NASA's Advanced Environmental Barrier Coatings Development for SiC/SiC Ceramic Matrix Composites: Understanding Calcium Magnesium Alumino-Silicate (CMAS) Degradations and Resistance

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Acknowledgements

Currently related NASA CMAS research activities:

- Advanced EBC development – composition design and developments for improved CMAS resistance
- NASA-Air Force Venture and Viper CMAS Collaborative programs - Zhu, James Smialek, Robert A. Miller, Bryan Harder
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- Fundamental NASA in-house CMAS properties - Narottam Bansal and Valerie Weiner

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The author is grateful to

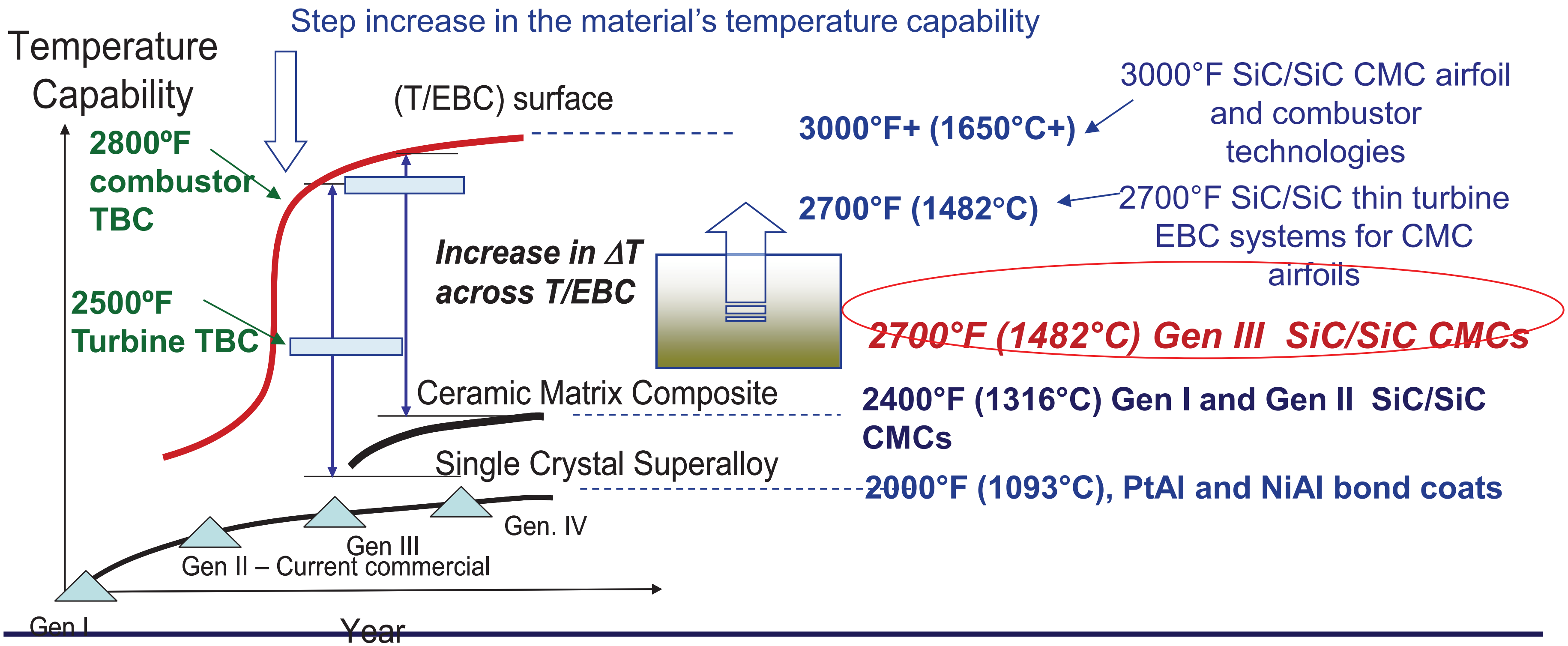
- Lynne M. Pfledderer and Oliver T. Easterday of the Air Force Research Laboratory, Managers of the Air Force Venture Program.
- Ralph Pawlik and Ron Phillips for their assistance in mechanical testing of EBC-CMC systems

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**

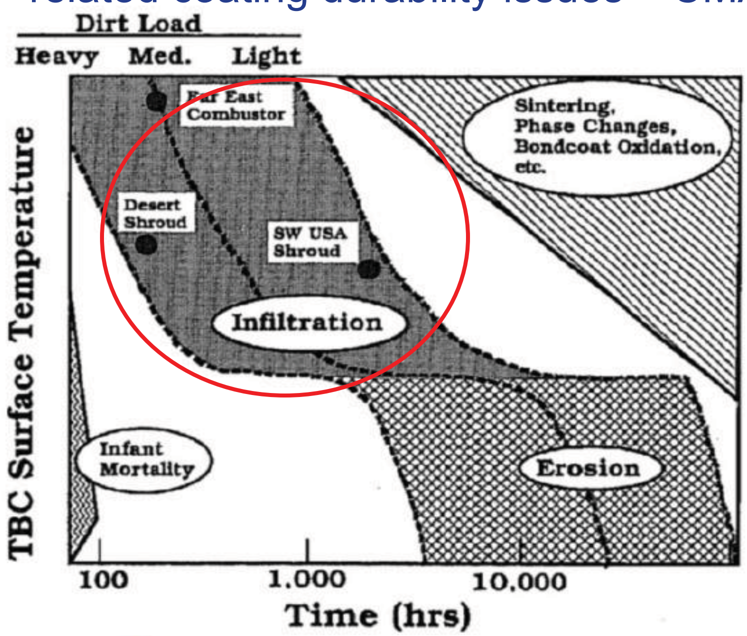
NASA Environmental Barrier Coatings (EBCs) and Ceramic Matrix Composite (CMC) System Development

- **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)

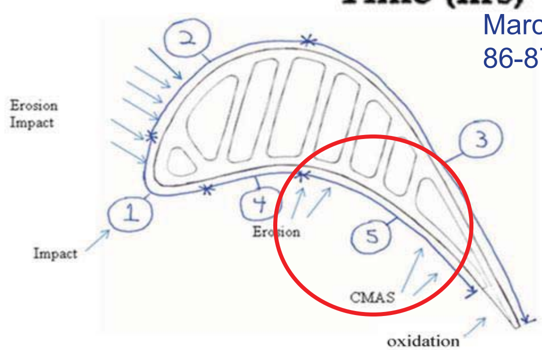


EBC-CMAS Degradation is of Concern with Increasing Operating Temperatures

– **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

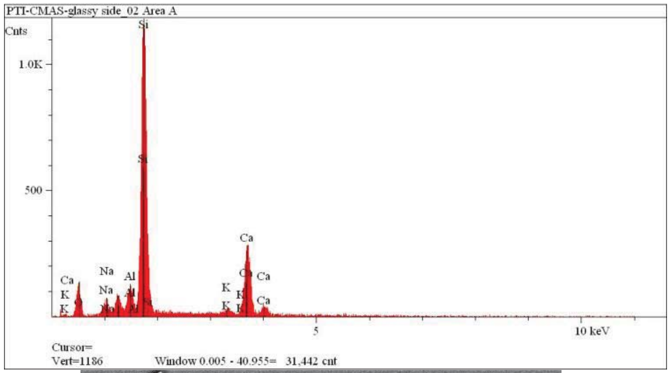


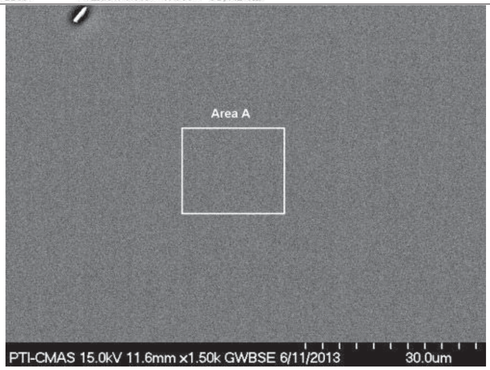
Current airfoil CMAS attack region - R. Darolia, International Materials Reviews, 2013

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

- Synthetic CMAS, modified version (NASA), the Air Force PTI 02 CMAS currently being used
- Saudi Sands used for past turbine TBC studies
- CMAS SiO_2 content typically ranging from 43-49 mole%
- Collaborations on-going with the Air Force; also planned DLR, ONEA etc on Volcanic Ash Composition selections

ARFL PTI 02 is also used at NASA for CMAS studies





Fully reacted

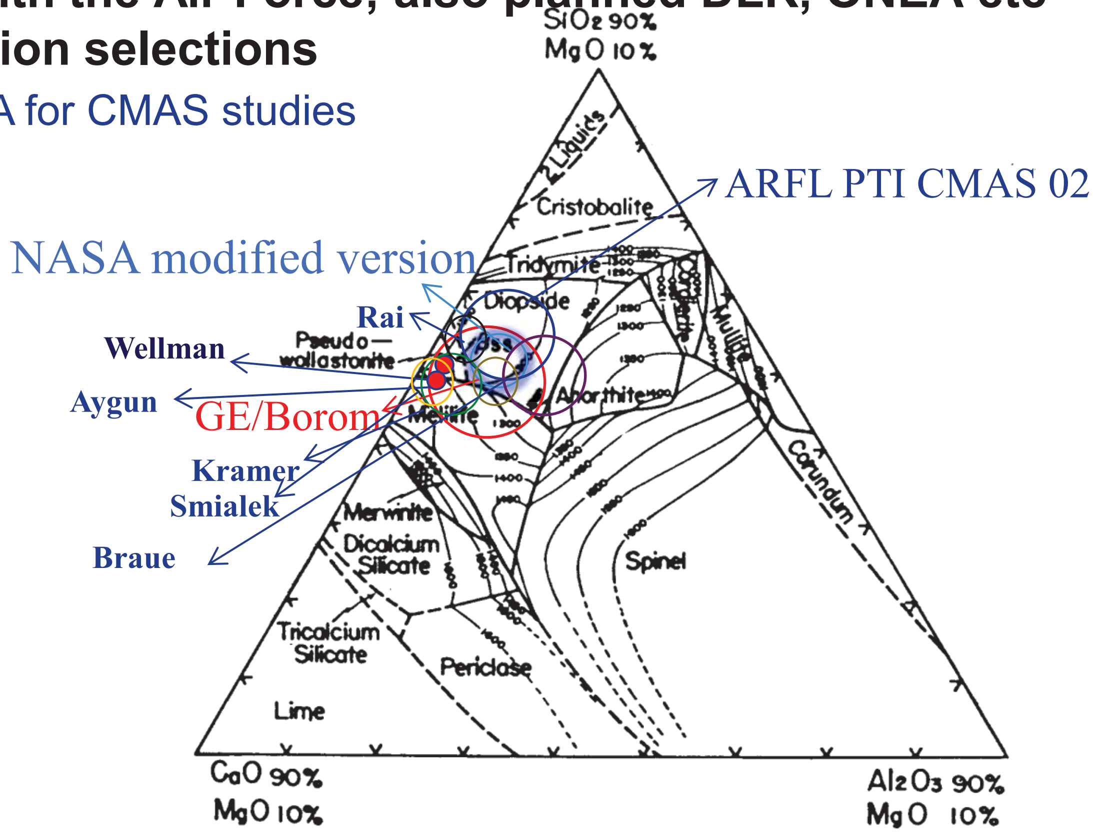
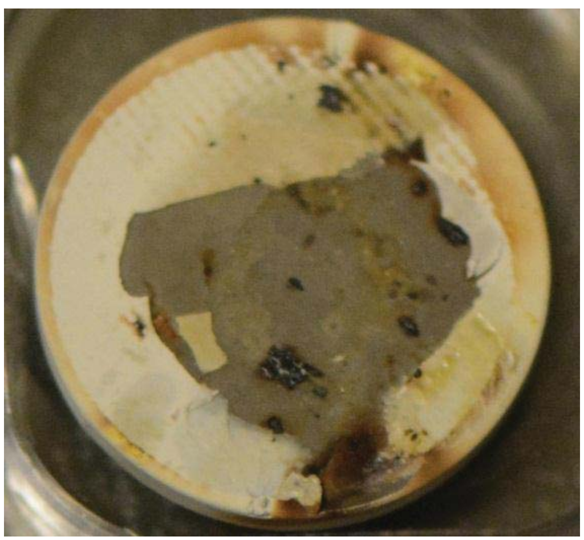


Fig. 4. The 10% MgO plane of the system $CaO-MgO-Al_2O_3-SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

Thermal Gradient Tests - Thermal Barrier Coating Degradations

— Coating cyclic failure with CMAS

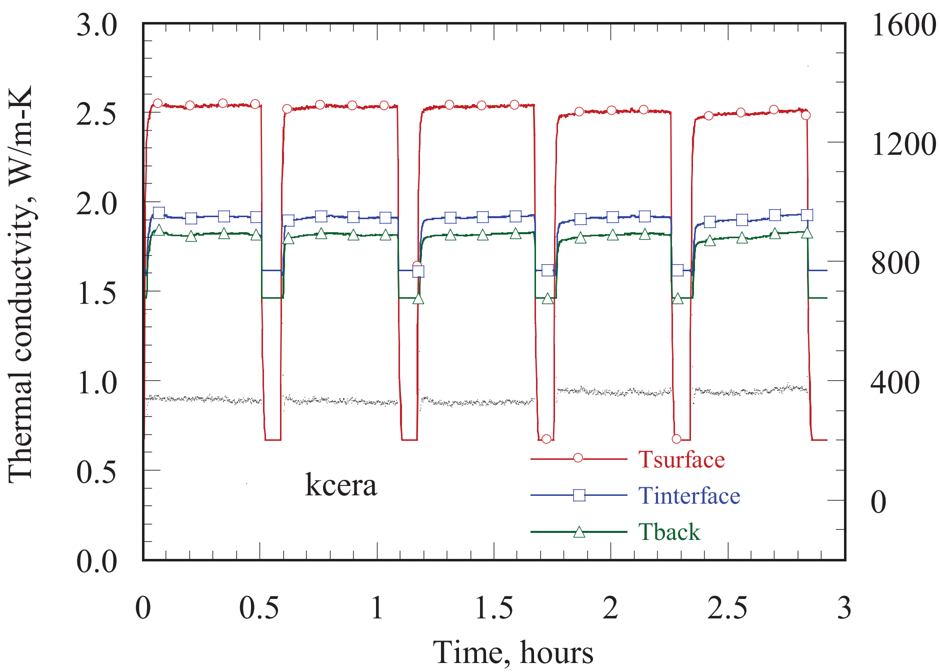


7YSZ turbine EB-PVD laser rig cyclic tested, after 50 hr cyclic test at $T_{surface}$ 1230°C and $T_{interface}$ 1170°C

Thermal Gradient Tests of Infiltrated and Reacted Apatite Phase under Cyclic Testing – Thermal Barrier Coating Degradations

— Coating surface layer spallation in infiltrated or highly reacted apatite phase layer in high rare earth dopant TBC systems

— Thermal gradient cyclic testing at Tsurface=1 316°F, Tinterface=950°F

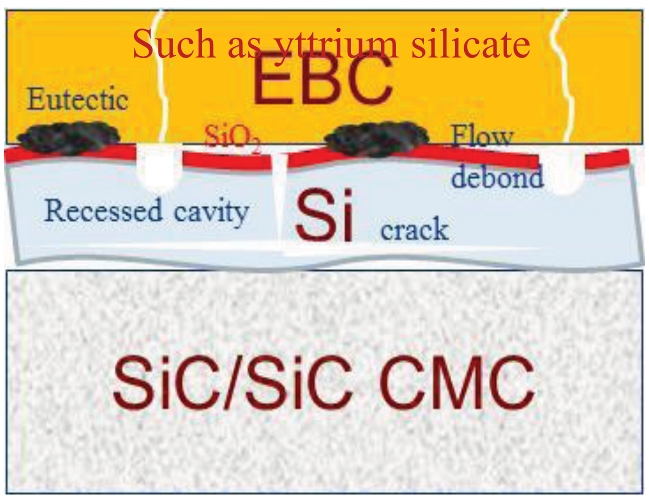


After thermal gradient cyclic testing

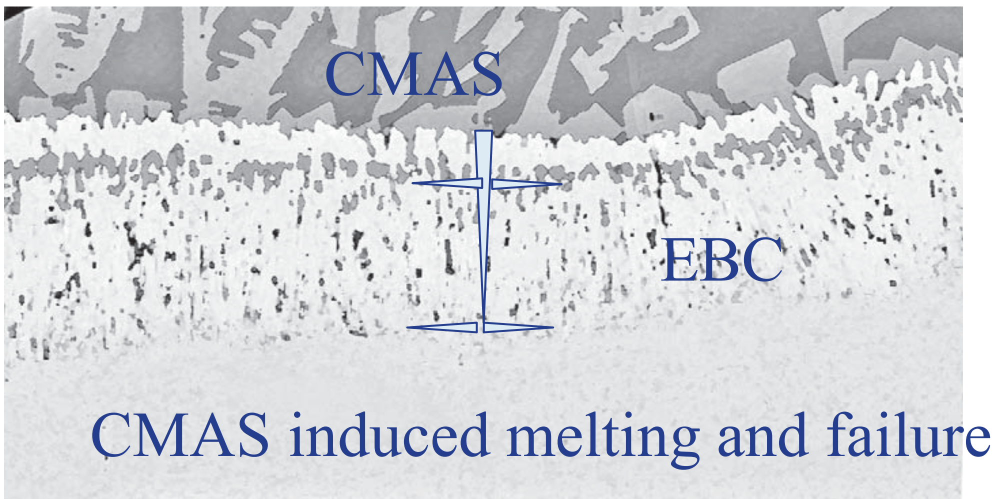
CMAS Related Degradations in EBCs

– **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

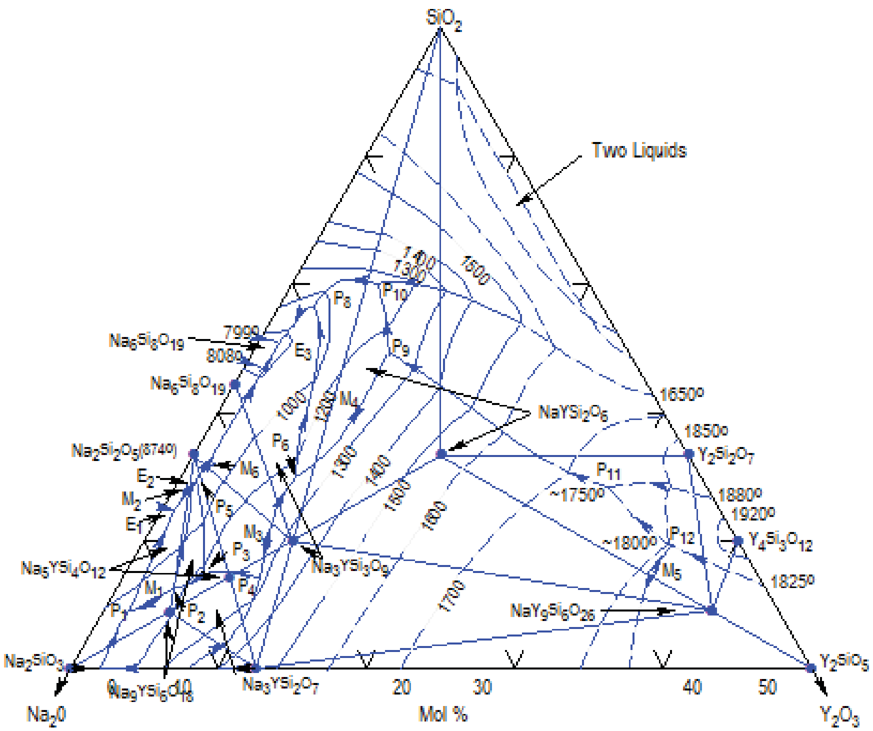


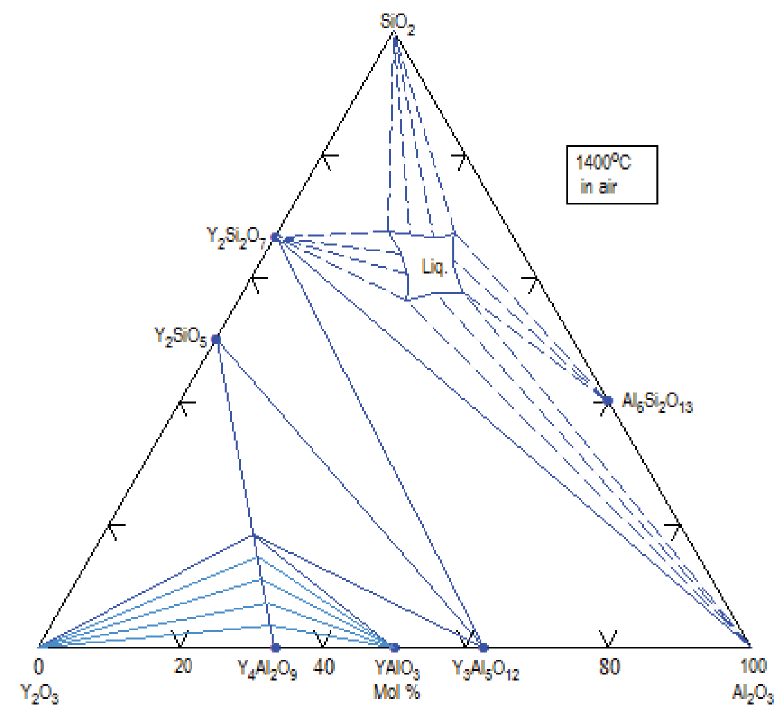
EBC and degradations



CMAS Related Degradations in EBCs - Continued

– **CMAS effects on EBC temperature capability**
  - Silicate reactions with NaO_2 and Al_2O_3 silicate

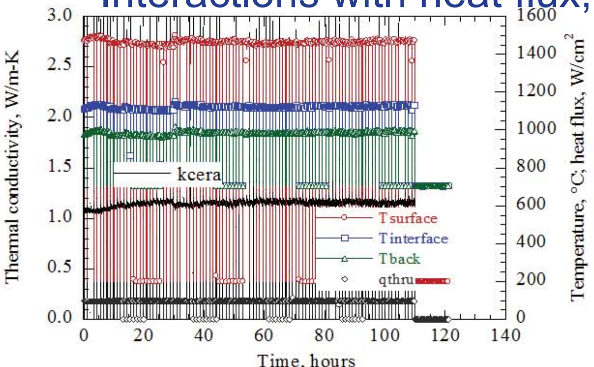


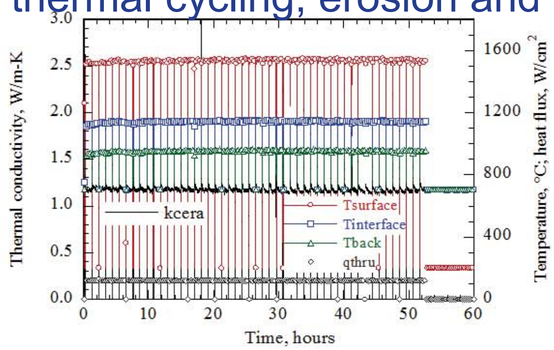


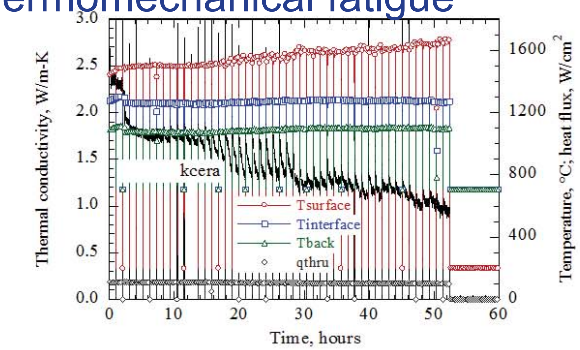
Phase diagrams showing yttrium di-silicate reactions with SiO_2, NaO and Al_2O_3

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



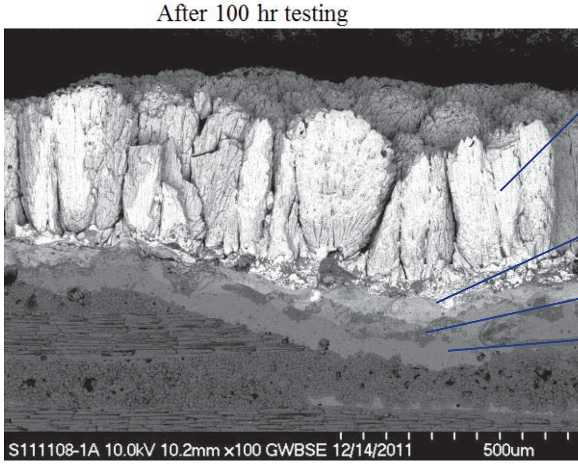




After 100 hr testing

After 50 hr testing

After 50 hr testing

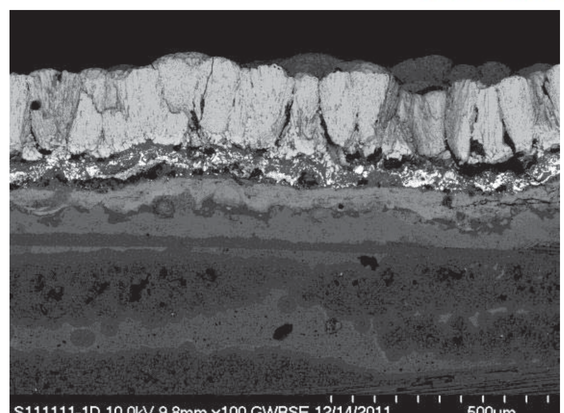


EB-PVD ZrO_2

HfO_2-Yb_2O_3-Aluminosilicate

$Yb_2Si_2O_7$

Si

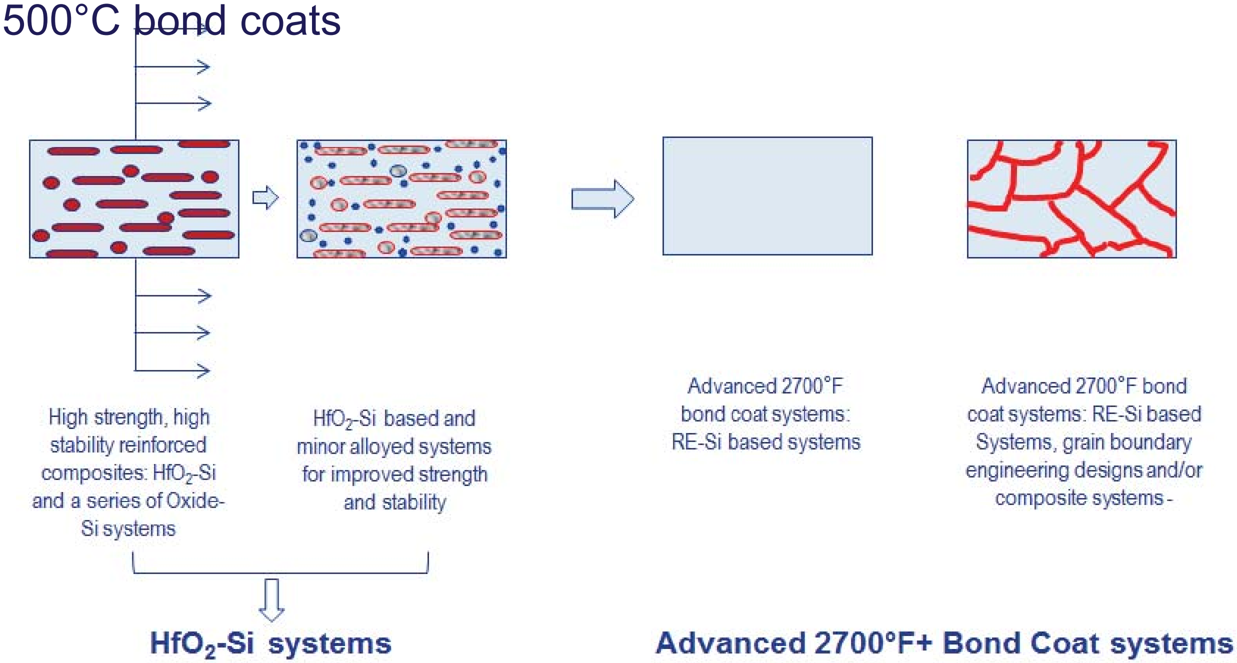


More severe degradation and delamination:
Tsurface 1500°C
Tinterface 1316°C

NASA EBC Systems

NASA EBC Systems

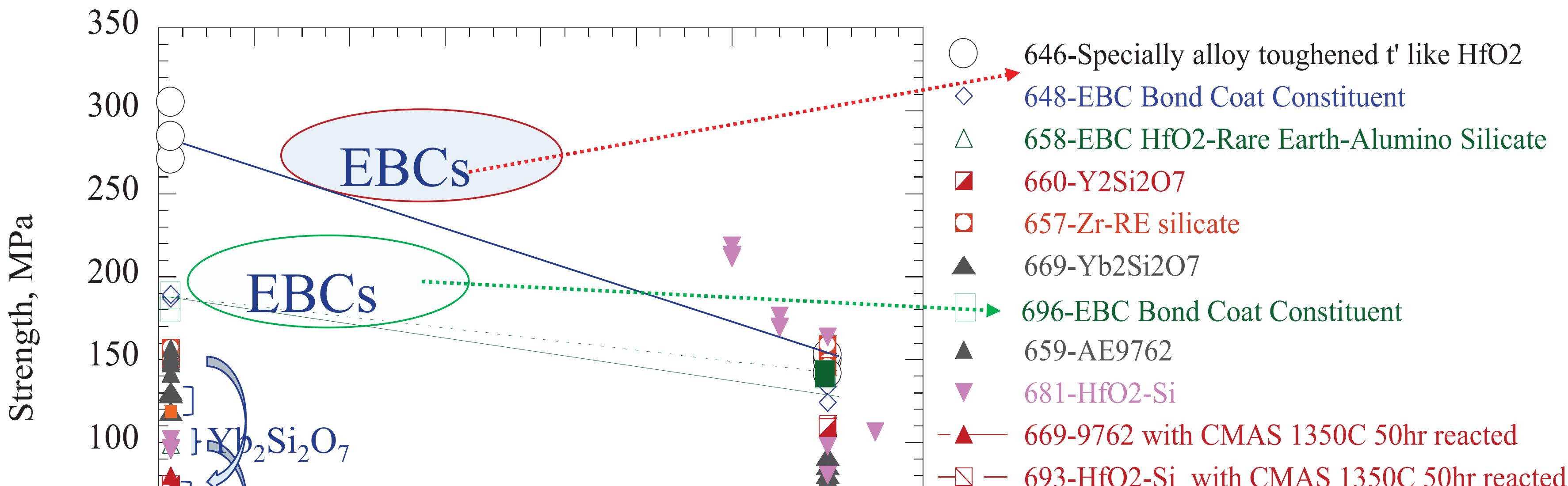
- HfO_2 -RE_2O_3-SiO_2/$RE_2Si_{2-x}O_{7-2x}$ environmental barrier systems
  - Controlled silica content and transition element and rare earth dopants to improve EBC stability and toughness
  - Develop HfO_2-Si based + X (dopants) and more advanced rare earth composite compound composition systems for 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



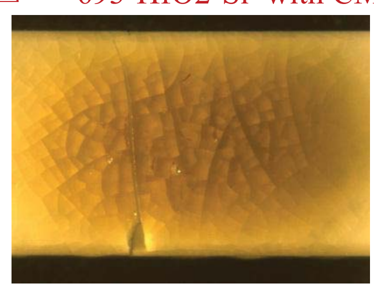
Strength Results of Selected EBC and EBC Bond Coats - CMAS Reaction resulted in Strength Reduction in Silicates

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



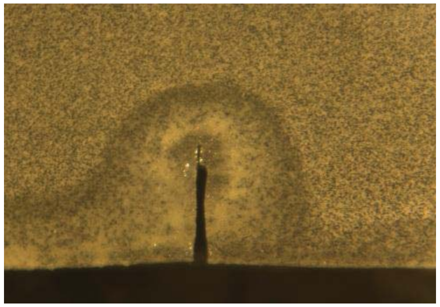
$Yb_2Si_2O_7$ CMAS reacted tensile surface

$Yb_2Si_2O_7$ CMAS reacted specimen fracture surface

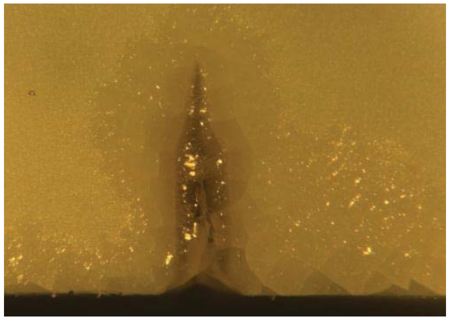
Effect of CMAS Reaction on Toughness of HfO_2-Si Bond Coat and $Yb_2Si_2O_7$ EBC

– 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

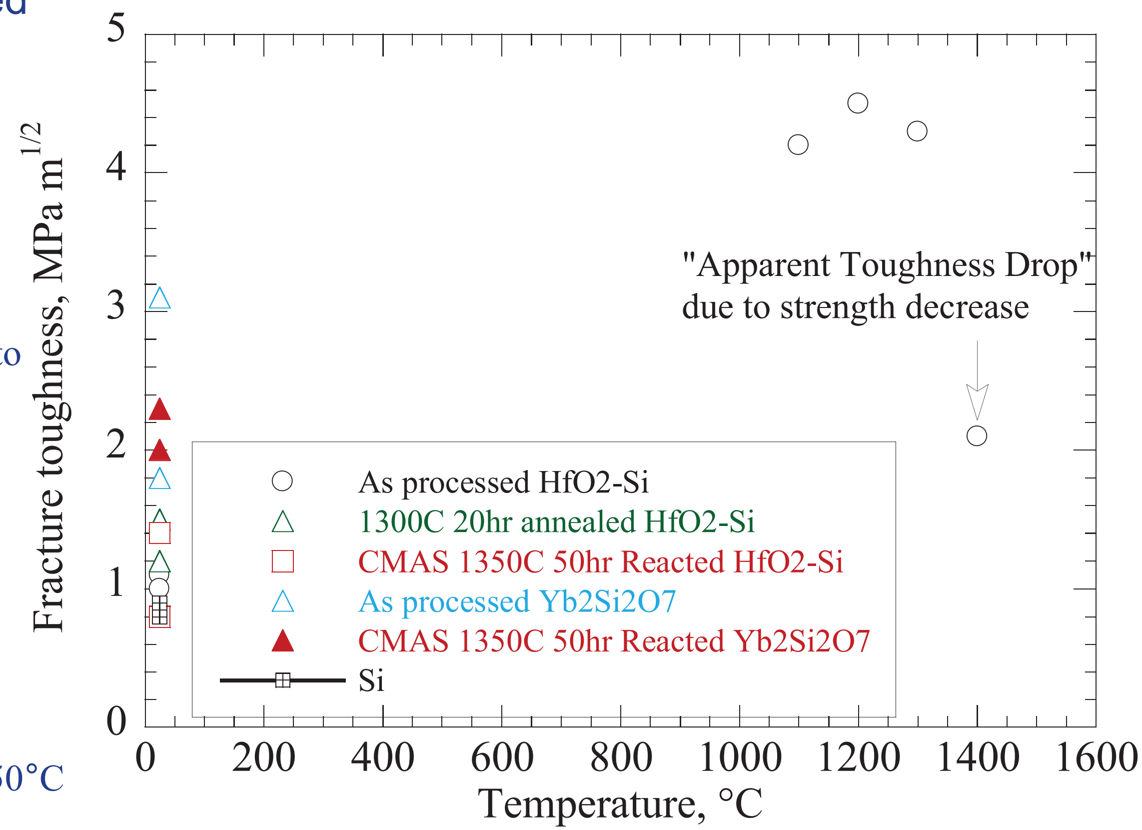
– Ytterbium silicate EBC toughness may also be reduced due to CMAS reactions
  - More measurements are needed



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

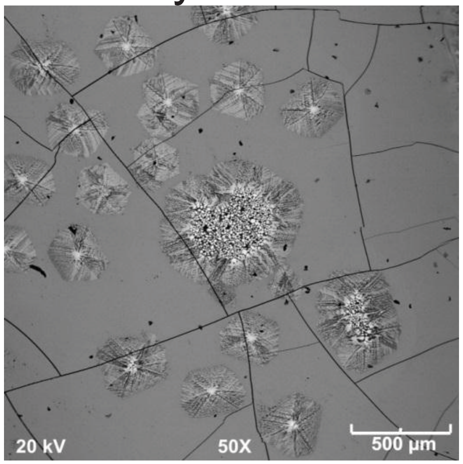


$Yb_2Si_2O_7$ notch after CMAS exposure at 1350°C for 50 hrs

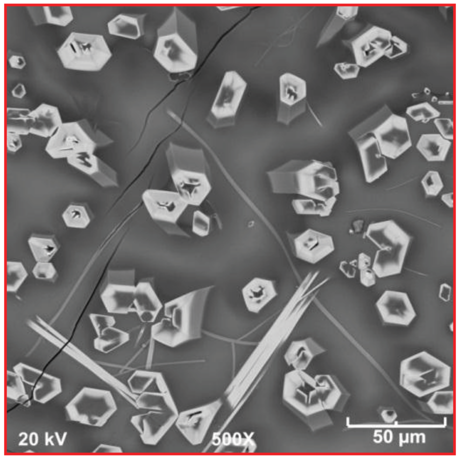


EBC CMAS Surface Reactions

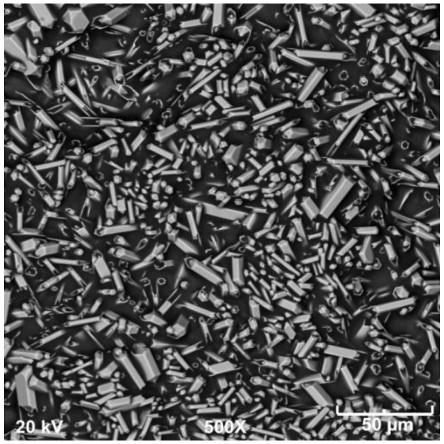
– Ytterbium and yttrium silicate reactions and dissolutions in CAMS



Ytterbium silicate surface CMAS melts: 50 hr 1300°C



Ytterbium silicate surface CMAS melts: 5 hr 1500°C

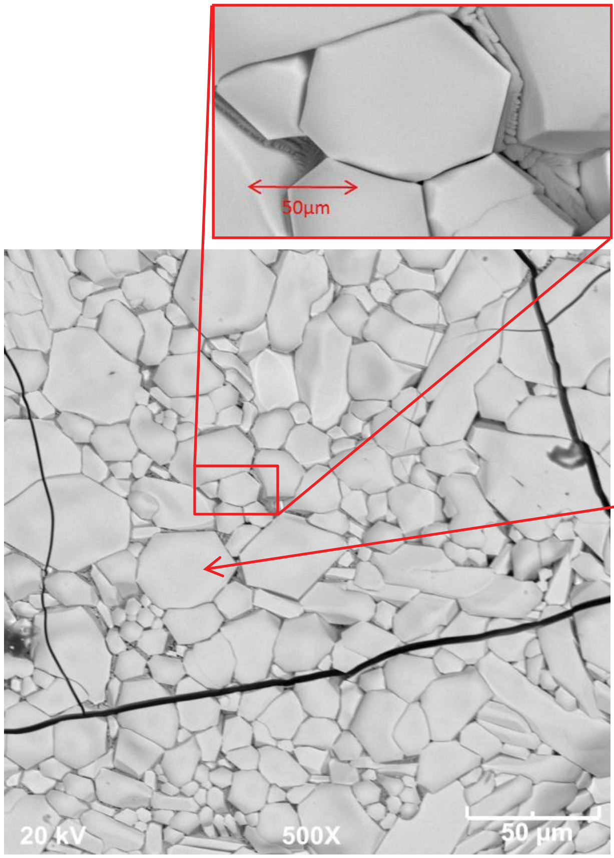


Yttrium silicate surface CMAS melts: 50 hr 1300°C

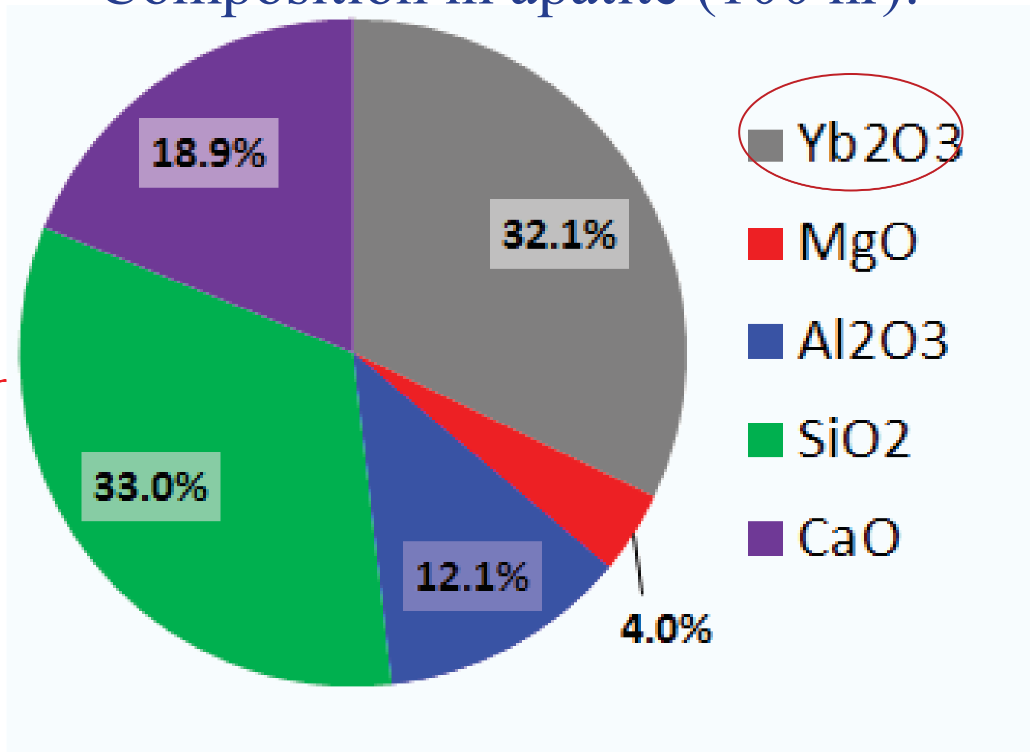
Yttrium silicate surface CMAS melts: 5 hr 1500°C

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

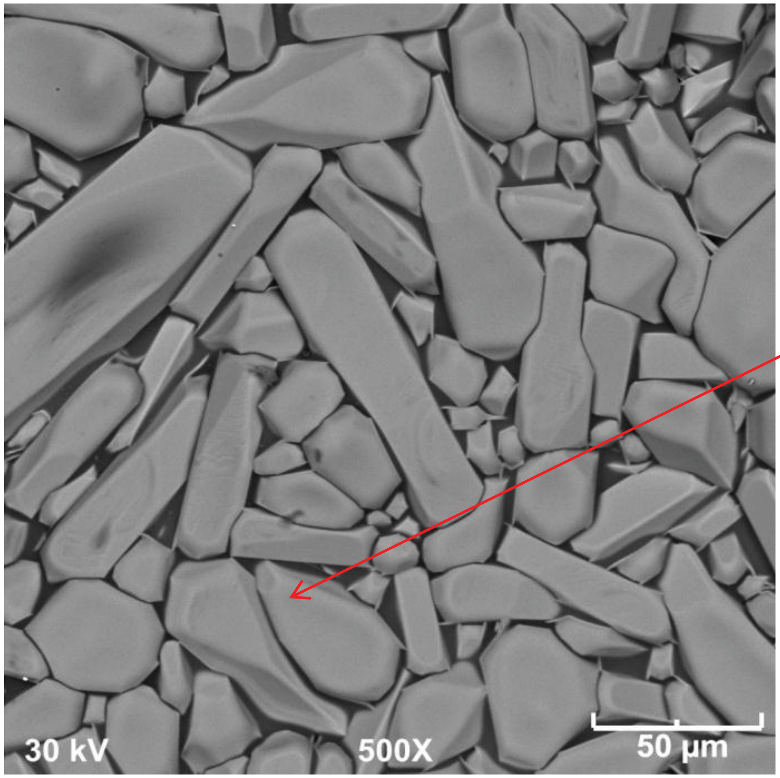


Composition in apatite (100 hr):

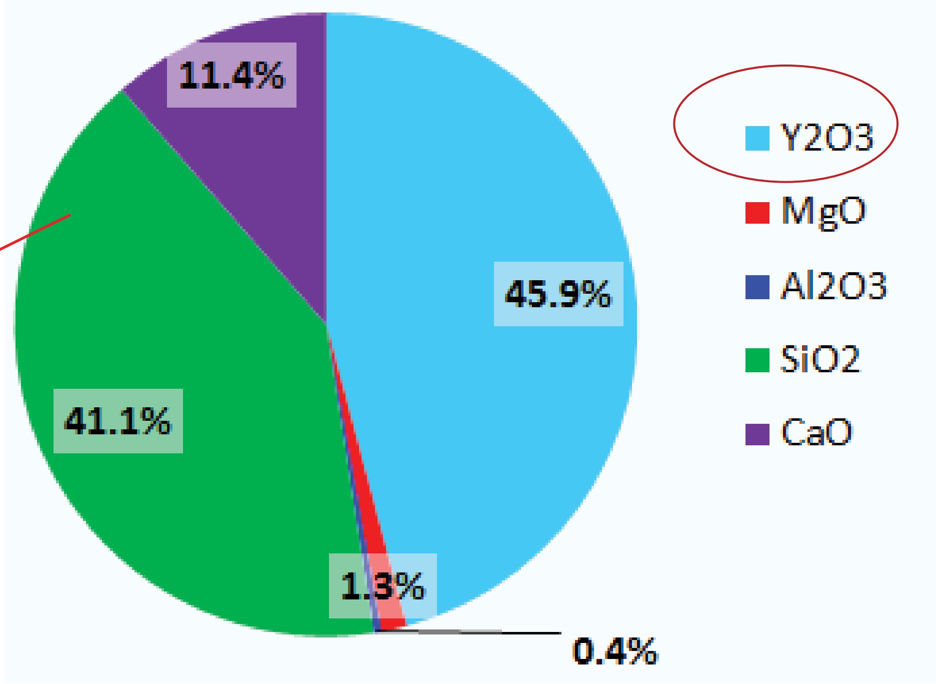


EBC Reacted Apatite Phases under Long-Term Testing at 1500°C: Yttrium Silicate EBC

– 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

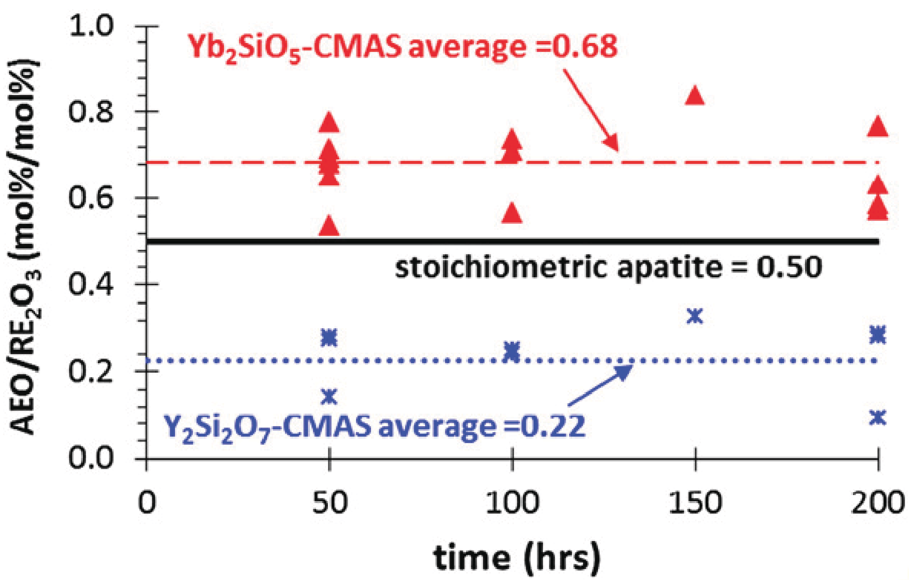


Composition in apatite (100 hr):

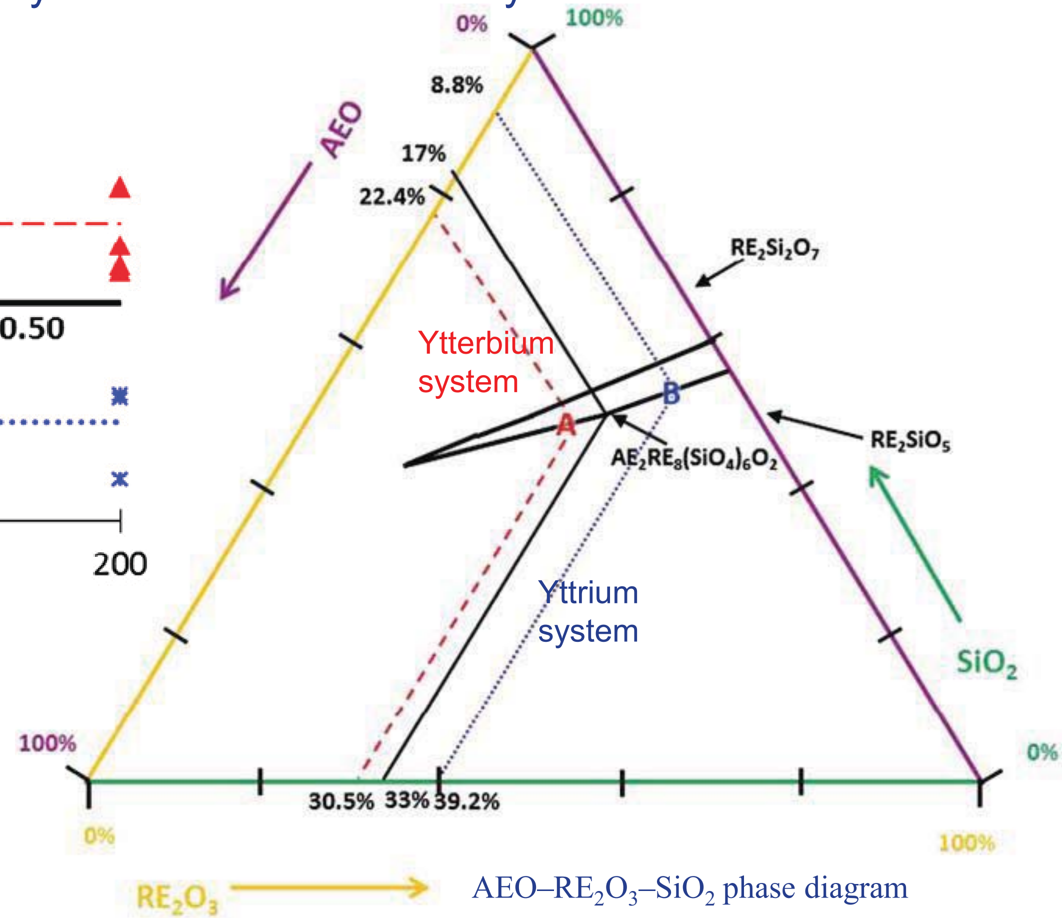


Stoichiometry of the Reacted Apatite Phases under Long-Term Testing at 1500°C

– 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

Partitioning of Rare Earths in Apatite in Geo Systems: Medium Ionic Rare Erath Reported higher Partitioning Coefficients

– Reported partition of Rare Earths in Apatite

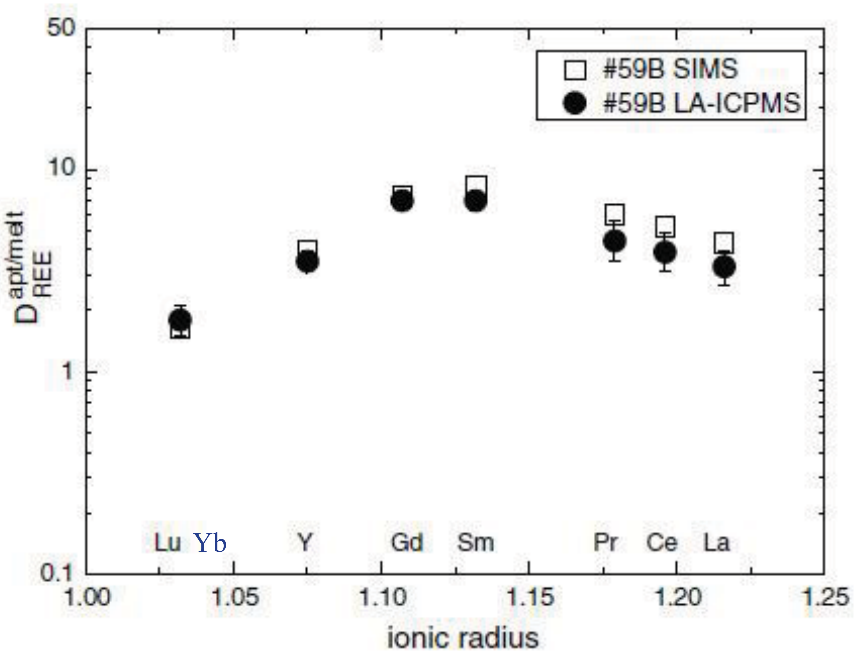


Fig. 1. Comparison of D_{REE} values calculated from SIMS analyses (open squares) and LA-ICPMS analyses.

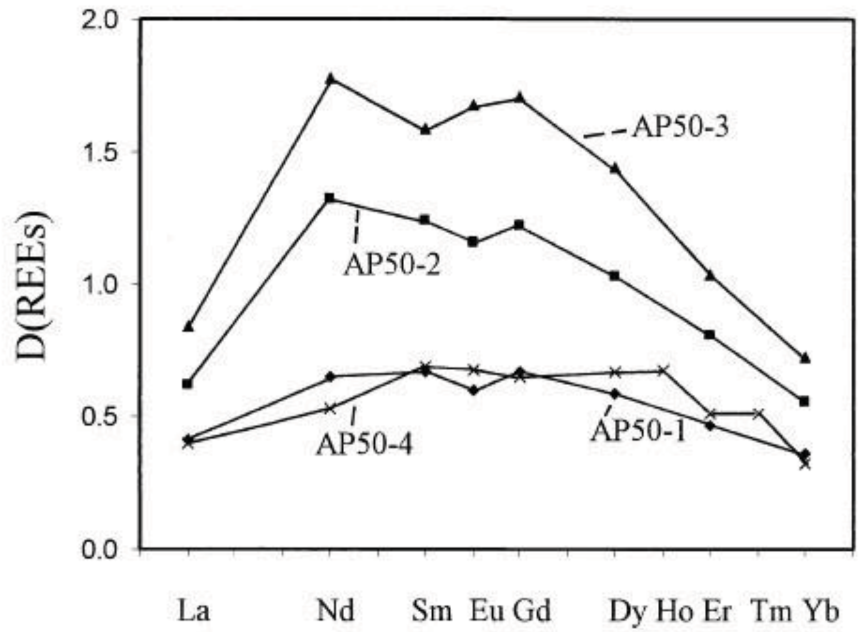


Fig. 3. Plots of D(REEs) as a function of atomic number for series AP50 experiments. Note that AP50-2 and AP30-3 with low total REE contents have more pronounced enrichments in middle REEs than AP50-1 and A P50-4.

Stefan Prowatke et al, Trace element partitioning between apatite and silicate melts., Geochimica et Cosmochimica Acta 70 (2006) 4513–4527

YUANMING PAN et al, Non-Henry's Law behavior of REE partitioning between fluorapatite.., Geochimica et Cosmochimica Acta, Vol. 67, No. 10, pp. 1889–1900, 2003

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

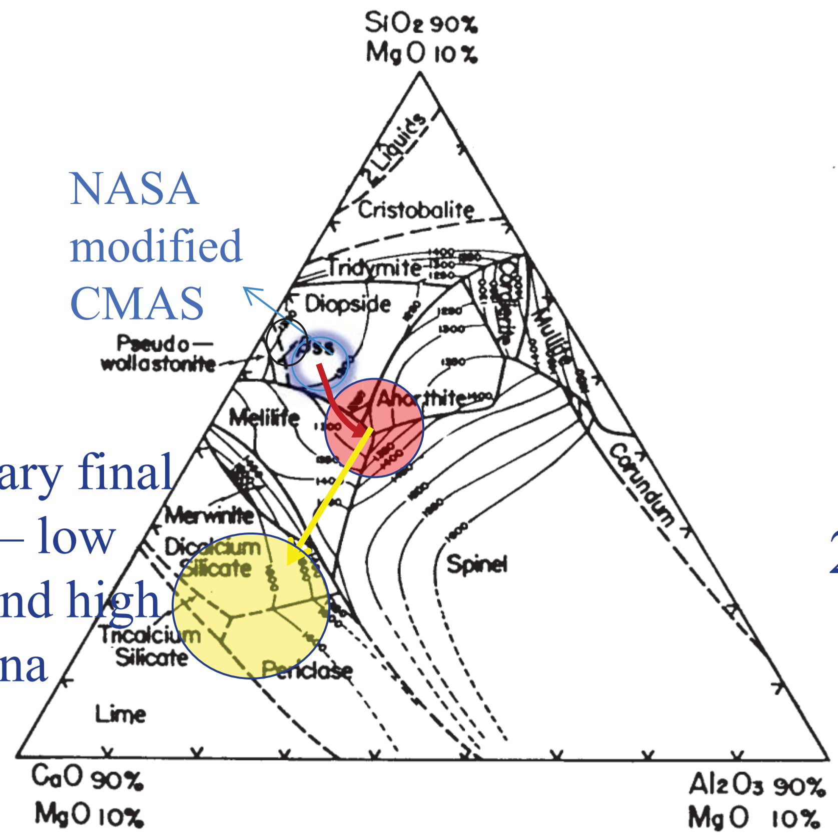
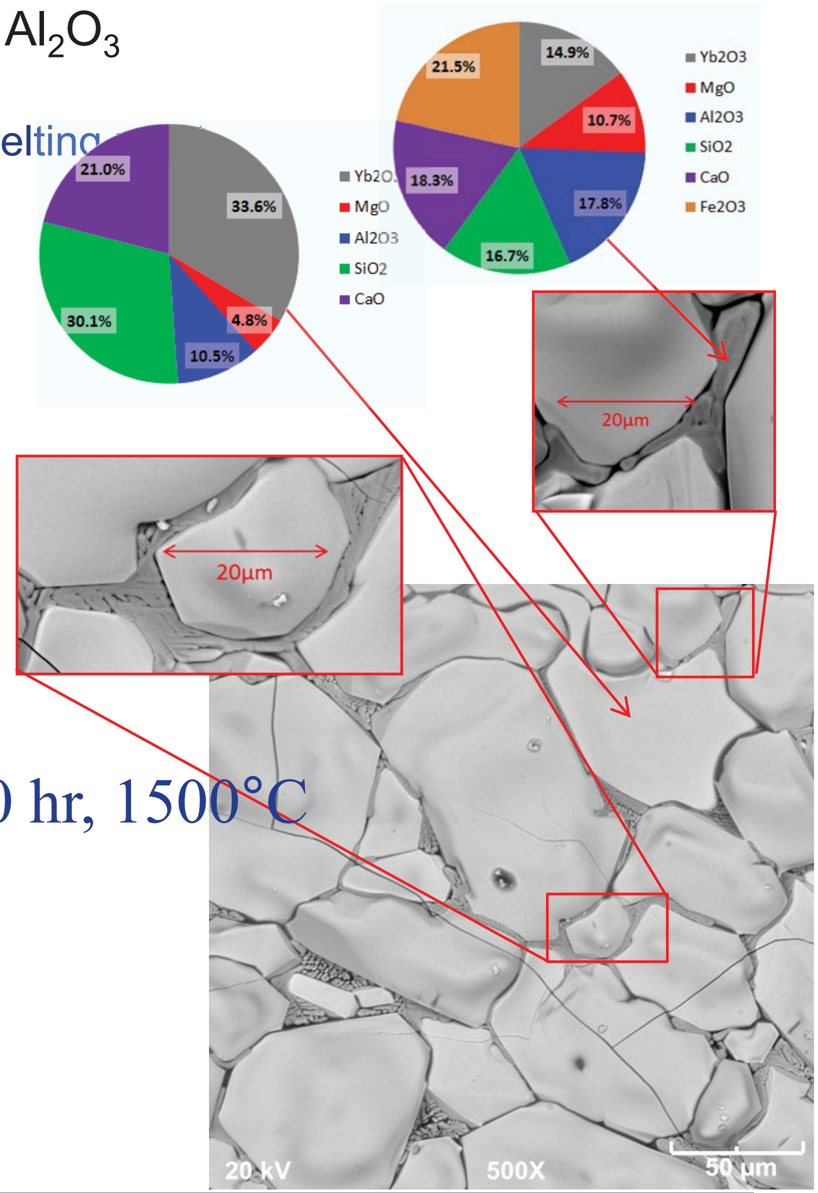


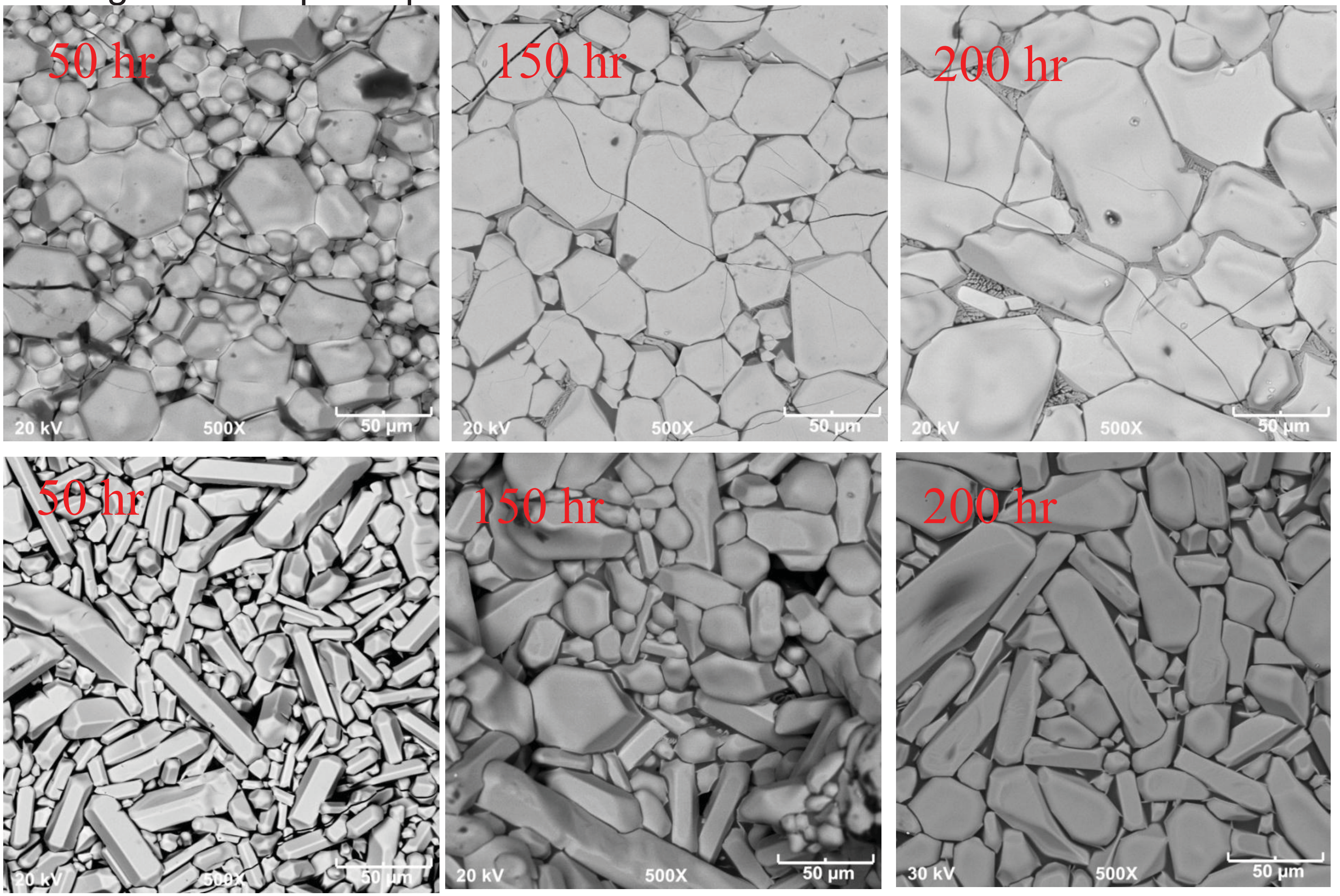
Fig. 4. The 10% MgO plane of the system CaO–MgO–Al_2O_3–SiO_2 showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

200 hr, 1500°C



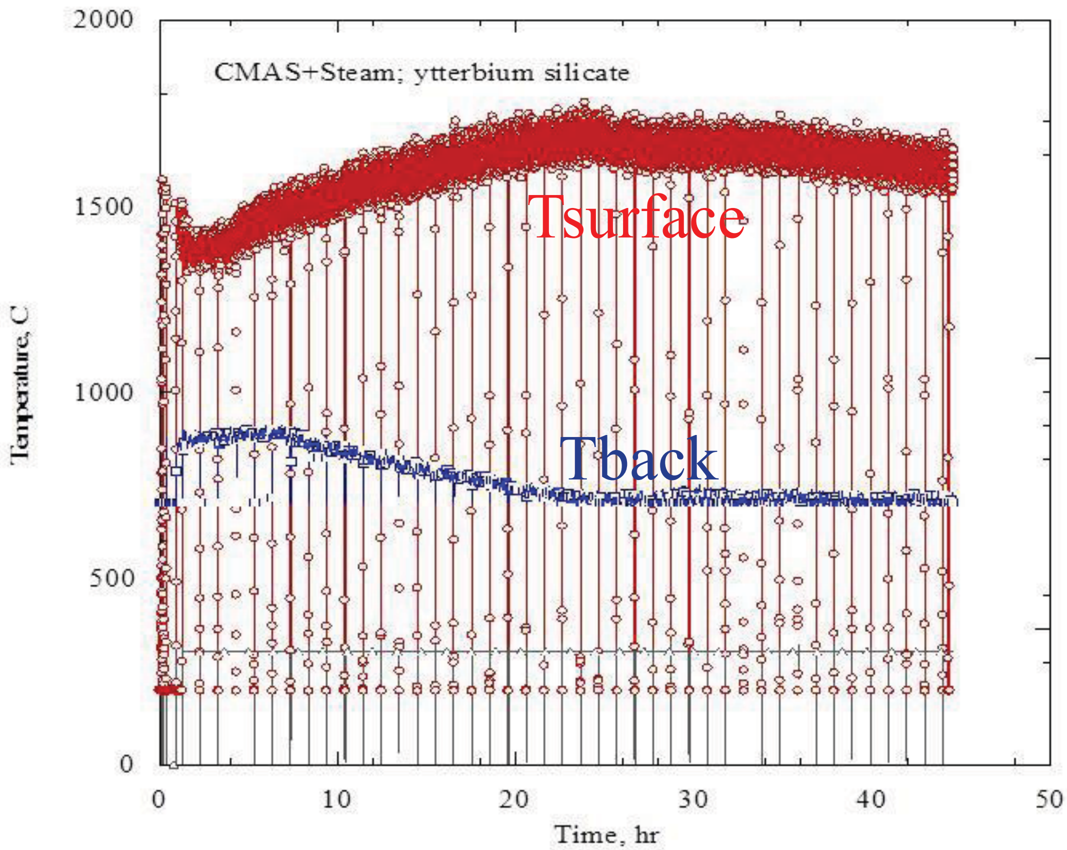
Rare Earth Apatite Grain Growth

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

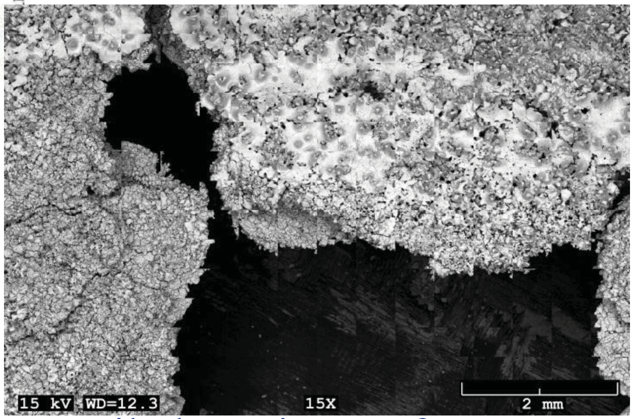


Effect of CMAS Reaction on EBC Cyclic Durability in Thermal Gradient Laser Steam Rig

- Ytterbium silicate EBC $Yb_2Si_2O_7$/Si on CMC
- CMAS fully infiltrated
- Failed after 40 cycles (1hr cycle) under combined laser thermal gradient CMAS+steam at 1400-1500°C
- Accelerated recession leading to cracking and porous coatings



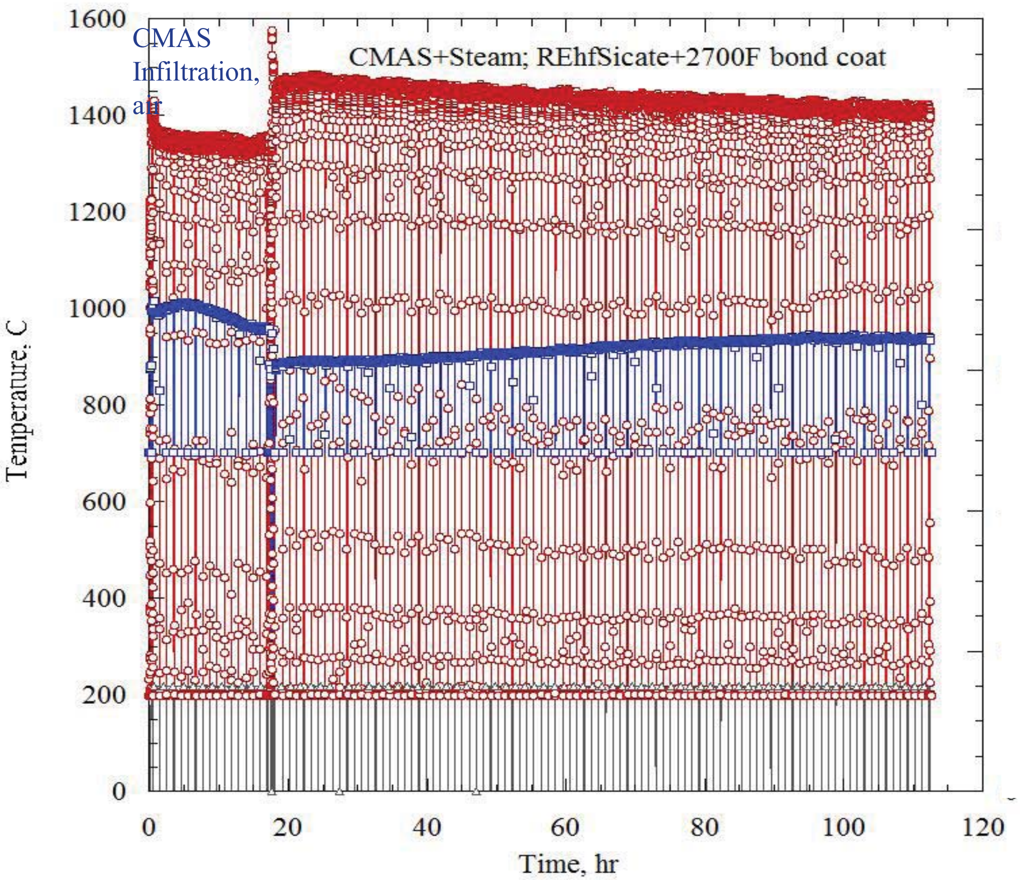
Coating spalled after 40 hr test



Failed coating surface

HfO_2-Rare Earth Silicate Composite EBC with Yb-Si Bond Coat Systems

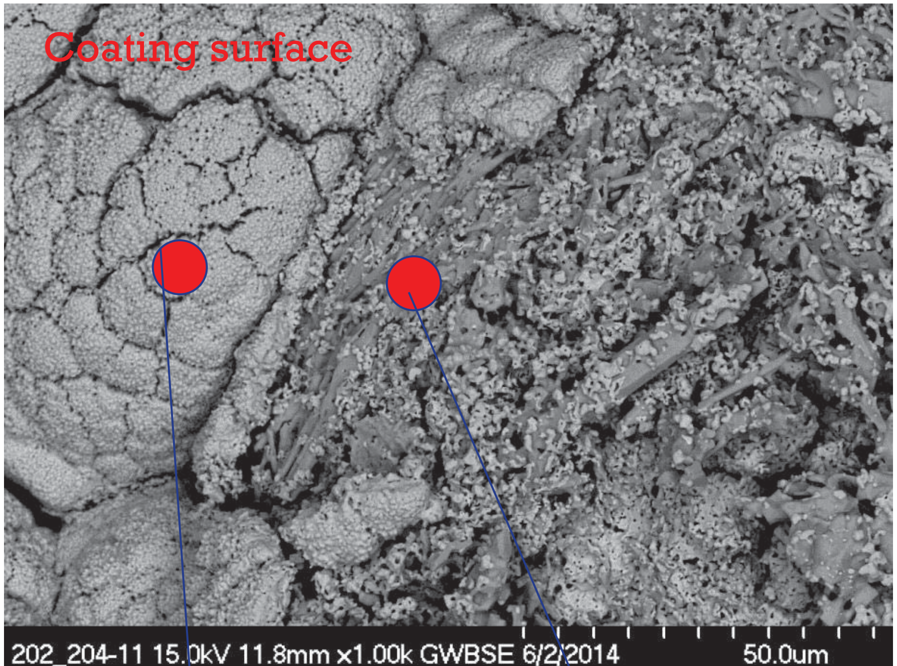
– Generally showed good resistance in CMAS and CMAS-steam tests
  - Composite system for achieving balanced CMAS resistance and water vapor stability at 1500°C
  - Compositions being further optimized

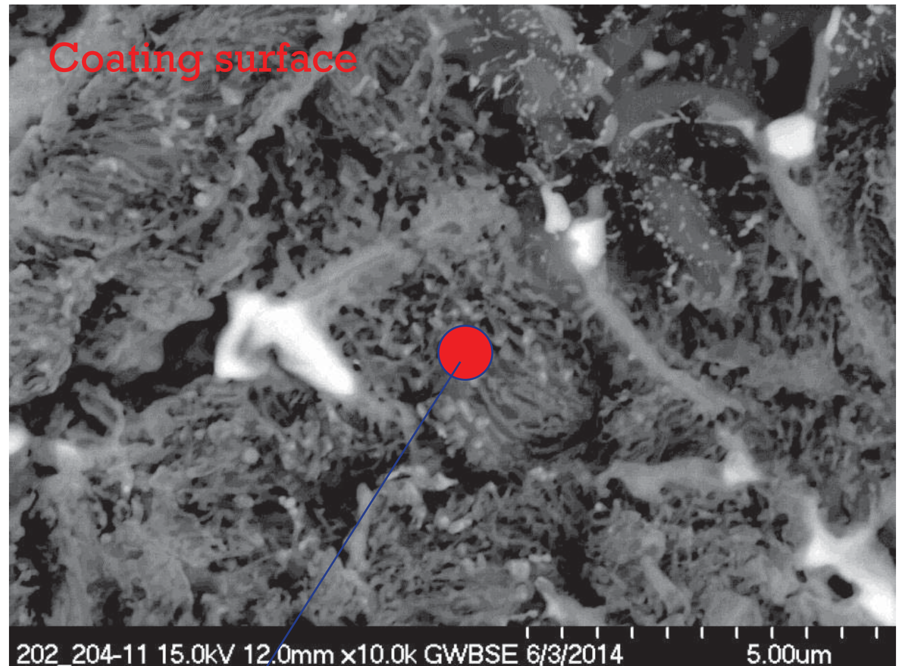


Specimen after testing

HfO_2-Rare Earth Silicate Composite EBC Systems - Continued

– Silica loss observed in the concentrated CMAS reacted regions

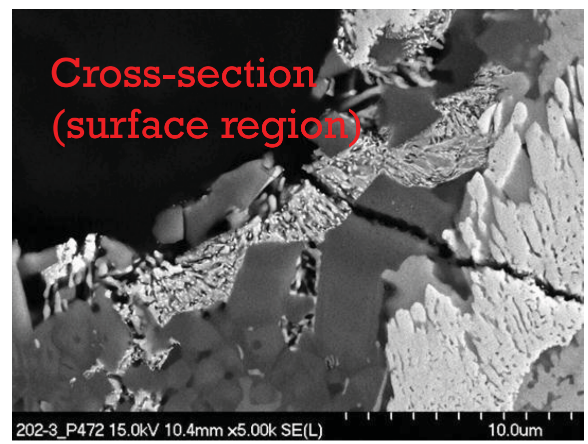




HfO_2 rich phase region

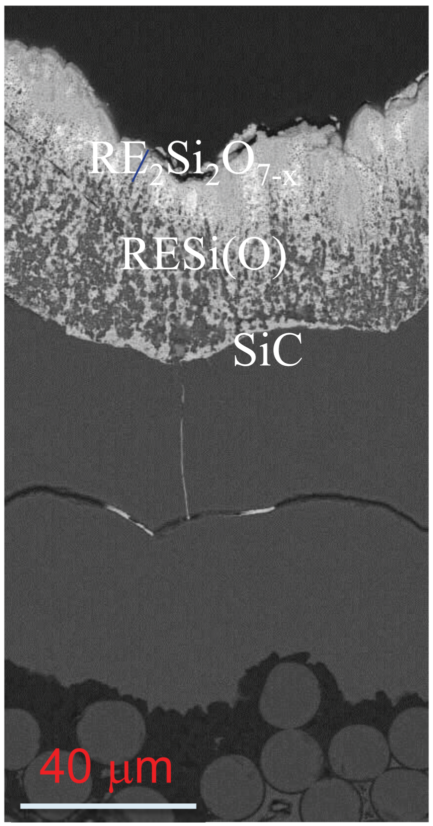
Rare earth silicate - apatite phase rich phase region

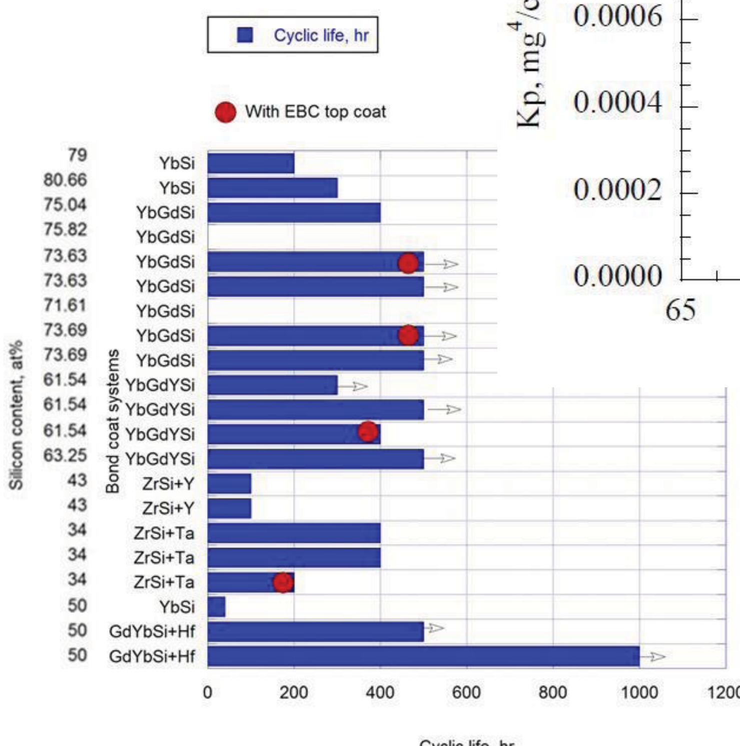
CMAS concentrated region, SiO_2 content 20-30 mol% (SiO_2 loss in the steam water vapor tests)



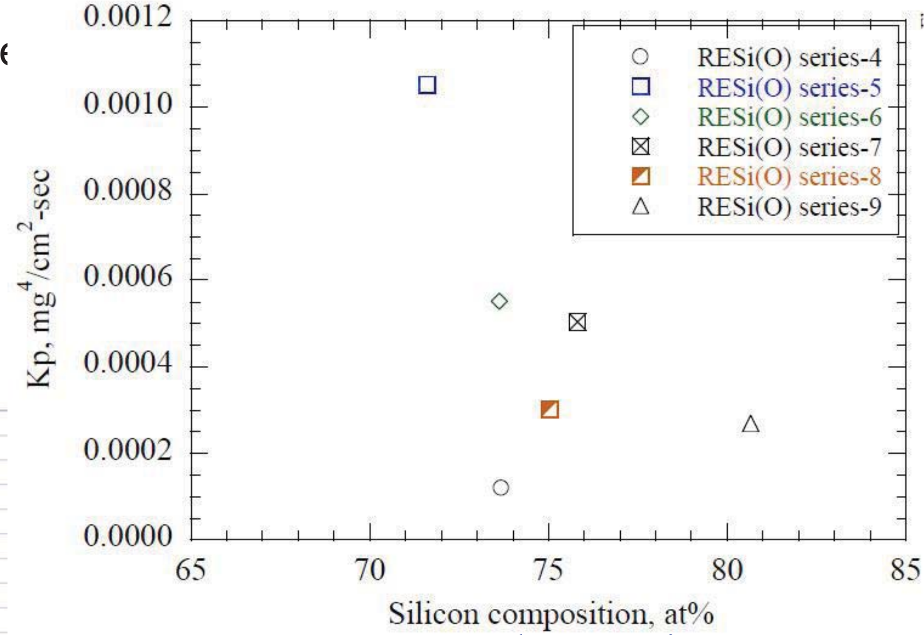
High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions

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





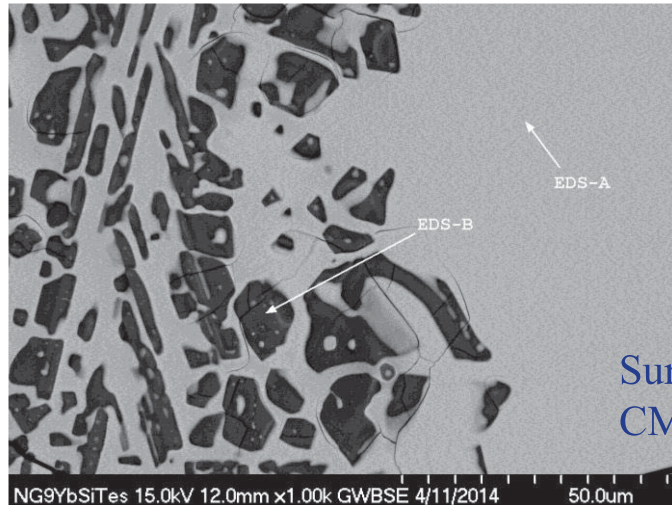
FCT life of RE-Si coatings



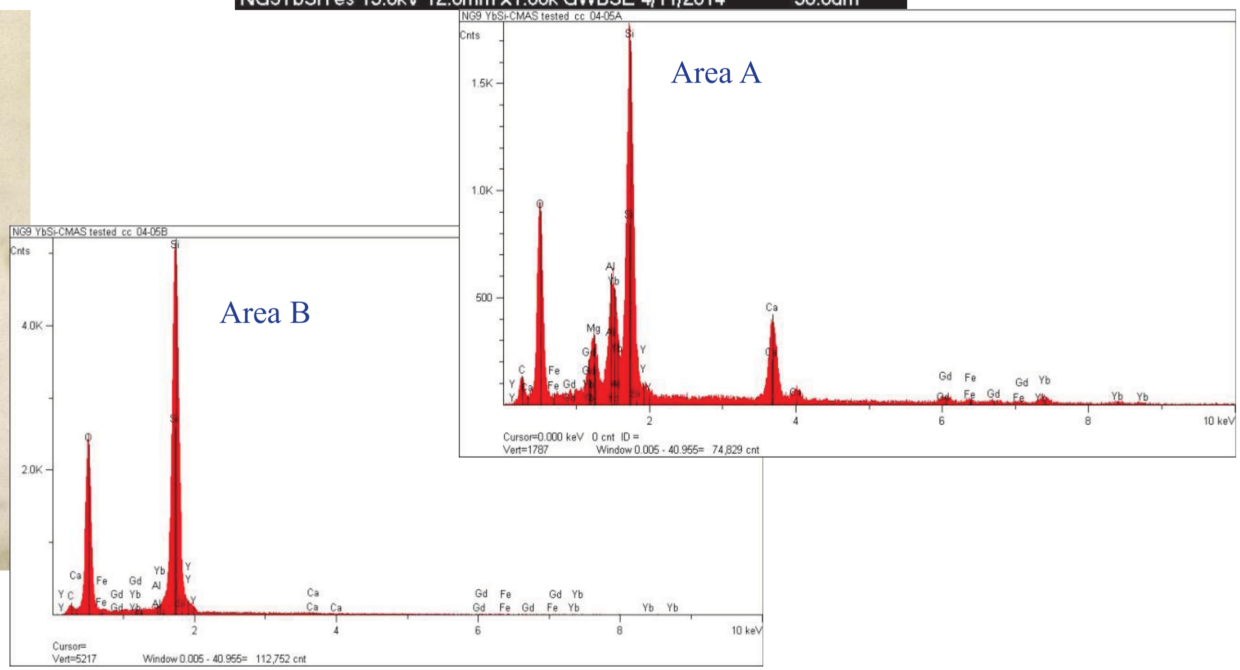
TGA results vs. Si content

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

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



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

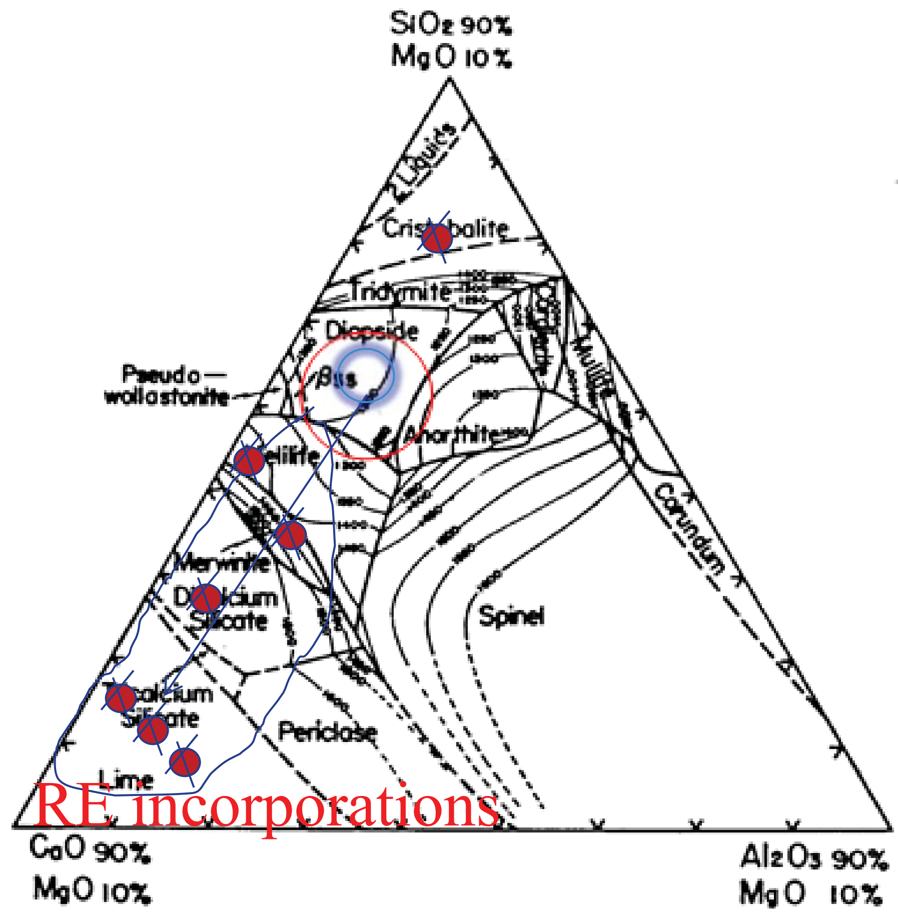
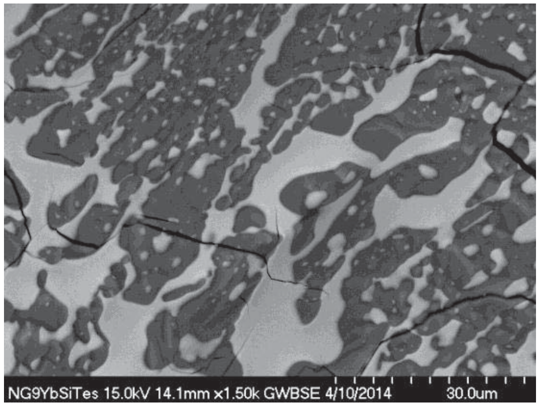


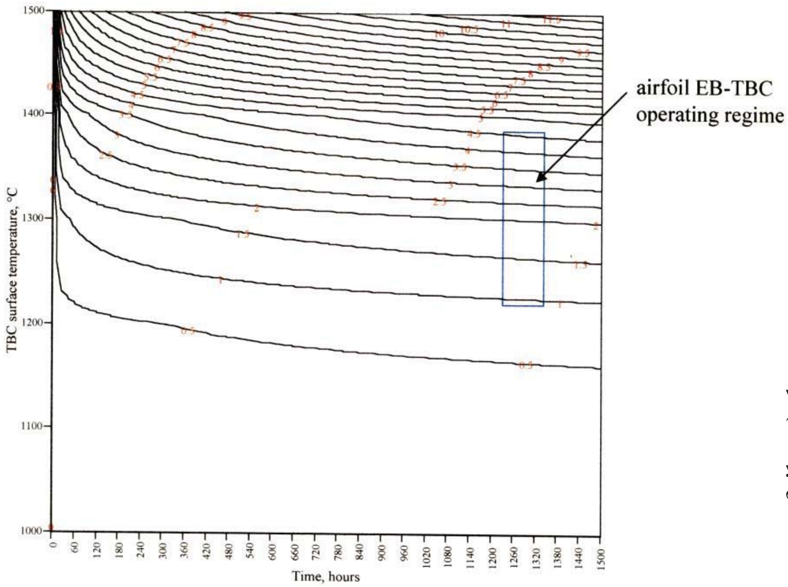
Fig. 4. The 10% MgO plane of the system CaO–MgO–Al₂O₃–SiO₂ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

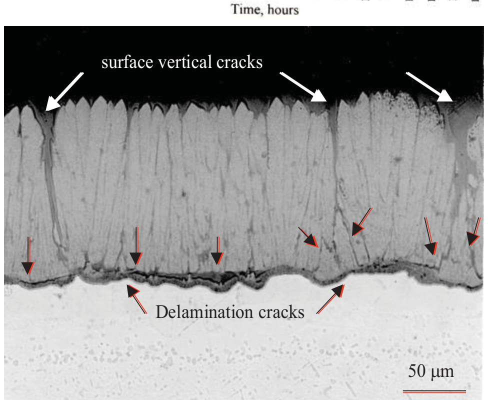
CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr

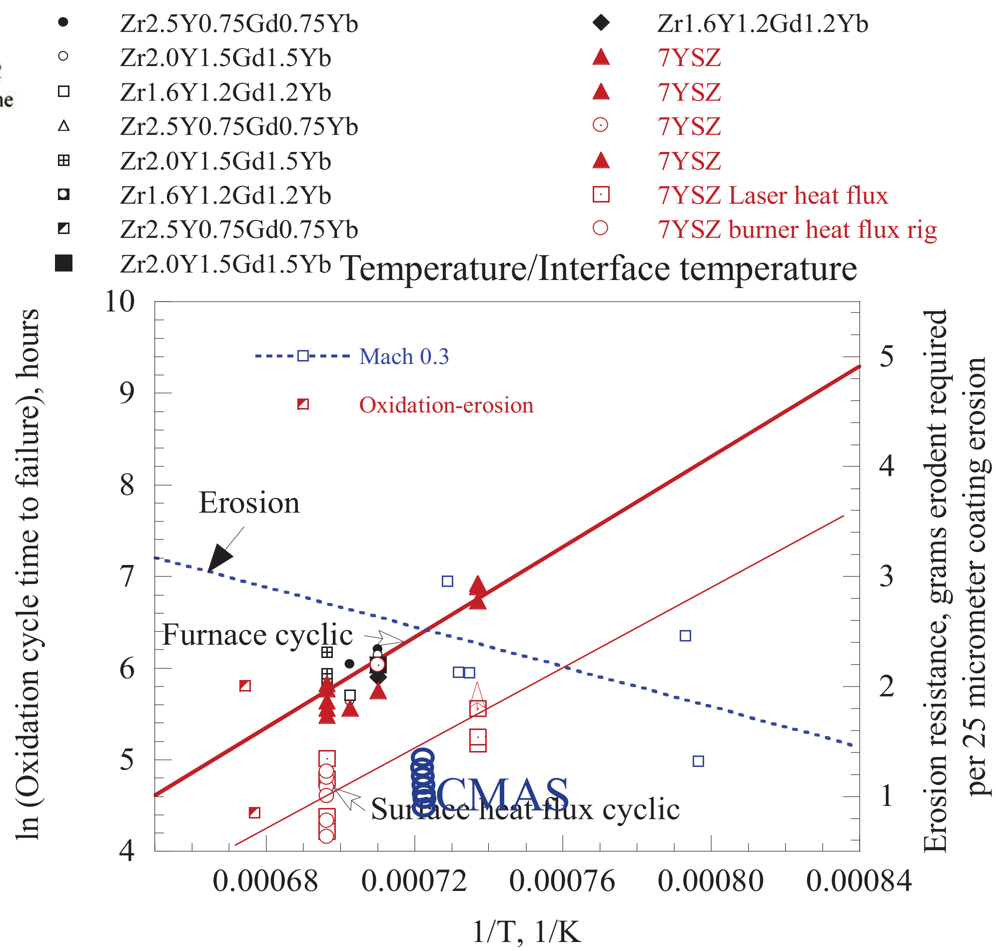


Turbine TEBC Life Aspects due to CMAS Degradations and Other Mechanisms

- Reduced cyclic life due to the CMAS infiltration







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 HfO_2-Si and, in particular Rare Earth - Silicon based bond coat compositions showed promise for CMAS resistance at temperatures up to 1500°C
- We have better understanding of CMAS integration 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