ORNL Thermal Barrier Coatings

TBC Research Activities Conducted Under The Materials/Manufacturing Program

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COGENERATION

Advanced Turbine Systems
Annual Review
1999

Several Materials Issues are Addressed in the Materials & Manufacturing Element

- **ATS prime contractors are responsible for the TBC technology needed for the demonstration projects**

- **Materials & Manufacturing element addresses materials issues raised by the longer-term goals**
  - **needs were identified and prioritized in collaboration with GT manufacturers and suppliers (M&M Plan, April 1994; needs assessment was revised Dec. 1996):**

1) coatings and process development	5) turbine airfoil development
2) SC airfoil manufacturing technology	6) ceramics development
3) materials characterization	7) catalytic combustor development
4) technology information exchange	

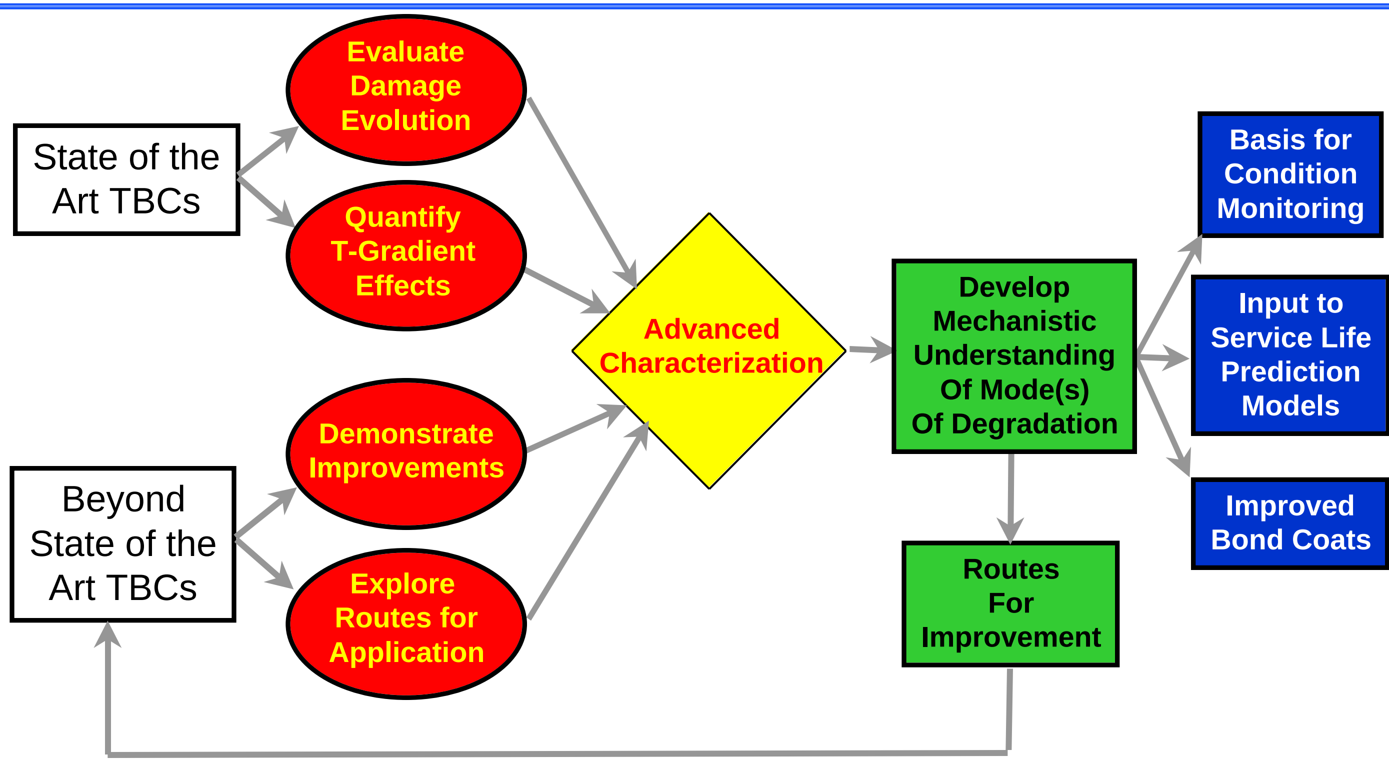
M/M Activities Include Both Subcontractor and In-House Programs

- Coatings and process development
  - Siemens Westinghouse Power Generation (SW): TBC development
  - Pratt & Whitney(PW): TBC development

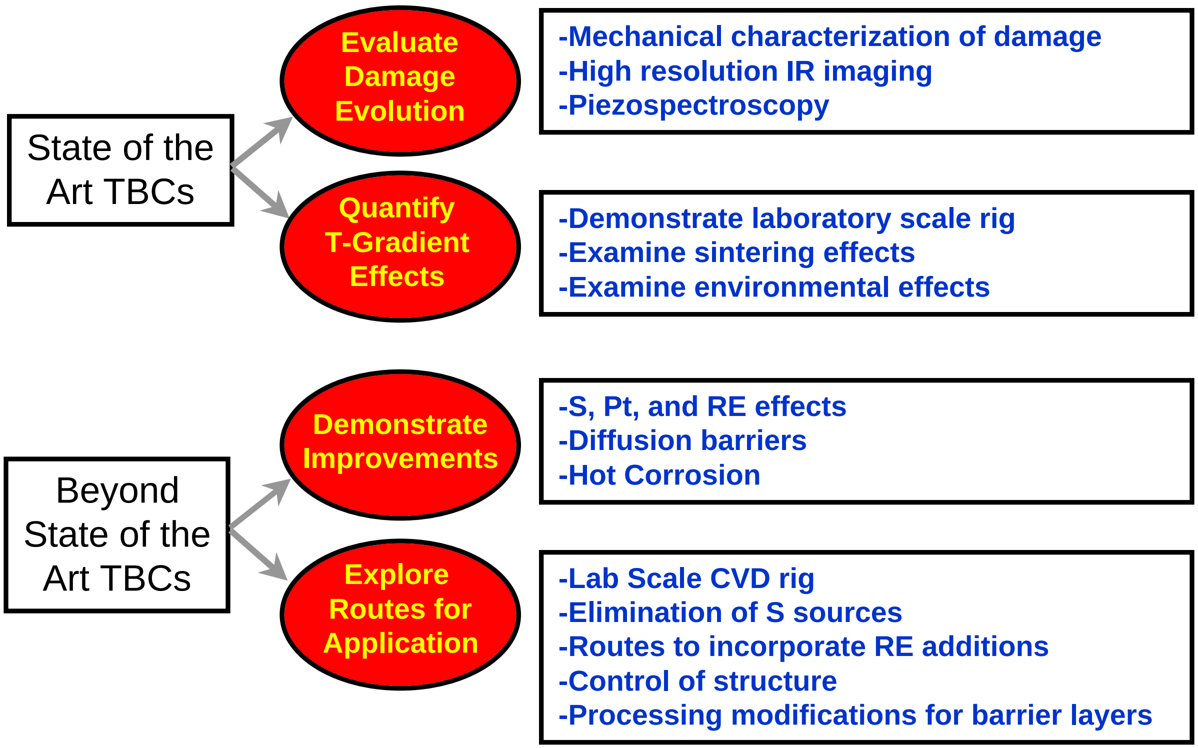
- Ceramics development
  - Solar Turbines: CMC combustor liners, ceramic vanes
  - Rolls-Royce Allison: ceramic vanes

- Materials characterization efforts mostly involve National Laboratories and universities (SCIES program)

ORNL's Overall Effort in TBCs



Key Issues


State of the Art TBCs
Evaluate Damage Evolution
-Mechanical characterization of damage
-High resolution IR imaging
-Piezospectroscopy
Quantify T-Gradient Effects
-Demonstrate laboratory scale rig
-Examine sintering effects
-Examine environmental effects
Beyond State of the Art TBCs
Demonstrate Improvements
-S, Pt, and RE effects
-Diffusion barriers
-Hot Corrosion
Explore Routes for Application
-Lab Scale CVD rig
-Elimination of S sources
-Routes to incorporate RE additions
-Control of structure
-Processing modifications for barrier layers

Three Technical Projects of the ATS Materials/Manufacturing Program Deal Specifically With Thermal Barrier Coating (TBC) Systems

- **Optimization of Bond Coating Alloys**
  - **Demonstrate Improvement in the High-Temperature Oxidation Lifetime of Bond Coating Alloys Possible Through the Incorporation of Alloy Composition and Structure Modifications**
  - **Translate These Improvements Into Practical Bond Coatings**

- **CVD Bond Coat Development Project**
  - **Examining Effects of Sulfur Impurities and Pt Additions on the Cyclic Oxidation Behavior of Low-sulfur Superalloys Coated With State-of-the-art NiAl and NiPtAl Bond Coatings Prepared by Chemical Vapor Deposition (CVD)**

- **TBC Characterization**
  - **Develop and Apply State-of-the-Art Characterization Techniques to the Evaluation of the Mechanical and Thermal Reliability of Thermal Barrier Coatings**

TBC Characterization Task Addresses Several Issues

- **What are the common failure modes?**
  - **Interplay between oxidation and thermally induced stresses**
  - **Role of bond coat chemistry**
  - **PVD versus APS coatings**

- **How does this damage influence properties (elastic modulus, thermal conductivity, residual stress, thermal expansion)?**

- **How is damage evolution influenced by exposure technique?**
  - **Isothermal aging versus thermal cycling**
  - **Thermal gradient testing**
  - **Mechanical loading**
  - **Thermal-mechanical loading**

The Current TBC Characterization Task Consists of Four Efforts

- **Characterization of Residual Stresses in TBC Systems**
- **Thermophysical Properties and Thermal NDE of Thermal Barrier Coatings**
- **Failure Mechanisms in Thermal Barrier Coatings**
- **Development of a Thermal Gradient Test Facility**

Current Projects Draw Heavily Upon Industrial and University Interactions

Materials
Manufacturing
Program

HTML User Projects
ATS Fellowship
MOU
CRADAs
WFO
Joint Proposals
Funded Research

General Electric
Siemens-Westinghouse
Solar Turbines
Pratt & Whitney UTRC
Rolls Royce Allison
Stoneybrook

Remainder of the Presentation will Highlight Several Activities

- **Optimization of Bond Coating Alloys**
- **CVD Bond Coat Development Task**
- **Characterization Task**
  - **Failure Mechanisms**
  - **Residual Stresses in TBC Systems**
  - **Development of a Thermal Gradient Test Facility**

Optimization of Bond Coating Alloys

Key Elements of Task

- **Objective**
  - Define the requirements of the bond coating alloy to enable it to form an 'ideal' alumina scale
  - Demonstrate the potential benefits on coating lifetime, using model alloy systems to investigate effects of composition and structure
  - Provide guidance to the complementary CVD coating development project

- **Approach**
  - Incorporation and distribution of the optimum amount of the specific reactive element
  - Minimization of the level of tramp sulfur in the coating (and superalloy substrate)
  - Additions of precious metals such as Pt and Rh, and the incorporation of diffusion barriers

Demonstrate Improvements Possible Over SOA

- **Quantification of Reactive Element Effects**
  - It has been demonstrated that Hf is the most potent reactive element addition to aluminide-type bond coat alloys
    - promotes an exclusively alumina scale
    - growth rate 10x slower than the previous 'ideal' alumina-forming alloy
    - exceptional resistance to scale spallation

    Next step is to define the limiting lower Al level where Hf can no longer help cyclic oxidation performance at 1100°C
- **Role of Precious Metals**
  - (Ni,Pt)Al is one of the best performing bond coats available, but the role of Pt is not understood
    - need for a mechanistic explanation for the role of precious metals

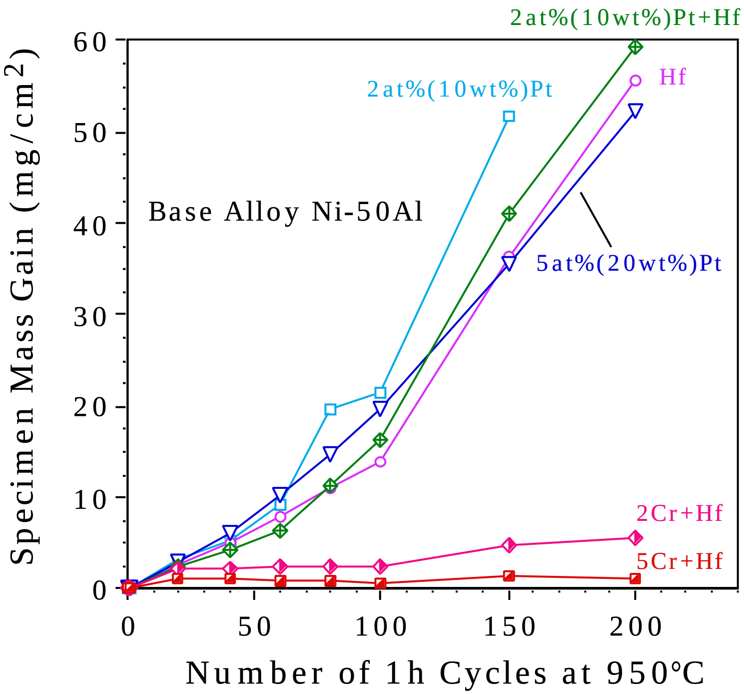
    Need to determine the effects of precious metal additions on factors affecting oxide growth and structure
    - location of the precious metals with respect to the metal-oxide interface
    - incorporation into the scale
    - effects on interface morphology and alumina phase transformation

Demonstrate Improvements Possible Over SOA

- **Influence of Small Additions of Cr on Hot Corrosion Resistance**
  - The aluminide bond coat alloys that demonstrate maximum resistance to high-temperature oxidation have been shown to be very susceptible to hot corrosion
    - › the only elemental addition found to improve hot corrosion resistance is Cr.
    - › when Cr is added at the levels attained in diffusion-processed bond coats, the hot corrosion resistance is improved, but
    - › *the scale spallation behavior in oxidation is degraded*

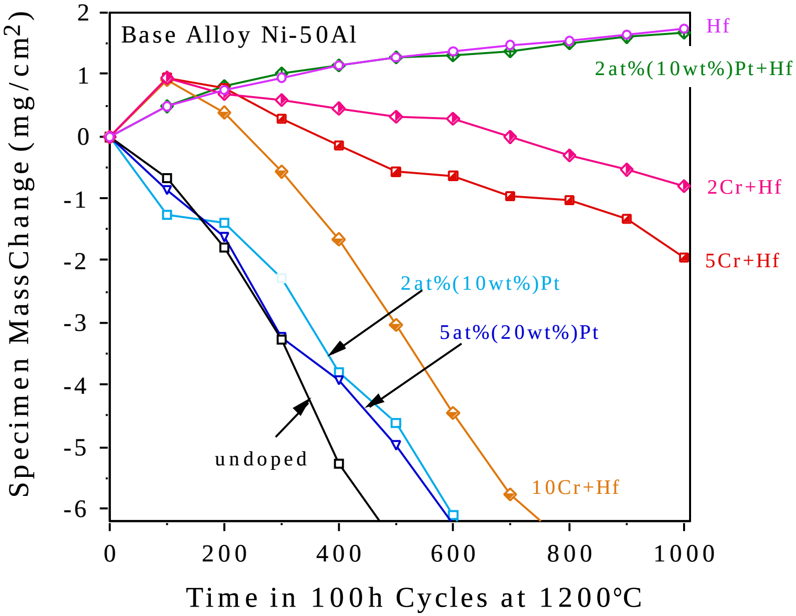
  The next effort will determine the minimum Cr levels to provide hot corrosion resistance (950°C), and their effects on high-temperature oxidation (1100-1200°C)

Cr (not Pt) controls hot corrosion resistance



NiAl is strongly attacked by Na2SO4 at 950°C. Additions of Hf or Pt do not alter behavior. Cr additions have a strong beneficial effect (commercial coatings contain approx. 5at%Cr).

Problem with Cr additions at higher temperatures



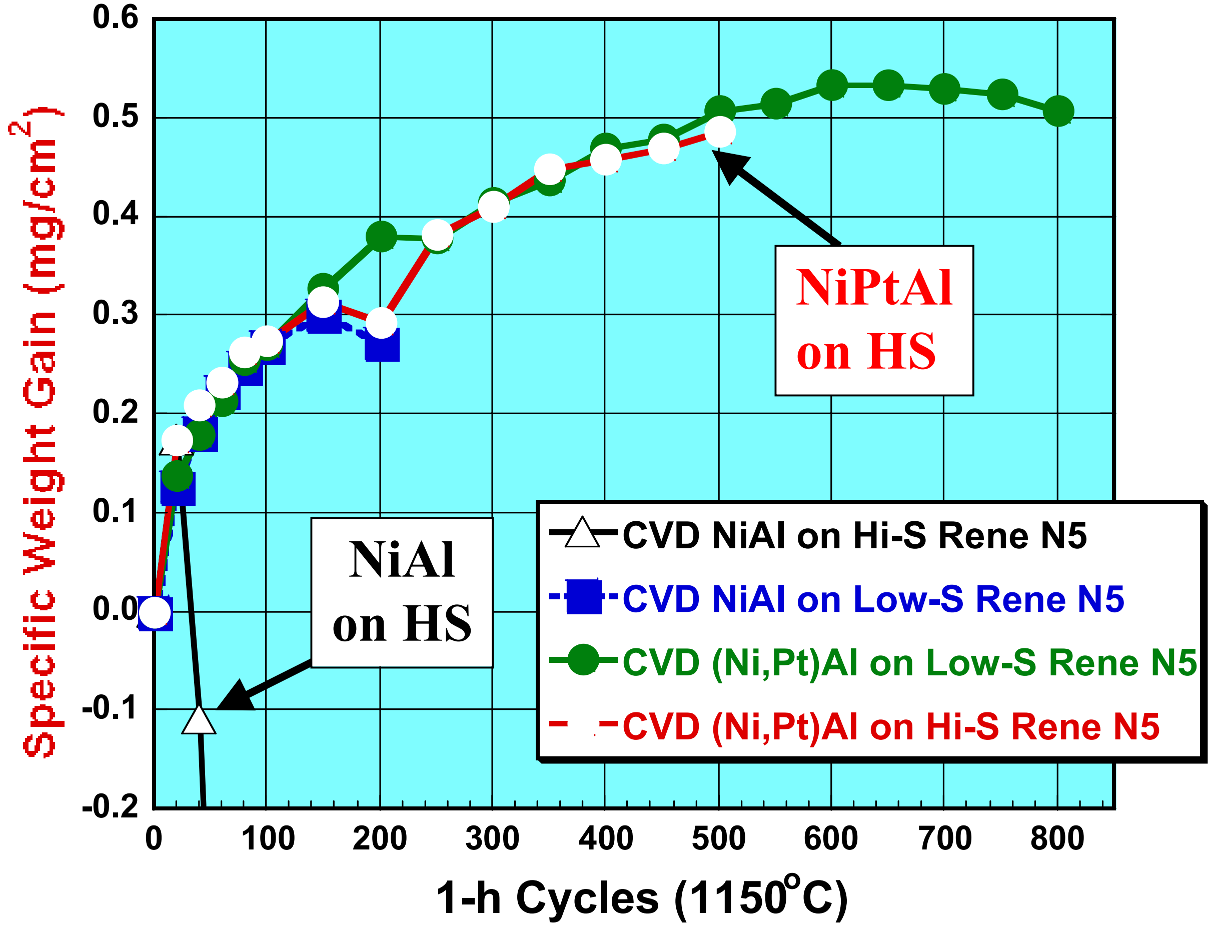
Hf-doped NiAl shows virtually no spallation. When co-doped with Cr, significant spallation occurs (commercial coatings contain approx. 5at%Cr). For these conditions, Pt shows no effect.

CVD Bond Coat Development Task

Key Elements of Bond Coat Task

- **Objectives**
  - **Develop and demonstrate coating design strategies for significantly improving protective oxide scale adherence to CVD aluminide bond coatings.**
  - **Investigate the influences of sulfur impurities and Pt alloying additions on the cyclic oxidation behavior of single-crystal superalloys coated with chemical vapor deposition (CVD) single-phase NiAl and NiPtAl.**
- **Approach**
  - **Single-phase CVD NiAl and NiPtAl coatings were fabricated on both high-sulfur and low-sulfur single-crystal superalloy substrates using the low-sulfur CVD reactor at ORNL.**
  - **Coatings were evaluated by isothermal and cyclic oxidation testing at 1150oC, combined with extensive characterization.**
  - **Recent efforts have focused on understanding and demonstrating the effects of Pt additions on coating oxidation behavior.**

Pt effectively mitigates the detrimental influence of S impurities on Al2O3 adherence



Bare CVD NiAl & (Ni,Pt)Al on Rene N5

HS = high sulfur
LS = low sulfur

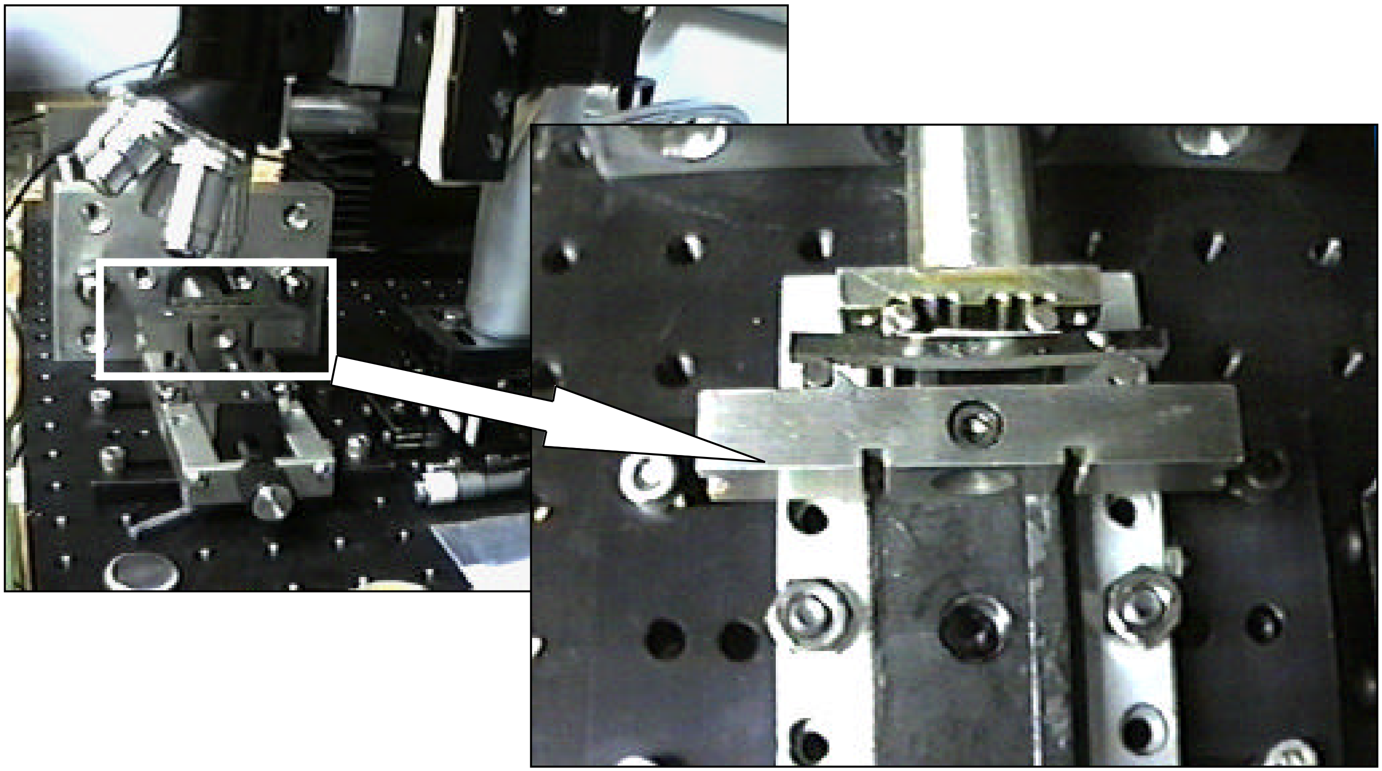
- **CVD NiAl on a high-sulfur superalloy experienced rapid and severe spallation of the protective oxide scale during oxidation testing.**
- **In contrast, CVD (Ni,Pt)Al coatings on the same superalloy have exhibited excellent scale adherence (testing still continuing).**

Results: Influence of Pt on CVD aluminide bond coat oxidation behavior

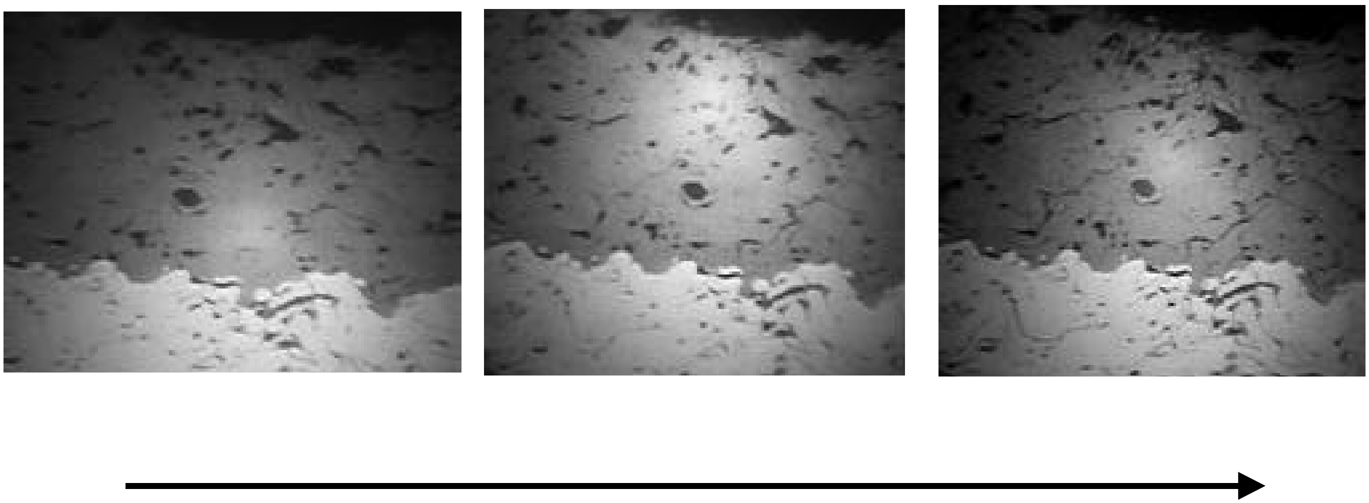
- **Based on the results of extensive oxidation testing, compositional analysis, and microstructural characterization of CVD NiAl and NiPtAl, it was concluded that Pt additions did not:**
  - **Reduce oxide scale growth rates or behave as a reactive element.**
  - **Prevent or reduce diffusion of alloying elements from the substrate.**
  - **Prevent coating surface deformation.**
- **Pt additions did appear to:**
  - **Dramatically improve oxide adherence on both low-sulfur and high-sulfur substrates.**
  - **Mitigate the detrimental effects of significant levels of sulfur impurities.**
  - **Eliminate void growth at the oxide-metal interface, especially at bond coating grain boundaries.**

Failure Mechanisms

Mechanical Testing is being used to Study Compressive TBC Failure

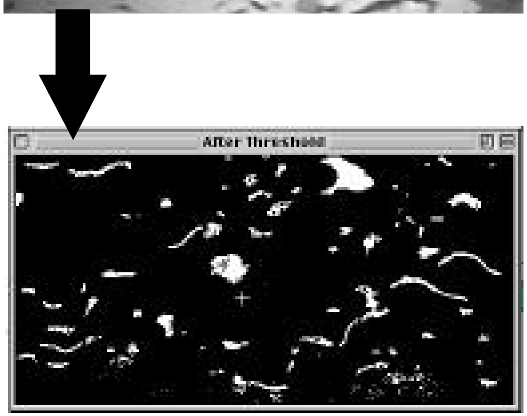


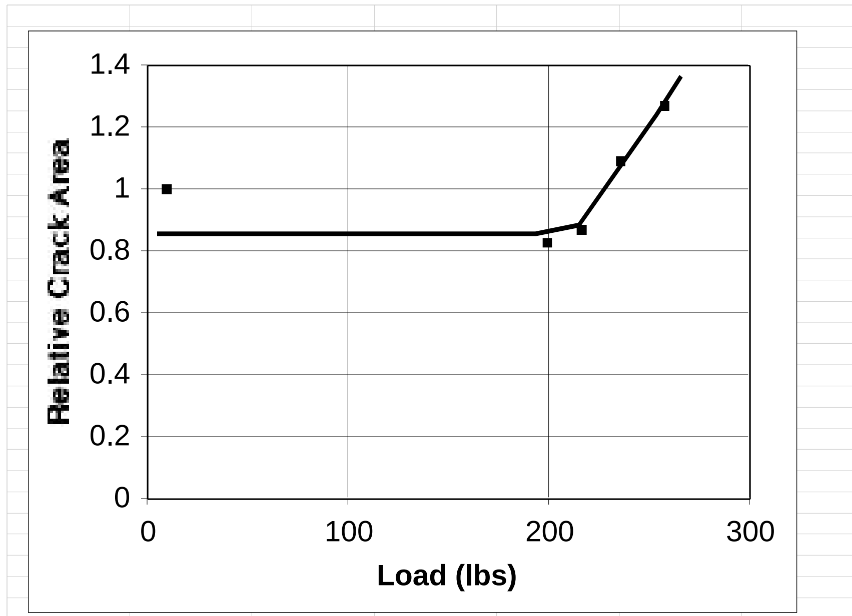
TBC Fracture Experiment-Results



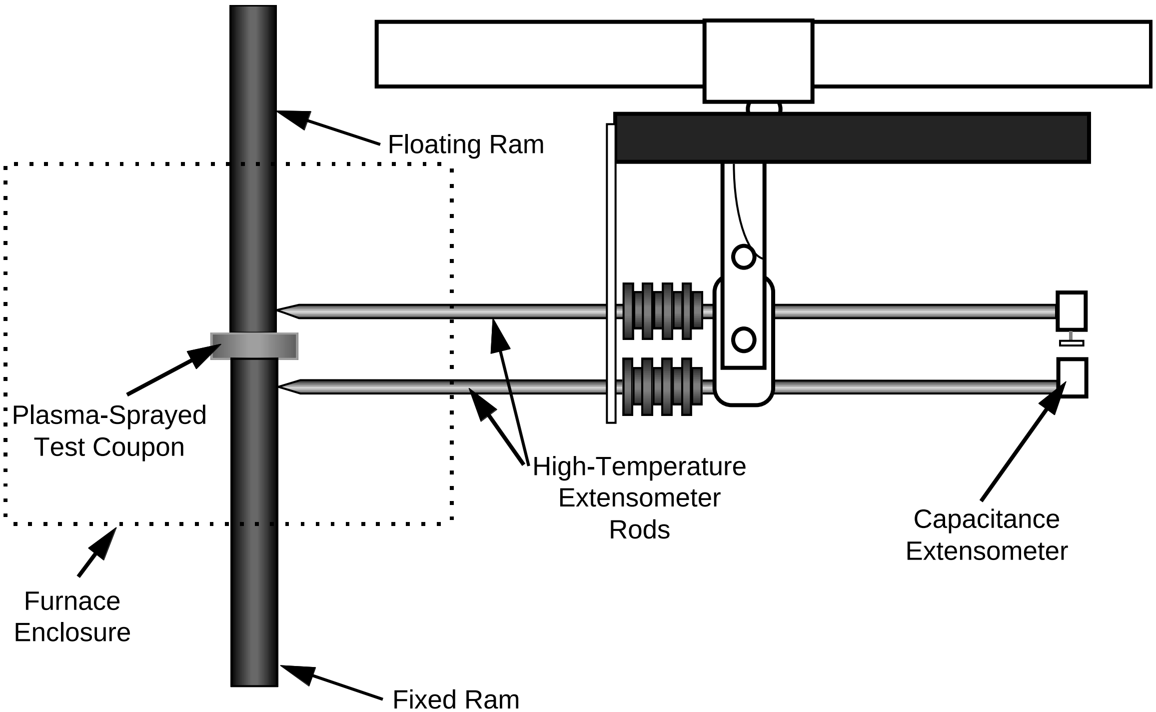
Increasing Compressive Load

TBC Fracture Experiment-Analysis

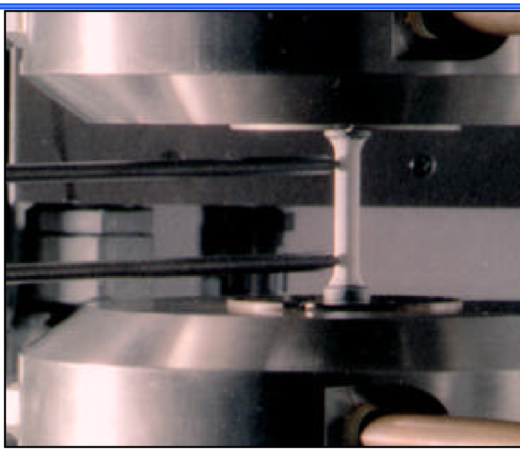


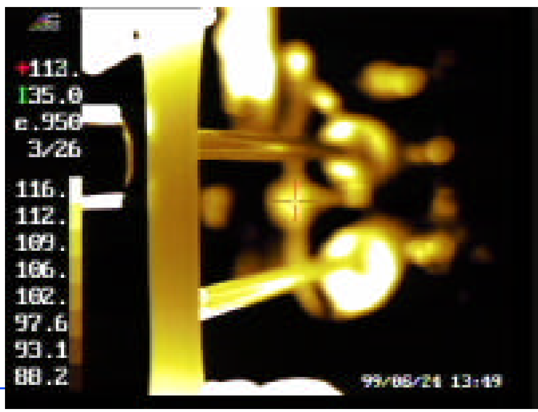


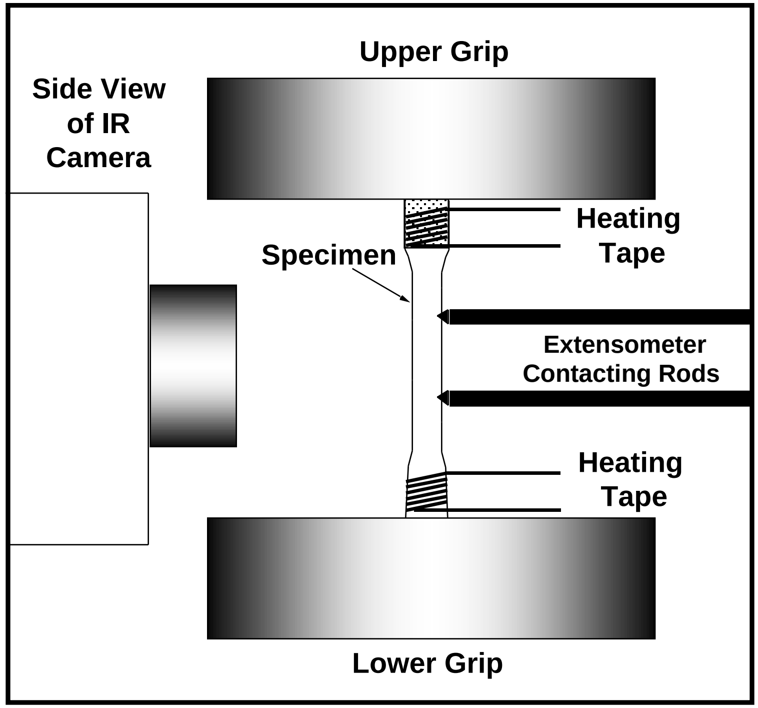
High-Temperature Extensometry



Fellowship Example: María A. Arana, Siemens Westinghouse Power Corporation

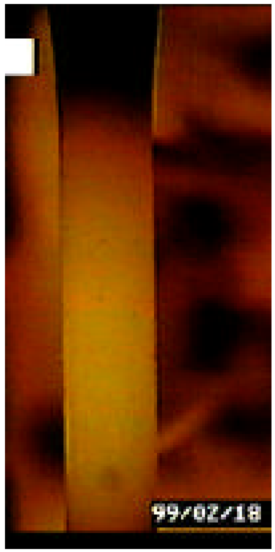




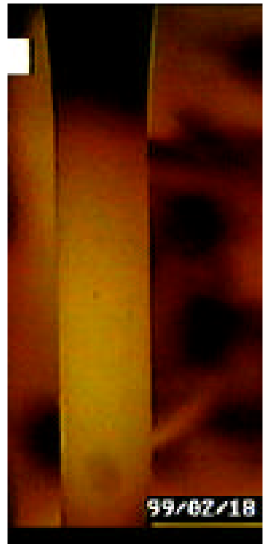


Debonding Decreases the Thermal Conductivity Which Reduces the Surface Temperatures

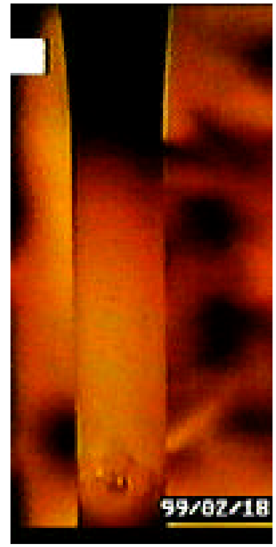
188
Cycles



196
Cycles



197
Cycles

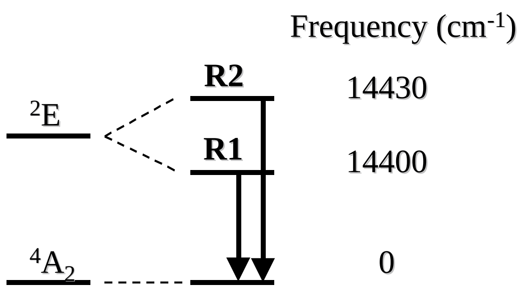


198
Cycles

Residual Stress Measurement

Basis for Piezospectroscopy

Fluorescence of Cr^{3+} in Al_2O_3

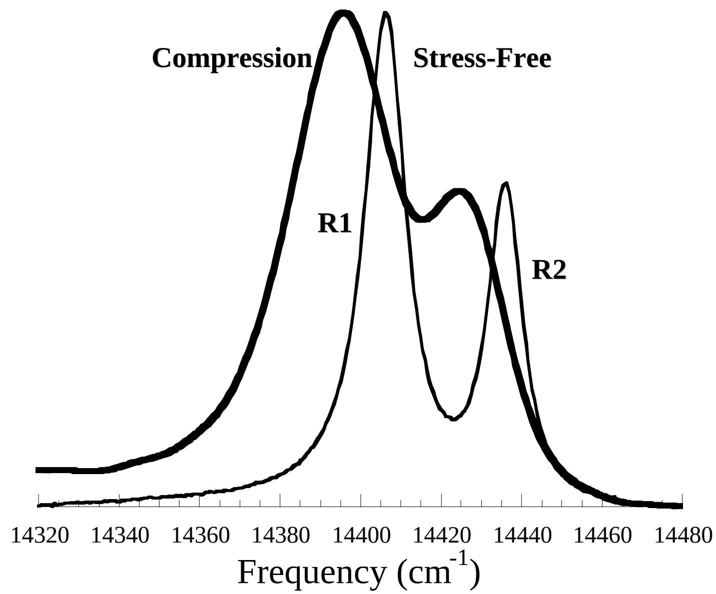


Stress alters the distance between the ion and the surrounding crystal which causes the energy levels to shift:

$$\Delta\nu = \Pi_{ij} a_{ik} a_{jl} \sigma_{kl}$$

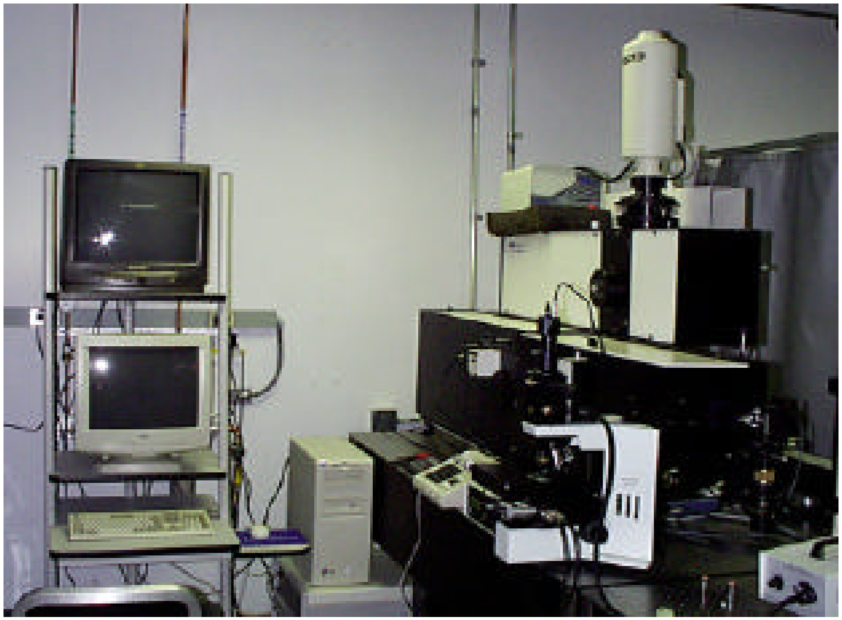
For polycrystalline alumina:

$$\Delta\nu = \tfrac{1}{3}\left(\Pi_{11} + \Pi_{22} + \Pi_{33}\right)\left(\sigma_{11} + \sigma_{22} + \sigma_{33}\right) = \Pi_{ii}\sigma_h$$



The peak shift gives the mean hydrostatic stress in polycrystalline alumina.

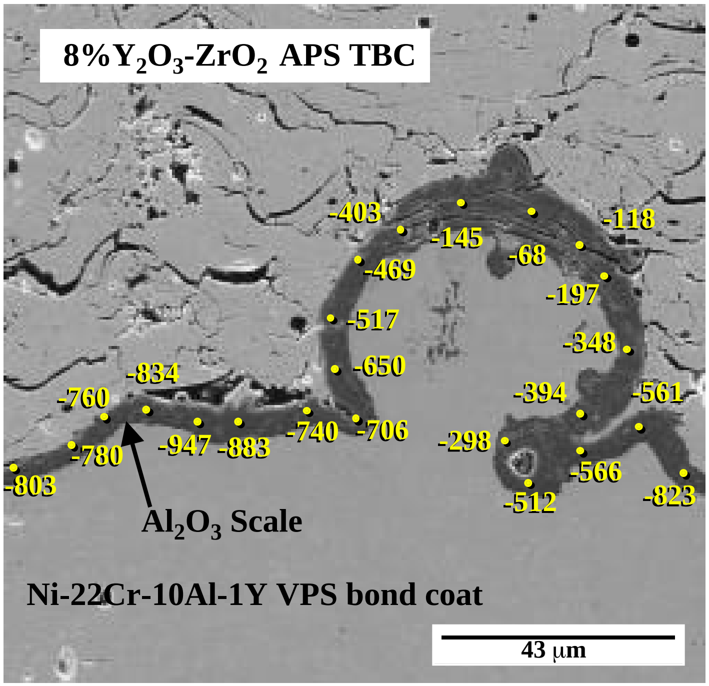
Dilor XY800 Raman Microprobe System



- Spatial resolution of ~2 μm and depth resolution of ~5 μm.
- Confocal line imaging for mapping phase content and stress on the surface and through the depth of a material.
- Laser and optics optimized for operation in the UV, which allows for Raman phase content measurements up to 1500°C.
- Fiber optic probe for remote measurements.

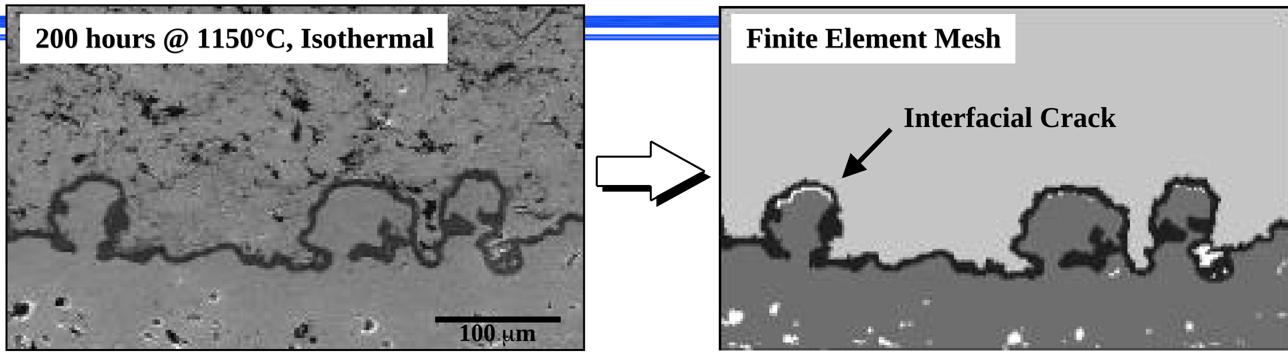
Air Plasma Sprayed Thermal Barrier Coating after Oxidation

Stress in Oxide Scale (MPa)

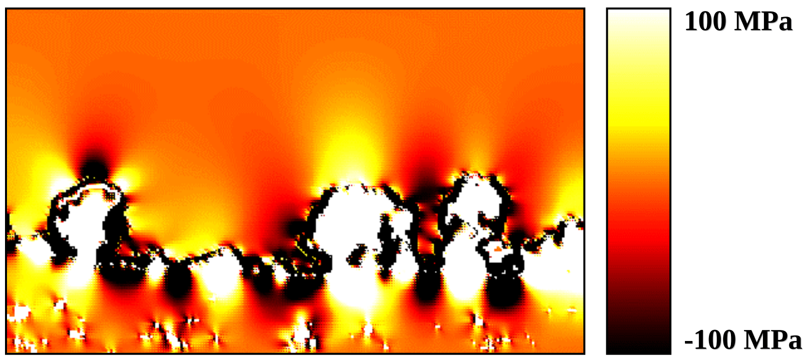


- An Al2O3 scale forms at the interface in thermal barrier coating (TBC) systems.
- Failure of the TBC has been linked to the onset of cracking in this scale.
- Piezospectroscopy was used to differentiate between concave and convex interfacial regions.
- Cracking on convex regions was reflected by a decrease in the compressive stress in the scale.

Object Oriented Finite Element (OOF) Modeling

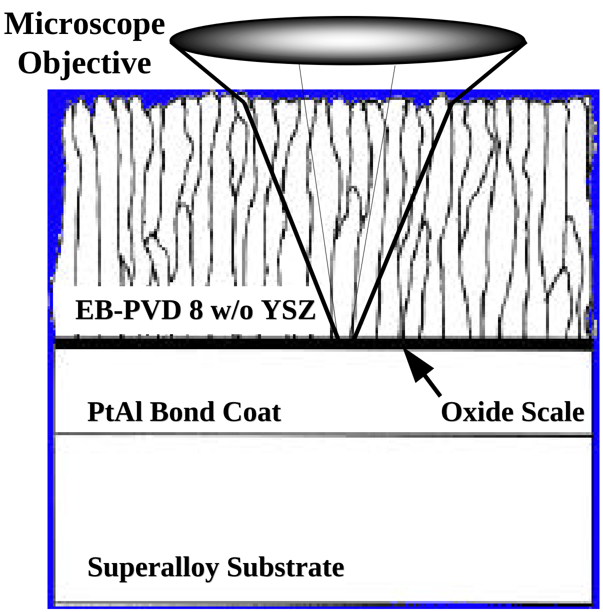


Stress normal to the interface:

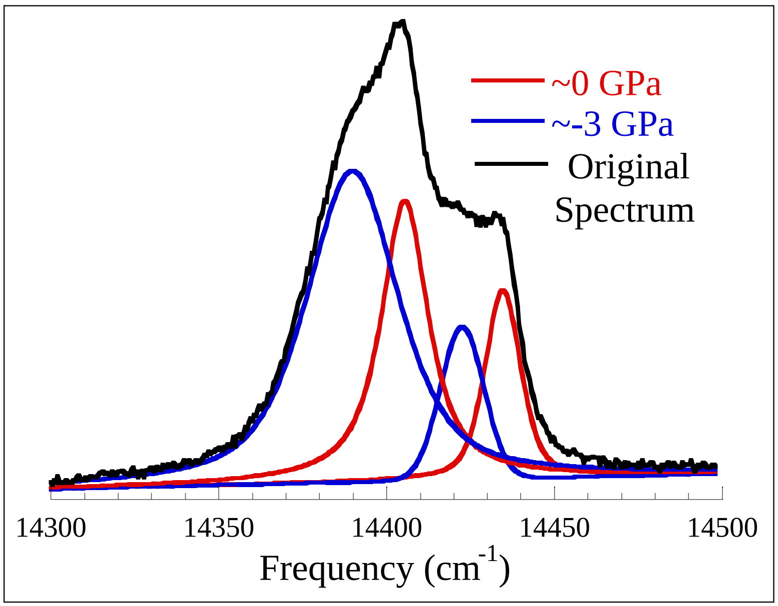


- The roughness produces tensile stresses normal to the interface which facilitate cracking.
- Interfacial cracks act as stress concentrators.

Stress Measurement at the Oxide Scale in Thermal Barrier Coatings



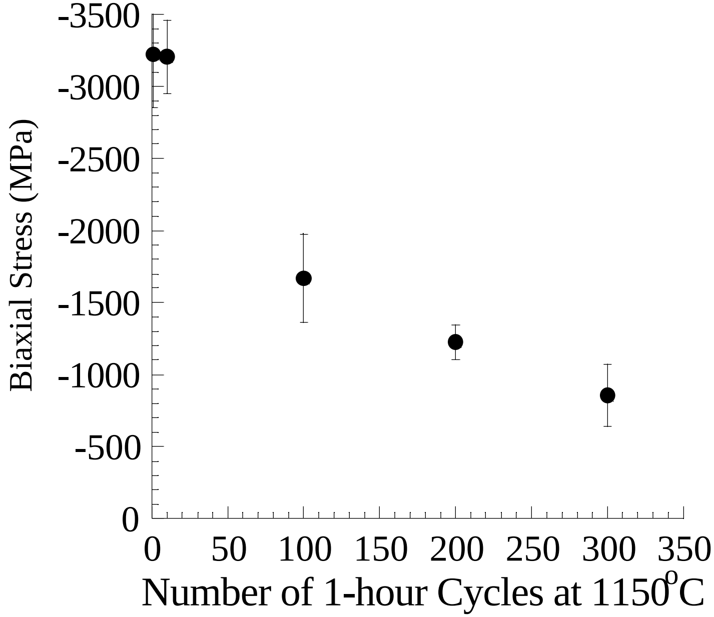
Spectrum Measured through TBC



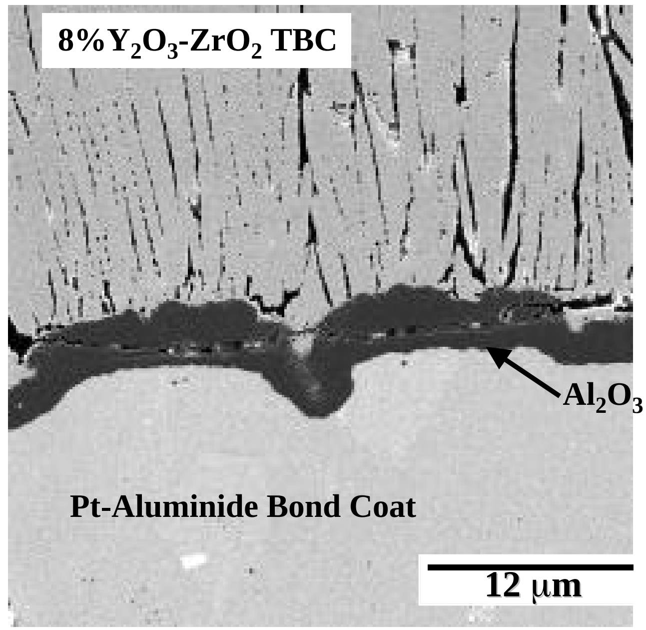
- Failure in EB-PVD TBCs occurs entirely within the oxide scale.
- Stress in the scale can be measured nondestructively through the top coat which makes piezospectroscopy an unparalleled technique for characterizing damage accumulation in TBCs.

Stress Measured at the Oxide Scale after Thermal Cycling

Thermal Cycling at 1150ºC

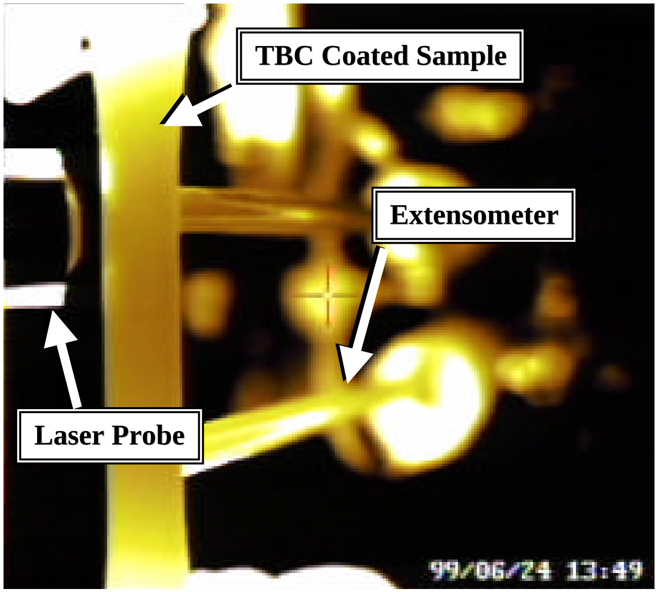


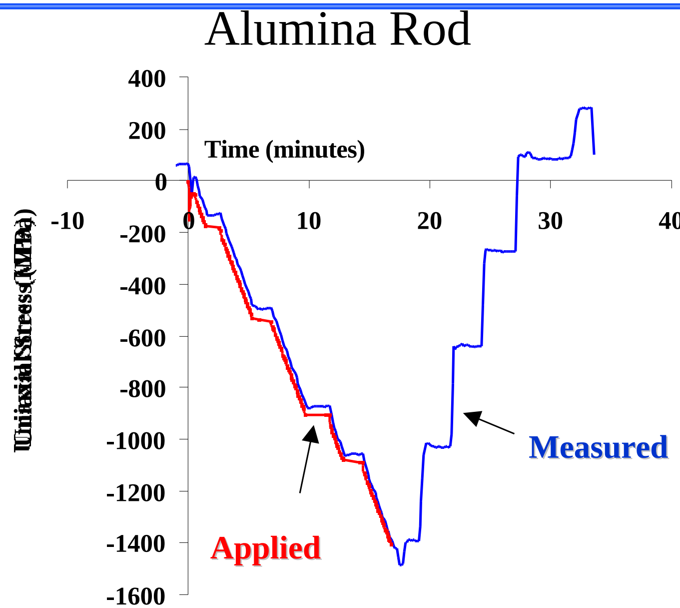
100 1-hr Cycles at 1150°C



- **The Al_2O_3 compressive stress gradually decreases during thermal cycling due to damage accumulation and interface roughening.**

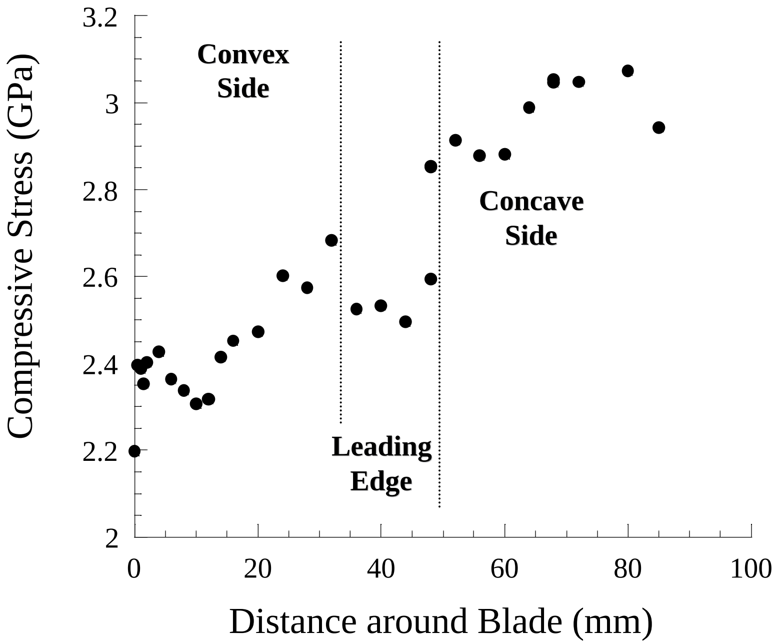
In situ Measurement of Stress in TGO under TBC





- Stress is measured in the TGO during compressive and cyclic loading using a fiber optic laser probe.

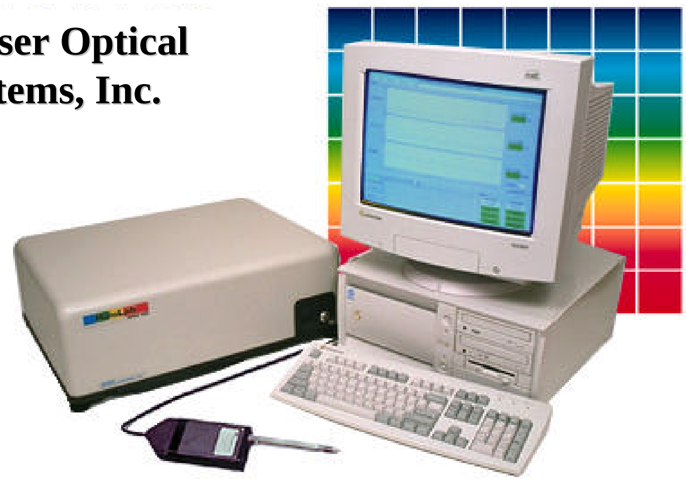
Effect of Curvature on Stress in an As-Deposited TBC-coated Blade



- **The concave side was under more stress than the convex side.**
- **More signal was obtained on the concave side.**

Portable Piezospectroscope

Kaiser Optical Systems, Inc.



- **Stress measurements were reproducible.**
- **Delamination on the leading edge of a turbine blade was detected nondestructively.**
- **Stress was measured through surface deposits.**

Thermal Gradient Rig

Current TBC Rig Test Methods

(1) Furnace Cycle Test

(2) Jet Engine Thermal Simulation Test (JETS)

(3) Becon High Velocity Burner Rig Tube Test

(4) Electron Beam Thermal Gradient Facility

(5) Arc Plasma System

Comments:

Current rig test methods have been and will continue to be valuable in the development and performance assessment of TBCs

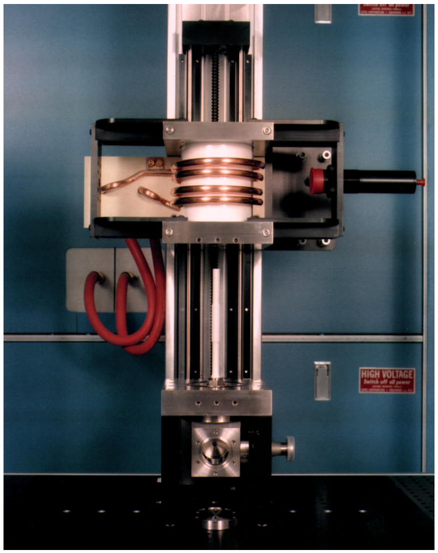
Methods 2,3, and 4 involve high capital or operating costs as well as significant safety issues and therefore, are not suitable most laboratory facilities

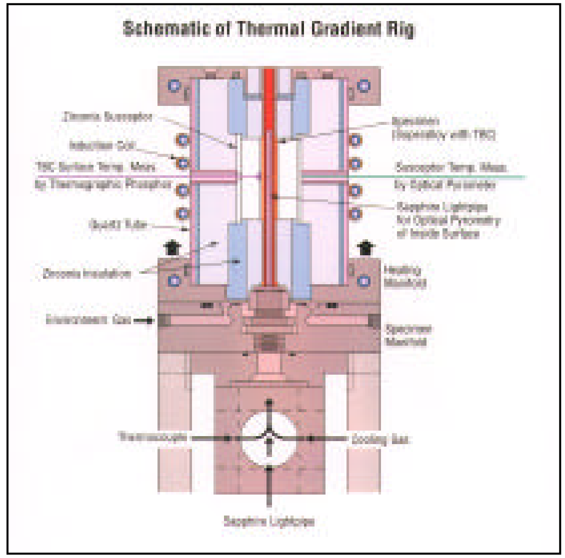
A thermal gradient rig suitable for laboratory use is being built at ORNL to assess long-term exposure of TBCs at realistic temperatures and temperature gradients

A Thermal Gradient Test Facility is Needed for Laboratory Assessment of Thermal Barrier Coatings

- **Compare oxidation rates and oxide scale morphologies to isothermal results**
  - **Thermal gradients are known to increase kinetics**
- **Assess variables controlling coating lifetime under thermal gradient and thermal cycling conditions**
- **Assess role of sintering on coating life and thermophysical property changes**
- **Assess the effect of deleterious environments**
- **Assess alternative cooling approaches**
- **Evaluate coating system diagnostics**

A New Thermal Gradient Rig is Under Development





Accomplishments

- **Start up of Zirconia Susceptor Heat Source to 50% Power Was Achieved**
- **Experiments Were Conducted to Determine Emissivity Versus Temperature at 920 nm Wavelength for Optical Pyrometry Measurement of Susceptor Temperature**
- **Specimen Fabrication Issues Were Resolved**
  - **Short (4 in.) Test Sections Will Be Inertia Welded to Inconel 718 End Sections Followed by Finish Machining**
- **A CRADA Was Established With Microwave Materials Technology, Inc. And VP Induction, Inc. To Complete the Development and Demonstration of the Prototype Unit and Offer a Commercial Unit**
- **Rig Is Physically Complete With Modifications Implemented to Prevent Electrical Arching at High Power As Was Experienced in the Last Start-up**

Summary

- **Optimization of Bond Coating Alloys**
  - Have Demonstrated Improvement in the High-Temperature Oxidation Lifetime of Bond Coating Alloys Through the Incorporation of Alloy Composition and Structure Modifications

- **CVD Bond Coat Development Project**
  - CVD NiAl Bond Coats Applied to Desulfurized Ni-based Superalloys Exhibited Distinct Improvements in Scale Adhesion
  - Once Scale Adhesion Was Improved by Reducing Sulfur Contents in CVD NiAl, the Bond Coat Grain Boundaries Became Preferred Sites for Al_2O_3 Scale Failure

- **TBC Characterization**
  - Residual Stress Measurement using Piezospectroscopy Shows Considerable Promise