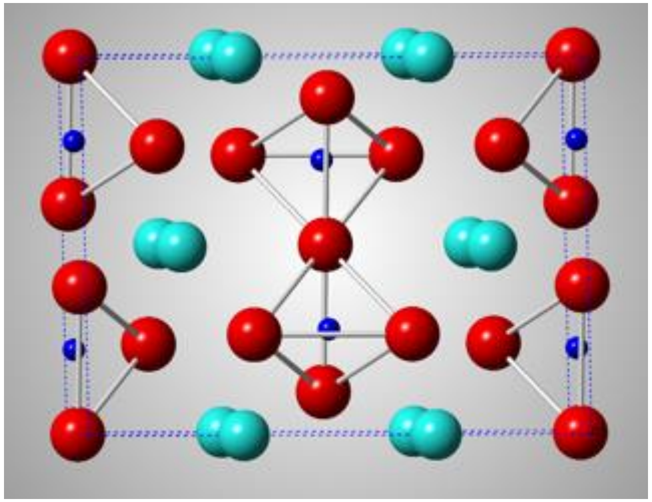
Approach:

- Process assumed thermally activated, consider vacancy and interstitial diffusion mechanisms.
- Migration barrier energies are computed using Density Functional Theory (DFT).
- Barrier energies are used to produce O2 diffusivities using a Kinetic Monte Carlo (kMC) code in candidate materials such as Yb2Si2O7, Y2Si2O7, and HfSiO4.

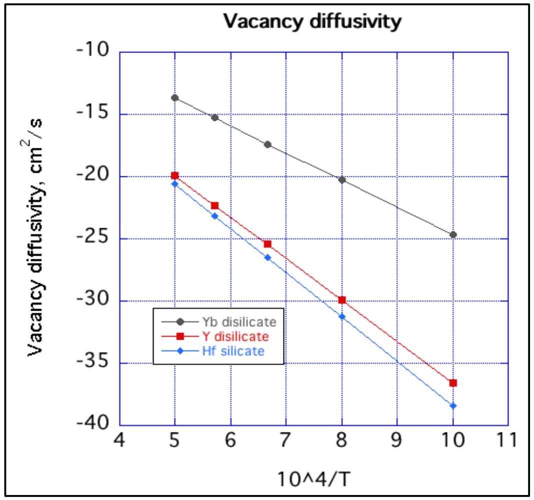
Results:

- Y and Y disilicates have very low vacancy-mechanism diffusion.
- Interstitial diffusivity is much larger, but solubility is low, so permeability will be small.
- Grain boundary diffusion still a concern.
- Prospective bond coat material, Hf silicate, has relatively low vacancy mechanism diffusivity, and may offer a degree of “last resort” protection in the case of coating cracking.

Oxygen diffusion via vacancy and interstitial mechanisms is not a significant problem in these materials.

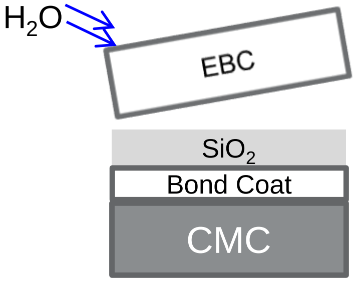


$Yb_2Si_2O_7$ Structure

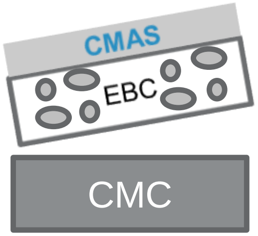


Extreme Environments Testing

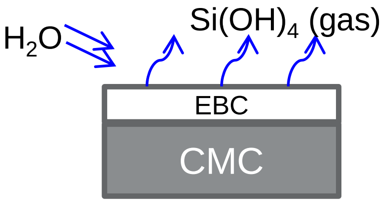
EBC Failure Modes



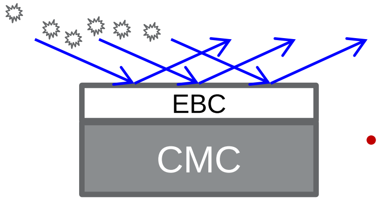
- Steam oxidation



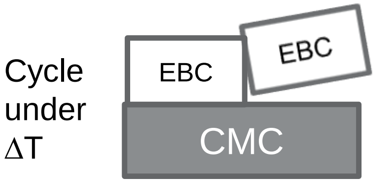
- Sand/Volcanic Ash Ingestion
- CMAS: Calcium-Magnesium-Alumino-Silicate



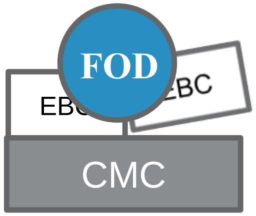
- Recession by water vapor



- Erosion



- Thermal fatigue
- Thermo-mechanical fatigue



- Foreign Object Damage

Synergies between failure modes lead to the ultimate EBC failure

K. N. Lee, "Environmental Barrier Coatings for CMC's"; in *Ceramic Matrix Composites*, Wiley, New York (2015)

NASA EBC Testing Rigs

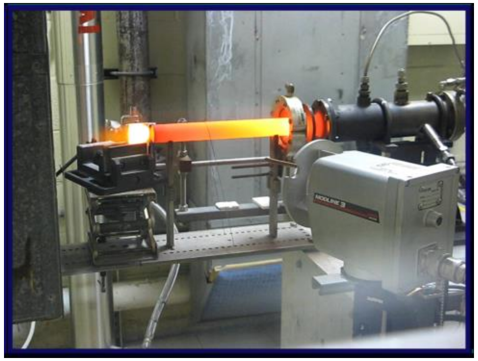
Rig	Capability	Failure modes to be tested
Mass Spectrometer	$P(H_2O)$ = N/A v = N/A P_{total} = N/A	Recession (High pressure measurement of reaction products and Low pressure measurement of activities)
Steam TGA	$P(H_2O)$ = up to ~0.5 atm v = a few cm/s P_{total} = 1 atm	Recession (Initial screening of candidate materials)
Mach 0.3 Burner rig	$P(H_2O)$ = ~0.1 atm v = 230 m/s P_{total} = 1 atm	CMAS, Erosion, FOD
Steam cycling rig	$P(H_2O)$ = up to ~1 atm v = a few cm/s P_{total} = 1 atm	Steam oxidation
High heat flux laser rig	$P(H_2O)$ = ambient air v = zero P_{total} = 1 atm	Thermal fatigue in temp gradient Thermo-mechanical fatigue in temp gradient
Natural gas burner rig	$P(H_2O)$ ~ 0.5 atm, v ~ 250m/s P_{total} = 1 atm	Recession Thermal fatigue in temp gradient (Coupons, Tensile bars, components)
CE-5 combustion rig	$P(H_2O)$ ~ 3 atm v ~ >30 m/s P_{total} ~ 30 atm	Steam oxidation w/ temperature gradient Recession (Coupons, Tensile bars, components)

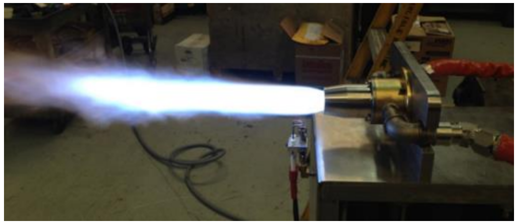
- **Combinations of rigs to investigate synergies between failure modes**

Environmental Durability Testing

Materials evaluated in relevant conditions with a wide range of facilities:

- **High Heat Flux Laser Rigs**
  - (4) rigs capable of up to 315 W/cm^2
  - Thermal-mechanical capability
  - Isothermal, thermal gradient, steam
  - In Situ Thermal Conductivity
- **Mach 0.3 Burner Rigs**
  - Jet fuel / air combustors (Mach 0.3 - 0.7)
  - Tgas over 3000°F / Tsrf up to 2700°F
  - Automated, thermal cycling, impact, loading
- **Dedicated Erosion Burner Rigs**
  - Alumina erodent particulates (1-600 micron)
  - Adapted for CMAS compositions
  - Continuous/uniform feeding (.08-60 gm/hr)
- **Steam Cyclic Oxidation Testing**
  - 90% water vapor (9 atm total pressure)
  - Temperatures up to 2700°F (1482 C)
- **Natural Gas / O2 Burner Rig**
  - Natural gas / O2 combustion
  - 4200 F, 250 m/s, up to 58% H2O, 160-215 W/m2
  - Versatile: water recession, full coverage high heat flux, complex geometries, film cooling, combine with erosion / CMAS

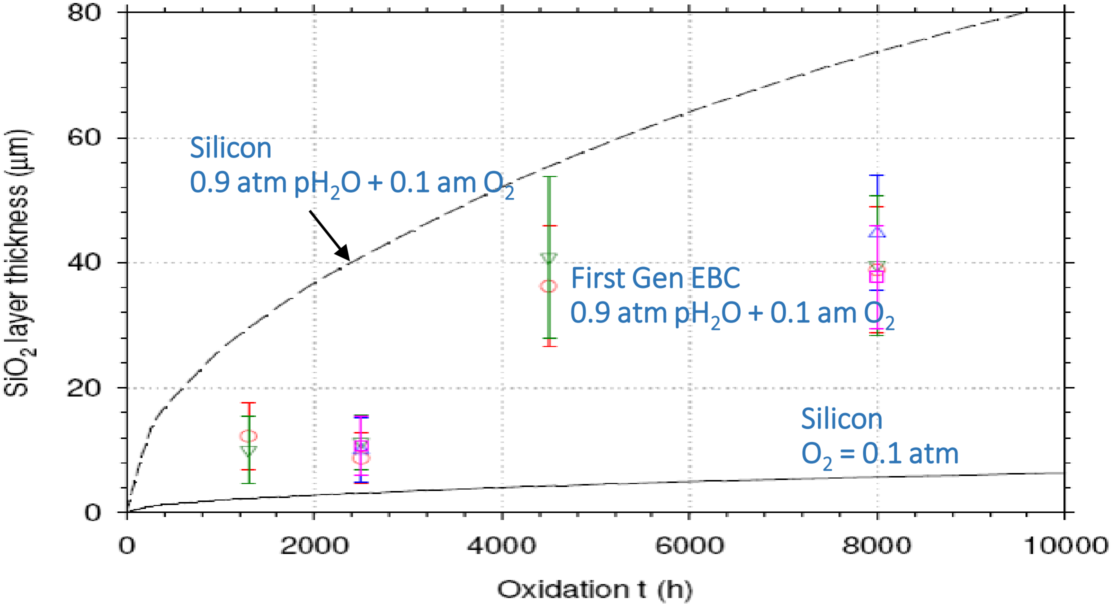




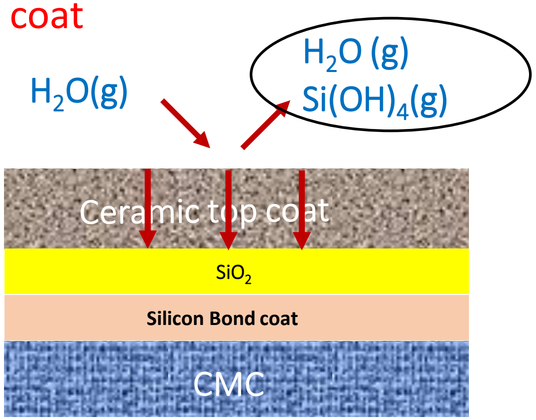
EBC Steam Oxidation

- Silicon oxidizes faster in $H_2O(g)$ than in air by an order of magnitude
- Attributed to high solubility of $H_2O(g)$ in SiO_2
- Ceramic top coat does not stop the transport of $H_2O(g)$ to Si bond coat

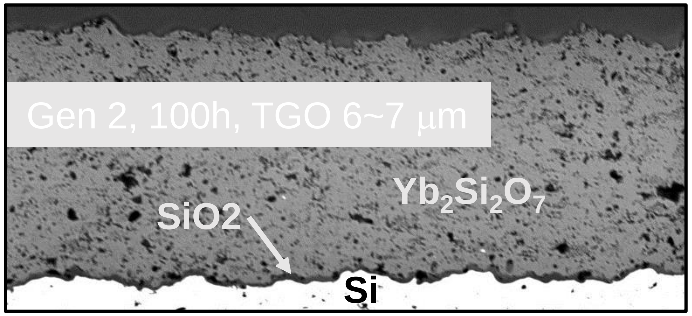
Isothermal Oxidation, T = 2200°F (1204°C)



GE Final Report – AMAIGT Program Dec. 2010



Cyclic Oxidation, 2400°F, 90% H_2O



NASA, Unpublished data

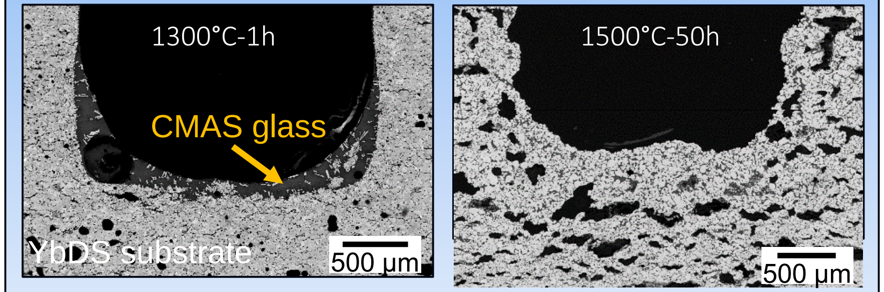
Oxidation of EBC/CMC system must be evaluated in H_2O environments

CMAS Studies for EBCs

CMAS Exposures of Ytterbium Disilicate (YbDS)

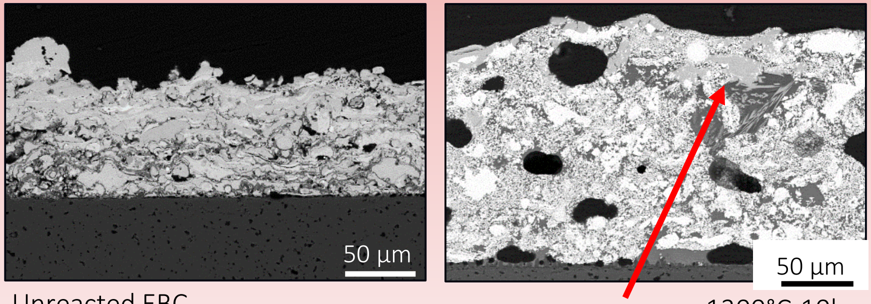
- Thermochemical interactions (1200-1500°C)

Hot-pressed YbDS substrate



No alternate phase detected

PS-PVD YbDS EBC on hexoloy substrate



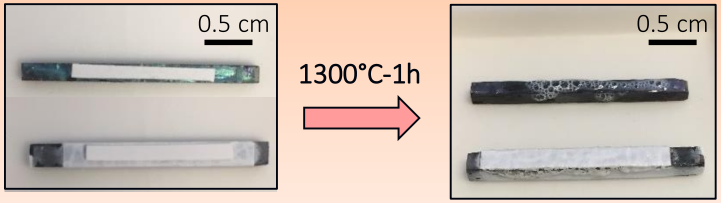
Unreacted EBC

Alternate Ca-containing phase

1300°C-10h

- Effect on EBC/CMC mechanical properties
  - PS-PVD YbDS on SiC/SiC CMC
  - Room-temperature flexure after CMAS exposure

CMAS exposure



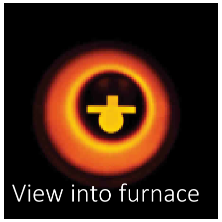
Before

After

Properties of CMAS Glasses

- Viscosity, crystallization, thermal and mechanical properties
  - Eyjafjallajökull volcanic ash
  - VIPR volcanic pumice
- CMAS wetting behavior on EBCs (IRAD Proposal)

Heating Microscope

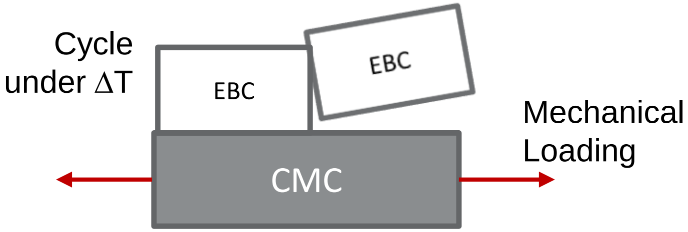


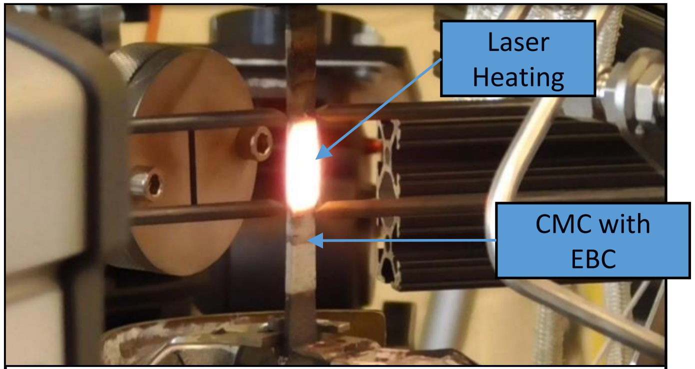
FY17: 1 journal paper, 5 conference presentations (as of Mar 7)

Thermomechanical Testing of NASA CMC/EBC System

- First integration and testing of NASA developed CMC with the NASA developed EBC system
- Sustained peak low cycle fatigue (SPLCF) test with laser gradient heating for thermomechanical validation
- Milestone set at 300 hours with a 2700°F CMC temperature and 10ksi load

EBC Surface Temperature: 2950°F
CMC Temperature: 2700°F
Load: 10ksi
Total Life: 487 hours

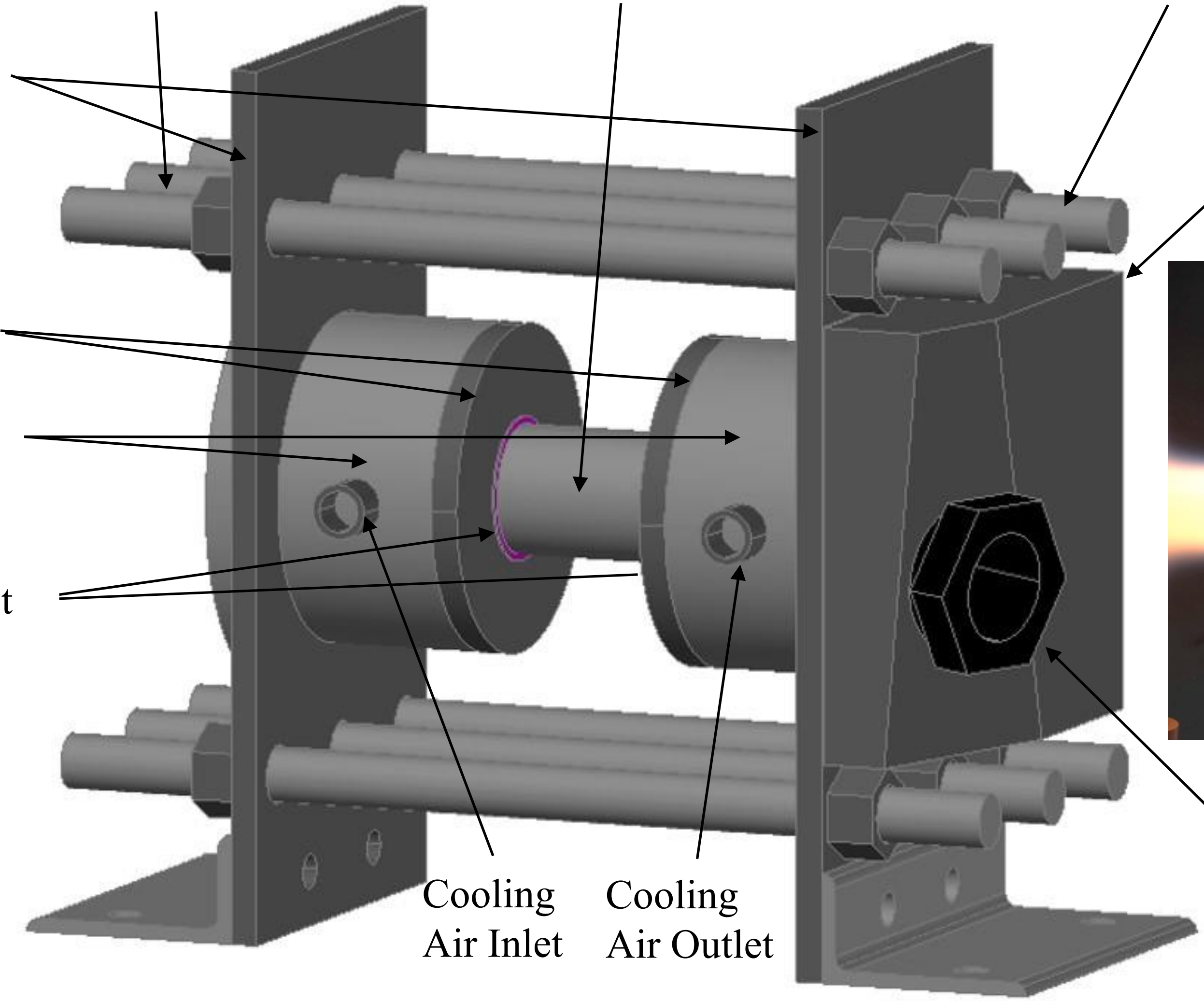




EBC coated CMC under stress heated by a high heat flux laser

After 487 hour testing

Natural Gas Burner Rig Test Fixture



Threaded rods
w/ Hex Nuts

Airfoil Sub-
component

Threaded rods
w/ Springs

Plate

Plate

Disk

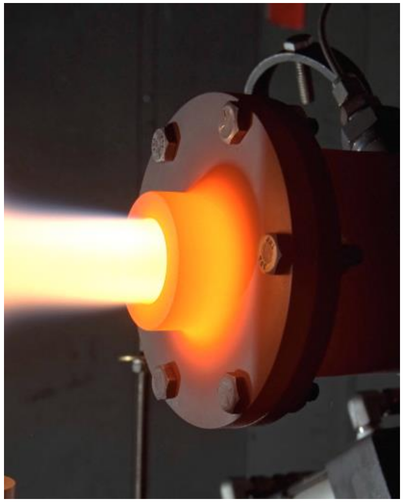
Tube

Gasket

Cooling
Air Inlet

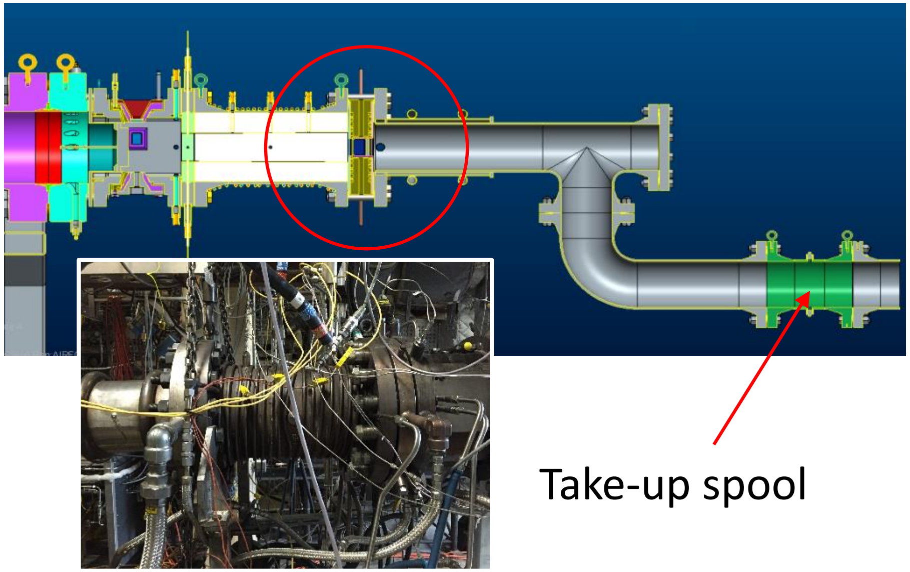
Cooling
Air Outlet

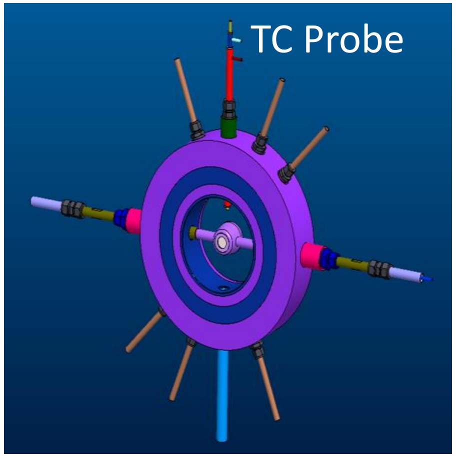
Sighting Glass

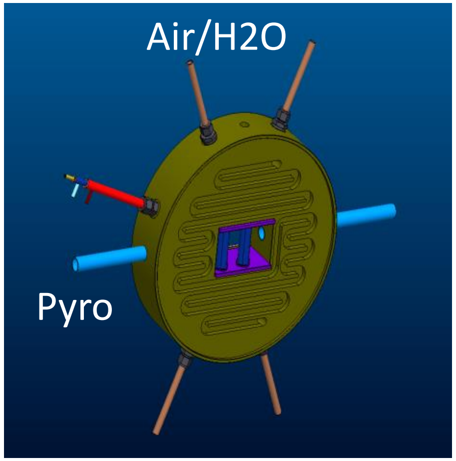


CE-5 Test Development

- GESS WO# 514
  - Labor on track: 1115/1726 WYE hrs
  - $75K TFOME PR in FM
- Coupon & Vane holder Designs
  - 1” cooled Button Sample Holder
    - Mech design & thermals complete
    - Fab Dwgs in progress
  - Vane pack near completion
    - Solving thermal issues with platforms
    - 2”x2” vanes accomodated
- Configuration Flexible
  - Either holder in downstream as piggy-back to injector testing
  - Coupon upstream + Vane downstream as stand alone customer.



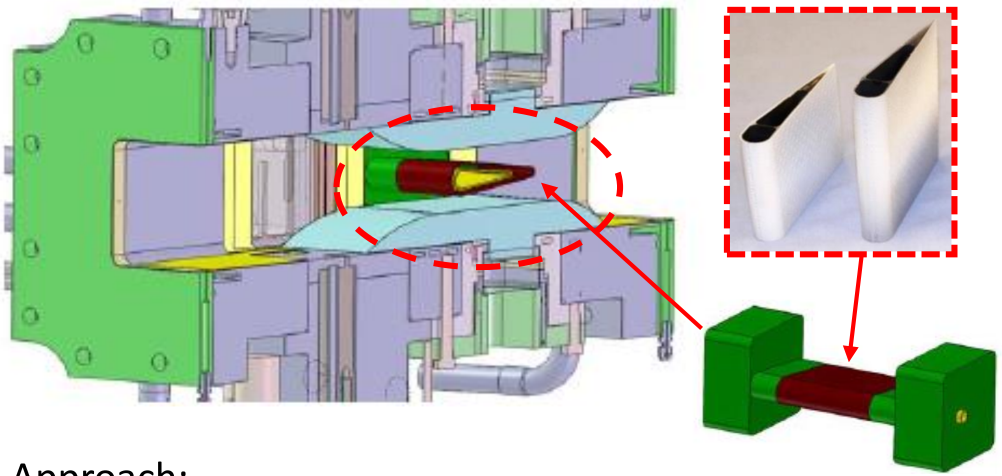




TTT TRL 5 Rig Test – PWA/UTRC

CMC/EBC sub-elements tested in simulated turbine engine environment

UTRC JBTS test rig



Approach:

- Airfoil-shaped test article, 3x3 inches
- Gas temps up to 3500°F / LE Temps 25-2700°F
- Mach No. 0.2 < M < 0.8 in test section
- 1.5 lb/s airflow at 220 psia, 10% H20 vapor
- Internal specimen cooling (900°F); TCs, pyrometers, & IR camera to monitor temp

Progress:

- PDR held 2-2-17
  - Setup article + (3) test vanes for 10 hr "hot" each
  - 6 min hot / 2 min cold test cycle
  - Analyses showed 5-600°F ΔT, 3100°F TE, 13.5 ksi w/ EBC
- Provided UTRC/PWA all requested data
- Vanes rec'd, NDE completed @ PWA, returned, and ready for machining
- HfO_2-Si + (Gd/Y)$Yb_2Si_2O_7$
- PR for coatings from DVTI targeting 3/31-4/15 delivery
  - Witness coupons being sprayed for other fundamental testing

Processing

Advanced Coatings: Processing

Develop in-house new techniques and partner with outside contractors in parallel paths:

- Rich history of Thermal and Environmental Barrier Coatings
- In-house facilities include:
  - Ambient / High Temperature Plasma Spray
  - Plasma Spray-Physical Vapor Deposition (PS-PVD)
  - Slurry Coating Deposition (new)
- Partner externally for developing EB-PVD, CVD, DVD

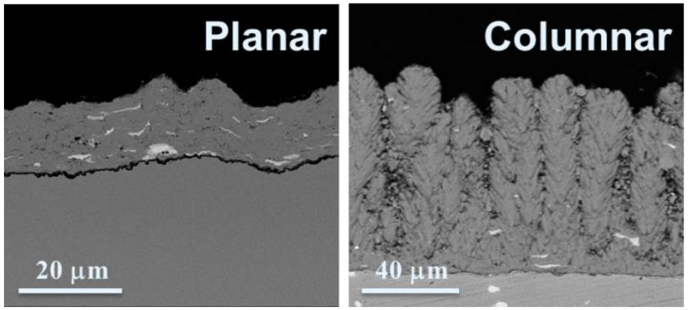

Ambient Plasma Spray


High Temp Plasma Spray

Plasma Spray-Physical Vapor Deposition:

- One of 5 systems worldwide, online in 2010
- Relatively high deposition rate over other methods
- Non line of sight deposition
- Wide range of applications

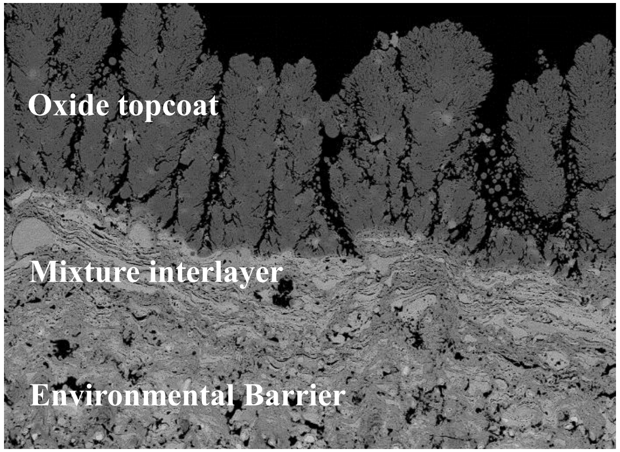

Plasma during vapor deposition



Same material, different processing parameters

Multiple materials

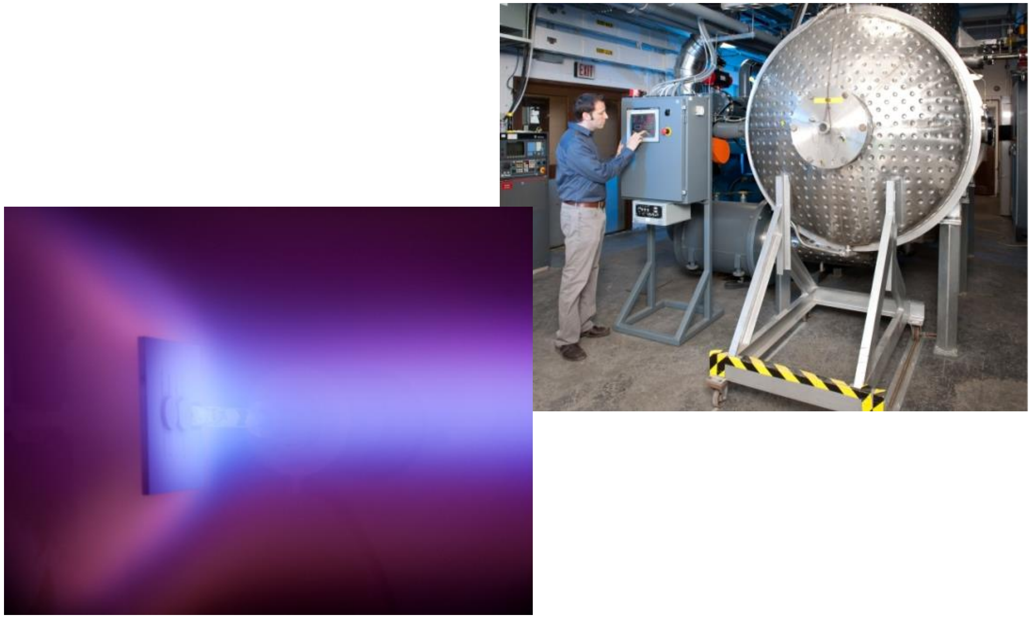
Different processing parameters

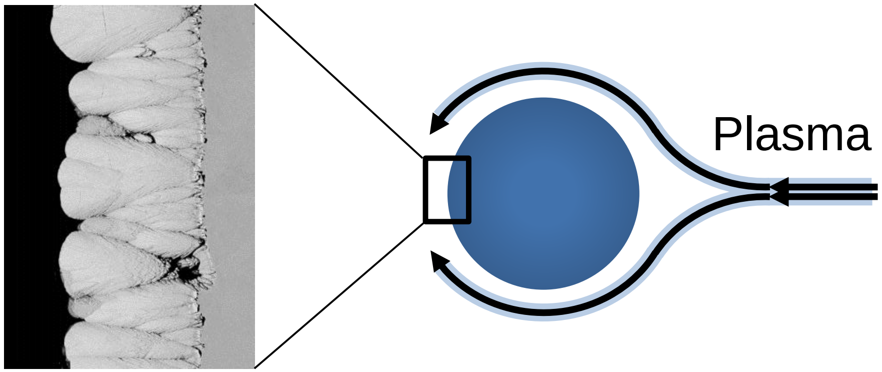


Plasma Spray-Physical Vapor Deposition (PS-PVD)

- Bridges the gap between plasma spray and vapor phase methods
  - Variable microstructure
  - Multilayer coatings with a single deposition
- Low pressure (70-1400 Pa)

  High power (>100 kW)
  - Temperatures 6,000-10,000K
- High throughput[1]
  - 0.5 m^2 area, 10 μm layer in < 60s
- Material incorporated into gas stream
  - Non line-of-sight deposition
- Attractive for a range of applications
  - Solid oxide fuel cells, gas sensors, etc.





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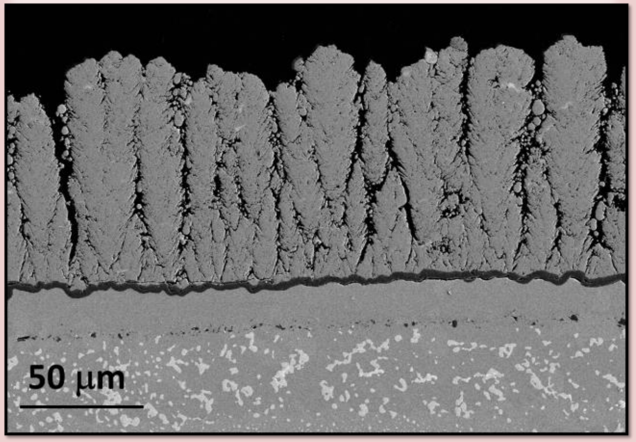
[1] **A. Refke, et al.** ***Proceedings of the International Thermal Spray Conference, May 14-18,*** **(Beijing, China), 705-10 (2007).**

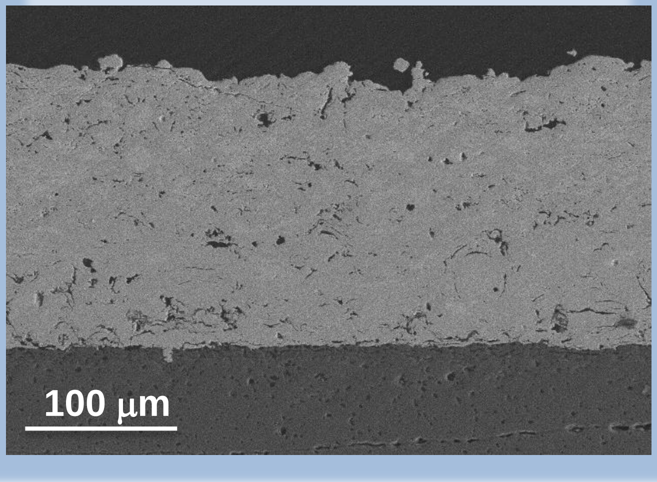
PS-PVD Architectures

- Thermal Barrier Coatings
  - Columnar and similar to EB-PVD
  - Good erosion performance and low thermal conductivity
- Environmental Barrier Coatings
  - Dense, similar to APS but smaller splats
- Hybrid (T/EBCs)
  - EBC base with a graded transition layer and a TBC topcoat
  - Flexible to coating chemistry

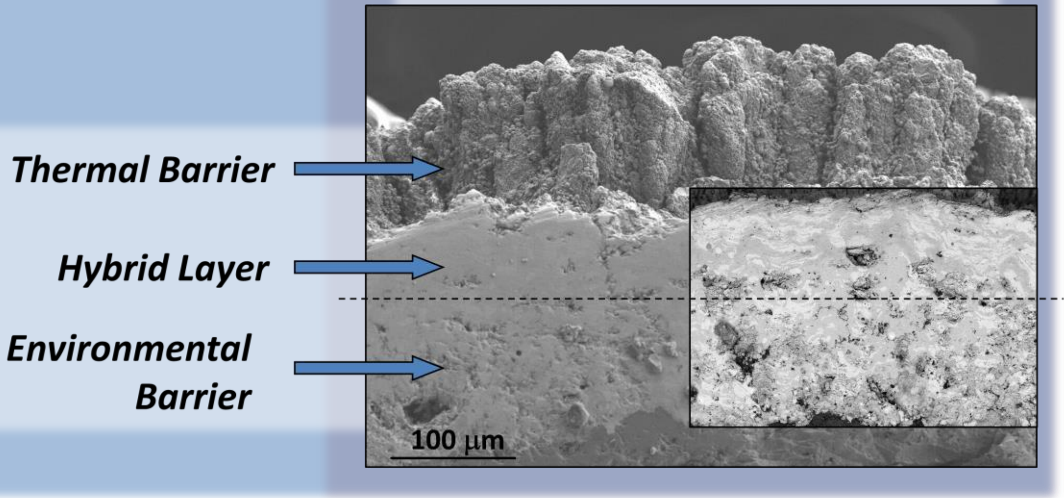
Thermal Barrier Coating



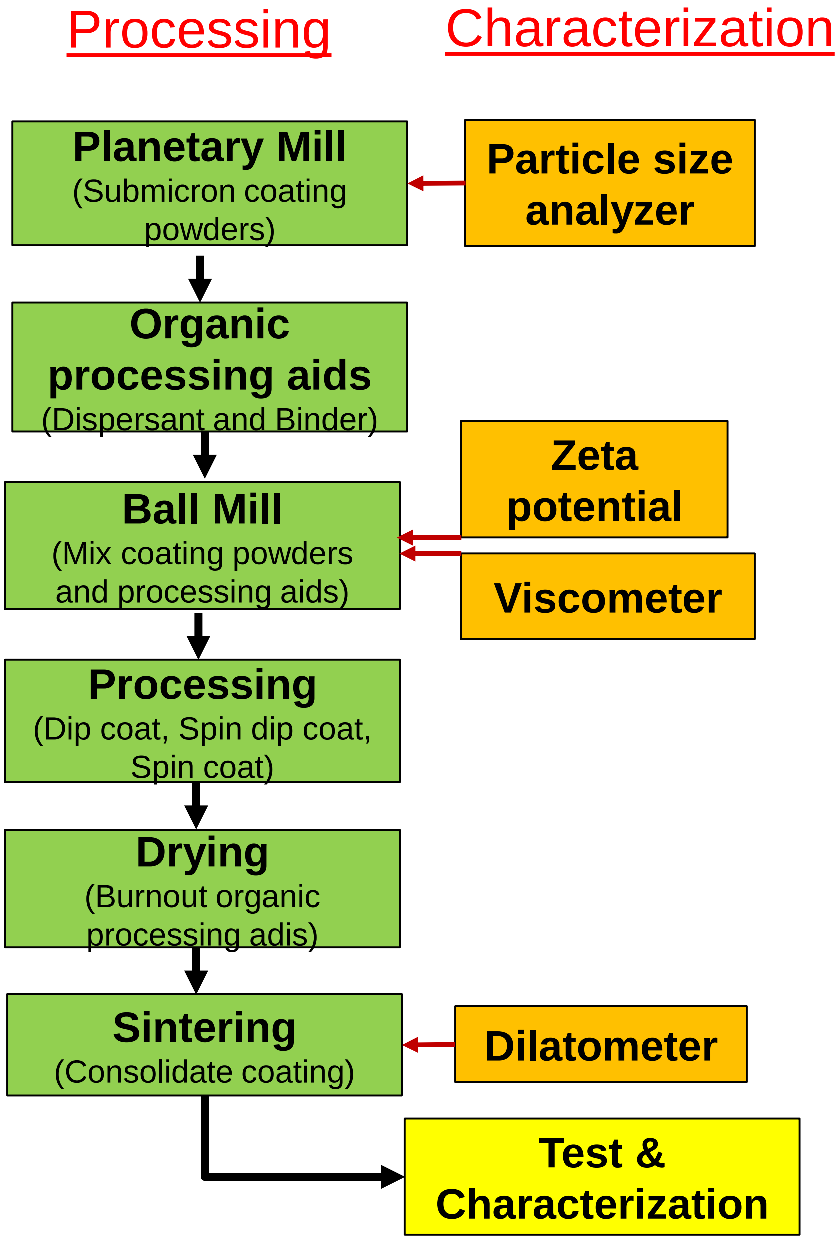
Environmental Barrier Coating



Hybrid Structure



Slurry EBC Process



Processing | Characterization

Planetary Mill
(Submicron coating powders)

Particle size analyzer

Organic processing aids
(Dispersant and Binder)

Ball Mill
(Mix coating powders and processing aids)

Zeta potential

Viscometer

Processing
(Dip coat, Spin dip coat, Spin coat)

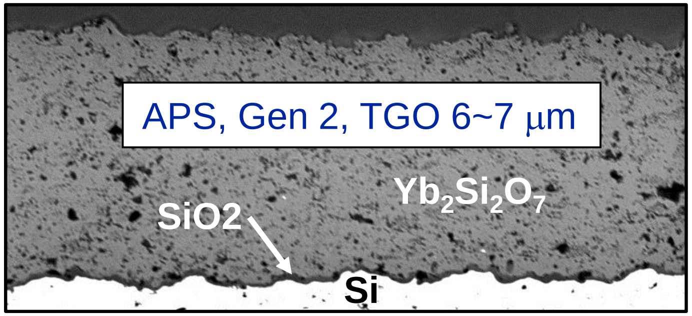
Drying
(Burnout organic processing adis)

Sintering
(Consolidate coating)

Dilatometer

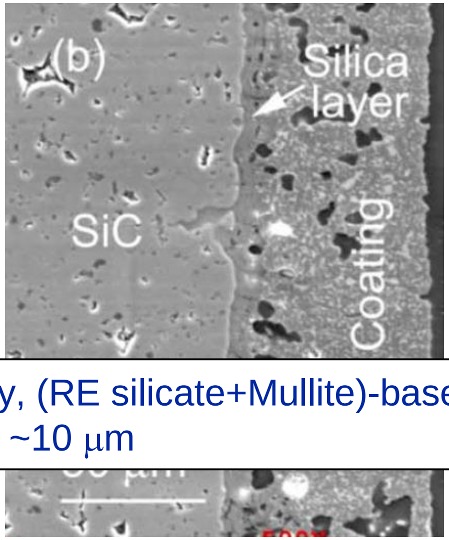
Test & Characterization

Steam Cycle, 1316°C, 90% H_2O, 100h



Lee, NASA, Unpublished data

Steam Cycle, 1350°C, 90% H_2O, 100h

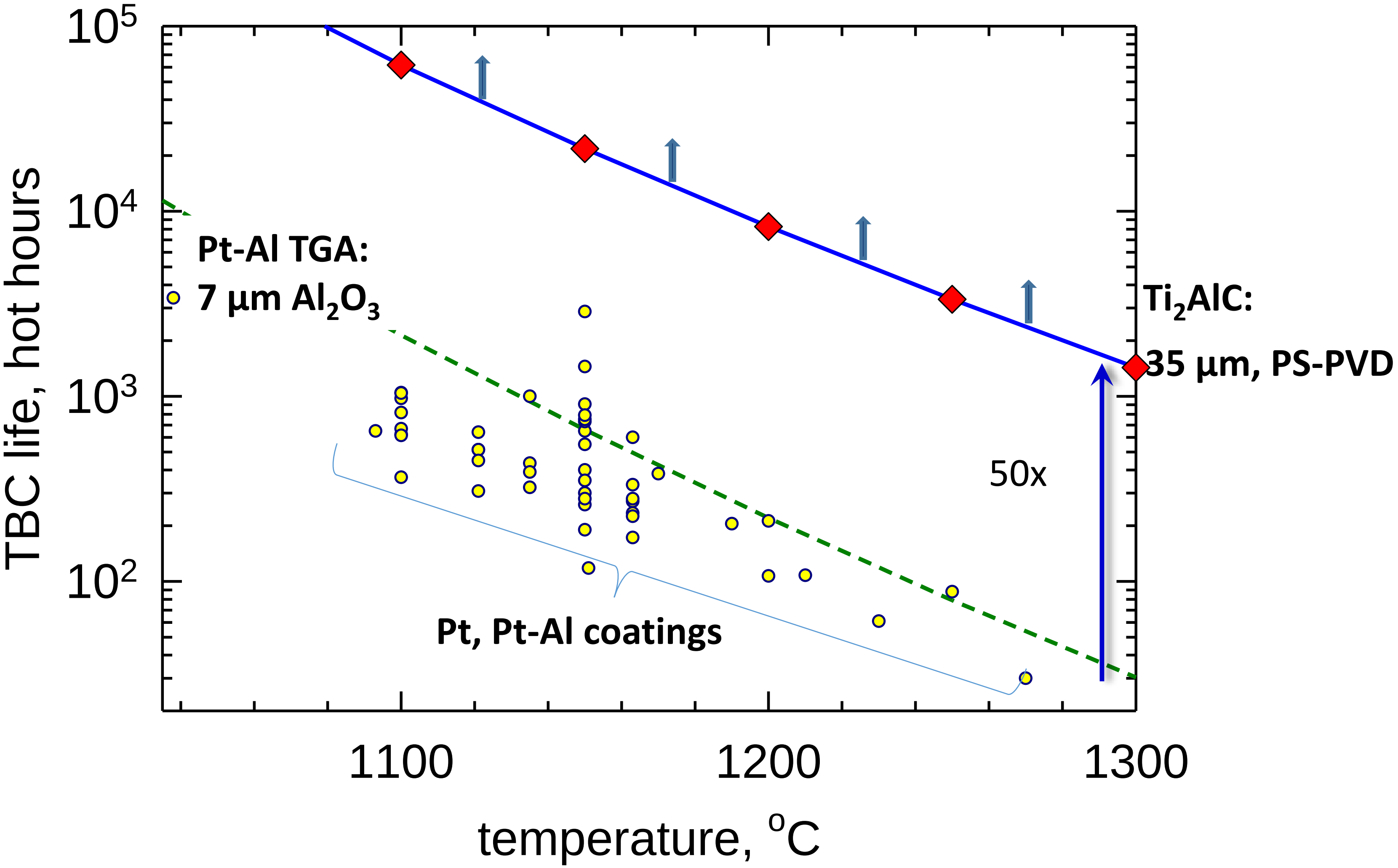


Slurry, (RE silicate+Mullite)-base, TGO ~10 µm

Cleveland State University - J. Euro. Ceram. Soc., 1123-1130 (2011)

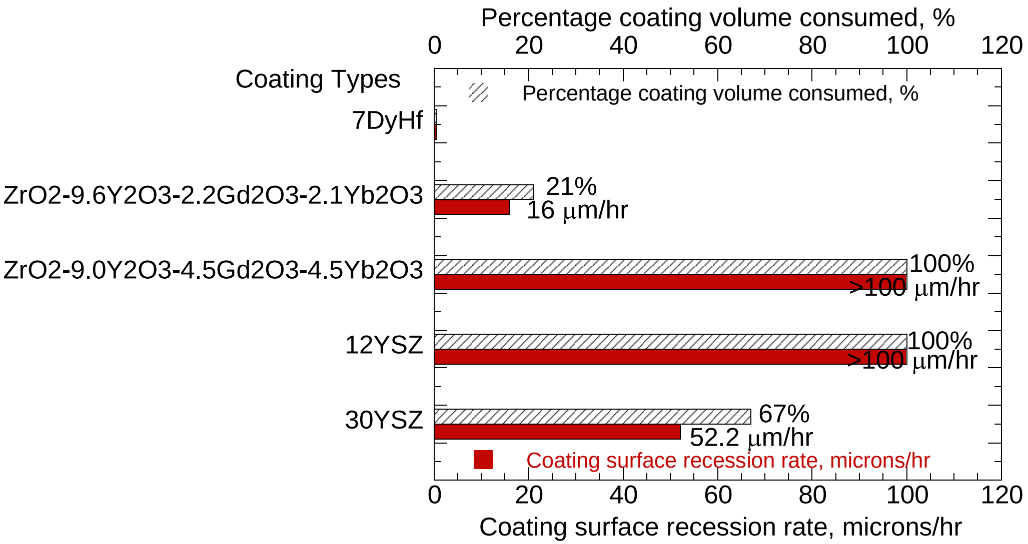
TBCs

EB-PVD TBC FCT Life on Alumina-Forming Systems

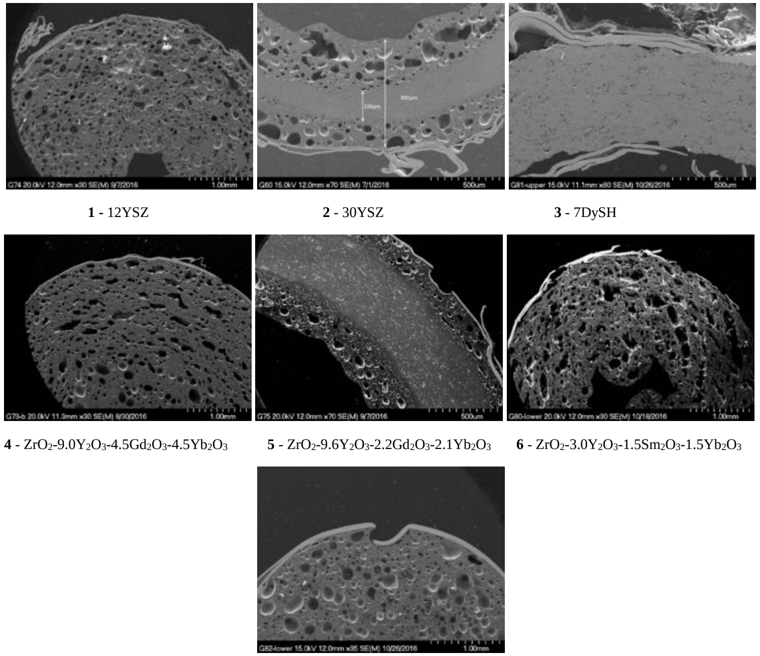


CMAS Studies for Advanced TEBCs

- CMAS reactions studied for selected coating candidate materials
- Preliminary results showed 7YSHf, ZrO_2-9.6Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3, and 30YSZ had the highest CMAS resistance
- Continued furnace tests in conjunction with the laser rig tests planned
- Incorporating large composition matrix and tests also planned



CMAS resistance of selected coating systems



1 - 12YSZ

2 - 30YSZ

3 - 7DySH

4 - ZrO_2-9.0Y_2O_3-4.5Gd_2O_3-4.5Yb_2O_3

5 - ZrO_2-9.6Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3

6 - ZrO_2-3.0Y_2O_3-1.5Sm_2O_3-1.5Yb_2O_3

SEM cross – sectional electron images ceramic coating reacted with CMAS at 1300 °C for 5 h

Challenges & Potential Collaborations

EBC Challenges

- **EBCs with 2700°F interfacial temperature capability to enable 2700°F CMC**
- **CMAS mitigation to break the upper temperature limit of EBCs due to CMC degradation**
- **A long-life EBC and a robust EBC lifing method to improve the reliability of CMC**
- **EBC Testing methods relevant to engines to validate EBC life**

Life Modeling Collaboration?

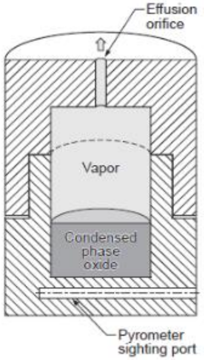
- Short Term: Empirical model
  - Steam oxidation
  - Steam oxidation + thermal fatigue
  - CMAS
  - …
- Long Term: Physics-based model in combination with empirical model
  - Generate time dependent EBC properties database
- Model validation
  - Combustion rig test data
  - Engine service data
- Pick a model EBC system that everyone can agree on
  - 1st Gen or 2nd Gen EBC

Backup

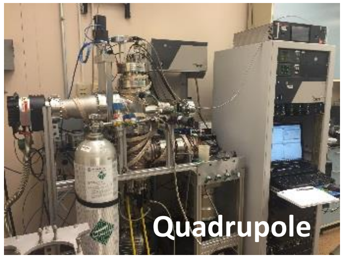
LME Mass Spectrometer Lab

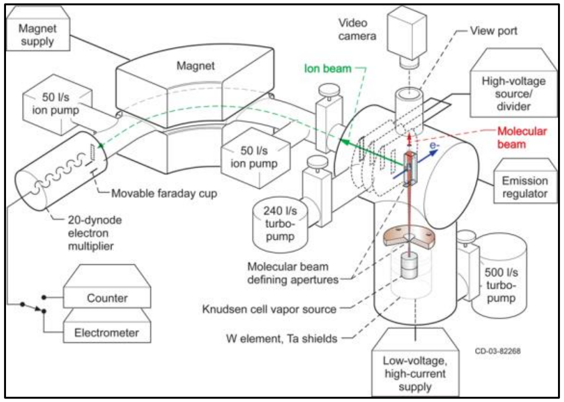
(3) unique instruments to identify gas and vapors at high temperatures. One-of-a-kind facility in US, only 2-3 worldwide.

- **Vacuum studies based on Knudsen cell**
  - Typical 1cm dia x 1cm high, 1 mm orifice, establish equilibrium, vapor effuses
  - Wt loss rates relates to pressure

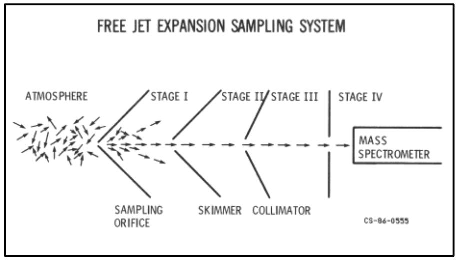


- **Knudsen Cell Mass Spectrometers**
  - Magnetic Sector KEMS
    - Magnet sorts ions by mass-to-charge ratio and ion intensity α vapor pressure
    - High stability / resolution
  - Fast Scanning Quadrupole KEMS
    - Electric field sorts the ions
  - Thermodynamic information provided:
    - Heats of Vaporization & composition of vapor phases
    - Activity measurements & phase diagram boundaries





- **High Pressure Mass Spectrometer**
  - Free Jet Expansion
    - Allows (10^{-6} atm) sampling at 1 atm
    - Series of differential chambers
    - Eliminates cold surface condensate
    - Chemical & dynamic integrity of gases
    - More qualitative (approx. amts)

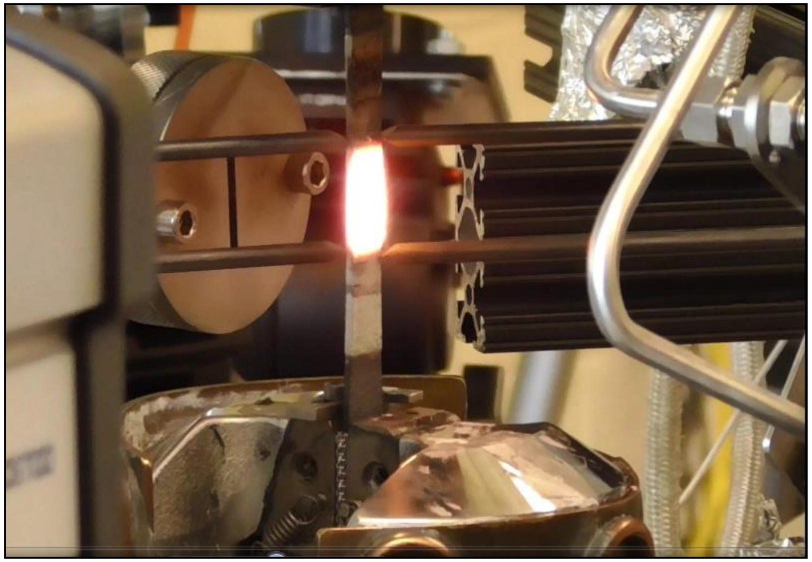


High Heat Flux Laser Rigs

Typical Laser Test Rig:

- Laser Heating (4000 W) on Front
- Backside Air Cooling
- Surface Temperature Measured with Pyrometers and/or IR Camera
- Surface Temperatures up to 3000 °F (Material Dependent)
- Thermal Fatigue and Combined Thermal Gradient and Axial Fatigue
- Uncoated / EBC Coated SiC/SiC CMCs


12/07/2015

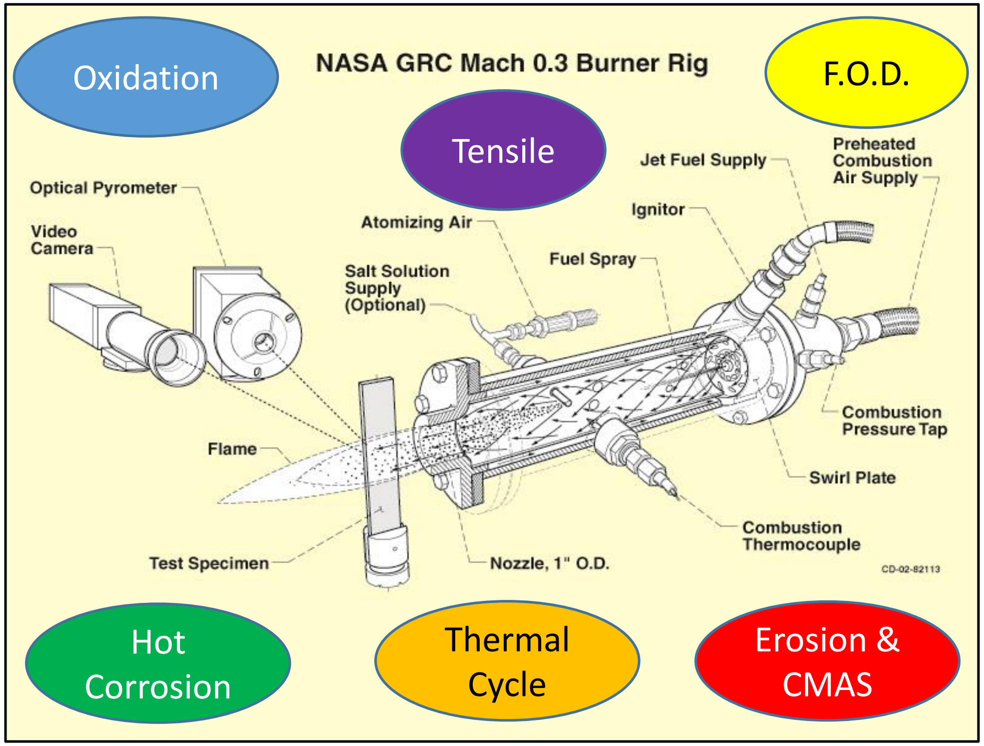


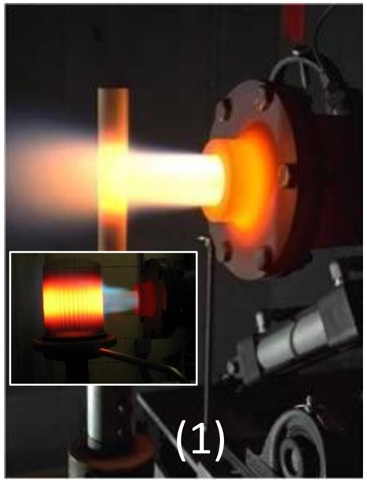
Testing Features:

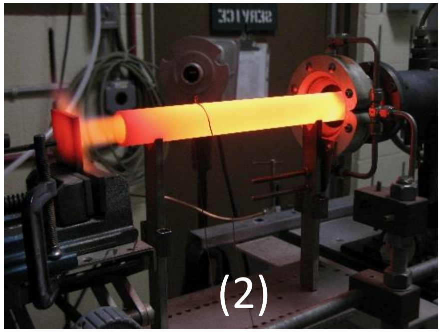
- Servo-hydraulic , 25 kN Load Cell
- Water-cooled Wedge Grips
- Two 1 in. Gage Length, Water-Cooled
- Extensometers; 6 in. Long Tensile Specimens
- Frequencies up to 30 Hz
- Load and Stroke Control
- Strain-Control capability in progress
- Tensile, flexural, HCF, LCF, SPLCF
- In situ thermal conductivity measurement

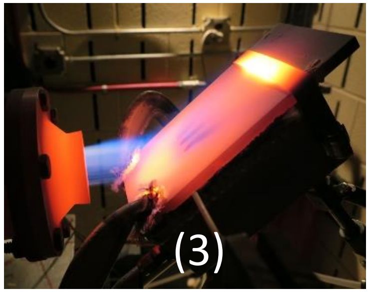
Mach 0.3 Burner Rig Facility

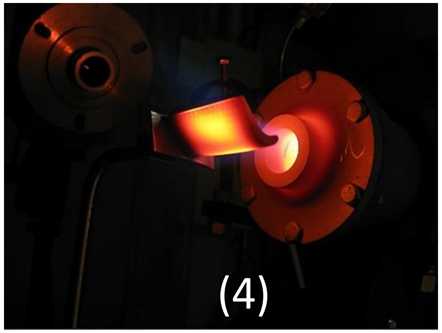
- 8 computer-controlled jet-fueled combustors in individual test cells Building 34
- Extremely efficient means of testing the durability of new jet engine materials
- Material test temperatures from 600° to 2700°F, flame temperatures to 3000ºF
- Creates the extremely hostile operating environment found in turbine engines
- Multiple or single samples tested using rotating carousels to compare materials
- Thermal cycling duplicates actual flight cycles: takeoffs, cruise, and landings







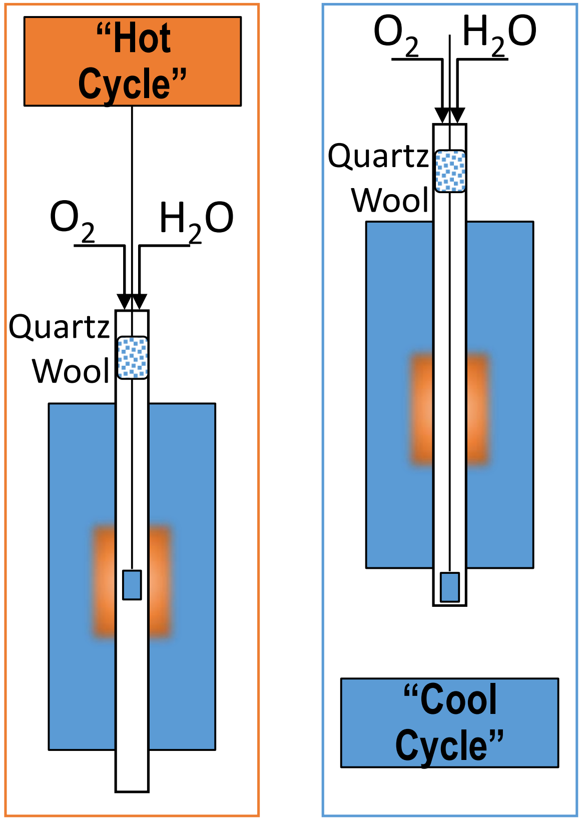


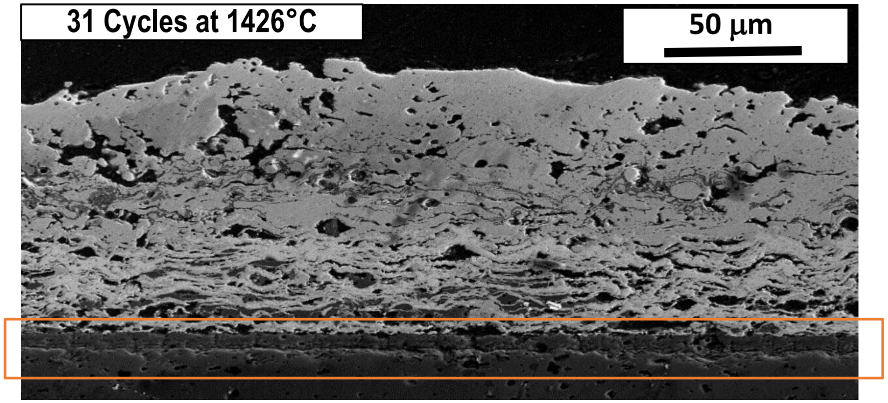


(1) TBC/Super-alloy, (2) Erosion, (3) Film-cooled monolithic ceramic, (4) Metal Turbine Blade

Cyclic Steam Oxidation Testing

- Steam oxidation required to determine durability of EBC
  - Limitation of formation and growth of SiO_2 layer critical to lifetime
  - Oxidation of Si-based ceramics (including Si) is an order of magnitude or more in steam
- Steam oxidation performed at NASA
  - “Hot cycle” temperature 1426°C
  - 0.9 atm H_2O bal. O_2
  - 2.2 cm/sec flow rate
  - 1 hour hot followed by 20 minute cool





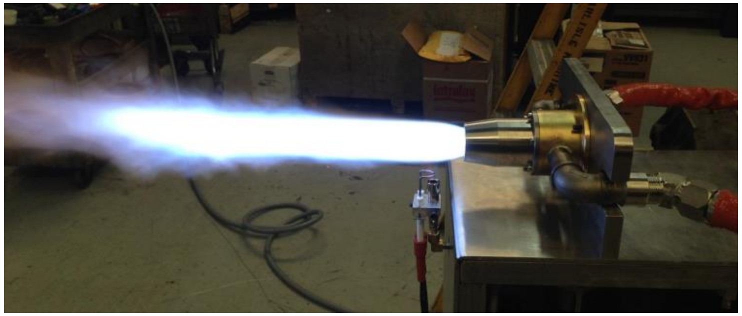
- Scales formed in cyclic steam oxidation are often much thicker and more porous
- TGO scales at coating interface lead to spallation failure

NG/O2 QARE Rig Development

B24 QARE Rig is being moved to B34 R126 and R127 with a few changes – Natural Gas and Oxygen from lines, not bottles

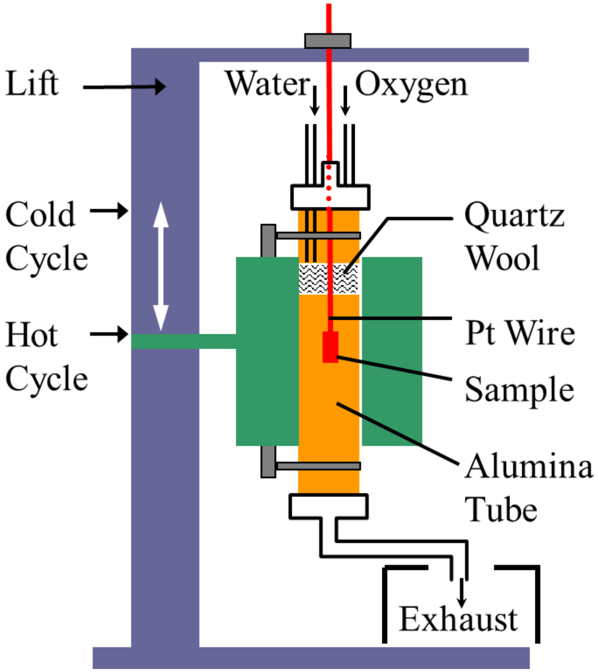
- Continuous supply of 700 SCFH Natural Gas / 1500 SCFH of 93% Oxygen
- Potential 24/7 operation using service natural gas, shop air and PLC Control – a switching zeolite system will concentrate the O2 supply
- Best guess 4200F, 250 m/s for 1.1” dia flame; 58% H_2O (g) – Heat Flux to 2700F
- Ideal for testing:
    - Rocket turbopump coating testing
    - Water-vapor inducted recession of CMCs
    - Complex geometries such as turbine vanes
    - Film cooled specimens
    - Testing of pre-spalled specimens
    - Possible future erosion or CMAS

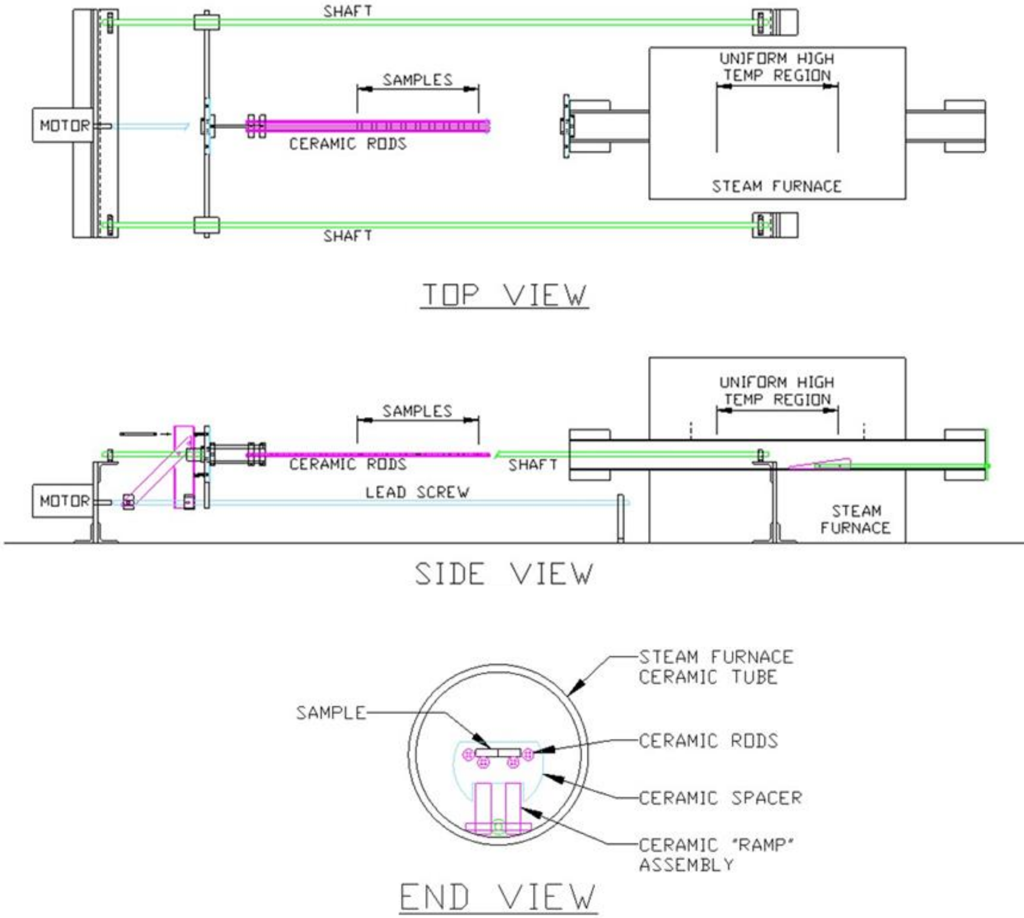
Status of rig – Contract is out for bid from Code F. Purchasing needed hardware such as FLIR IR camera and other items for testing and safety.



Steam Cycling Rig Progress Update (Lee, Harder)

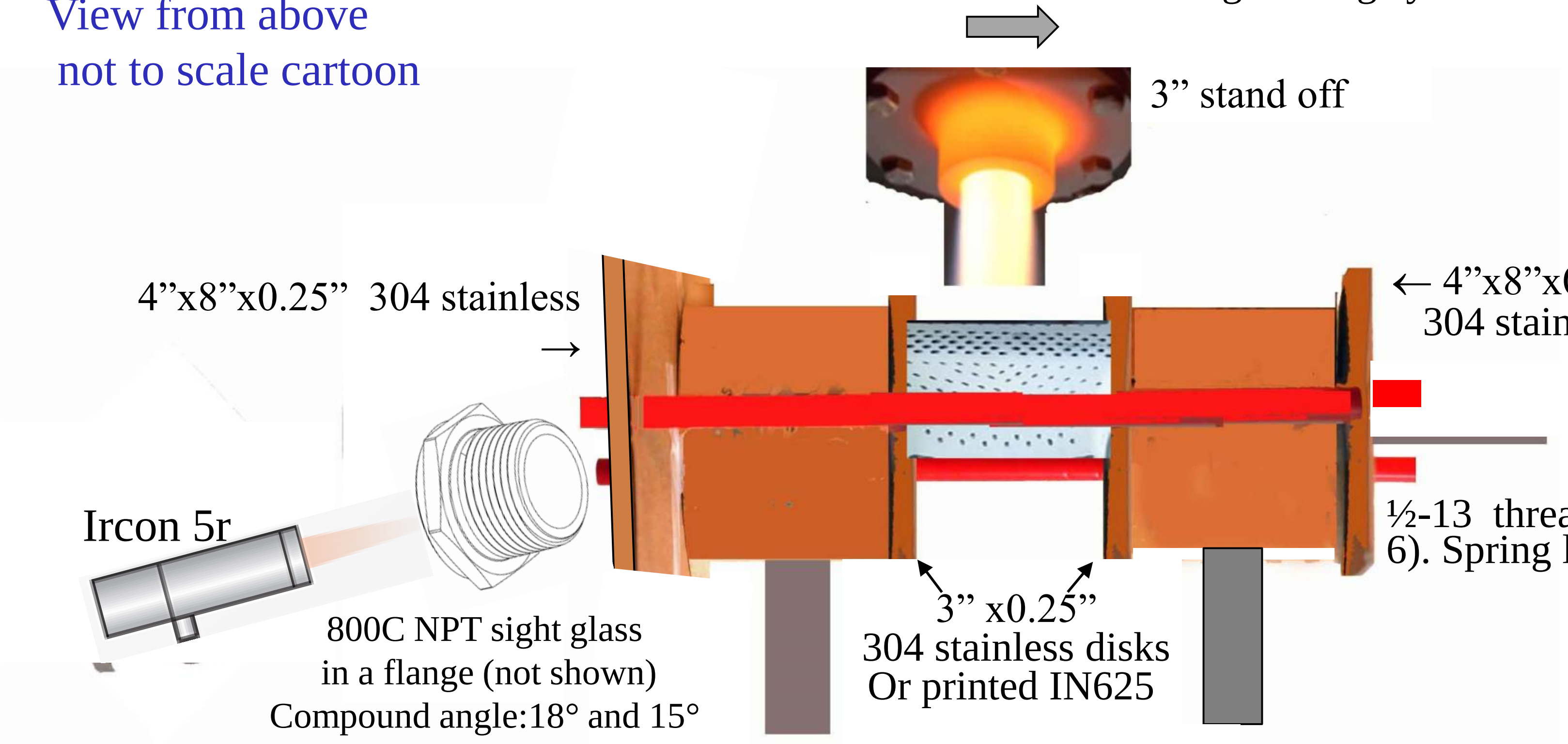
- Four steam cycling rigs employing a vertical tube furnace coupled with a mechanical lift are in operating conditions
- A new higher capacity steam cycling rig employing a horizontal tube furnace coupled with a mechanical actuator is being designed (Ed Sechkar)





NG QARE Airfoil Test Fixture

View from above
not to scale cartoon



Burner moves during cooling cycle

3" stand off

4"x8"x0.25" 304 stainless →

← 4"x8"x0.25"
304 stainless

Ircon 5r

½-13 threaded rods (
6). Spring loaded nuts

800C NPT sight glass
in a flange (not shown)
Compound angle:18° and 15°

3" x0.25"
304 stainless disks
Or printed IN625

Colling
Air out

Cooling
Air In

Flame deflected upward towards
viewer by vane
Use symmetric vane with NG QARE

Switch to 6 threaded rods

Set on a lift table, pedestal, or large lab jack
Angle brackets for bolting or C-clamping to table