# Coating Issues in Coal-Derived Synthesis Gas/Hydrogen-Fired Turbines

B. A. Pint
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

Research sponsored by DOE, Office of Coal and Power R&D
Office of Fossil Energy (B. White, project monitor)

# Acknowledgments

I. G. Wright - architect of ORNL syngas project (2005)

Task leaders: J. A. Haynes - coatings (Y. Zhang, Tenn. Tech.)

K. Unocic - characterization (TEM, etc.)

K. Cooley - coating fabrication

G. Garner, M. Stephens - oxidation experiments

T. Lowe - characterization

D. W. Coffey - TEM specimen preparation, FIB

H. Longmire, T. Jordan - metallography

D. Leonard - EPMA

Ken Murphy, Howmet - X4 superalloy substrates

Jacqui Wahl, Cannon-Muskegon - CMSX7,X8 substrates

Anand Kulkarni, Siemens - 1483 superalloy substrates

Ben Nagaraj, GEAE - N515 alloy, EB-PVD YSZ deposition

S. Sampath, Stonybrook U. - HVOF,APS coatings

Research sponsored by: U. S. Department of Energy, Office of Coal and Power R&D, Office of Fossil Energy

# 12MWh/yr per U.S. resident

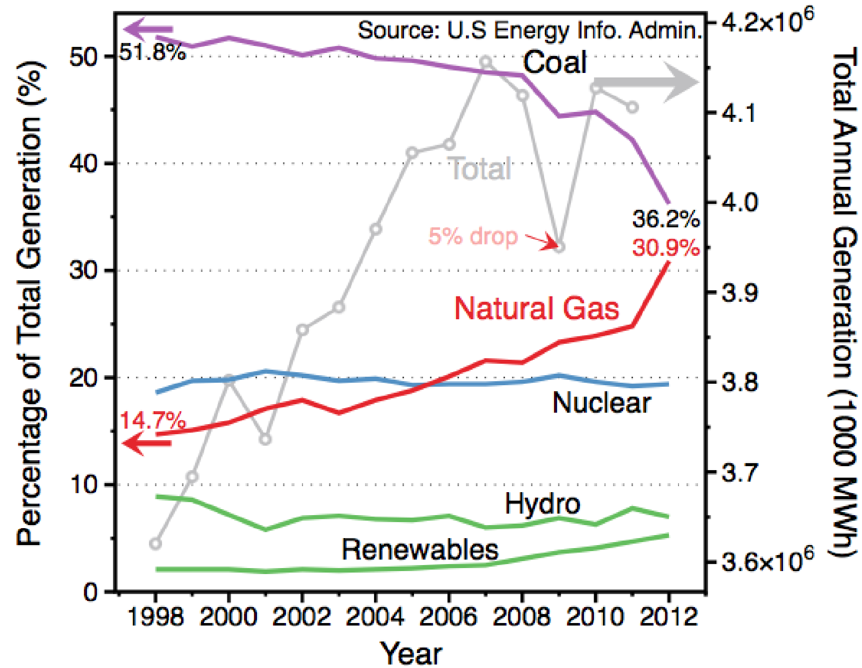
## From where?

## coal?

## how?

Integrated gasification combined cycle (IGCC):

- similar to NGCC
- control $NO_x$, $SO_x$, Hg...




Kemper County, MS (Southern Co.)

\$2.67 billion, ~60% $CO_2$ capture (oil recovery)

550MW, Siemens turbines, 2014 start

Edwardsport, IN (Duke Energy)

\$2.88 billion (Carbon capture ready)

618MW, GE Energy turbines, 2012 start

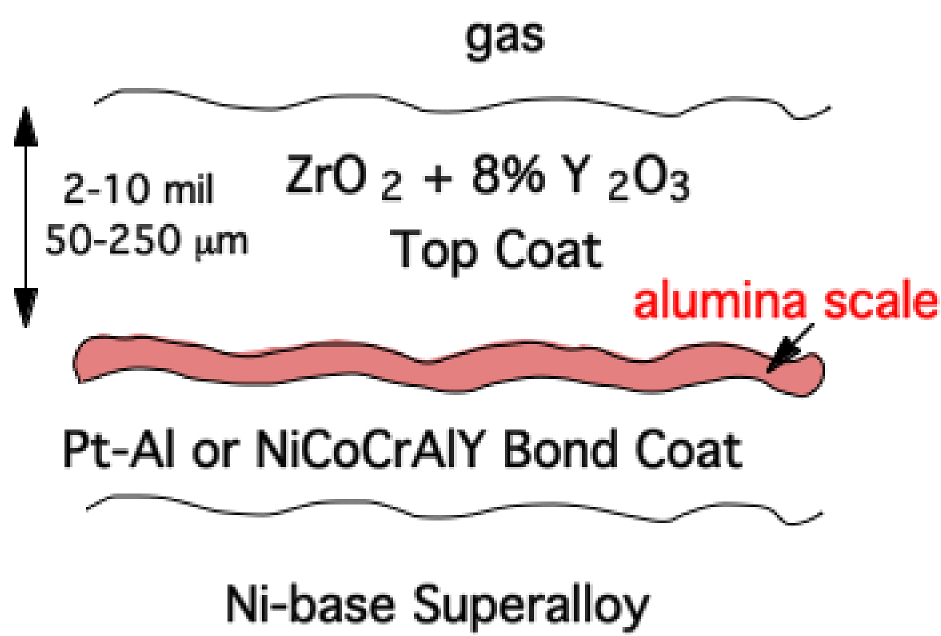
# De-rating of syngas turbines

Current project: more durable coatings
- coal-derived synthesis gas or syngas
- syngas turbines operating ~100°F(C?) less
- eliminating de-rating will improve efficiency

Reasons for de-rating*:
- higher water vapor content (fuel+diluent) (~10vol.%$H_2O$ for natural gas vs. 30-60%)
- higher S levels (imperfect syngas cleanup)
- increased deposits
- syngas lower caloric value: higher fuel/air 5-10X more fuel, magnifying impurities

*See Gibbons & Wright, "A review of materials for gas turbines firing syngas fuels," 2009 ORNL report & *International Journal of Hydrogen Energy* 32 (2007) 3610

# TBC requires “perfect” scale adhesion




Spallation of the scale has catastrophic effect (loss of YSZ)
scale is key to extending coating performance/reliability

Failure assumption:
- Many possibilities but when other problems corrected the “weak link” will be the metal-scale interface
- Thinner scale more “strain tolerant” – less strain energy

## Focus on alumina scale growth and adhesion

# Outline

FY10 (initiated 3 related "pre-competitive" tasks)

- Task 1: water vapor effects
- Task 2: superalloy dopant effects
- Task 3: characterization

FY12

- Task 1: repeating results from first 2 groups
  - Two issues: Dry vs. Wet and Wet vs. Wetter
- Task 2: Completed, no significant benefit in X4
- Task 3: dopant & $H_2O$ effects on alumina scale
- Task 4: New compositions and processes
  - model bond coating (NiCrAlX) alloys
  - low Re superalloys

FY13

- Future directions

# Recent Presentations

8th Int. Charles Parsons Conf. (Sept. 2011, UK)

- Effect of water vapor content on TBC lifetime

(publication in *Materials Science and Technology*)

ICMCTF (April 2012, San Diego)

- Effect of Water Vapor on the 1100°C Oxidation Behavior of Plasma-Sprayed TBC's with HVOF NiCoCrAlX Coatings
- Effect of Water Vapor on Thermally Grown Alumina Scales on Bond Coatings

(publication in *Surface & Coatings Technology*, Dec. 2012)

*Advanced Materials and Processing* (May 2012 issue)

- Effect of water vapor content on TBC lifetime

Microscopy & Microanalysis (August 2012, AZ)

- Microstructure and Chemistry of the Oxide Scale and Pt-containing Coatings Deposited on Superalloy N5

Superalloys 2012 (Sept. 2012, PA)

- The Effect of Water Vapor and Superalloy Composition on Thermal Barrier Coating Lifetime (Proceedings)

# Several TBC groups investigated

## (3 YSZ samples per condition + 1 without YSZ)

| Group | Alloy | Bond coating | Top coating | Comment |
|---|---|---|---|---|
| 1 | N5 | Diffusion $\beta/\gamma+\gamma'$ | EB-PVD | "quick start" |
| 2 | X4±RE | HVOF Y±Hf | APS | RE/$H_2O$ effect |
| 3 | N5/N515 | Diffusion $\beta/\gamma+\gamma'$ | EB-PVD | repeat/low Re |
| 4* | 1483/X4 | HVOF YHf | APS | rougher,1483 |

* 5 YSZ samples per condition + 1 without YSZ

HVOF: High velocity oxygen fuel (plasma spraying)
EB-PVD: electron-beam physical vapor deposition
APS: Air plasma spraying
N5 - GE SX (single crystal) ~3 wt.%Re; N515 - 1.5%Re
X4/1483 - Siemens recommended

# Does water vapor explain de-rating?

## Motivation for Task 1 on water vapor:

- Experiments done in dry $O_2$ or air - convenience
- All turbines contain some $H_2O$
  - Natural gas - 10-15 vol.%
  - Syn. gas - ~30%
  - Hydrogen - ~60%
    - higher levels with diluent
- Recent literature discussion on $H_2O$ effect on TBC
  - Anomaly of testing without $H_2O$
  - Negative effect on lifetime when $H_2O$ added
  - Syngas-firing question:

What is difference in TBC lifetime when $H_2O$ increased from 10% to 30%-50%?

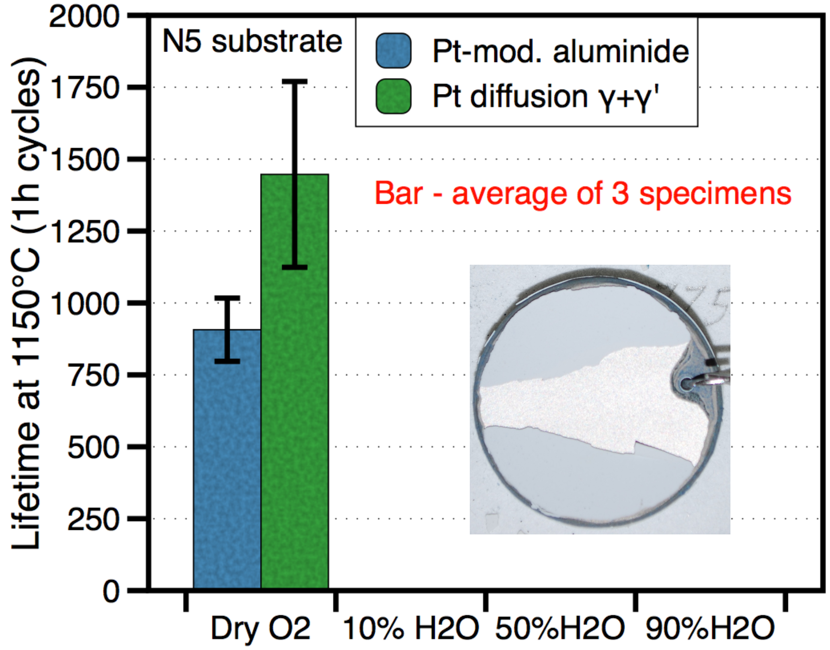
(not dry vs. wet, but wet vs. wetter)

# Well controlled coating procedures

16mm disks: single crystal substrates (all at.%):

N5: 13.3Al,8Co,8Cr,0.9Re,70Y-17S-540Hf-132Zr

X4: 13.0Al,10Co,8Cr,0.9Re,1.2Ti,17S-270Hf




$ZrO_2$-$Y_2O_3$ coated (1 side)

1. N5, Pt diffusion/EB-PVD

β: CVD at ORNL (7μm Pt)

γ-γ': 7μm Pt, 2h, 1175°C

2. X4, HVOF/APS

MCrAlY & MCrAlYHfSi:

41Ni,18C0,16Cr,23Al,0.4Y

or 0.4Y, 0.07Hf, 0.65Si

Oxidation testing: 1h cycles (10min cooling)

1150°C or 1100°C: dry $O_2$, air + (10,50,90%) $H_2O$

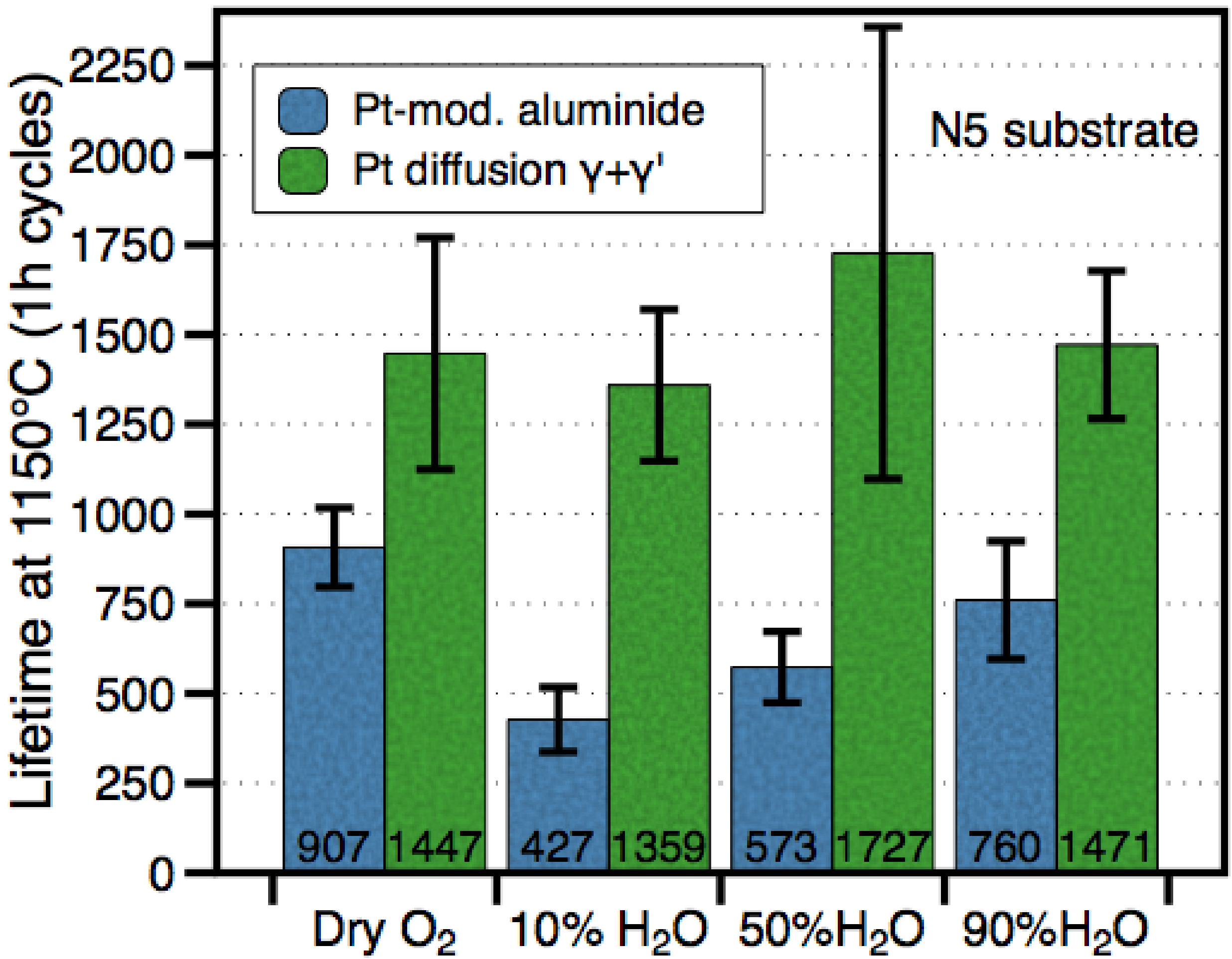
Characterization: Laser & optical profilometry ($R_q$)

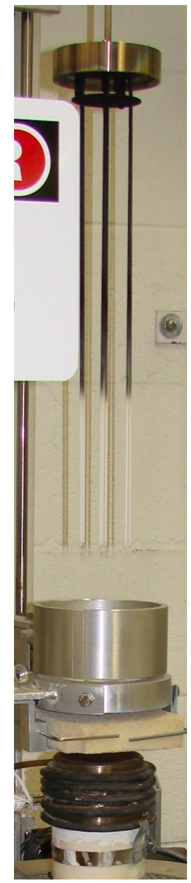
Metallographic cross-sections, EPMA, PSLS...

# TBC Group 1: more effect on β life

1h cycles, 1150°C, air with 10-90 vol.% $H_2O$

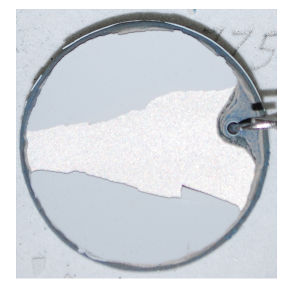
1150°C, 2102°F



lid

alumina rods (7)



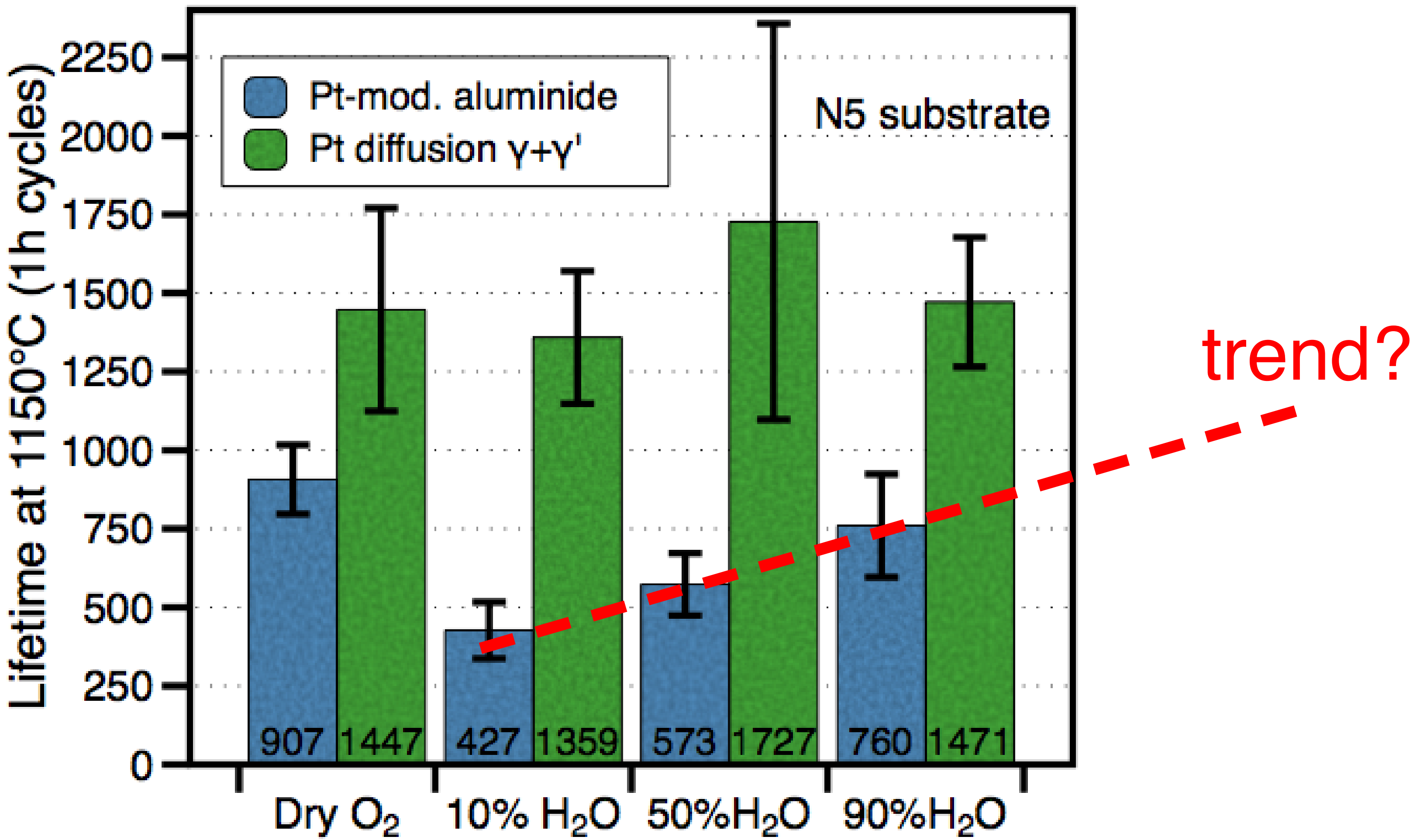
vertical tube

β-NiAl bond coating: >50% decrease with 10%$H_2O$

γ-γ' Pt diffusion: no statistical change in life

# Higher $H_2O$: not what I expected

1h cycles, 1150°C, air with 10-90 vol.% $H_2O$



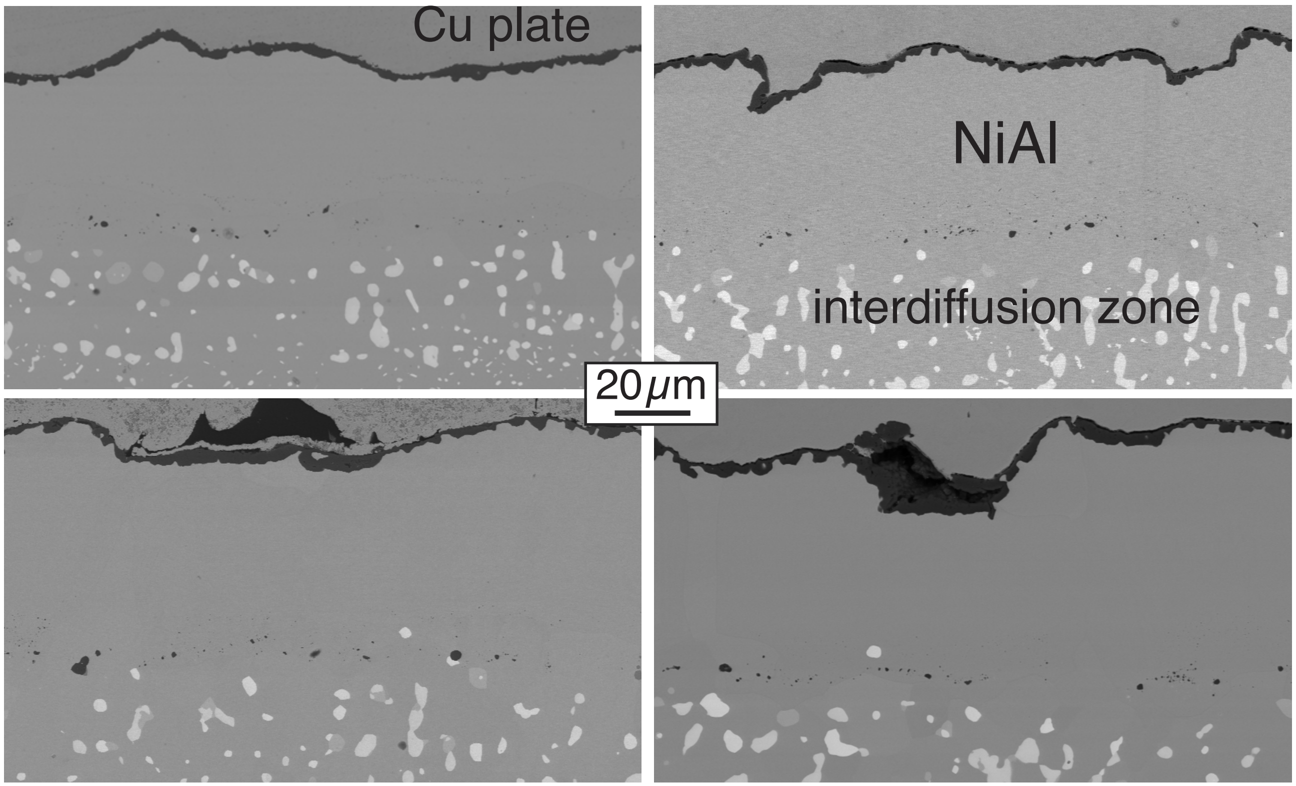

β-NiAl bond coating: expected more $H_2O$ resistance

γ-γ' Pt diffusion: lower Al, expected $H_2O$ problem

# β coatings have non-uniform scale

## Backscattered SEM, 1-h cycles at 1150°C

dry $O_2$, 900h  10%$H_2O$, 400h




50%$H_2O$, 900h  90%$H_2O$, 800h

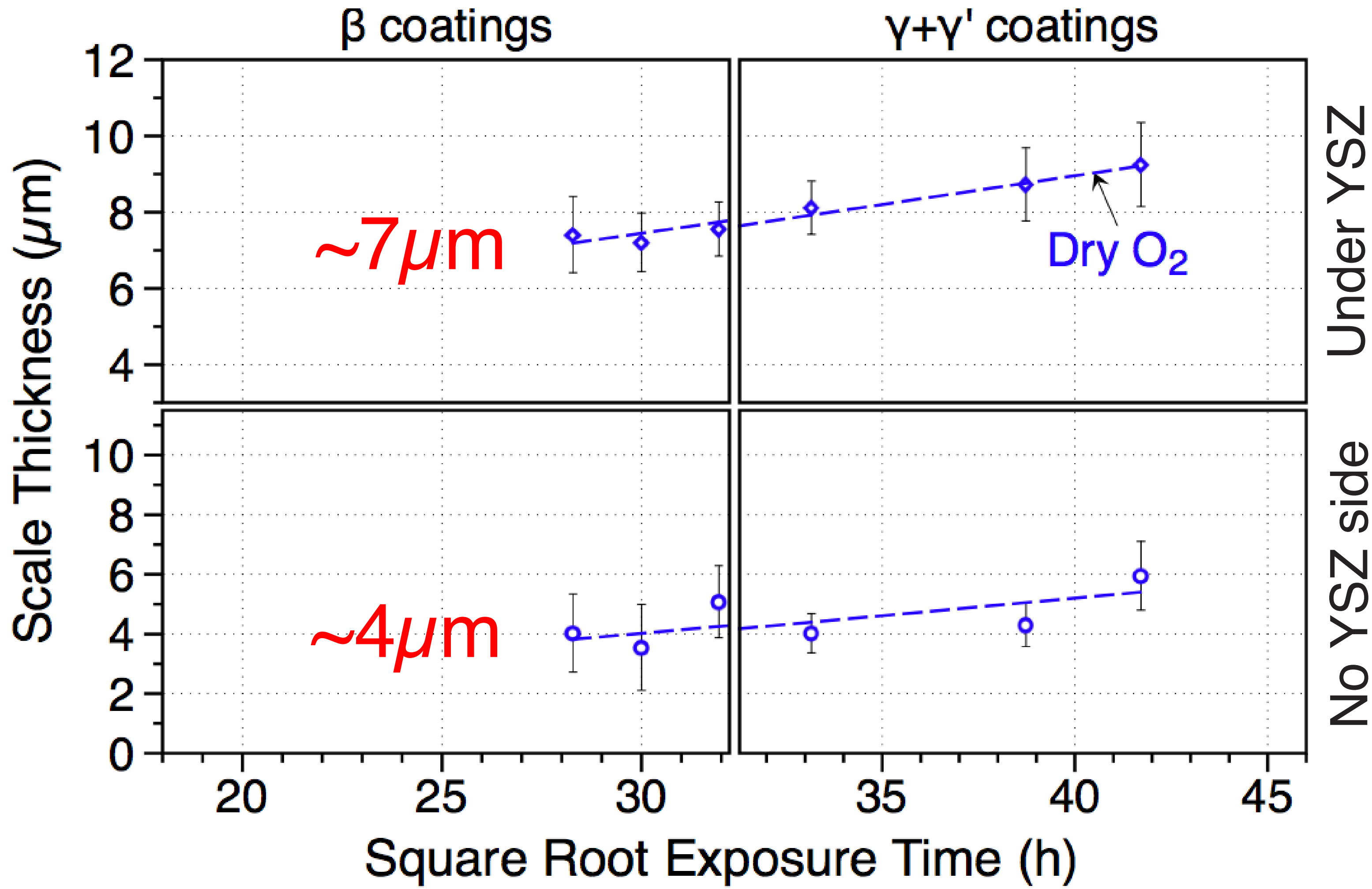
Images from: 4th specimen in each group without YSZ

Difficult to assess thickness/roughness differences

More quantitative method needed to compare

# Thicker oxide beneath YSZ

## Average of 40 measurements from SEM images

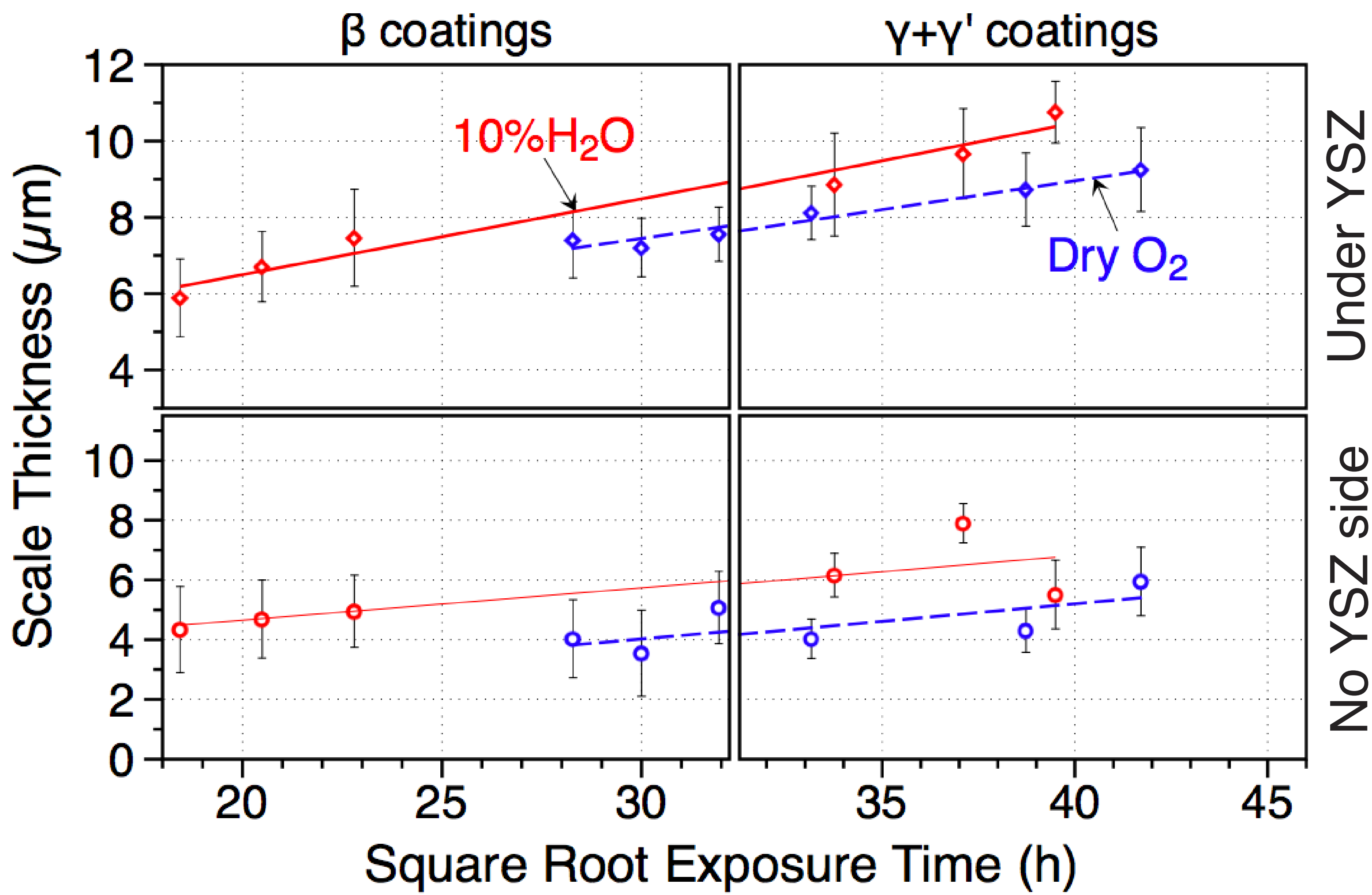



Failed TBC specimens plotted versus exposure time

Standard deviation shown

# Thicker oxide with 10% $H_2O$

## Average of 40 measurements from SEM images

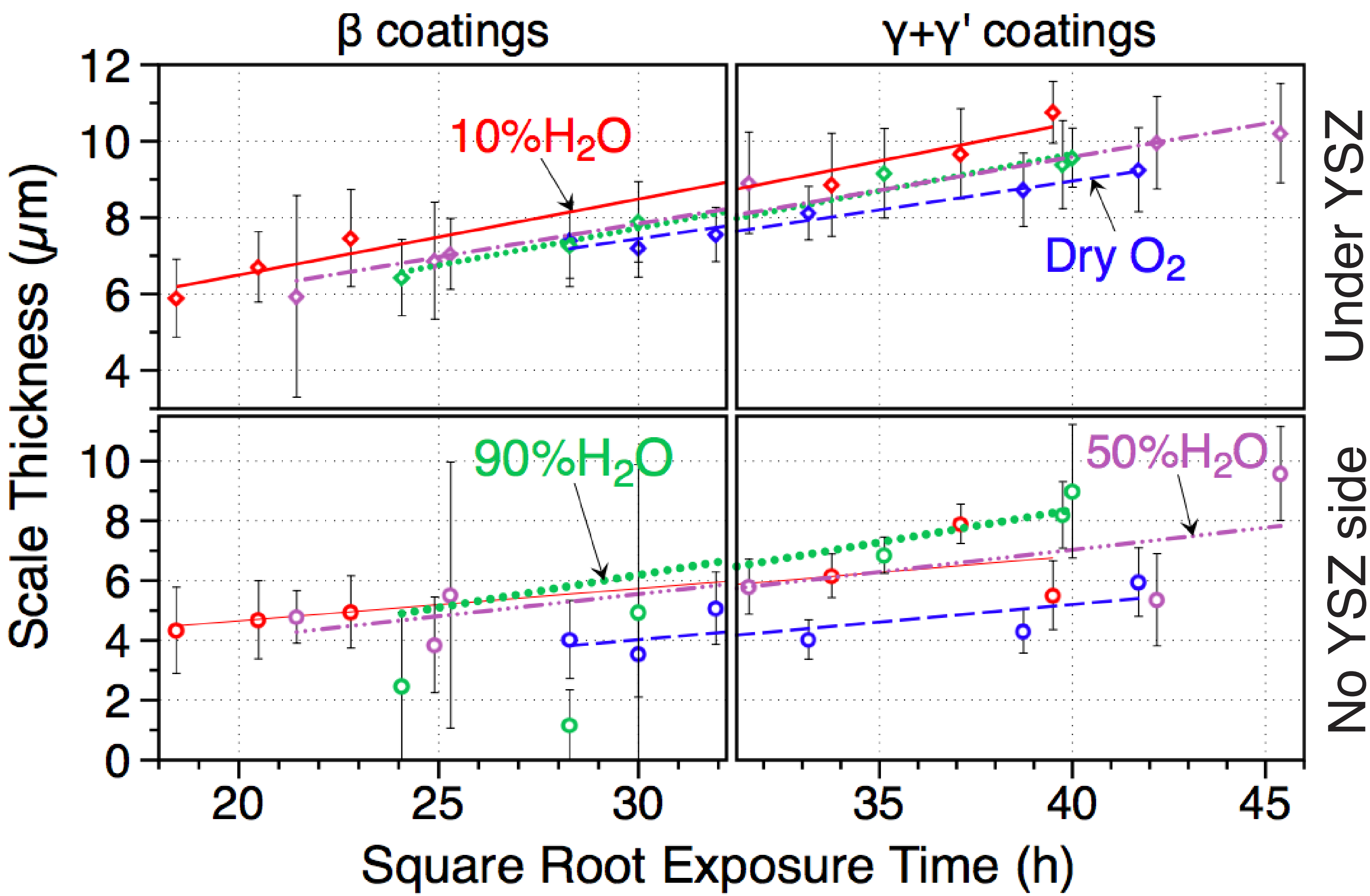



Similar thicker oxide formed with and without YSZ

Rate similar in both cases

# Higher $H_2O$ - no further trend

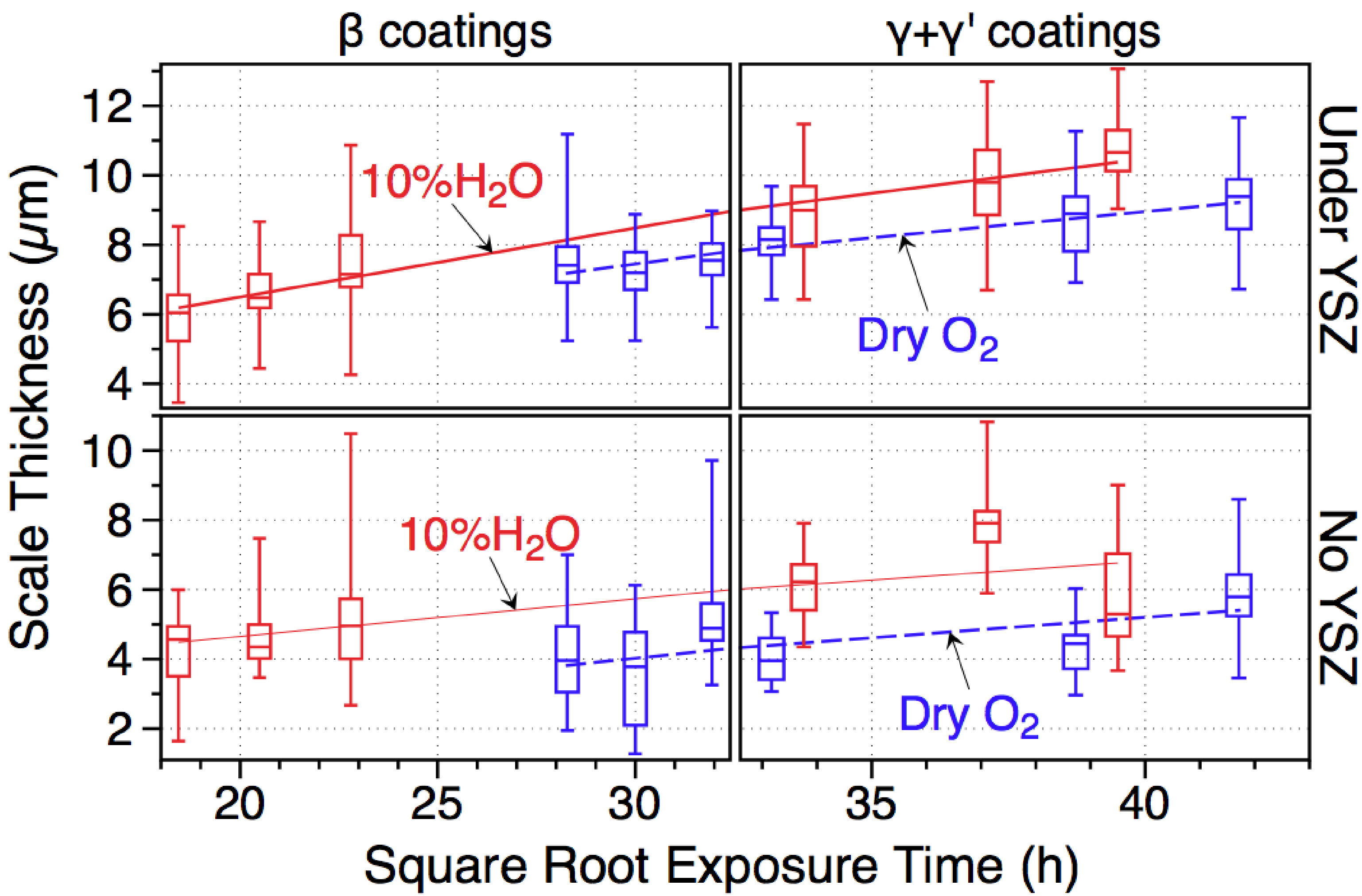
## Average of 40 measurements from SEM images




Oxide not thicker with higher water vapor content

# Box plots better represent data

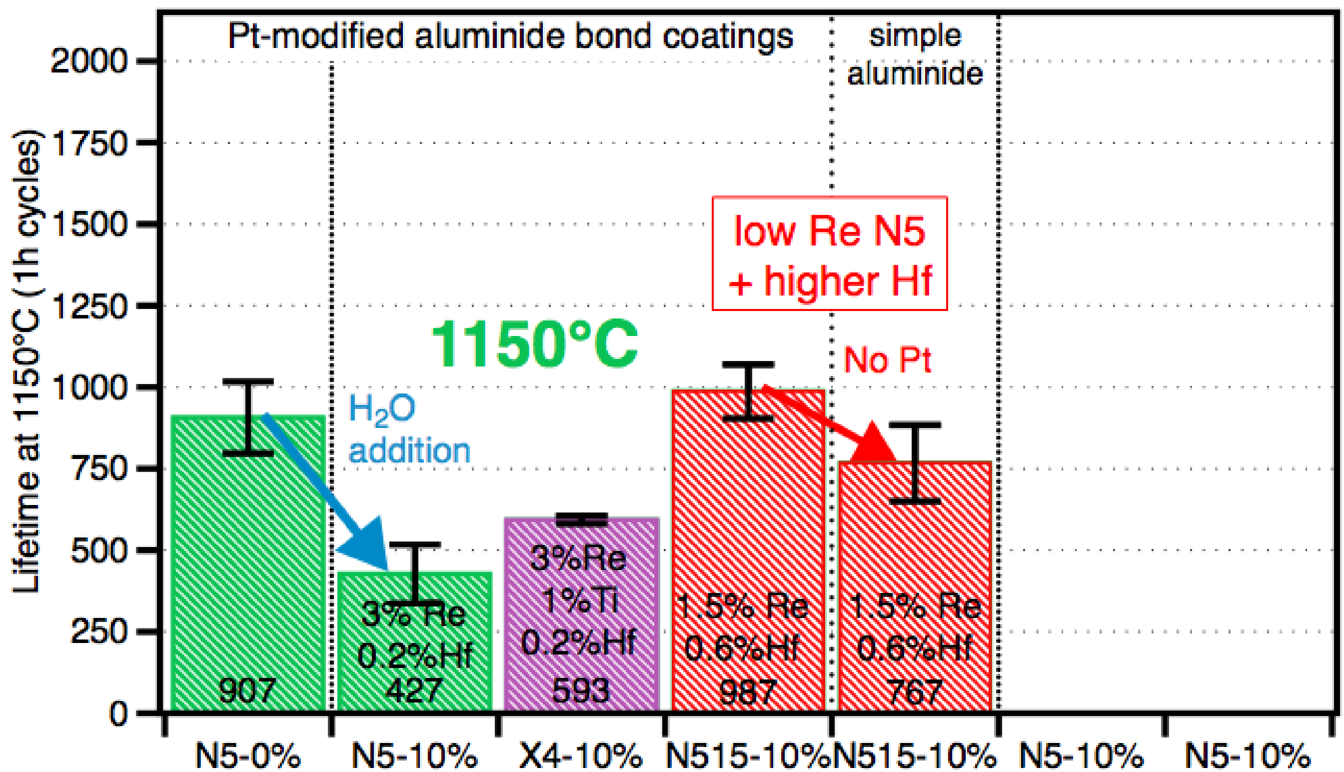
## Box of same 40 measurements from SEM images




Not much statistical difference between two cases

# TBC Group 3: in depth repeat

## 1h cycles, 1150°C, air with 0 & 10 vol.% $H_2O$

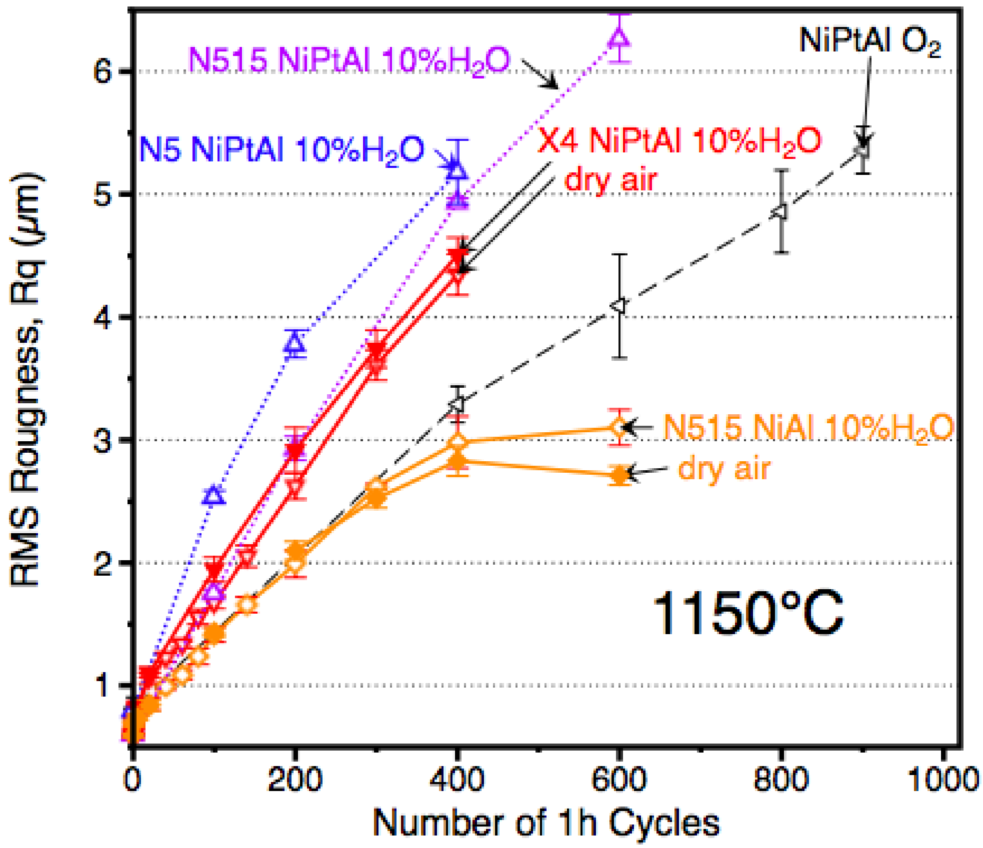



New: Superalloy composition (X4 1%Ti, N515)

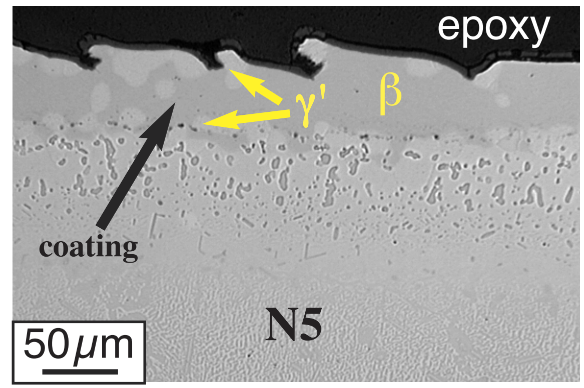
- similar lifetime with X4 substrate, no Ti debit
- higher Hf (2000 ppma) in N515 increased lifetime
- observed higher life with and without Pt

# New data: no $H_2O$ roughness effect

## β coating: 4th (no YSZ) specimen cut in half




1150°C, 2102°F




10%$H_2O$: 340 cycles

bars: standard deviation of 6 lines or 5 areas

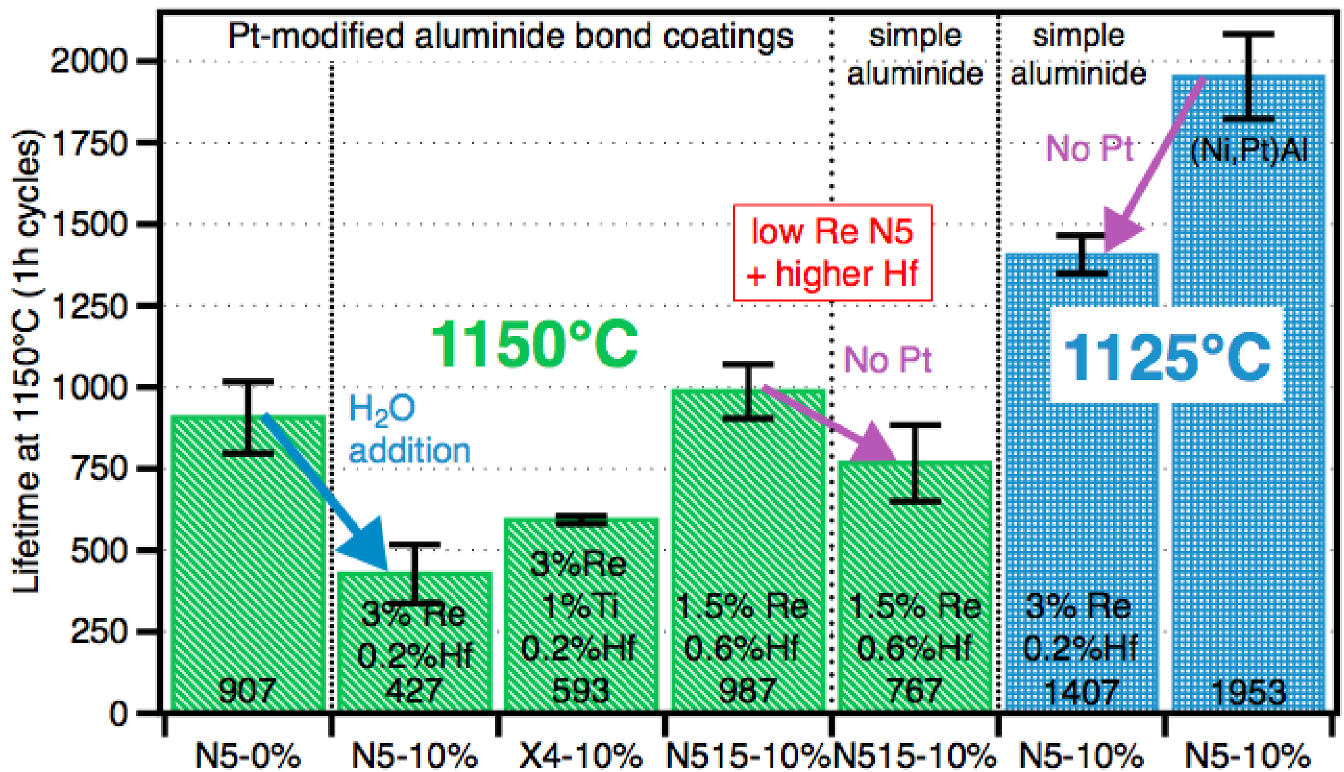
Previously: Observed large difference with $H_2O$ for β

- Specimens from different batches, test in 2 rigs
- No mechanistic reason for such an effect

Both X4 (NiPtAl) and N515 (NiAl) showed little effect

# Effect of lower temperature

## 1h cycles, 1125°C, air with 10 vol.% $H_2O$

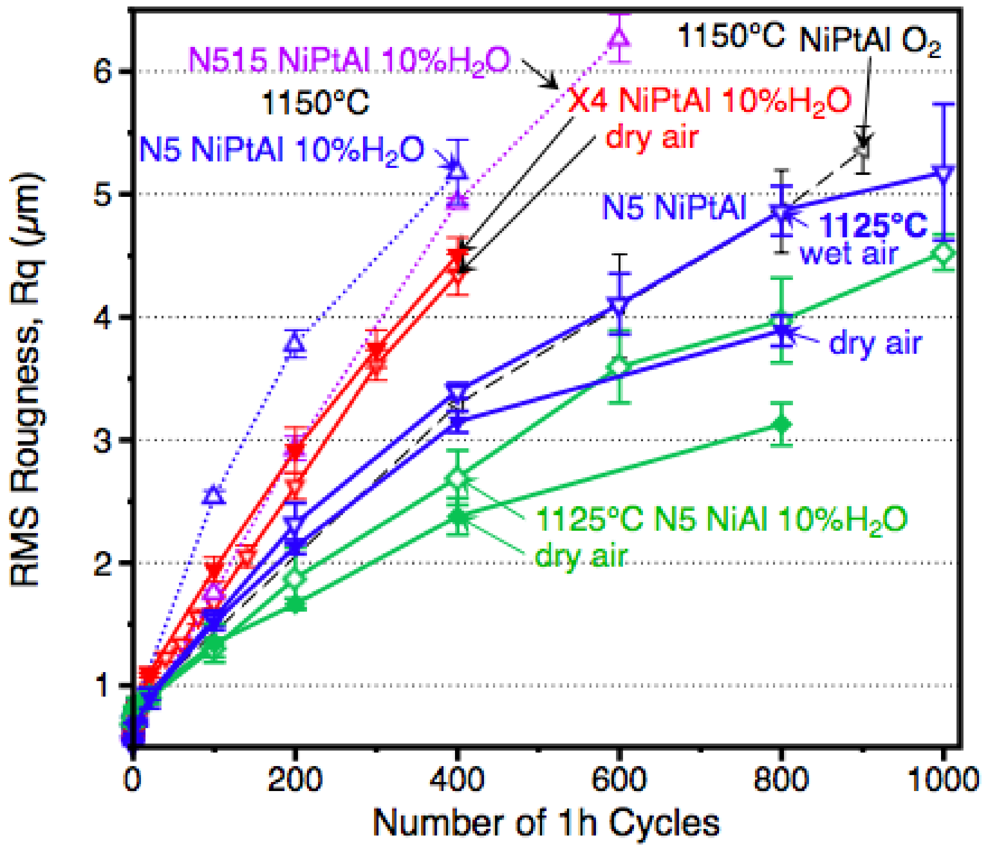



1125°C: reduced temperature to lower rumpling

- 4.5X higher life than 1150°C
- Pt increased life by 40%

# 1125°C: did not eliminate rumpling

## 4th (no YSZ) specimen cut in half (in progress)

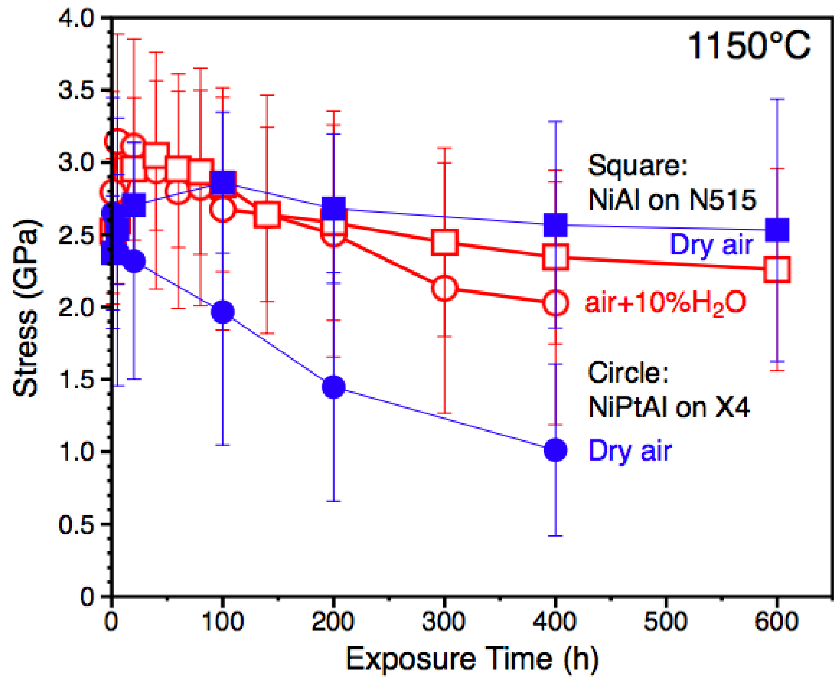



Specimens stopped after 1000 cycles (TBC 1400-1950h)

- similar roughness for NiAl and NiPtAl on N5
- somewhat lower roughness in dry air vs. wet air

# Group 3: stress measurements too

## Residual stress in alumina by PSLS




NiAl on N515 (low Re)

NiPtAl on X4

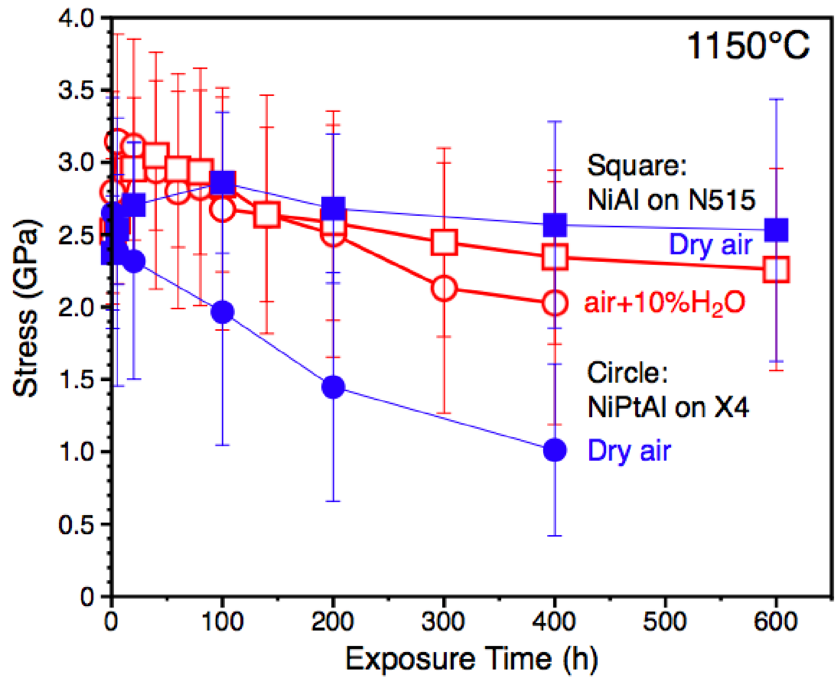
Same specimen used for roughness (no YSZ, cut in half)

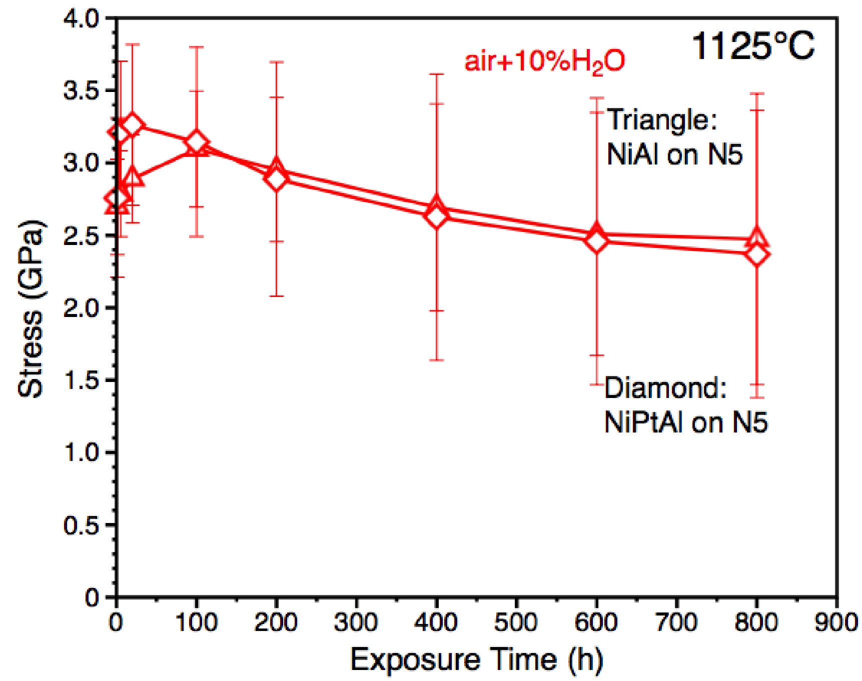
1150°C - NiAl on N515 (high Hf): little $H_2O$ effect

- NiPtAl on X4: lower stress in dry air

# 1125°C: no effect of Pt on stress

## In progress: alumina residual stress by PSLS



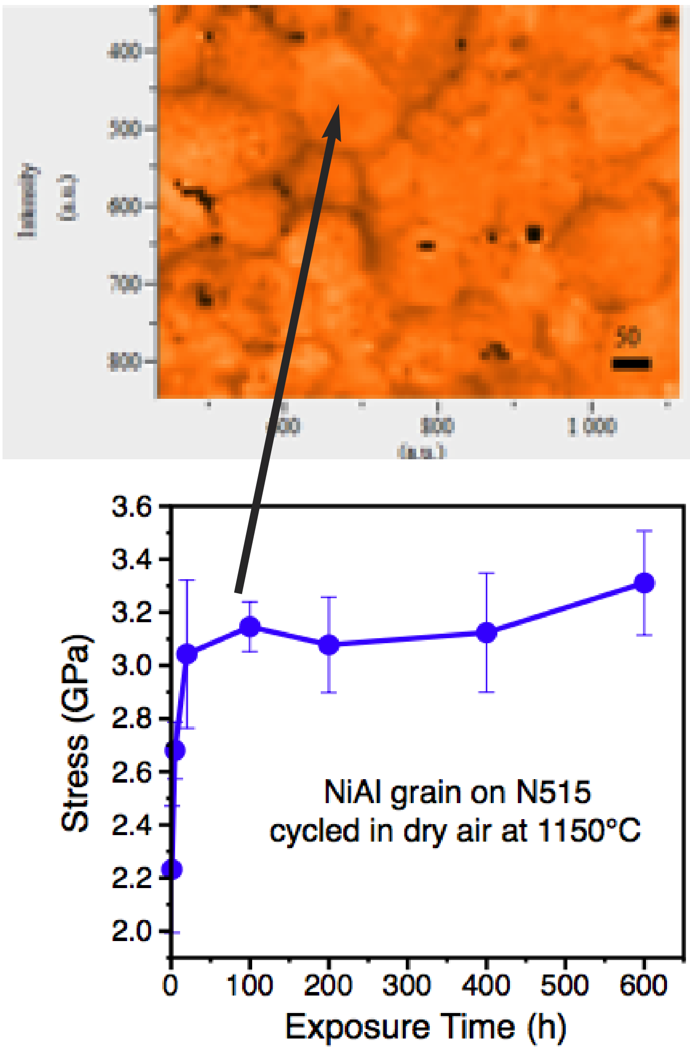

Same specimen used for roughness (no YSZ, cut in half)

- 1125°C - N5 with NiAl/NiPtAl: same stress
- Data still being crunched for 1125°C dry air exposure

# Next gen. stress measurements

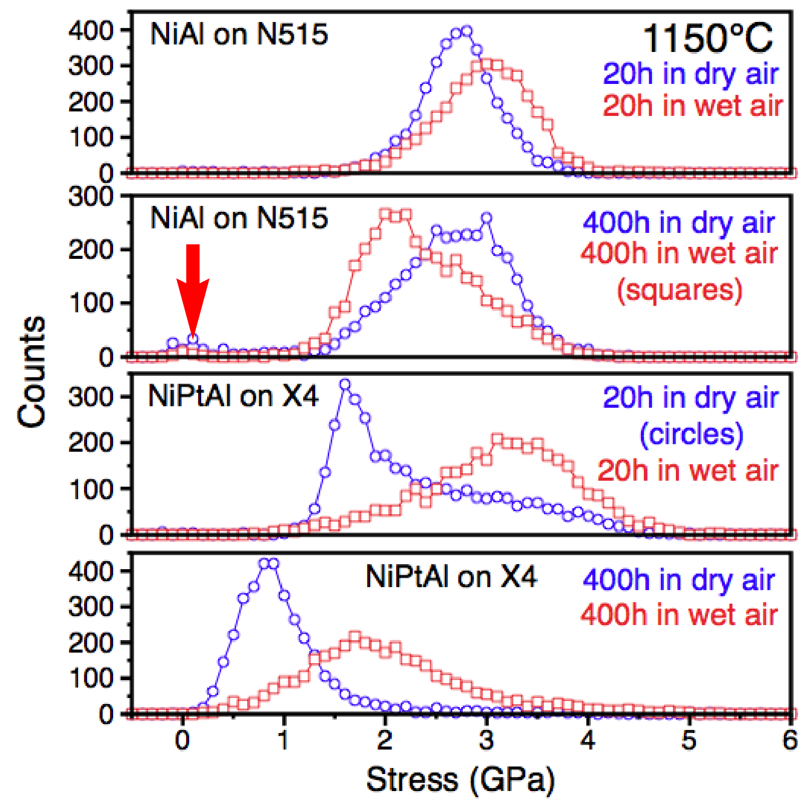
## PSLS measurement as a function of location

NiAl on N515 after 5h at 1150°C in dry air



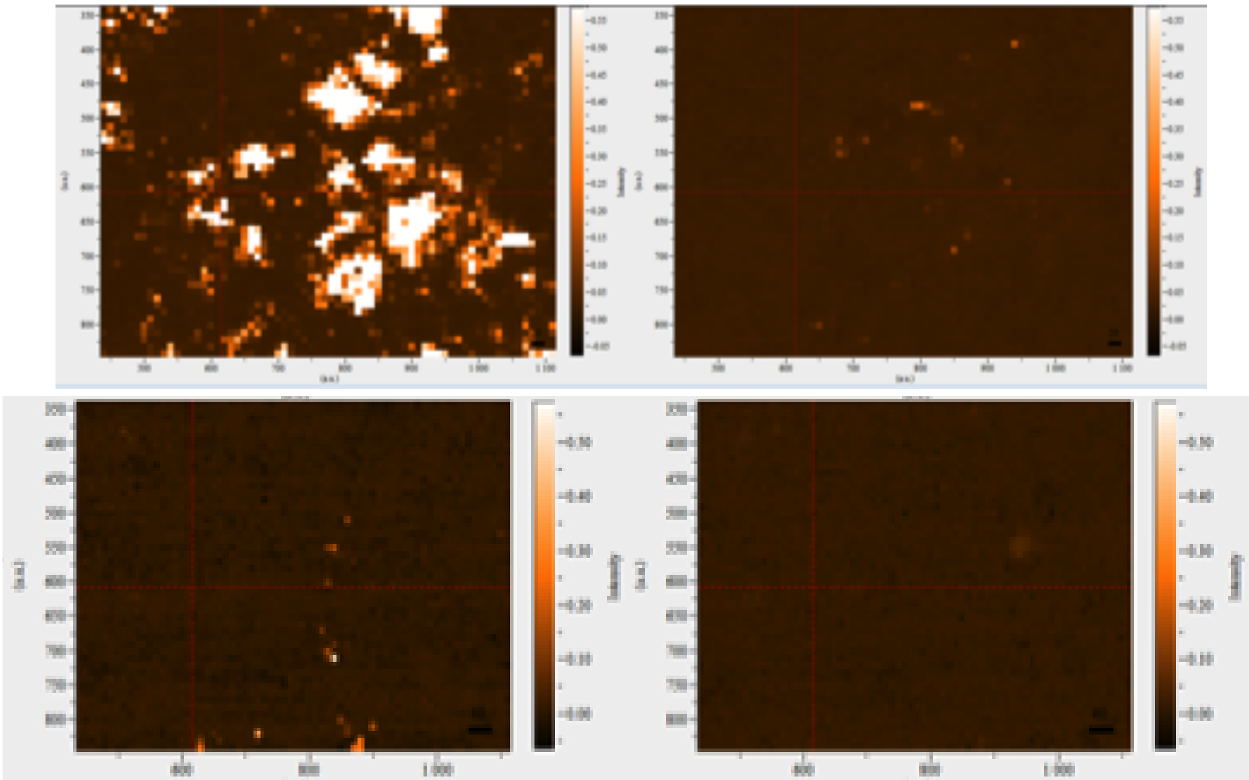

stress in single grain

wet vs. dry air histograms



# PSLS identified alumina phase

Theta map: 1h 5h

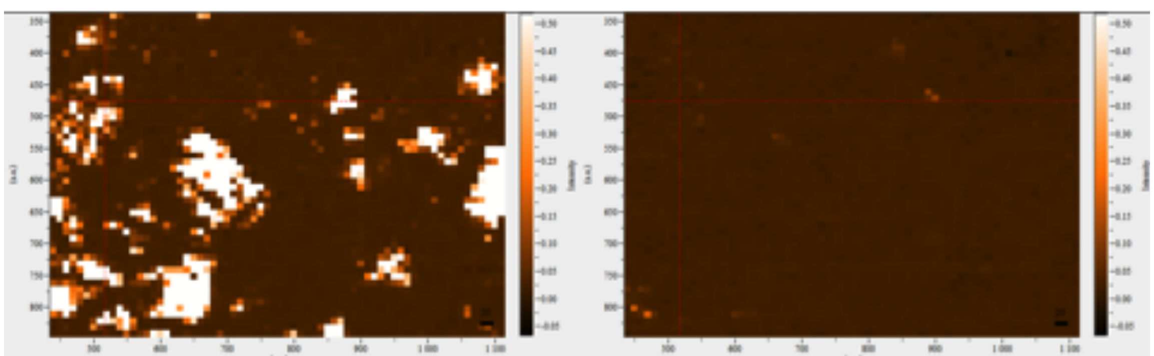


1150°C wet air

X4 NiPtAl

1150°C dry air

## Water vapor stabilized faster growing $\theta$-$Al_2O_3$

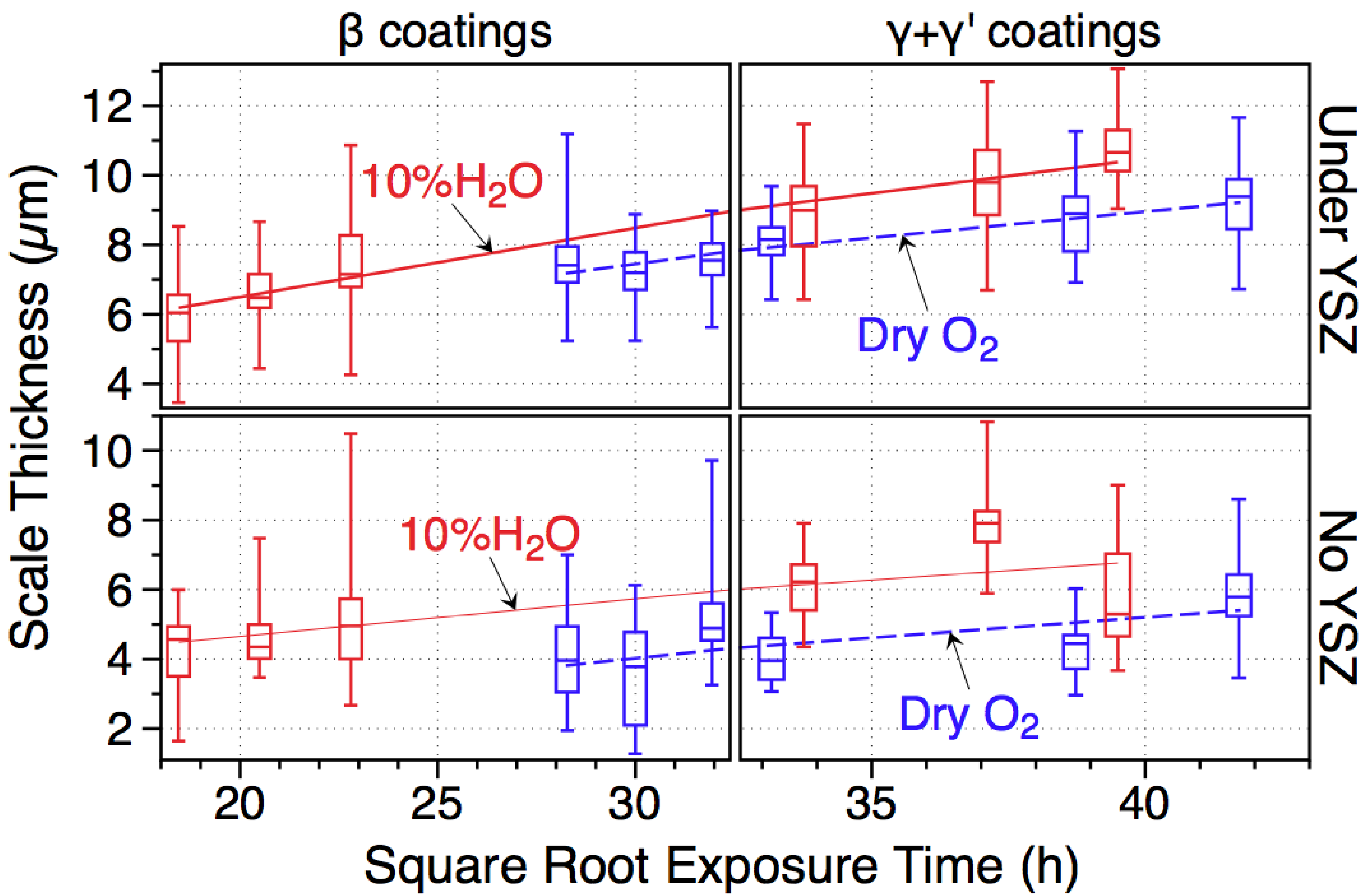


N5 NiPtAl

1125°C wet air

# Initial θ-$Al_2O_3$ explains thickness

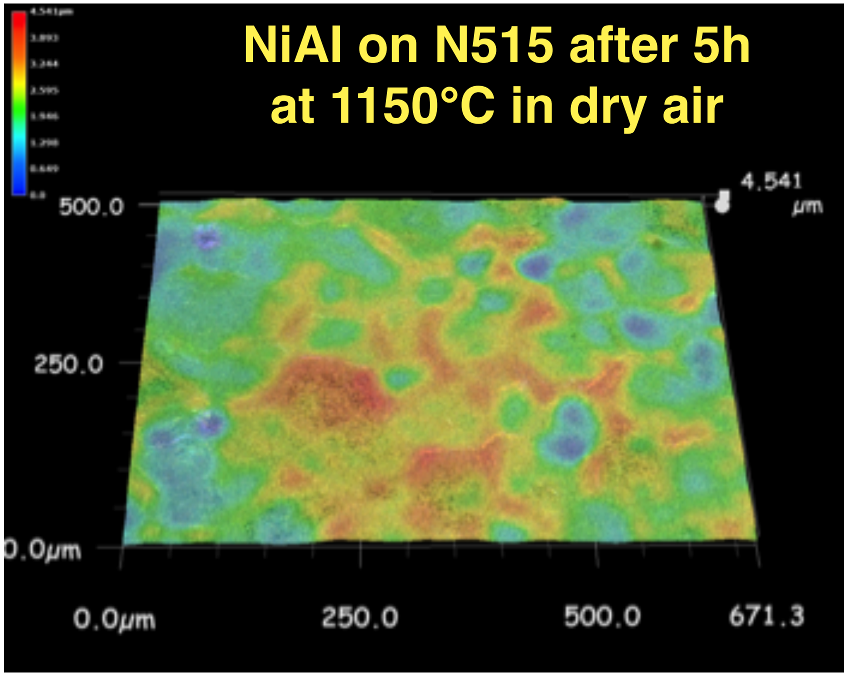
## Alumina thickness measured from SEM images



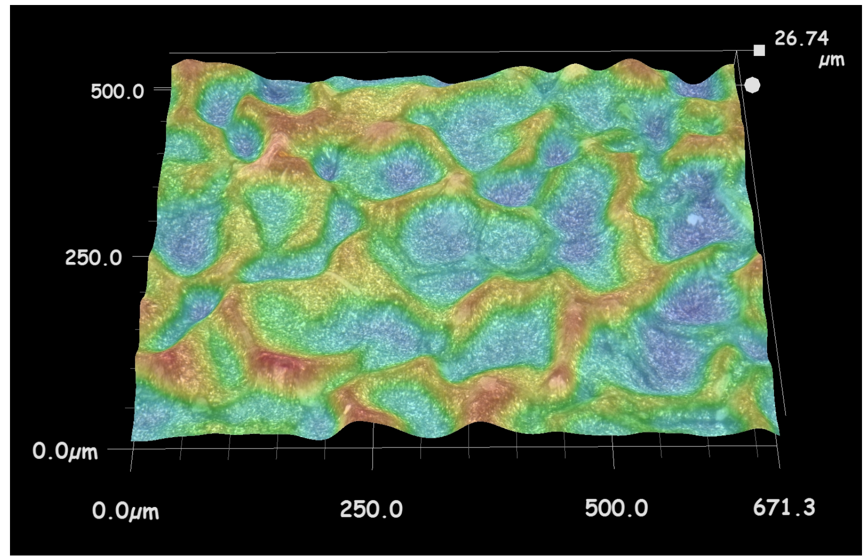

Increase due to initial faster-growing θ-$Al_2O_3$ formation

# 3D microscopy links stress/location

## Keyence examined same location as PSLS




NiPtAl on N5 after 400h
at 1150°C in wet air



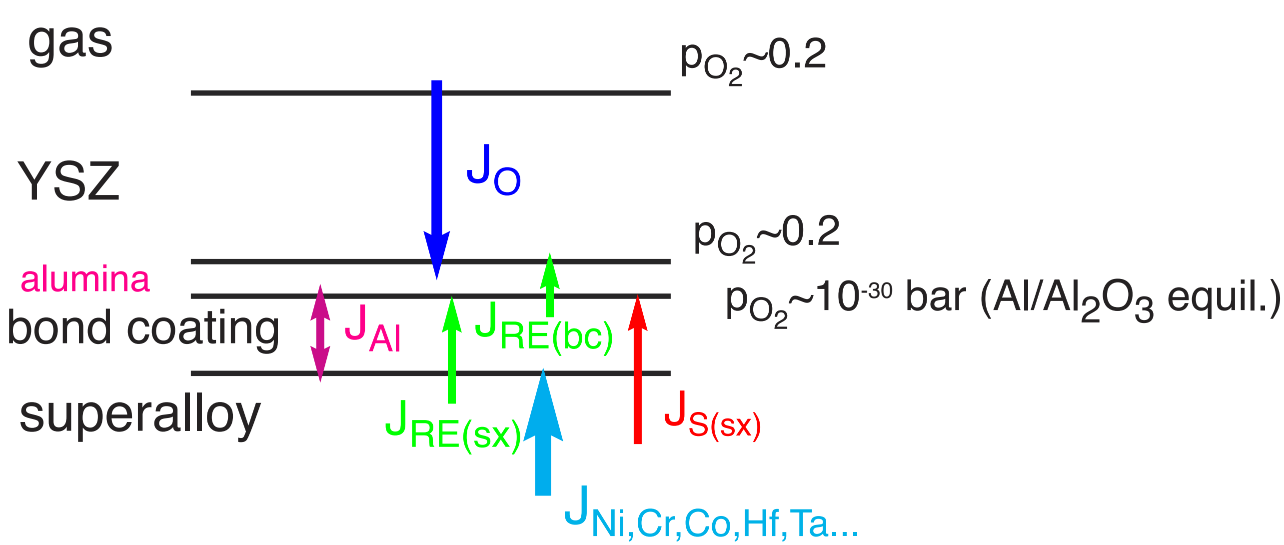

- Can link stress and deformation as a function of time
- Similar analysis done for wet and dry air
- Supports hypothesis that coating grain size affects rumpling (Dryepondt): small grains “shrink and sink”
- Last step: microstructure at key locations (FIB)

# Are doped superalloys a solution?

## Motivation for Task 2 on doped superalloys:

Difficult to develop/commercialize new alloy/coating
- is there a solution available?

Cannon-Muskegon has commercial CMSX4+Y,La
- reported to increase TBC lifetime by 2-3X
- little independent verification
- little mechanistic understanding
- Proposed Impurity flux mechanism for S,RE:



# Three alloys & one coating examined

CMSX4: 6-7at.%Cr-9-13Al-1Re-10Co-2W-2Ta-1Ti

Baseline:

X4: 13.0Al-270Hf-17S

disks: 16 x 2mm thick

1Y (ppma) 2Y
2La 3La

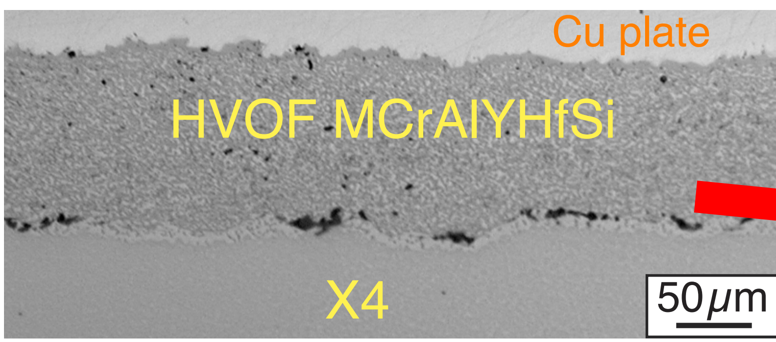
X4-1: 12.8Al-340Hf-<1S

X4-2: 12.8Al-270Hf-<1S

10Y (ppma) 14Y
6La 9La

MCrAlYHfSi (PWA286) by high-velocity oxygen-fuel

41at.%Ni-18.4Co-16.2Cr-22.9Al-0.39Y-0.07Hf-0.65Si



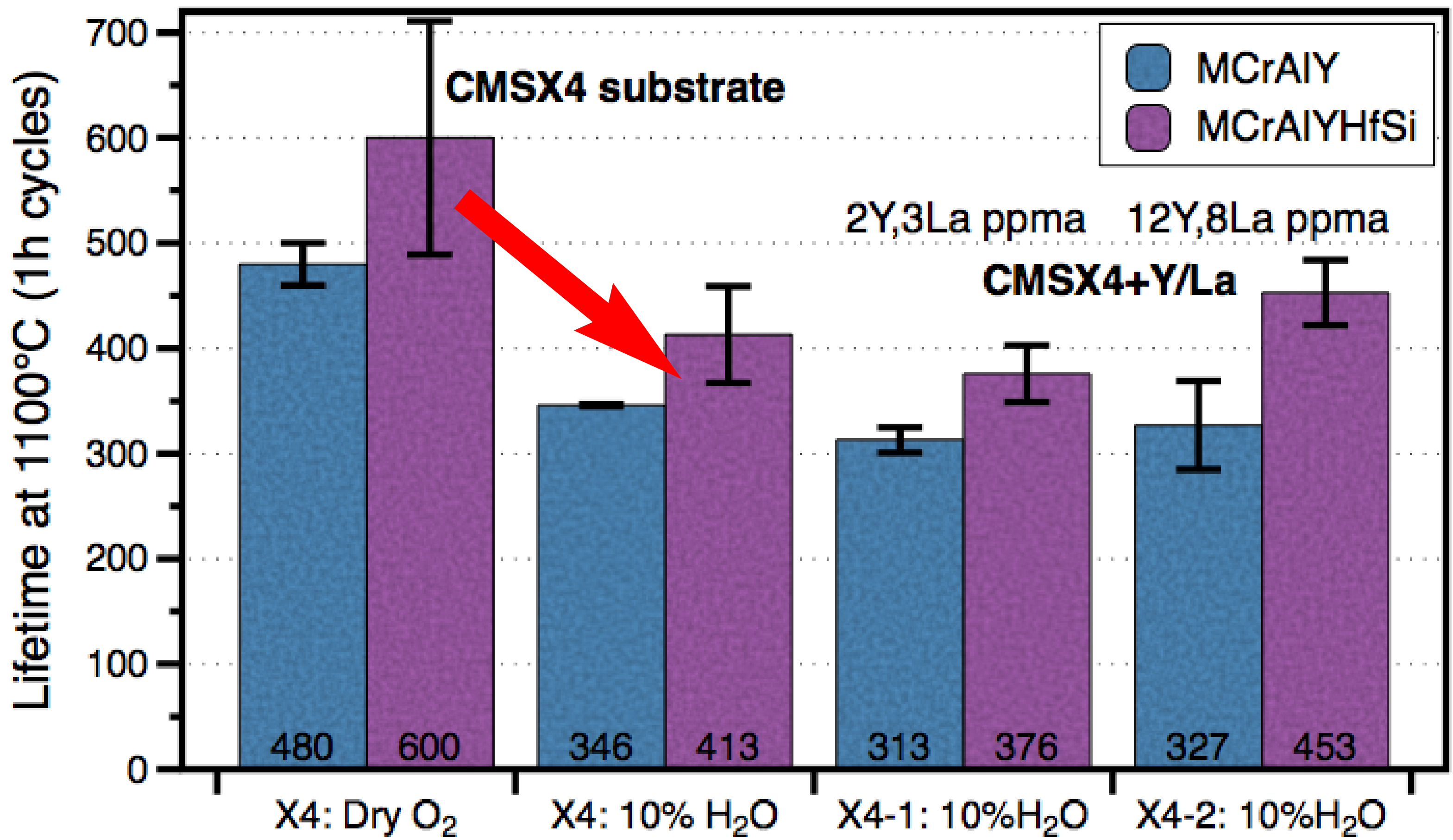

HVOF: Stonybrook Univ.
ORNL: vacuum anneal 4h/1080°C

<u>1h cycles:</u>
1100°C
flowing, dry $O_2$ or air + 10, 50% $H_2O$

<u>100h cycles:</u>
1100°, air+10% $H_2O$

# Group 2: no Y/La benefit in X4

## Two bond coatings on CMSX4 + APS YSZ



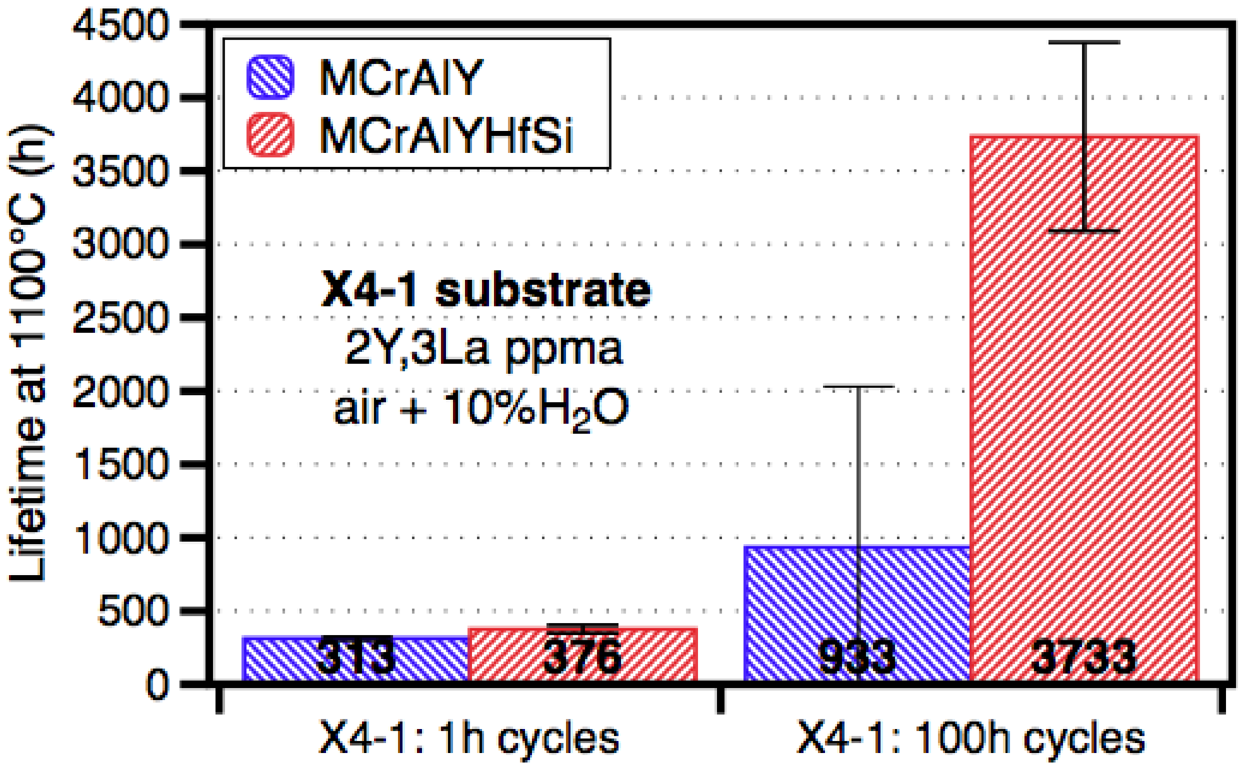

30% drop in lifetime in 10% $H_2O$ for both bond coats

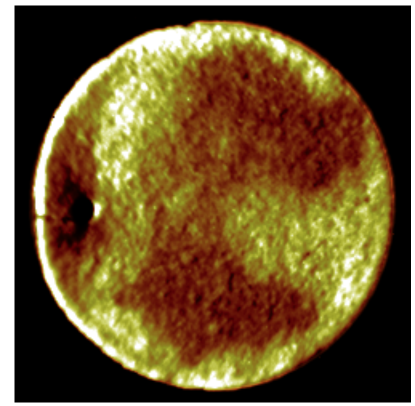
No increase in lifetime with Y/La addition to CMSX4

# 100h cycles increased lifetime

## 1100°C: two bond coatings on X4-1 + APS YSZ

FY12 Milestone



bright areas delaminated in thermal flash at 42 cycles

Cycle more representative of land-based turbine

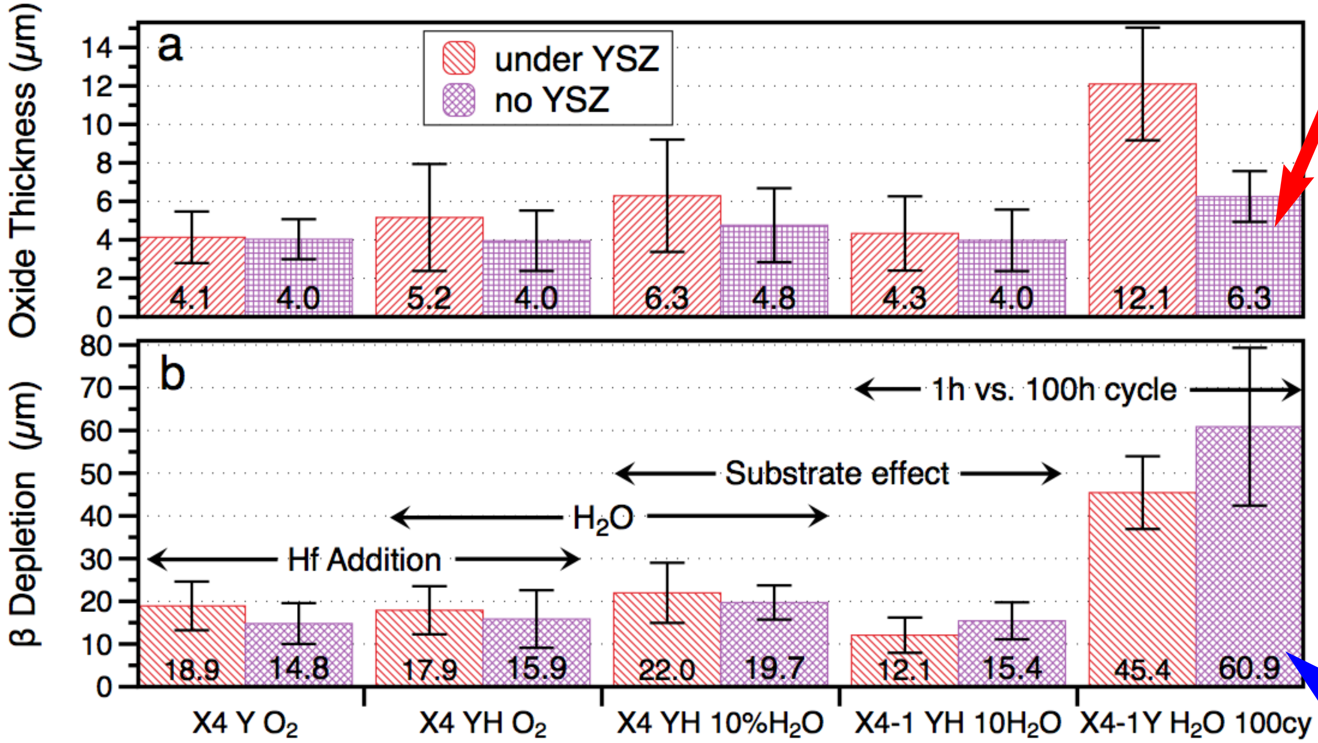
100h cycles in tube furnace with slow heat/cool

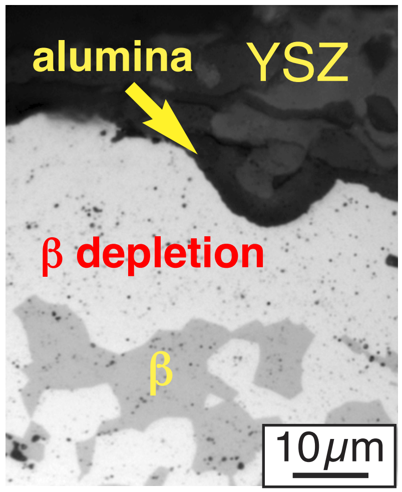
Results support 1h accelerated testing

# HVOF characterization: few trends

## Interdiffusion and oxide thickness on both sides

FY12 Milestone




MCrAlY coating

- Subset of large number of HVOF specimens
- Since many specimens fell within scatter, not all specimens were examined

## Conclude doped superalloy task:

- No evidence of Y/La benefit in these tests
- Y+Hf bond coat more effective benefit
  Increased lifetime compared to MCrAlY
- Perhaps, Y+La benefit clearer with higher S
  Low S superalloys are now more common
  Also, Howmet X4 contained higher Hf, which may overshadow Y and La effects
  Expect more effect with diffusion coatings

# Characterization helps understanding

## Motivation for Task 3 characterization:

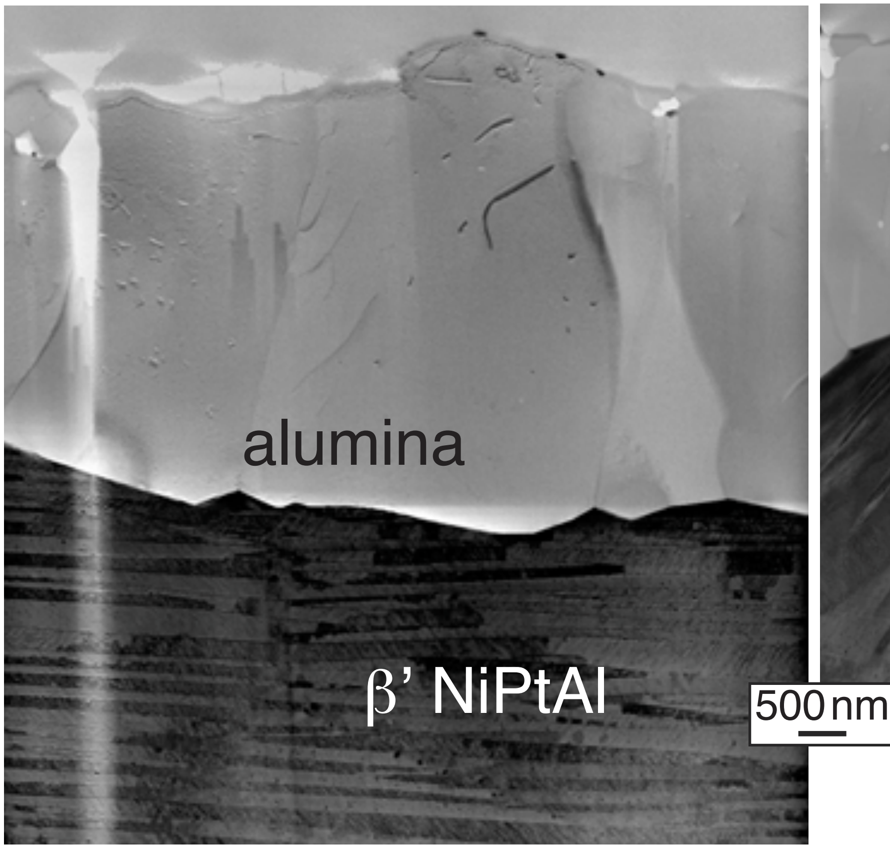
- Developing mitigation strategies is very difficult without understanding the role of dopants & $H_2O$
- Strong interest in the alumina scale but typically <10$\mu$m in thickness
- Imaging from light microscopy to SEM to TEM
- Also PSLS and roughness

## FY12 tasks:

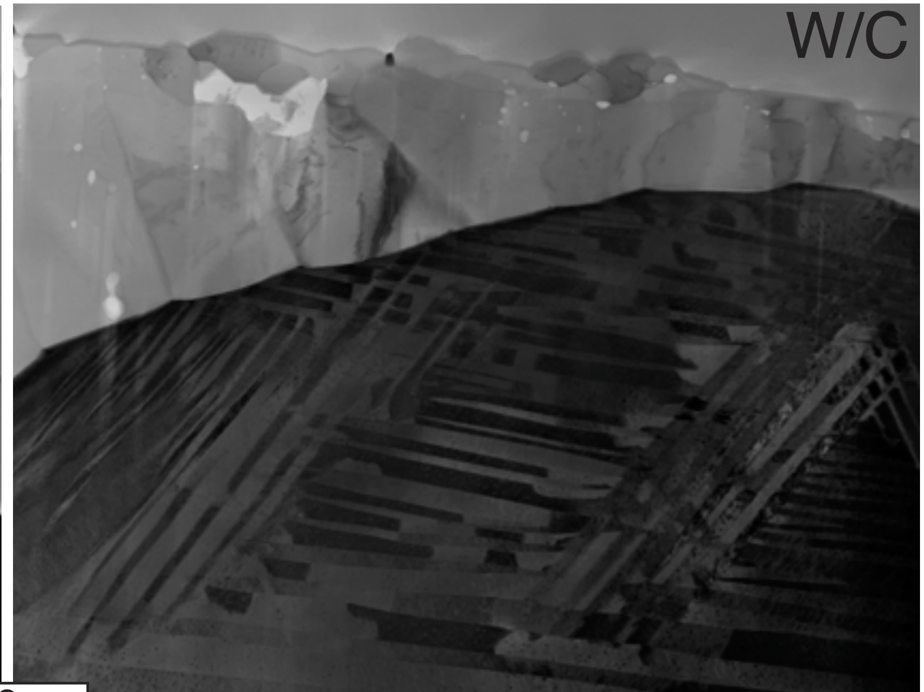
- complete TBC Group 1 characterization
- complete TBC Group 2 characterization
- broader characterization on Group 3 (PSLS...)
- continue characterization of model alloys

# TEM: variable scale thickness on β

## After 900 1-h cycles at 1150°C




900h in dry $O_2$



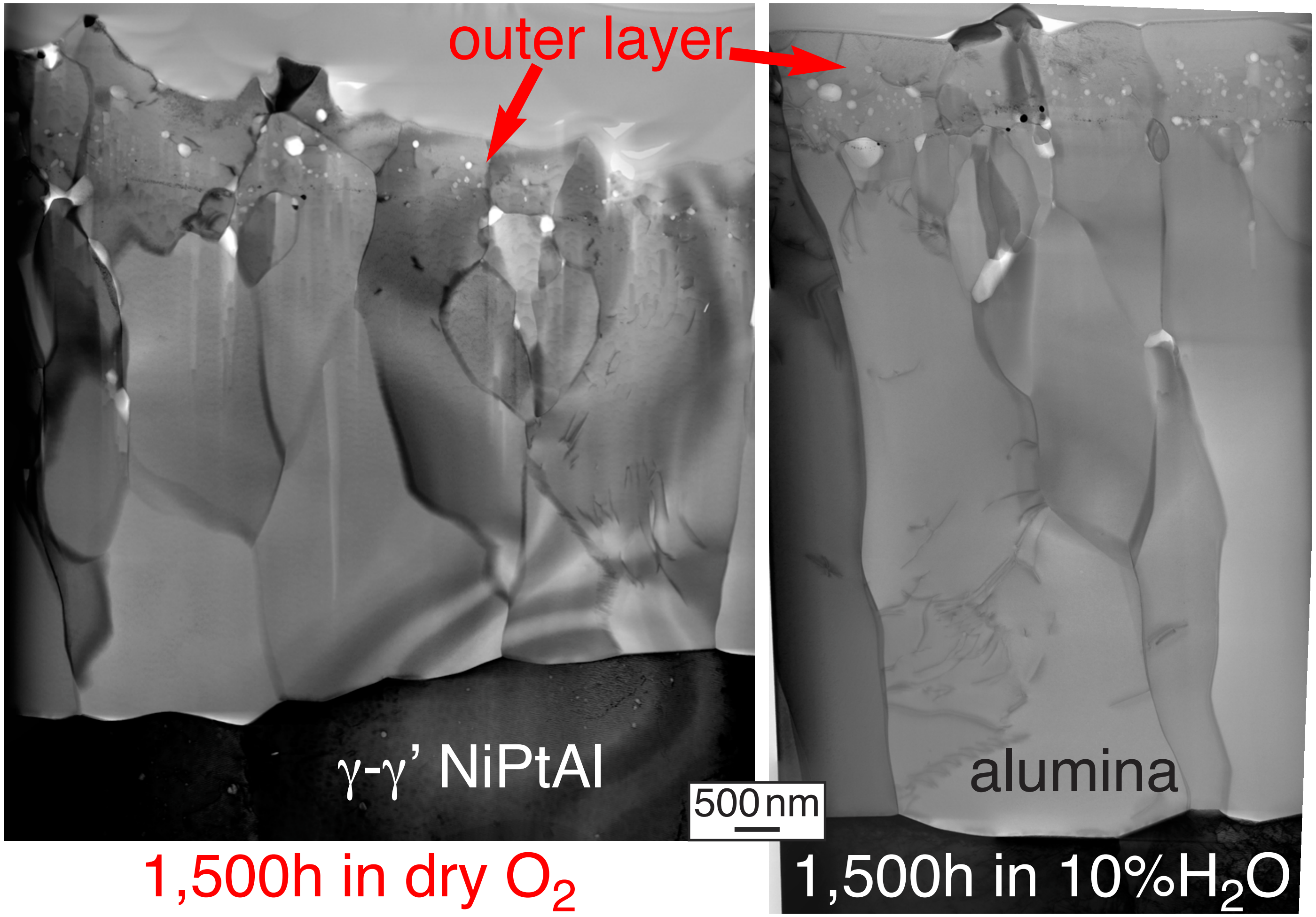

900h in 50% $H_2O$

Martensitic β apparent

Only minor changes in microstructure

# TEM: thicker oxide on γ-γ’ in $H_2O$

After 1500 1-h cycles at 1150°C

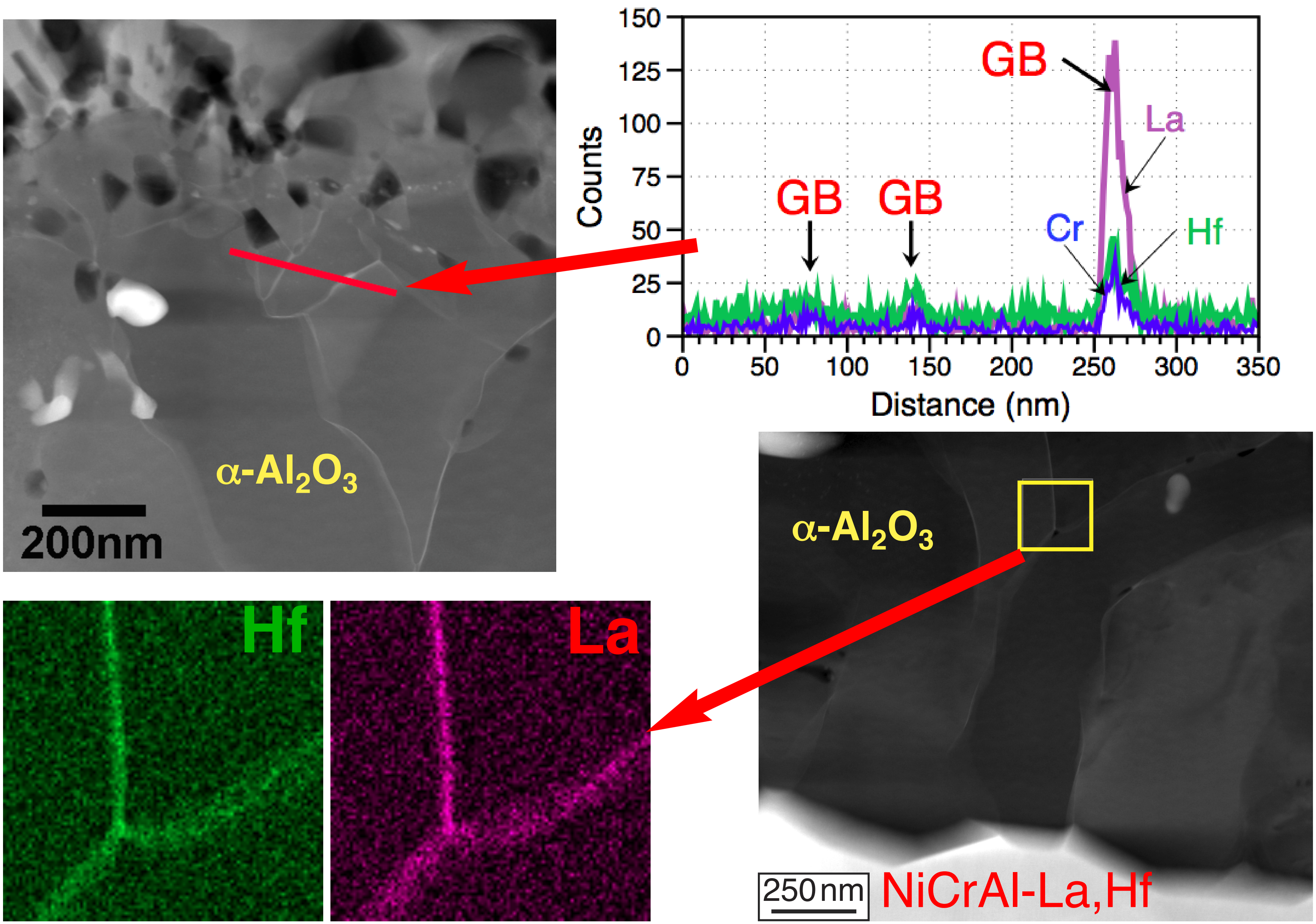



Columnar grains typical of γ-γ’ coatings

Thicker oxide, otherwise few differences

# TEM: model NiCrAl+La,Hf

## Oxidized 100h at 1100°C in dry $O_2$



# Task 4 focused on solutions for syngas

## Motivation for task:

- Other tasks concern understanding
- This task added to develop solutions
- Also to investigate new coating technologies
  (often difficult to get specimens)

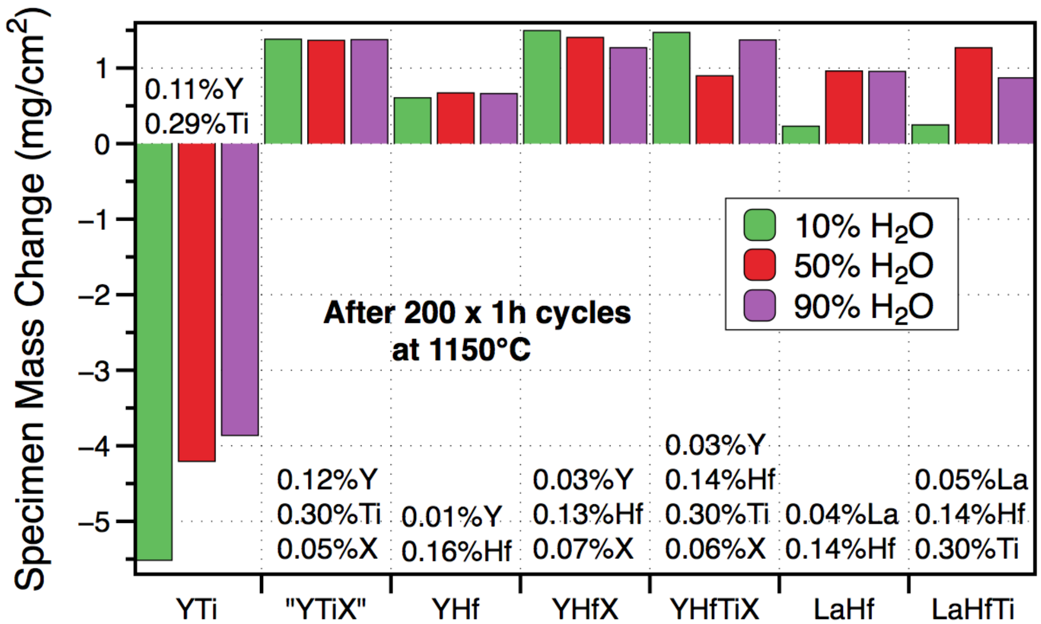
## FY12 work:

- more oxidation resistant MCrAlY coatings:
  initial work on model NiCrAlX cast alloys
  invention disclosure filed
- different superalloys (N515, 1483)
  N515, X7, X8:  lower Re
  1483:  higher Cr (hot corrosion resistance)

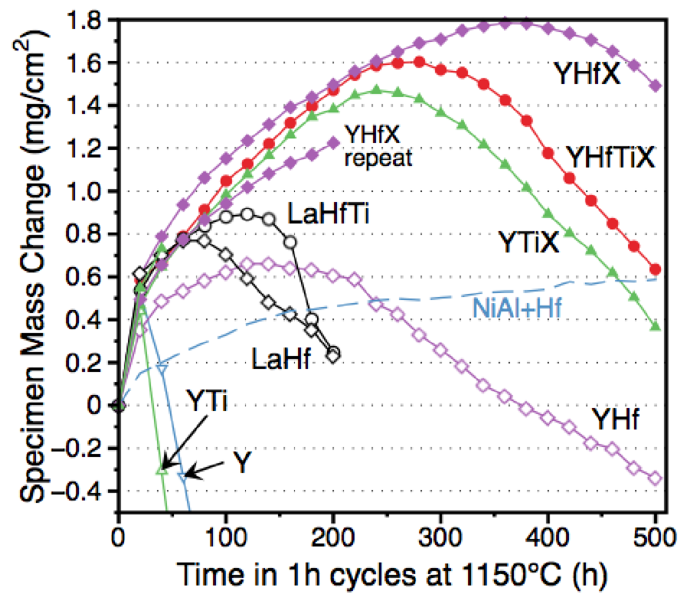
# Cast NiCrAl show benefit of "X"

## 1h cyclic oxidation testing at 1150°C

after 200 cycles:




air + 10%$H_2O$



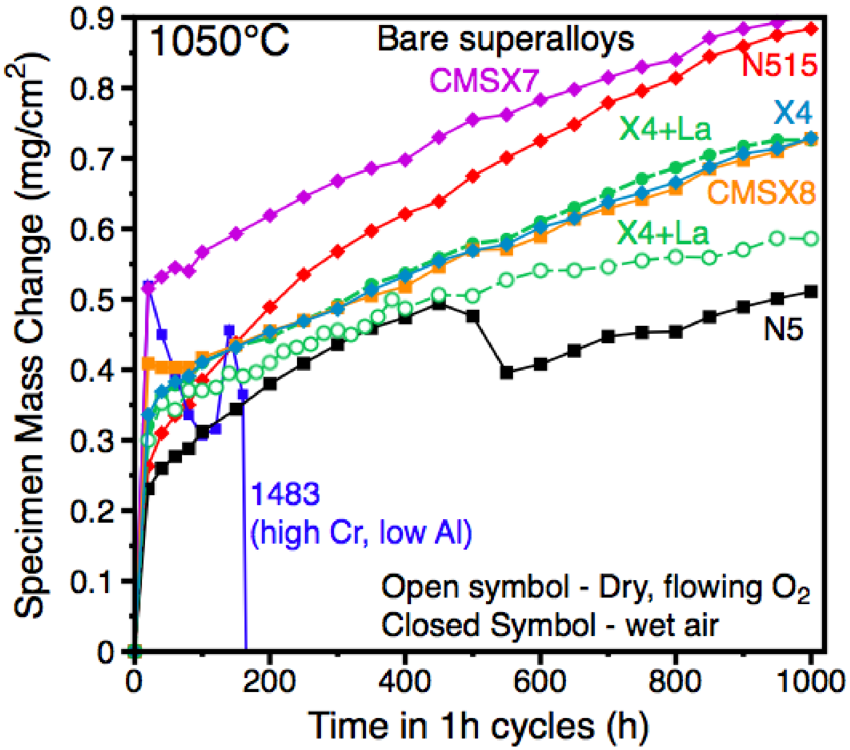

Higher temperature used for short time evaluation

Bar graphs at 200 cycles do not reflect behavior

Next step is to make powder/spray coatings

# Bare superalloy tests in progress

## 1h cyclic oxidation testing at 1050°-1150°C




1050°C example

All similar, little Re effect

1483 poor (low Al)

Comparison of low Re alloys with conventional 2nd generation single crystal alloys

# FY13 directions

FY10 (initiated 3 related “pre-competitive tasks)

(1) water vapor effects
(2) superalloy dopant effects
(3) characterization

FY13

Task 1: Broadening environment effects
Including $CO_2$ and $SO_2$ (late FY13 or FY14)
Task 2: Effect of superalloy composition
Higher Cr and lower Re effects (market pull)
Task 3: Characterization (continue key role)
Task 4: New bond coatings/processes
Validate model alloy performance in coating
Work with industry for new directions
- OEM/utilities, S-rich deposits, new processes

# Summary–take away points

Higher water vapor does not appear to explain de-rating although $H_2O$ effect is detrimental
- continue to study role of $H_2O$ on TBC life
- more relevant/better understanding

Doped superalloys do not appear to be a solution
- conventional SX alloys may have improved

Co-doped (Y+Hf) bond coatings appear to be very effective and should be further explored

Promising solution for new bond coating

Scope evolving to include performance of new superalloys and effect of $CO_2$ and $SO_2$

# CLEAN COAL.
# COOL.

backups

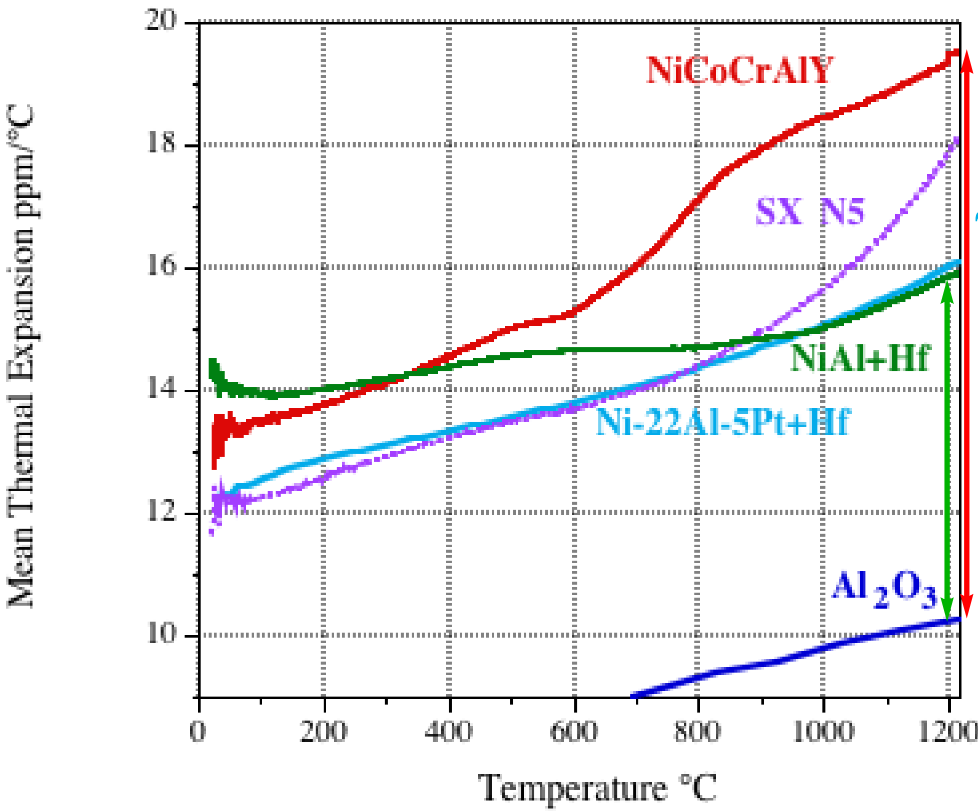
# TBC Group 4 in progress

Coatings (w/YSZ) received from Stonybrook
- mostly 1483 substrate, some X4 to compare
- only HVOF NiCoCrAlYHfSi bond coatings
- APS top coating on one side
- increased roughness compared to Group 2
- closer to industry standard
- 5 specimens per condition (3 for Group 2)

Experiments (complete Task 1 on $H_2O$ effect)
- 1h cycles 1100°C: 0%, 10%, 50%$H_2O$
  (compare to previous work)
- 100h cycles 1150°C: 0%, 10%, 50%$H_2O$
  (increased temperature to reduce test time)
- 1h cycles 1150°C: 0%, 10%
  (link experiments)

# 1100°C used for MCrAlY coatings

## Thermal expansion difference among coating classes




MCrAlY

$\gamma+\gamma'$ NiPtAl, Pt diffusion

$\beta$-(Ni,Pt)Al, CVD

$$\text{stress} = f(\Delta\alpha_{M\text{-}O})$$

$$W \propto \xi_{oxide}$$

(strain energy) (thickness)

$$\xi^* \propto (\Delta T \Delta\alpha)^{-2}$$

thickness at spallation

MCrAlY bond coatings (industry standard)

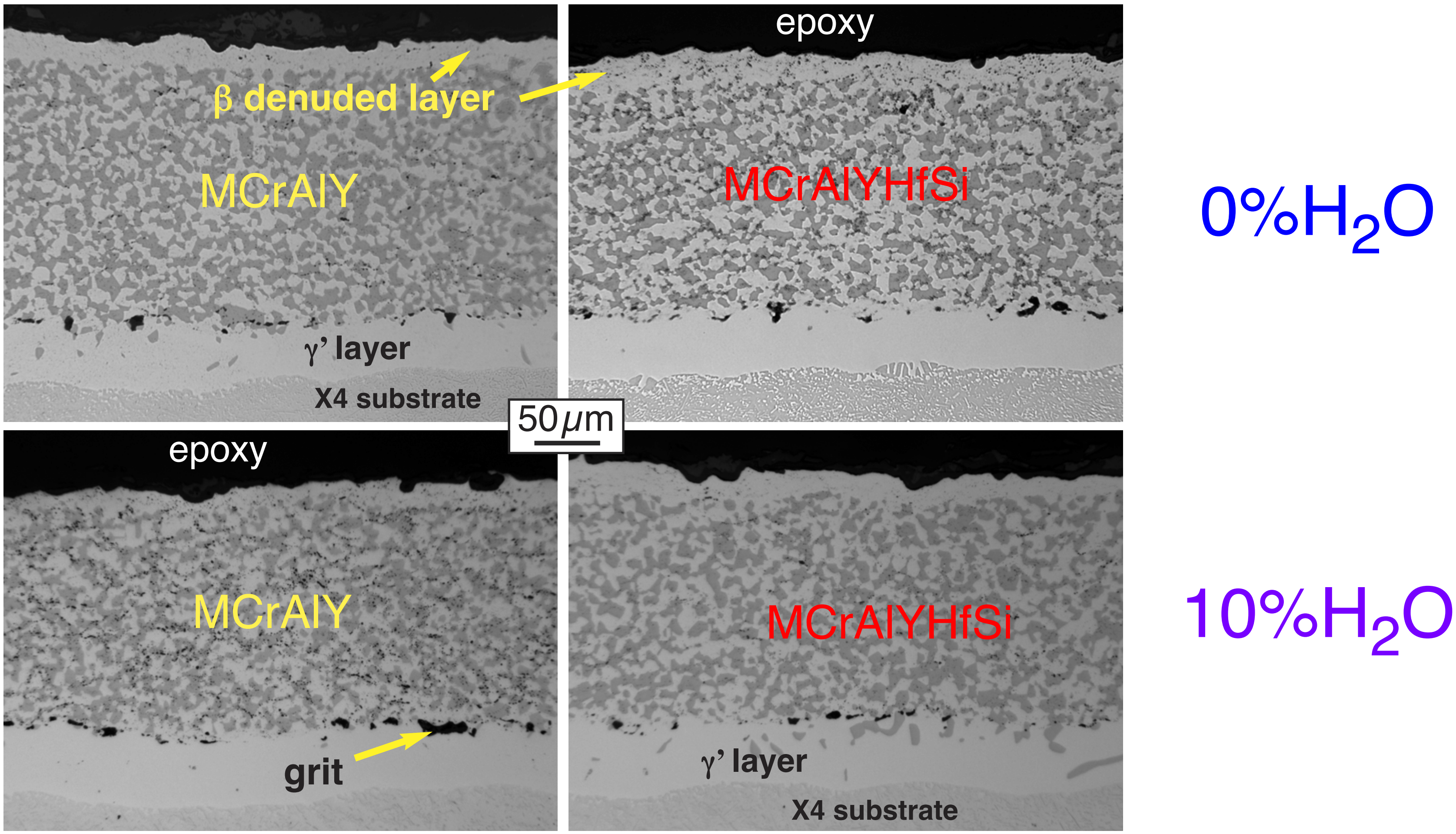
X4: 13.0Al,10Co,8Cr,0.9Re,1.2Ti,17S-270Hf

MCrAlY & MCrAlYHfSi: 41Ni,18C0,16Cr,23Al,0.4Y

or 0.4Y, 0.07Hf, 0.65Si

# Morphology of HVOF MCrAl

## Epoxy-mounted polished cross-sections after failure

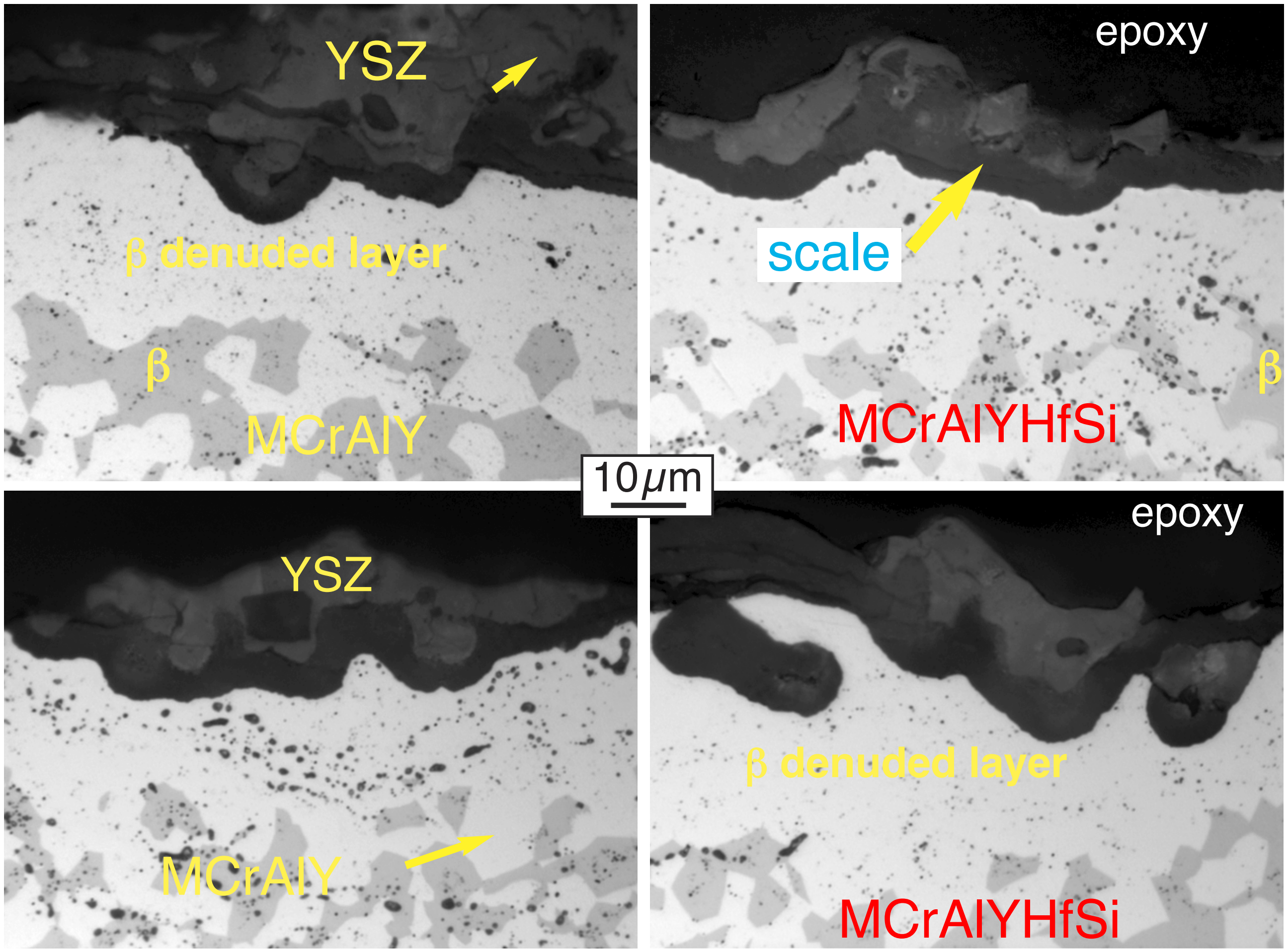



Relatively small β denuded zone

Low roughness of $R_a$~5.5, not industrial standard

# Scale on HVOF MCrAl

## Epoxy-mounted polished cross-sections after failure




0%$H_2O$

10%$H_2O$

Rougher areas: more alumina scale + YSZ attached

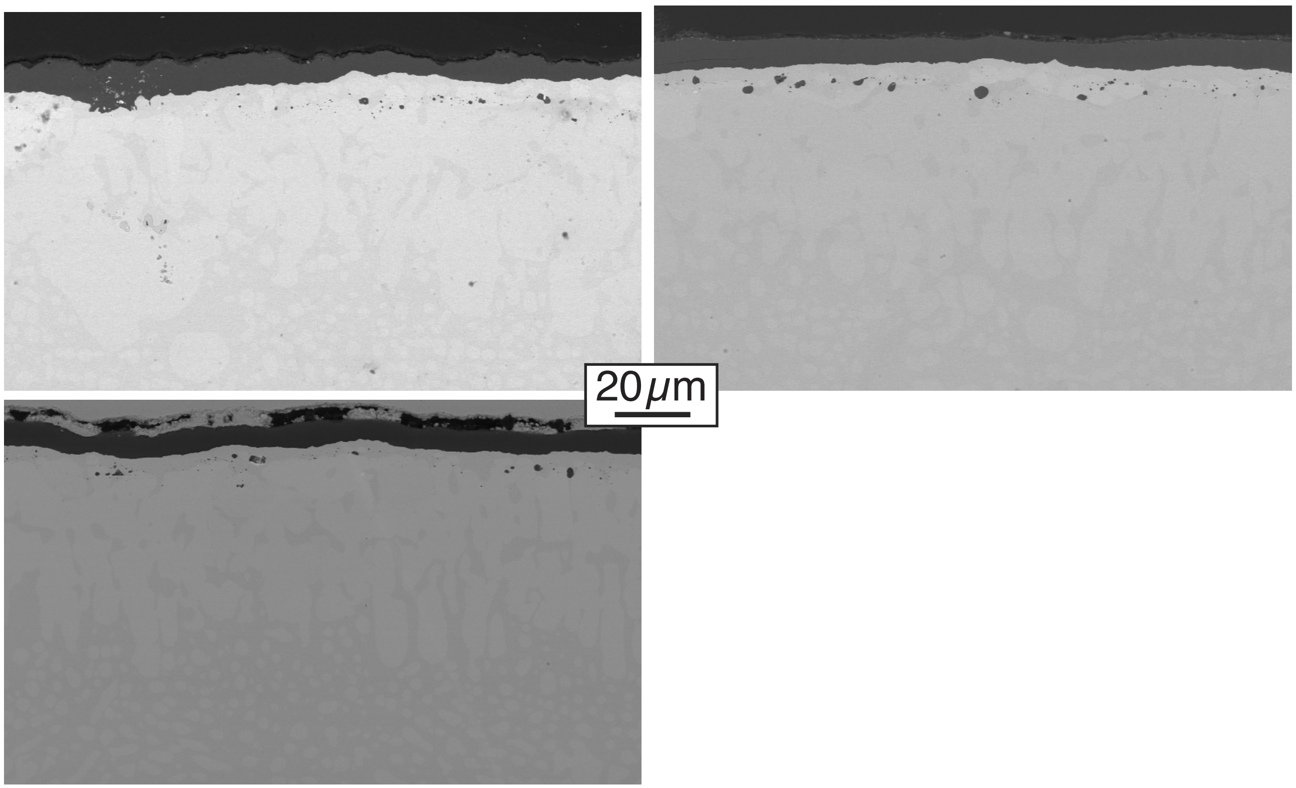
~100% APS YSZ spallation leaves little to analyze

# $\gamma+\gamma'$ coatings: more uniform scale

## Backscattered SEM, 1-h cycles at 1150°C

dry $O_2$, 1,500h

10%$H_2O$, 1,500h




50%$H_2O$, 1,500h

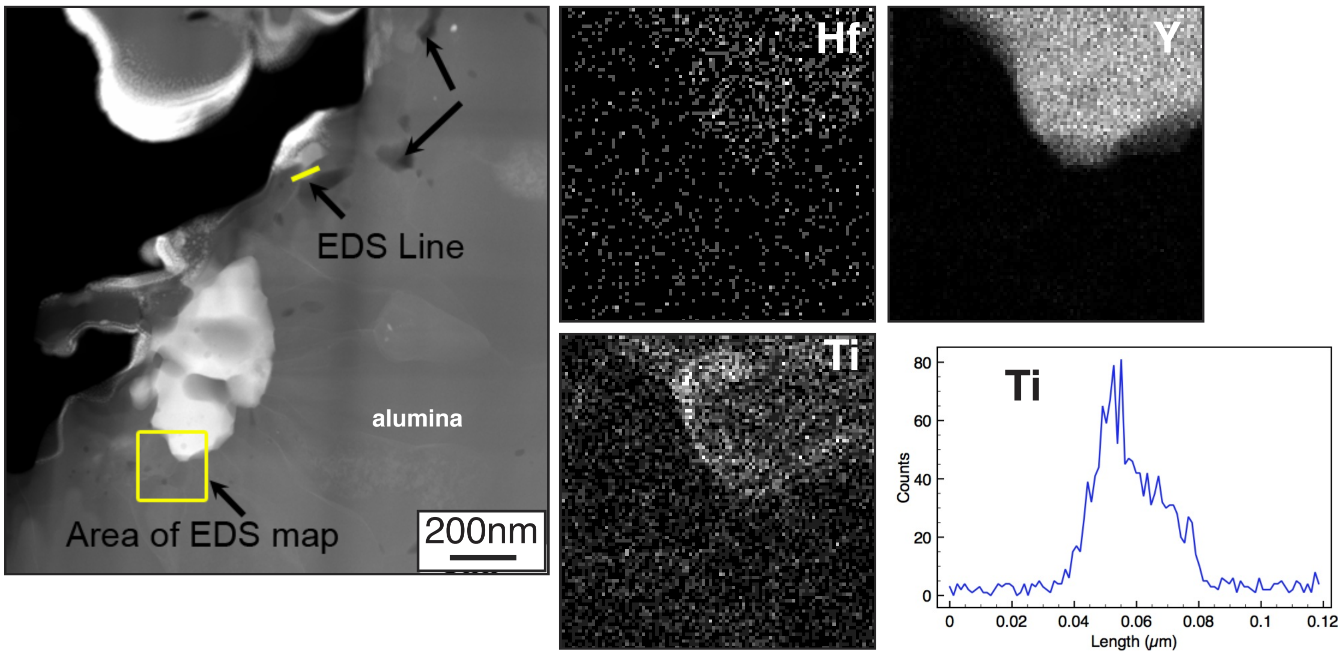
90%$H_2O$, 1,500h

Relatively uniform oxide formed on $\gamma+\gamma'$ coatings

More variation for scale formed in 0% $H_2O$:  spall?

# Coated X4-2 - found Ti in scale

## Oxidized for 100h at 1100°C in dry $O_2$

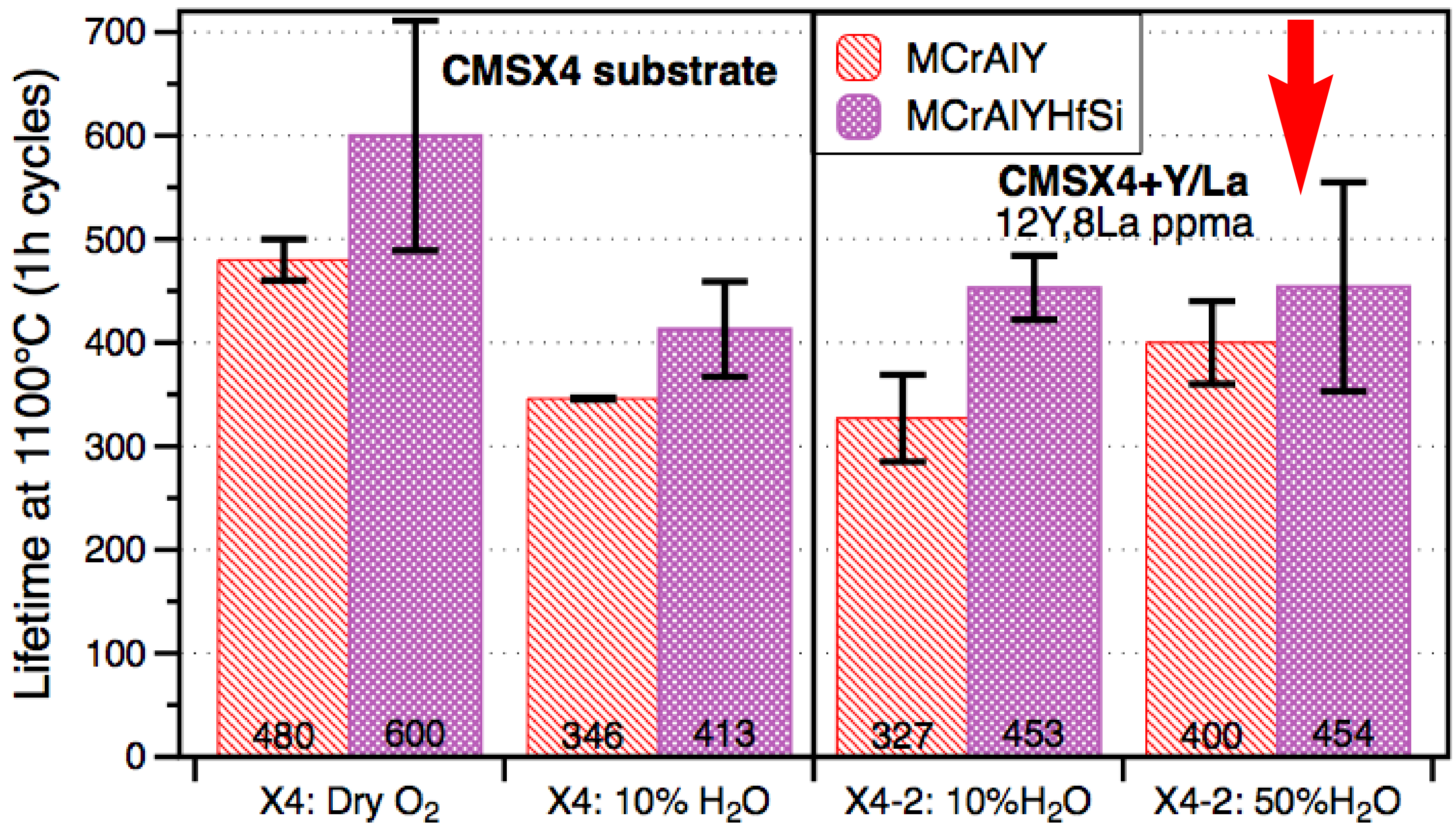



Demonstrates that Ti diffused through coating

(No Ti in MCrAlYHfSi coating, 1% in X4-2)

# 50% $H_2O$: no effect on TBC life

## 1100°C: two bond coatings on X4-2 + APS YSZ




Similar to diffusion coatings, higher water vapor content did not reduce TBC lifetime.

Characterization in progress

# FY12-13 milestones

FY2012

- Complete TBC lifetime testing at two different cycle frequencies. (Met).
- Complete characterization of the coated CMSX4 variants (with and without dopants) (Met).

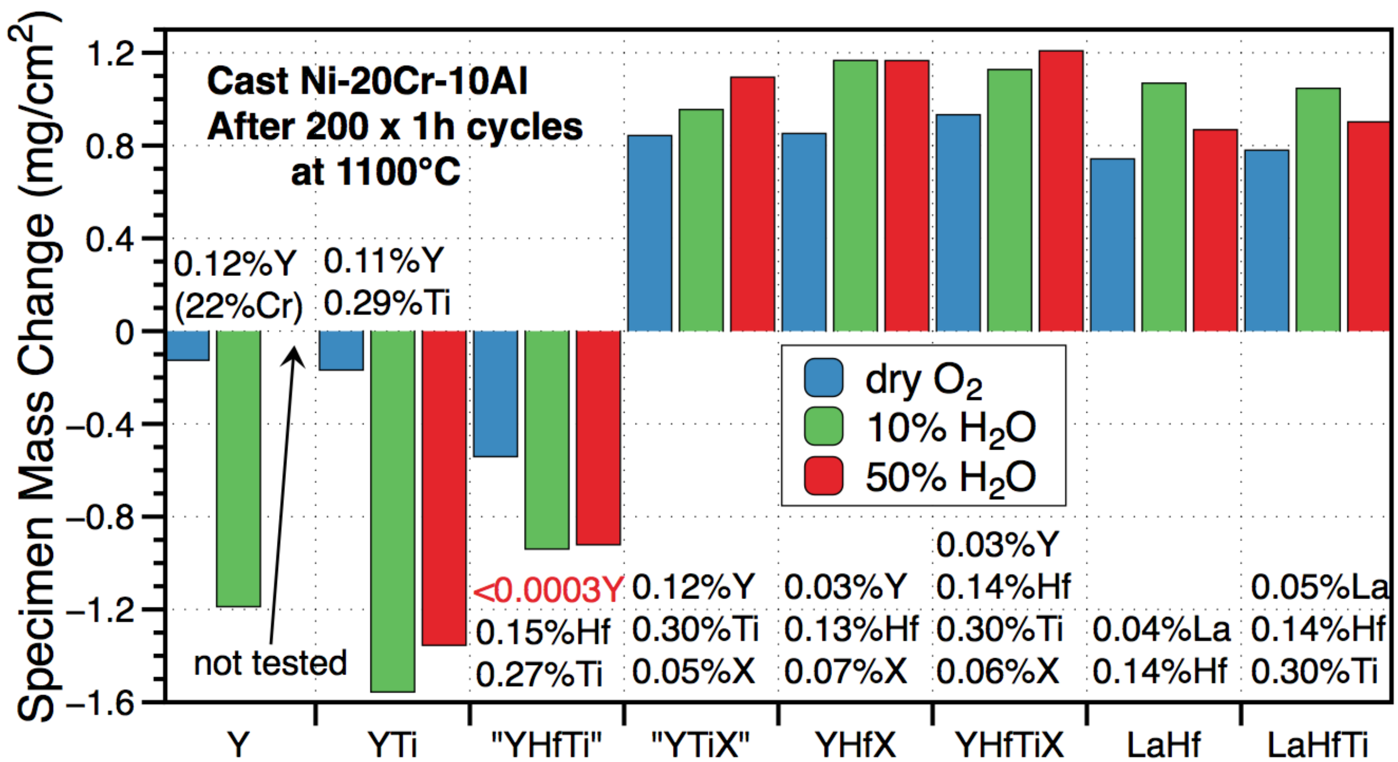
3. Complete initial assessment of model alloy oxidation results (Progressing, 9/30/12).

FY2013

1. Complete oxidation evaluation of bare superalloys with higher Cr or lower Re (12/31/2012)
2. Complete TBC lifetime testing and characterization in the presence of $CO_2$ and $H_2O$ (5/31/2013)
3. Fabricate bond coatings with new composition and complete initial cyclic oxidation evaluation (9/30/2013)

# Model alloys show benefit of “X”

## 1h cyclic oxidation testing at 1100°C




Testing in dry and wet air

La/Hf compositions also worked well without X

# Path forward for MCrAlY+X

Invention disclosure filed in June 2012

- patent review being conducted
- more data needed to file strong patent

Next steps:

Identify vendor, obtain non-disclosure agreement

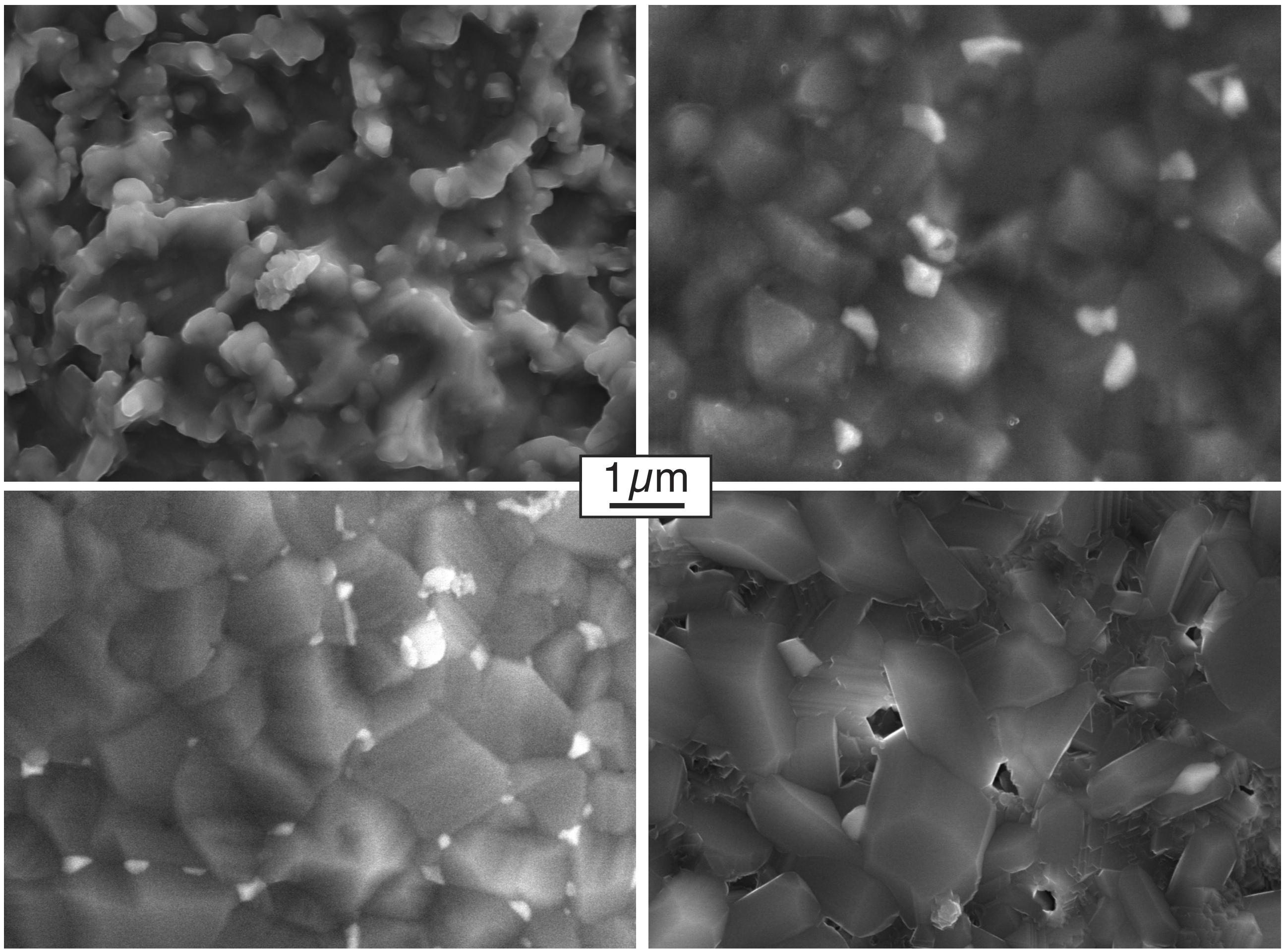
Make two powders, spray coatings (FY13 funds)

Test coatings, compared to current coatings

# Change in $Al_2O_3$ morphology on $\gamma$-$\gamma$'

## Plan view SEM, all 1,500, 1-h cycles at 1150°C

dry $O_2$ (0% $H_2O$) 10%$H_2O$



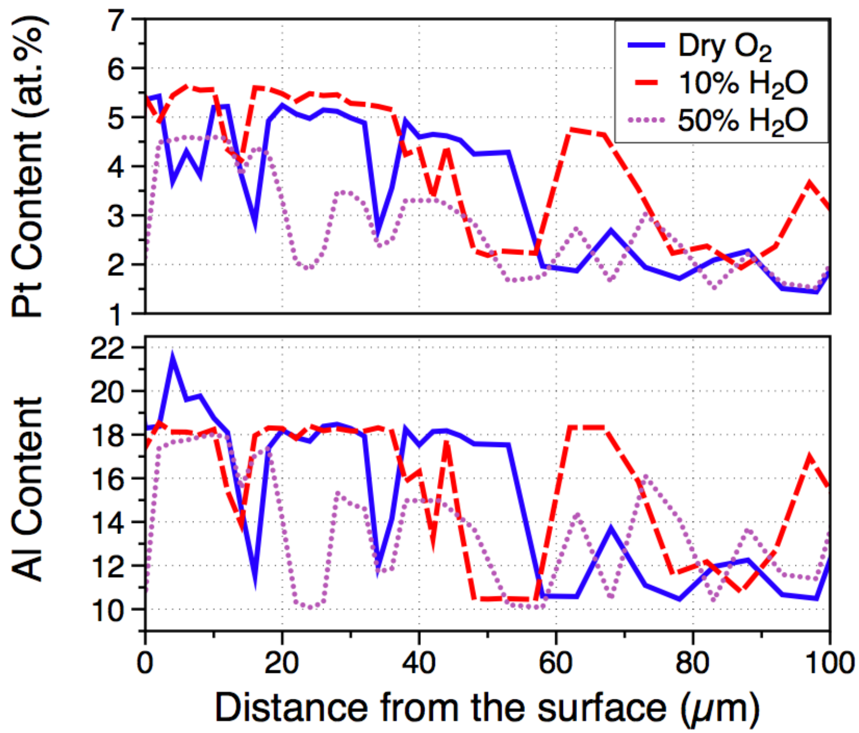

50%$H_2O$ 90%$H_2O$

Spinel(?) at surface except 0% -> spall at 0%(?)

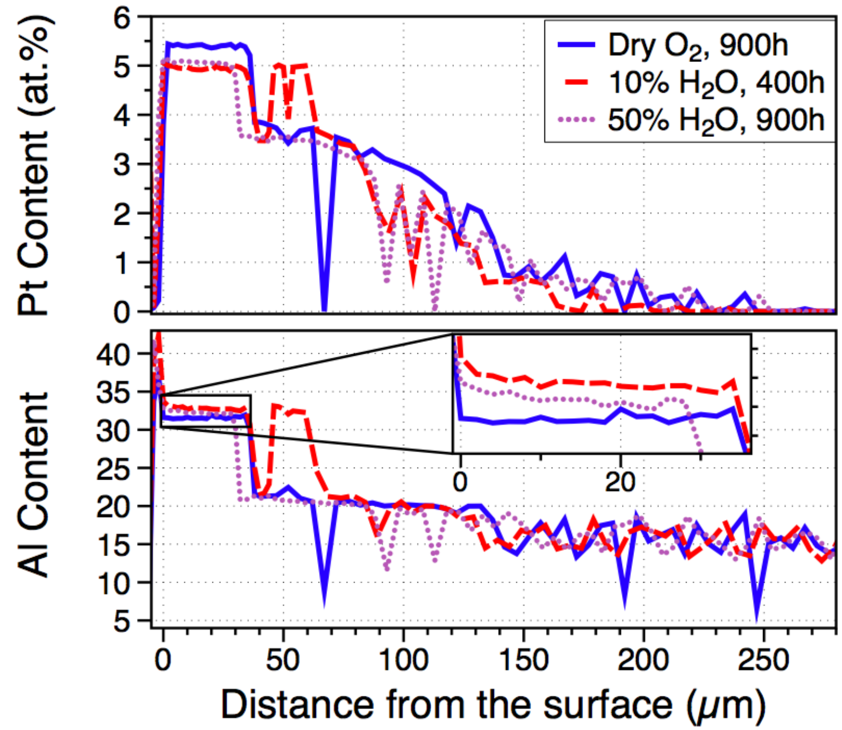
# EPMA: no clear differences

## Line traces from specimens without YSZ

γ-γ' coatings (1500h)




β coatings




No apparent effect of water vapor on interdiffusion

β coatings exposed for different times at 1150°C