Understanding Corrosion Mechanisms in Advanced Coal-Fired Boilers

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T. Jordan - metallography

T. Lowe - SEM, image analysis

K. Perry, D. Leonard - EPMA

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)
4. Coatings
   - fabrication, model, mechanical properties

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

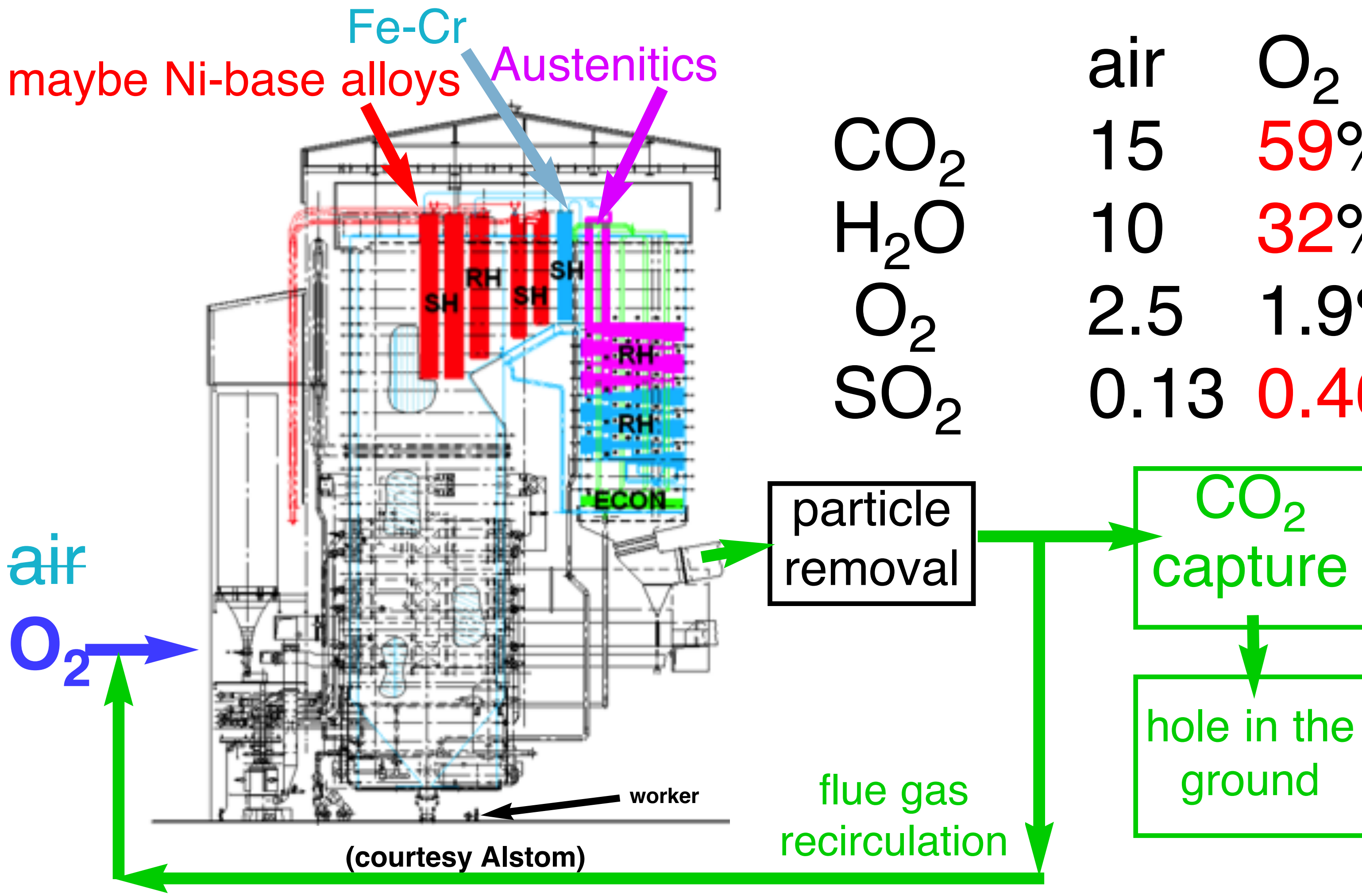
B. ~650°-700°C austenitic steels (FY11-13)

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

Oxy-firing: strategy to facilitate CO_2 C+S

Germany: 30MW oxy-fired pilot plant (Alstom)

	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)

Oxy-firing literature tends to focus on worst case

Not just commercial alloys

Model alloys: better composition understanding

Ni Content (wt.%)

Cr Content (wt.%)	0	10	15	20	25	30	35	45
15	X	(new 347mods)						
16		OOO	o	o	o	o		
18		OOO	o	o	o	o	→ Ni+Al,Ti	
20	X	OOO	o	o	o	o	→ Ni+Al,Ti	
25	X							
30	X							
35								
40	X							

↓ chromizing

Cast 400g, hot-roll to 8mm: cut coupons & rods

Corrosion testing w/o ash

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

1bar testing

gas only, no ash

- H_2O only (~0.06 µS/cm; ISO <1 µS/cm)
- Ar-50%CO_2*
- H_2O-50%CO_2*

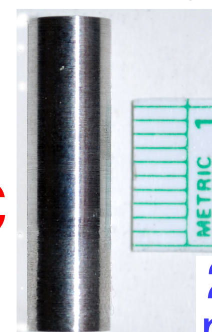
(*CO_2+1500ppmO_2)

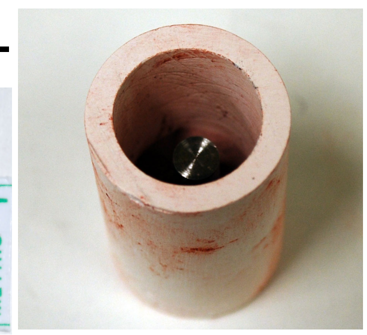
Synthetic ash: 30%Fe_2O_3-30%Al_2O_3-30%SiO_2-5%Na_2SO_4-5%K_2SO_4

Gas: N_2-CO_2-H_2O-O_2-SO_2

Temperature: 600°-800°C

Time: 500 h





25x6mm rod in porous alumina

Many different procedures for ash testing

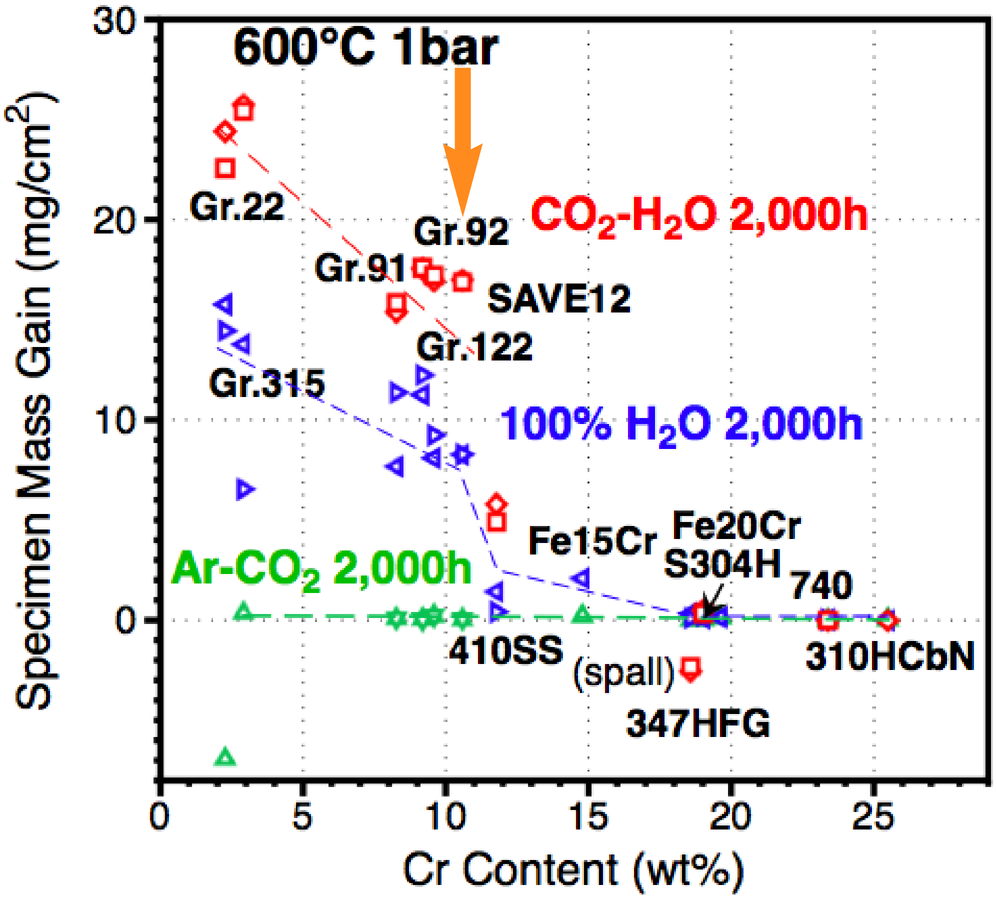
- Focus on one to explore effect of temperature

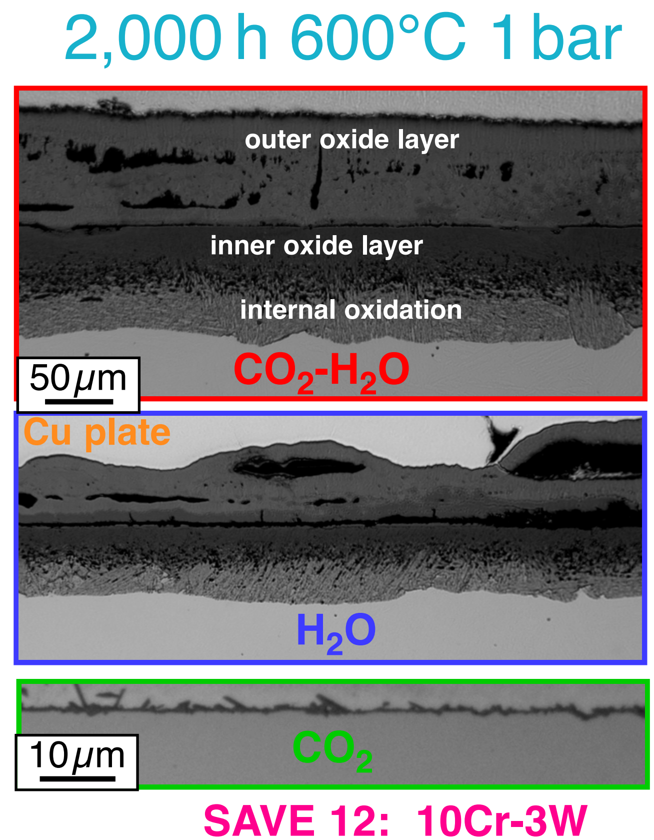
Summary: Gas only exposure

1. 600°C:
   a. steam 1 bar — FY11, 2kh
   b. Ar-50%(CO_2-0.15O_2)(buffer) — FY11, 2kh
   c. 50%(CO_2-0.15O_2)-50%H_2O — FY11, 5kh
   d. 50%CO_2-50%H_2O(no buffer) — FY12, 2kh
   e. Ar-10%(CO_2-0.15O_2)-50%H_2O — FY12, 2kh
   f. Ar-50%H_2O — FY12-13, 2kh
2. 650°C:
   a. steam 1 bar — FY11-12, 5kh
   b. 50%(CO_2-0.15O_2)-50%H_2O — FY12-13
   c. Ar-50%(CO_2-0.15O_2) — FY13, 2+kh
3. 800°C steam 17bar (A-USC): — FY12-13
4. 550°C steam 1bar (compare 17 bar) — FY12-13

600°C: CO_2-H_2O thicker scale

SAVE12 after 2,000h (4 x 500h) exposures





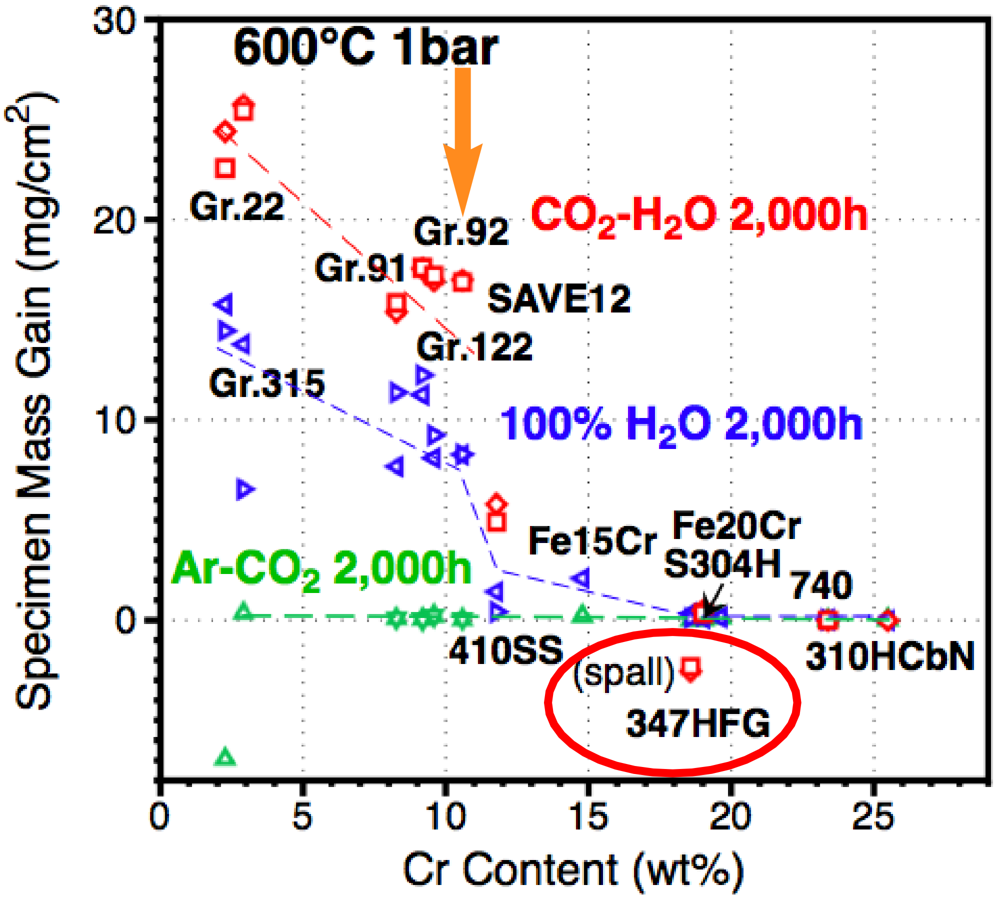
Ar-CO_2 thin oxide consistent with mass gain

CO_2-H_2O: thicker outer oxide compared to H_2O

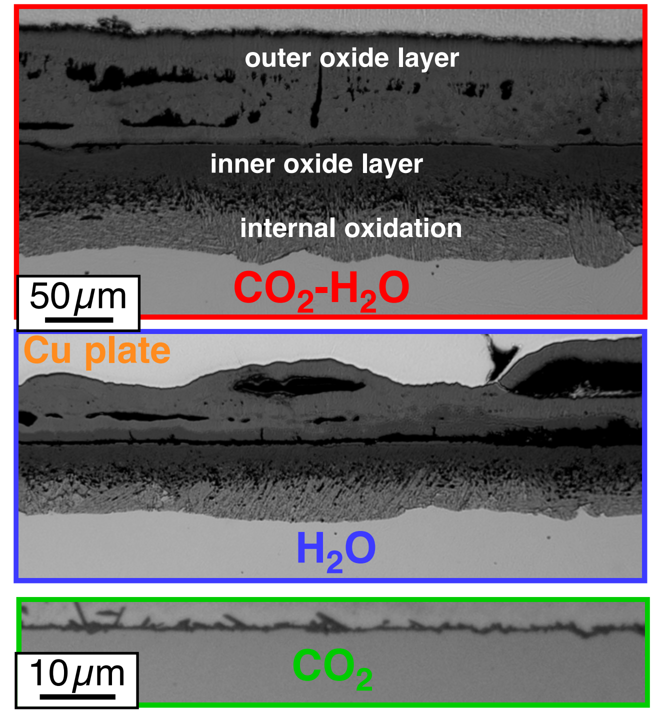
- no internal carburization detected by EPMA

600°C: CO_2-H_2O thicker scale

SAVE12 after 2,000h (4 x 500h) exposures



2,000 h 600°C 1 bar



SAVE 12: 10Cr-3W

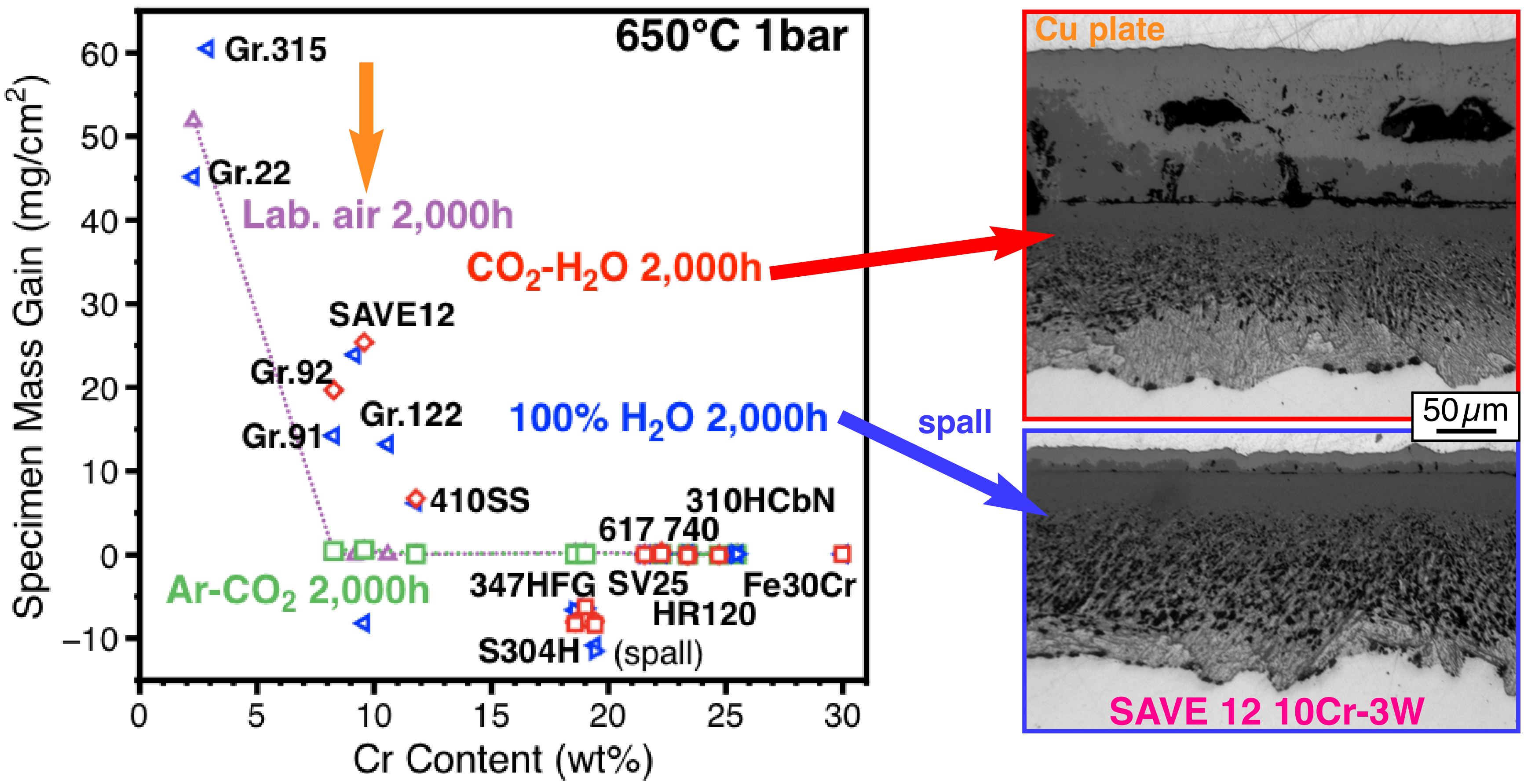
Ar-CO_2 thin oxide consistent with mass gain

CO_2-H_2O: thicker outer oxide compared to H_2O

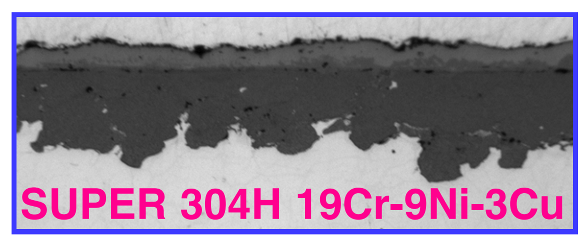
- spalled oxide for 347HFG

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)



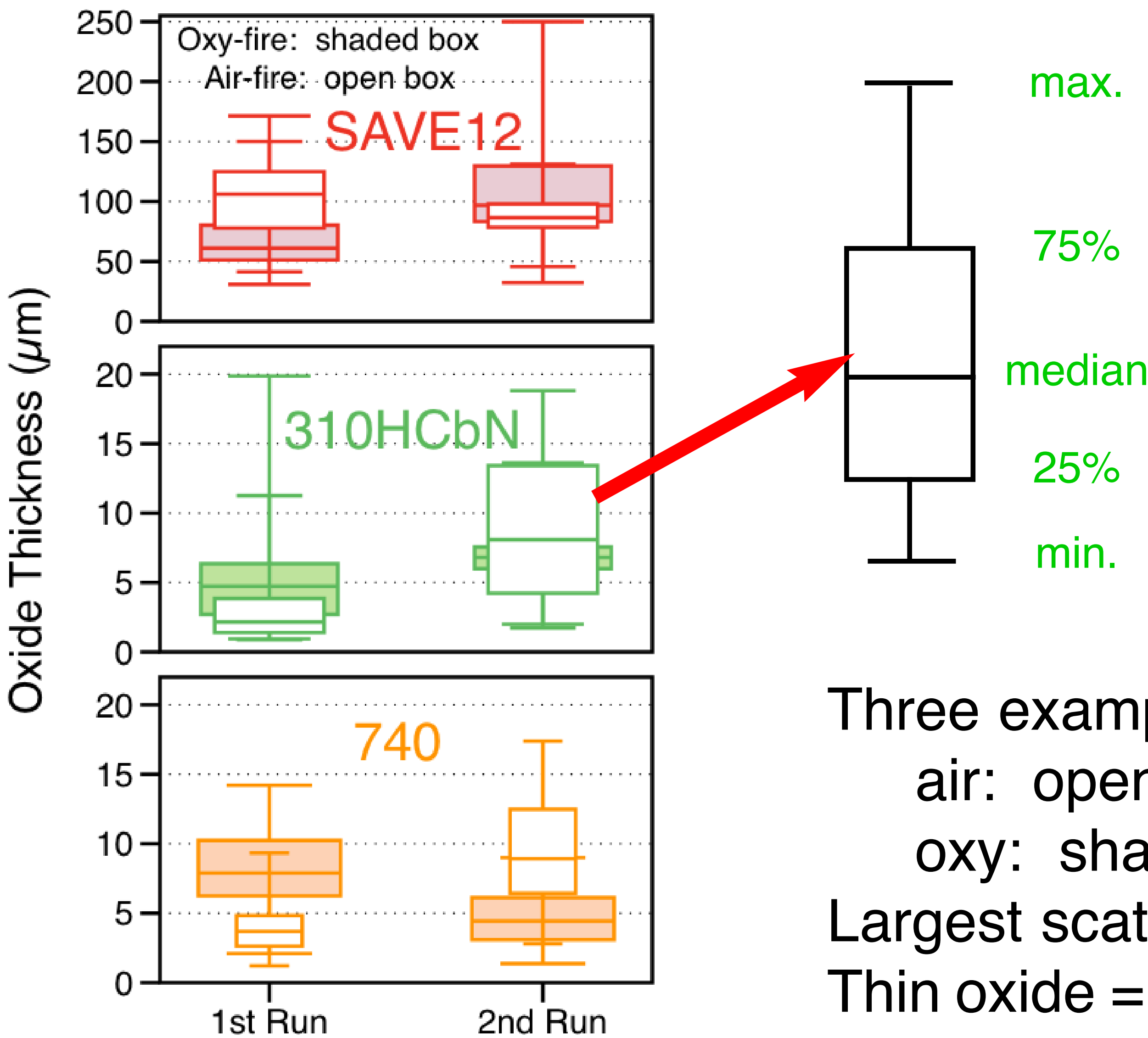
Pint & Thompson, Mater. Corr. in press

Summary: Ash exposure

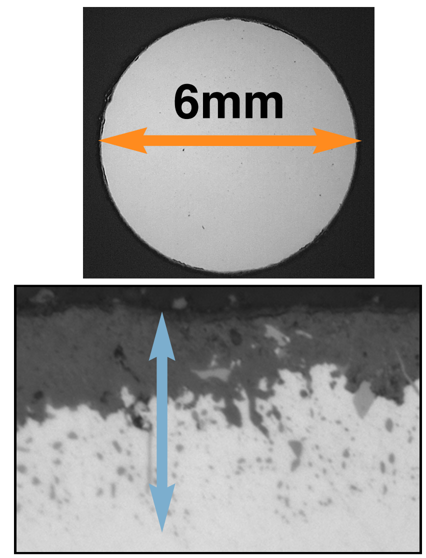
1. 600°C: (oxy-fire retrofitting current plants)
   air/oxy-firing (hot gas recirculation) (FY11)
   low H_2O/low SO_2 (FY11)
   FY12: low H_2O/low SO_2 (cold gas recirculation)
2. 650°C: (current USC plants)
   air/oxy-firing (FY12)
3. 700°C
   air/oxy-firing (FY12-13)
4. 750°C: (A-USC range)
   air/oxy-firing (FY12)
5. 800°C: (A-USC range)
   air/oxy-firing (FY12-13)

Repeated experiments at 600°C

Check reproducibility of 500h experiments



Box and whisker plots: oxide thickness



Three examples provided

air: open box

oxy: shaded box

Largest scatter for SAVE 12

Thin oxide = small mass gain

Similar results for others

500h ash tests

“air-firing” open box (40 pts)

“oxy-firing” shaded box

“Oxy-firing” did not consistently increase reaction rates

SAVE12+304 baseline data

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

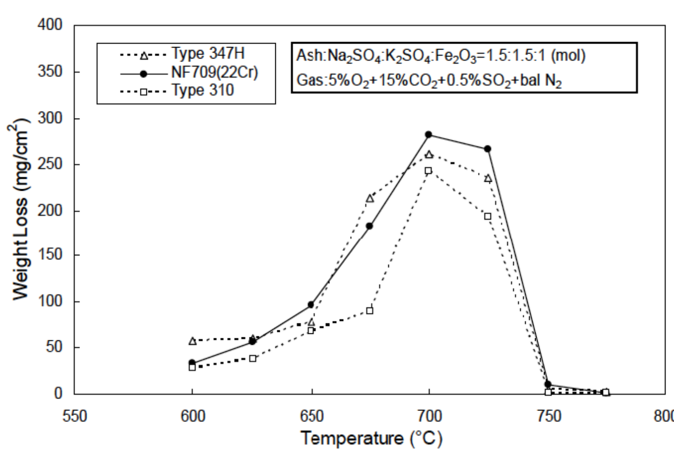
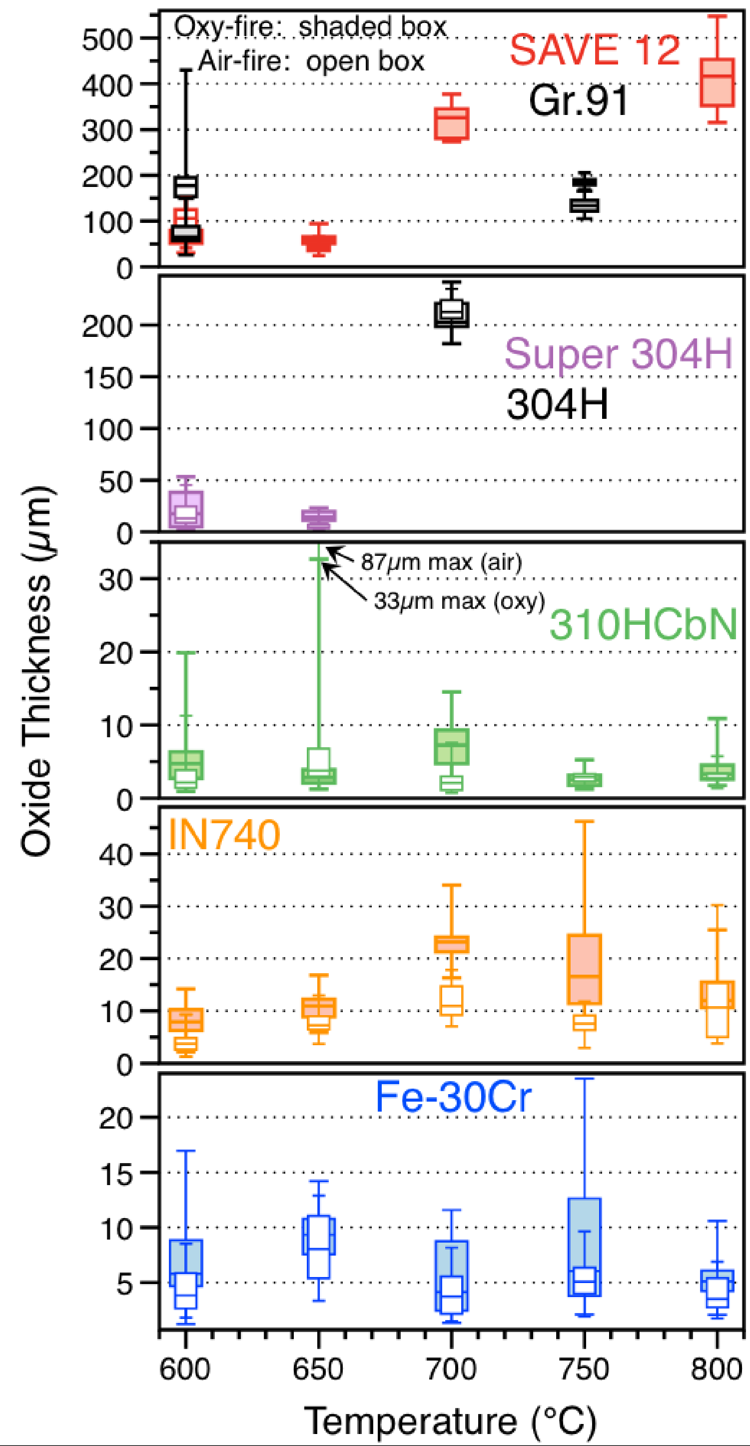


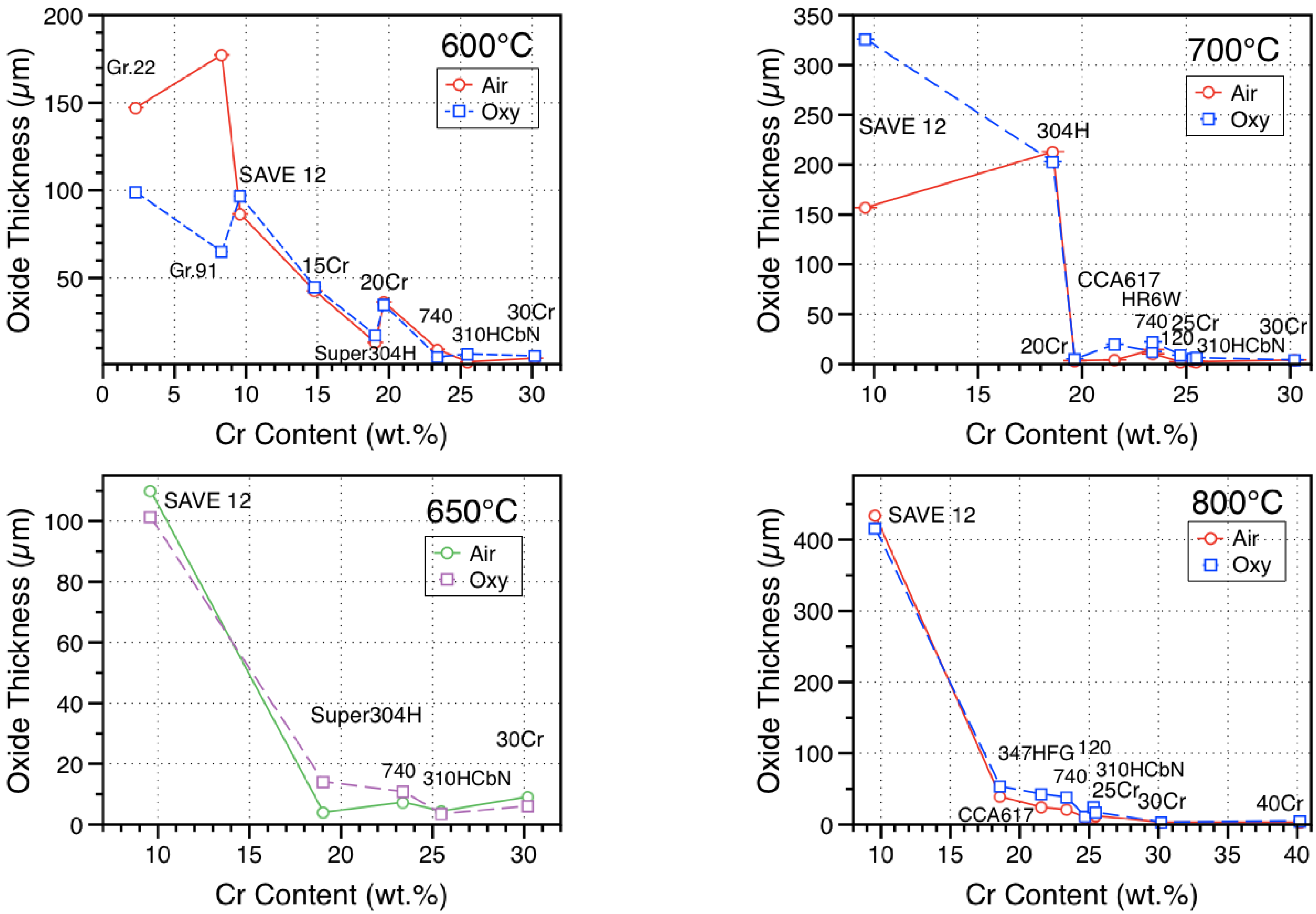
Fig. 3-7 Hot corrosion of NF709 in simulated coal ash environment.
(Test duration : 100h)



Pint & Thompson, NACE 2013

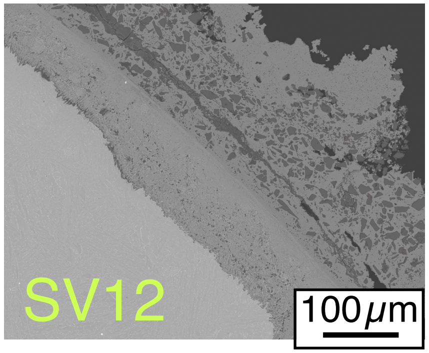
Obvious benefit of higher alloy Cr

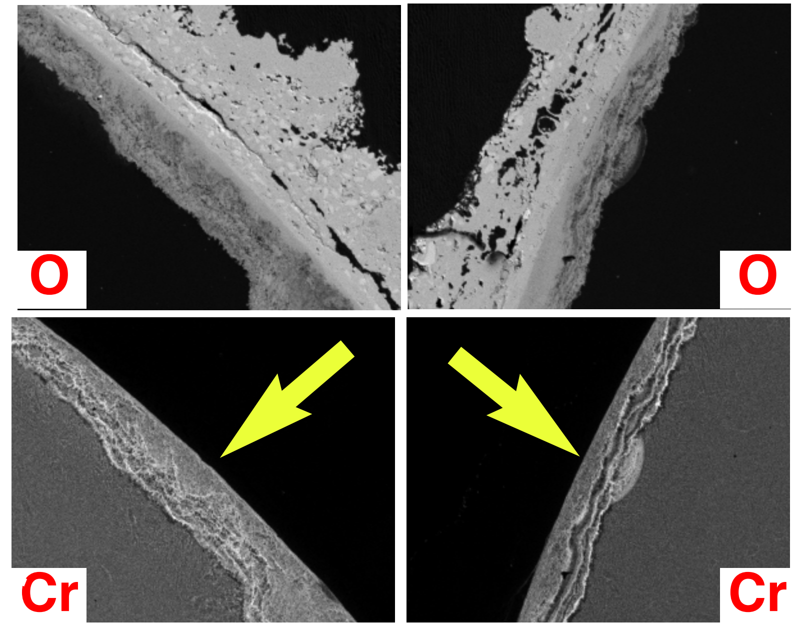
Median oxide thickness to compare air and “oxy”

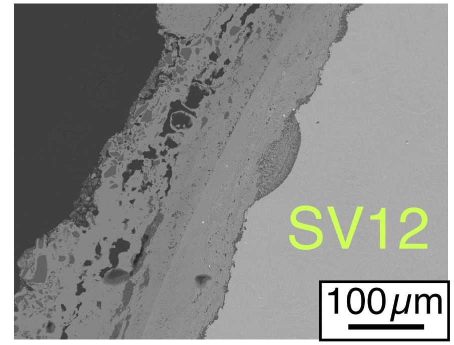


Pint & Thompson, NACE 2013

SAVE12 650°C ash: oxy not worse

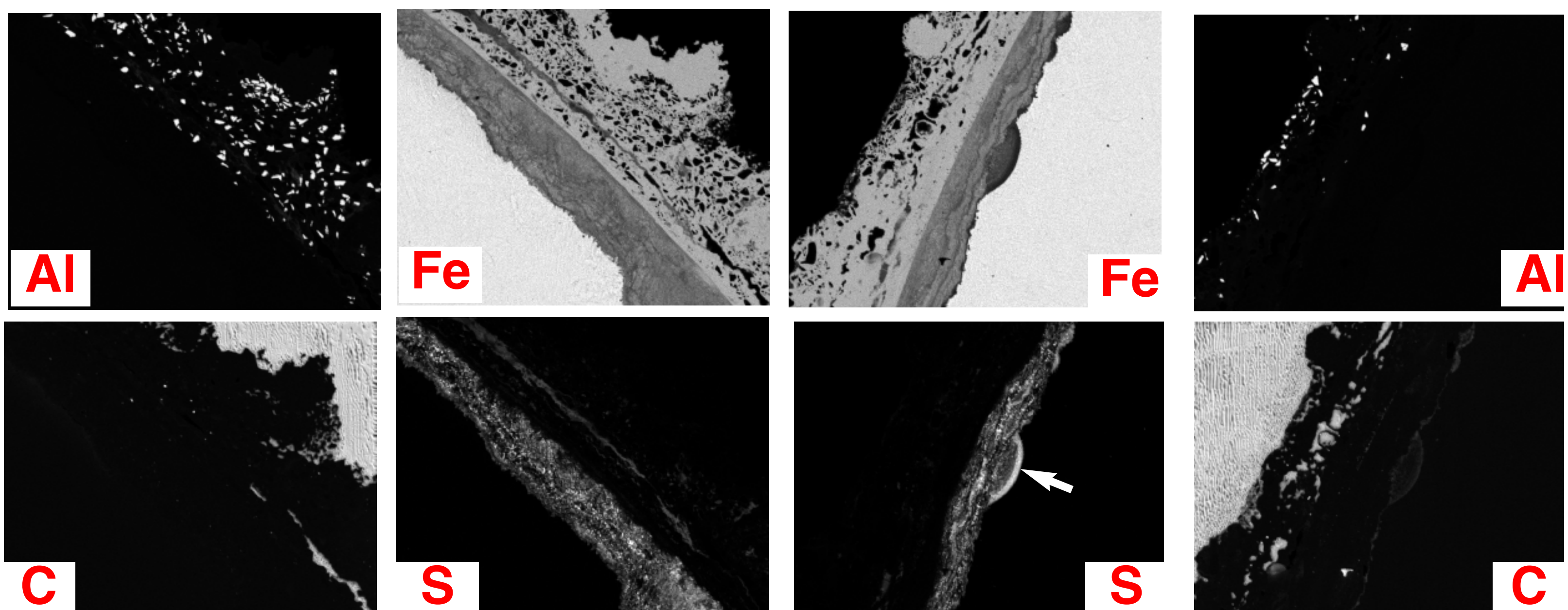






“air-firing”
15%CO_2-10%H_2O-0.15%SO_2

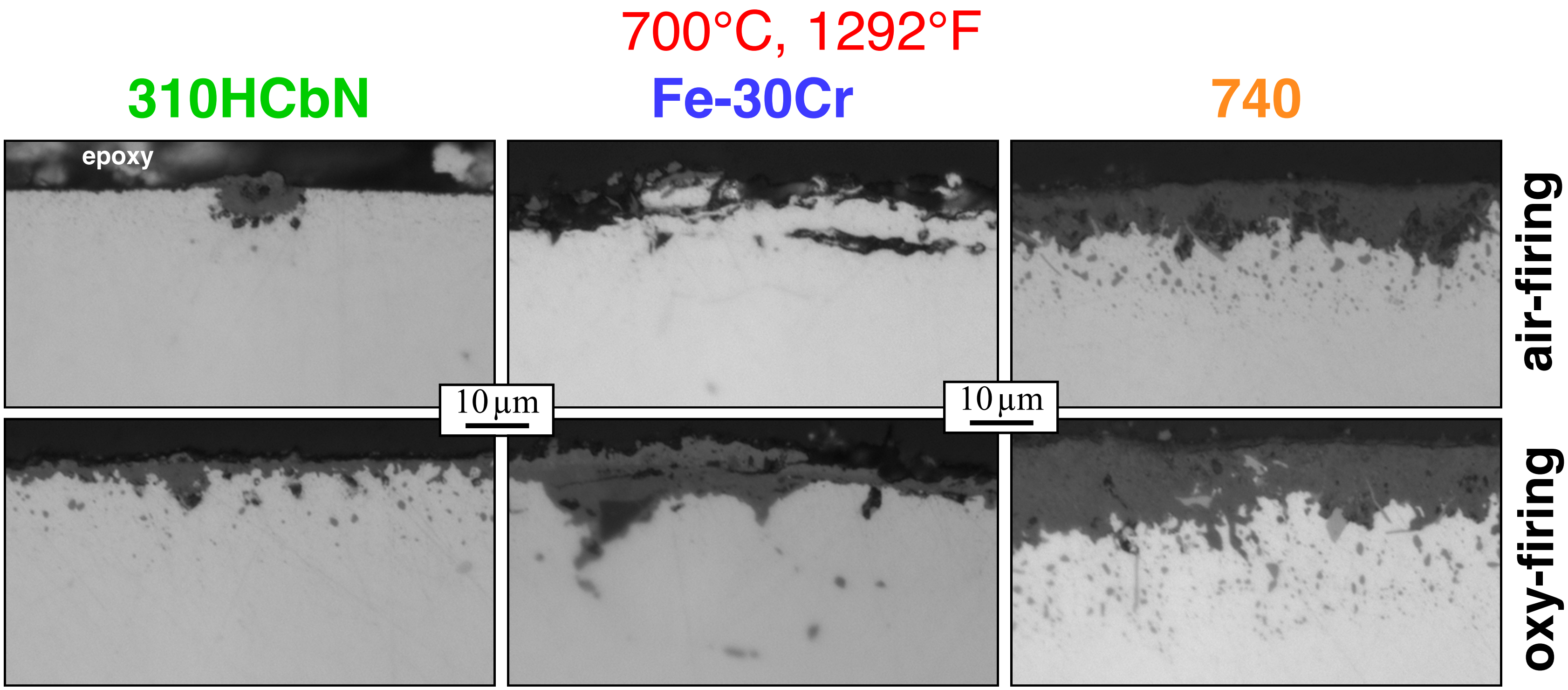
“oxy-firing”
61%CO_2-30%H_2O-0.45%SO_2



Pint & Thompson, Mater. Corr. in press

700°C: thin reaction products

500h, synthetic ash, light microscopy



Pint & Thompson, NACE 2013

Peak temperature for the molten alkali iron trisulfates

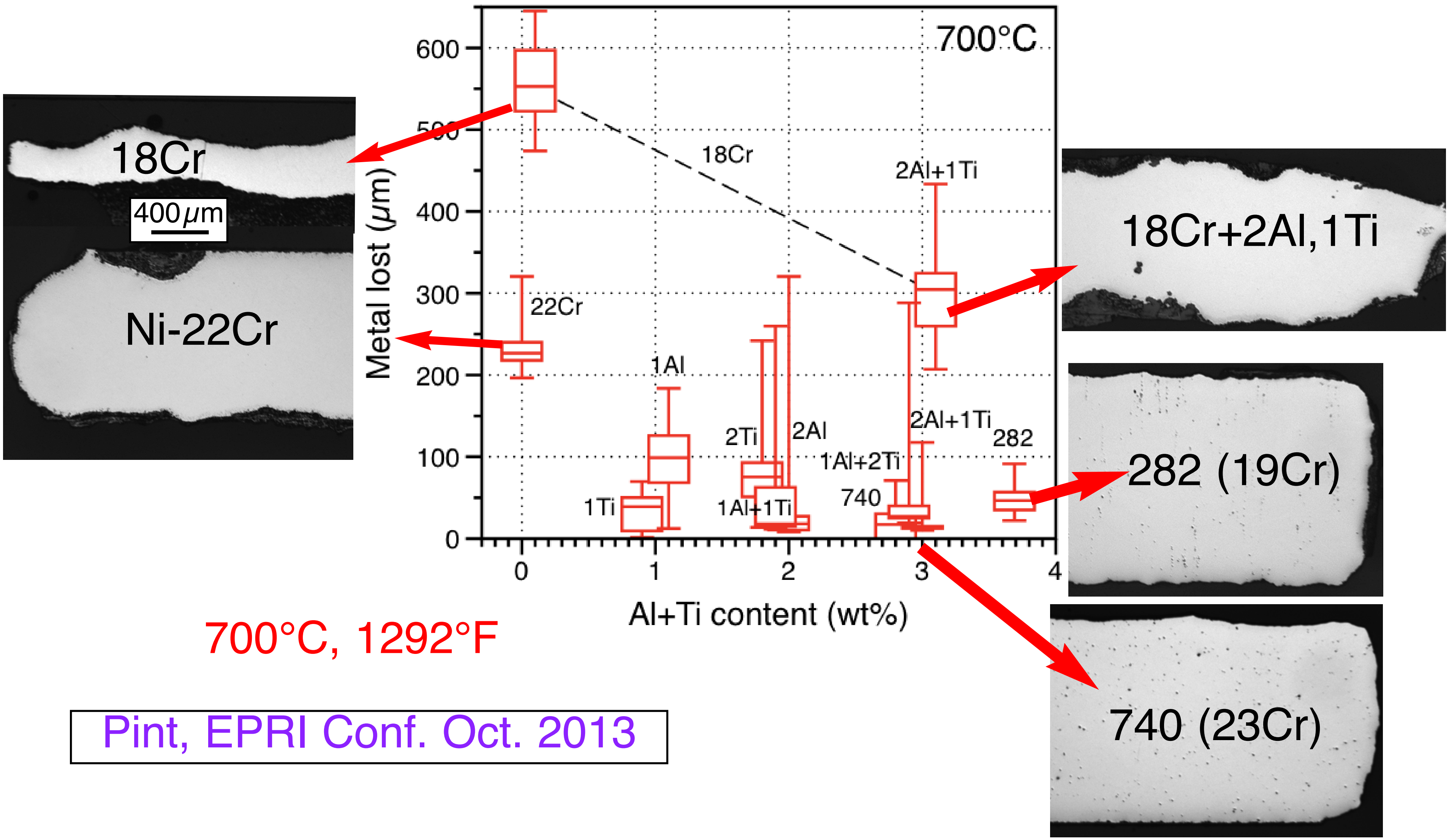
310CbN: smaller pits

740: deeper internal oxides (presumably Al and Ti)

Fe-30Cr: less uniform oxide (but no Ni)

Model NiCr alloys: sensitive to Cr

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



700°C, 1292°F

Pint, EPRI Conf. Oct. 2013

Al and Ti additions do not explain everything...

Summary: Creep in steam

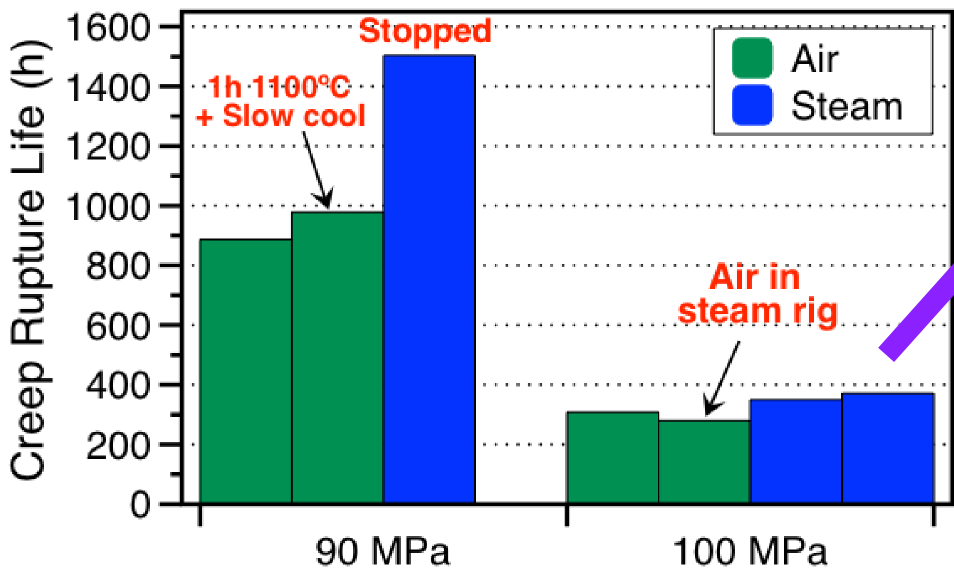
1. 800°C (completed): Dryepondt, et al. Mater. Corr. 2012
   740 (Ni-23Cr-20Co); 230 (Ni-22Cr-14W)
   air vs. steam
   in-situ vs. ex-situ
   anneal (thermal effect)
   microstructure analysis

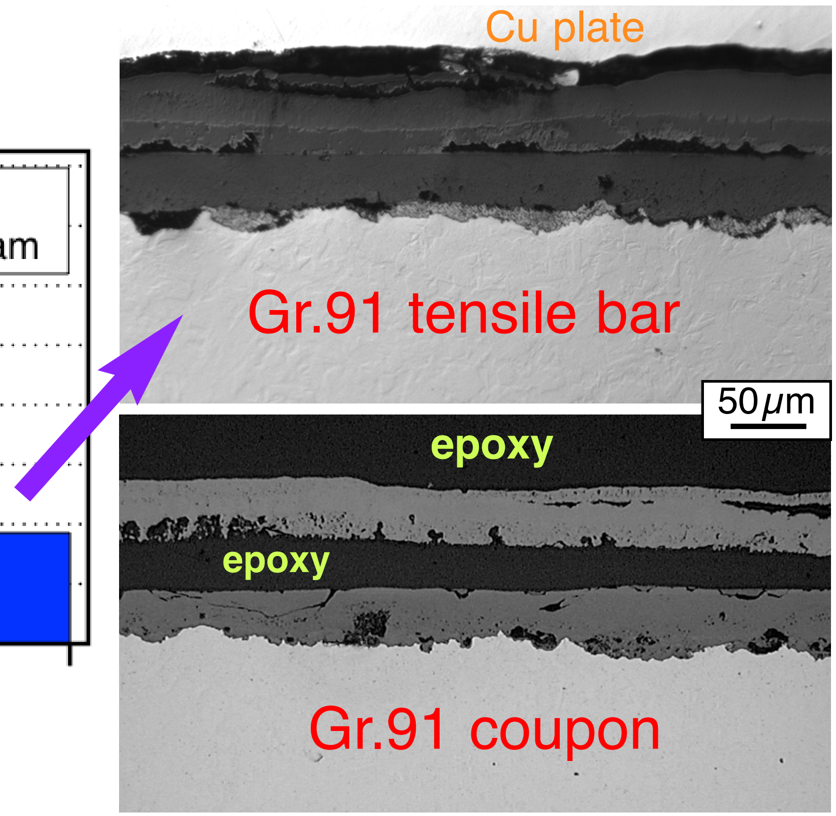
2. 650°C:
   Grade 91 (9Cr-1Mo)
   air vs. steam
   role of thick scale

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

Two concerns: temperature & load transfer

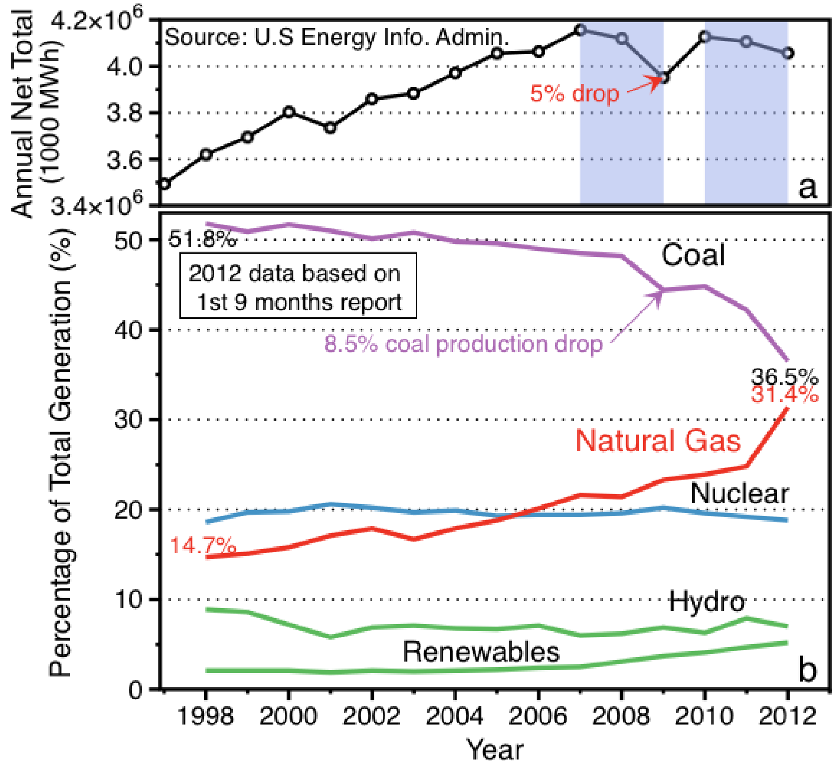
Verified similar oxide formed on coupon in steam

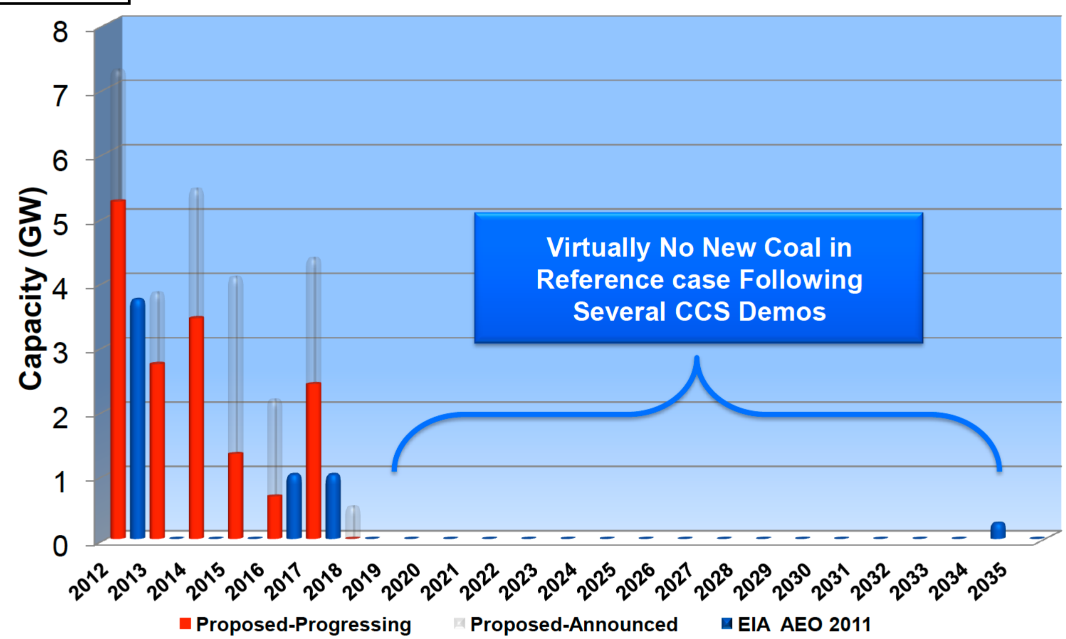
2nd test on alloy with improper anneal: 1h/1100°C

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 tasks

1) complete oxy-fire reporting

2) continue "in-situ" work
   - perhaps fatigue testing in steam (A-USC)

3) H-induced stress corrosion cracking
   - Grades 22,23,24
   - significant for industry
   - little "science"

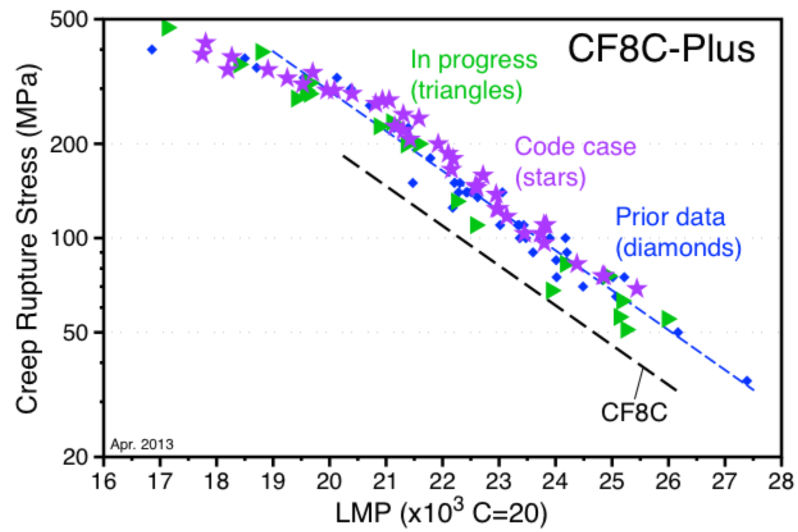
Cracks in longitudinal direction

Cracks in transversal direction

FY14 tasks

4) Complete code case on CF8C-Plus

- new cast alloy (347)
- pumps/valves
- EPRI wrought version
- EERE started effort



Milestones

FY11

Done (9/12) - Initial in-situ 650°C creep testing

FY12

Done - Report CO_2-H_2O effects (12/11)

Done - Complete 600°-650°C steam tests (3/12)

Done - Complete in-situ Ni-base creep test (6/12)

Done - Complete 700°C coal ash testing (9/12)

Milestones

FY13

Done - Assess temp. effect on ash testing (12/12)

Done - Complete Ni-Cr+Al,Ti ash testing (3/13)

- 650°C creep effect of steam-formed oxide (6/13)
- Compare C-ring & Jones test for SCC (9/13)

Summary

Three FY13 tasks: gas only, with ash, creep

- Concluding focus on oxy-firing
- Gas only: CO_2-H_2O similar to H_2O at 650°C
- Coal ash corrosion:
  - Completed 600°-800°C matrix early
  - Oxy-firing no worse with same ash
  - Followup on NiCr model alloys (A-USC)
- Creep: T91 work at 650°C in progress
  - Ni-base: 800°C work complete

Four FY14 tasks: oxy, creep, SCC, CF8C-Plus

CLEAN COAL.
COOL.

Why don't I expect an answer soon?

1. It's complicated (O_2-H_2O-CO_2-SO_2...)
- complicated experiments = more errors

2. Community is still struggling with H_2O effect
- answer may be at hand but no agreement
- little agreement between steam lab. vs. field

3. No agreement on experimental procedure (parameters are usually not even reported)
- steam: Ar-H_2O, 100%H_2O
- water chemistry: 0.055 vs <1 μS/cm (ISO)
- CO_2: O_2 buffer (boiler: always residual O_2)
- coal ash: time, cycle, cover vs. slurry, Pt catalyst, accelerated test vs. actual conditions

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?

Extensive use of commercial alloys

measured by inductively coupled plasma analysis and combustion analysis

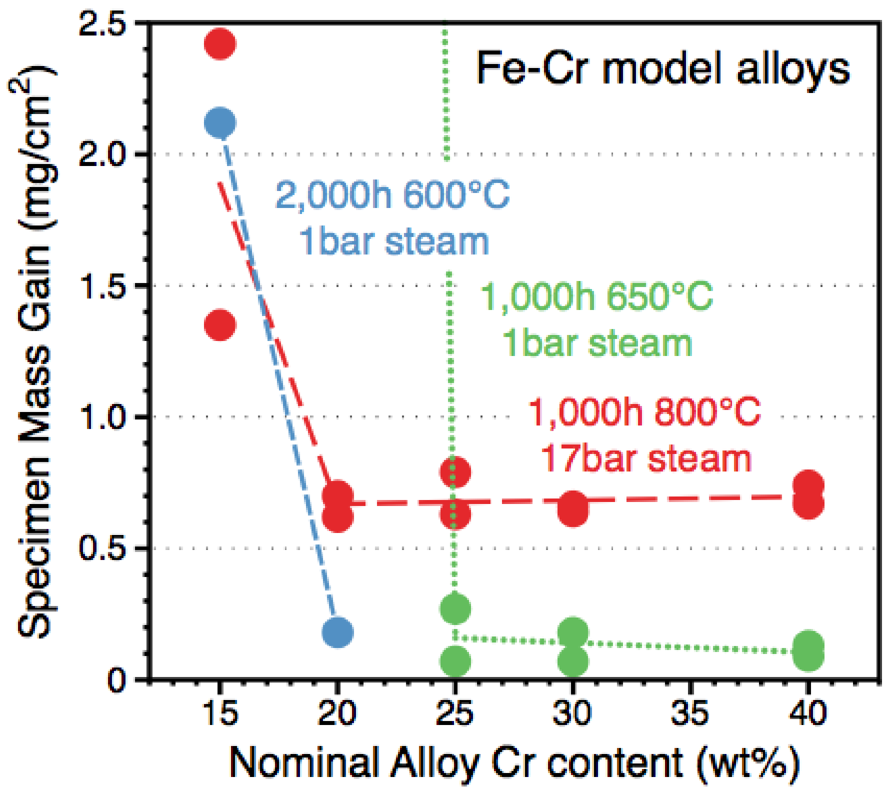
Alloy chemical compositions (weight %)

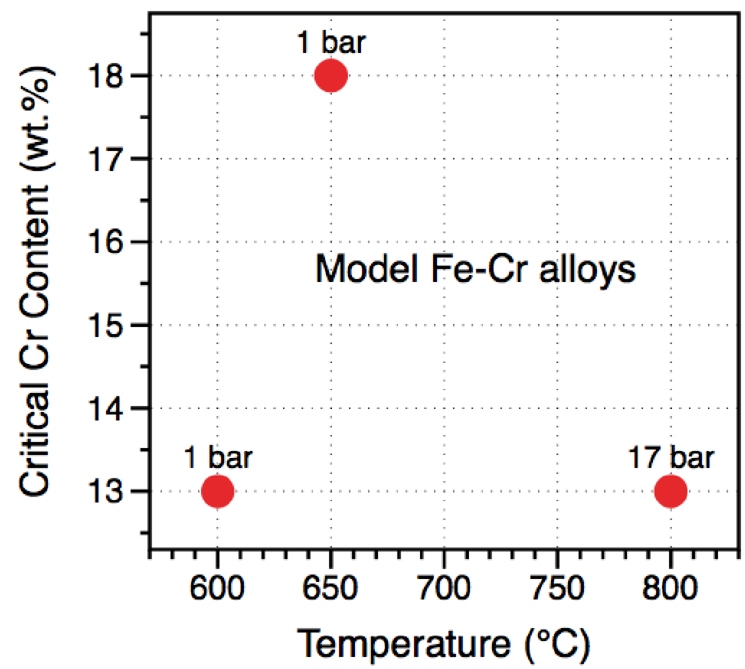
Alloy	UNS#	Fe	Cr	Ni	Mo	W	Mn	Si	C	N	Other
Gr.22	K21590	95.5	2.3	0.2	0.9	<	0.6	0.1	0.14	0.01	0.2Cu
Gr.91	S90901	89.7	8.3	0.1	0.9	0.01	0.3	0.1	0.08	0.05	0.3V,0.07Nb
Alloy12	——	83.4	9.6	0.3	0.05	3.0	0.4	0.1	0.11	0.01	2.6Co,0.3V
Fe-15Cr	——	85.1	14.8	<	<	<	<	<	<	<	
Fe-20Cr	——	80.3	19.7	<	<	<	<	0.01	<	<	
Fe-25Cr	——	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	<	<	
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
310HCbN	S31042	51.4	25.5	20.3	0.1	0.01	1.2	0.3	0.05	0.27	0.4Nb
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

< indicates below the detectability limit of <0.01%

Fe-xCr model binary alloys

1 and 17bar steam, 1-2 kh exposures

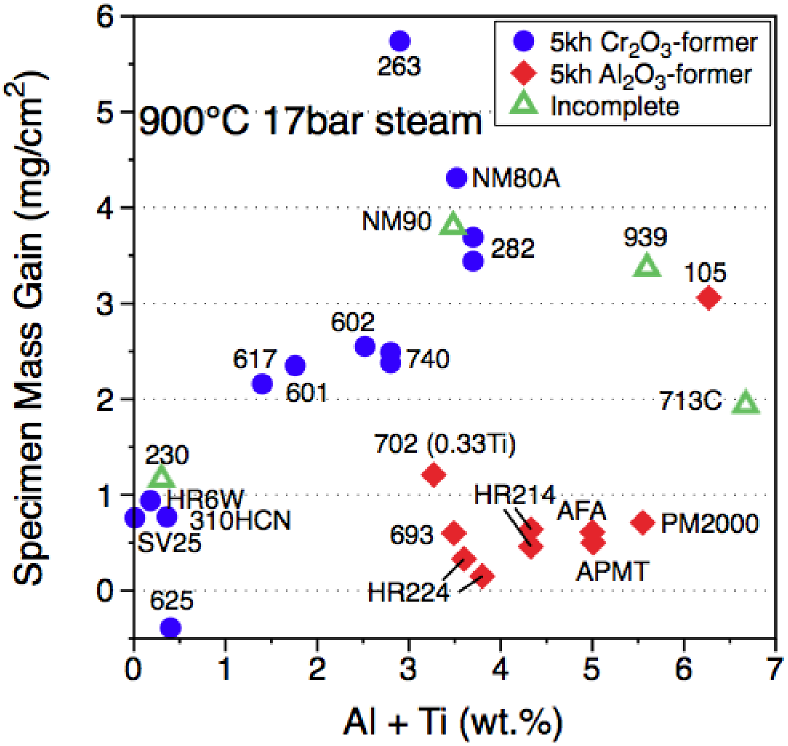




Here, model alloys perform worse than expected
Need to fill in with additional temperatures
Next question is about ternary additions (Mn, Si...)

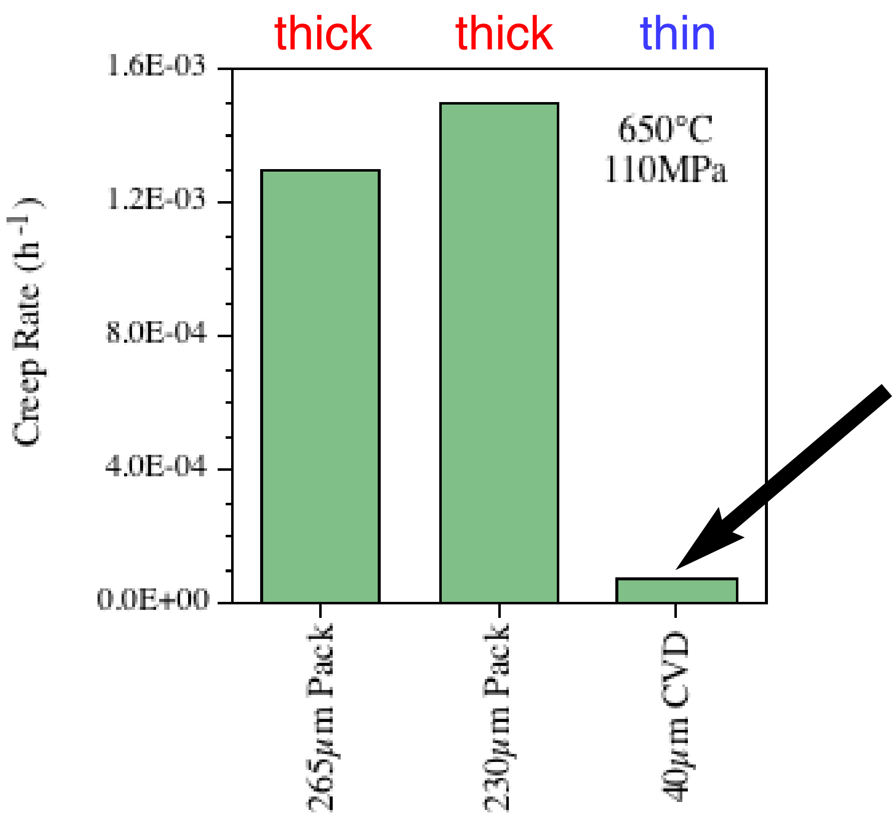
900°C steam

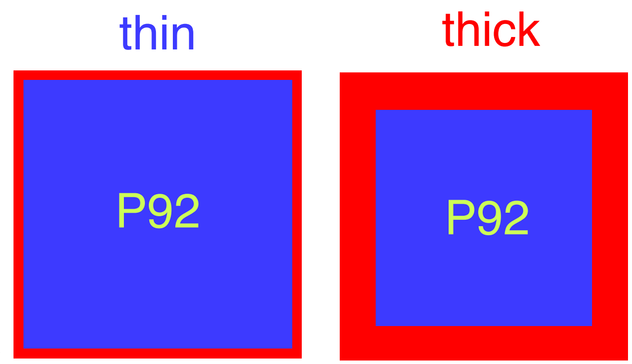
5,000h



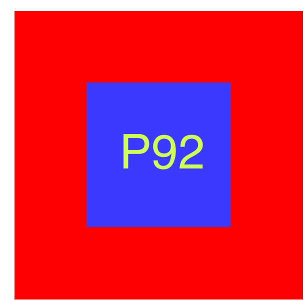
Creep Testing of P92 (Fe-9Cr-2W)

Effect of as-deposited coating thickness





as coated



650°C, 1202°F; gage: 2 x 2 mm

after long exposure

Specimen with thin coating has better creep resistance

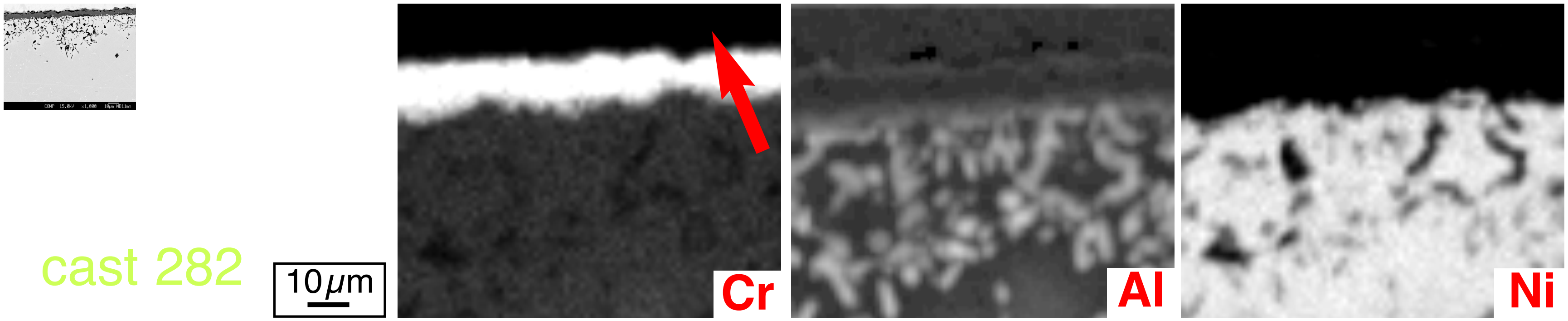
Effect of coating can be modeled as if coated layer absent

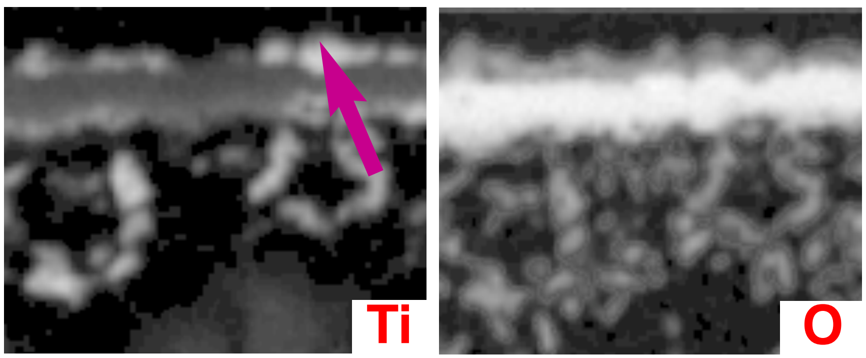
Suggests that thin coatings are preferable

Dryepondt et al., Surf. Coat. Tech. (2006)

Unusual Ti distribution in scale

Cast alloy 282 after 5kh in steam at 800°C



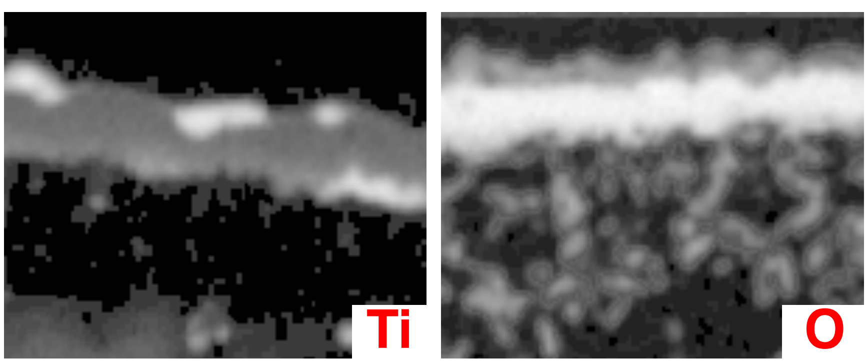


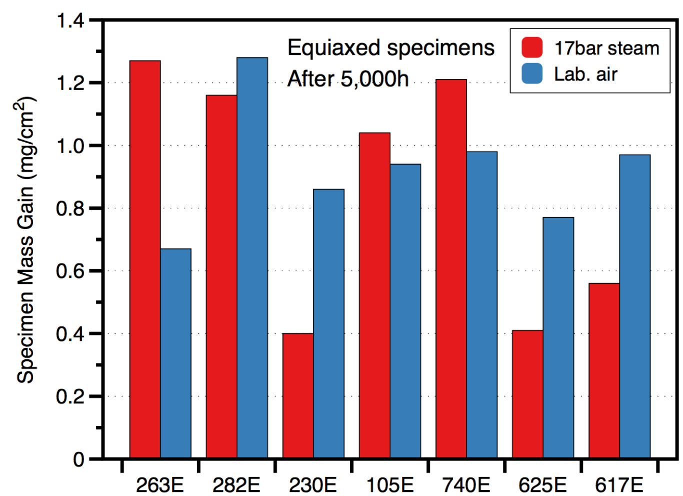
Electron probe analysis:

Typical internal Al + Ti oxidation

Ti “layer” at both gas & metal side

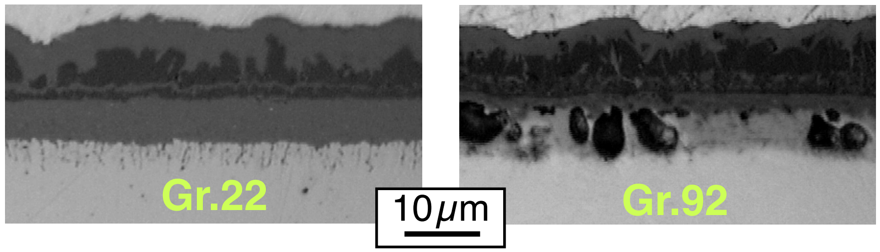
Scale after 5kh lab air:



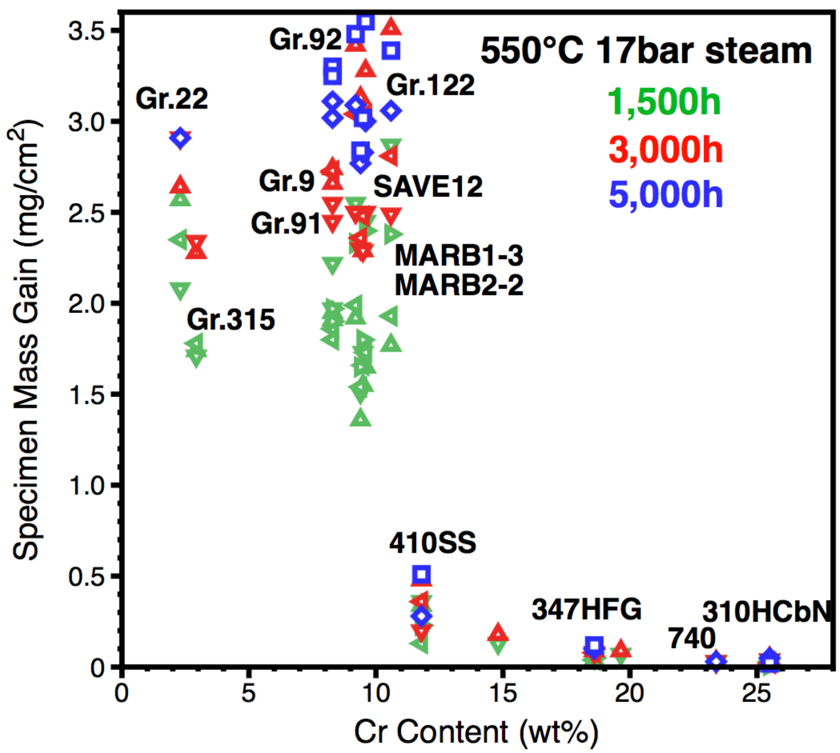


~12%Cr needed at 550°C

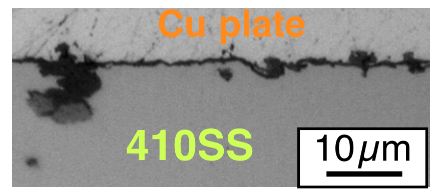
For protective behavior at 17bar steam



dual oxide layer



2,000 h 550°C

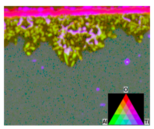


Surprisingly, little difference in 2.25-11%Cr steels

5,000h cross-sections in progress

800°C steam follow up work

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



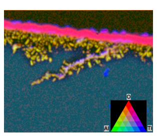
Ni~20Cr

Al+Ti->γ’

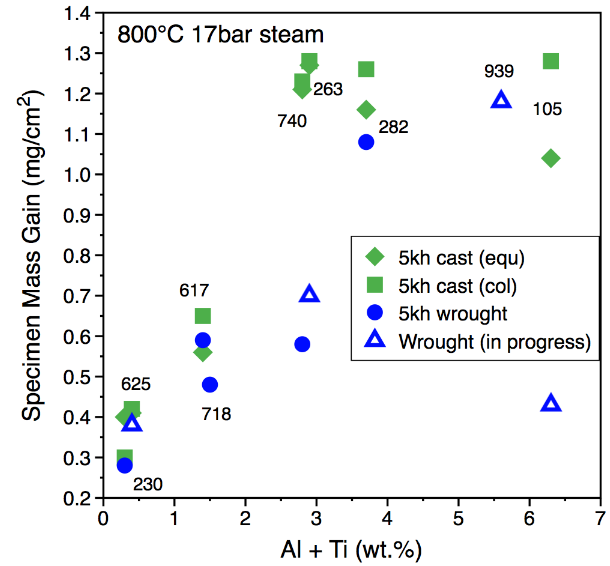
Cr_2O_3 TiO_2 Al_2O_3

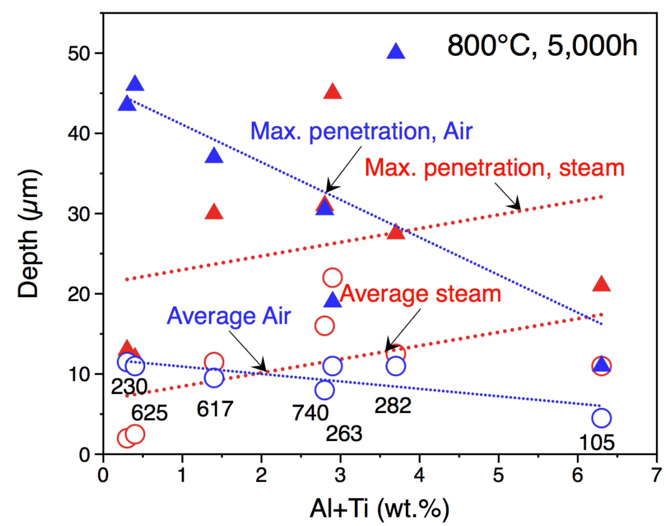
Synergy

Al-Ti ?



5 μm





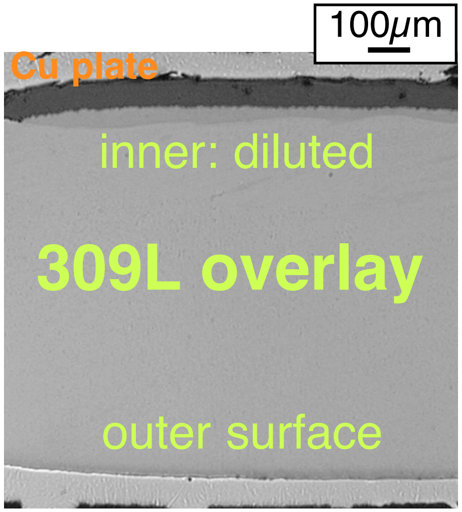
Model alloys: Ni-22Cr + Al +/- Ti in steam

Evaluated weld-overlay coupons

Air- and Oxy-firing conditions: 600°C, 500h

Nominal composition wt.% from Titanova

	Fe	Ni	Cr	other
309L	60	14	23	1Mn, 1Si
8020		80	20	
33	33	31	33	2Mo,1Cu
52	9	63	29	
72		57	43	0.3Ti
C22	3	58	23	13Mo,3W



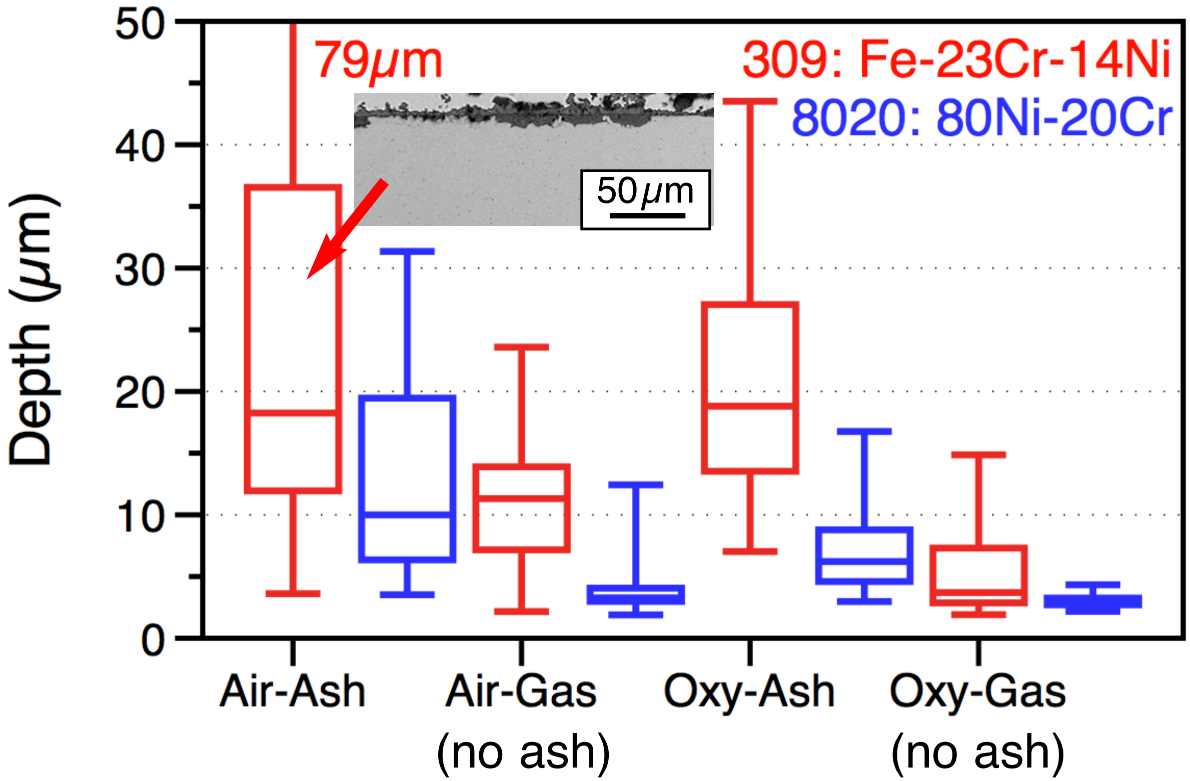
Rectangular coupons: removed overlay from tube

~1mm thick

- face adjacent to substrate has some dilution
- mass change data meaningless

Box plots to quantify attack

Air- and Oxy-firing conditions: 600°C, 500h

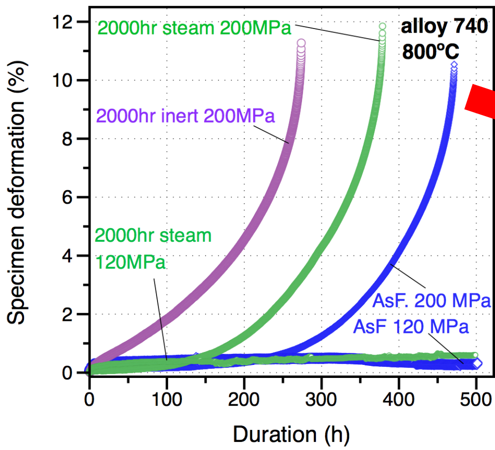


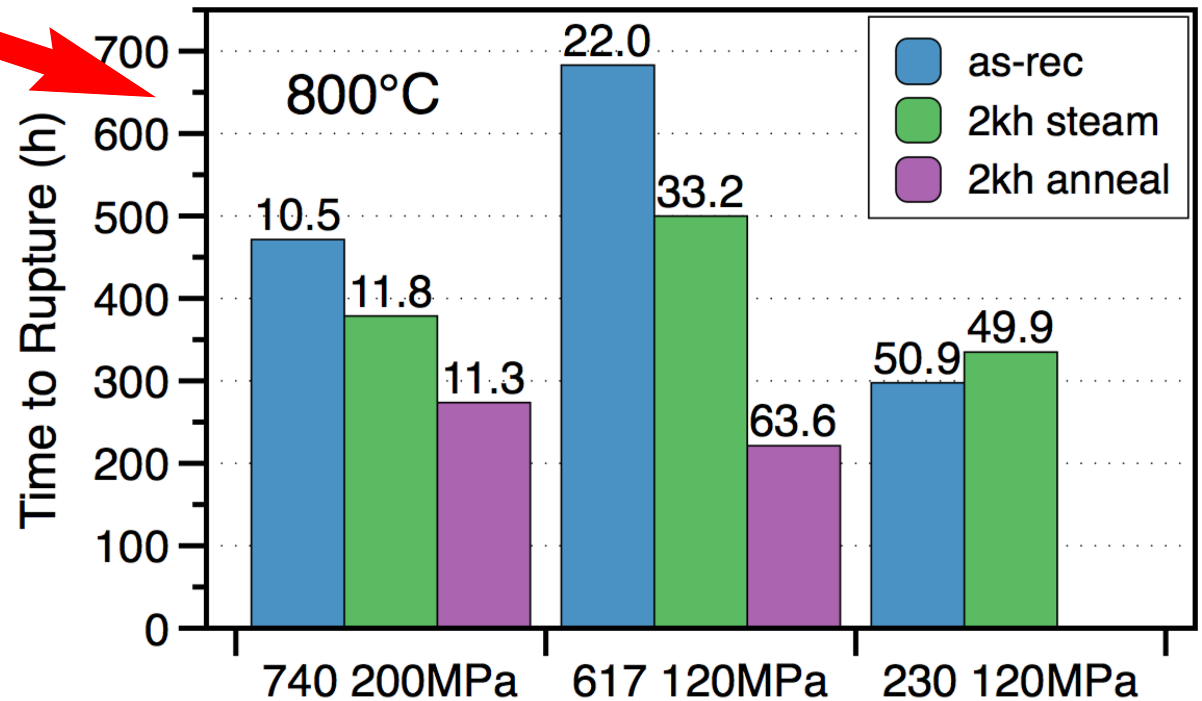
40 data points taken from 500X pictures

- including scale + internal oxidation
- high Ni coating more oxidation resistant
- attack not increased in oxy-firing conditions

Ex-situ testing: anneal vs. steam

2kh anneal to account for thermal effect





230: no effect of 2kh in steam at 800°C

740/617: decrease life after 2kh steam

larger decrease with 800°C 2kh anneal (?)

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

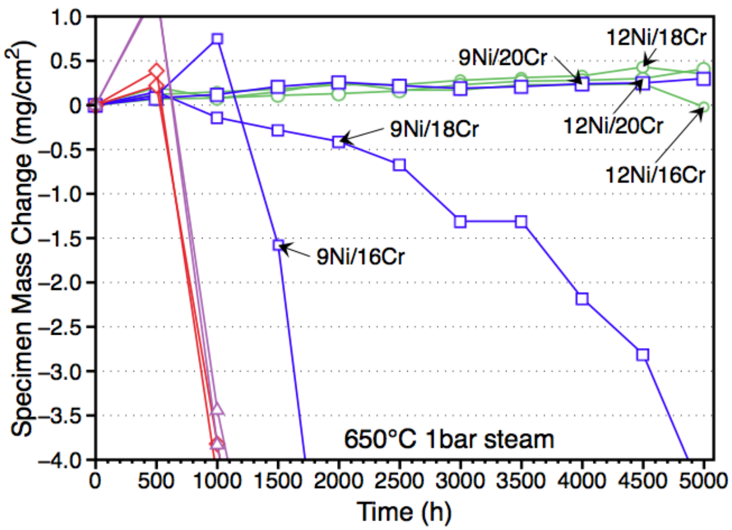
Was it an effect of Cu or other element(s)?

* Model alloys to better understand composition

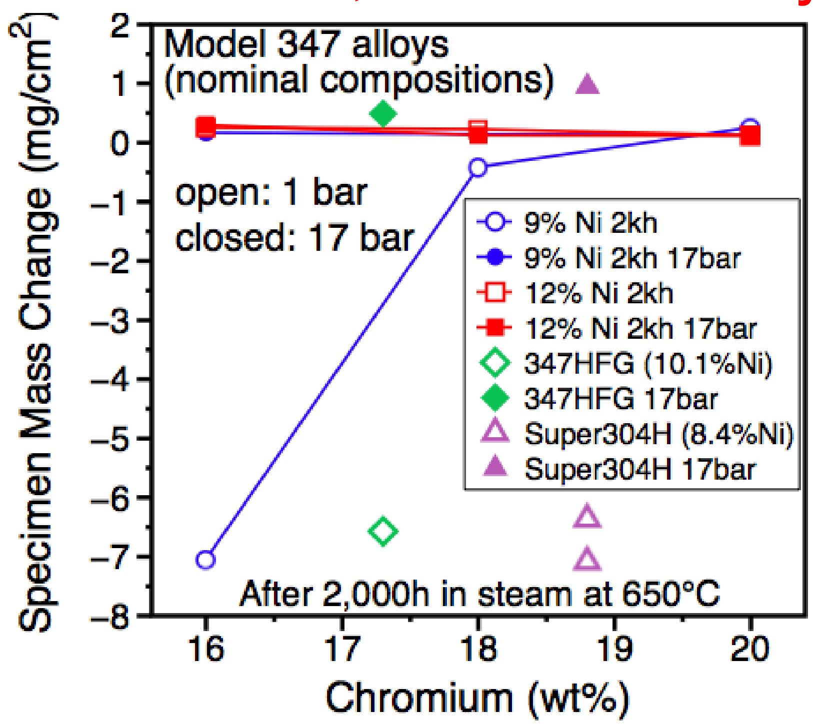
Model 347 alloys: 650°C steam

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

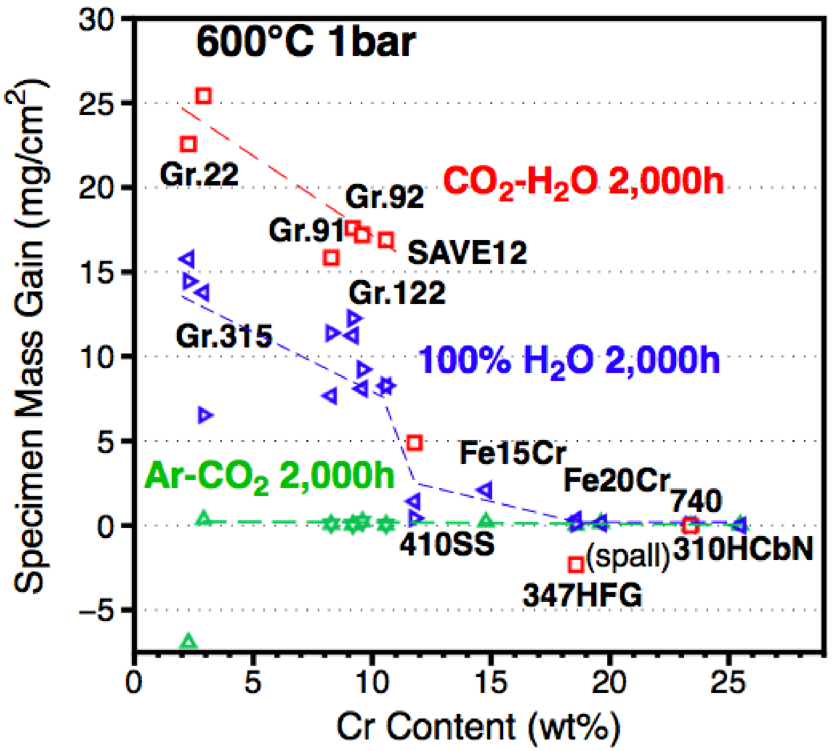
2000h 17bar completed April 2012 (no effect)

Concern: model alloys better than 347HFG & S304H

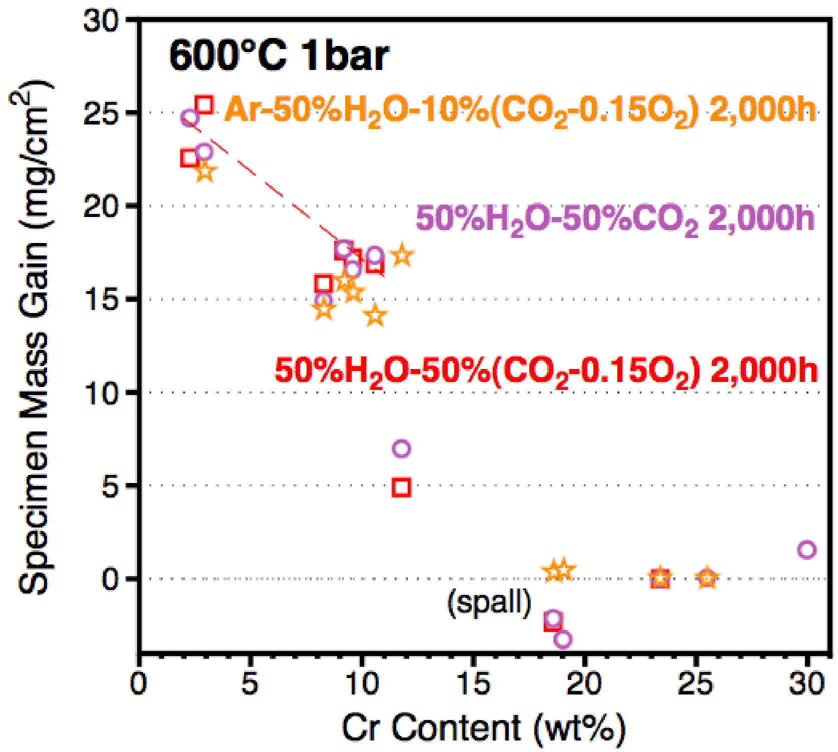
Little effect of $C(CO_2)$ & buffer

600°C, 4 x 500h cycles, 1bar

FY11 results



FY12 results



No buffer: 50%H_2O-50%CO_2

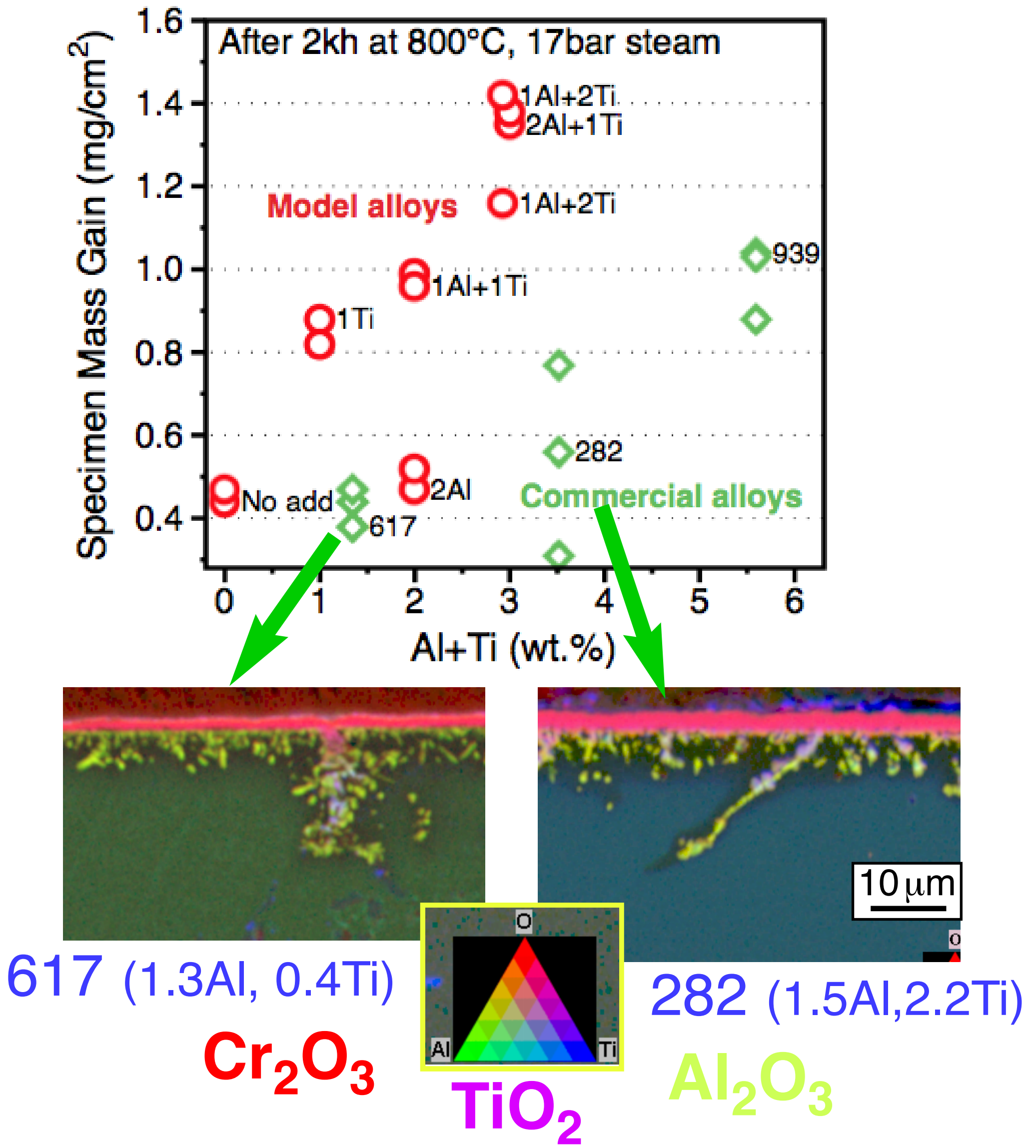
Lower CO_2: Ar-50%H_2O-10%(CO_2-0.15O_2)

Both: little effect on 2,000h mass change

Need to complete metallography comparison

800°C model Ni-22Cr alloys

17bar steam, 2,000h exposure



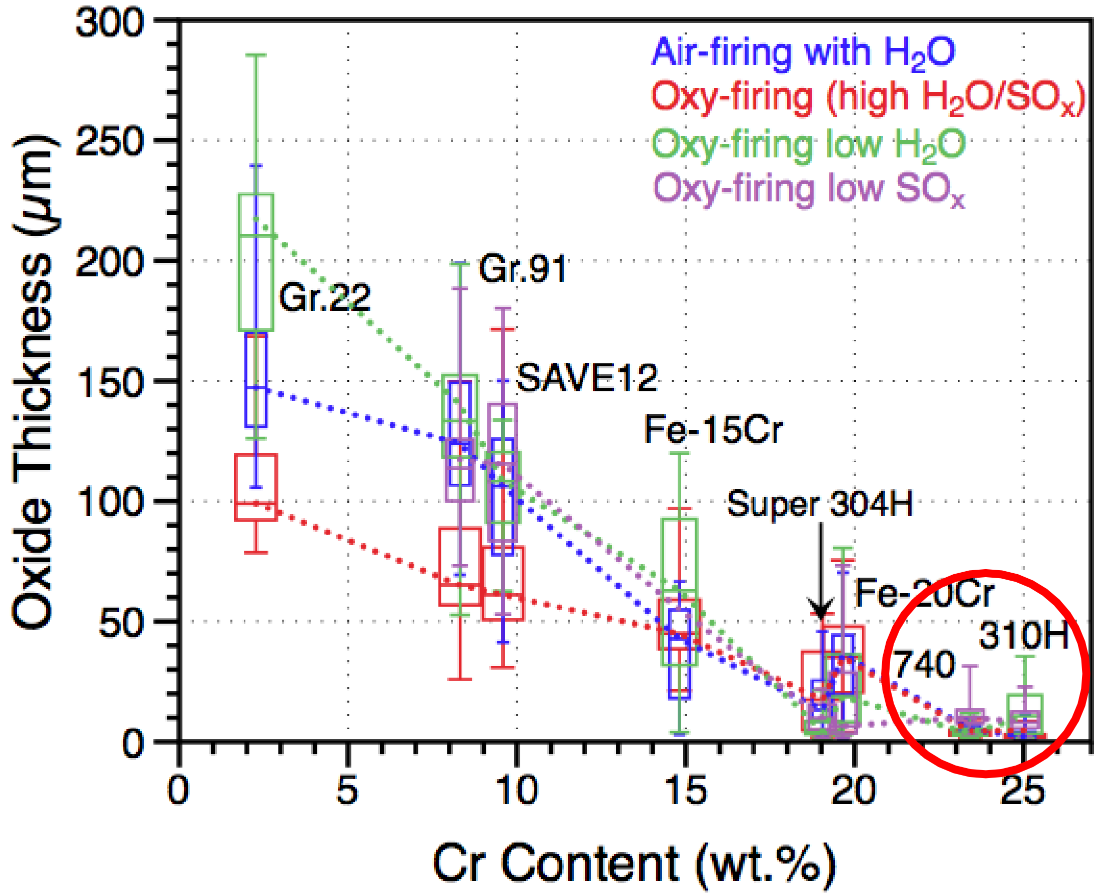
Model alloys:
simulate Al,Ti effect on internal oxidation

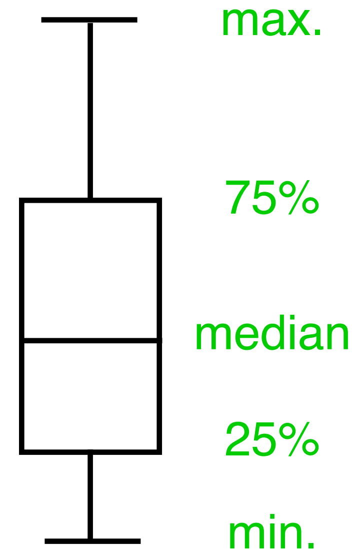
Ni-18Cr alloys (282) fabricated (2)

Future:
quantify depth of attack
continue to 5,000h
expose to coal ash

Little effect of gas at 600°C

Synthetic coal ash, 500h exposures in 4 gases





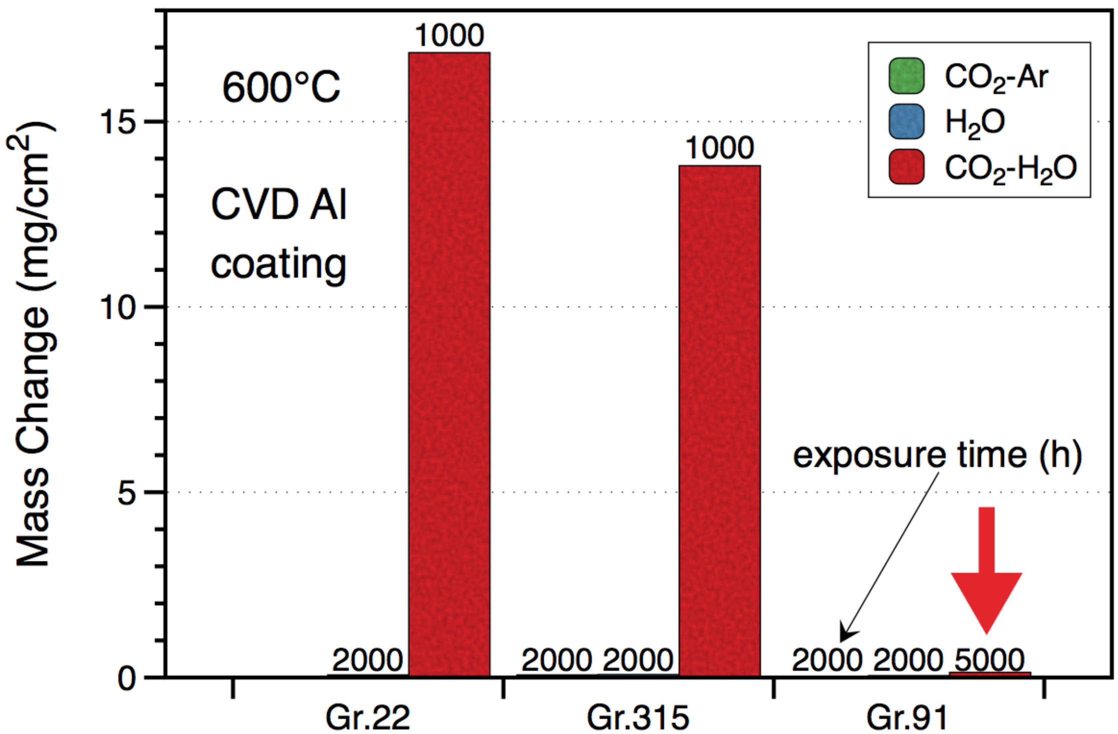
Higher CO_2 environments not detrimental

Expected the lower SO_2 environment to lower attack

- same synthetic ash used in all cases

Coating results at 600°C

Low Al content chemical vapor deposition coating



Conclusions:

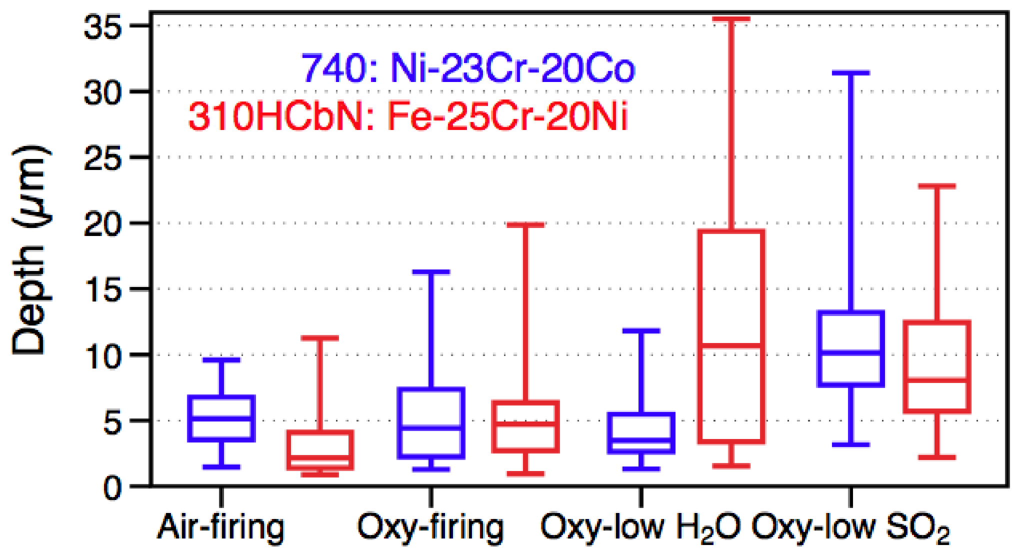
Coating prevents thick oxide formation in steam

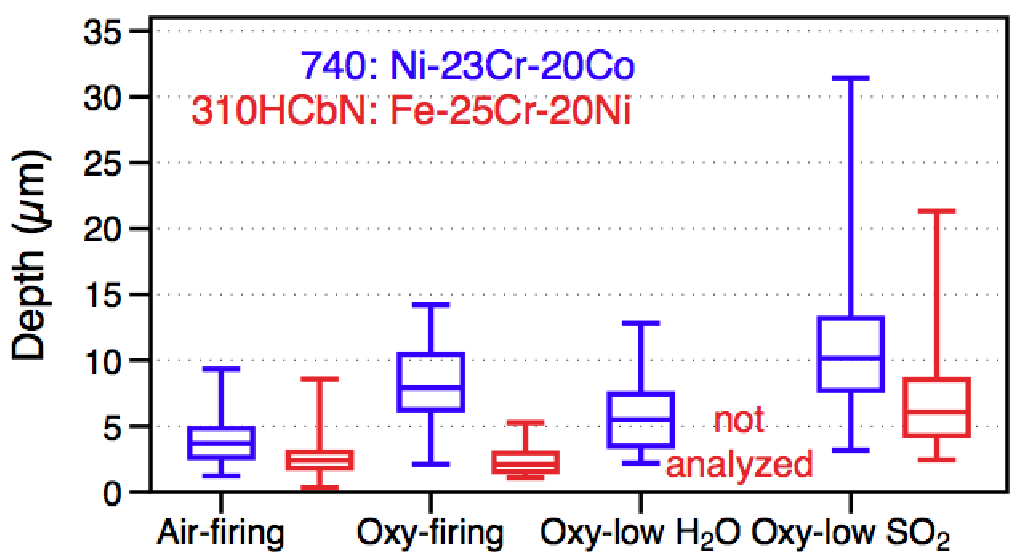
Coating less effective on low Cr substrates

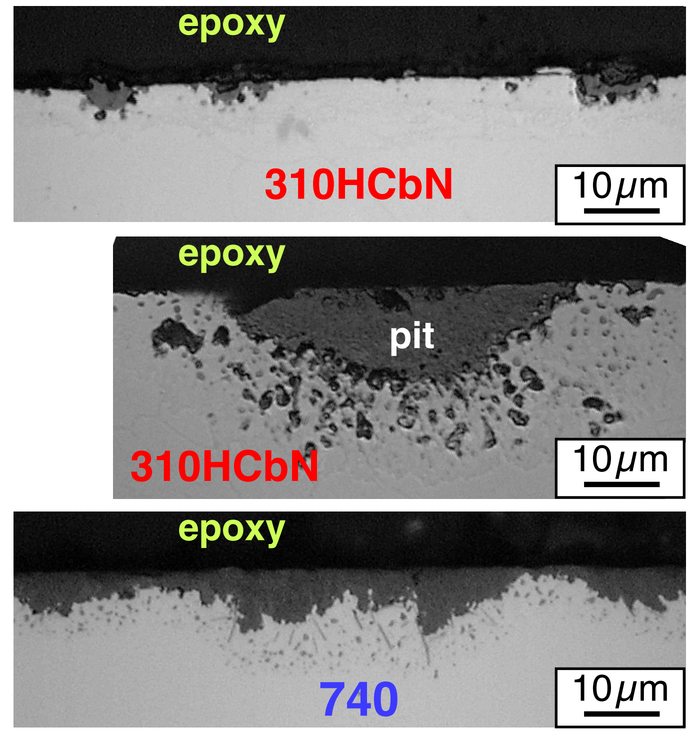
CO_2-H_2O is most aggressive environment

Reanalyzed: 310HCbN < 740

High Ni-content alloy not most protective at 600°C



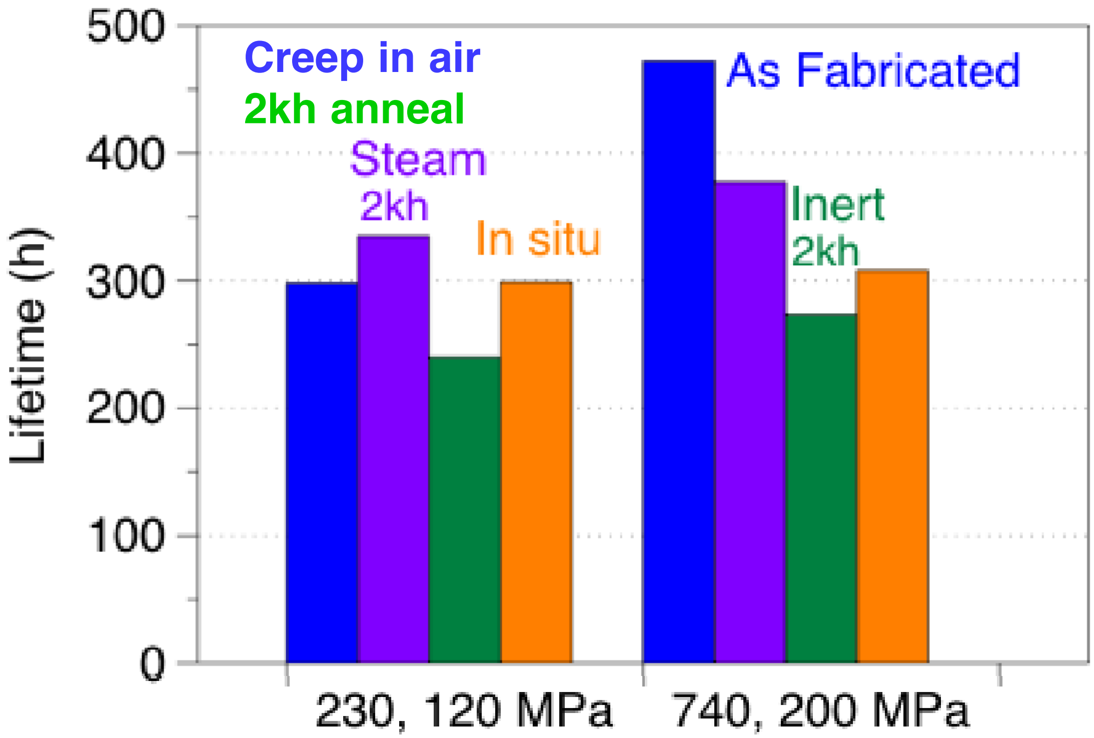


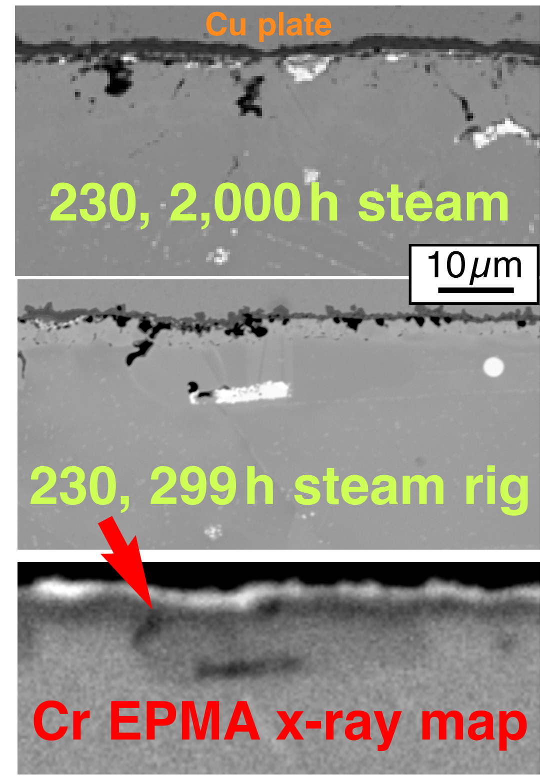


More accurate distributions from new images

800°C: 230/740 limited steam effect

Creep rupture tests in air and 1 bar steam





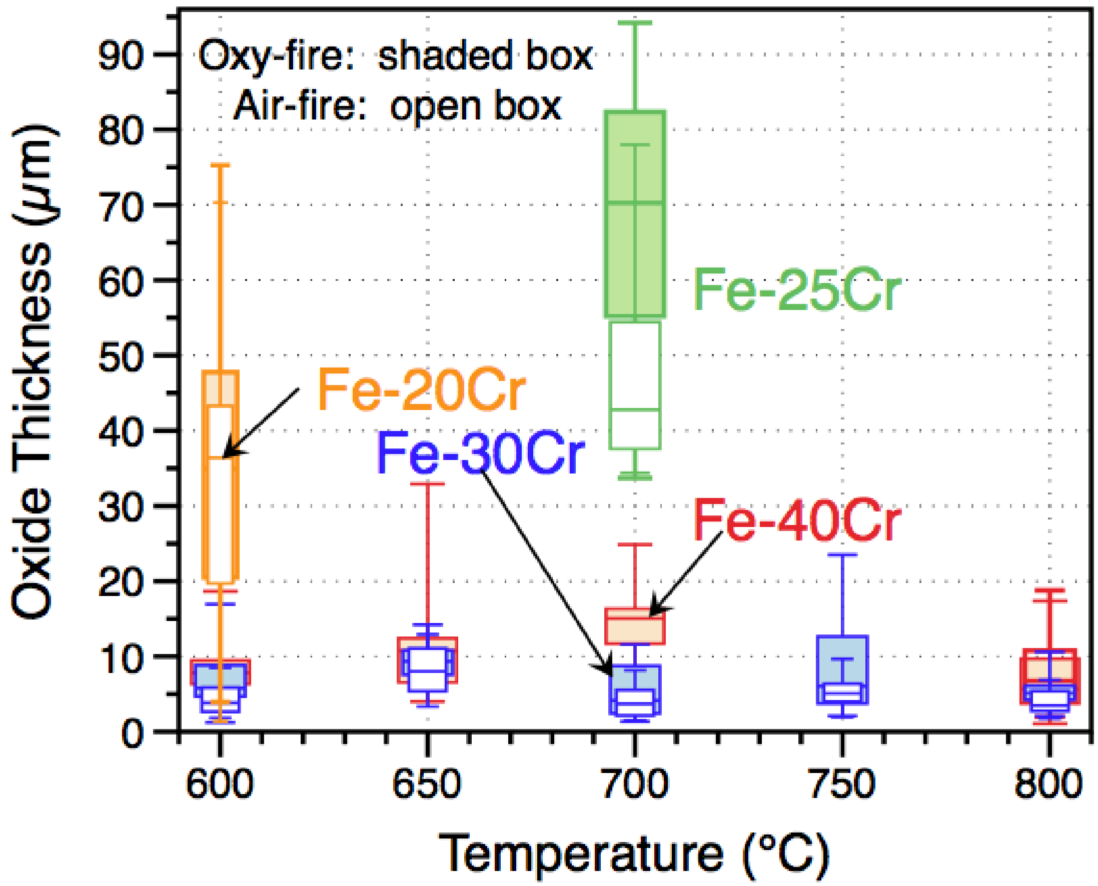
230: no effect of in-situ or ex-situ steam

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

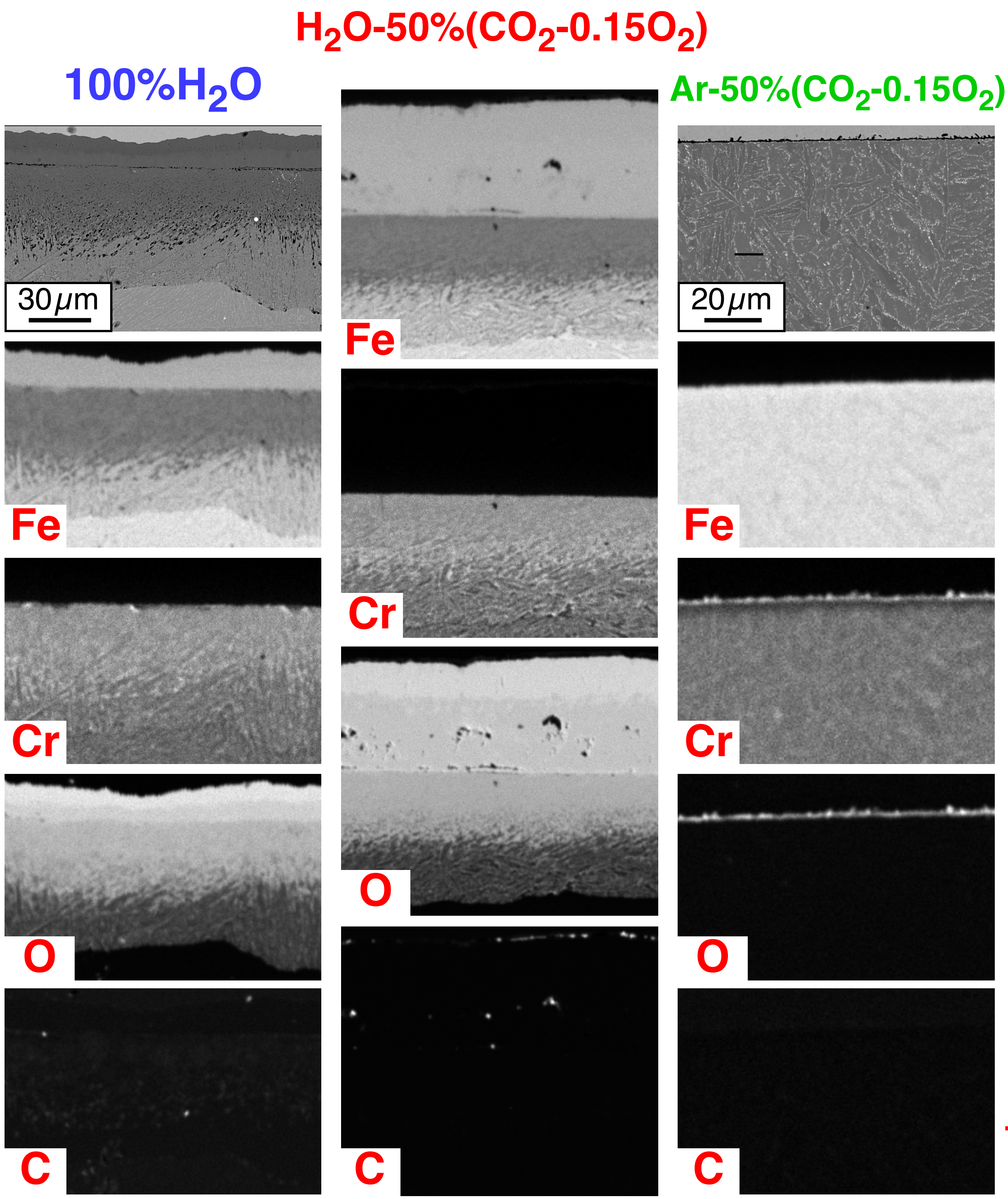
Fe-40Cr casting had problems with Cr rich phases

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

SAVE12

EPMA

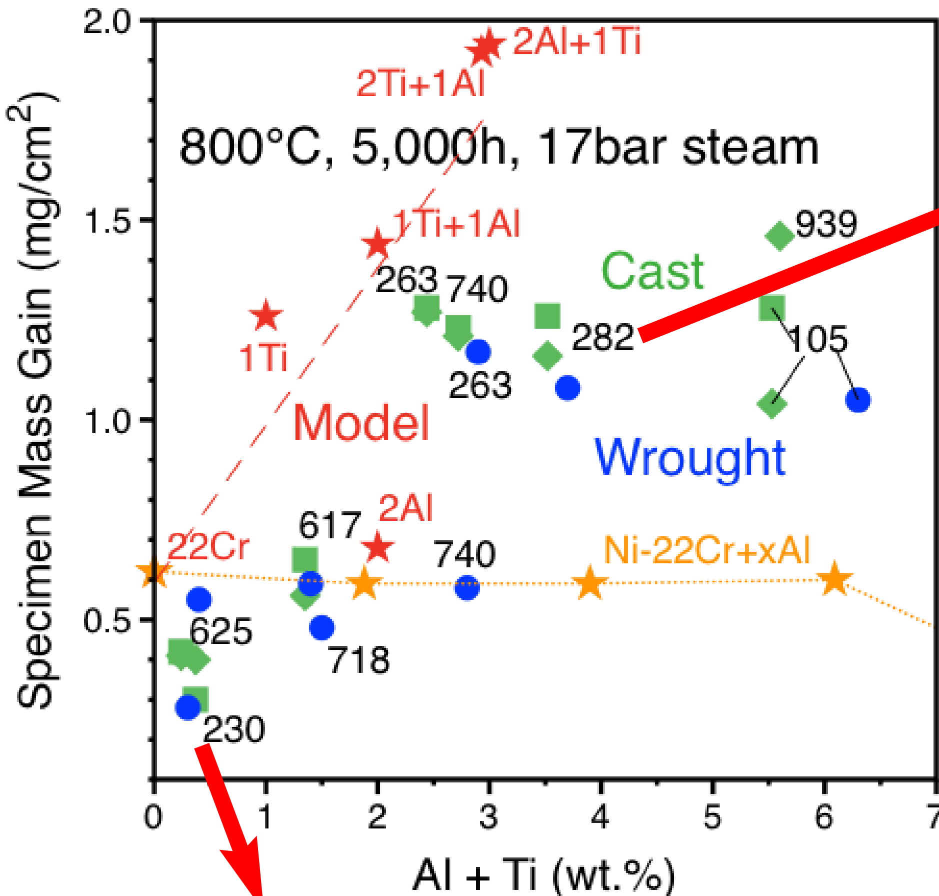
2,000h 600°C

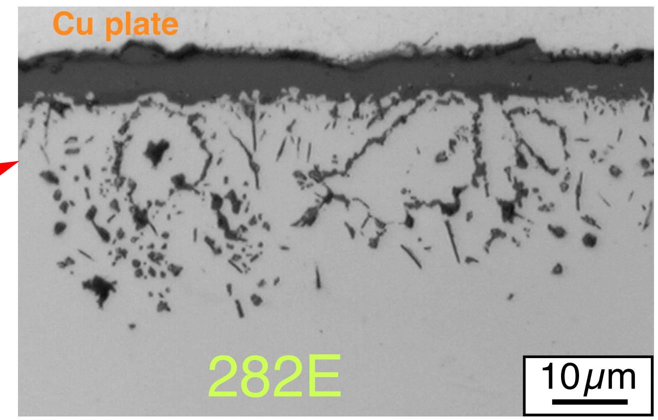


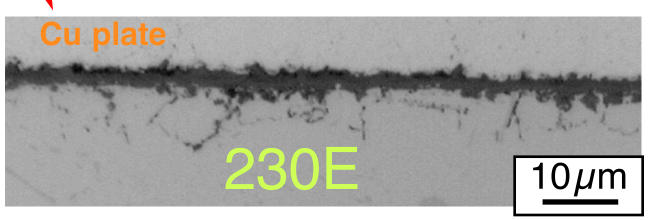
not high enough magnification to see carbides?

800°C steam: Ti sensitive

5,000h steam testing at 17 bar, 800°C





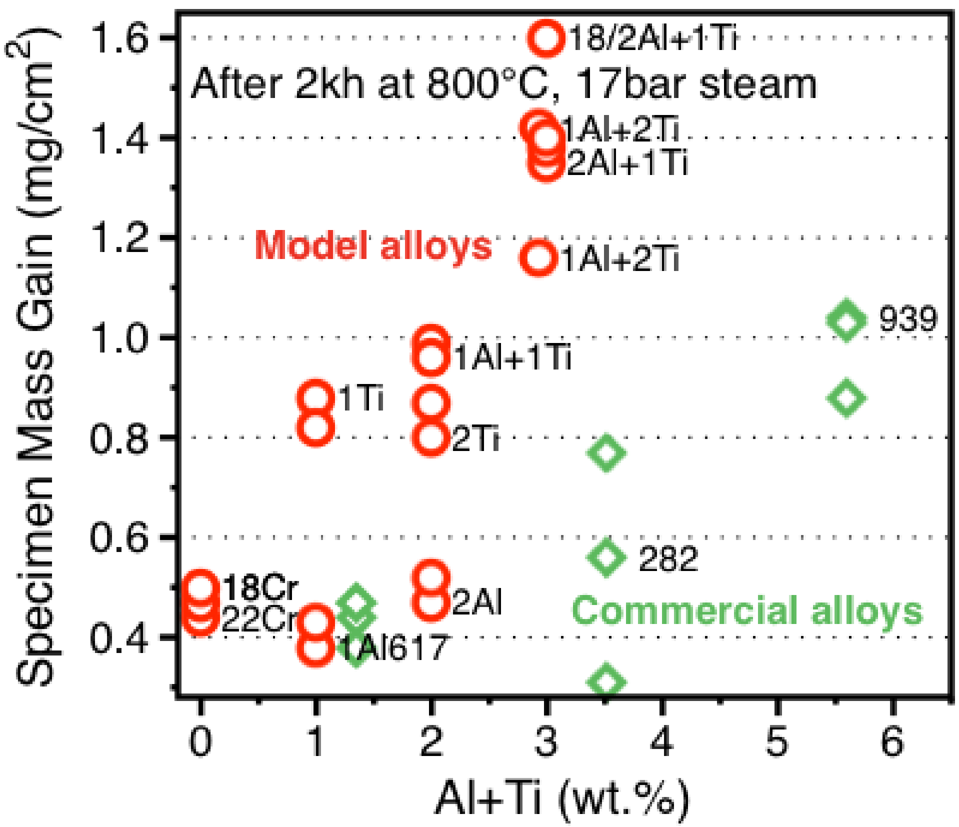


Model alloys: need to complete metallography

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.

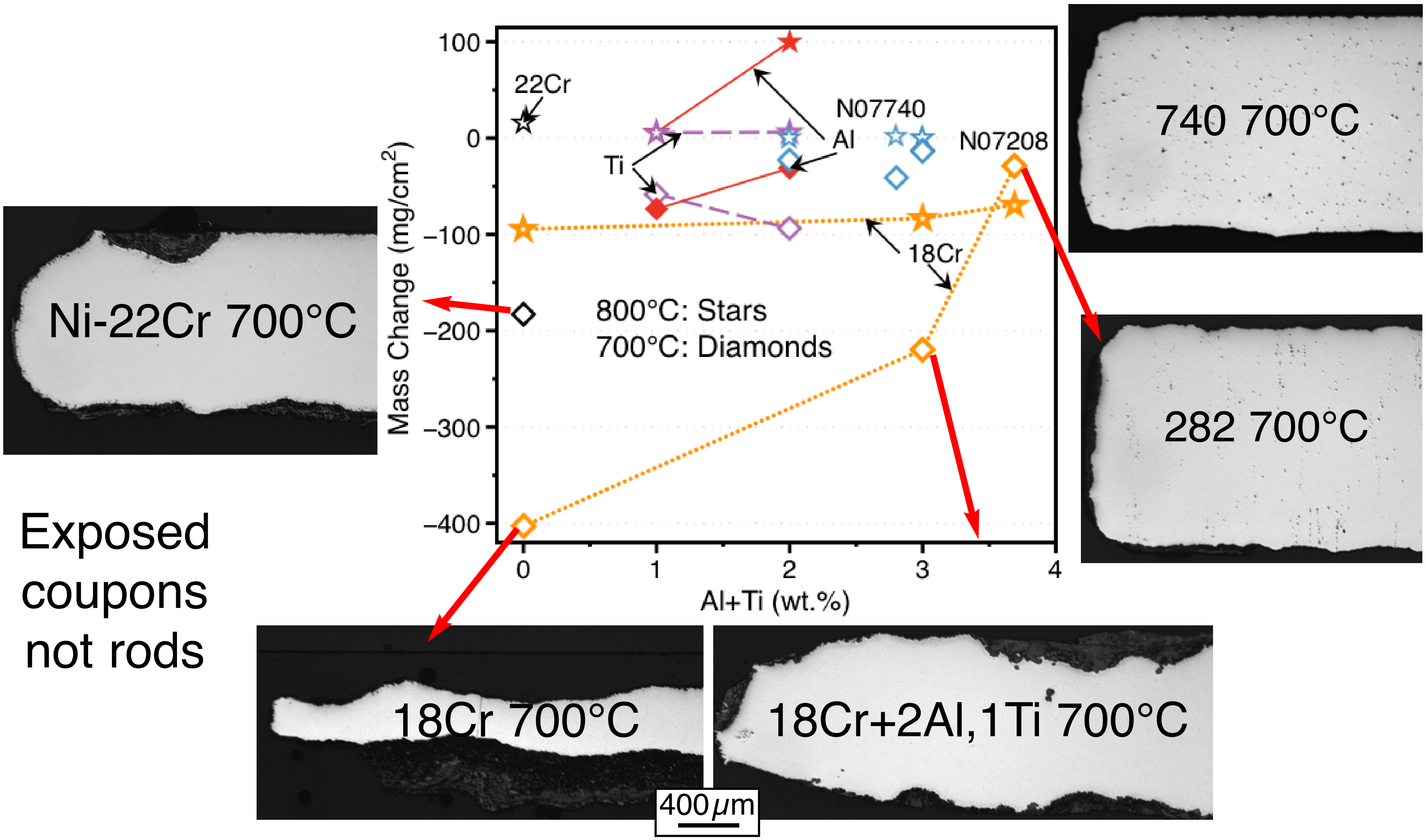
800°C steam: Ti sensitive

2,000h steam testing at 17 bar, 800°C



Model NiCr alloys: more sensitive to Cr

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



Exposed coupons not rods

Al and Ti additions do not explain everything...