# Materials Issues for (1) Advanced Supercritical $CO_2$ Cycles and (2) High Efficiency Gas Turbines

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# Acknowledgments

- TBC task leaders:
  - J. A. Haynes - coating procurement
    - G. Garner, M. Stephens - oxidation experiments
  - M. J. Lance - characterization (PSLS)
  - S. Sampath, Stonybrook U. – processing
  - K. Kane, Virginia Commonwealth U. – modeling

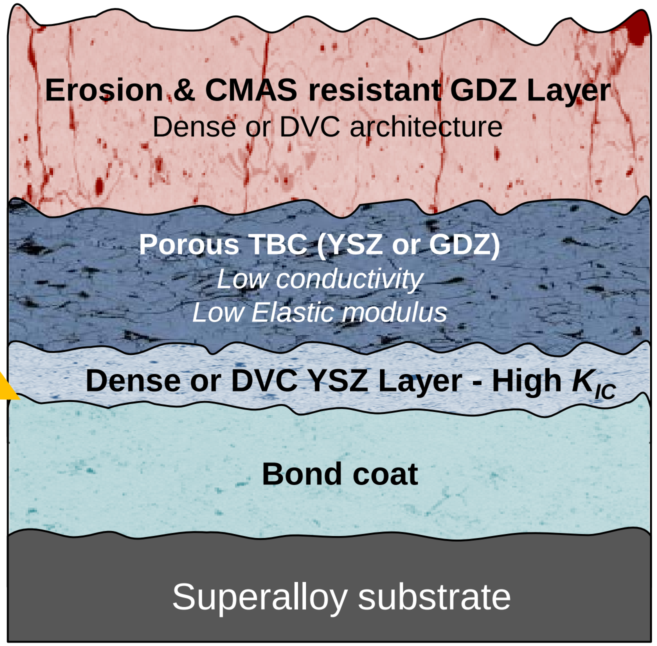

- $sCO_2$ team:
  - Jim Keiser - autoclave design
  - Mike Howell - construction and operations
  - Characterization: R. Brese, T. Lowe, T. Jordan (metallography), M. Lance (GDOES)
- Alloys: Howmet, Siemens, Capstone Turbines, Haynes, Special Metals, Sandvik
- Research sponsored by: U. S. Department of Energy, Office of Fossil Energy
  - TBC project: Turbine Program (Rin Burke)
  - $sCO_2$ project: Crosscutting Technology Program (Vito Cedro)

# Looking for coating solutions

- More durable coatings will benefit
  - NGCC (natural gas combined cycle)
  - IGCC (i.e. coal syngas/$H_2$)
- Focus on alumina scale as "weak link"
- Partner with industry to advance testing
  - **pursue deployment of advanced TBC**
- Project transitioning to EBC
  - Protection for Si-based ceramic composites
  - Initial coating studies on high purity CVD SiC

Environmental barrier coating =
durable, $H_2O$ stable, ceramic coating

ORNL: New environments (higher $H_2O$, $CO_2$, $SO_2$)




CTSR: Multi-layer top coatings

$Al_2O_3$ scale

Optimal bond coating: PWA286 Y+Hf+Si

Explored different superalloy substrates

Thermal barrier coating =
oxidation-resistant, metallic bond coating +
durable, low conductivity, ceramic top coating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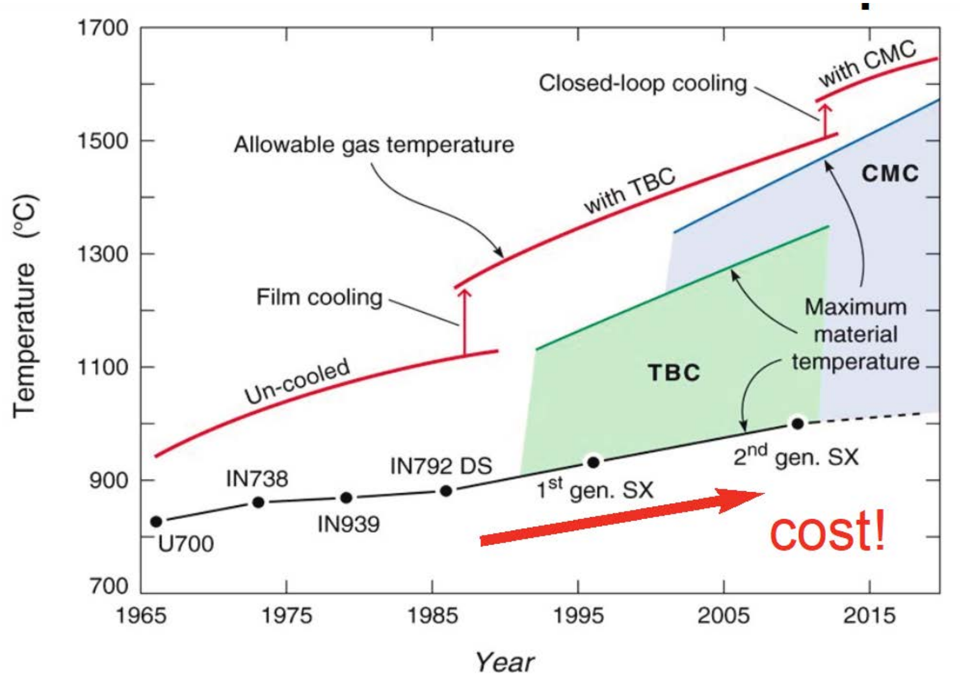
# Coatings for Land-Based Turbines

- Focus on thermally-sprayed coatings
  - HVOF: high-velocity oxy-fuel
  - APS: air plasma spray
  - VPS: vacuum plasma spray
- Current land-based turbine issues:
  - first cost drives sales
  - temperature/efficiency
    - Not as important in US with cheap gas
  - hot corrosion in blade root
    - want higher Cr content alloys or coatings




MarM247 <- PWA1483 <- CMSX4

8Cr+1Hf 12Cr+4Ti 6Cr+3Re

Land-based ← → Aircraft

| Material | Ni | Co | Cr | Al | Y | Hf | Si | Ti | W | Ta | Mo | C | Other (ppmw) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| YHfSi Bond Coating | 48.0 | 21.6 | 16.7 | 12.3 | 0.68 | 0.25 | 0.36 | < | 0.01 | < | < | < | 2 S |
| Y-only Bond Coating | 47.1 | 23 | 16.6 | 12.8 | 0.42 | < | 0.04 | < | 0.02 | < | < | < | 8 S |
| Alloy 247 | 59.1 | 10.2 | 8.5 | 5.6 | < | 1.32 | 0.06 | 1.0 | 10.0 | 3.2 | 0.6 | 0.2 | 200 Re, 11 S |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# All testing done in simulated exhaust gas: air + 10%$H_2O$

- Many studies have shown that water vapor decreases FCT life

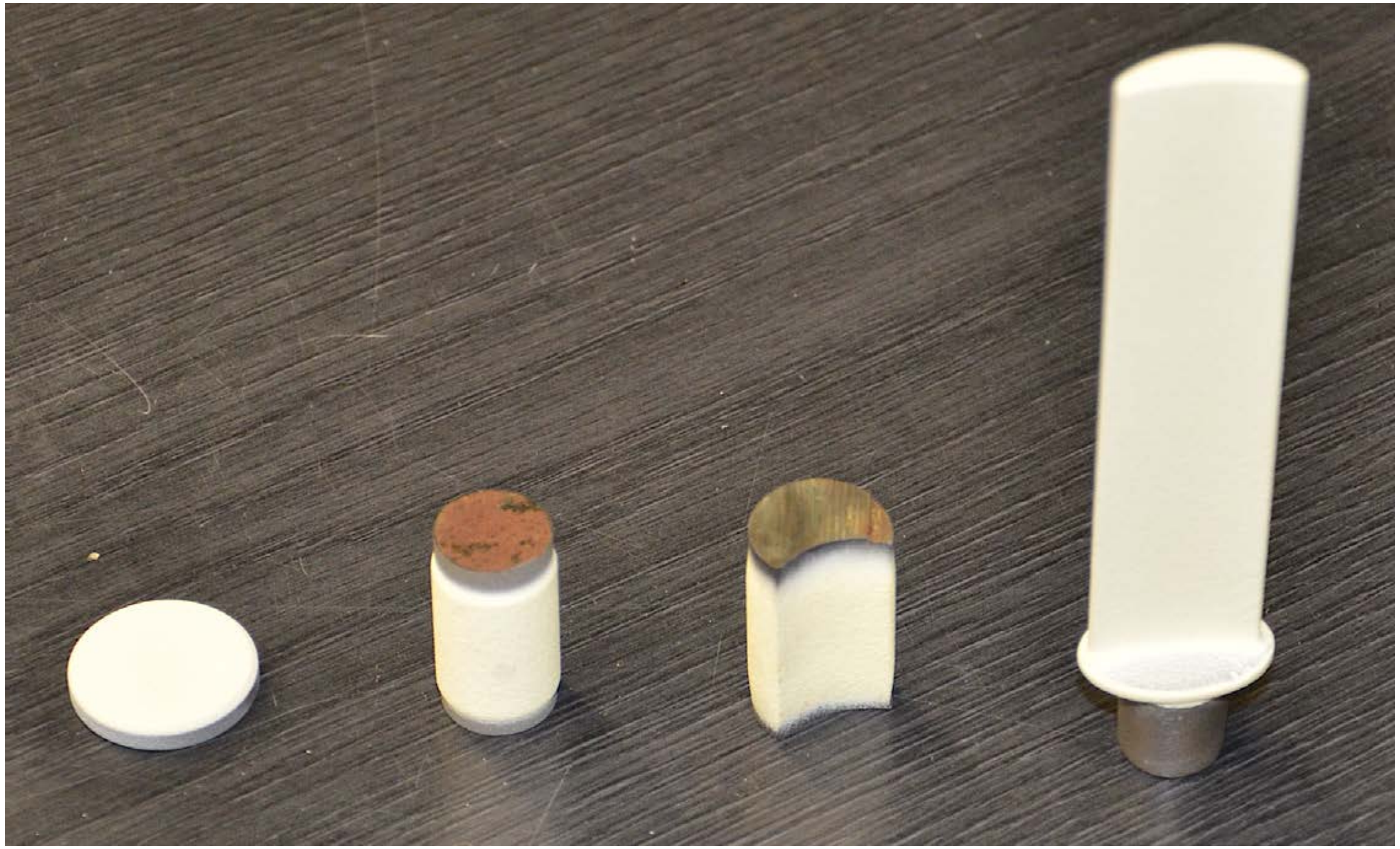
lid

furnace

1-h cycles:
automated cyclic rig
(10 min cool in lab. air)
20 cycles/day

100-h cycles (base-load):
Tube furnace with endcaps
1 cycle/week

# 2015:  Moving towards coating more realistic substrates



AM 718 “blade”

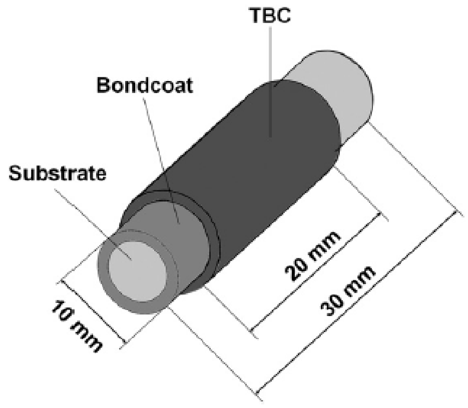



Fig. 1. Geometry of used TBC specimens.

Jülich 2014

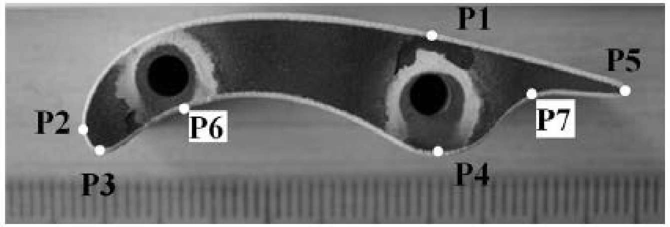
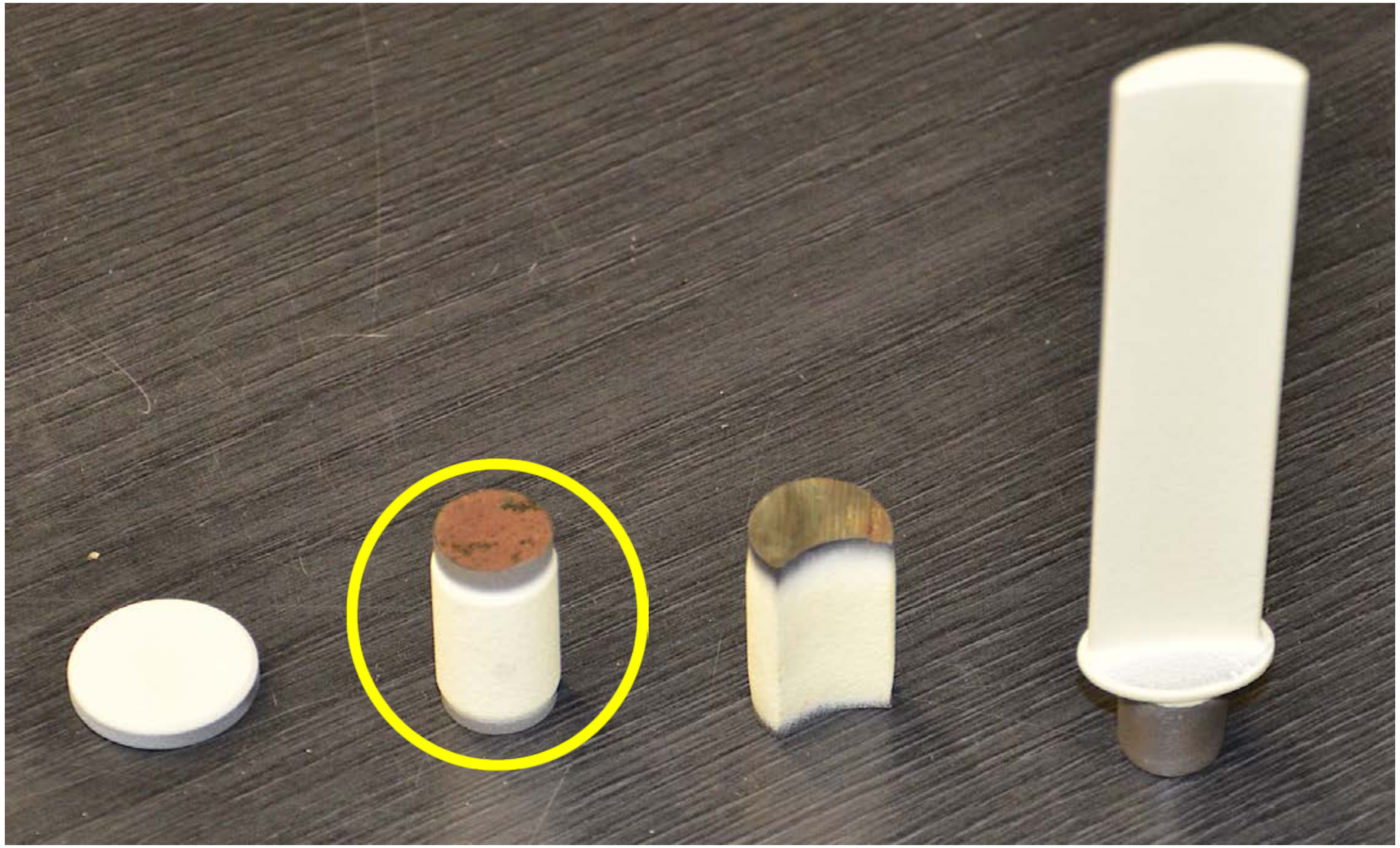



Fig. 1. Picture of a modified aerofoil-shaped specimen. P1, P2, P3, P4 and P5 are convex areas whereas P6 and P7 are concave.

Cranfield 2013

# I thought it would be easy to switch to "rodlet" specimens
# It was easier to imagine than to coat...

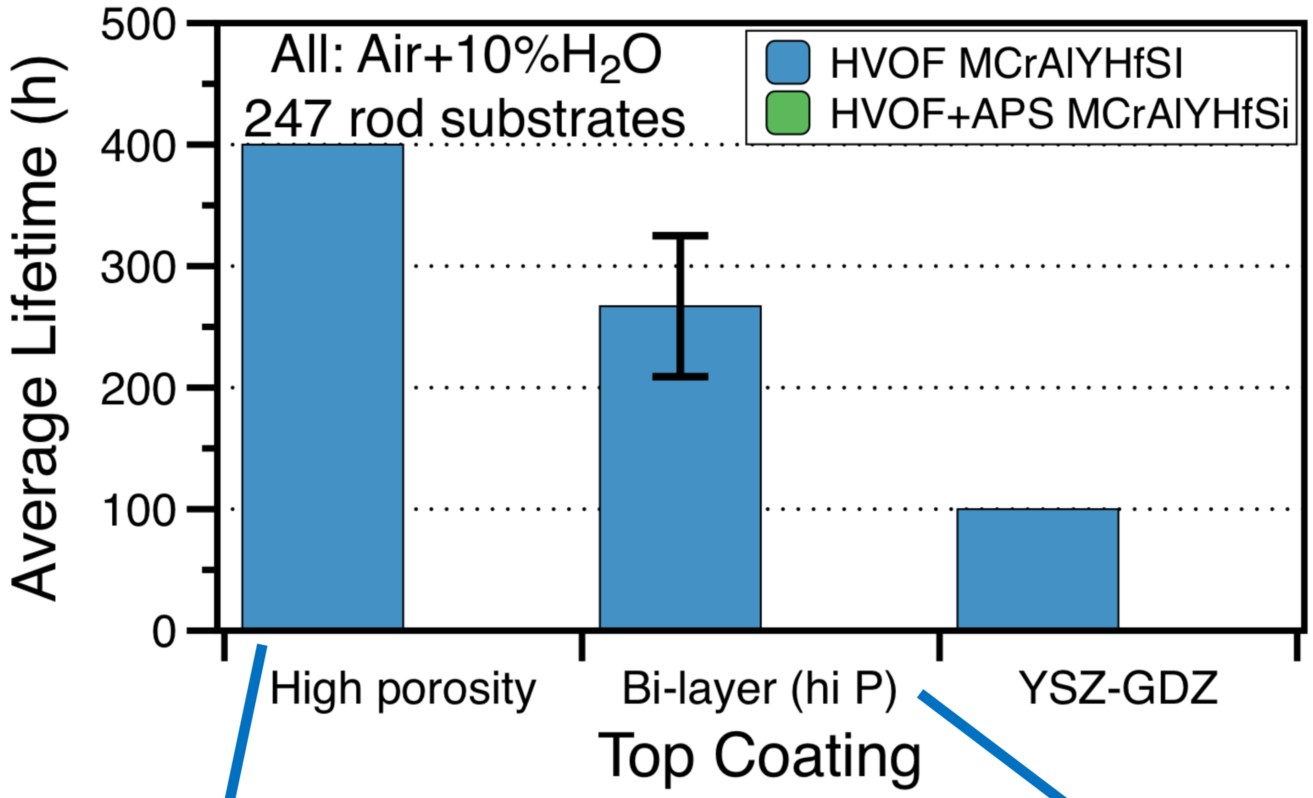


AM 718 "blade"

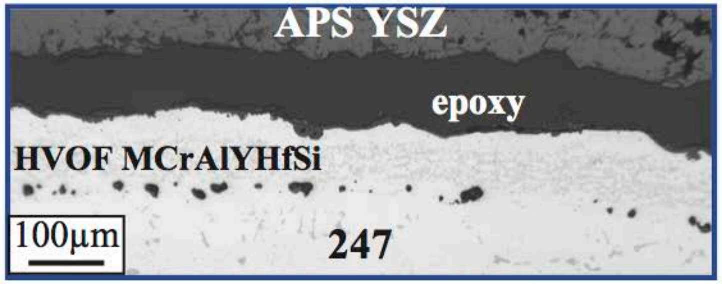
2015: 247 rods

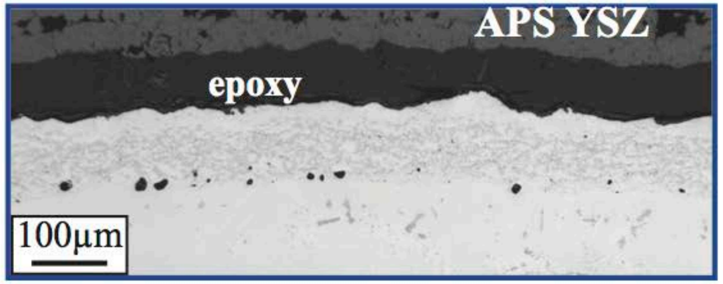
**Coating development not linear with time**

# HVOF bond coatings performed poorly



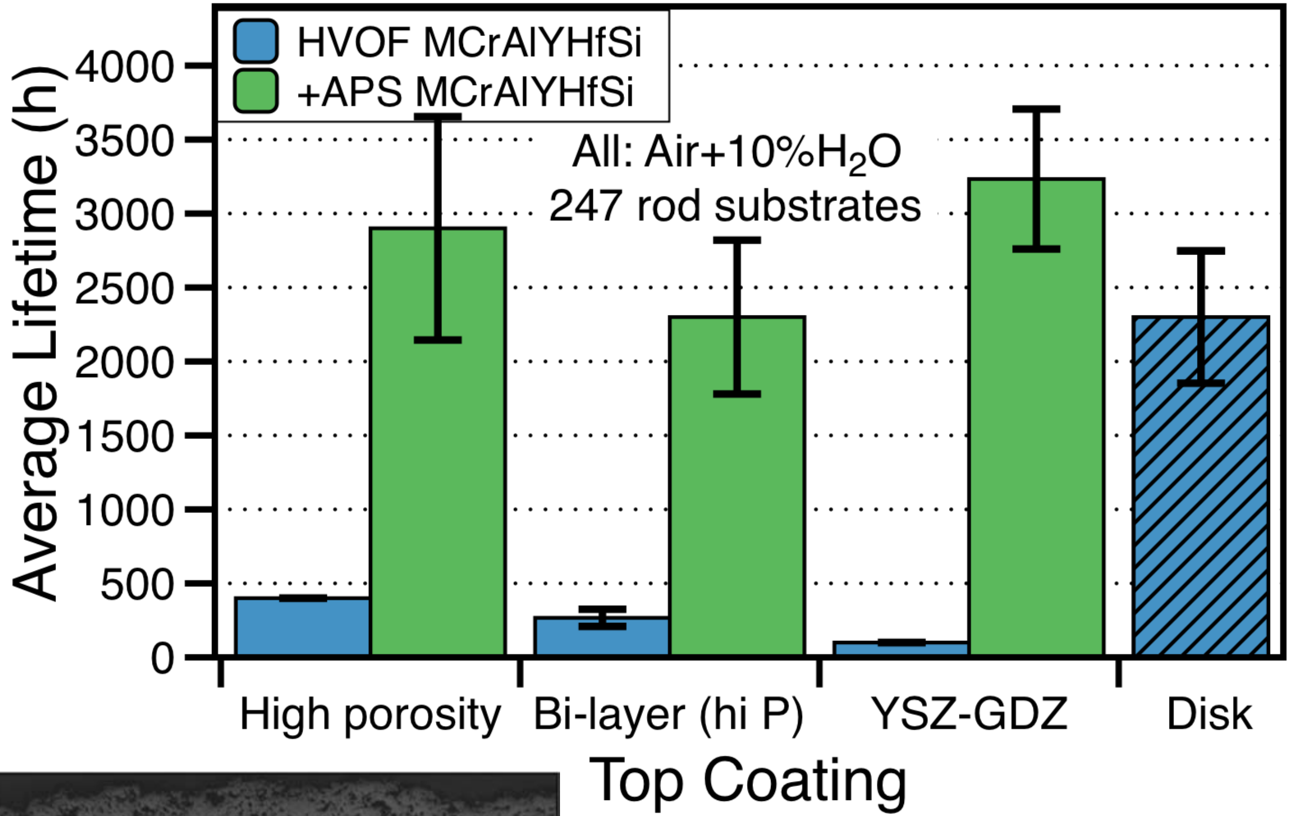

- CTSR parametric study
- Three top coat variations
  - 1 layer: high porosity YSZ
  - 2 layer: dense inner layer
  - 3 layer: outer $Gd_2Zr_2O_7$
- Concern about low bond coating roughness

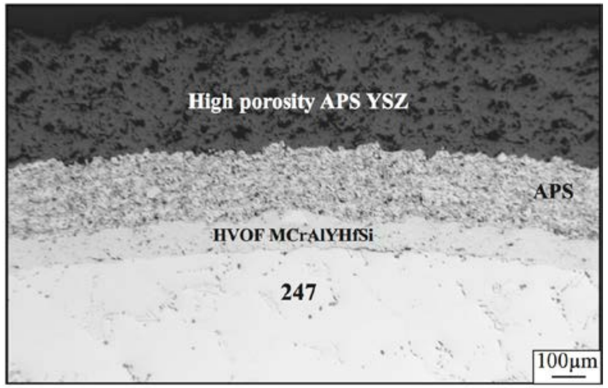



# Excellent results with APS layer on top of HVOF bond coating

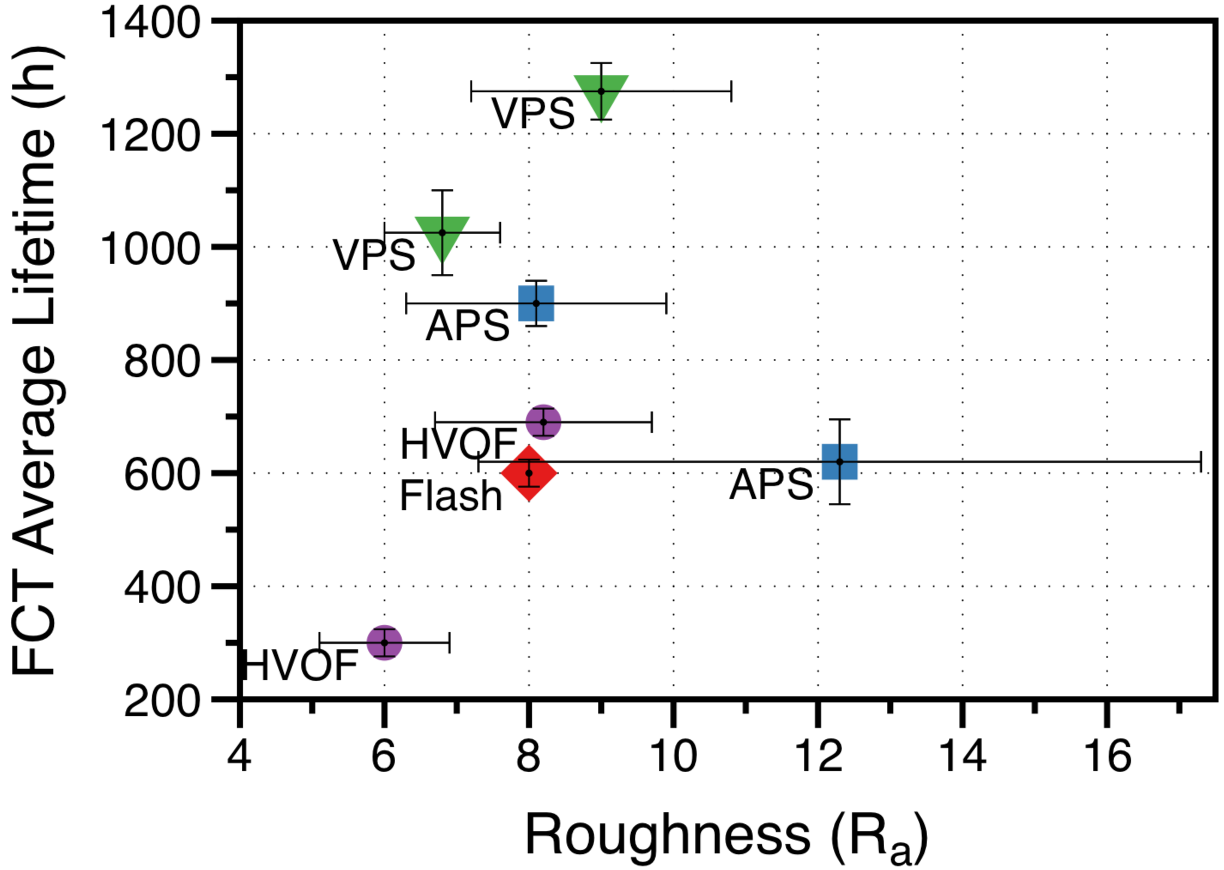
- Standard testing at 1100°C
  - Air + 10%$H_2O$
  - 100-h cycles
- Rod specimens
  - Three different top coatings
    - 1 layer: extra porous
    - 2 layer: dense inner YSZ
    - 3 layer: add $Gd_2Zr_2O_7$ outer layer
  - Two bond coatings
    - Standard HVOF
    - HVOF+ ~200 µm APS "flash"




**Not really an APS "flash" coating on HVOF**

# Is roughness really the “flash” coating advantage? Stony Brook: could not correlate roughness with lifetime




- 1100°C (2102°F)
- 24-h cycles
- Laboratory air
- 3 specimens/group
- 15 profilometry measurements to determine roughness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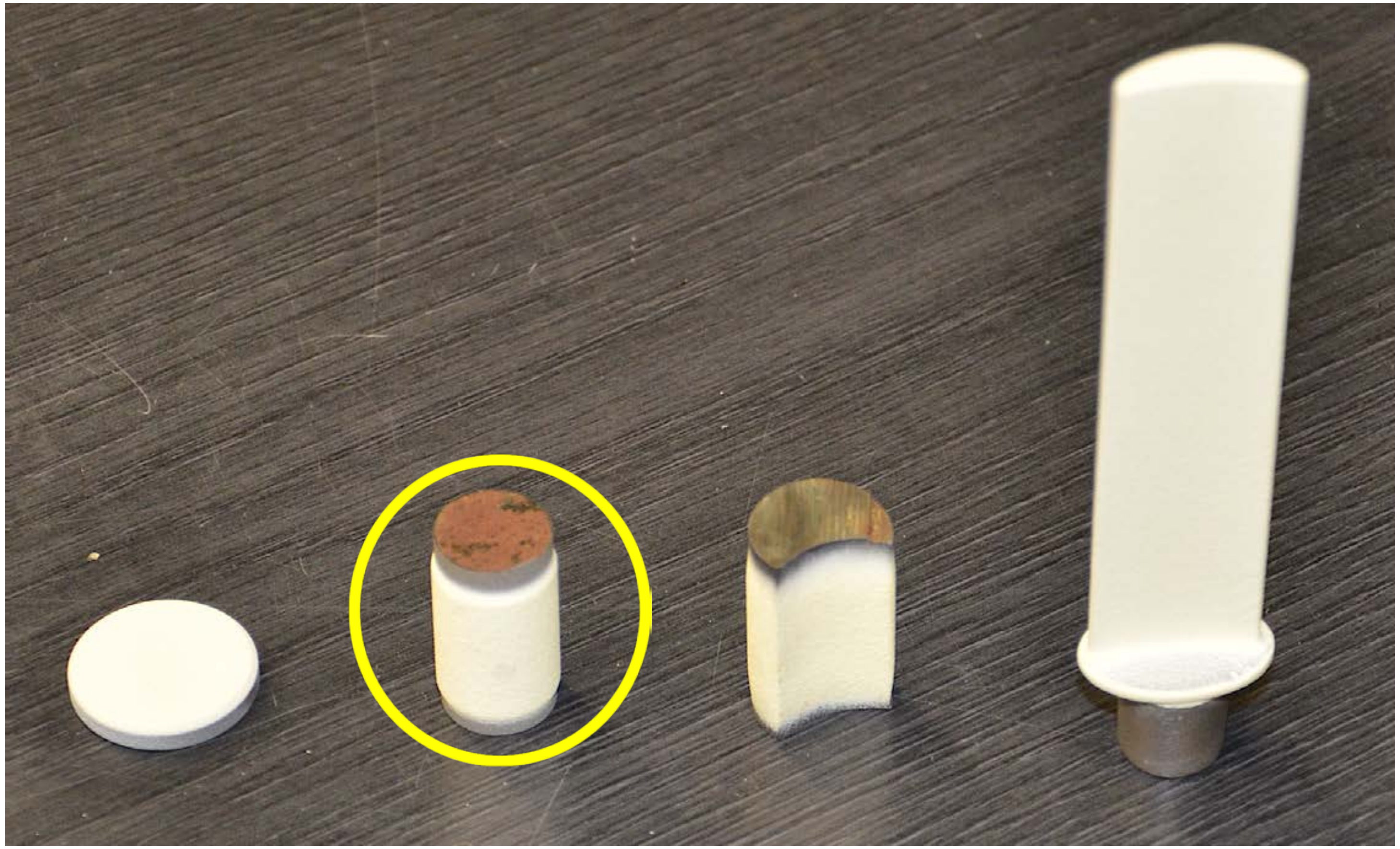
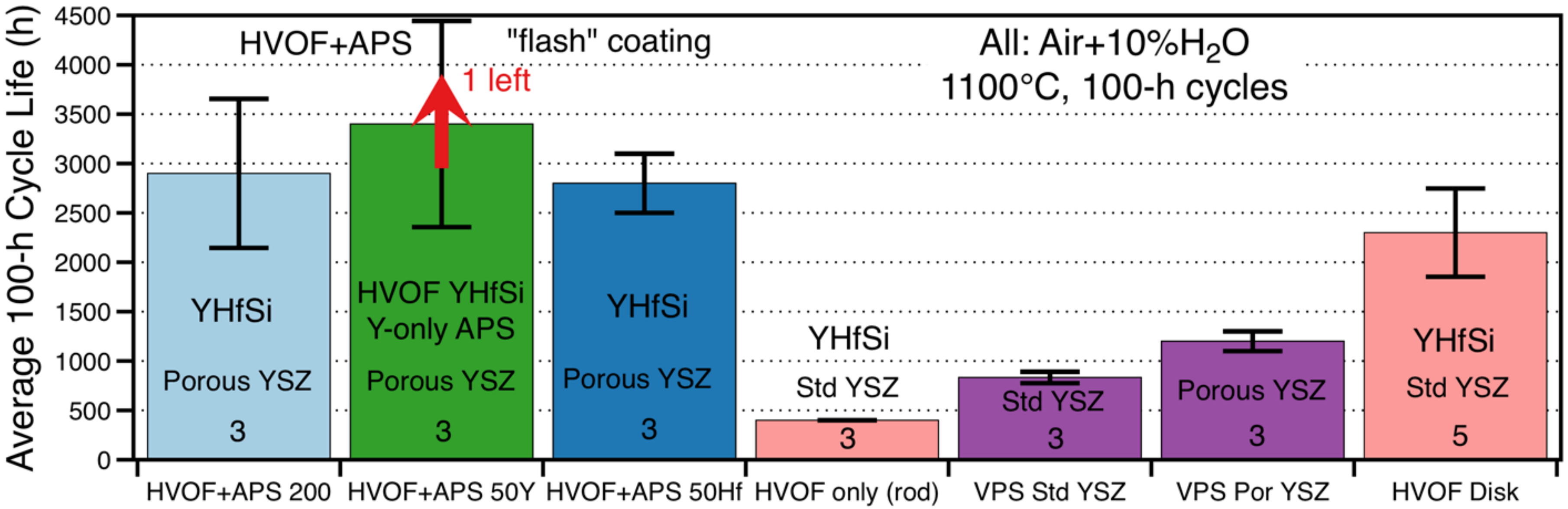
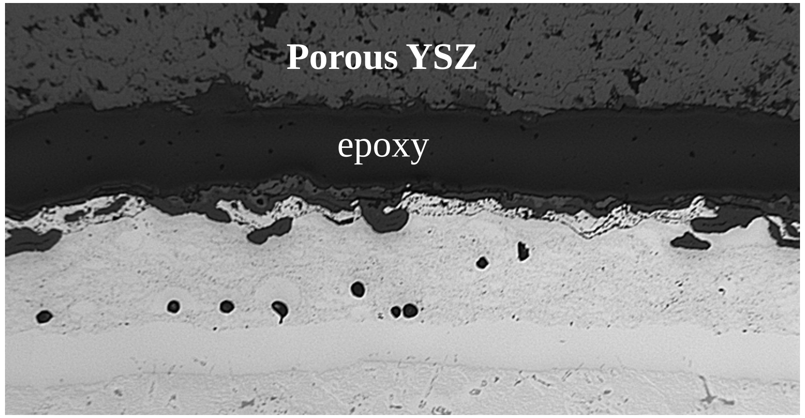
# Last phase: what about ~50 μm flash coating?
# If roughness is key, is Y-Hf-Si needed?
# Was longer life due to extra-thick bond coating?

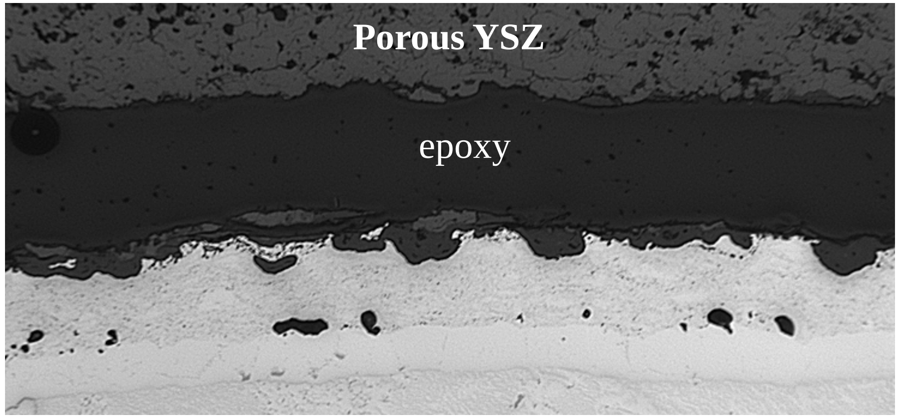


# Similar lifetime for both Y-only and YHfSi-flash coated rods Outperformed VPS bond coatings



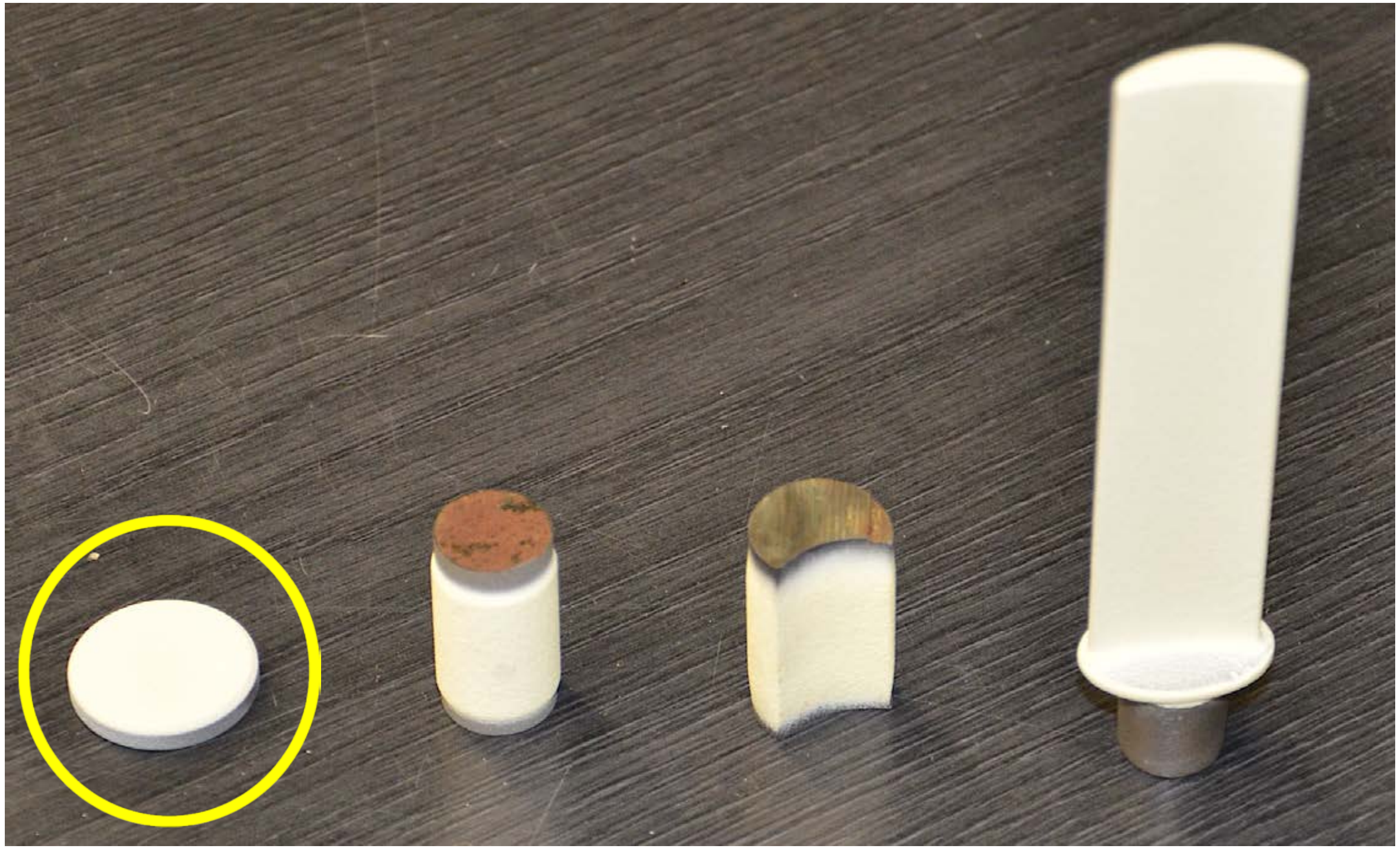




Flash Y-only Rod (2900 h)



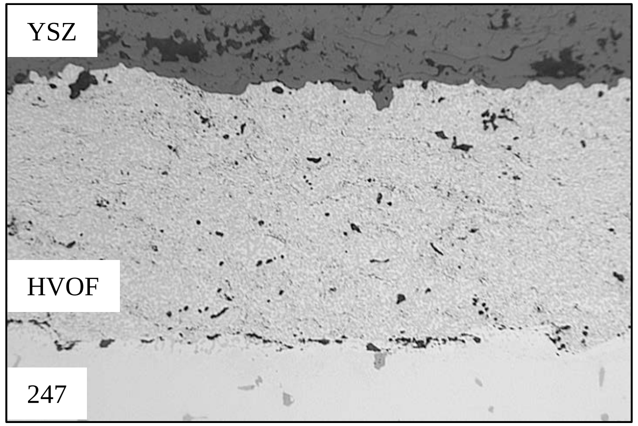

Flash YHfSi Rod (2800 h)

# How would ~50 μm flash coating do in 1-h cycles? If roughness is key, is Y-Hf-Si needed?

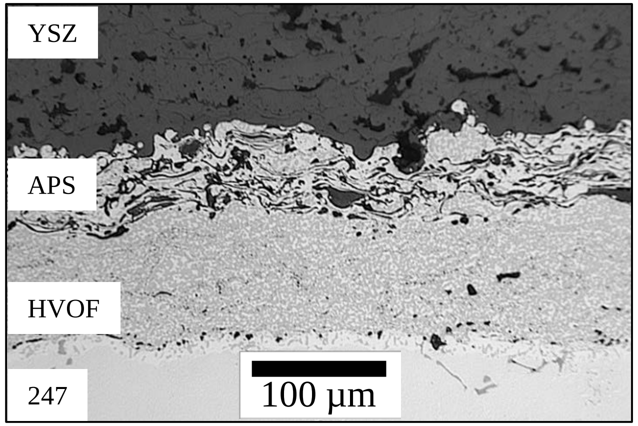


# Light microscopy of as-sprayed disks

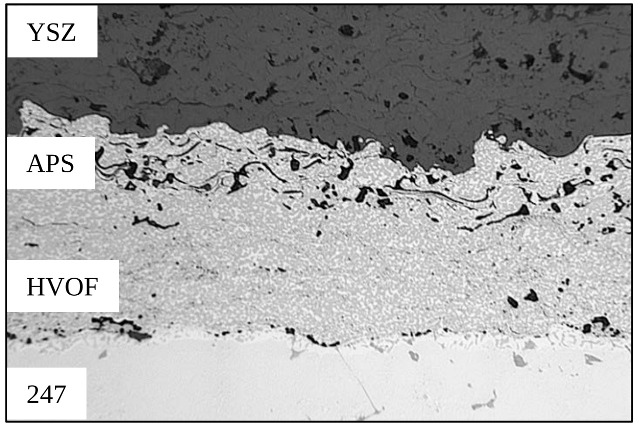
<u>YHfSi HVOF-only</u>
(0.68 Y, 0.25 Hf, 0.36 Si)




<u>YHfSi Flash Coating</u>
(0.68 Y, 0.25 Hf, 0.36 Si)




<u>Y-only Flash Coating</u>
(0.42 Y)




- Dense YHfSi HVOF layer in each case
- Outer APS flash coatings contain internal oxidation generated during APS deposition
- More internal oxidation in YHfSi APS layer
  - Sprayed same powder size
  - Due to higher RE content?

| Material | Ni | Co | Cr | Al | Y | Hf | Si | Ti | W | Ta | Mo | C | Other (ppmw) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| YHfSi Bond Coating | 48.0 | 21.6 | 16.7 | 12.3 | 0.68 | 0.25 | 0.36 | < | 0.01 | < | < | < | 2 S |
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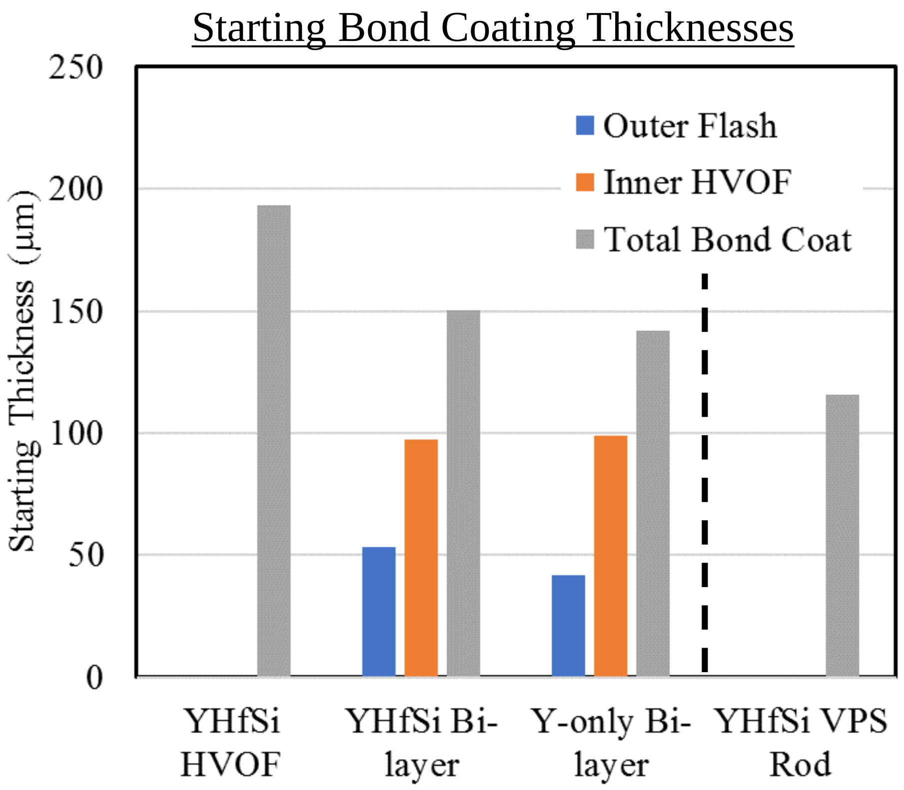
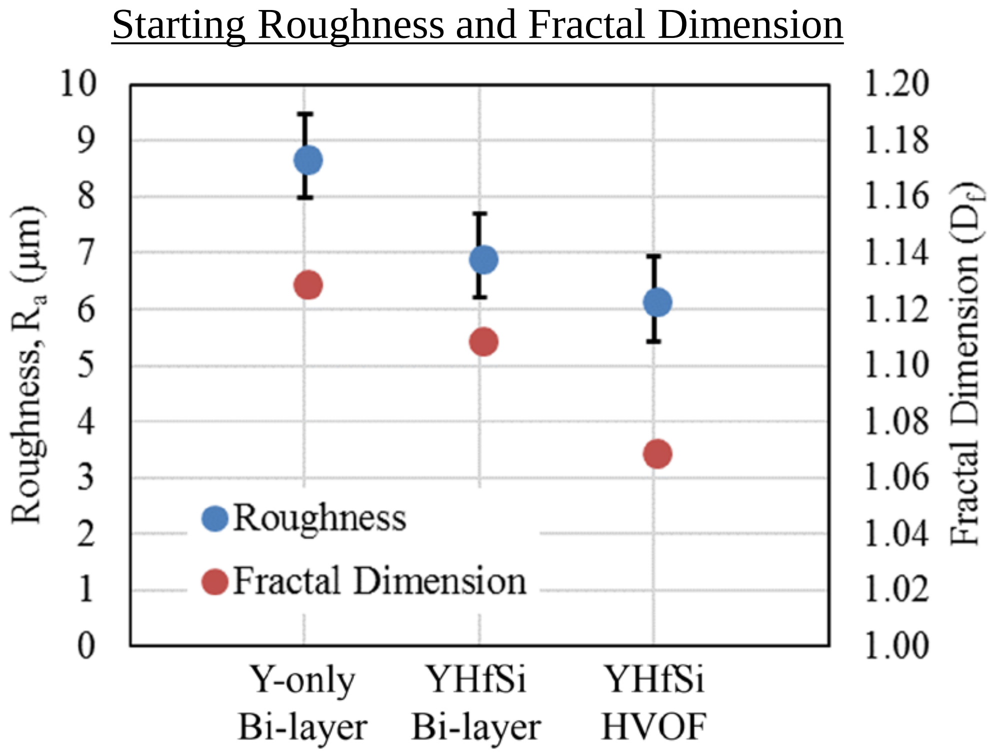
| Alloy 247 | 59.1 | 10.2 | 8.5 | 5.6 | < | 1.32 | 0.06 | 1.0 | 10.0 | 3.2 | 0.6 | 0.2 | 200 Re, 11 S |

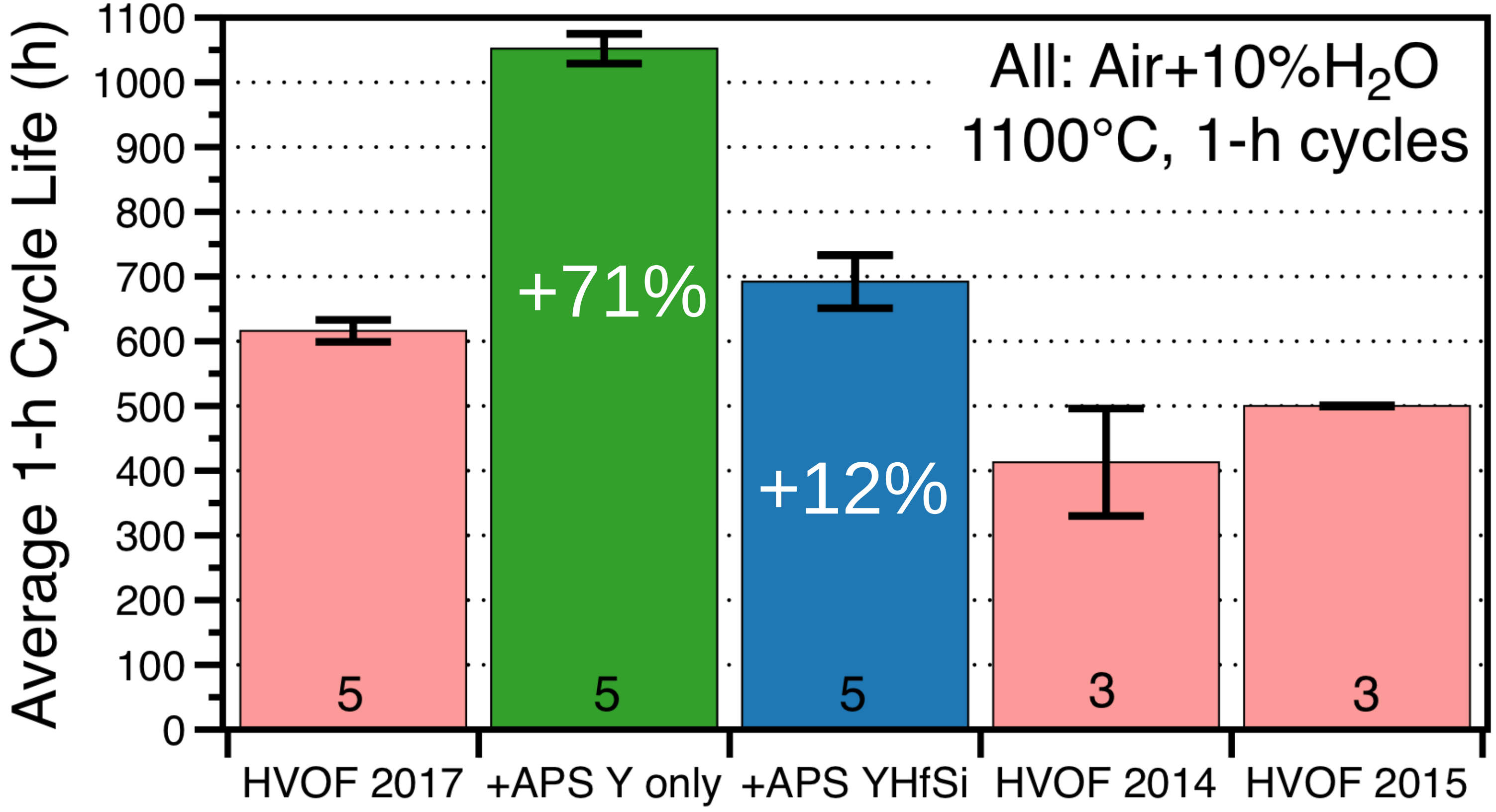
# Starting bond coating conditions




- HVOF-only coating slightly thicker (but had lowest life)
- Roughness did increase with flash coating
- Measured fractal dimension ($D_f$) as described by Nowak et al. (Jülich)
  - Fairly small differences measured to explain 12% and 71% increase in lifetime

# Y-only flash coating out-performed HVOF by 71%




HVOF as baseline

50 µm APS flash coating

Y only vs. YHfSi

5 specimens of each coating

1-h cycles

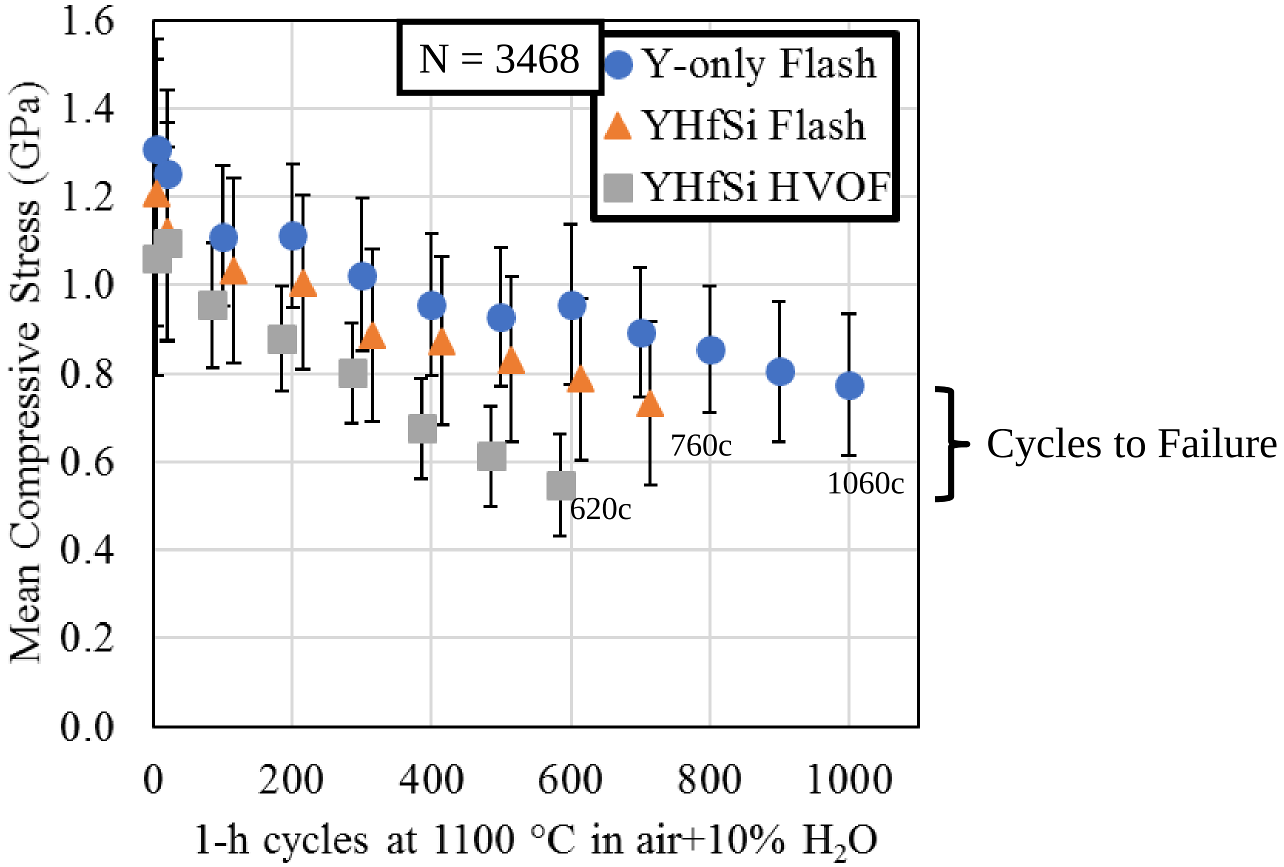
1100°C

Air+10%$H_2O$

Statistically significant results!

Manuscript submitted to *Oxidation of Metals*

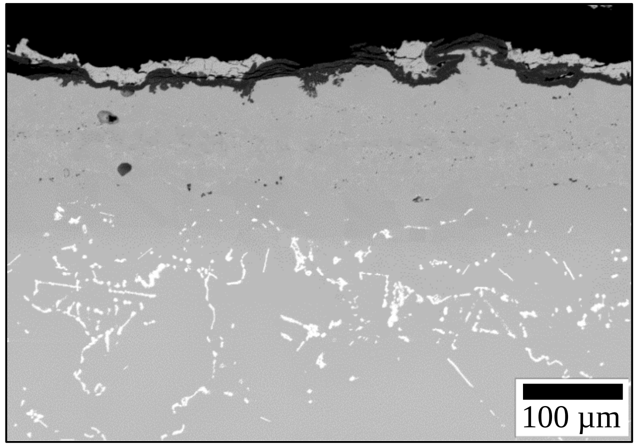
# Average compressive residual stress in the $Al_2O_3$ scale declines with cycling as damage accumulated



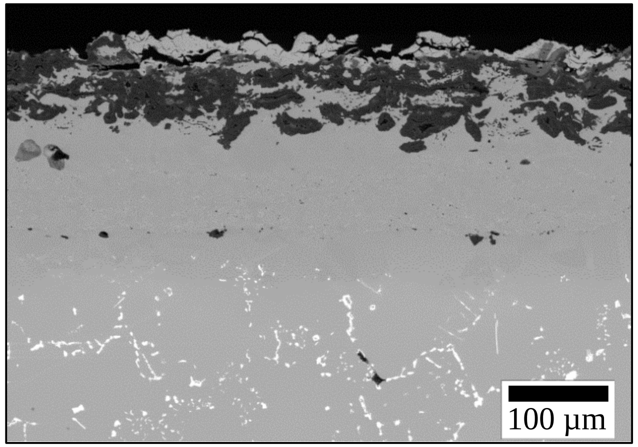

- The rate of stress decline was fastest for the HVOF-only bond coating which reaches a lower mean compressive stress prior to failing than the two bi-layer coatings.

# Failure microscopy: HVOF and flash-coat differences

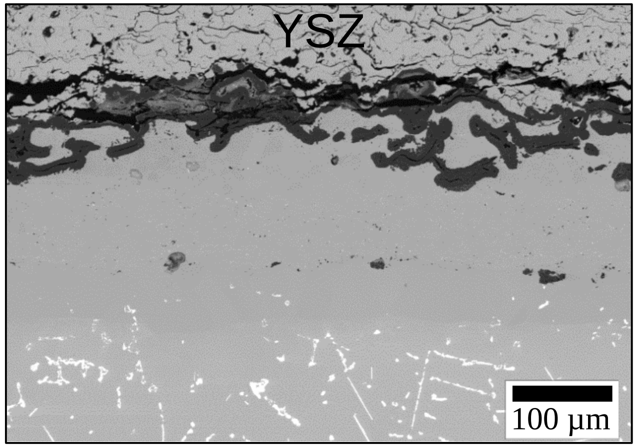
YHfSi HVOF-only, 620 cycles




YHfSi Flash, 760 cycles

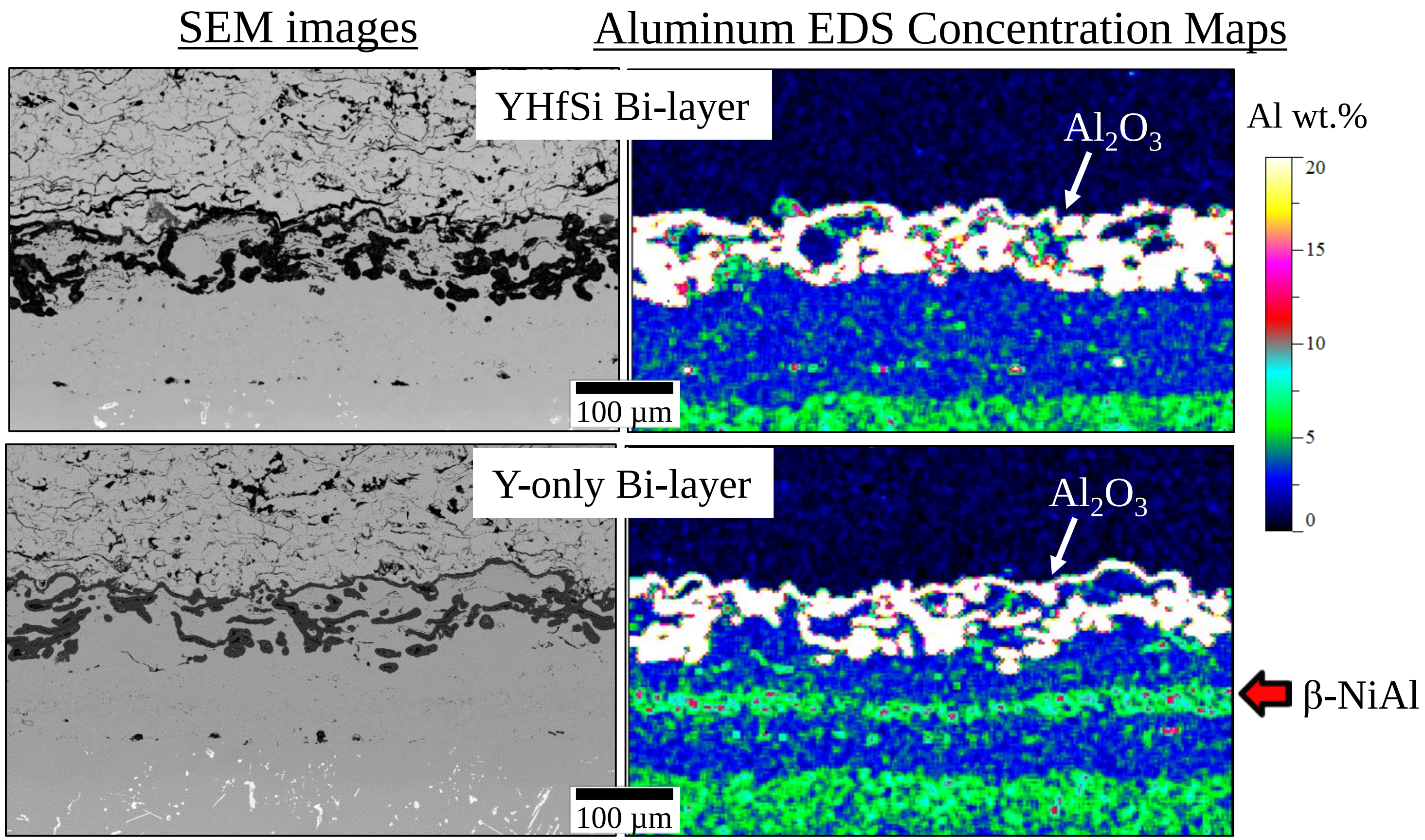



Y-only Flash, 1080 cycles




- HVOF-only: smoother interface, more uniform oxide
- Much more oxide formed with flash coatings
- Underlying HVOF layer inhibited superalloy oxidation
- Intermixed metal/oxide layer:  inhibited interface crack growth
- Intermixed metal-oxide layer:  did it create a graded interface & reduce CTE mismatch?

# Ran two more flash-coated specimens to 300 cycles: YHfSi flash coating: Al was more depleted in HVOF layer




After 300 1-h cycles at 1100°C in air+10%$H_2O$

YHfSi: more oxide = more Al consumed = shorter life



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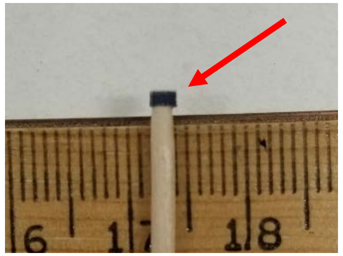
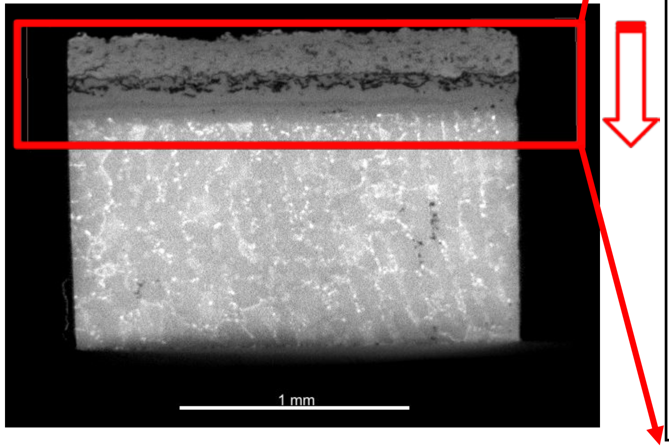
# Micro-X-ray Computed Tomography (µCT) shows promise for characterizing plasma sprayed coatings

2 X 2 mm sample



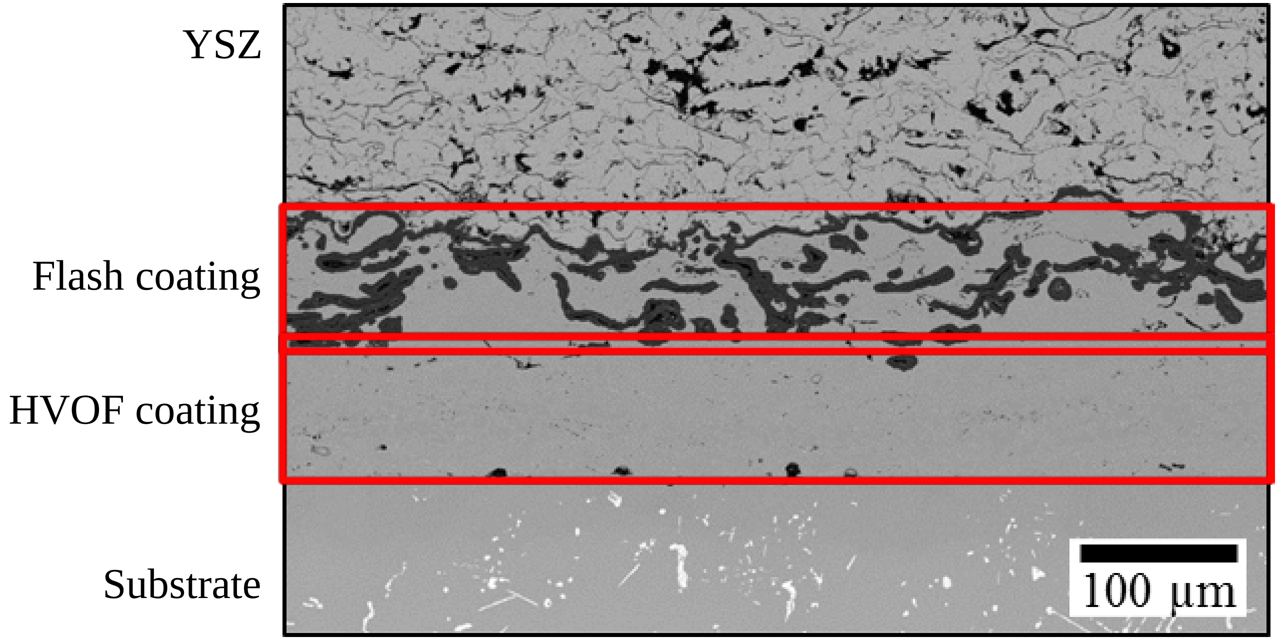
Sliced Section




Y-only Bi-layer, 300 cycles, 1100°C (Top to Bottom slices)

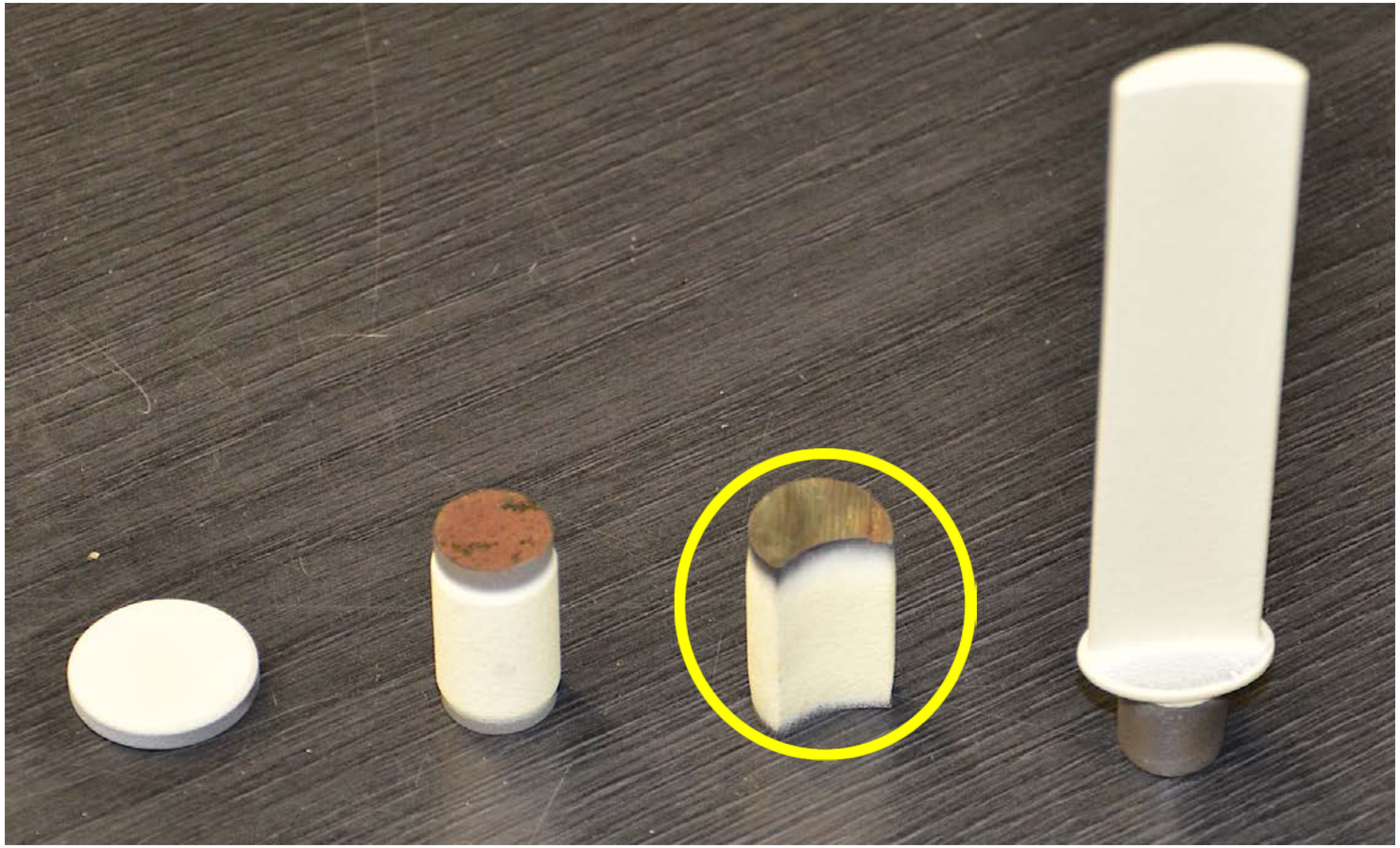
- Zeiss Xradia 520 Versa µCT has a resolution from 20 µm down to 1 µm
- PS splat size, porosity shape and size, oxide scales and β-NiAl regions can all be characterized non-destructively.

# Why did the Y-only flash coating increase lifetime 71%?




1. Intermixed alumina-metal layer inhibited crack growth; possibly acted to reduce CTE mismatch in system
2. Dense HVOF layer was a barrier for substrate attack and provided an Al reservoir for the flash coating (inhibited Ni-rich oxide).
3. Less reactive element in the Y-only flash coating reduced the rate of Al consumption, thereby increasing lifetime

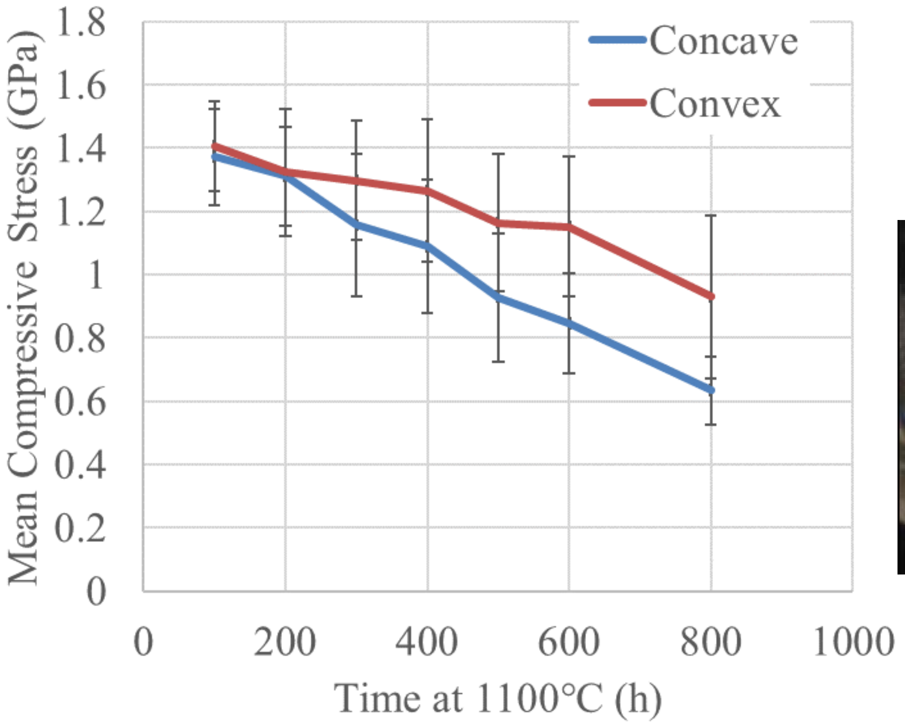
# Convex surface provided a coating challenge

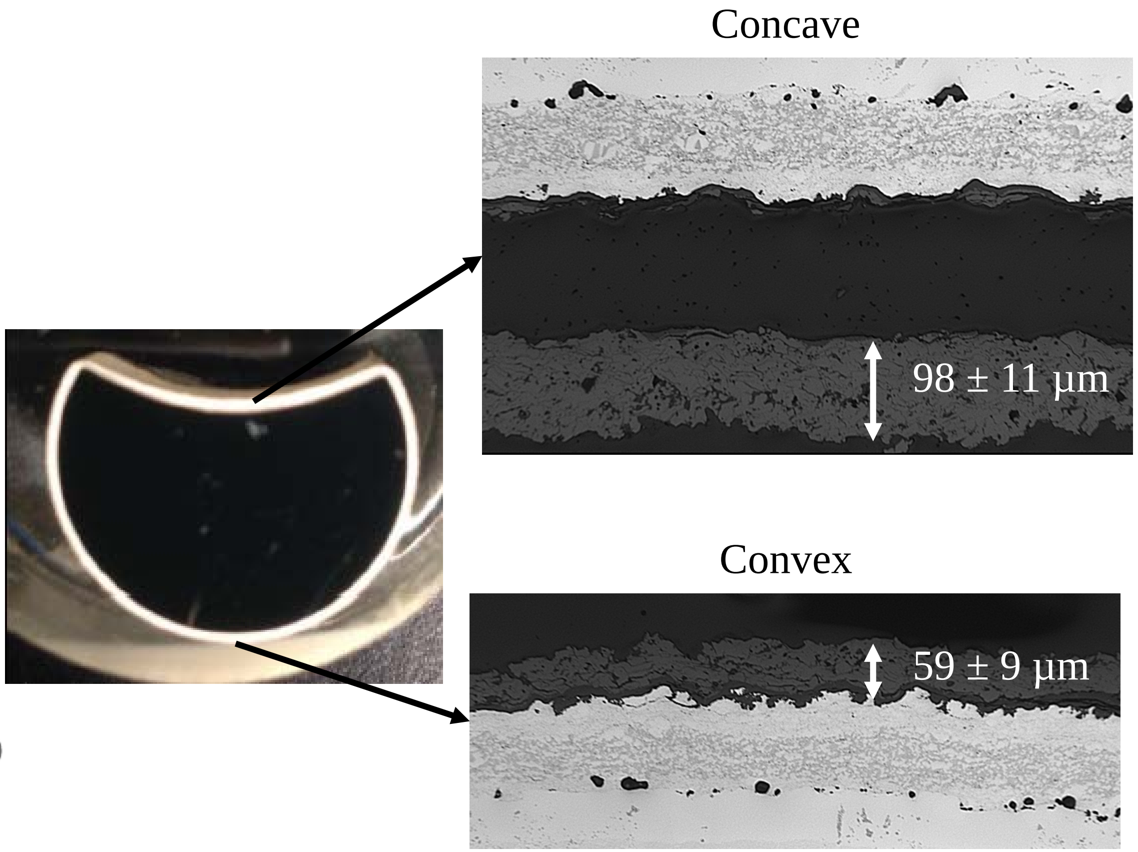


2017:  industry feedback helped achieve uniform coating
(Feedback was “blade” was too difficult to uniformly coat)

# Scale on the concave side decreased in residual stress more rapidly than the convex side

Stress measured is PLPS

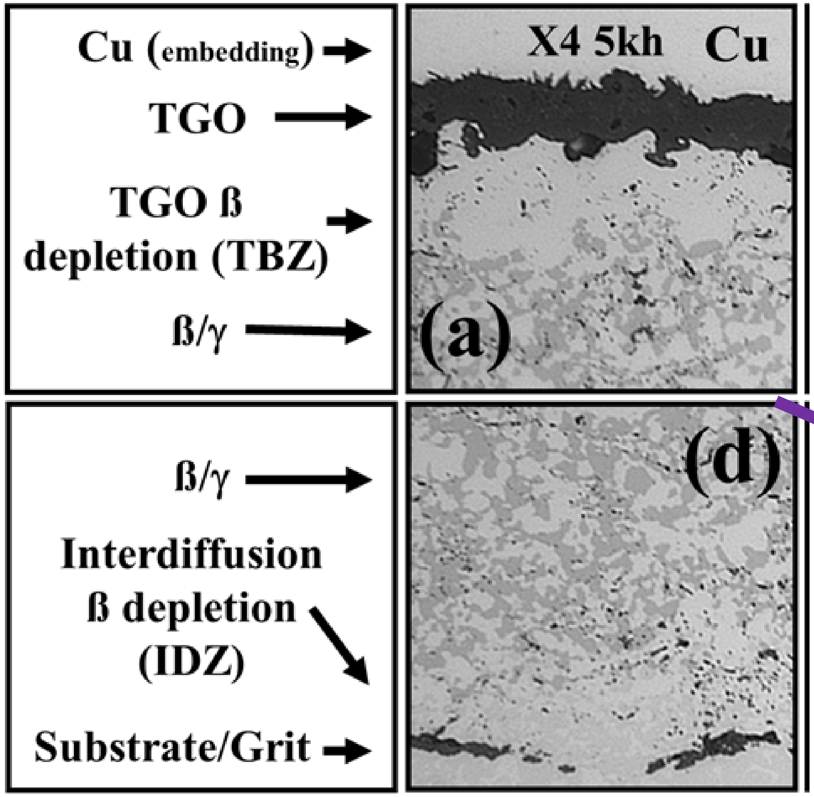


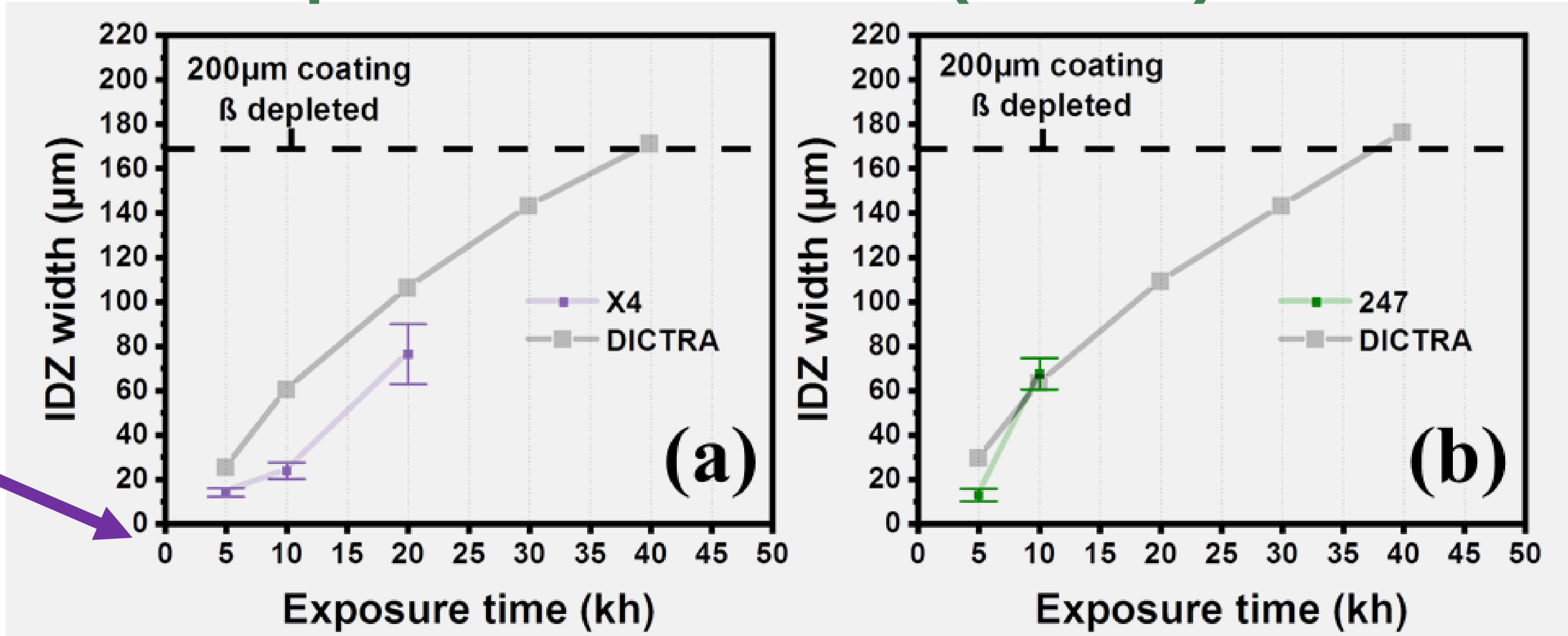

- Geometry taking us closer to real components
- Much more difficult to coat uniformly
- Coating failed after 9 x 100-h cycles

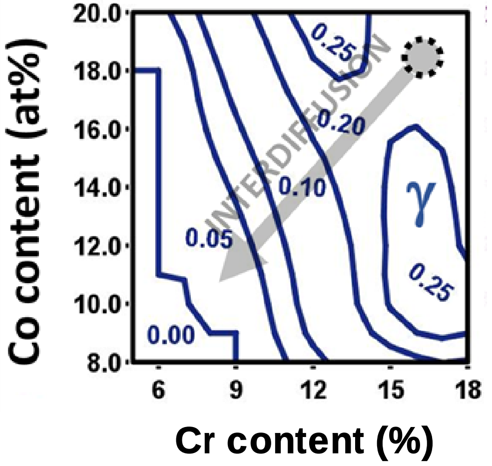
# 2nd Iteration Modeling of 900°C coating performance

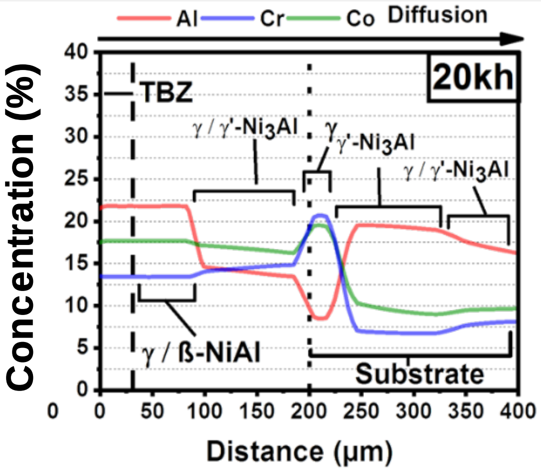
## Experiments (isothermal)

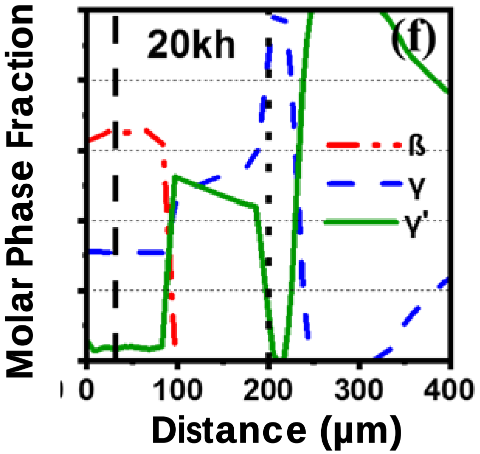



## Model predictions at 900°C (DICTRA)




**Results by K. Kane (VCU) and R. Pillai (ORNL)**

# ORNL coating project converting to EBC study in 2019

- FY18 defined an initial task to coat CVD SiC with silicate coating
  - Continuing to partner with Stony Brook University
- Building new cyclic rig for >1500°C steam testing
- Focus on next generation EBC
  - 1425°C (2600°F) without Si bond coating used at ≤1300°C
  - Initial topic:  role of EBC porosity on SiC substrate reaction

# Supercritical $CO_2$ Allam cycle: first clean fossil energy?

NetPower 25MWe demo plant (Texas)

Exelon, Toshiba, CB&I, 8Rivers Capital: $140m

The prototype NET Power plant near Houston, Texas, is testing an emission-free technology designed to compete with conventional fossil power. CHICAGO BRIDGE & IRON

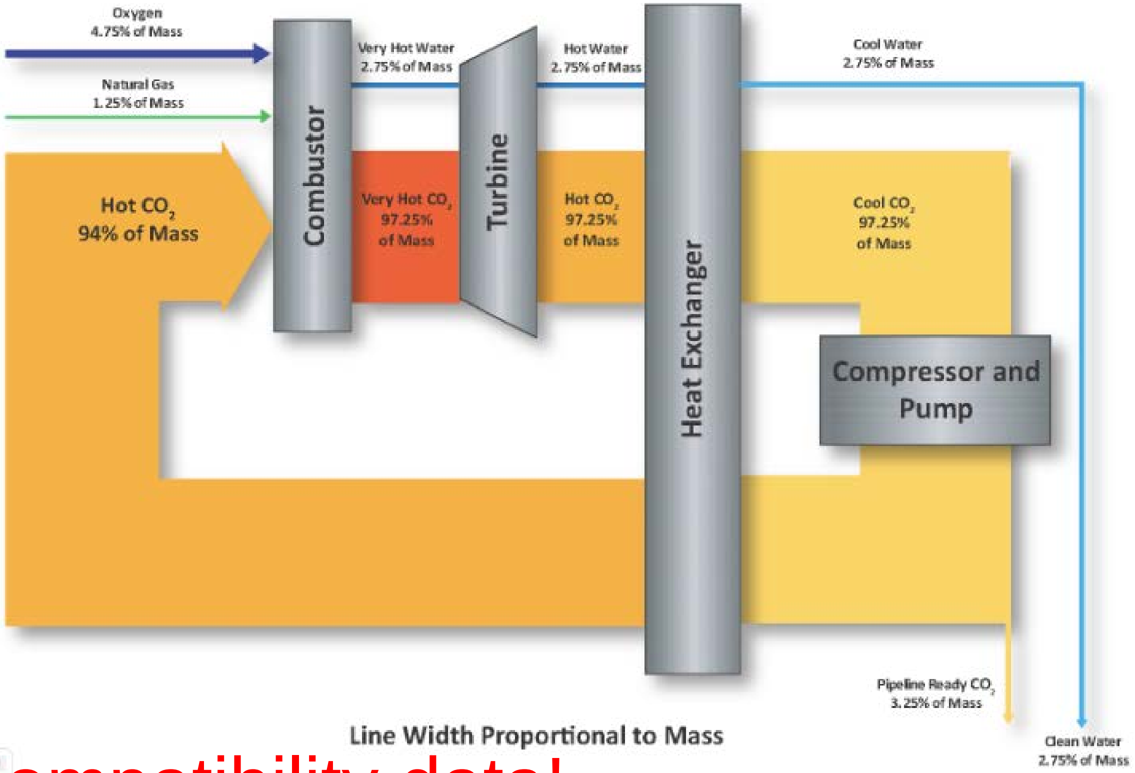
**May 2018: announced first firing**

**Material challenges:**

Combustor: 1150°C (!?!)

Turbine exit: 750°C/300 bar

**Combustion impurities: $O_2$, $H_2O$, $SO_2$**

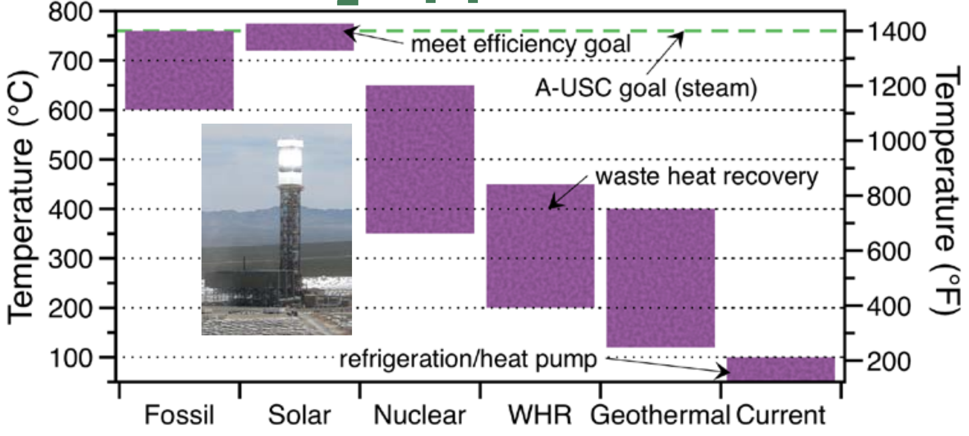


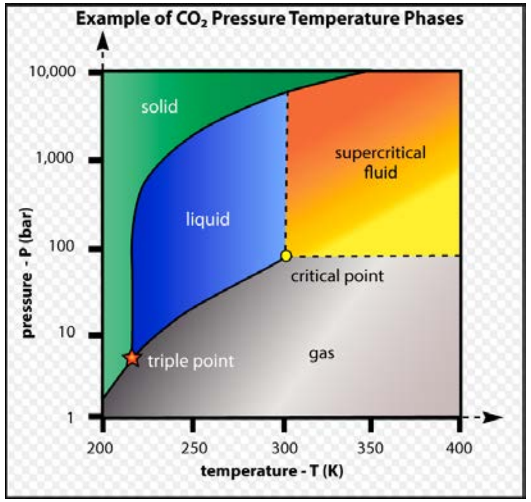

Moving forward with limited compatibility data!

As audacious as Eddystone in 1960

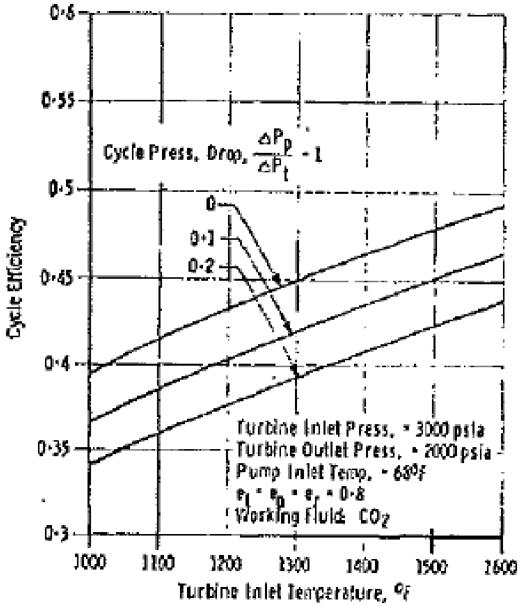
# Fossil/Solar focus on >700°C for high efficiency $sCO_2$

## $sCO_2$ applications



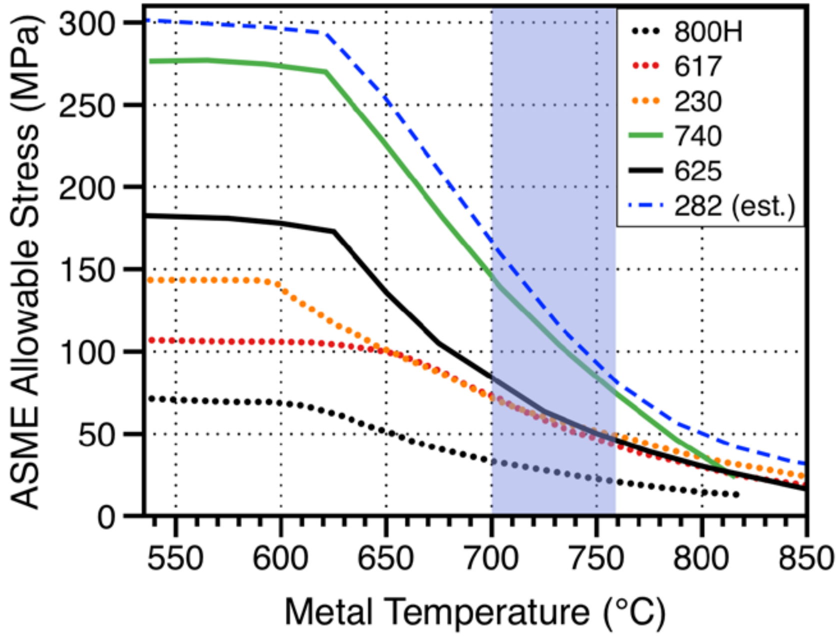

- **Low critical point (31°C/7.4 MPa)**
- **High, liquid-like density**
- **Flexible, small turbomachinery**




**Feher, 1965**

**50% $sCO_2$ eff @ >720°C**

## >700°C: favors precipitation-strengthened **Ni-based alloys**



# Cooperation between two $sCO_2$ projects at ORNL

## DOE Fossil Energy

- 750°C/300 bar: 500-h cycles
- Focus on impurity effects for direct-fire
  - Baseline research grade (RG) $CO_2$
  - New autoclave with controlled $O_2$+$H_2O$
- Alloys
  - 310HCbN (HR3C, Fe-base SS)
  - 617
  - 230
  - 247 ($Al_2O_3$-forming superalloy)
  - 282 (Heat #1)
  - 740

## DOE SunShot (CSP)

- 750°C/300 bar: 500-h cycles
  - Including 750°C/1 bar, 10-h cycles
- Focus on industrial grade (IG) $CO_2$
  - Indirect fired (closed loop)
- Alloys
  - Alloy 25 (Fe-base SS Sanicro 25)
  - 625
  - 740
  - 282 (Heat #2)

Cooperative test matrix:

| | Air | RG $CO_2$ | IG $CO_2$ | FE: $CO_2$+$O_2$/$H_2O$ |
|---|---|---|---|---|
| 1 bar | 5,000 h | 5,000 h | 5,000 h | — |
| 300 bar | — | 5,000 h | 5,000 h | 4,000+ h |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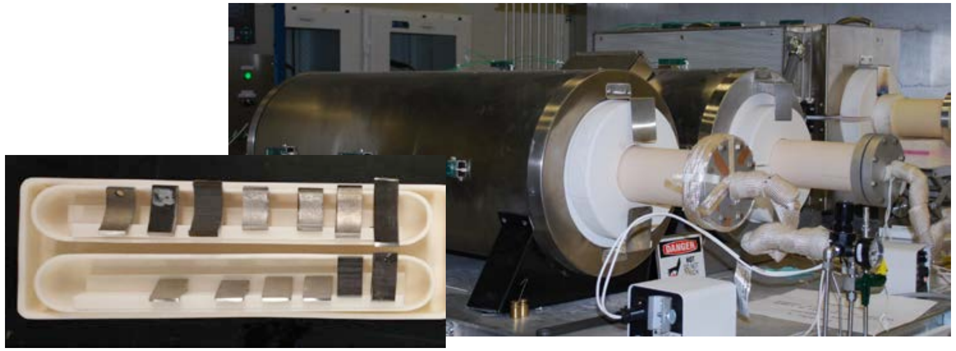
# $CO_2$ compatibility evaluated three ways at 700°-800°C

**Autoclave: 300 bar $sCO_2$**
**500-h cycles**

Correct temperature and pressure

4-5 $cm^2$ alloy coupons

**Tube furnace: 1 bar $CO_2$**
**500-h cycles**



Same cycle frequency as autoclave

**Box furnace:**
**Lab. Air**
**500-h cycles**
**(baseline)**

**"Keiser" rig:**
**500-h cycles, 1-43 bar $CO_2$**

Study impurities at 1-43 bar

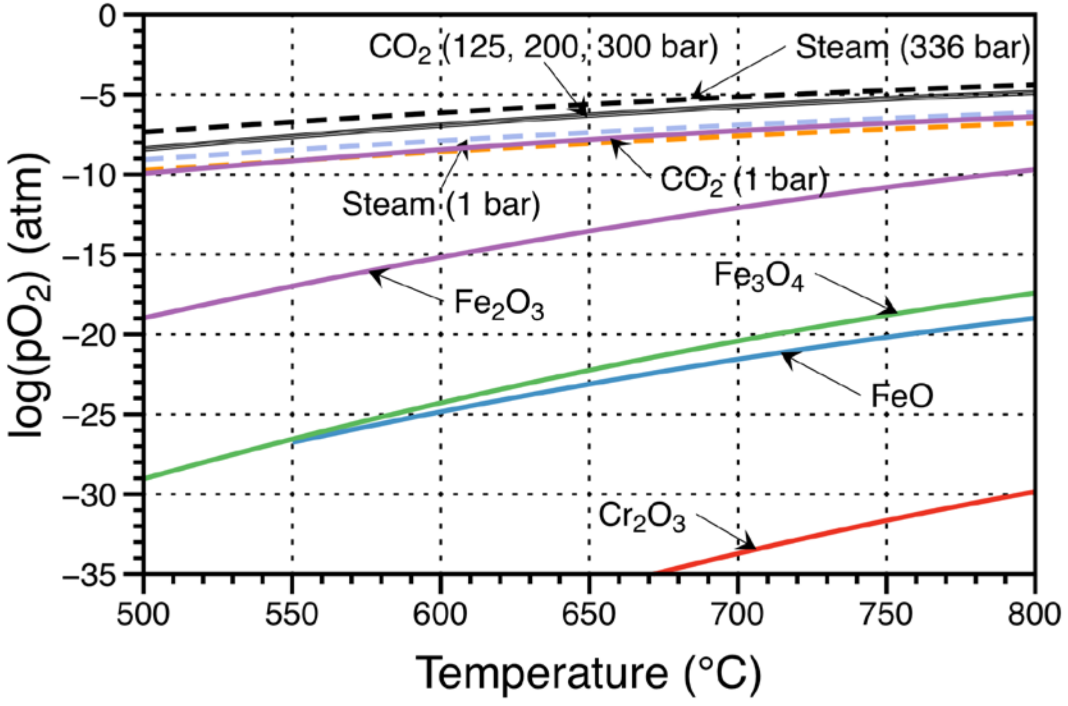
Baseline of research grade (RG) $CO_2$: ≤ 5 ppm $H_2O$ and ≤ 5 ppm $O_2$
industrial grade (IG) $CO_2$: 18±16 ppm $H_2O$ and ≤ 32 ppm $O_2$

# Range of alloys have been evaluated

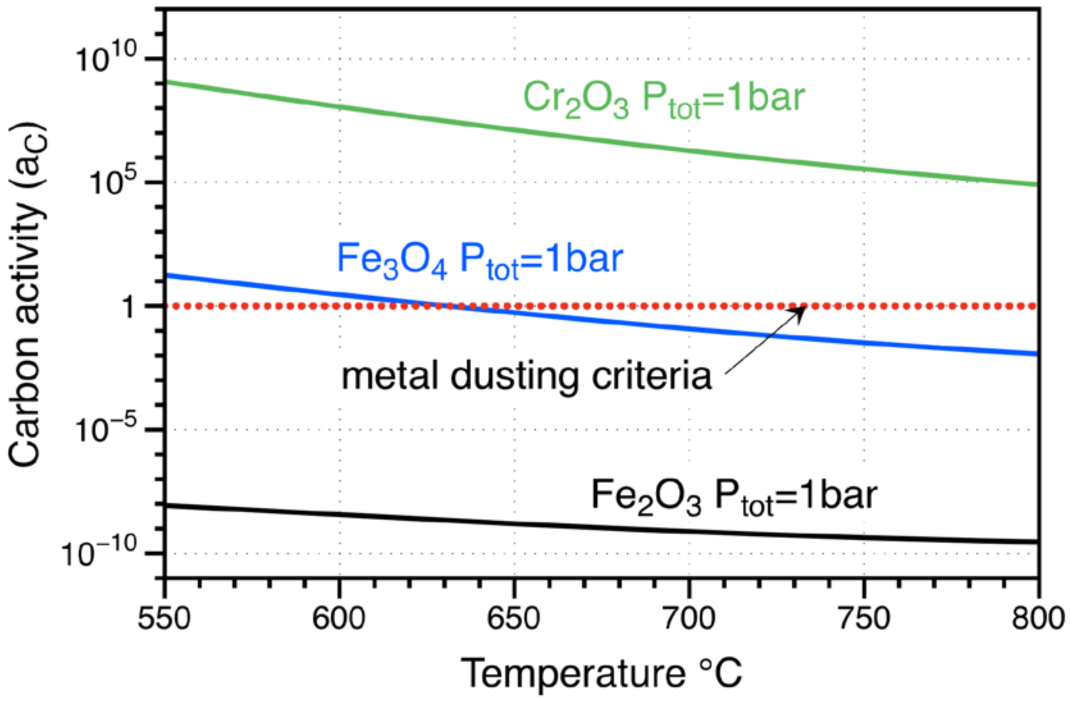
| | Ni | Cr | Fe | Co | Refractories | Ti | Al | S | Other |
|---|---|---|---|---|---|---|---|---|---|
| Grade 91 | 0.1 | 8.3 | 90 | 0.01 | 0.9Mo,0.1Nb | <0.01 | <0.01 | 10 | 0.03Cu,0.3Mn,0.1Si,0.3V |
| 304H | 8.4 | 18 | 70 | 0.1 | 0.3Mo,0.01Nb | <0.01 | <0.01 | 29 | 0.4Cu,1.6Mn,0.3Si,0.07N |
| 25 | 25 | 22 | 43 | 1.5 | 3.5W,.5Nb,.2Mo | 0.02 | 0.03 | 8 | 3.0Cu, 0.5Mn, 0.2Si, 0.2N |
| 310HCbN | 20 | 25 | 51 | 0.3 | 0.1Mo,0.4Nb | 0.01 | <0.01 | <10 | 0.1Cu,1.2Mn,0.3Si,0.3N |
| **230** | **61** | **23** | **2** | **0.1** | **1Mo, 12W** | **0.01** | **0.3** | **9** | **0.02La** |
| **625** | **61** | **22** | **4** | **0.1** | **9Mo, 4Nb** | **0.2** | **0.1** | **<10** | **0.2Si,0.1Mn,0.02C** |
| 617 | 54 | 22 | 1 | 13 | 9Mo, 1Nb | 0.3 | 1.1 | <3 | |
| **740** | **48** | **23** | **2** | **20** | **0.3Mo, 2Nb** | **2.0** | **0.8** | **<10** | **0.5Si,0.3Mn,0.03C** |
| **282** | **58** | **19** | **0.2** | **10** | **8Mo** | **2.2** | **1.5** | **<1** | **0.1Si,0.1Mn,0.06C** |
| 247 | 60 | 8 | 0.03 | 10 | 10W,3Ta,1Mo | 1.1 | 5.3 | <1 | 1.3Hf,0.14C |

Compositions measured using ICP-OES and combustion analyses

# Thermodynamics: Oxygen levels similar in steam/$CO_2$
# Concern about high C activity at m-o interface




Factsage calculations




High carbon activity at $P_{total}$ = 1 bar

What is $P_{interface}$?



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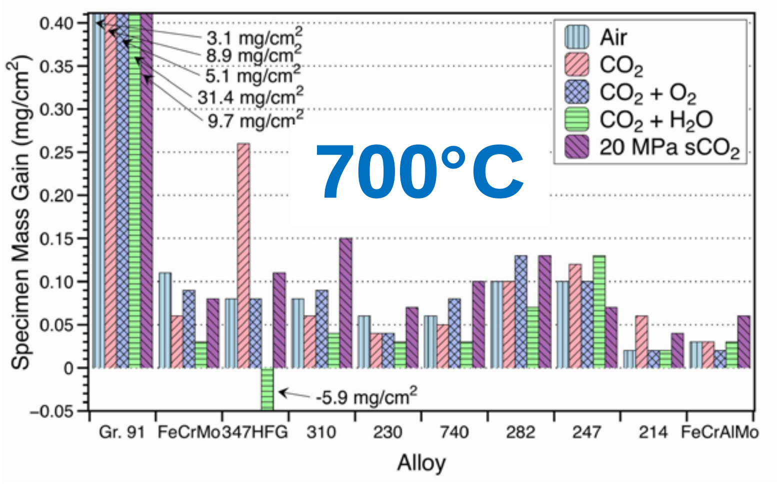
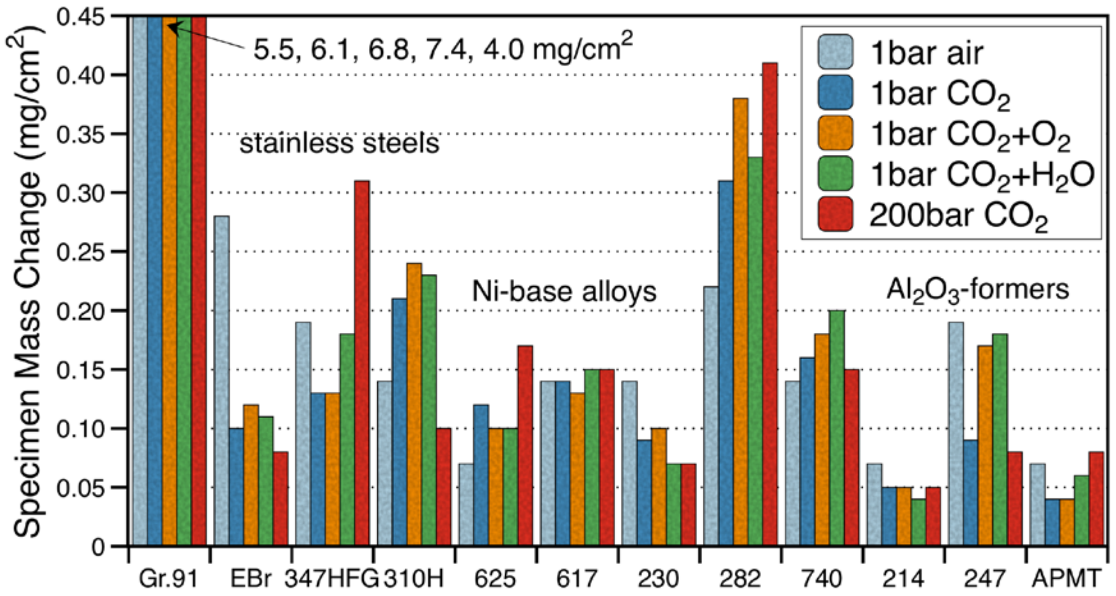
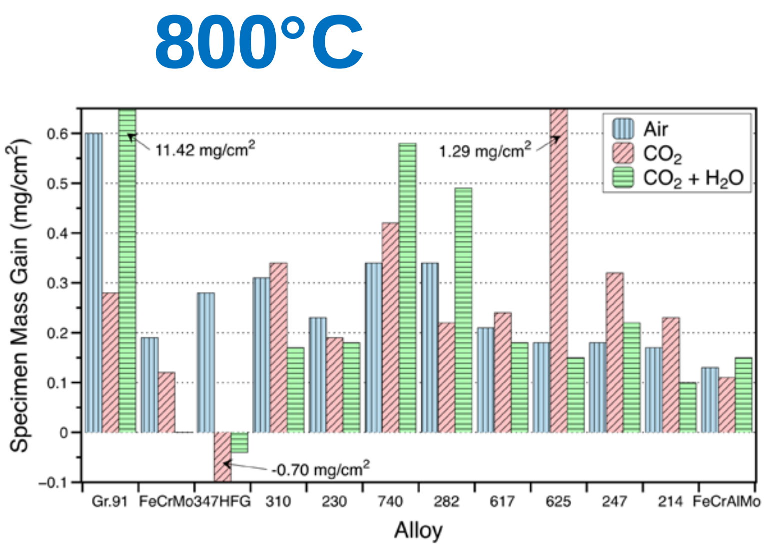
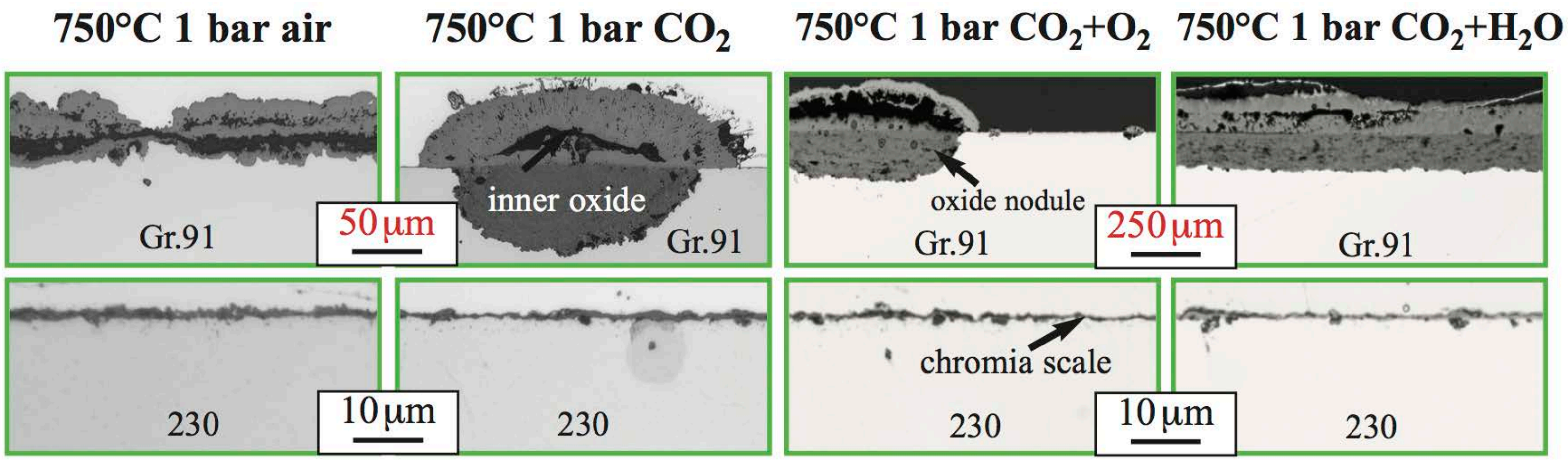
# Impurities (2015): 1atm, 500 h, many alloys (1 of each)



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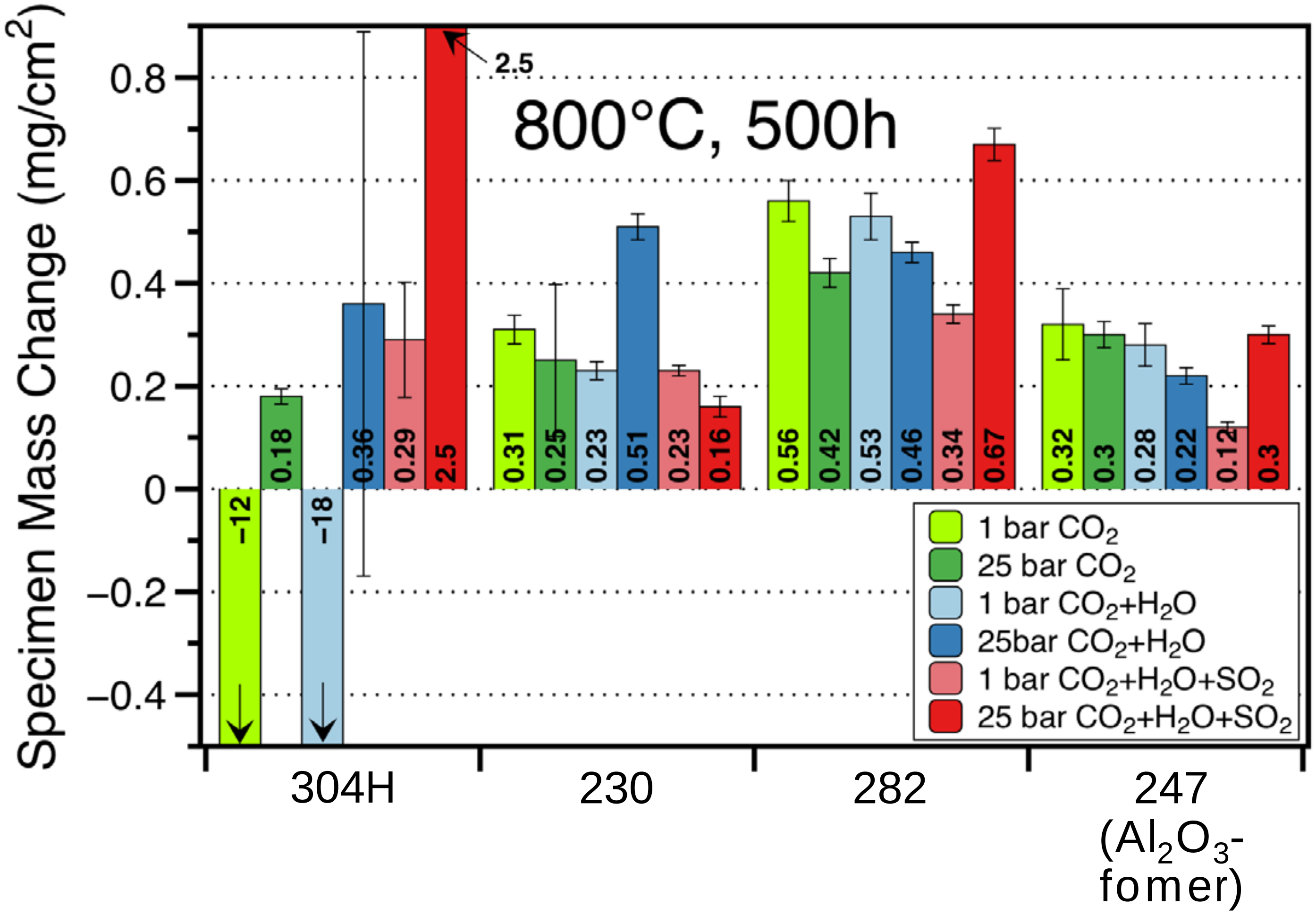
# Impurities (2017): fewer alloys (3 of each), 1 and 25 bar




Two alloy 230 reaction tubes:

Pressure: 1 and 25 bar

Gas: RG $CO_2$
$CO_2$+10%$H_2O$
$CO_2$+10%$H_2O$+0.1%$SO_2$



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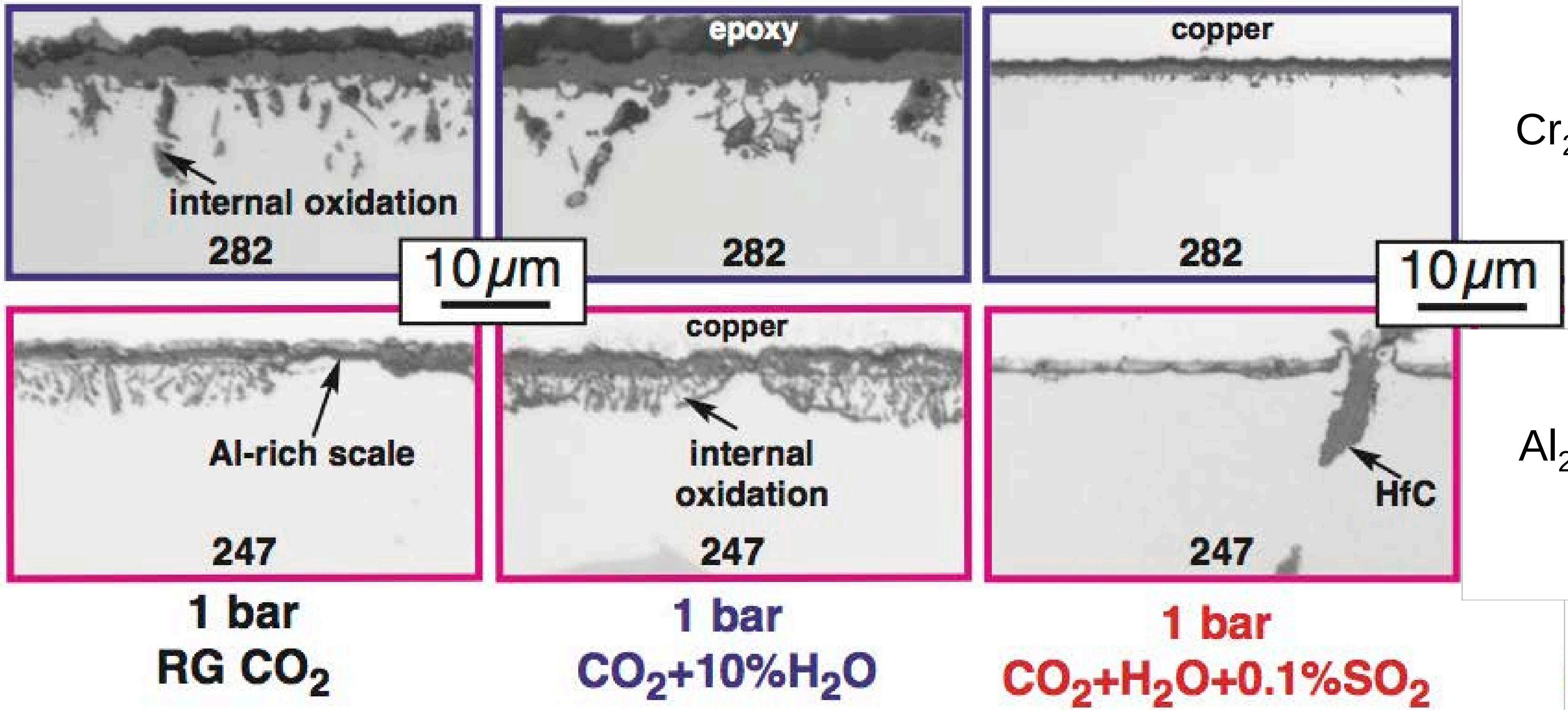
# 500h at 800°C: $SO_2$ suppressed internal oxidation at 1 bar




1000 ppm $SO_2$

$Cr_2O_3$-former

$Al_2O_3$-former

Similar results for $SO_2$ reported by Young (UNSW) and Quadakkers (Jülich)



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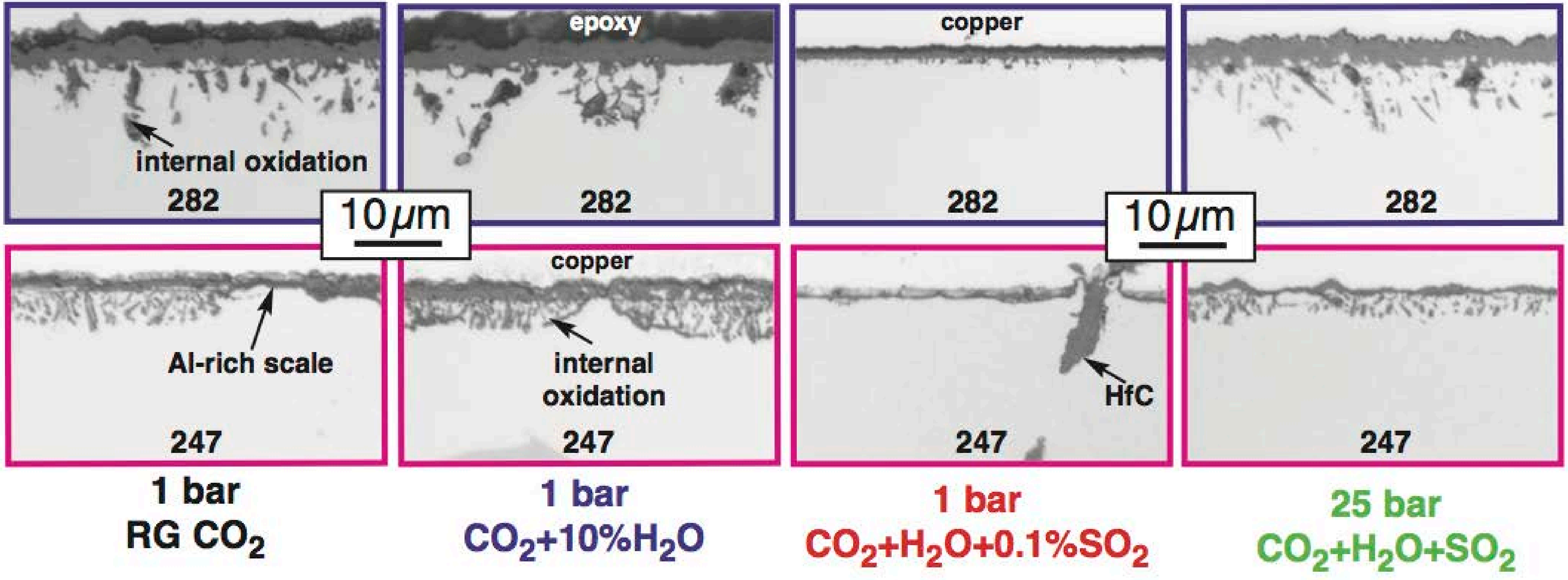
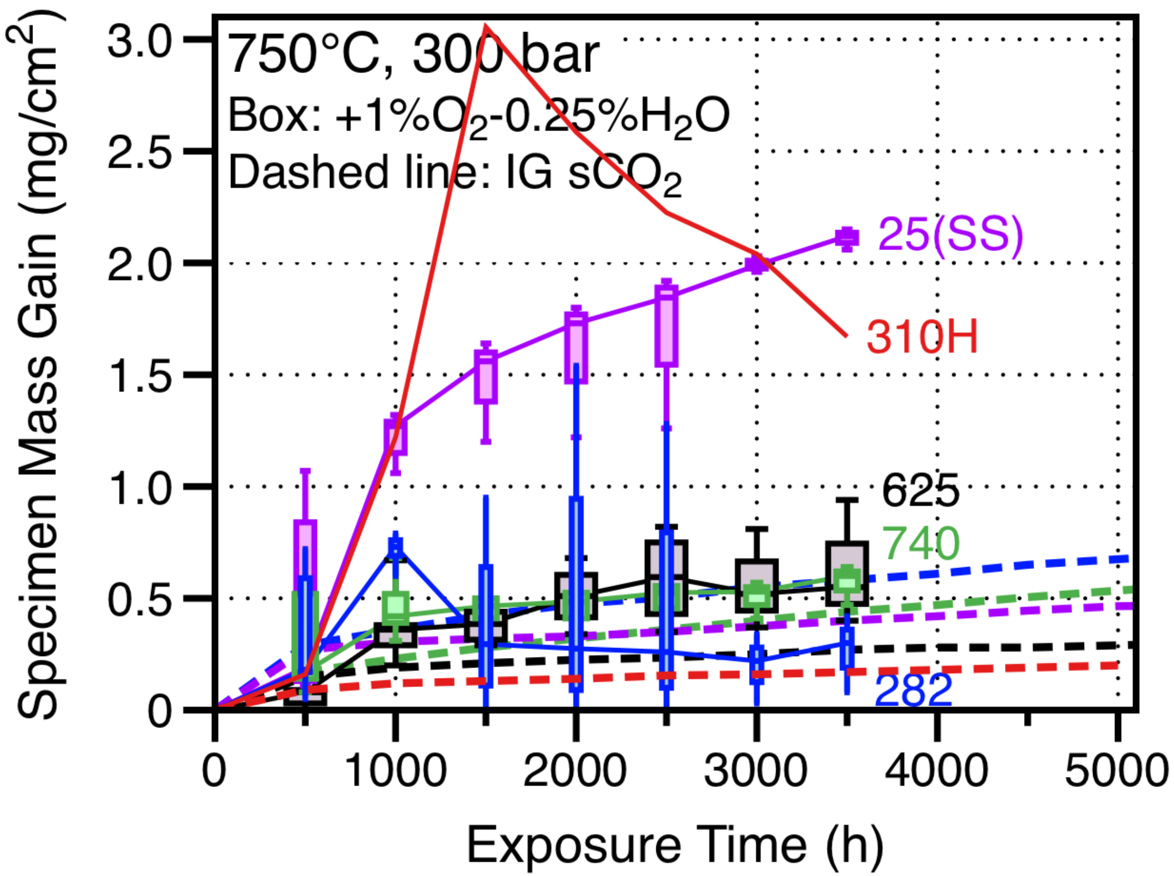
# 500h at 800°C: at 25 bar, 0.1%$SO_2$ resulted in more attack

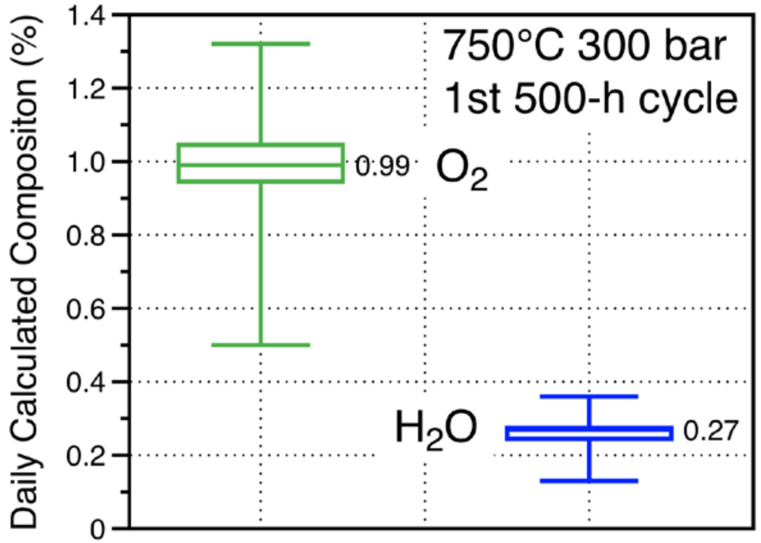



Haynes 282: Ni-20Cr-11Co-9Mo-1.6Al-2.2Ti

MarM247 superalloy: Ni-9Cr-10Co-1Mo-6Al-10W-3Ta-1.4Hf

# 2018: finally completed multi-pump 300 bar autoclave
# Clearly see an effect of impurities

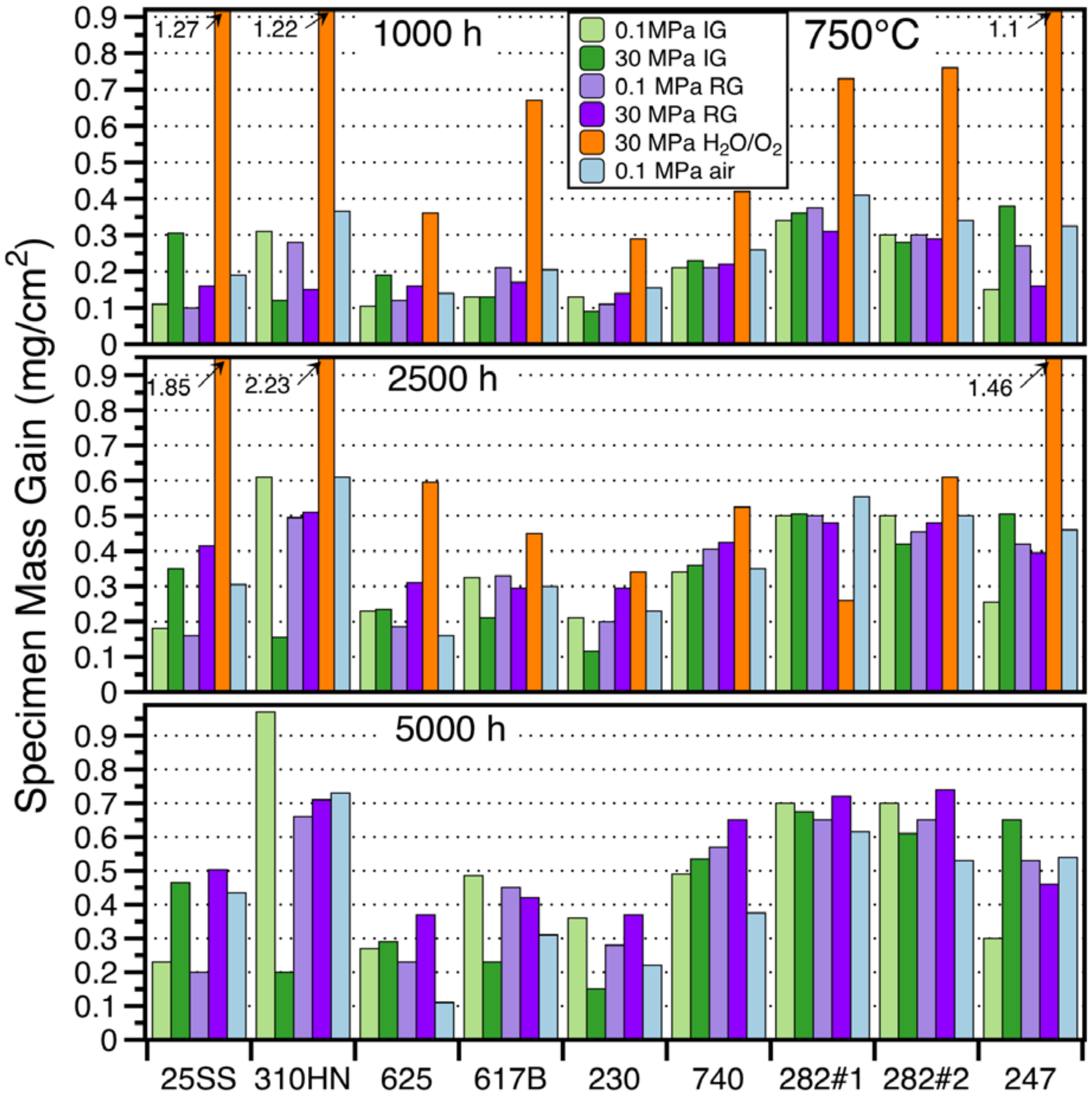



**Goal: 1%$O_2$+0.25%$H_2O$ (industry suggestion)**
**Not easy to control at 300 bar**

Research grade (RG) $CO_2$: ≤ 5 ppm $H_2O$ and ≤ 5 ppm $O_2$

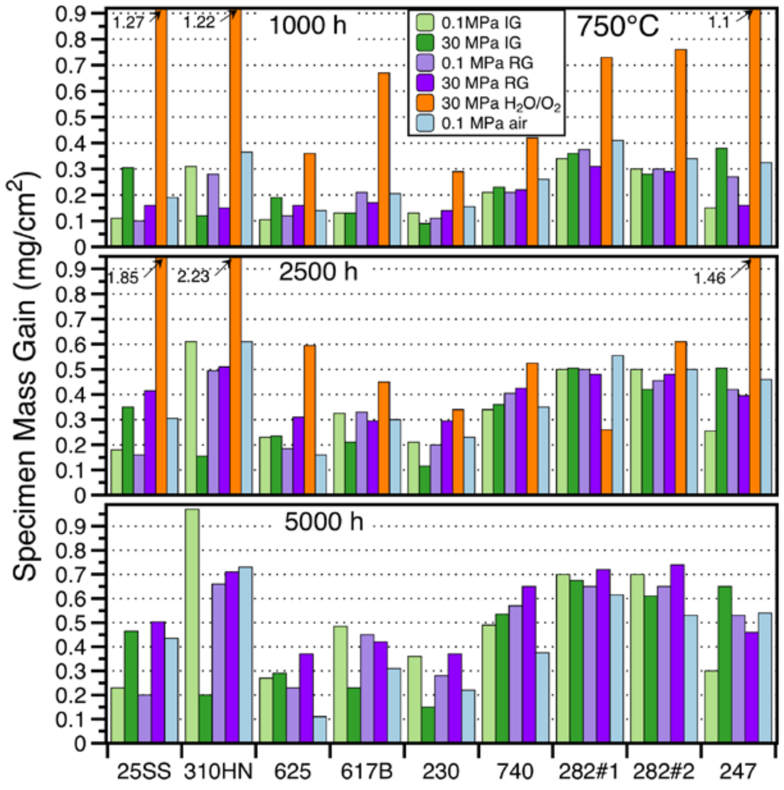
# First time: impurities caused a higher mass gain

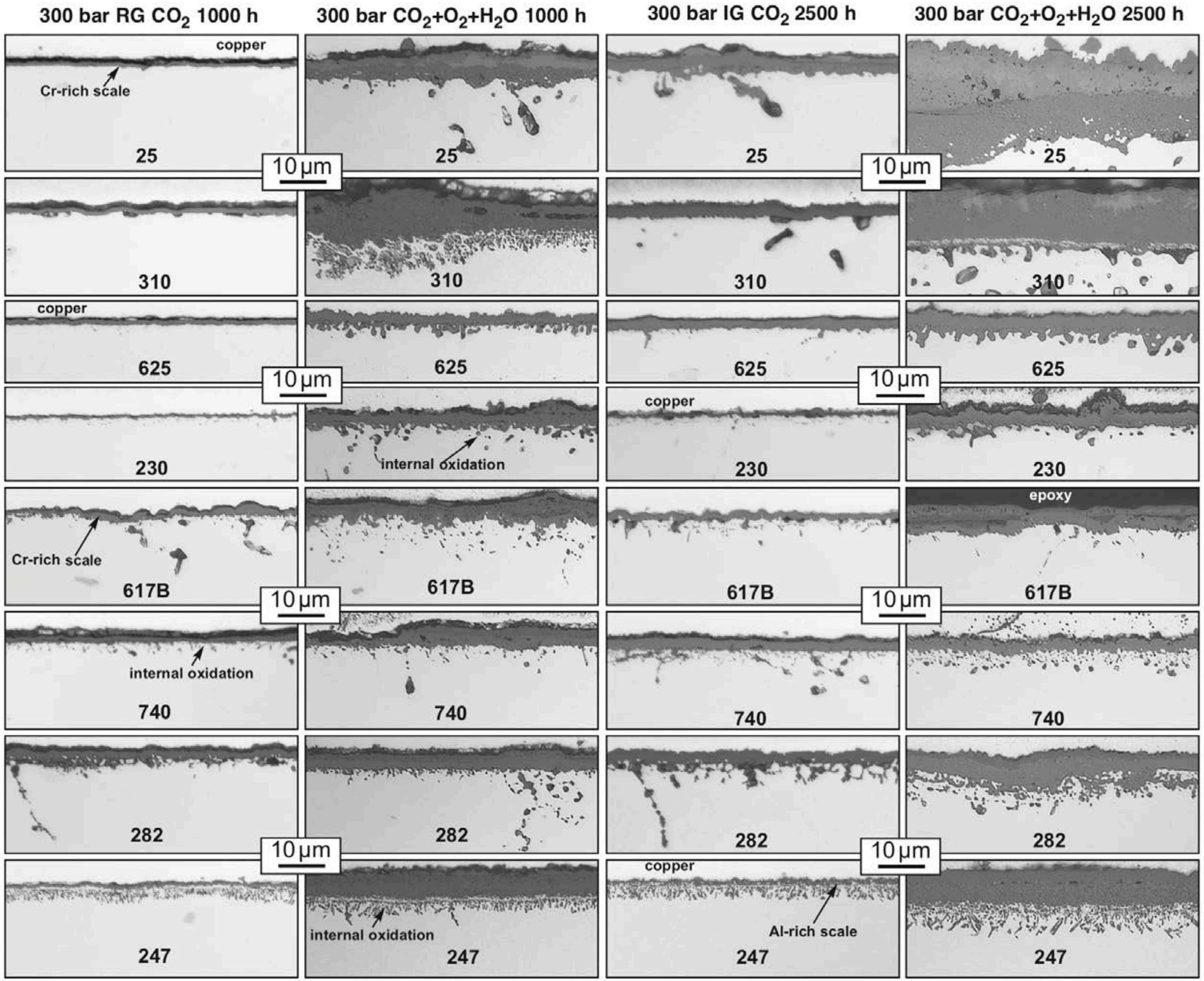



RG $CO_2$ + 1%$O_2$ + 0.25% $H_2O$

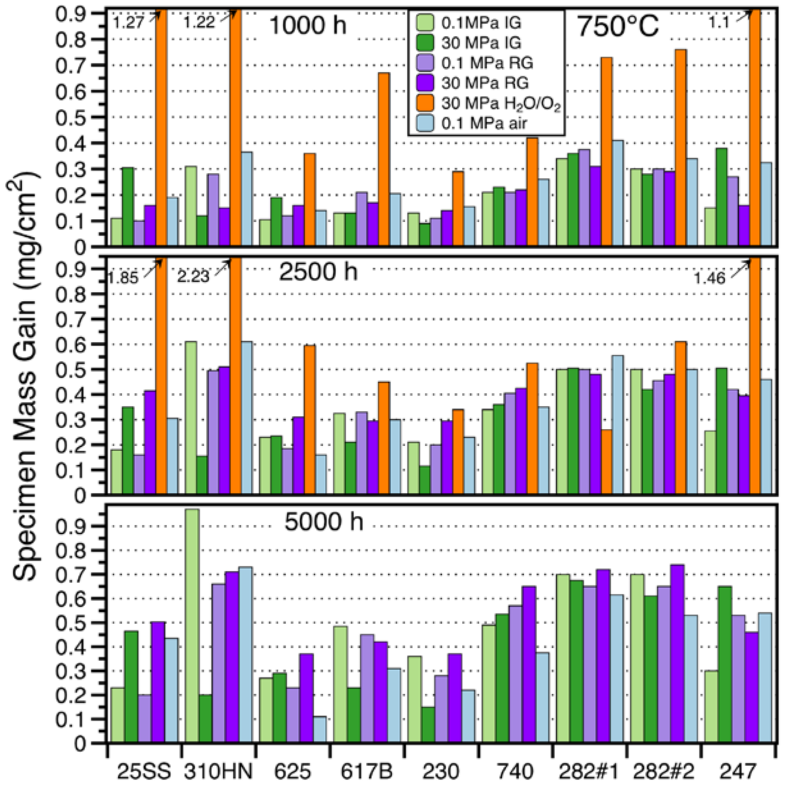
Only 4000 h completed

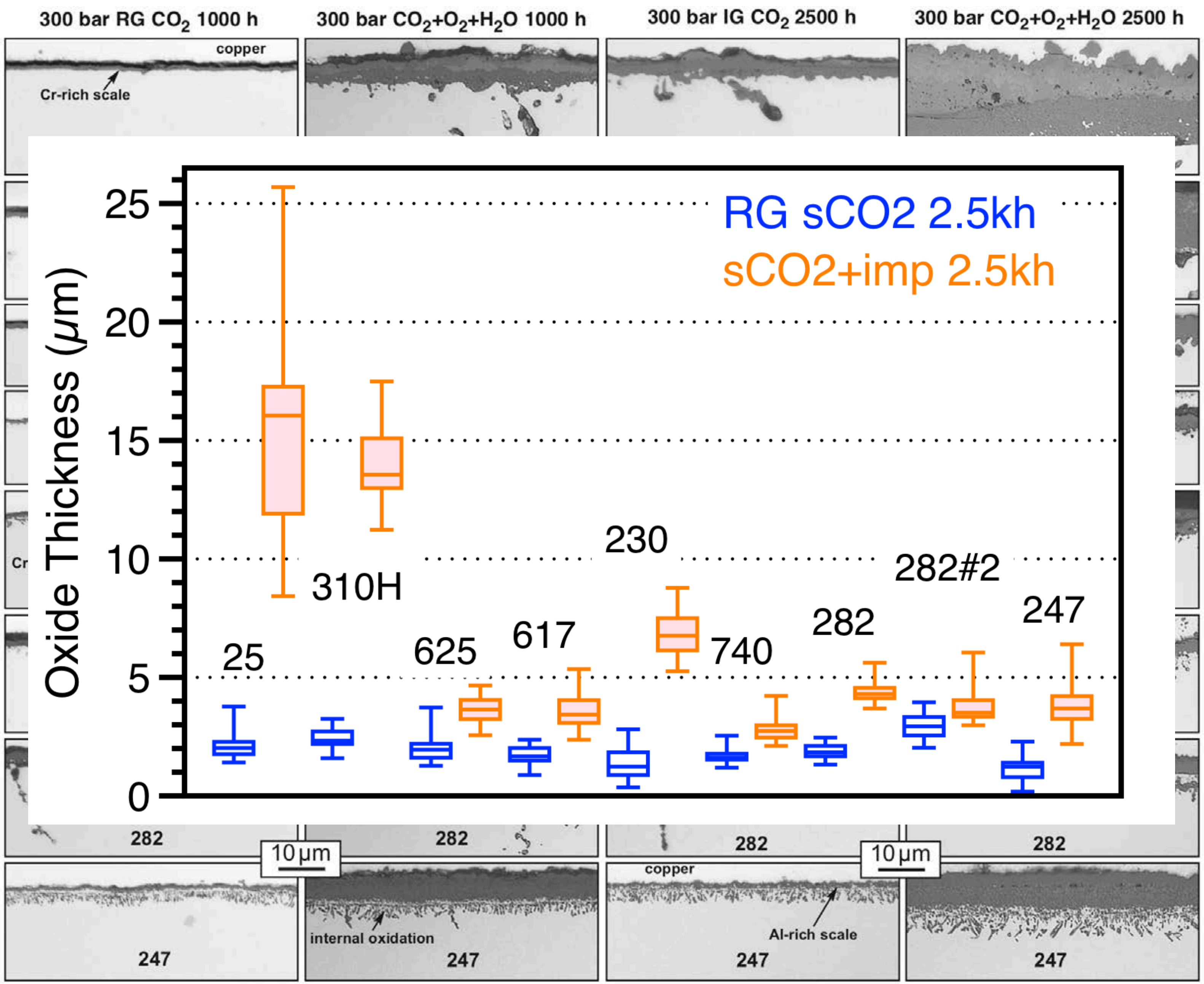
# 300 bar effect



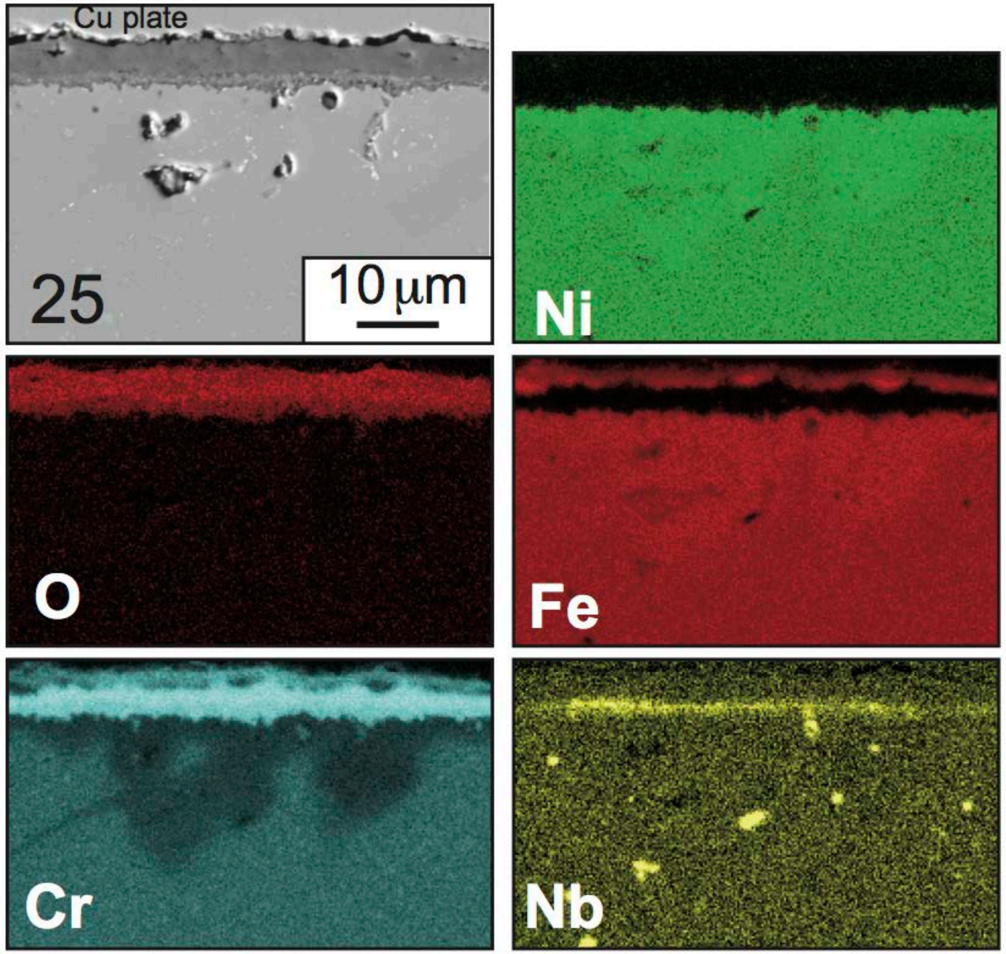



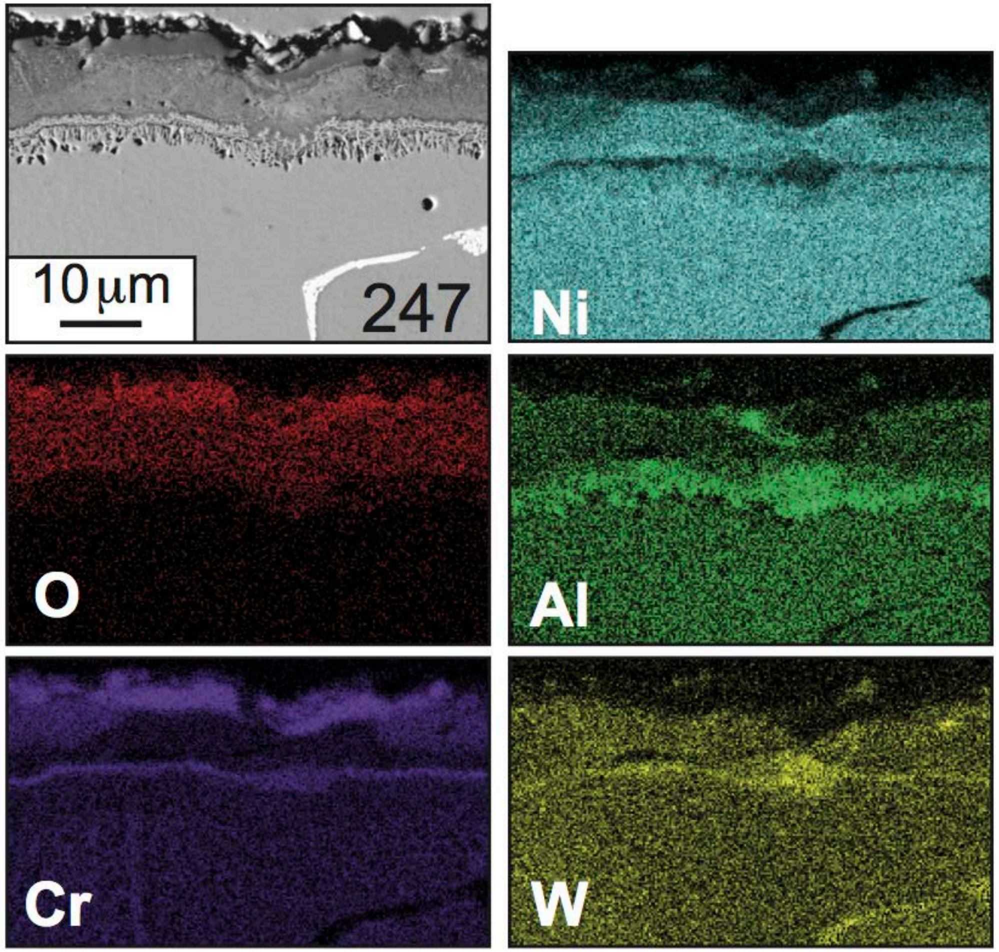
# Fe-based alloys: strongest effect



# SEM/EDS: Fe/Ni-rich oxide forming with impurities



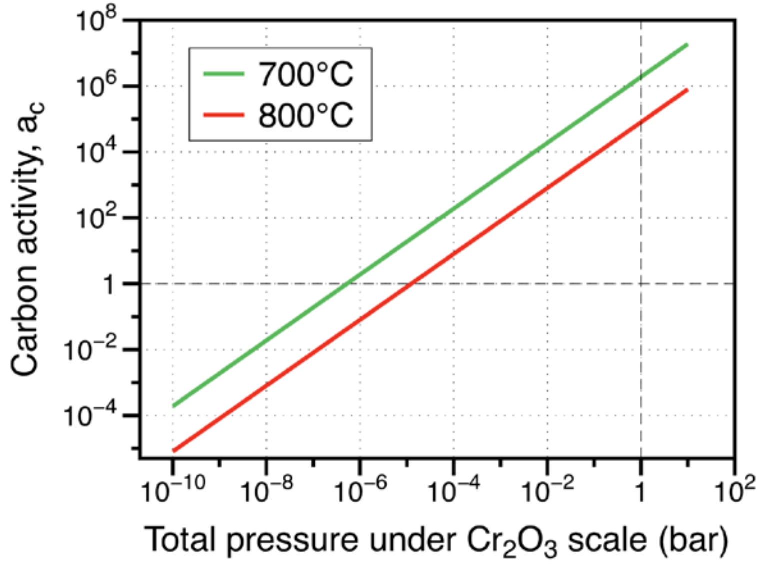




Additional characterization in progress…

# Summary: impurity and pressure effects

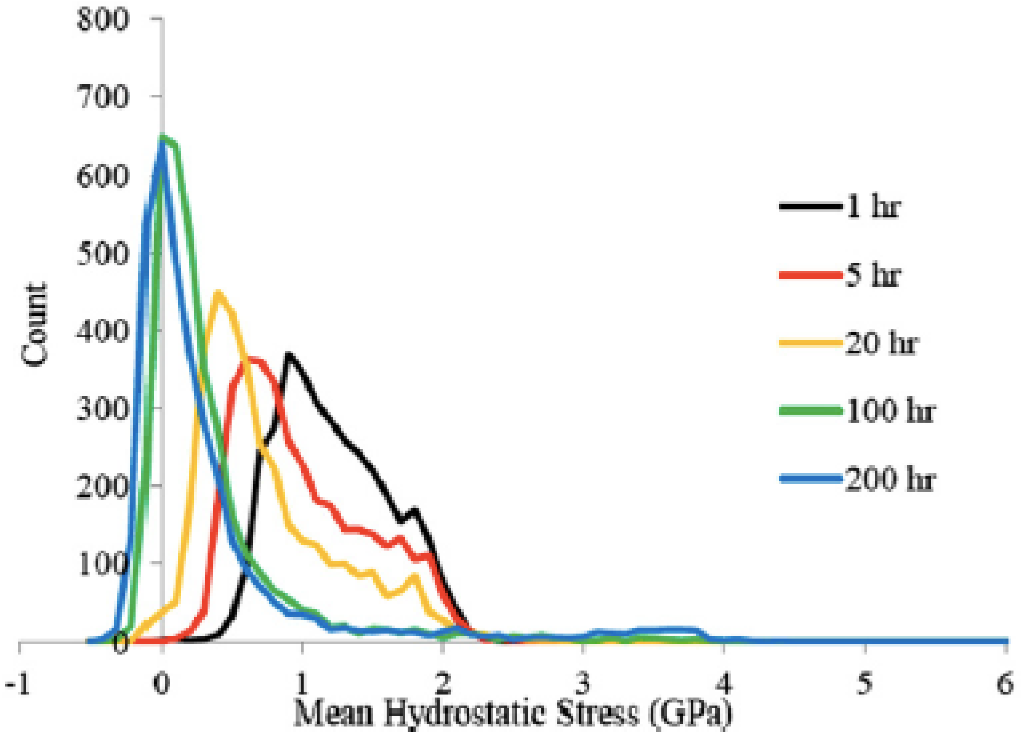
- Want to study impurities in $sCO_2$ for direct-fired concept at 750°C
  - Comparison of industrial and research grade $CO_2$ at 1 and 300 bar
    - 2018 $sCO_2$ symposium paper
  - Effect of $H_2O$ and 0.1%$SO_2$ at 1 and 25 bar
    - 2018 NACE Corrosion paper
- 300 bar $sCO_2$+1%$O_2$+0.25%$H_2O$
  - Increased mass gains observed for most alloys
  - Higher Fe/Ni incorporated into scale
- Current hypotheses
  - Higher P = denser, more protective scale
    - More characterization of thin scales required
  - $SO_2$ suppresses C & OH effects (Young & Quadakkers): can we take advantage?
- Future work at lower temperatures and more Fe-based alloys

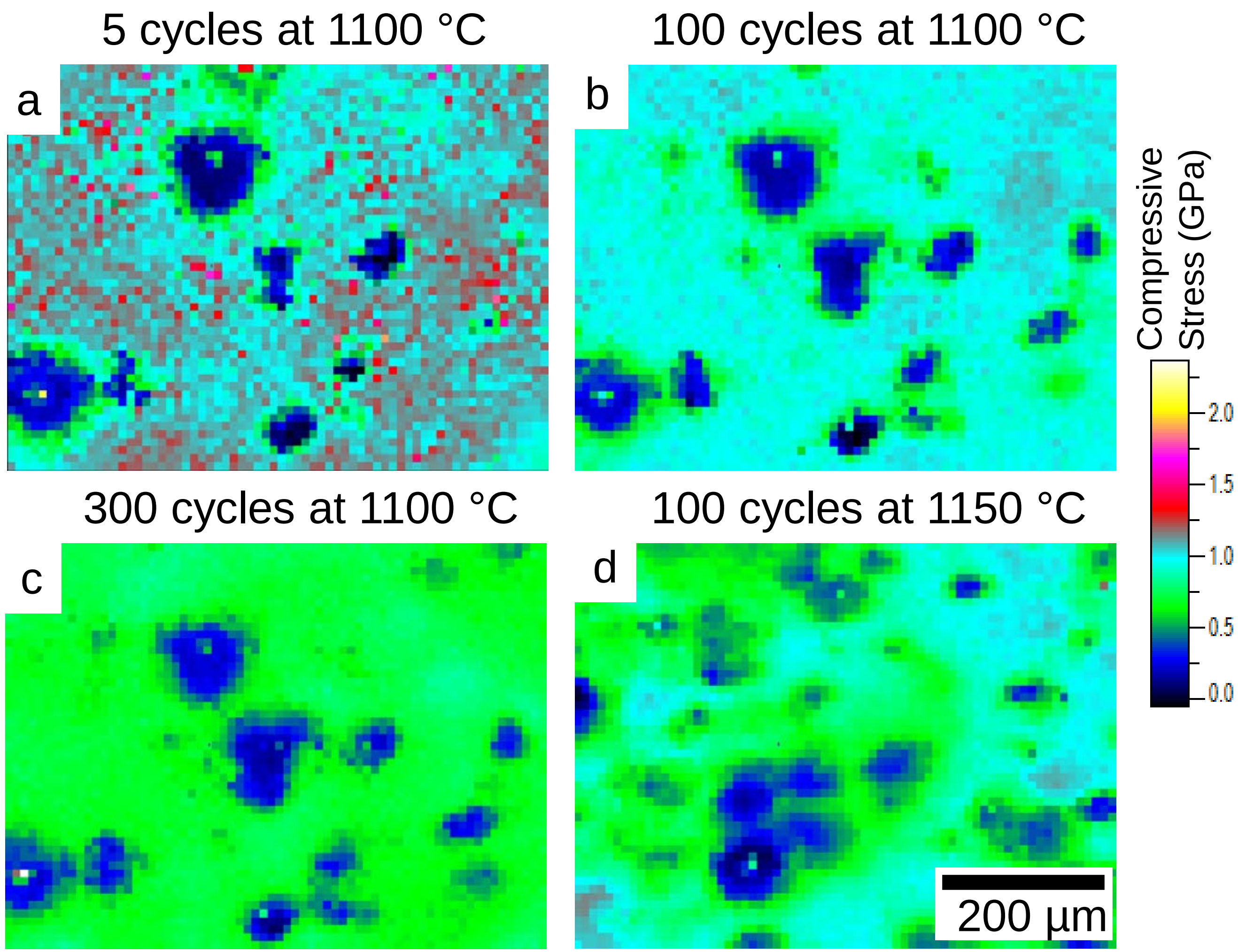
# Backup slides



# In-situ coating characterization using PLPS through YSZ

1-h cycles in ”wet” air (10%$H_2O$)

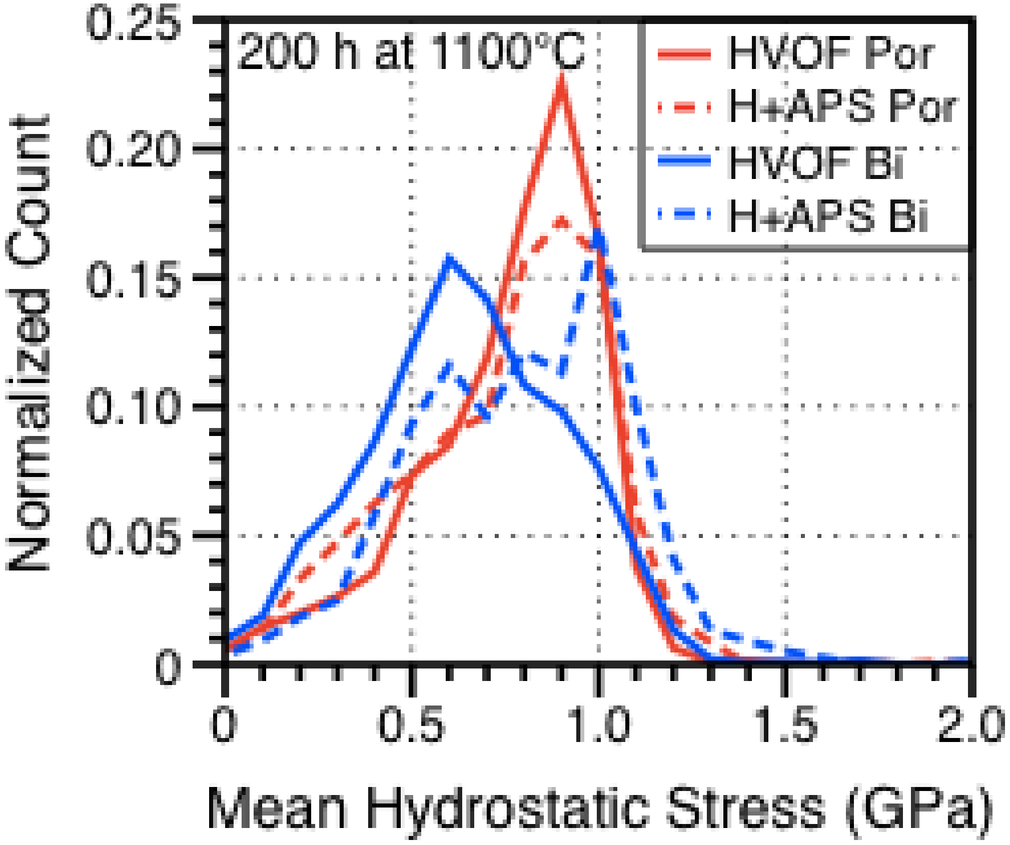


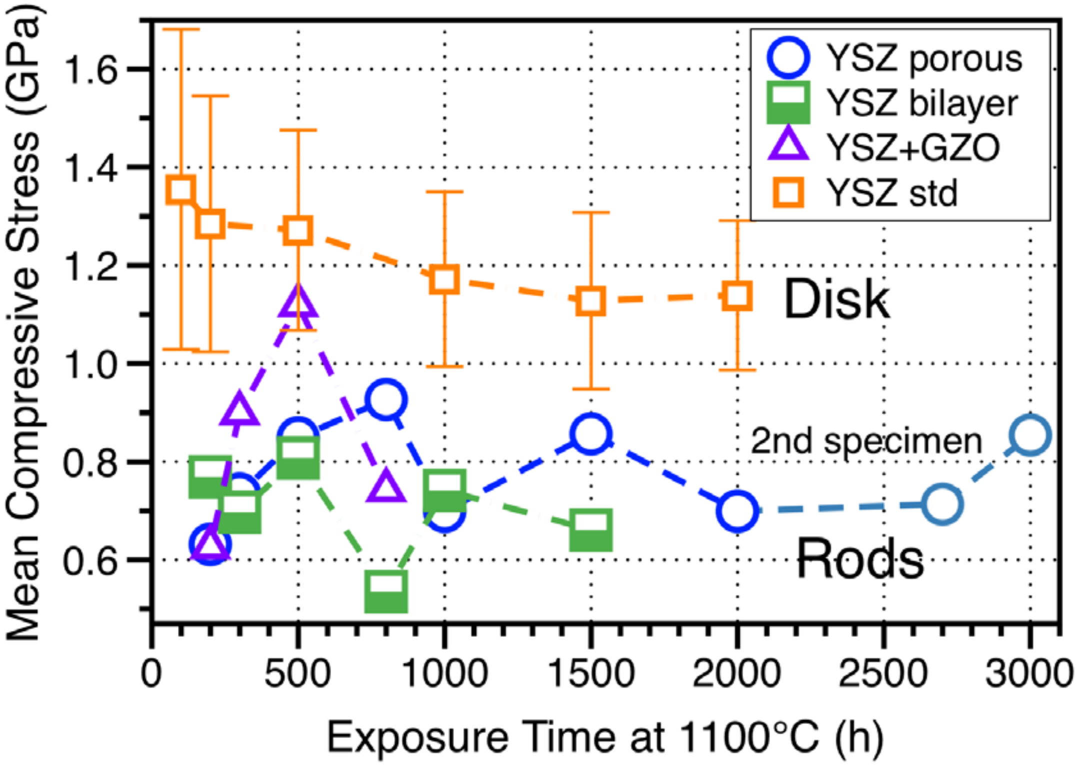

PLPS: photo-stimulated luminescence piezospectroscopy

# PLPS results: very weak signal through 300µm top coating

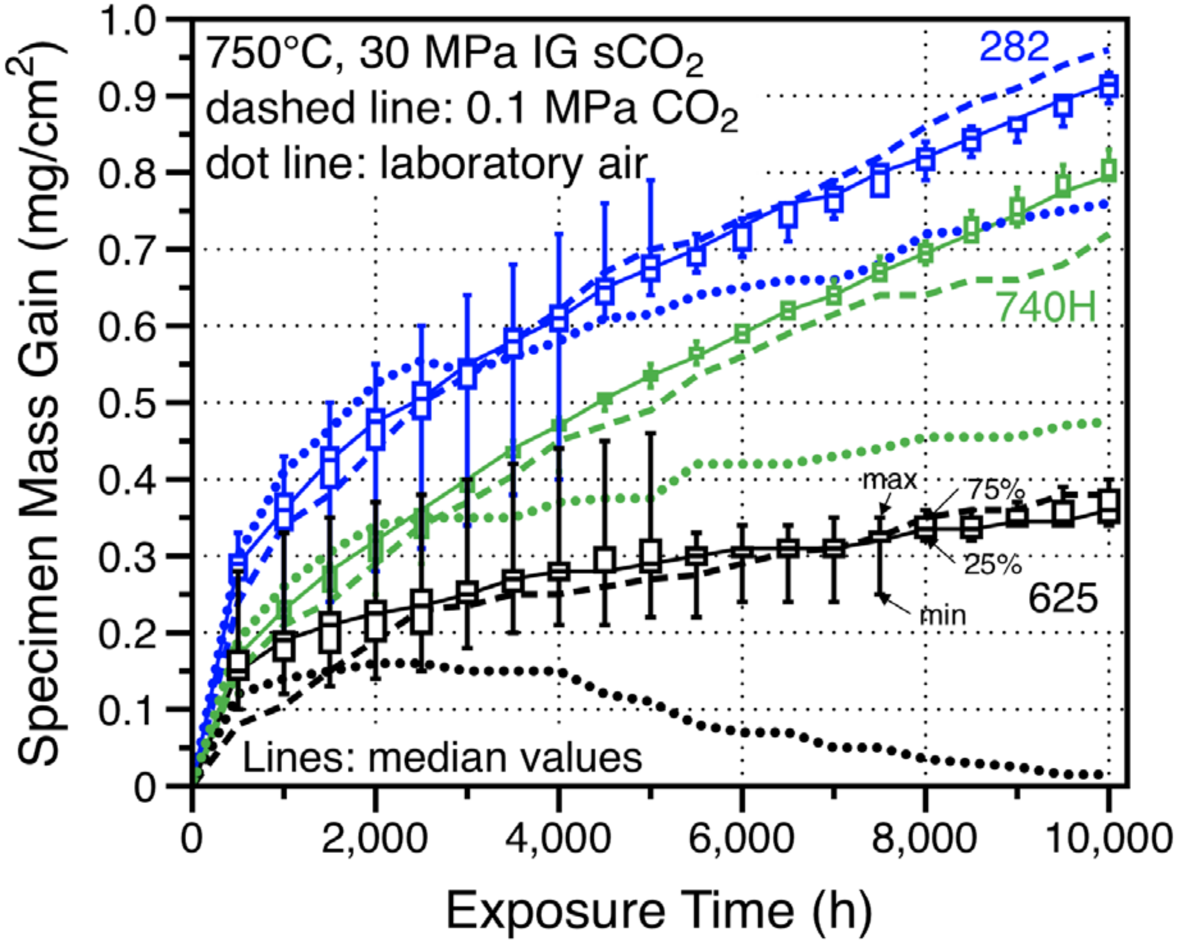
## Similar residual stress in alumina scale on both bond coatings

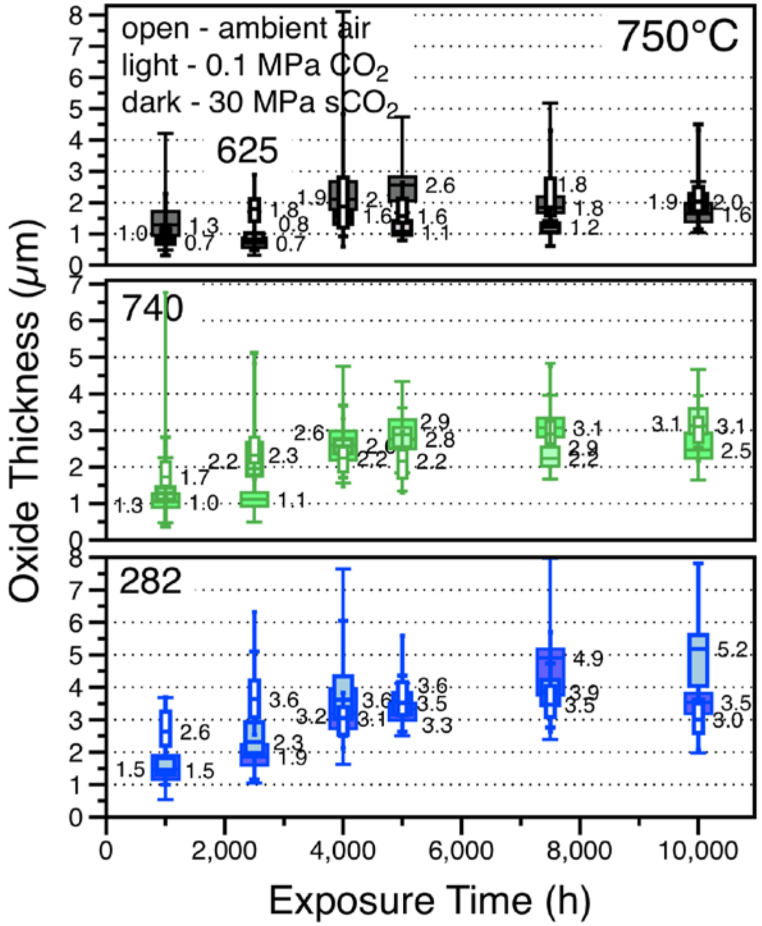



## Higher residual stress in flat disk specimen compared to rods



# 2015-2018: created a baseline in IG $sCO_2$ and $CO_2$

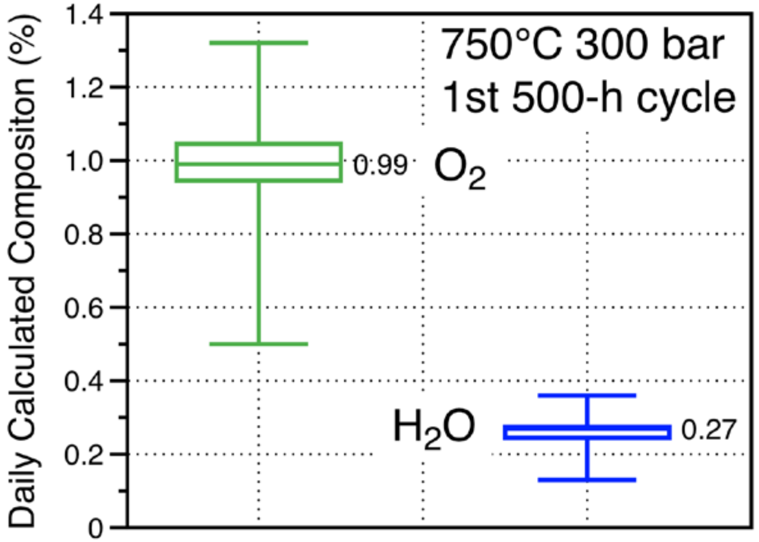



**Lines: median values Box: 25-75% Whiskers: min./max.**

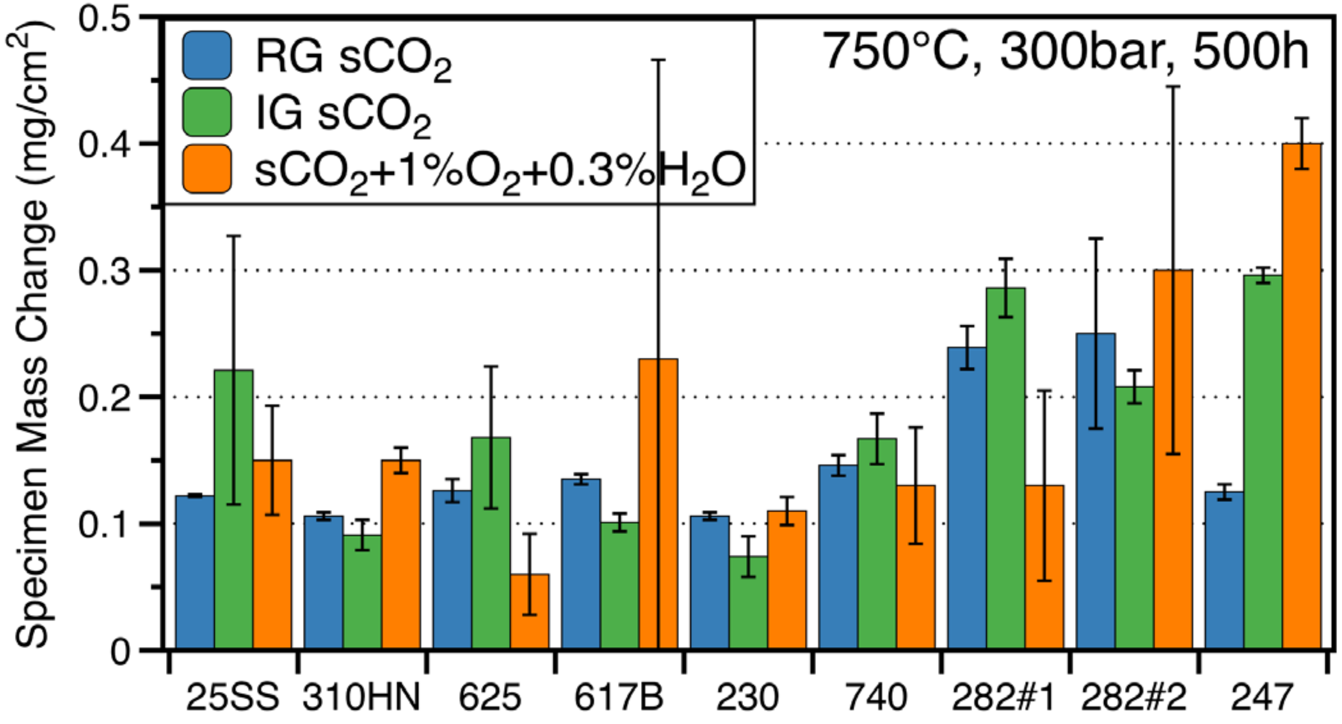
Industrial grade (IG) $CO_2$: 18±16 ppm $H_2O$ and ≤ 32 ppm $O_2$

# First 300 bar impurity data obtained
# New rig completed first cycle in February 2018
# Second cycle completed March 27




**Goal: $1\%O_2+0.25\%H_2O$ (industry suggestion)**

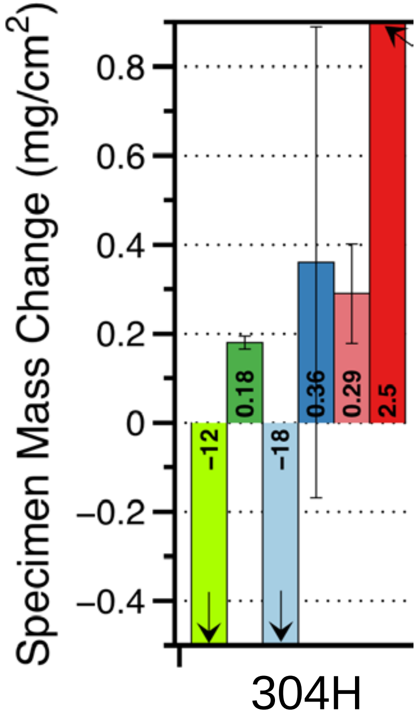
**Not easy to control at 300 bar**




**Average of 3 specimens in first experiment**

**No plans to add $SO_2$ to autoclave**

# 800°C light microscopy: strong variations observed for 304H

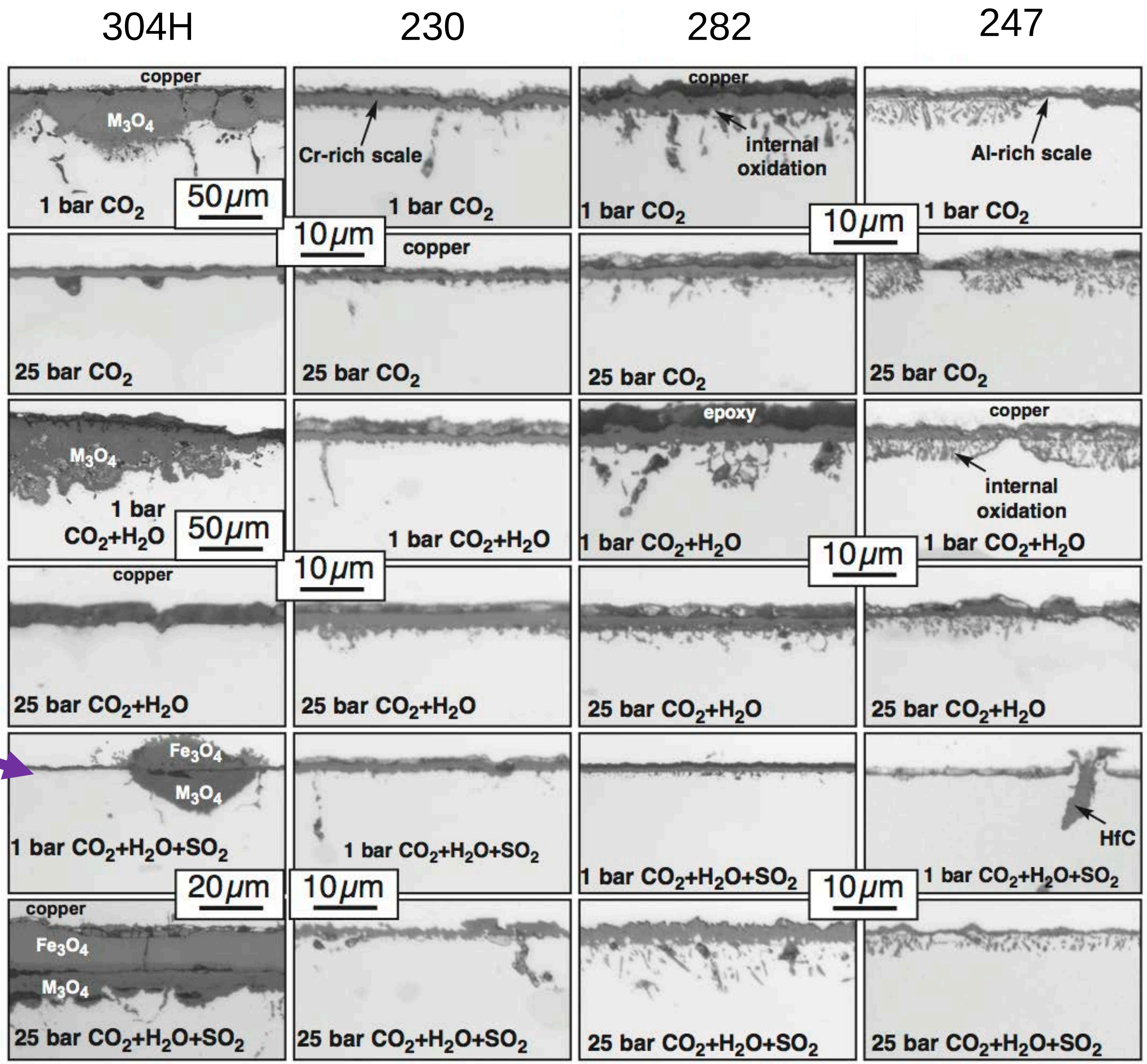



RG $CO_2$

+10%$H_2O$

Almost Protective!

+10%$H_2O$ +0.1%$SO_2$



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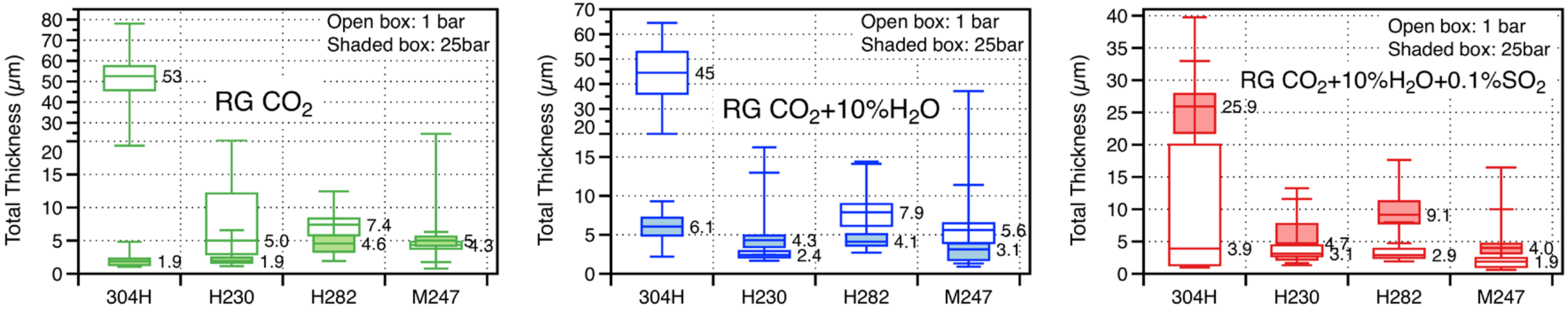
# 800°C Total Reaction (including internal oxidation): reduced in 25 bar except with 0.1%$SO_2$




**0.1%$SO_2$ 1 bar: inhibited negative $CO_2$/$H_2O$ effect, especially for 304H**

- **Similar result for Young ($CO_2$+$H_2O$) and Quadakkers ($H_2O$) on Fe-Cr**
- **Like $SO_2$ poisoning of metal dusting**

**0.1%$SO_2$ 25 bar: sulfidation attack with 25X higher $p_{S_2}$**

# Eddystone (1960): when coal-fired boiler progress stopped

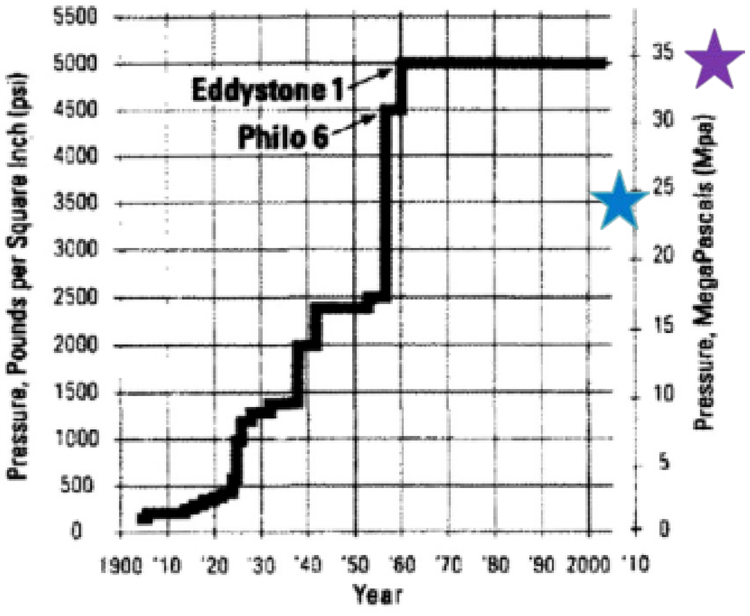



**Figure 1** Illustrating the progress in the working steam pressure for utility-type boilers over the last 100 years.

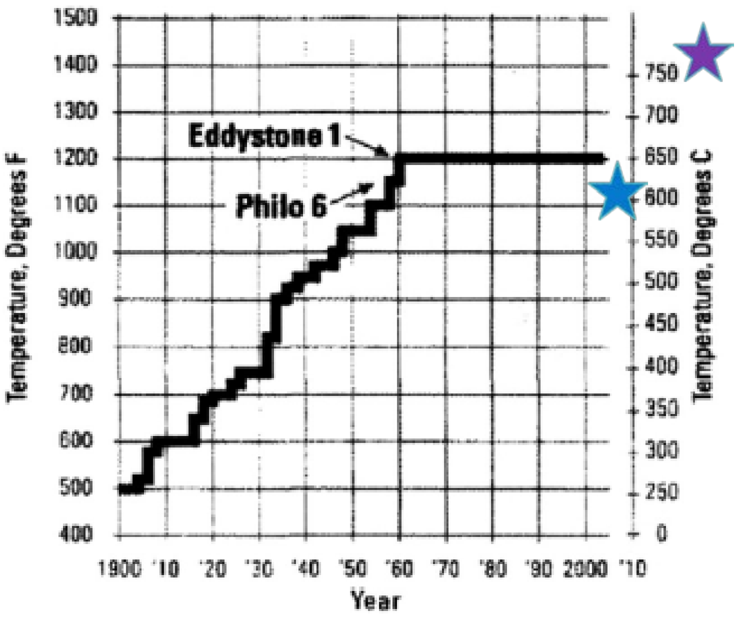



**Figure 2** Illustrating the progress in final steam temperature for utility-type boilers over the last 100 years.

AEP's John W. Turk Plant (Arkansas, US) 2013

Source: J. Henry (2007) Mater. High Temp.

Eddystone (1960): 613°C/34.5 MPa (1135°F, 5000 psi)

Turk (USC, 2013): 599°/607°C SH/RH, 25.3MPa (1110/1125°F, 3400 psi)

A-USC: 760°C/34.5 MPa (1400°F/5000 psi)

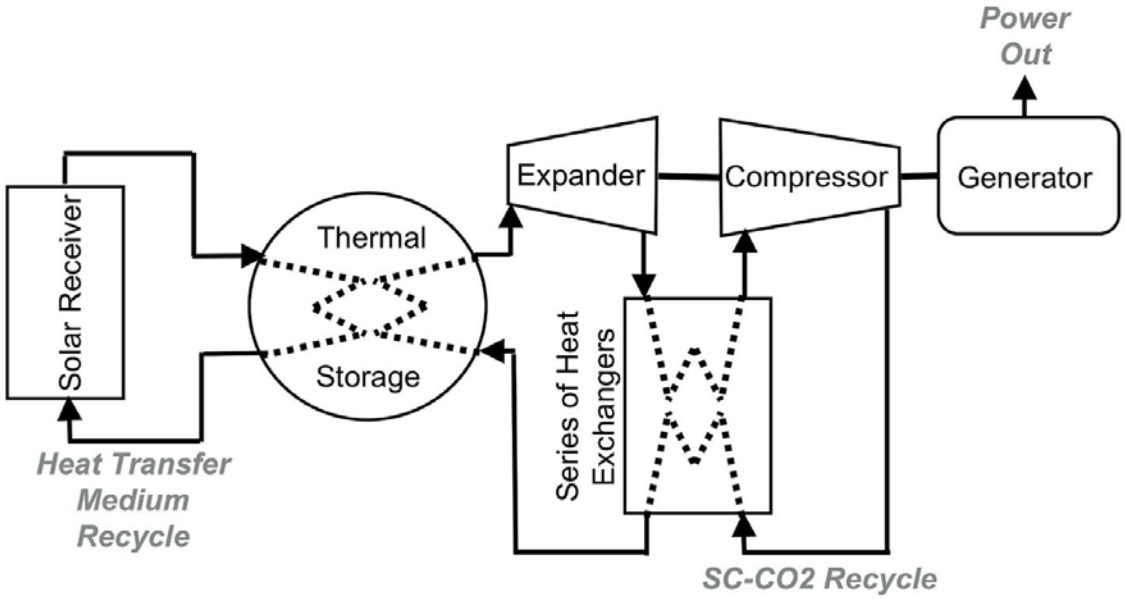
# Many variables can be considered

- Temperature
  - $Cr_2O_3$ better C barrier at higher T (?)
  - Steels more T limited than in steam
- Pressure
  - No strong effect of increasing P
- Thermal cycling
  - Stainless steel attacked at 700°-750°C

- Oxygen
  - ORNL & UW different results
- $H_2O$
  - Negative, especially for steels
- CO
  - UW 1%CO results
- $SO_2$
  - Complicated…

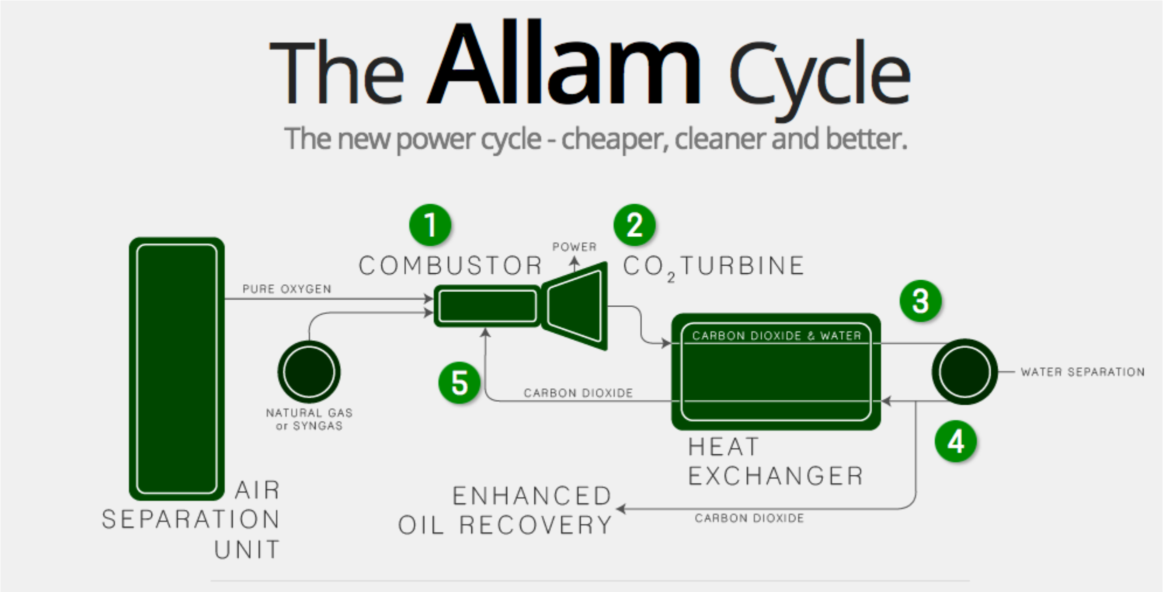
# Indirect- vs. direct-fired $sCO_2$ systems (i.e. closed vs. open)

**Closed cycle:**
**"pure" $CO_2$ 100-300 bar**



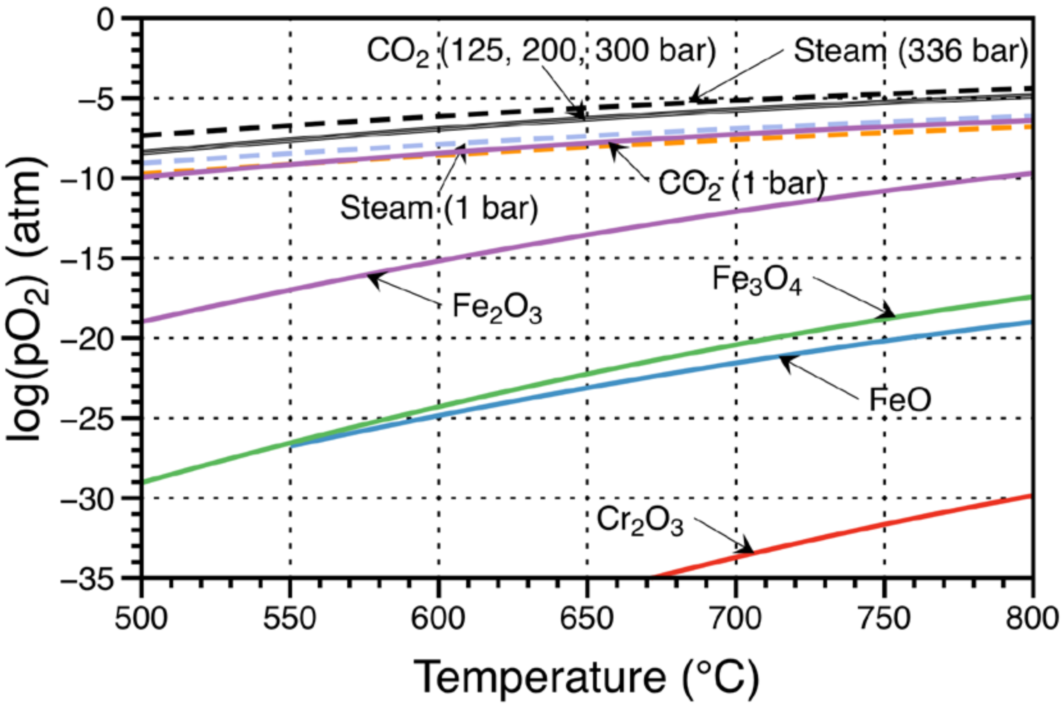

DOE SunShot funding

**Open cycle:**
**$sCO_2$ + impurities ($O_2$,$H_2O$...)**

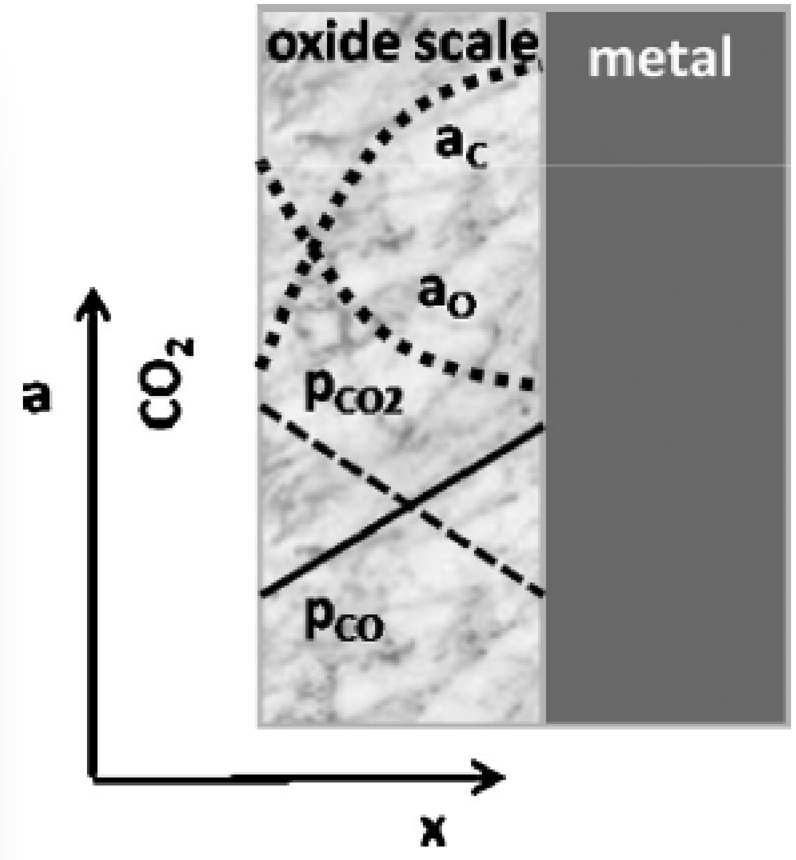



DOE Fossil Energy funding

# Thermodynamics: Oxygen levels similar in steam/$CO_2$ Concern about high C activity at m-o interface



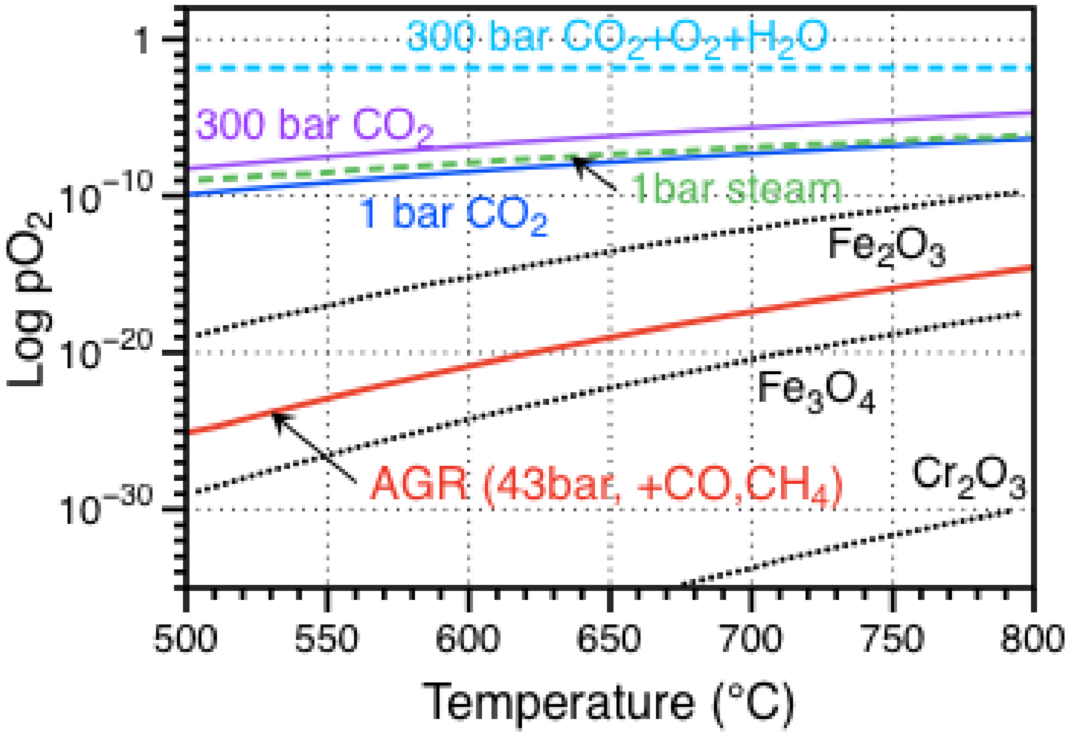

Factsage calculations

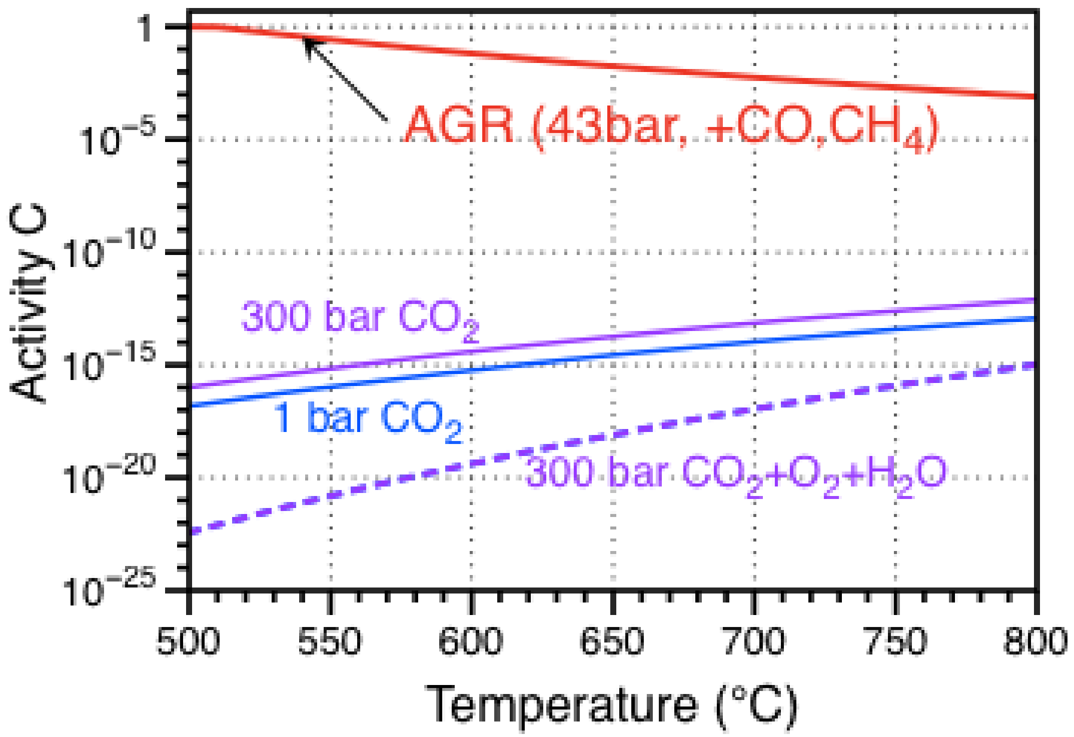



From Young et al. 2011
Also Fujii and Muessner, 1967

# AGR gas composition is highly carburizing, unlike $sCO_2$

43 bar, $CO_2$ +1%CO-0.03%$H_2O$-0.03%$CH_4$-0.01%$H_2$



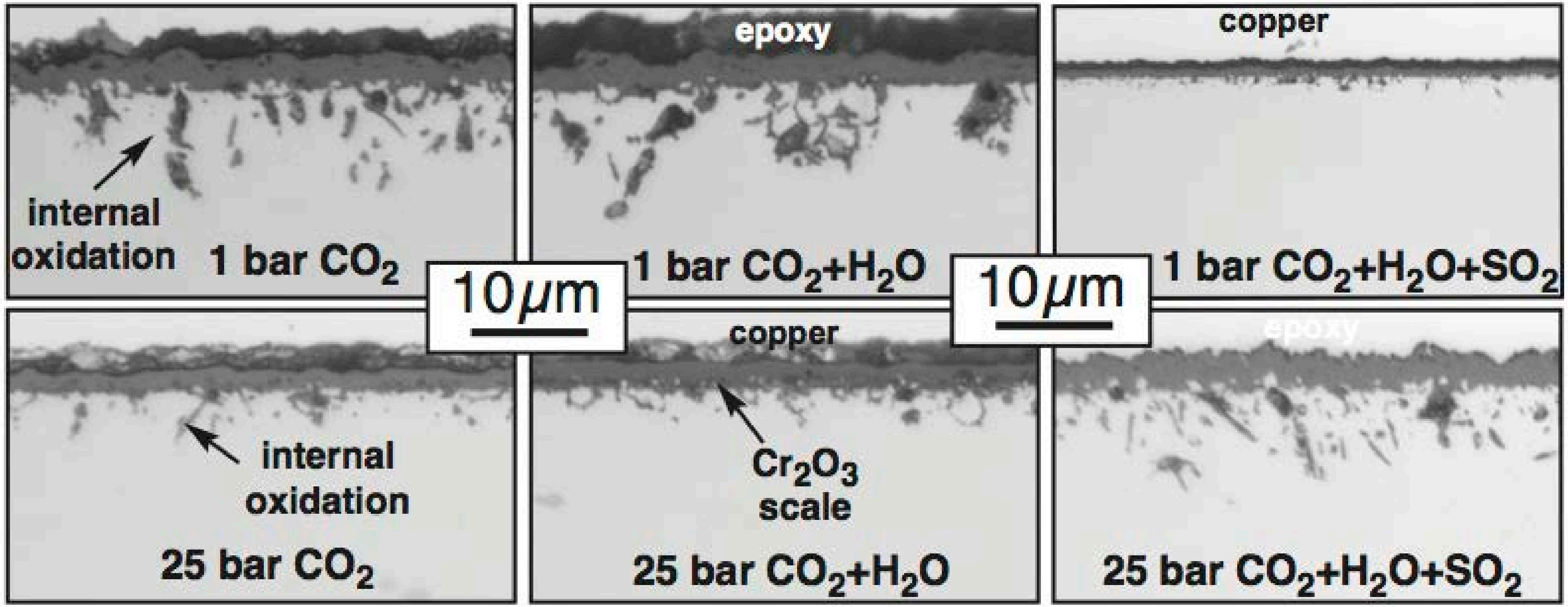




Similar $pO_2$ in steam and $CO_2$

Direct-fired gas: $CO_2$-1%$O_2$-0.25%$H_2O$

**AGR: Advanced Gas-cooled Reactor**

# 500h at 800°C: 1 bar, 0.1%$SO_2$ reduced internal oxidation at 25 bar, 0.1%$SO_2$ resulted in more attack




Similar results for $SO_2$ reported by Young (UNSW) and Quadakkers (Jülich)
Hypothesis that S inhibits absorption of C species