UCIrvine | The Henry Samueli School of Engineering

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

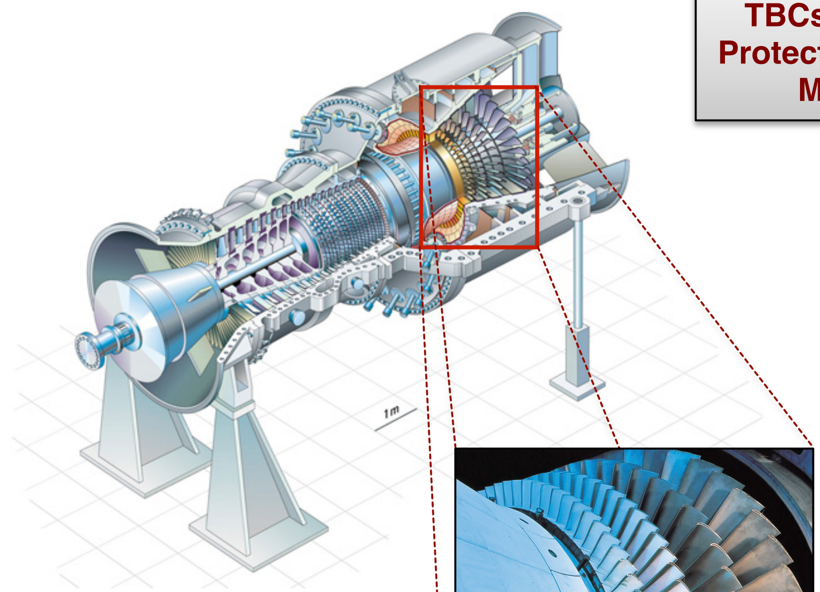
2012 University Turbine Systems Research Workshop
Irvine, CA; October 2nd – 4th, 2012

U.S. Department of Energy; National Energy Technology Laboratory
Agreement # DE-FE0004727; Project Manager: Dr. Patcharin Burke

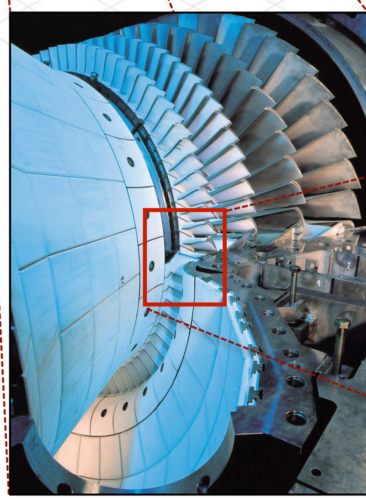
U.S. DEPARTMENT OF ENERGY

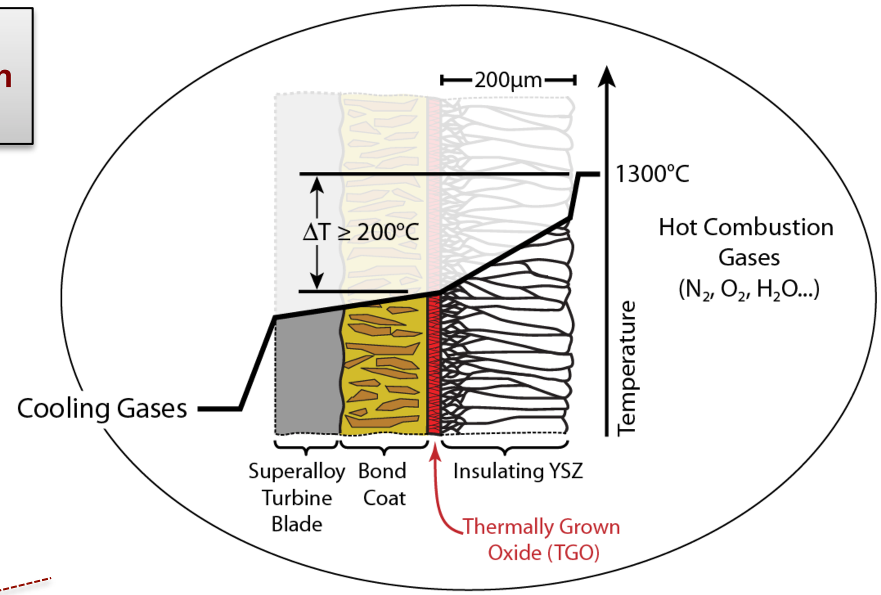
Introduction

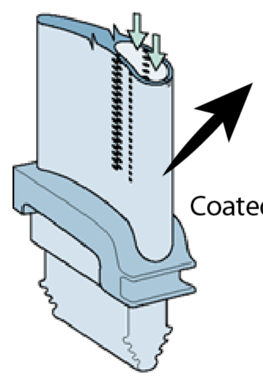
TBCs and TGOs Protect Hot-Section Materials



Siemens SGT5-4000F Gas Turbine Engine 287 MW





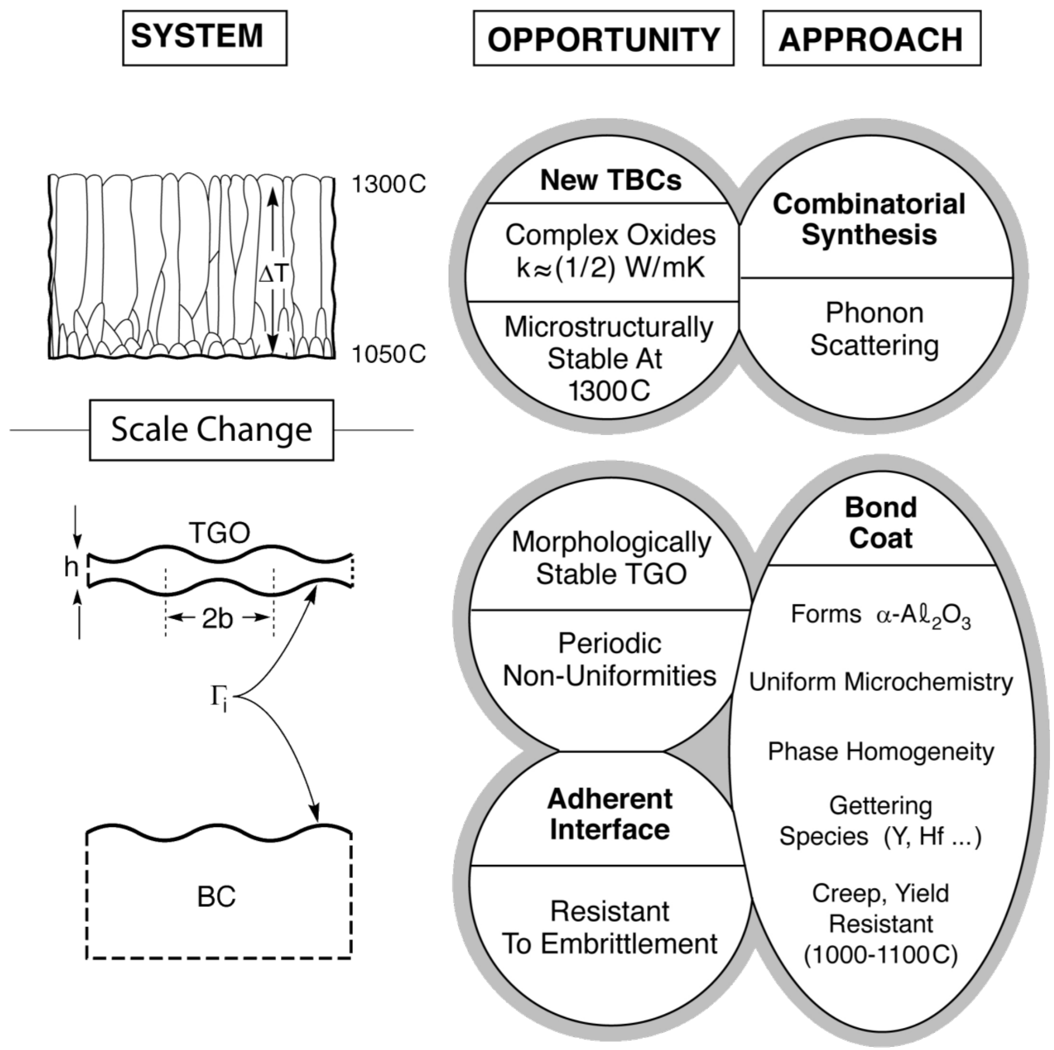


Thermally Grown Oxides and TBCs

Thermal Barrier Coating
Low Thermal Conductivity
Strain Tolerance
Microstructural Stability

Thermally Grown Oxide
Lowest Thickness
Controlled Defects
Adherent To BC

Bond Coat
Chemically Homogenous
Selectively Form Alumina
Creep/Yield Resistant

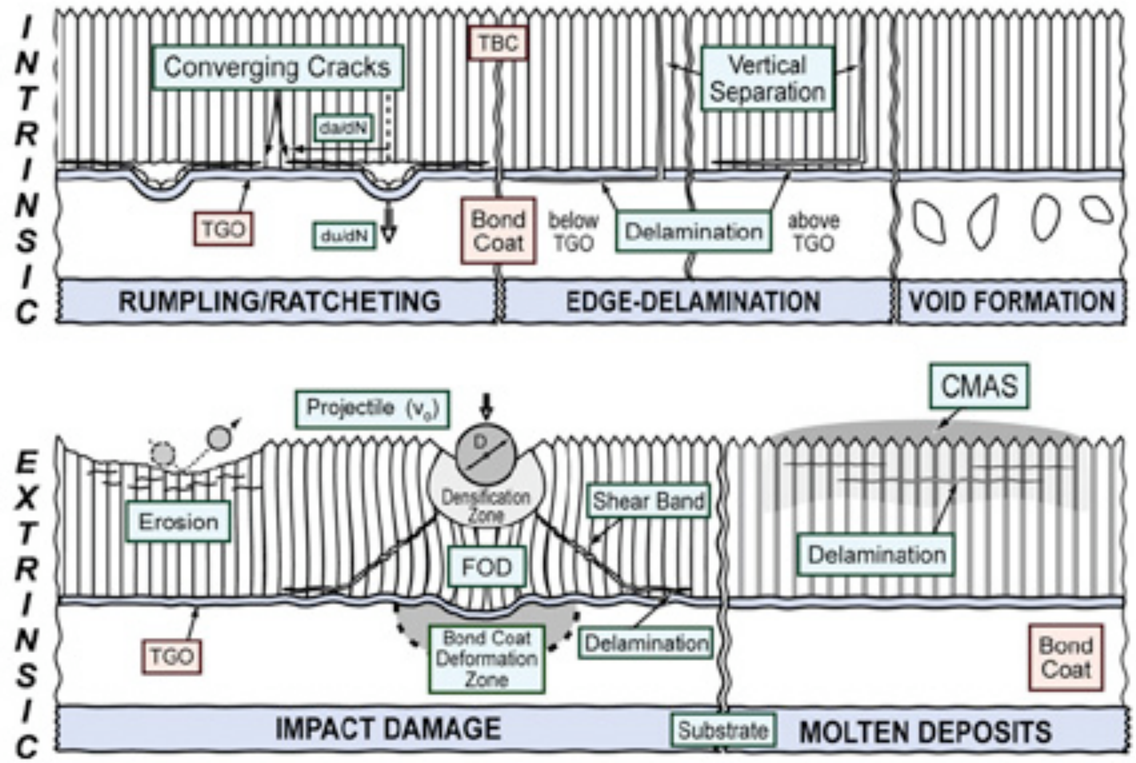


Potential Challenges in Transitioning to Alternative Fuels

A.G. Evans (2007)

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

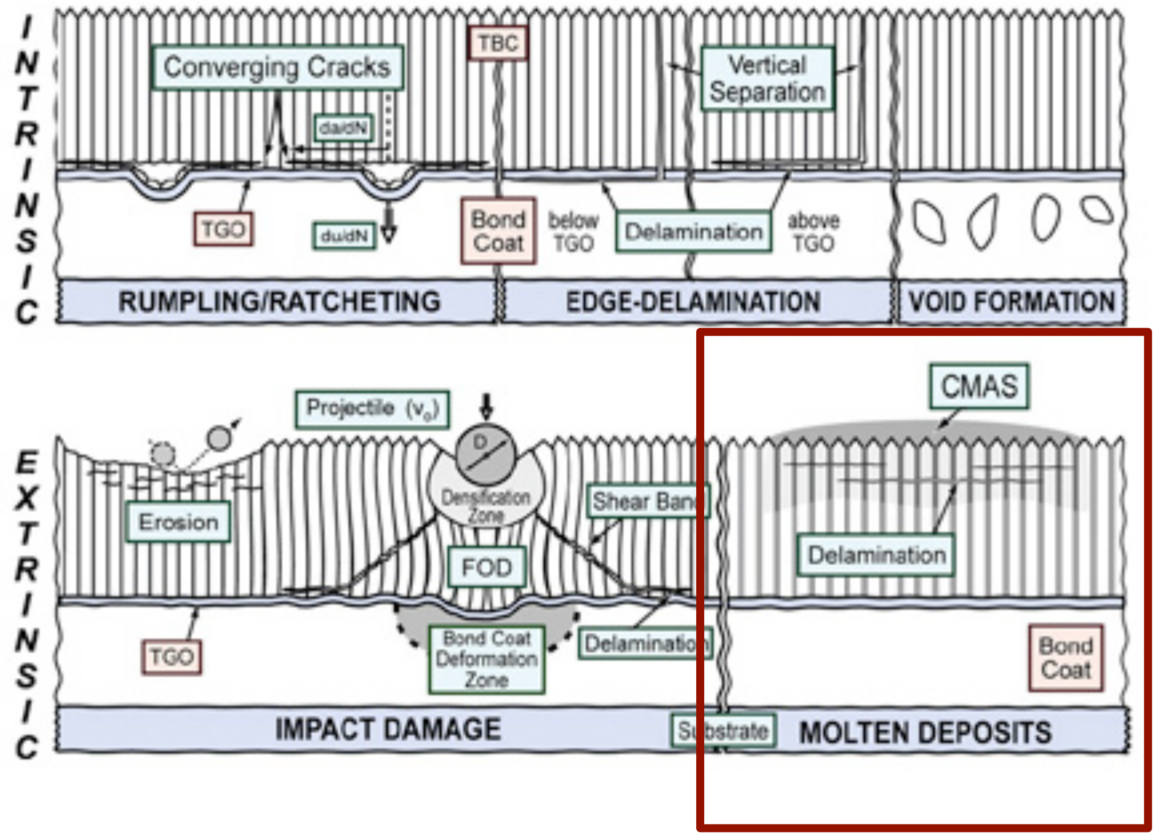
A.G. Evans, D.R. Mumm, J.W. Hutchinson, G. Meier and F.S. Pettit (2001)
Progress in Materials Science, 46, 505-53.

Deposit Formation and Infiltration

A.G. Evans (2007)

Deposit Formation

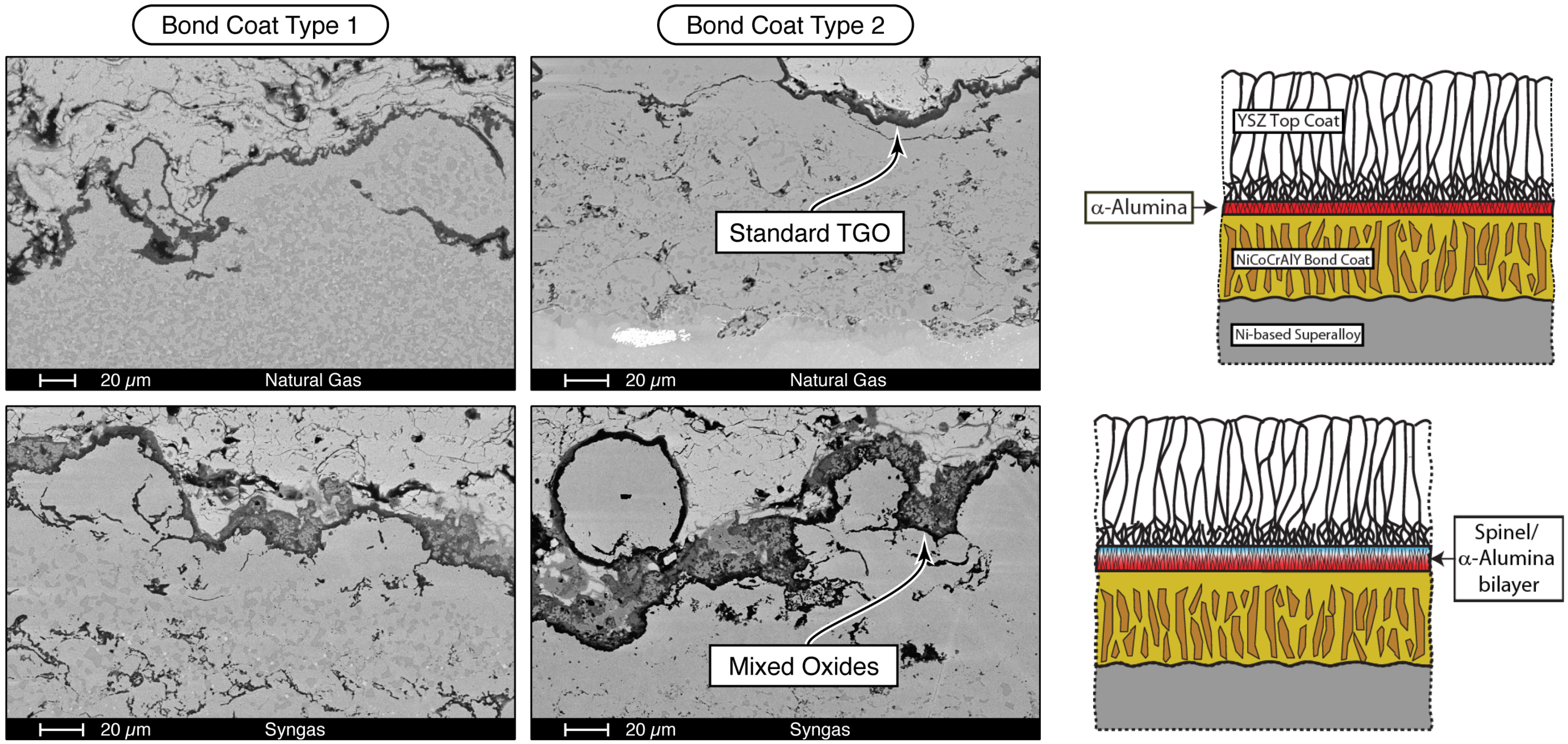
What potential analogies to CMAS degradation arise with use of syngas or HHC fuels and intrinsic combustion by products ?



Project Motivation: Non-Ideal TGO Growth

Natural Gas

Syngas Blend

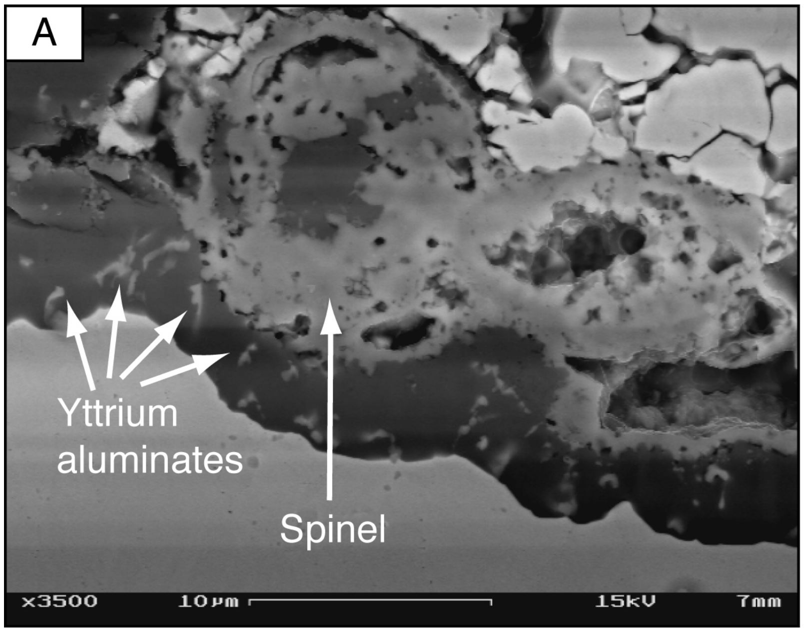


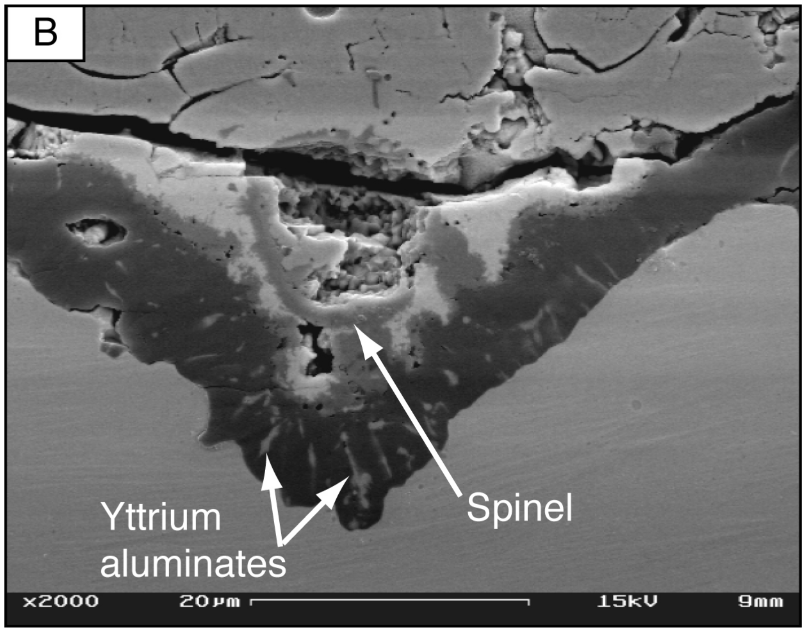
- Note location of new (spinel) phases – above the alumina
- Requires Ni transport **through** the alumina layer…

Non-Ideal Oxide Formation: Thermo-Mechanical Implications

So why are we concerned with external spinel formation?

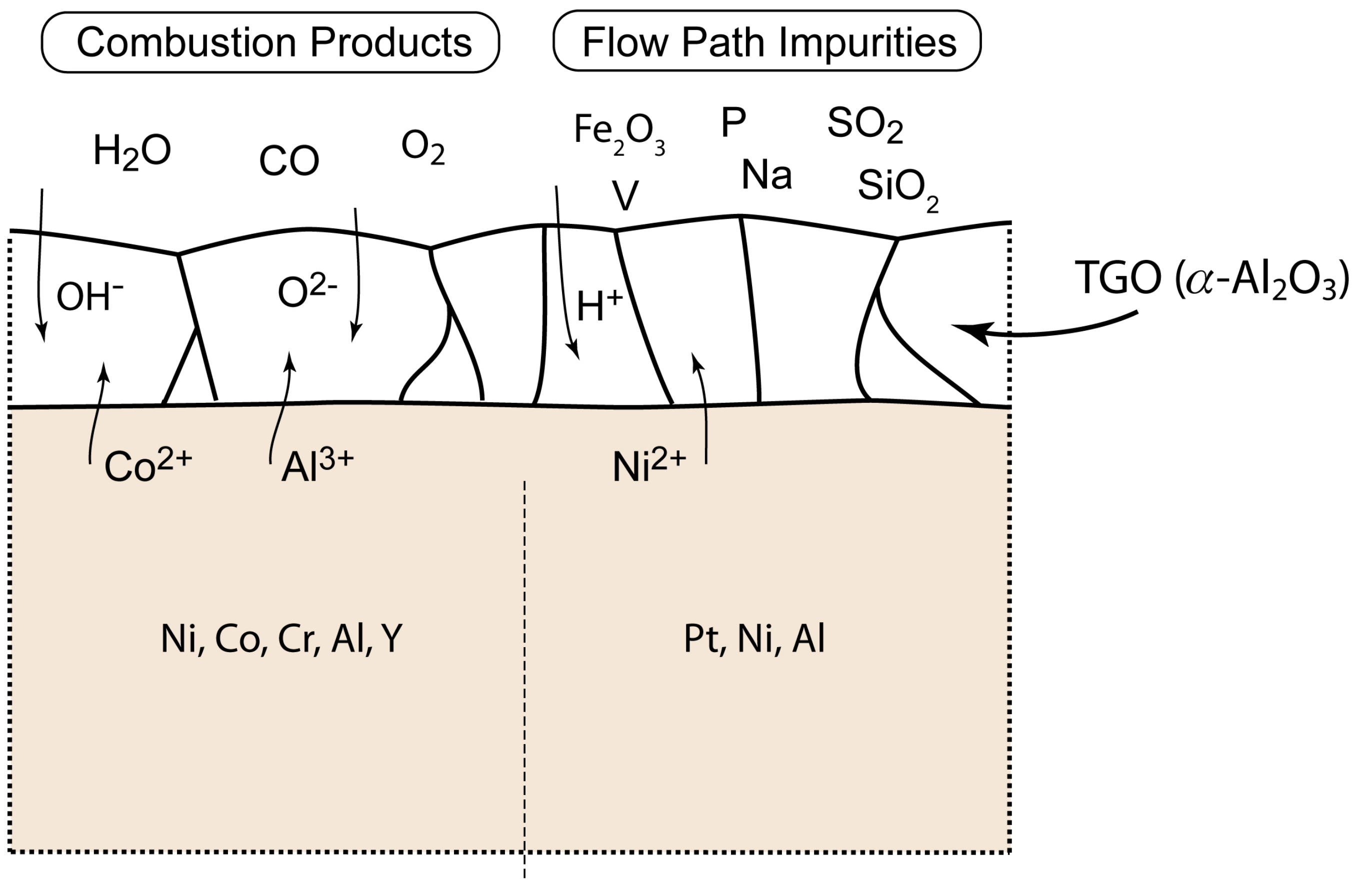
Spinel Formation in Plasma Sprayed TBCs
Preferential Crack Propagation Pathways





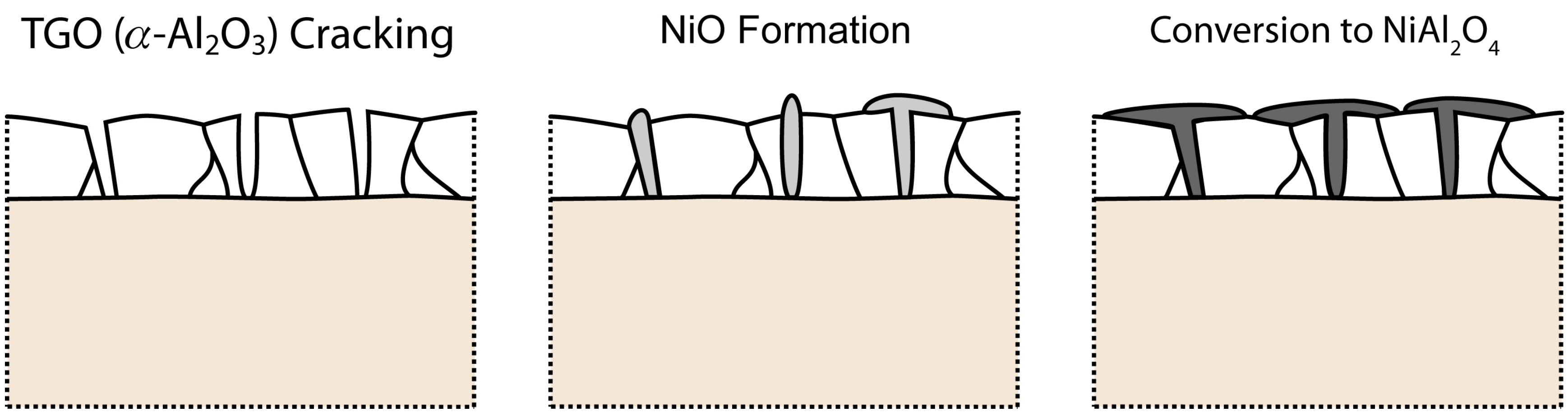
A. Rabiei and A.G. Evans (2000), Acta Materialia, 48, 3963-76.

TGO growth Mechanisms and Effects of Combustion Environment



TGO Development Studies: Non-Ideal Growth Mechanisms

Observed spinel formation not simply due to depletion of Al….



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

Microstructural features inconsistent with behavior observed in previous isothermal experiments

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.

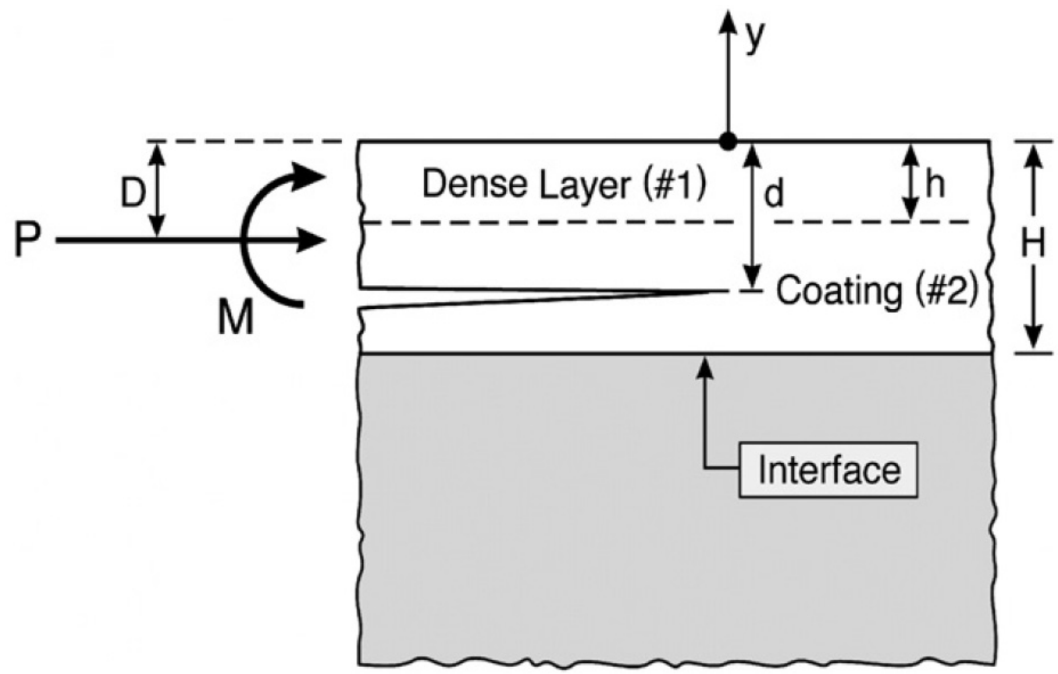
- **Spinel Formation Dominated by Ni activity in growing TGO**

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

Project Motivation: Enhanced TBC Degradation

TBC Sintering and Phase Destabilization

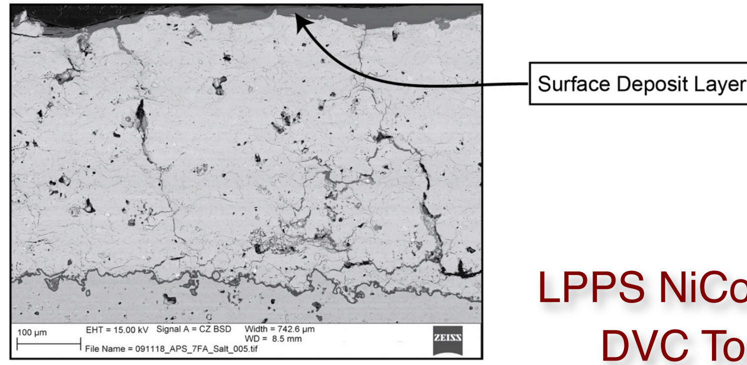
Does HHC/syngas combustion environment lead to enhanced sintering and destabilization of thermal barrier top coats?



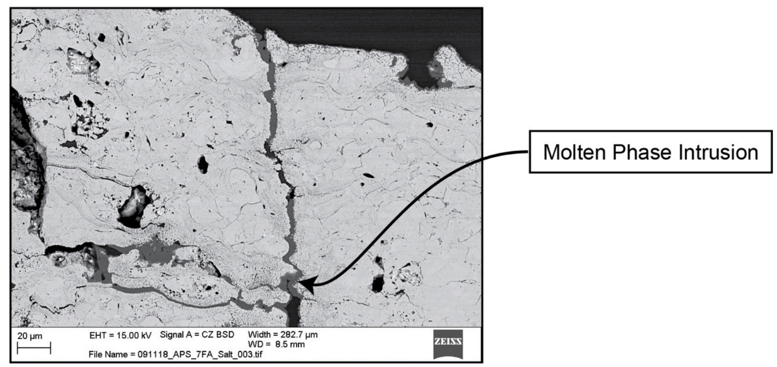
Project Motivation: Deposit-Induced Failure

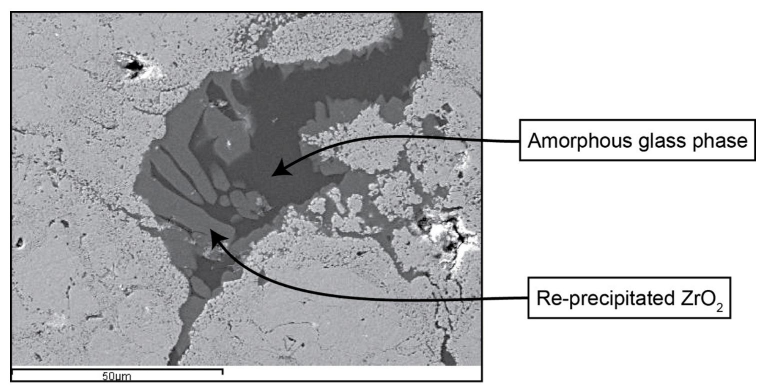
What is the potential for CMAS-based failure in HHC/syngas environments?

What are the characteristic chemistries of deposits and the associated thermo-physical and thermo-chemical properties and thermo-mechanical failure mechanisms?



LPPS NiCoCrAlY BC
DVC Top Coat





Current Discussion

Assessment of the stability of current hot-section materials in emerging HHC/syngas fueled turbine systems.

- Non-Ideal oxide formation and water-vapor effects on TGO development
- TBC stability studies in high pH_2O environments
- Characteristic surface deposits and CMAS-based degradation

New materials and processing approaches directed at mitigating damage evolution.

Project Overview: Goals and Objectives

- Derive a mechanisms-based understanding of protective TGO layer and TBC system degradation associated with turbine operation with syngas and high hydrogen content fuels, and develop a knowledge base upon which design of coatings more resistant to the observed attack mechanisms may be based.
  - Link and quantify the effects of higher water vapor content, modified combustion gas composition, higher sulfur concentrations, and exposure to flow stream impurities characteristic of syngas and HHC fuels on hot section materials stability.
  - Identify any synergism among these factors influencing materials stability.
  - Investigate novel materials solutions to mitigate materials degradation.
  - Educate the next generation of scientists and engineers trained in materials design for advanced turbine systems.

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.

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

Project Overview: Scope of Work

The scope of work was developed such that:

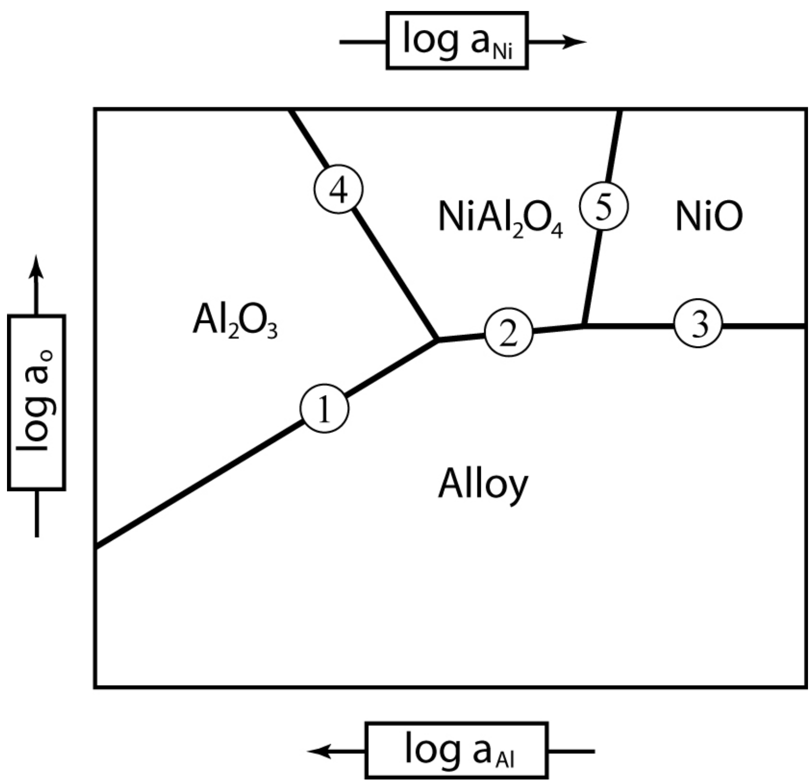
- The suitability of 'baseline' hot-section materials for use with syngas and HHC fueled turbines could be critically assessed.
- The mechanisms underpinning syngas and HHC fuel specific effects could be elucidated – and used as the basis for developing materials design protocols for improved materials.
- Within the time constraints of extended test protocols (accelerated, but ≥ 1000hr), meaningful comparisons can be made between new/alternative materials and baseline systems through focusing on underlying mechanisms.

The project is responsive to overall program goals in that:

- The effort is aligned with maximizing system lifetime under increasingly harsh conditions and avoiding premature maintenance.
- Allowing for the extension of operational conditions to more aggressive regimes (higher temperatures, etc.)

TGO Development Studies: Explore Elevated pH_2O Effects

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

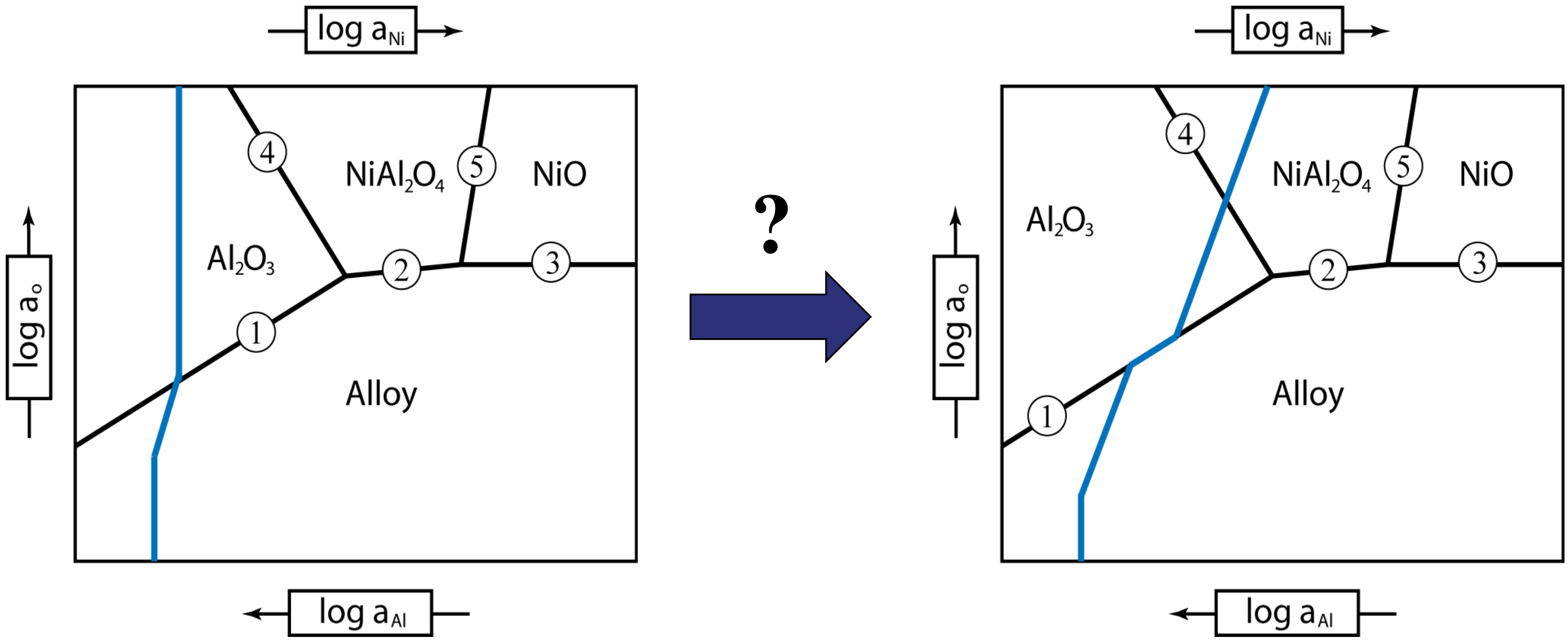


1. $$2Al + 3O \rightleftharpoons Al_2O_3$$
2. $$Ni + 2Al + 4O \rightleftharpoons NiAl_2O_4$$
3. $$Ni + O \rightleftharpoons NiO$$
4. $$Al_2O_3 + 3Ni \rightleftharpoons 3NiAl_2O_4 + 2Al$$
5. $$NiAl_2O_4 + 3Ni \rightleftharpoons 4NiO + 2Al$$

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.

TGO Development Studies: Explore Elevated pH_2O Effects

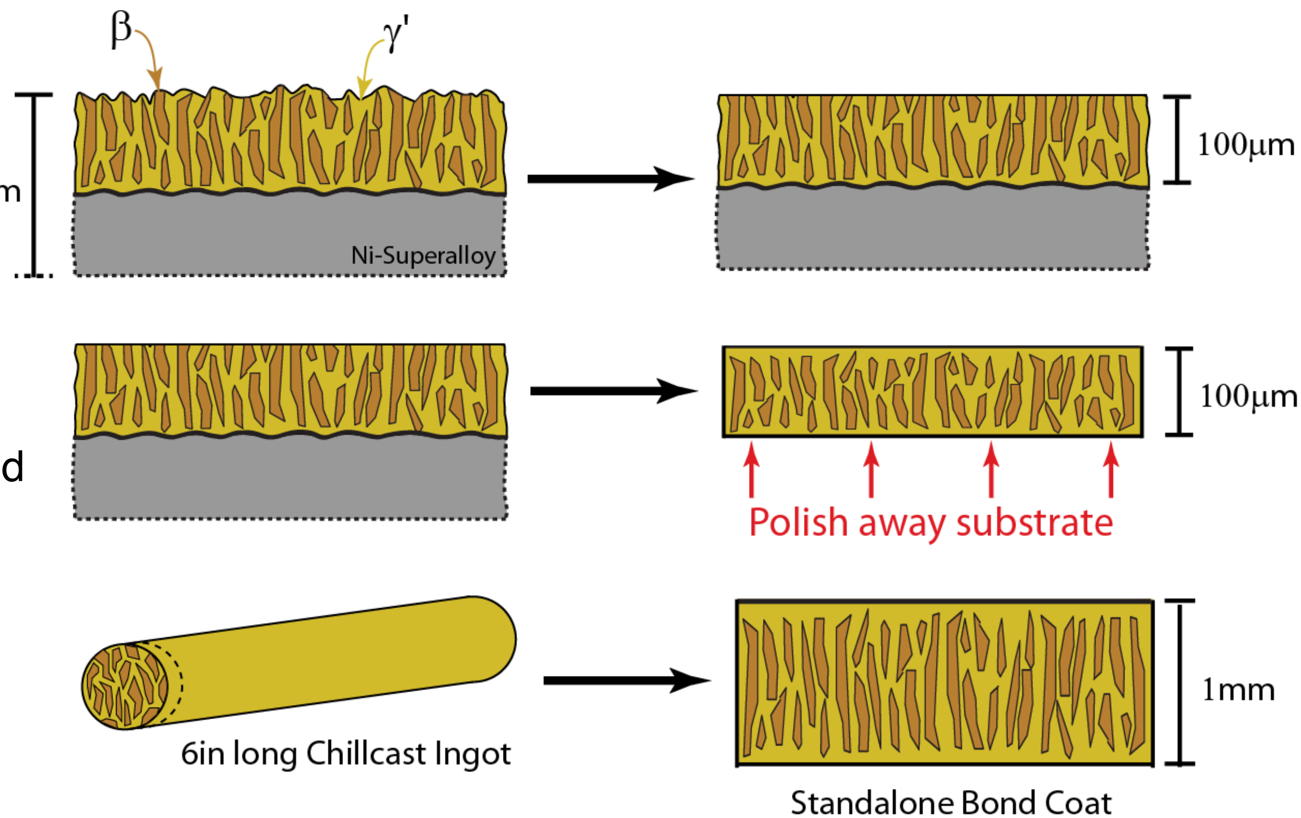


- Modification of the combustion environment alters reaction kinetics
- Dependence on partial pressures of gas stream constituents

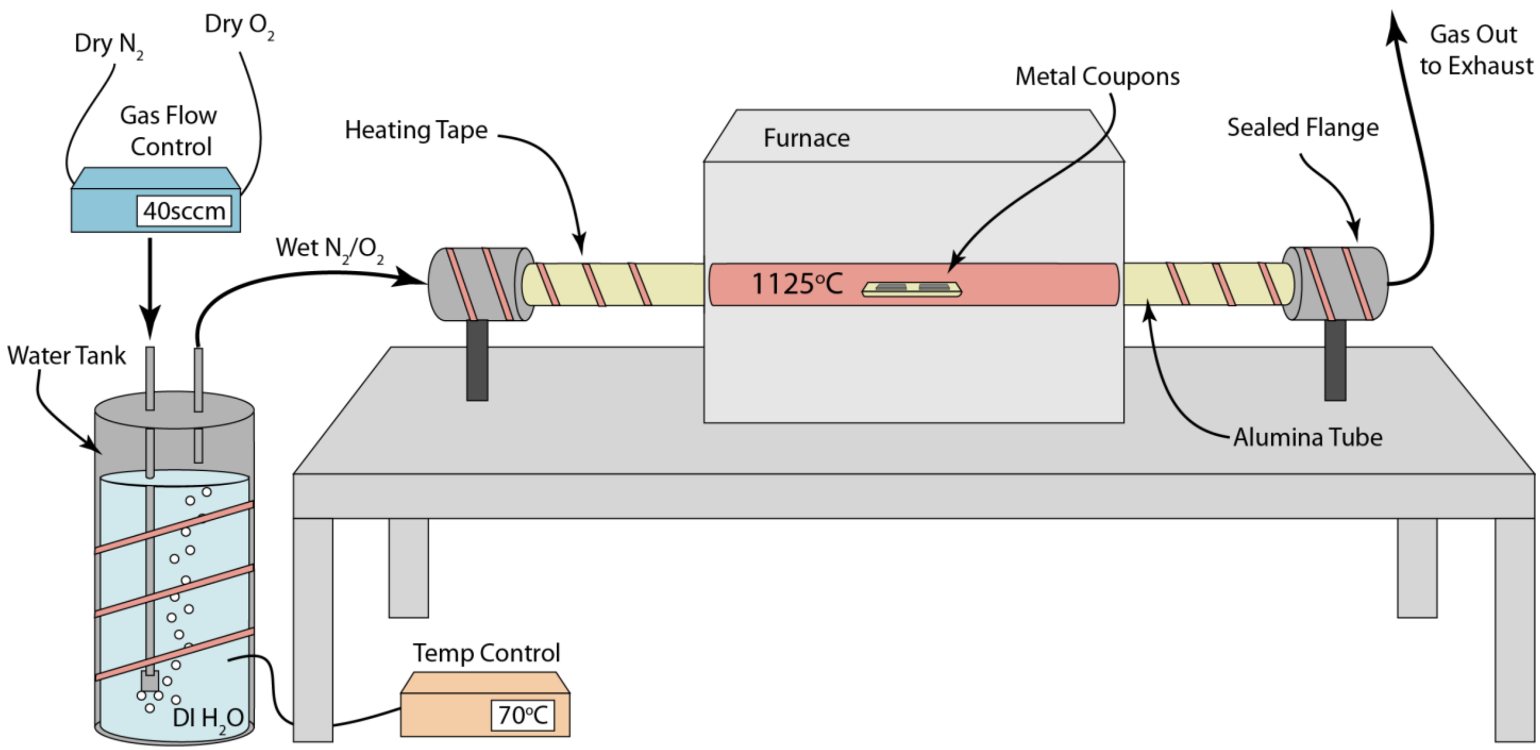
TGO Development Studies: Explore Elevated pH_2O Effects

Isothermal oxidation at 1125°C in variable vol% H_2O environment

1. Sprayed BC, With Substrate
2. Sprayed BC, Substrate Removed
3. Standalone BC



Methods



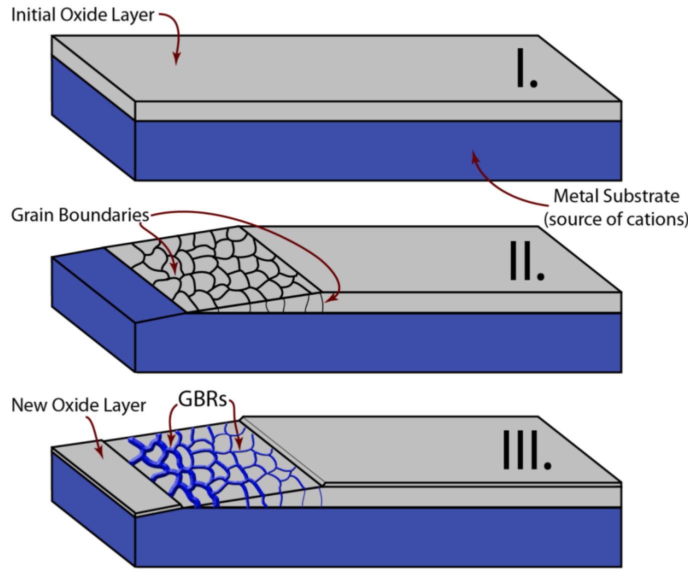
- Water tank temperature determines vol% H_2O via gas-liquid equilibrium exchange
- For 0% H_2O, the water tank is bypassed completely

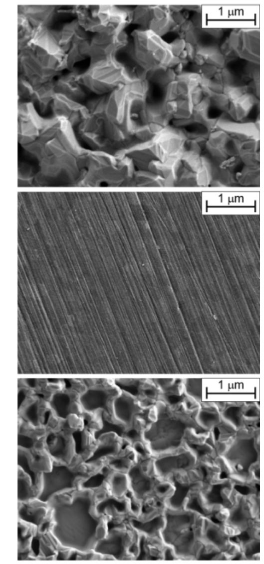
TGO Development Studies: Tapered Specimen Studies

I. Grow an initial oxide layer via isothermal exposure @ 1125°C

II. Polish at a slight angle to create linearly variable diffusion lengths along the wedge

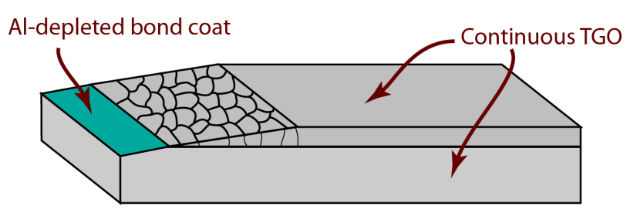
III. Re-oxidize the sample to grow new oxide



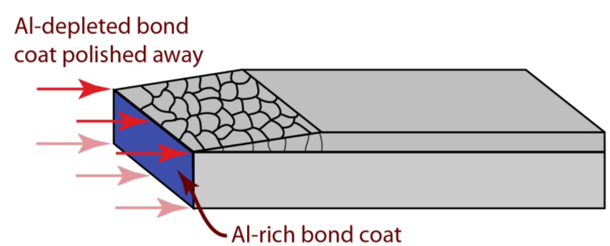


Examples from FeCrAlY

Original Wedge Geometry



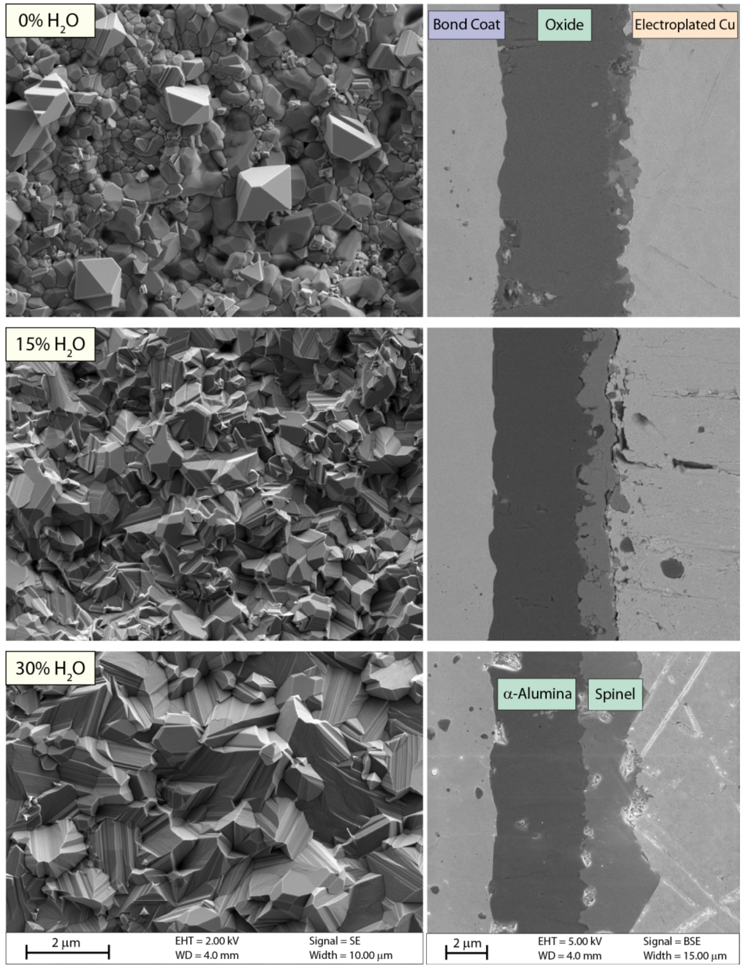
Modified Wedge Geometry

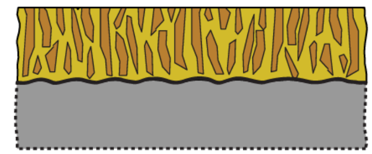


TGO Development Studies: Tapered Specimen Studies

Plan view images ▸

- 0% H_2O sample shows smooth, equiaxed a-alumina grains at surface, with cubic spinel grains scattered on top
- 15 and 30% H_2O samples show that the surface is completely covered with cubic spinel phase

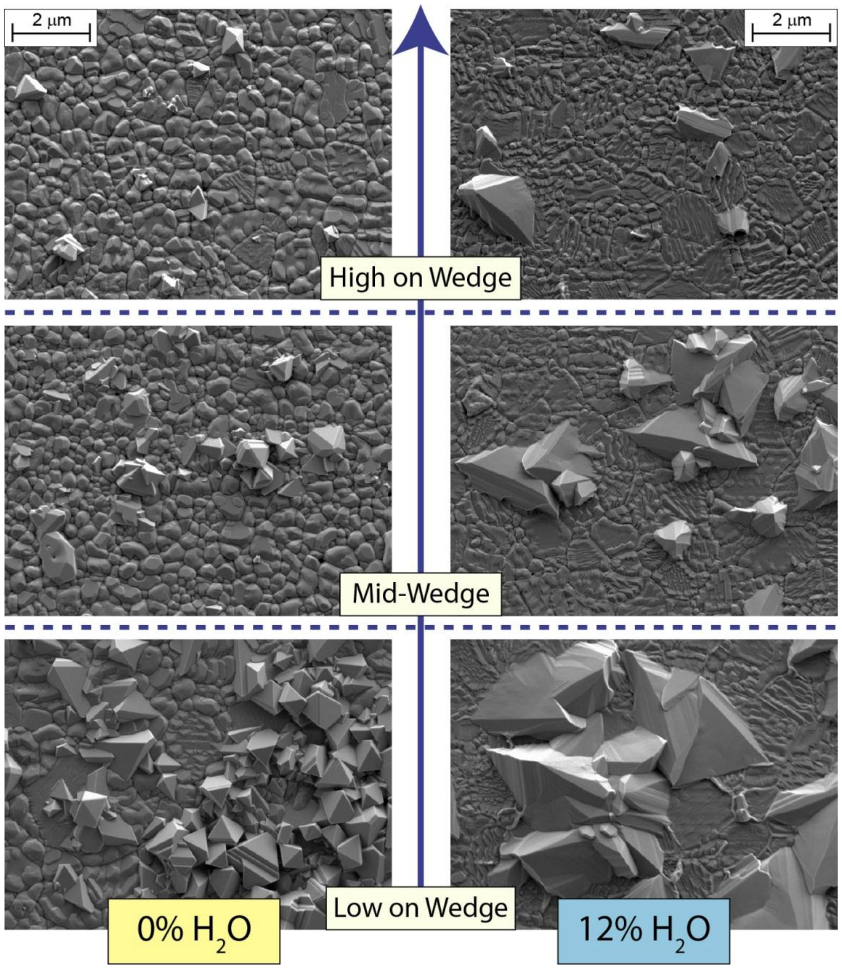


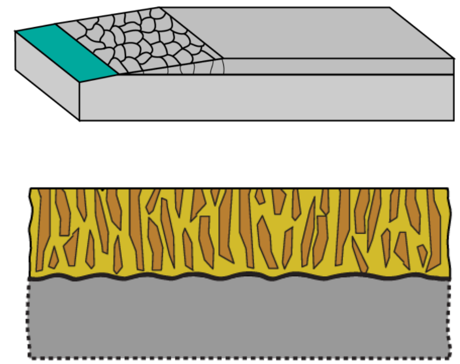


◂ Cross-Section images

- Overall TGO thickness stays virtually the same at all %H_2O
- Spinel top layer is continuous, gets thicker with increasing %H_2O

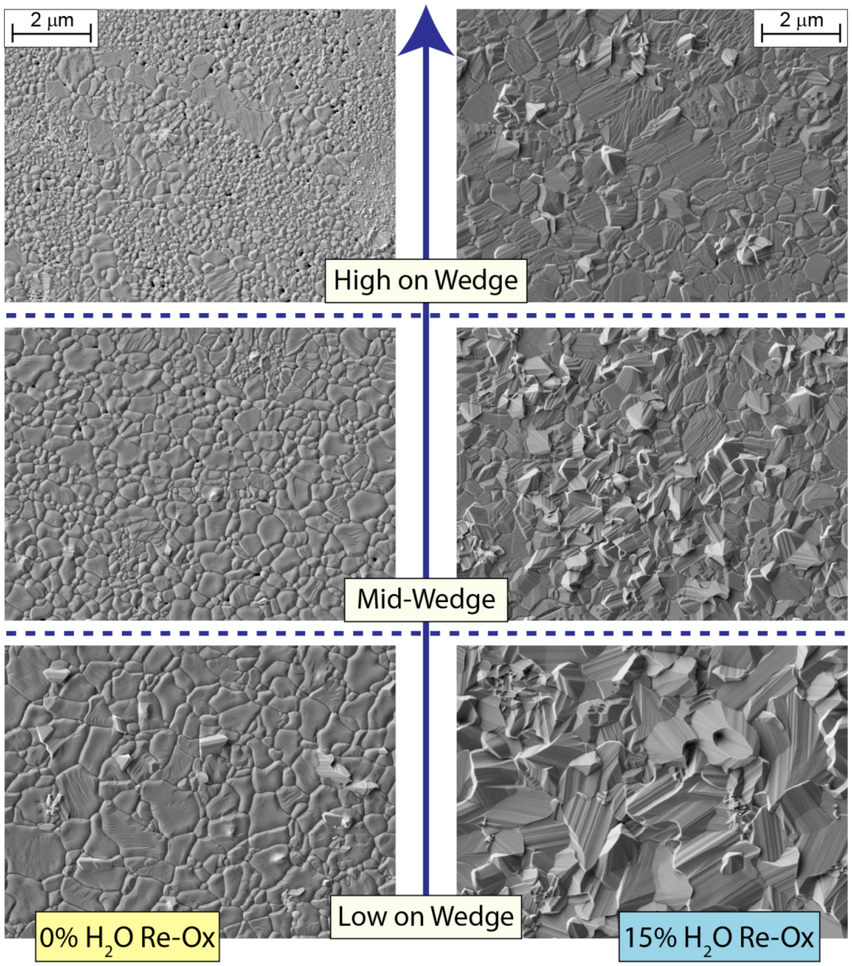
TGO Development Studies: Tapered Specimen Studies

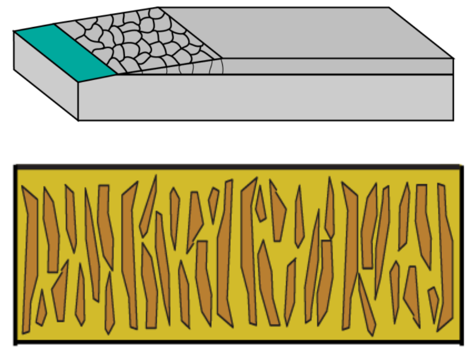




- After polishing and re-oxidation, spinel grains grow above the alumina wedge; grains are larger at the bottom where diffusion lengths through alumina are shortest
  - Water vapor promotes spinel growth at all wedge positions

TGO Development Studies: Tapered Specimen Studies





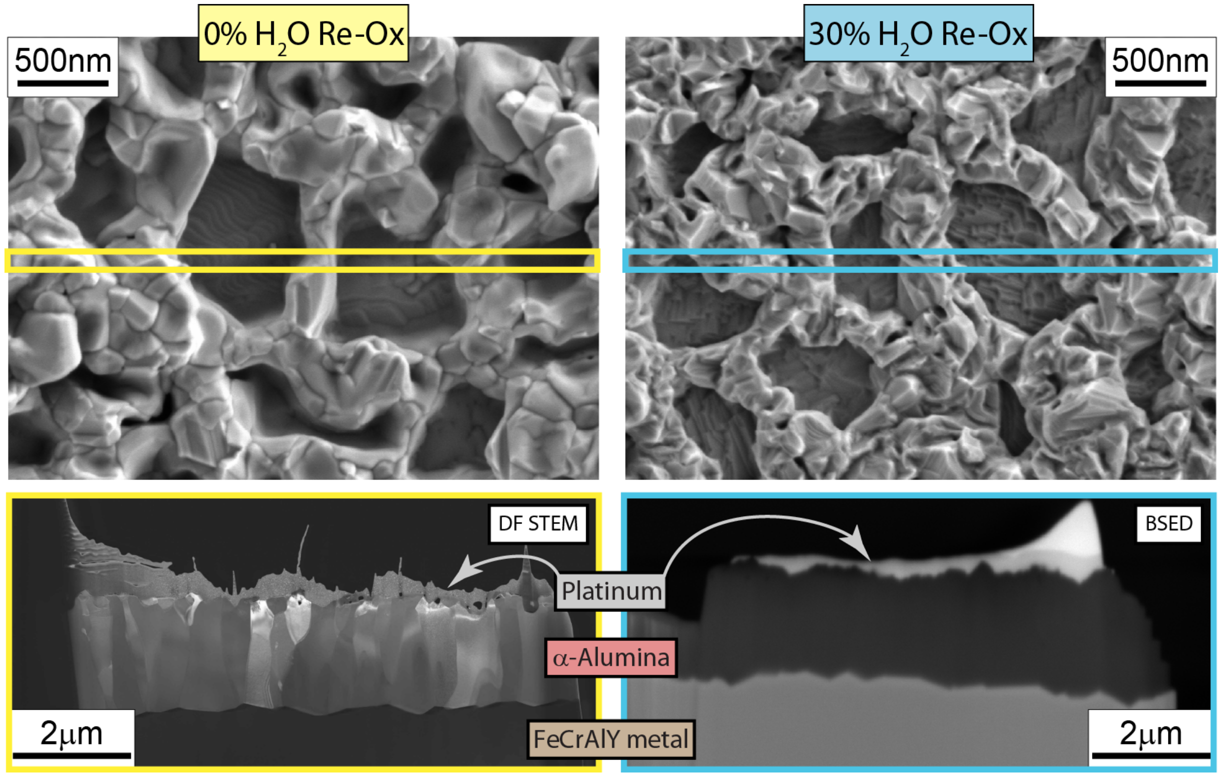
Standalone BC

* Same results using a substrate-mounted vs. a standalone bond coat

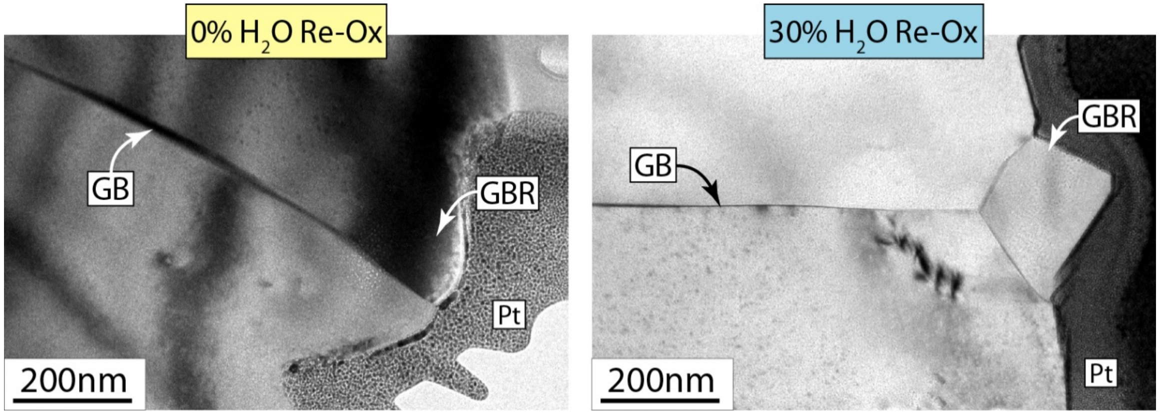
TGO Development Studies: FIB and (S)TEM Studies

Use FeCrAlY to evaluate GBR chemistry in variable H_2O atm

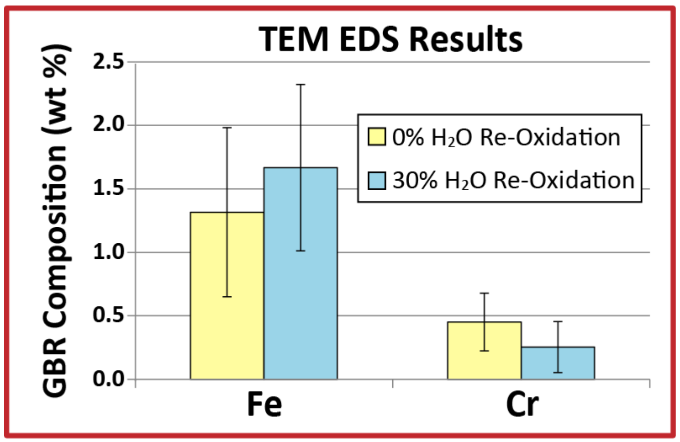
- Expect to see heightened Fe in wet atm, as Fe^{2+} may substitute for Al^{3+} with proton incorporation.
- Prepare TEM cross-sections with FIB and Omniprobe



TGO Development Studies: FIB and (S)TEM Studies

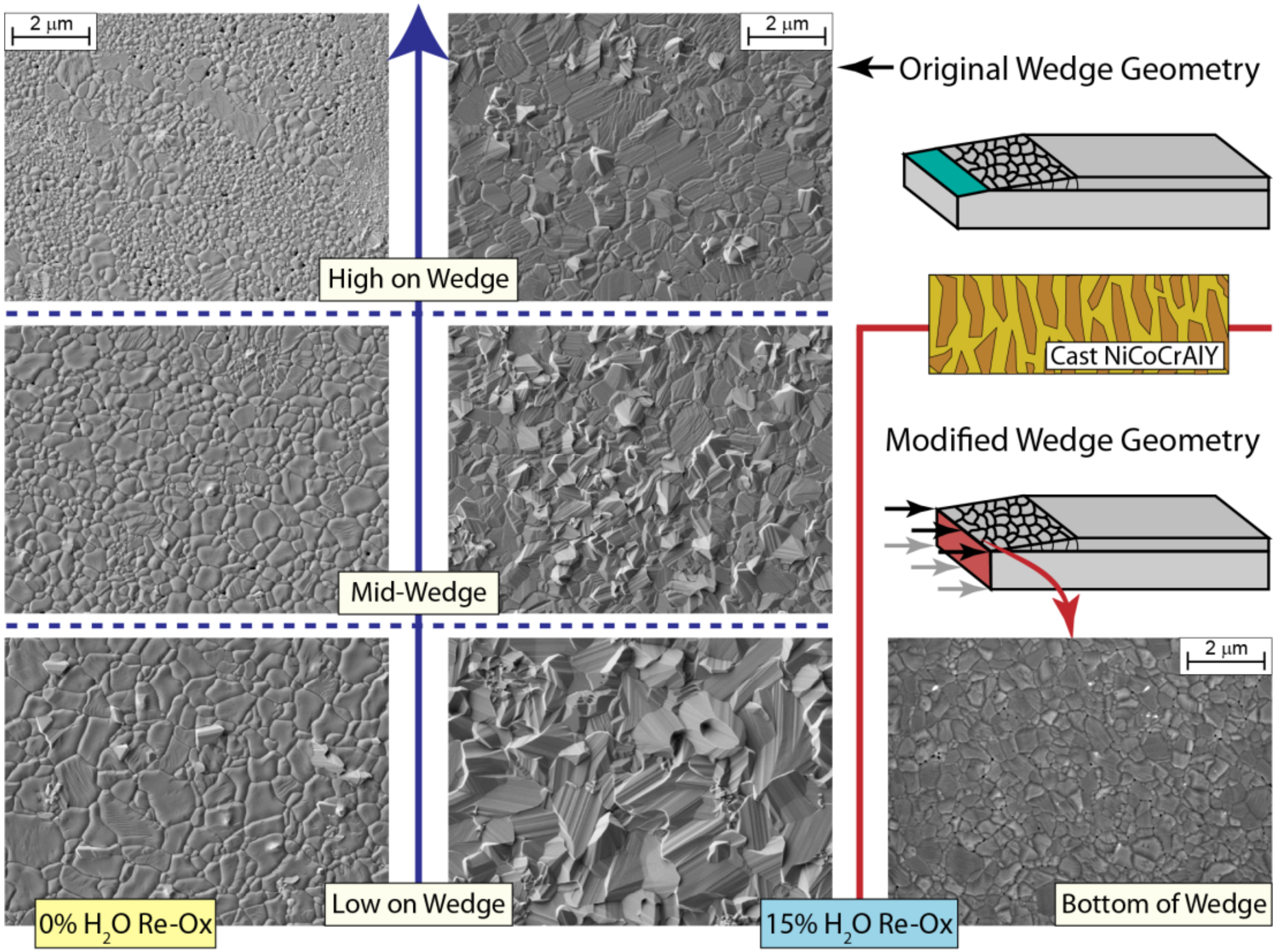


TEM

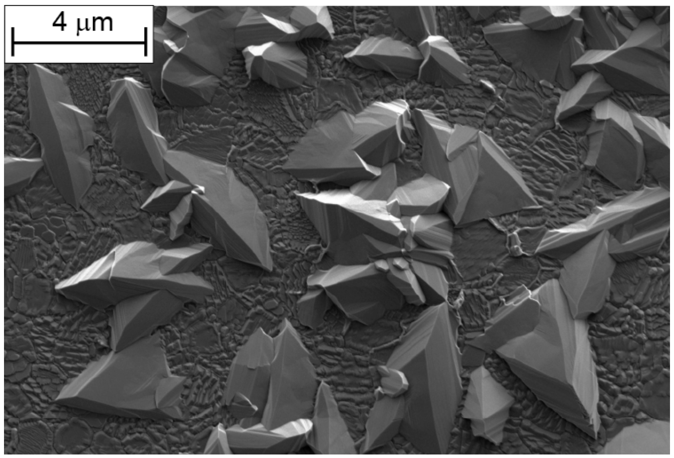


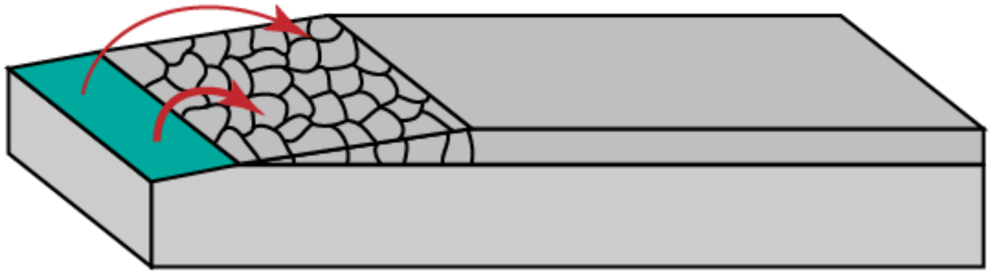
- ▲ Water vapor induces faceting of the grain boundary ridges.
- ◄ Fe and Cr composition of GBRs is statistically equivalent in dry and wet re-oxidation atm, indicating no change in cation diffusion.

TGO Development Studies: Tapered Specimen Studies

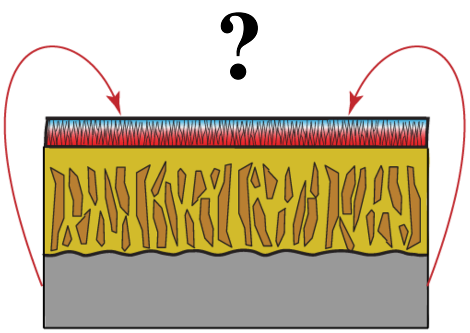


TGO Development Studies: Volatilization Effects



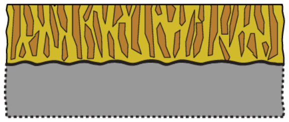


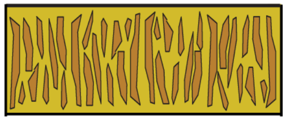
- The exposed, Al-depleted wedge (rich in Ni, Cr and Co) grows non-ideal oxides that volatilize and redeposit via vapor phase proportionately up the wedge



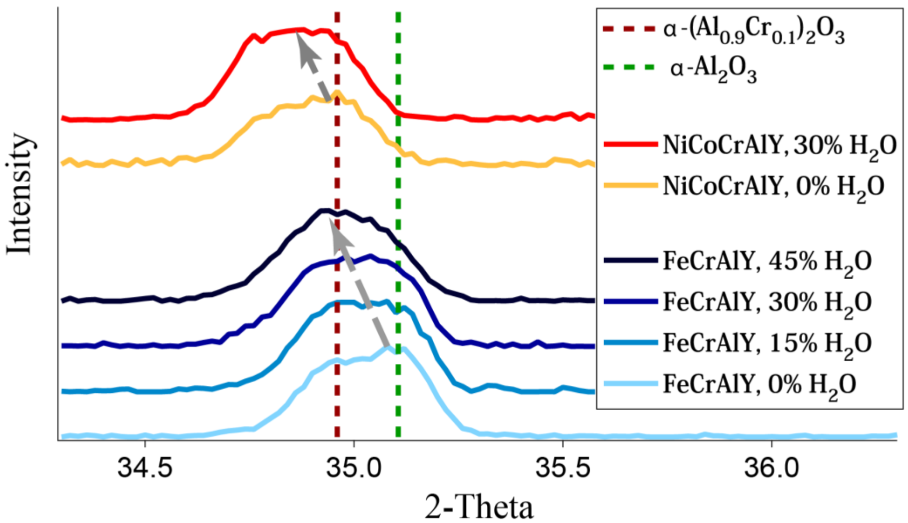
TGO Development Studies: XRD Measurements

XRD Results:

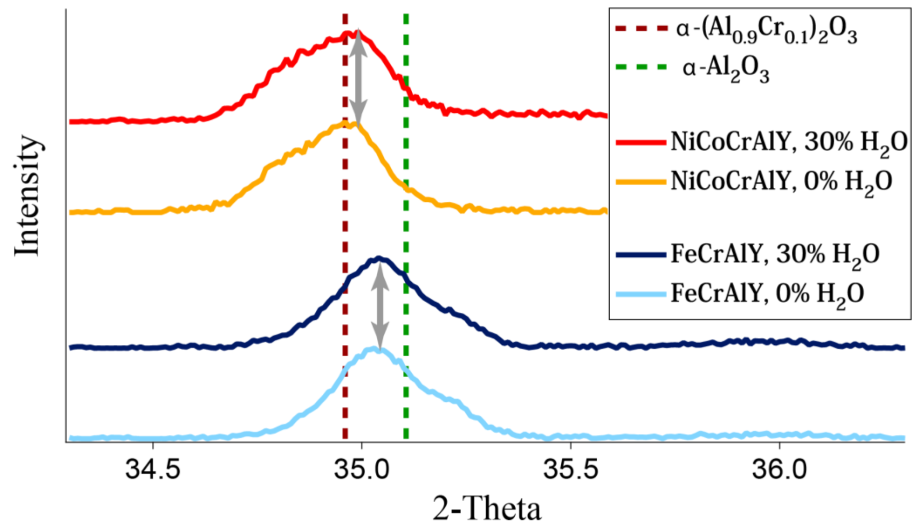




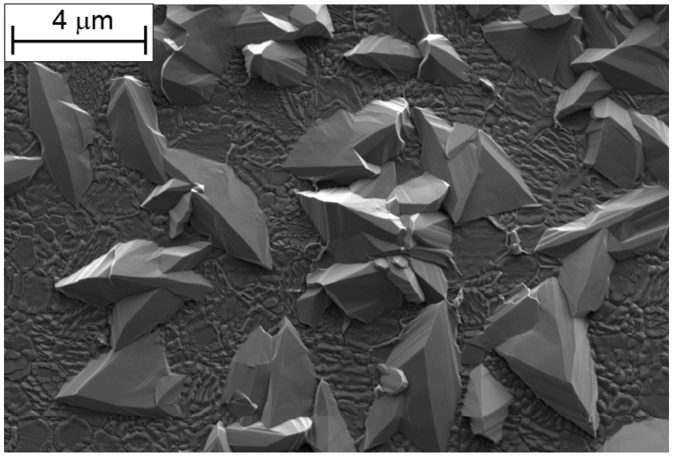
Same Furnace

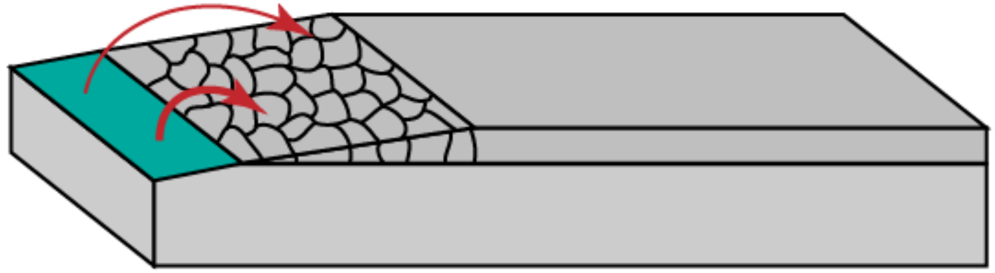


Separate Furnaces



Volatilization



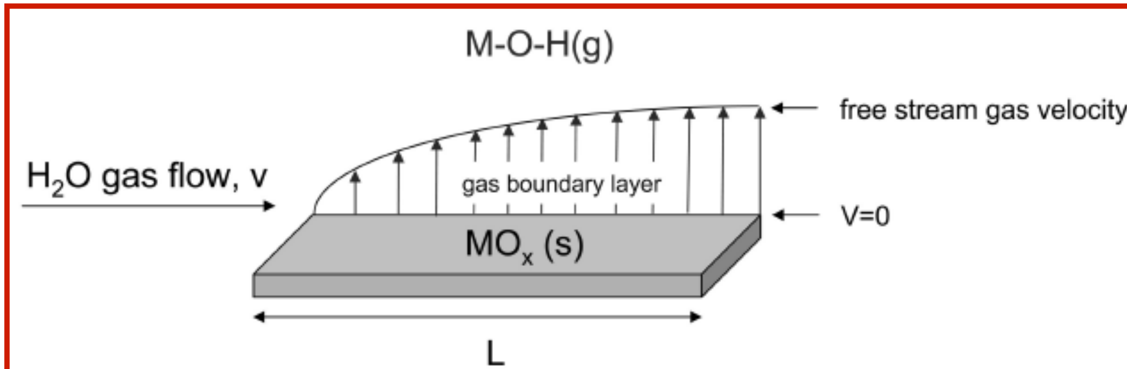


- The exposed, Al-depleted wedge (rich in Ni, Cr and Co) grows non-ideal oxides that volatilize and redeposit via vapor phase proportionately up the wedge

$$MO_x + nH_2O(g) + mO_2(g) = MO_{(x+n+2m)}H_{(2n)}(g)$$

e.g. $2NiO(s) + H_2O(g) + 1/2O_2 = 2Ni(OH)_2(g)$

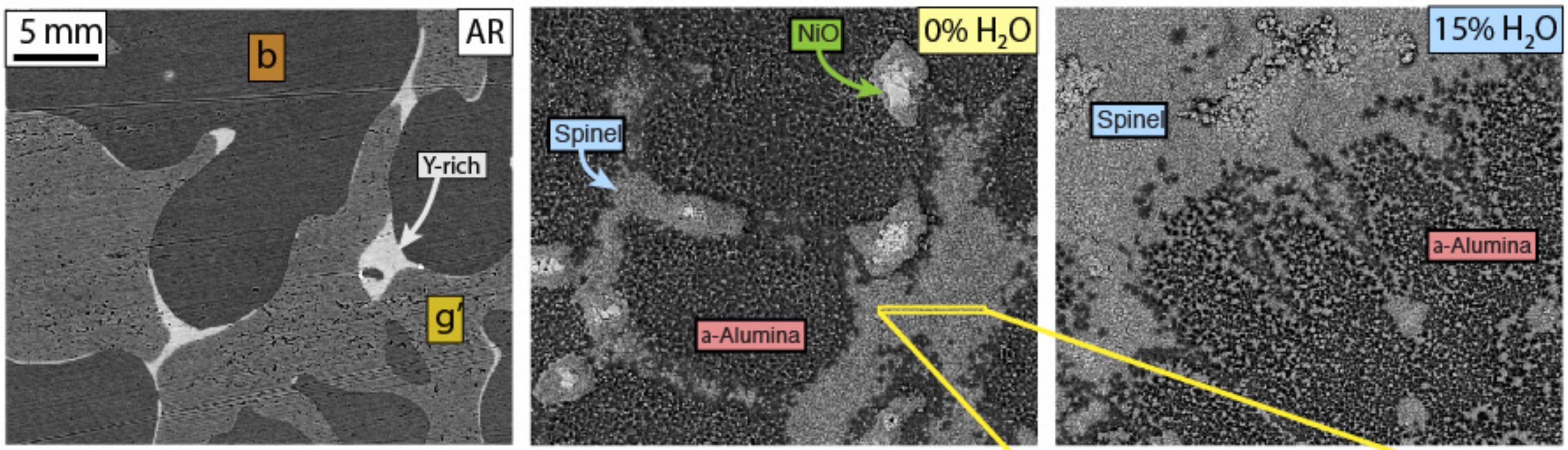
$1/2Cr_2O_3(s) + H_2O(g) + 3/4O_2 = CrO_2(OH)_2(g)$



- Solid spinels can be synthesized via vapor phase combination of M^{2+} and M^{3+} metal hydroxides (e.g. Ni^{2+} and Cr^{3+})

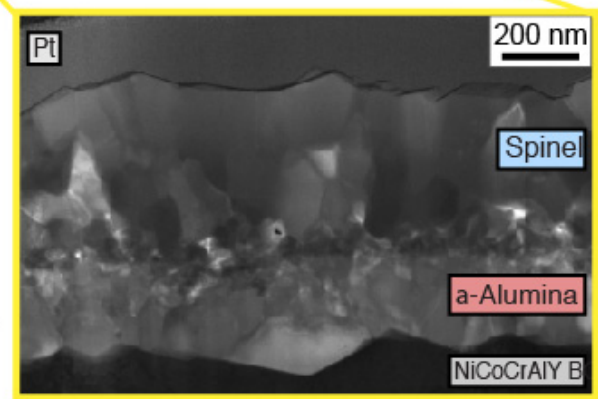
Opilia EJ, JOM (2006)

NiCoCrAlY & CoNiCrAlY:



▲ Backscatter electron images show coarse b/g′/Y-rich phase distribution in as received (AR) NiCoCrAlY. When oxidized for "0 hours" at 1125°C (i.e. ramp up, ramp down at 5°C/min), coarse distribution of alumina (dark), spinel (medium), and NiO (light gray) results. More spinel is promoted at the TGO surface in 15% vs. 0% H_2O.

A thin lamella cross-section cut from the 0% H_2O sample ▶ reveals a bilayer TGO via dark field STEM imaging. Thickness of transient stage spinel is roughly equal in all H_2O environments; spinel surface coverage varies most.

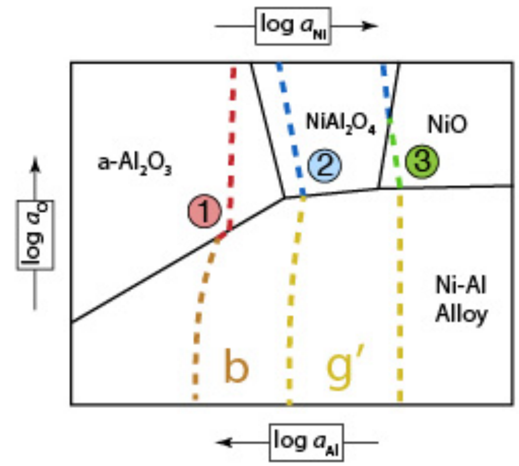


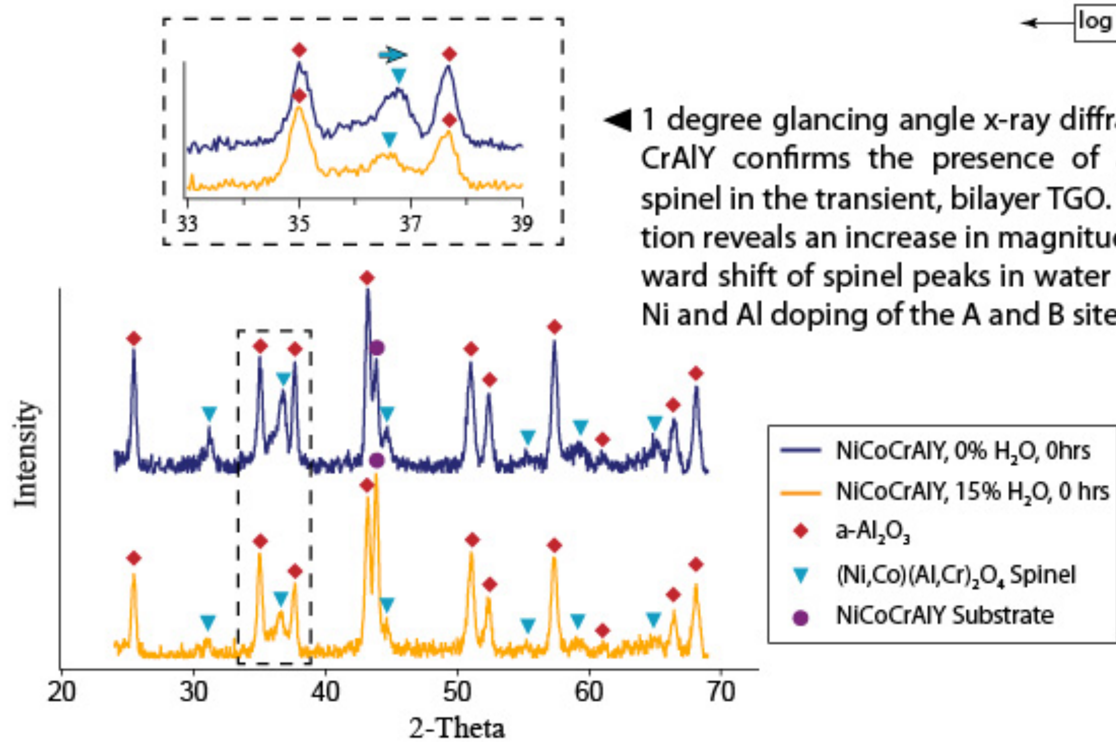
TGO Development Studies – Transient Stages

An activity diagram for a Ni-Al alloy system, shows three ▶ potential reaction pathways:

1. Al-rich phase (e.g. b) forms a-alumina under steady state conditions
2. Ni-rich phase (e.g. g′) forms spinel during high P_{H_2O}/P_{O_2} transient stage
3. Ni-rich phase + high effective P_{O_2} grows transient NiO, which evolves into spinel via reaction with a-alumina / diffusing Al

(Schematic adapted from MJ Stiger et al, 1999)

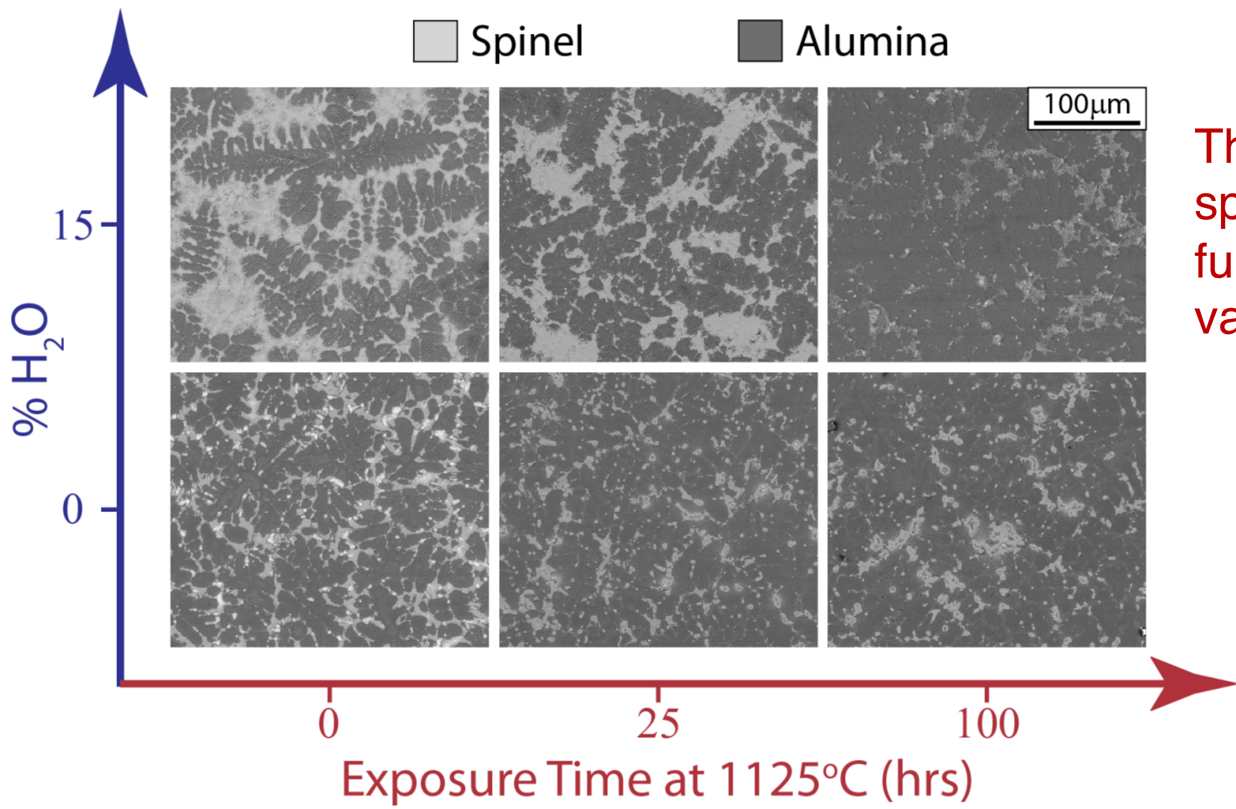




◀ 1 degree glancing angle x-ray diffraction of NiCoCrAlY confirms the presence of a-alumina and spinel in the transient, bilayer TGO. A close inspection reveals an increase in magnitude and a rightward shift of spinel peaks in water vapor, towards Ni and Al doping of the A and B sites, respectively.

TGO Development Studies: Evidence of Ni Volatilization

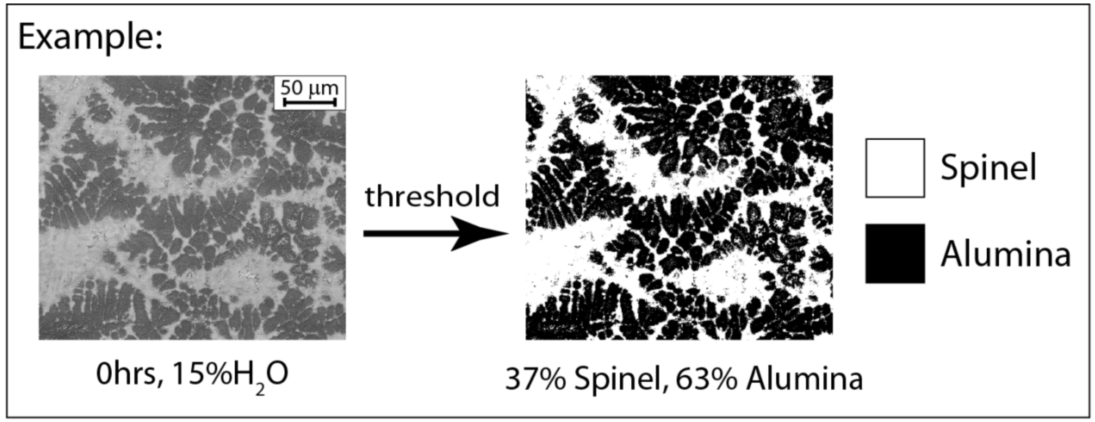
Visual inspection of low magnification, plan view, backscatter electron images shows the relative distribution of alumina and spinel on the surface of the TGO –



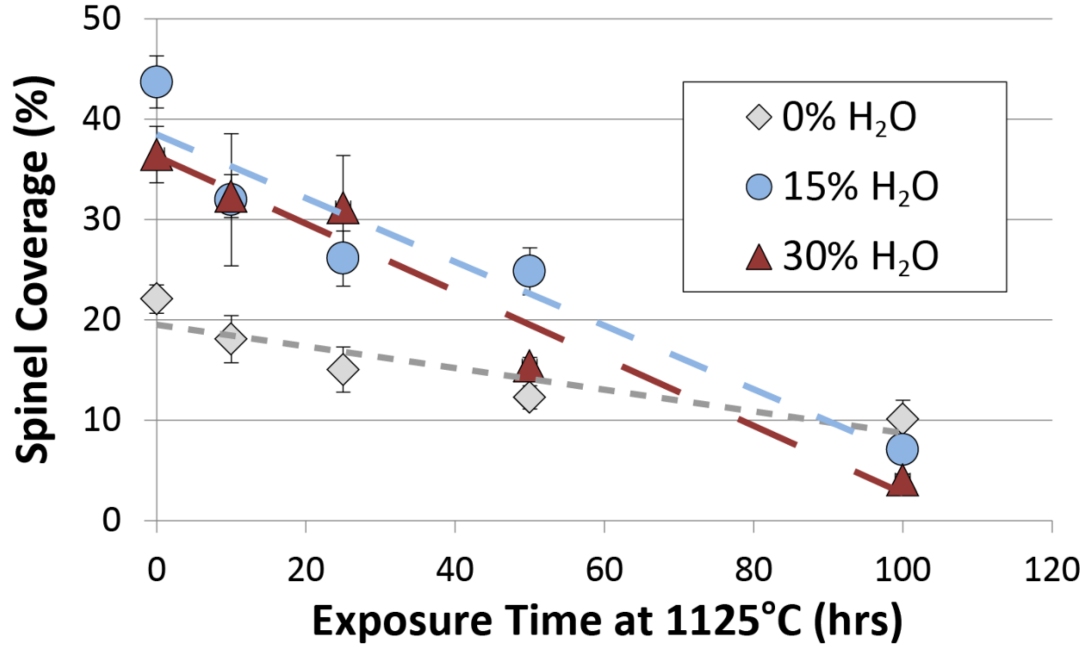
The amount of surface spinel *decreases* as a function of time in water vapor

TGO Development Studies: Evidence of Ni Volatilization

By thresholding plan view images, the amount of surface spinel (measured as a % of surface area coverage) can be quantified and plotted for many samples:

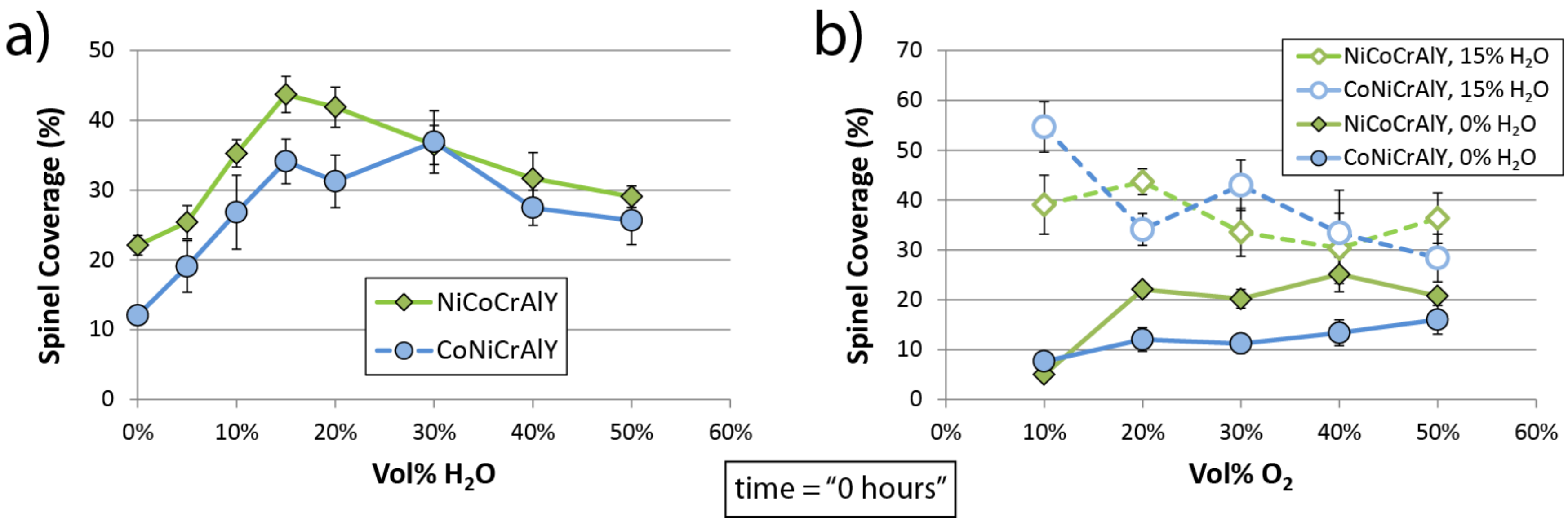


For all environments, spinel coverage decreases as a function of time. In water vapor, more spinel exists early in oxidation, but also disappears more rapidly.



TGO Development Studies: Transient Oxidation & Volatilization

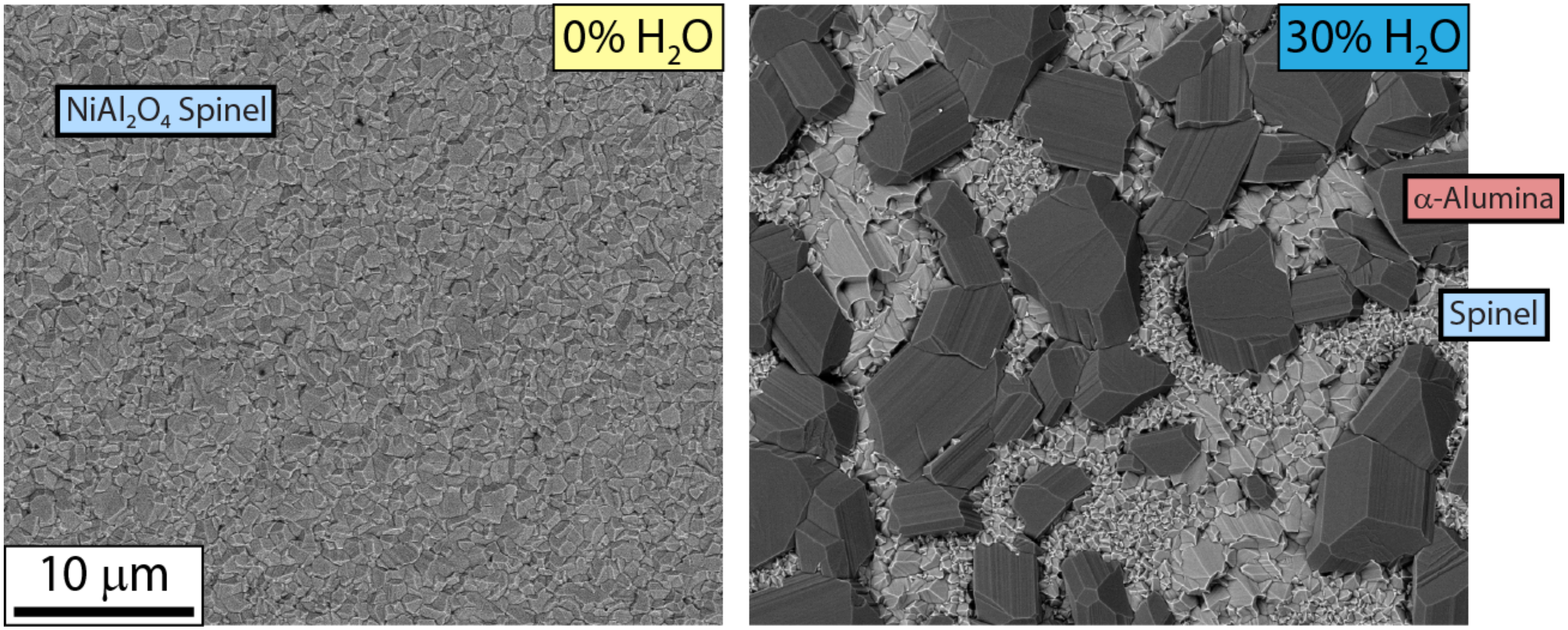
Focusing on the early stage of oxidation (0 hours at 1125°C), where spinel coverage is always highest with no top coat, spinel coverage can be plotted as a function of a) H_2O and b) O_2.



a) For both NiCo- and CoNiCrAlY, spinel coverage increases as a function of water vapor to a point, before decreasing. It is likely that the decrease is due to volatilization: the rate of volatilization outstrips the rate of spinel growth at high enough H_2O. Experiments must be repeated with a top coat present to verify this.

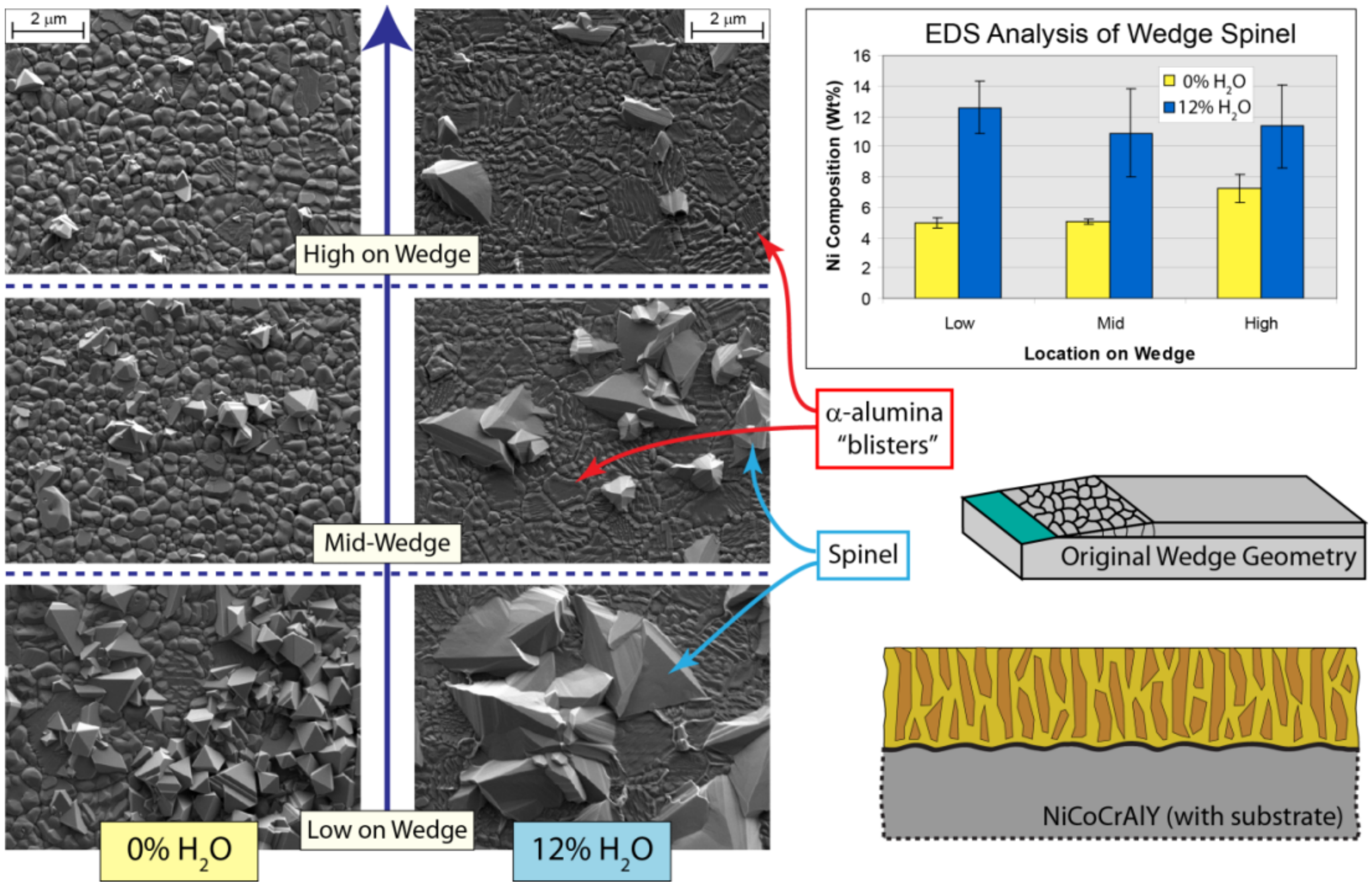
b) Spinel coverage also increases as a function of O_2; adding water vapor to any O_2 composition increases spinel coverage as well.

$Ni_{70}Al_{30}$ 100hrs, Plan View



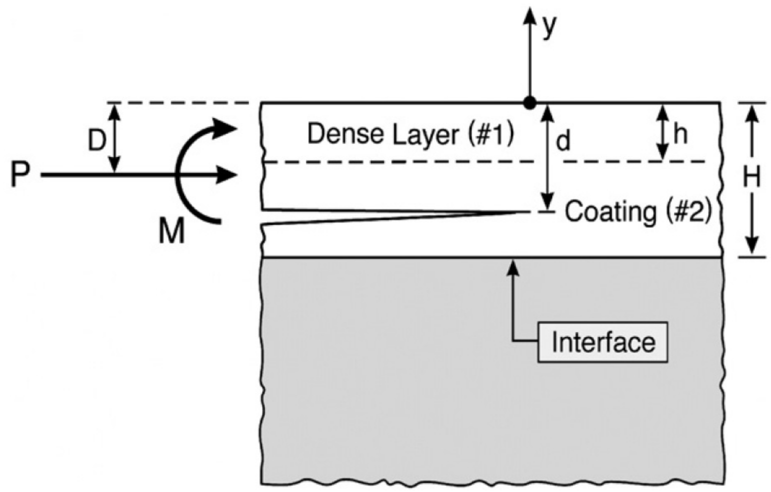
In a simple Ni-Al alloy, a bilayer oxide forms in 0% H_2O, with $NiAl_2O_4$ spinel covering the entire surface (alumina is beneath, not pictured). At 30% H_2O, large alumina grains protrude from the surface, possibly the result of Ni volatilizing away, causing $NiAl_2O_4$ to reduce to Al_2O_3. This could be similar to what is observed in NiCoCrAlY, only more severe because the amount of spinel is so much greater for an alloy not designed to prevent its formation. The heavily faceted alumina grains are characteristic of a water vapor interaction.

Evidence of Ni-species Redeposition



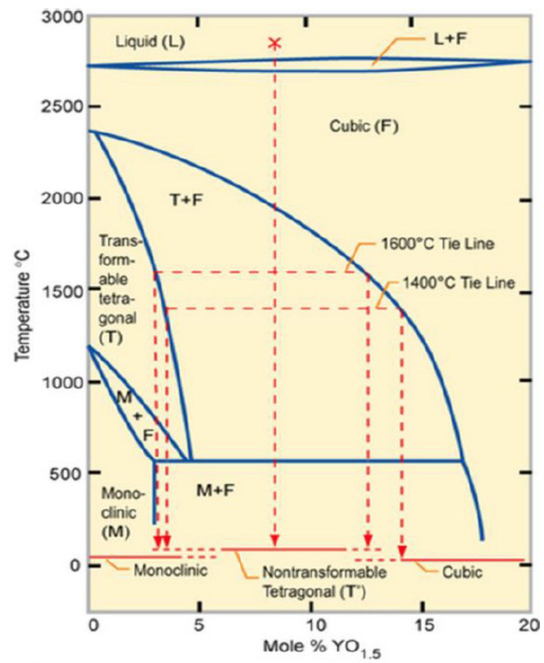
Running a wedge re-oxidation experiment on NiCoCrAlY with the "original wedge geometry" (i.e. exposed, Al-depleted bond coat surface at base of wedge), large spinel domains form on the wedge surface after just 4 hours. Ni is detected in the spinel by EDS.

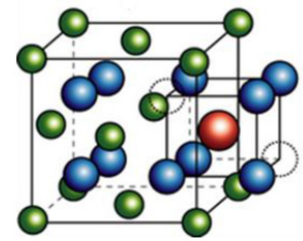
TBC Degradation Studies: Destabilization w/ high pH_2O



Sintering Effects

Y-stabilized ZrO_2

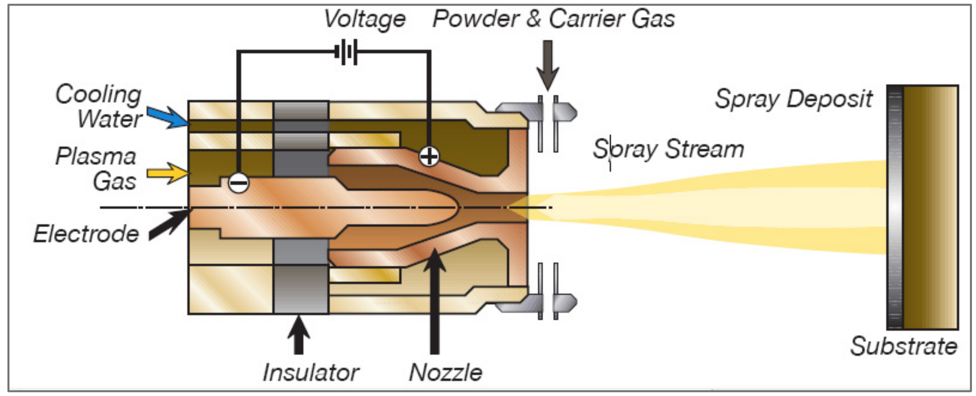




Fluorite

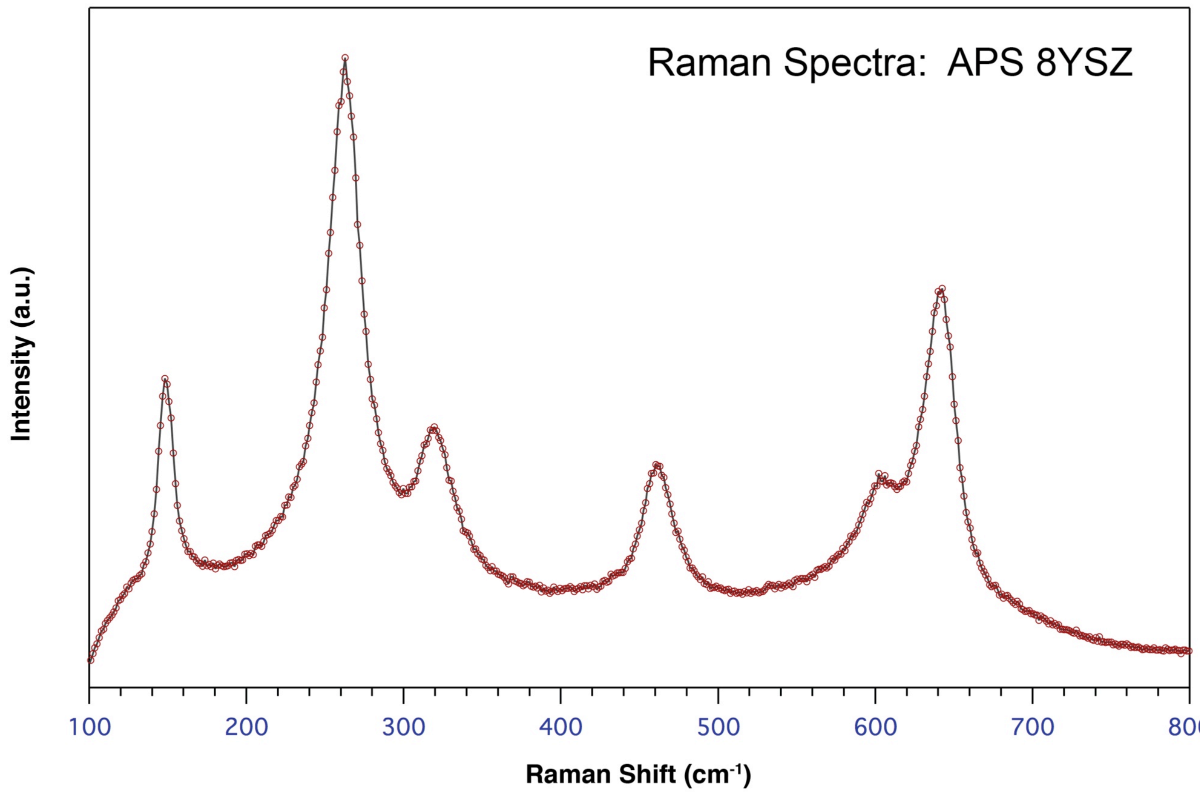
Phase Instability

TBC Degradation Studies: Materials Preparation



JÜLICH
FORSCHUNGSZENTRUM

TBC Degradation Studies: Raman and XRD Measurements



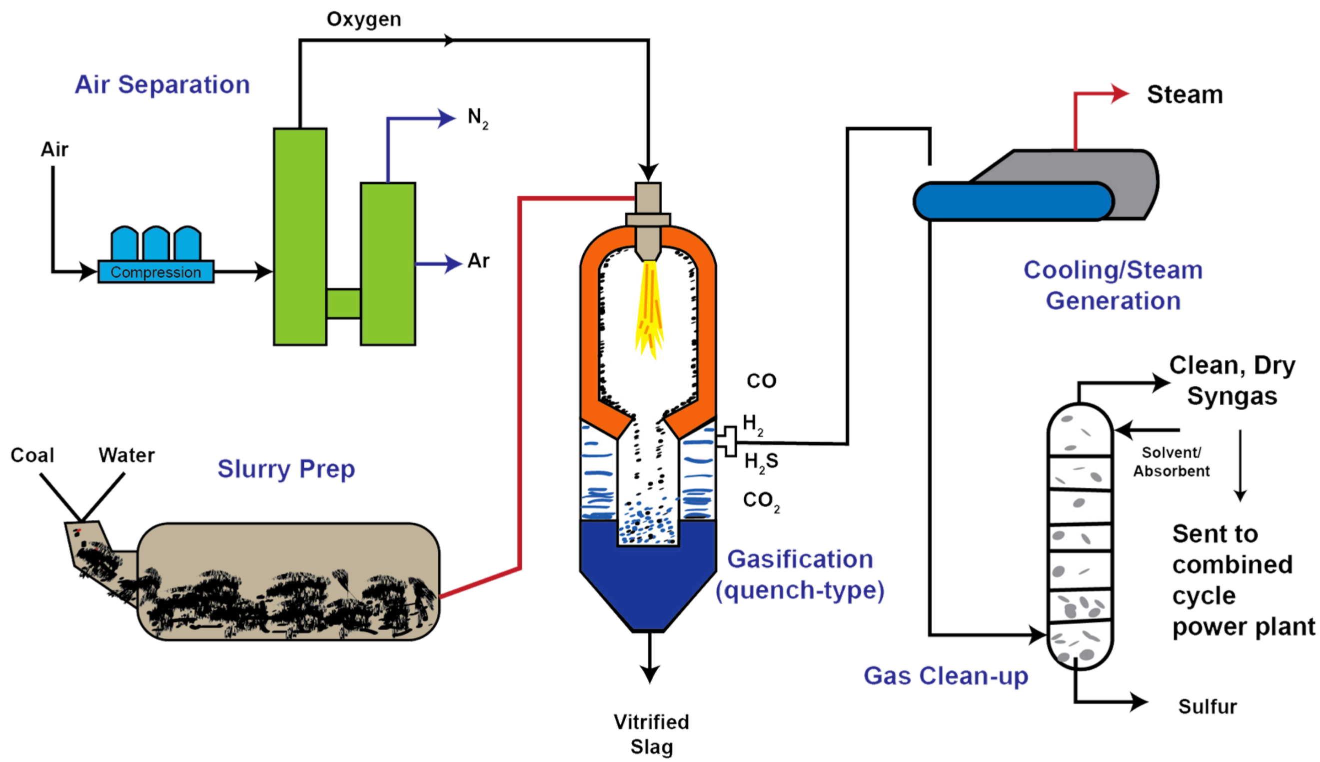
Raman spectroscopy is being used to monitor phase evolution as a function of environmental parameters under extended aging exposures

In-situ XRD Measurements are also being utilized for such measurements

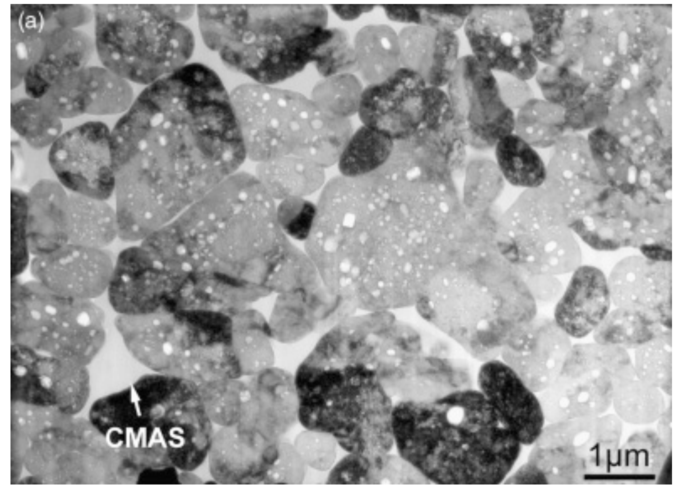
TBC Degradation Studies: Fly Ash and CMAS Studies

Coal gasification may leave residual fuel impurities to combine with non-combustibles in the intake air to form surface deposits and infiltrating phases.

Understanding the deposit thermo-chemical and thermo-physical properties, and the resulting thermo-mechanical affects is critical to ensuring hot-section materials durability.



CMAS (CaO-MgO_2-Al_2O_3-SiO_2) – Analogous Failure Processes?



Carlos Levi, A.G. Evans (UCSB)

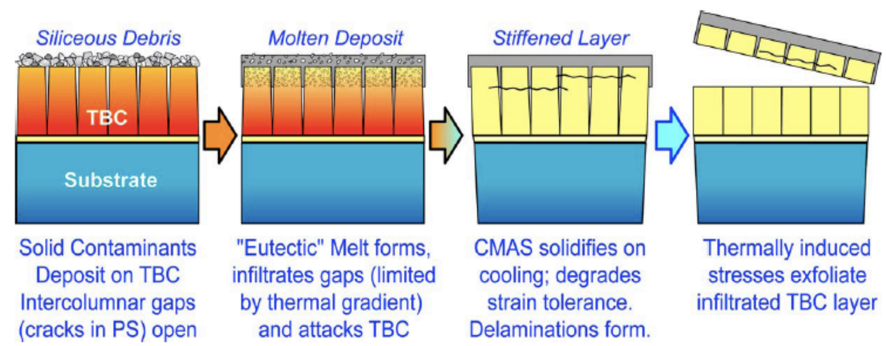
Nitin Padture (Ohio State)

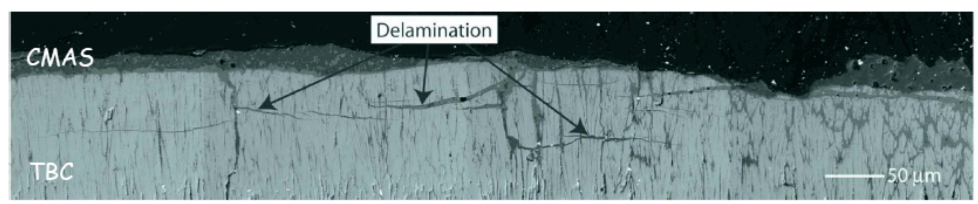
Comprehensive Understanding of Mechanistic Basis of Coating Degradation

Dissolution of YSZ

Melt Infiltration

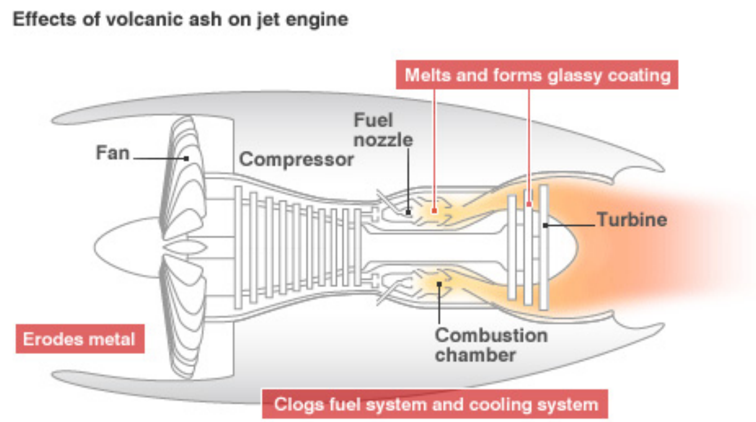
Mitigation Strategies

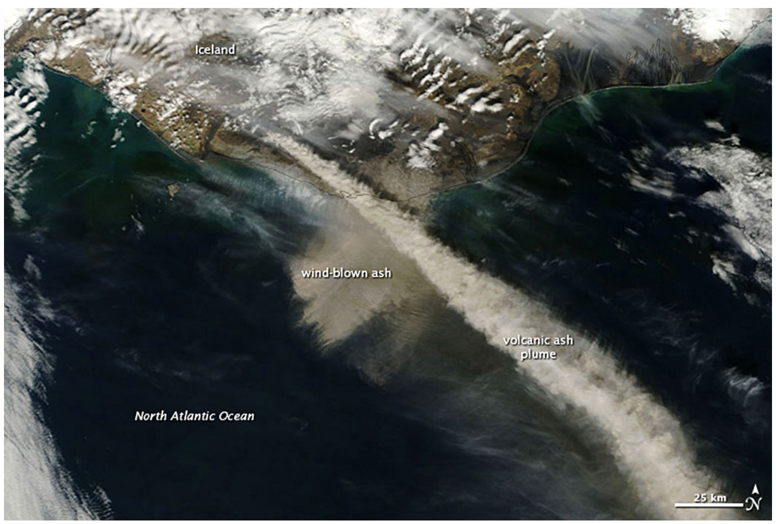


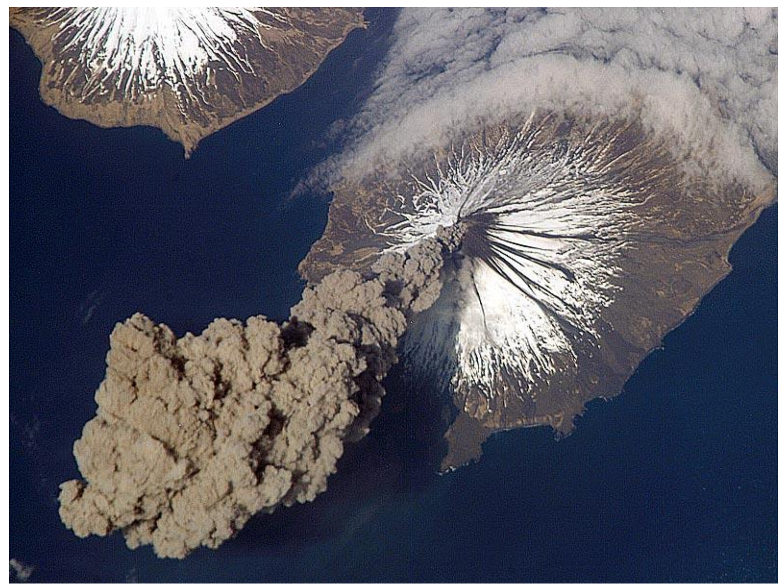


Mercer, Faulhaber, Evans, Darolia, 2005

Eyjafjallajokull Volcano Eruption - Iceland



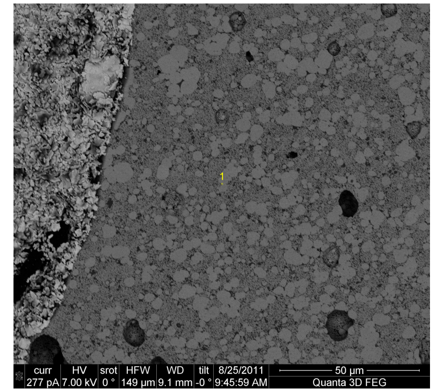




TBC Degradation Studies: Fly Ash and CMAS Studies

Wt%	Spectrum 1	Spectrum 2	Spectrum 3	Average
Al	9.07	9.40	8.97	9.15
Ca	4.93	5.20	5.01	5.05
Fe	7.39	8.90	7.45	7.91
K	1.52	1.77	1.52	1.60
Mg	0.80	0.76	0.79	0.78
Na	2.56	2.24	2.15	2.30
O	49.03	45.68	47.35	47.35
Si	25.91	26.49	25.56	25.99
Ti	0.35	0.46	0.36	0.39

Compound	Wt%
Al2O3	17.28
CaO	7.23
Fe2O3	11.31
K2O	1.93
MgO	1.30
Na2O	3.10
SiO2	56.31
TiO2	0.65



Energy Dispersive Spectroscopy of Petcoke/Coal blend bottom ash. Contains a high weight percent of silica and iron differentiation it from CMAS.

Compound	Wt%
Al2O3	19.79
C	5.40
CaO	4.40
Fe2O3	4.26
K2O	3.53
MgO	0.78
Na2O	0.59
P2O5	0.44
S	1.21
SiO2	58.65
TiO2	0.56

Data obtained from a study of fly ash obtained from the IGCC plant in Puertollano Spain.

Oriol Font et.al

TBC Degradation Studies: Fly Ash and CMAS Studies

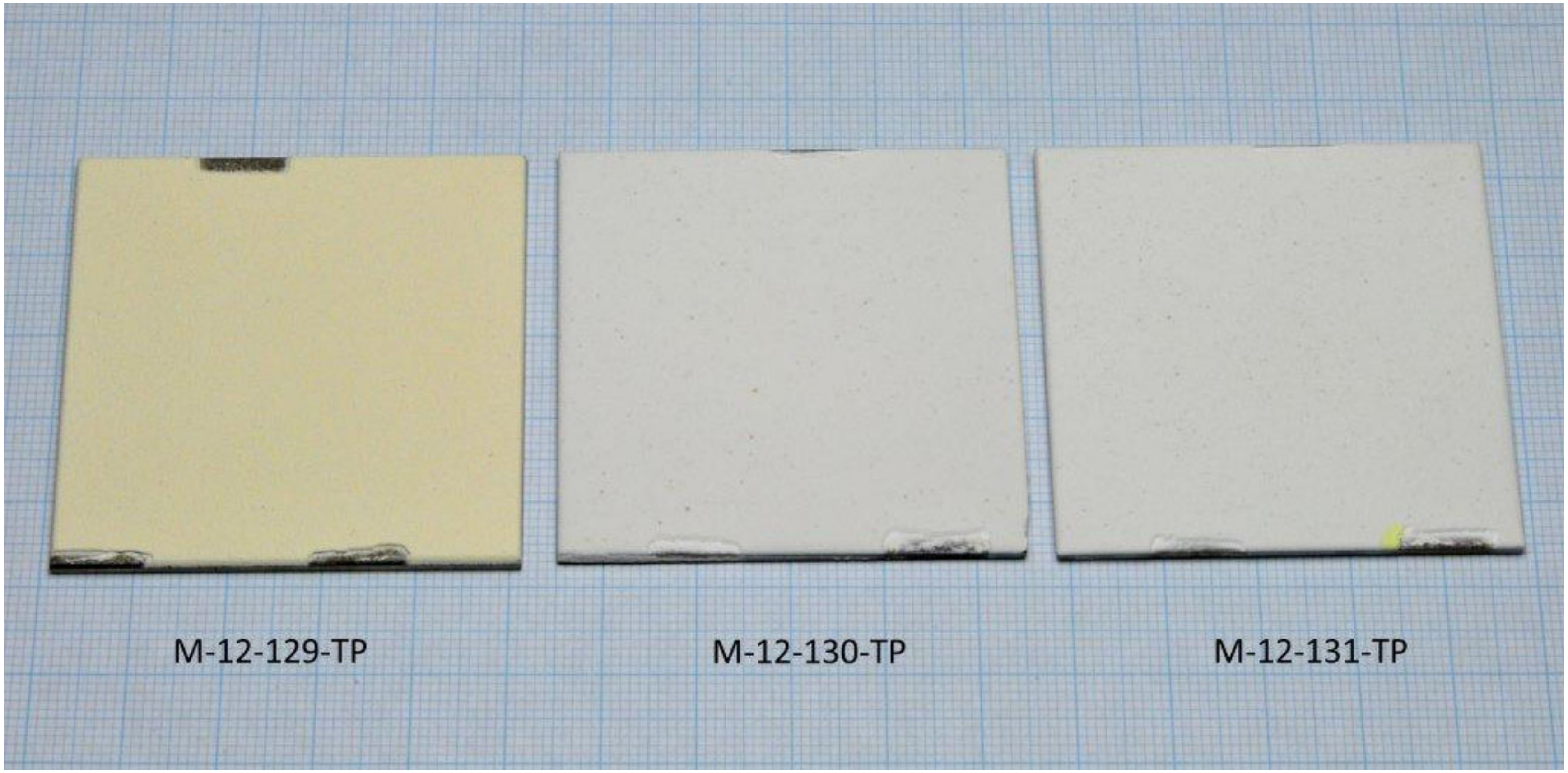
Component (wt %)	Fly Ash Type			
	Typical Coal	Synthetic Coal	Biomass (Pulverized Wood)	Lab Fly Ash
SiO_2	40.0	55.0	14.1	58.0
Fe_2O_3	17.0	10.0	2.7	4.0
Al_2O_3	24.0	25.0	2.9	19.0
CaO	5.8	5.0	20.7	4.0
Na_2O	0.8	1.0	1.0	0.0
K_2O	2.4	1.0	8.1	3.5 (K_2SO_4)
MgO	> 0.2	> 0.2	4.0	0.0

A representative CMAS composition (believed to be relevant for HHC/syngas fueled systems) is being synthesized, characterized, and utilized in TBC degradation studies.

Ca	Mg	Al	Si	Fe
12	5	4	6	20

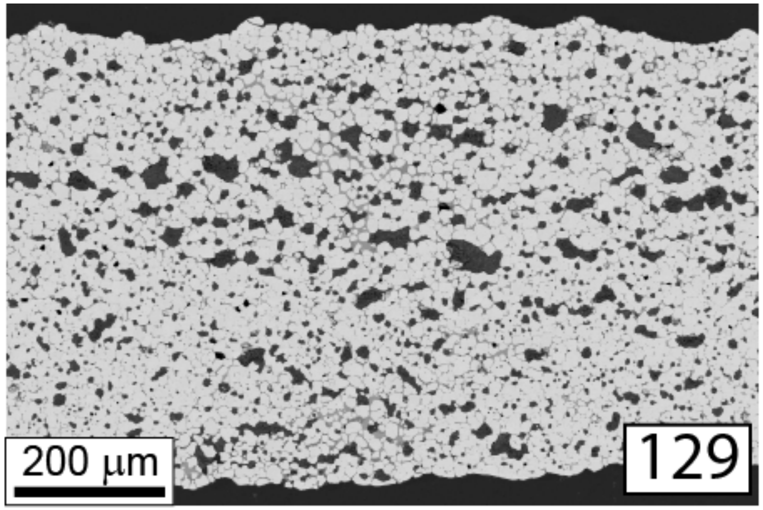
Free-standing APS TBC materials are being subjected to CMAS deposit melting and infiltration exposures under isothermal conditions. Also preparing Nitrate-based solutions for burner-rig based exposures (under thermal gradient conditions).

CMAS Degradation of YSZ: Microstructure Dependence

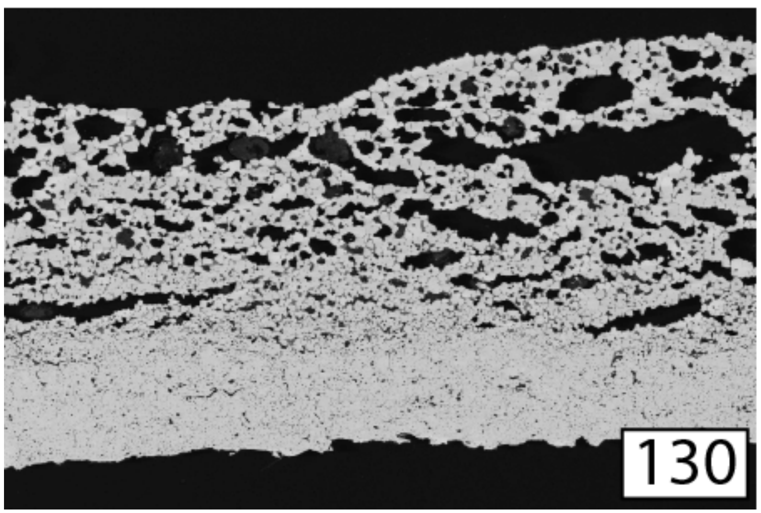


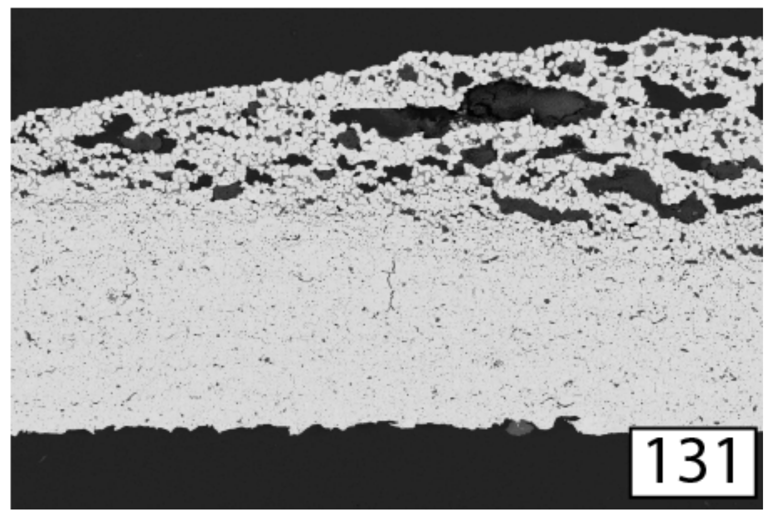
- Materials were sprayed at three distinct conditions to systematically control microstructural characteristics, and were then removed from substrate to carry out experiments on free-standing layers.

CMAS Degradation of YSZ: Microstructure Dependence



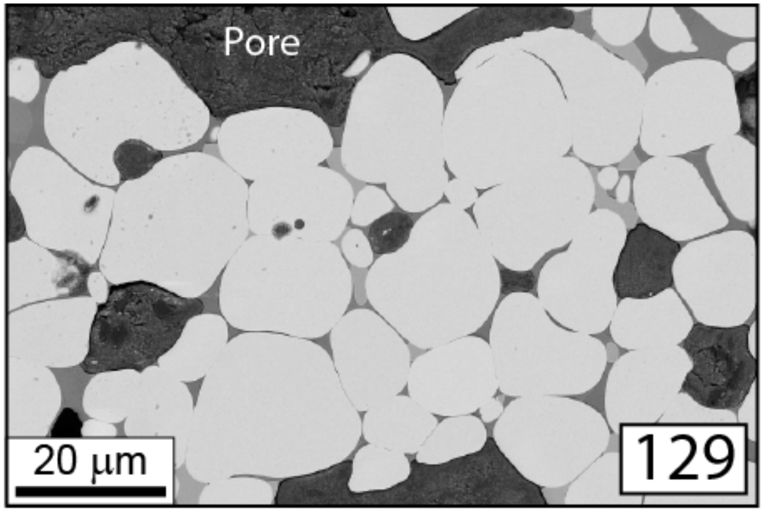
View of full sample thicknesses (image widths = 1mm)



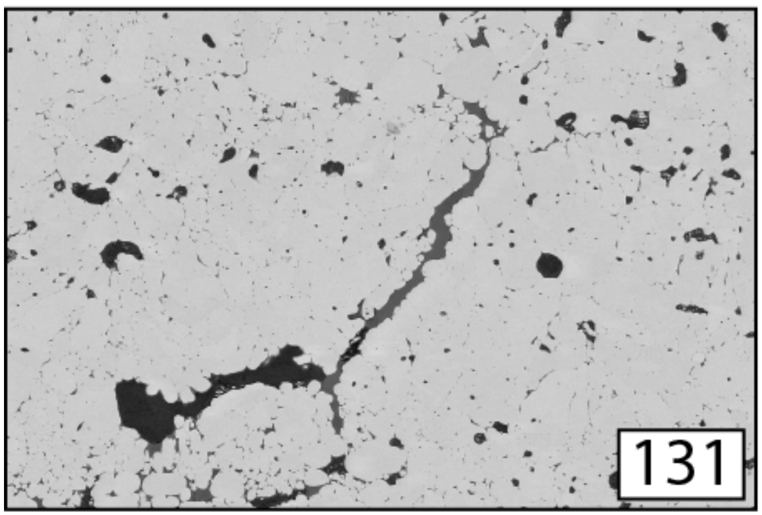


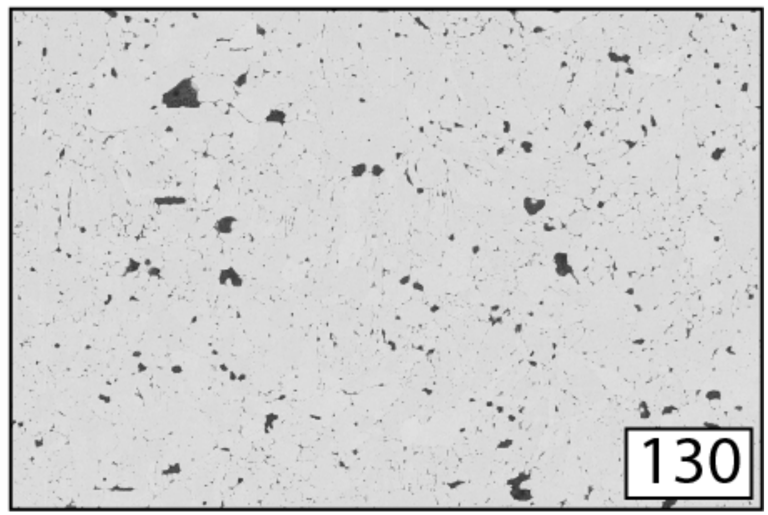
- These images represent the worst areas of CMAF attack on three samples

CMAS – Based Degradation of YSZ: Thermo-Chemical Interactions



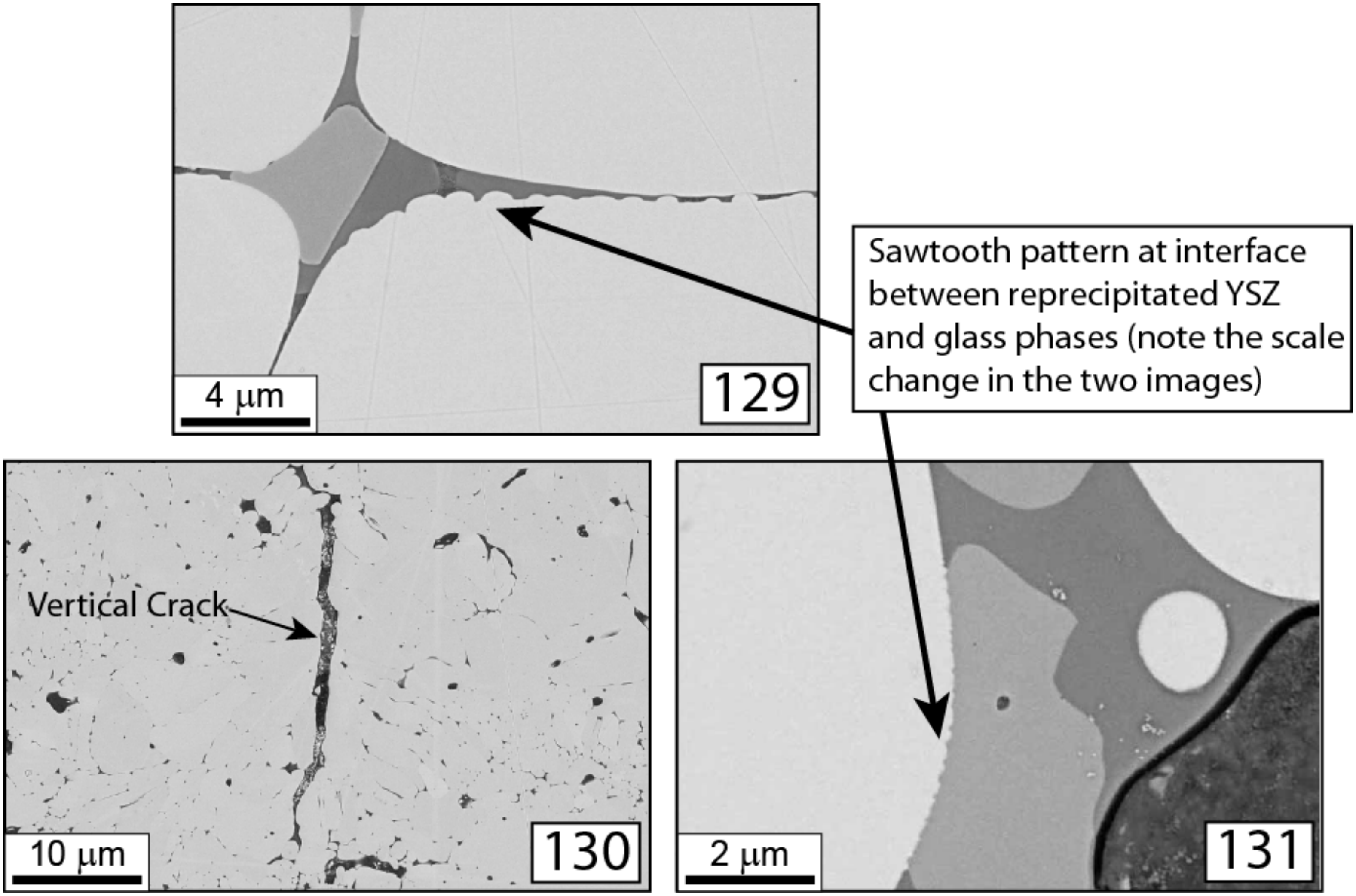
View from middle of cross-section (image widths = 100mm)





- Evidence of reprecipitation of YSZ phase after CMAF attack in all three samples, with glassy phases interspersed between (also in vertical cracks)

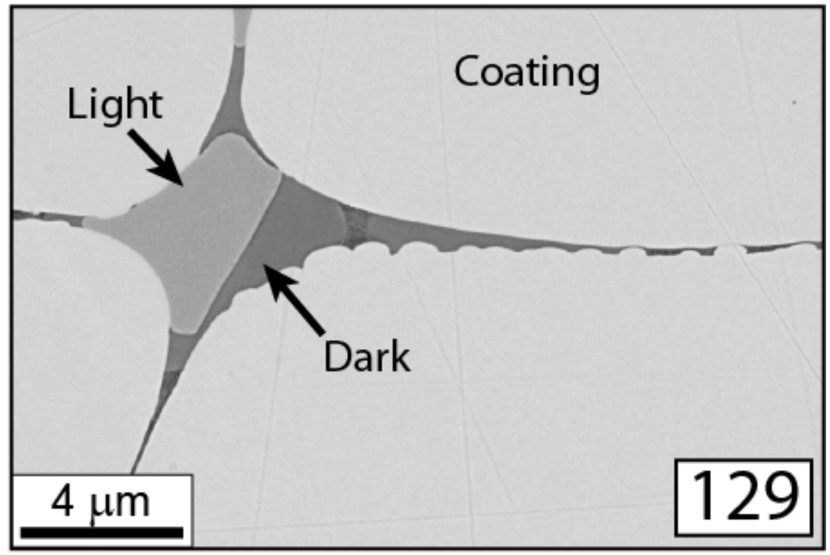
CMAS – Based Degradation of YSZ: Thermo-Chemical Interactions



- Some interesting features seen at higher magnification

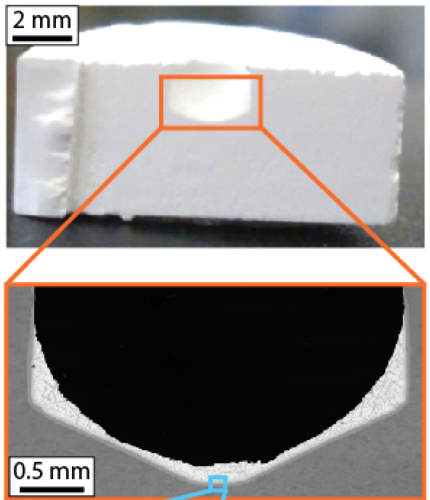
CMAS – Based Degradation of YSZ: Thermo-Chemical Interactions

M-12-129-TP-CMAF EDS Weight %			
	Coating	Light CMAF	Dark CMAF
Y	3.2	0.3	1.5
Zr	64.9	3.7	9.0
O	27.6	34.4	41.6
Ca	1.1	0.6	13.1
Mg	0.2	0.6	2.2
Al	0.0	1.7	5.3
Fe	3.0	57.9	13.9
Si	0.0	0.9	13.5



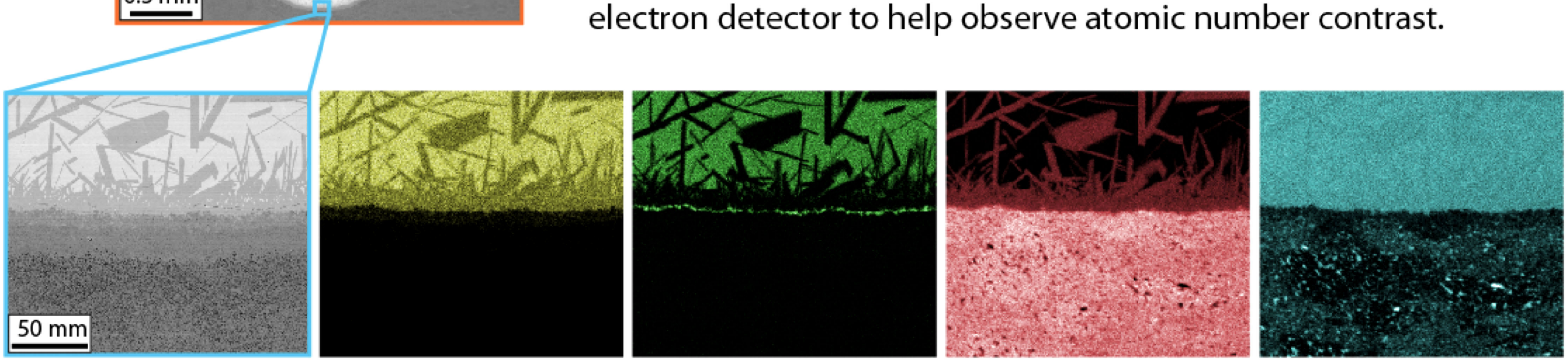
- Chemical composition of the reprecipitated APS YSZ coating and the light and dark glassy CMAF phases for sample -129 (APS)

New Materials – Rapid Assessment of Thermo-Chemical Interactions



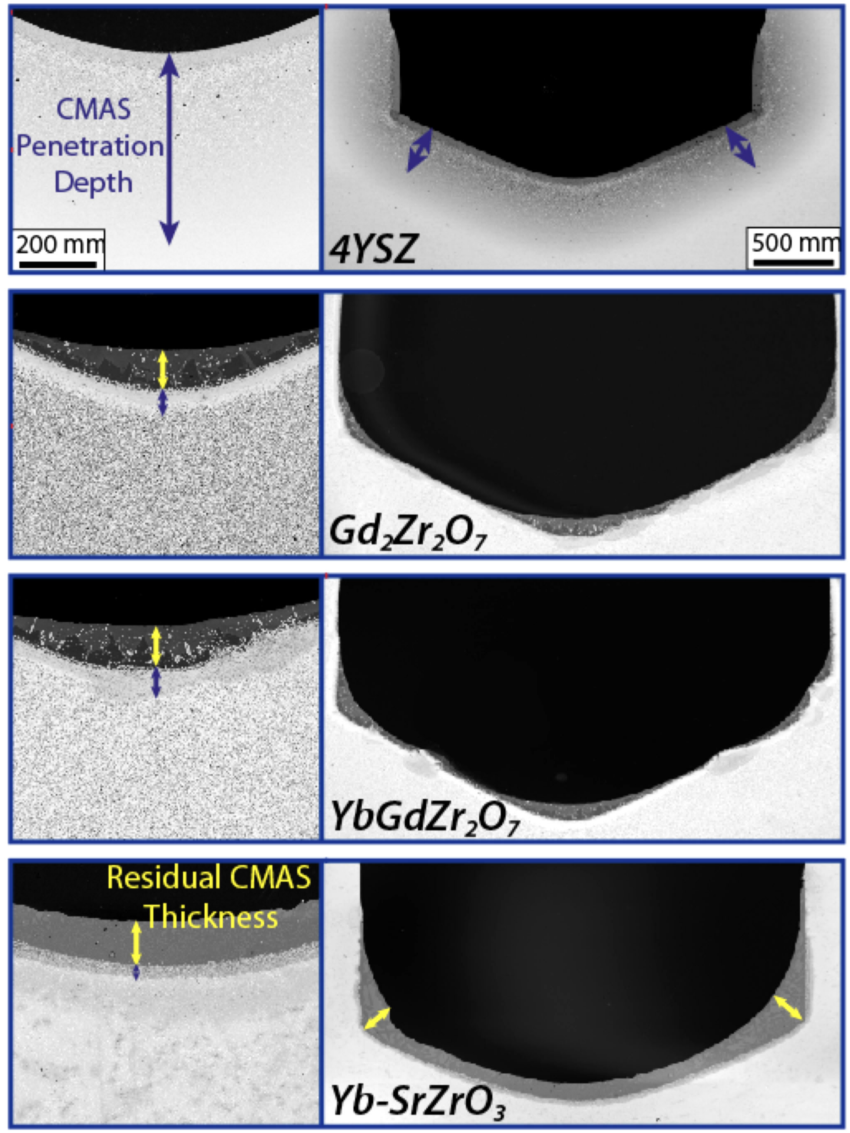
While this study was mainly focused on the CMAS resistance of TBC candidate ceramics, the same methodology can be applied to environmental barrier coating (EBC) materials as well. The results for one such material, Mullite ($3Al_2O_3 : 2SiO_2$), are shown here, apart from the TBC results, to serve as an example of the methodology used.

An infiltrated, cross-sectioned pellet appears at top left and, below it, an SEM micrograph of the entire drill bit hole with the CMAS reaction zone along the bottom surface. All SEM images presented here were captured with a backscatter electron detector to help observe atomic number contrast.



New Materials – Rapid Assessment of Thermo-Chemical Interactions

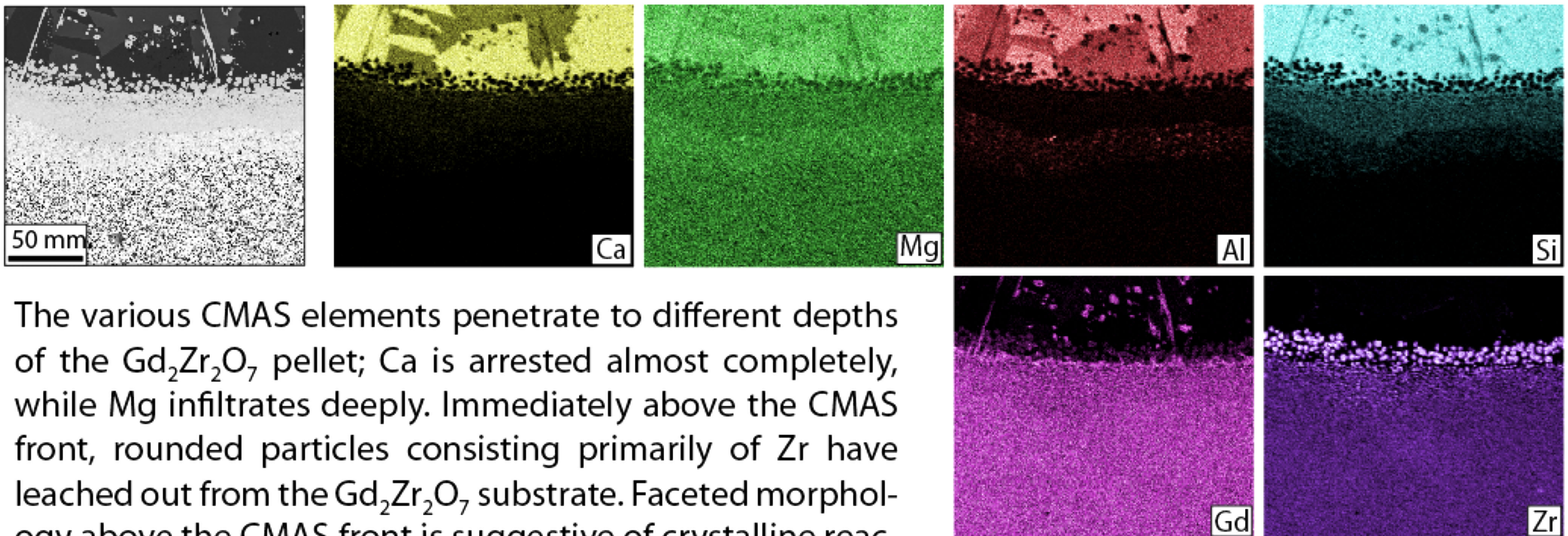
After sintering, any CMAS that has not infiltrated the substrate is observed as solidified glass at the surface of the drilled hole. Both the average CMAS penetration depth (blue arrows) and the average thickness of residual CMAS glass above the oxide (yellow arrows) can be calculated by taking measurements along the entire radial penetration front. Values for all four TBC candidate materials are listed in the table below. Not surprisingly, there is an inverse correlation between the two measurements. 5Yb-$SrZrO_3$ best resisted CMAS, 4YSZ the worst.



Ceramic Oxide	Avg. CMAS Penetration Depth (μm)	Avg. Thickness of Residual CMAS Glass Above Oxide (μm)
4YSZ	500	0
$Gd_2Zr_2O_7$	90	75
$GdYbZr_2O_7$	75	80
5Yb-$SrZrO_3$	55	110

New Materials – Rapid Assessment of Thermo-Chemical Interactions

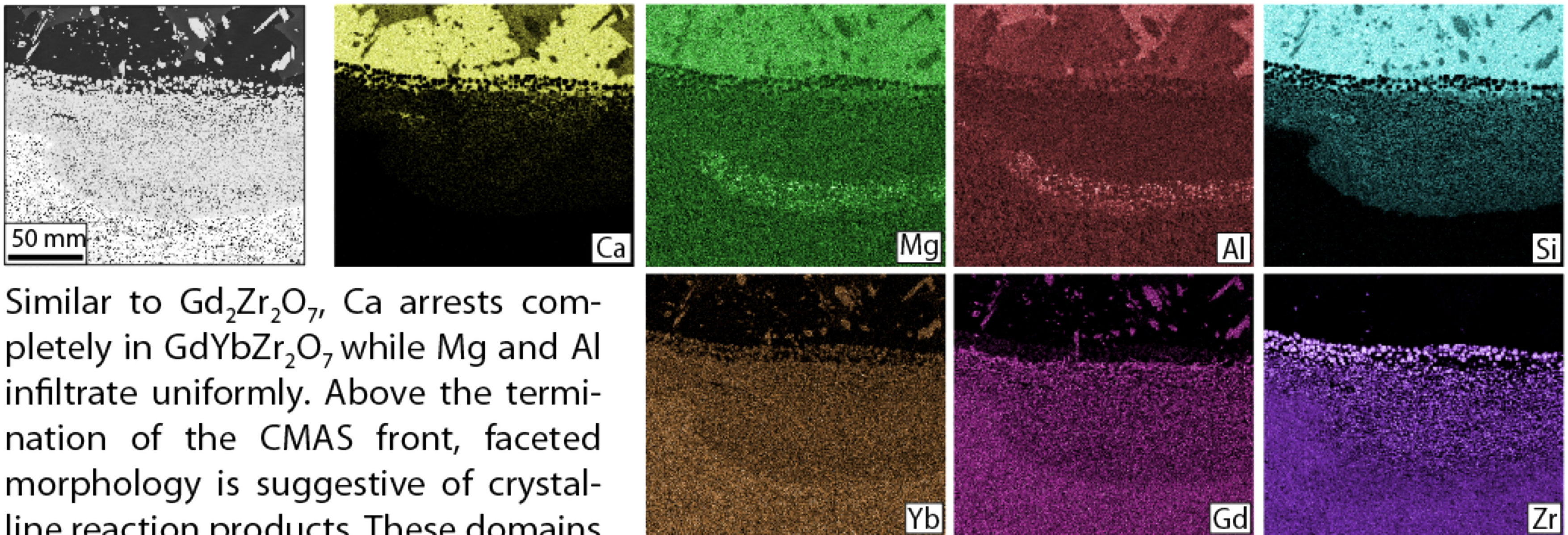
$Gd_2Zr_2O_7$



The various CMAS elements penetrate to different depths of the $Gd_2Zr_2O_7$ pellet; Ca is arrested almost completely, while Mg infiltrates deeply. Immediately above the CMAS front, rounded particles consisting primarily of Zr have leached out from the $Gd_2Zr_2O_7$ substrate. Faceted morphology above the CMAS front is suggestive of crystalline reaction products that consist mostly of Gd.

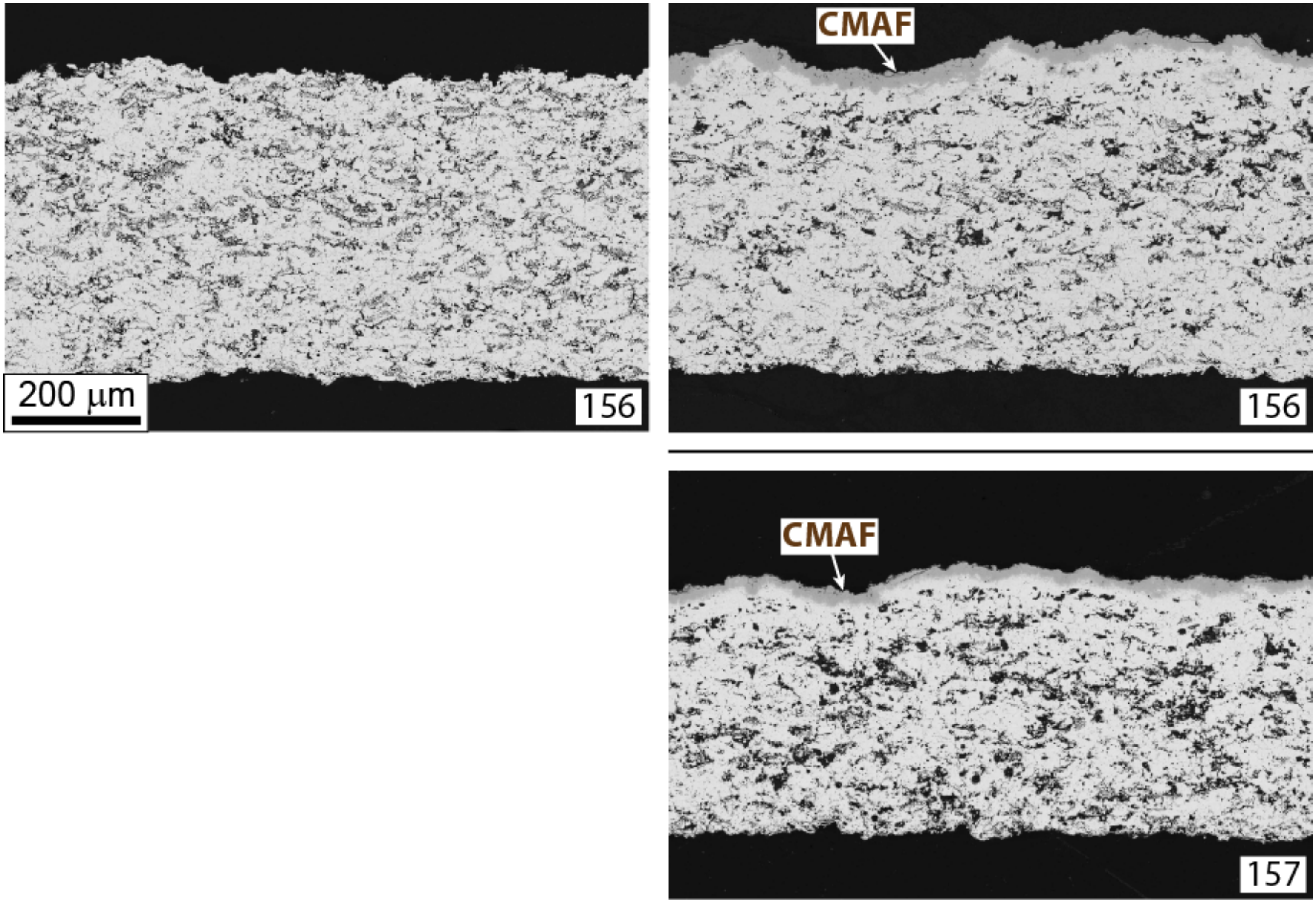
New Materials – Rapid Assessment of Thermo-Chemical Interactions

$GdYbZr_2O_7$



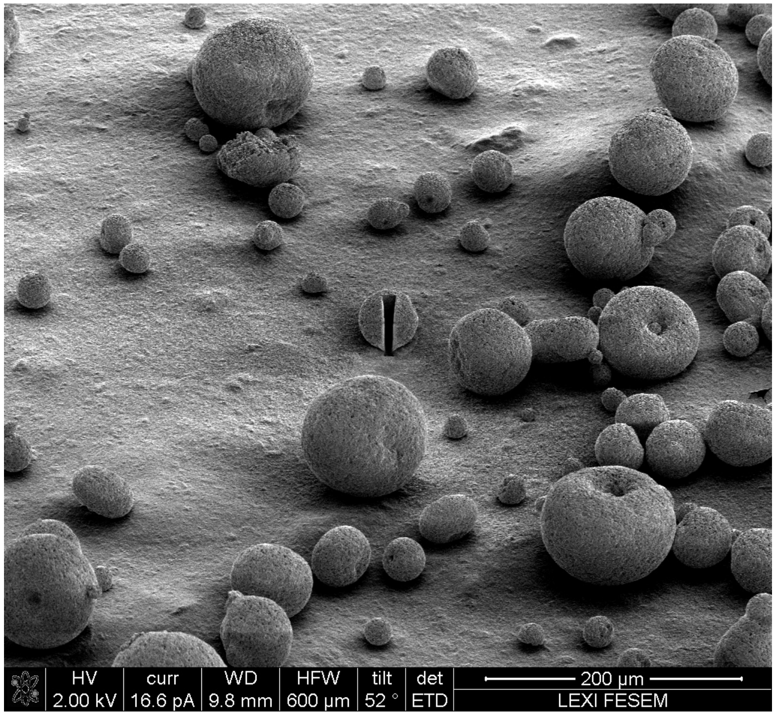
Similar to $Gd_2Zr_2O_7$, Ca arrests completely in $GdYbZr_2O_7$ while Mg and Al infiltrate uniformly. Above the termination of the CMAS front, faceted morphology is suggestive of crystalline reaction products. These domains consist mostly of Gd and Yb with little evidence of CMAS elements or Zr being incorporated.

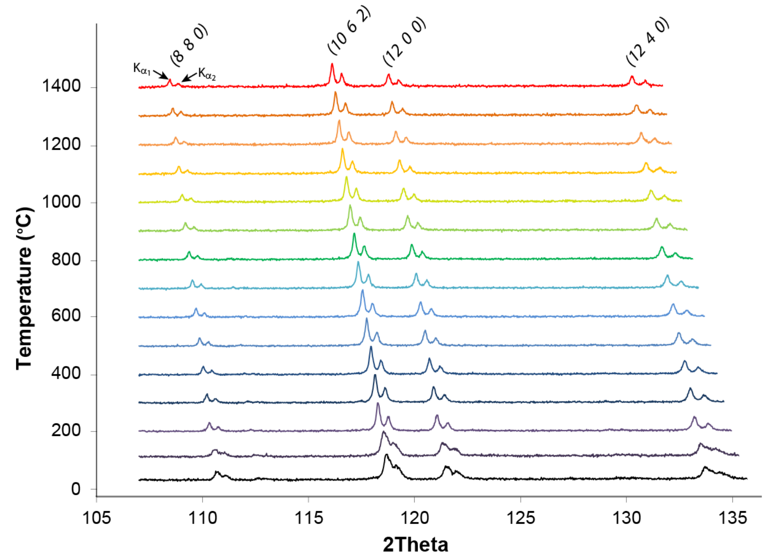
New Materials – Free Standing TBC Materials (Zirconate)

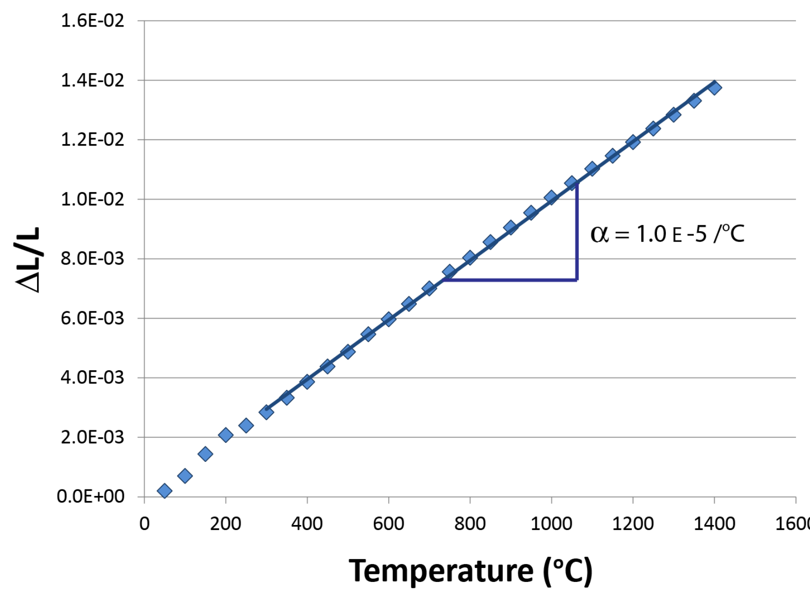


- -157 has larger pores than -156; CMAF does not penetrate too deeply into either sample

New Materials – TEC Determinations (Zirconate)







Alternative materials are being processed and basic material parameters determined as precursors for systematic stability studies.

Summary: Accomplishments and Key Findings

- Investigated isolated effects of elevated water vapor levels on TGO formation, investigated in a manner intended to isolate *mechanisms* responsible for observed behavior. In BC systems that are not 'borderline' alloys for alumina formation, water vapor exposures do not lead directly to sustained spinel formation through enhanced Ni^{2+} ion transport along grain boundaries.
- Work with taper-polished geometries, combined with (S)TEM-based analysis, has shown that - for systems evaluated to date - spinel formation is not highly localized at through-thickness grain boundaries.
- However, a strong correlation between pH_2O and transient spinel formation is observed. Furthermore, there is a strong dependence of TGO growth kinetics on pH_2O, but volatilization effects counteract these effects and complicate analysis of mechanisms. Care must be taken during laboratory experimental procedures to avoid vapor-phase transport contributions to non-ideal oxide formation (irrelevant to TBC-coated materials degradation processes).
- Development of protective thermally grown oxides is highly dependent upon the relative partial pressures of combustion by products, and therefore varies with transitions to syngas-based systems. More work is needed to isolate mechanistic details and correlations with controllable materials design parameters.

Questions?