Advanced Materials Issues for Supercritical CO_2 Cycles (FEAA123)

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Acknowledgments

sCO_2: Jim Keiser - autoclave design
Mike Howell - construction and operations
Robert Brese - UTenn PhD student

G. Garner, M. Stephens - oxidation experiments
T. Lowe - characterization;   T. Jordan - metallography
D. W. Coffey - TEM specimen preparation, FIB
D. Leonard - EPMA

Alloys: Haynes, Special Metals, ATI, Sumitomo, Sandvik...

Research sponsored by: U. S. Department of Energy, Office of Fossil Energy, Crosscutting Research Program

Project is focused on studying materials in direct-fired supercritical CO_2

Goals and Objectives

Address materials issues for scaling up direct-fired sCO_2 Brayton cycle systems to higher temperatures for increased efficiency and larger size for commercial power production

Milestones

FY16

Data analysis on effect of temperature on reaction rates	6/2016 (done)
1 and 25 bar testing at three different impurity levels	2 of 3 complete
Complete construction of impurity effects test rig	in progress

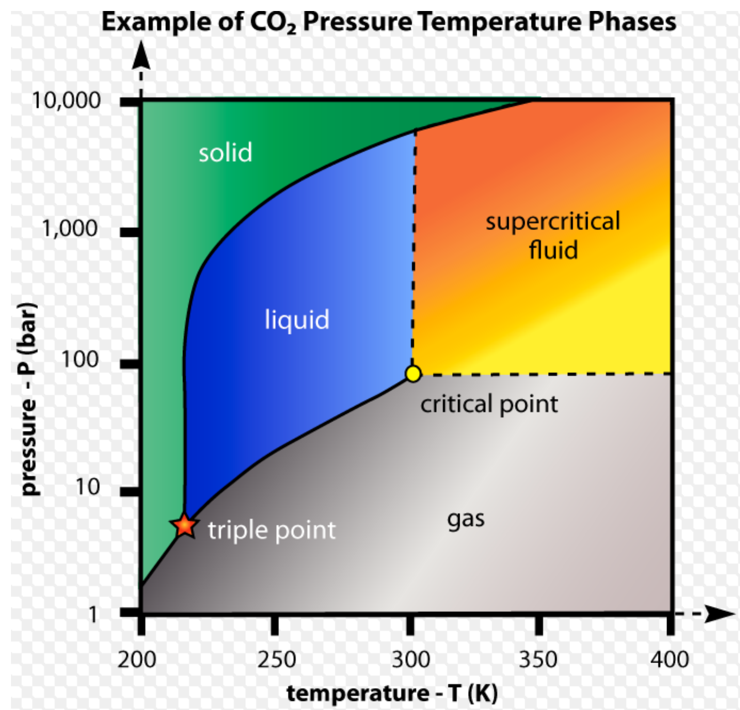
FY17

Complete analysis of reaction products as a f(T,P,...)	3/2017
Complete 500h, 300 bar exposures at 3 impurity levels	6/2017
Complete 2,500 h sCO_2 at a high H_2O content	9/2017

Why use supercritical CO_2?

Potential supercritical CO_2 (sCO_2) advantages:

- no phase changes
- high efficiency
- more compact turbine
- short heat up
- less complex
- lower cost (?)



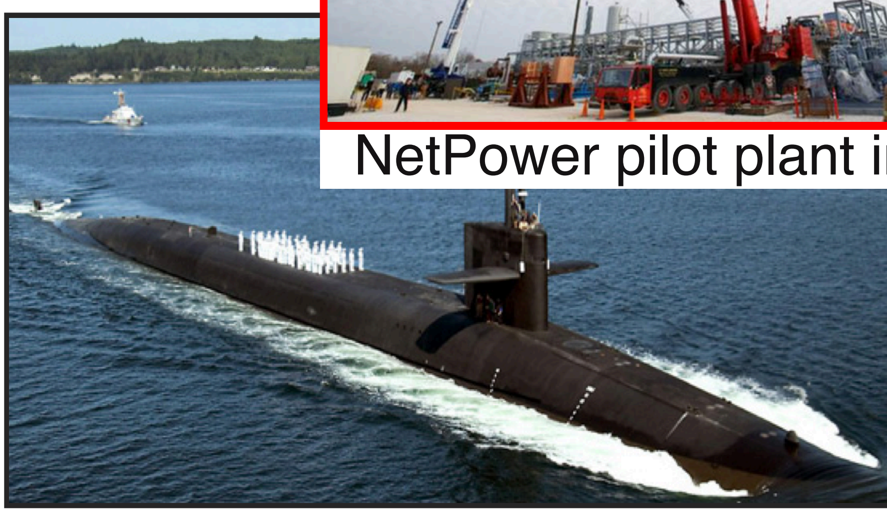
Direct- and indirect-fired sCO_2 Brayton cycles for:

- fossil energy (coal or natural gas)
- concentrated solar power
- nuclear (paired with sodium for safety)
- waste heat recovery/bottoming cycle

Many possible applications

Smaller fossil systems

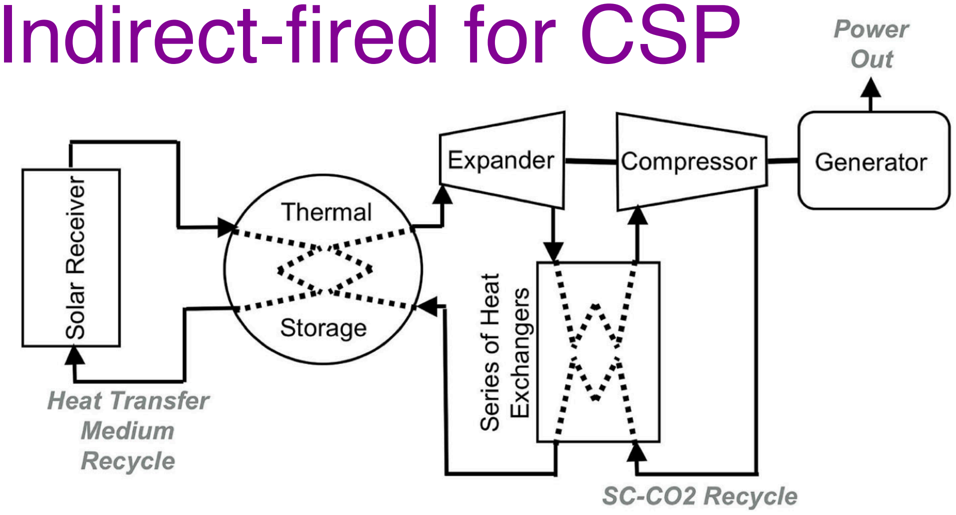
NetPower pilot plant in Texas



7MW Echogen, waste heat

Direct-fired system of special interest

Indirect-fired for CSP



Closed loop of relatively pure CO_2
- primary HX (>700°C)
- recuperators (<600°C)

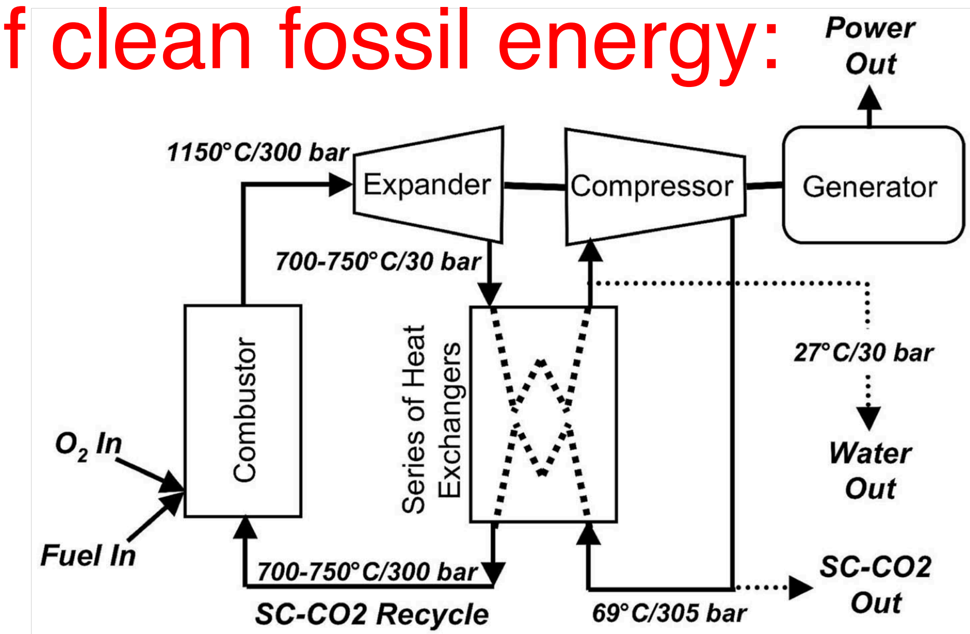
Also, waste heat recovery, bottoming cycle for Fossil

Direct-fired (e.g. Allam cycle by Netpower) offers the promise of clean fossil energy:

In: natural gas + O_2

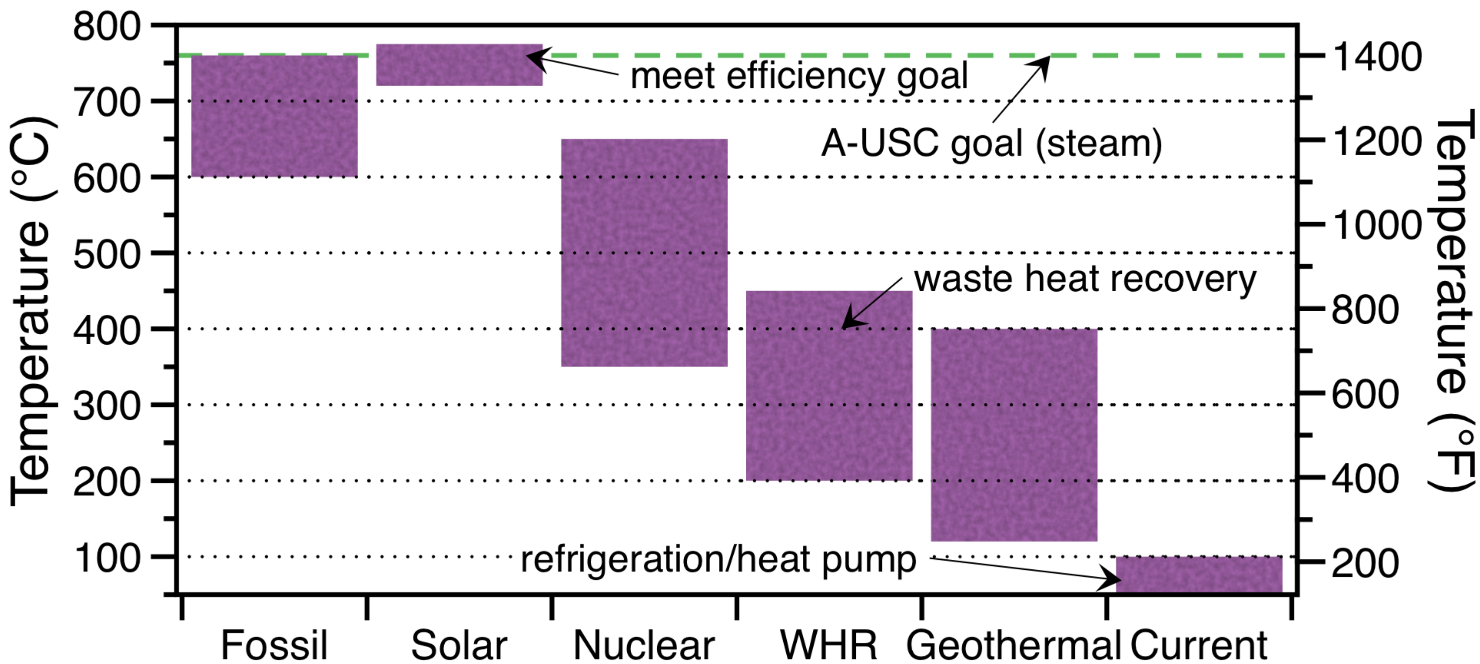
Impurities: ~10%H_2O ~1%O_2, CH_4?, SO_2?

Out: CO_2 for EOR (enhanced oil recovery)



Different temperature targets

- Uncertainty about peak T for sCO_2 applications
- Fossil energy interest for power generation
  coal/natural gas: replace steam with closed cycle
- Direct-fired system may have very high peak T's:
  1150°C combustor
  750°C/300 bar turbine exit
- Indirect-fired: Primary HX operating at higher T

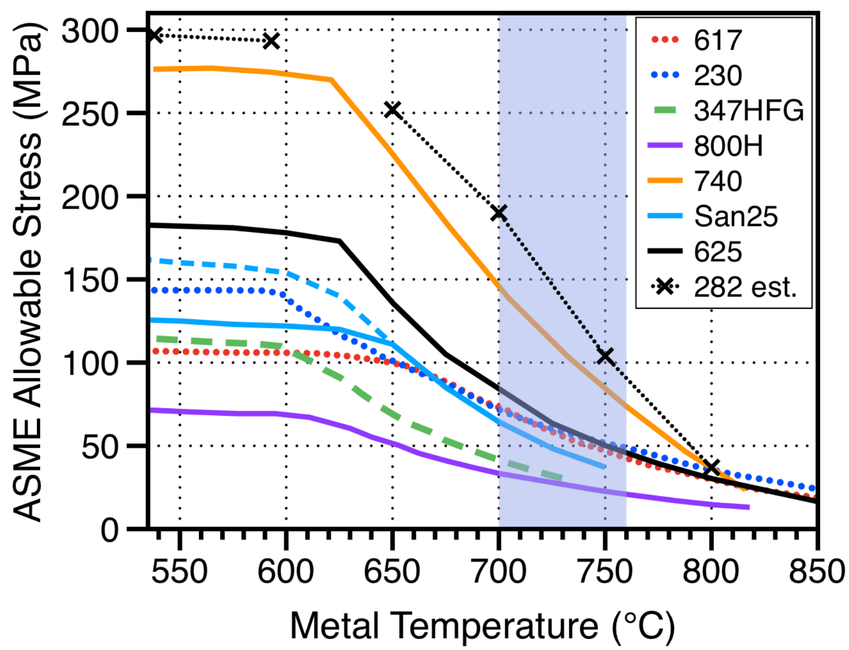


Materials for sCO_2 ~ A-USC steam

Temperatures (600°-750+°C) and pressures:
- challenge for strength
- limited number of materials available
- ! Adv. Ultra-supercritical (steam) same T range

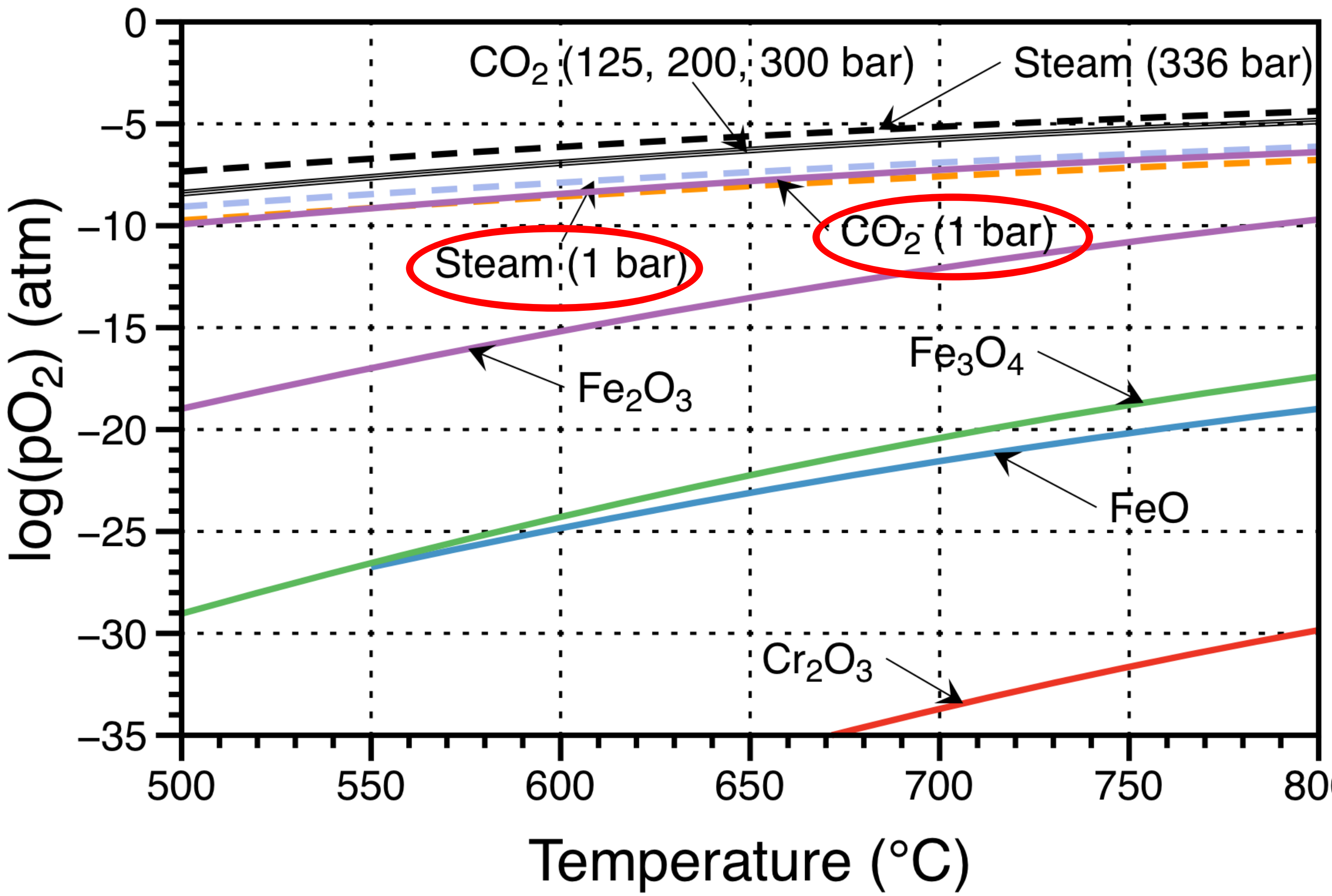
Limited materials choices:
- capability
- ASME Boiler & Pressure Vessel Code:

Materials are key to:
- reliability
- availability
- maintainability



Oxygen levels similar in steam/CO_2

Factsage calculations: CO_2 <-> $1/2O_2$ + CO



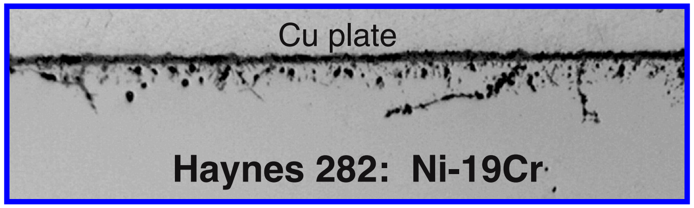
Similar pO_2 levels in steam & CO_2, higher at 200bar

All oxides of interest are stable

Why worry about 740/282?

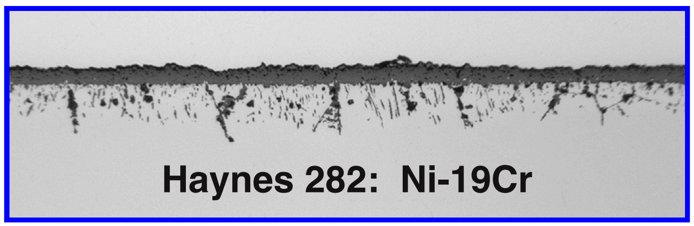
5-10kh at 800°C still form thin reaction product in air

$CO_2 = CO + 1/2O_2$ $C(s) + O_2(g) = CO_2$

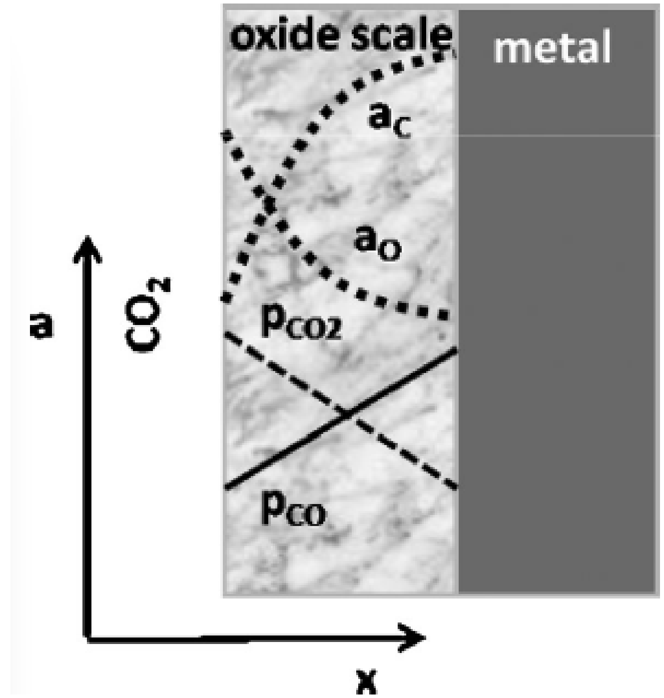


800°C, 5,000h in air+10%H_2O

10 µm



800°C, 10,000h in dry air
both exposures: 500h cycles
Al+Ti internally oxidize beneath
Cr_2O_3 oxide scale



from Young, et al. 2011

Gas only: C activity (a_C) relatively low, favors oxidation

C in alloy ties up Cr, not available to form protective scale

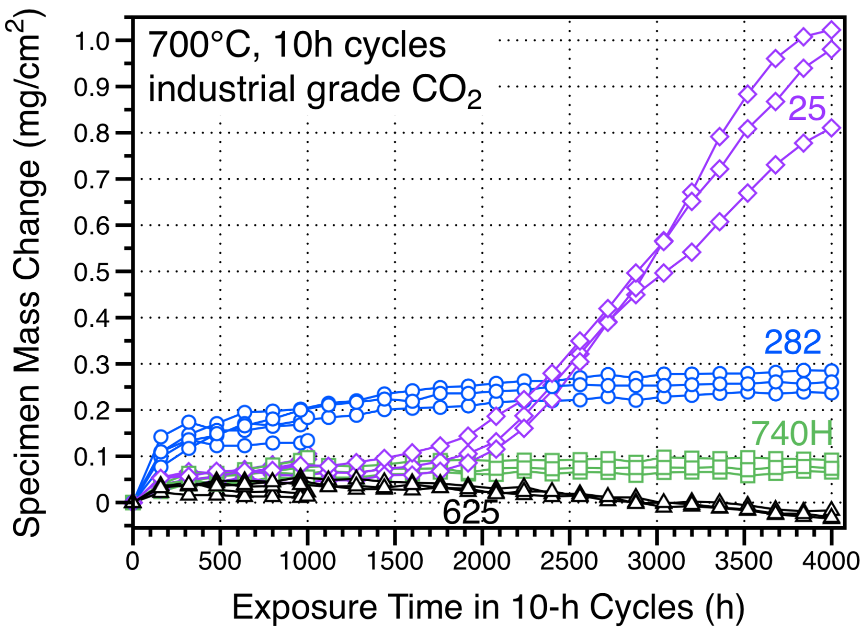
McCoy 1965: 600 & 18Cr-8Ni SS internally carburized in 1bar CO_2

High a_C predicted - what about NiCr in sCO_2 + 1%H_2O?

Maybe we should be worried

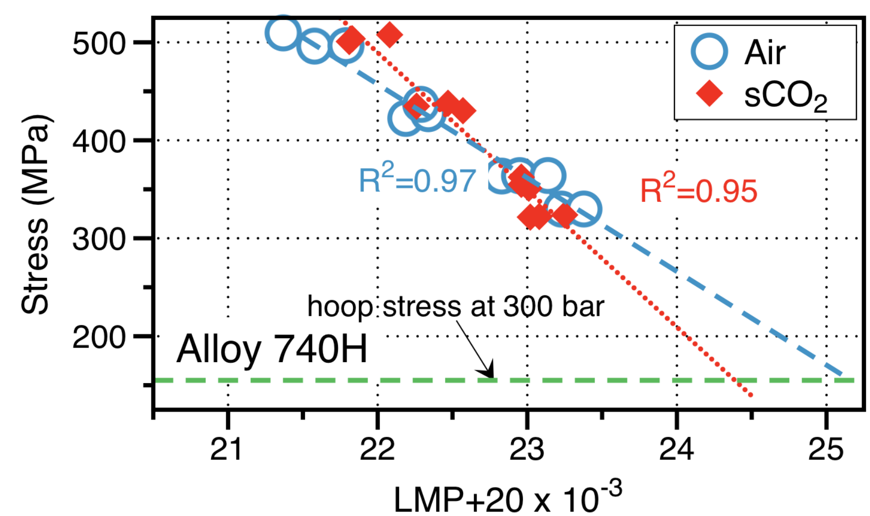
Year 1 results from concentrated solar power study

Laboratory simulation of CSP duty cycle (700°C, 1 bar)



Sanicro 25 (Fe-22Cr-25Ni-3W-3Cu) showed accelerated mass gain (Fe_2O_3) after ~1500 h in 10-h cycles in industrial grade CO_2

Tube creep rupture testing in supercritical CO_2

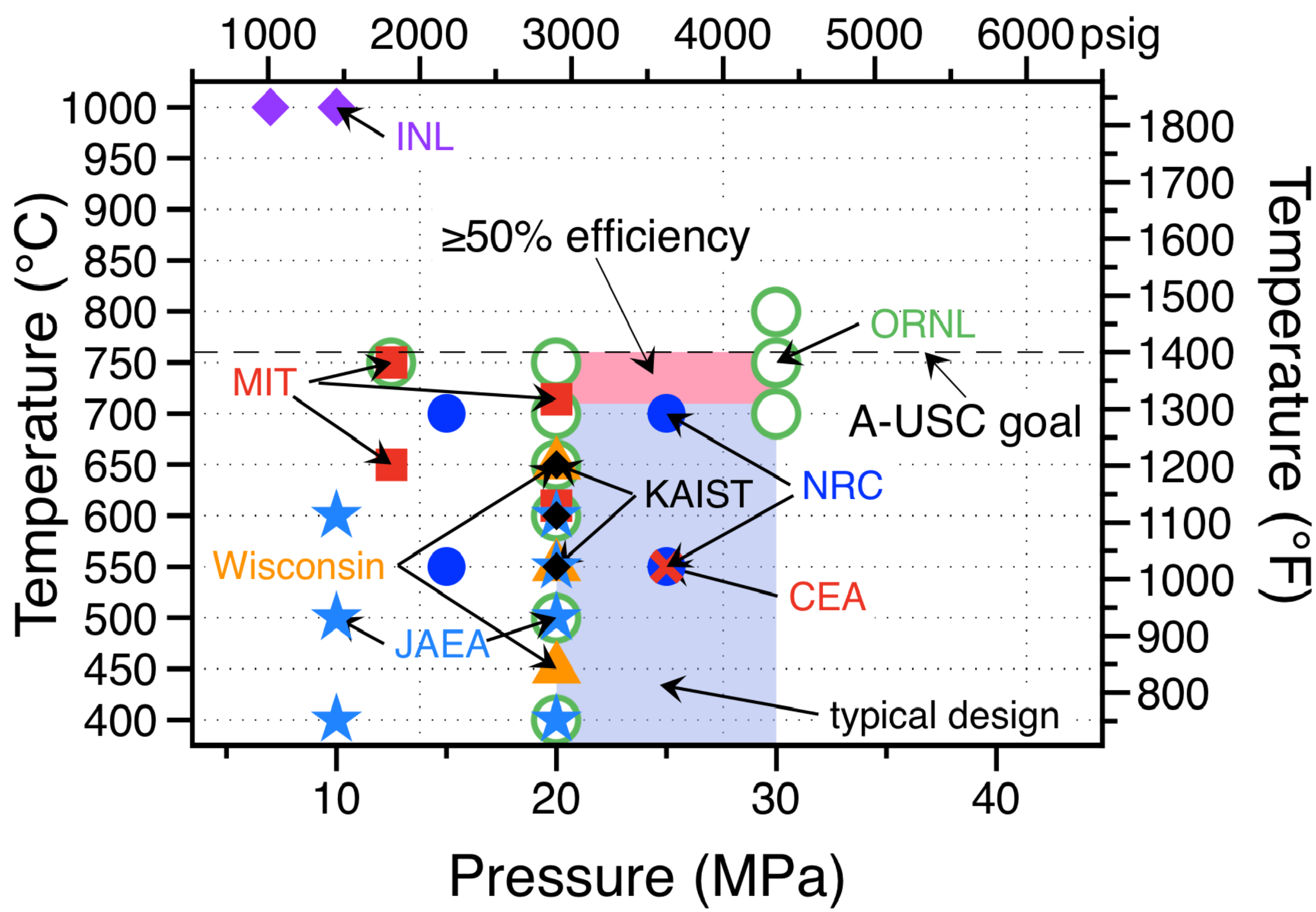


LMP = T(in K) (20 + log(time in h))

Ni-base 740H showed decreased creep rupture lifetime at 750°C at longest exposure time in sCO_2 compared to high pressure air

Relatively little prior sCO_2 work

Especially at >650°C and >200 bar



Several groups active in the past 10 years

U. Wisconsin group has published the most results

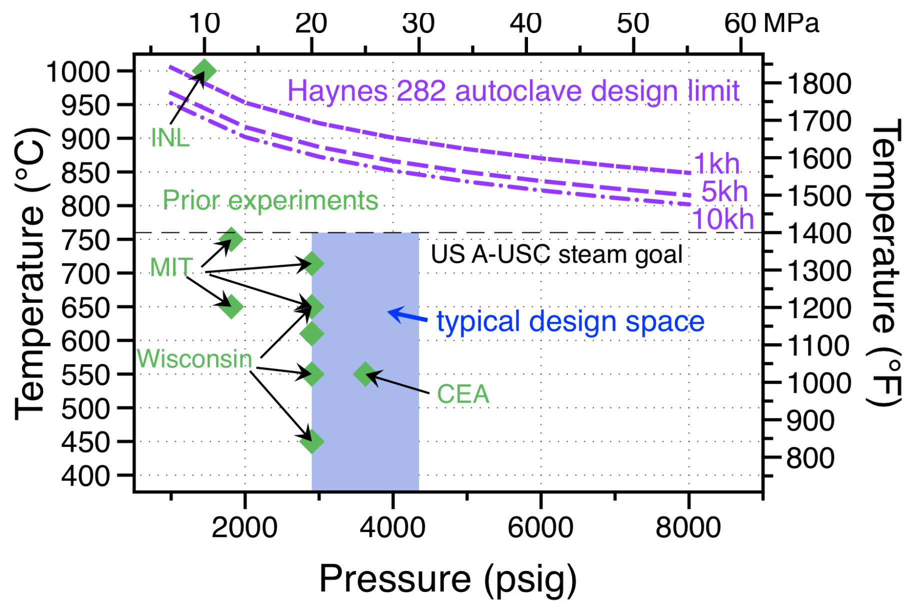
Temperature/pressure limited by autoclave design

ORNL sCO_2 rig finished in 2014

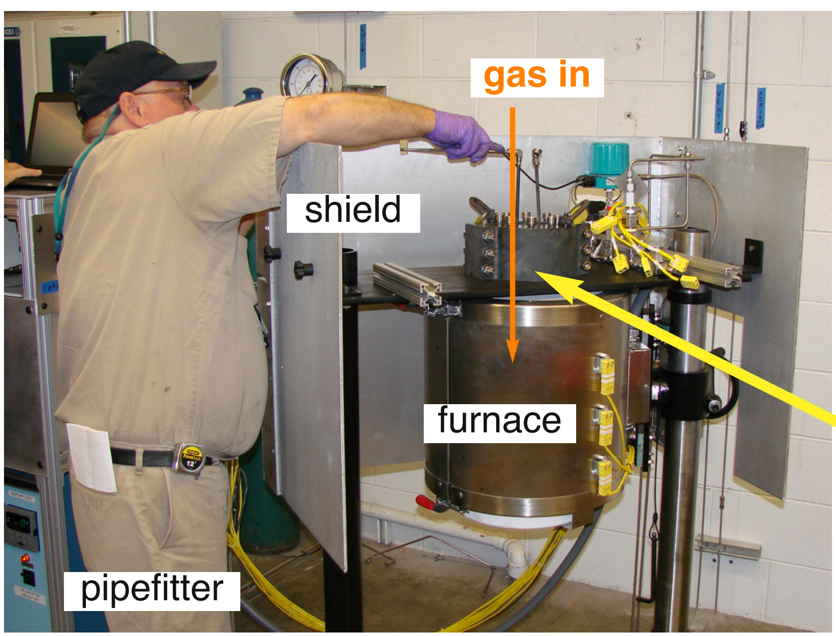
- ORNL design team: 100+ years of experience
- Haynes 282 autoclave

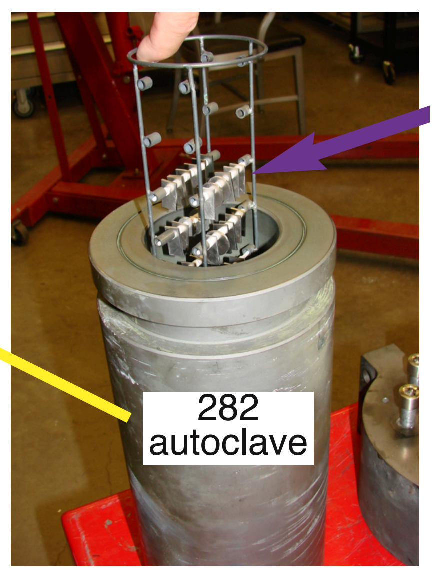
  152mm (6”) dia.

  1ml/min flow

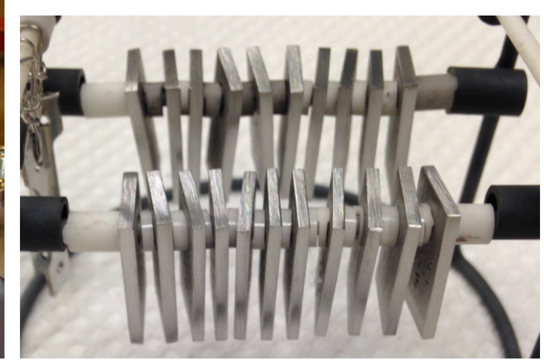


ORNL sCO_2 rig:



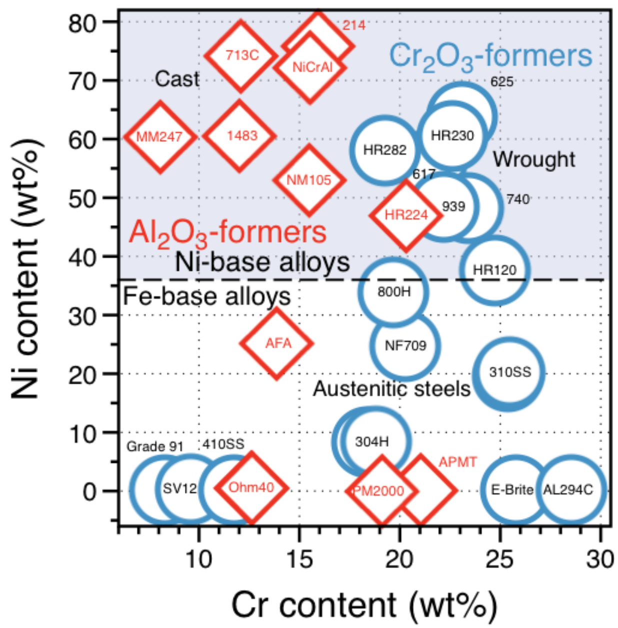


specimen holder



Range of alloys exposed

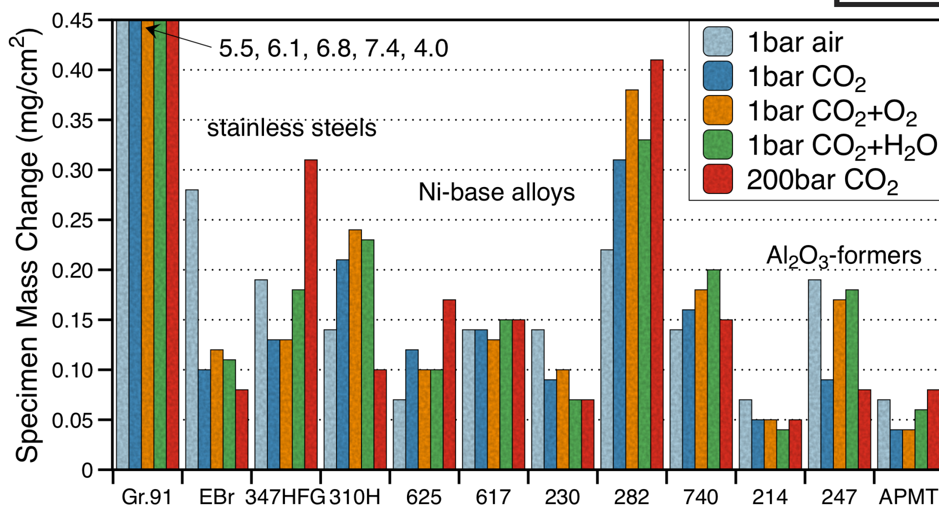
Narrowing scope as project progresses



2014: 30 alloys screened

2015: 12 alloys studied

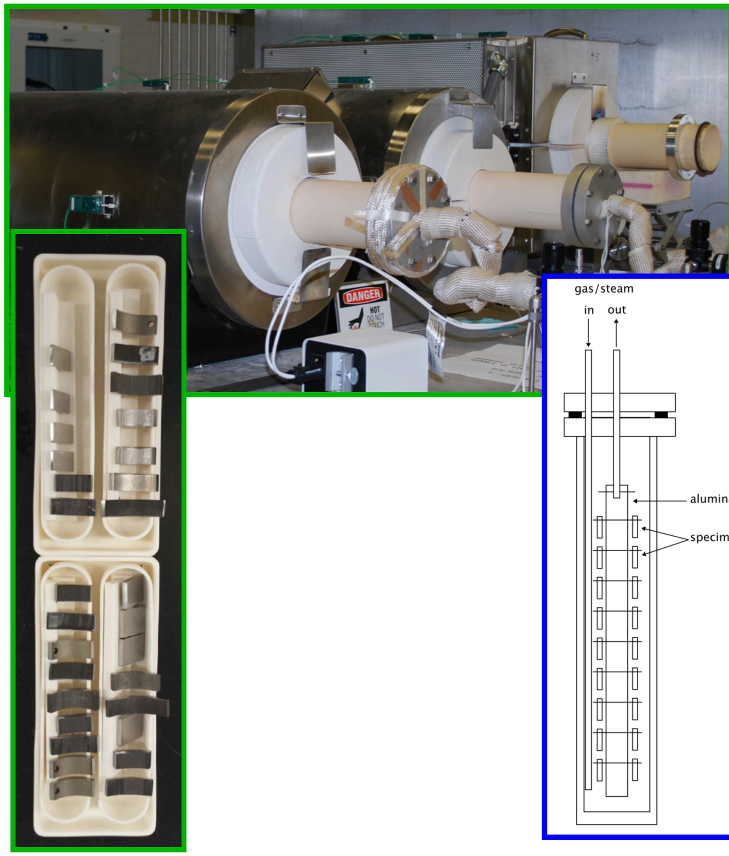
2016-17:
6 alloys:
310HCbN
617
230
740H
282
247



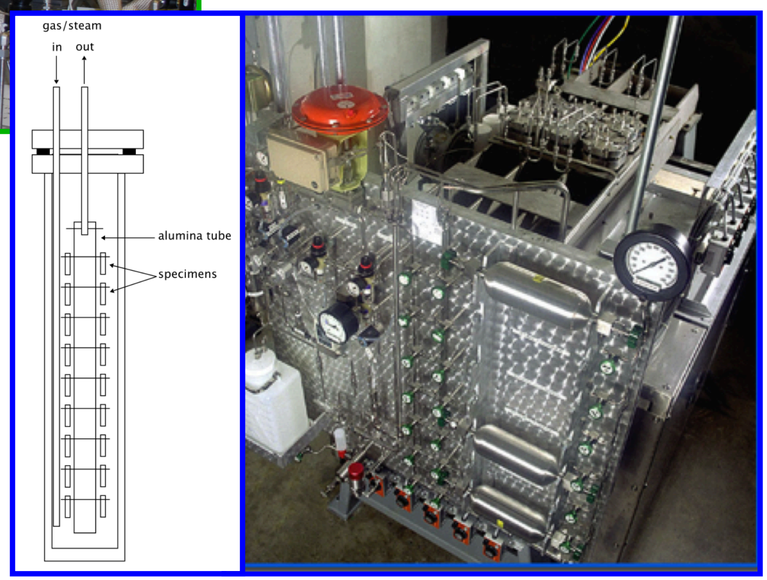
Several testing options

High temperature exposure in controlled gas environment

3-zone tube furnace



“Keiser” rig



282 autoclave

1 bar
500°-1200°C
500 h cycles

1 + 25 bar
500°-1300°C
500 h cycles

300 bar
200°-800°C
500 h cycles

Want to study sCO_2 impurity effects

Goal: study effect of H_2O & O_2 on sCO_2 corrosion

BUT, we can't pump impurities into sCO_2 gas

AND can't monitor H_2O or O_2 level at pressure

(1) 1 bar dry air,CO_2(99.995%),CO_2+0.15%O_2,CO_2+10%H_2O

2014-2015 results

(2) Constructing rig for 300 bar/750°C testing

Pumping system and detector being built

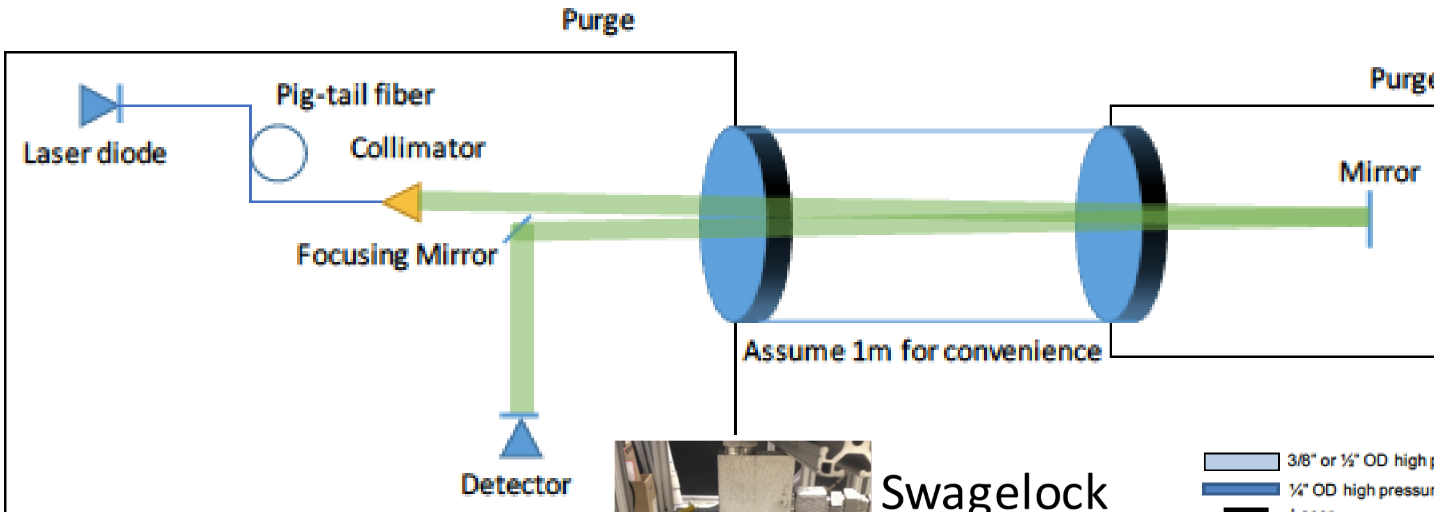
(3) 1 & 300 bar: industrial vs. research grade CO_2

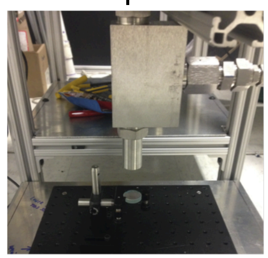
Starting experiments (IG sCO_2 for SunShot project)

(4) 1 & 25 bar CO_2 vs. CO_2+H_2O vs. +SO_2?

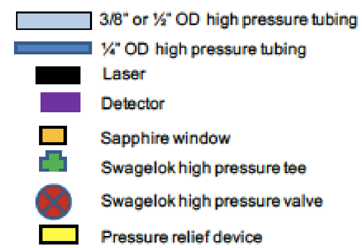
Test matrix in progress

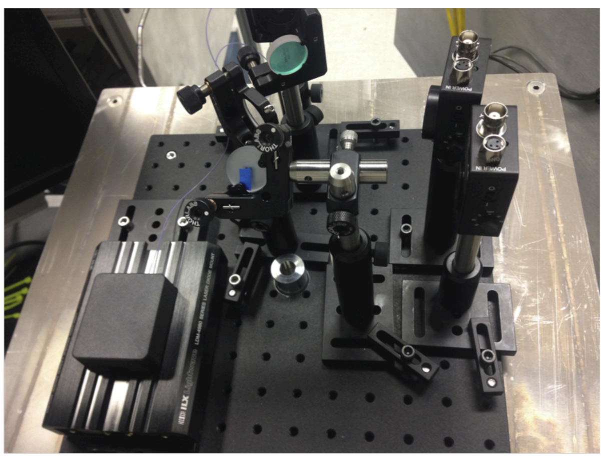
New system under construction



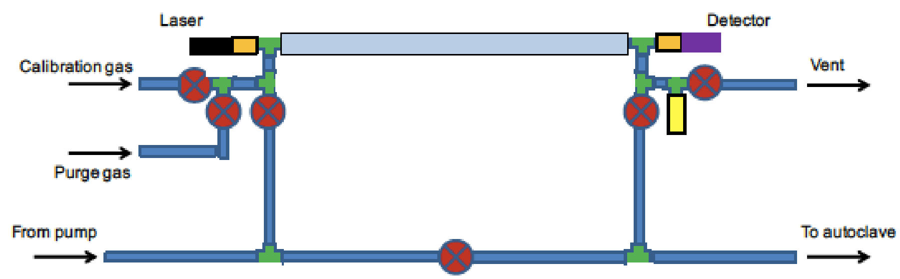


Swagelock High Pressure Tee



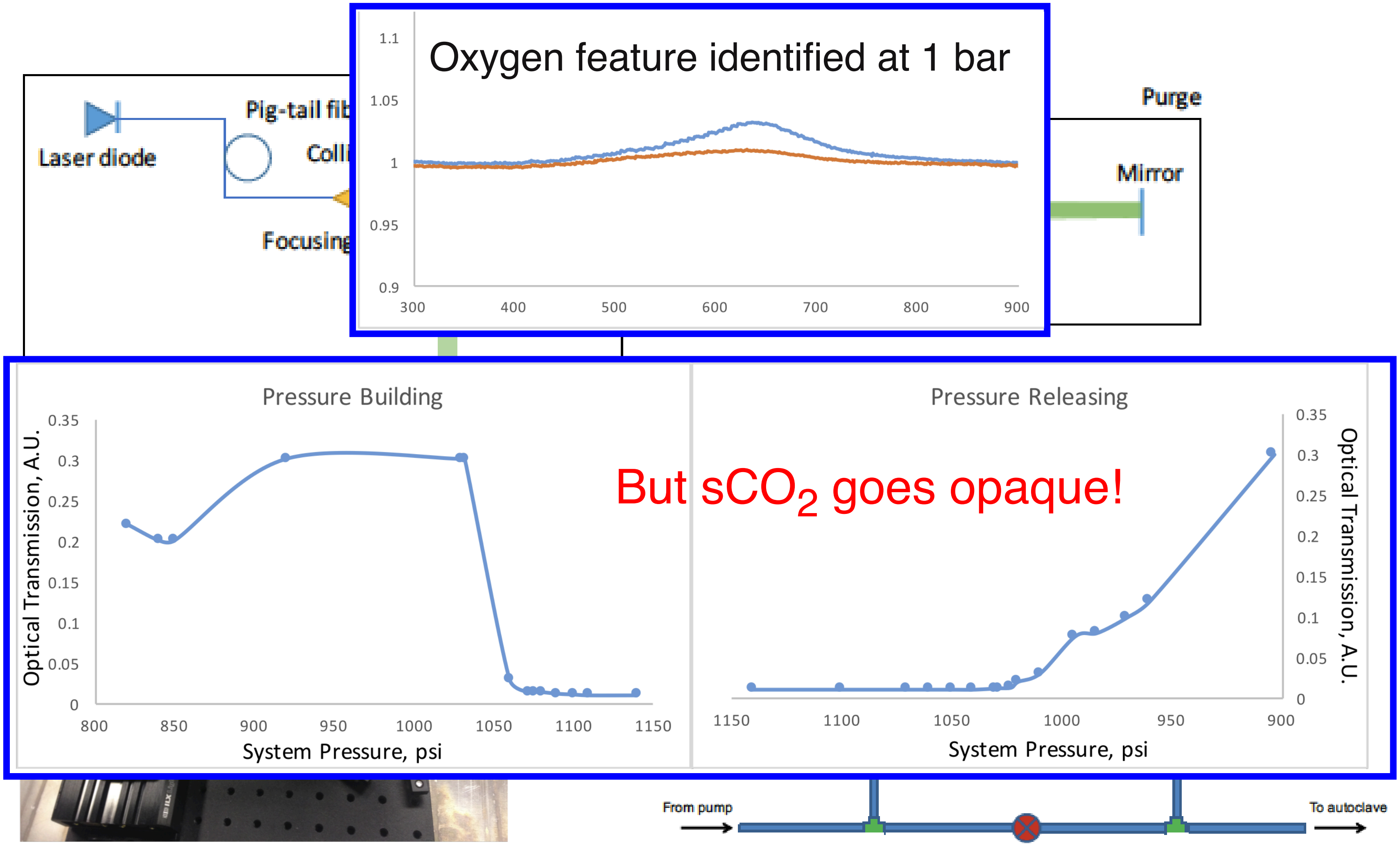


Optical Detection Set-Up



Laser-based system to detect O_2 and H_2O in CO_2 at pressure (200-300 bar)

New system under construction

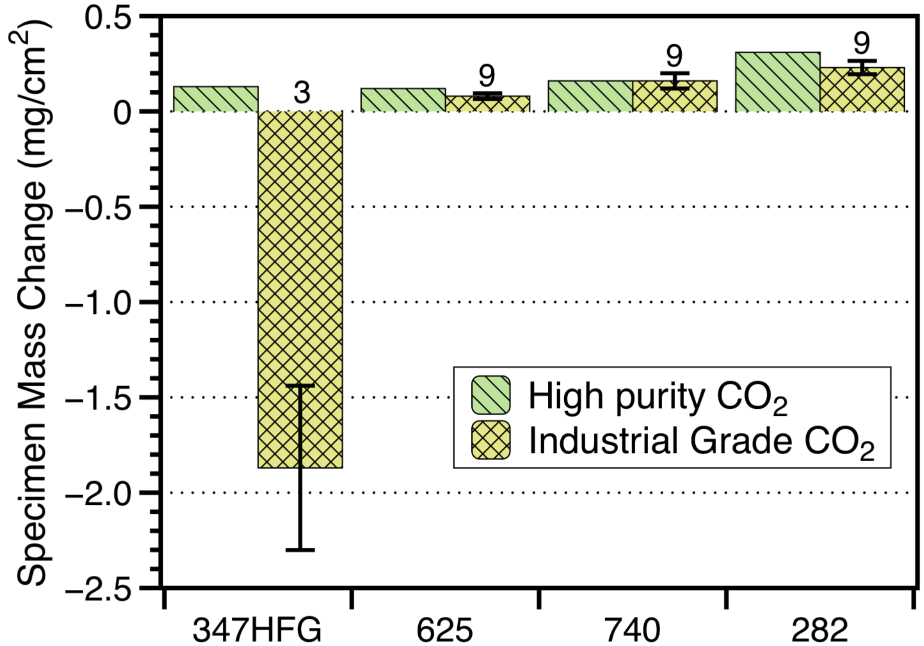


Optical Detection Set-Up

Laser-based system to detect O_2 and H_2O in CO_2 at pressure (200-300 bar)

RG vs. IG CO_2: initial comparison

FE/CSP collaboration: 750°C: 500 h cycles



Initial results: 1 bar

Pressure	FE: RG CO_2	CSP: IG CO_2
1 bar	5,000 h	5,000 h
300 bar	5,000 h	5,000 h

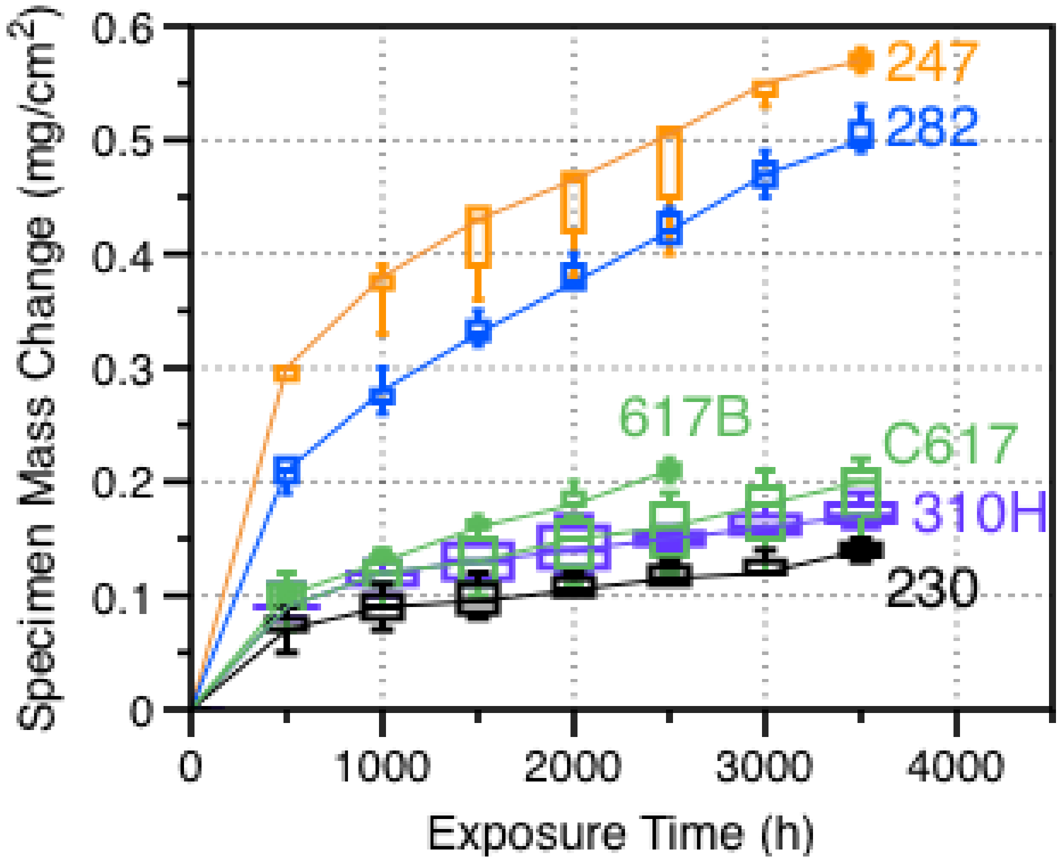
test matrix

1 sample of each in first RG 200 bar exposures
Multiple samples in future for better statistics

Industrial grade: ≤ 50 ppm H_2O and ≤ 32 ppm O_2
Research grade: < 5 ppm H_2O and < 5 ppm hydrocarbons

300 bar IG sCO_2: complete June

10 x 500 h cycles at 750°C w/SunShot



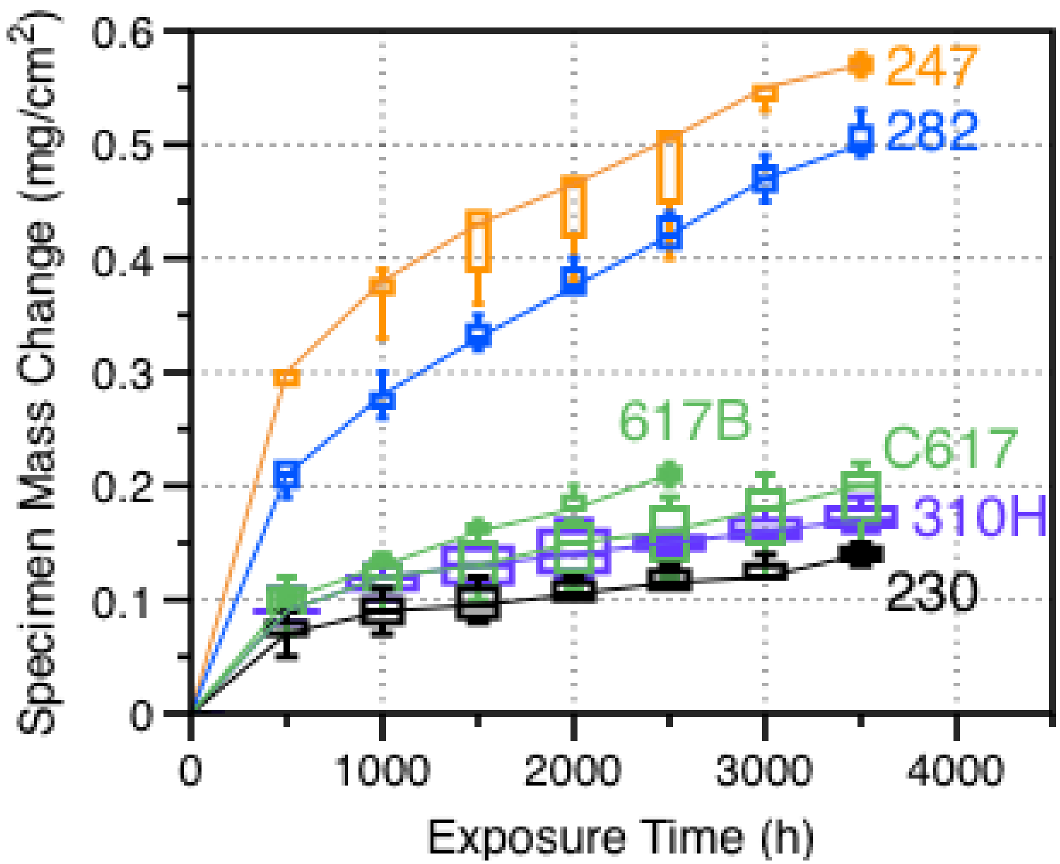
High mass gain for 282 and 247

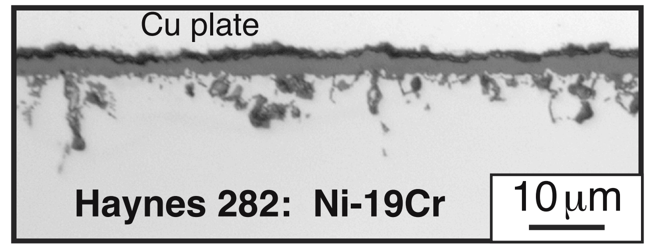
617: both CCA617 and VDM 617B in test

Industrial grade: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

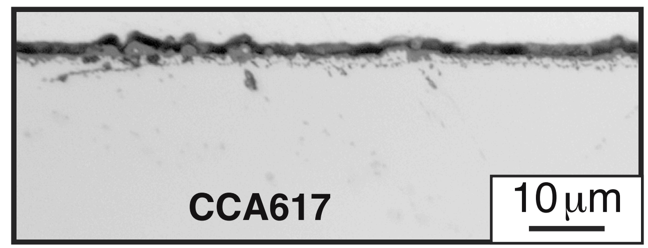
300 bar IG sCO_2: next RG sCO_2

10 x 500 h cycles at 750°C w/SunShot





750°C 300 bar 2,500 h



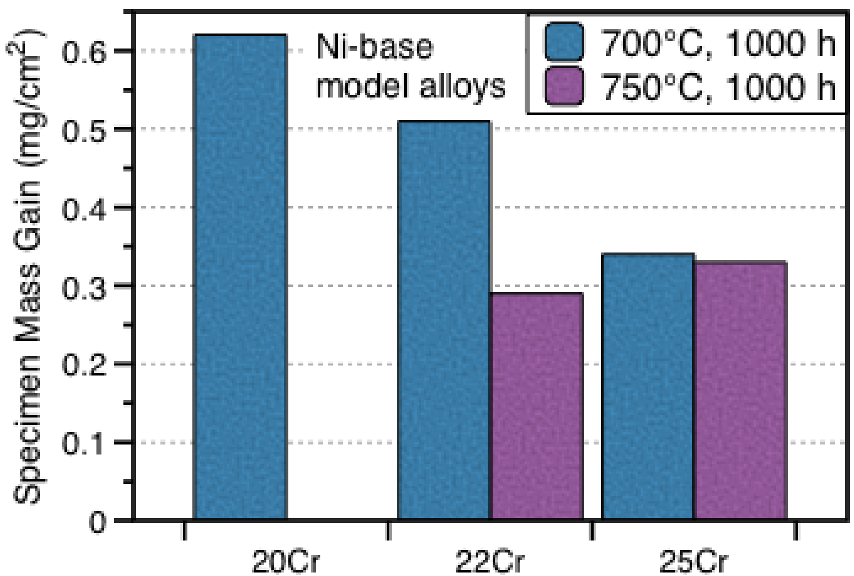
High mass gain for 282 and 247

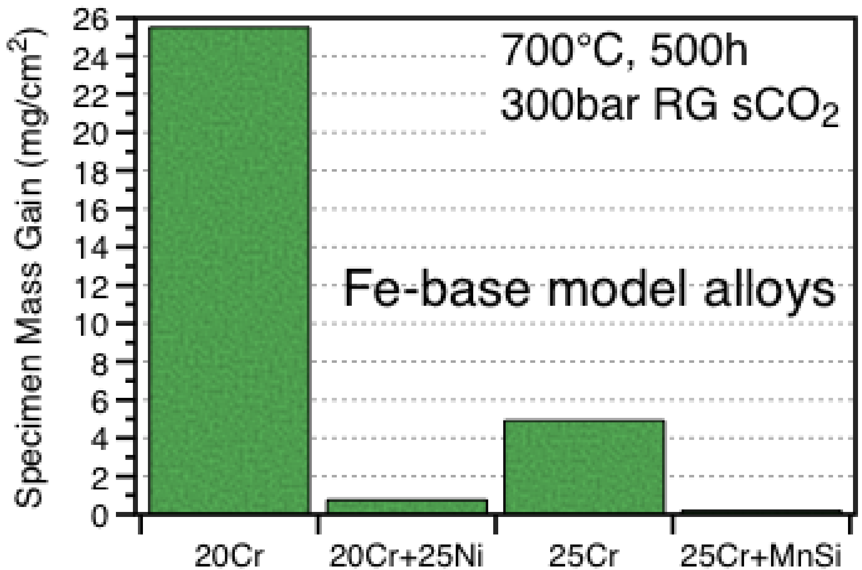
617: both CCA617 and VDM 617B in test

Industrial grade: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

Also exposing model alloys

500-1000 h exposures, 300 bar 700°+750°C





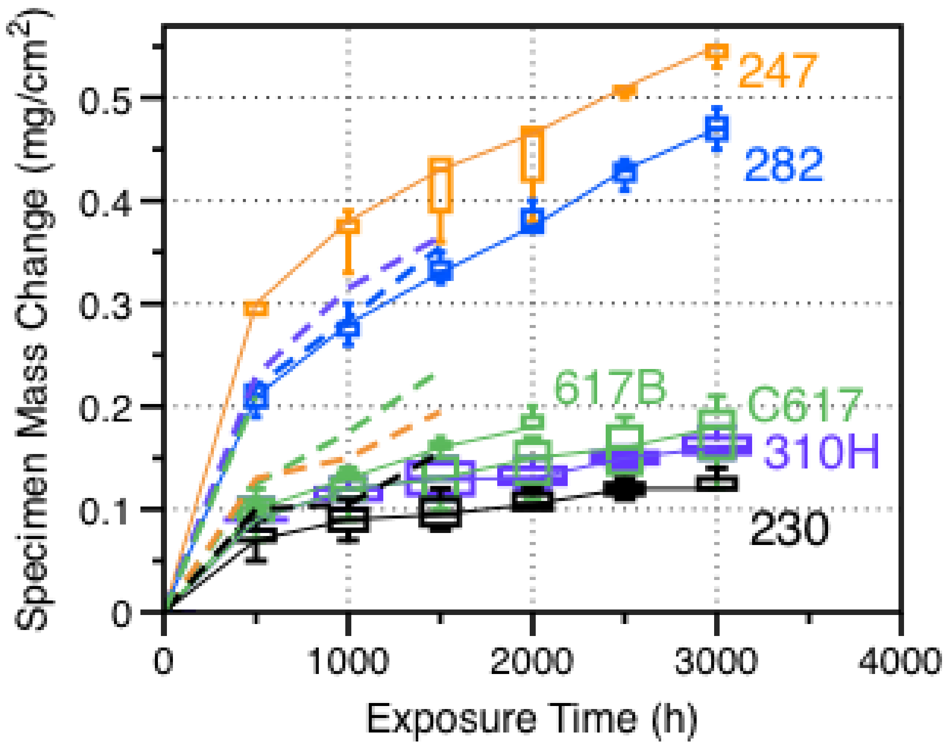
Cast and rolled M-Cr alloys

- Ni-Cr alloys more protective
- Several Fe-base alloys stopped at 500h
  - Fe-20Cr-25Ni - protective (FCC slower D_{Cr})
  - Fe-25Cr+Mn,Si - protective

Characterization in progress

Comparing 1 + 300 bar IG sCO_2

If P not important, large 1 bar database!

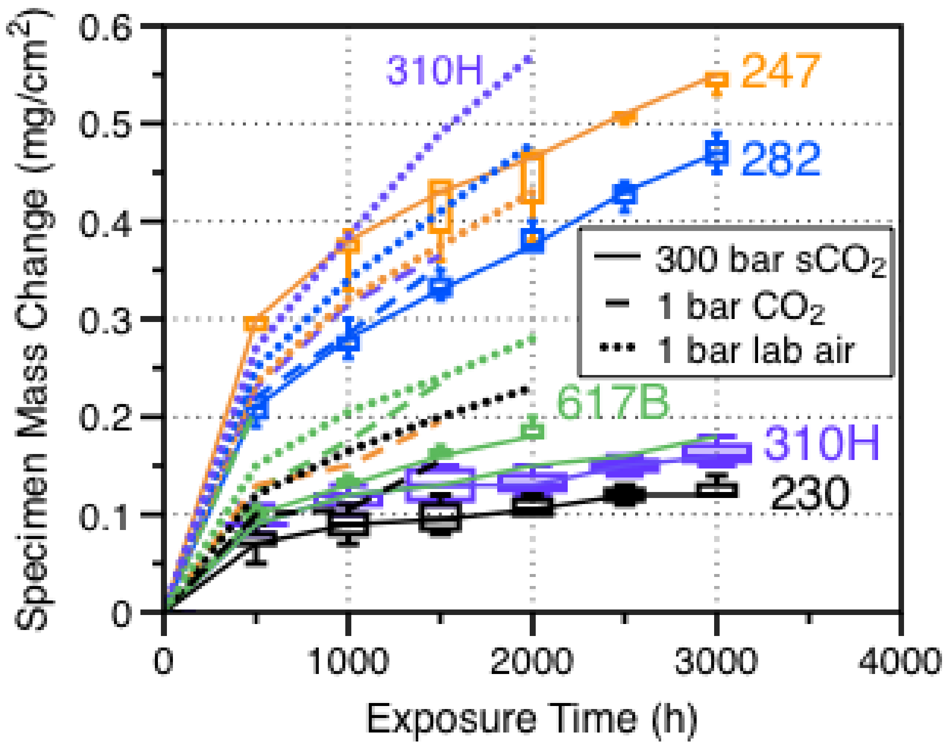


Dashed lines - median value of 4-5 1 bar specimens
Initial results: slightly different ordering (310,247)
Now starting 1 bar RG CO_2

Industrial grade: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

Baseline of laboratory air

500 h cycles at 750°C



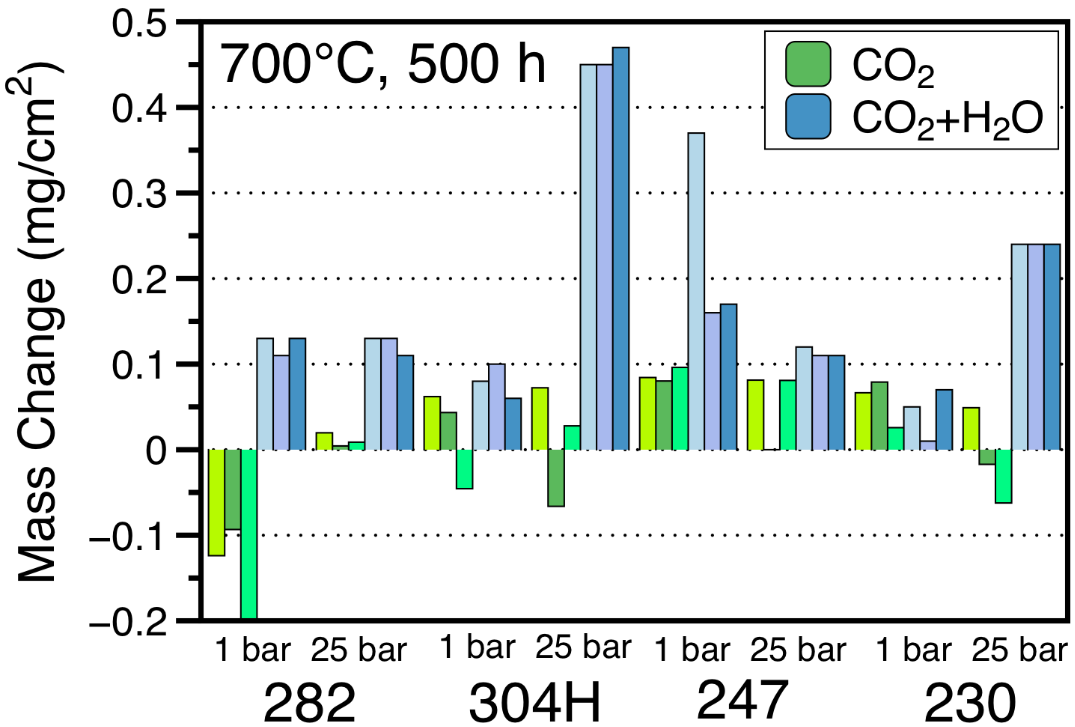
Dotted lines - median value of 4-5 1 bar specimens

Initial results: air similar to 1 bar CO_2

Need to compare rates & ignore transient effects

Initial results in 1 & 25 bar

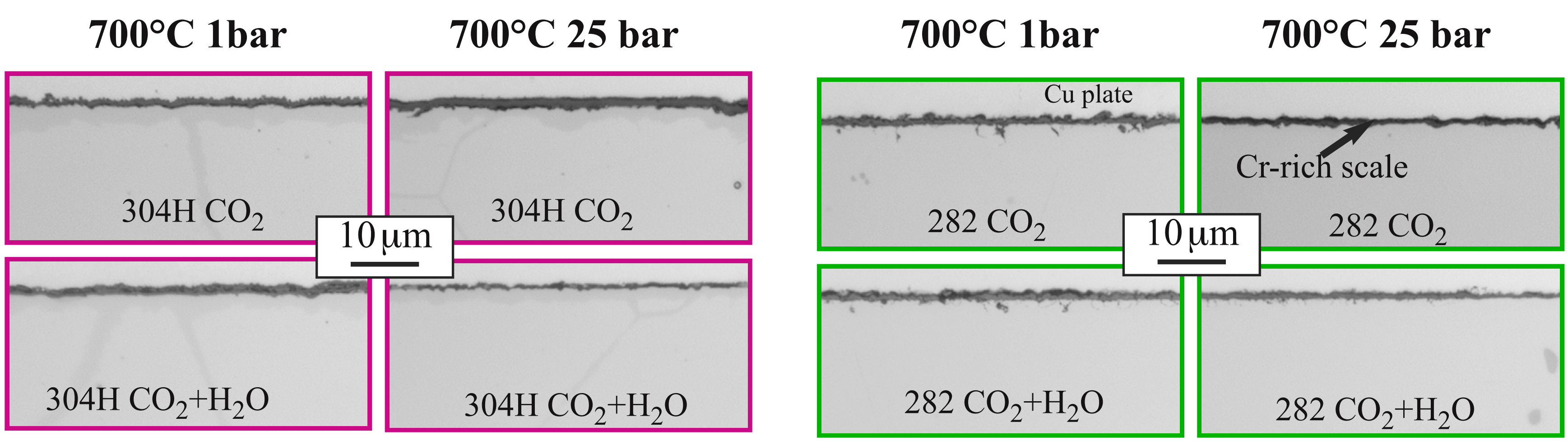
Three specimens of each alloy per condition



700°C, 1292°F

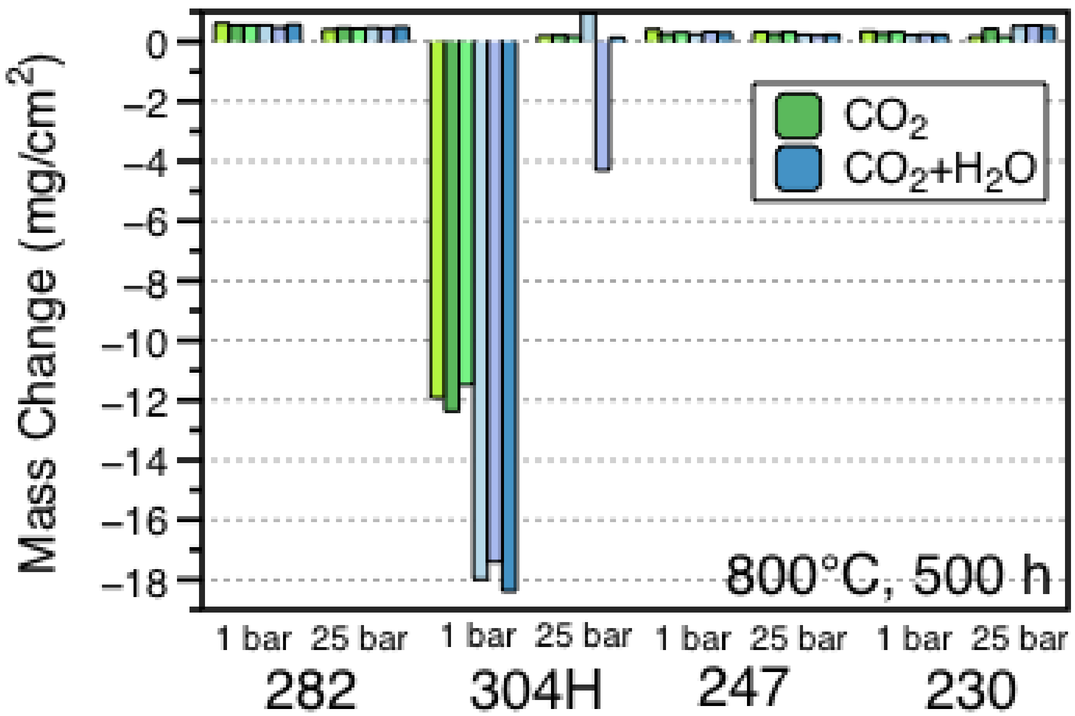
RG CO_2±10%H_2O

500 h exposure



800°C: only 304H showed P effect

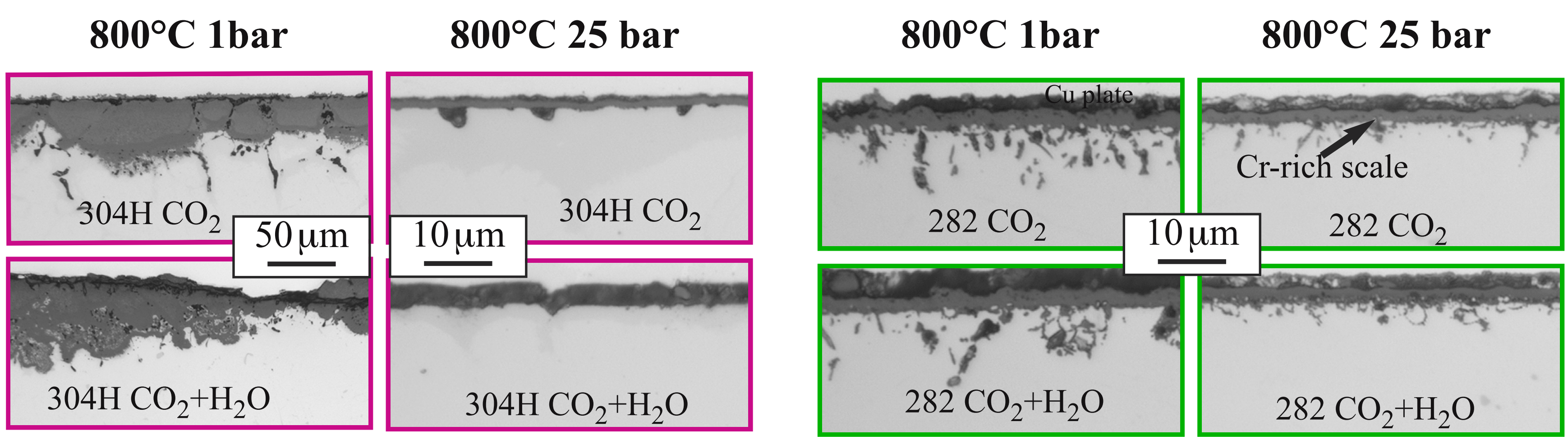
Odd that higher pressure showed less attack



800°C, 1472°F

RG CO_2±10%H_2O

500 h exposure



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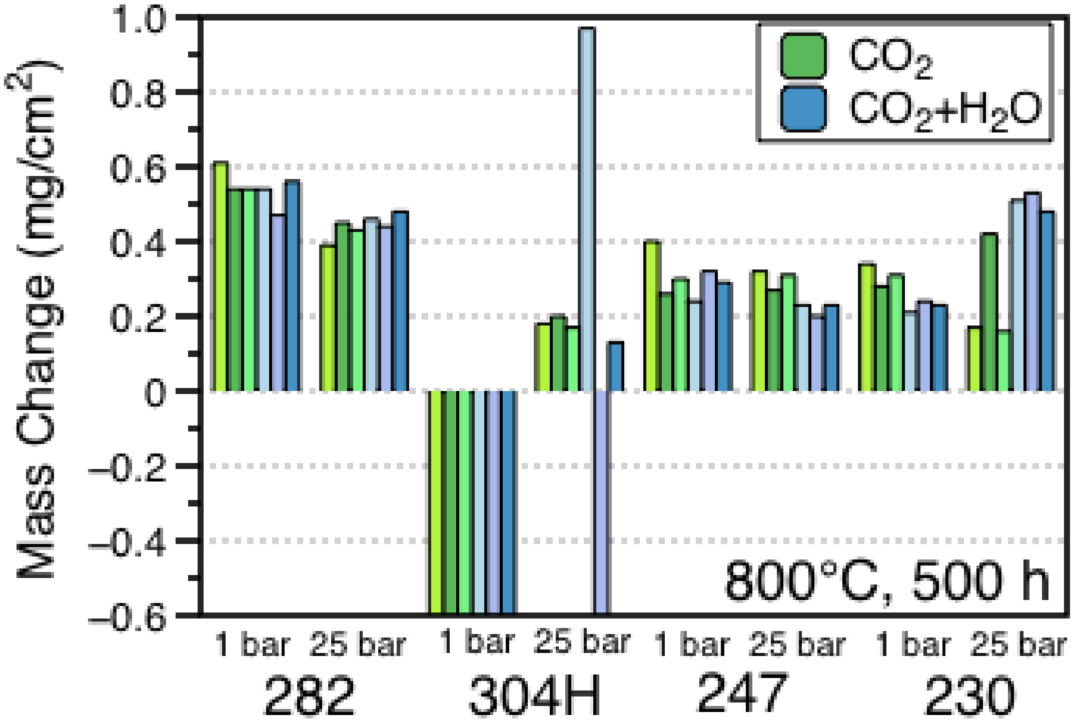
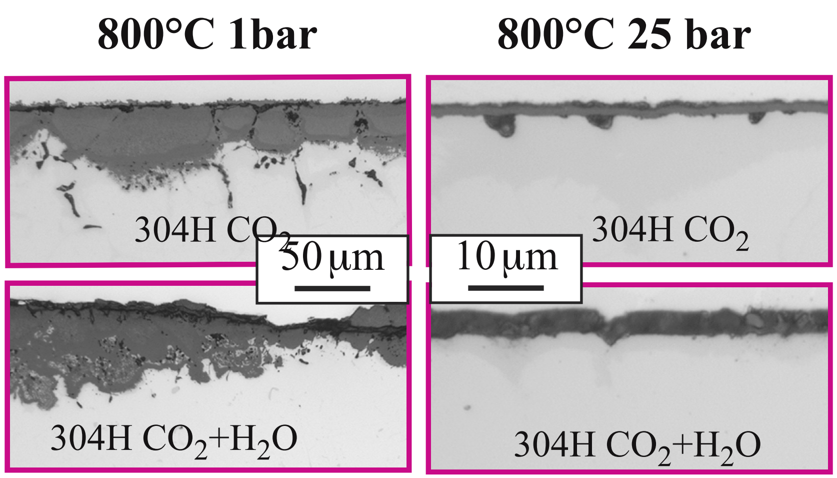
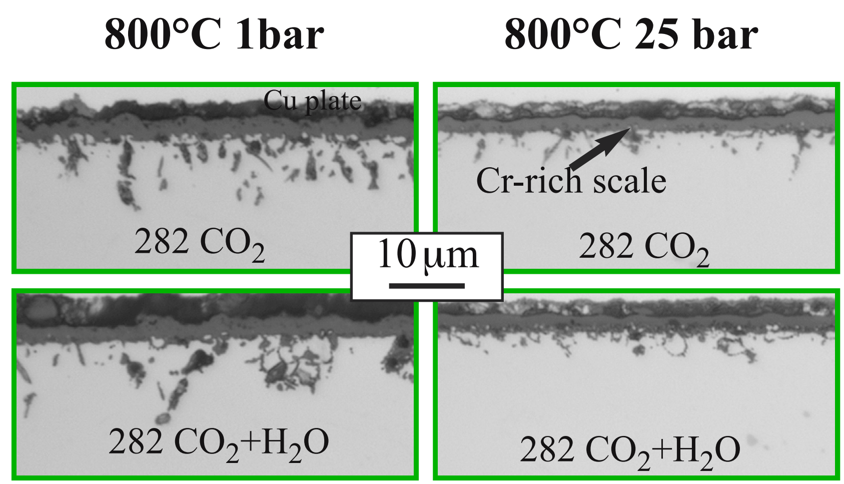


800°C, 1472°F

RG CO_2±10%H_2O

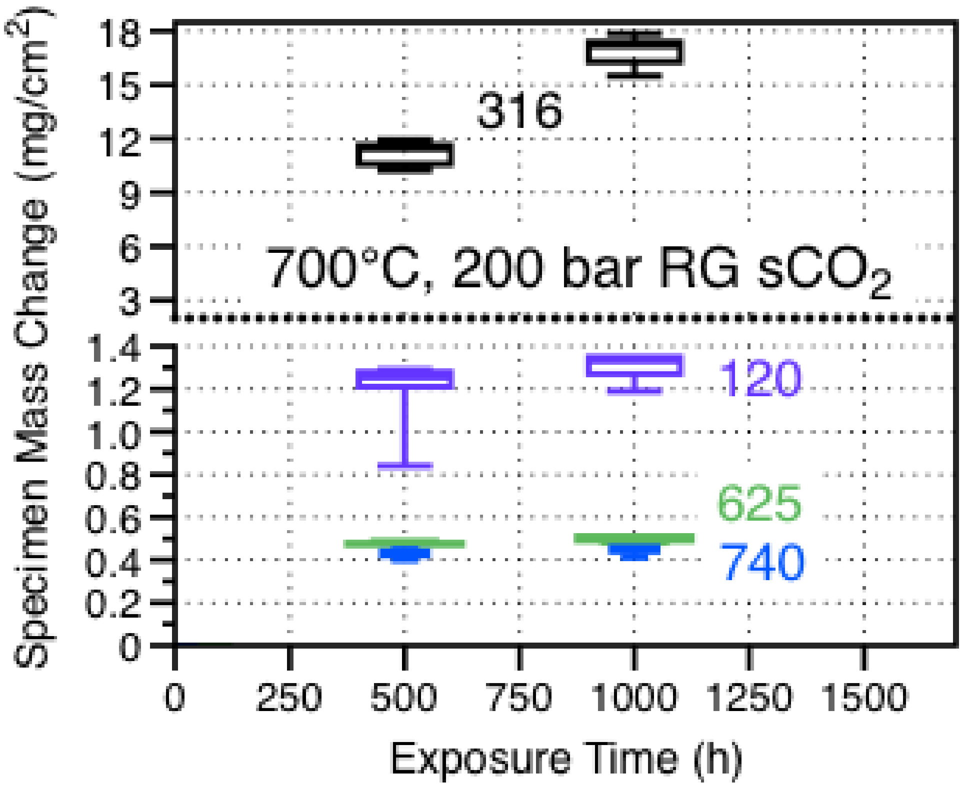
500 h exposure





Round robin testing starting

Project led by Oregon State, including NETL + UW



200 bar RG sCO_2
550° and 700°C
3 x 500 h cycles
4 alloys each
6 specimens

Two cycles complete at 700°C

- specimens removed at 500 and 1000 h
- high mass gain for 316SS

550°C: IN740 replaced by T91

Summary: direct-fired sCO_2 project

Several experiments planned to study H_2O and O_2 effects in supercritical CO_2, need a system that:
- can pump control impurity levels at 300 bar?
- detect levels entering and leaving autoclave

to study conditions relevant to direct-fired cycles

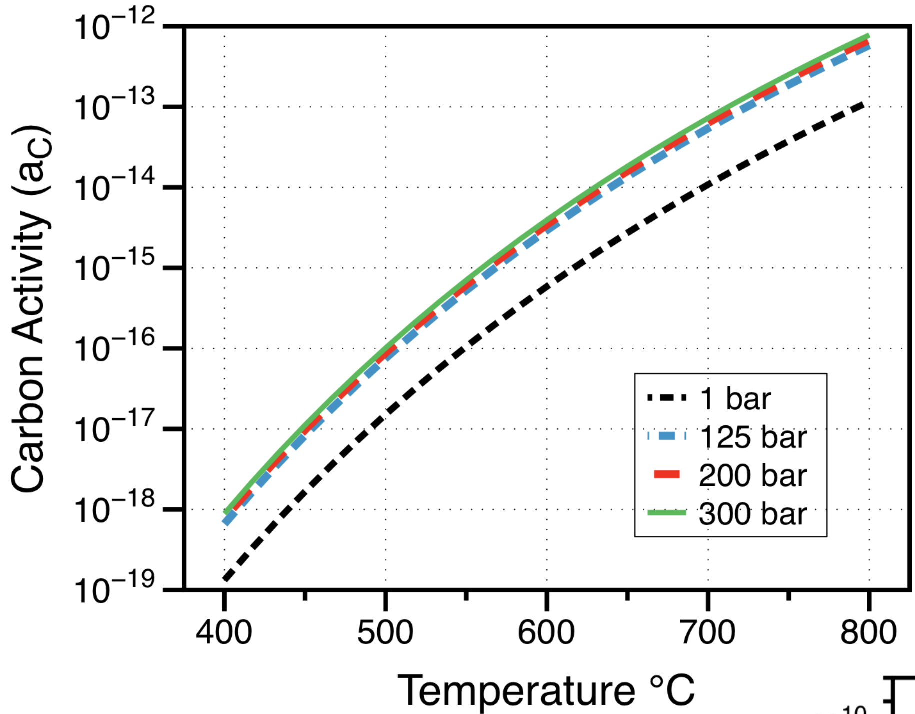
Additional experiments:

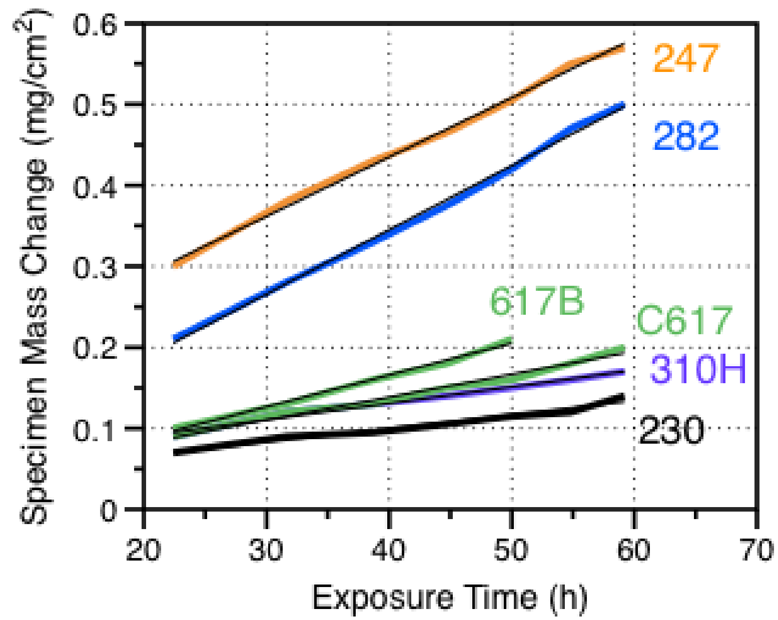
(1) comparing industrial and research grade CO_2
- 1 and 300 bar
- collaboration with DOE SunShot-funded project

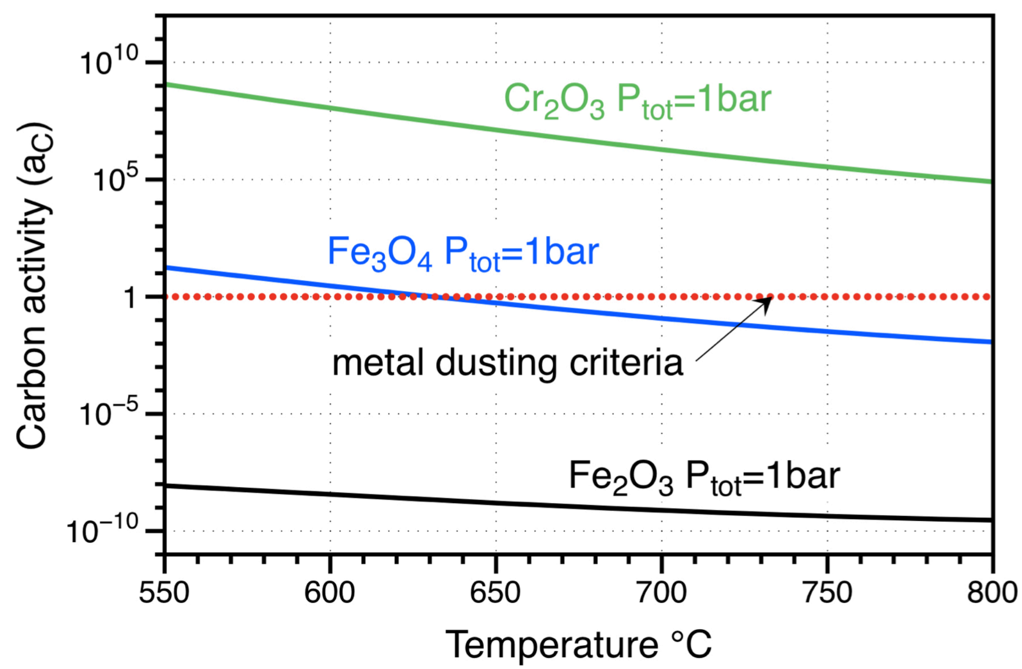
(2) comparing 1 & 25 bar CO_2 & CO_2+10%H_2O
- thin oxides formed on higher-alloyed materials
- no clear effect of impurities from this data
- last condition to be run CO_2+10%H_2O+0.1%SO_2

More characterization: TEM & GDOES

backup slides

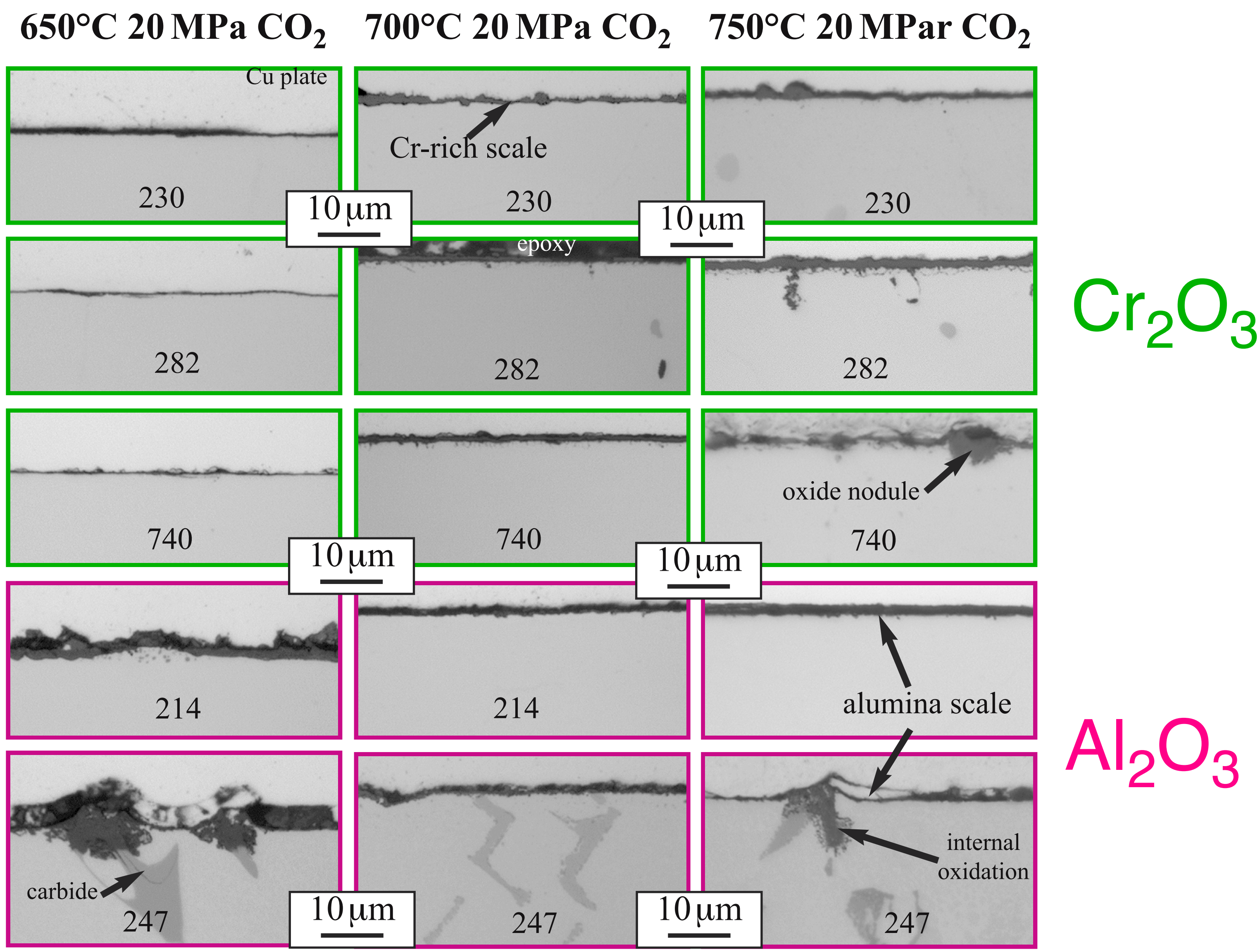






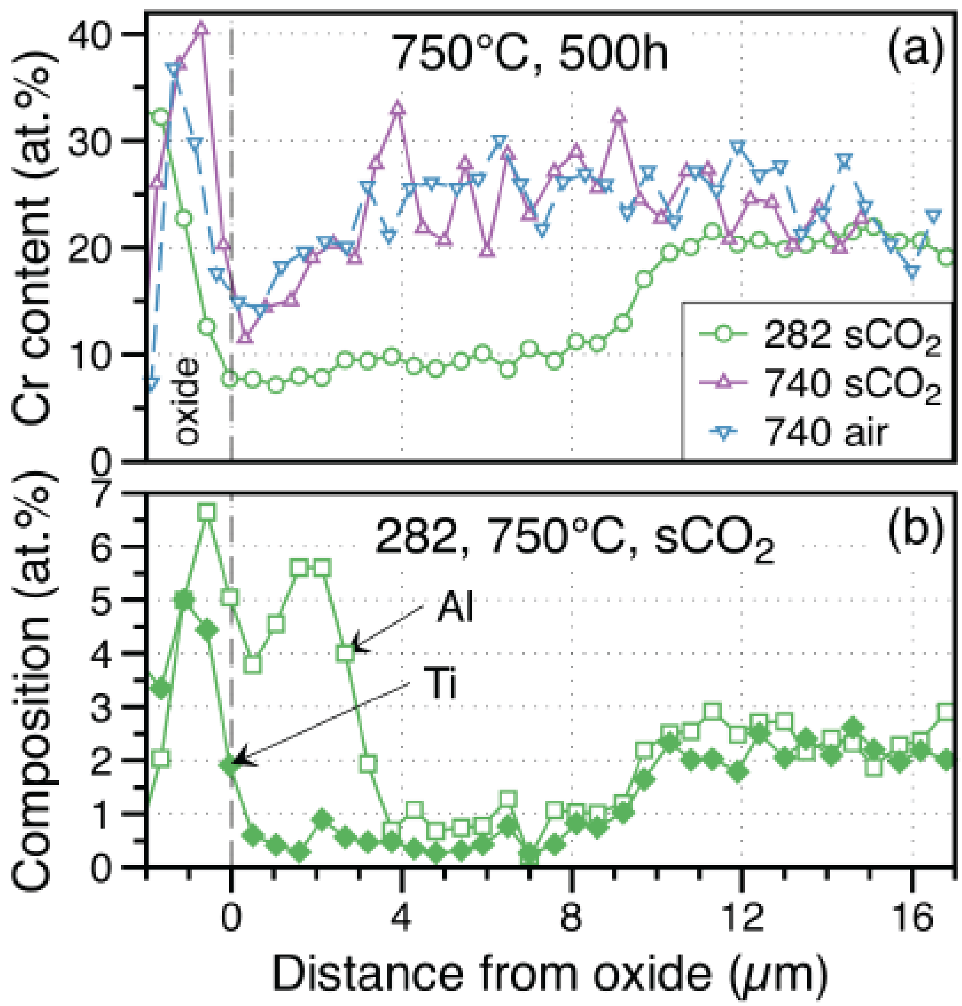
Ni-base alloys: thin scales

All thin Cr-rich or Al-rich scales in 20 MPa sCO_2

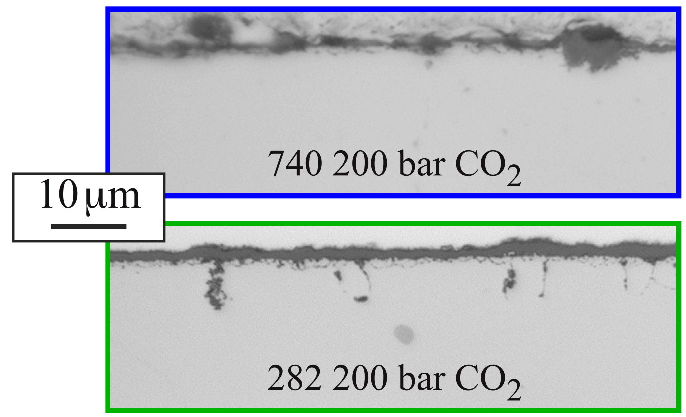


282 deeper Cr depletion than 740

EPMA depth profiles beneath scale at 750°C



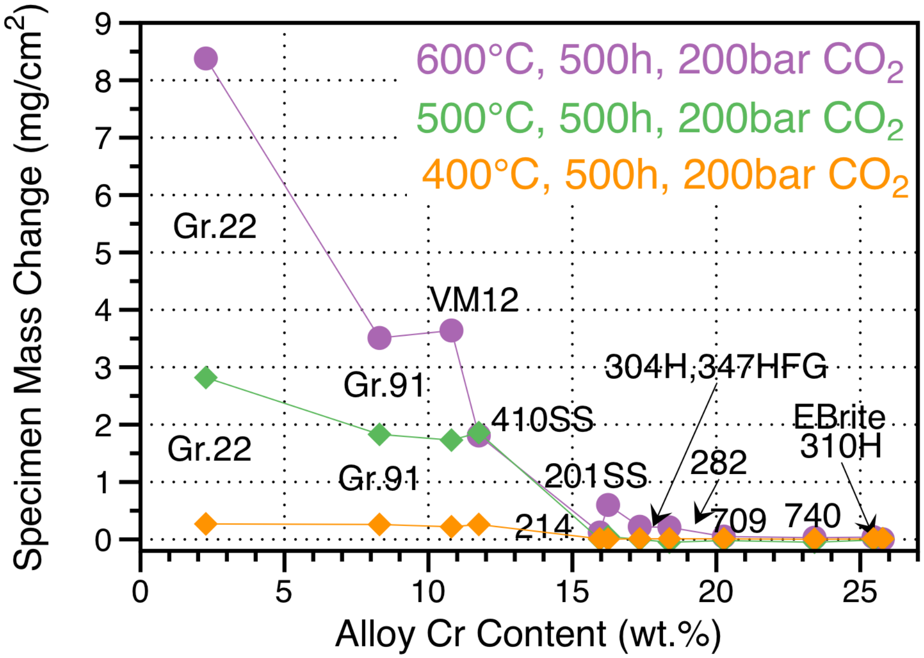
1 bar air vs. 200bar CO_2

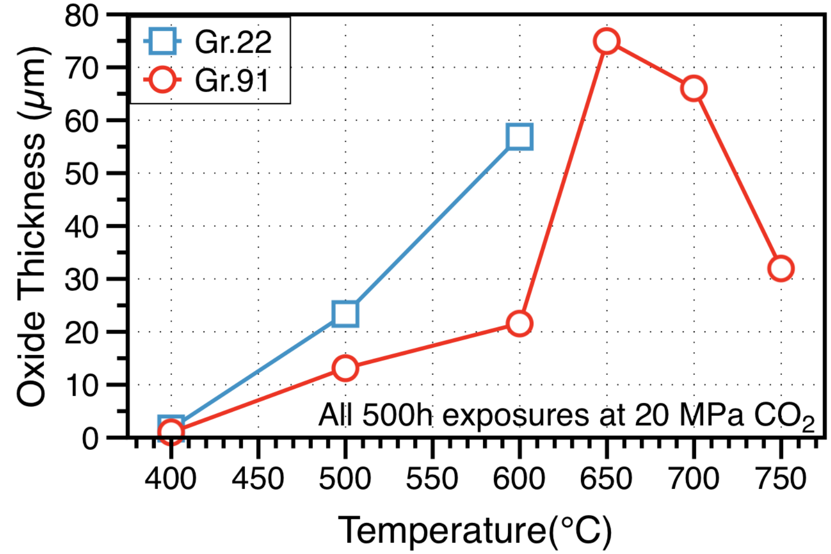


282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti

740: 49Ni-24.6Cr-20Co-0.5Mo-1.3Al-1.5Ti

Steels exposed at 400°-600°C
500h exposures in 20 MPa CO_2



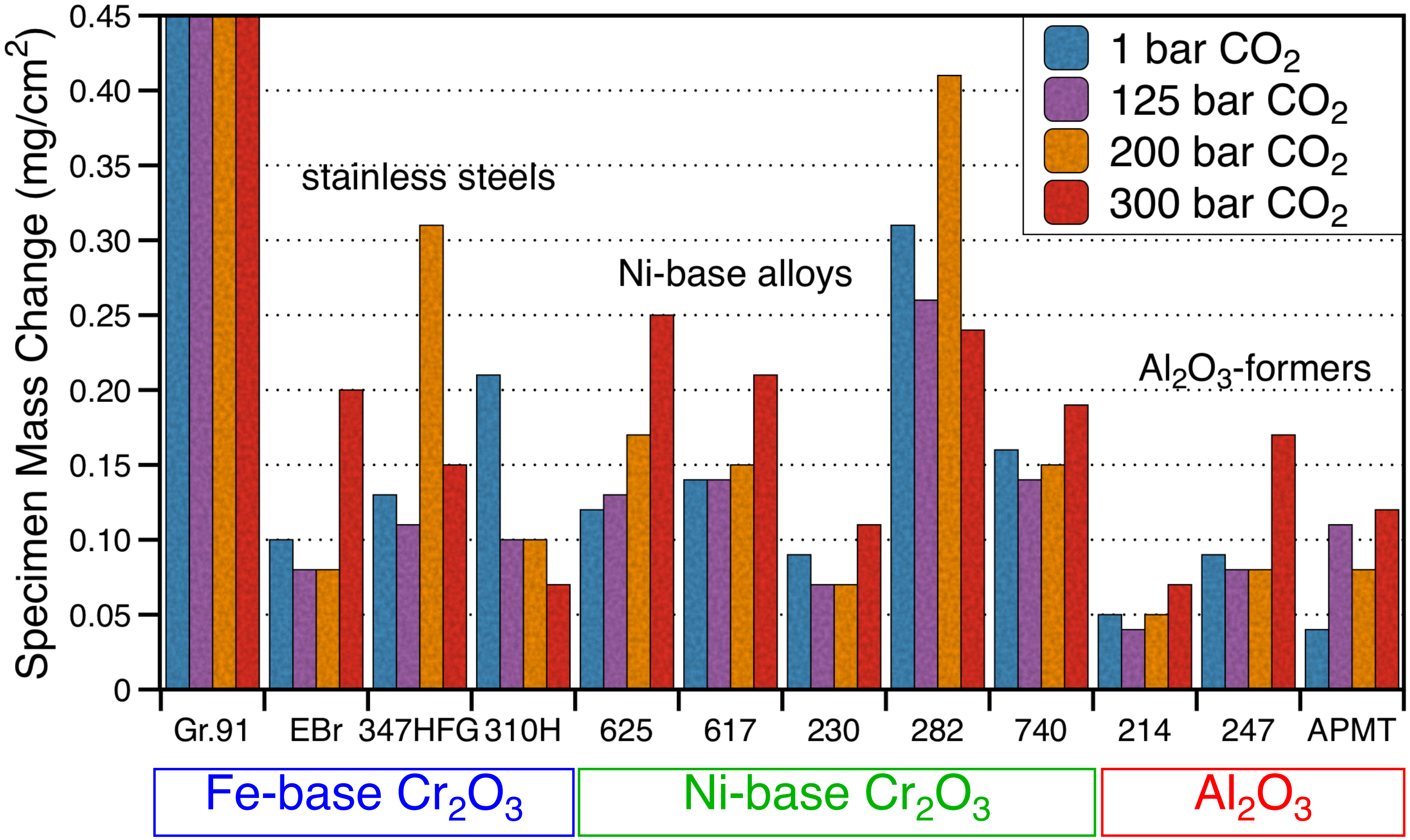


Industry interested in where low-cost alloys can be used

Little effect of pressure observed

500h exposures at 750°C

Core group of 12 alloys evaluated



All 500h tests

0.1 mg/cm^2 ~ 0.5 μm surface oxide

10 mg/cm^2 ~ 50 μm (2 mils)

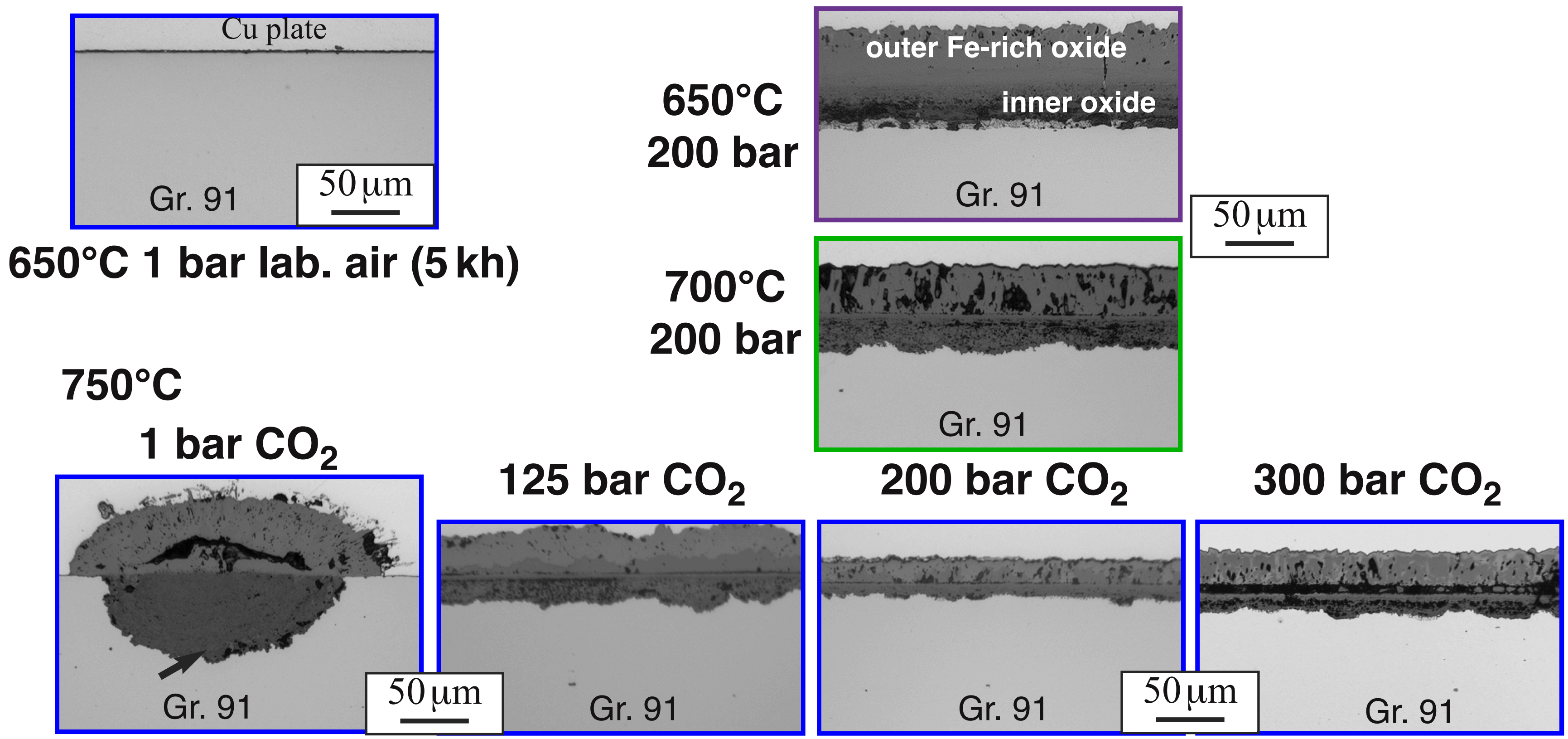
Typical Fe-rich oxide on Gr.91

However, inner/outer ratio appears to change with P

- Outer Fe_2O_3/Fe_3O_4 layer
- Inner $(Fe,Cr)_3O_4$ layer

Grade 91: Fe-9Cr-1Mo

Some thin-protective Cr-rich scale at 1bar



light microscopy of polished cross-sections

750°C: initial tensile experiments showed little effect of sCO_2

25mm tensile bars exposed at each condition

Tensile test at room temperature: 10^{-3}/s strain rate