Environmental Barrier Coatings for Ceramic Matrix Composites – An Overview

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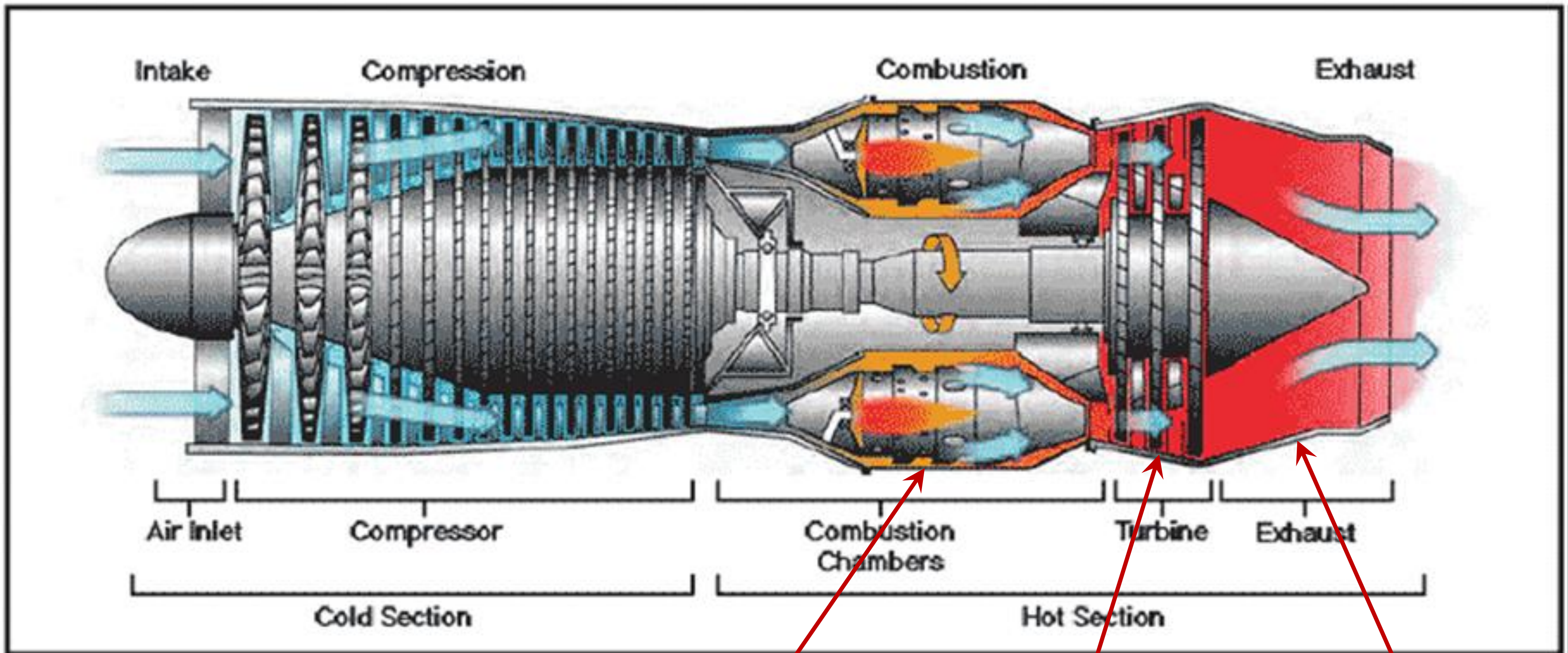
CMC is a game changer

- **Higher temperature capability**
  - Mechanical properties (Creep rupture, Fatigue)
  - Oxidation resistance
  - ➢ Reduced cooling and/or higher turbine firing temperature
- **Light weight**
  - 1/3 of Ni-base superalloys

➢ Reduced fuel consumption
➢ Higher thrust
➢ Reduced NOx and CO emissions

CMC's are the most promising material option for significant fuel and pollution reductions

CMC turbine engine components



Combustor liners

Bladetracks
Blades
Vanes

Exhaust components

SiC/SiC

Ox/Ox

Outline

- **CMC and EBC Background**
- **Gen 1 EBC & Gen 2 EBC**
- **Engine Test Experience**
- **Summary & Conclusion**

Acknowledgements

This presentation is based on the EBC section of CMH-17 (Composite Materials Handbook)

What is Composite Materials Handbook 17

CMH-17
COMPOSITE MATERIALS HANDBOOK

CMH-17 Mission

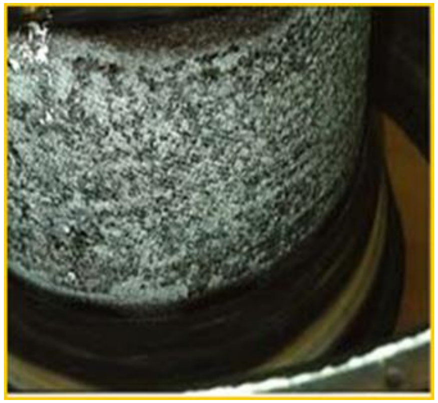
The Composite Materials Handbook organization creates, publishes and maintains proven, reliable engineering information and standards, subjected to thorough technical review, to support the development and use of composite materials and structures.

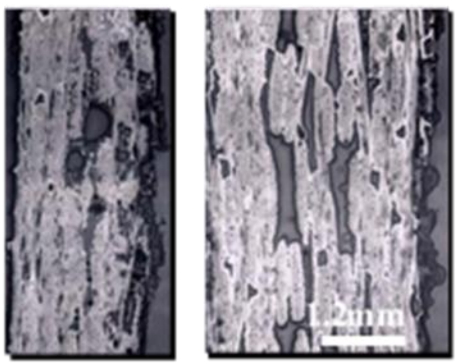
CMH-17 Vision

The Composite Materials Handbook will be the authoritative worldwide focal point for technical information on composite materials and structures.

Achilles' Hill of SiC/SiC CMCs

- **Recession in $H_2O(g)$**



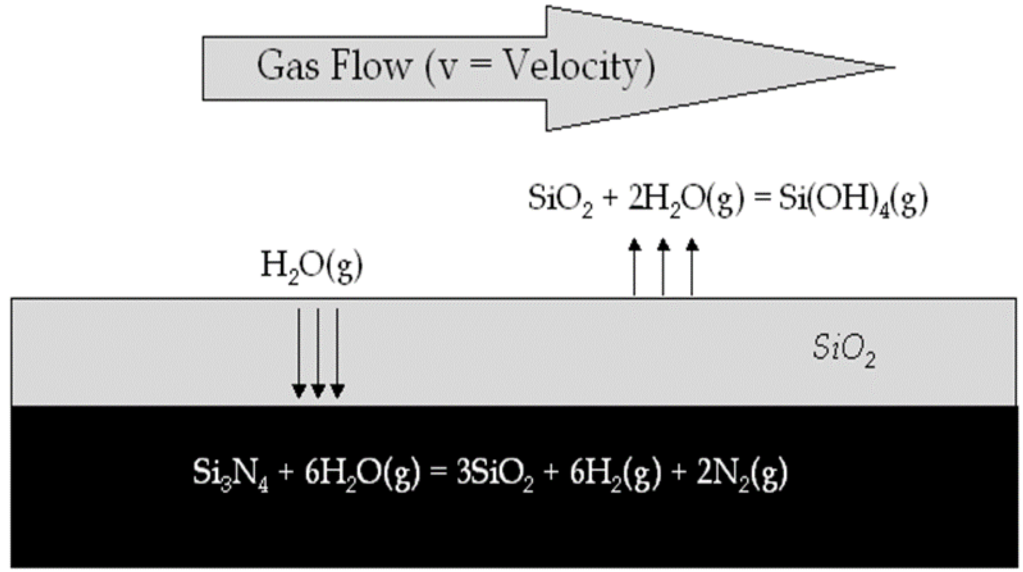


Inner liner (left)
Outer liner (right)

M. van Roode, et al., Transactions of the ASME, J. Eng. Gas Turbines & Power, 129 [1],21-30, 2007.

- **NASA Recession Model**

Based on "E. J. Opila et al., Am. Ceram. Soc., 80[1], 197-205 (1997)"

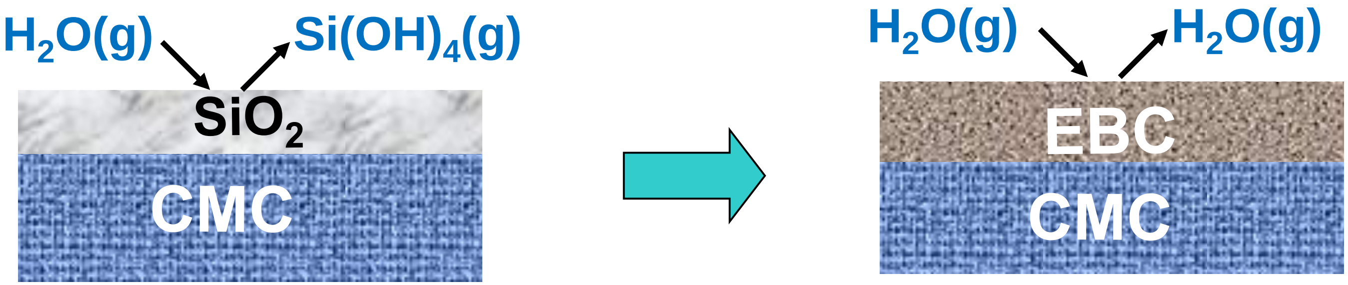


$$R = \text{rate } (\mu m/h) = 465 \exp(-111 \text{ kJ/mole}/RT)\, v^{1/2}\, P_{H2O}^{2}\, P_{total}^{-1/2}$$

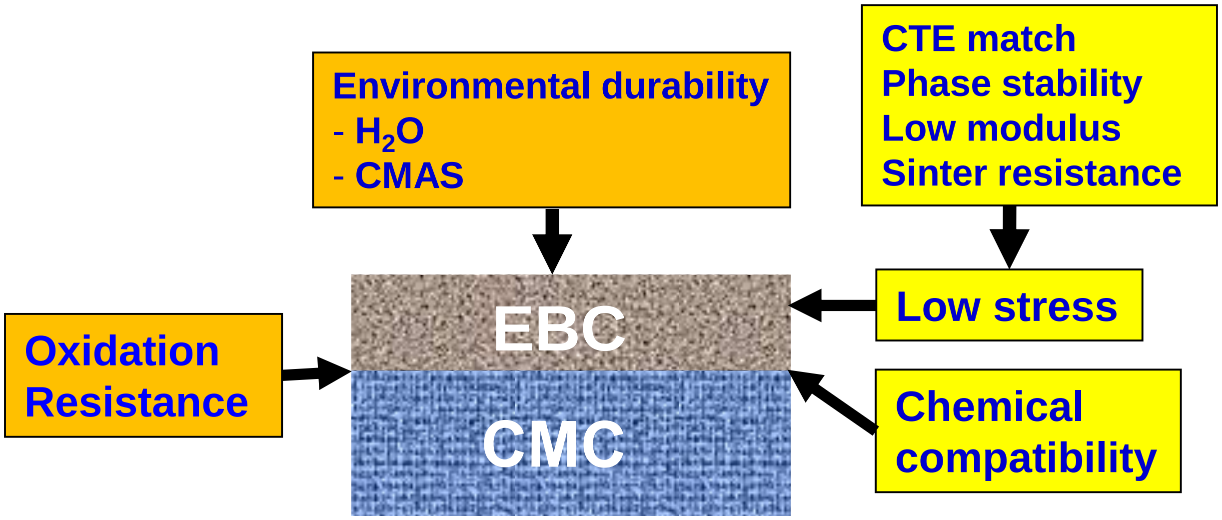
Maximum SiC/SiC CMC combustor liner life at ~1200C: ~ 5,000h

Environmental Barrier Coating (EBC)

- **An external coating to protect CMC from water vapor**



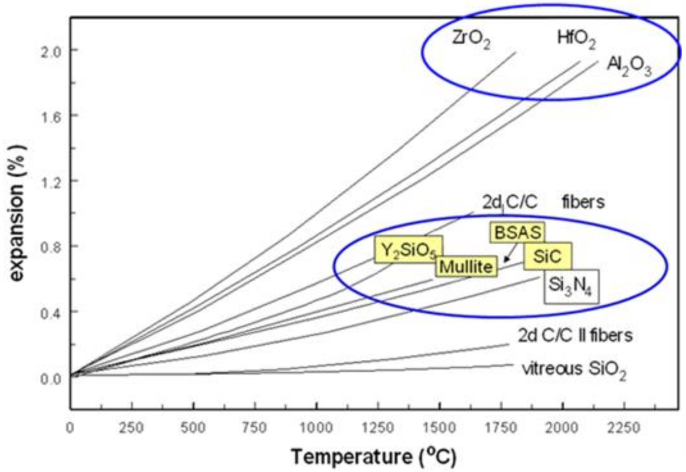
SiO_2 (s) + $2H_2O$ (g) = $Si(OH)_4$ (g)



K. N. Lee, Surface and Coatings Technology, 133-134 1-7 (2000).

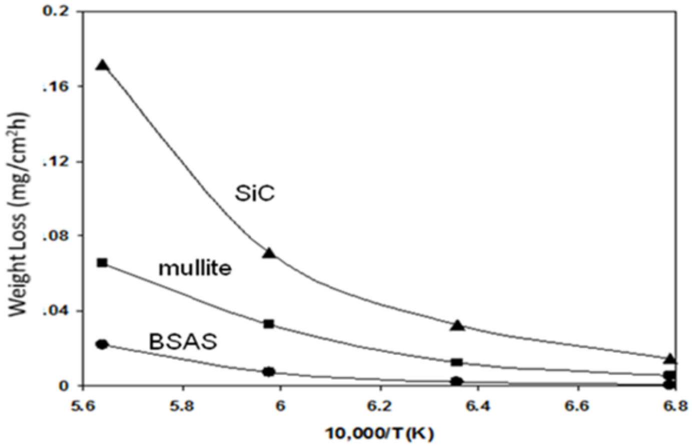
Gen 1 Environmental Barrier Coatings

CTE



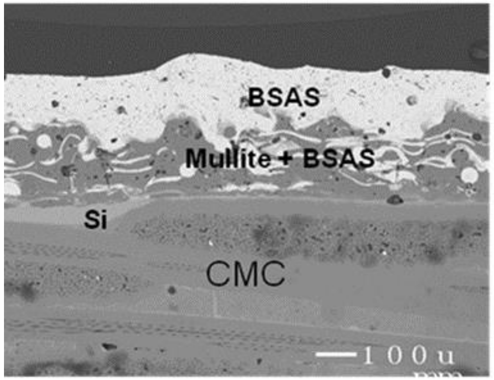
K. N. Lee et al., Progress in Ceramic Gas Turbine Development, Vol. 2. ASME PRESS, New York, NY, 641-664 (2003).

Volatility



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

3-layer EBC



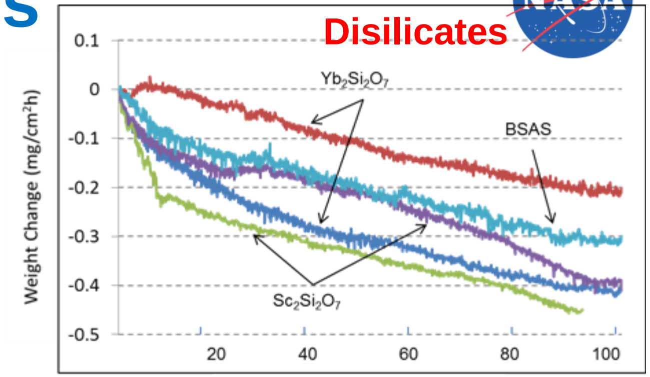
K. N. Lee et al., J. Am. Ceram. Soc. 86 [8] 1299-1306 (2003).

- **Developed at NASA Glenn in collaboration with GE and P&W – 1990s**
- **From early work on mullite coatings on SiC (Solar, GTE, NASA) – 1980s/1990s**
- **Si/mullite+BSAS/BSAS – deposited by plasma spraying**
  - **BSAS: (1-xBaO·xSrO·Al_2O_3·$2SiO_2$, $0 \le x \le 1$: barium-strontium-aluminosilicate)**
    - **High stability in water vapor, CTE match with SiC/SiC, low modulus**
  - **Si Bond coat: Improve oxidation life of EBC by forming slow growing SiO_2 TGO**
  - **Mullite: intermediate coat that separates BSAS from SiO_2 TGO**
    - **SiO_2 reacts with BSAS to form eutectic melt at T ~ 1300°C**
    - **BSAS addition reduces thermal stress: 20 wt% ~ 50 wt%**

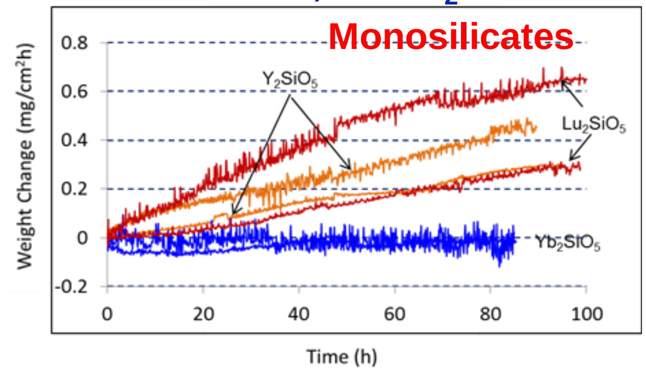
K. N. Lee et al., J. Am. Ceram. Soc. 86 [8] 1299-1306 (2003).

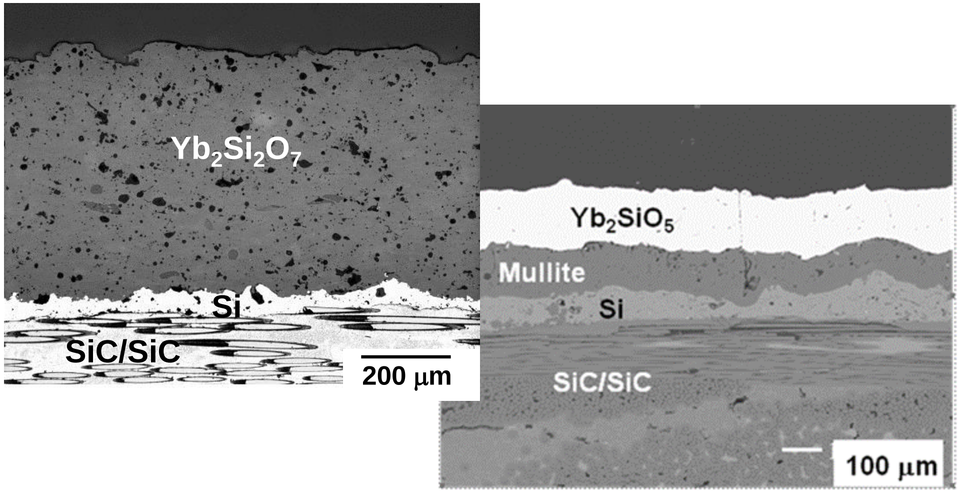
Gen 2 Environmental Barrier Coatings

- **NASA Ultra Efficient Energy Technology (UEET) program - Early 2000's**
- **Low CTE Rare Earth silicates:**
  - **Monosilicates (RE_2SiO_5)and Disilicates ($RE_2Si_2O_7$)**
  - **RE = ytterbium (Yb), scandium (Sc), lutetium (Lu), yttrium (Y)**
- **Higher H_2O stability and m.p. compared to Gen 1**

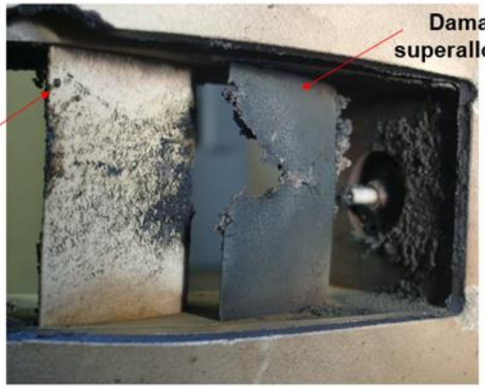


1500C, 90% H_2O





K. N. Lee et al., J. Euro. Ceram. Soc. 25, 1705-1715 (2005).



K. N. Lee, 3rd EBC Workshop Nashville, TN (2004).

M. Verrilli et al., ASME TURBO EXPO 2004, June 14-17, 2004 – Vienna, Austria.

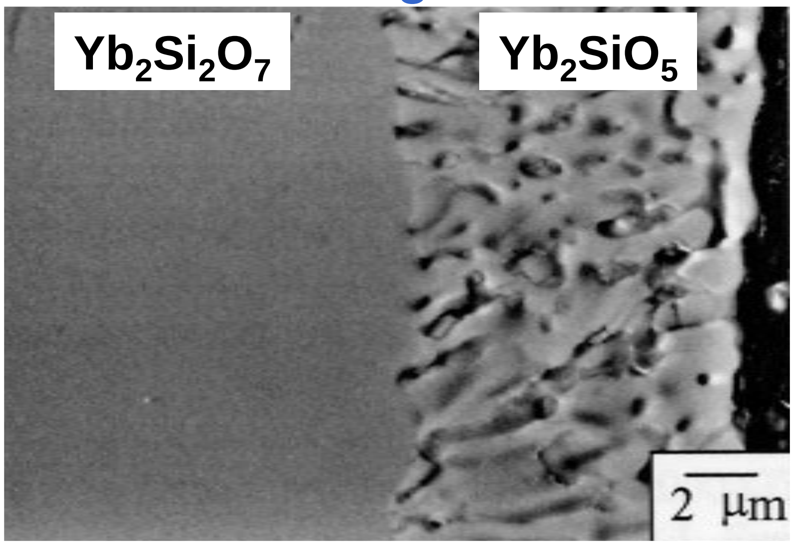
Gen 2 EBC-coated SiC/SiC CMC and superalloy vanes after 5 h with 2 min cycles at T=(~1260°C - ~1316°C), P_{TOTAL} = 6 atm, and v = 24 m/s

Recession of RE Disilicates

$RE_2Si_2O_7 + 2H_2O\ (g) \rightarrow RE_2SiO_5 + Si(OH)_4\ (g)$

$RE_2SiO_5 + 2H_2O\ (g) \rightarrow RE_2O_3 + Si(OH)_4\ (g)$

Burner rig test



1450°C, $P(H_2O)$=0.27 atm, 100 m/s, P(total)=1 atm, 224h

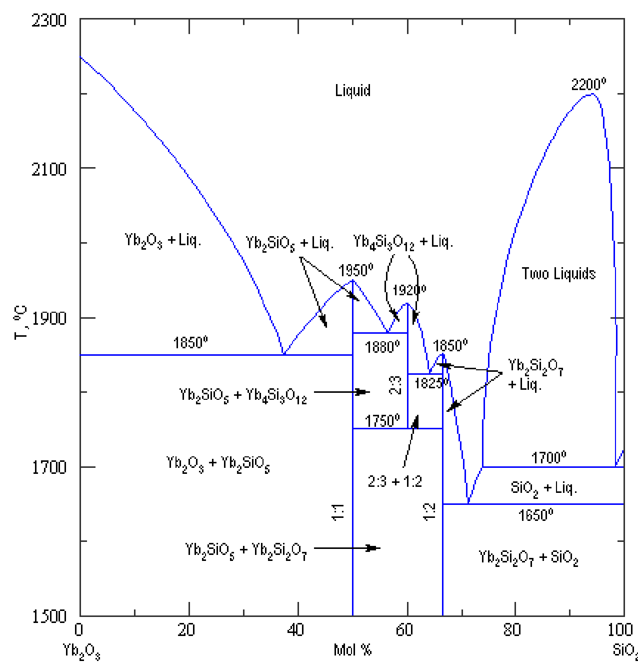
- Volatilization of $Yb_2Si_2O_7$ results in Yb_2SiO_5 surface layer
- Monosilicate layer slows down volatility

Klemm et al., Fraunhofer Institute, Proc. 2004 Cocoa Beach Meeting

Silica Activity of RE Silicates at 1377C

	RE = Y	RE = Yb
$a(SiO_2)_{RE2Si2O7}$	0.281	0.194
$a(SiO_2)_{RE2SiO5}$	0.000804	0.00298
$\frac{a(SiO_2)_{RE2Si2O7}}{a(SiO_2)_{RE2SiO5}}$	350	65

G. Costa and N.S. Jacobson, J. Eur. Ceram. Soc. 2015

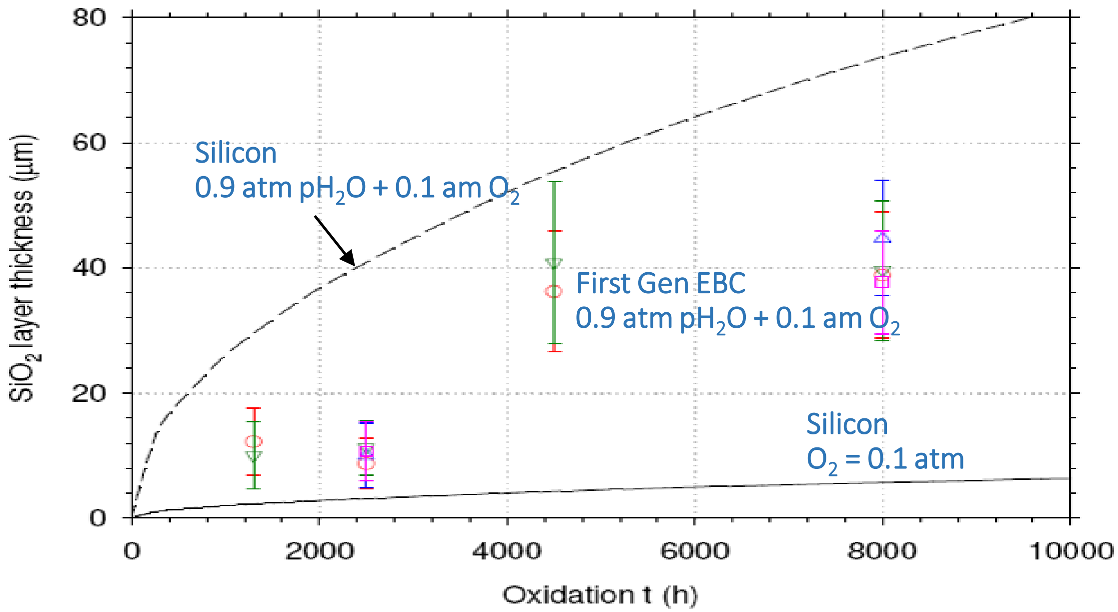


Phase Equilibria Diagrams, American Ceramic Society, Westerville, OH, 1998.

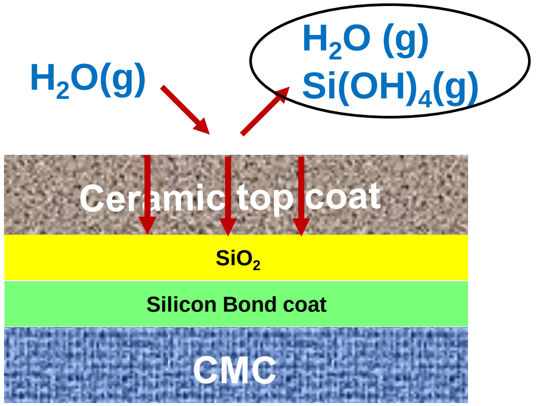
Oxidation of EBC in engines is dominated by $H_2O(g)$

- Silicon oxidizes faster in $H_2O(g)$ than in air by an order of magnitude (Deal and Grove)
- 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

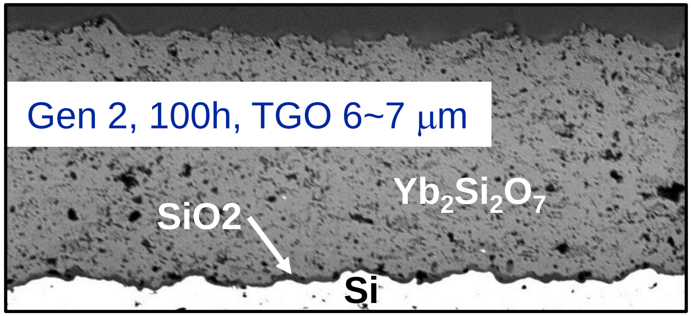
Isothermal Oxidation, T = 2200ºF (1204ºC)



GE Final Report – AMAIGT Program Dec. 2010



Cyclic Oxidation, 2400ºF, 90% H_2O



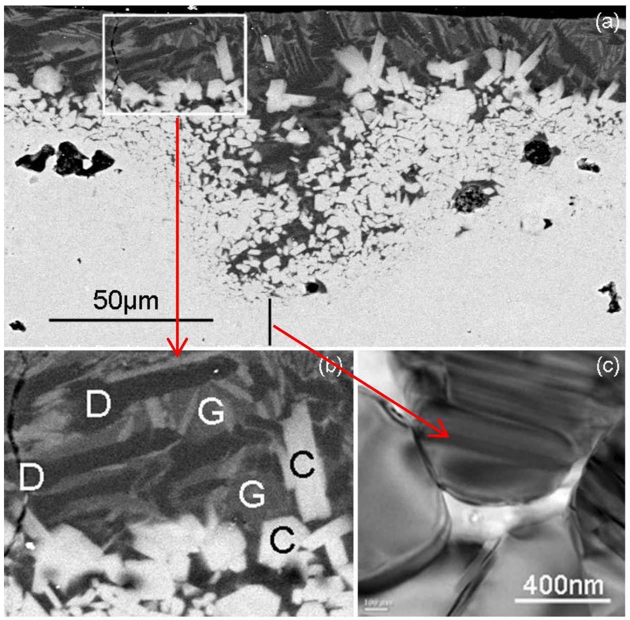
NASA, Unpublished data

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

CMAS Degradation of Gen 1 EBC (BSAS)

K. Grant et al., Surf & Coat Tech 202 653-657 (2007)

Hot-pressed BSAS
4h,1300C,10 mg/cm^2 CMAS



(b) C=celsian G=CMAS D=diopside.
(c) a Sr-rich pocket at the bottom of the infiltrated crevice in (a)

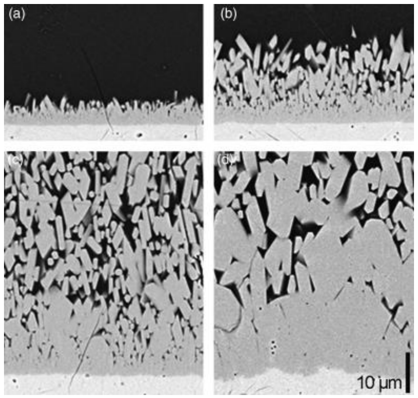
K. Grant et al., Surf & Coat Tech 202 653-657 (2007)
B. Harder et al., J. Am. Ceram. Soc. 94[S1] S178-S185 (2011)

- CMAS dissolves BSAS (celsian and hexacelsian) and re-precipitates as modified celsian plus other phases, such as anorthite
  - CMAS penetrates the BSAS grains boundaries to depths much larger than the apparent reaction front
- CMAS reaction with BSAS also affects the EBC residual stress state negatively
  - The surface of BSAS became increasingly compressive with CMAS exposure time
- The primary form of CMAS degradation of EBCs appears to be thermochemical, yielding phases that compromise chemical and mechanical properties

CMAS: $33CaO\text{-}9MgO\text{-}13AlO_{1.5}\text{-}45SiO_2$ (mol%)

CMAS Degradation of Gen 2 EBC (Y_2SiO_5, Yb_2SiO_5)

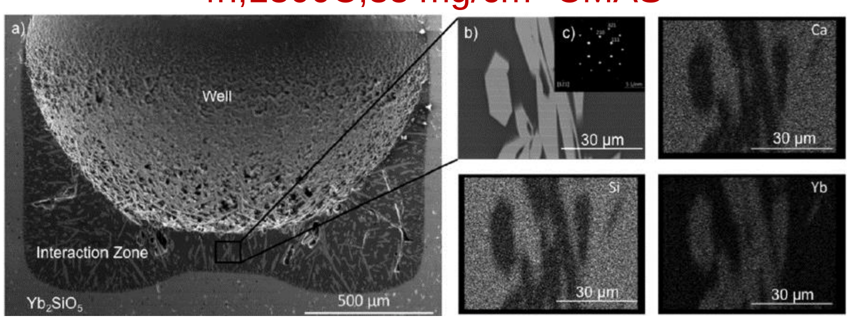
Hot-pressed Y_2SiO_5 (YMS)
1300C,12~13 mg/cm^2 CMAS



Apatite layer after (a) 1h, (b) 4h, (c) 24h, and (d) 100h.

K. Grant et al., J. Am. Ceram. Soc. 93 3504-3511 (2010)

APS Yb_2SiO_5 (YbMS)
4h,1300C,35 mg/cm^2 CMAS



(a) Dark phase: CMAS; Precipitates: Apatite.
(b) EDS map
(c) SAED pattern of precipitate: $Ca_2Yb_8(SiO_4)_6O_2$

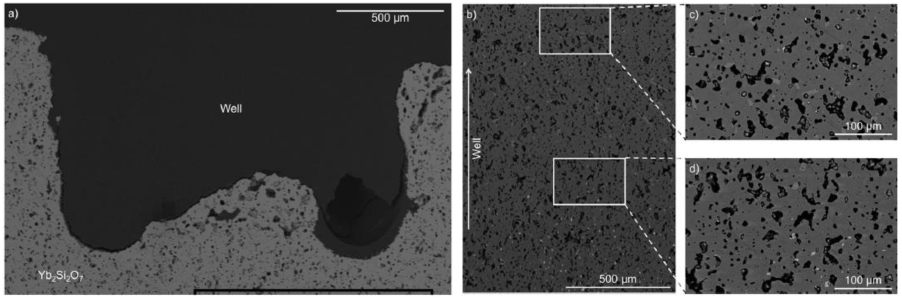
F. Stolzenburg et al, Surf. & Coat. Tech., 284 44-50 (2015)

CMAS: 33CaO-9MgO-13$AlO_{1.5}$-45SiO_2 (mol%)

- YMS and YbMS dissolve into molten CMAS and re-precipitates as apatite
  - $Ca_2Y_8(SiO_4)_6O_2$, $Ca_2Yb_8(SiO_4)_6O_2$
- No CMAS penetration of the EBC grain boundaries unlike BSAS
- Recession after 4h at 1300C (Grant et al.):
  - YMS: ~40 µm
  - EB-PVD $Gd_2Zr_2O_7$: ~10 µm
  - EB-PVD $Y_4Zr_3O_{12}$: ~15 µm or less
- Two other studies showed similar CMAS-YbMS reactions
  - Ahlborg and Zhu, Surf and Coat Tech, (2013)
  - Zhao, et al, Surf and Coat Tech, 288 151-162 (2016)

CMAS Degradation of Gen 2 EBC ($Y_2Si_2O7_7$, $Yb_2Si_2O_7$)

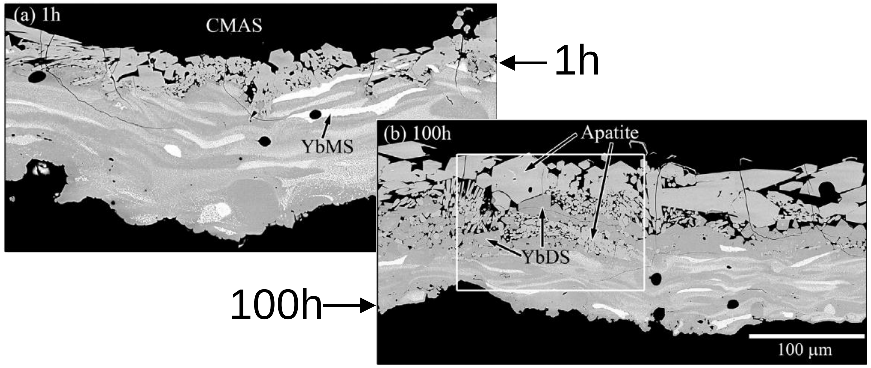
APS $Yb_2Si_2O_7$ (YbDS)
96h,1300C,35 mg/cm^2 CMAS



(a) Well filled with epoxy
(b & c) Light gray: $Ca_2Yb_8(SiO_4)_6O_2$
(b & d) White features near bottom: Yb_2SiO_5

F. Stolzenburg et al, Surf. & Coat. Tech., 284 44-50 (2015)

APS $Yb_2Si_2O_7$ (YbDS)
1300C, 30-35 mg/cm^2 CMAS

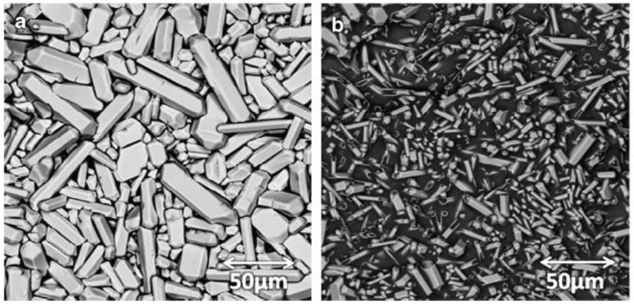


CMAS reacted preferentially with YbMS segregates

CMAS: 33CaO-9MgO-13$AlO_{1.5}$-45SiO_2 (mol%)

- Little or no reaction occurs with YbDS (Stolzenburg)
  - Yb_2O_3 activity of YbDS is lower than YbMS by more than three orders of magnitude (Costa and Jacobson)
  - YbMS should react more readily than YbDS
- Reaction intruded into the interior by the preferential reaction with surface-connected YbMS segregates, leaving peninsulas of less reacted YbDS (Zhao et al.)

Hot Pressed $Y_2Si_2O_7$ (YDS)
1300C and 1500C,40 mg/cm^2 CMAS



Apatite on the surface

CMAS: 35 CaO-10 MgO-7 Al_2O_3–48 SiO_2 (mol%) w/ minor Fe_2O_3 & NiO

Ahlborg and Zhu, Surf and Coat Tech, (2013)

CMAS reactions appear to be influenced by coating composition, microstructure, and CMAS chemistry

Summary of EBC Coated SiC/SiC CMC Engine Field Tests

GE CMC Shroud Engine Tests
Solar Turbines Inc. CMC Combustor liner Engine Tests

Gen 2 (red box) Ox/Ox (green box)

Start Test - End Test	CMC	EBC	Hours/Starts
GE/7FA engine/stage 1 inner shrouds			
Dec. 19, 2002-Aug. 17, 2003 rainbow test, S.Florida (9 CMC shrouds)	HiPerComp® MI prepreg, slurry cast (GRC, HACI, BFG)	Si/mullite+BSAS/BSAS (GRC)	5,366/14
April 17, 2006-End Sept. 2010[a] JEA test, Jacksonville, Florida (96 shrouds)	HiPerComp® MI prepreg (CCP,GRC)	Si/mullite+BSAS/BSAS, Rare Earth silicates (GRC,MP&E)	1,537/497
Solar/Centaur 50S engine/inner (top) and outer (bottom) annular combustor liners			
April 1999-Nov. 2000, Texaco, Baskerville, California	HiNi SiC/BN/SiC MI (ACI) HiNi SiC/PyC/SiC CVI(ACI)	Si/mullite/BSAS (UTRC) Si/mullite+BSAS/BSAS (UTRC)	13,937/61
Aug. 1999-Oct. 2000, Malden Mills, Lawrence, Massachusetts	HiNi SiC/BN/SiC MI (BFG) HiNi SiC/PyC/SiC CVI (ACI)	Si/mullite+BSAS/BSAS (UTRC) Si/mullite+BSAS/BSAS (UTRC)	7,238/159
Nov. 2001-May 2002, Texaco, Bakersfield, California	HiNi SiC/BN/SiC MI (BFG) HiNi SiC/PyC/SiC CVI (ACI)	Si//BSAS (UTRC) Si/mullite+BSAS/BSAS (UTRC)	5,135/43
Aug. 2000-July 2002, Malden Mills, Lawrence, Massachusetts	TyZM/BN/SiC MI (BFG) HiNi/PyC/SiC CVI (HACI)	Si/mullite+BSAS/BSAS (UTRC) Si/mullite+BSAS/BSAS (UTRC)	15,144/92
July 2002-July 2003, Malden Mills, Lawrence, Massachusetts	TyZMI/BN/SiC MI (HACI) TyZMI/BN/SiC MI (HACI)	Si//SAS Si/mullite+SAS/SAS (UTRC)	8,368/32
May 2003-Nov. 2004, ChevronTexaco, Bakersfield, California	HiNi/BN/SiC (DLC/ACI) N720/Al_2O_3 (COIC/SWPC)	Si/mullite/BSAS (UTRC) Aluminosilicate FGI (COIC)	12,582/63
Jan. 2005-Oct. 2006, ChevronTexaco, Bakersfield, California	HiNi/BN/SiC (GE PSC) N720/Al_2O_3 (COIC/SWPC)	Si/mullite+BSAS/BSAS (GRC) Aluminosilicate FGI (COIC)	12,822/46
June 2006-May 2007, Tipton, California	TyZMI/BN/SiC MI (CCP) TyZMI/BN/SiC MI (CCP)	Si/mullite/SAS (UTRC) Si/YS (UTRC)	7,784/43

[a] Marks end of the govt. program; testing was continued under GE in-house effort.

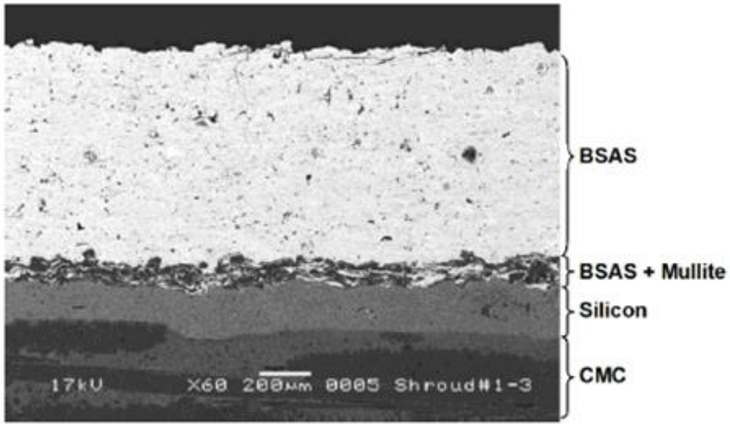
GE Final Report – DOE AMAIGT Program, Dec. 2010

Final Report, Solar Turbines Incorporated, DOE Contract Number DE-FC26-00CH11049, May 28, 2009.

Two Variants of Gen 1EBCs

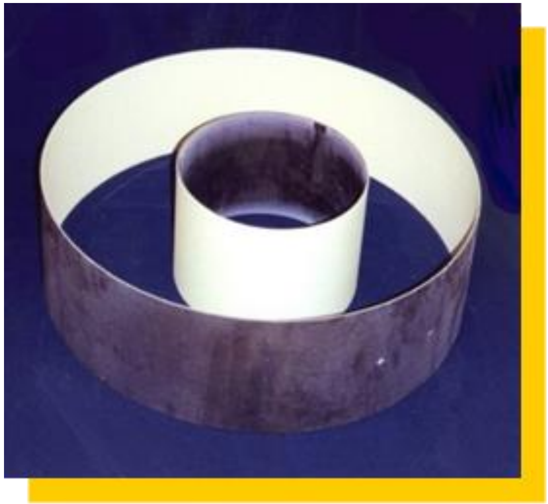
GE Shroud
Total: 6,903h

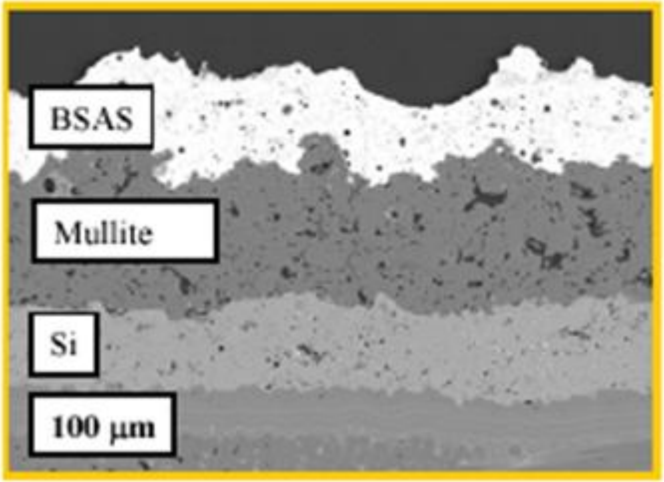
GE Final Report – DOE AMAIGT Program, Dec. 2010



Solar Combustor Liner Set
Total: 83,010h

M. van Roode et al., Transactions of the ASME, J. Eng. Gas Turbines & Power, 129[1],21-30, 2007.



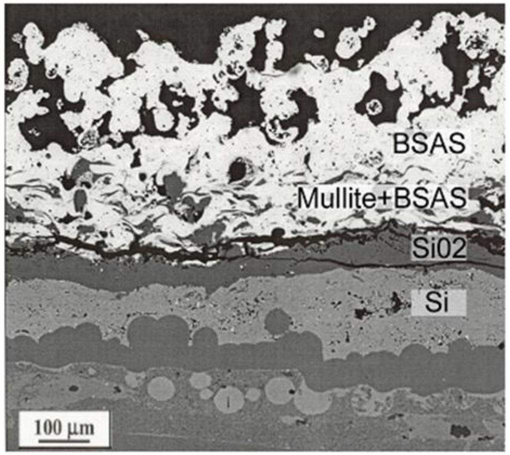


Limit of Gen1 Standard EBC @~1200C: ~ 15,000h

Oxidation-Induced Degradation

15,144-h Solar Combustor Liner Engine Test

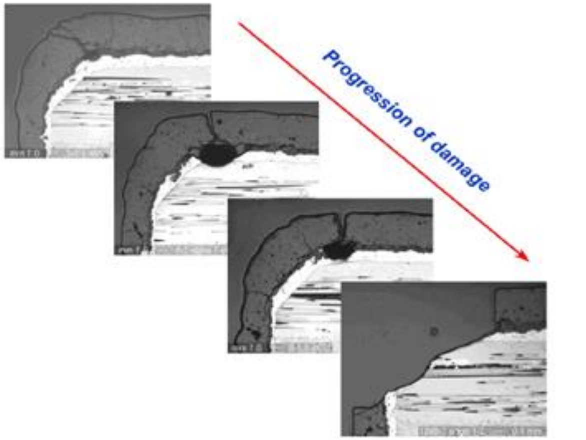
- Ingress of water vapor through EBC
- Bond coat oxidation: SiO_2 TGO formation
  - TGO has different CTE from EBC layers
- Horizontal cracks at Si-SiO_2/mullite+BSAS interface
  - Thermal cycles aggravate crack formation
  - Cracks may also go vertically into the Si bond coat



J. Kimmel et al., ASME paper GT2003-38920, ASME TURBO EXPO, Atlanta, GA, USA, June 16-19, 2003.

5,366-h GE "rainbow" test – progression of degradation

- Edge EBC is more porous; cracks form at surface
- Pathway for ingress of water vapor
- Bond coat oxidation, SiO_2 TGO formation
- Lateral crack formation ->debonding, spallation

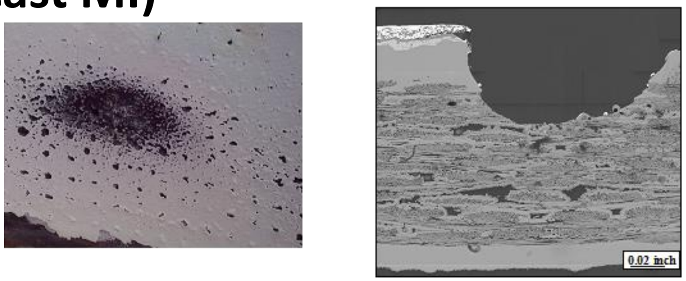


GE Final Report – DOE AMAIGT Program, Dec. 2010

Recession-Induced Degradation

13,937-h Solar Combustor Liner Engine Test

- **Tooling bumps cause EBC processing defects (Slurry cast MI)**
- **Pathway for ingress of water vapor in EBC**
- **Rapid recession of CMC, creating craters, where EBC is breached**

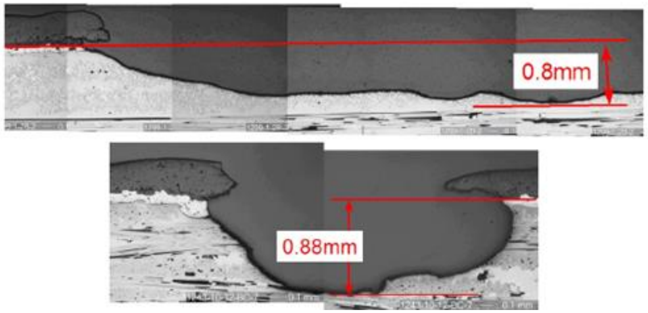


(a) (b)

Final Report Phase III, Solar Turbines Incorporated, October 1, 1996 – September 30, 2001, DOE Contract DE-AC02-92CE40960, September 30, 2003.

5,366-h GE "rainbow" test

- **Slurry cast MI showed similar behavior to Solar Turbines' liner shown above**

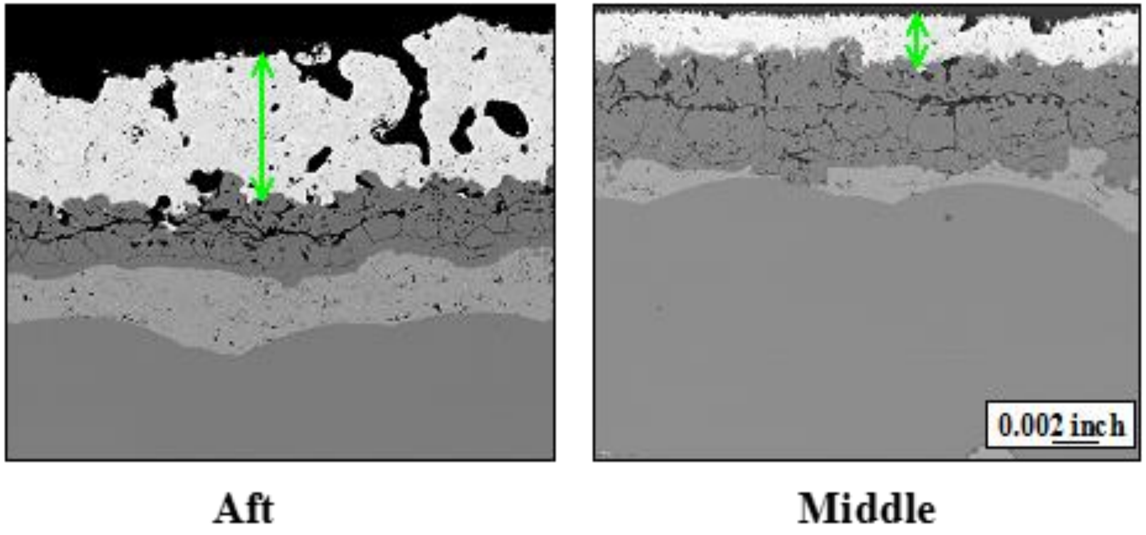


GE Final Report – DOE AMAIGT Program, Dec. 2010

Combination of Recession and Oxidation

13,937-h Solar Combustor Liner Engine Test

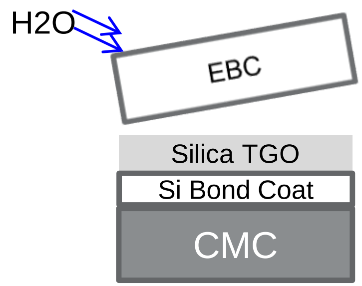
- **Recession of BSAS top layer**
- **Recession more severe in hot middle section**
- **Severe oxidation of Si bond coat**



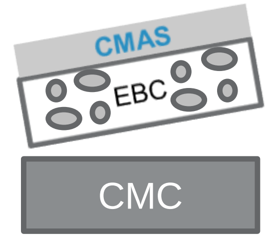
M. van Roode et al., Transactions of the ASME, J. Eng. Gas Turbines & Power, 129[1],21-30, 2007.

Final Report Phase III, Solar Turbines Incorporated, October 1, 1996 – September 30, 2001, DOE Contract DE-AC02-92CE40960, September 30, 2003.

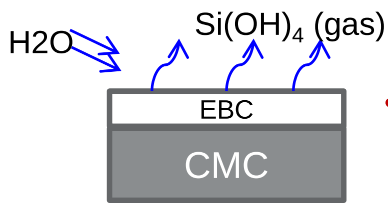
EBC Failure Modes



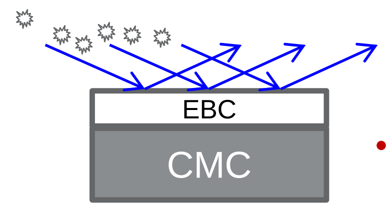
- Steam oxidation



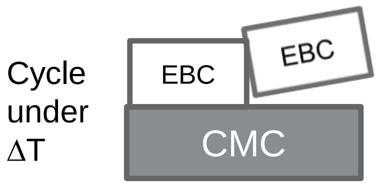
- CMAS degradation



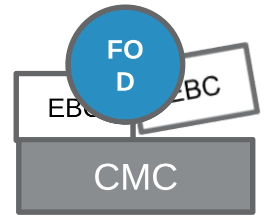
- Recession by water vapor



- Erosion



- Thermal fatigue
- Thermo-mechanical fatigue



- FOD

Synergies between failure modes lead to the ultimate EBC failure

- **Combination of empirical and mechanism-based life modeling**
- **Engine test is the ultimate validation**

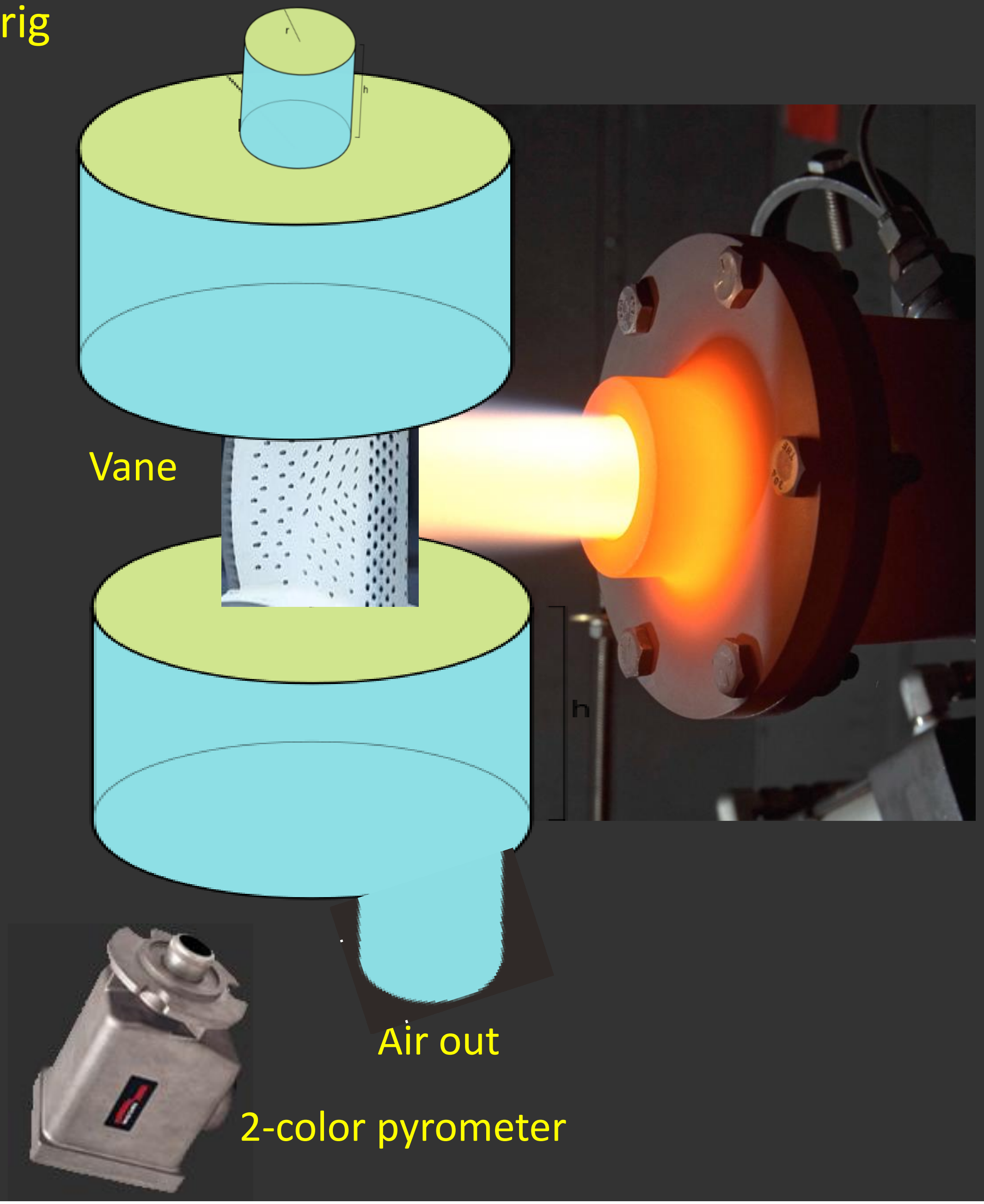
K. N. Lee, "Environmental Barrier Coatings for CMC's"; in *Ceramic Matrix Composites*, Wiley, New York (2015)

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**
- **The only test vehicle that has all key variables is an engine**

Vane/Blade Airfoil Fixture for NG Burner rig



Conclusion

- CMCs are a game changer for next generation gas turbine engines due to high temperature capability
  - Improves SFC, thrust, and emission
  - EBC is an enabling technology for CMCs

- The first and second Gen EBCs developed in mid 1990s- early 2000s laid the foundations for current EBCs
  - A number of rig and engine tests have been successfully completed

- The introduction of CMCs represents significant challenges as failure of the EBC means significant reduction in component life
  - A reliable EBC life model is required
  - Testing methods relevant to engine conditions is critical to validate life model