

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

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Acknowledgments

- G. Garner, M. Stephens, M. Howell — oxidation experiments
- T. Lowe — SEM, image analysis
- T. Jordan — metallography, hardness
- D. Leonard — EPMA
- A. Willoughby, R. De Las Casas Aranda, S. Pearson — 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, complete 2019)
- Compare oxide microstructure formed on steam at 1 & 200 bar (6/30/17, complete 8/2018)
- Demonstrate in-situ crack growth measurements in 200°C water (9/30/17, delayed)

- FY18

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

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)
 - CO₂ 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



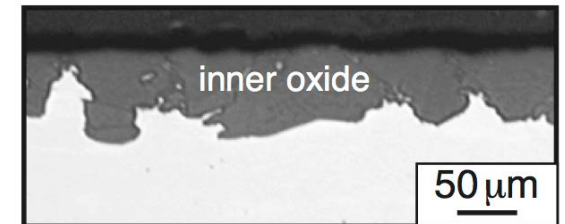
- 600MW, ~39% LHV efficiency
- \$1.8billion (\$2.8b?)
- Steam: 599°/607°C SH/RH
25.3MPa (1110/1125°F)
 - Eddystone (1960): 613°C/34.5MPa
- Superheater: shot-peened 347H
 - 17.5Cr-10Ni-0.5Nb-1.5Mn-0.4Si-0.07C

Task 1: Why focus on shot peening?

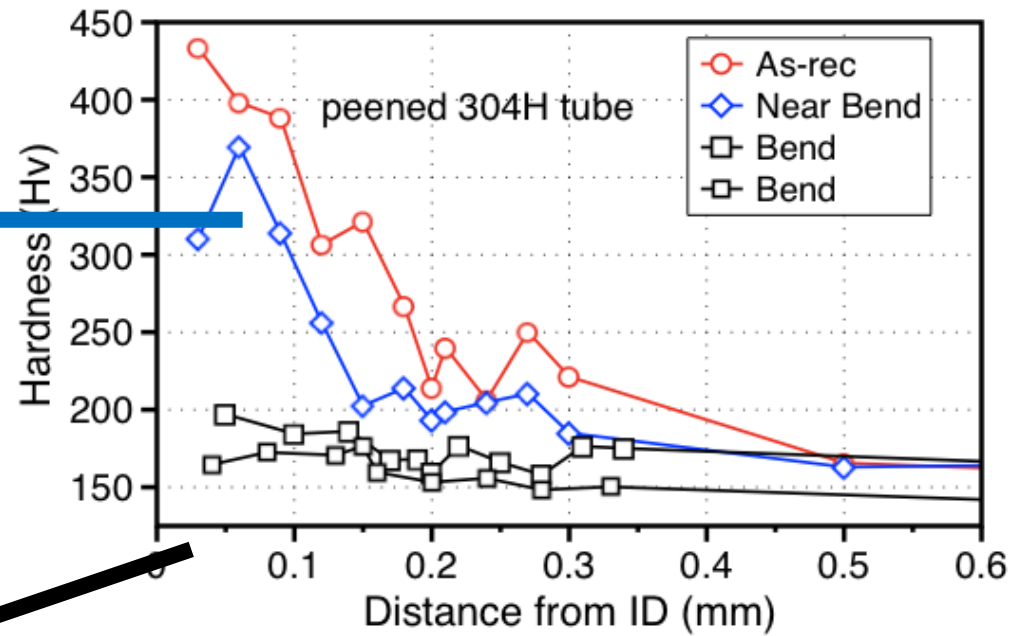
- Scale exfoliation is the main driver for this task
 - H₂O-accelerated oxidation of steels (steam-side)
 - Simultaneous spallation of thick oxide
 - Tube failures & erosion damage
 - Costs: unplanned shutdowns, mitigation
- Shot peening of austenitic tubes
 - Industry standard to address exfoliation
 - Reduced scale growth: avoids exfoliation issue
 - Limited understanding of benefit and procedure



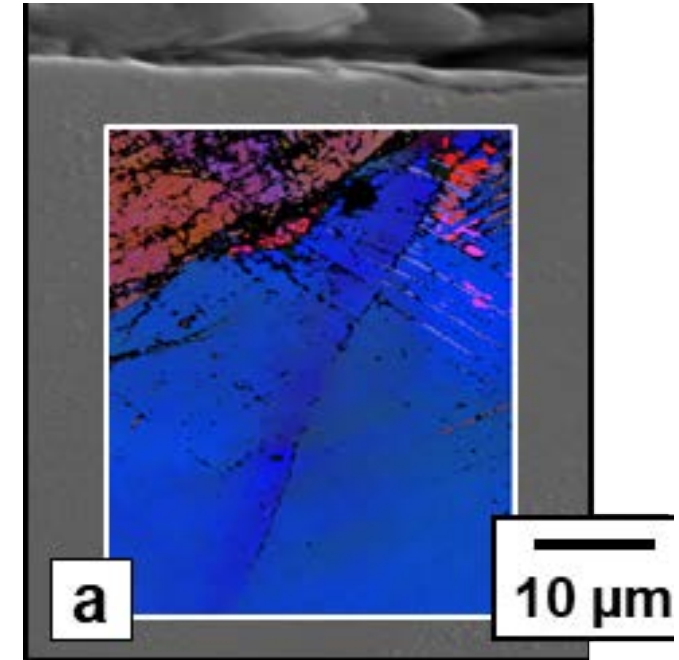
TP304H
22,000 h



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



2011 EPRI-funded project

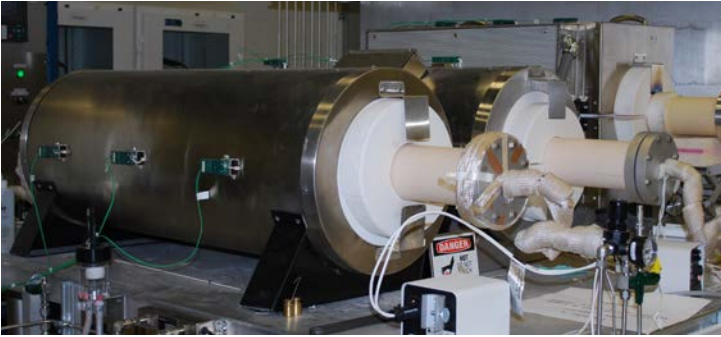


Recent EBSD
Electron Back Scattered
Diffraction

ASME-specified 1100°C annealed U-bend

Several options for steam exposures

Tube furnace: 1 bar
500-h cycles

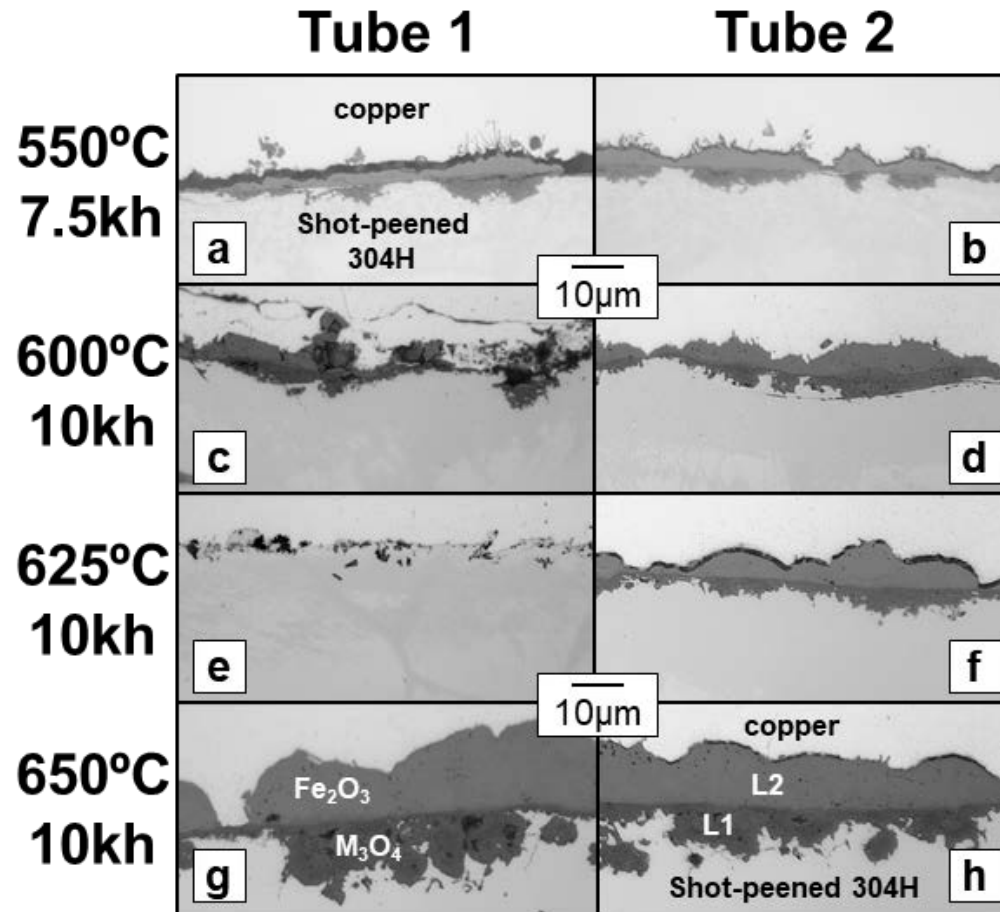
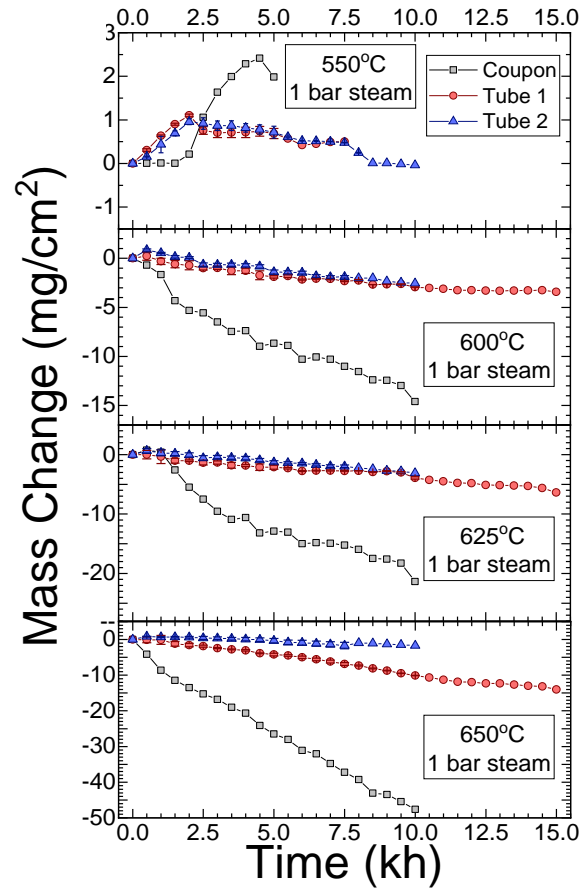


Standard procedure

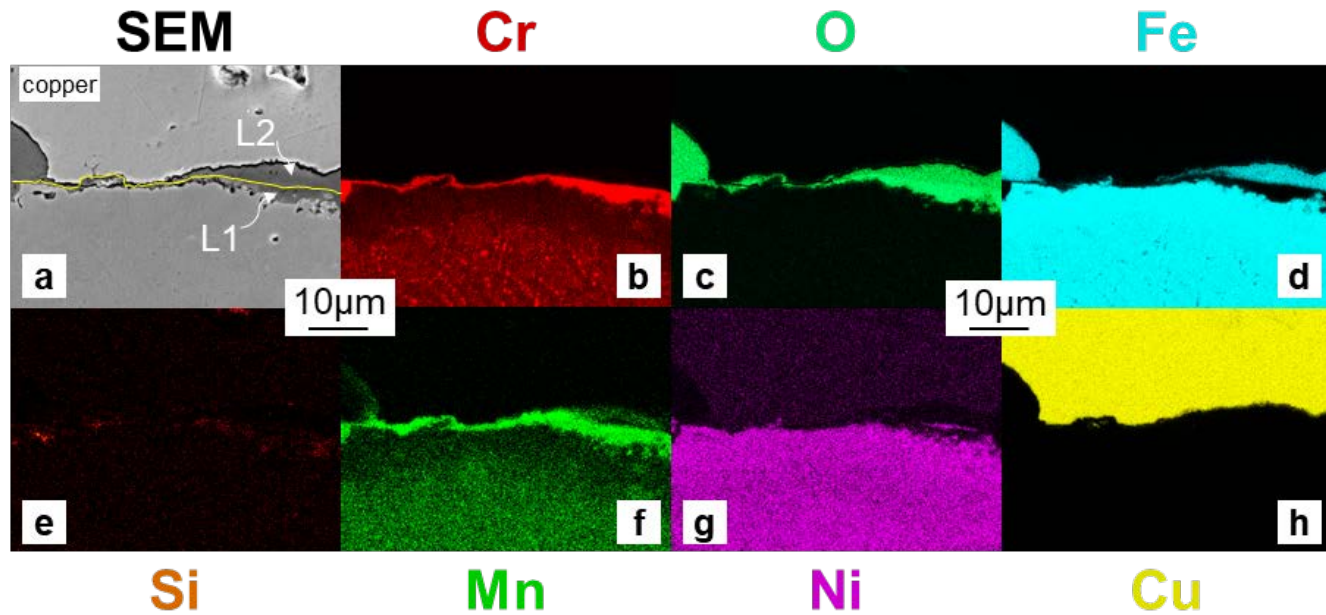


High purity Ar-bubbled, filtered water with conductivity $<0.1\mu\text{S}$ and $<10\text{ ppb O}_2$

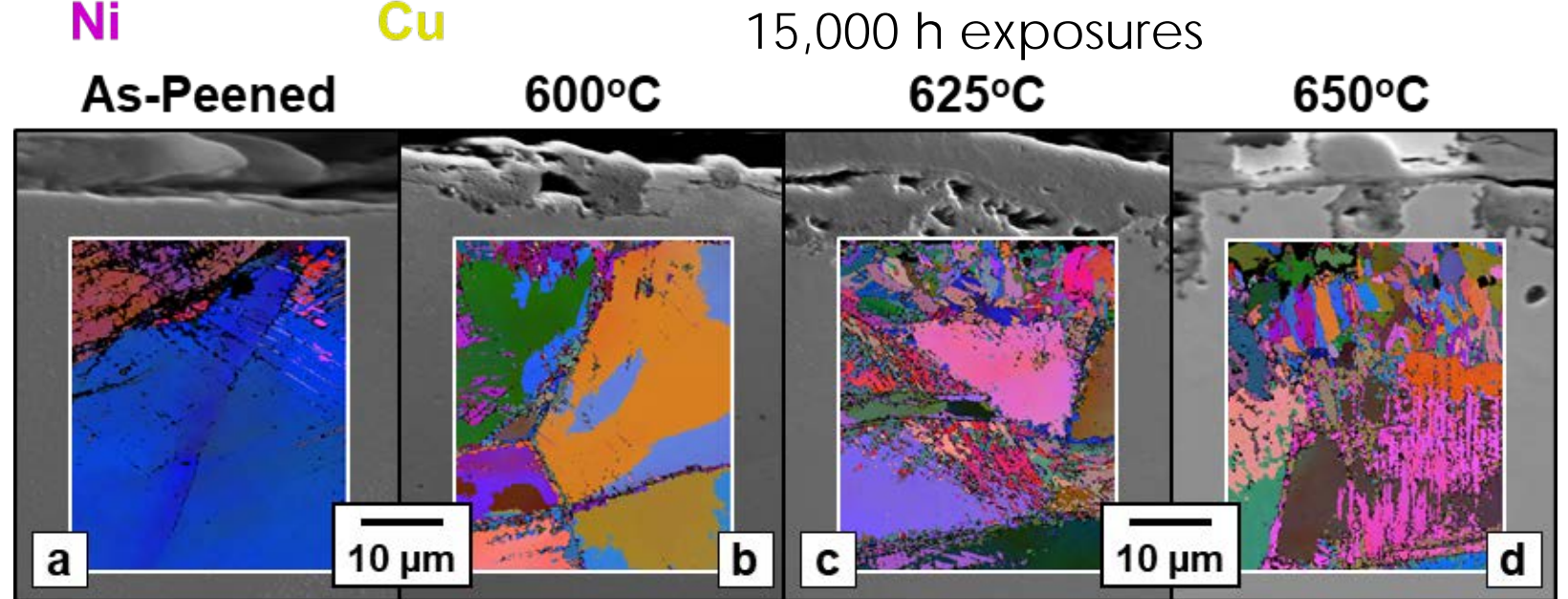
Final results assembled on two 304H tubes for publication



Characterization completed for publication

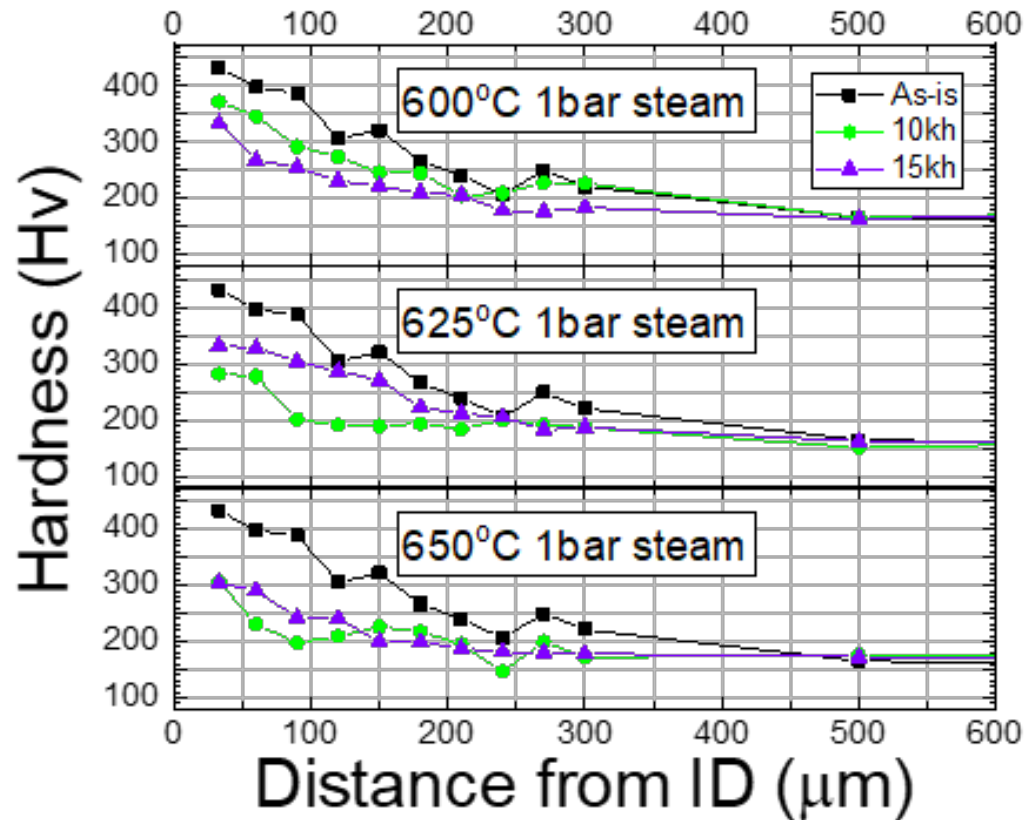


Shot-peened ID
2,500 h at 650°C
Nodules beginning to form
Significant Cr depletion

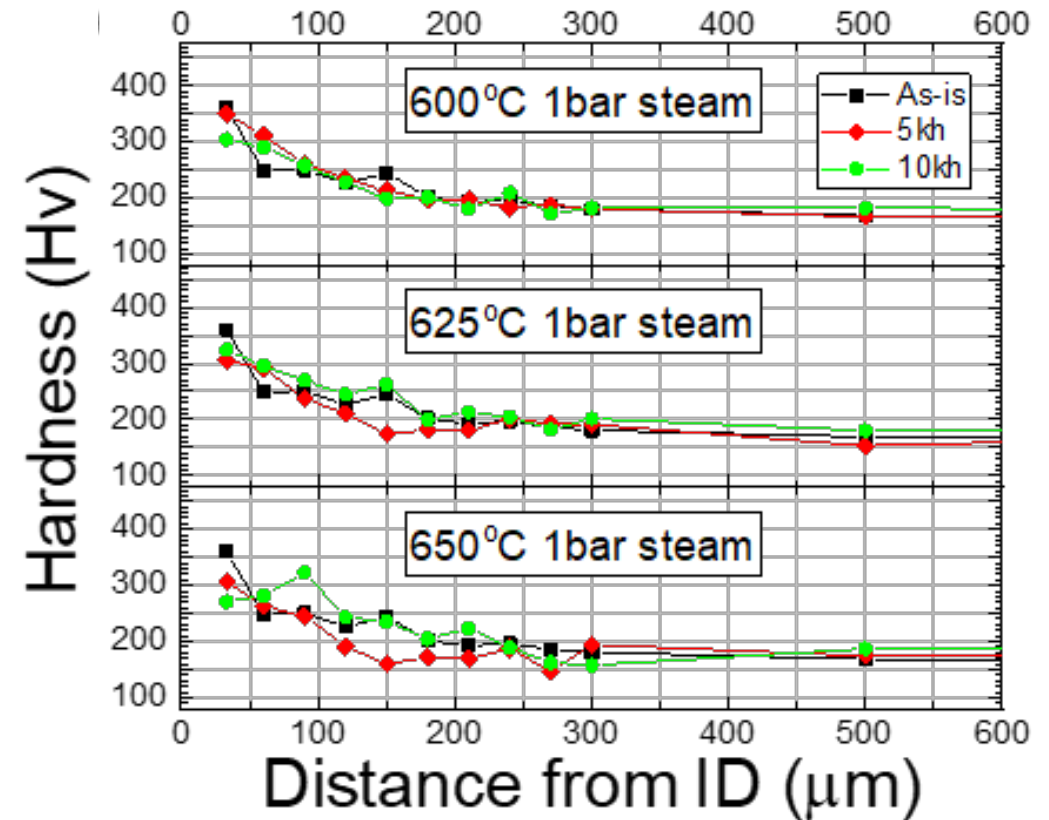


Some drop in hardness at highest temperatures

304H Tube #1

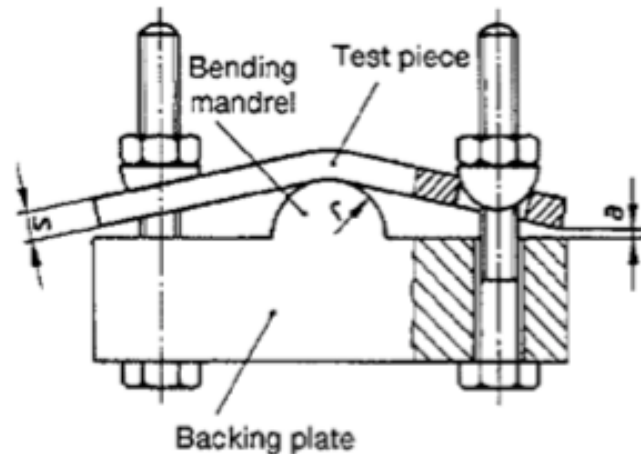


304H Tube #2



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

1st water loop built to have better environment control

Recirculating water system
- based on GE systems

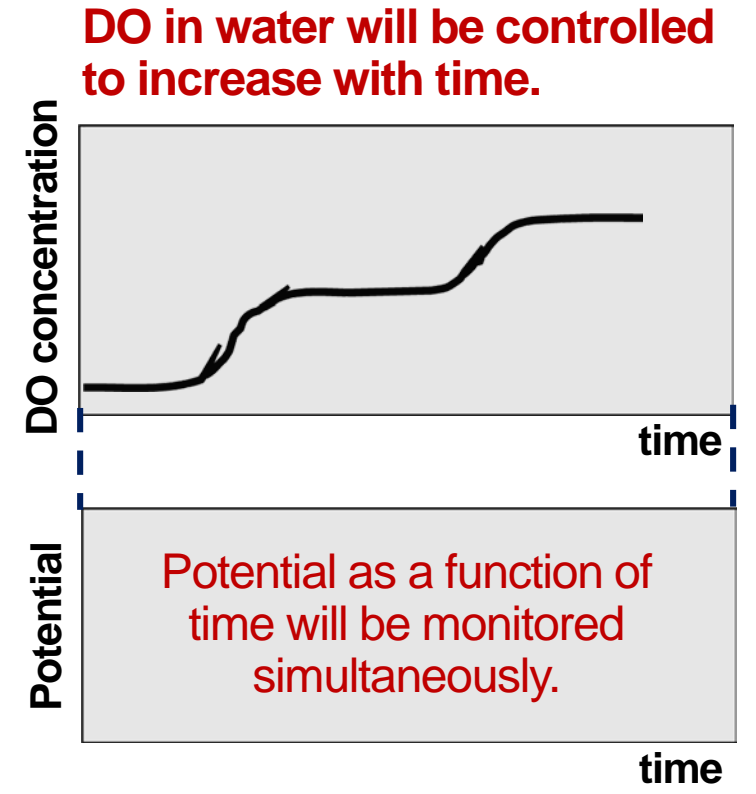
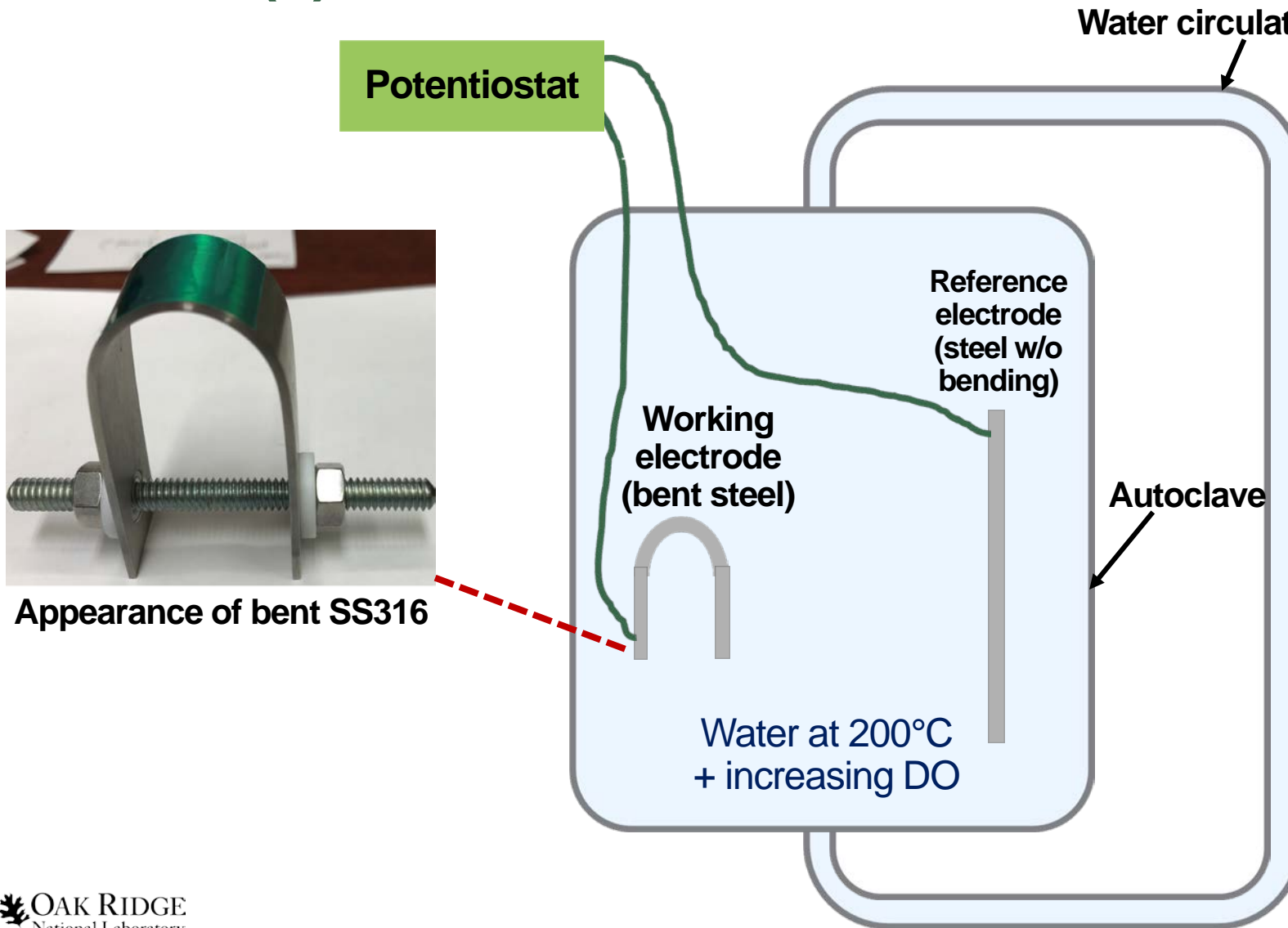


200°C autoclave



Simulate actual fossil environments with controlled pH and pO_2 levels

Experiment redesigned due to issues with autoclave/electrode: Electrochemical noise measurement will detect the potential transient(s) associated with crack initiation as O₂ increased



Any potential transient could indicate the initiation of cracking.

Specimens being prepared for experiment this quarter

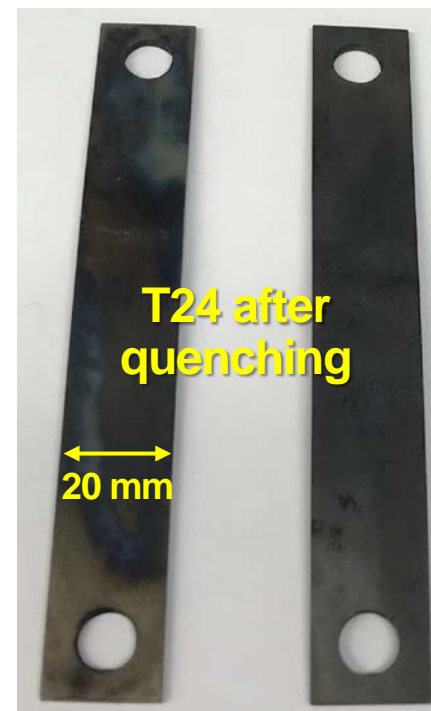
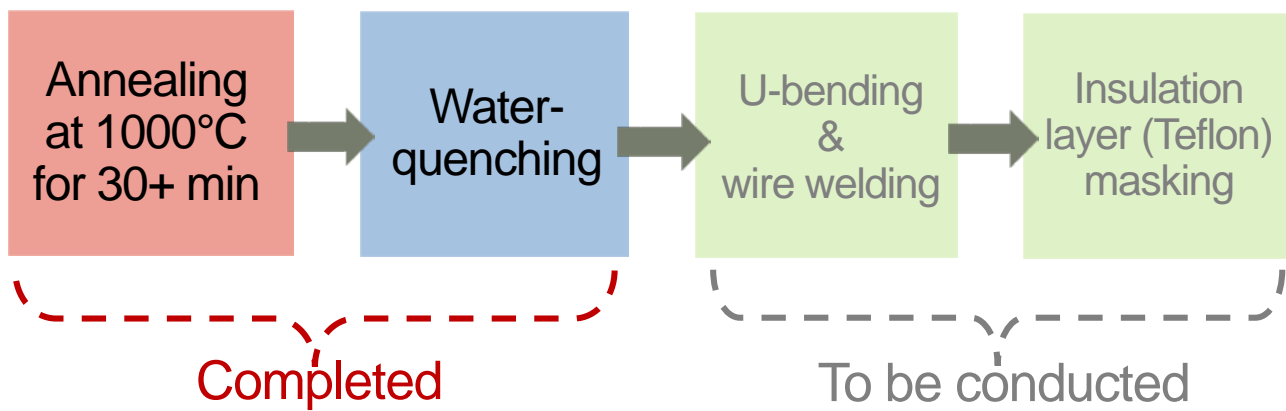
Increasing DO →

Quenched Alloy	Stagnant deaerated (~0 ppb DO)	Circulating w/ 50 ppb DO	Circulating w/ 100 ppb DO	Stagnant aerated (~8400 ppb DO)
T23	No crack	No crack	No crack	Cracking
T24	No crack	No crack	Cracking	Cracking
T91	No crack	Cracking	Cracking	Cracking

Previous Jones test results with increasing dissolved oxygen (DO) in 200°C water

T24 and T91 selected due to their cracking susceptibility

Pre-treatment for T24 and T91



T24 steel Vickers Hardness (Hv)	
ASTM standard	Measured after quenching
265	455

~72% increase in hardness

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

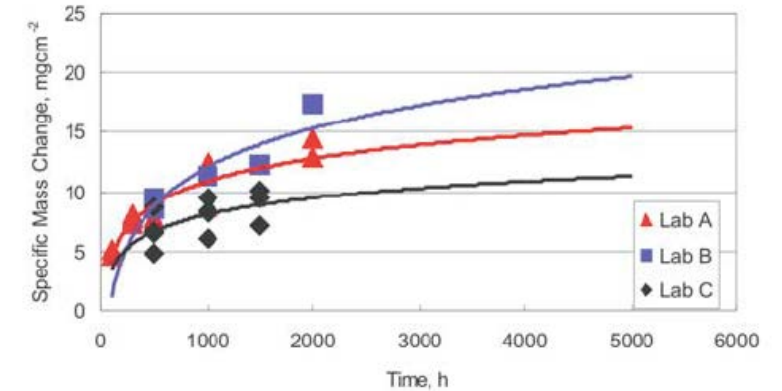
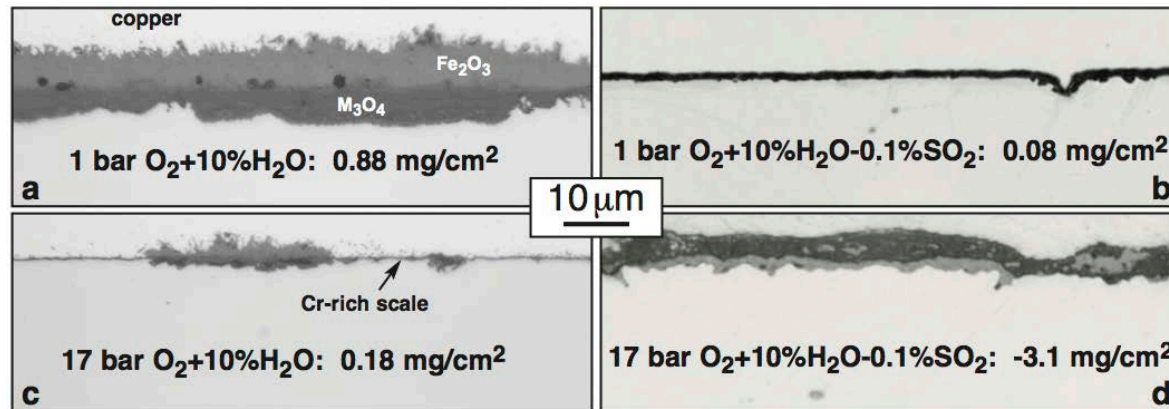
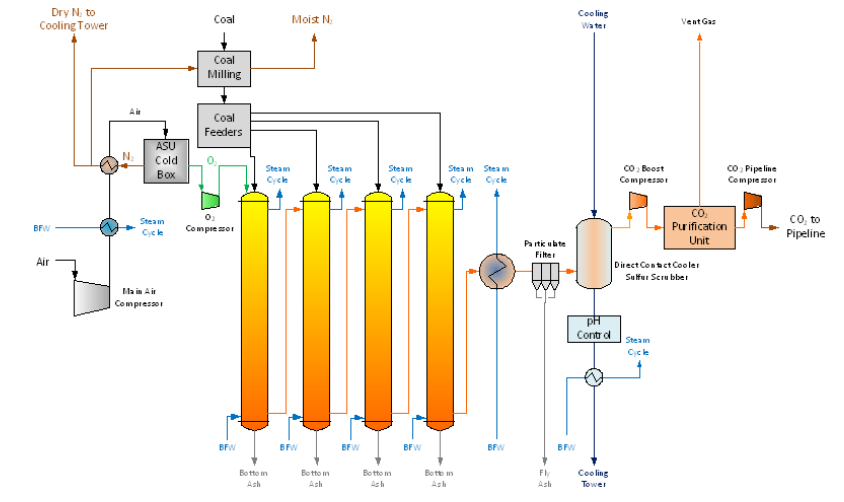


Figure 2 Intercomparison of specific mass change measurements on T92 martensitic steel after exposure to steam for up to 2000 h at 600°C (after [4]).



Partnered 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
 - Sensors in and out of autoclave

Loop completed in Spring 2018



500-h cycles: 1L volume restricts number of specimens



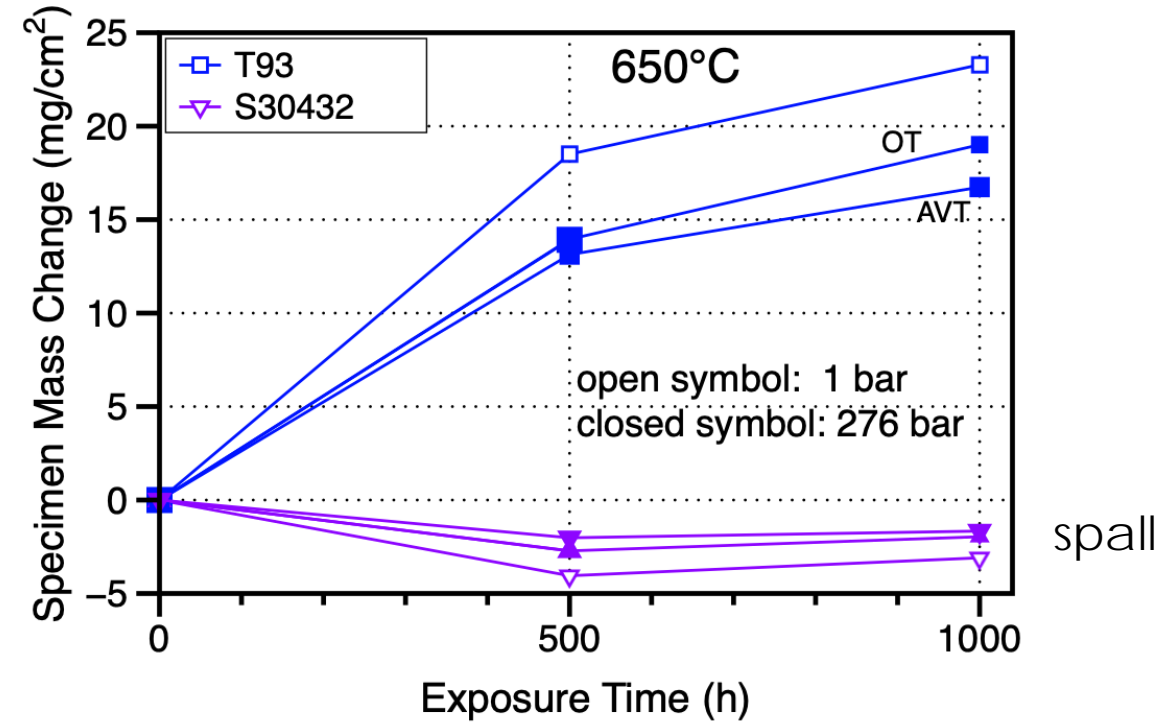
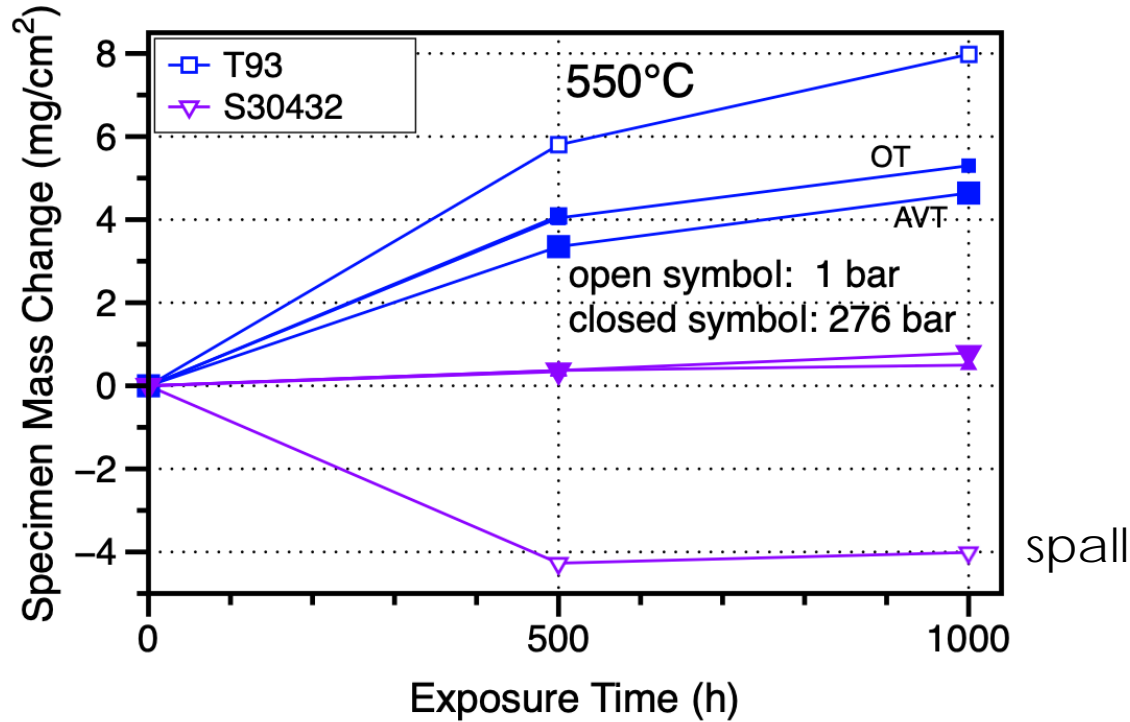
Issues resolved with:
Heater
Gasket
Back pressure regulator

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 O₂
Typical for sub-critical
Oxygenated treatment (OT)
50-150 ppb O₂
Typical for super-critical
Oxide to prevent erosion

Differences in mass change observed at 550°-650°C comparing 1 and 276 bar

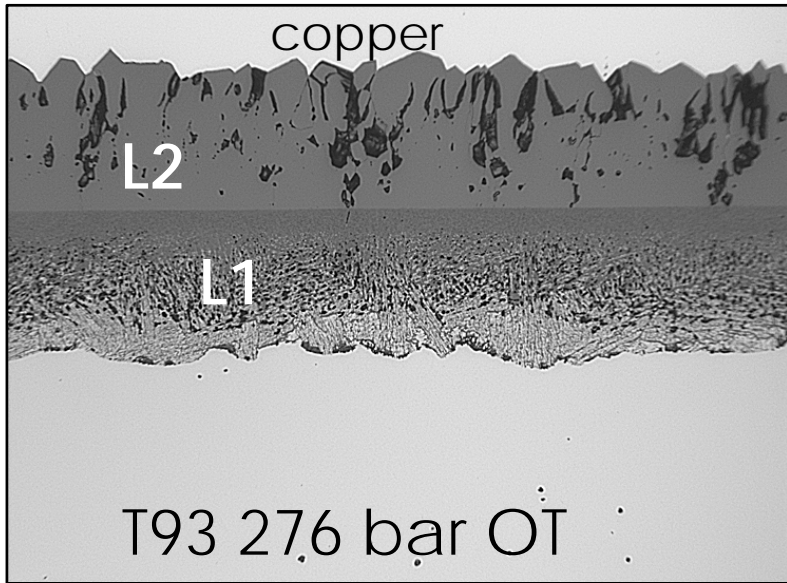


T93: 84wt.%Fe-8.9Cr-**3.1Co**-**3.1W**-0.5Mn-0.2Si-0.2V-0.1Ni-0.06Nb-0.09C

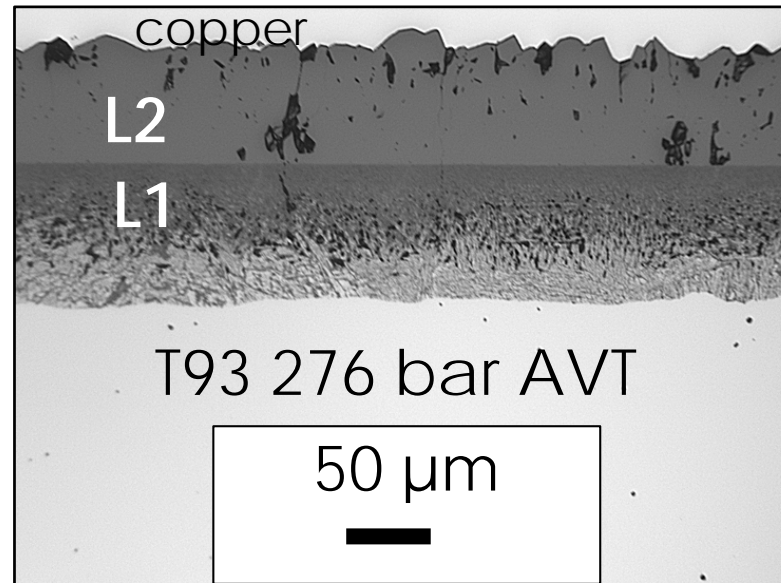
Super 304H: 67Fe-18.8Cr-8.4Ni-**2.8Cu**-0.8Mn-0.3Si-0.5Nb-0.3Mo-0.09C-**0.11N**



T93: 1000h 650°C 276 bar vs 1 bar

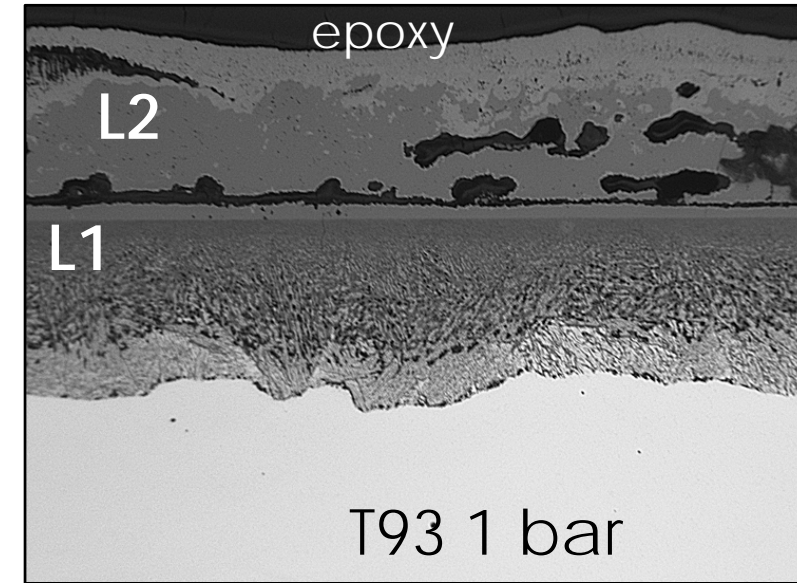


Mass change:
19.0 mg/cm²



Mass change:
16.7 mg/cm²

Hematite in 1 bar steam

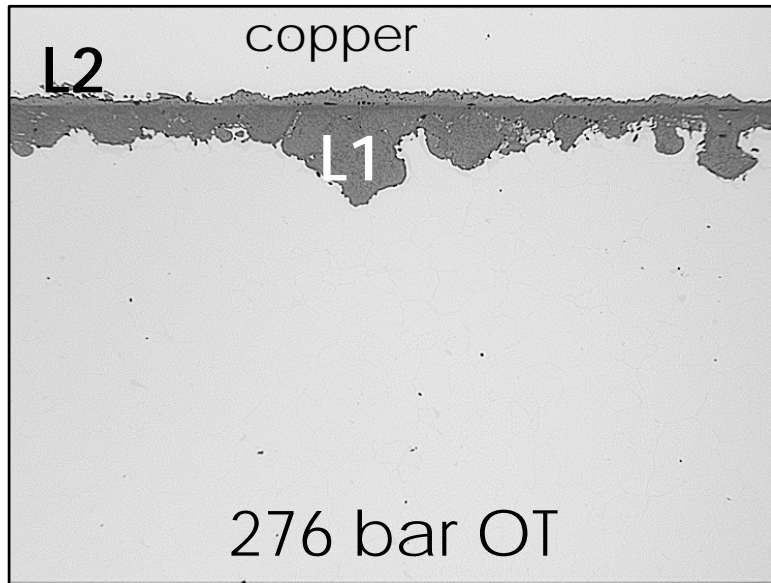


Mass change:
23.3 mg/cm²

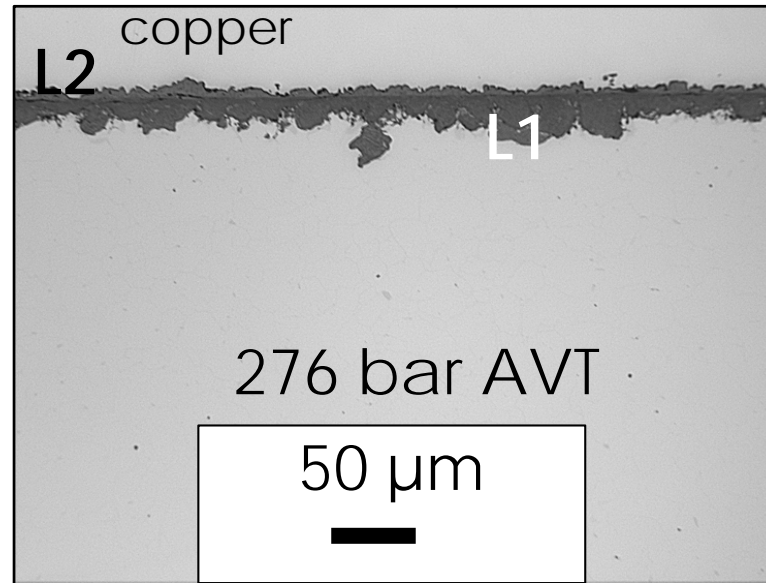
Super 304H: 1000h 650°C 276 bar vs 1 bar

L2 (FeO_x layer) spalled after first cycle in all cases

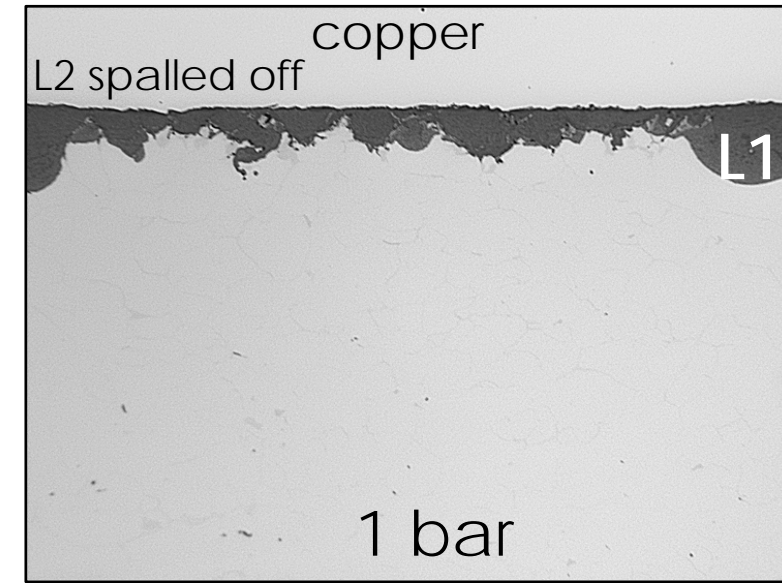
OT: Hematite in L2?



Mass change:
-2.0 mg/cm²



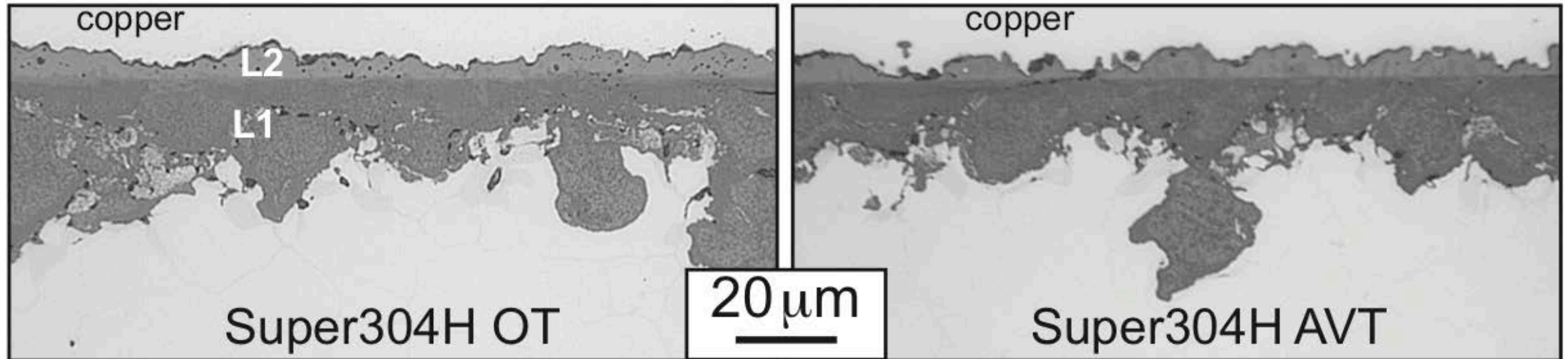
Mass change:
-1.7 mg/cm²



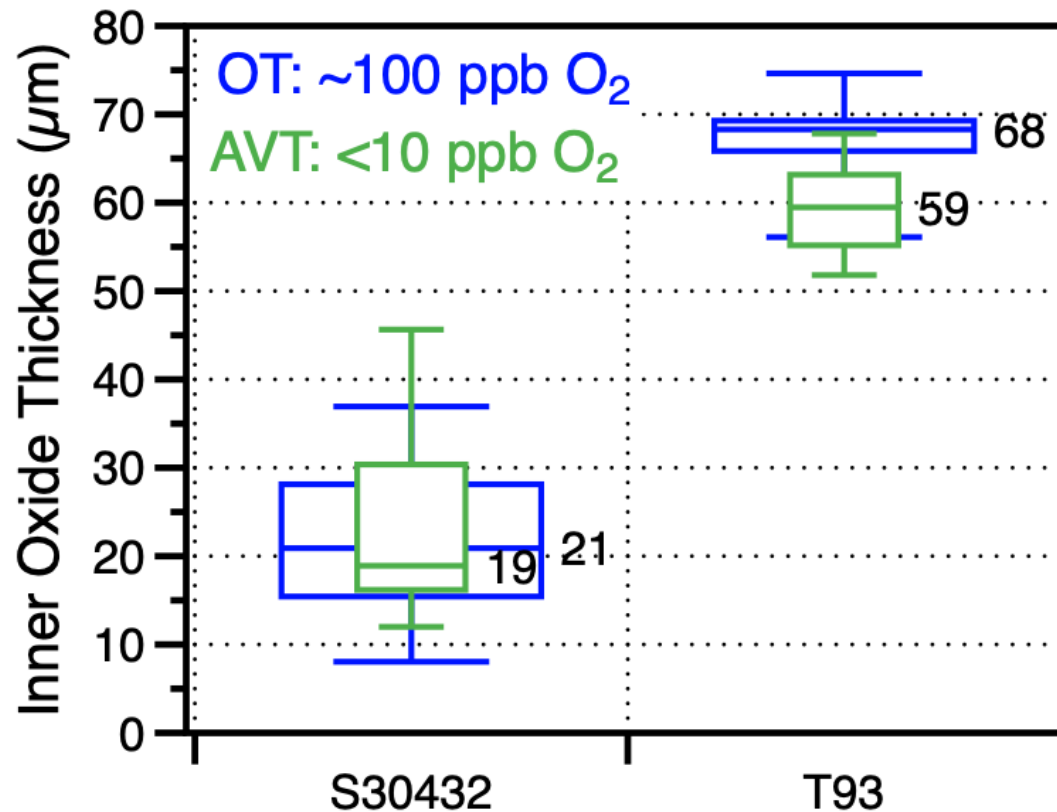
Mass change:
-3.1 mg/cm²

Super 304H: 1000h 650°C 276 bar

OT: Hematite in L2



Inner oxide (L1): slightly thinner oxides formed in AVT compared to OT



Plot (~30 measurements):

- Median value marked
- Whiskers: Min/max
- Box: 25%-75% values

Project has addressed several issues

1. Quantify shot-peening benefit on 304H
 - Completed 10-15 kh exposures at 550°-650°C
 - Compared to polished coupons
 - Manuscript drafted for journal submission
 2. SCC issue in current waterwalls
 - Redesigned for electrochemical noise monitoring
 - Experiment prepared to identify critical cracking O content
 3. Effect of pressure on steam oxidation
 - Matrix complete: 276 bar, 550°/650°C, two O₂ levels
 - Final report being completed
- Expecting to complete all tasks in 2019



Backups

Industrial collaborations

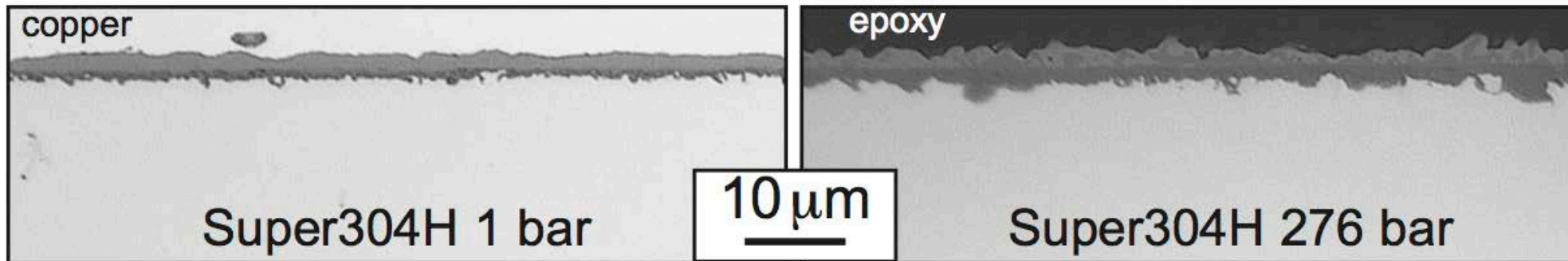
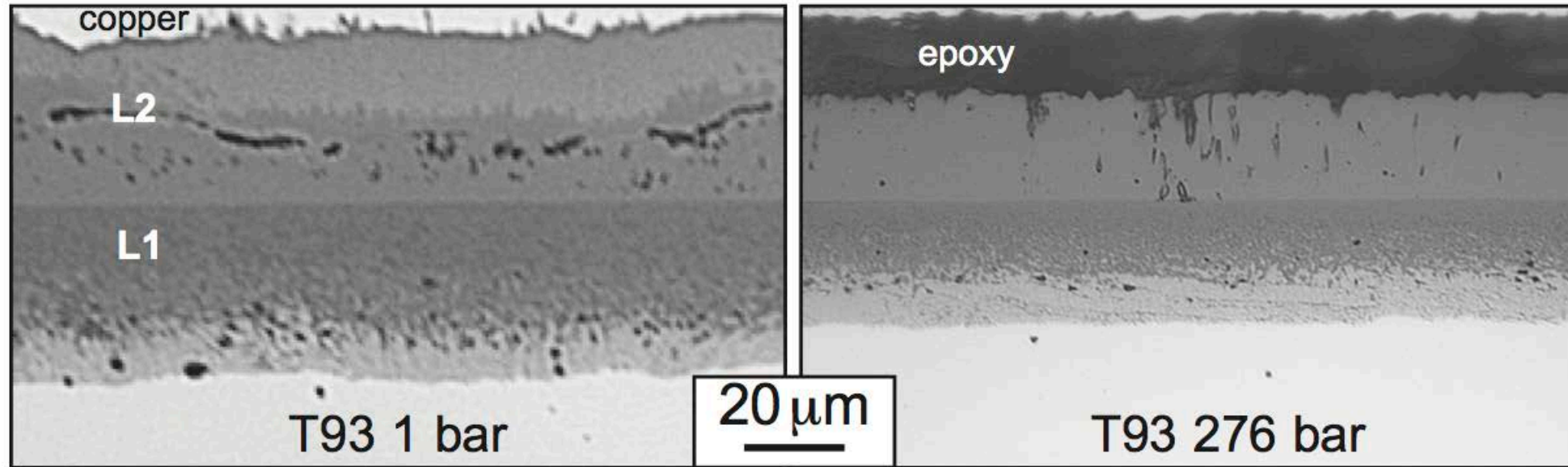
- Strong collaboration with EPRI
 - EPRI Atlas
 - EPRI shot-peen study
 - EPRI water loop project (\$125K in late 2016)
- Shot-peened material from American Electric Power
 - Two 304H tubes using commercial process



Relation to other relevant projects/activities

- Steam testing performed for FEAA114 and AFA/CAFA development
- Legacy coal ash testing performed for FEAA114
- Effect of pressure also considered in CO₂ studies (FEAA123)

550°C: changes observed between 1 and 276 bar (OT)



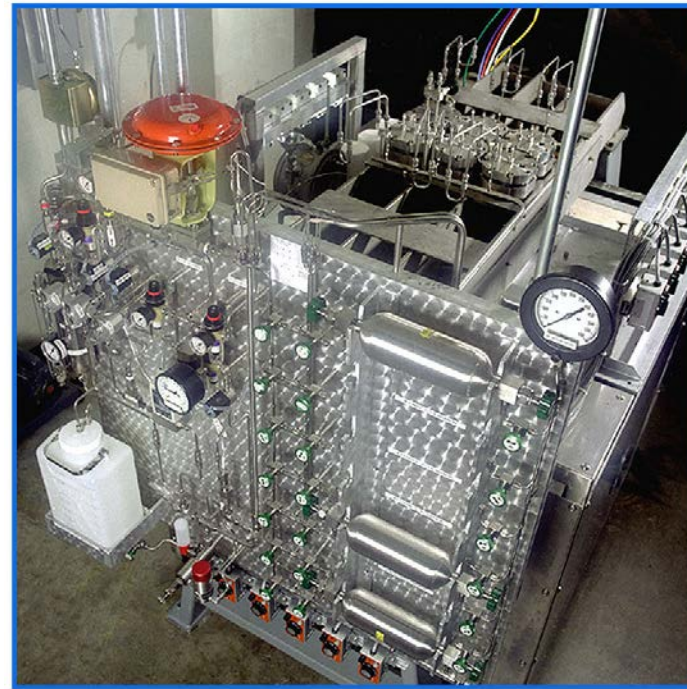
Several options for steam exposures

Tube furnace: 1 bar CO₂
500-h cycles



Standard procedure

"Keiser" rig:
500-h cycles, 1-43 bar
CO₂



Pressures of 1-43 bar

Autoclave: 275 bar water
500-h cycles

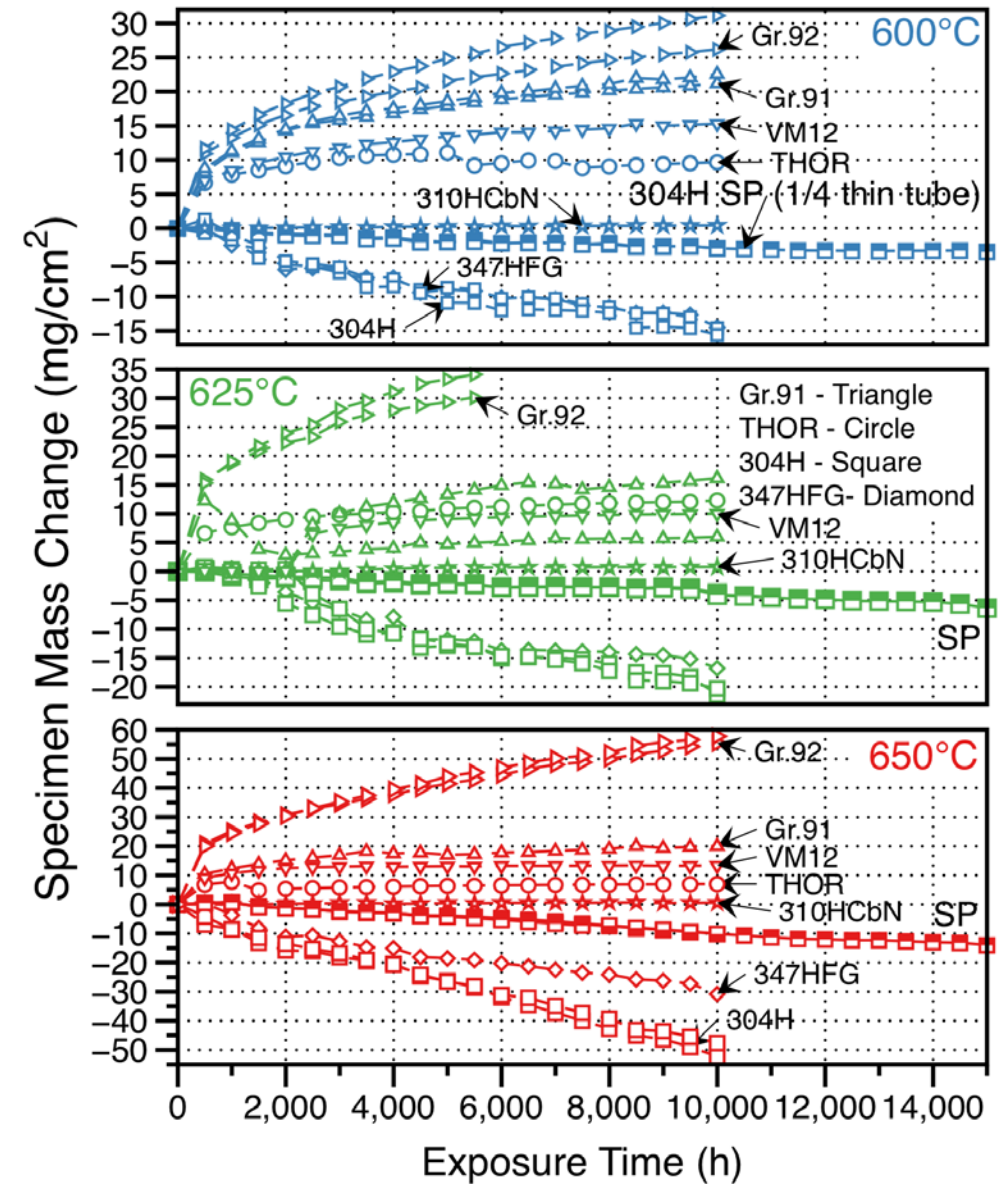
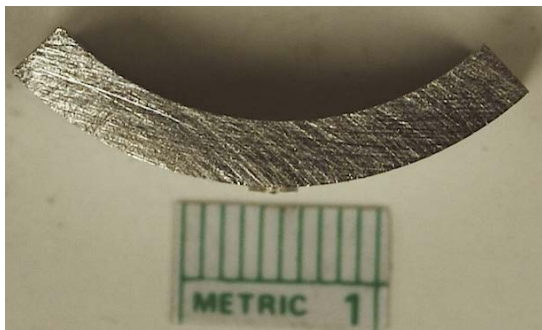


1L volume restricts exposure

High purity Ar-bubbled, filtered water with conductivity $<0.1\mu\text{S}$ and $<10\text{ ppb O}_2$

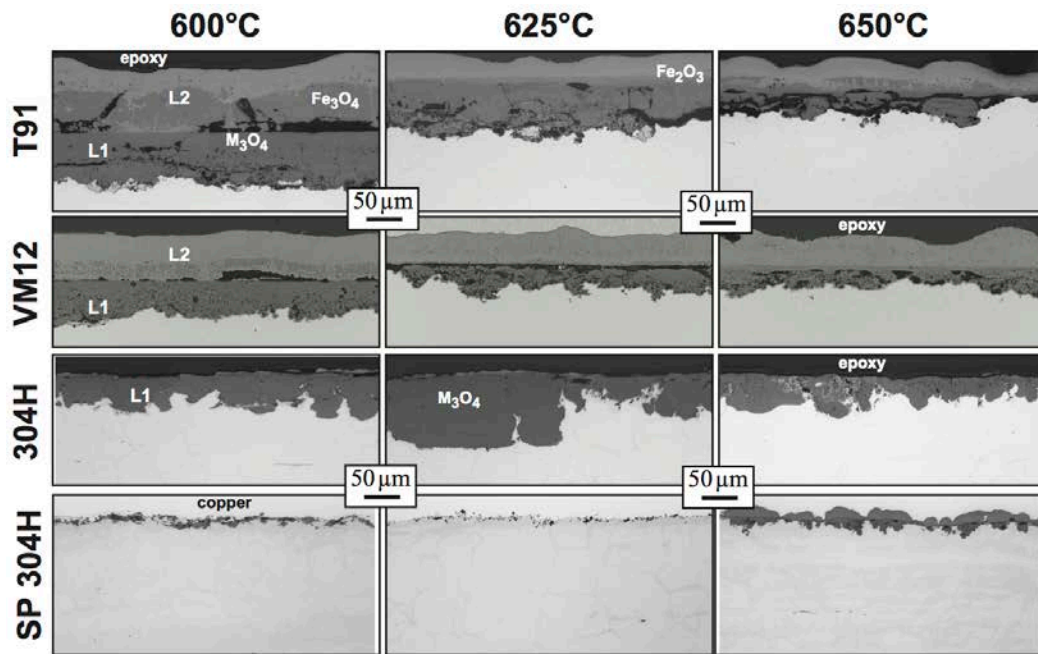
Completed 15,000 h of testing

- Tube sections removed at various times
- Polished alloy coupons for comparison
 - Gr.91
 - Gr.92
 - THOR
 - VM12
 - Gr.93 (new CSEF steel)
 - CPJ7 (started in 2018)

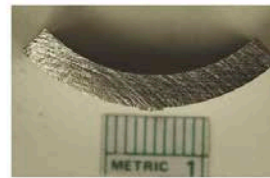


Dramatic benefit of shot peening 304H

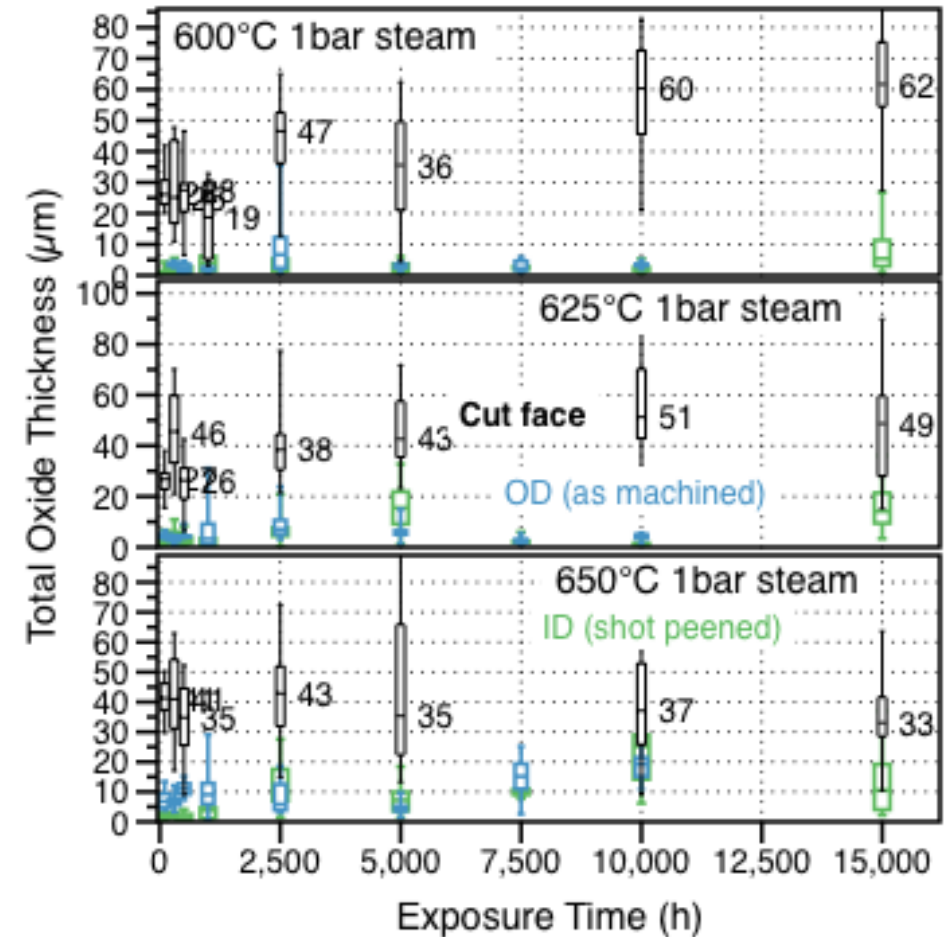
- Fe-18.3wt.%Cr-8.6Ni-1.8Mn-0.3Si-0.3Mo
- Effect starting to fade at 650°C
- Additional exposure running at 550°C
- **Final characterization in progress**



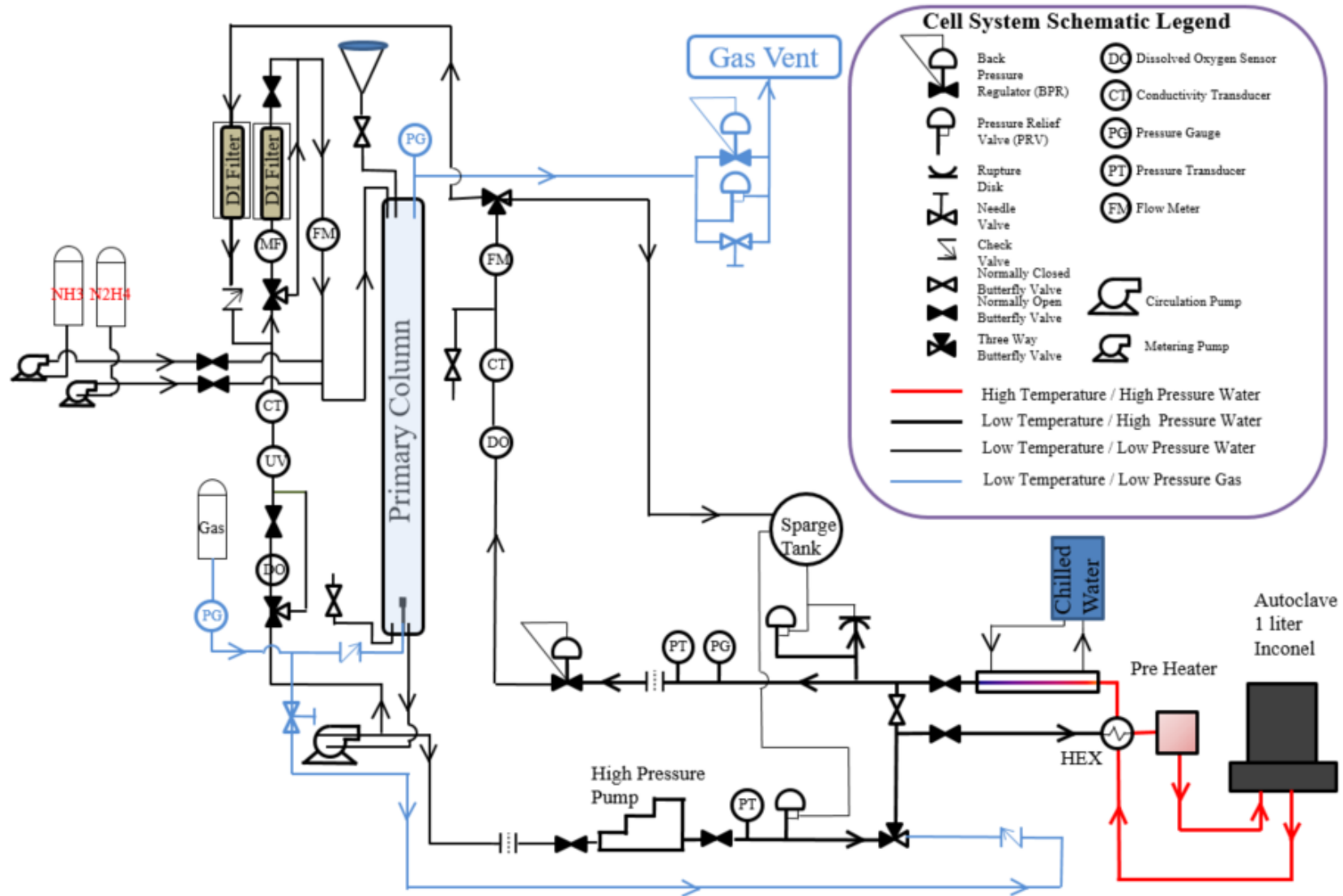
10,000 h exposures



1 Specimen: shot peened ID
 machined OD
 polished "cut" sides (like coupon)



Raiman: loop architect



pH is controlled with ammonia addition

