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Oxy-combustion Environmental Characterization: Fire- and Steam-side Corrosion

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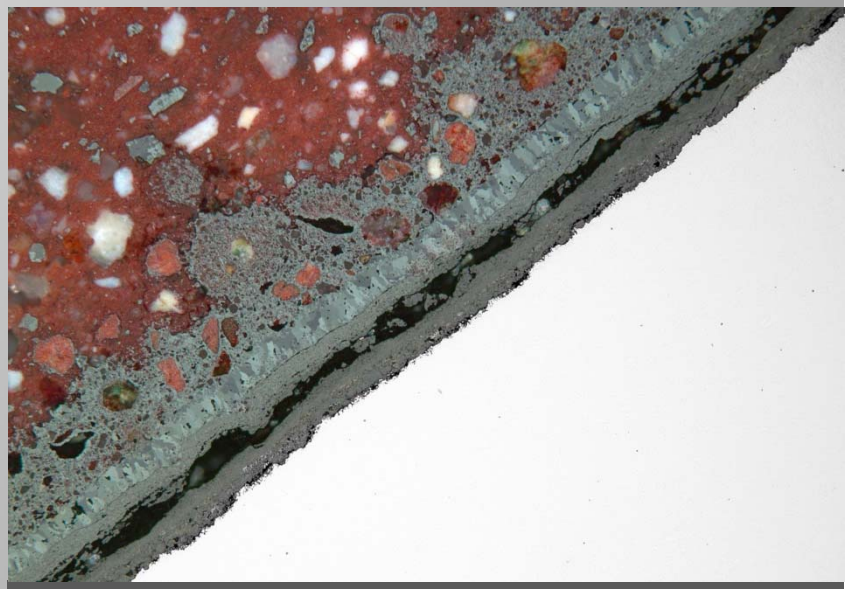

the **ENERGY** lab

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- Jeffrey Hawk, NETL, ORD, Technical Coordinator, ORD's Advanced Combustion FWP

Disclaimer

Outline

Fireside Corrosion in Oxy-Fuel Combustion

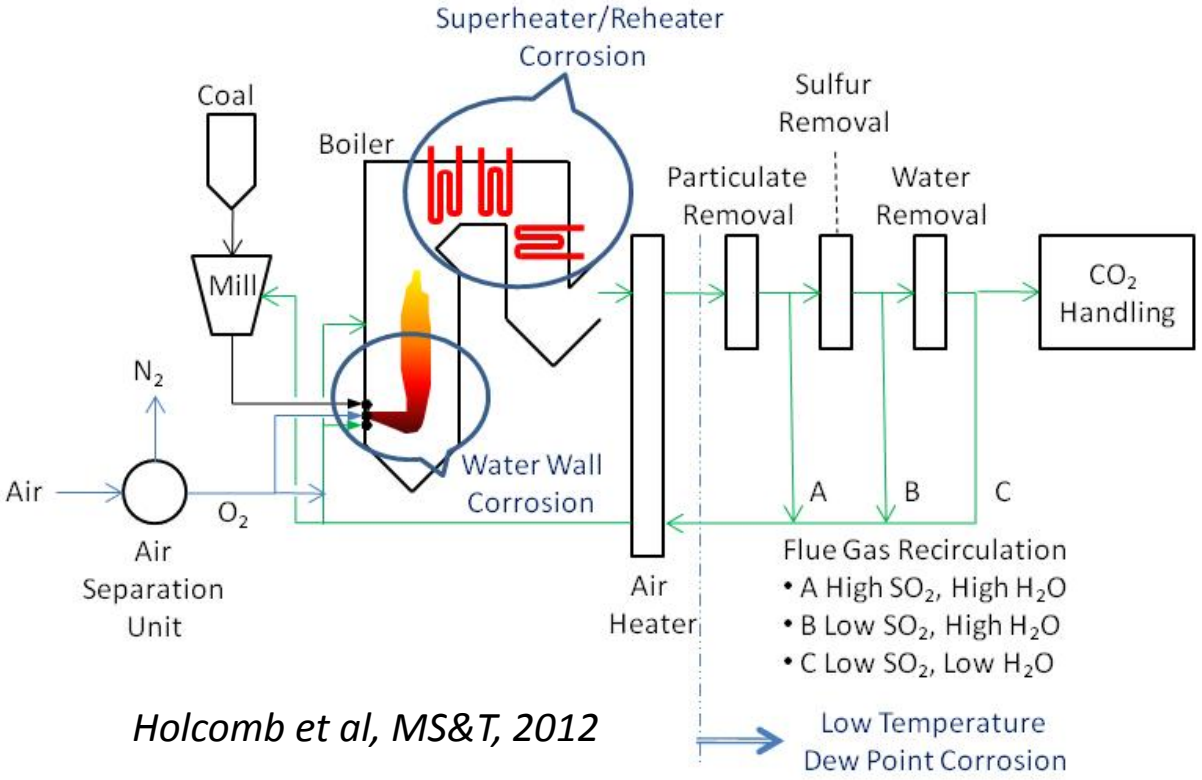
- Brief Background
- Experimental Procedures
- Results
- Conclusions
- New FY14 Research Efforts
- Initial Results

Hydrogen Tracking During Oxidation

- Background
- Experimental Procedures
- Results

Brief Update of Steam Oxidation in A-USC Conditions

Fireside Corrosion Associated with Oxy-Combustion



Holcomb et al, MS&T, 2012

- CO_2 replaces N_2 as the primary flue gas
- This changes the heat balance in the boiler
- Flue gas recirculation mimics air-fired heat balance

A primary goal was to examine the corrosion effects from flue gas composition changes arising from oxy-combustion

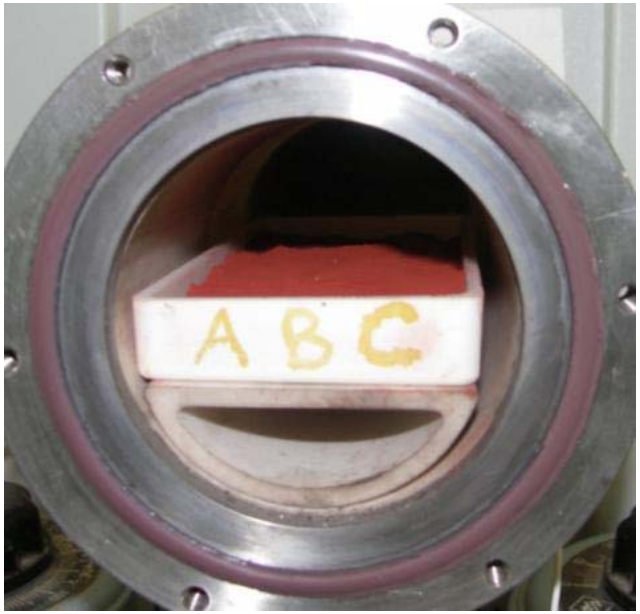
Laboratory Fireside Corrosion—Gas Phase FY12-13

Conditions		700°C, SH/RH Conditions			
		Air-Fired	Oxy-Fired		
			FGD <H_2O	FGD	wo FGD
Input Gas	N_2	Bal	8	8	8
	CO_2	14	Bal	Bal	Bal
	H_2O	9	9	20	20
	O_2	2.5	2.5	2.5	2.5
	SO_2	0.3	0.3	0.3	0.9
Calc SO_x	SO_2	0.215	0.215	0.215	0.649
	SO_3	0.085	0.085	0.085	0.252

Kung (2010) showed that a SO_2+SO_3 level of 0.3 results from a coal with a sulfur content of 4.3, such as a high sulfur Gatling (OH) bituminous coal

Long-term Laboratory Fireside Corrosion Tests, FY12-13

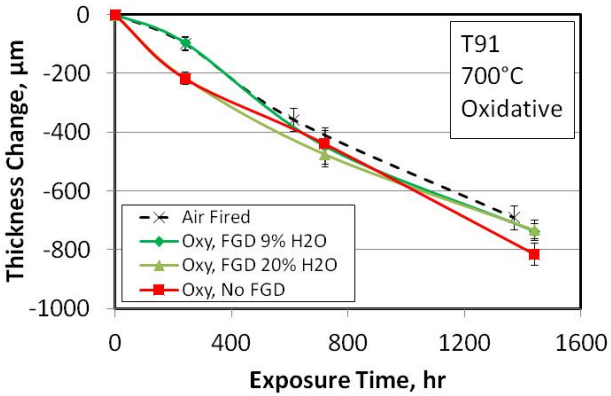
- **Ash Composition**
  30 Fe_2O_3 30 Al_2O_3 30 SiO_2 5 Na_2SO_4 5 K_2SO_4
- **Ash Application**
  - One side coverage, 3mm thick, 40 g/cm^2 compaction
- **Triplicate samples**
- **240 hour test segments**
  Clean samples of ash after each segment
  Weigh, photograph, reapply ash, and test again
- **Special Ash-Retained Samples after 240hr of Exposure**

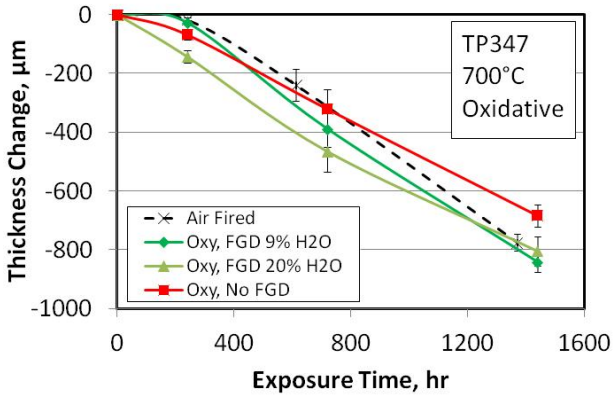


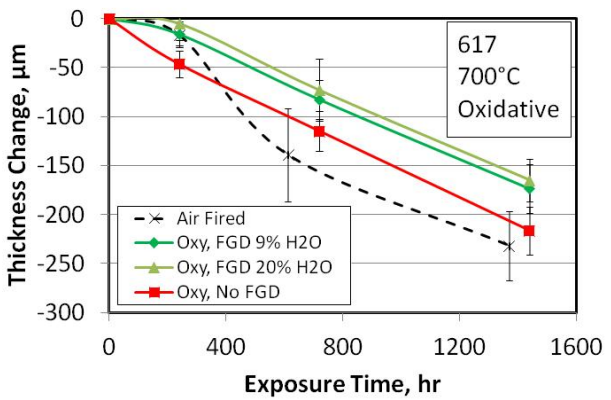
- **One of the triplicates available for periodic removal of 2 mm of sample for section-loss analysis**
- **25 cm/min gas phase velocity (at temperature)**
- **Pt catalyst for SO_2-O_2-SO_3 equilibrium**
  - Used to keep laboratory gas environment constant and reproducible

Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Ti	Al	Mn	V	Nb+Ta	Cu	Other
T91	Bal	8.46	0.14		0.95	0.10	0.36		0.01	0.44	0.22	0.08	0.16	0.05 N
TP347H	Bal	17.55	11.04	0.10	0.39	0.08	0.57	0.01	0.02	1.57	0.07	0.95	0.35	0.04 W
IN617	0.39	21.87	Bal	11.46	9.65	0.10	0.01	0.47	0.98	0.04		0.03	0.01	

SH/RH Temperatures (700°C)







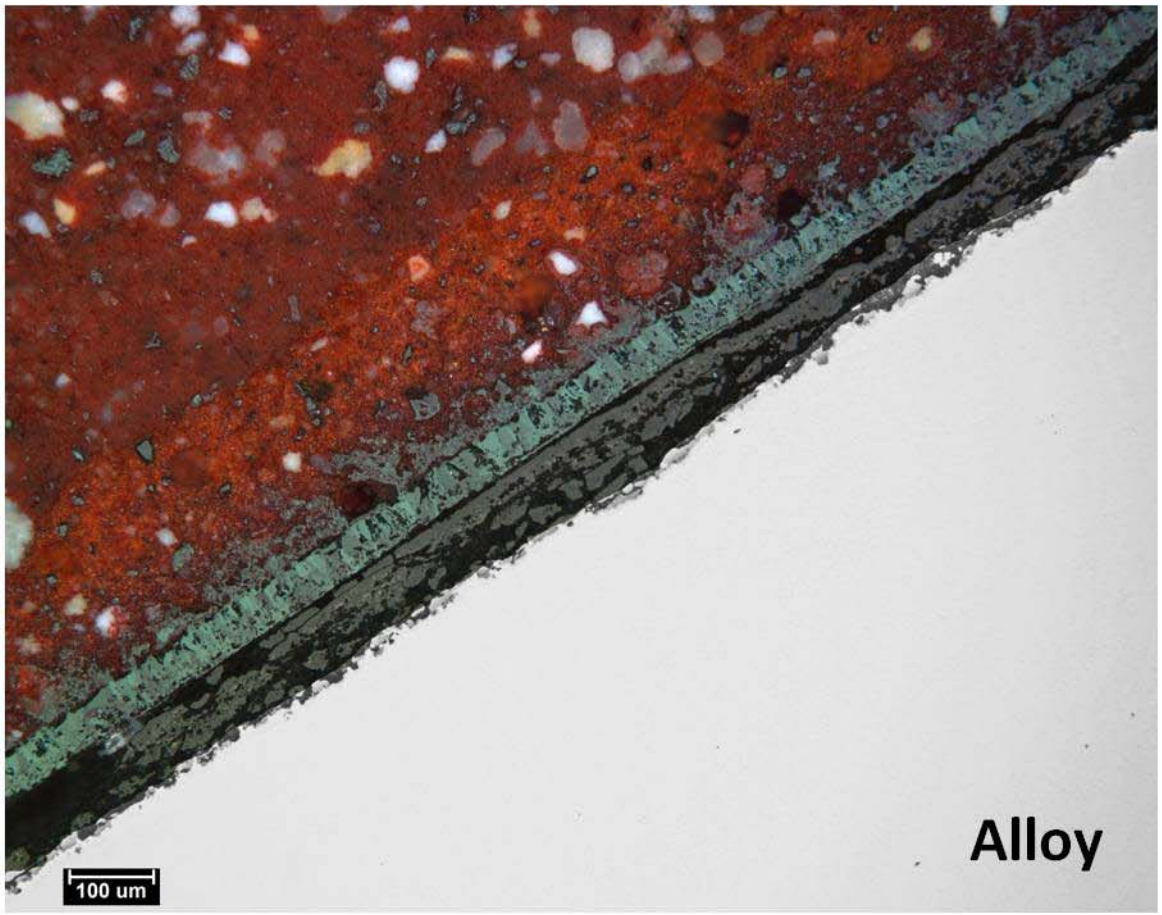
- Linear corrosion rates
- No significant differences in section loss measurements between air- and oxy-firing at 700°C
- Early trends disappeared with longer exposure times

Conditions		700°C, SH/RH Conditions			
		Air-Fired	Oxy-Fired		
			FGD <H_2O	FGD	no FGD
Input Gas	N_2	Bal	8	8	8
	CO_2	14	Bal	Bal	Bal
	H_2O	9	9	20	20
	O_2	2.5	2.5	2.5	2.5
	SO_2	0.3	0.3	0.3	0.9

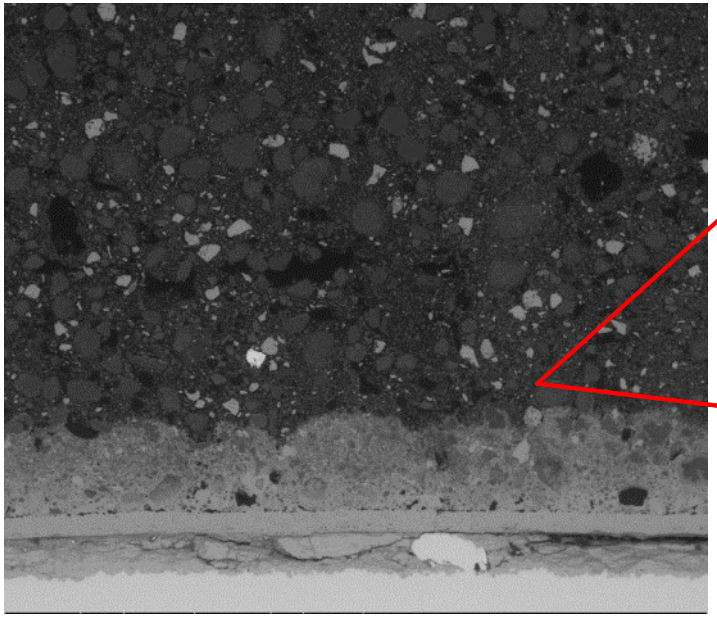
T91 (Oxy FGD 20% H_2O) 240hr at 700°C

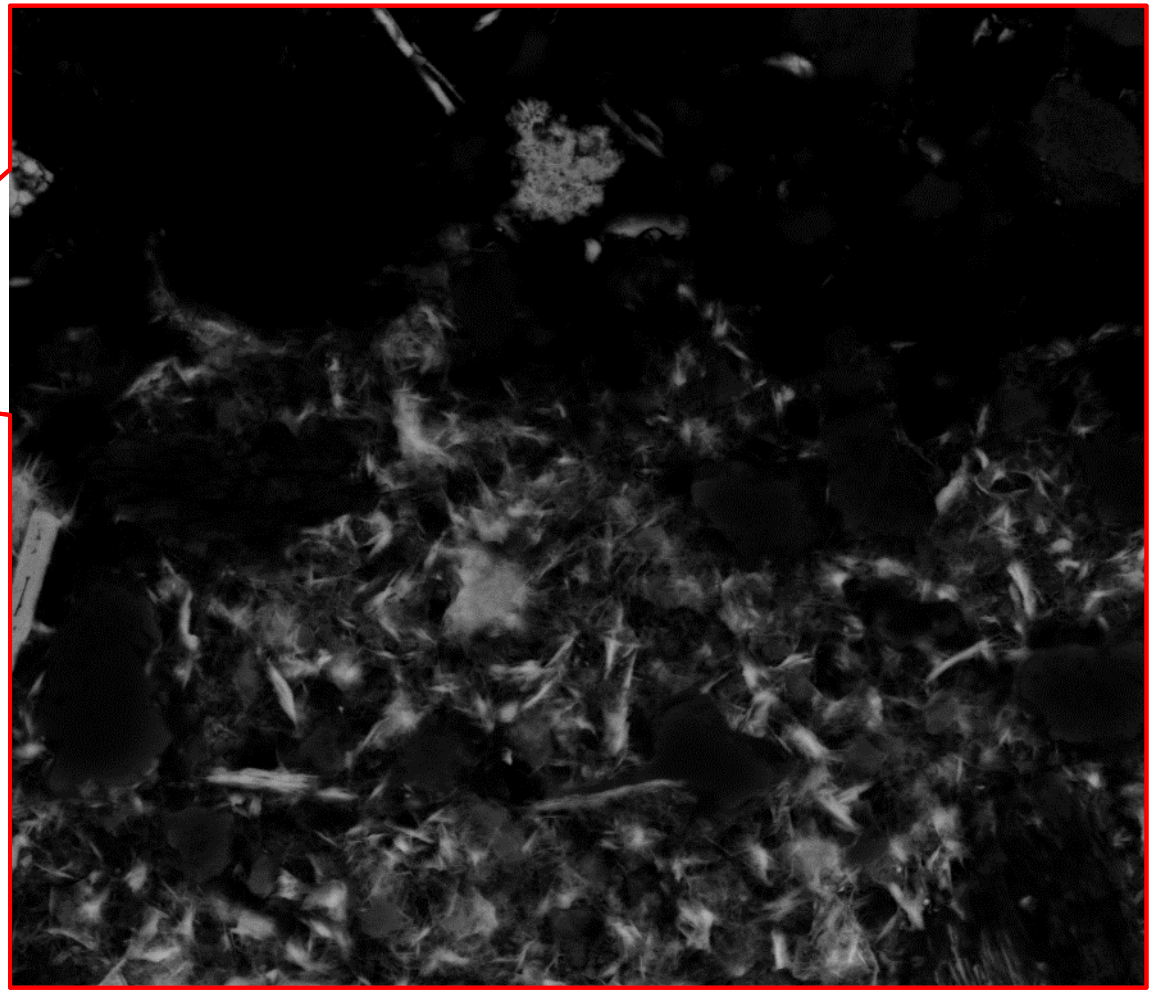
CO_2+8%N_2+20%H_2O+2.5%O_2+0.3%SO_2

Special test with ash retained



T91, Oxy-fired, CO_2+8%N_2+**20%H_2O**+2.5%O_2+**0.3%SO_2**, 700°C, 240h



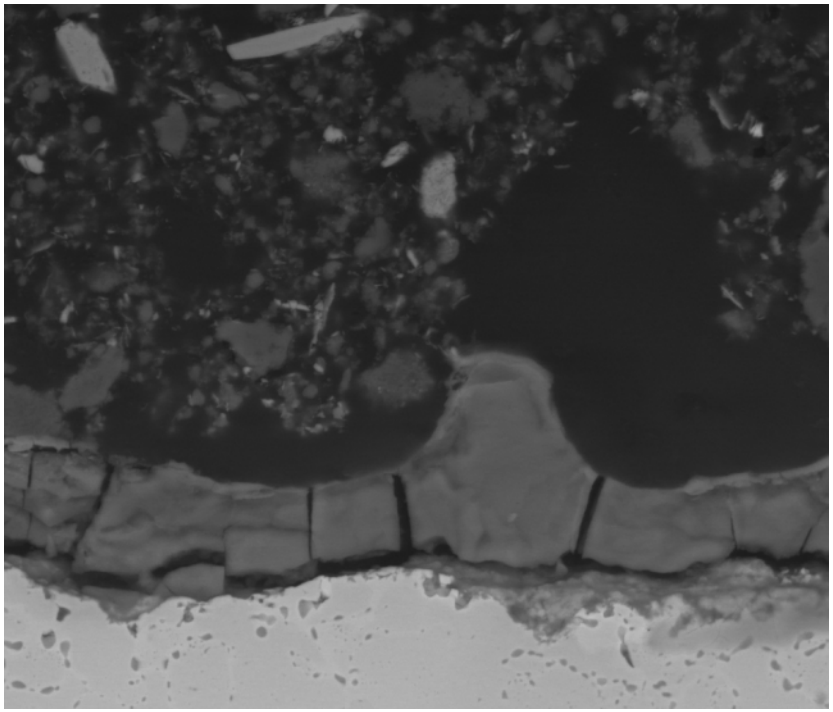


Needle shaped Fe-rich oxides through the pores between the ash particles

617, 240hr at 700°C

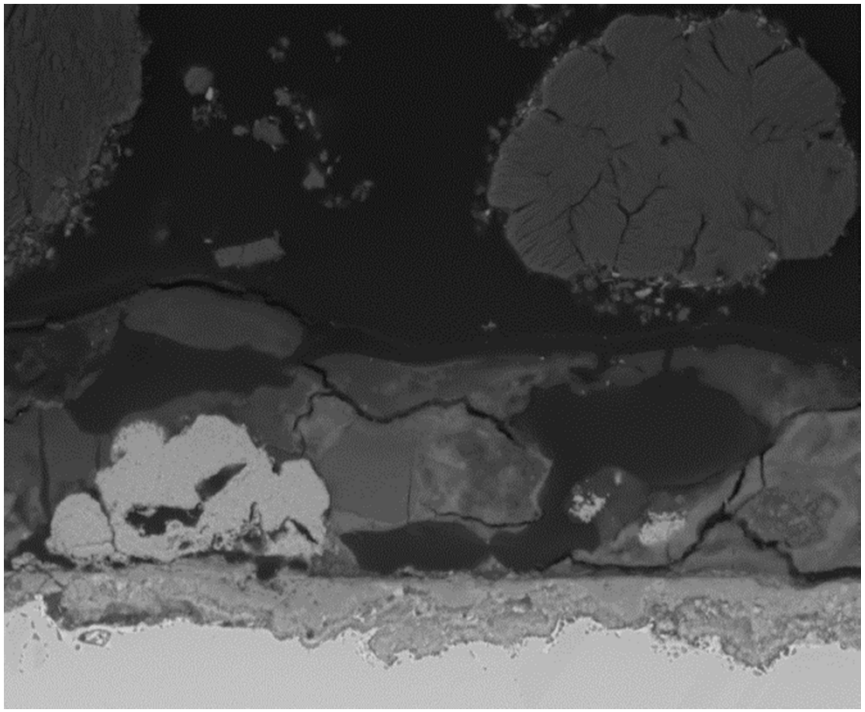
(Oxy FGD 20% H_2O)

CO_2+8%N_2+20%H_2O+2.5%O_2+0.3%SO_2



(Oxy no FGD)

CO_2+8%N_2+20%H_2O+2.5%O_2+0.9%SO_2



50 µm

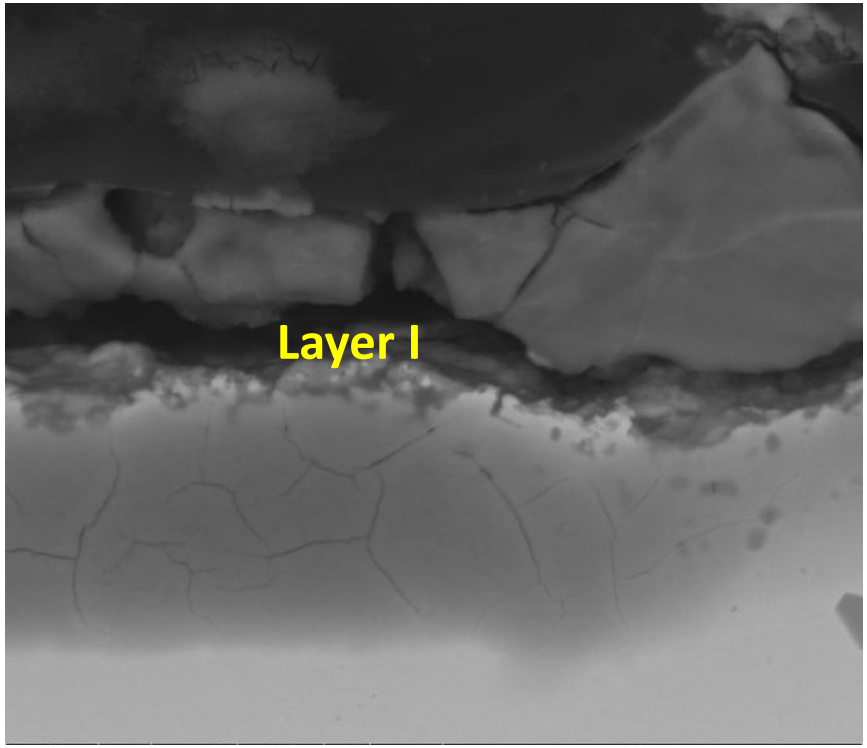
- External scale fused with ash
- More discrete internal sulfide particles beneath the inner scale layer

- External scale fused with ash
- Thicker external scale
- Large NiO particles present
- Large pores present
- Thicker inner S-rich layer

617, 240hr at 700°C

(Oxy FGD 20% H_2O)

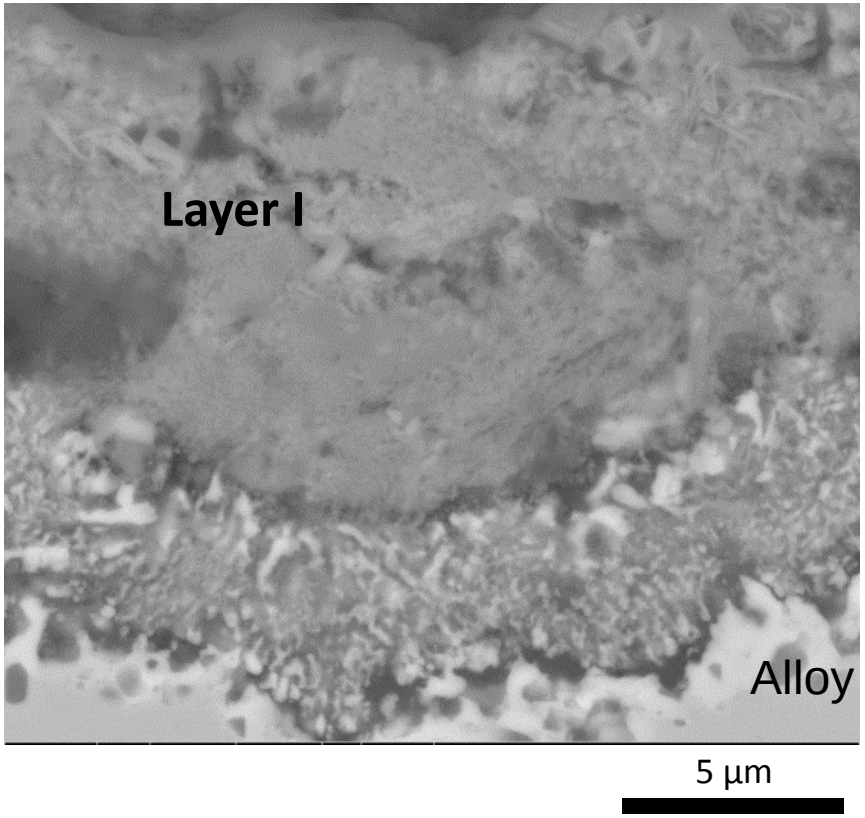
CO_2+8%N_2+20%H_2O+2.5%O_2+0.3%SO_2



- **Much thinner layer I**
- **Intergranular internal sulfides**

(Oxy no FGD)

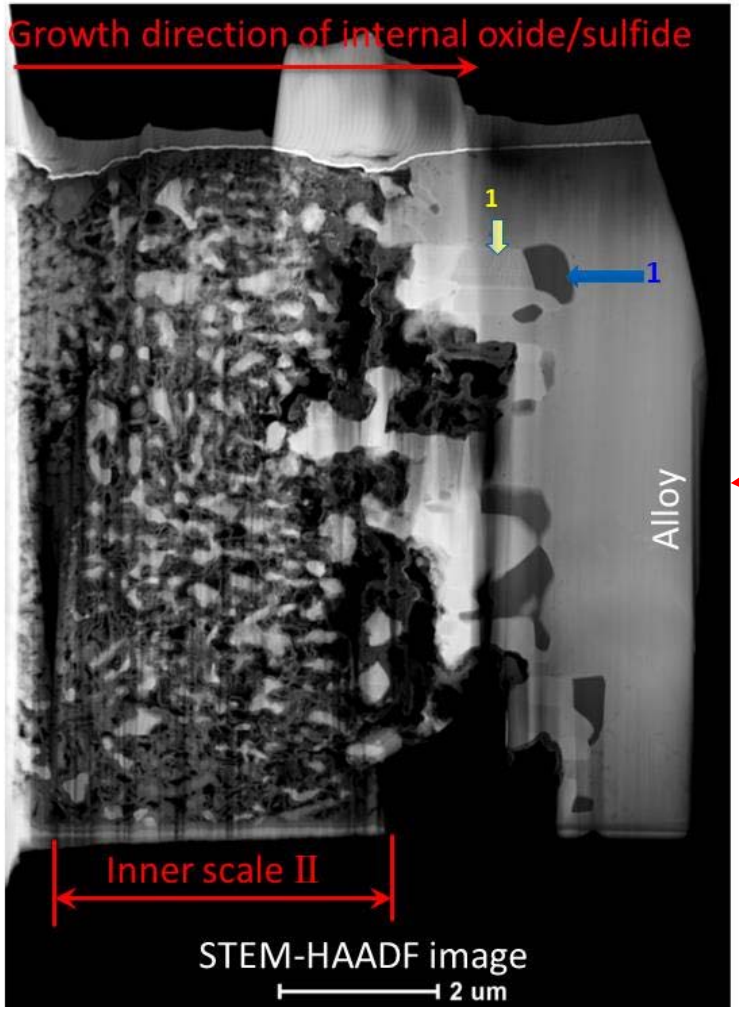
CO_2+8%N_2+20%H_2O+2.5%O_2+0.9%SO_2

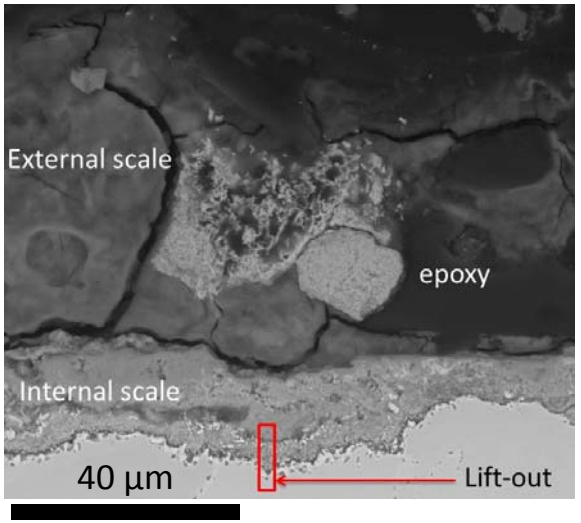


- **Internal sulfidation morphology**

Transmission Electron Microscopy (TEM) Analyses

IN617 oxy-fired: CO_2+8%N_2+**20%H_2O**+2.5%O_2+**0.9%SO_2** 700°C & 240 hr





at %	1	1
O(K)	5.86	25.73
S(K)	11.66	33.40
Cr(K)	0.13	40.74
Fe(K)	0.37	0.03
Co(K)	15.54	0.01
Ni(K)	44.35	0.05
Mo(K)	22.06	0

- Internal oxidation, sulfidation of Cr (blue).
- Alloy above internal sulfides are low in Cr (yellow).
- Rapid corrosion.

Conclusions: 700°C Oxy-combustion Corrosion

Overall

- Corrosion rates at 700°C did not change with flue gas composition (ash chemistry held constant)
- Substantial metal loss, linear with time

T91

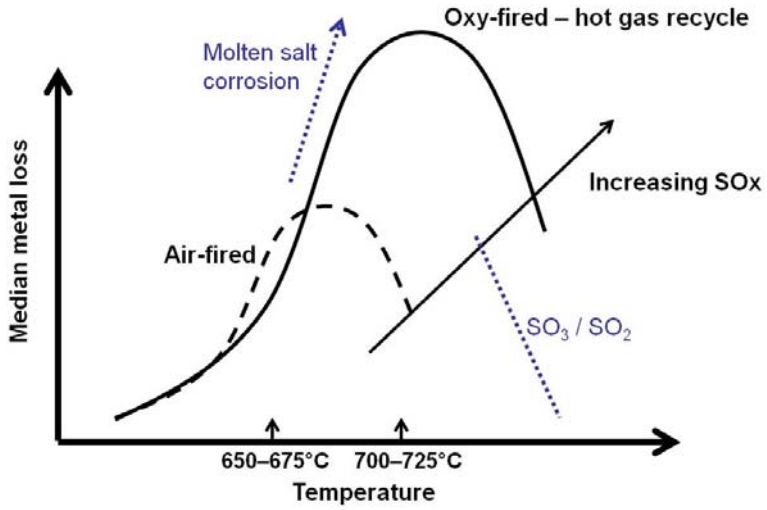
- Ash attachment, needle-shaped iron oxide growing into and infiltrating the ash

617

- Morphology change at high SO_2—more internal sulfidation of Cr
- Internal sulfidation leads to low Cr levels in the alloy between the internal sulfide and scale, which may lead to increased corrosion at longer times

New FY 14 Research Effort

- **Focus is on these items**
  - Examine reports of a shift upwards in the temperature of maximum corrosion for oxy-combustion conditions. Implications for A-USC steam boilers.
  - Use model alloys to examine the effect of Mo in Ni-Cr alloys. Several A-USC Ni-base alloys of interest contain up to 8-10% Mo.
  - Compare NETL's CPJ7B to T92
  - Look at sulfate flux as a variable in the ash as a tool to address oxy-combustion ash changes
- **Ni-base alloys**
  - Model alloys Ni-22Cr, Ni-22Cr-1Mo and Ni-22Cr-8Mo
  - Commercial A-USC alloy 740H
- **9Cr Ferritic/Martensitic Steels**
  - T92 and CPJ7B
- **Gas Compositions**
  - Air-firing: N_2-14CO_2-9H_2O-2.5O_2-0.3SO_2
  - Oxy-firing: CO_2-8N_2-20H_2O-2.5O_2-0.9SO_2 (hot gas recycle case)
- **Temperatures**
  - 650, 675, 700, 725, 750, 775, 800°C



N. Simms, T. Hussain and A. Syed (2012.)

Additional Test Details

- **Ash Composition (see table)**
  - Maintain 3:1 ratio of $(Na,K)_2SO_4$:Fe_2O_3 as found in lowest melting point alkali iron trisulfates
  - S20 closest to prior ash composition (30 Al_2O_3 30 SiO_2 30 Fe_2O_3 5 Na_2SO_4 5 K_2SO_4)
- **Special Ash-Retained Samples after 24hr of Exposure**

ID	Al_2O_3	SiO_2	Fe_2O_3	Na_2SO_4	K_2SO_4
SCM	0	0	25	37.5	37.5
S80	10	10	20	30	30
S60	20	20	15	22.5	22.5
S40	30	30	10	15	15
S20	40	40	5	7.5	7.5

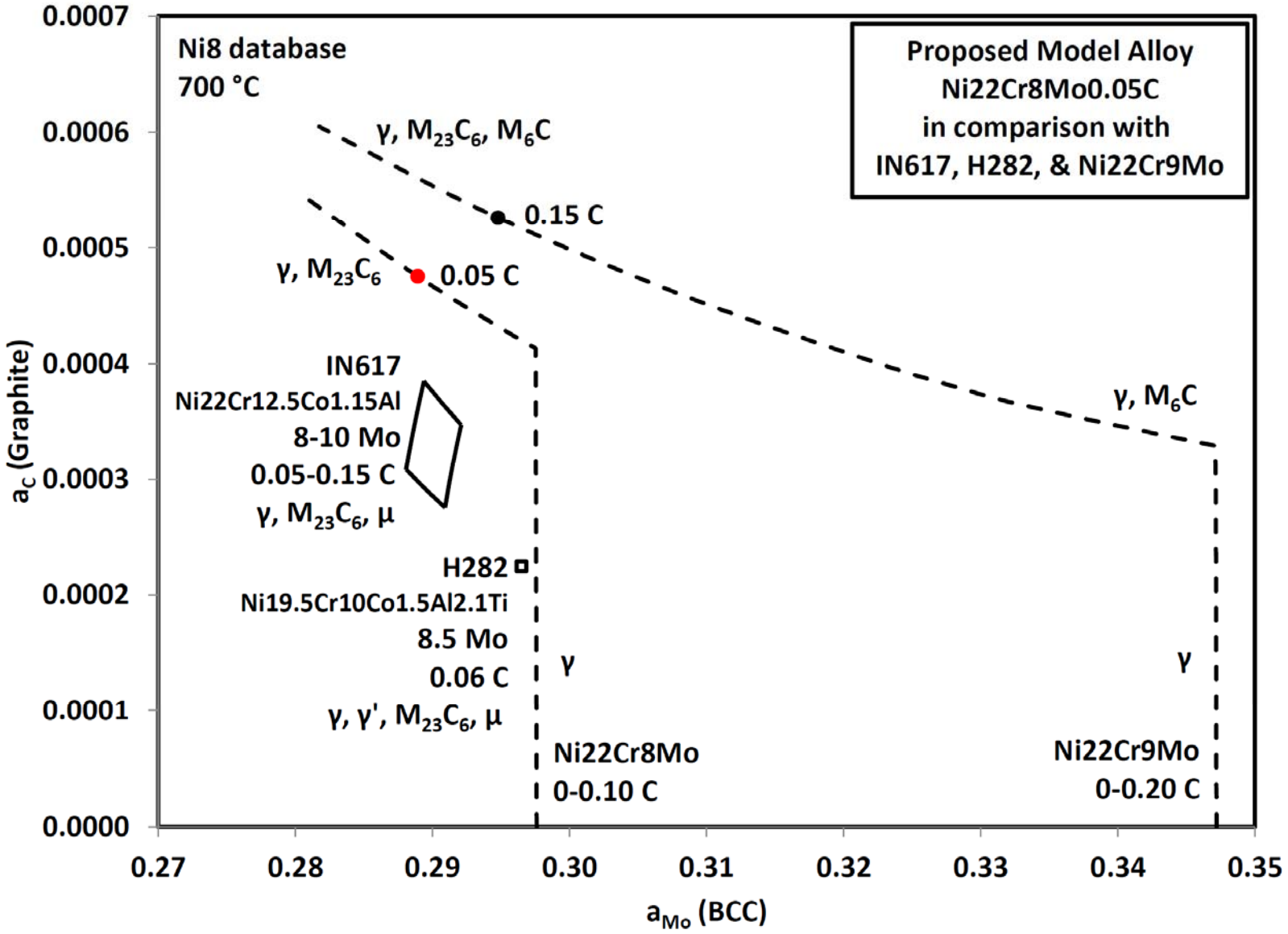
Effect of Mo in Ni-Cr Alloys

- **Hot Corrosion Research, focused primarily on turbine applications, reports severe degradation with Mo in Ni-base superalloys**
  - MoO_2 reacted with Na_2SO_4 to produce an acid (SO_2-rich) salt, leading to acidic fluxing, Pettit and Meier (1985)
  - MoO_3 incorporated into Na_2SO_4 by the formation of compounds such as Na_2MoO_4, $Na_2MoO_4 \cdot MoO_3$, and $Na_2MoO_4 \cdot 2MoO_4$ can be liquid and have a high solubility for Cr_2O_3, Fyrburg et al (1982)
  - A reported threshold for Mo below which catastrophic attack is not encountered. For Ni-15% Cr at 900°C the threshold was between 3-4% Mo, Peters et al (1976)
- **Mo is significant in many Ni-base A-USC superalloys:**

Significant Mo	Modest Mo
263: Ni 20.0Cr 6.0Mo	230: 22.0Cr 2.0Mo
282: Ni 19.5Cr 8.5Mo	740: 25.0Cr 0.5Mo
617: Ni 22.0Cr 9.0Mo	
625: Ni 21.5Cr 9.0Mo	

- **Model Ni-22Cr-XMo alloys will be used to assess corrosion initiation and propagation as a function of Mo. 15 lb heats of each were made by Paul Jablonski.**

Ni-22Cr-8Mo-0.05C Model Alloy



Alloys Tested—Alloys Compositions (wt%)

FY14

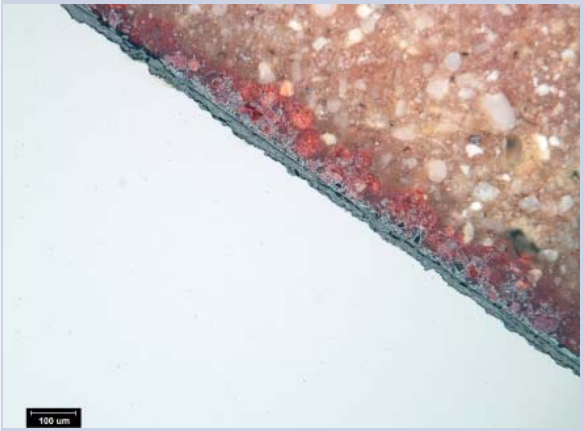
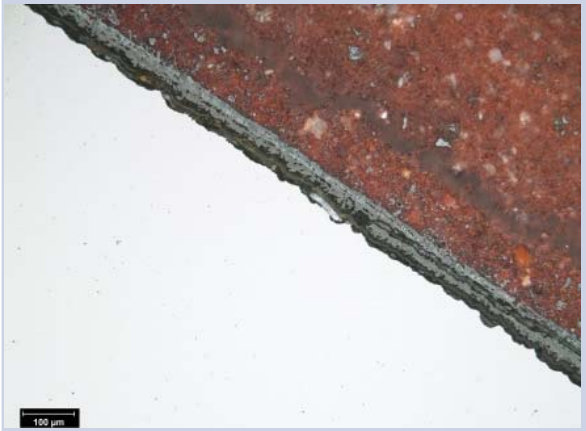
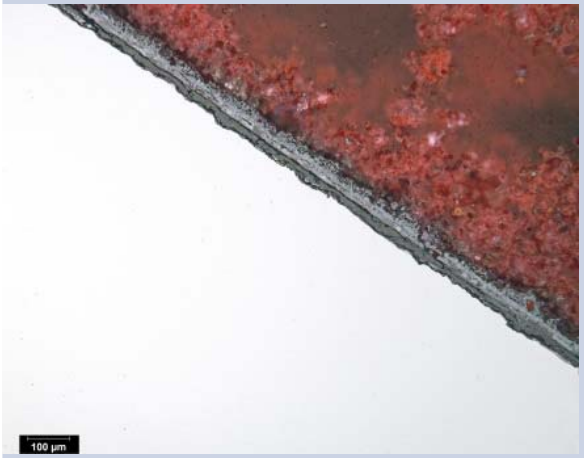
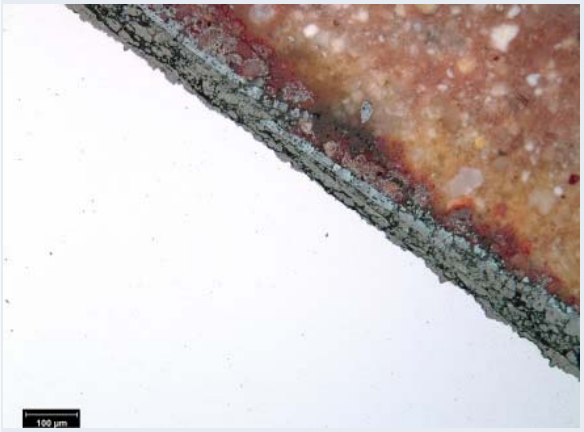
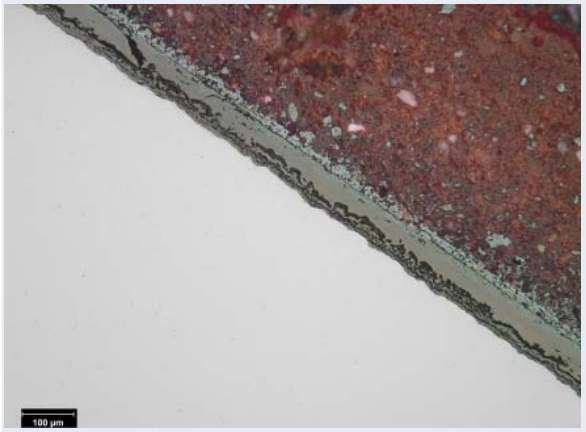
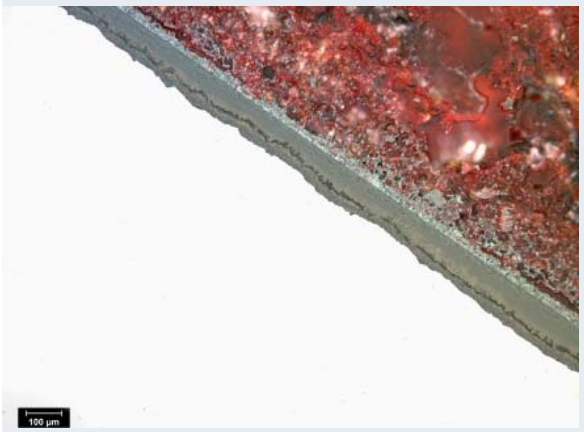
Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Ti	Al	Mn	V	Nb+Ta	Cu	Other
T92	Bal	9.08	0.25	0.01	0.45	0.081	0.09		0.01	0.40	0.21	0.07		1.80 W
CPJ7B In Dev	Bal	9												
740H Nominal	0.7	25	Bal	20	0.5		0.15	1.35	1.35	0.3		1.5		
Ni22Cr 0Mo		22.18	Bal		0.02	0.043		0.01	0.08			0.01	0.01	11 ppm S
Ni22Cr 1Mo		22.04	Bal		0.99	0.050			0.07			0.02	0.01	4 ppm S
Ni22Cr 8Mo		22.04	Bal		7.77	0.052			0.07			0.01		11 ppm S

Met target Cr, Mo, and C levels in Ni-22Cr-xMo model alloys
Low S levels obtained

Preliminary Results

- **Light microscopy images from ash-retained 24hr tests**
  - Iron oxide fluxing evident in T92
  - Effect of Mo on corrosion initiation

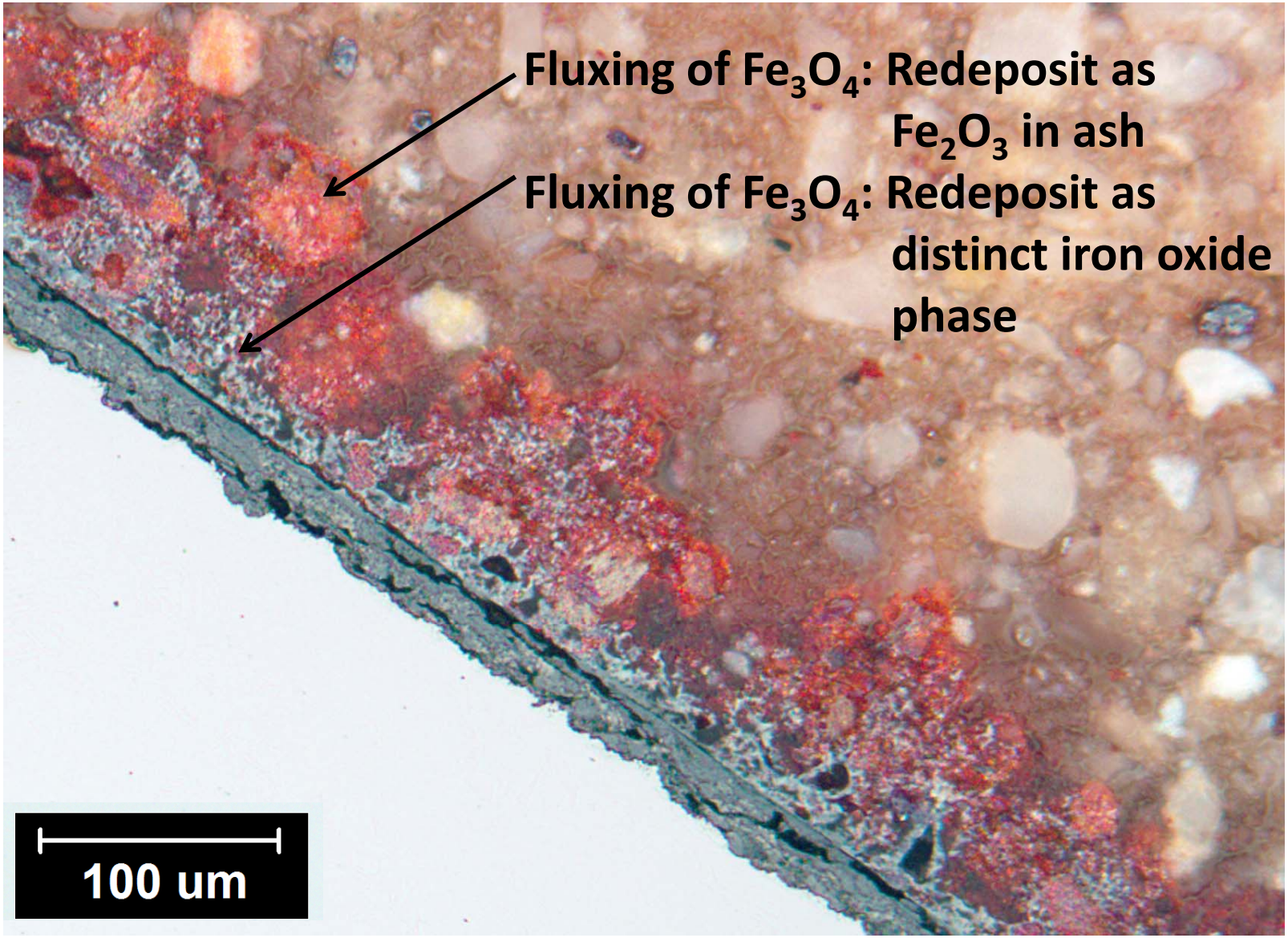
24 hr Ash-Retained Tests – T92 at 700°C

	20% alkali iron trisulfate	80% alkali iron trisulfate	100% alkali iron trisulfate
Air-fired (0.3% SO_2)			
Oxy-fired (0.9% SO_2)			

Little effect from Ash Content on Scale Thickness

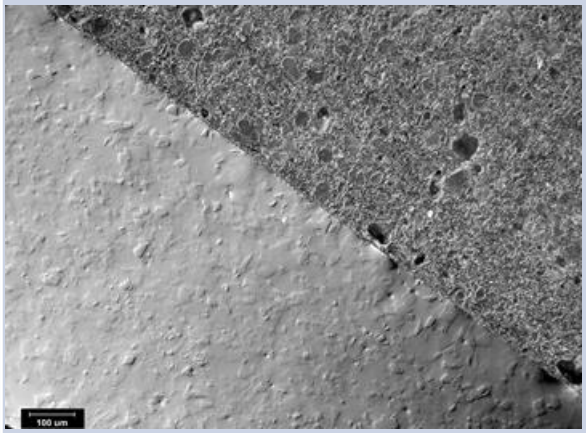
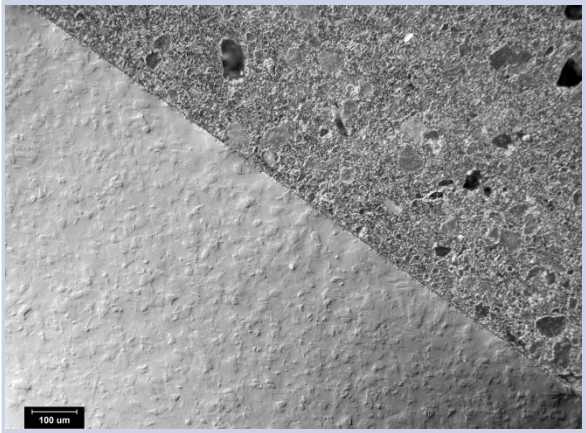
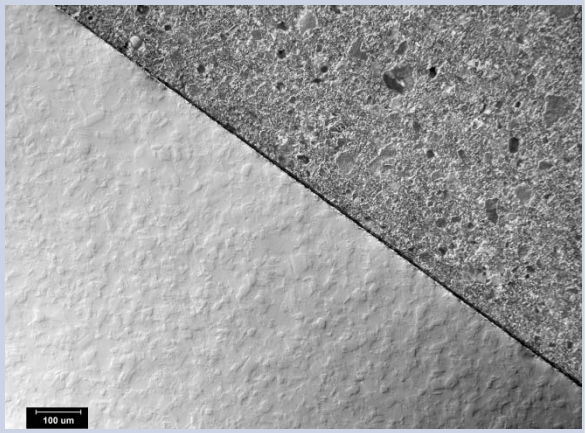
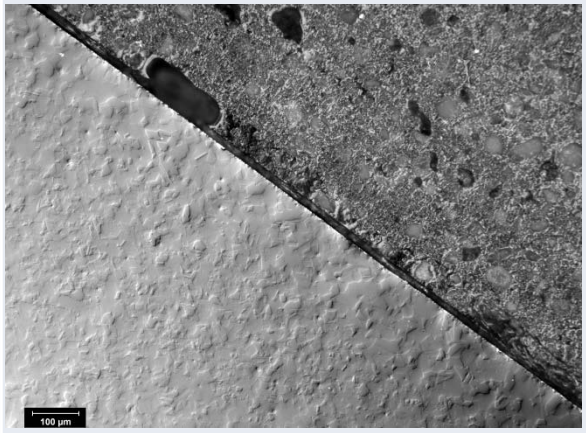
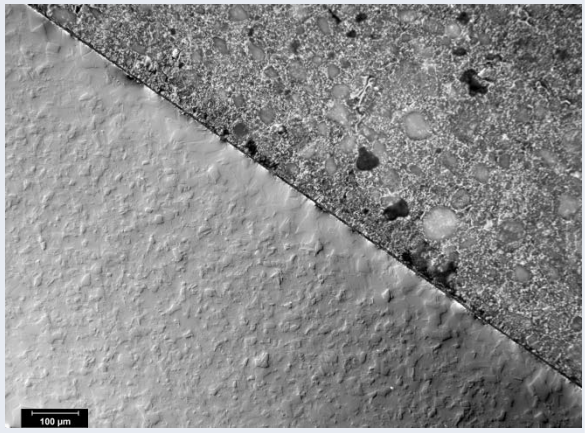
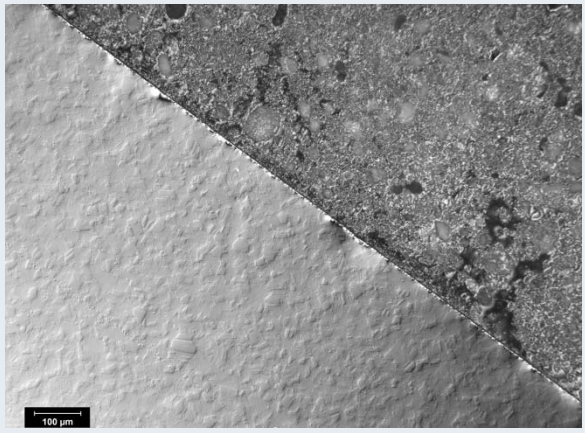
Some effect from Gas Phase (SO_X, H_2O, CO_2) on Scale Thickness

24 hr Air-Fired Exposure of T92 at 700°C with a 20% alkali iron trisulfate ash



Effect of Mo

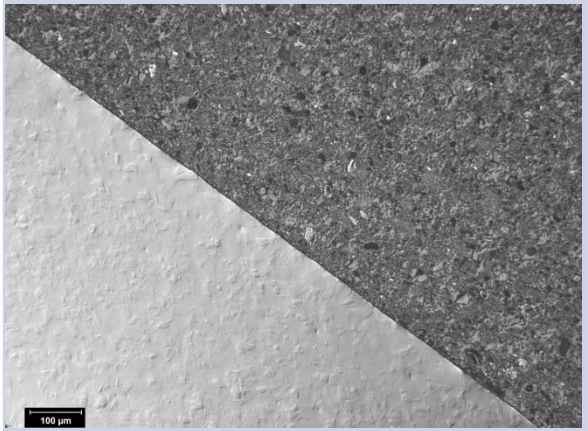
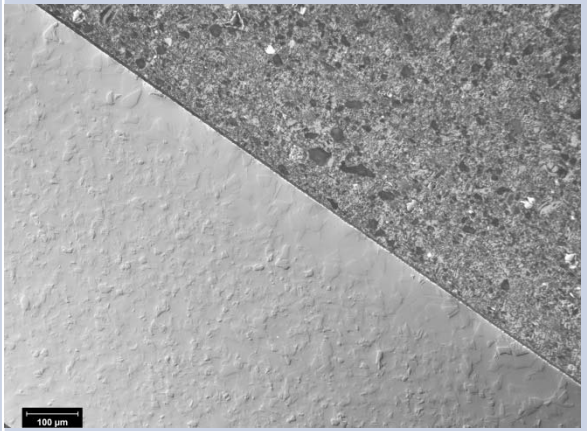
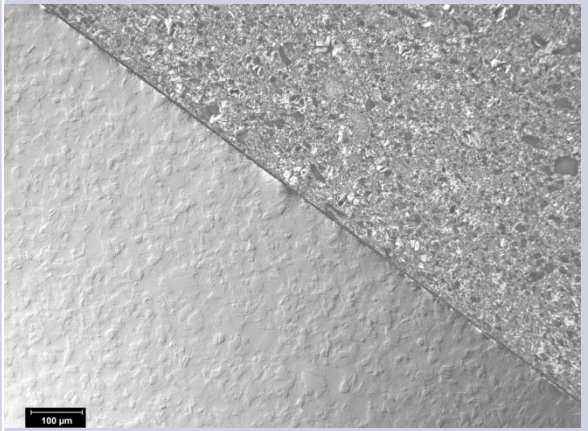
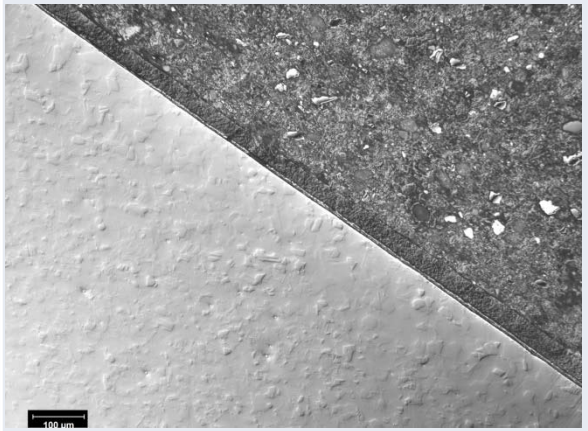
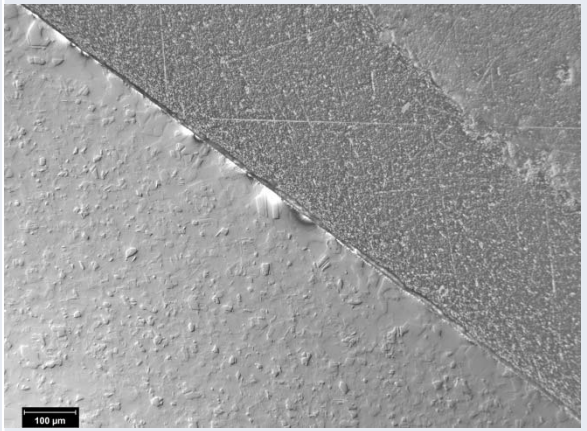
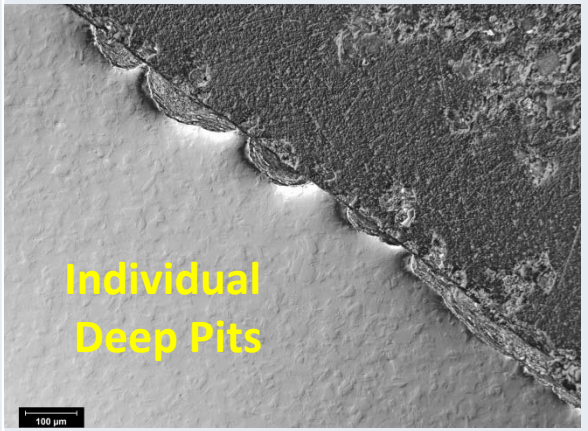
24 hr Exposure at 700°C with a 20% alkali iron trisulfate ash

	Ni 22Cr 0Mo	Ni 22Cr 1Mo	Ni 22Cr 8Mo
Air-Fired (0.3% SO_2)			
Oxy-Fired (0.9% SO_2)			

No effect from Mo or Gas Phase (SO_X, H_2O, CO_2) with a 20% alkali iron trisulfate ash

Effect of Mo

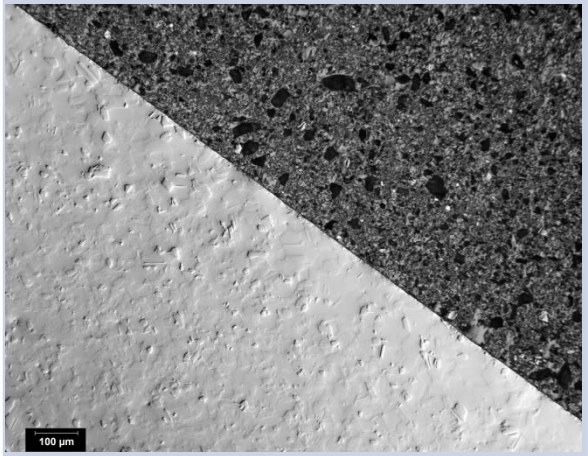
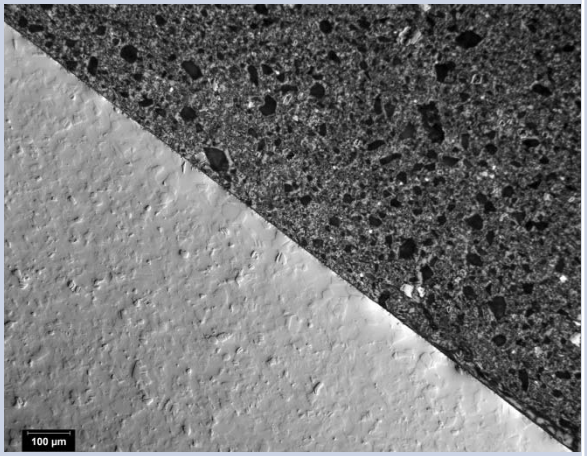
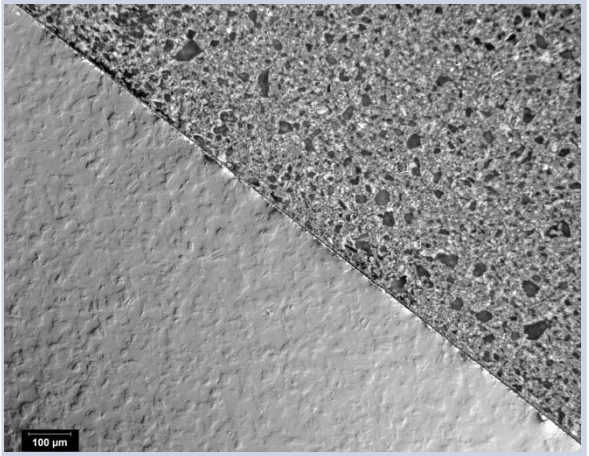
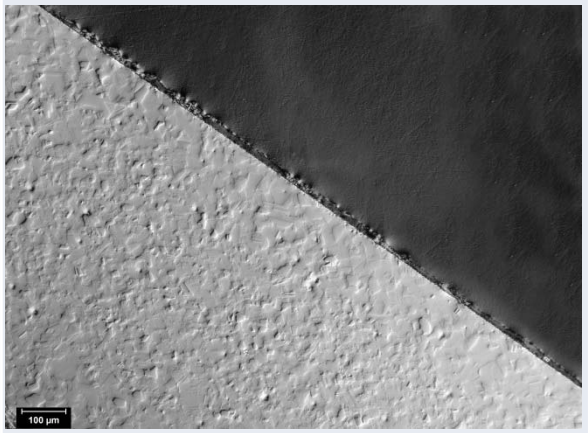
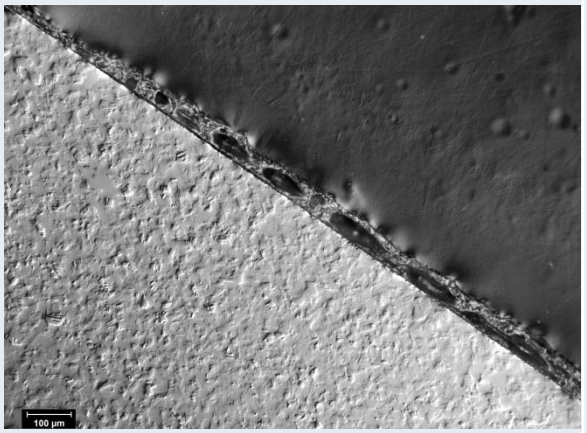
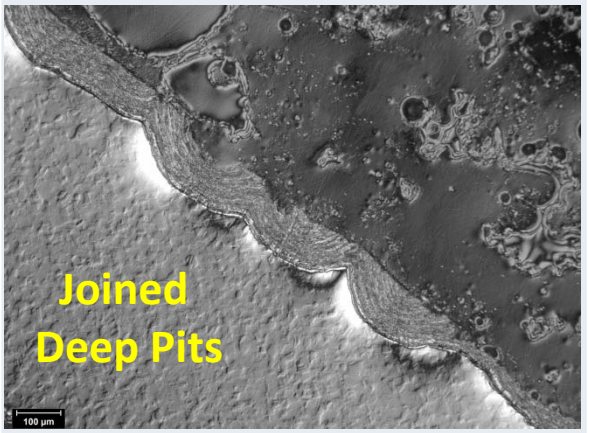
24 hr Exposure at 700°C with an 80% alkali iron trisulfate ash

	Ni 22Cr 0Mo	Ni 22Cr 1Mo	Ni 22Cr 8Mo
Air-Fired (0.3% SO_2)			
Oxy-Fired (0.9% SO_2)			

Large effect from 8 Mo and Gas Phase (SO_X, H_2O, CO_2) with an 80% alkali iron trisulfate ash

Effect of Mo

24 hr Exposure at 700°C with a 100% alkali iron trisulfate ash

	Ni 22Cr 0Mo	Ni 22Cr 1Mo	Ni 22Cr 8Mo
Air-Fired (0.3% SO_2)			
Oxy-Fired (0.9% SO_2)			

Large effect from 8 Mo and Gas Phase (SO_X, H_2O, CO_2) with a 100% alkali iron trisulfate ash

Summary of New FY14 Oxy-Combustion Fireside Corrosion Research

Aims

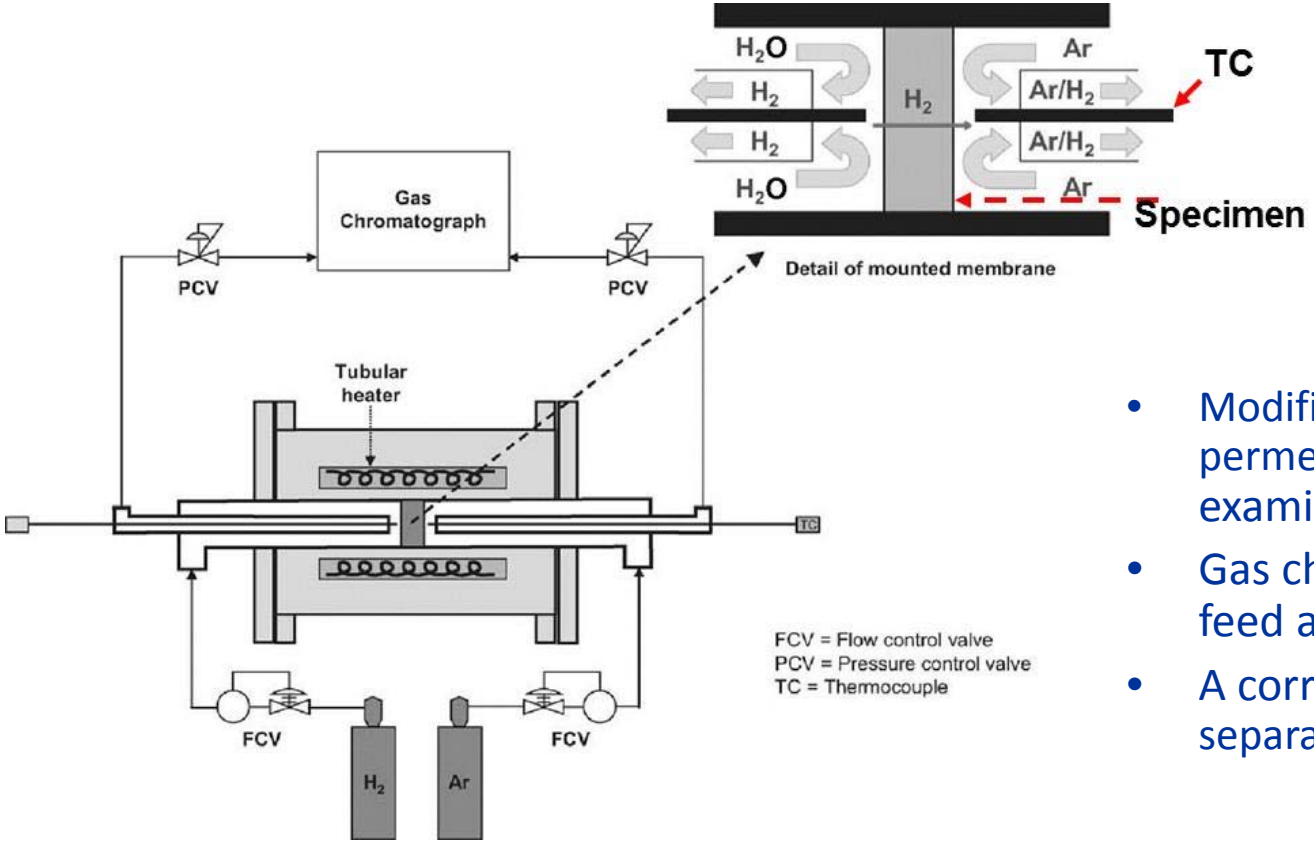
- Temperature effects
- Mo effects with Ni22CrXMo Alloys
- Compare NETL's CPJ7B to T92
- Sulfate flux

Progress

- Fluxing of Fe_3O_4 found for T92 in ash
- Early corrosion initiation with 8Mo in Ni22CrXMo alloys with high sulfate ash levels when combined with high SO_X gases

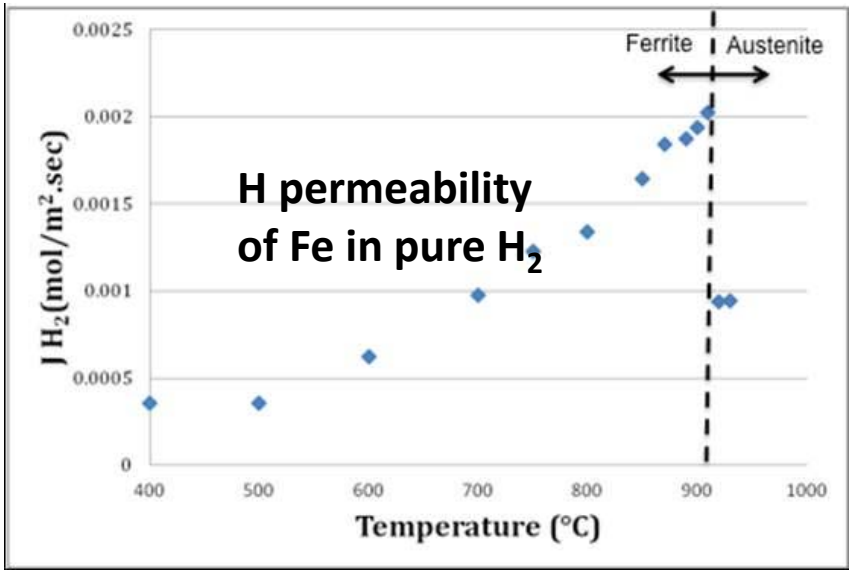
Hydrogen Tracking During Oxidation

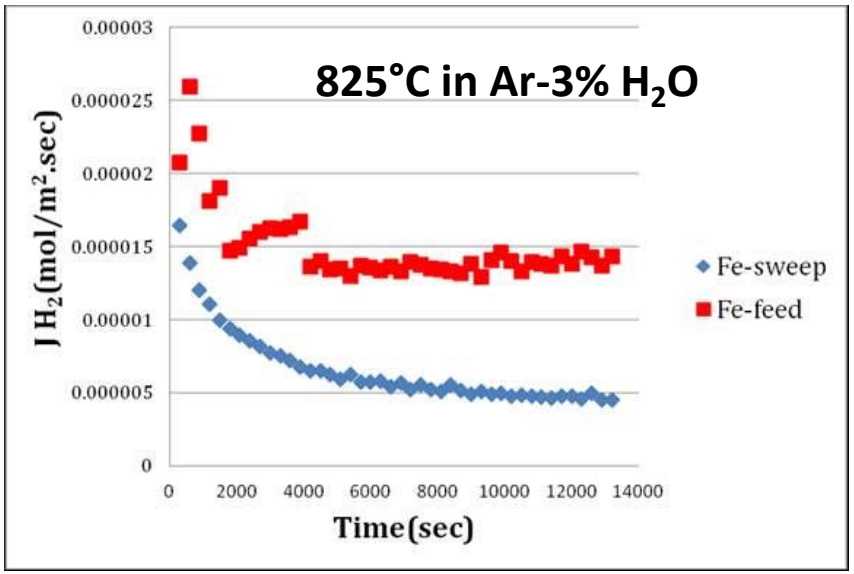
- SH/RH boiler corrosion occurs in a mixed oxidant atmosphere (O_2, CO_2, H_2O, SO_2)
- Oxyfuel combustion changes the amounts and ratios of oxidants
- This research examines, in a more fundamental nature, the influence of individual oxidants in mixed oxidant gases, and the transport path of hydrogen when it is a product of water oxidation



- Modification of a hydrogen permeability apparatus to examine corrosion
- Gas chromatography (GC) of feed and sweep gases
- A corrosion sample foil separates the two gas streams

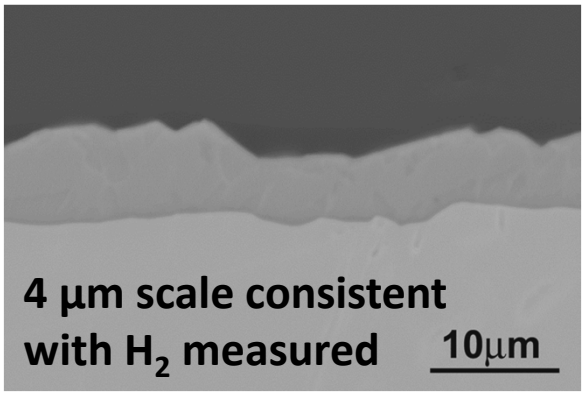
Results for Fe in Ar-3%H_2O



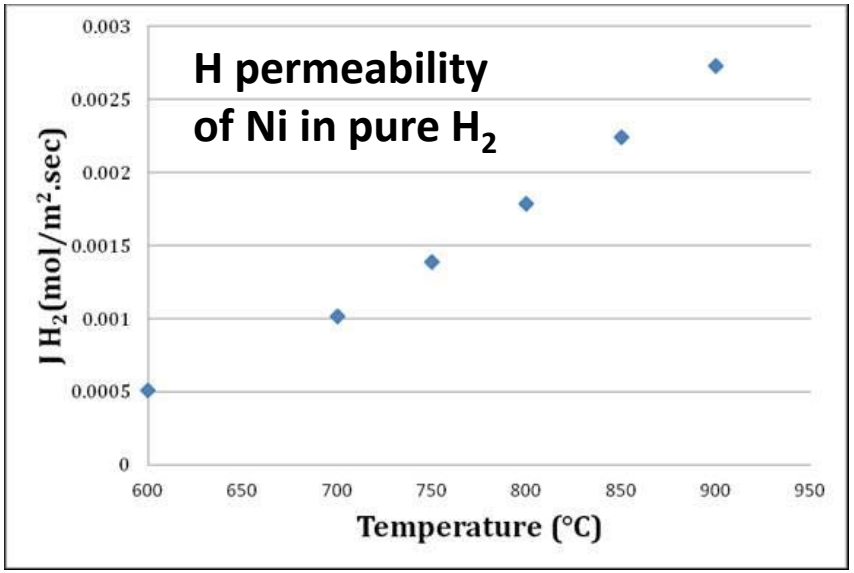


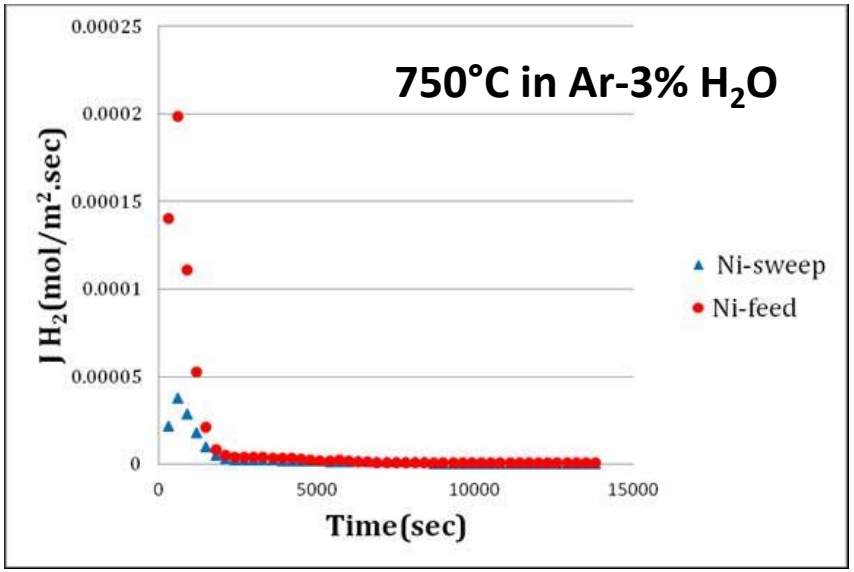
After initial rapid scale growth at 825°C:

- ~25% of H_2 is injected into and through the metal
- ~75% of H_2 is desorbed back into the feed gas
- Tomlinson and Cory (1989) found the fraction of injected H decreased with increased T
- Short term exposures of Fe at these temperatures in H_2O have linear kinetics and are surface reaction controlled (Turkdogan 1965).
- Estimated fugacities at the Fe/FeO interface using Sievert's law and H permeability data (825°C):
  - H_2 1 ×10^{-5} atm
  - O_2 4 ×10^{-19} atm
  - H_2O 5 ×10^{-6} atm



Results for Ni in Ar-3%H_2O



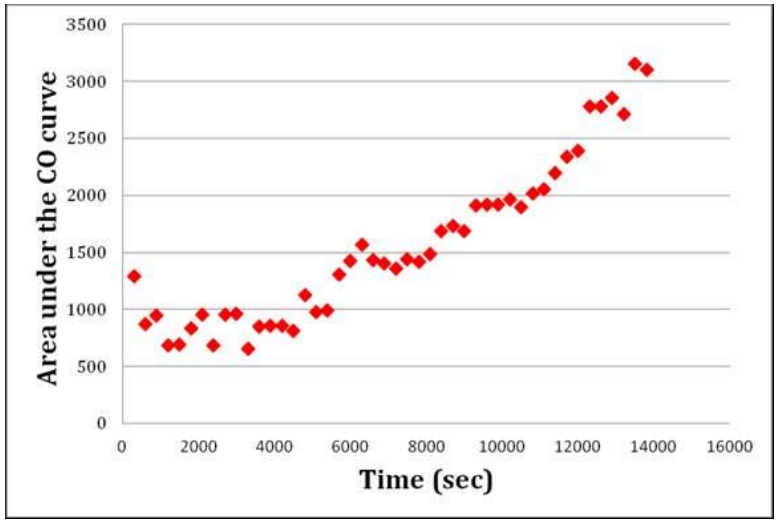


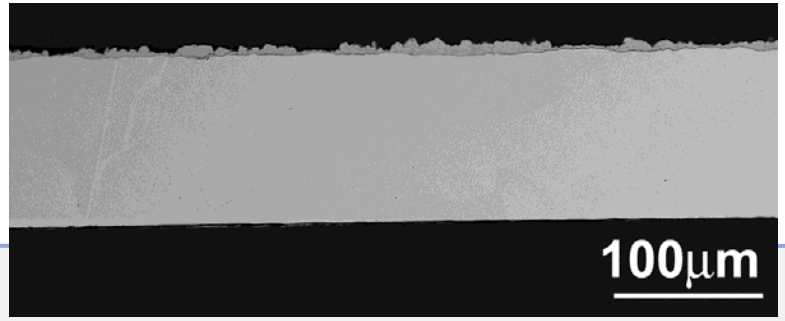
- After initially high fluxes, the feed and sweep H_2 levels become quite low
- Estimated fugacities at the Ni/NiO interface using Sievert's law and H permeability data:
  - H_2 7 ×10^{-8} atm
  - O_2 8 ×10^{-16} atm
  - H_2O 1 ×10^{-5} atm

Results for Fe at 750°C in Ar-CO_2-H_2O

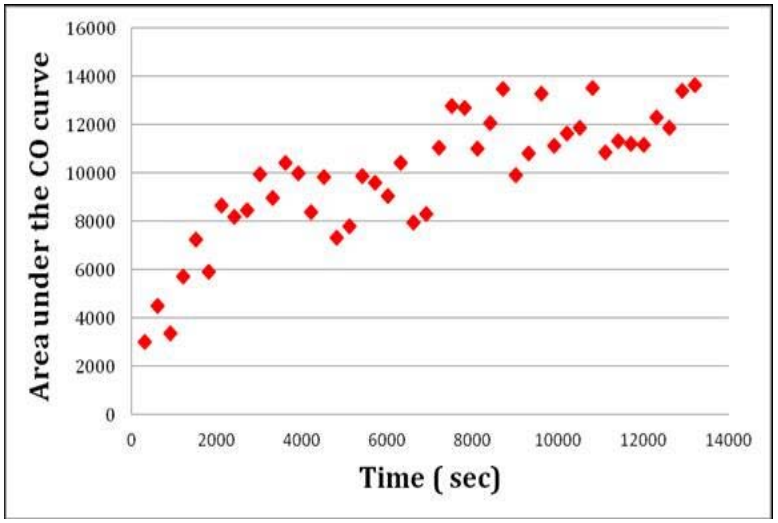
- Unlike in Ar-H_2O, these rates continue to increase with time
- Much more oxidation in CO_2 with H_2O than without H_2O
- Sweep and feed gases also contain H_2
- In these short exposures, both H_2O and CO_2 are adsorbing and contributing to the surface reactions, which control the rate of scale growth.

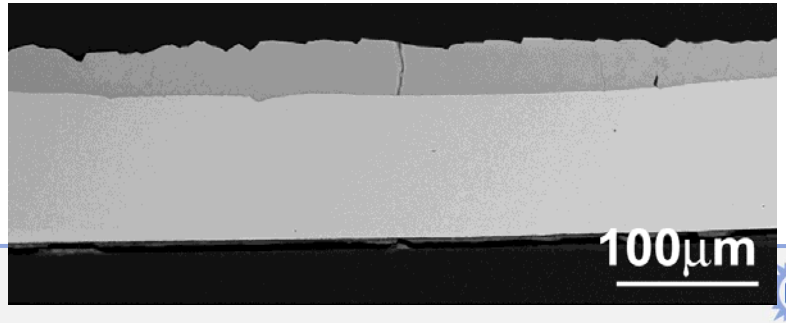
CO Flux in at 750°C in Ar-10%CO_2





CO Flux in at 750°C in Ar-10%CO_2-3%H_2O





Summary of Hydrogen Tracking During Oxidation

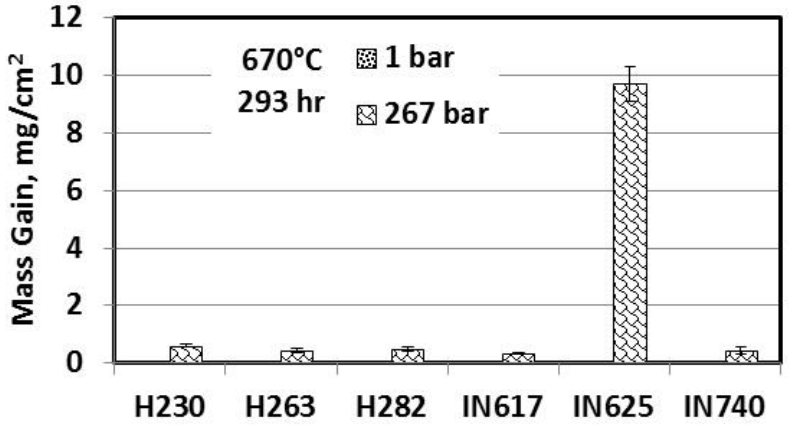
Oxidation in Ar-H_2O

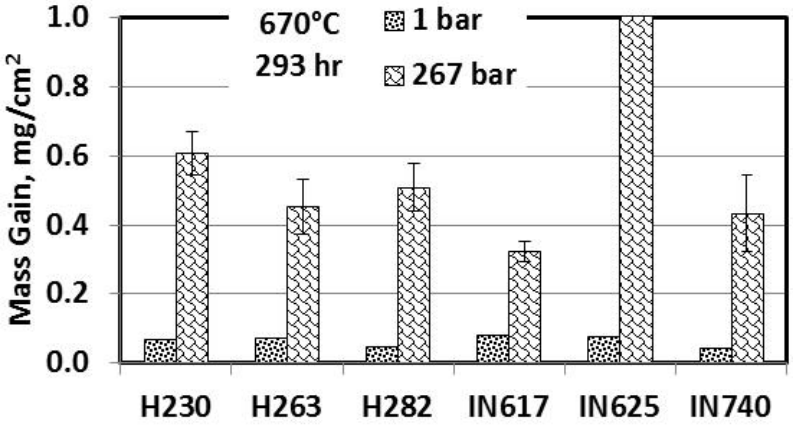
- For Fe, significant hydrogen permeates through.
- Of the H_2 generated, 25% permeated through the foil.
- For Ni, the hydrogen flux drops to very low levels as NiO forms on the surface.
- Activities of H_2, O_2, and H_2O were able to be calculated at the metal-scale interface.

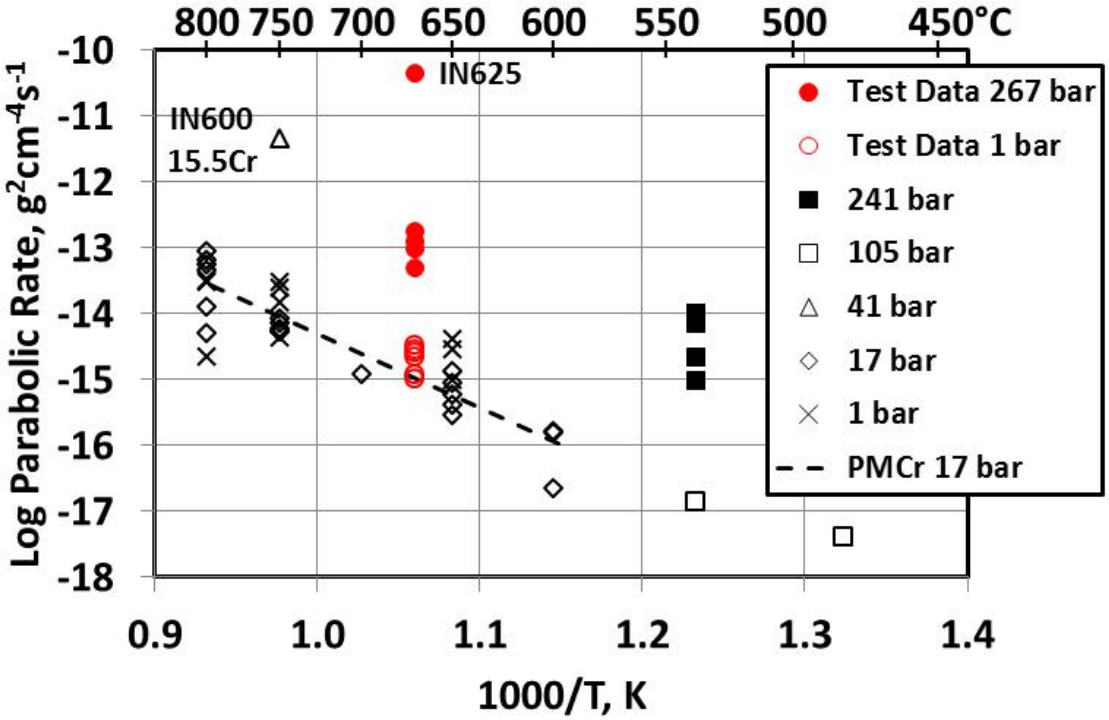
Oxidation in Ar-CO_2 and Ar-CO_2-H_2O

- Oxidation was accelerated in the presence of both CO_2 and H_2O.
- In Ar-CO_2-H_2O, both CO and H_2 were observed in the feed gas.
- Both H_2O and CO_2 absorb and contribute to the surface reactions, which control scale growth.

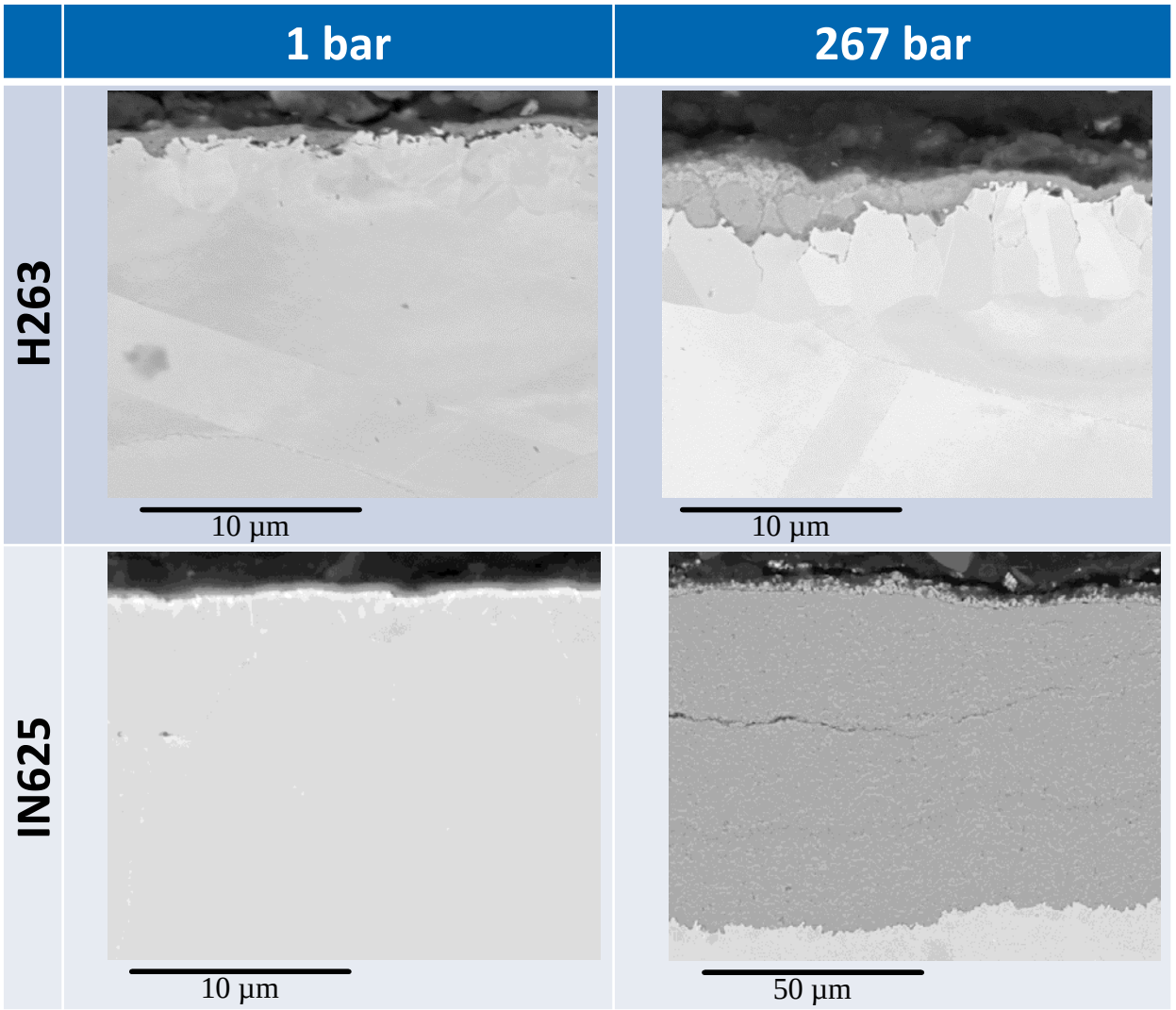
Update on Steam Oxidation at High Pressure







- Increase in oxidation with pressure
- For all but IN625 the scales are thicker but still high in chromia
- IN625 has much thicker scale, with metal ratios close to that of the alloy



Selected for TEM Analysis

- Why does higher pressure increase corrosion?
- What is going on with IN625?
- IN625 has high Mo precipitates near the surface, not found for other alloys

Compositions of alloys (wt%) measured by x-ray fluorescence

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Nb	Cu
H263		20.0	Bal	20.1	5.7	0.3	2.1	0.3	0.5	0.1	
IN625	4.4	21.4	Bal	0.1	8.4	0.3	0.3	0.2	0.1	3.3	0.3