

# Steamside Oxidation Issues in Current Coal-Fired Boilers

Bruce Pint and Rishi Pillai

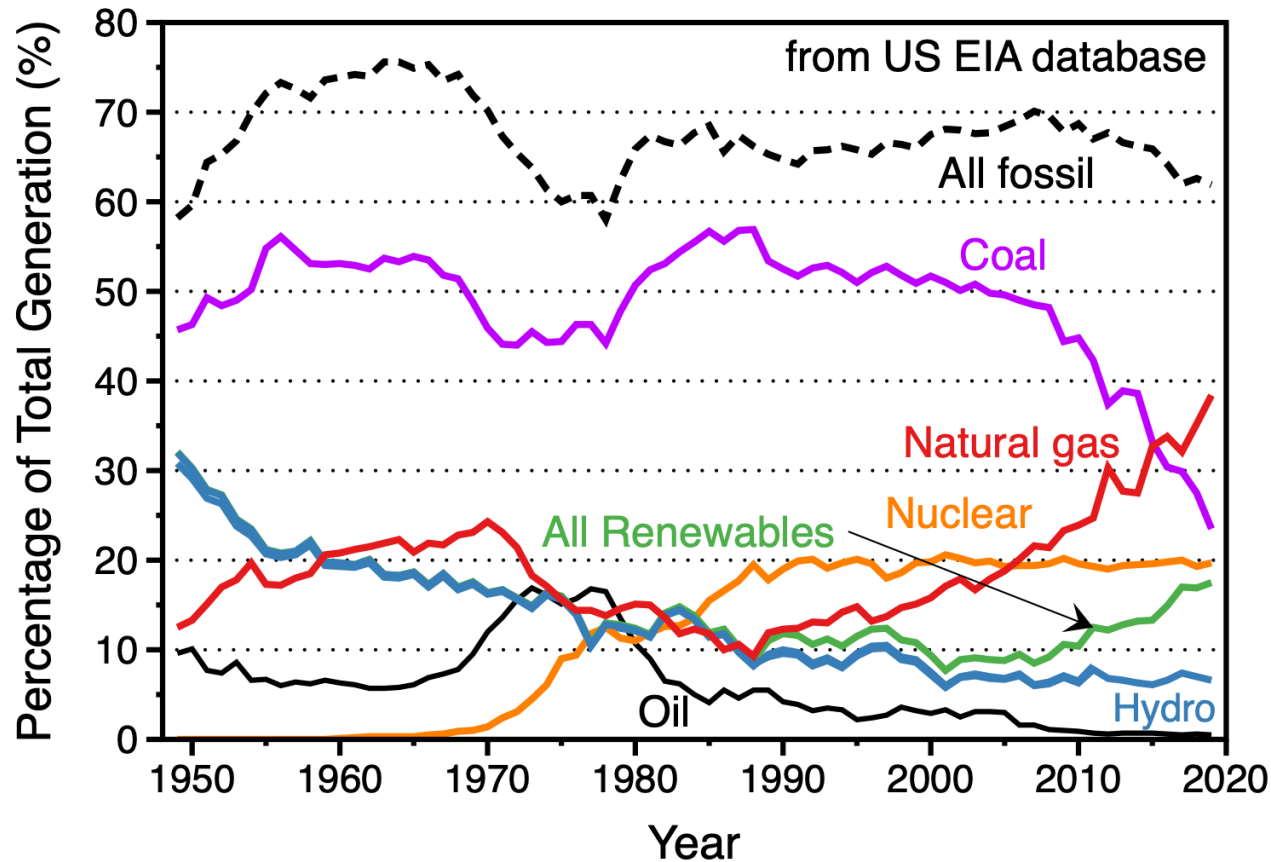
Corrosion Science and Technology Group  
Materials Science and Technology Division  
Oak Ridge National Laboratory

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

# Acknowledgments

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

# Steam oxidation still relevant in 2020

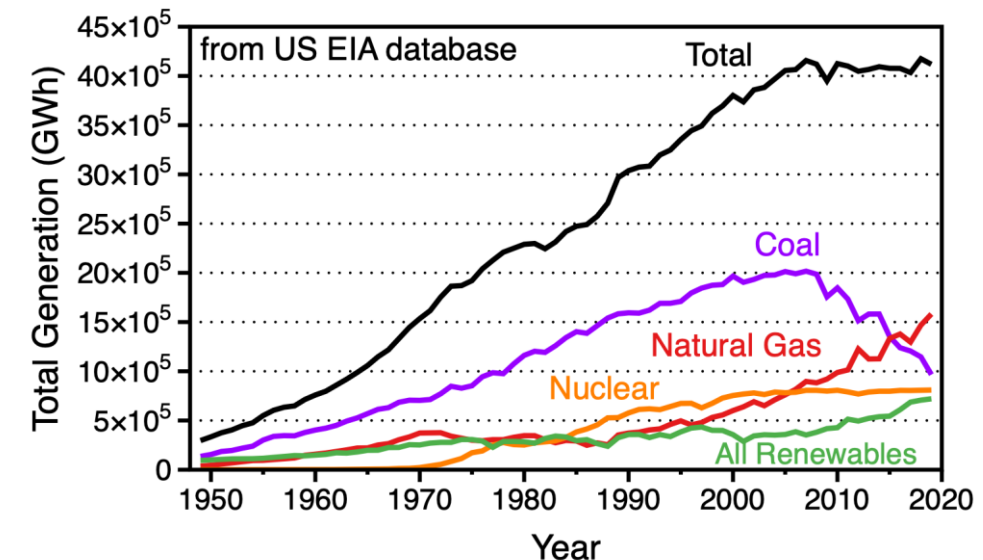


Coal: Fewer boilers operating

Gas: More HRSGs (combined cycle)  
Heat Recovery Steam Generators

DOE FE Strategic goals 1 and 2:

1. Develop **secure and affordable fossil energy** technologies to realize the full value of domestic energy resources.
2. Enhance U.S. economic and energy security through prudent policy, **advanced technology**, and the use of strategic reserves.



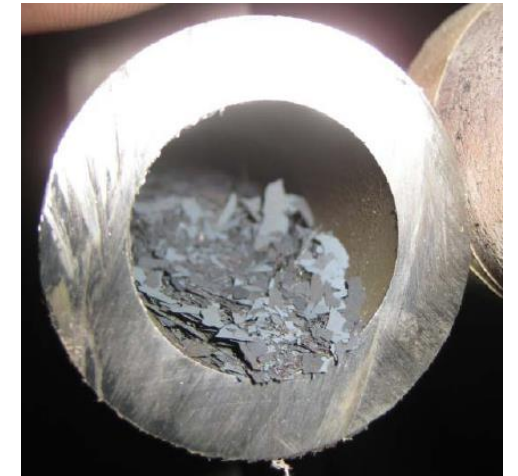
# Science approach to “real world” corrosion issues

- Stress corrosion cracking at 200°C
  - 2¼ %Cr waterwall steels: Grades 22, 23, 24
  - Significant issue in many recent boilers
- Shot-peening solution for exfoliation
  - Study of baseline alloys and shot-peened tubes
  - Long term testing in 1 atm steam at 550°-650°C
- Effect of pressure on corrosion
  - Steam-side difference between laboratory and field
    - Phase 1: does water chemistry play a role? (2017-2019)
    - Phase 2: do water additives (e.g. amines) play a role? (2020-2022)
  - Fire-side effects
    - SPOC: staged pressurized oxy-combustion (with Wash. U @ St. Louis)
  - CO<sub>2</sub> effects from related project FEAA144

Cracks in longitudinal direction



Cracks in transversal direction



Scale exfoliation blockage



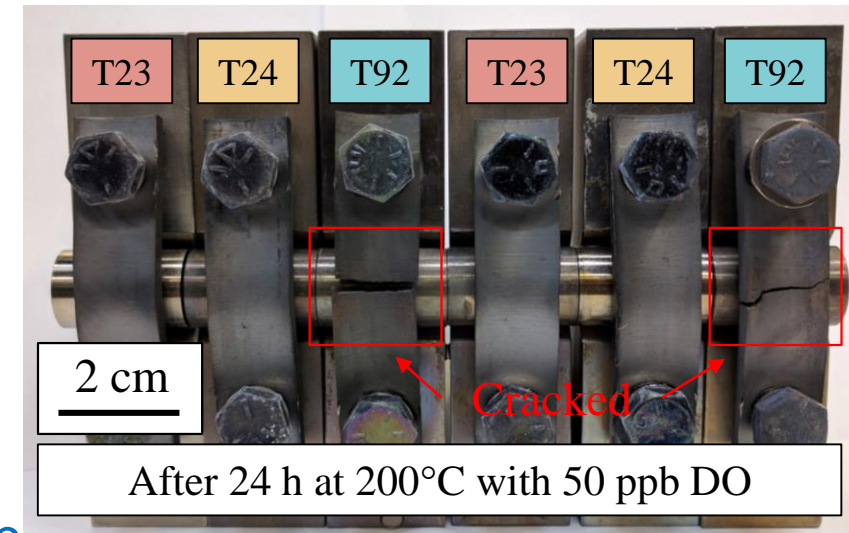
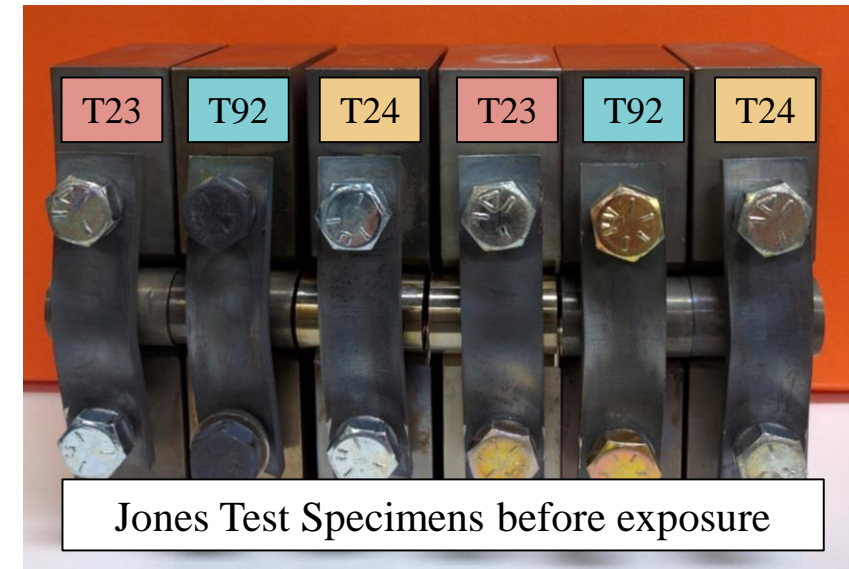
# Stress corrosion cracking: demonstrated O<sub>2</sub> effect

- “Jones” test conducted in 200°C water
  - Normalized steel (0.5h, 1065°C WQ) (no temper)
  - 50 ppb O<sub>2</sub> (autoclave)
  - 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

- Final task to measure cracking in-situ
  - As O<sub>2</sub> increased in water, can crack be detected in autoclave?



# “USC” John W. Turk Plant (commissioned 2013) used shot-peened 347H tubing to prevent exfoliation issues

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



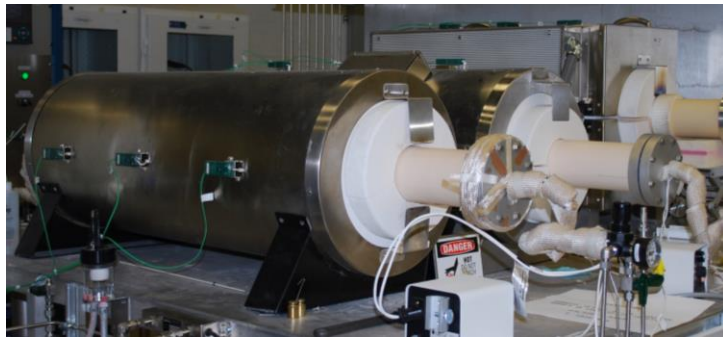
- 600MW, ~39% LHV efficiency
- \$1.8billion (\$2.8b?)
- Steam: 599°/607°C SH/RH  
25.3MPa (1110/1125°F)
  - Eddystone (1960): 613°C/34.5MPa
- Superheater: shot-peened 347H
  - 17.5Cr-10Ni-0.5Nb-1.5Mn-0.4Si-0.07C



Multi-billion dollar plant protected by shot peening with little published literature

# Shot peened tube ID: benefit to 625°C/15,000 h

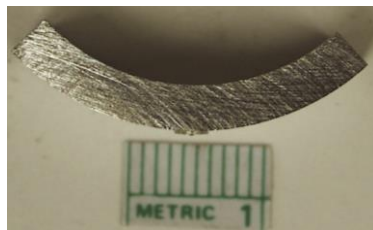
Tube furnace: 1 bar steam  
500-h cycles



Water:  $<0.1\mu\text{S}$  and  $<10\text{ ppb O}_2$



Alloy coupon



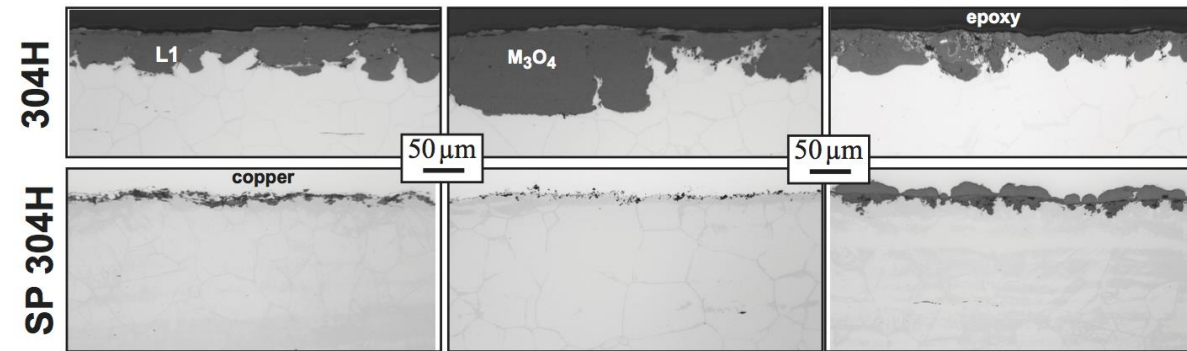
Shot peened  
tube specimen

**Task Complete:** J. M. Kurley and B. A. Pint,  
“The Effect Of Shot Peening On Steam  
Oxidation Of 304H Stainless Steel,” *Oxidation  
of Metals*, 93 (2020) 159-174.

10,000 h: 600°C

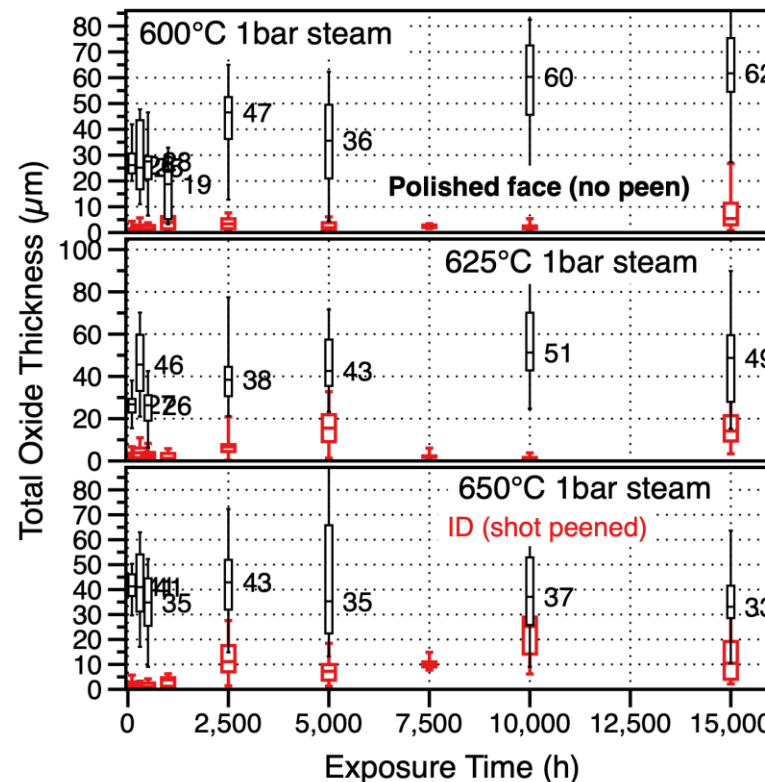
625°C

650°C

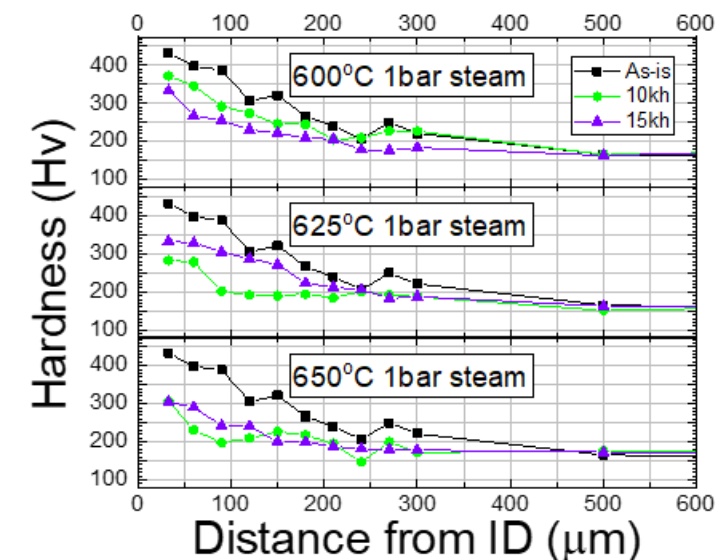


No SP:  
Spalled  
outer oxide

SP: Thinner,  
adherent,  
little spall

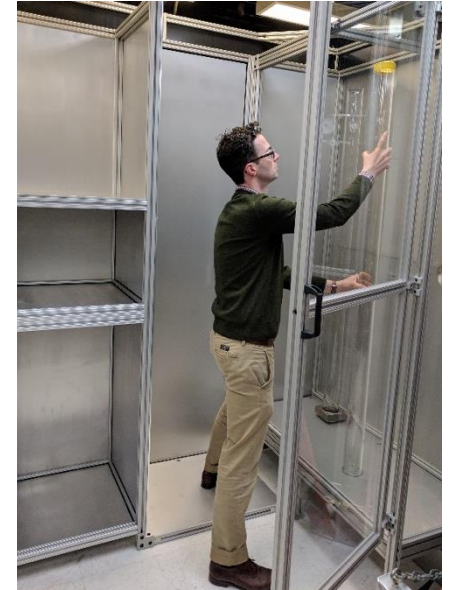
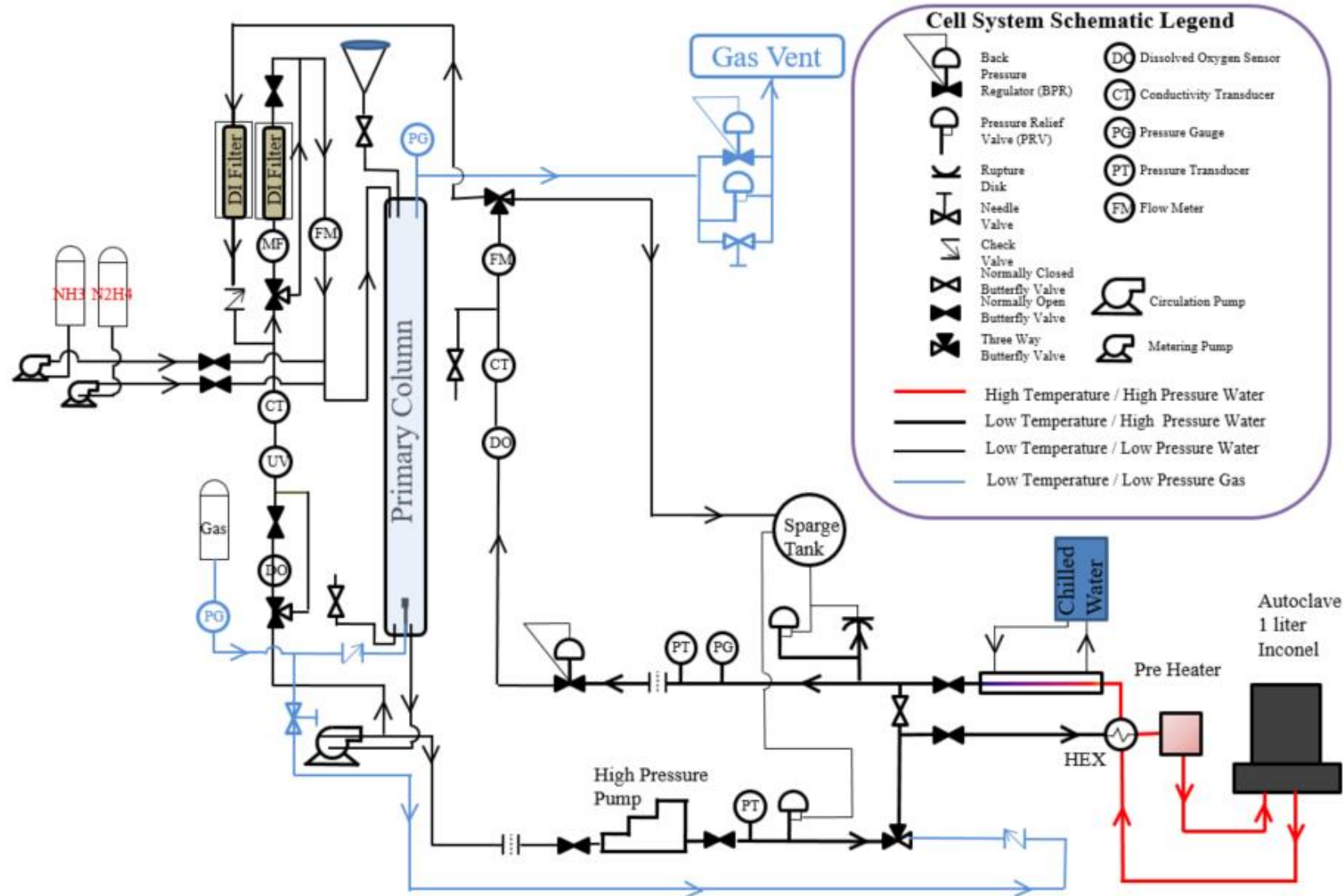


High hardness from peening  
Hardness drop with exposure:





# Water loop constructed for pressure & water chemistry



Raiman: loop architect



Similar system used for SCC experiments



# Phase 1: 4 x 1000 h experiments all 276 bar (4000 psi) 1L autoclave volume restricts specimens in 500-h cycles



	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

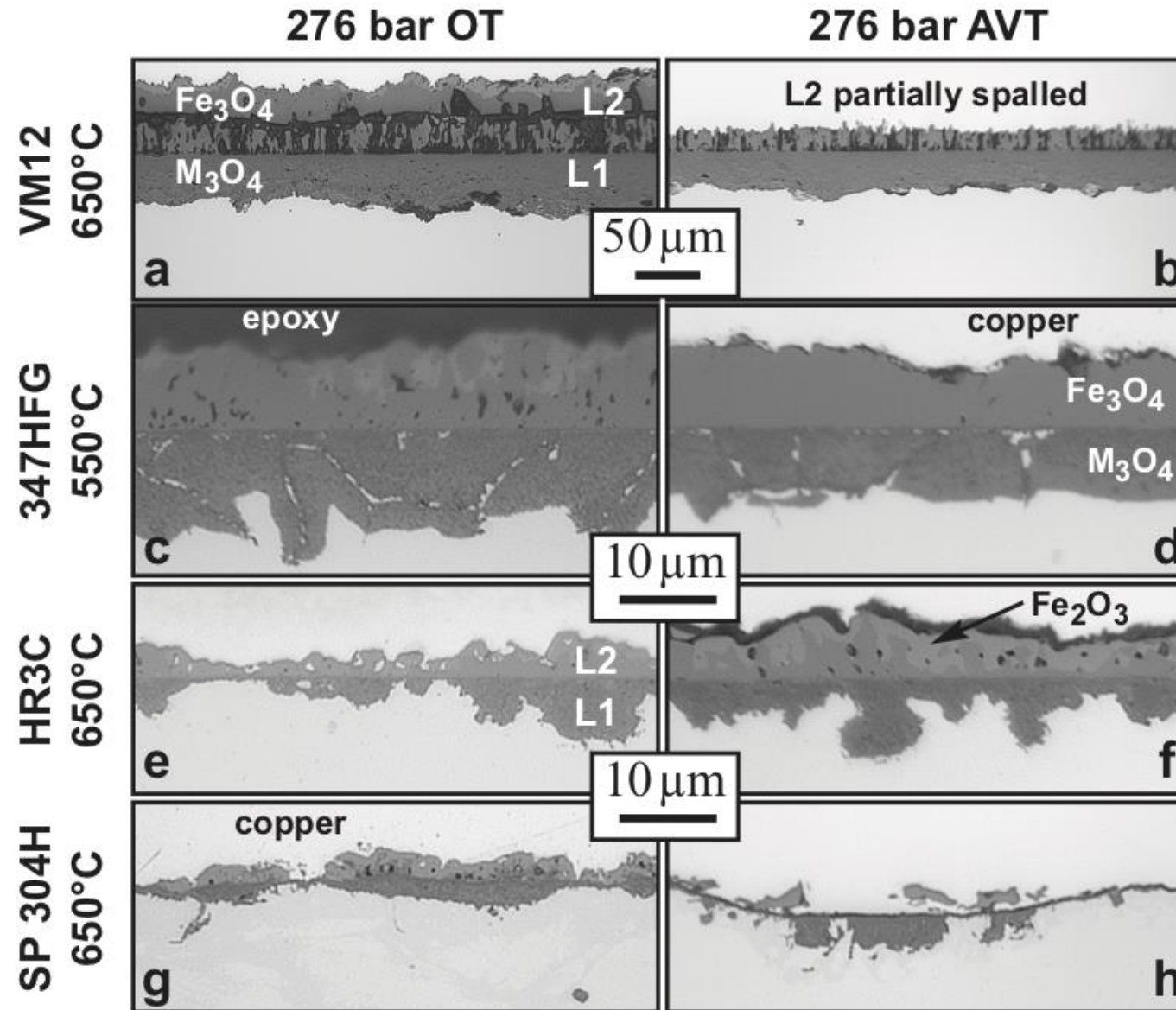
# OT vs. AVT: slight differences observed, similar reaction rates

High  $O_2$ :  
Some  $Fe_2O_3$   
Light oxide

High  $O_2$ :  
Some  $Fe_2O_3$   
Light oxide

No  $Fe_3O_4$

$Fe_2O_3$  outer layer



Spall?

Low  $O_2$ :  
Only  $Fe_3O_4$

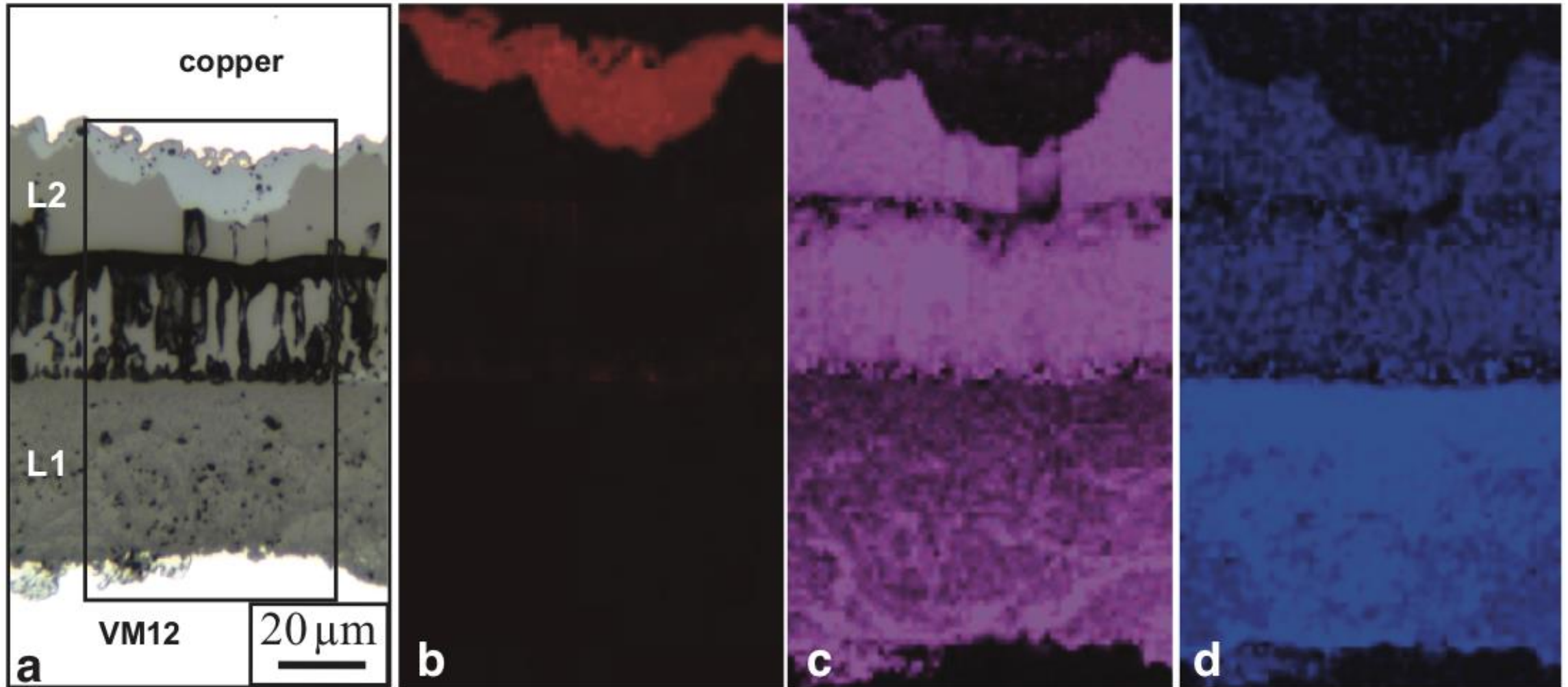
Some  $Fe_3O_4$

Some  $Fe_2O_3$   
Inner layer inhibits  
Cr transport?

Light microscopy, all 1000 h

# Raman spectroscopy confirms lighter oxide is $\text{Fe}_2\text{O}_3$

VM12: 276 bar OT 650°C 1000 h



$\text{Fe}_2\text{O}_3$

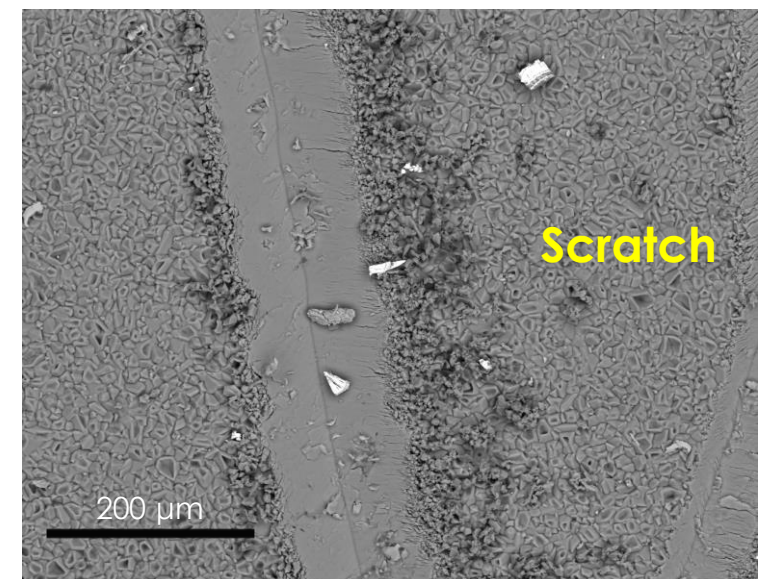
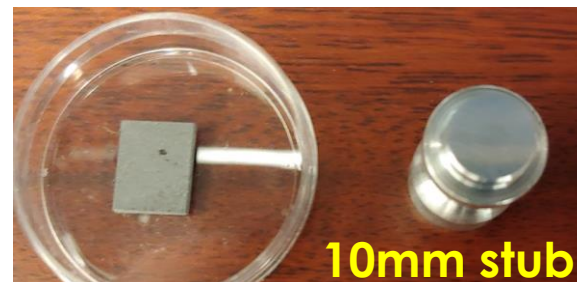
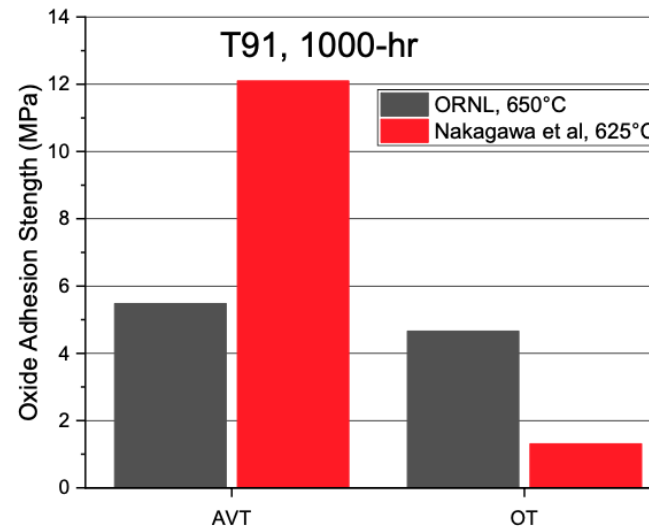
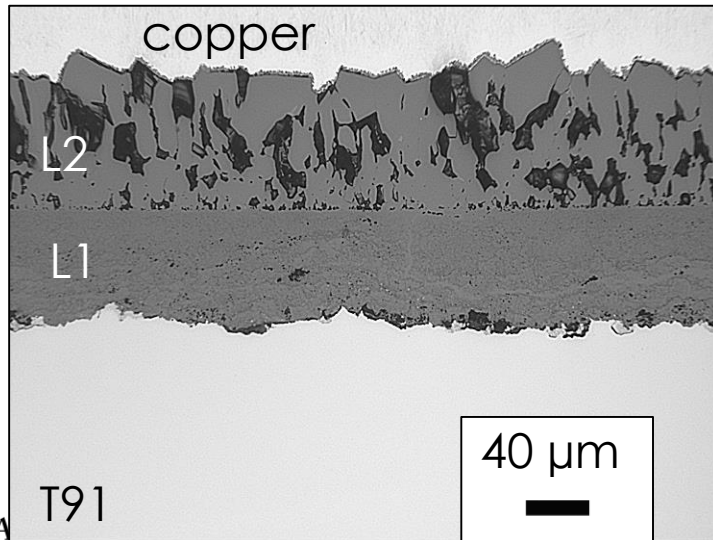
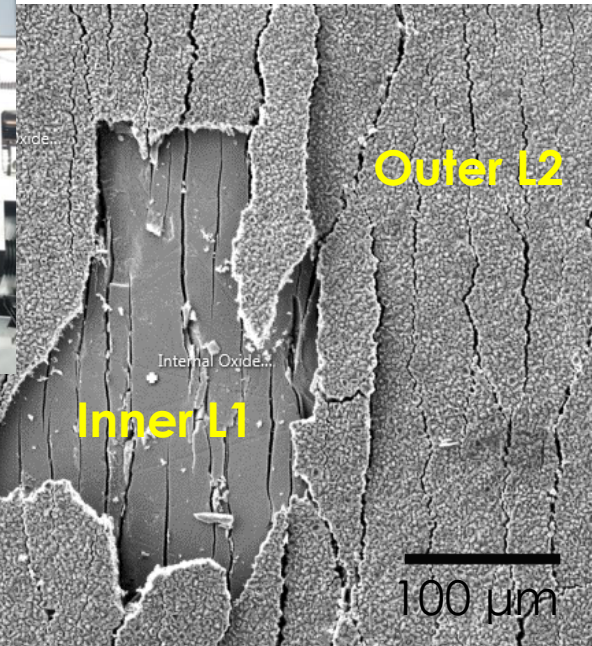
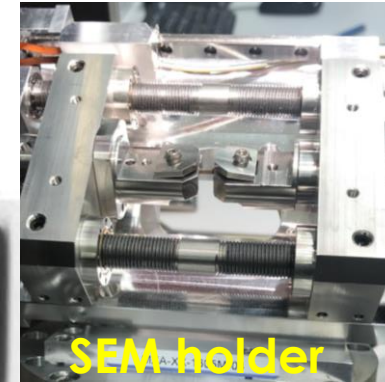
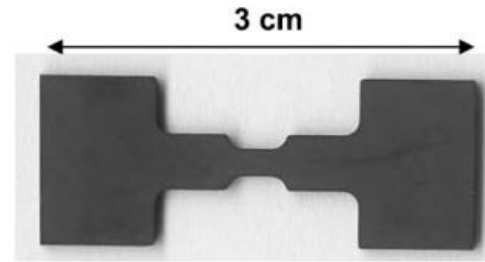
Ordered  $\text{M}_3\text{O}_4$

Disordered  $\text{M}_3\text{O}_4$



# Current task to explore different methods to test adhesion

- Adhesion between L1 and L2 oxide layers
  - Key factor in exfoliation
- ASTM pull test (10 mm stub)
  - Values obtained
- In-situ SEM tensile testing
- Scratch test
  - Need larger load cell



# Controlled chemistry steam oxidation-exfoliation studies are continuing

- Three-year project started in FY20, delayed by COVID response
- Industrial partner EPRI (S. Kung)
  - Co-funding research: \$125K Phase 1, \$100K Phase 2
    - Based on utility interest in exfoliation issues
  - Phase 2: effect of water additives on steam oxidation (e.g. amines)
    - Challenge: Currently working on non-disclosure agreements with additive suppliers
    - Exploring several strategies to measure scale adhesion
    - Emphasis on modeling steam oxidation
      - Autoclave experiments expensive and require significant system maintenance
- Shot peened tubes donated by American Electric Power
- Relation to other projects
  - Effect of pressure on corrosion relevant to sCO<sub>2</sub> and SPOC (Wash. U.)  
(supercritical CO<sub>2</sub> and stage pressurized oxy-combustion)

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



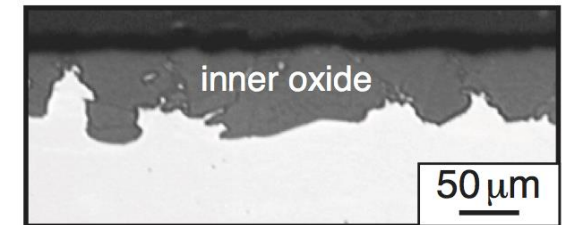


# Why focus on shot peening?

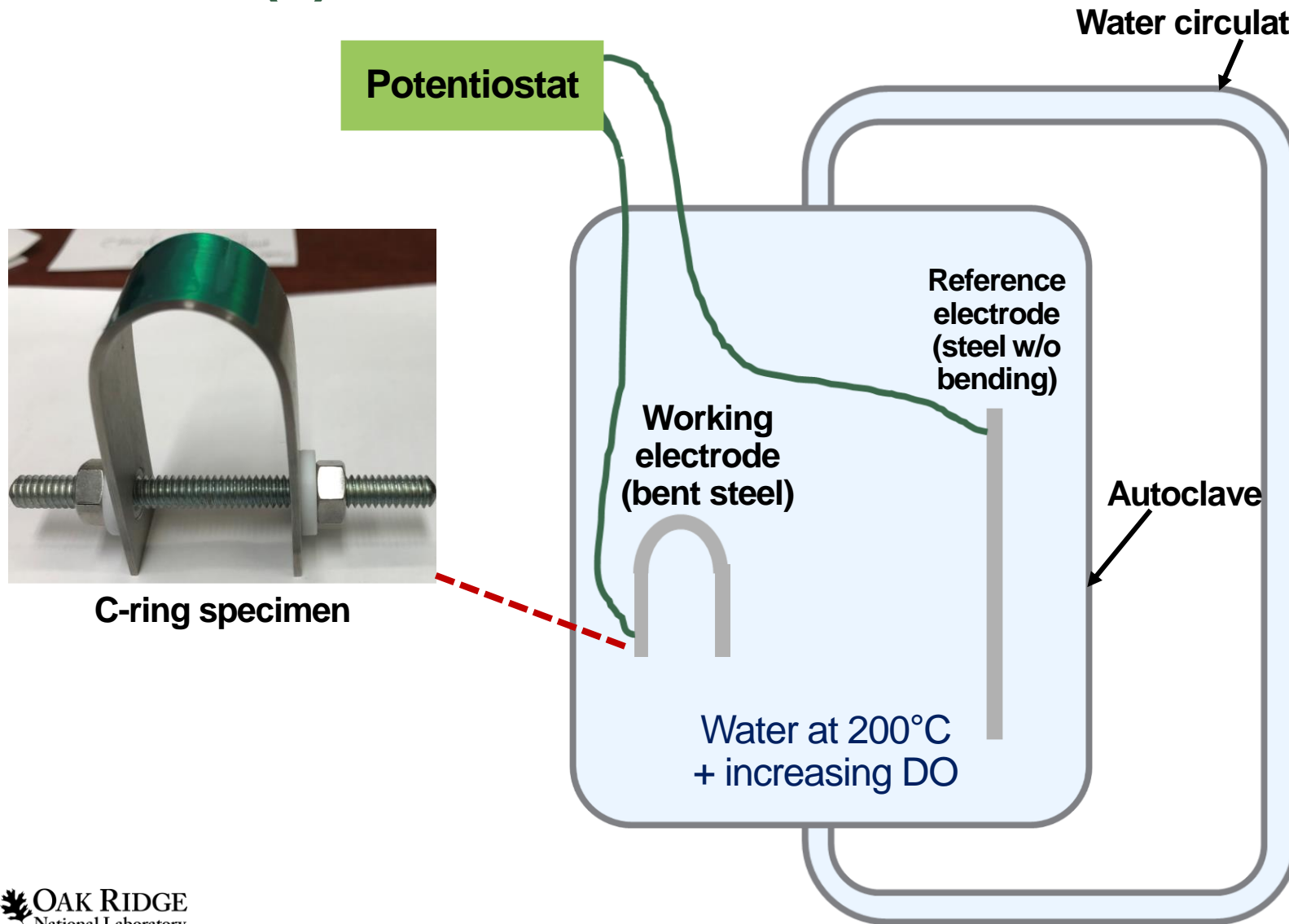
- Scale exfoliation is the main driver for this task
  - $\text{H}_2\text{O}$ -accelerated oxidation of steels (steam-side)
  - Simultaneous spallation of thick oxide
  - Tube failures & erosion damage
  - Costs: unplanned shutdowns, mitigation
- Shot peening of austenitic tubes
  - Industry standard to address exfoliation
  - Reduced scale growth: avoids exfoliation issue
  - Limited understanding of benefit and procedure



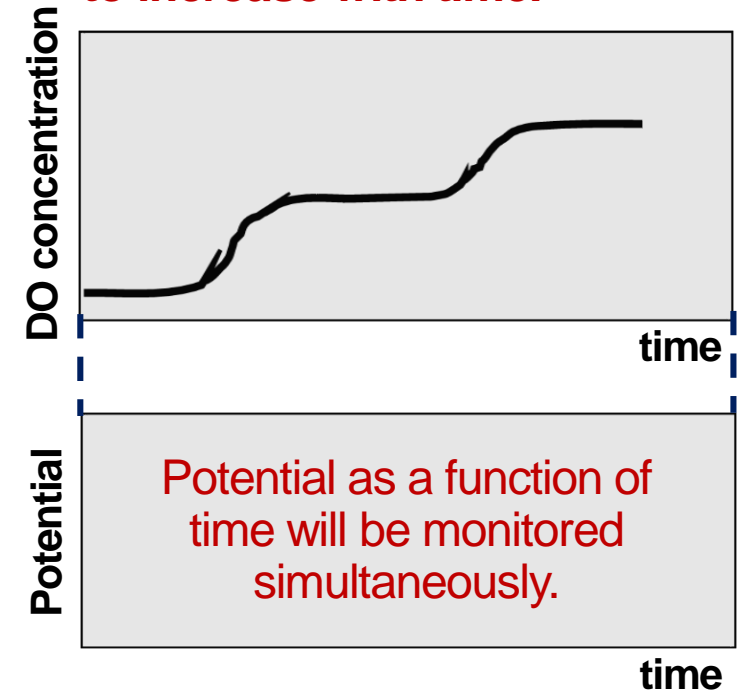
TP304H  
22,000 h



# In-situ SCC experiment redesigned: Electrochemical noise measurement will detect the potential transient(s) associated with crack initiation as O<sub>2</sub> increased



DO in water will be controlled to increase with time.



Any potential transient could indicate the initiation of cracking.