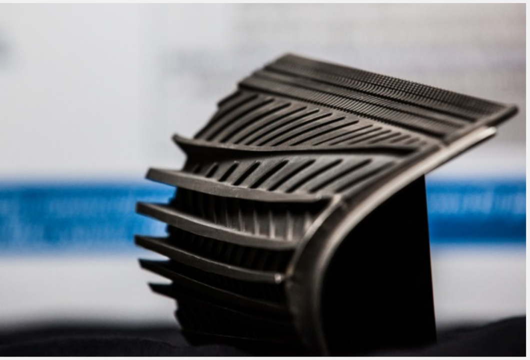
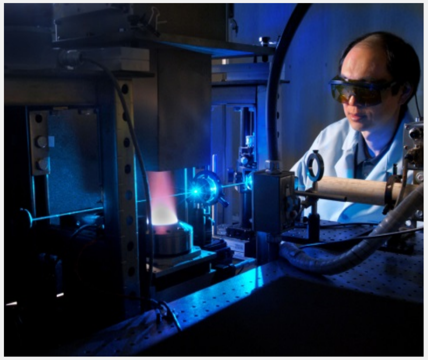
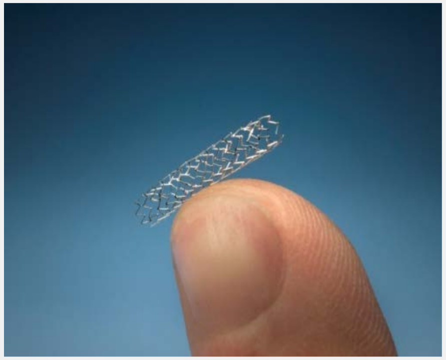
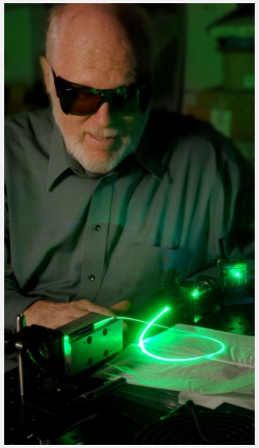







Materials Performance in Supercritical CO_2 in Comparison with Atmospheric CO_2 and Supercritical Steam

Gordon R Holcomb,
Ömer N. Doğan, Casey Carney,
Kyle Rozman, Jeffrey A. Hawk,
and Mark Anderson

The 5th International Symposium - Supercritical CO2 Power Cycles
March 28-31, 2016, San Antonio, TX

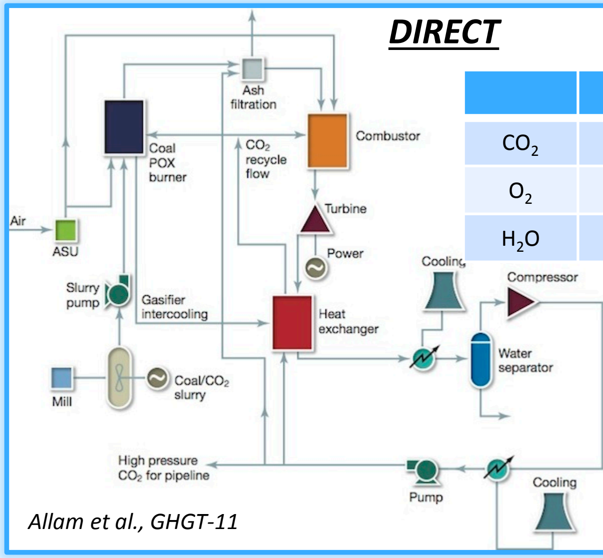
Acknowledgements

- **University of Wisconsin-Madison Collaboration**
  - Arjun Kalra and Paul Brooks
- **Funding and Support**
  - This work was funded by the Advanced Combustion Program at the National Energy Technology Laboratory (Richard Dennis and Daniel Driscoll, Technology Managers and Briggs White, Project Monitor). The Research was executed through NETL's Research and Innovation Center's Advanced Combustion Field Work Proposal.
- **Disclaimer**
  - "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

Outline

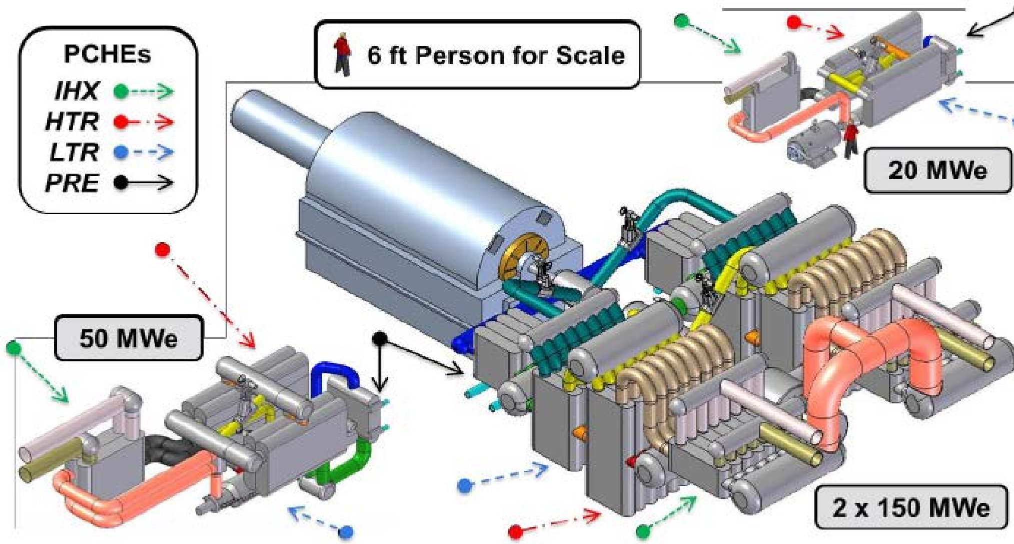
- **Background**
  - Power cycles utilizing sCO_2
  - Comparison with steam system parameters
- **sCO_2, sH_2O, and aCO_2 Oxidation**
  - Experimental procedures
  - Results
  - Comparisons with other results
- **Summary/Conclusions**

sCO_2 Power Cycles

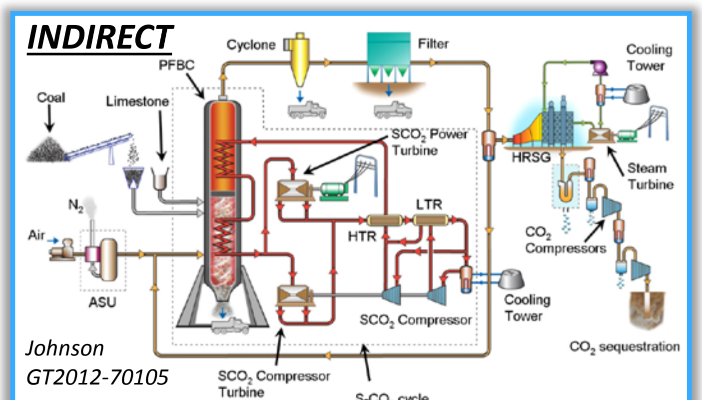


	mol %
CO_2	85-95
O_2	1-5
H_2O	2-10

Allam et al., GHGT-11



J.P. Gibbs et al., MIT Report, MIT-GFR-037, 2006



Johnson GT2012-70105

Cycle/Component		Inlet T (C)	Inlet P (bar)	Outlet T (C)	Outlet P (bar)
Indirect	Heater	450-535	10-100	650-750	10-100
	Turbine	650-750	200-300	550-650	80-100
	HX	550-650	80-100	100-200	80-100
Direct	Combustor	750	200-300	1150	200-300
	Turbine	1150	200-300	800	30-80
	HX	800	30-80	100	30-80

Coal-based Steam Systems and Efficiency

Steam conditions and net plant efficiencies for pulverized coal power plants

Nomenclature	Conditions	Net Plant Efficiency (HHV)
Subcritical	2400 psi/1050°F/1050°F (165 bar/566°C/566°C)	35%
Supercritical (SC)	3600 psi/1050°F/1075°F 248 bar/566°C/579°C)	38%
Ultra-Supercritical (USC)	>3600 psi/1100°F/1150°F (>248 bar/593°C/621°C)	>42%
Advanced Ultra-Supercritical (A-USC)	4000-5000 psi/1300-1400°F (276-345 bar/704-760°C)	>45%

adapted from EPRI Report 1022770, 2011

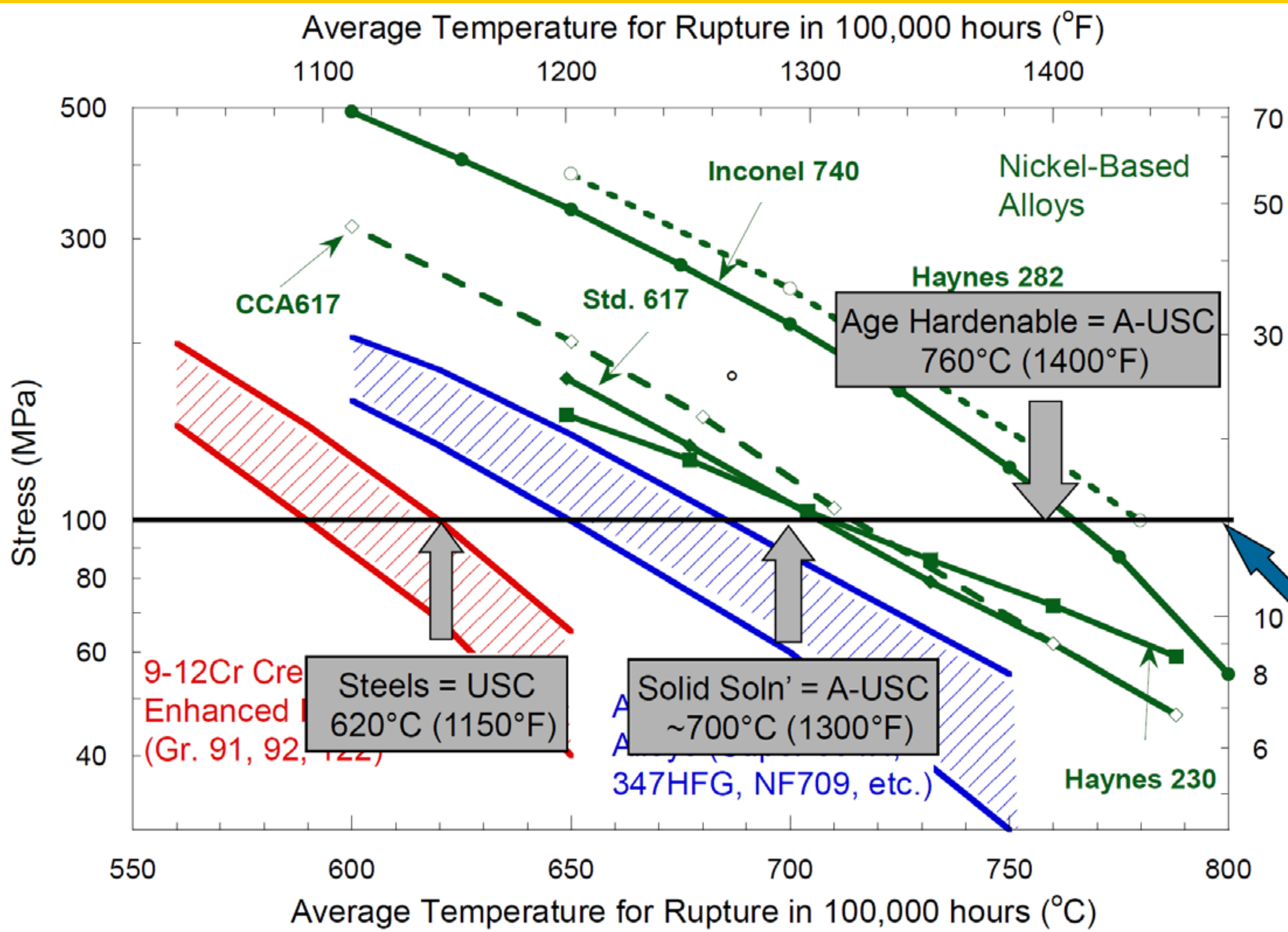
Categories are materials related, largely due to creep strength

- **USC: advanced ferritic & austenitic steels required**
- **A-USC: nickel-base superalloys required**

Each 1% increase in efficiency eliminates ~1,000,000 tons of CO_2 emissions over the lifetime of an 800-MW plant

Viswanathan, Armor, and Booras, 2003

Creep Rupture Advantages of Ni-Base Superalloys



Minimum Desired Strength at Application Temperature

Shingledecker, Purgert, and Cedro, 2013

sCO2 Components/A-USC Conditions

Nomenclature	Conditions
Subcritical	2400 psi/1050°F/1050°F (165 bar/566°C/566°C)
Supercritical (SC)	3600 psi/1050°F/1075°F 248 bar/566°C/579°C)
Ultra-Supercritical (USC)	>3600 psi/1100°F/1150°F (>248 bar/593°C/621°C)
Advanced Ultra-Supercritical (A-USC)	4000-5000 psi/1300-1400°F (276-345 bar/704-760°C)

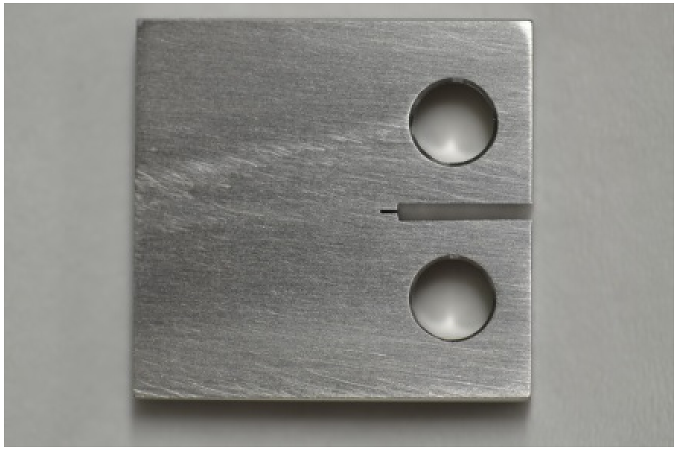
adapted from EPRI Report 1022770, 2011

Similarities in temperature and pressure suggests similar alloy candidates

Cycle/Component		Inlet		Outlet	
		T (C)	P (bar)	T (C)	P (bar)
Indirect	Heater	450-535	10-100	650-750	10-100
	Turbine	650-750	200-300	550-650	80-100
	HX	550-650	80-100	100-200	80-100
Direct	Combustor	750	200-300	1150	200-300
	Turbine	1150	200-300	800	30-80
	HX	800	30-80	100	30-80

Alloys and Samples

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
347H	Bal	17.6	9.1	0.1	0.2	0.3			1.1	0.1	0.1	0.7	0.05
282	0.2	19.4	Bal	10.1	8.7		2.2	1.4					0.06
625	3.4	22.1	Bal		8.9	0.1	0.2	0.1	0.1	0.2		3.3	0.05



Compact Tension Specimens
Nominally 22 × 23 × 3 mm

Ground surfaces to 600 grit

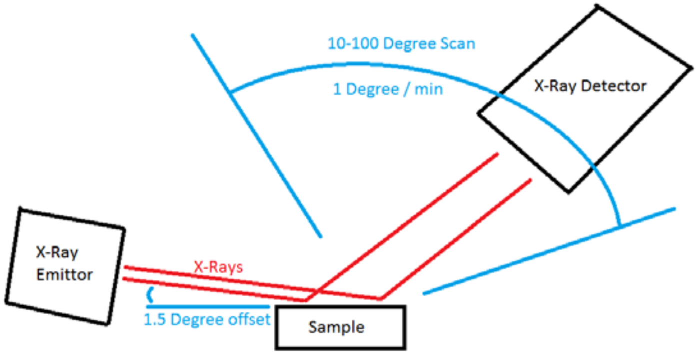
Triplicate Specimens in each test

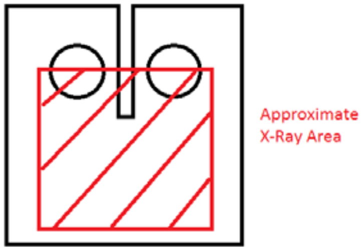
Experimental Conditions for 500 h Tests

Test	T, °C	P, bar	Environment	ρ, g/cm³	u, cm/min	Re
sCO_2	730	207	99.999% CO_2	1.04×10^{-1}	0.40	10.4
sH_2O	726	208	Deaerated H_2O	4.77×10^{-2}	0.21	1.8
aCO_2	730	1	CO_2 with 0.25% O_2	5.28×10^{-4}	33.0	4.8

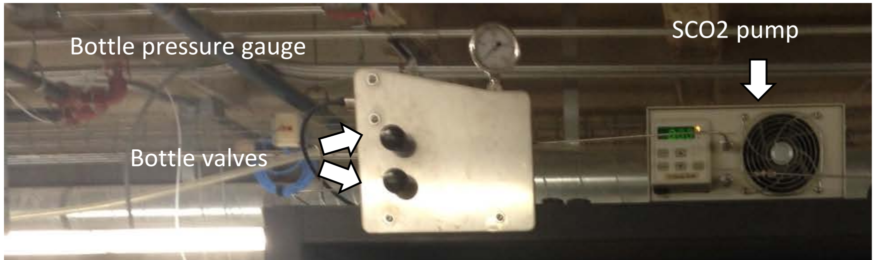
Results

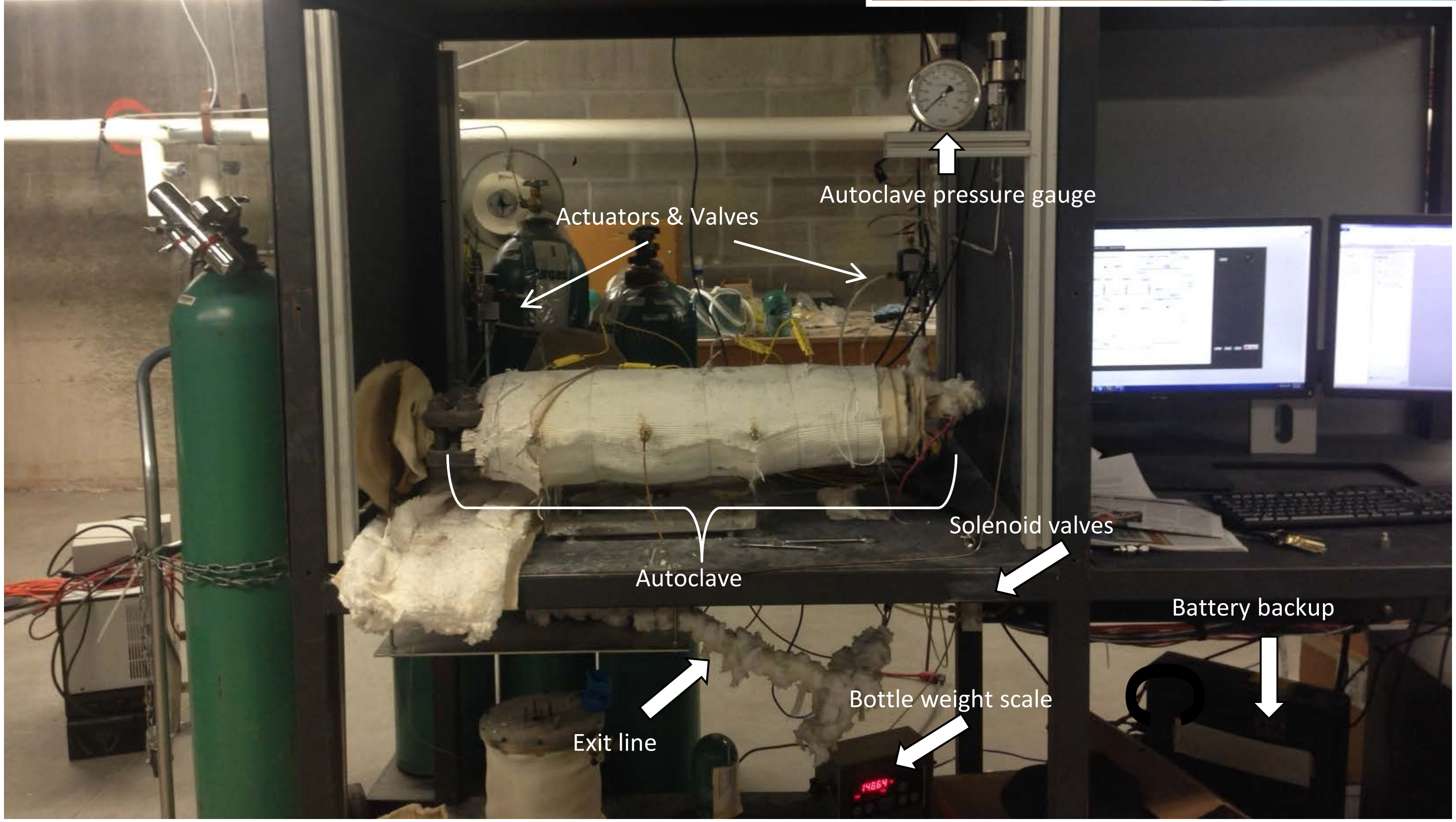
- Mass change
- Surface SEM
- Glancing angle (1.5°) XRD
- Cross-section SEM





System for sCO2 Exposures

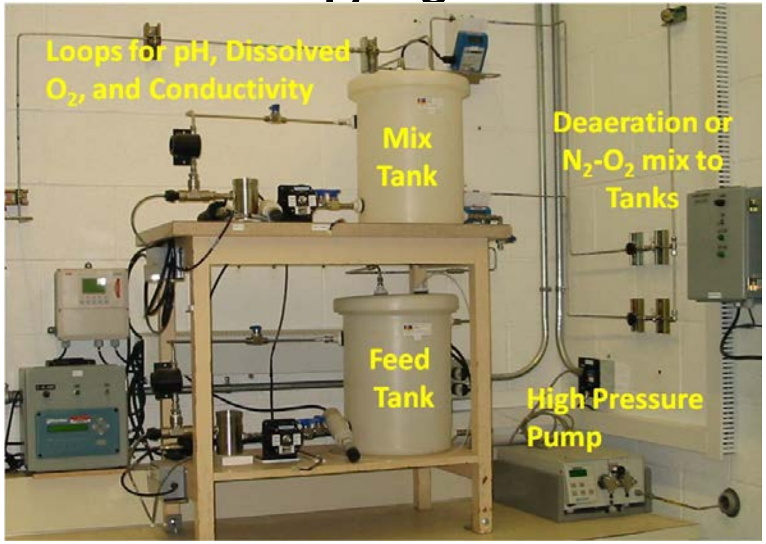




THE UNIVERSITY of WISCONSIN MADISON

USC Autoclave for sH2O Exposures

Feed Water Prep/High Pressure Pump



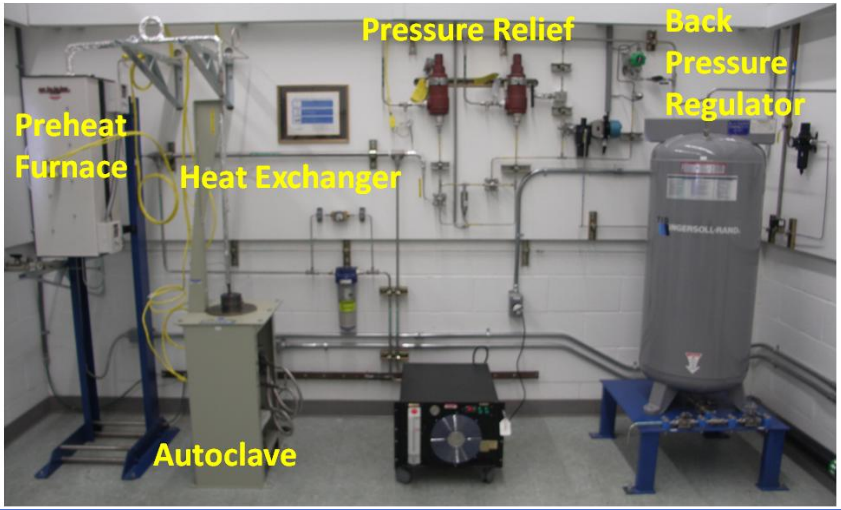
Flow Rate Controlled by Pump

Pressure Controlled by Back Pressure Regulator

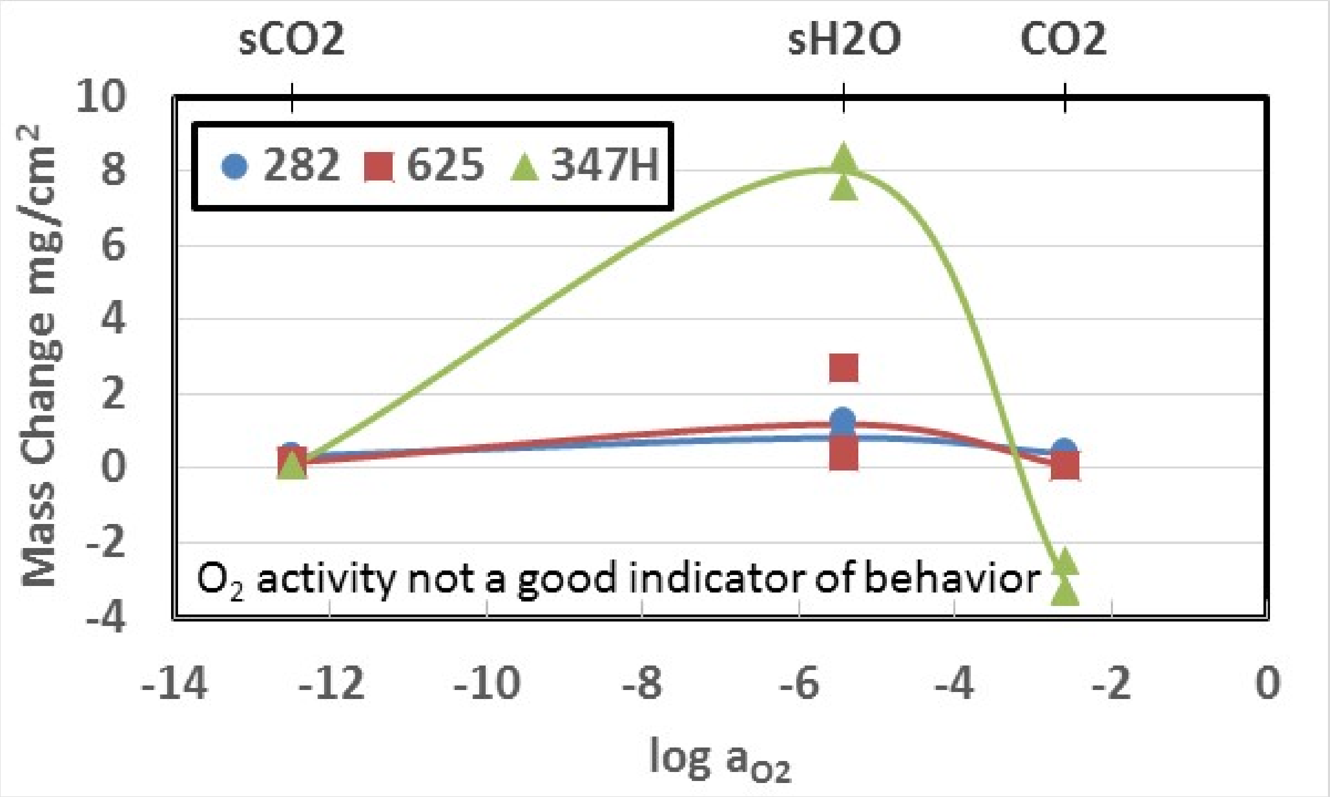
Autoclave

High Pressure Side

Autoclave
1 Liter
6.35 cm ID
31.75 cm L



Mass Change Results



Mass Change, mg/cm^2

Test	282	625	347H
sCO2	0.36	0.16	0.10
	0.33	0.15	0.08
	0.33	0.21	0.08
sH2O	0.87	2.73	8.44
	1.25	0.53	7.58
	0.39	0.31	0.79*
CO2	0.40	0.09	-2.47
	0.42	0.08	-3.33
	0.37	0.07	-3.23

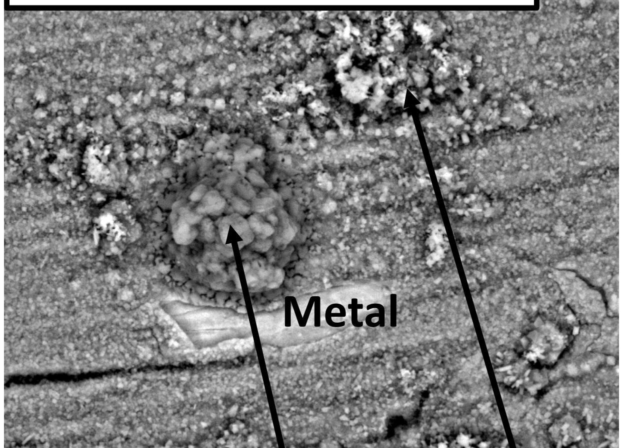
*SEM revealed significant spalling, so not used in plots or k_p calculations

Surface SEM – 347H

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
347H	Bal	17.6	9.1	0.1	0.2	0.3			1.1	0.1	0.1	0.7	0.05

sCO2 +0.08 mg/cm^2

57O-21Fe-16Cr-2Ni*, at%



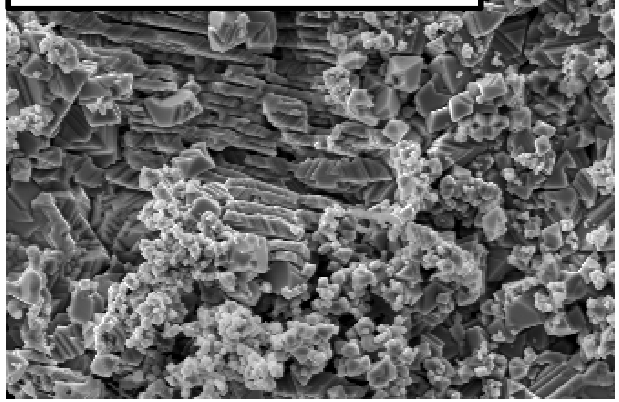
20 µm

Nb-Rich & Low Cr

Mn-Rich & Low Cr

sH2O +7.62 mg/cm^2

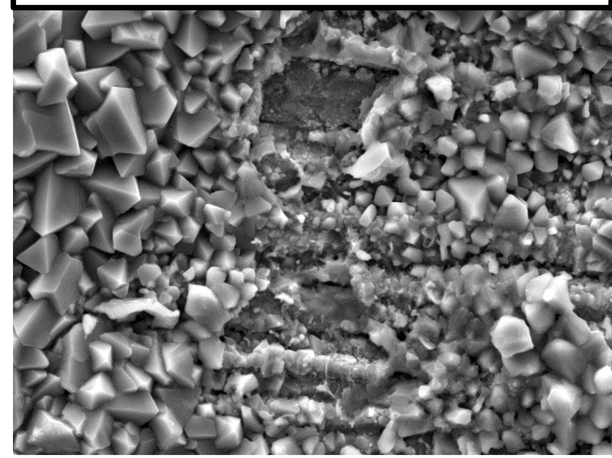
Fe Oxide with small amounts of Cr, Mn, Ni



20 µm

CO2 -3.33 mg/cm^2

61O-35Fe-1Cr-2Ni-1Mn, at%



20 µm

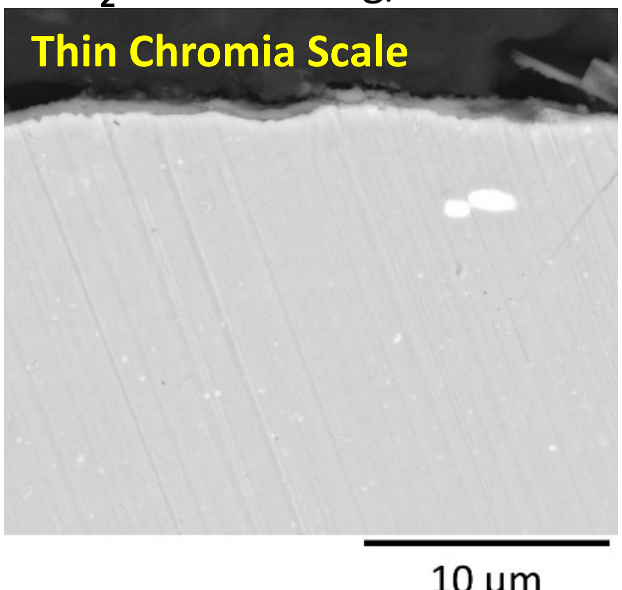
***Glancing angle XRD confirms Cr_2O_3 and M_3O_4 as the primary surface phases**

Chromia with nodule formation of Low Cr oxides
Scale spalling tendencies

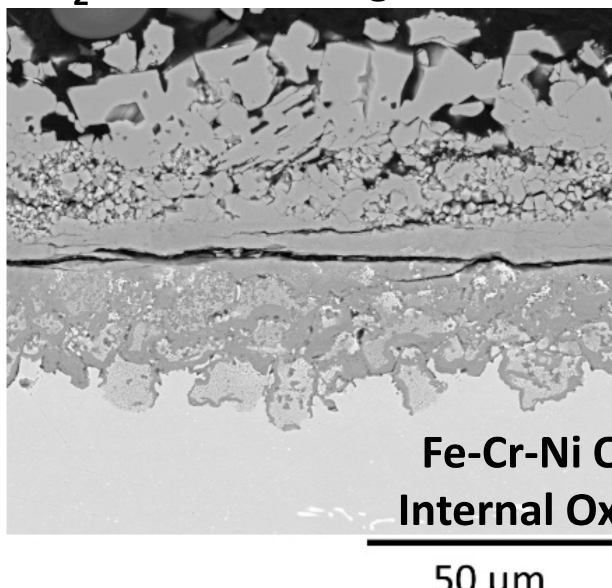
Cross-section SEM – 347H

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
347H	Bal	17.6	9.1	0.1	0.2	0.3			1.1	0.1	0.1	0.7	0.05

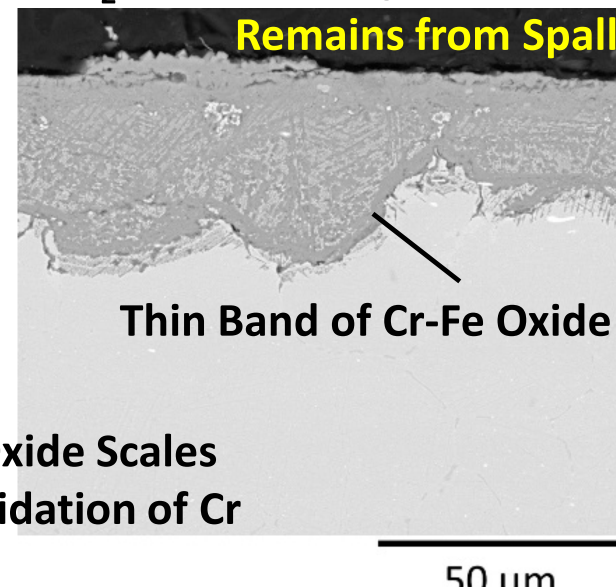
sCO_2 +0.10 mg/cm^2



sH_2O +8.44 mg/cm^2



aCO_2 -2.47 mg/cm^2

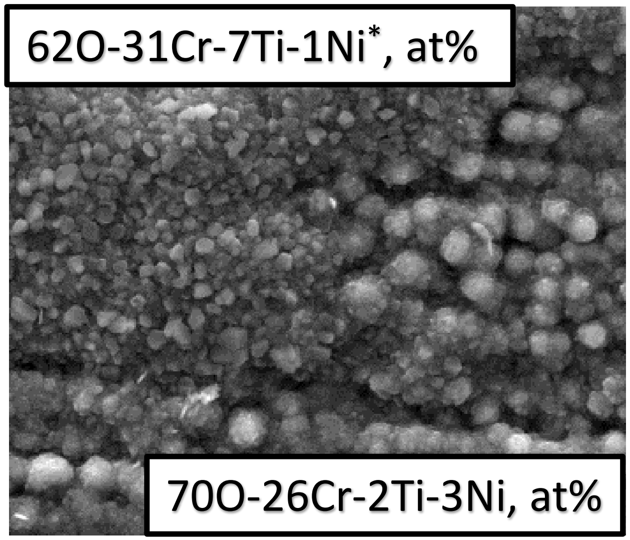


- Protective oxide in sCO_2
- Less protective oxides in sH_2O and aCO_2
- Will show later that this switch from protective oxidation is typical

Surface SEM - 282

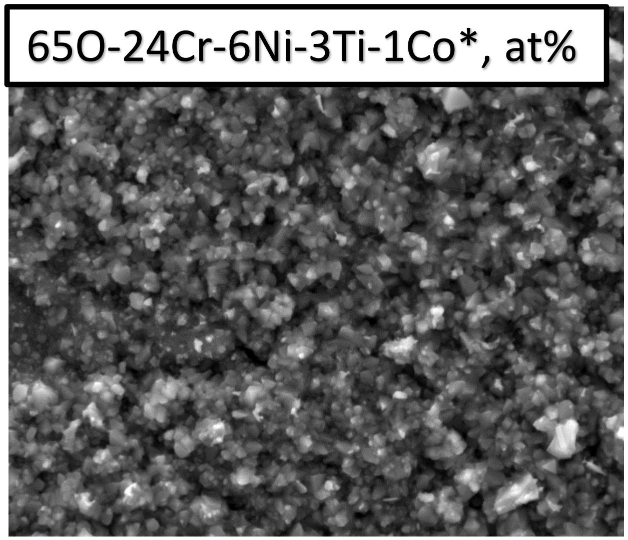
Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
282	0.2	19.4	Bal	10.1	8.7		2.2	1.4					0.06

sCO_2 +0.33 mg/cm^2



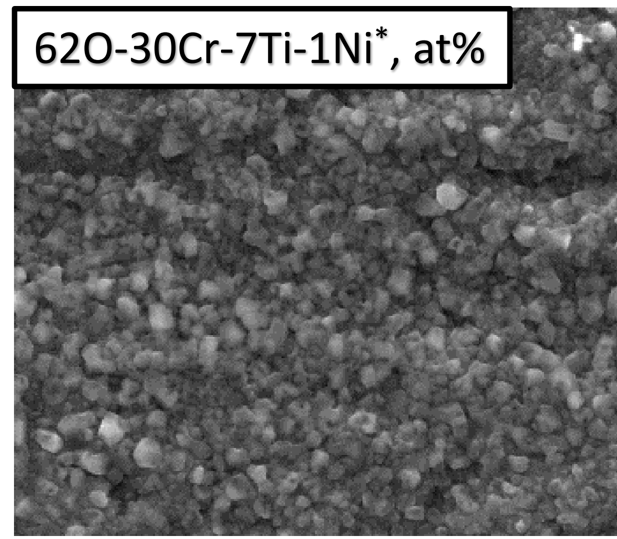
10 µm

sH_2O +1.25 mg/cm^2



10 µm

a**CO_2** +0.42 mg/cm^2



10 µm

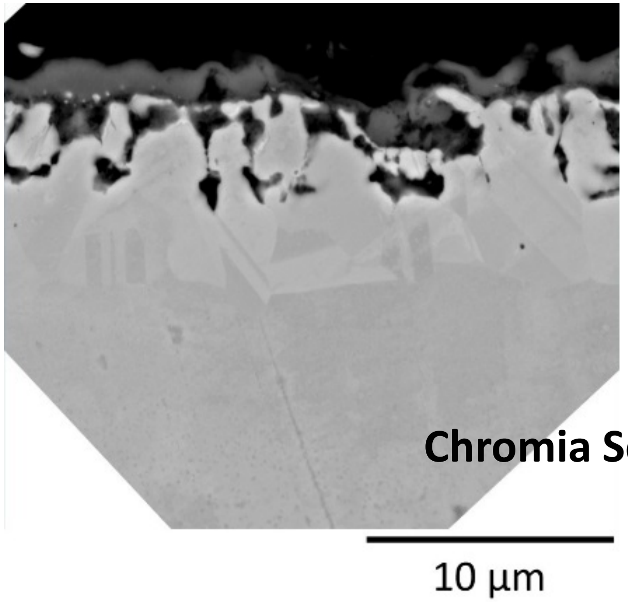
Chromia scale with TiO_2 on outer surface

***Glancing angle XRD confirms Cr_2O_3 and TiO_2 as the primary surface phases**

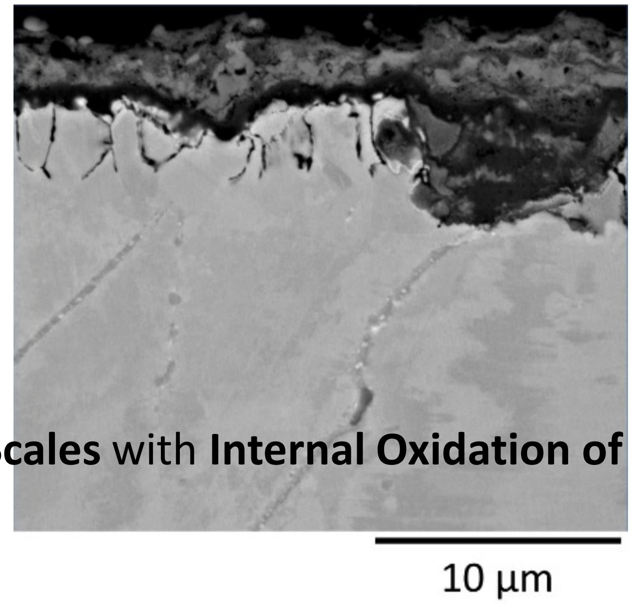
Cross-section SEM - 282

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
282	0.2	19.4	Bal	10.1	8.7		2.2	1.4					0.06

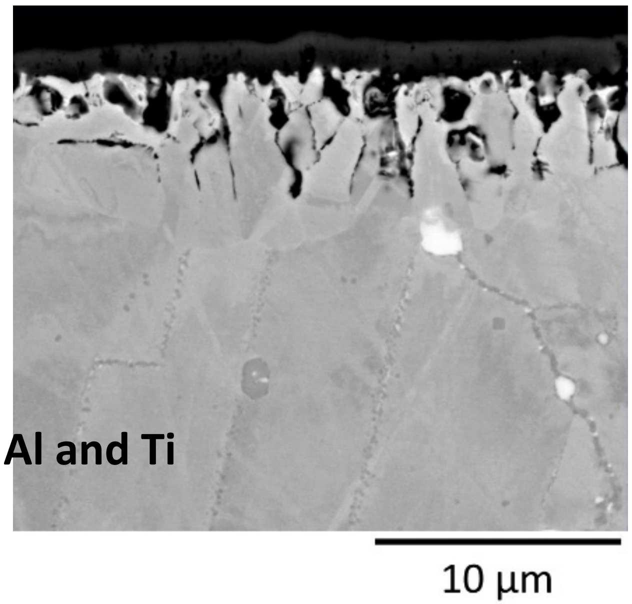
sCO_2 +0.36 mg/cm^2



sH_2O +0.87 mg/cm^2



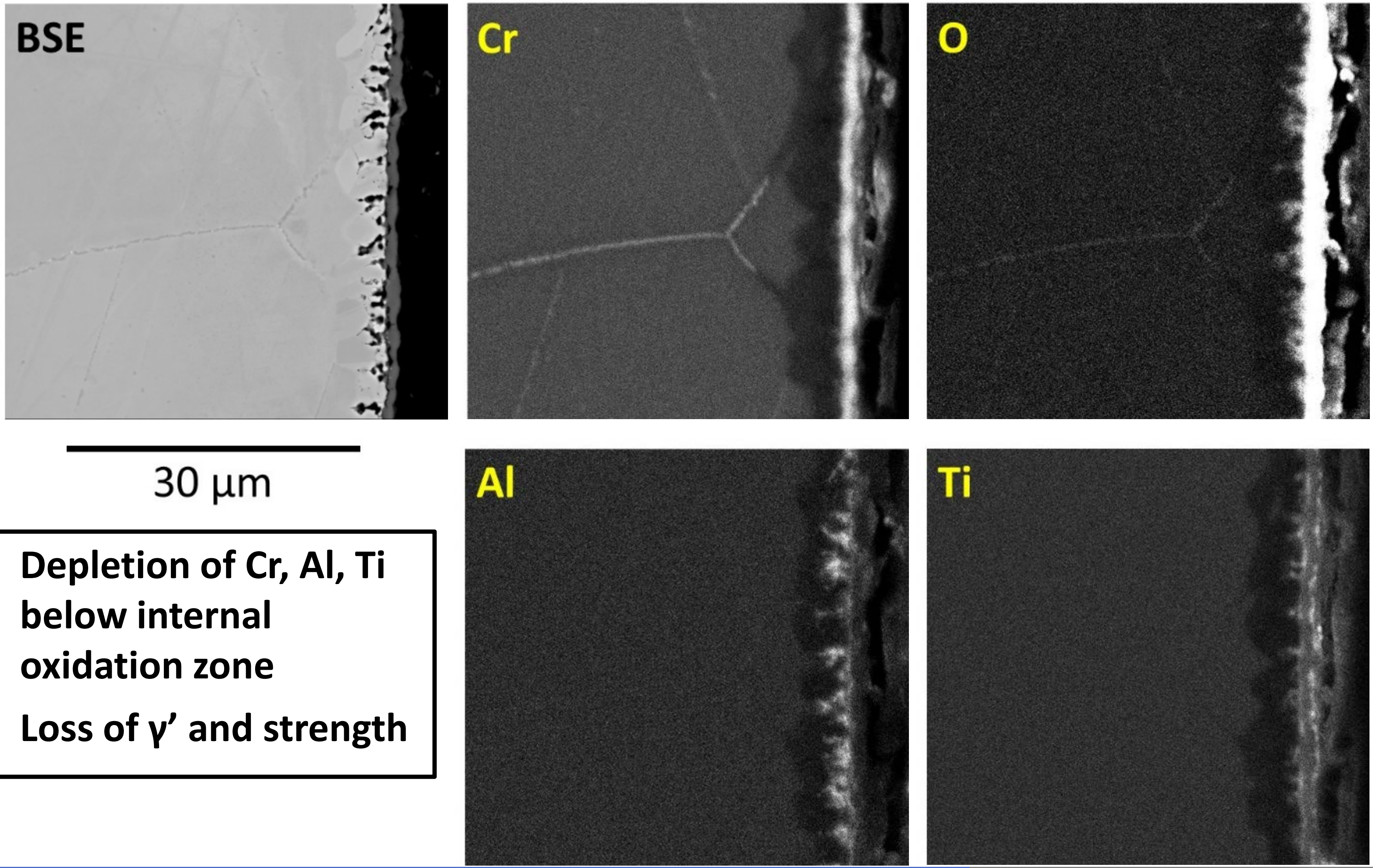
a**CO_2** +0.40 mg/cm^2



Chromia Scales with **Internal Oxidation of Al and Ti**

- **Protective chromia scale thicker in sH_2O**
- **Internal oxidation deeper and more extensive in CO_2**

EDS Mapping of 282 in sCO_2

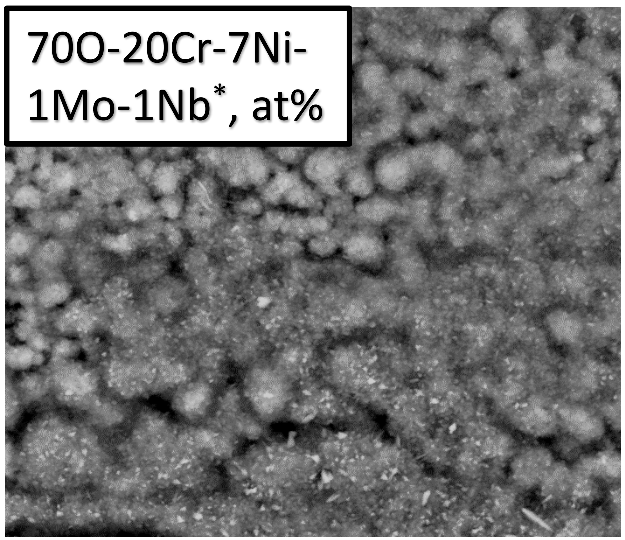


- **Depletion of Cr, Al, Ti below internal oxidation zone**
- **Loss of γ’ and strength**

Surface SEM - 625

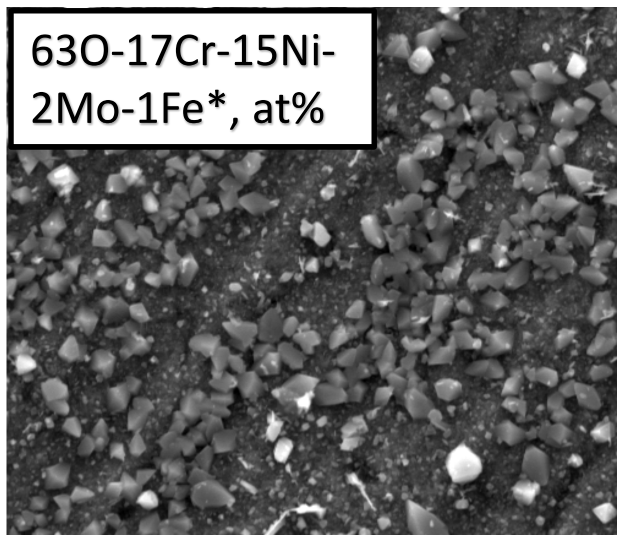
Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
625	3.4	22.1	Bal		8.9	0.1	0.2	0.1	0.1	0.2		3.3	0.05

sCO_2 +0.15 mg/cm^2



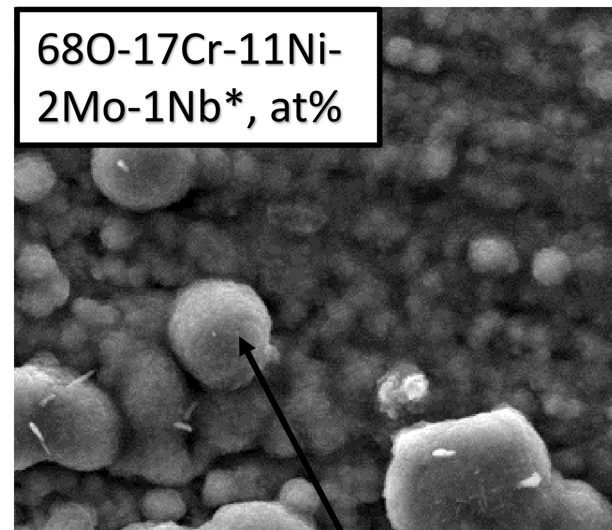
10 µm

sH_2O +0.53 mg/cm^2



10 µm

a**CO_2** +0.08 mg/cm^2



10 µm

71O-28Cr-1Ni-1Nb, at%

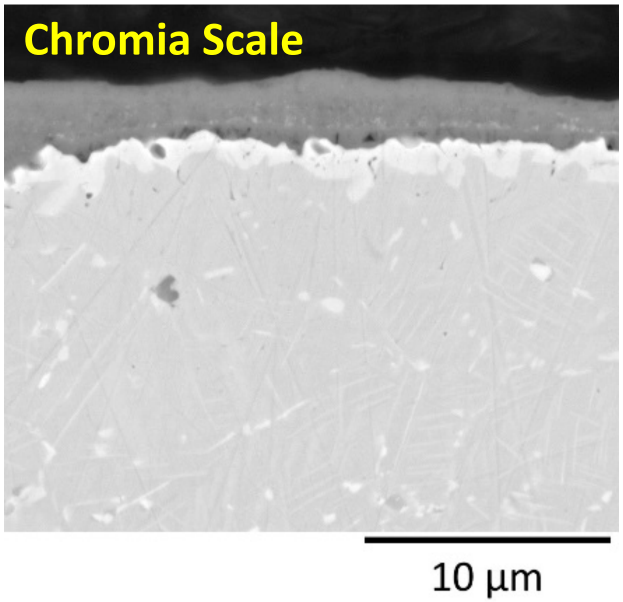
Chromia scale with some underlying alloy Ni content showing in analysis

***Glancing angle XRD confirms Cr_2O_3 as the primary surface phase**

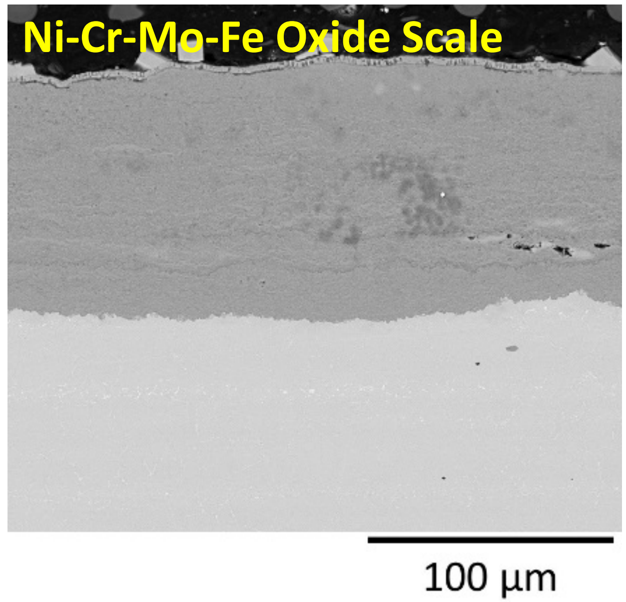
Cross-section SEM - 625

Alloy	Fe	Cr	Ni	Co	Mo	Si	Ti	Al	Mn	Cu	V	Nb	C
625	3.4	22.1	Bal		8.9	0.1	0.2	0.1	0.1	0.2		3.3	0.05

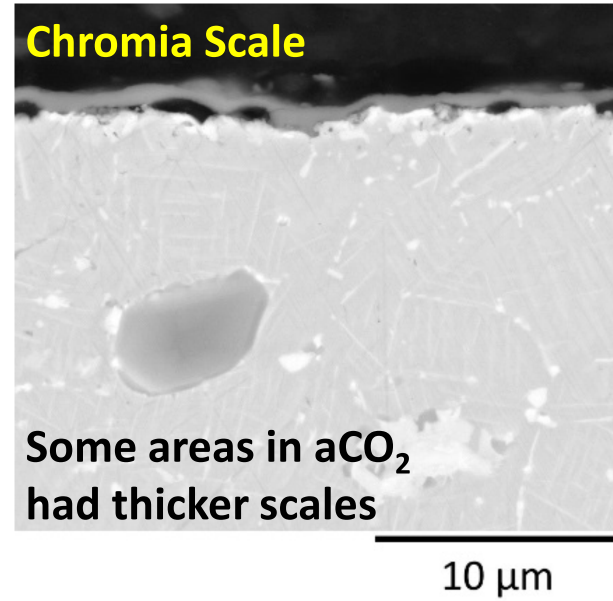
sCO_2 +0.16 mg/cm^2



sH_2O +2.73 mg/cm^2



a**CO_2** +0.09 mg/cm^2



- **Other 2 replicates in sH_2O had much smaller mass gains and chromia was detected on the surface by XRD**
- **Bright second phases are Nb/Mo rich**

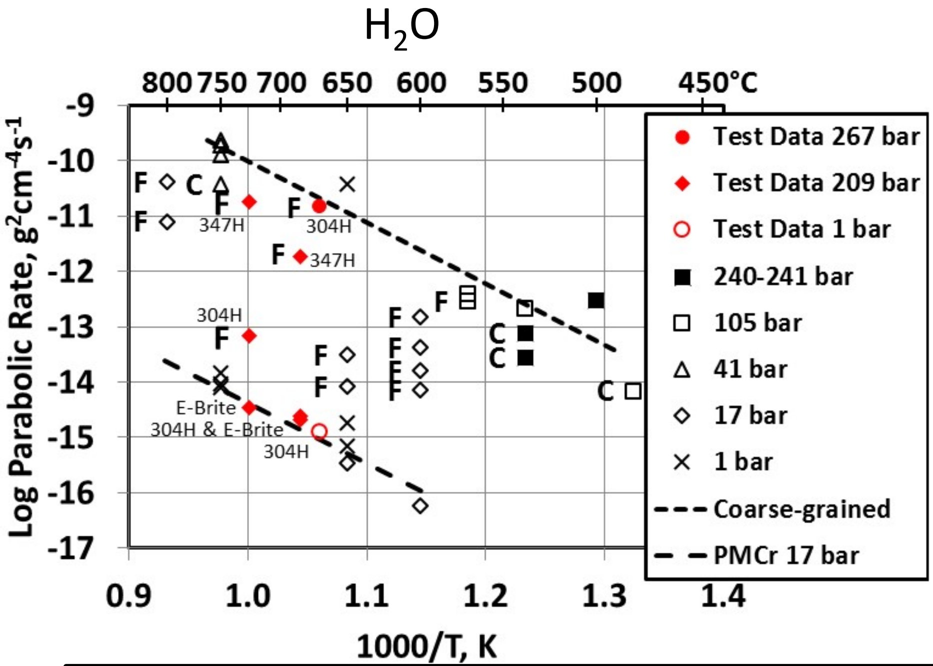
Parabolic Behavior

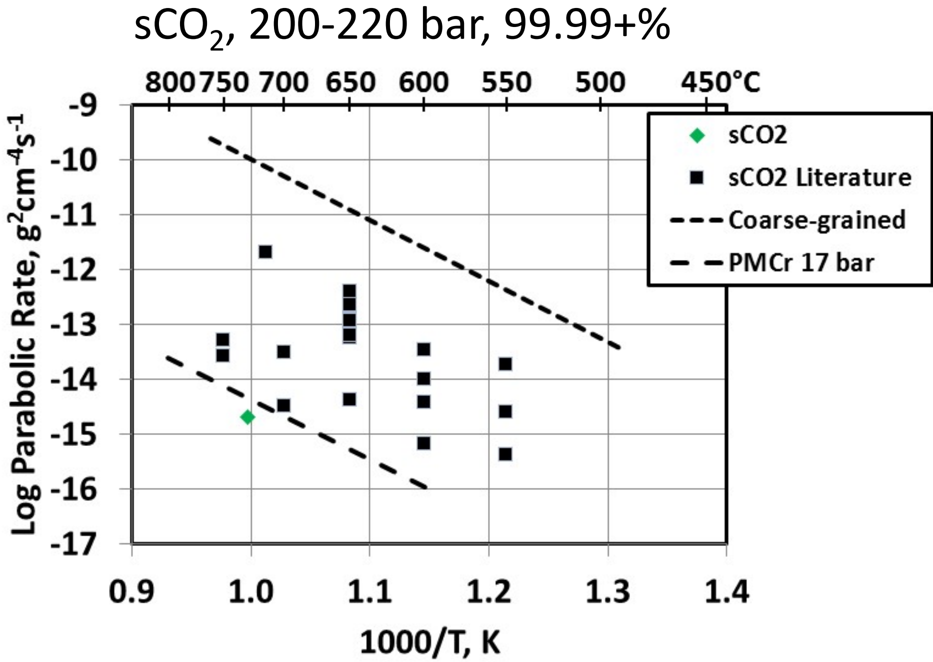
- **Parabolic rate constants were estimated using**

$$k_p = \frac{\Delta M^2}{2t}$$

  – Where ΔM is the mass change and t is the time
- **Time series tests are planned to verify such behavior**
- **Not applied in cases where spalling was evident**

300 Series (18Cr-8Ni)/E-Brite



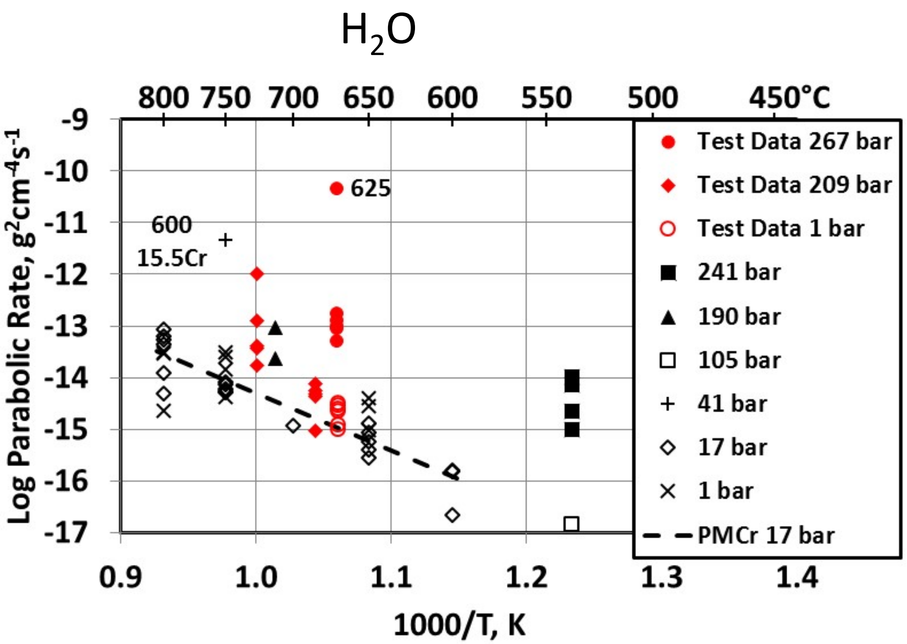


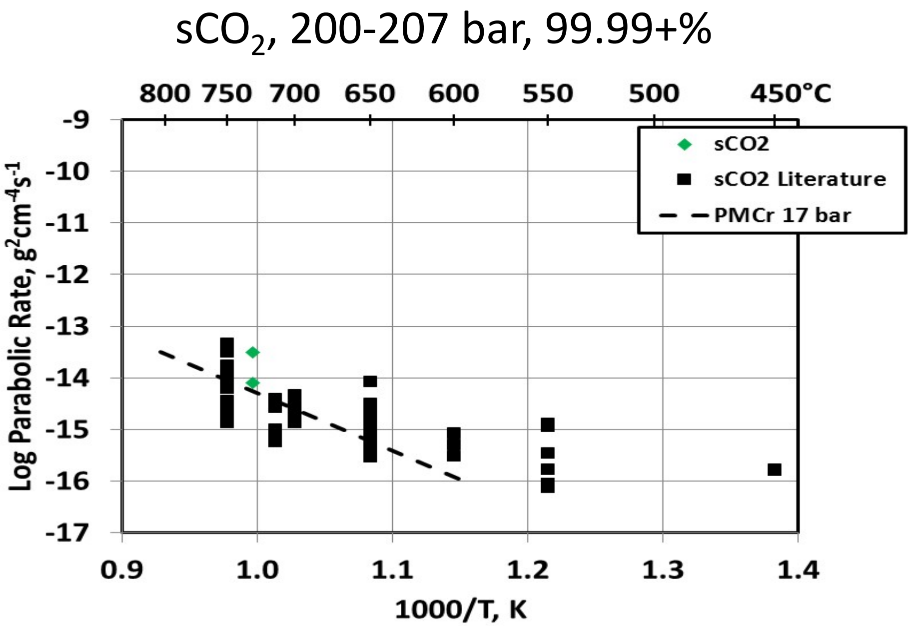
- **Similar behavior in both sH_2O and sCO_2 (but note the gap in sCO_2)**
- **A variable increase in oxidation of fine-grain alloys with pressure**
- **Variability arises from Fe-rich nodule formation and lateral growth to disrupt protective chromia scale**

H_2O adapted from the compilation of Wright & Dooley (2010), plus Holcomb (2014) and Holcomb (2016)
sCO_2 adapted from Furukawa (2011), Cao (2012), Pint (2014), Lim (2008), Olivares (2015), Dunlevy (2007), and Lee (2015)

Note: PMCr forms pure chromia scale

Ni-base Alloys



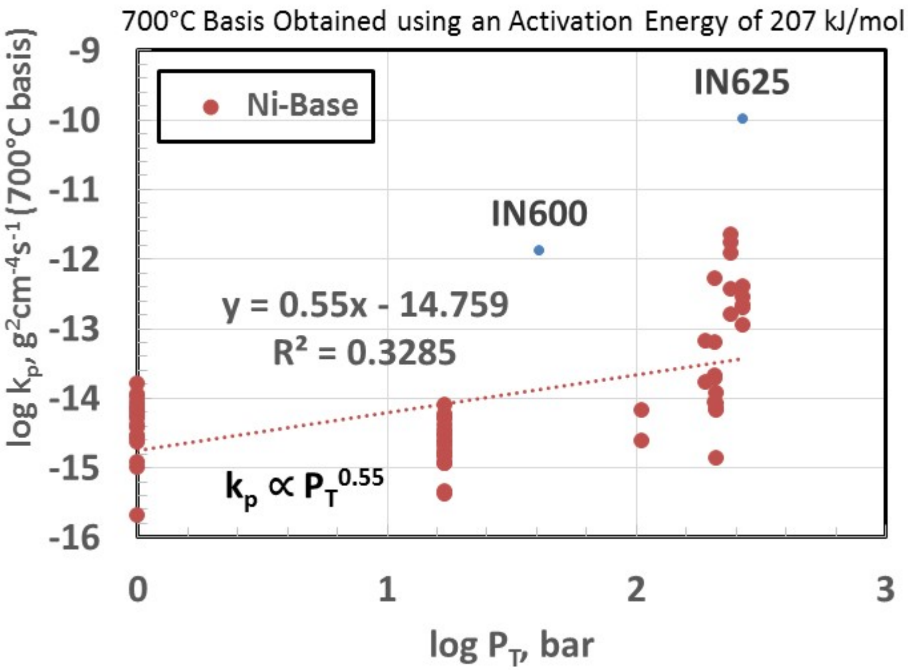


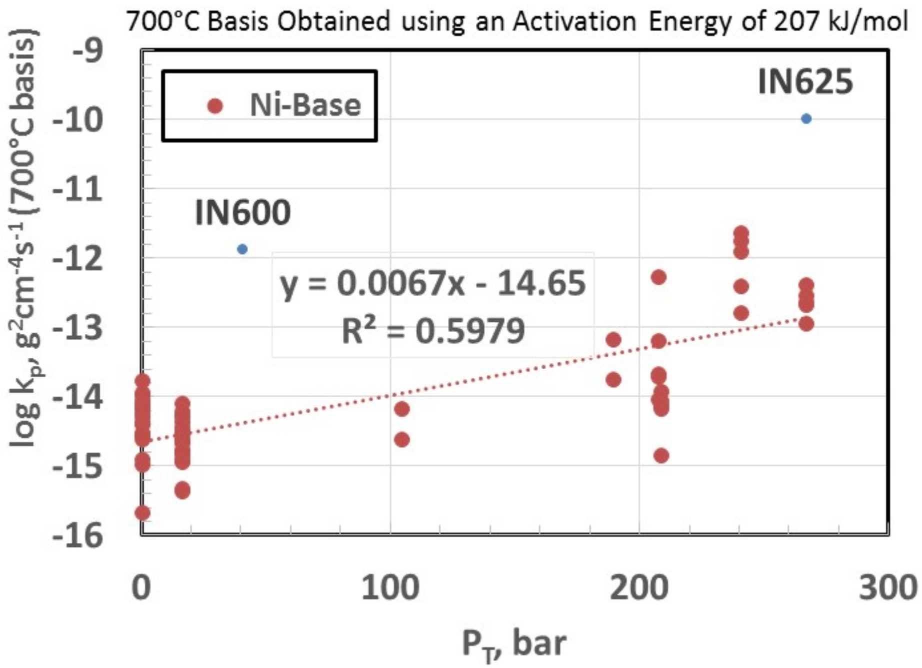
- **The highest pressures in sH_2O show an increased oxidation rate**
- **No evidence of increased oxidation rates at high pressure in sCO_2 (at temperatures of interest)**
- **625 has ~8000 h in a steam superheater at ~713°C/190 bar with good performance Knödler (2014)**

H_2O adapted from the compilation of Wright & Dooley (2010), plus Knödler (2014), Holcomb (2014) and Holcomb (2016)
sCO_2 adapted from Pint (2014), Dunlevy (2007), Lee (2014, 2015), Firouzdor (2013), Dheeradhada (2015), and Mahaffey (2015)

Note: PMCr forms pure chromia scale

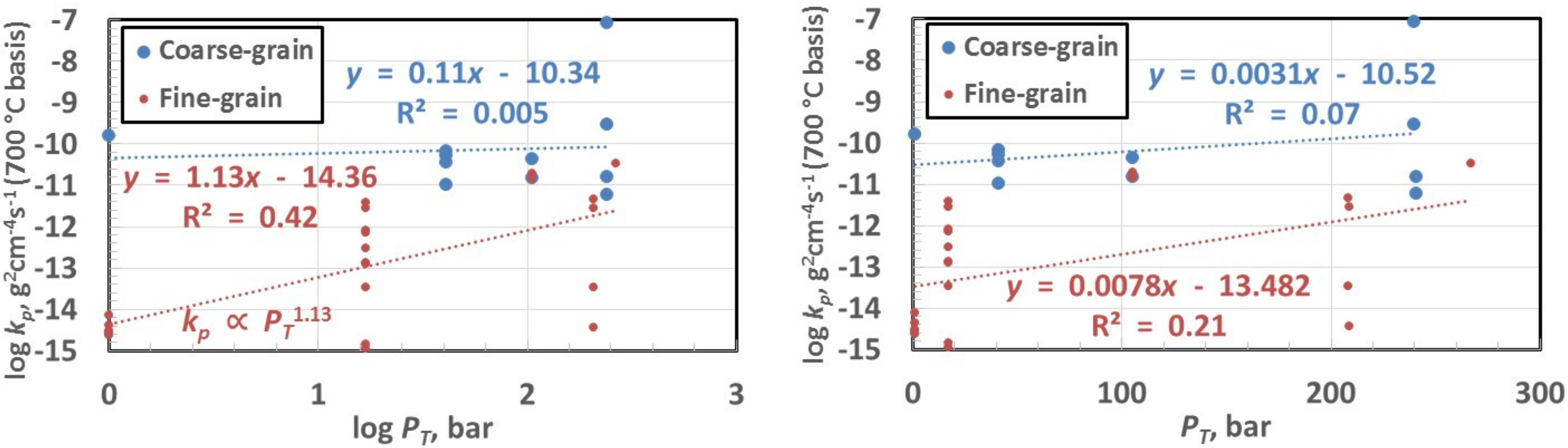
Effect of Pressure in Steam for Ni Alloys





- **Arrhenius behavior used to translate oxidation data to a 700°C basis**
- **Oxide defect models tend to predict $k_p \propto P_T^X$**
- **Better fit with $\log k_p \propto P_T$**

Effect of Pressure in Steam for Austenitics



- **Arrhenius behavior used to translate oxidation data to a 700°C basis**
- **Oxide defect models tend to predict $k_p \propto P_T^X$**
- **Fine Grain Alloys: Better fit with log $k_p \propto$ log P_T ($k_p \propto P_T^{1.13}$)**
- **Coarse Grain Alloys: No measurable dependence on pressure**

Summary/Conclusions

- **High Pressure sH_2O and sCO_2 Exposures**
  - Over 200 bar and 726-730°C
- **Preliminarily Results Indicate:**
  - Nickel-base alloys
    - Unlike in sH_2O, there is no evidence of significant increased oxidation rates at high pressure in sCO_2
  - Fine-grain austenitic steels
    - Similar increase in oxidation with pressure in both sH_2O and sCO_2
    - More Fe-rich oxide nodule formation with pressure
    - Variability in results associated with nodule formation/lateral growth
  - Coarse-grain austenitic steels
    - No measurable increase in oxidation with pressure in sH_2O
    - Not examined in sCO_2