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

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NETL

EPRI

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  Mr. Balaji Jayaraj, Nan Mu, Chris Petorak, Sungkeun Seo
  Miss Abby Elliot and Xia Li

Program Objectives

- Evaluate Commercial Production Thermal Barrier Coatings (TBCs) During Thermal Cyclic Oxidation with:
  - Concurrent Non-Destructive Evaluation (NDE):
    - ✓ Photostimulated Luminescence Spectroscopy (PSLS).
    - ✓ Electrochemical Impedance Spectroscopy (EIS).
  - State-of-the-Art Microstructural Characterization including:
    - ✓ Focused Ion Beam – Micromanipulator Lift Out (FIB-MLO).
    - ✓ High Resolution Transmission Electron Microscopy (HR-TEM).
    - ✓ Nano-Spot Energy Dispersive Spectroscopy (n-EDS).
- Establish Relationship Between NDE Techniques, Microstructural Development and Failure Mechanisms for TBCs.

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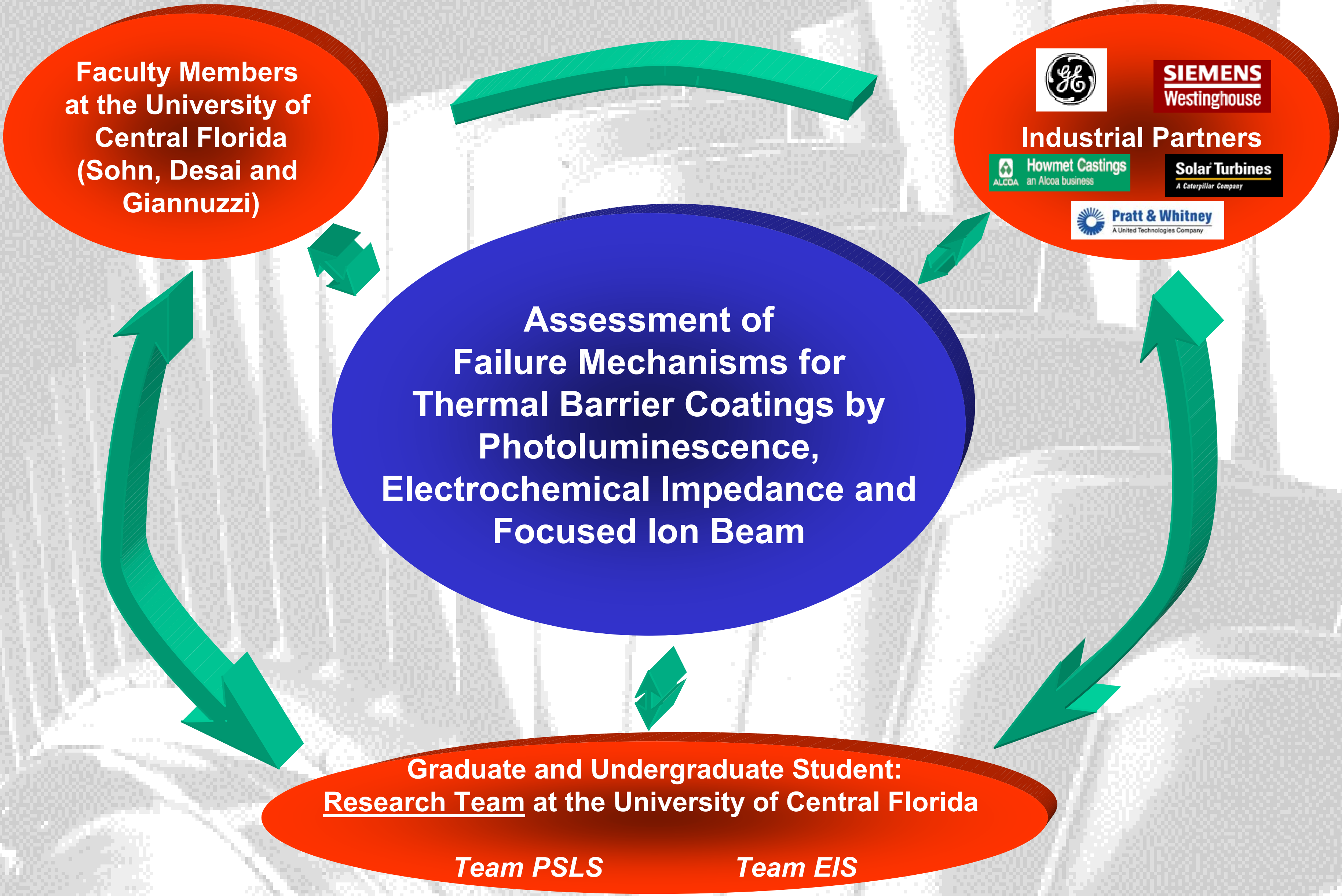
Program Objectives (Continued)

- Technology / Knowledge Transfer to Industrial Partners.
  - Identification of Failure Mechanisms
  - Refinement of NDE Techniques
  - Basis for Lifetime Improvement Methods and Prediction Models
- Research and Education for Two Student-Research-Teams:
  - Pair of Graduate and Undergraduate Students.
  - Collaboration / Competitive Team-Based Research Activities.
  - Direct Collaboration / Communication with Industrial Partners.
  - Education in Technology and in Professionalism.

Program Organization



Task Based Program Flowchart

Task I
Thermal Cyclic Oxidation of Thermal Barrier Coatings

Task II
NDE by Photostimulated Luminescence and Electrochemical Impedance Spectroscopy

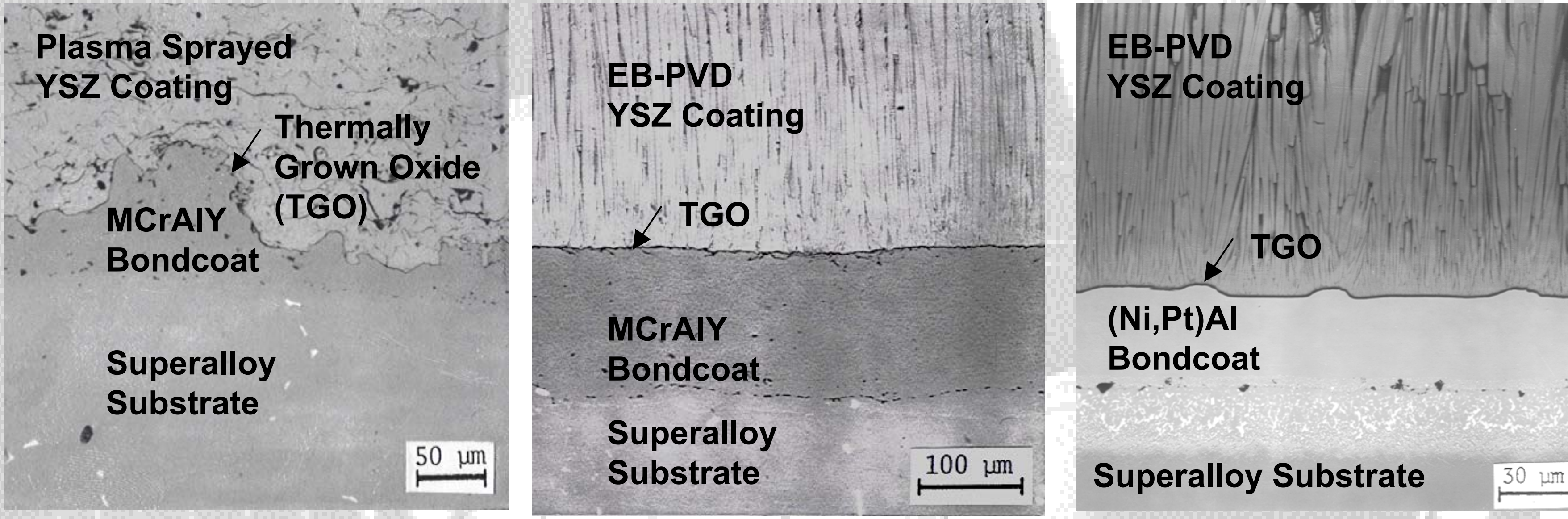
Task III
Advanced Microstructural and Failure Analysis

Task VI
Organization and Operation of Student Research Team

Task IV
Identification of Failure Mechanisms
Refinement of PSLS and EIS
Identify / Demonstrate Lifetime Improvement / Prediction Approach

Task V
Reports, Industrial Briefing and Technology Transfer

Thermal Barrier Coatings (TBCs)



- **Insulating Ceramic Layer Provides Thermal Protection of Hot Components (e.g. Blades and Vanes) in Gas Turbine Engines → Increase in Performance and Efficiency and Reduced Emission.**
- **Requires Reliable and Durable TBC as an Integral Part of Component Design System with High Confidence that TBC will Last Life of Part.**
- **Understanding of Failure Mechanisms and Development of Mechanisms–Based Lifetime Prediction Models.**
- **Develop Non-Destructive Evaluation Techniques for Quality Assessment, Life Prediction and Life-Remain Assessment.**

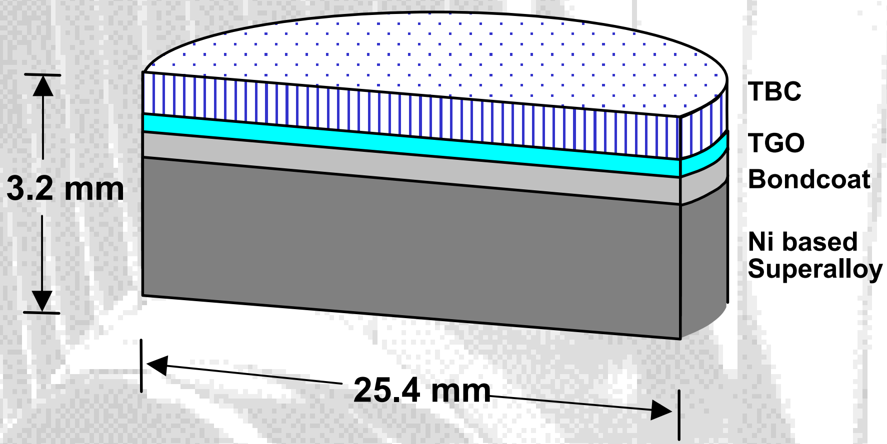
Non-Destructive Evaluation and Microstructural Analysis Techniques Related to Failure of TBCs

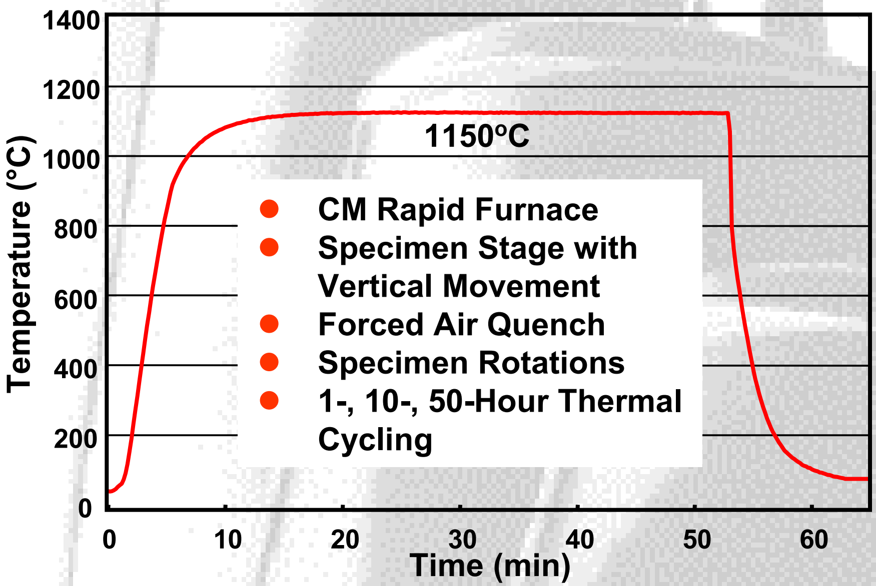
Main Factors Associated with TBC Failure	Potential NDE Technique	Microstructural Analysis
Thickness / Growth of TGO	EIS	SEM, TEM
Polymorphic Transformation of Al_2O_3 TGO	PSLS	XRD, TEM
Residual Stress of α-Al_2O_3 TGO	PSLS	-
Formation of Ni/Co Rich TGO	PSLS	SEM, TEM, n-EDS
Sintering of YSZ Coating	EIS	SEM
Phase Transformation of YSZ Coating	XRD, RS	
Bond Integrity of TGO/Bondcoat Interface	EIS, PSLS	SEM, TEM
Bond Integrity of YSZ/TGO Interface	EIS	SEM, TEM
Sulfur Segregation	N.A.	AES, XPS, SIMS

EIS: Electrochemical Impedance Spectroscopy; PSLS: Photostimulated Luminescence Spectroscopy; SEM: Scanning Electron Microscopy; TEM: Transmission Electron Microscopy; n-EDS: nano-spot Energy Dispersive Spectroscopy; XRD: X-ray Diffraction; RS: Raman Spectroscopy; AES: Auger Electron Spectroscopy; XPS: X-ray Photoelectron Spectroscopy; SIMS: Secondary Ion Mass Spectroscopy

Commercial Production TBC Specimens* and Thermal Cyclic Oxidation

TBC ID	7YSZ Type	Bondcoat	Superalloy	Notes
I	APS	NiCoCrAlY	Haynes 230	-
II	EB-PVD	NiCoCrAlY	CMSX-4	-
IIIa	EB-PVD	(Ni,Pt)Al	CMSX-4	As-Coated Bondcoat
IIIb	EB-PVD	(Ni,Pt)Al	Rene'N5 (SX)	Surf. Mod. Bondcoat

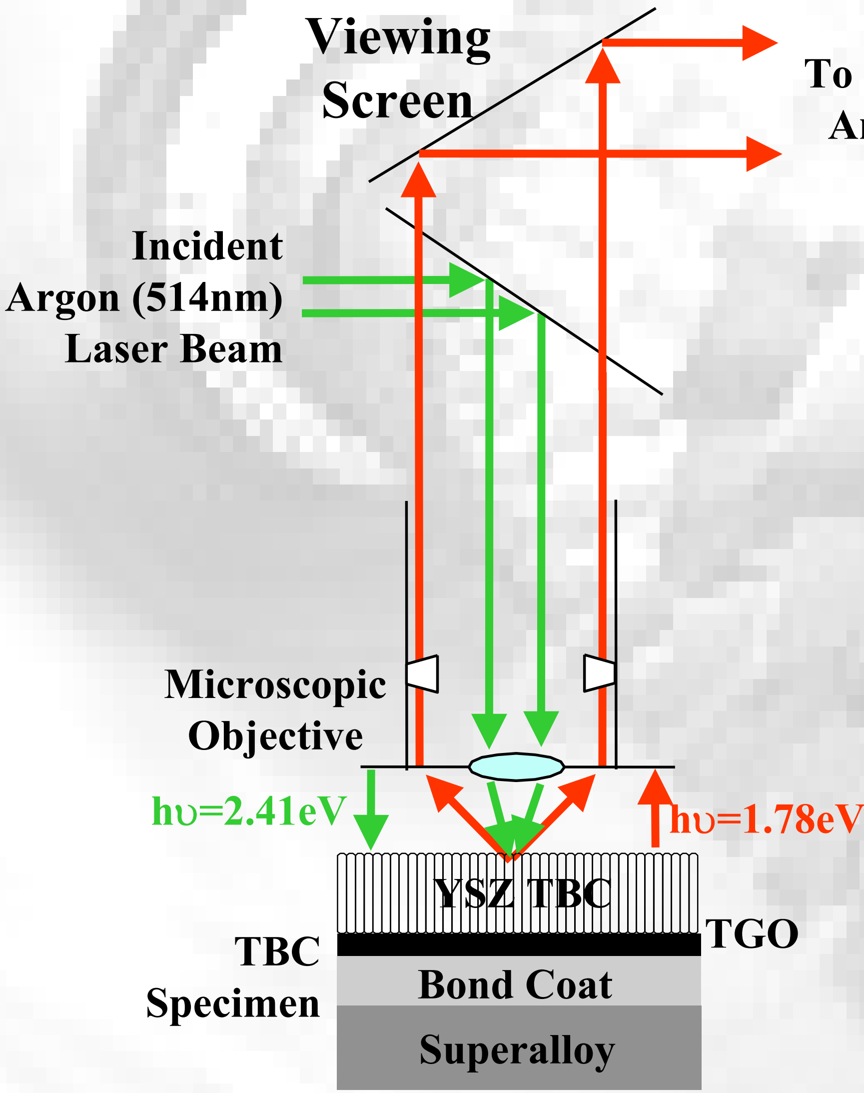




- CM Rapid Furnace
- Specimen Stage with Vertical Movement
- Forced Air Quench
- Specimen Rotations
- 1-, 10-, 50-Hour Thermal Cycling

*Supplied by Industrial Partners.

Photo-Stimulated Luminescence Spectroscopy (PSLS) for Thermal Barrier Coatings



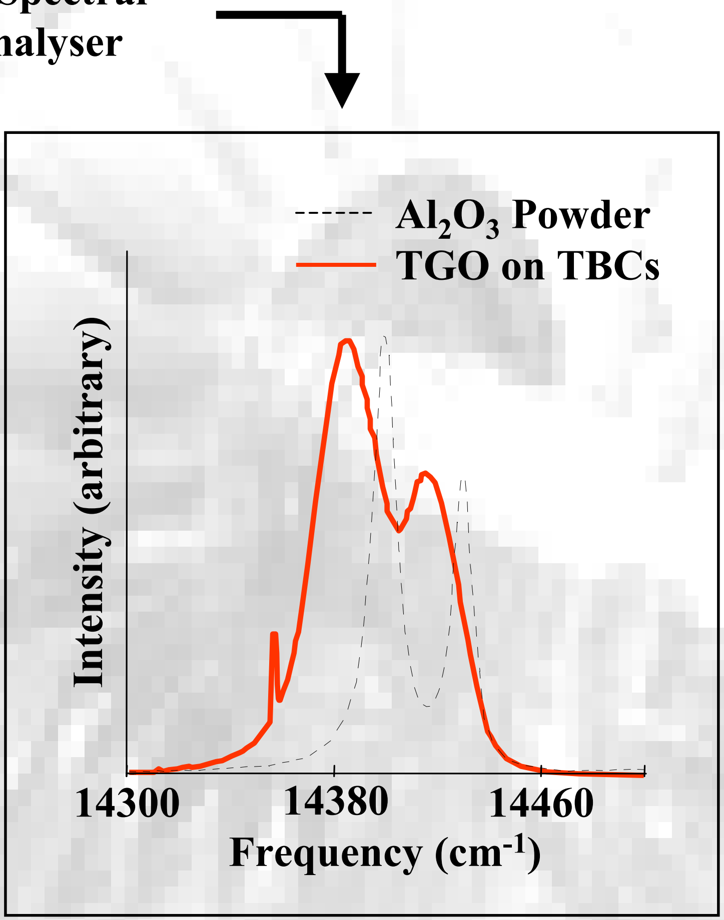
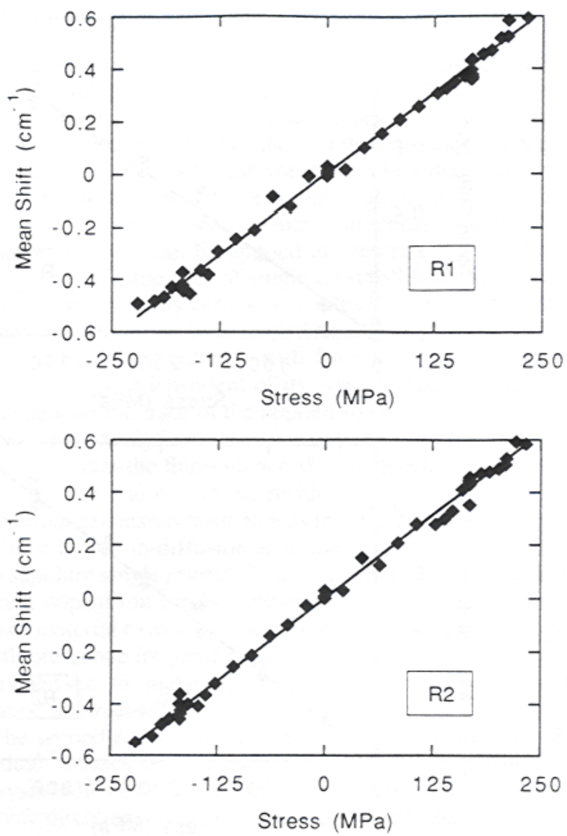


Photo-Stimulated Luminescence Spectroscopy (PSLS) for Thermal Barrier Coatings



Frequency Shift, $\Delta\upsilon$ of R_1 and R_2 Cr^{3+} Luminsecence Can Be Related To the Average Stress, $\overline{\sigma}$ of the α - Al_2O_3 by :

$$\overline{\Delta\upsilon} = \frac{2}{3}\Pi_{ii}\overline{\sigma}$$

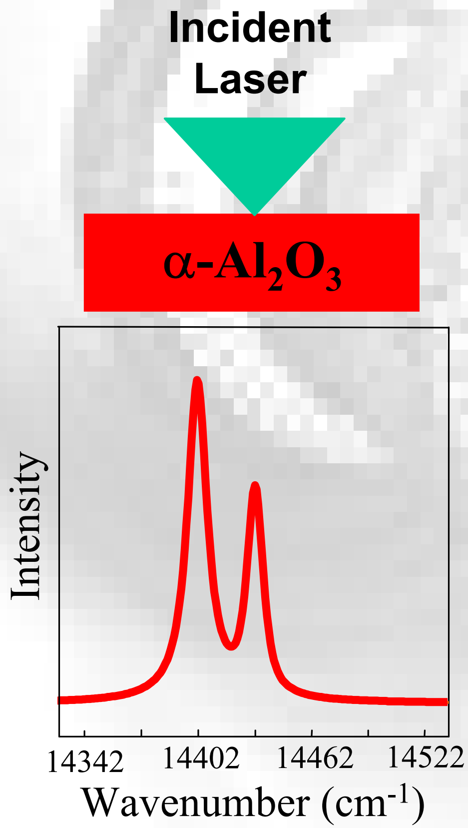
where Π_{ii} is the piezospectroscopic coefficients

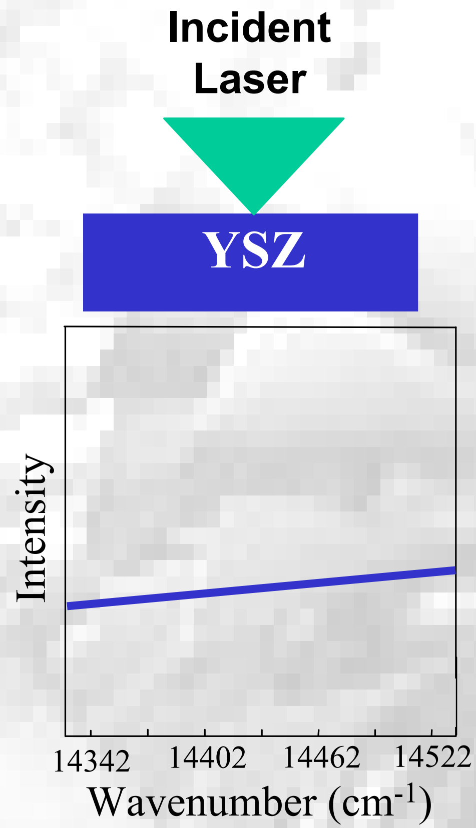
Assumptions :

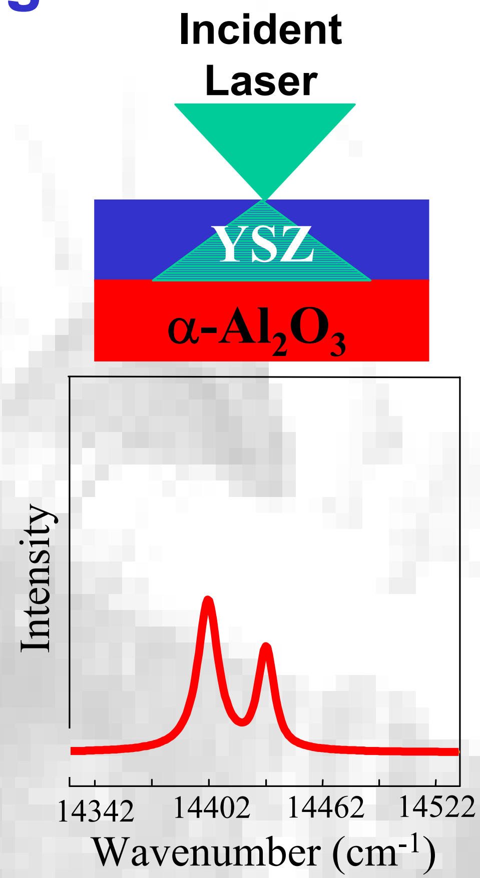
- **Untextured Polycrytallline α-Al_2O_3**
- **Thin Scale**
- **Biaxial Stress**

*** Q. Ma and D. R. Clarke, J. Am. Ceram. Soc., 76 (1993) 1433; 77 (1994) 298.**

Photo-Stimulated Luminescence Spectroscopy (PSLS) for Thermal Barrier Coatings







σ = 0.00 ± 0.01 GPa

R_2 Fluorescence Intensity:

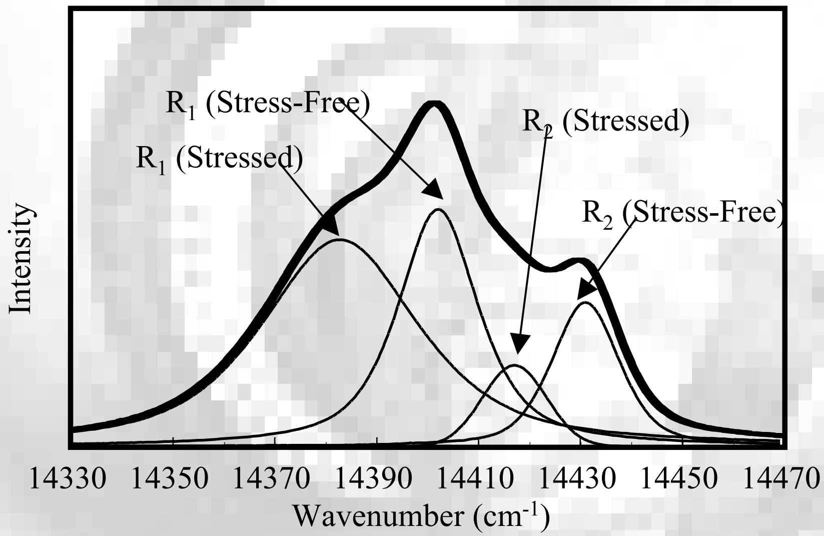
Std. Dev. = 1.4 Percent

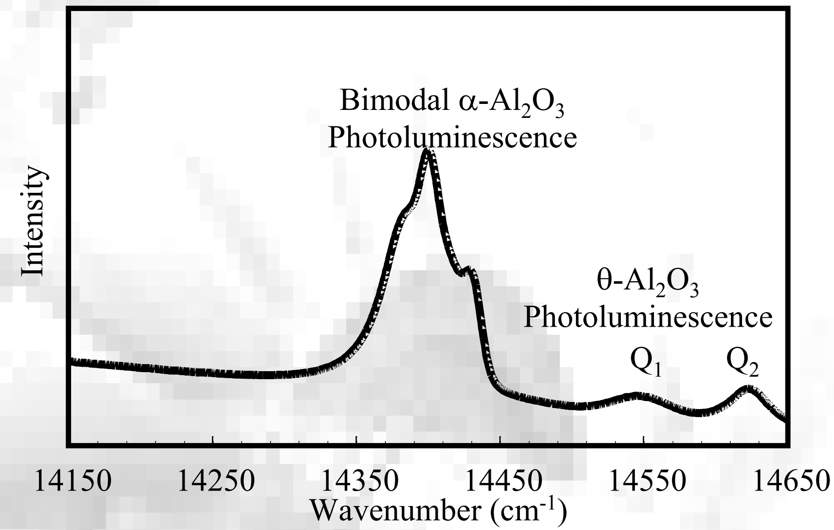
σ = 3.61 ± 0.02 GPa

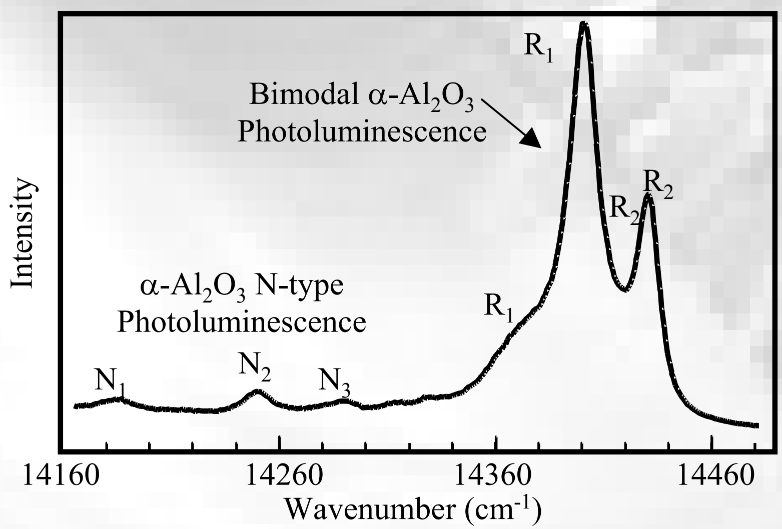
R_2 Fluorescence Intensity:

Std. Dev. = 2.6 Percent

Characteristics Photostimulated Luminescence from Thermally Grown Oxides in TBCs



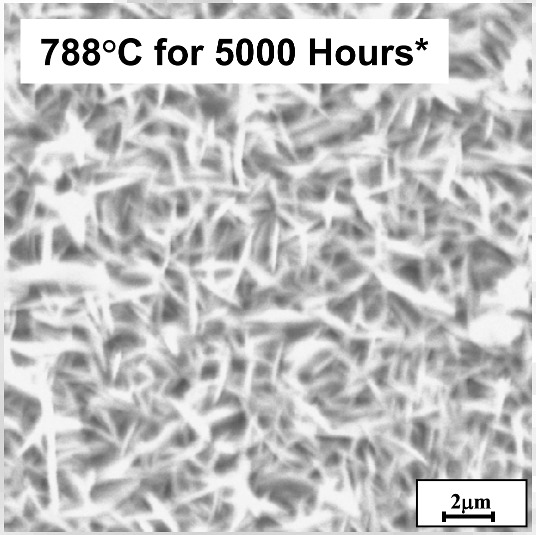


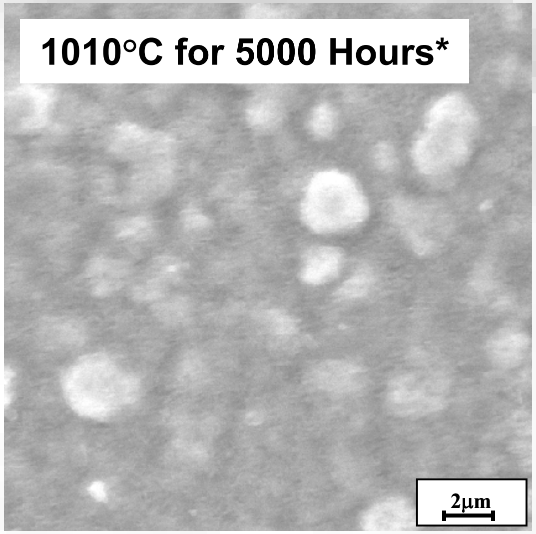


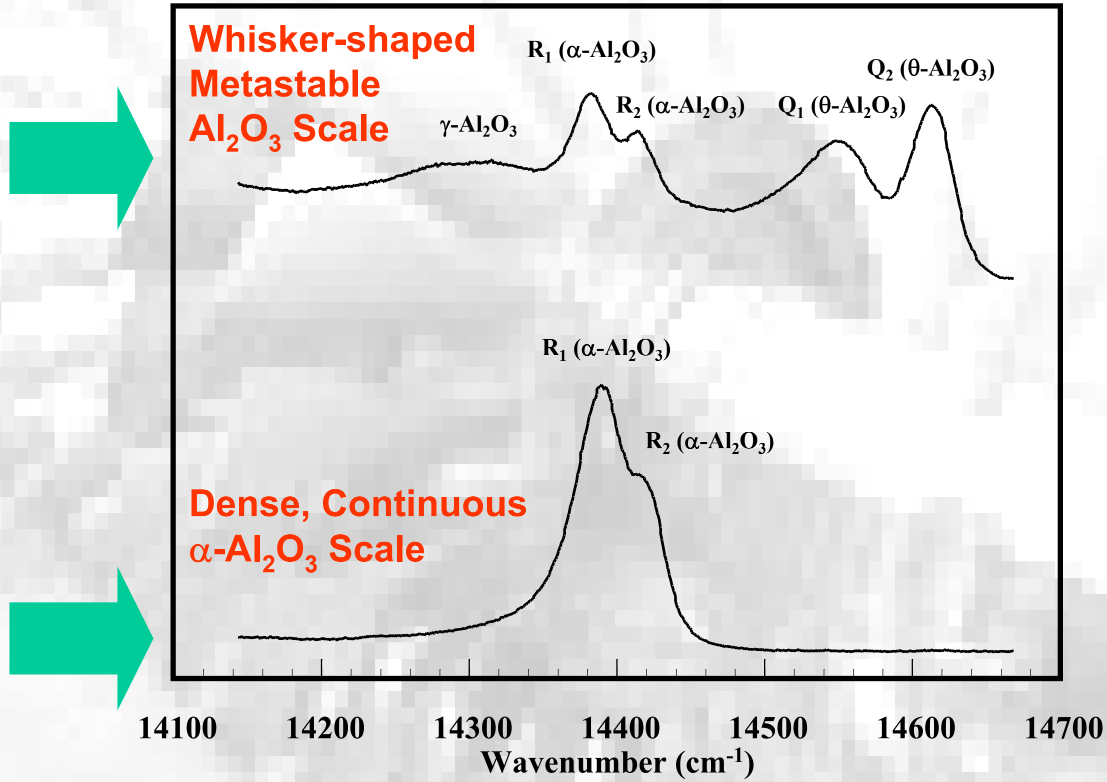
- **Bimodal R-Luminescence from α-Al_2O_3 (R_1 and R_2)**
  - **Stress (Shifted)**
  - **Stress-Free (Not-Shifted)**
- **Q-Luminescence from θ-Al_2O_3 (Q_1 and Q_2)***
- **N-Luminescence from α-Al_2O_3 (N_1, N_2 and R_2)****

***D.R. Clarke, J. Am. Ceram. Soc., 81 (1998) 3345; ** A. Schawlow et al, Phys. Rev. Lett., 3 (1959) 271.**

Characteristics Photostimulated Luminescence from Thermally Grown Oxides

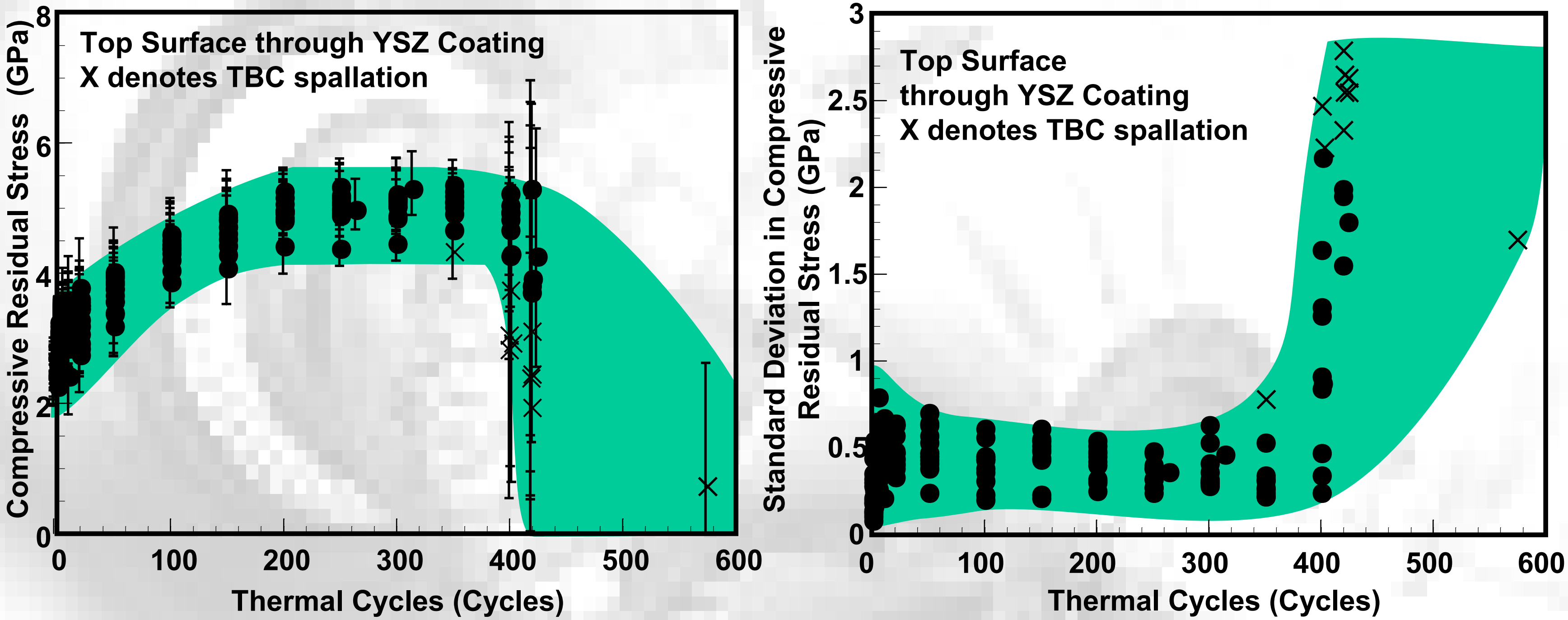






* Isothermal Oxidation of Aluminized CMSX-4

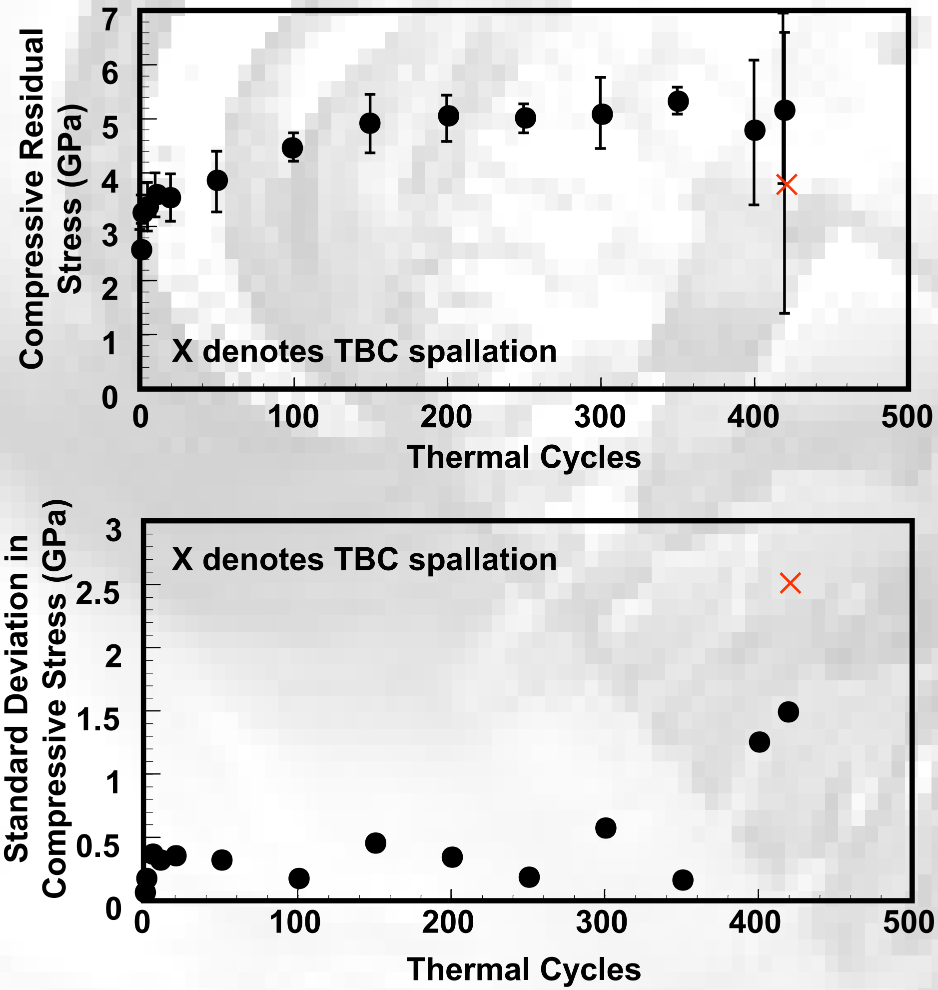
Evolution of Residual Stress of TGO in TBCs*



- Initial Increase in the Compressive Residual Stress of TGO up to 200 Cycles.
- Stable Compressive Residual Stress of TGO between 200 and 400 Cycles
  - 4.5 ~ 5.0 GPa.
- Decrease (or Fluctuation) in the Compressive Residual Stress of TGO after 400 Cycles.
  - Majority of TBC Spallation Begins at 400 Cycles.
  - Increase in the Standard Deviation of Compressive Residual Stress.

*Y.H. Sohn et al., Surf. Coat. Technol., 146-7 (2001) 102-109.

Evolution of Residual Stress of TGO in TBCs*

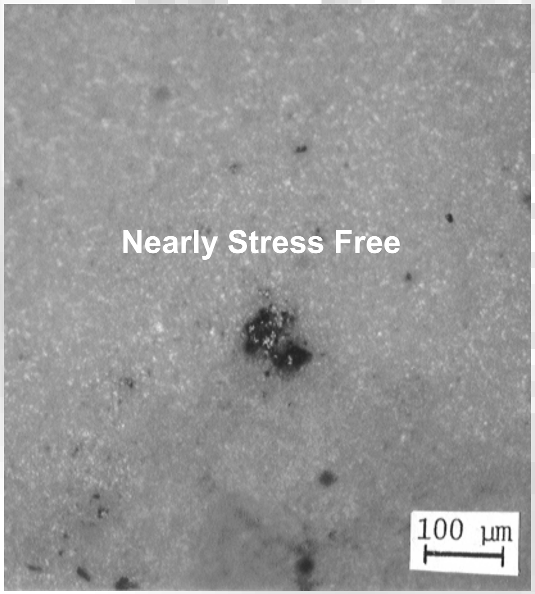


- Initial Increase in the Compressive Residual Stress of TGO up to 200 Cycles.
- Stable Compressive Residual Stress of TGO between 200 and 400 Cycles
    - 5.0 GPa.
- Fluctuation in the Compressive Residual Stress of TGO after 400 Cycles.
- Increase in the Standard Deviation of Compressive Residual Stress.

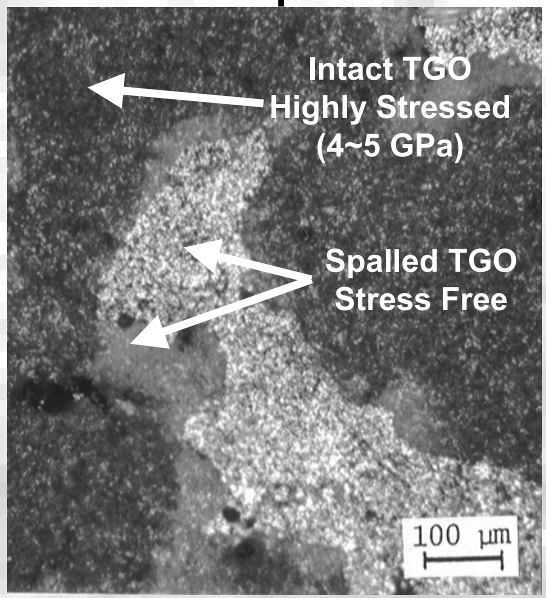
*Y.H. Sohn et al., Surf. Coat. Technol., 146-7 (2001) 102-109.

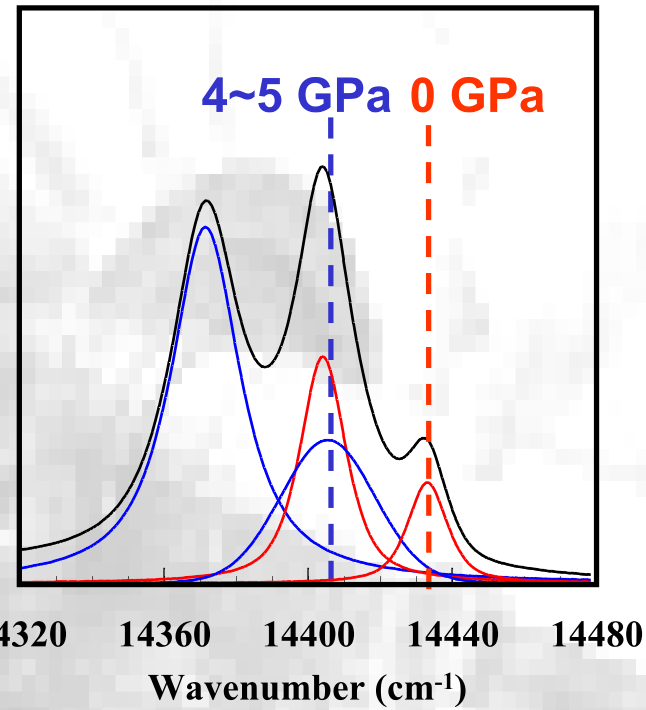
Bimodal R-Luminescence from Spallation of TBC*

Bottom of Spalled YSZ



Top of Bond Coat After YSZ Spallation

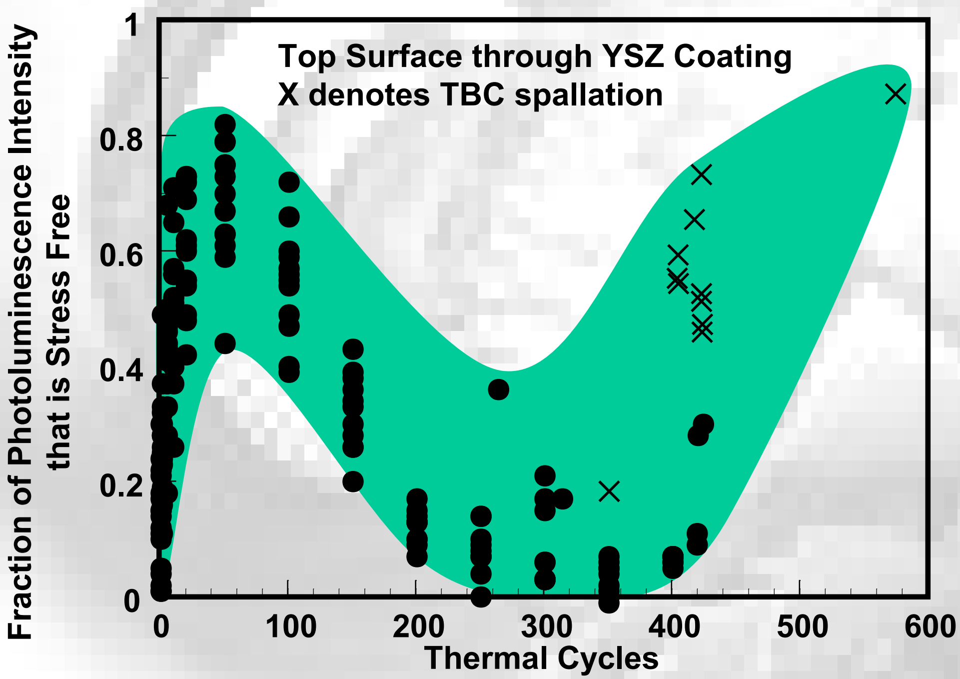




- **Stress Relief Caused by Spallation of TGO from Bond Coat:**
  - **Thermal Expansion Mismatch.**
  - **Intact TGO with Compressive Residual Stress (4~5 GPa).**

*Y.H. Sohn et al., Surf. Coat. Technol., 146-7 (2001) 102-109.

Evolution of Bimodal R-Luminescence*



- Sharp Initial Increase in the Fraction of R-Luminescence that is Stress-Free up to 50 Cycles.
- Gradual Decrease in the Fraction of R-Luminescence that is Stress-Free from 100 to 350 Cycles.
- Sharp Increase in the Fraction of R-Luminescence that is Stress-Free from 400 Cycles.

- Possible Explanation for the Initial Evolution in the Fraction of Stress-Free R-Luminescence:
  - Polymorphic Transformation of Al_2O_3 (θ-to-α)**
  - Morphology (constrained and unconstrained) of Al_2O_3 (θ and α)**
  - θ- Al_2O_3 Luminescence (Q_1 and Q_2) Absent After 150 Thermal Cycles.

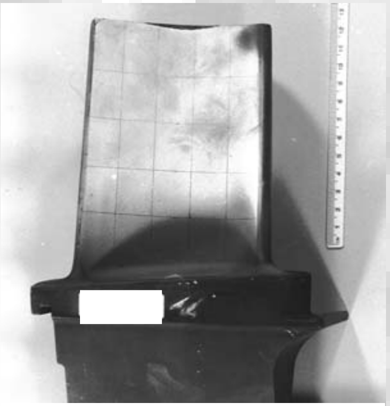
*Y.H. Sohn et al., Surf. Coat. Technol., 146-7 (2001) 102-109.
**V.K. Tolpyog and D.R. Clarke, Mater. High Temp., 17 (2000) 59.

Application of Photo-Stimulated Luminescence Spectroscopy on Thermal Barrier Coated Turbine Blades*

3.14 ± 0.25 GPa
Pressure Surface

3.15 ± 0.12 GPa
Suction Surface

As-Coated



1.64 ± 0.18 GPa
Pressure Surface

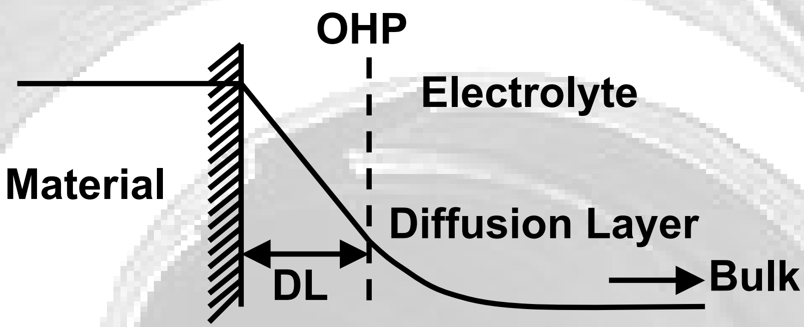
1.41 ± 0.21 GPa
Suction Surface

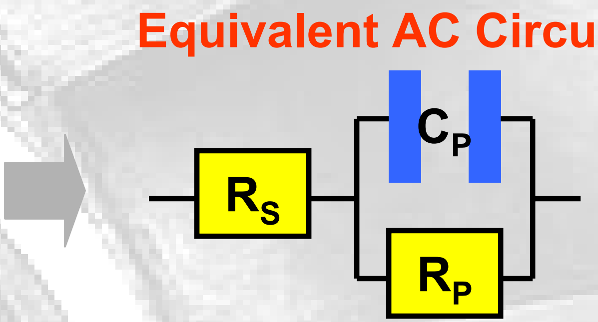
27000 Service Hours

*Y.H. Sohn et al., Metall. Mater. Trans. A, 31A (2000) 2388-2391.

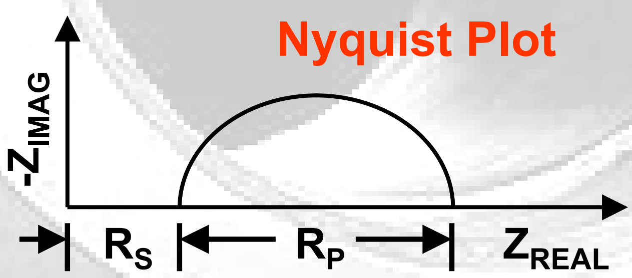
Electrochemical Impedance Spectroscopy (EIS)

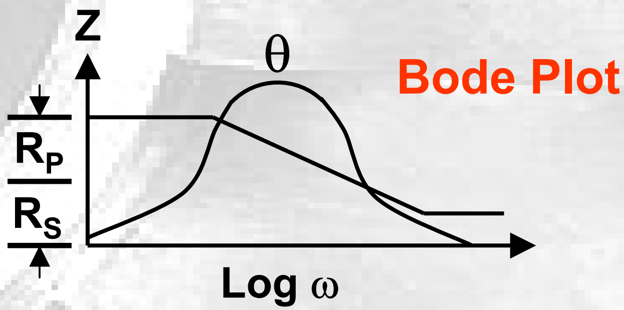
- Material When Exposed to an Electrolyte Develops an Electrified Interface Called Double Layer (DL).



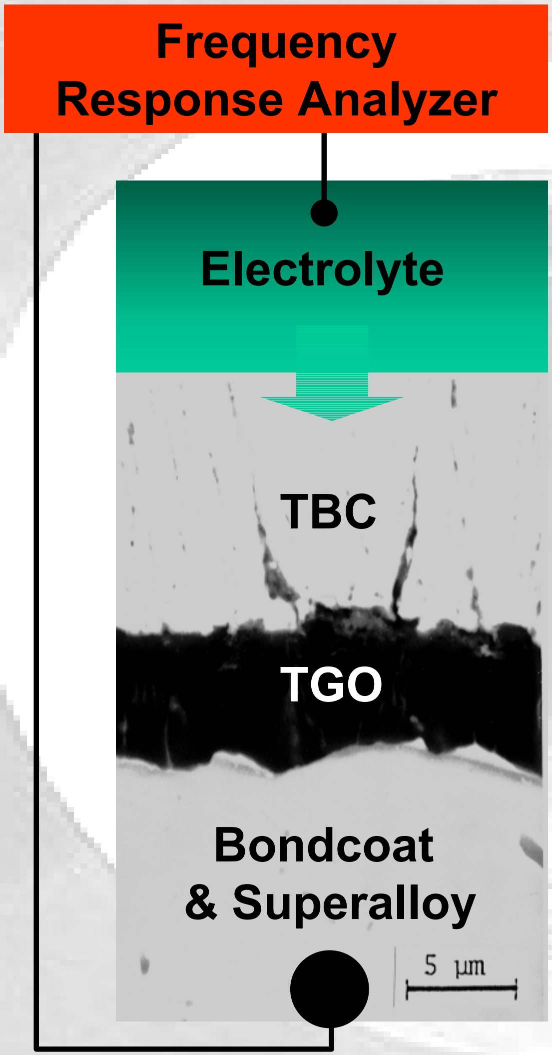


- In Response to AC Stimulation for Various Frequencies, Nyquist and Bode Plots are Obtained:

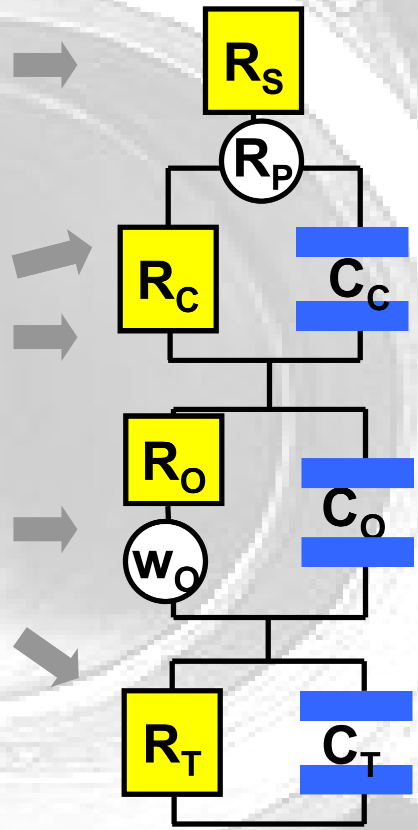




Thermal Barrier Coatings (TBCs) and Electrochemical Impedance Spectroscopy (EIS)



Each AC Circuit Component Corresponds to Physical Parameter of TBC Constituents Quantitatively.



AC Circuit: A Model

R_S: Electrolyte Solution Resistance

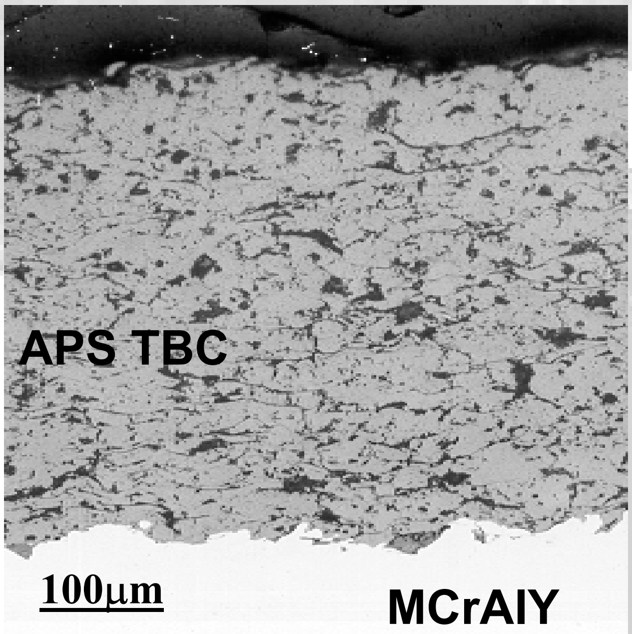
R_P: Pore (Porous Electrode) Resistance

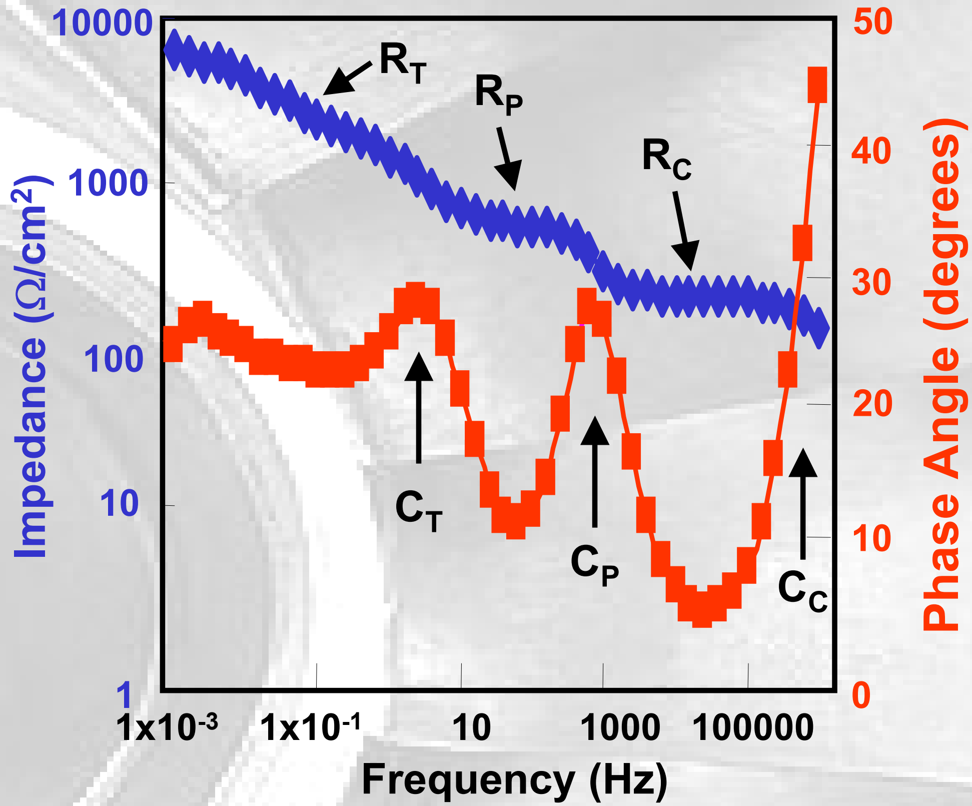
R_C: Ceramic Top Coat Resistance
C_C: Ceramic Top Coat Capacitance

R_O: Oxide Scale (TGO) Resistance
C_O: Oxide Scale (TGO) Capacitance
W_O: Warburg Coefficient

R_T: Interface Transmittance Resistance
C_T: Interface Transmittance Capacitance

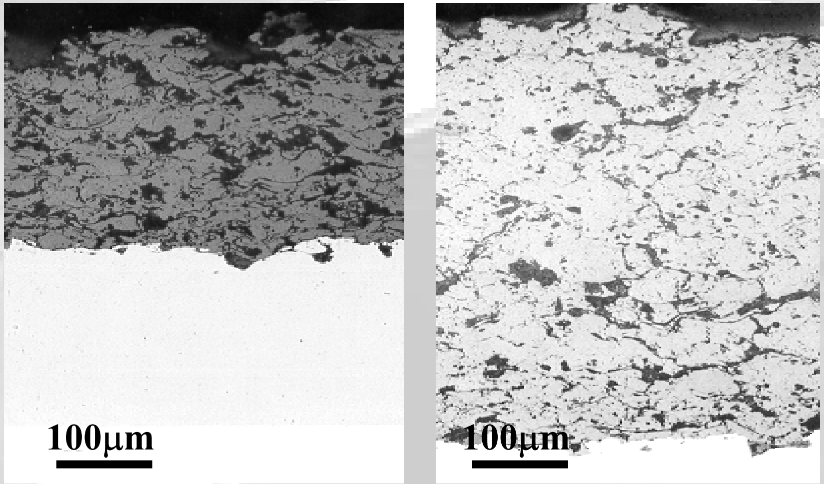
Air Plasma Sprayed (APS) Thermal Barrier Coatings (TBCs) and Electrochemical Impedance Spectroscopy (EIS)

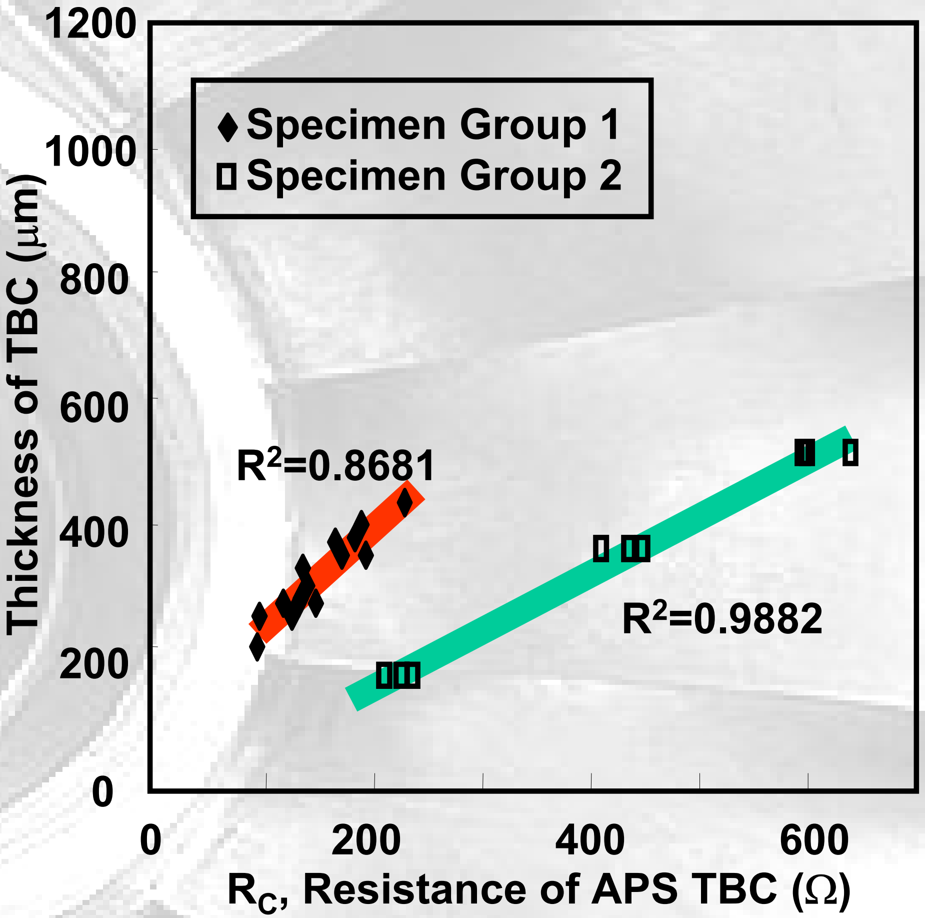




Typical Bode Plot from As-Coated APS TBC with Various Value of Resistance and Capacitance Corresponding to the Multilayer Structure of TBC.

APS TBCs and EIS:
Thickness of APS TBC and Ceramic Resistance, R_C

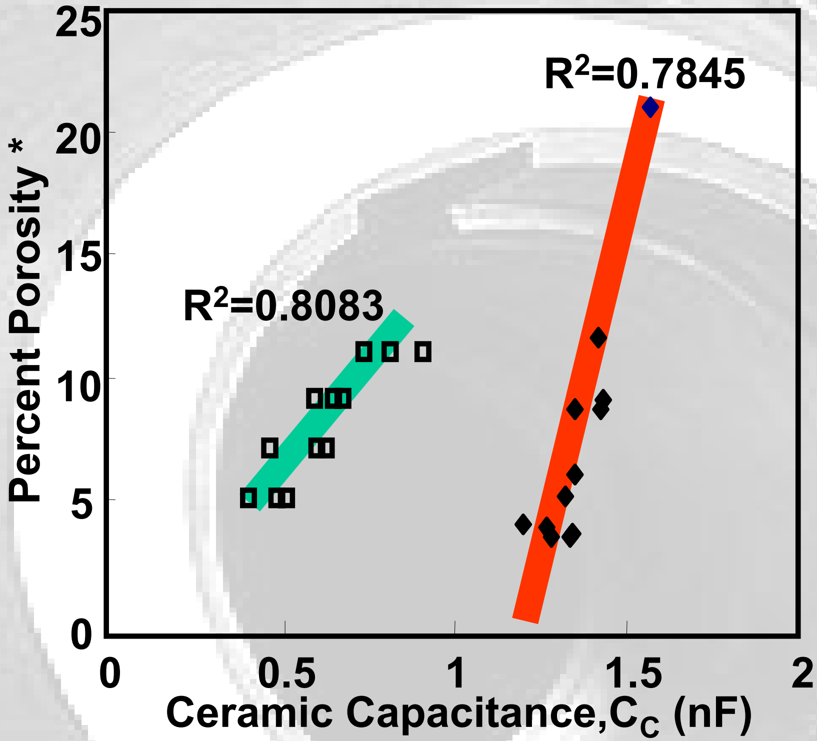




Linear Relationship between the Thickness and the Resistance, R_c for As-Coated APS TBCs

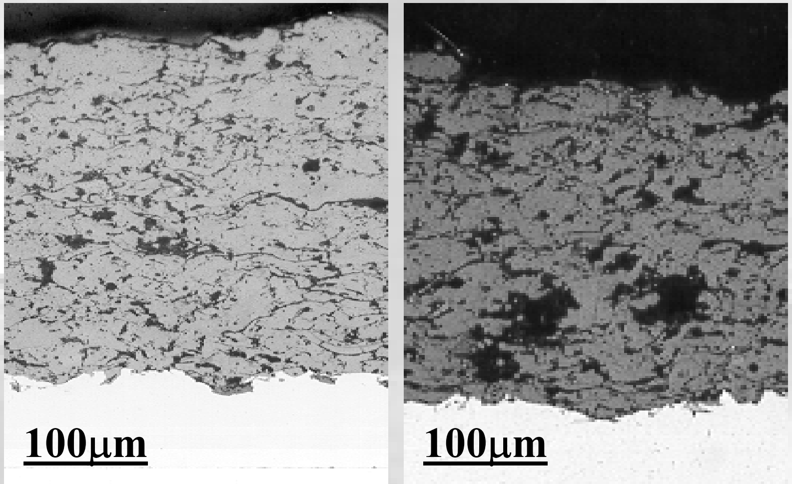
APS TBCs and EIS

Porosity of APS TBC and Ceramic Capacitance, C_C



Linear Relationship between the Percent Porosity and the Capacitance, C_c for As-Coated APS TBCs.

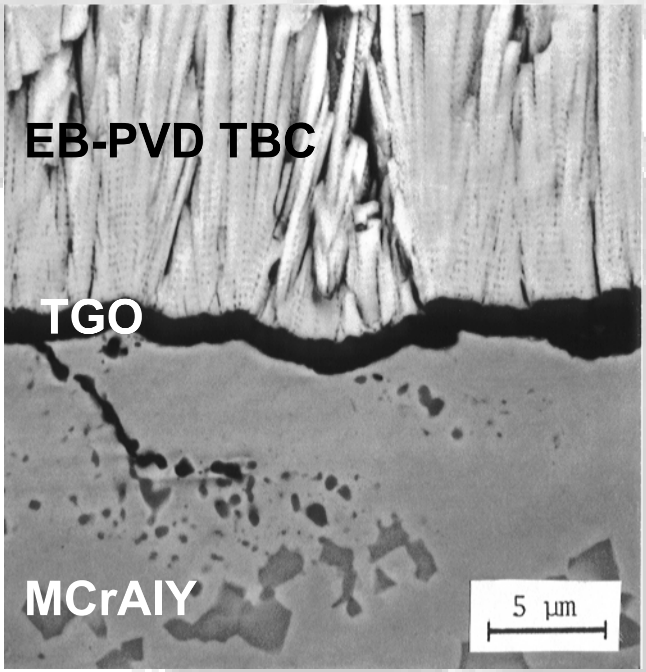
* Image Analysis

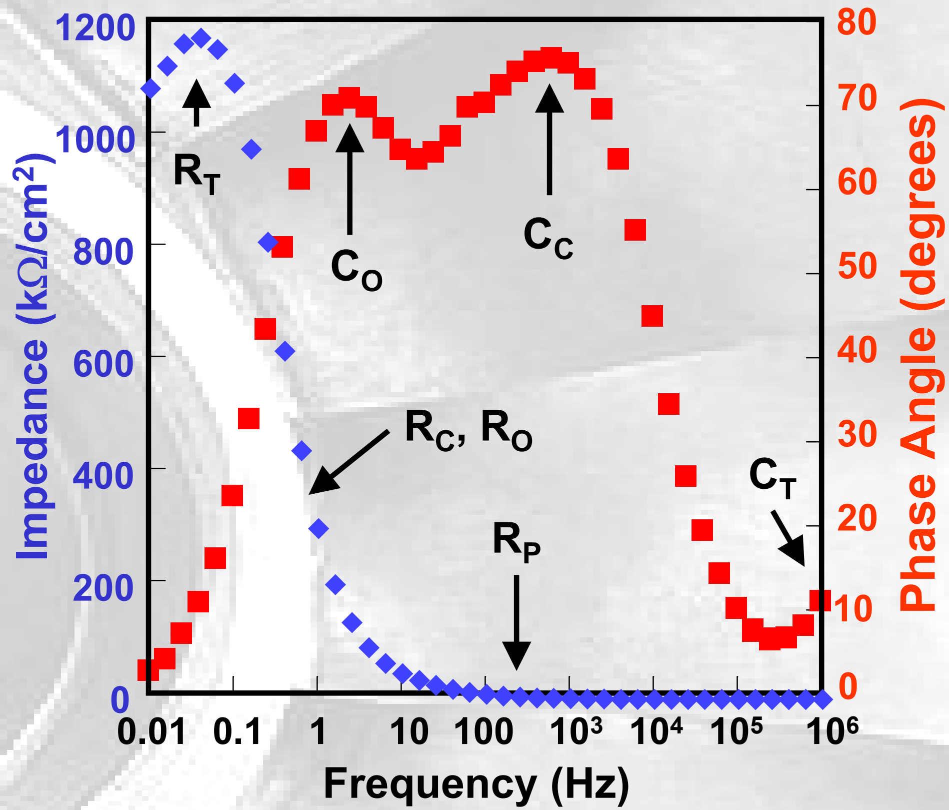


Pore Shape in APS TBCs and Pore Resistance, R_P:

- Transverse Cracks: $R_P > 550\ \Omega$
- Small Oval Pores: $R_P \approx 500\ \Omega$
- Intermediate Oval Pores: $355 < R_P < 450\ \Omega$
- Large Oval Pores: $R_P < 355\ \Omega$

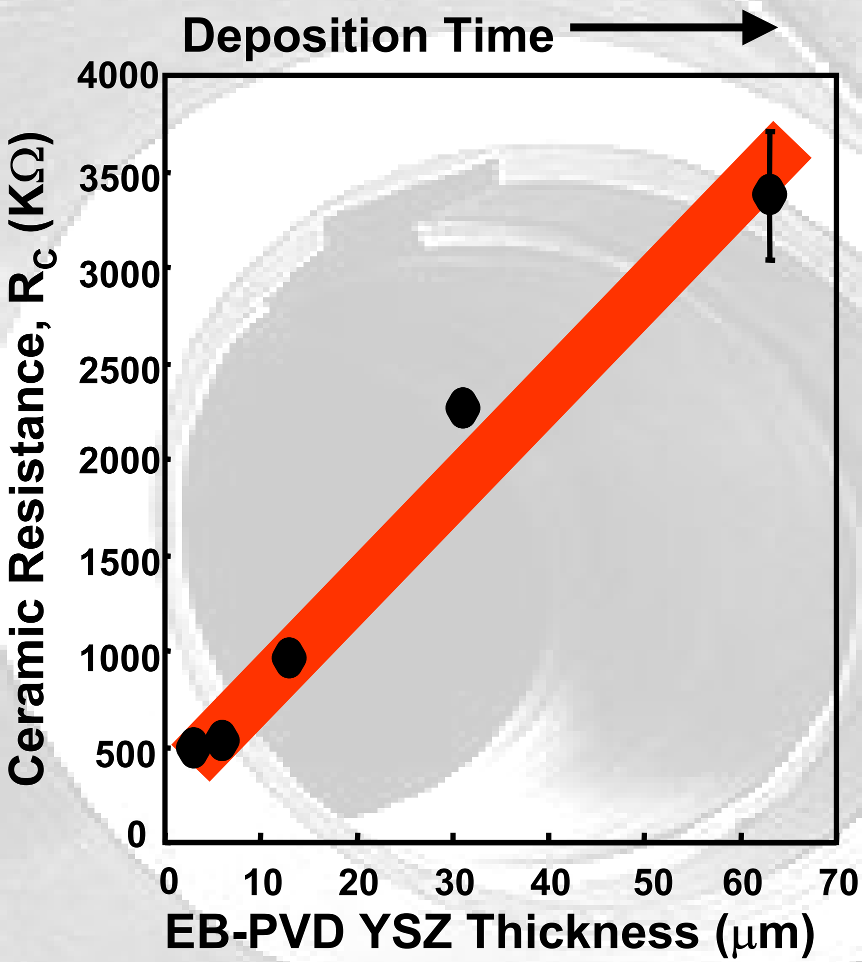
EB-PVD Thermal Barrier Coatings (TBCs) and Electrochemical Impedance Spectroscopy (EIS)

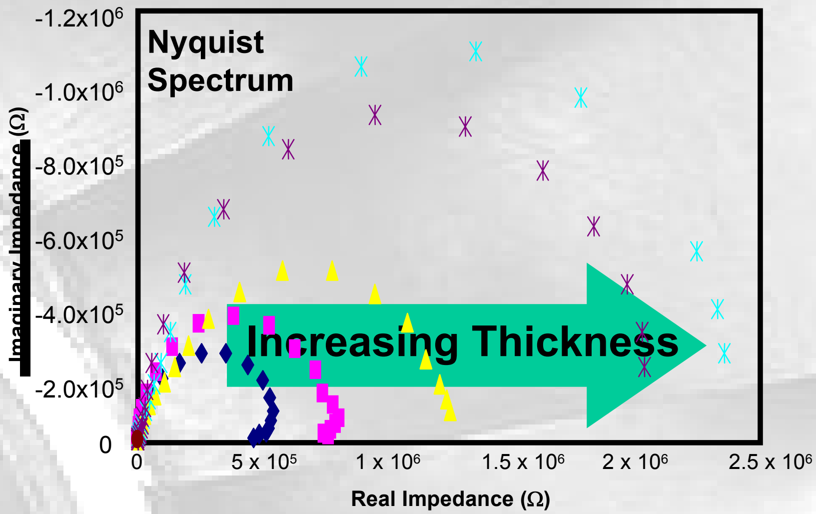




Typical Bode Plot from EB-PVD TBC with Various Value of Resistance and Capacitance Corresponding to the Multilayer Structure of TBC.

As-Coated EB-PVD TBCs and EIS
Thickness of EB-PVD TBC and Ceramic Resistance, R_C

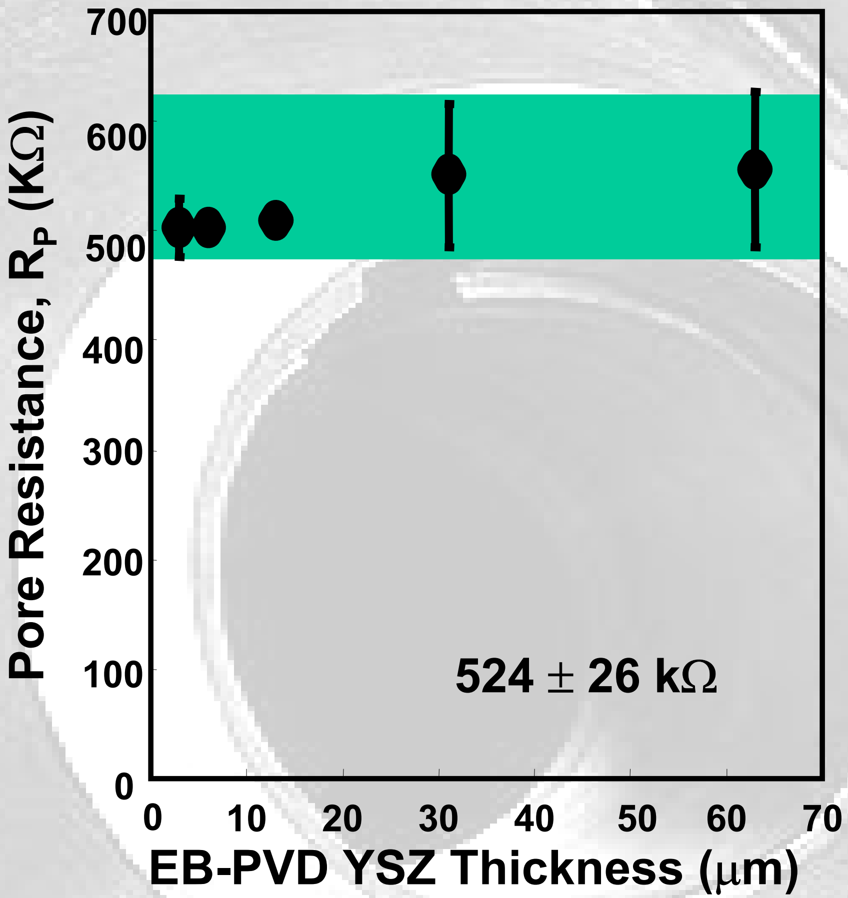




- Variation in Thickness of EB-PVD TBCs was Achieved by Varying the Deposition Time.
- Linear Relationship between the Thickness and the Resistance, R_c for As-Coated EB-PVD TBCs.

* EB-PVD 7YSZ with (Ni,Pt)Al Bondcoat and CMSX-4 Superalloy Substrate

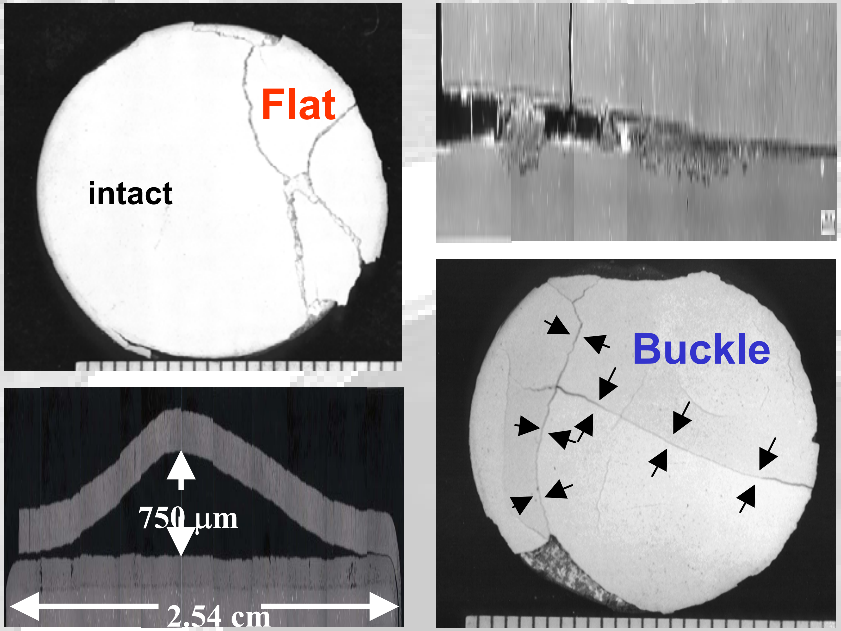
As-Coated EB-PVD TBCs and EIS
Thickness of EB-PVD TBC and Other Variables

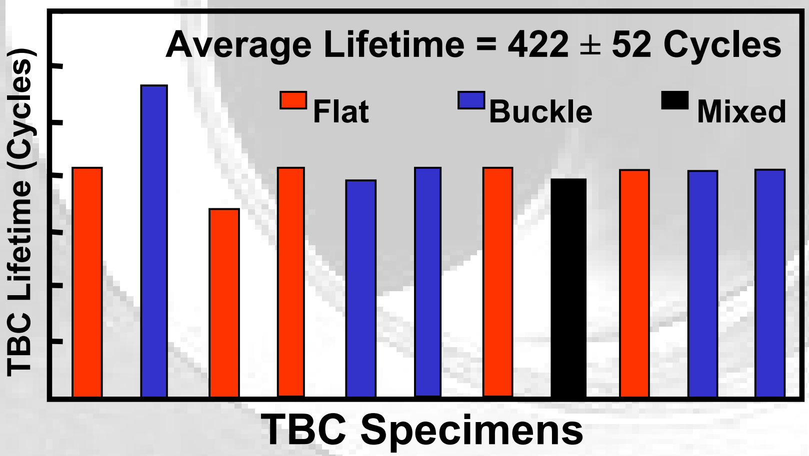


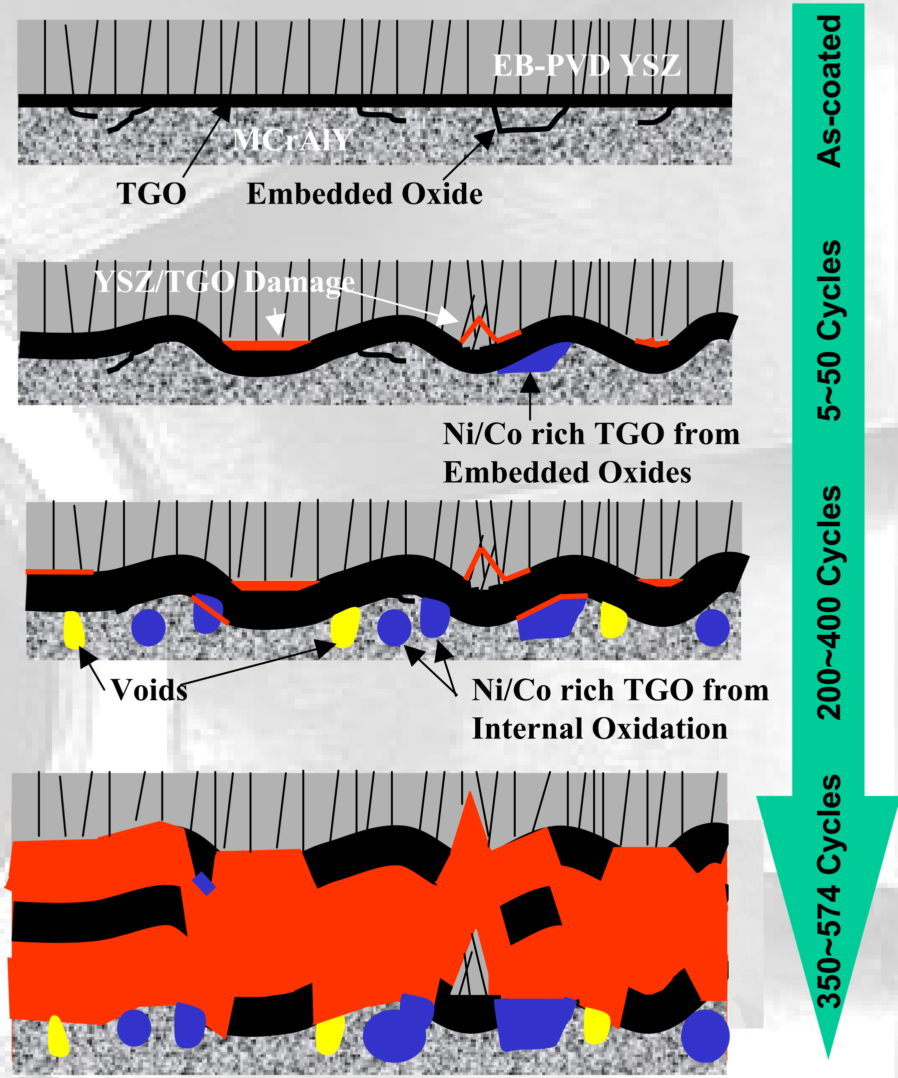
* EB-PVD 7YSZ with (Ni,Pt)Al Bondcoat and CMSX-4 Superalloy Substrate

- **Other Components of the AC Circuit Remained Constant within ± 5 ~ 30%:**
- **C_C and R_P Related to EB-PVD YSZ:**
  - **No Change in Fraction of Porosity and Porosity Shape.**
- **R_O , C_O, R_T and C_T Related to TGO and TGO/Bondcoat Interface:**
  - **No Significant Change in Thickness or Integrity.**
  - **Some Fluctuations due to Incomplete TGO Coverage/Growth**

Thermal Cycling of EB-PVD TBCs*: Damage Initiation and Progression**

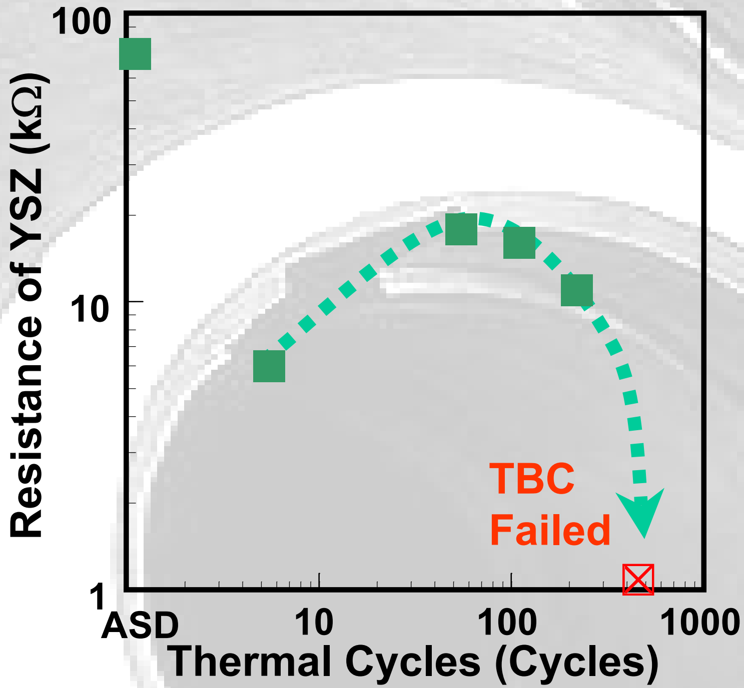


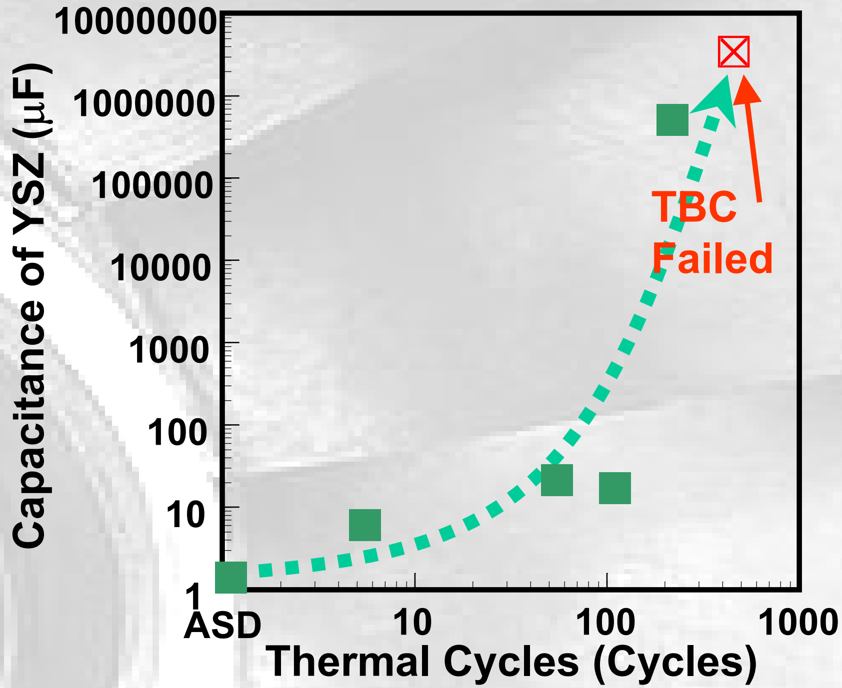




*EB-PVD 7YSZ; MCrAlY; IN-738; Thermal Cycling of 10-min. heat-up to 1121C; 40-min. at 1121C; 10-min. quench.
**Y.H. Sohn et al., Surf. Coat. Technol., 146-7 (2001) 70-78.

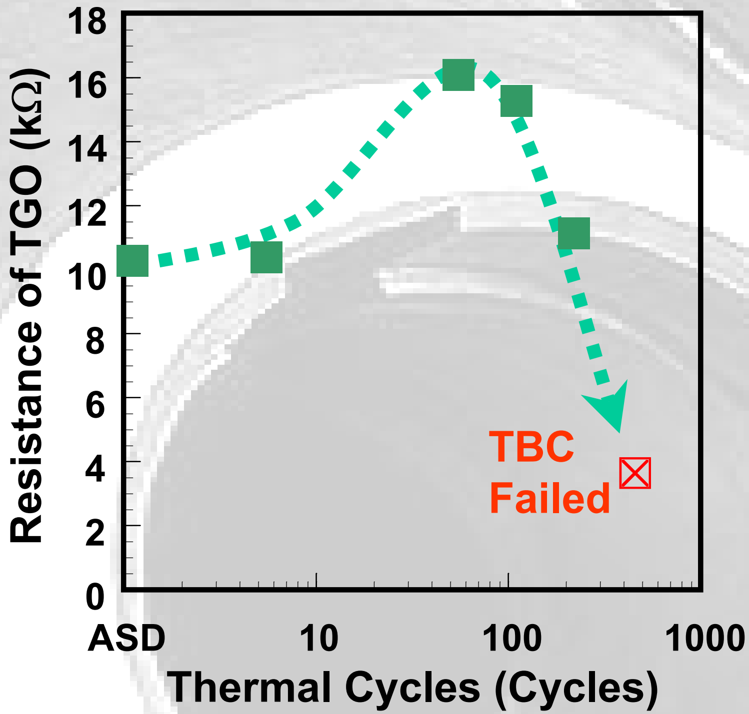
Thermally Cycled EB-PVD TBCs and EIS:
Evaluation of EB-PVD YSZ Top Coat

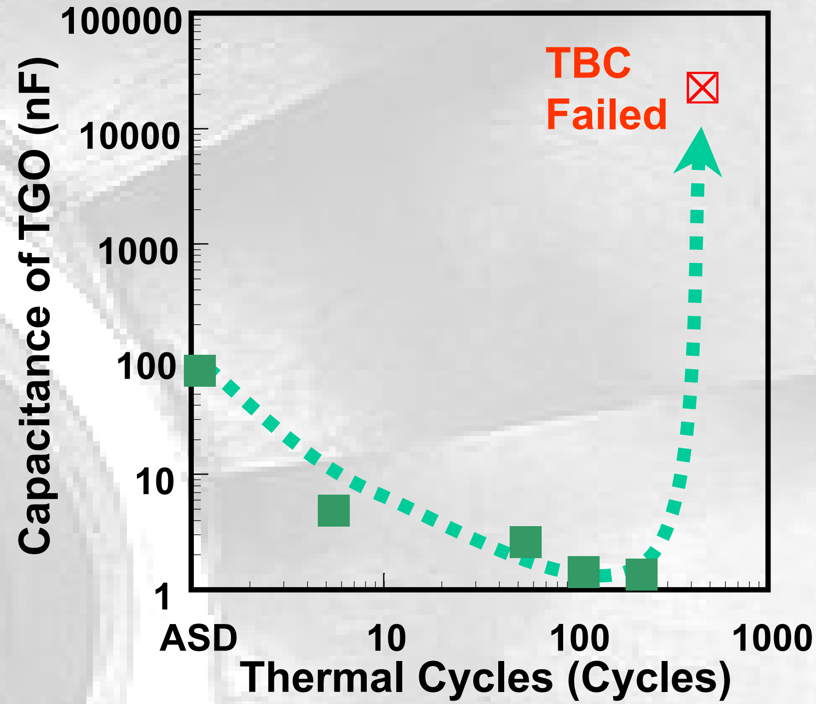




- **Decrease in YSZ Resistance and Increase in YSZ Capacitance by Several Orders of Magnitude:**
  - **Not Likely Due to Decrease in Thickness or Increase in Porosity in YSZ.**
  - **Initiation and Accumulation of Damage in TBC.**
  - **Electrolyte Penetration.**

Thermally Cycled EB-PVD TBCs and EIS:
Evaluation of Thermally Grown Oxide (TGO)

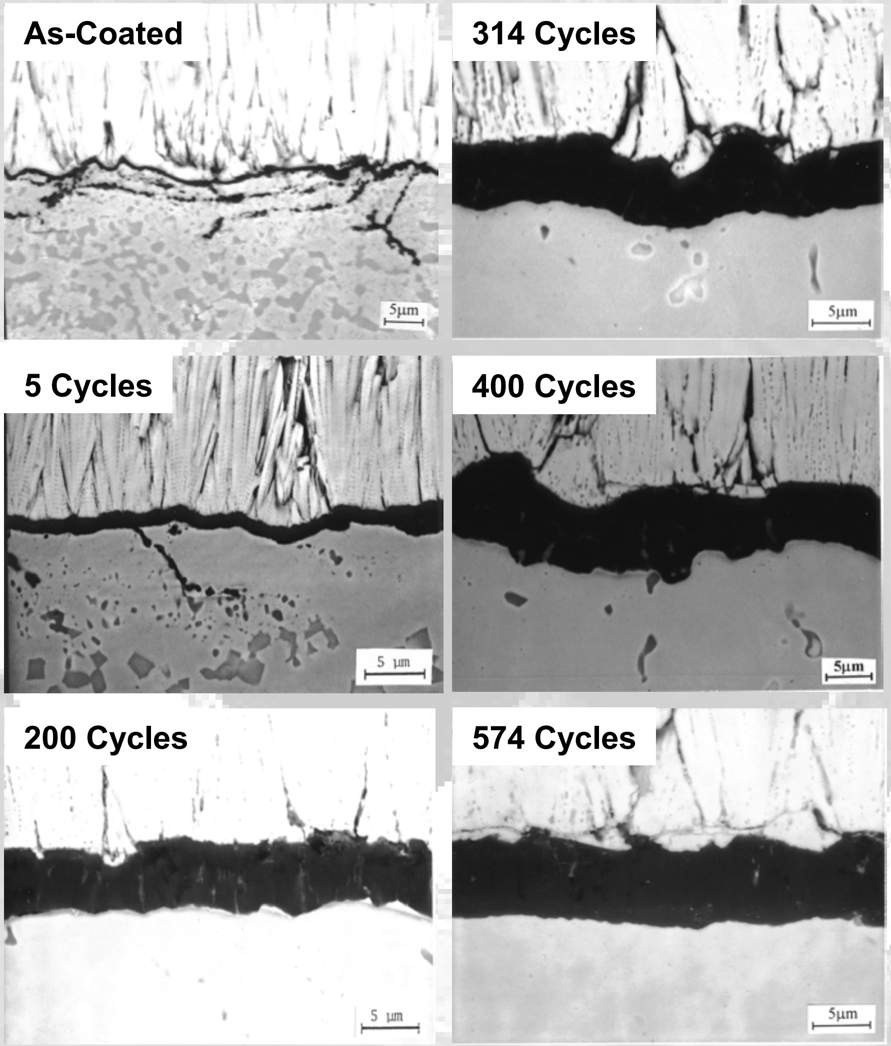


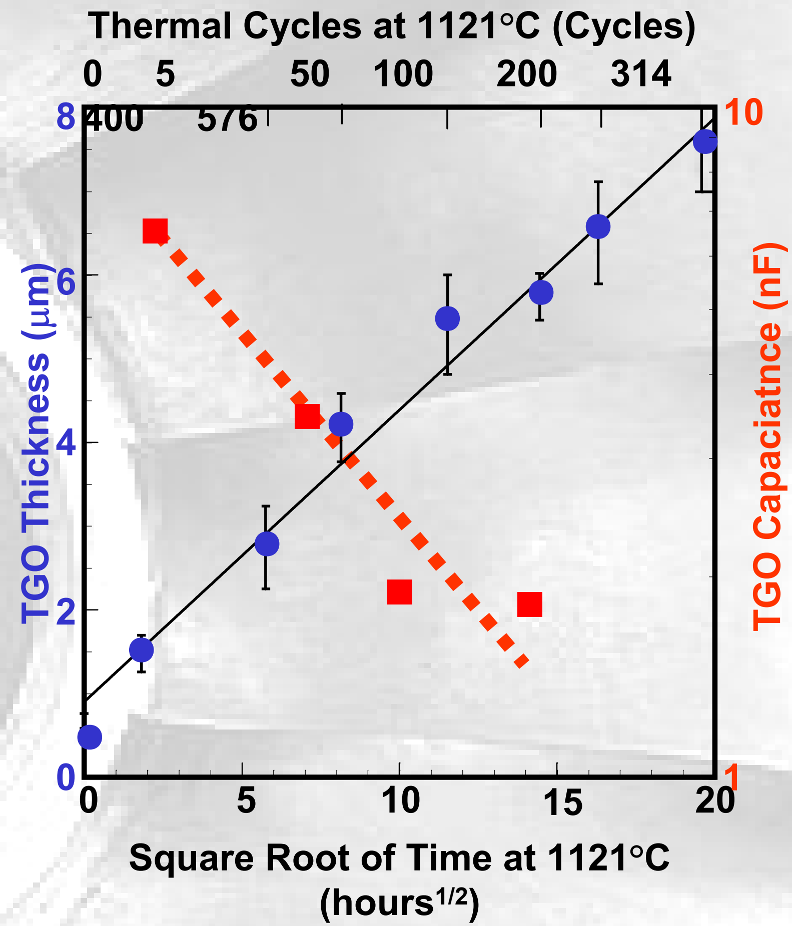


- Initial Increase and Decrease of TGO Resistance:
  - Growth of TGO.
  - TBC Damage and Electrolyte Penetration.

- Decrease of TGO Capacitance by Several Orders of Magnitude Before Failure:
  - Growth of TGO.
  - TBC Damage and Electrolyte Penetration.

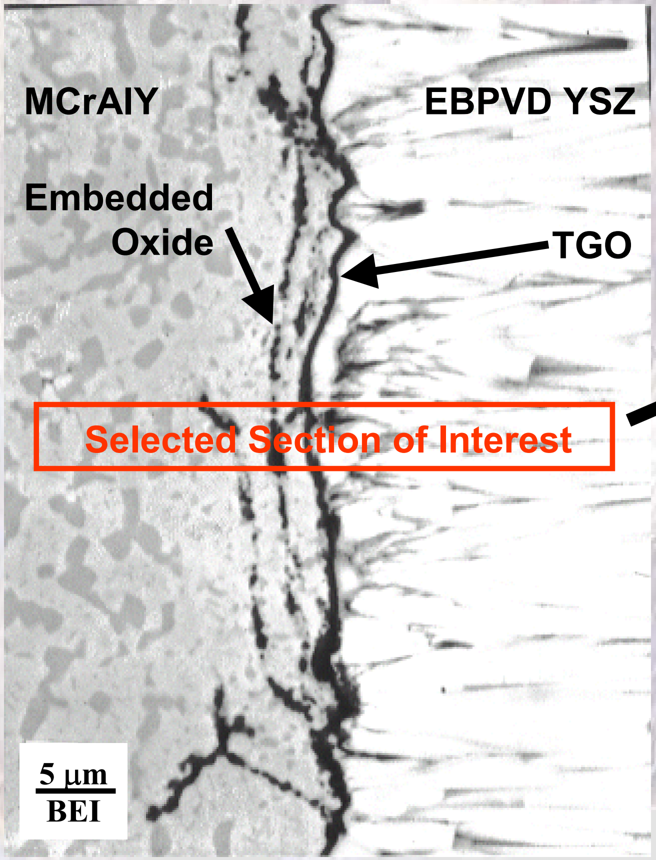
Thermally Cycled EB-PVD TBCs and EIS:
Evaluation of Thermally Grown Oxide (TGO)



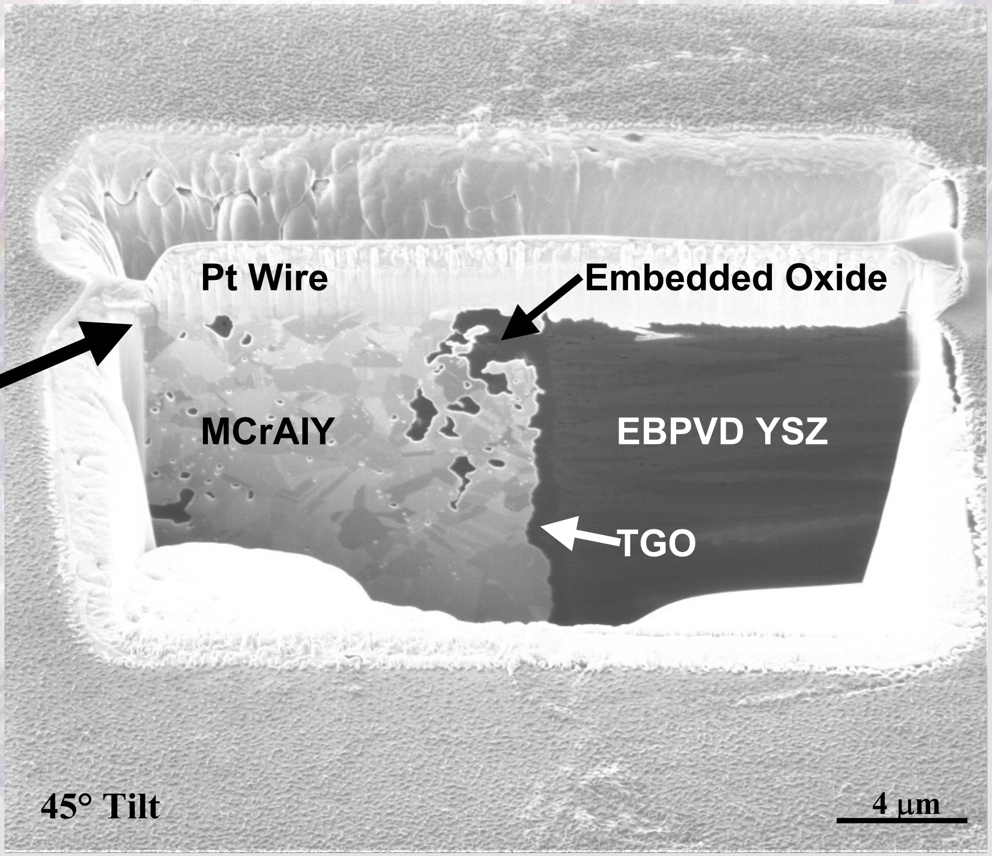


Thickness of TGO Measured 10 Times at Magnification of 3000X or Higher

High Resolution Transmission Electron Microscopy (HRTEM) Specimen Preparation of Thermal Barrier Coatings (TBCs) by Focused Ion Beam Technique (FIB)

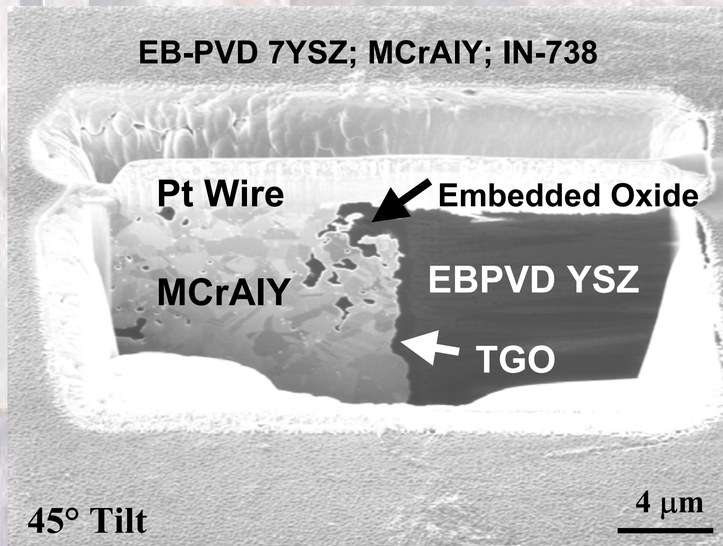


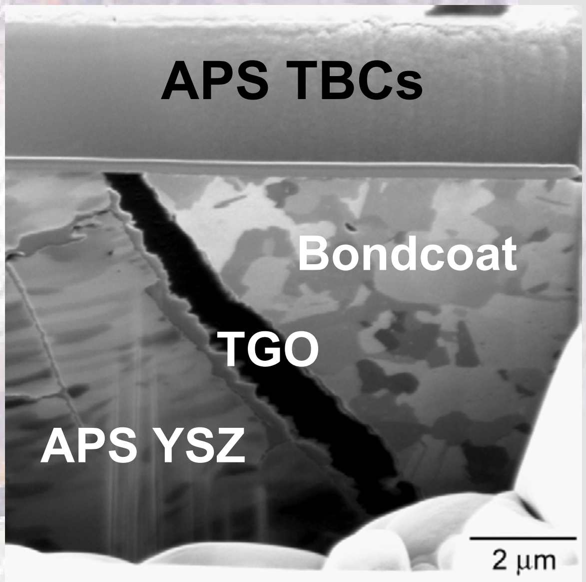
EB-PVD 7YSZ; MCrAlY; IN-738

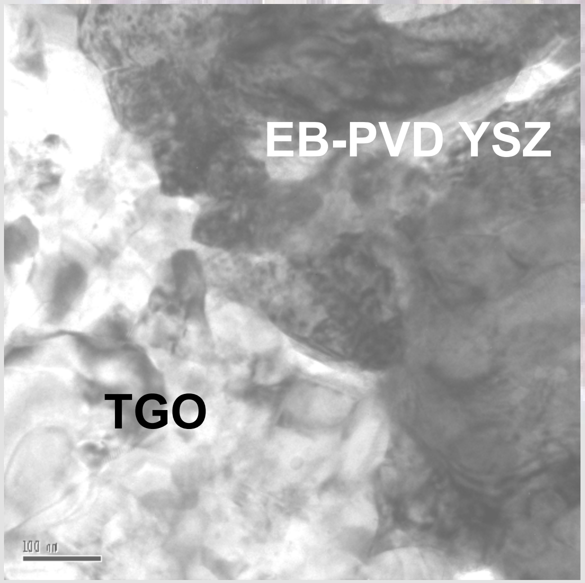


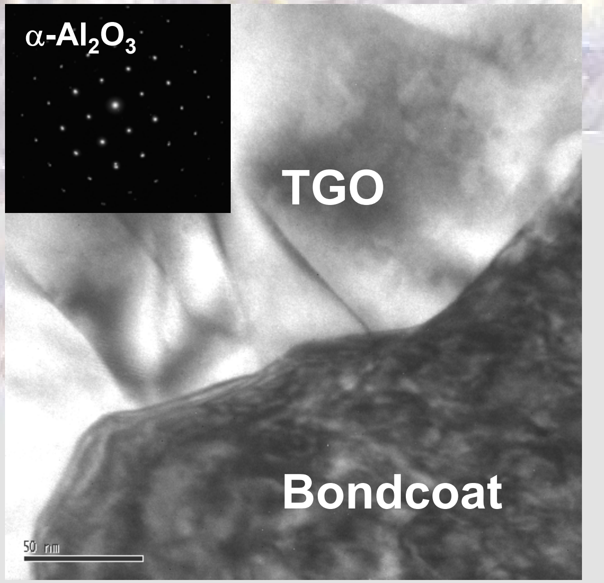
FIB Image of EB-PVD TBC Showing Cross-Sectional View (45 degree tilt) of YSZ, TGO, and Bondcoat During FIB Process.

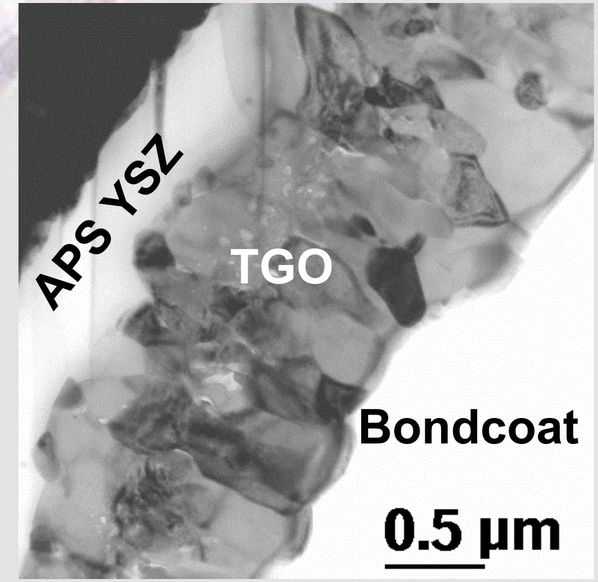
Preliminary Results from HRTEM of TBCs by Focused Ion Beam Technique (FIB)



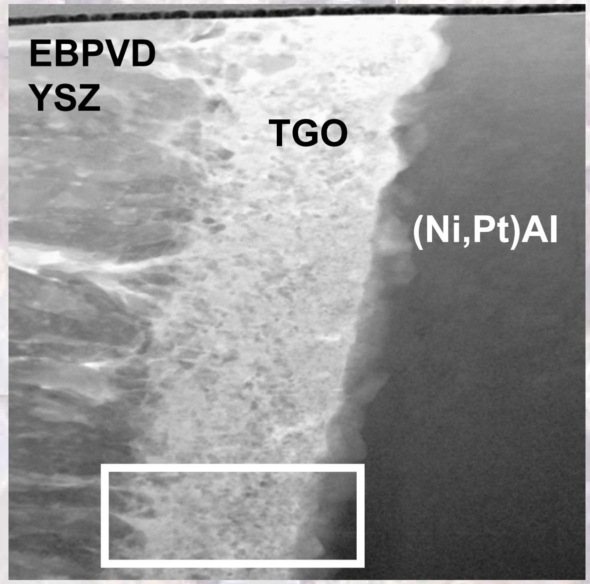




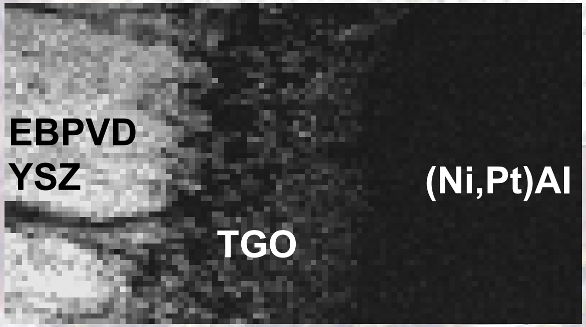




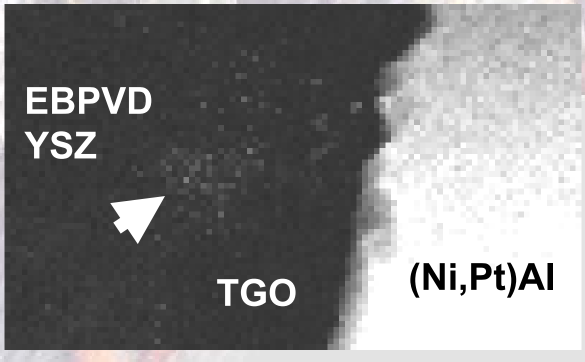
Preliminary Results from HRTEM of TBCs by FIB-MLO Technique: Nano-Spot (~10 nm) Energy Dispersive Spectroscopy (n-EDS) with Automated Point Mapping



EB-PVD 7YSZ; (Pt,Al)Ni; CMSX-4



Zr Map: Presence of Mixed-Oxide Zone* (ZrO_2 and Al_2O_3)



Ni Map: Presence of Transient Oxide Containing Ni** on Top of TGO

*M.J. Stiger, Elev. Temp. Coatings, TMS, 1999, 51-65 and *K. Murphy et al., Surf. Coat. Technol., 146-7 (2001).
** Currently Being Examined by Electron Energy Loss Spectroscopy (EELS) for Oxidation State.

Currently In-Progress:
Calibration – Refinement of NDE Techniques

- **Photostimulated Luminescence Spectroscopy (PSLS):**
  - Lateral Resolution and Probe Penetration.
  - Metastable and Equilibrium Al_2O_3.
  - Coupled Effect (Residual Stress and Composition) of Cr^{3+} in Al_2O_3.
  - Scale Formation - Spallation on Al_2O_3 Forming Alloys without TBCs.
- **Electrochemical Impedance Spectroscopy (EIS).**
  - Calibration using Monolithic 7YSZ with Open Pores as a Function of Thickness and Porosity.
  - Scale Formation - Spallation on Al_2O_3 Forming Alloys without TBCs.
- **Processing Parameters of As-Coated APS and EB-PVD:**
  - Thickness and Porosity / Microstructure.
  - TGO Phase Constituents and Residual Stress.
  - Thermal Conductivity.
- **Thermal Cyclic Oxidation:**
  - Lifetime Prediction / Remain Assessment based on Relation to Microstructural Evolution and Failure Modes / Mechanisms.

Currently In-Progress:
Advanced Microstructural Characterization

- **Development and Refinement (Perfection!) of HR-TEM Specimen Preparation Procedure by Two FIB-MLO (FEI 200TEM and FEI 611TEM):**
  - **As-Coated and Thermally Cycled TBC Specimens.**
  - **Emphasis on YSZ/TGO/Bondcoat Interfaces.**
- **High Resolution Transmission Electron Microscopy (FEI Tecnai F30):**
  - **Bright-Field (BF) and Dark-Field (DF) Imaging with Selected Area Diffraction (SAD).**
  - **Nano-Spot Energy Dispersive Spectroscopy and Mapping.**
  - **Installed Detection Capability Currently Being Examined for TBC Applications:**
    - ✓ **High Angle Annular Dark Field (HAADF) Imaging.**
    - ✓ **Electron Holography (EH).**
    - ✓ **Electron Energy Loss Spectrometer (EELS).**
    - ✓ **Gaton Image Filter (GIF).**
    - ✓ **Orientation Imaging Microscopy (OIM).**

Currently In-Progress:
Advanced Microstructural Characterization

- **Standard/Conventional Microstructural Characterization Techniques:**
  - X-ray Diffraction (XRD)
  - Two Field Emission Scanning Electron Microscopy (FE-SEM)
  - Energy Dispersive Spectroscopy (EDS)
  - Electron Probe Microanalysis (EPMA)
- **Other Techniques Being Examined and Available for TBC Applications:**
  - Auger Electron Spectroscopy (AES)
  - Rutherford Backscatter Spectroscopy (RBS)
  - Secondary Ion Mass Spectroscopy (SIMS)
  - X-ray Photoelectron Spectroscopy (XPS)
- **Other Critical Facilities Available:**
  - Renishaw 1000B MicroRaman Spectroscopy (NDE: PSLS).
  - Electrochemical Impedance Analyzer (NDE: EIS)
  - CM Rapid Furnaces with Vertical Stage Cycling Package.
  - Automated Specimen Preparation

Summary

- **Two Non-Destructive Evaluation (NDE) Techniques, Photostimulated Luminescence Spectroscopy (PSLS) and Electrochemical Impedance Spectroscopy (EIS) are Being Developed and Refined for Applications in Thermal Barrier Coatings (TBCs):**
  - **Specification / Quality Control.**
  - **Lifetime Prediction / Remain Assessment.**
  - **Insight to Failure Mechanisms.**
- **Detailed Failure Mechanisms of TBCs are Investigated using Advanced Characterization Techniques including:**
  - **High Resolution Transmission Electron Microscopy (HRTEM) via Focused Ion Beam (FIB) - Micromanipulator Lift-Out (MLO).**
  - **Two NDEs, PSLS and EIS.**

AMPAC "Bridging the technology gap"

Summary

- Active Participation and Strong Support of Industrial Partners:
  - Technical Collaboration and Specimen Preparation.
  - Education of Students Technically and Professionally through Direct Communication.
- Research and Education for Two Student-Research-Teams:
  - Pair of Graduate and Undergraduate Students.
  - Collaboration / Competitive Team-Based Research Activities.
  - Direct Collaboration / Communication with Industrial Partners.
  - Education in Technology and in Professionalism.

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