

Department of Chemical Engineering and Materials Science

Abradable Sealing Materials for Emerging IGCC-Based Turbine Systems

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> 2016 University Turbine Systems Research Workshop Blacksburg, VA: November 2nd, 2016

DOE NETL Grant # DE-FE0011929 Project Manager: Dr. Robin Ames



Clearance Control is Critical to Obtaining High Efficiency



Abradable Materials for Clearance Control

- To reduce rotor-shroud clearance (an extra gap of .005" between the rotating blades and the engine casing can increase fuel consumption by as much as 0.5%).
 - Lower consumption of engine fuel
 - Improves engine-efficiency
- To achieve high temperature stability, low thermal conductivity, chemical stability, and erosion resistance at operating temperatures



Active Cooling Control for Clearance Control



R.E. Chupp, et al., Journal of Propulsion and Power Vol. 22, No. 2, March–April 2006

Abradable Seal Coatings



Sulzer Metco: SF-0015.0, July 2012

Abradable Seal Coatings

Schematic of a section through a gas turbine engine high pressure stage, showing where an abradable coating is used and how gas leaks through this seal leads to performance loss.



D. Sporer, S. Wilson and M. Dorfman, "Ceramics for Abradable Shroud Seal Applications." *Proceedings of the* 33rd *International Conference on Advanced Ceramics and Composites, volume 3, 2009,*

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Potential Benefits of Abradables for Clearance Control

- Ideally, turbine/housing distance should be kept close to zero.
- Blade movement due to force and high heat would cause rubbing with housing
- Abradable designed to deform to form "trenches" where blades contact
- Theoretical efficiency increase of 1% or saves .39 trillion cubic feet of natural gas per year (calculated from IER estimate 2013)



Sulzer Metco, Solutions Flash Improve Efficiency and Reduce Emissions with Abradable Coatings for Steam Turbines, SF-0016.0, July 2012 http://instituteforenergyresearch.org/topics/encyclopedia/fossil-fuels/

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Abradable Materials

- Metal matrix (T<700 degree C)
- Ceramic materials (T>700 degree C)
- Lubricant/dislocator agent (hBN)
- Porous materials
- Ni/Graphite and AlSi/hBN for compressor
- CoNiCrAlY/hBN/Polyester for LP turbine sections of engines.
- YSZ, spinel or similar ceramics for HPT sections



Figure 1: Cross section of a typical abradable coating (dark phase: porosity, grey phase: bentonite, bright phase: NiCrAl metal matrix)

What is a Ceramic Abradable Coating?

- Abradable coatings in turbines are generally made of a ceramic matrix with a fugitive phase and a release agent.
- Alternative release agent phases proposed are LaPO₄ and Spinels as a replacement for the whole system or in small concentration in YSZ.
- Mechanisms of mechanical degradation and microstructural evolution in corrosive and wet environments are not well documented.



Schematic representation of the abradable mechanism in service.

- Sulzer Metco, Solutions Flash Improve Efficiency and Reduce Emissions with Abradable Coatings for Steam Turbines, SF-0016.0, July 2012
- Ebert S, Mücke R, Mack D, Vaßen R, Stöver D, Wobst T, and Gebhard S, J. Eur. Ceram Soc. 33, (December 2013): 3335–43.
- Lyalin A, Nakayama A, Uosaki K, and Taketsugu T. *PCCP* 15, (January 31, 2013): 2809–20.

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Abradability vs. Erosion – A Balancing Act (and Evolving)



 Concerns include: excessive blade-tip wear, macrorupture in coatings, transfer of materials from blade to shroud.

Abradability vs. Erosion – A Balancing Act (and Evolving)

- Housing coating must be 'soft' enough to wear away during startup.
- Must also be hard enough to not be eroded by debris

Too Soft

Too Hard



Heavy coating rupture after initial blade material transfer



Coating rupture



Slight coating rupture mixed with cutting and some blade material transfer



Mixed coating rupture and blade material transfer



Heavy blade material transfer

Sulzer Metco: SF-0015.0, July 2012

Ideal Wear Patterns – Tipped and Non-Tipped Blades

Ideal Wear Tracks **Un-tipped Blades** cBN-tipped Blades



cBN Abrasive Coating: As-processed



cBN Abrasive Coating: Oxidized

Sulzer Metco: SF-0015.0, July 2012

Scrinzi, E. et al. Development of New Abradable/Abrasive Sealing Systems for Clearance Control in Gas Turbines. ASME 2013 Proceedings.

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The Role of Porosity on Abradability of Current Coatings

Porosity is optimized for reduced blade wear – but at the cost of erosion resistance.



Sulzer Metco: SF-0015.0, July 2012

Abradability vs. Erosion – A Balancing Act (and Evolving)



Sulzer Metco: SF-0015.0, July 2012

Motivation

Are prominent degradation modes for turbine hot-section materials exacerbated through the use of alternative fuels?

- High-Hydrogen Content (HHC) fuels may result in substantial increases in the water vapor content.
- Alternative fuels may introduce unique impurities that play a role in deposit-induced corrosion.

What are the mechanisms by which elevated water vapor contents may affect the durability and degradation of hot-section materials?

Project Overview

- Reducing the gap between rotating and stationary parts in gas turbine engines, and mitigating gas leakage via these paths, can significantly increase the performance and attendant efficiency. One approach to maintaining a minimum gap is to use abradable coatings on the stationary shroud components as seals.
 - Abradable coatings must be able to withstand high temperature oxidation, thermal cycling, and erosion, while providing optimal controlled abrasion and associated shape retention.
 - Syngas and high-hydrogen-content (HHC) fired turbines has shown that the stability of hot-section materials may be substantially altered due to characteristic changes in the combustion by-products (partial pressures of water vapor, etc.) as well as characteristic impurities and particulate matter entrained in the fuel.

Project Objectives

- Investigate the impacts of coal-derived syngas combustion environments on the performance, durability and degradation of existing abradable coatings used on turbine shroud structures.
- Assess the potential of alternative materials sets for improving performance of hot-section abradable seals in IGCC-based gas turbine power plants.
- Derive a mechanisms-based understanding of factors controlling the performance and degradation of abradable seals used in the hightemperature turbine sections of gas turbine engines in relation to emerging IGCC-based combustion environments, and evaluate the potential of alternative materials as abradable seal coatings – ultimately with the goal of developing a knowledge base upon which the design of coatings that retain optimal sealing characteristics and are more resistant to the observed wear/attack mechanisms.
- Educate the next generation of scientists and engineers trained in materials design for advanced turbine systems.

Outline

The research community has developed a mechanistic understanding of many (sometimes synergistic) prominent degradation modes. How are these mechanisms influenced or modified by elevated water vapor content service conditions?

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- Bond coat oxidation and TGO formation, and volatilization issues
- Phase evolution of the TBC top coat – loss of beneficial t' phase, and attendant monoclinic phase development



A.G. Evans, D.R. Clarke and C.G. Levi (2008) Journal of the European Ceramic Society, 28, 1405-1419.

Adapted from A.G. Evans (2007)

IGCC Process – High Hydrogen Content Fuels



Predicted Increased Water Content in Power

"Plug In, Charge Up, Drive Off" by Douglas L. Smith (calteches.library.caltech.edu/709/2/Drive.pdf)

		Gas Composition								
	Flow Segment ID	Units	GE Case 2	CoP Case 4	Shell Case 6	Range				
		H ₂	91%	76%	86%	76-91%				
		H ₂ O	0%	14%	3%	0- 4%				
	Clean High-H ₂ Syngas	со	2%	1%	3%	1-3%				
	-)g	CO ₂	4%	2%	2%	2-4%				
		Ar	1%	1%	1%	1%				
		N2	1%	1%	5%	1-5%				
		N ₂	75%	74%	75%	74-75%				
	Turt ine	H ₂ O	12%	14%	13%	12 <mark>14%</mark>				
	LAIN	O ₂	11%	10%	11%	10-11%				
		CO ₂	1%	1%	1%	1%				
		Ar	1%	1%	1%	1%				

- 15-18 vol% H₂O in turbine exhaust when using dry, high-H₂ syngas fuel
- If steam is used for NO_x suppression, H₂O could run as high as <u>30%</u>
- Represents a 2-4x increase over H₂O in natural gas combustion (5-7%)

White, Ames and Burke. National Energy Technology Laboratory (NETL) Report, 2013.

Spectrum of Possibilities for Accelerated Degradation



Accelerated Degradation in High pH₂0 Environments

High Temp Aging of YSZ TBCs – Dependence on pH₂O ?

- Yttria content puts the 8YSZ in the tetragonal + cubic phase field
- *t'* phase will eventually decompose to the equilibrium tetragonal and cubic phases
- Rate is dictated by aging time and temperature
- Can normalize the influence of time and temperature by the use of the Larson-Miller or the Hollomon-Jaffe parameter of the form:

 $T[C + \ln(t)]$



Redrawn from Levi *et al., J. Am. Ceram. Soc.*, 96 [1] 290-298 (2013)

Prior Studies of Elevated Temp Aging of YSZ



Lipkin *et al., J. Am. Ceram.* Soc., 96 [1] 290-298 (2013)

How does a humid environment influence the destabilization of the t'phase during aging?

Isothermal Aging Under Controlled pH₂O Conditions







- Water tank temperature determines vol%
 H₂O via gas-liquid equilibrium exchange.
- For 0% H₂O, the water tank is bypassed completely.
- Exposed to dry or humid aging (30 vol%) in a controlled environment.
- Air plasma spray, 8 wt.% Yttria-Stabilized Zirconia.
- All test specimens cut from the same sample plate.

Aging Protocols and Materials Characterization



Post-test characterization by XRD, Raman, XPS and microstructural analysis via TEM/STEM imaging.

Rietveld refinement of XRD spectra to quantify evolving phase fractions. The refinement employed a four phase model (t', tetragonal, cubic and monoclinic)

XRD Analysis of Aging to LMP = 15.2k (88 hours exposure)



- XRD peak positions gradually shift from t' toward tetragonal and cubic positions.
- Indicates a range of lattice parameters as the *t*' is destabilized.
- No significant difference observed between 'dry' and 'humid' conditions.

Further Aging to LMP = 18.2k (570 hours exposure)



Raman Spectroscopy Analysis Corroborates XRD Results



- For dry aging, the monoclinic modes not observed until LMP = 18.2 K (570 h)
- For humid aging, the monoclinic modes appear as soon as 15.9 K (140 h)

Quantitative Phase Fraction Analysis of XRD Results

- Full-pattern Rietveld fitting
- Examples of the peak deconvolution shown
- Selected peaks corresponding to the t', tetragonal and cubic phases
- Weighted profile R value (a metric for quality of fit) was consistently less than 7%



Average Phase Fractions at LMP = 15.2k (88 hours exposure)



Accelerated decomposition of the t' phase, with associated formation of the monoclinic phase.

Evolution of the Phase Fractions with Exposure Time



Evolution of the Phase Fractions with Exposure Time

- In early stages of evolution, coherency strains prevent Y-rich and Y-lean phases from relaxing to equilibrium lattice structures; system appears as single-phase t'
- Interfacial coherency provides a driving force for coarsening; a wide variation in tetragonality develops with an associated variation in lattice parameters



Krogstad *et al., J. Am. Ceram. Soc.*,94 [S1] S168-S177 (2011)

Evolution of the Phase Fractions with Exposure Time

- Continued coarsening results in larger fractions of the system relaxing to equilibrium lattice parameters, and a sharpening of the strain gradient at domain boundaries
- Misfit dislocations are introduced to relieve coherency strains, allowing further development of the Y-lean (tetragonal) and Yrich (cubic) phases. The Ylean domains are now transformable to monoclinic



Krogstad *et al., J. Am. Ceram.* Soc.,94 [S1] S168-S177 (2011)

Potential Mechanism for pH₂O Dependence

Clarke et al., J. Am. Ceram. Soc., 92 [9] 1901-1920 (2009)

 $2H^+ + O^{2-} + V_O^{\bullet\bullet} \xleftarrow{ZrO_2} 2H^+ + O_O^x$ $H_2O + V_0^{\bullet} + O_0^X \leftarrow ZrO_2 \rightarrow 2(OH)_0^{\bullet}$

Prinz et al., Chem. Mater., 22 5366-5370 (2010)

 $Y_2O_2 \leftarrow ZrO_2 \rightarrow 2Y'_{zr} + 3O_0^x + V_0^{II}$

 $H_2O + Y_2O_3 \leftarrow ZrO_2 \rightarrow 2Y'_{Zr} + 2O_O^x + 2(OH)_O^i$



Dissociation of water, and incorporation of protons and oxygen ions, may be accommodated through changes in the defect chemistry.

 $H_0 \rightarrow 2 H^+ + 0^=$

Rate Controlling Defects & Potential Interactions w/ Water Species



Lattice diffusion kinetics in Y_2O_3 -stabilized cubic ZrO_2 single crystals: A dislocation loop annealing study

F. R. Chien & A. H. Heuer

To cite this article: F. R. Chien & A. H. Heuer (1996) Lattice diffusion kinetics in Y_2O_3 -stabilized cubic ZrO₂ single crystals: A dislocation loop annealing study, Philosophical Magazine A, 73:3, 681-697, DOI: <u>10.1080/01418619608242990</u>

- Studied cation diffusion through measurements of shrinkage rates of prismatic dislocation loops introduced through plastic deformation.
- Noted that cation diffusion in 18 mol% YSZ is 15 times slower than in 9.4 mol% YSZ; however, activation energies for both materials nearly identical.
- Studies suggested that a charged vacancy cluster, the divacancy: $(V_o^{ii} V_{Zr}^{m})$ is rate controlling.
- Furthermore, the lower cation diffusivities of the higher-solute compositions are attributed to the higher density of yttrium-containing trapping and blocking centers: $(Y'_{zr} V_o^{ii})^i$ and Y'_{zr} respectively.

Raman Consistent w/ Relaxing of Interface Coherency Strain



Peak fitting of the A_{1g} mode shows peak shifting in both environments

- Indicates a continuous change in the lattice parameters
- Peak shifts faster for humid-aging condition

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Confirmation of High Temp Effect (not LTD Artifact)



Structural Verification of Accelerated Coarsening/Aging

- Previous work investigated the microstructure of aged APS 8YSZ
- Dark-field images used to highlight the modulated structure
- EDX in the TEM used to determine the Y content in the domains
- SAD patterns used to determine the local phases



Krogstad et al., J. Am. Ceram. Soc., 96 [1] 299-307 (2013)

Selected Area Diffraction (SAD) of 140 hour Specimens

- Bright-field images are difficult to interpret alone
- The SAD patterns match the simulated tetragonal pattern
- The (112) reflections confirm the presence of the tetragonal phase, and are used to perform Dark Field imaging



Domain Structure Viewed Utilizing a Tetragonal Reflection



- TEM imaging and diffraction of the 15.9 K (140 h) humid aged sample
- Use an indexed SAD pattern to form an image from a known reflection
- Here use one of the (112) tetragonal variants to form an image
- Resulting dark-field images highlight the domains of the sample

Differences observed in domain structure:

- For dry exposures, domains exhibit ~ 3-7nm width
- For high pH_2O exposures, domains ranges from ~ 12- 17nm in width

Comparison of Domain Coarsening with Aging Time

15.2 K (88 h) 15.9 K (140 h) 16.7 K (224 h) b Dry 100 nm 100 nn Humid DO nm

- Domains increase with increasing aging time
- At the same aging time, humid aging causes larger domains
- Larger domains are more susceptible to monoclinic transformation

Comparison of Domain Coarsening with Aging Time



Higher water vapor exposures show larger domain widths as measured by EDS line profiles of yttrium content

Evidence of Link Between Gas Partial Pressure and Aging



Evidence of Link Between Gas Partial Pressure and Aging

Another Variation in Exposure Environment....

- Performed aging in a reducing environment with the same pH₂O
- Purpose was to evaluate the influence of the partial pressure of oxygen.
- Utilized forming gas as the carrier gas instead of air.
- Obtained intermediate effects relative to Dry/Humid exposures.



XPS Analysis – Evidence of Proton Incorporation



Prinz *et al.*, *Chem. Mater.*, 22 [18] 5366-5370 (1986)



- XPS has been used to identify the formation of hydroxyl groups on YSZ.
- Can identify these groups by the increase in the binding energy due to a chemical shift.
- Can identify hydroxyl groups for various elements based on their XPS spectral lines.



Badwal *et al., J. Mater. Chem.*, 4 [2] 257-263 (1994)

XPS Analysis – Direct Evidence of Proton Incorporation

- XPS was done on the 10.9 K (6 h), 15.2 K (88 h), and 15.9 K (140 h) thermally aged samples.
- Purpose was to determine if water derived species were incorporated into the structure.
- Evidence of hydroxyl group formation for multiple elemental shells.



Thermally Sprayed Abradable Coating Samples



Ceramic Matrix Phase

- TBC compositions
- Stabilized zirconia (Y or Dy)

Porosity

- 30-45%
- Polymer pore former (polyester)

Dislocator Phase

- Hexagonal boron nitride (< 1 wt. %)
- Magnesium spinel
- Lanthanum phosphate



Steinke, T. et al. Process Design and Monitoring for Plasma Sprayed Abradable Coatings. J. Thermal Spray Tech. (2014) 19, 756-64. Ren, X. et al. Thermal Conductivity and Mechanical Properties of YSZ/LaPO4 Composites. J. Mater. Science (2014) 49, 2243-51.

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Thermally Sprayed Abradable Coating Samples

Sample coupons were prepared by Air Plasma Spraying (APS) techniques:





Solar Turbines

A Caterpillar Company

University of California, Irvine

Ceramic Abradable Coating Studies

Pure 8YSZ
 8YSZ + PE
 8YSZ + PE + hBN





Air plasma sprayed (APS) 9.5Dy₂O₃-ZrO₂, hBN, polymer (DySZPB)

- Tetragonal DySZ provides thermal shock resistance and improved erosion resistance
- Hexagonal BN and polymer pore former increase coating abradability

Sulzer	Const	tituent	Operating		
Metco		(w	Temp.		
Durabrade	ZrO ₂	Dy ₂ O ₃	hBN	Polyester	1200°C
2192	85.3	9.5	0.7	4.5	



As-Processed Microstructure: DySZ-PE-BN



As-Processed Coating Characterization



As-Processed Coatings Incorporating BN

Amorphous B-based phase present at splat boundaries



TEM imaging credit: Irvine Materials Research Institute staff, Kenta Ohtaki.

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Experimental – Accelerated Degradation Studies

High temperature, controlled atmosphere tube furnace exposures

- Exposed at 1100°C, 10°C/min. ramp for 10, 25, 50 hrs.
- Natural gas: 9.5% H₂O (v)
- Syngas: 30% H₂O (v)



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Low and High Water Vapor Environment Exposures

Exposures in 9.5% H_20 (V)





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Exposures in $30\% H_20$ (V)

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Low and High Water Vapor Exposures Compared

Compaction at surface.

Steady increase in splat size.

- 50% in low water vapor for 50 hrs.
- 60% in high water vapor for 50 hrs.

Anticipated Effects of Elevated Water Vapor on YSZ/BN

- Enhanced sintering (porosity removal)
- Tetragonal phase transformation
- Development of significant volatility in water vapor containing environments – Oxidation, volatilization of hBN

 $BN(s) + \frac{3}{4}O_2(g) \rightarrow \frac{1}{2}B_2O_3(I) + N_2(g)$

 $B_2O_3 \rightarrow BOOH, B(OH)_3, (BOOH)_3, BO_2(g)$

Metscher, Opila, Jacobson. Water Vapor Mediated Vaporization of High Temperature Materials (2013). Yu, Hou. Effect of Water Vapor Content on Reaction Rate of hBN powder at 1273K.

Anticipated Effects of Elevated Water Vapor Levels

Development of significant volatility in water vapor containing environments

P.J. Meschter, E.J. Opila and N.S. Jacobson, Annual Review of Materials, 2013

Water Vapor Effects: Volatilization of Lubricious Phases?

Transpiration experiments will be used to verify volatilization of second phase constituents (hBN species) via atomic absorption spectroscopy:

Effect of Porosity and Hardness on Exposure Conditions

- Porosity decreases with Exposure time and temperature
- Hardness increases with decrease in porosity

Coating Evolution – High Water Vapor Content Exposures

High Water Vapor Enhances Pore Sintering, and Reduces Abradability

Thermo-Mechanical Degradation

Sintering Effects

Pore Evolution, Volatilization and Interface Degradation

Hardness Measurements of Abradable Systems

Boron Nitride acts as the lubricant phase and makes the composite more machinable and less robust.

> Durabrade 2192 Indentation ~0.347 GPa No cracks (9 Kgf load)

Tz8Y indentation: ~7.78 GPa Cracks visible 9 Kgf load

Mechanical Property Evaluations

Tension

'Barb' Test System at UCI

Mechanical Property Evaluations

a) Median Crack

b) Bending And Lateral Cracking

Wedge Impression Test

A. Rabiei, et al, Materials Science and Engineering A, 369 (1999) 152

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Abradability Test Rig

Design features will be vetted with the OEMs and coating vendors with experience in carrying out such tests, to ensure that representative wear behavior and high temperature seal material behavior can be assessed

- Simulates the rubbing of blade tips against the coated casing as occurs during engine service.
- Stepper motor force the coated coupon into the moving rotor.
- Incursion rates can be accurately controlled.
- Abradability results are determined by measuring incursion depth of the blade into the coating, blade wear and abradable roughness.

D. Sporer, S. Wilson and M. Dorfman, "Ceramics for Abradable Shroud Seal Applications." *Proceedings of the 33rd International Conference on Advanced Ceramics and Composites, volume 3, 2009,*

Changes to the Thermal Conductivity

Purpose: To calculate the change in heat flow using a specimen that has been exposed to simulated water vapor environment

Current laboratory set-up

*A steady-state Bi-substrate technique for measurement of the thermal conductivity of ceramic coatings J.C. Tan, S.A. Tsipas, I.O. Golosnoy, J.A. Curran, S. Paul, T.W. Clyne

Summary and Key Developments and Conclusions

- YSZ aging appears accelerated in higher pH₂O environments. A strong correlation between pH₂O and accelerated transformation of the desired t' phase to equilibrium phases is found. XRD, Raman Spectroscopy and TEM/STEM analysis give consistent evidence of the role of high pH₂O environments on the aging/degradation process. Exposure conditions that were interrupted ("dried") at elevated temperature provide evidence that the accelerated aging is not a lowtemperature artifact.
- Degradation studies relevant to abradable coatings (hBN included) are underway. Elevated water vapor combustion environments appear to accelerate materials evolution that will lead to abradable coating loss or performance degradation.
- Mechanical and thermomechanical test approaches— for evaluation of abradable coating performance in relation to IGCC systems – are also under development
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- Use of IGCC combustion systems brings up additional issues in oxidation, corrosion volatilization and deposit-based degradation; the underlying mechanisms must be better understood in order to develop effective materials design strategies.

Questions?

