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

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K. Unocic - TEM characterization

K. Cooley - coating fabrication

G. Garner, M. Stephens - oxidation experiments

T. Lowe - characterization

D. W. Coffey - TEM specimen preparation, FIB

H. Longmire - metallography

L. Walker, D. Leonard - EPMA

Ken Murphy, Howmet - CMSX4 substrates

Ben Nagaraj, GEAE - YSZ deposition

S. Sampath, C. Weyant, Stonybrook U. - HVOC,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

Where will it come from?

50% coal now

Cleaner coal?

vs.

2 coal gasification plants being built:

- Indiana (GE turbines)
- Mississippi (Siemens turbines)

Why de-rating syngas turbines?

- syngas turbines operating ~100°F(C?) less

Reasons for de-rating*:

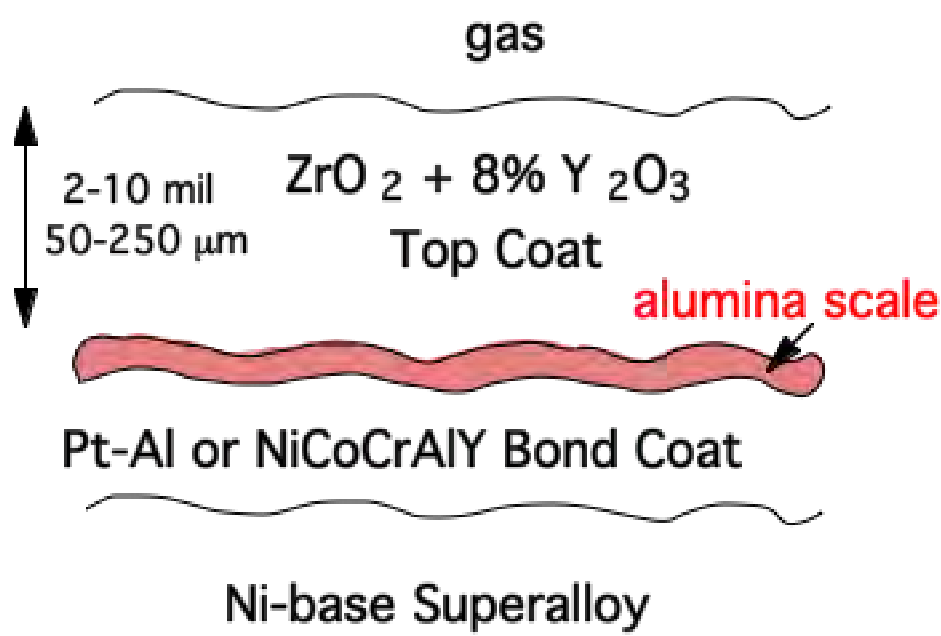
- higher water vapor content (fuel+diluent) (~10vol.%H_2O for natural gas vs. 30-60%)
- higher S levels (imperfect cleanup)
- increased deposits
- syngas lower caloric value: higher fuel/air
  5-10X more fuel, magnifying impurities

*See Gibbons & Wright (2009) "A review of materials for gas turbines firing syngas fuels," ORNL report

Project goal: eliminate syngas turbine de-rating

- need more durable coatings

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)

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

FY11

Nearly complete superalloy dopant study
- Y+La additions to CMSX4

Complete/characterization for two TBC series
- 0-90% H_2O with Pt diffusion bond coatings
- 0-50% H_2O with MCrAlY/APS YSZ

Characterization
- dopant ionic segregation in alumina scales

FY12

Future directions

Recent Presentations

TMS Annual (March 2011, San Diego)
- Cyclic Oxidation Behavior of HVOF MCrAlY Coatings Deposited on La- and Y-doped Superalloys

8th Microscopy of Oxidation (April 2011, Liverpoool)
- Ionic Segregation on Grain Boundaries in Thermally Grown Alumina Scales

ICMCTF (May 2011, San Diego)
- Effect of increased water vapor levels on TBC life-time with Pt-containing bond coatings
- Characterization of the Alumina Scale formed on Coated and Uncoated Doped Superalloys

8th Int. Charles Parsons Conf. (Sept. 2011, UK)
- Effect of water vapor content on TBC lifetime

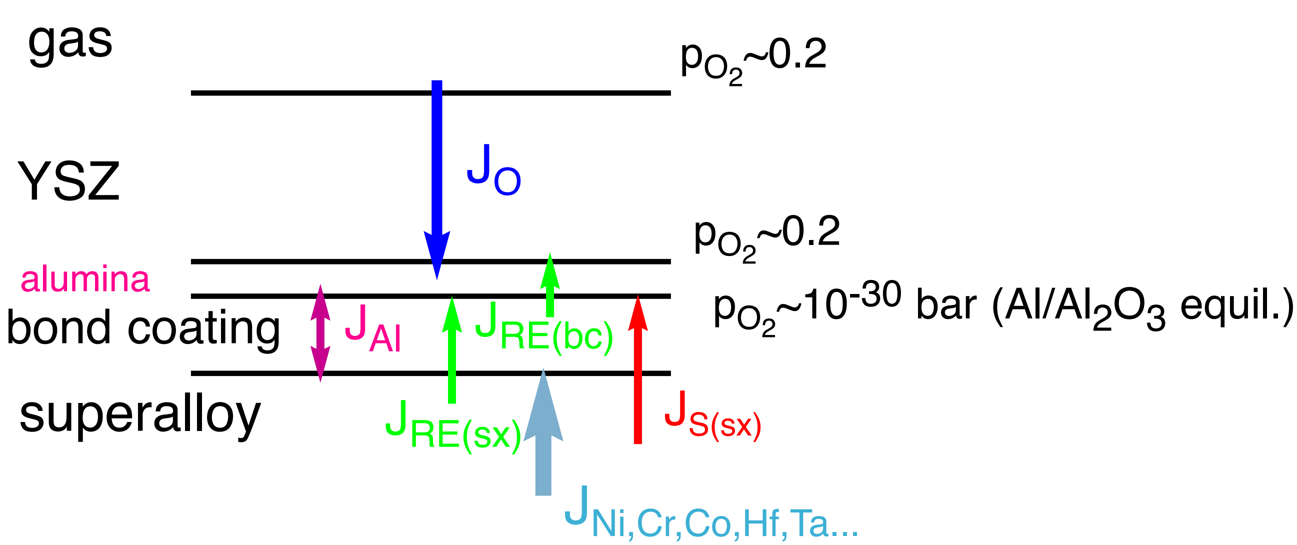
NEXT: Superalloys 2012?

Are doped superalloys a solution?

Motivation for doped superalloy task:

Difficult to develop/commercialize new bond coating
- dozens of current MCrAlY coating compositions

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

X4: 9.5Al-620Hf-3Y

All <1ppma S

disks: 16 x 2mm thick

1Y 2La	(ppma) GDMS	2Y 3La

X4-1: 12.8Al-340Hf

X4-2: 12.8Al-270Hf-3Y

10Y 6La	(ppma)	14Y 9La

MCrAlYHfSi (PWA286) by high-velocity oxygen-fuel

48Ni-21.6Co-16.7Cr-12.3Al-0.68Y-0.25Hf-0.36Si

HVOF: Stonybrook Univ.

ORNL: vacuum anneal 4h/1080°C

1h cycles:

1050°,1100°,1150°C

Pt-Rh

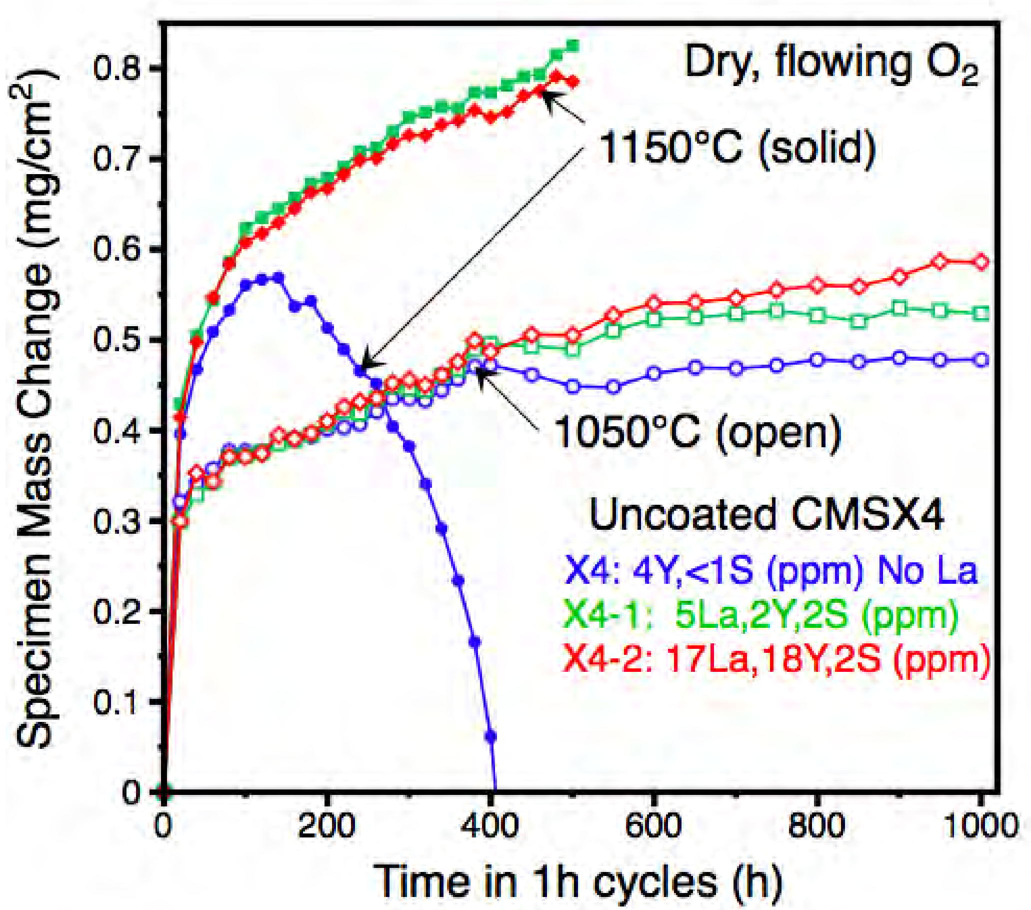
flowing, dry O_2

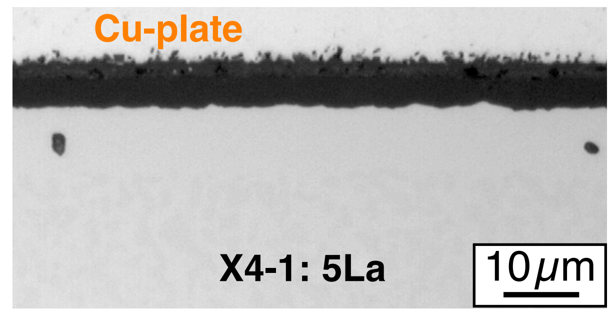
100h cycles:

1100°, lab. air

Bare alloys spall transient oxide

Three different alloys oxidized in 1h cycles





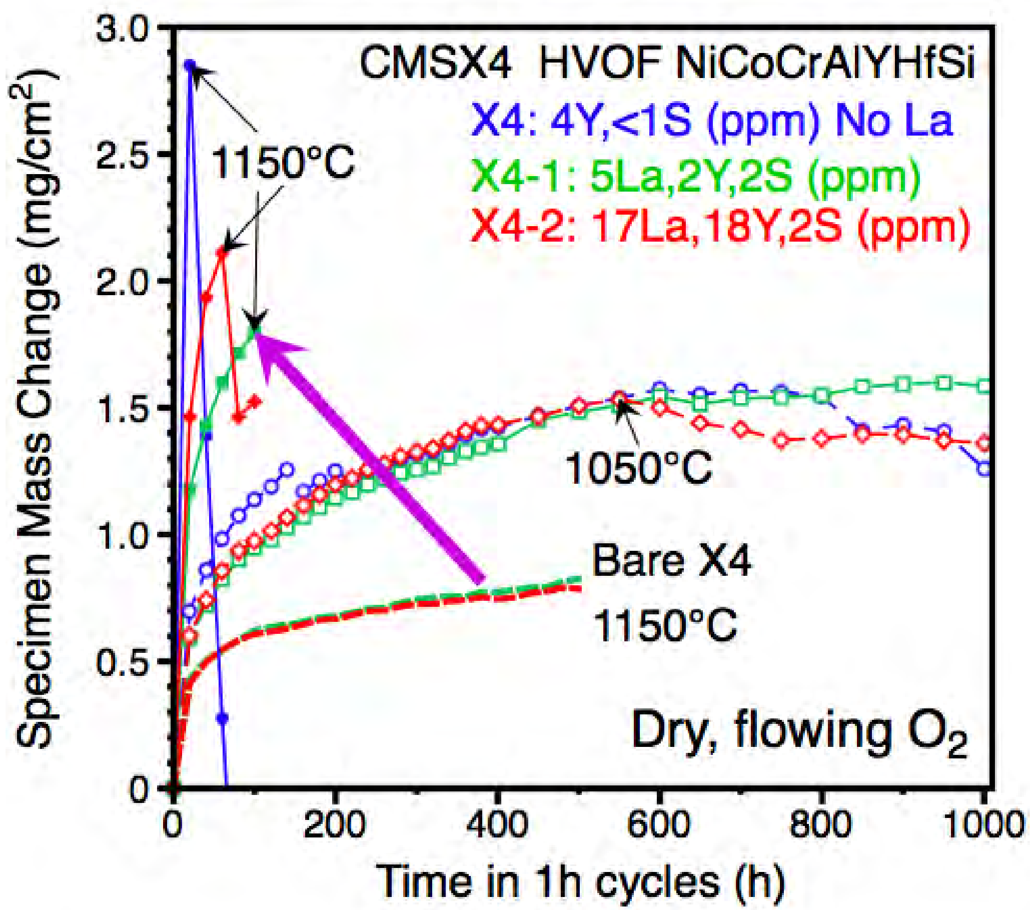
after 500 cycles at 1150°C

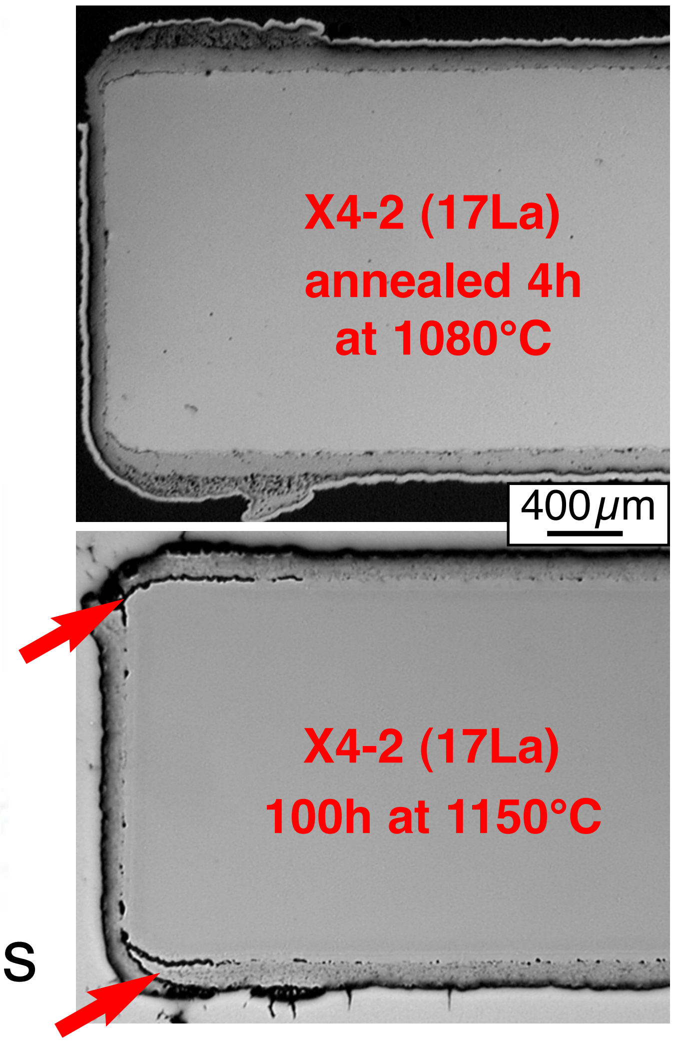
1050°C: little difference

1150°C: No La X4 mass loss due to lower Al content in X4 compared to X4-1,X4-2

Oversprayed edges problem

HVOF MCrAlYHfSi bond coating on doped alloys





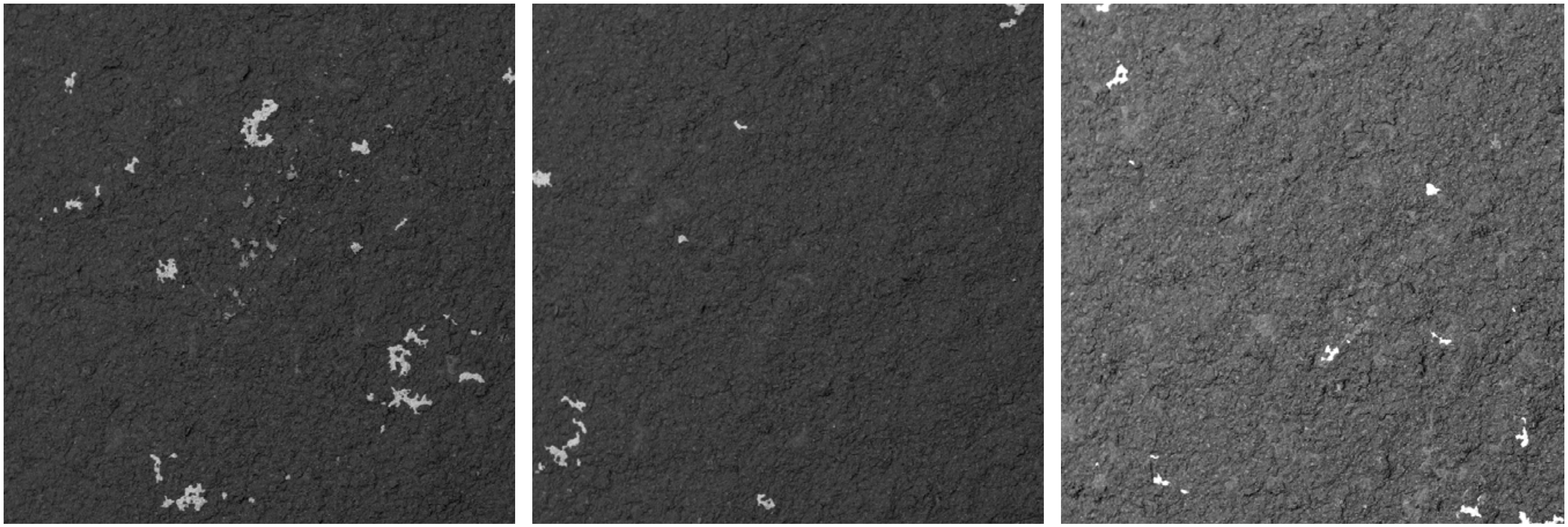
High velocity oxygen fuel coatings

Mass gains higher than bare alloy due to oxidation of oversprayed region

Little indication of differences

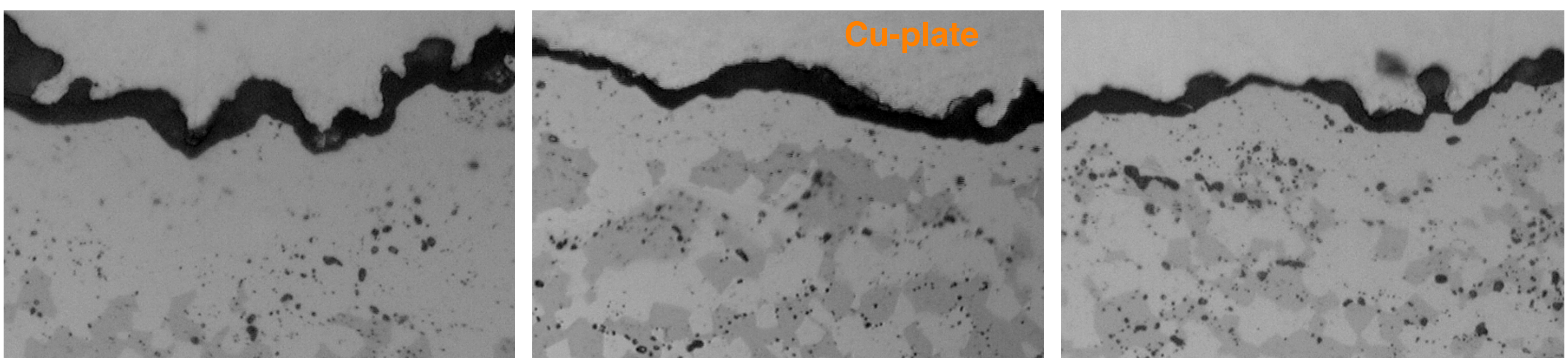
Three different alloys after 1h cycle exposures

SEM backscattered plan views after 600x1h at 1050°C



X4 X4+5La X4+17La

Polished sections after 100x1h at 1150°C



Learning during 1st HVOF phase:

- Need base X4 with same Al content
  (more X4 obtained from Howmet)
- Need to eliminate overspray on sides
  (done, but spinel formed...)
- Did Y+Hf bond coat overshadowed Y+La?
- Many not familiar with Y+Hf co-doping
  (include MCrAlY in next group)
- Y+La doping benefit not easily seen
  Phase 2: deposit APS YSZ to measure dopant effect on TBC lifetime
  AND test in the presence of water vapor

Does water vapor explain de-rating?

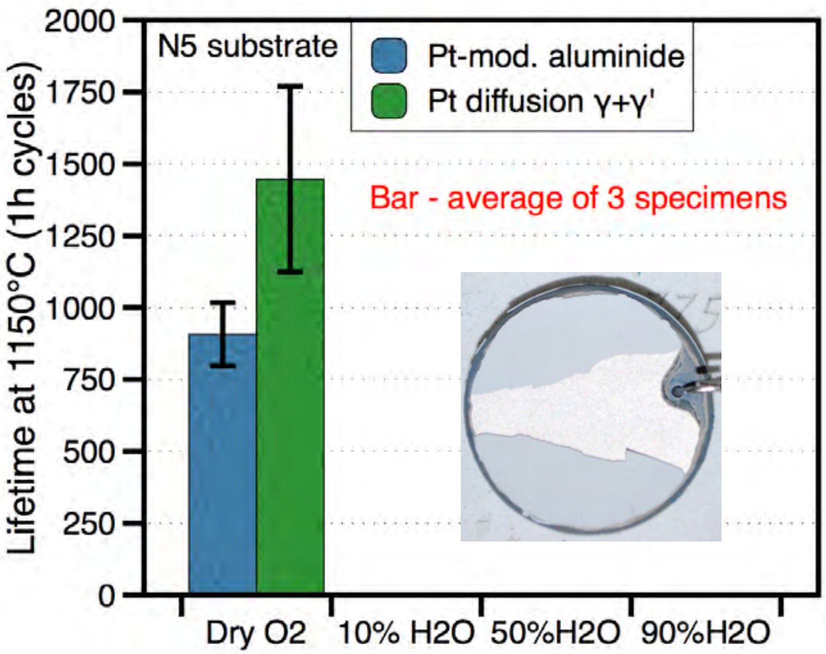
Motivation for water vapor task:

- Current work 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%?

Keep procedure very uniform

16mm disks: single crystal substrates (all at.%):
N5: 13.3Al,8Co,8Cr,0.9Re,70Y-17S-540Hf-132Zr
Grit blasted 7±1μm Pt layer at Tenn. Tech.



β: CVD at ORNL, 6h at 1100°C, low S process

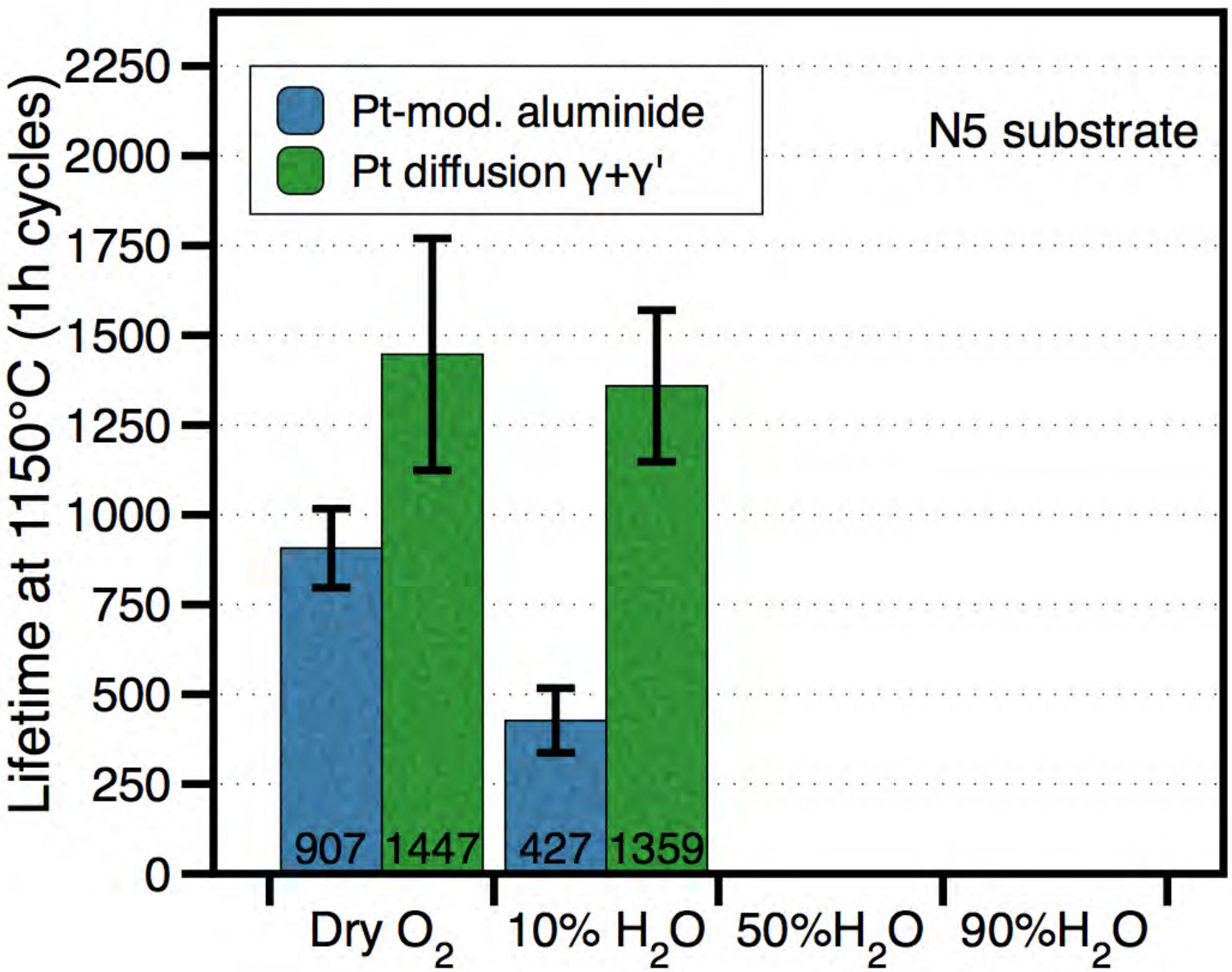
γ-γ': anneal 2h, 1175°C, ~10^{-4} Pa vacuum

ZrO_2-Y_2O_3 coated (1 side) comm. EB-PVD process

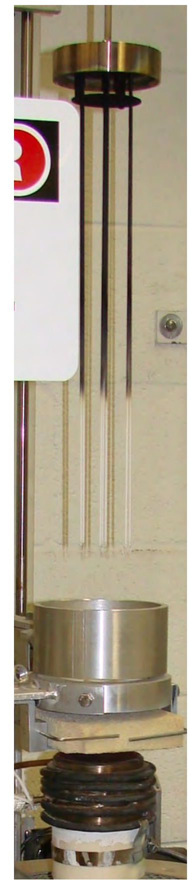
Oxidation testing: 1h cycles (10min cooling),1150°C
Characterization: Laser & optical profilometry (R_q)
Scanning electron microscopy (SEM)
Metallographic cross-sections

Switching to wet air: major β drop

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



1150°C, 2102°F

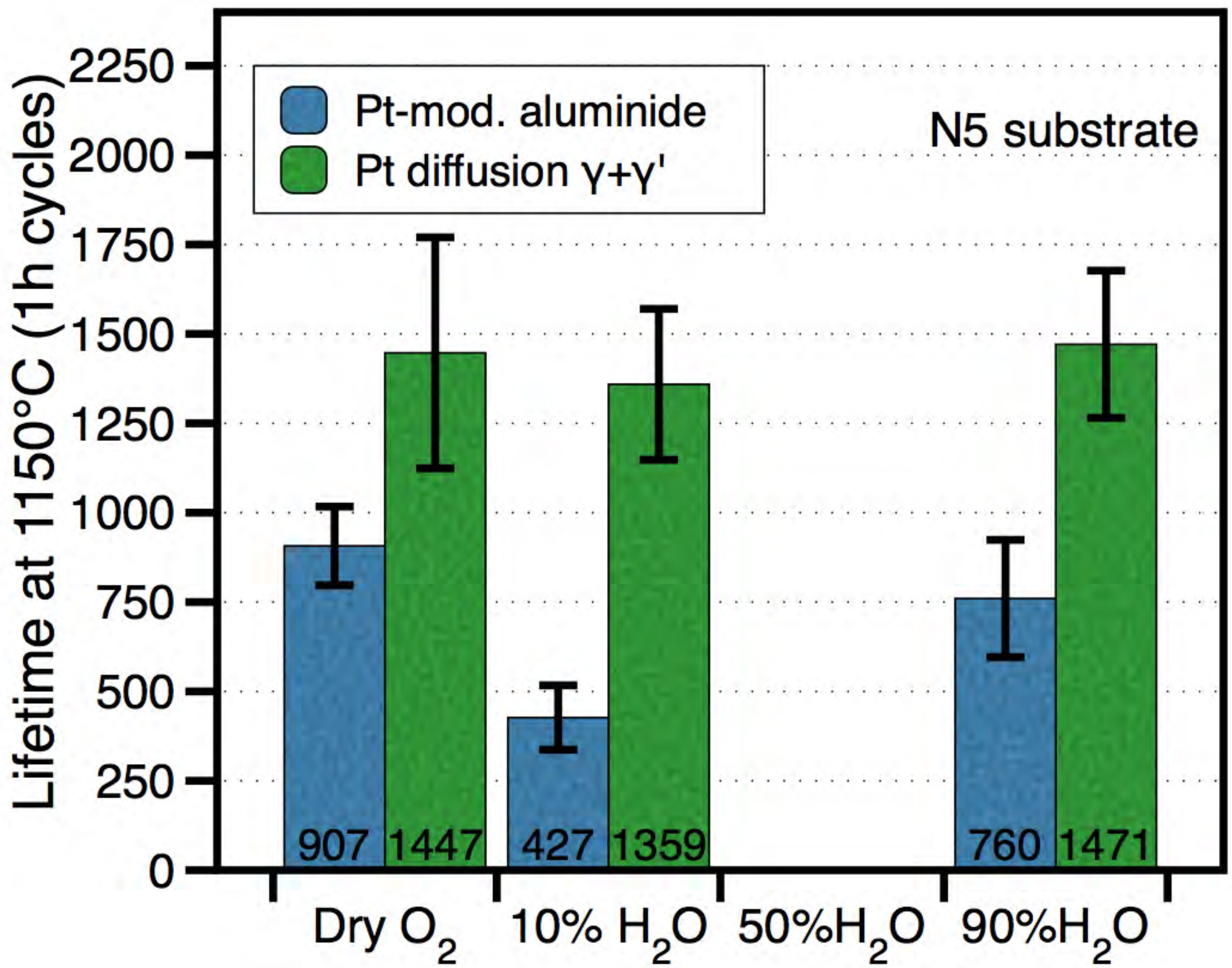


β-NiAl bond coating: >50% decrease in lifetime

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

Increasing to 90%: not as bad

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

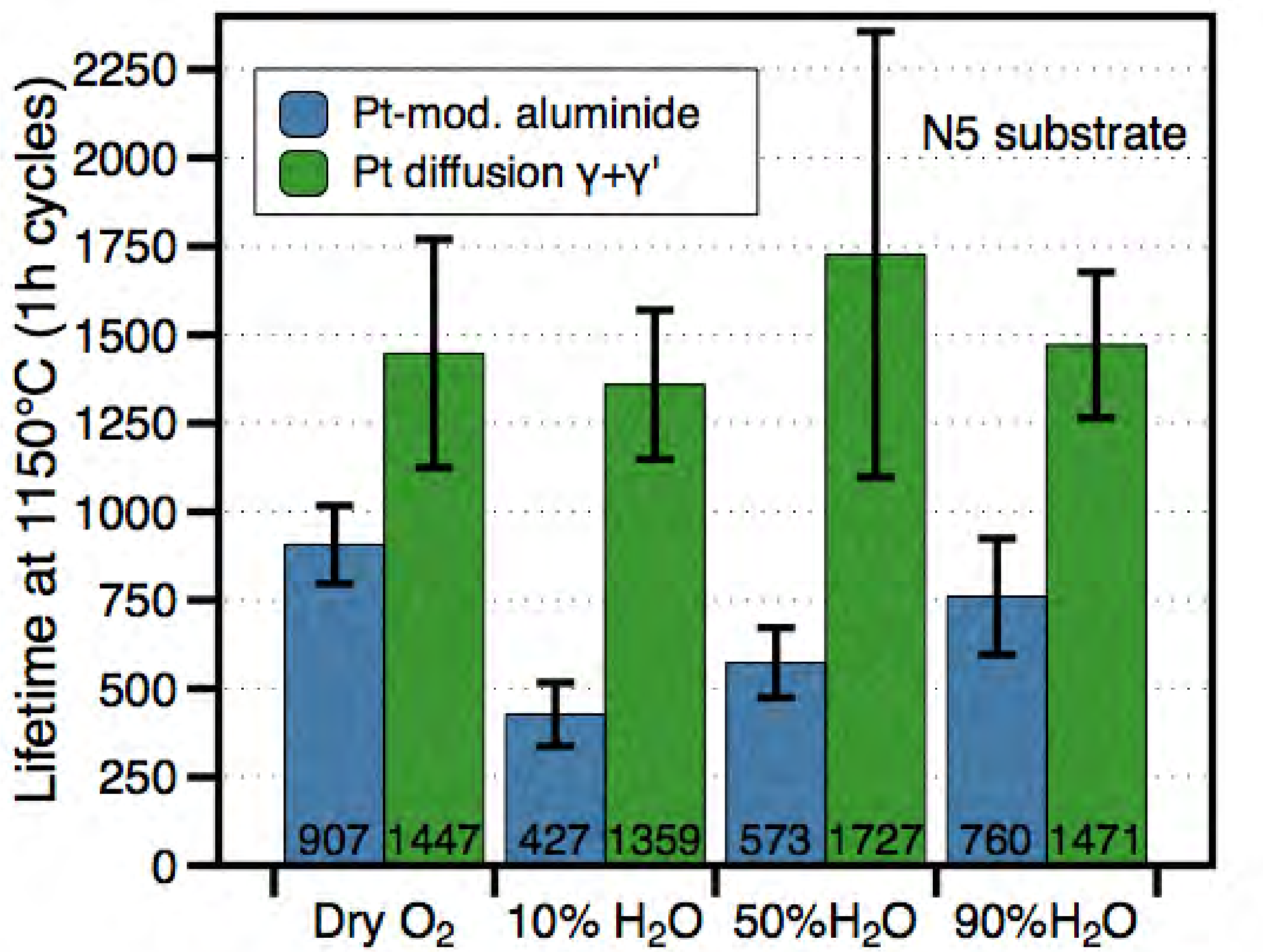


β-NiAl bond coating: slight change in life

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

50% H_2O: intermediate effect

1h cycles, 1150°C, air with 50 vol.% H_2O

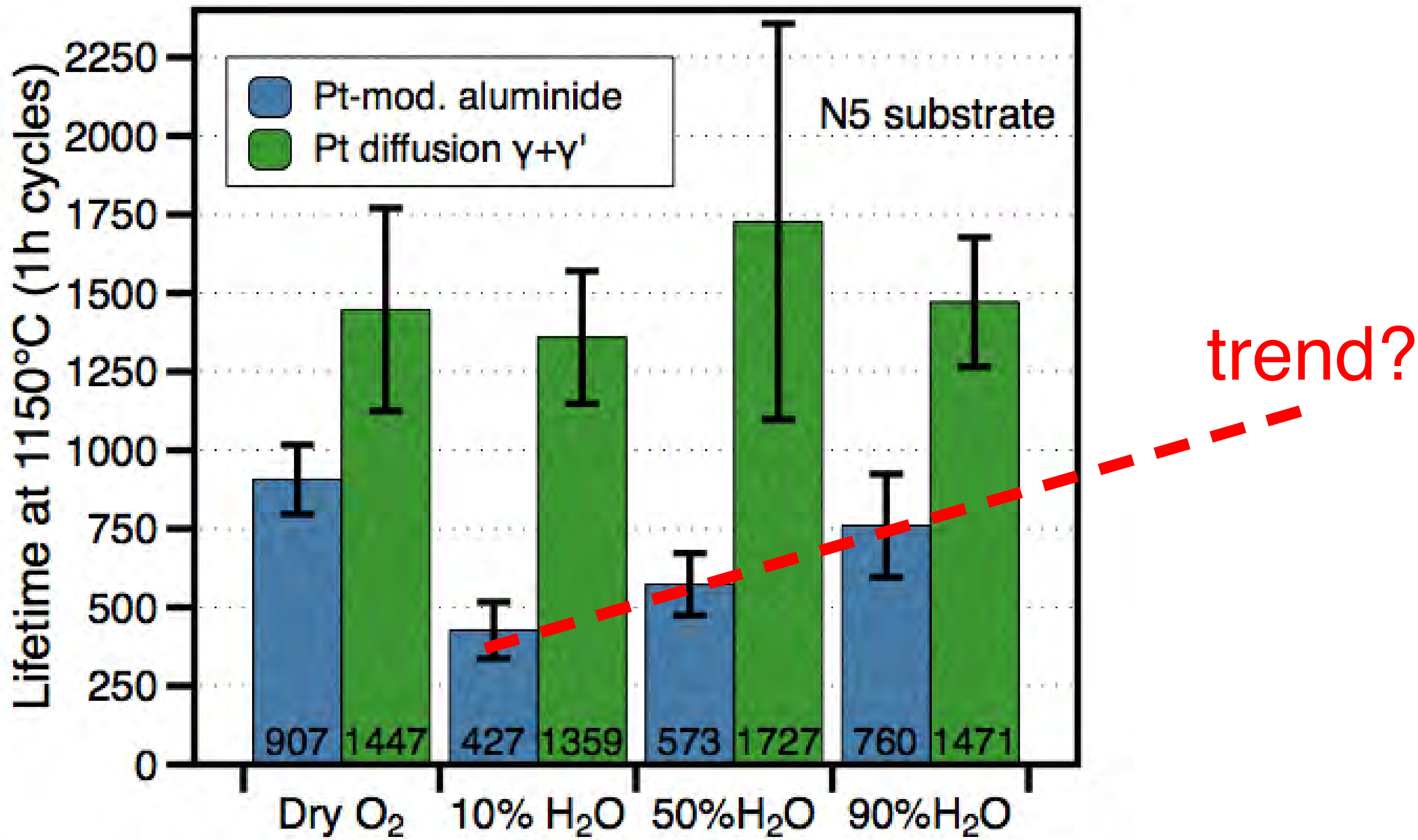


β-NiAl bond coating: 37% decrease in average life

γ-γ' Pt diffusion: higher average but larger variation

50% H_2O: intermediate effect

1h cycles, 1150°C, air with 50 vol.% H_2O



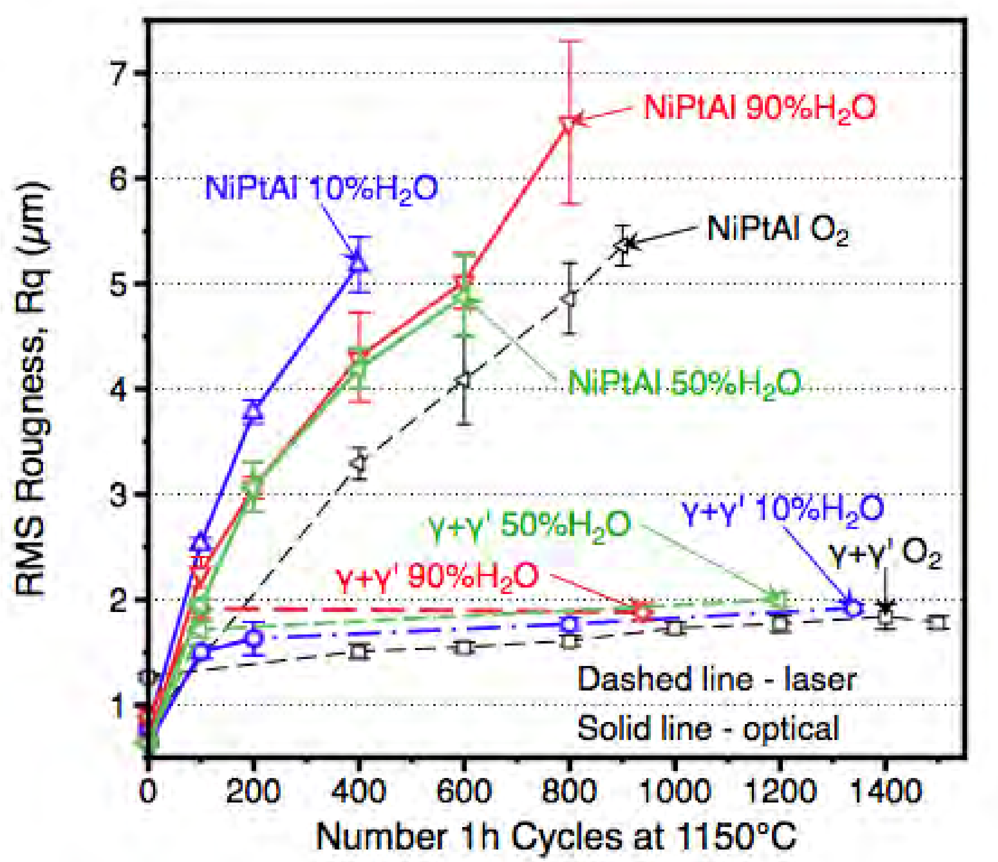
β-NiAl bond coating: 37% decrease in average life

γ-γ' Pt diffusion: higher average but larger variation

β explanation: rapid roughening

Profiled 4th specimen without YSZ coating

1150°C, 2102°F



bars: standard deviation of 6 lines or 5 areas

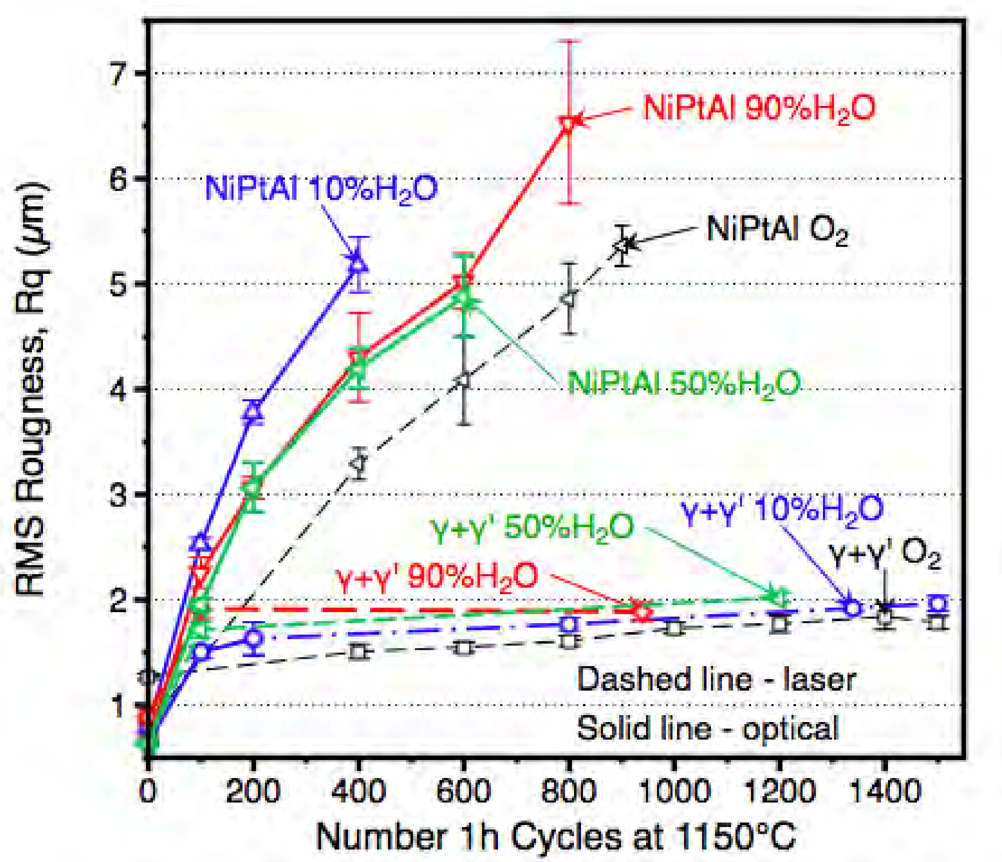
Laser profilometry: dashed lines
Optical profilometry: solid lines

Some variation in Rq

γ-γ' Pt diffusion: little effect of water vapor on Rq

β explanation: rapid roughening

Profiled 4th specimen without YSZ coating



1150°C, 2102°F

Time to Rq=5		Life
0%H_2O:	820h	907h
10%H_2O:	360h	427
50%H_2O:	600h	573
90%H_2O:	600h	760

bars: standard deviation of 6 lines or 5 areas

Laser profilometry: dashed lines

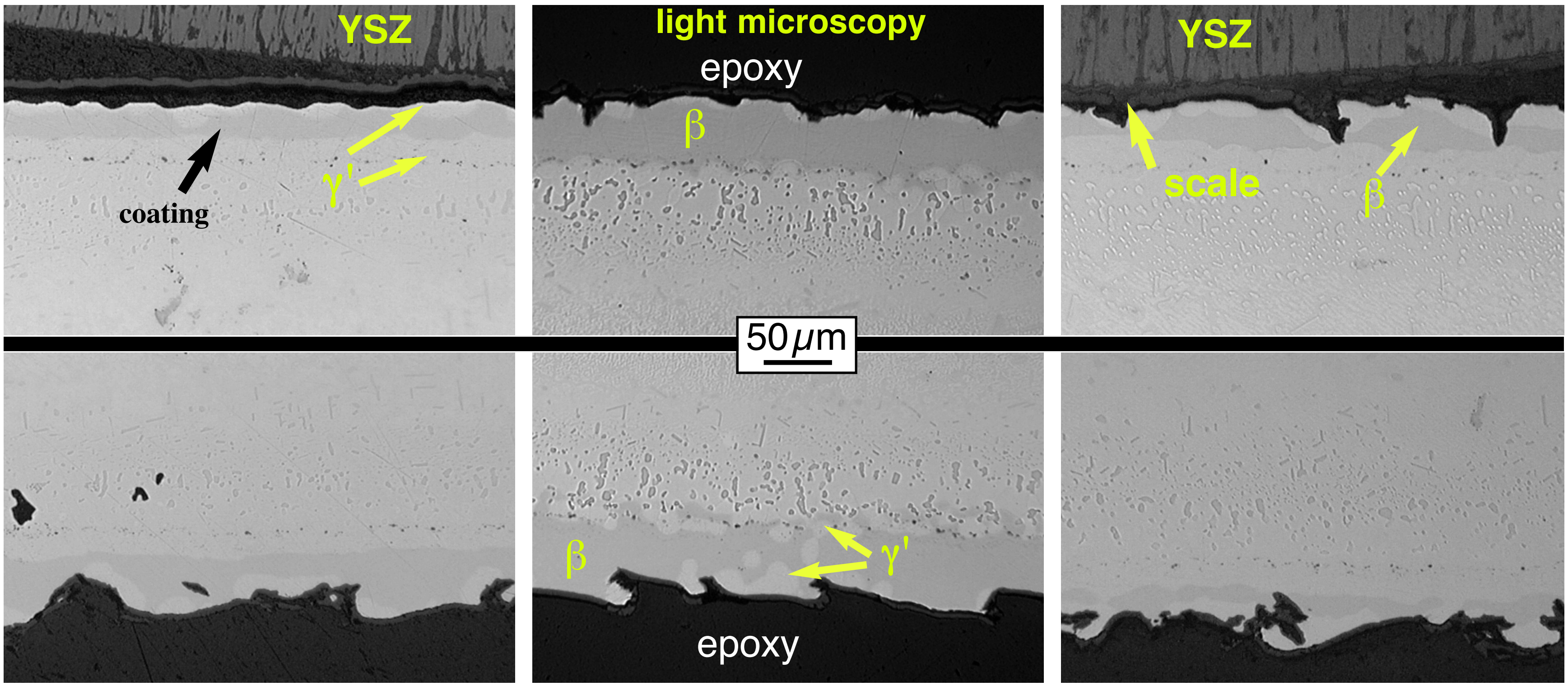
Optical profilometry: solid lines

γ-γ' Pt diffusion: little effect of water vapor on Rq

Why does water vapor make β-NiPtAl rumple more?

Morphology of β-(Ni,Pt)Al

Epoxy-mounted polished cross-sections after failure



0%H_2O: 800 cycles | 10%H_2O: 340 cycles | 90%H_2O: 800 cycles

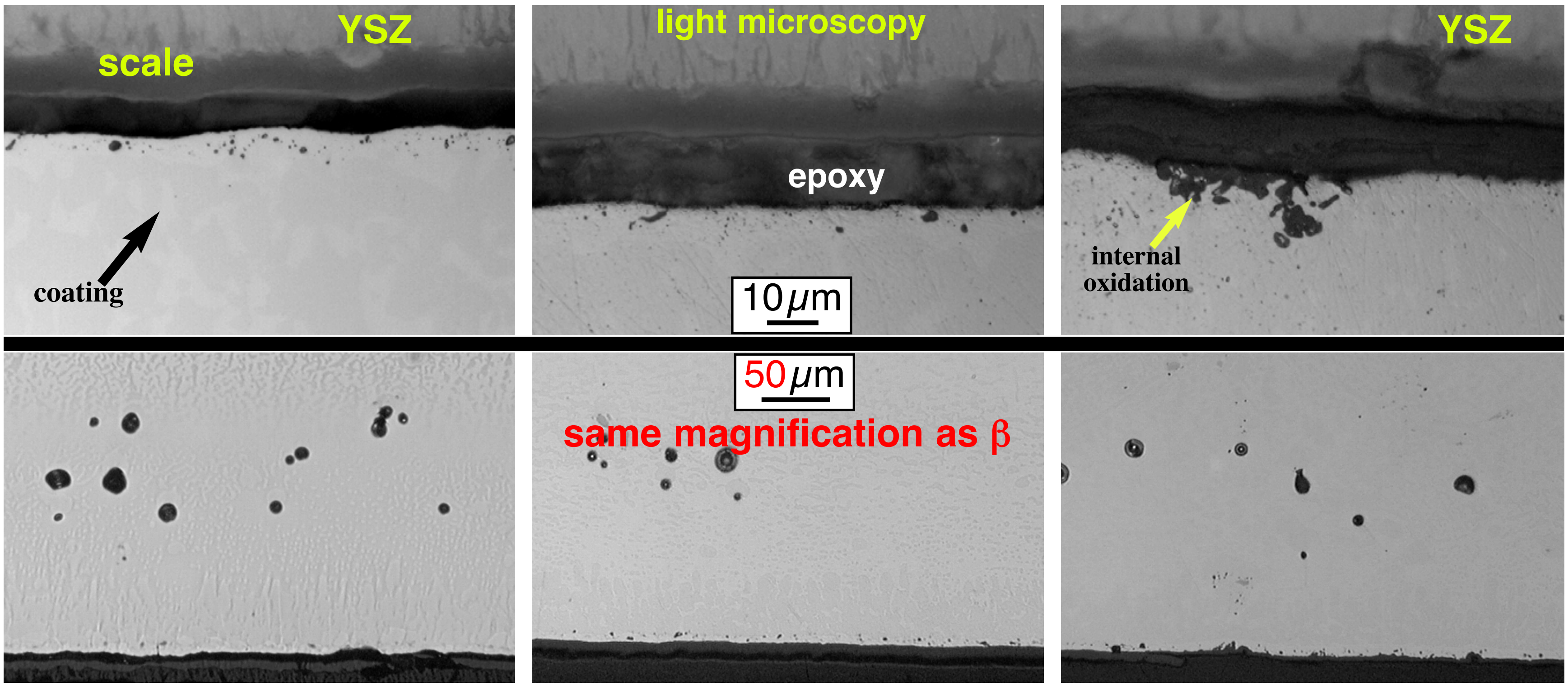
10%H_2O - much shorter time, rougher, more β phase

0% & 90% H_2O - same failure time, β similar (?)

Uncoated rougher, but YSZ-side ratcheted with H_2O

Much flatter γ-γ' coatings

Epoxy-mounted polished cross-sections after failure

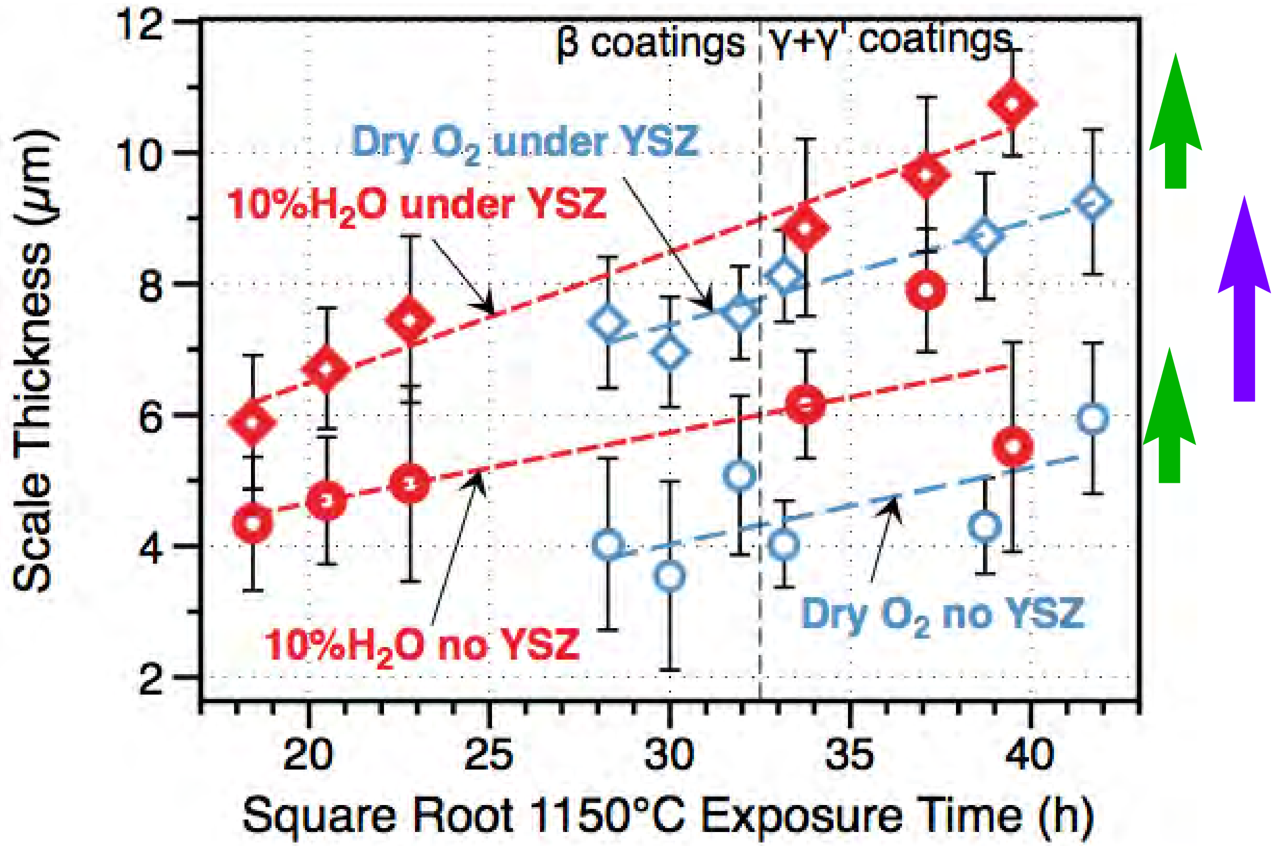


0%H_2O: 1100 cycles 10%H_2O: 1377 cycles 90%H_2O: 1234 cycles

In all cases:
- Continuous γ layer at metal interface
- Some internal oxidation observed
- Scale thickness similar, thinner in O_2?

Scale thicker in 10% H_2O

Average after each 0%+10% TBC failure at 1150°C



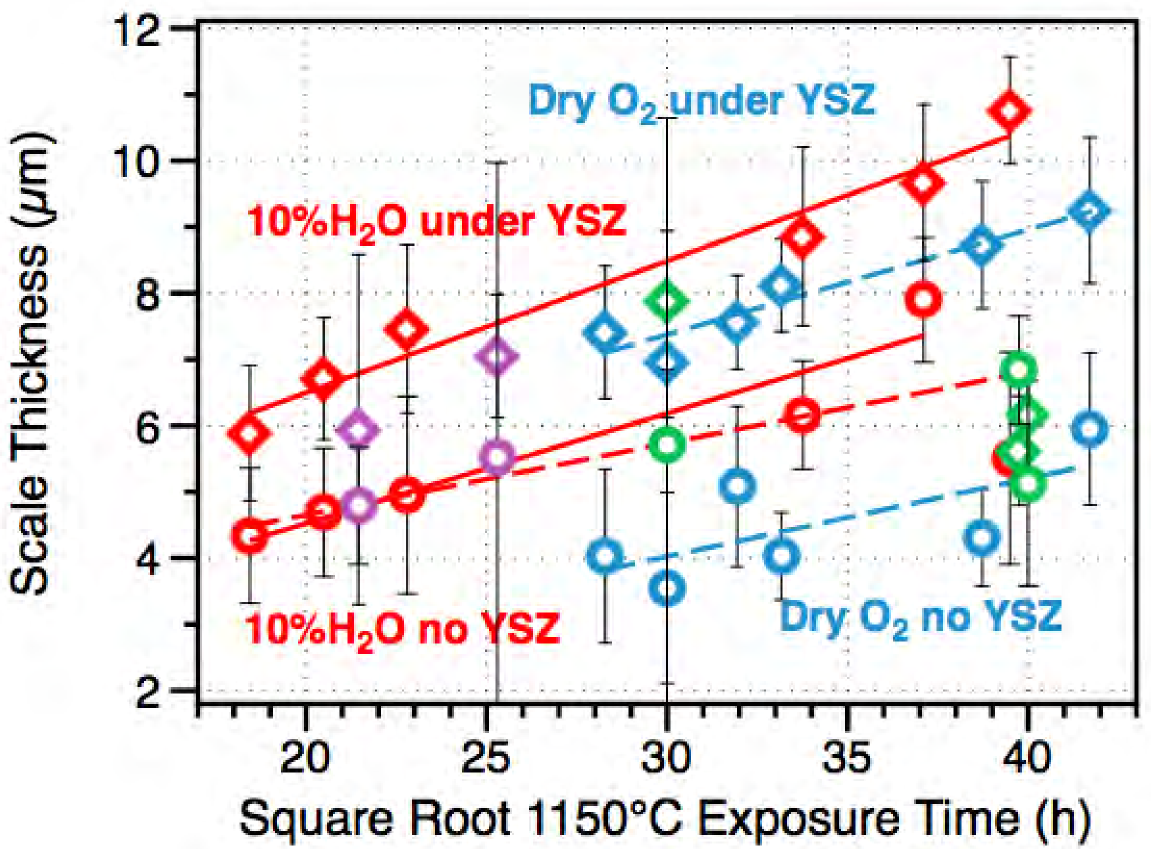
Two observations:

#1 scale thicker underneath YSZ layer

#2 scale thicker with the addition of water vapor

More water vapor - less clear

Average after more TBC failures at 1150°C



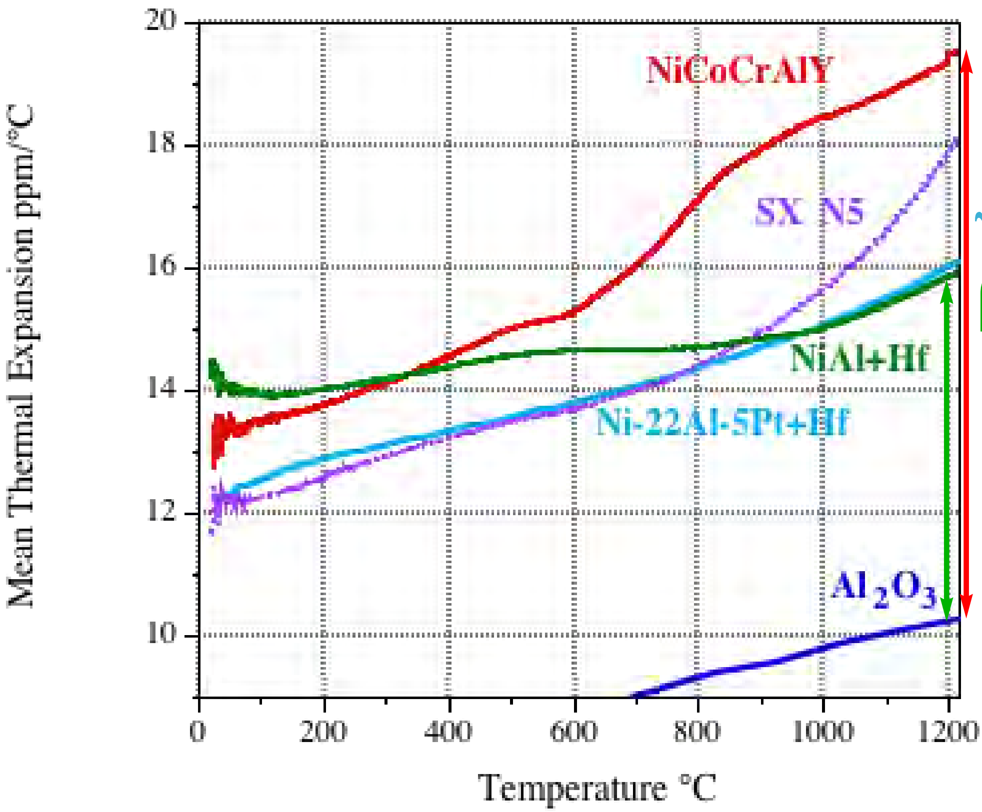
0%
10%
50%
90%

Another observation:

#3 Scale was same as 10% or thinner at higher H_2O

1100°C used for MCrAlY coatings

Thermal expansion difference among coating classes



MCrAlY

γ+γ' NiPtAl, Pt diffusion

β-(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)

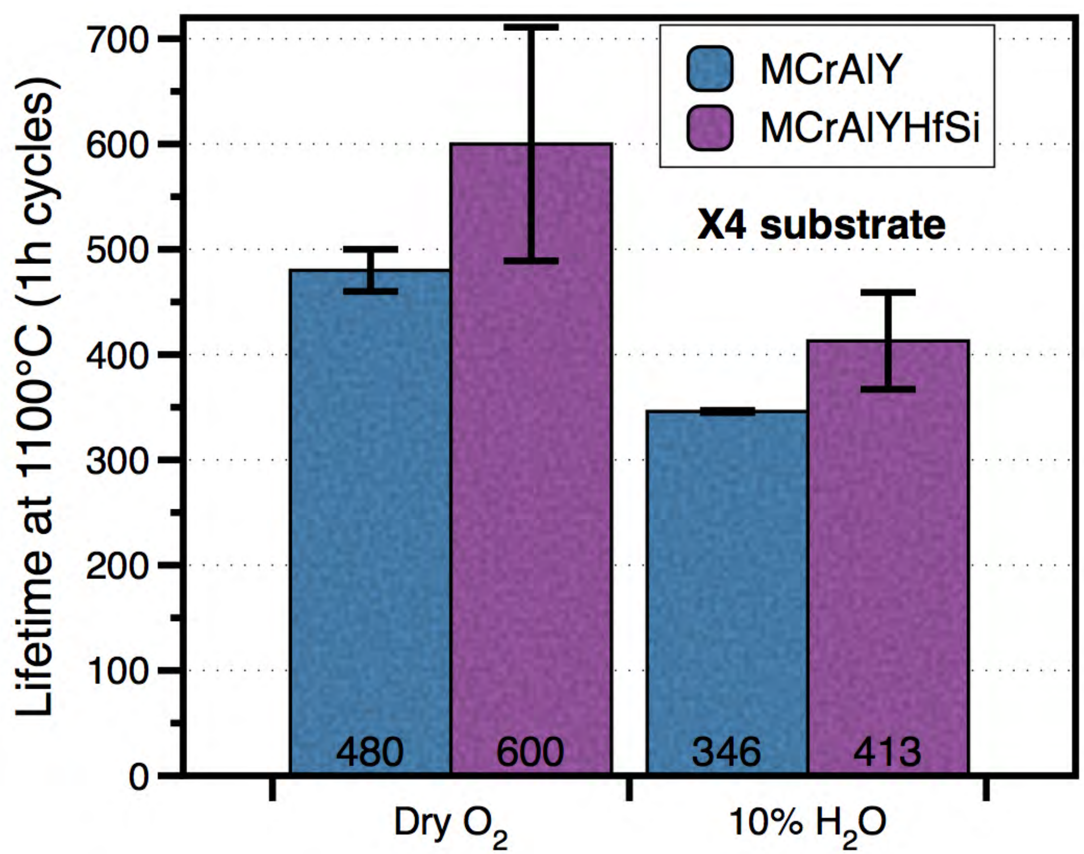
X4: 13.0Al,10Co,8Cr,0.9Re,1.2Ti,17S-270Hf

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

or 0.4Y, 0.07Hf, 0.65Si

10% H_2O reduced TBC life ~30%

1100°C: two bond coatings on CMSX4 + APS YSZ



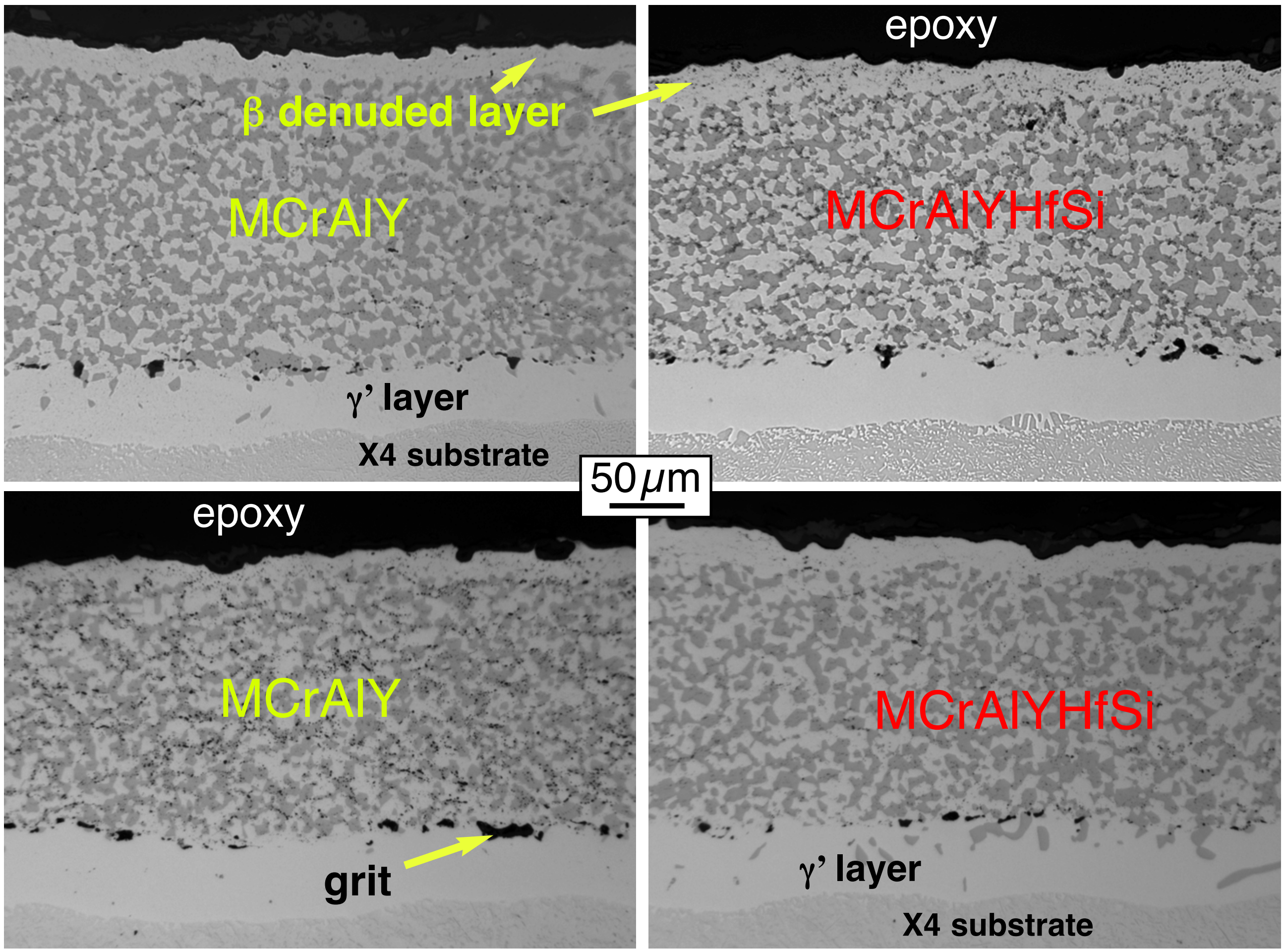
H_2O reduced coating lifetime by 30% in each case

Longer lifetime with MCrAlYHfSi in both cases

same composition except for Hf and Si

Morphology of HVOF MCrAl

Epoxy-mounted polished cross-sections after failure



0% H_2O

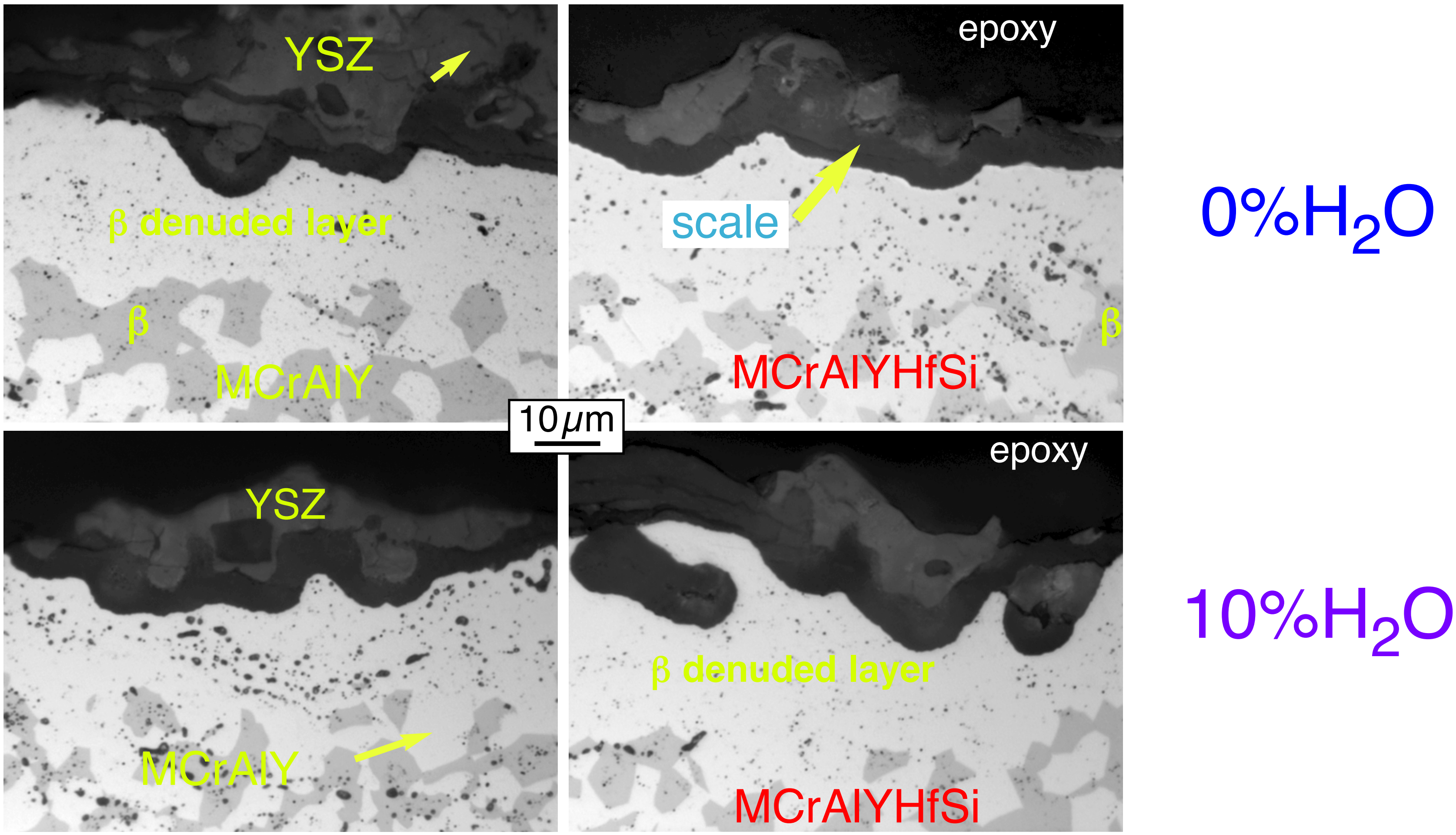
10% H_2O

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

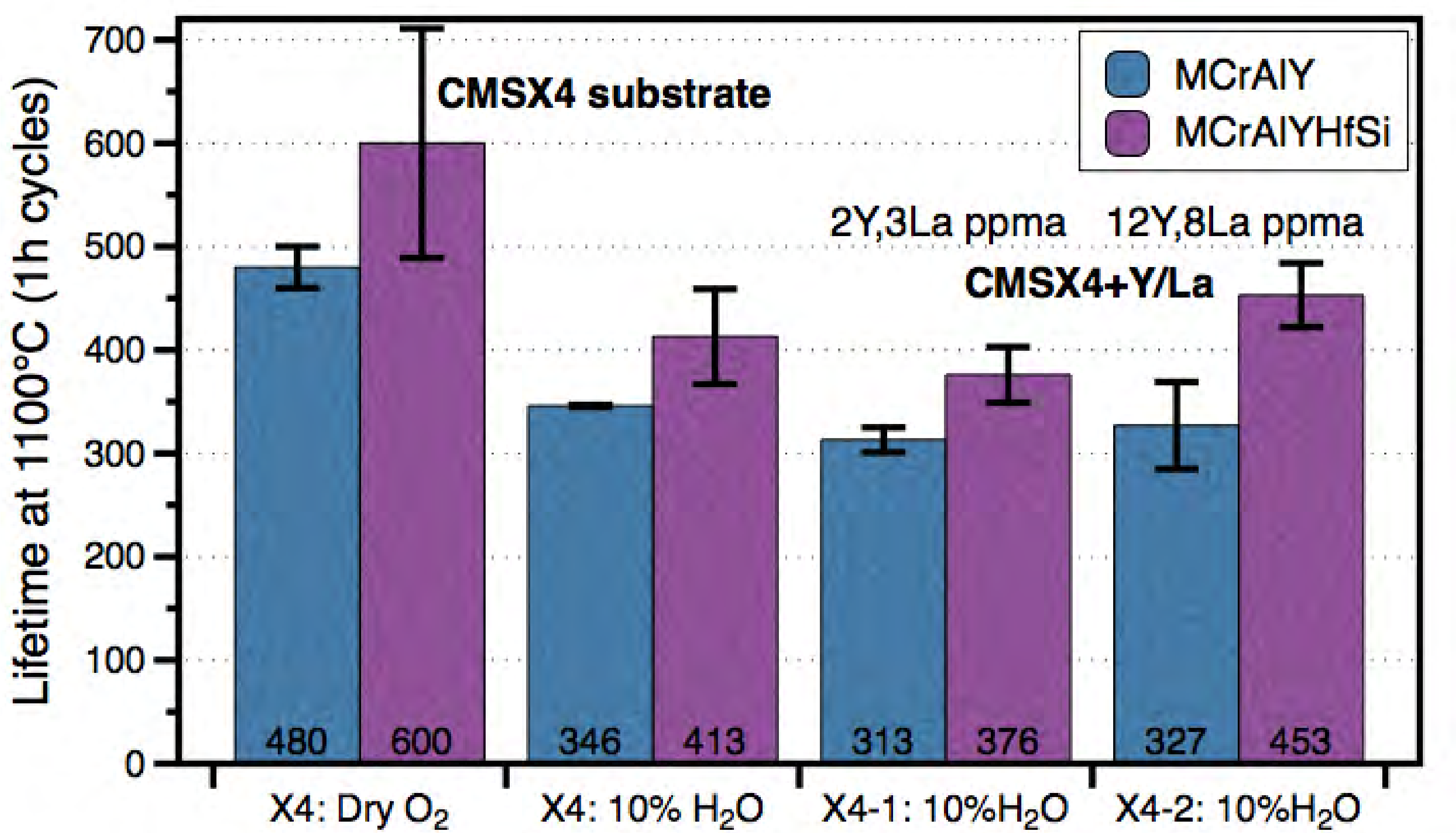


Rougher areas: more alumina scale + YSZ attached

~100% APS YSZ spallation leaves little to analyze

10% H_2O: no dopant effect

1100°C: two bond coatings on CMSX4 w/o Y-La

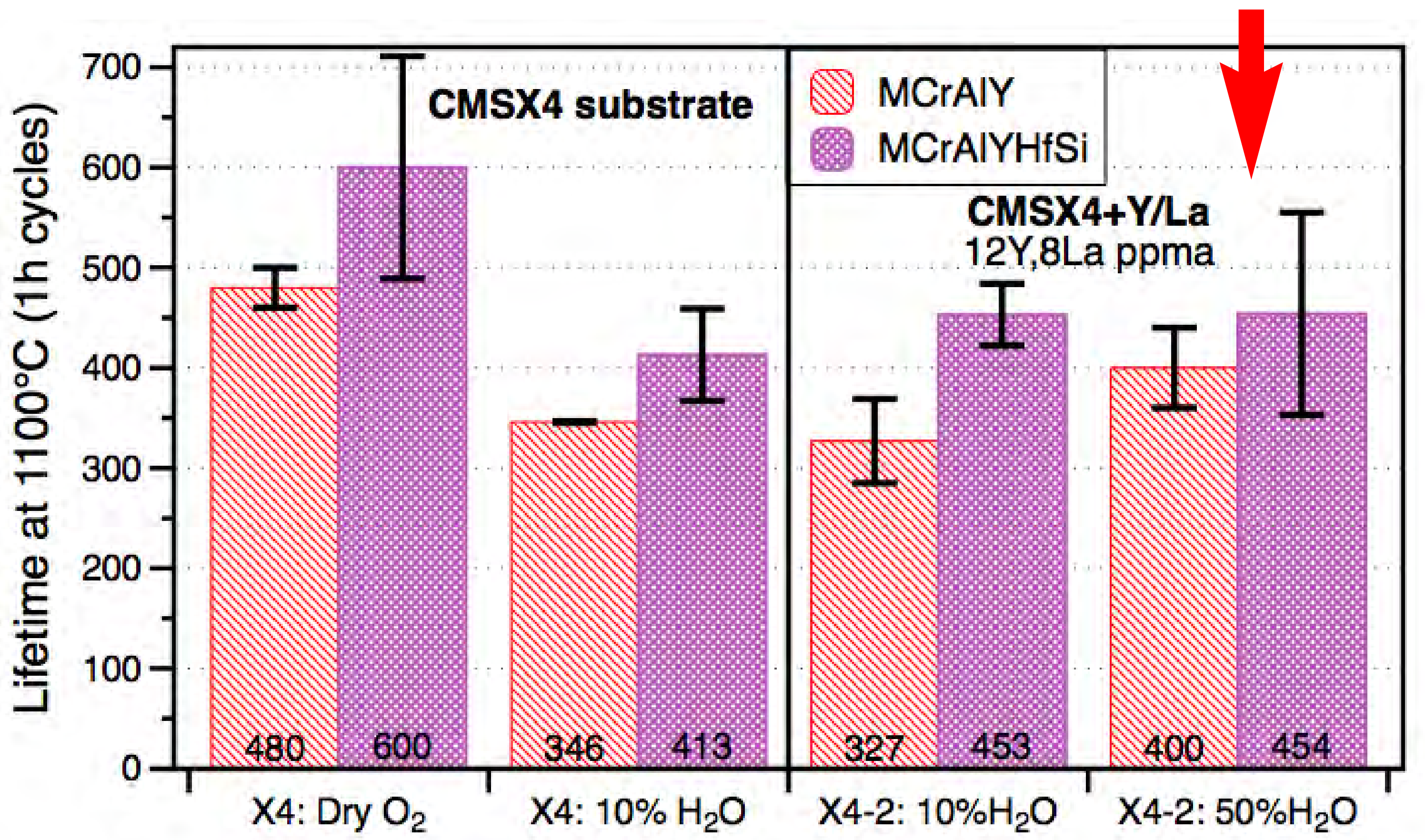


No change in average lifetime among three alloys

(New X4 baseline alloy with similar Al content)

50% H_2O: no effect on TBC life

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

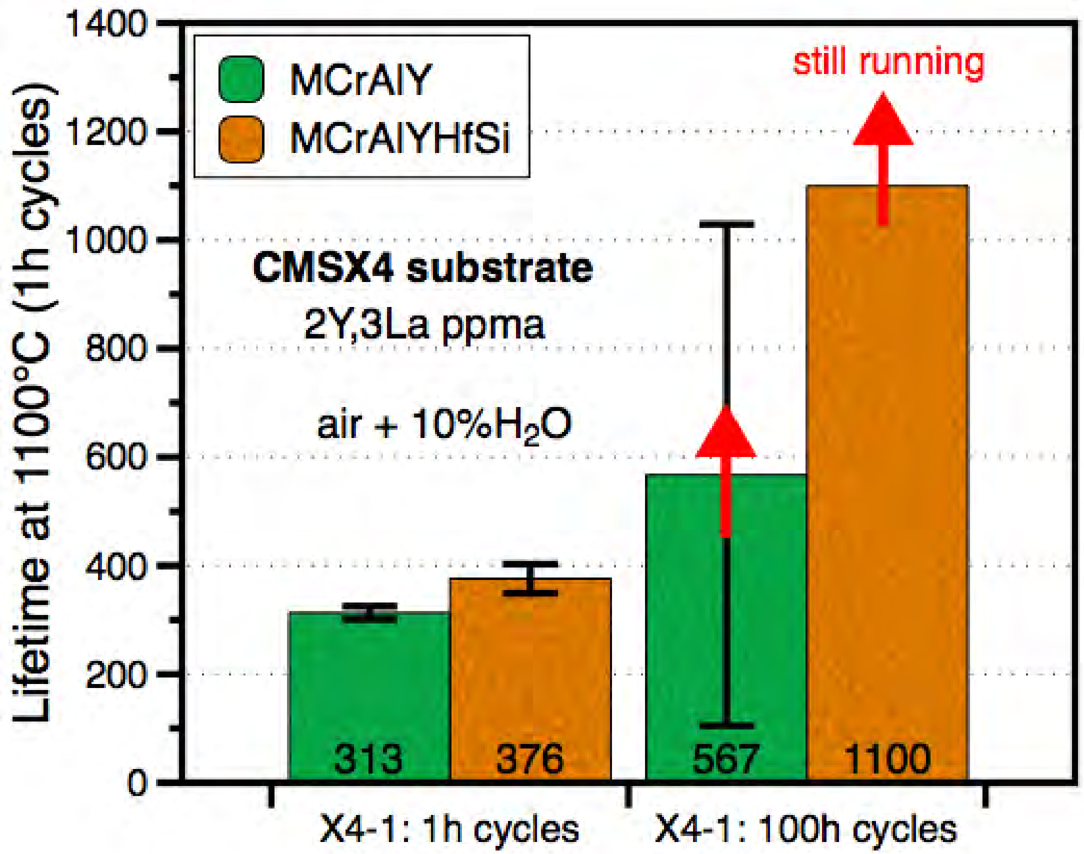


Similar to diffusion coatings, higher water vapor content did not reduce TBC lifetime.

Characterization in progress

100h cycles increased lifetime

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



100h cycles in tube furnace with slow heat/cool

4 of 6 coatings still running.

Characterization helps understanding

Motivation for characterization task:

- Developing mitigation strategies is very difficult without understanding the role of dopants & H_2O
- Strong interest in the alumina scale but typically <10μm in thickness
- Worked from light microscopy to SEM to TEM

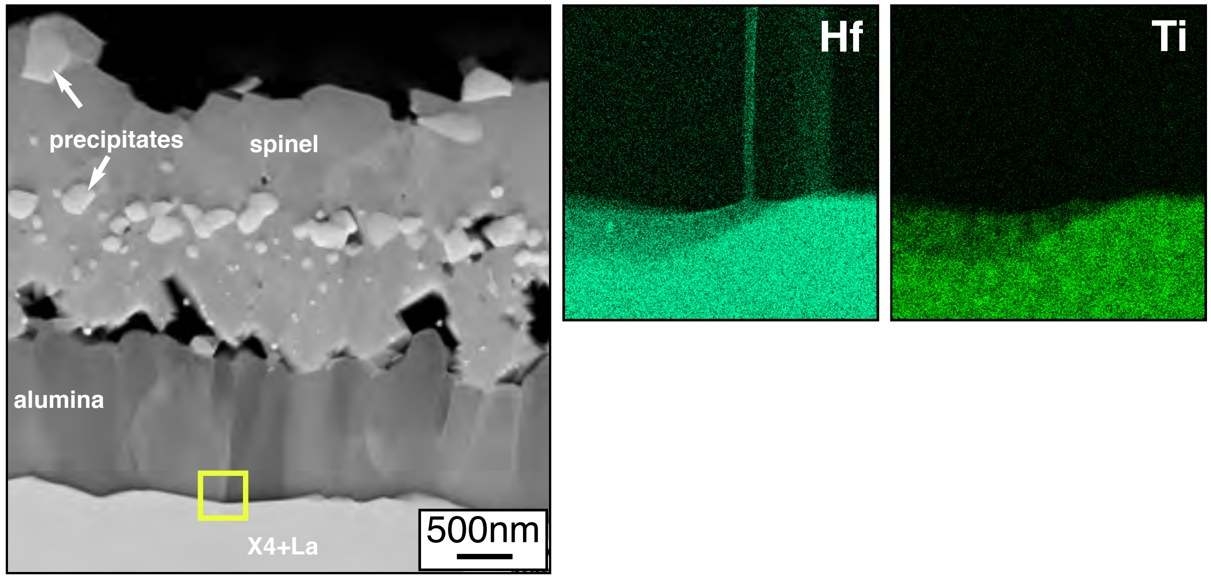
FY11 tasks:

- bare and coated X4 and X4-2 (with Y and La)
- model alloys to understand co-segregation with substrate containing Hf, Ti, Y and La
- SEM characterization of scale thickness in different H_2O environments

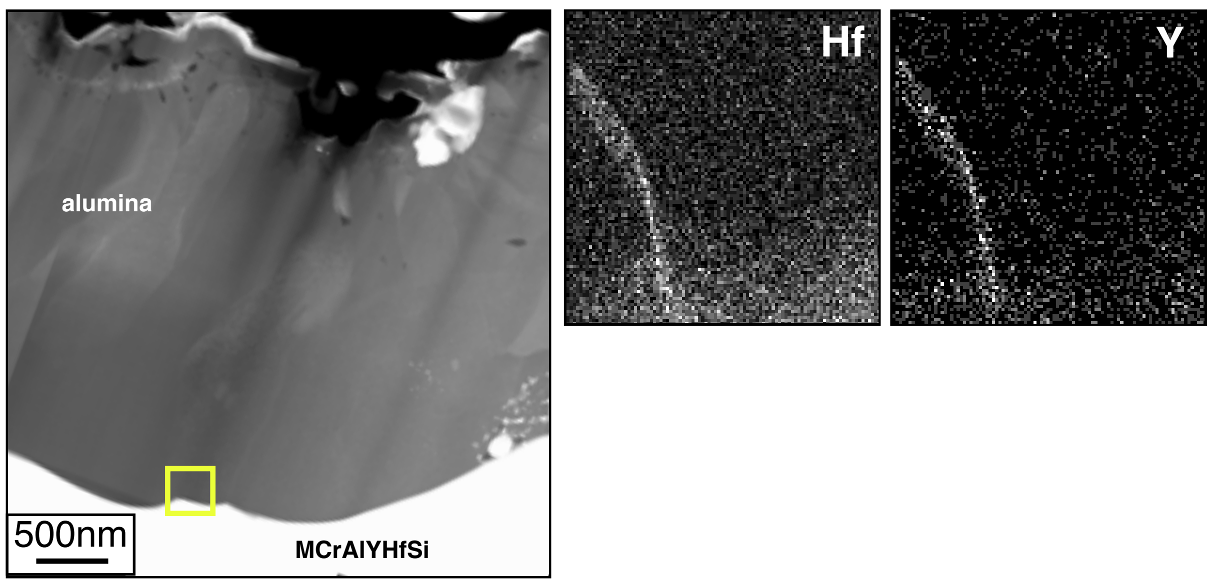
Segregation in bare & coated X4-2

Oxidized for 100h at 1100°C in dry O_2

Bare

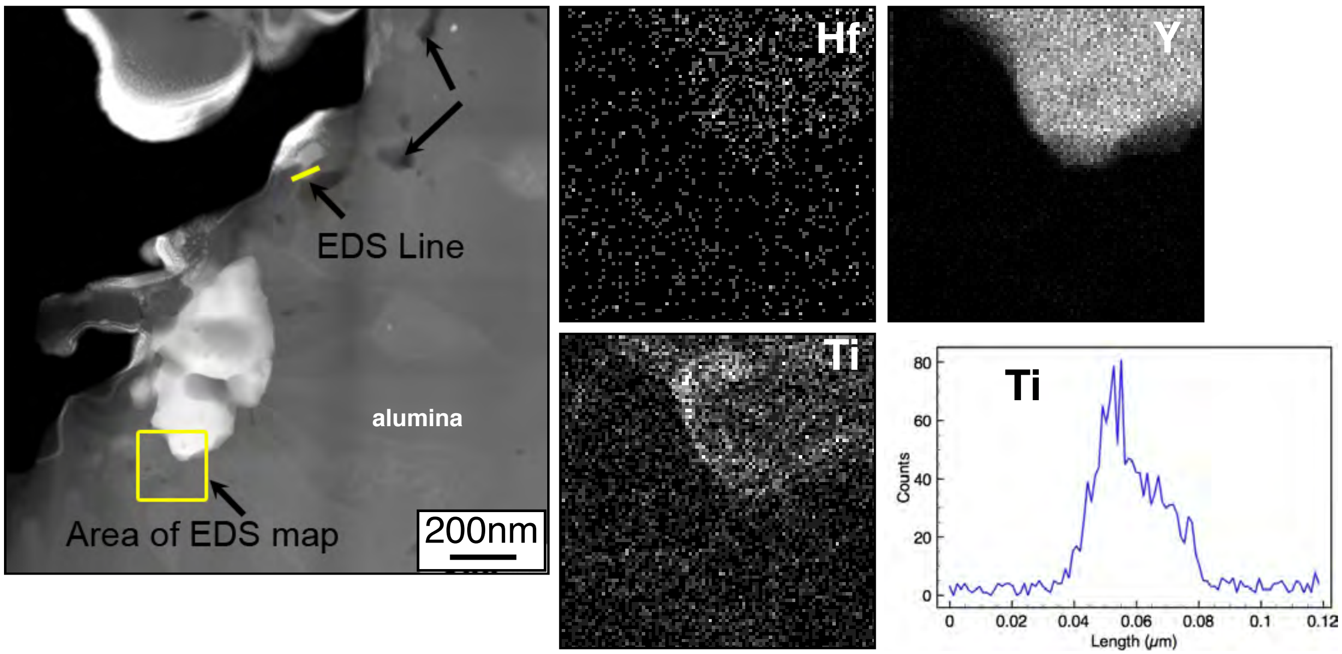


HVOF MCrAlYHfSi



Coated X4-2 - found Ti in scale

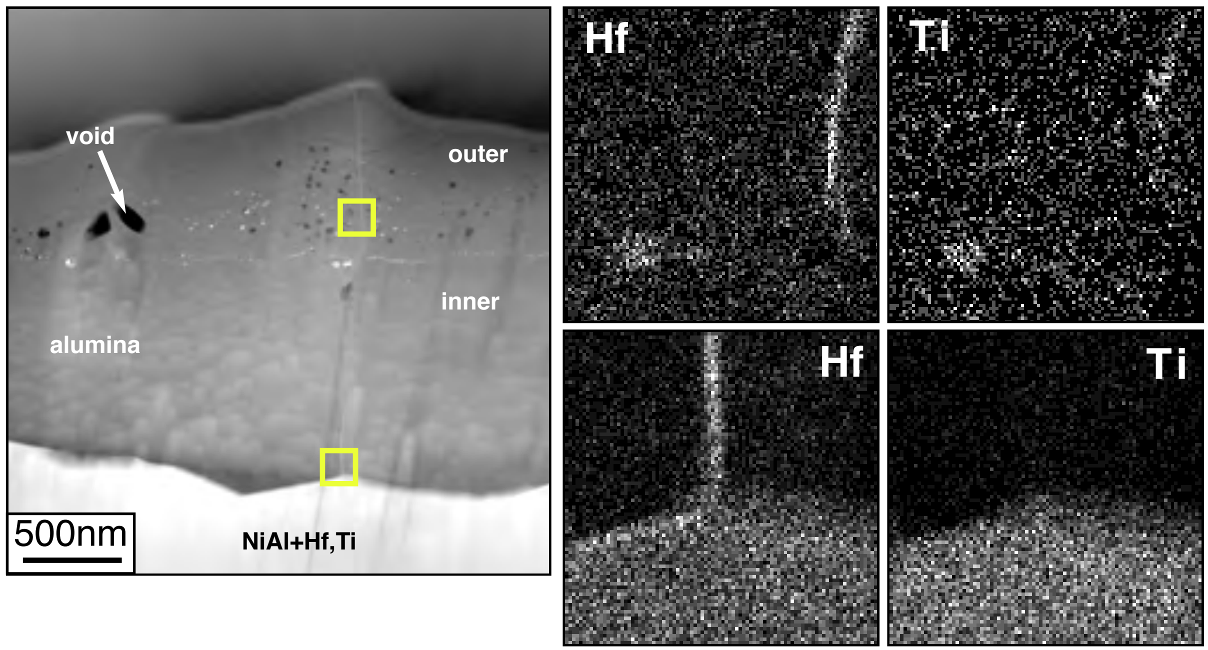
Oxidized for 100h at 1100°C in dry O_2



Demonstrates that Ti diffuses through coating
(No Ti in MCrAlYHfSi coating, 1% in X4-2)

Hf+Ti co-segregation in NiAl

Oxidized for 100h at 1100°C in dry O_2



Alumina scale complicated by θ-α transformation

Hf strongly segregated

Ti segregation in outer layer only

FY12 Work

New set of diffusion coatings being fabricated
- repeat 10% result and try additional gases

Model alloys to explore composition effects
- identify improved compositions (?)
- define role of Si in MCrAlYHfSi bond coating

HVOF/APS primary focus:
Coat 1483 (low Cr, no Ti) superalloy
Focus on MCrAlYHfSi bond coating
More testing with longer cycles
Include testing at lower temperature (900°C)
Increase to 5 specimens/condition
Explore coating pins (bars) rather than coupons
- more alloys available in ≤12mm bar (low Re)

Summary–take away points

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

10% water vapor appears to be more detrimental to TBC performance than 50 or 90% H_2O

Demonstrated that Ti from superalloy diffused through coating

At 1150°C, γ-γ' coatings were the most resistant to higher water vapor contents

Further work needed to identify H_2O mechanism
Understanding may suggest mitigation strategy