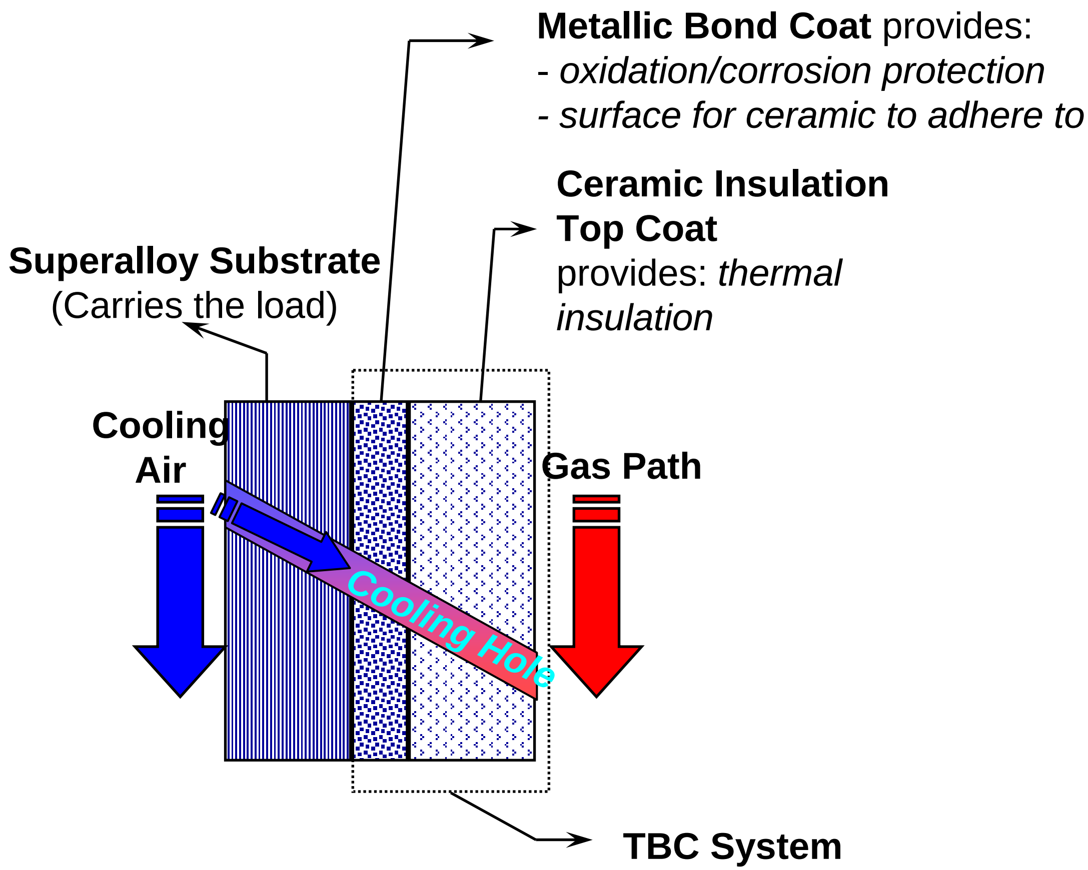
Turbine Material Studies
(Supported by DOE-NETL)



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Introduction

Improved gas turbines demand materials that operate in high hostile environment. Thermal barrier coatings (TBCs) provide solution for meeting such a demand. The TBCs have the most complex structure with a minimum of four layers made of different materials with specific properties and functions. They are the substrate, the bond-coat, thermally grown oxide (TGO), and the ceramic top-coat. The thermally-insulating ceramic bonded to an oxidation-resistant metal coating, which is applied to the superalloy substrate. The current TBC of choice consists of zirconia, partially stabilized by yttria (YSZ) with a bond coating such as MCrAlY.

NETL Programs

NETL has/is managing materials research at organizations such as GE, Siemens, Pratt & Whitney, ORNL (national lab) etc. NETL manages various turbine materials research projects through programs such as University turbine systems research (UTSR), University coal research (UCR).

The major development issues:

(i) the mechanical and chemical stability of the ceramic and bond coating interface, which is the likely focus of stresses developed as a result of mismatch of the coefficients of thermal expansion of the ceramic and metallic bond coating, and as a result of oxidation of the bond coating,

(ii) changes in the thermal conductivity across the thickness of the ceramic as a result of service exposure.

(iii) These studies indicate the research need on new materials, deposition procedures and new TBC structures with improved physical properties. Other coatings such as environmental barrier coating (EBC) and ceramic matrix composite (CMC) are also important.

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Required important research tasks

1) Identify and evaluate TBC compositions for improved corrosion resistance over that of conventional YSZ TBC's, but with no increase in thermal conductivity or decrease in life
2) Further clarify TBC failure mechanisms for turbines operating with conventional fuels and expand understanding to include failure mechanisms for turbines operating with alternate fuels especially under high heat flux (HHF) conditions. Exploit this knowledge to show feasibility of approaches for improved lifetimes and/or to improve TBC lifing models for both conventional and alternate fuels such as syngas
3) Identify deposition (condensation) kinetics for critical vapor species on high temperature surfaces – and consequent corrosion effects. For higher material surface temperatures, condensation of corrosive species will differ significantly from historic data for metals. Quantification of these rates under realistic turbine conditions is required. (cont'd)

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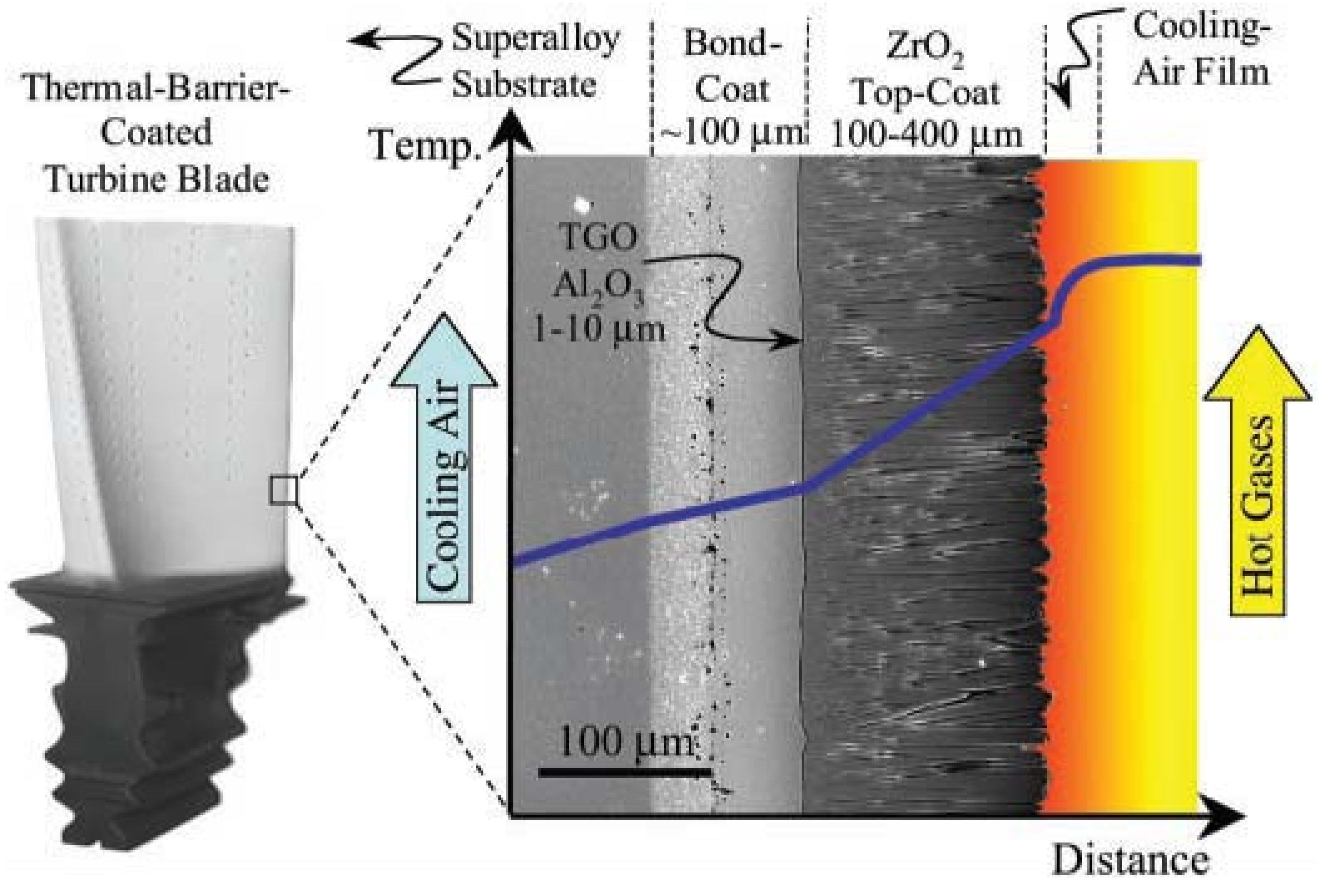
Required important research tasks

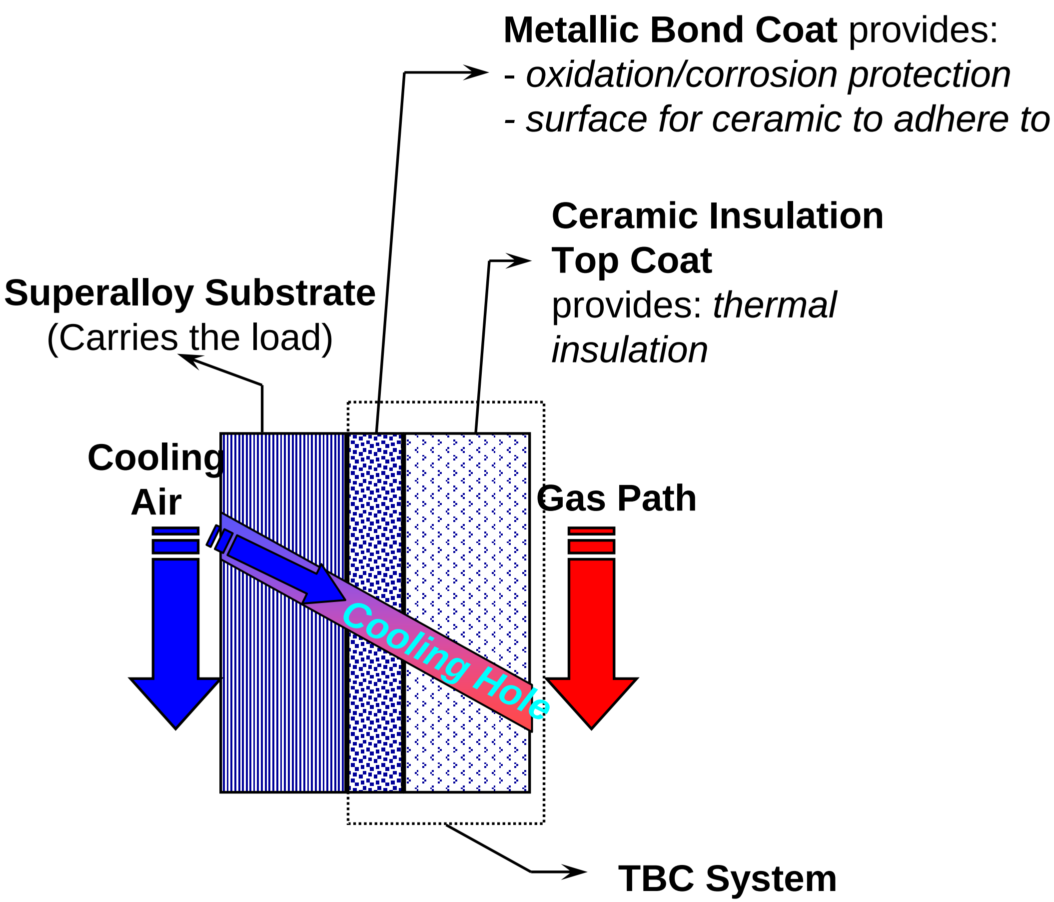
4) Water Vapor activated recession of TBC's
5) Develop a fundamental understanding of degradation processes and determine combined moisture/contaminant limits for materials environments produced by alternate fuels
6) Determine Effect of Cooling Strategy (Temperature Gradient through the Thermal Barrier Coating) and thermal cyclic lives on TBC degradation modes
7) Quantify effects of high Hydrogen on engine materials, i.e. hydrogen embrittlement mechanisms and metal dusting effects
8) Understanding the factors limiting the firing temperatures of syngas turbines
9) Evaluate the potential for deposition, erosion, or corrosion (D-E-C) when firing syngas
10) Coatings for most robust hot gas path components
11) Coatings vulnerable to CMAS (Calcium-Magnesium-Alumino-Silicate) infiltration
12) Nondestructive examination (NDE) techniques for inspection of the coatings, especially, *in situ* are required

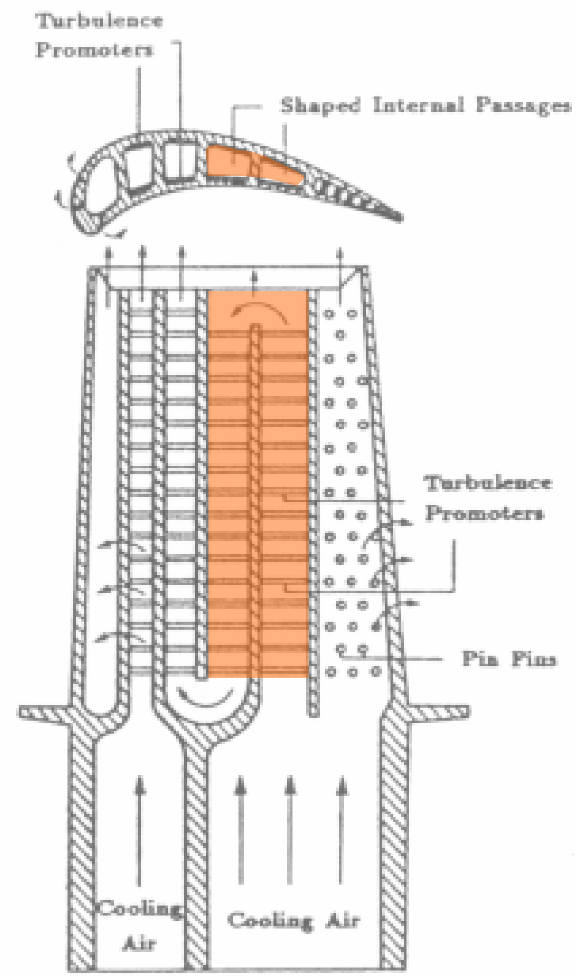
TBC Architecture



Nitin P Padture et.al, SCIENCE, P-280 VOL 296, (2002)

TBCs and Internal Cooling Manage Blade Strength





(J.C. Han 1988)

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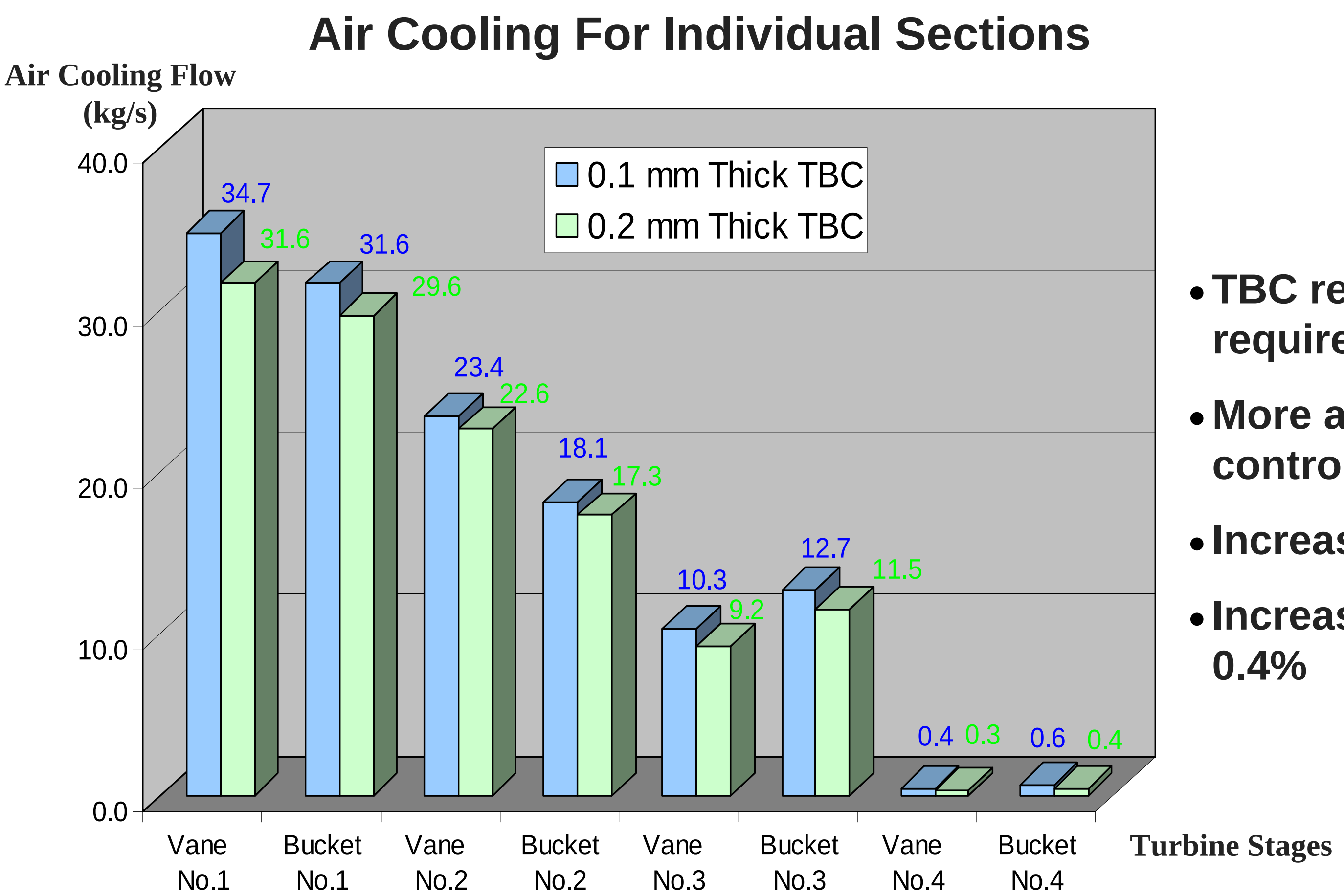
Improved TBC Has Synergistic Benefits

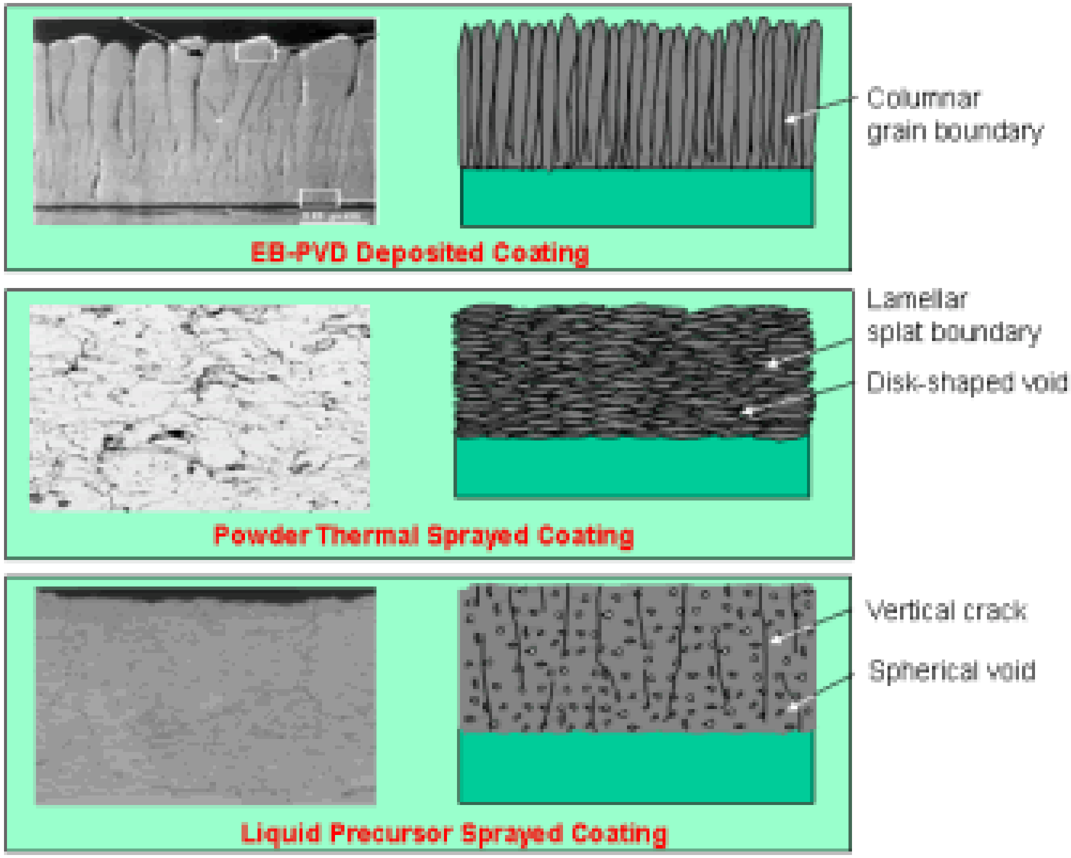


- **TBC reduces cooling flow requirements by 7%**
- **More air available for NOx control**
- **Increase expansion work out**
- **Increase CC efficiency by 0.4%**

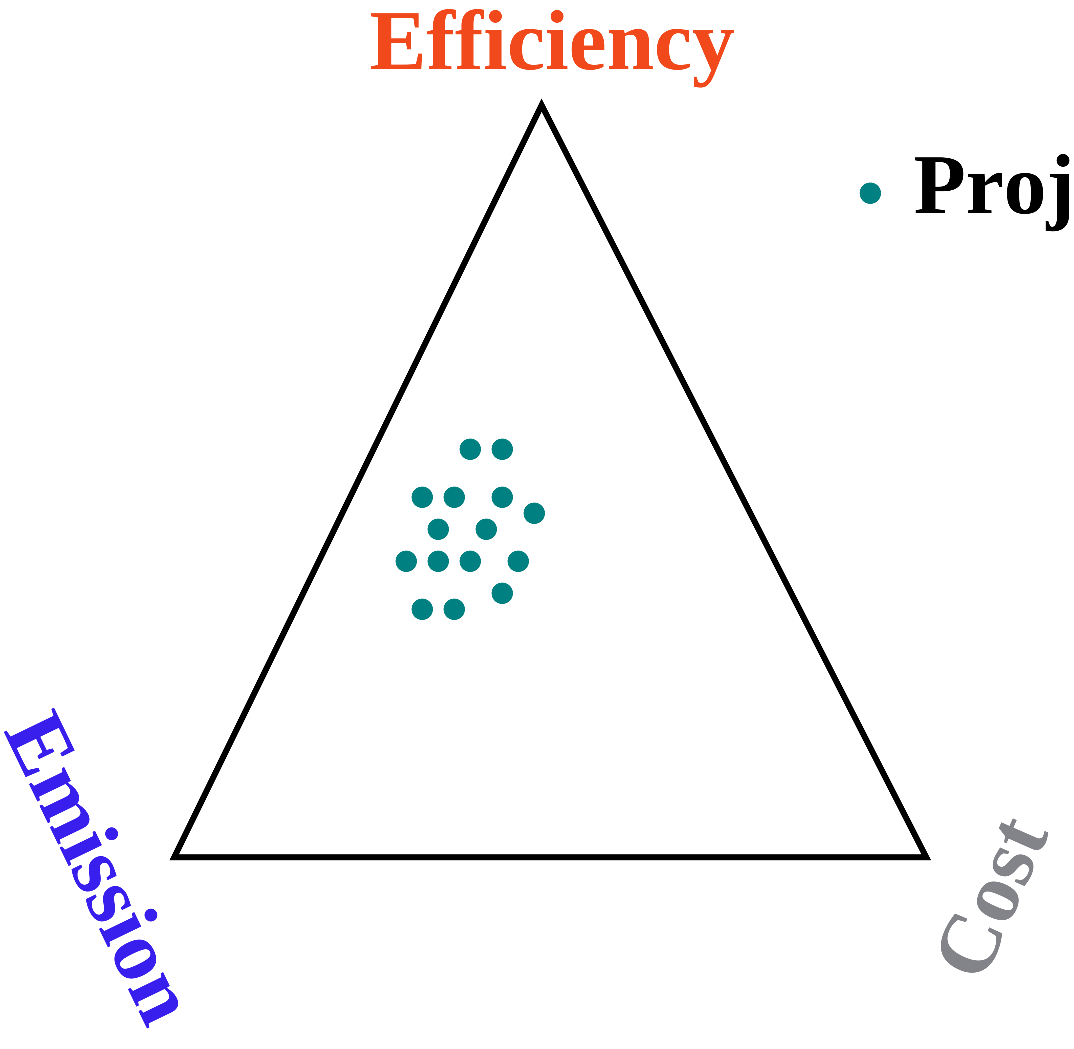
Note: For a 4 stage machine, F machines have 3 stages

Ref: Fig.5.2 of VDI-Report 448, 2001

Microstructure of Ceramic TBC's by Various Processes



Materials to help solve the Puzzle



- Projects aimed

Industry Views

Directions for Coatings (SIEMENS)

Material Requirements for Advance Turbines

- **Higher temperature capability – reduced cooling, increased TIT**
- **Improved oxidation resistance – post coating spallation life**
- **Enhanced prime reliance – reliable system integrity**
- **Better hot corrosion resistance – IGCC and low grade fuels**
- **Improved coating life: erosion/FOD/steam oxidation resistance**

Potential Solutions

- **Oxidation resistant metallic coatings - Larger aluminum reservoir, Slow diffusion/depletion rate of aluminum**
- **Thermal barrier coatings – Design-based input for thermal conductivity, heat flux and structural integrity**
- **Functional coatings – Coatings providing functional resistance against steam oxidation (Environmental barrier coatings (EBCs)), erosion, hot corrosion and foreign object damage.**

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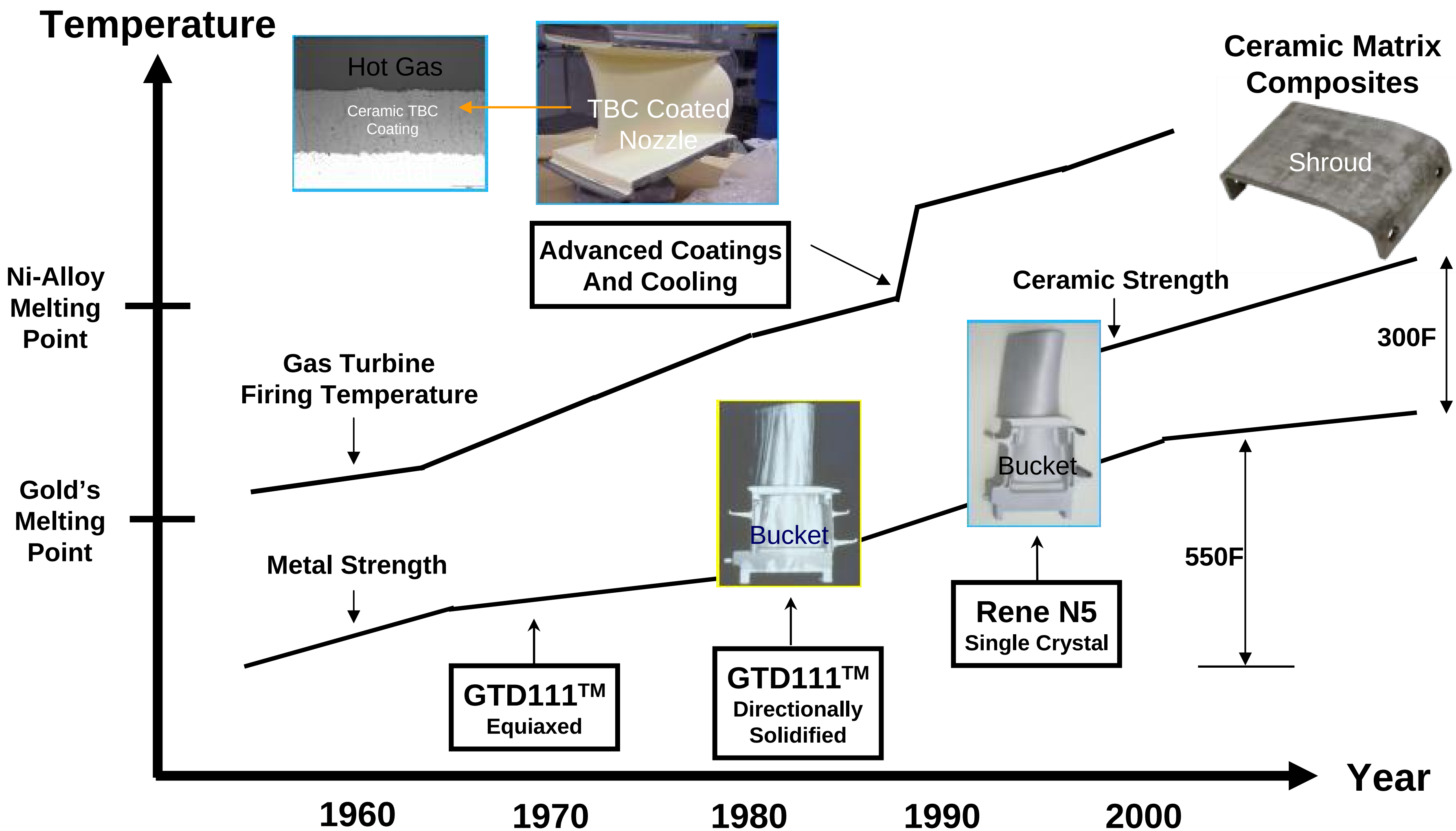
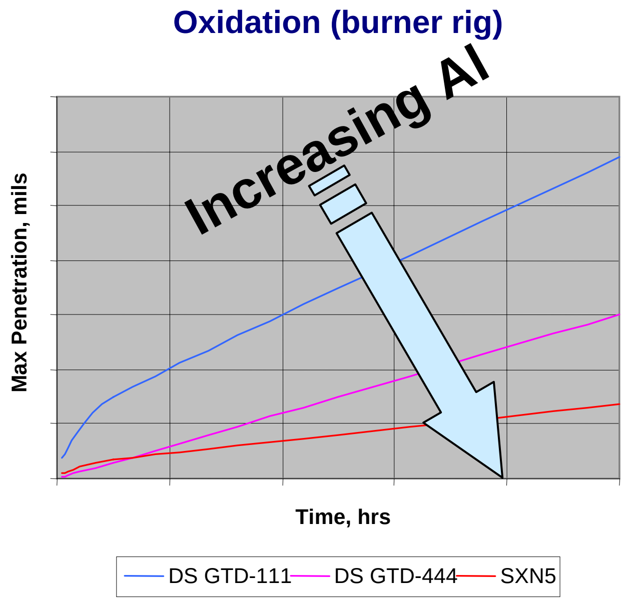
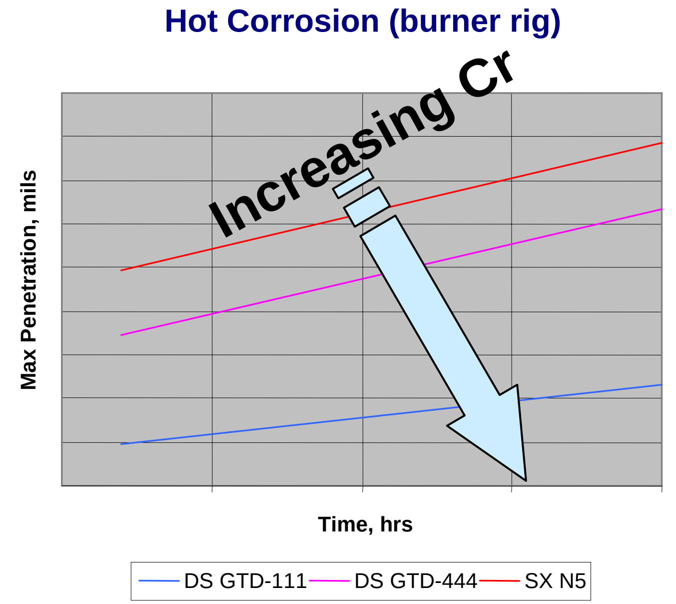
Materials Define Turbine Technology



Alloy Development History





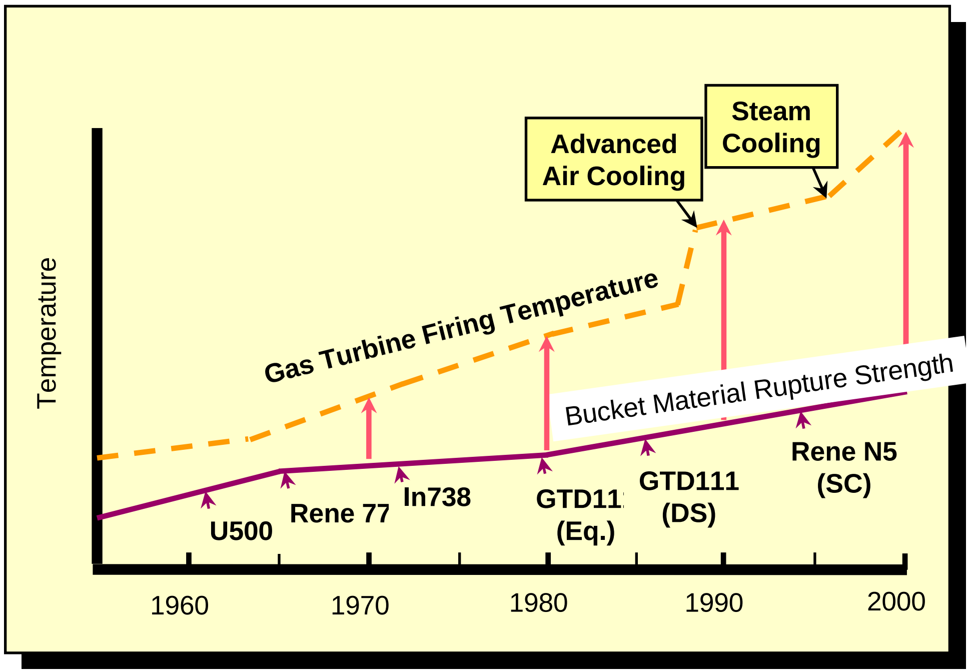
Increasing firing temperature / decreasing fuel contaminates →

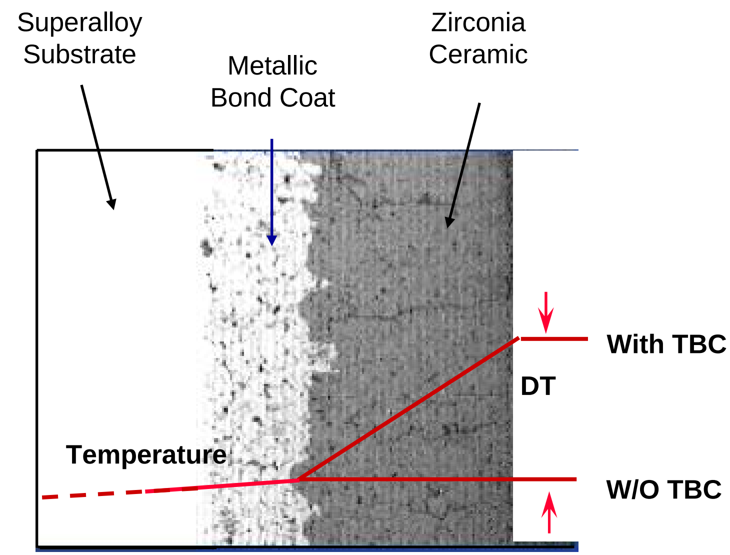
Alloy development / firing condition timeline

Increasing oxidation resistance / decreasing hot corrosion resistance →

Result: Alloy development focused entirely on increasing oxidation resistance because operating conditions dictated (high temperature and clean fuel).

Thermal Barrier Coatings





Benefits of TBC

Higher firing temperature

Reduced cooling air required

Longer component life.

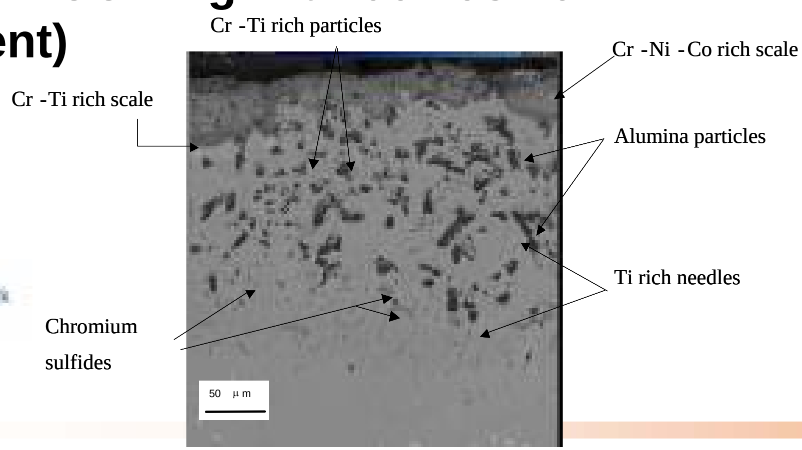
TBC needed as the gap between the turbine firing temperature and substrate alloy capability increases

Advanced Turbine Materials

- Modified MCrAlY coatings (rare earth & precious metals) for environmental protection
- Low thermal conductivity (k) TBC
- Advanced application and processing

Current progress is with the laboratory test development

- Deposit corrosion (sulfate deposit at elevated temperatures)
- Gaseous corrosion (low contaminant “hot corrosion” test)
- Erosion (BECON rig with corrosive environment)



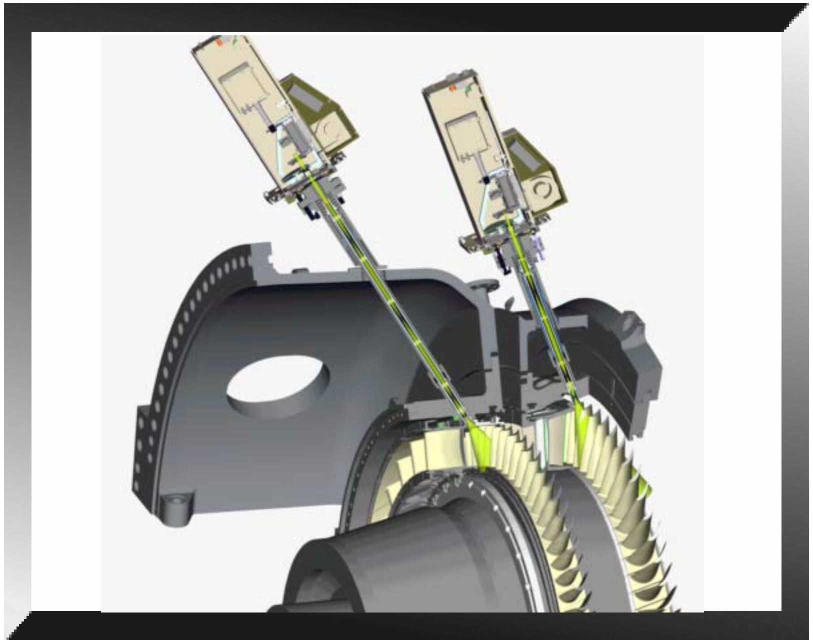
Buckets	Gas Turbine	Material	Coatings	
S1B	7FA TECo Baseline	DSGTD-111	CoCrAlY	Aluminide
	2010/2015	SC N5	NiCoCrAlY	DVC TBC*
			Enhanced NiCoCrAlY	Advanced TBC
				EBPVD TBC
S2B	7FA TECo Baseline	GTD-111*	CoCrAlY	
	2010/2015	DSGTD-111	NiCoCrAlY	
		DSGTD-444	Enhanced NiCoCrAlY	
S3B	7FA TECo Baseline	GTD-111	Chromide	
	2010/2015	DSGTD-111	Chromide	
		DSGTD-444		
Nozzles	Gas Turbine	Material	Coatings	Coatings
S1N	7FA TECo Baseline	FSX-414	CoCrAlY	TBC
	2010/2015	GTD-111	NiCrAlY	DVC TBC
		GTD-111W		Advanced TBC
				EBPVD TBC
S2N	7FA TECo Baseline	GTD-222*	Aluminide	
	2010	GTD-111	Aluminide	
		GTD-111W	Modified Aluminide	
		GTD-241+		
	2015	CMC	Gen 1 EBC	
			Gen 2 EBC	
S3N	7FA TECo Baseline	GTD-222		
	2010/2015	GTD-241+	Slurry Aluminide	
			Aluminide	
Shrouds	Gas Turbine	Material	Coatings	Coatings
S1S	7FA TECo Baseline	Alloy 738	CoCrAlY	DVC TBC
	2010	GTD-741	NiCoCrAlY	DVC TBC
		N5	NiCrAlY	
	2015	CMC	Gen 1 EBC	
			Gen 2 EBC	
S2S	7FA TECo Baseline	Alloy 738 or Haynes 214		
	2010	GTD-741		
		GTD-333		
	2015	CMC	Gen 1 EBC	
S3S	7FA TECo Baseline	SS310		
	2010/2015	SS310		
Combustion	Gas Turbine	Material	Coatings	Coatings
Liner	7FA TECo Baseline	Nimonic(R) 263	NiCrAlY	Class B TBC
	2010	Nimonic(R) 263	NiCrAlY	Class B TBC
	2015	Cast U500	NiCrAlY	Super B TBC
Nozzle	7FA TECo Baseline	304L SS		
	2010/2015	304L SS		
End Cove	7FA TECo Baseline	304L SS		
	2010/2015	304L SS		
		347 SS		
TP Body	7FA TECo Baseline	Nimonic(R) 263	NiCrAlY	Super B TBC
	2010/2015	Nimonic(R) 263	NiCrAlY	Super B TBC
		Haynes(R) 282		

*Trademark of General Electric Company

TBC Monitoring Projects

On-Line TBC Monitoring for Real-Time Failure Protection

Siemens Westinghouse Power Corporation, (41232)



Objectives

Design build and install a gas turbine blade and vane thermal barrier coating (TBC) monitor for real time detection / formation and progression of critical TBC defects. The monitor will track and report on the progression of TBC defects, estimate remaining TBC life, and notify operations of impending damage.

Duration: 4 Year Program

Total Project Cost

DOE: $5.118M

Non-Government: $1.280M

Benefits

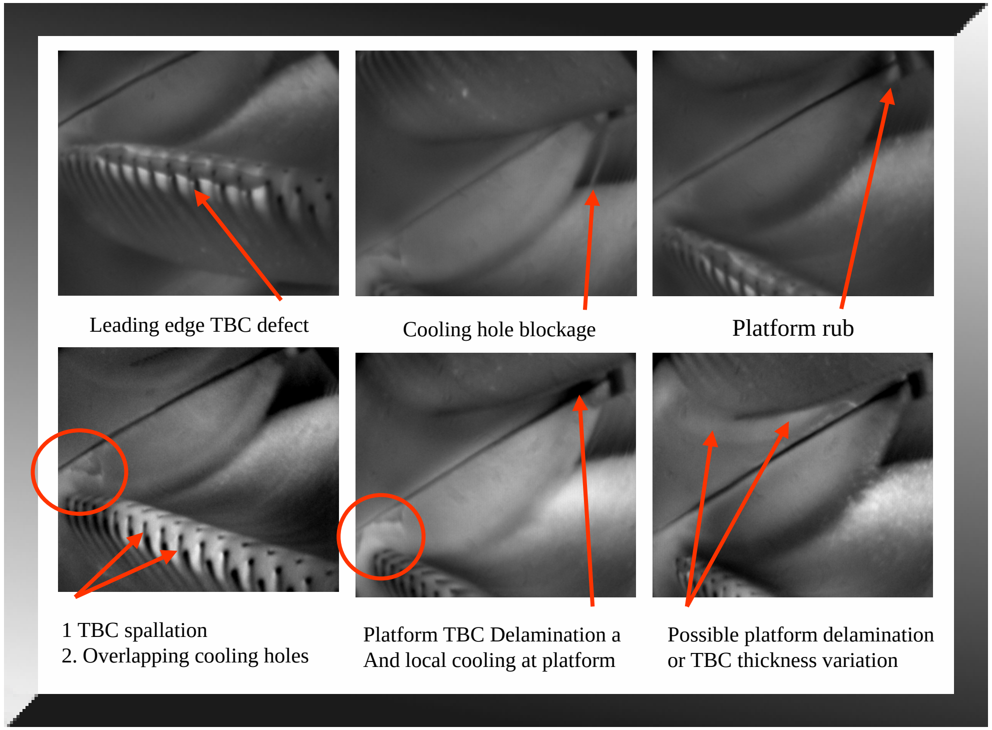
- Higher equipment availability
- OEM design tool
- Reduced Maintenance Costs

On-Line TBC Monitoring for Real-Time Failure Protection

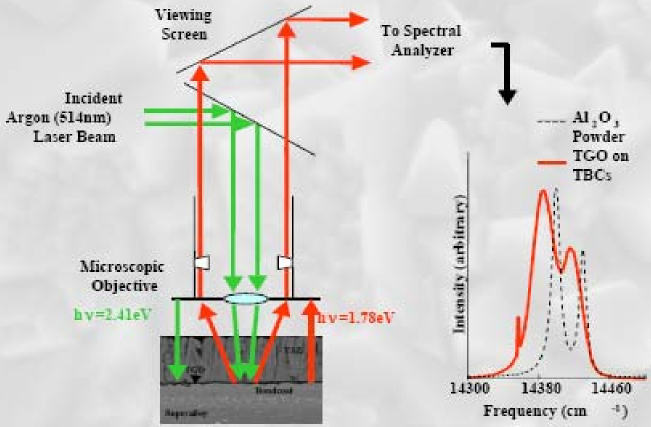
Siemens Westinghouse Power Corporation, (41232)

Results

- Proof-of-concept tests (2001) profiled key interactions between infrared instrumentation, and absorption characteristic
- Characterize emissions from TBC defects (APS)-Infrared emission from TBC and associated progressions of deterioration was characterized, (debond growth, spall). The deteriorating TBC emission demonstrates a local step change in emissivity.
- Installation (2003) of the prototype dual spectral response On-line TBC Monitor
- Developed TBC Remaining Life Prediction Model / completed prototype testing (5/03)
- Installation (10/04) of full scale system at Empire State-Line Unit (501FD2) monitored in real-time, the condition and performance of row 1 and row 2 turbines blades



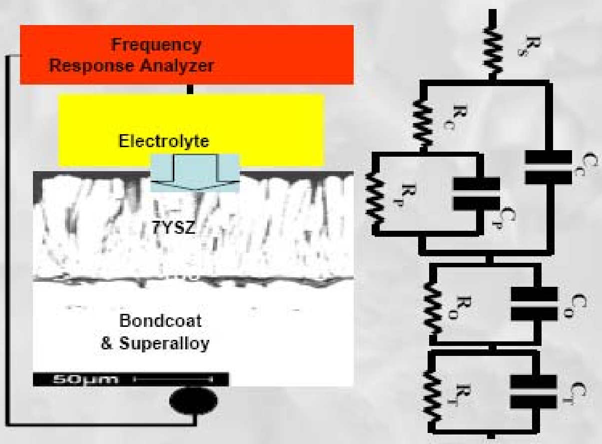
Non-Destructive Evaluation of TBCs During Furnace Thermal Cycling Test by PSLS and EIS



Photostimulated Luminescence:

Critical Characteristics of TGO Scale Associated with TBC Failure:

- Phase Constituents in the TGO Scale.
- Residual Stress in the TGO Scale.
- Stress Relief and/or Relaxation Associated with Spallation of TBCs.



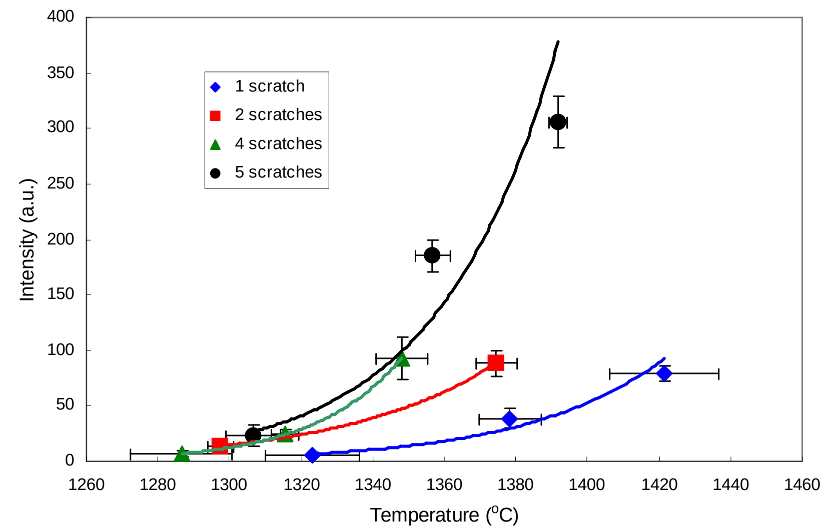
Electrochemical Impedance:

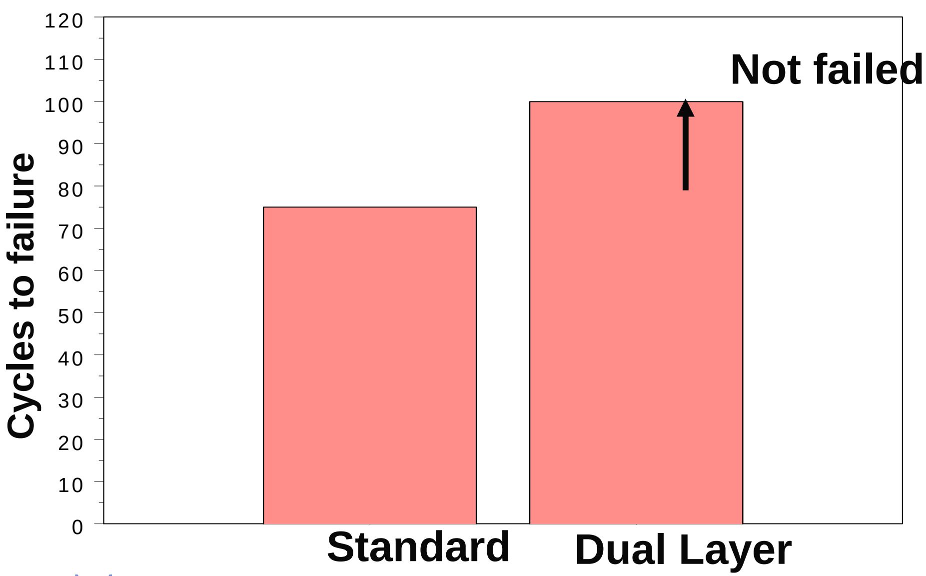
- Each AC Circuit Component Corresponds to Physical Parameter of TBC Constituents Quantitatively.
- Measured Electrochemical Impedance is Simulated According to Equivalent AC Circuit.

Spectroscopic In-Sitsu Health monitoring of TBCs

Cleveland State U.
Kang Lee #042

- Dual layer TBC's (doped YSZ / undoped YSZ) show strong dependence of emissions intensity on TBC health (simulated cracks)
- This shows feasibility of in-sitsu health monitoring via spectroscopy.





- Dual layer TBC's show as good as or better then standard TBC's at 1115C / 20h thermal cycling
- Other testing at different frequencies underway to confirm results
- Progress has been forwarded to sponsoring companies Solar, Honeywell and Rolls-Royce

Advanced optical sensor for monitoring and control of multiple gas and turbine-blade properties

University of Wisconsin – Madison

Department of Mechanical Engineering

Principal Investigator: Scott T. Sanders

SCIES Project 03 - 01 - SR105

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

Tom George, Program Manager, DOE/NETL

Richard Wenglarz, Manager of Research, SCIES

Project awarded 7/1/2003, 36 month duration

$418,961 total contract value ($418,961 DOE)

Project Objective

- Develop fiber-optic sensors that can be readily attached to "research-grade" gas turbine engine test facilities
- Contribute to maturation of "production-grade" sensor designs

Gas Turbine Needs Met

- Researchers provided with a tool that enables more rapid evaluation of new engine designs

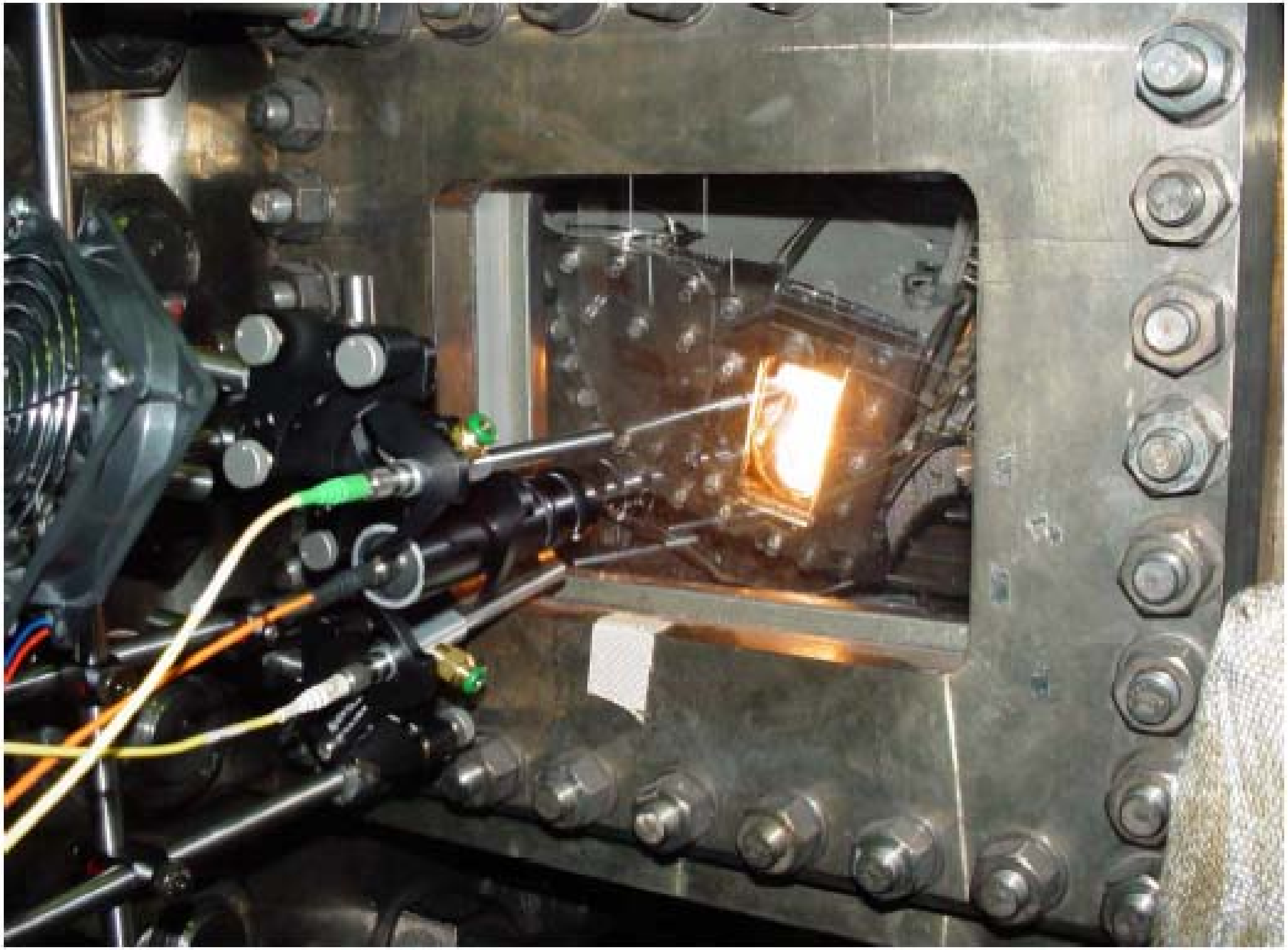
will lead to reduced engineering time

- Useful information becomes available, ultimately in production engines. For example, the ability to monitor or control the temperature distribution of gases entering the turbine

will lead to…

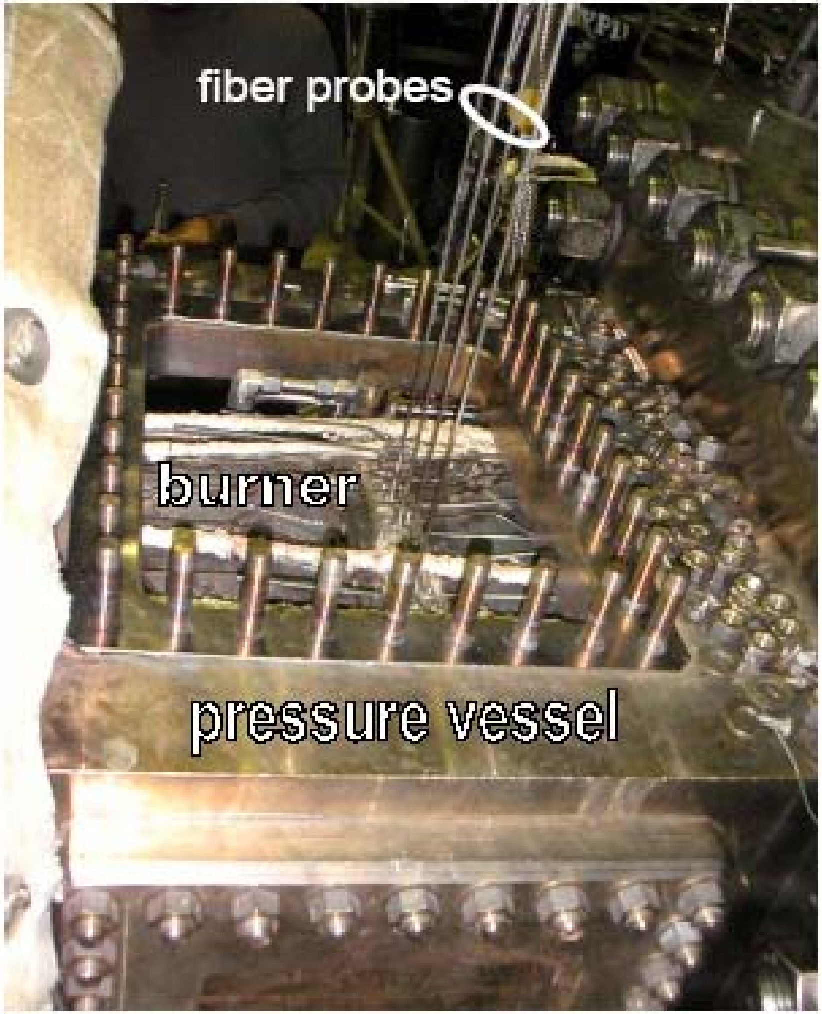
- increased efficiency
- reduced emissions

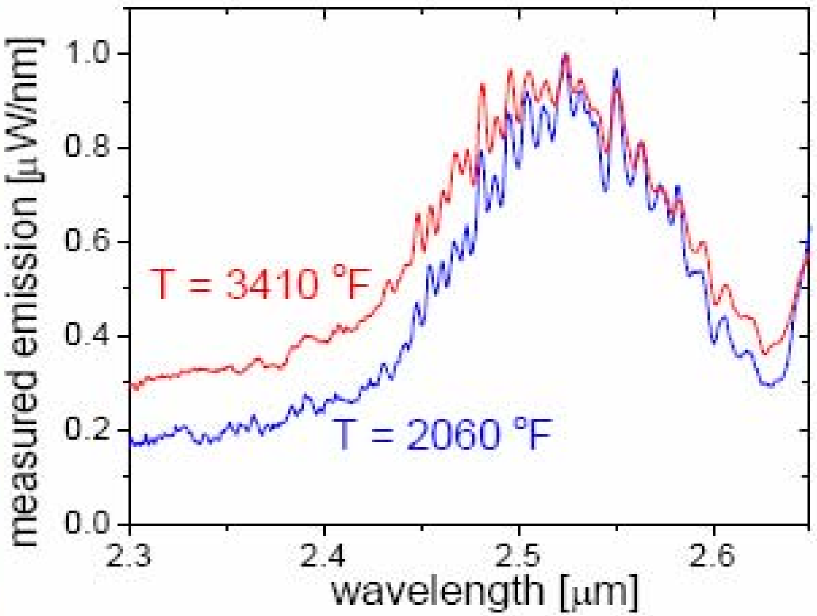
Dual-Clad Fiber Installed at WPAFB (using window)



- Each fiber represents a different sensor

Ruggedized Installation at WPAFB (no window)





- Gas temperatures inferred from optical measurements

TBC* Testing with NG and SG Combustion Using HADES

Parameter	High Temperature Testing	Low Temperature Testing
TBC Surface Temperature	1150°C (2100°F)	1050°C (1920°F)
Combustor Exit Temperature	Up to 1650°C (3000°F)	Up to 1650°C (3000°F)
Gas Pressure	Up to 350 psi	Up to 350 psi
Coolant Temperature	~ 412°C (775°F)	~ 412°C (775°F)
Mechanical Loading	None	None
Test Duration	10, 100 and 400 hours	10, 100 and 400 hours

* APS and EB-PVD TBCs: Tubular Specimens with 0.5" Diameter, 0.0375" Wall-Thickness and 8" Length.

Assessment of Failure Mechanisms for Thermal Barrier Coatings by Photoluminescence, Electrochemical Impedance and Focused Ion Beam

UNIVERSITY OF CENTRAL FLORIDA

FROM PROMISE TO PROMINENCE
CELEBRATING 40 YEARS

Y.H. Sohn, B. Jayaraj and V.H. Desai

SCIES Project 02- 01- SR103

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

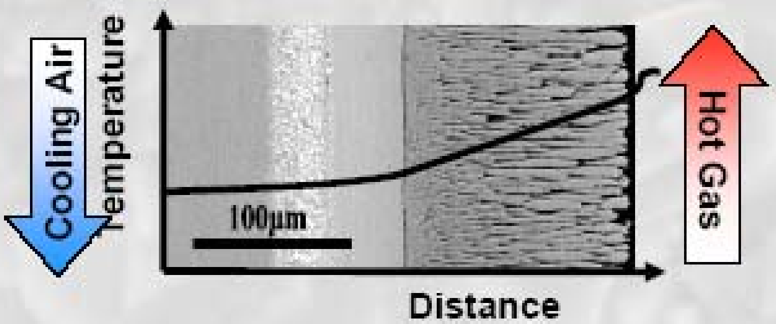
Tom J. George, Program Manager, DOE/NETL

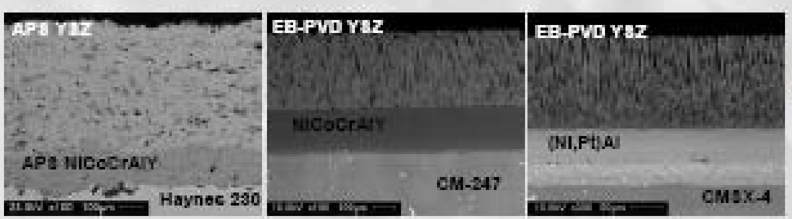
Richard Wenglarz, Manager of Research, SCIES

Project Awarded (May 1, 2002, 36 Month Duration)

$249,766 Total Contract Value ($208,228 DOE UTSR)

Gas Turbine Needs: Reliable and Durable Thermal Barrier Coatings (TBCs)





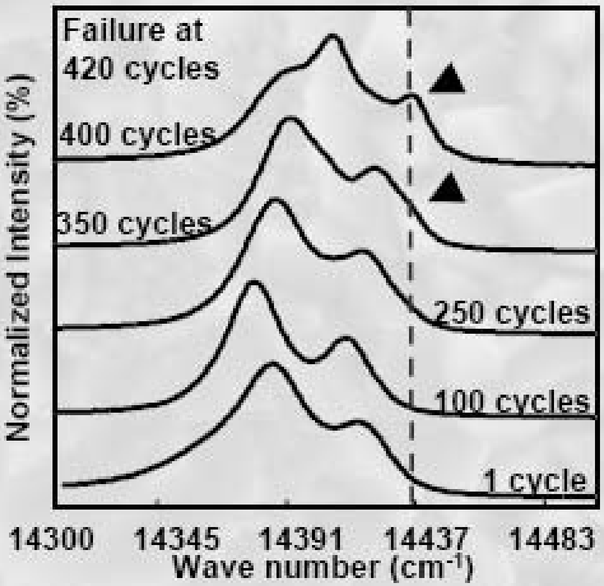
- TBCs Provide Thermal Protection of Hot Components in Advanced Gas Turbine Engines
  - Increase in Performance, Efficiency, Reliability and Maintainability.
  - Reduction Life Cycle Costs.
- Reliable and Durable TBCs Needed as An Integral Part of Component Design.
- Needs Refined Understanding of **Failure Mechanisms** to Develop a Mechanisms–Based Lifetime Prediction Models.
- Develop **Non-Destructive Evaluation** Techniques for Quality Assessment, Life Prediction and Life-Remain Assessment.

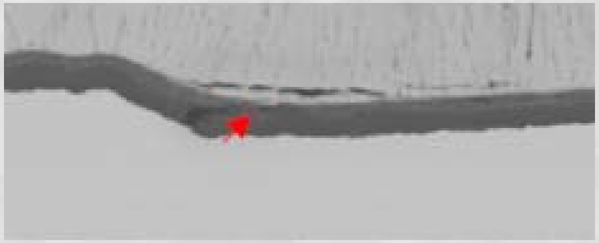
Program Objectives

- Complimentary Non-Destructive Evaluation (NDE) Techniques:
  - ✓ Photostimulated Luminescence Spectroscopy (PL).
  - ✓ Electrochemical Impedance Spectroscopy (EIS).
- State-of-the-Art Microstructural Characterization including:
  - ✓ Focused Ion Beam (FIB) In-Situ Lift-Out (INLO).
  - ✓ Transmission Electron Microscopy (TEM); Scanning TEM (STEM), Analytical TEM/STEM
- Establish Relationship Between NDE Techniques, Microstructural Development and Failure Mechanisms for TBCs.
- Technology / Knowledge Transfer to Industrial Partners.
- Education for Graduate and Undergraduate Students Through Research in Science, Technology and Professionalism.

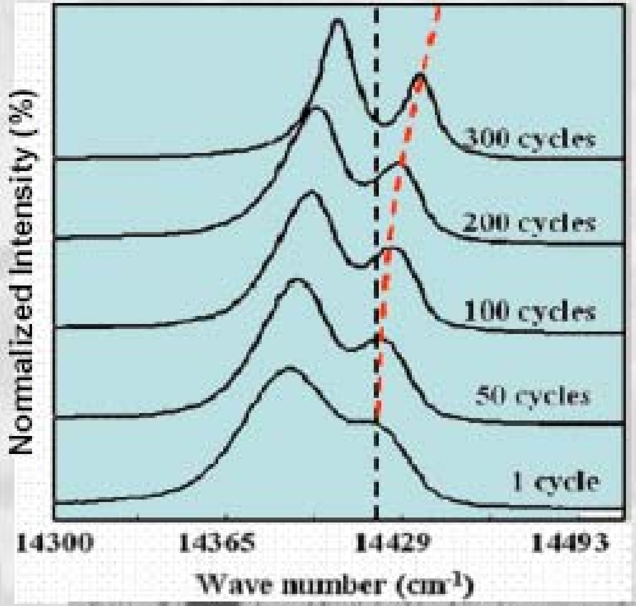
Accomplishments (1): PL

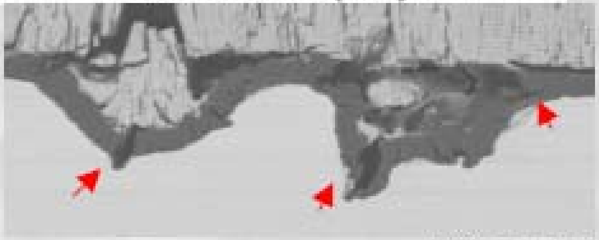
Stress Relief due to the TGO Cracking Detected Prior to Spallation.





Stress Relaxation due to Lengthening of the TGO (Racheting) Detected Prior to Spallation).

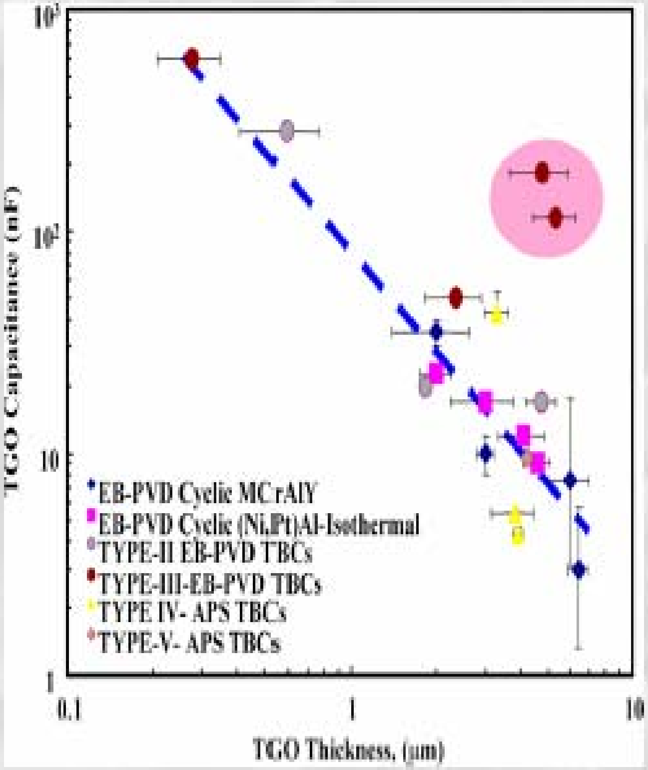




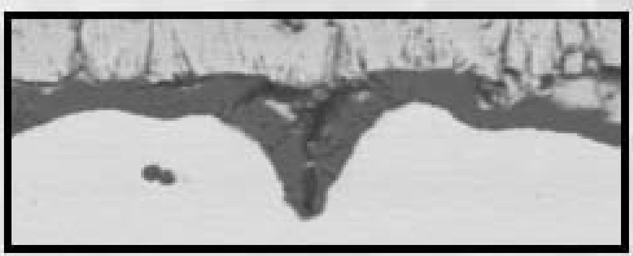
YHS@UCF,10/17/05

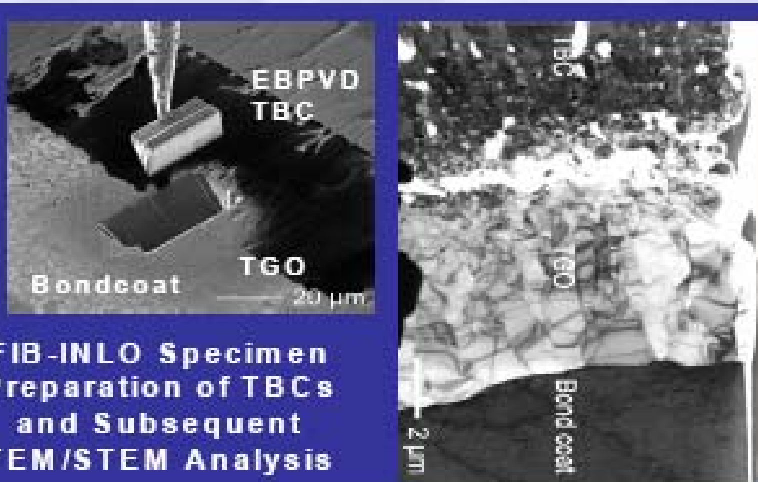
NETL

Accomplishments (2): EIS & TEM/STEM



- Increase in Electrochemical Capacitance of TGO Scale with TGO Thickness.
- Deviation in Trend with the TGO Scale Damage and Electrolyte Exposure.
- FIB-INLO Specimen Preparation for TEM/STEM Microstructural Analysis.

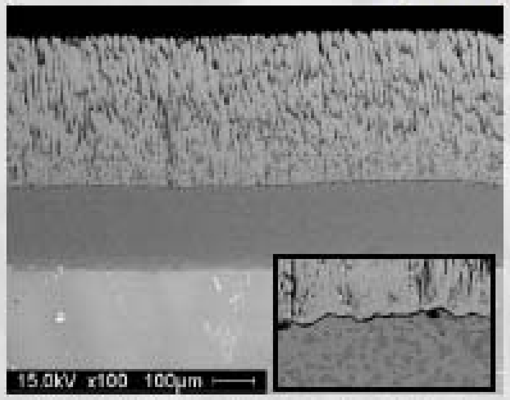




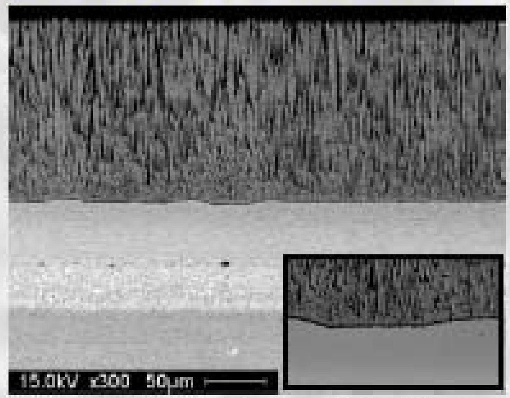
FIB-INLO Specimen Preparation of TBCs and Subsequent TEM/STEM Analysis

Typical Microstructure of As-Coated TBCs

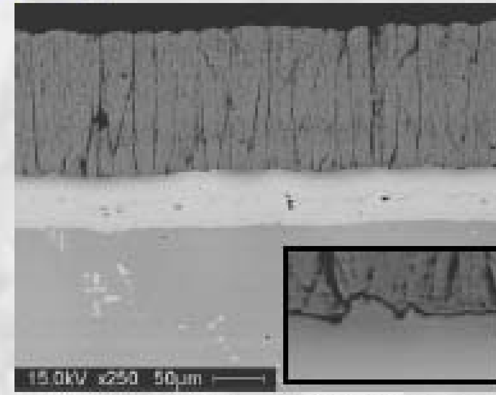
(SEM: Backscatter Electron Images)



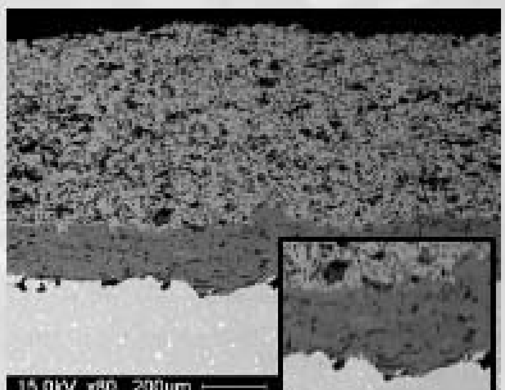
I: EBPVD, Shot-Peened NiCoCrAlY Bondcoat



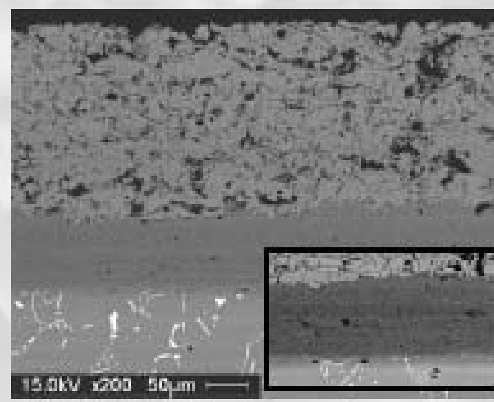
II: EBPVD, As-Coated (Ni,Pt)Al Bondcoat



III: EBPVD, Grit-Blasted (Ni,Pt)Al Bondcoat



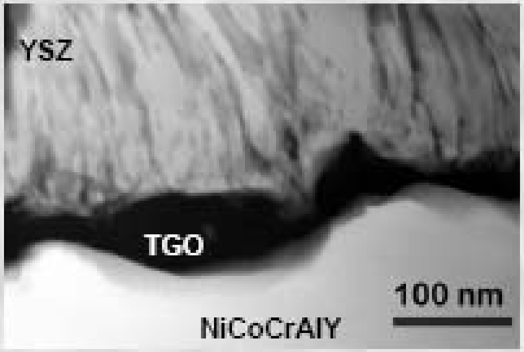
VI: APS, NiCoCrAlY with Oxide Inclusions



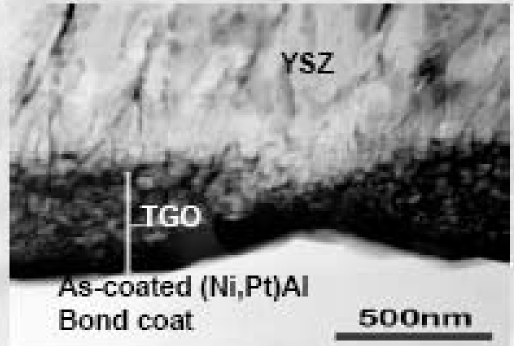
V: APS, NiCoCrAlY Bondcoat

Typical Microstructure of As-Coated TBCs

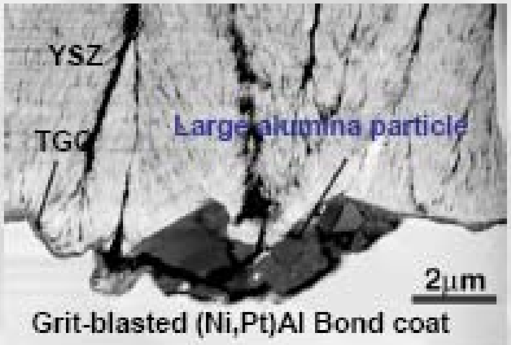
(TEM/STEM: Bright & High Angle Annular Dark Field Images)



Type I



Type II



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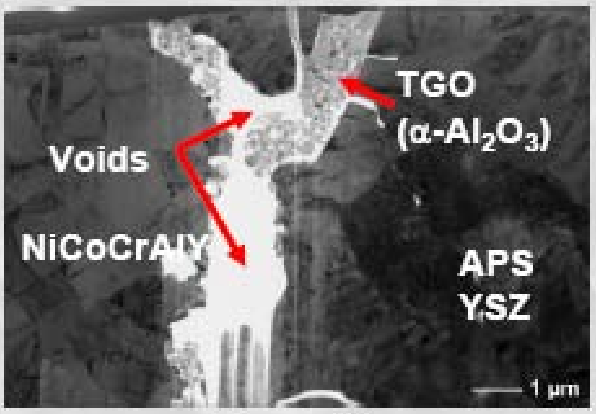

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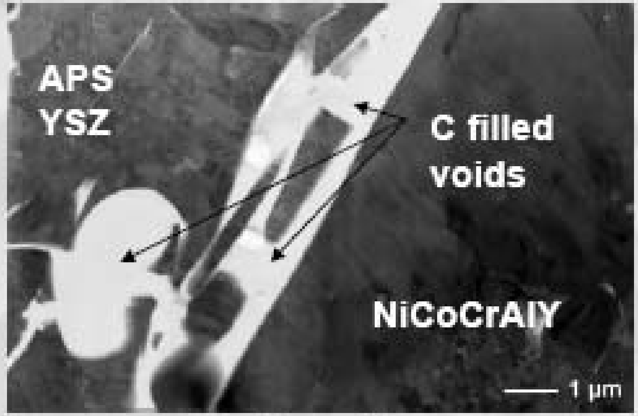
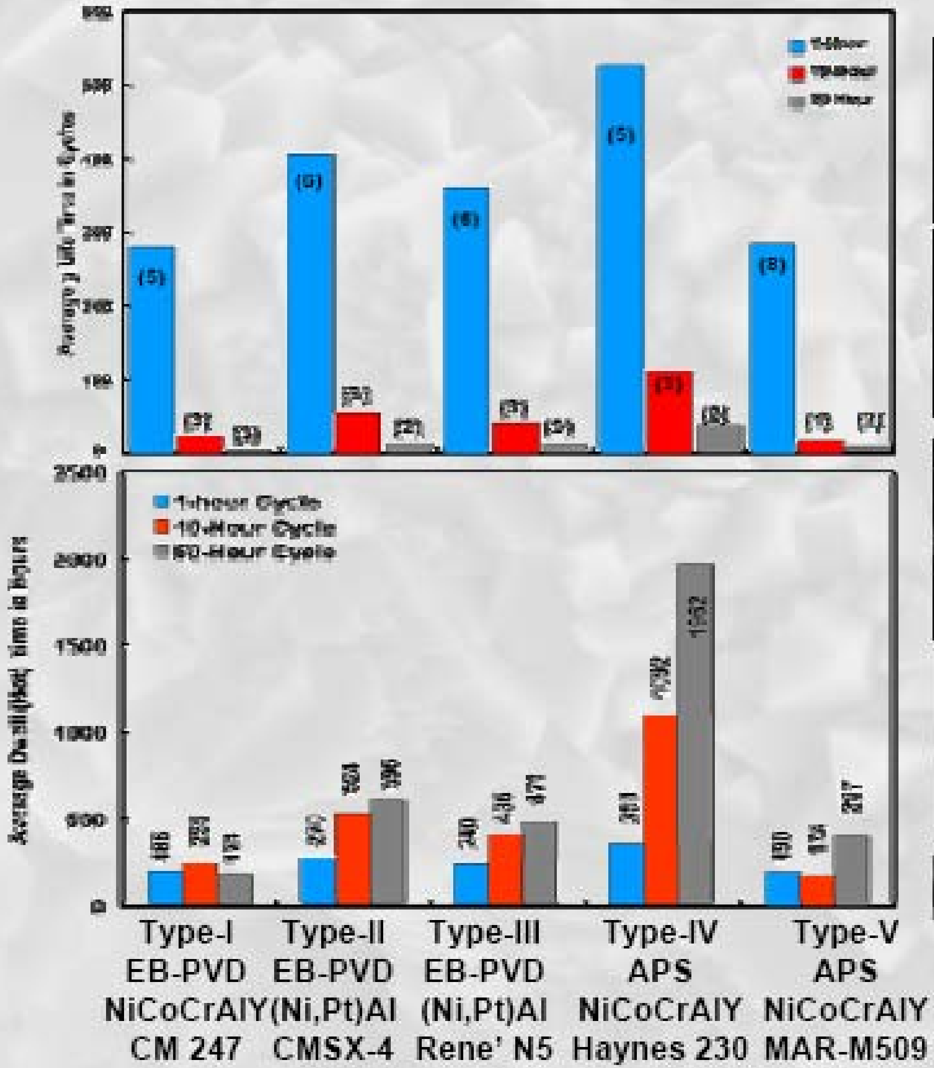
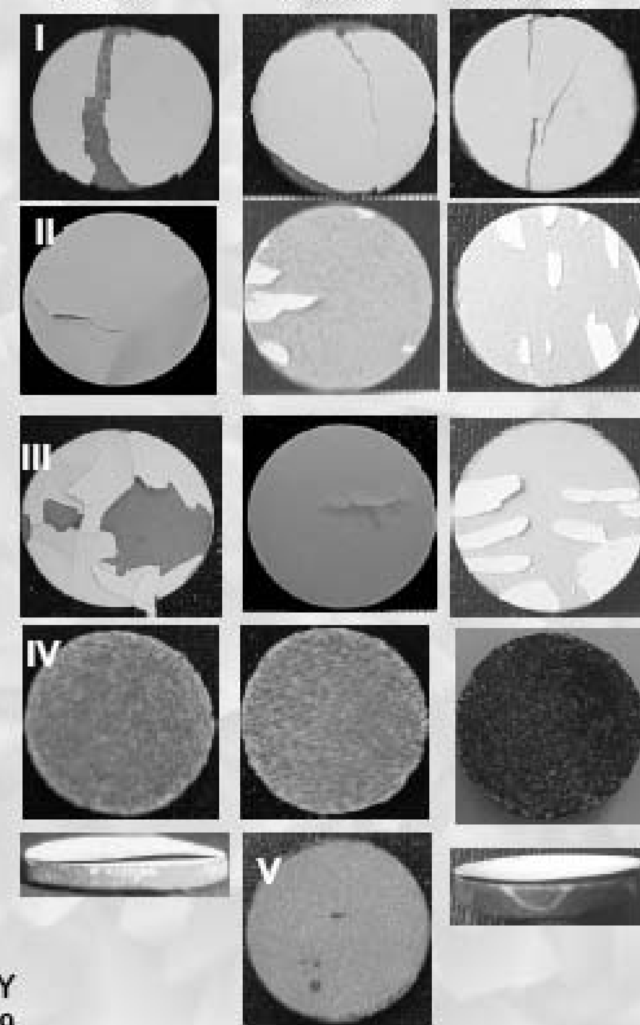


Type V

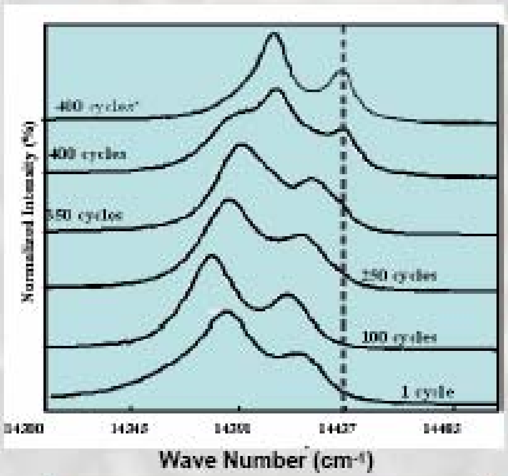
Thermal Cycling Lifetime / Dwell Time of TBCs

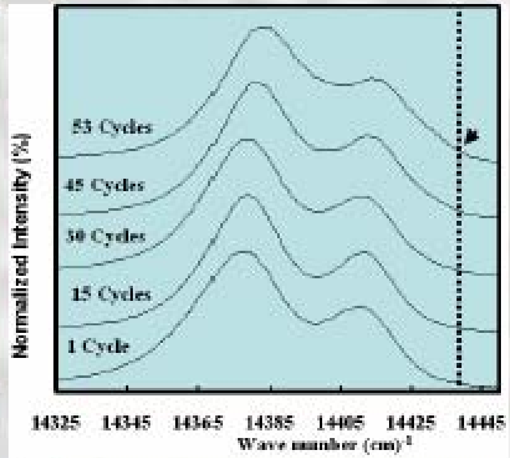


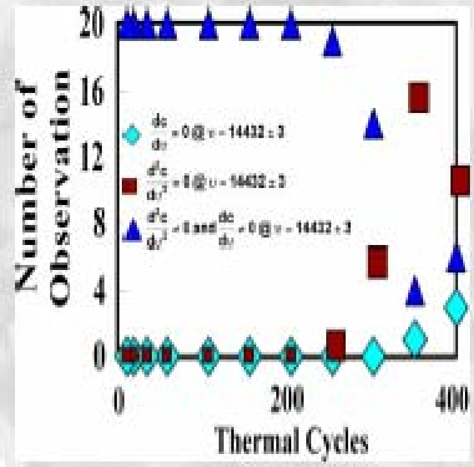


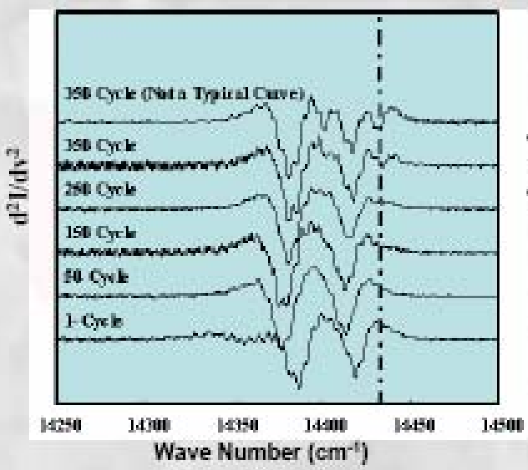
YHS@UCF,10/17/05

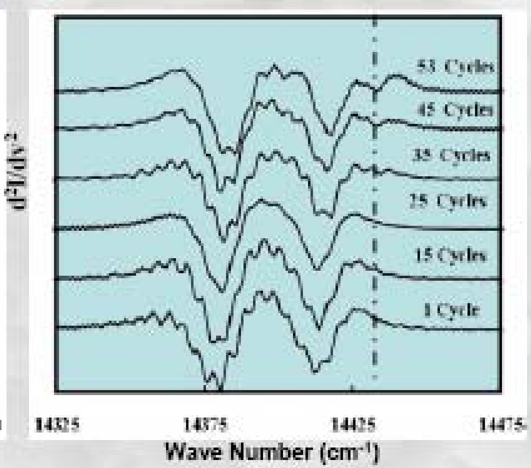
Luminescence from the TGO with Thermal Cycling {Type II TBC: EB-PVD / As Coated (Ni,Pt)Al / CMSX-4}







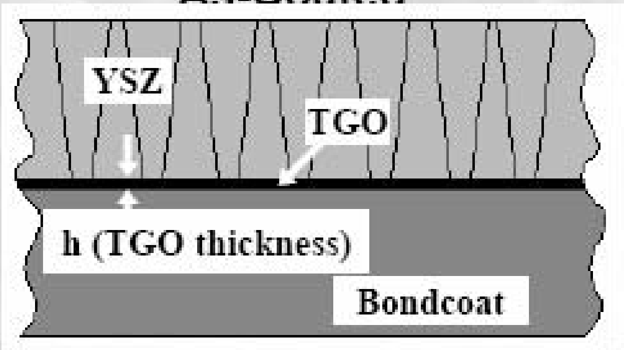




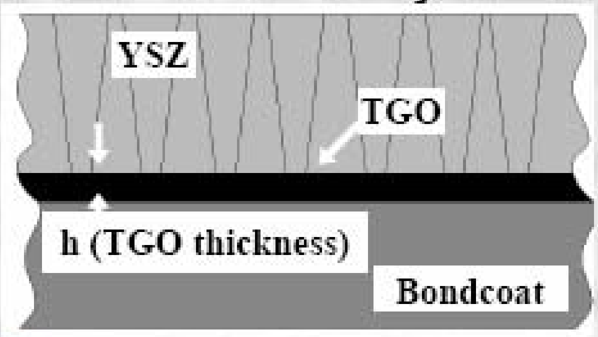
- Stress Relief Detected Prior to Spallation (420 Cycles).
- Both 1 and 10 Hour Thermal Cycles.

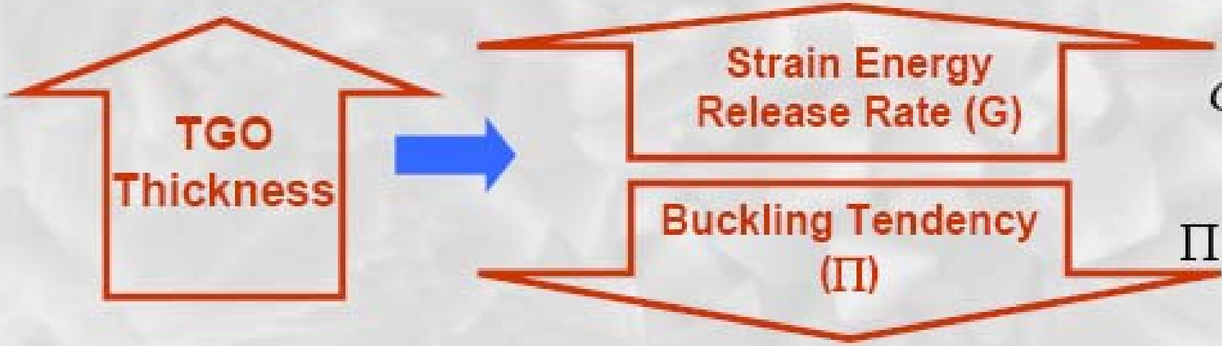
Effective Thickness of Oxide (YSZ and TGO) Governing the Failure of TBCs

As-Coated



After Thermal Cycles





$$G = \frac{Z\sigma^2 h(1-\upsilon^2)}{E} \; *$$

$$\Pi = (1-\upsilon^2)\left(\frac{\sigma_0}{E_0}\right)\left(\frac{b}{h}\right)^2 \; *$$

Z = Geometry Constant for the TGO; E = Young's Modulus of Al_2O_3; ν = Poisson's ratio; h = TGO Thickness; G = Strain Energy Release Rate; σ or σ_0 = In-Plane Compressive Stress (due to Thermal Mismatch); Π = Buckling Index; b = Crack Width.

**A.G.Evans et al, Progress in Materials Science 46 (2001) 505-553; M.C.Shaw Design of Power Electronics Reliability.*

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Summary

- Thermal Cycling Lifetime for Each Type of TBC was Determined and Characteristics of Failure was Examined.
  - Rating (e.g., Thermal Cycles or Dwell Time) Among 5-Types of Commercial Production TBCs Remained the Same for 1,10 and 50-Hour Thermal Cycling.

- Great Potential Exists for PL and EIS as Complimentary NDE Techniques for TBCs:
  - PL: Stress Relief of the Highly Stressed TGO due to Subcritical Cracking Prior to Final TBC Spallation.
  - PL: Stress Relaxation of the TGO due to Racheting or Stress-Retention due to No-Racheting.
  - EIS: Subcritical Damage Detection by Electrolyte Penetration.
  - EIS: Correlation between Thickness of the TGO and C_{TGO}.

- TBC Specimens for (S)TEM Can Be Prepared Routinely and Within 2~3 Hours Regardless of Thermal Cycling History:
  - Detailed Microstructural Information on Critical Constituents of TBCs.
  - Refined Understanding of TBC Failure Mechanisms:
    - Importance of YSZ/TGO Interface on the Failure at the TGO/Bond Coat Interface.

Spectroscopic In-Situ Non-Destructive Evaluation to Monitor the Health of Thermal Barrier Coatings

Cleveland State University

Guofeng Chen, Kang Lee and Surendra Tewari

SCIES Project 03-01-SR106

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

Tom J. George, Program Manager, DOE/NETL

Richard Wenglarz, Manager of Research, SCIES

Project Awarded (07/01/03, 36 Month Duration)

$391,615 Total Contract Value ($391,615 DOE)

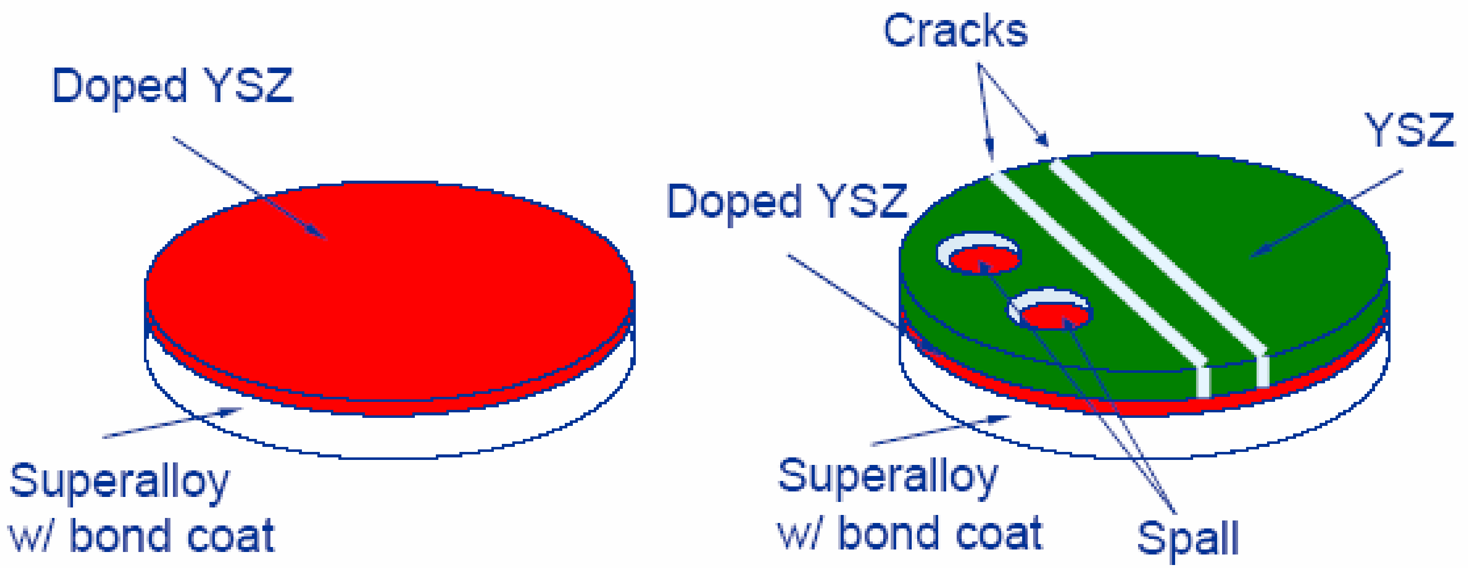
Approach

- TBC is doped with a marker material that can be detected by spectroscopy when exposed to combustion environment
- As TBC degrades (cracking, spallation, etc.), marker material is exposed to combustion environment and becomes airborne.
- TBC health-spectral response relationship is calibrated by exposing pre-damaged TBC to combustion environment.
- TBC health-spectral response calibration is used to determine the TBC health by continuously monitoring spectral response

Accomplishments

- The correlation between intensity of Li emission and degree of TBC degradation confirmed
- Optimal Li_2O dopant concentration and doped layer thickness determined
- The effect of Li_2O dopant on TBC durability determined
- A flat flame burner having much improved temperature stability compared with a welding torch has been set up

TBC Design

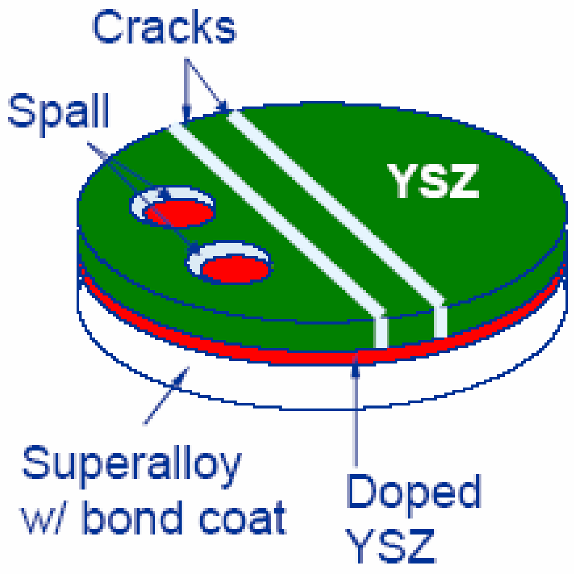


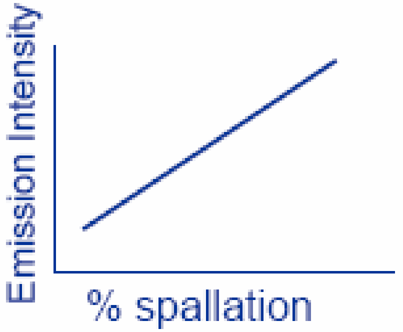
- Place doped YSZ at a location where it is most likely to be exposed to the flame when TBC spalls

TBC Health vs. Spectral Intensity Calibration

TBC with cracks/ spallation is exposed to combustion flame

Determine TBC health-Spectral response relationship



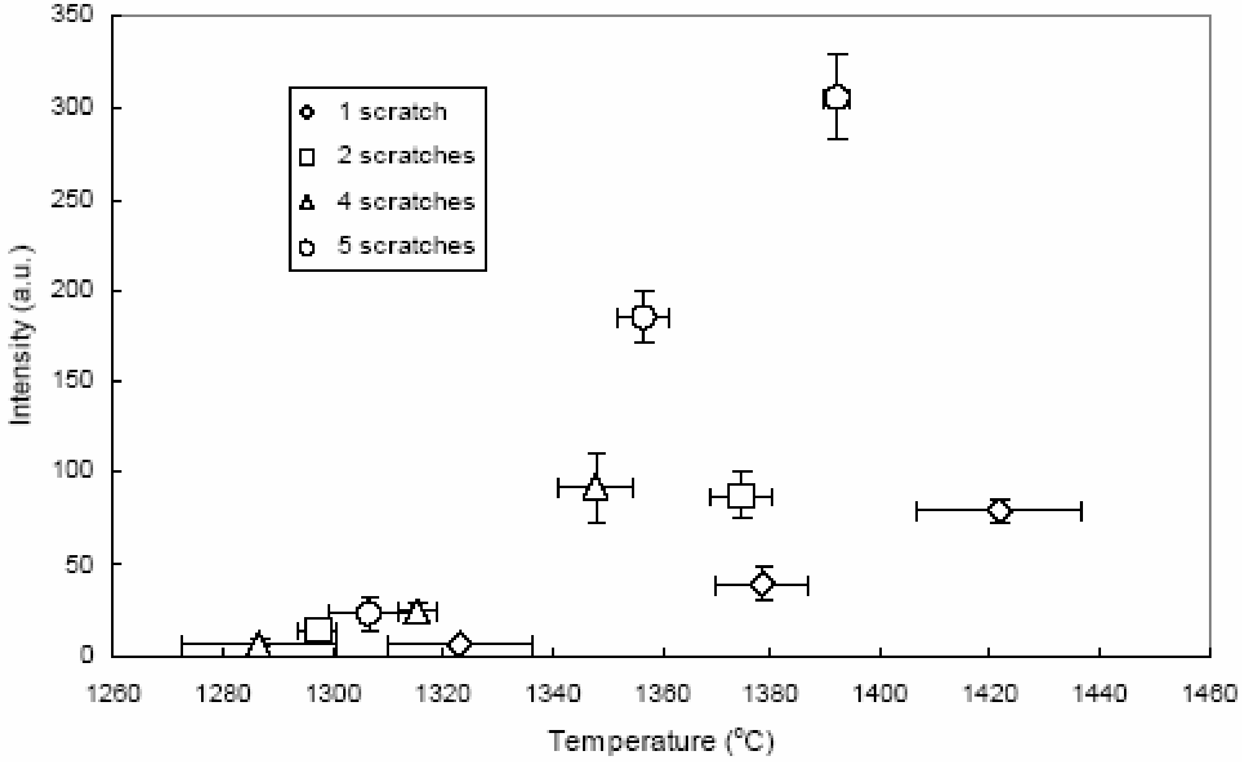


TBC health-spectral response relationship is used in conjunction with in-situ emission spectroscopy To monitor TBC degradation

Emission Spectroscopy Setup

• The emitted light from lithium atoms in flame travels into an input fiber, which carries the light information to the spectrometer. The spectrometer then transmits the information to the PC for data acquisition of measured spectra

Intensity vs. Simulated cracks (Plasma - 1 w/o Li_2O-Doped YSZ/YSZ TBC)



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Conclusions

- The intensity of Li emission correlates well with temperature, Li_2O dopant concentration, and degree of TBC degradation
- A flat flame burner provides much improved temperature stability compared with a welding torch
- Optimal Li_2O dopant concentration is 1 ~ 3 wt%
  - Li_2O-doped inner YSZ layer does not cause a debit in TBC thermal cycling life if the thickness is kept within ~1mil
- Emission spectroscopy is a promising tool for in-situ TBC health monitoring

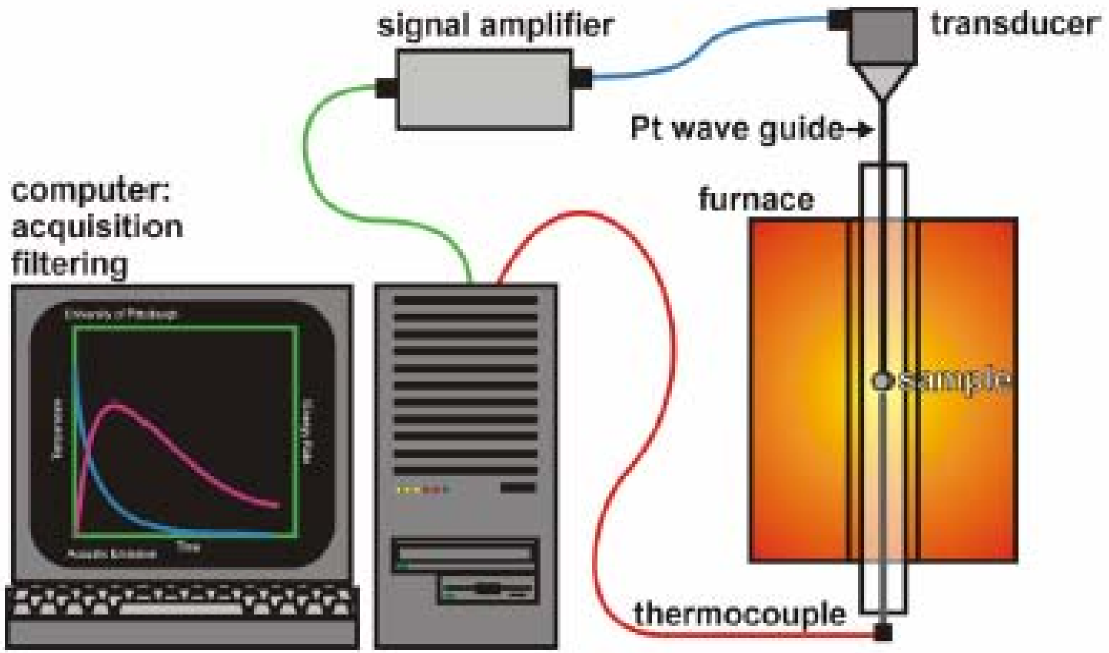
Program Objectives

The overall objectives of this program are to establish a mechanistic understanding of how the durability of oxidation resistant coatings and TBCs is affected by exposures to degradation conditions likely to be encountered in the operation of advanced gas turbines and develop approaches for minimizing detrimental effects on component lifetimes and predicting remaining lives of exposed coatings.

More specifically the goals are to use existing testing techniques and develop new techniques, particularly nondestructive ones, to

1. Evaluate the adhesion of alumina to MCrAlY and aluminide coatings.
2. Understand the degradation mechanisms of TBCs under thermal cycling conditions.
3. Use the test data to model the degradation mechanisms of the coatings and extend the experimental results in a predictive manner.
4. Propose a limited number of improvements to existing coatings (compositions and processing) and evaluate their performance.

Acoustic Emission Testing Apparatus



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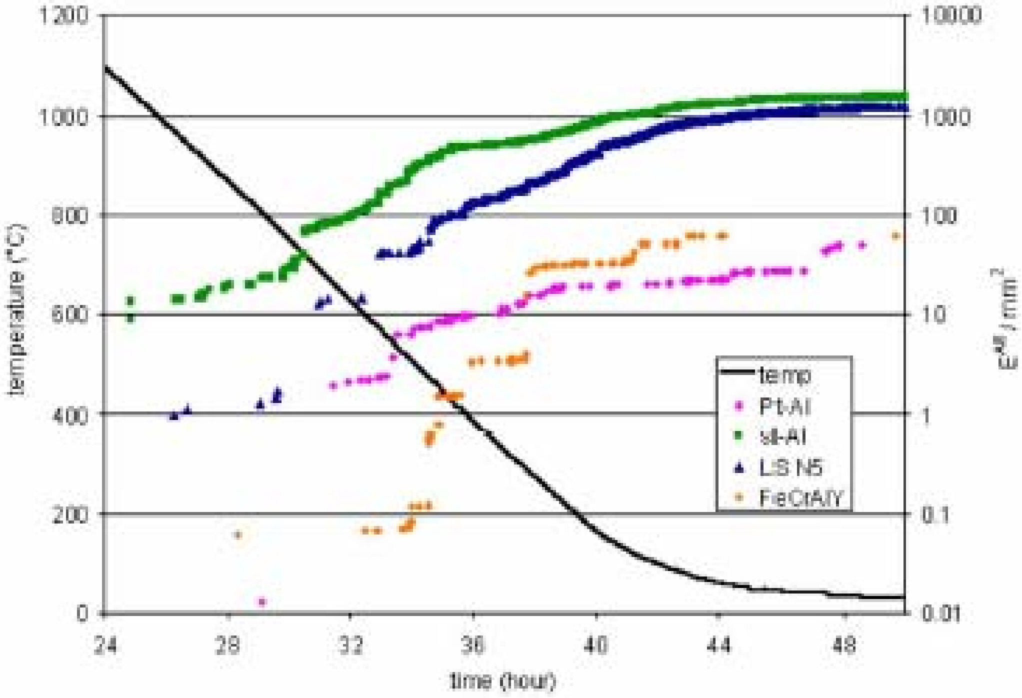
Acoustic Emission Summary

Acoustic Emission Tests:

- 24hour isothermal exposure to 1100°C
- 1°C/min cool
- acoustic events (cracking and spallation) only detected curing cooling



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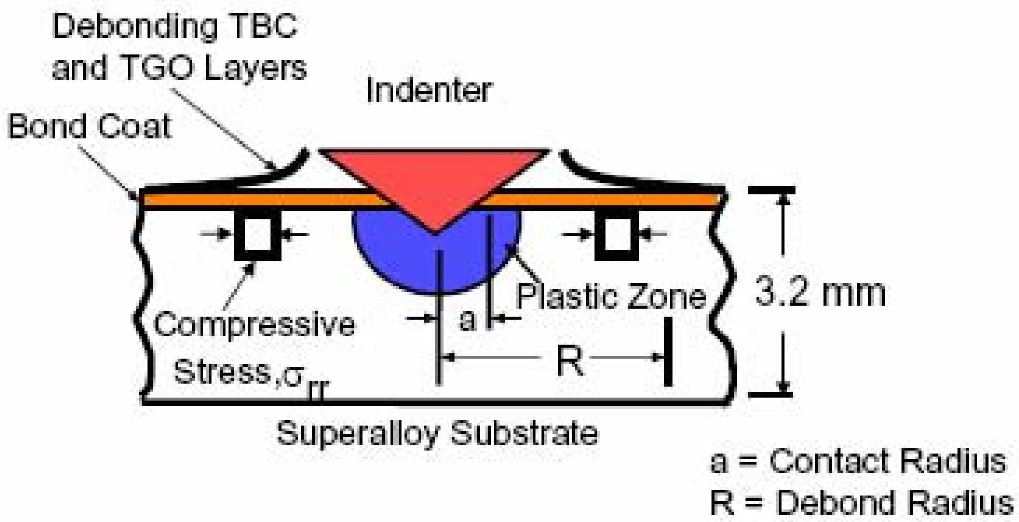
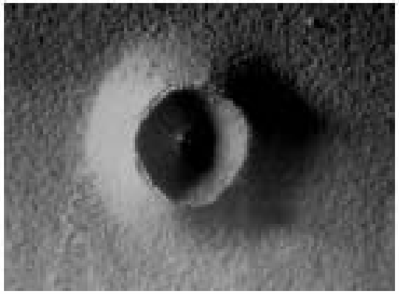
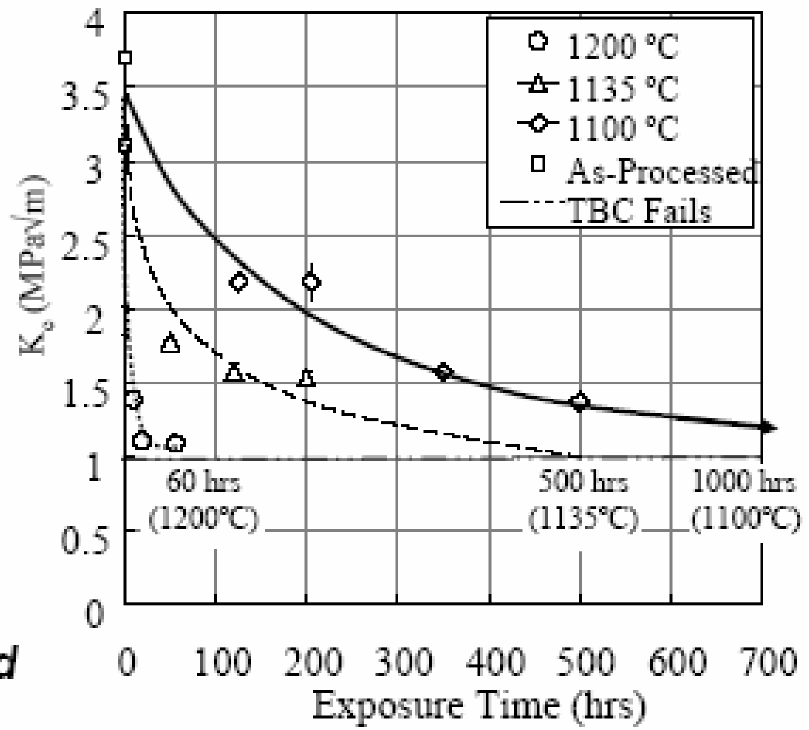
Indentation Test for Interfacial Toughness





- A Rockwell Hardness Indent: Debond Radii 1-3 mm
- TBC and Oxide Layers are Penetrated; Plastic Deformation Induced In Bond Coat/Superalloy Substrate
- Compressive Radial Stress Drives Axisymmetric Delamination
- Radius of Debonding is Determined by Interfacial Toughness
- Based on Work for Diamond Films on Ti Alloys:
  - M.D. Drory and J.W. Hutchinson, Proc. R. Soc. Lond. A (1996)

Isothermal Exposures: Apparent Toughness Loss



- **Mapped Toughness Dependence on Time and Temperature**
- ***Changes in TBC System Not Included in Fracture Mechanics Calculations***
- **Substantial (Apparent) Toughness Loss for Short Exposure Times**
- **Explains Substantial Variability in Life: Toughness is Near That for Failure Over Last 1/2 of Life**
- **Note: G (J/m^2) = 3.58 K^2 (K in $MPam^{1/2}$)**

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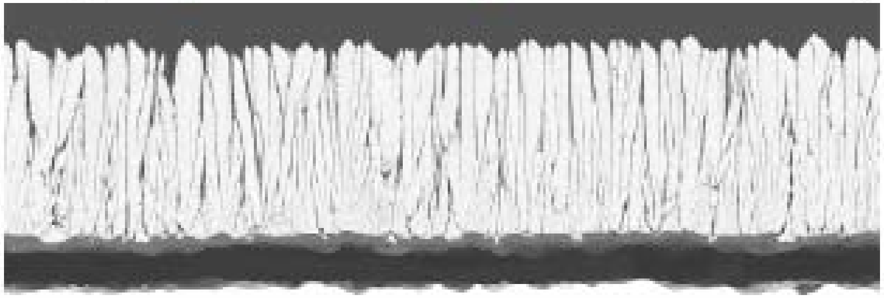
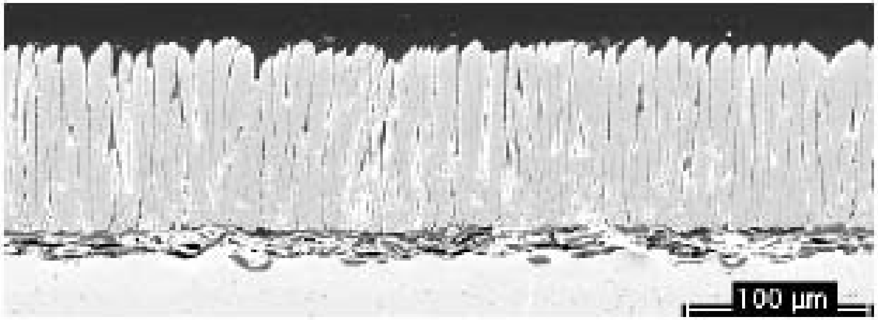
Sectioned Micrograph
Isothermal, Dry Air vs. Cyclic Thermal, Dry Air



Isothermal Dry Air 500 hrs 100 μm



Cyclic Dry Air 500 hrs

- Cycle-Induced Damage is Clearly Occurring
- Damage Causes Cracking In, Below and Above the Oxide; However, Net Toughness is Not Affected
- What Can Fracture Tests Tell Us?

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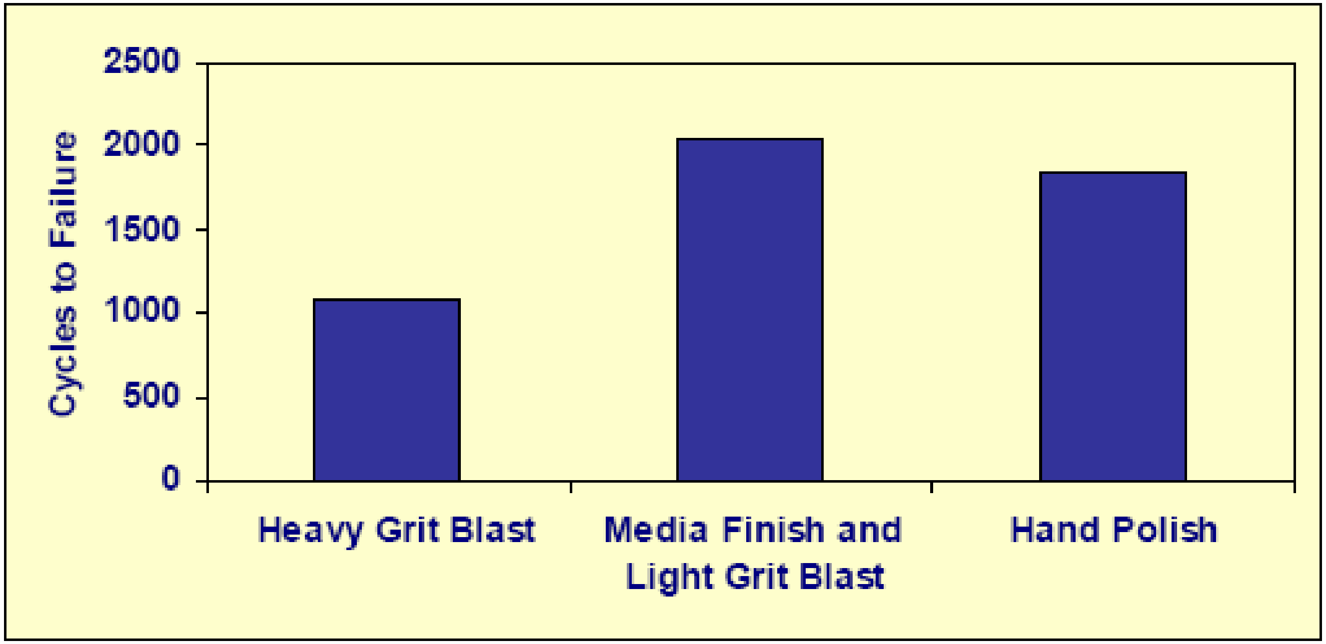
TBC Failures - Smooth Bond Coat Surfaces

Platinum Aluminide Bond Coats



Smooth bond coat surfaces prevent ratcheting and result in long TBC lives as a result of the high fracture toughness of the alumina/Pt-aluminide interface as indicated directly by indentation and indirectly by acoustic emission.

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Summary

Significant progress has been made in:

- Stress measurements in alumina (XRD, Luminescence)
- Indentation technique has been improved as an accelerated testing technique.
- Good results have been obtained in cyclic oxidation life prediction (AE, modified COSP model)

Ongoing work:

- Definition of coating improvements.

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Measurement of Three Critical Parameters As A Basis for A Simple Thermal Barrier Coating Life Prediction Methodology

University of Connecticut

Eric Jordan and Maurice Gell

SCIES Project 02- 01- SR 097

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

Tom J. George, Program Manager, DOE/NETL

Richard Wenglarz, Manager of Research, SCIES

Project Awarded (05/01/02, 36 Month Duration)

$ 478,495 Total Contract Value ($ 478,495 DOE)

Project Objectives

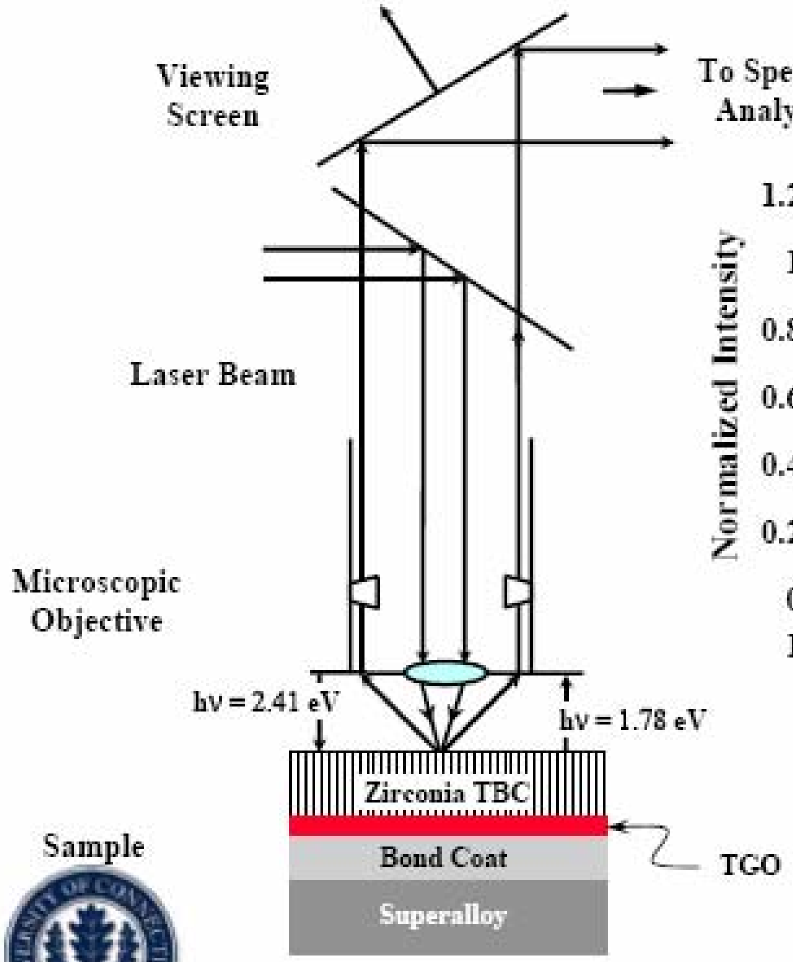
To develop and experimentally validate a method for the nondestructive prediction of remaining life of by measurement of :

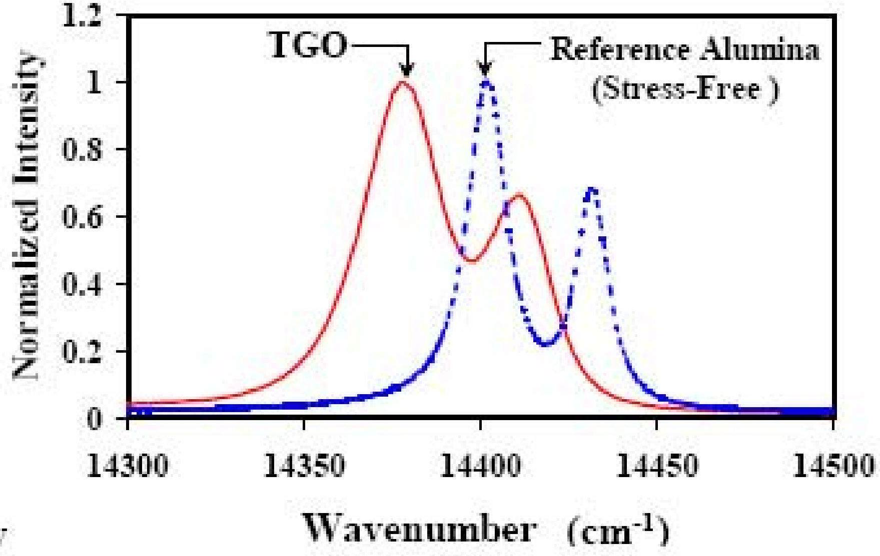
- Initial Surface Geometry
- Thermally Grown Oxide (TGO) Stress
- TGO Thickness

ACOMPLISHMENTS

- An accurate remain life NDI based on TGO Stress measurement
  - Showed a direct relation to damage and failure
- A new surface metric more related to damage than RMS etc.
- Transferred Technology to Industry

Photoluminescence Piezospectroscopy (PLPS) for Measuring TGO Stress





$$\overline{\Delta\nu}_{stress} = \frac{2}{3}\Pi_{ij}\sigma_o$$

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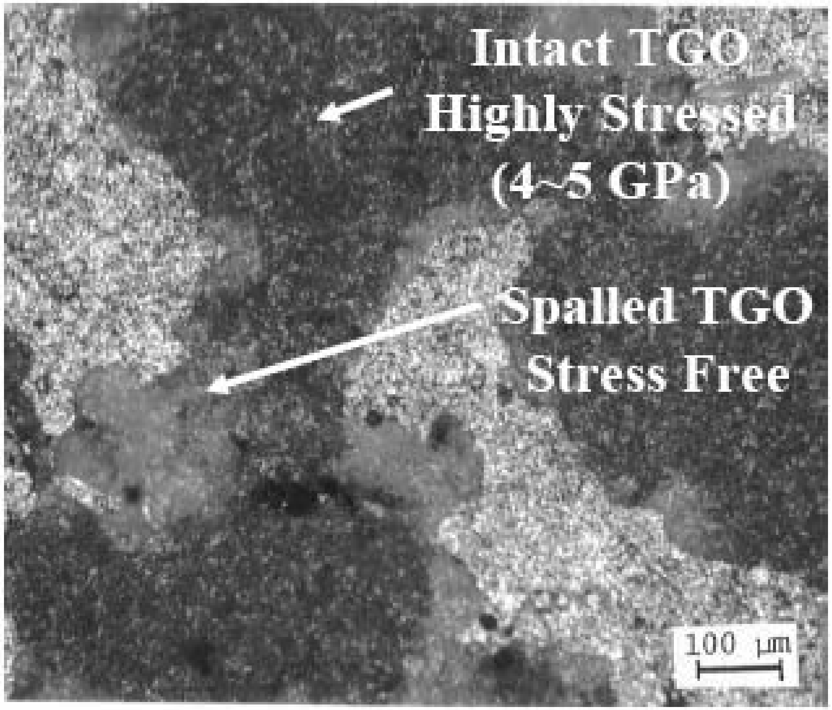
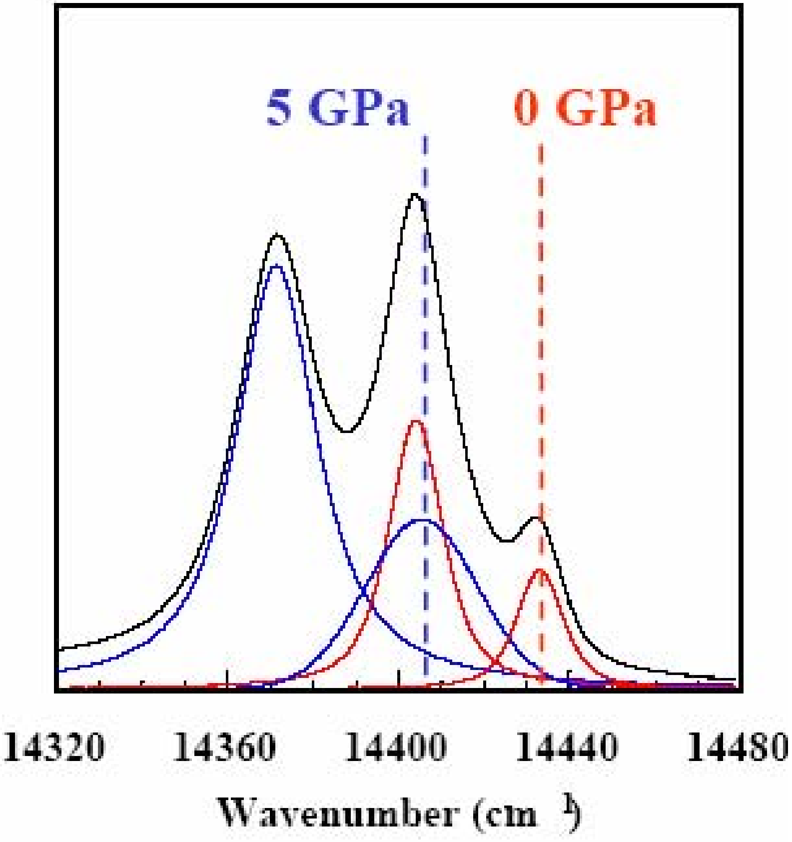
Bimodal Spectra

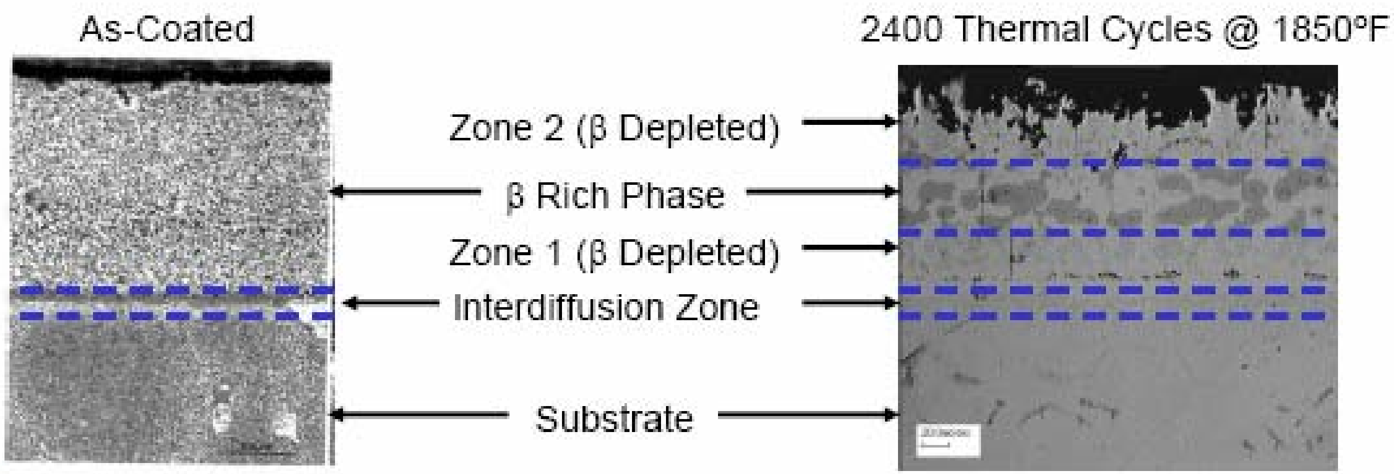


Top of MCrAlY Bond Coat Surface
After Spallation of 7YSZ



TGO Thickness Measured by Advanced AC Potential Drop

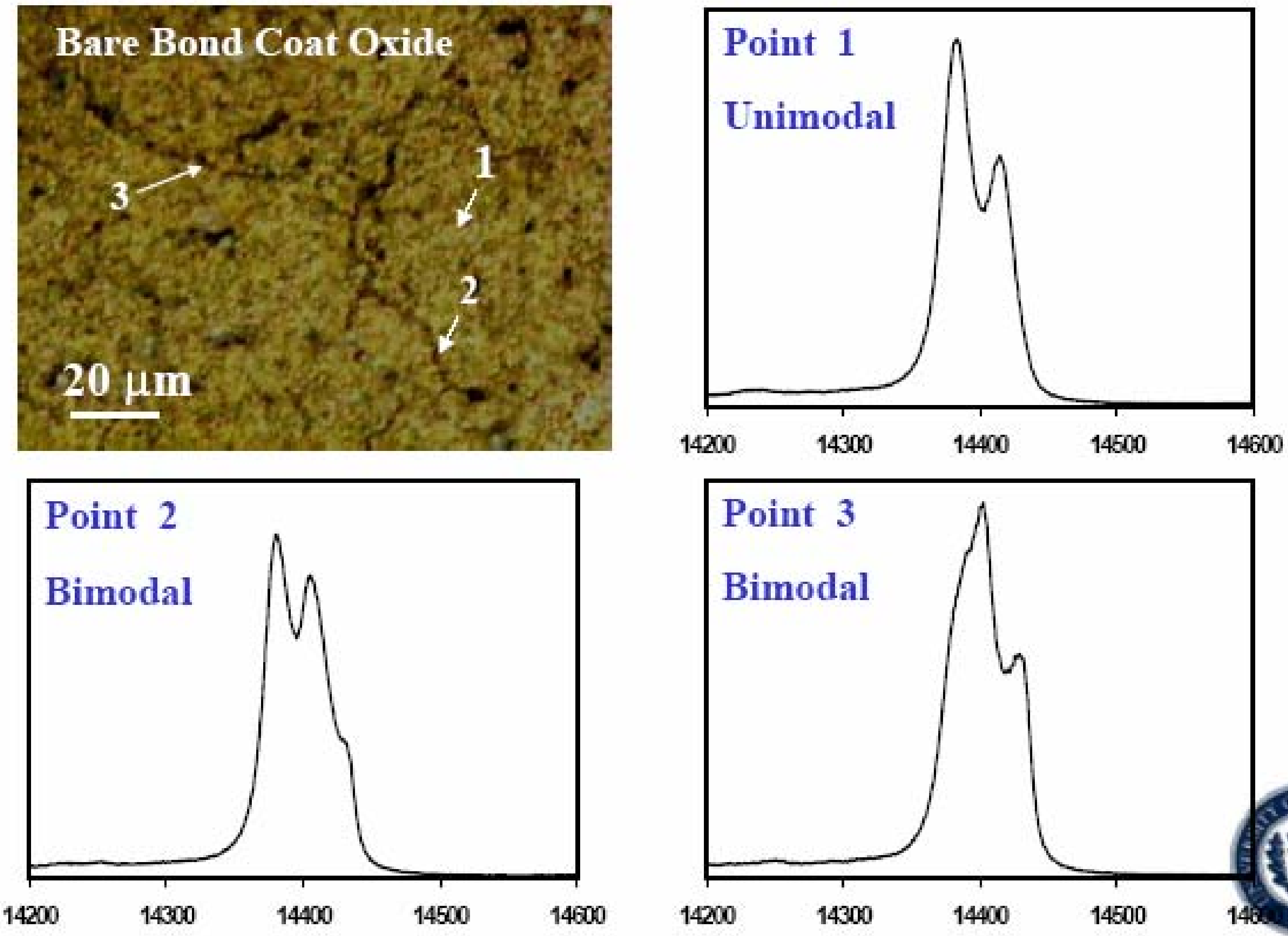
- Beta depletion zone thickness determined from electrical resistivity vs. depth inferred from AC Potential Drop.
- JENTEK measurement system deemed best in Round-Robin Test



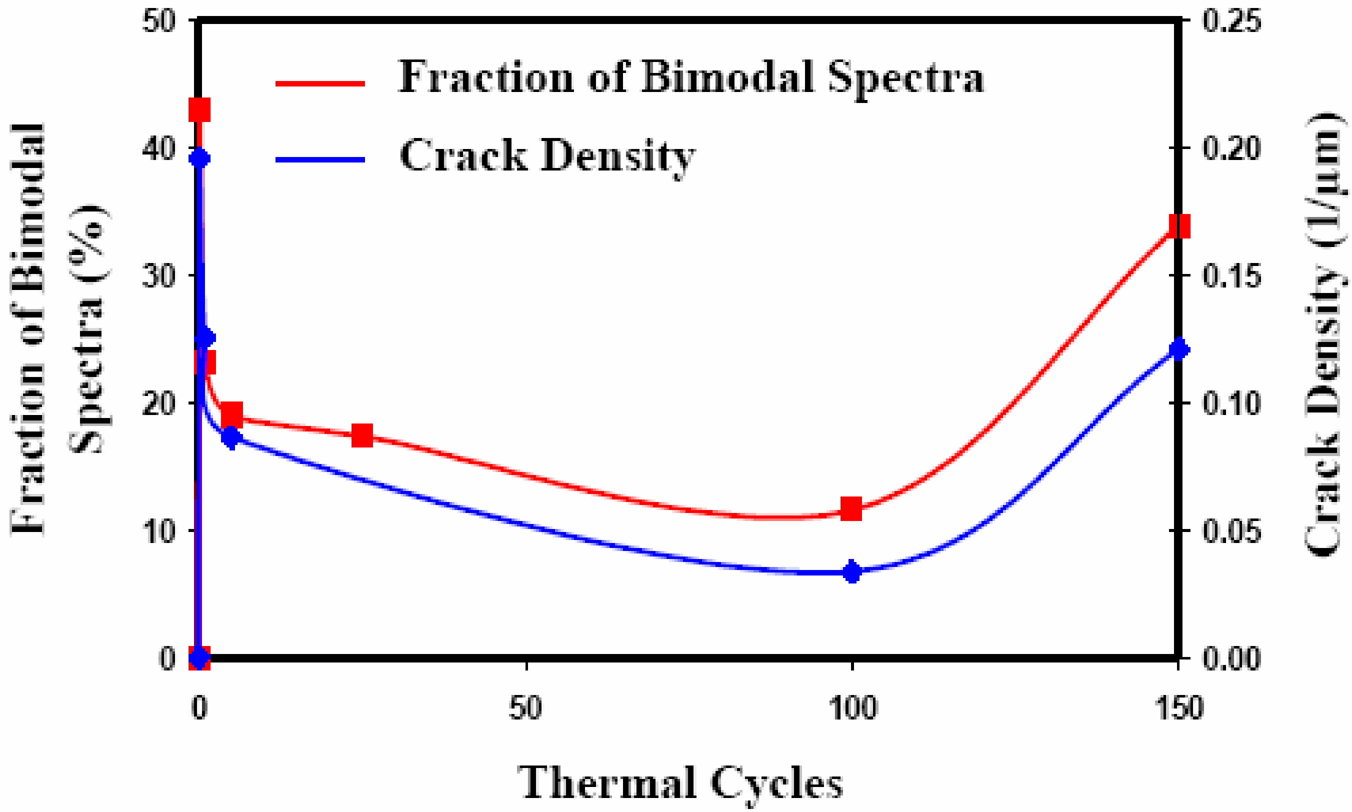
JENTEK Sensors Inc.

University of Connecticut

Bimodal Luminescence Related To TGO Cracking

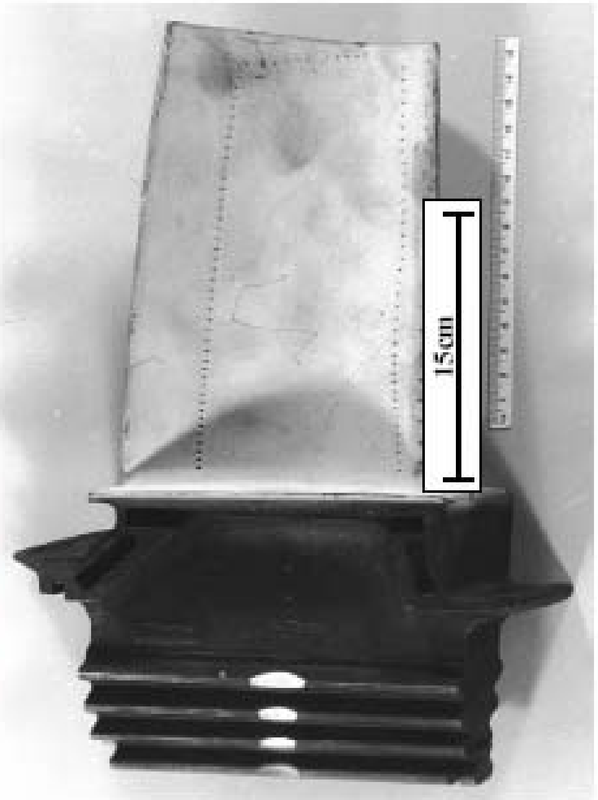


Fraction of Bimodal Spectra and Crack Density



- Fraction of Bimodal Spectra and Crack Density Change in a Similar Manner with Thermal Cycles

Portable PLPS NDI Instrument Available



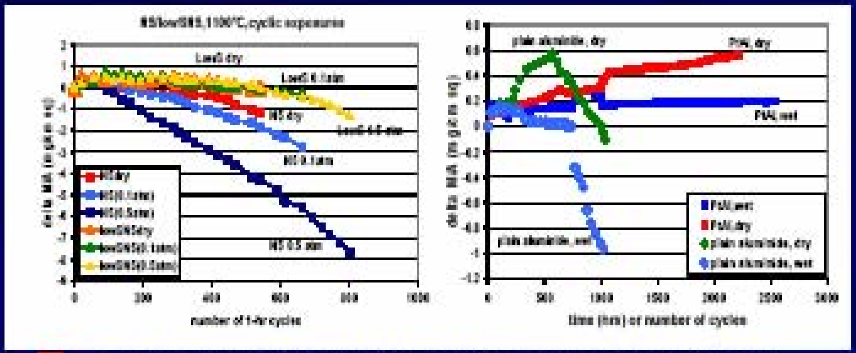
TBC Performance

Control of Water Vapor Effects on the Oxidation of Gas Turbine Alloys and Coatings

U. of Pittsburgh

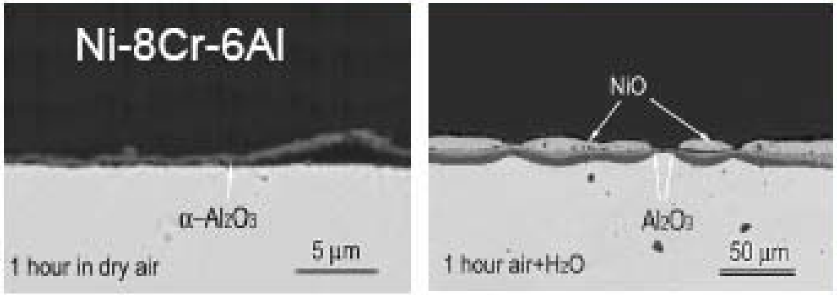
Fred Pettit #077

- Water Vapor Causes α-Al_2O_3 Scales to Crack and Spall More Profusely



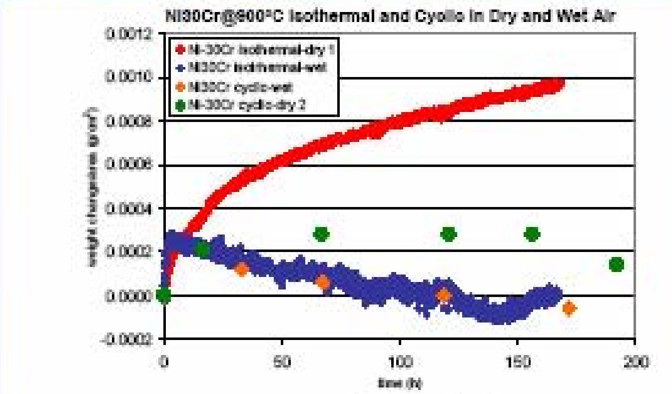
- The Adverse Effects of Water Vapor are Inhibited by Using Alloys (Low S) or Coatings (Pt Mod.) with Improved α-Al_2O_3 Adherence

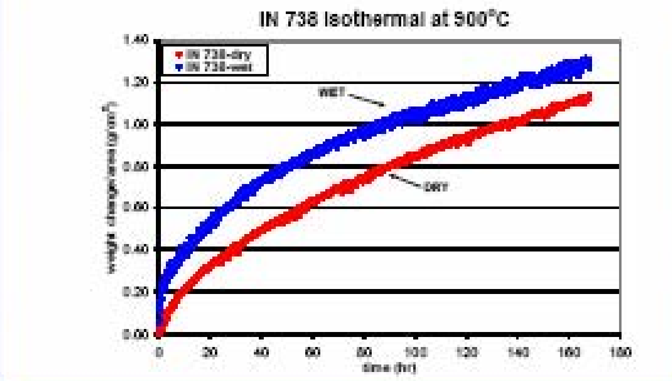
- Water Vapor Inhibits the Selective Oxidation of Aluminum on Nickel Base Superalloys



- In environments Containing Water Vapor Superalloys with High Aluminum Concentrations (>6wt%) must be used to Inhibit Oxidation Degradation

- In the Case of Chromia-forming Superalloys Water Vapor Causes the Vaporization of Cr_2O_3 to be Increased.





- The Use of Alloys Such as IN 738 Inhibits this Form of Degradation Due to the Formation of a Layer of TiO_2 on Top of the Cr_2O_3 Scale.

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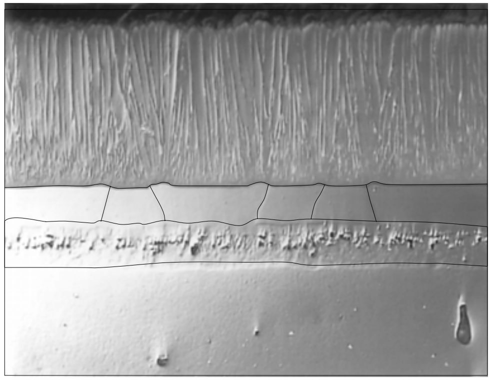
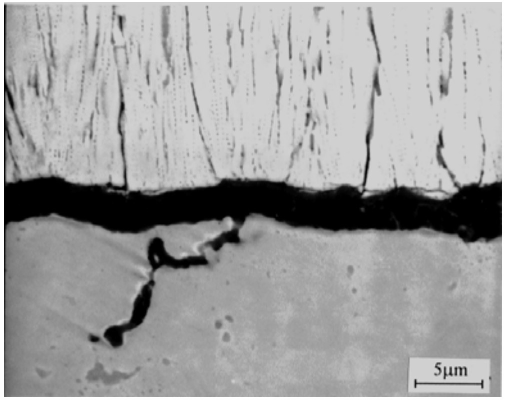
4:1 Improvement in Life of Thermal Barrier Coatings

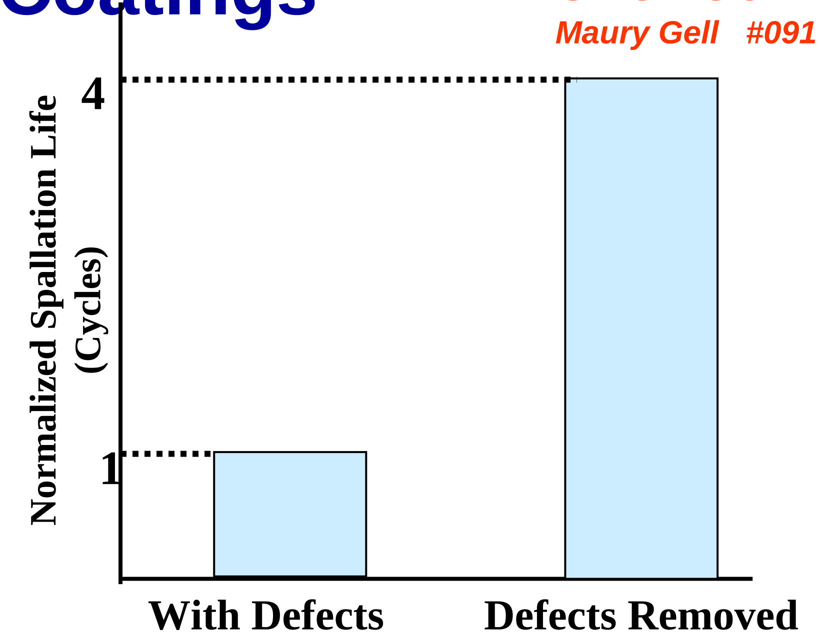
U. Of Connecticut
Maury Gell #091



Pt-Al/EB-PVD TBC
Defect:Bond Coat Ridges



MCrAlY/EB-PVD TBC
Defect: Embedded Oxides

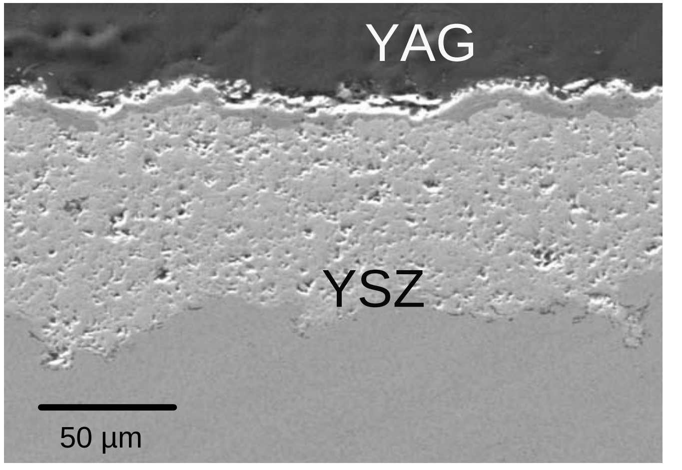


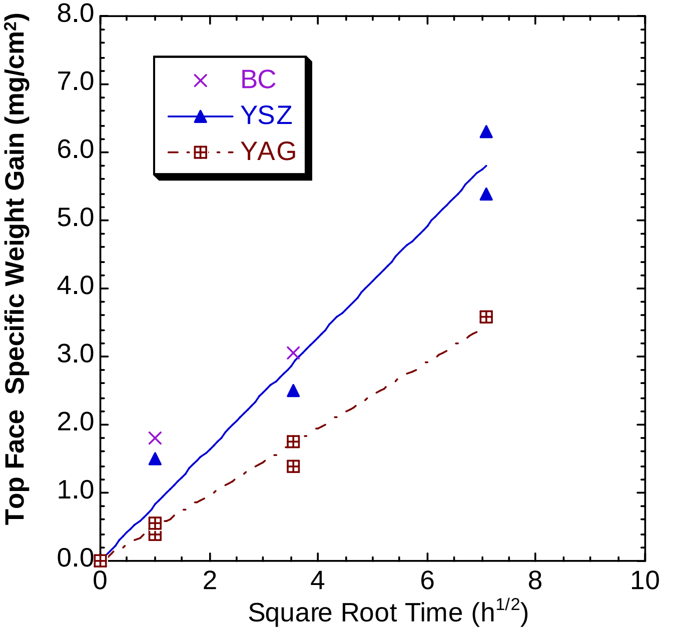
- This project applies to EBPVD (electron beam physical vapor deposition) thermal barrier coatings.
- Demonstrated that the spallation life (cycles) of TBCs is controlled by processing defects on the bond coat surface.
- When these defects are removed by polishing or slight process modification, the spallation live of is improved by 4 times.
- Two gas turbine manufacturers are using the technology.
- Subsequent development by industry has extended the improvements up to 10 times the original spallation life.

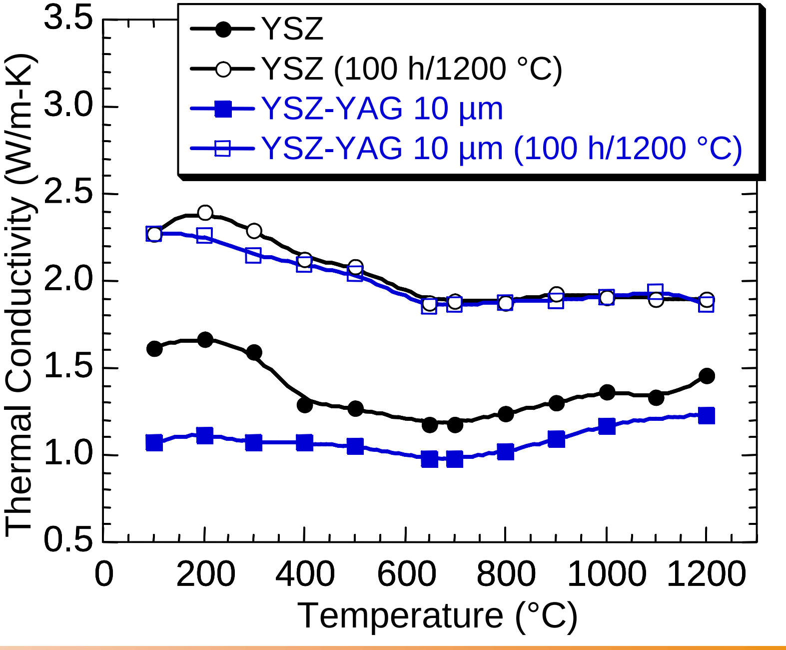
Improved Oxidation Resistance with YAG Layers in TBCs

Northwestern Univ.
Katherine Faber #047

- **Designed Yttrium Aluminum Garnet (YAG)/Yttria Stabilized Zirconia (YSZ) multilayer coatings and produced by Small-Particle Plasma Spray**
- **Demonstrated that the oxidation resistance of the bond coat (BC) is improved by a factor of ~3 with YAG coating.**
- **Proved that YAG does not compromise thermal conductivity of TBC.**



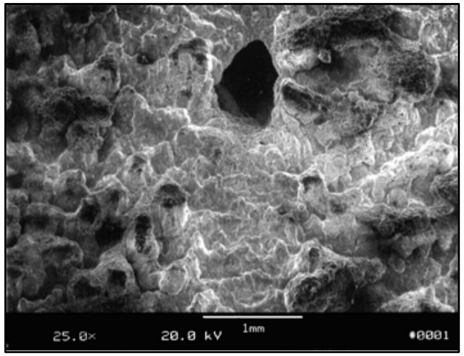


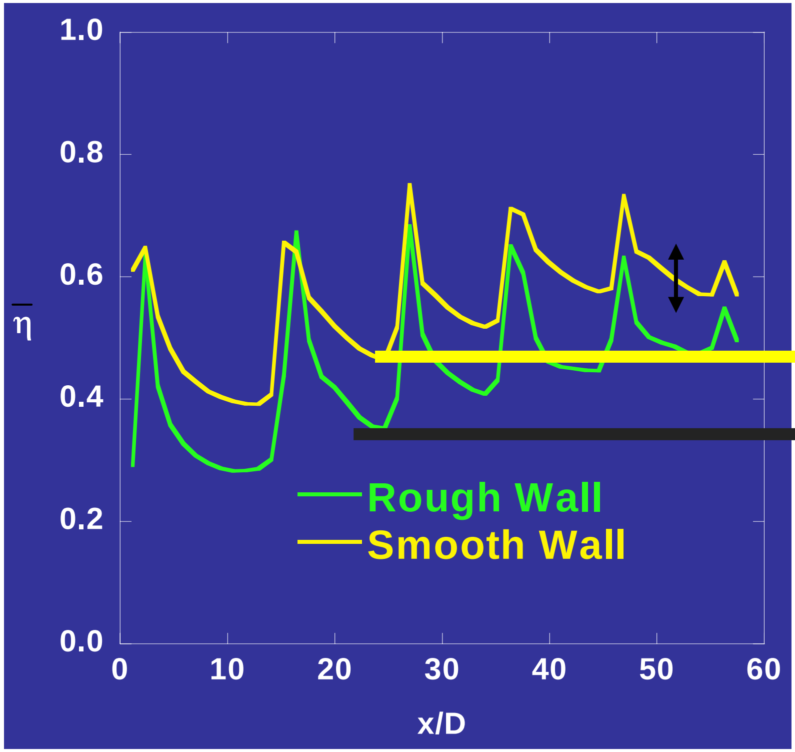


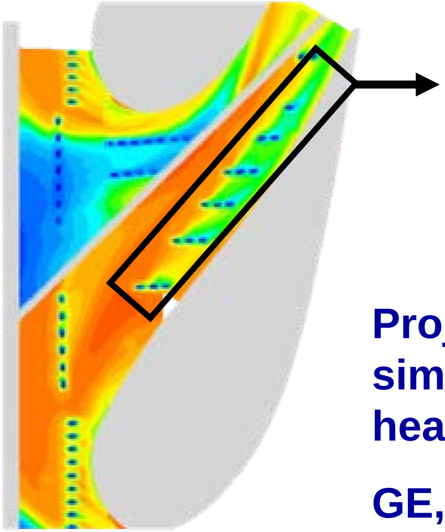
Evaluation of Turbine Vanes and Endwalls with Realistic Surface Conditions

Picture of cooling hole with surface roughness for actual operating conditions

Virginia Tech, K. Thole
University of Texas, D. Bogard #110





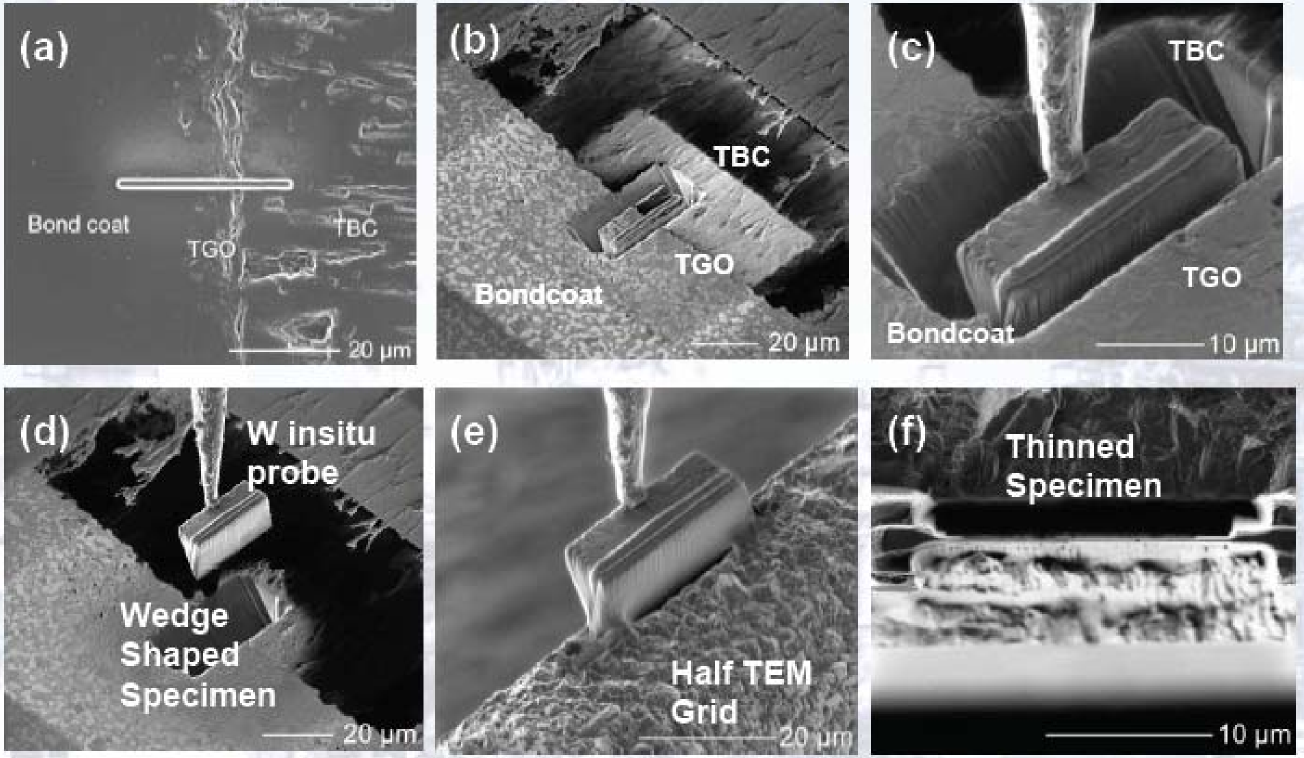


Reduction in cooling results in more than a 2X reduction in life

Project showed the effect of surface roughness levels from simulations of engine operating conditions on airfoil and endwall heat transfer will be to reduce cooling effectiveness and airfoil life

GE, Pratt & Whitney, and Rolls-Royce have participated in this project

Focused Ion Beam IN-Situ Lift-Out (FIB-INLO) for TEM/STEM Specimen Preparation of TBCs



Sequential ion beam images from TEM specimen preparation of TBCs by focused ion beam (FIB) in-situ lift out (INLO) technique: (a) Pt wire is deposited at a site of specific interest; (b) focused ion milling is carried out to create a wedge-shaped specimen, (c) specimen is welded to a micromanipulator, and (d) lifted out, (e) specimen is welded to a TEM grid, and (f) thinned further for TEM analysis.

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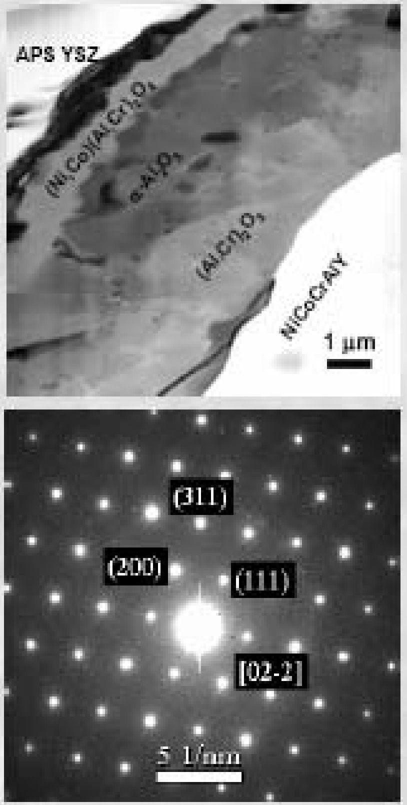
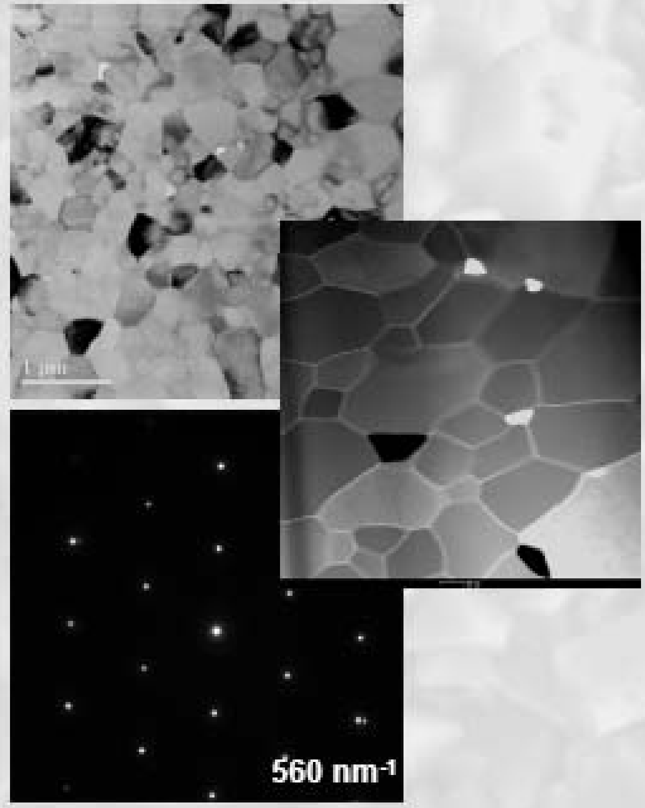
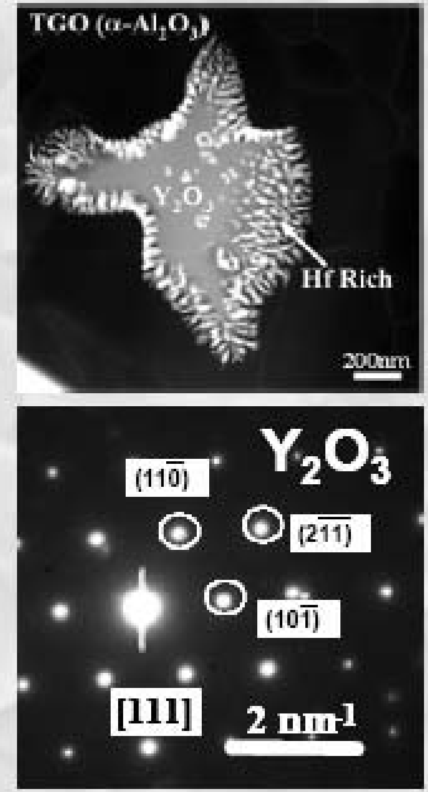
TEM/STEM on Thermally Cycled TBCs



$(Ni,Co)(Al,Cr)_2O_4$ Oxide Layer Near the YSZ/TGO Interface with a Spinel Structure and Lattice Parameter of 8.0317Å.



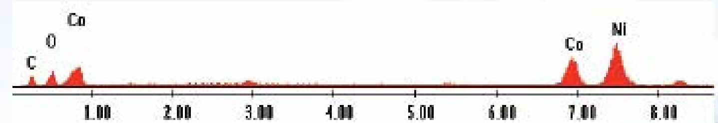
Controlling Hf Content in the Superalloy Substrate Increases Lifetime of TBCs by 4X: Excellent YSZ/TGO Interface and Suppression of Rumpling.

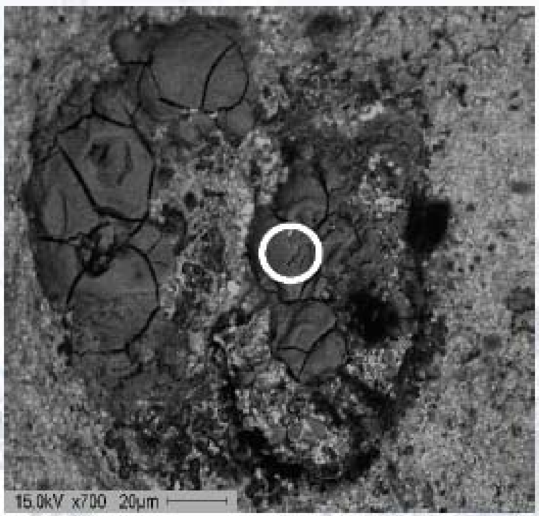


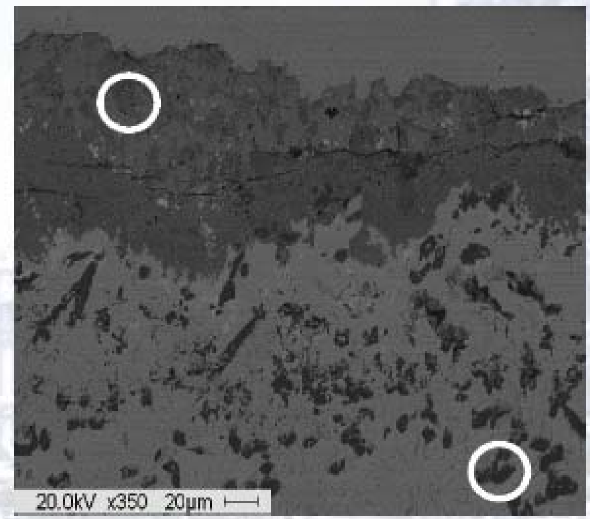
Oxide Stringers Observed as Y_2O_3 on Several TBC Specimens of Different NiCoCrAlY Bond Coats.

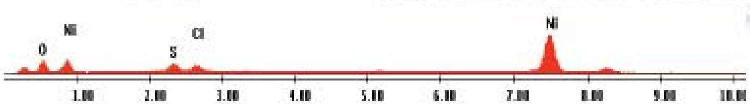
Preliminary Characterization* of Degradation in NiCoCrAlYs under Syngas Combustion Environment

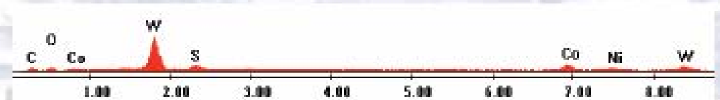
Observation of Sulfidation, Ni/Co-Rich Oxide Scale (e.g., Spinel) and Internal Degradation for NiCoCrAlY Coatings











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* Specimens and Testing Courtesy of IRB Members. *YHS@UCF*

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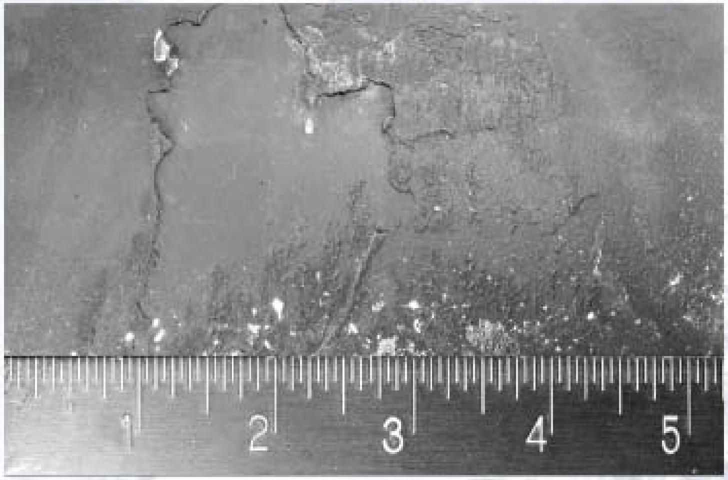
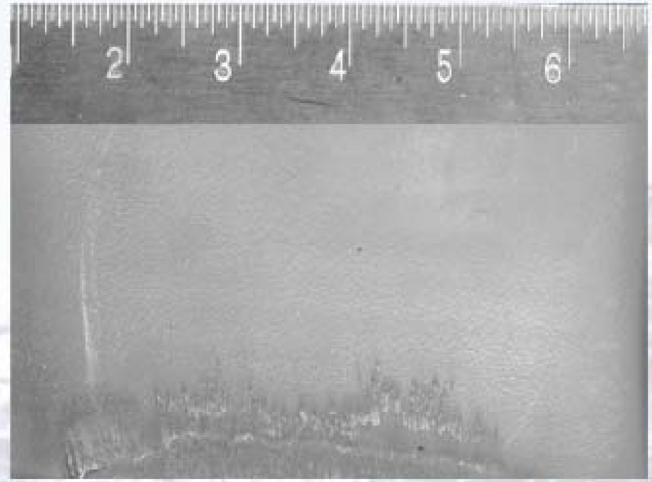
Preliminary Characterization* of Degradation in TBCs under Syngas Combustion Environment





- TBC Specimen was Covered with Brown-Gray Deposits, Containing Fe, Si, Al, Ca, Mg, Na, K and Sulphate Anions (SO_4^{2-}). Primary Constituents is Fe_2O_3.
- Significant Presence of Spinel Compounds such as $NiFe_2O_4$, $NiCr_2O_4$ and $CoCr_2O_4$ in Spalled Area was Observed.
- Oxides of Co, Cr, Si and Mg were Observed through the 8YSZ coating thickness.

* Specimens and Testing Courtesy of IRB Members.

Summary

- Provide Performance Data and Fundamental Understanding of Degradation for TBCs in Natural Gas (NG) and Syngas (SG) Combustion Environment:
  - ✓ Identify Degradation (e.g., hot corrosion) Mechanisms (e.g., YSZ Destabilization, Deposit Penetration and Reaction, etc.).
  - ✓ Generate Critical Materials Data (e.g., Solubility, Eutectic Compositions and Degradation Kinetics for Realistic NG and SG Combustion Turbine Environment).
  - ✓ Provide Feasible Approaches to Improve Resistance Against TBC Degradation in Fuel-Flexible Combustion Environment.

- Testing of TBCs by FTT's HADES Rig and Advanced Microstructural Analysis:
  - ✓ Comparison of NG and SG Combustion in HADES.
  - ✓ Detailed Documentation of Microstructural Degradation in TBCs by Using Scanning Transmission Electron Microscopy (TEM/STEM).
  - ✓ Better Understanding of Failure Mechanisms/Characteristics and Approaches for Enhanced TBCs and other Coatigs Schemes in NG-SG Flexible Environment.
  - ✓ Preliminary Characterization of SG Combustion TBCs in Progress.

- Benefits for Gas Turbine Engineers:
  - ✓ Prime-Reliant Application of TBCs in Fuel-Flexible Environment.
  - ✓ Development of Enhanced and Durable TBCs Based on Fundamental Understanding of Microstructural Development.

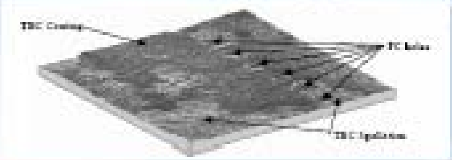
Motivation

- Alternate fuels (e.g. coal, petcoke, and biomass) are being considered to produce syngas fuels to replace natural gas in power turbines

- Despite gas cleanup, small levels of airborne particulate (e.g. 0.1 ppmw) produce significant quantities (e.g. 2 tons) of ingested material in a large utility power plant during an 8000 hour operating year

- Previous studies of deposits from "dirty fuels" (e.g. Wenglarz et al., Wright et al., Patnaik et al., etc…) were conducted in the 1980s, before the advent of G and H class machines with…
  - Higher firing temperatures (1400C)
  - Broader use of EB and APS TBCs
  - Heavier reliance on innovative film cooling strategies

- The impact of depositing synfuel contaminants may present unforeseen viability issues for modern high performance turbines. For example…

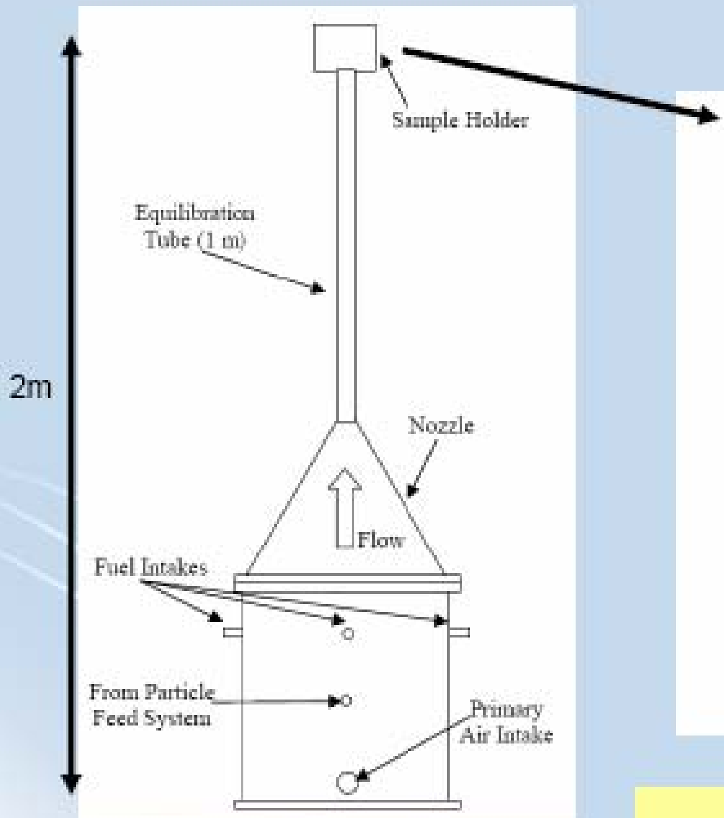


Spallation near a film cooling hole

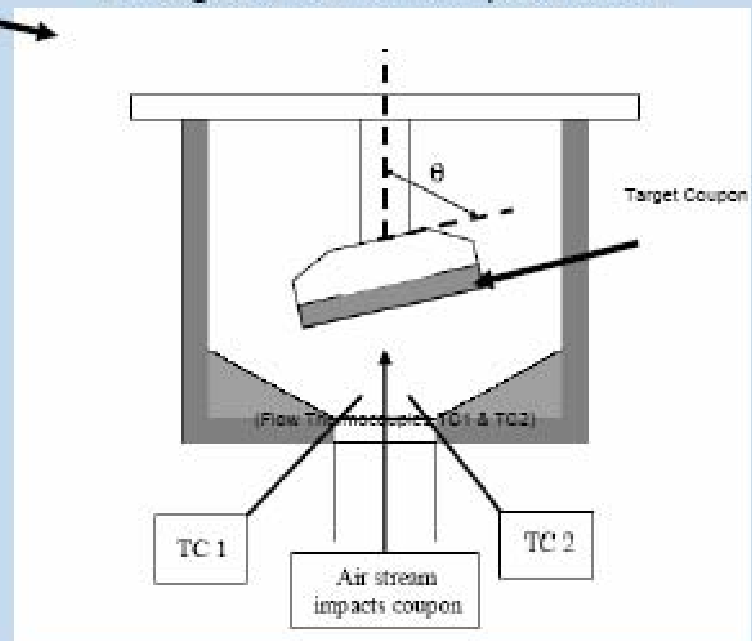
"Furrows" downstream of a film cooling hole

Deposits in the mouth of a film cooling hole

Schematic of Turbine Accelerated Deposition Facility (TADF) at BYU



Enlarged View of Sample Holder

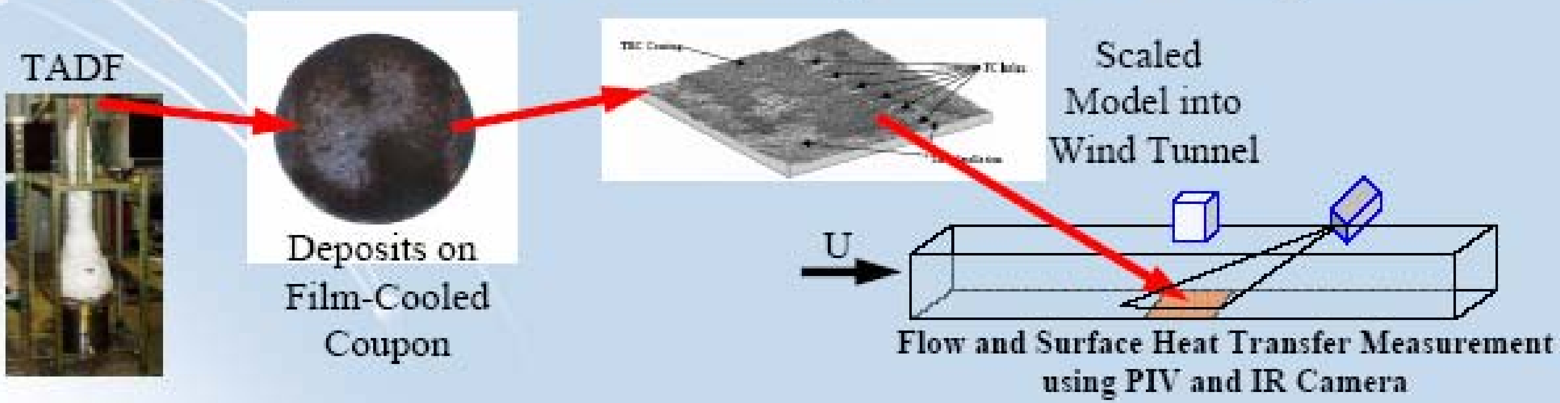


(Jensen et al. IGTI 2004 in Vienna
Paper #GT2004-53324.)

Coupons obtained from industrial partners, including oxidation resistant coating and thermal barrier coating (TBC)

Project Summary

- Deposits in accelerated facility (4 hrs) match accumulated deposits in industrial facilities (8000-25,000 hrs)
- Synfuel deposits generated to date show fuel-type dependence
  - Composition is fuel-type dependent
    - Enhanced deposition of unique elements (e.g., Fe for petcoke, Ca for sawdust)
    - Deposition in TBC cracks has different composition than deposit on surface
  - Physical structure is also fuel-type dependent
    - Strands detected in voids in petcoke flyash deposit
- Making progress on thermal conductivity measurement
- Redesign of facility for cooled coupons is underway
- Work on deposits around film cooling holes will start in year two



Superior Thermal Barrier Coatings for Industrial Gas-Turbine Engines Using a Novel Solution-Precursor Plasma-Spray Process

University of Connecticut
Principal Investigator: Prof. Eric H. Jordan

The Ohio State University
Co-Principal Investigator: Prof. Nitin P. Padture

SCIES Project 03- 01- SR107

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

Tom J. George, Program Manager, DOE/NETL

Richard Wenglarz, Manager of Research, SCIES

Project Awarded: 07/01/03 (36 Months Duration)

$546,000 Total Contract Value ($546,000 DOE)

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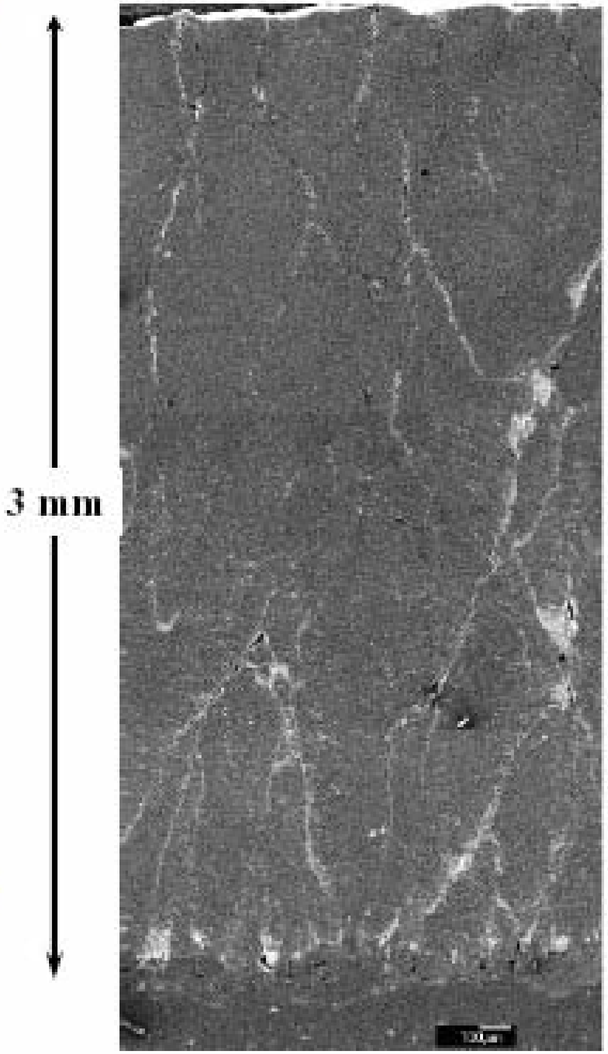
Objectives and Approach

- To Demonstrate Feasibility of Ultra-Thick (~3 mm) TBCs Using Solution-Precursor Plasma-Spray (SPPS)
- To Determine Mechanical Properties, Thermal Cond., Durability, and Hot-Corrosion Resistance
- To Elucidate Failure Mechanisms and Microstructural Thermal Stability
- To Identify Microstructural and Architectural Characteristics for Optimum Ultra-Thick SPPS TBCs
- To Obtain TBCs with Improved Durability, Thermal Resistivity and Hot-Corrosion Resistance

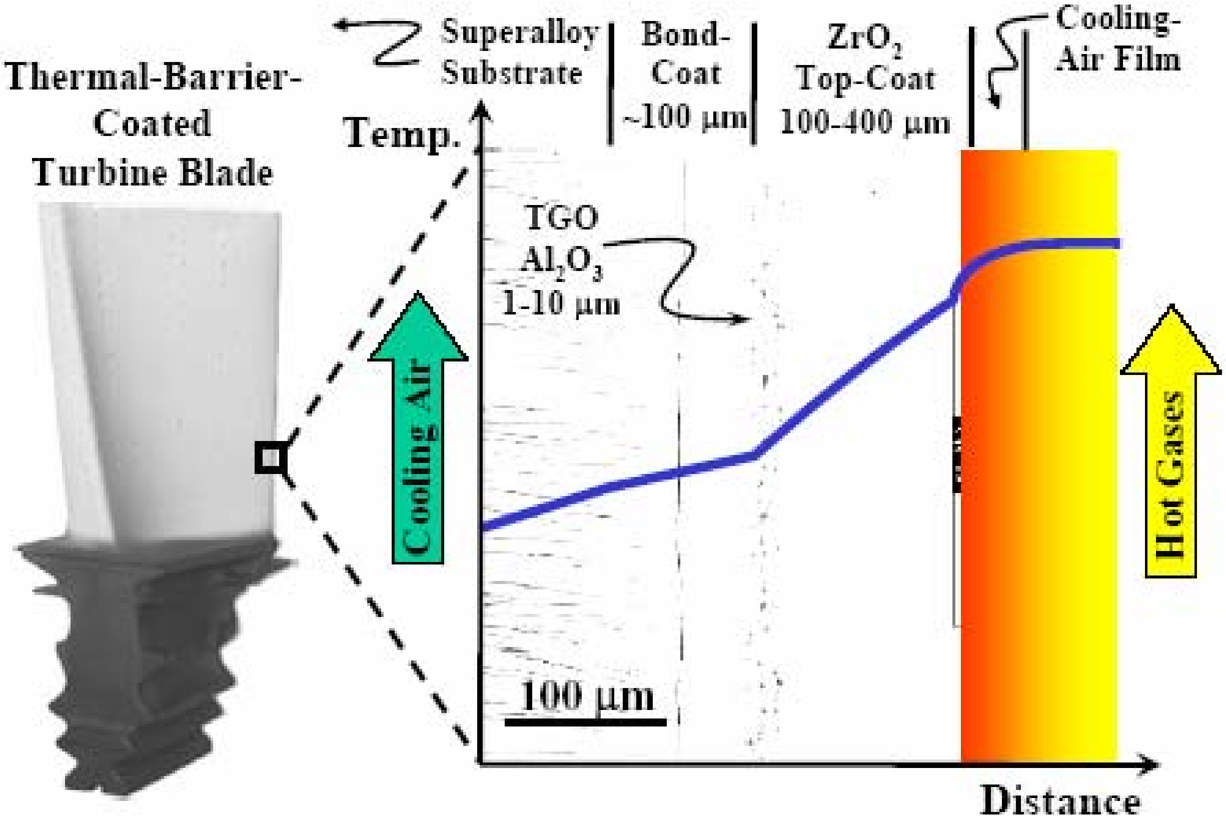
Accomplishments

- Demonstrated the Feasibility of Depositing Ultra-Thick (~3 mm) TBCs Using the SPPS Process
- Determined Mechanical and Thermal Properties of SPPS Ultra-Thick TBCs
- Demonstrated Improved Durability in SPPS Ultra-Thick TBCs
- Deposited Layered TBCs for Lower Thermal Conductivities



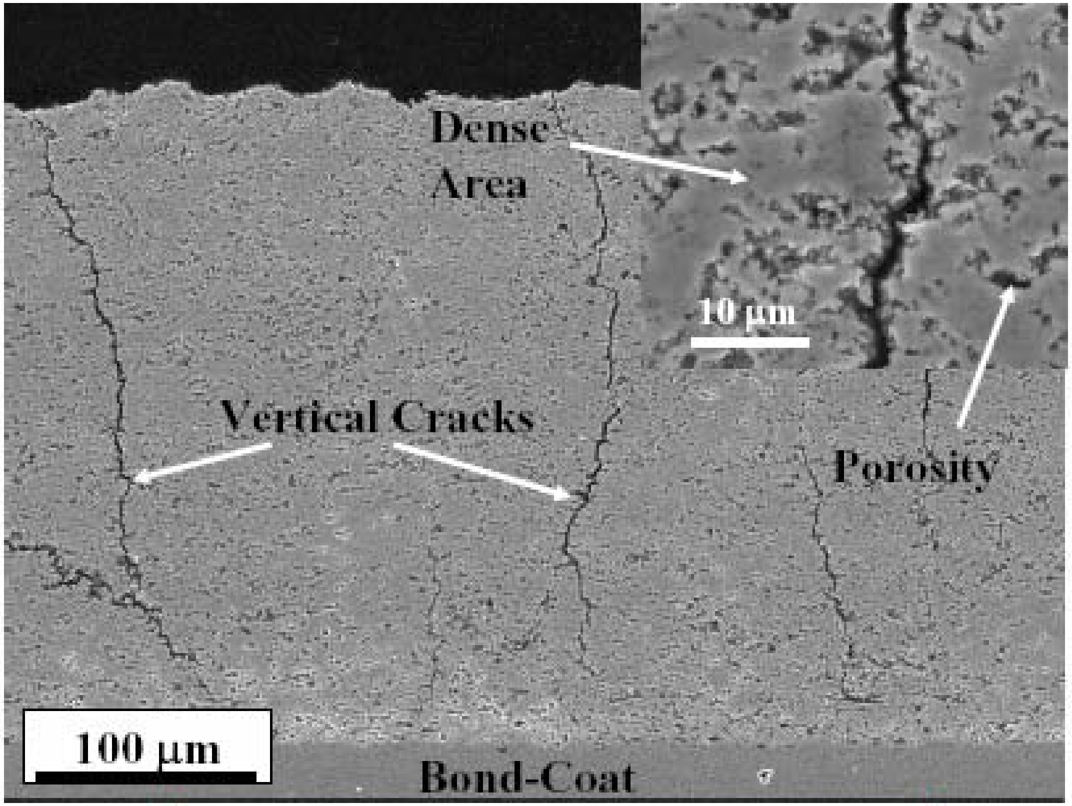
Thermal Barrier Coatings

- Hot-Section Metal Comp.
- Blades
- Vanes
- Combustors
- Temp. Redn. Up to 300 °C



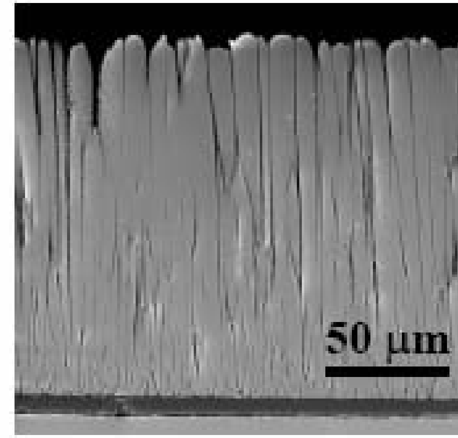
Padture *et al.*, *Science*, 2002

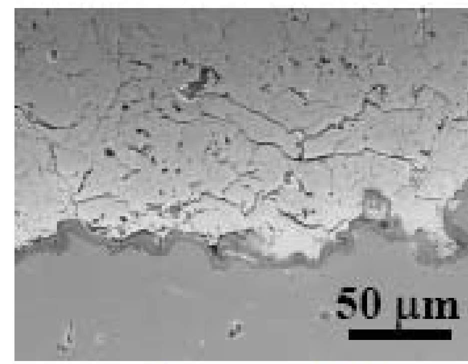
SPPS TBCs: ZrO_2-7 wt% Y_2O_3



- No Macro-Splat Boundaries
- Vertical Cracking
- Porosity (18-20%)

EB-PVD



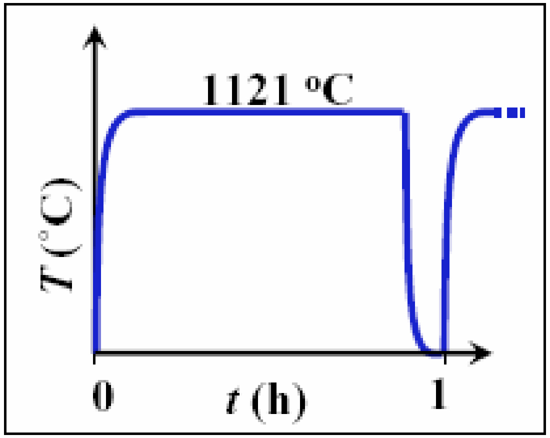


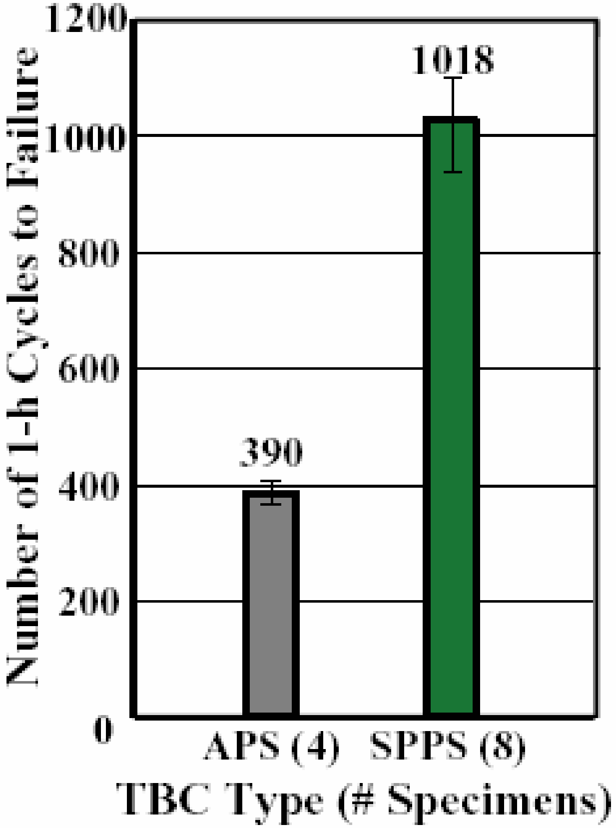
Conv. APS

Durability of SPPS TBCs

- Same Bond-Coat for APS and SPPS
- TBC Thickness: ~250 μm

Thermal-Cycling Life Test

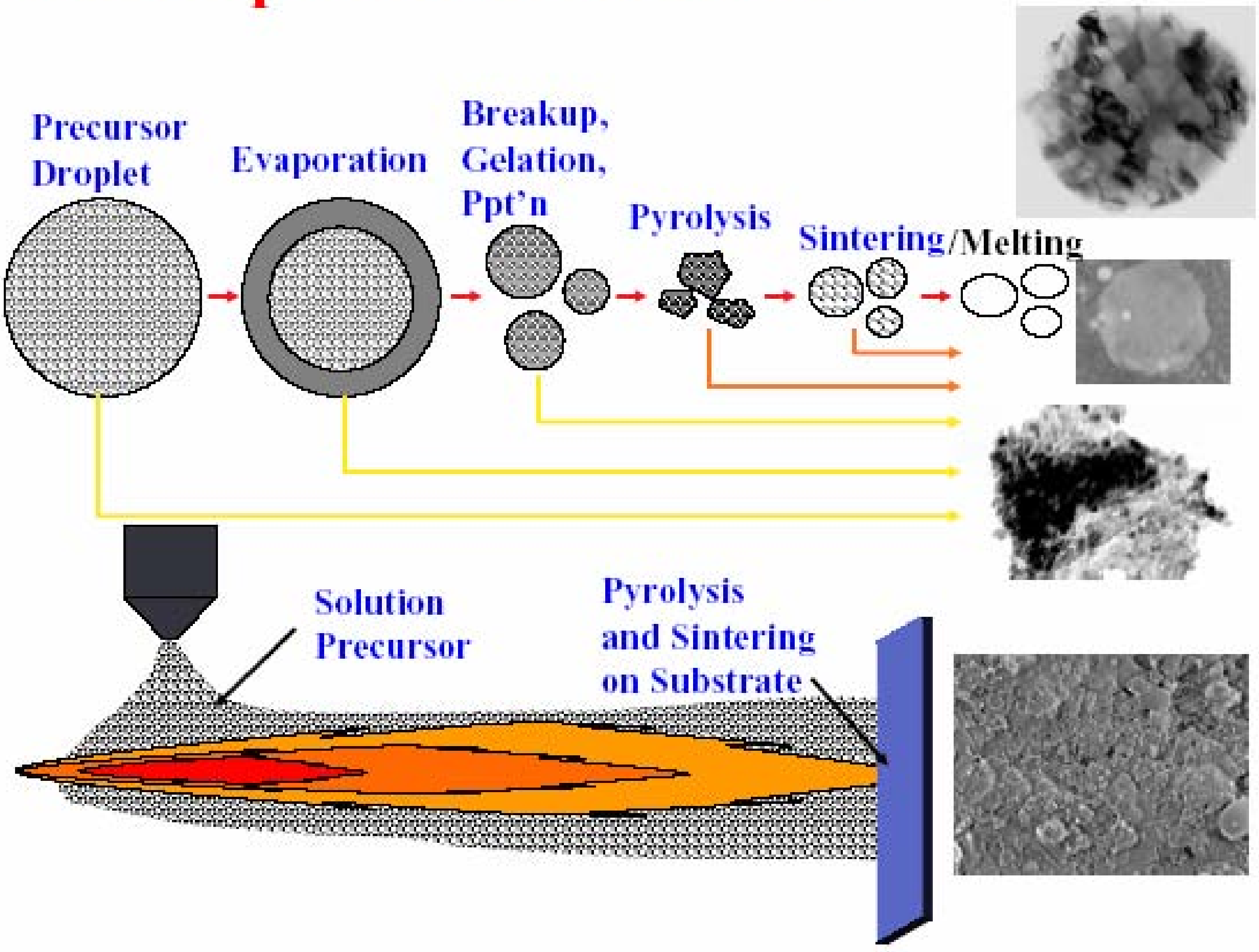




- No Macro-Splat Boundaries
- Vertical Cracking
- Porosity (18-20%)

Surf. & Coat. Techol., 2004

SPPS Deposition Mechanisms



Ultra-Thick TBCs

SPPS Process Uniquely Suited for Ultra-Thick TBCs

Advantages

- Lower Thermal Diffusivities
- Increased Engine Operating Temperatures
- Improved Efficiency
- Lower Cooling Requirements

Applications

- Turbine Blades Out-of-Air-Seals
- Turbine Airfoils
- Combustors

Current Limitations

- Ultra-Thick TBCs Difficult To Deposit Using APS
- Need Graded Interfaces

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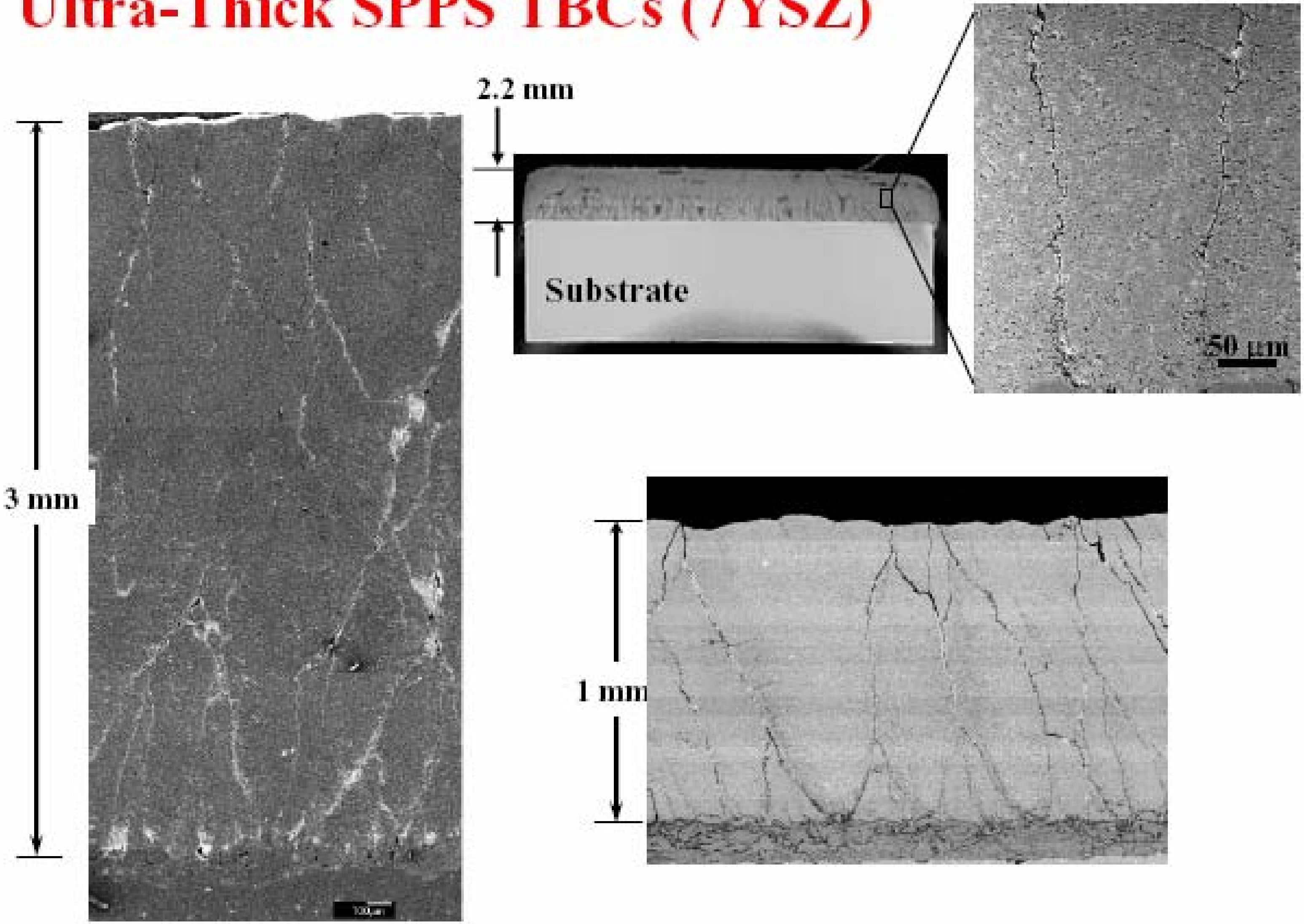
Ultra-Thick SPPS TBCs (7YSZ)



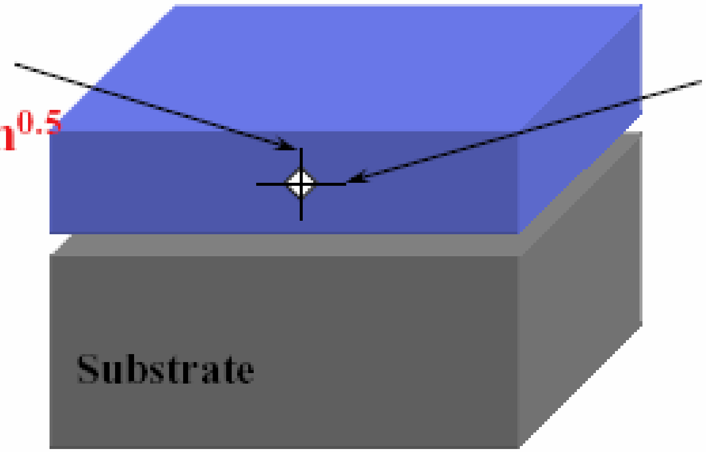
Toughness

$$K_{IC} = 0.016(E/H)^{0.5}Pc^{-1.5}$$ (Lawn *et al.*)

(P=49 N)

(H from Hardness Test and E from Comp. Test)

Out-of-Plane
SPPS: 1.17 MPa.m$^{0.5}$
APS: N/A

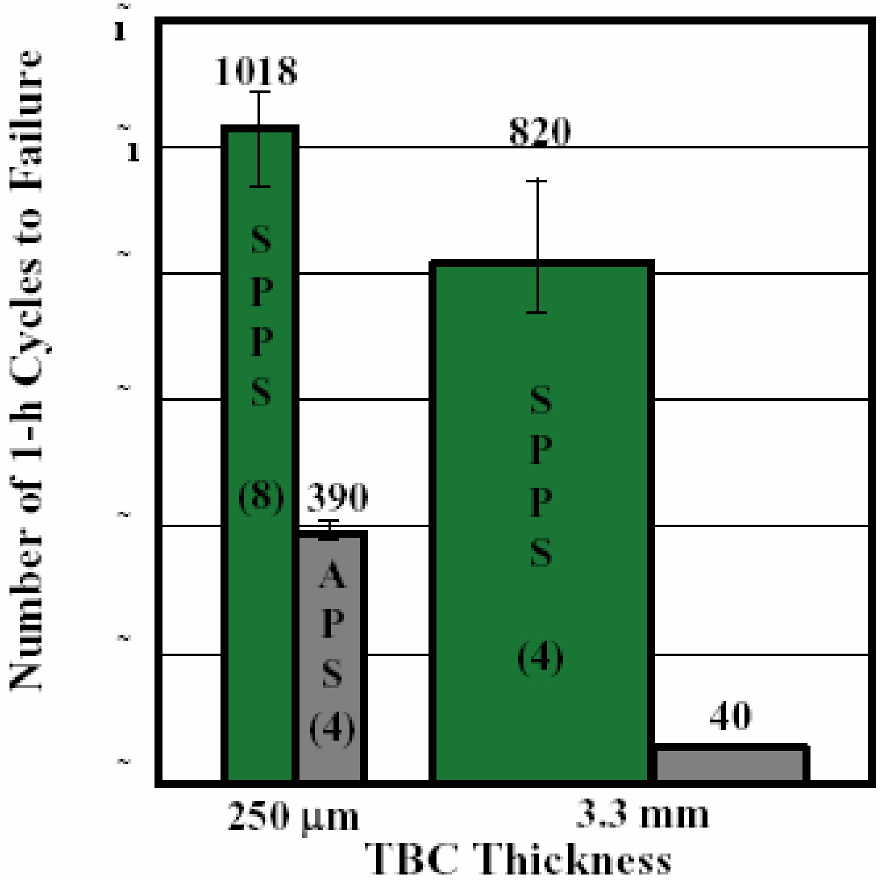


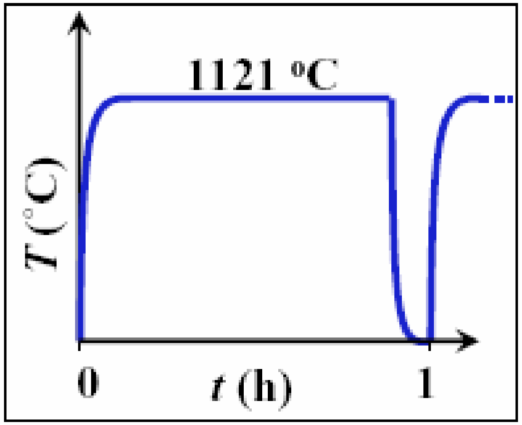
In-Plane
SPPS: 1.72 MPa.m$^{0.5}$
APS: 0.26 MPa.m$^{0.5}$

SPPS TBCs 6 Times Tougher in the Important In-Plane Direction: Lack of Macro-Splat Boundaries

Mater. Sci. Engr. A, 2005

Thermo-Mechanical Durability





- Vertical Cracks: Strain Tolerance
- Lack of Macro-Splat Boundaries: In-Plane Toughness

Mater. Sci. Engr. A, 2005

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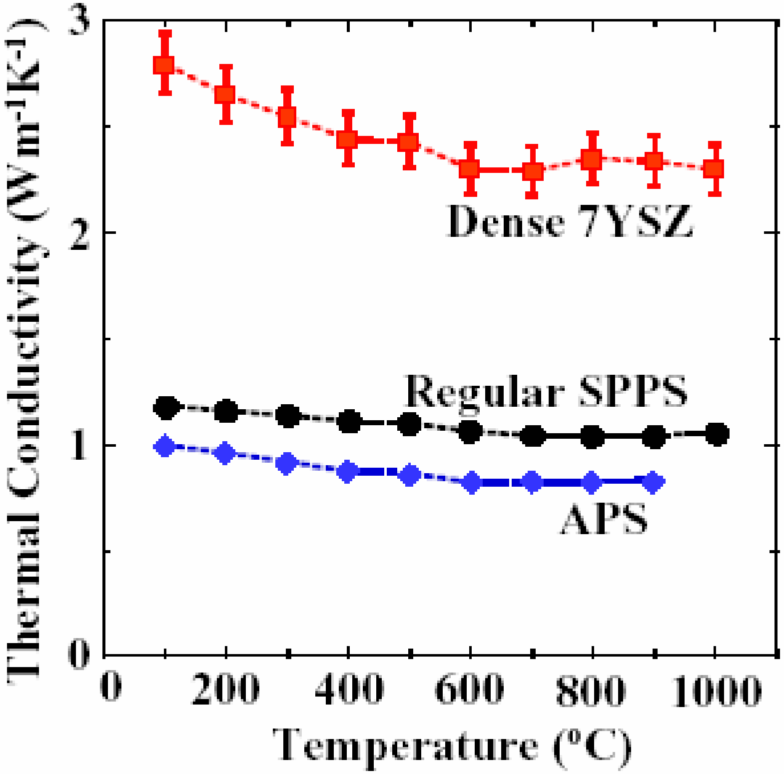
Thermal Conductivity

- Free-Standing Coatings (~1 mm)
- Laser-Flash Method

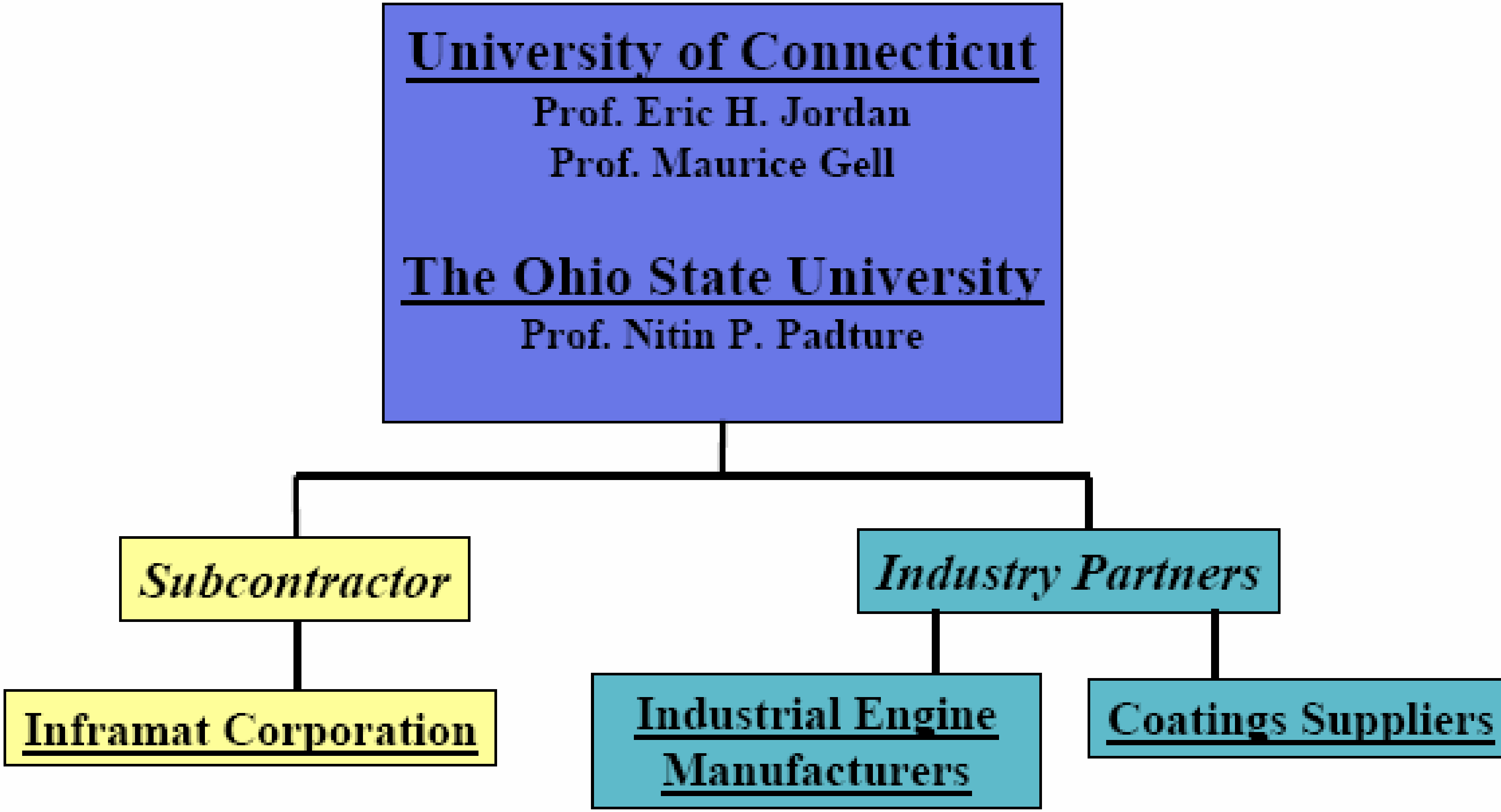


- SPPS Conductivity Higher Than APS
- Lack of Macro-Splat Boundaries

Summary

- Demonstrated Feasibility of Depositing Ultra-Thick (~3 mm) TBCs Using the SPPS Process
- Demonstrated High Durability in Ultra-Thick TBCs
- Demonstrated Feasibility of Depositing Layered TBCs with Low Thermal Conductivities
- Modeled Effect of Microstructure on Th. Cond.
- Demonstrated Feasibility of Depositing SPPS TBCs with Layered Architecture for Low Th. Cond. and High Durability

Teaming Arrangements



Investigation of materials performances in high moisture environments including corrosive contaminants typical of those arising by using alternative fuels in gas turbines

Gerald Meier, Frederick Pettit and Keeyoung Jung

Department of Materials Science and Engineering,

University of Pittsburgh

Pittsburgh, PA 15260

Peer review Workshop III

UTSR Project 04 01 SR116

October 18-20, 2005

NETL

Project Approach

Schematic Flow Diagram for the Present Project

Task I
Selection and Preparation of Specimens

Task II
Selection of Test Conditions
Specimens : GTD111+CoNiCrAlY and Pt Aluminides, N5+Pt Aluminides
Deposit : No Deposit, CaO, $CaSO_4$, Na_2SO_4

1150°C Dry	1150°C Wet	950°C Dry	950°C Wet	750°C SO_3

Selection of Test Temperature, T_1, Gas Environment and Deposit Composition, D_1

Task III
Comparison of Alloys and Coatings
GTD111, N5, IN738
GTD111 + NiCrAlY,
N5 + CoNiCrAlY and NiCrAlY
IN738 + 3 coatings
@ T_1, D_1

Task IV
Determine Moisture/Contaminants Limits
Specimens Described in Task II
T_1, variable
Water Vapor Pressure and Deposit Amount

Task V
TBC Testing @ T_1 and D_1

Task VI
CMC Testing @ T_1 and D_1

Program Objectives

1. Develop a fundamental understanding of the degradation process in moisture environments and in such environments where the specimens have deposits which are typical of deposits that will be encountered from the use of alternate fuels.

2. Attempt to describe how moisture/contaminant levels and temperature affect the corrosion processes.

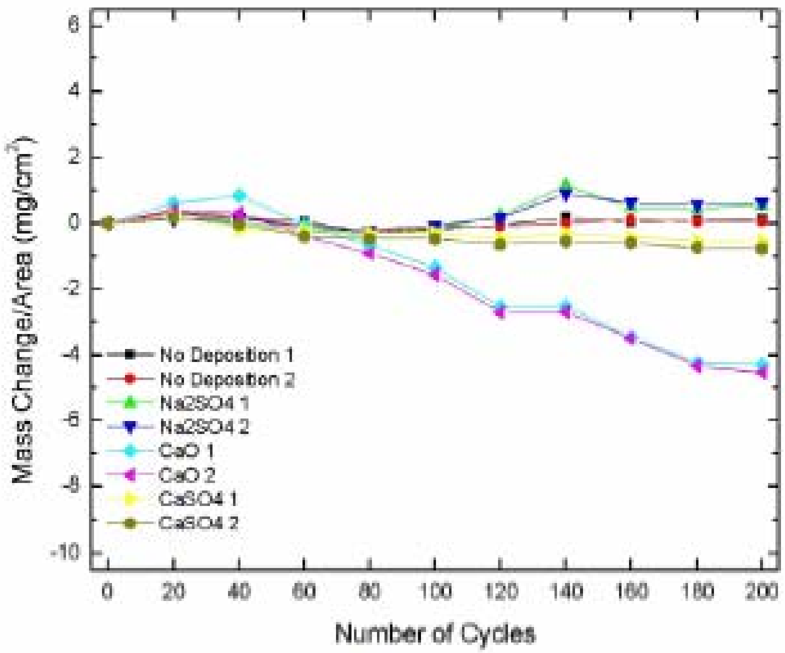
3. Determine the alloy compositions and coatings that are most resistant to corrosion induced by deposits from alternative fuels.

4. Compare and describe the failure mechanisms of state-of-art TBCs (Thermal Barrier Coatings) operating with conventional fuels and with alternative fuels.

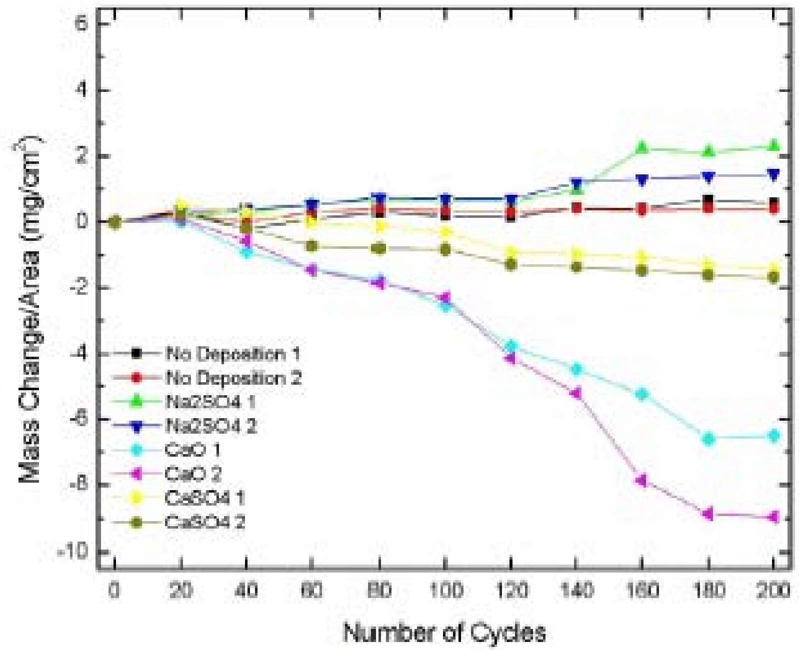
5. Compare the degradation of a CMC(Ceramic Matrix Composite) under conditions typical of gas turbines using conventional fuels and environments containing water vapor and contaminants representative of turbines using alternate fuels.

Weight change versus time measurements

Rene' N5 + Platinum Aluminide samples
with different deposits cyclically exposed at 950°C for 200 hours



(a) In wet air

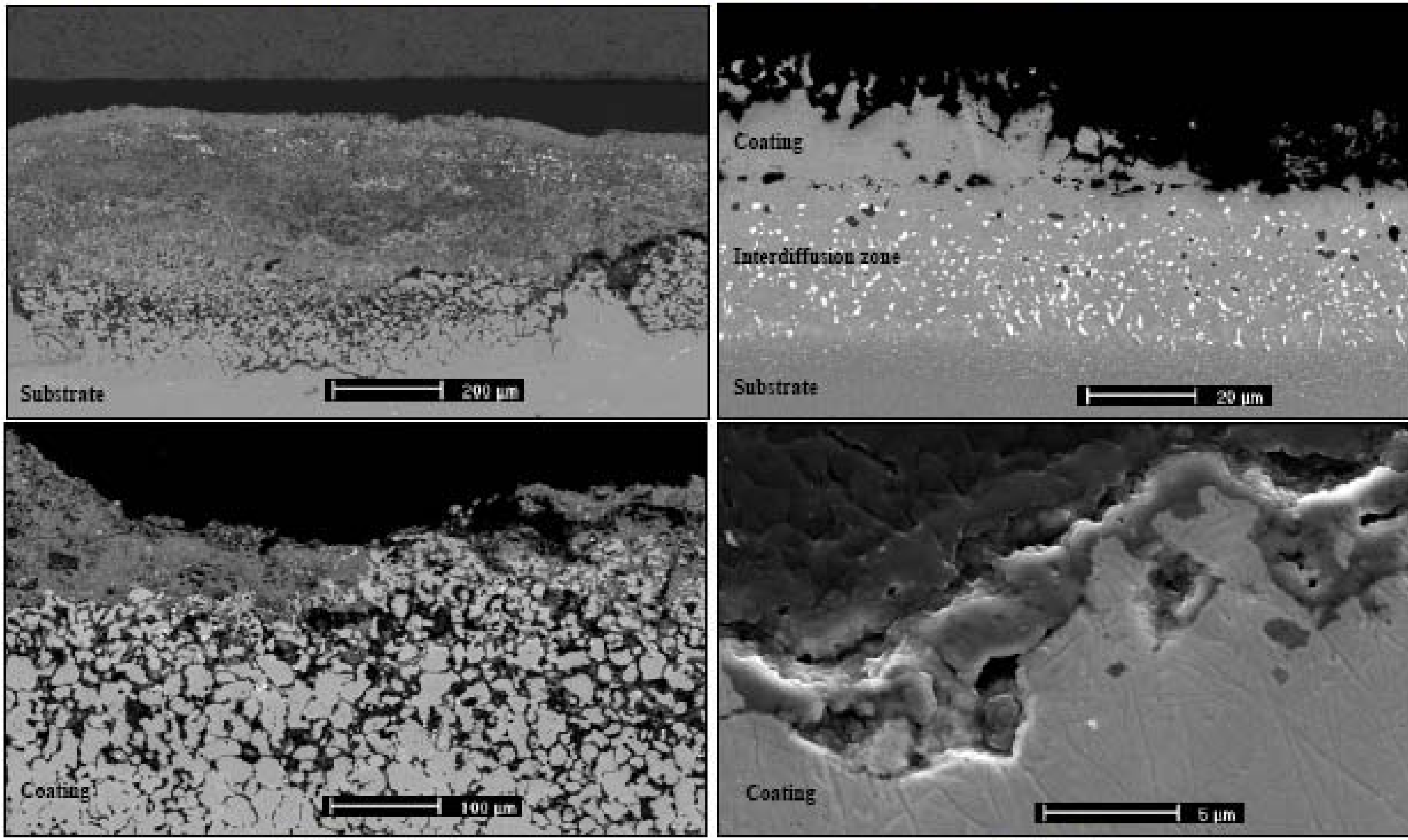


(b) In dry air

Substantially large weight losses for specimens with CaO deposits compared to Na_2SO_4 and $CaSO_4$ deposits as well as specimens with no deposits.

Scanning Electron Micrographs (Cross-section, cont'd)

Rene' N5 + Platinum Aluminide / 950°C / **CaO** / after 200 hours exposure



(a) In wet air **(b) In dry air**

Summary of Key Results

Obtained to date (First Year) for Platinum Aluminide Coatings on Rene′ N5

1. Deposits from gas turbine burning syngas have been analyzed.
   - Deposits of Fe_2O_3 with traces of Ca and S were determined.
   - Substantial erosion was observed.

2. Cyclic oxidation test have been performed with deposits of Na_2SO_4, CaO and $CaSO_4$ at 750°C, 950°C and 1150°C in dry and wet air.
   - At 750°C, severe attack (low temperature hot corrosion) was induced by Na_2SO_4 deposits.
   - At 750°C, CaO and $CaSO_4$ deposits did not cause substantial degradation.
   - At 950°C, CaO deposits caused more severe degradation than Na_2SO_4 and $CaSO_4$ deposits.
   - This attack induced by CaO was more severe in wet compared to dry air.
   - The CaO deposits also caused more severe degradation compared to Na_2SO_4 and $CaSO_4$ deposits at 1150°C.

3. The mechanism by which CaO cause increased degradation has not been determined as yet. Less attack by Na_2SO_4 above 900°C is probably being caused by evaporation.

Summary of Results

For Platinum Aluminide coatings on Rene′ N5 at 950°C

1. Substantial attack induced by deposits of CaO compared to other deposits.
2. Attack with all deposits was more severe in wet air.
3. In case of no deposits, significant amount of degradation in wet air.

Concluding Remarks

For Platinum Aluminide coatings on Rene' N5 at 750°C

1. Testing conditions for the remaining tasks (III, IV, V, VI) should be using CaO deposits at a temperature of either 950°C or 1150°C.

2. The test temperature will be selected based upon the results obtained with CoNiCrAlY coatings.

3. The gas environment should be wet air (p_{H2O}=0.1atm), but Task IV will examine moisture/contaminant limits at the selected test temperature.

4. The effects of other deposits (e.g. CMAS) may be considered based on any information that becomes available from gas turbines using syngas.