UCIrvine | The Henry Samueli School of Engineering

Abradable Sealing Materials for Emerging IGCC-Based Turbine Systems

2015 University Turbine Systems Research Workshop
Atlanta, GA: November 4th, 2015

Daniel R. Mumm

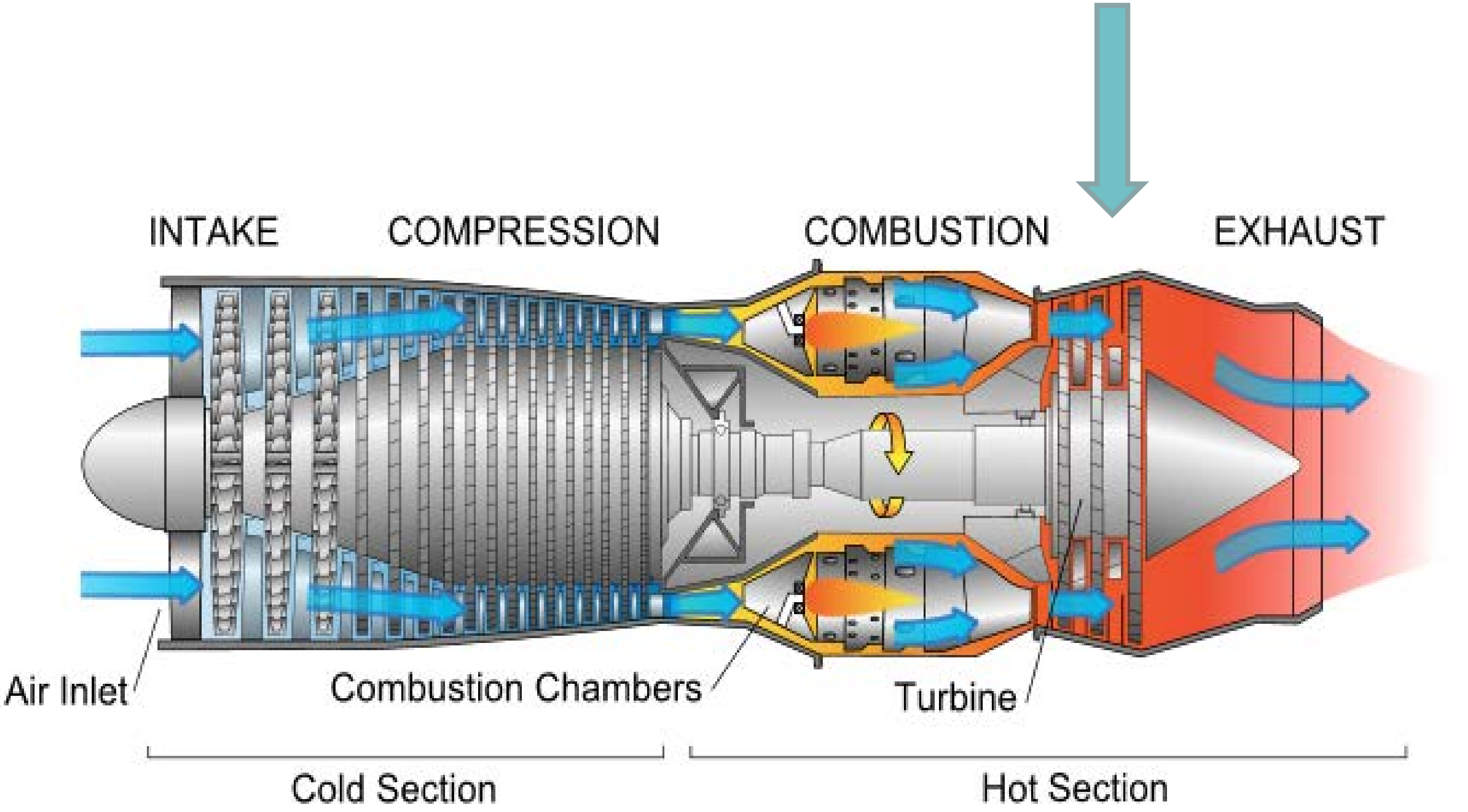
Chemical Engineering and Materials Science
Advanced Power and Energy Program (APEP)
University of California, Irvine
Tel: (949) 824-3858; Fax: (949) 824-2541
mumm@uci.edu

U.S. Department of Energy; National Energy Technology Laboratory
Agreement # DE-FE0011929; Project Manager: Dr. Robin Ames

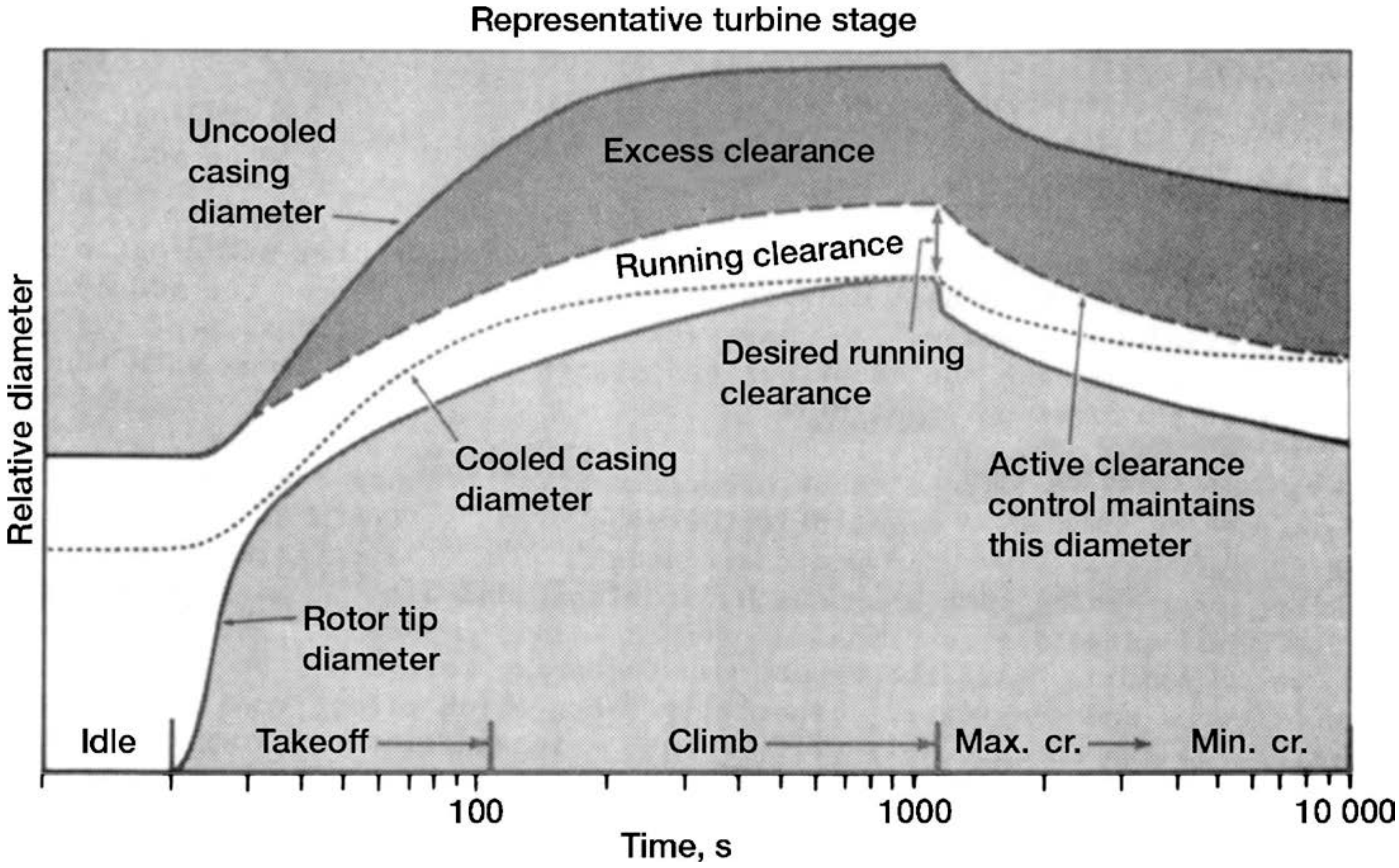
U.S. DEPARTMENT OF ENERGY

Clearance Control is Critical to Obtaining High Efficiency

Rotor-Shroud Clearance



Active Cooling Control for Clearance Control

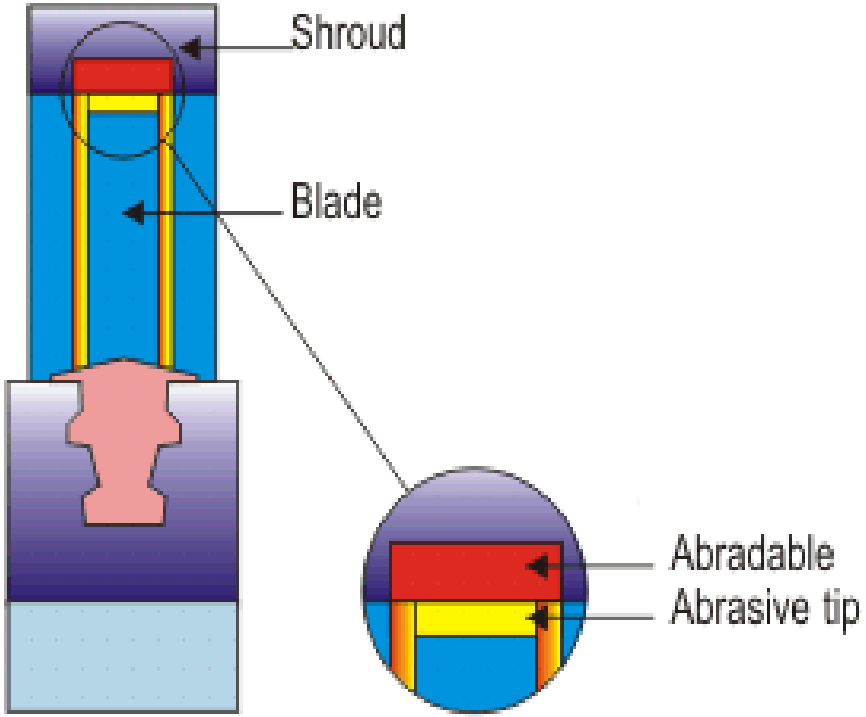


R.E. Chupp, et al., Journal of Propulsion and Power
Vol. 22, No. 2, March–April 2006

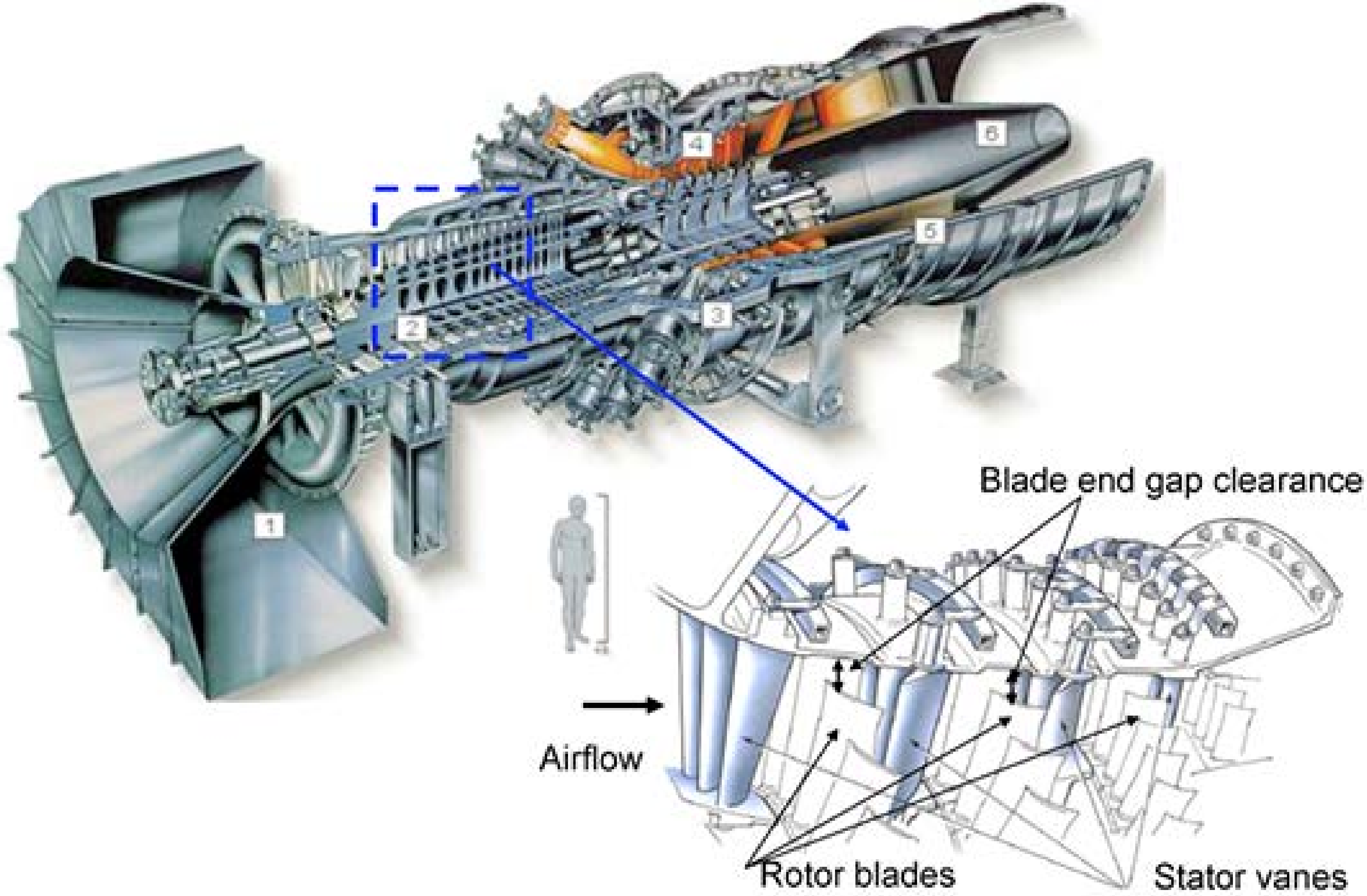
Abradable Materials for Clearance Control

- To reduce rotor-shroud clearance (an extra gap of .005" between the rotating blades and the engine casing can increase fuel consumption by as much as 0.5%).
  - Lower consumption of engine fuel
  - Improves engine-efficiency

- To achieve high temperature stability, low thermal conductivity, chemical stability, and erosion resistance at operating temperatures

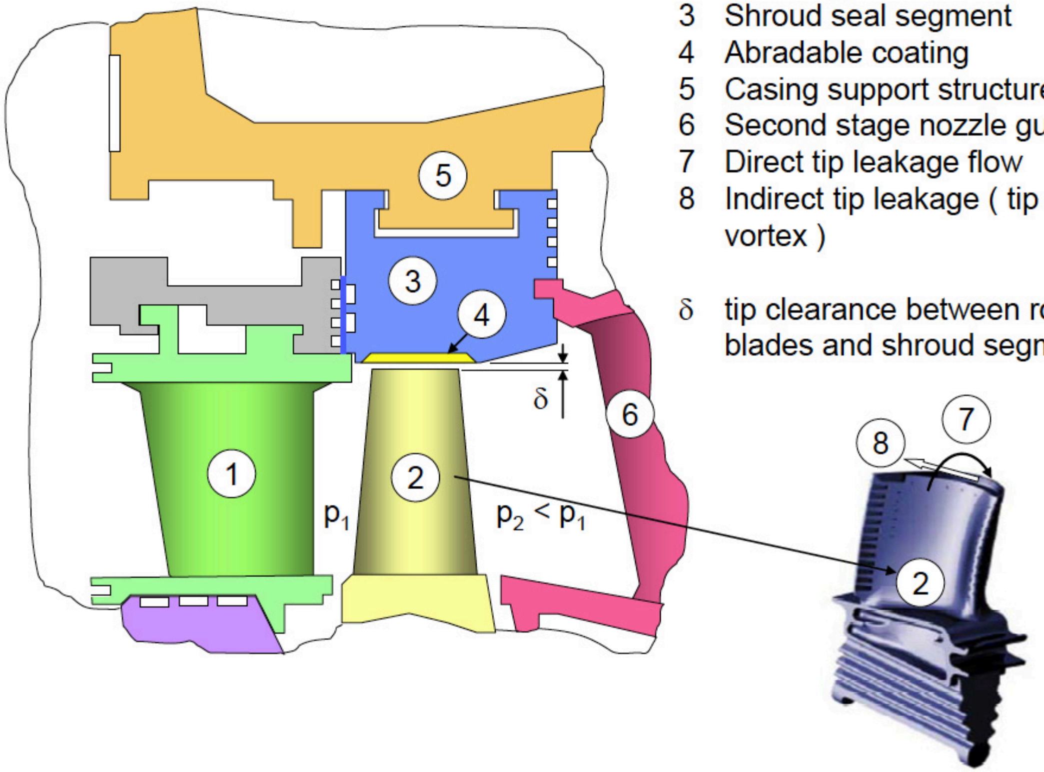


Abradable Seal Coatings



Abradable Seal Coatings

Schematic of a section through a gas turbine engine high pressure stage, showing where an abradable coating is used and how gas leaks through this seal leads to performance loss.



1 First stage nozzle guide vane
2 First stage turbine blade
3 Shroud seal segment
4 Abradable coating
5 Casing support structure
6 Second stage nozzle guide vane
7 Direct tip leakage flow
8 Indirect tip leakage (tip clearance vortex)

δ tip clearance between rotating blades and shroud segment

D. Sporer, S. Wilson and M. Dorfman, “Ceramics for Abradable Shroud Seal Applications.” *Proceedings of the 33rd International Conference on Advanced Ceramics and Composites, volume 3, 2009,*

Project Overview:

- Reducing the gap between rotating and stationary parts in gas turbine engines, and mitigating gas leakage via these paths, can significantly increase the performance and attendant efficiency. One approach to maintaining a minimum gap is to use abradable coatings on the stationary shroud components as seals.
  - Abradable coatings must be able to withstand high temperature oxidation, thermal cycling, and erosion, while providing optimal controlled abrasion and associated shape retention.
  - Syngas and high-hydrogen-content (HHC) fired turbines has shown that the stability of hot-section materials may be substantially altered due to characteristic changes in the combustion by-products (partial pressures of water vapor, etc.) as well as characteristic impurities and particulate matter entrained in the fuel.

Abradable Materials

- Metal matrix (T<700 degree C)
- Ceramic materials (T>700 degree C)
- Lubricant/dislocator agent (hBN)
- Porous materials
- o Ni/Graphite and AlSi/hBN for compressor
- o CoNiCrAlY/hBN/Polyester for LP turbine sections of engines.
- o YSZ, spinel or similar ceramics for HPT sections

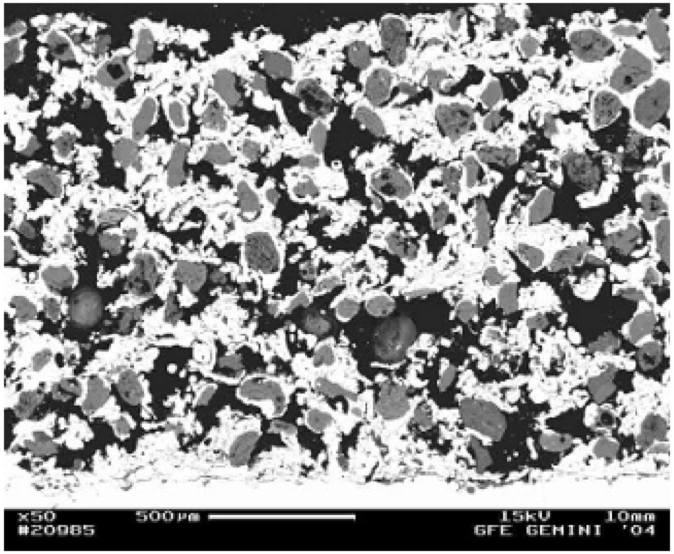
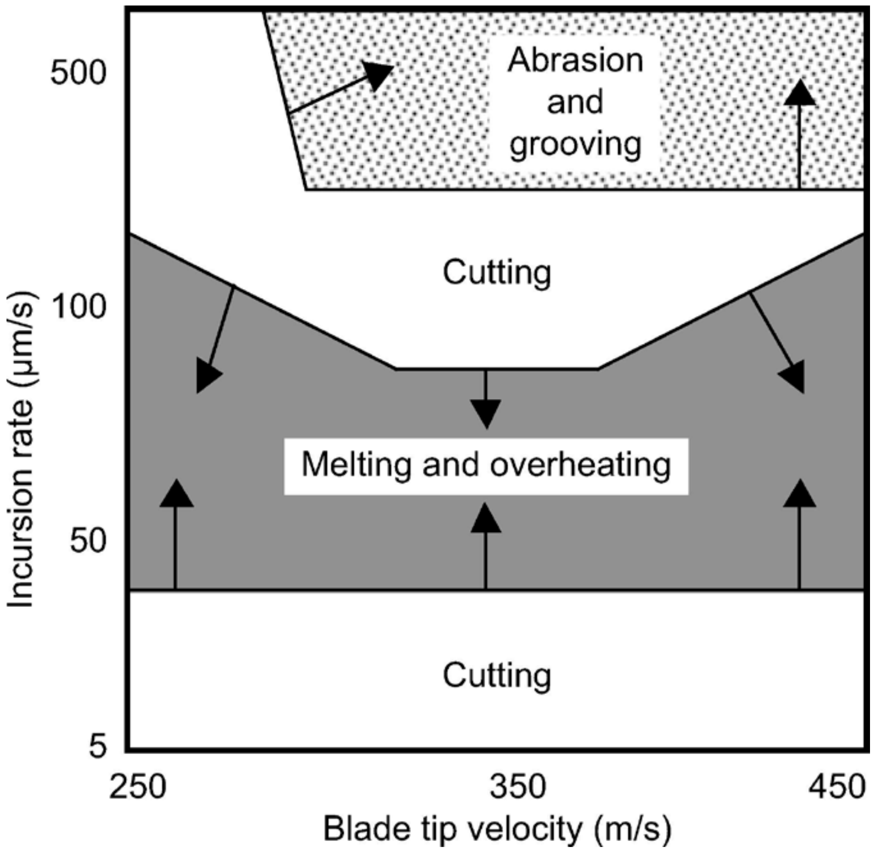


Figure 1: Cross section of a typical abradable coating (dark phase: porosity, grey phase: bentonite, bright phase: NiCrAl metal matrix)

Metallic Abradable Seal Wear and Recession – A Balancing Act



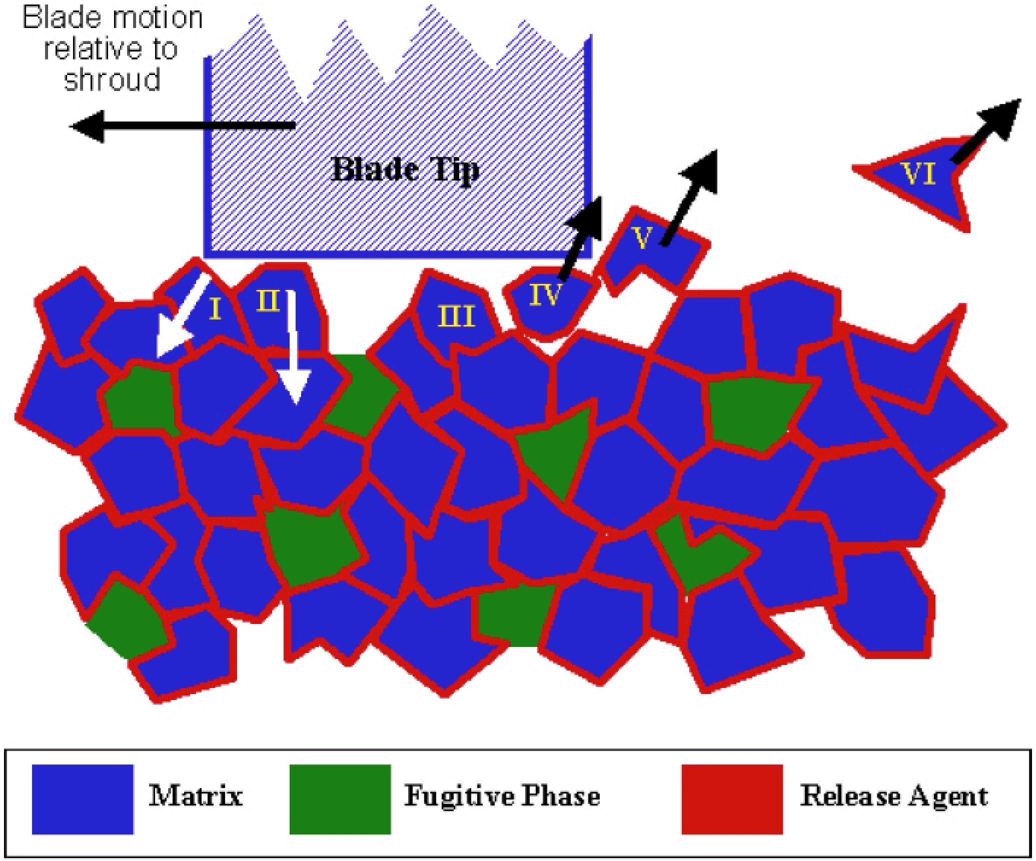
Abradable Coating response is dependent upon operational parameters of the engine

R.E. Chupp, et al., Journal of Propulsion and Power, Vol. 22, No. 2, March–April 2006

- Concerns include: excessive blade-tip wear, macrorupture in coatings, transfer of materials from blade to shroud.

Ceramic Abradable Seal Wear and Recession – A Balancing Act

The ideal wear and recession behavior of an abradable coating consisting of a ceramic matrix (YSZ), a fugitive pore-forming phase, and a release agent that creates weak interfaces.



D. Sporer, S. Wilson and M. Dorfman, "Ceramics for Abradable Shroud Seal Applications." *Proceedings of the 33rd International Conference on Advanced Ceramics and Composites, volume 3, 2009,*

Project Objectives

- Investigate the impacts of coal-derived syngas combustion environments on the performance, durability and degradation of existing abradable coatings used on turbine shroud structures.

- Assess the potential of alternative materials sets for improving performance of hot-section abradable seals **in IGCC-based gas turbine power plants**.

- Derive a mechanisms-based understanding of factors controlling the performance and degradation of abradable seals used in the high-temperature turbine sections of gas turbine engines in relation to emerging IGCC-based combustion environments, and evaluate the potential of alternative materials as abradable seal coatings – ultimately with the goal of developing a knowledge base upon which the design of coatings that retain optimal sealing characteristics and are more resistant to the observed wear/attack mechanisms.

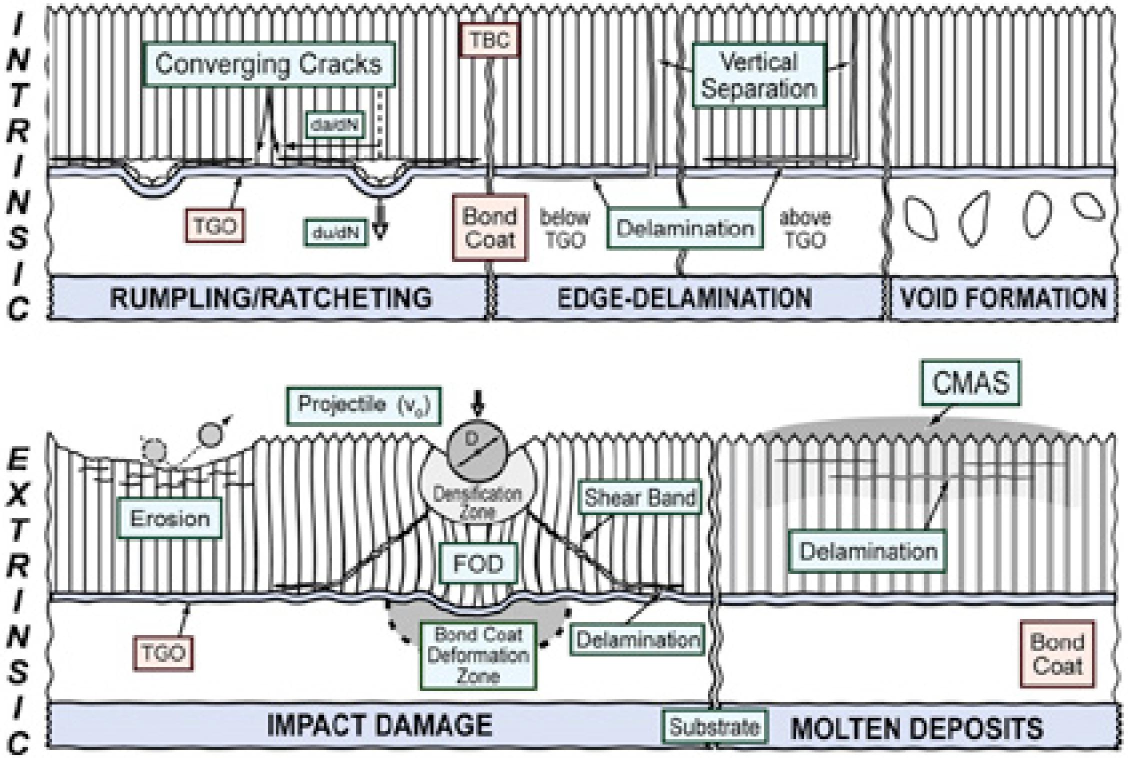
- Educate the next generation of scientists and engineers trained in materials design for advanced turbine systems.

Potential Challenges in Transitioning to Alternative Fuels

There has been extensive research efforts directed toward the development and improvement of Thermal Barrier Coating (TBC) materials.

Our understanding of these Degradation Mechanisms forms a basis for understanding performance of Abradable Seals.

A.G. Evans (2007)



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

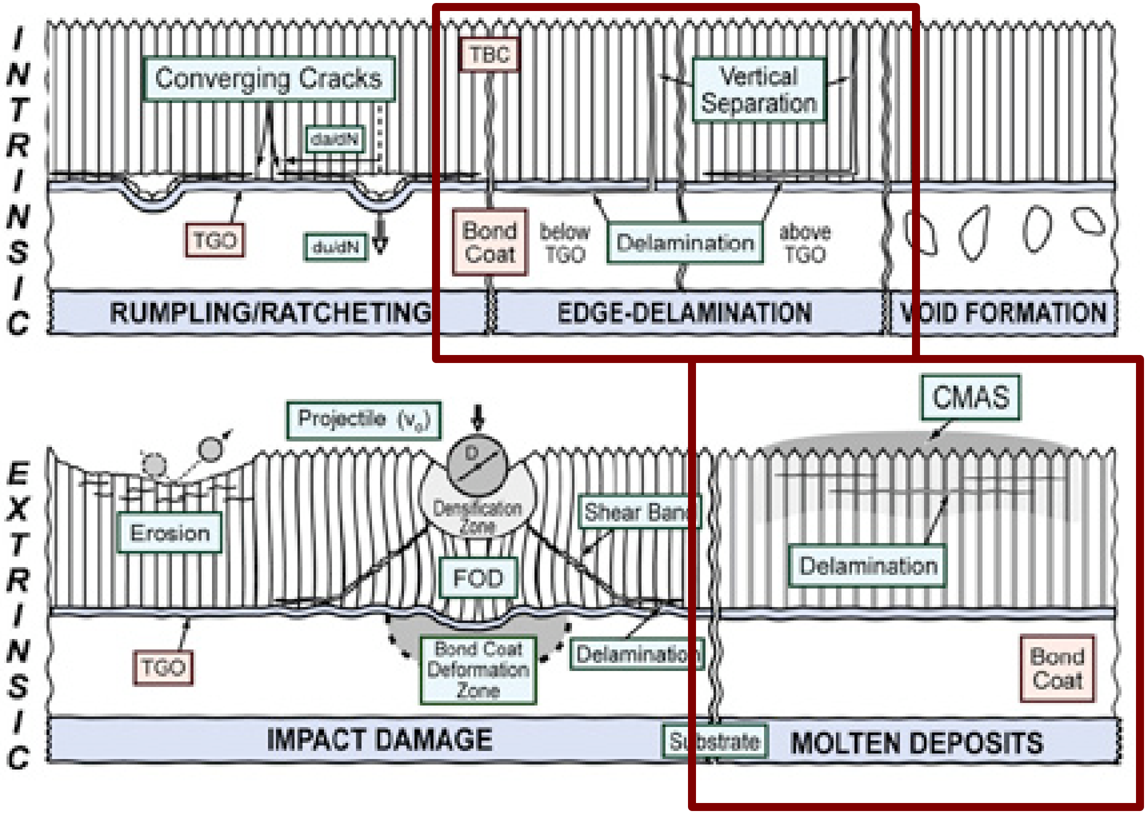
A.G. Evans, D.R. Mumm, J.W. Hutchinson, G. Meier and F.S. Pettit (2001)
Progress in Materials Science, 46, 505-53.

Abradable Coating Degradation

Deposit Formation
Edge Delamination

What potential analogies to existing TBC thermomechanical damage and CMAS degradation mechanisms arise for abradable coatings with use of syngas or HHC fuels and intrinsic combustion by products ?

A.G. Evans (2007)



General Project Structure

Assessment of the stability of current abradable seal 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
- Mechanisms underpinning environment-dependent degradation (volatilization, etc.)
- Characteristic surface deposits and CMAS-based degradation

New materials and processing approaches directed at mitigating damage evolution and optimizing system performance.

Development of improved thermo-mechanical models to guide development of abradable – but erosion resistant – seal coating systems.

Power Generation – Integrated Gasification Combined Cycle System

- ❑ IGCC plant

  -Produces syn-gas; $3C + O_2 + H_2O \rightarrow H_2 + 3CO$

  -lowers the emission of CO_2, particulate matters, SO_2, NOx using filters

  -re-uses the heat generated in the system.

- ❑ Synthetic gas is used as the fuel for combustion

  -H_2, CO, CO_2, CH_4, N_2 and H_2O.

  -the composition remains relatively constant despite changes in coal composition.

- ❑ Synthetic gas fuel introduces

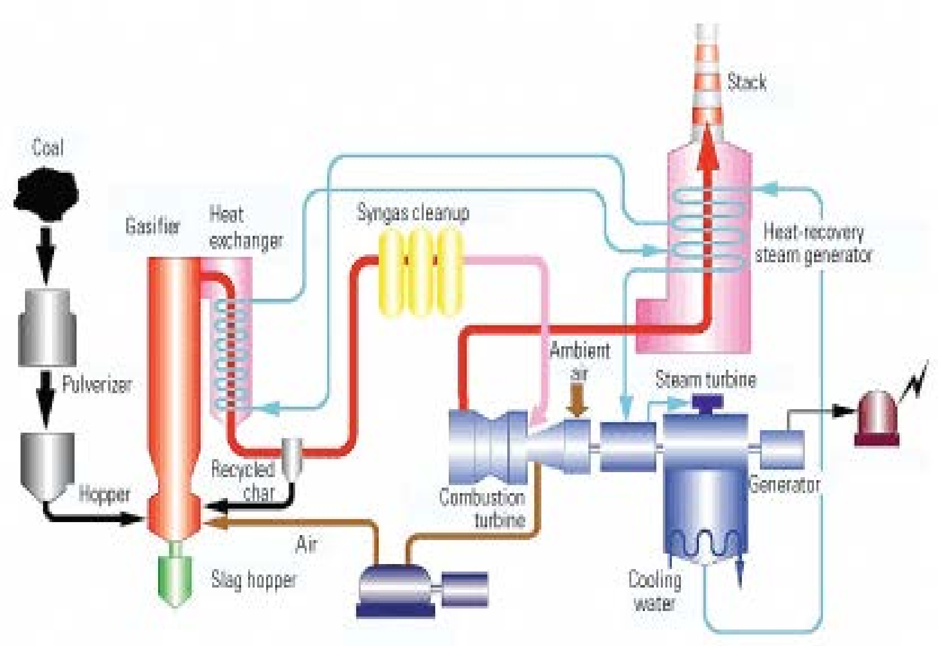
  -15%-30% water vapor in the turbine stages

  which will affect the coating systems of turbine.

  *CONDITIONS IN ADVANCED TURBINES FOR IGCC POWER PLANTS WITH CARBON CAPTURE

  Briggs M. White, Robin W. Ames, Patcharin Burke

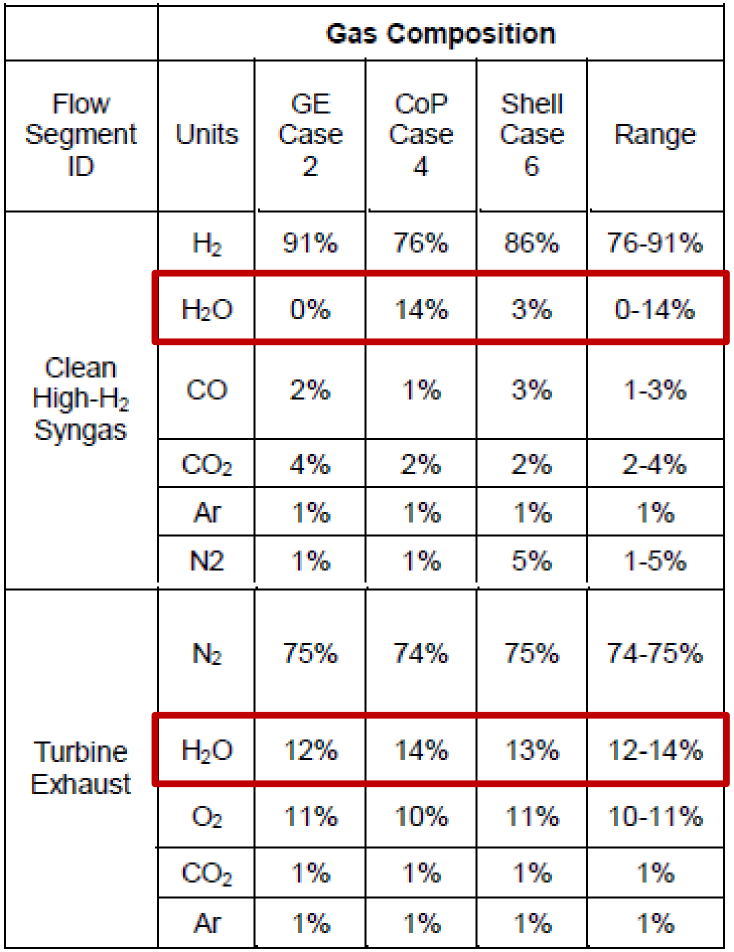
Direct incorporation of coal gasification



NETL

Motivation – Hot-Section Combustion Environment Modifications

Predicted Increased Water Content in Power Generation Turbines by the Use of Synthetic Gas (Syngas)



	Gas Composition				
Flow Segment ID	Units	GE Case 2	CoP Case 4	Shell Case 6	Range
Clean High-H_2 Syngas	H_2	91%	76%	86%	76-91%
	H_2O	0%	14%	3%	0-14%
	CO	2%	1%	3%	1-3%
	CO_2	4%	2%	2%	2-4%
	Ar	1%	1%	1%	1%
	N2	1%	1%	5%	1-5%
Turbine Exhaust	N_2	75%	74%	75%	74-75%
	H_2O	12%	14%	13%	12-14%
	O_2	11%	10%	11%	10-11%
	CO_2	1%	1%	1%	1%
	Ar	1%	1%	1%	1%

General Combustion Rxns:

$2H_2 + O_2 \rightarrow 2H_2O$

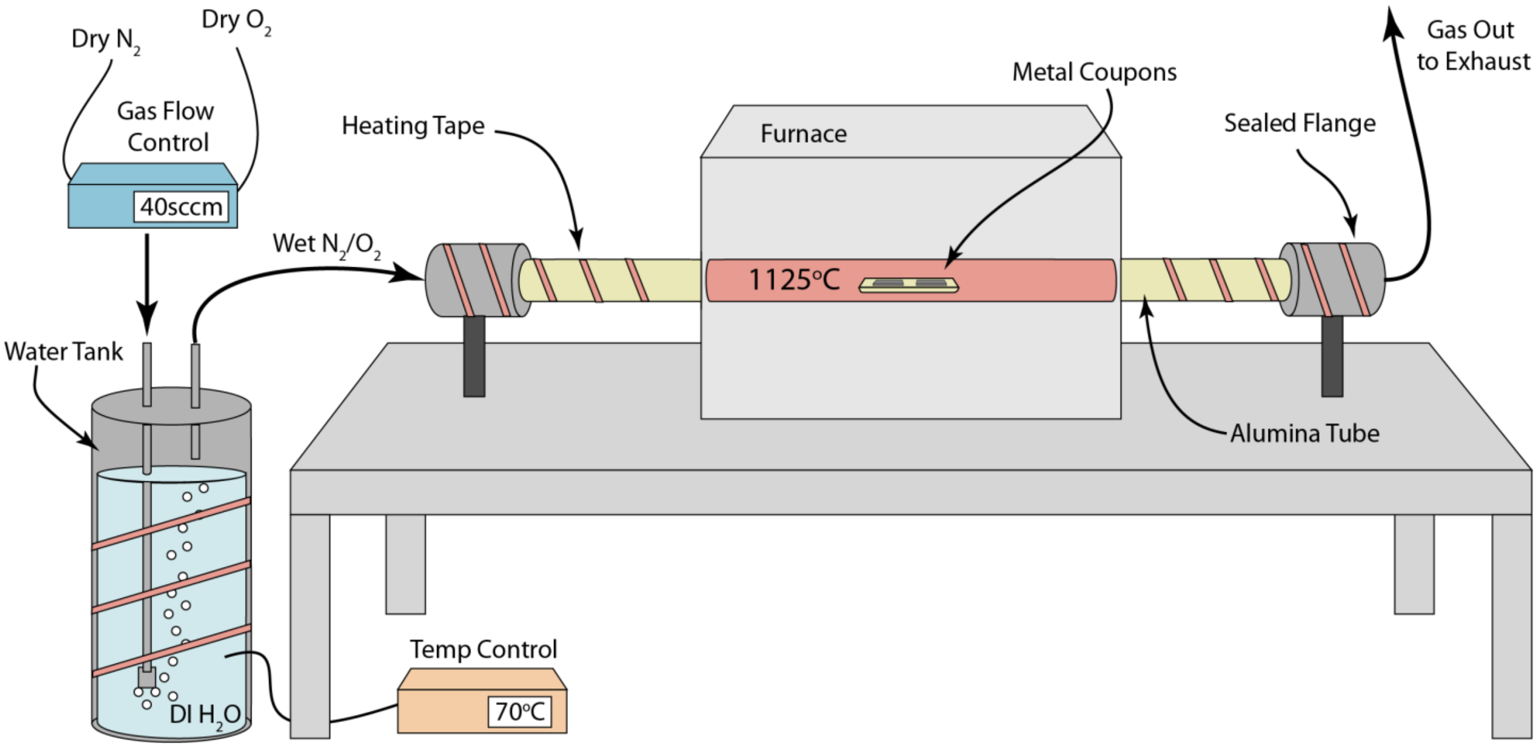
$CO + O_2 + H_2 \rightarrow CO_2 + H_2O$

$CO + H_2O \rightarrow CO_2 + H_2$

- *15-18 vol% H_2O* in turbine exhaust when using dry, high-H_2 syngas fuel
- If steam is used for NO_x suppression, H_2O could run as high as *30%*
- Represents a 2-4x increase over H_2O in natural gas combustion *(5-7%)*

White, Ames and Burke. National Energy Technology Laboratory (NETL) Report, 2013.

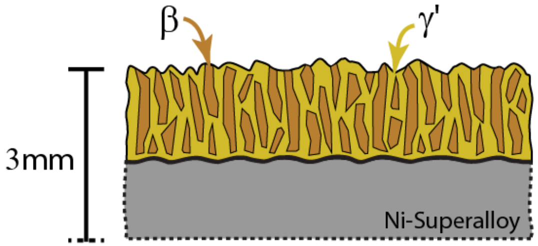
Methods



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

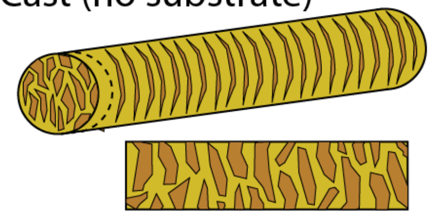
Materials

1) Sprayed (with substrate)

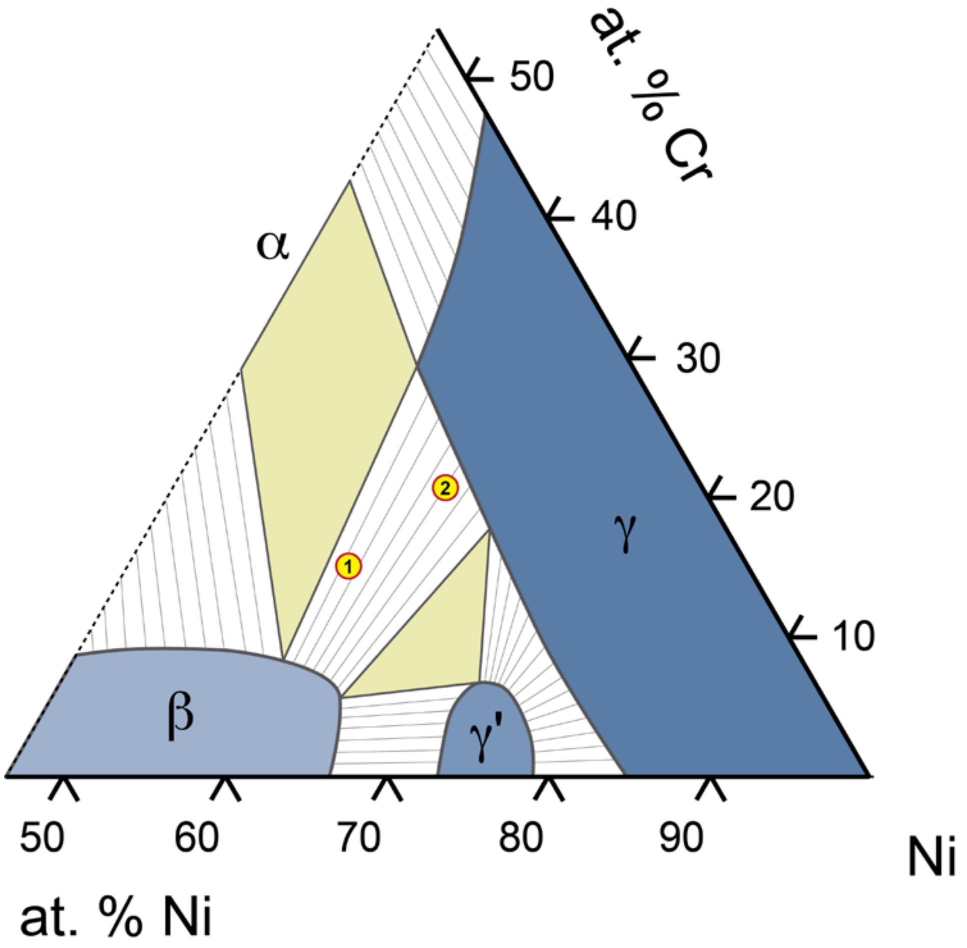


2) Sprayed (without substrate)

3) Cast (no substrate)



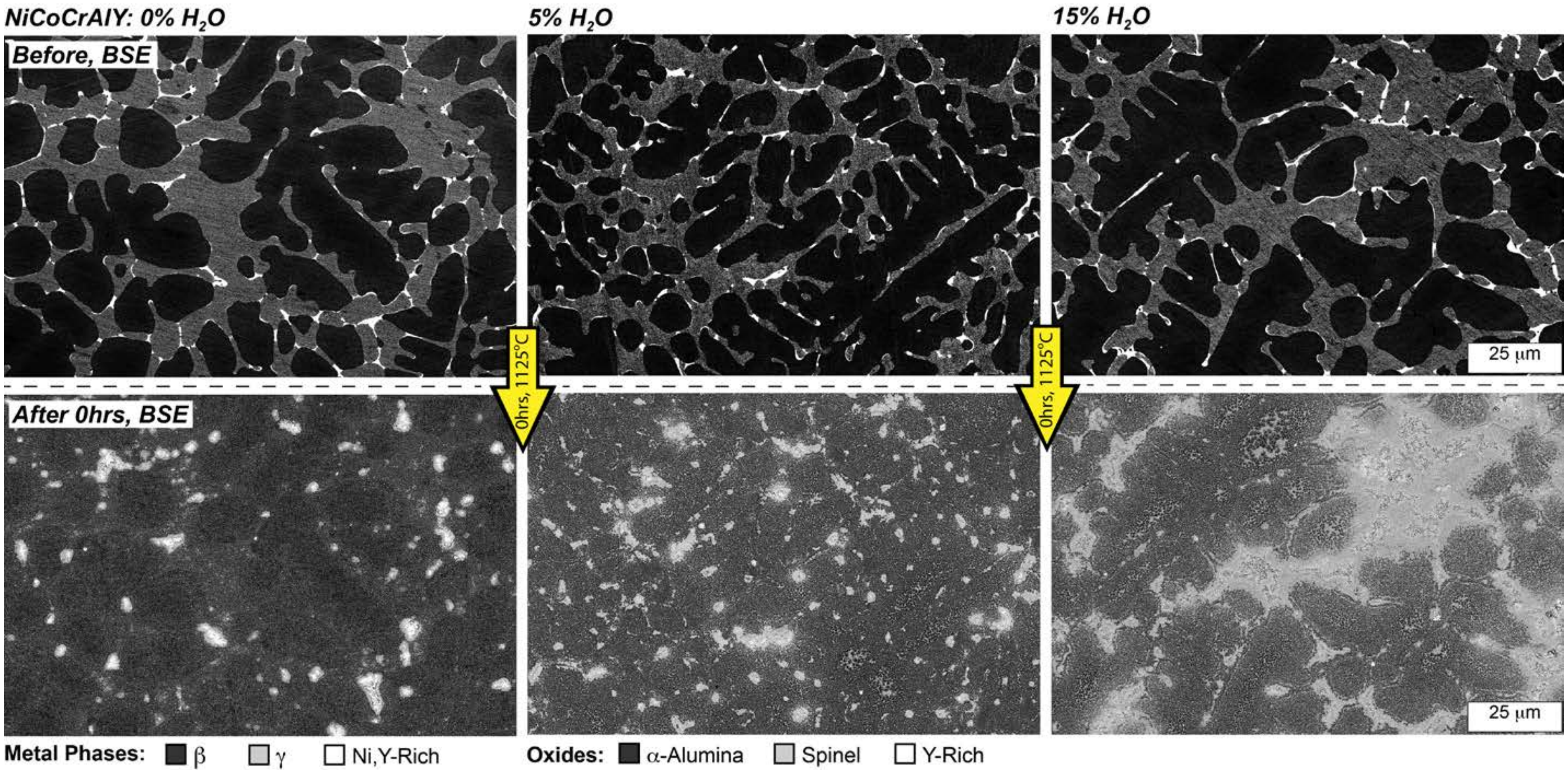
Ingot sectioned and polished



① Ni–20Co–23Al–16.5Cr–0.3Y

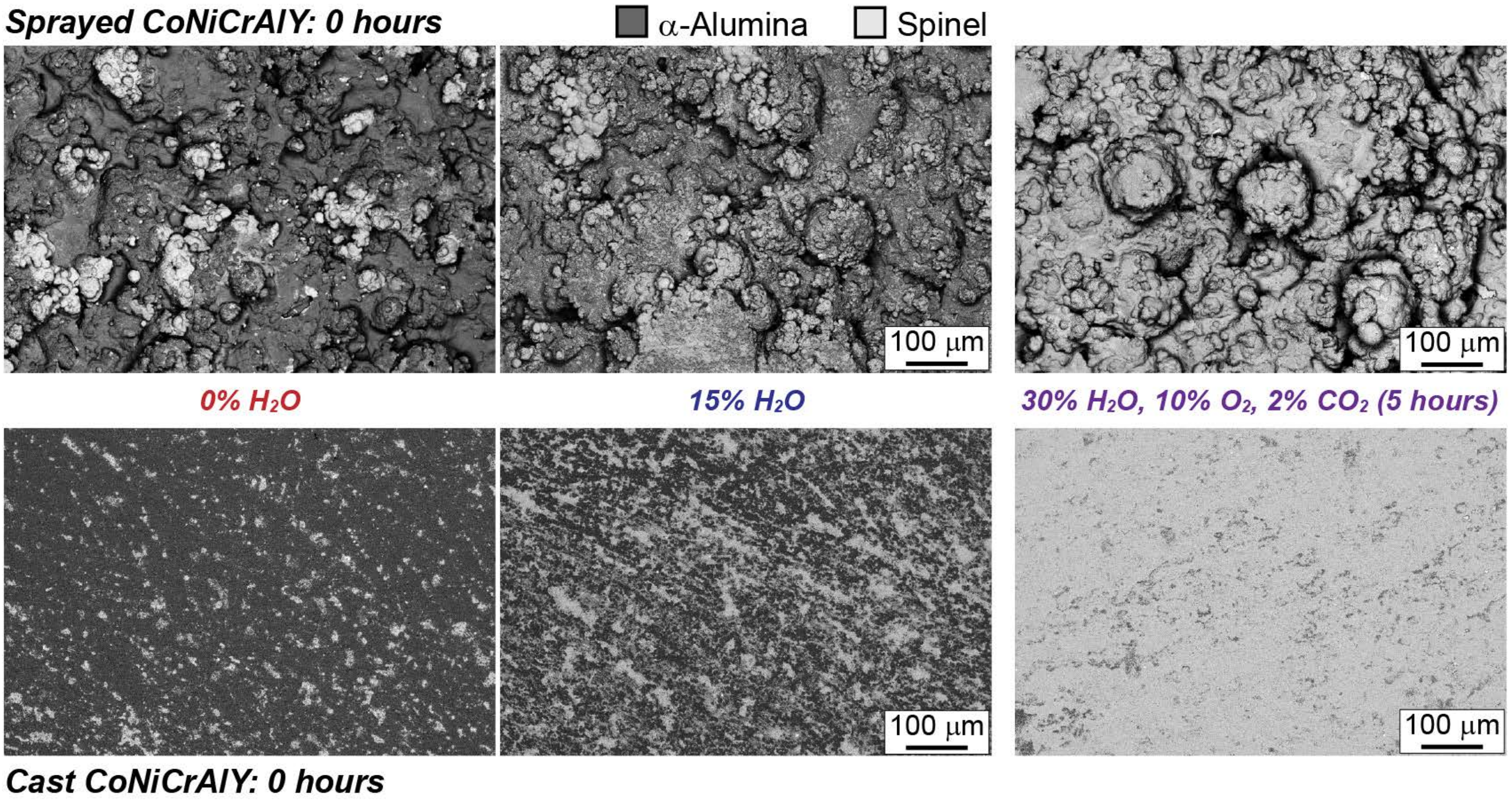
② Co–28.6Ni–15.6Al–21.2Cr–0.3Y

Transient Oxidation



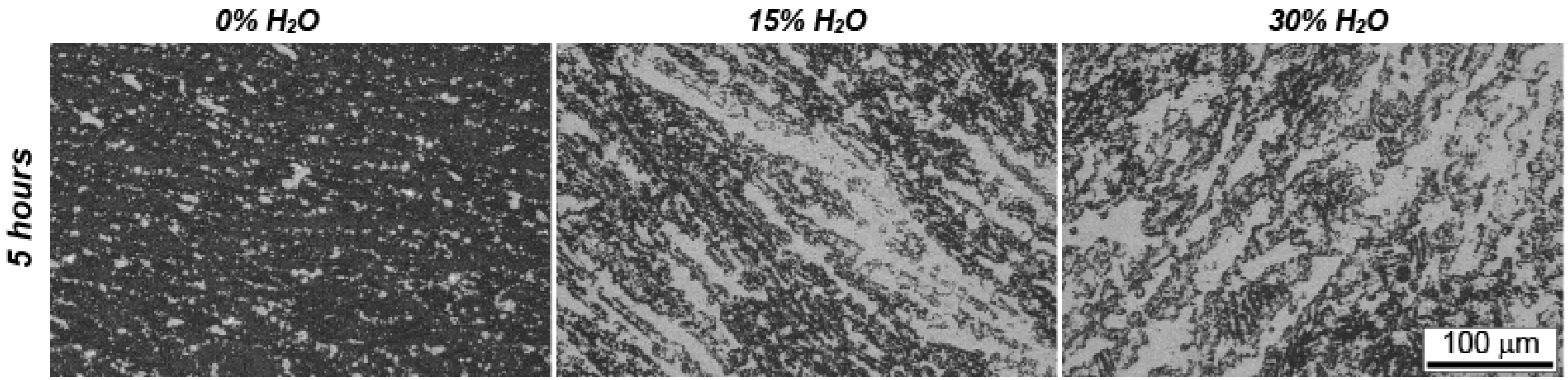
- Increasing H_2O allows for spinel to grow over progressively more Al-rich alloy phases

Transient Oxidation

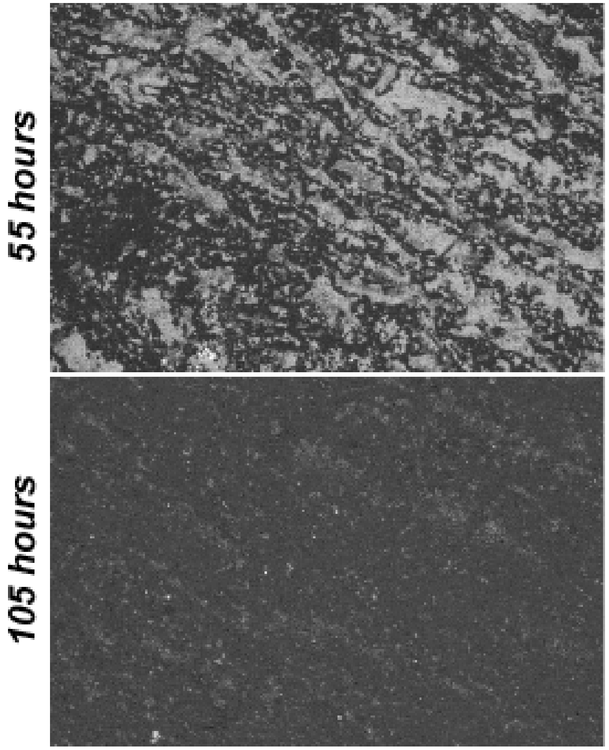


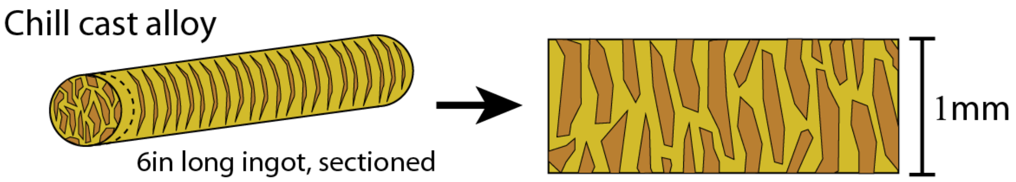
- The highest H_2O scenario with syngas combustion matches the worst-case spinel coverage scenario in the lab.
- Adding 2% CO_2 to the worst case scenario yields *complete* spinel coverage.

TGO Development: Water Vapor and Volatilization



■ Alumina ☐ Spinel

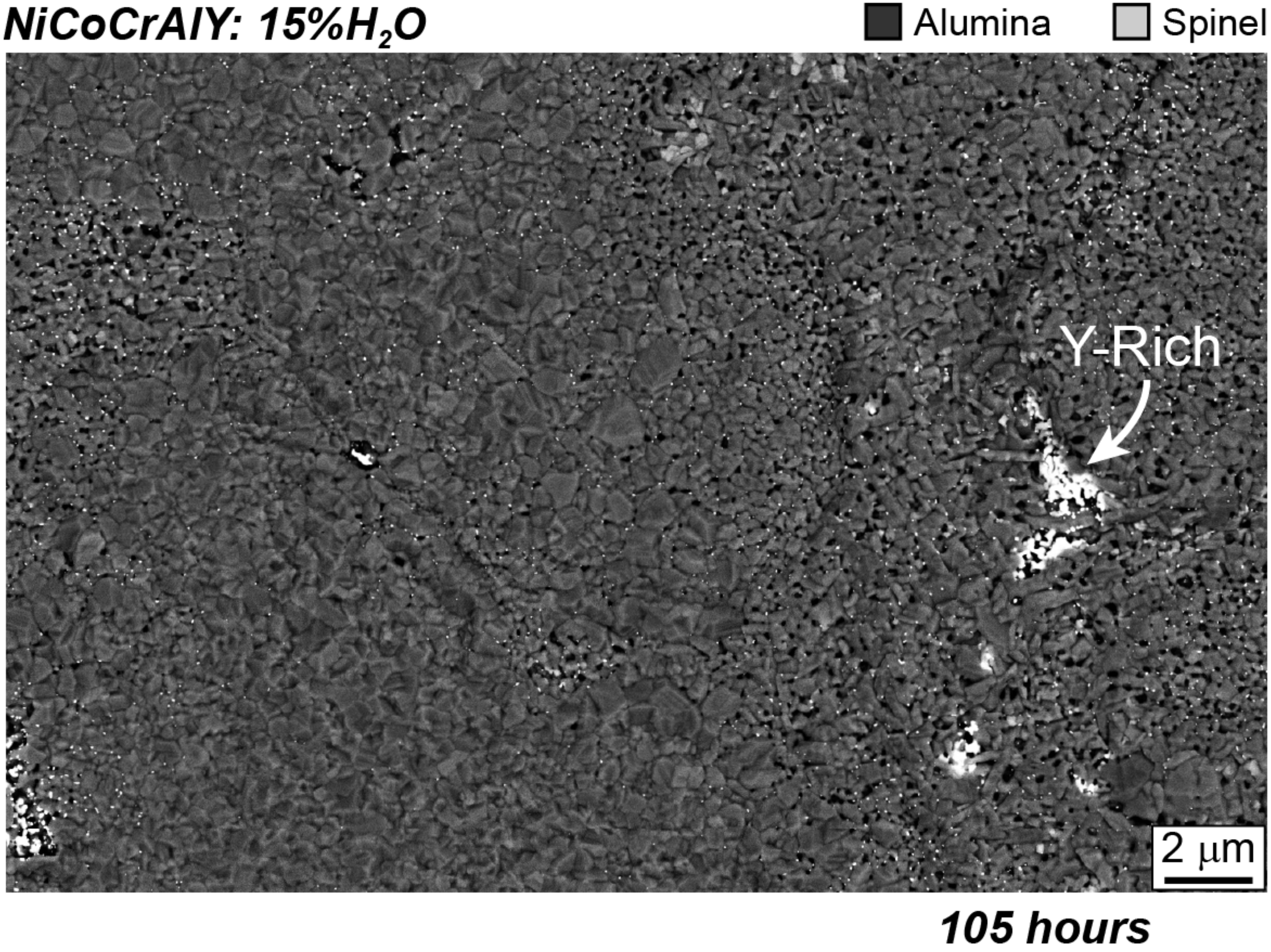




1. Amount of spinel varies as a function of *%H_2O*

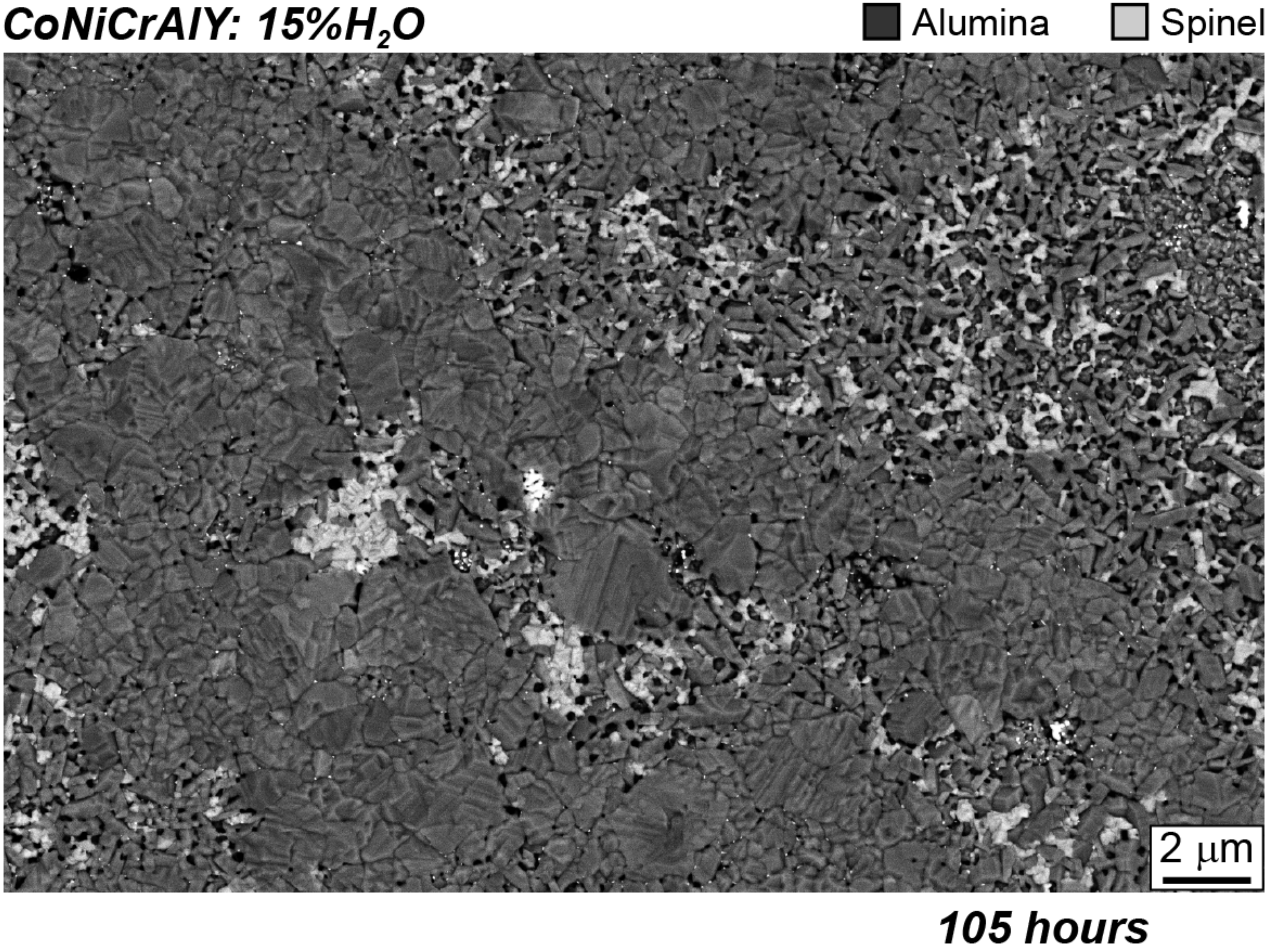
2. Amount of spinel varies as a function of *time*, too

H2O-Related Artifacts



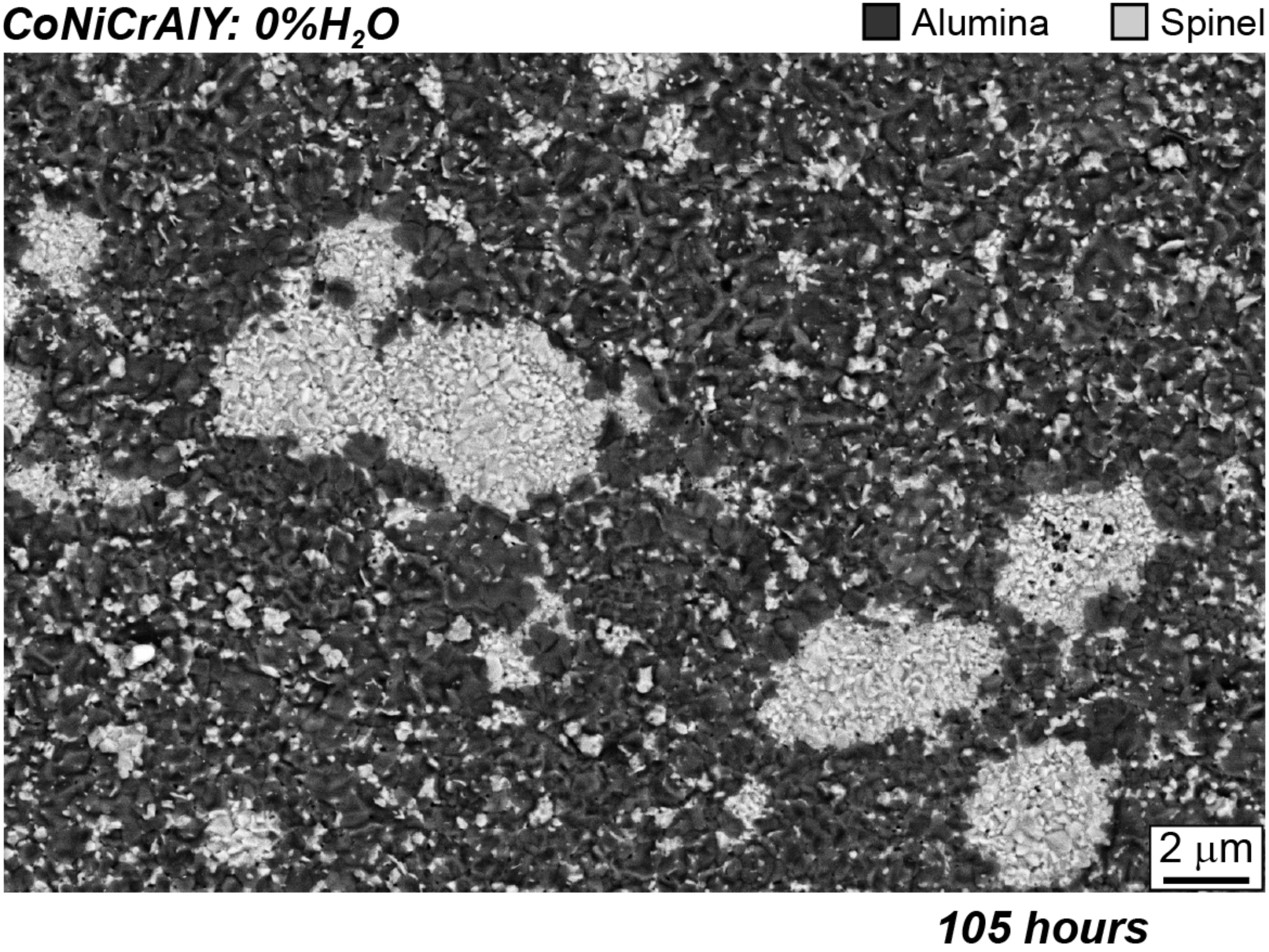
- Spinel disappears from surface as a function of time in a wet environment

H2O-Related Artifacts



- ➢ Spinel disappears from surface as a function of time in a wet environment

H2O-Related Artifacts



- Surface spinel is unchanged as a function of time in a dry environment

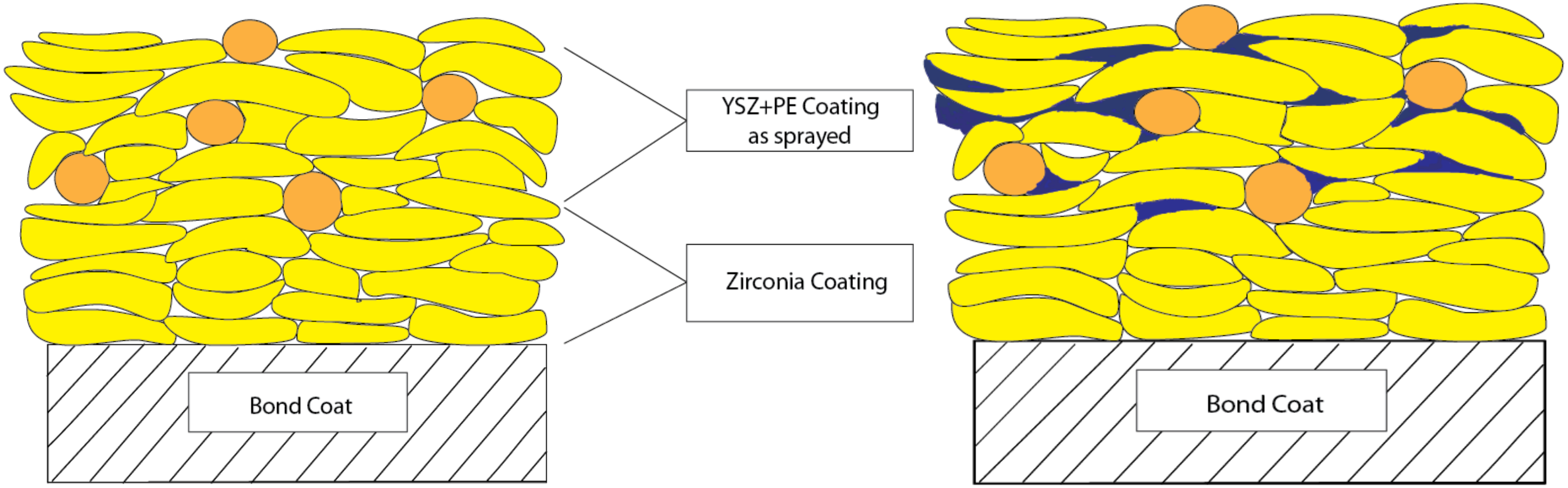
Ceramic Abradable Coating Studies

- Pure 8YSZ
- 8YSZ + PE
- 8YSZ + PE + hBN

🟨 **YSZ**

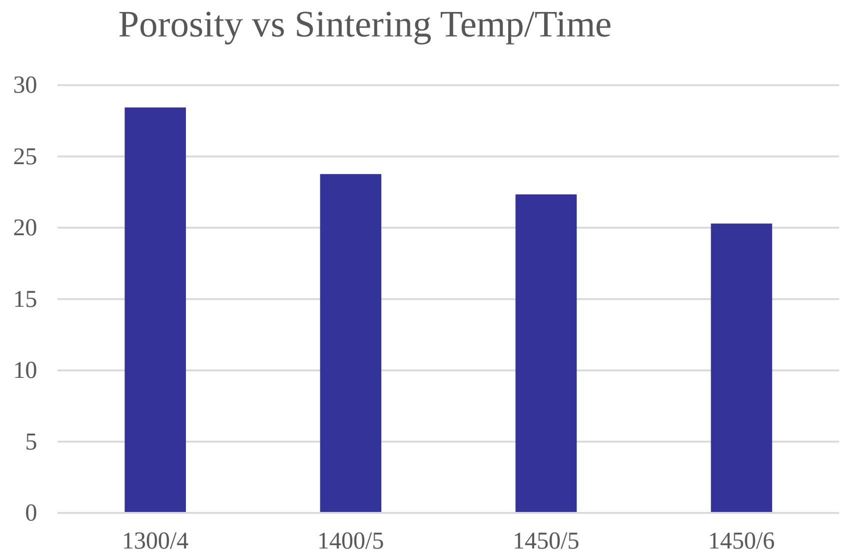
■ **hBN**

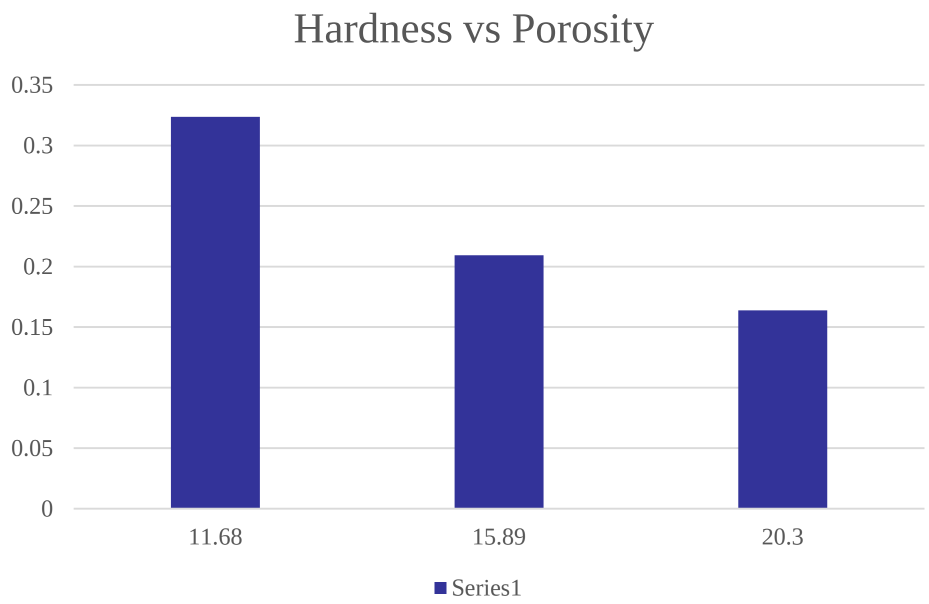
● **PE**



Effect of Porosity and Hardness on Exposure Conditions

- ☐ Porosity decreases with Exposure time and temperature
- ☐ Hardness increases with decrease in porosity





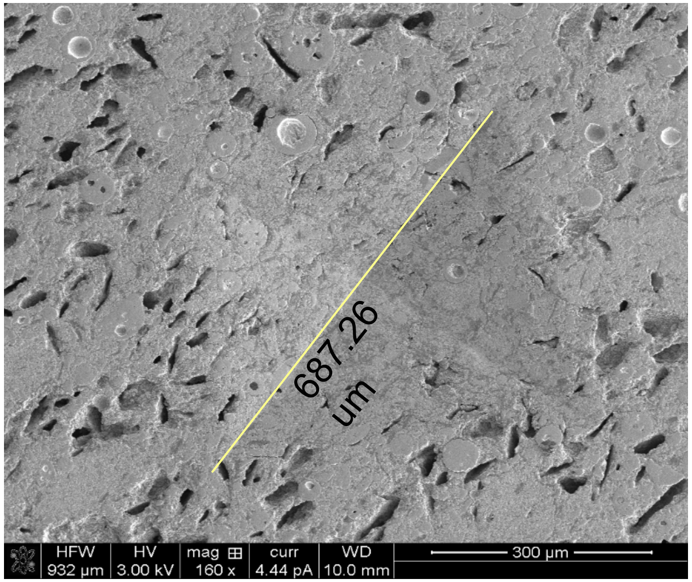
Hardness Measurements of Abradable Systems

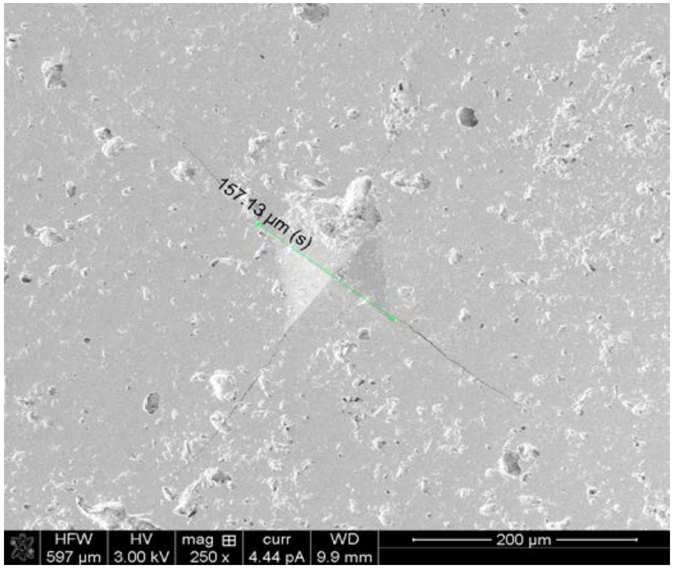
Boron Nitride acts as the lubricant phase and makes the composite more machinable and less robust.

Durabrade 2192 Indentation
~0.347 GPa

No cracks

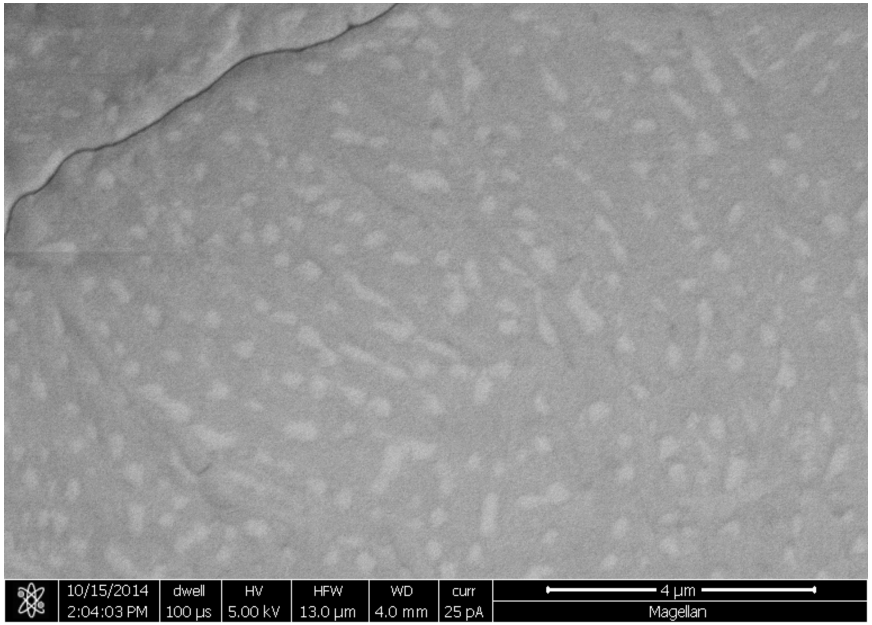
(9 Kgf load)

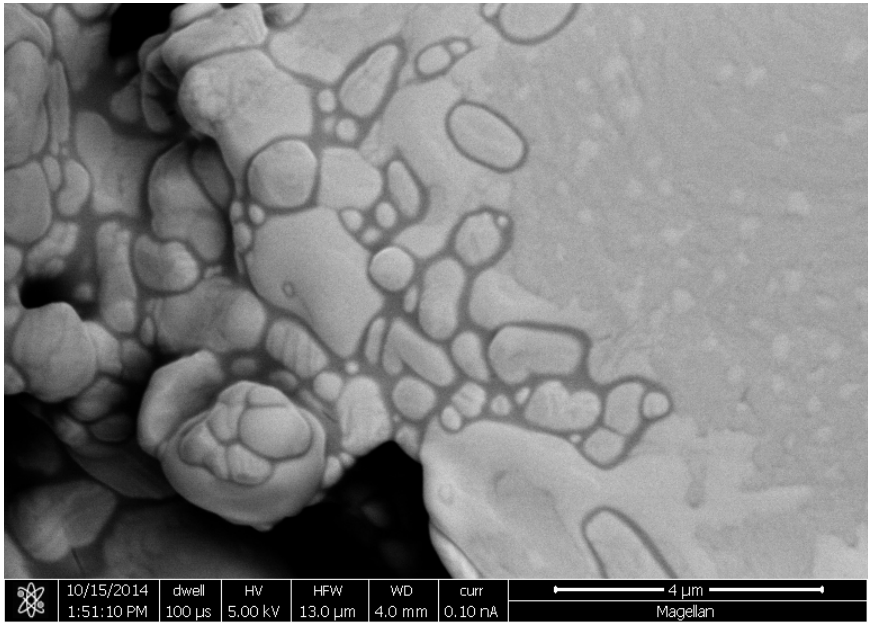




Tz8Y indentation:
~7.78 GPa
Cracks visible
9 Kgf load

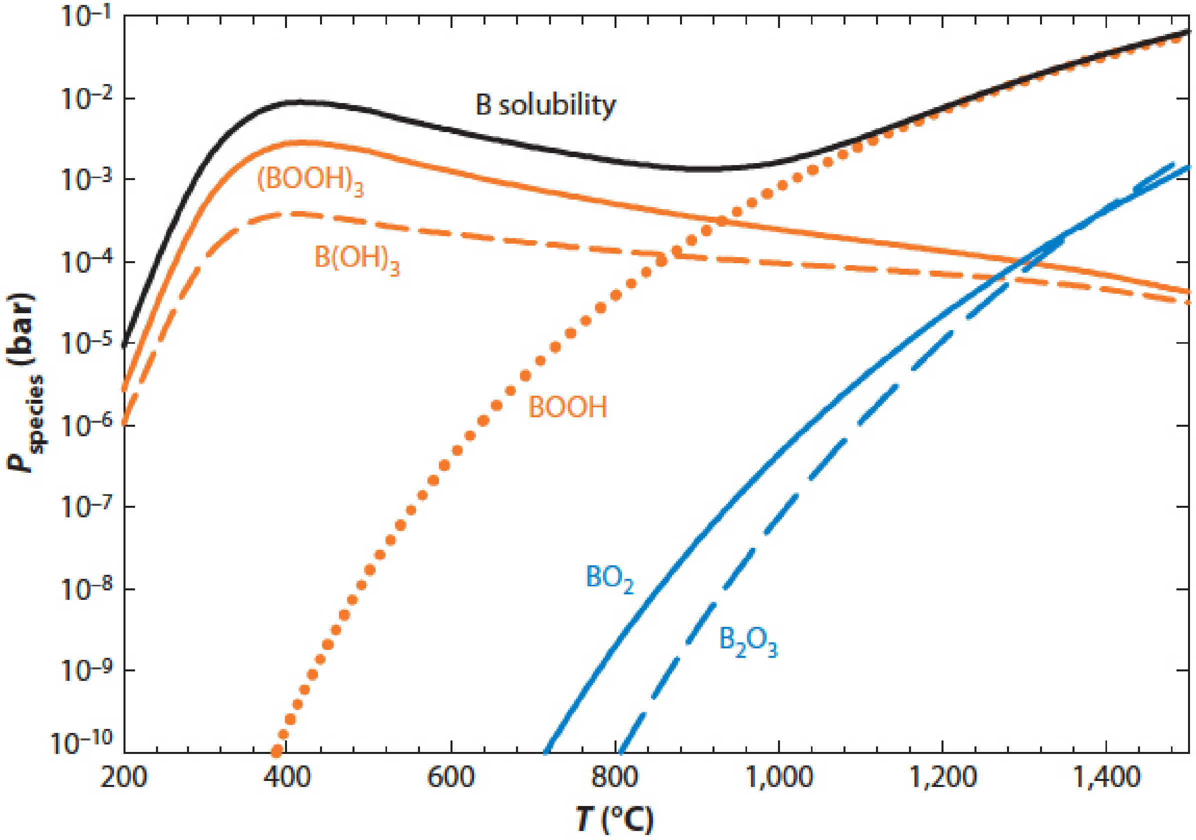
YSZ/hBN/Polyester Abradable System Behavior





- As processed materials show uniform distribution of BN phase
- Exposed samples show development of boron oxide or boro-silixate glass phases (developed in dry air exposure).
- Potential volatility with elevated pH_2O levels

YSZ/BN System Behavior

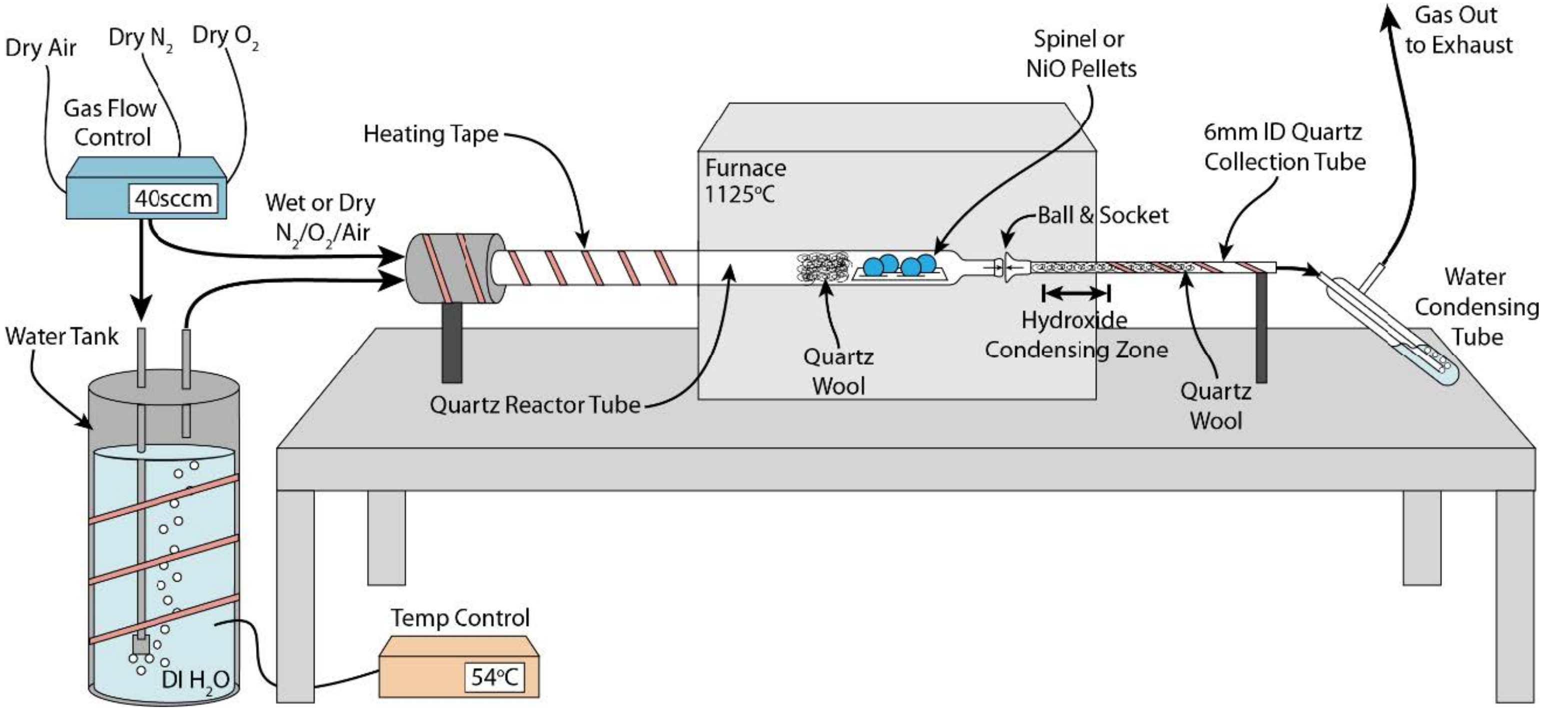


- Development of significant volatility in water vapor containing environments

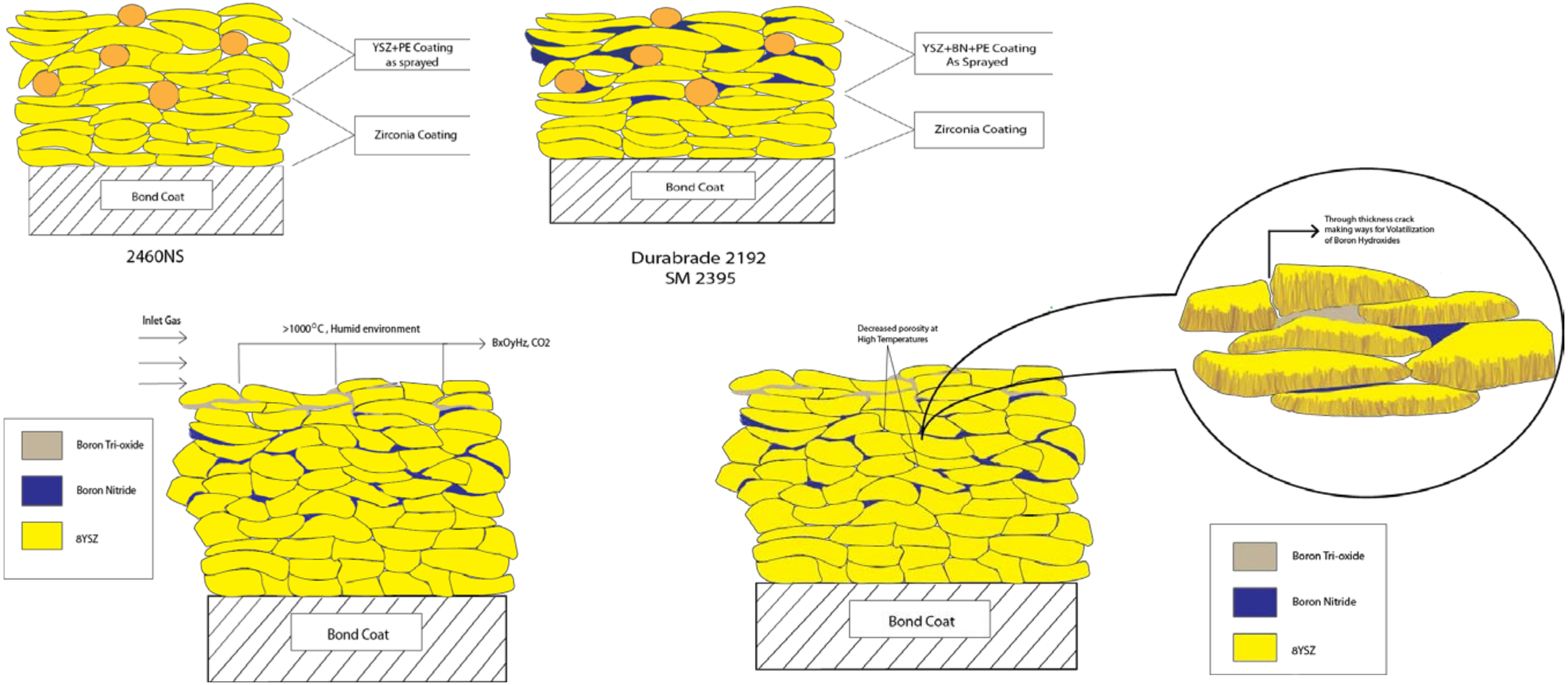
P.J. Meschter, E.J. Opila and N.S. Jacobson,
Annual Review of Materials, 2013

Water Vapor Effects: Preferential Volatilization of Lubricious Phases?

Transpiration experiments will be used to verify volatilization of second phase constituents (hBN species) via atomic absorption spectroscopy:



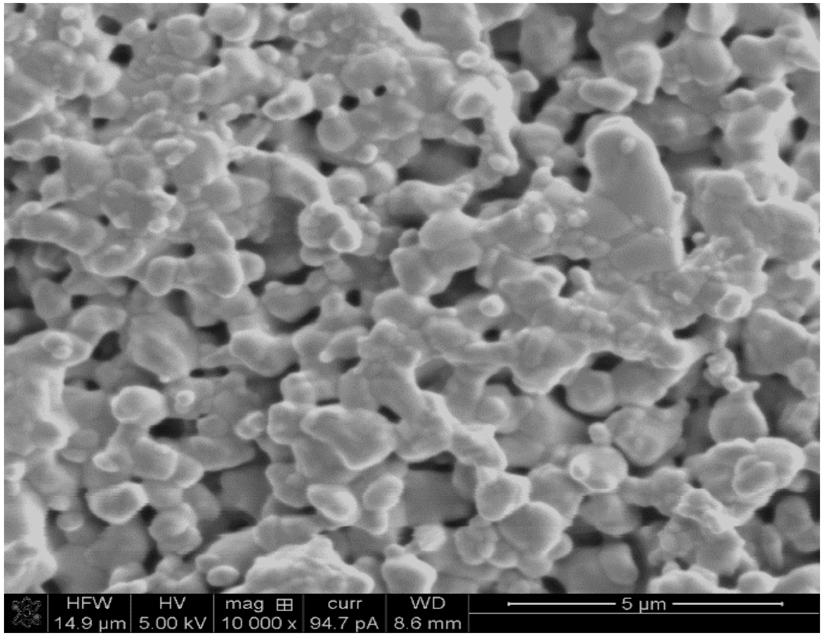
Coating Evolution under High Water Vapor Content Exposures



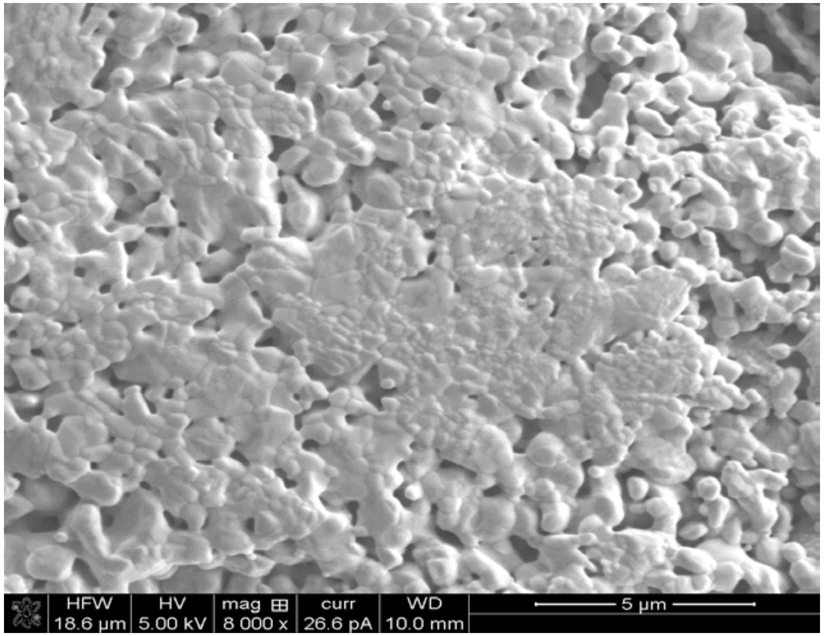
High Water Vapor Enhances Pore Sintering, and Reduces Abradability

Coating Evolution under High Water Vapor Content Exposures

- The grains after exposure at higher temperature in air seems to have grown a very porous network.
- The wet run made the specimen more dense, less porous and the surface more closed porosity.



Dry

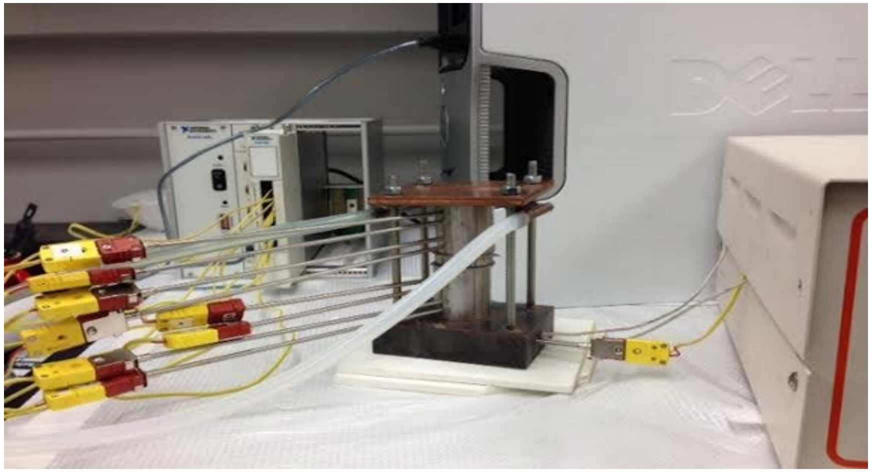


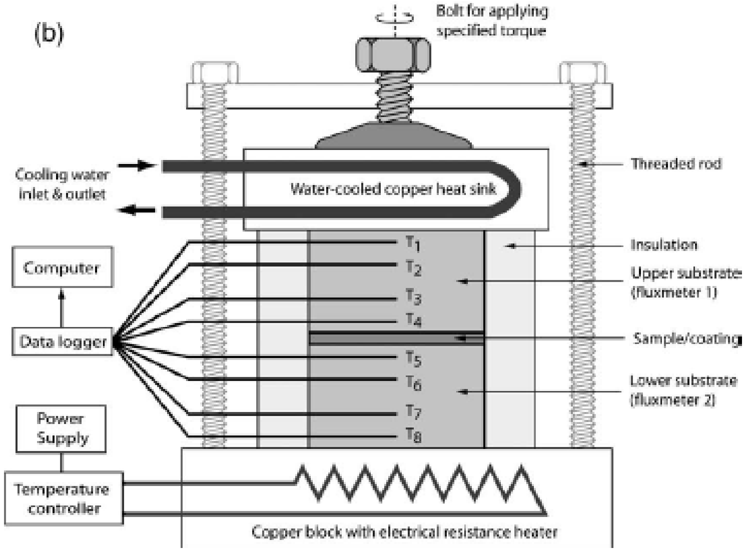
Wet

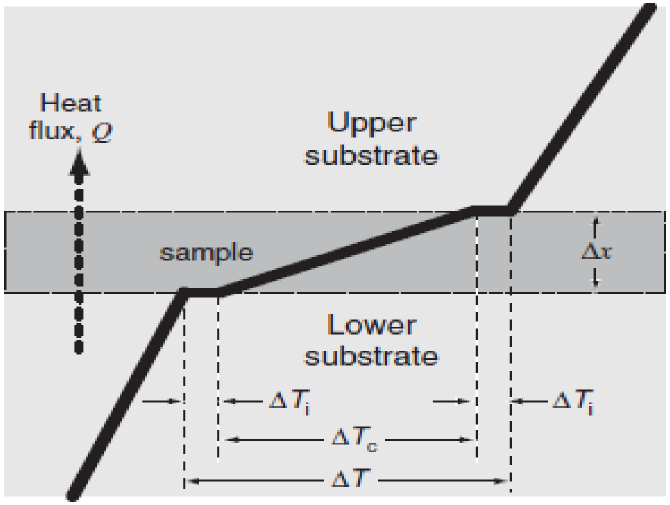
Changes to the Thermal Conductivity

- Purpose: To calculate the change in heat flow using a specimen that has been exposed to simulated water vapor environment

Current laboratory set-up





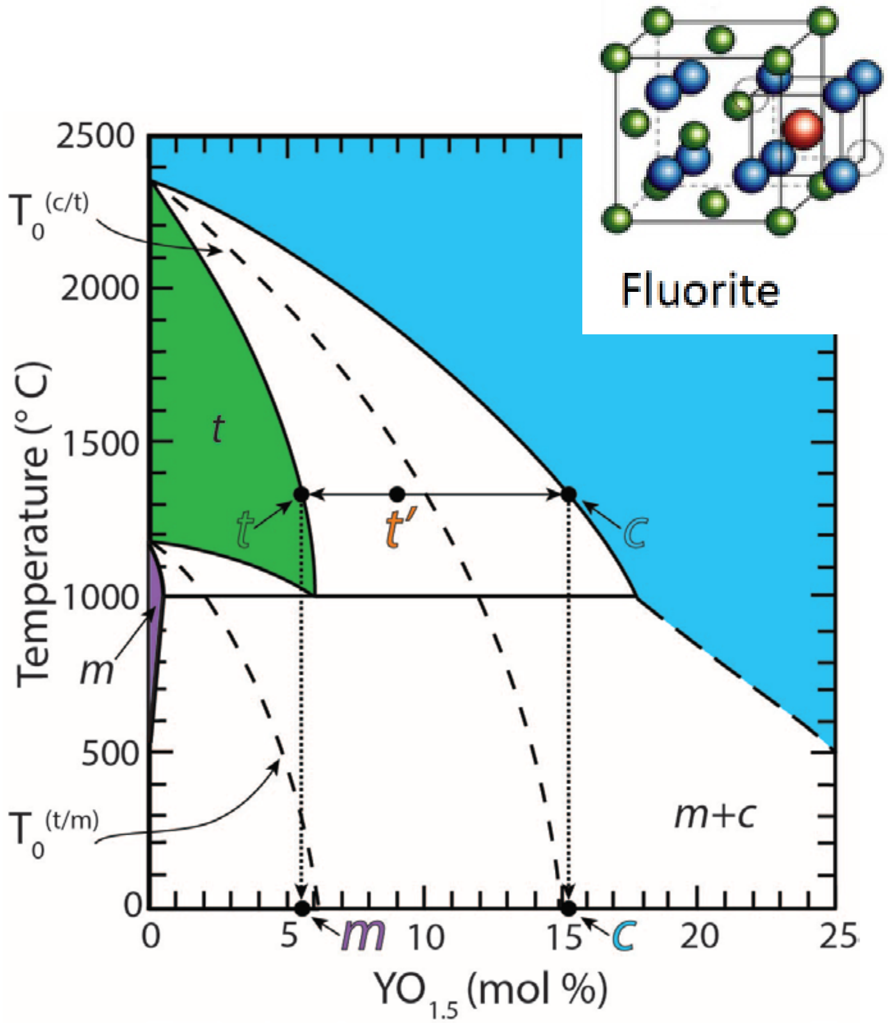


*A steady-state Bi-substrate technique for measurement of the thermal conductivity of ceramic coatings
J.C. Tan, S.A. Tsipas, I.O. Golosnoy, J.A. Curran, S. Paul, T.W. Clyne □

Aging of YSZ under IGCC-Relevant Environments

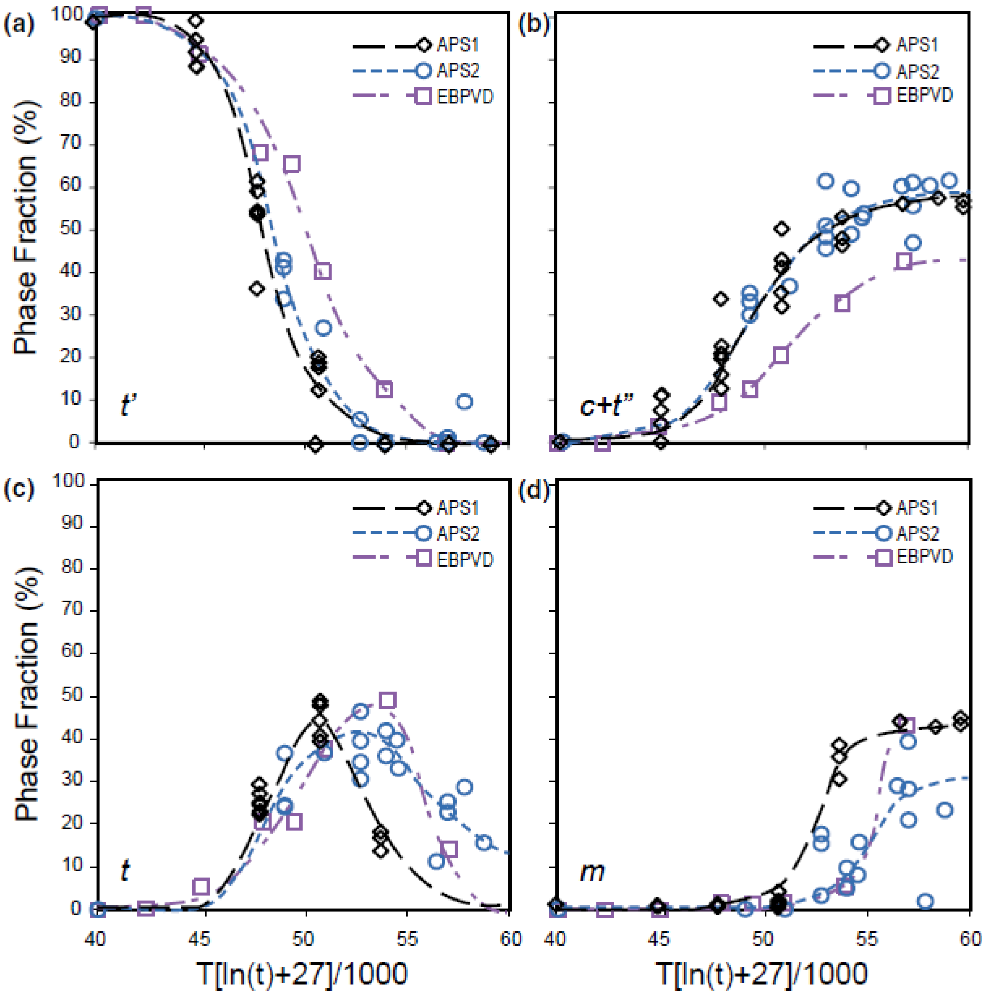
- Yttria content puts the 8YSZ in the tetragonal + cubic phase field
- *t'* phase will eventually decompose to these equilibrium phases
- Rate is dictated by aging time and temperature
- Can normalize the influence of time and temperature by the use of the Larson-Miller or the Hollomon-Jaffe Parameter of the form:

$$T[C+\ln(t)]$$

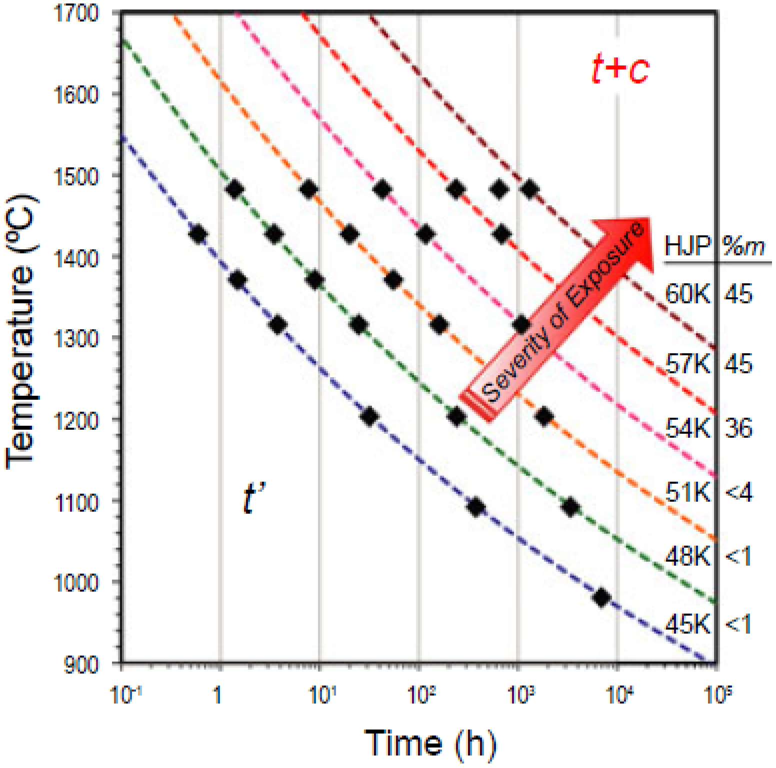


Redrawn from Levi *et al.,*
J. Am. Ceram. Soc., 96 [1] 290-298 (2013)

Prior Research Findings

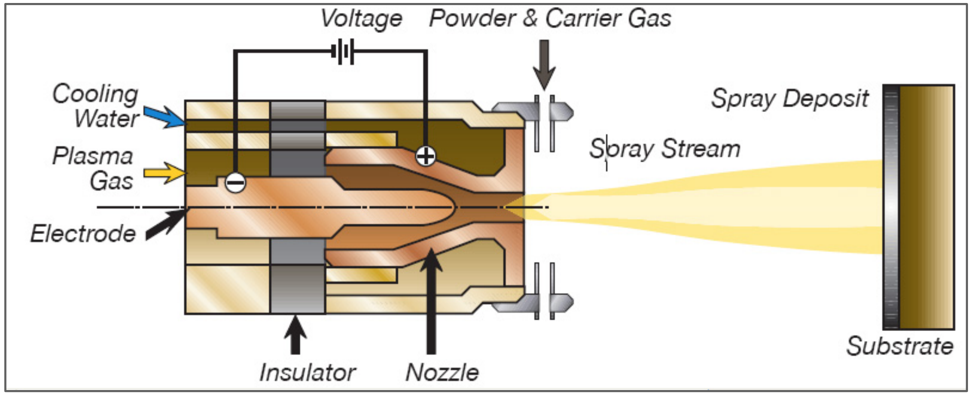


Lipkin *et al., J. Am. Ceram. Soc.*,
96 [1] 290-298 (2013)



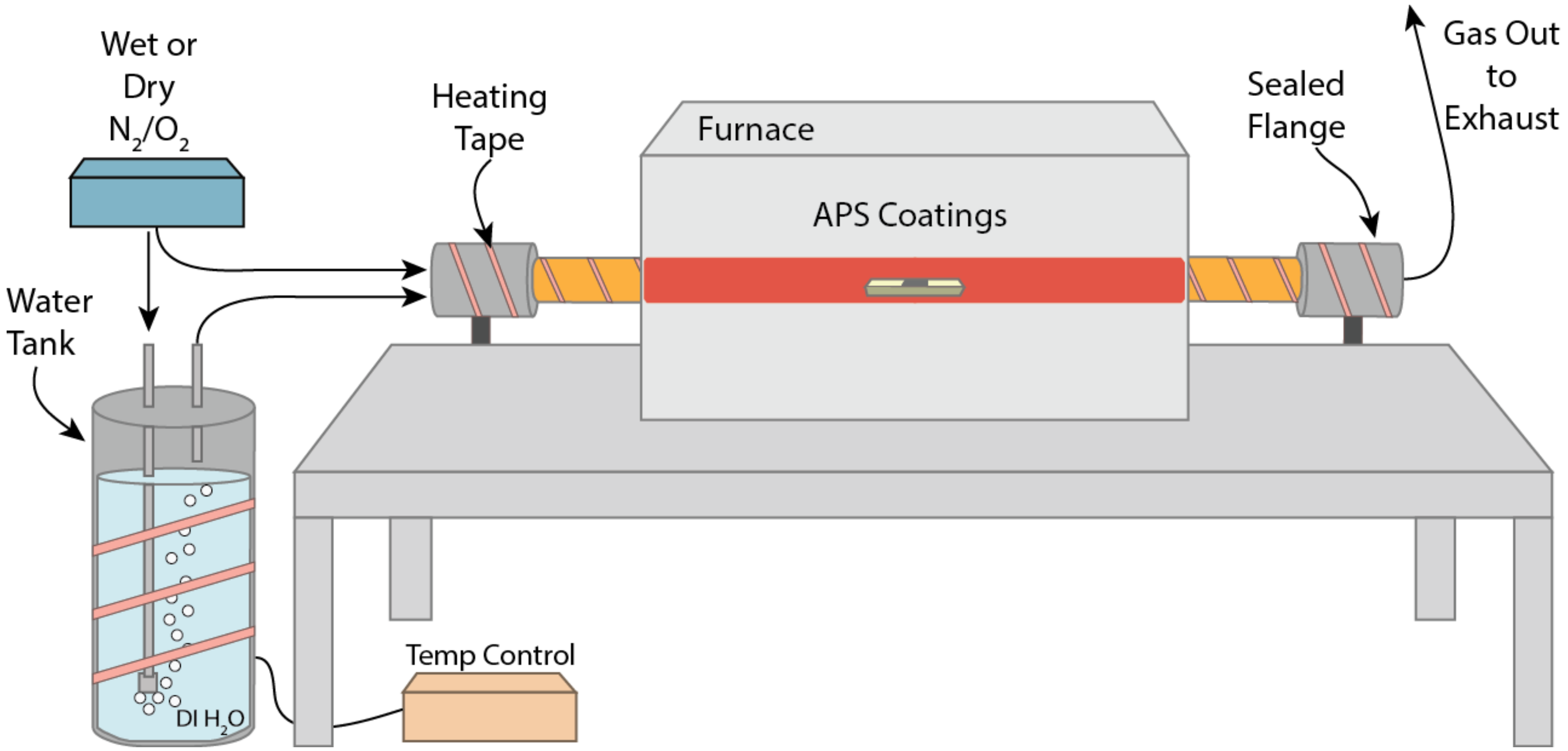
How does a humid environment influence the destabilization of the *t'* phase during aging?

TBC Degradation Studies: Materials Preparation



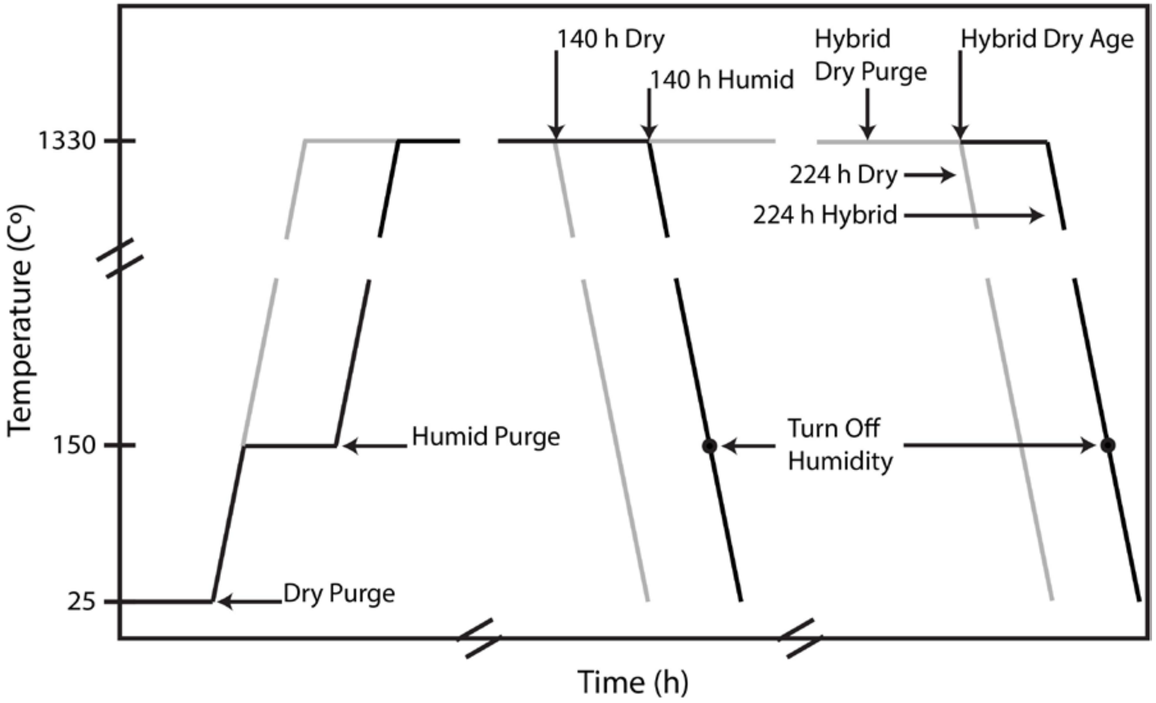
JÜLICH
FORSCHUNGSZENTRUM

Isothermal Exposures with Environmental Control



- Water tank temperature determines vol% H_2O via gas-liquid equilibrium exchange
- For 0% H_2O, the water tank is bypassed completely
- Exposed to dry or humid ageing (45 vol. %) in a controlled environment
- Air plasma spray, 8 wt.% Yttria-Stabilized Zirconia

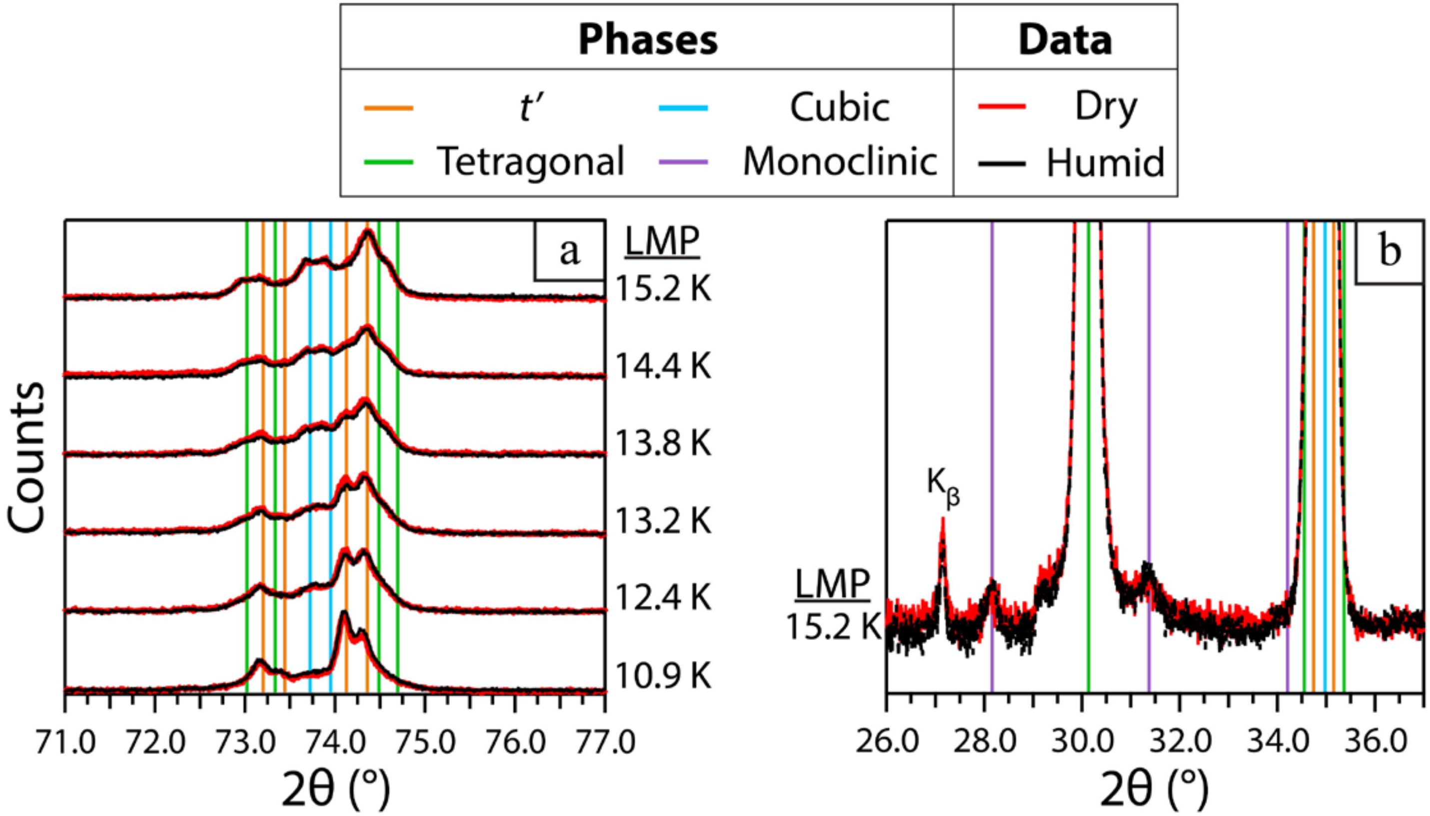
Aging Protocols and Characterization



- Post-test characterization by XRD, Raman and Microstructural analysis (TEM/STEM)
- Rietveld refinement of XRD spectra carried out to quantify evolving phase fractions
- The refinement employed a four phase model (t’, tetragonal, cubic and monoclinic)

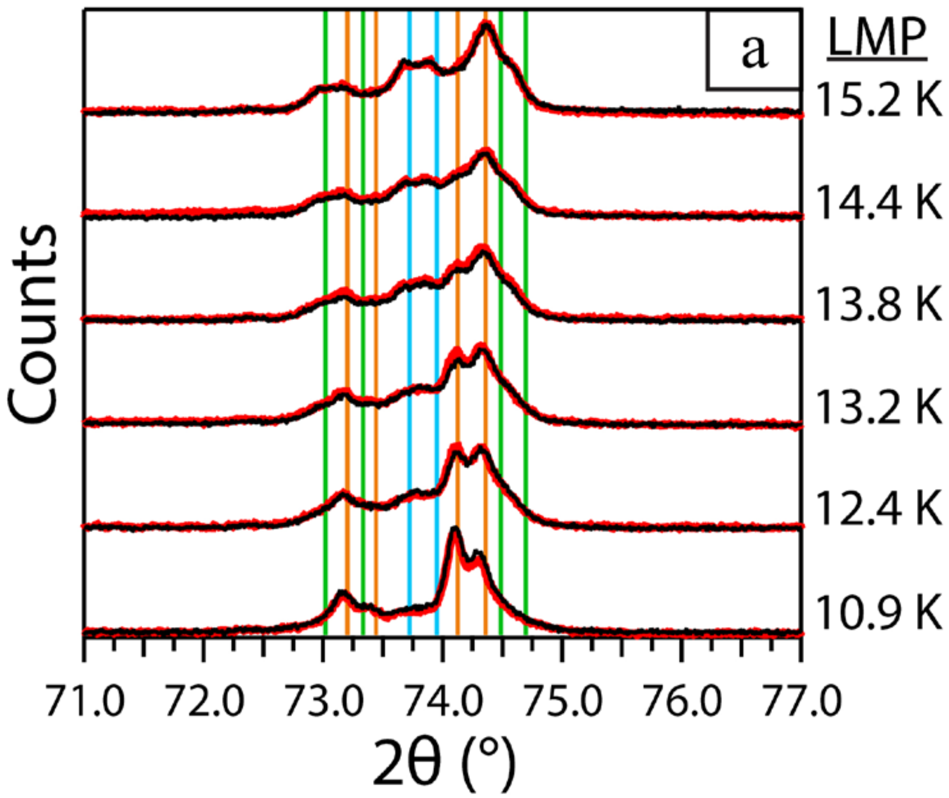
Aging to a Max LMP of 15.2k (88 hours at this Temp)

- Dry and humid environments appear to decompose the *t’* phase at the same rate, for exposure times to 88 hours



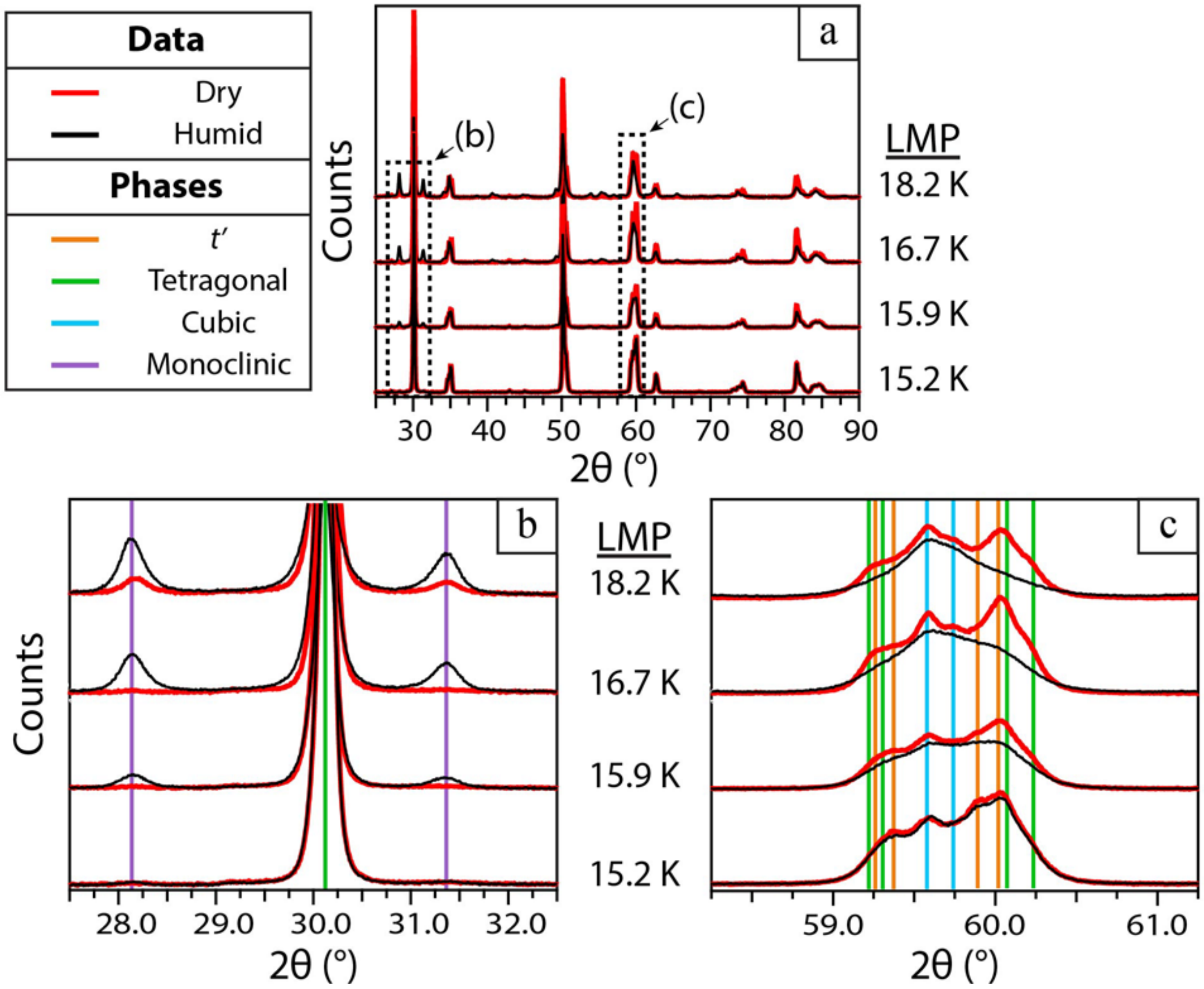
- XRD peak positions gradually shift from t’ to tetragonal and cubic positions

Evidence in Support of Spinodal Decomposition During Aging



- Gradual shifting of the XRD peaks
- Indicates a range of lattice parameters as the *t'* destabilizes to the tetragonal and cubic phases

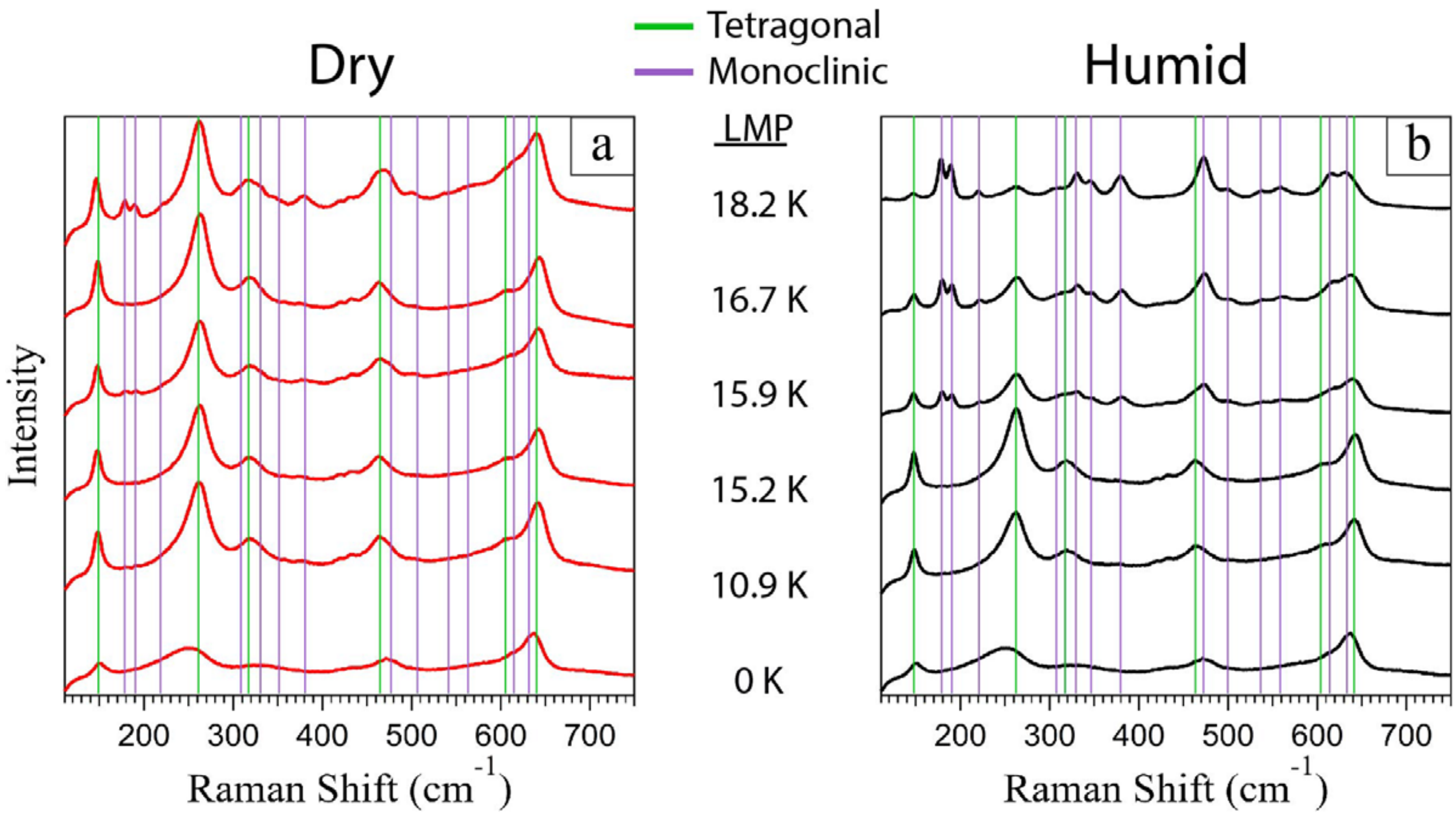
Further Aging to LMP = 15.9k [Environmental Dependence Observed]



- Accelerated formation of the monoclinic phase under high pH_2O exposure conditions

Raman Spectroscopy Analysis

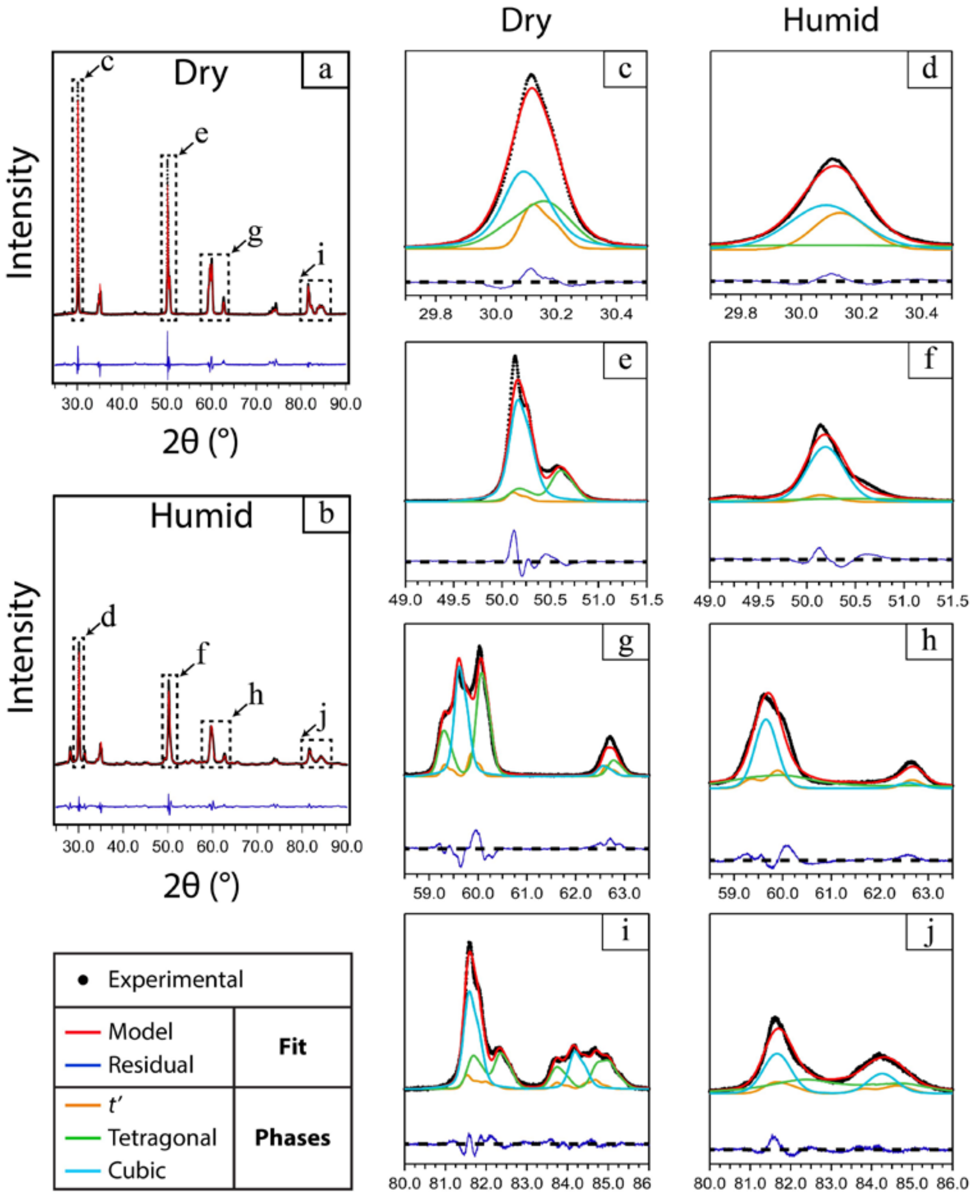
Raman spectroscopy results corroborate the XRD results



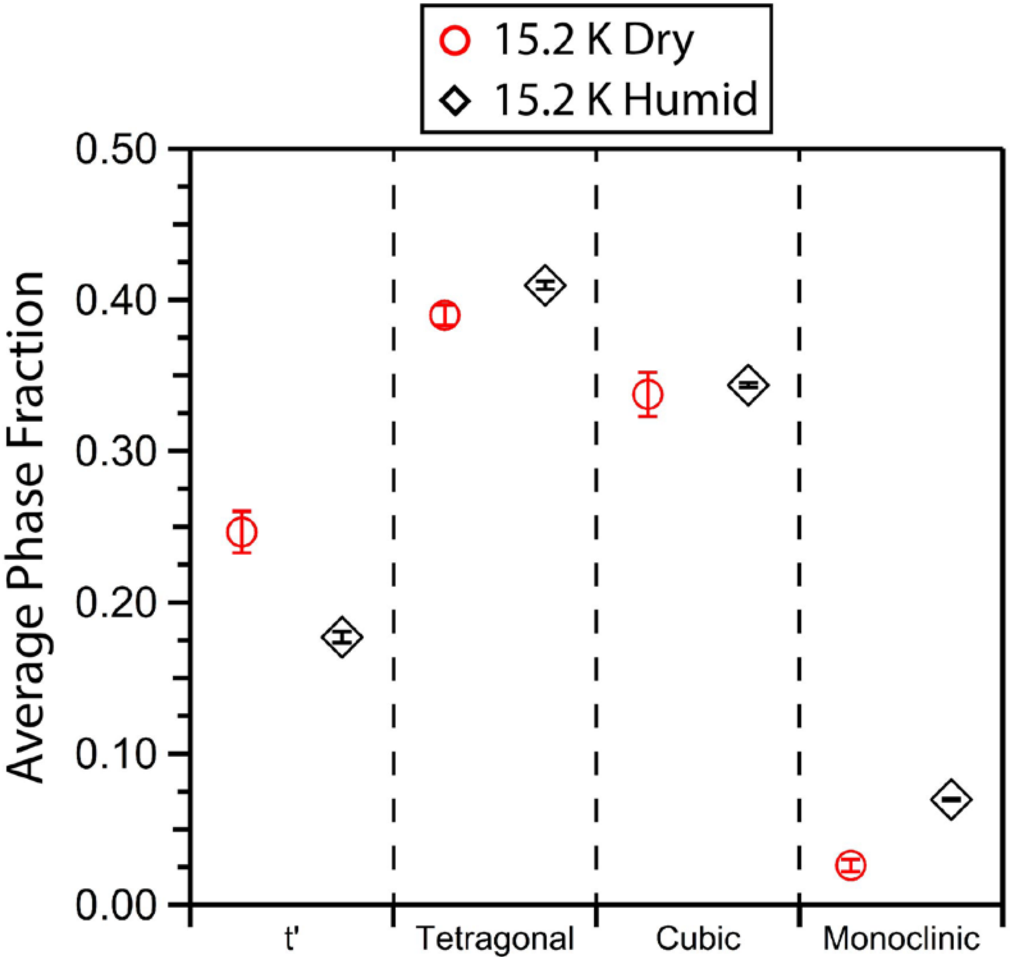
- Only the tetragonal modes are observed up to a LMP of 15.2 K
- For LMPs 15.9 K and 16.7 K , the monoclinic modes are now present

Quantitative Phase Analysis

- Full-pattern Rietveld fitting
- Examples of the peak deconvolution shown
- Selected peaks corresponding to the t’, tetragonal and cubic phases
- Weighted profile R value (a metric for quality of fit) was consistently less than 7%

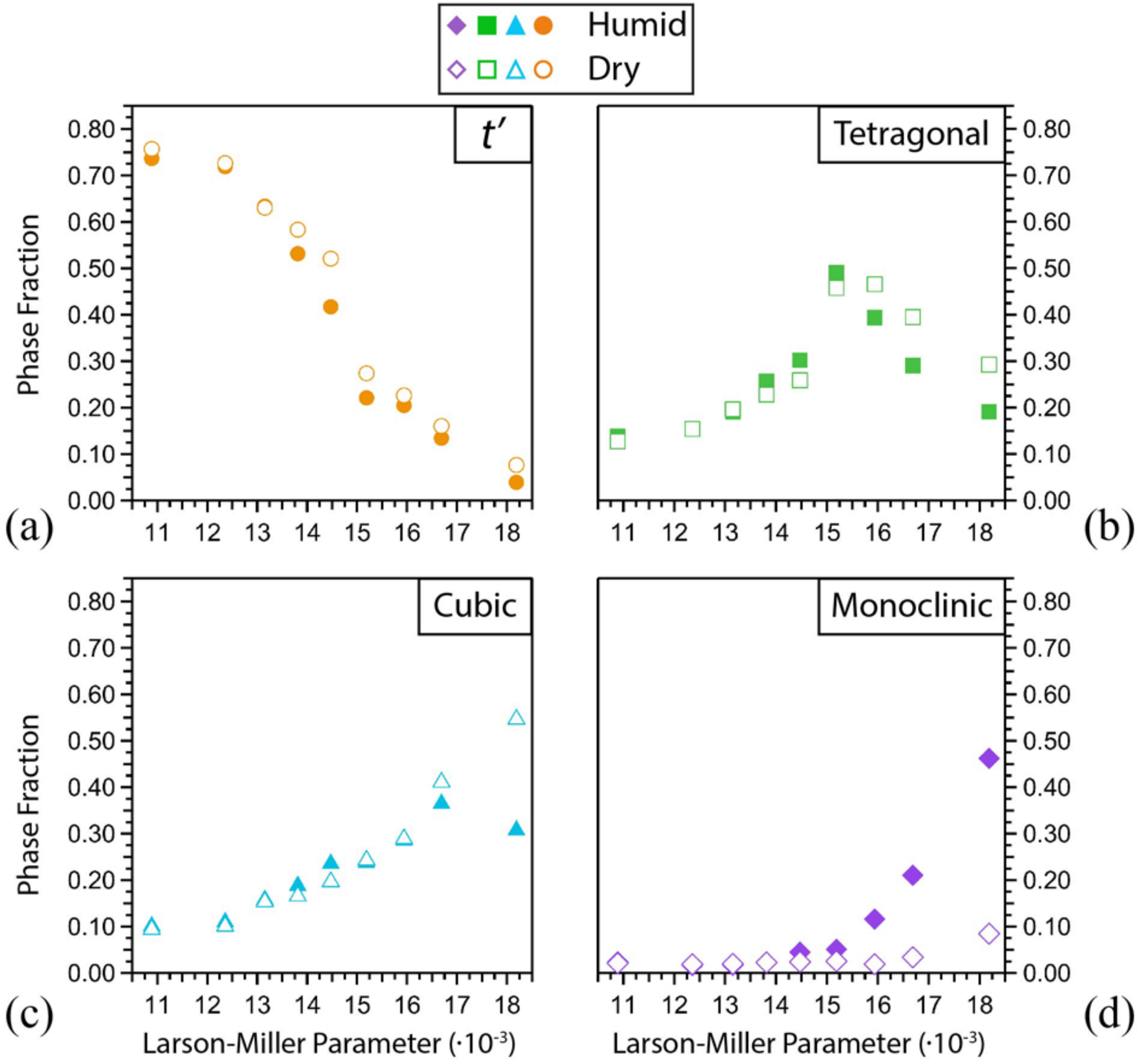


Average Phase Fractions (at 88 hours Exposure)

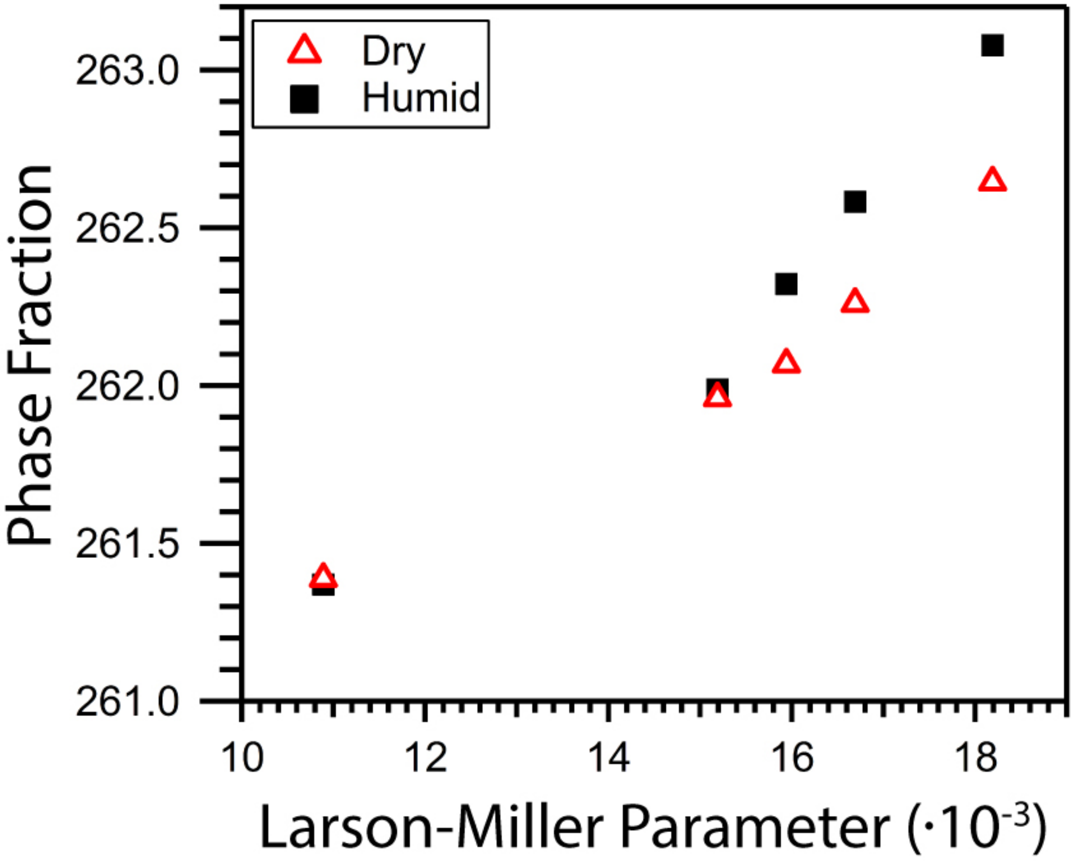


- Accelerated decomposition of the t’ phase, with associated formation of the monoclinic phase

Evolution of the Phase Fractions



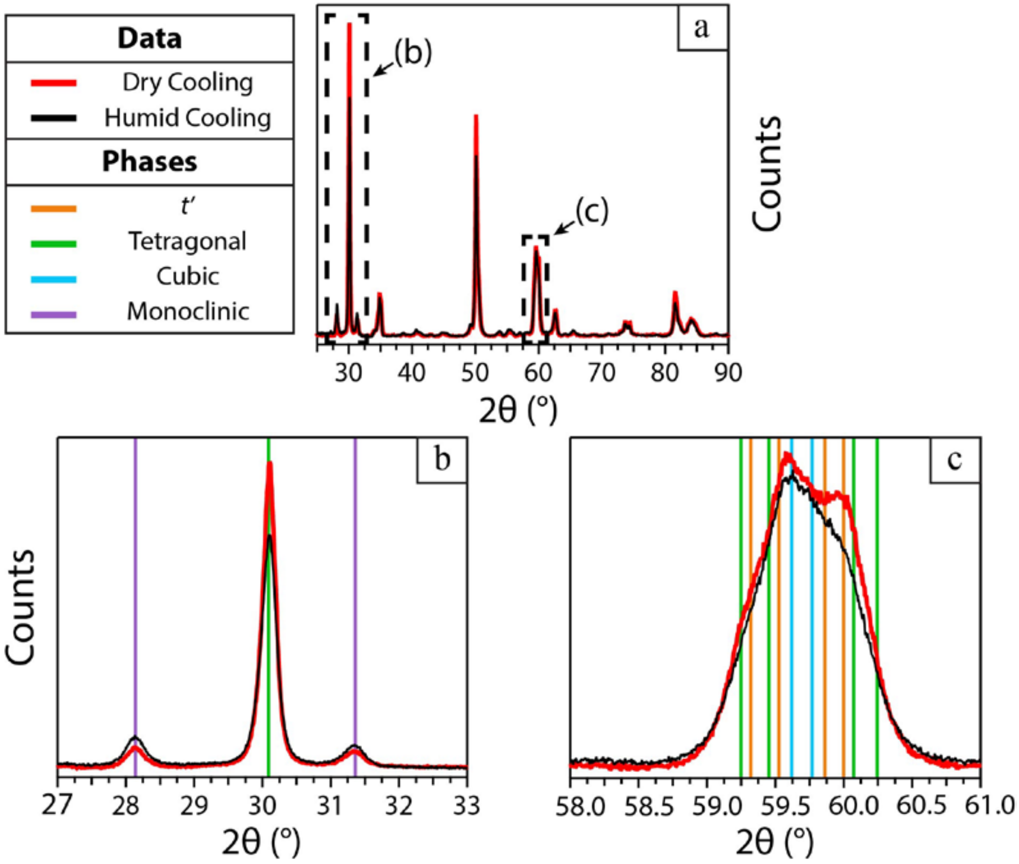
Raman Spectroscopy Supports Spinodal Decomposition Mechanism

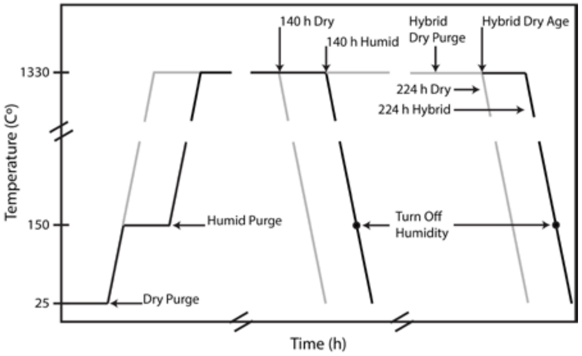


Peak fitting of the A_{1g} mode shows peak shifting in both environments

- Indicates a continuous change in the lattice parameters
- Peak shifts faster for humid-ageing condition

Cooling Under High pH_2O Conditions vs. Cooling Under Dry Conditions

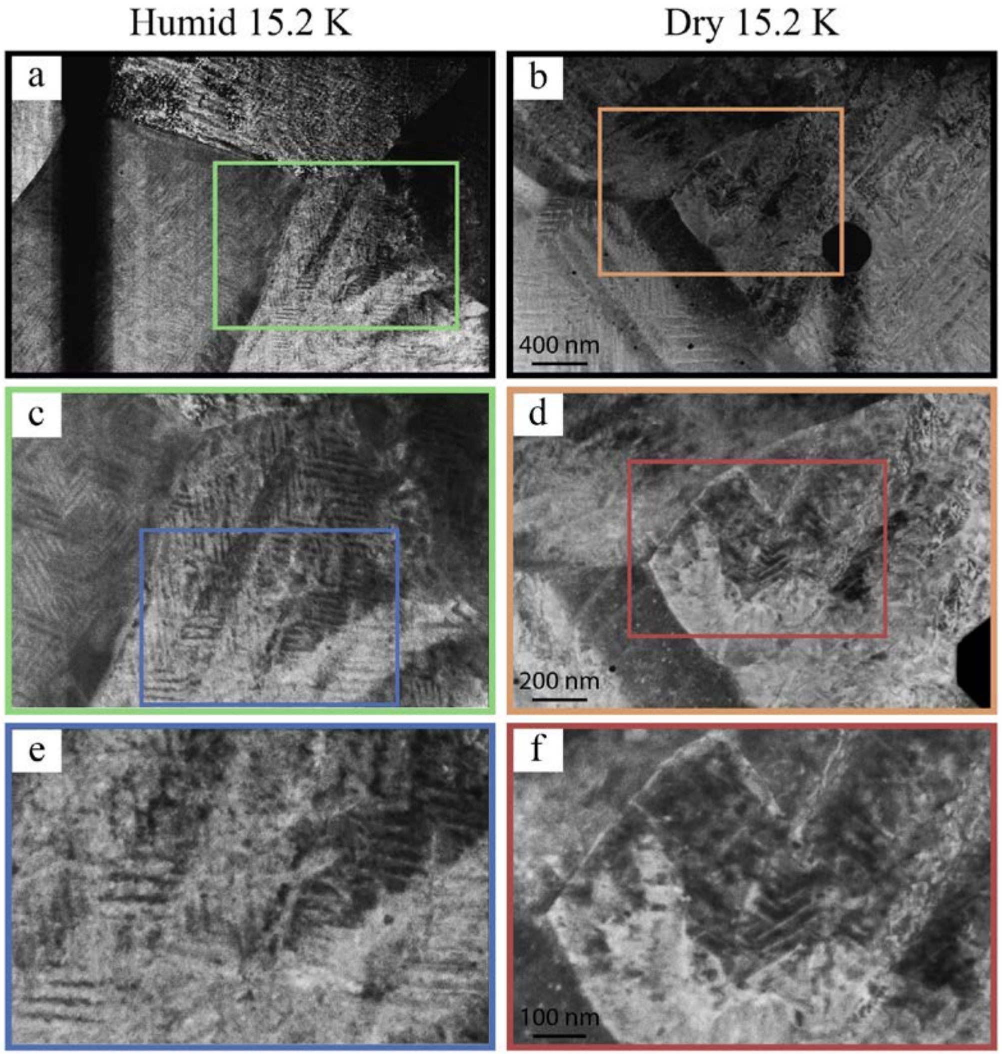




Observed monoclinic formation appears to play out at high temperature, not as an artifact of low temperature exposure to high pH_2O conditions

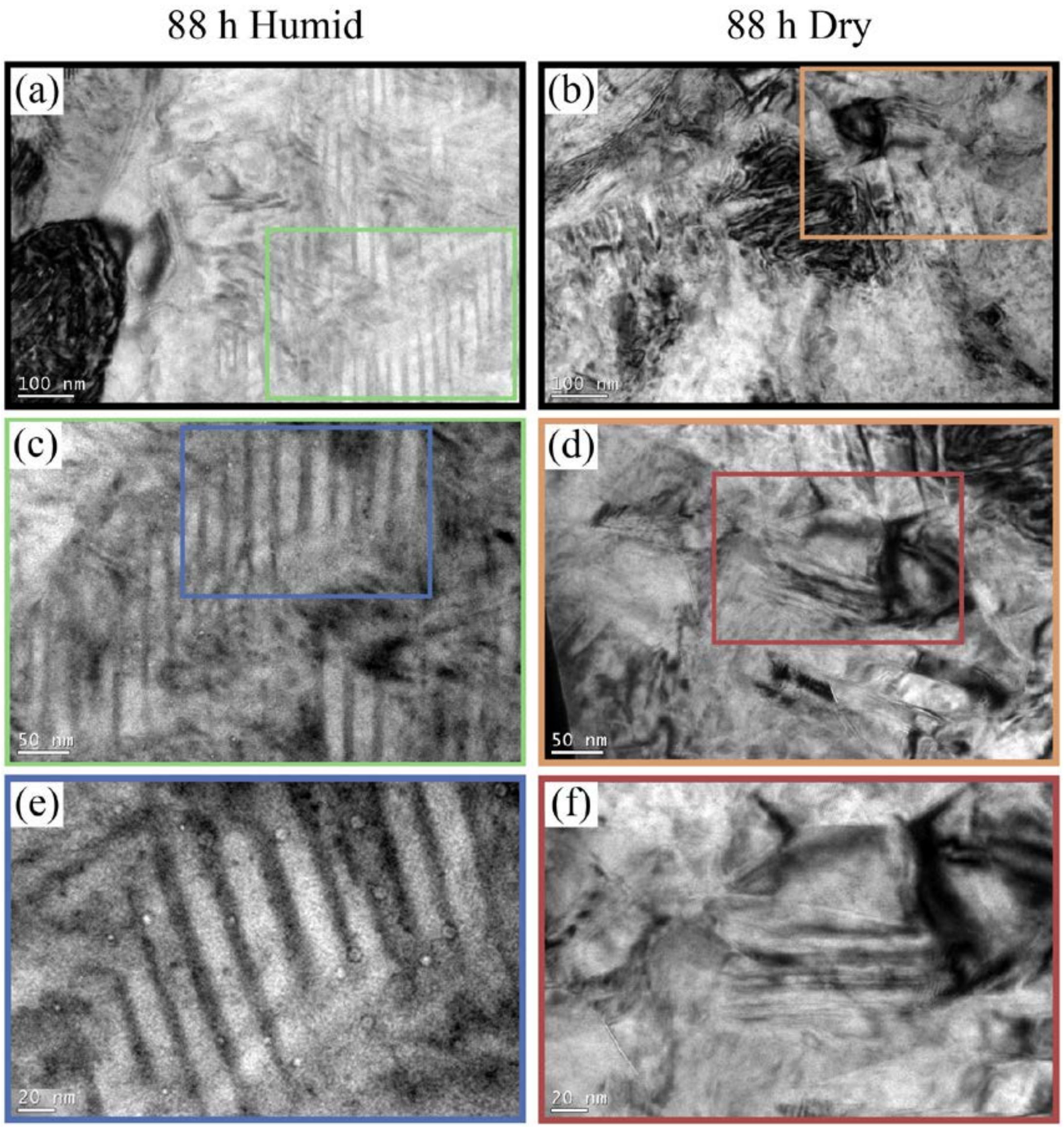
HAADF Imaging

- Differences observed in domain structure
- For dry exposures, domains exhibit ~ 3-7nm width
- For high pH2O exposures, domains ranges from ~ 12- 17nm in width

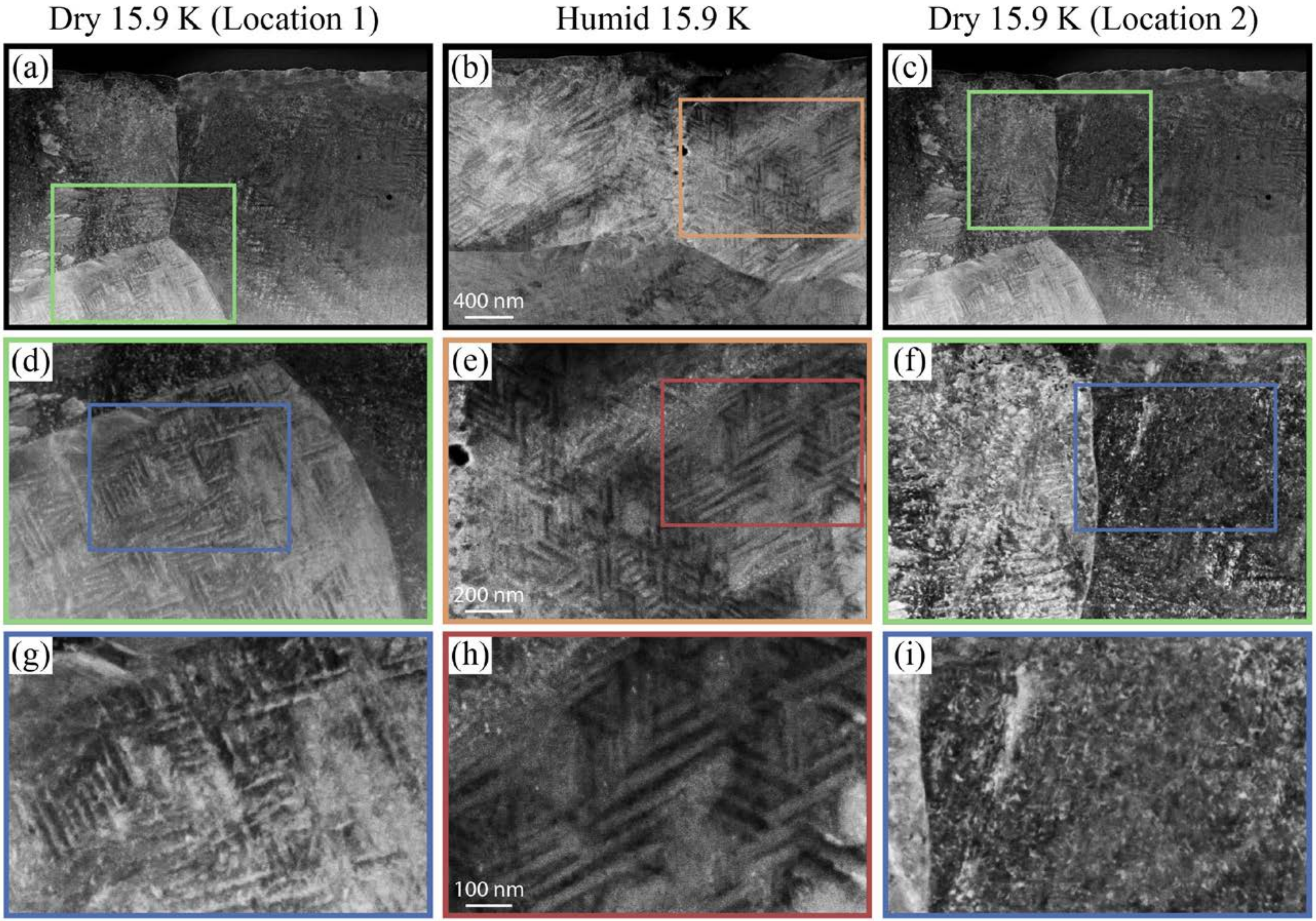


Bright-Field TEM Imaging

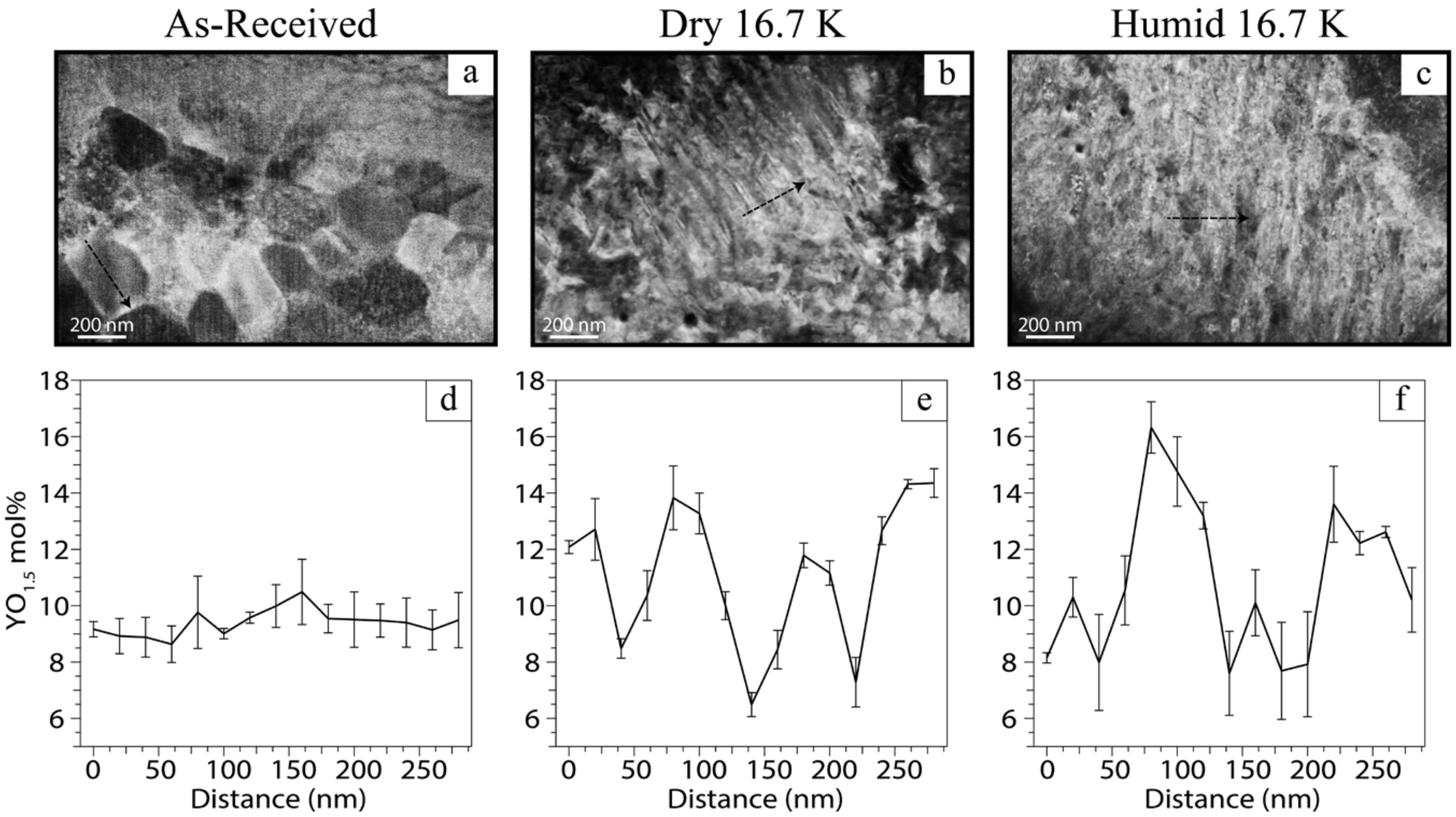
- Differences observed in domain structure
- For dry exposures, domains exhibit ~ 3-7nm width
- For high pH2O exposures, domains ranges from ~ 12- 17nm in width



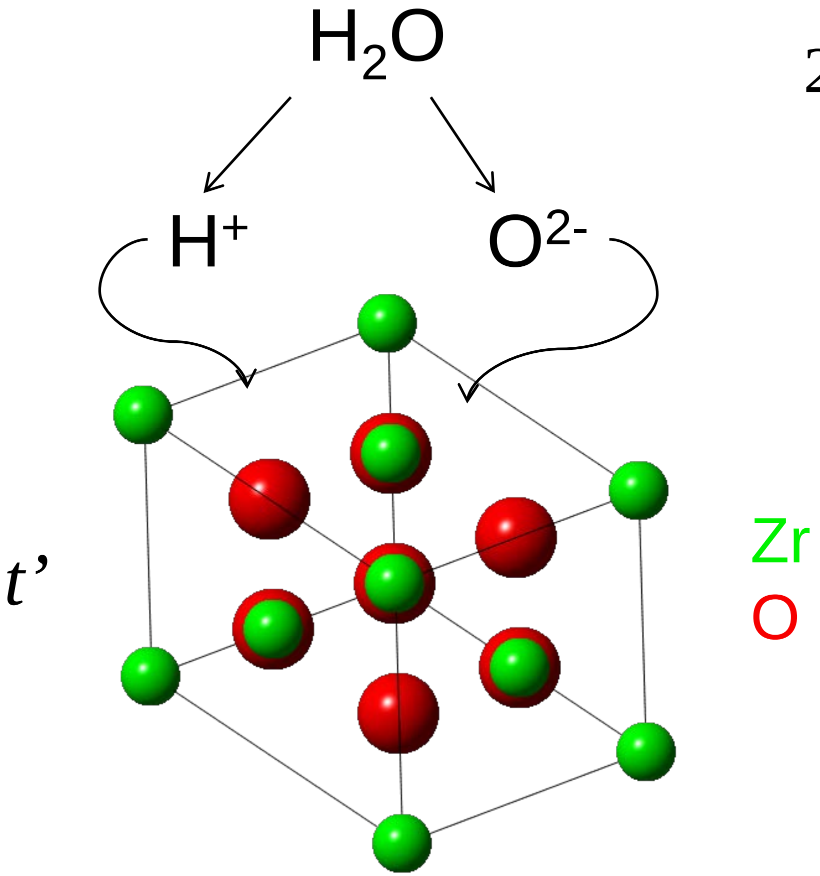
HAADF TEM Imaging – Longer Exposures



EDS Line Profile Across Domain Structures



Possible Underpinning Mechanisms for Observed pH_2O Dependence

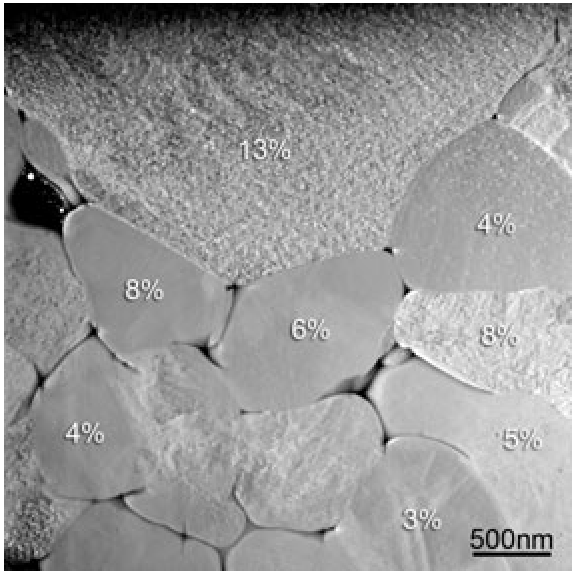


$$2H^{+} + O^{2-} + V_O^{\bullet\bullet} \xleftrightarrow{ZrO_2} 2H^{+} + O_O^{x}$$

And/Or

$$H_2O + V_O^{\bullet\bullet} + O_O^{X} \xleftrightarrow{ZrO_2} 2(OH)_O^{\bullet}$$

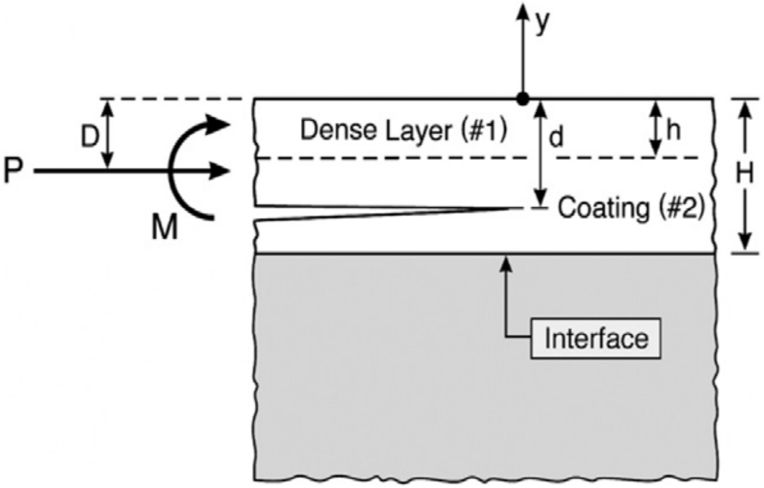
Clarke *et al., J. Am. Ceram. Soc.*, 92 [9] 1901-1920 (2009)



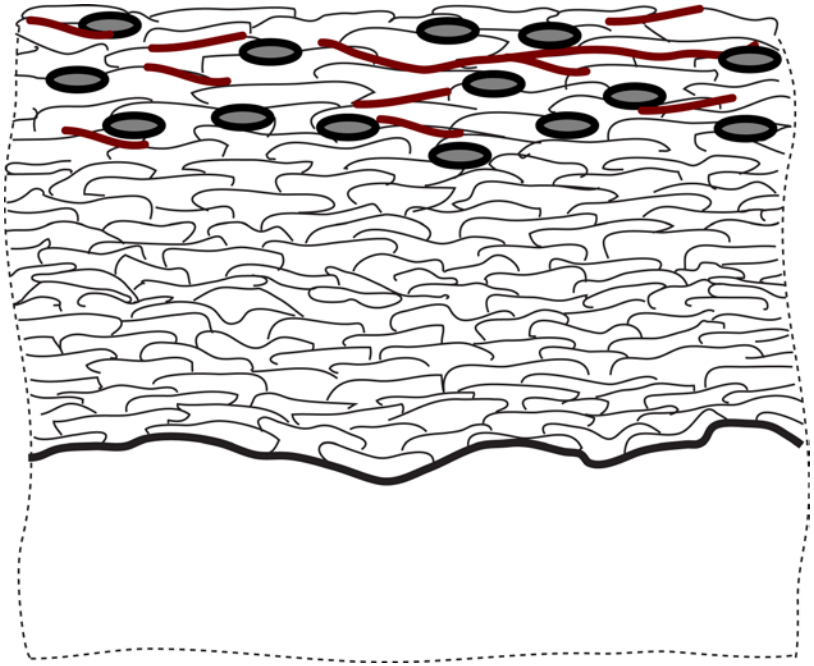
Levi *et al., J. Am. Ceram. Soc.*, 96 [1] 299-307 (2013)

Silica impurities at grain boundaries may incorporate water species and enhance yttrium diffusion

Microstructural Degradation

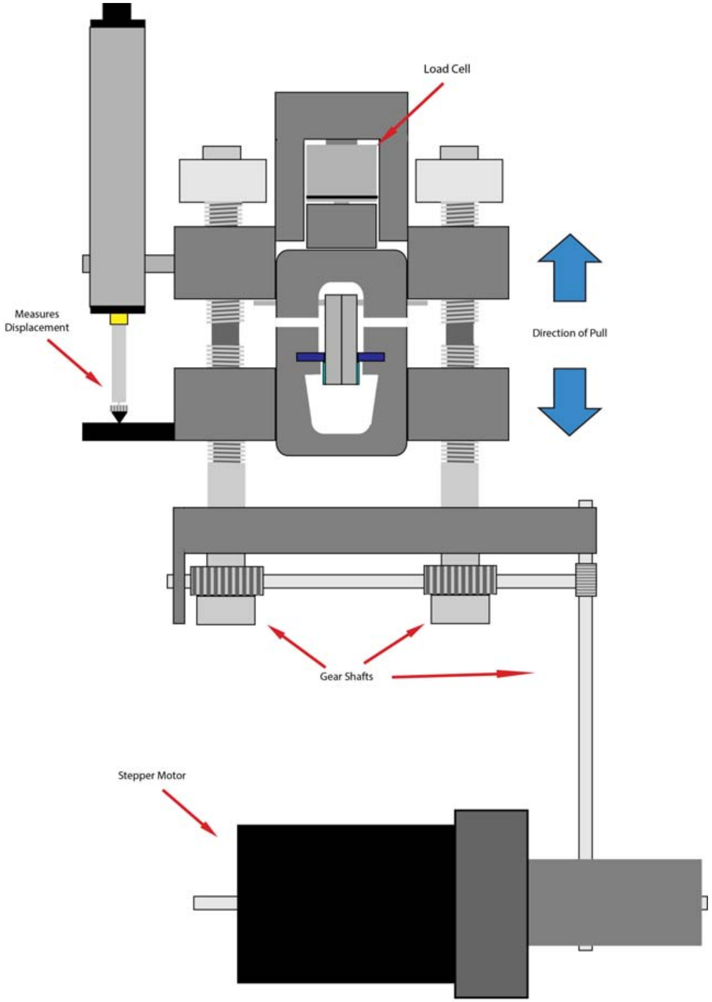


Sintering Effects

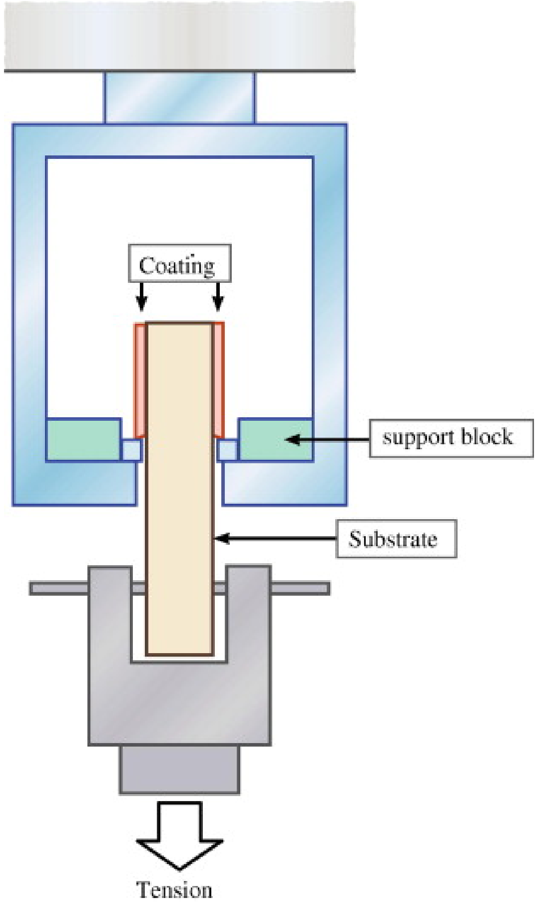


Pore Evolution,
Volatilization and
Interface Degradation

Mechanical Property Evaluations

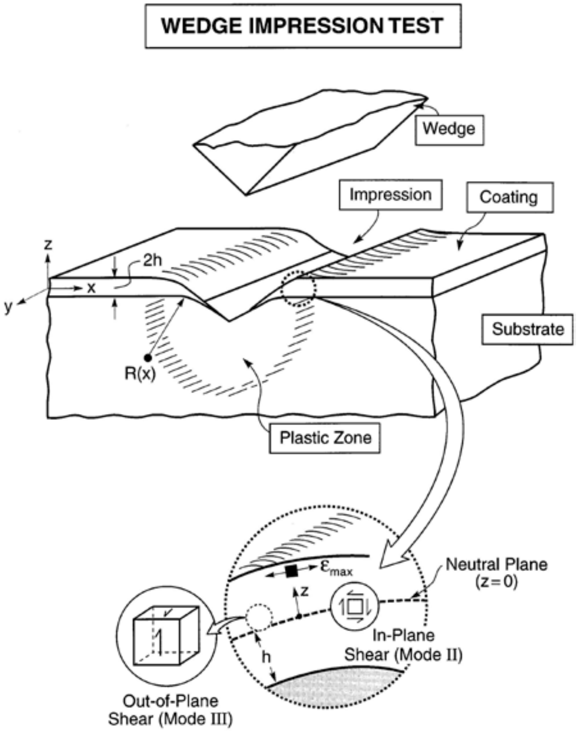


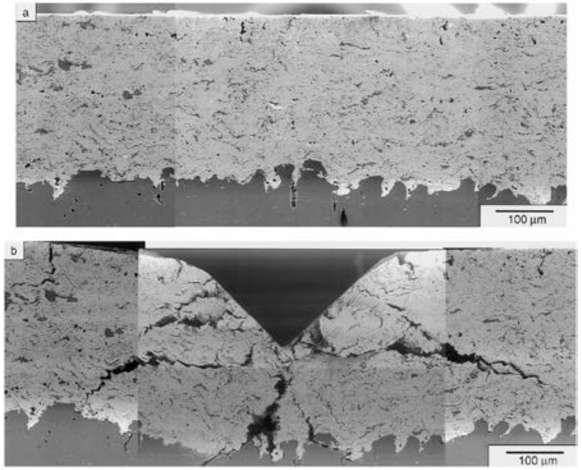
Full Barb Pullout Test Rig With Loaded Sample and Gauges

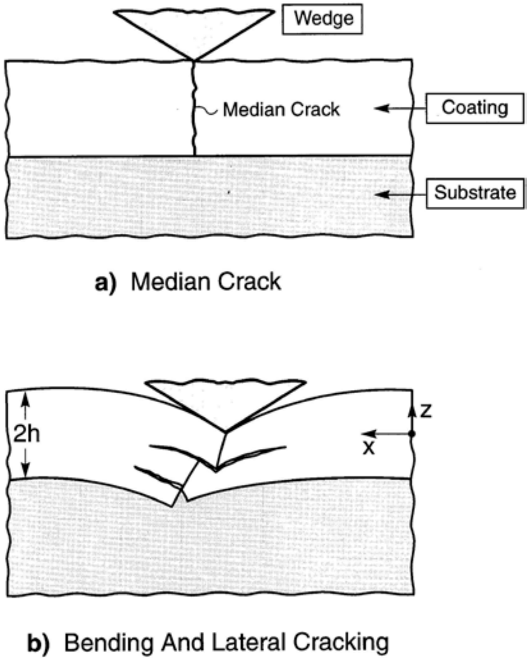


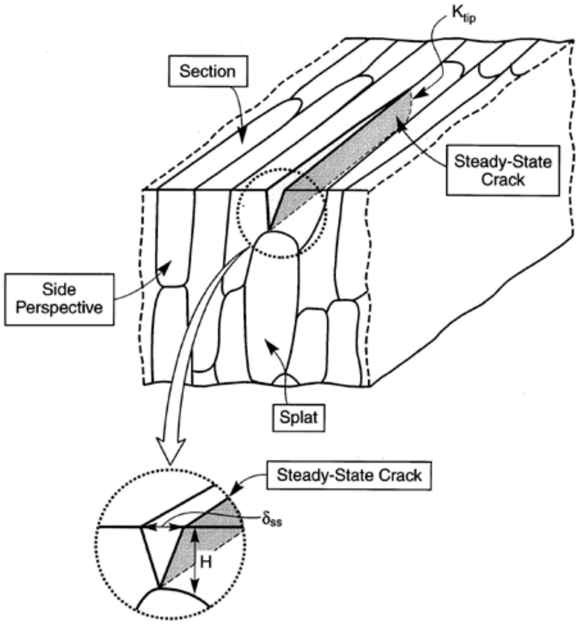
'Barb' Test

Mechanical Property Evaluations





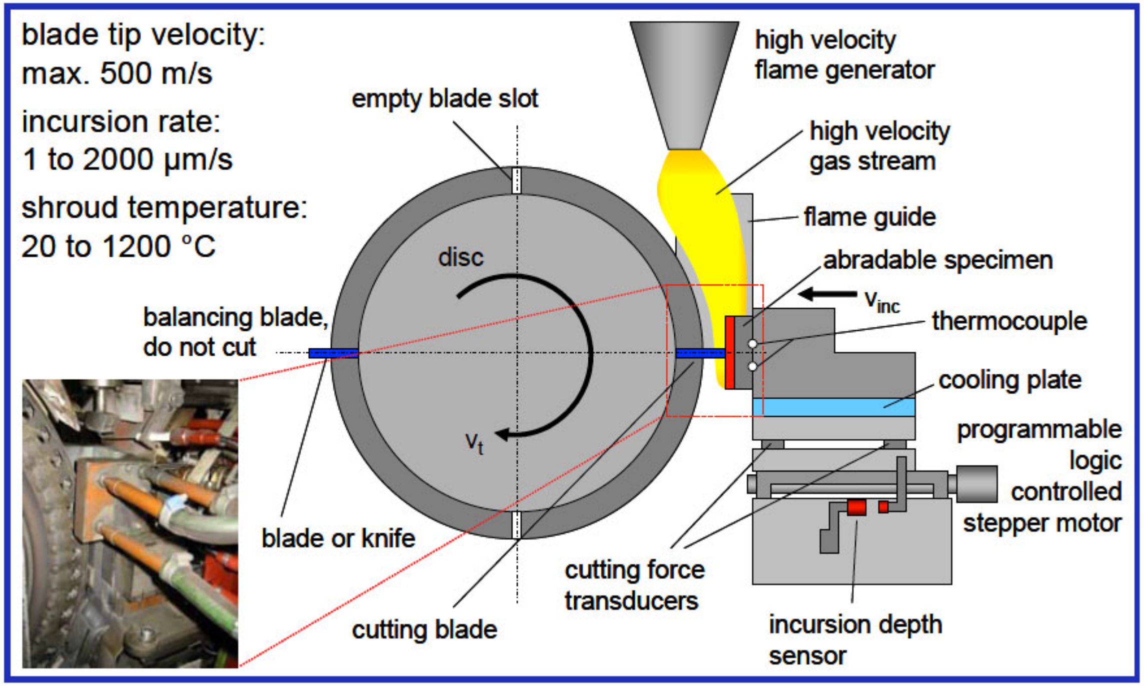




Wedge Impression Test

A. Rabiei, et al, Materials Science and Engineering A, 369 (1999) 152

Abradability Test Rig



Design features will be vetted with the OEMs and coating vendors with experience in carrying out such tests, to ensure that representative wear behavior and high temperature seal material behavior can be assessed

- Simulates the rubbing of blade tips against the coated casing as occurs during engine service.
- Stepper motor force the coated coupon into the moving rotor.
- Incursion rates can be accurately controlled.
- Abradability results are determined by measuring incursion depth of the blade into the coating, blade wear and abradable roughness.

D. Sporer, S. Wilson and M. Dorfman, “Ceramics for Abradable Shroud Seal Applications.” *Proceedings of the 33rd International Conference on Advanced Ceramics and Composites, volume 3, 2009,*

Summary and Key Developments and Conclusions

- Evaluated effects of elevated water vapor environments on TGO development for alumina-forming alloys. A strong correlation between pH_2O and *transient* spinel formation is observed. Furthermore, there is a strong dependence of TGO and spinel growth kinetics on pH_2O, but *volatilization effects counteract* these effects and complicate analysis of mechanisms.
- YSZ aging appears accelerated in higher pH_2O environments.
- CMAS degradation studies relevant to abradable coatings (hBN included) are underway.
- Mechanical and thermomechanical test approaches– for evaluation of abradable coating performance in relation to IGCC systems – are also under development
- **Use of IGCC combustion systems brings up additional issues in oxidation, corrosion volatilization and deposit-based degradation; the underlying mechanisms must be better understood in order to develop effective materials design strategies.**

Questions?