

Corrosion Issues in Advanced Coal-Fired Boilers (FEAA116)

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Crosscutting Research Program (V. Cedro, project manager)

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Acknowledgments

ORNL

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Z. Burns - oxidation experiments

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T. Lowe - SEM, image analysis

D. Leonard - EPMA

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Special thanks for shot peening task:

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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

FY16

Complete shot peened SS characterization after 10,000h (5/31/16 Met)

Complete initial SCC assessment in 2 water chemistries (12/31/16 Met)

Complete steel characterization in 3 steam pressures (in progress)

FY17

Complete final report on shot peened stainless steel oxidation (3/31/17)

Demonstrate in-situ crack growth measurements in 200°C water (9/30/17)

Compare oxide microstructure formed on steam at 1 & 200 bar (6/30/17)

FY16-17: science approach to “real world” corrosion issues

1) Steam oxidation

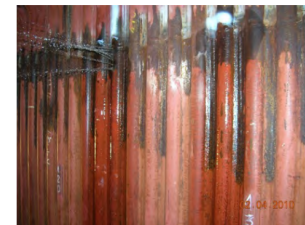
- study of shot-peening “solution”



2) H-induced stress corrosion cracking

- 2.25%Cr waterwall steels: Grades 22,23,24
- significant problem in new boilers
- need for more detailed understanding

Cracks in longitudinal direction



Cracks in transversal direction



3) Effect of pressure on corrosion

- relevant for steam oxidation (lab. vs. field)
- SPOC: staged pressurized oxy-combustion (with Wash.U@StL) also relevant on fireside

John W. Turk Plant (2013) solution

“Ultra-supercritical” coal-fired steam plant by B&W/AEP



Fulton, Arkansas

600 MW

2013 commission

~40% LHV efficiency

\$1.8 billion (\$2.8b?)

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

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

Turk superheater tubes: shot-peened 347H

Fe-17.5Cr-10Ni-0.5Nb-1.5Mn-0.4Si-0.07C

Task 1: Why shot peening?

Exfoliation problem is a main driver for research

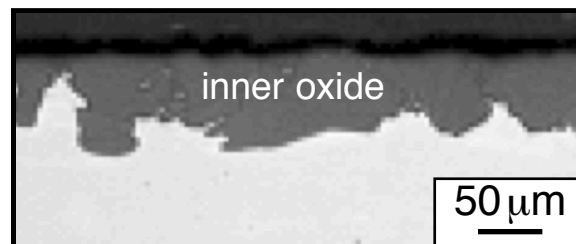
H₂O-accelerated oxidation of steels (steam-side)

Simultaneous spallation of thick oxide

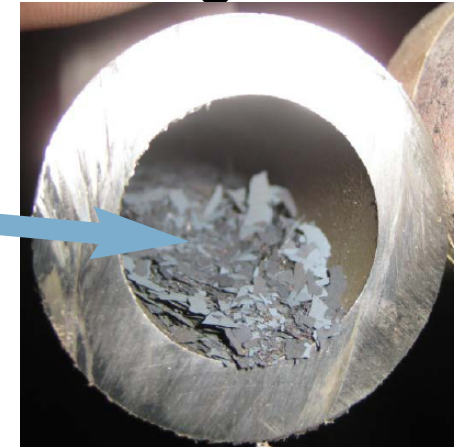
Tube failures & erosion damage

Cost: planned/unplanned shutdowns, mitigation

TP304H (22,000h)



outer oxide



Source: EPRI

Shot peening of austenitic tubes

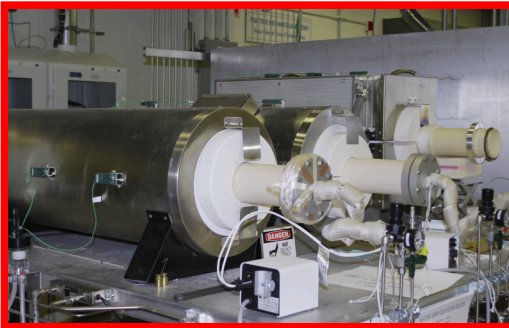
Reduced scale growth: avoids exfoliation issue

Limited understanding of benefit and procedure

Ex: How do oxide nodules evolve at 600°-650°C?

Specimens exposed in laboratory

ORNL has several options



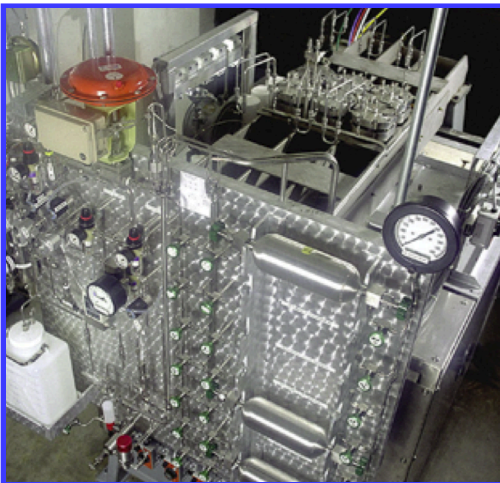
1 bar steam

Atomized deionized water (no carrier gas)

H₂O: ~0.065 μS/cm, filtered, deaerated

Temperature: 550°-650°C

Time: 500 h cycles



1-30 bar steam testing

H₂O: ~0.065 μS/cm, filtered, deaerated, deionized

Temperature: 550°-900°C

Time: 500 h cycles



≤ 275 bar steam testing (in 2017)

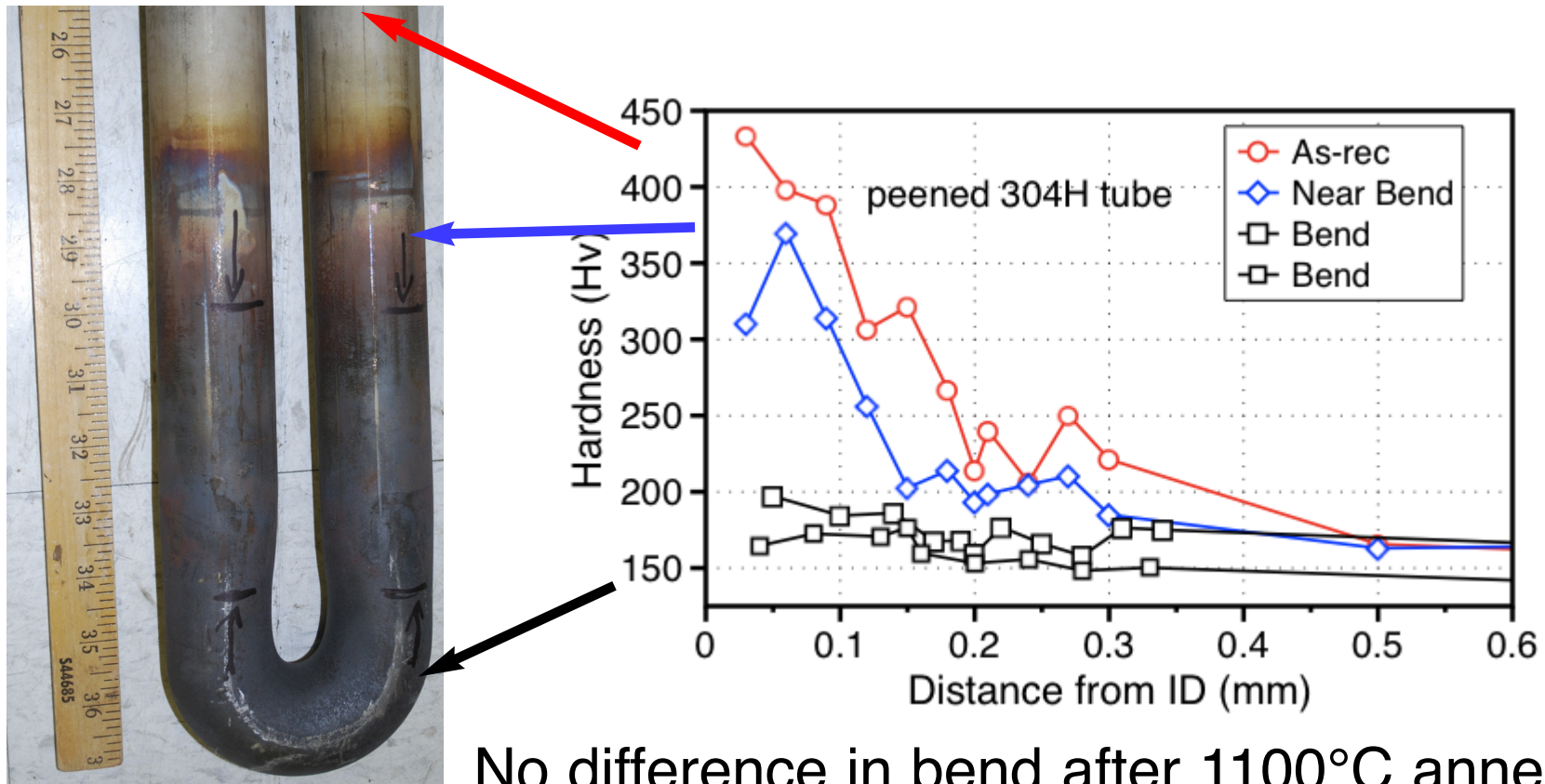
Controlled water chemistry loop

Temperature: 450°-650°C

Time: 500 h cycles

Cold work–hardness–fast D_{Cr}

Well known cold working affects transport



No difference in bend after 1100°C anneal

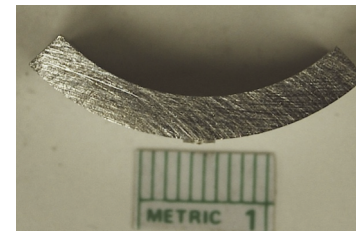
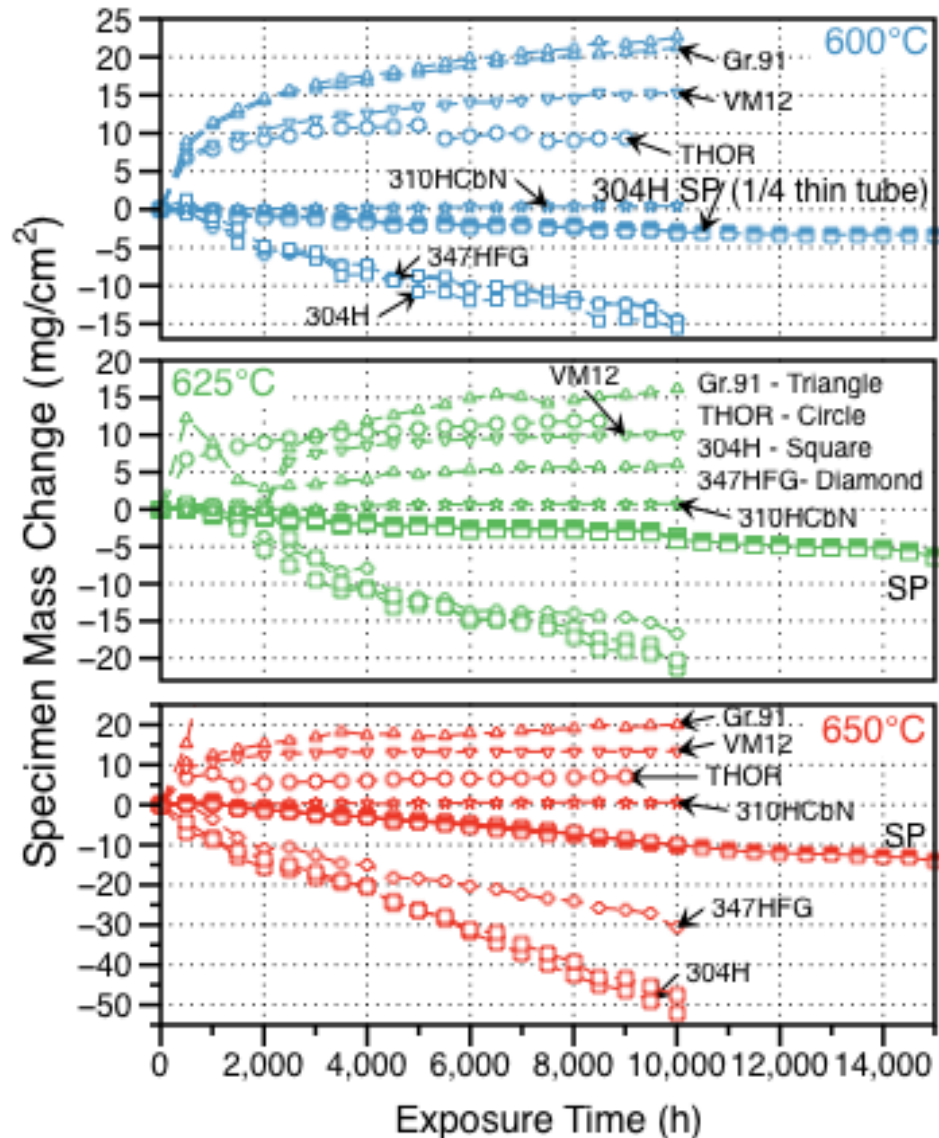
304H tube from an EPRI partner:

No hardness difference remained in the bend after required 1100°C annealing

Completed 15kh of exposures

600°,625°,650°C 1bar steam; 500-h cycles

Shot peened coupons: commercial 304H from a utility

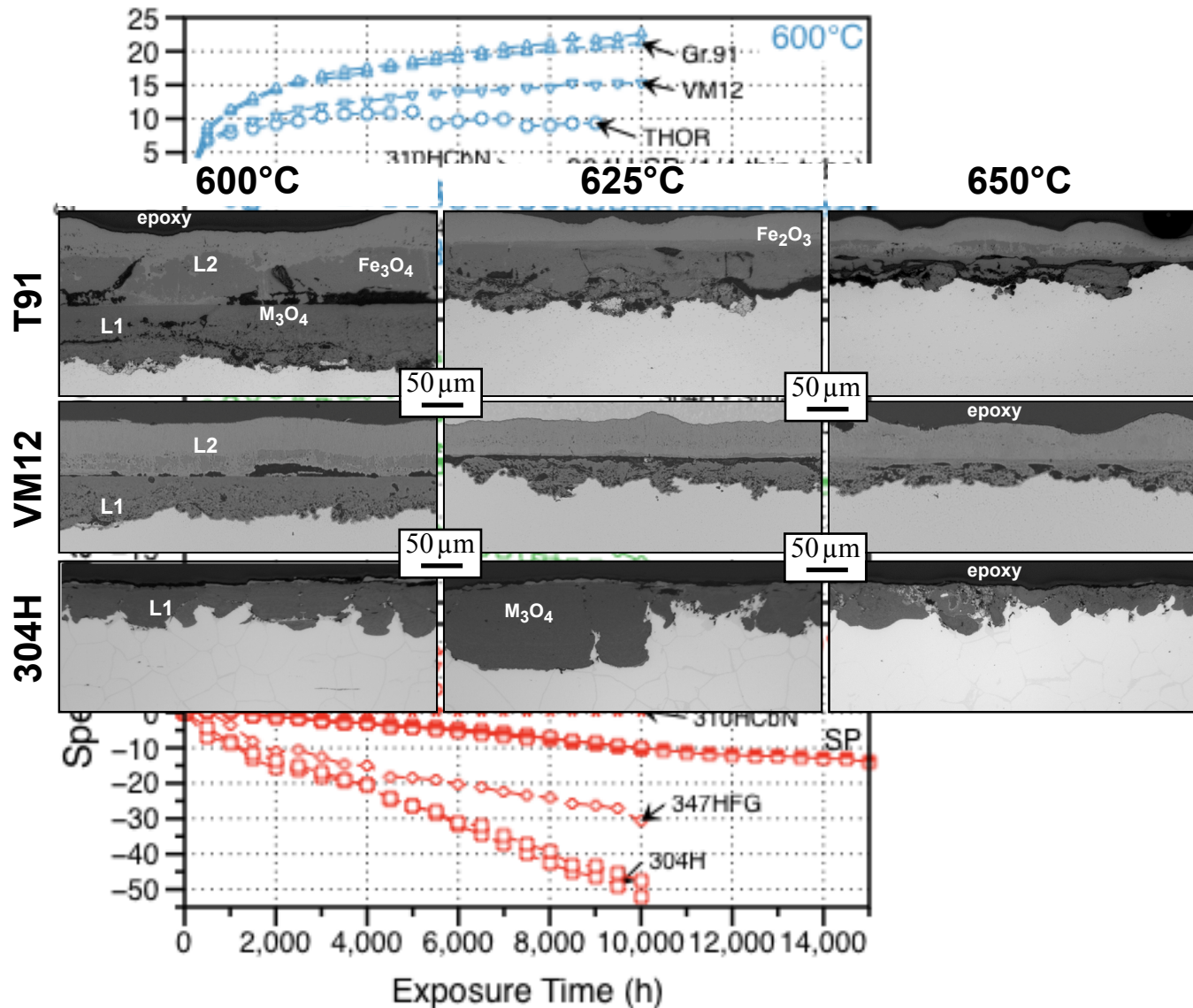


Shot peened coupons:
tube sections
reduced wall thickness
Polished alloy coupons:
comparison



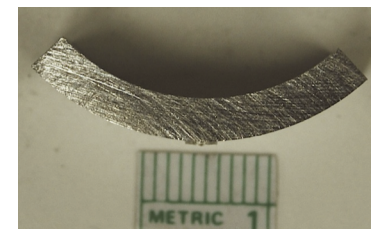
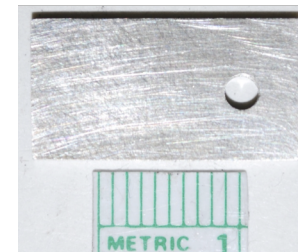
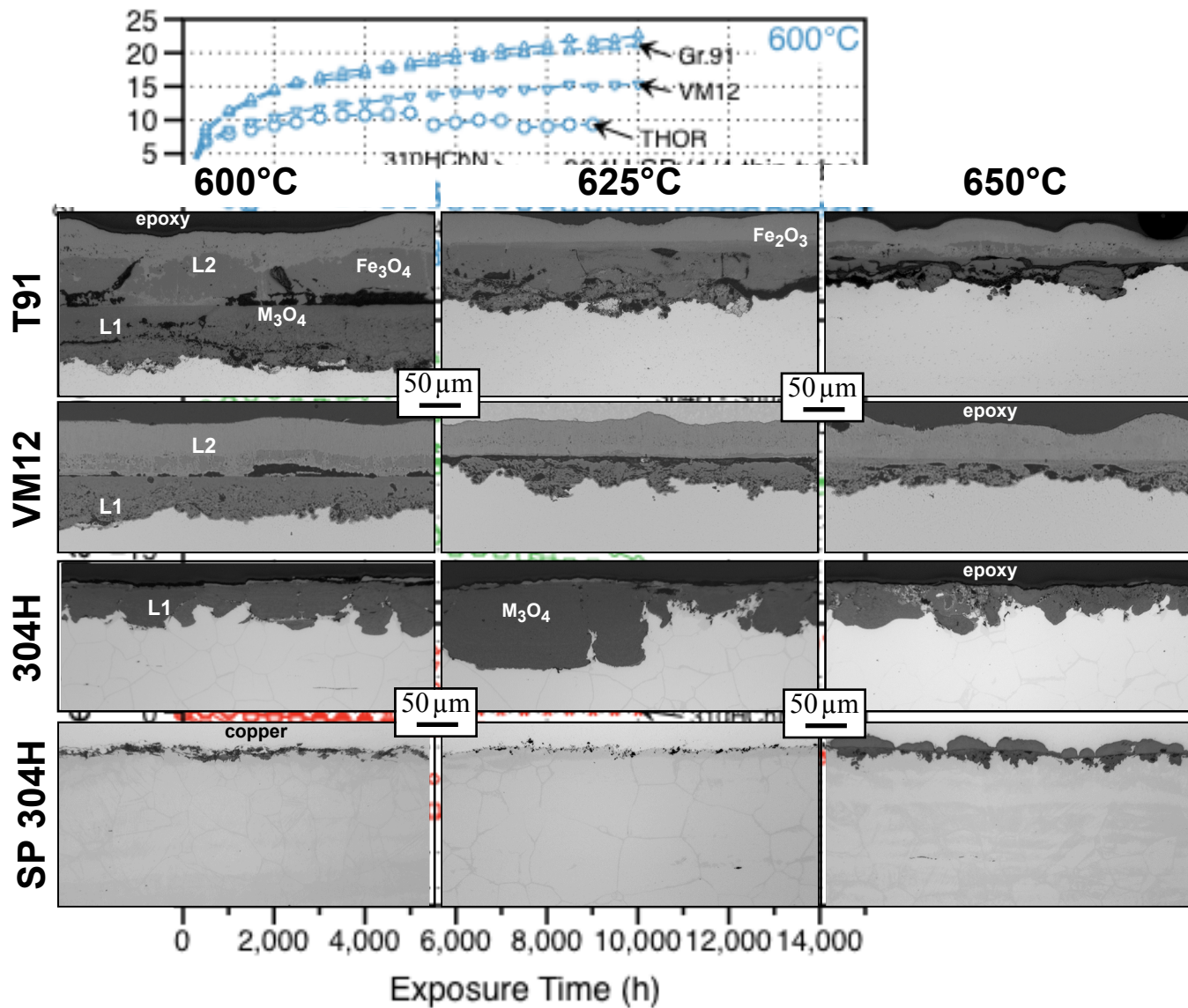
Alloy coupons stopped at 10,000h

Alloy coupons: conventionally polished



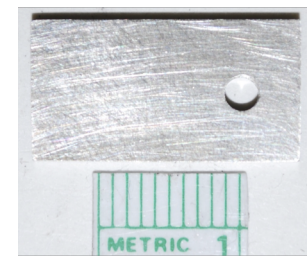
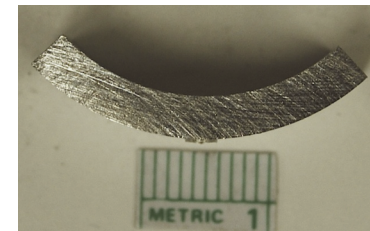
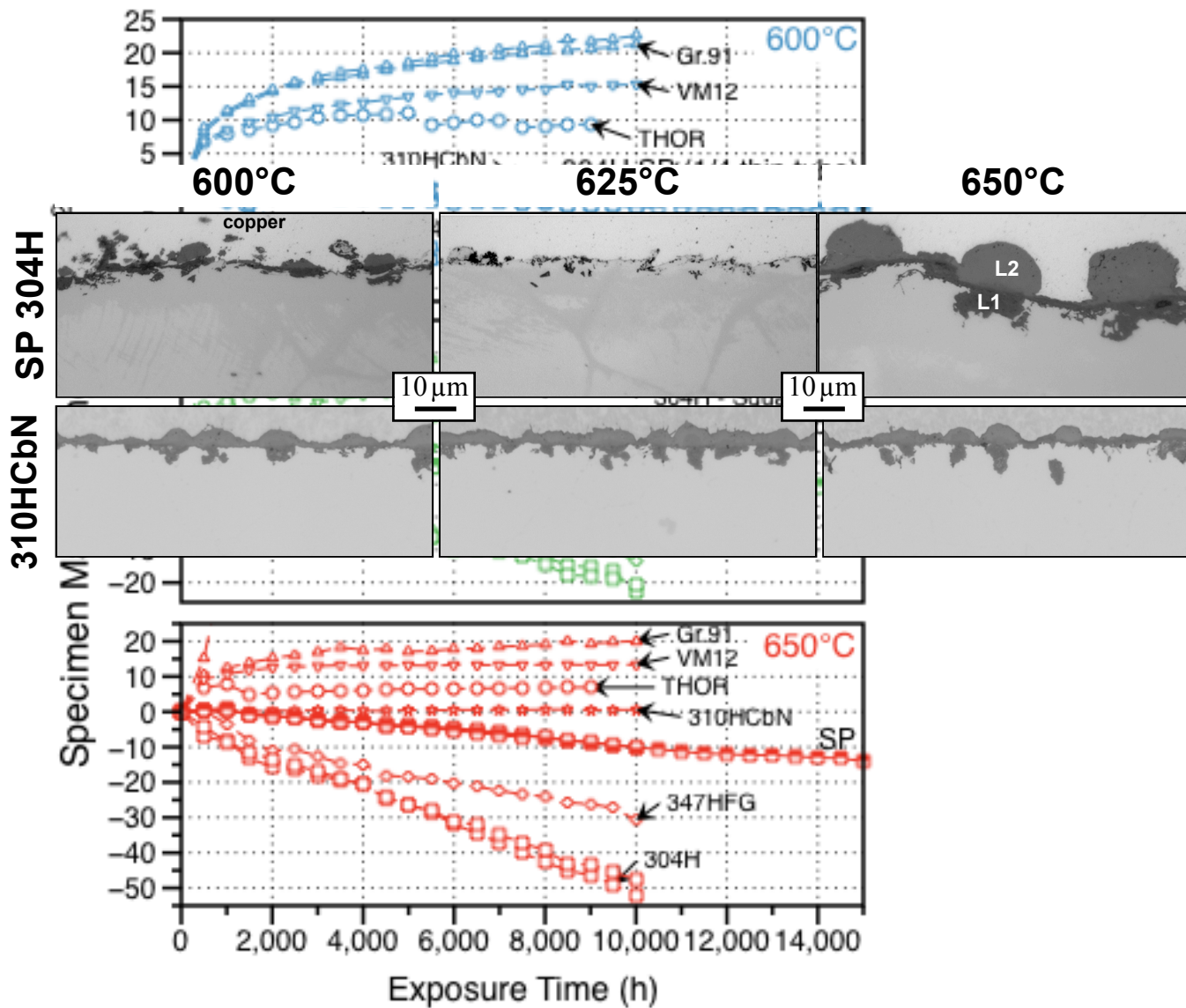
10,000h: Clear shot peening benefit

600°, 625°, 650°C 1bar steam; 500-h cycles



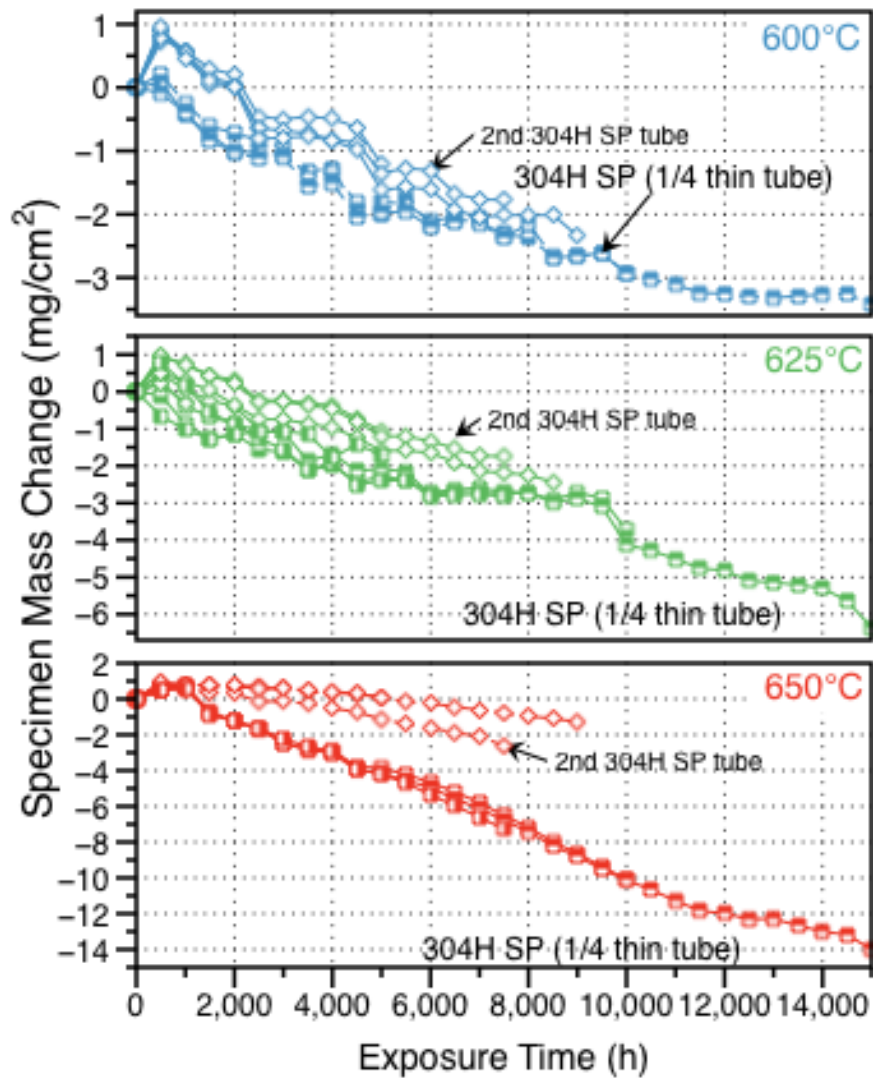
10,000h: thin scale like on 310SS

600°, 625°, 650°C 1bar steam; 500-h cycles



Two differentiated peened tubes

600°, 625°, 650°C 1bar steam; 500-h cycles



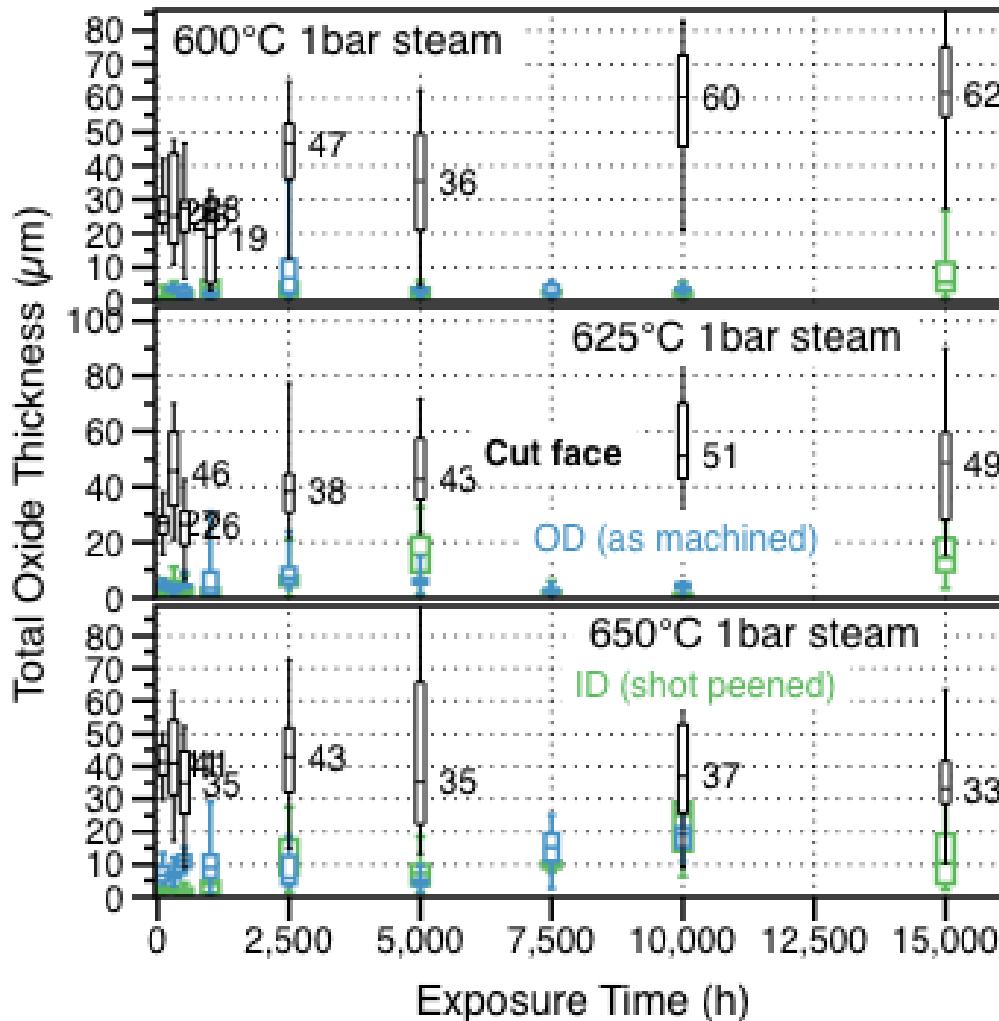
commercial shot-peened 304H

Each: 0.5, 1, 2.5, 5, 7.5, 10, 15 kh specimens

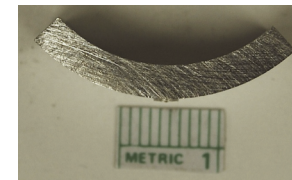
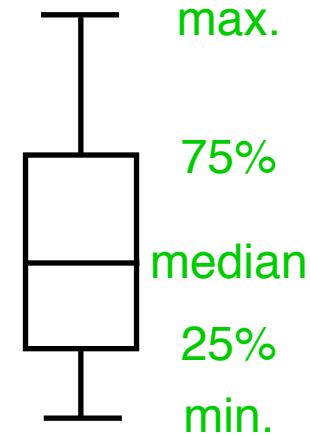
Series of SP specimens exposed

Oxide thickness measurements from polished sections

commercial shot-peened 304H

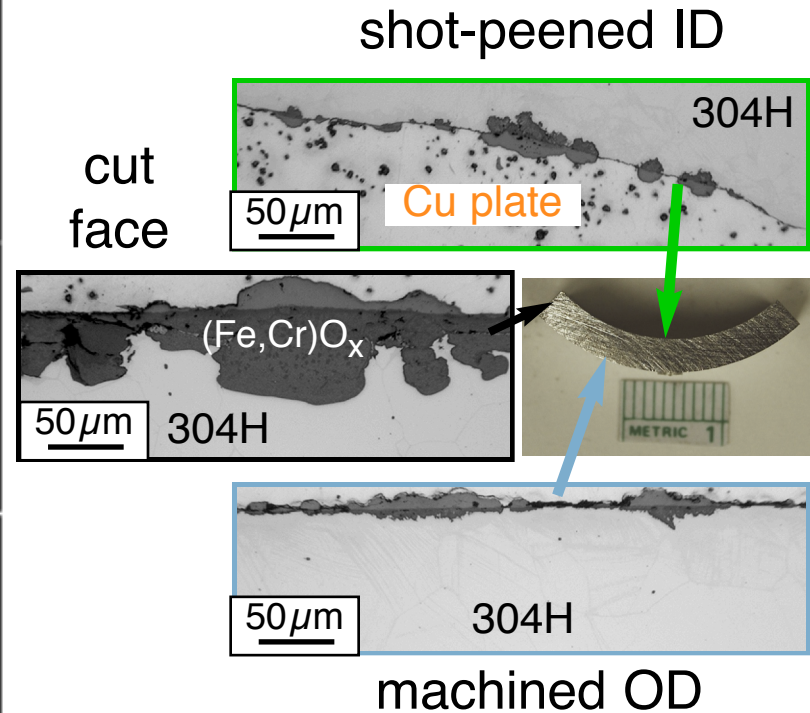
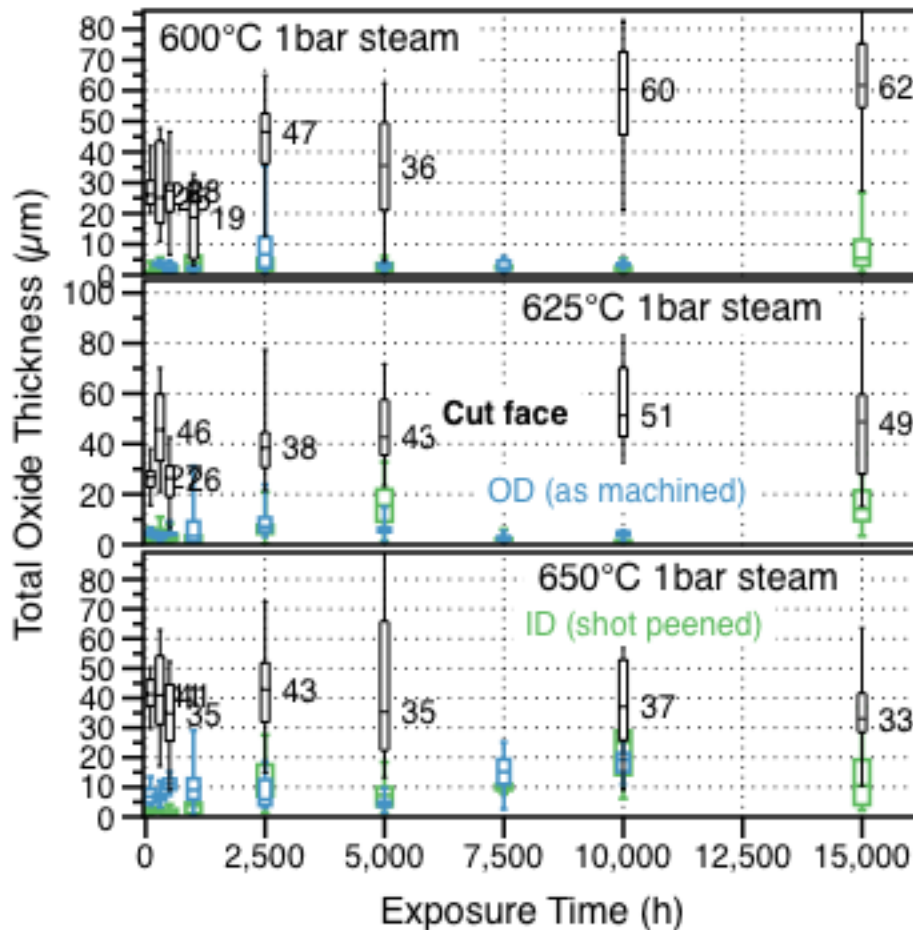


Box & whisker plot



“Cut” face grows thick oxide

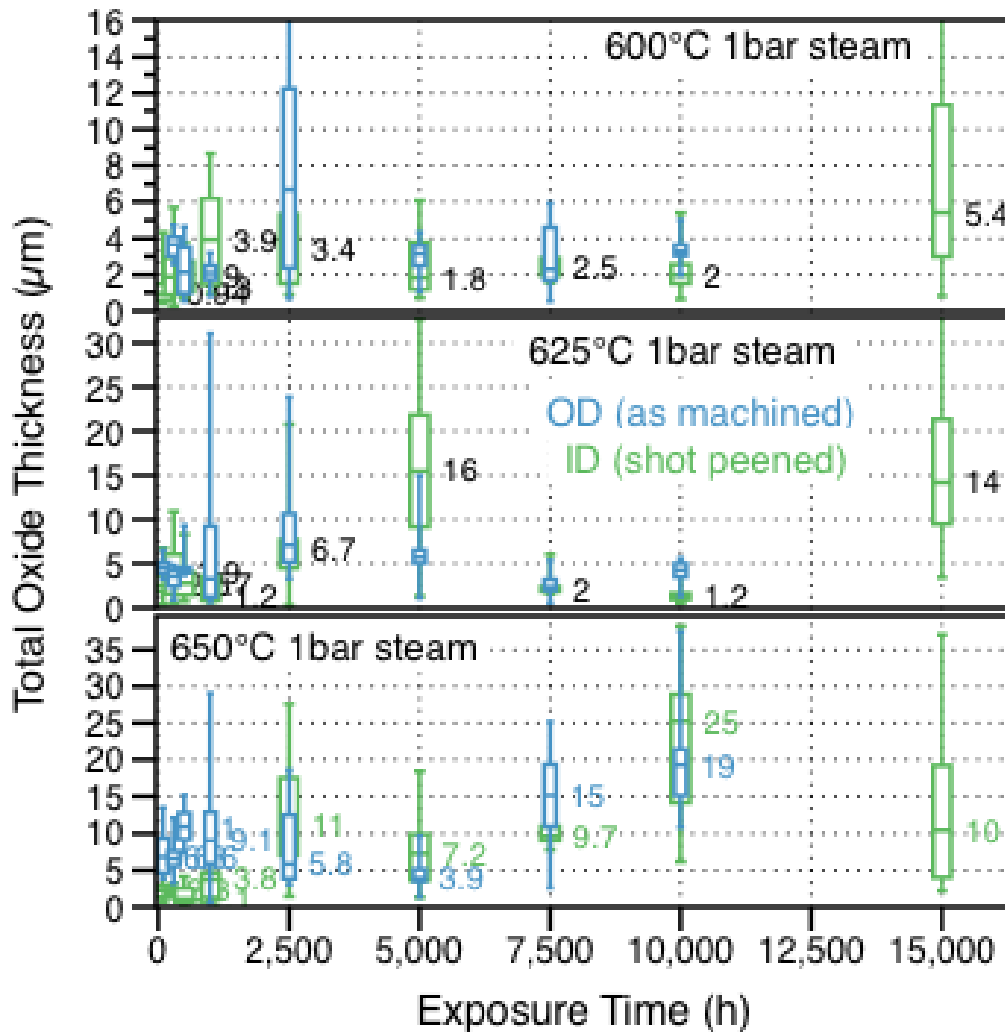
Oxide thickness measurements from polished sections



Example: 2,500h, 625°C

Similar benefit on machined OD

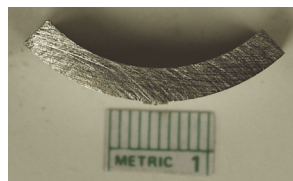
Oxide thickness measurements from polished sections



600°-625°C

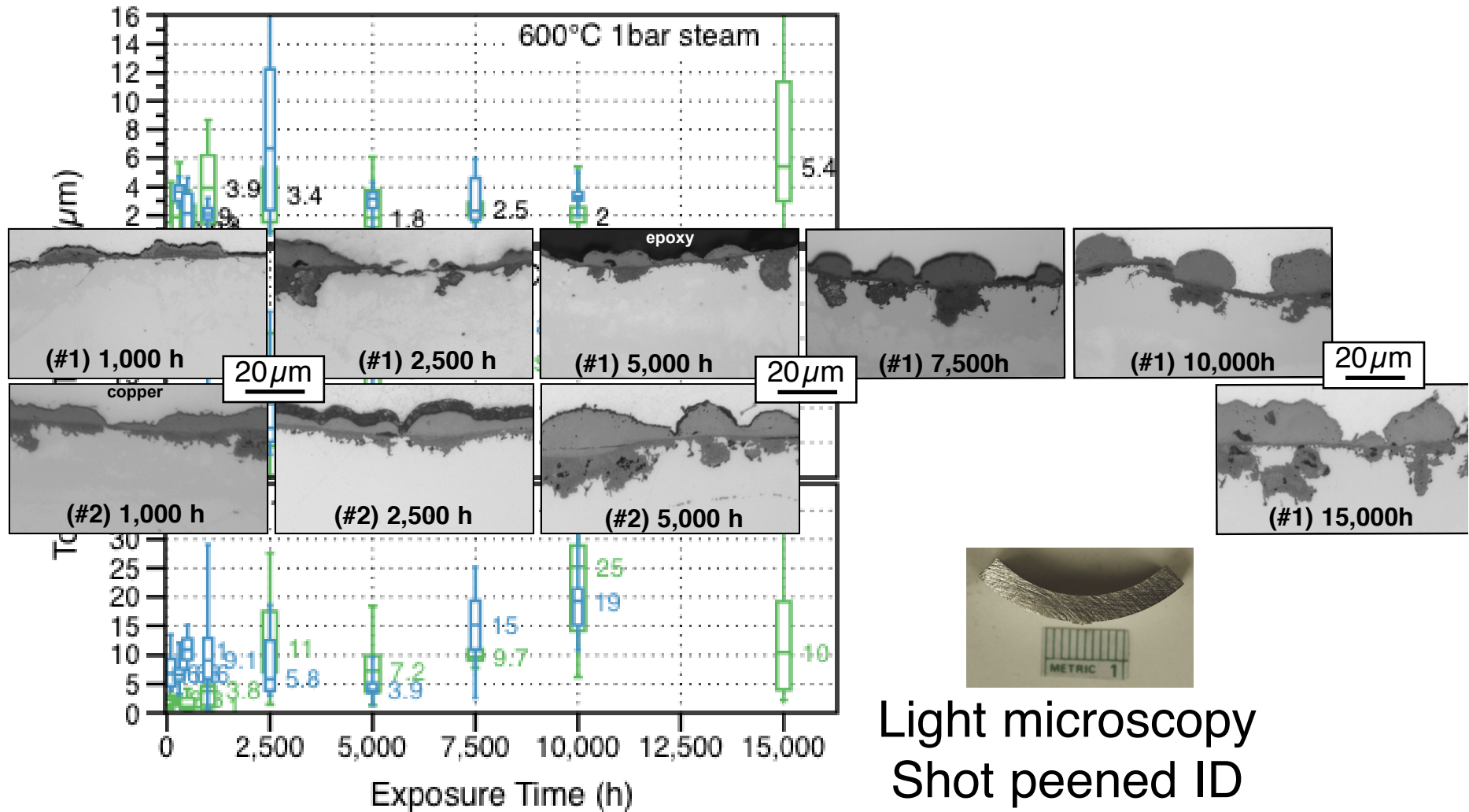
- thin ID oxide

- similar thin OD oxide



Losing peening benefit at 650°C

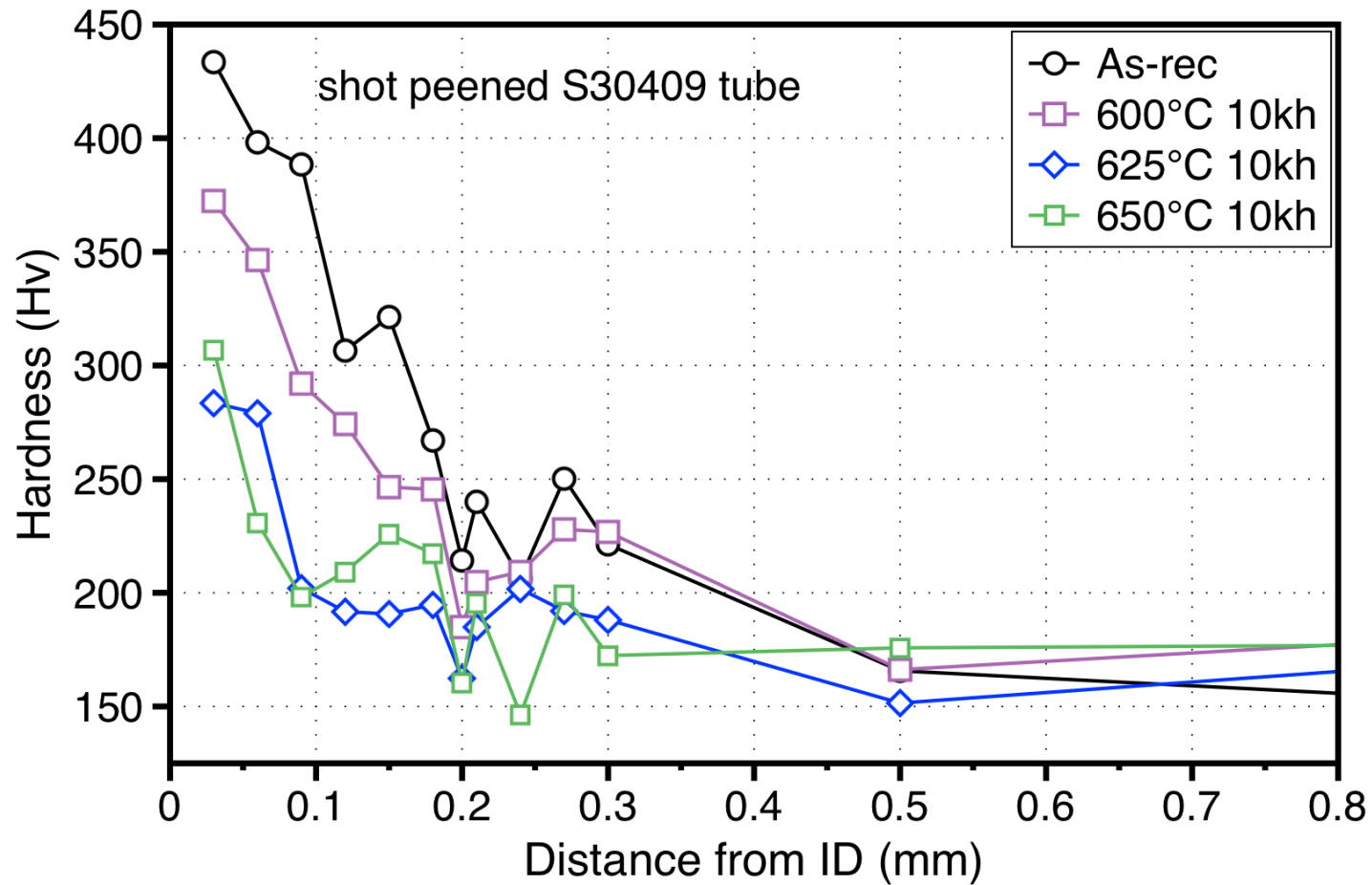
650°C 1bar steam; 500-h cycles



Each: 0.5, 1, 2.5, 5, 7.5, 10, 15 kh specimens

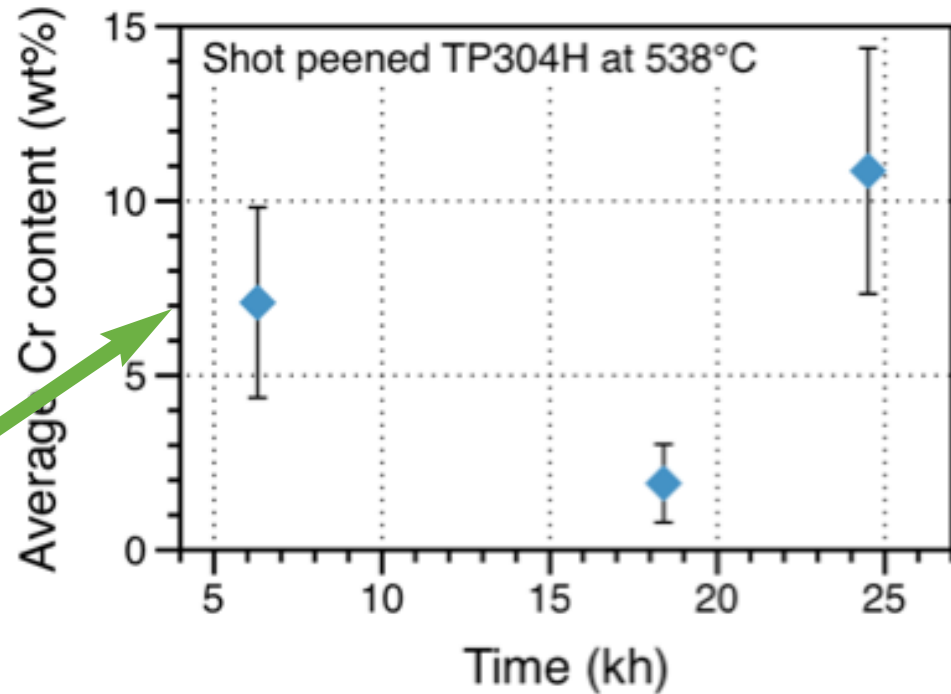
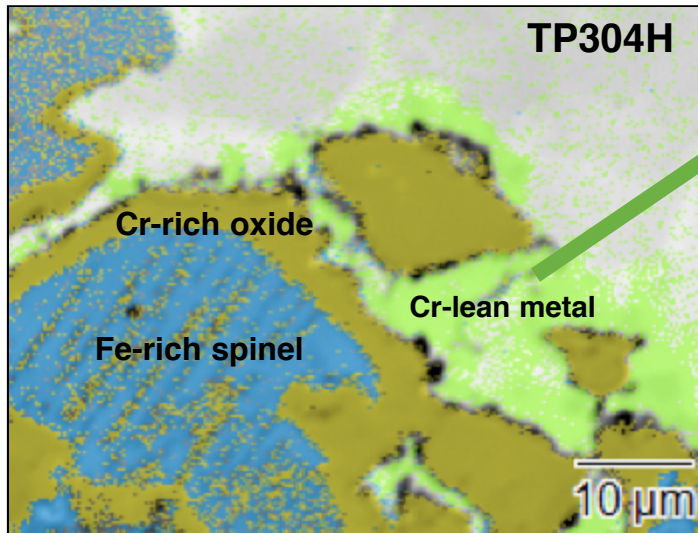
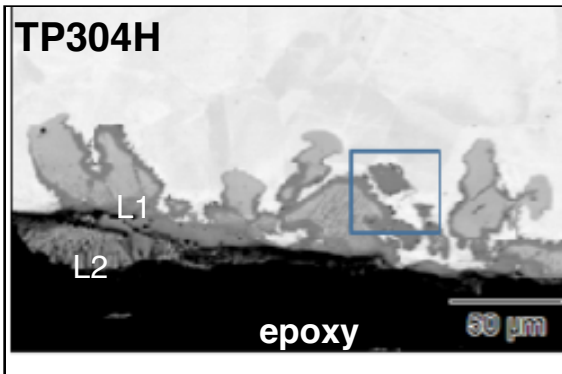
Hardness changed with exposure

Measurements on 10,000 h specimens



Field (EPRI): high Cr depletion beneath scale

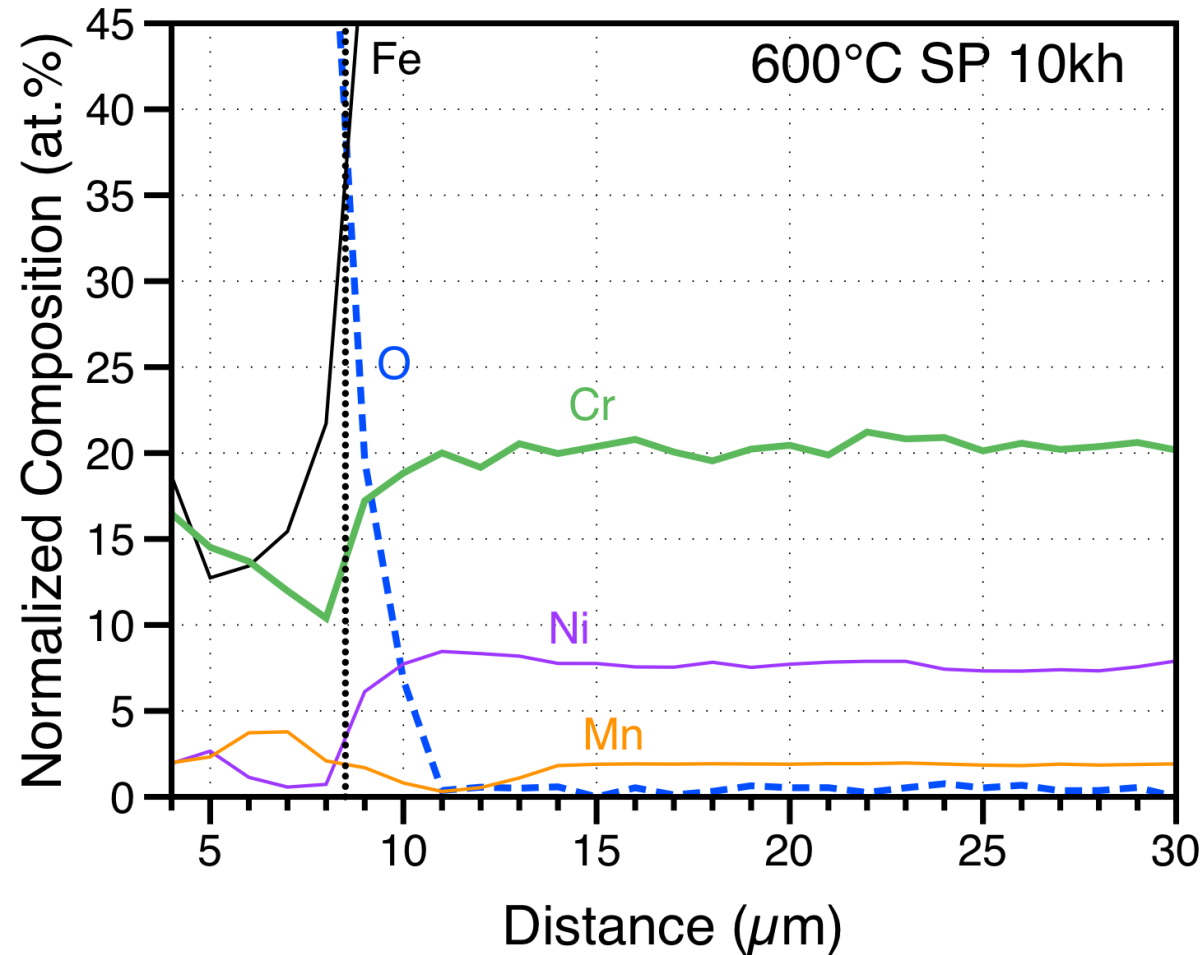
Shot peened TP304H: up to 24,500 h, 538°C steam



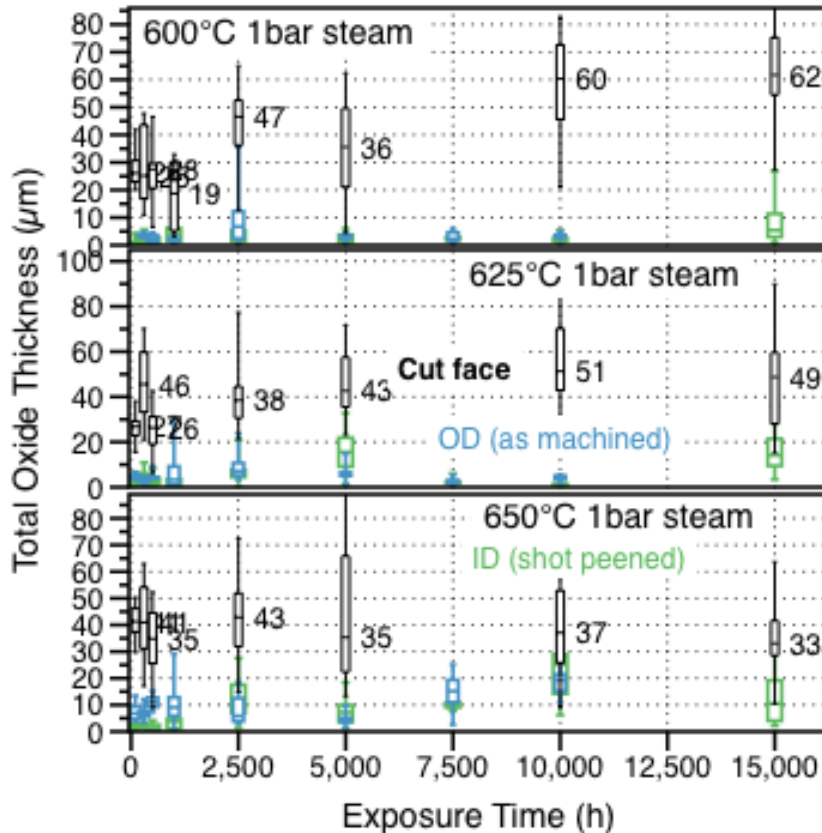
Models: 10-15%Cr is susceptible to form FeO_x
Higher Cr depletion here: unstable situation
- any disruption in Cr-rich oxide likely to grow nodule

Minimal depletion in lab specimens

EPMA line profile after 10,000 h at 600°C



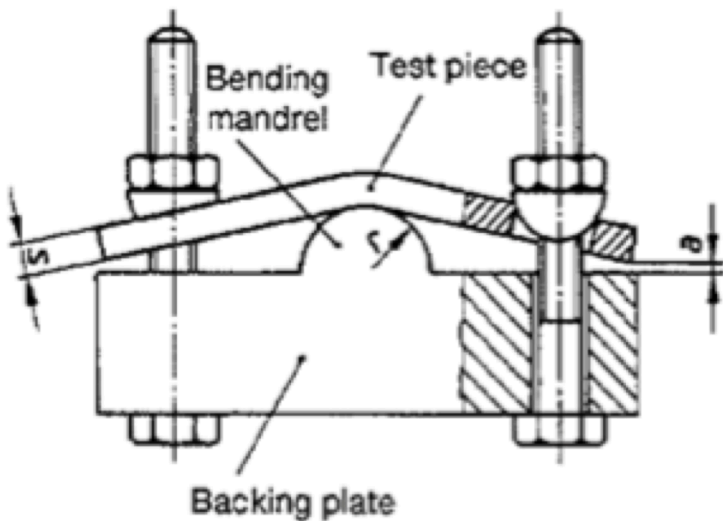
Wrapping up Task 1



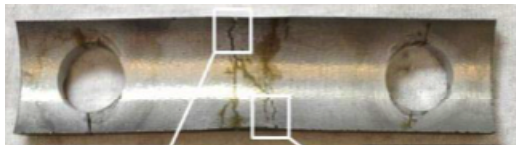
- Second SP tube specimen running to 10,000 h
- Alloy coupon specimens running to 10,000 h
- **More characterization**
 - complete measurements
 - improved image statistics
 - 15kh hardness check
 - 15kh Cr depletion (EPMA)
 - EBS

Task 2: stress corrosion cracking

- 2.25%Cr waterwall steels: Grades 22,23,24 high strength steels susceptible
- significant problem for new boilers
- Stress-environment interaction: 25°-300°C
- Jones test to apply stress (complicated)
- prior results in aerated and deaerated water



Jones Test



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"/>

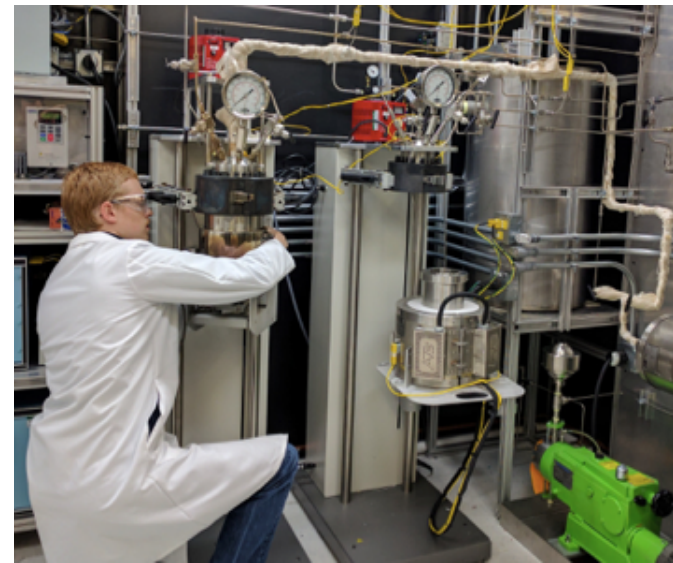
- Did Not Crack
- Cracked

Water loop: next level of testing

Simulate actual fossil environments
with controlled pH and pO_2 levels



water control system
- based on GE systems



200°C autoclave

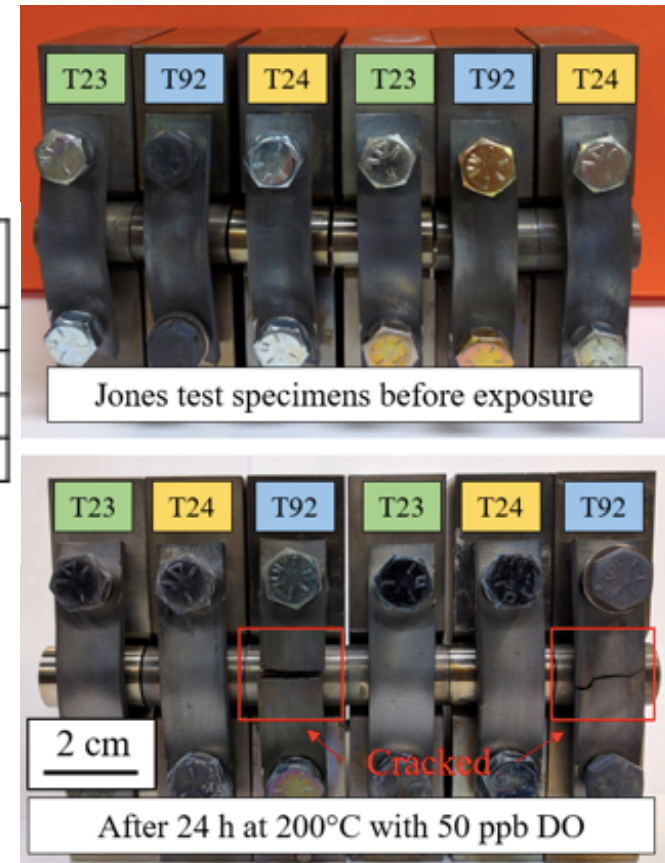
O content affected cracking

1st Jones tests with controlled water chemistry at ORNL

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
T92	O	X	X	X

O: Uncracked X: Cracked

200°C, untempered steels
Normalized (0.5h, 1065°C WQ)



Earlier work concluded no need to run 72-168h
100ppb O 24h test conducted first
Reduced O to 50ppb for second experiment

Next steps

SCC = microstructure + stress + environment

In-situ crack growth monitoring (FY17)

exploring electrochemical methods

incrementally change water chemistry

determine when crack begins in Jones test

Controlled stress experiments (tensile tests)

(GE downsizing their laboratory)

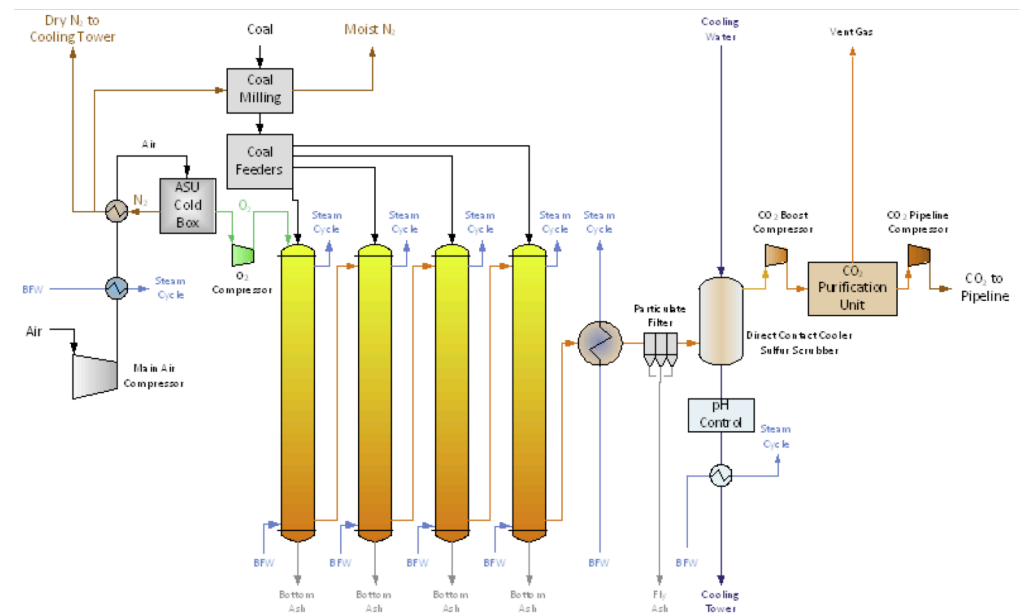
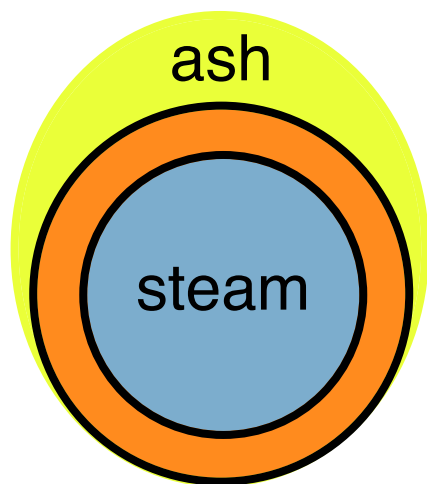
Change crack growth rate with chemistry

Are there critical temperature and hardness values for susceptibility?

Are there solutions for Grades 23 and 24?

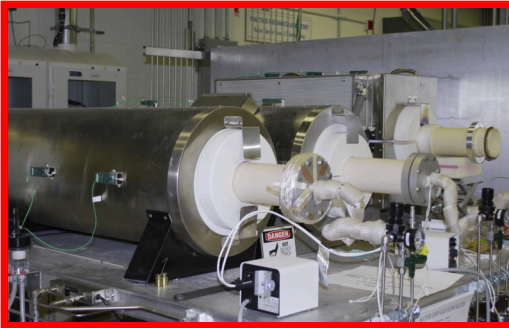
Task 3: effect of pressure

- Steamside
 - steam oxidation field-lab disconnect
 - field (high pressure) \neq lab (typically 1 bar)
 - need uniform test procedure to study
- Fireside (future topic)
 - for Staged-Pressurized Oxy-Combustion (SPOC)
 - previous work with Washington Univ. (St. Louis)
 - R. Axelbaum and B. Kumfer



Specimens exposed in laboratory

ORNL has several options



1 bar steam (tube test)

Atomized deionized water (no carrier gas)

H₂O: ~0.065 μS/cm, filtered, deaerated

Temperature: 550°-650°C

Time: 500 h cycles

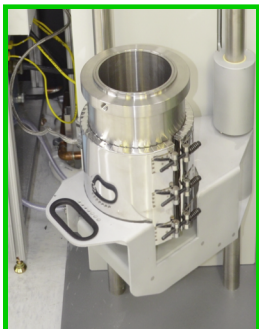


1-30 bar steam testing (Keiser rig)

H₂O: ~0.065 μS/cm, filtered, deaerated, deionized

Temperature: 550°-900°C

Time: 500 h cycles



≤ 275 bar steam testing (in 2017)

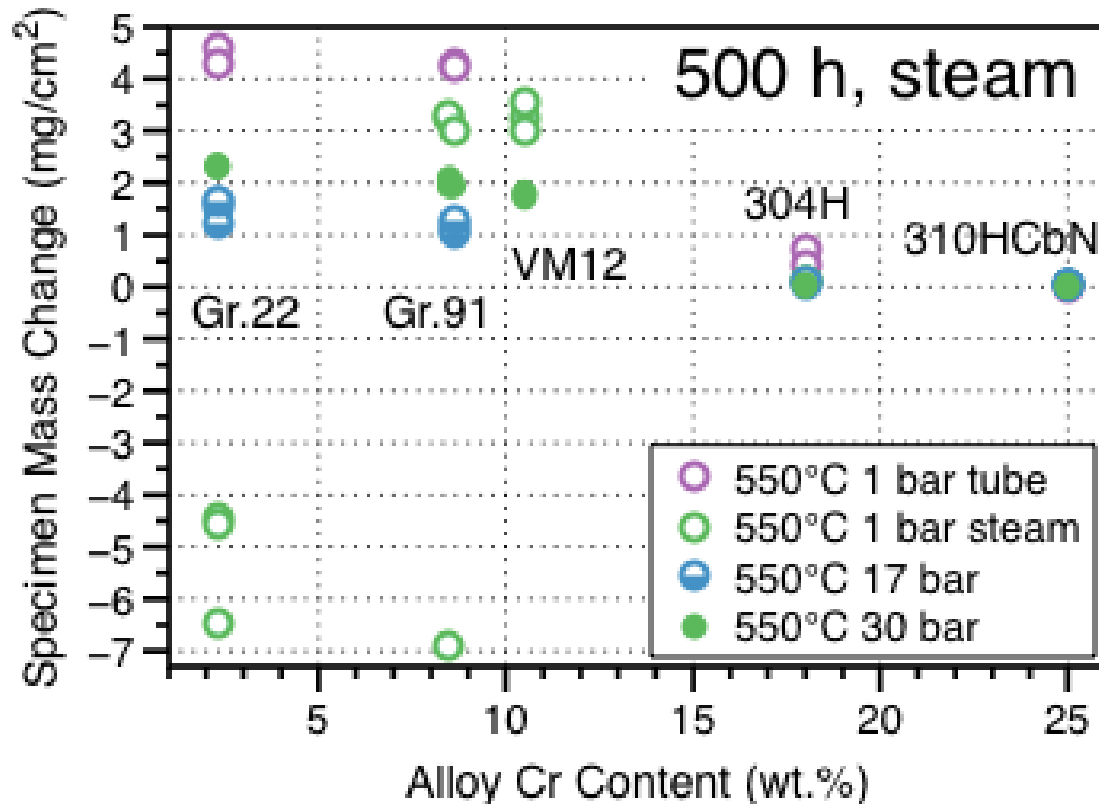
Controlled water chemistry loop

Temperature: 450°-650°C

Time: 500 h cycles

Initial results in 550°C steam

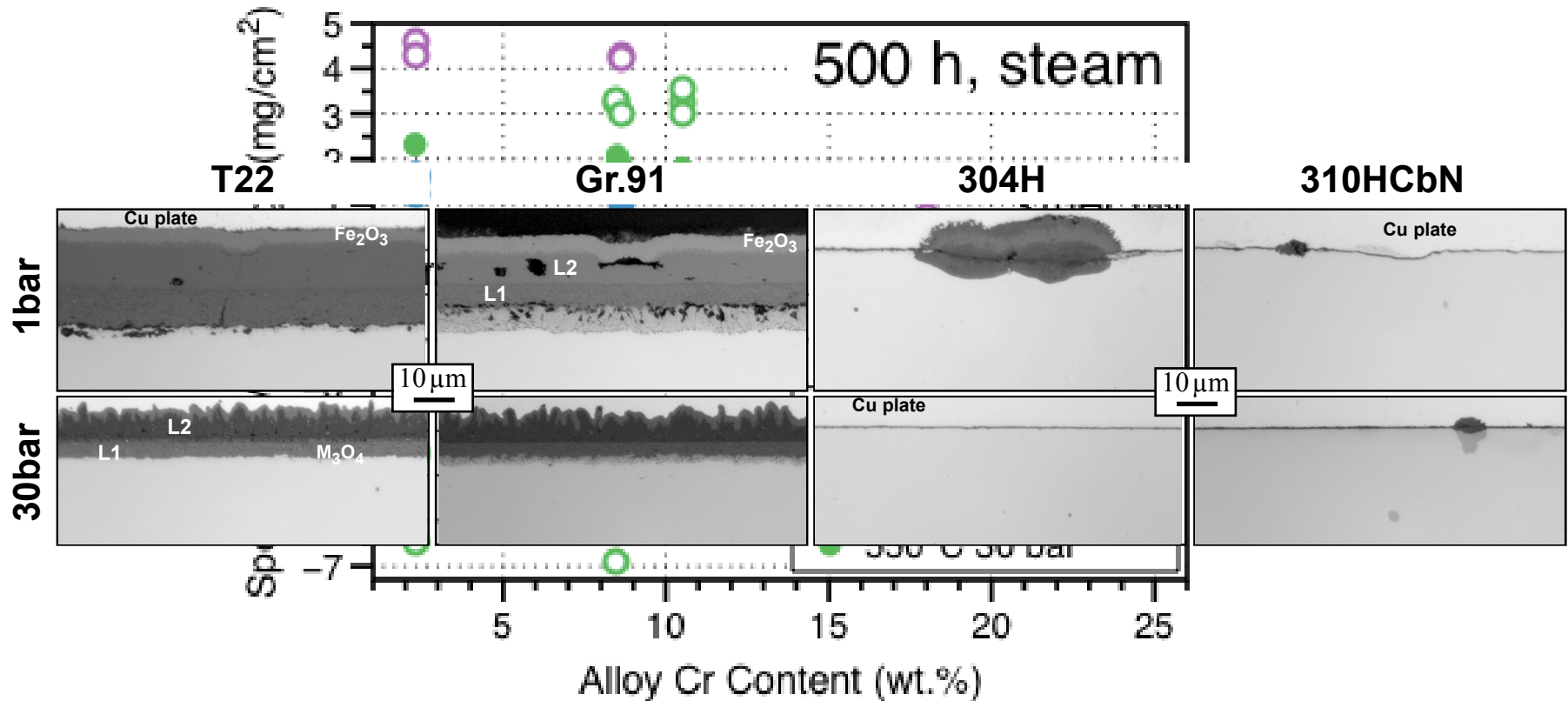
500 h exposures: Tube vs. Keiser rig



- 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 (?)

Initial results in 550°C steam

500 h exposures: Tube vs. Keiser rig

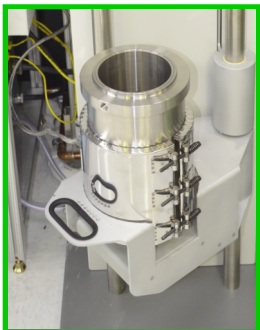


- 1 bar steam in tube: higher mass than Keiser rig
- 1 bar Keiser rig - scale spallation for T22
- 17 bar less mass gain than 30 bar (?)

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

Initial investigation of water chemistry effect

1st EPRI experiment (2017)
- compare oxygenated water to all-volatile treatment (10 vs. 150 ppb O, plus pH control)



≤ 275 bar steam testing

Controlled water chemistry loop

Temperature: 450°-650°C

Time: 500 h cycles



Summary

Corrosion task addressing several issues

1. Quantify shot-peening benefit on 304H
 - completed 15 kh specimens
2. SCC issue in current waterwalls
 - testing in controlled water chemistry
 - next step is in-situ monitoring
3. Effect of pressure
 - initial comparison steam, 500 h at 550°C
 - next work: steam, 650°C

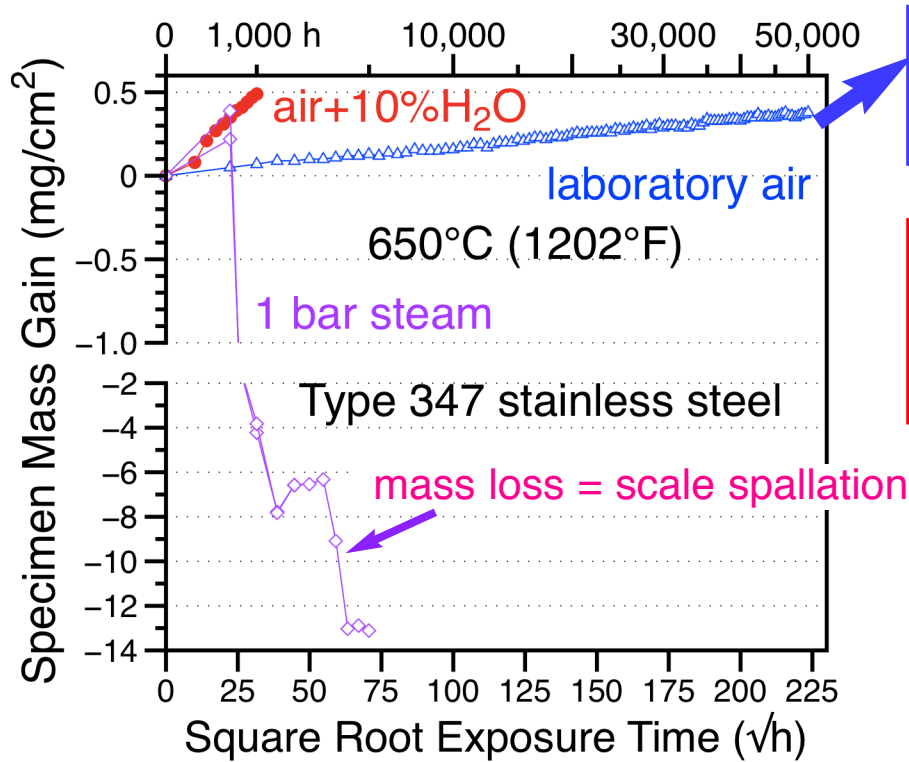
Task 1 is finishing in 2017, Task 3 expanding
Seeking industry feedback on Task 2

CLEAN COAL.
COOL.



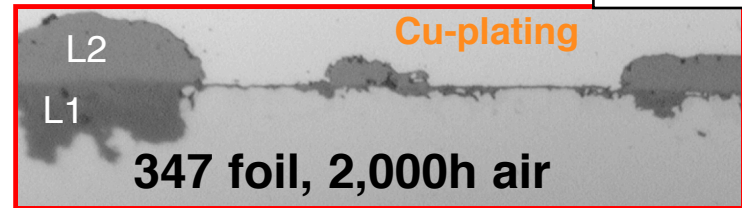
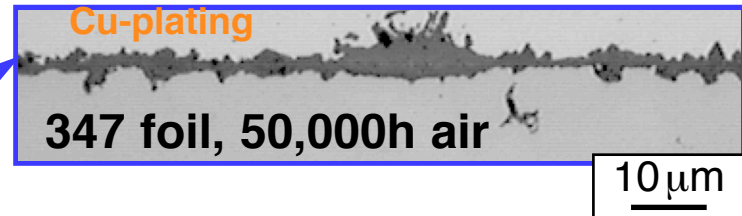
H₂O drives steels crazy

Steam or exhaust gas accelerate oxidation

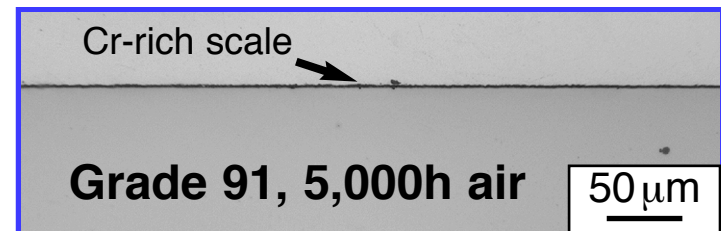
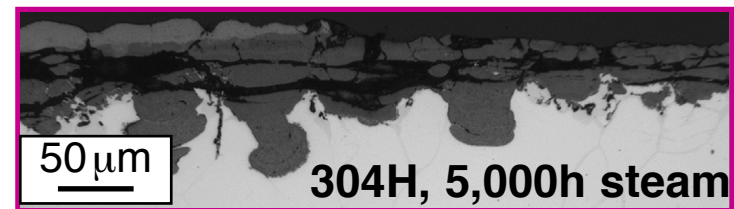


650°C, 1202°F

91: Fe-9Cr-1Mo



347: Fe-18Cr-10Ni+Nb



Laboratory air - thin, Cr-rich oxide

+ H₂O - thick, Fe-rich oxide

Specimen type showed minor effects

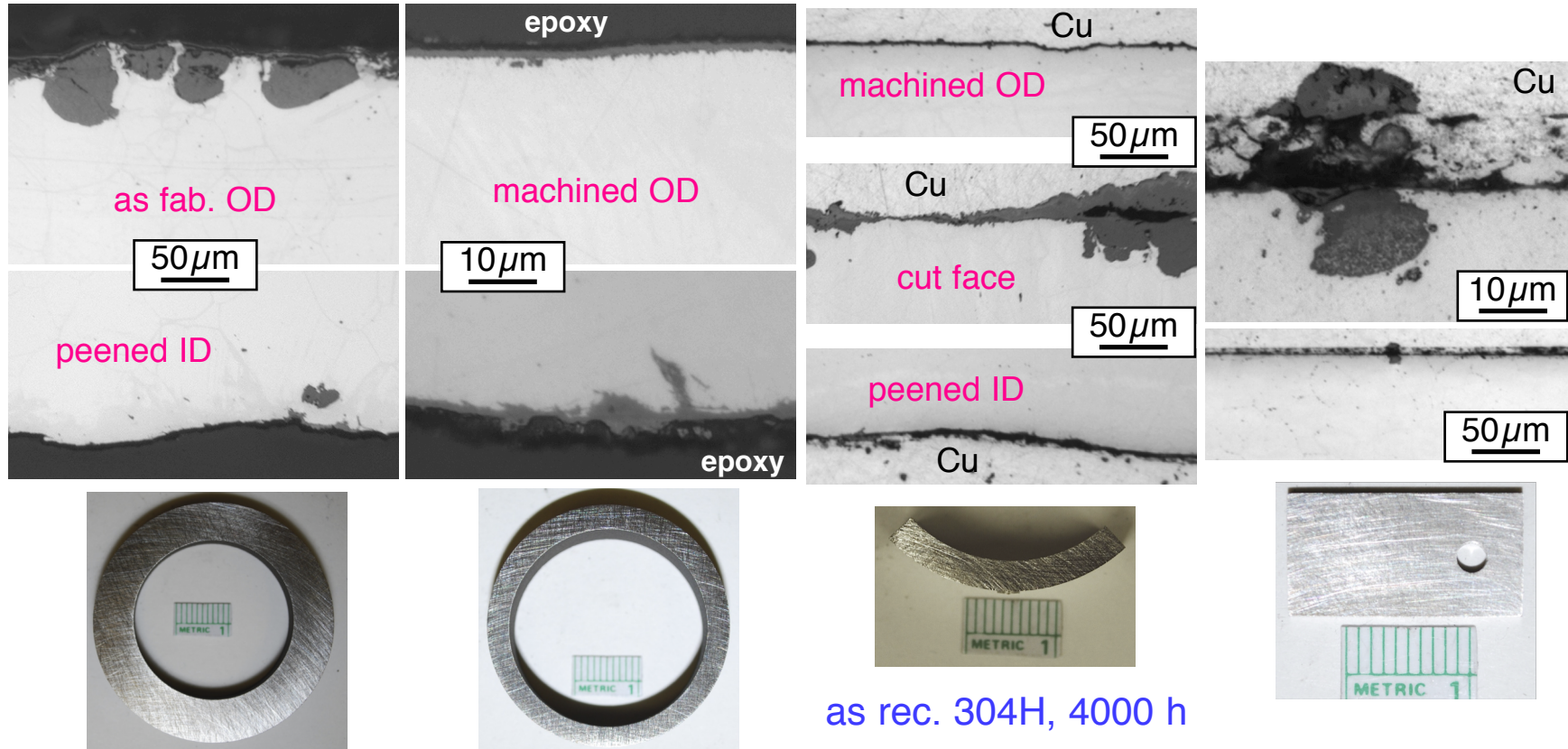
peened 304H 650°C 17bar steam 4,000h

full ring

thin ring

1/4 thin ring

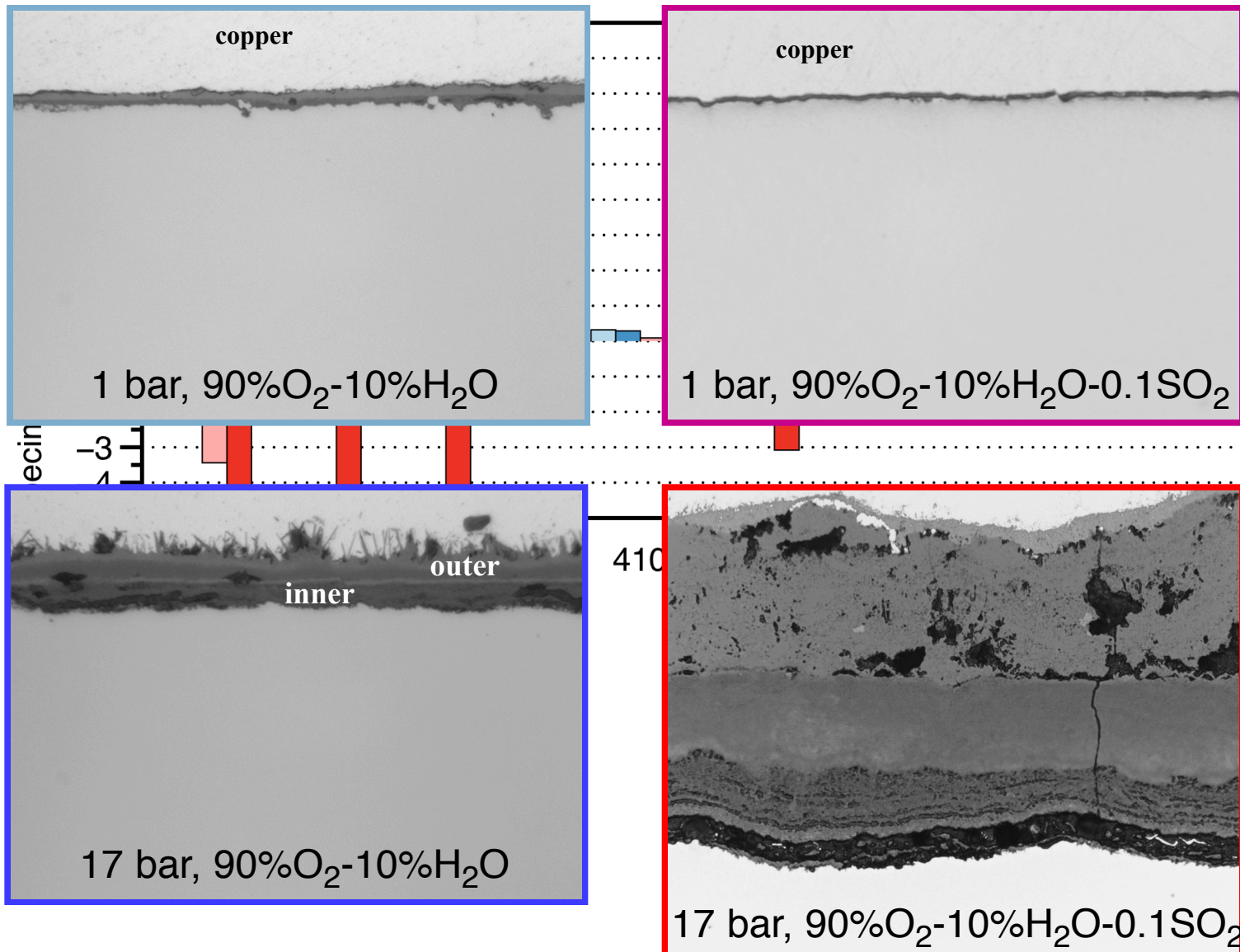
coupon



Peened ID: no effect of specimen geometry
 OD difference: as-received vs. machined (thin ring)
 - cold work due to machining similar to peen-

Initial ORNL study of pressure

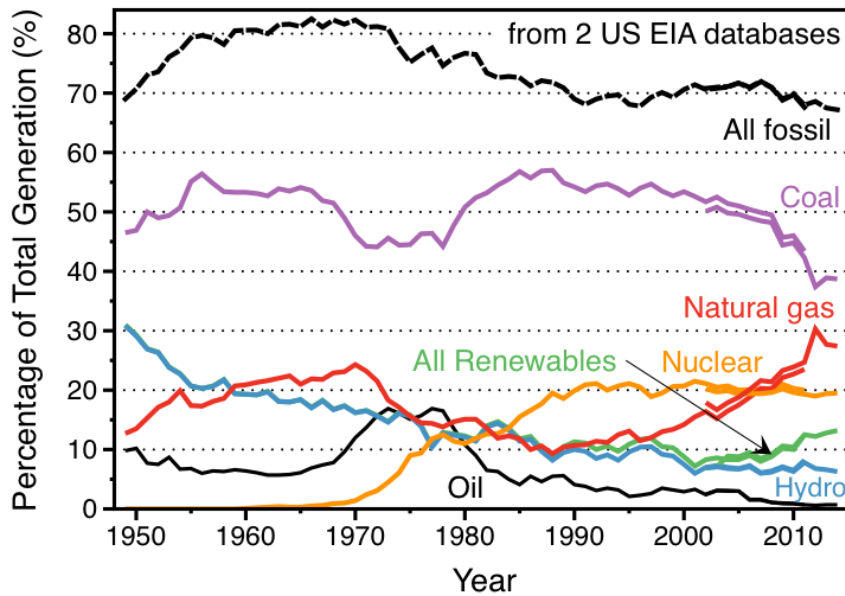
VM12: ~11Cr-1.5Co-1.5W steel



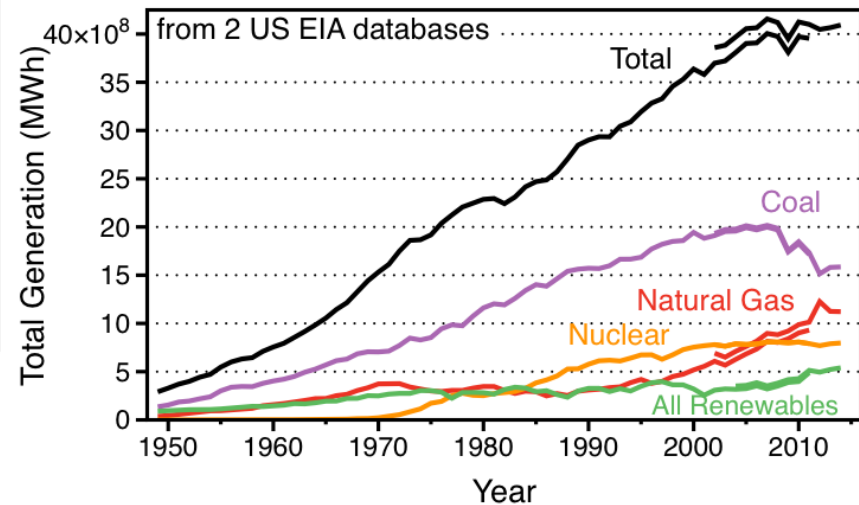
Fossil energy continues to dominate

Source mix is changing & demand is stagnant

How does US generate electricity?



How much does US use?



Prior work with EPRI

Characterizing field exposed shot-peened tubes

