# Environmental Stability and Oxidation Behavior of $HfO_2$-Si and YbGd(O) Based Environmental Barrier Coating Systems for SiC/SiC Ceramic Matrix Composites

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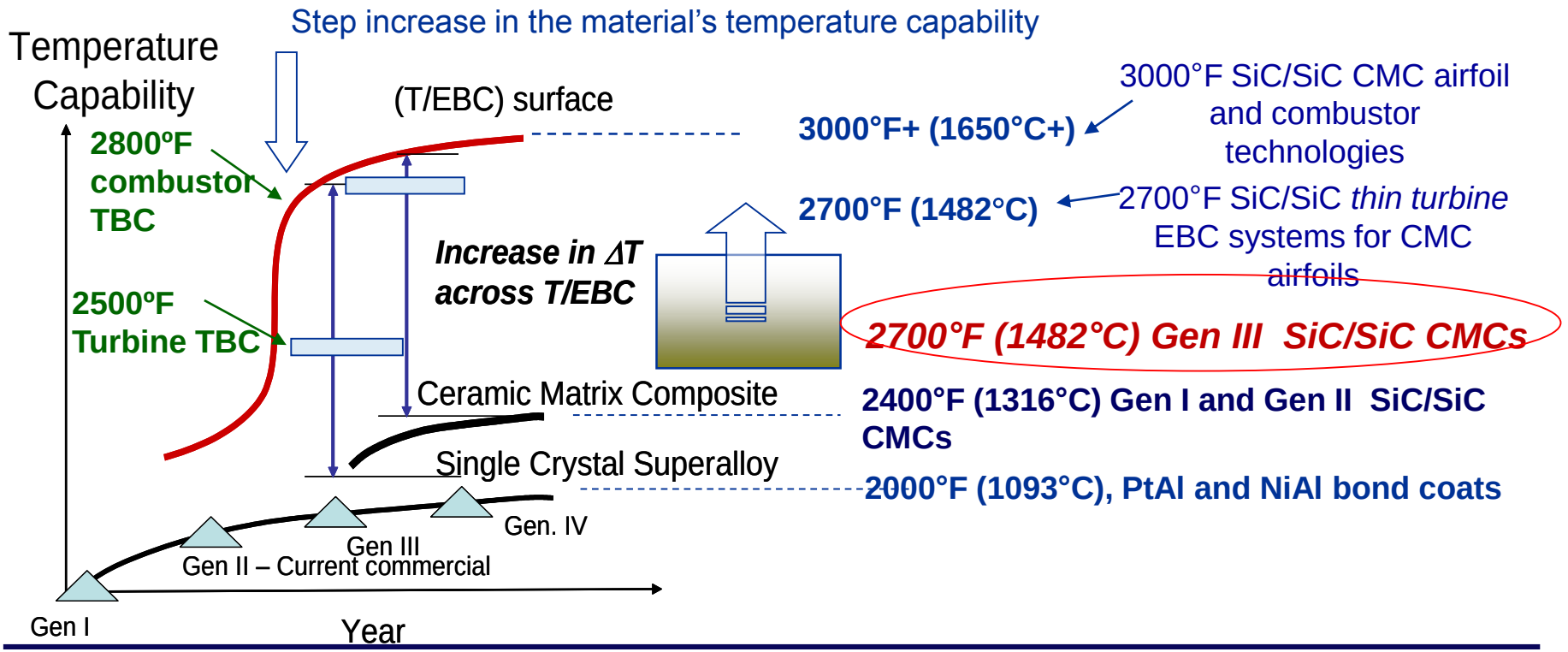
# NASA EBC and CMC System Development

- **Emphasize temperature capability, performance and *long-term* durability**
  - Highly loaded EBC-CMCs - Prime-reliant coatings
  - 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
  - 2700°F (1482°C) EBC bond coat technology for supporting next generation
    - Recession: <5 mg/cm$^2$ per 1000 h
    - Coating and component strength requirements: 15-30 ksi, or 100- 207 MPa
    - Resistance to Calcium Magnesium Alumino-Silicate (CMAS), impact and erosion



# Outline

- **Advanced 2700°F capable EBC and bond coat developments**
  - Rare Earth – Silicon, i.e., YbGd-Si (O) and YbGd-Lu-Si (O) and Hafnia-Si ($HfO_2$-Si) systems
  - Early systems cyclic oxidation results and Si composition optimizations
  - Focus on oxidation kinetics studies of selected EB-PVD coatings using TGA
  - Oxidation mechanisms and degradation mechanisms

- **EBC - CMC system thermomechanical - environment testing, particularly using laser rigs**
  - A Key step and capability for developments, and help composition optimization and

- **Summary**

# NASA Advanced 2700°F Silicide Based Bond Coats – and EBC Systems Processing for Various Component Applications

- Advanced coating systems developed for various processing to improve Technology Readiness Levels (TRL)
- Composition ranges studied mostly from 50 – 80 atomic% silicon
  - PVD-CVD processing, for composition downselects - also helping potentially develop a low cost CVD or laser CVD approach
  - Compositions initially downselected for selected EB-PVD and APS coating composition processing

## PVD-CVD

| | | |
|---|---|---|
| YSi | YbGdYSi | GdYSi |
| ZrSi+Y | YbGdYSi | GdYSi |
| ZrSi+Y | YbGdYSi | GdYSi |
| ZrSi+Ta | YbGdYSi | GdYSi |
| ZrSi+Ta | YbGdSi | GdYSi-X |
| HfSi + Si | YbGdSi | GdYSi-X |
| HfSi + YSi | YbGdSi | |
| HfSi+Ysi+Si | YbGdSi | |
| YbSi | YbGdSi | |
| HfSi + YbSi | YbSi | |
| GdYbSi(Hf) | | |
| YYbGdSi(Hf) | YbYSi | |
| | YbHfSi | |
| | YbHfSi | |
| | YbHfSi | |
| | YbHfSi | |
| | YbHfSi | |
| | YbSi | |

Process and composition transitions

## EB-PVD

$HfO_2$-Si [1];
REHfSi
GdYSi
GdYbSi [2]
GdYb-LuSi
NdYSi

[1,2] Subelment demos

## APS*

HfO2-Si
YSi+RESilicate
YSi+Hf-RESilicate

Hf-RESilicate — Used in ERA components as part of bond coat system

Hf-RE-Al-Silicate — Used in ERA components as part of bond coat system

## FurnaceLaser/CVD/PVD

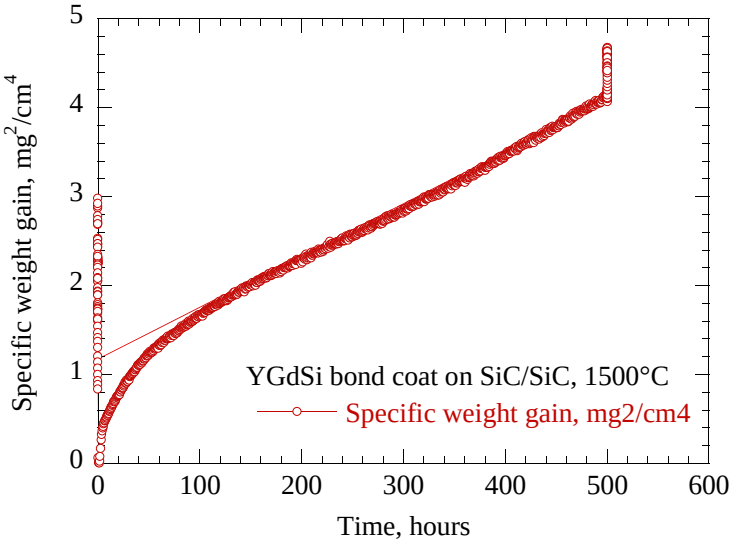
REHfSi

APS*: or plasma spray related processing methods

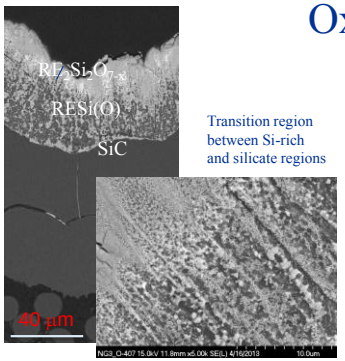
US Patent Application S/N: 13/923,450 (LEW 18949-1), US Provisional Patent Serial No.: 62/329,500 (LEW 18949-2), LEW 19435-1.

# Oxidation Kinetics and Furnace Cyclic Behavior of RESi EBC Bond Coats -

- Some early multi-component PVD processed systems showed excellent oxidation resistance and furnace cyclic test (FCT) durability at 1500°C
- FCT and steam tests also performed for more advanced RESiO-Hf systems

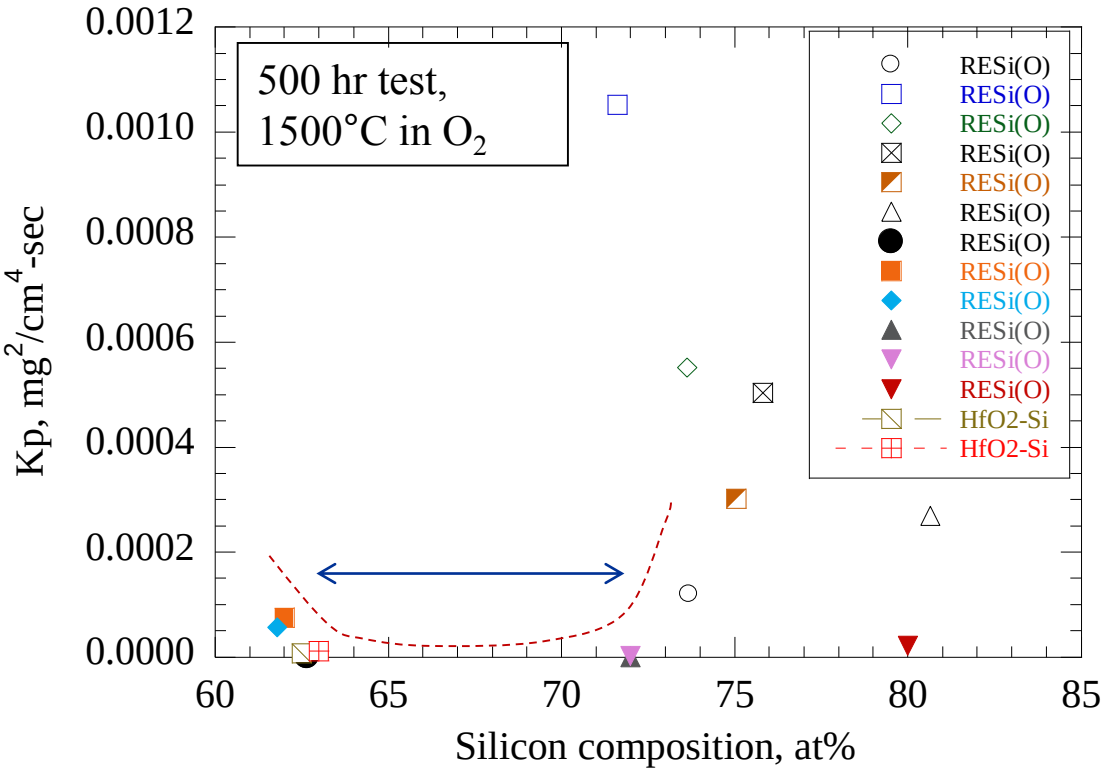



Oxidation kinetics




Transition region between Si-rich and silicate regions

An example of cross-sectic
TGA tested specimen
-

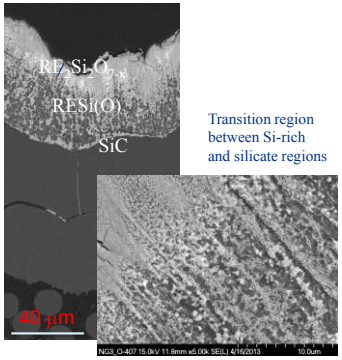


# Oxidation Kinetics and Furnace Cyclic Behavior of RESi EBC Bond Coats - Continued

- Some early multi-component PVD processed systems showed excellent oxidation resistance and furnace cyclic test (FCT) durability at 1500°C
- FCT and steam tests also performed for more advanced RESiO-Hf systems
- FCT durability found to be closely related to temperature capability and oxidation resistance of the coating systems

Di-silicides/disilicates

Monosilicides/monosilicates




Transition region between Si-rich and silicate regions

An example of cross-section TGA tested specimen

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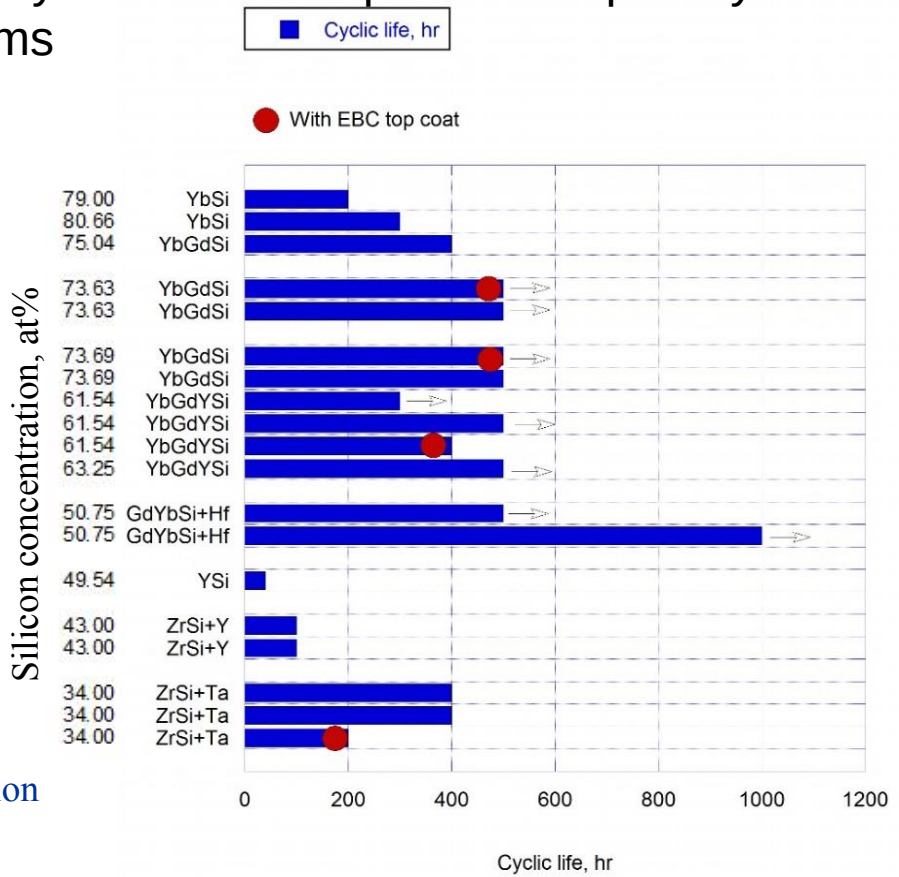
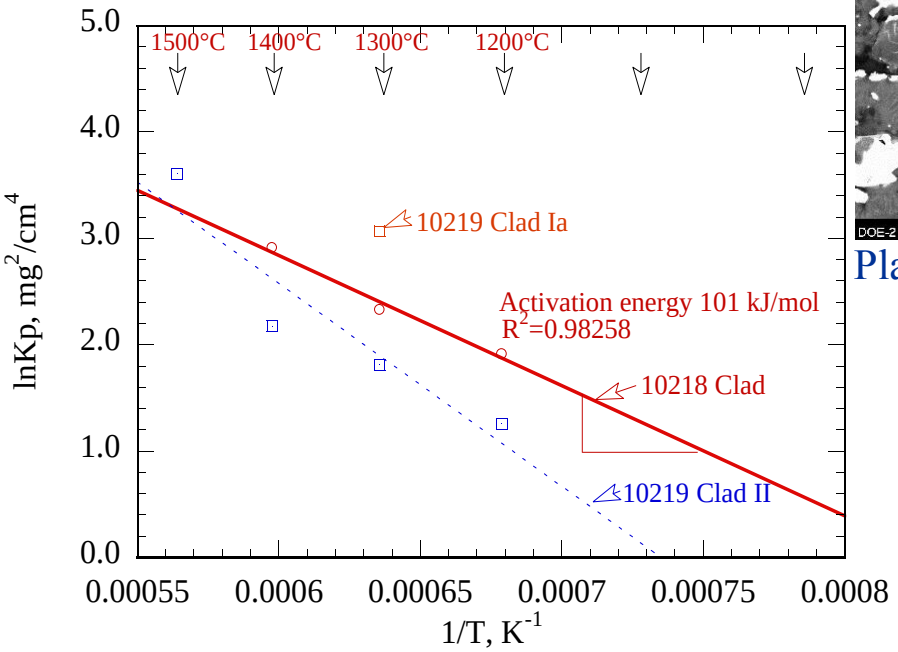
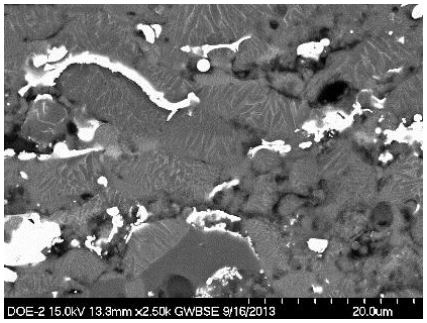



FCT life, Testing in Air at 1500°C, 1 hr cycles

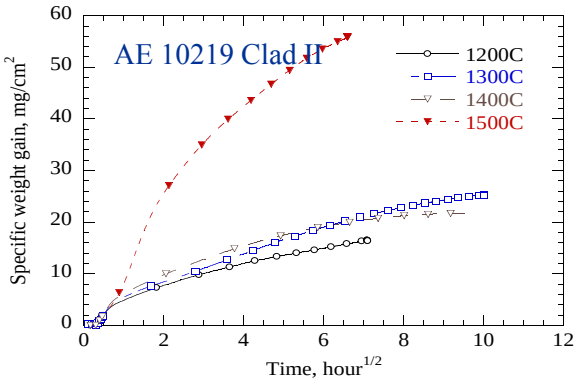
# Oxidation Resistance of Plasma sprayed Based $HfO_2$-Si

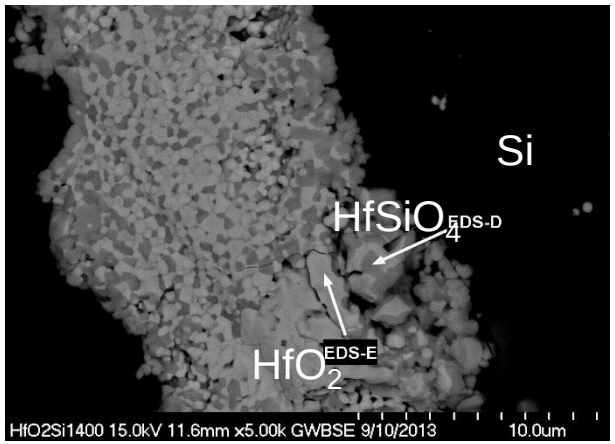
- TGA weight change measurements in flowing $O_2$
- Parabolic oxidation kinetics generally observed
- Solid-state reaction is also involved with the systems, and more complex behavior at 1400 and 1500°C
- Improved oxidation resistance through APS plasma spray powder processing optimization (AE10219 II; Sulzer/Oerlikon Metco)




Plasma spray processed



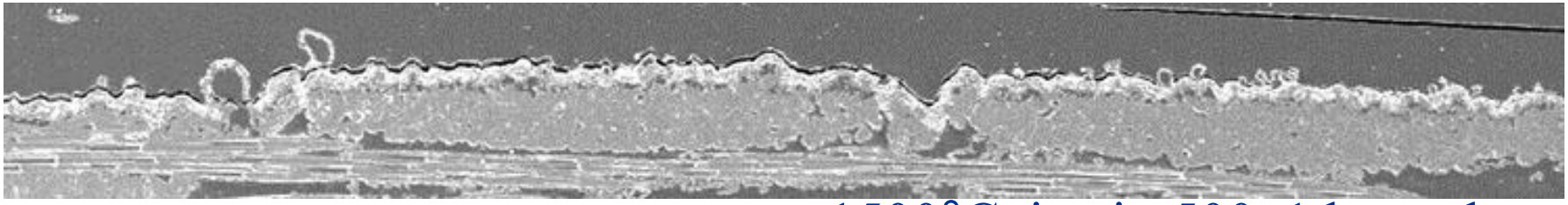




Polished specimen microstructure after 1400°C test (Hot pressed sample)

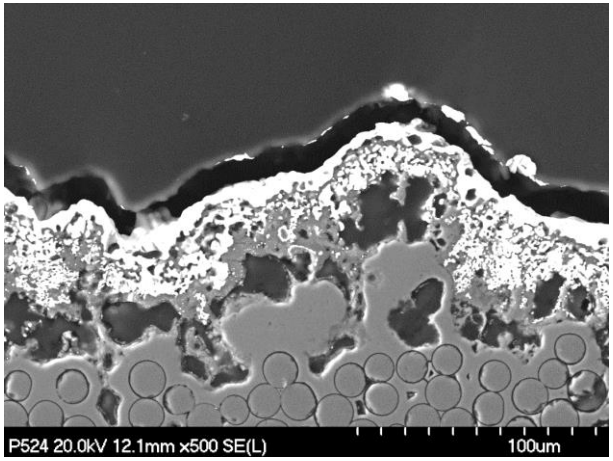
- AE 10219: first Generation $HfO_2$-30wt%Si composite APS powders
- AE 10218 is $HfO_2$-30wt%Si composite APS powders used in NASA ERA liner component demonstrations
- AE 10219 Clad II is second Generation $HfO_2$-30wt%Si composite APS powders

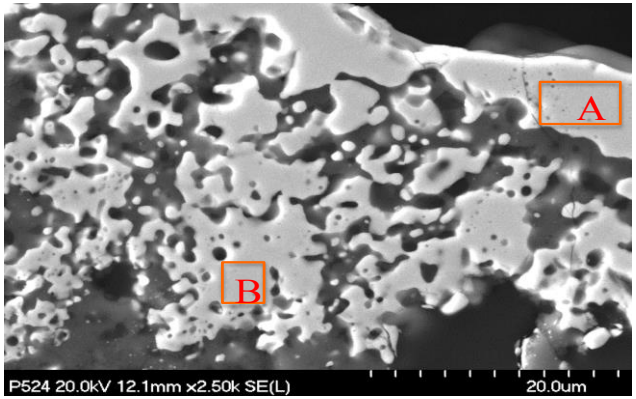
# Microstructures of Furnace Cyclic Tested GdYbSi(O) EBC Systems

- Cyclic tested cross-sections of early PVD processed YbGdSi(O) bond coat
- Self-grown rare earth silicate EBCs and with some RE-containing $SiO_2$ rich phase separations
- Relatively good coating adhesion and cyclic durability



1500°C, in air, 500, 1 hr cycles



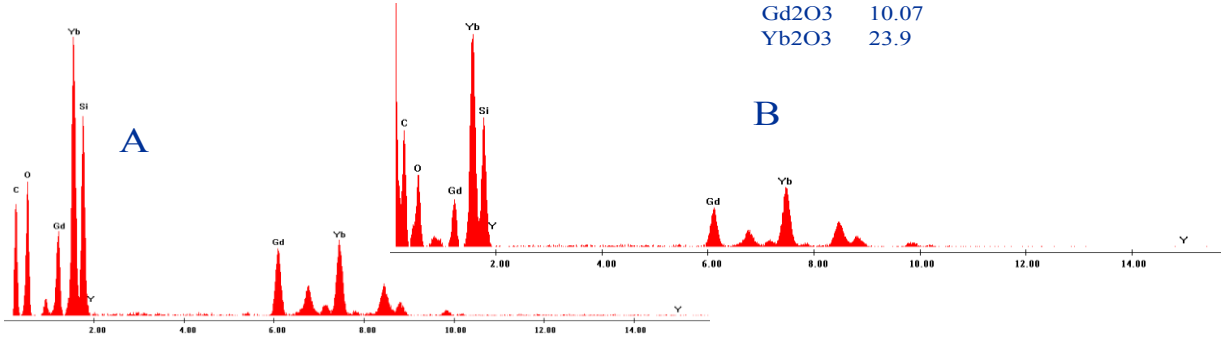

- Complex coating architectures after the testing
- Designed with EBC like compositions – Self-grown EBCs

Composition (mol%) spectrum Area #1

| | |
|---|---|
| SiO2 | 67.98 |
| Gd2O3 | 11.95 |
| Yb2O3 | 20.07 |

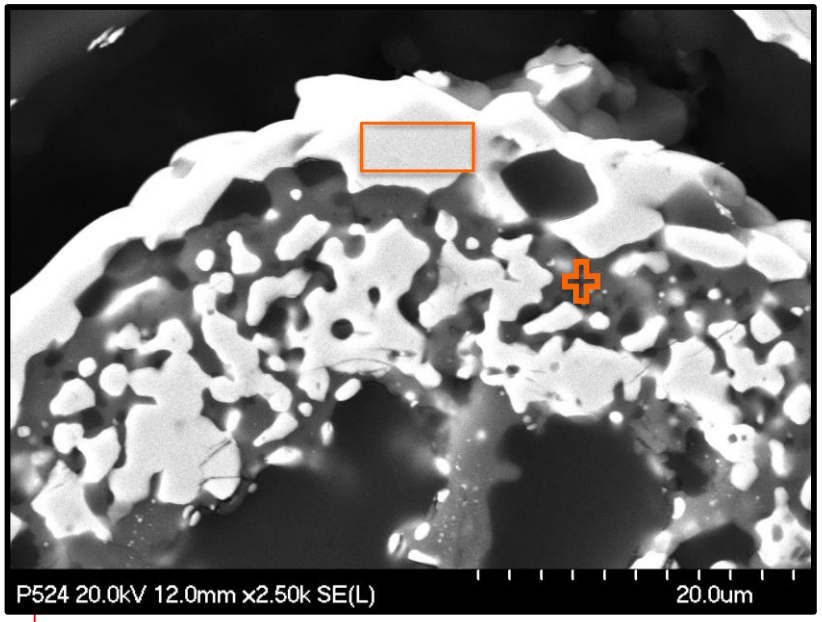
Composition (mol%) spectrum Area #2

| | |
|---|---|
| SiO2 | 66.03 |
| Gd2O3 | 10.07 |
| Yb2O3 | 23.9 |



# Microstructures of Cyclic Tested GdYbSi(O) EBC Systems- Continued

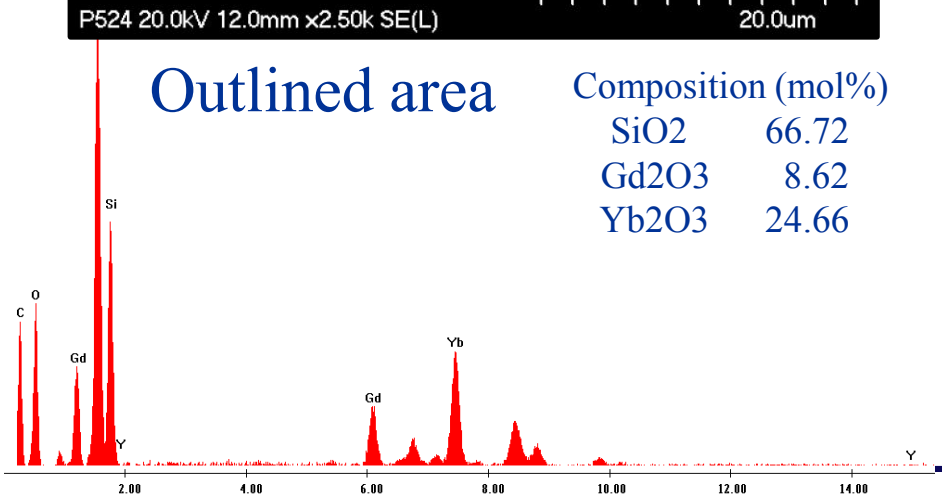
- Cyclic tested cross-sections of early PVD processed YbGdSi(O) bond coat
- Self-grown rare earth silicate EBCs and with some RE-containing $SiO_2$ rich phase separations
- Relatively good coating adhesion and cyclic durability




1500°C, in air, 500, 1 hr cycles

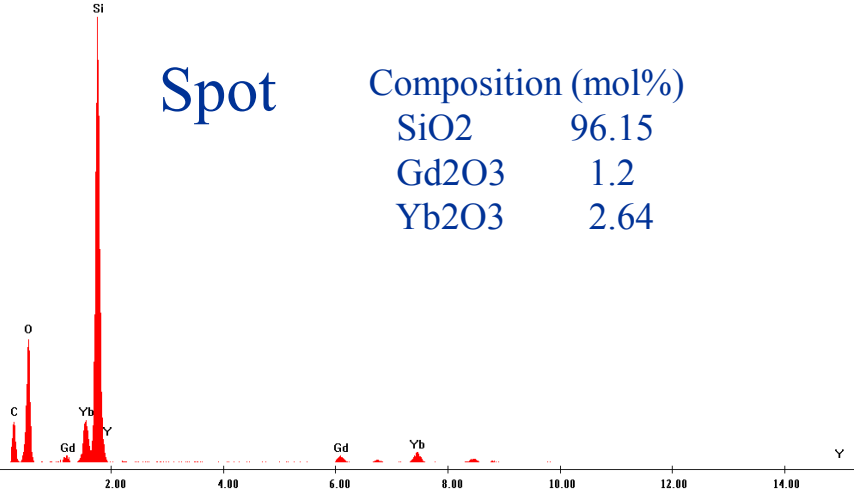
Outlined area

| Composition (mol%) | |
|---|---|
| SiO2 | 66.72 |
| Gd2O3 | 8.62 |
| Yb2O3 | 24.66 |



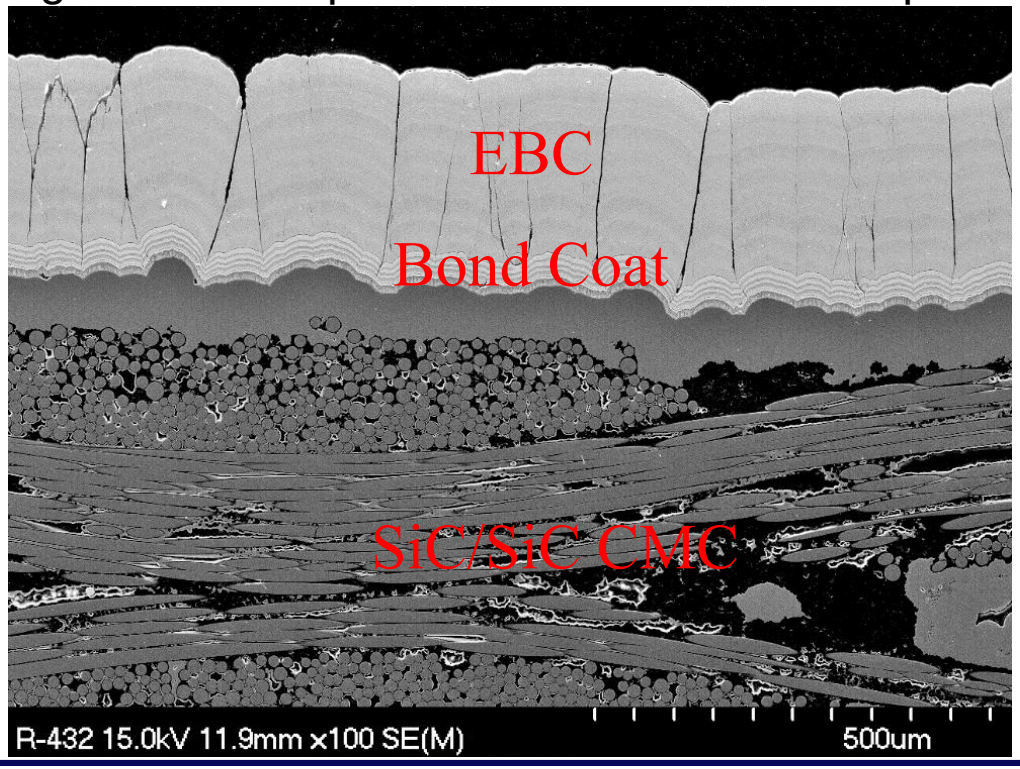

Spot

| Composition (mol%) | |
|---|---|
| SiO2 | 96.15 |
| Gd2O3 | 1.2 |
| Yb2O3 | 2.64 |



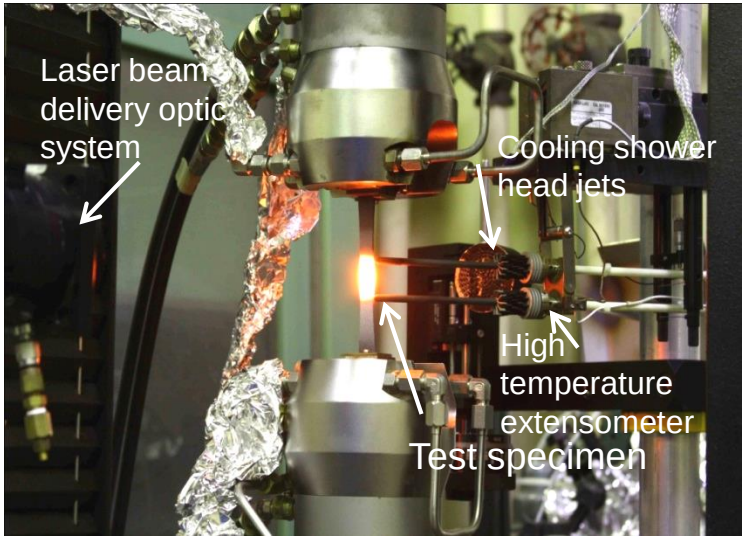
# Experimental: NASA Yb,Gd,Y Rare Earth Silicate EBCs

- Yb,Gd(Nd),Y (or RE-Silicate) Multi-Component Rare Earth Silicate EBCs
- Sometime using fine alternating $HfO_2$ and the silicates for top coats
- EB-PVD bond coat systems mostly focused on YbGdSi, YbGd-LuSi, and YbNdSi, and $HfO_2$-Si
- Initial compositions optimized for the EBC bond coats: RE:Si 1:2; and Hf:Si 1:2 – 1:1
- Coating processed on SiC/SiC ceramic matrix composites for studies
- Processed using Directed Vapor EB-PVD at Directed Vapor Technologies

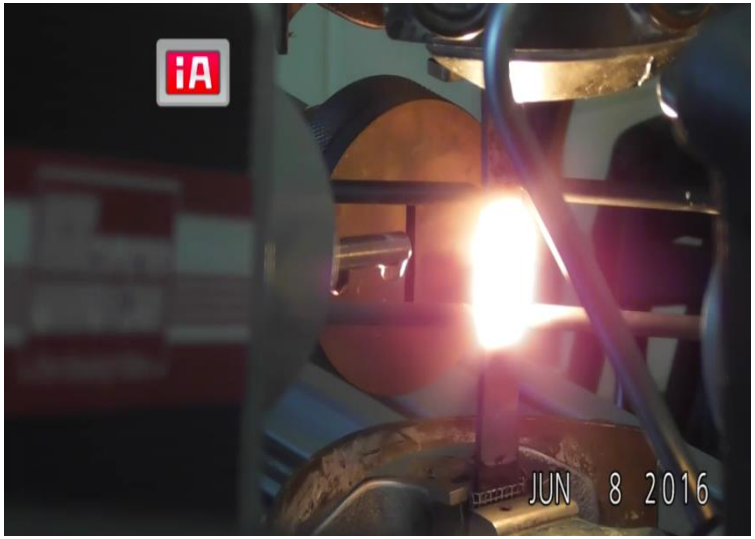


# Experimental: Oxidation and Durability Tests

- Test specimens with dimensions 25 mm diameter disc  specimens for oxidation, laser heat flux and furnace cyclic test (FCT) – briefly reviewed
- Thermogravimetric analysis (TGA), using 0.5”x1” CVI SiC/SiC specimens
- Laser long-term thermomechanical fatigue + steam/CMAS water vapor cyclic test using 0.5”x6” dogbone specimens



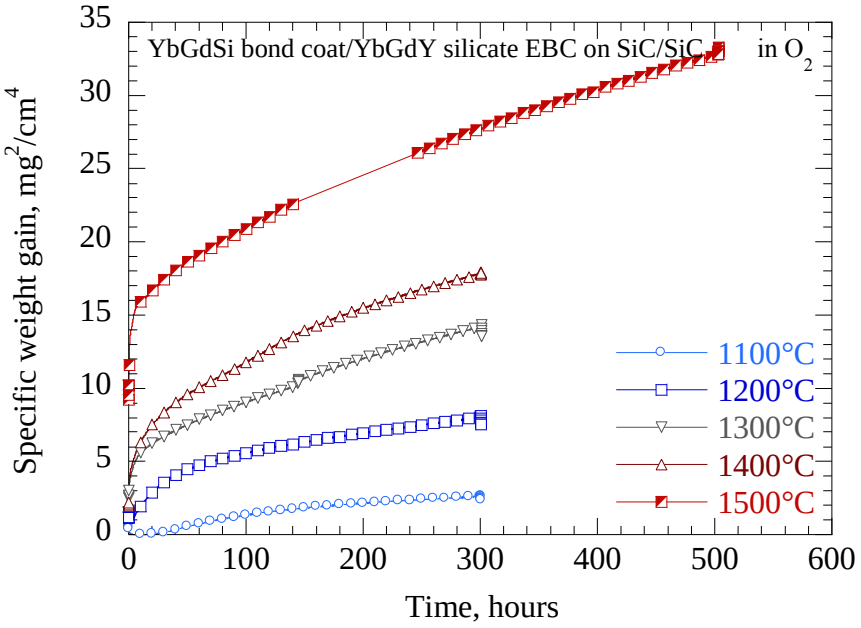

High heat flux tensile TMF and rupture testing

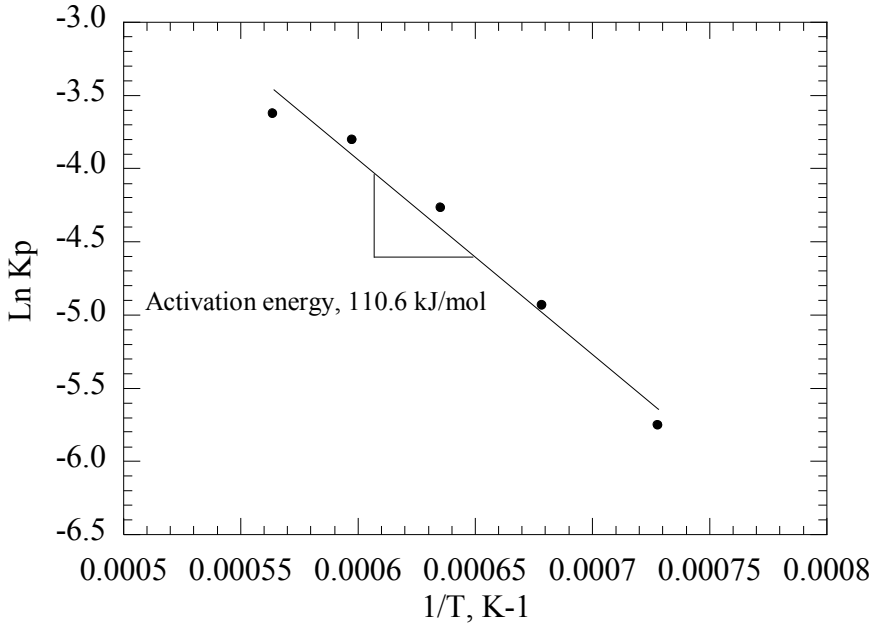



High heat flux tensile TMF and rupture, with high velocity steam testing

# Oxidation Kinetics of EB-PVD Processed YbGdSi(O) Based Coating

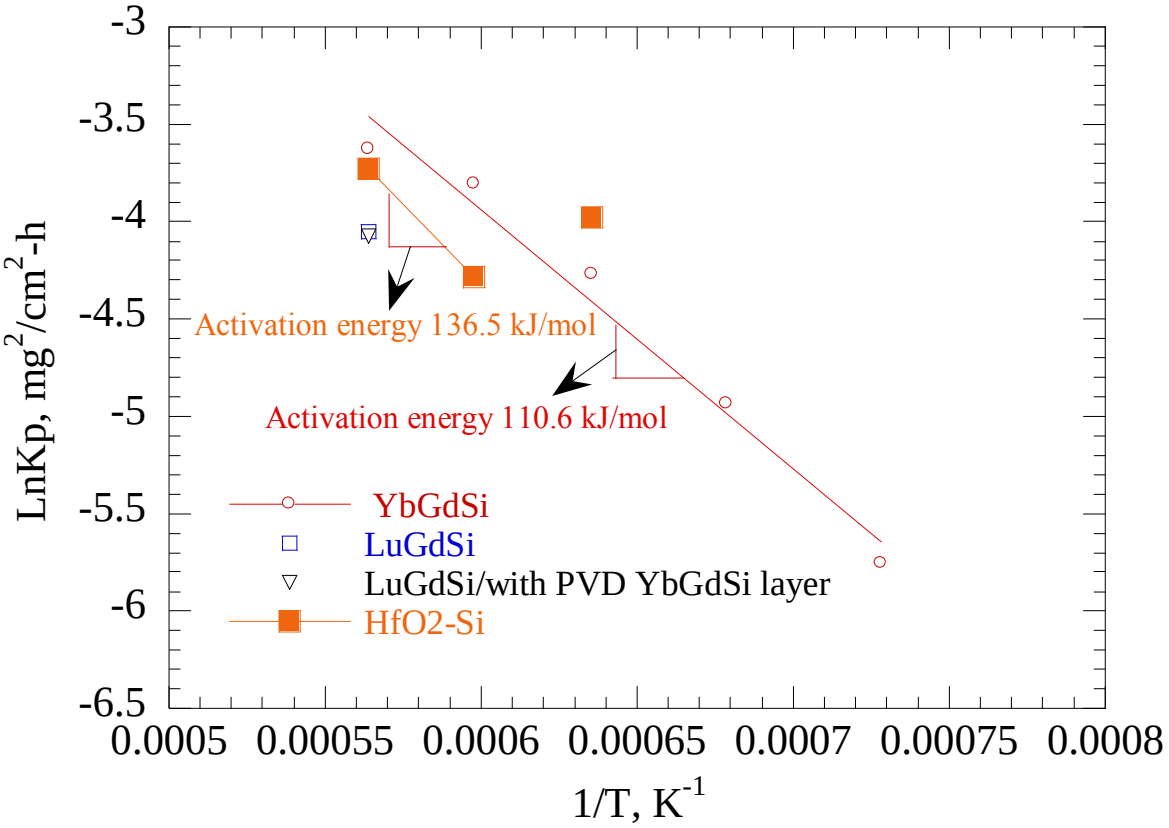
- Oxidation kinetics obtained at various temperatures in flowing $O_2$ for YbGdSi(O) (not necessarily processing optimized)
- Parabolic oxidation kinetics generally observed after initial transient stages
- Activation energy determined 110 kJ/mol



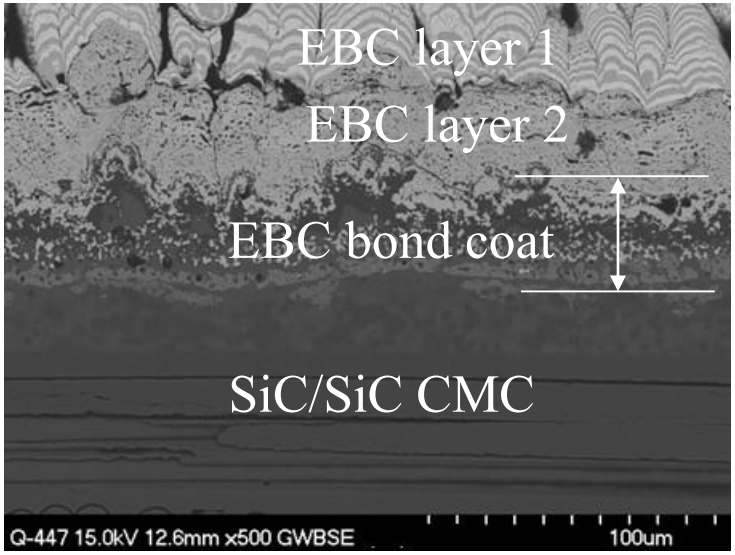
# Oxidation Kinetics Comparisons of Several Advanced EB-PVD Processed EBC Systems Compared

- The EB-PVD Systems showed comparable oxidation rates and good oxidation resistance, tested up to 500 h
- Kinetics compared with LuGdSi (O) and $HfO_2$-Si (O) systems
- Further process improvements help improved oxidation resistance and durability

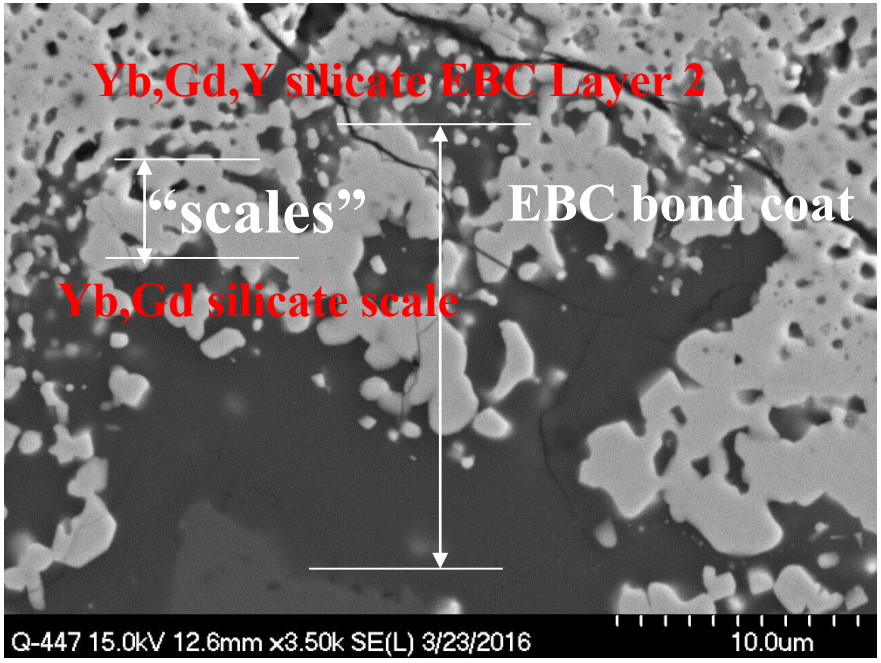


# Microstructures of the Advanced EBCs after the Oxidation Tests

- RE-Si system: forming RE silicate "scales", fully compatible with EBCs
- Reaction and oxidation mechanisms are being further studied, particularly RE containing $SiO_2$ phase stability
- Further process improvements can help improve the oxidation resistance and durability

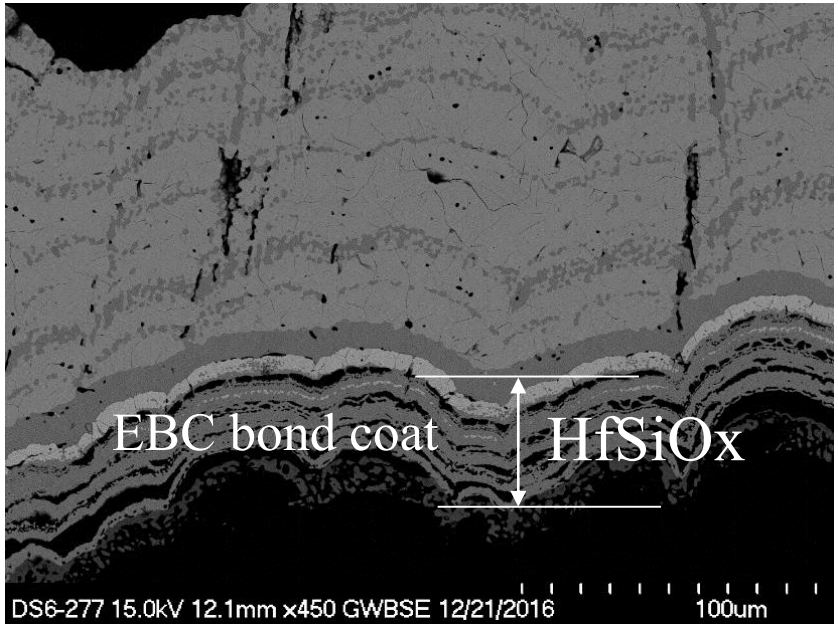



Cross-section micrograph of YbGdSi(O) tested at 1500°C, 500hr



# Microstructures of the Advanced EBCs after the 500 hr Oxidation Tests in $O_2$- Continued

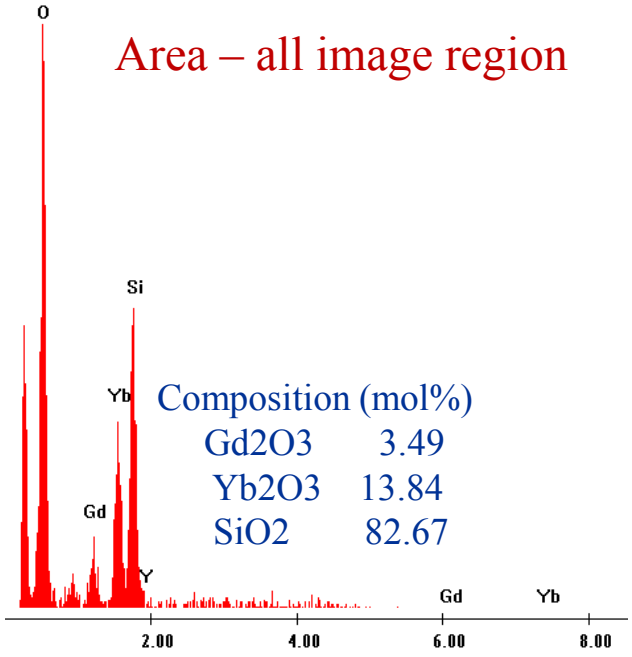
- $HfO_2$-Si bond coat: forming $HfSiO_x$ based scales bond coat, compatible with EBCs
- Reaction and stability being studied
- Further process improvements can help improve the oxidation resistance and durability




Cross-section micrograph of $HfO_2$-Si tested at 1500°C, 500hr

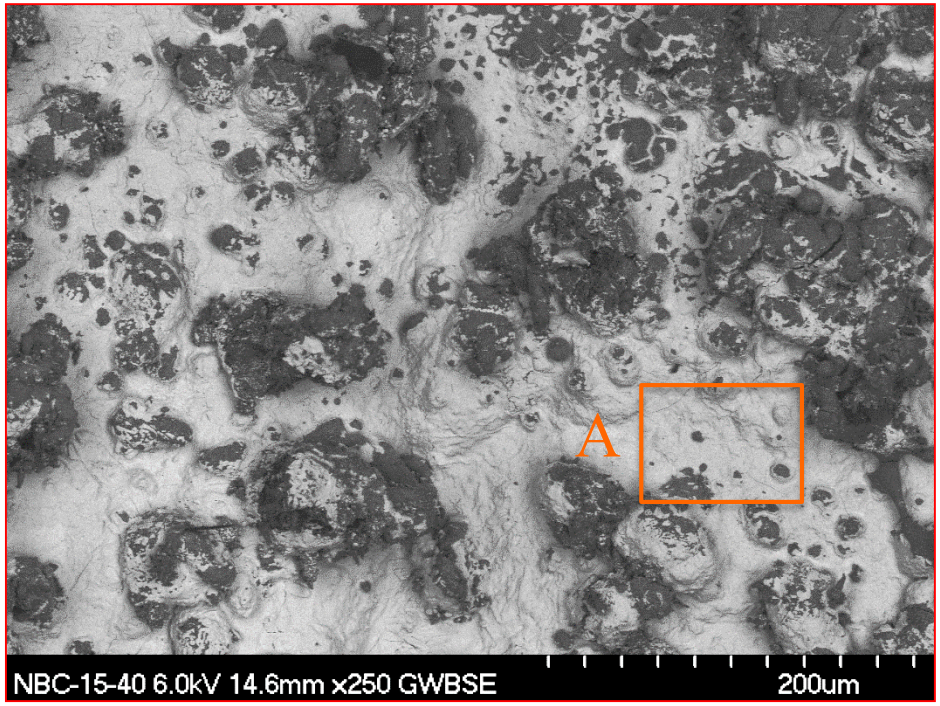
# Microstructures of the Advanced EBCs after the Oxidation Tests - Continued

– Surface Morphologies of YbGdSi Bond Coat only on CMC after Oxidation at 1400C, 300 hr




Area – all image region

| Composition (mol%) | |
|---|---|
| Gd2O3 | 3.49 |
| Yb2O3 | 13.84 |
| SiO2 | 82.67 |

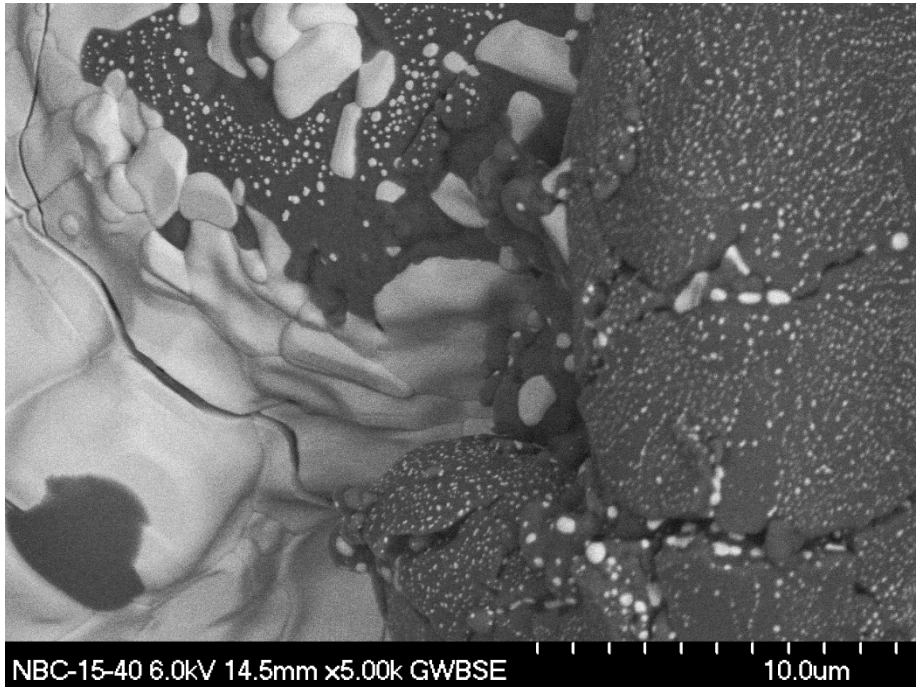


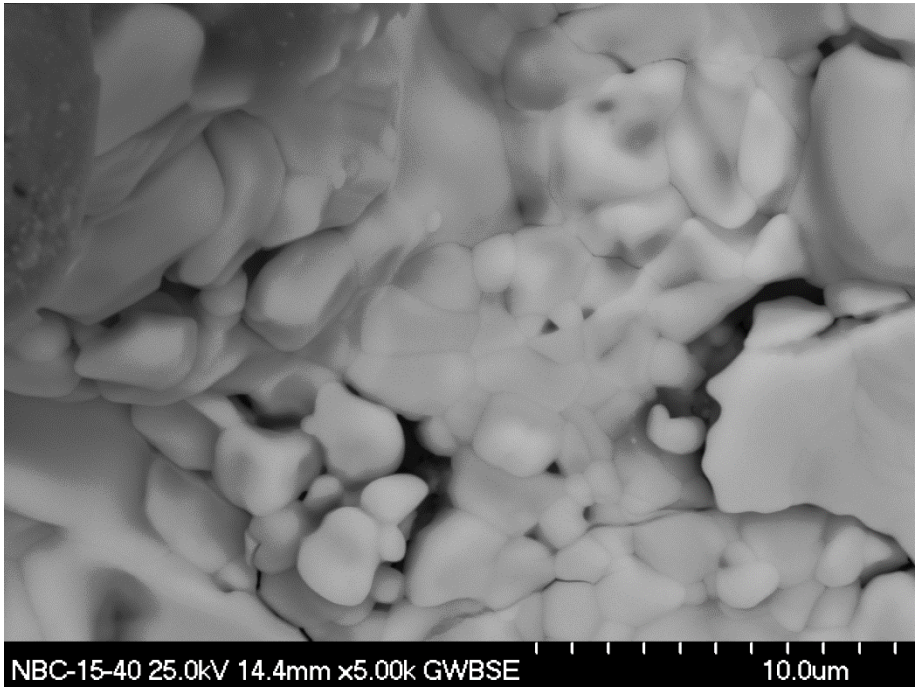

| Composition (mol%) | |
|---|---|
| Gd2O3 | 7.73 |
| Yb2O3 | 30.54 |
| SiO2 | 61.73 |

Area A Composition

# Microstructures of the Advanced EBCs after the Oxidation Tests - Continued

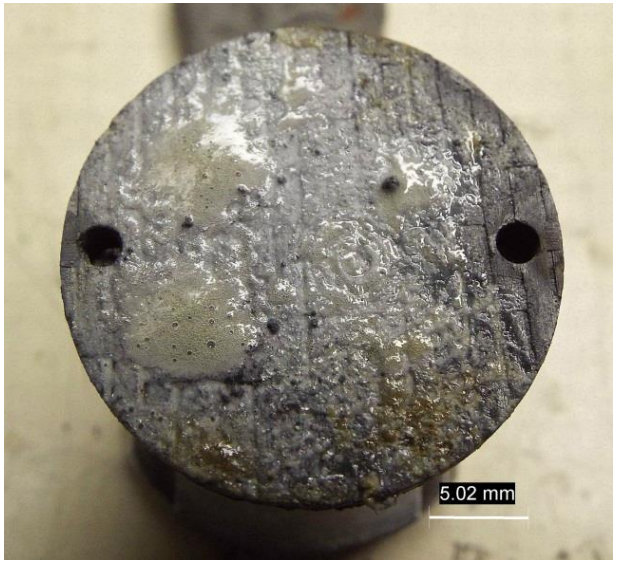
- Surface Morphologies of YbGdSi Bond Coat only on CMC after Oxidation at 1400°C, 300hr
- Observed $SiO_2$ rich phase separation with fine rare earth silicate phases
- Solubility of $HfO_2$ and rare earth oxides/silicates also being studied using TEM

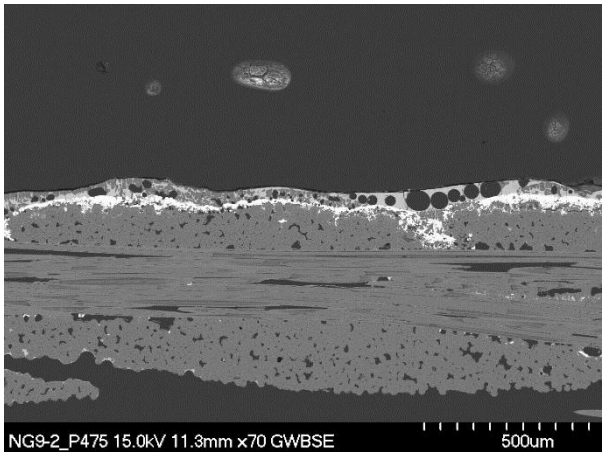


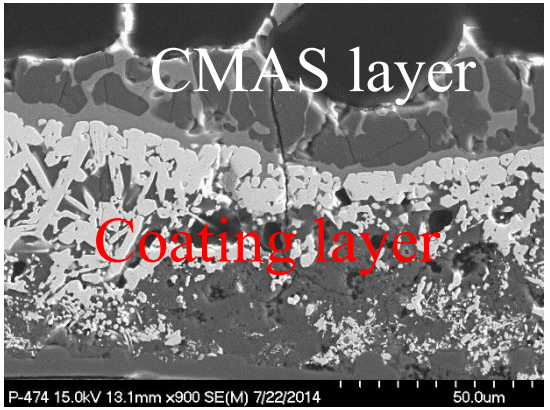



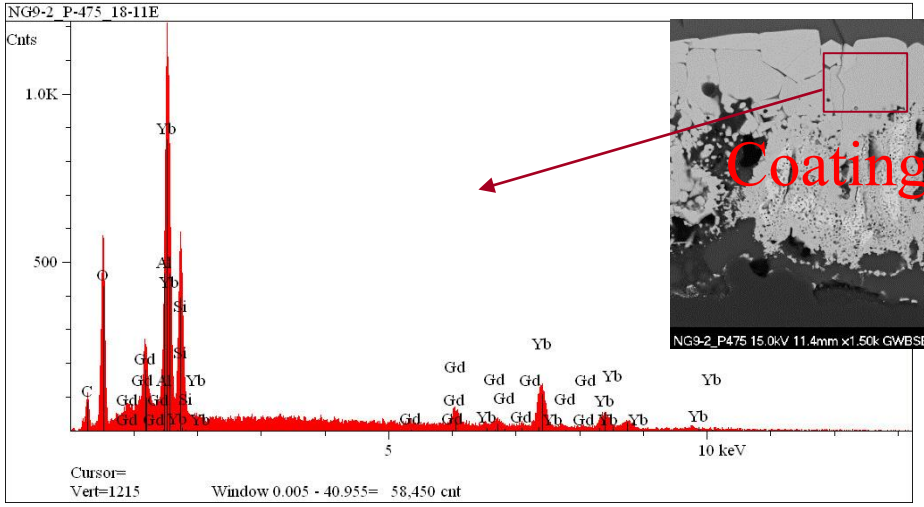
# CMAS Resistance for the Rare Earth-Silicon Coatings

- CMAS resistance of Yb-GdSi (O) at 1500°C, 100 hr
- Higher stability and CMAS resistance observed due to its High Melting Point Coating Compositions
- Observed the Apatite phase formation



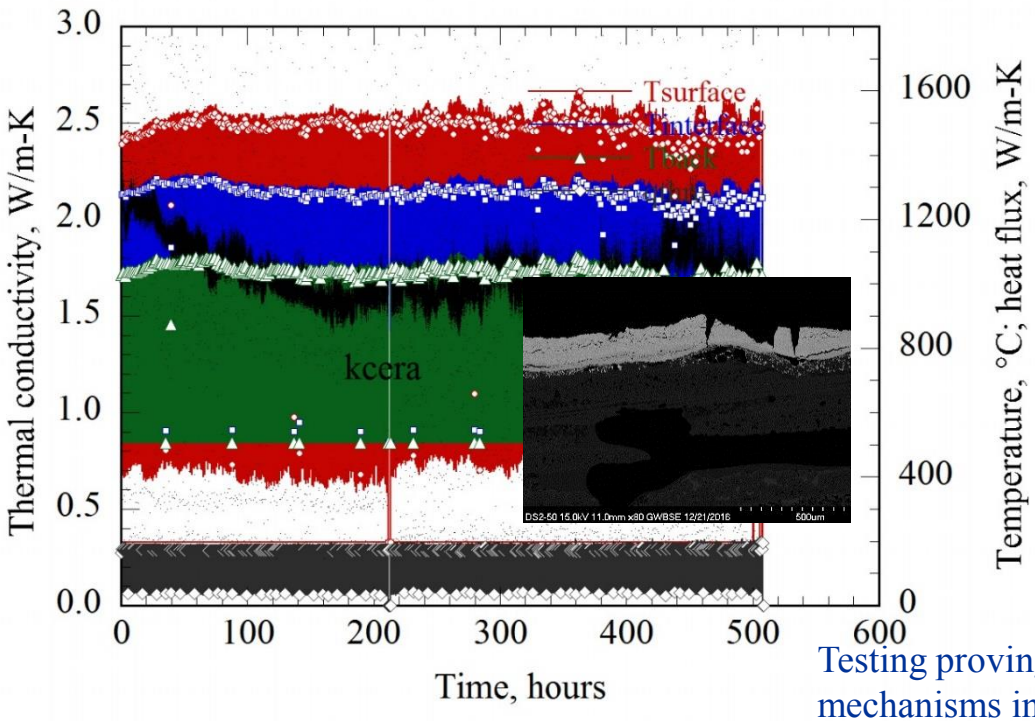



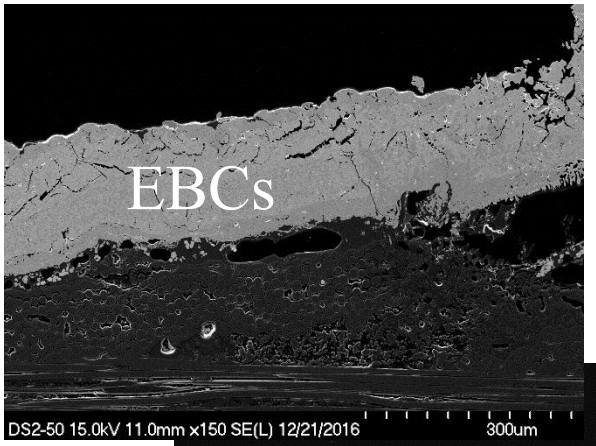
# High Heat Flux Thermomechanical fatigue Tests of Advanced NASA EBC-Bond Coats Systems on CMCs

- Laser High Heat Flux themomechanical fatigue testing of a $HfO_2$-Si and NASA advanced EBC baseline with steam at 3 Hz, 2600-2700°F, and 69 MPa maximum stress with stress ratio 0.05, completed 500 h testing

- Tsurface = 1500-1600°C
- Tinterface= 1320-1350°C
- Heat Flux = 170 W/cm$^2$
- Specimen had some degradations

3hz fatigue testing at 10 ksi loading
Completed 500 hr testing



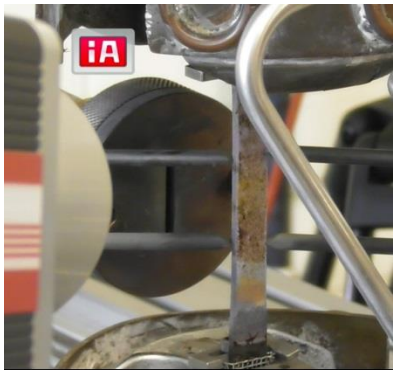



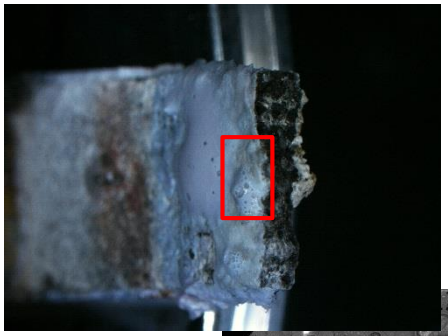


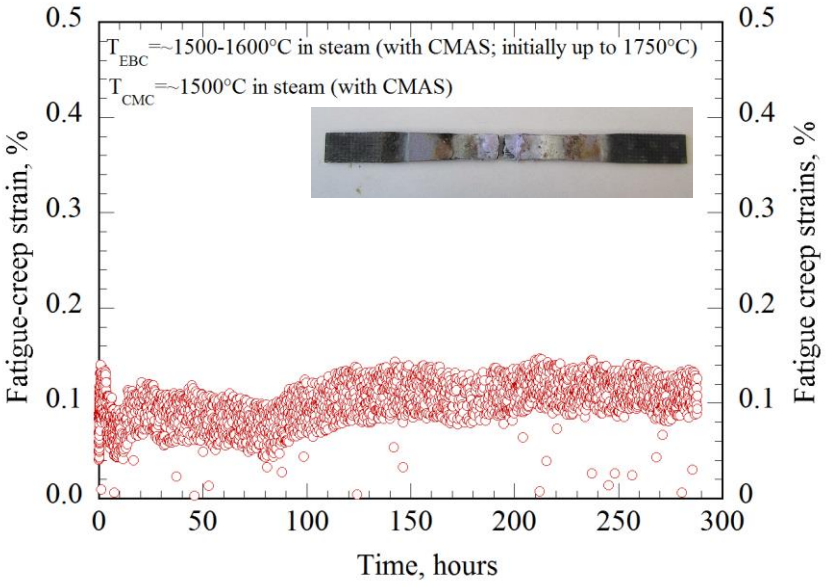
Testing proving vital failure mechanisms in a simulated test environments

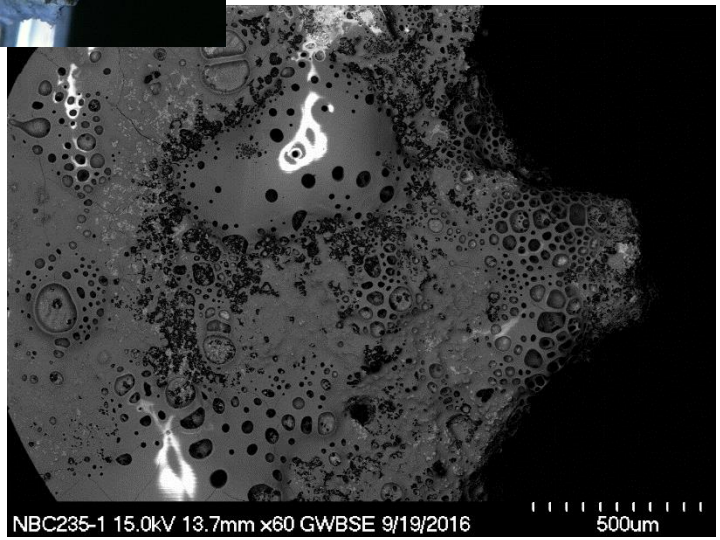
# High Heat Flux Thermomechanical fatigue Tests of Advanced NASA EBC-Bond Coats Systems on CMCs - Continued

- NdYb silicate EBC-RESi bond coat EBC coatings on 3D-architecture CVI-PIP SiC-SiC CMC (EB-PVD processing), tested in combined CMAS and steam thermomechanical fatigue, completed ~300 h testing



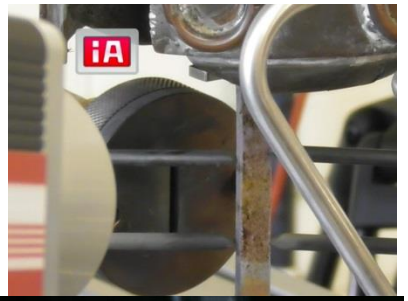


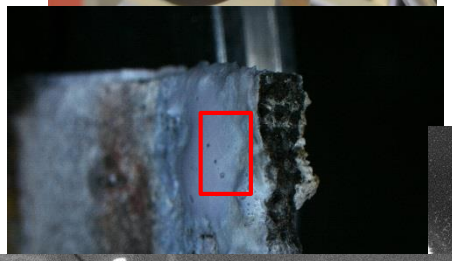



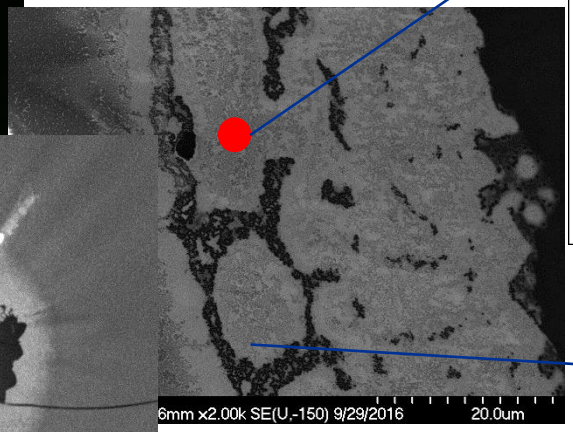

Steam and CMAS attacked coating surface at 2700°F

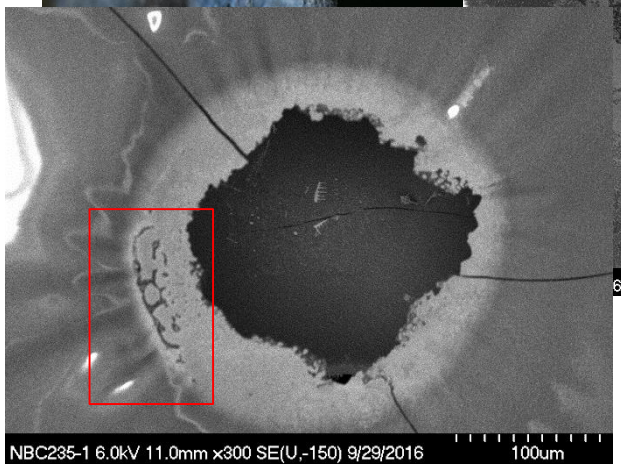
# High Heat Flux Thermomechanical fatigue Tests of Advanced NASA EBC-Bond Coats Systems on CMCs - Continued

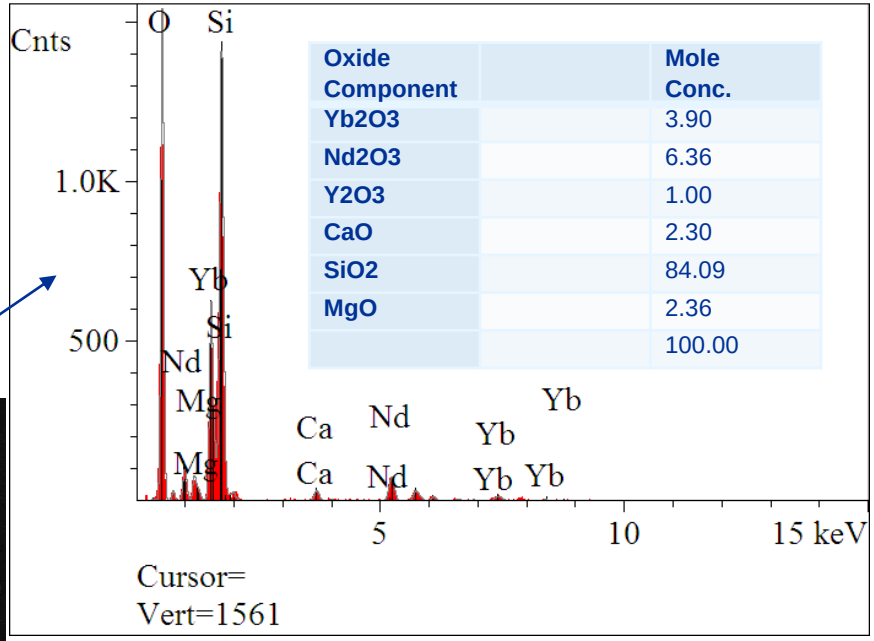
- NdYb silicate EBC-RESi bond coat EBC coatings on 3D architecture CVI-PIP SiC-SiC CMC (EB-PVD processing), tested in combined CMAS and steam thermomechanical fatigue, completed ~300 h testing






| Oxide Component | | Mole Conc. |
|---|---|---|
| Yb2O3 | | 3.90 |
| Nd2O3 | | 6.36 |
| Y2O3 | | 1.00 |
| CaO | | 2.30 |
| SiO2 | | 84.09 |
| MgO | | 2.36 |
| | | 100.00 |

$SiO_2$ rich phases separation in CMAS
Nd and Yb dissolutions

Steam and CMAS attacked coating surface at 2700°F

# Summary

- RE - Silicon and $HfO_2$-Si bond coats with multicomponent rare earth silicate EBCs processed using EB-PVD, and the oxidation kinetics investigated
- The coatings generally showed very good oxidation and cyclic resistance for CMCs with targeted designed bond coat compositions, at 1500°C and up to 500 h tests
- The EBC bond coats grow rare earth silicates or $HfSiO_x$ “scales”, compatible with the EBC systems
- Stability of RE, Hf containing $SiO_2$ rich phases from the phase separation being further evaluated
- Long-term environment durability testing conducted to evaluate the coatings in more complex load, CMAS and/or steam environments, simulating turbine airfoil conditions
- The results helping further design and processing improved environmental barrier coating systems, for achieving more robust, prime-reliant EBC systems

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