

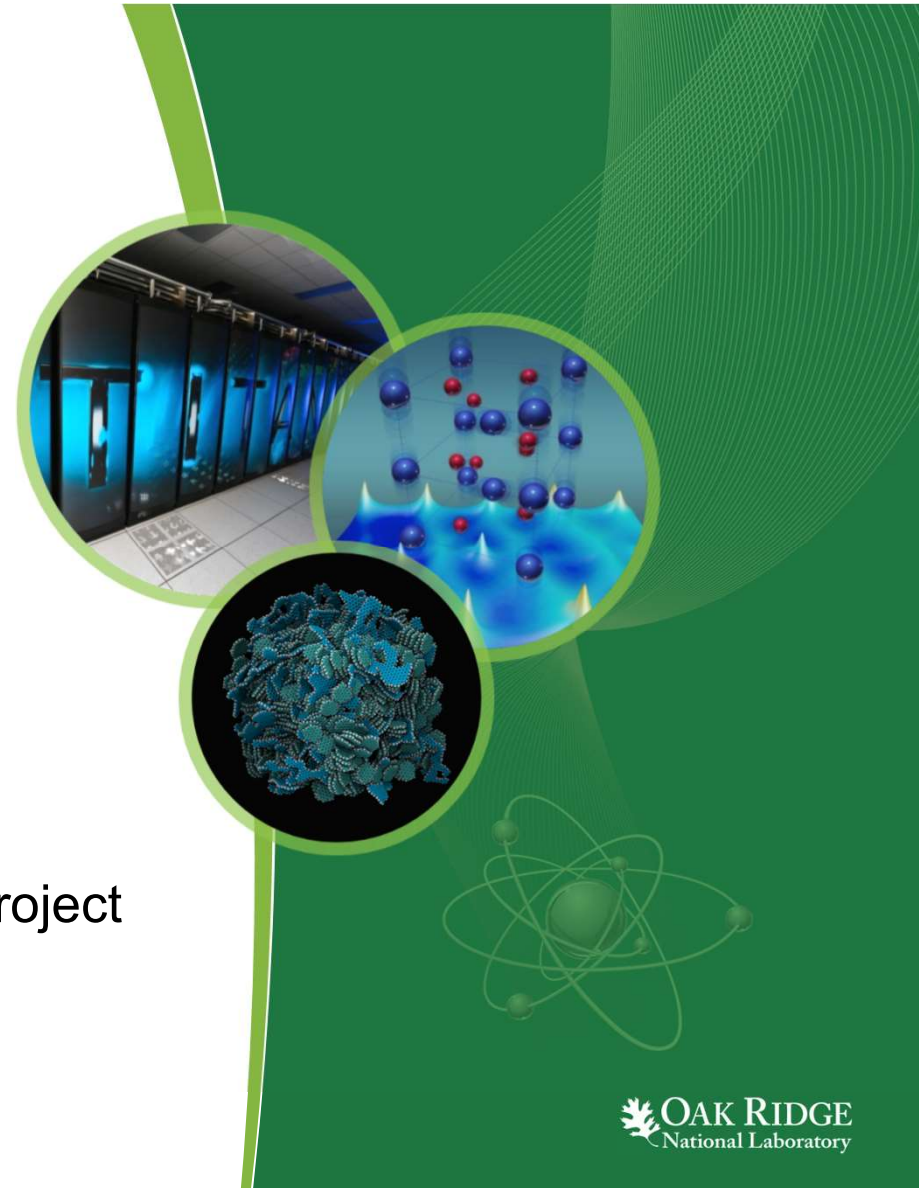
# Corrosion Issues in Advanced Coal-Fired Boilers FEAA116 (2014 – 2018?)

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Presentation for 2018 Crosscutting Research Project  
Review Meeting  
April 11, 2018

ORNL is managed by UT-Battelle  
for the US Department of Energy



# Acknowledgments

- G. Garner, M. Stephens, M. Howell — oxidation experiments
- T. Lowe — SEM, image analysis
- T. Jordan — metallography, hardness
- D. Leonard — EPMA
- A. Willoughby, P. Doyle, R. De Las Casas Aranda — water loop
- Special thanks for shot peening and steam oxidation tasks:
  - American Electric Power (commercial 304H tubes)
  - EPRI (J. Shingledecker, I. Wright, S. Kung)
  - Barry Dooley (Structural Integrity Assoc.)
  - Steve Paterson (PIKA Solutions)

# Project is studying corrosion issues relevant to current and advanced boilers

- Goals and Objectives

- This project is addressing critical corrosion & environmental effects issues in current and future coal-fired boilers focusing on the water-steamside for waterwalls and superheaters

- Milestones

- FY17

- Complete final report on shot peened stainless steel oxidation (3/31/17, **delayed**)
- Compare oxide microstructure formed on steam at 1 & 200 bar (6/30/17, **delayed**)
- Demonstrate in-situ crack growth measurements in 200°C water (9/30/17, **delayed**)

- FY18

- Submit publication comparing crack growth behavior of 2.25 & 9%Cr in flowing water (6/18)
- Report on the effect of pressure and water chemistry on oxide scale growth (9/30/18)
- Complete a report assessing current importance of oxide scale exfoliation (9/30/18)

# Science approach to “real world” corrosion issues

- Task 1: Steam oxidation
  - Study of baseline alloys and shot-peening “solution” at 550°-650°C
- Task 2: Stress corrosion cracking
  - 2¼ %Cr waterwall steels: Grades 22, 23, 24
  - Significant issue in new boilers
  - Need for more detailed understanding
- Task 3: Effect of pressure on corrosion
  - Steam-side difference between laboratory and field
    - EPRI: does water chemistry also play a role?
  - Fire-side effects
    - SPOC: staged pressurized oxy-combustion (with Wash. U @ St. Louis)
  - CO<sub>2</sub> effects from related project FEAA123

Cracks in longitudinal direction



Cracks in transversal direction



# “USC” John W. Turk Plant solution (commissioned 2013)

“Ultra-supercritical” coal-fired steam plant by B&W/AEP in Fulton, AR



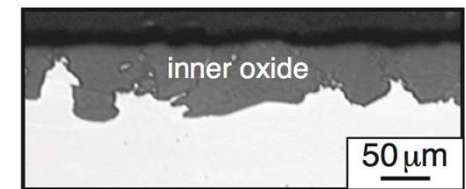
- 600MW, ~39% LHV efficiency
- \$1.8billion (\$2.8b?)
- Steam: 599°/607°C SH/RH  
25.3MPa (1110/1125°F)
  - Eddystone (1960): 613°C/34.5MPa
- Superheater: shot-peened 347H
  - 17.5Cr-10Ni-0.5Nb-1.5Mn-0.4Si-0.07C

## Task 1: Why focus on shot peening?

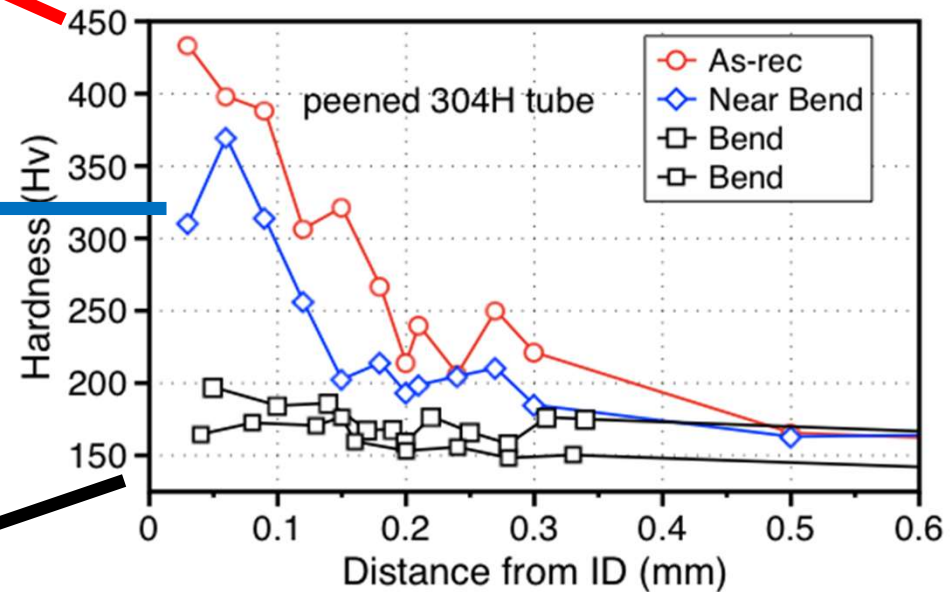
- Scale exfoliation is the main driver for this task
  - H<sub>2</sub>O-accelerated oxidation of steels (steam-side)
  - Simultaneous spallation of thick oxide
  - Tube failures & erosion damage
  - Costs: unplanned shutdowns, mitigation
- Shot peening of austenitic tubes
  - Industry standard to address exfoliation
  - Reduced scale growth: avoids exfoliation issue
  - Limited understanding of benefit and procedure



TP304H  
22,000 h



# Shot peening increases the near-surface dislocation density which increases hardness and Cr diffusivity

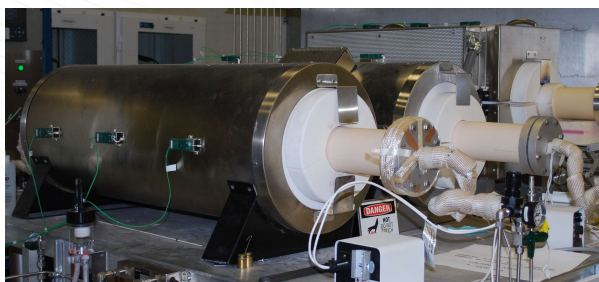


2011 EPRI-funded project

ASME-specified 1100°C annealed U-bend

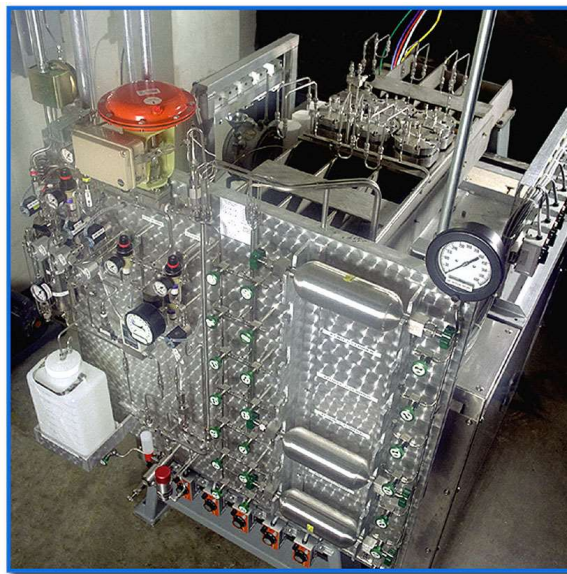
# Several options for steam exposures

Tube furnace: 1 bar CO<sub>2</sub>  
500-h cycles



Standard procedure

"Keiser" rig:  
500-h cycles, 1-43 bar CO<sub>2</sub>



Pressures of 1-43 bar

Autoclave: 275 bar water  
500-h cycles



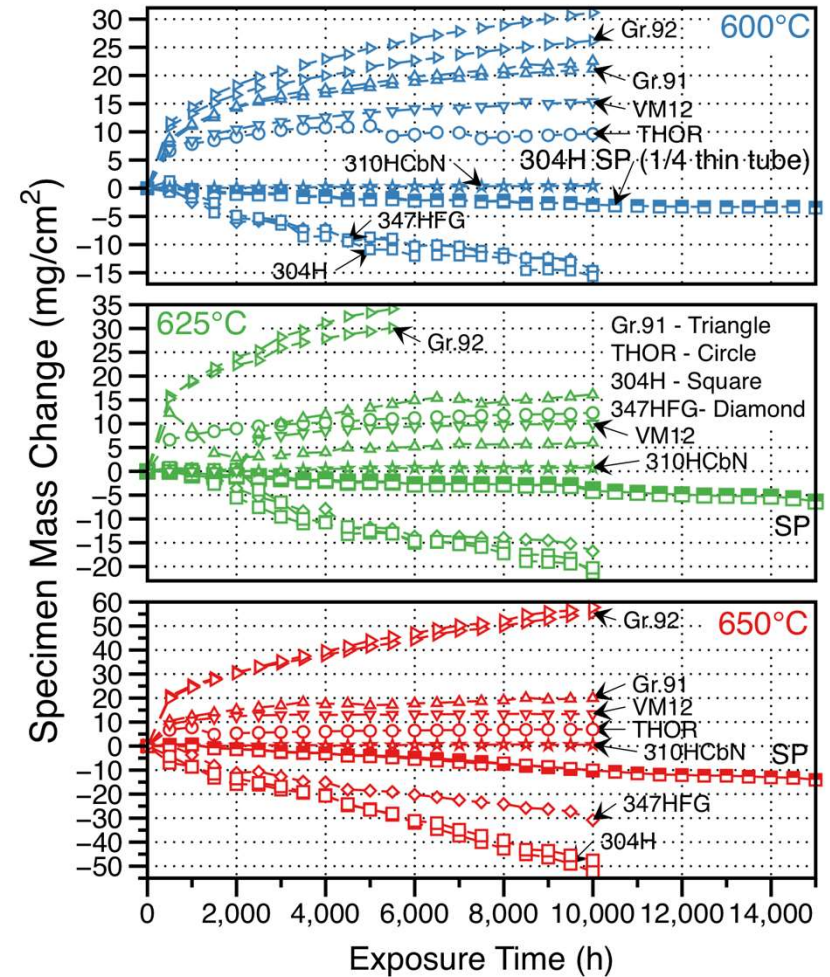
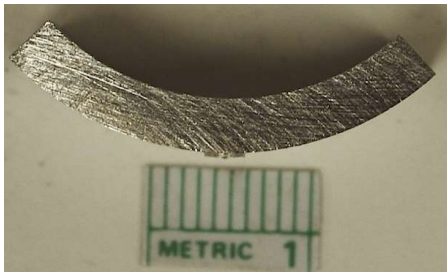
1L volume restricts exposure

High purity Ar-bubbled, filtered water with conductivity  $<0.1\mu\text{S}$  and  $<10$  ppb O<sub>2</sub>

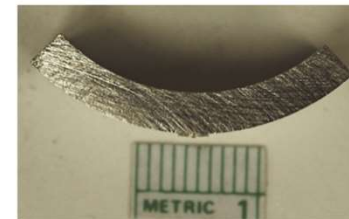
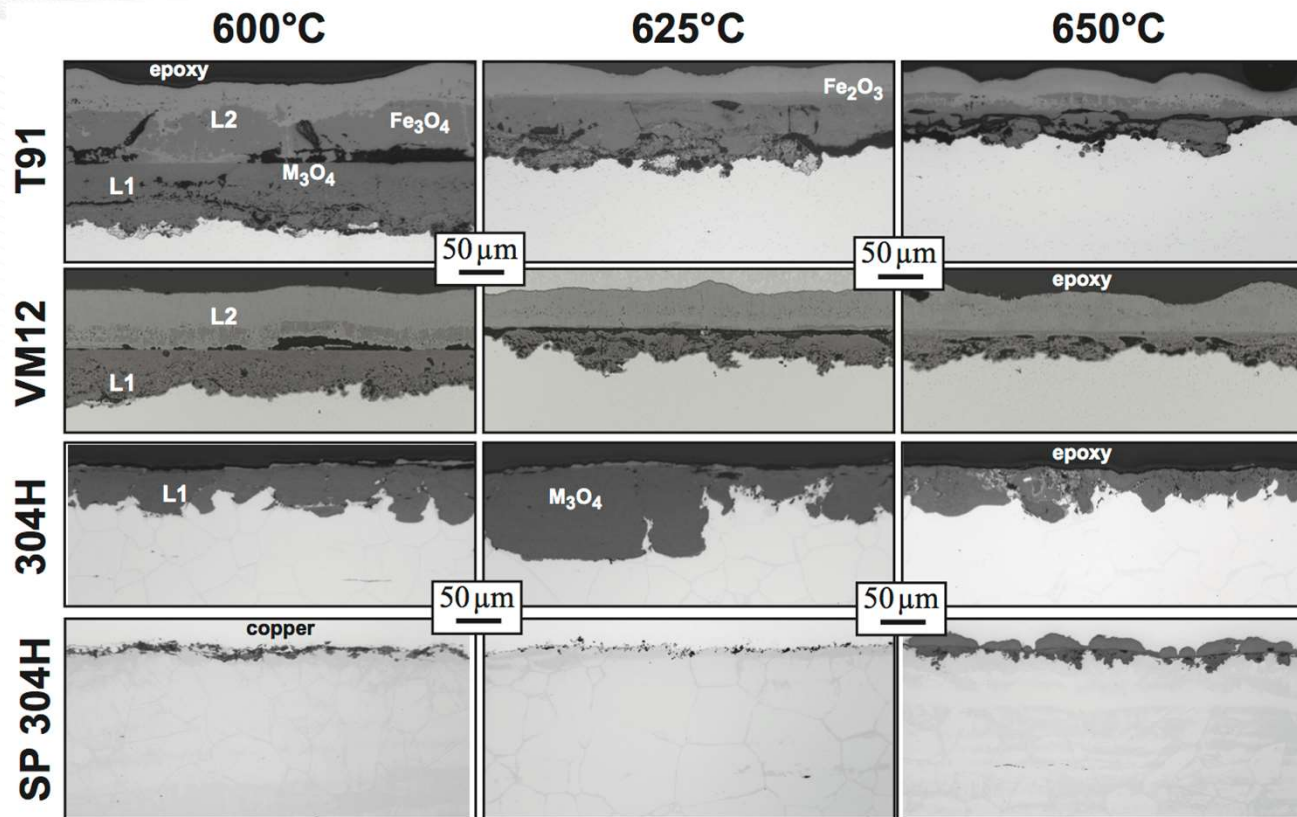


# Completed 15,000 h of testing

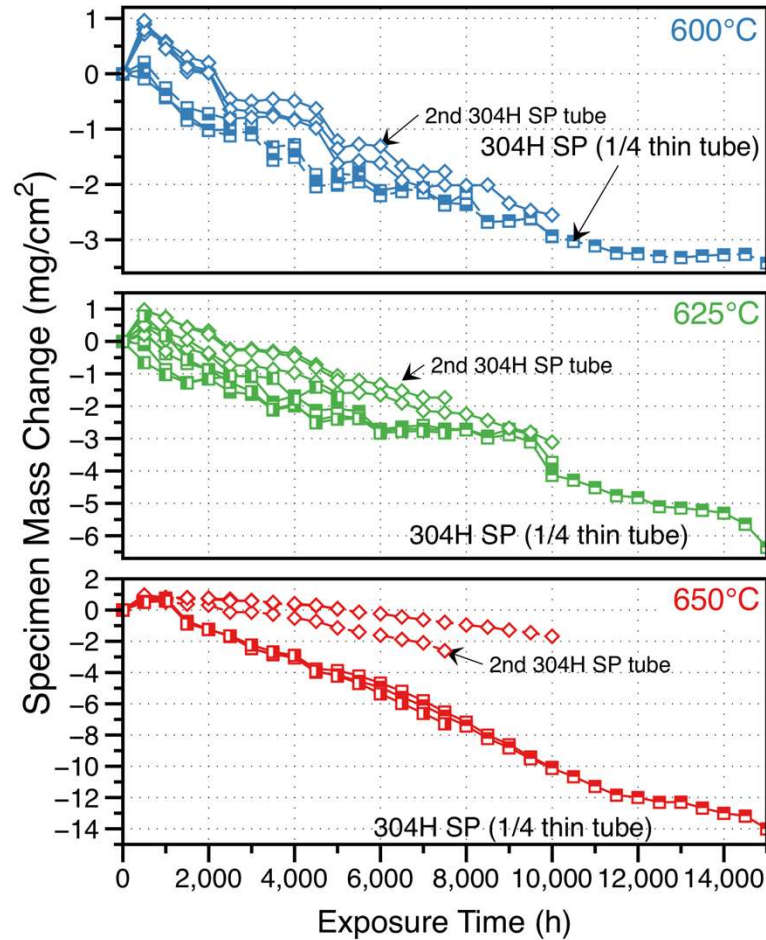
- Tube sections removed at various times
- Polished alloy coupons for comparison
  - Gr.91
  - Gr.92
  - THOR
  - VM12
  - Gr.93 (new CSEF steel)
  - CPJ7 (just started)



# Clear shot-peening benefit at 10,000 h but oxide growing thicker at 650°C

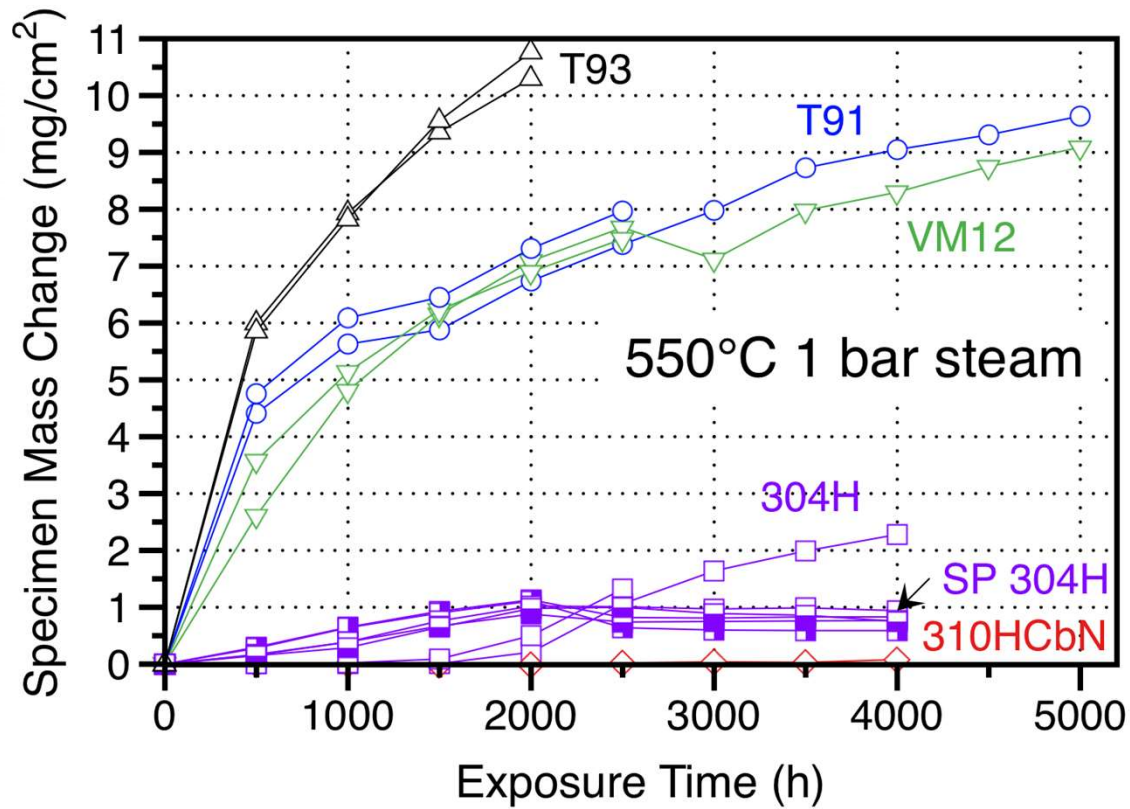


# Specimens from 2<sup>nd</sup> 304H tube finished 10,000 h in 2017



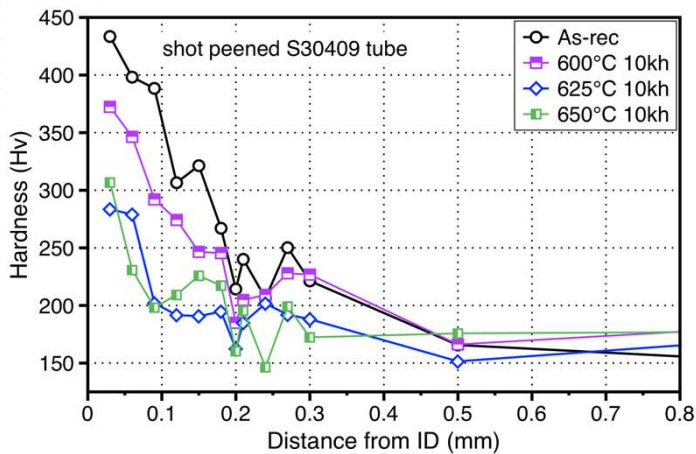
Specimens removed at:  
0.5, 1, 2.5, 5, 7.5, 10 kh  
(15 kh only for 1<sup>st</sup> tube)

## Currently running 550°C (relevant to more boilers)

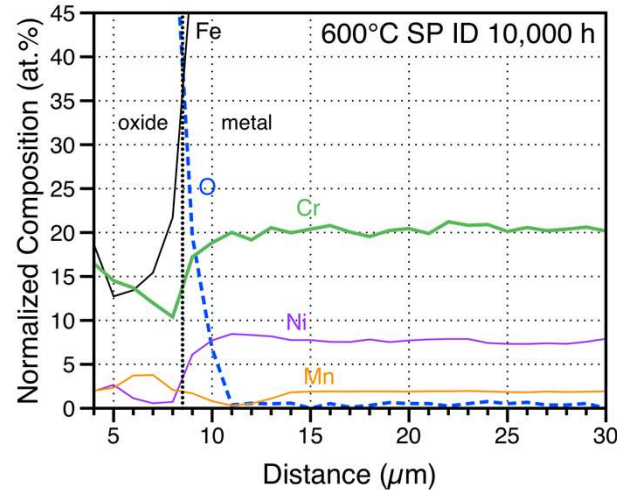


# Considerable characterization work remains to complete journal article

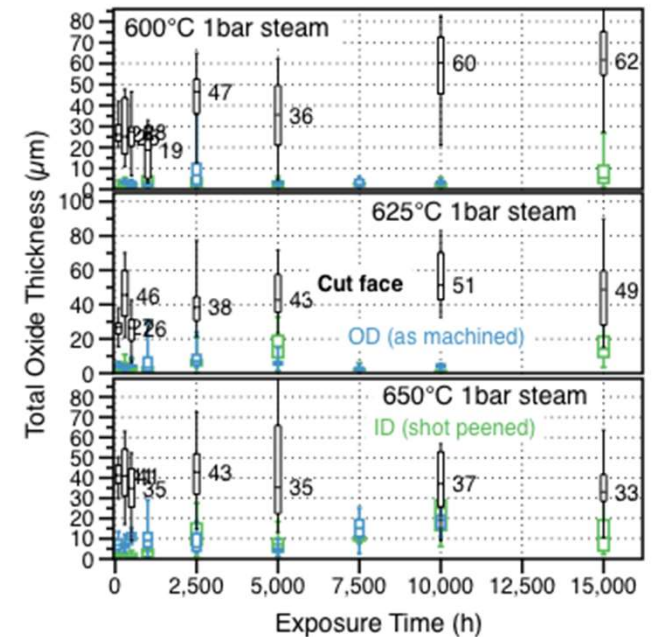
## Post-exposure hardness measurements



## Microprobe of scale and Cr depletion



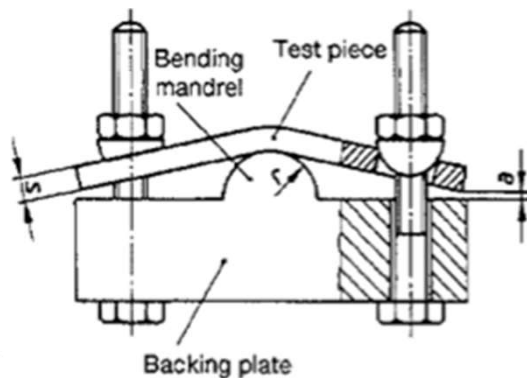
## Quantified oxide thickness on 1<sup>st</sup> tube



Finish similar work for 2nd tube and microscopy (e.g. EBSD)

## Task 2: stress corrosion cracking

- 2.25%Cr waterwall steels: Grades 22,23,24
  - High strength steels are susceptible
  - Including 9Cr steels (Grades 91,92)
- significant problem for new boilers in US (T23) and EU (T24)
- Stress-environment interaction: 25°-300°C
- Jones test to apply stress (complicated)
- prior results in aerated and deaerated water



Alloy	Test Condition			
	As Received		Normalized	
	Aerated	Deaerated	Aerated	Deaerated
T23	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
T24	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
T92	<input type="checkbox"/>		<input checked="" type="checkbox"/>	<input type="checkbox"/>

Did Not Crack  
 Cracked

# Water loop built to have better environment control

Recirculating water system  
- based on GE systems



200°C autoclave



Simulate actual fossil environments with controlled pH and pO<sub>2</sub> levels

## Next phase of testing completed in 2017

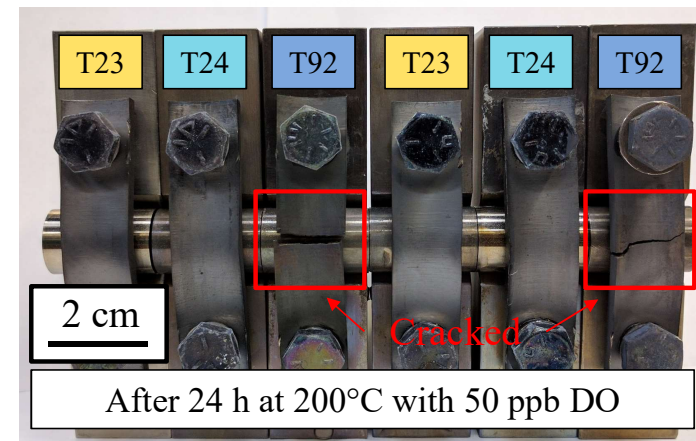
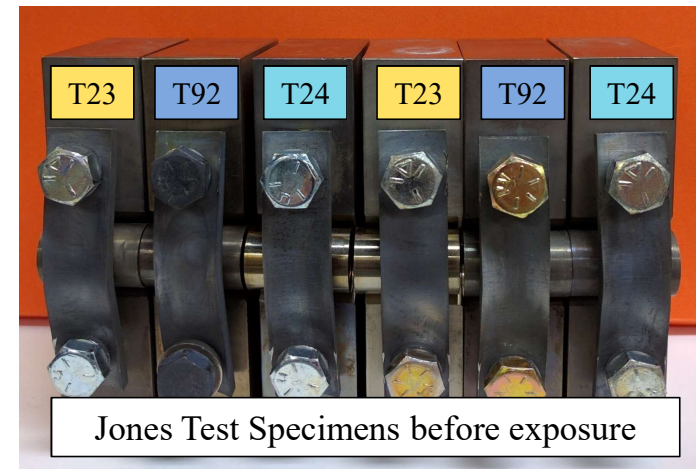
- Jones test conducted in 200°C water
  - Normalized steel (0.5h, 1065°C WQ)
  - 50 ppb O<sub>2</sub>
  - 100 ppb O<sub>2</sub>
- Increasing attack as O<sub>2</sub> level increased
- Previous work concluded only 24 h needed

DO	Deaerated*	50 ppb	100 ppb	Air saturated* (~8400 ppb DO)
Time	72 h	24 h	24 h	72 h
T23	O	O	O	X
T24	O	O	X	X
T91	O	X	X	X

O: Uncracked

X: Cracked

\*J.K. Thompson, S.J. Pawel, 2015





## Progression of SCC testing planned

**SCC = stress + environment + microstructure**

- Closed autoclave
  - Aerated or deaerated water (no cracking without O<sub>2</sub>)
- Autoclave with controlled flowing water
- In-situ probe to monitor crack growth in autoclave
  - Monitor Jones test while incrementally increasing O<sub>2</sub> content in water
  - Task deferred to 2018 to explore electrochemical methods
- Controlled stress in flowing water
  - Tensile test frame needed
  - Monitor crack growth rate changes with water chemistry
  - GE Global Research specialty that was downsized
- Are their critical temperatures? Hardness? Any solutions?

# Task 3: effect of pressure (adding water chemistry)

- Steamside

- steam oxidation field-lab disconnect
- field (high pressure)  $\neq$  lab (typically 1 bar)
- need uniform test procedure to study

- - Fireside

- for Staged-Pressurized Oxy-Combustion (SPOC)
- previous work with Washington Univ. (St. Louis)
  - R. Axelbaum and B. Kumfer

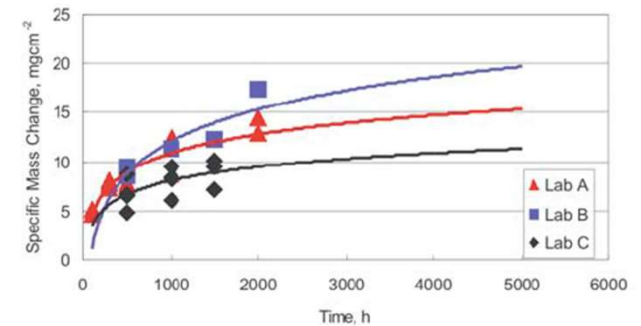
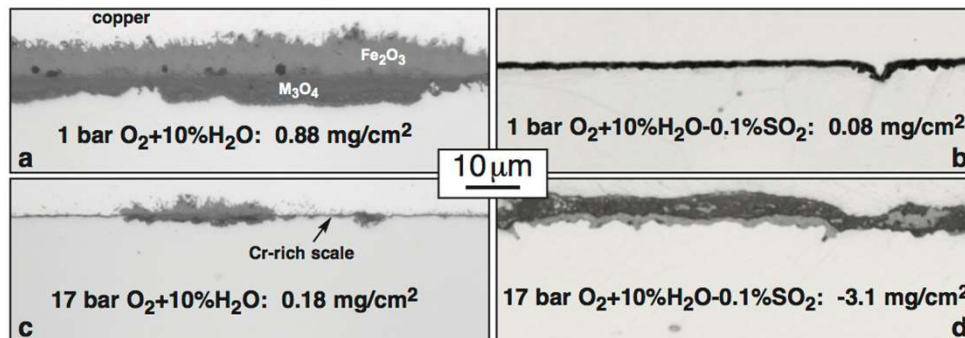
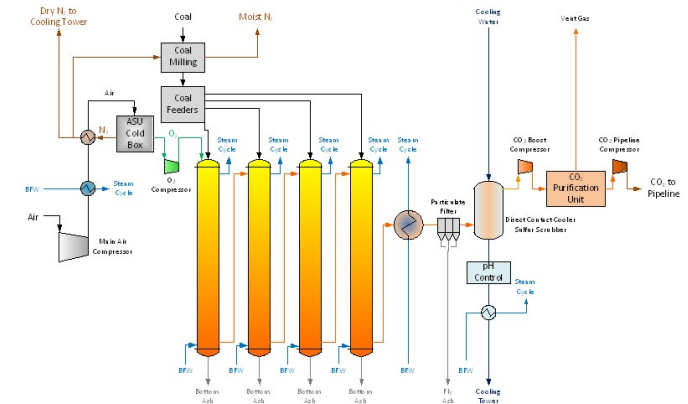
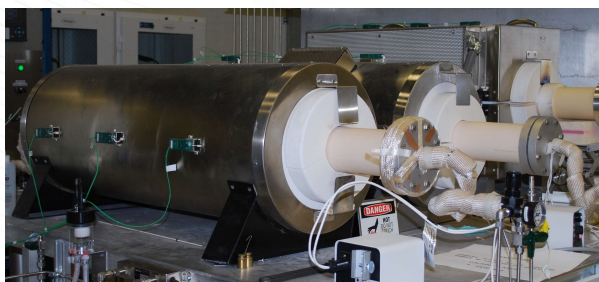


Figure 2 Intercomparison of specific mass change measurements on T92 martensitic steel after exposure to steam for up to 2000 h at 600°C (after [4]).



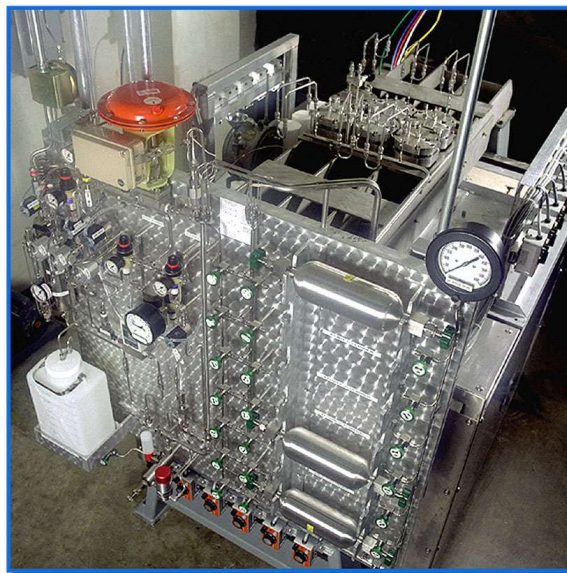
# Several options for steam exposures

Tube furnace: 1 bar CO<sub>2</sub>  
500-h cycles



Standard procedure

"Keiser" rig:  
500-h cycles, 1-43 bar CO<sub>2</sub>



Pressures of 1-43 bar

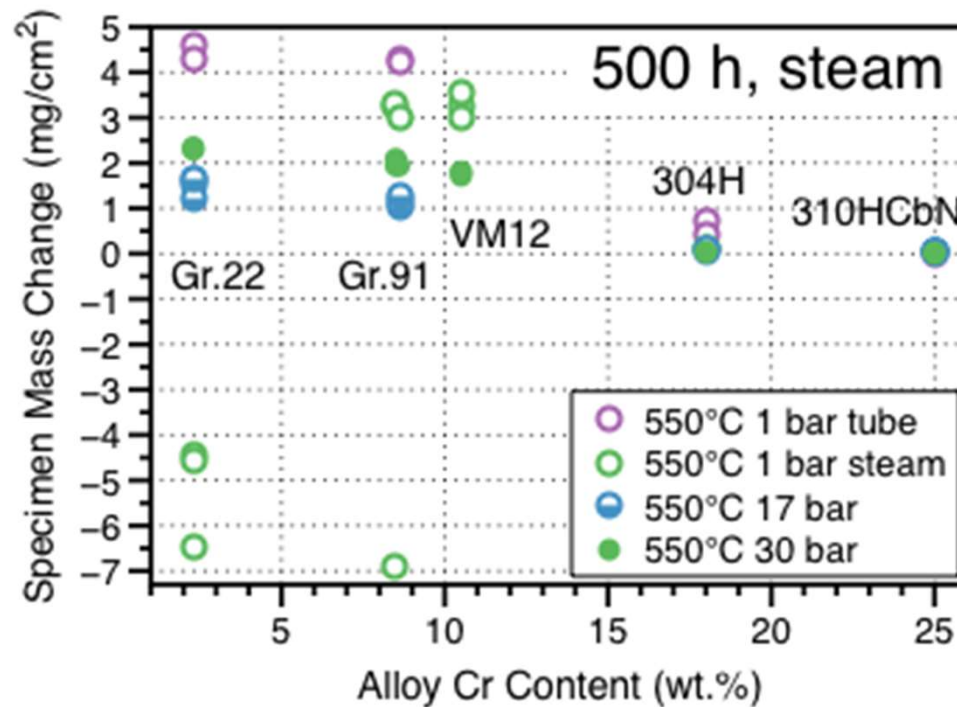
Autoclave: 275 bar water  
500-h cycles



1L volume restricts exposure

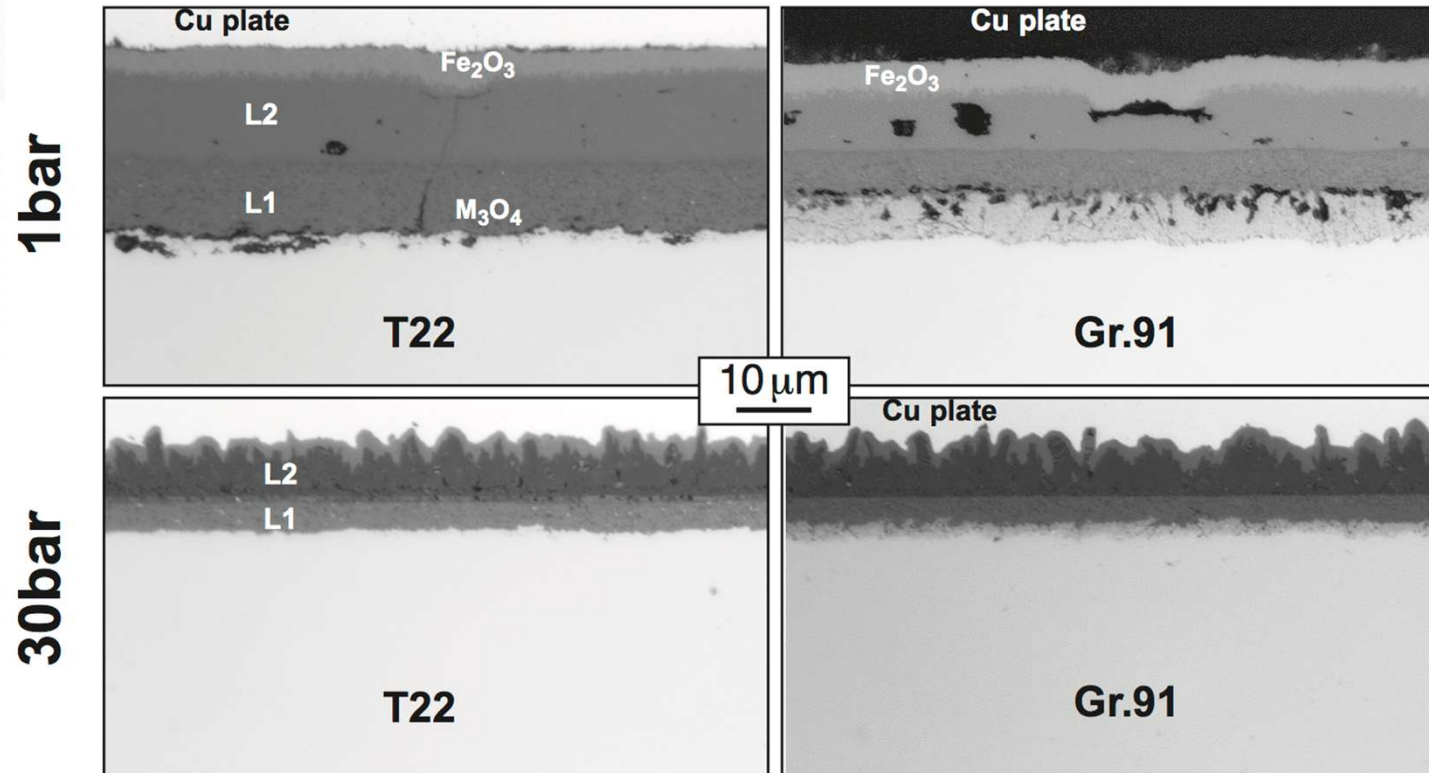
High purity Ar-bubbled, filtered water with conductivity  $<0.1\mu\text{S}$  and  $<10$  ppb O<sub>2</sub>

## 2017: 550°C, 500 h comparison of 1, 17 and 30 bar



- 1 bar steam in tube: higher mass than Keiser rig
- 1 bar Keiser rig - scale spallation for T22
- 17 bar less mass gain than 30 bar (run at different times)

Whoa. I wonder what scale at 275 bar looks like.



Cr content means little at this temperature: diffusion is too slow

# Partnering with EPRI to go supercritical (650°C/27.5MPa)

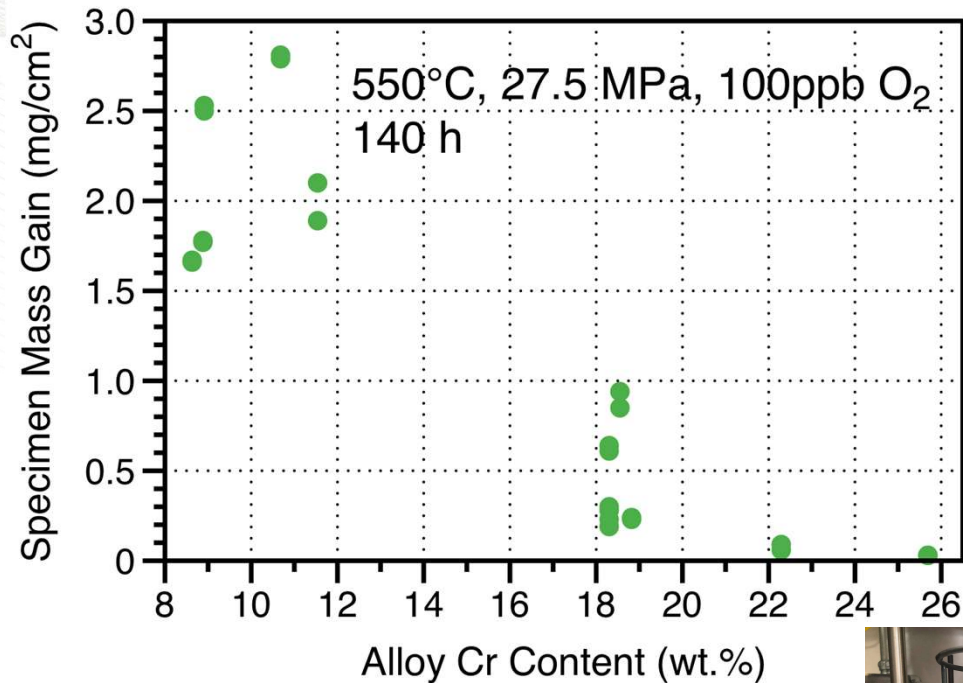
- 1L alloy 625 autoclave
- Temperature up to 650°C
- Pressure to 27.5 MPa (4000 psi)
- Controlled & monitored water chemistry
  - Purified water loop for start
  - $<0.06 \mu\text{S}/\text{cm}$
  - UV, deionization, gas sparging
  - pH controlled by ammonia addition
  - Novel ammonia and hydrazine injection

## Two conditions:

- (1) All volatile treatment (hydrazine)
- (2) Oxygenated treatment (100 ppb  $\text{O}_2$ )



# First 500-h cycle aborted after 140 h



Issues resolved with:  
 Heater  
 Gasket  
 Back pressure regulator



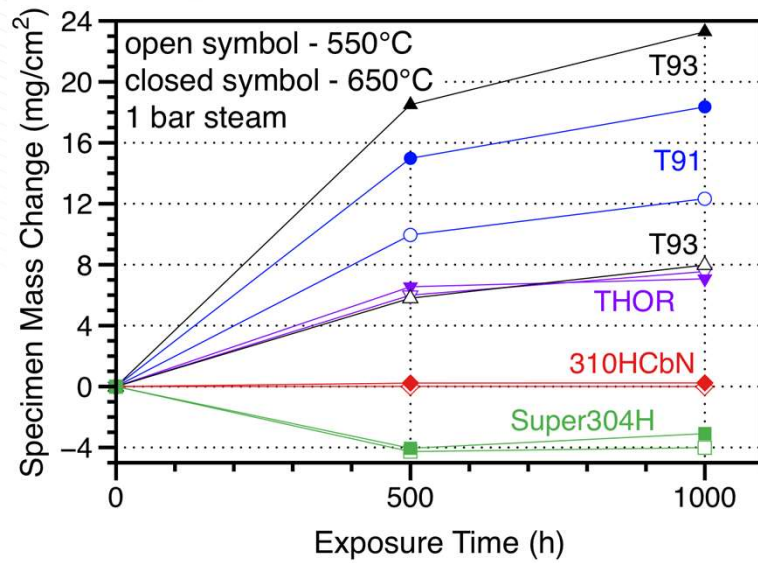
Planned test matrix:

	AVT	OT
550°C	1,000 h	1,000 h
650°C	1,000 h	1,000 h

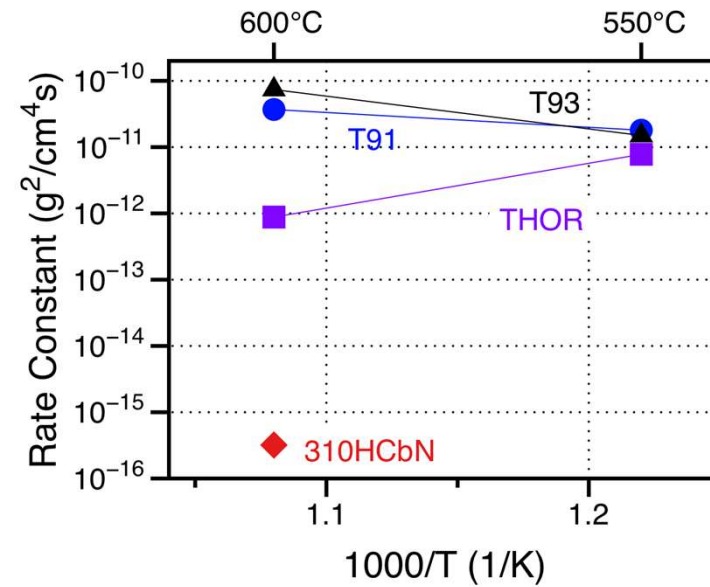
All volatile treatment (AVT)  
 < 10 ppb O<sub>2</sub>  
 Typical for sub-critical  
 Oxygenated treatment (OT)  
 50-150 ppb O<sub>2</sub>  
 Typical for super-critical  
 Oxide to prevent erosion

# Created baseline 1,000 h exposures in 1 bar steam

## Two 500-h cycles



## Calculated rates





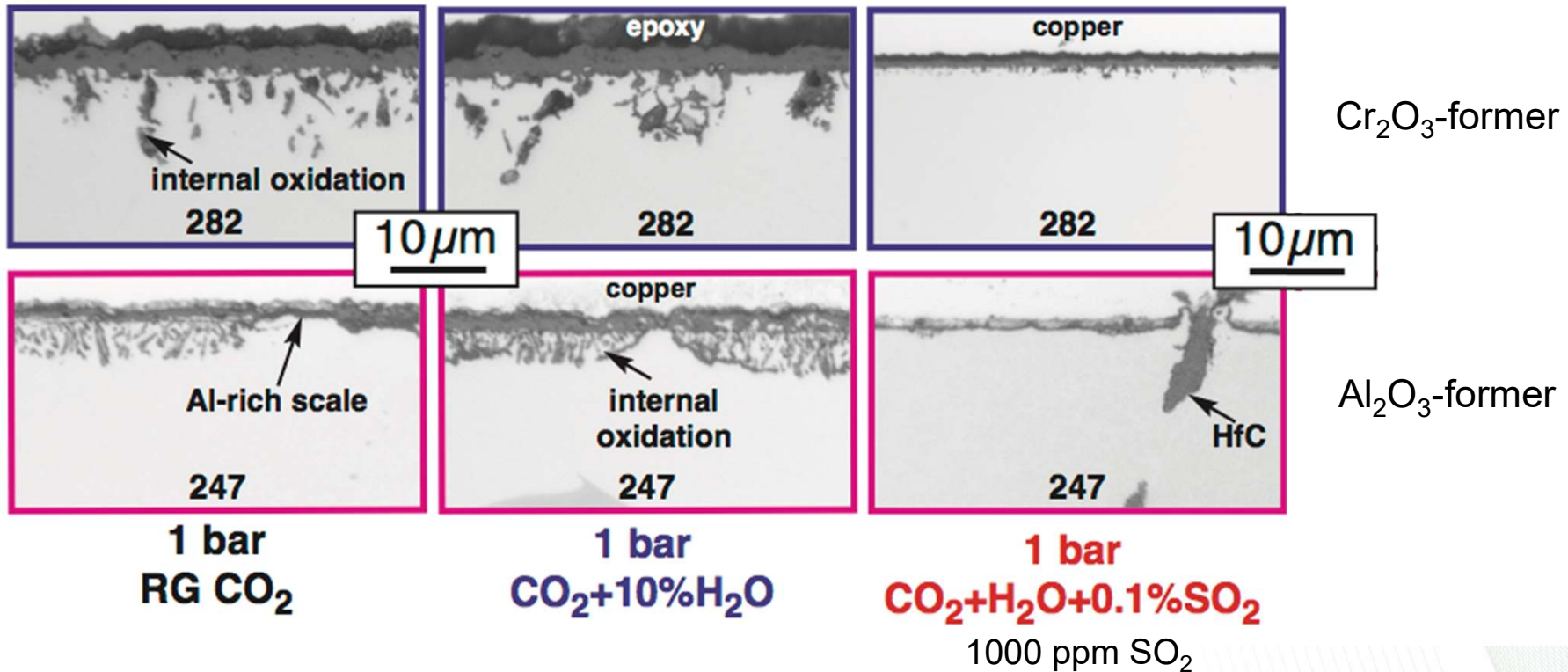
# Corrosion task addressing several issues

1. Quantify shot-peening benefit on 304H
    - Completed 15 kh exposures at 600°-650°C
    - Now exposing at 550°C
    - Baseline alloy coupons also being exposed
  2. SCC issue in current waterwalls
    - Testing completed in controlled water chemistry
    - Next task is in-situ monitoring
  3. Effect of pressure on steam oxidation
    - Initial comparison: 500 h at 550°C, 1-30 bar
    - New matrix: 1000 h at 550° and 650°C in two water chemistries
- Expecting to complete all tasks in 2018



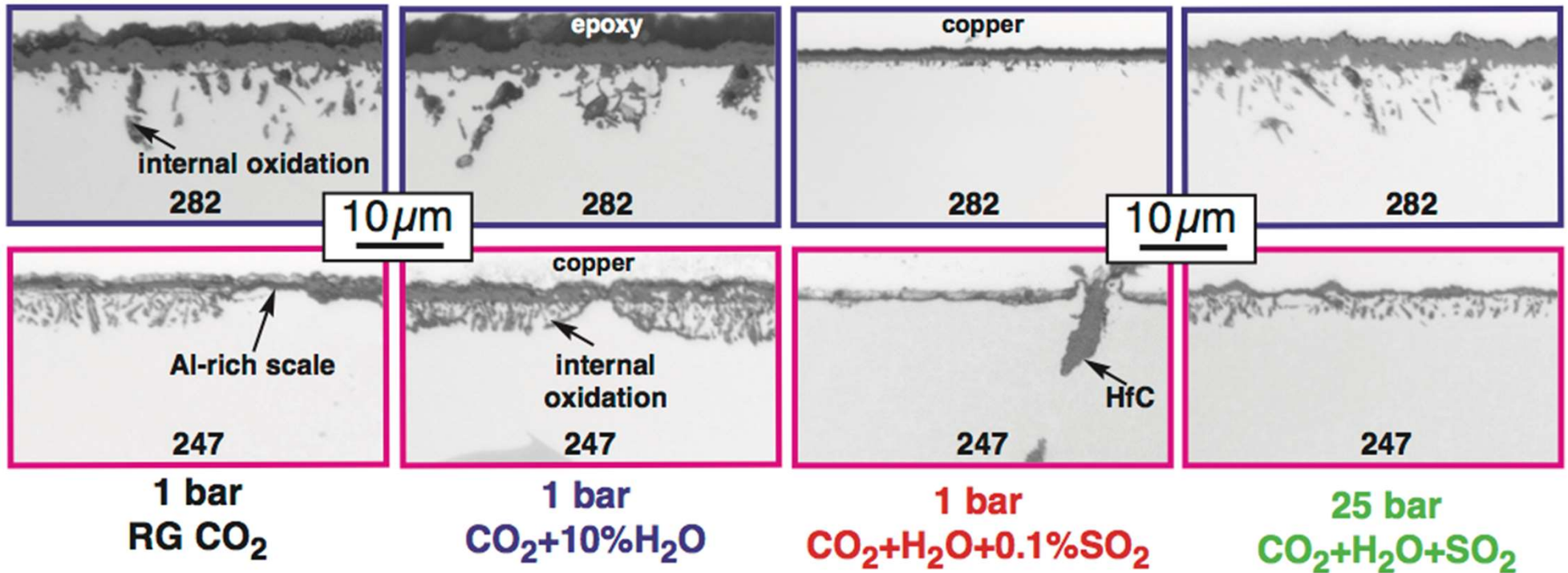
# Backup slides

# 500h at 800°C: SO<sub>2</sub> suppressed internal oxidation at 1 bar



Similar results for SO<sub>2</sub> reported by Young (UNSW) and Quadakkers (Jülich)

# 500h at 800°C: at 25 bar, 0.1%SO<sub>2</sub> resulted in more attack



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

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

## Similar observation with 600°C ORNL study for staged pressurized oxy-combustion (SPOC):

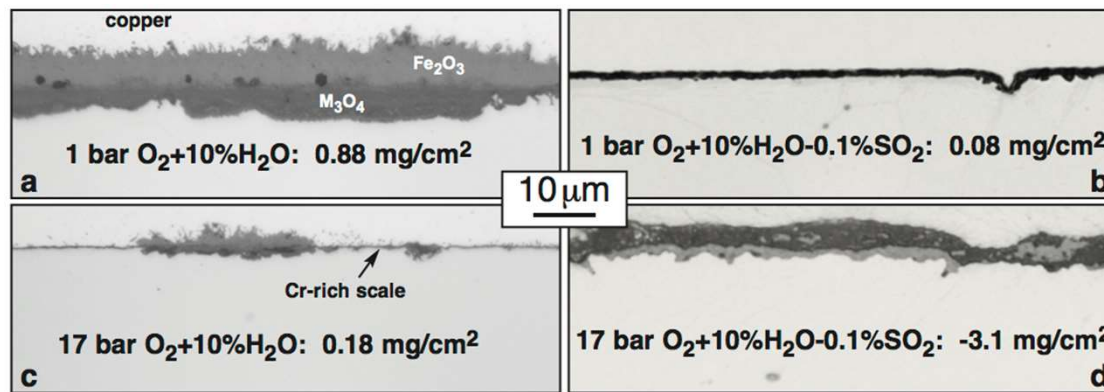


Figure 5: Light microscopy of S30409 specimens exposed at 600°C for 500 h in two environments and two pressures.

**No CO<sub>2</sub>  
in this  
study**

**O<sub>2</sub>-10%H<sub>2</sub>O: reduced attack at 17 bar compared to 1 bar**  
**0.1%SO<sub>2</sub> 1 bar: inhibited negative CO<sub>2</sub>/H<sub>2</sub>O effect (protective scale)**  
**Similar result for Young (CO<sub>2</sub>+H<sub>2</sub>O) and Quadakkers (H<sub>2</sub>O)**  
**0.1%SO<sub>2</sub> 17 bar: sulfidation attack with 17X higher p<sub>S<sub>2</sub></sub>**