

# Corrosion Issues in Advanced Coal-Fired Boilers (FEAA116)

B. A. Pint and S. S. Raiman

Corrosion Science & Technology Group

Materials Science and Technology Division

Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156

e-mail: [pintba@ornl.gov](mailto:pintba@ornl.gov)

Project performance period: FY15-FY19

Research sponsored by DOE, Office of Fossil Energy  
Crosscutting Research Program (V. Cedro, project manager)

Presentation for 2017 Crosscutting Research Project Review Meeting  
March 23, 2017

# Acknowledgments

## ORNL

G. Garner, T. Lowe, M. Stephens, M. Howell,  
Z. Burns - oxidation experiments

T. Jordan - metallography, hardness

T. Lowe - SEM, image analysis

D. Leonard - EPMA

S. Shipilov, A. Willoughby, P. Doyle - water loop

## Special thanks for shot peening task:

American Electric Power

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

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

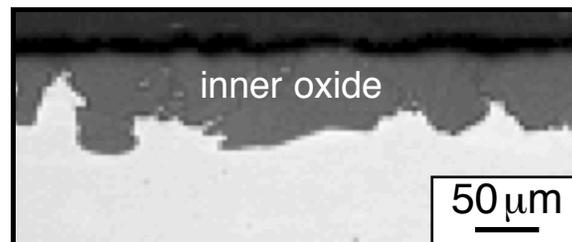
H<sub>2</sub>O-accelerated oxidation of steels (steam-side)

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)

H<sub>2</sub>O: ~0.065 μS/cm, filtered, deaerated

Temperature: 550°-650°C

Time: 500 h cycles



## 1-30 bar steam testing

H<sub>2</sub>O: ~0.065 μS/cm, filtered, deaerated, deionized

Temperature: 550°-900°C

Time: 500 h cycles



## ≤ 275 bar steam testing (in 2017)

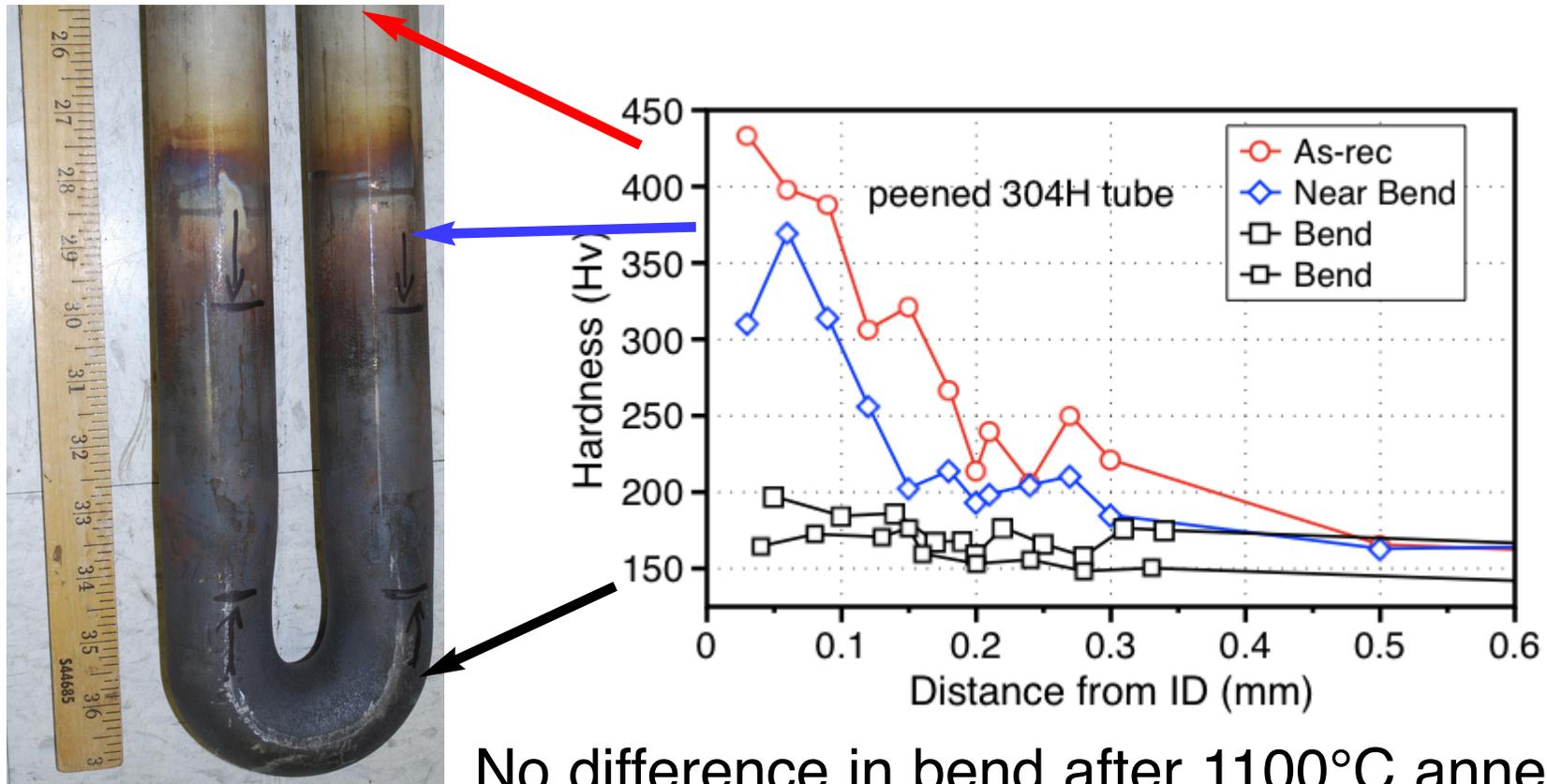
Controlled water chemistry loop

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

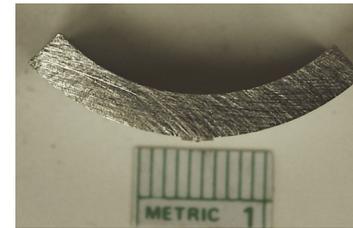
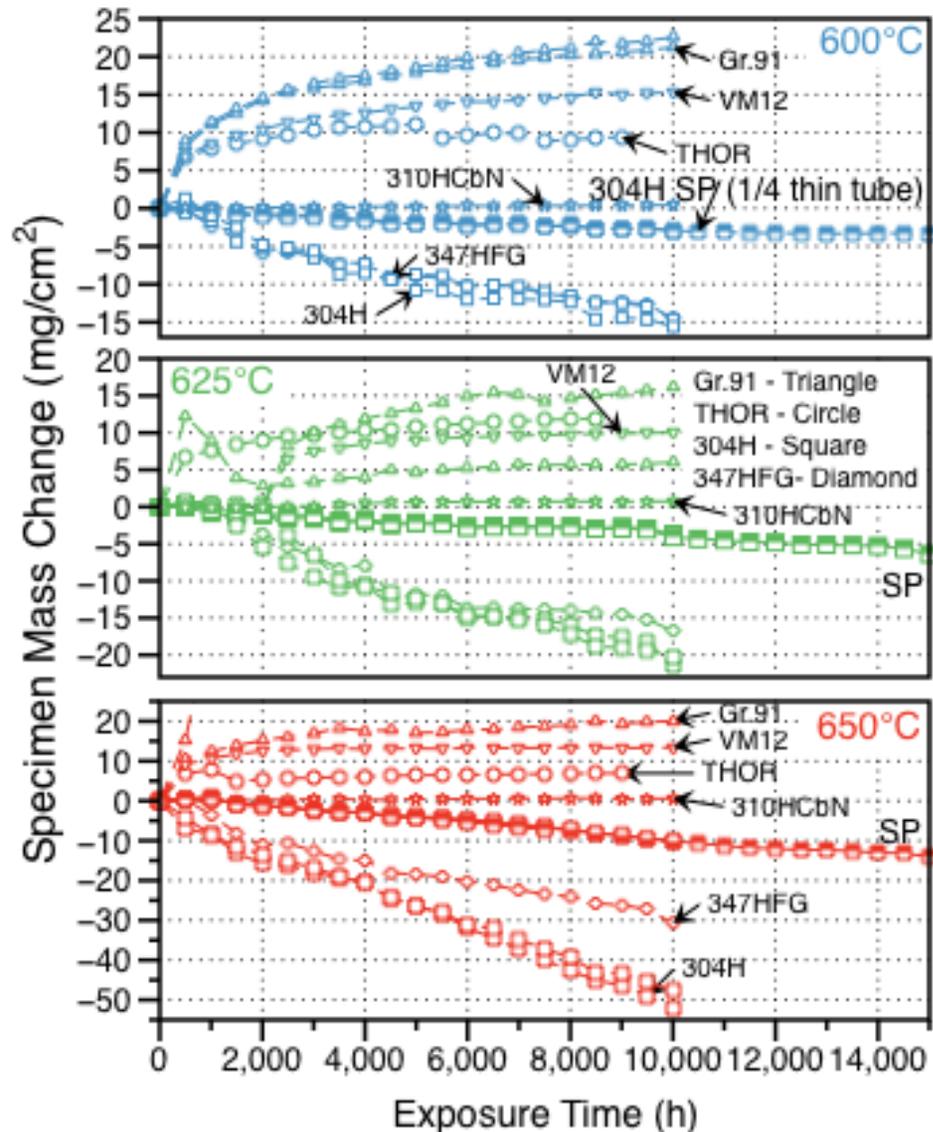
304H tube from an EPRI partner:

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

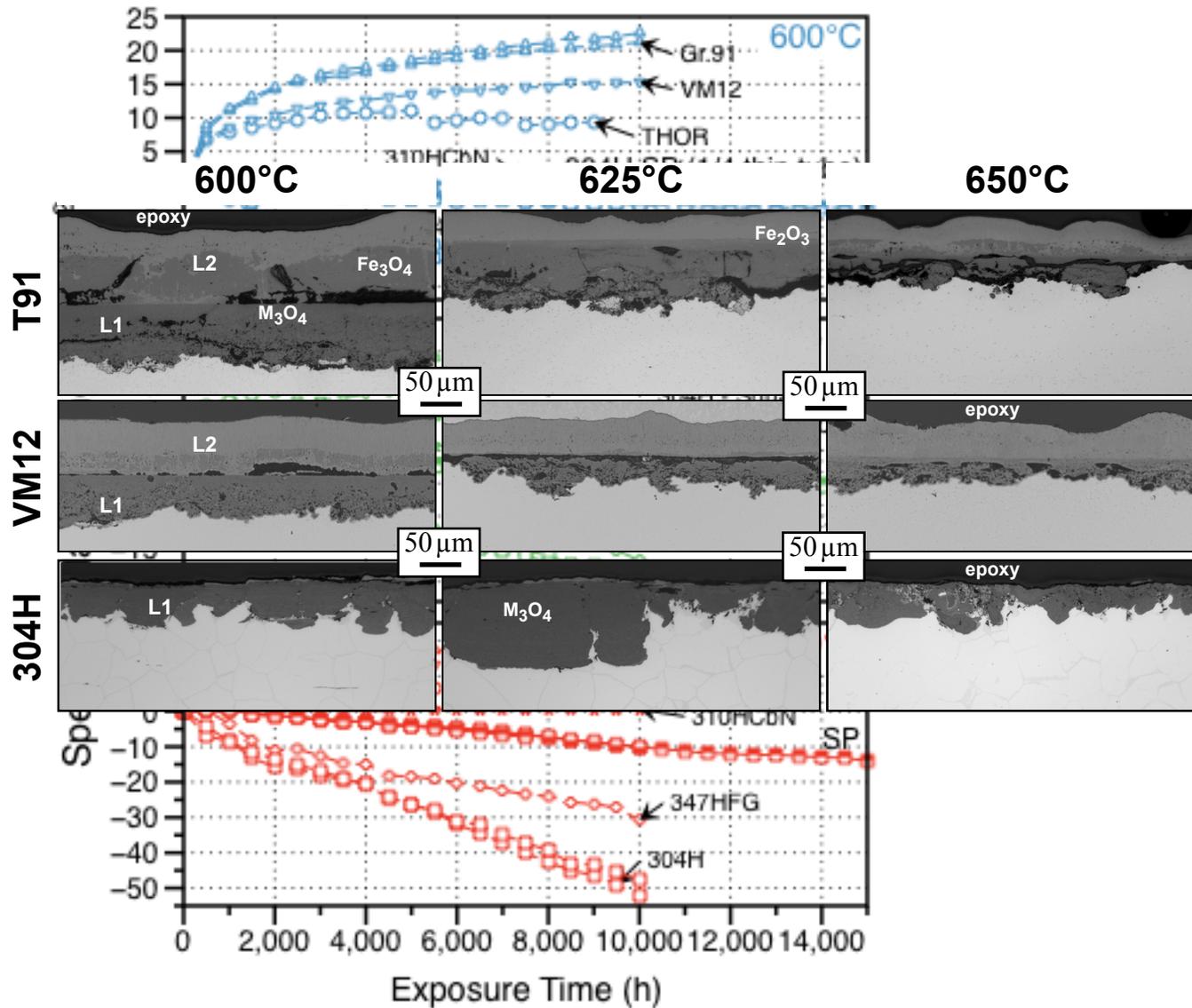


Shot peened coupons:  
tube sections  
reduced wall thickness  
Polished alloy coupons:  
comparison



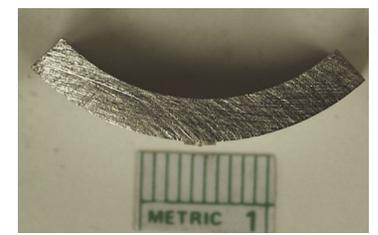
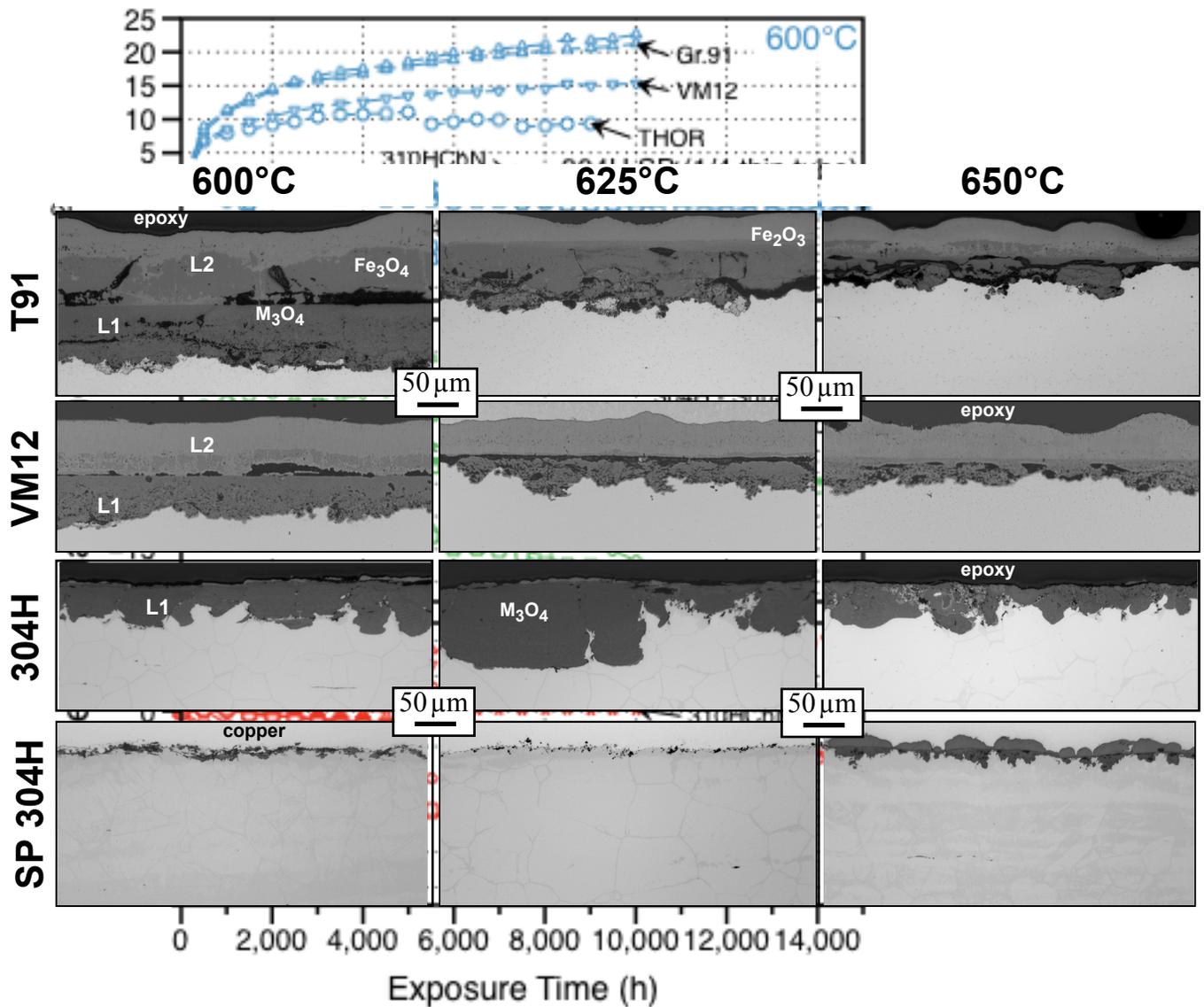
# Alloy coupons stopped at 10,000h

Alloy coupons: conventionally polished



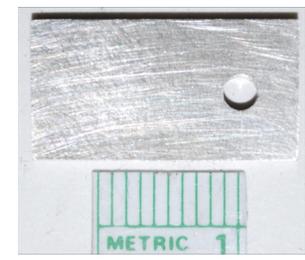
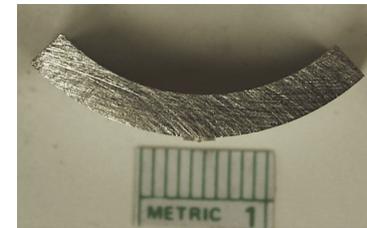
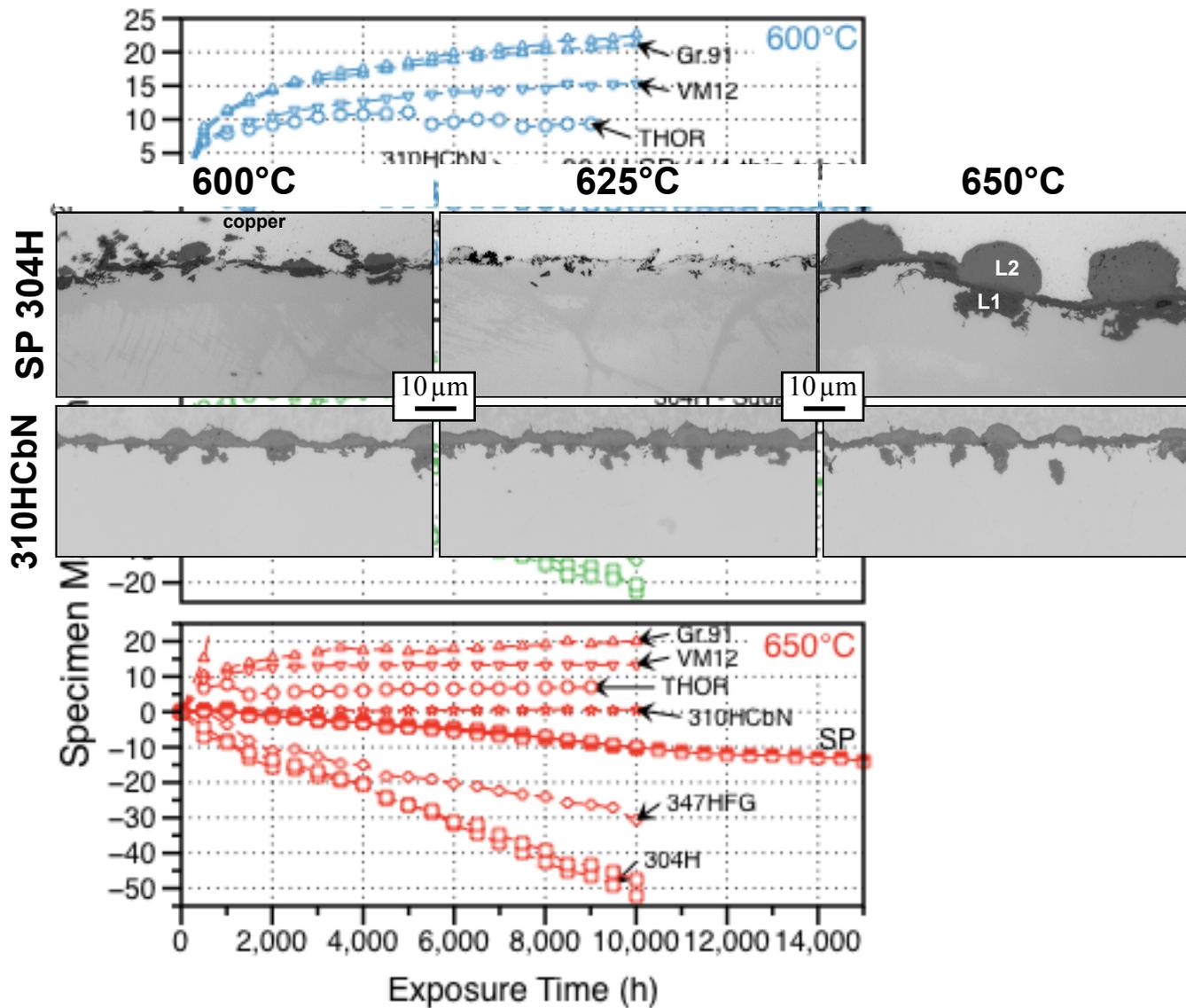
# 10,000h: Clear shot peening benefit

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



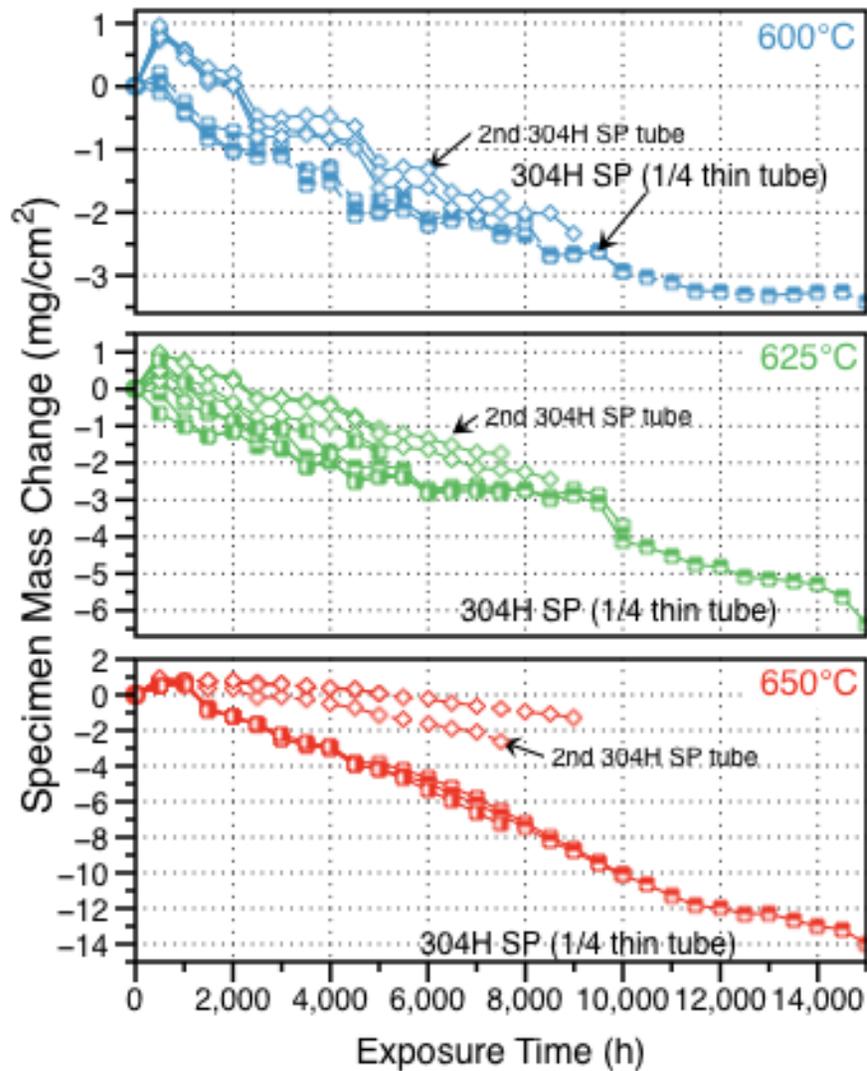
# 10,000h: thin scale like on 310SS

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



# Two differentiated peened tubes

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



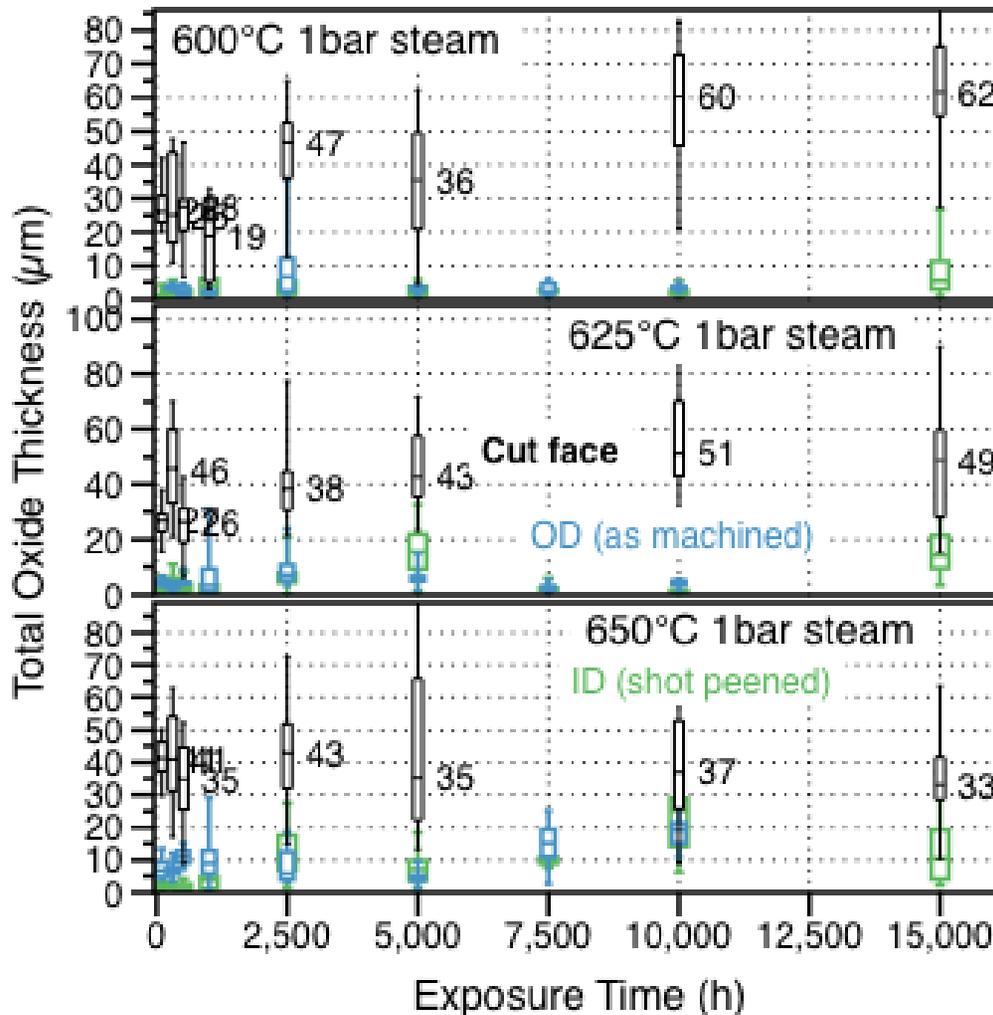
commercial shot-peened 304H

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

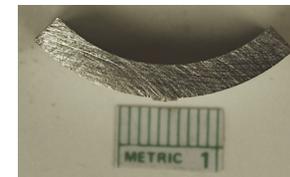
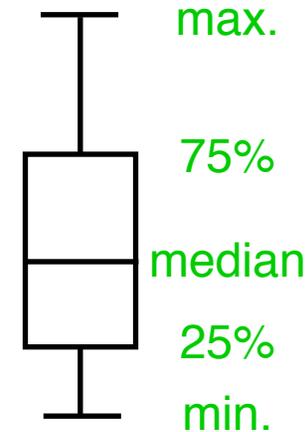
# Series of SP specimens exposed

Oxide thickness measurements from polished sections

commercial shot-peened 304H

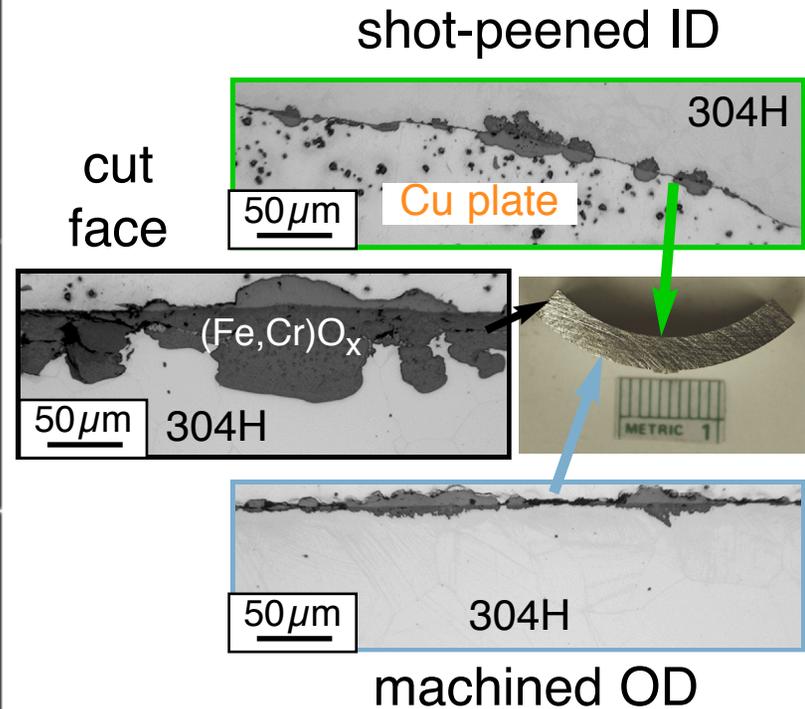
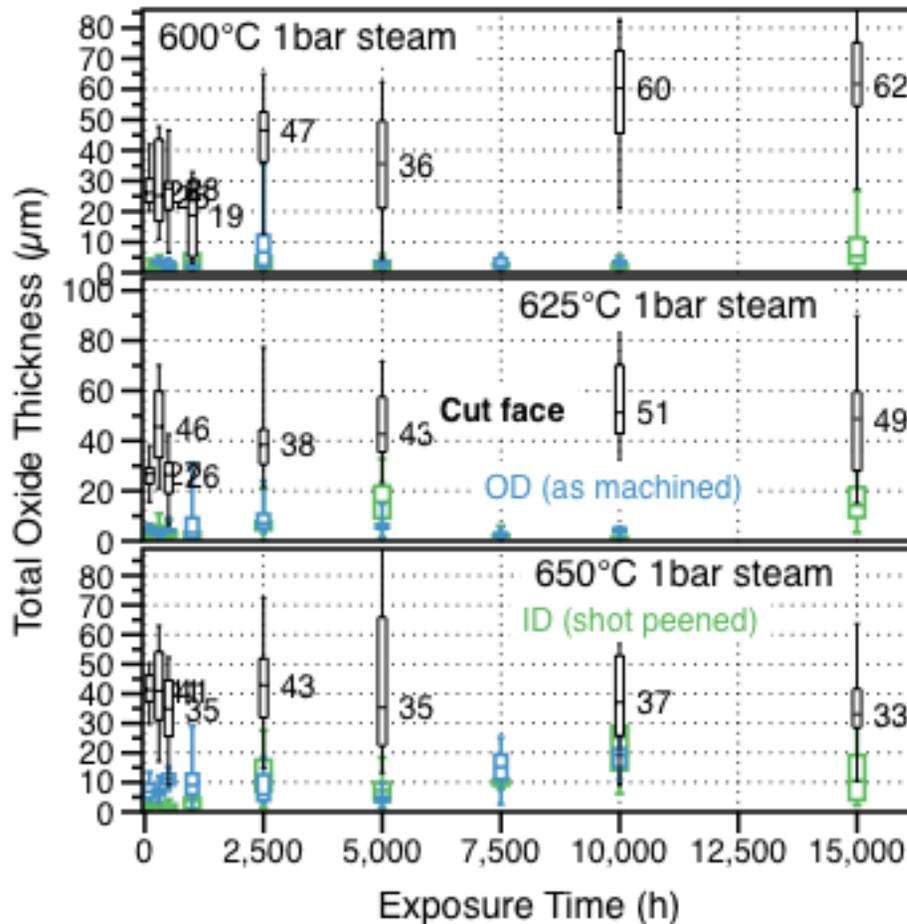


Box & whisker plot



# “Cut” face grows thick oxide

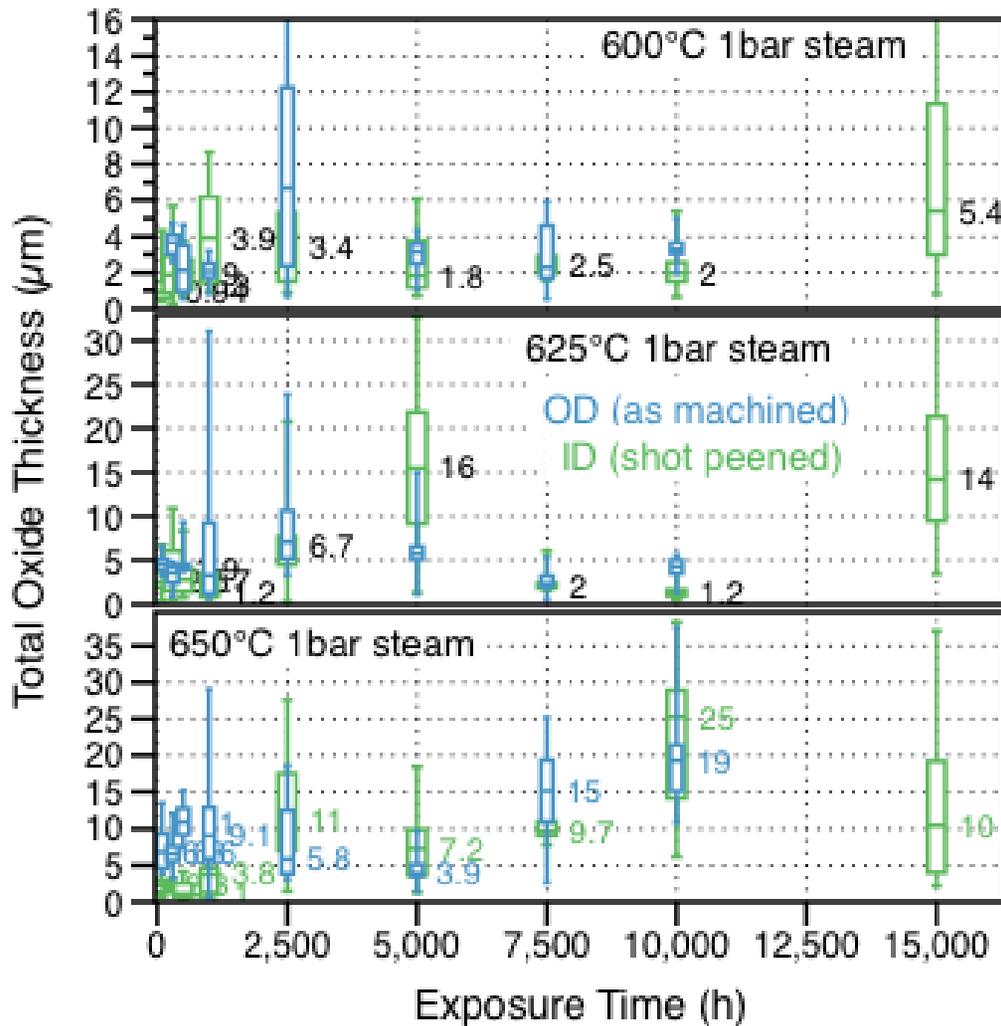
Oxide thickness measurements from polished sections



Example: 2,500h, 625°C

# Similar benefit on machined OD

Oxide thickness measurements from polished sections



600°-625°C

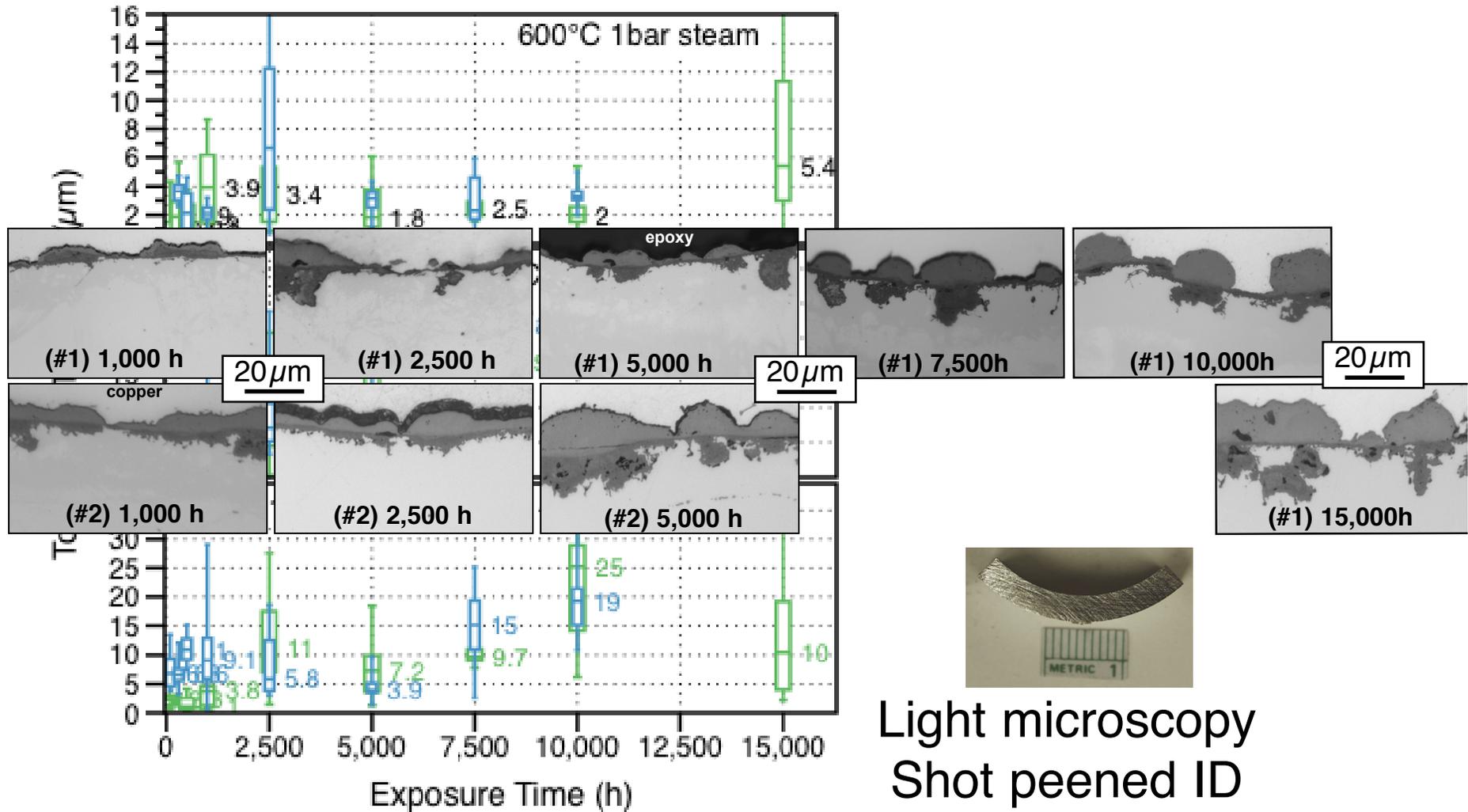
- thin ID oxide

- similar thin OD oxide



# Losing peening benefit at 650°C

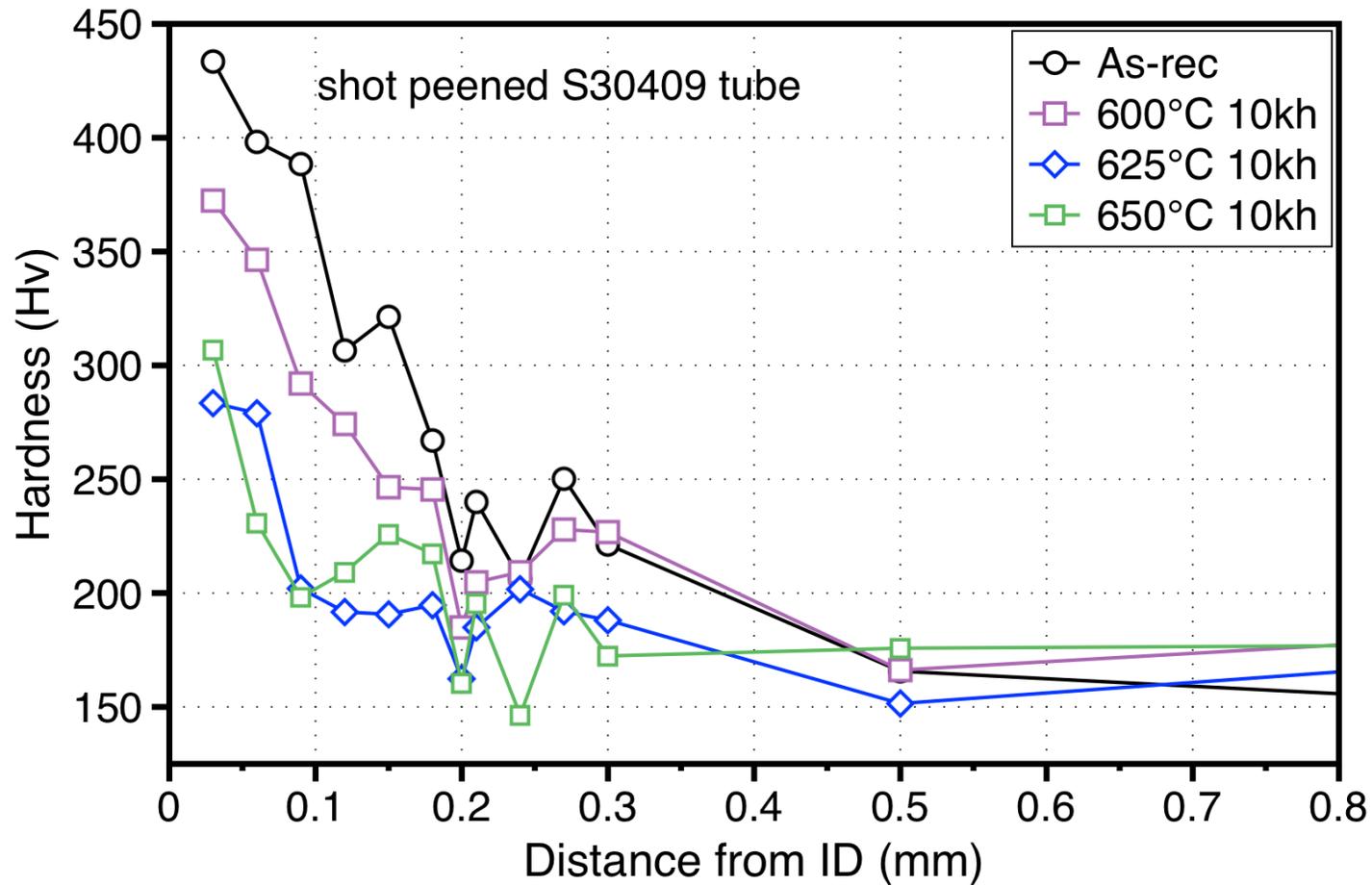
650°C 1bar steam; 500-h cycles



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

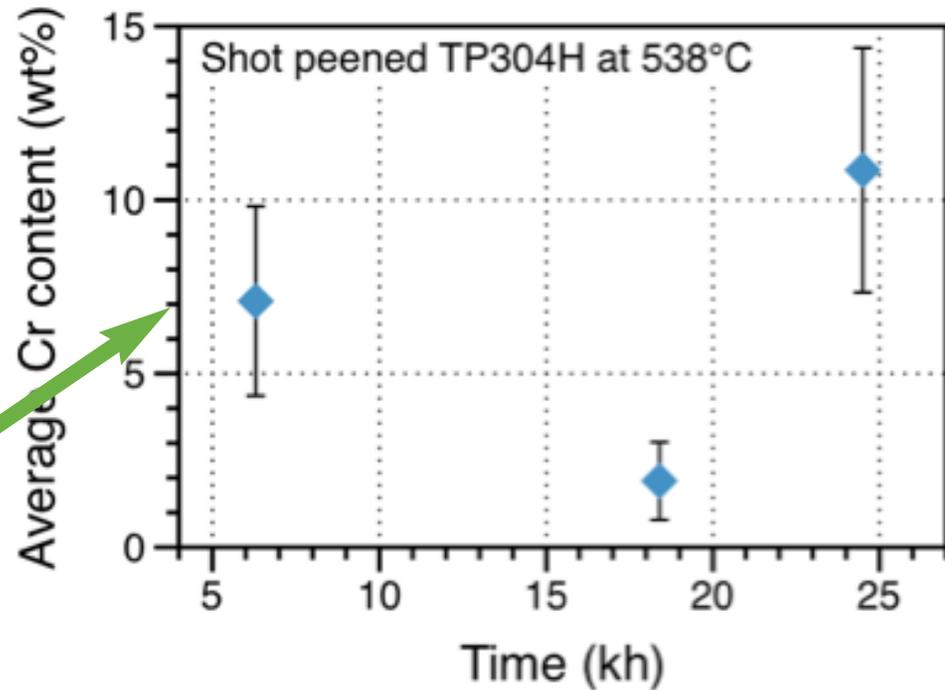
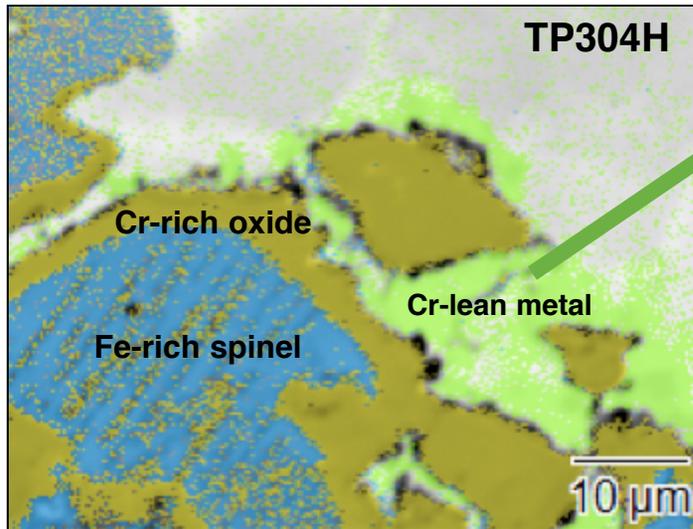
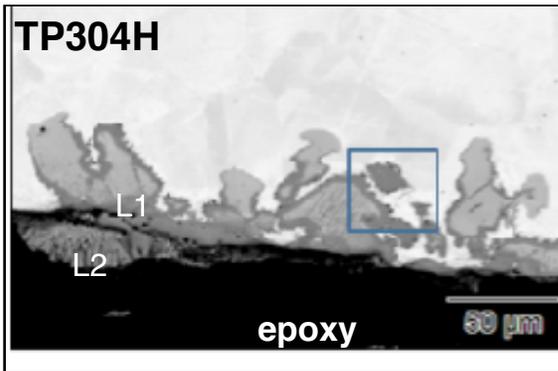
# Hardness changed with exposure

Measurements on 10,000 h specimens



# Field (EPRI): high Cr depletion beneath scale

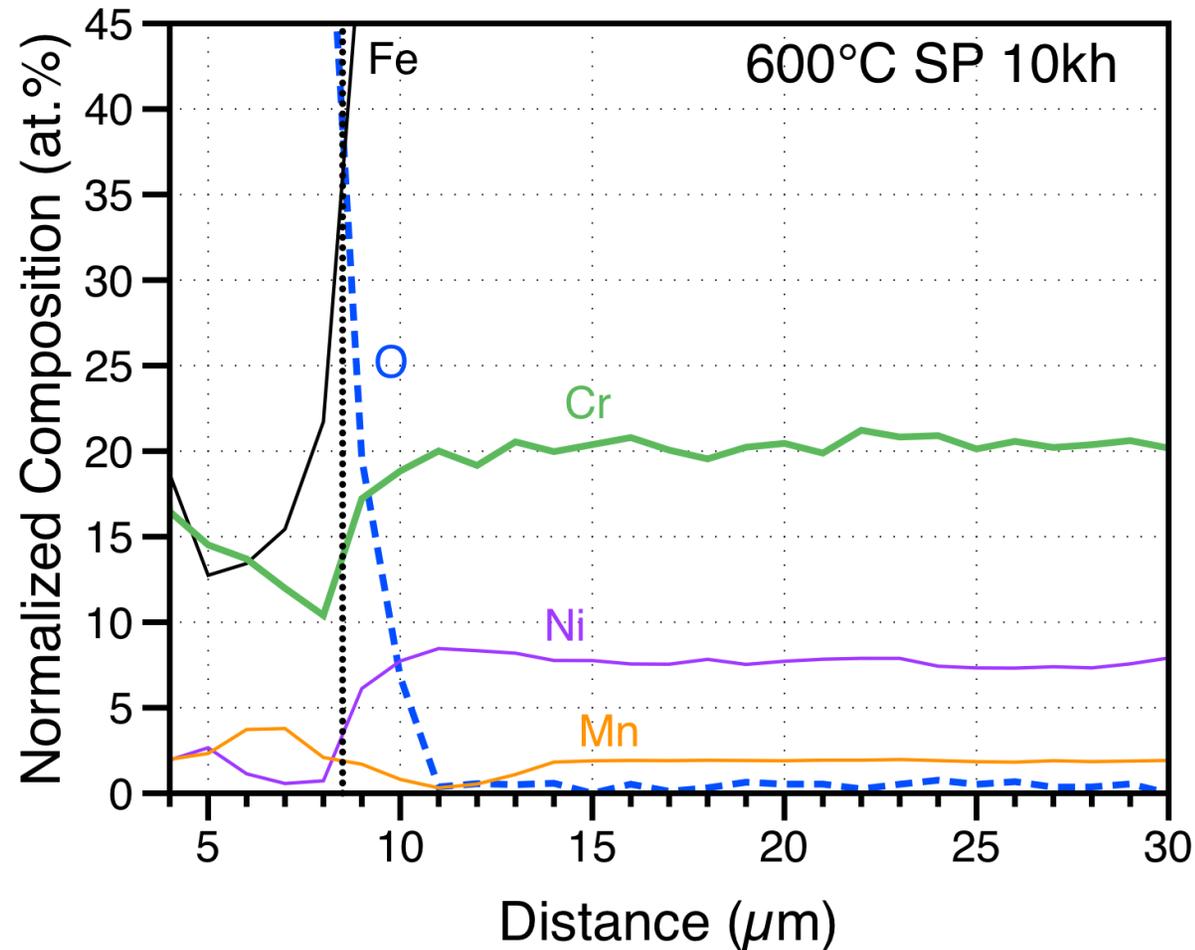
Shot peened TP304H: up to 24,500 h, 538°C steam



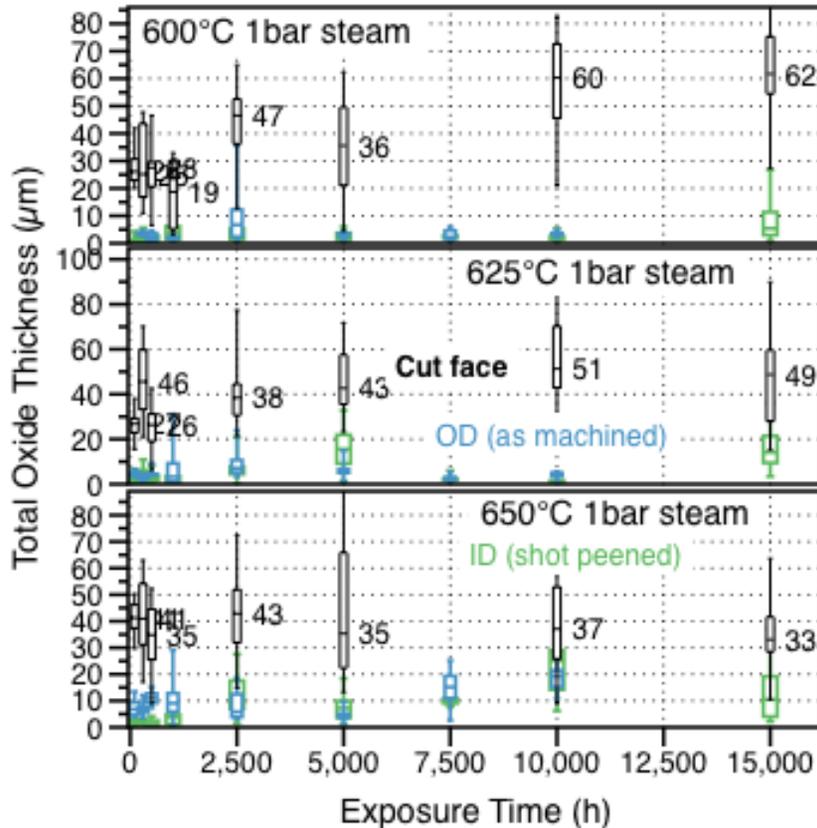
Models: 10-15%Cr is susceptible to form  $FeO_x$   
Higher Cr depletion here: unstable situation  
- any disruption in Cr-rich oxide likely to grow nodule

# Minimal depletion in lab specimens

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



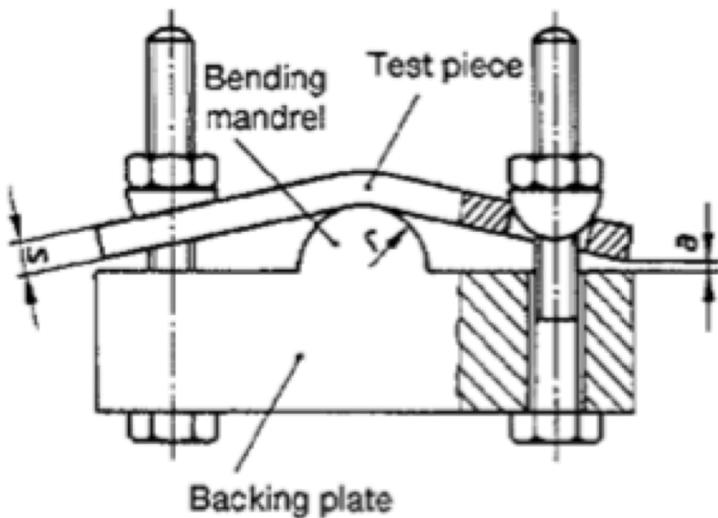
# Wrapping up Task 1



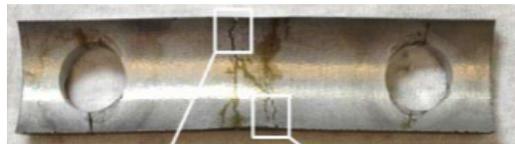
- Second SP tube specimen running to 10,000 h
- Alloy coupon specimens running to 10,000 h
- **More characterization**
  - complete measurements
  - improved image statistics
  - 15kh hardness check
  - 15kh Cr depletion (EPMA)
  - EBSD

## 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

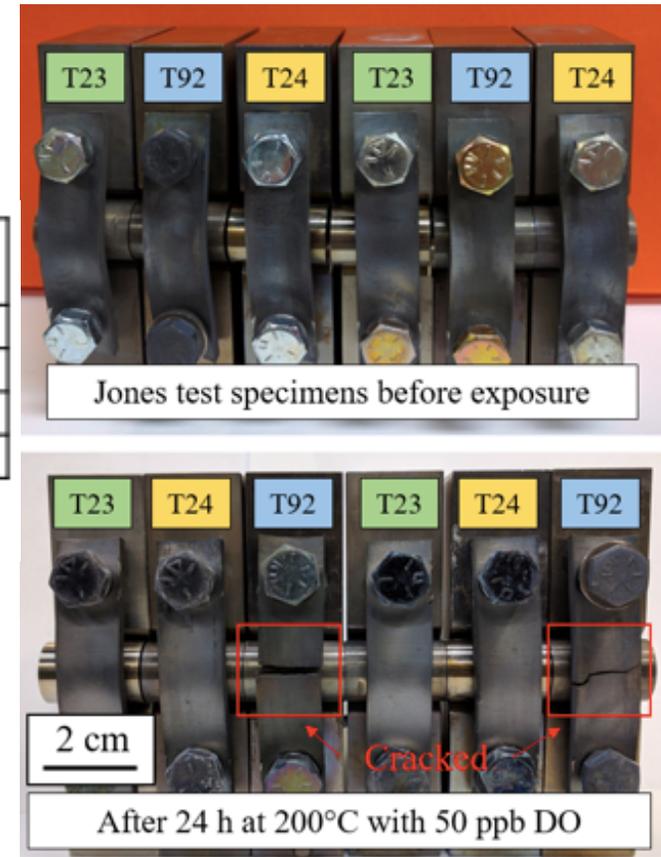
# O content affected cracking

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)

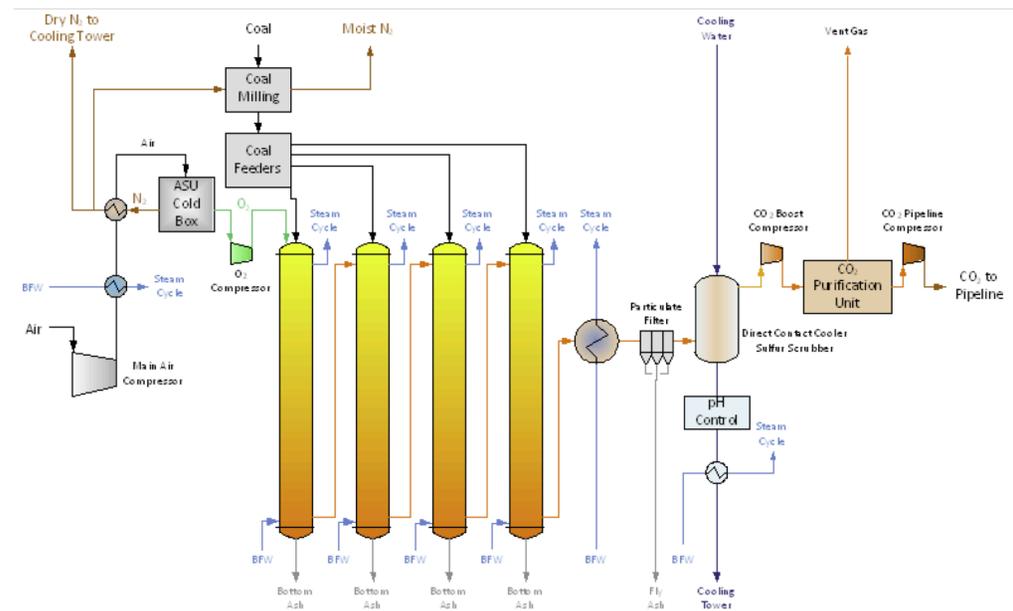
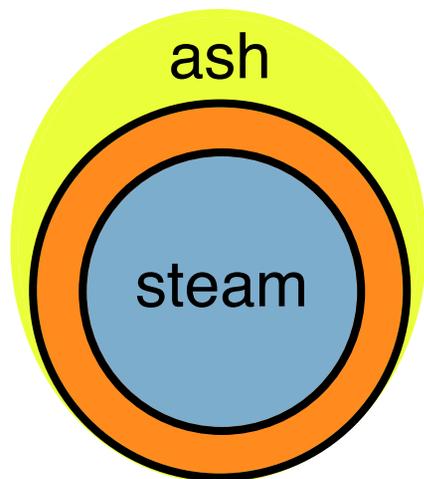
Change crack growth rate with chemistry

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)

H<sub>2</sub>O: ~0.065 μS/cm, filtered, deaerated

Temperature: 550°-650°C

Time: 500 h cycles



## 1-30 bar steam testing (Keiser rig)

H<sub>2</sub>O: ~0.065 μS/cm, filtered, deaerated, deionized

Temperature: 550°-900°C

Time: 500 h cycles



## ≤ 275 bar steam testing (in 2017)

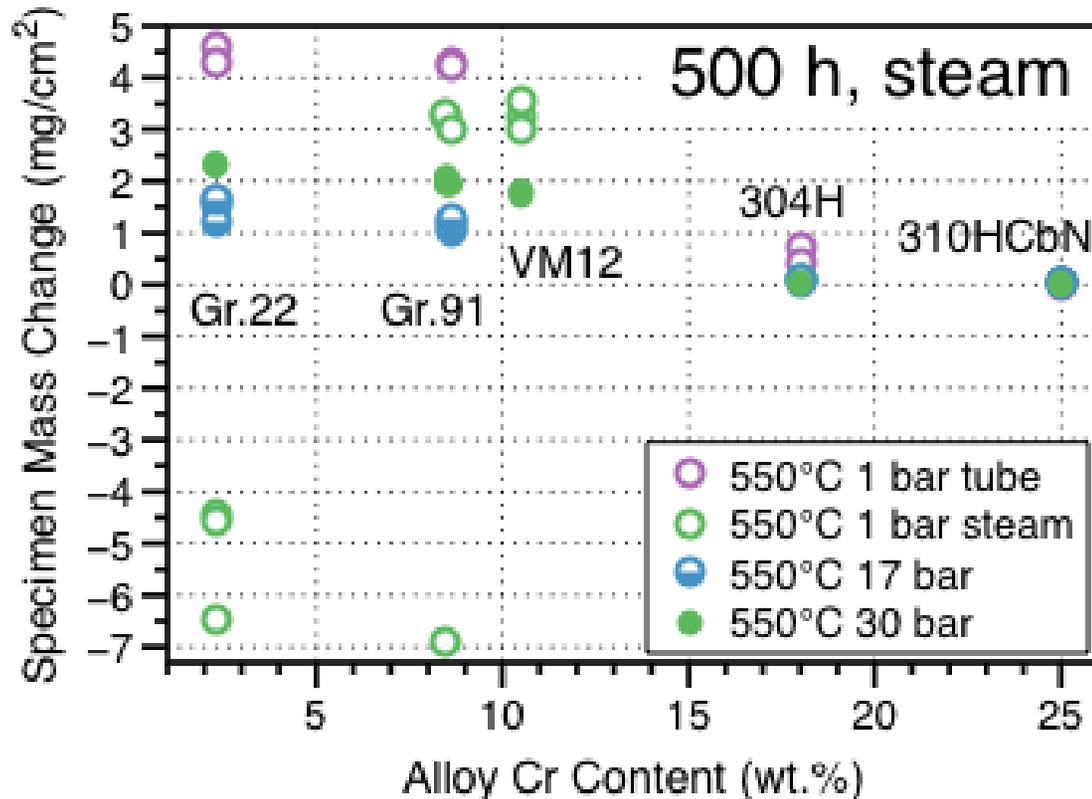
Controlled water chemistry loop

Temperature: 450°-650°C

Time: 500 h cycles

# Initial results in 550°C steam

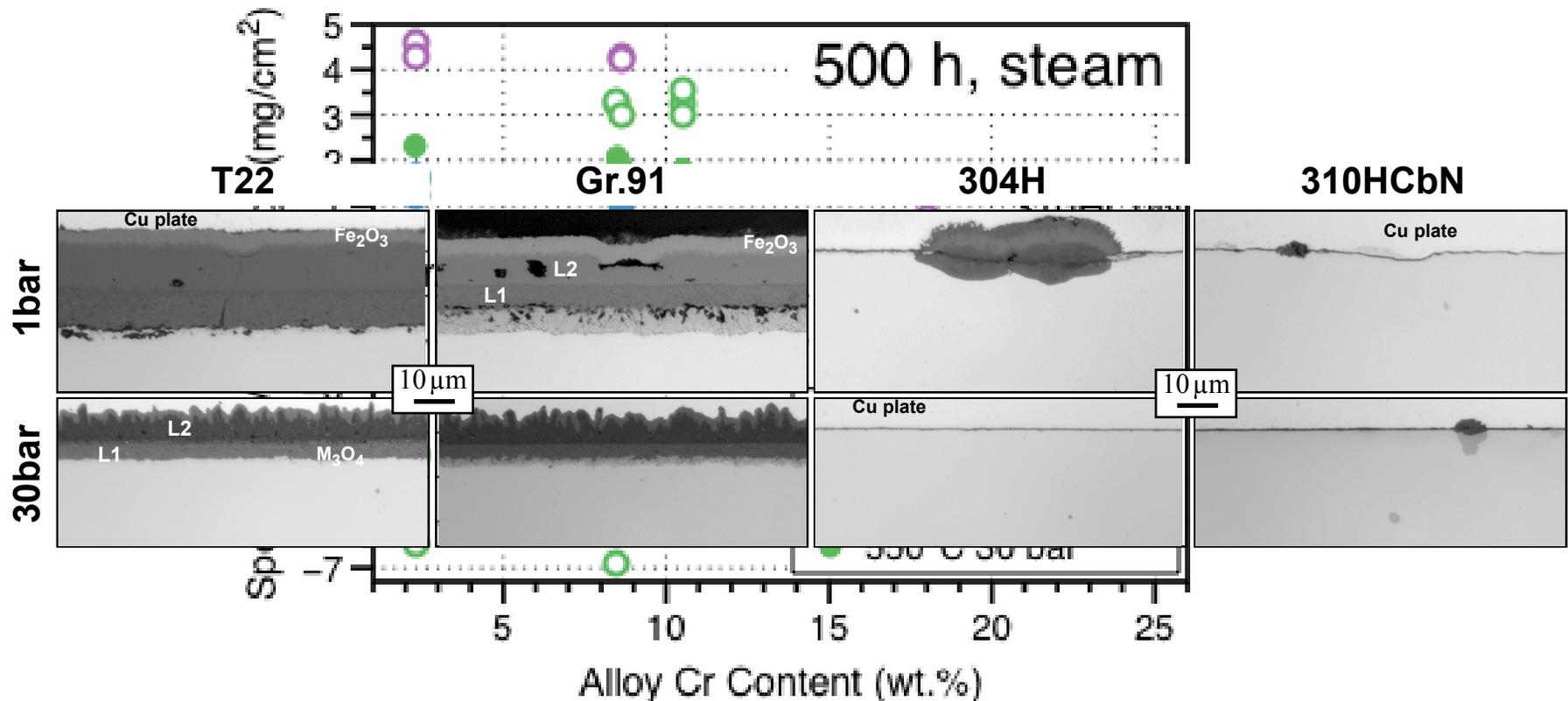
500 h exposures: Tube vs. Keiser rig



- 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

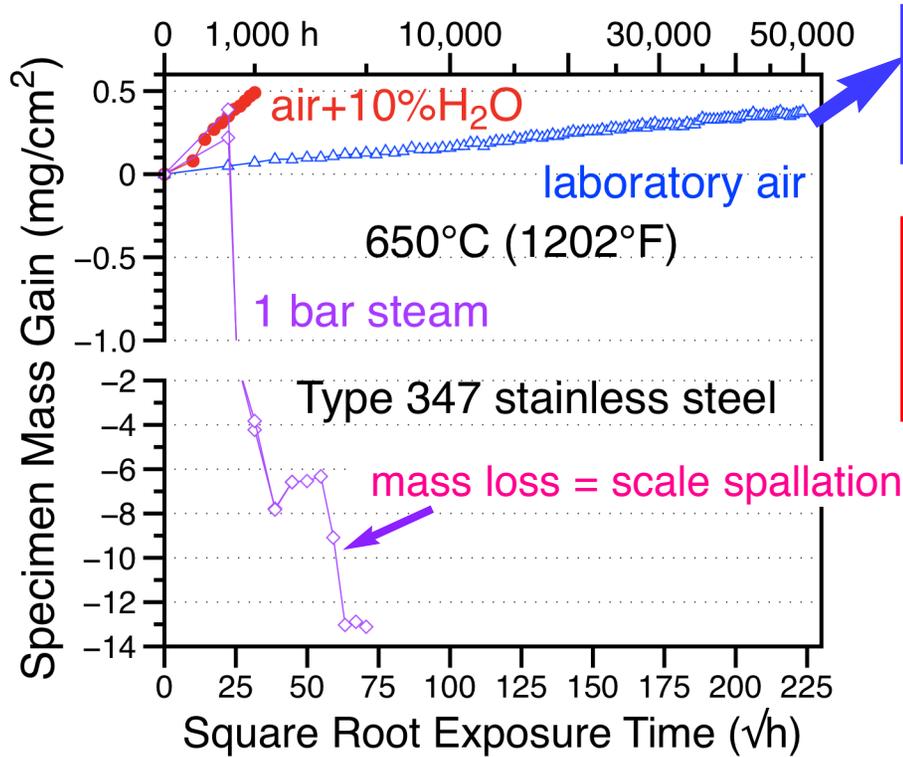
Task 1 is finishing in 2017, Task 3 expanding  
Seeking industry feedback on Task 2

**CLEAN COAL.**  
**COOL.**



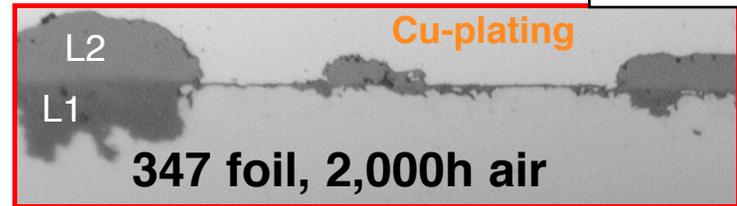
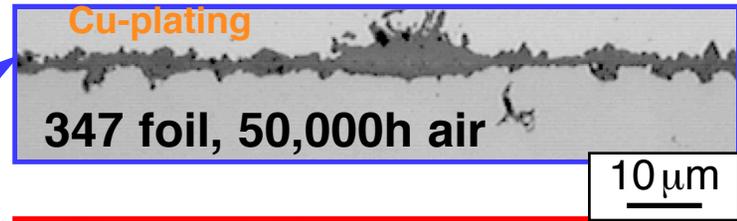
# H<sub>2</sub>O drives steels crazy

Steam or exhaust gas accelerate oxidation

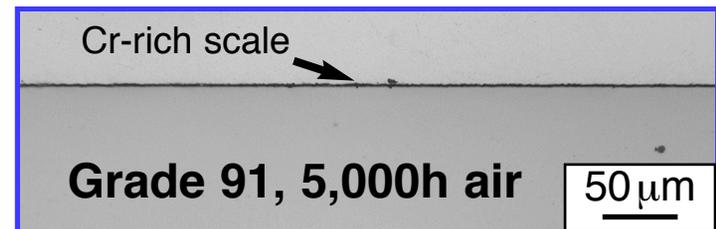
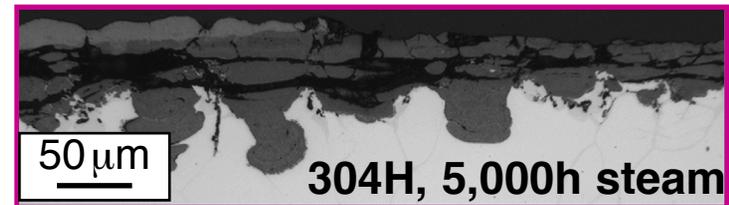


650°C, 1202°F

91: Fe-9Cr-1Mo



347: Fe-18Cr-10Ni+Nb



Laboratory air - thin, Cr-rich oxide

+ H<sub>2</sub>O - thick, Fe-rich oxide

# Specimen type showed minor effects

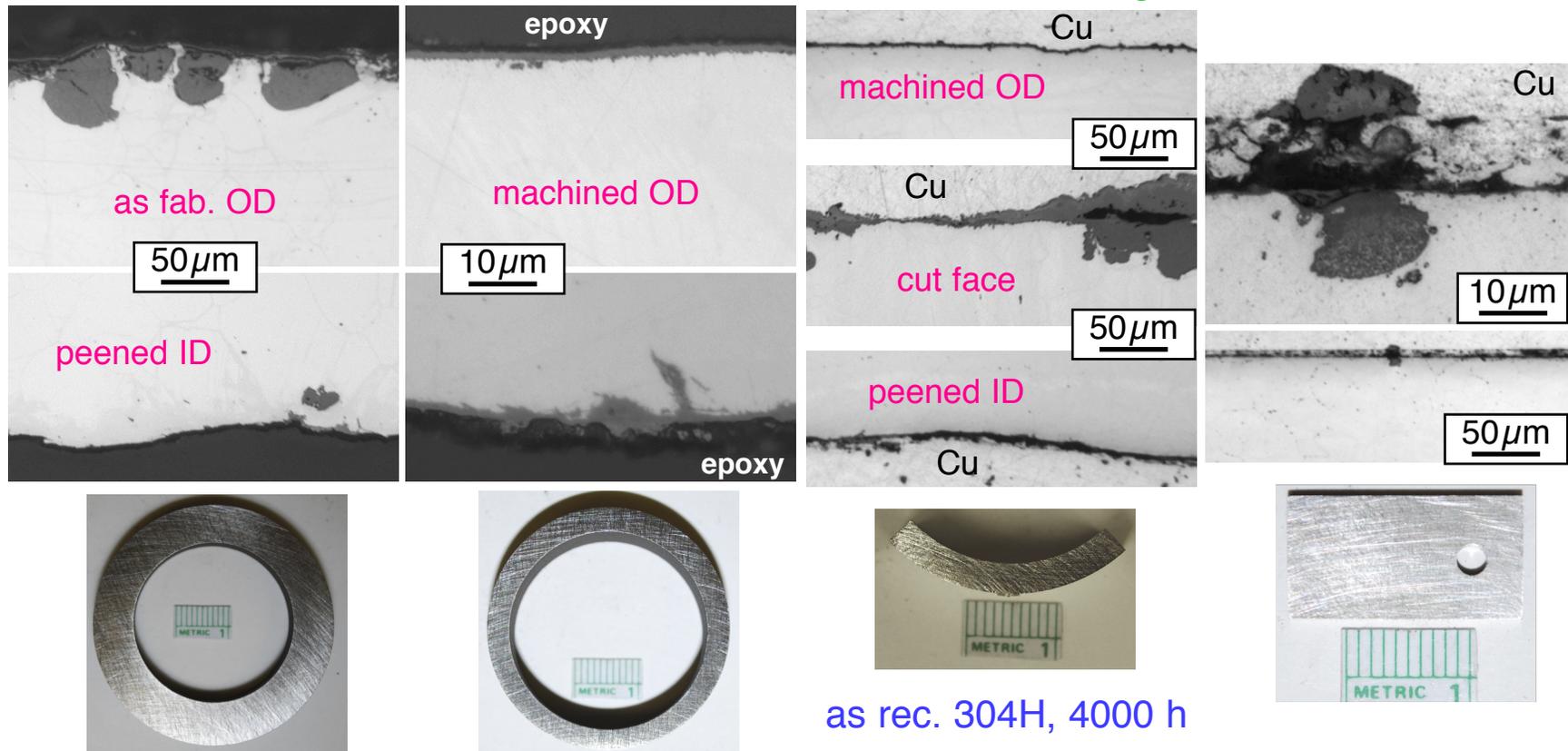
peened 304H 650°C 17bar steam 4,000h

full ring

thin ring

1/4 thin ring

coupon



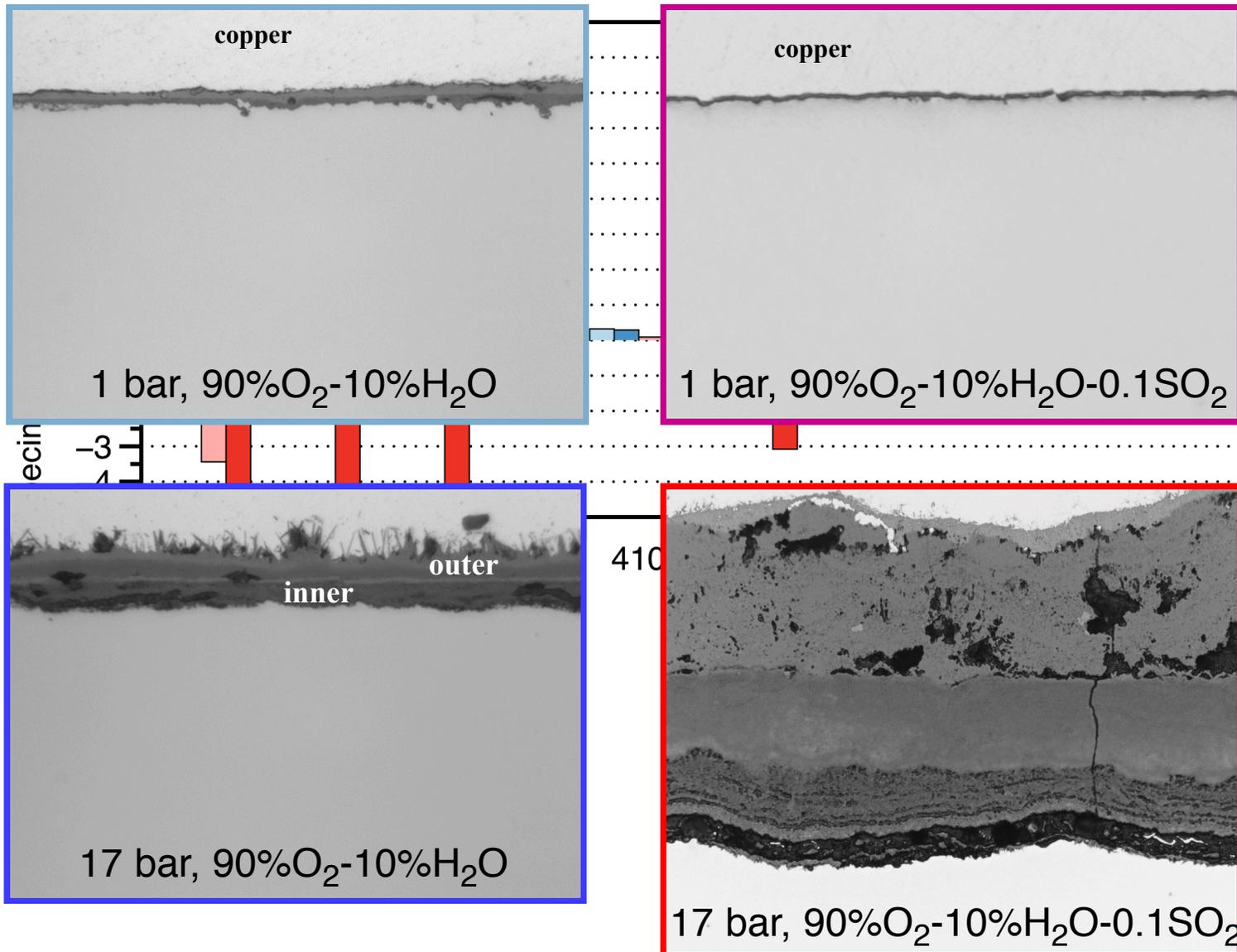
Peened ID: no effect of specimen geometry

OD difference: as-received vs. machined (thin ring)

- cold work due to machining similar to peen-

# Initial ORNL study of pressure

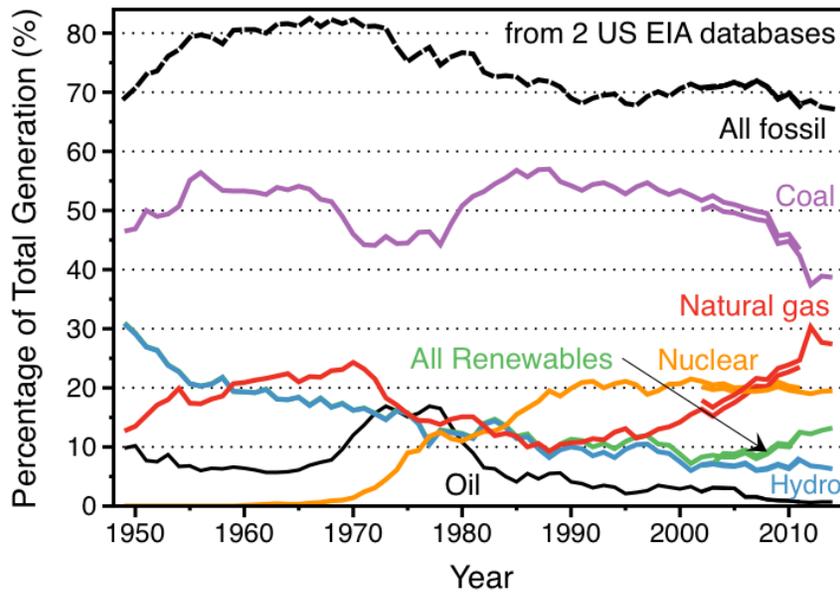
VM12: ~11Cr-1.5Co-1.5W steel



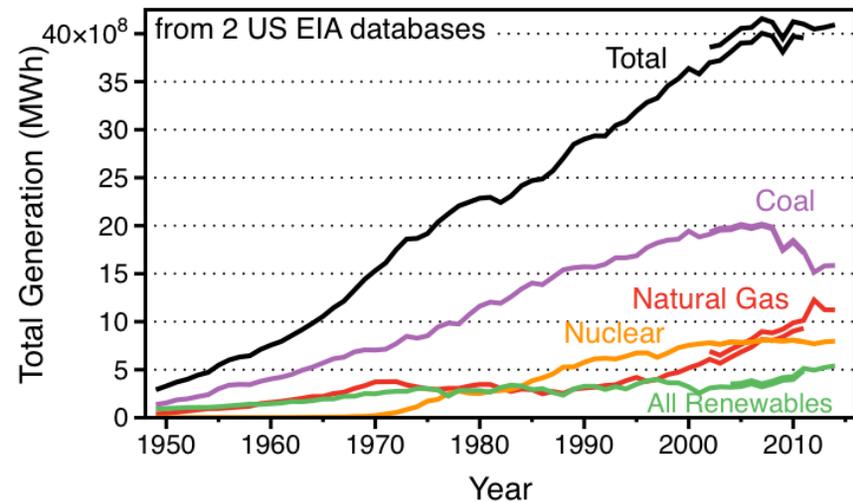
# Fossil energy continues to dominate

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

