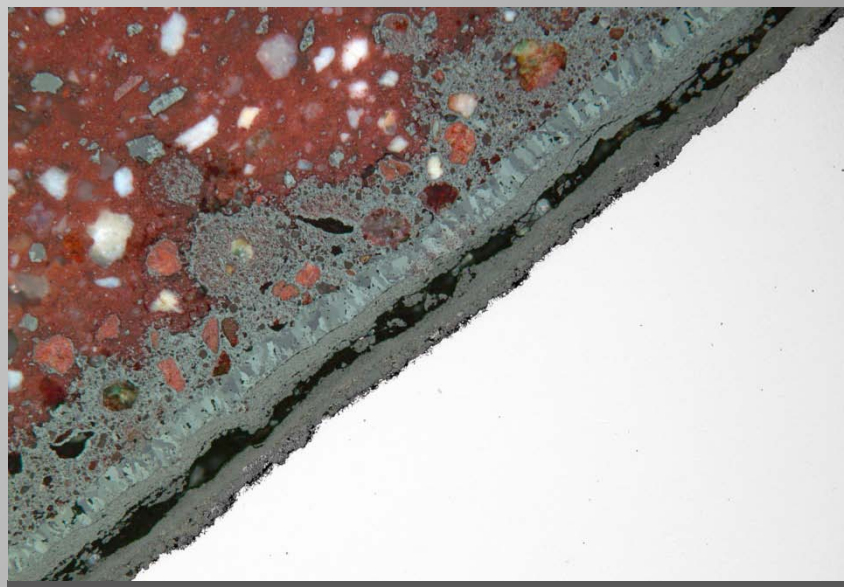
June 19, 2013

Oxy-Combustion Environmental Characterization: Fire- and Steam-Side Corrosion in Advanced Combustion

Gordon R. Holcomb, NETL

Gerald H. Meier & Bradley S. Lutz, University of Pittsburgh



the **ENERGY** lab

U.S. DEPARTMENT OF ENERGY

Acknowledgements

- Funding from the Strategic Center for Coal, Advanced Energy Systems, Advanced Combustion
- Scott Smouse, NETL Technology Manager, Advanced Combustion

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Advanced Combustion Tasks

FY12 SCC Program Guidance	Advanced Combustion Project Tasks
Advanced Combustion	1. Project Management
	2. Oxy-Combustion Environment Characterization 2.1 Steamside Oxidation 2.2 Fireside Corrosion 2.3 Development of New Capabilities
	4. Alloy Manufacturing and Process Development

2.1 Steamside Oxidation

- **Conduct Steam Oxidation Tests (NETL)**
- Perform Transmission Electron Microscopy Analyses of Selected Steam Oxidation Test Specimens (CMU)
- Conduct Atmospheric Steam Oxidation Tests on T92 (NETL)
- Conduct Scale Adhesion Tests in Steam (NETL)

2.2 Fireside Corrosion

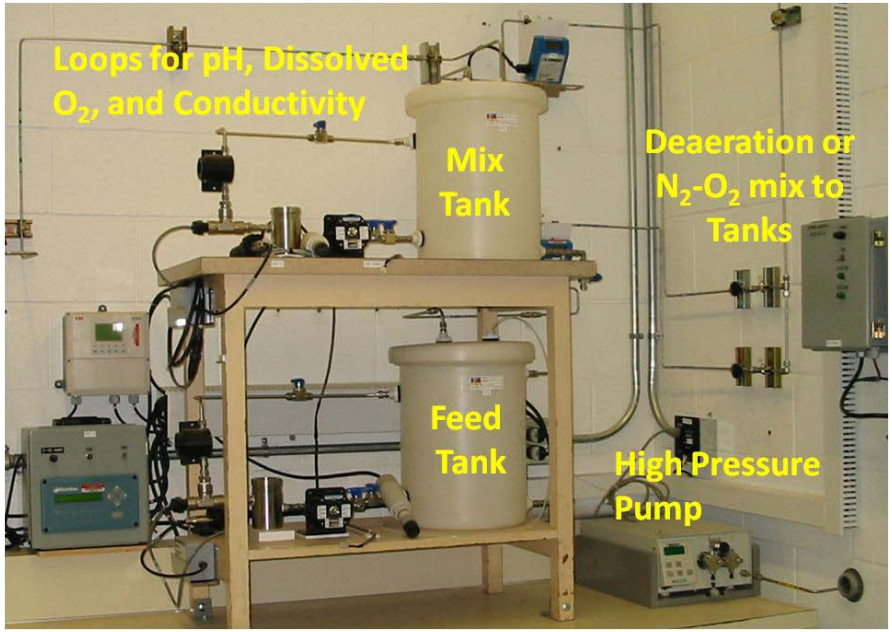
- Conduct and Analyze Long-term Laboratory Fireside Corrosion Tests (NETL)
- **Conduct and Analyze Short-term Laboratory Fireside Corrosion Tests (Pitt)**
- Perform Transmission Electron Microscopy Analyses of Selected Fireside Test Specimens (CMU)
- Conduct Mixed Oxidant Exposure Tests Measuring Hydrogen Permeability (Pitt)
- Conduct Low Temperature Corrosion Tests Simulating Post Economizer Environments (NETL)
- Conduct Tests on Thermal Barrier Coating Protected Alloys (NETL)

Conduct Steam Oxidation Tests (NETL)

- **First High Pressure Steam Autoclave Test Completed**
  - Ran for 293 hr at 3874 psi (267 bar) and 670 C.
  - 27 Samples (9 alloys with triplicate samples):
    - Ferritic Steels T22 and T91; Austenitic Steel TP304H
    - Ni-base Alloys H230, H263, H282, IN617, IN625, and IN740
  - Parallel test at 1 bar for direct comparison.
- **Experimental Issues**
  - Inconsistent high pressure pump:
    - Required re-priming during test with a interruption of P, but not T.
    - The pump started to leak, which terminated the test prior to the desired 500 hr.
    - New filters and cleaner type I water seems to have solved the problem. Will monitor.
  - Heater failure: Custom heater assembly on order.

USC Autoclave

Feed Water Prep & High Pressure Pump

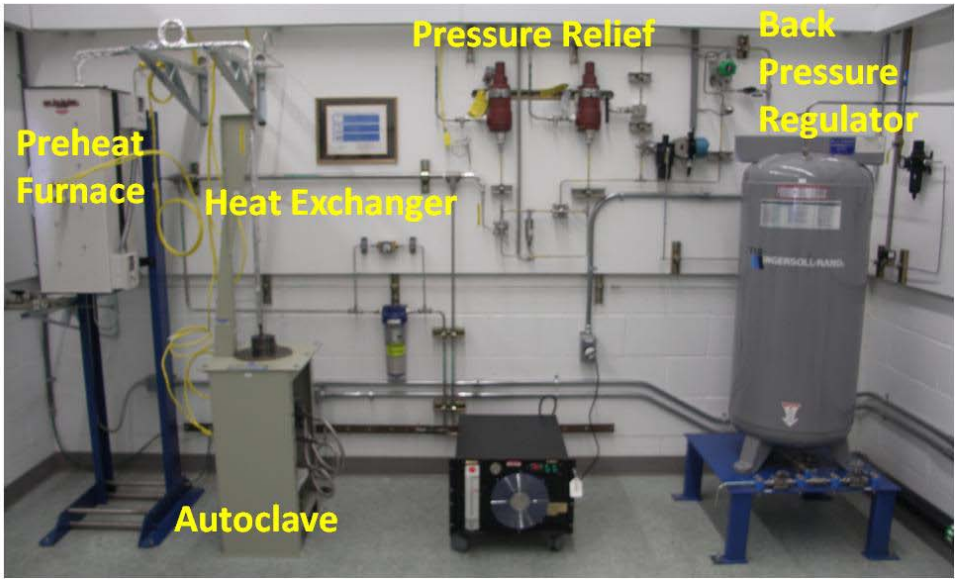


Flow Rate Controlled by Pump

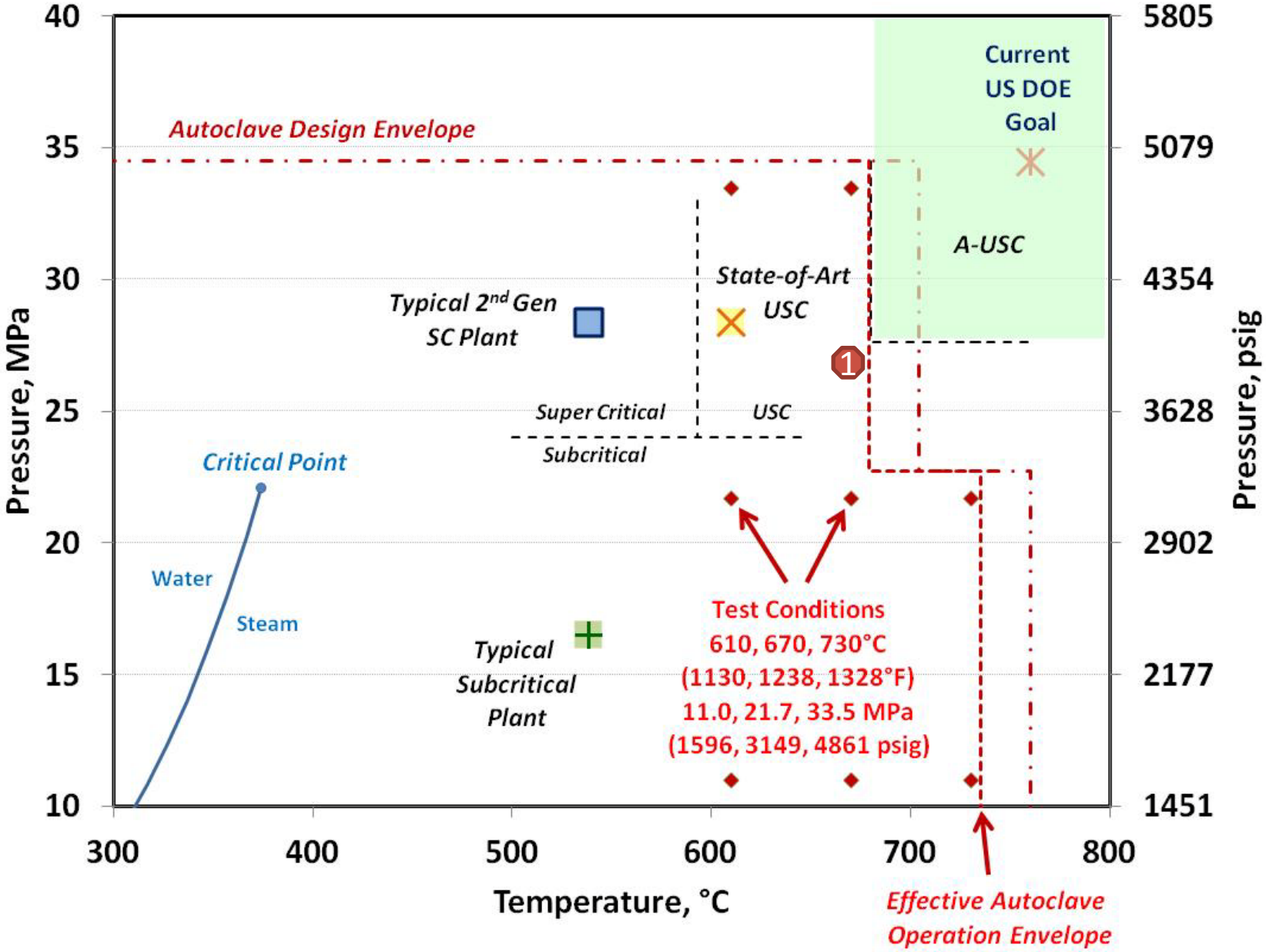
Pressure Controlled by Back Pressure Regulator

Autoclave

High Pressure Side



NETL Autoclave Temperature & Pressure Envelope



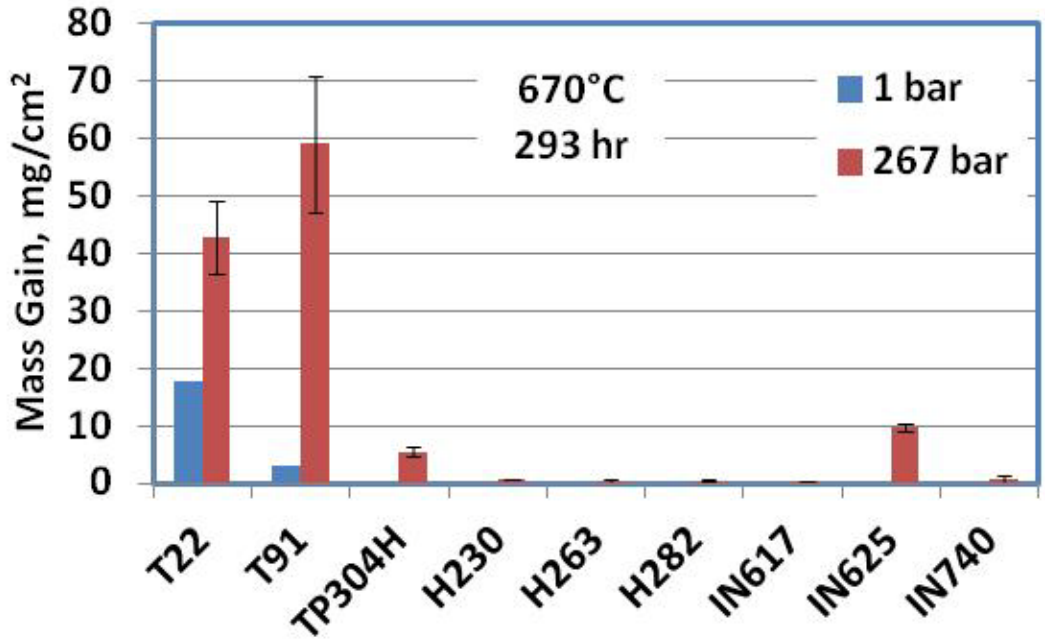
USC Steam Oxidation Alloys Nominal Compositions, wt%

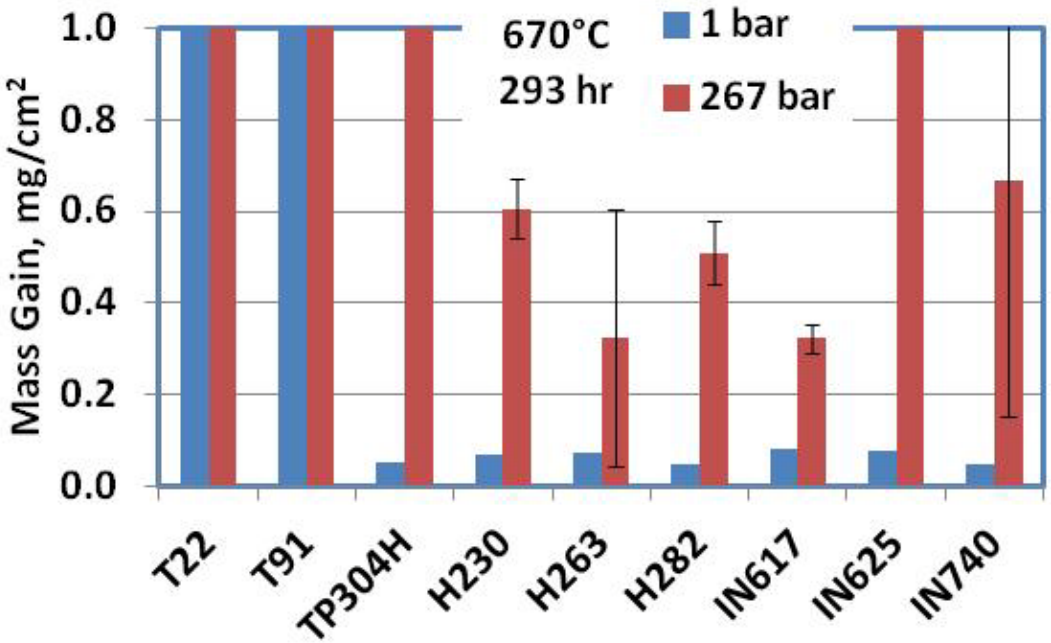
Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Ti	Al	B ppm	Mn	Nb	Other
T22	Bal	2.25			1.0	0.12	0.3				0.45		
T91	Bal	9.0	0.8		1.0	0.10	0.4				0.45	0.08	0.20 V 0.05 N
TP304H	Bal	18.0	8.0			0.08	0.6				1.60		
H230	1.5	22.0	Bal	2.5	2.0	0.10	0.4		0.3	75	0.50		14 W 0.02 La
H263	0.35	20.0	Bal	20.0	6.0	0.03	0.2	1.2	0.3		0.30		
H282	0.75	19.5	Bal	10.0	8.5	0.06	0.075	2.1	1.5	50			0.15 Cu
IN617	1.5	22.0	Bal	12.5	9.0	0.10	0.5	0.3	1.15	30	0.50		0.25 Cu
IN625	2.5	21.5	Bal	0.5	9.0	0.05	0.25	0.2	0.2		0.25	3.65	
IN740	0.7	25.0	Bal	20.0	0.5	0.03	0.5	1.8	0.9		0.30	2.0	

Source values that were ranges are listed as the midpoint of the range. Source values that were maximums are listed as half the maximum. Only Nb is listed for sources that gave a value or range for Nb+Ta. Values for Pb, P, and S are omitted. For economic reasons it is not unusual for actual chemical compositions of materials delivered for use in power plants to be near the lower end of the specification. For some alloys (such as the 9Cr ferritic steels) the oxidation behavior significantly change over the specification range.

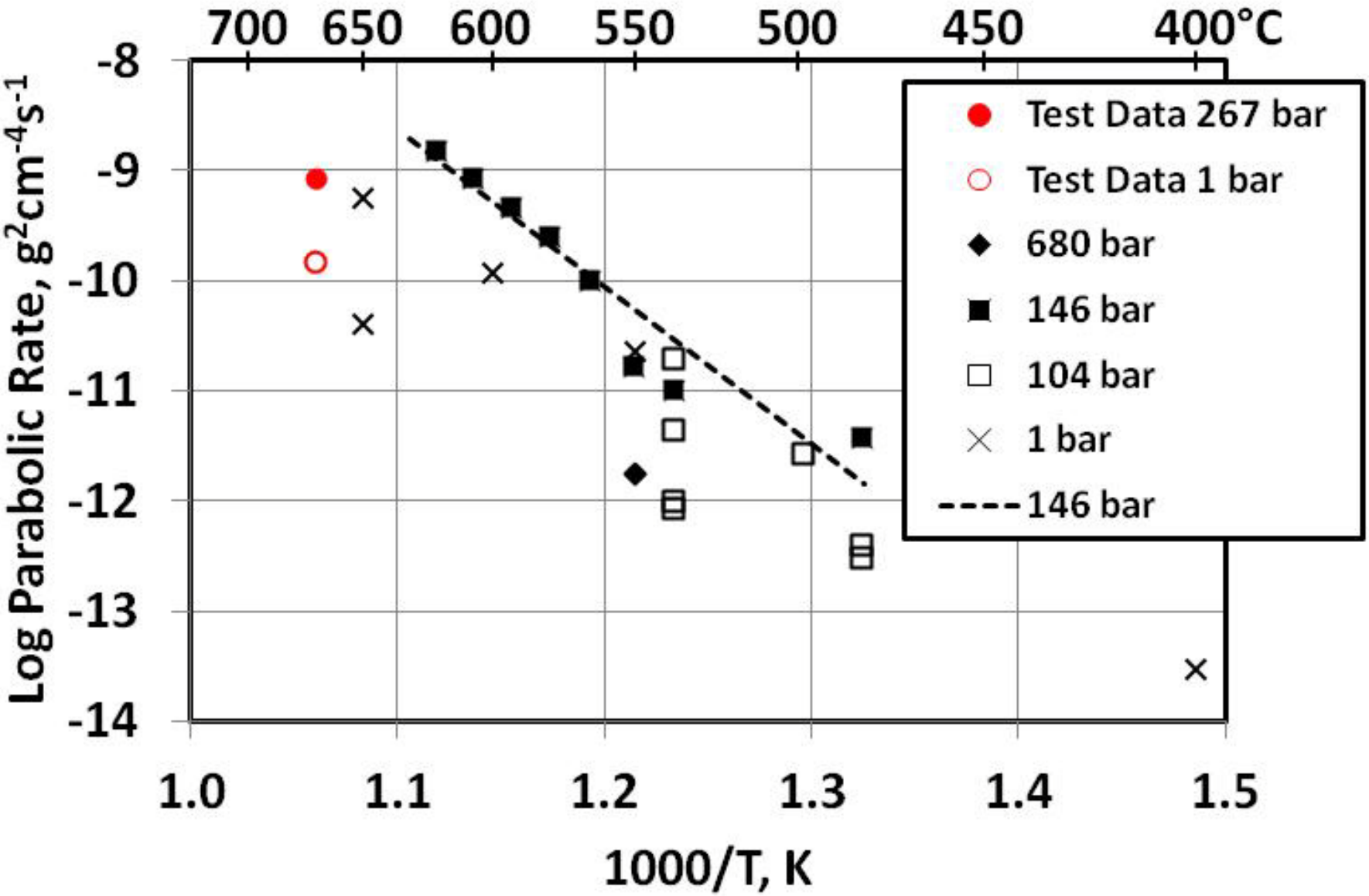
Compositions from Viswanathan and Bakker (2001), Haynes International (2002, 2008, 2008) and Special Metals Corporation (2004, 2005, 2006)

Test 1 Results





T22 Test Data

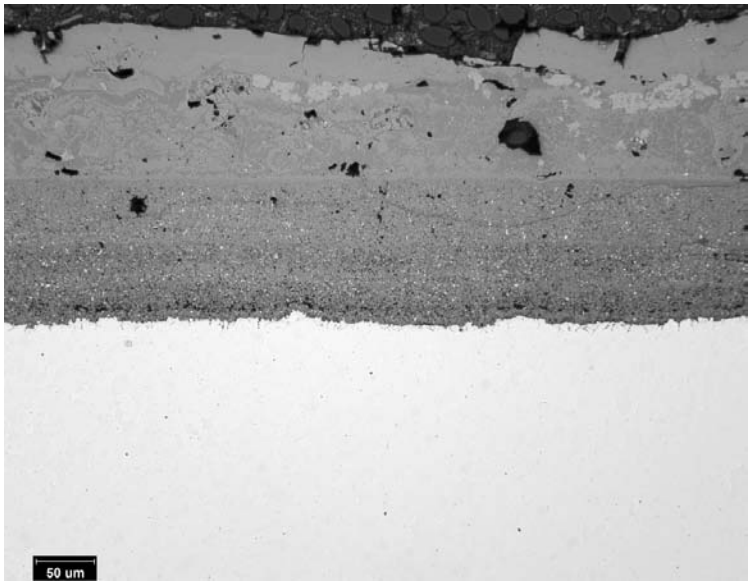


T22 data adapted from Wright and Dooley, 2010

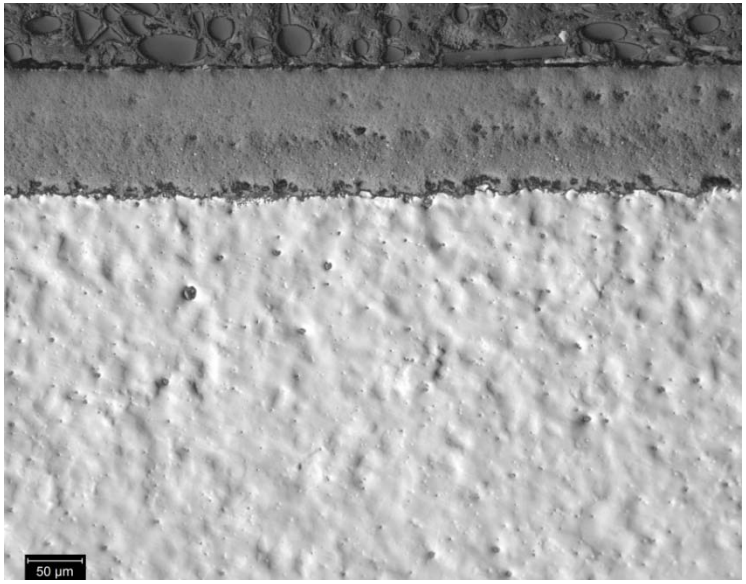
T22 Light Microscopy

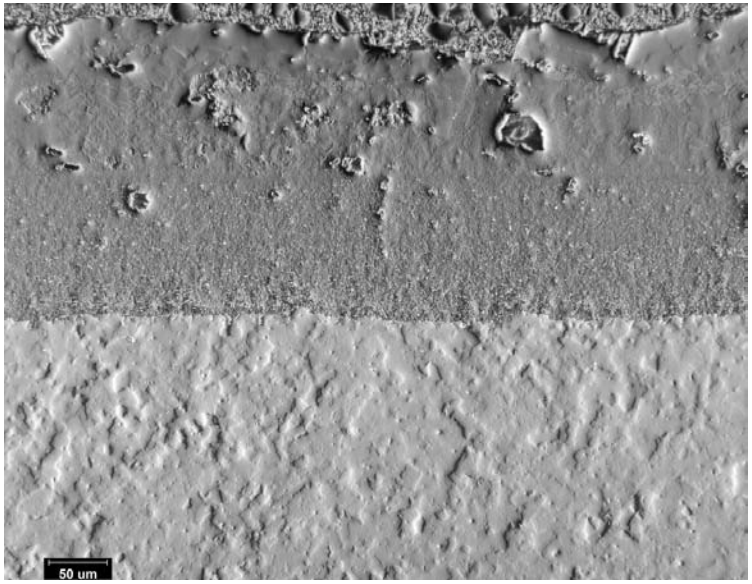
1 bar (670°C, 293 hr) 267 bar

BF

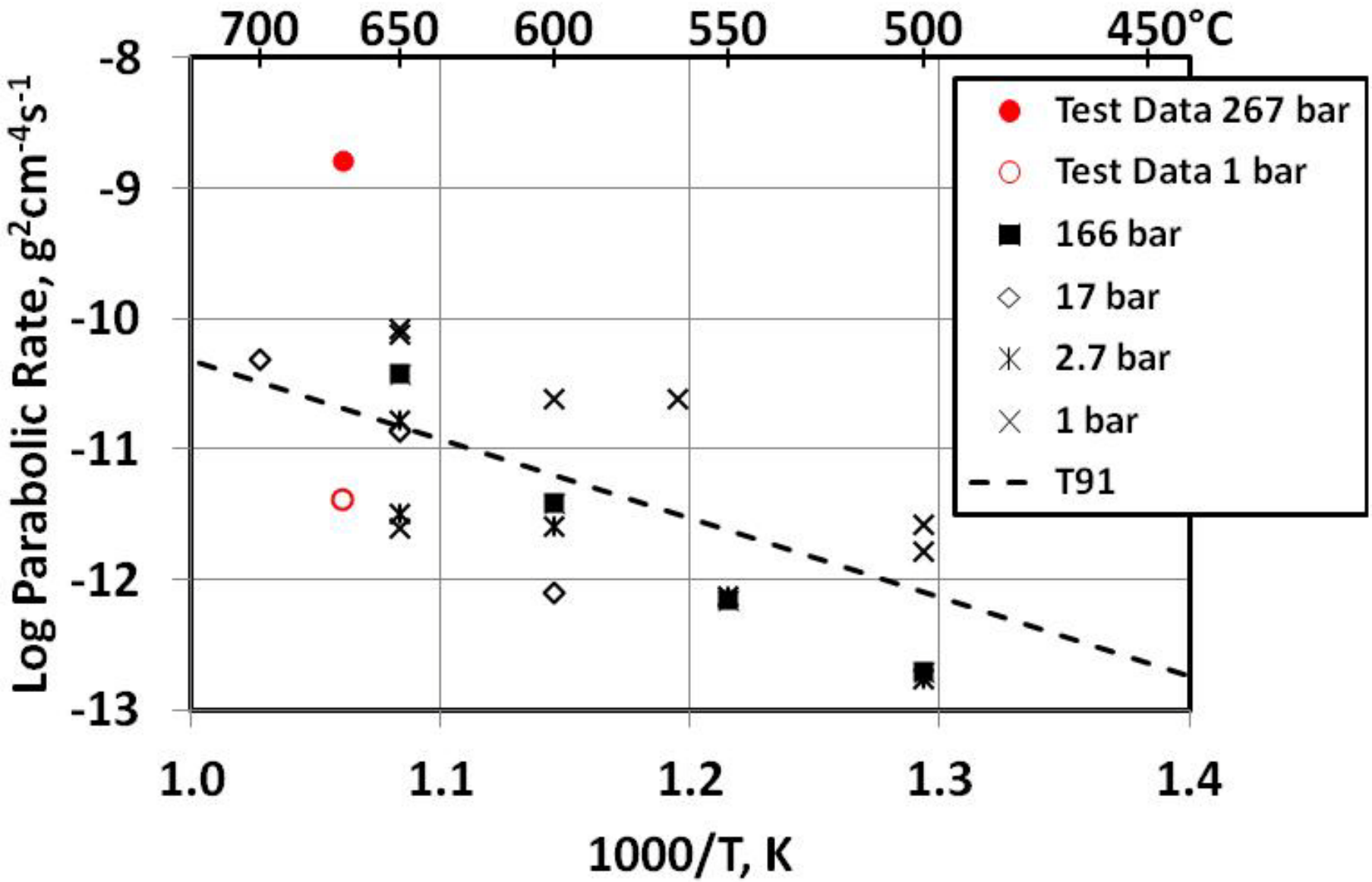


DIC





T91 Test Data



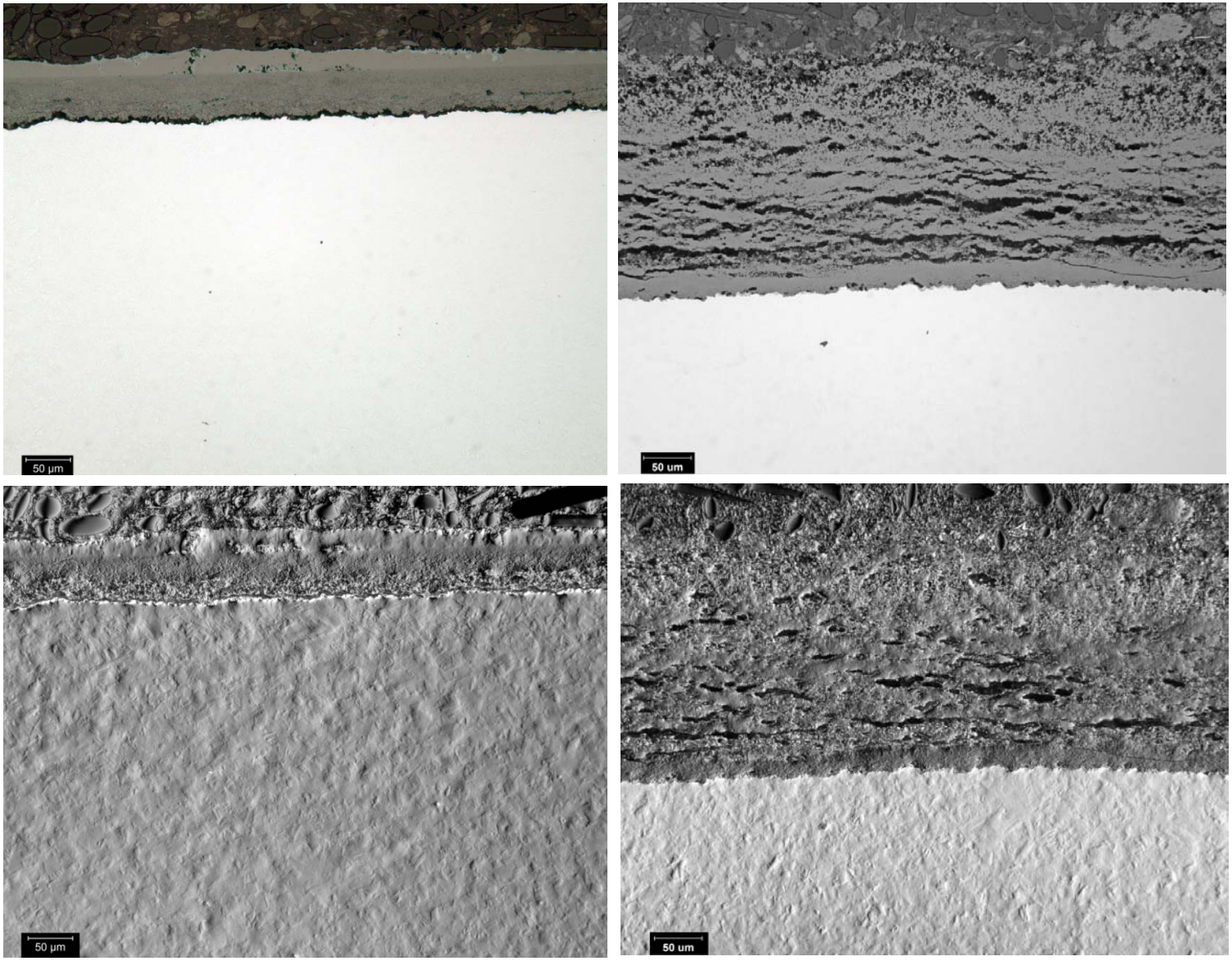
T91 data adapted from Wright and Dooley, 2010

T91 Light Microscopy

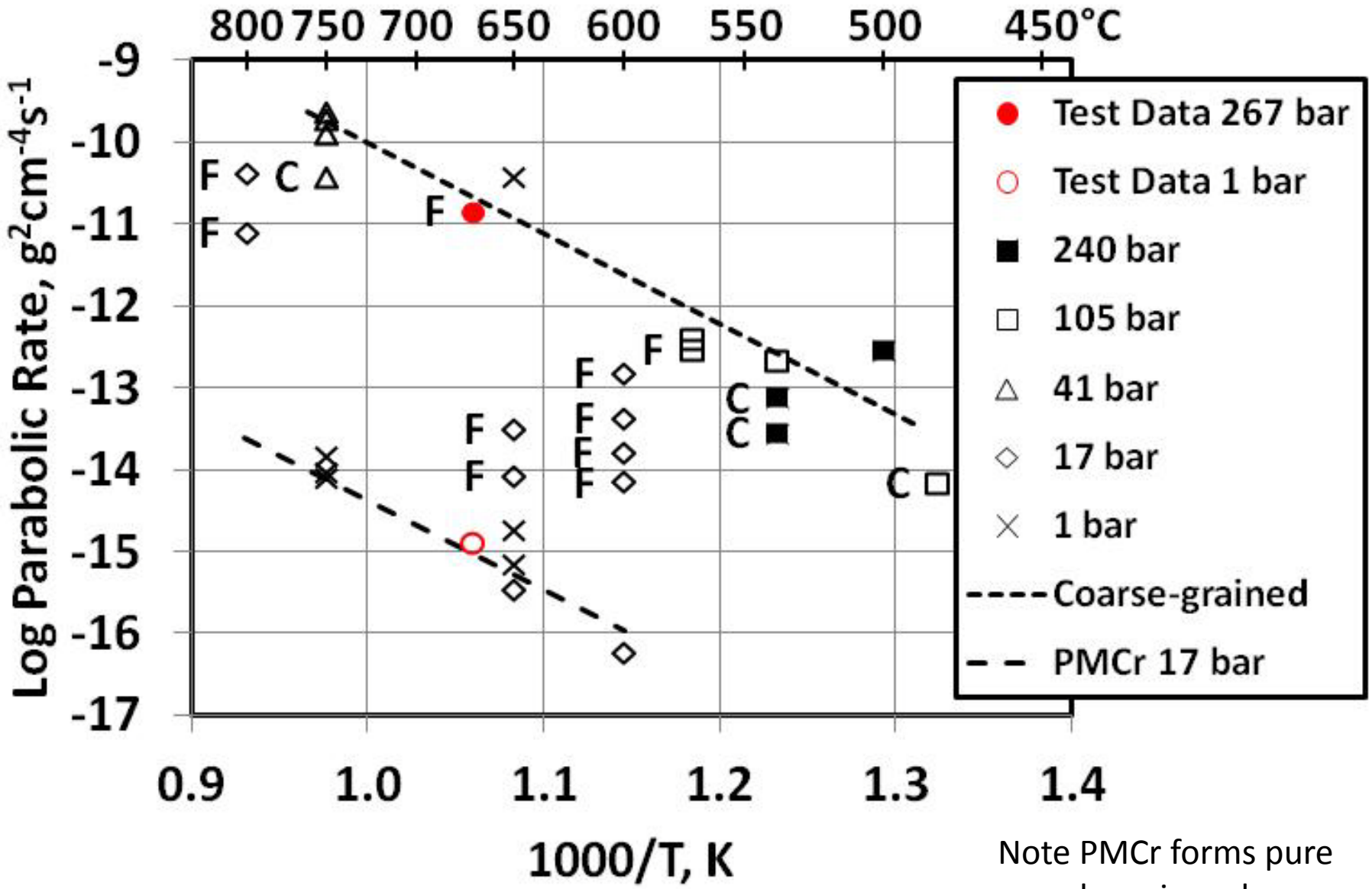
1 bar (670°C, 293 hr) 267 bar

BF

DIC



TP304H Test Data



Note PMCr forms pure chromia scale

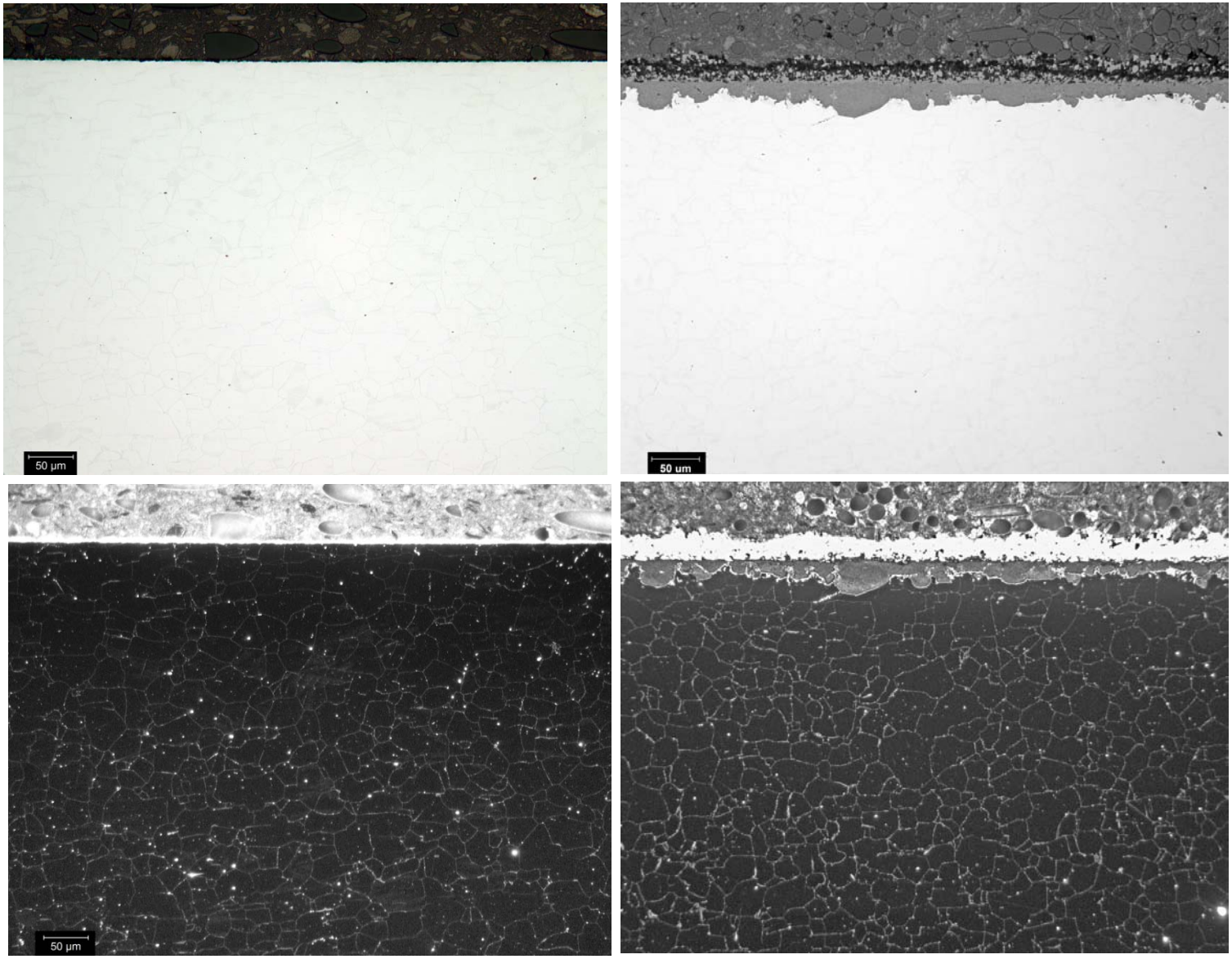
300 series stainless steel data adapted from Wright and Dooley, 2010

TP304H Light Microscopy

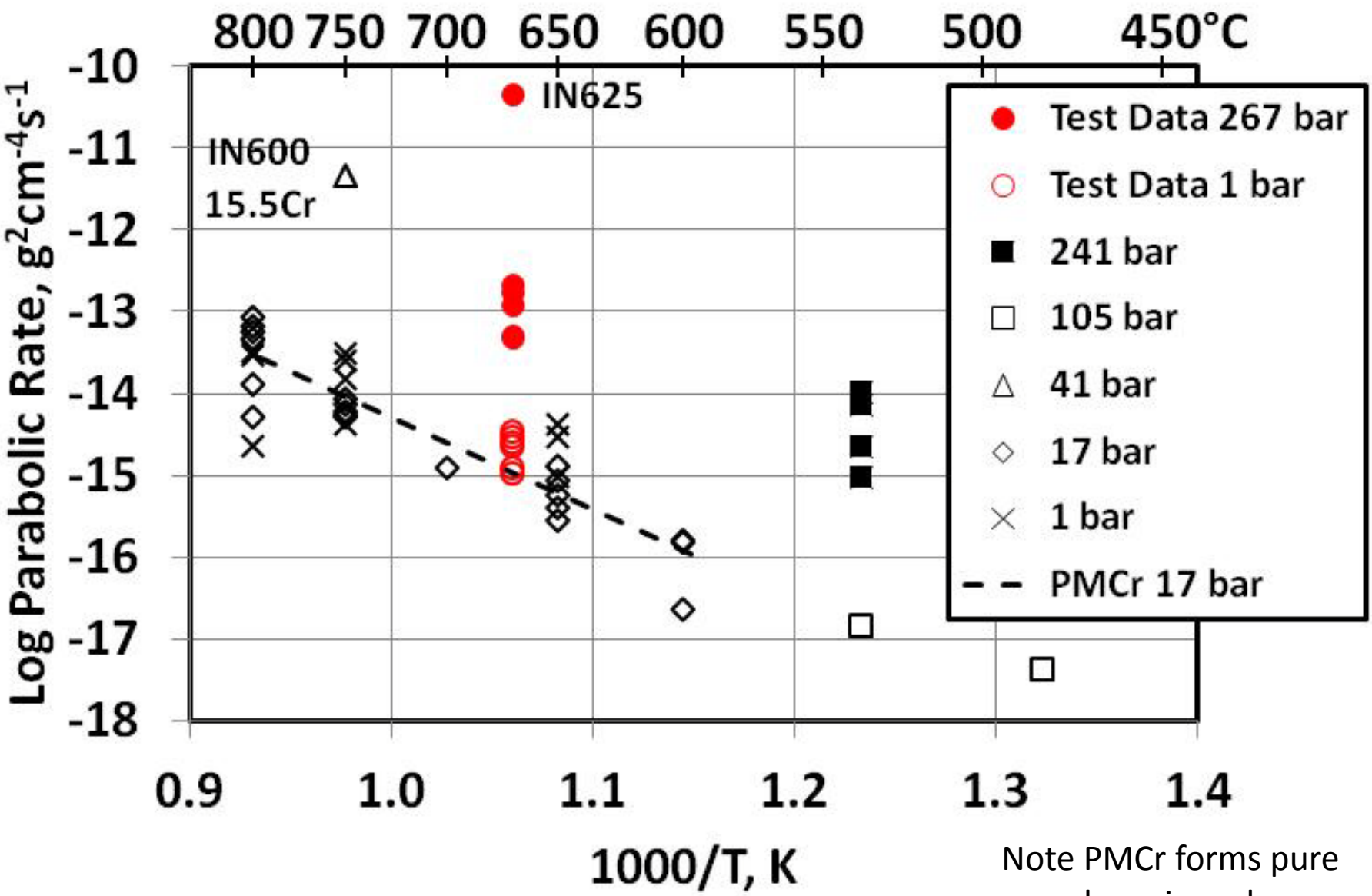
1 bar (670°C, 293 hr) 267 bar

BF

DF



Ni-base Test Data



Note PMCr forms pure chromia scale

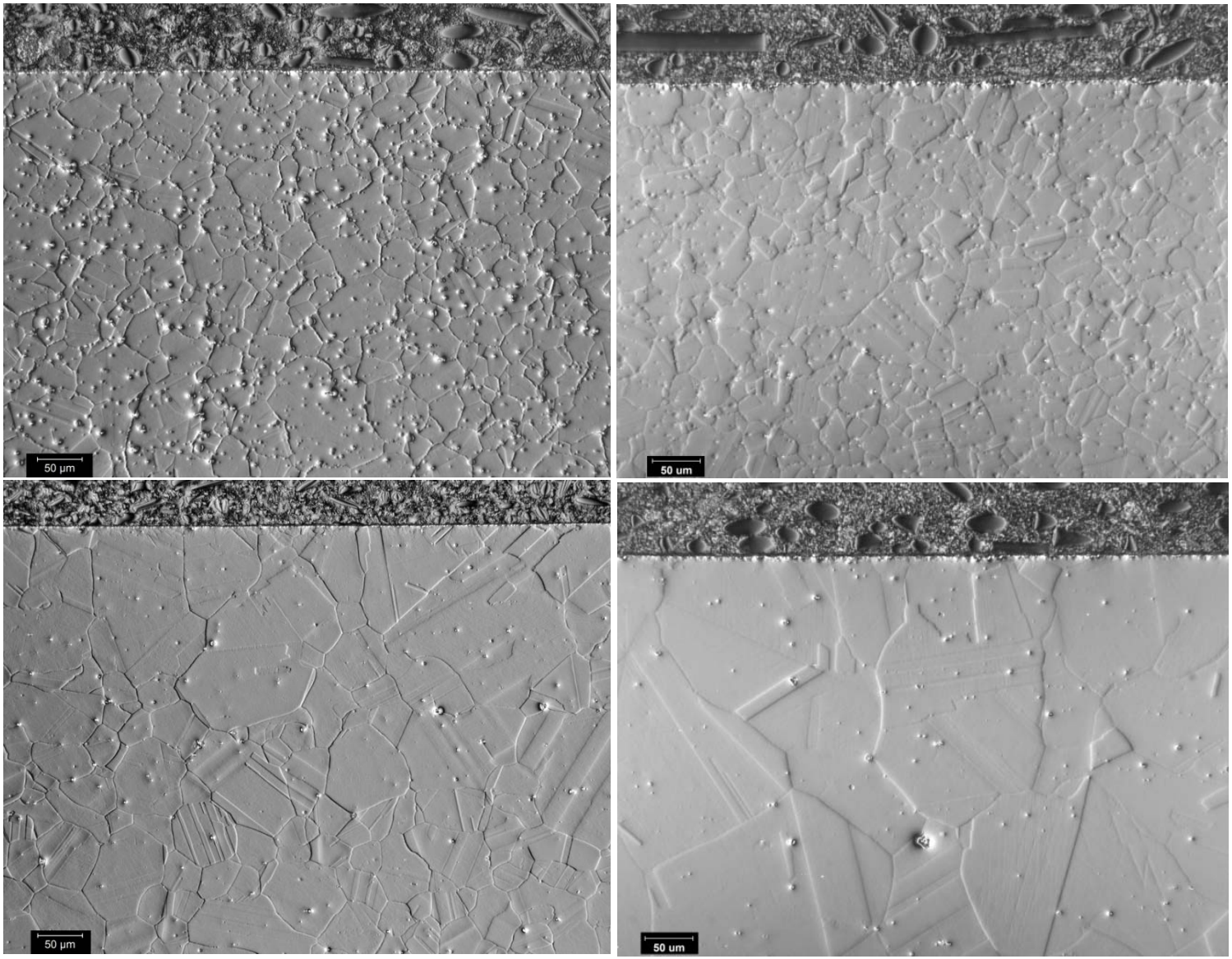
Ni-base data adapted from Wright and Dooley, 2010

Ni-Base Alloy Light Microscopy (DIC)

1 bar (670°C, 293 hr) 267 bar

H230

H263

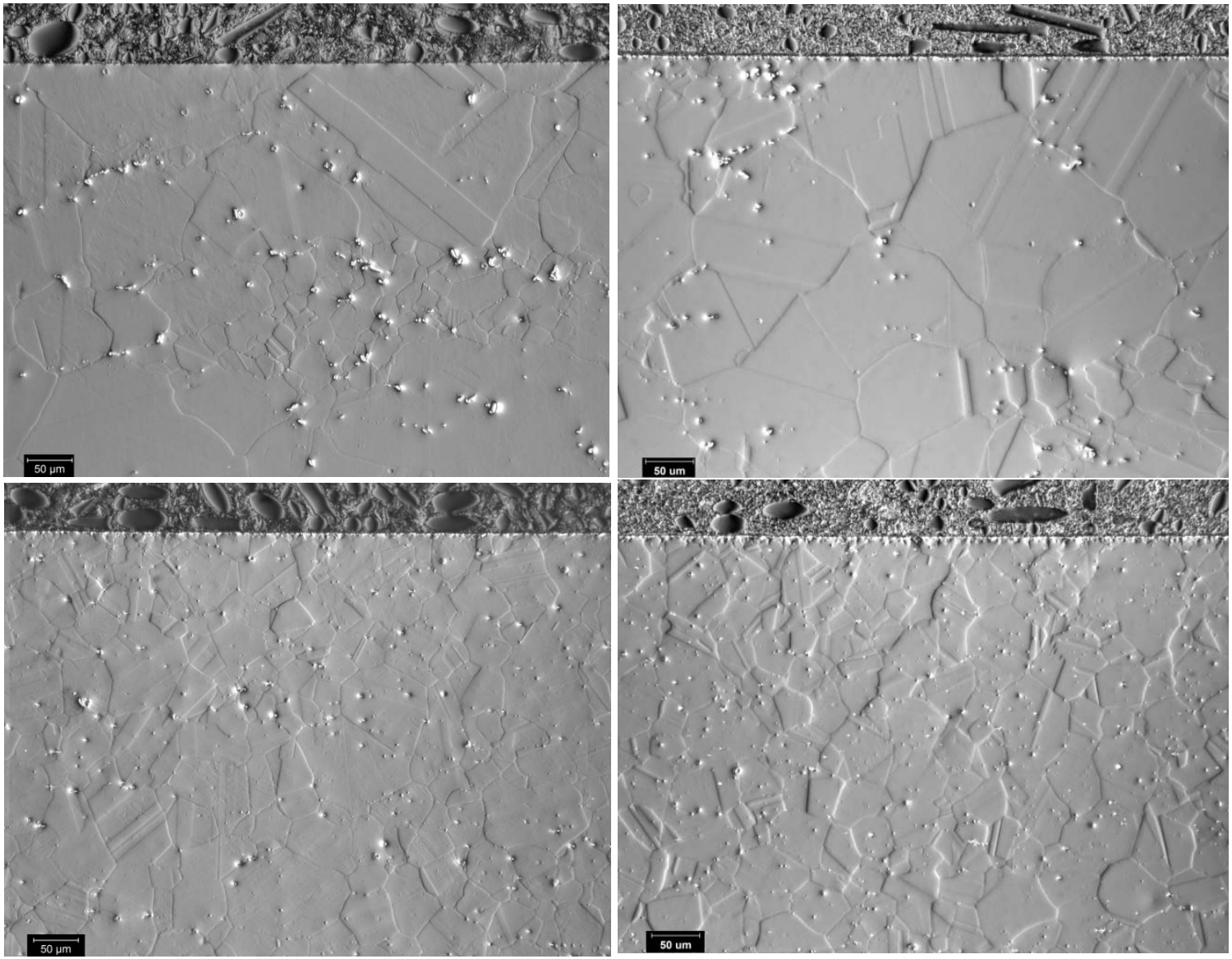


Ni-Base Alloy Light Microscopy (DIC)

1 bar (670°C, 293 hr) 267 bar

H282

IN617

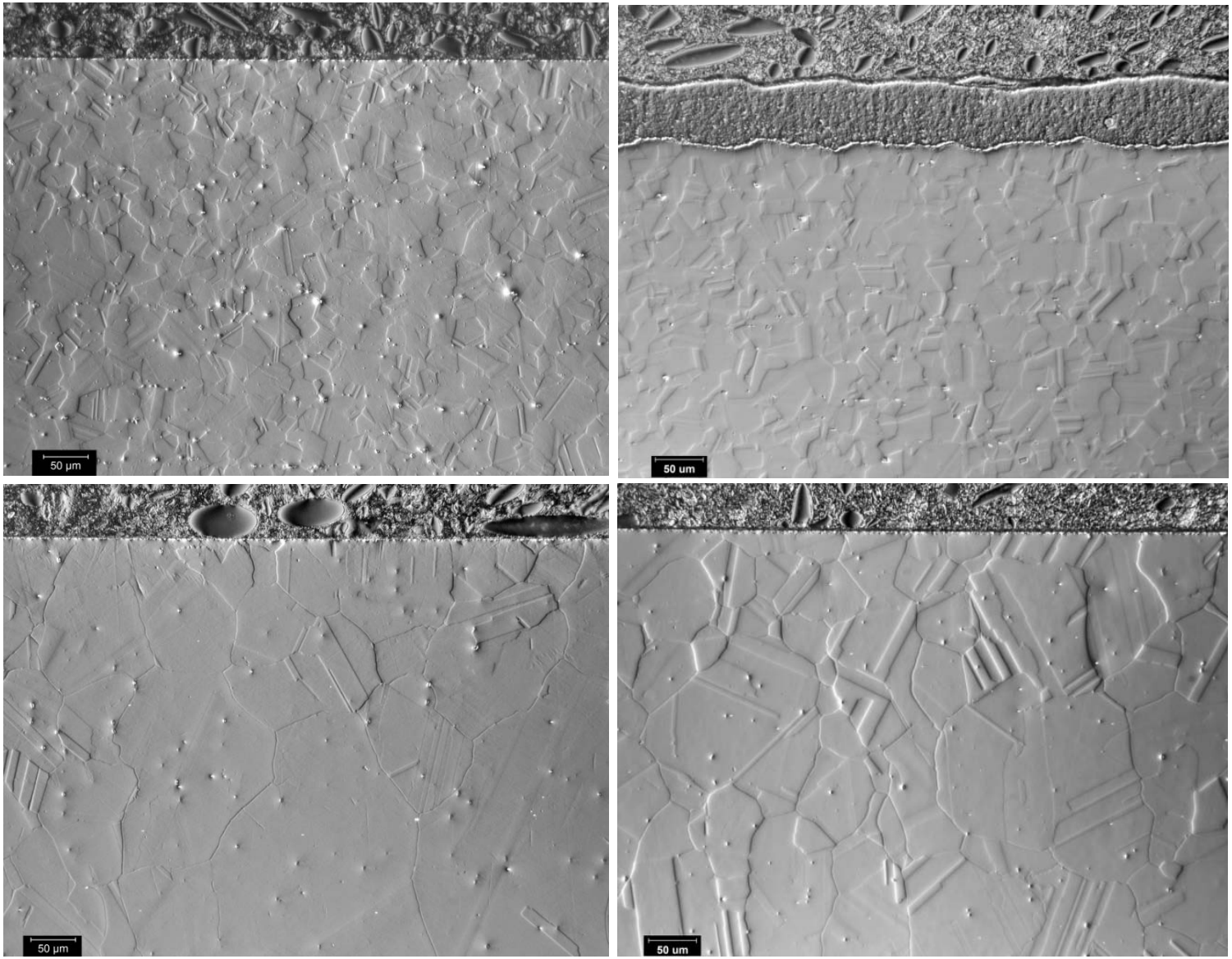


Ni-Base Alloy Light Microscopy (DIC)

1 bar (670°C, 293 hr) 267 bar

IN625

IN740



Conclusions—Steamside Oxidation

- **A first high pressure test was completed**
  - 293 hr at 267 bar and 670°C
  - A parallel 1 bar test was done for comparison
  - Mass gains were higher for all alloys at 267 bar than at 1 bar
- **A comparison was made with longer-term literature data**
  - Ferritic steels—no consistent pressure effect
  - Austenitic steels—fine grain alloys less able to maintain protective chromia scale as pressure increases
  - Ni-base alloys—more mass gains above 105 bar than below. Not based on many data points

2.1 Fireside Corrosion

- Conduct and Analyze Long-term Laboratory Fireside Corrosion Tests (NETL)
- **Conduct and Analyze Short-term Laboratory Fireside Corrosion Tests (Pitt)**
- Perform Transmission Electron Microscopy Analyses of Selected Fireside Test Specimens (CMU)
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- Conduct Low Temperature Corrosion Tests Simulating Post Economizer Environments (NETL)
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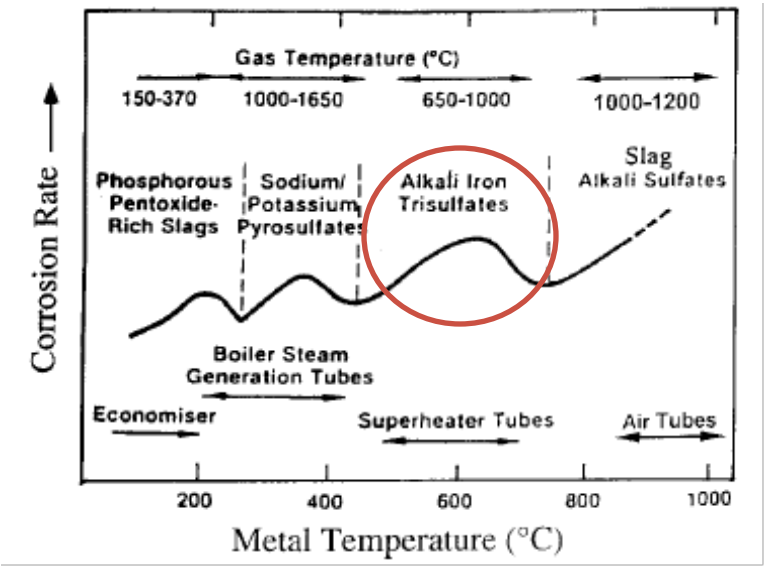
Fireside Corrosion Atmosphere

- **Deposit:** coal ash rich in alkalis
- **Temperature:** 650-750°C (bell-shaped curve)
- **Gas Atmosphere:** products of combustion, high in SO_2 due to S in the coal



$$3K_2SO_4 + Fe_2O_3 + 3SO_3 = 2K_3Fe(SO_4)_3$$

$K_3Cr(SO_4)_3$ typically not found in deposits

Compound	Melting Point, F
$K_3Fe(SO_4)_3$	1145 (618°C)
$K_3Al(SO_4)_3$	1210 (654°C)
$KFe(SO_4)_2$	1281[a] (694°C)
$Na_3Fe(SO_4)_3$	1155 (624°C)
$Na_3Al(SO_4)_3$	1195 (646°C)
$NaFe(SO_4)_2$	1274[a] (690°C)

Reid, W.T., *External Corrosion and Deposits Boilers and Gas Turbines.* 1971, New York: American Elsevier Publishing Company, Inc

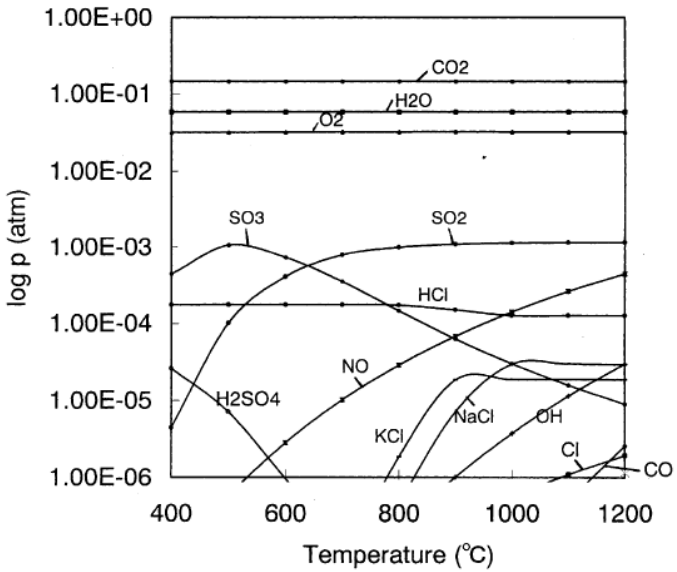
SO_3 Formation

- The main source of SO_3 in the flue gas is by the oxidation of SO_2

$$SO_2 + O = SO_3$$

$$SO_2 + ½\ O_2 = SO_3$$

- The amount of SO_3 that can be formed from SO_2 depends on the temperature



- The amount of SO_3 present in the flue gas is a major factor on the formation of alkali iron trisulfates (threshold value?)

Otsuka, N., *Effects of fuel impurities on fireside corrosion of boiler tubes in advanced power generating systems – a thermodynamic calculation of deposit chemistry.* Corrosion Science, 2002. 44: p. 265-283

Experimental

Nominal Composition Alloys Tested (wt%)

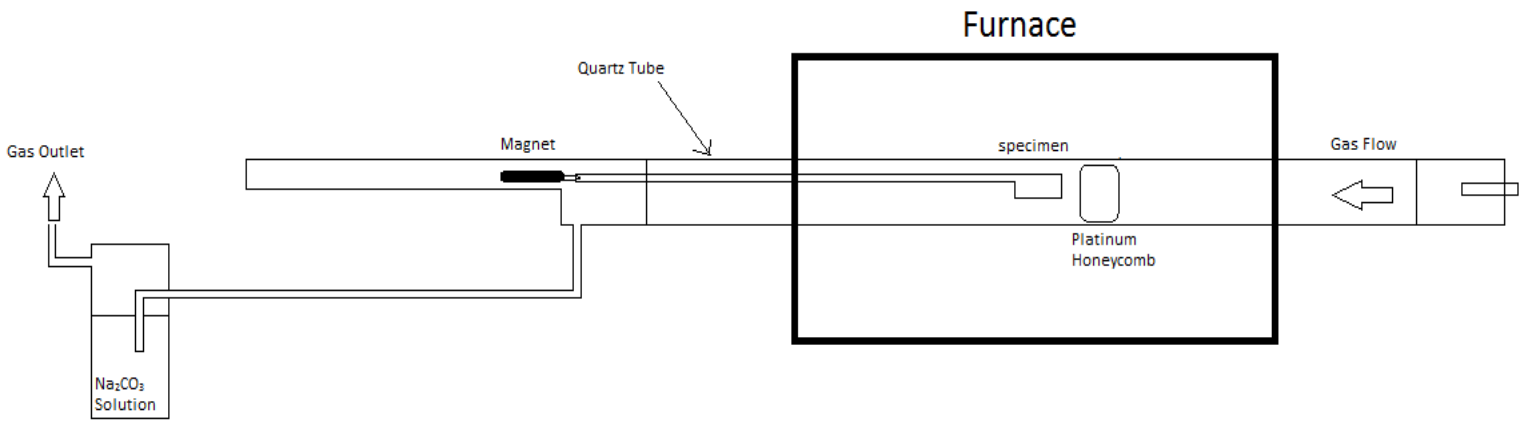
	Ni	Fe	Co	Cr	Al	Mo	Ti	W	Other(Nb, Ta, Hf, Y)
NiCrAl	Balance	-	-	8	6	-	-	-	-
NiCrAlMo	Balance	-	-	8	6	6	-	-	-
NiCr	Balance	-	-	22	-	-	-	-	-
IN-617	Balance	-	12	22	1.2	9	0.3	-	-
T92	0.32	Balance	-	8.84	-	0.32	-	1.83	-
FeNiCr	12	Balance	-	18	-	-	-	-	-

Equilibrium SO_3 Partial Pressures

	O_2 + 100ppm SO_2	O_2 + 1000ppm SO_2
650°C	8.3×10^{-5} atm	8.3×10^{-4} atm
700°C	7.2×10^{-5} atm	7.2×10^{-4} atm

Experimental Procedure: Fireside Corrosion

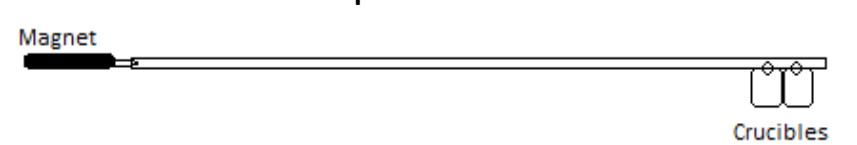
Selected Alloys: FeNiCr, T92, NiCr, NiCrAl, NiCrAlMo, and IN-617
Deposit: Standard Corrosion Mix: Na_2SO_4:K_2SO_4:Fe_2O_3 in a 1.5:1.5:1.0 molar ratio
Gas Atmospheres: O_2 + 100ppm SO_2 and O_2 + 1000ppm SO_2
Duration: 20, 40, 80, and 160 hours



Deposition Procedure

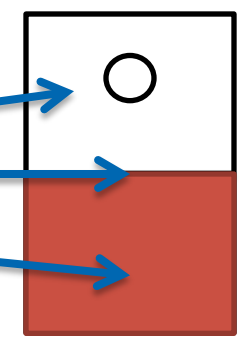
Powder Crucible Method

- Place deposit powder in crucibles
- Place specimen in crucible so half is covered in powder



Deposit thickness effect

- No deposit zone
- Thin Deposit zone
- Thick deposit zone



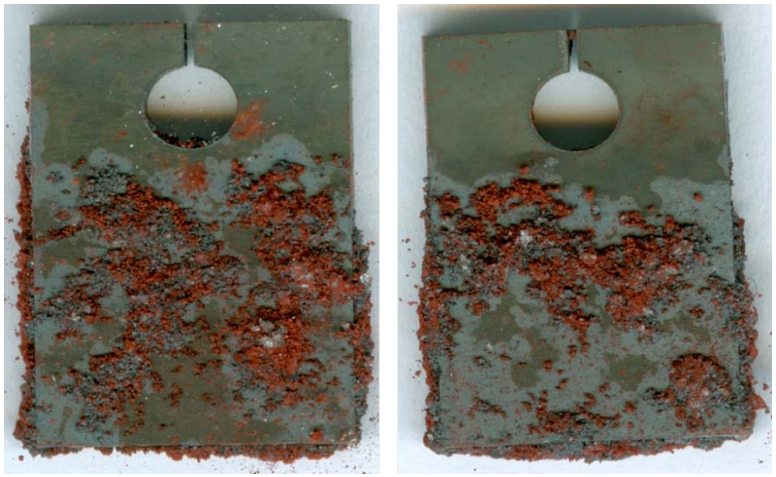
Fireside Corrosion Conditions

Conditions for most severe corrosion (established by FeNiCr alloy):

- Temperature: 700°C (bell-shaped curve)
- Deposit: Standard Corrosion Mix
- Duration: 160 hours
- Gas Atmosphere: O_2 + 1000ppm SO_2 (SO_2 threshold)
- Pt-catalyst placed close to the hot zone next to the specimens
- Thin Deposit (deposit thickness effect)

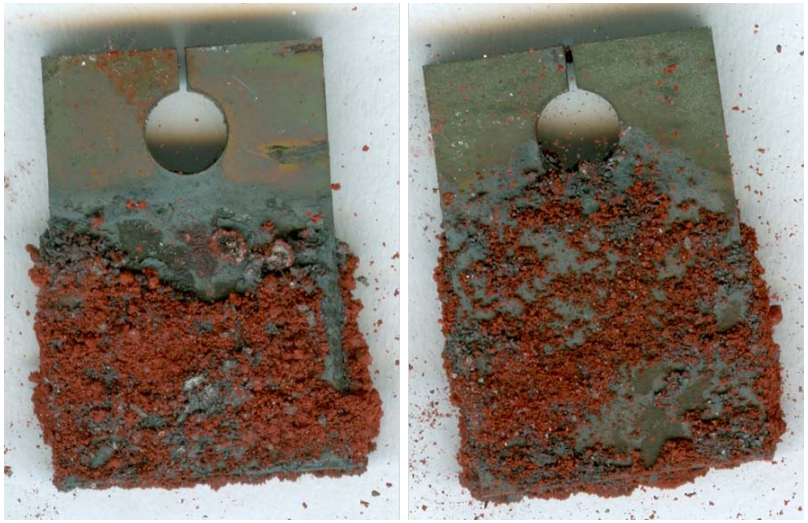
Fireside Corrosion: Fe-12Ni-18Cr

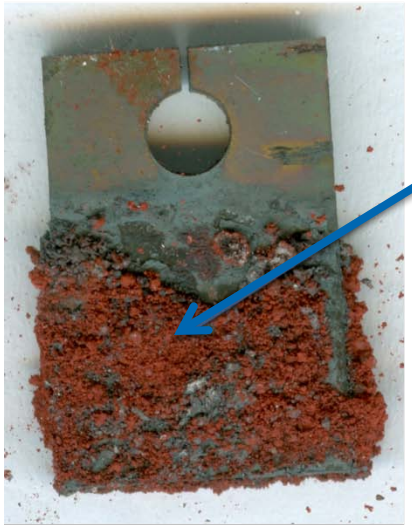
O_2 + 100ppm SO_2



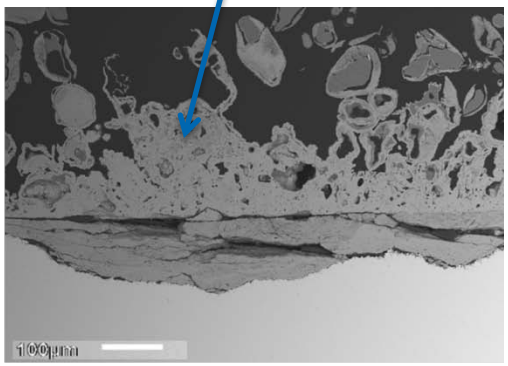
SO_2 threshold between 100 and 1000ppm SO_2

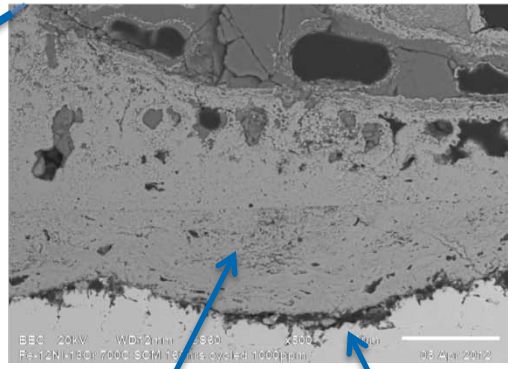
O_2 + 1000ppm SO_2





Fe_2O_3





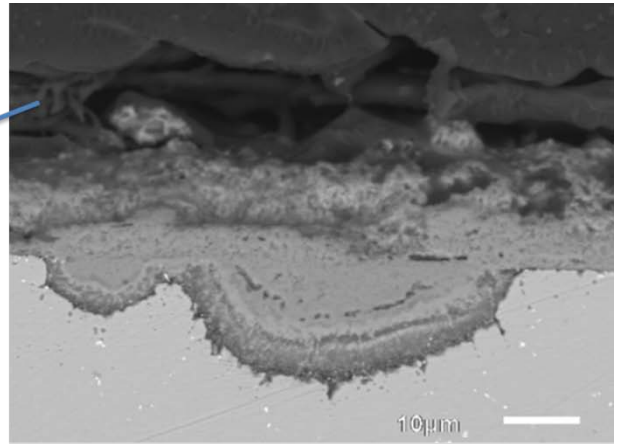
Cr, S, O rich

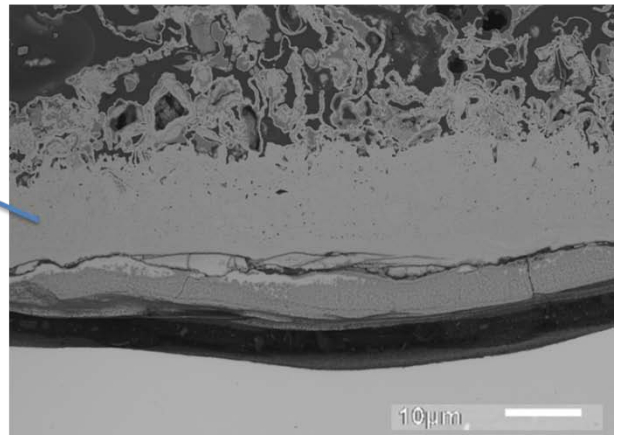
sulfides

Fireside Corrosion: T92 (9%Cr)

O_2 + 100ppm SO_2

SO_2 threshold less than 100ppm



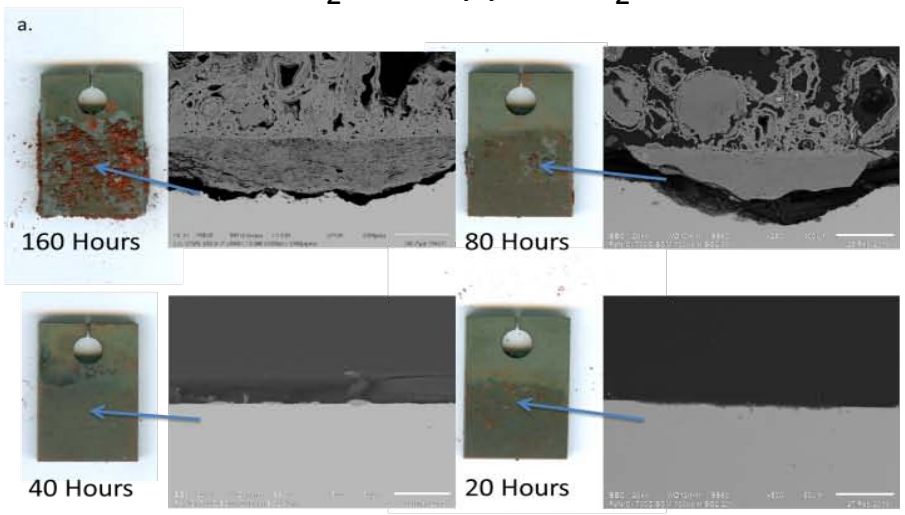


O_2 + 1000ppm SO_2

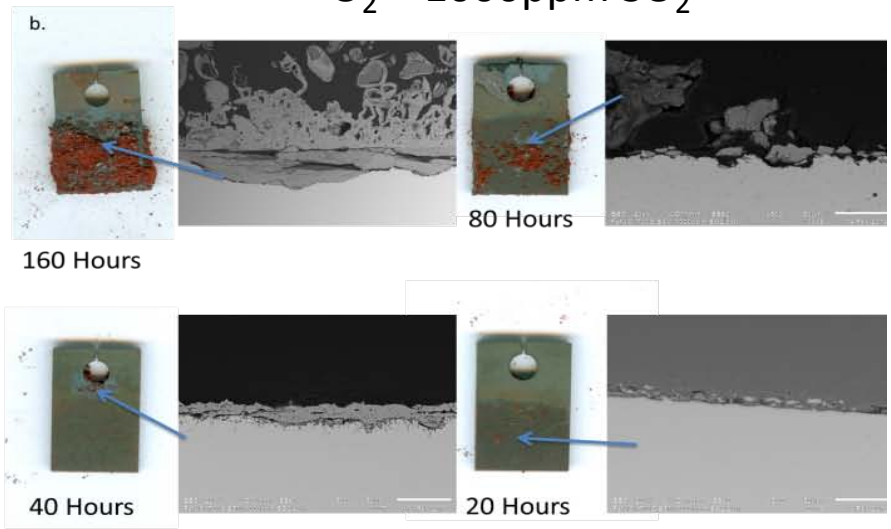
Fireside Corrosion: Results

FeNiCr

O_2 + 100ppm SO_2

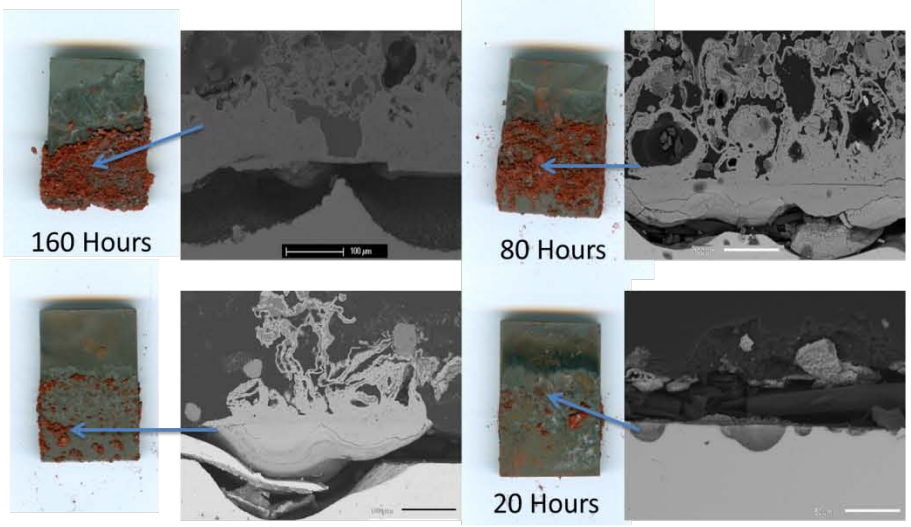


O_2 + 1000ppm SO_2

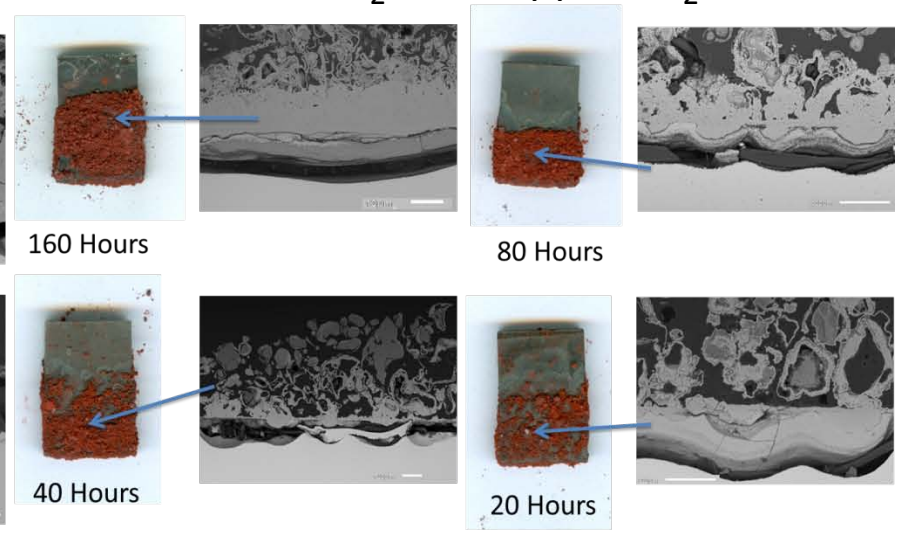


T92

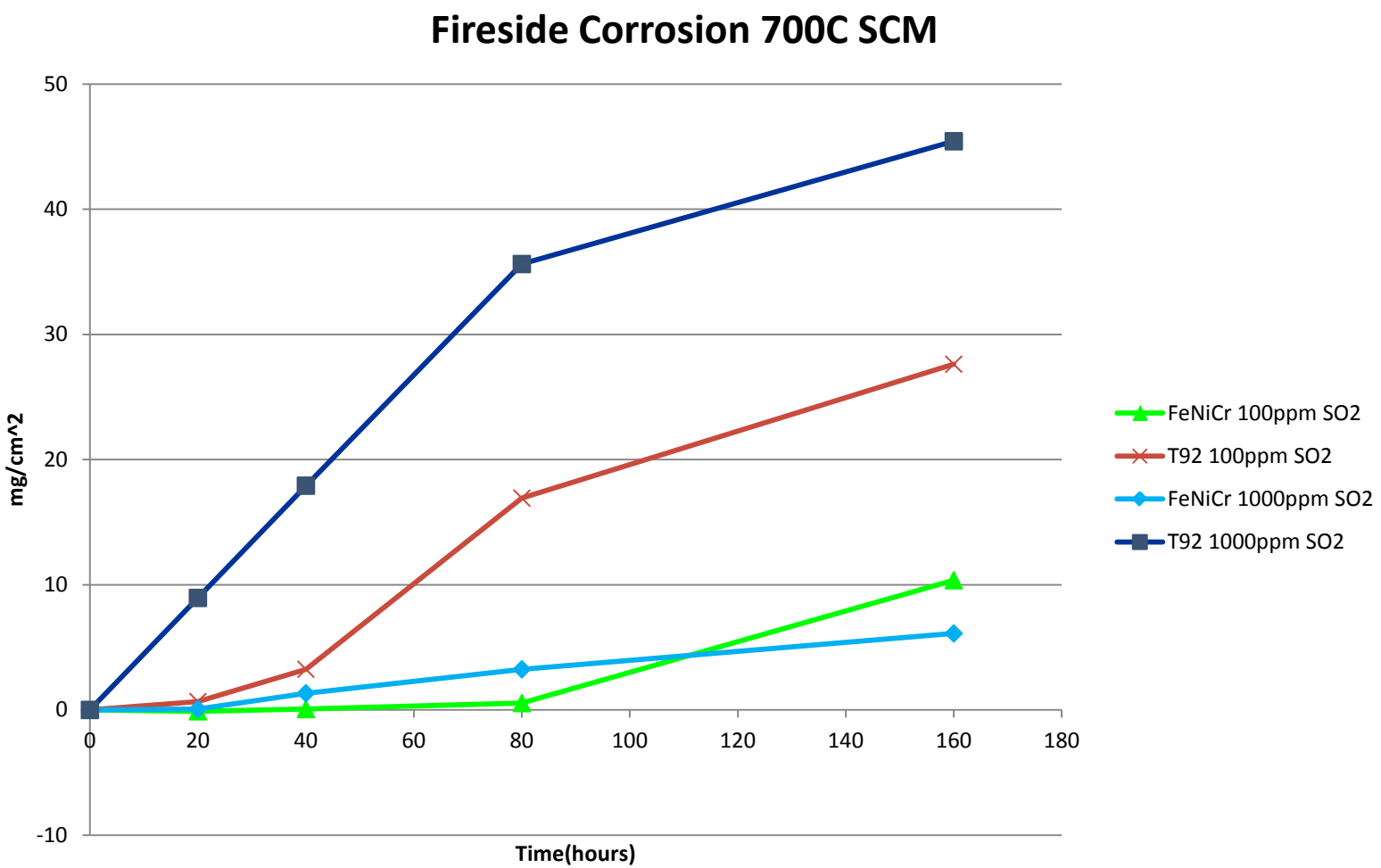
O_2 + 100ppm SO_2



O_2 + 1000ppm SO_2



Fireside Corrosion: Kinetics



Weight change measurements may be exaggerated and inaccurate measure of corrosion due to adherence of deposit on corrosion products

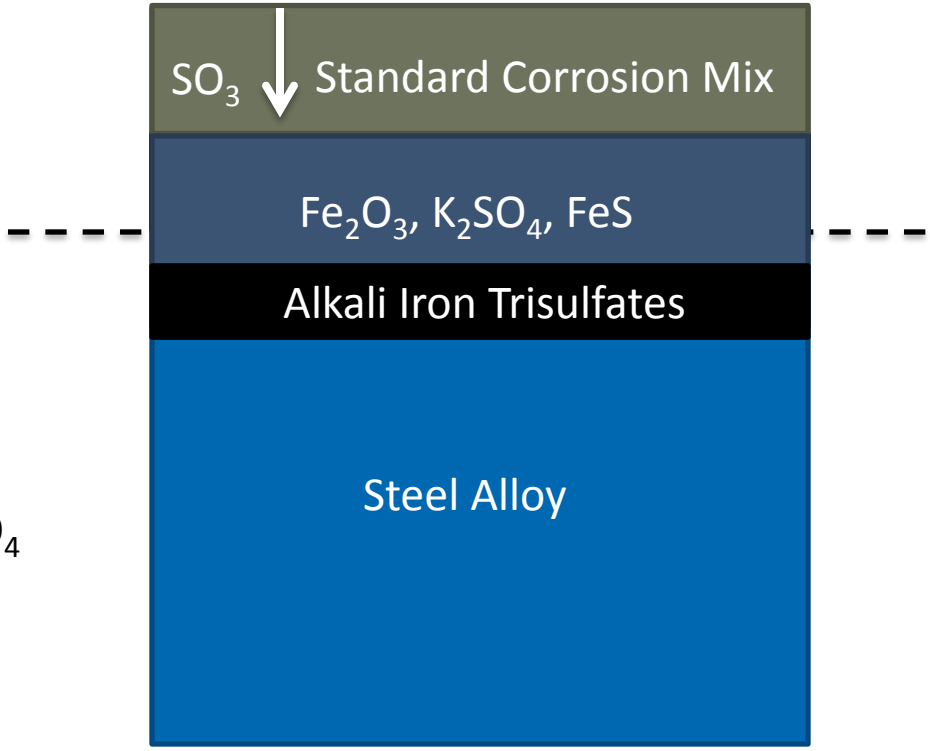
Fireside Corrosion Mechanism: Steel Alloys

$4Fe + 3O_2 = 2Fe_2O_3$
$4Cr + 3O_2 = 2Cr_2O_3$

Standard Corrosion Mix:
K_2SO_4:Na_2SO_4:Fe_2O_3 in a 1.5:1.5:1.0 molar ratio

$3K_2SO_4 + Fe_2O_3 + 3SO_3 = 2K_3Fe(SO_4)_3$

$9Fe + 2K_3Fe(SO_4)_3 = 4Fe_2O_3 + 3FeS + 3K_2SO_4$

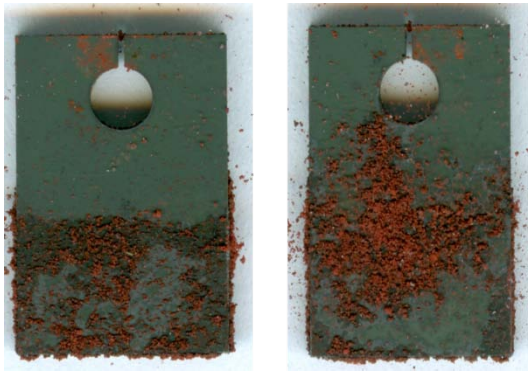


Fireside Corrosion: Ni-22Cr, IN-617(22%Cr)

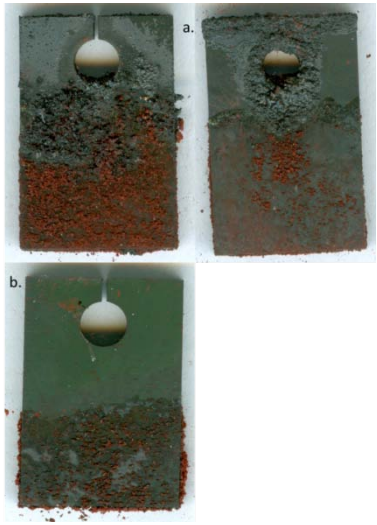
O_2 + 100ppm SO_2

O_2 + 1000ppm SO_2

O_2 + 100ppm SO_2

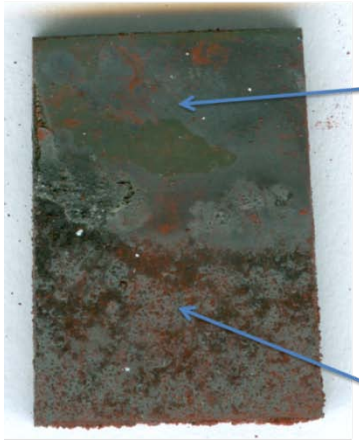


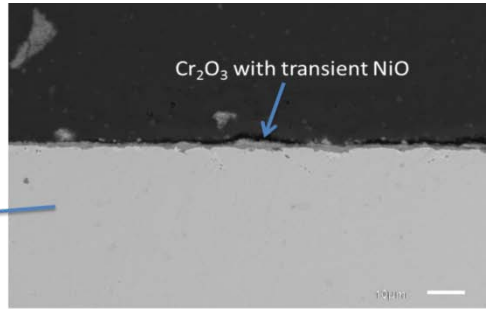
O_2 + 1000ppm SO_2

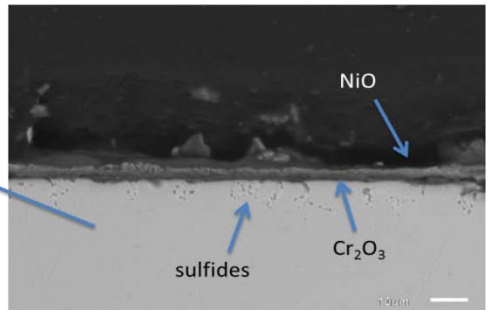


- SO_2 threshold greater than the steel alloys' threshold
- Greatest amount of corrosion in thin deposit zone

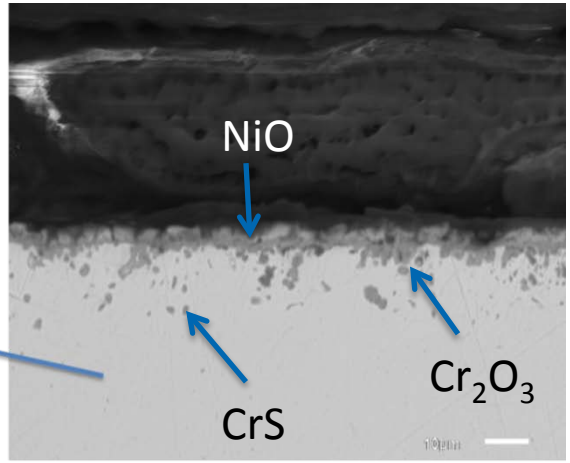
IN-617







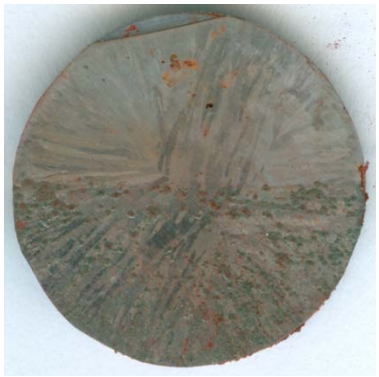
NiCr

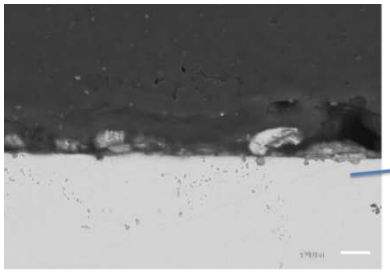


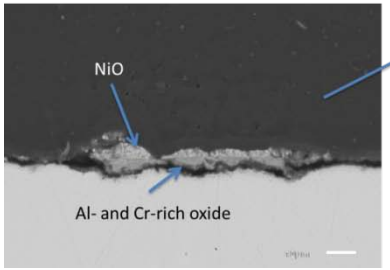
Fireside Corrosion: Ni-8Cr-6Al, Ni-8Cr-6Al-6Mo

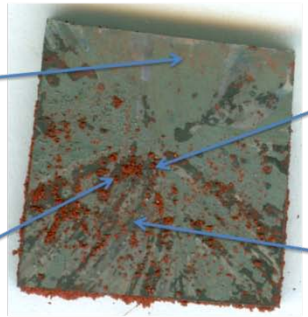
O_2 + 100ppm SO_2

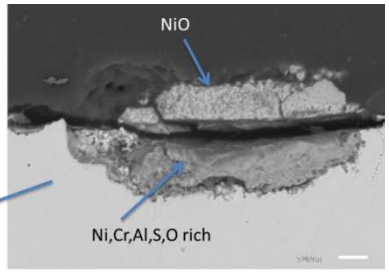
O_2 + 1000ppm SO_2

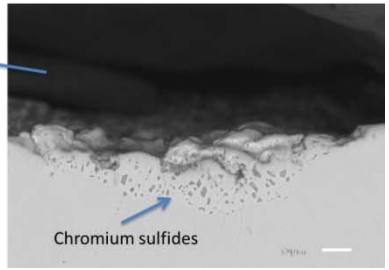




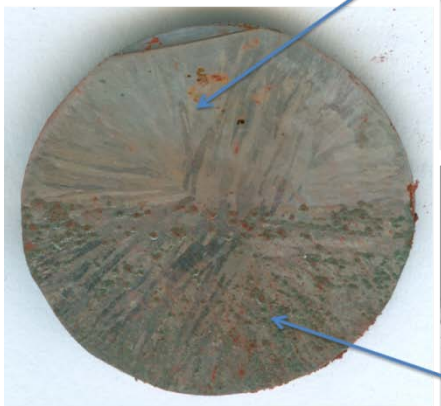


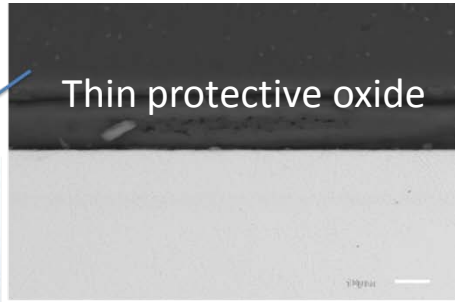


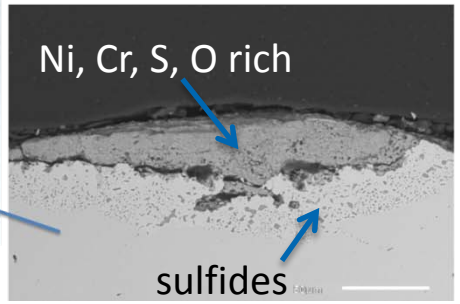




NiCrAl

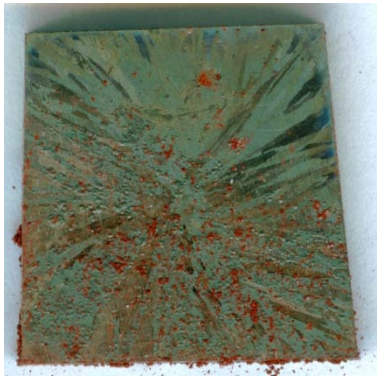




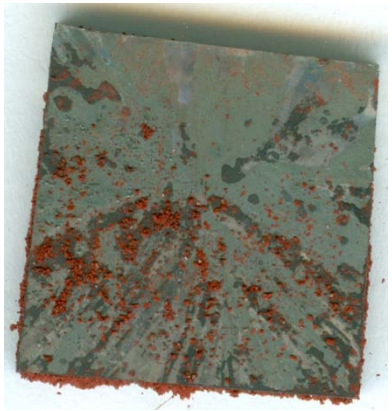


NiCrAlMo

O_2 + 100ppm SO_2



O_2 + 1000ppm SO_2



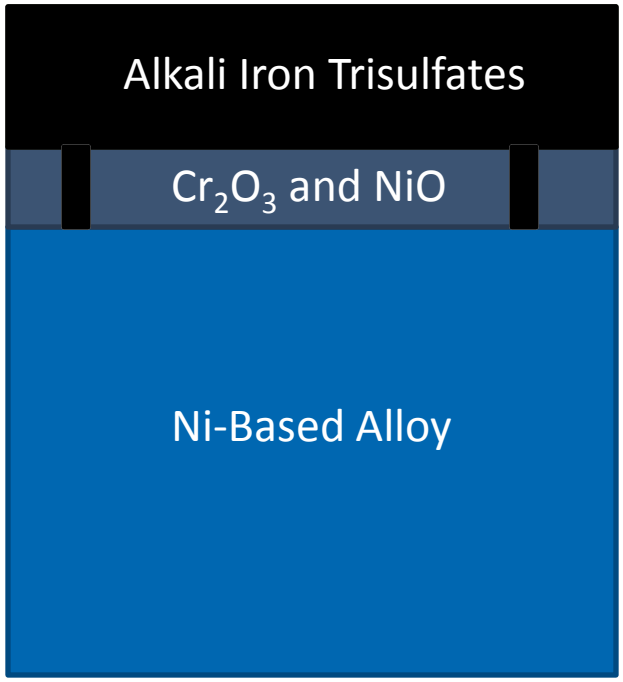
Fireside Corrosion Mechanism: Ni-Based Alloys

1. $Ni + ½ O_2 = NiO$
   $2Cr + 3/2 O_2 = Cr_2O_3$

   Standard Corrosion Mix:
   K_2SO_4:Na_2SO_4:Fe_2O_3 in a
   1.5:1.5:1.0 molar ratio

2. Na_2SO_4-Induced Type II Hot Corrosion

3. Combination of both



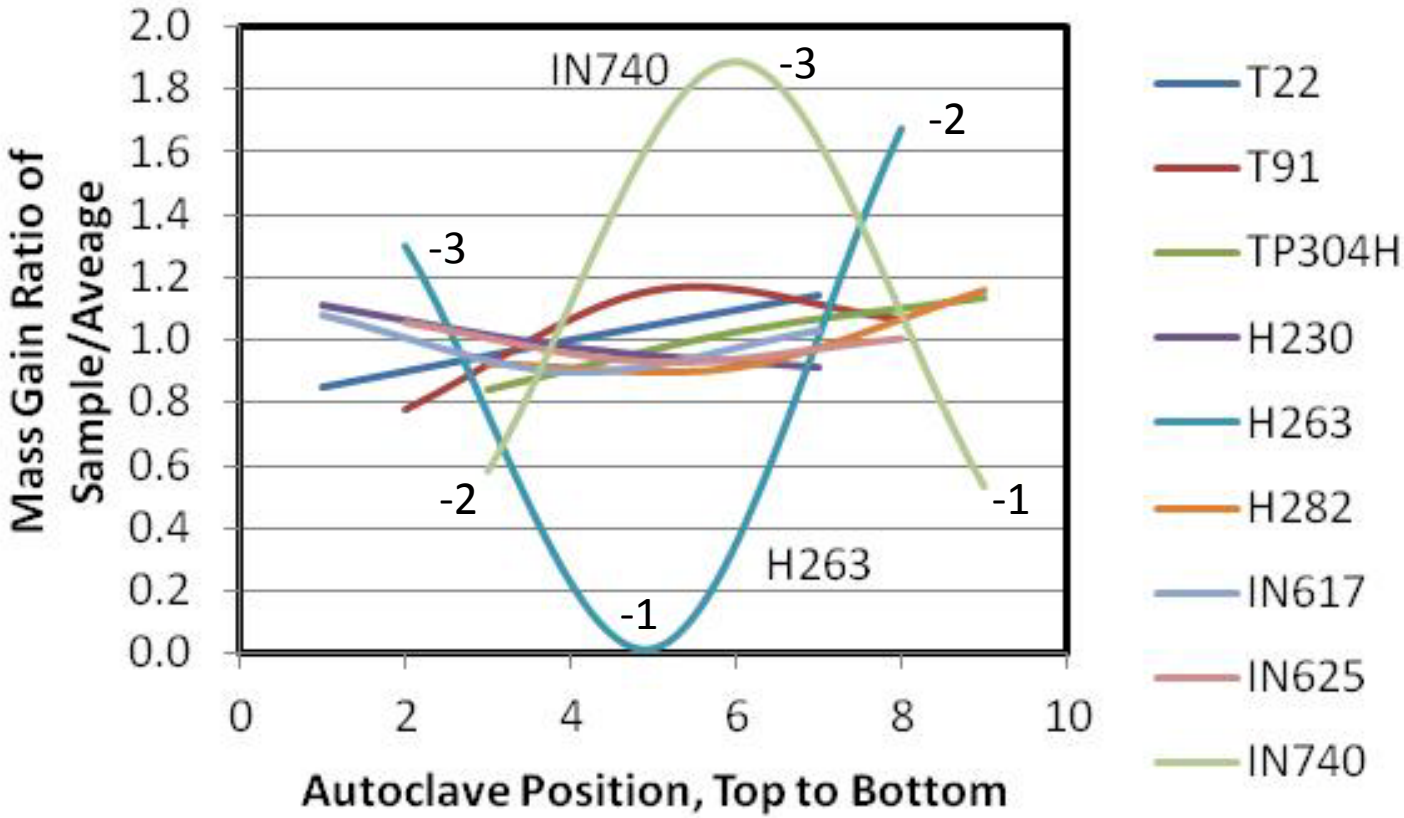
Conclusions—Fireside Corrosion

Fireside Corrosion:

1. Conditions for most severe corrosion:
   - Temperature: 700°C
   - Deposit: Standard Corrosion Mix
   - Duration: 160 hours
   - Gas Atmosphere: O_2 + 1000ppm SO_2
   - Pt-catalyst placed in the hot zone next to the specimens
2. Possible SO_2 threshold in gas atmosphere for corrosion
3. Corrosion greater in steel alloys than Ni-based alloys
4. Corrosion mechanism proposed for steel alloys and Ni-based alloys

Test 1 Results, Autoclave Position

The steam density at 670°C and 267 bar is 0.0675 g/cm^3
A pump flow of 4.5 g/min resulted in a steam velocity of 2.1 cm/min in the autoclave
Some concern that this low flow would create location effects within the autoclave



No consistent top to bottom positioning effects