Understanding Corrosion Mechanisms in Oxy-Fired Systems

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T. Lowe - SEM, image analysis

D. Leonard - EPMA

12MWh/yr per U.S. resident

Where will it come from?

coal?

how?

Conventional: “USC”

-PC Turk, AR, 595°C

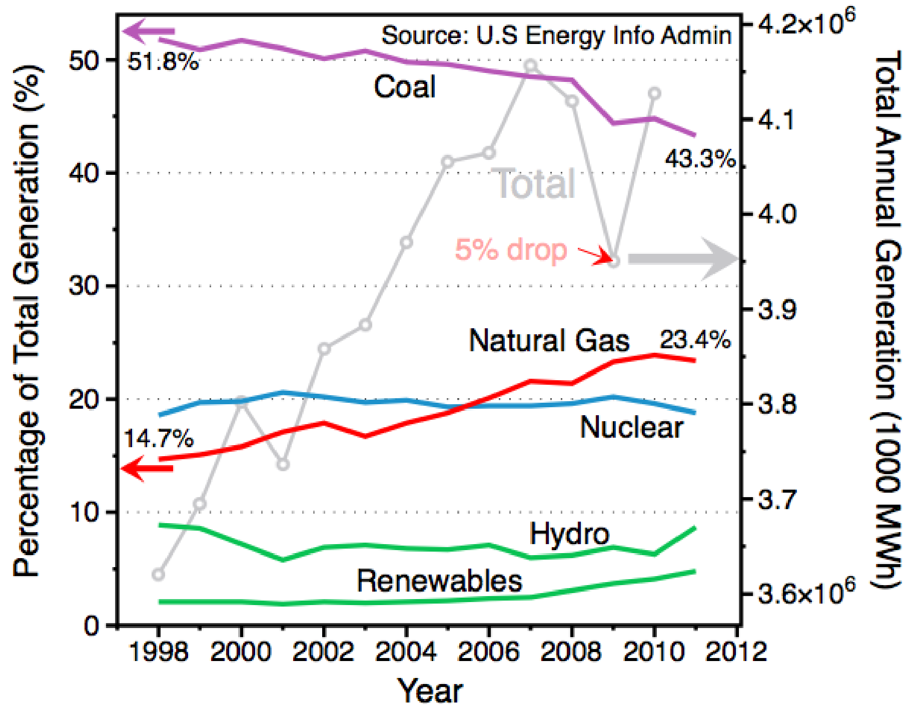
Gasification:

-IGCC Kemper Co., MS

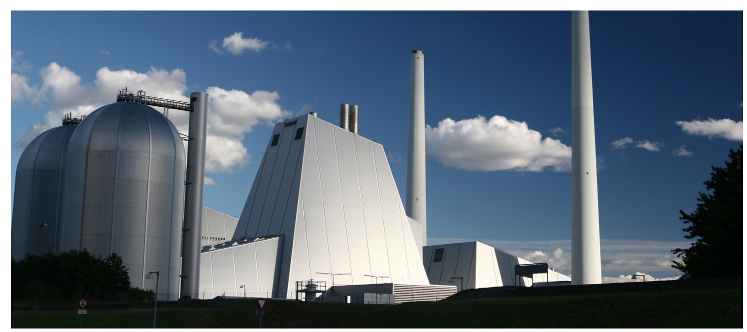
-IGCC Edwardsport, IN

Oxy-firing:

-FutureGen 2.0 (?)



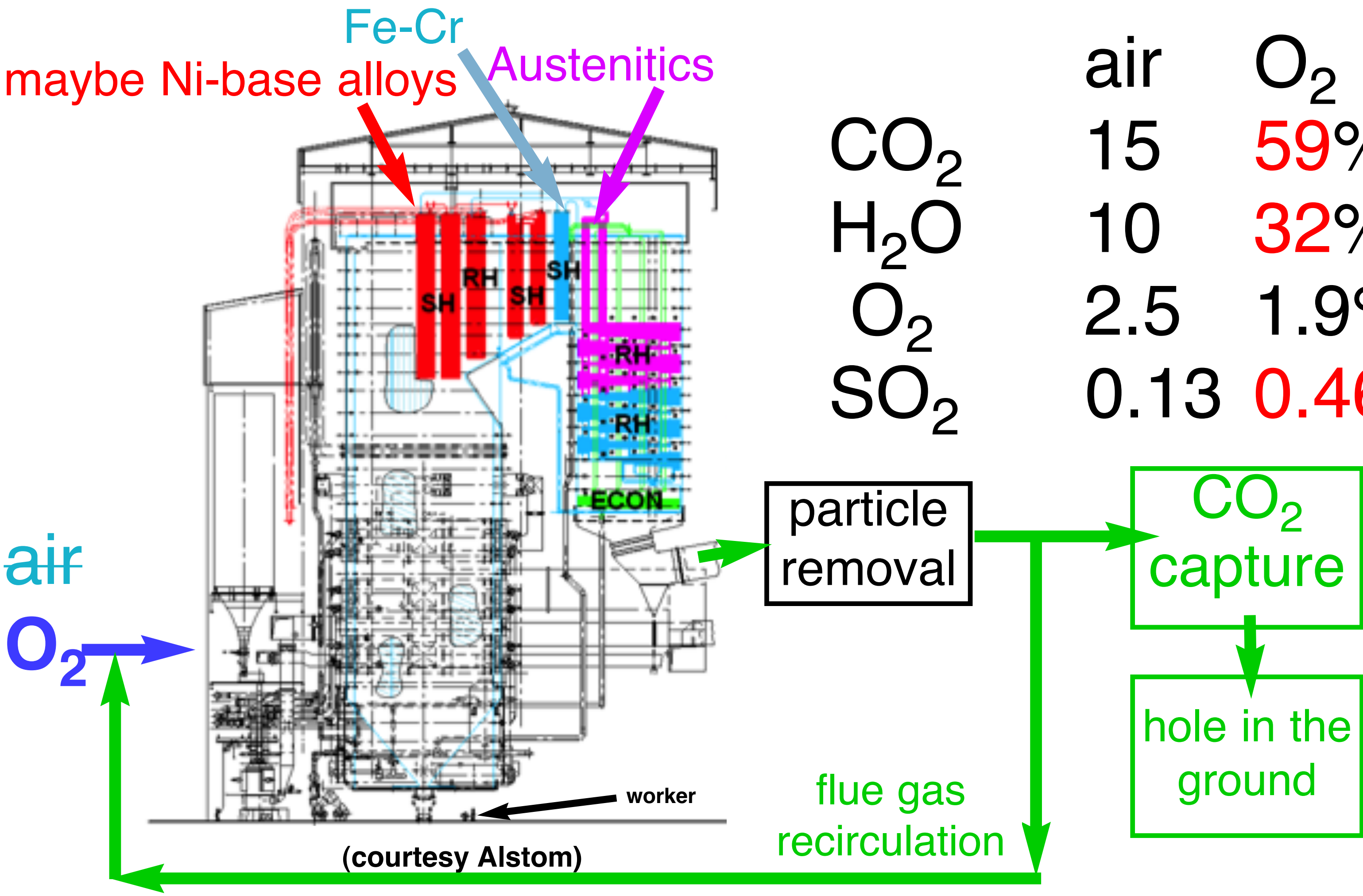
vs.



FutureGen 2.0: U.S. demo of oxy-firing

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

Current 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 and model (TTU subcontract)
   - effect on mechanical properties (Dryepondt)

A. ~600°C ferritic/martensitic steels (FY10-12)

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)

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

Not just commercial alloys

Model alloys: better composition understanding

Ni Content (wt.%) across, Cr Content (wt.%) down

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	(2001 set)	
20	X	OOO	o	o	o	o		
25	X				X		X	X
30	X				(overlay coatings) → 622,625			
35					X		X	X
40	X							

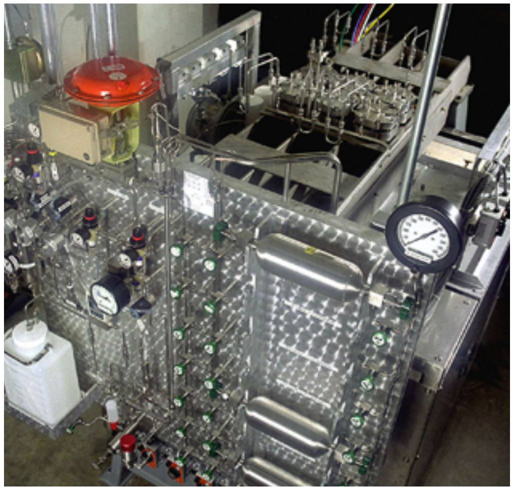
chromizing

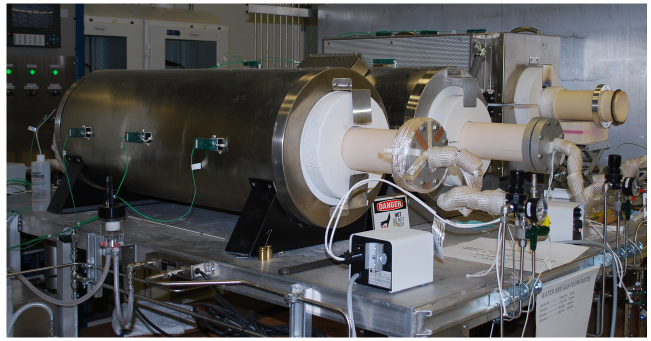
Alloy 33

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

Corrosion testing w/o ash

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





17bar or 1bar

gas only, no ash
- H_2O only
- Ar-50%CO_2*
- H_2O-50%CO_2*

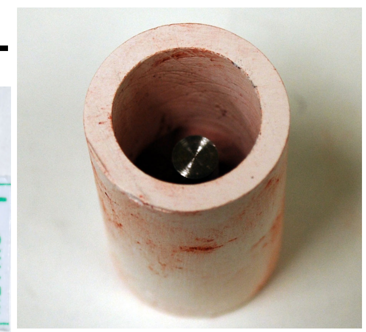
(*CO_2+1500ppmO_2)

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°C

Time: 500 h (1 cycle)



25x6mm rod in porous alumina

Continuing to establish methodology + procedure

- Current focus on characterization process

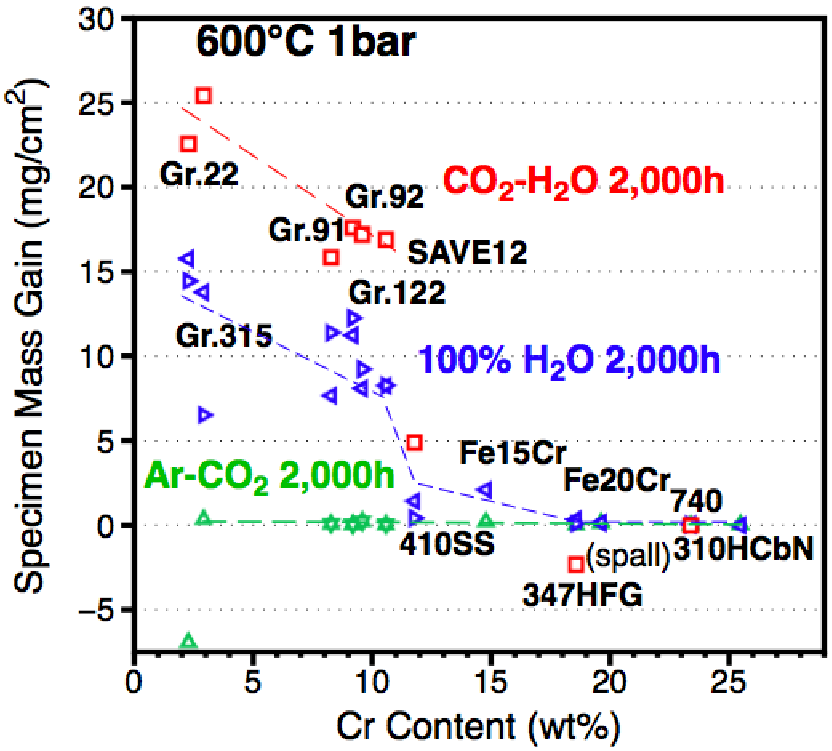
Summary: Gas only exposure

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 — started
2. 650°C:
   a. steam 1 bar — FY11-12, 5kh
   b. 50%(CO_2-0.15O_2)-50%H_2O — started
   c. Ar-50%(CO_2-0.15O_2) — next
3. 800°C steam 17bar: A-USC follow on, started
4. 550°C steam 1bar (compare 17bar) started

600°C: CO_2 content and buffer

Followup on H_2O-50%(CO_2-0.15O_2)

FY11 results



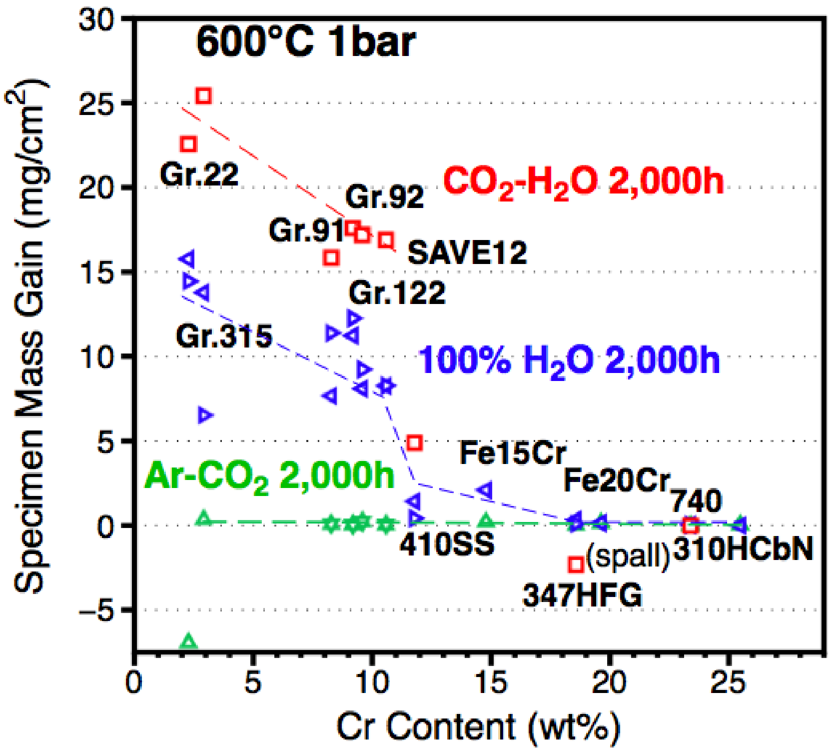
Mass gain after 2,000h
Worst case (fastest rate):
O_2 buffered
50%H_2O-50%CO_2

Most other groups do not use buffer, what is its role?

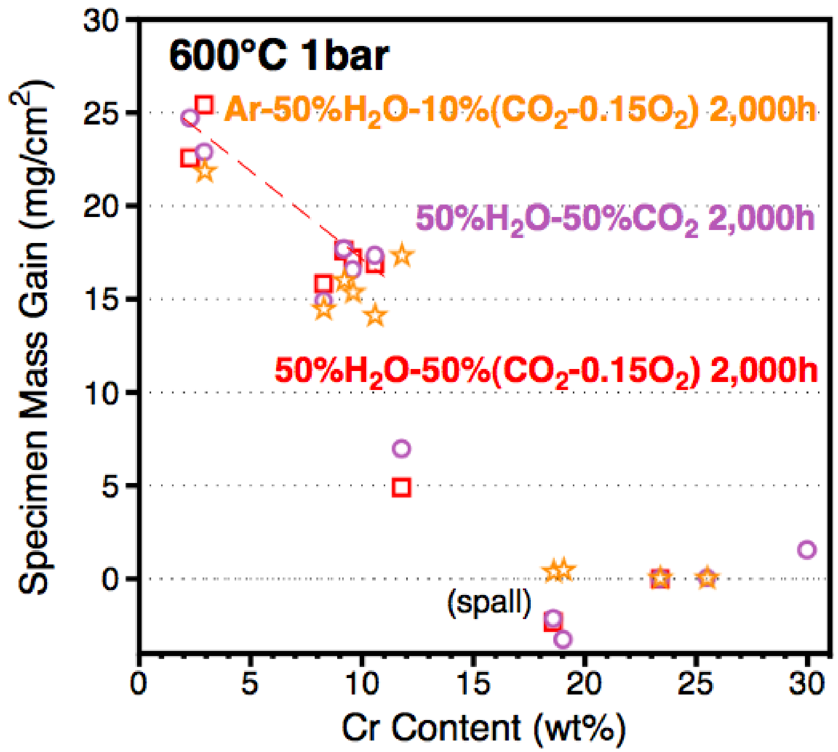
Little effect of $C(CO_2)$ & buffer

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)

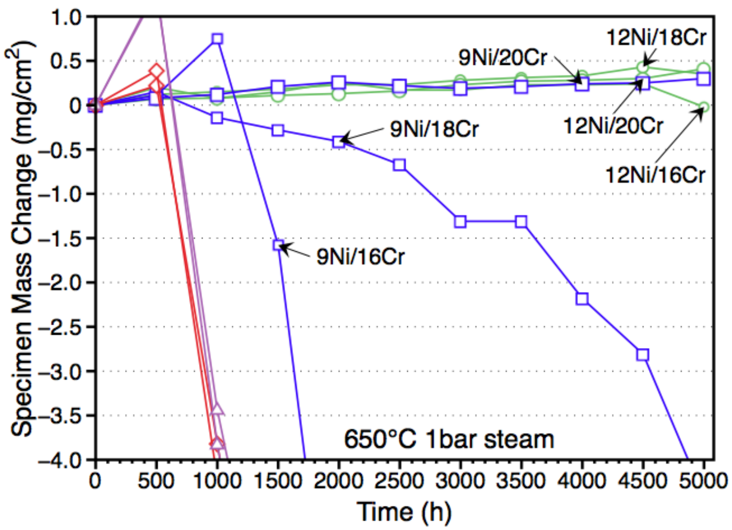
Both: little effect on 2,000h mass change

Need to complete metallography comparison

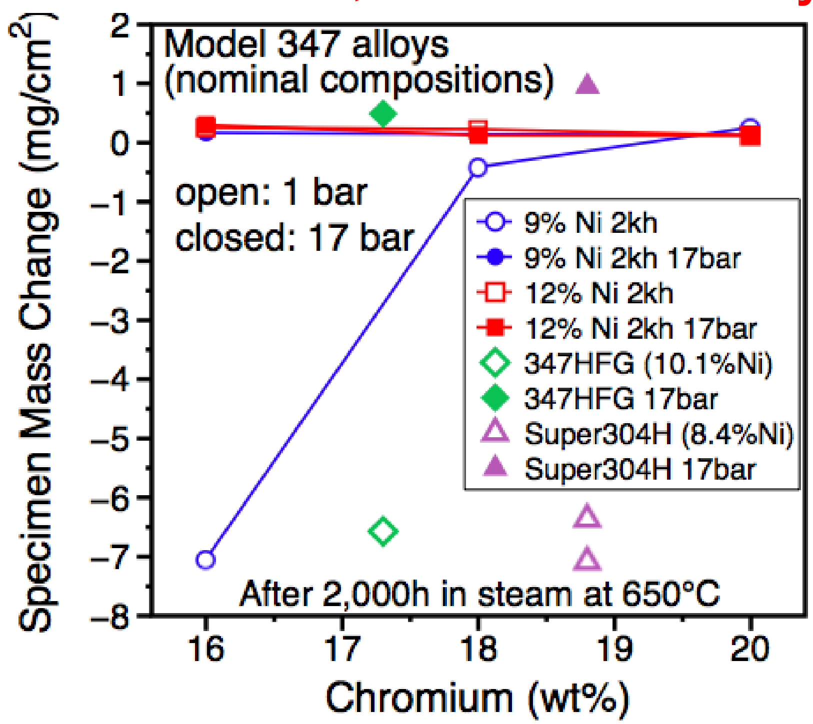
Model 347 alloys: 650°C steam

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)

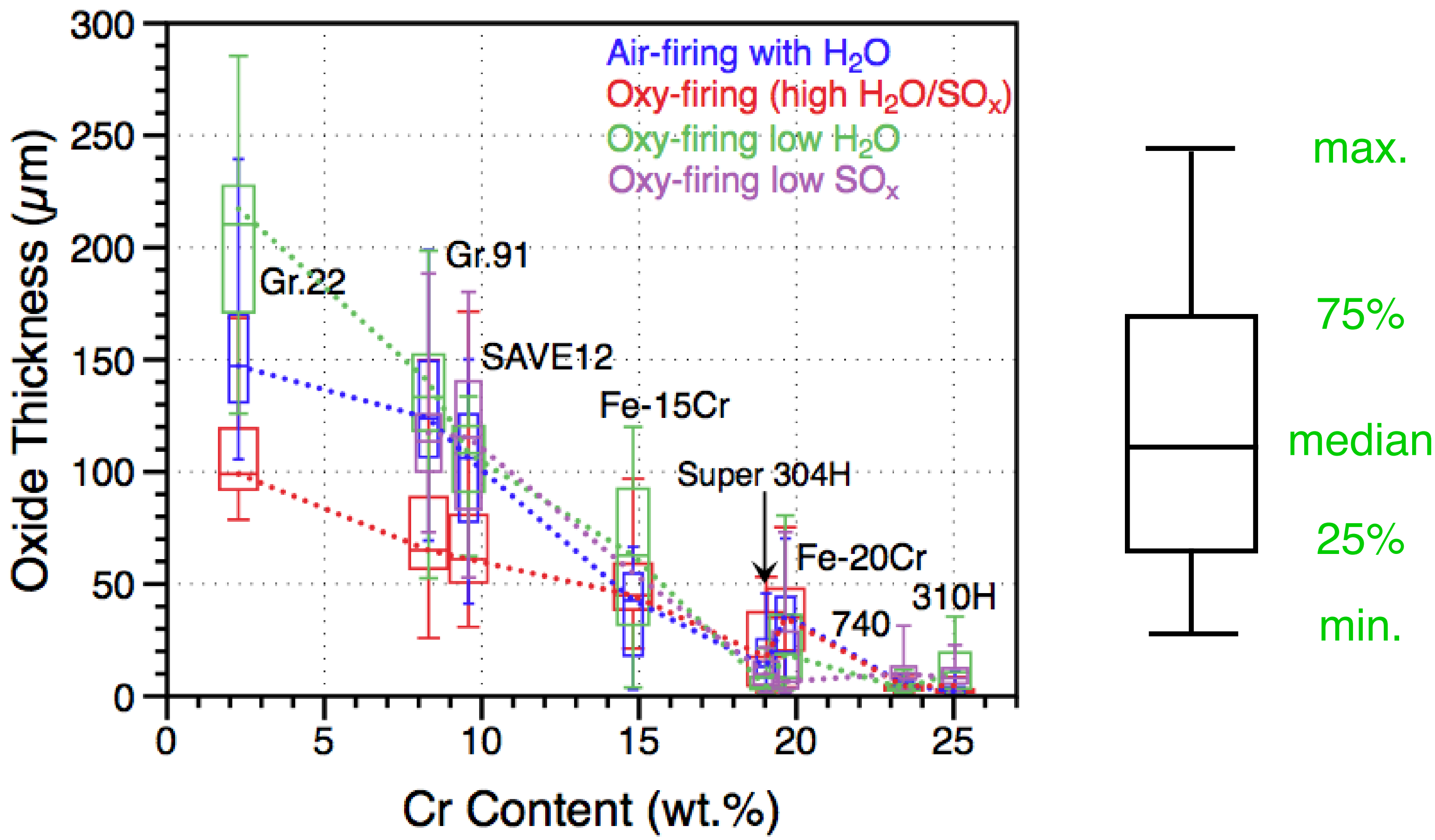
Concern: model alloys better than 347HFG & S304H

Summary: Ash exposure

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

Little effect of gas at 600°C

Synthetic coal ash, 500h exposures in 4 gases



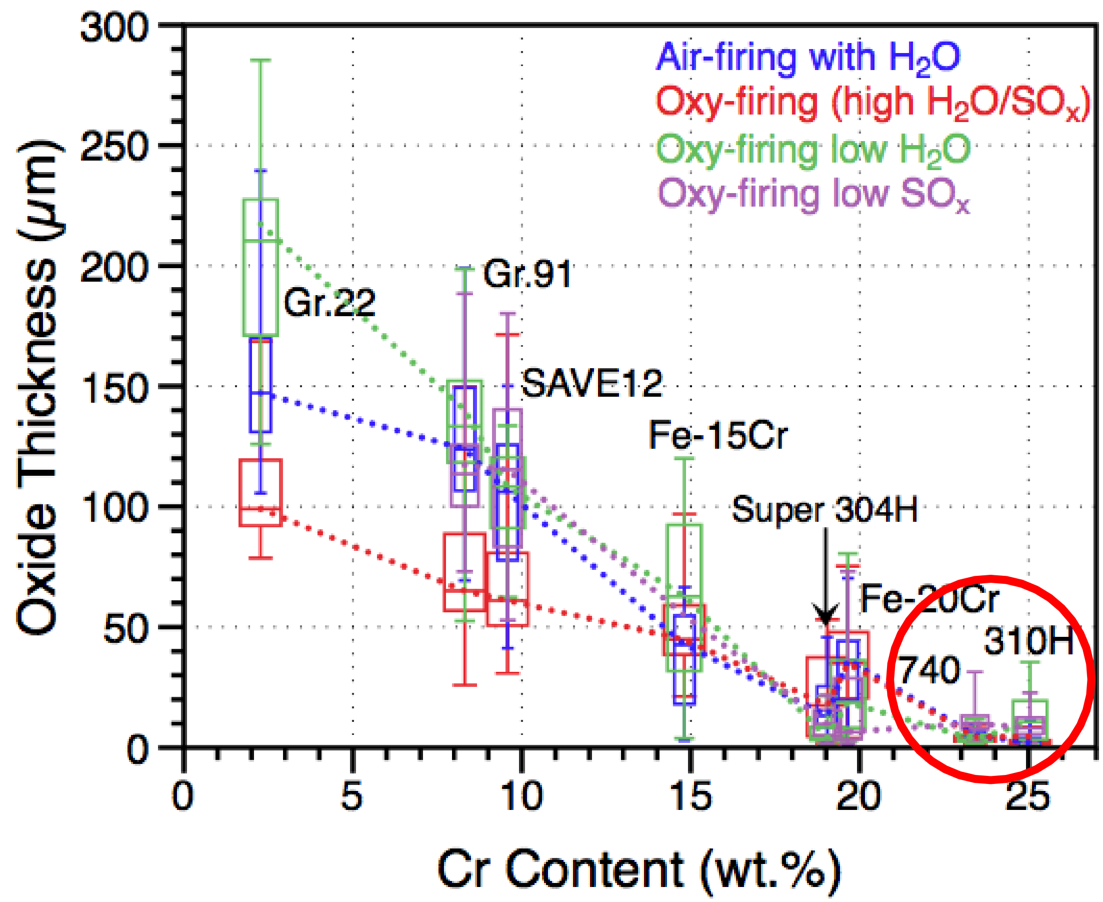
Higher CO_2 environments not detrimental

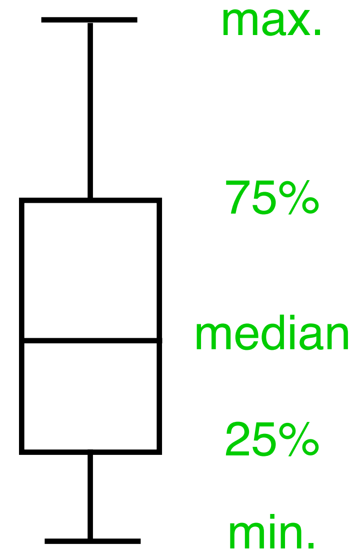
Expected the lower SO_2 environment to lower attack

- same synthetic ash used in all cases

Little effect of gas at 600°C

Synthetic coal ash, 500h exposures in 4 gases





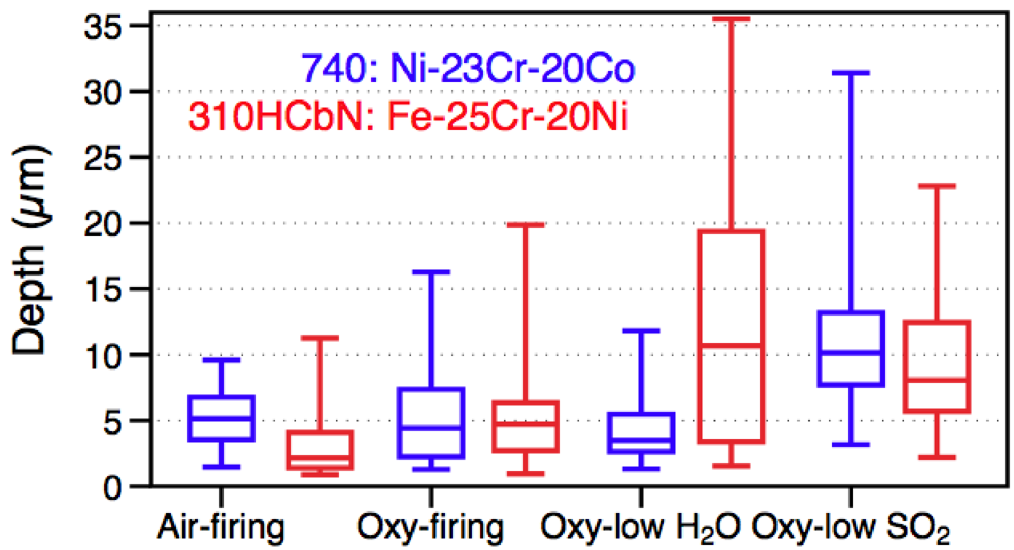
Higher CO_2 environments not detrimental

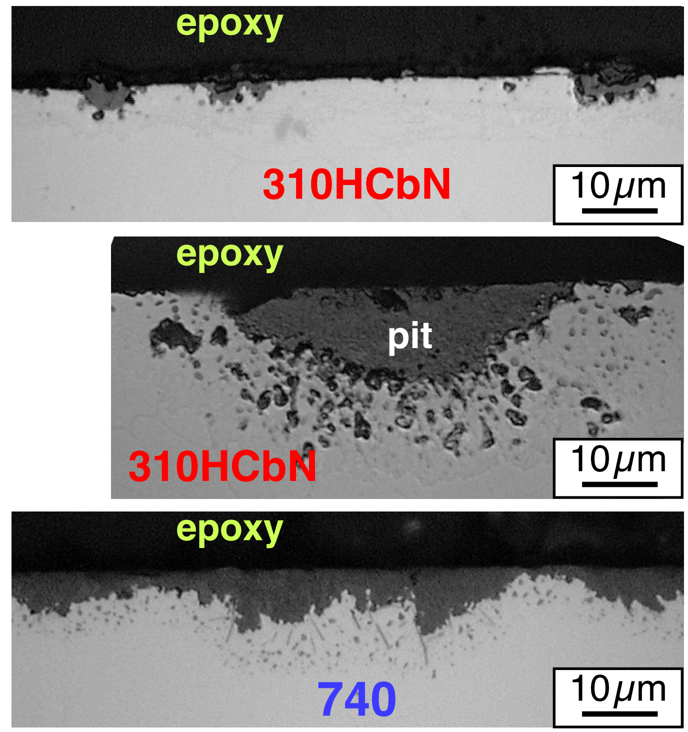
Expected the lower SO_2 environment to lower attack

- same synthetic ash used in all cases

310-740 differences accurate?

Highest alloyed examples with minimal attack

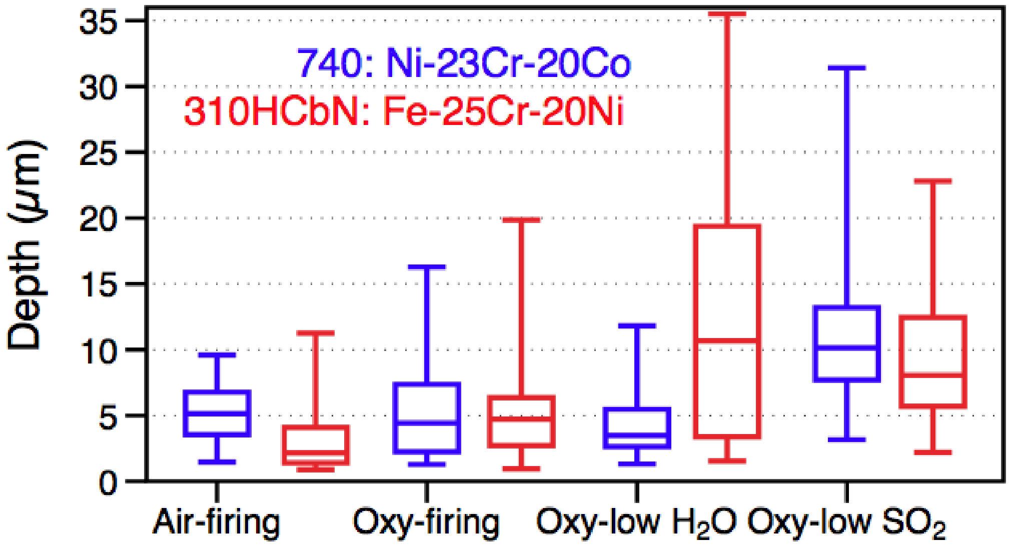


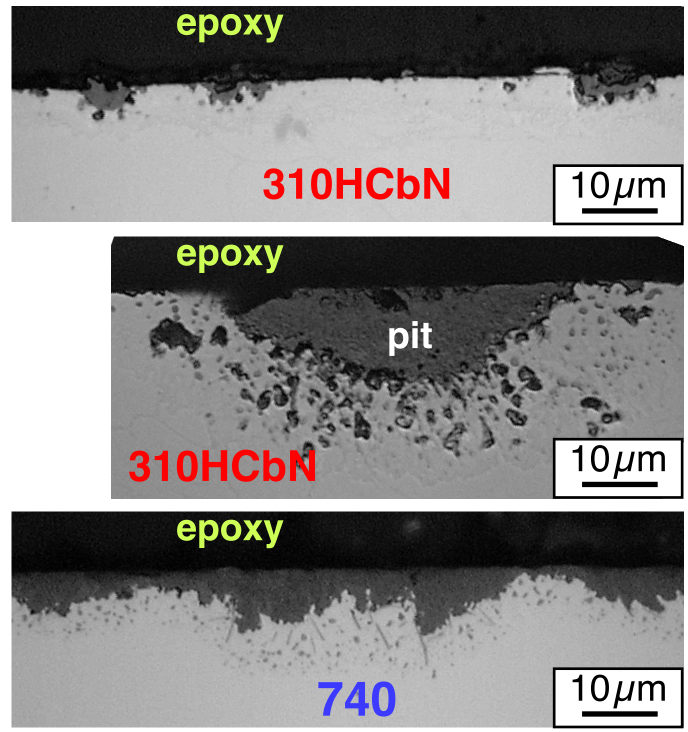


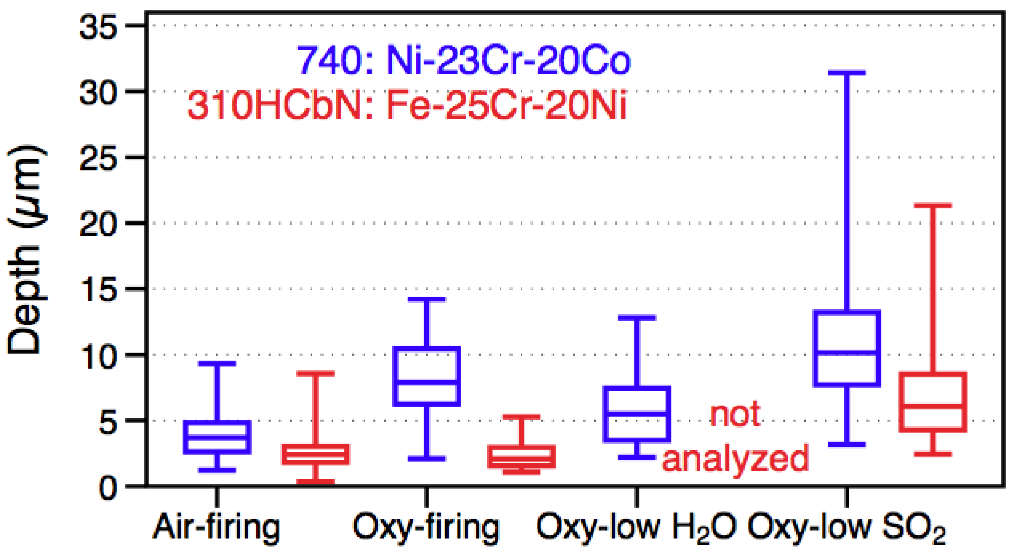
Sometimes focus on deepest penetrations
Need more images at “medium” magnification
Metal loss from 6mm diameter rod is minimal

Reanalyzed: 310HCbN < 740

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







More accurate distributions from new images

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?

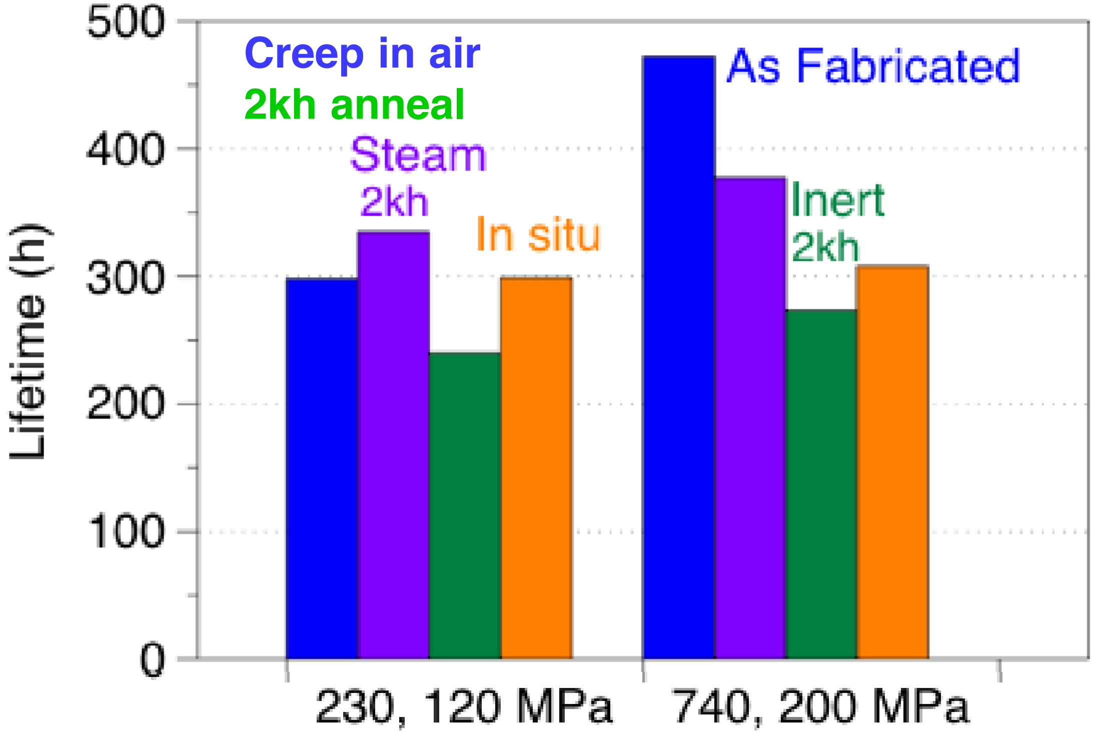
Summary: Creep in steam

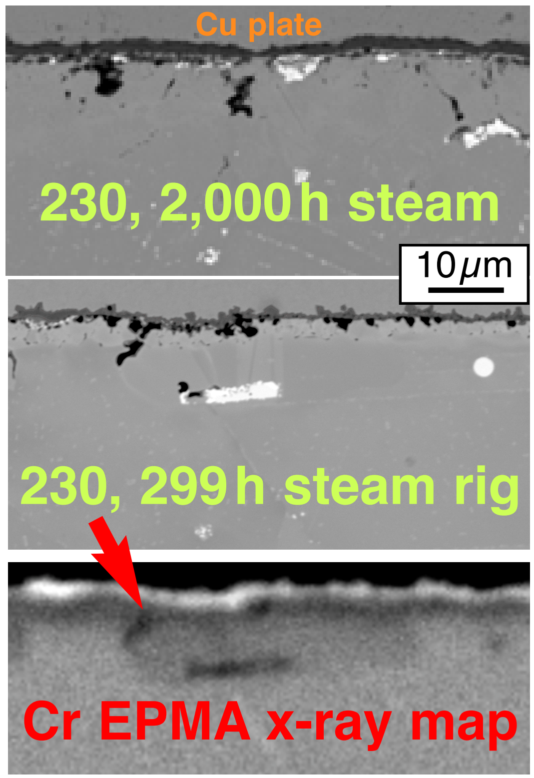
1. 800°C:
   completing work on Ni-base
   740 (Ni-23Cr-20Co); 230 (Ni-22Cr-14W)
   air vs. steam
   in-situ vs. ex-situ
   anneal (thermal effect)
2. 650°C:
   Grade 91 (9Cr-1Mo)
   air vs. steam
   coated vs. uncoated

two in-situ creep rigs

800°C: 230/740 limited steam effect

Creep rupture tests in air and 1 bar steam





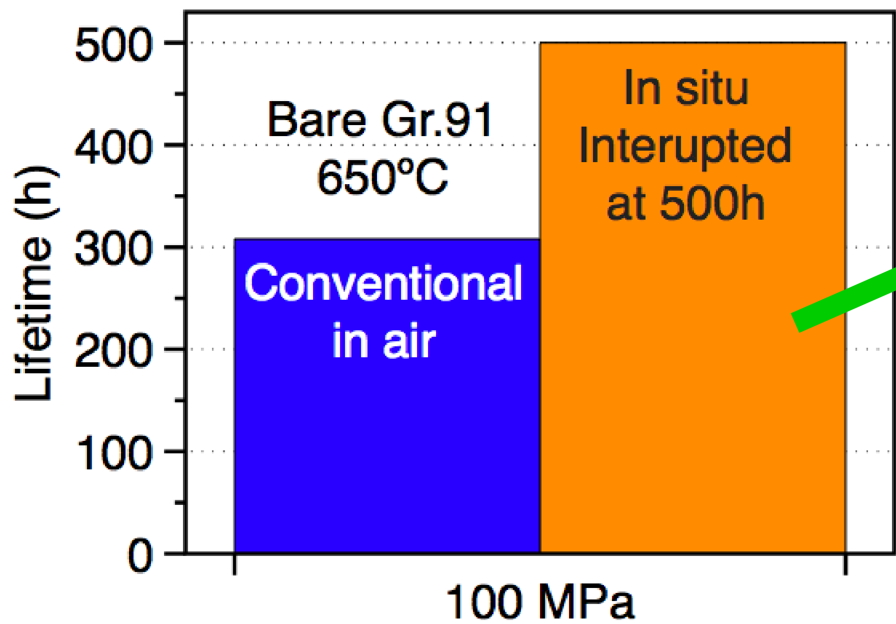
230: no effect of in-situ or ex-situ steam

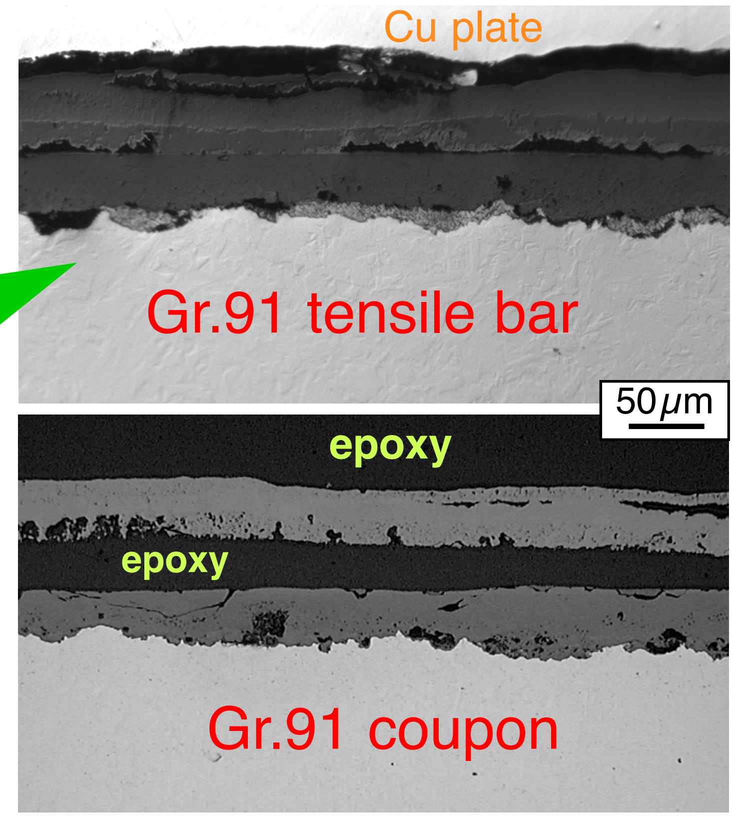
740: microstructural reason for decreased life?

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

Grade 91: higher lifetime in steam

650°C 100MPa 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

Milestones

FY11

Done - Procure coatings for creep testing (12/10)
Done - Initial assessment of CO_2 role (6/11)
Done - Complete 600°C coal ash testing (6/11)
Delayed (9/11)- In-situ 650°C creep testing
(Resource delays/followup on results)

FY12

Done - Report CO_2-H_2O effects (12/11)
Done - Complete 600°-650°C steam tests (3/12)
- Complete in-situ Ni-base creep testing (6/12)
- Complete 700°C coal ash characterization(9/12)

Summary

Four tasks: gas only, with ash, creep, coatings

Gas only: further work on 600°C CO_2 effect
650°C steam testing complete

Coal ash corrosion:
further data analysis of 600°C results
- Oxy-firing no worse with same ash
FY12 focus on temperature series
add "cold" oxy-firing conditions

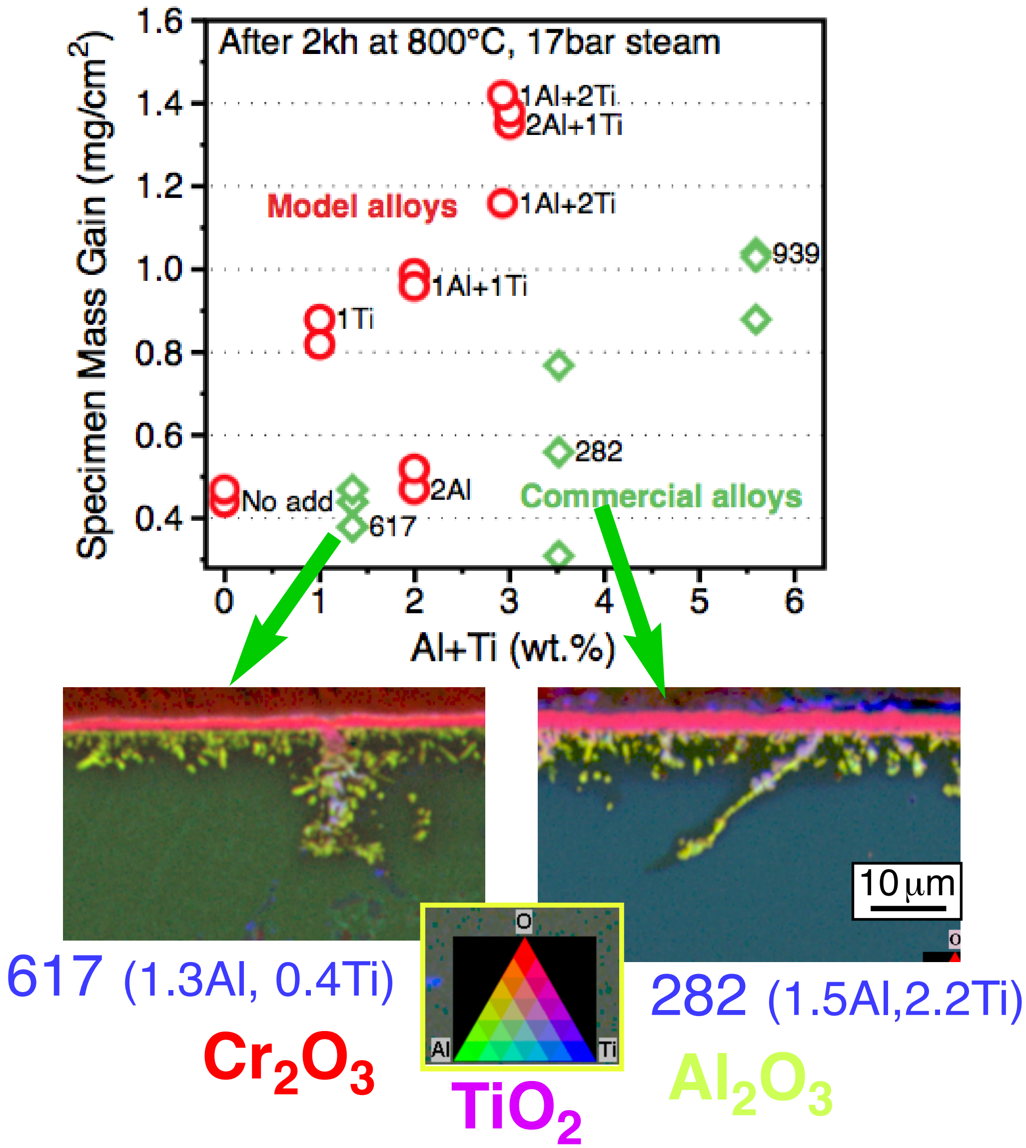
Creep: T91 work at 650°C in progress
Ni-base: completing characterization

Coatings - final work on model/creep effects

CLEAN COAL.
COOL.

800°C model Ni-22Cr alloys

17bar steam, 2,000h exposure



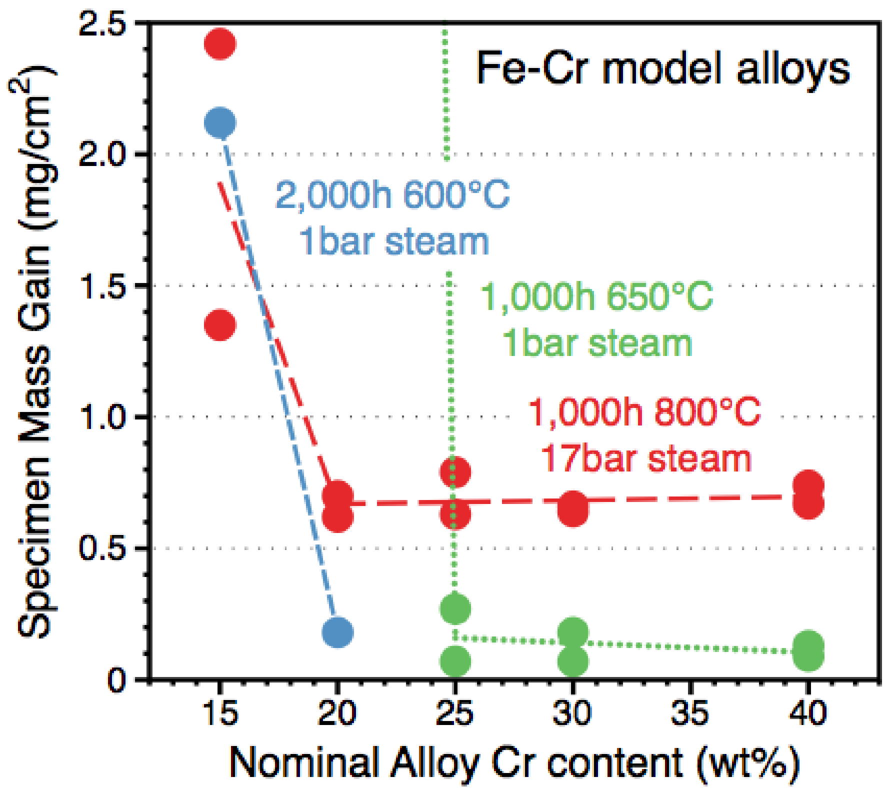
Model alloys:
simulate Al,Ti effect
on internal oxidation

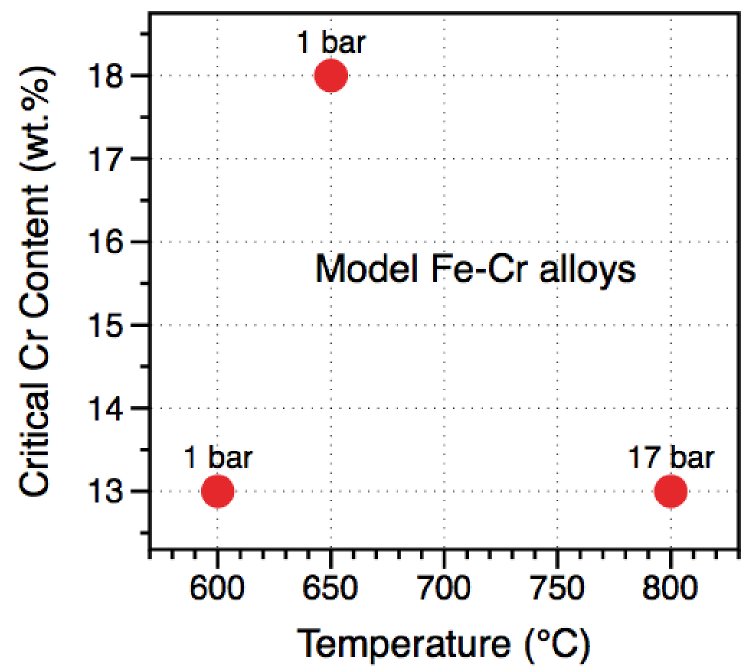
Ni-18Cr alloys (282)
fabricated (2)

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

Fe-xCr model binary alloys

1 and 17bar steam, 1-2 kh exposures



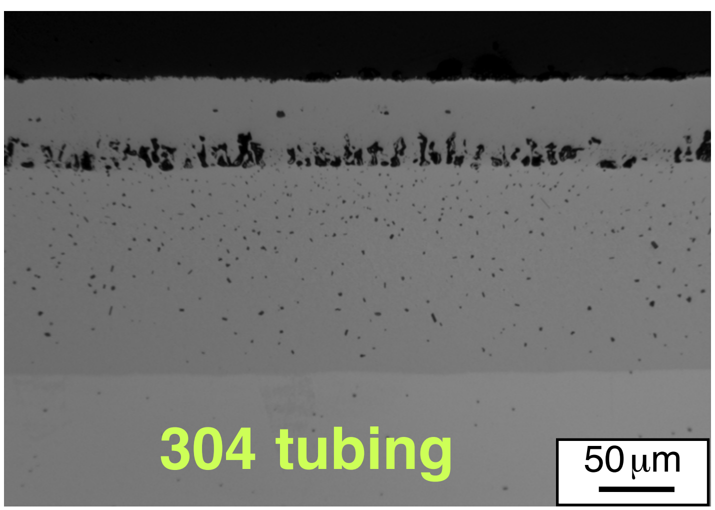


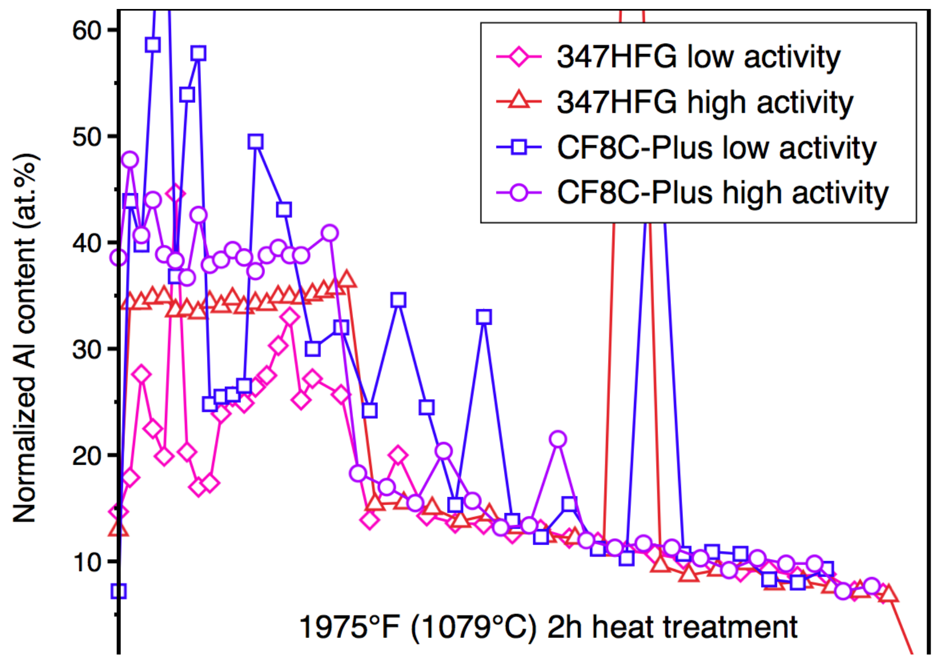
Here, model alloys perform worse than expected
Need to fill in with additional temperatures
Next question is about ternary additions (Mn, Si...)

Coating commercialization (slow)

- No industry interest in coating 8-11%Cr steels
  peak application is ~600°C - no interdiffusion
- More interest for austenitics (304, 347, etc.)
  boiler application limited to ~650°C
  phase boundary will limit interdiffusion
  304H/347H tube explosions created interest
  EPRI funding for coating demonstration:

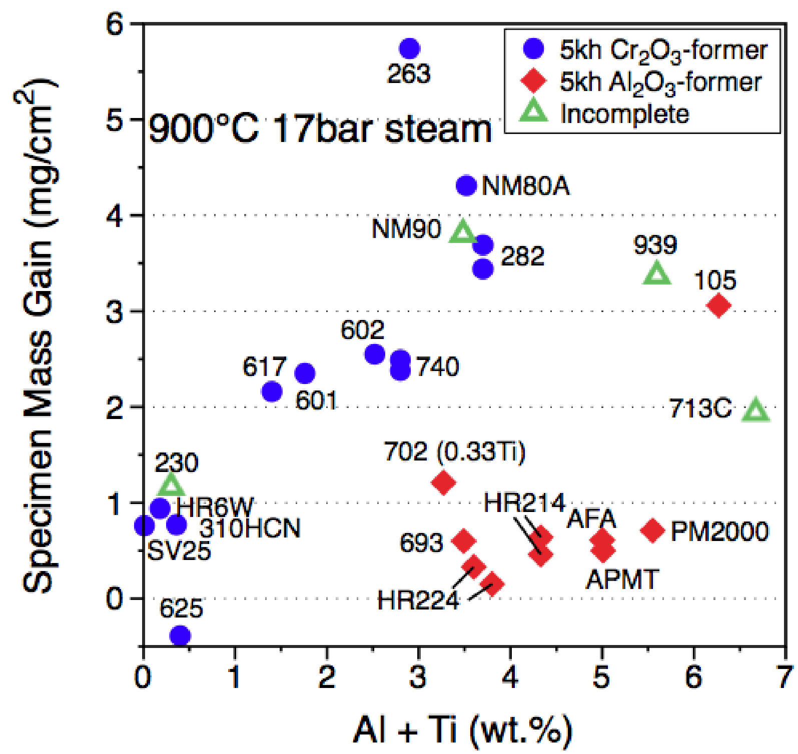
Vapor slurry coating





900°C steam

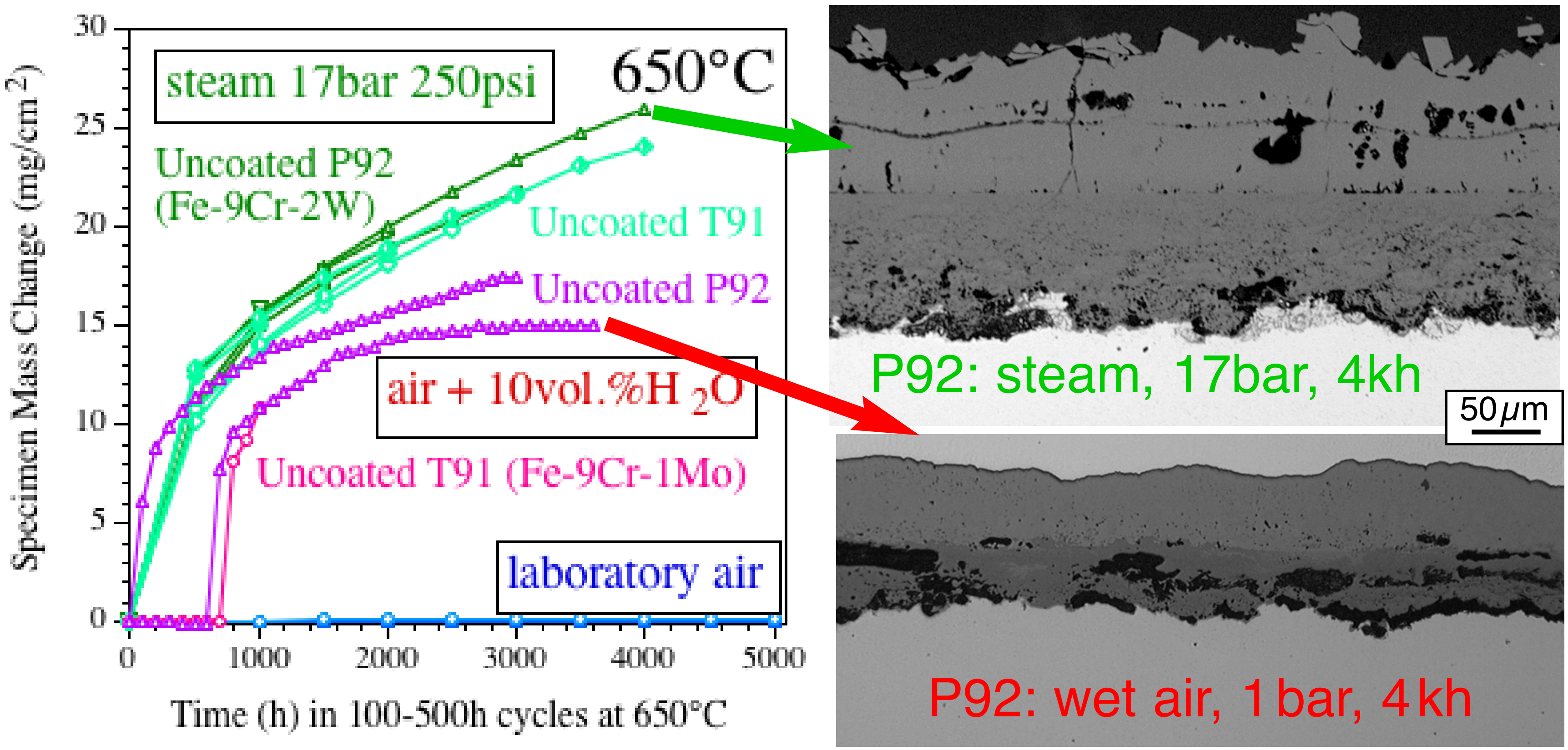
5,000h



Fe-9Cr in Steam vs. Humid Air

comparison of mass gain and reaction products

650°C, 1202°F



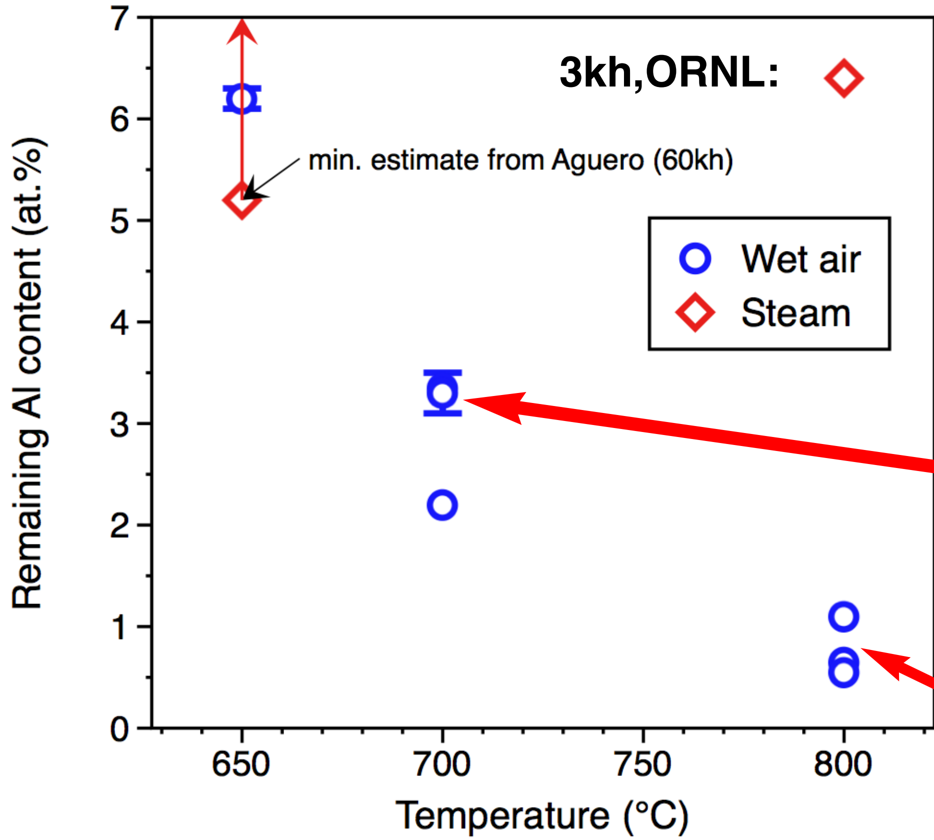
Similar attack in steam and wet air (10±1 vol.% H_2O)

Define failure: must have environment that attacks substrate

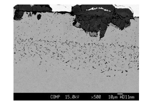
Prior work in lab. air could not define coating lifetime

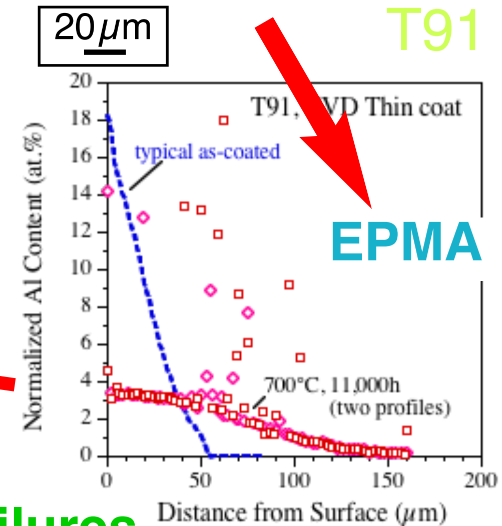
Effect of temperature on C_b

~40μm coatings on Fe-Cr at 650°-800°C in H_2O



coating failure





T91

EPMA

3 800°C failures
T91, T92, T122
(Fe-8-11%Cr)

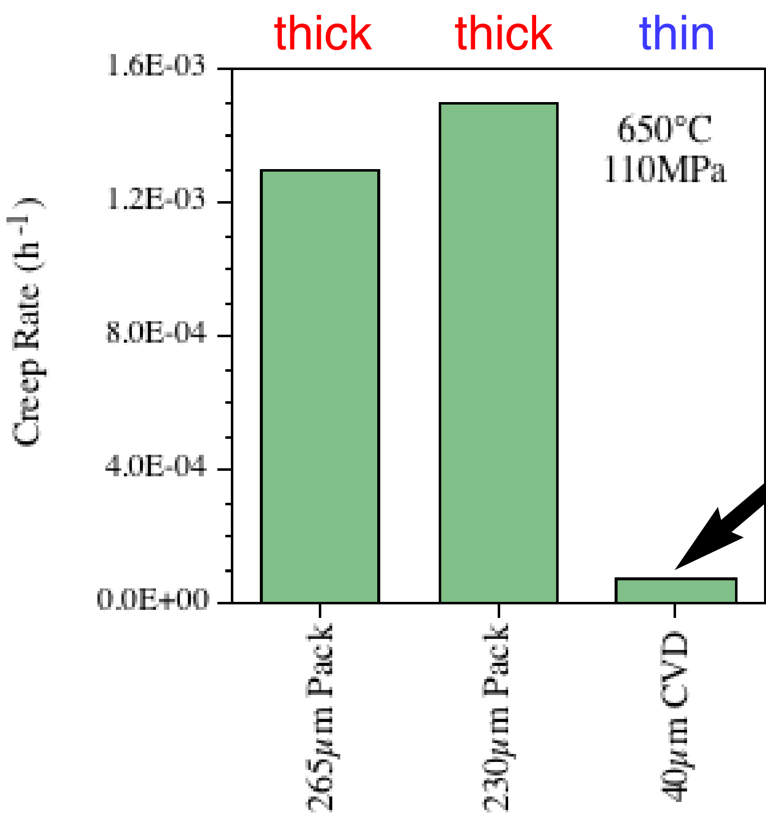
Six failures of thin coatings, one higher Al activity coating

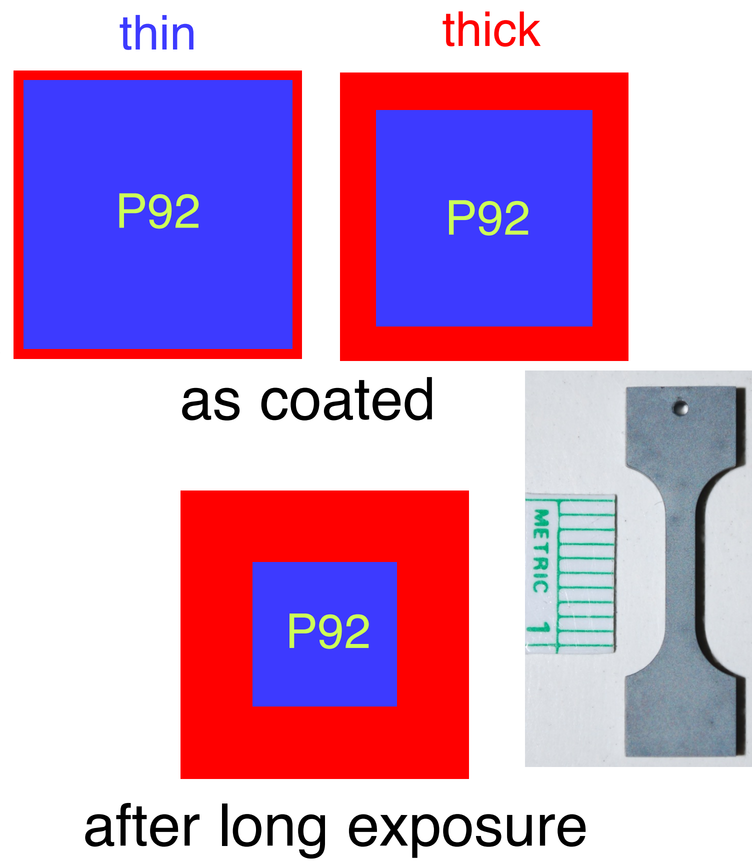
Agüero: 650°C slurry coating failed at ~60kh in steam

If temperature relationship is understood, this data set forms the basis for a comprehensive lifetime model

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

Effect of as-deposited coating thickness





650°C, 1202°F; gage: 2 x 2 mm

Specimen with thin coating has better creep resistance

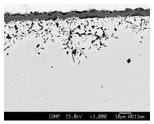
Effect of coating can be modeled as if coated layer absent

Suggests that thin coatings are preferable

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

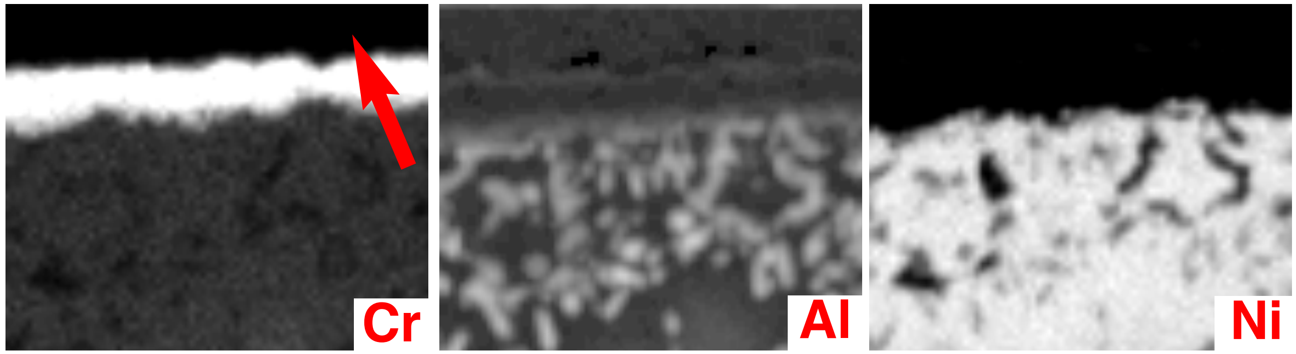
Unusual Ti distribution in scale

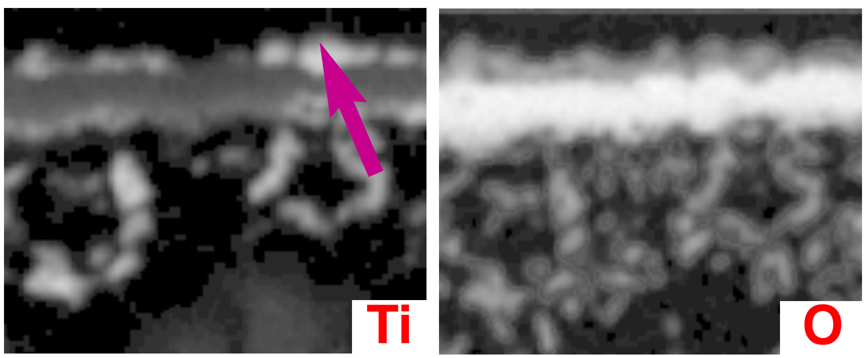
Cast alloy 282 after 5kh in steam at 800°C



cast 282

10μm



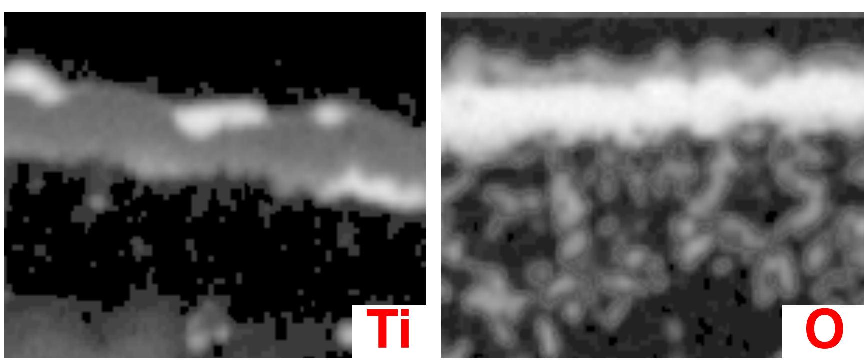


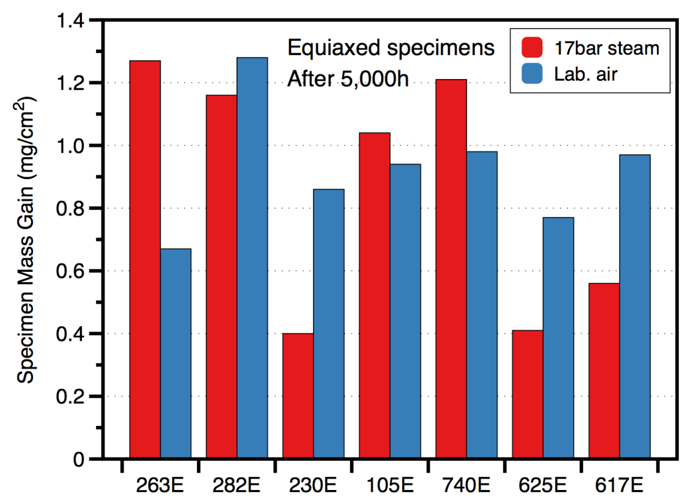
Electron probe analysis:

Typical internal Al + Ti oxidation

Ti “layer” at both gas & metal side

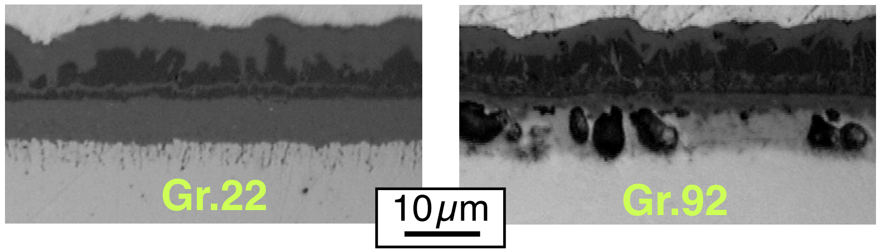
Scale after 5kh lab air:



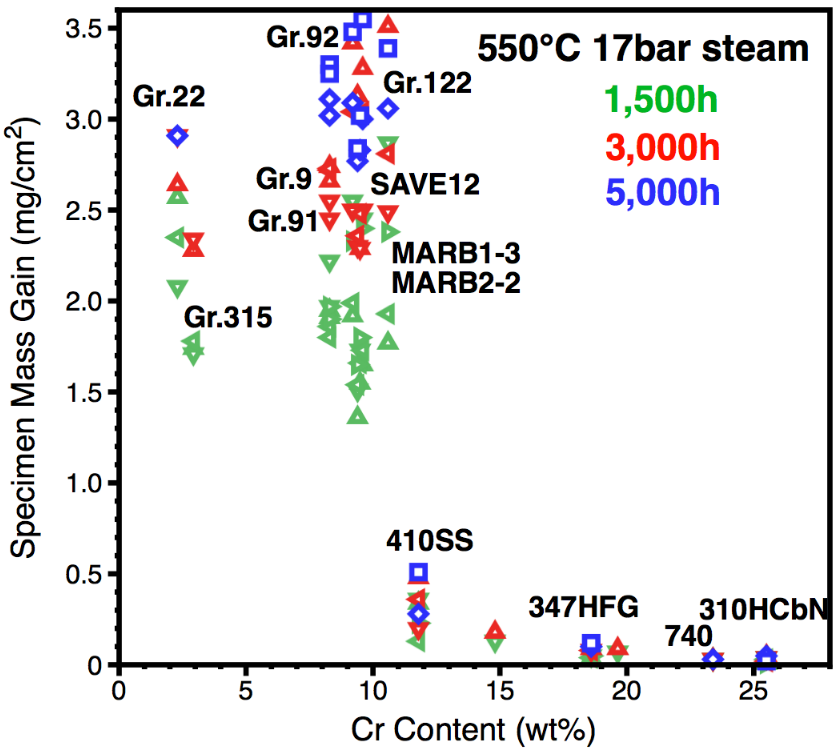


~12%Cr needed at 550°C

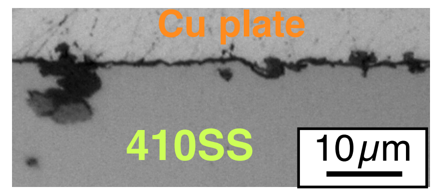
For protective behavior at 17bar steam



dual oxide layer



2,000 h 550°C

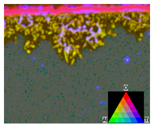


Surprisingly, little difference in 2.25-11%Cr steels

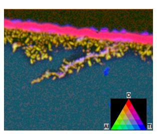
5,000h cross-sections in progress

800°C steam follow up work

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



Cr_2O_3 TiO_2 Al_2O_3



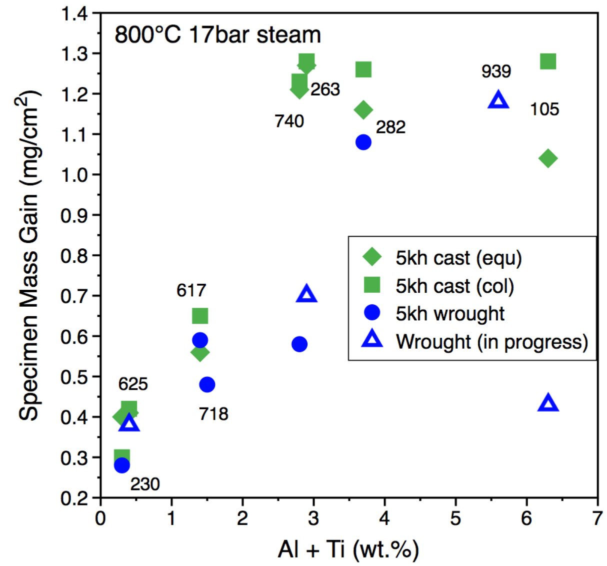
5 µm

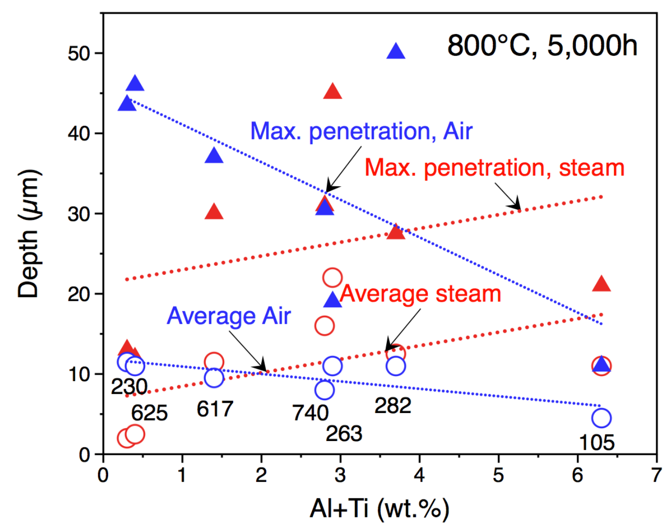
Ni~20Cr

Al+Ti->γ'

Synergy

Al-Ti ?

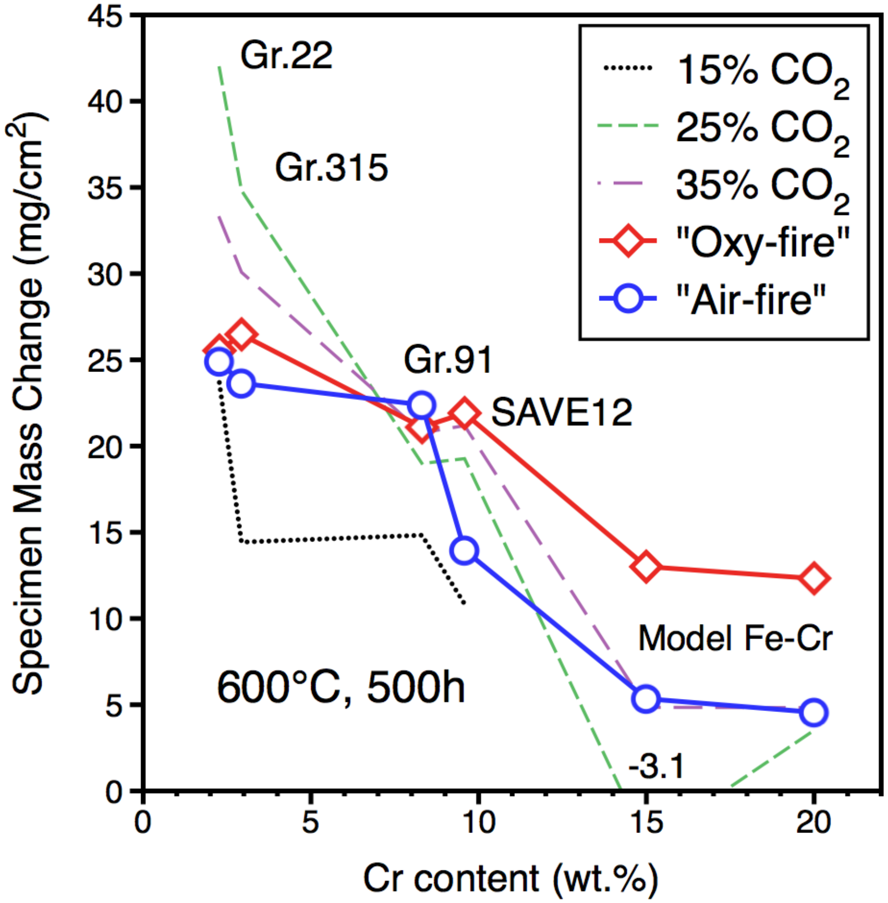




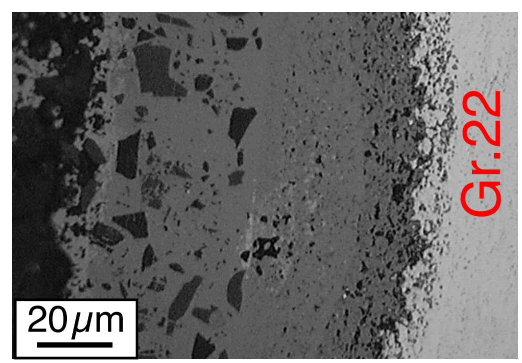
Model alloys: Ni-22Cr + Al +/- Ti in steam

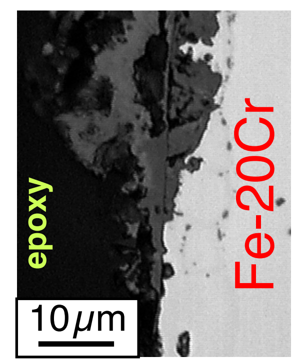
New coal ash tests: H_2O added

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



	air	O_2
CO_2	16	61%
H_2O	10	32%
O_2	2	2%
SO_2	0.15	0.45%





Modified gas train to add H_2O to test

Mass gain: not a strong effect of H_2O

Change to oxy-firing had strongest effect on high Cr

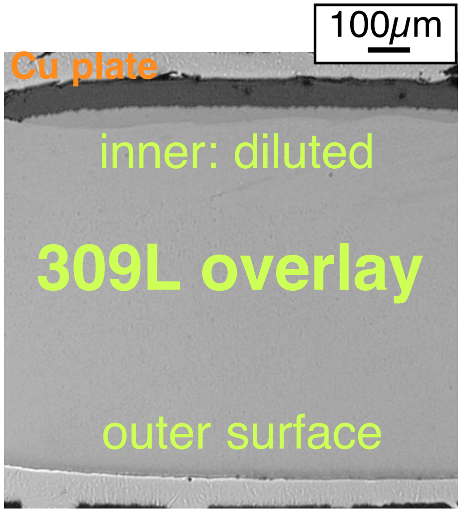
Evaluated weld-overlay coupons

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

from Titanova

Nominal composition wt.%

	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



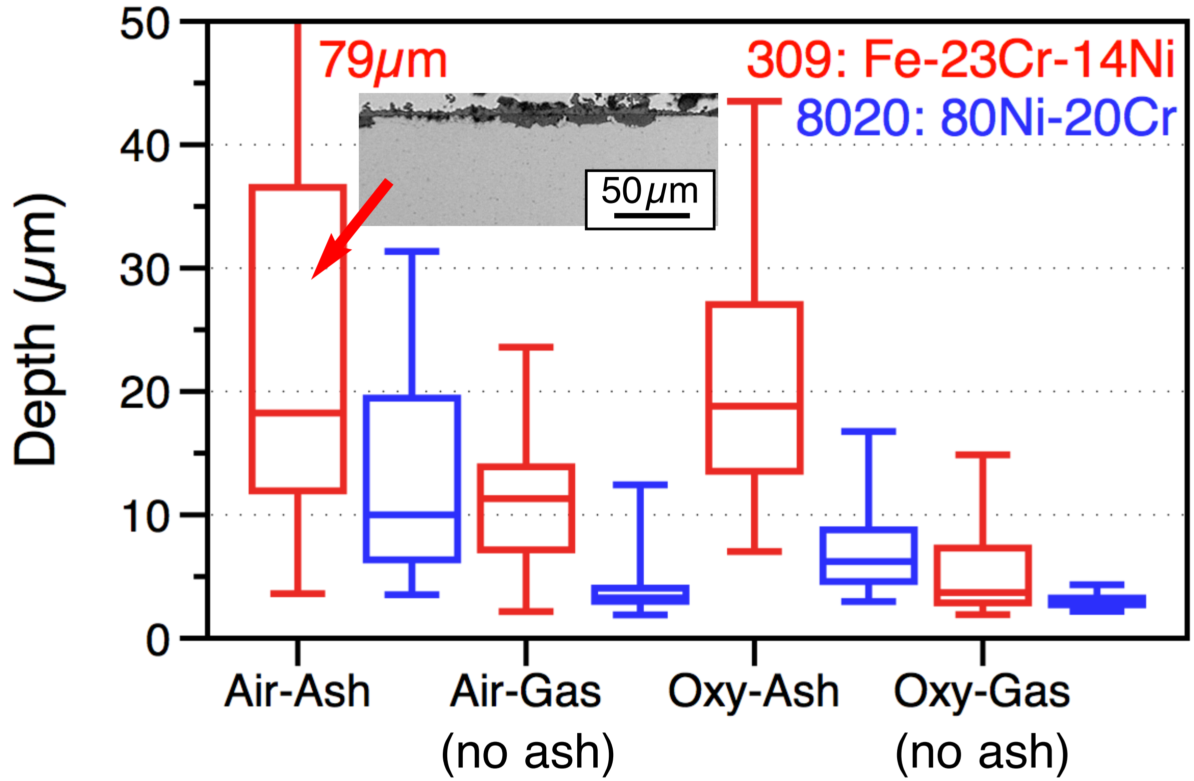
Rectangular coupons: removed overlay from tube

~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

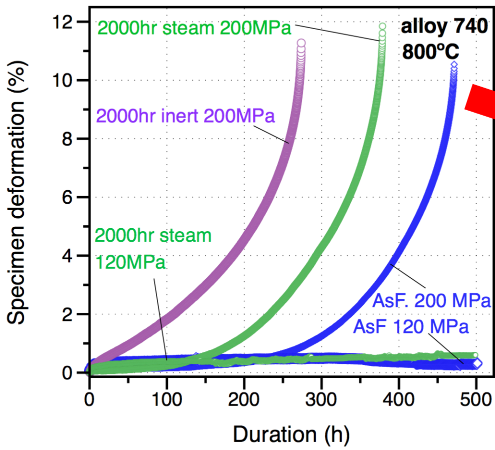


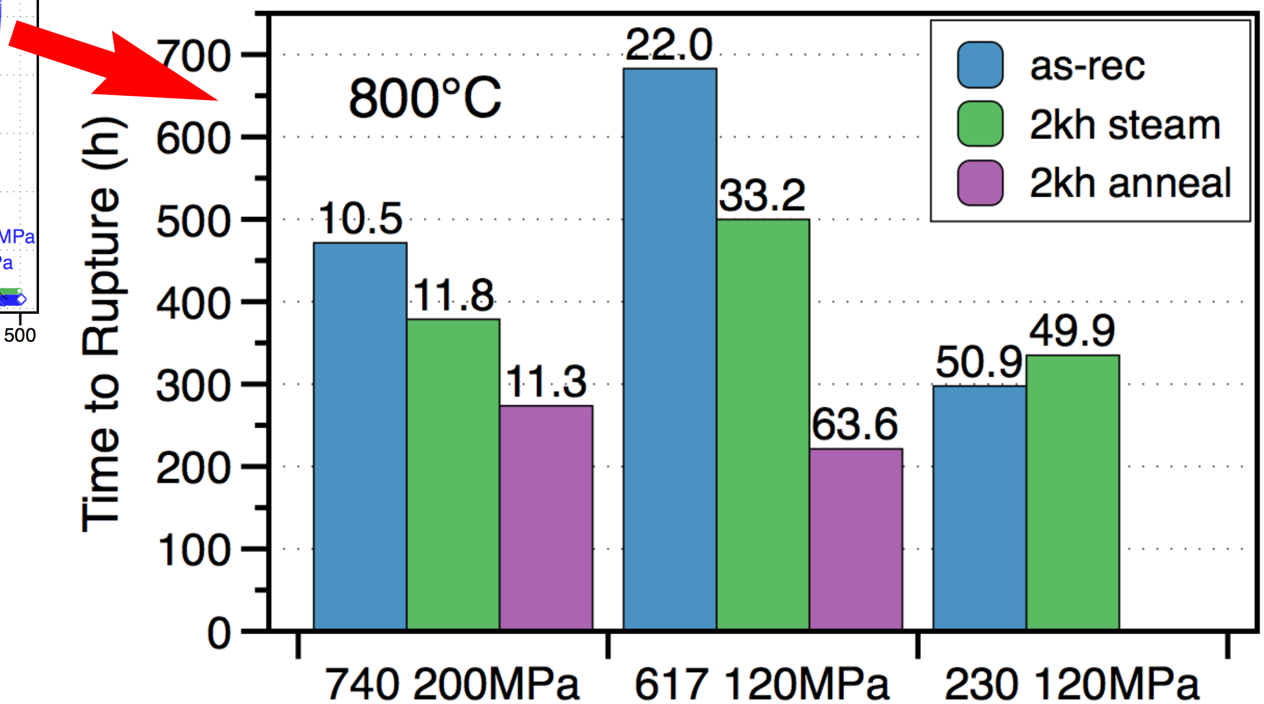
40 data points taken from 500X pictures

- 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





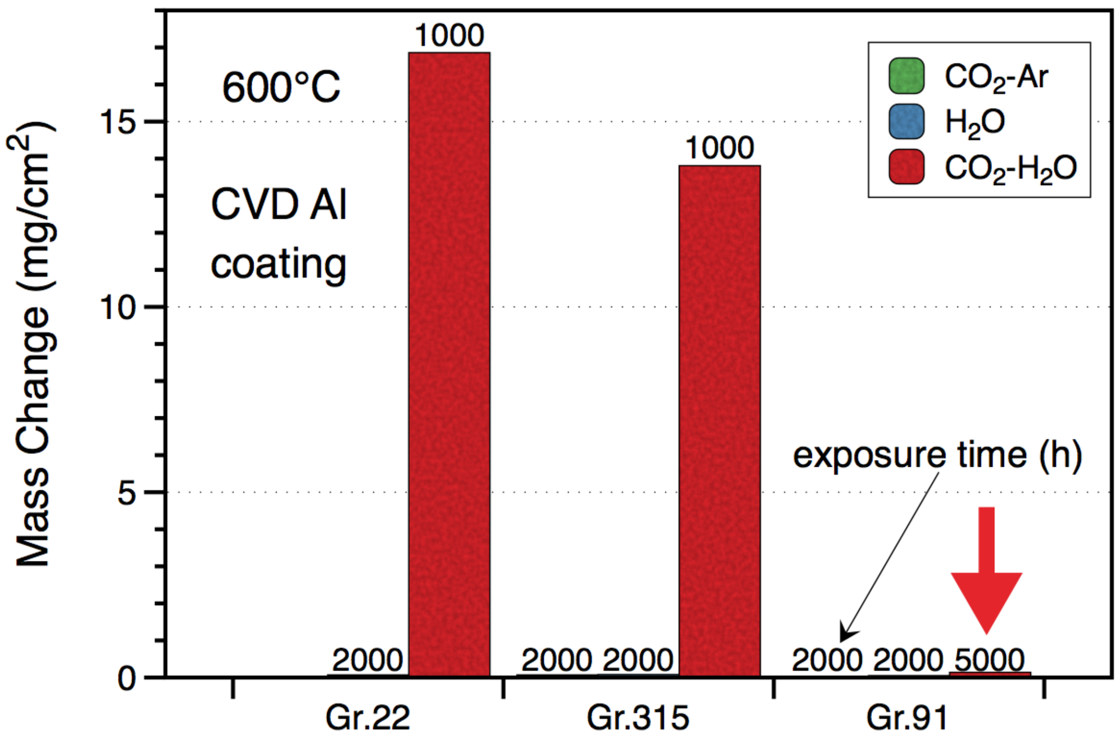
230: no effect of 2kh in steam at 800°C

740/617:   decrease life after 2kh steam

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

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