

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

B. A. Pint

Corrosion Science & Technology Group
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

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Office of Fossil Energy (B. White, project monitor)

Acknowledgments

Task leaders: **J. A. Haynes** - coatings
 K. A. Unocic - characterization (TEM)

M. Lance - PSLS, 3D LM

G. Garner, M. Stephens - oxidation experiments

T. Lowe - characterization

D. W. Coffey - TEM specimen preparation, FIB

T. Jordan - metallography

D. Leonard - EPMA



George Garner

Ken Murphy, Howmet - X4 superalloy substrates

Anand Kulkarni, Siemens - 1483 superalloy substrates

Dan Vicario, Capstone Turbines - 247 superalloy substrates

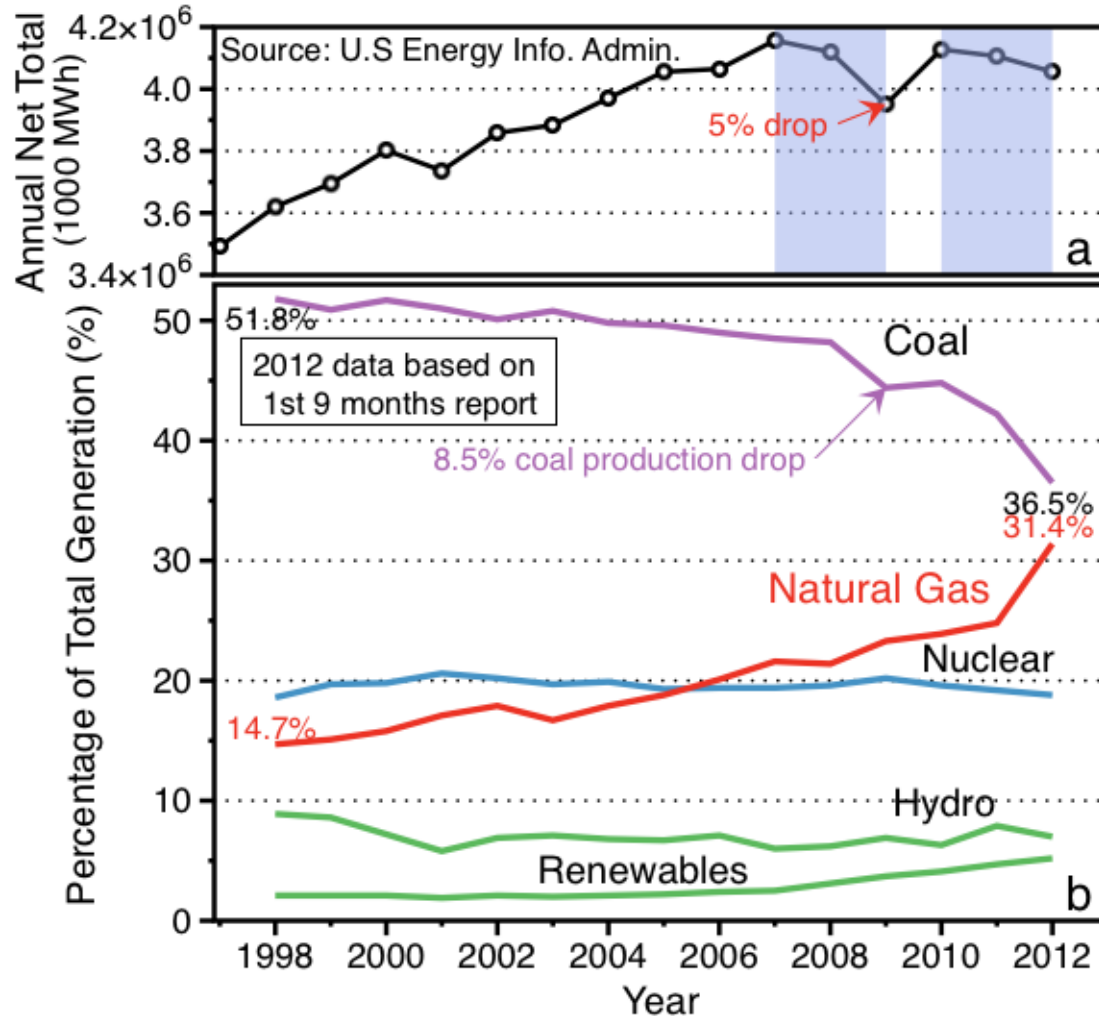
Jacqui Wahl, Cannon-Muskegon - CMSX7,X8 substrates

Ben Nagaraj, GEAE - N515 alloy, 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

How does coal compete?



Demand not growing

NGCC + Renewables increasing

In a stagnant U.S. market where natural gas is cheap?

Is coal gasification the solution?

Integrated gasification combined cycle (IGCC)

- similar turbine/steam generator as NGCC
- method to control NO_x , SO_x , Hg, CO_2 ...
- two full size IGCC plants coming on line in the US



Edwardsport, IN (Duke Energy)
\$2.88 billion (Carbon capture ready)
618MW, GE Energy turbines, 2013 start



Kemper County, MS (Southern Co.)
\$2.67 billion, ~60% CO_2 capture (oil recovery)
550MW, Siemens turbines, 2015 start

The U.S. will find out.

What are the issues with IGCC?

#1 IGCC “syngas” turbines are “de-rated”

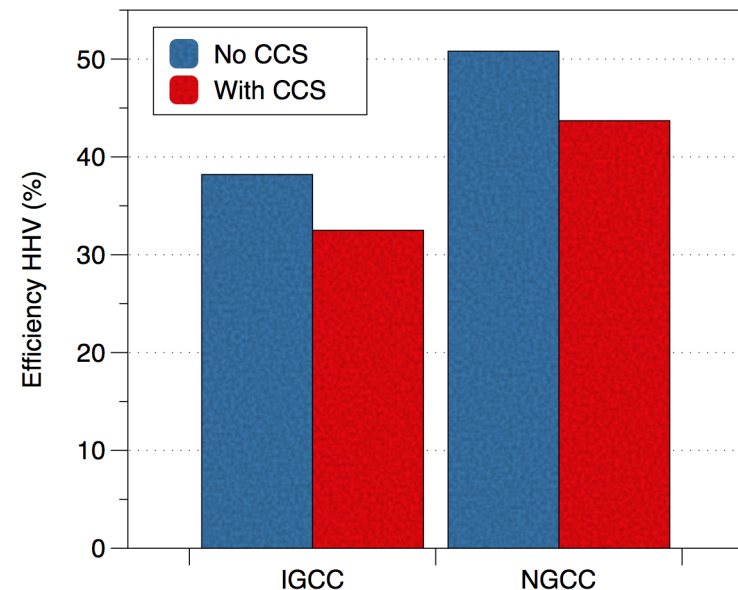
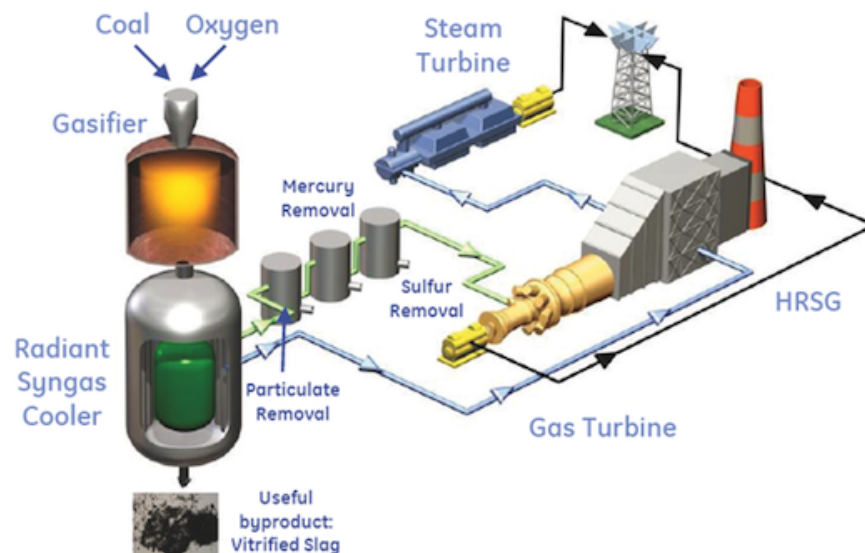
Need to understand what drives that decision

- higher H_2O , sulfur and/or ash from coal?

5-10X more fuel (syngas lower caloric value)

Current ORNL focus: more durable coatings

- potential IGCC and NGCC benefit



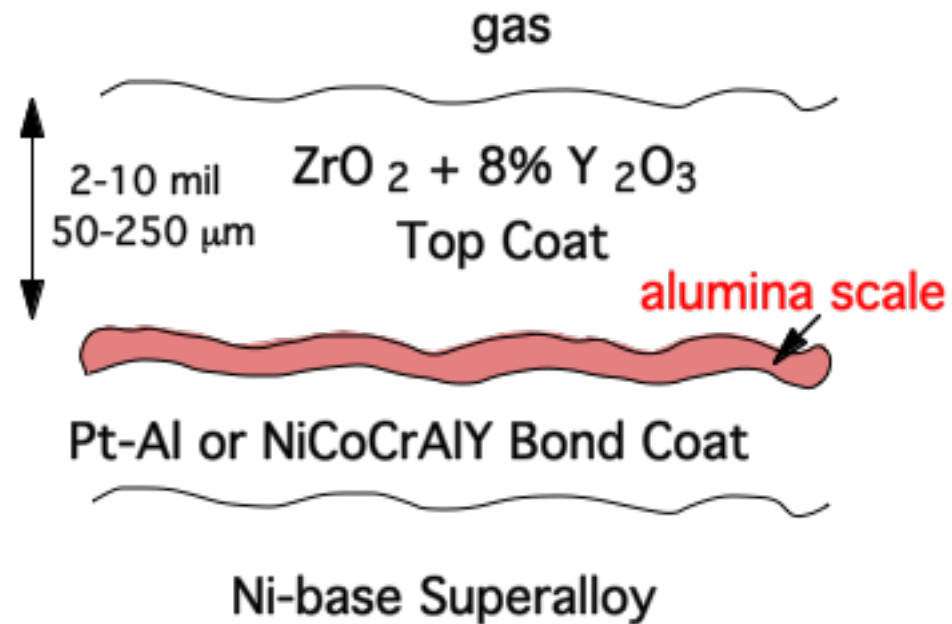
Looking for coating solutions

New environments (higher H₂O, CO₂, SO₂)

CTSR: new top coat

New bond coatings?

Different substrates



#1 More durable coatings will benefit
IGCC and NGCC

#2 Focus on alumina scale as “weak link”

Outline

FY10 (initiated 3 related “pre-competitive” tasks)

Task 1: superalloy ppm Y, La dopant effects

Task 2: water vapor effects “Wet vs. Wetter”

Task 3: characterization

FY14

Task 1: Superalloy effects (Cr, Re, Hf, Ti...)

Task 2: Environment effects (H₂O, CO₂, SO₂)

Task 3: Characterization

- supports other tasks

Task 4: New compositions and processes

- B-doped bond coating

FY15

Future directions

- Partnership with Stonybrook

Several TBC groups investigated (3 YSZ samples per condition + 1 without YSZ)

Group	Alloy	Bond coating	Top coating	Comment
	N5	Diffusion $\beta/\gamma+\gamma'$	EB-PVD	“quick start”
1	X4±RE	HVOF Y±Hf	APS	RE/H ₂ O effect
	N5/N515	Diffusion $\beta/\gamma+\gamma'$	EB-PVD	repeat/low Re
2	1483/X4	HVOF YHfSi	APS	rougher, 1483
3	247/83/X4	HVOF YHfSi	CTSR APS	add 247
4	247	VPS ±B, ±Si	APS	rcvd 10/2014

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

X4/1483/247 - Siemens recommended

Task #1: Superalloy de-evolution

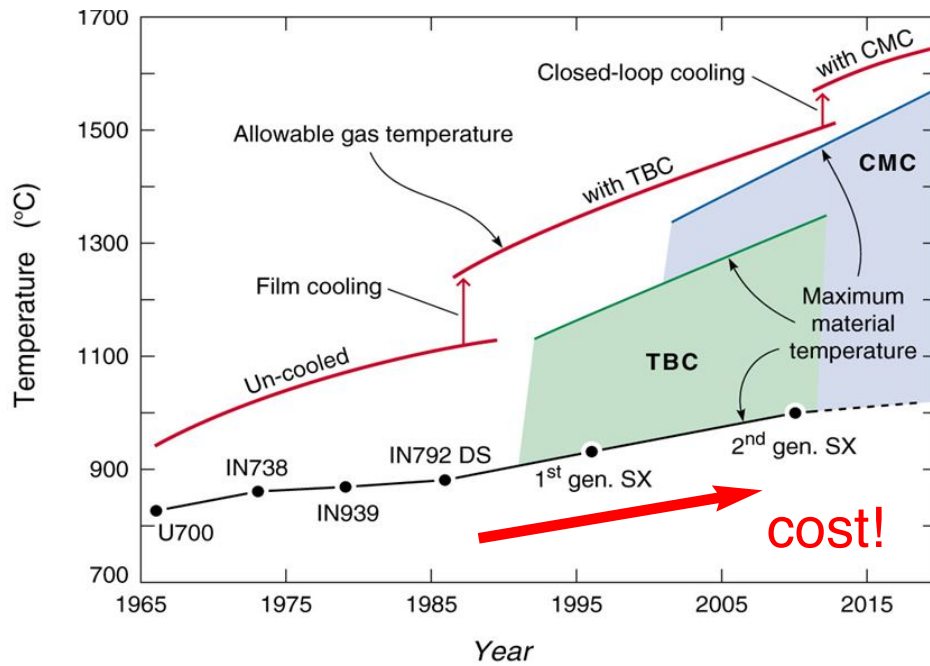
Land-based turbine drivers:

first cost drives sales

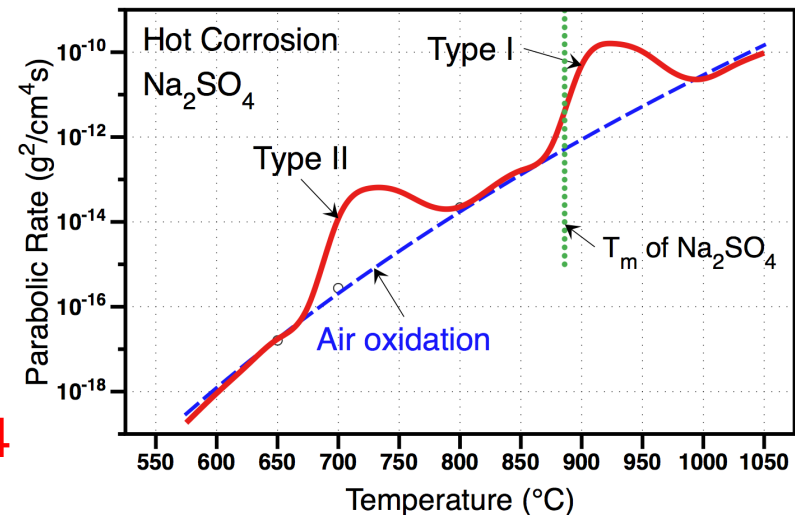
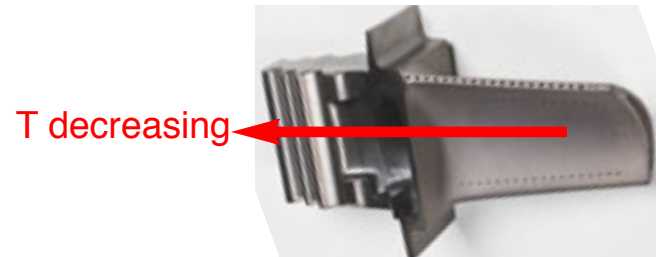
temperature/efficiency (not with cheap gas)

low-k TBC (lowers blade temperature)

hot corrosion in blade root (want higher Cr)

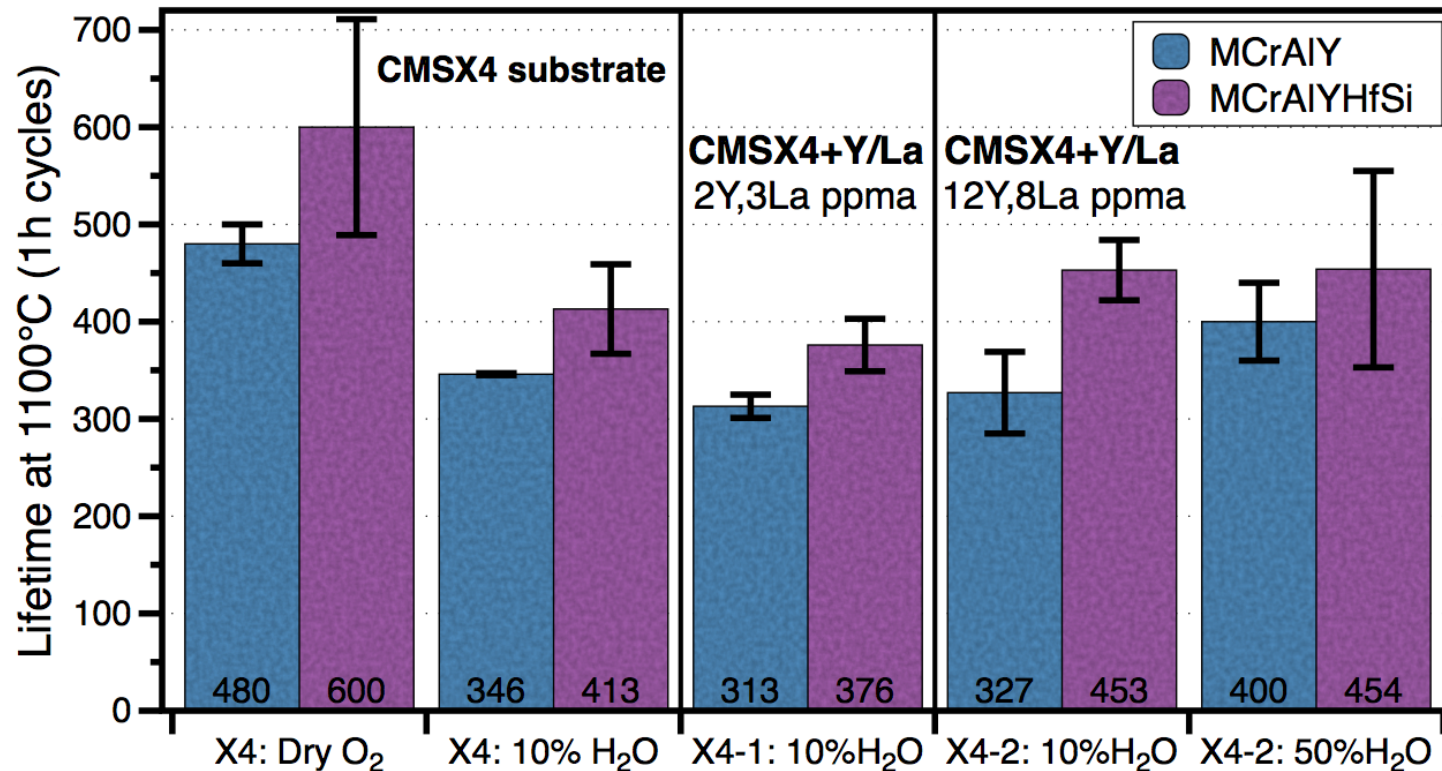


MarM247 \leftarrow PWA1483 \leftarrow CMSX4
 8Cr+1Hf 12Cr+4Ti 6Cr+3Re



Superior YHfSi bond coating used

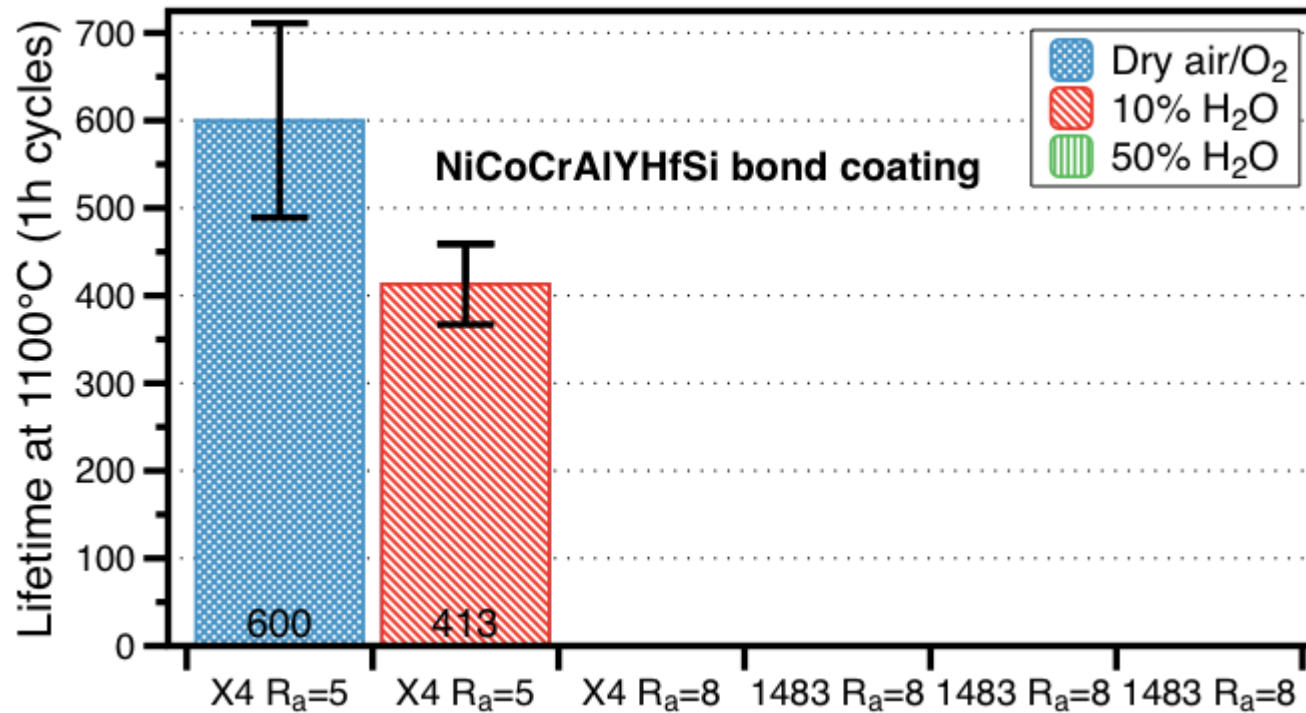
CMSX4 + APS YSZ: compared HVOF Y vs. YHfSi



Average lifetime of 3 similarly coated specimens
All conditions/substrates higher lifetime than
NiCoCrAlY bond coat made by same process

APS/HVOF: 1st batch baseline

1100°C, 1-h cycles: average 3 samples



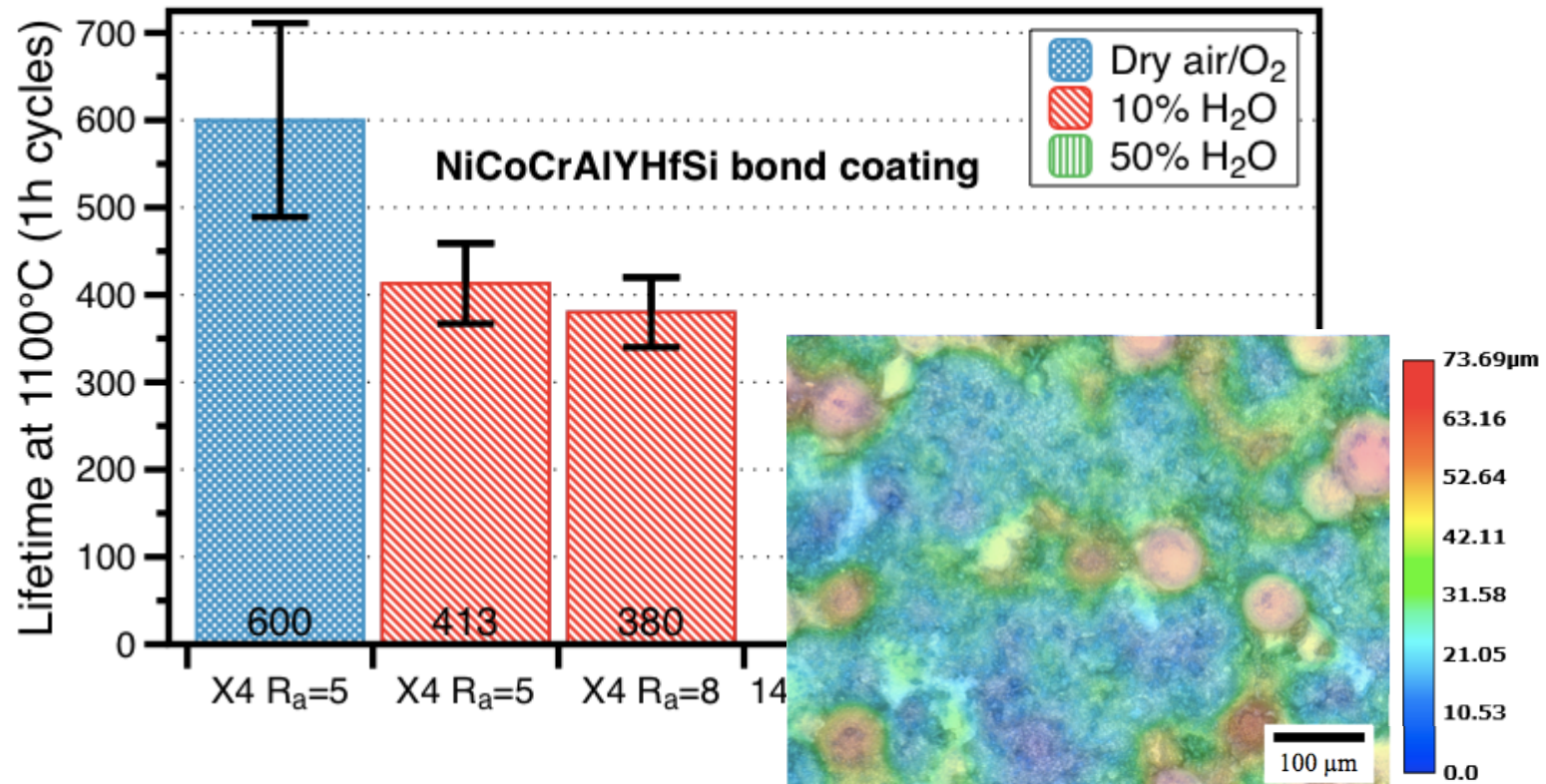
X4 substrate (2nd generation SX with 3%Re, 1%Ti)

Negative effect of H₂O observed

Air plasma spray YSZ top coating

Batch 2: $R_a \sim 8\mu\text{m}$ -similar lifetime

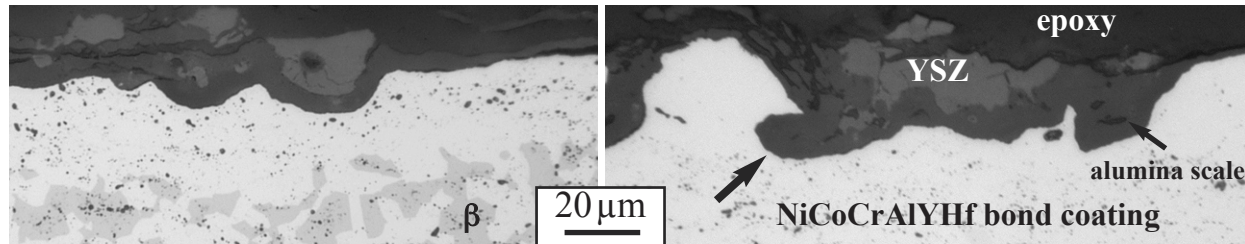
Air+10% H_2O : 1100°C, 1-h cycles



Higher roughness ($R_a \sim 8\mu\text{m}$) closer to industry
Lower coating thickness likely reduced lifetime

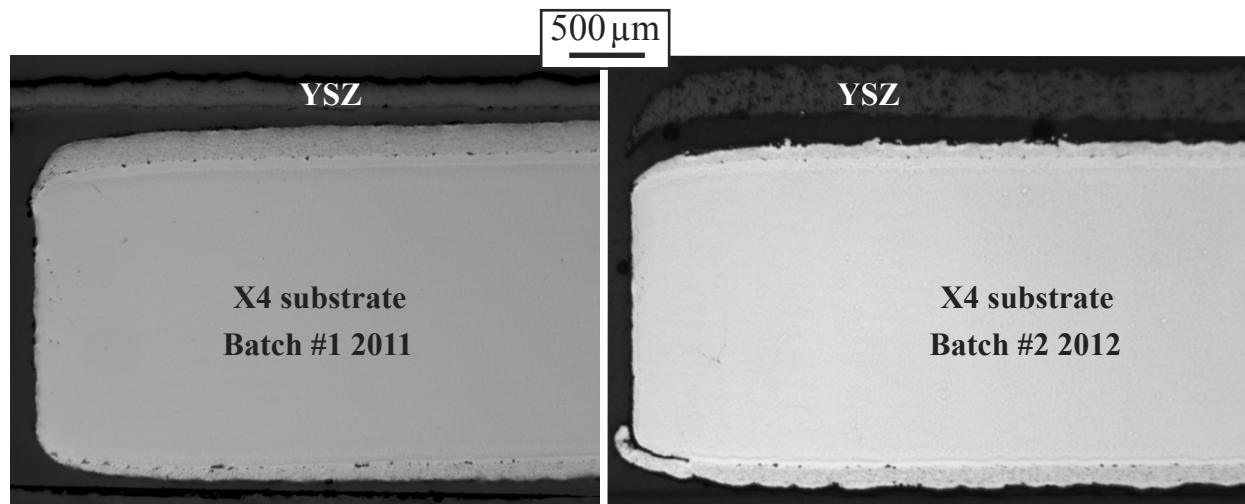
1 vs. 2: thickness & roughness varied

HVOF NiCoCrAlYHfSi on X4, 10%H₂O at 1100°C



Ra~5 440 cycles

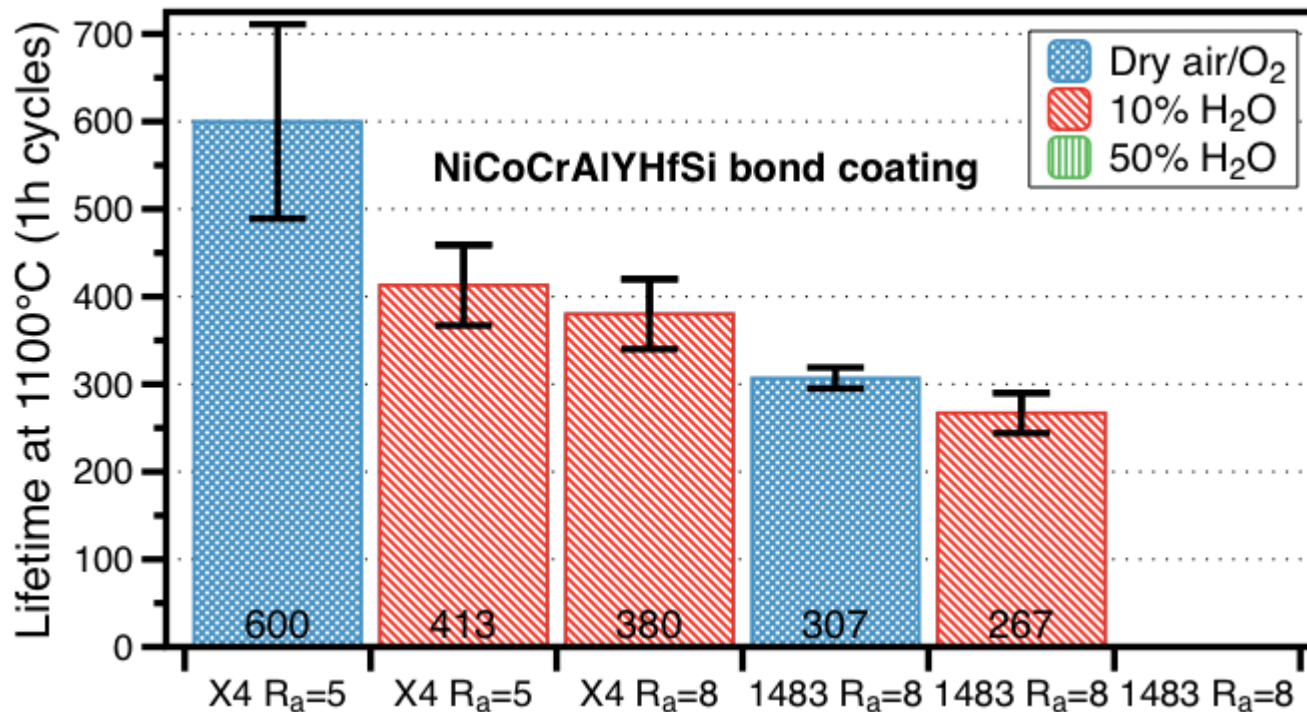
Ra~8 380 cycles



Rougher coating had similar $\sim 150\mu\text{m}$ coating
highest peak to substrate!
Much lower Al reservoir than prior coating

1483: lower lifetimes

Air+10% H_2O : 1100°C, 1-h cycles



Compare batch #2: R_a to ~8 μm

Lower cost 1483 substrate: no Re, 3.4%Al, 4%Ti

1st generation single-crystal superalloy

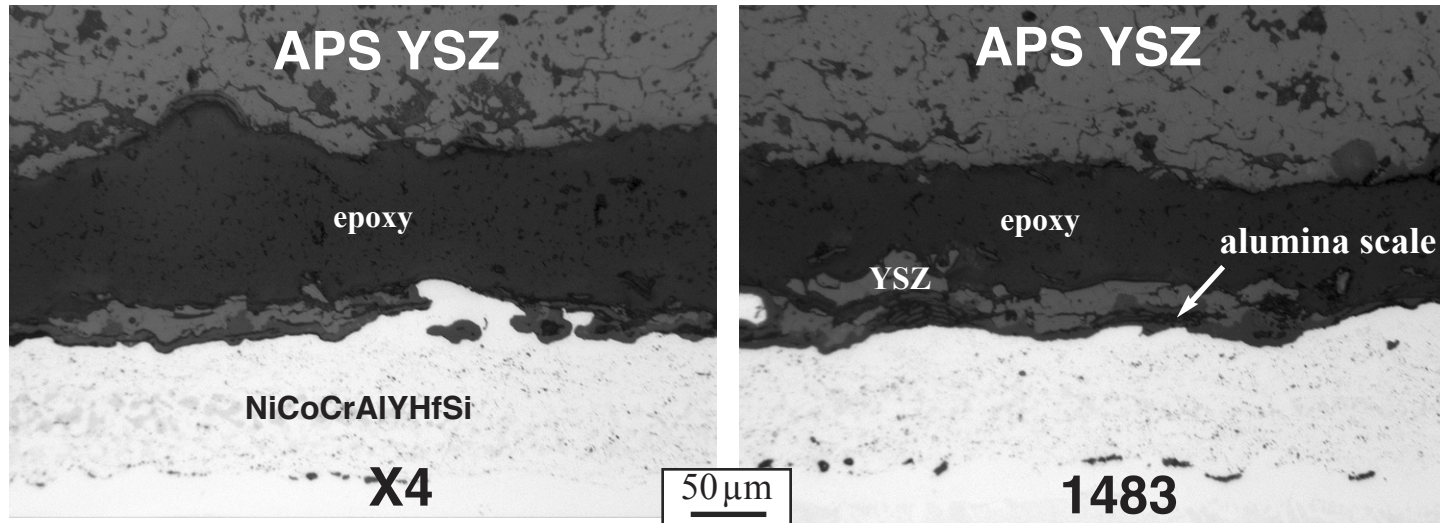
X4: 2.9%Re, 5.8%Al, 1%Ti

Similar morphologies with 1483

Light microscopy after exposure in air+10%H₂O

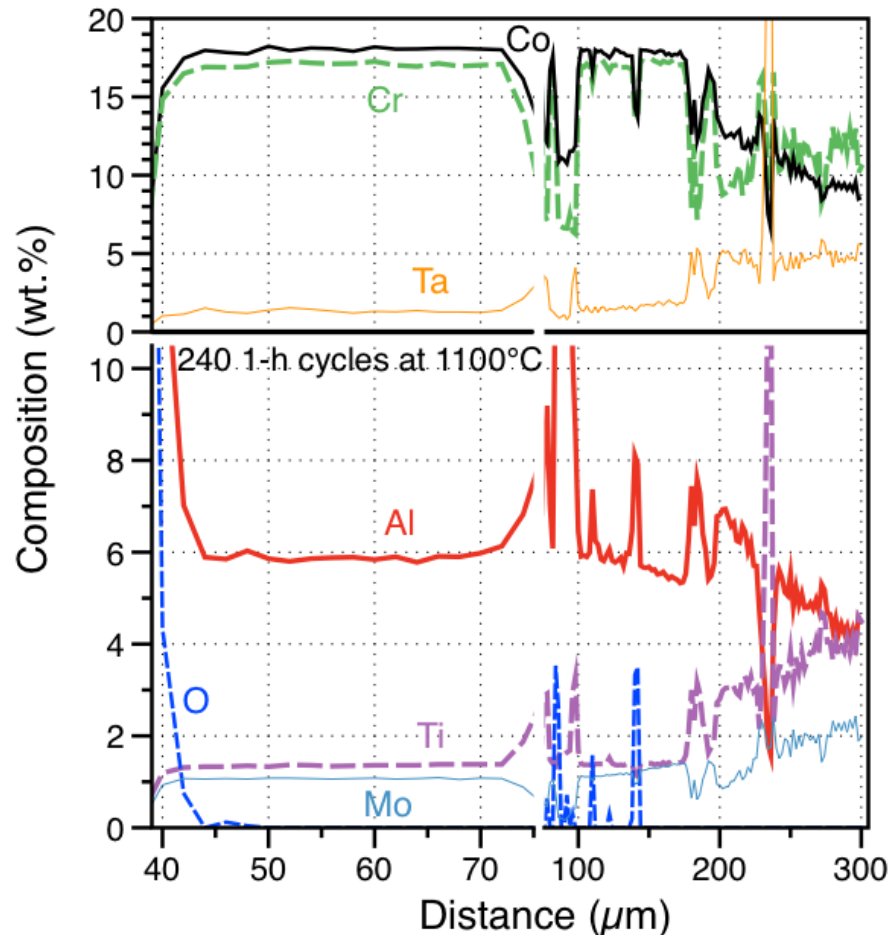
340, 1-h cycles, Ra~8

280, 1-h cycles, Ra~8



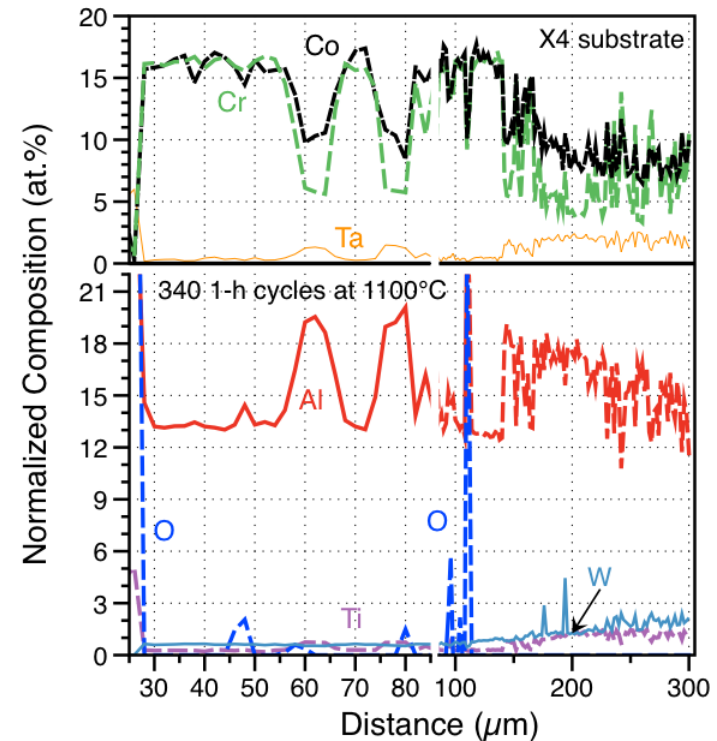
Lower Al content in 1483: more interdiffusion

Significant interdiffusion with 1483 1100°C, 240 1-h cycles, 50%H₂O



1483 substrate

X4 substrate



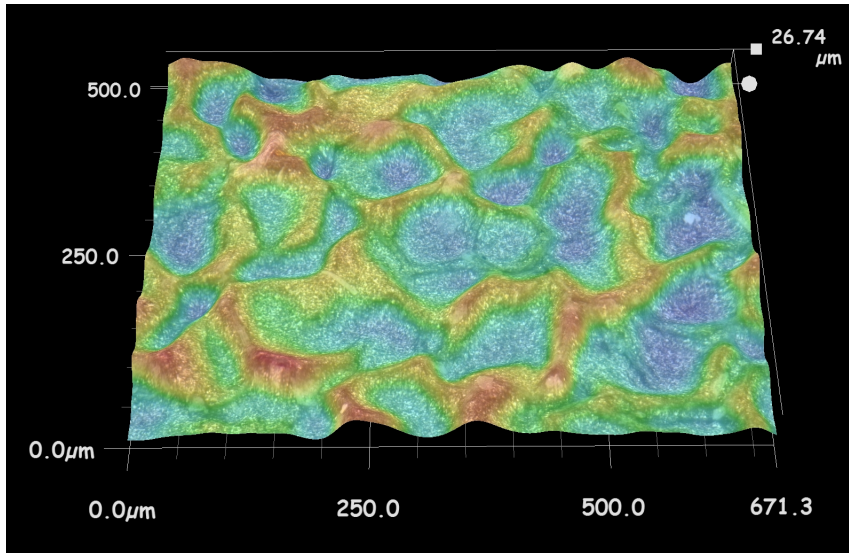
Al content dropped from 12% to 6wt%

1.4%Ti in the coating: what effect?

- 0.3%Ti in model NiCrAlYHf alloys: no debit

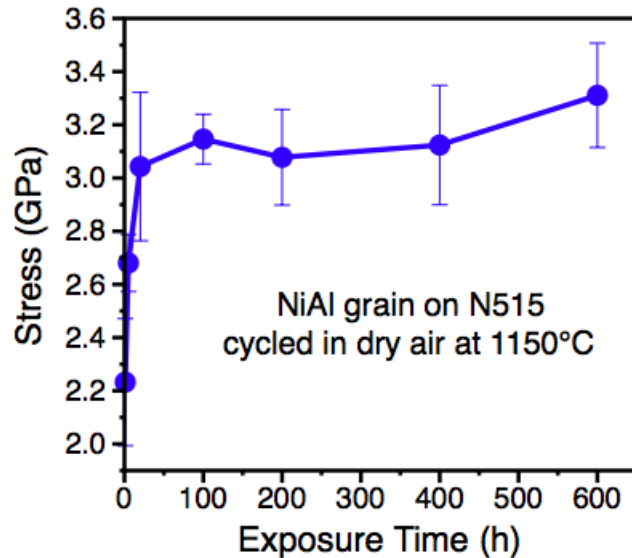
Next gen. stress/3D measurements

PSLS/Z measurement as a function of location

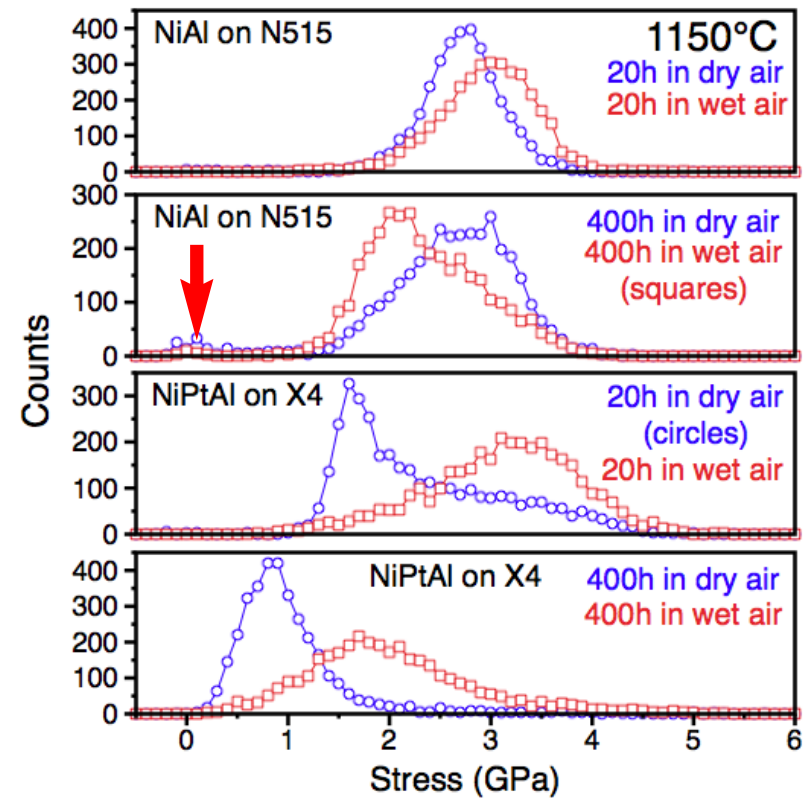


NiPtAl on N5 after 400h
at 1150°C in wet air

wet vs. dry air histograms



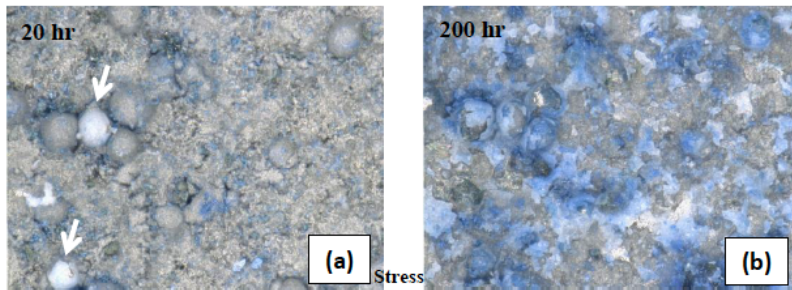
stress in single grain in β coating



Last step: microstructure
at key locations (FIB)

3D image + PSLS: maps & histograms

1483: 1100°C, dry air, 1h cycles



3D Light microscopy (Keyence)

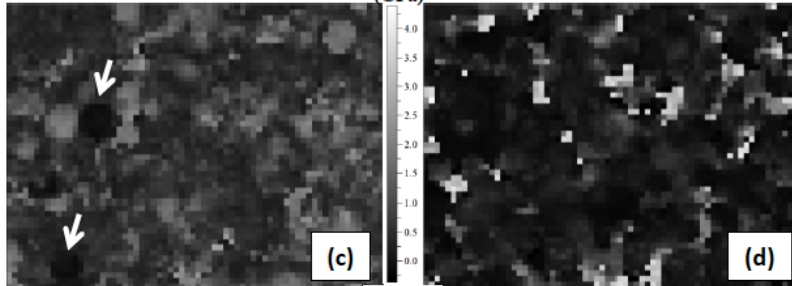
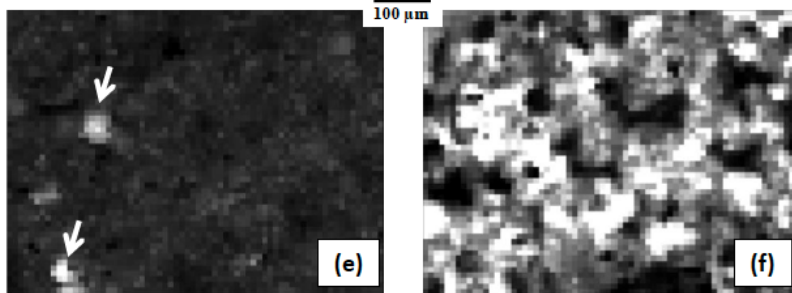


Photo-Stimulated Luminescence Spectroscopy: mean stress

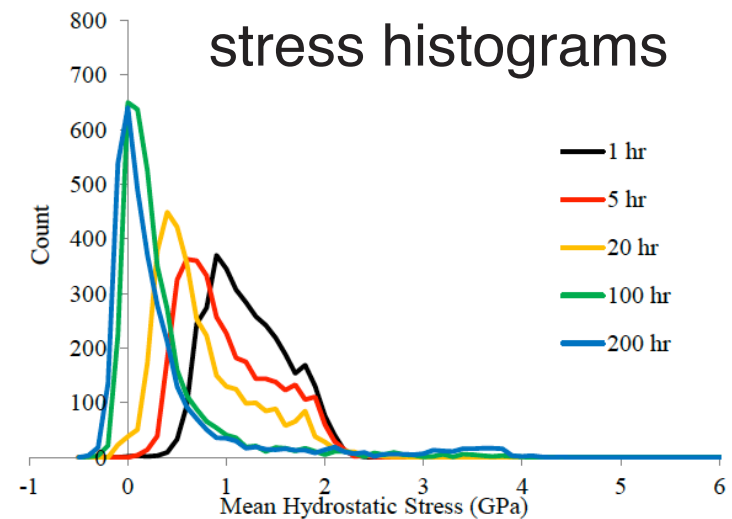


PSLS: total R-line area

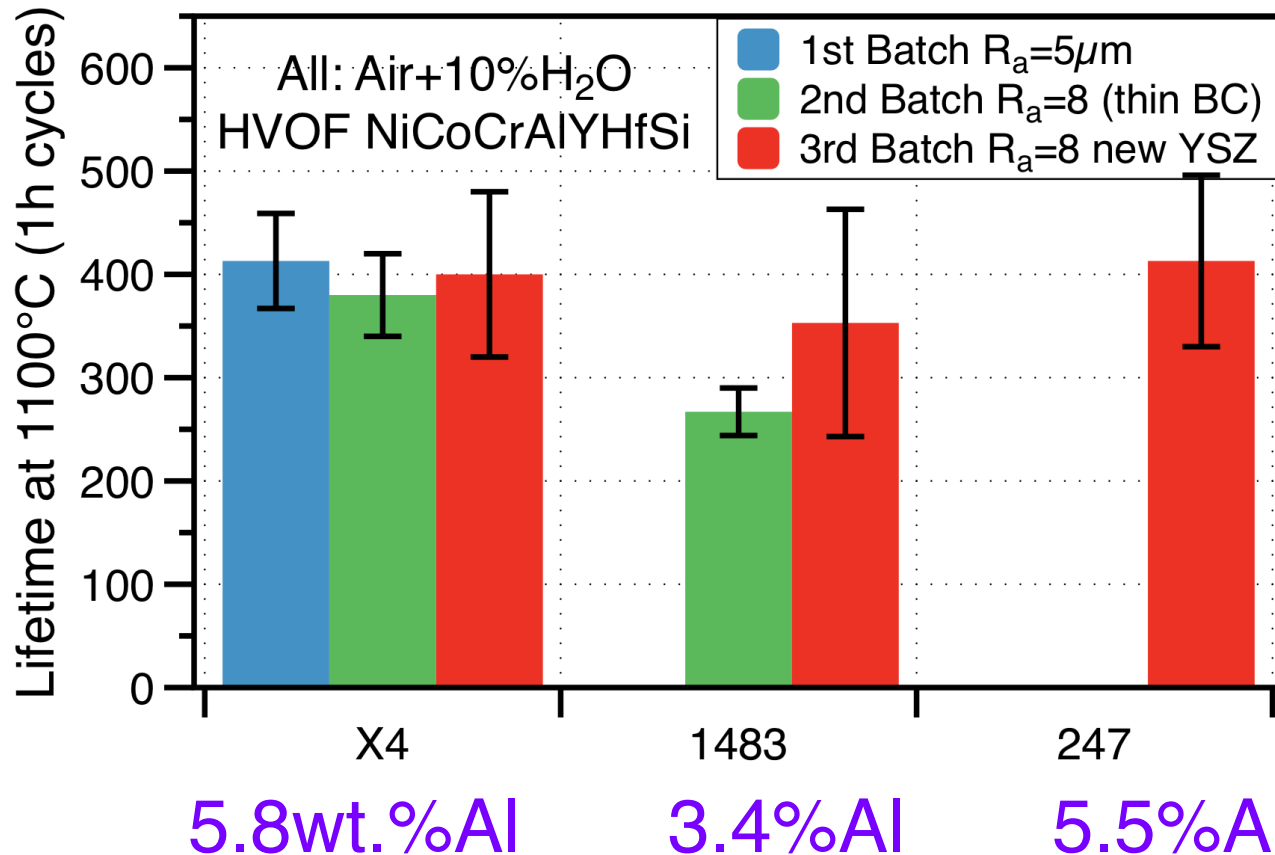
20 cycles

200 cycles

No YSZ top coat:
nothing to constrain spallation



DS MarM247 similar to X4 HVOF NiCoCrAlYHfSi/APS YSZ coatings

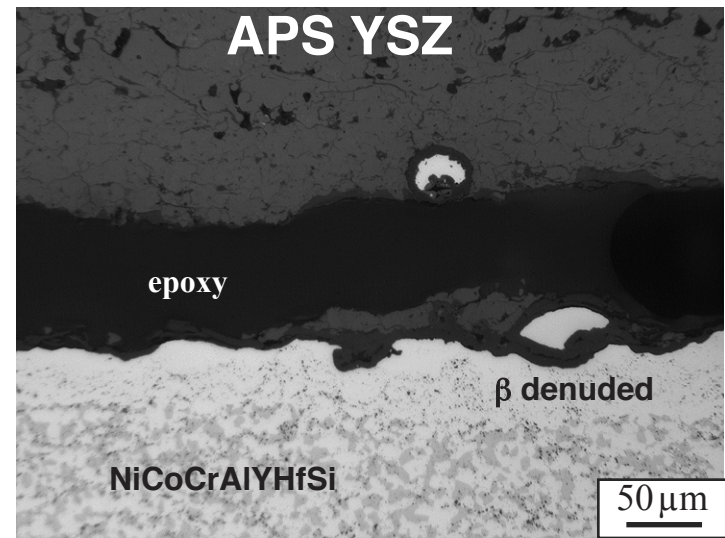
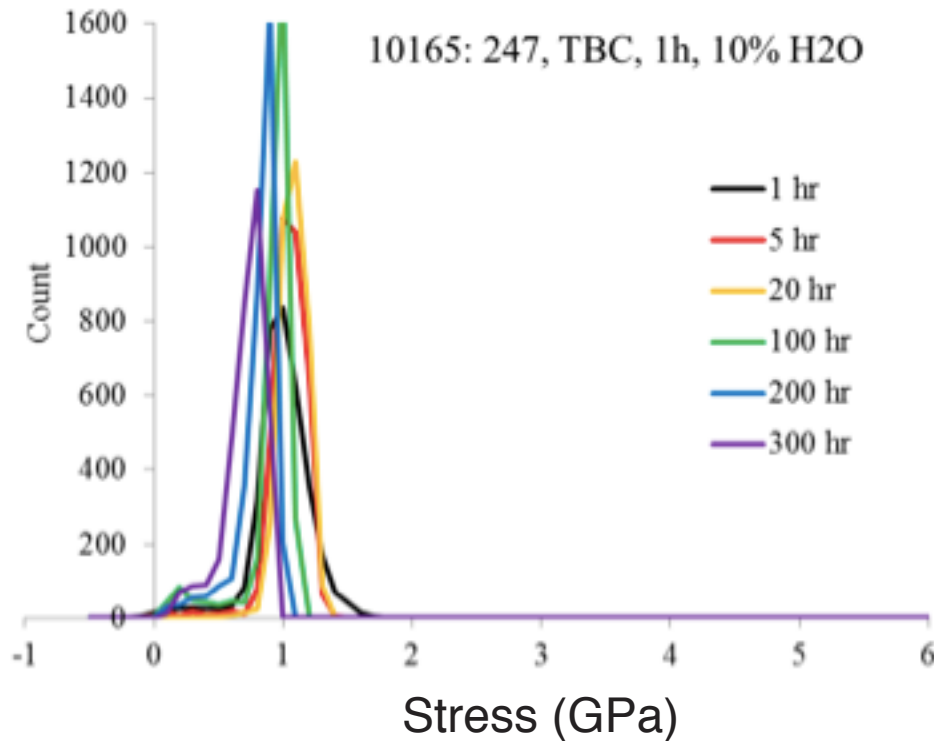


Average lifetime of 3 similarly coated specimens
Characterization of failed specimens in progress

Stress/failure: substrate independent

1100°C, 1-h cycles, 10%H₂O

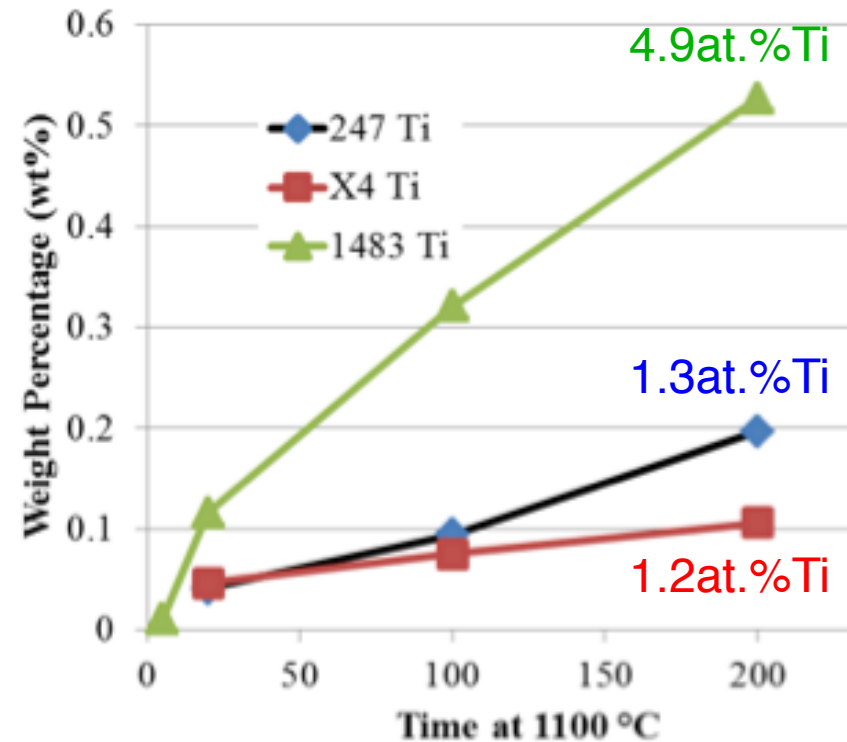
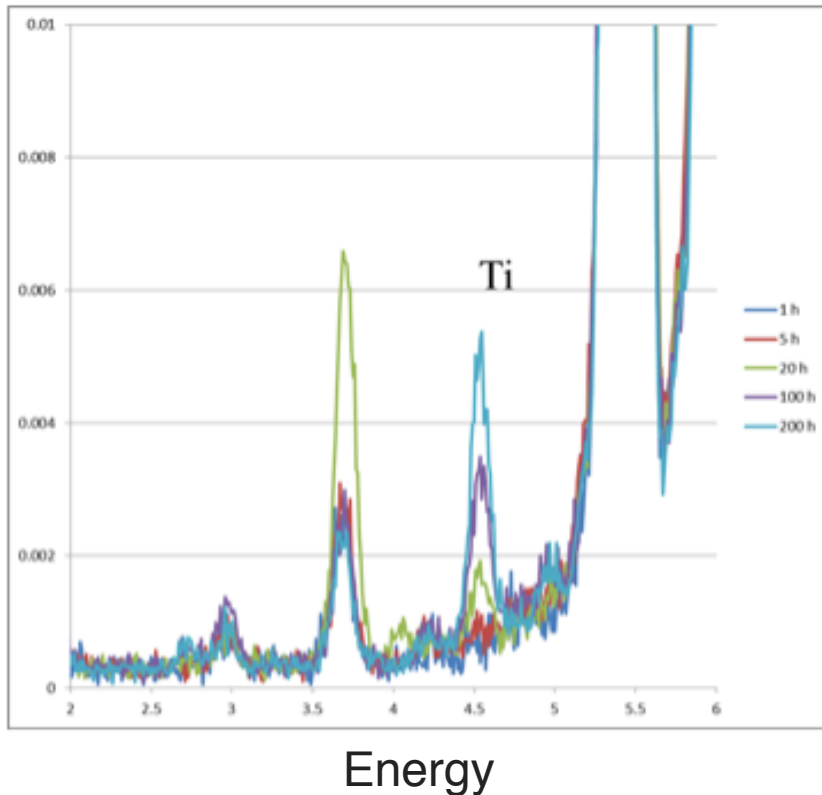
PSLS: through the YSZ top coat



1483 substrate: 280 cycles

Similar results for X4, 1483 and 247

New micro-XRF spectrometer tracked interdiffusion on bare bond coating



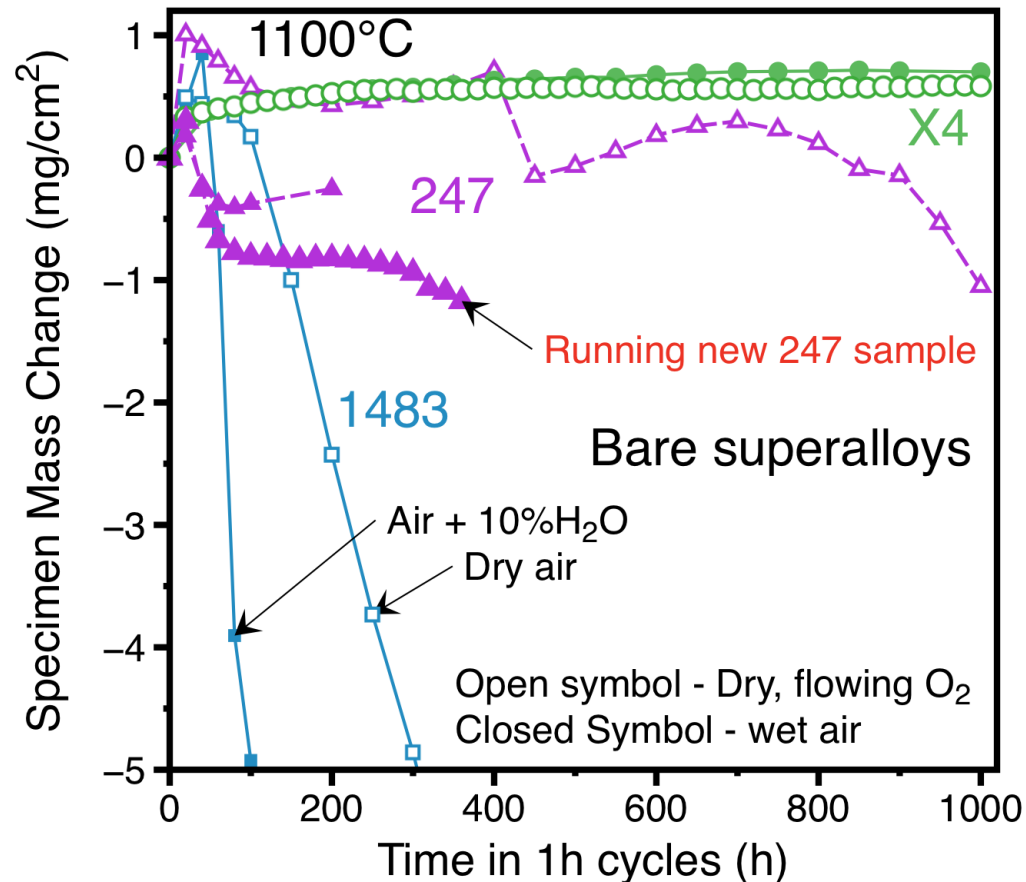
Signal from $\sim 10\mu\text{m}$ into substrate

Surprising increase for 247 compared to X4

How much does Ti play a role?

Concern testing 1483 at high T

Bare 1483 severely attacked at 1050°/1100°C



1h cycles: dry O₂ and wet air (worse)

247 a little bit worse than X4

Component metal temperature ~900°C

Task 2: Does H₂O explain de-rating?

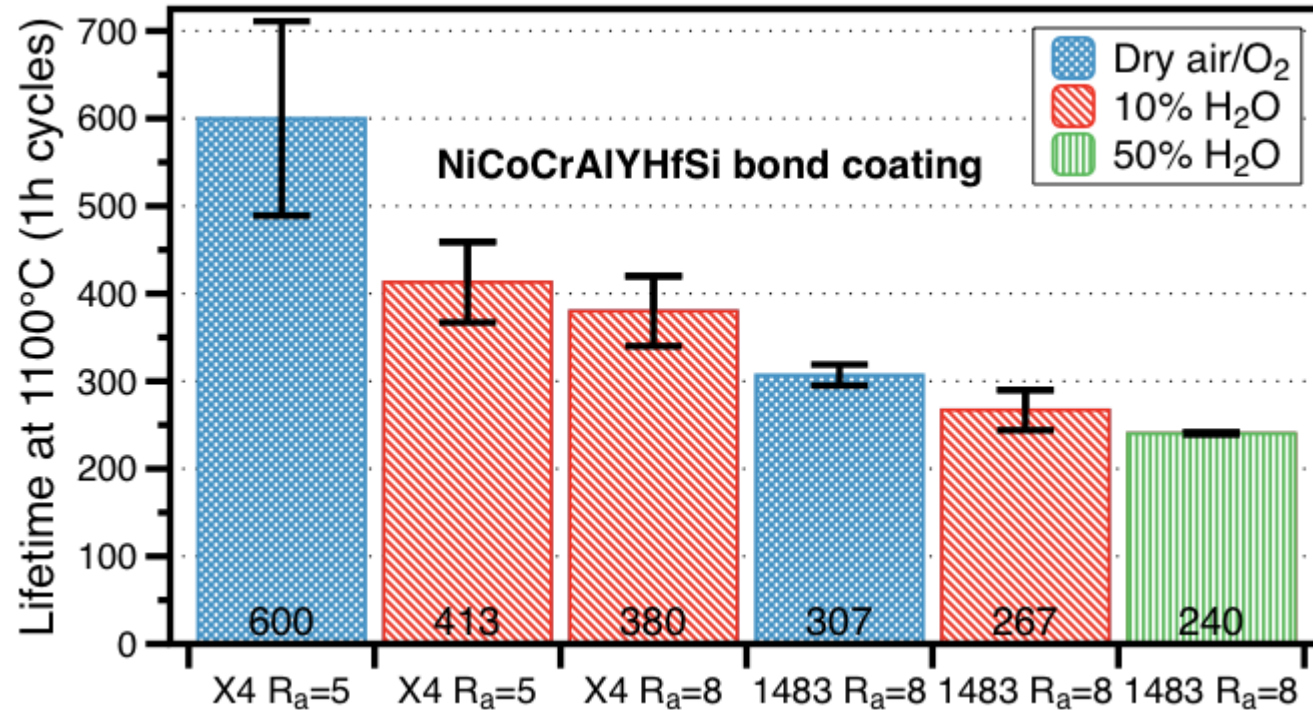
Motivation for original task:

- Experiments done in dry O₂ or air - convenience
 - All turbines contain some H₂O
 - Natural gas - 10-15 vol.%
 - Syn. gas - ~30%
 - Hydrogen - ~60%
 - higher levels with diluent
 - Literature discussion on H₂O effect on TBC
 - Anomaly of testing without H₂O
 - Negative effect on lifetime when H₂O added
- Syngas-firing question:

What is difference in TBC lifetime when H₂O increased from 10% to 30%-50%?
(not dry vs. wet, but wet vs. wetter)

50% H₂O: slight lifetime reduction

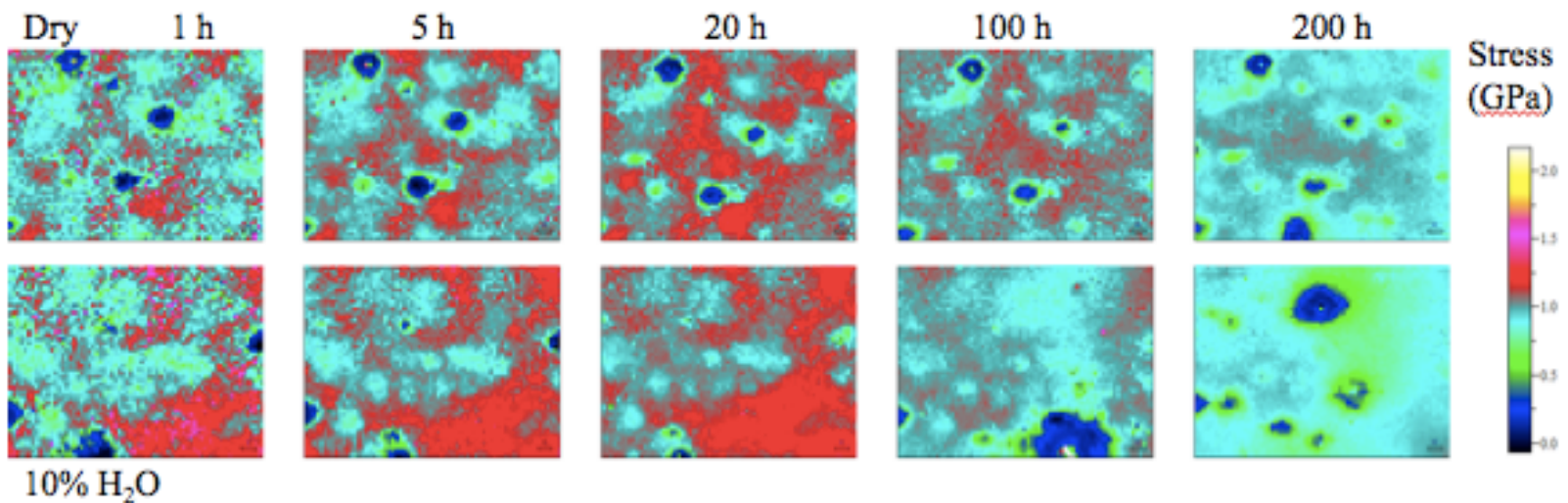
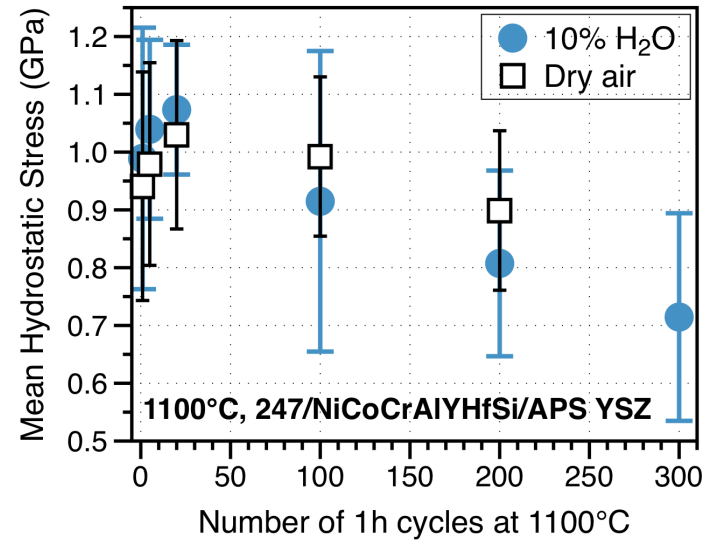
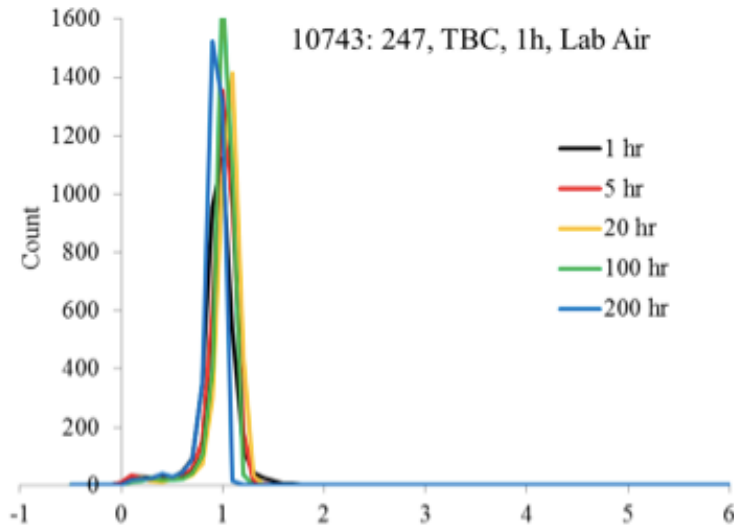
1483 substrate, 1100°C, 1-h cycles



Lower scatter in the 1483 specimens (groups of 3)

Current: tracking 247 dry/wet air

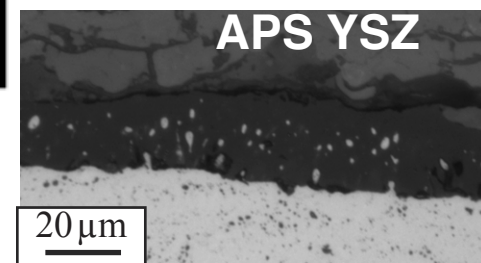
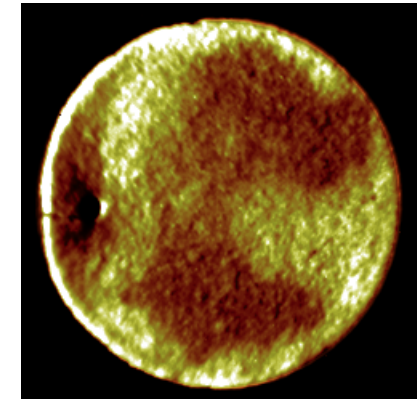
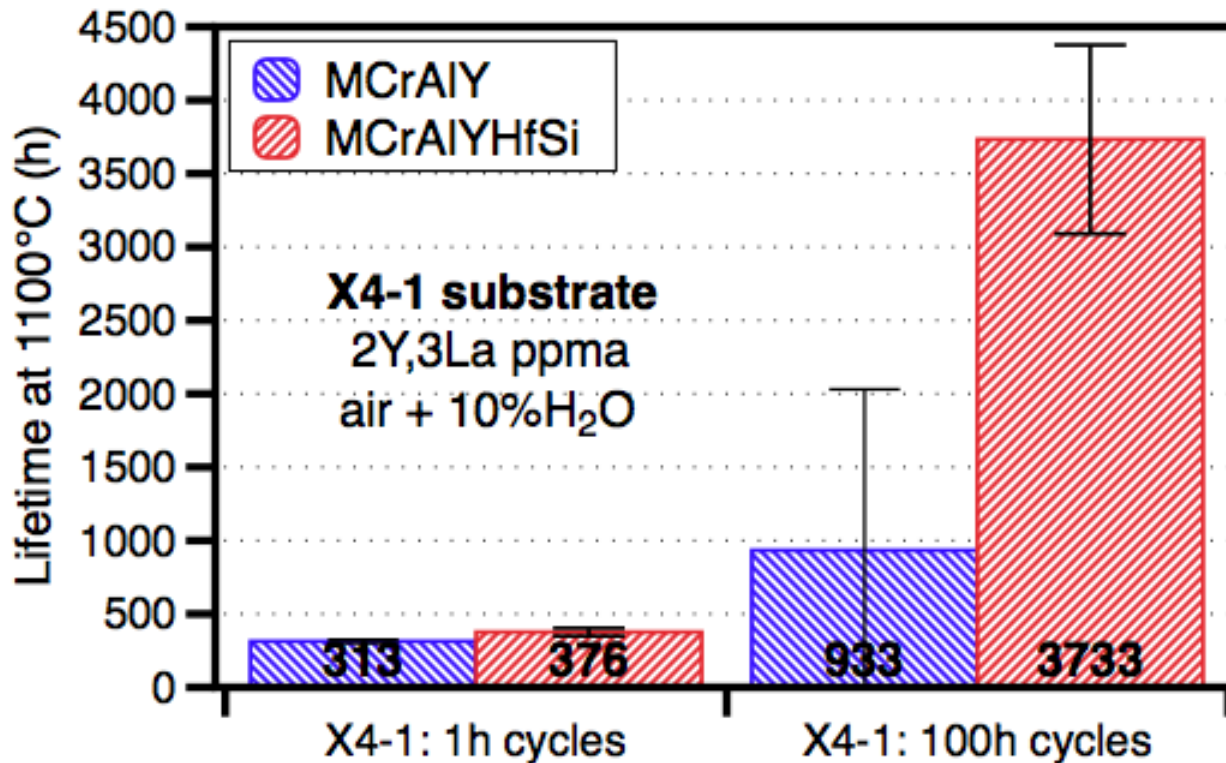
DS 247 substrate, 1100°C, 1-h cycles



Coatings failed ~400h in both environments

100h cycles increased lifetime

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



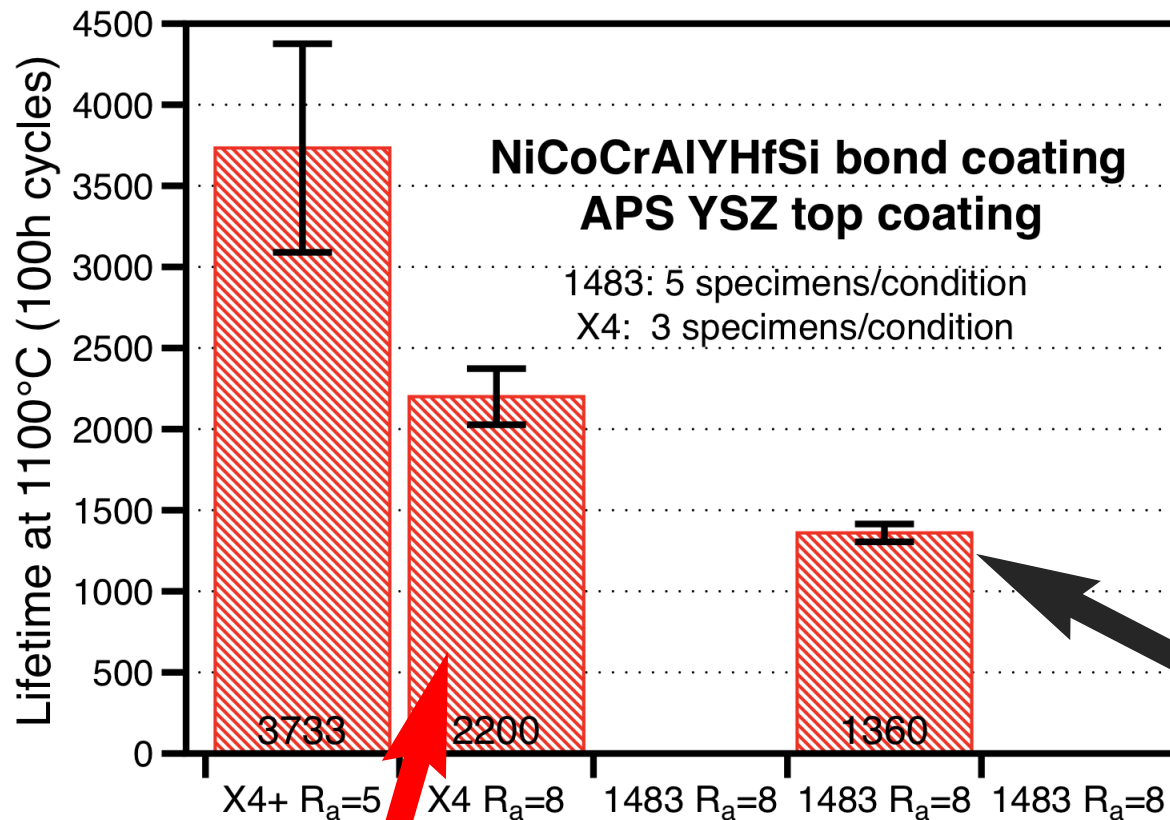
Cycle more representative of land-based turbine

Aero-engine (~15 kh); Power-gen (~25-50 kh)

100h cycles in tube furnace with slow heat/cool

100h: similar trends as 1h cycles

1100°C: HVOF NiCoCrAlYHfSi + APS YSZ

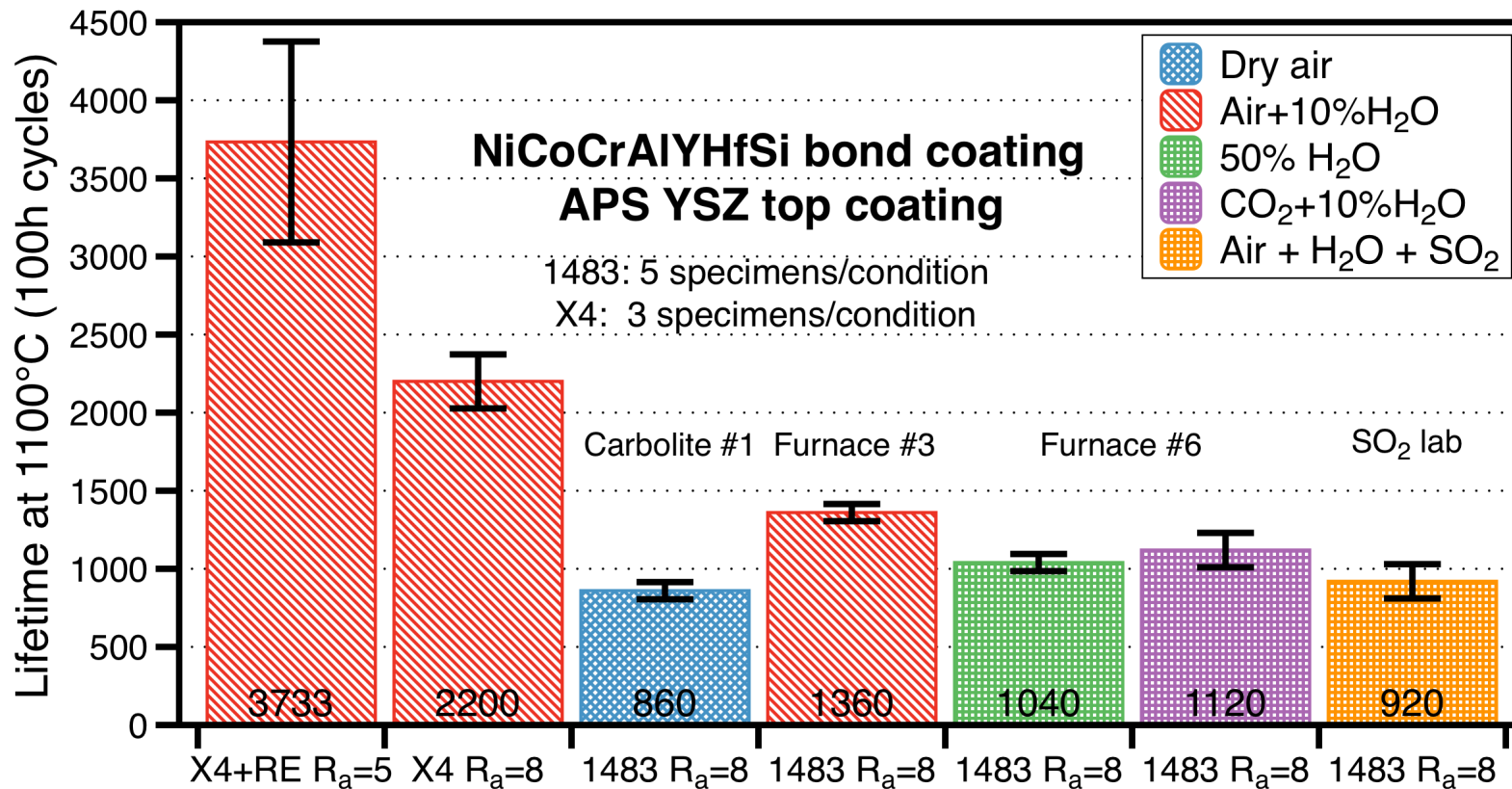


2nd batch: rougher, thinner BC = shorter life

1483: shorter life

1483, 100h: environment no factor

1100°C: HVOF NiCoCrAlYHfSi + APS YSZ



Five samples per 1483 group

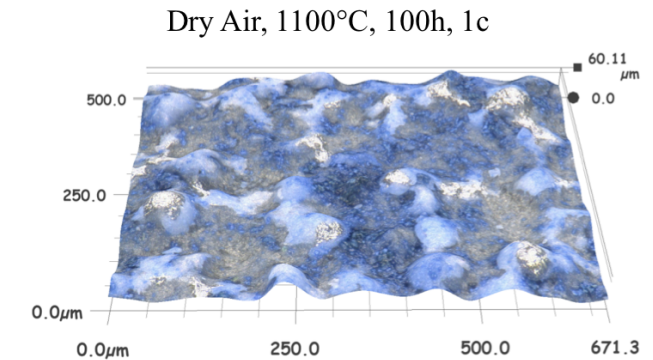
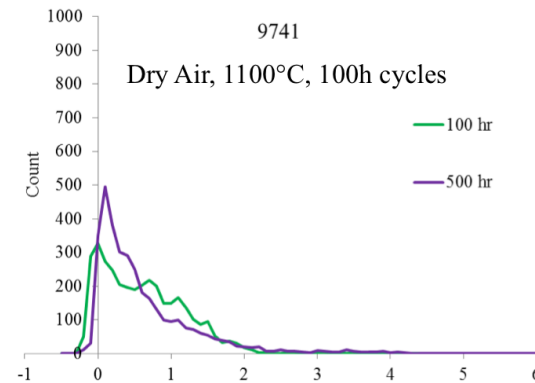
Longest life in 10%H₂O

Test with 10%H₂O and 1000ppm SO₂ in progress

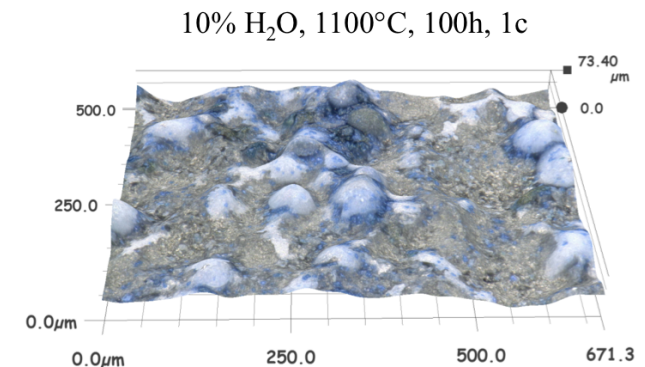
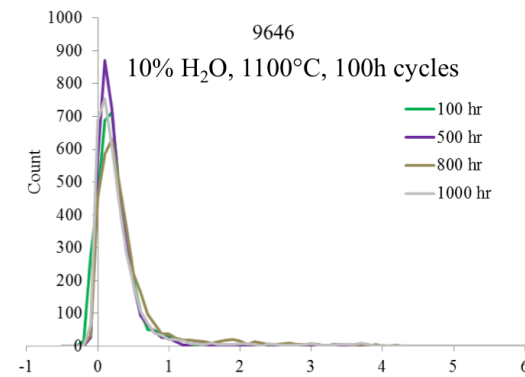
PSLS: maps & histograms

1483: 1100°C

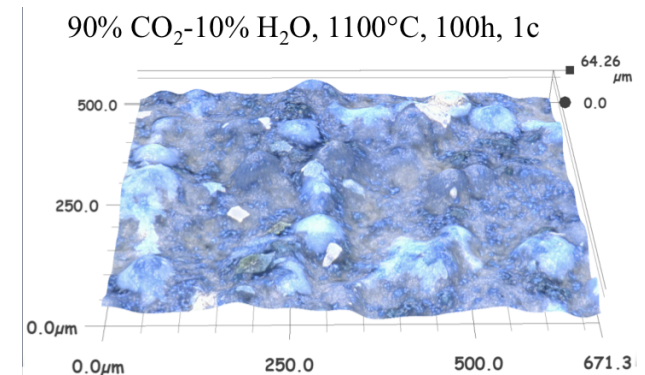
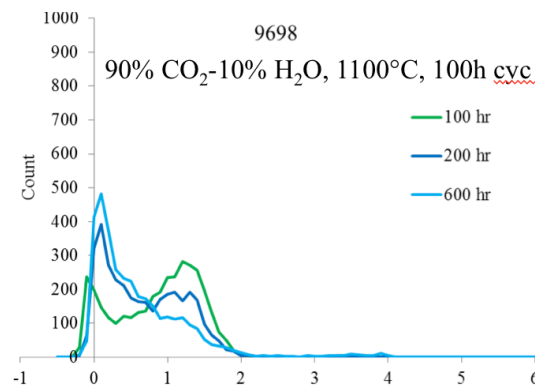
Dry air



air+10% H_2O

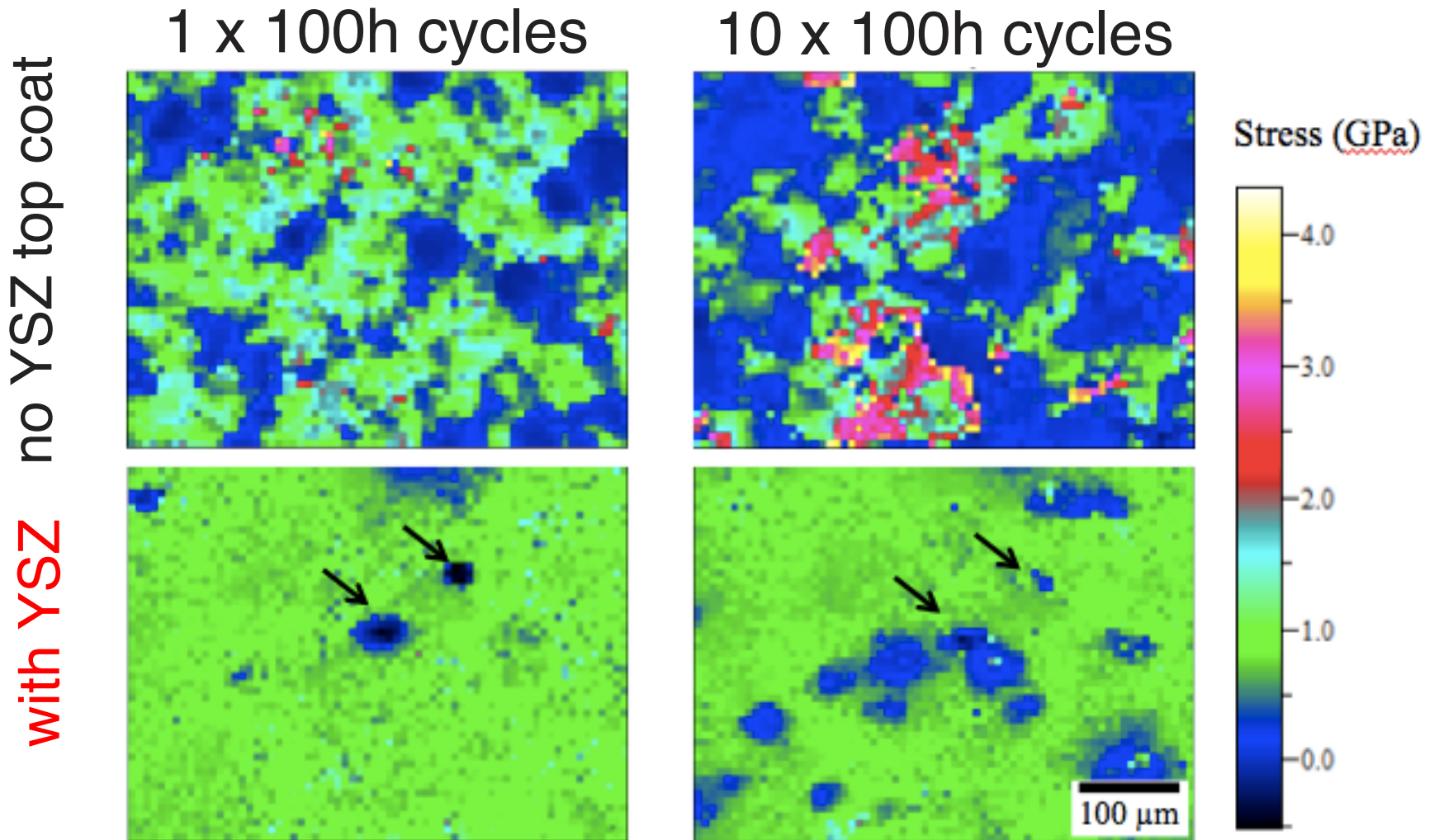


CO_2 +10% H_2O



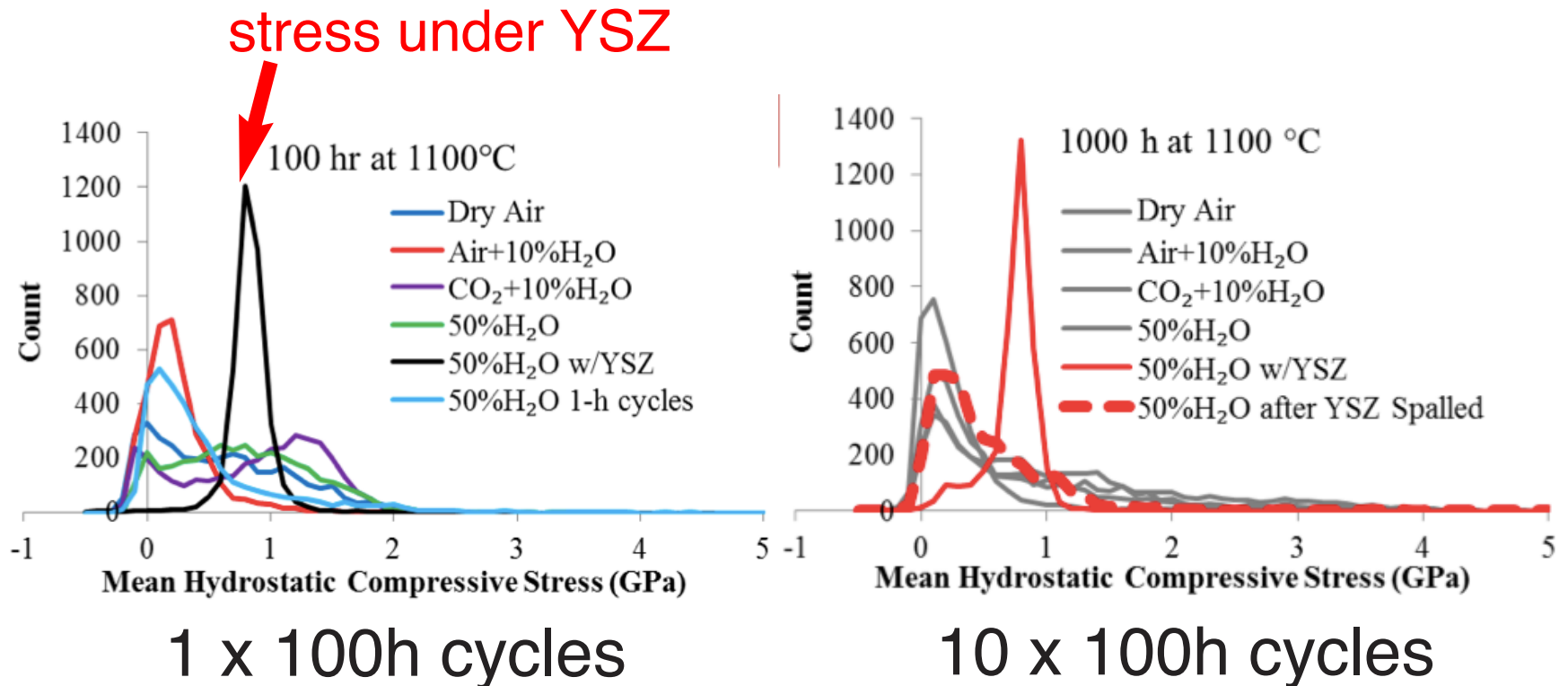
Measuring stress under APS YSZ

HVOF NiCoCrAlYHfSi on 1483 in 50% H_2O



Stress in alumina scale measured by PSLS or PLPS

Measuring stress under APS YSZ HVOF NiCoCrAlYHfSi on 1483 in 50%H₂O

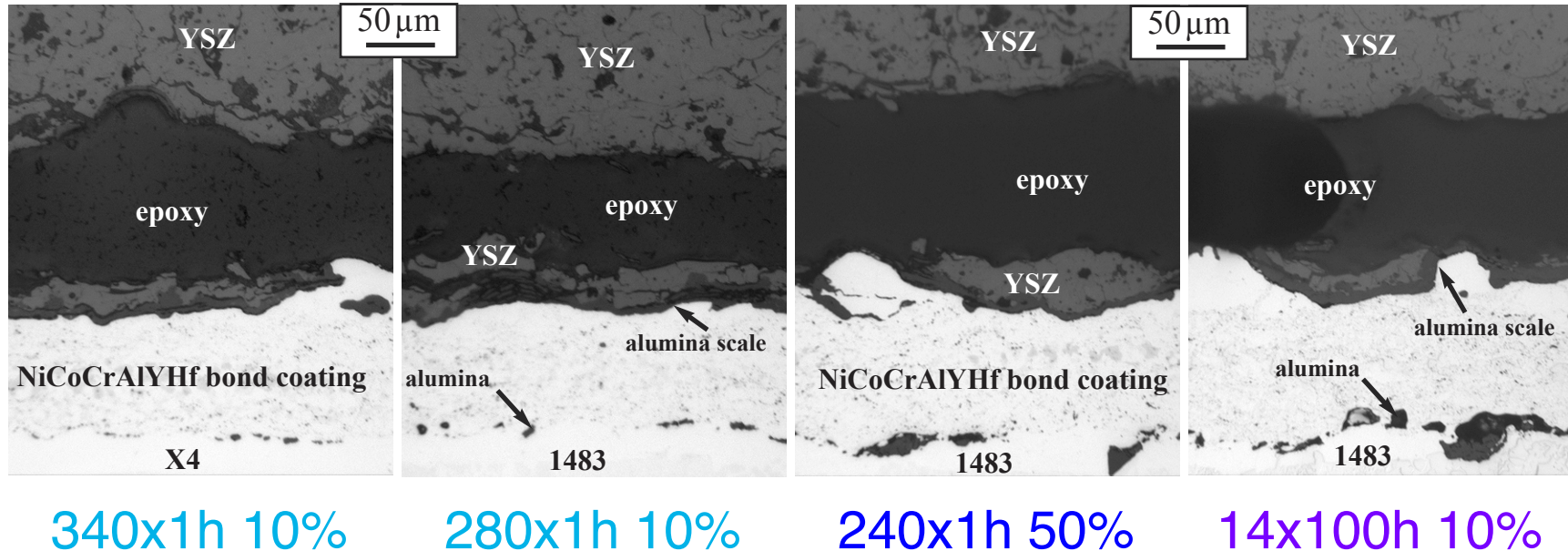


11 cycles spall: stress distribution just like no YSZ

Future: no more PSLs on bare bond coatings

General concern about 1483 results

Various 1100°C exposures



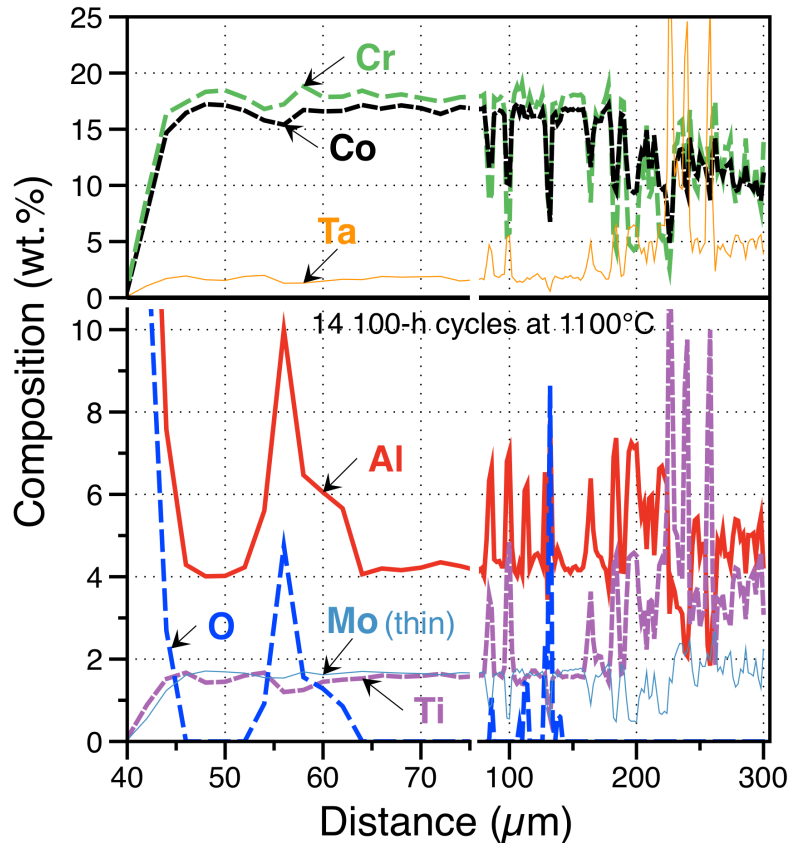
Higher alumina formation at coating-1483 interface

- was interface compromised?
- 1483 very poor behavior at 1100°C without coating

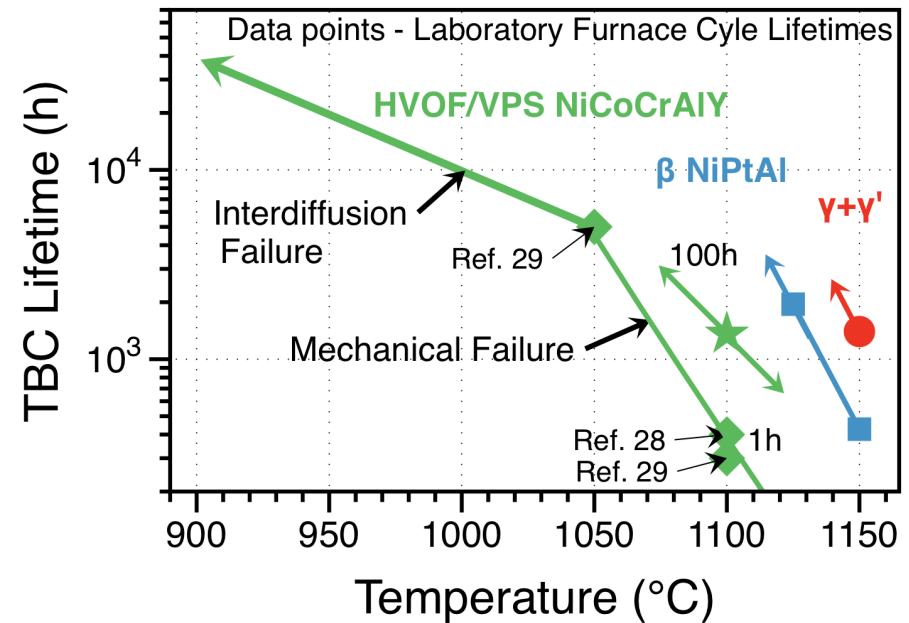


Al diffusion limits 100h cycle life

Especially interdiffusion with 3%Al 1483



1483 substrate: 1400h 1100°C



Eschler, Rensch, Schütze 2004+2008

If interdiffusion limits life, does environment matter?

Could other bond coatings do better?

Task 4 focused on solutions for syngas

Motivation for task:

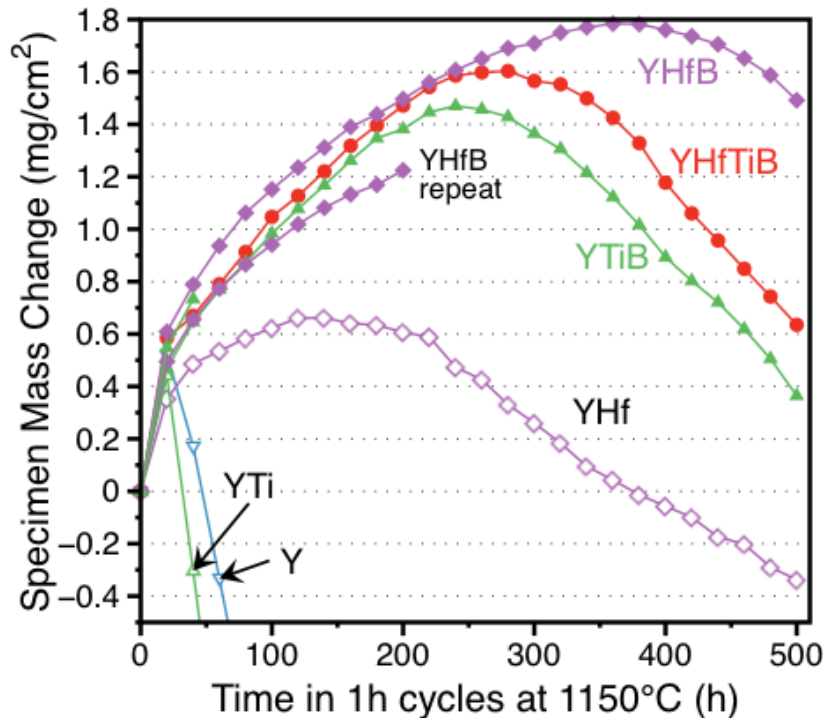
- Other tasks concern understanding
- This task added to develop/study coating solutions
- Also to investigate new coating technologies
(often difficult to get specimens)

FY14 work:

- followup on B improving oxidation resistance
making MCrAlYHfSi coatings with B

Is B a bond coating solution?

Cast NiCrAl: 1h cyclic testing at 1150°C



air + 10%H₂O

0.01wt%Y-0.16Hf vs.
0.03wt%Y-0.13Hf-0.07B
0.03Y-0.14Hf-0.3Ti-0.06B

PWA286 (YHfSi, AMDRY 386) base, ±B, ±Si

- VPS deposition at Stonybrook

coatings arrived last week

- if B promising, look for industrial partner

Coating summary–take aways

Environment:

H₂O is relevant & detrimental for furnace cycle life

Higher water vapor does **not** appear to explain
IGCC de-rating

No indication that CO₂ is detrimental to TBC life

100h cycles: environment less important (?)

Bond coating:

Y + Hf in bond coating yields higher TBC lifetimes

- Does B affect performance?

Substrate:

- Land-based turbines focused on cheaper alloys

Lower TBC life for 1483 compared to X4 substrates

- lower Al, higher Ti in 1483: not surprising

FY15: develop understanding

Begin coating/testing round specimens

