Corrosion Issues in Advanced Coal-Fired Boilers

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J. Moser, T. Jordan, A. Willoughby, D. McClurg - creep testing

T. Jordan - metallography

T. Lowe - SEM, image analysis

D. Leonard - EPMA, image analysis

FY10-13 Tasks & Timeline

Goal: Mechanistic understanding to enable accurate oxy-fired corrosion modeling

1. Steam/gas corrosion (no ash)
2. Fireside corrosion (with ash)
3. Environment-mechanical property effect
   - effect of steam on creep (Dryepondt)

A. ~600°C ferritic/martensitic steels (FY10-12)
   - creep testing at 650°C (FY12-13)

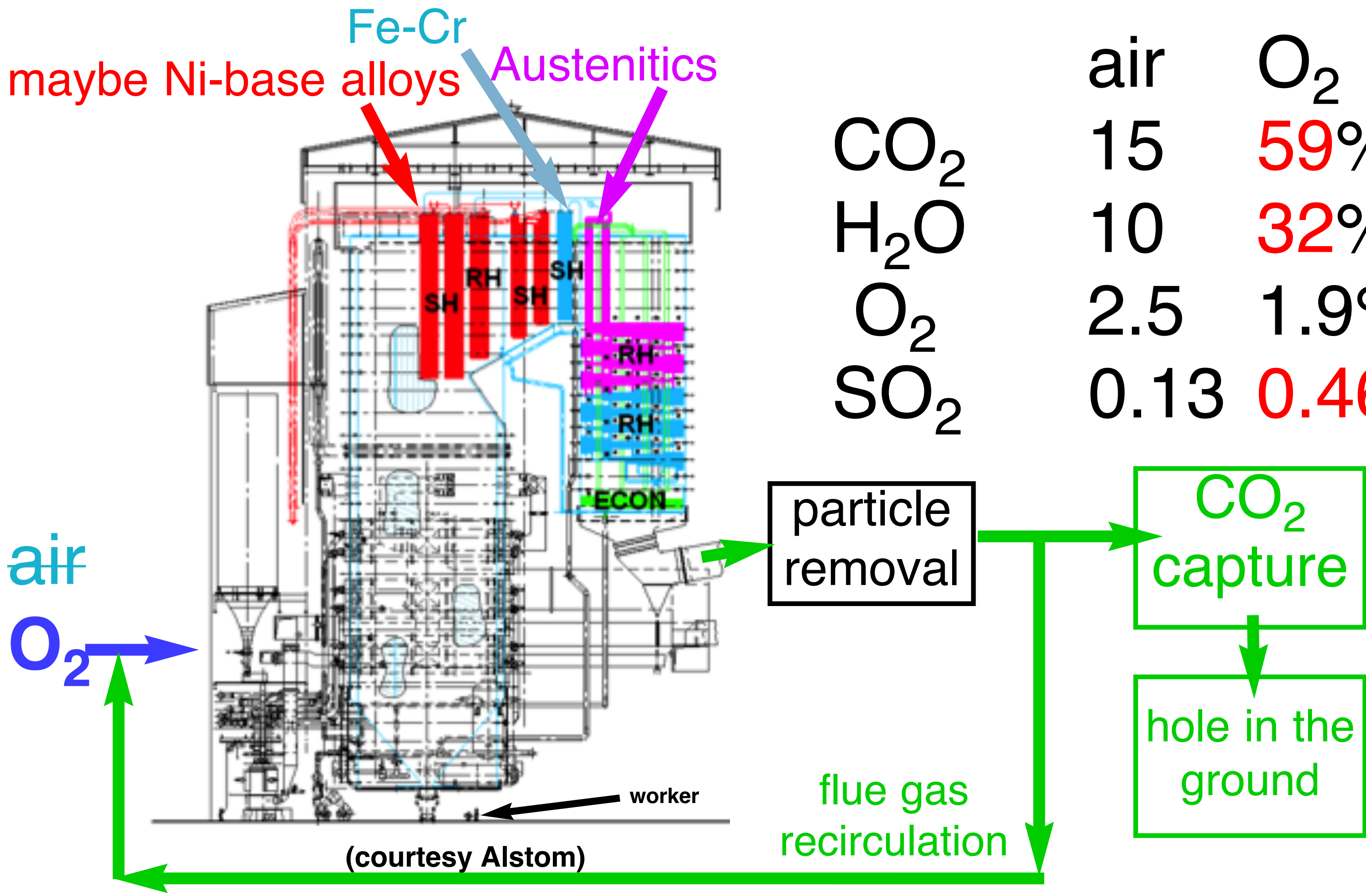
B. ~650°-700°C austenitic steels (FY11-13)

C. ~700°-750+°C Ni-base alloys
   - creep testing at 800°C (FY11-12)
   - ash testing 600°-800°C (FY12-13)

Advanced: Oxy-firing to facilitate CO_2 C+S

Retrofit current plants or advanced 760°C (below)

	air	O_2
CO_2	15	59%
H_2O	10	32%
O_2	2.5	1.9%
SO_2	0.13	0.46%



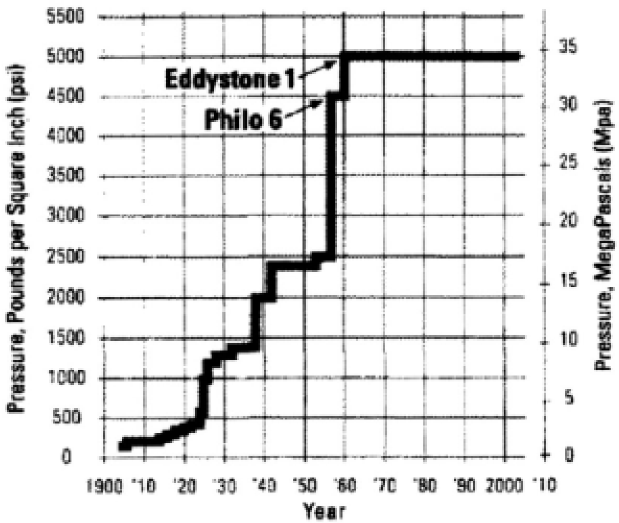
Several studies published by Alstom (Bordenet)

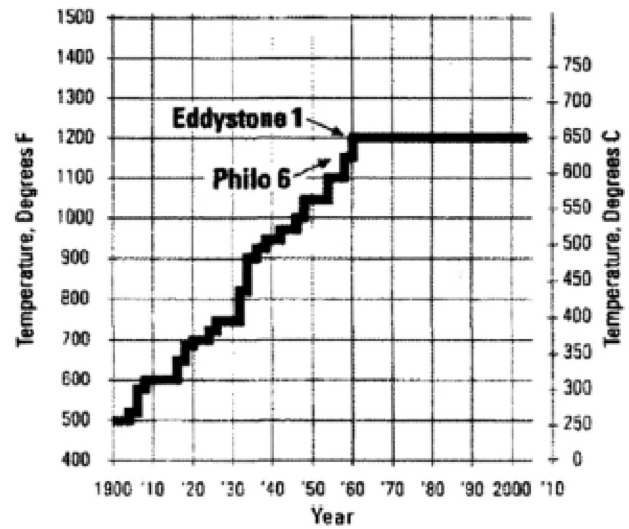
What is the effect of oxy-firing on fireside corrosion?

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)

Corrosion testing with ash

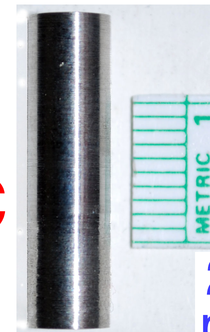
Determine effect of Temp., CO_2, H_2O, SO_2...

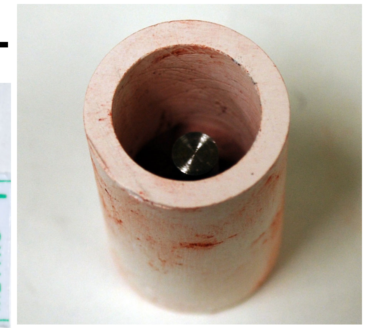
Synthetic ash: 30%Fe_2O_3-30%Al_2O_3-30%SiO_2-5%Na_2SO_4-5%K_2SO_4

Gas: N_2-CO_2-H_2O-O_2-SO_2

Temperature: 600°-800°C

Time: 500 h

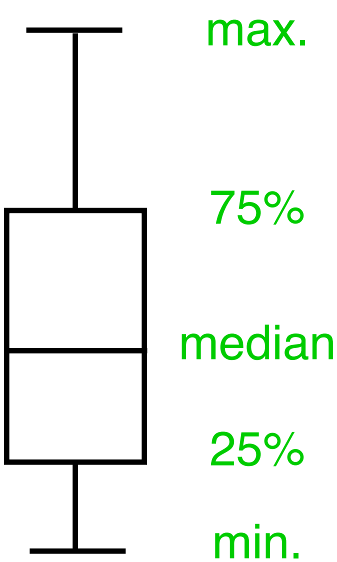


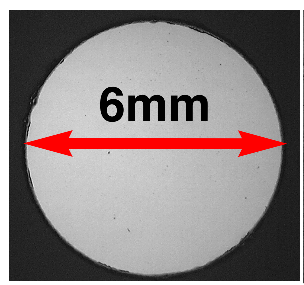


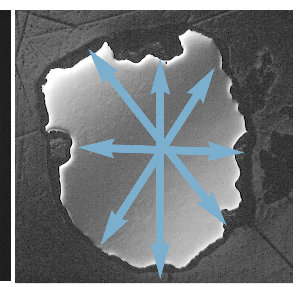
25x6mm rod in porous alumina

Box and whisker plots

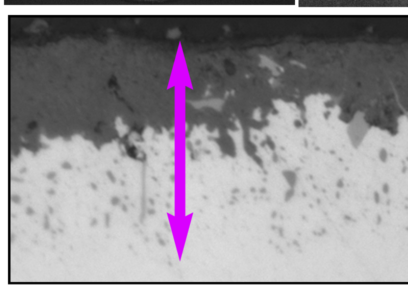
oxide thickness or metal loss (128)







remaining metal (radii)



oxide thickness = scale + internal oxide

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%

Oxy-firing is complicated

Bordenet (Alstom) published worst case
- hot flue gas recycle with no cleaning
  (unlikely, flue gas cools oxy-fired boiler)
- options: cooling flue gas + de-sulfurization

	air-fire	O_2-fire (hot)	(w/Flue Gas De-S) (warm)	(cold)
CO_2	15	61%	61%	83%
H_2O	10	30%	30%	10%
O_2	3	3%	3%	3%
SO_2	0.15	0.45%	0.15%	0.15%

500h: Oxy not worse

“air-firing” open box (128 radii)

“oxy-firing” shaded box

“Oxy-firing” did not consistently increase metal loss

SAVE12+304H baseline data

Most protective: 310HCbN, 740 and Fe-30Cr do not show peak at 700°C:

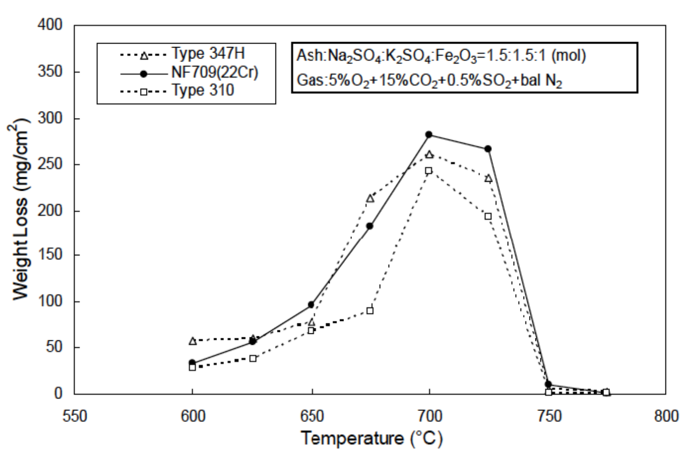
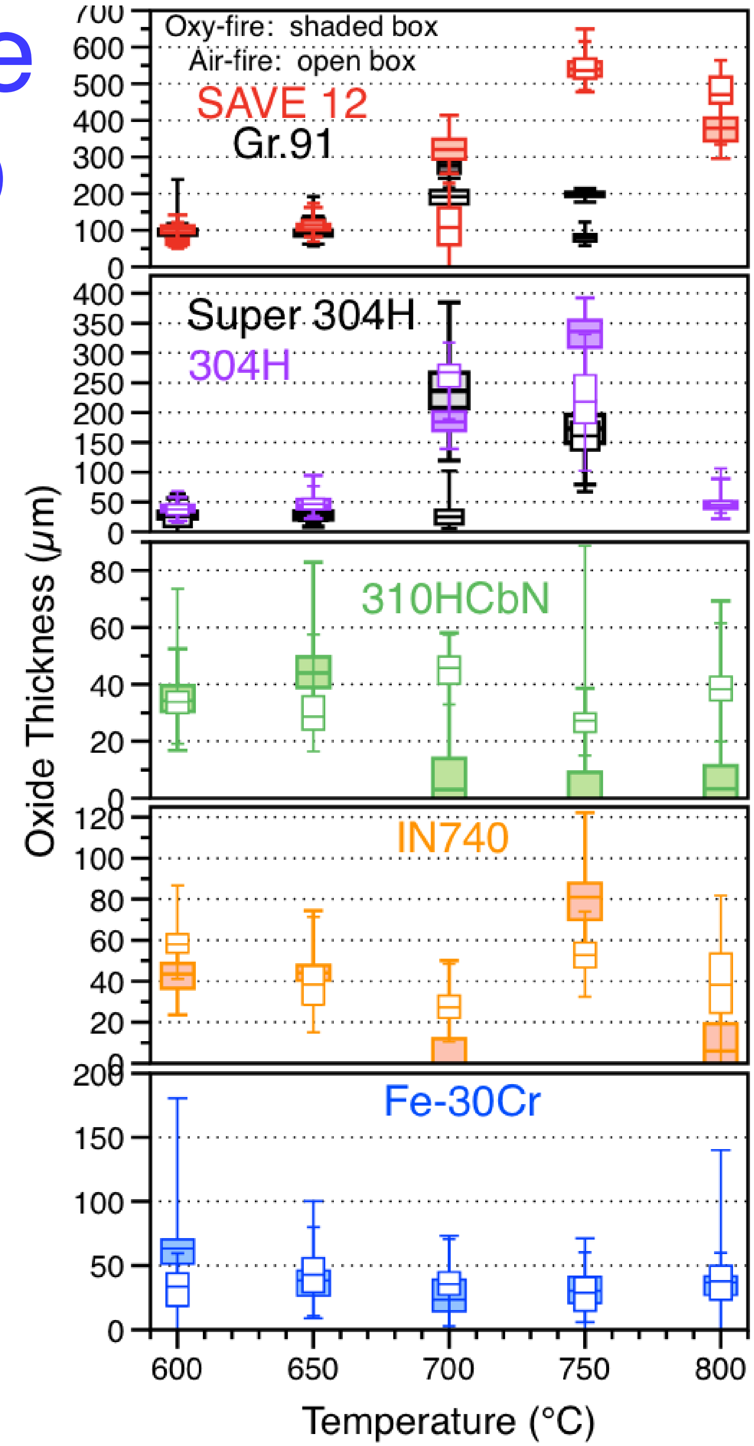
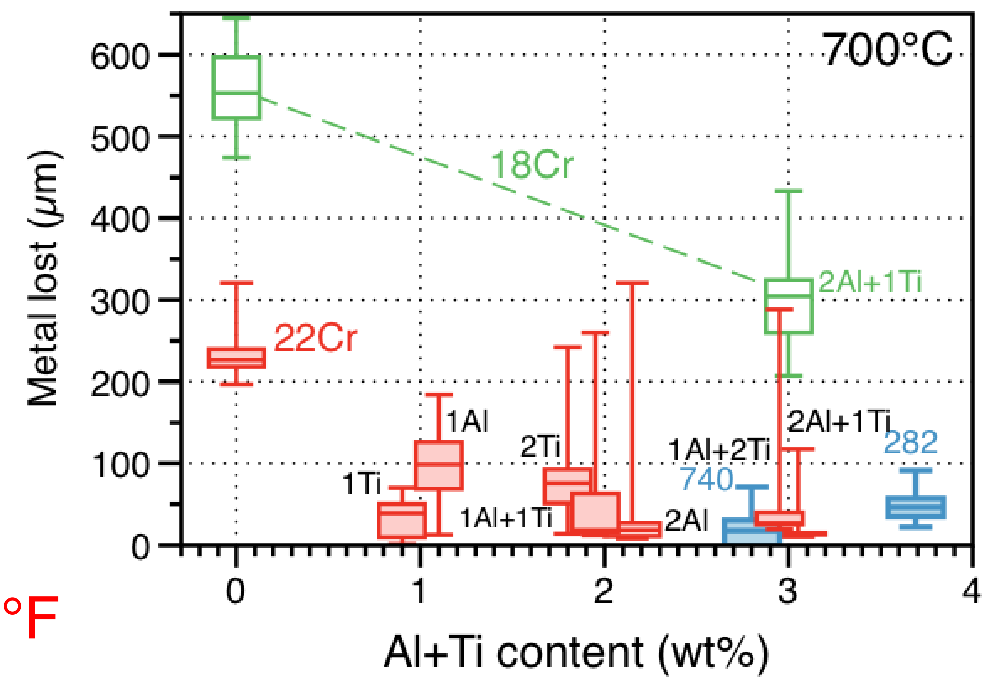


Fig. 3-7 Hot corrosion of NF709 in simulated coal ash environment.
（Test duration：100h）



Model NiCr+Al,Ti: Cr key, Ti,Al good

Coupons: 500 h in synthetic coal ash + “oxy-firing” gas



700°C, 1292°F

1.5mm thick coupons (not rods)

282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti

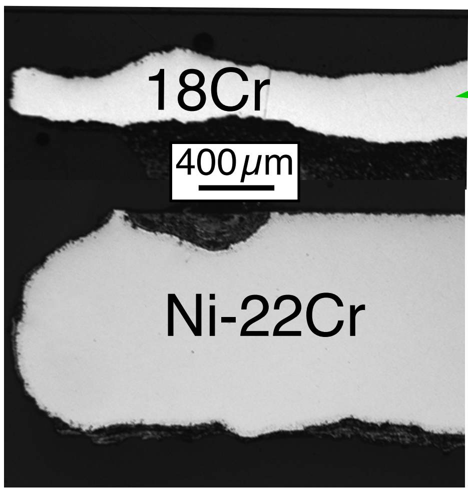
740: 48Ni-23Cr-20Co-0.5Mo-0.8Al-1.5Ti

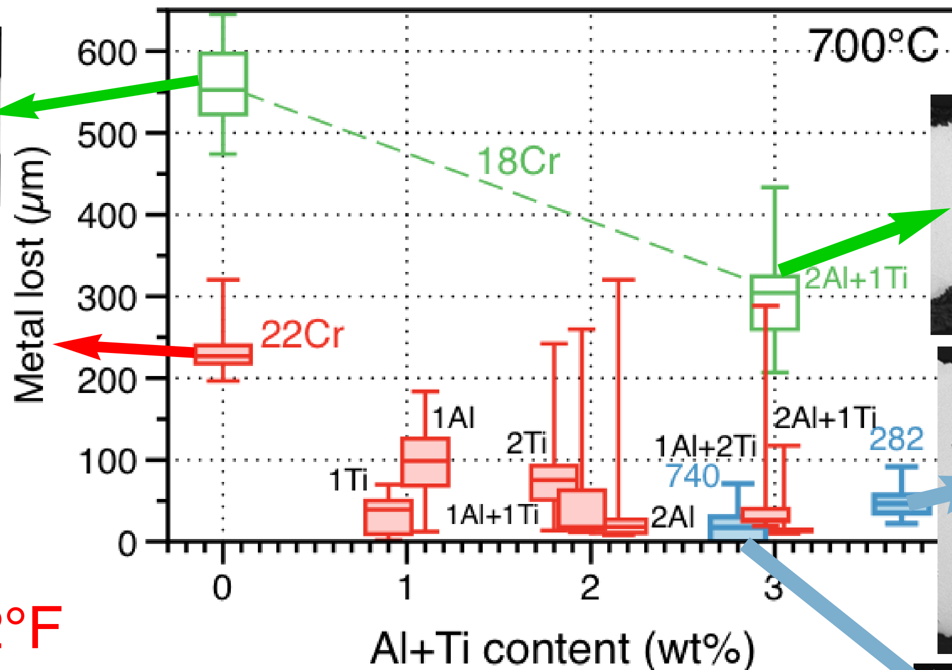
Al and Ti additions do not explain 740/282 performance

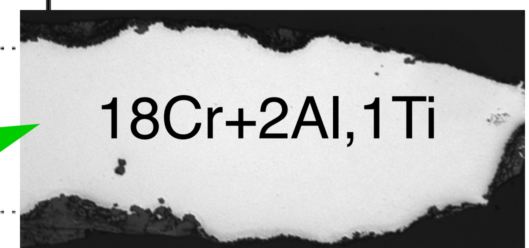
Model NiCr+Al,Ti: more sensitive to Cr

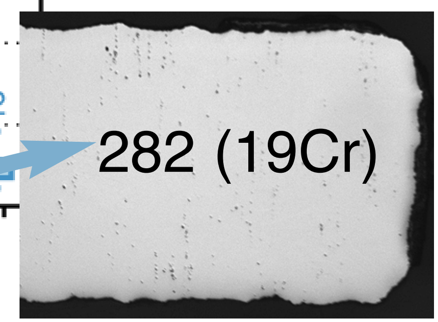
Coupons: 500 h in synthetic coal ash + “oxy-firing” gas

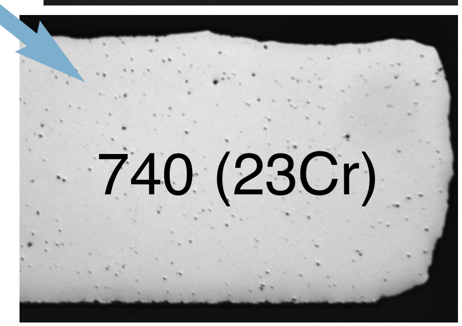
Pint, EPRI Conf. Oct. 2013











700°C, 1292°F

1.5mm thick coupons (not rods)

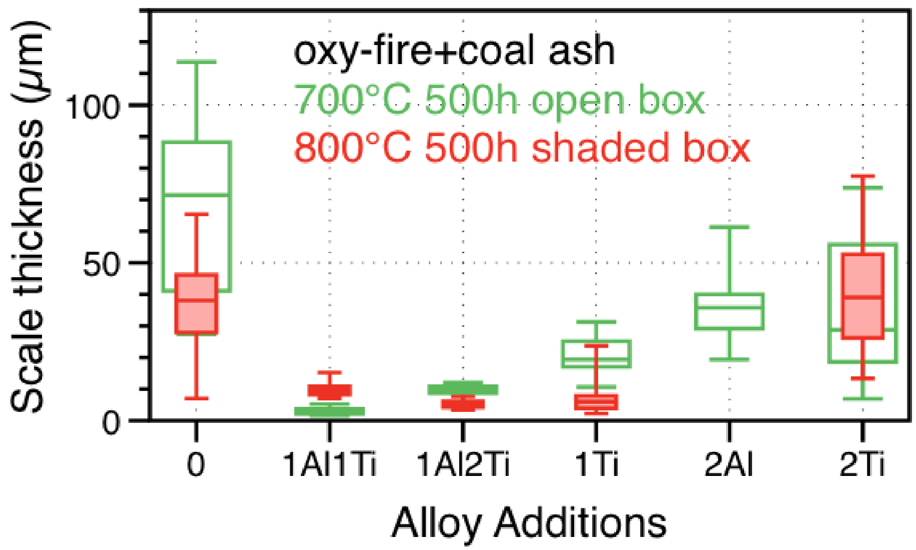
282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti

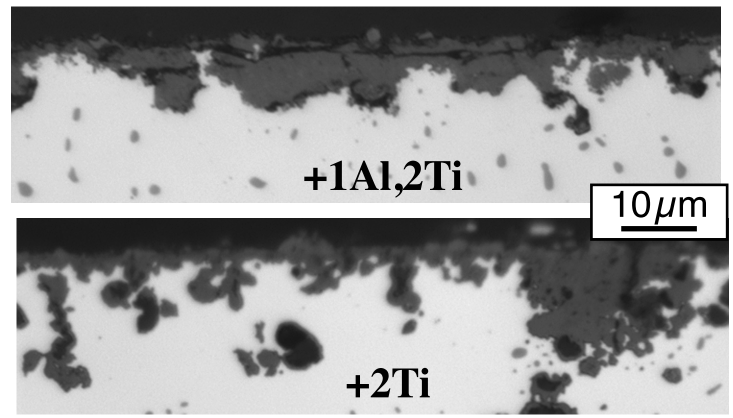
740: 48Ni-23Cr-20Co-0.5Mo-0.8Al-1.5Ti

Al and Ti additions do not explain 740/282 performance

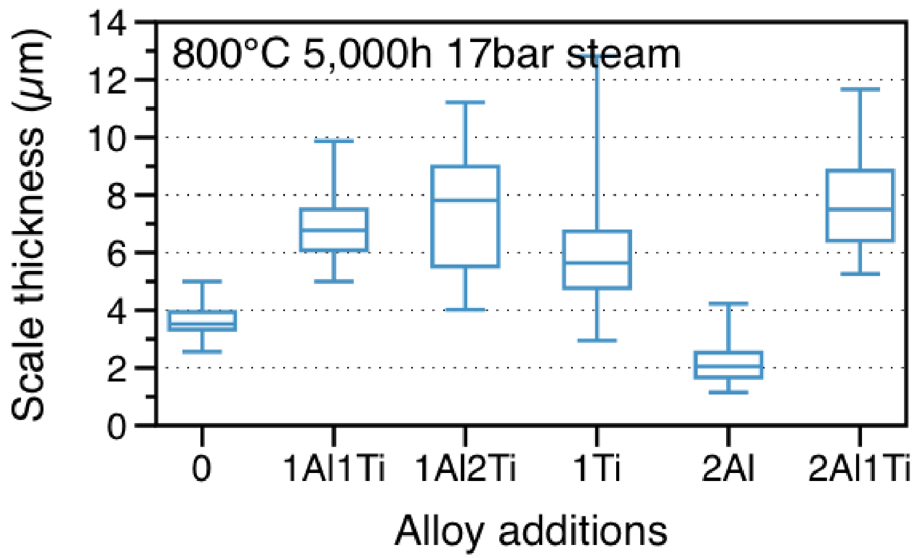
Ti: thicker scale in steam

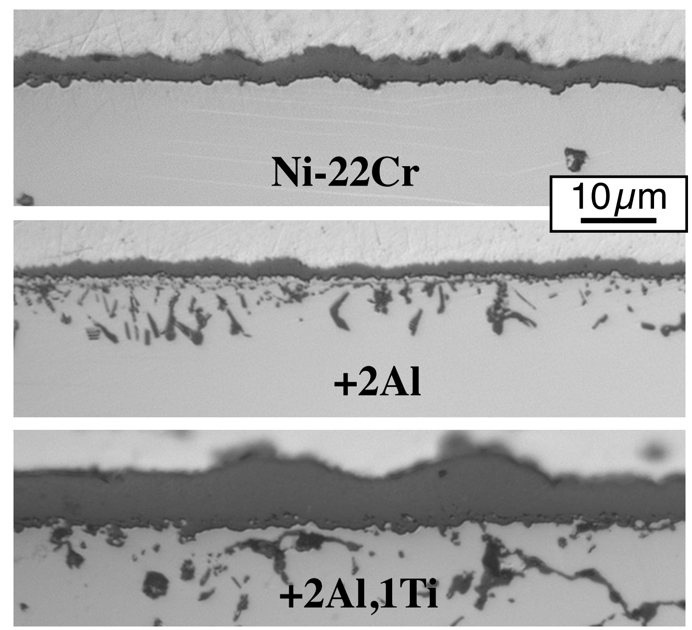
Barrier layer prevents direct metal-ash contact





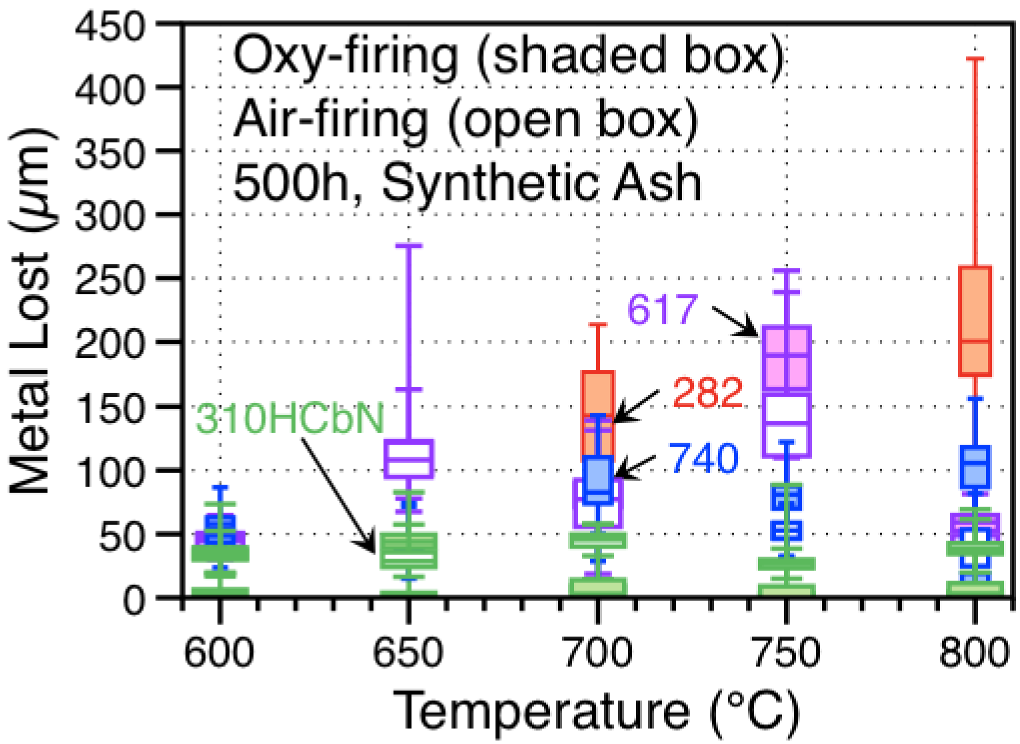
Pint, NACE 2014





Range of behaviors for Ni-base alloys

But none as good as Fe-base 310 stainless steel



282: 58Ni-19Cr-10Co-8Mo
740: 48Ni-23Cr-20Co-0.5Mo
617: 54Ni-22Cr-10Co-9.2Mo

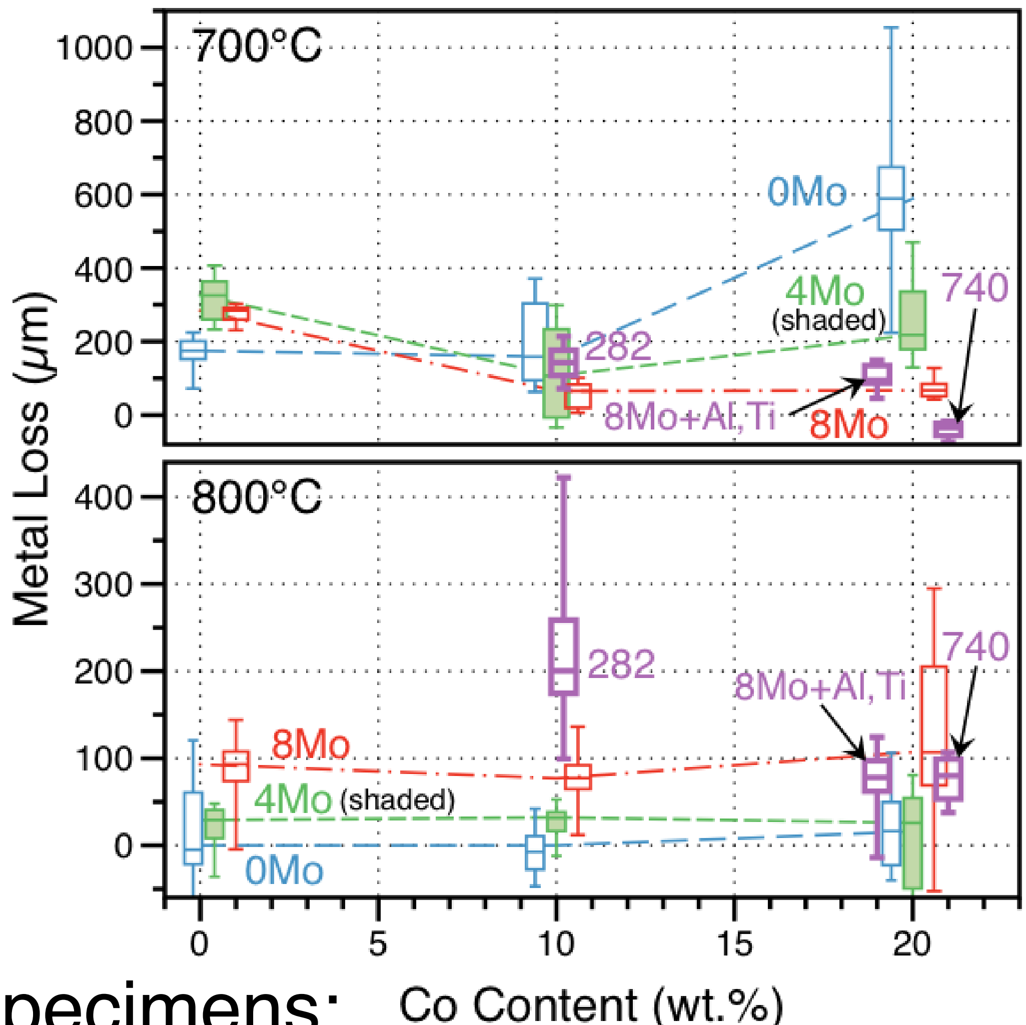
All rod specimens

If Al and Ti are not important:

How much do Co and Mo affect performance?

Model NiCrCoMo alloys: muddled

Rods: 500 h in synthetic coal ash + “oxy-firing” gas



700°C, 1292°F

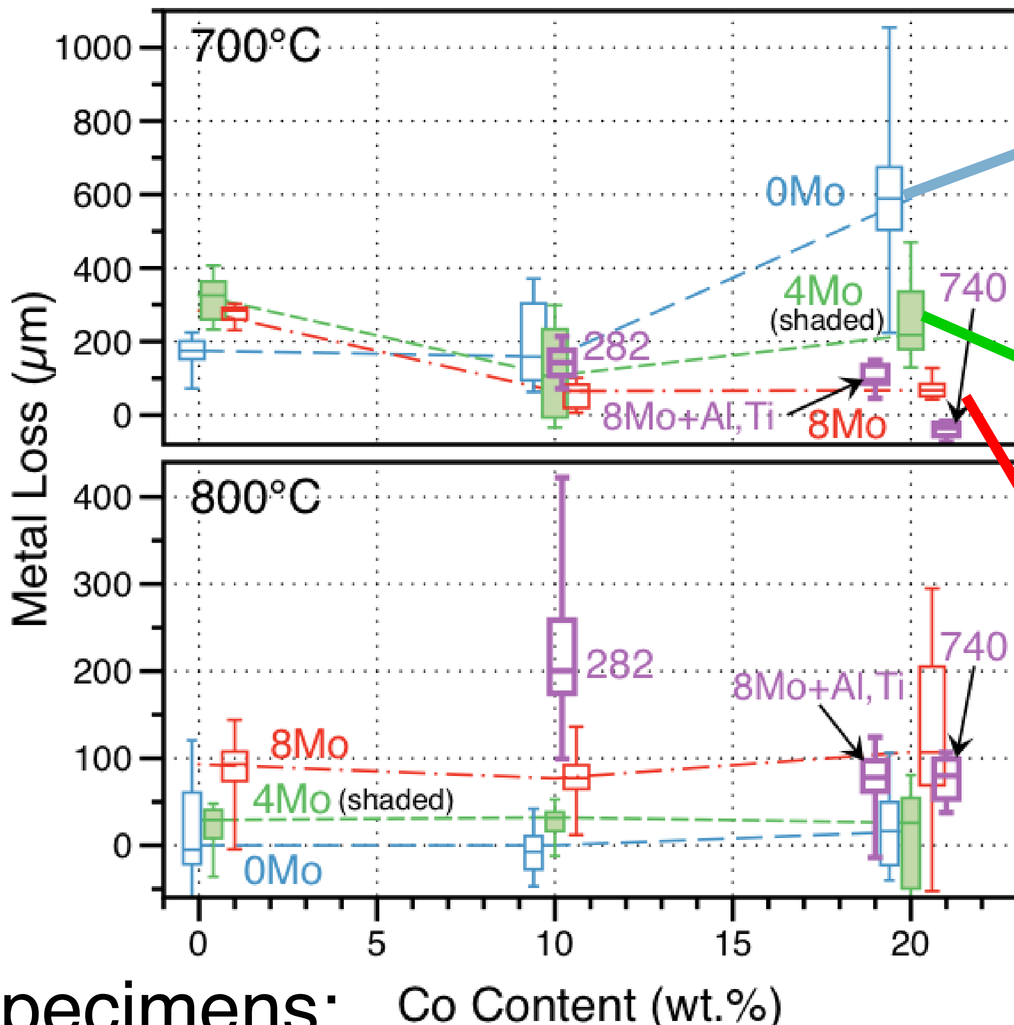
800°C, 1472°F

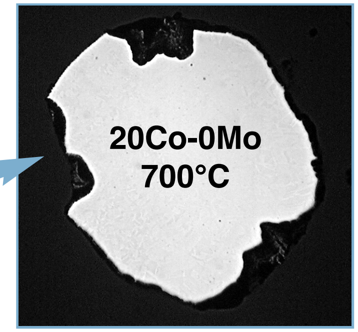
Rod specimens:

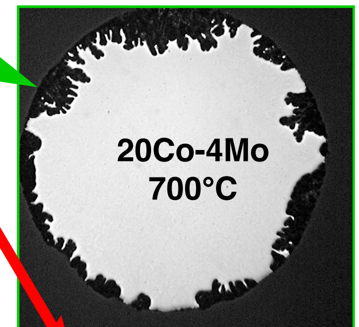
Ni-20Cr-(0-20)Co-(0-8)Mo

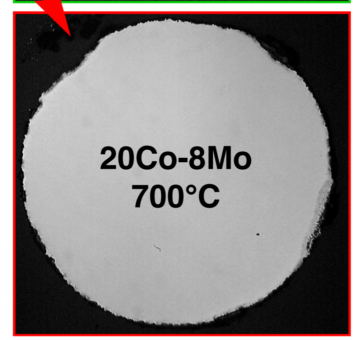
Model NiCrCoMo alloys: muddled

Rods: 500 h in synthetic coal ash + “oxy-firing” gas





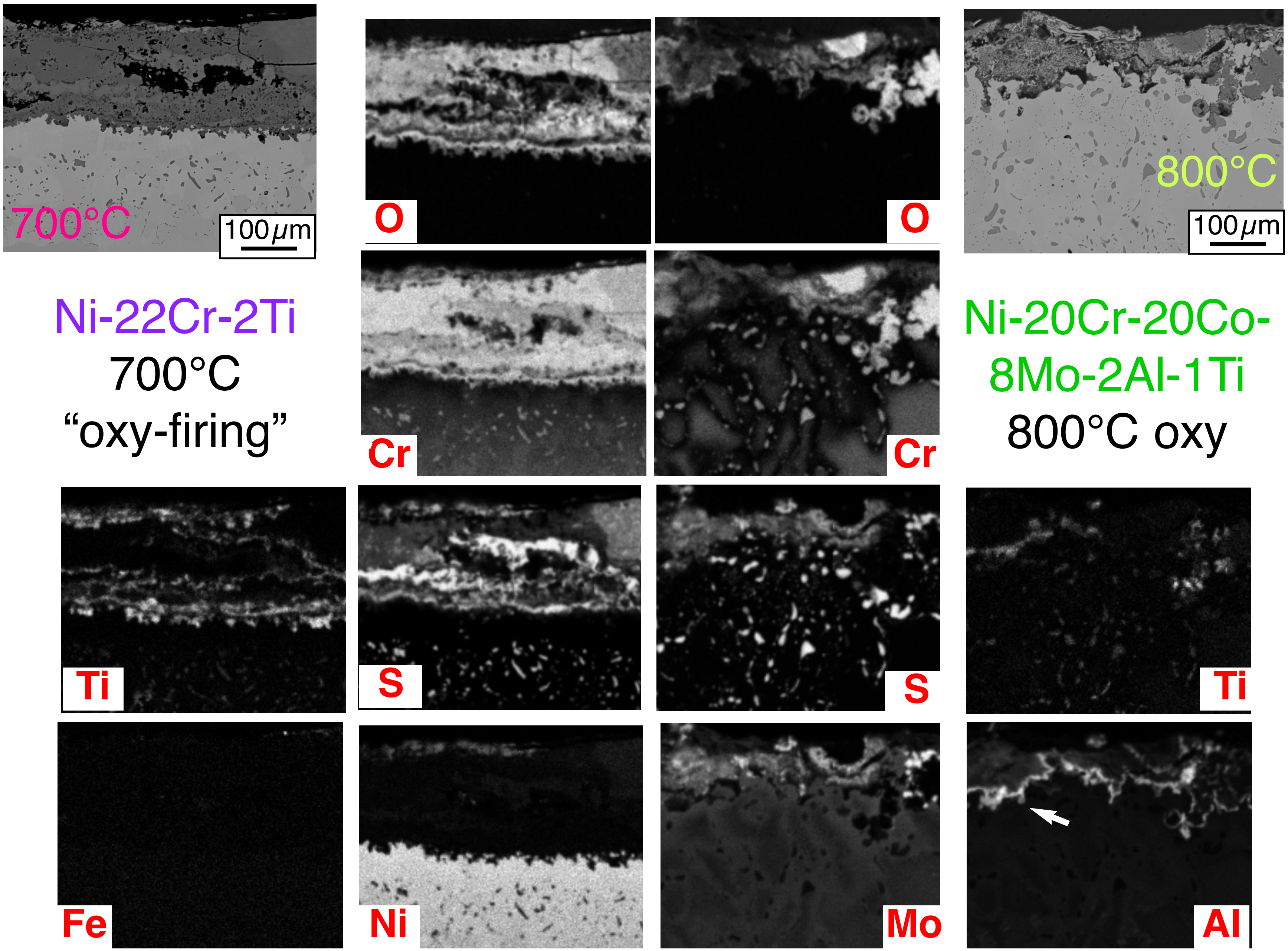




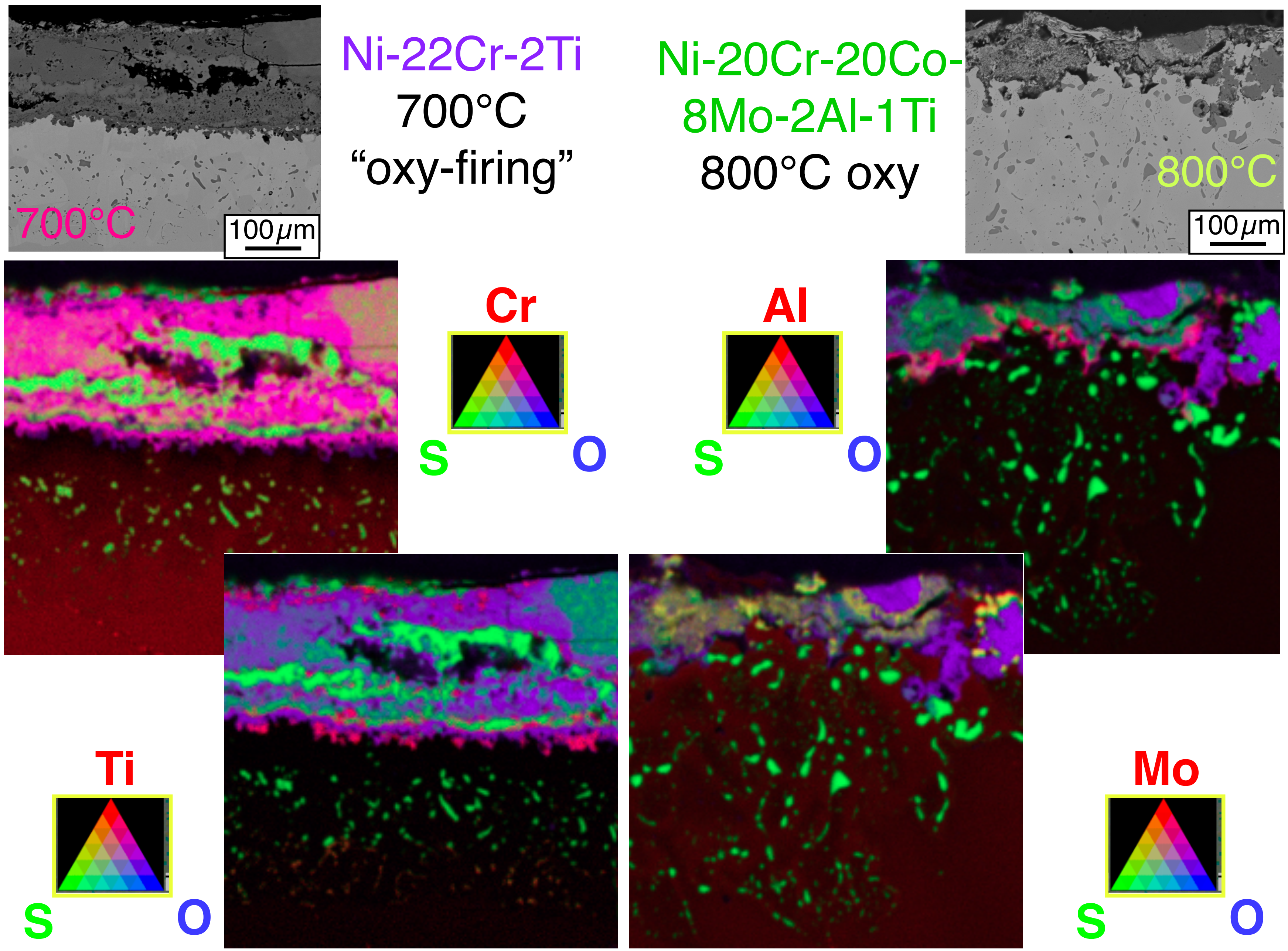
Rod specimens:
Ni-20Cr-(0-20)Co-(0-8)Mo

Pint, ASME 2014

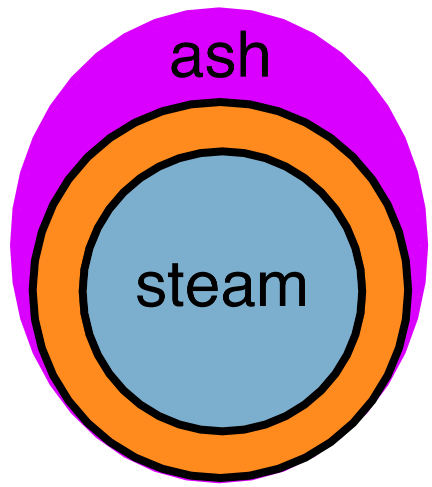
Ni-Cr+ash EPMA: Ti,Al in scale



Ni-Cr+ash EPMA: Ti,Al in scale



Boiler tubes see two harsh environments



Expect steam-side oxide to grow by OH^- transport

Any concern about H affecting alloy properties?

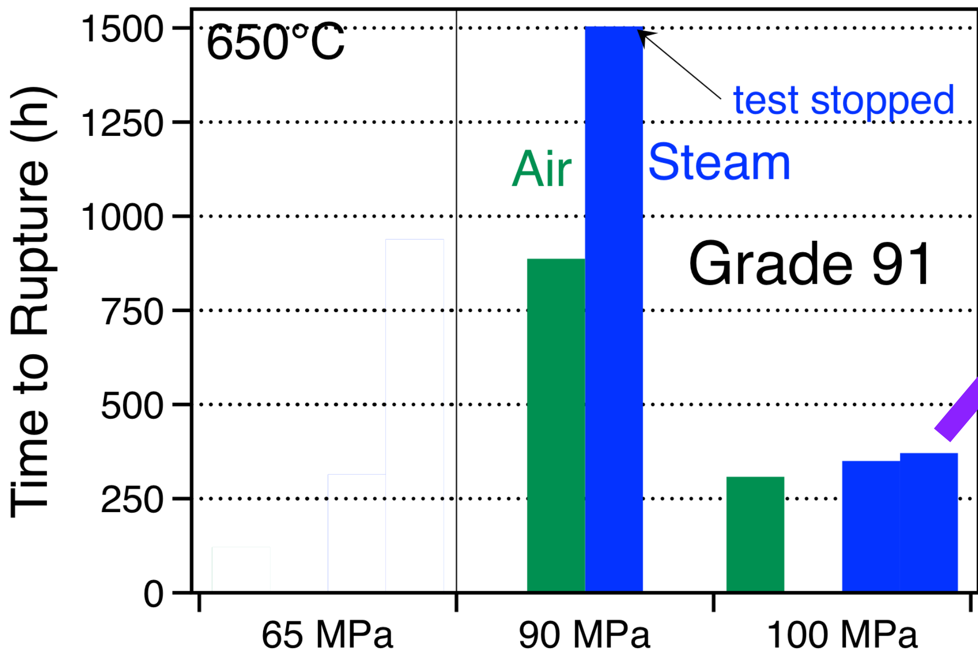
Summary: Creep in steam

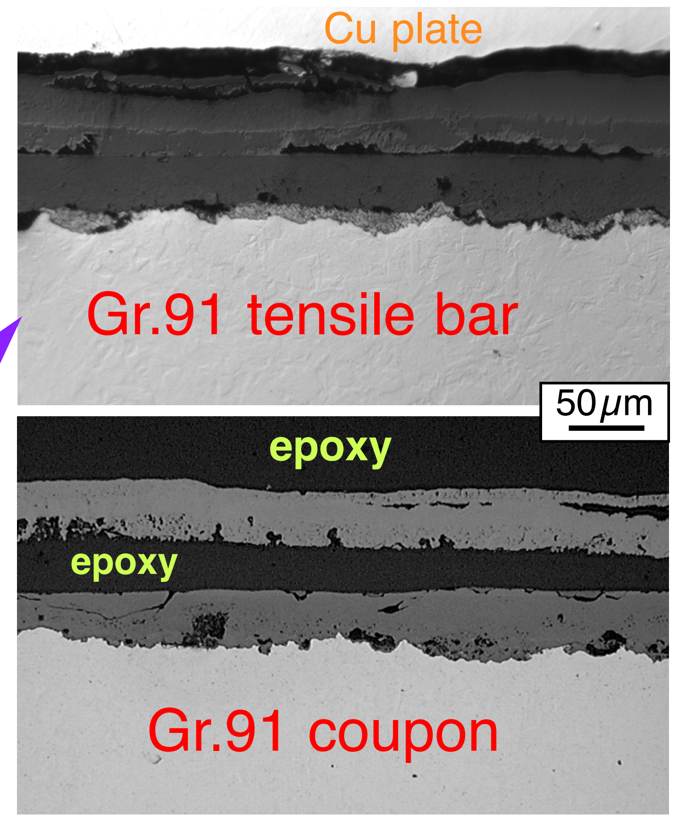
1. 800°C (completed): Dryepondt, et al. Mater. Corr. 2012
   740 (Ni-23Cr-20Co); 230 (Ni-22Cr-14W)
   air vs. steam
   in-situ vs. ex-situ
   anneal (thermal effect)
   microstructure analysis
2. 650°C:
   Grade 91 (9Cr-1Mo)
   air vs. steam
   role of thick scale

two in-situ creep rigs

Grade 91: higher lifetime in steam

650°C 90/100 MPa in air and 1 bar steam

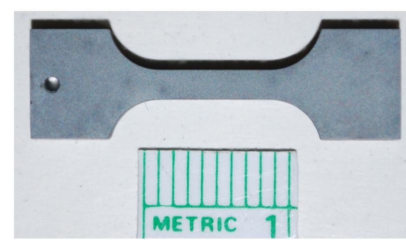




650°C, 500h, 1 bar steam

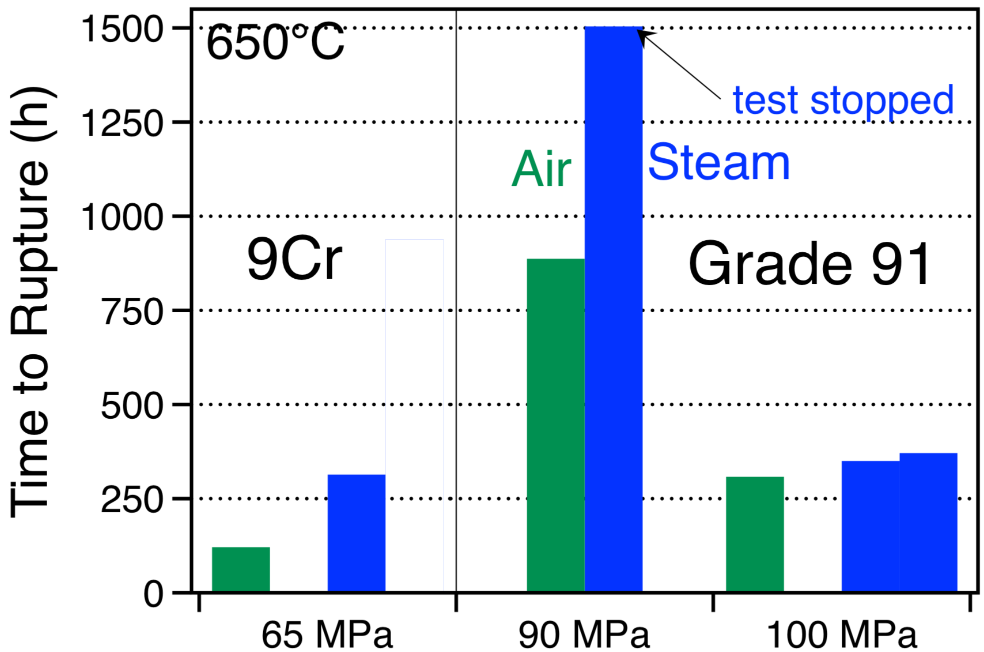
Grade 91: Fe-9Cr-1Mo

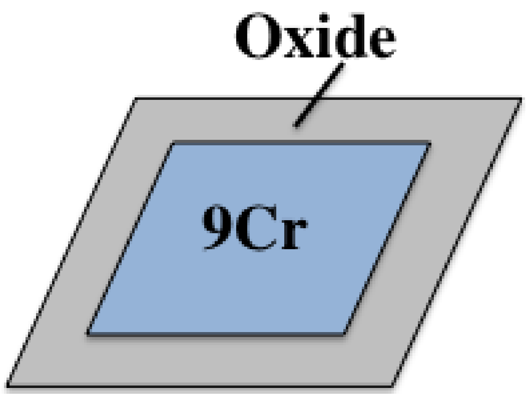
Verified similar oxide formed on coupon and on creep specimen



More impact for weak substrate

"9Cr" fully ferritic: slow cool from 1100°C





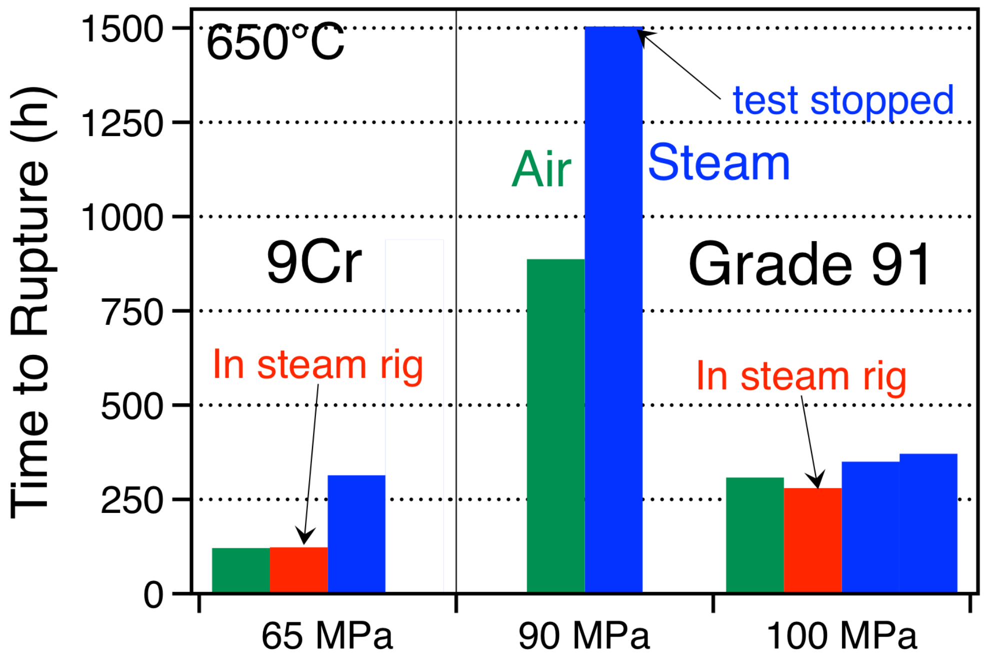
$$F = \sigma_{oxide}\frac{S_{oxide}}{S} + \sigma_{9Cr}\frac{S_{9Cr}}{S}$$

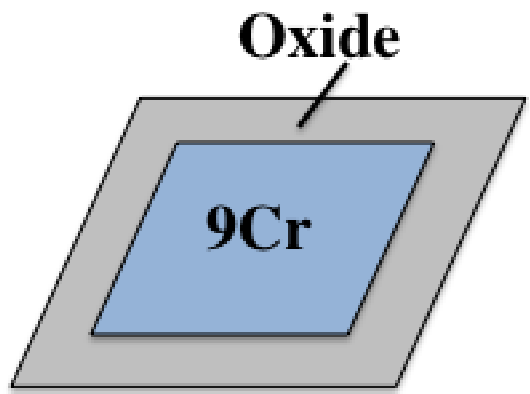
Higher effect of steam when substrate is weaker

Suggests that the oxide scale may be load bearing

Repeated air test in steam rig

650°C 90/100 MPa in air and 1 bar steam



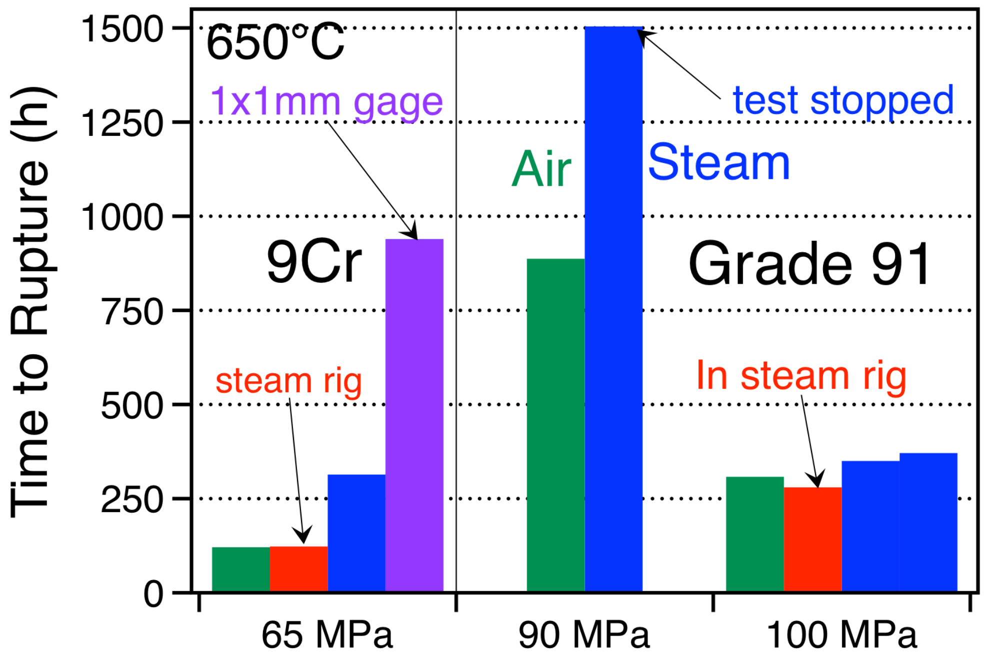


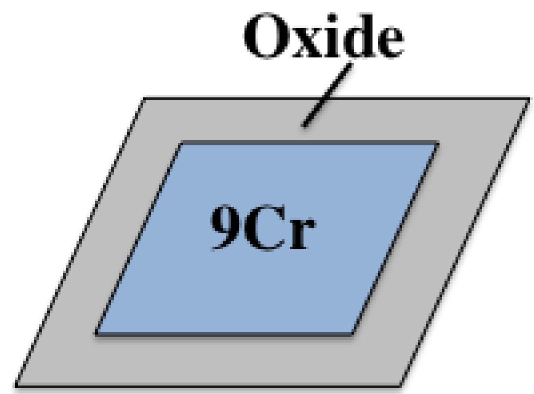
$$F = \sigma_{oxide}\frac{S_{oxide}}{S} + \sigma_{9Cr}\frac{S_{9Cr}}{S}$$

Verified that there was no effect of the in-situ creep rig compared to conventional creep rig test in air

8X increase in lifetime for 1mm gage

Reduced gage from 2x2mm to 1x1mm





$$F = \sigma_{oxide}\frac{S_{oxide}}{S} + \sigma_{9Cr}\frac{S_{9Cr}}{S}$$

More of the load on the oxide scale with small gage
Clear evidence of load-bearing scale on 9Cr steel

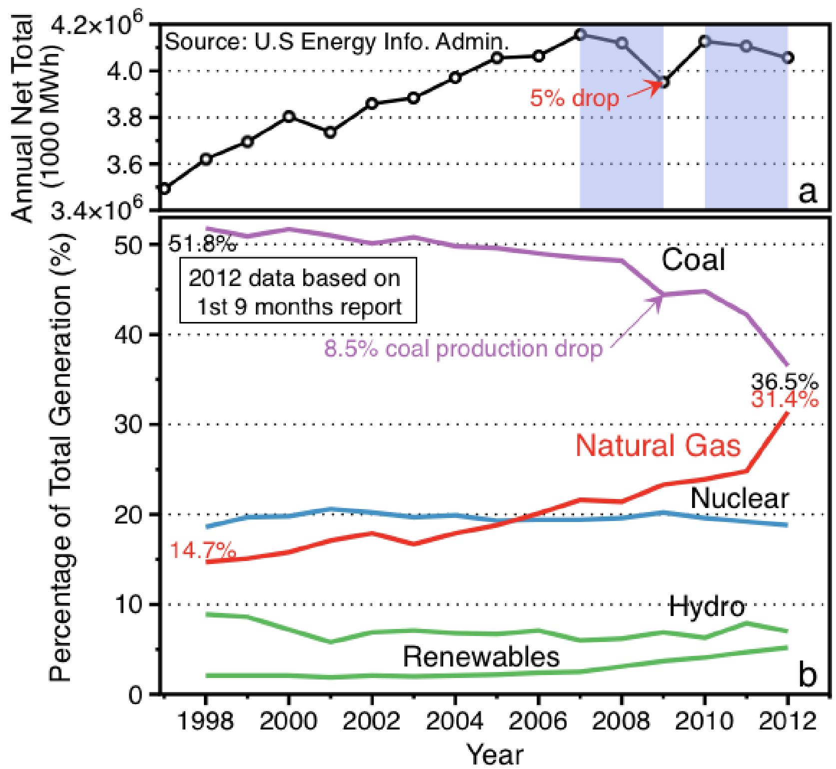
No evidence of creep debit in steam environment

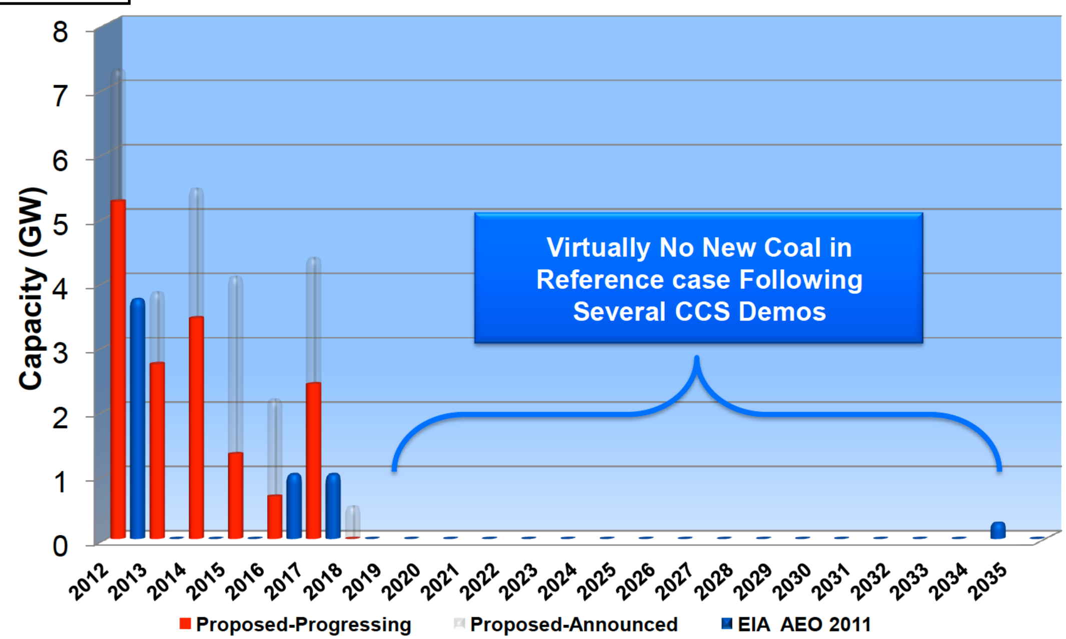
Task completed

Why stop working on oxy-firing?

- no indication of effect
- scarce research $
- stagnant US demand
- new regulations
- no plants planned

Pint, JOM Aug. 2013





FY14: more "real world" issues

1) complete oxy-fire reporting
   1+) quantify internal oxidation of NiCr alloys in different environments

2) more detailed study of shot peening solution for steam-side scale exfoliation

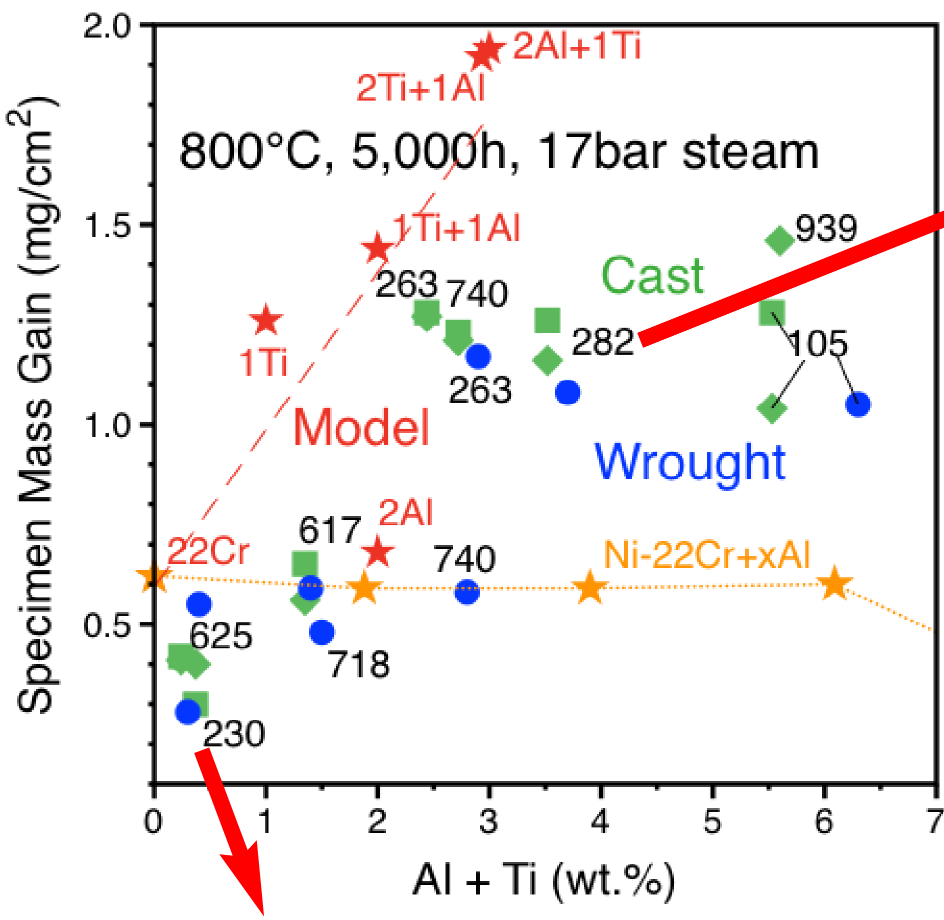
3) H-induced stress corrosion cracking
   - 2.25%Cr steels: Grades 22,23,24
   - significant for industry
   - little "science"
   - need solutions

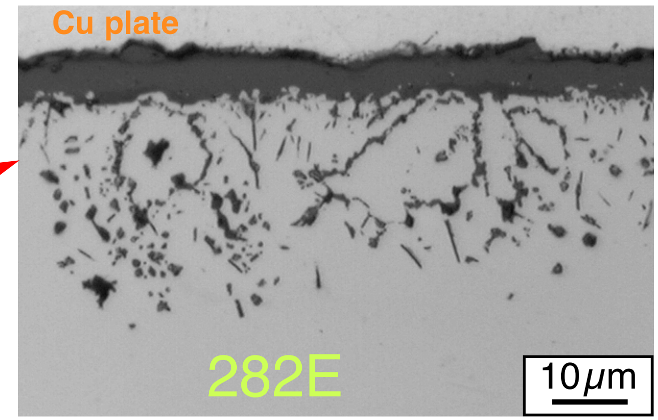
Cracks in longitudinal direction

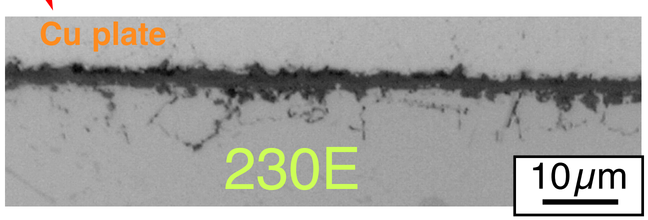
Cracks in transversal direction

NiCr+Al,Ti: mostly Ti effect

5,000h steam testing at 17 bar, 800°C







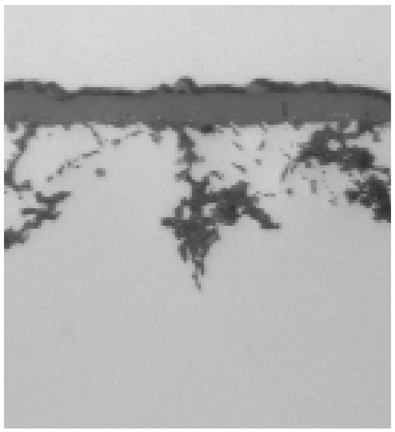
Commercial vs. model &
Cast vs. wrought alloys

E. Essuman, L. R. Walker, P. J. Maziasz and B. A. Pint, "Oxidation Behavior of Cast Ni-Cr Alloys in Steam at 800°C," Materials Science and Technology, in press.

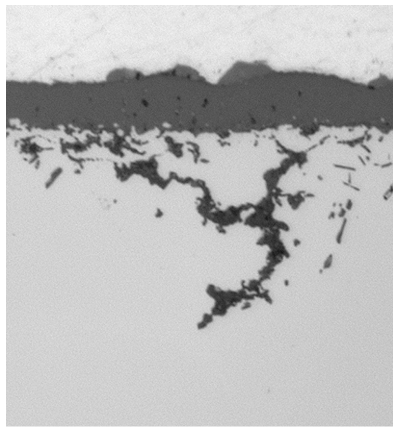
Ex: Ni-18Cr-2Al-1Ti comparison

Coupons tested at 800°C in three environments

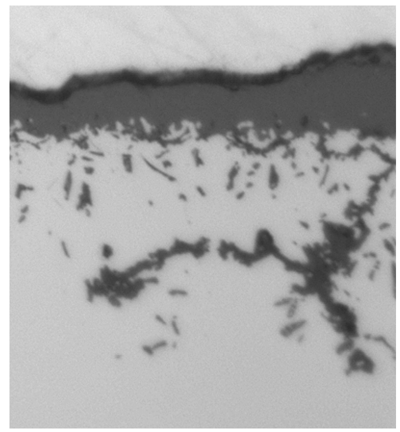
Steam, 1000h



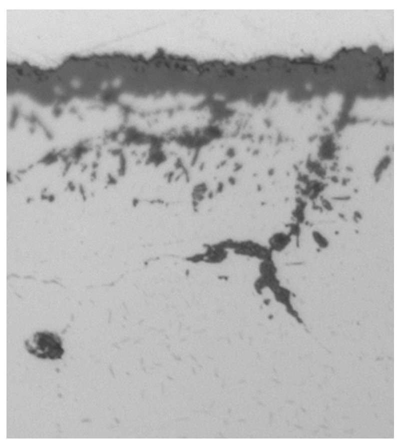
Steam, 2000h



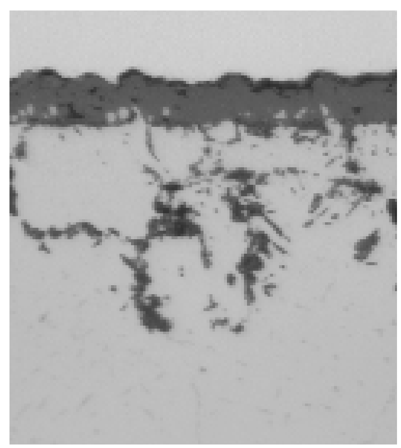
Steam, 5000h

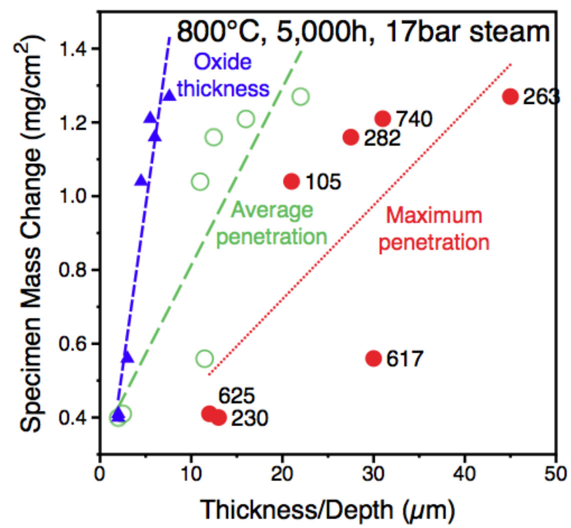


Wet air, 2000h



Dry air, 5000h





Why shot peening?

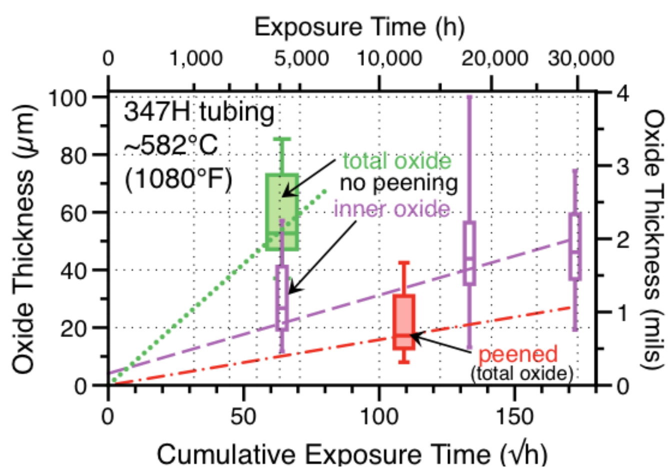
Exfoliation problem is a main driver for research

- H_2O-accelerated oxidation of steels (steam-side)
- Tube failures & erosion damage
- Cost: planned/unplanned shutdowns, mitigation
- Realization of limited understanding

Shot peening of austenitic tubes

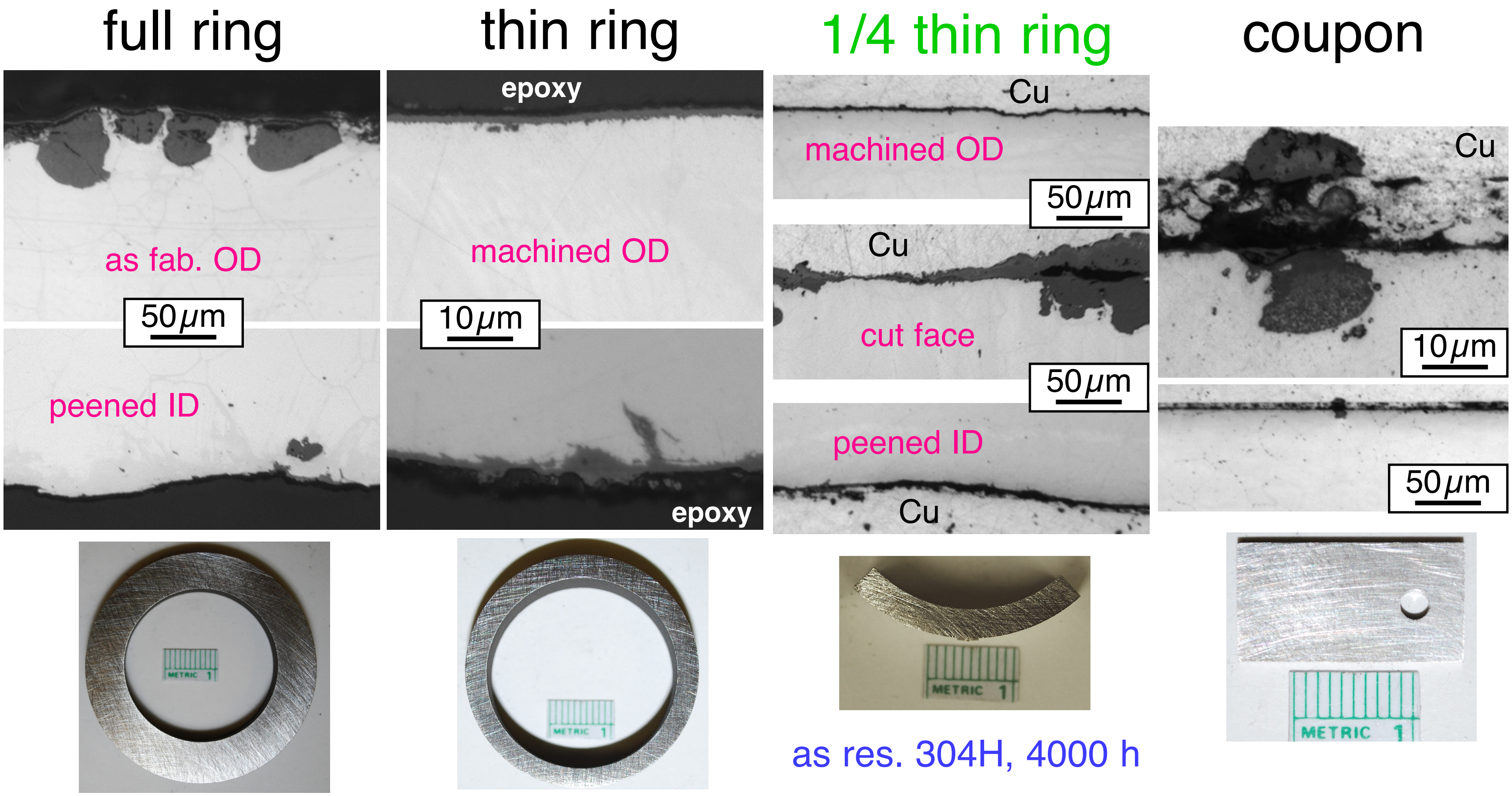
- Reduced scale growth: avoids exfoliation issue
- Limited understanding of benefit and procedure
- Ex: How do oxide nodules evolve at 600°-650°C?

Prior field/lab work with EPRI:



Specimen type showed minor effects

peened 304H 650°C 17bar steam 4,000h



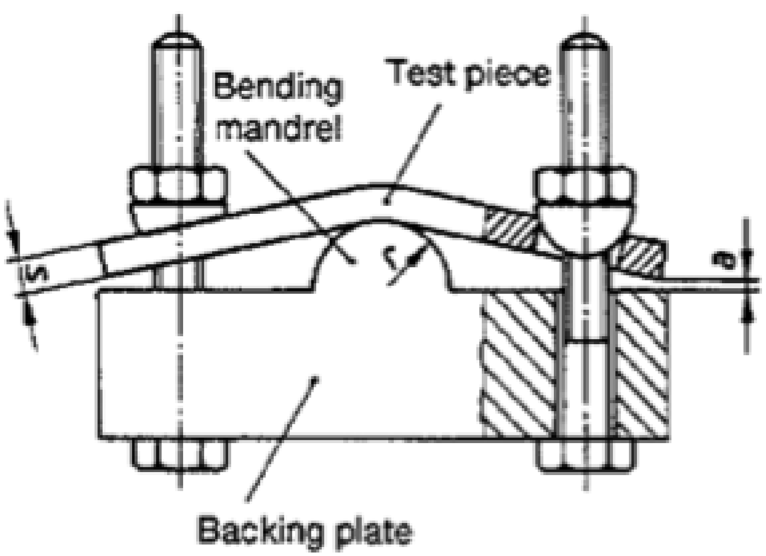
Peened ID: no effect of specimen geometry

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

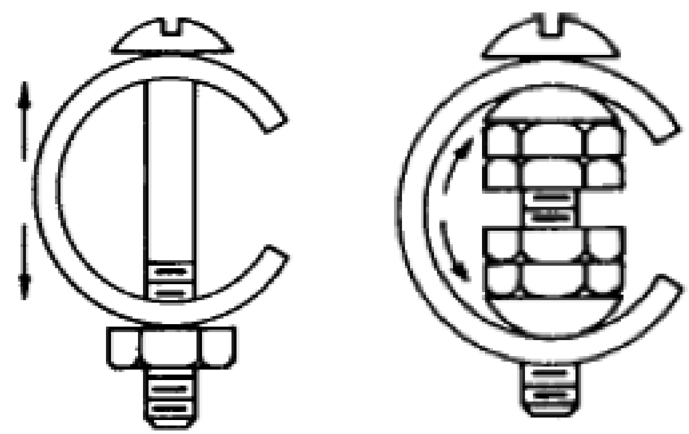
- cold work due to machining similar to peen-

Stress corrosion cracking testing

1. Stress-environment interaction: 25°-300°C with controlled water chemistry
2. Two tests: U.S. (C-ring) and E.U. (Jones) have very different stress states
3. Do they produce the same result?



Jones Test Longitudinal



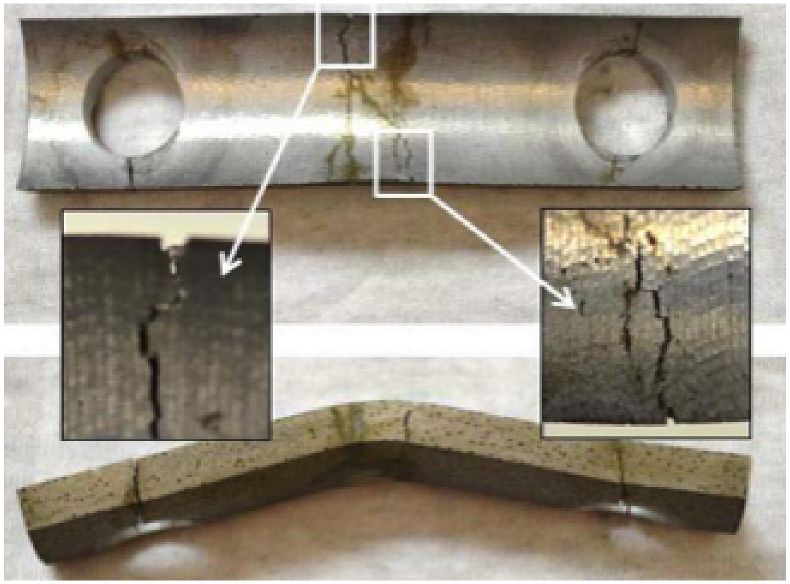
C-Ring Test Circumferential

Both tests showed same results

200°C $H_2O \pm O_2$ 168h

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

☐ Did Not Crack
☑ Cracked



Harder (350 vs 220 DPH), Normalized (0.5h,1065°C WQ) steels are more susceptible to cracking

Normalized T24
after inhibited acid clean

FY14+ SCC Testing

1. Characterization of cracking

2. Do higher strength super-bainitic 3Cr steels show the same behavior?
    - no Grade 315 tubing available

3. Are there critical temperature and hardness values for susceptibility?

4. Controlled chemistry water loop needed to identify critical O_2 content for cracking
    - loop under construction (due FY15)

5. Explore potential solutions

Milestones

FY13

Done - Assess temp. effect on ash testing (12/12)
Done - Complete Ni-Cr+Al,Ti ash testing (3/13)

Done - creep effect of steam-formed oxide (12/13)
Done - Compare SCC C-ring & Jones test (2/14)

FY14

- Complete Ni-base alloy coal ash eval. (2014)
- Assess shot peening at 600°-650°C (2014)
- Compare SCC of 2.25Cr and 3Cr steels (2014)

Summary

ORNL corrosion task transitioning

Prior focus on oxy-firing + in-situ creep testing

- Wrapping up: oxy-firing no worse than air
- Model NiCr alloys: Cr, Co, Mo, Al, Ti effects
- No detrimental effect of steam on creep

FY13-14 transitioning to “real world” issues

- Shot peening - study exfoliation solution
- SCC - study current waterwall issue
- Followup - quantify internal oxidation of NiCr
  - compare air, wet air, steam

CLEAN COAL.
COOL.

Ash experiment issues

Experiments:

- air/oxy: worst case comparison
- "milder" oxy-firing: lower H_2O or SO_2
- add cold recirculation: low H_2O/low SO_2

Test protocols to be evaluated:

- use of Pt catalyst
- crucible (covered sample) vs. ash slurry
- cycle frequency 10 x 100h vs. 500h x ?
- goal: "actual" rate or accelerated?

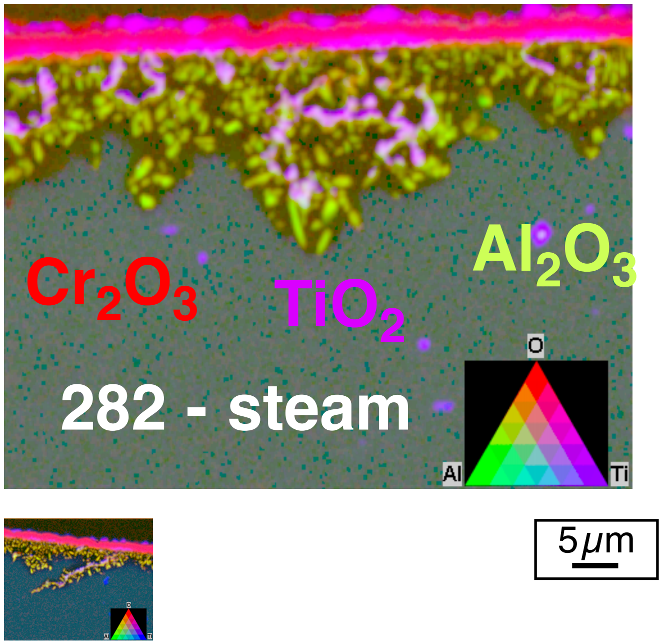
Metal loss measurement

- box plots capture variable attack
- scale thickness (not rod diameter)

Ash composition: how changed by oxy-firing?

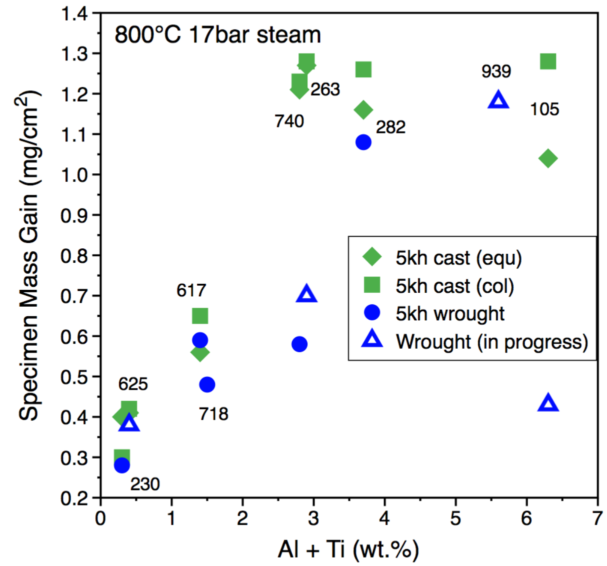
800°C steam follow up work

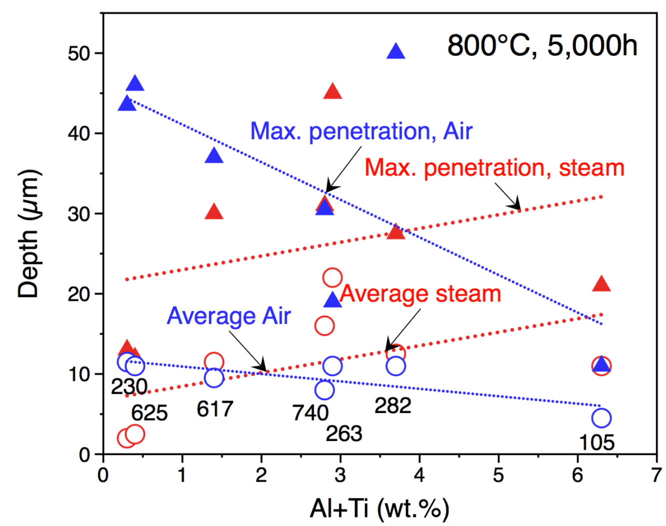
Alloy 282: 5kh in 17bar steam or lab. air



Ni~20Cr
Al+Ti->γ'

Synergy
Al-Ti ?





Model alloys: Ni-22Cr + Al +/- Ti in steam

What's different here?

Many previous & current studies of oxy-firing & CO_2

- "Oxy" worse: Speigel (2006) + Corvino (2008)
- Complicated: boiler OEMs have advantage
- CO_2 effect: Jülich, U. Pitt & Australia (Young)

Issues with fireside corrosion experiments:

Different experimental conditions (if published)

1000h vs. 10 x 100h (ash re-supply)

Ash/gas/temp. variables

Use of Pt catalyst (SO_2/SO_3)

* Evaluate experimental parameters (FY12)

Typically, only commercial alloys evaluated

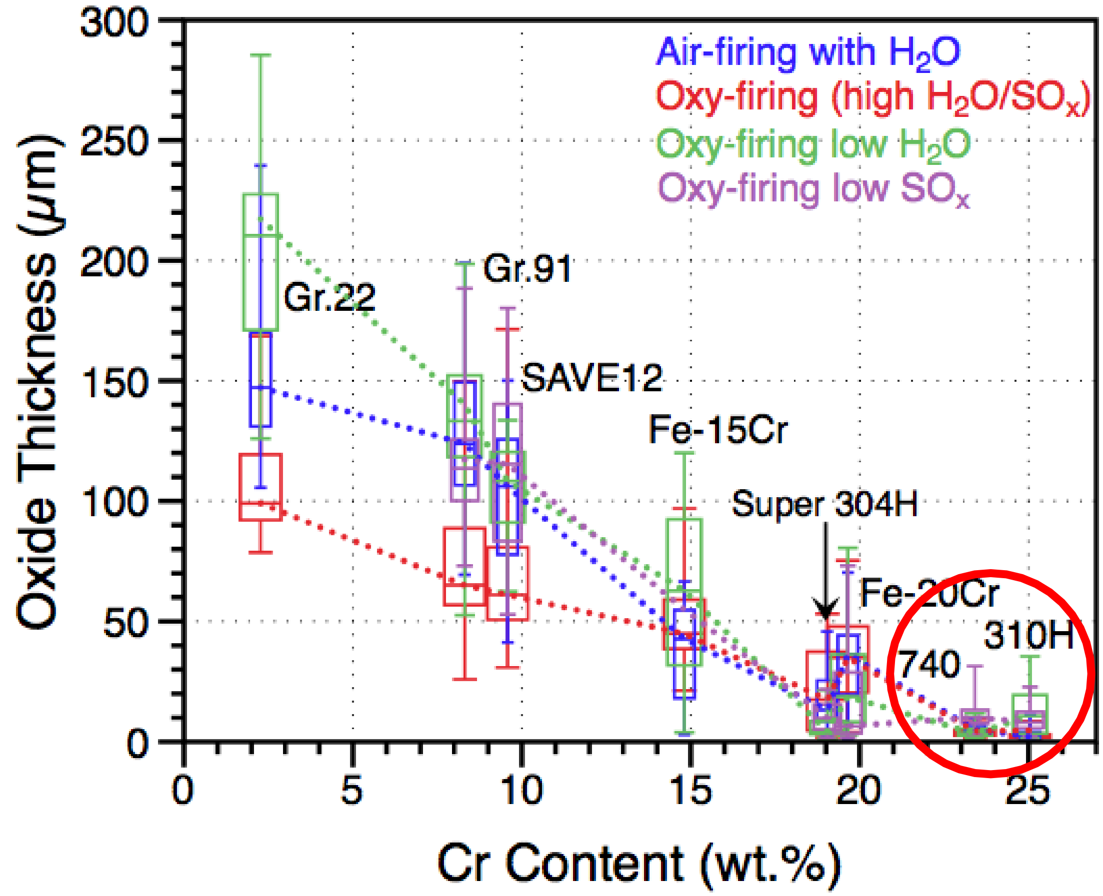
Prior work showing Cu-containing alloy attacked

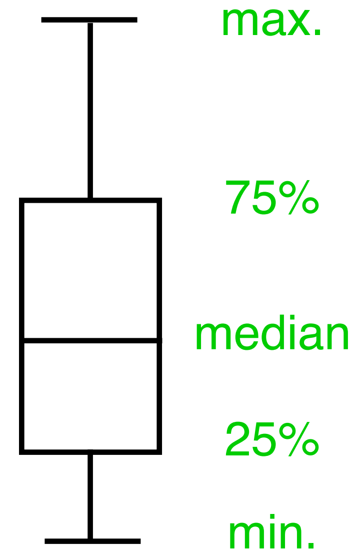
Was it an effect of Cu or other element(s)?

* Model alloys to better understand composition

Little effect of gas at 600°C

Synthetic coal ash, 500h exposures in 4 gases





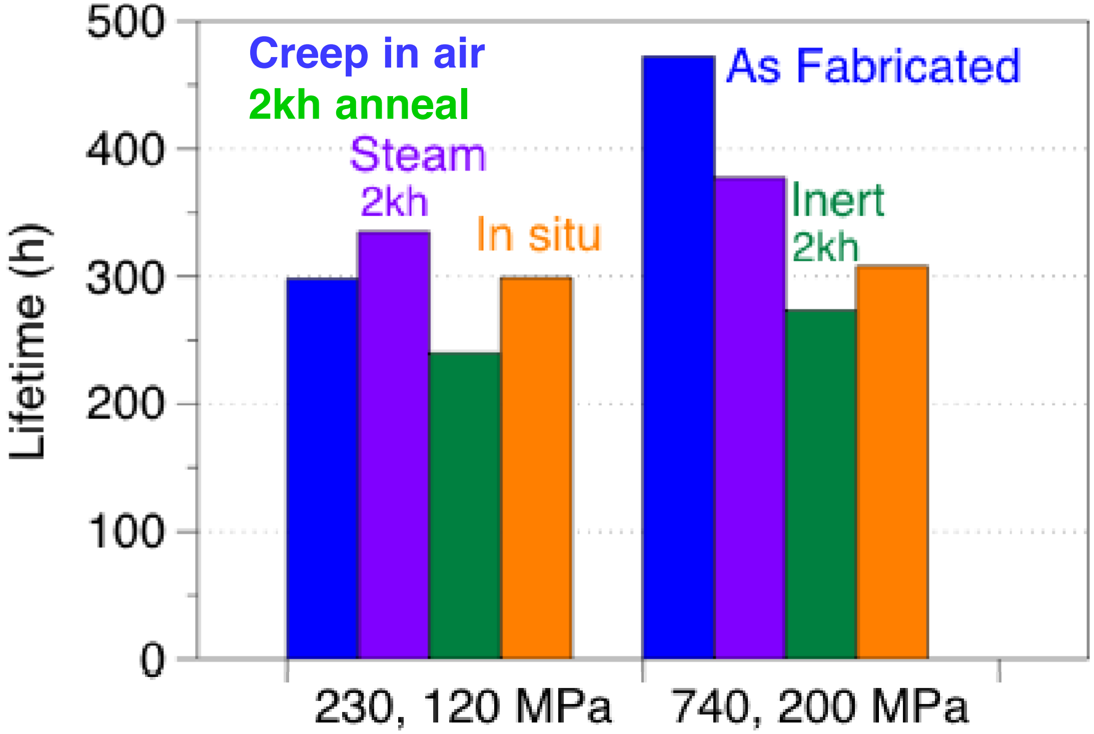
Higher CO_2 environments not detrimental

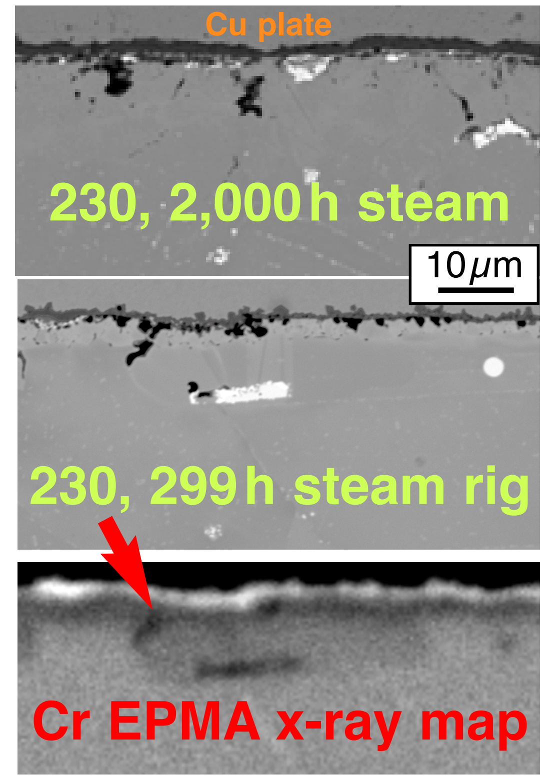
Expected the lower SO_2 environment to lower attack

- same synthetic ash used in all cases

800°C: 230/740 limited steam effect

Creep rupture tests in air and 1 bar steam





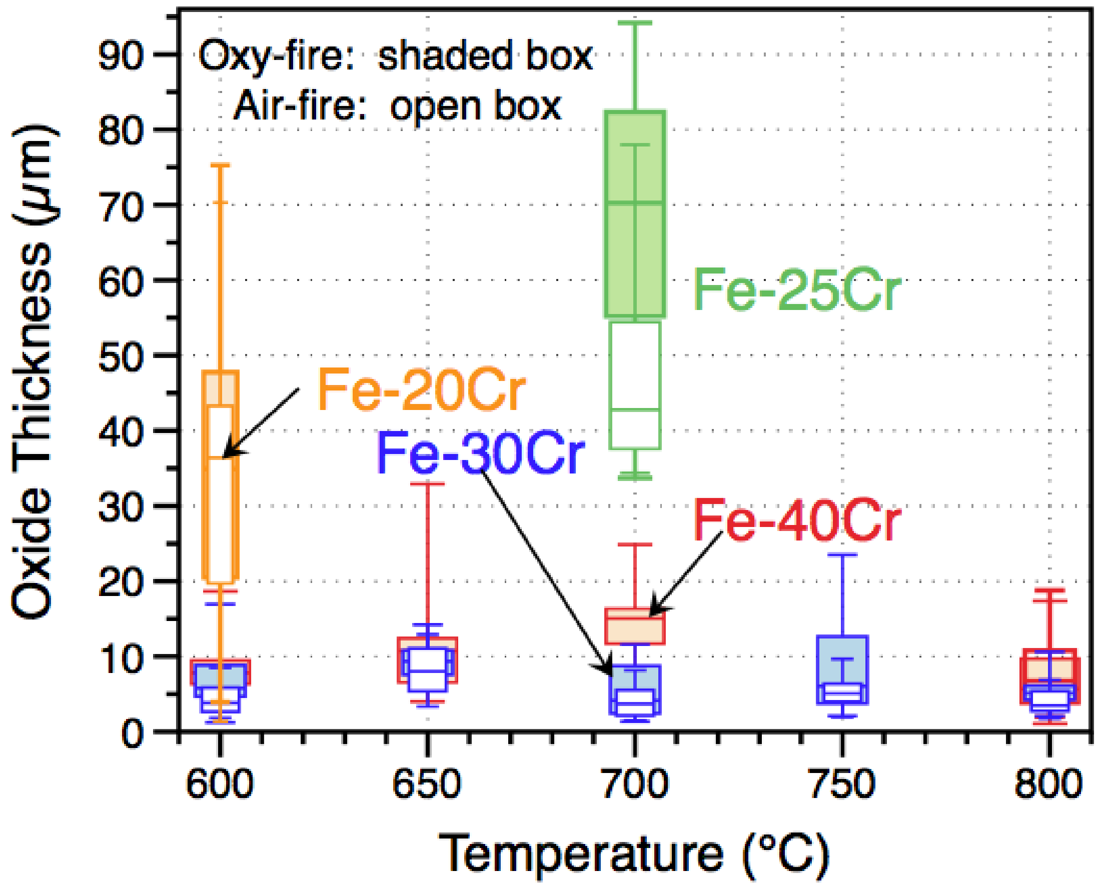
230: no effect of in-situ or ex-situ steam

740: microstructural reason for decreased life?

- alloy/oxide characterization in progress
- task will conclude this summer with paper

Model Fe-Cr alloys show Cr benefit

Provide guidance for Cr-rich coatings



Fe-30Cr chosen for more study

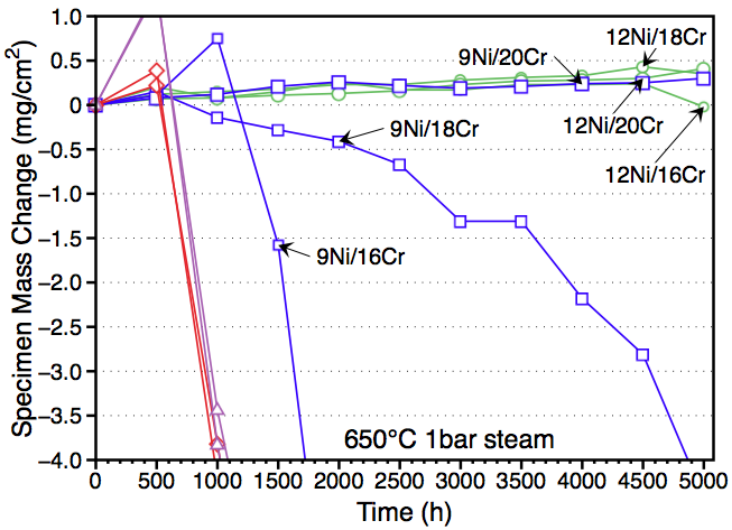
Fe-40Cr casting had problems with Cr rich phases

Currently, filling in matrix for Fe-20Cr and 25Cr.

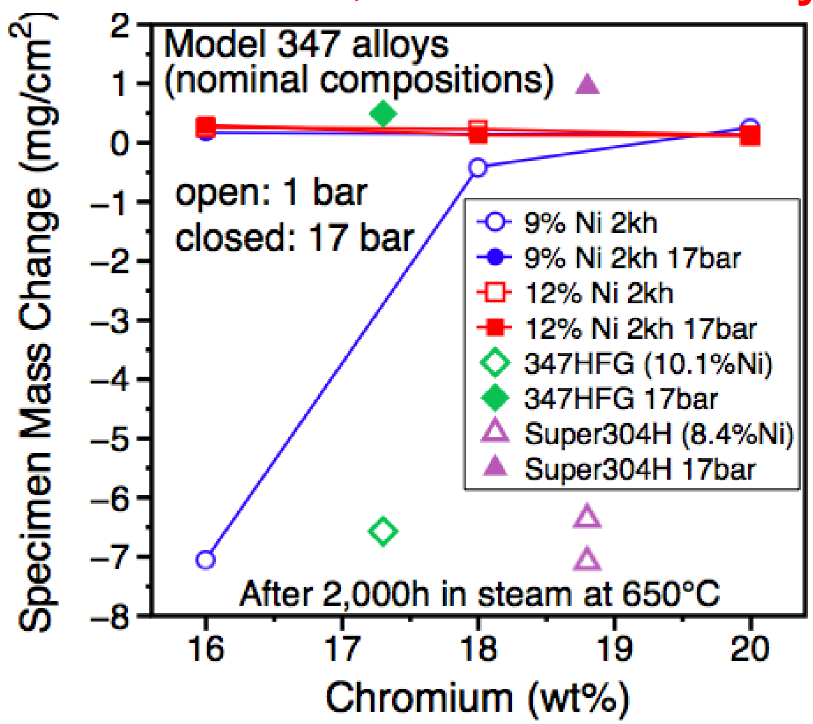
Model 347 alloys: 650°C steam

Cast, hot rolled Fe-Cr-Ni-1.5Mn-0.4Si-0.8Nb-0.09C

1 bar mass gain:



1 & 17bar 2,000h summary:



5,000h 1bar exposure completed in March 2012

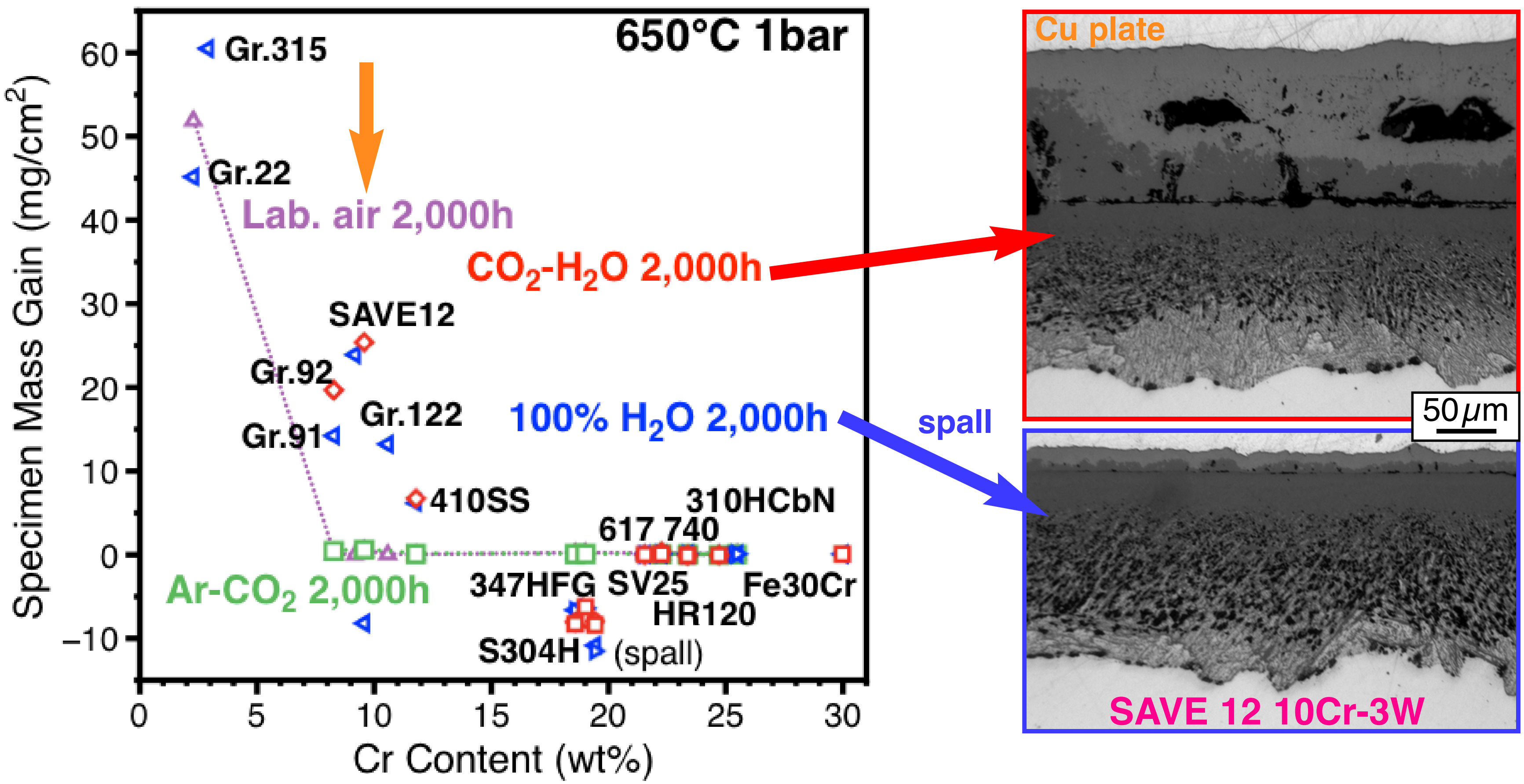
Higher (12%) Ni content very beneficial

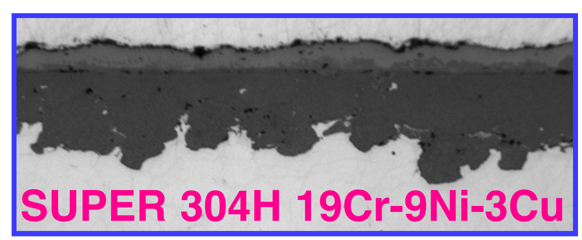
2000h 17bar completed April 2012 (no effect)

Concern: model alloys better than 347HFG & S304H

650°C: CO_2-H_2O not any worse

After 2,000h (4 x 500h) exposures



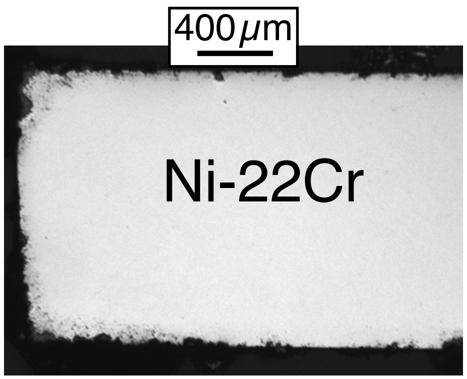


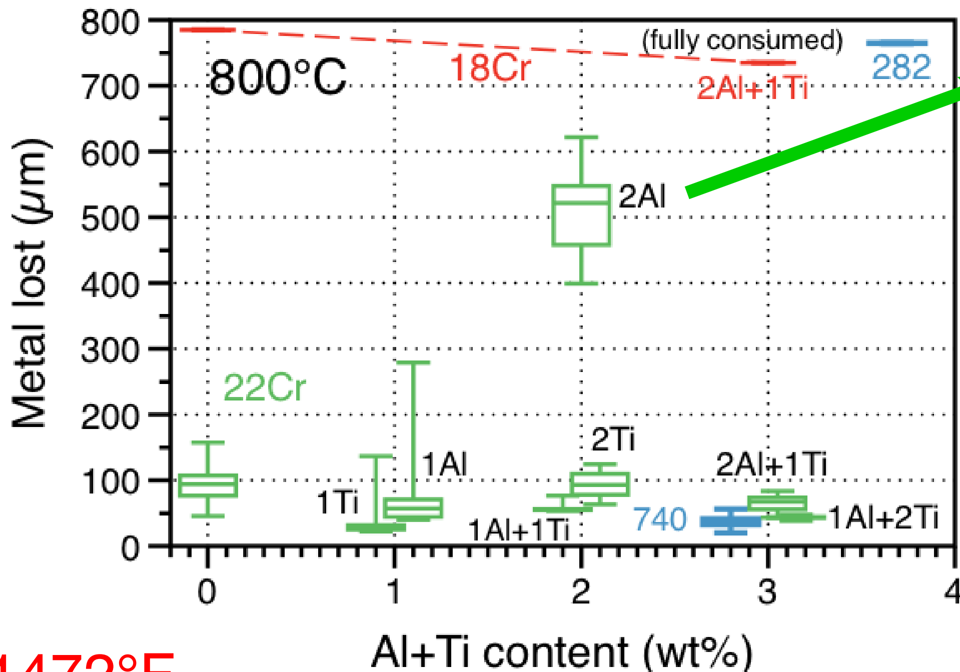
Spalled outer oxide in 100%H_2O
(both SAVE 12 & Super304H)

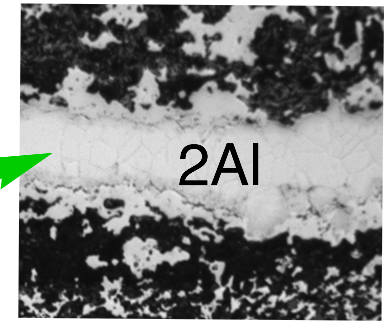
Pint & Thompson, Mater. Corr. in press

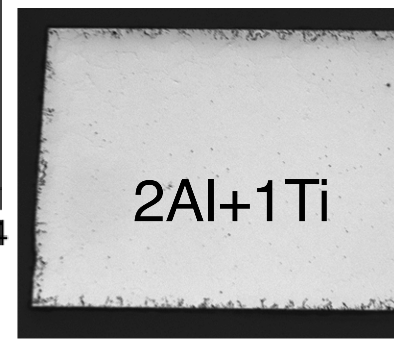
NiCr+Al,Ti 800°C: complete destruction

Coupons: 500 h in synthetic coal ash + "oxy-firing" gas









800°C, 1472°F

1.5mm coupons (not rods)

282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti

740: 48Ni-23Cr-20Co-0.5Mo-0.8Al-1.5Ti

Serious problem for 282 at 800°C