# Corrosion Issues in Advanced Coal-Fired Boilers

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T. Jordan - metallography

T. Lowe - SEM, image analysis (oxide thickness)

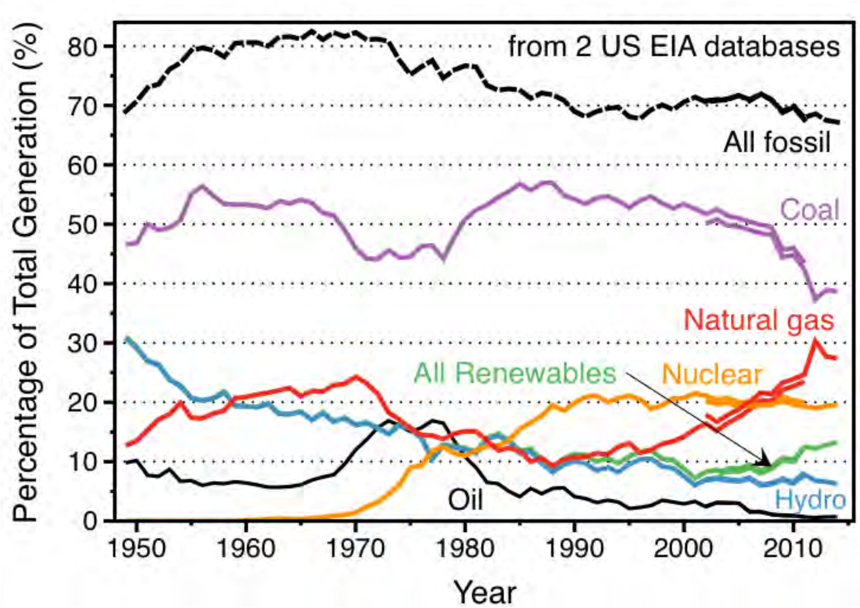
D. Leonard - EPMA, image analysis (metal loss)

B. Thiesing (post-MS) - image analysis (int. oxid.)

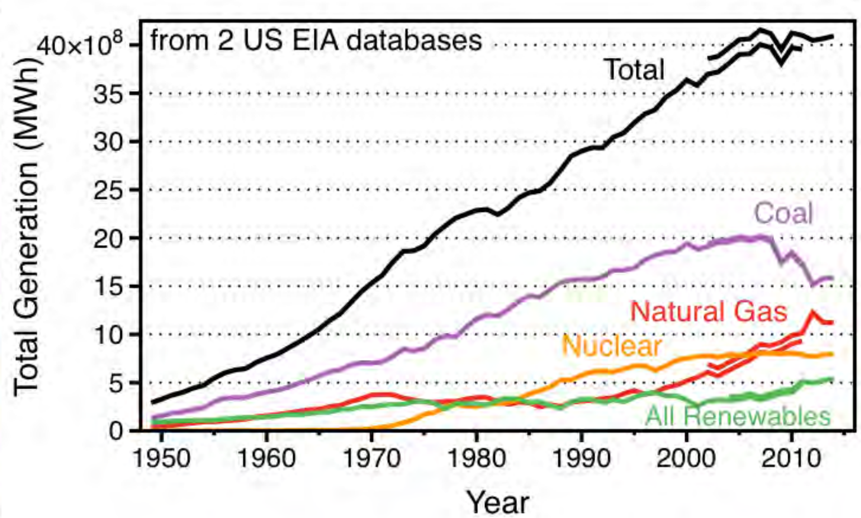
# Fossil energy continues to dominate

## Source mix is changing & demand is stagnant

How does US generate electricity?




How much does the US use?



# FY14-15: “real world” corrosion

1) complete oxy-fire reporting
    - 1a) quantify internal oxidation of NiCr alloys in different environments
    - 1b) one last test of Ni-Cr model alloys

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
    - conflicting results
    - need solutions

Cracks in longitudinal direction

Cracks in transversal direction

# Corrosion testing with ash

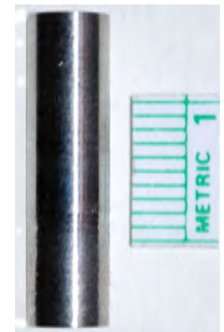
## Laboratory test of rods buried in ash

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

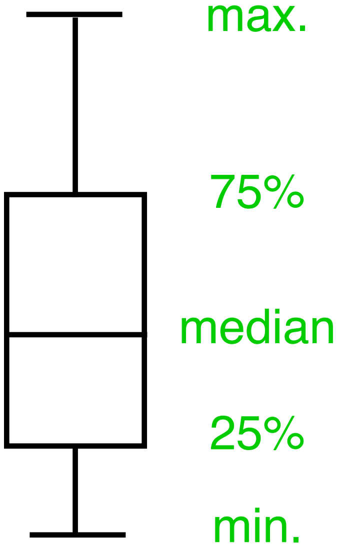
"Oxy-Firing" Gas: $CO_2$-5%$N_2$-32%$H_2O$-3%$O_2$-0.45%$SO_2$

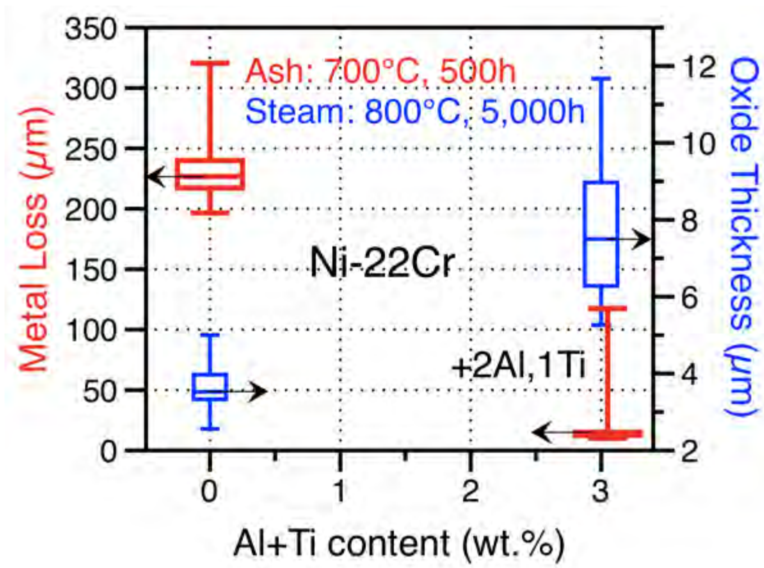
Temperature: 700°C bell "peak"

Time: 500 h

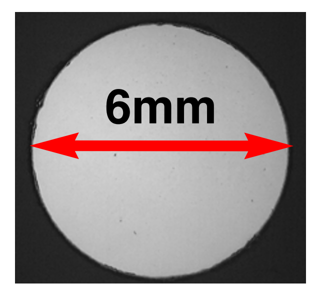


Before, Al+Ti: thicker oxide = less metal loss



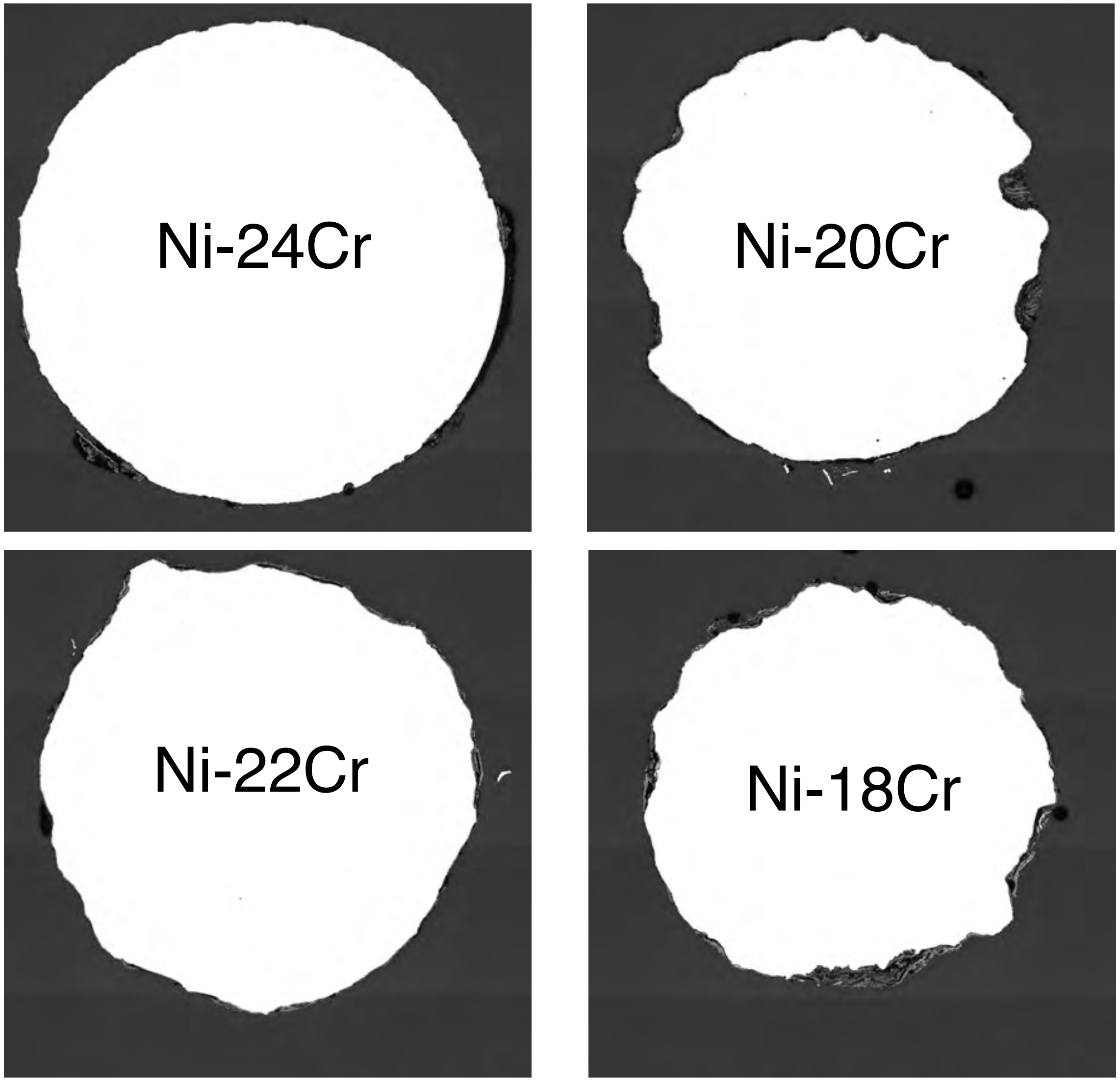




25x6mm rod in porous alumina



# Model Ni-Cr alloys: 700°C ash

## 500h isothermal, synthetic ash + oxy-fire gas



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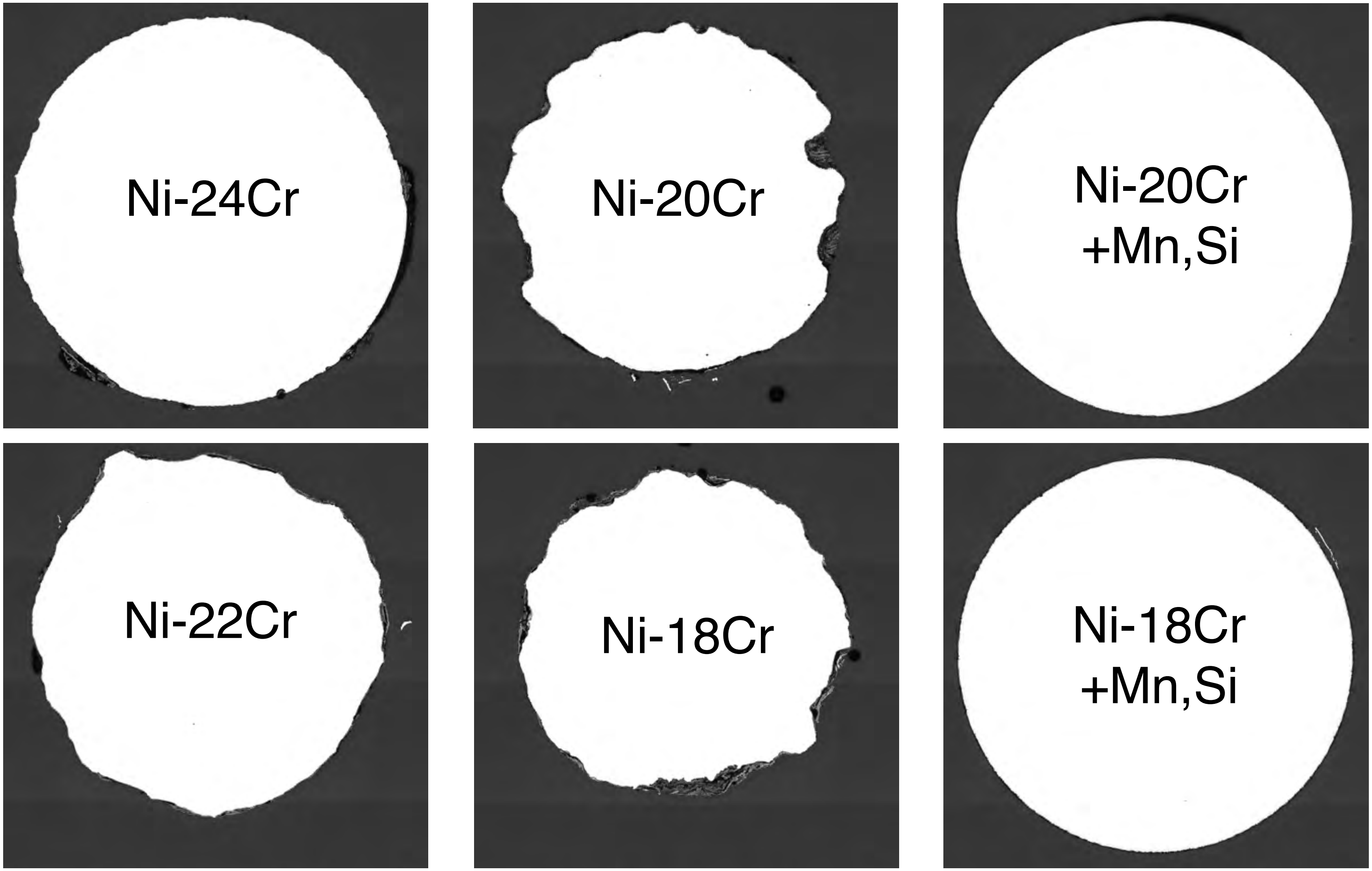

# Model Ni-Cr alloys: 700°C ash

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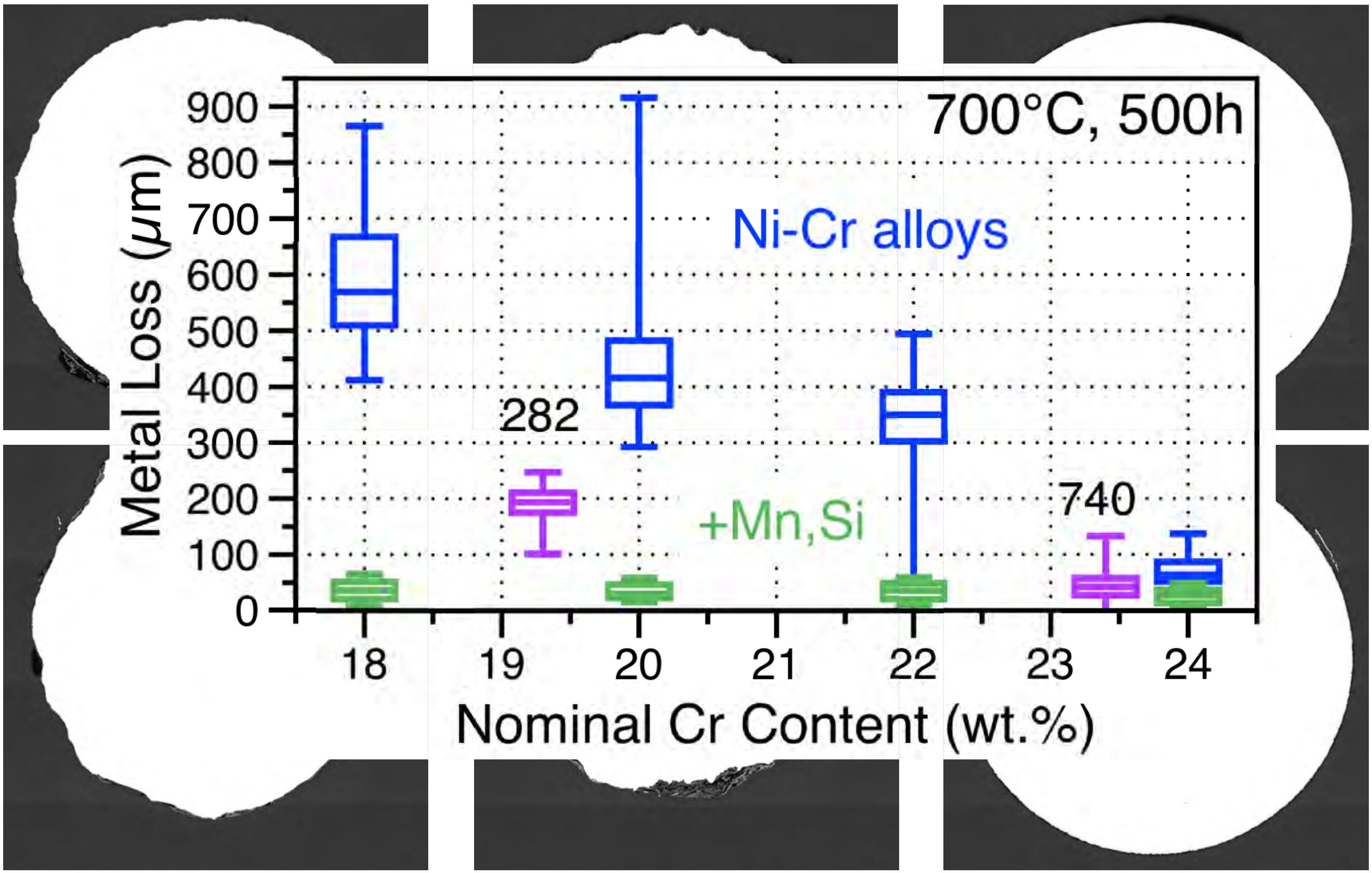


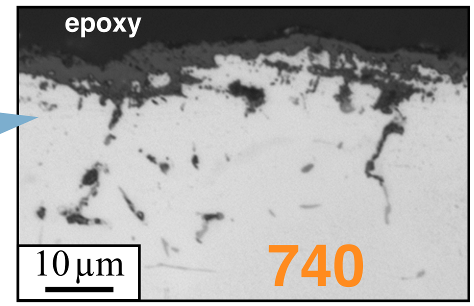
# Quantification: Ni-base alloys

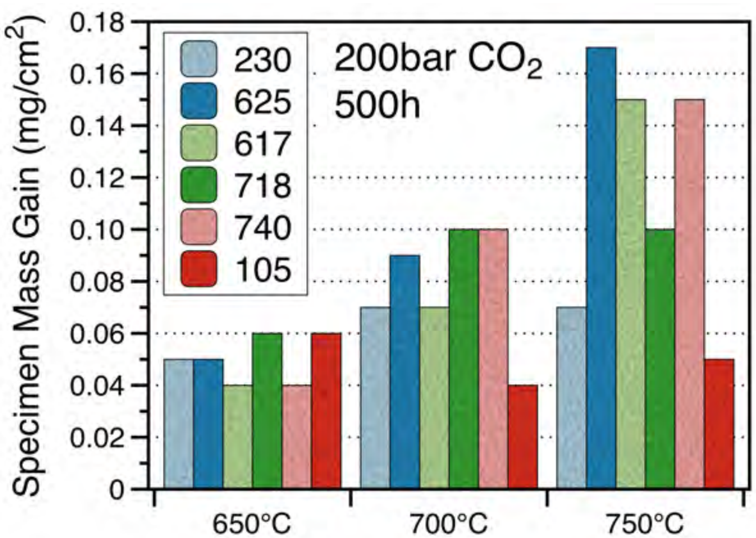
Quantified internal oxidation (and scale thickness) of Ni-base alloys after 1-10 kh 800°C exposures in:

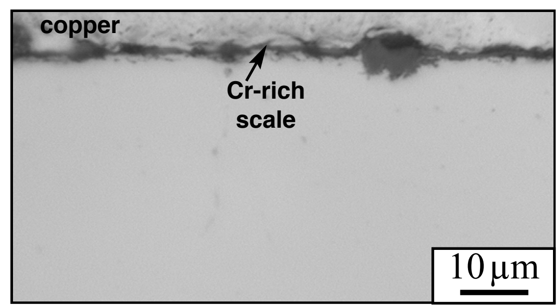
- 17bar steam
- 1 bar lab. air
- 1 bar “wet” air (simulate exhaust gas)

Not able to make comparisons with:

- coal ash: only 500h exposures
- supercritical $CO_2$ (500h, <800°C)




740 750°C 200bar $CO_2$

# Alloy oxidation coupons exposed

## ~1.5x10x20mm in all cases

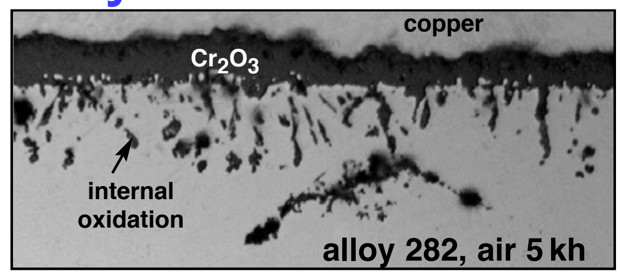
### 17bar steam testing

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

Temperature: 800°C or 900°C

Time: 2-20 x 500 h cycles

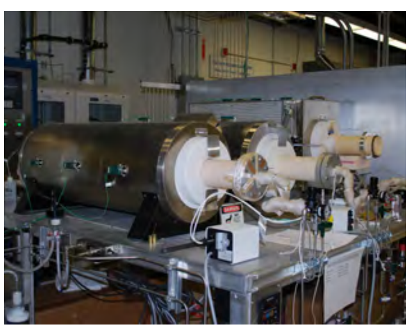
**~20 measurements per image**




### 1bar laboratory air

Temperature: 800°C or 900°C

Time: 100h or 500 h cycles



### 1bar “wet” air - 10%$H_2O$

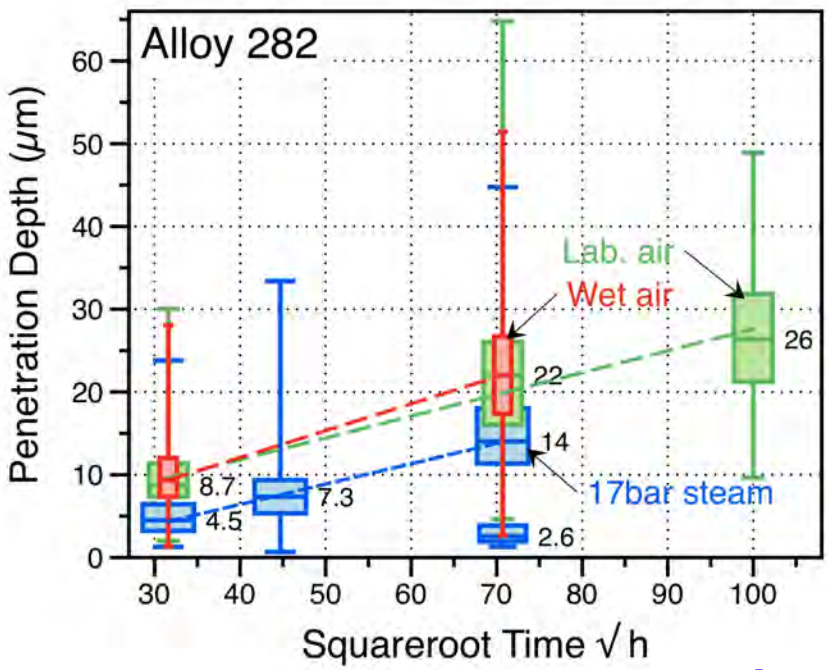
Deionized water atomized into flowing (1.8 cm/s) air

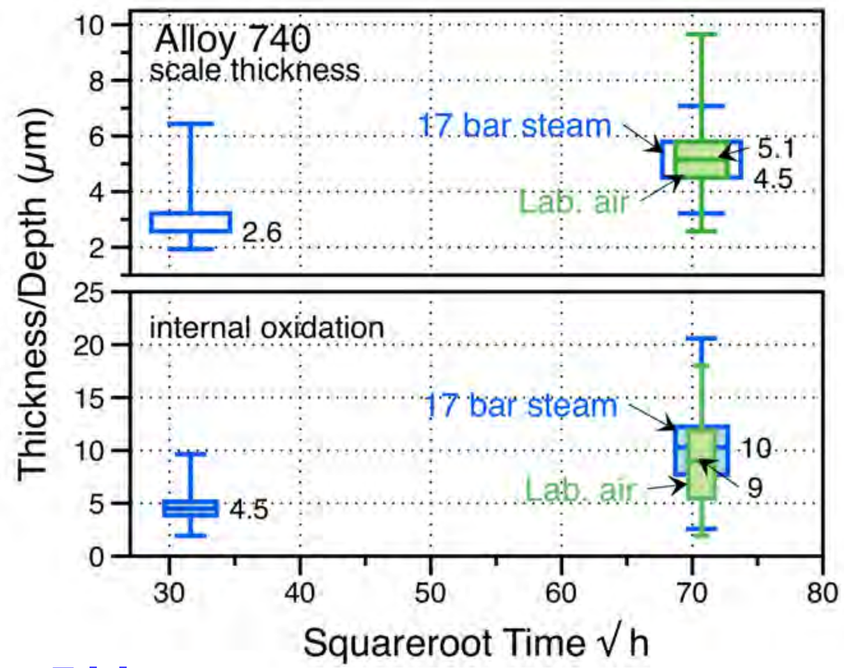
Temperature: 800°C

Time: 100h or 500 h cycles

# Commercial Ni-base alloys: little environment effect

## Depth of internal attack & external scale thickness

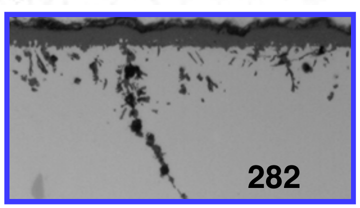


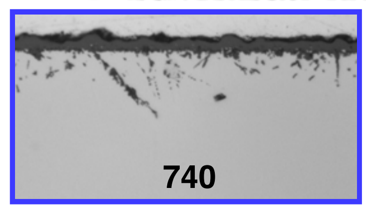




**steam 5 kh**

20μm

**19.3Cr-1.5Al-2.2Ti**



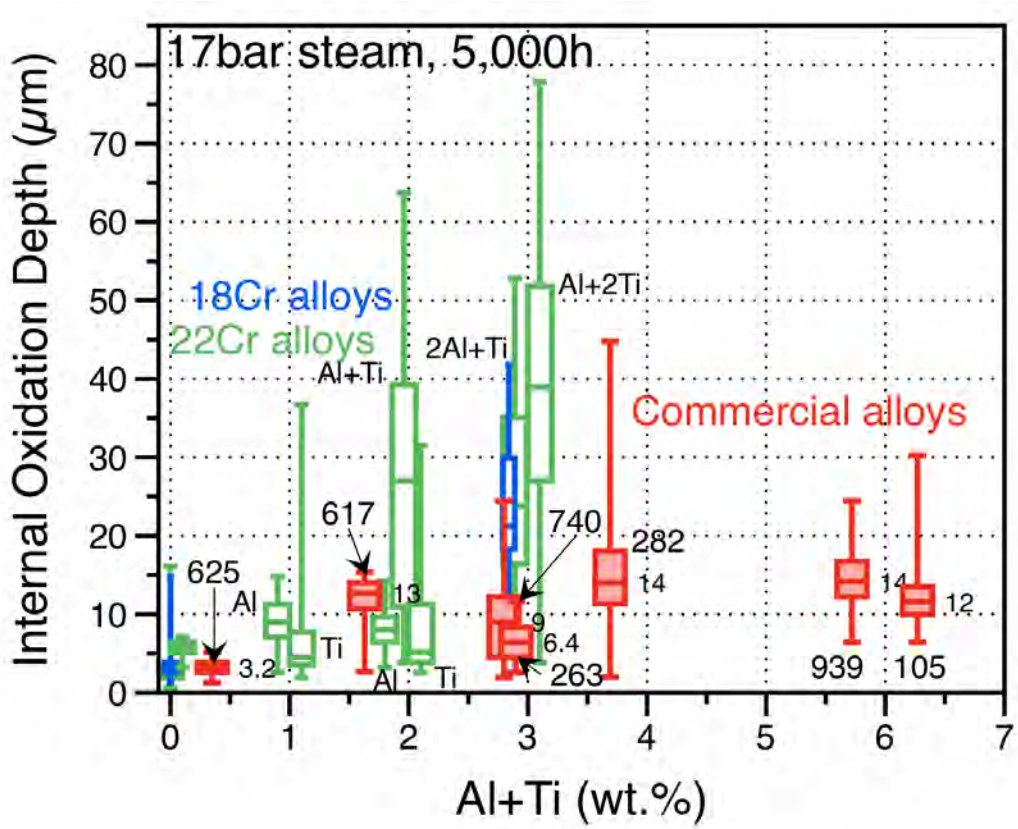



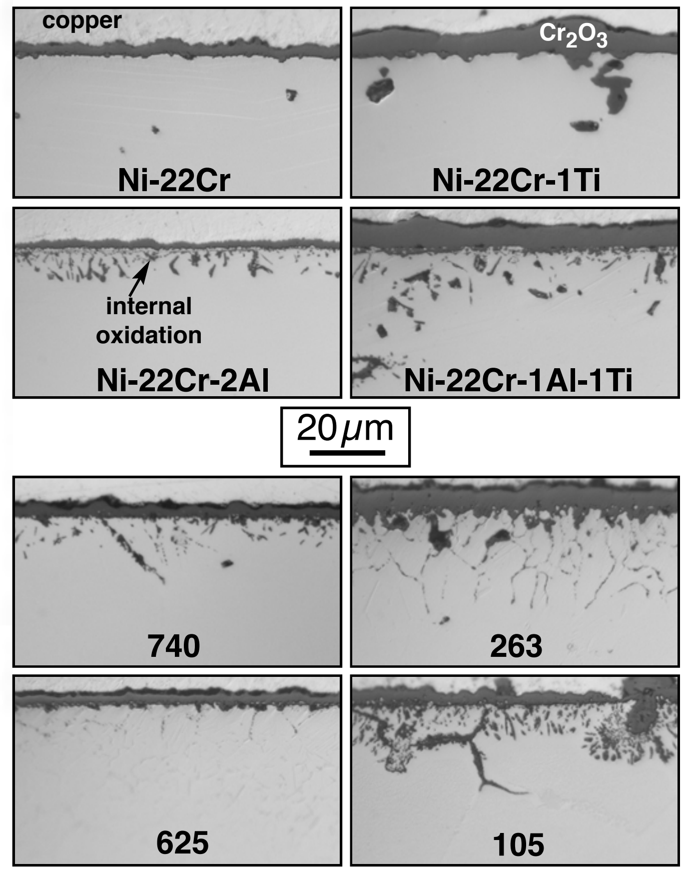

**23.4Cr-0.8Al-2.0Ti**

Most extensive exposures for alloy 282
many different potential applications beyond coal
Similar trend for alloy 740

# Model alloys: deeper penetrations

## Standard 5,000h exposure at 800°C in 17bar steam



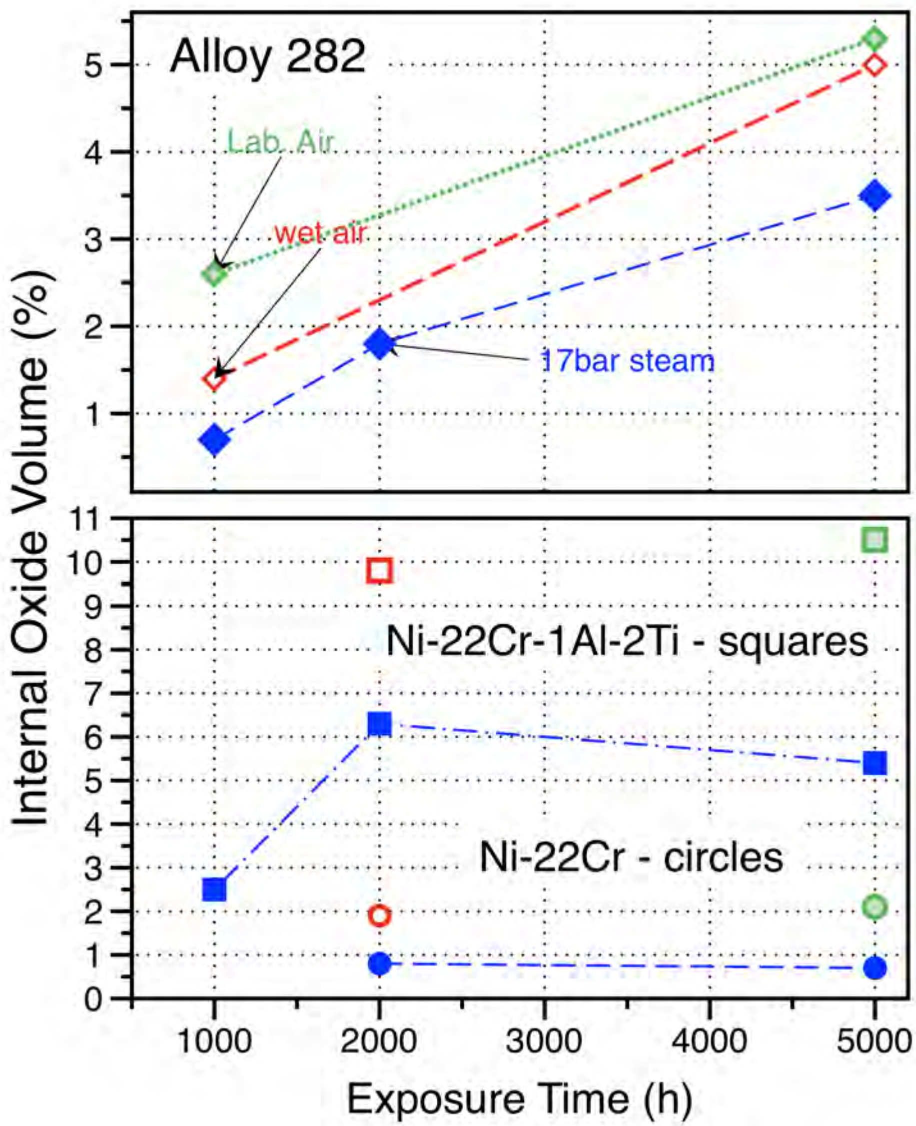




Peak median/maximum with alloy 282

Model alloys: deepest penetrations with highest Ti

# Internal oxide volume quantified

## % relative to standard area beneath scale




282:
- volume highest in air
- lowest in steam

Model alloys:
- less oxide in steam

Ni-22Cr - least oxide

+1Al-2Ti - most oxide

even more than 282

# Task 2: Why shot peening?

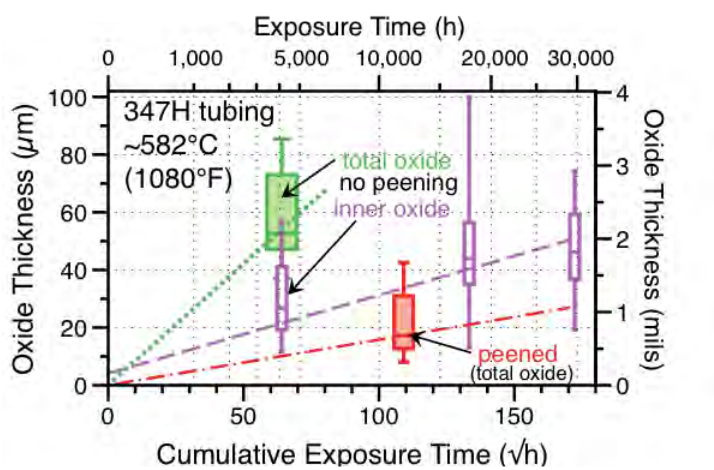
Exfoliation problem is a main driver for research

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

Shot peening of austenitic tubes

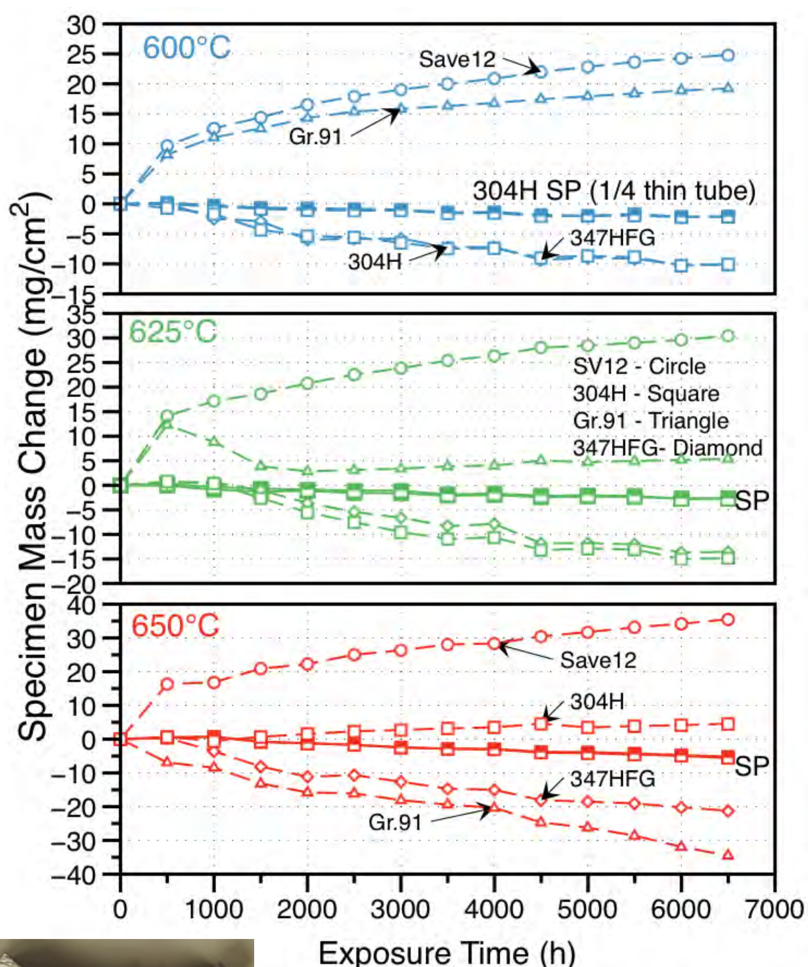
- Reduced scale growth: avoids exfoliation issue
- Limited understanding of benefit and procedure
- Ex: How do oxide nodules evolve at 600°-650°C?

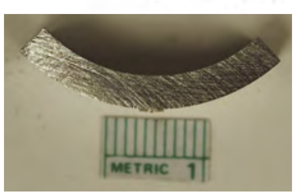
Prior field/lab work with EPRI:



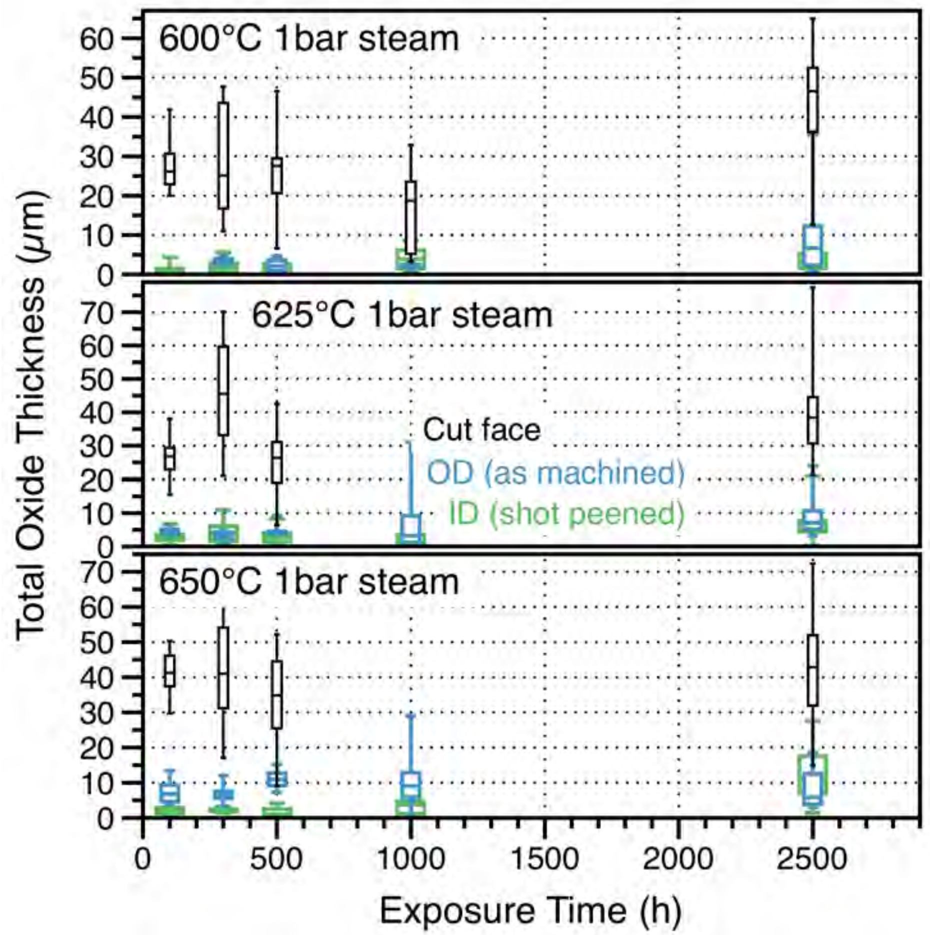

# 600°-650°C 1bar steam exposures

## Coupon mass change + oxide measurements



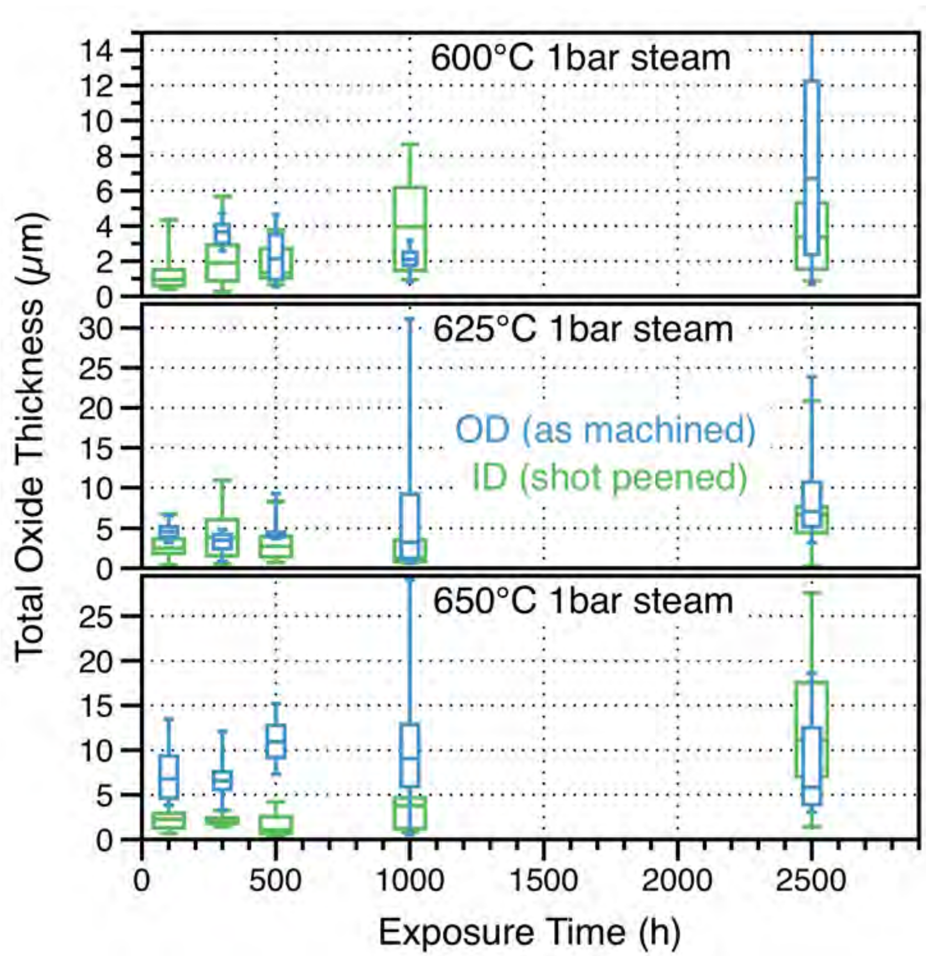

commercial shot-peened 304H

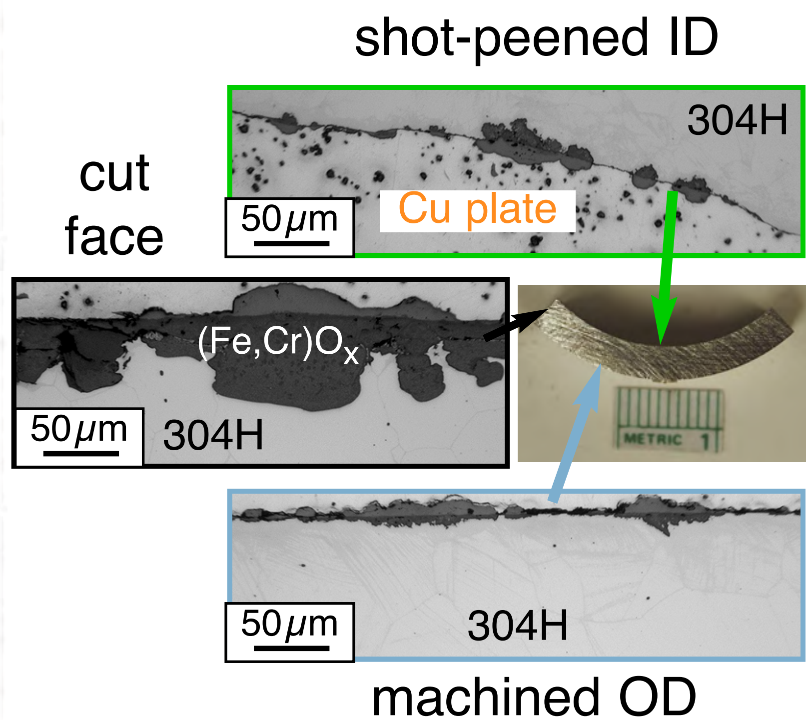


# 600°-650°C 1bar steam exposures

## Oxide measurements on each specimen

commercial shot-peened 304H




Example: 2,500h, 625°C

304H-SP: 5, 7.5, 10, 10+kh specimens in progress

# Task 3: stress corrosion cracking

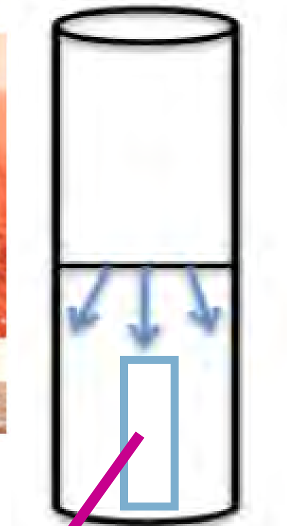
1. Recent massive failures of waterwall tubes T23 (in US) and T24 (in EU) caused by SCC, primarily during plant startup has created interest in this topic.

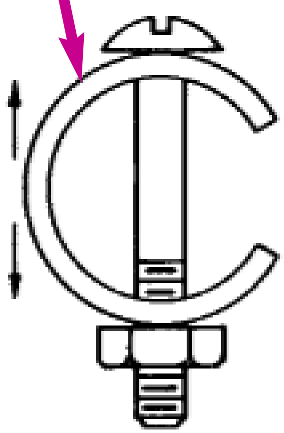
2. SCC susceptibility requires several factors:
   - tensile stress (applied or residual)
   - “wrong” microstructure (e.g. improper PWHT)
   - corrosive environment (~200°C, $O_2$ in water...)

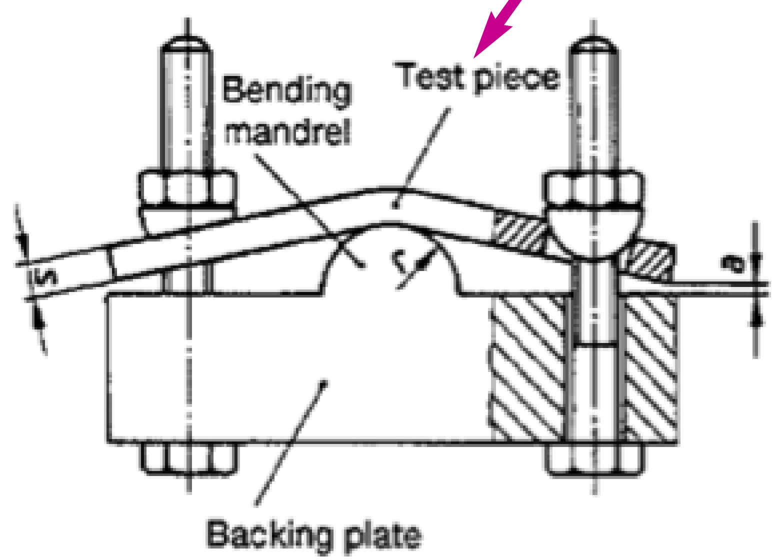
# Two tests address two failure modes

Cracks in longitudinal direction

Cracks in transversal direction








**C-Ring Test** Longitudinal

**Jones Test** Circumferential

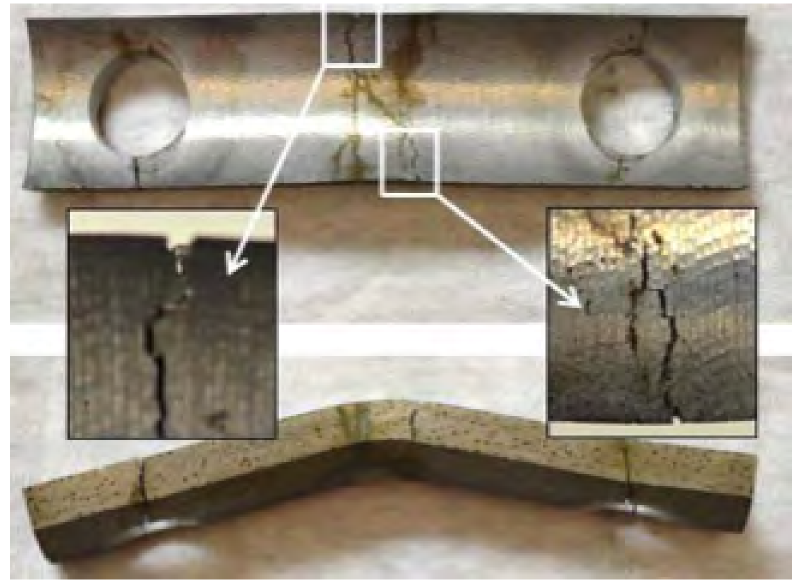
# Both tests showed same results

## 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

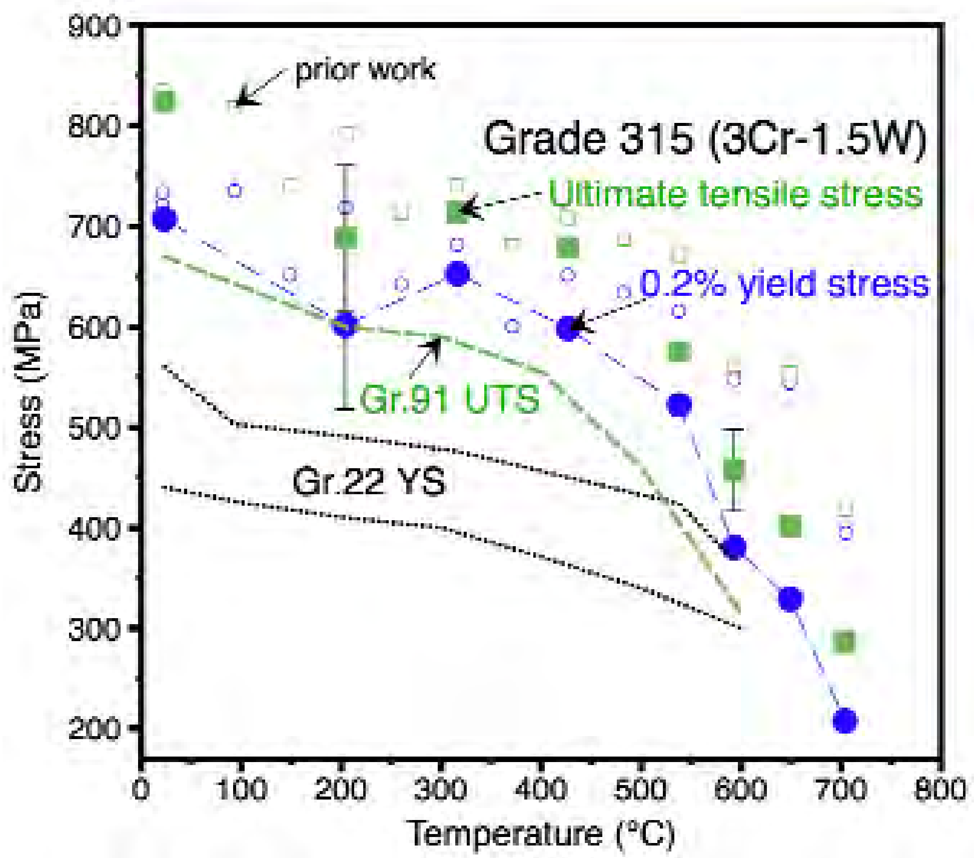
Harder (350 vs 220 DPH), Normalized (0.5h,1065°C WQ) steels are more susceptible to cracking



Normalized T24
after inhibited acid clean

# Excellent properties of Grade 315

3Cr-1.7W-0.7Mo data from abandoned code case

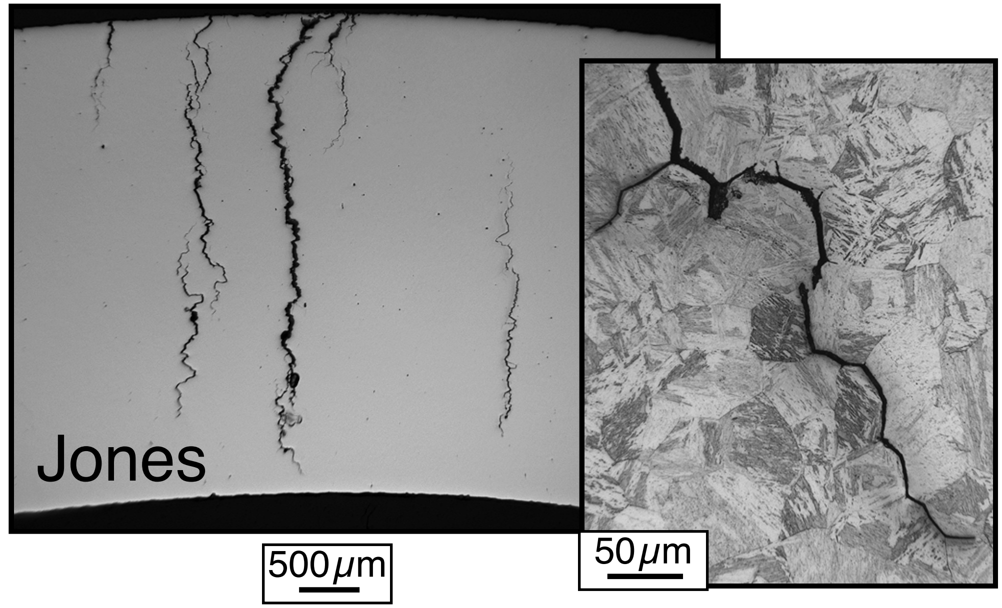


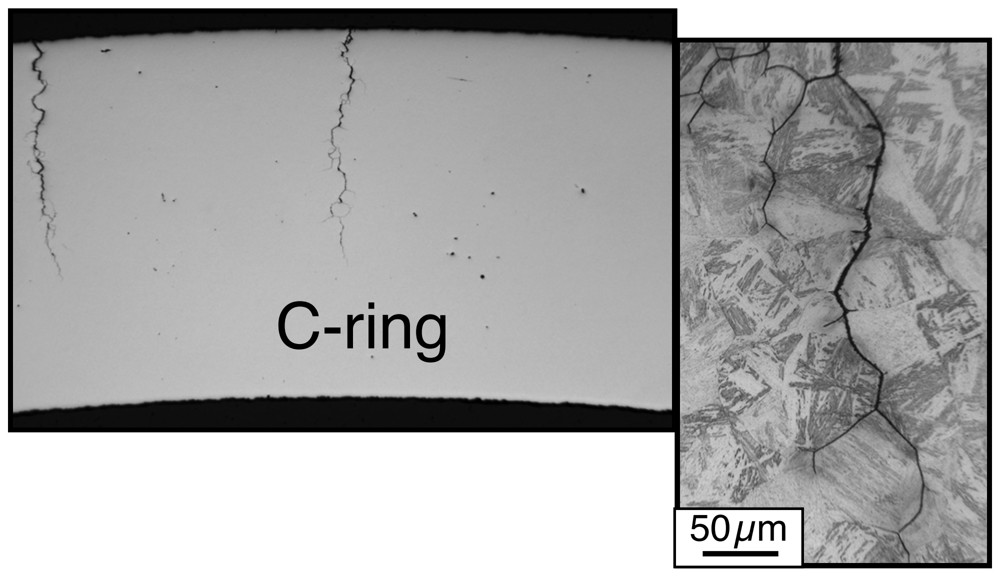

Higher yield & ultimate tensile stress than Grades 22 & 91

# Similar cracking for Grade 315

## 3Cr-1.7W-0.7Mo, 200°C $H_2O \pm O_2$ 168h

Grade 315 Jones and C-ring test specimens in aerated $H_2O$, 200°C, 168h



# Future SCC Work

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

2. Controlled chemistry water loop needed to identify critical $O_2$ content for cracking
    - loop under construction

3. Explore potential solutions

# Water loop: next level of testing

## Simulate actual fossil environments and controlled $pO_2$ levels

On-line in summer 2015, joint work with nuclear project

# Milestones

## FY14

Done - Complete comparison of Ni-base 740, 617 & 282 alloys in coal ash corrosion and evaluate need for surface treatment (9/14)

Done - Complete microstructural assessment of effect of shot peening on steam oxidation at 600°-650°C (9/14)

Done - Compare SCC of 2.25Cr and 3Cr steels (11/14)

## FY15

Done - Complete quantification of Ni-base alloy attack (12/14)

Complete relative assessment of 3Cr steels in static testing (in progress, 6/15)

Complete initial assessment of SCC in water loop with at least two different water chemistries (in progress, 9/15)

# Summary

Corrosion task transitioned from oxy-firing

Current work involves several sub-tasks:

1. Wrap up: internal oxidation of Ni-Cr alloys
   - little effect of environment 1-10kh
2. Quantify shot-peening 304H benefit
   - 2500h complete, 5kh, 7.5kh, 10kh running
3. SCC issue in current waterwalls
   - transitioning to water loop testing
   - want to define critical $O_2$ content

- October EPRI Power Plant Corrosion Conf. may identify future topics to explore

# CLEAN COAL.
# COOL.

# FEAA120: Phase 1 with WashUStL

Work supports Staged Pressurized Oxy-Combustion

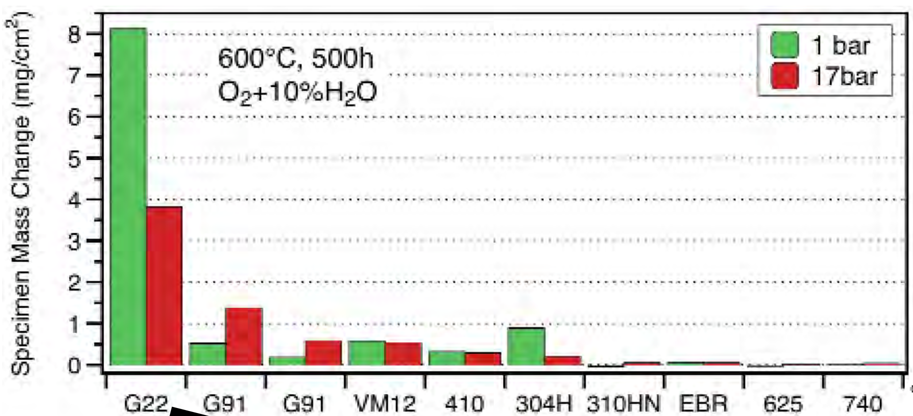
Side-by-side reaction tubes: 1 and 17bar

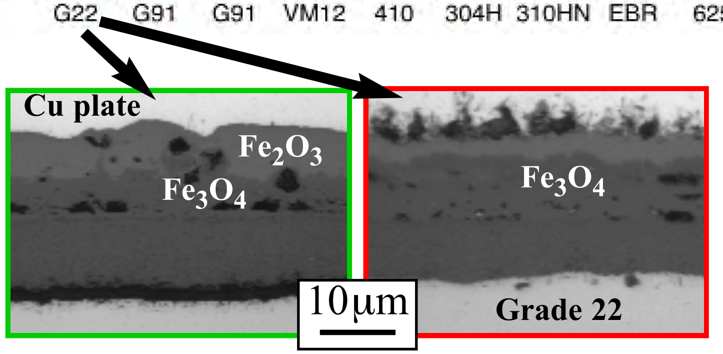
600°C (Fe-base alloys) $90\%O_2-10H_2O$ complete

$90\%O_2-10H_2O+0.1\%SO_2$ running

800°C (Ni-base alloys) $90\%O_2-10H_2O$ complete

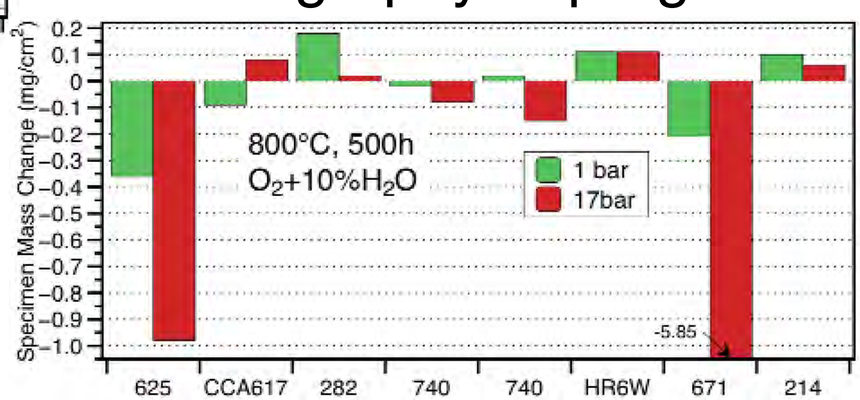
$90\%O_2-10H_2O+0.1\%SO_2$



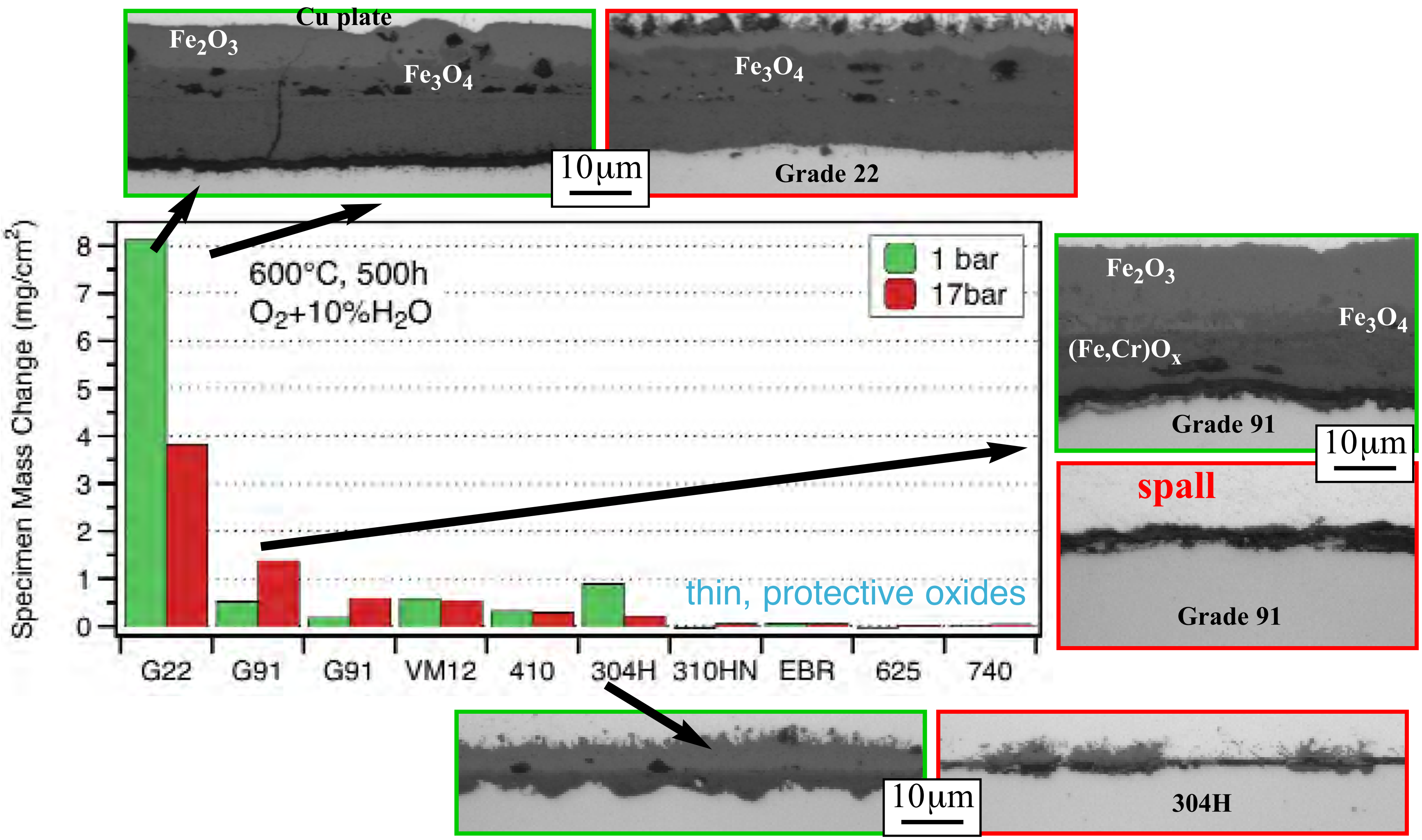

Subtle pressure effects observed

metallography in progress:



# Phase 1: subtle effects of pressure

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

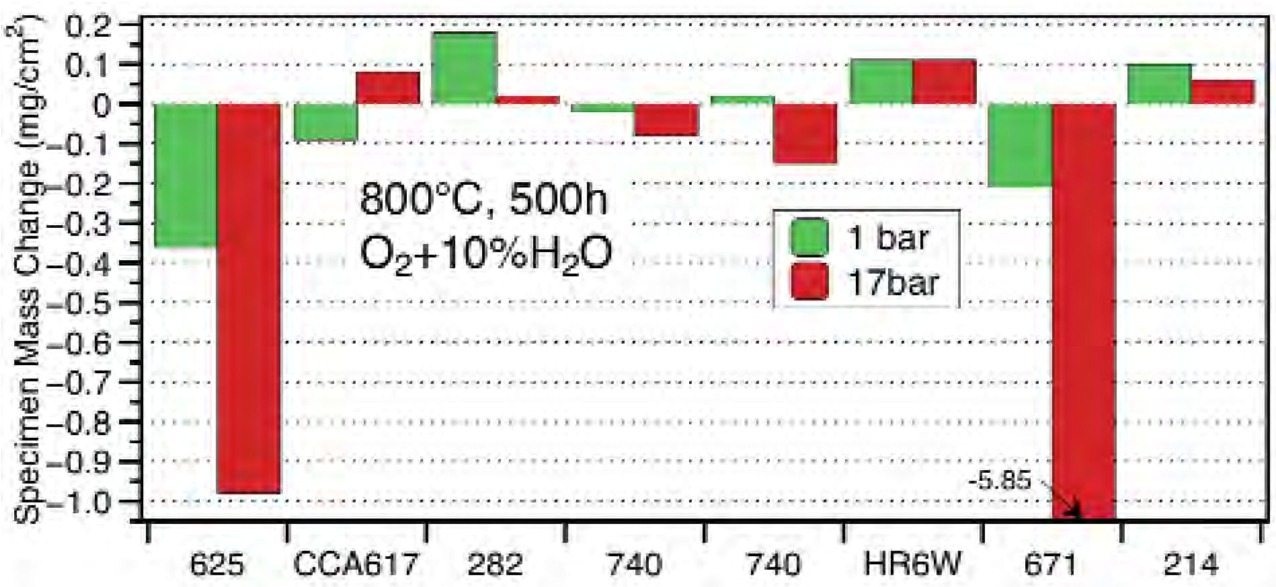



Thick oxides on Fe-Cr spall: mass change unreliable

Higher-alloyed materials: very thin oxide, low mass gains

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

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




Specimens unloaded at end of February
metallography in progress

Next 500h experiment running: 600°C, $O_2$-10%$H_2O$-0.1%$SO_2$

# Range of commercial & model alloys

measured by inductively coupled plasma analysis and combustion analysis

**Alloy chemical compositions (weight %)**

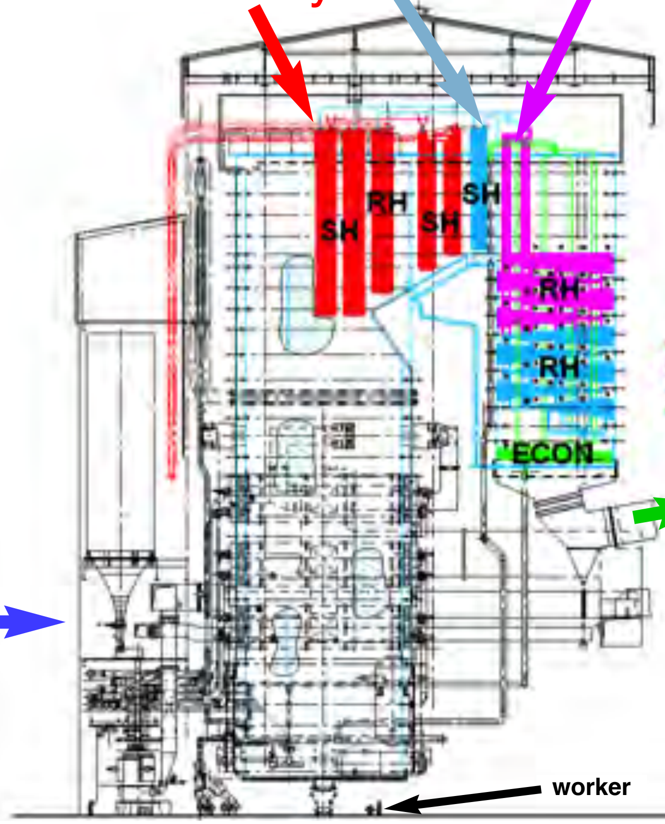
| Alloy | UNS# | Fe | Cr | Ni | Mo | W | Mn | Si | C | N | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Gr.22 | K21590 | 95.5 | 2.3 | 0.2 | 0.9 | < | 0.6 | 0.1 | 0.14 | 0.01 | 0.2Cu |
| Gr.33 | | | | | | | | | | | |
| Gr.91 | S90901 | 89.7 | 8.3 | 0.1 | 0.9 | 0.01 | 0.3 | 0.1 | 0.08 | 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%

# Advanced: Oxy-firing to facilitate $CO_2$ C+S

Retrofit current plants or advanced 760°C (below)




(courtesy Alstom)

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

~~air~~ $O_2$ → particle removal → $CO_2$ capture → hole in the ground

flue gas recirculation

Several studies published by Alstom (Bordenet)

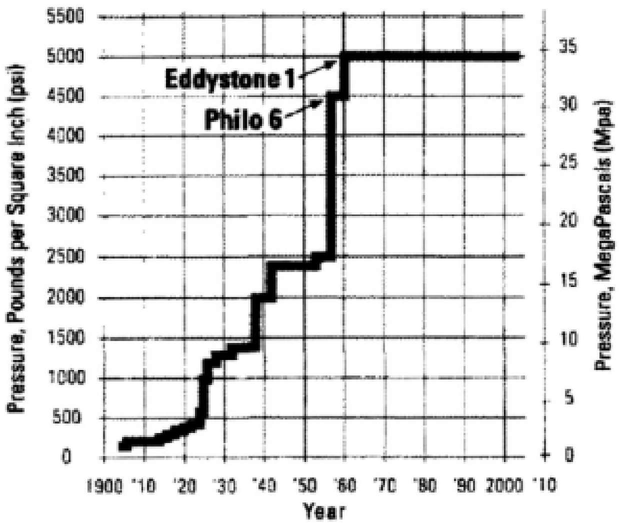
What is the effect of oxy-firing on fireside corrosion?

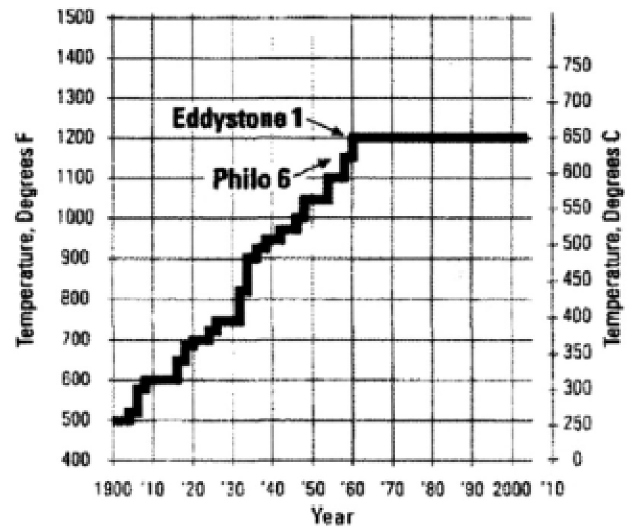
# Ultimate goal is to marry Oxy + A-USC

"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

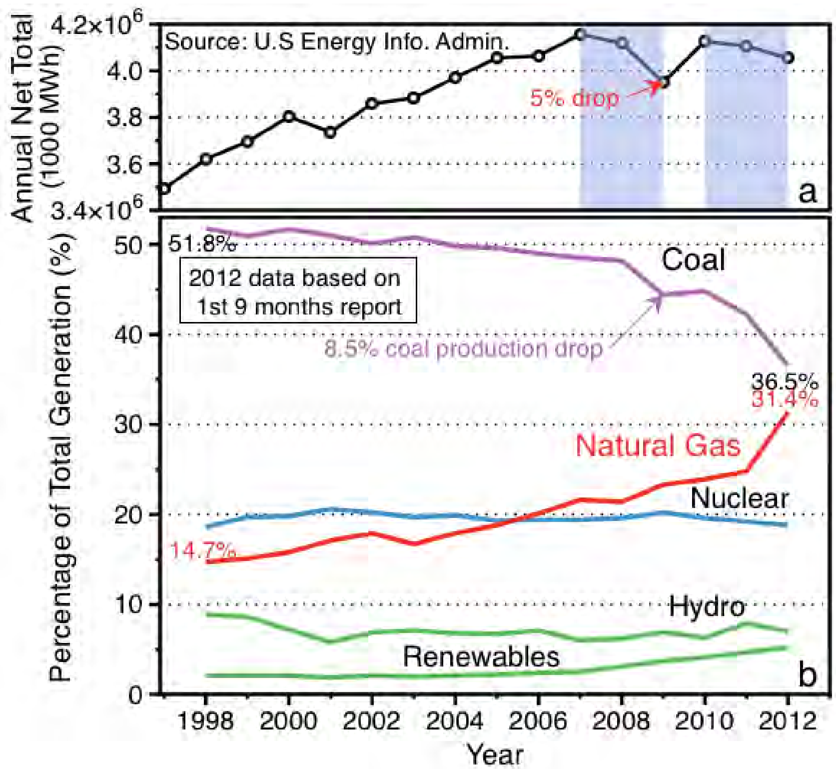
Eddystone (1960): 654°C/36.5MPa (1210°F/5300psi)
settled for 613°C/34.5MPa (1135°F/5000psi)

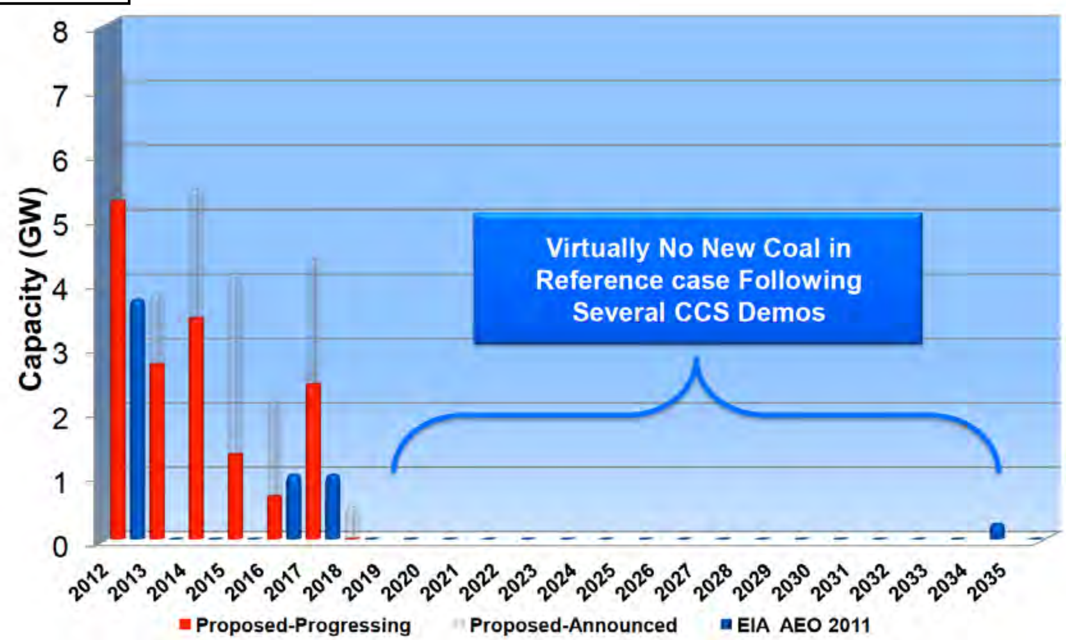
Turk (2013): 599°/607°C SH/RH 25.3MPa (1110/1125F)

# Why stop working on oxy-firing?

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

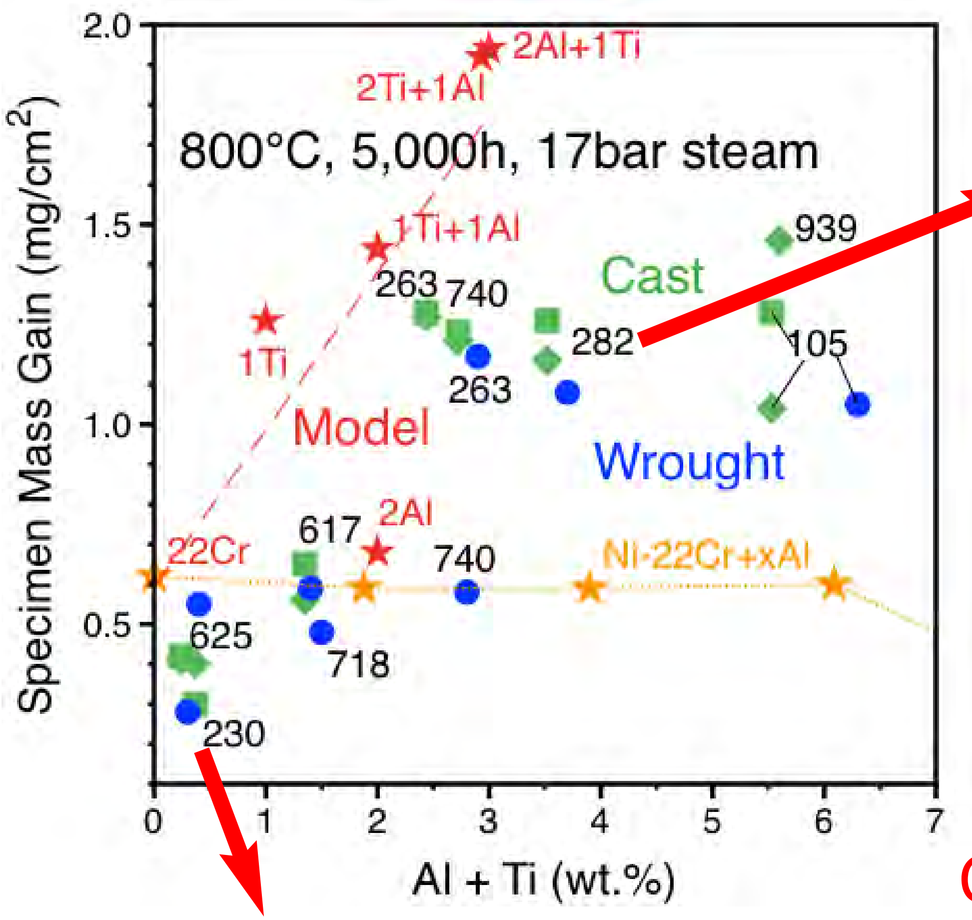
Pint, JOM Aug. 2013

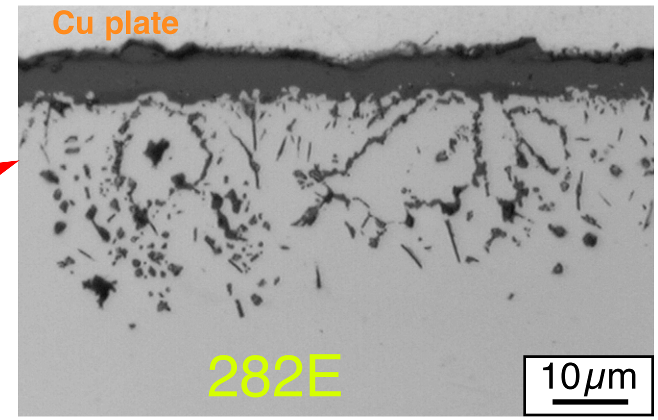


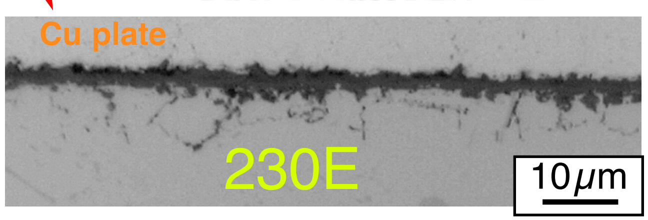



# NiCr+Al,Ti: mostly Ti effect

## 5,000h steam testing at 17 bar, 800°C



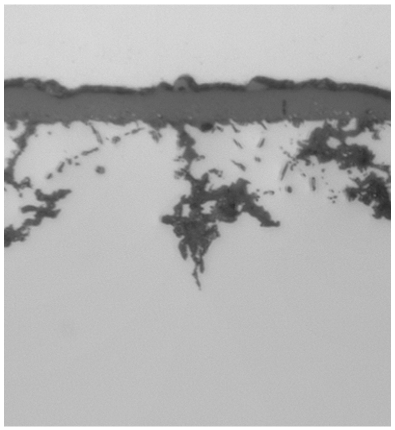

Commercial vs. model &
Cast vs. wrought alloys

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.

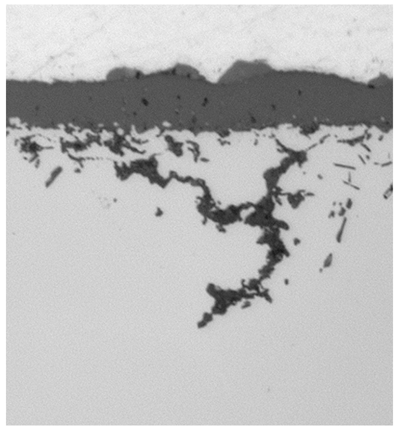
# Ex: Ni-18Cr-2Al-1Ti comparison

## Coupons tested at 800°C in three environments

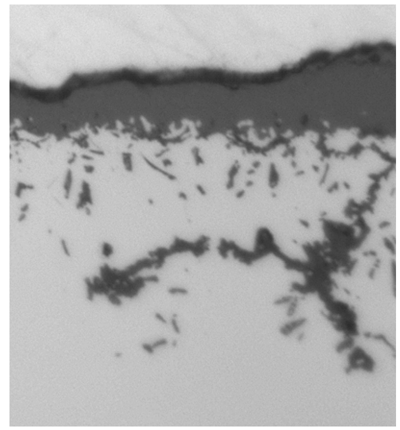
Steam, 1000h



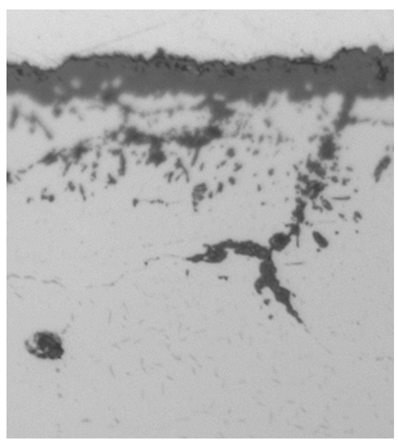
Steam, 2000h



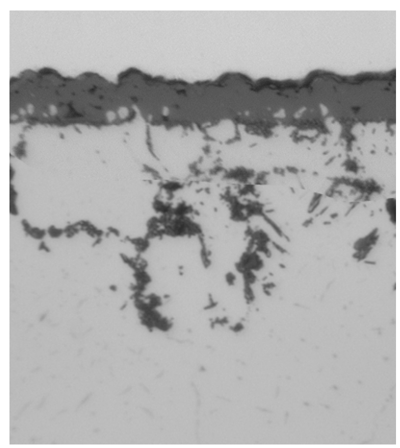
Steam, 5000h

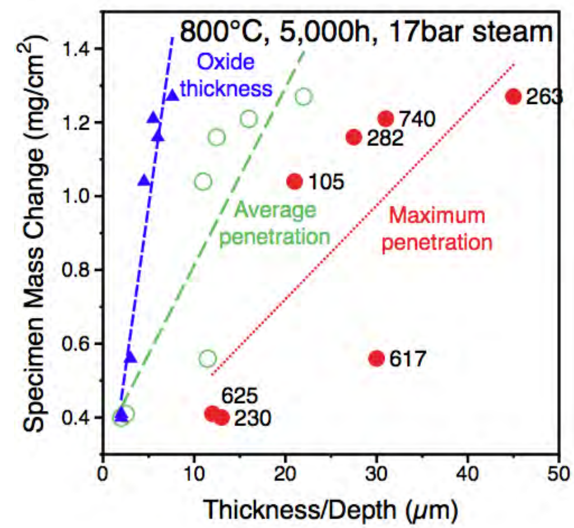


Wet air, 2000h



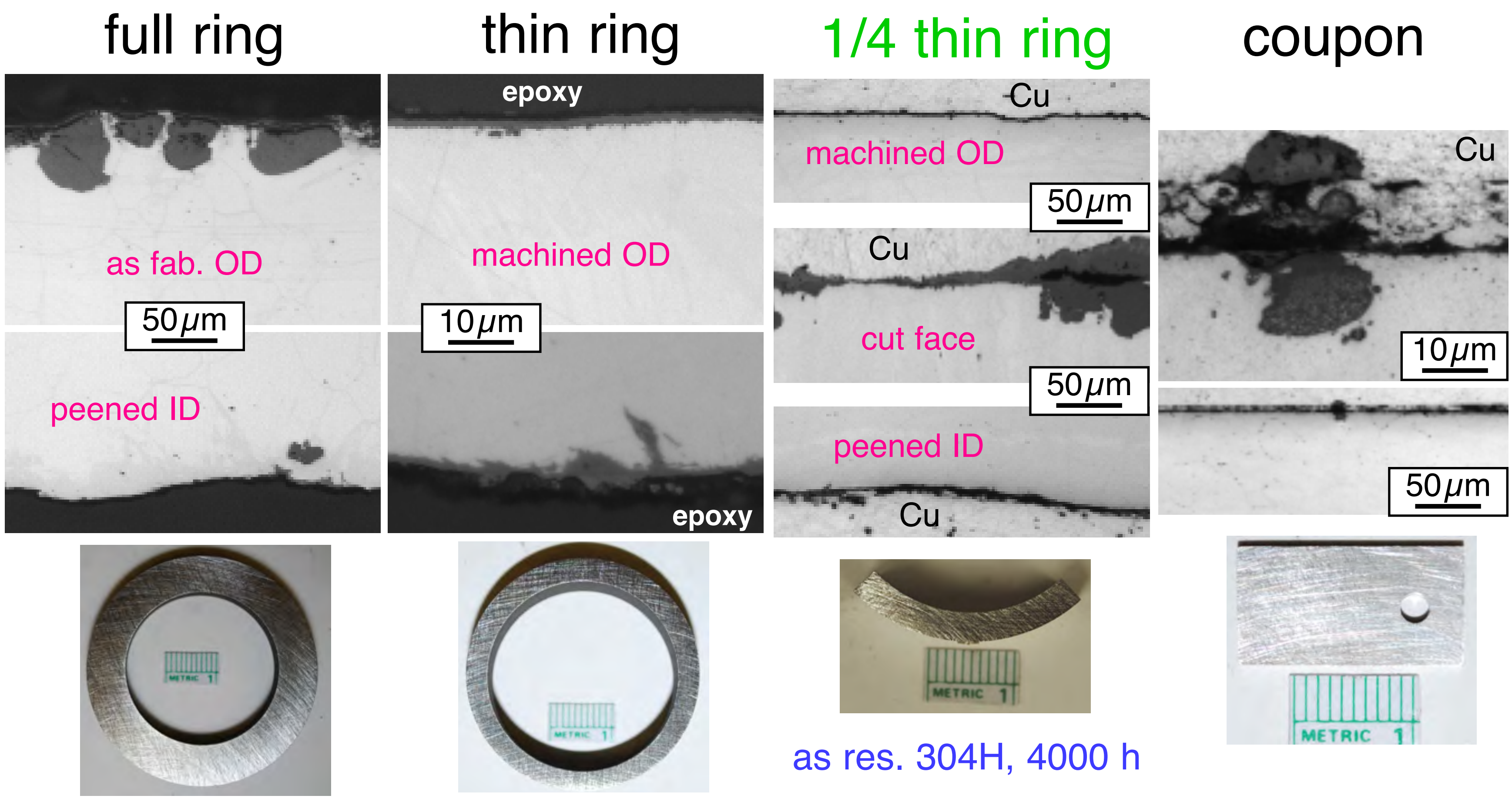
Dry air, 5000h





# 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-