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Environmental Barrier Coatings for Ceramic Matrix Composites – An Overview

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Progression of High Temperature Materials Capability



Improving efficiency and reducing emissions are main driving forces behind ever increasing demands for higher gas turbine inlet temperatures (TIT).
CMCs can provide a step change in materials capability.



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
- \searrow Reduced NOx and CO emissions

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





Commercialization Challenges

Design of Components

- Adequate attachment compliance to account for thermal expansion mismatch
- Adequate part sealing to realize cooling air flow and leakage goals

Life of MI-CMC Components

- Industrial applications require tens of thousands of hours
- Damage propagation after initial damage
- Requires minimization of processing defects in components

Coating Life

- Required minimum of 24,000 hours
- Damage propagation after FOD or otherwise localized damage

Component Cost

Target is 1 - 2 times the metallic component cost

K. L. Luthra, Ceramic Leadership Summit 2011



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)





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.



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Moving Forward

- FAA CLEEN Program accelerating commercial CMC technology development
 - Aircraft component certification beginning in 2016
- FAA is exploring potential CMC certification issues with industry
- CMH-17 Handbook is a resource
 - Lessons learned in PMC certification apply
 - All stakeholders may contribute
- Building consensus for key tasks/timeframes





Representative Non-oxide CMC Systems with Constituents

Fabrication	Fiber	Matrix	Interface	Compositions
Process				
CVI	SiC (~40%)	SiC (60%)	Pyrocarbon (PyC)	SiC/PyC/SiC,
			Boron Nitride (BN)	SiC/BN/SiC,
				SiC/PyC,BN/SiC
MI (prepreg)	SiC(20-25%)	SiC(70-63%)	BN,Si ₃ N ₄ (8-10%)	SiC/BN/SiC
MI (slurry cast)	SiC(35%)	CVD SiC(25%),	BN,SiC(6%)	SiC/BN,SiC/SiC
		SiC slurry cast		
		(16%), Si(12%)		
PIP	C,SiC(40%)	SiNC,SiC,	PyC,BN	SiC/BN/SiC, C/SiC
		SiC+ Si ₃ N ₄		

CVI: Chemical Vapor Infiltration, MI; Melt Infiltration, PIP: Polymer Impregnation and Pyrolysis, 2D/3D: 2/3-dimensional,

J. Lamon, et al., "Chemical Vapor Infiltrated SiC/SiC Composites (CVI SiC/SiC)," in Handbook of Ceramic Composites, 2005.

J.A. DiCarlo et al., "SiC/SiC Composites for 1200°C and Above," in Handbook of Ceramic Composites, 2005..

G.S. Corman et al., "Silicon Melt Infiltrated Ceramic Composites (HiPerComp™)," in Handbook of Ceramic Composites, 2005.

A. Szweda et al., "Ceramic Matrix Composites for Gas Turbine Applications," Volume II of Progress In Ceramic Gas Turbine Development, ASME Press, New York, 2003.

J.A. DiCarlo et al., "Ceramic Composite Development for Gas Turbine Engine Hot Section Components," ASME Paper GT2006-90151, ASME TURBO EXPO 2006.



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GE's Melt Infiltrated, Prepreg CMC Process



K. L. Luthra, Ceramic Leadership Summit 2011



Standard Slurry Cast Melt-Infiltrated (MI) 2D&3D Woven Composites



G. N. Morscher et al., Composites at Lake Louise, Canada 2007



CMC Microstructure

Microstructure of Prepreg MI Composites



K. L. Luthra, Ceramic Leadership Summit 2011

Slurry Cast MI Composites



G. N. Morscher et al., Composites at Lake Louise, Canada 2007



Degradation of SiC/SiC CMCs

- Major application: Hot section components of advanced gas turbines
 - Combustor liners, nozzles, shrouds, rotors, blades, etc.
- Water vapor degradation in hot section NASA Model



R = rate (μ m/h) = 465 exp(-111 kJ/mole/RT) v^{1/2} P_{H20}² P_{total}^{-1/2}

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



SiC/SiC CMC combustor liner after 1048h of Solar engine testing





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.



Effect of Water Vapor on SiC Degradation¹³



Stagnant water vapor – Oxidation of Si High velocity water vapor – Recession of SiC



Calculations Based on *"Robinson and Smialek, J. Am. Ceram. Soc.*, 82 [7] 1817–25 (1999)"

Calculations based on "B. E. Deal and A. S. Grove, J. Appl. Phys., 36 [12] 377078 (1965)" High oxidation rate in water vapor is due

to high permeability of water vapor in SiO_2 (~10 times larger than that of oxygen) Several mils of recession per 100h is projected at 1400°C and 7 atm



Environmental Barrier Coating (EBC)

- An external coating to isolate CMC from water vapor
- EBC is an enabling technology for CMC



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



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EBC Test Rigs

Rig	Typical Test Condition	Capability
Steam thermal cycle rig	$P(H_2O) = up \text{ to } 1 \text{ atm}$	Steam oxidation test
(NASA Glenn)	v = a few cm/s	
	P _{total} = 1 atm	
High steam burner rig	$P(H_2O) \sim 0.3 \text{ atm},$	Recession test
(Fraunhofer, Dresden)	v ~ 100m/s	
	P _{total} = 1 atm	
High pressure burner rig	$P(H_2O) \sim 0.6 atm$	Steam oxidation test
(NASA Glenn)	v ~ 24 m/s	Recession test
	P _{total} ~ 6 atm	
Steam Jet Rig	$P(H_2O) = 1 \text{ atm},$	Recession test
(Teledyne)	v = up to ~300 m/s	
	P _{total} = 1 atm	
High heat flux laser rig	$P(H_2O) = ambient air,$	Thermal fatigue test
(NASA Glenn)	v = zero, P _{total} = 1 atm	

The only test vehicle that includes all the variables is an engine or an expensive combustor test rig, which means real validation can only occur in an engine or an expensive combustor rig

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



Gen 1 Environmental Barrier Coatings (EBCs)



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

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

- 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 standard Gen 1 EBC deposited by plasma spraying
 - BSAS: $(1-xBaO \cdot xSrO \cdot Al_2O_3 \cdot 2SiO_2, 0 \le x \le 1$: 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 SiO₂ TGO
 - Mullite: intermediate coat that separates BSAS from SiO₂ TGO
 - SiO₂ reacts with BSAS to form eutectic melt at T \sim 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).

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Upper Temperature Limit of Gen 1 EBC

- Long-term durability at >~1300°C is an issue
- Glass formation due to BSAS-silica eutectic reaction
- Glass-silica TGO reaction accelerates oxidation rate



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



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1000-1h Cycles @1316°C, 90% H₂O-Bal. O₂

Gen 2 EBCs

- NASA Ultra Efficient Energy Technology (UEET) program Early 2000's
- EBC surface temperature goal: 1482°C (2700°F)
- EBC/CMC interface temperature goal: 1316°C (2400°F)
- Candidate materials: Low CTE Rare Earth silicates
 - Monosilicates: RE₂SiO₅ and Disilicates: RE₂Si₂O₇
 - RE = yttrium (Y), ytterbium (Yb), scandium (Sc), lutetium (Lu), etc.
- higher H₂O stability and m.p. compared to BSAS, CTE match with CMC

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



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

Cross section of Si/mullite/Yb₂SiO₅-coated CMC after 1000h with 1h cycles at T=1380°C (2516°F), $pH_2O = 0.9$ atm, $P_{TOTAL} = 1$ atm, and v = 2.2 cm/s



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

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



Silica Activity of Rare Earth Silicates at 1377C 19

	RE = Y	RE = Yb		
a(SiO ₂) _{RE2Si2O7}	0.281	0.194		
a(SiO ₂) _{RE2SiO5}	0.000804	0.00298		
$a(SiO_2)_{RE2Si2O7} / a(SiO_2)_{RE2SiO5}$	350	65		

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G. Costa and N.S. Jacobson, ICACC, Daytona Beach, Jan 2015



Phase Equilibria Diagrams, **CD-ROM Database Version** 2.1, American Ceramic Society, Westerville, OH, 1998.



Recession of RE disilicates

$\begin{aligned} \mathsf{RE}_2\mathsf{Si}_2\mathsf{O}_7 + 2\mathsf{H}_2\mathsf{O}\ (\mathsf{g}) & \rightarrow \mathsf{RE}_2\mathsf{Si}\mathsf{O}_5 + \mathsf{Si}(\mathsf{OH})_4\ (\mathsf{g}) \\ \mathsf{RE}_2\mathsf{Si}\mathsf{O}_5 + 2\mathsf{H}_2\mathsf{O}\ (\mathsf{g}) & \rightarrow \mathsf{RE}_2\mathsf{O}_3 + \mathsf{Si}(\mathsf{OH})_4\ (\mathsf{g}) \end{aligned}$



High velocity burner rig test: 1450°C, 100 m/s, P(H₂O)=0.27 atm, P(total)=1 atm

- Volatilization of Yb₂Si₂O₇ results inYb₂SiO₅ surface layer (~224h test)
- Monosilicate layer slows down volatility

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



Summary of EBC Coated SiC/SiC CMC Engine Field Tests

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

Start Test - End Test	CMC	EBC	Hours/Starts			
GE/7FA engine/stage 1 inner shrouds						
Dec. 19, 2002-Aug. 17, 2003	HiPerComp® MI prepreg,	Si/mullite+BSAS/BSAS (GRC)	5,366/14			
rainbow test, S.Florida	slurry cast					
(9 CMC shrouds)	(GRC, HACI, BFG)					
April 17, 2006-End Sept. 2010a	HiPerComp® MI prepreg	Si/mullite+BSAS/BSAS,	1,537/497			
JEA test, Jacksonville, Florida	(CCP,GRC)	Rare Earth silicates (GRC,MP&E)				
(96 shrouds)						
Solar/Centaur 50S engine/inner	(top) and outer (bottom) annular o	combustor liners				
April 1999-Nov. 2000, Texaco,	HiNi SiC/BN/SiC MI (ACI)	Si/mullite/BSAS (UTRC)	13,937/61			
Baskerville, California	HiNi SiC/PyC/SiC CVI(ACI)	Si/mullite+BSAS/BSAS (UTRC)				
Aug. 1999-Oct. 2000, Malden	HiNi SiC/BN/SiC MI (BFG)	Si/mullite+BSAS/BSAS (UTRC)	7,238/159			
Mills, Lawrence, Massachusetts	HiNi SiC/PyC/SiC CVI (ACI)	Si/mullite+BSAS/BSAS (UTRC)				
Nov. 2001-May 2002, Texaco,	HiNi SiC/BN/SiC MI (BFG)	Si//BSAS (UTRC)	5,135/43			
Bakersfield, California	HiNi SiC/PyC/SiC CVI (ACI)	Si/mullite+BSAS/BSAS (UTRC)		C:		
Aug. 2000-July 2002, Malden	TyZM/BN/SiC MI (BFG)	Si/mullite+BSAS/BSAS (UTRC)	15,144/92			
Mills, Lawrence, Massachusetts	HiNi/PyC/SiC CVI (HACI)	Si/mullite+BSAS/BSAS (UTRC)		Τι		
July 2002-July 2003, Malden	TyZMI/BN/SiC MI (HACI)	Si//SAS	8,368/32	D		
Mills, Lawrence, Massachusetts	TyZMI/BN/SiC MI (HACI)	Si/mullite+SAS/SAS (UTRC)		D		
May 2003-Nov. 2004,	HiNi/BN/SiC (DLC/ACI)	Si/mullite/BSAS (UTRC)	12,582/63			
ChevronTexaco, Bakersfield,	N720/A12O3 (COIC/SWPC)	Aluminosilicate FGI (COIC)		IV		
California						
Jan. 2005-Oct. 2006,	HiNi/BN/SiC (GE PSC)	Si/mullite+BSAS/BSAS (GRC)	12,822/46			
ChevronTexaco, Bakersfield,	N720/Al ₂ O ₃ (COIC/SWPC)	Aluminosilicate FGI (COIC)				
California						
June 2006-May 2007, Tipton,	TyZMI/BN/SiC MI (CCP)	Si/mullite/SAS (UTRC)	7,784/43			
California	TyZMI/BN/SiC MI (CCP)	Si/YS (UTRC)				

GE Final Report – DOE AMAIGT Program, Dec. 2010

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

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



Two Variants of Gen 1EBCs



GE Shroud Total: 6,903h

GE Final Report – DOE AMAIGT Program, Dec. 2010





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



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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.

Degradation of Gen 1 EBC Coated SiC/SiC CMCs

15,144-h Solar Combustor Liner Engine Test

- Pathway for ingress of water vapor (e.g. cracks in EBC)
- Bond coat oxidation: SiO₂ TGO formation
 - TGO has different CTE from EBC layers
- Horizontal cracks at Si-SiO₂/mullite+BSAS interface
 - Hypothesis: transient thermal stresses+bond coat oxidation
 - Many thermal cycles aggravate crack formation
 - Cracks may also go vertically into the Si bond coat

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, SiO₂ TGO formation
- Lateral crack formation ->debonding, spallation



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

GE Final Report – DOE AMAIGT Program, Dec. 2010



Degradation of Gen 1 EBC Coated SiC/SiC CMCs

13,937-h Solar Combustor Liner Engine Test

- Pinhole formation from CMC fabrication tooling bumps Slurry cast CMC
- Tooling bumps cause EBC processing defects
- Pathway for ingress of water vapor in EBC and CMC
- Pinholes extend 1.25-1.50 mm (i.e. into EBC)





(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

- Pinhole formation from CMC fabrication tooling bumps Slurry cast CMC
- Pathway for ingress of water vapor
- EBC degradation undercutting of EBC
- Rapid degradation of CMC when EBC is breached





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GE Final Report – DOE AMAIGT Program, Dec. 2010

Degradation of Gen.1 EBC Coated SiC/SiC CMCs

13,937-h Solar Combustor Liner Engine Test

- Edge defect, present in thermal diffusivity NDE
- Present after CMC fab., increased after EBC deposition
- Defect pattern duplicated in NDE after test
- Defect pattern also in post-test digital photograph

13,937-h Solar Combustor Liner Engine Test

- Recession of BSAS top layer
- Recession more severe in hot middle section
- Recession less severe in cool aft section

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.





Aft

Middle

0.002 inch





Gen 2 EBCs - Field Test Data

GE 1,537-h shroud engine test

GE Final Report – DOE AMAIGT Program, Dec. 2010

2001, DOE Contract DE-AC02-92CE40960, September 30, 2003.

- Boroscope inspection: 1122h/169 start/stops
- Complete edge-to-edge spall
- Post coating heat treat at 1300°C gives desired C-polymorph
- At op. temperature of 1200°C: conversion to D-polymorph
 - Grain growth, expansion anisotropy -> cracking EBC and EBC spallation
- Remedy: composition modification to prevent D-phase formation
 - Verified by steam rig test

Solar 7,784-h combustor engine test

- Some discoloration at aft edge, minor edge spallation at fore edge-otherwise effective
 Final Report Phase III, Solar Turbines Incorporated, October 1, 1996 – September 30,
- Published engine data on Gen 2 EBCs very limited
- Next Gen EBCs under development –1480-1650°C (2700-3000°F) mostly proprietary





CMAS Attack on EBCs

- Particulates (sand, volcanic ash, other silicate) ingested by air-breathing turbine engines
- T>~1200°C: forms glassy deposits of calcium-magnesium-aluminosilicate (CMAS) with other minor oxides
- Molten CMAS deposits adhere to EBC-coated CMC components, cause compositional and property degradation
- Gen 1 EBC <u>BSAS is not CMAS resistant</u>
- Model CMAS system: 33CaO-9MgO-13AlO_{1.5}-45SiO₂ + BSAS -> dissolves both hexacelsian and celsian phases and reprecipitates thermodynamically stable celsian phase
- Penetrates the BSAS layer at 1300°C
- CMAS reacted with BSAS also affects the EBC residual stress state negatively
- Gen 2 EBCs (Yttrium silicates, ytterbium silicates) <u>insufficiently resistant to CMAS</u> <u>penetration</u>
- CMAS mitigation needs to be developed Pyrochlore (e.g. Gd₂Zr₂O₇) shows promise , but mechanical properties are inferior to RE-silicates and large CTE mismatch
- Research for CMAS mitigation is ongoing

B. Harder et al., J. Am. Ceram. Soc. 94 (2011)

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

K. Grant et al., Surf & Coat Tech 201 (2007)

F. Stolzenburg et al, Surface and Coatings Technology, 284 44-50 (2015)



EBC Failure Modes

- Cyclic Steam Oxidation
- Recession by Water Vapor
- Stress Cracking
- CMAS Degradation
- Erosion
- Foreign Object Damage (FOD)

Synergies between failure modes are likely to lead to the ultimate EBC failure

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



Summary

- SiC/SiC CMCs for advanced power generation hot section components ~5,000h life limit
 - Water vapor attacks CMC to form volatile components
 - CMC consumption by water vapor recession leads to component thinning, property degradation. Component loses functionality and becomes life-limited
- Gen 1 EBCs: Si/mullite+BSAS/BSAS increase SiC/SiC CMC life to ~15,000h
- A number of EBC issues have surfaced in CMC/EBC component field testing by GE and Solar Turbines Inc. under US government programs: EBC degradation through various mechanisms leads to pathways for water vapor ingress, bond coat oxidation, cracking at the bond coat/intermediate layer interface, EBC debonding and spallation. BSAS recession is additionally life-limiting
- Gen 2 EBCs focuses on Rare Earth monosilicates and disilicates which have lower volatilities under water vapor conditions. Lab and rig data and limited engine test data indicate improved performance compared to Gen 1 EBCs, but more development and validation will be required.
- CMAS formation in air-breathing turbines results in degradation of EBC which lose their effectiveness. A fully CMAS-resistant EBC has yet to be demonstrated.



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 a significant challenges as failure of the EBC means significant reduction in component life
 Development of a reliable EBC life model required

