Durability and CMAS Resistance of Advanced Environmental Barrier Coatings Systems for SiC/SiC Ceramic Matrix Composites

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Environmental Barrier Coating - CMAS Interaction Research Efforts

- Advanced EBC development – composition design and developments for improved CMAS resistance; thermomechanical-CMAS Interactions and durability – Zhu et al
- NASA-Air Force Venture and Viper Turbine Coating-CMAS Collaborative programs - Zhu, James Smialek, Robert A. Miller, Bryan Harder
- Formal NASA Intern Undergraduate Students – Nadia Ahlborg and Dan Miladinovich
- Fundamental NASA in-house CMAS properties - Narottam Bansal and Valerie Weiner

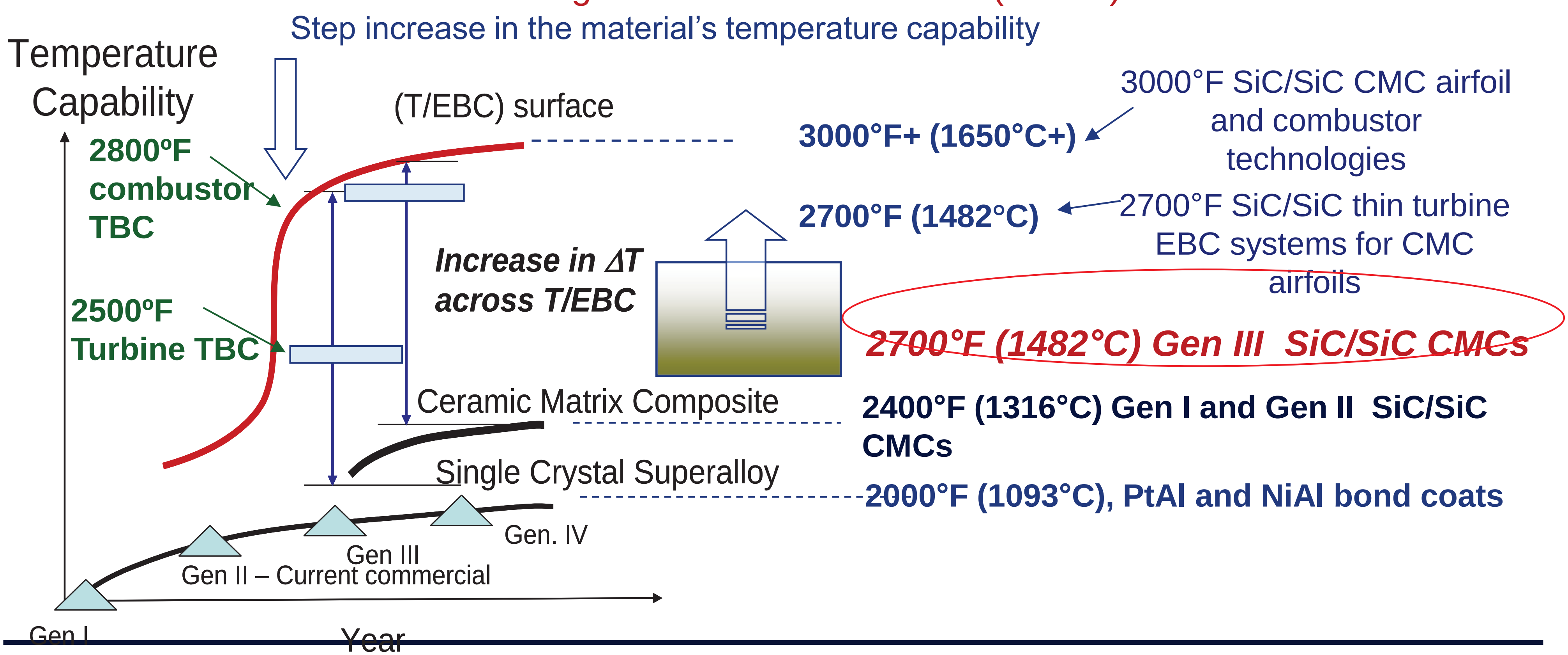
Outline

- **Environmental barrier coating (EBC) development: the CMAS relevance**
- **Some generalized CMAS related failures**
- **CMAS degradation of environmental barrier coating (EBC) systems: rare earth silicates**
  - Ytterbium silicate and yttrium silicate EBCs
  - Some reactions, kinetics and mechanisms
- **Advanced EBCs, HfO_2- and Rare Earth - Silicon based 2700°F+ capable bond coats**
- **Summary**

NASA Environmental Barrier Coatings (EBCs) and Ceramic Matrix Composite (CMC) System Development

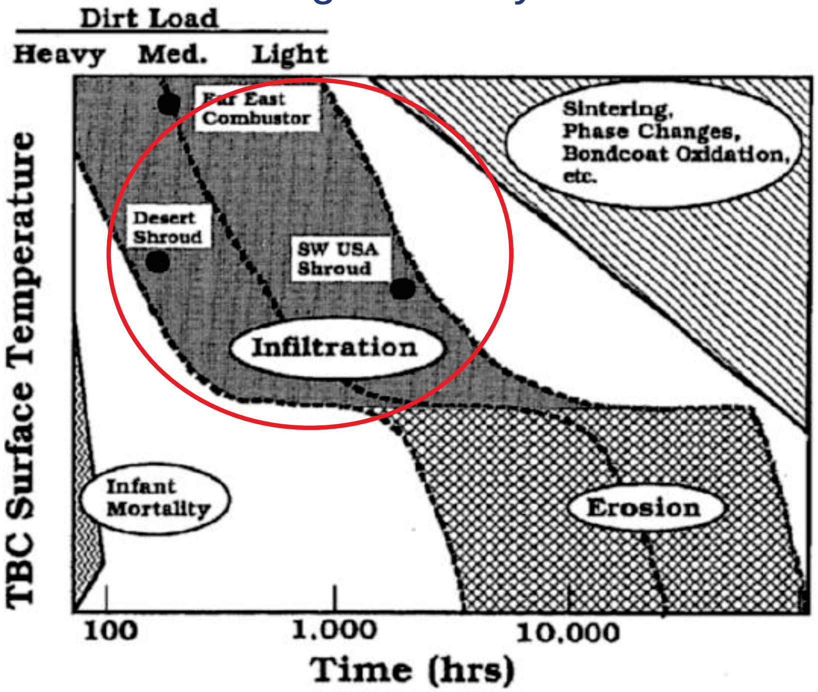
– **Emphasize material temperature capability, performance and *long-term* durability-** Highly loaded EBC-CMCs with temperature capability of 2700°F (1482°C)

- 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)

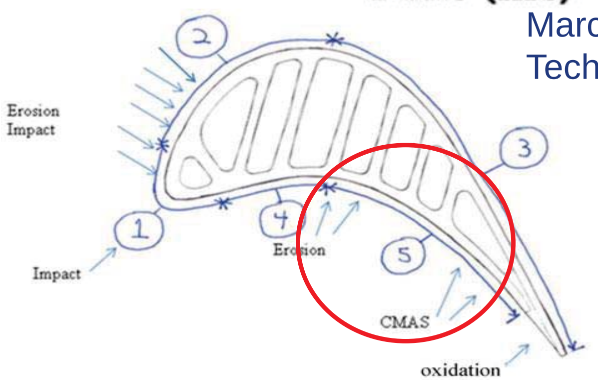


EBC-CMAS Degradation is of Concern with Increasing Operating Temperatures

- **Emphasize improving temperature capability, performance and *long-term* durability of ceramic turbine airfoils**
  - Increased gas inlet temperatures for net generation engines lead to significant CMAS -related coating durability issues – CMAS infiltration and reactions



Marcus P. Borom et al, Surf. Coat. Technol. 86-87, 1996

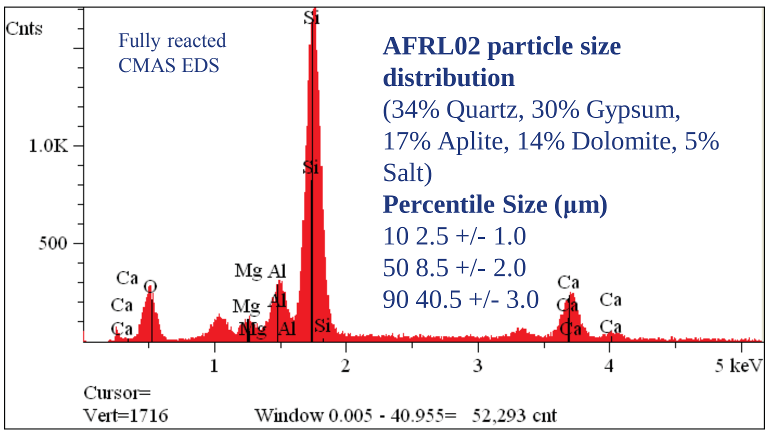


Current airfoil CMAS attack region - R. Darolia, International Materials Reviews, 2013

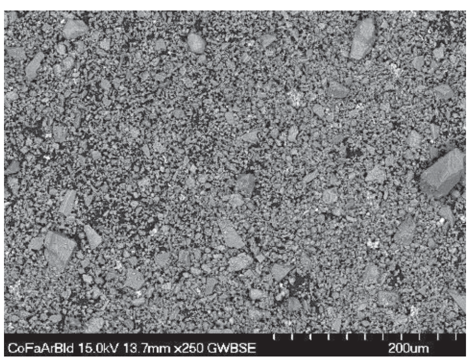
Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests

- Synthetic CMAS compositions, in particular, NASA modified version (NASA CMAS), and the Air Force Powder Technology Incorporated PTI 02 CMAS currently being used
- Saudi Sands used for past turbine coating studies
- CMAS SiO_2 content typically ranging from 43-49 mole%; such as NASA's CMAS (with NiO and FeO)
- Collaborations on-going with the Air Force; also planned DLR, ONERA etc on Volcanic Ash Composition selections

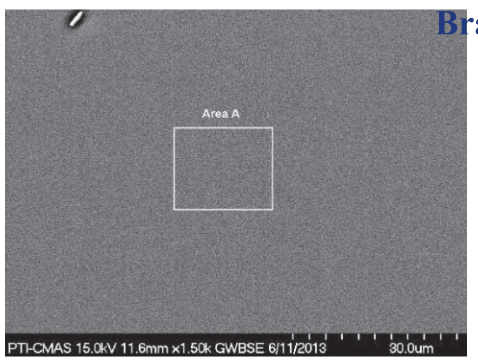
ARFL PTI 11717A 02 used at NASA for CMAS studies



AFRL02 particle size distribution
(34% Quartz, 30% Gypsum, 17% Aplite, 14% Dolomite, 5% Salt)
Percentile Size (µm)
10 2.5 +/- 1.0
50 8.5 +/- 2.0
90 40.5 +/- 3.0



As received



Fully reacted

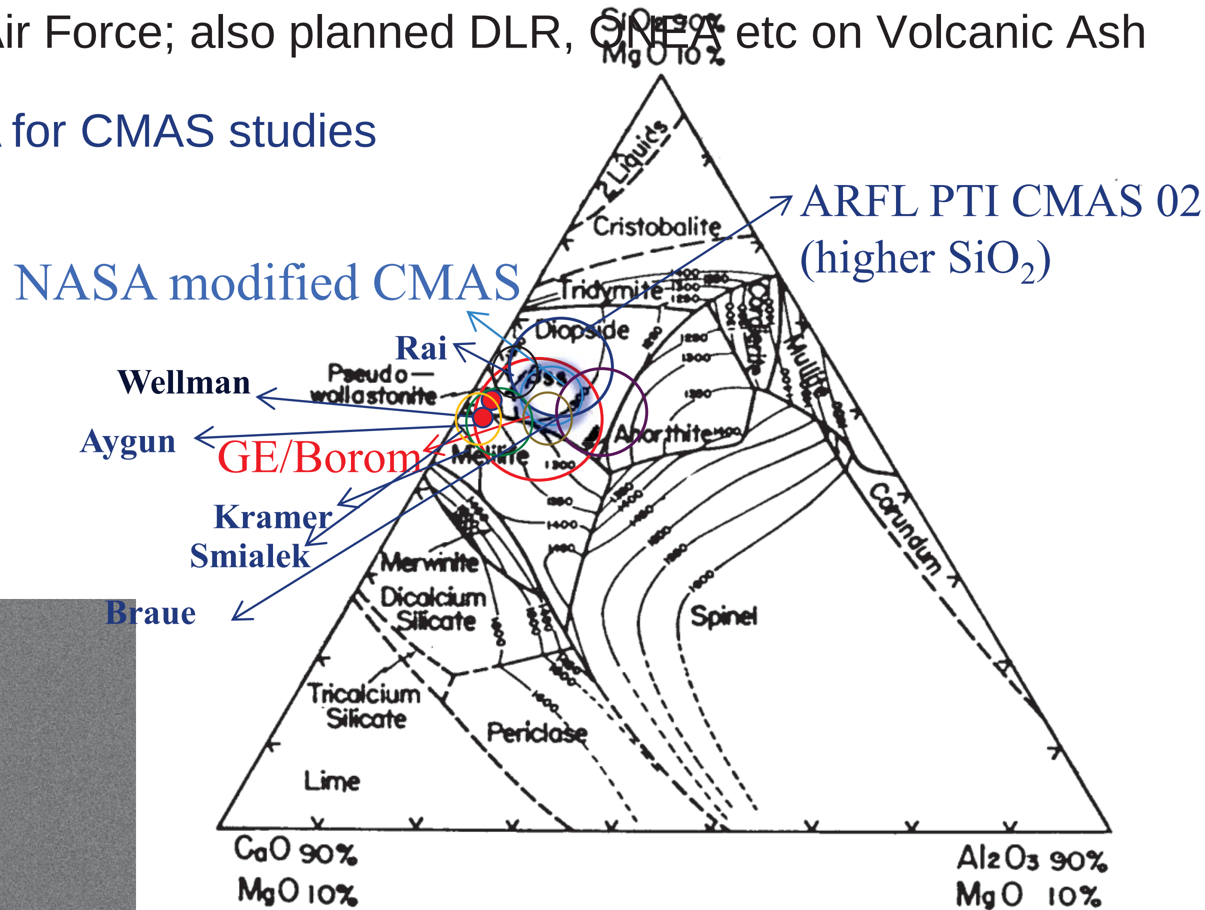
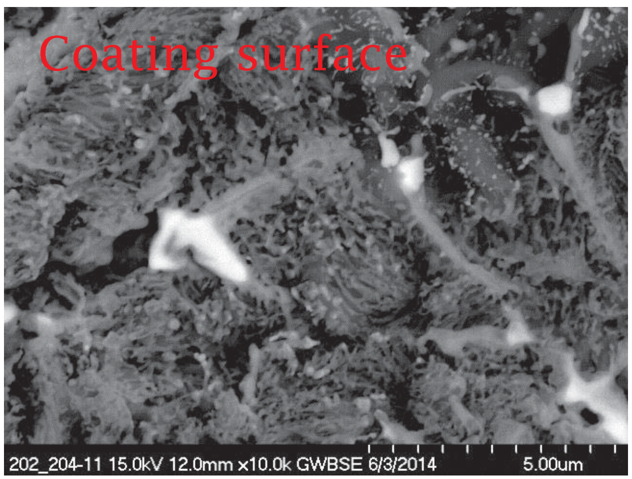


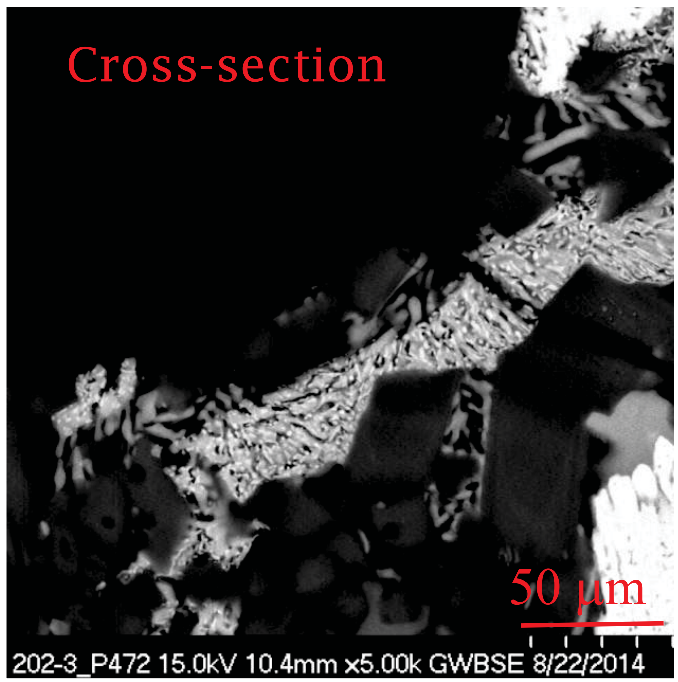
Fig. 4. The 10% MgO plane of the system $CaO-MgO-Al_2O_3-SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

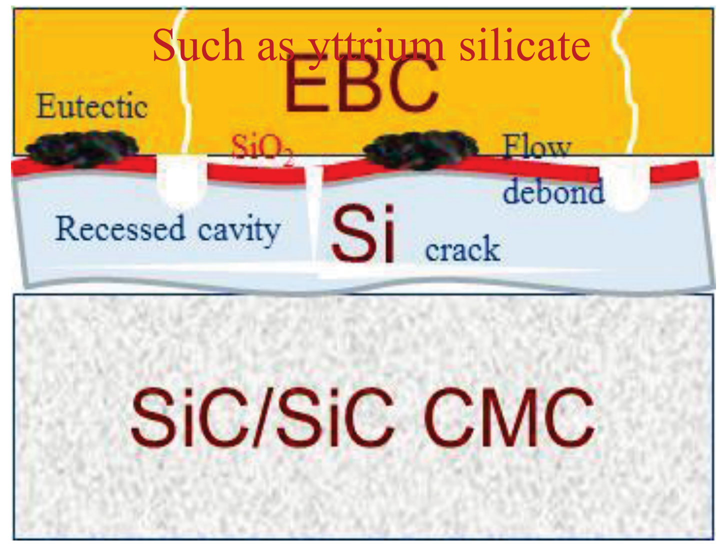
CMAS Related Degradations in EBCs

– CMAS effects

- Significantly reduce melting points of the EBCs and bond coats
- Cause more severe degradations with thin airfoil EBCs
- CMAS increase EBC diffusivities and permeability, thus less protective as an environmental barrier
- Reduced mechanical properties: such as strength and toughness reductions
- Leads to grain boundary attack thus disintegrate EBCs
- CMAS interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue







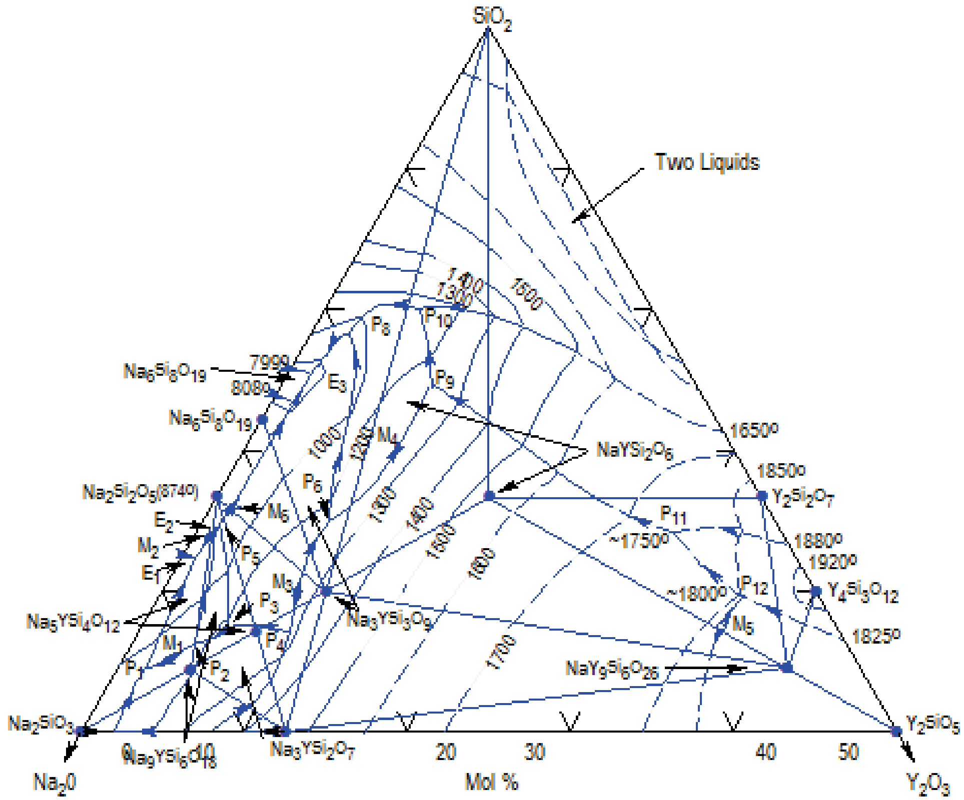
EBC and degradations

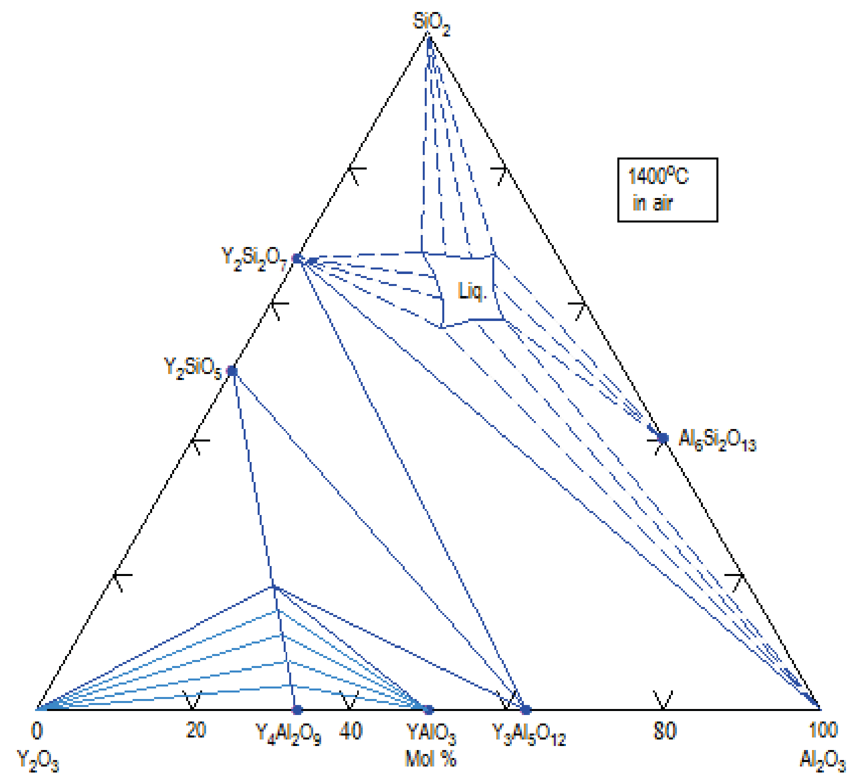
CMAS induced melting and failure

CMAS Related Degradations in EBCs - Continued

– CMAS effects on EBC temperature capability

- Silicate reactions with NaO_2 and Al_2O_3 silicate

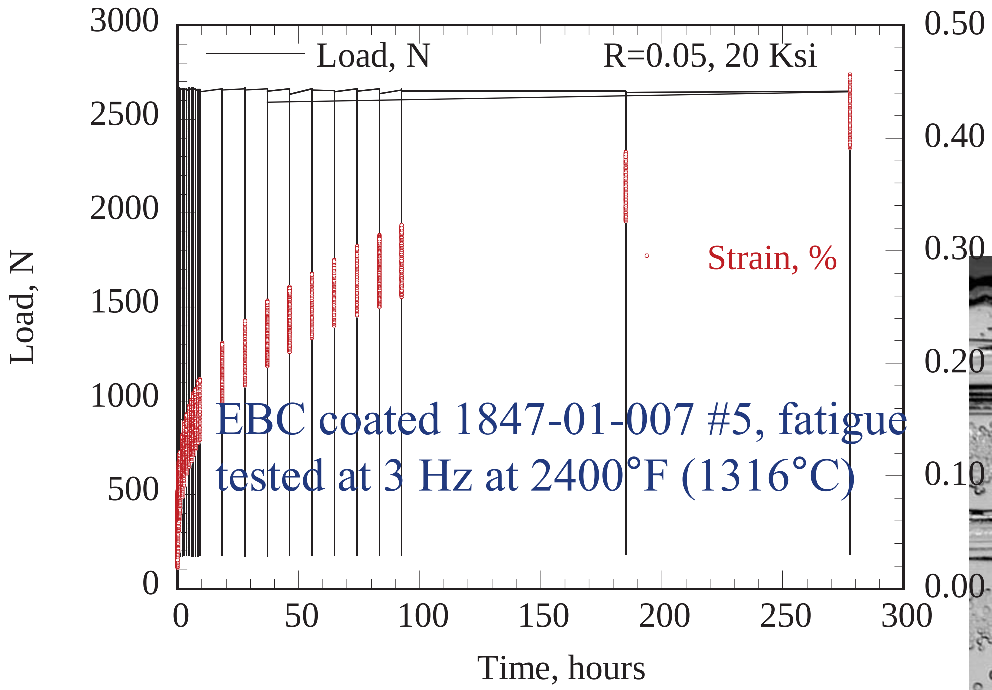


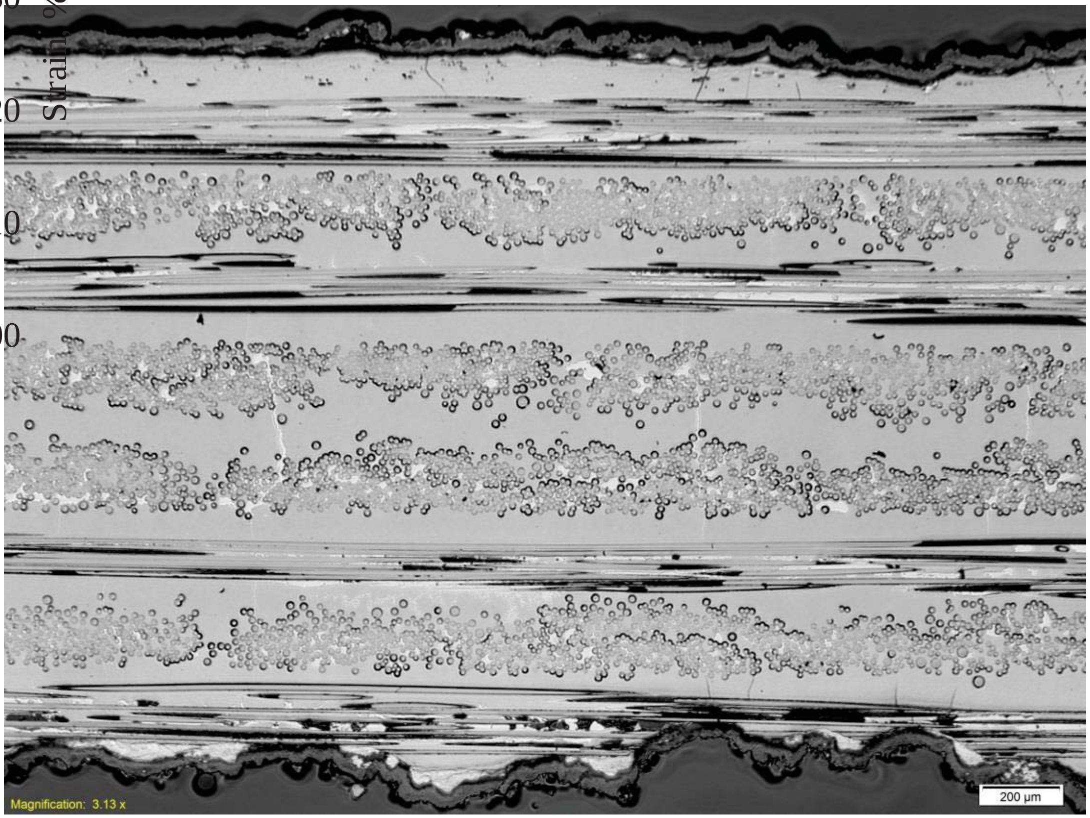


Phase diagrams showing yttrium di-silicate reactions with SiO_2, NaO and Al_2O_3

CMAS Related Degradations in EBCs

- **Fatigue – environmental interaction is of great concern**





A 20 micrometer thick EBC bond coated Prepreg SiC/SiC CMC after 40 hr, 20 Ksi, stress ratio R=0.05 fatigue testing in air

Environmental Barrier Coating Development Limitations and Requirements

- Current EBCs limited in their temperature capability, water vapor stability and long-term durability, especially for advanced high pressure, high bypass turbine engines

- Advanced EBCs also require higher strength and toughness
  - In particular, resistance to combined high-heat-flux, engine high pressure, combustion environment, creep-fatigue, loading interactions

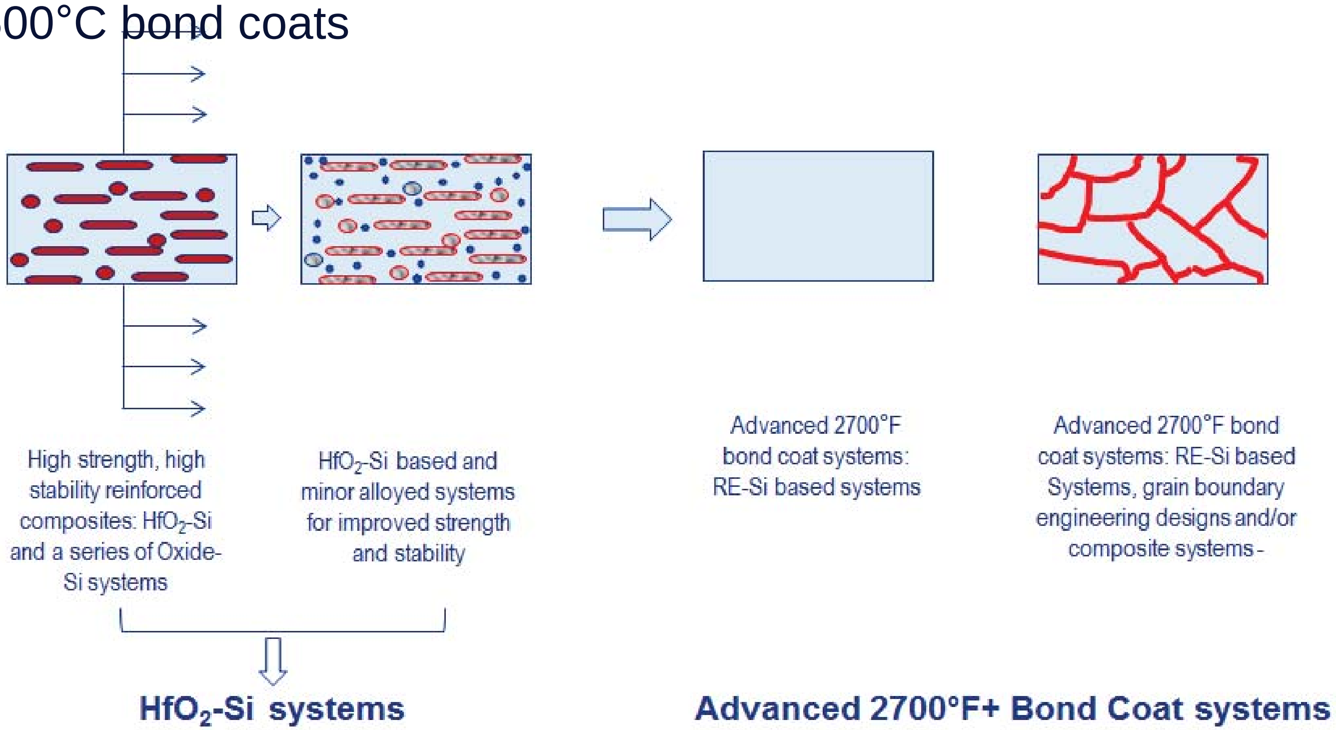
- EBCs need improved erosion, impact and calcium-magnesium-alumino-silicate (CMAS) resistance and interface stability
  - Critical to reduce the EBC Si/SiO_2 reactivity and their concentration tolerance

- EBC-CMC systems need advanced processing for realizing complex coating compositions, architectures and thin turbine configurations for next generation high performance engines
  - Advanced high temperature processing of high stability cluster and nano-composites

NASA EBC Systems

NASA EBC Systems

- HfO_2 -RE_2O_3-SiO_2/$RE_2Si_{2-x}O_{7-2x}$ environmental barrier systems
  - Controlled silica content and transition element and rare earth dopants to improve EBC stability and toughness
  - Develop HfO_2-Si based + X (dopants) and more advanced rare earth composite compound composition systems for 2700°F+ long-term applications
  - Develop prime-reliant composite EBC-CMC interfaces for fully integrated EBC-bond coat systems
- RE_2O_3-SiO_2-Al_2O_3 Systems
- Develop advanced NASA high toughness alternating layered systems
- Advanced 1500°C bond coats

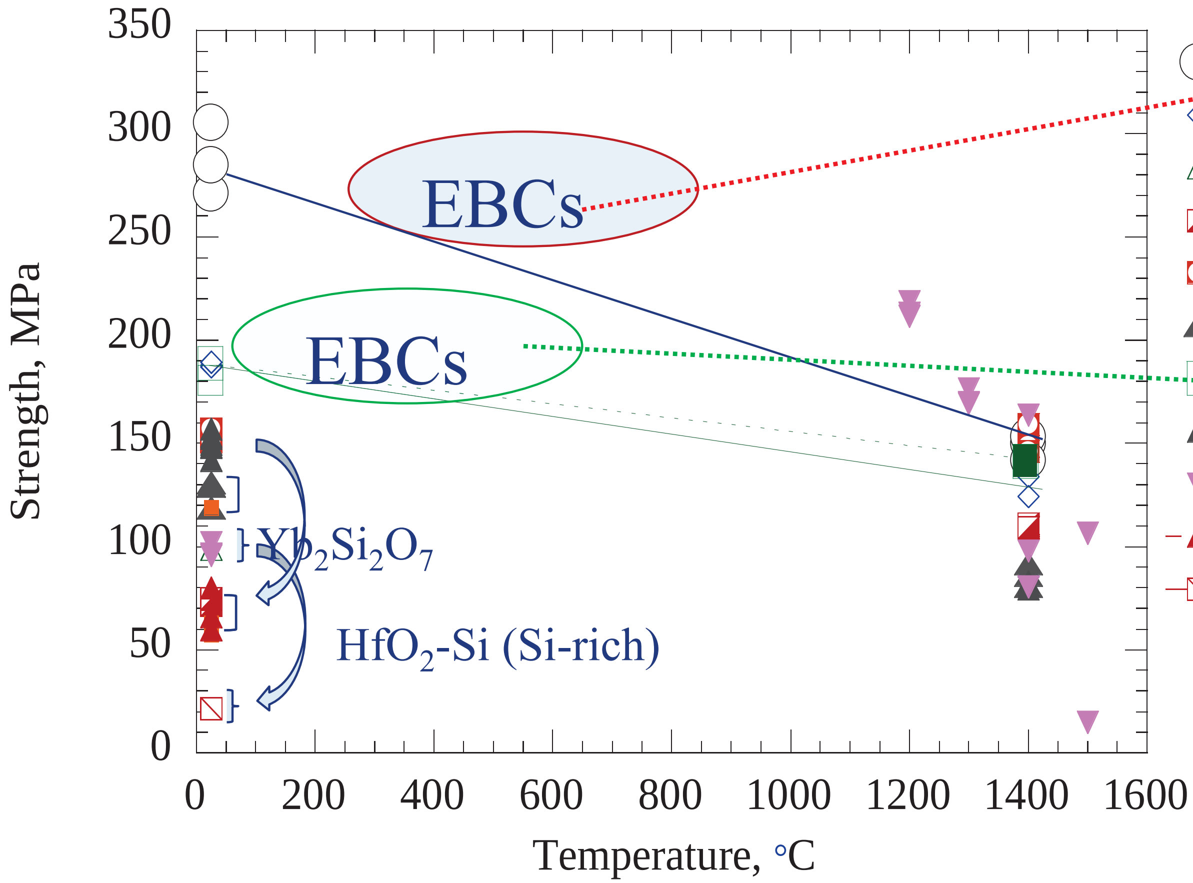


Strength Results of Selected EBC and EBC Bond Coats - CMAS Reaction resulted in Strength Reduction in Silicates

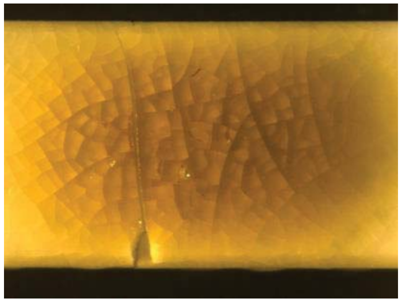
Selected EBC systems

– HfO_2-RE-Si, along with co-doped rare earth silicates and rare earth alumino-silicates , for optimized strength, stability and temperature capability

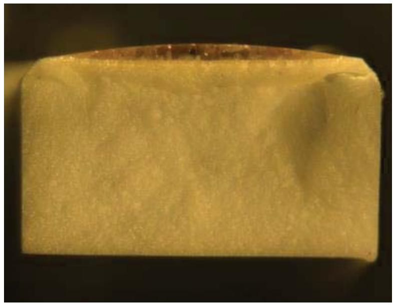
– CMAS infiltrations can reduce the strength



Strength test data compared



$Yb_2Si_2O_7$ CMAS reacted tensile surface

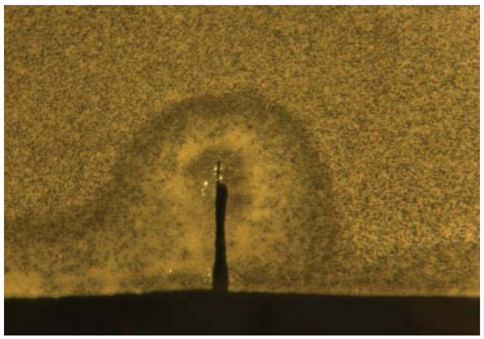


$Yb_2Si_2O_7$ CMAS reacted specimen fracture surface

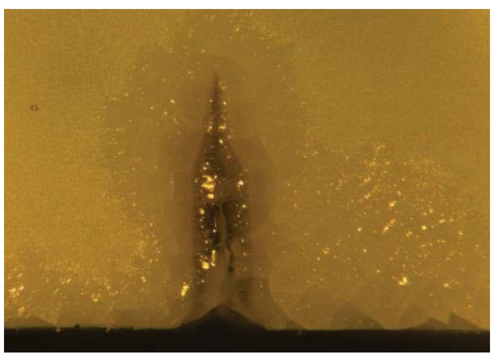
Effect of CMAS Reaction on Toughness of HfO_2-Si Bond Coat and $Yb_2Si_2O_7$ EBC

– HfO_2-Si bond coat and ytterbium di-silicate fracture toughness studied
  - HfO_2-Si toughness >4-5 MPa $m^{1/2}$ achieved at higher temperature
  - Annealing heat treatments at 1300°C improved lower temperature toughness
  - CMAS effect unclear due to the compounded effects of possible 1350°C CMAS reaction degradation and annealing

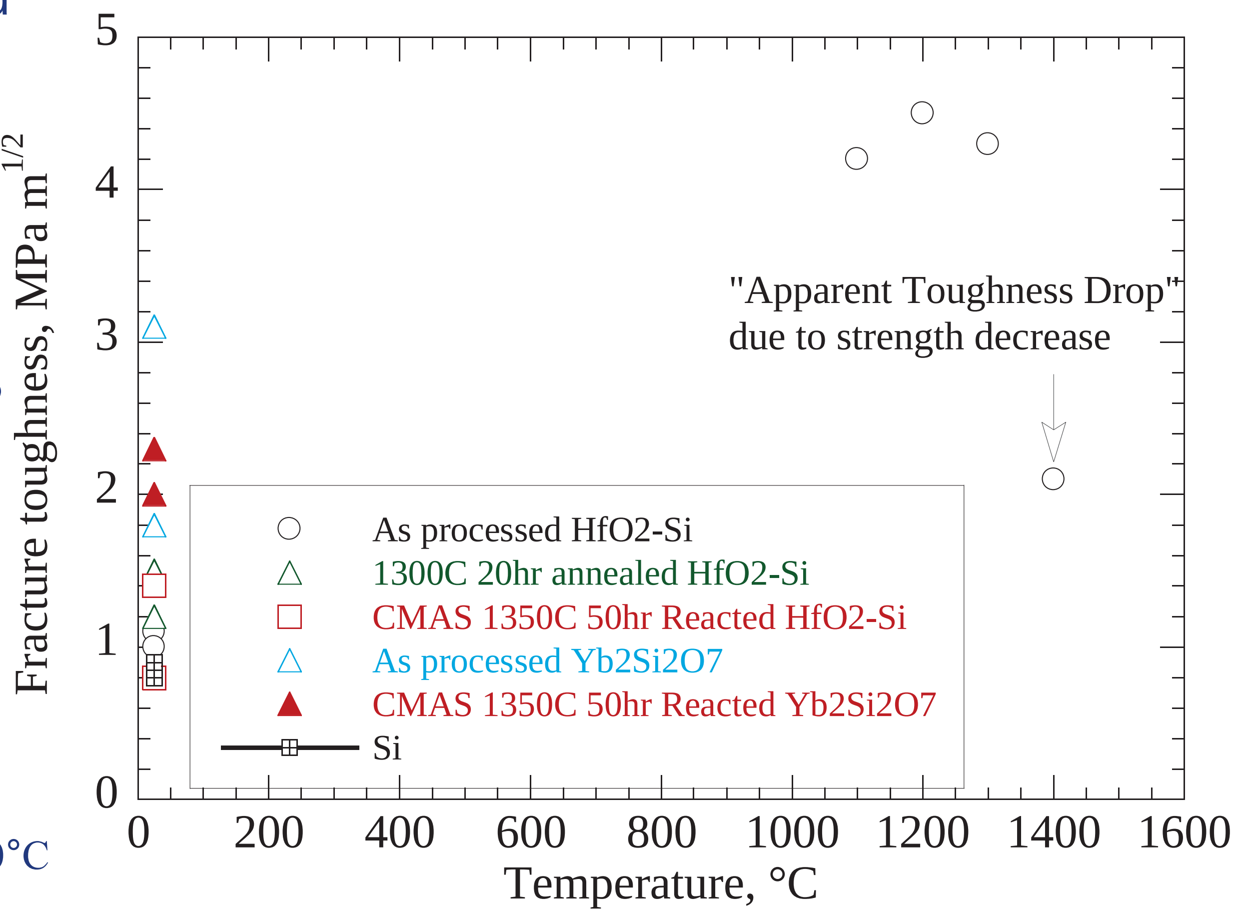
– Ytterbium silicate EBC toughness may also be reduced due to CMAS reactions
  - More measurements are needed



HfO_2-Si illustrating notch distortion due to CMAS exposure at 1350°C for 50 hrs

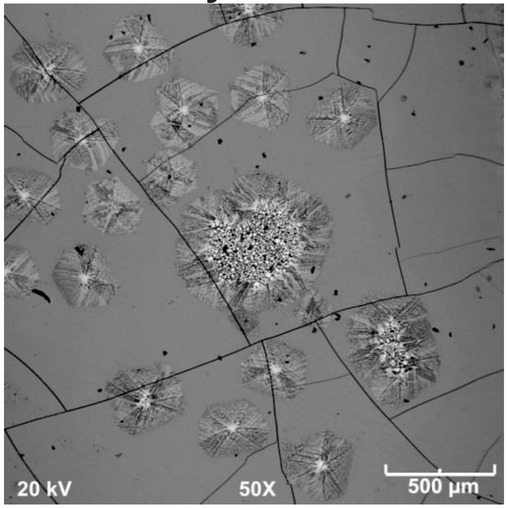


$Yb_2Si_2O_7$ notch after CMAS exposure at 1350°C for 50 hrs

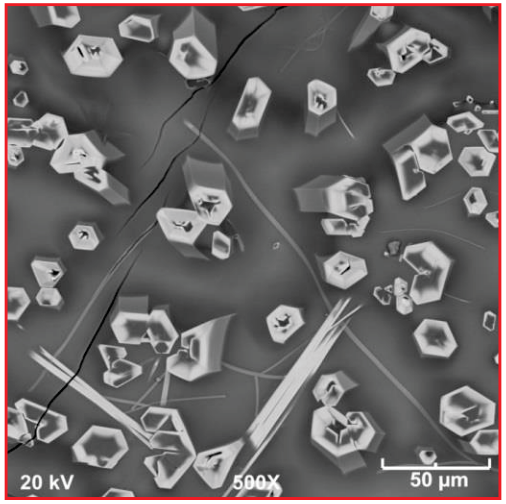


EBC CMAS Surface Reactions

– Ytterbium- and yttrium-disilicate silicates reactions and dissolutions in CAMS



Ytterbium silicate surface CMAS melts: 50 hr 1300°C



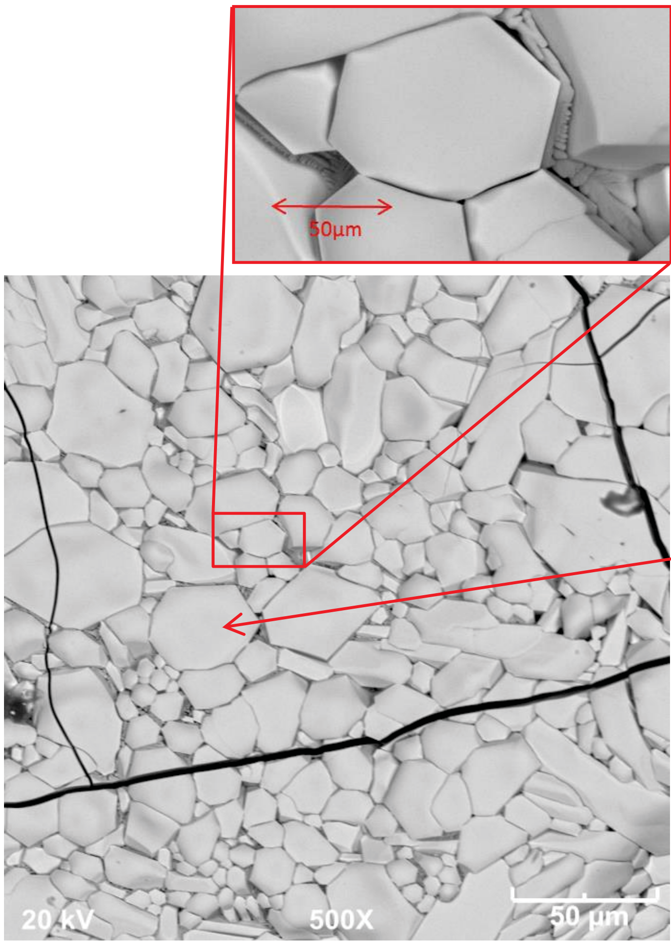
Ytterbium silicate surface CMAS melts: 5 hr 1500°C

Yttrium silicate surface CMAS melts: 50 hr 1300°C

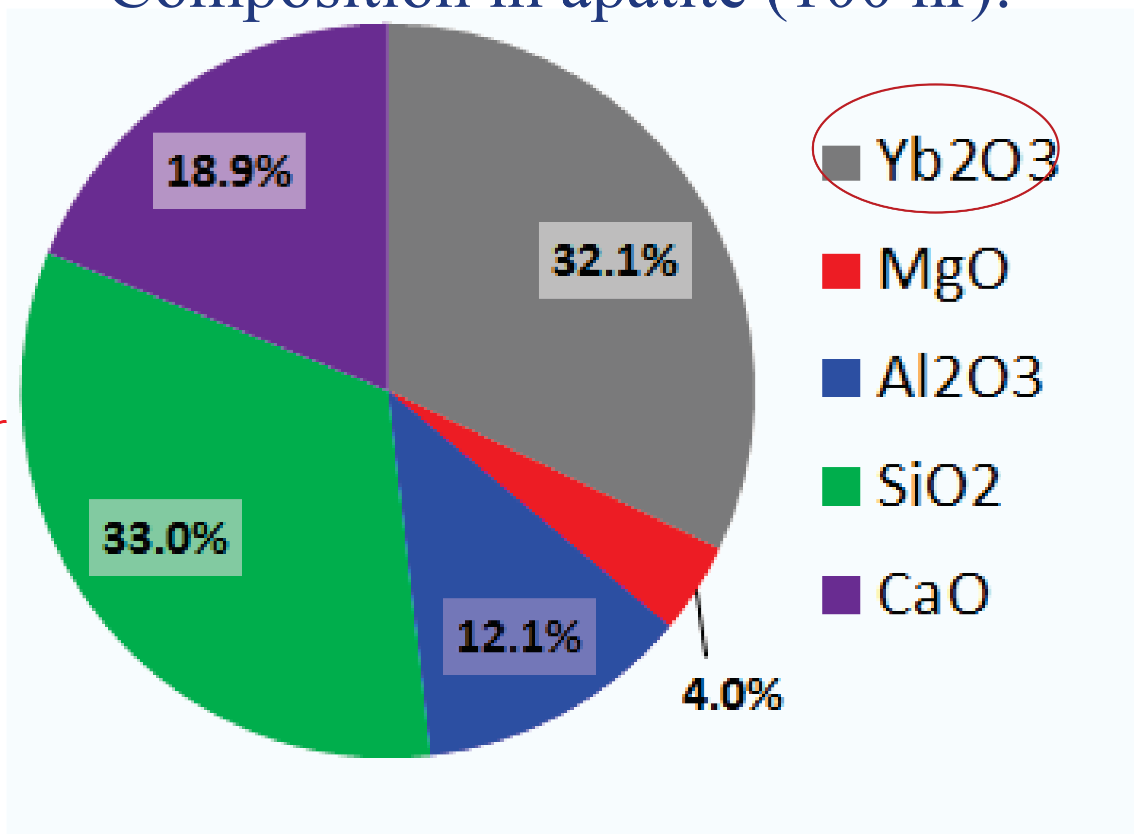
Yttrium silicate surface CMAS melts: 5 hr 1500°C

EBC Reacted Apatite Phases under Long-Term Testing at 1500°C – Ytterbium silicate EBC

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases
- Difference in partitioning of ytterbium vs. yttrium in apatite

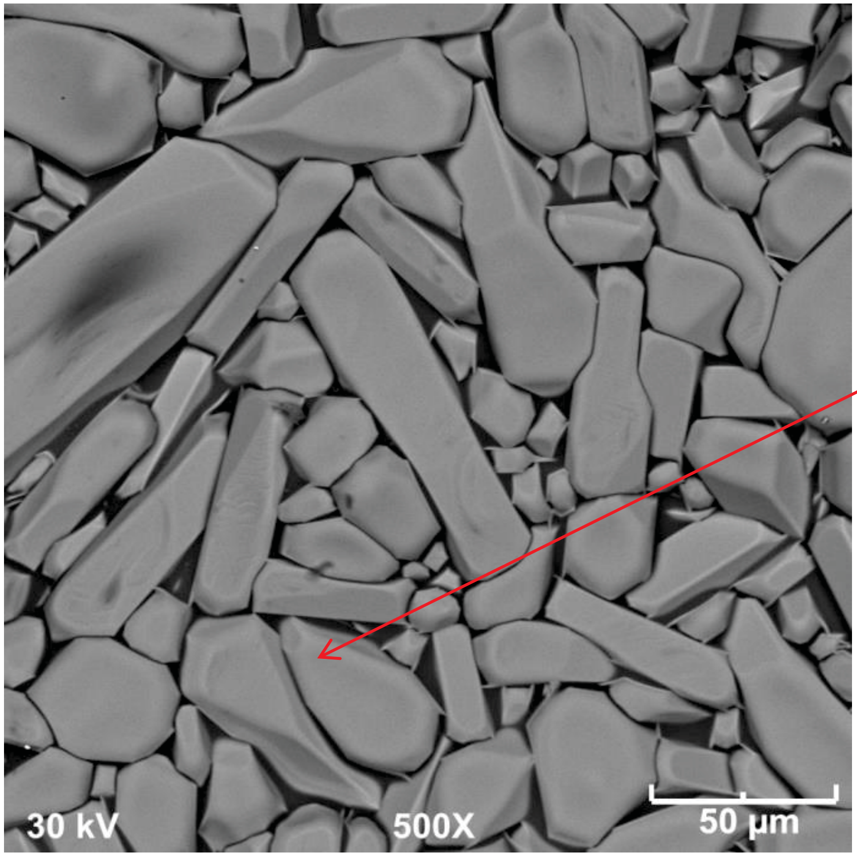


Composition in apatite (100 hr):

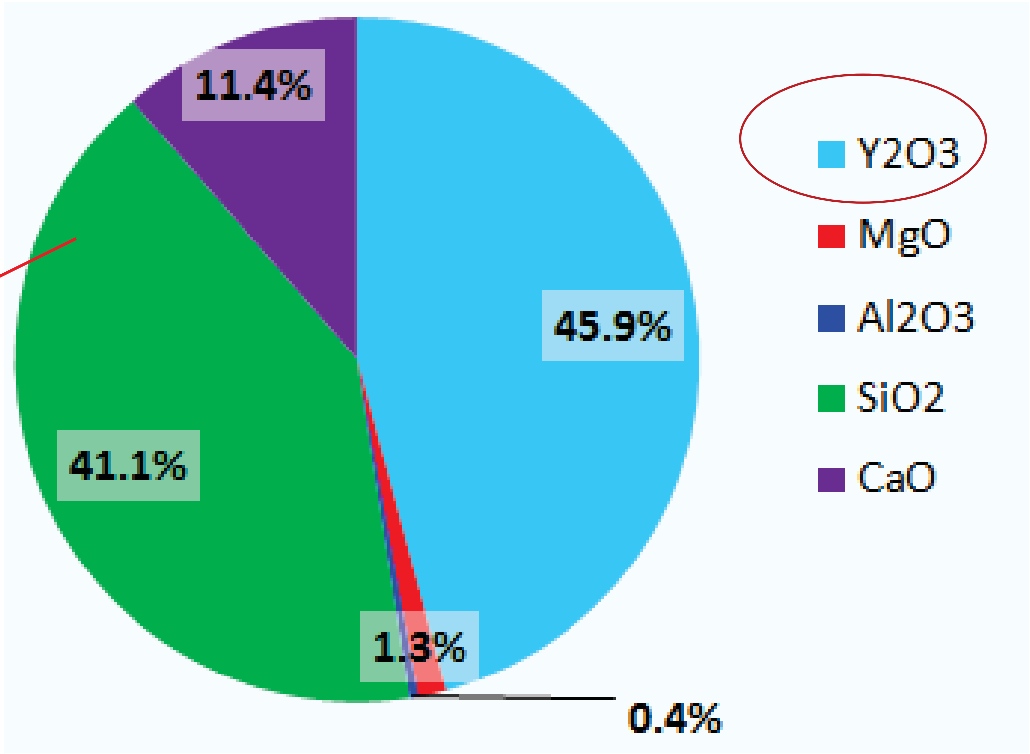


EBC Reacted Apatite Phases under Long-Term Testing at 1500°C: Yttrium Silicate EBC

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases
- Difference in partition of ytterbium vs. yttrium
  - Average AEO/RE_2O_3 ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE_2O_3 ratio ~ 0.22 for yttrium silicate – CMAS system

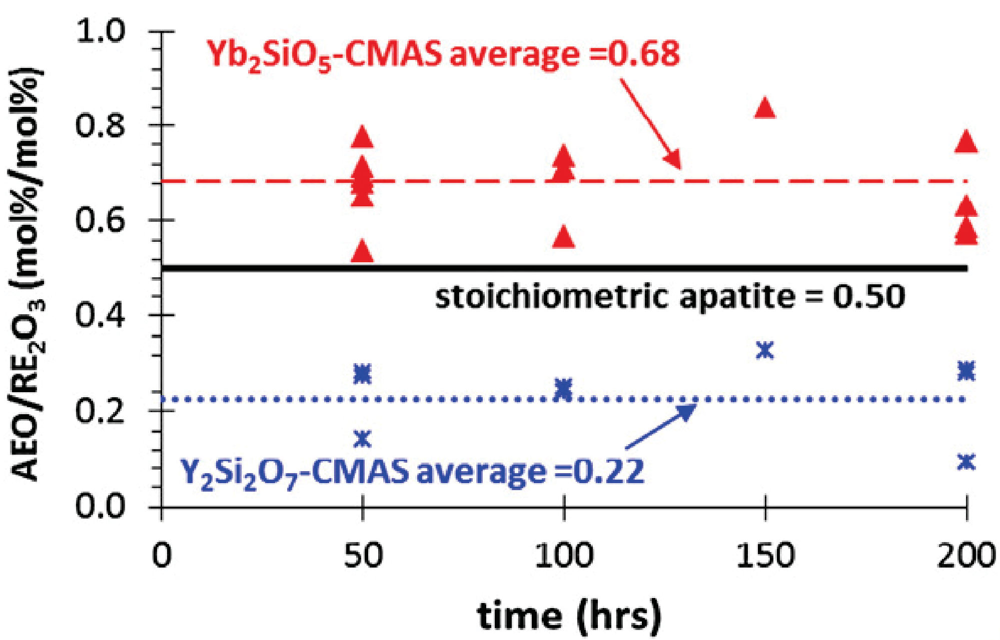


Composition in apatite (100 hr):

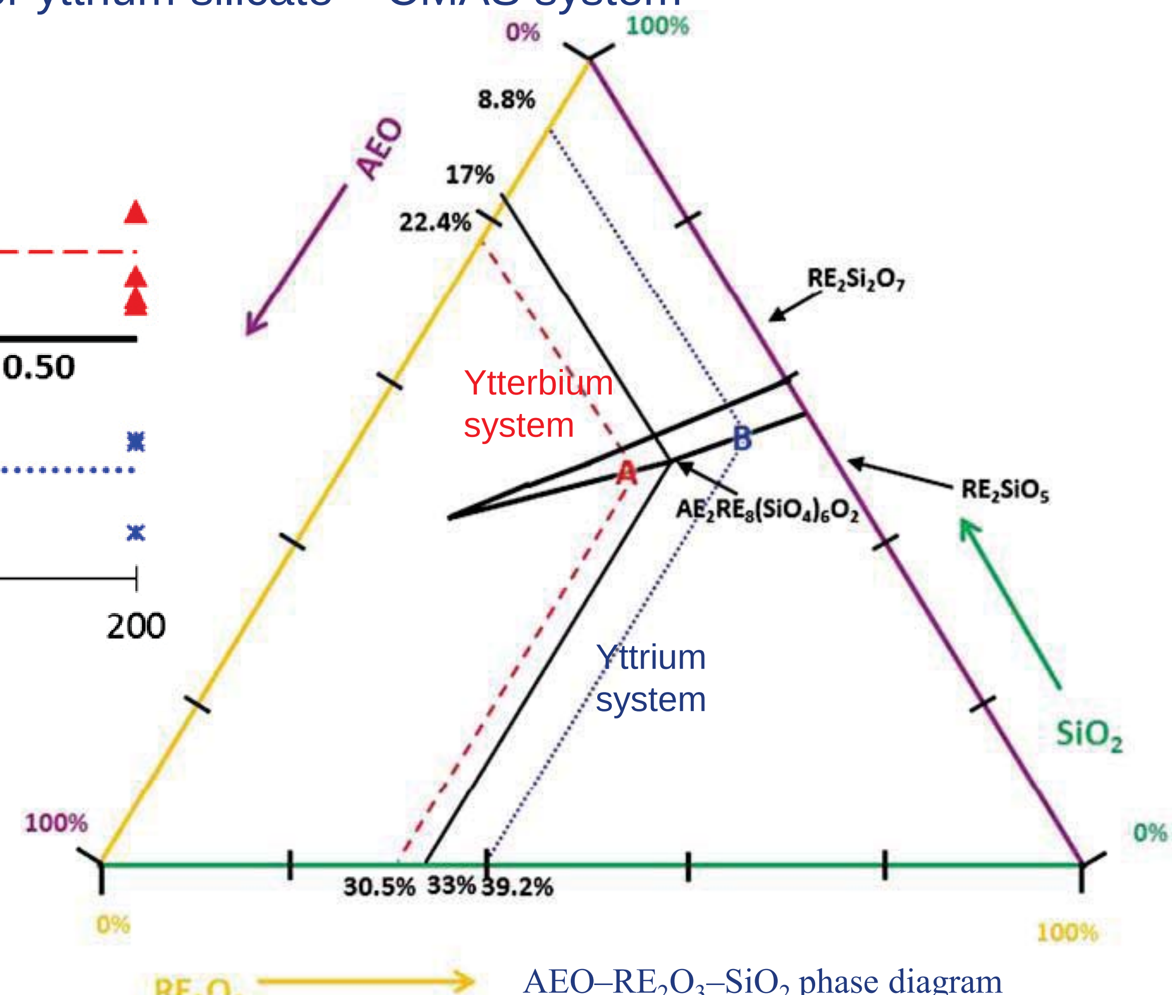


Stoichiometry of the Reacted Apatite Phases under Long-Term Testing at 1500°C

– Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases – up to 200 hr testing
– Difference in partitioning of ytterbium vs. yttrium in apatite
  - Average AEO/RE_2O_3 ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE_2O_3 ratio ~ 0.22 for yttrium silicate – CMAS system



Ahlborg and Zhu, Surface & Coatings Technology 237 (2013) 79–87.

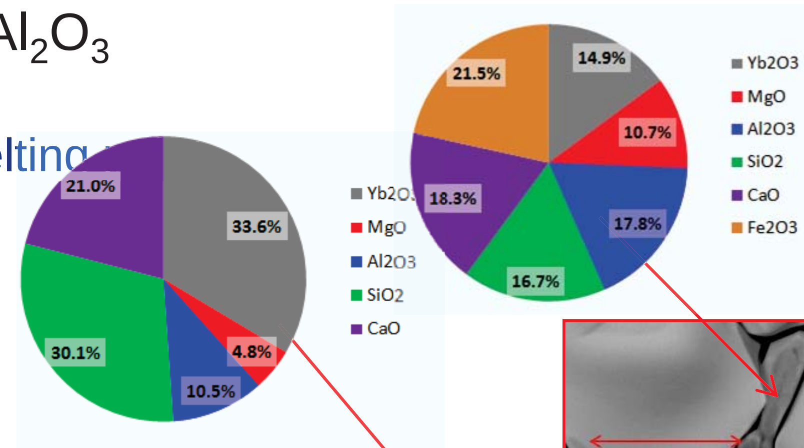


AEO–RE_2O_3–SiO_2 phase diagram

From Zhu Irsee Presentation Pages 18-19: "NASA's Advanced Environmental Barrier Coatings Development for SiC/SiC Ceramic Matrix Composites: Understanding Calcium Magnesium Alumino-Silicate (CMAS) Degradations and Resistance", June 2014

Effect of CMAS Reactions on Grain Boundary Phases

– CMAS and grain boundary phase has higher Al_2O_3 content (17-22 mole%)
  - Eutectic region with high Al_2O_3 content ~1200°C melting
  - Loss of SiO_2 due to volatility



NASA modified CMAS

Grain boundary final phase – low SiO_2 and high Alumina

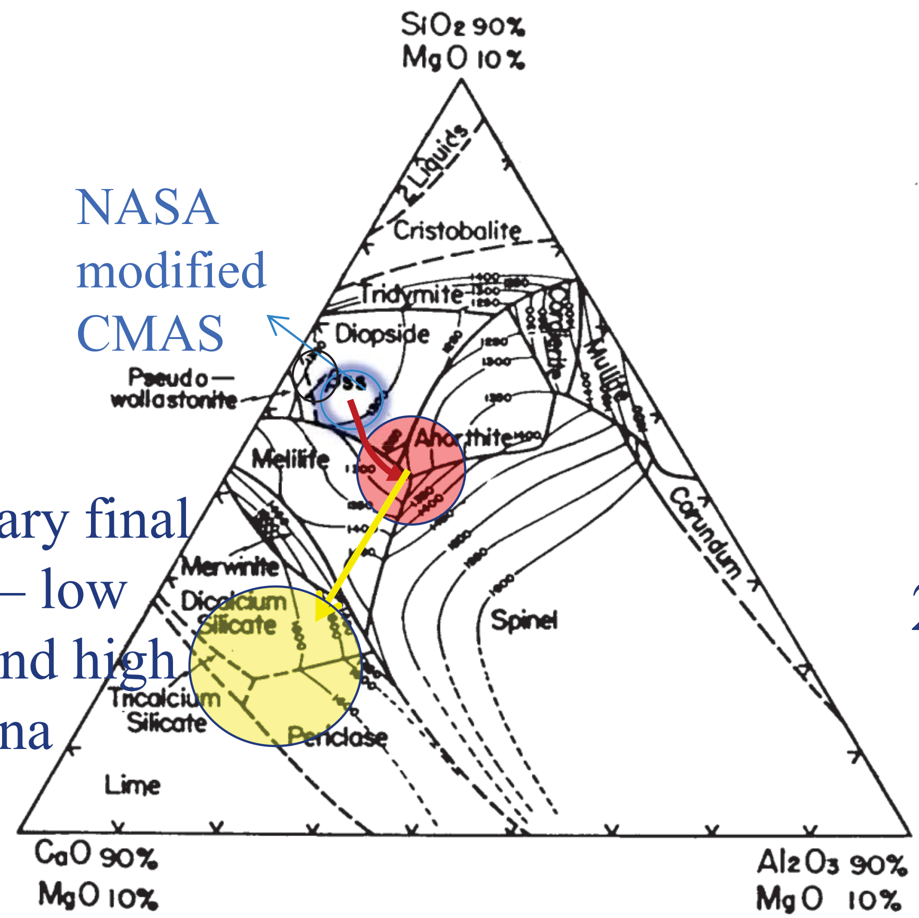
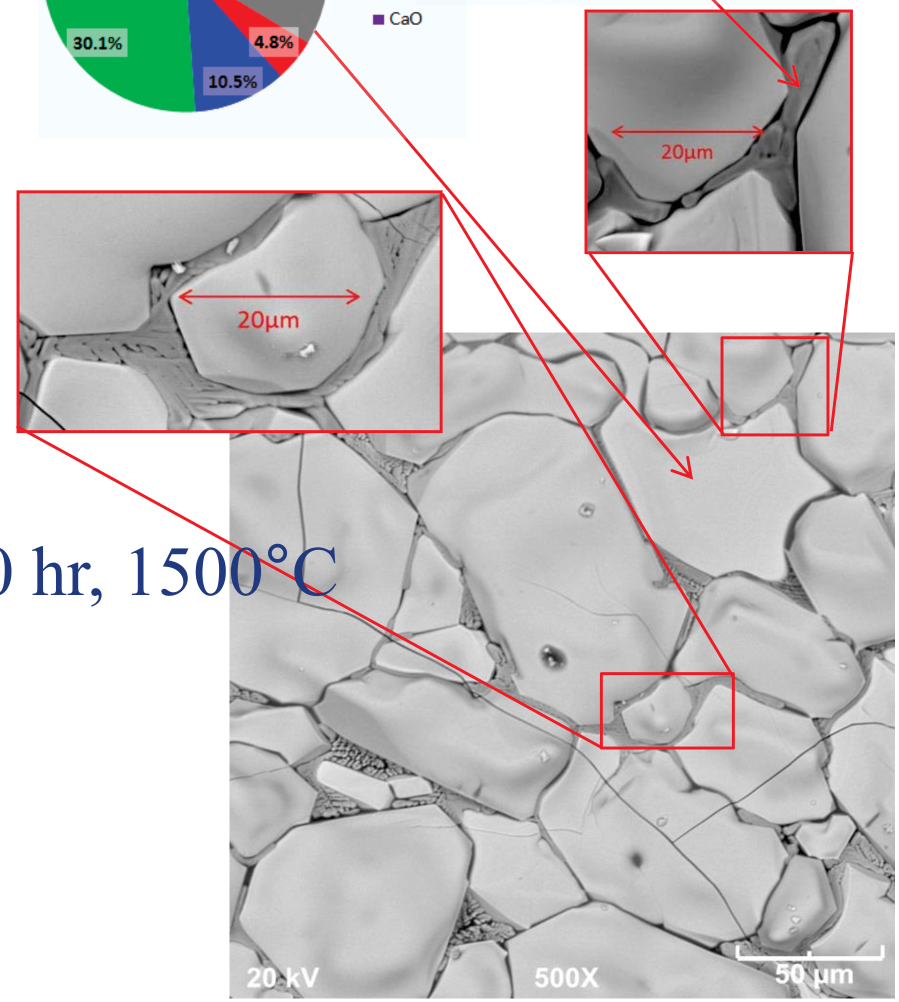


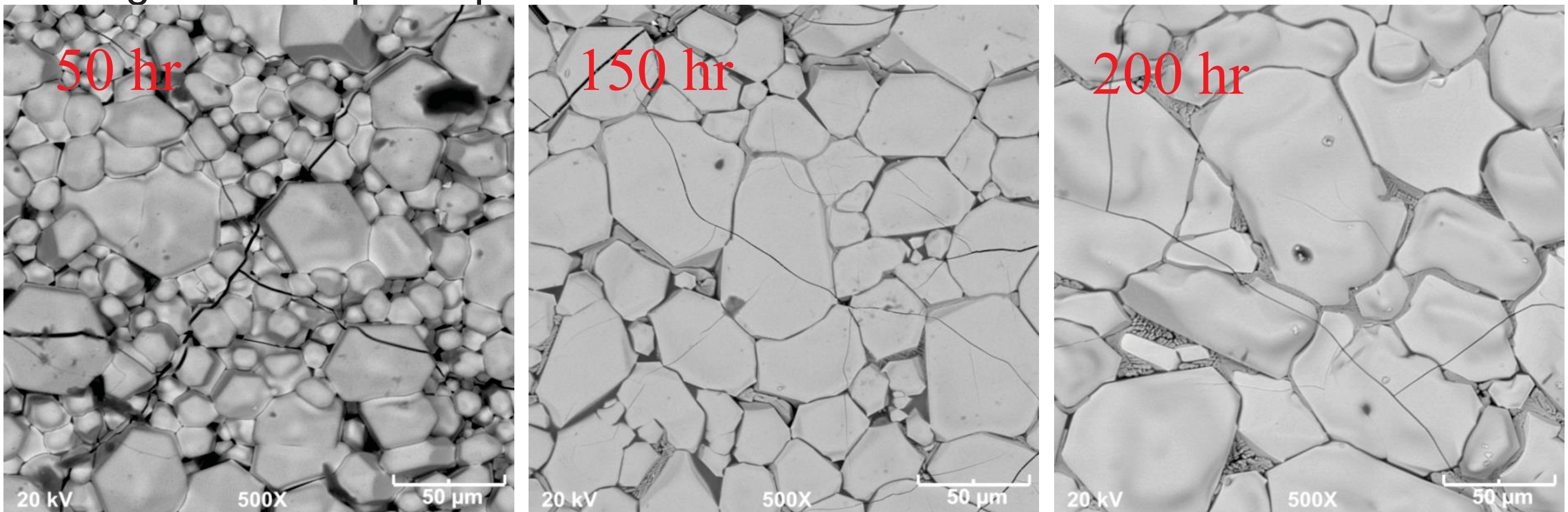
Fig. 4. The 10% MgO plane of the system CaO–MgO–Al_2O_3–SiO_2 showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

200 hr, 1500°C

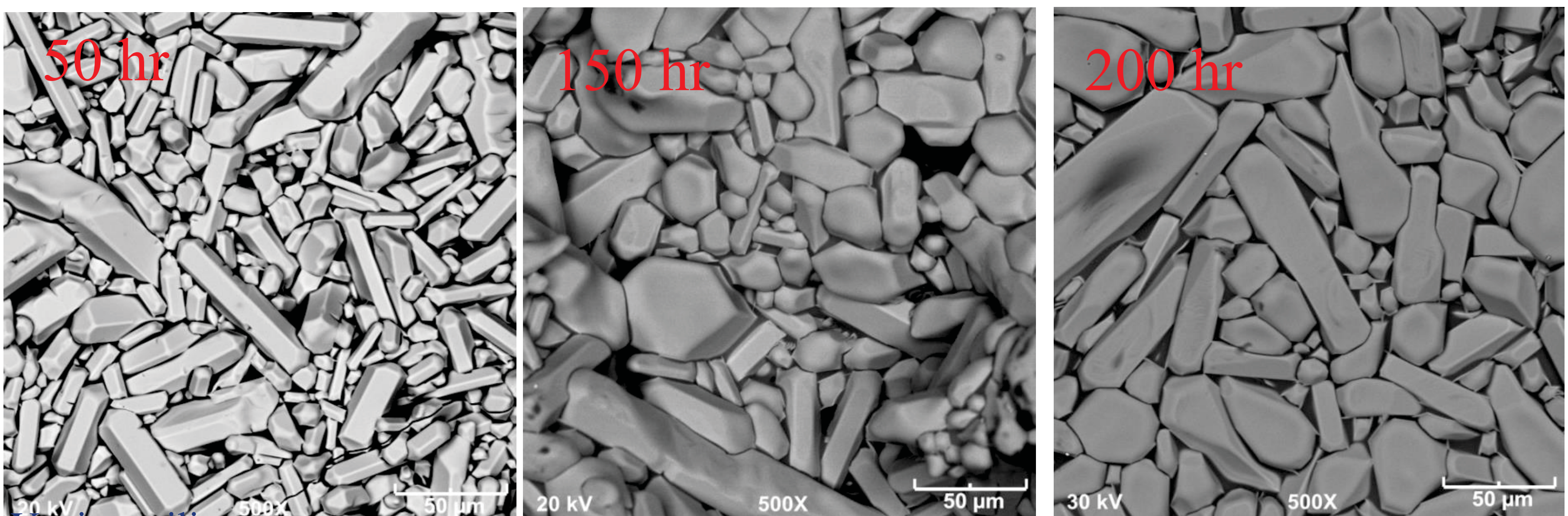


Rare Earth Apatite Grain Growth

– Grain growth of apatite phase at 1500°C at various times



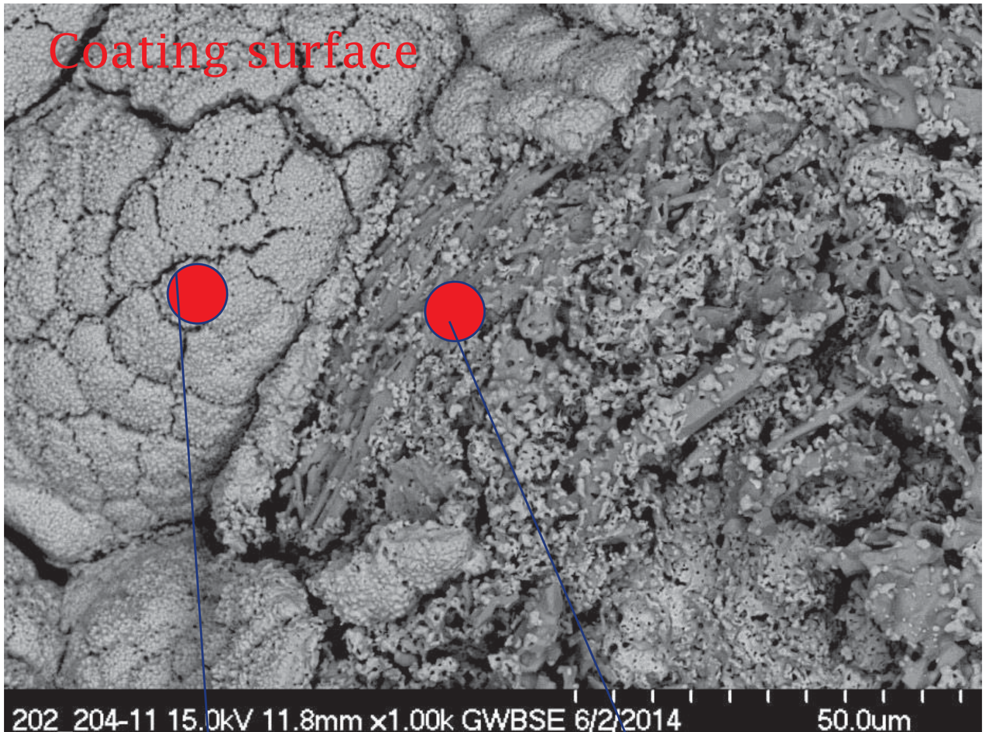
Ytterbium silicate system

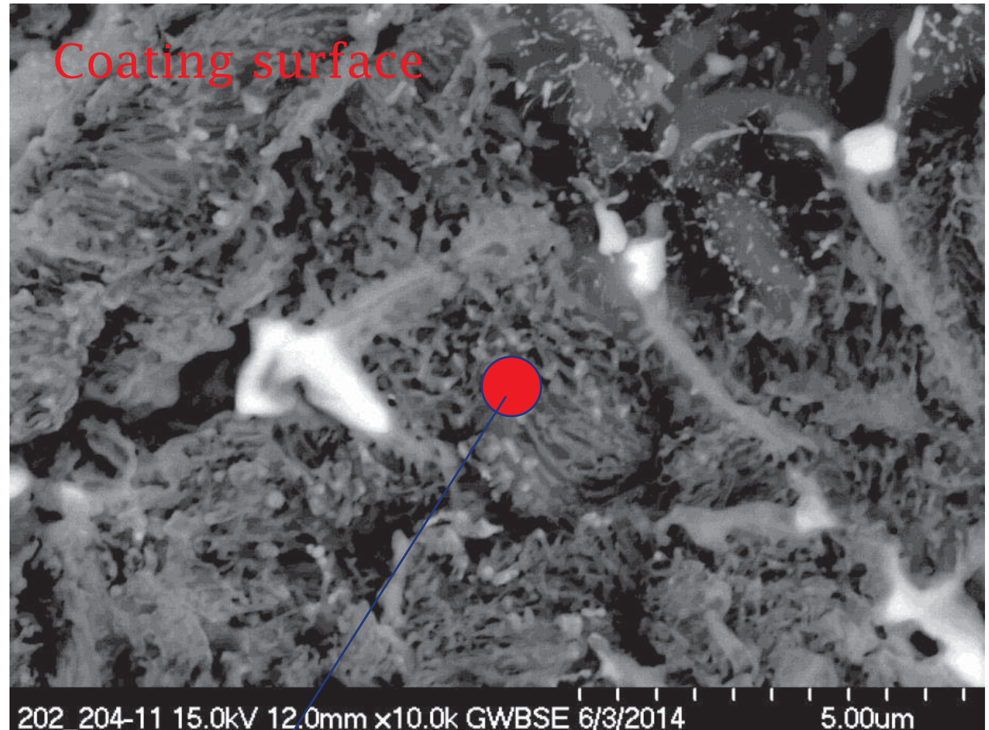


Yttrium silicate system

HfO_2-Rare Earth Silicate Composite EBC Systems - Continued

– Silica loss observed in the concentrated CMAS reacted regions

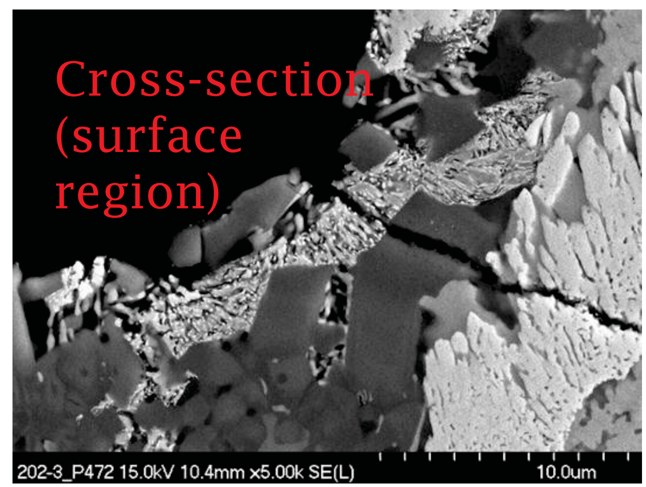




HfO_2 rich phase region

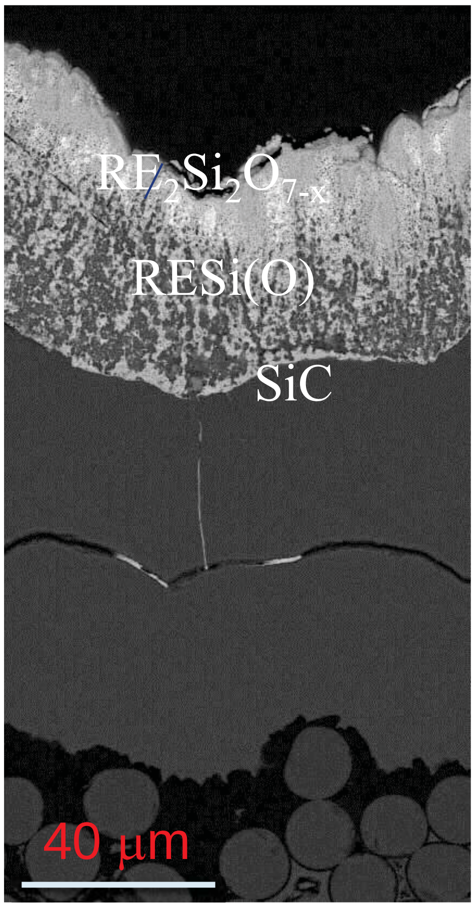
Rare earth silicate - apatite phase rich phase region

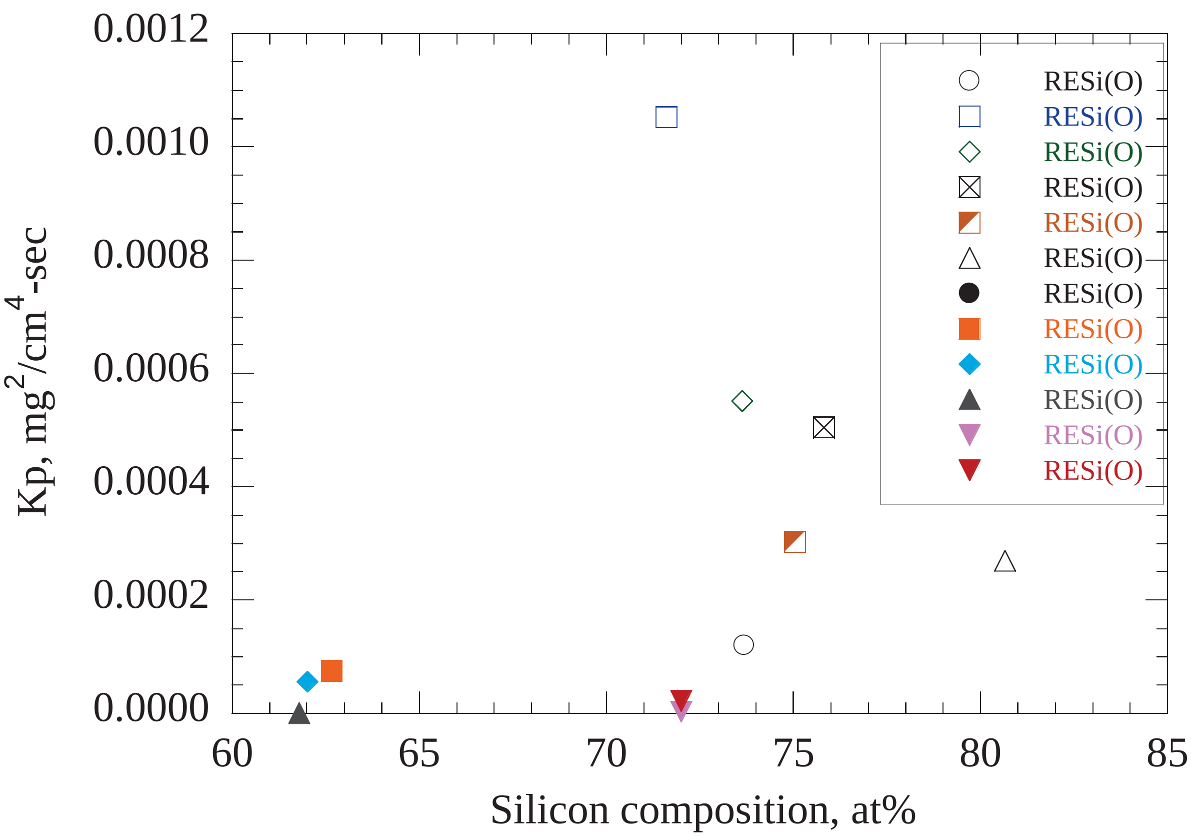
CMAS concentrated region, SiO_2 content 20-30 mol% (SiO_2 loss in the steam water vapor tests)



High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions: Designed with Improved Temperature capability and CMAS Resistance

- Thermogravimetric analysis (TGA) in dry O_2 at 1500°C, tested up to 500 hr
- "Protective" scale of rare earth di-silicate formed in oxidizing environments
- Furnace cyclic test life also evaluated at 1500°C

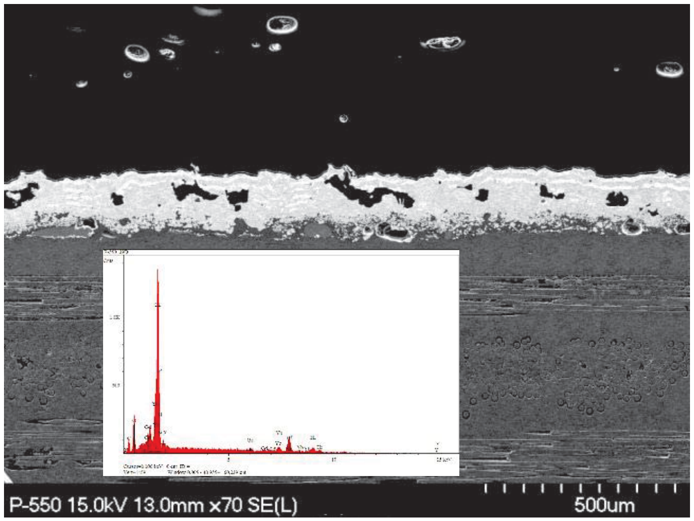


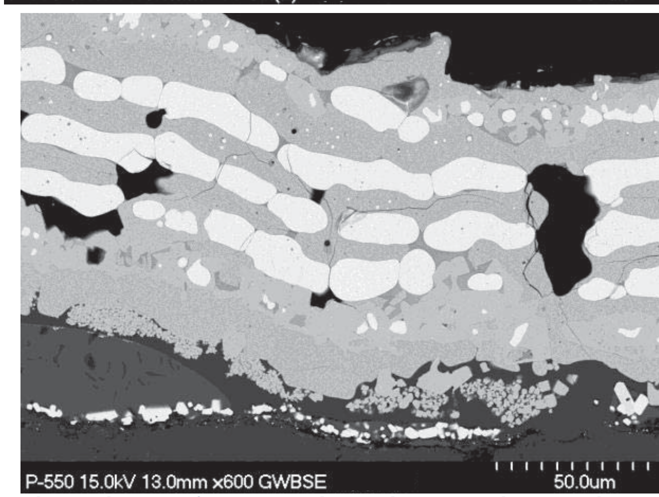


Oxidation kinetics vs Si content

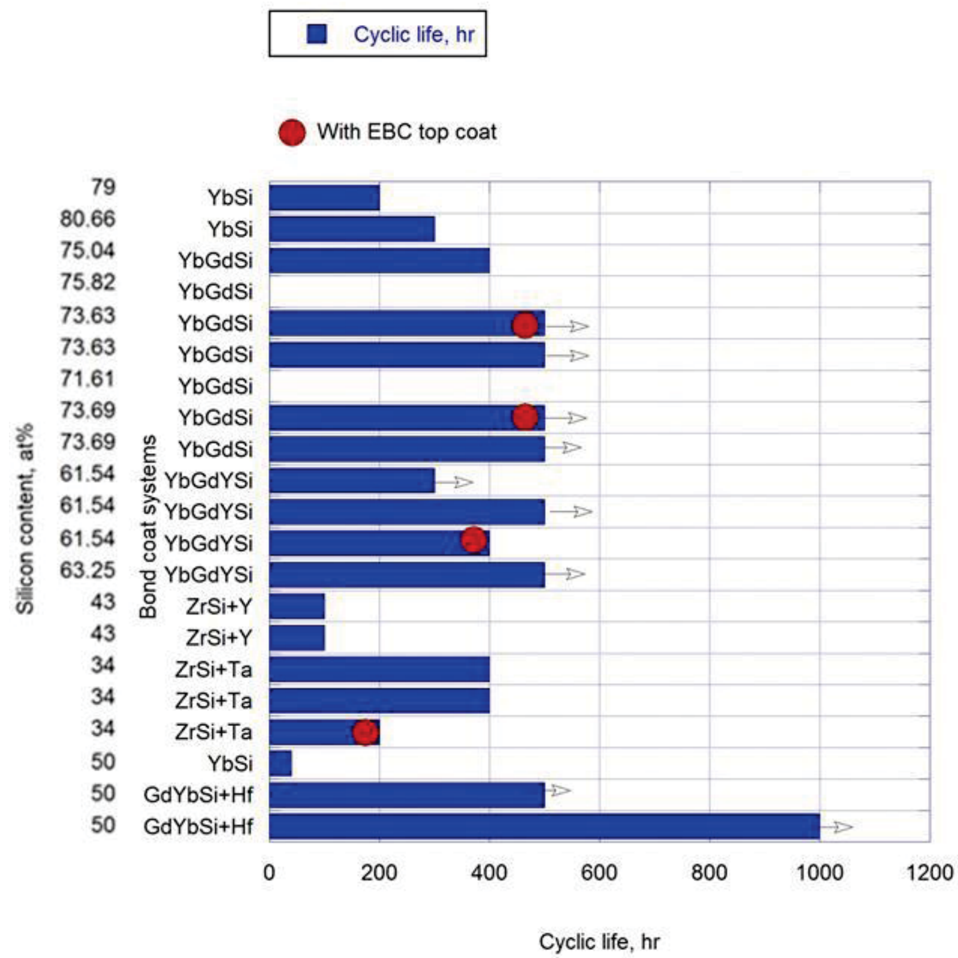
High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions: Designed with Improved Temperature capability and CMAS Resistance - Continued

- Thermogravimetric analysis (TGA) in dry O_2 at 1500°C, tested up to 500 hr
- “Protective” scale of rare earth di-silicate formed in oxidizing environments
- Furnace cyclic or high heat flux test life evaluated at 1500°C up to 1000 hours with or without CMAS





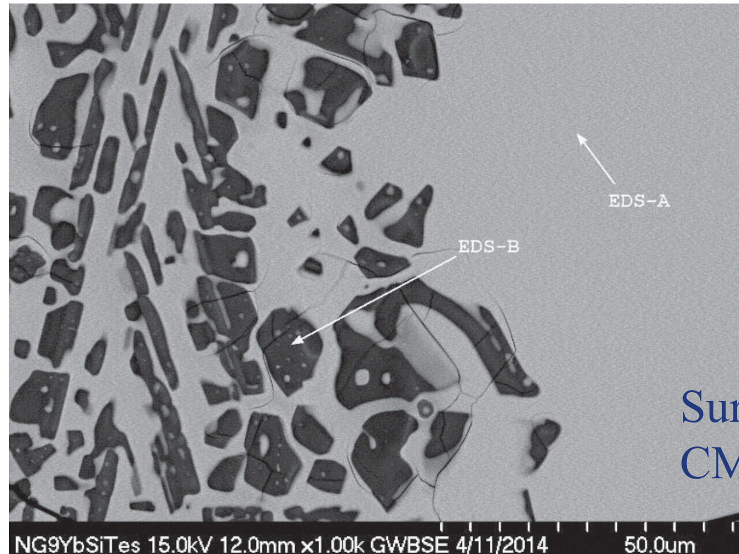
An Yb-Gd2700°F EBC bond coat showed 500hr cyclic durability



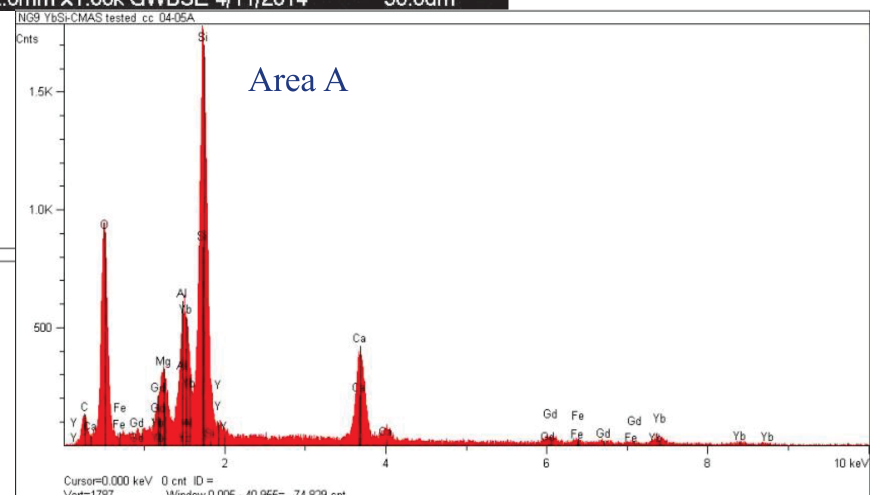
FCT life of RE-Si coatings

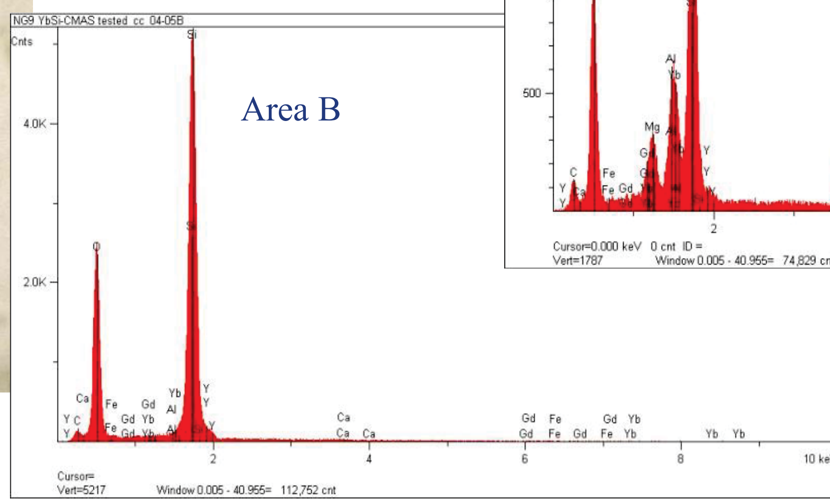
High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

- Demonstrated CMAS resistance of NASA RE-Si System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration ~9 mol%)



Surface side of the CMAS melts





CMAS Reaction Kinetics in Bond Coats

- SiO_2 rich phase partitioning in the CMAS melts
- Rare earth content leaching low even at 1500°C
- More advanced compositions are being implemented for improved thermomechanical – CMAS resistance

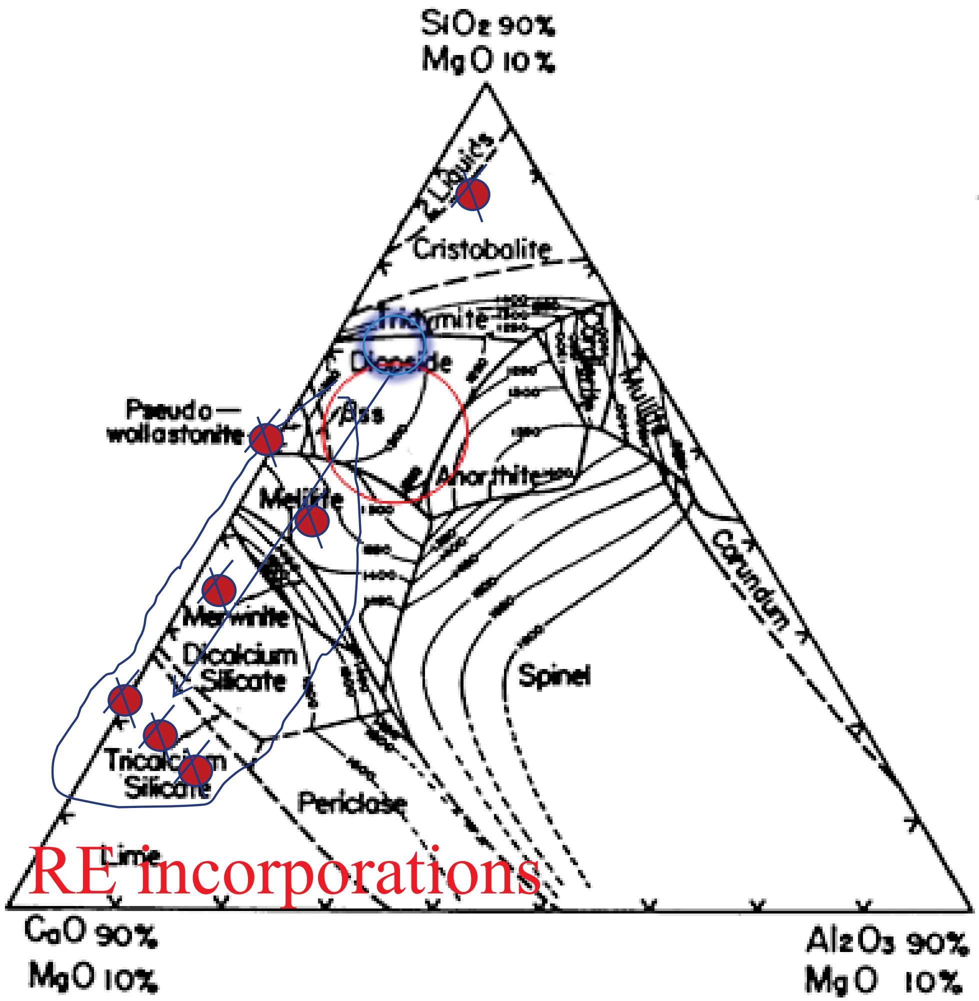
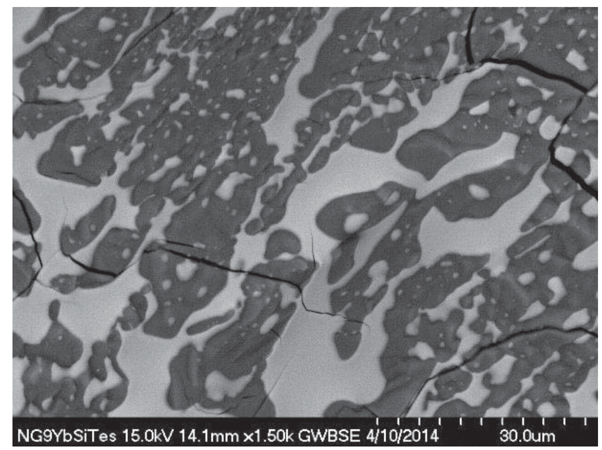


Fig. 4. The 10% MgO plane of the system $CaO–MgO–Al_2O_3–SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr



Advanced EBC Compositions Improve the Resistance to CMAS

- Controlling CMAS wetting, viscosity, stability and melting points
- Providing better EBC protections for CMCs in CMAS environments
- EBC durability being validated under CMAS-mechanical loading

400 hr, 69 Mpa creep rupture at EBC surface temperature 1400°C

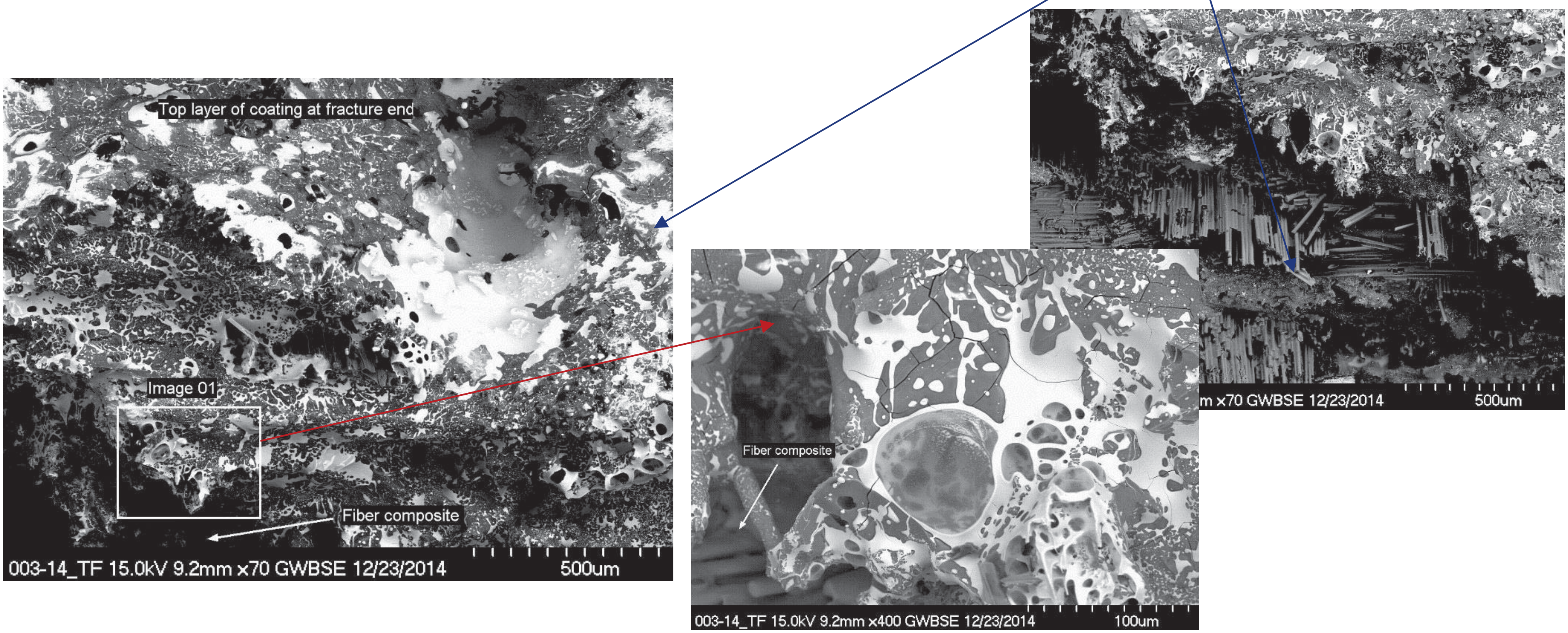
202 hr, 69 MPa creep rupture at EBC surface temperature 1540°C; CMC failure

Advanced EBC Compositions Improve the Resistance to CMAS - Continued

- Controlling CMAS wetting, viscosity, stability and melting points
- Providing better EBC protections for CMCs in CMAS environments
- EBC durability initially validated under long-term CMAS-mechanical loading

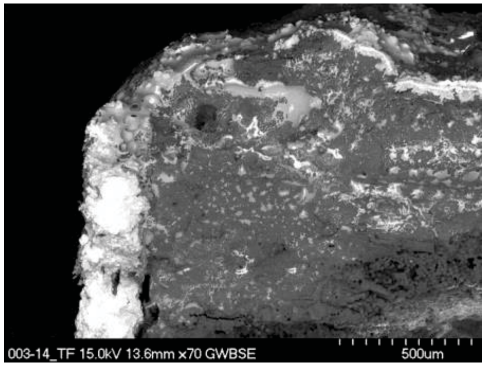
400 hr, 69 Mpa creep rupture at EBC surface temperature 1400°C

202 hr, 69 MPa creep rupture at EBC surface temperature 1540°C; CMC failure

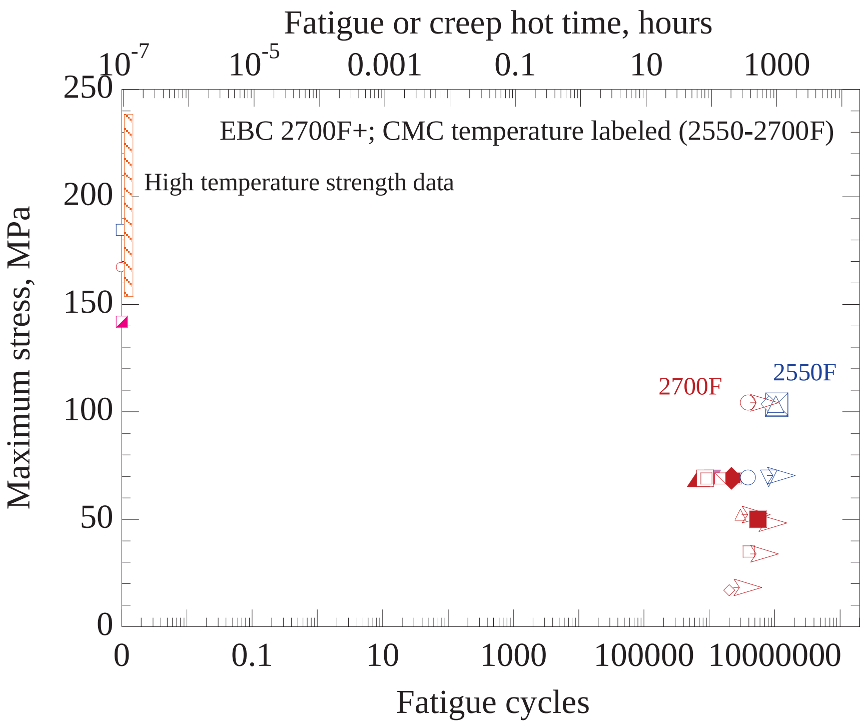


Creep-Fatigue of EBCs-CMCs in Complex Heat Flux and Simulated Engine Environments

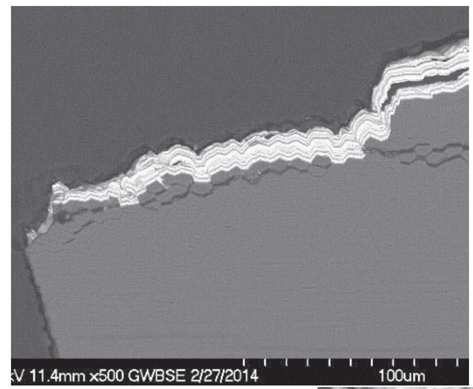
- Long-term creep and fatigue used to validate EBCs at various loading levels
- Demonstrated 2700°F EBC and bond coat capability in complex environments



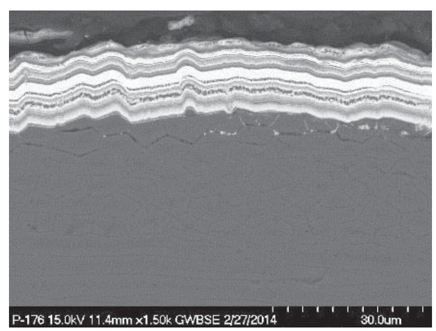
Fracture surface; 200+ hr at 2700°F+ creep rupture testing with CMAS; Advanced EBC protected CMCs

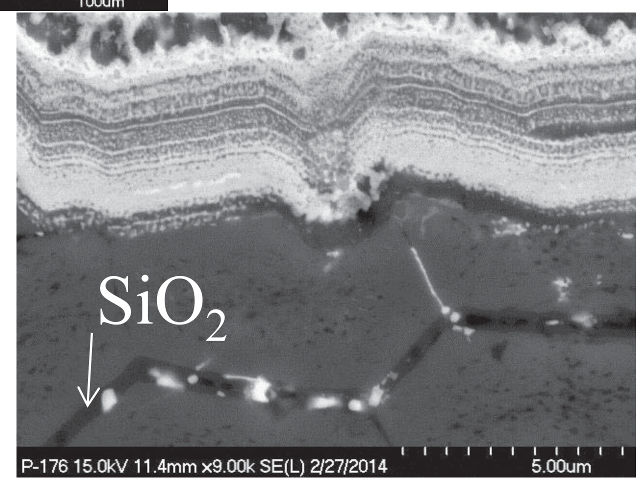


Stress-oxidation and stress-CMAS environmental testing



Advanced Bond Coat on CMC – intact after fatigue test with 15 ksi load and 2600-2700°F surface temperature for 460 hot hours





Advanced Bond Coat on CMC – intact after fatigue test with 15 ksi load and 2600-2700°F surface temp for 460 hot hours

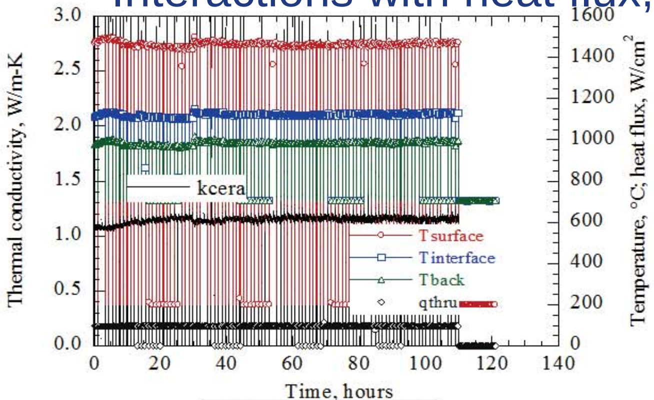
Summary

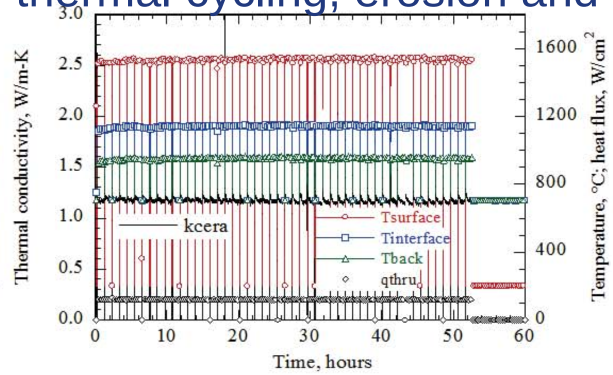
- CMAS degradation remains a challenge for emerging turbine engine environmental barrier coating – SiC/SiC CMC component systems
- CMAS leads to lower melting point of EBC and EBC bond coat systems, and accelerated degradations
- NASA advanced EBC compositions showed promise for CMAS resistance at temperatures up to 1500°C+, and in combined with mechanical loading
- We have better understanding of CMAS interaction with rare earth silicates, and in controlling the compositions for CMAS resistance while maintaining high toughness
- We are developing better standardized CMAS testing, and working on CMAS induced life reductions, helping validate life modeling

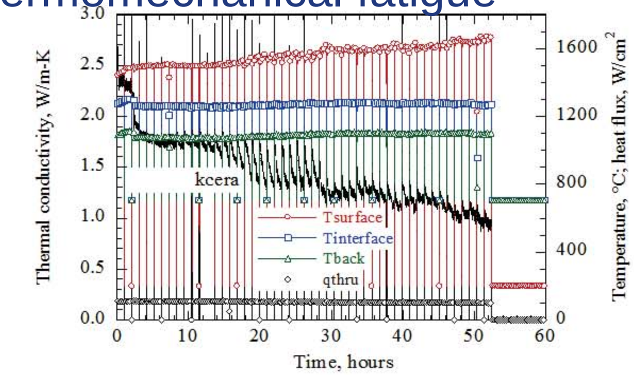
EBC-CMAS Degradation under Thermal Gradients

– **Effect of CMAS concentration on EBC-CMC system cyclic durability**

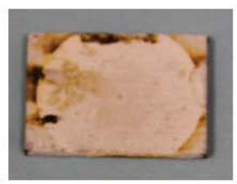
- CMAS reacts with high SiO_2 activity layer and reducing melting point
- Low tough reaction layers such as apatite phases
- Interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue





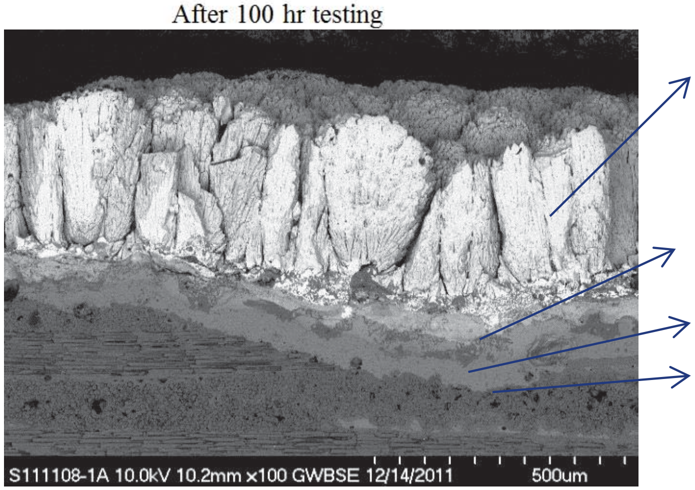


After 100 hr testing



After 50 hr testing

After 50 hr testing

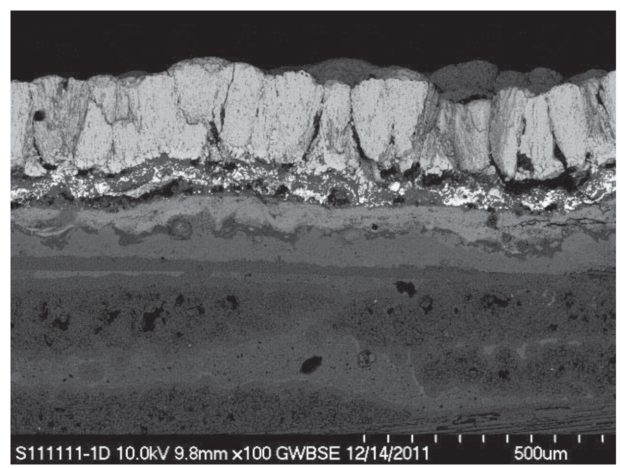


EB-PVD ZrO_2

HfO_2-Yb_2O_3-Aluminosilicate

$Yb_2Si_2O_7$

Si



More severe degradation and delamination: Tsurface 1500°C Tinterface 1316°C