Corrosion Issues in Advanced Coal-Fired Boilers

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Acknowledgments

ORNL

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

T. Jordan - metallography

T. Lowe - SEM, image analysis

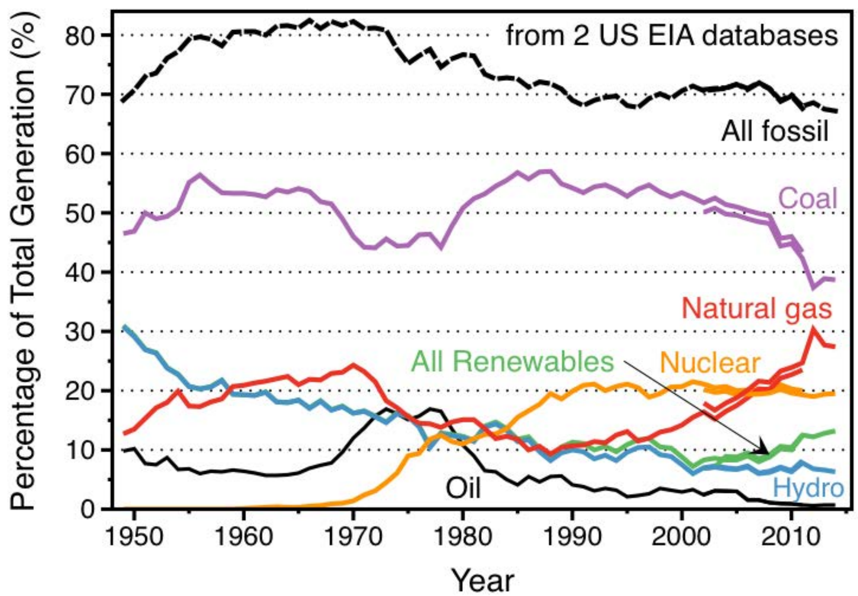
D. Leonard - EPMA

S. Shipilov, A. Willoughby - water loop

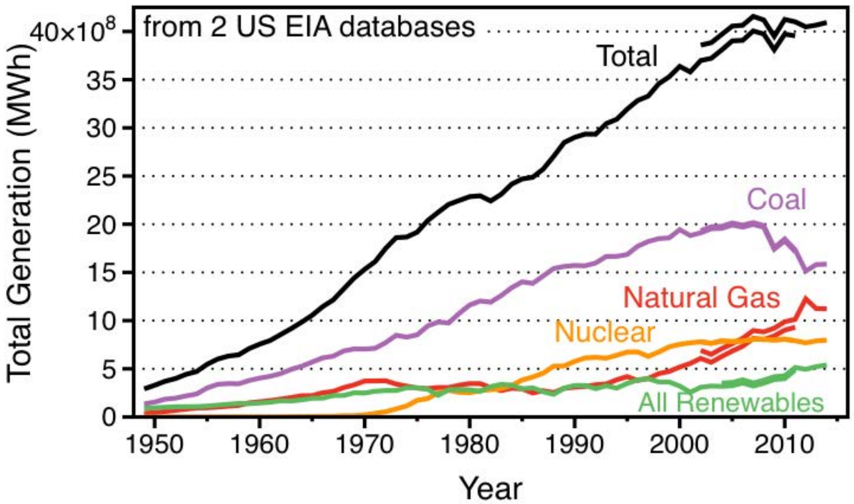
Fossil energy continues to dominate

Source mix is changing & demand is stagnant

How does US generate electricity?



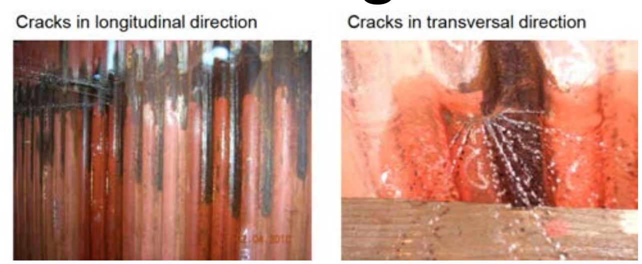
How much does US use?



FY15-16: 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



3) Effect of pressure on corrosion
   - relevant for steam oxidation (lab. vs. field)
   - SPOC: staged pressurized oxy-combustion
   (FEAA120 subcontract with Wash.U@StL)

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

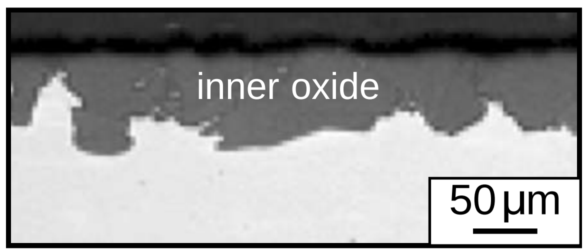
Fe-17.5Cr-10Ni-0.5Nb-1.5Mn-0.4Si-0.07C

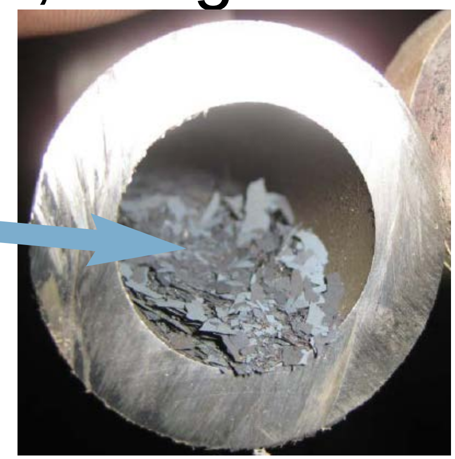
Task 1: Why shot peening?

Exfoliation problem is a main driver for research

- H_2O-accelerated oxidation of steels (steam-side)
- Simultaneous spallation of thick oxide
- Tube failures & erosion damage
- Cost: planned/unplanned shutdowns, mitigation

TP304H (22,000h)





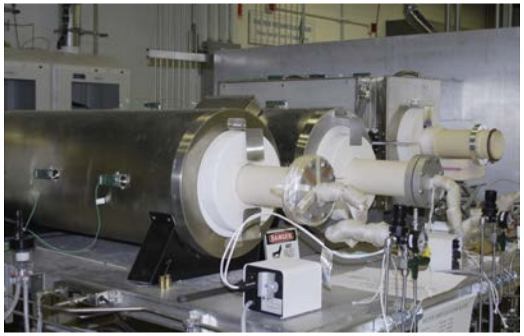
Source: EPRI

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?

Alloy oxidation specimens exposed

~1.5x10x20mm in most cases



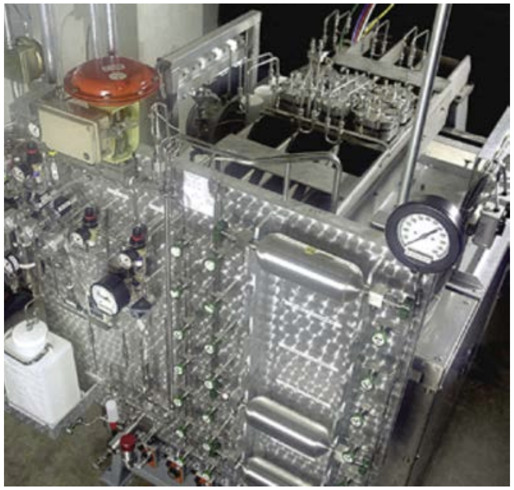
1bar steam

Atomized deionized water (no carrier gas)

H_2O: ~0.065μS/cm, filtered, deaerated

Temperature: 550°-650°C

Time: 500 h cycles



17bar steam testing

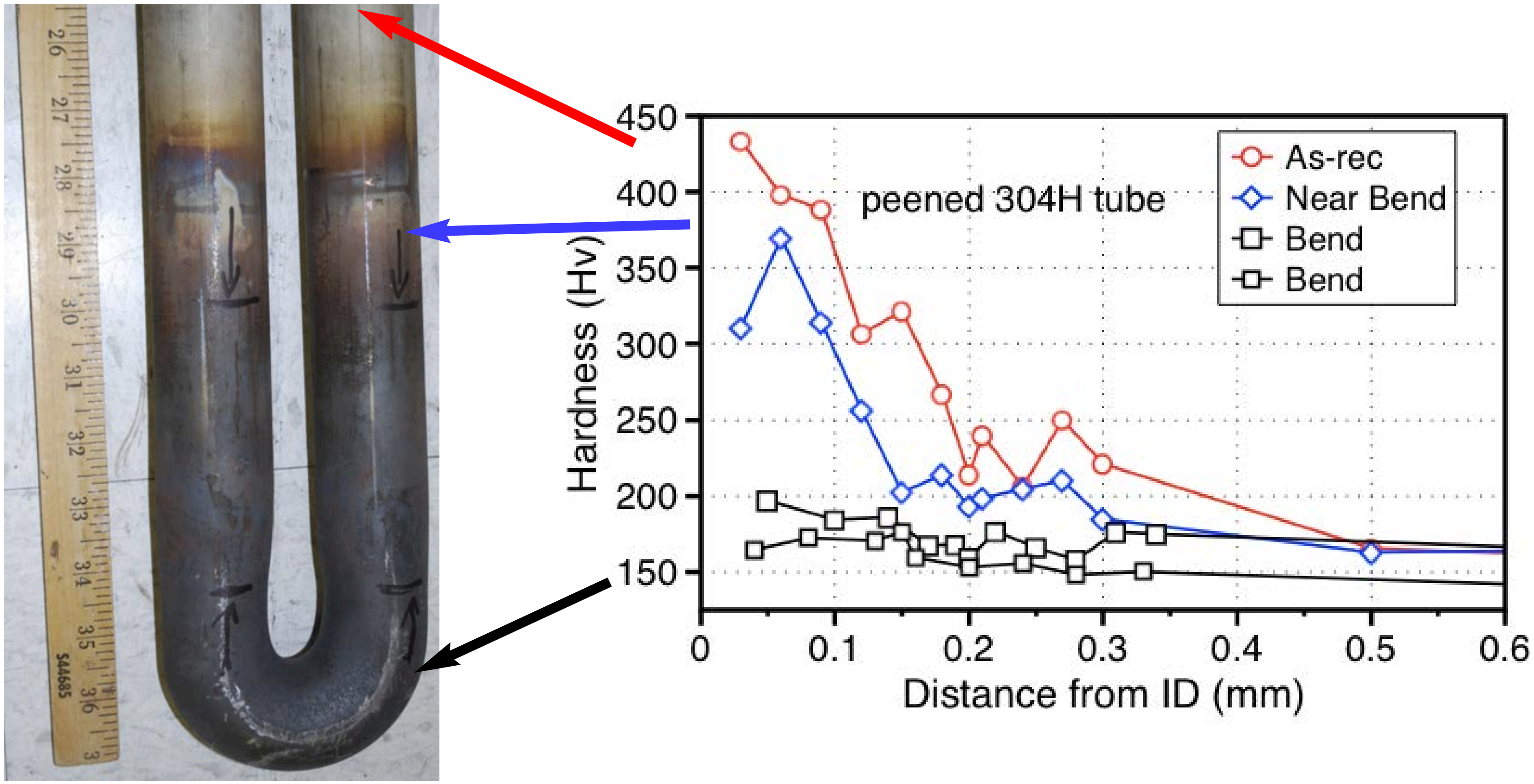
H_2O: ~0.065μS/cm, filtered, deaerated, deionized

Temperature: 550°-900°C

Time: 500 h cycles

Shot peening hardness profiles

Required 1100°C solution annealing of bend



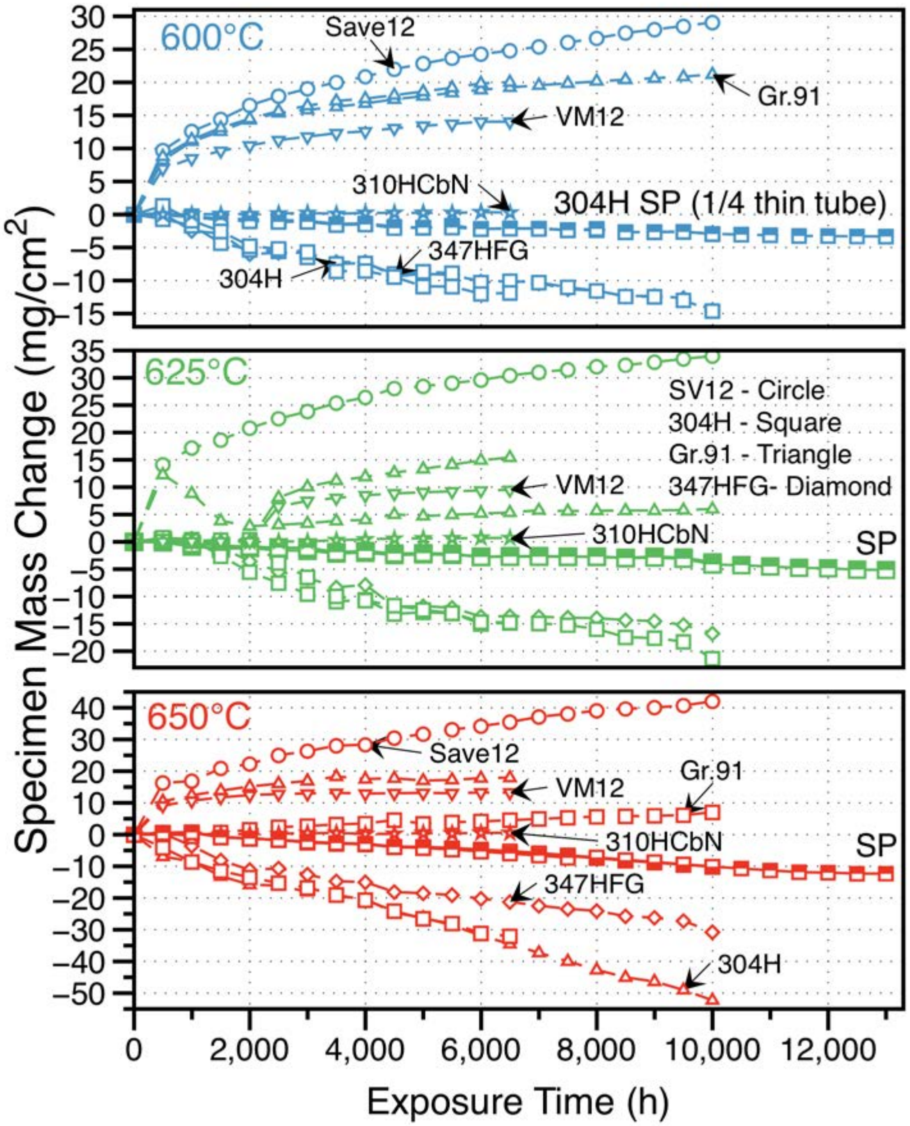
304H tube from an EPRI partner:

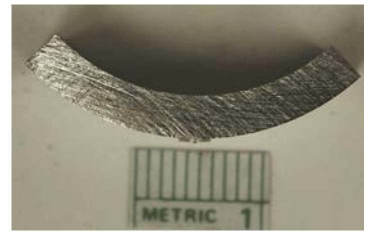
No hardness difference remained in the bend after annealing at 1100°C

Completed 13kh of exposures

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

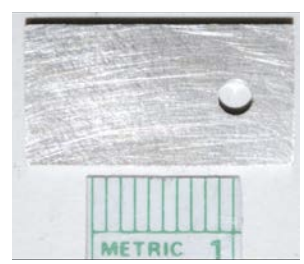
Shot peened coupons: commercial 304H from a utility





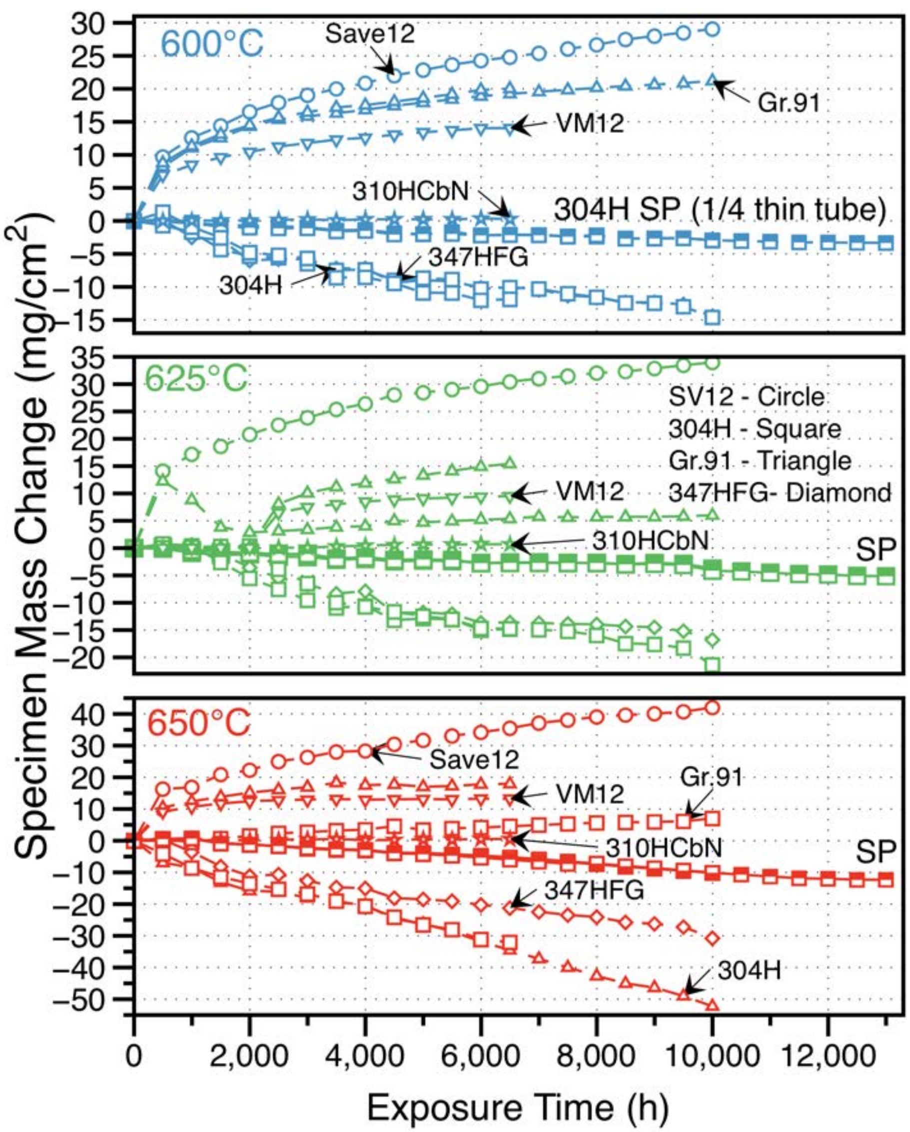
Shot peened coupons:
- tube sections
- reduced wall thickness

Polished alloy coupons:
- comparison

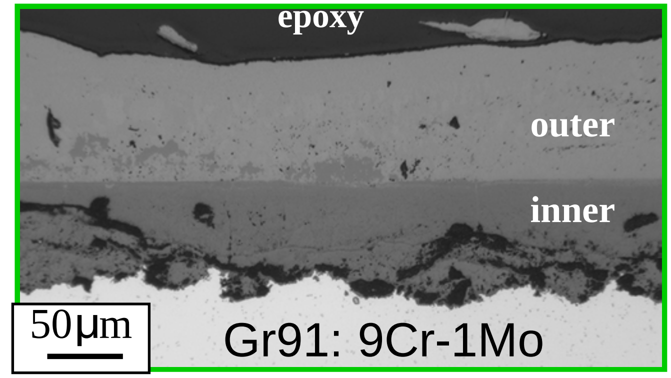


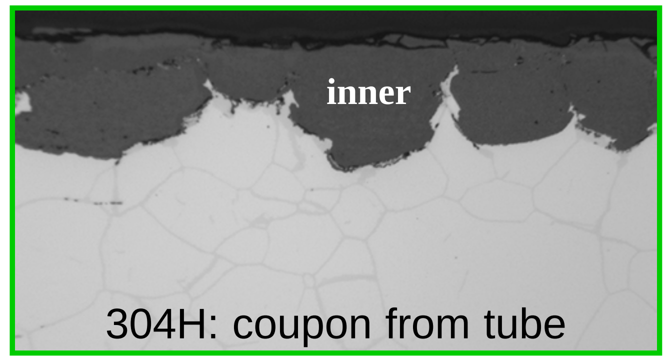
Alloy coupons stopped at 10,000h

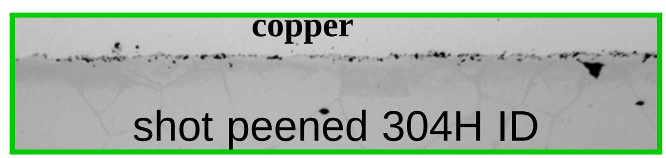
Shot peened coupons: commercial 304H from a utility

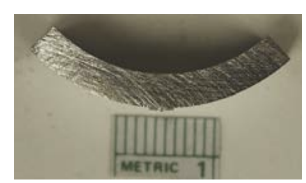


10,000 h 625°C steam





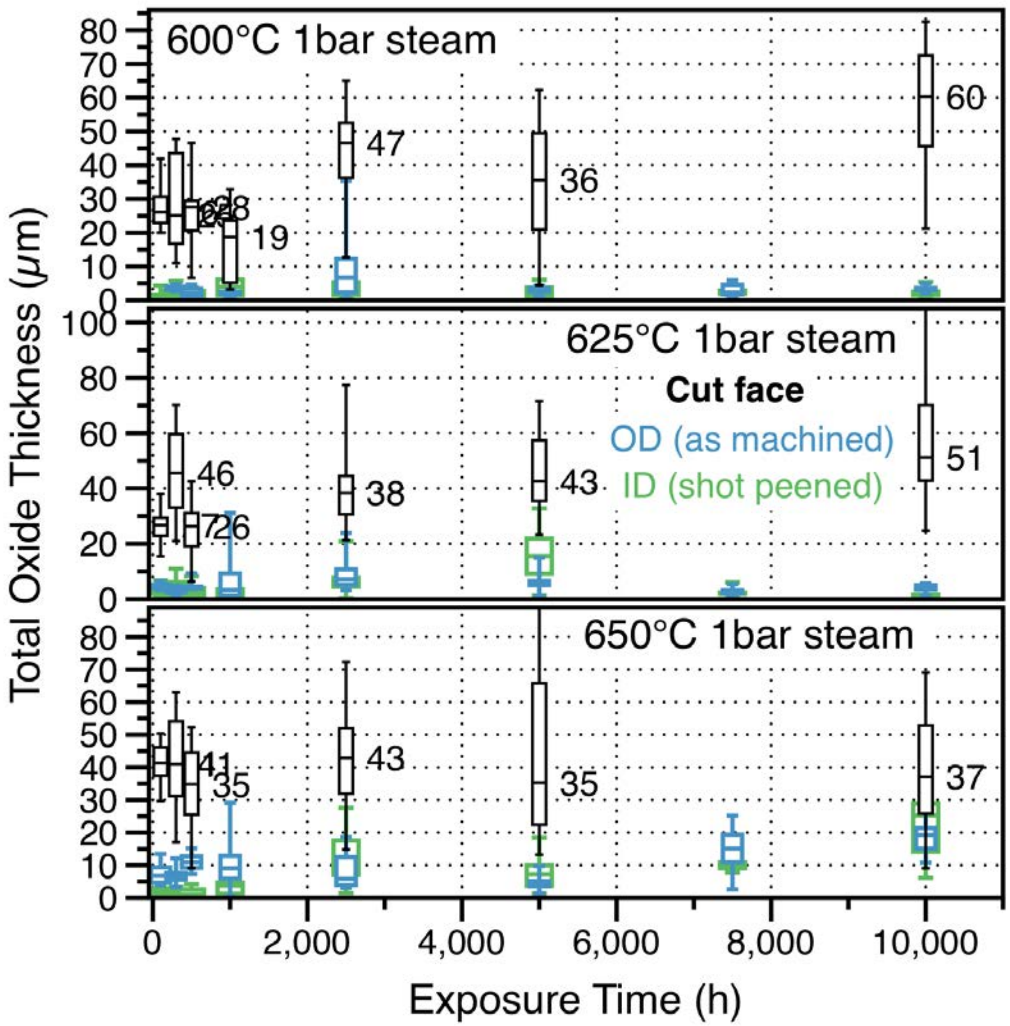




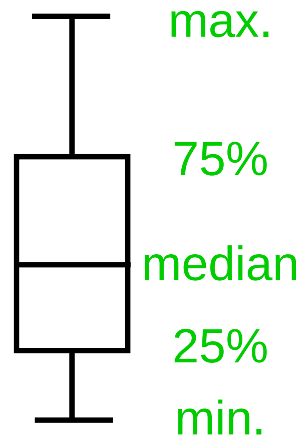
Series of SP specimens exposed

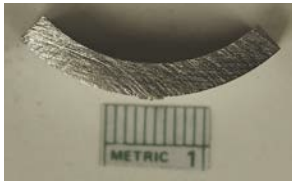
Oxide thickness measurements from polished sections

commercial shot-peened 304H



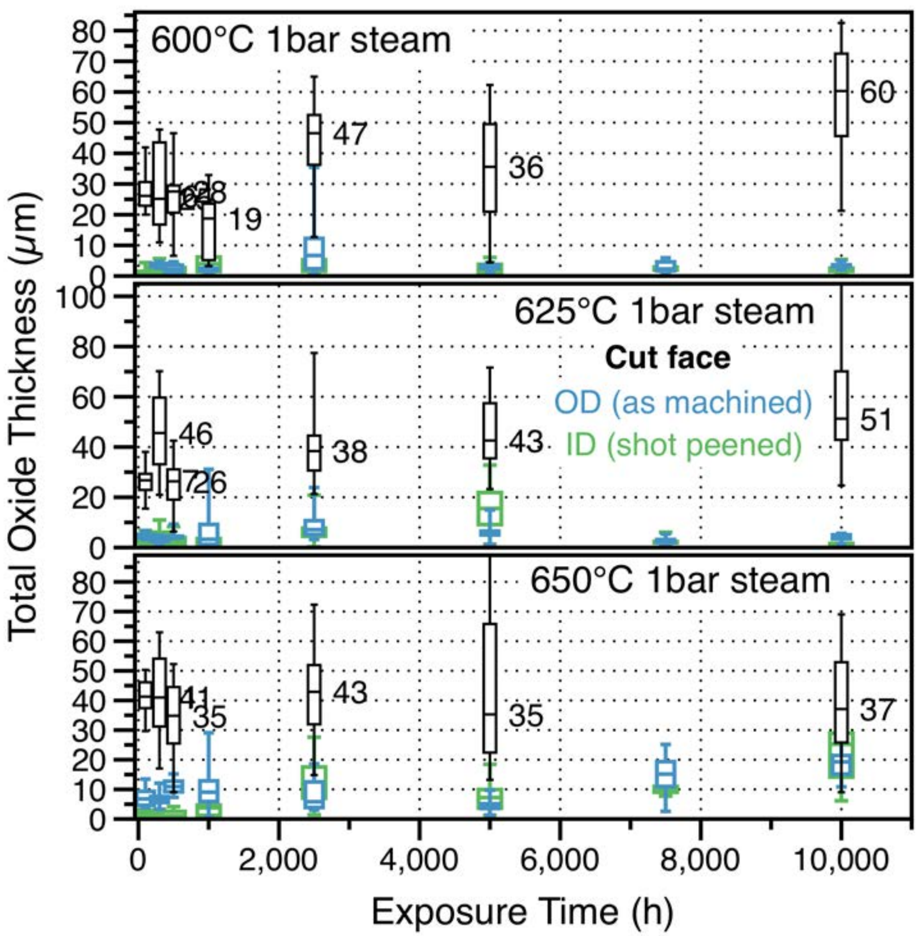
Box & whisker plot

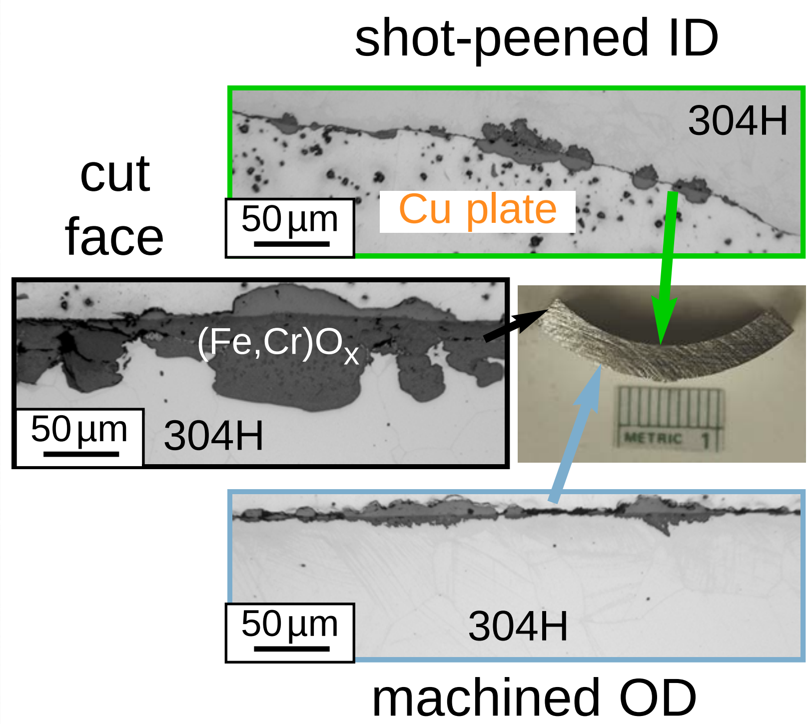




“Cut” face grows thick oxide

Oxide thickness measurements from polished sections

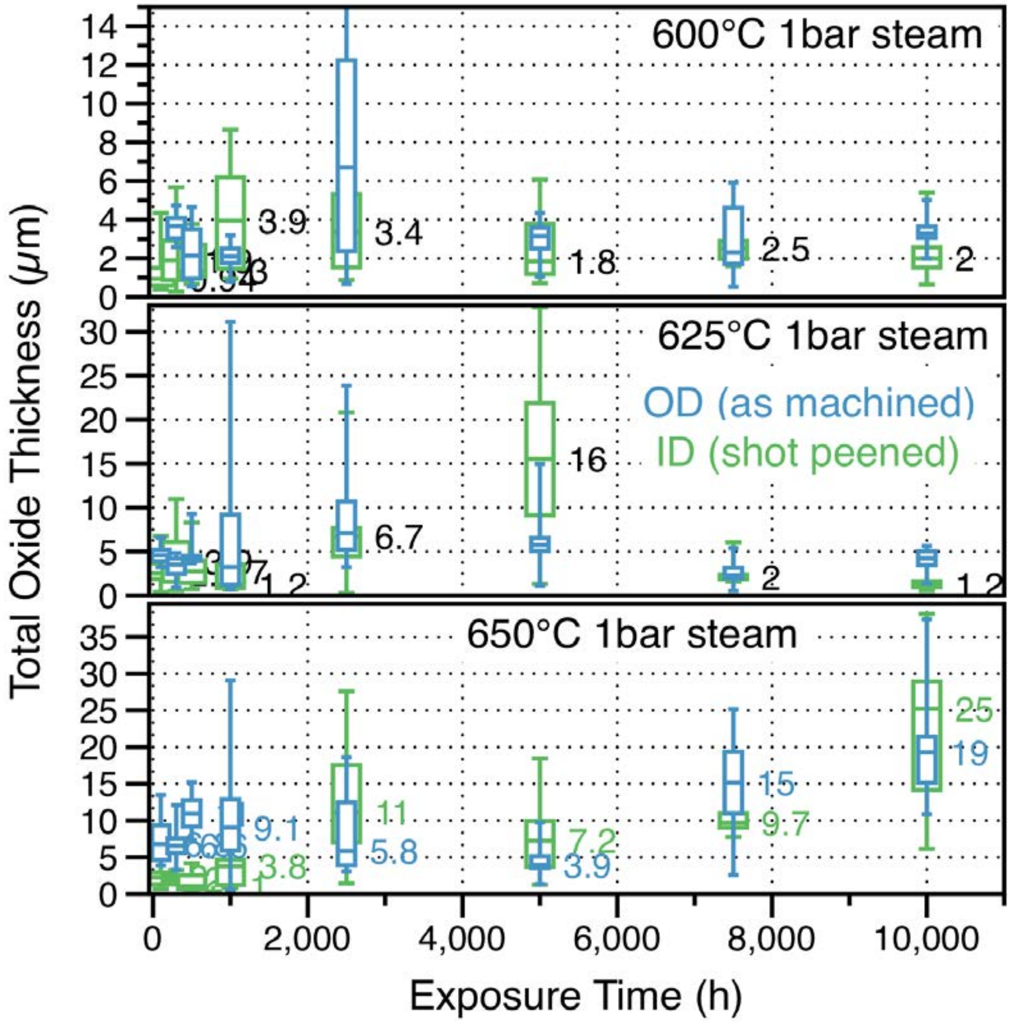


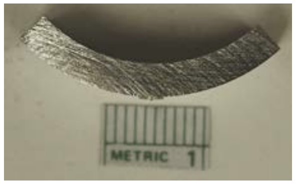


Example: 2,500h, 625°C

Similar benefit on machined OD

Oxide thickness measurements from polished sections

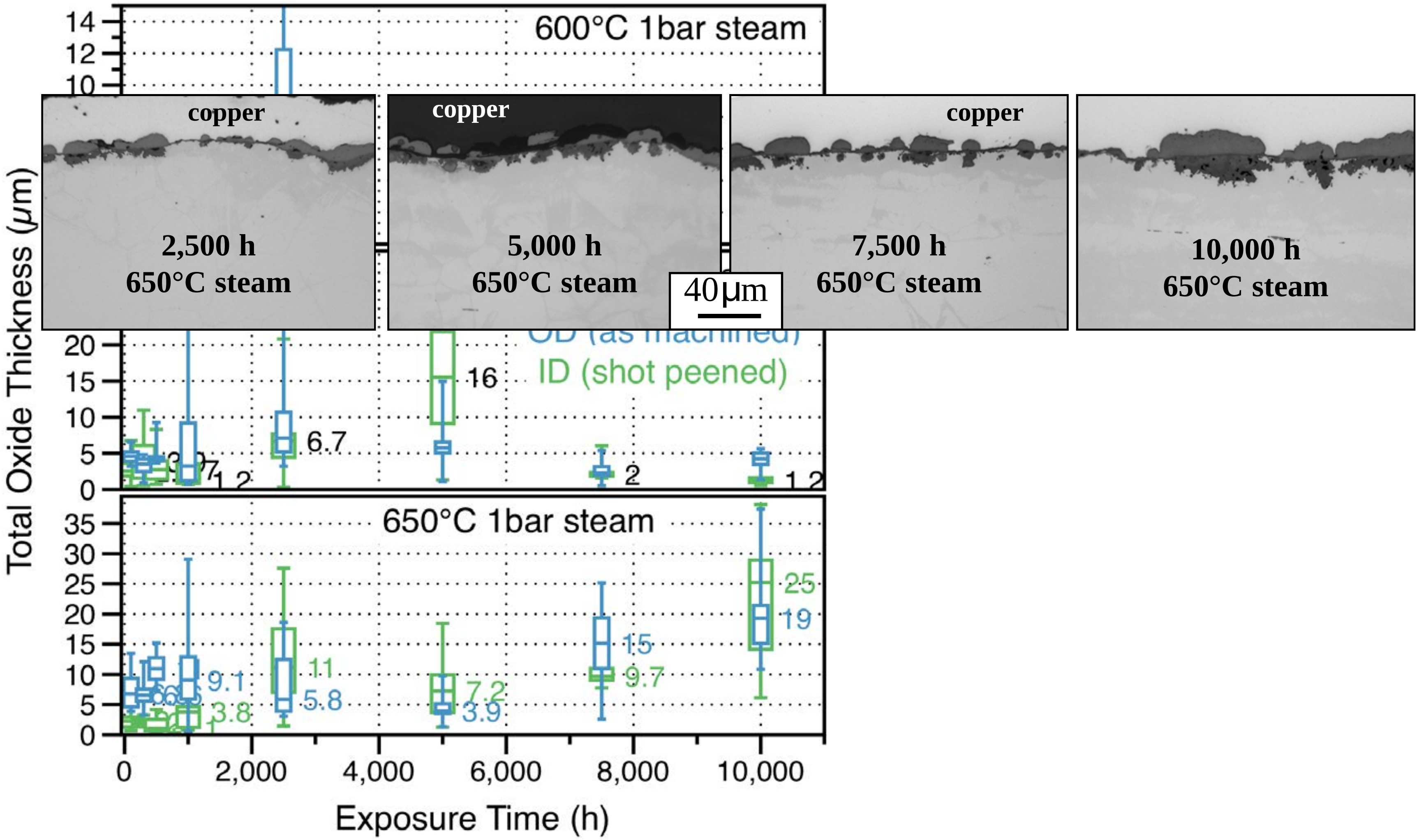


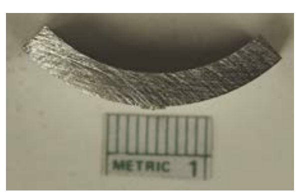


600°-625°C
- thin ID oxide
- similar thin OD oxide

Losing benefit at 650°C ?

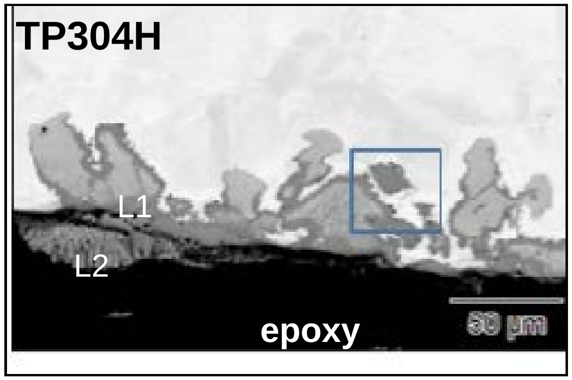
Oxide thickness measurements from polished sections

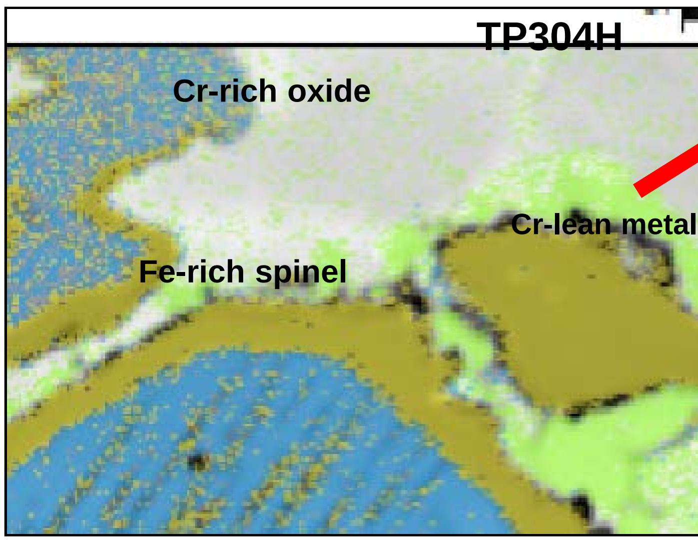


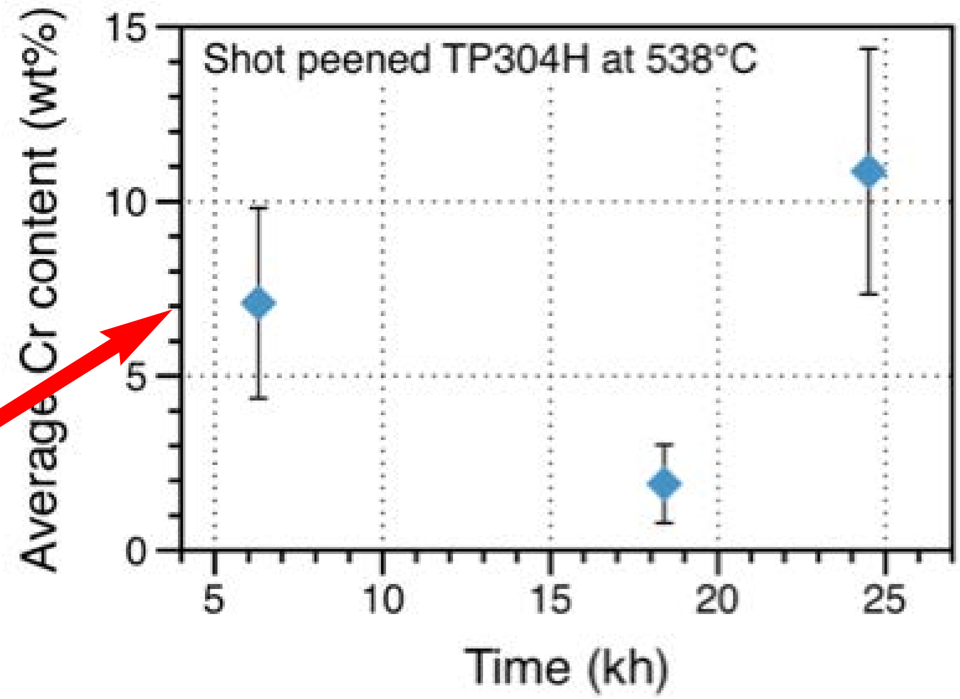


Previous: high Cr depletion beneath scale

Shot peened TP304H: 24,500 h, 538°C steam (EPRI)





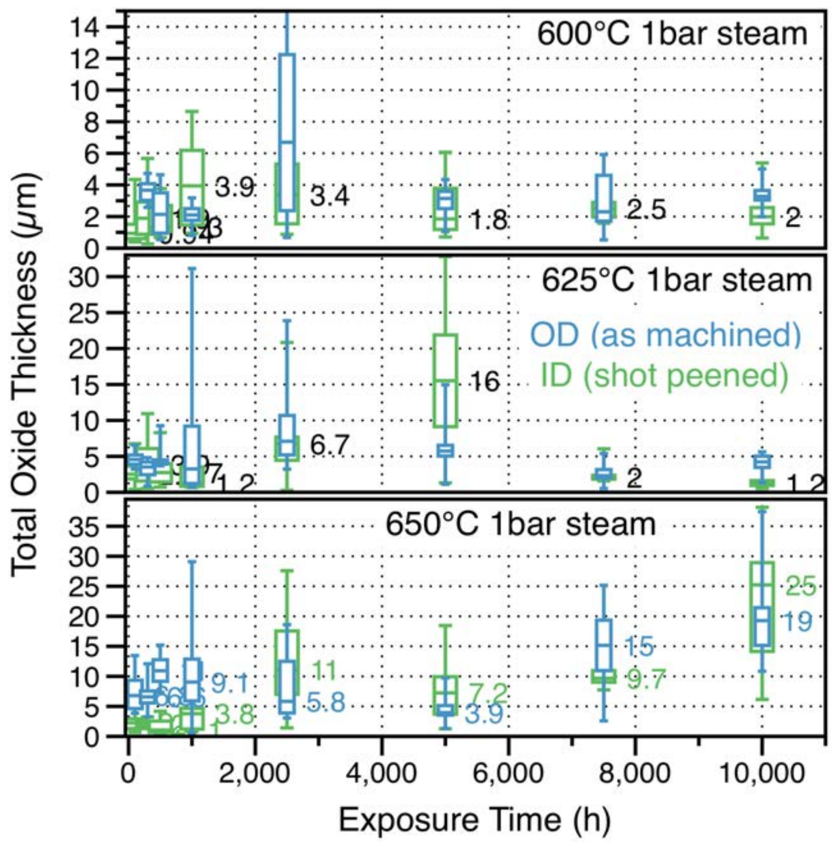


Models: 10-15%Cr is susceptible to form FeO_x

Higher Cr depletion here: unstable situation

- any disruption in Cr-rich oxide likely to grow nodule

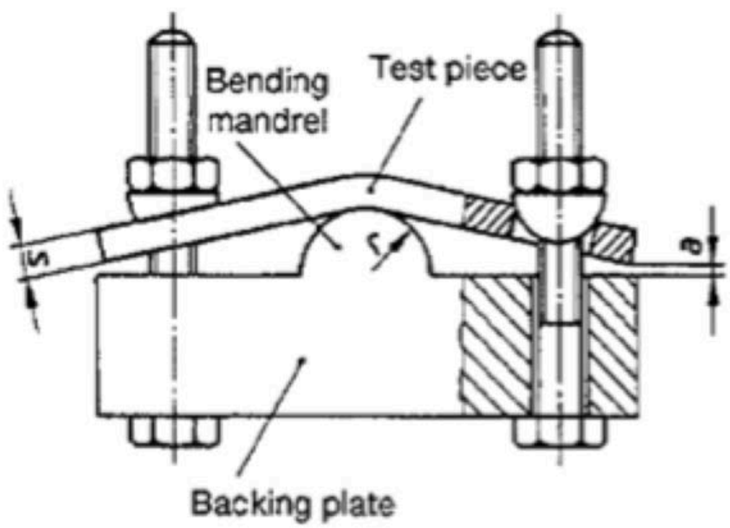
Wrapping up Task 1



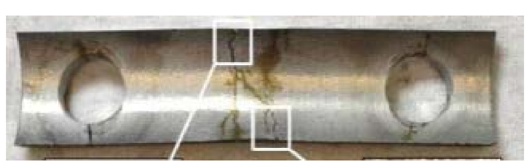
- Last SP specimens running stop at 15,000 h
- Second SP tube obtained specimens running to 7,500 h
- 2nd set alloy specimens running to 10,000 h
- More characterization improved image statistics hardness vs. time at temp. Cr depletion (EPMA)

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



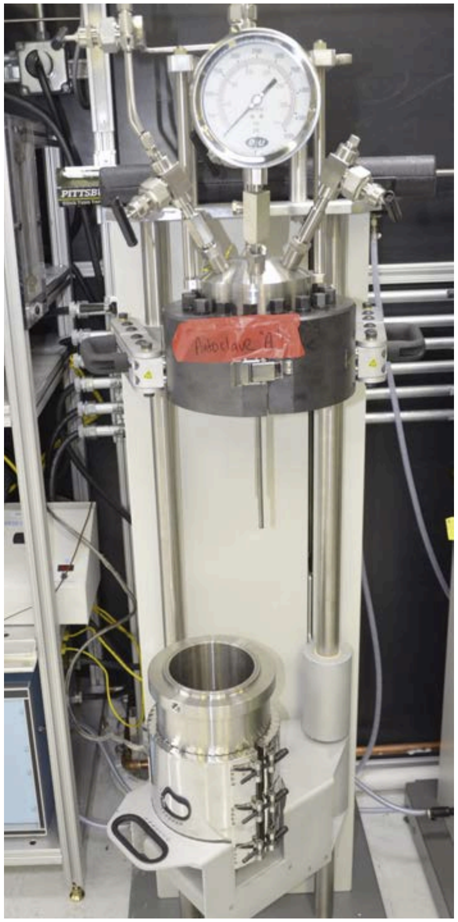
Alloy	Test Condition			
	As Received		Normalized	
	Aerated	Deaerated	Aerated	Deaerated
T23	☐	☐	☑	☐
T24	☐	☐	☑	☐
T92	☐		☑	☐

☐ Did Not Crack
☑ Cracked

Water loop: next level of testing

Simulate actual fossil environments
and controlled pO_2 levels

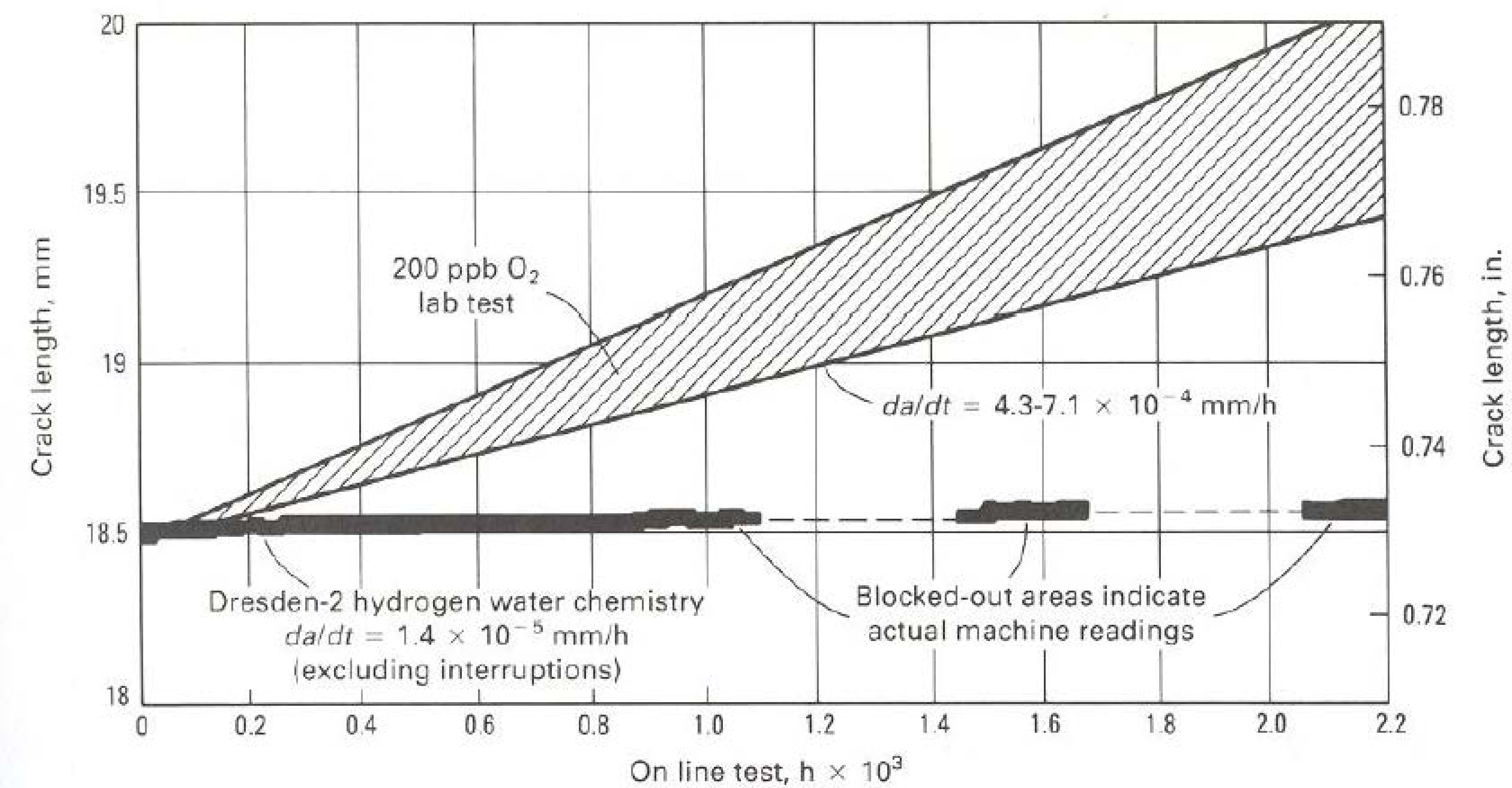
water control system
- based on GE systems



200°C autoclave

Qualitatively: O affects cracking

Example: 304SS from nuclear industry



Source: B. M. Gordon 1986 ANS Proc. Operab. Nucl. Power Syst. in Normal & Adverse Env.

Current & Future SCC Testing

FY14: Grade 315 9(3Cr) also susceptible

FY15: loop under construction

FY16:

- testing at 150ppb O_2 ("oxygenated" water)
- second O_2 level based on 1st results

Future:

More precise crack growth monitoring

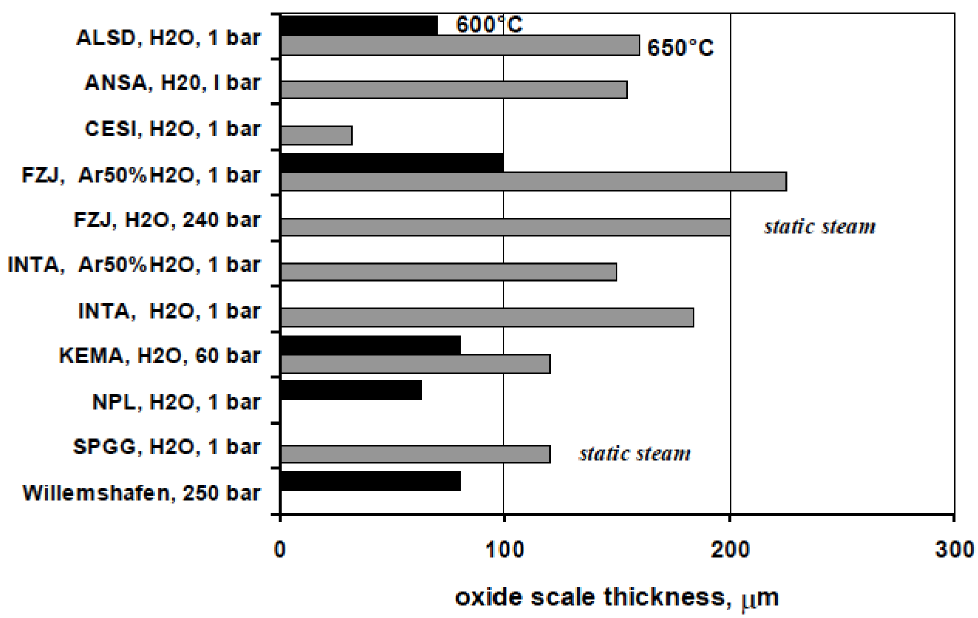
Are there critical temperature and hardness values for susceptibility?

Are there solutions for Grades 23 and 24?

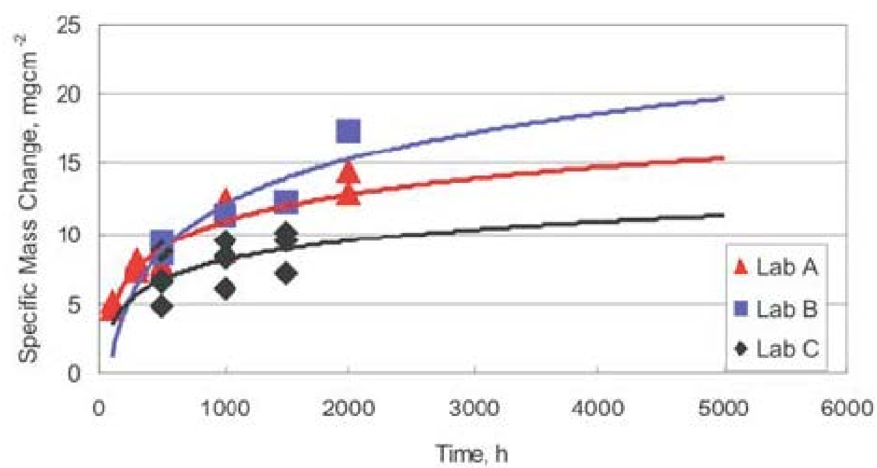
Task 3: effect of pressure

- steam oxidation field-lab disconnect
  field (high pressure) ≠ lab (typically 1 bar)
- what is the effect of pressure?
  need uniform test procedure

Saunders 2006 MSF, etc.
P92, 1000h, 600°-650°C

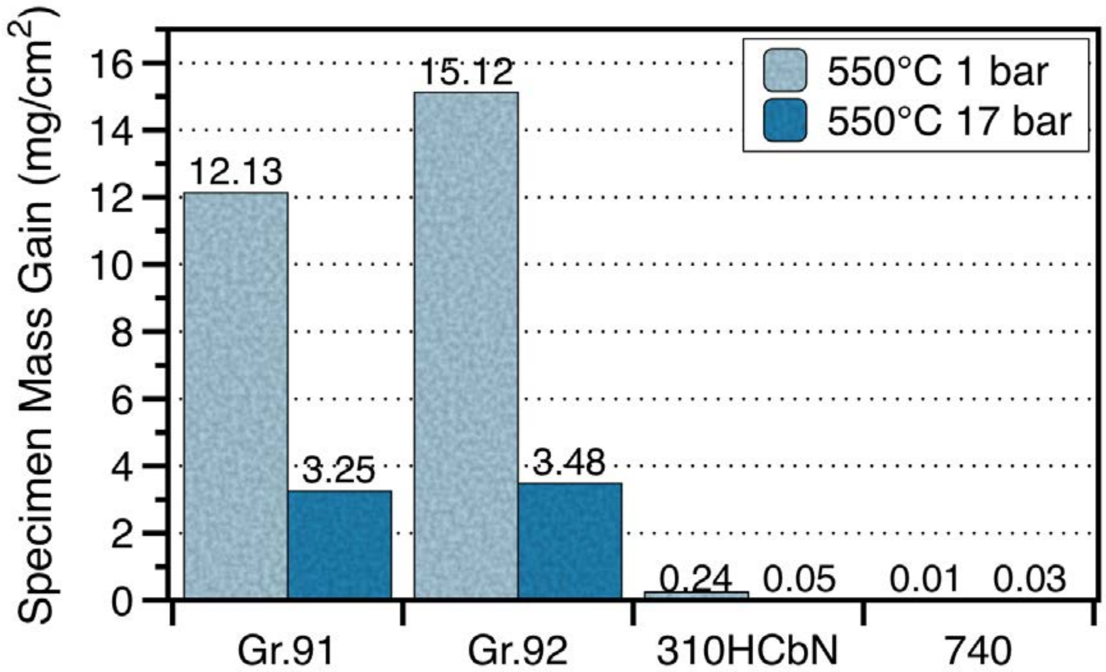


Fry 2006 MHT
T92, 600°C, "steam"



Initial results in 550°C steam

5,000 h exposures (10 x 500-h cycles)



Higher mass gain in 1 bar steam

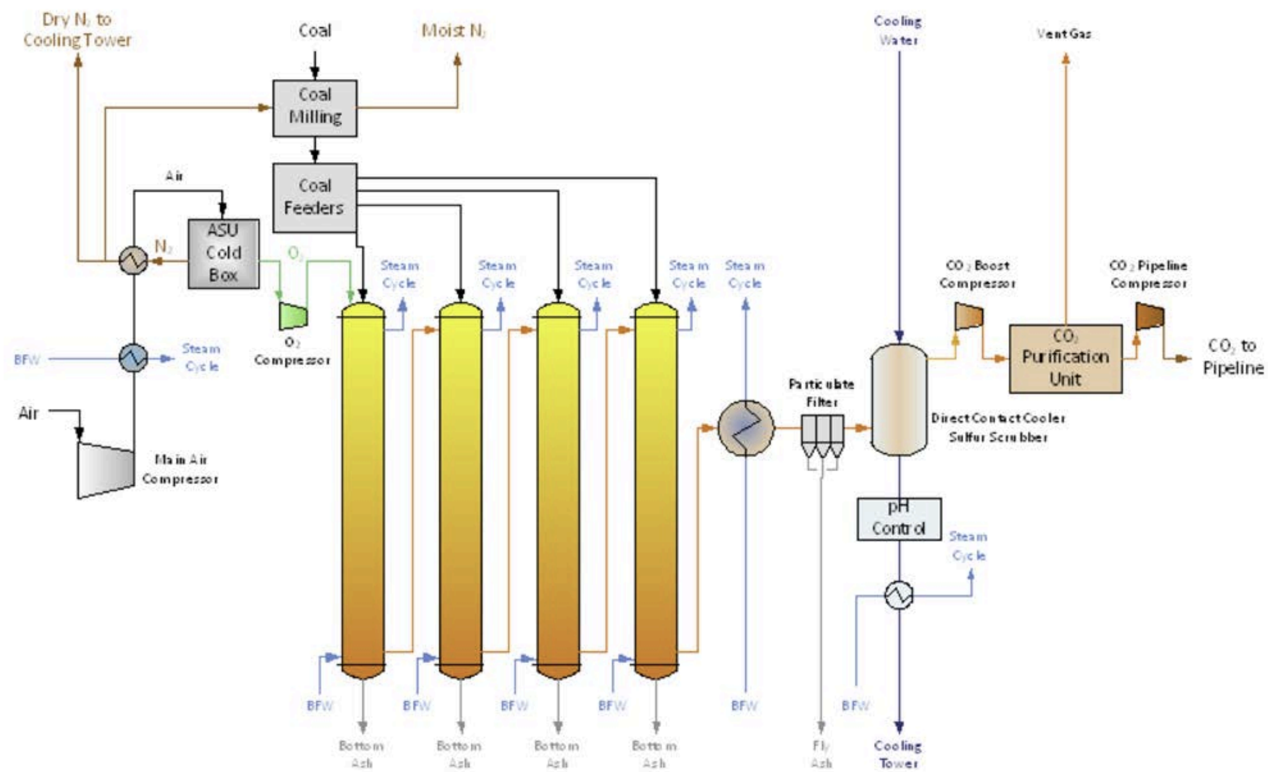
oxygen contamination (?)

Two tests in two different test rigs

what did we learn?

Interest in P effect for SPOC

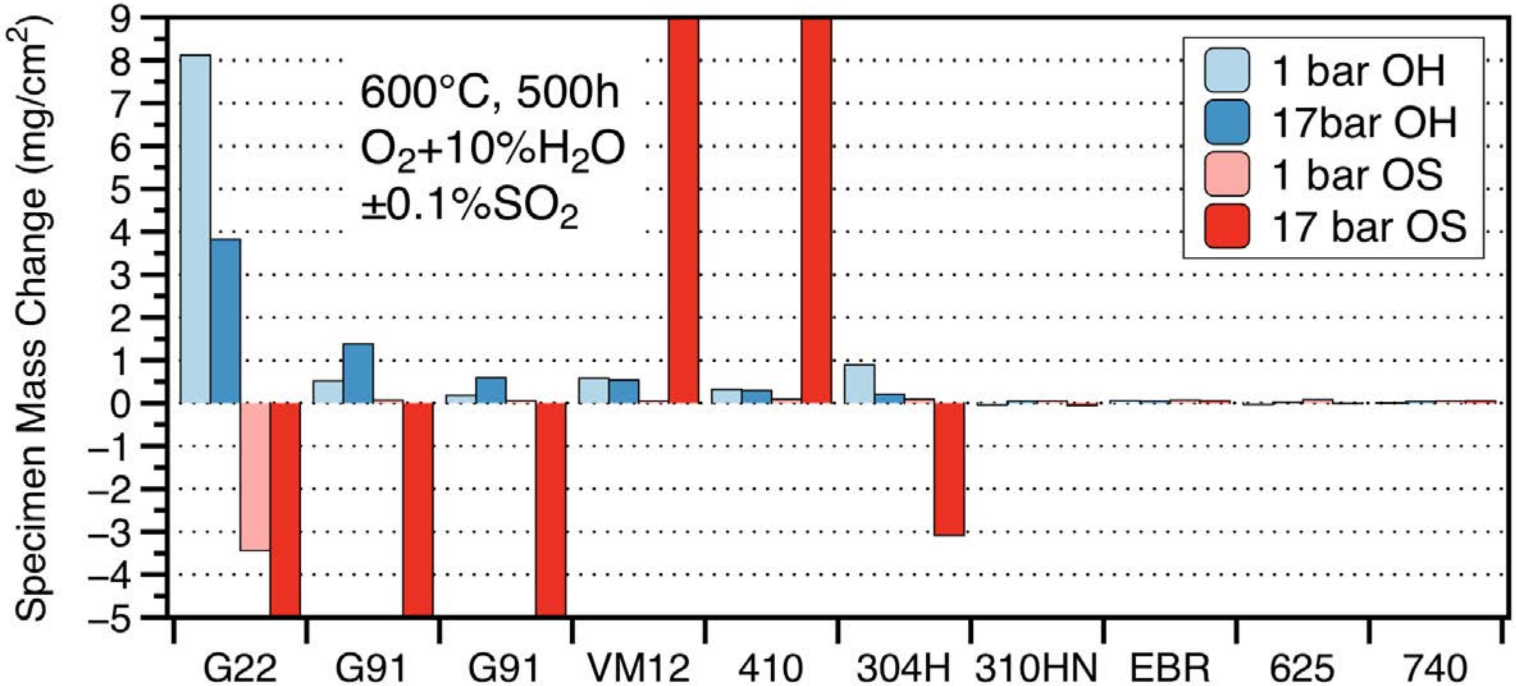
Staged-Pressurized Oxy-Combustion
(Pressure effect on fireside)



Project led by Washington University (St. Louis)
R. Axelbaum and B. Kumfer

Initial ORNL study of pressure

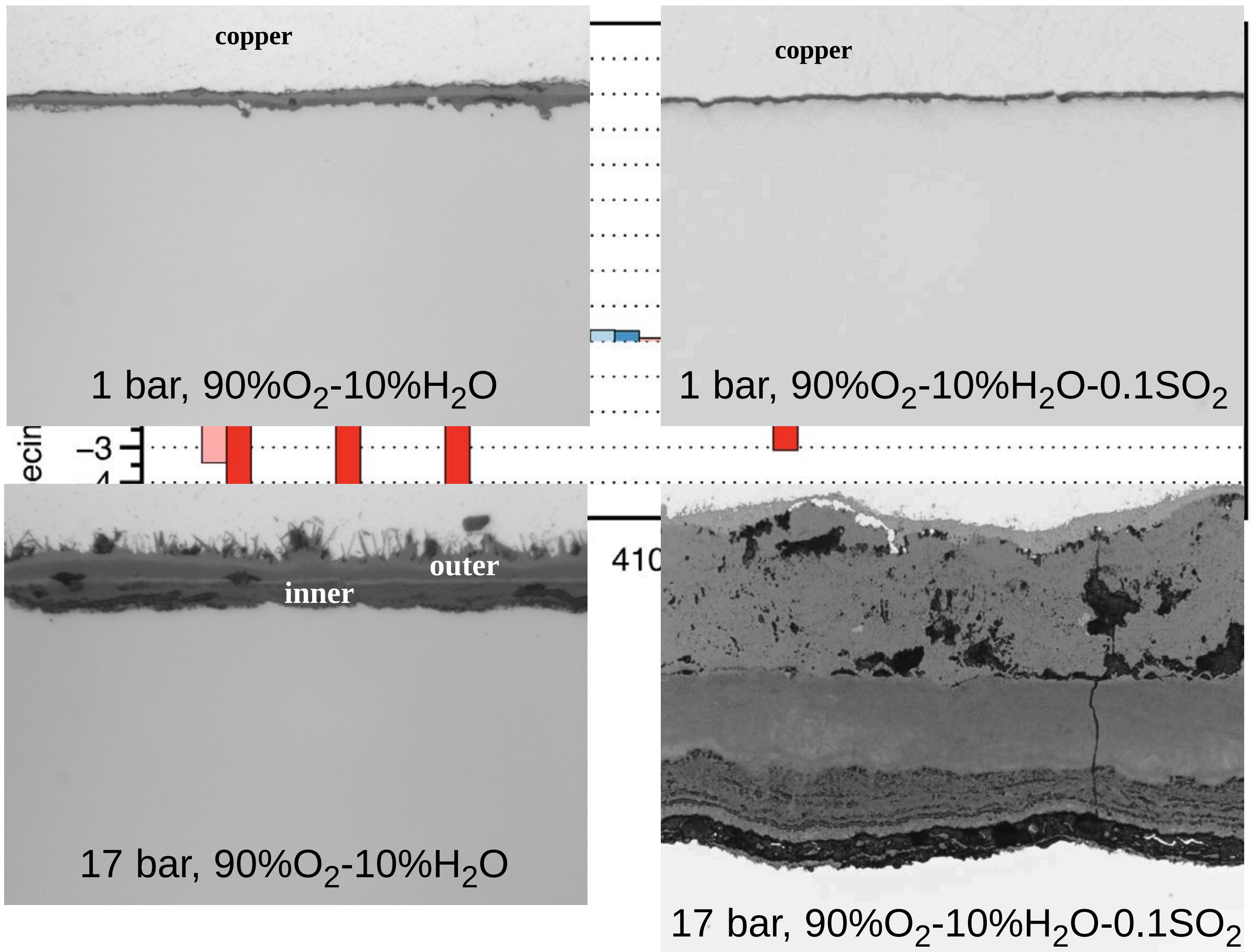
FEAA120: SPOC materials study: 500h



600°C	1 bar	90%O_2-10%H_2O (OH)
	17 bar	90%O_2-10%H_2O
	1 bar	90%O_2-10%H_2O-0.1%SO_2 (OS)
	17 bar	90%O_2-10%H_2O-0.1%SO_2

Initial ORNL study of pressure

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



Summary

Corrosion task addressing “real-world” issues

1. Quantify shot-peening benefit on 304H
   - completed 10 kh specimens

2. SCC issue in current waterwalls
   - next step is testing in water loop

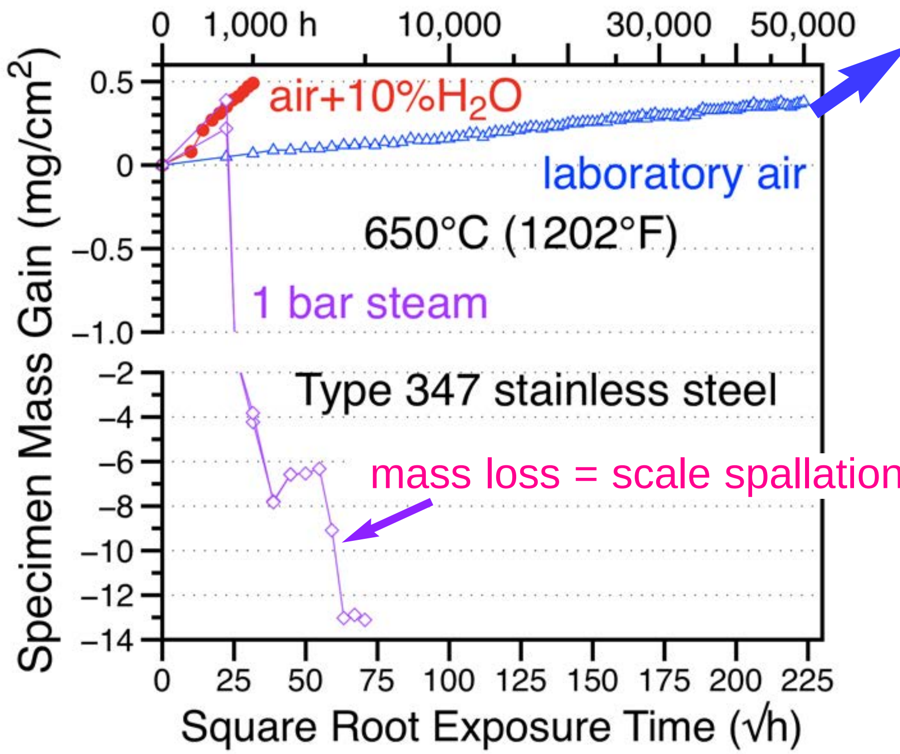
3. Effect of pressure
   - 1st exposure: 550°C steam
   - 2nd project for SPOC

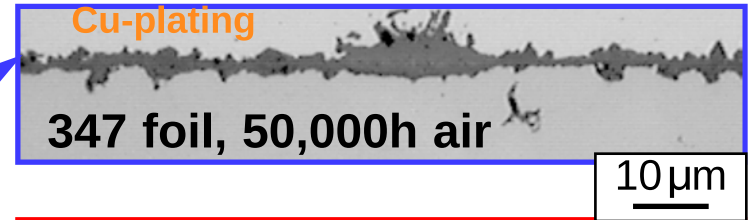
Future possibilities:
   - Corrosion issues with dry cooling (?)

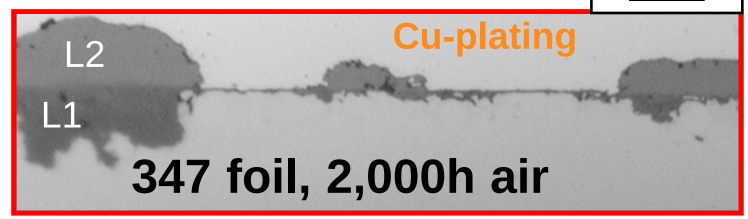
CLEAN COAL.
COOL.

H_2O drives steels crazy

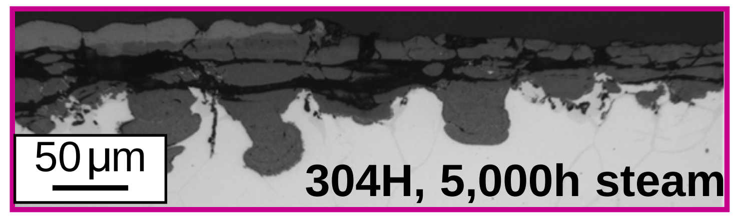
Steam or exhaust gas accelerate oxidation





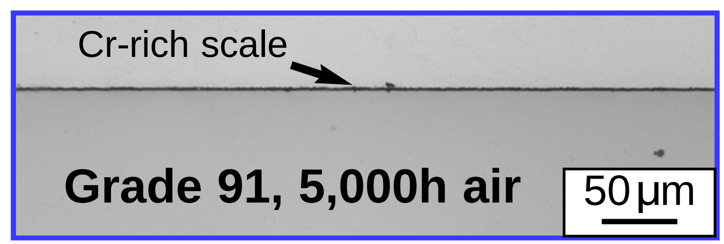


347: Fe-18Cr-10Ni+Nb



650°C, 1202°F

91: Fe-9Cr-1Mo

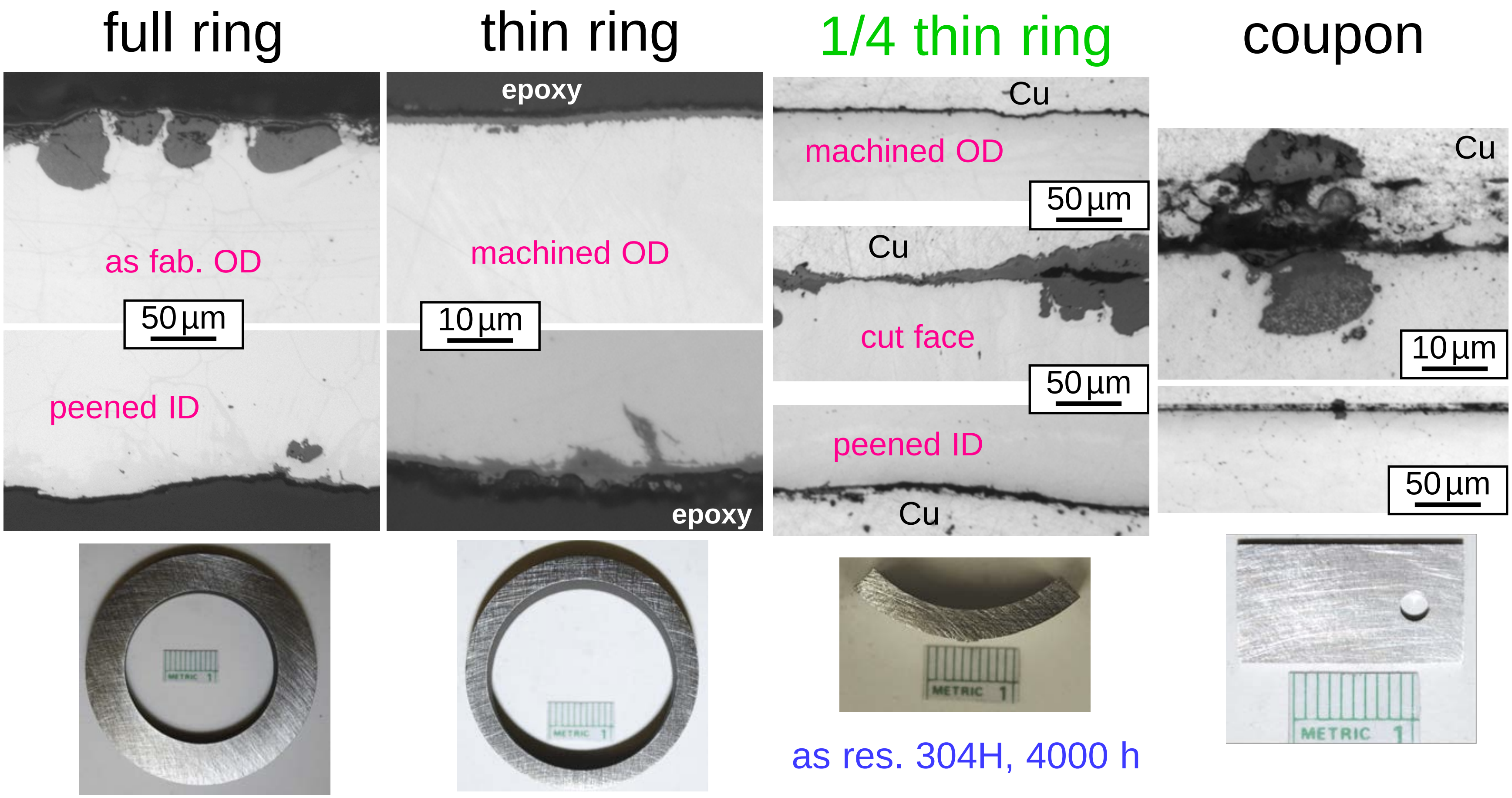


Laboratory air - thin, Cr-rich oxide

+ H_2O - thick, Fe-rich oxide

Specimen type showed minor effects

peened 304H 650°C 17bar steam 4,000h



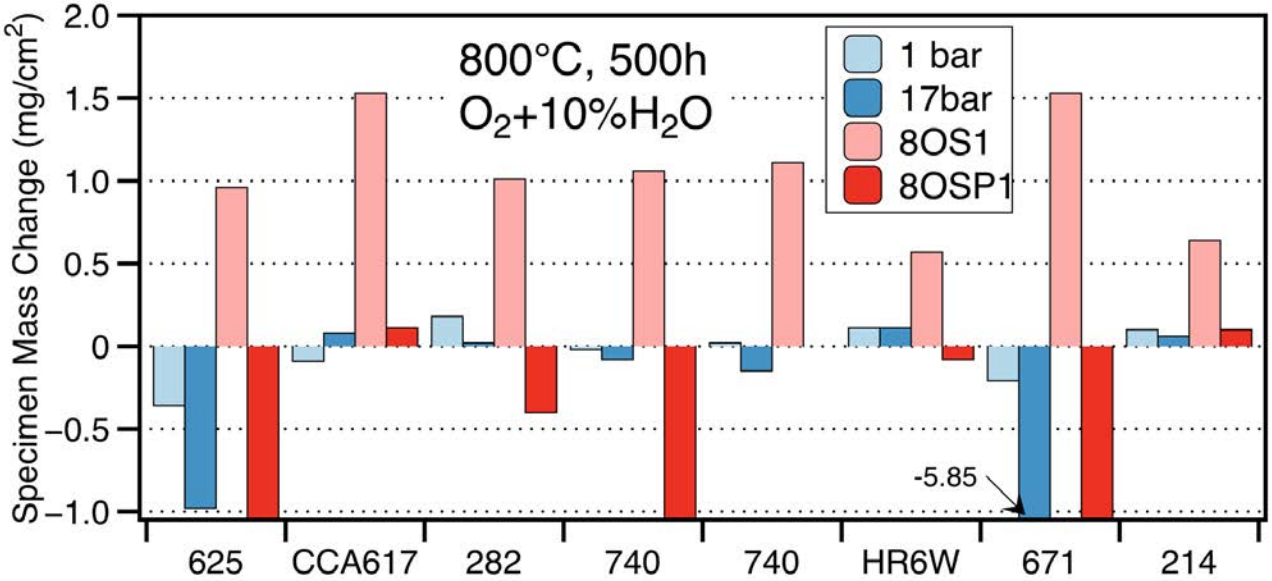
Peened ID: no effect of specimen geometry

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

- cold work due to machining similar to peen-

Phase 1: smaller mass changes for Ni-base alloys at 800°C

Side-by-side reaction tubes: 1 + 17bar, 90%O_2-10H_2O



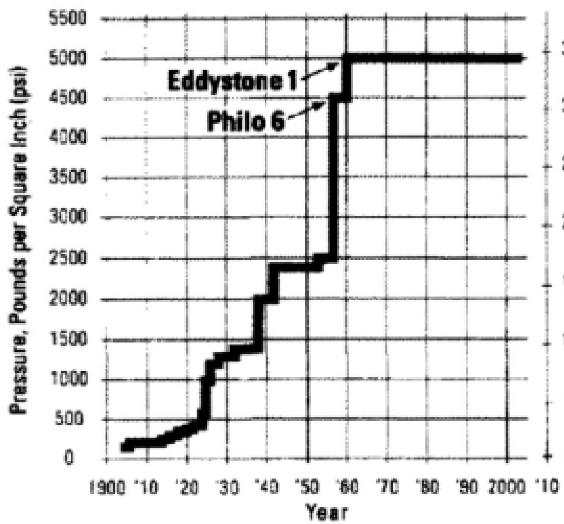
Specimens

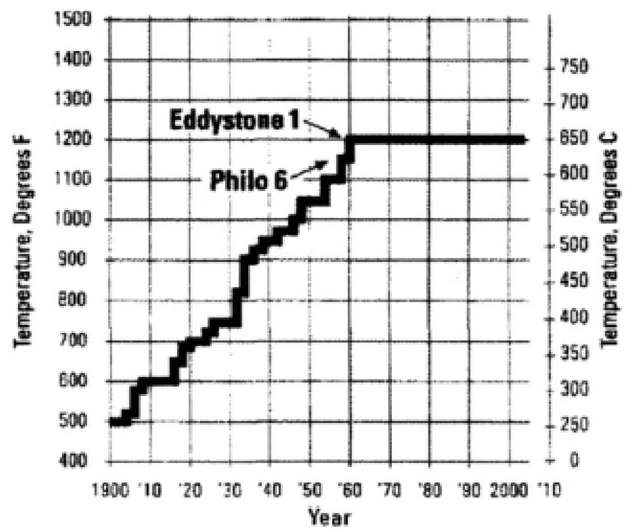
Ultimate goal is to marry Oxy + A-USC

"least regret" CO_2 strategy: higher efficiency

A-USC: 760°C (1400°F) + 34.5 MPa (5000psi)

(Advanced ultra-supercritical)





Henry MHT 2007
(Alstom/CE)

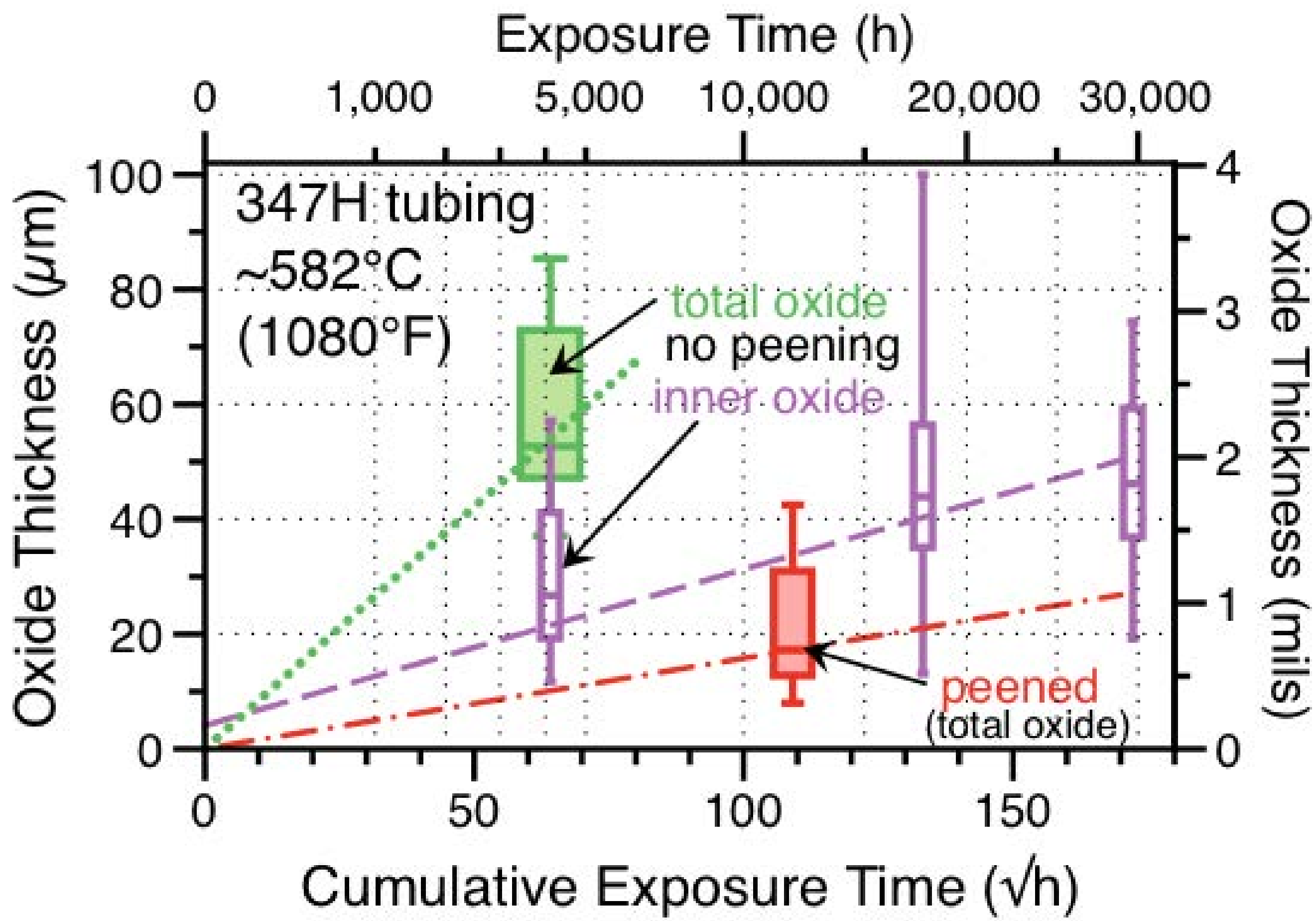
History: 1960 - the year progress stood still

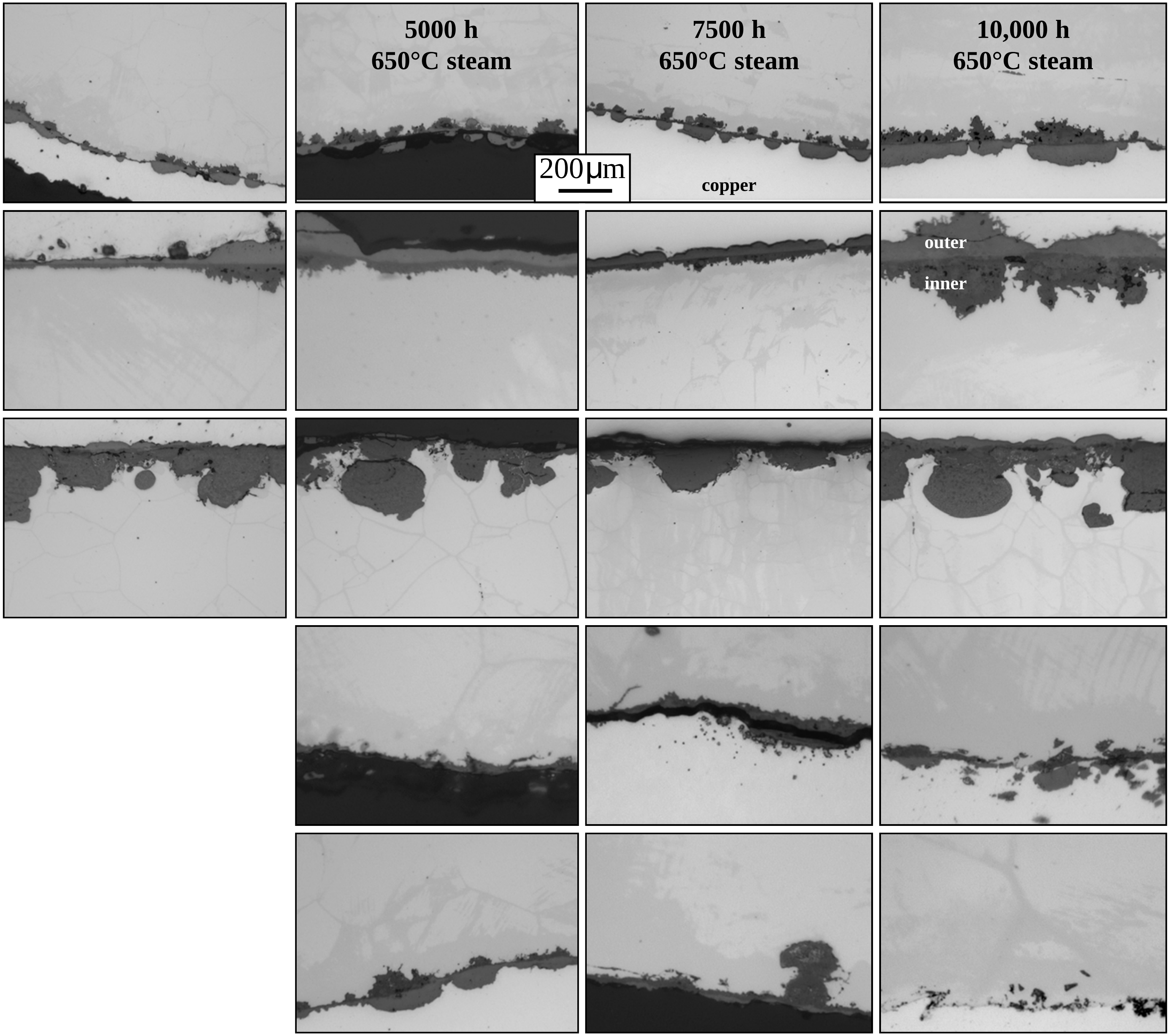
Eddystone (1960): 654°C/36.5MPa (1210°F/5300psi)
settled for 613°C/34.5MPa (1135°F/5000psi)

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

Prior work with EPRI

Characterizing field exposed shot-peened tubes




5000 h
650°C steam
7500 h
650°C steam
10,000 h
650°C steam
200 μm
copper
outer
inner

Range of commercial & model alloys

measured by inductively coupled plasma analysis and combustion analysis

Alloy chemical compositions (weight %)

Alloy	UNS#	Fe	Cr	Ni	Mo	W	Mn	Si	C	N	Other
Gr.22	K21590	95.5	2.3	0.2	0.9	<	0.6	0.1	0.14	0.01	0.2Cu
Gr.33											
Gr.91	S90901	89.7	8.3	0.1	0.9	0.01	0.3	0.1	0.08	0.05	0.3V,0.07Nb
SAVE12	——	83.4	9.6	0.3	0.05	3.0	0.4	0.1	0.11	0.01	2.6Co,0.3V
304H	S30409	69.7	18.9	8.5	0.3	0.04	1.0	1.1	0.05	0.02	0.3Cu,0.1Co
Super304H	S30410	68.0	19.0	8.9	0.1	<	0.4	0.1	0.08	0.11	2.9Cu,0.1Co
347HFG		66.0	18.6	11.8	0.2	0.02	1.5	0.4	0.09	0.06	0.8Nb,0.2Co,0.2Cu
310HCbN	S31042	51.4	25.5	20.3	0.1	0.01	1.2	0.3	0.05	0.27	0.4Nb
800H		43.2	19.7	33.8	0.2	0.02	1.0	0.3	0.08	0.01	0.7Al,0.5Ti,0.3Cu
SAVE25		51.5	22.3	20.0	0.1	1.0	0.7	0.2	0.07	0.22	3.4Cu,0.3Nb,0.2Co
SANICRO25		42.6	22.5	25.4	0.2	3.4	0.5	0.2	0.06	0.21	2.9Cu,0.5Nb,1.4Co
HR120		35.0	24.7	37.6	0.3	0.05	0.7	0.2	0.06	0.21	0.6Nb,0.2Cu,0.1Al
HR6W		23.3	23.4	44.6	0.2	6.3	1.0	0.2	0.07	0.01	0.4Co,0.2Nb,0.1Ti
740	N07740	1.9	23.4	48.2	0.5	<	0.3	0.5	0.08	0.01	20Co,2Nb,2Ti
617(CCA)	N06617	0.6	21.6	55.9	8.6	0.09	0.02	0.12	0.05	0.01	11Co,1.3Al,0.4Ti
282	N07208	0.2	19.3	58.0	8.3	<	0.1	0.1	0.06	0.01	10Co,1.5Al,2.2Ti
Fe-15Cr	——	85.1	14.8	<	<	<	<	<	<	<	
Fe-20Cr	——	80.3	19.7	<	<	<	<	0.01	<	<	
Fe-25Cr	——	74.6	25.3	<	<	0.01	<	0.02	<	<	
Fe-30Cr	——	69.7	30.2	<	<	<	<	0.02	<	<	
Fe-40Cr	——	59.6	40.2	0.01	<	<	<	0.09	<	<	

Ni-(18-22)Cr additions of 0-2%Al, 0-2%Ti, 0-20%Co, 0-8%Mo

< indicates below the detectability limit of <0.01%