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

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SCIES Project 02- 01- SR103

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

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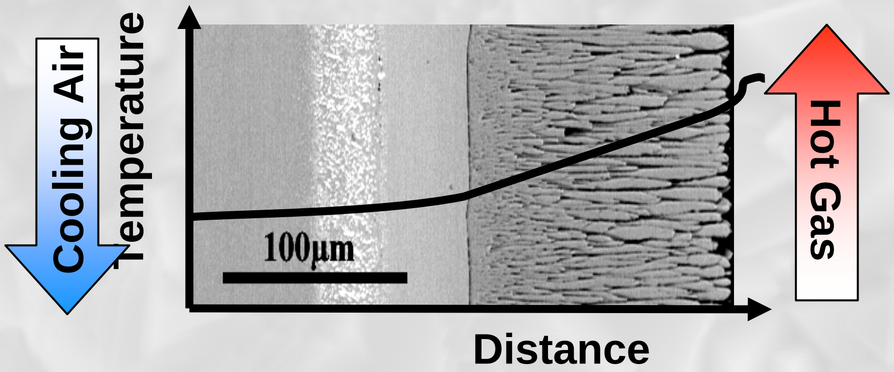
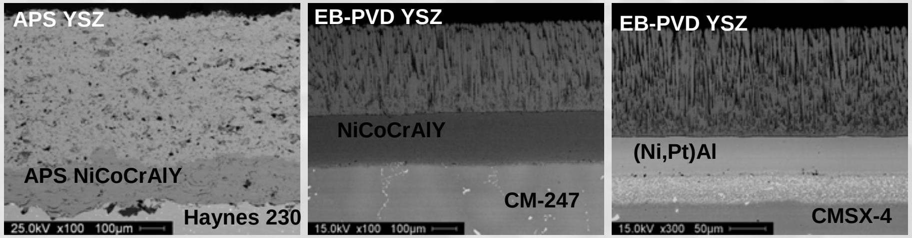
Project Awarded (May 1, 2002, 36 Month Duration)

$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.**

Approach: Tasks and Schedule

Task I
Thermal Cyclic Oxidation of Thermal Barrier Coatings

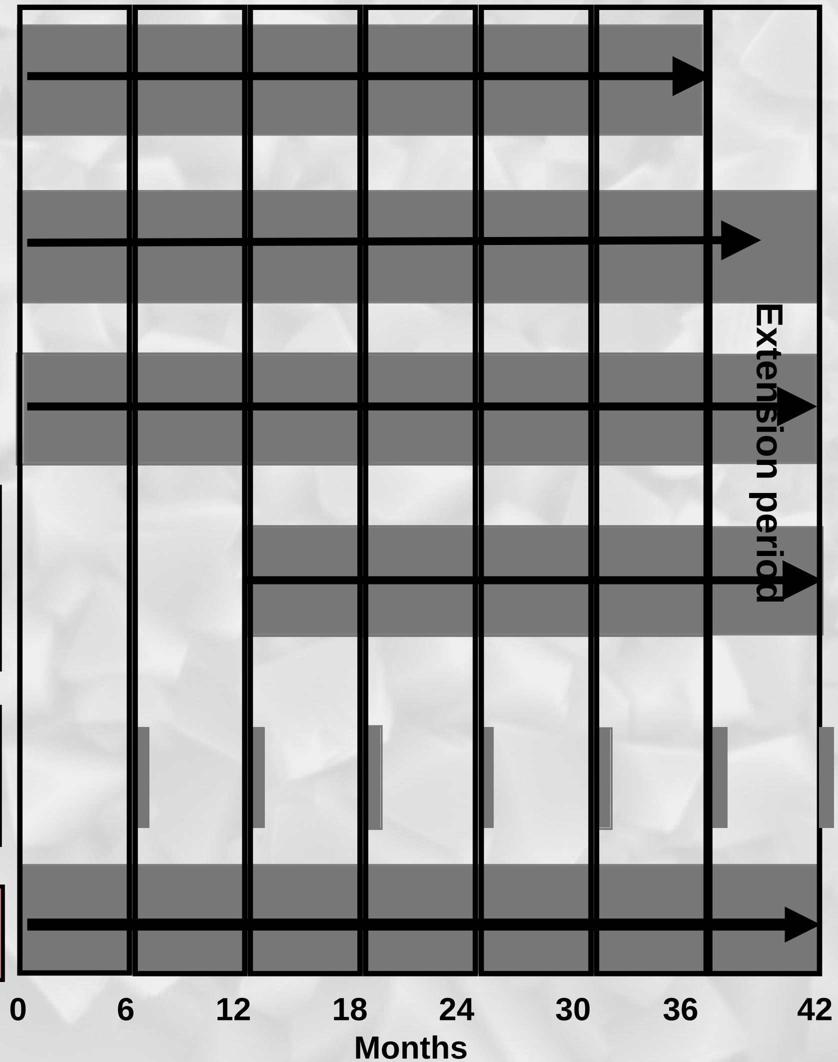
Task II
NDE by Photostimulated Luminescence and Electrochemical Impedance Spectroscopy

Task III
Advanced Microstructural and Failure Analysis

Task IV
Failure Mechanisms; Refinement of PL and EIS; Identify / Lifetime Improvement / Prediction Approach

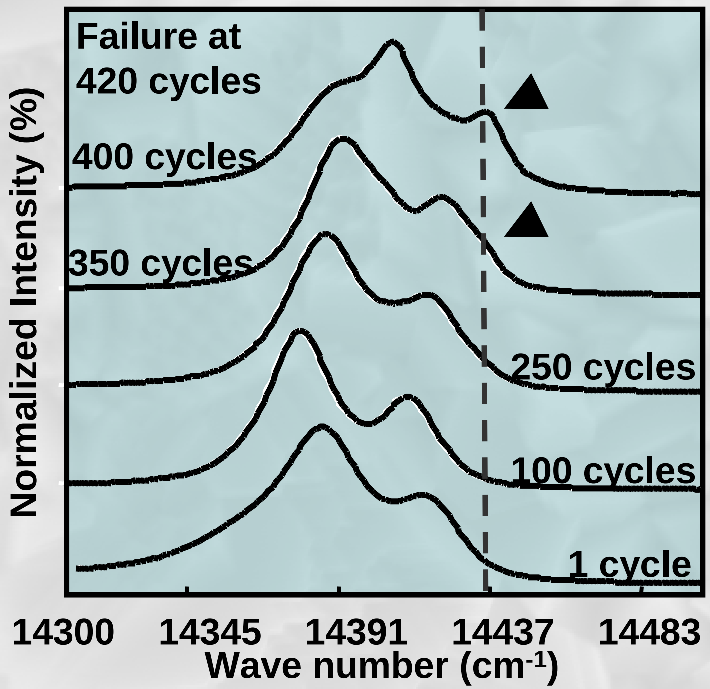
Task V
Reports, Industrial Briefing and Technology Transfer

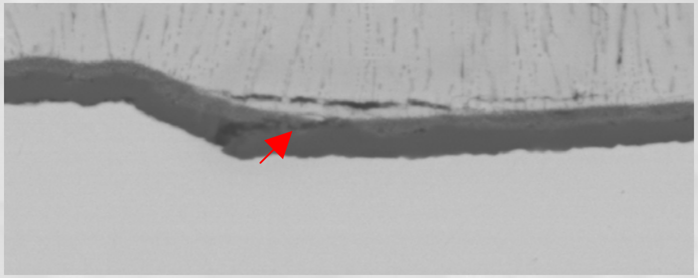
Task VI
Organized Operation of Student Research Team



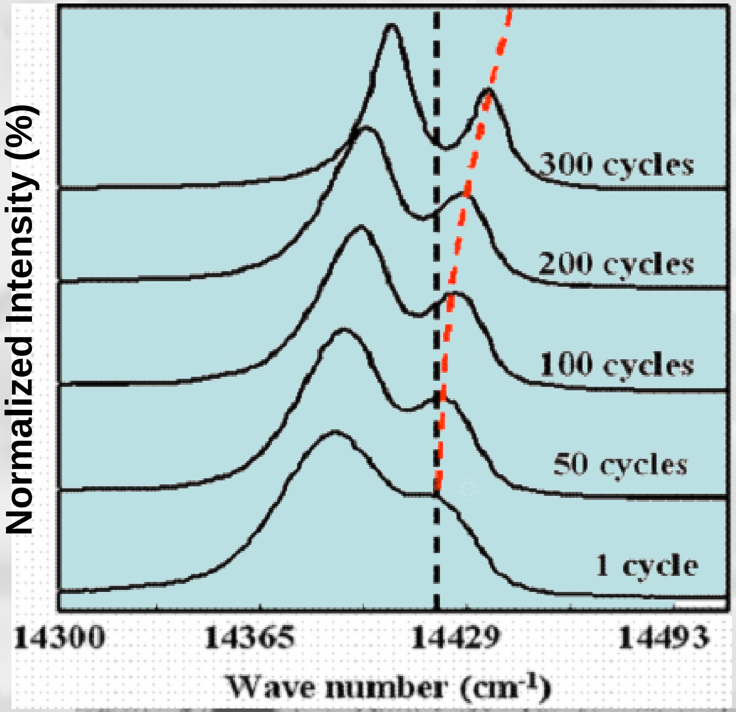
Accomplishments (1): PL

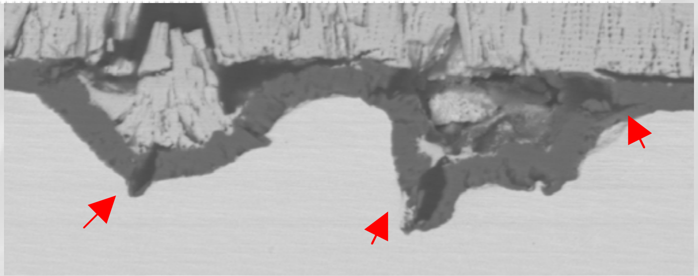
Stress Relief due to the TGO Cracking Detected Prior to Spallation.



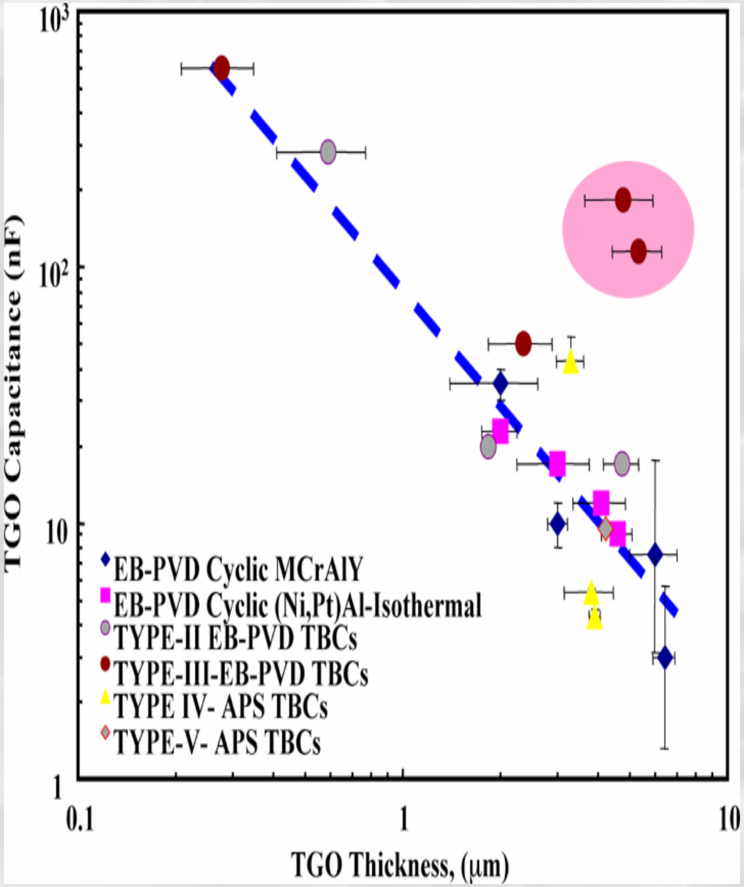


Stress Relaxation due to Lengthening of the TGO (Racheting) Detected Prior to Spallation).

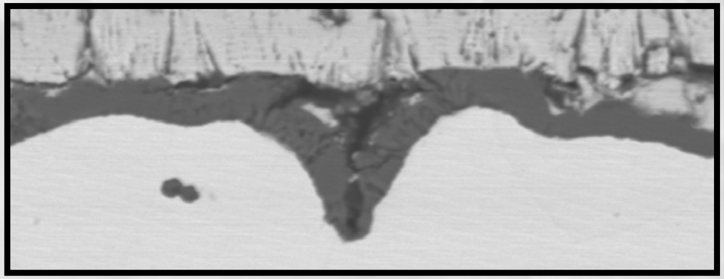


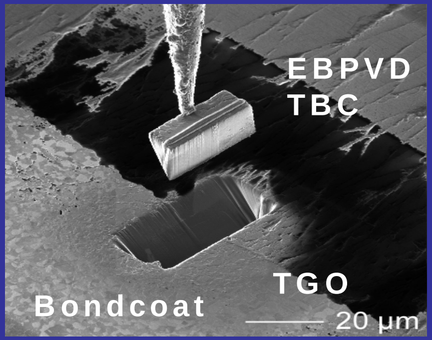


Accomplishments (2): EIS & TEM/STEM

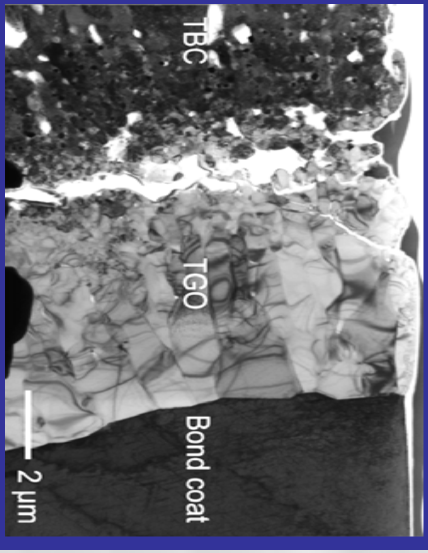


- Increase in Electrochemical Capacitance of TGO Scale with TGO Thickness.
- Deviation in Trend with the TGO Scale Damage and Electrolyte Exposure.
- FIB-INLO Specimen Preparation for TEM/STEM Microstructural Analysis.



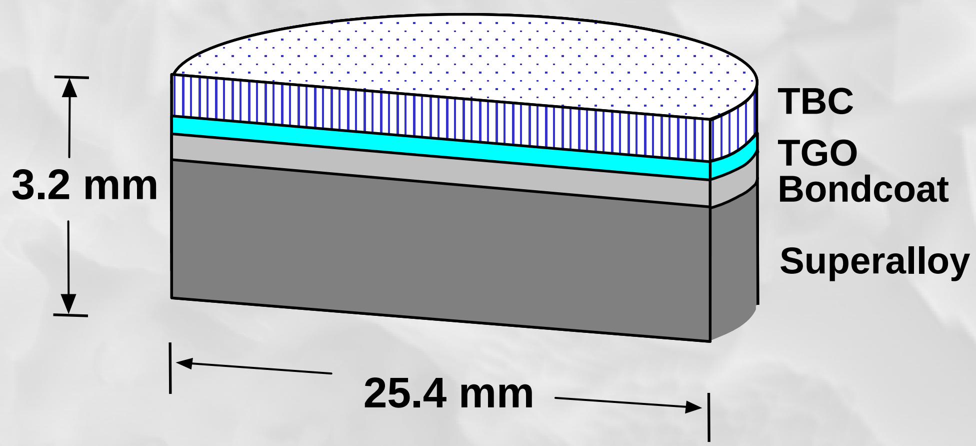


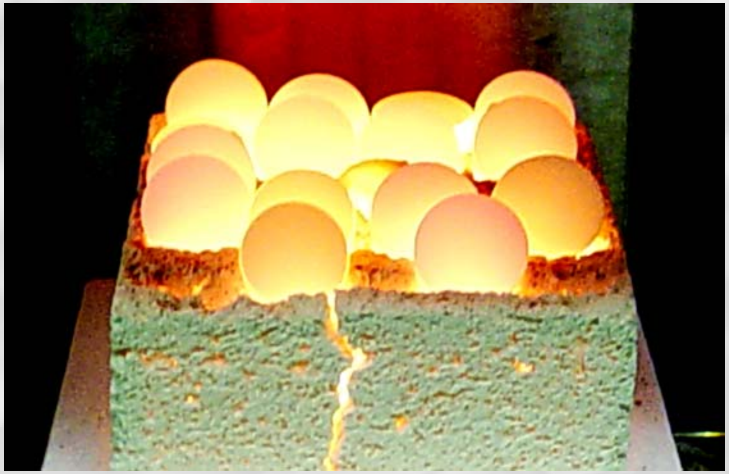
FIB-INLO Specimen Preparation of TBCs and Subsequent TEM/STEM Analysis



Specimen Description* and Testing

TBC System Type	7YSZ Deposition and Thickness (μm)	Bond Coat Type and Thickness (μm)	Superalloy Substrate	Notes
I	EB-PVD; 380	NiCoCrAlY; 200	CM247	Shot-Peened Bondcoat
II	EB-PVD; 150	(Ni,Pt)Al; 50	CMSX-4	As-Coated Bondcoat
III	EB-PVD; 145	(Ni,Pt)Al; 35	Rene'N5	Grit-Blasted Bondcoat
IV	APS; 600	NiCoCrAlY; 180	Haynes 230	APS Bondcoat
V	APS; 240	NiCoCrAlY; 100	MAR-M-509	VPS Bondcoat

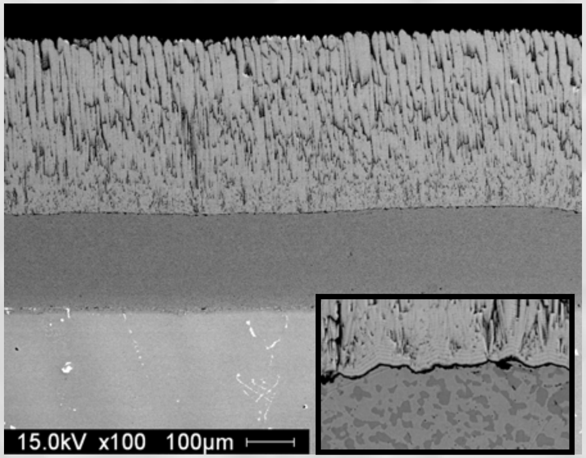




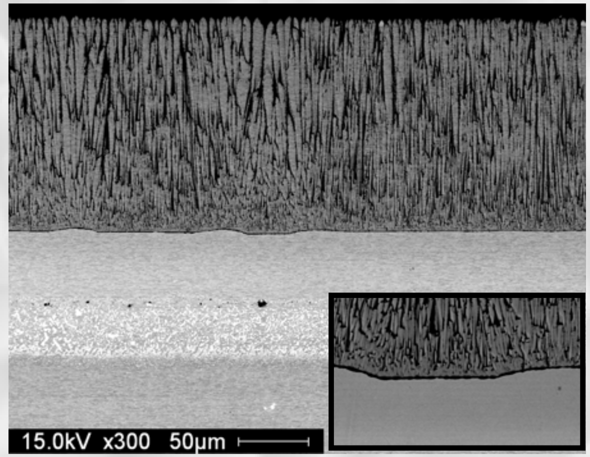
* Courtesy of Industrial Partners

Typical Microstructure of As-Coated TBCs

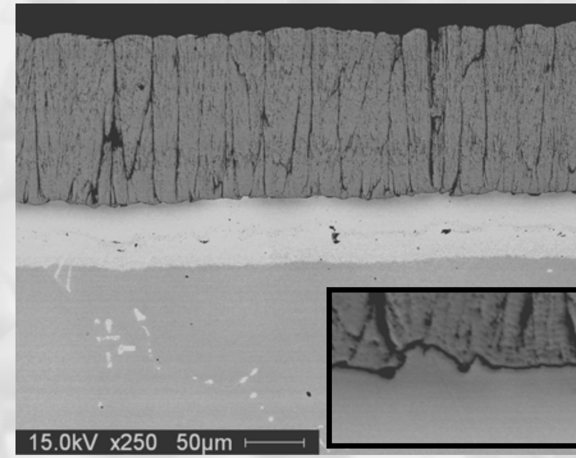
(SEM: Backscatter Electron Images)



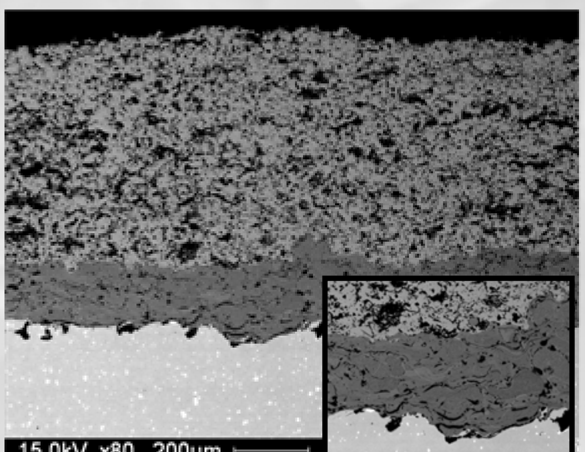
I: EBPVD, Shot-Peened NiCoCrAlY Bondcoat



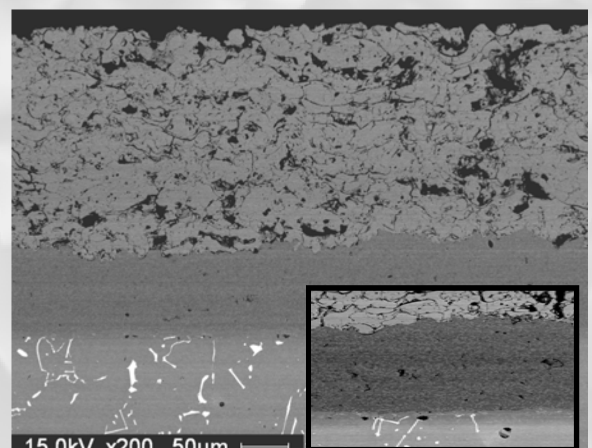
II: EBPVD, As-Coated (Ni,Pt)Al Bondcoat



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



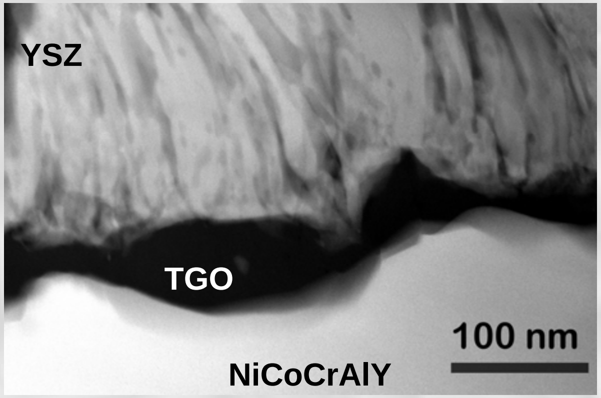
VI: APS, NiCoCrAlY with Oxide Inclusions



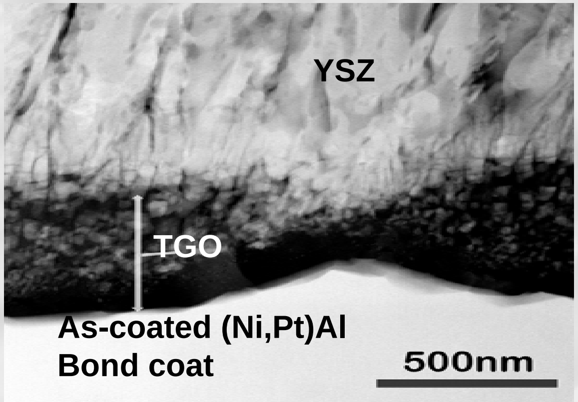
V: APS, NiCoCrAlY Bondcoat

Typical Microstructure of As-Coated TBCs

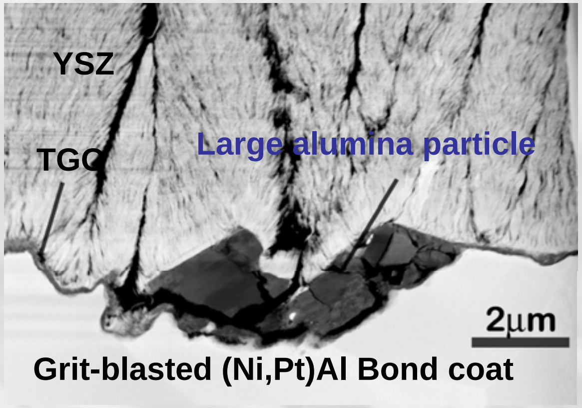
(TEM/STEM: Bright & High Angle Annular Dark Field Images)



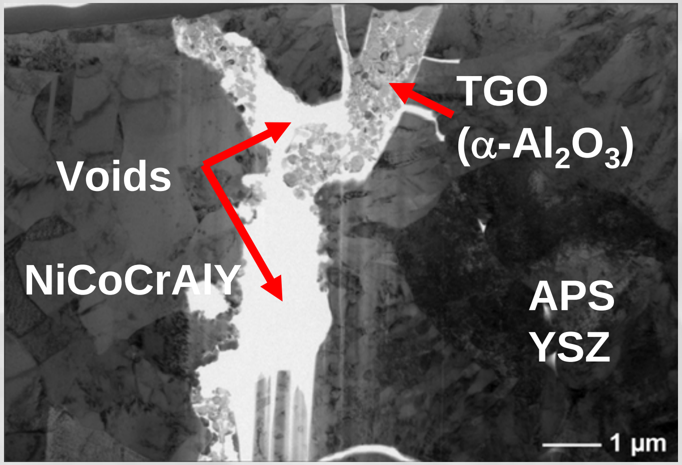
Type I



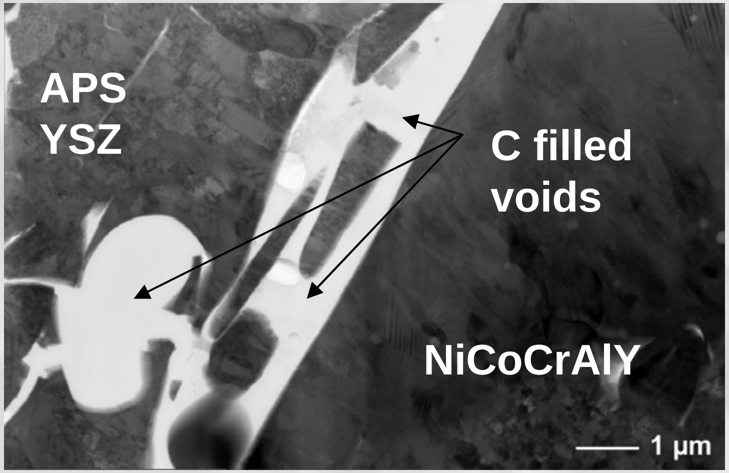
Type II



Type III

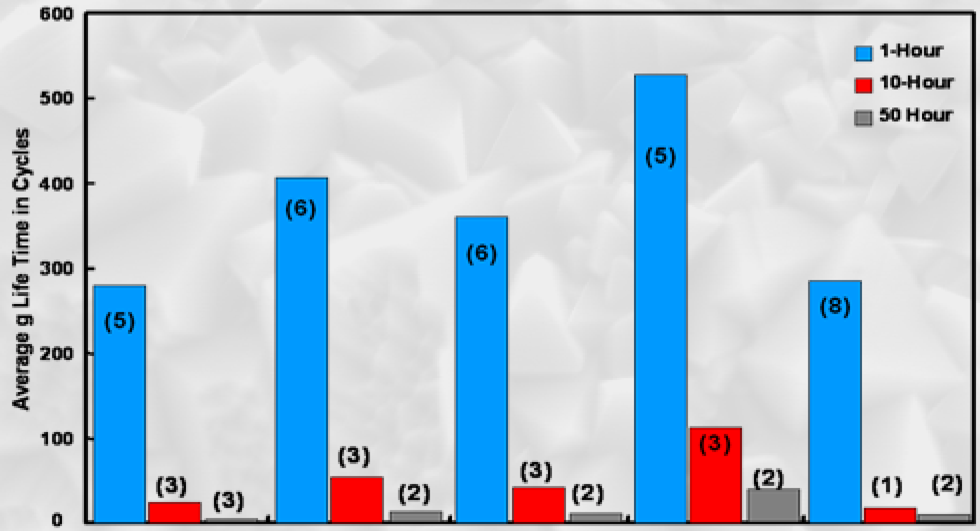


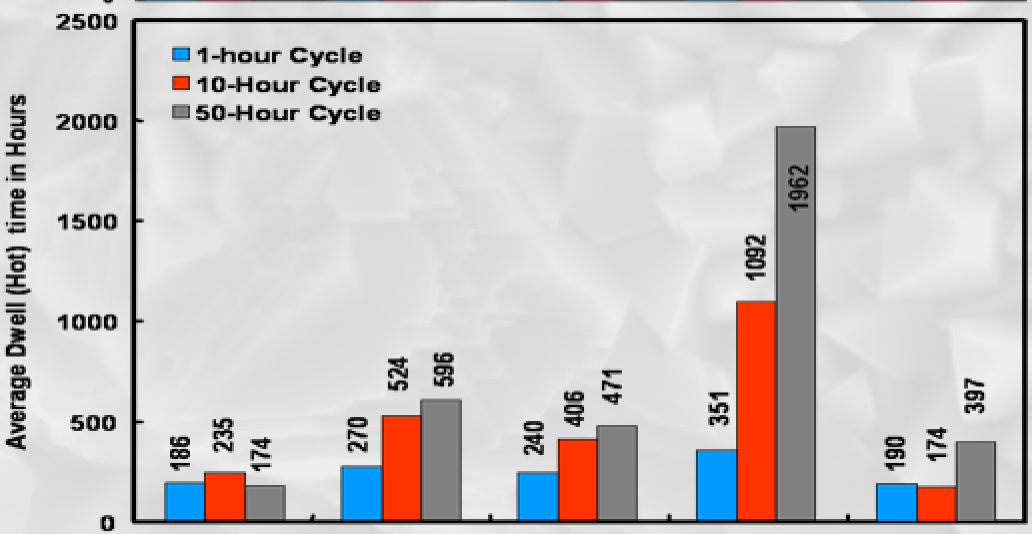
Type IV



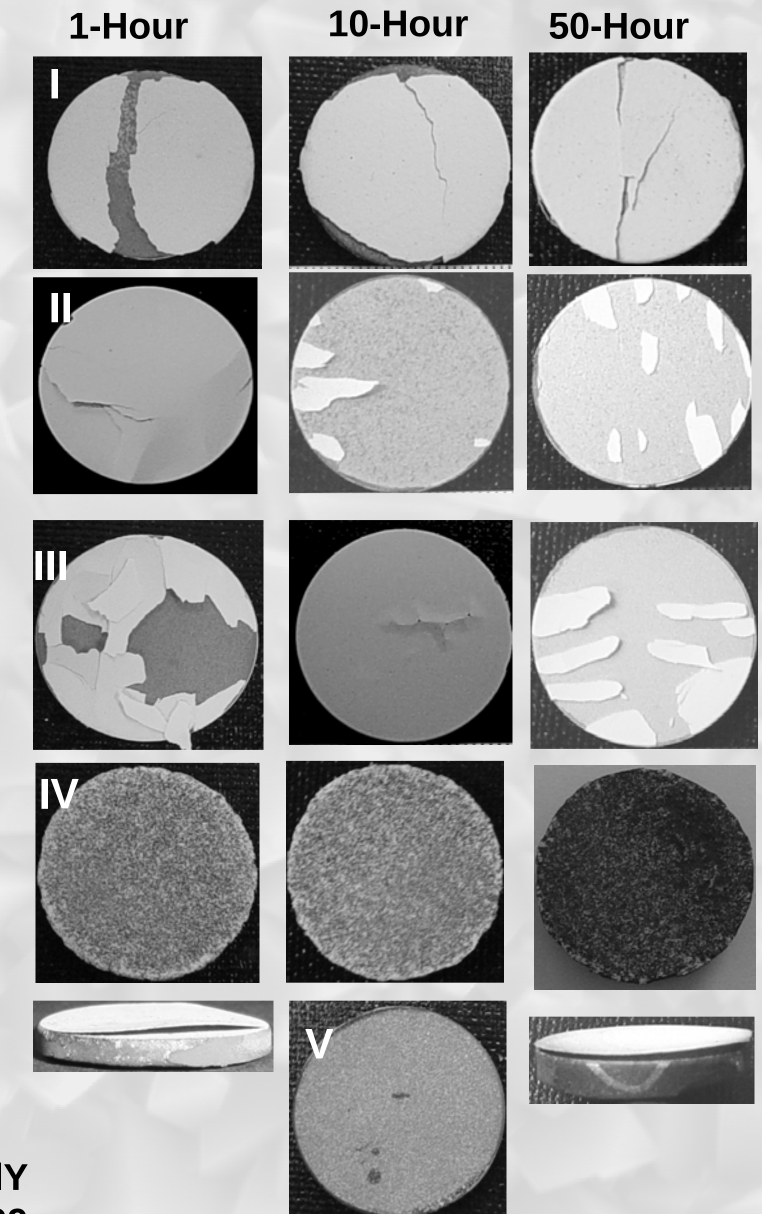
Type V

Thermal Cycling Lifetime / Dwell Time of TBCs

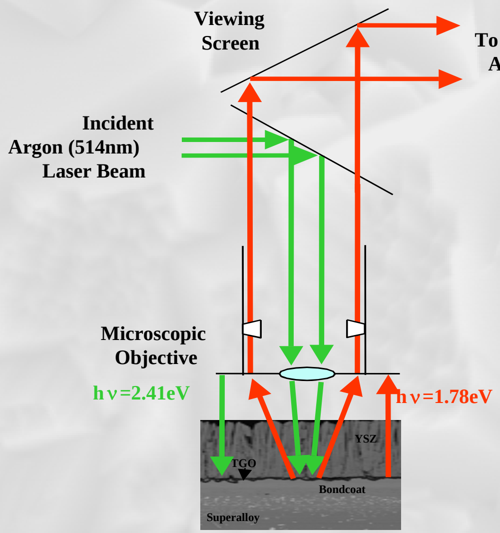


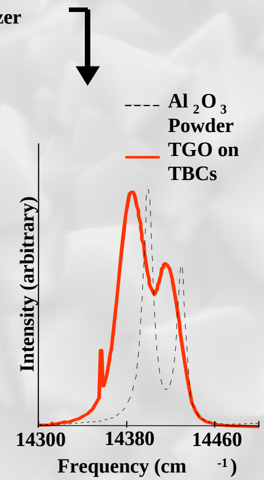


Type-I	Type-II	Type-III	Type-IV	Type-V
EB-PVD	EB-PVD	EB-PVD	APS	APS
NiCoCrAlY	(Ni,Pt)Al	(Ni,Pt)Al	NiCoCrAlY	NiCoCrAlY
CM 247	CMSX-4	Rene' N5	Haynes 230	MAR-M509



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

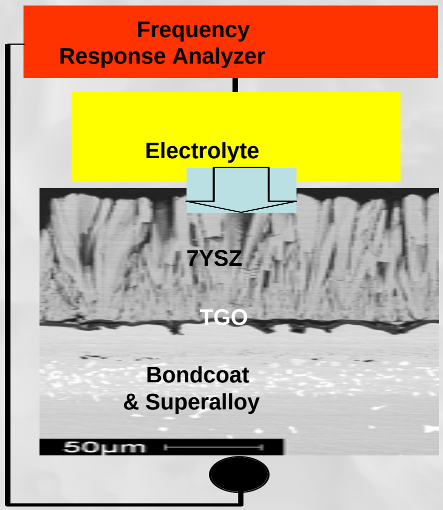


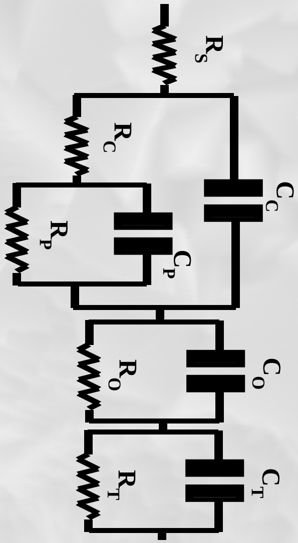


<u>Photostimulated Luminescence:</u>

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.**

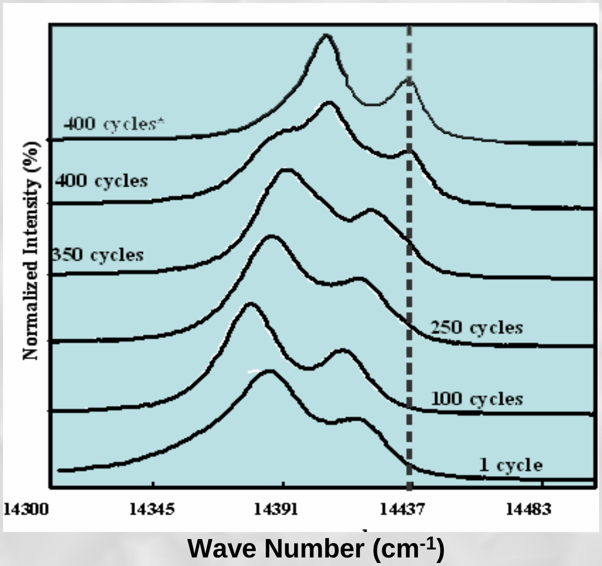


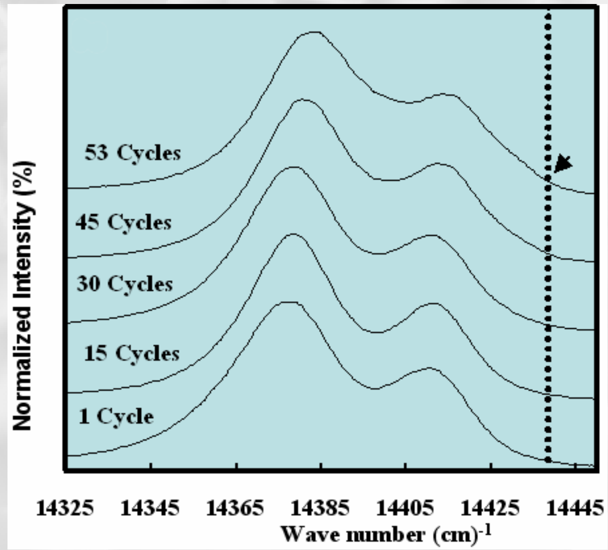


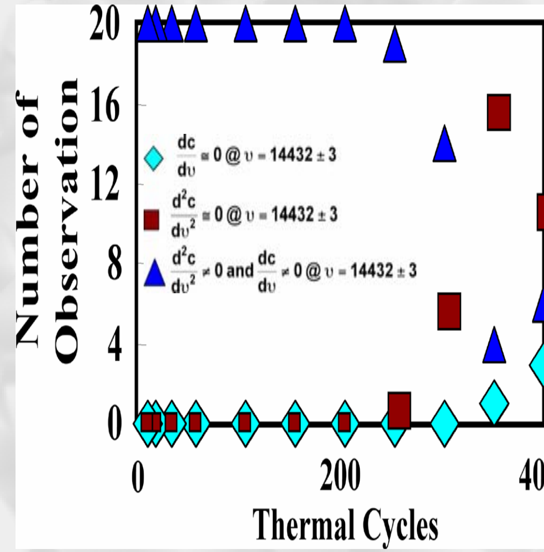
<u>Electrochemical Impedance:</u>

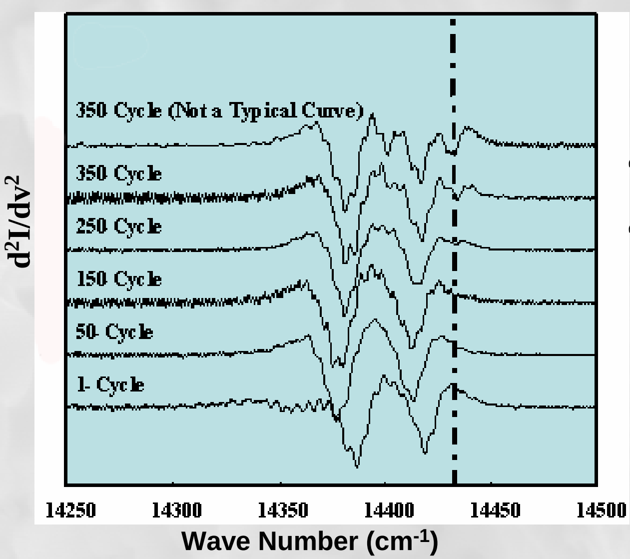
- **Each AC Circuit Component Corresponds to Physical Parameter of TBC Constituents Quantitatively.**
- **Measured Electrochemical Impedance is Simulated According to Equivalent AC Circuit.**

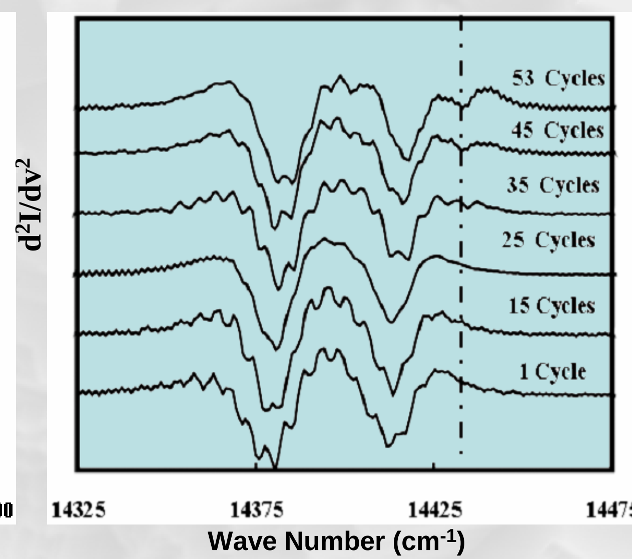
Luminescence from the TGO with Thermal Cycling {Type II TBC: EB-PVD / As Coated (Ni,Pt)Al / CMSX-4}





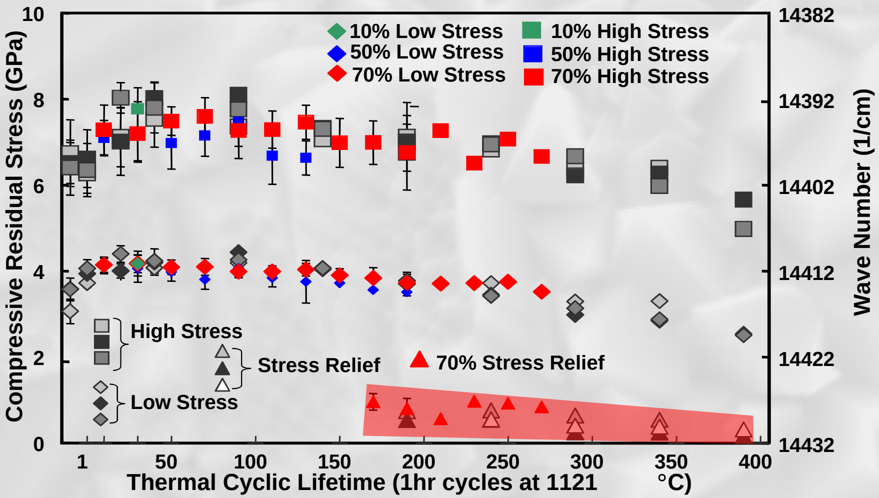


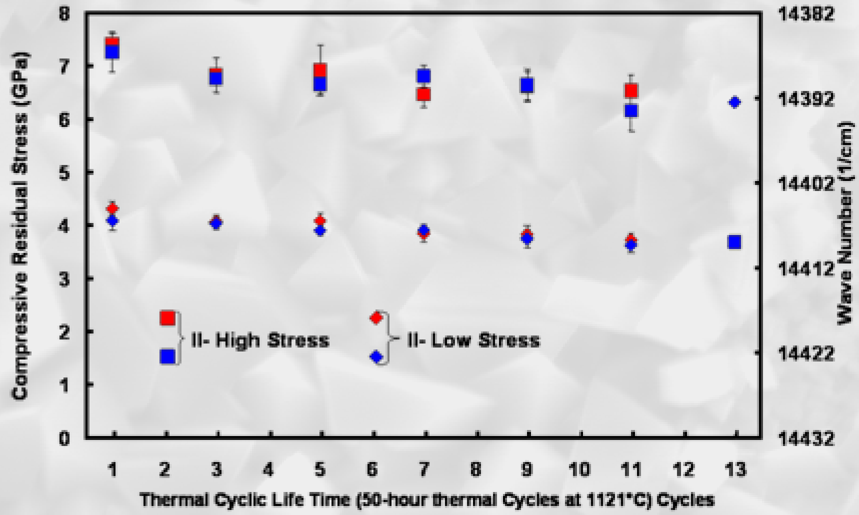


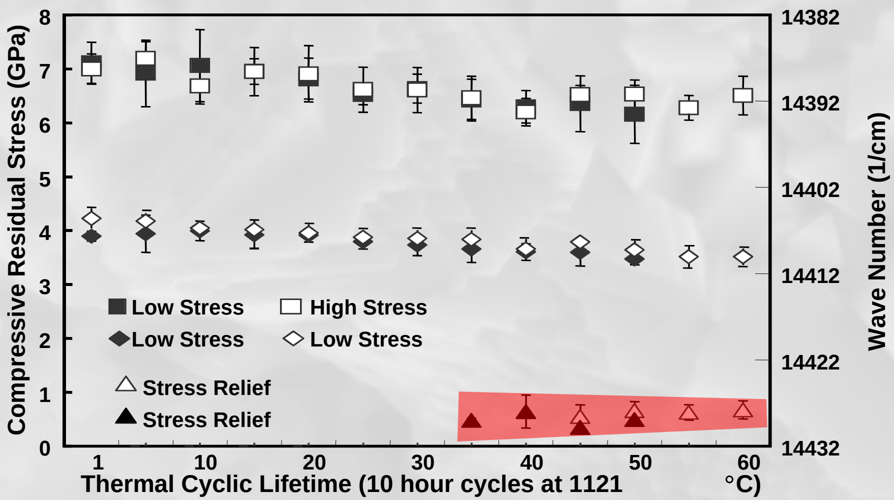


- **Stress Relief Detected Prior to Spallation (420 Cycles).**
- **Both 1 and 10 Hour Thermal Cycles.**

Evolution of Compressive Residual Stress within the TGO with Stress Relief {Type II TBC: EB-PVD / As Coated (Ni,Pt)Al / CMSX-4}



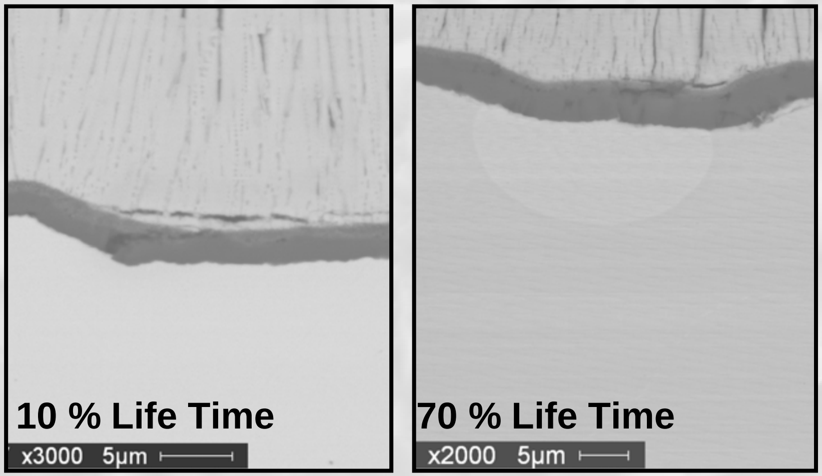




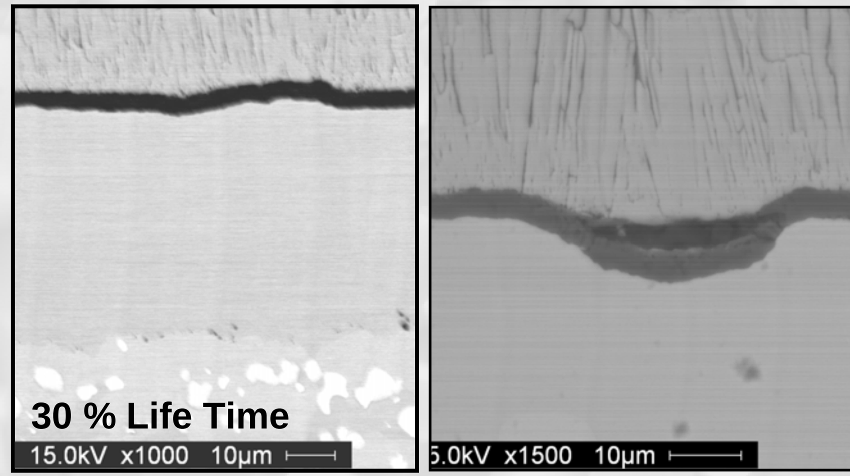
- **Initial Rise in the Magnitude of the Compressive Residual Stress In TGO.**
- **TGO Stress Relief Accompanied by Sub Critical Damages at YSZ/ TGO Interface or Within TGO.**

Microstructural Development During Thermal Cycling {Type II TBC: EB-PVD / As Coated (Ni,Pt)Al / CMSX-4}

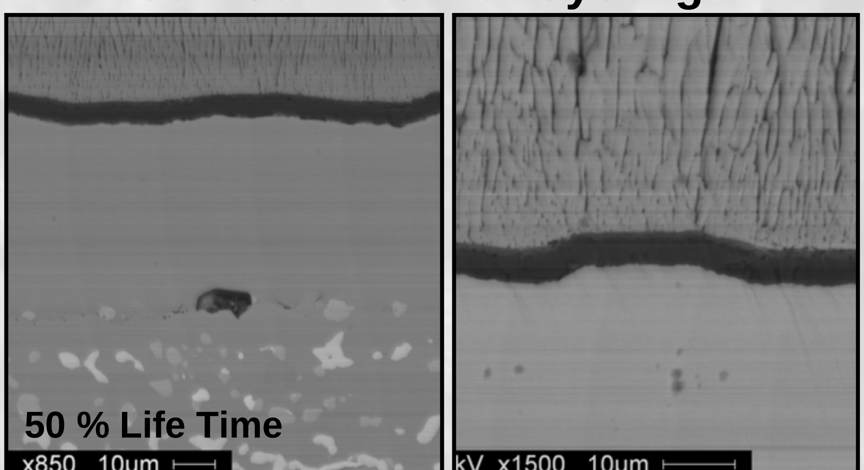
1-Hour Thermal Cycling



10-Hour Thermal Cycling



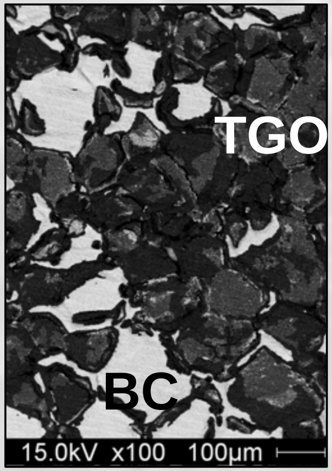
50-Hour Thermal Cycling



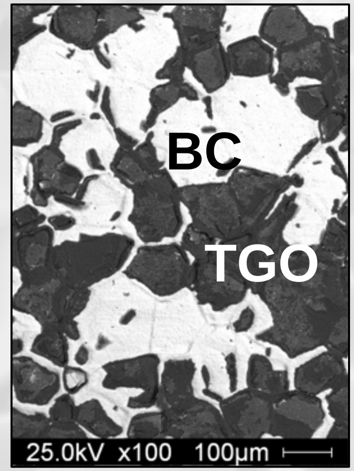
- **Damages Near the (Ni,Pt)Al Bondcoat Ridges.**
- **Damages within the TGO (Mixed Oxide Zone) and at the TGO/Bondcoat Interface.**

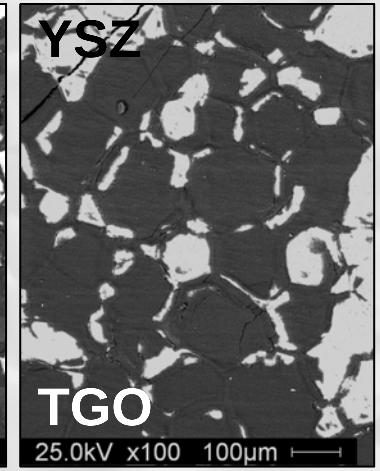
Fractographic Characteristics of TBC Spallation
{Type II TBC: EB-PVD / As Coated (Ni,Pt)Al / CMSX-4}

1-Hour Thermal Cycling

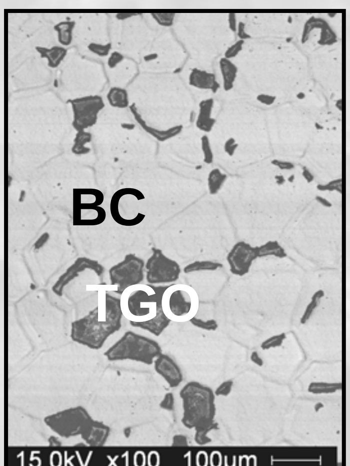


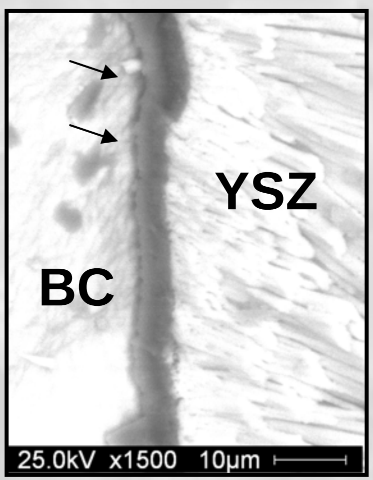
10-Hour Thermal Cycling





50-Hour Thermal Cycling

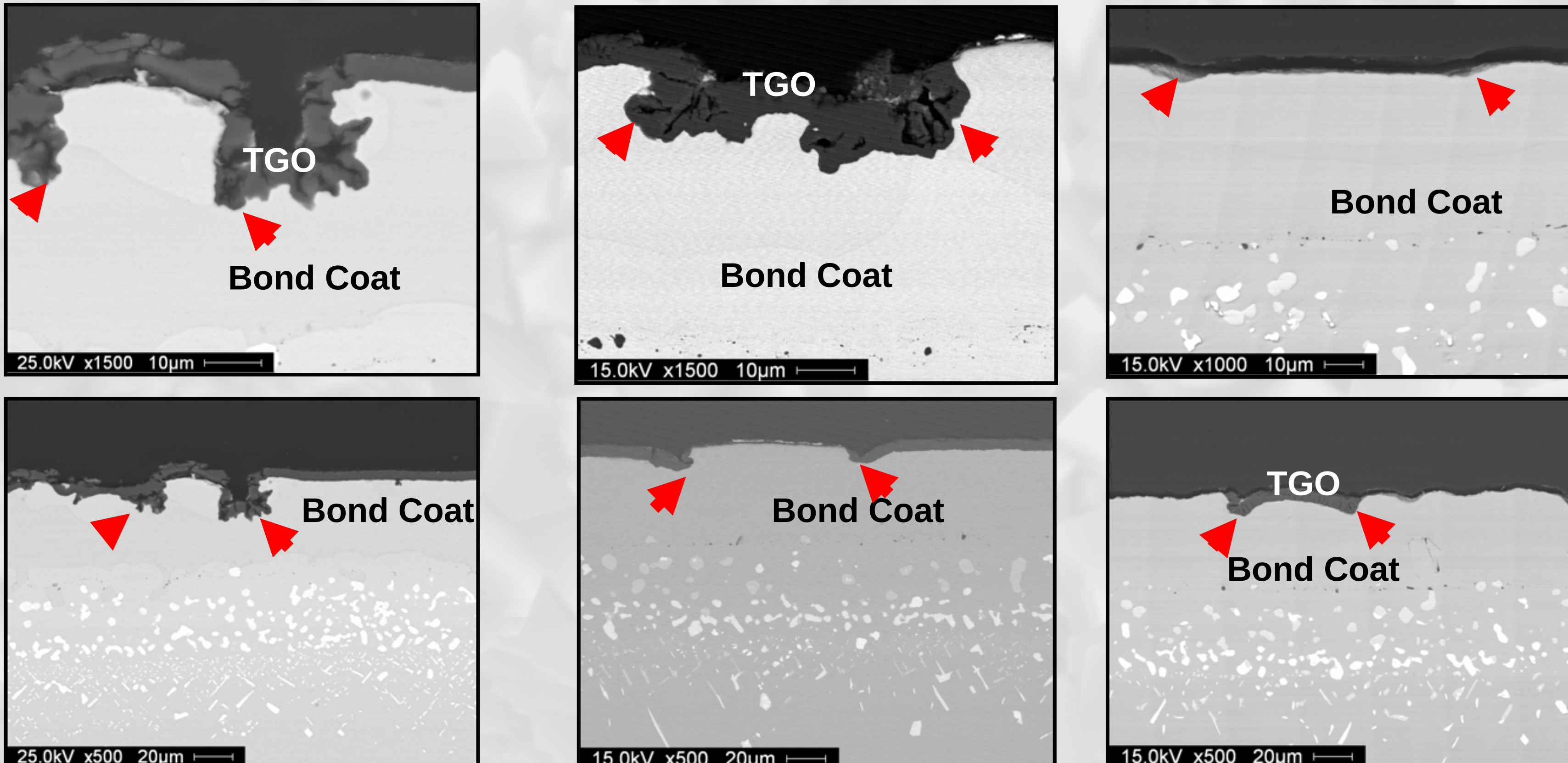




- **With an Increase in Dwell Time the Fracture Predominantly Occurs at the TGO/Bond coat Interface**
- **TGO with Mixed Oxide Zone (MOZ).**
- **Grain Boundary Ridges.**

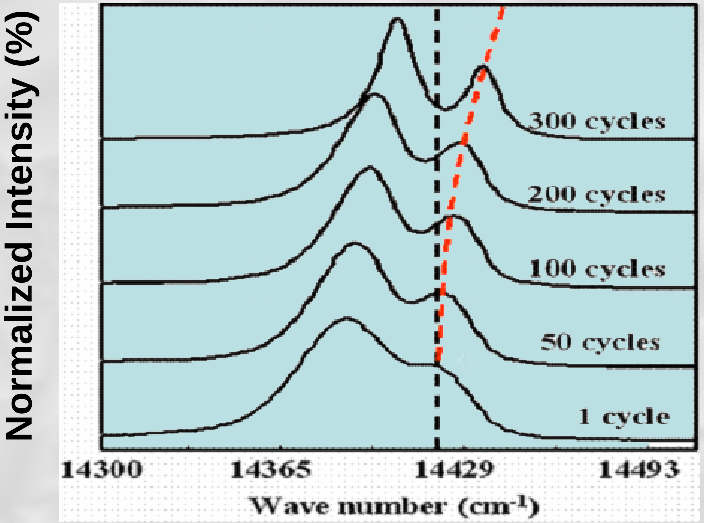
Cross-Sectional Microstructure
{Type II TBC: EB-PVD / As Coated (Ni,Pt)Al / CMSX-4}

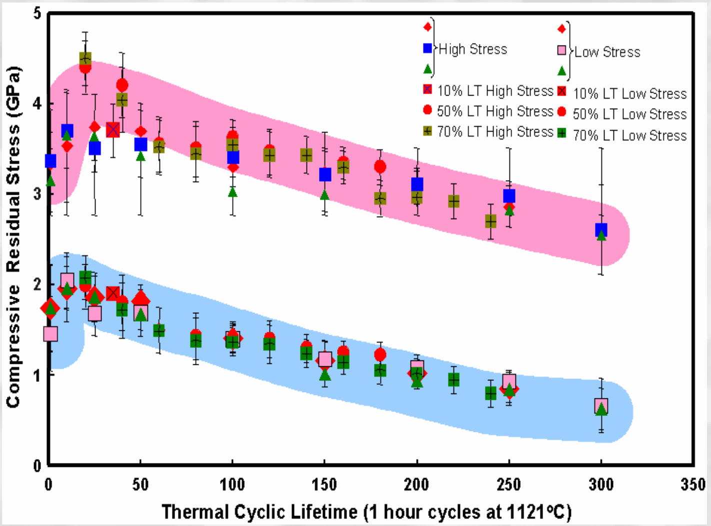
1-Hour Thermal Cycles (420 Cycles) | **10-Hour Thermal Cycles (55 Cycles)** | **50-Hour Thermal Cycles (12 Cycles)**

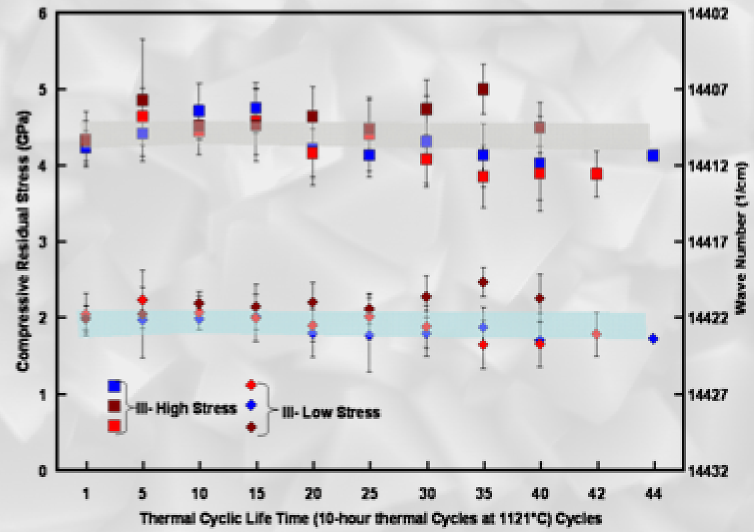


Preferential Oxidation of Grain Boundaries Occurs Significantly During 1-Hour Thermal Cycling, But Not during 10- and 50-Hour Thermal Cycling.

Compressive Residual Stress within the TGO with Stress Relaxation during Thermal Cycling {Type III TBC: EB-PVD / Grit-Blasted (Ni,Pt)Al / Rene'N5}



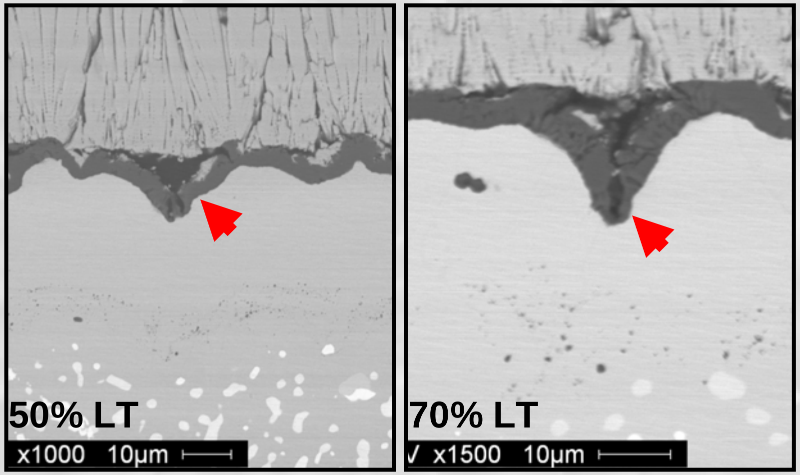




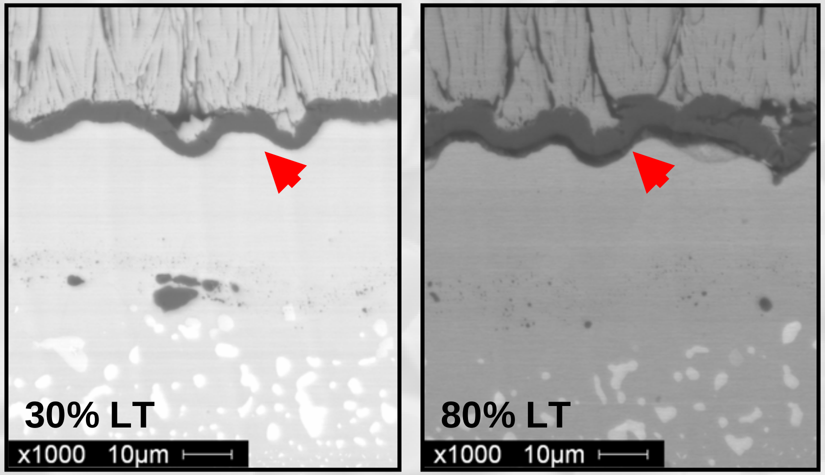
- **Gradual Decrease in the Magnitude of the Compressive Residual Stress in the TGO: Stress Relaxation Associated with Lengthening of TGO and Racheting of TGO/Bondcoat Interface.**
- **However, such a Relaxation was not Observed during 10- and 50-Hour Thermal Cycling.**

Microstructural Development During Thermal Cycling {Type III TBC: EB-PVD / Grit-Blasted (Ni,Pt)Al / Rene'N5}

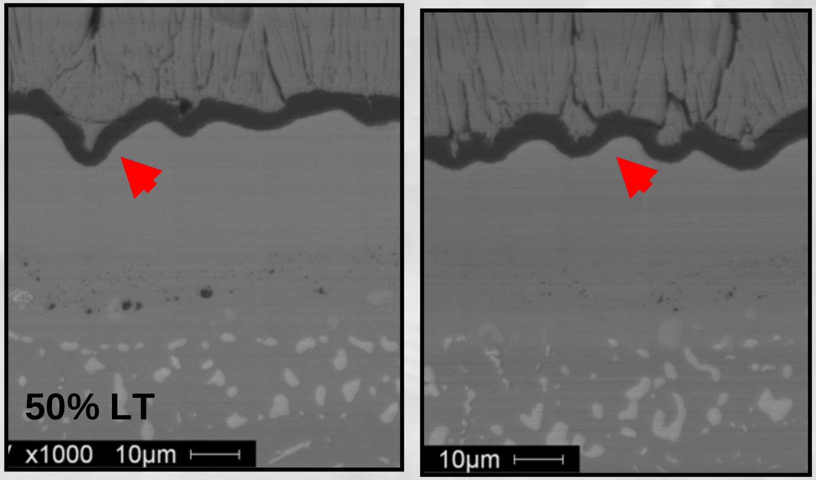
1-Hour Thermal Cycling



10-Hour Thermal Cycling



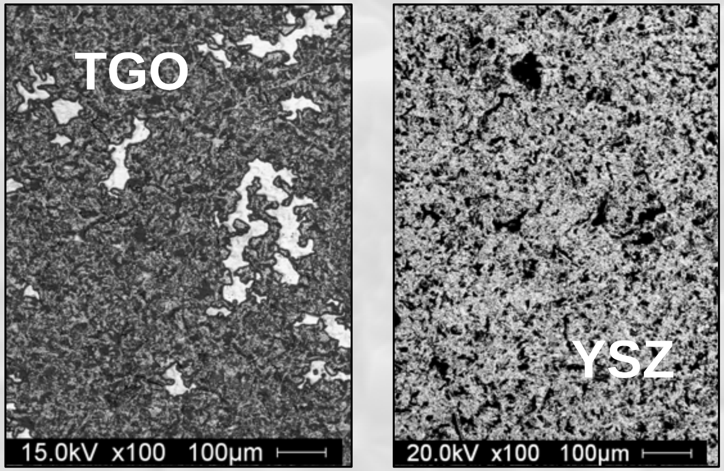
50-Hour Thermal Cycling



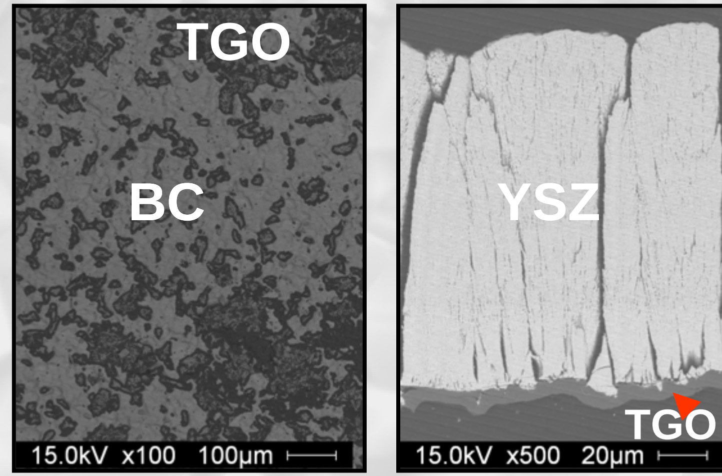
- **No Significant Evidence of Racheting at the TGO/Bondcoat Interface with Increase in Dwell Time.**
- **Limited Rumpling Observed during 10- and 50-Hour Thermal Cycling.**

Fractographic Characteristics of TBC Spallation {Type III TBC: EB-PVD / Grit-Blasted (Ni,Pt)Al / Rene'N5}

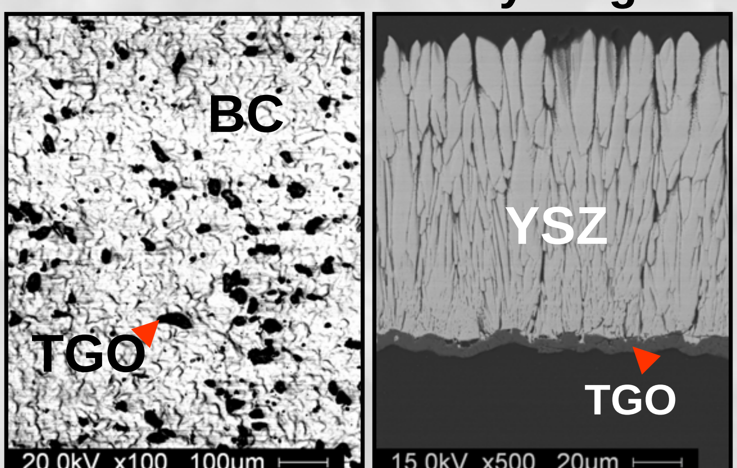
1-Hour Thermal Cycling



10-Hour Thermal Cycling



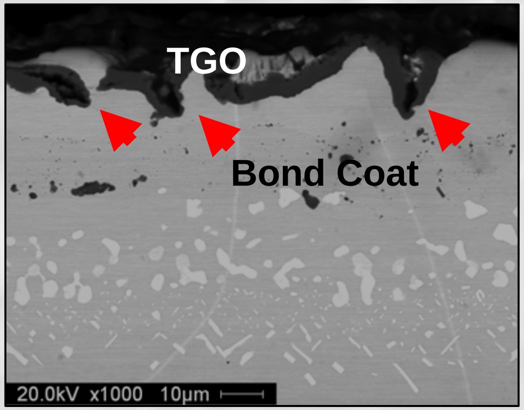
50- Hour Thermal Cycling

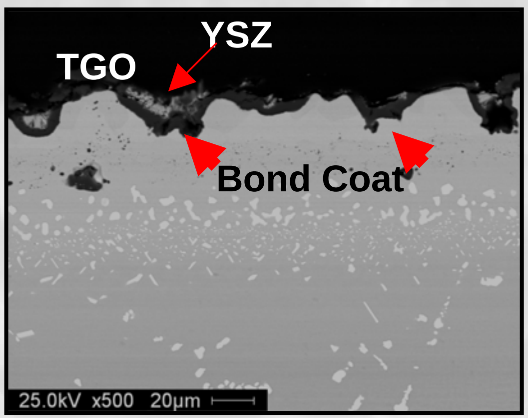


- **<u>1-Hour Thermal Cycling:</u> Fracture Mostly at the YSZ/TGO Interface; Little within the TGO and at the TGO/Bond Coat Interface.**
- **<u>10 and 50-Hour Thermal Cycling:</u> Fracture Mostly at the TGO/Bond Coat Interface; Little within the TGO and at the YSZ/TGO Interface.**

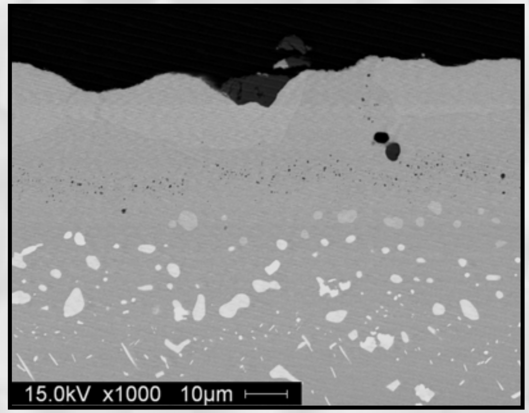
Cross-Sectional Microstructure from Failed TBCs {Type III TBC: EB-PVD / Grit-Blasted (Ni,Pt)Al / Rene'N5}

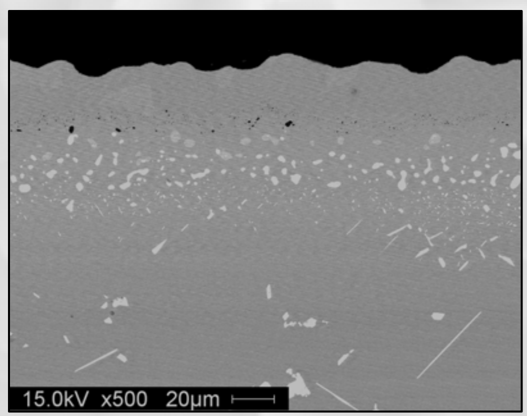
1-Hour Thermal Cycles (360 Cycles)



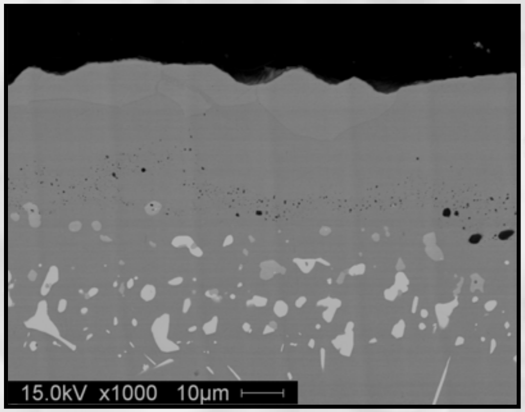


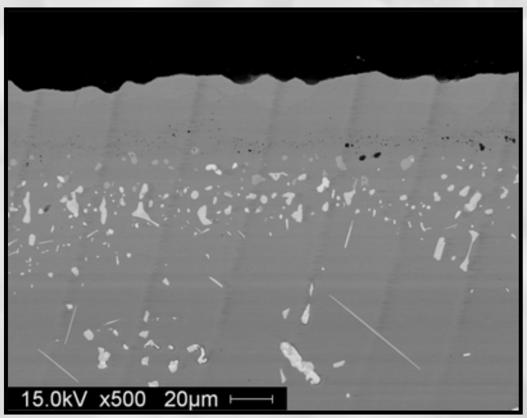
10-Hour Thermal Cycles (42 Cycles)





50-Hour Thermal Cycles (10 Cycles)

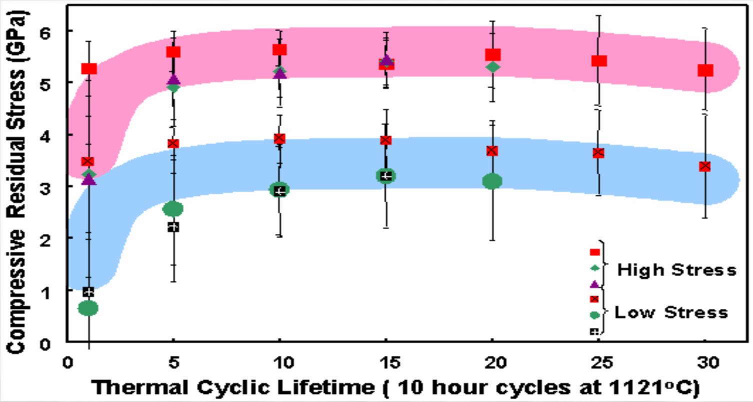


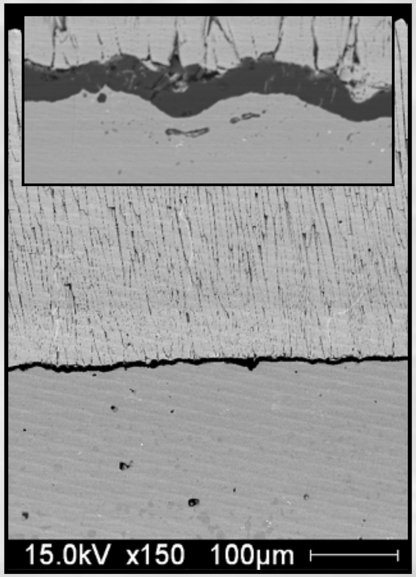


Fracture Mostly at the YSZ/TGO Interface; Racheting.

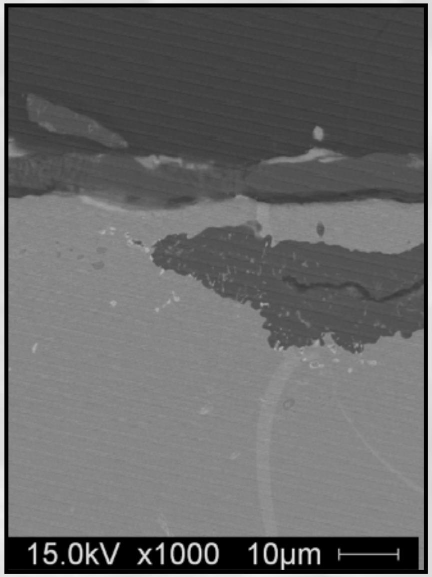
Fracture Mostly at the TGO/Bond Coat Interface; No Racheting, but Limited Rumpling.

PL and Microstructural Analysis of Type I TBCs (Type I TBC: EB-PVD / NiCoCrAlY / CM-247)





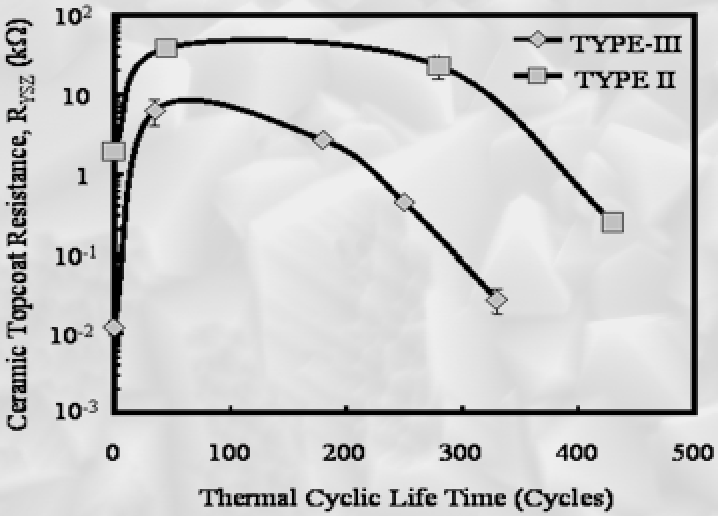
140 1-Hour Cycles

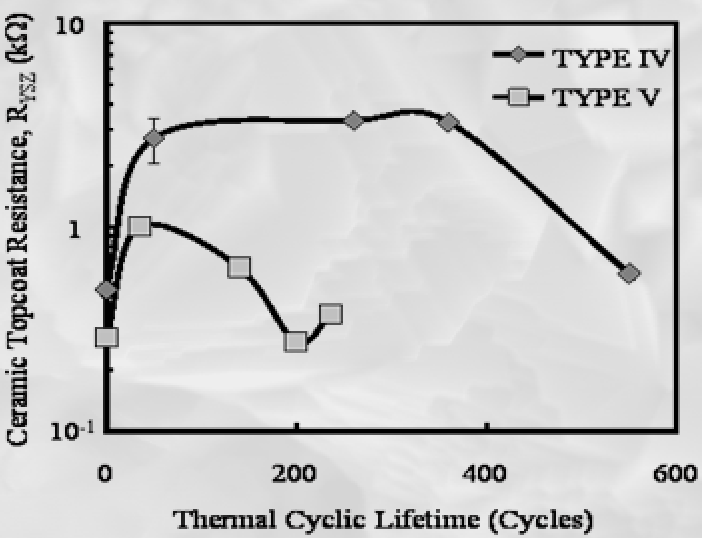


20 10-Hour Cycles

- **PL: The Magnitude of Compressive residual Stress/Standard Deviation Remains Relatively Constant Regardless of Dwell Time.**
- **Initial Increase in Compressive Residual Stress Potentially due to the Initial Development of the TGO.**
- **Short Lifetime Due to Internal Oxidation and Premature Formation of Spinel.**
- **Premature Failure Occurred at the YSZ/TGO Interface.**
- **Fracture Preferentially Occurred at the TGO/Bond Coat Interface with Longer Dwell Time.**

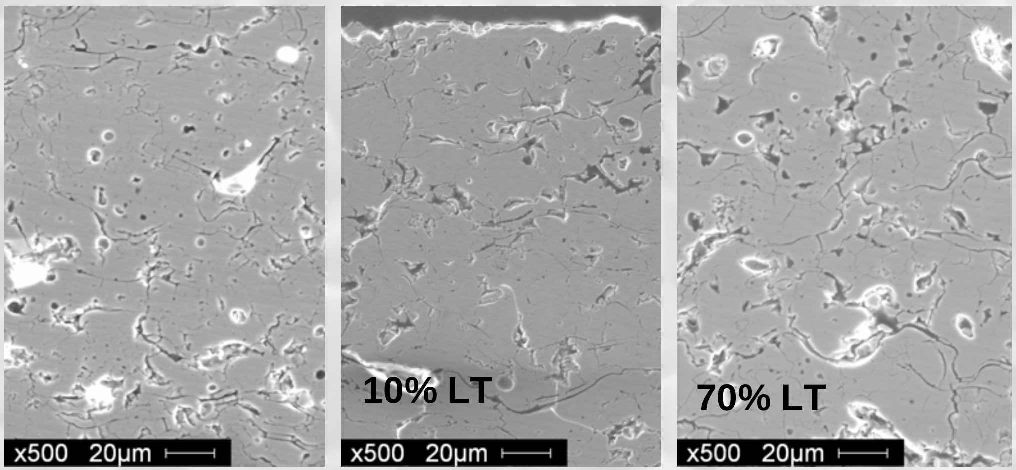
Evolution of EIS with Thermal Cycling of TBCs





Type-V; APS; As-Coated

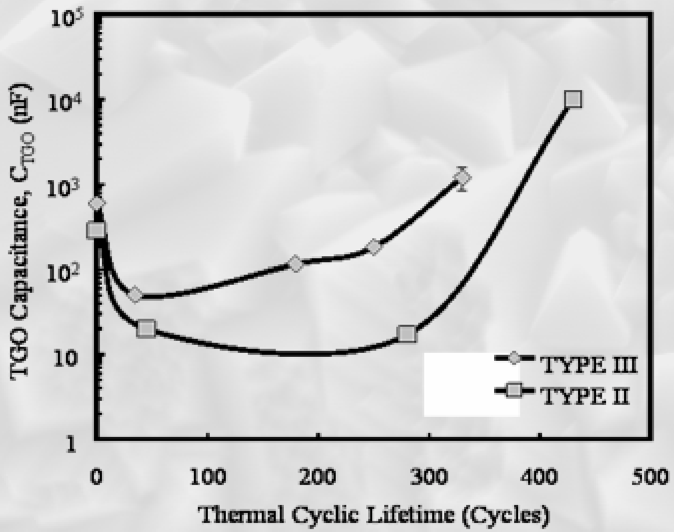
Type-V; APS; Thermally Cycled

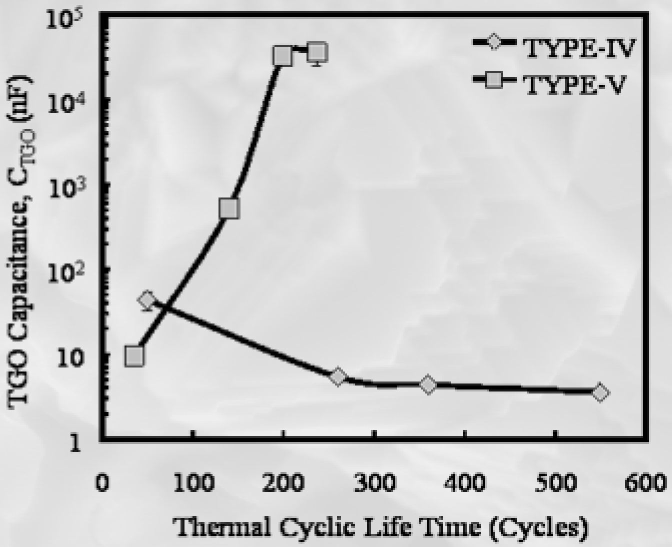


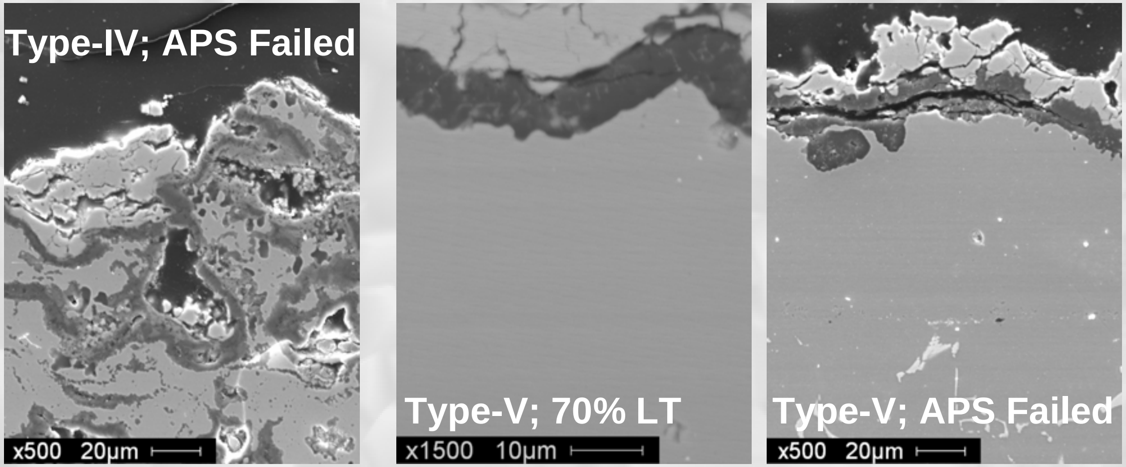
Sintering Initially Increase the R_{YSZ}, but a Gradual Decrease in R_{YSZ} is Observed with Further Thermal Exposure Due to YSZ Micro-cracking.

Jayaraj et al., JOM, in Press.
Byeon et al., MSEA, 407 (2005) 213.
Y.H. Sohn et al., JOM, 56 (2004) 53.
Jayaraj et al., MSEA, 372 (2004) 278.
Jayaraj et al., SCT, 177/78 (2004) 140.

Evolution of EIS with Thermal Cycling of TBCs







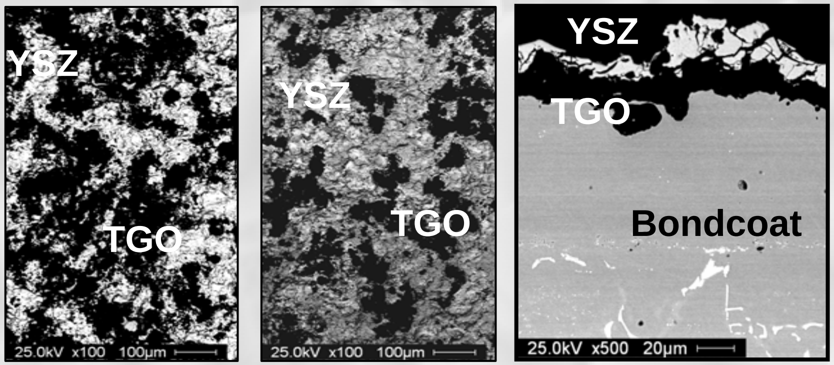
- Abrupt Increase in C_{TGO} was Not Observed When the Fracture Occurred with the YSZ Coating (No Bond Coat Surface Exposed) for Type IV APS TBCs (with Significant Internal Oxidation of APS NiCoCrAlY Bond Coat).

- A Continuous Increase in C_{TGO} was Observed with Progressive Microcracking in the TGO Scale for Type V APS TBCs.

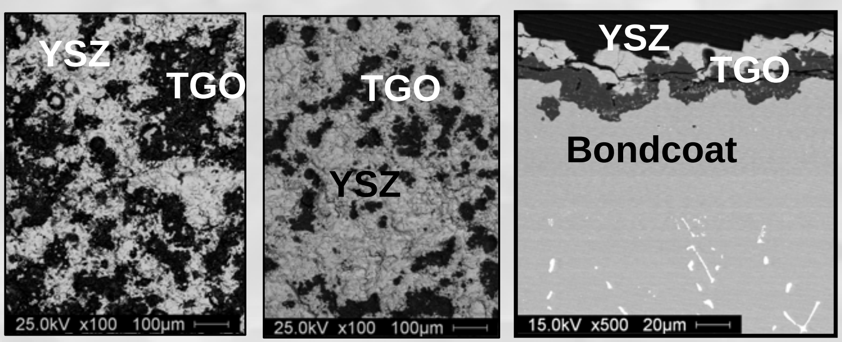
Jayaraj et al., JOM, in Press.; Byeon et al., MSEA, 407 (2005) 213.
Y.H. Sohn et al., JOM, 56 (2004) 53.
Jayaraj et al., MSEA, 372 (2004) 278.
Jayaraj et al., SCT, 177/78 (2004) 140.

Fractographic Characteristics of APS TBC

TYPE-V: APS TBCs with NiCoCrAlY Bond Coat and MAR-M509

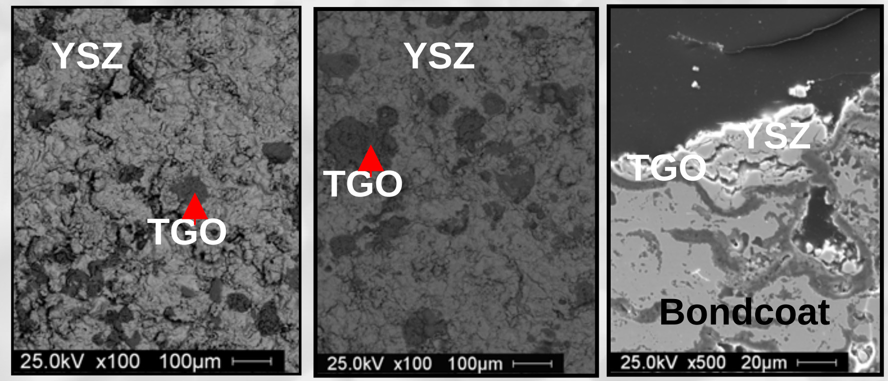


1-Hour Thermal Cycling

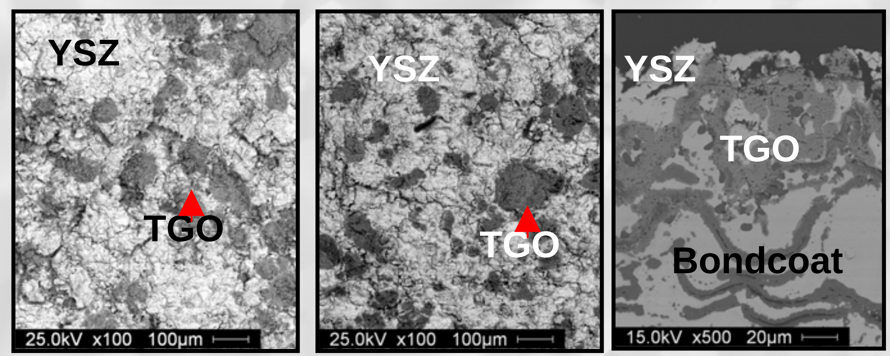


10-Hour Thermal Cycling

TYPE-IV: APS TBCs with APS NiCoCrAlY Bond Coat and HAYNES 230



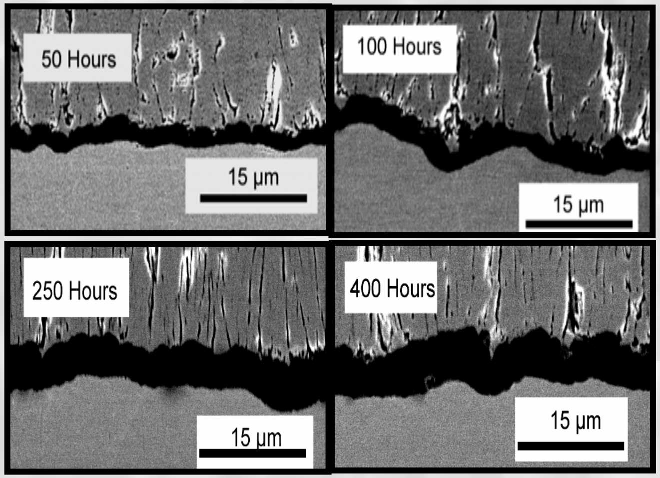
1-Hour Thermal Cycling

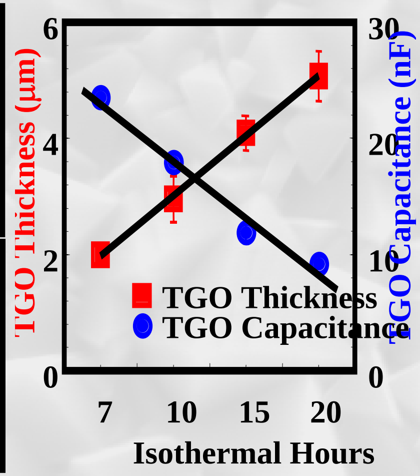


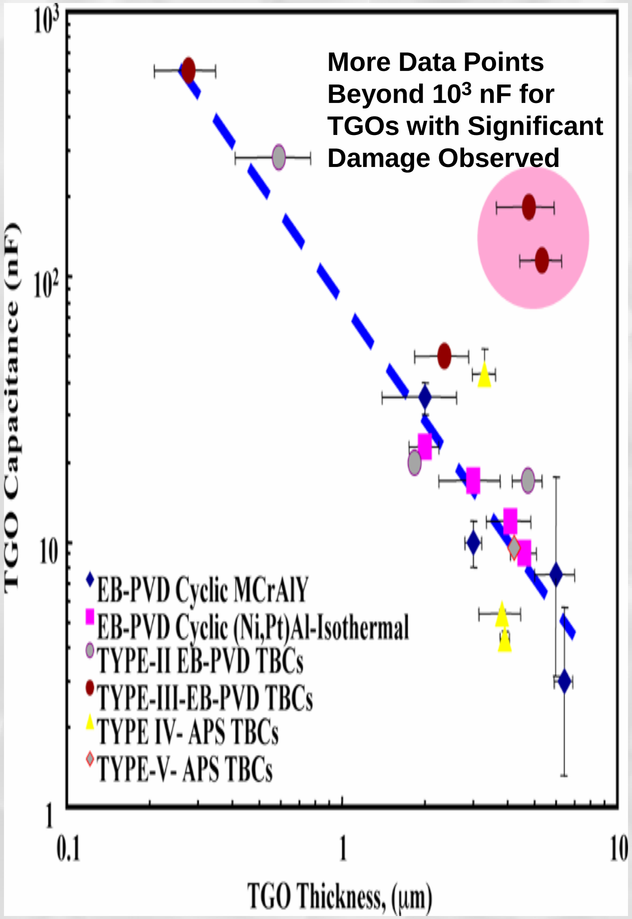
10-Hour Thermal Cycling

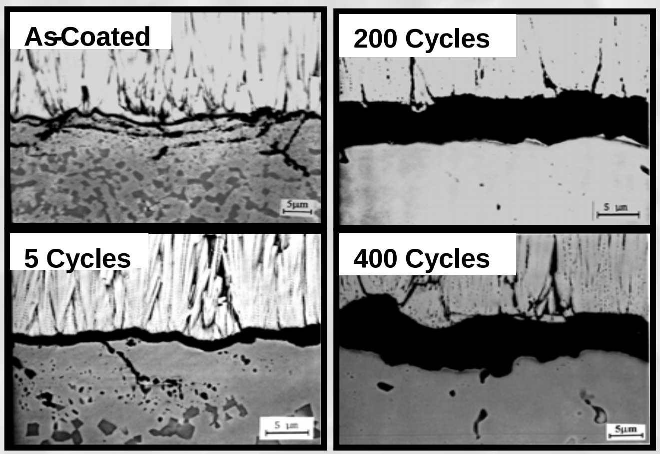
Fracture Within the YSZ and at the YSZ/TGO Interface for APS TBCs Regardless of Dwell Time.

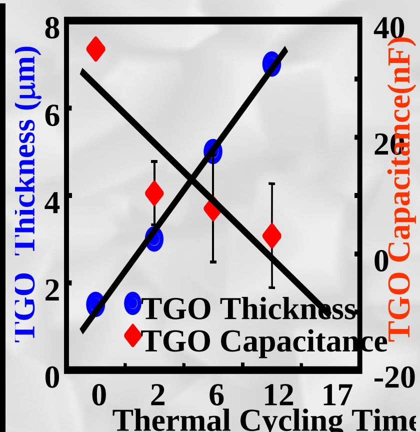
TGO Capacitance and TGO Thickness









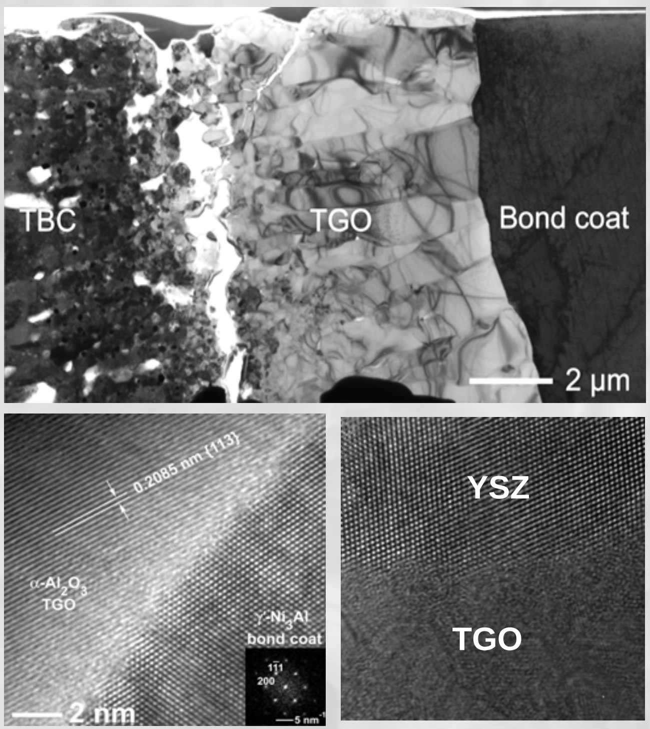


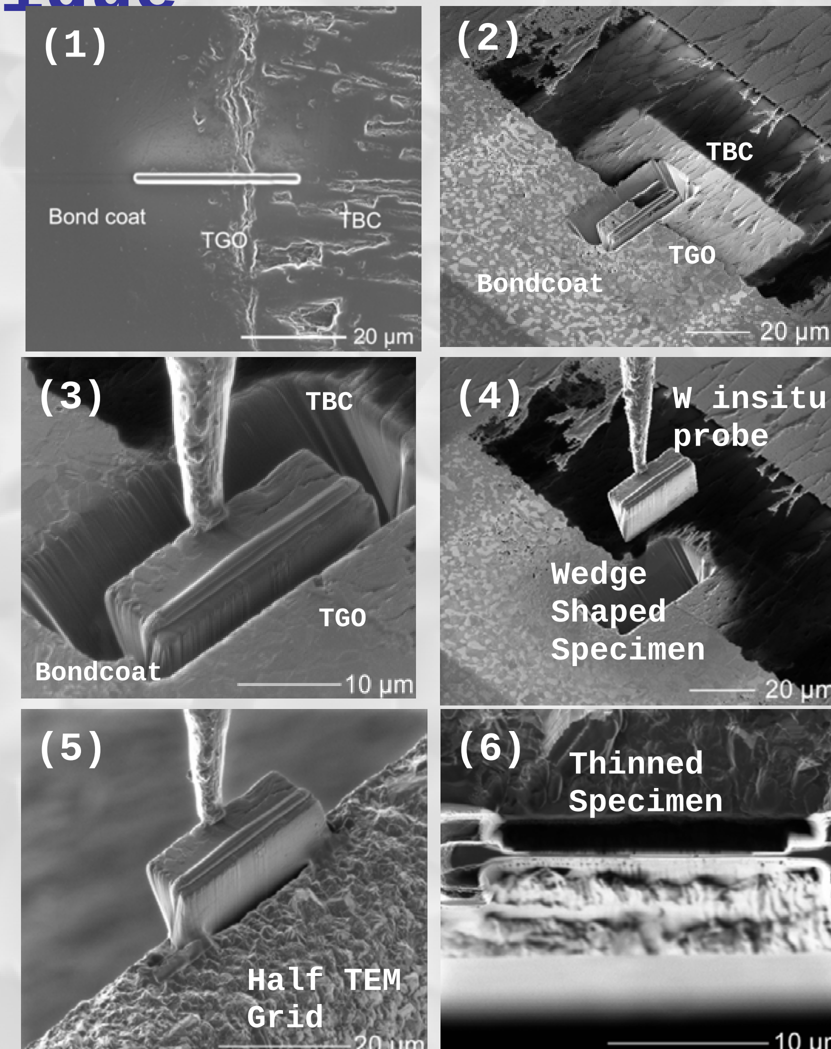
$$C = \varepsilon_V \bullet \varepsilon \frac{A}{t}$$

B. Jayaraj et al., Surface and Coatings Technology, 177/8 (2004) 140.
Y.H. Sohn et al., Journal of Metals, October (2004) 54.
B. Jayaraj et al., Materials Science and Engineering, A372 (2004) 278.
J. Byeon et al., Materials Science and Engineering A, in Press (2005).

TEM Specimen Preparation by Focused Ion Beam (FIB) In-Situ Lift-Out (INLO) Technique

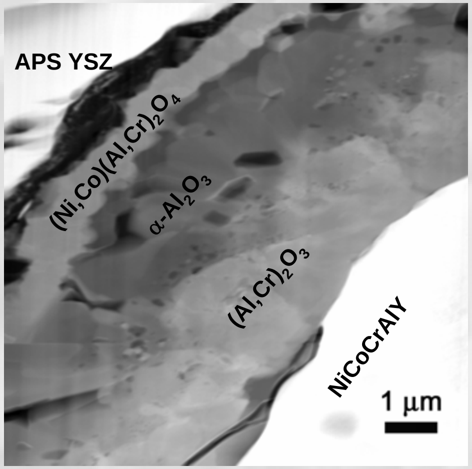
TBC Specimens for HR-STEM Investigation Can Be Prepared Routinely and Within 2~3 Hours Regardless of Thermal Cycling History (both As-Coated and Thermally Cycled).

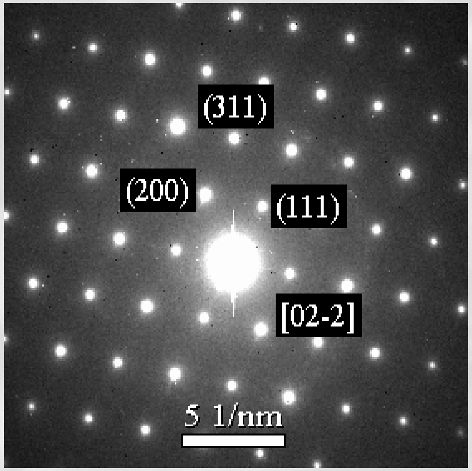




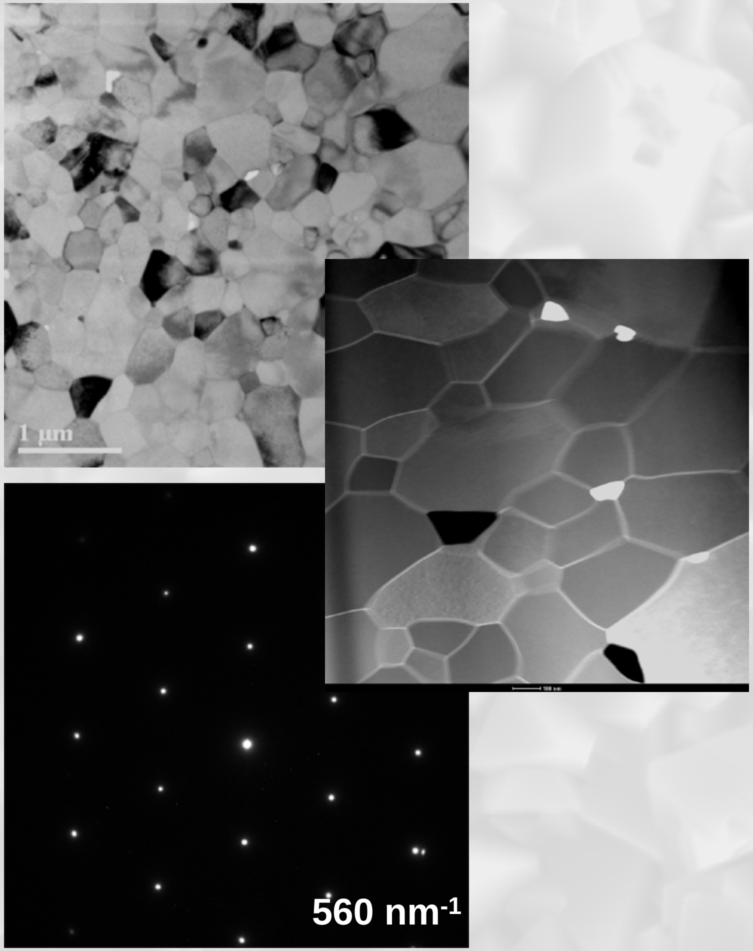
B. Kempshall et al., Thin Solid Films, 466 (2004) 128.

TEM/STEM on Thermally Cycled TBCs

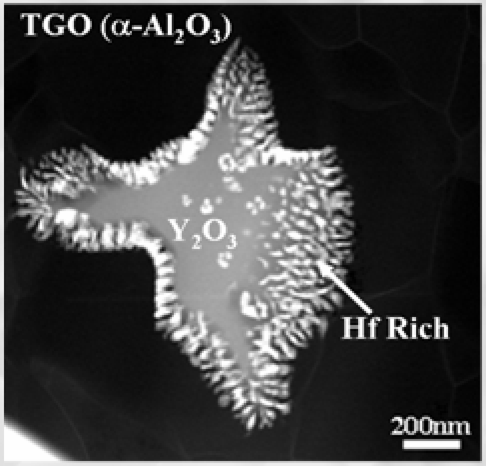


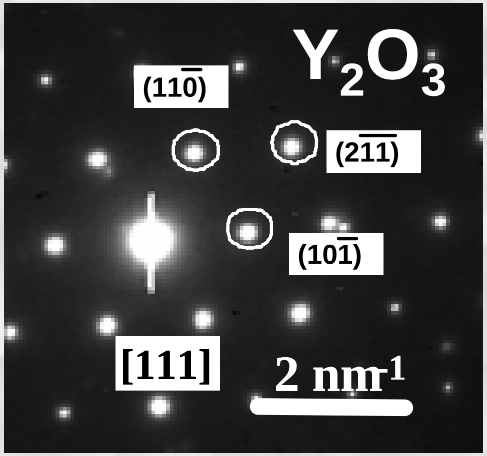


$(Ni,Co)(Al,Cr)_2O_4$ Oxide Layer Near the YSZ/TGO Interface with a Spinel Structure and Lattice Parameter of 8.0317Å.



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

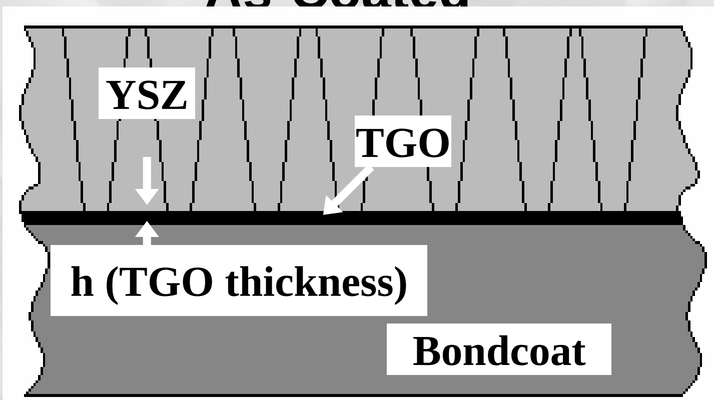




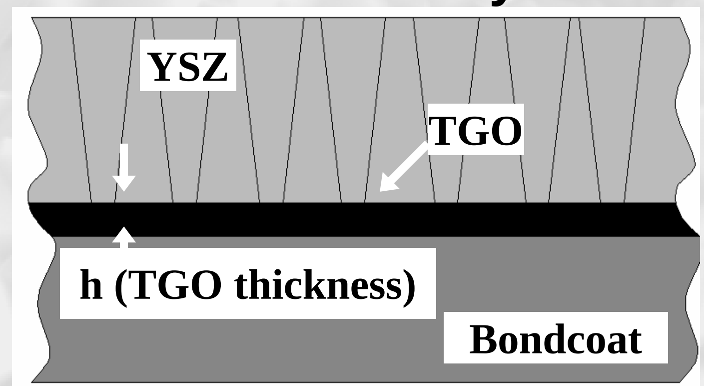
Oxide Stringers Observed as Y_2O_3 on Several TBC Specimens of Different NiCoCrAlY Bond Coats.

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

As-Coated



After Thermal Cycles



TGO Thickness → **Strain Energy Release Rate (G)** / **Buckling Tendency ($\prod$)**

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

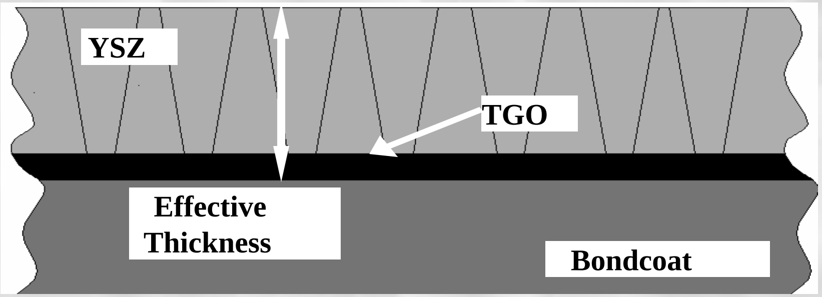
$$\Pi = (1-\upsilon^2)\left(\frac{\sigma_0}{E_0}\right)\left(\frac{b}{h}\right)^2 \; *$$

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); ∏ = Buckling Index; b = Crack Width.

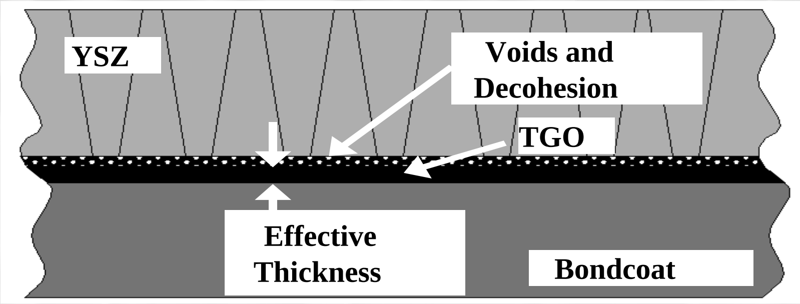
A.G.Evans et al, Progress in Materials Science 46 (2001) 505-553; M.C.Shaw Design of Power Electronics Reliability.

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

Situation I



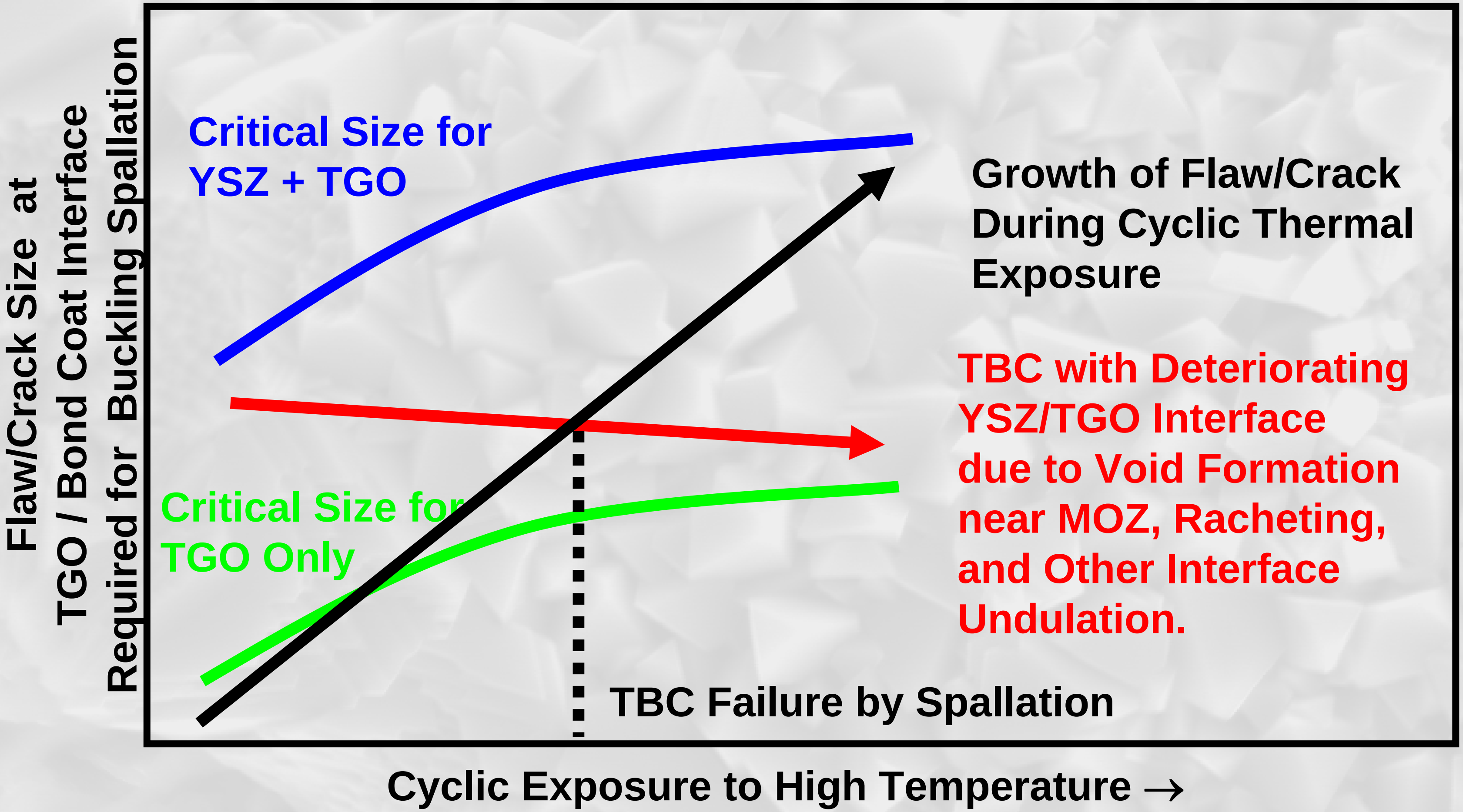
Situation II



Situation	TGO/YSZ Interface or TGO Near YSZ	Effective Thickness for Resisting Buckling	Strain Energy Release Rate (G)	Buckling Tendency (∏)	Results
I	Good	YSZ + TGO	Similar	Low	Difficult to Fail
II	Flawed	TGO + Partially YSZ		High	Easy to Fail

- The Thickness Governing the Buckling Failure May Include that of TGO and YSZ Combined.
- The Microstructure at or near the YSZ/TGO Interface May Play a Significant Role in Thermo-Mechanical Behavior of Thermal Barrier Coatings During Thermal Cycling.

Buckling Failure Mechanisms of TBCs*
(Incorporating SEM/TEM/STEM Observations)



**Y.H. Sohn, B. Jayaraj, S. Laxman, B. Franke, J. Byeon, A.M. Karlsson, Journal of Metals, October (2004) 54.*

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.

Related Highlights From This Program

- 9 Journal Publications (A Few More Coming) and 9 Conference Proceedings.
- 7 Invited Presentations including at ACERS, AVS-ICMCTF, TMS, ASM, ORNL and NIST and 27 Presentations .

- Supported 2 M.S. and 1 Ph.D.:
  - Ms. Barb Franke: Now with Solar Turbines.
  - Mr. Sankar Laxman: Now with Vasologen.
  - Mr. Balaji Jayaraj: Ph.D. Expected in April, 2006.

- Several UG Research Assistants including:
  - Mr. Chris Petorak, Now with Purdue for Ph.D.
  - Ms. Barb Franke, Now with Solar after MS at UCF.
- UTSR Summer Fellows:
  - Ms. Barb Franke, 2003 (Solar) & 2004 (Solar), Now with Solar.
  - Mr. Manny Perez, 2004 (E-M) & 2005 (GE), Now at UCF for Ph.D.
  - Mr. Travis Patterson, 2005 (SPC), Committed for Ph.D. at UCF.
- UCF’s M.S. Thesis of 2004 by Mr. Balaji Jayaraj.
- UCF’s Distinguished Researcher Award by Sohn, 2005.
- Significant Additional Interaction with IRB Members Through Research Contracts and Collaborations.