Mechanism-Based Testing Methodology For Improving the Oxidation, Hot Corrosion and Impact Resistance of High-Temperature Coatings for Advanced Gas Turbines

University of Pittsburgh - Carnegie Mellon University

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Subcontractor: J. L. Beuth

SCIES Project 02- 01- SR101

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

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Project Awarded (05/01/02, 36 Month Duration + 6 mo No-Cost Extension)

$ 458,420 Total Contract Value ($ 412,695 DOE)

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Gas Turbine Needs

In the next generation gas turbine, resistance to thermal cycling damage may be as important as resistance to long isothermal exposures. Moreover, metallic coatings and Thermal Barrier Coatings (TBCs) may encounter attack by deposits arising from combustion of low-grade fuel and air borne impurities. Finally, there is currently a need for nondestructive techniques to assess metallic coating and TBC degradation and damage as a result of exposure to cyclic oxidation and hot corrosion conditions.

Program Focus

Development of a mechanism-based testing methodology for improving the oxidation resistance of high temperature metallic coatings and TBCs

Incorporation of a significant number of nondestructive tests in this methodology directed at assessing coatings degradation and damage accumulation.

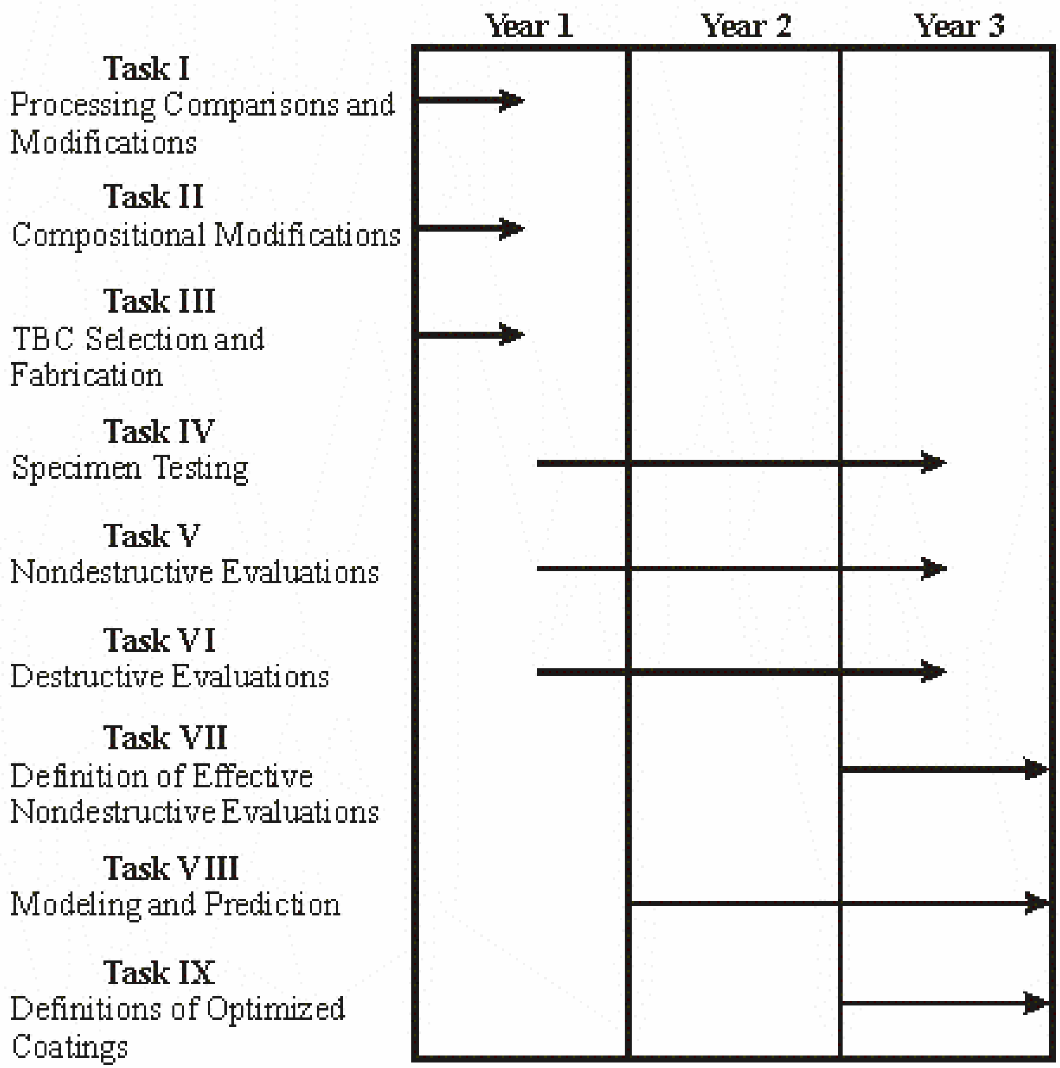
Program Objectives

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.

Approach


Year 1
Year 2
Year 3
Task I
Processing Comparisons and Modifications
Task II
Compositional Modifications
Task III
TBC Selection and Fabrication
Task IV
Specimen Testing
Task V
Nondestructive Evaluations
Task VI
Destructive Evaluations
Task VII
Definition of Effective Nondestructive Evaluations
Task VIII
Modeling and Prediction
Task IX
Definitions of Optimized Coatings

Accomplishments

Obj#1
Extensive cyclic oxidation data.
Advances in oxide stress measurement.

Obj#2
Advances in indentation of TBCs as an accelerated testing technique.

- **Debond Imaging**
- **FEM Modeling (including stress measurements)**

Obj#3
COSP model modified to incorporate stress measurements.
Acoustic emission used to obtain spall parameter (Q_0).
Good agreement between predicted and measured lives.

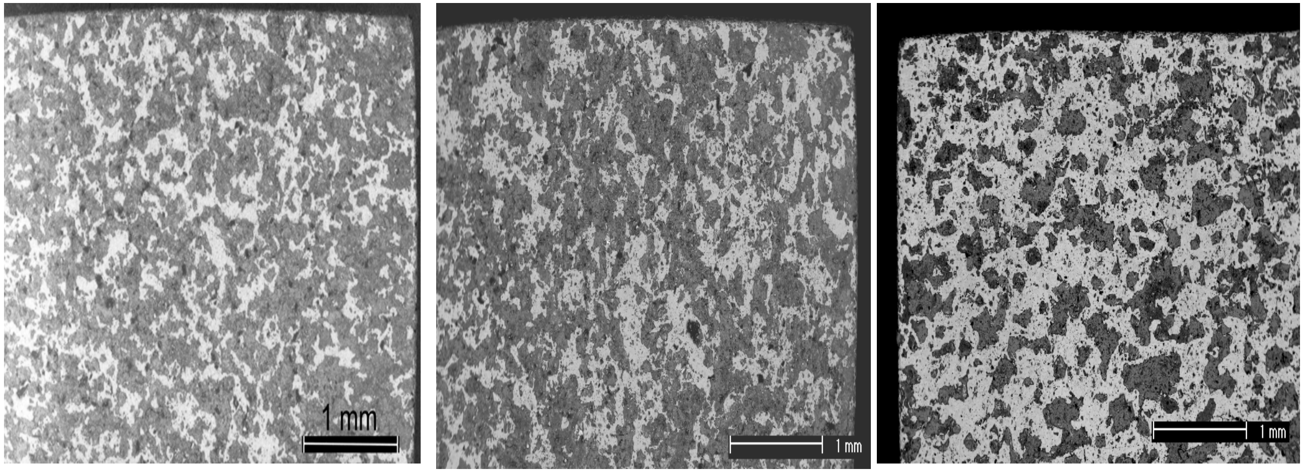
Obj#4
In Progress.

Subsequent Slides Illustrate Results from # 2 and # 3.

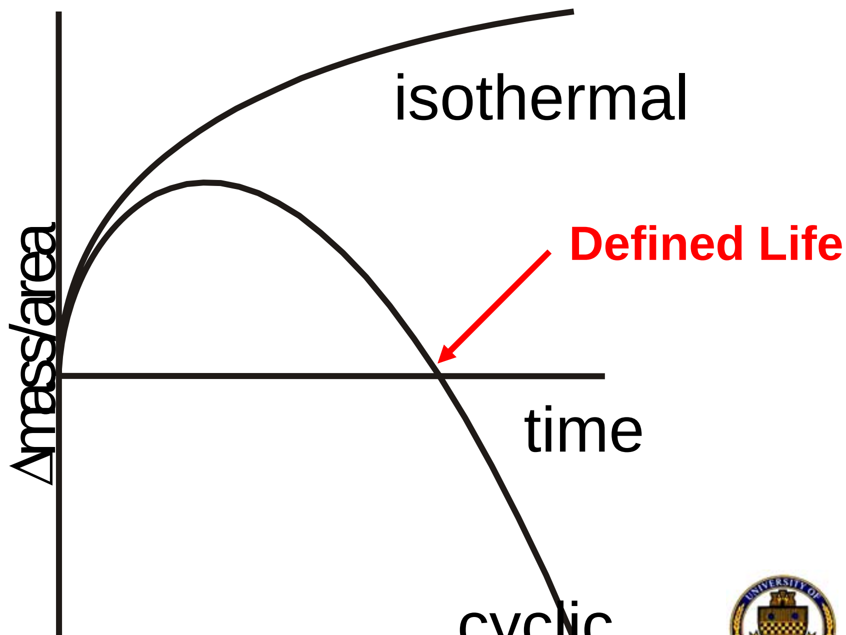
Cyclic Oxidation of Alumina-Formers

1 h Cycles

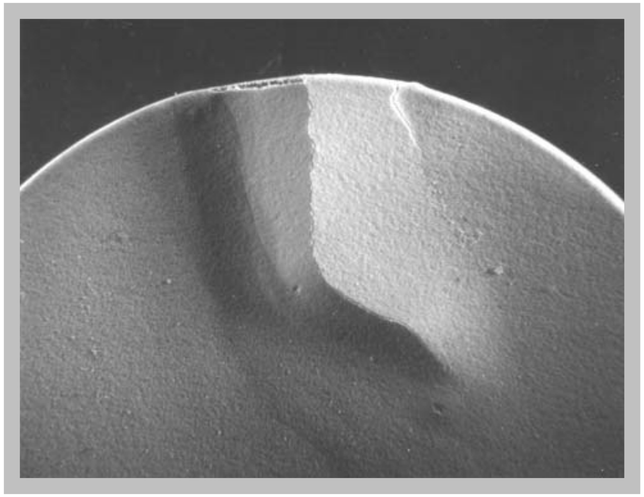
1100°C

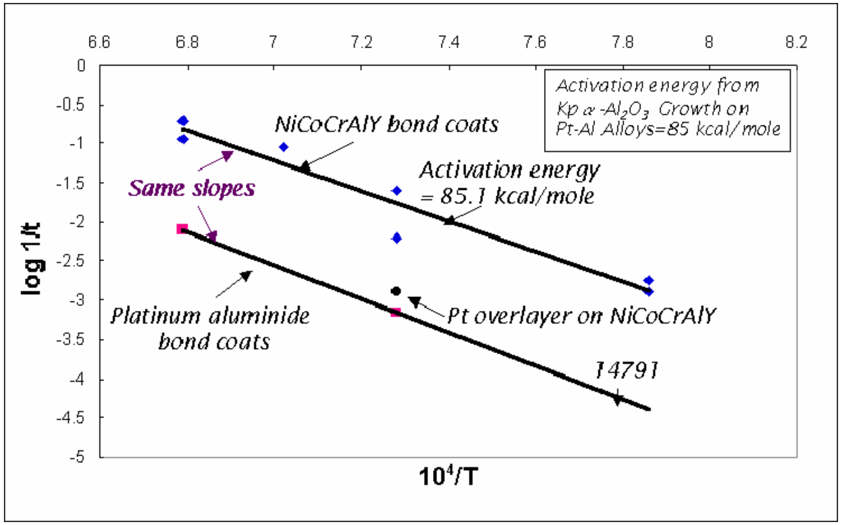


N5 dry 615cycles | 0.1atm 664cycles | 0.5atm 802cycles



Cyclic Exposure of TBCs





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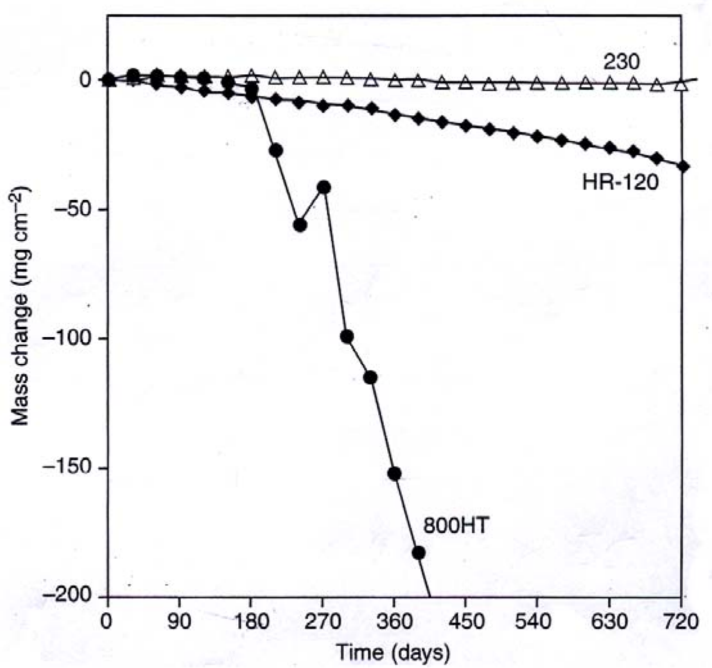
Cyclic Oxidation Degradation and Breakaway

- Alloys initially are Cr_2O_3-formers

982°C 30 day cycles

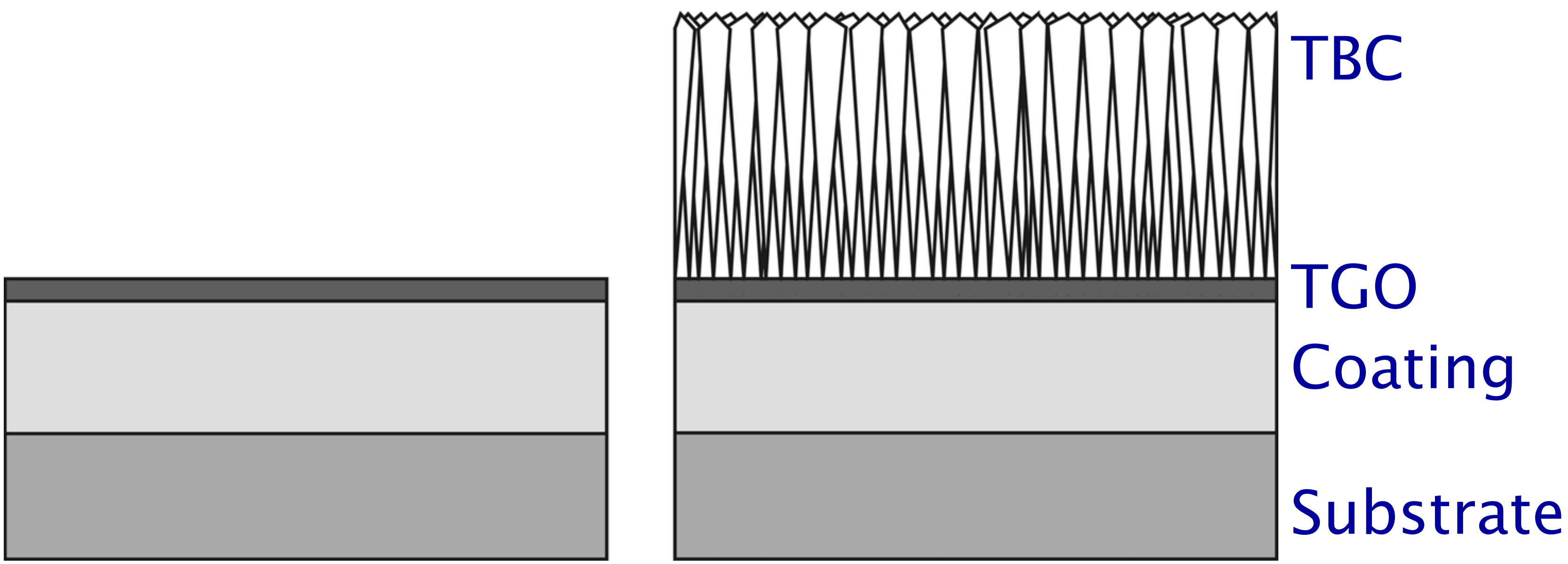


wt%

Alloy	Cr	Ni	Fe	Co	Mo	W	C	Others
800HT	21	32.5	Bal.	—	—	—	0.08	0.8Mn, 0.5Si, 0.4Cu, 0.4Al, 0.4Ti
HR–120	25	37	Bal.	3*	2.5*	2.5*	0.05	0.7Mn, 0.7Nb, 0.6Si, 0.2N, 0.1Al, 0.005B
230	22	Bal.	3*	—	2	14	0.1	0.5Mn, 0.4Si, 0.3Al, 0.02La, 0.015B*

More adherent oxide

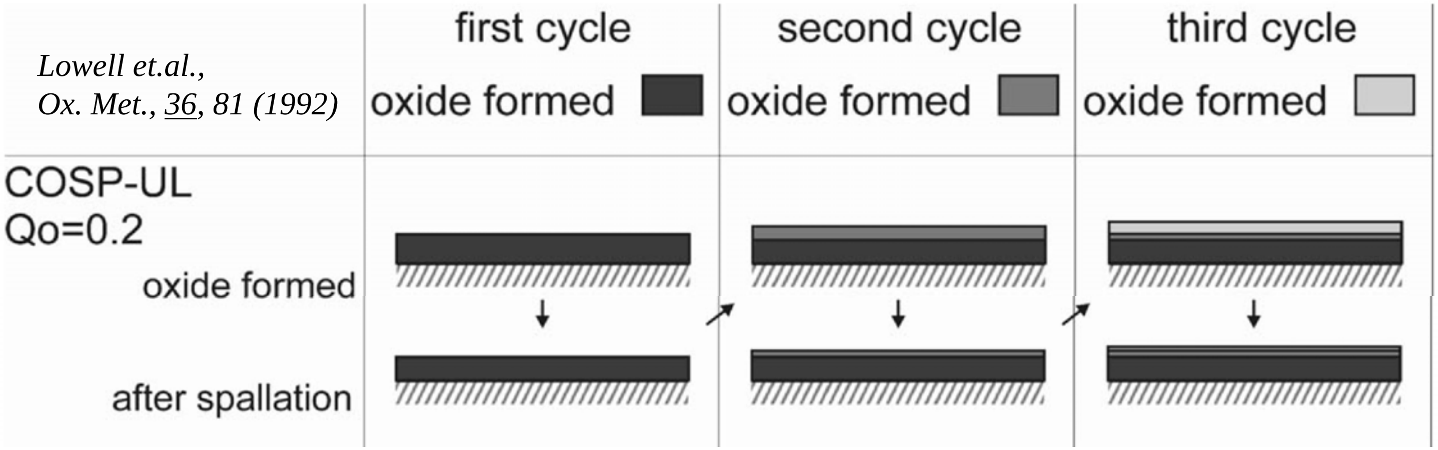
Important Parameters

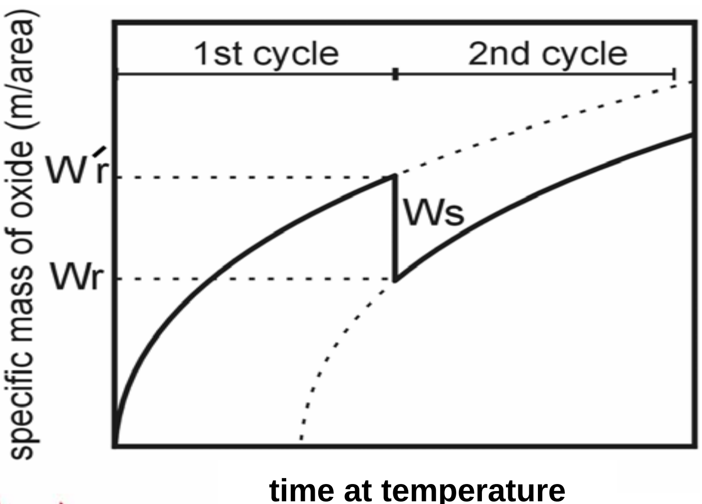


- Oxide Thickness
- Stress in Al_2O_3 (and TBC)

- Fracture Toughness of Interfaces
- Interface Morphology

Model: COSP-Uniform Layer





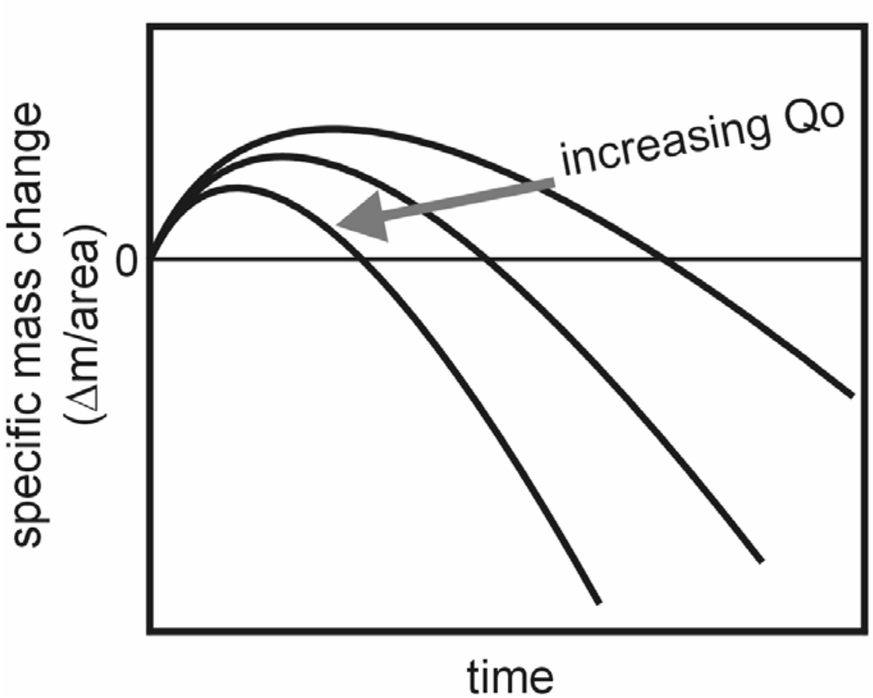
$$F = Q_o \cdot W'r$$

$$Ws = F \cdot W'r$$

$$Wr = W'r - Ws$$

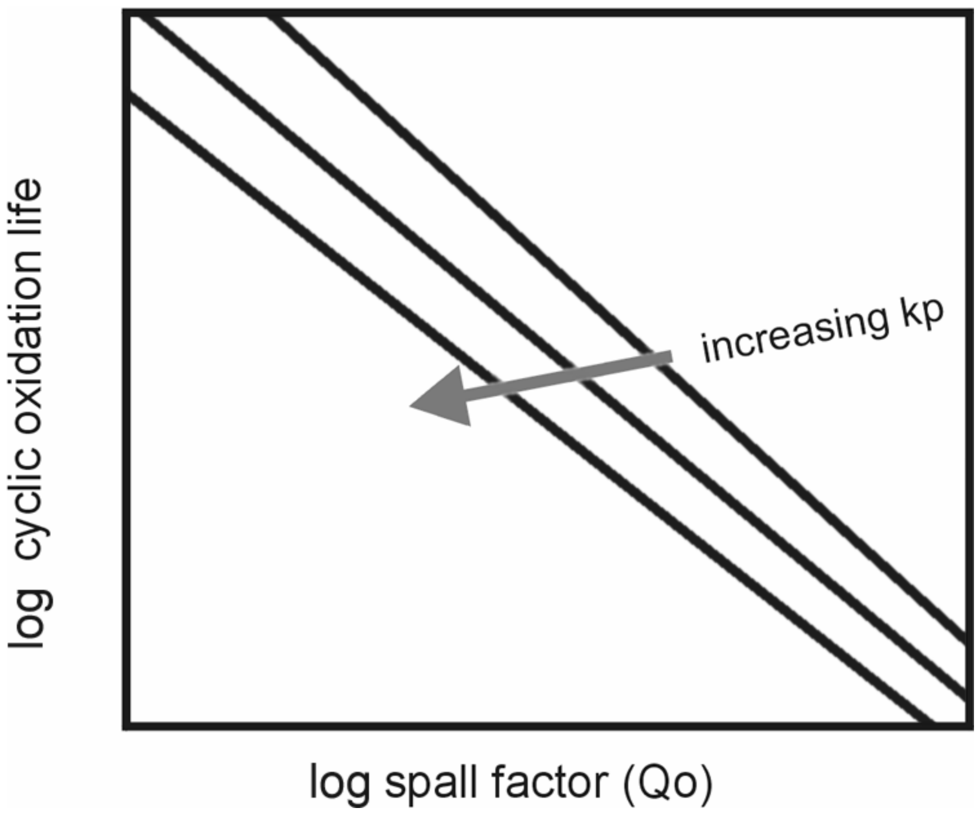
- *W'r*, weight of oxide that forms during the high temperature dwell
- *Ws*, weight of oxide that spalls during cooling
- *Wr*, remaining oxide, the starting point of the next cycle
- *F*, fraction of oxide that spalls
- Q_o, spall parameter

Model: COSP



With known oxide growth kinetics and *Qo*, mass change versus time curves can be constructed

Model: COSP (Life-Time Curves)



<u>Cyclic Oxidation Life</u>

•Cyclic oxidation life is defined as cross over to negative weight change in mass change versus time curves

•Life as a function of oxidation kinetics and spall behavior

<u>Life-Time Curves Inputs</u>

•oxide type (α-alumina)

•cycle frequency

•scale growth rate (k_p)

COSP and Short-Term Testing

spall factor (Qo) and experimental variables

$$Q_o = \frac{E^{AE}/A \cdot \rho_{ox}}{B \cdot (W_r')^2 \cdot \Omega_{ox}}$$

ρ_{ox}	oxide density
W_r'	weight of retained oxide prior to spallation
E^{AE}	acoustic energy
Ω_{ox}	elastic strain energy density $\Omega_{ox} = \frac{(1-\nu)}{E}\sigma_o^2$
B	ratio of E^{AE} to the fracture energy of oxide spallation

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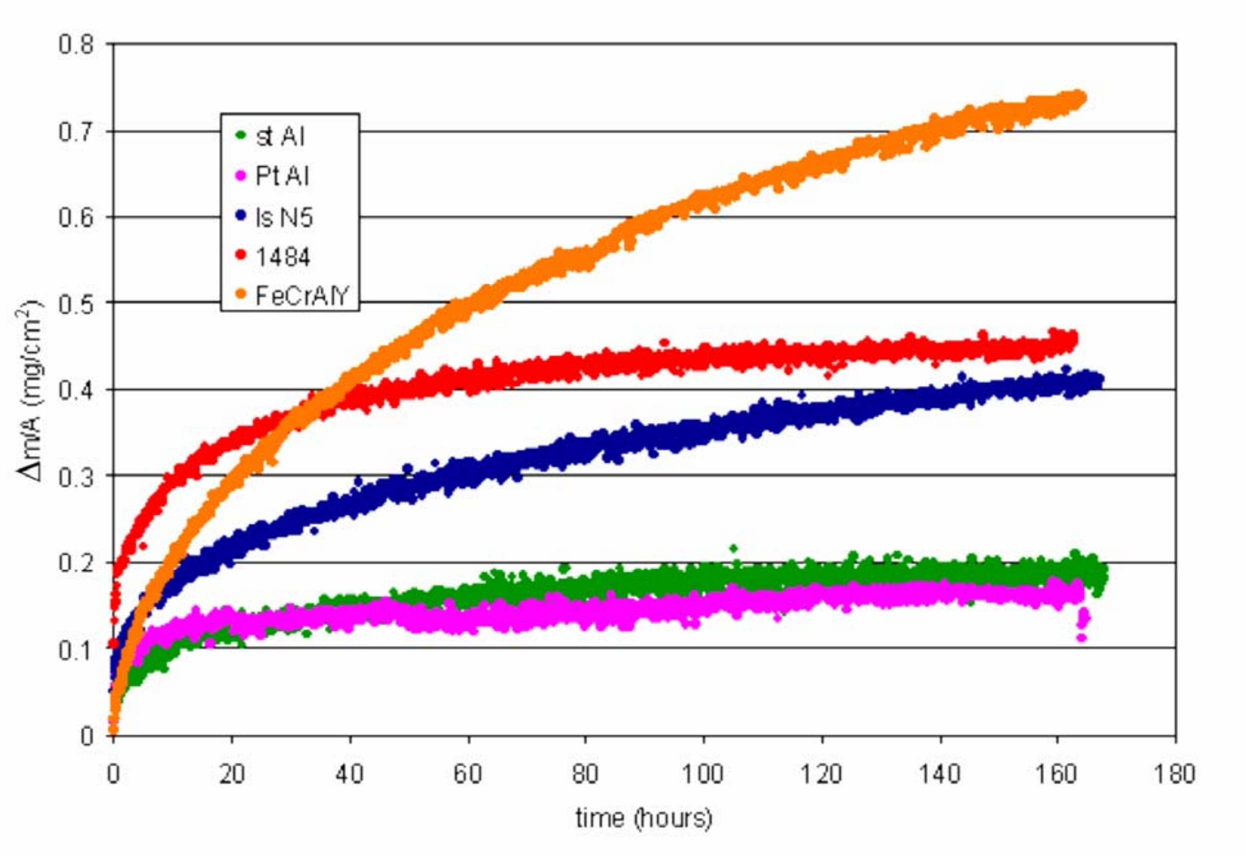
Oxide Growth Kinetics



Isothermal TGA results at 1100°C

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Stress Measurement Result

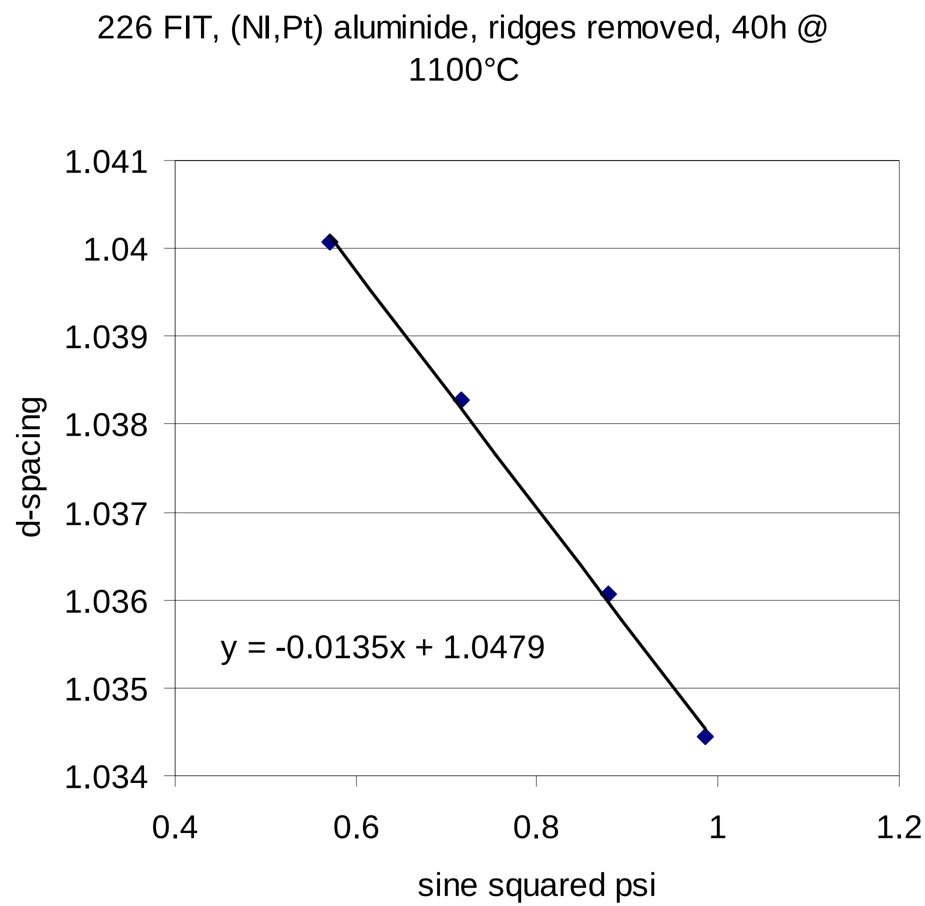
- d-spacing as a function of the biaxial stress and the tilt angle

$$d_\psi = \tfrac{1}{2} s_2 \cdot \sigma_o \cdot d_o \cdot \sin^2 \psi + d_o \left(2 s_1 \cdot \sigma_o + 1\right)$$

- Calculation of Stress

$$\text{slope} = \tfrac{1}{2} s_2 \cdot \sigma_o \cdot d_o$$

- -4.14 +/- 0.21GPa



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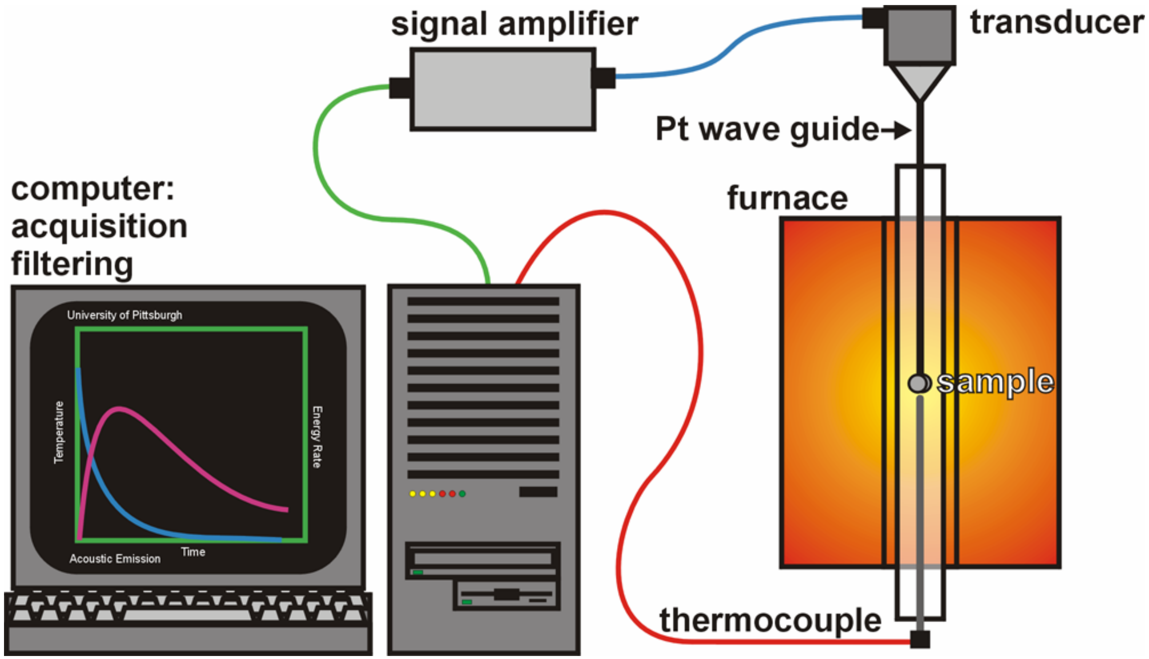
Acoustic Emission Testing Apparatus



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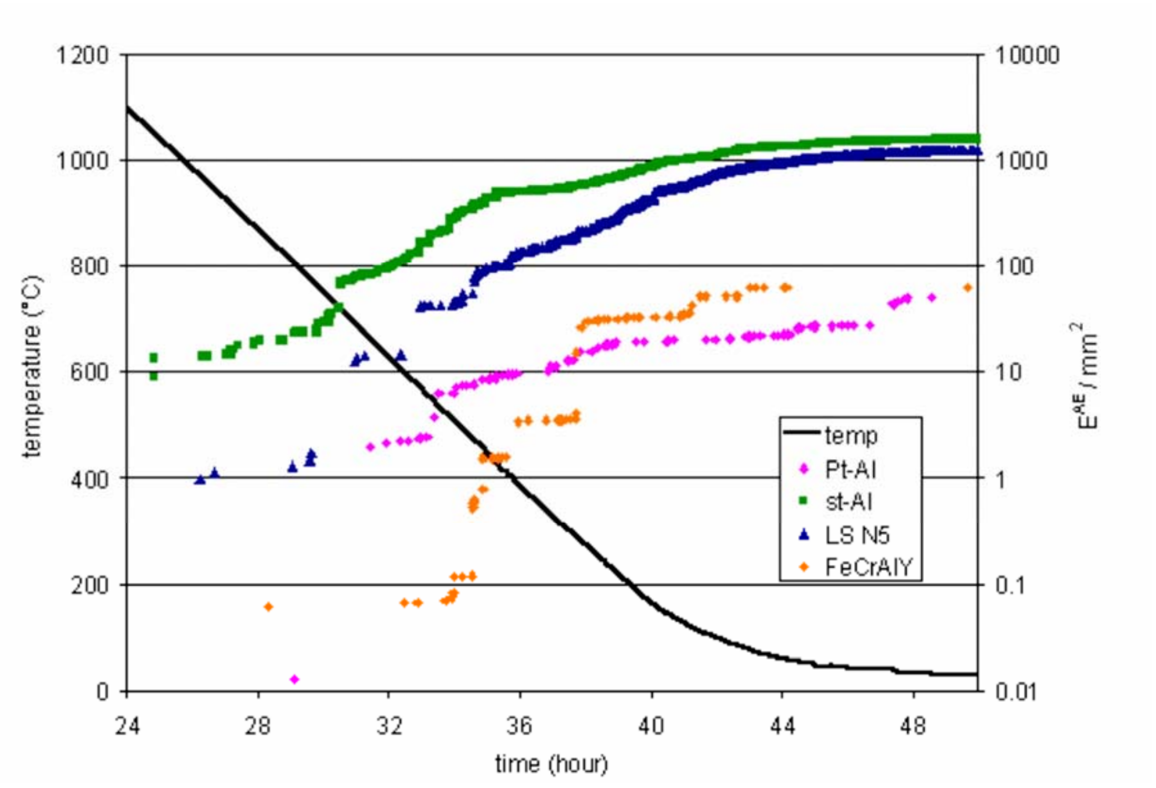
Acoustic Emission Summary

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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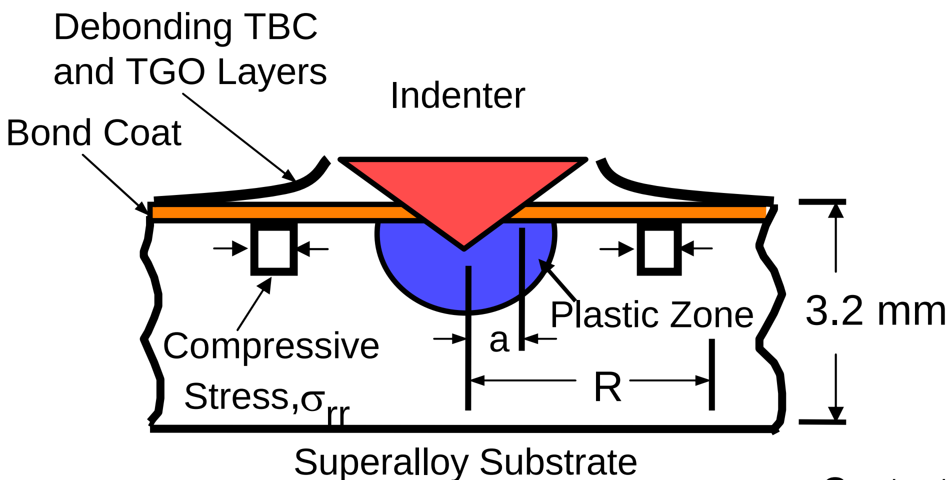
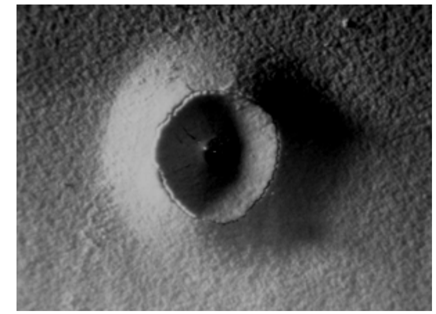
Model Results with Inputs from Short-Term Testing

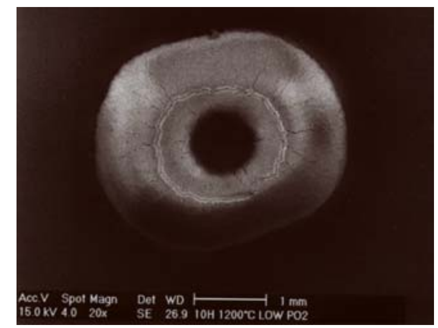
alloy/coating	cycles to failure (n)	
	experimental long-term test	short-term tests and model
1484	24	64
ls-N5	690	950
st-Al	1000	560
FeCrAlY	>2000 (~4000)	3850
Pt-Al	>4000	10000

Indentation Test for Interfacial Toughness



a = Contact Radius
R = Debond Radius





- **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)**

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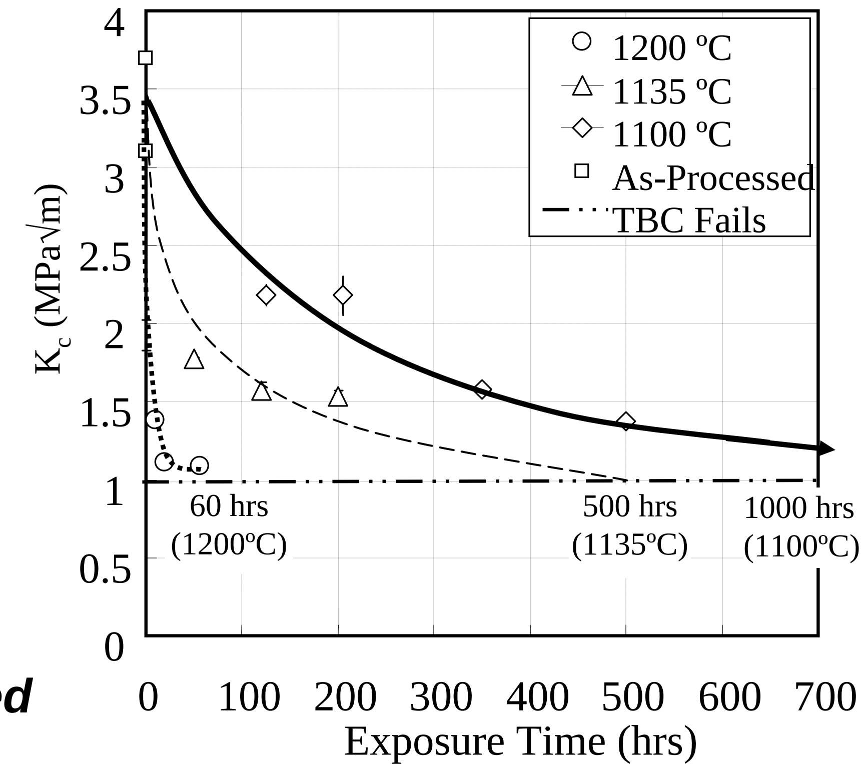
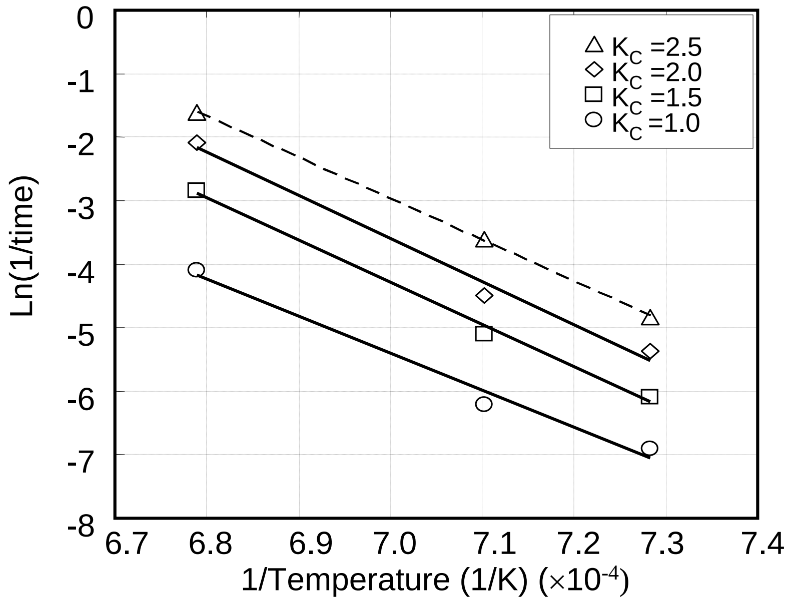
Isothermal Exposures: Apparent Toughness Loss



- **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 $MPam^{1/2}$)**

Fracture Toughness Measurements



- **Failure Times follow an Arrhenius Relationship (Error Bars not Shown): Rate = $Ce^{-Q/RT}$**
- **Suggests Thermally Activated Failure Mechanism(s) That Do Not Change with Temperature**
- **Apparent Toughnesses Have Similar Slopes - Apparent Toughness Loss Appears to be Linked to the Same Thermally-Activated Mechanism(s)**

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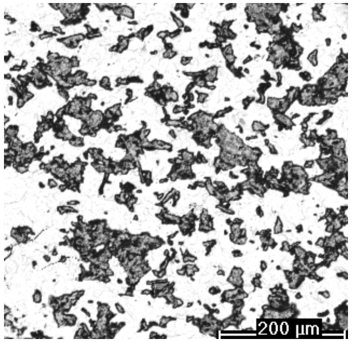
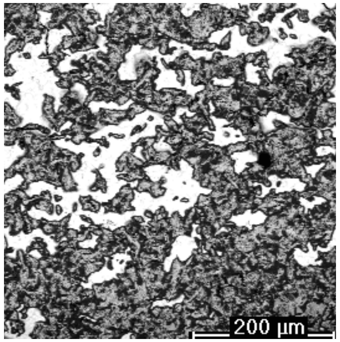
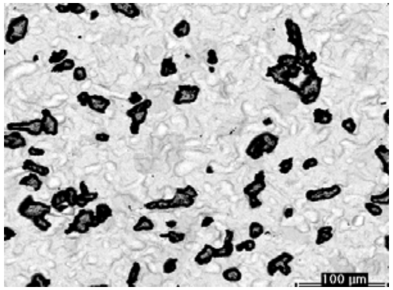
Fracture Surfaces: Isothermal, Dry Air vs. Cyclic Thermal, Dry Air (1100° C)



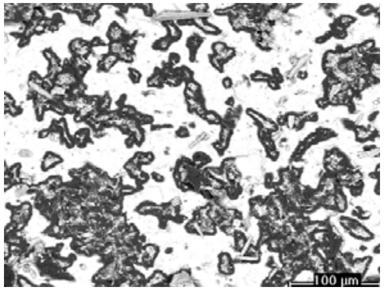
Isothermal Dry Air 120 Hrs



Cyclic Dry Air 120 Hrs



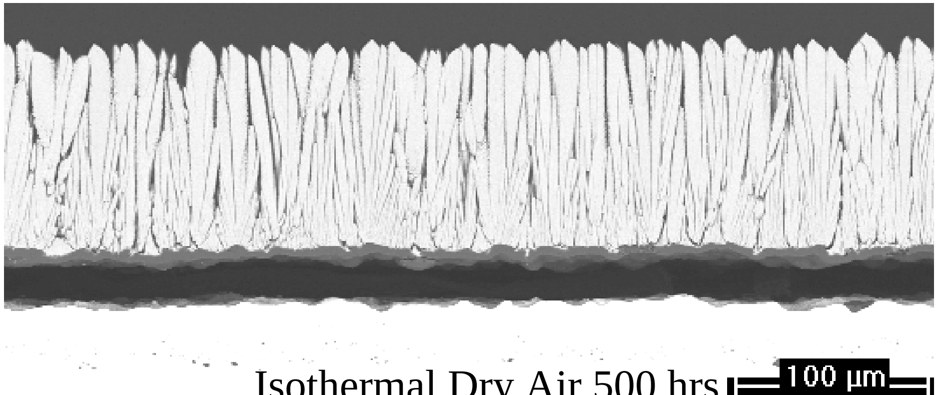
Isothermal Dry Air 500 hrs



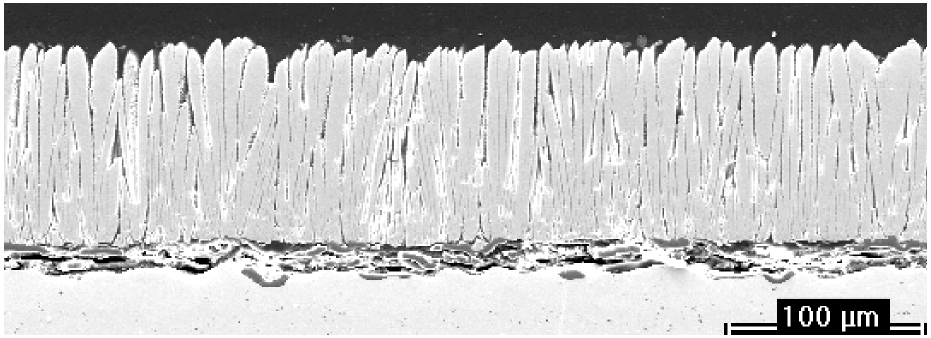
Cyclic Dry Air 500 hrs

- **White is Bond Coat, Black is Oxide, Grey is TBC**
- **Significant Difference Between Isothermal and Cyclic Dry Air**
- **Difference Between Isothermal and Cyclic Dry Air Even More Pronounced Near End of Life**
  - **Cycles are Approx. 10 min heat/ 45 min at temp/ 10 min cool**
  - **Cycles Yield More of a Mixed Fracture Surface**

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



Isothermal Dry Air 500 hrs



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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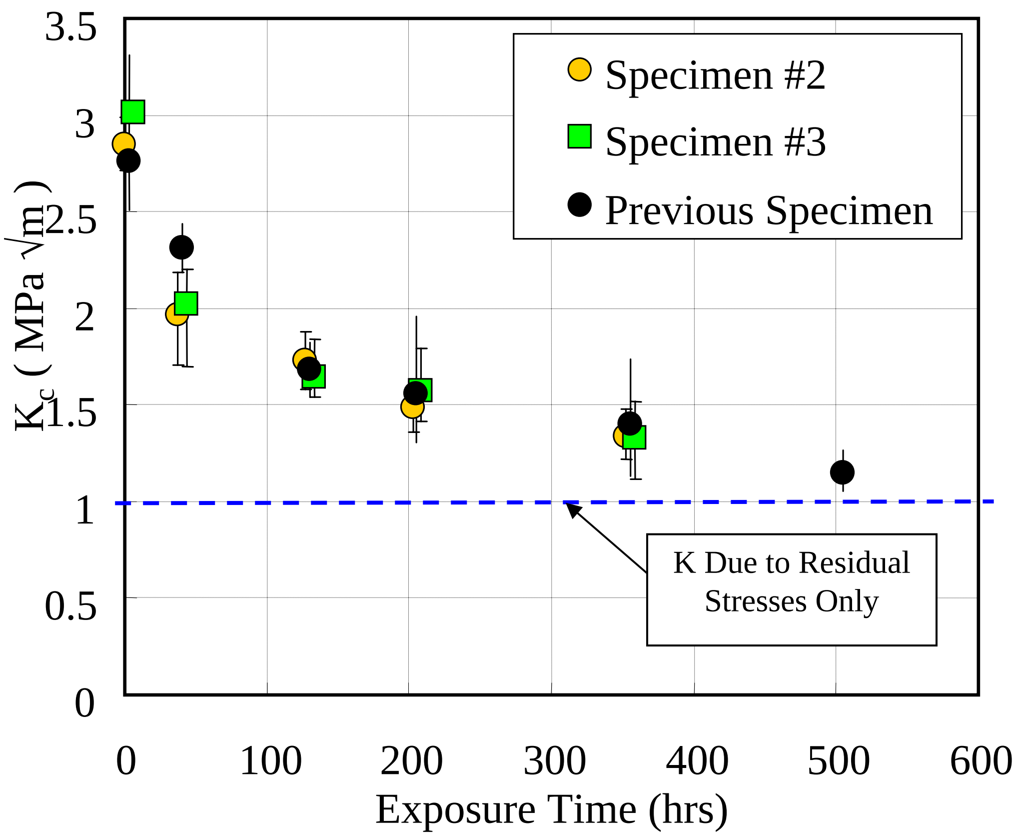
Fracture Test Results
Cyclic Dry Air Exposures (1100° C)

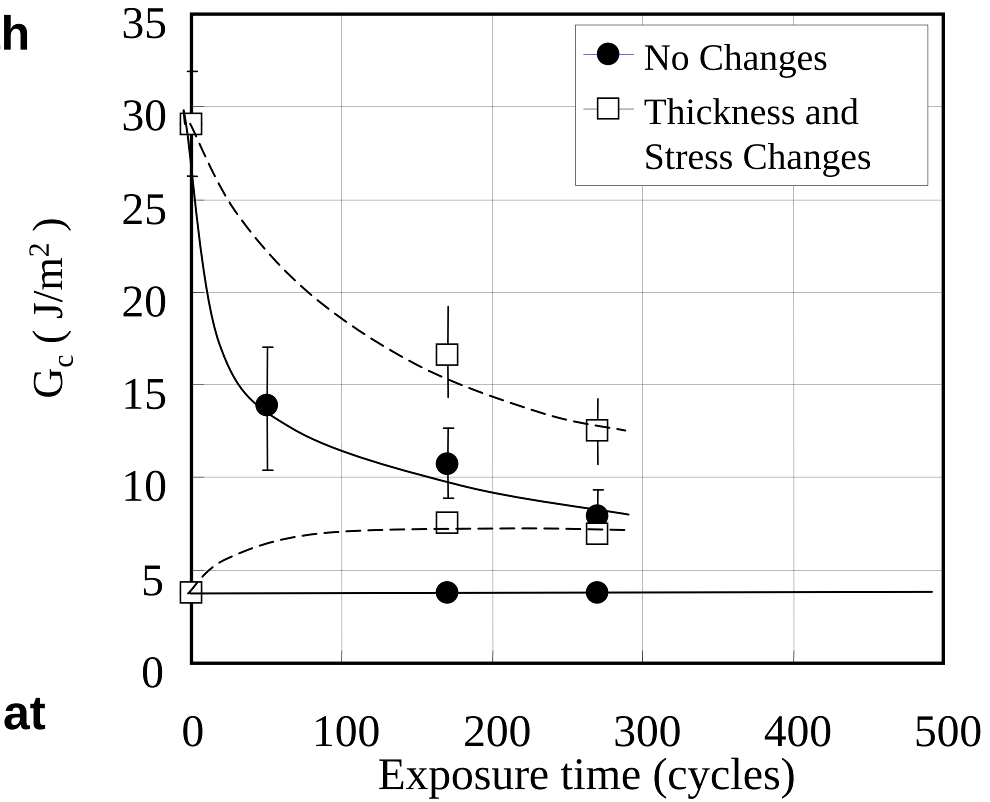
- **Results from 3 Specimens**
- **2 of 3 Tests with Oxide Stress Measurements via Piezospectroscopy (Michael Lance, ORNL)**
- **Stress Values:**
  - **0 hrs: 3.86 GPa**
  - **128 hrs: 1.46 GPa**
  - **202 hrs: 1.27 GPa**
- **Try to Account for This in Fracture Analysis of Tests**



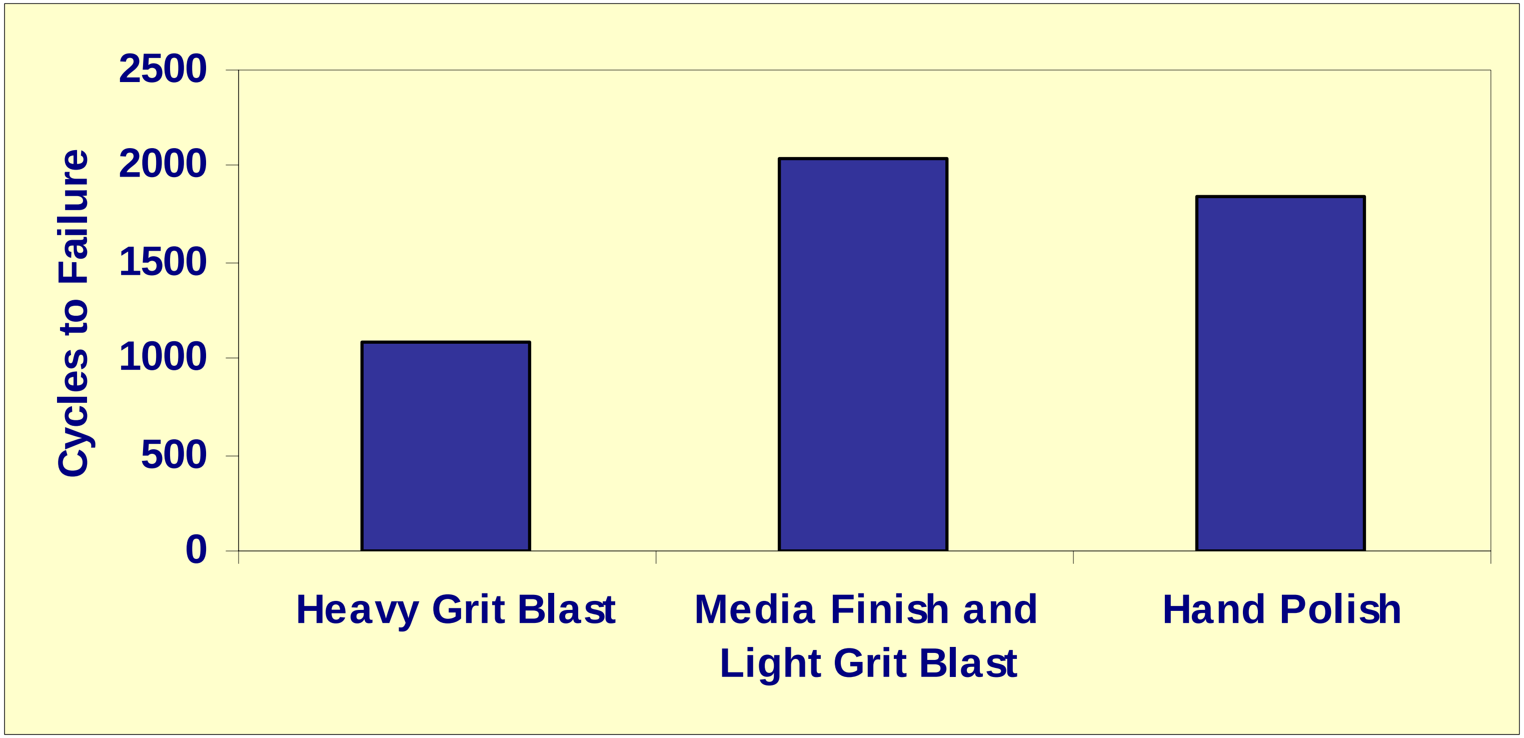
Fracture Test Results
Accounting for Oxide Stress and Thickness Changes

(1100° C)

- **Results Including Oxide Growth and Oxide Stress Reduction**
- **Now There is a "True" Loss of Toughness**
- **Critical Energy Release Rates Scale with Bonded Area**
- **% Reduction in Bonded Area:**
  - **170 Cycles: 45%**
  - **270 Cycles: 60%**
- **Results Suggest Large-Scale Damage is Occurring Prior to Spontaneous Spallation**
- **Similar Results for Debonding at the TBC/Alumina Interface**



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.

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.**

Project Team

The general approach is to leverage the talents of a multi-disciplinary, multi-organization team to achieve the project objectives.

Program Team

- Prof. F. S. Pettit, Department of Materials Science and Engineering, University of Pittsburgh (Pitt-MSE)
- Prof. G. H. Meier, Department of Materials Science and Engineering, University of Pittsburgh
- Prof. J. L. Beuth, Department of Mechanical Engineering, Carnegie Mellon University (CMU)
- Dr. M. Lance, Oak Ridge National Laboratory (ORNL)
- Dr. W. Ellingson, Argonne National Laboratory (ANL)
- Graduate Students: Two Ph. D Degrees Awarded
- Industrial Partners:Praxair & Howmet

QUESTIONS?

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