Mechanisms Underpinning Degradation of Protective Oxides and Thermal Barrier Coatings in High Hydrogen Content (HHC) – Fueled Turbines

Daniel R. Mumm

Chemical Engineering and Materials Science
Advanced Power and Energy Program (APEP)
University of California, Irvine
Tel: (949) 824-3858; Fax: (949) 824-2541
mumm@uci.edu

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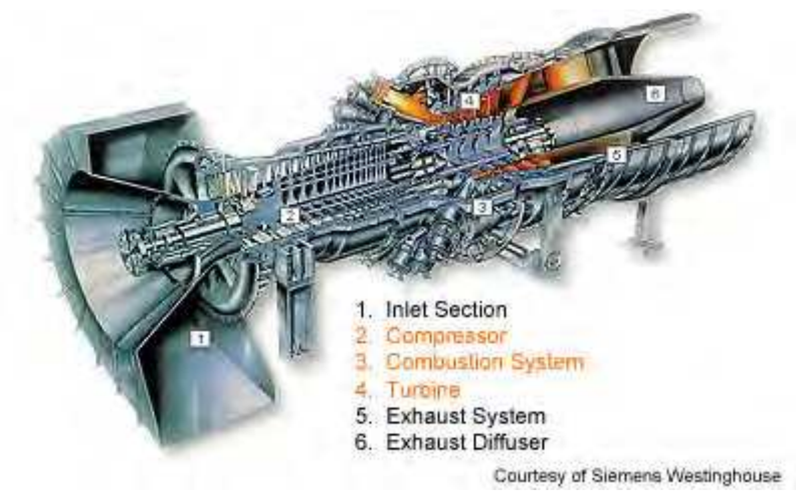
Agreement # DE-FE0004727; Project Manager: Dr. Patcharin Burke

Project Objectives

- Derive a mechanisms-based understanding of TGO layer and TBC system degradation associated with turbine operation with syngas and HHC fuels

- Develop a knowledge base upon which the design of protective oxides and thermal barrier coatings more resistant to the observed attack modes may be based.

- Link and quantify the effects of modified combustion by product constituent partial pressures, higher water vapor levels, varied sulfur concentrations, and exposure to flow stream impurities characteristic of syngas and HHC fuels, and identify any synergism among these factors influencing materials stability.



Thermal Barrier Coating Failure

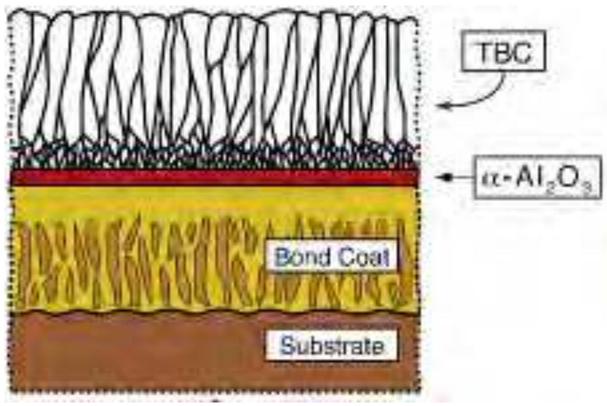
Delamination and Spallation with Thermal Cycling

Photo Courtesy of D. Wortman, GE CR&D

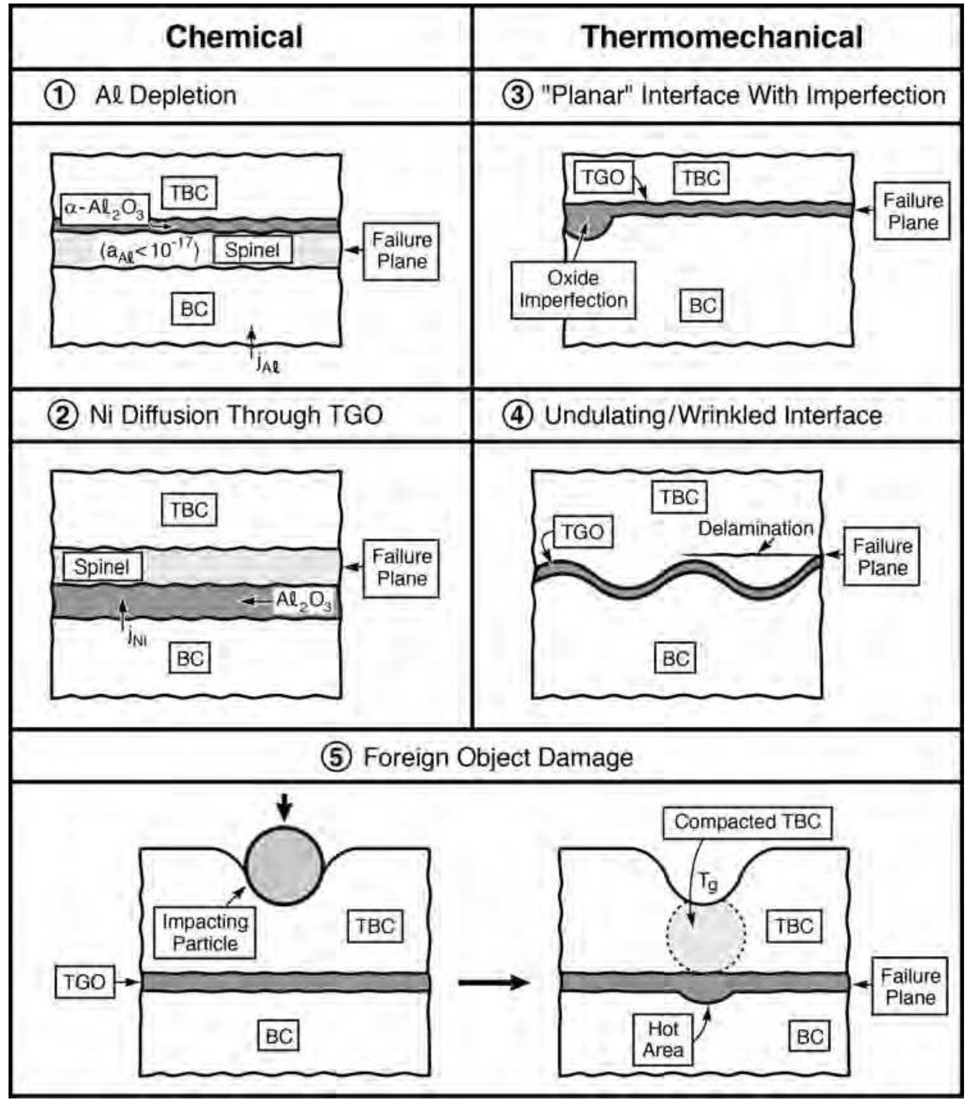
FOD (?)

Mechanistic Understanding Needed to Relate Failure To Intrinsic Characteristics of Materials, Microstructure and Operational Variables

Project Relevancy – Determining Underpinning Mechanisms

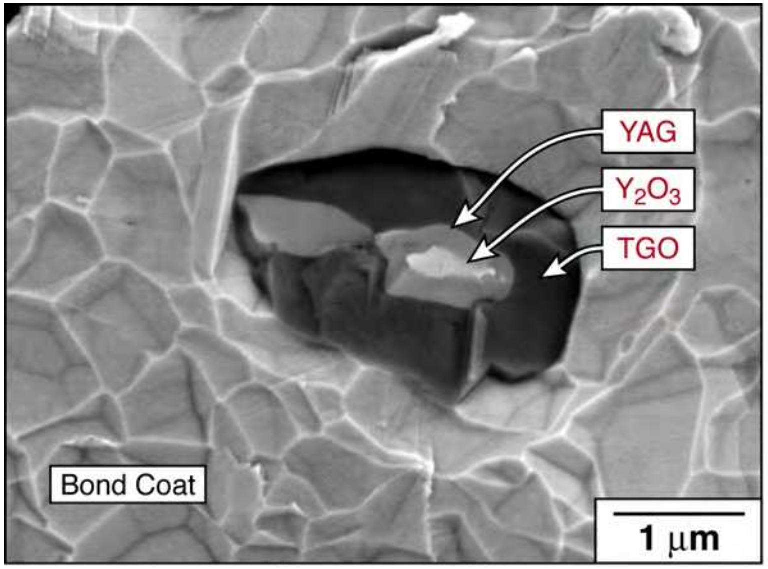


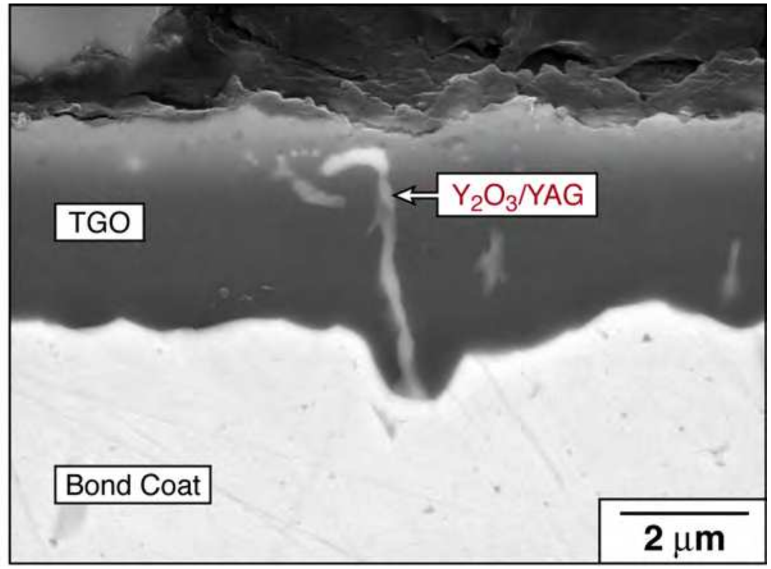
Mechanistic Understanding Needed to Relate Failure To Intrinsic Characteristics of Materials, Microstructure and Operational Variables



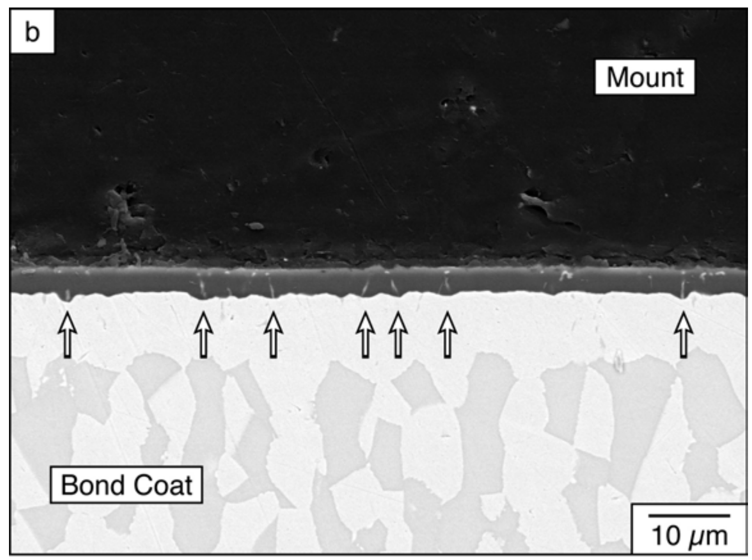
A.G. Evans, D.R. Mumm, J.W. Hutchinson, G. Meier and F.S. Pettit (2001) Progress in Materials Science, 46, 505-53.

Examples from Previous Work: TGO Heterogeneities & Role of Yttrium

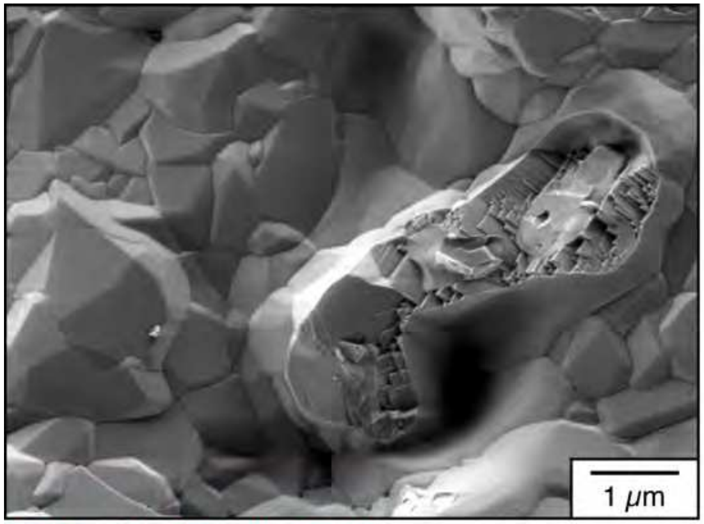




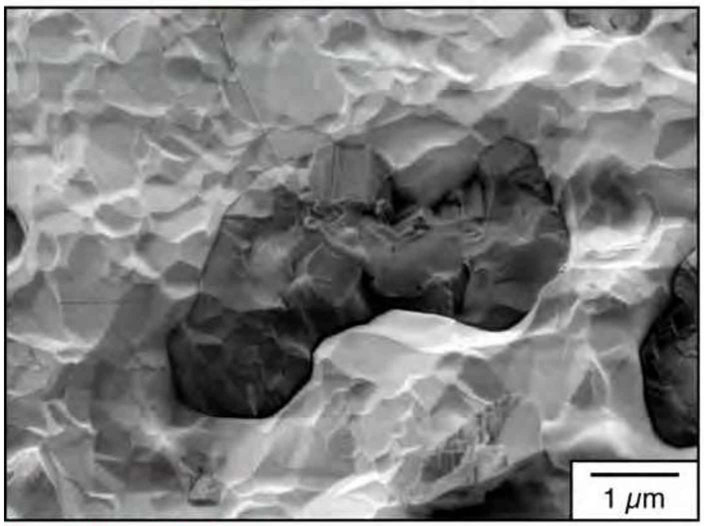
Chemical heterogeneities result in potential thermo-mechanical drivers for interfacial failure



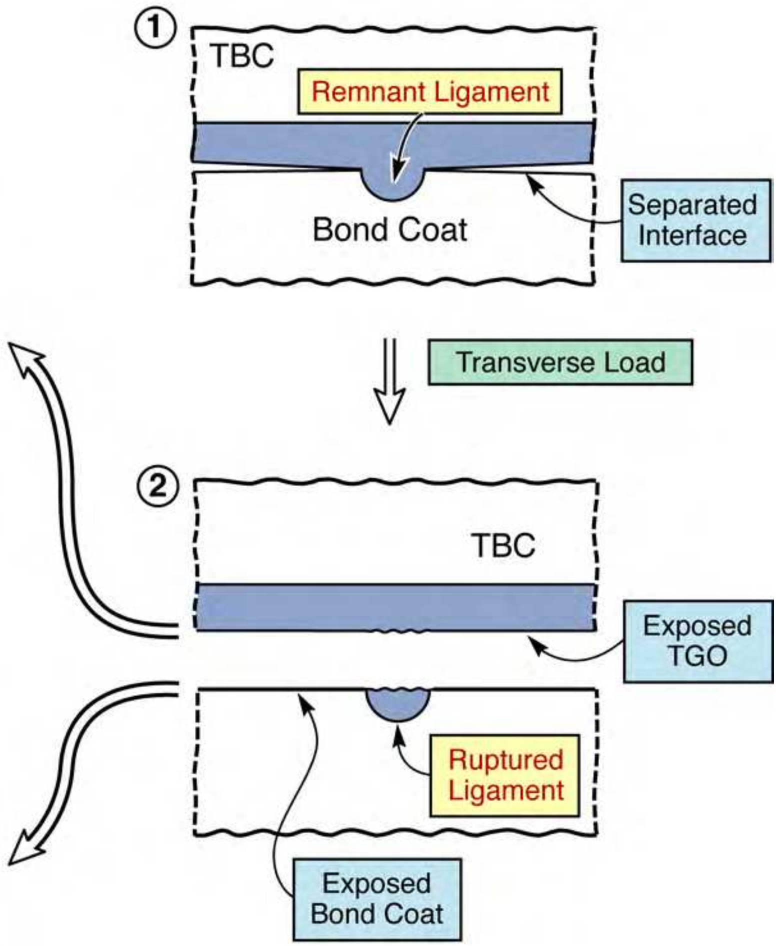
Role of Thickness Heterogeneities – Pinning?



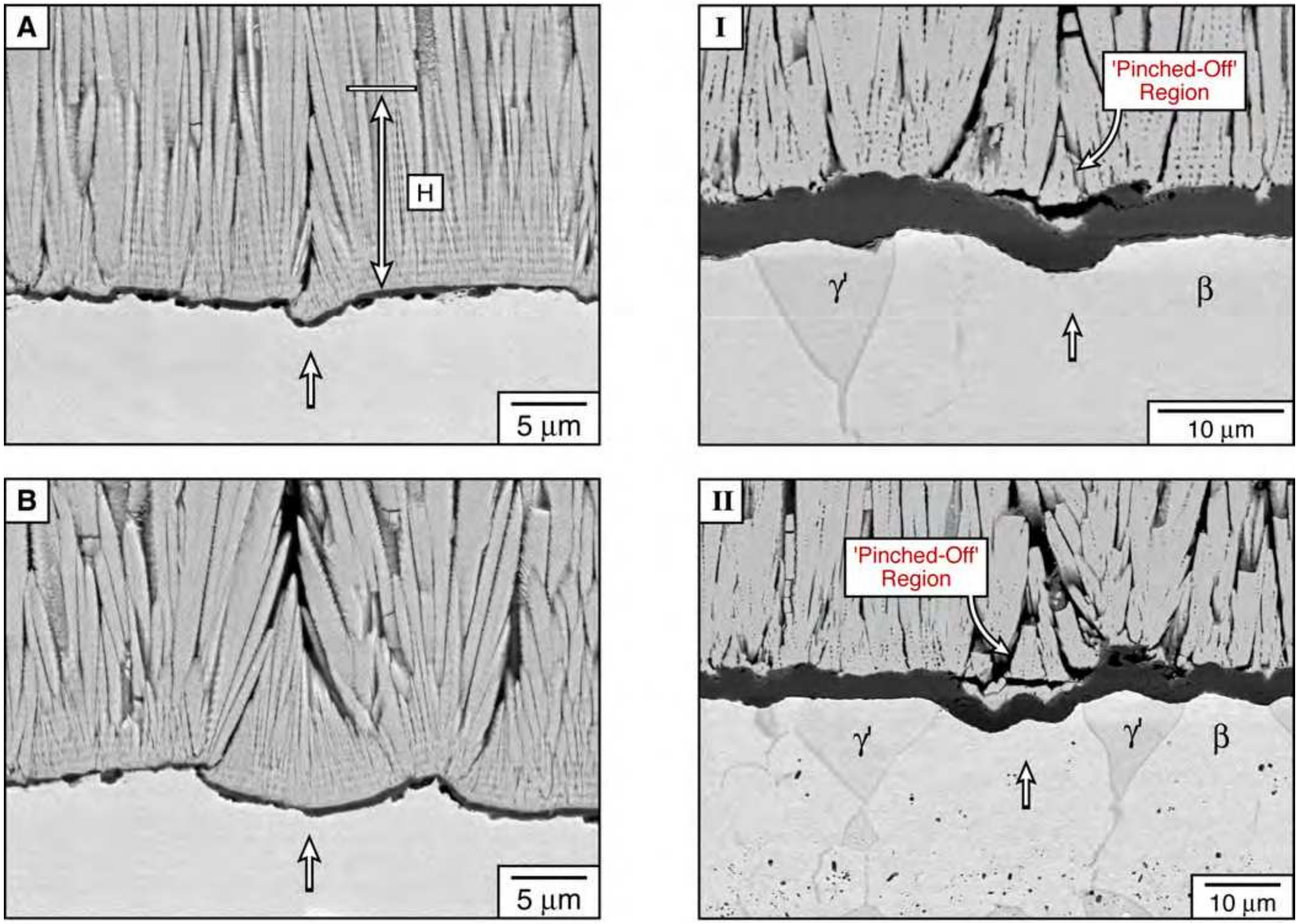
Underside of Spalled Oxide



Bond Coat Surface



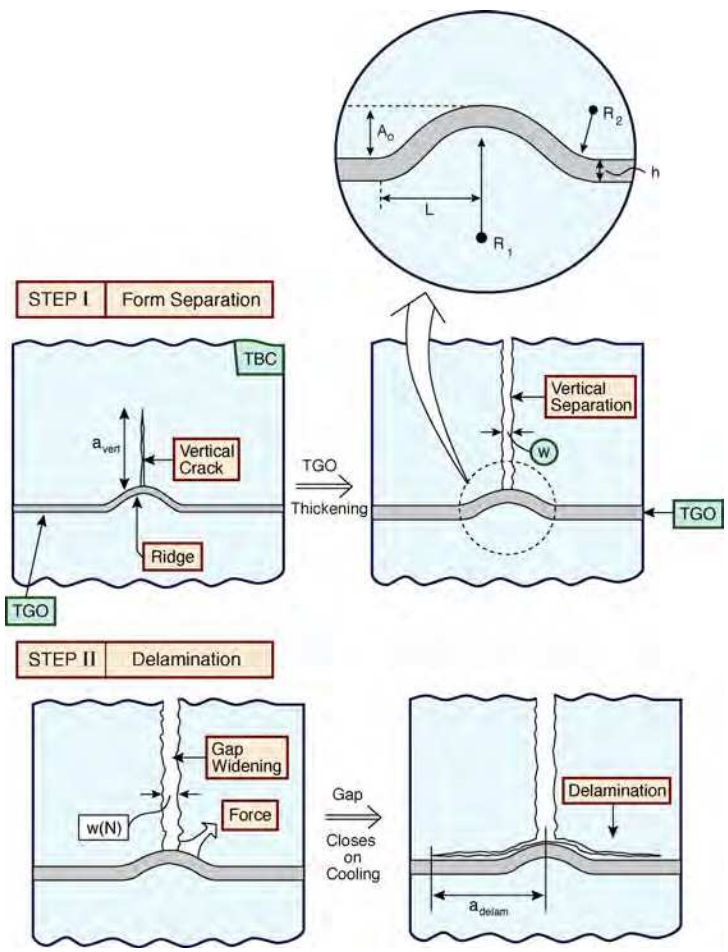
Initial Imperfections and Crack Nucleation Sites

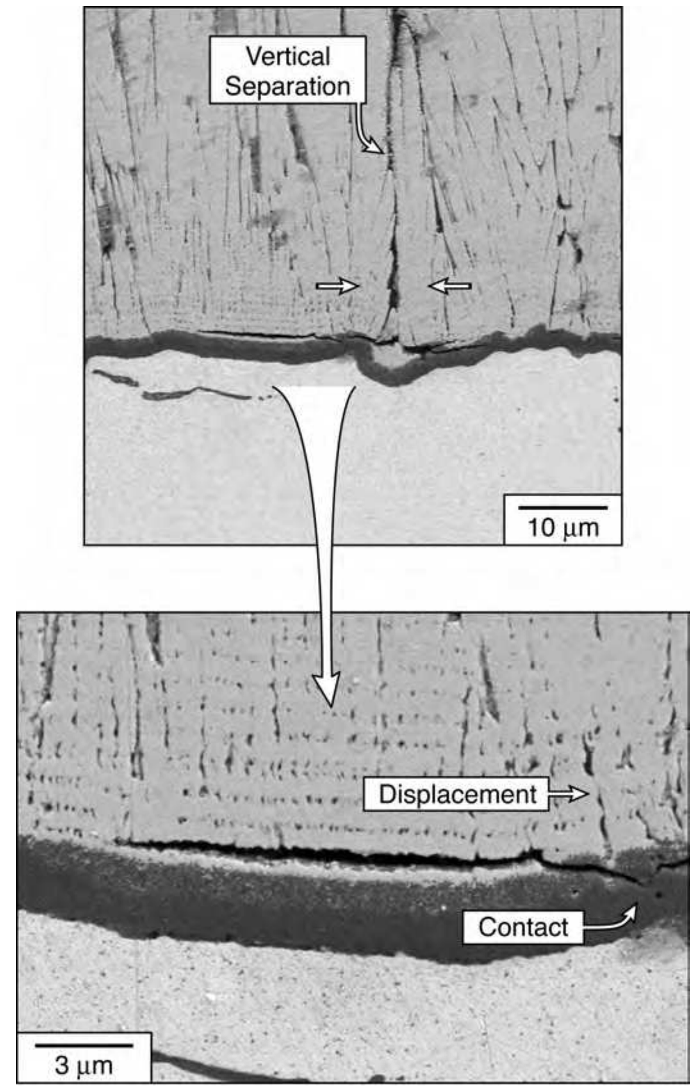


Cracking at interfaces between metals and porous ceramics initiates at pre-existing morphological features.

D.R. Mumm, A. G. Evans and I.T. Spitsberg (2001), Acta Materialia, 49, 2329-2340

Thermo-Mechanical Drivers for Coating Failure – Processing Defects

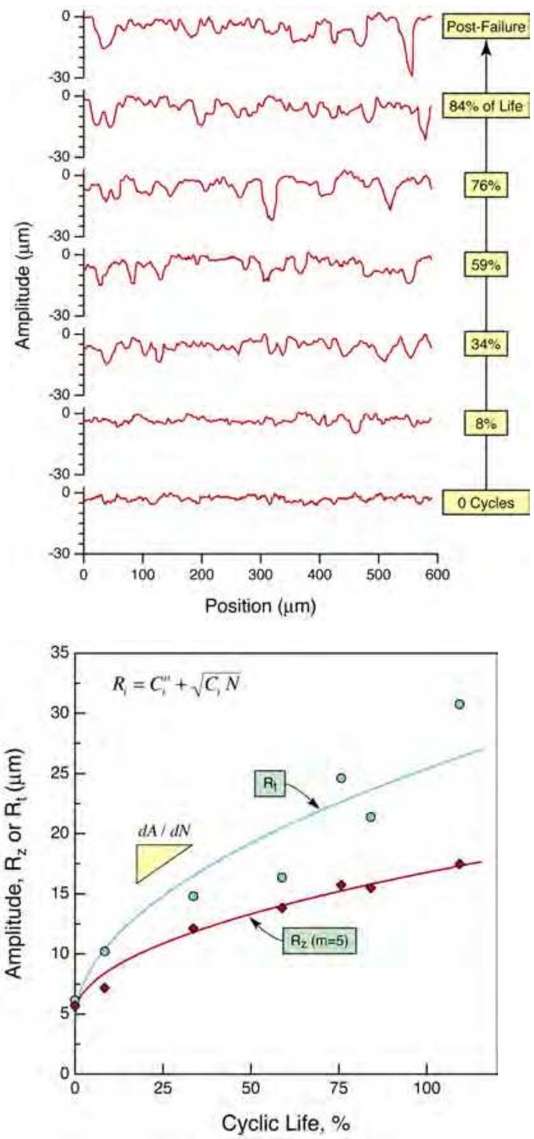


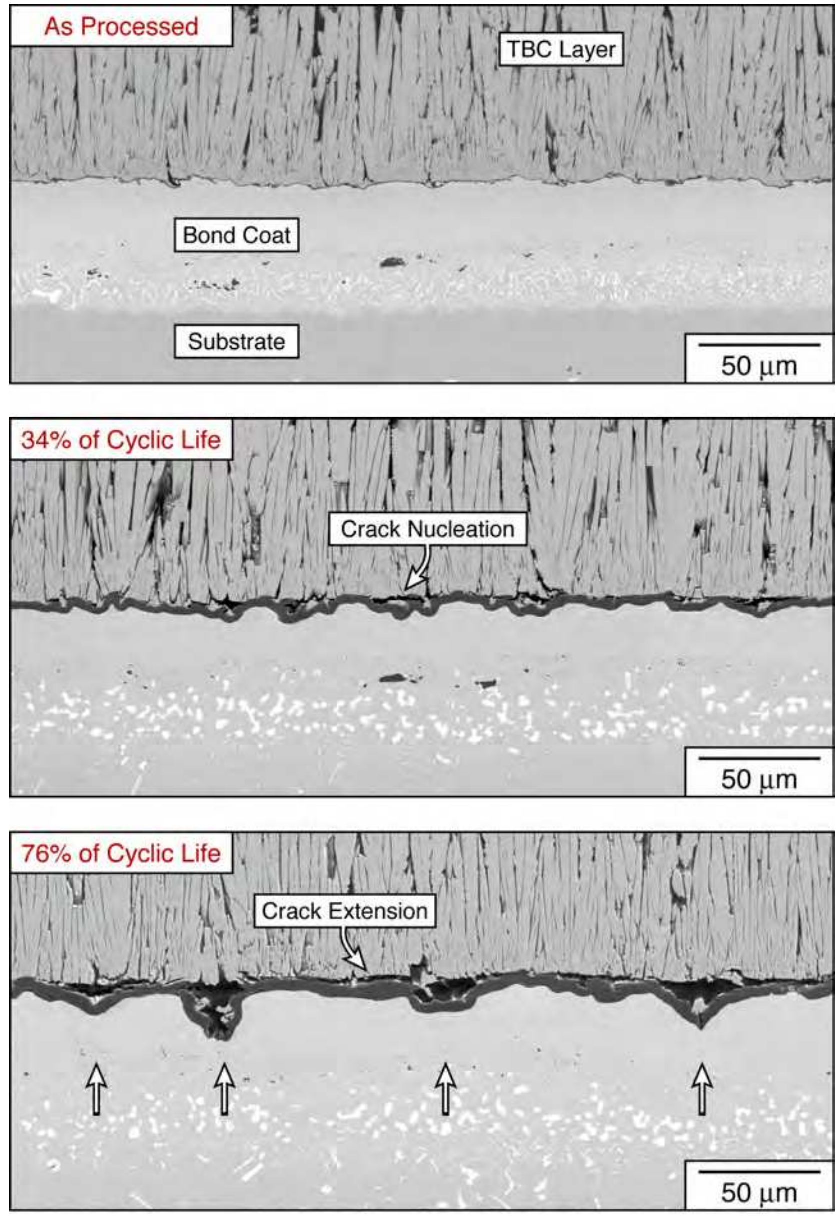


He, Mumm and Evans, Surface and Coatings Technology, 185, 184-193 (2004)

Materials Evolve in Service: Incubation Time for Observable Failure

Mumm, Evans and Spitsberg, Acta Materialia, 49, 2329 (2001)





Alternative Fuels in Turbine Engine Systems

Transitions to Alternative Fuels

- Drivers for transition
- General considerations from Power Generation Systems perspective
- Domestic supplies of fuels for power and propulsion
- Potentially more control over compositional consistency

Potential Impacts of Alternative Fuels on Materials Stability

- Effects on TGO development (thermo-chemical)
- Impacts on TBC stability (thermo-chemical, thermo-mechanical)
- Non-intuitive contaminant sources associated with Alt Fuels
- Altered combustion product streams
- Characteristic non-combustibles and residual ash
- Fuel additives that are unique to a particular fuel type

Experimental Methodologies and Studies

- Deposit formation and infiltration
- Oxidation in elevated water vapor content
- Efforts to isolate correlations between water vapor and transport

Project Scope

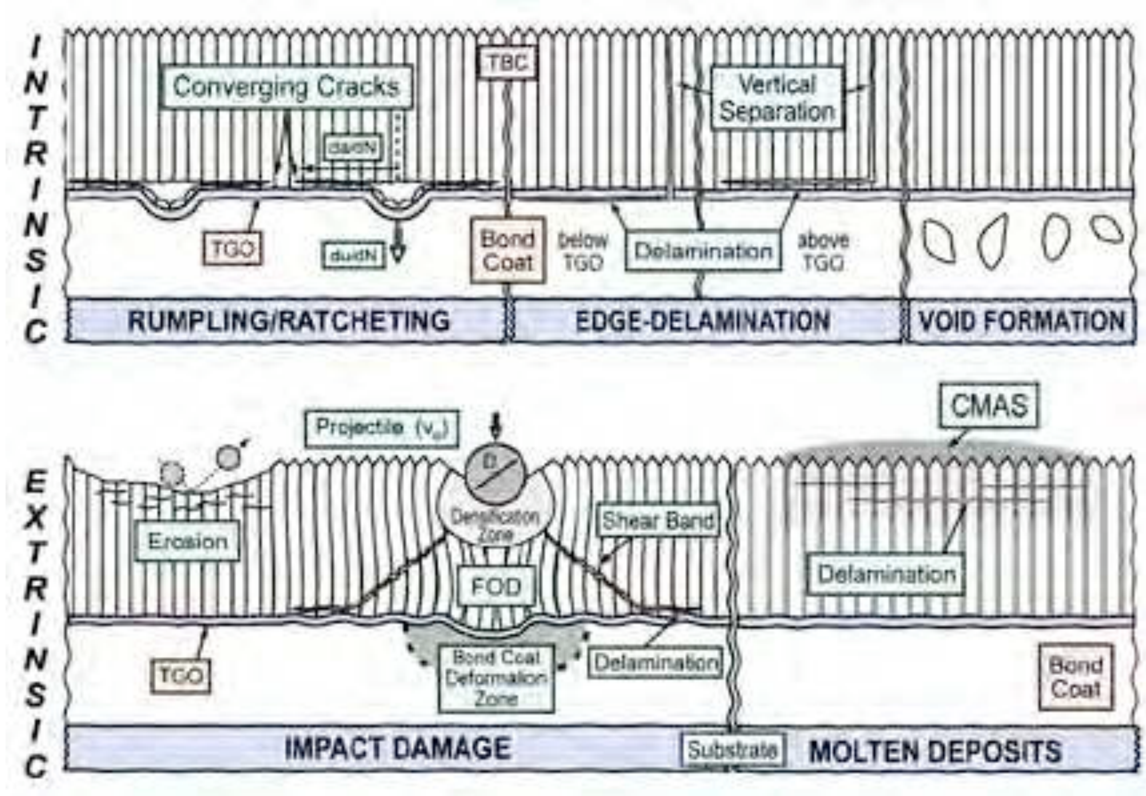
- **Project has an overarching goal of attaining a stable, durable TBC system for use in coal-derived syngas and HHC environments.**
- To achieve this goal, the project is organized around six inter-related themes:
  - Evaluating the role of HHC combustion in modifying hot-section component surface temperatures, heat transfer, and resulting thermal gradients within the TBC coatings.
  - Understanding the instability of TBC coatings in syngas and high hydrogen environments, with regards to decomposition, phase change and sintering.
  - Characterizing ash deposition, molten phase development and infiltration, and associated corrosive / thermo-chemical attack mechanisms.
  - Developing a mechanics-based analysis of driving forces for crack growth and delamination, based on molten phase infiltration, misfit upon cooling, and loss of compliance
  - Understanding changes in thermally grown oxide (TGO) development associated with these emerging combustion product streams
  - Identifying degradation resistant alternative materials for use in mitigating the observed degradation modes.

Potential Challenges in Transitioning to Alternative Fuels

How is this behavior modified with adoption of alternative fuels or blends?

How prevalent are these damage mechanisms for power generation turbine systems in association with HHC fuels?

A.G. Evans (2007)



A.G. Evans, D.R. Clarke and C.G. Levi (2008)
Journal of the European Ceramic Society, 28, 1405-1419.

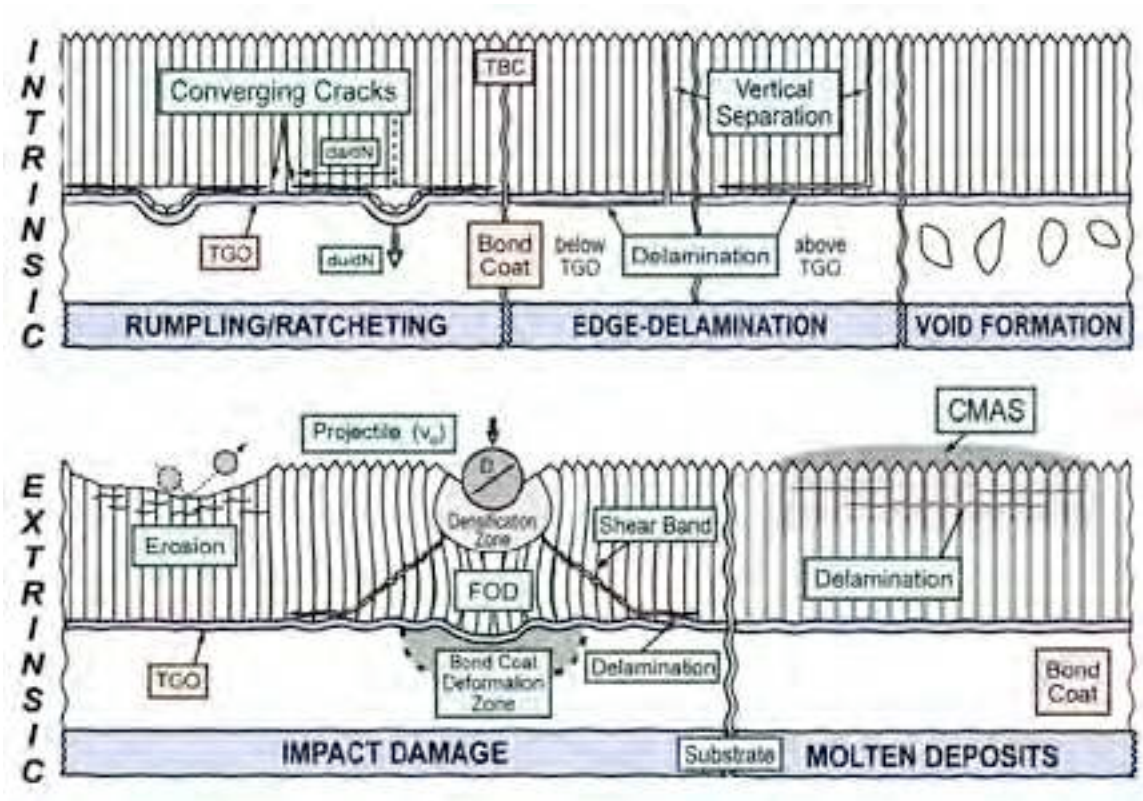
A.G. Evans, D.R. Mumm, J.W. Hutchinson, G. Meier and F.S. Pettit (2001)
Progress in Materials Science, 46, 505-53.

Deposit Formation and Infiltration

A.G. Evans (2007)

Deposit Formation

What potential analogies to CMAS degradation arise with use of syngas or HHC fuels and intrinsic combustion by products
?



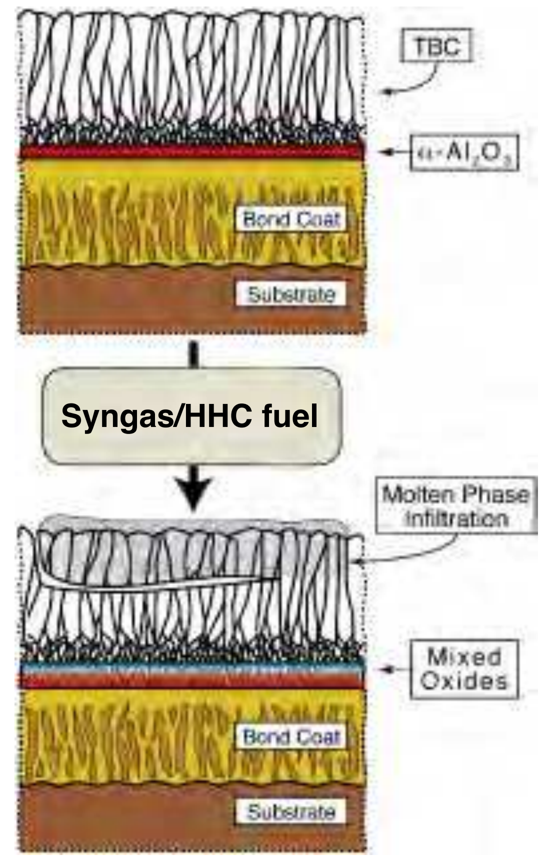
What are the Potential Impacts of Alternative Fuels?

- May have unique impurities and non-combustibles
  - Metal cation incorporation with various fuel storage possibilities?
  - Metals inherent in fuel source? Fe_2O_3, SiO_2
  - FT fuels normally considered "perfectly clean"

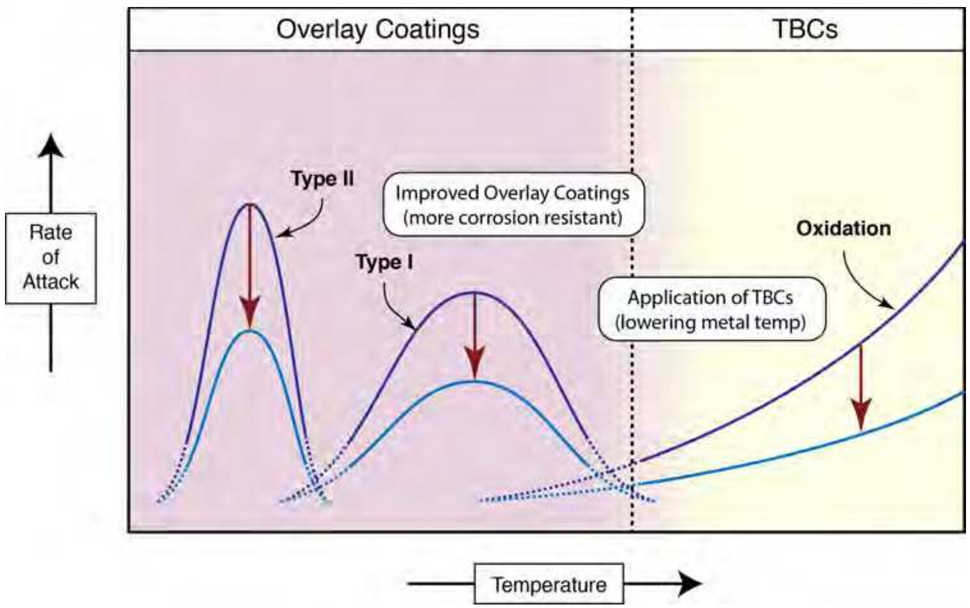
- May modify the combustion environment
  - high temperatures
  - modified partial pressures of gas species? (water vapor, oxygen, hydrogen)
  - modified heat transfer characteristics to surfaces?

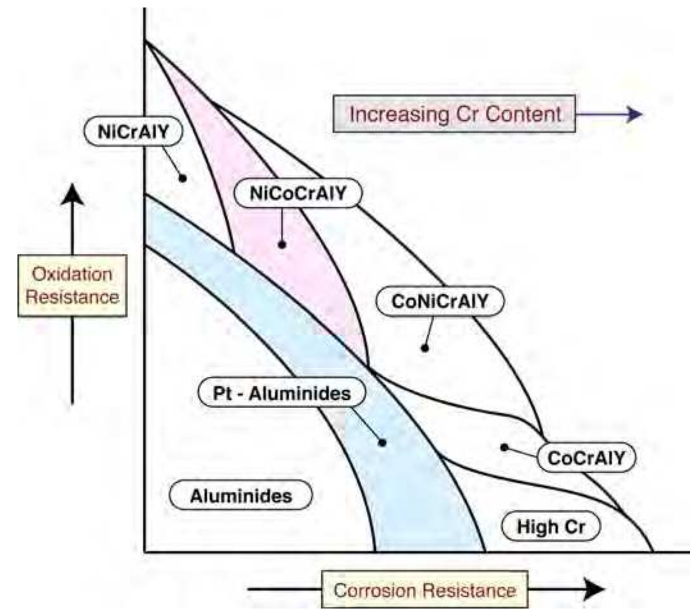
- May be 'seeded' with catalysts, etc

- May have different additives
  - Anti-icing compounds
  - Anti-bacterial compounds
  - Copper additives



Degradation of Hot-Section Materials





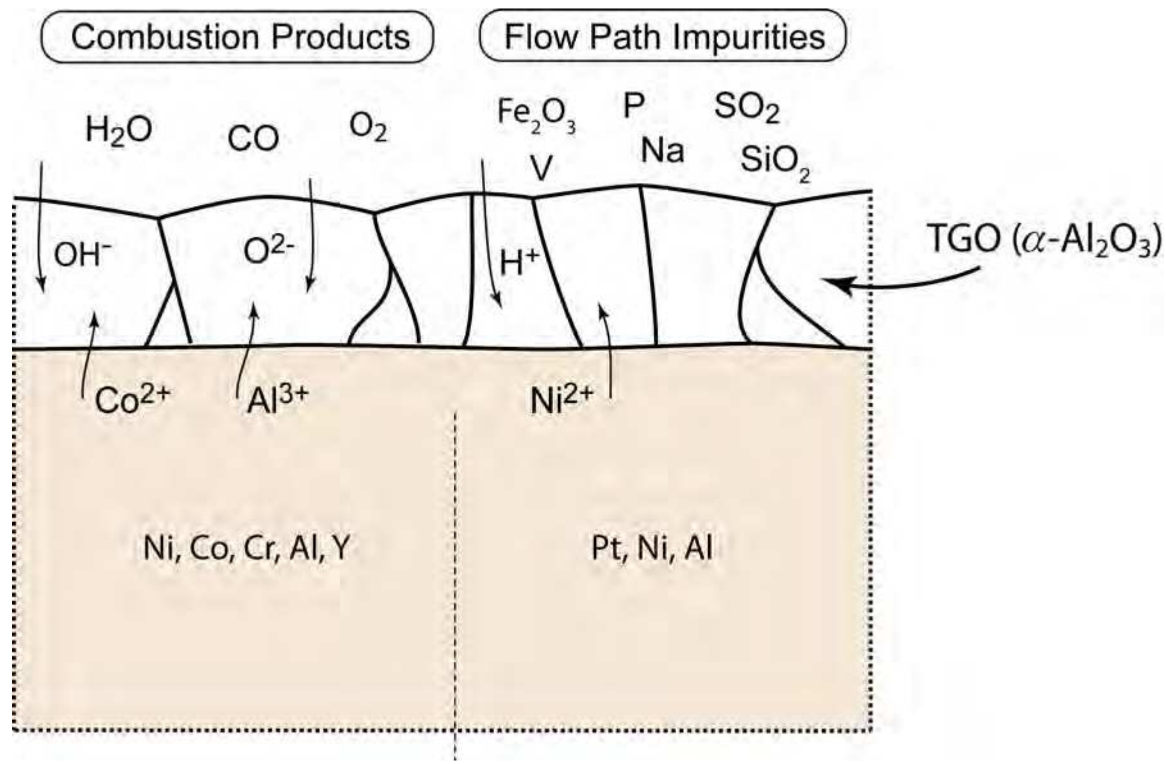
How is this behavior effected by alternative fuels?

What can be expected in TBC coatings are utilized in emerging combustion environments systems?

Candidate Synthetic and Bio-Derived Fuels

Ideal:

Fischer-Tropsch



Realistic:

Algae-Derived

Camolina-Derived

BioMass-Derived

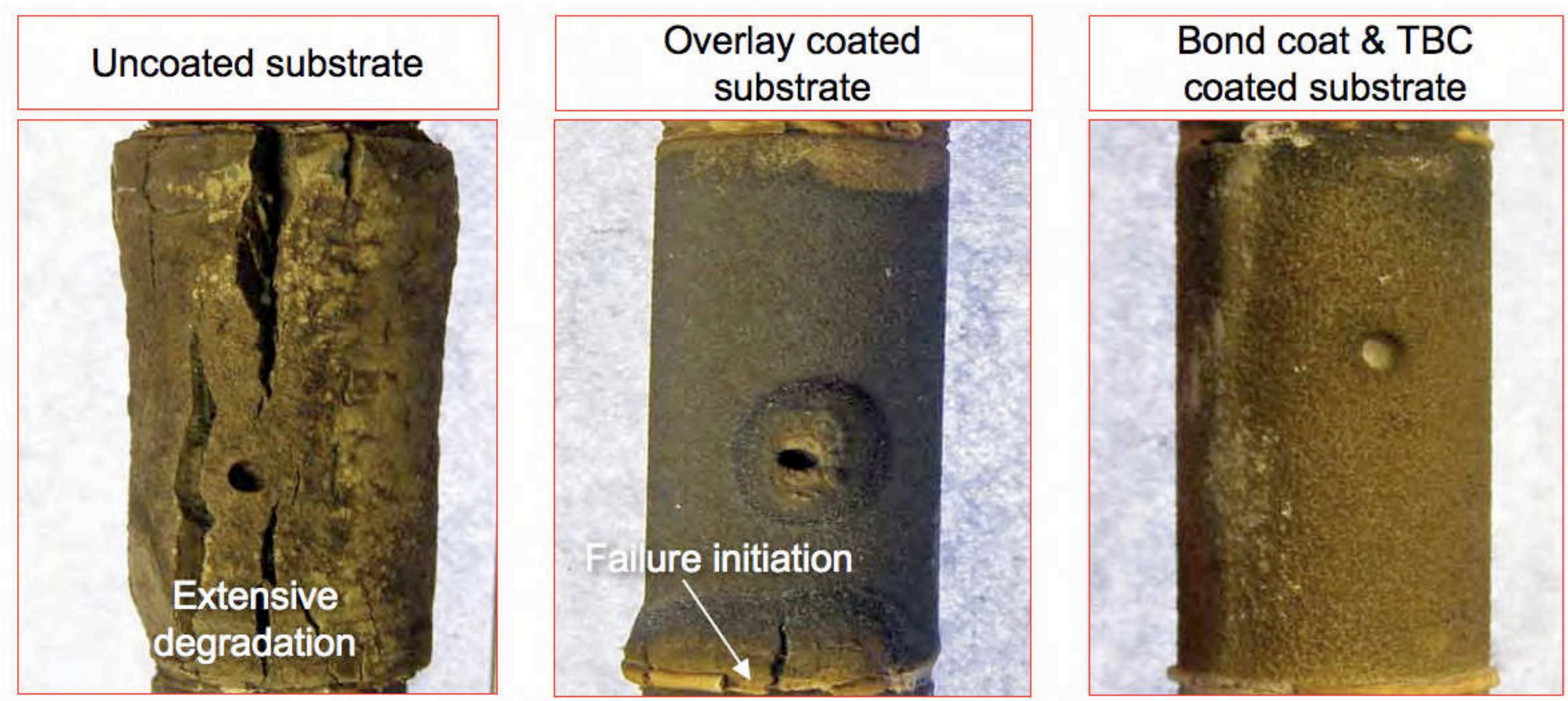
Coal-Derived Syngas

Potential Ash Constituents – Alternative Fuels

Component (wt %)	Fly Ash Type		
	Typical Coal	Synthetic Coal	Biomass (Pulverized Wood)
SiO_2	40.0	55.0	14.1
Fe_2O_3	17.0	10.0	2.7
Al_2O_3	24.0	25.0	2.9
CaO	5.8	5.0	20.7
Na_2O	0.8	1.0	1.0
K_2O	2.4	1.0	8.1
MgO	> 0.2	> 0.2	4.0

- Not clear what to expect in terms of impurities/non-combustibles associated with alternative fuel blends
- However, **ppm levels are sufficient** to degrade materials durability and lower duty cycle lifetime

Materials Durability Issues Arising w/ Alternative Fuel Combustion

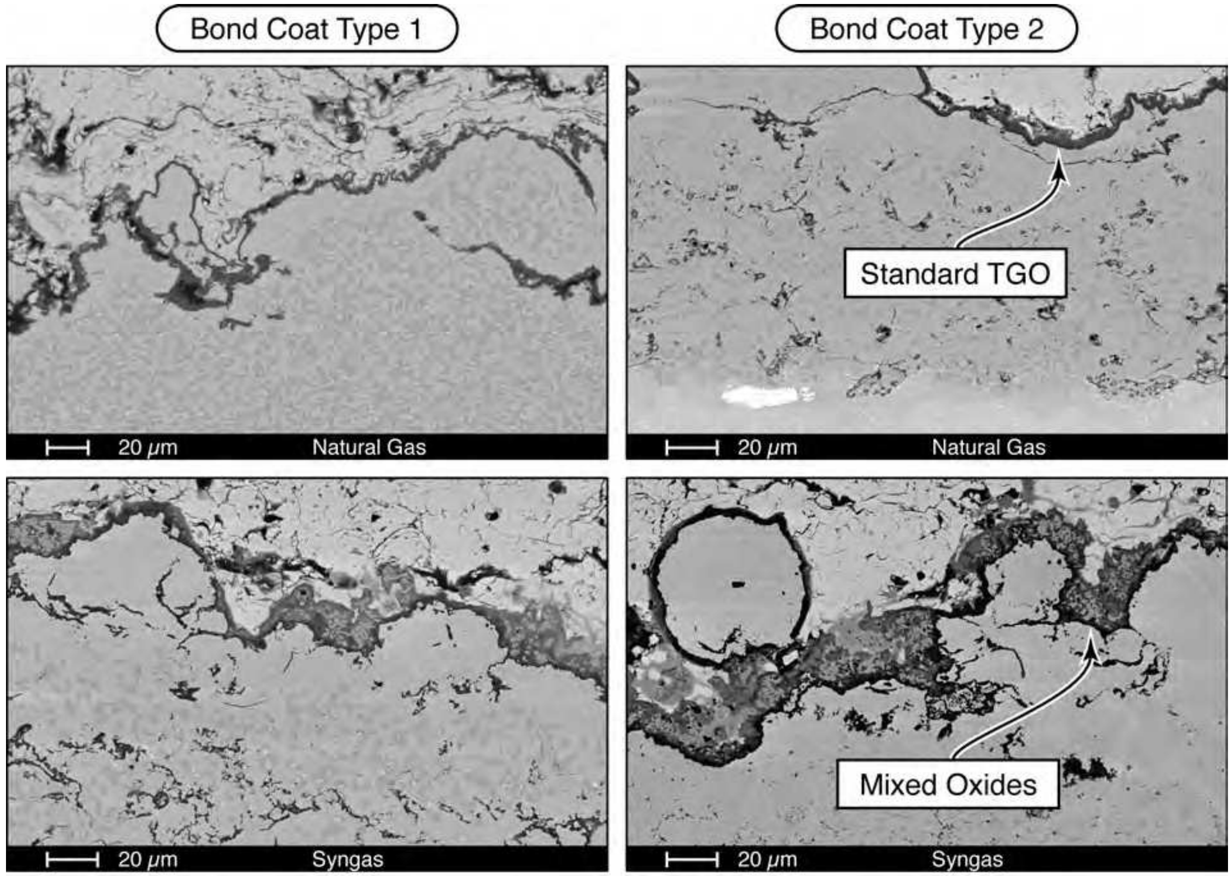


- Test coupons were exposed to simulated power generation turbine combustion environments, utilizing syngas blends in place of natural gas.
- Severe and unexpected materials degradation was observed.

Oxide Formation Under the TBC with Fuel Variation

Natural Gas

Syngas Blend



- Note location of new (spinel) phases – above the alumina
- Requires Ni transport **through** the alumina layer…

Synthetic Fuels and the Combustion Environment

		Volume Fraction					
Fuel	**Temp (°C)**	**O_2**	**H_2O**	**CO_2**	**H_2**	**CO**	**CH_4**
CH_4	1538	0.104	0.068	0.083	3.14×10^{-7}	8.43×10^{-6}	4.07×10^{-25}
Solar #10	1538	0.109	0.078	0.085	3.60×10^{-7}	8.57×10^{-6}	5.31×10^{-25}
HHC (H_2)	1538	0.126	0.115	0	5.04×10^{-7}	0	0

**chart courtesy the McDonnell group*

~21% higher than in natural gas

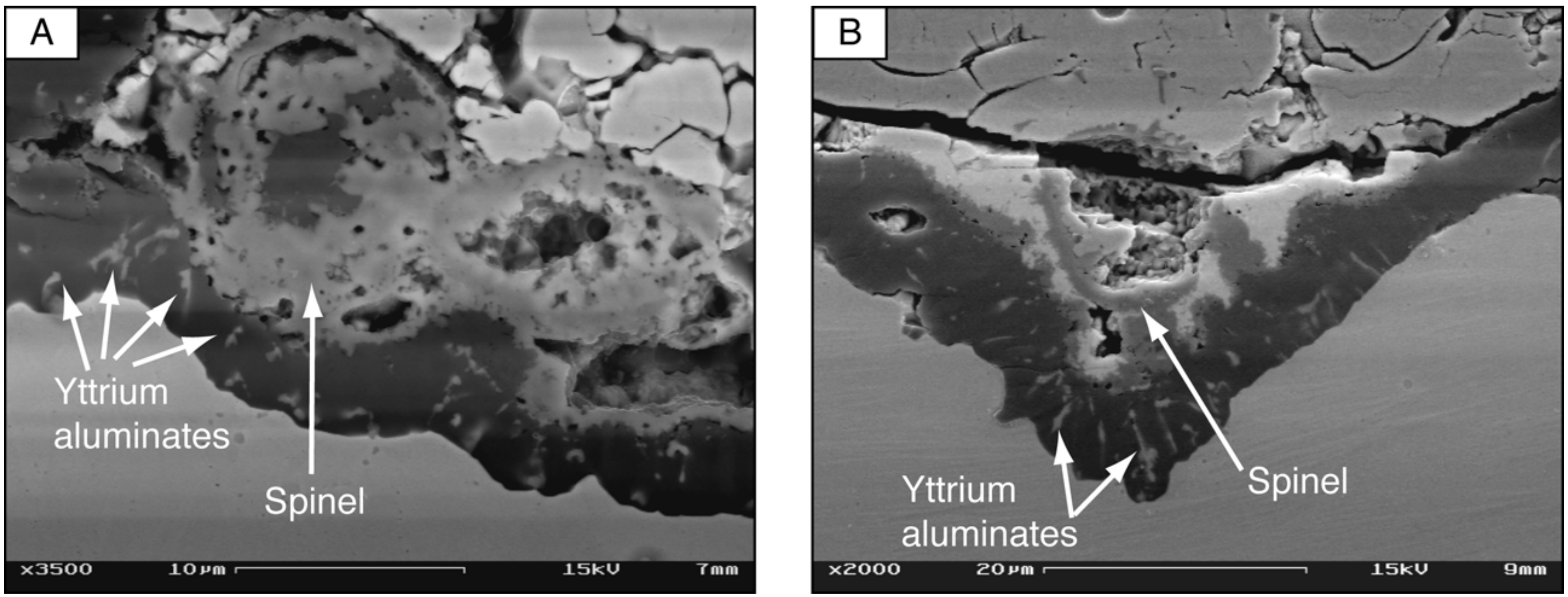
Nearly 70% higher than in natural gas

Combustion flow paths constituents and concentrations vary greatly with fuel composition. Many candidate alternative fuels induce high water vapor content.

Non-Ideal Oxide Formation: Thermo-Mechanical Implications

So why are we concerned with external spinel formation?

Spinel Formation in Plasma Sprayed TBCs
Preferential Crack Propagation Pathways



A. Rabiei and A.G. Evans (2000), Acta Materialia, 48, 3963-76.

Project Scope – Technical Approach

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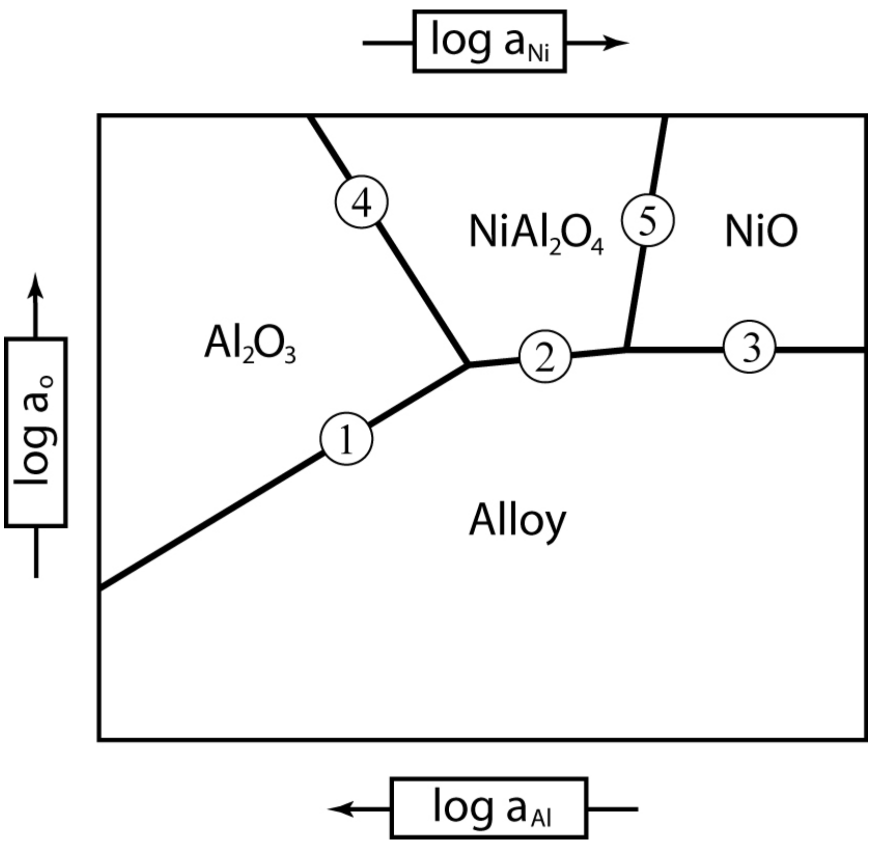
Thermodynamic Assessment of Oxide Development

- Schematic Thermodynamic Stability Diagram – Ni-Al-O system
- Boundaries represent various equilibrium reactions



① $$2Al + 3O \rightleftharpoons Al_2O_3$$

② $$Ni + 2Al + 4O \rightleftharpoons NiAl_2O_4$$

③ $$Ni + O \rightleftharpoons NiO$$

④ $$Al_2O_3 + 3Ni \rightleftharpoons 3NiAl_2O_4 + 2Al$$

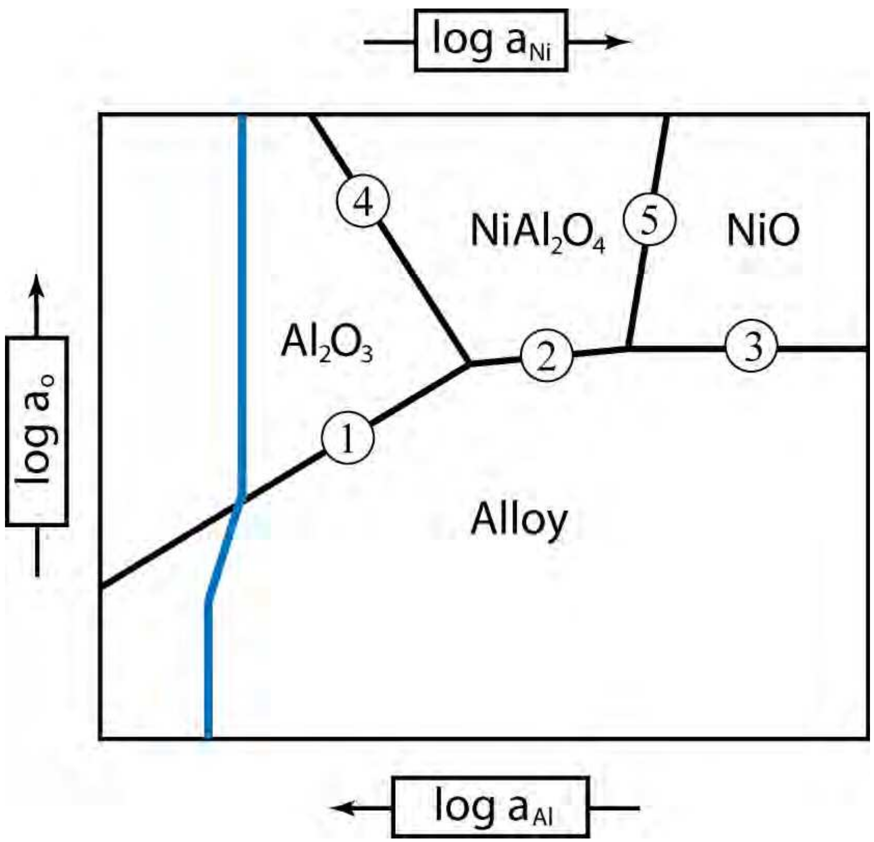
⑤ $$NiAl_2O_4 + 3Ni \rightleftharpoons 4NiO + 2Al$$

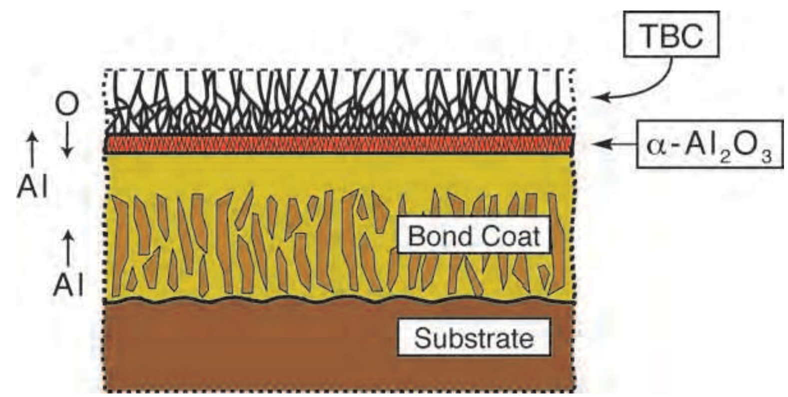
M.J. Stiger, N.M. Yanar, M.G. Topping, F.S. Pettit and G.H. Meier (1999) *Zeitshrift für Metallkunde*, 90 [12], 1069-1078.

A.G. Evans, D.R. Mumm, J.W. Hutchinson, G. Meier and F.S. Pettit (2001) *Progress in Materials Science*, 46, 505-53.

Thermodynamic Assessment of Oxide Development

- Mechanistic description of ‘pure’ alumina TGO formation





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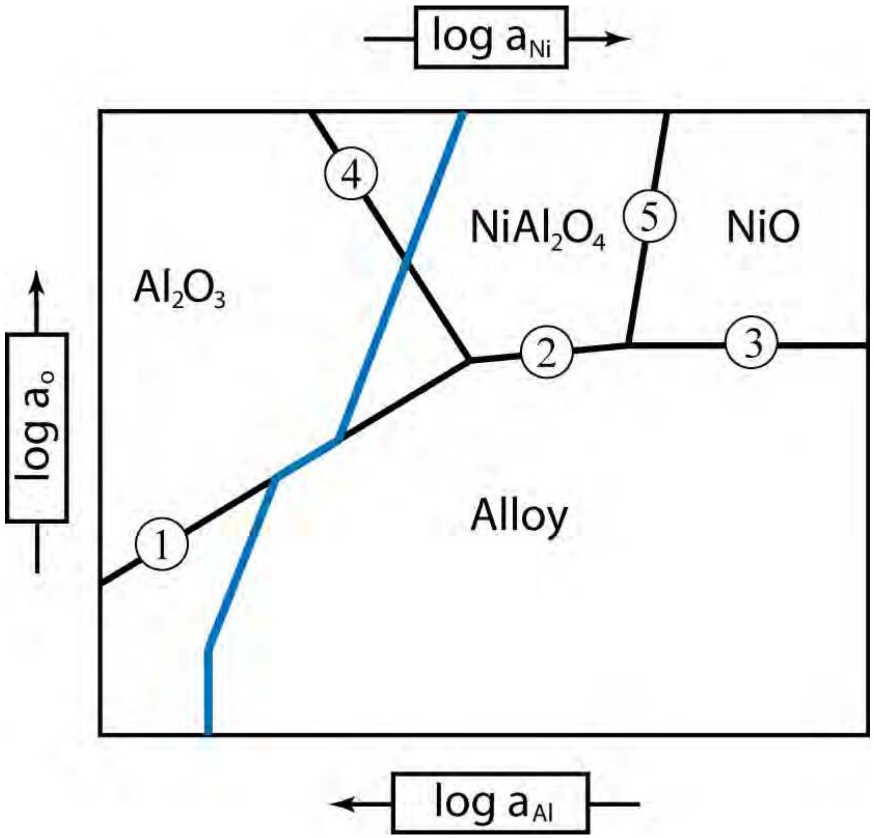
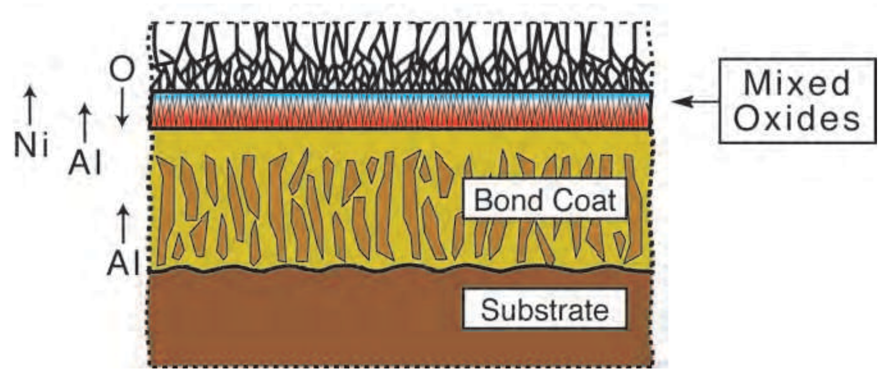
Thermodynamic Assessment of Oxide Development

- Mechanistic description of bilayer TGO formation (with spinel formation)

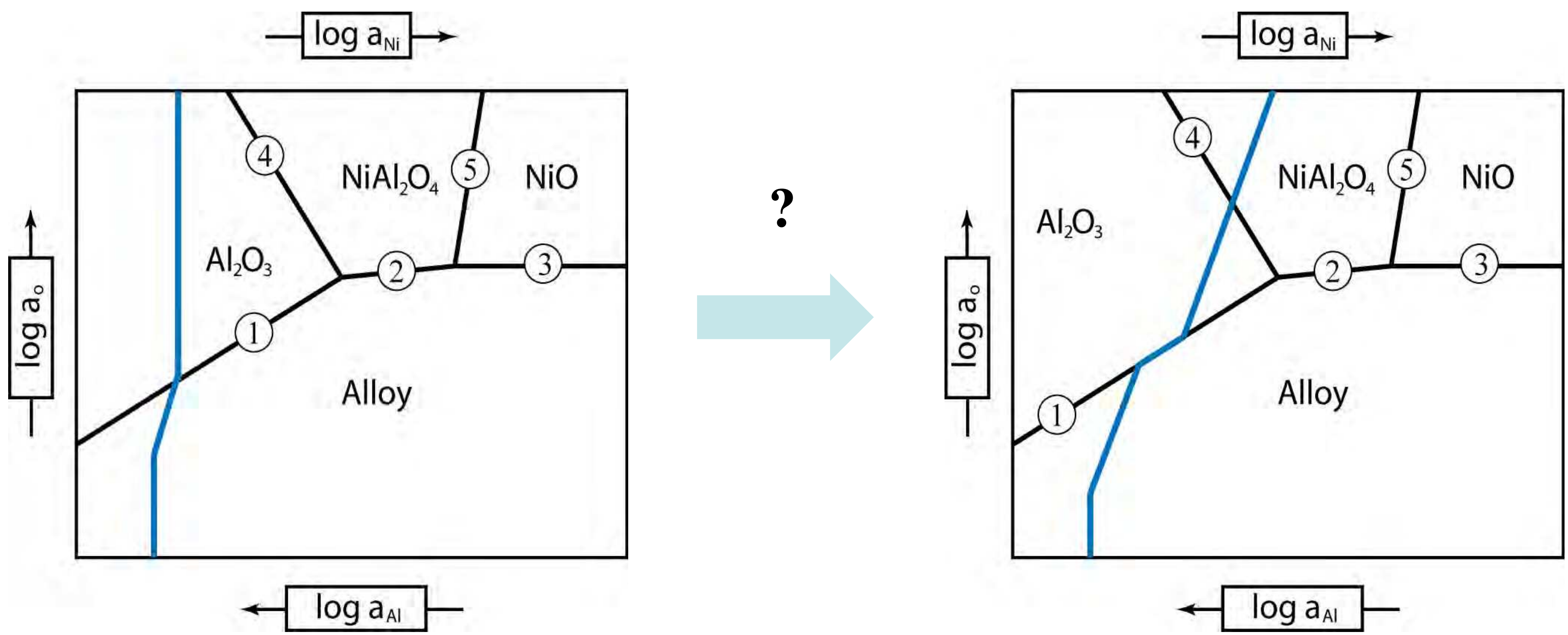




- **Nickel diffusion through alumina**
- **Enhanced solubility/transport**

M.J. Stiger, N.M. Yanar, M.G. Topping, F.S. Pettit and G.H. Meier (1999) *Zeitshrift für Metallkunde*, 90 [12], 1069-1078.

Effect of Alternative Fuels on Oxide Development

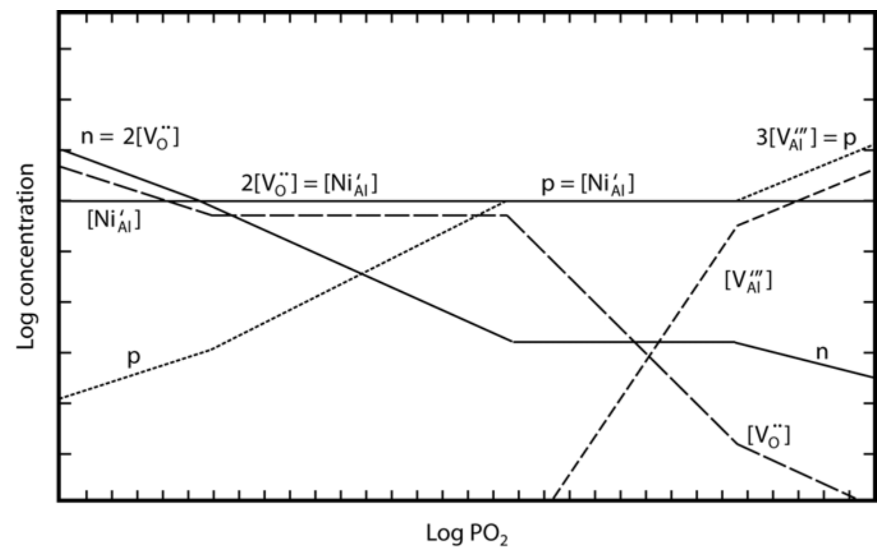


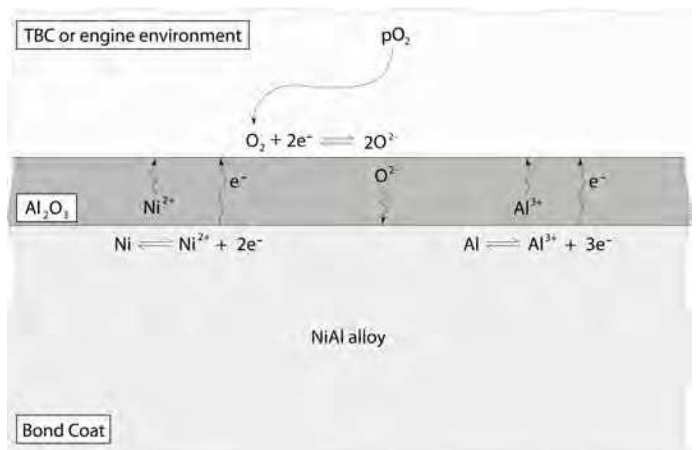
- Modification of the combustion environment alters reaction kinetics
- Dependence on partial pressures of gas stream constituents

Ni Activity and Undesirable Phase Formation (Spinel)

- Activity of Ni and Al vary with combustion conditions
- Defect populations change with oxygen/hydrogen partial pressures

Brouwer Diagram

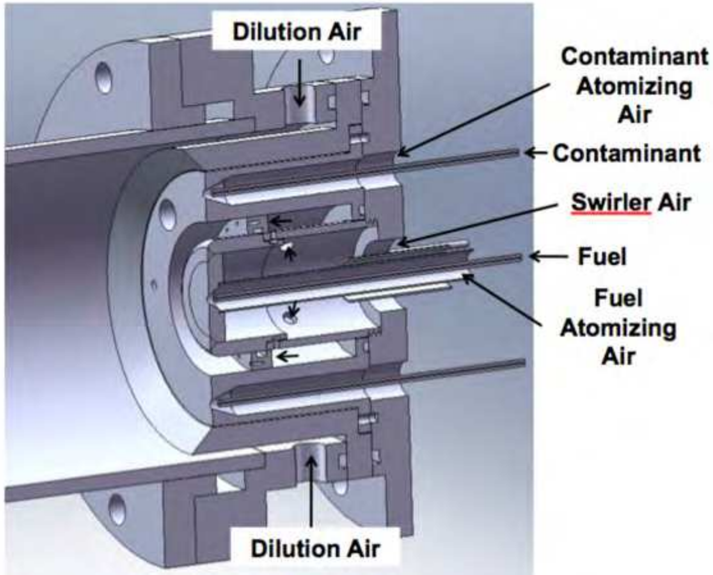




Approach: Alternative Fuel Effects and Synergistic Effects with Ash

- **Controlled isothermal exposures to simulated combustion gases**
  - Varying partial pressures of combustion products
  - Varying water vapor contents
- **Extended thermal exposures with ash constituents**
  - Exploration of molten phase formation, composition, and infiltration
  - Exposure to relevant impurities
  - Synergistic effects of water vapor content
- **Low velocity, low pressure burner rig testing**
  - Evaluation of deposit formation
  - Seeding with impurities, additives, etc
- **Examination of hardware removed from field service**
  - Compare and contrast power system hardware tested under Traditional and syngas/HHC combustion environments

Low Velocity Burner Rig Development – Alternative Fuels Evaluations



ONR Grant: N000141010591
Program Manager: D. Shifler

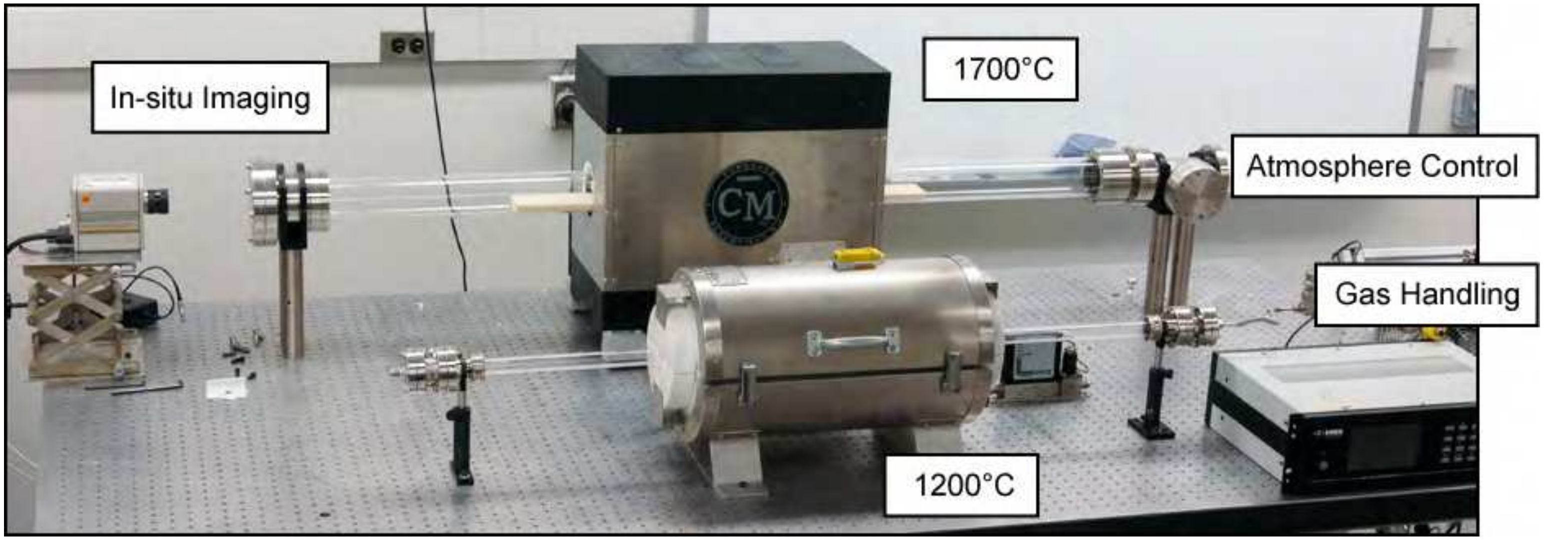
UC Irvine Combustion Laboratory (APEP)

Low Pressure Combustion Stand May Be Configured for Materials Exposure and Deposit Formation Studies

High Pressure Test Stand Also Available

Micro-Turbines May Also be Employed for Future Studies

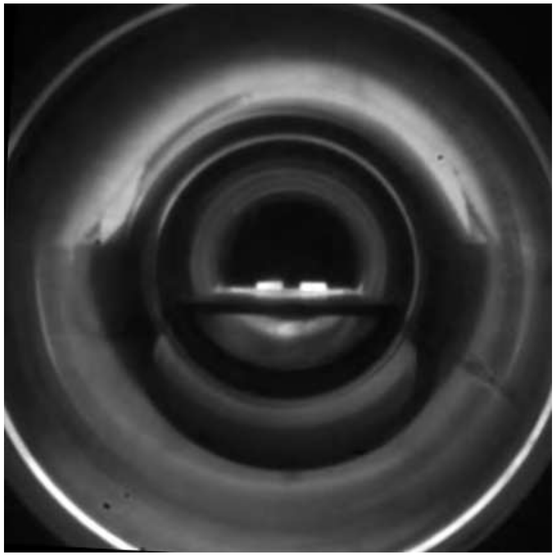
Controlled-Environment Tube Furnace Systems



Multiple Platforms for Controlled-Environment Thermal Exposure Now Being Configured

Controlled Water Vapor Content, Salt Exposures and Gas Mixtures

In-situ Imaging for Monitoring Melt Infiltration



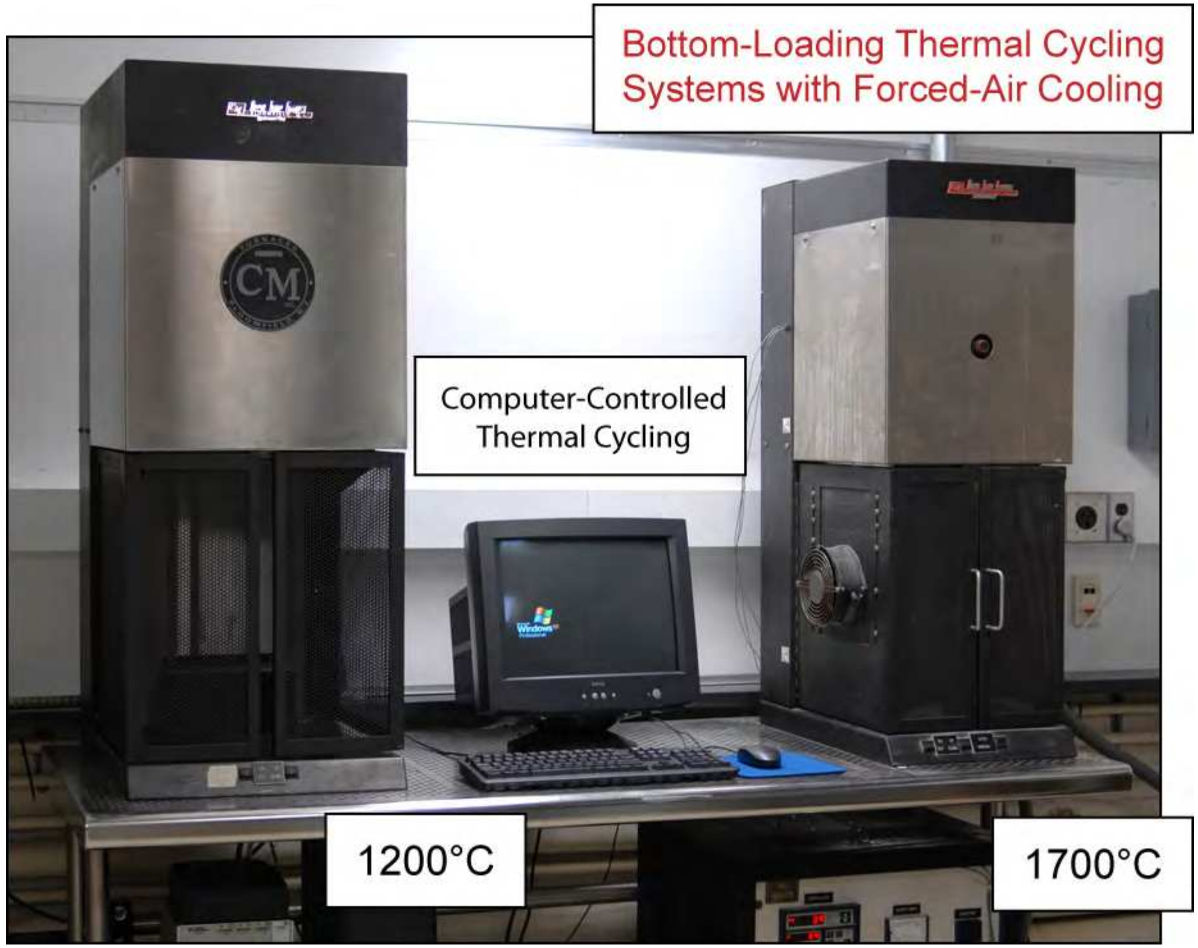
Thermal Cycling Furnace Systems

Multiple Platforms for Cyclic Thermal Exposure

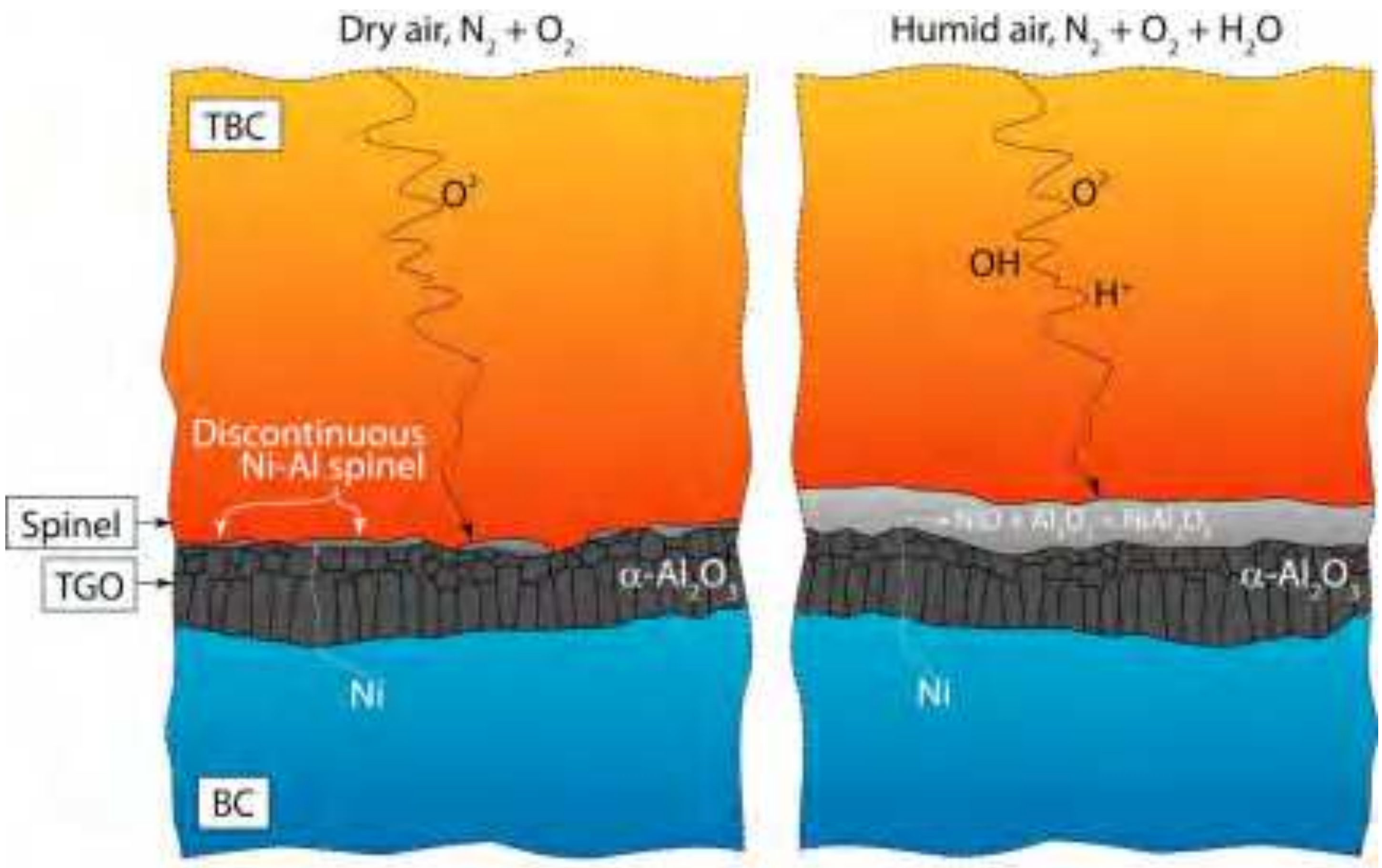
Developing a Thermal Gradient Specimen Rig

Forced-Air Cooling for Rapid Cycling

Computer-Controlled Temperature-Time History



Understanding Water Vapor Effects on Bilayer TGO Formation

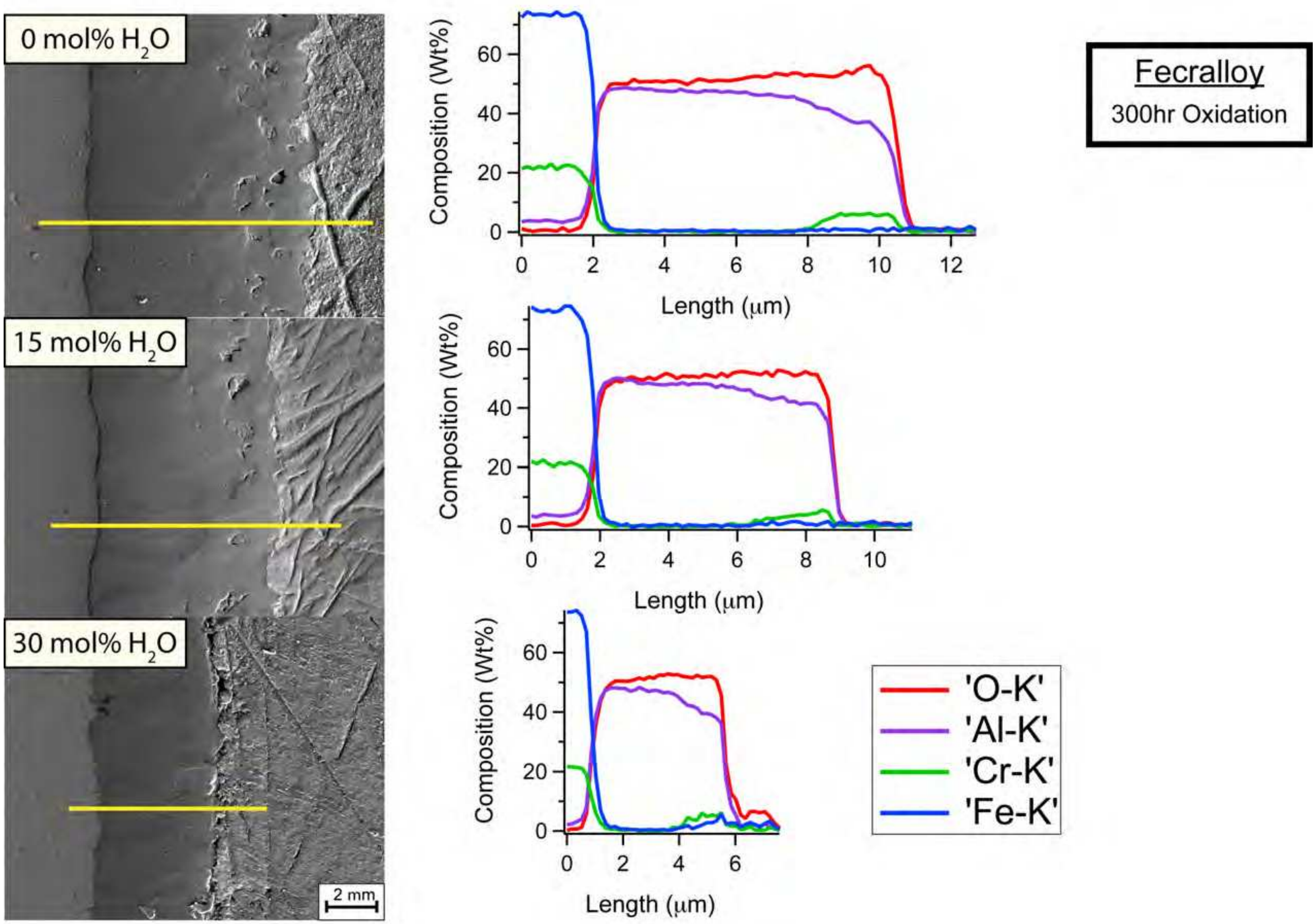


Investigations of TGO Growth: Function of Water Vapor

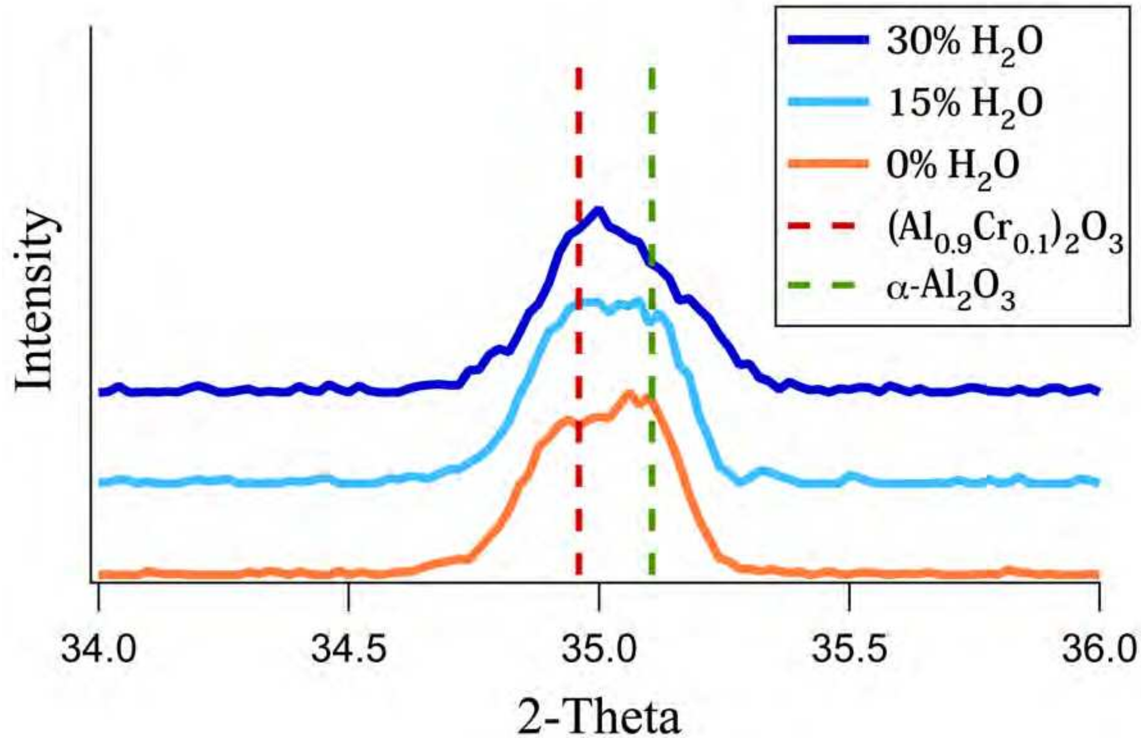
- Compared behavior of NiCoCrAlY and Pt-NiAl coated systems, as well as FeCrAlY
- Test matrix included YSZ TBC-coated samples of each bond-coat system
- Specimens exposed to varying water vapor content, and compared to dry oxidation
- All exposures involved total flow rates or 100 mL/min at 1 atm total pressure
- All exposures comprised 100 hours at 1125°C

	Input Gas Composition (mol %)		
	N_2	O_2	H_2O
Baseline	80	20	0
Humidity Level 1	74	18.5	7.5
Humidity Level 2	68.8	17.2	14
Humidity Level 3	61.6	15.4	23

Variation in Cr Incorporation

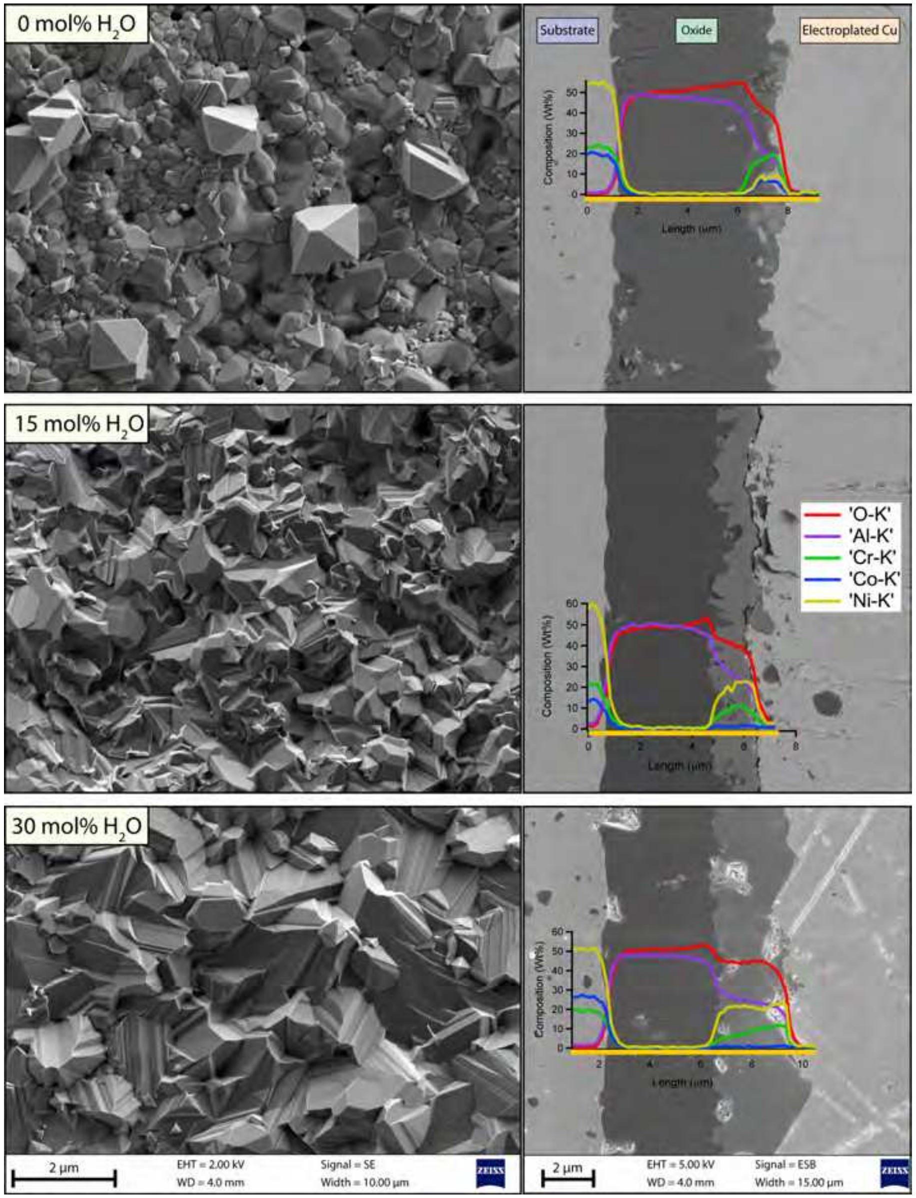


Variation in Cr Incorporation



Further inspection of α-alumina reveals a peak shift toward a Cr-doped phase as %H_2O is increased.

Extended Exposure to Varying Water Vapor Content



Surface images of oxidized NiCoCrAlY from 0% (top) to 30% H_2O (bottom)

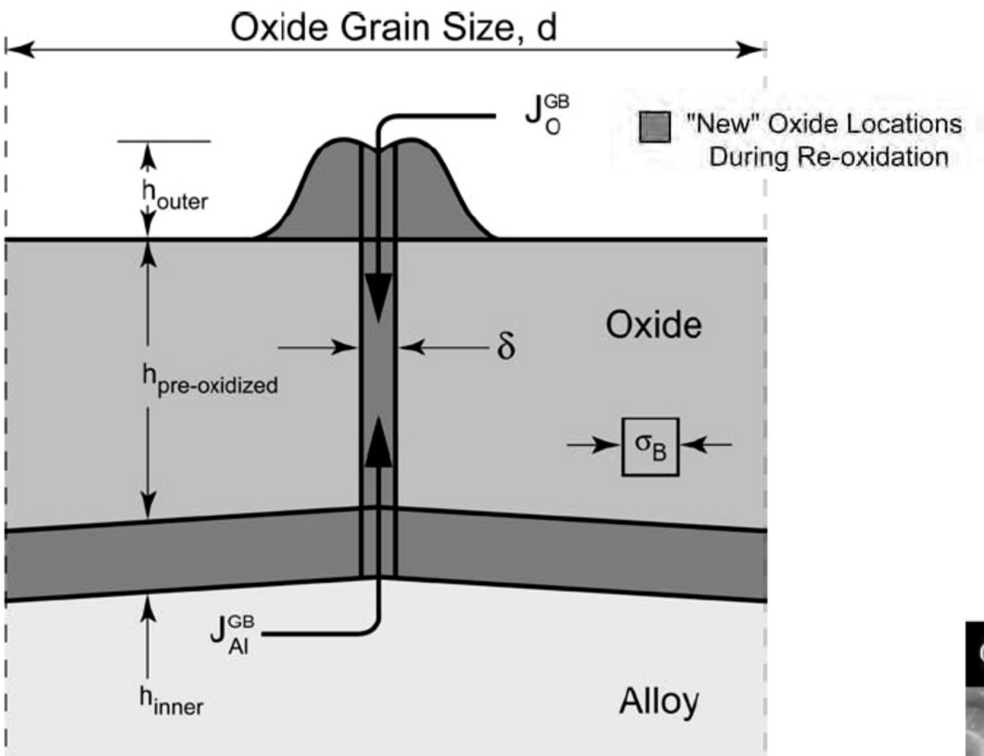
Spinel is diffuse at 0%; pervasive in elevated H_2O atm.

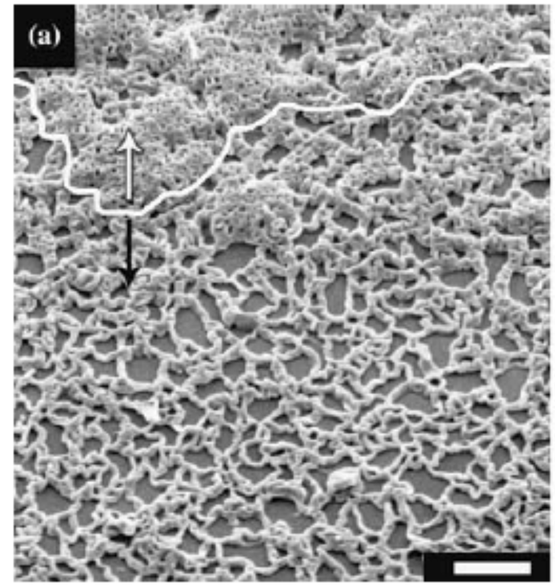
BSE images of corresponding cross-sections, showing phase contrast between alumina and spinel, but little difference in overall oxide thickness.

EDS maps indicate chemical composition in spinel layer; Ni diffusion appears consistently preferential to Cr diffusion in wet environments, whereas Cr diffusion is enhanced in a dry environment.

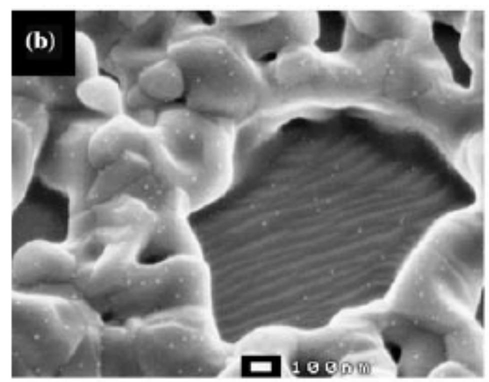
Taper Re-Oxidation Technique (Clarke, et al.)

J.A. Nychka and D.R. Clarke





Schematic of GBR formation: new oxide forms at alumina-atm and alumina-alloy interfaces according to ratio of magnitude of Al and O diffusion rates

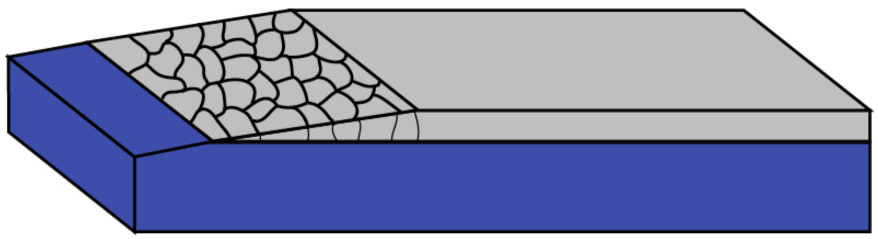


Wedge re-oxidation forms GBRs, pictured here at two different magnification factors

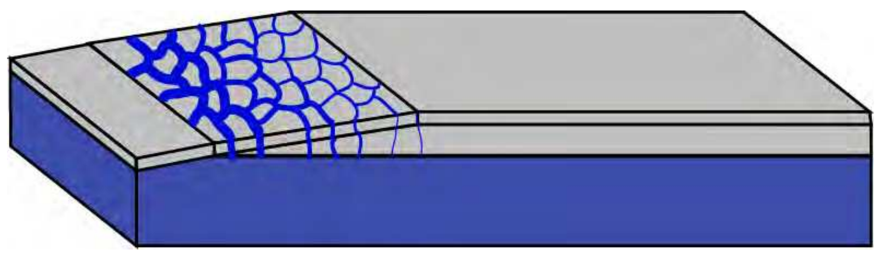
Taper Re-Oxidation Technique

I. Grow an initial oxide layer (25-50 hrs @ 1125ºC)

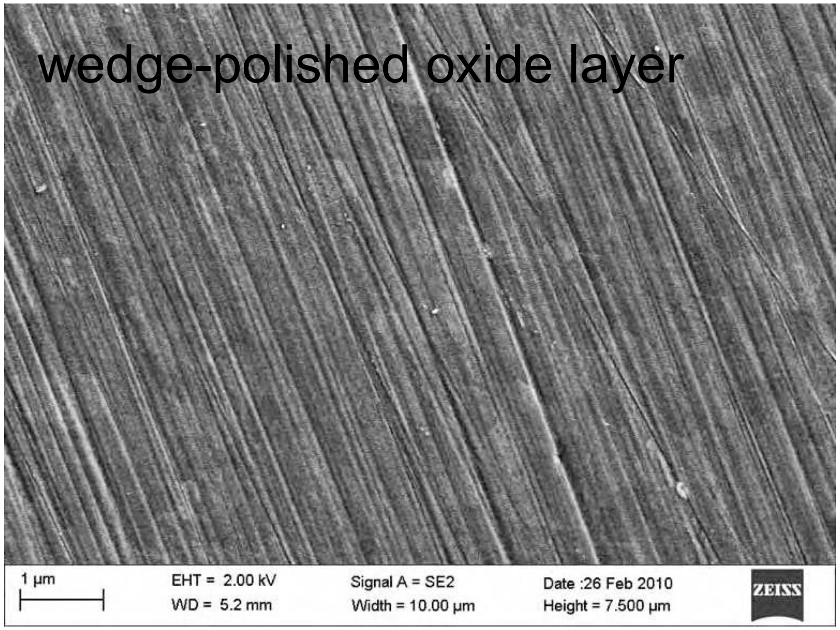
II. Polish at an angle (~0.1º) to create linearly variable diffusion lengths along the wedge

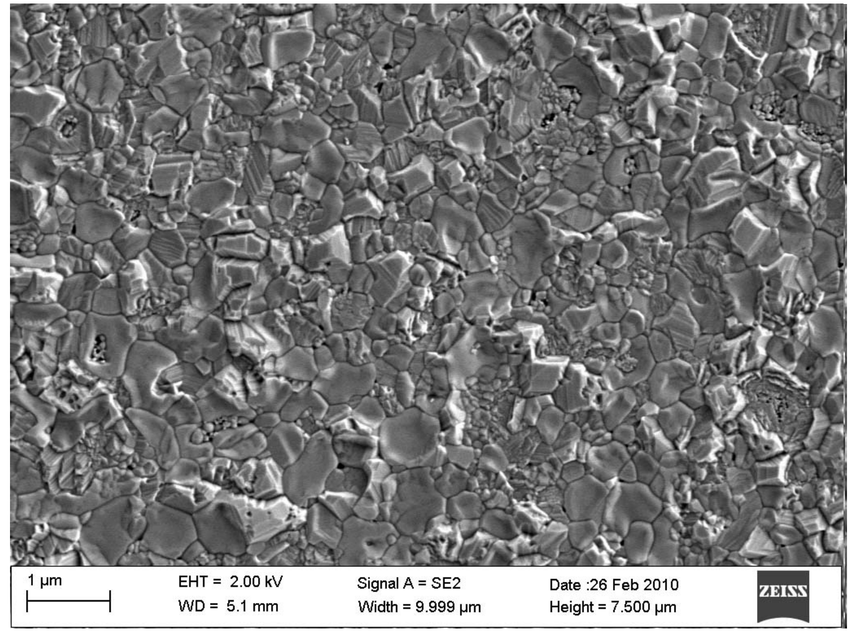


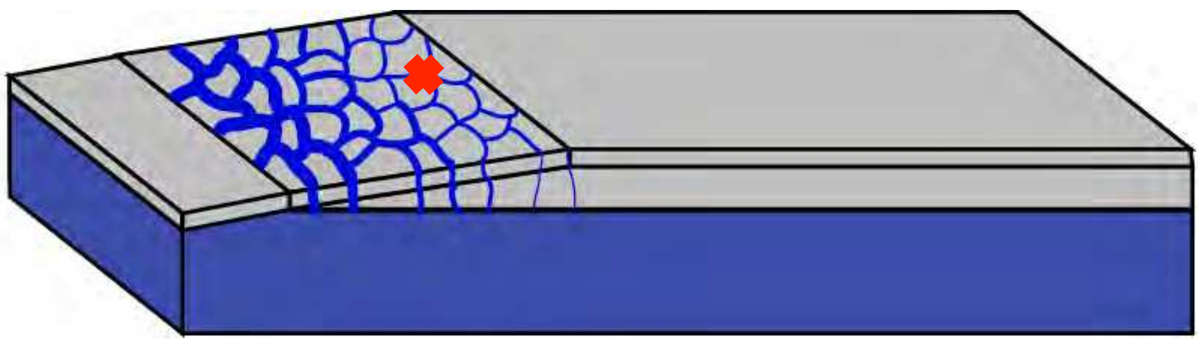
III. Re-oxidize the sample (1-3 hrs @ 1125ºC) to grow grain boundary ridges (GBRs)



Application of Taper Technique to Study Water Vapor Effects - FeCrAlY

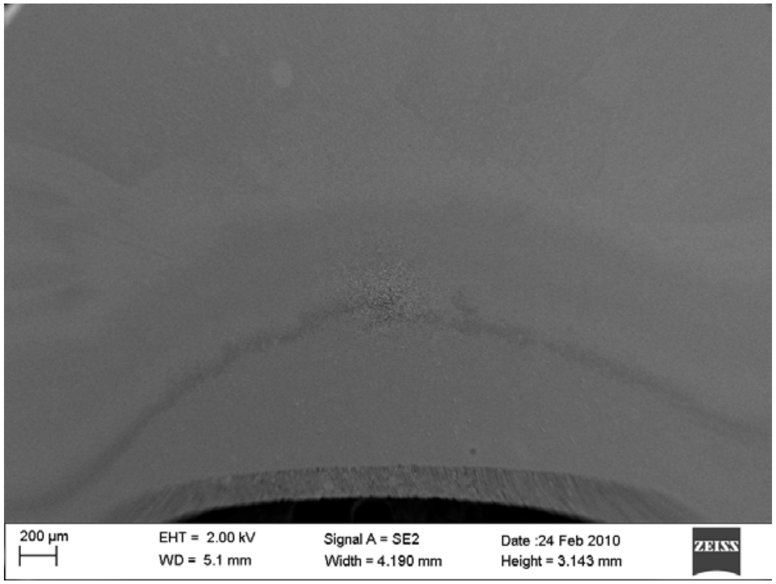




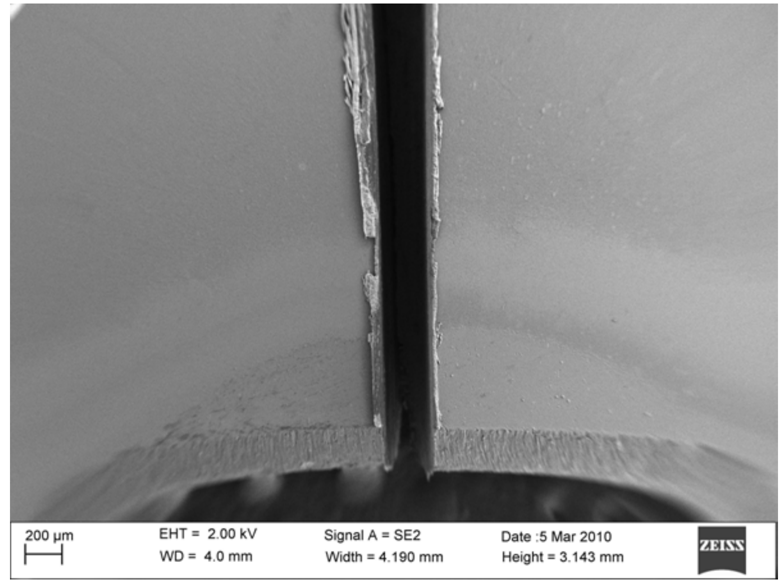


Wedge Oxidation Technique

Oxidized 25h then wedge polished

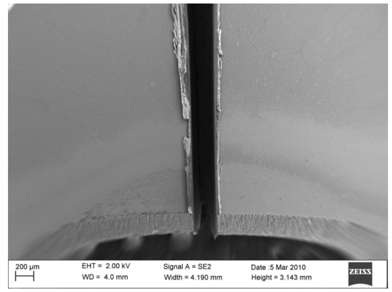


Cut in half…

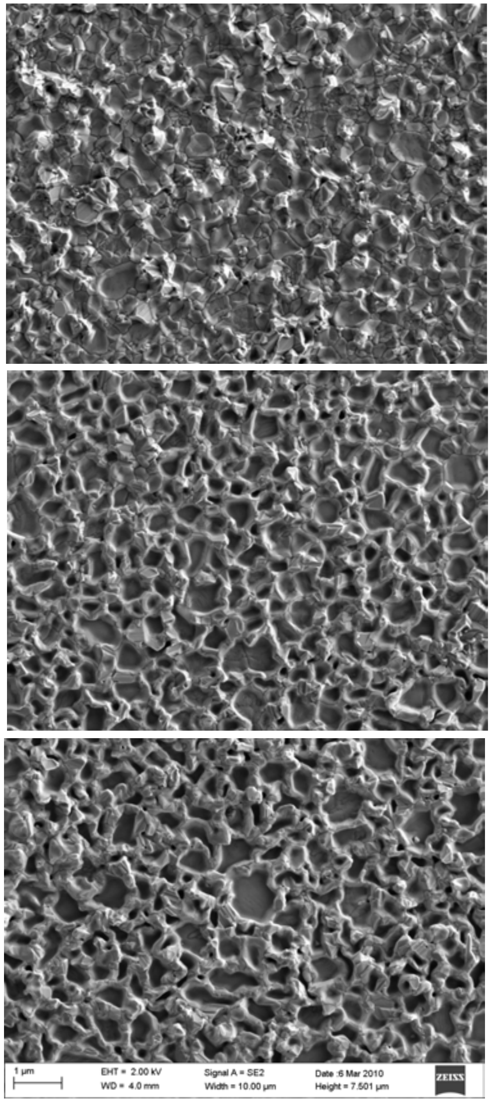


Dry vs. Wet
Re-oxidation

Re-Oxidation Exposures of FeCrAlY



0 mol% H_2O

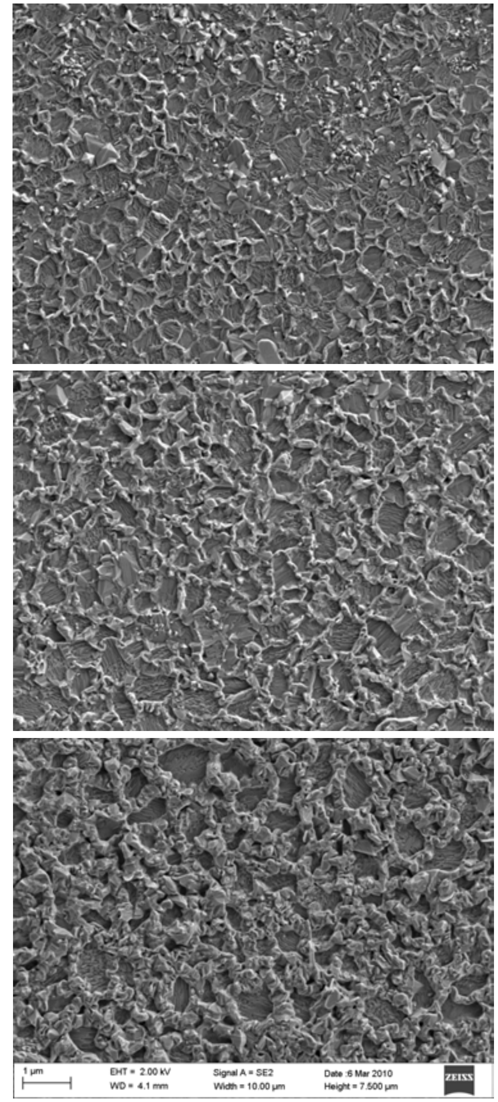


◄ High on Wedge ►

◄ Mid Wedge ►

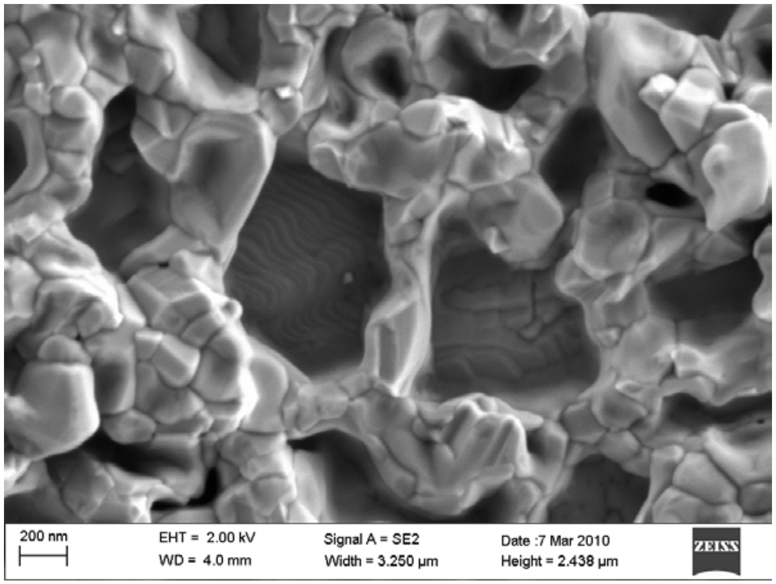
◄ Low on Wedge ►

30 mol% H_2O

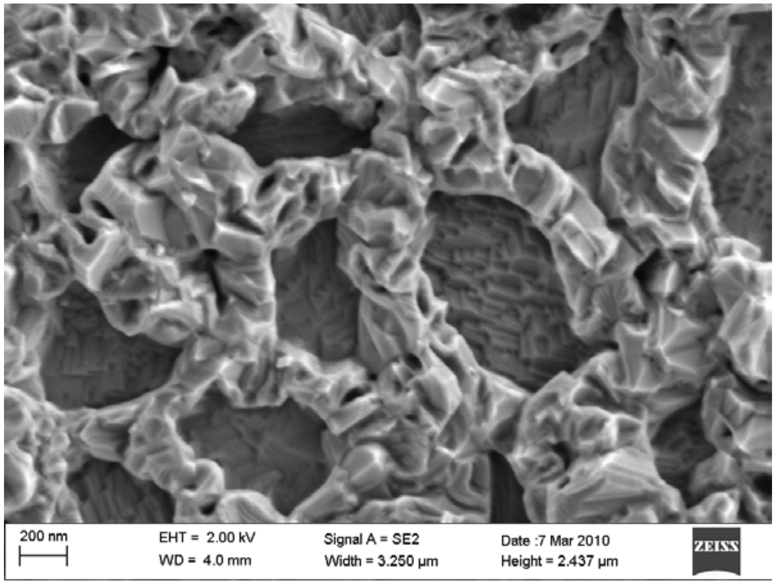


Individual Ridges and Analysis

0 mol% H_2O



30 mol% H_2O

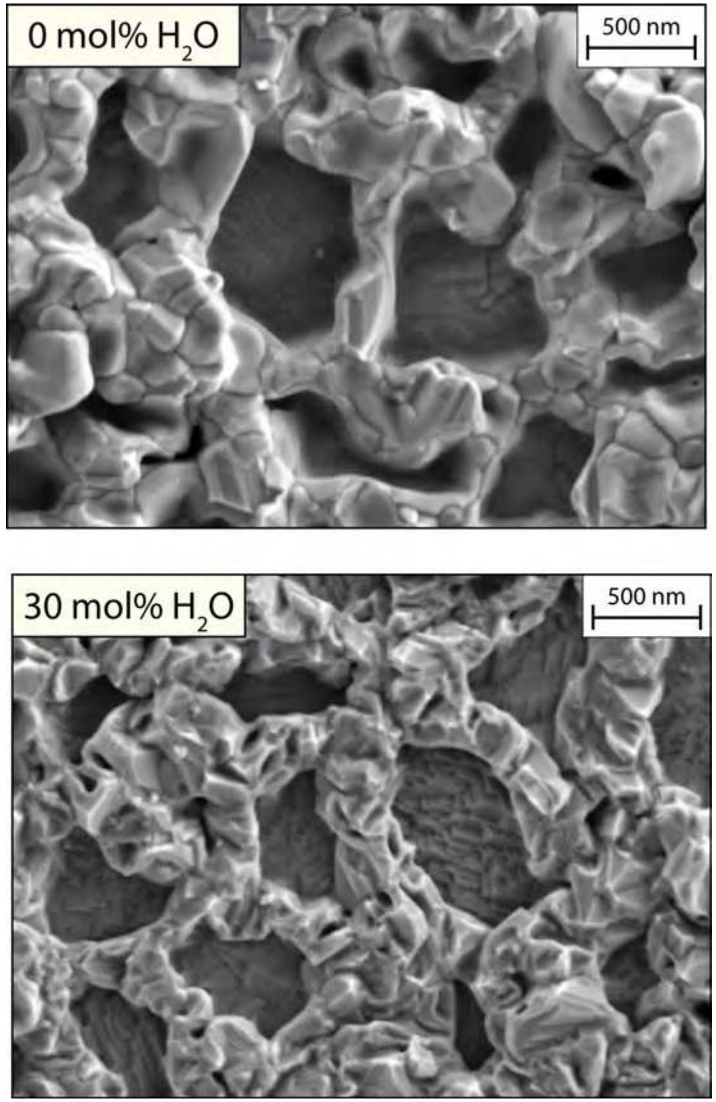


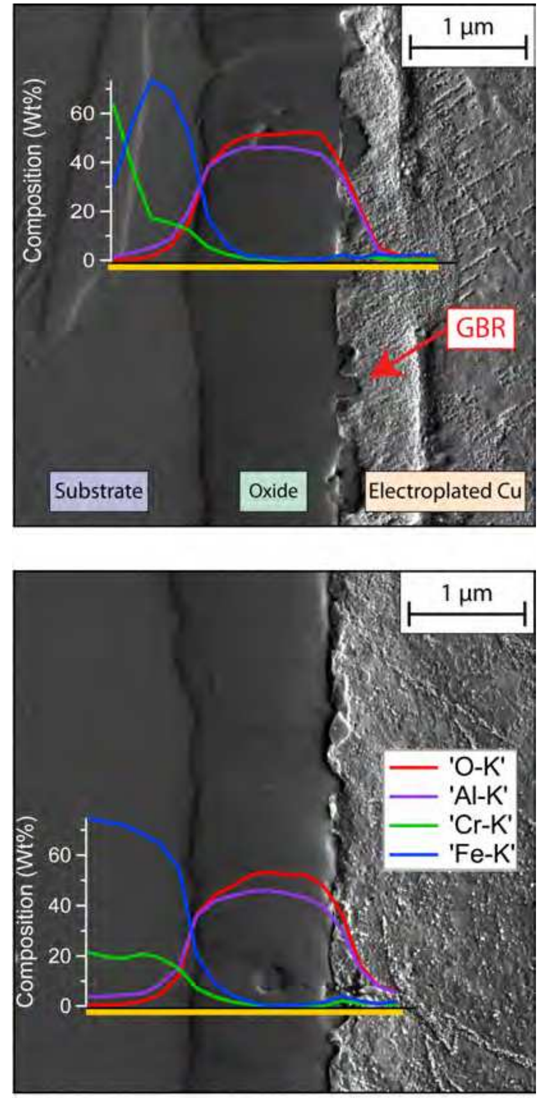
Low on Wedge

Quantitative Analysis of Oxide and Ridge Composition

Enhanced Fe and Cr Transport to Developing GB Ridge

(?)

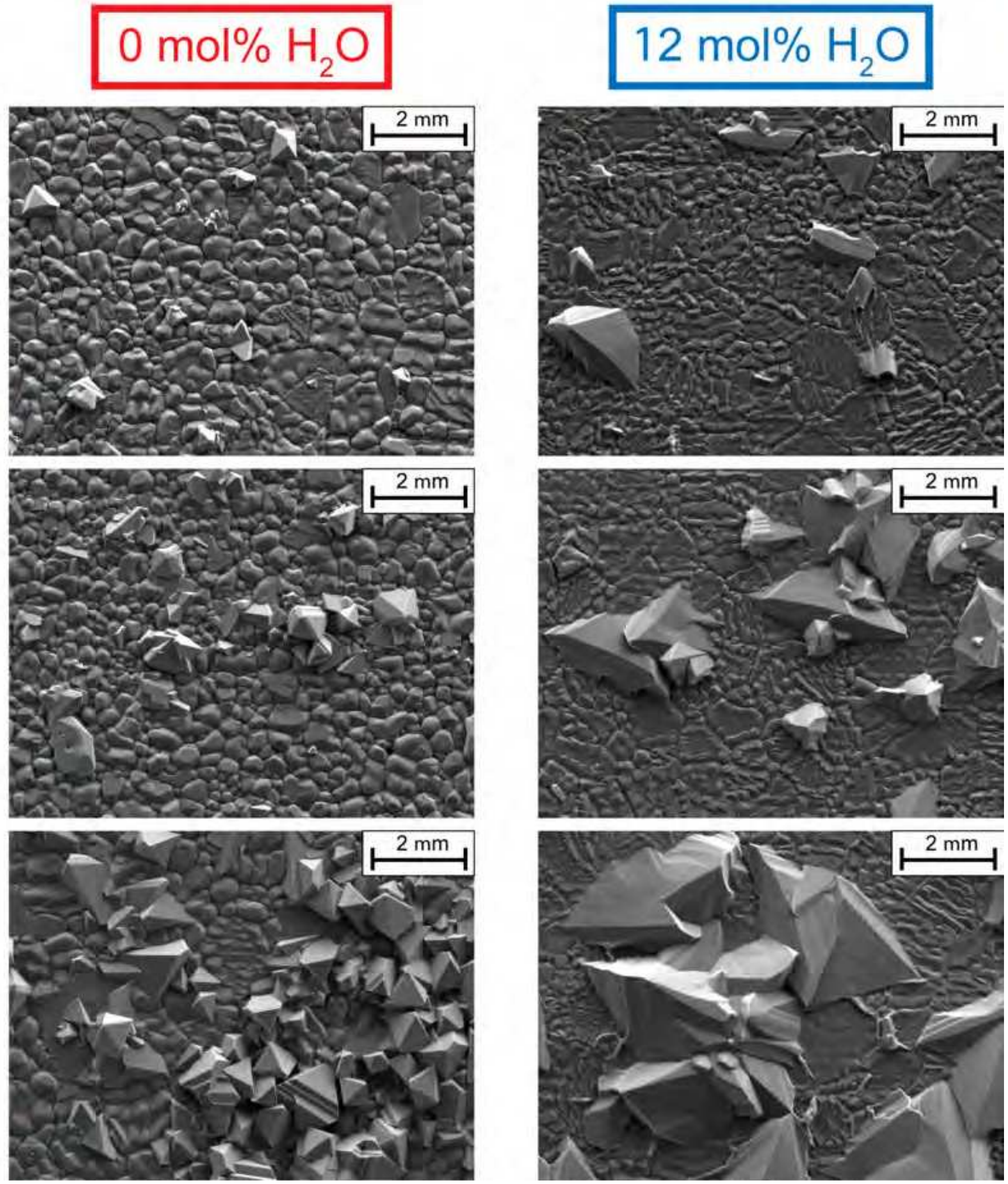




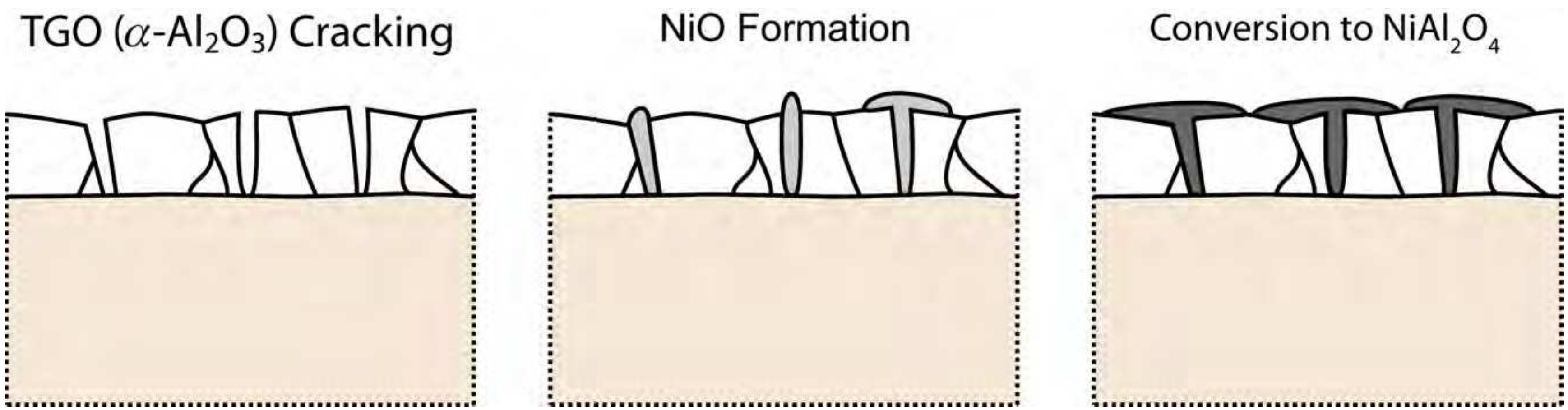
NiCoCrAlY – Increased Spinel with Further 'Wet' Exposure

NiCoCrAlY:

1. 300hr Oxidation, *in 15 mol% H_2O*
2. 4hr Re-Oxidation



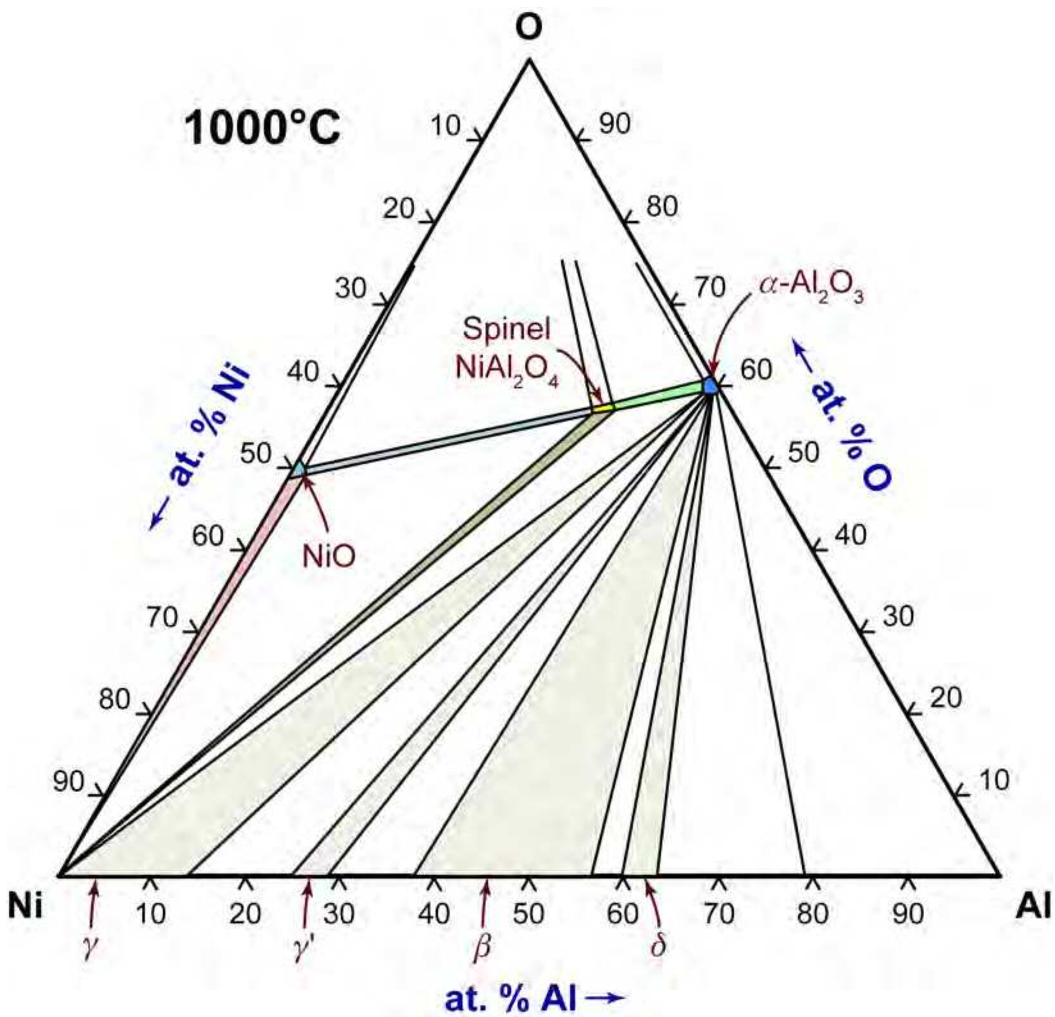
Spinel Formation Through Short Circuit Pathways



Schematic describes an accepted mechanisms for formation of spinel through NiO intermediate phases

Microstructural features inconsistent with behavior observed in previous isothermal experiments

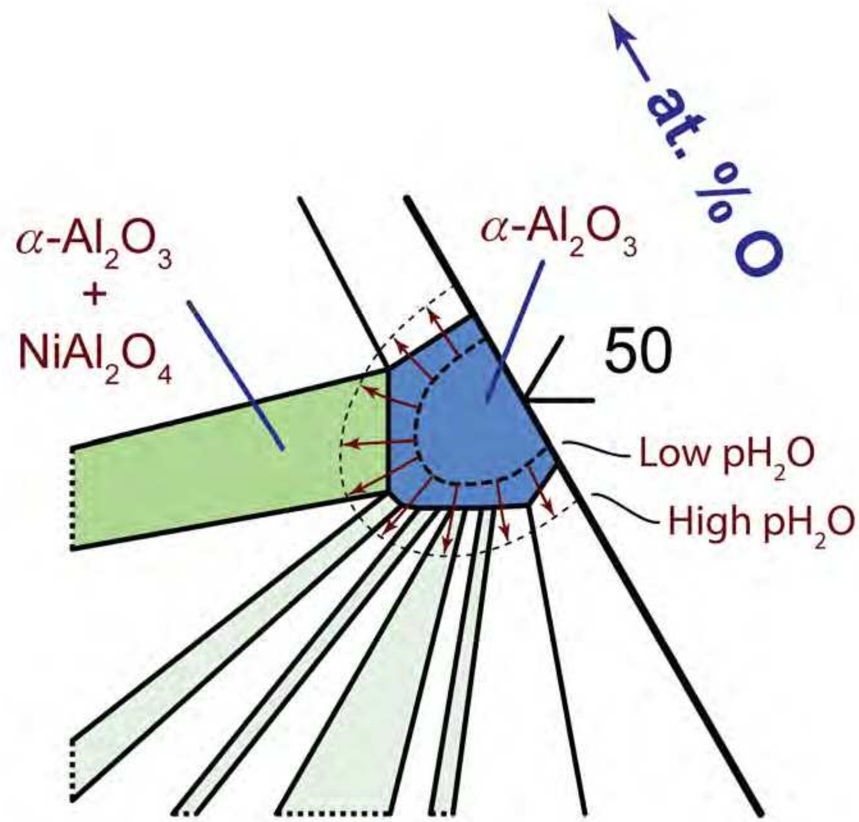
External Spinel Formation in the Absence of Short-Circuit Pathways



In the absence of TGO cracks, attendant NiO formation, and solid state reaction to form spinel, formation of this phase is dependant upon the composition of the alumina.

How is the activity of Ni in the alumina TGO layer dependant upon the exposure environment?

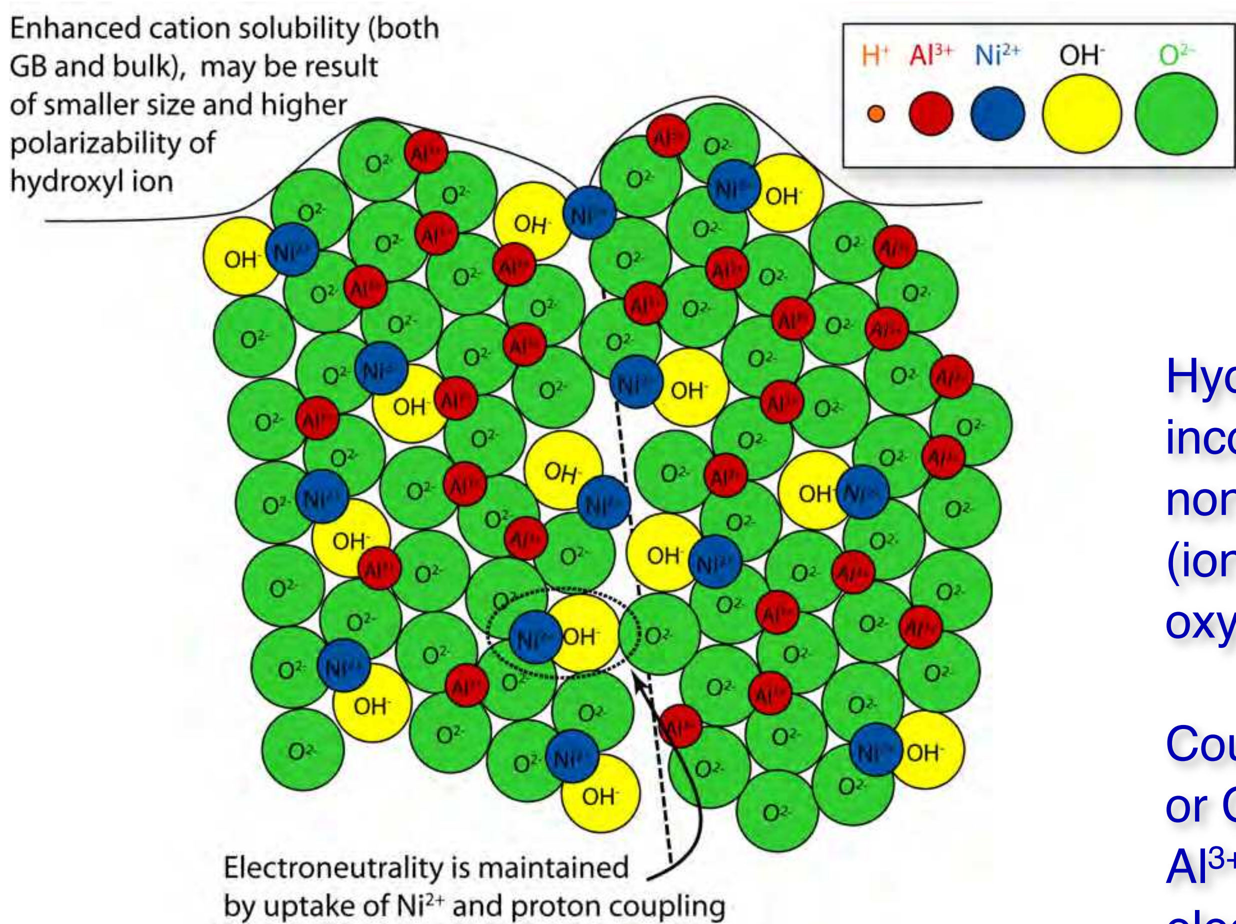
The Role of Water Vapor on Ni Solubility



Under low pH_2O exposure, the solubility of Ni in the developing α-Al_2O_3 is sub-critical for spinel formation.

Under high pH_2O exposure, the effective solubility of Ni in the developing α-Al_2O_3 is above the concentration necessary for spinel formation.

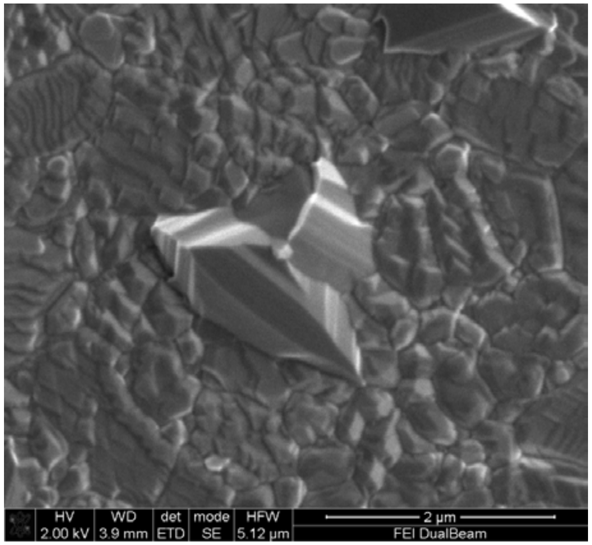
A Possible Mechanistic View of Enhanced Ni Solubility



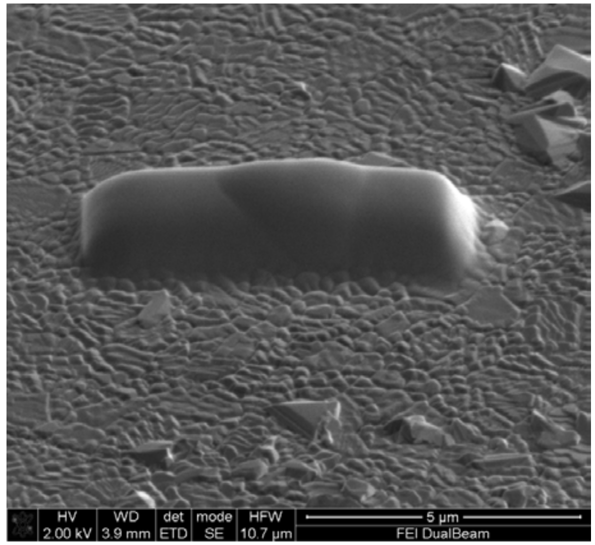
Hydroxyl ions are easily incorporated into some non-stoichiometric oxides (ion is actually smaller than oxygen ion….)

Coupled with protons, Ni^{2+} or Co^{2+} ions substitute for Al^{3+} to maintain local electro-neutrality

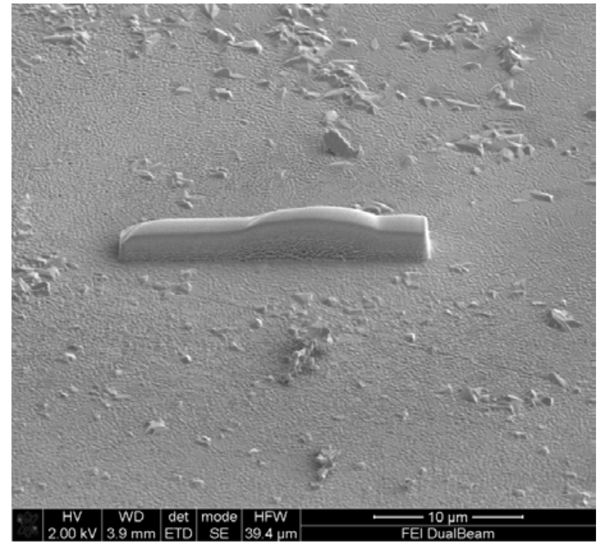
Substructural Examination of Spinel Domains



Spinel grains on surface

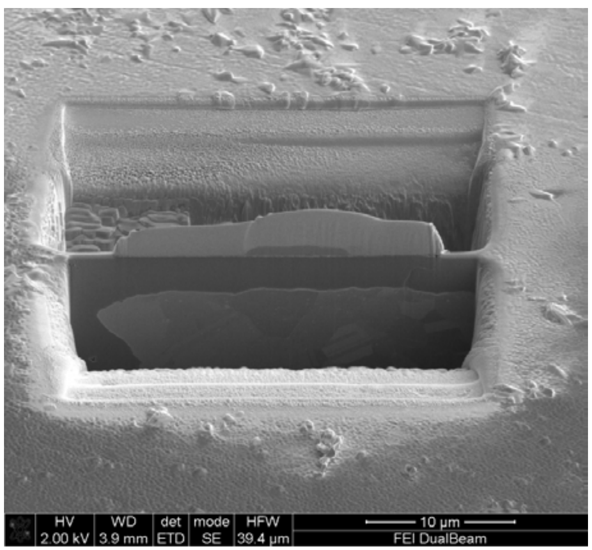


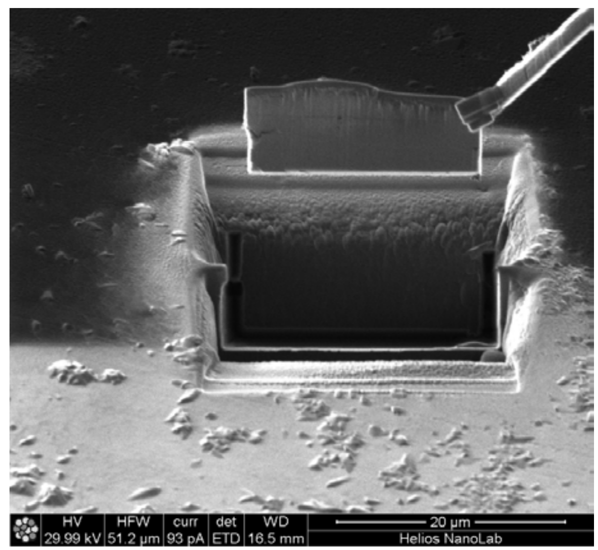
Grain after e-beam Pt deposition



FIB Pt deposition

Lamella prepared at site of interest

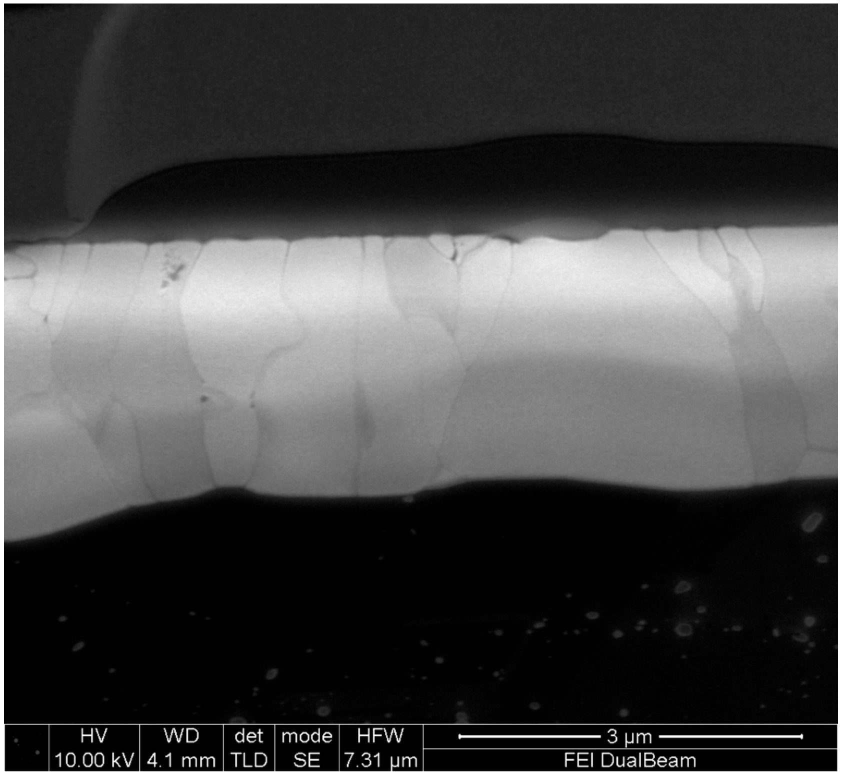




Lamella liftout from bulk

Substructural Examination of Spinel Domains

STEM imaging: extracted lamella



Implications of Proposed Mechanisms – Mitigation Strategies

- **Spinel Formation Dominated by Short-Circuit Pathways**

  Materials design strategies focus on preventing aluminum depletion in bond coat and preferential formation of NiO in cracks and 'open' diffusion paths.

- **Spinel Formation Dominated by Mechanisms Allowing Ni GB Diffusion**

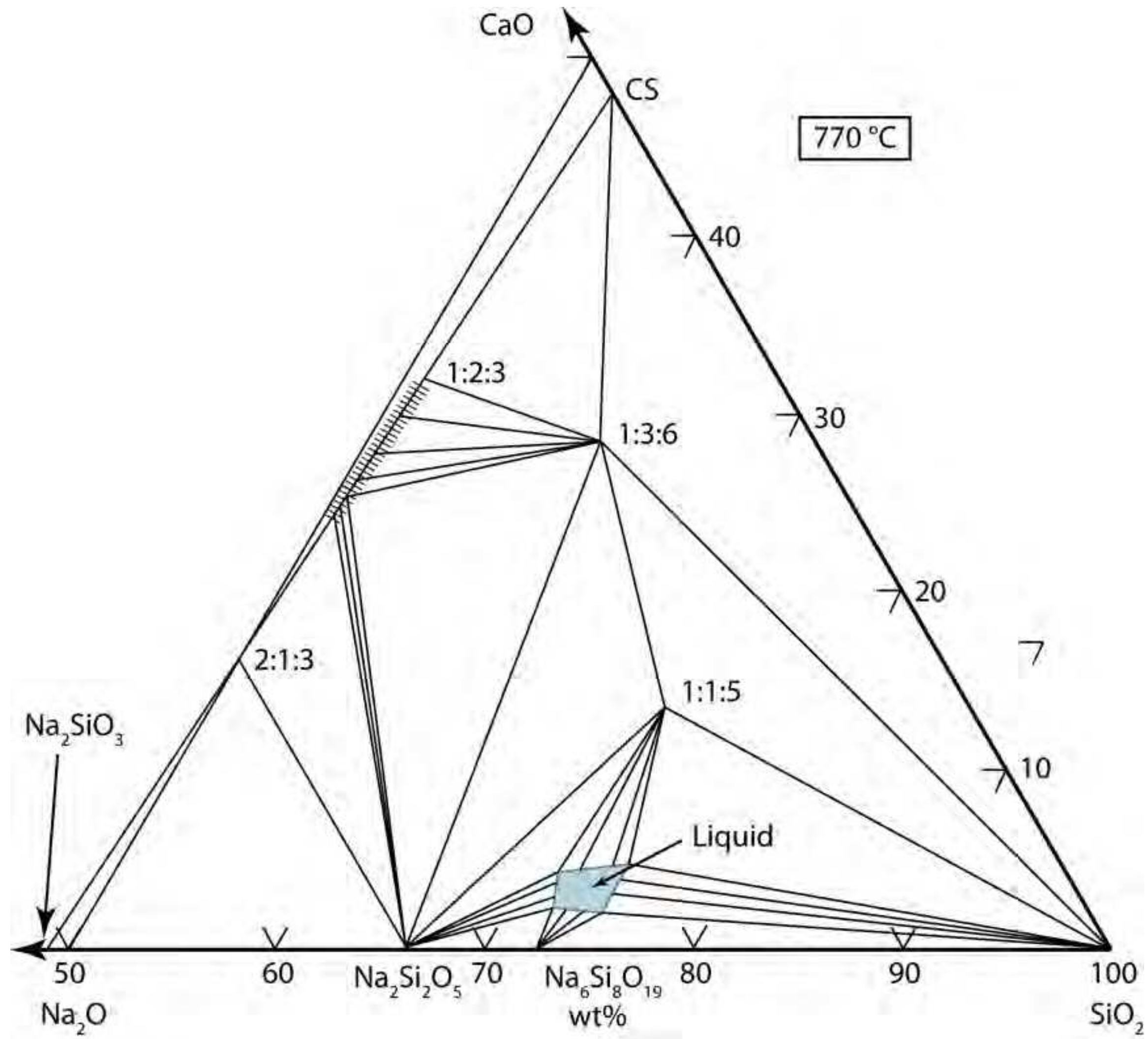
  Materials design strategies focus on mechanisms affecting GB transport, along lines of RE doping additions.

- **Spinel Formation Dominated by Ni activity in growing TGO**

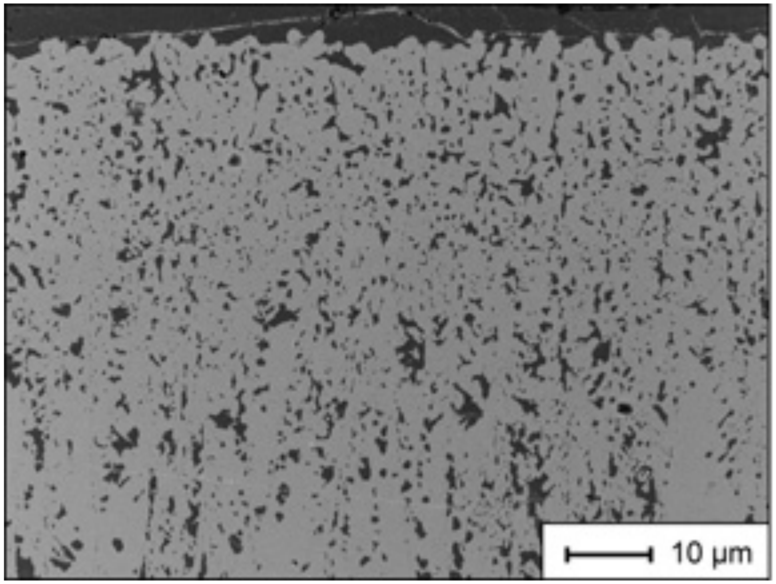
  Materials design strategies focus on changing defect chemistry to limit solubility and potential for reaching critical activity necessary for new phase formation.

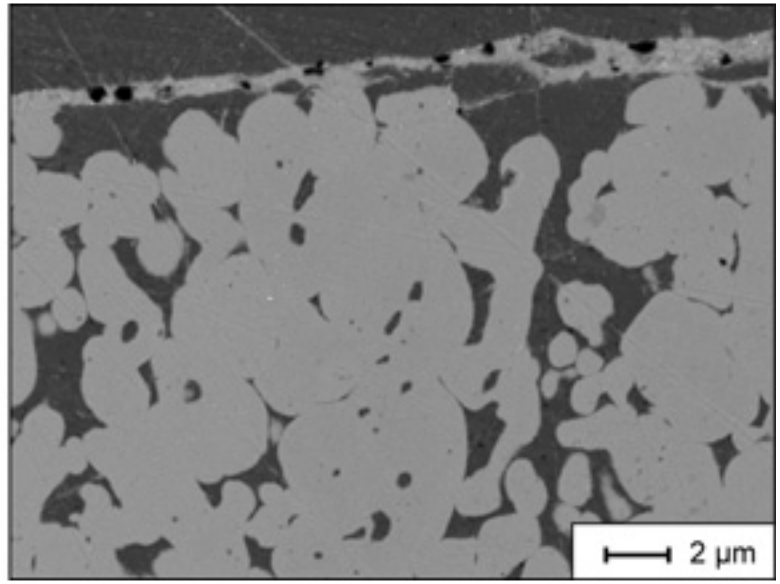
Exploration of Potential Low Melting Point Phases – Ternary Systems

Sodium
Silica
&
Calcium



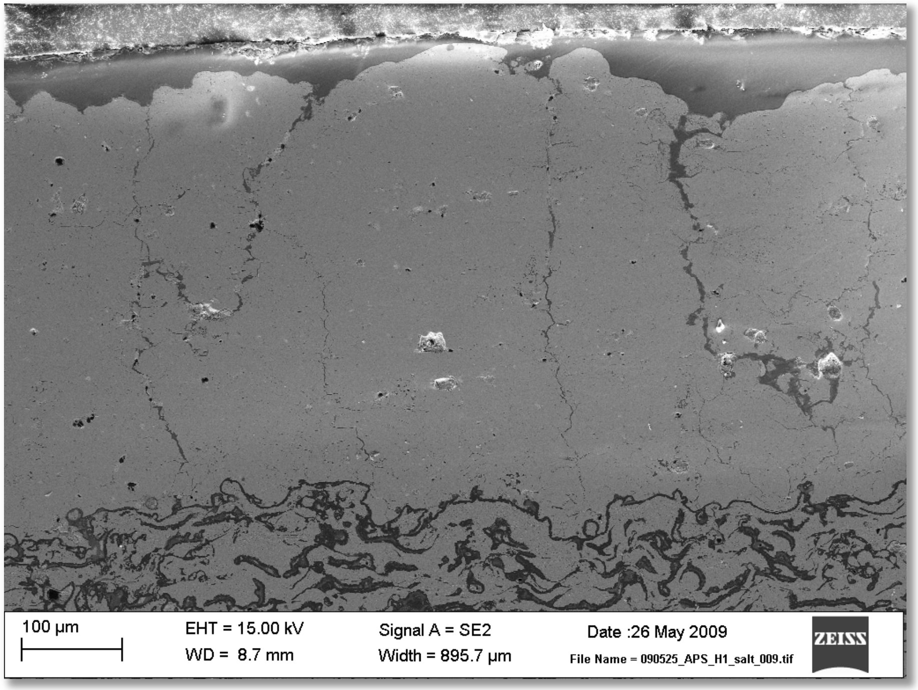
Molten Phase Infiltration Studies – EBPVD Systems



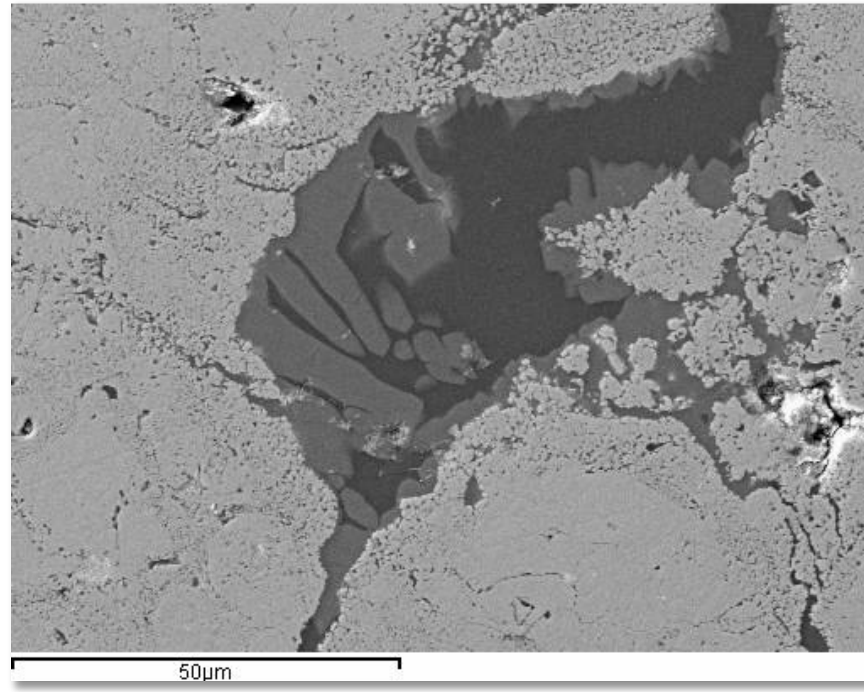


- Infiltrates Found to Cause Dissolution of YSZ
- Morphological Changes to YSZ Columnar Microstructure
- Complete Infiltration of YSZ with Attendant Loss of Compliance

Molten Phase Formation and Infiltration: NaCl and Silica



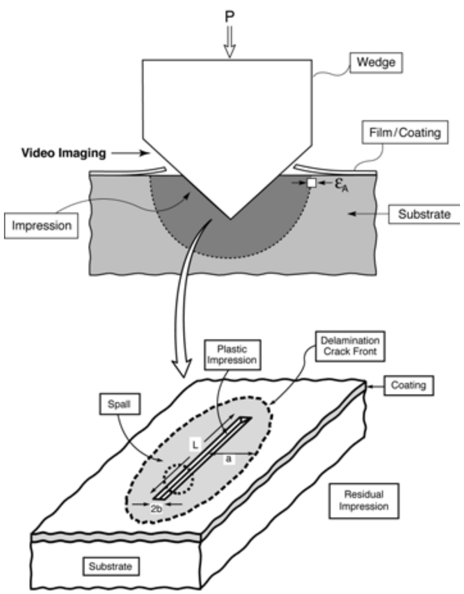
APS NiCoCrAlY BC – DVC Top Coat



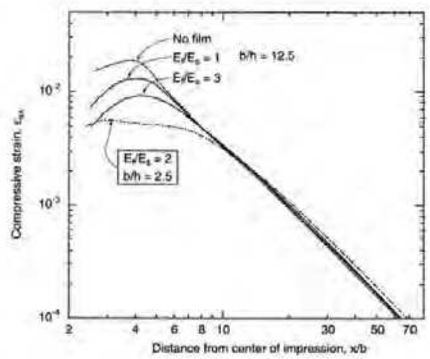
LPPS NiCoCrAlY BC – DVC Top Coat

- Deposition from vapor phase and extensive infiltration of TBC porosity
- Low melting point phase (Na-Si-O) with apparent dissolution and re-precipitation of YSZ

Constituent Mechanical and Thermo-Mechanical Behavior

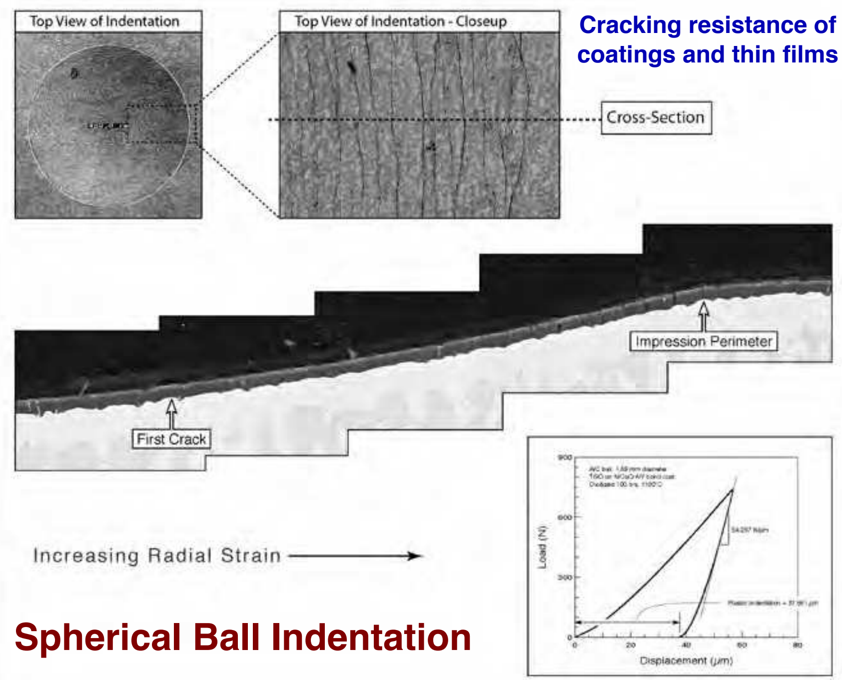


Wedge Indentation

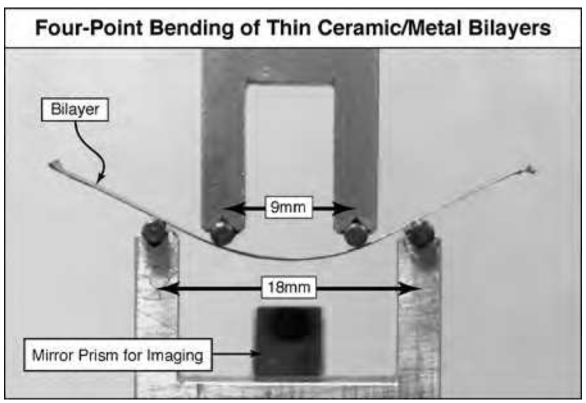


Provides a quantitative measurement of interfacial toughness and degradation due to materials evolution in service

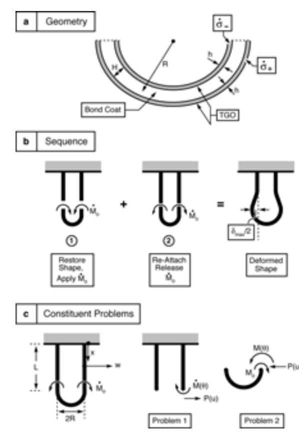
Cracking resistance of coatings and thin films



Spherical Ball Indentation



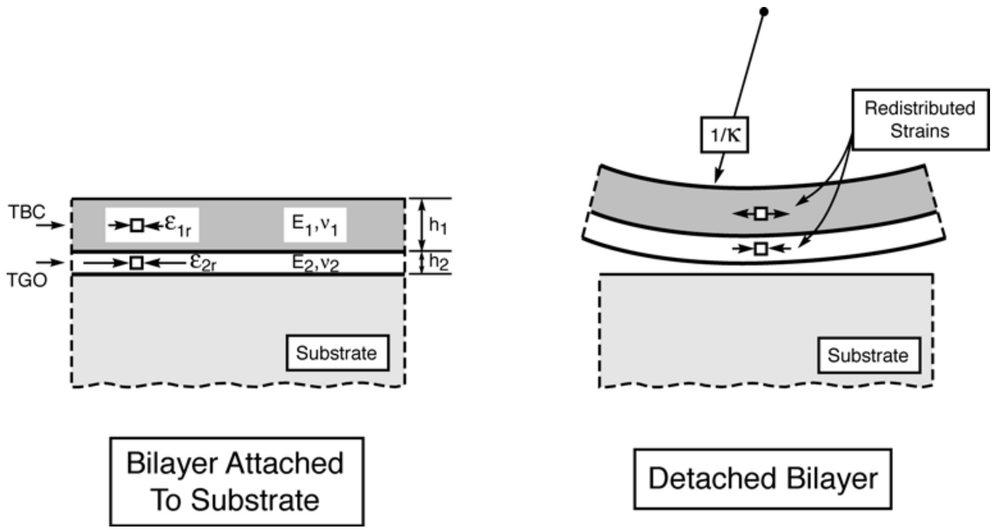
Bilayer or Multilayer Bending

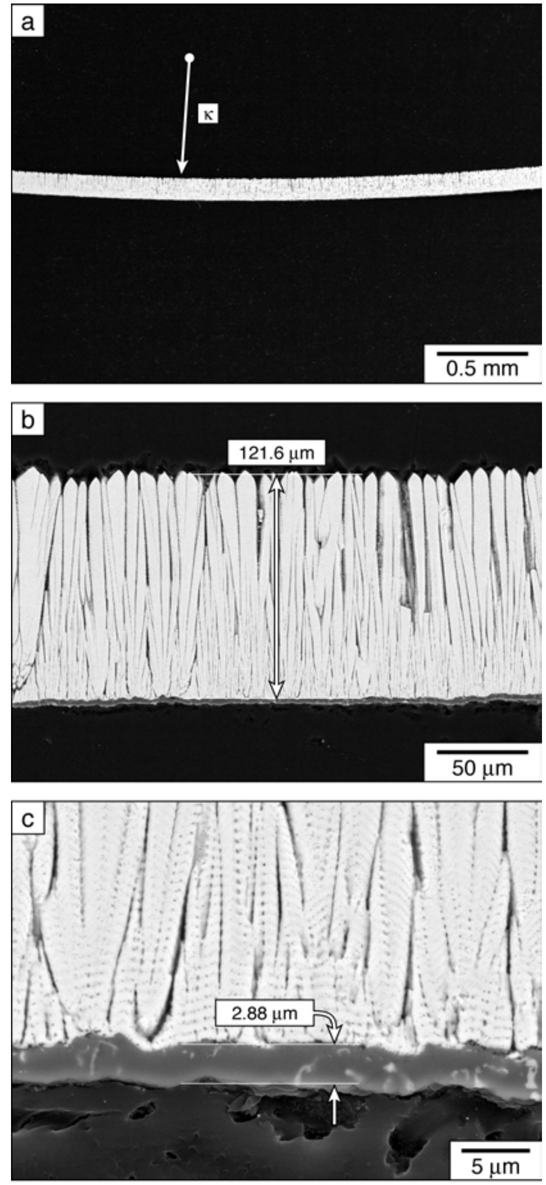


Loop shape change during high temperature treatment is an indication of constraints that develops within thermally grown oxide

Loop Oxidation Studies

TBC Layer Elastic Properties Determined via Bilayer Bending





In-Plane Modulus of TBC: **E = 15 GPa**

(100 hr Oxidation)

In-Plane Modulus of TBC: **E = 40 GPa**

(200 hr Oxidation)

Dense Zirconia: **E ~ 200 GPa**

Summary

- Materials exposure under oxidation conditions with elevated water vapor will be investigated and related to transport processes and defect chemistry.
- Potential deposits that may arise from use of alternative fuels in syngas/HHC environments will be identified, and laboratory studies of materials degradation by deposit formation and molten phase infiltration will be carried out.
- Mechanisms underpinning observed modified oxide formation (spinel) will be explored, and possibilities for relating this behavior to defect chemistry and effects on transport will be pursued.
- The impacts of HHC and syngas environments on hot-section materials degradation will be elucidated.

Questions?