The Effect of O_2 and H_2O on oxidation in CO_2 at 700°-800°C

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(R. Dennis, program manager; P. Burke, project monitor)

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M. Stephens, T. Lowe - specimen preparation/handling

T. Jordan - metallography

ORNL craft workers

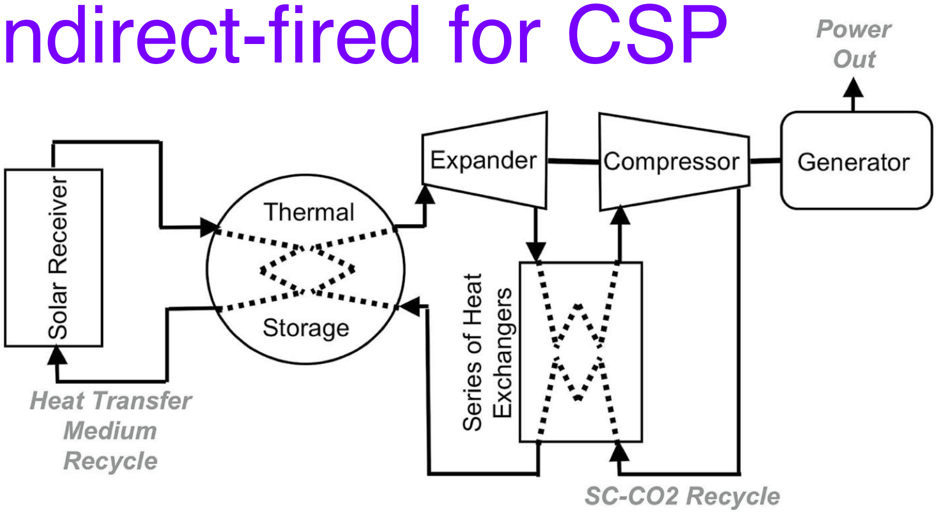
Alloy coupons:

- Haynes International
- Special Metals
- Sandvik (Kanthal)
- Allegheny-Ludlum
- Sumitomo Metals
- Capstone Turbines

Research sponsored by: U. S. Department of Energy, Office of Coal and Power R&D, Office of Fossil Energy

Direct-fired system of special interest

Indirect-fired for CSP



Closed loop of relatively pure CO_2

- primary HX (>700°C)
- recuperators (<600°C)

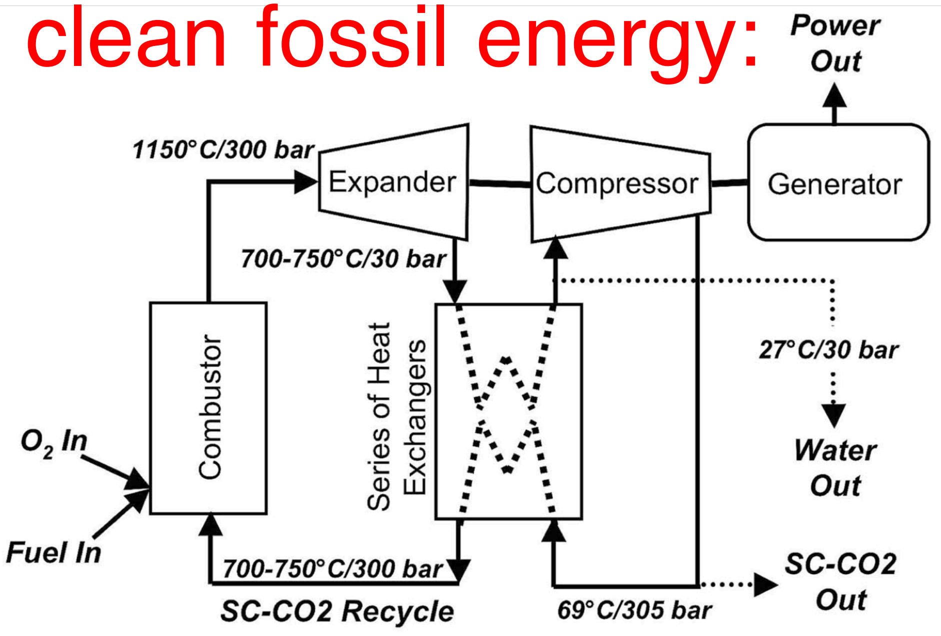
Also, waste heat recovery, bottoming cycle

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

In: natural gas + O_2

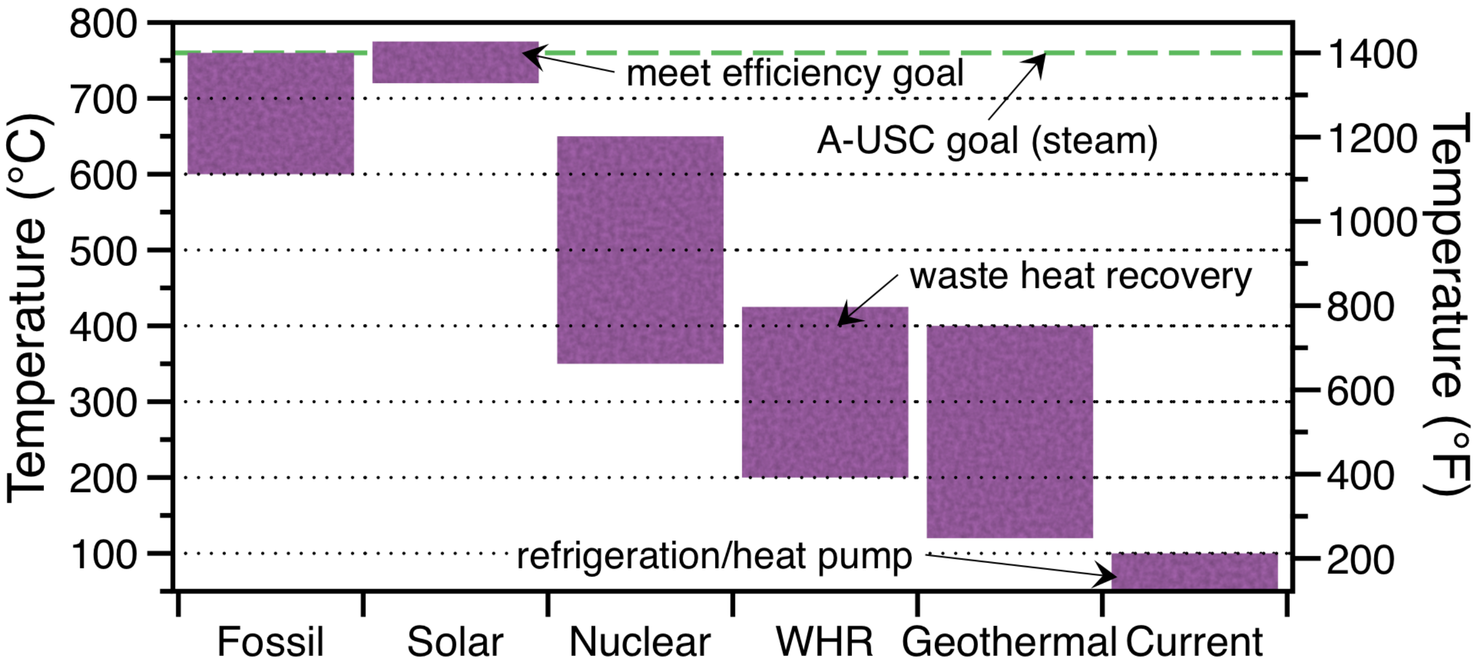
Impurities: ~10%H_2O
~1%O_2, CH_4?, SO_2?

Out: CO_2 for EOR (enhanced oil recovery)



Different temperature targets

- Uncertainty about ranges 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 T's:
  1150°C combustor
  750°C/300 bar turbine exit
- Primary HX operating at higher T than turbine inlet



Materials for sCO_2

Temperatures (600°-750+°C) and pressures:

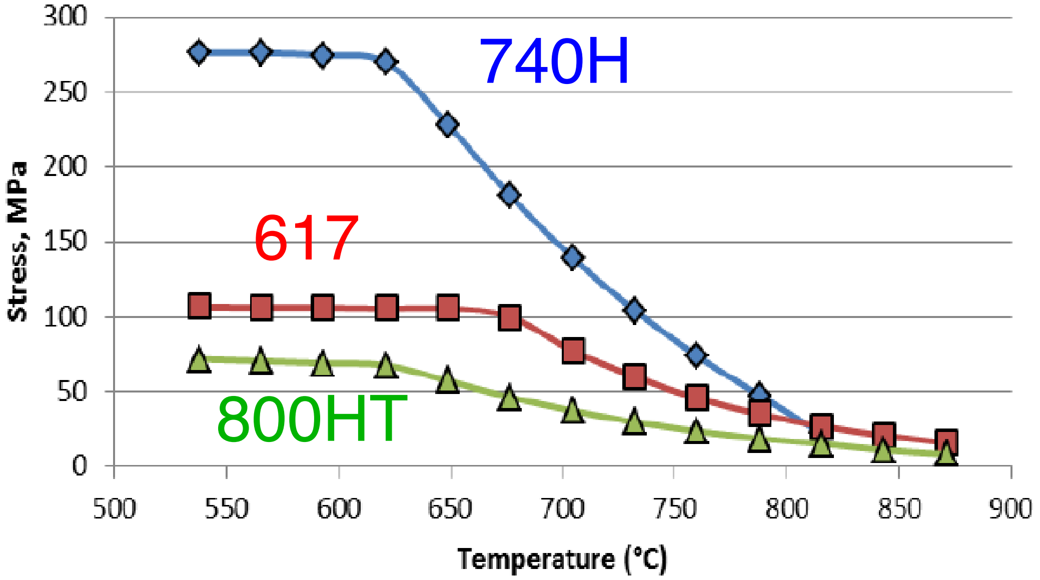
- challenge for strength
- limited number of materials available
- ! Adv. Ultra-supercritical (steam) same T range

Limited materials choices:

- - capability
- - ASME Boiler & Pressure Vessel Code:

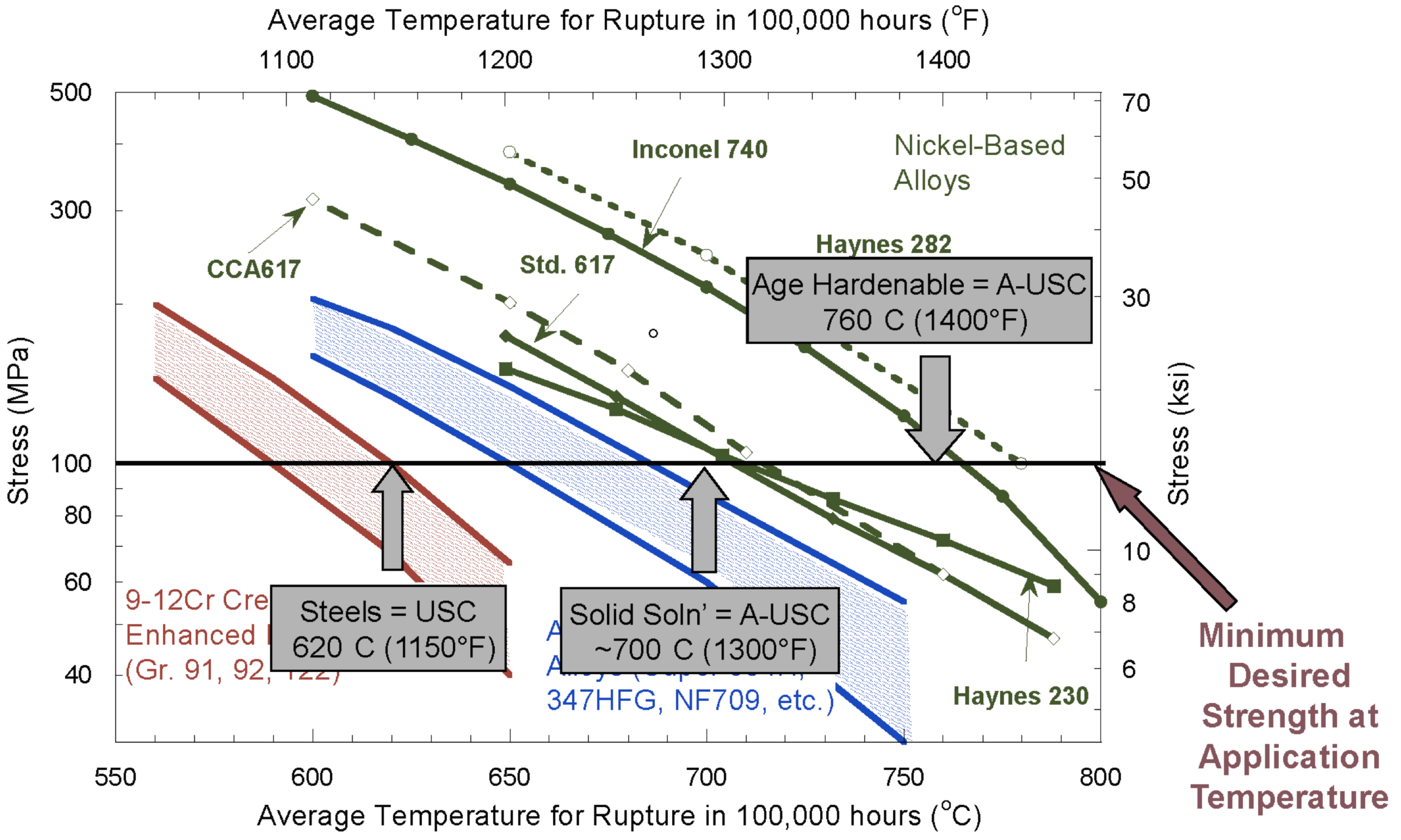
Materials are key to:

- reliability
- availability
- maintainability



A-USC materials for 700-760°C

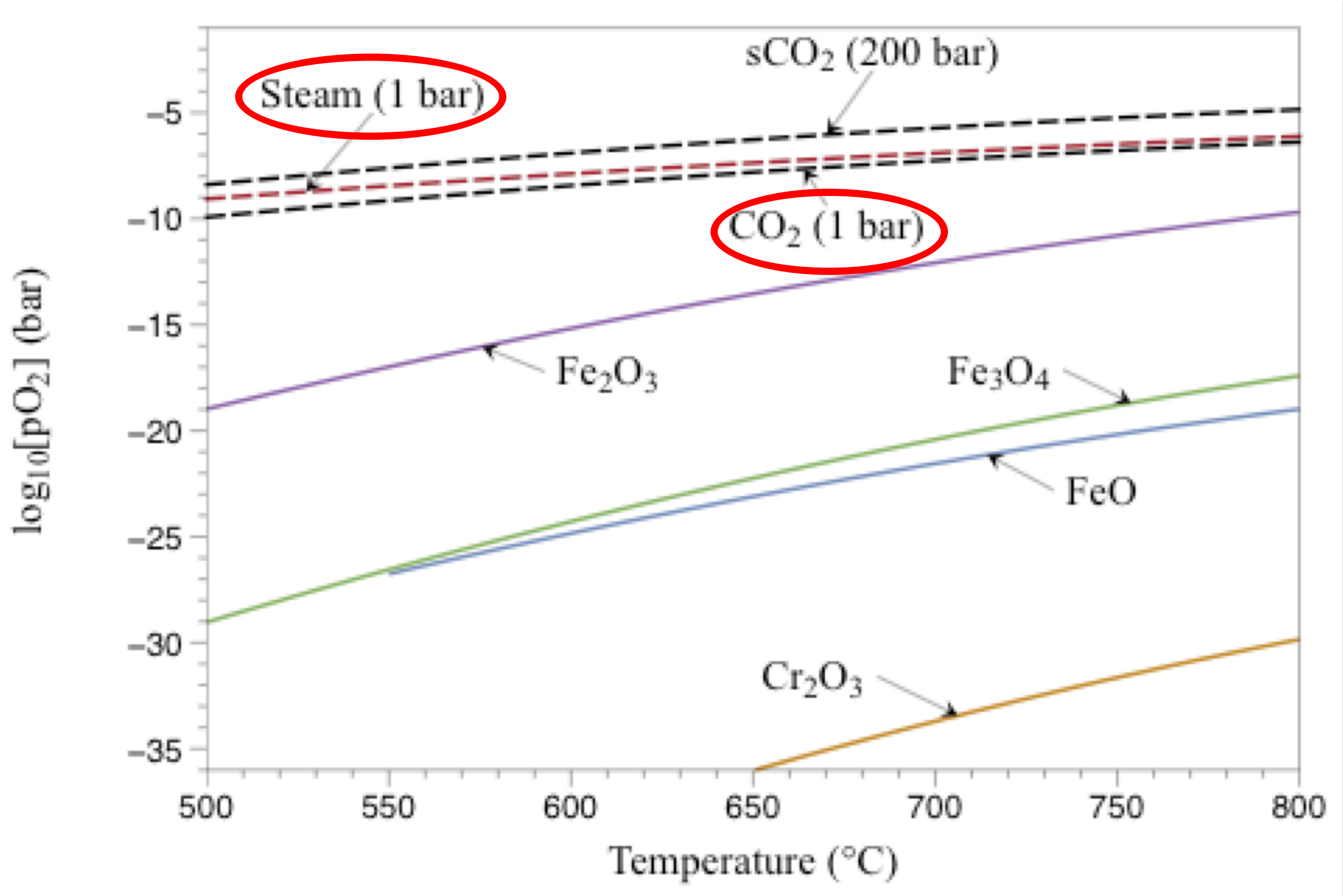
100MPa/100,000h creep rupture lifetime needed



U.S. Advanced Ultra-Supercritical (steam) Consortium

Oxygen levels similar in steam/CO_2

Factsage calculations

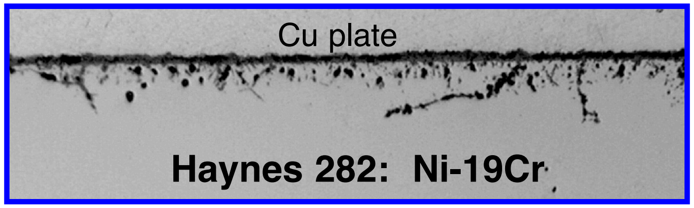


Similar pO_2 levels in steam & CO_2, higher at 200bar

All oxides of interest are stable

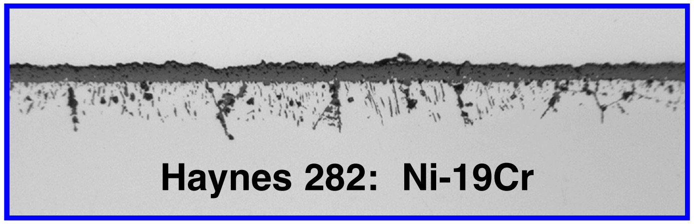
Why worry about 740/282?

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



800°C, 5,000h in air+10%H_2O

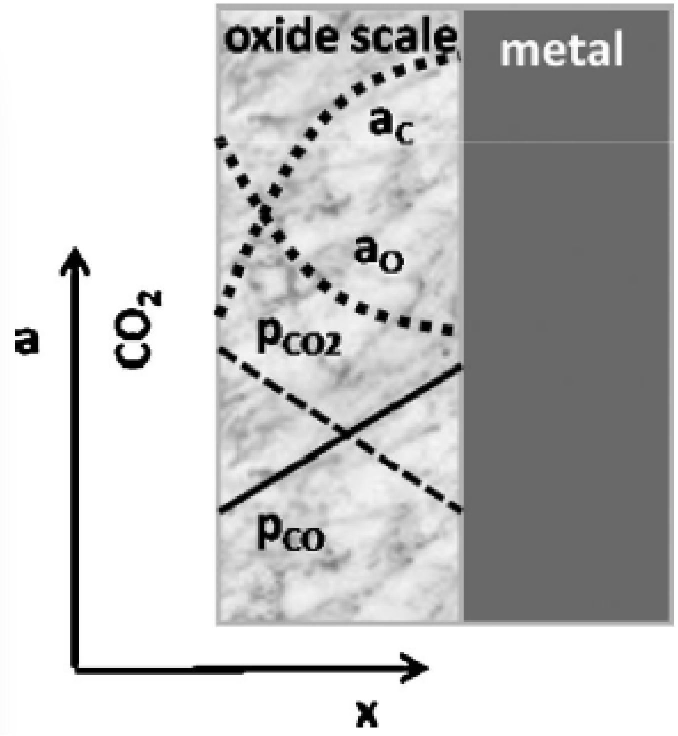
10 µm



800°C, 10,000h in dry air
both exposures: 500h cycles

Al+Ti internally oxidize beneath Cr_2O_3 oxide scale

$CO_2 = CO + 1/2O_2$



from Young, et al. 2011

General: C activity (ac) relatively low, favors oxidation

McCoy 1965: Inconel 600 and 18Cr-8Ni steel internally carburized in 1bar CO_2

High ac predicted - what about NiCr in sCO_2 + 10%H_2O?

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

2016 project goals:

- build H_2O & O_2 detection system at pressure
- build dual pumping system for incorporating
  H_2O & O_2 in sCO_2

2017 goals:

- operate system

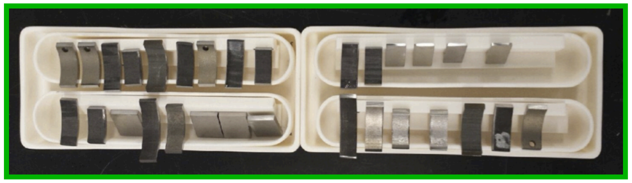
Several testing options

High temperature exposure in controlled gas environment

automated
cyclic rigs

1 bar
500°-1200°C
0.1-24 h cycles

3-zone tube furnace



1 bar
500°-1200°C
100-500 h cycles

282 autoclave

300 bar
200°-800°C
500 h cycles

Some impurity results while we wait

- Create a 1 bar baseline
  - 500 h exposures
  - dry air,CO_2(99.995%),CO_2+0.15%O_2,CO_2+10%H_2O
  - Coupons 11 x 19 x 1.5mm
    - 600 grit SiC finish
    - Ultrasonically cleaned in acetone & methanol
  - Held in alumina boat in alumina reaction tube
  - 100 cc/min flow rate, heat to temperature in argon
  - Mass change
    - Mettler Toledo model XP205 balance
    - ±0.04 mg (±0.01 mg/cm^2) accuracy
  - Post exposure characterization:
    - Light microscopy (Cu-plating to protect scale)

Wide range of alloys examined

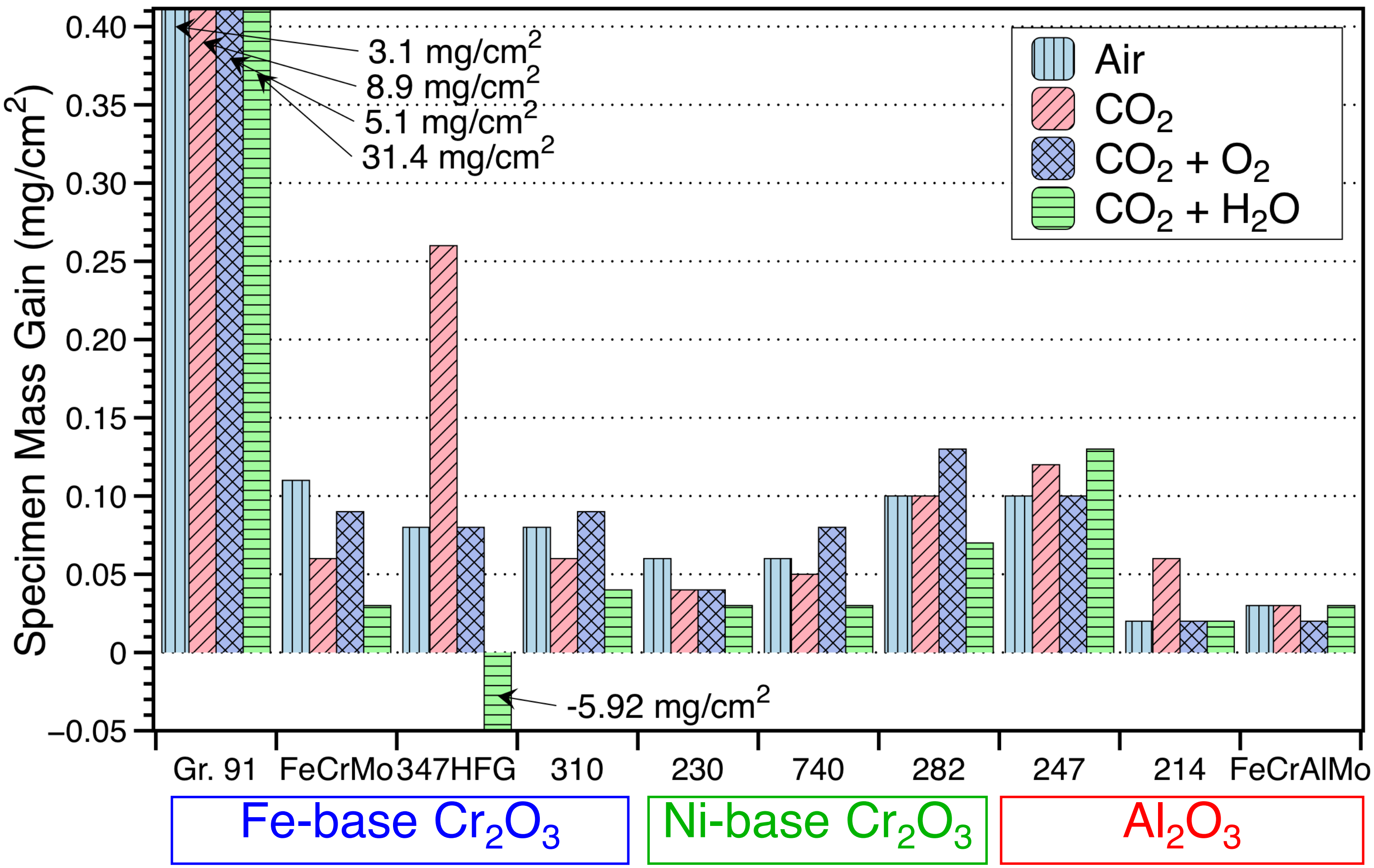
Alloy	Fe	Ni	Cr	Al	Other
Ferritic chromia-forming steels					
Gr.91 (S90901)	89.7	0.1	8.3	<	1Mo,0.3Mn,0.1Si, 0.08C
FeCrMo (S44735)	72.6	0.1	25.8	<	1.0Mo,0.2Si,0.1V
Fe-12.5Cr	86.7	<	12.4	0.01	0.6Mn,0.2Si,0.005Y
Fe-15Cr	84.1	<	14.9	0.02	0.6Mn,0.3Si,0.012Y
Fe-17.5Cr	81.6	<	17.5	0.02	0.6Mn,0.3Si,0.011Y
Fe-20Cr	79.0	<	20.0	0.02	0.7Mn,0.3Si,0.010Y
Fe-22.5Cr	76.6	<	22.5	0.01	0.2Mn,0.7Si,0.002Y
Fe-25Cr	74.0	<	25.0	0.01	0.7Mn,0.3Si,0.002Y
Austenitic Fe-base chromia-forming steels					
347HFG (S34710)	66.0	11.8	18.6	0.01	1.5Mn,0.8Nb,0.4Si,0.2Mo,0.2Co,0.09C
310HCbN (S31042)	51.3	20.3	25.5	<	0.3Co,0.4Nb,1.2Mn,0.3Si,0.3N,0.05C
Fe-base alumina-forming alloys					
FeCrAlMo	69.2	0.2	21.1	5.0	0.2Hf,0.1Mn,2.8Mo,0.6Si,0.3Y,0.1Zr
AFA OC4	49.1	25.2	13.9	3.5	2.5Nb,2W,1.9Mn,2Mo,0.5Cu,0.2Si,0.1C
CAFA	48.4	25.2	14.6	3.5	1.0Nb,1.3W,2Mn,1.9Mo,0.6Cu,0.9Si,0.4C
DAFA	44.5	33.3	14.0	2.7	2.8Nb,1.7Ti,0.2Mn,0.4Si,0.1C
Ni-base chromia-forming alloys					
625 (N06625)	4.0	60.6	21.7	0.09	9.4Mo,3.6Nb,0.2Ti,0.2Si,0.1Mn
230 (N06230)	1.5	60.5	22.6	0.3	12.3W,1.4Mo,0.5Mn,0.4Si
CCA617 (N06617)	0.6	55.9	21.6	1.3	11.3Co,8.6Mo,0.4Ti,0.1Si
282 (N07208)	0.2	58.0	19.3	1.5	10.3Co,8.3Mo,0.06Si,2.2Ti,0.1Mn
740 (N07740)	1.9	48.2	23.4	0.8	20.2Co,2.1Nb,2.0Ti,0.3Mn,0.5Si
Ni-base alumina-forming alloys					
214 (N07214)	3.5	75.9	15.6	4.3	0.2Mn,0.1Si,0.02Zr
247 (N07247)	0.07	59.5	8.5	5.7	9.8Co,9.9W,0.7Mo,3.1Ta,1.0Ti,1.4Hf

< indicates less than 0.01%

Baseline created at 700°C 1bar

10 representative alloys were focus of metallography

1bar: dry air, CO_2, CO_2+0.15O_2, CO_2+10%H_2O



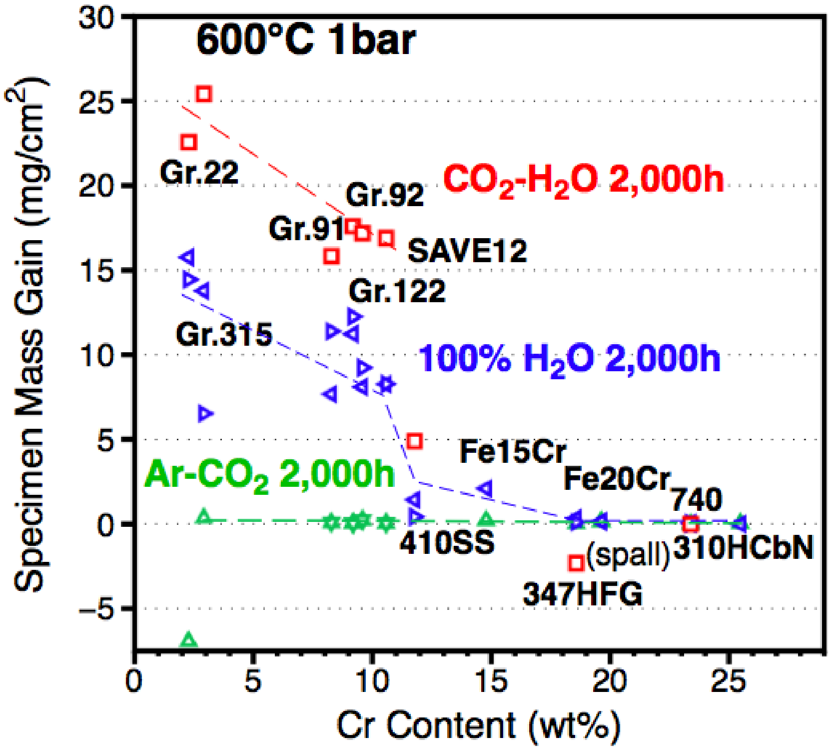
All
500h
tests

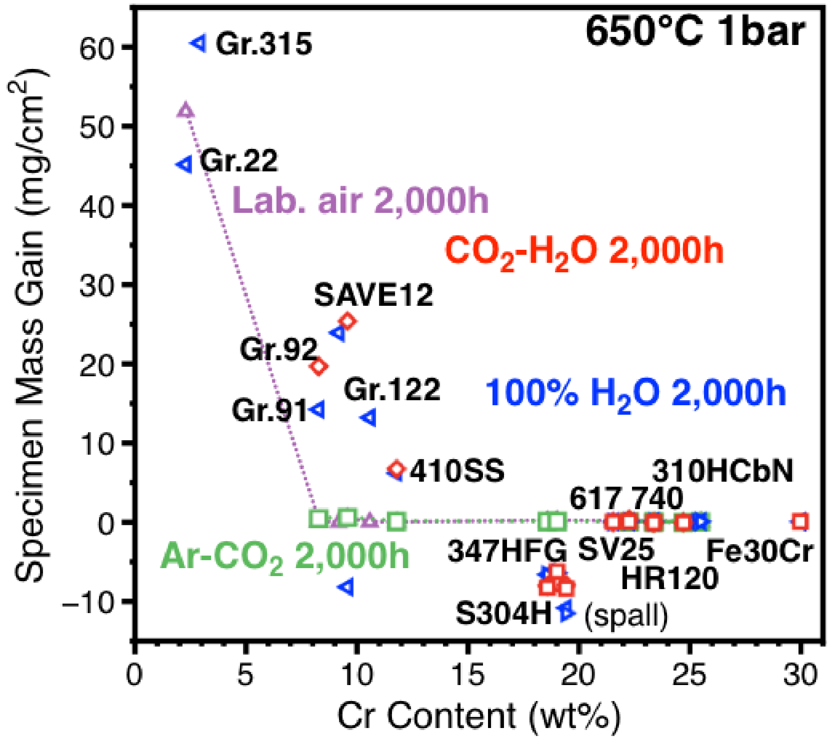
0.1 mg/cm^2 ~ 0.5 μm surface oxide
10 mg/cm^2 ~ 50 μm (2 mils)

Similar H_2O effect observed before

Similar alloys evaluated for oxy-firing (gas only)

1bar: dry air, 100%H_2O, Ar+50%(CO_2+0.15O_2), 50%(CO_2+0.15O_2)+50%H_2O

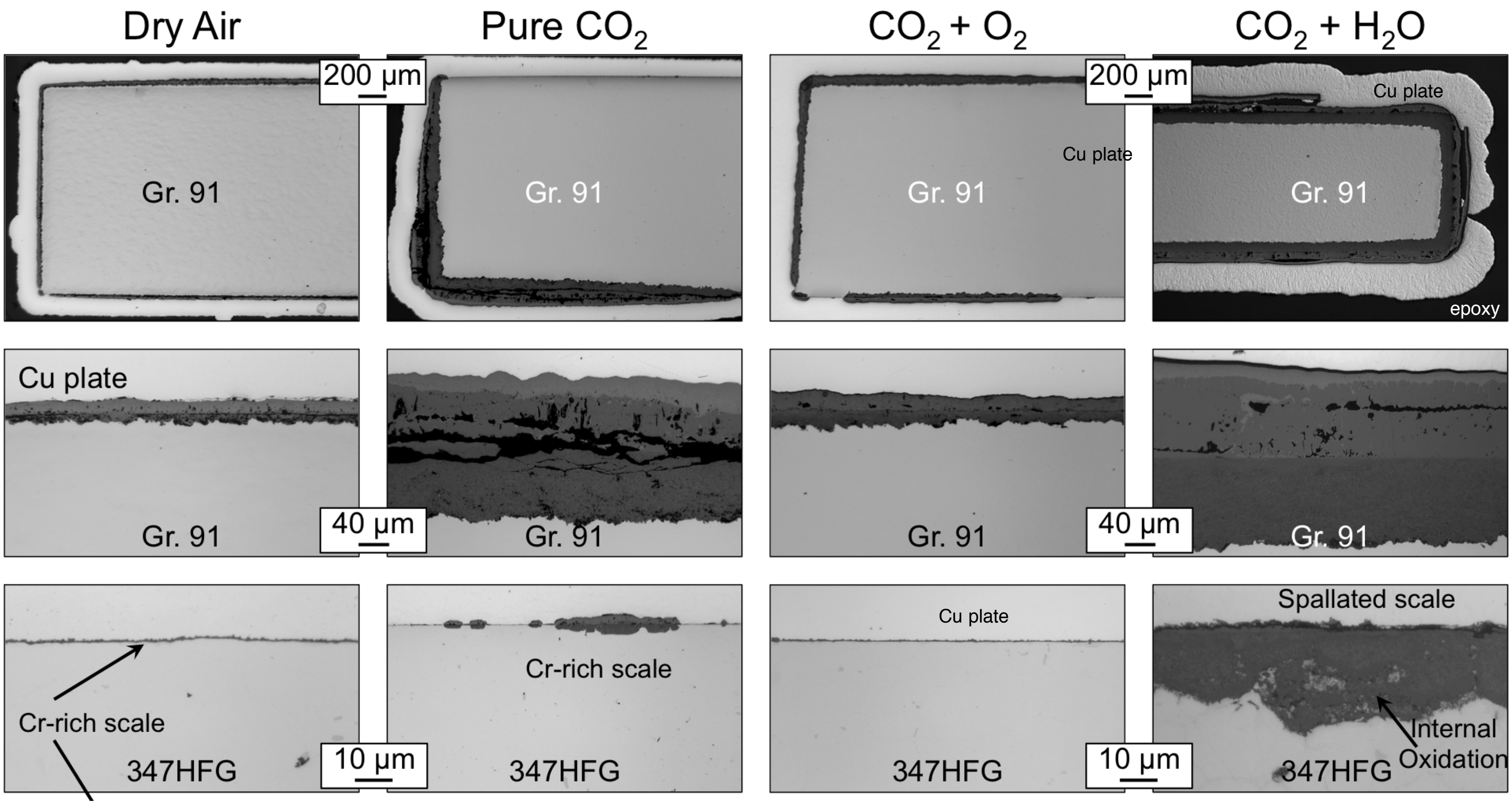




Pint and Thompson, Mater. Corros. 2014

Especially H_2O caused thick oxide

Light microscopy after 500h exposures at 700°C



Dry Air

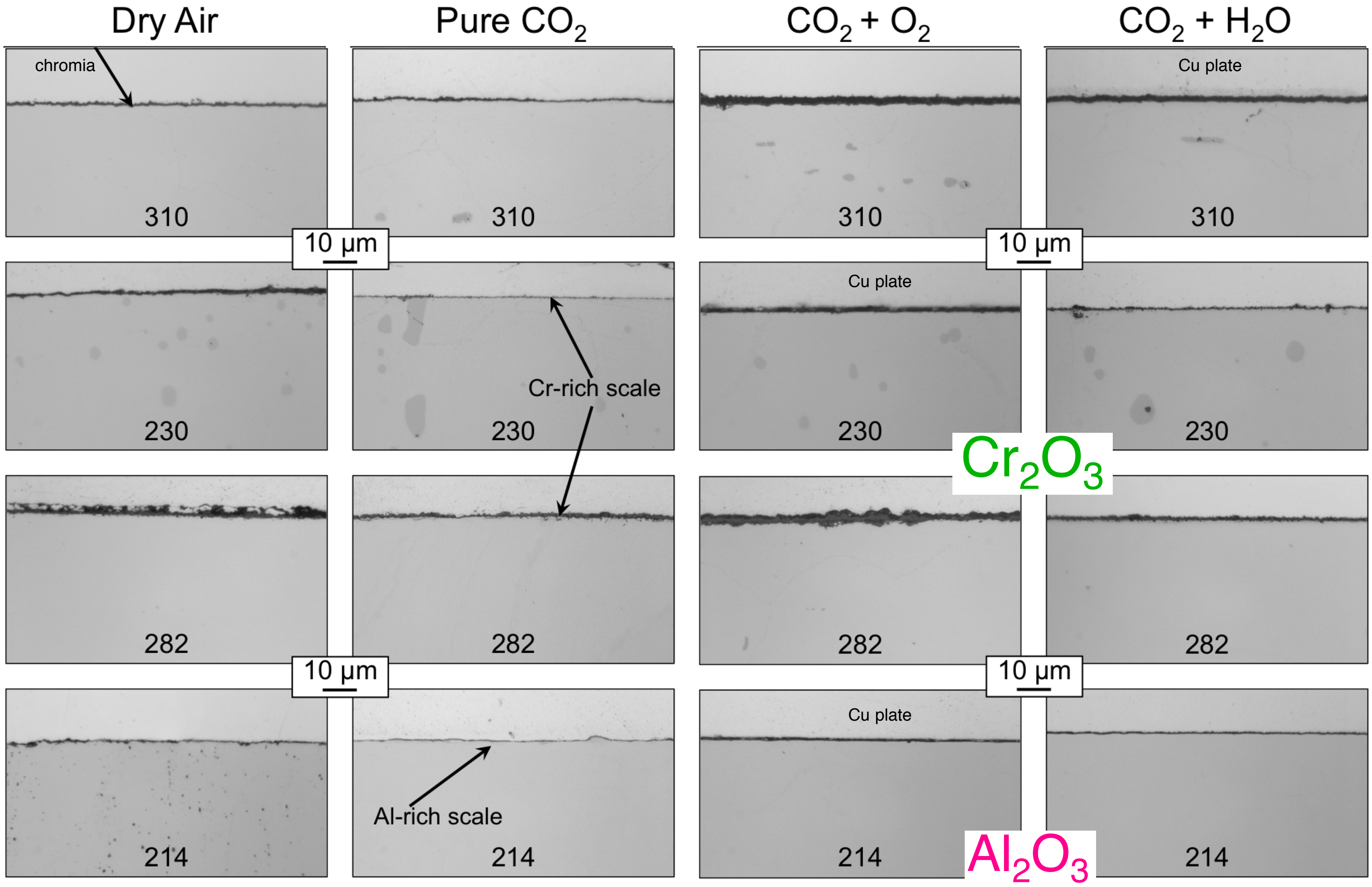
Pure CO_2

$CO_2 + O_2$

$CO_2 + H_2O$

Thinner oxides formed on others

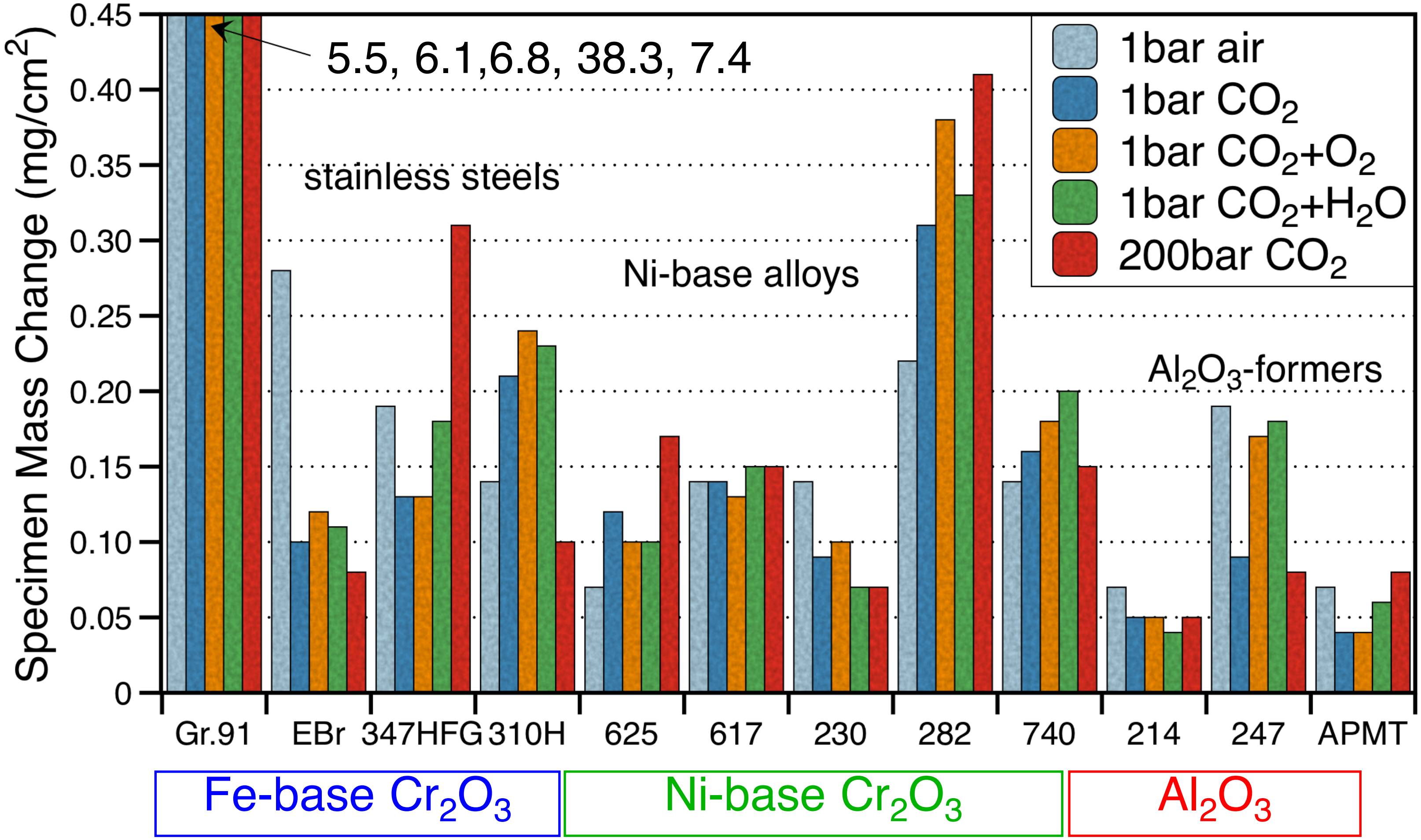
Light microscopy after 500h exposures at 700°C



750°C 1bar: baseline + impurities

1bar: dry air, CO_2, CO_2+0.15O_2, CO_2+10%H_2O

Consistently higher mass gains for alloy 282



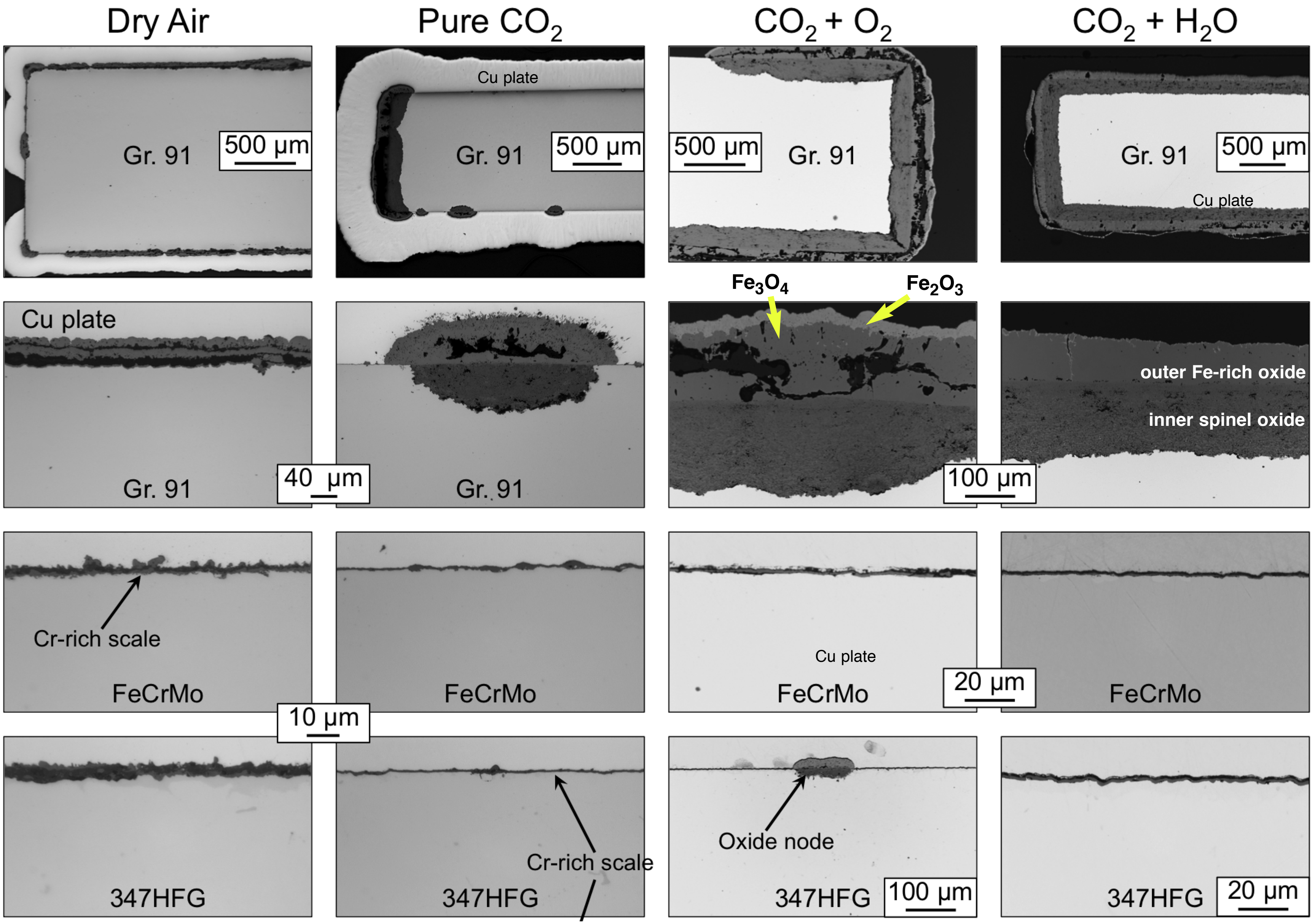
All
500h
tests

0.1 mg/cm² ~ 0.5 μm surface oxide

10 mg/cm² ~ 50 μm (2 mils)

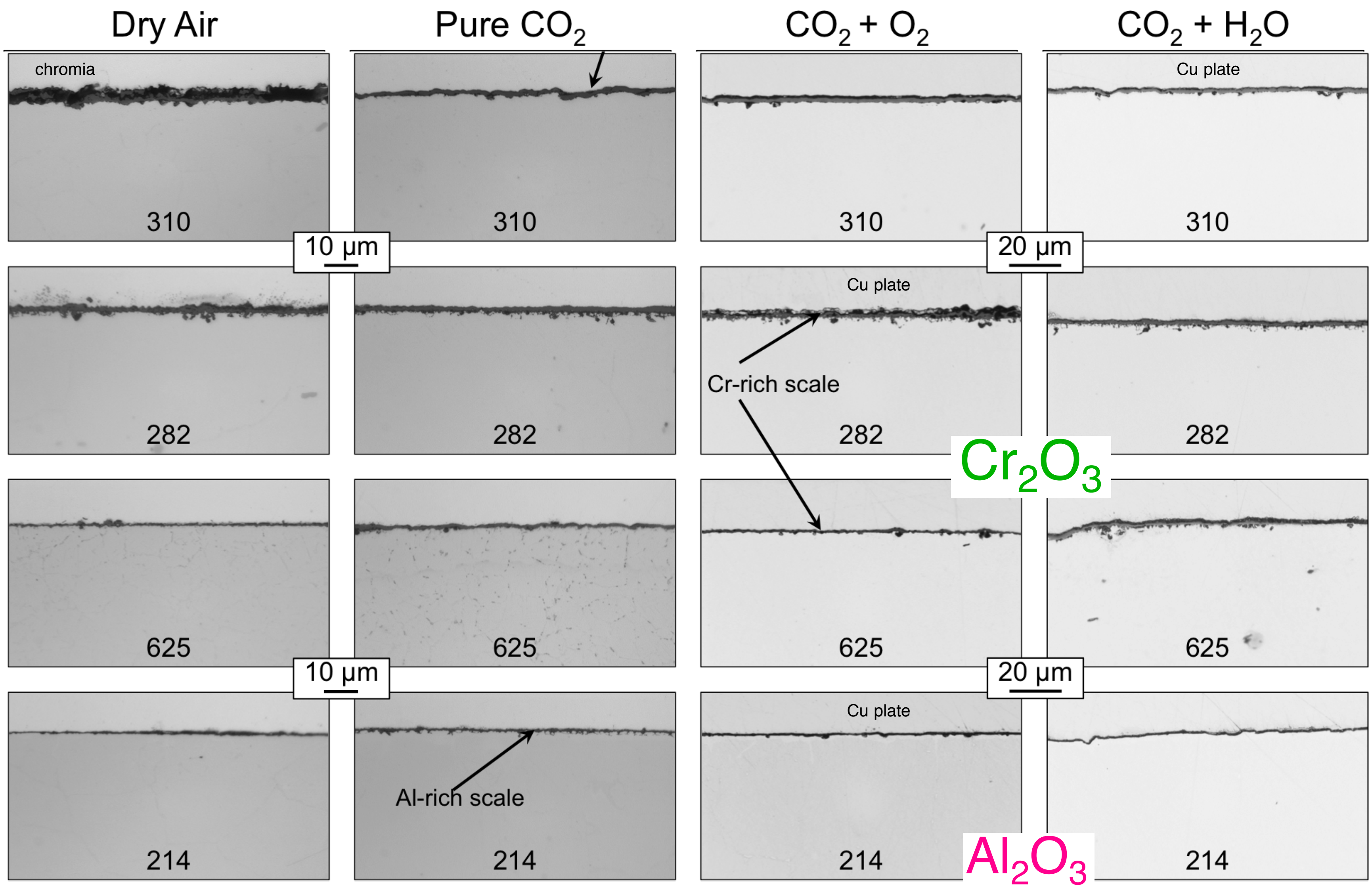
Only Gr.91 formed thick oxide

Light microscopy after 500h exposures at 750°C



Thinner oxides formed on others

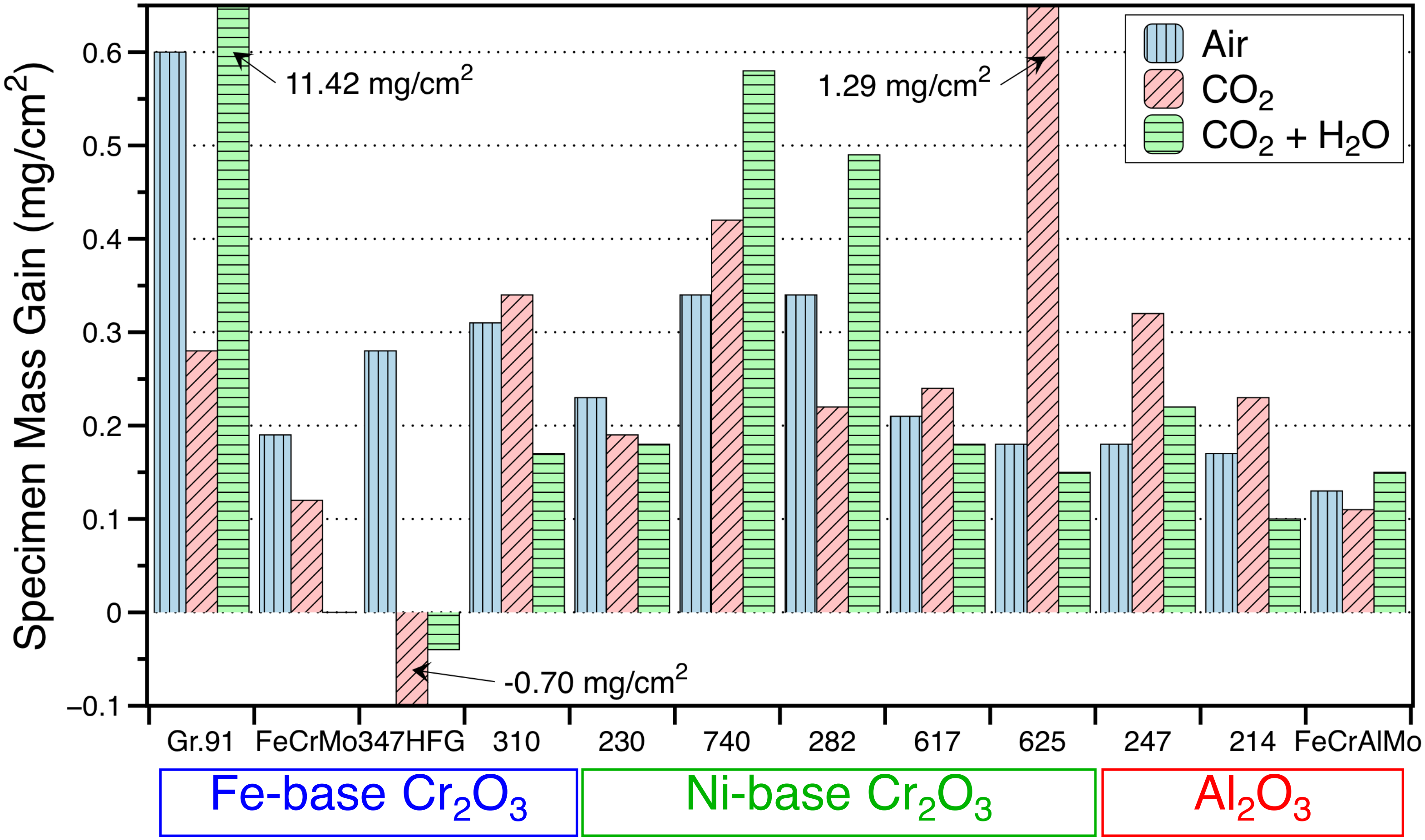
Light microscopy after 500h exposures at 750°C



800°C 1bar: different behavior

1bar: dry air, CO_2, CO_2+10%H_2O

Consistently higher mass gains for alloy 282



All
500h
tests

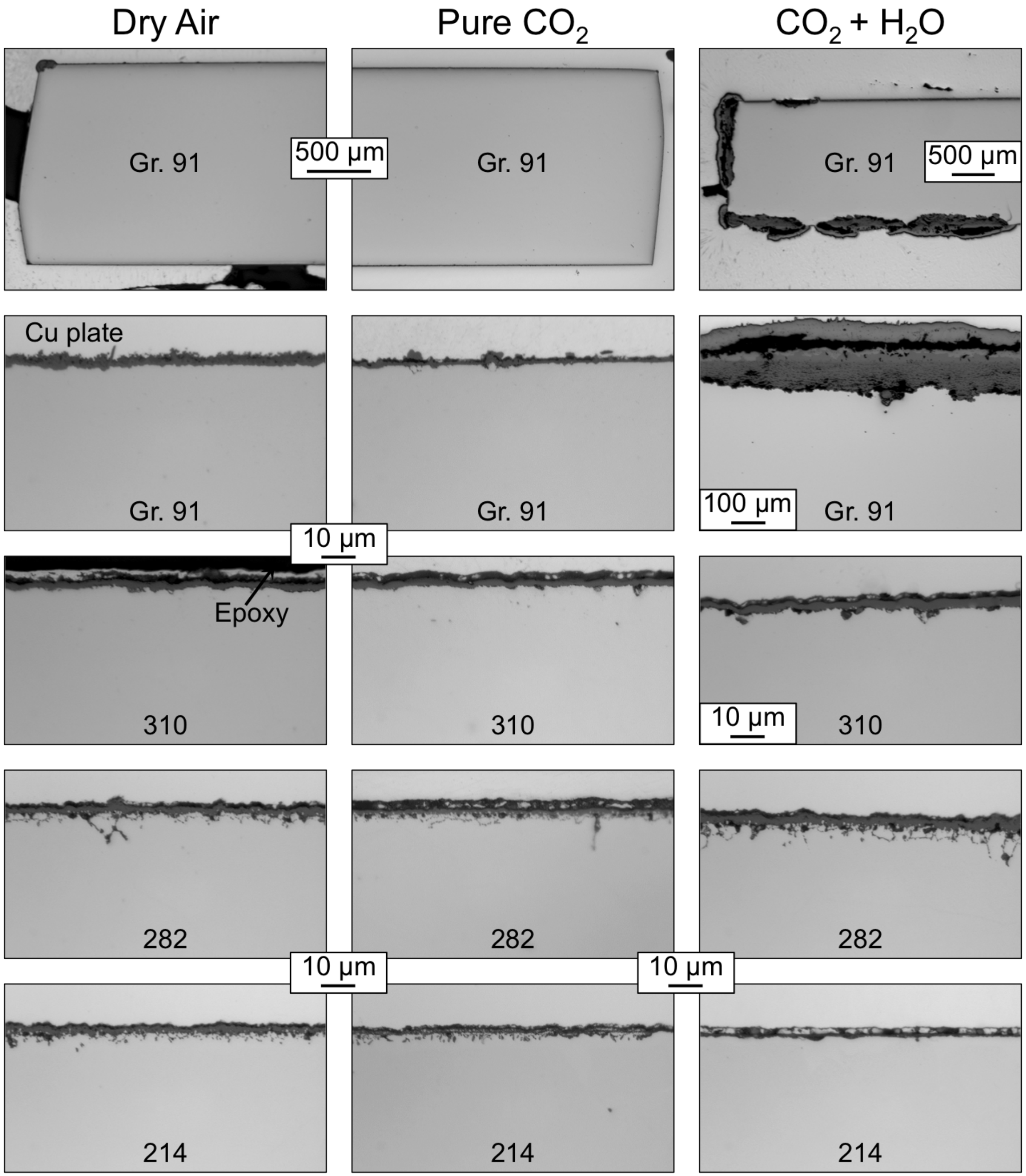
0.1 mg/cm^2 ~ 0.5 μm surface oxide

10 mg/cm^2 ~ 50 μm (2 mils)

Gr.91 + H_2O: only thick oxide

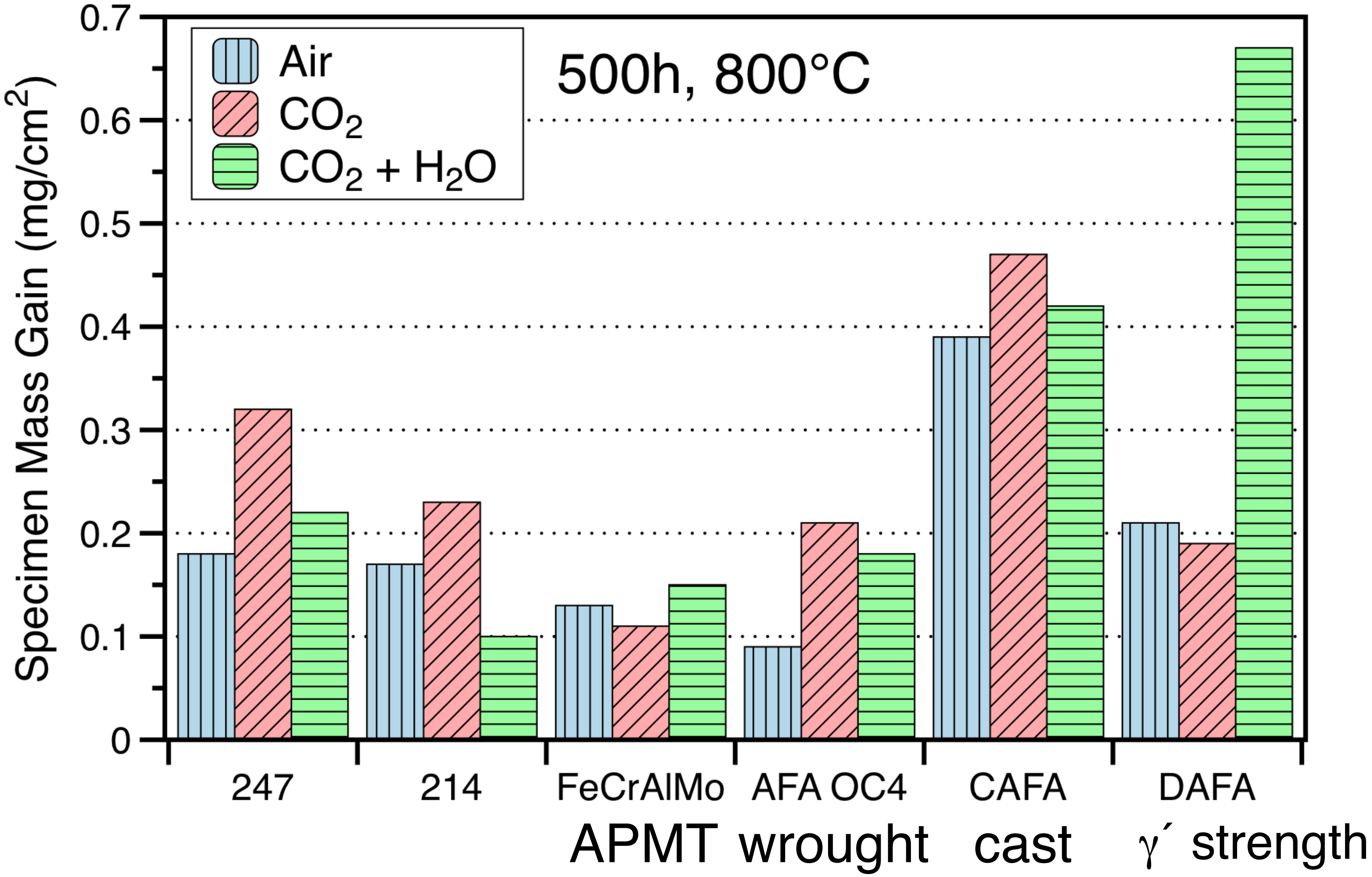
Light microscopy

500h at 800°C



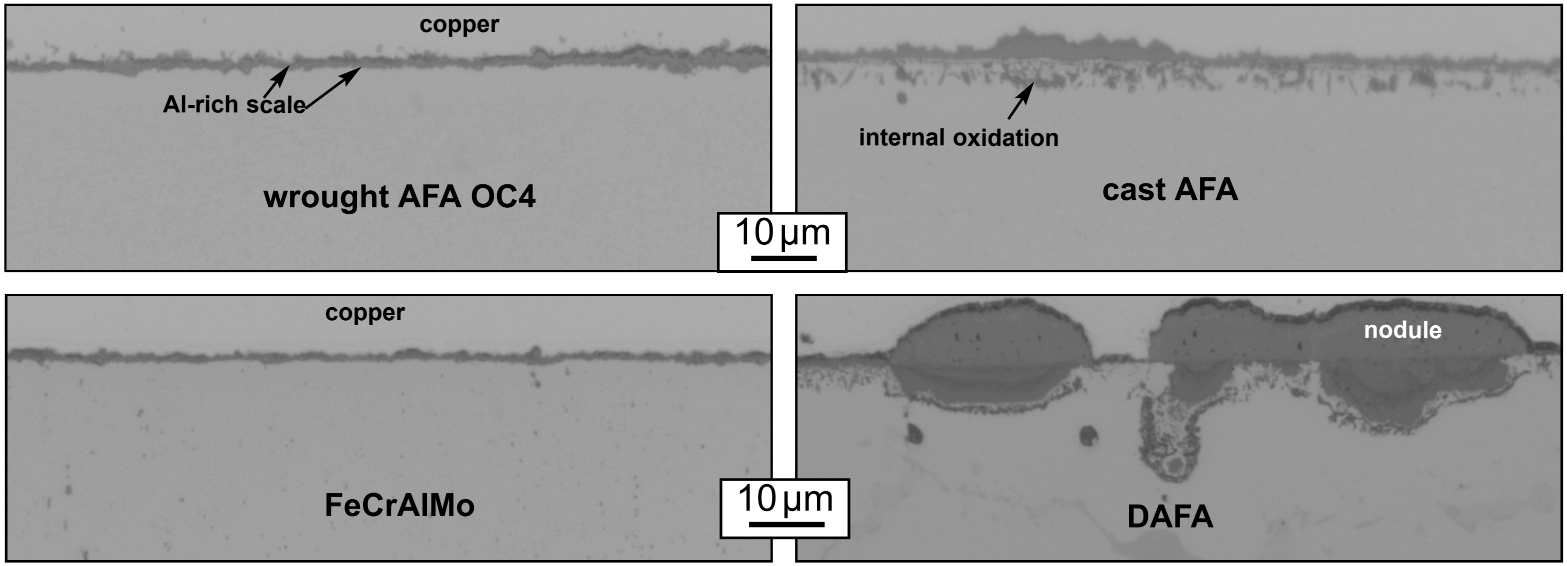
800°C: wide range of Al_2O_3-former

AFA: alumina-forming austenitic steel
wrought AFA (OC4) performed best



H_2O affected AFA variants

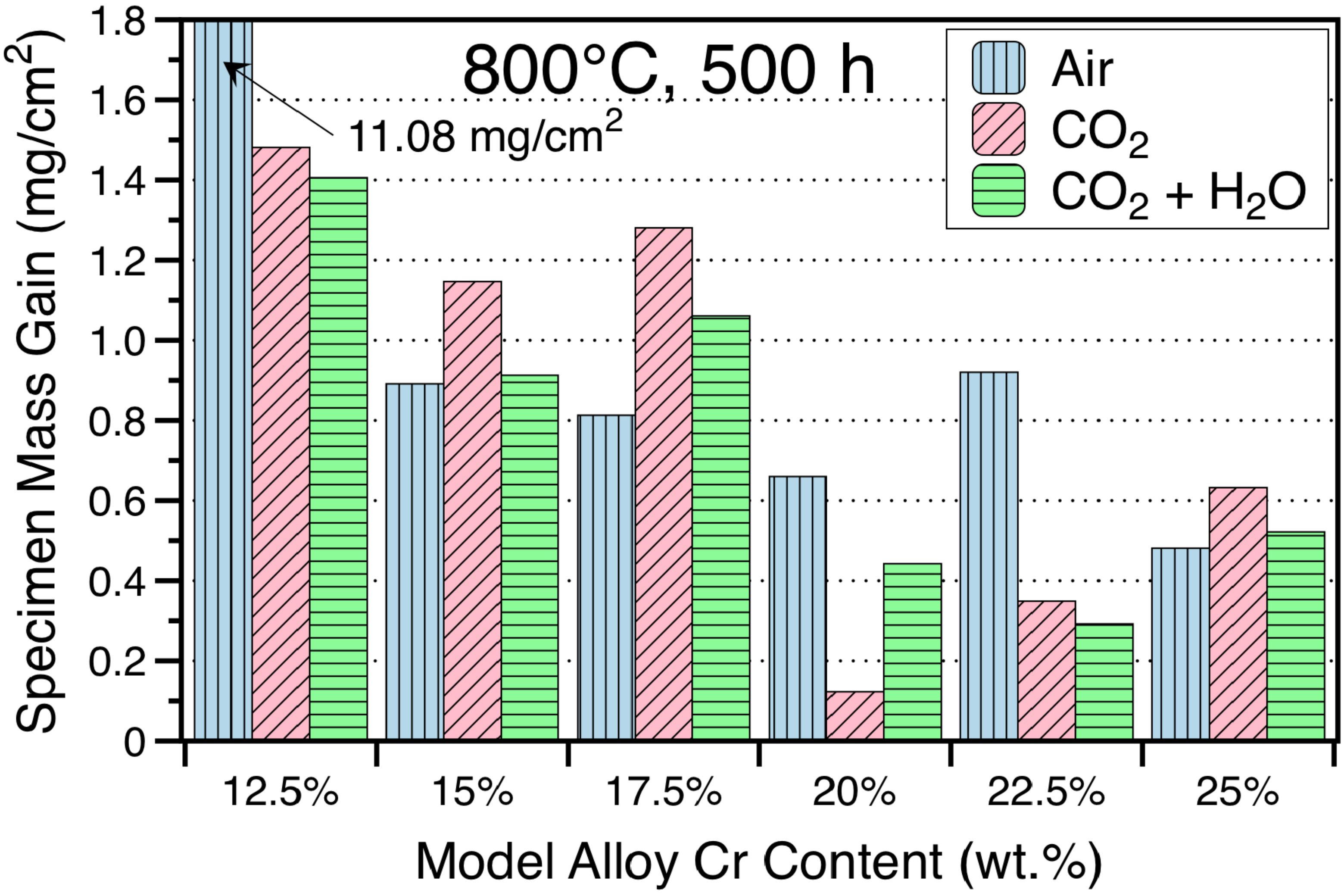
Light microscopy: 500h, 800°C, CO_2+10%H_2O



Hoping to find critical Cr content

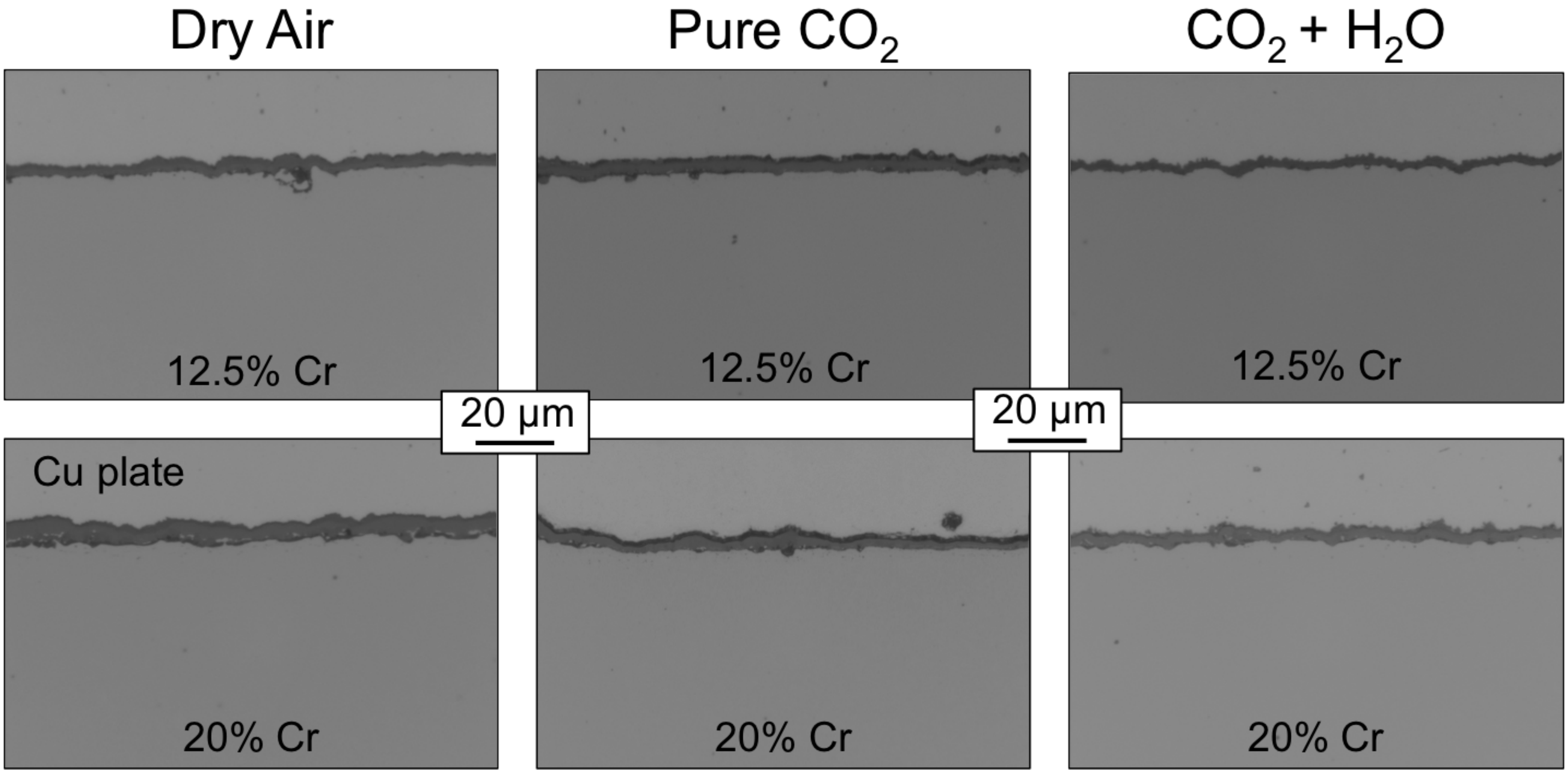
Model Fe-Cr alloys with Mn,Si,Y additions

Not a strong affect of environment on performance



Thin oxides formed in most locations

Light microscopy after 500h exposures at 800°C



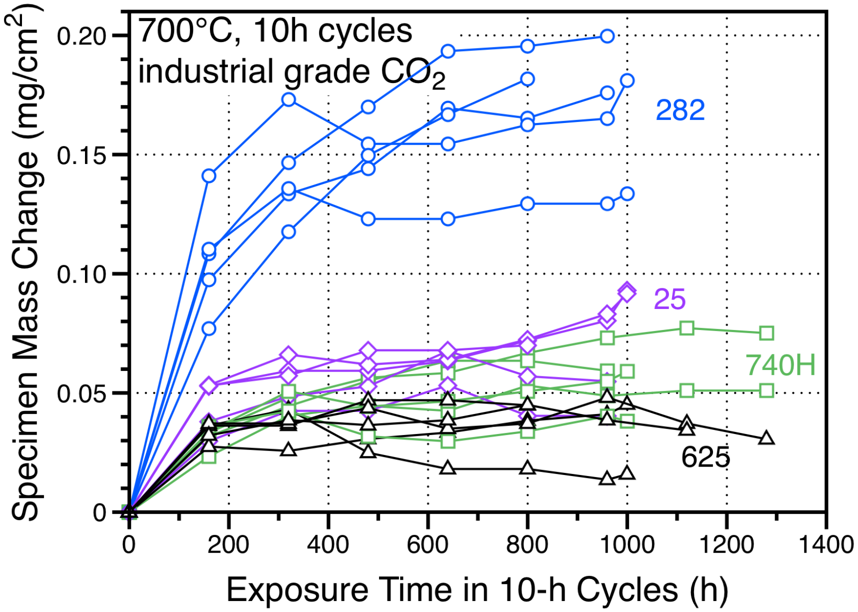
Nodule formation dominated mass change

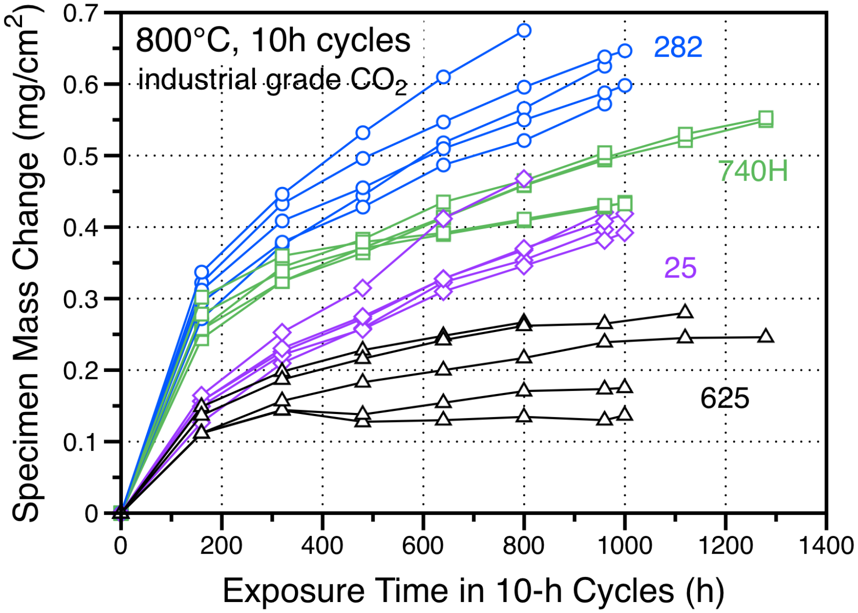
Other work in 2016

#1 Built longer 282 autoclave

#2 SunShot: sCO_2 lifetime model

- 1 bar CO_2, 10-h cycles to simulate solar duty cycle
- 300 bar CO_2, 500-h cycles to 1kh at 700°-800°C





Summary

Completed 500h 1 bar CO_2 tests at 700°-800°C

- dry air, CO_2, CO_2+0.15%O_2 and CO_2+10%H_2O
- Some information on H_2O and O_2 for direct-fired
- Wide range of alloys exposed
- 700°-750°C H_2O had most negative effect
  - similar result observed in other studies
  - thick oxide formed on Fe-9Cr specimens
  - 347HFG thick oxide + spall only at 700°C
  - thin oxides on higher-alloyed materials
- 800°C
  - only thick oxide formed on Gr.91 with H_2O
  - additional alumina-forming alloys evaluated
  - Fe-Cr model alloys did not show clear effect

questions?

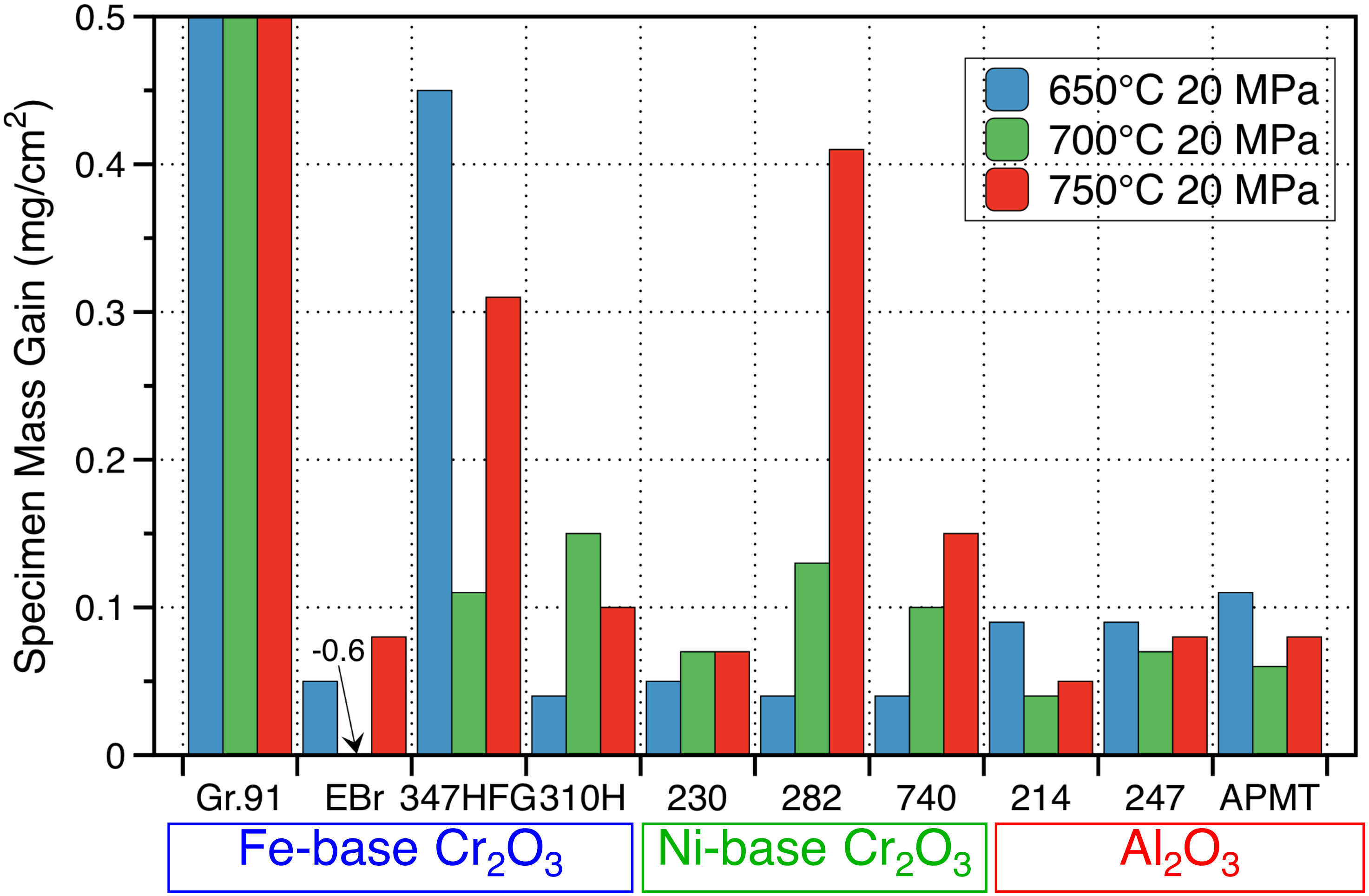
Thoughts

More characterization needed of current results
  - Better understand some unusual results

Concern:
  - Degradation by C penetration through Cr_2O_3
    - H. McCoy 1965 at 1bar
    - D. J. Young et al. (2011-2014) at 1bar
  - Need to evaluate longer times + ex-situ ductility
  - Al_2O_3 thought to be better barrier to C ingress
    - Pre-oxidation may assist in Al_2O_3 formation
    - Al-containing alloys can be difficult to fabricate

1st: 20MPa runs, most low gains

10 representative alloys were focus of metallography

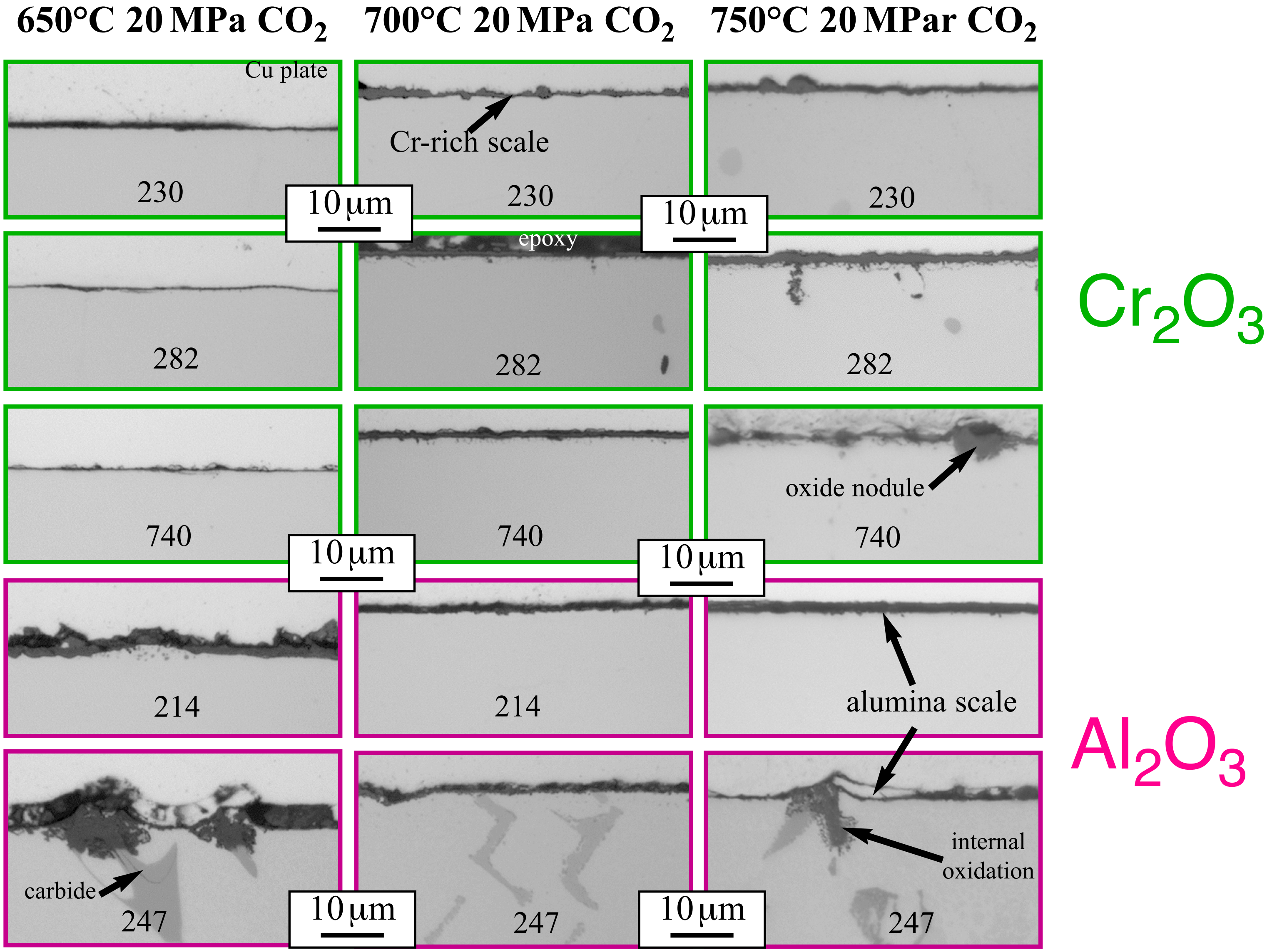


0.1 mg/cm^2 ~ 0.5 μm surface oxide

10 mg/cm^2 ~ 50 μm (2 mils)

Ni-base alloys: thin scales

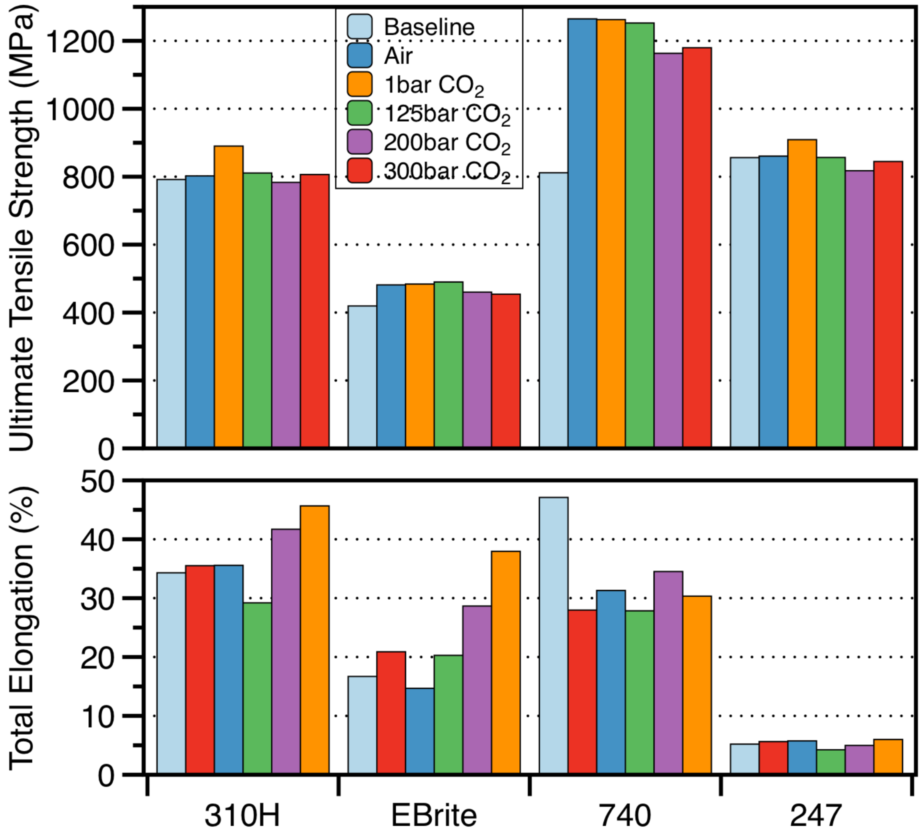
All thin Cr-rich or Al-rich scales in 20 MPa sCO_2

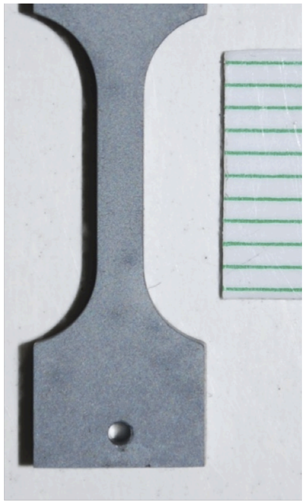


750°C: initial tensile experiments showed little effect of sCO_2

25mm tensile bars exposed at each condition

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





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 (?)

load following

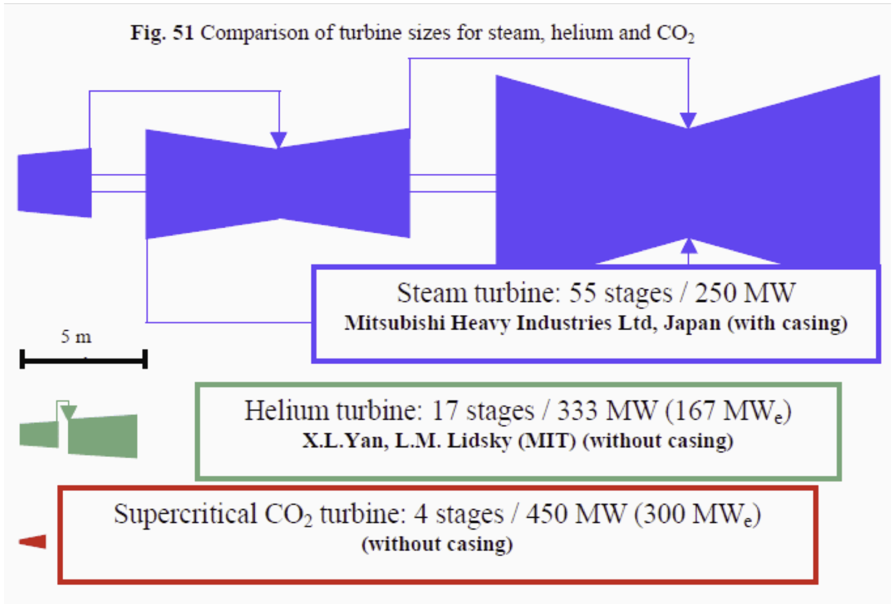


Fig. 51 Comparison of turbine sizes for steam, helium and CO_2

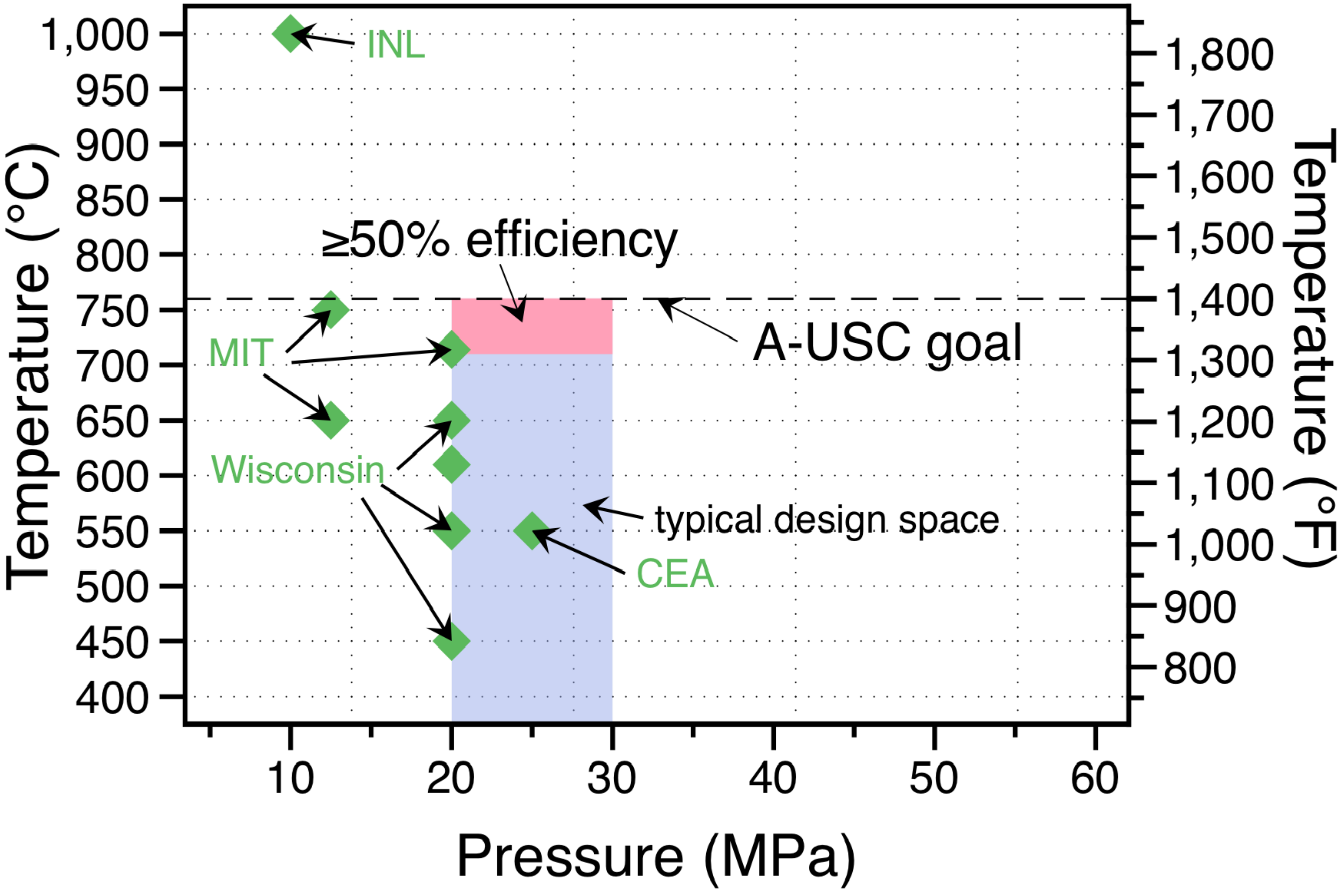
Source: MIT report

Direct- and indirect-fired sCO_2 Brayton cycles for:

- fossil energy (coal or natural gas) FY13- FY16+
- concentrated solar power FY16-FY18
- nuclear (paired with sodium for safety)
- waste heat recovery/bottoming cycle

Relatively little prior sCO_2 work

Especially at >650°C and 300 bar



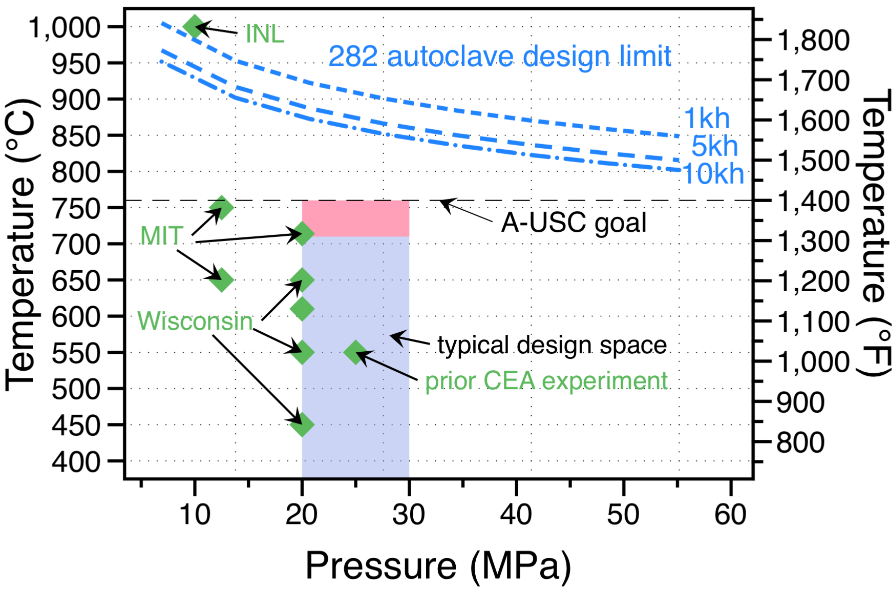
Several groups active in the past 10 years

U. Wisconsin group has published the most results

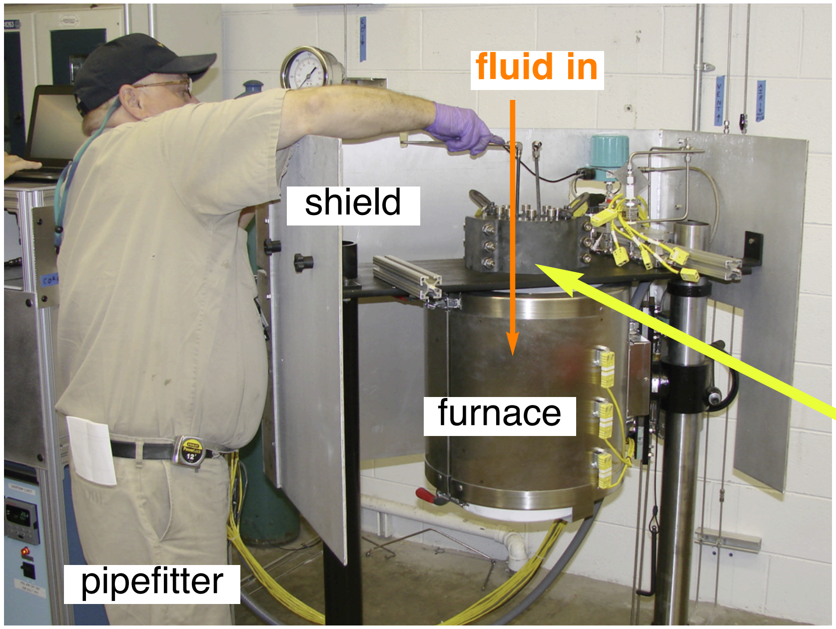
Temperature/pressure limited by autoclave design

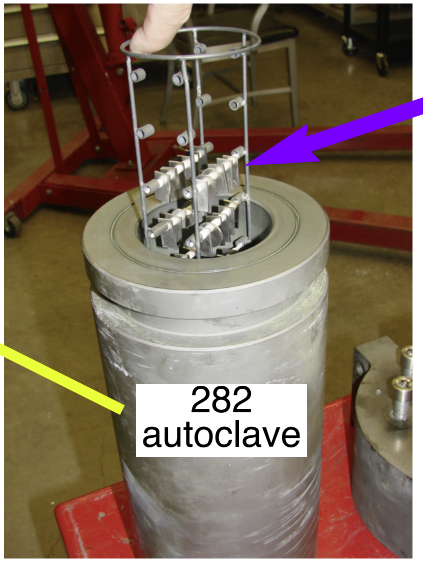
ORNL designed new sCO_2 rig

- Haynes 282 autoclave
  152mm (6”) dia.
- Hight purity CO_2
  99.995%, <5 ppm H_2O
  1ml/min flow
- 10x20x1.5mm coupons

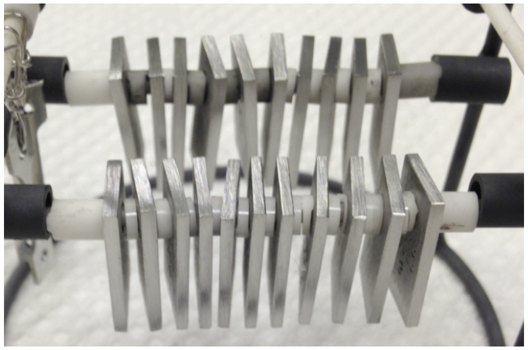


ORNL sCO_2 rig:

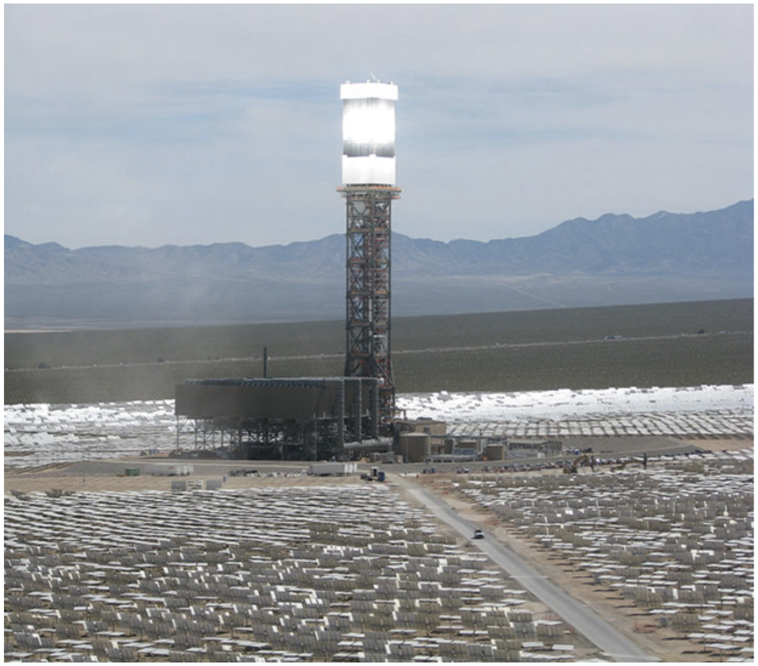




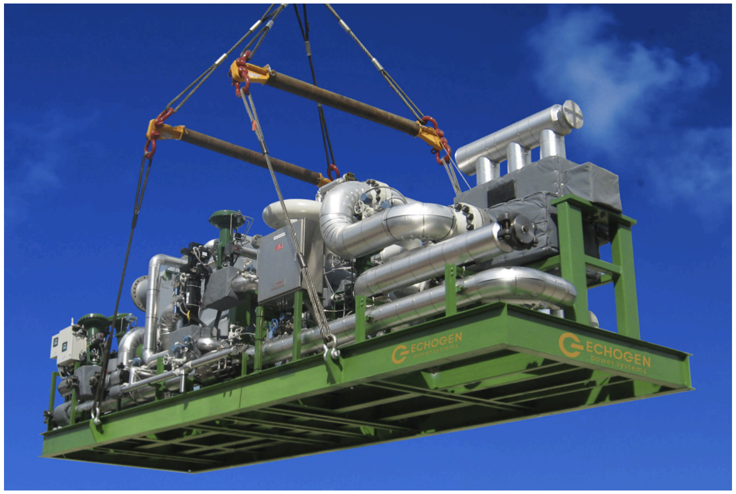
specimen
holder



Many possible applications



Smaller fossil fuel turbines



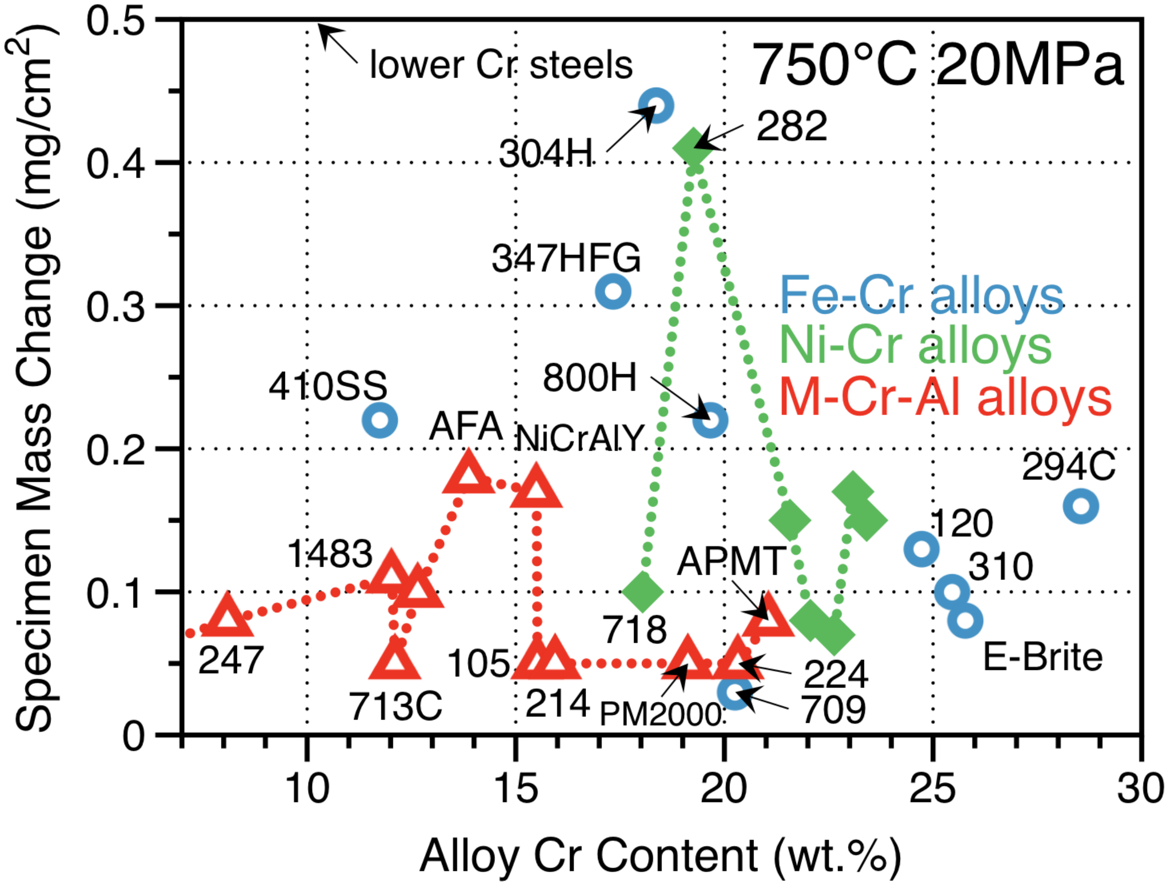
7MW Echogen (WHR)

200 bar mass change by %Cr

~30 alloys exposed in first 750°C experiment

Alumina-forming alloys typically lower mass than chromia-forming alloys

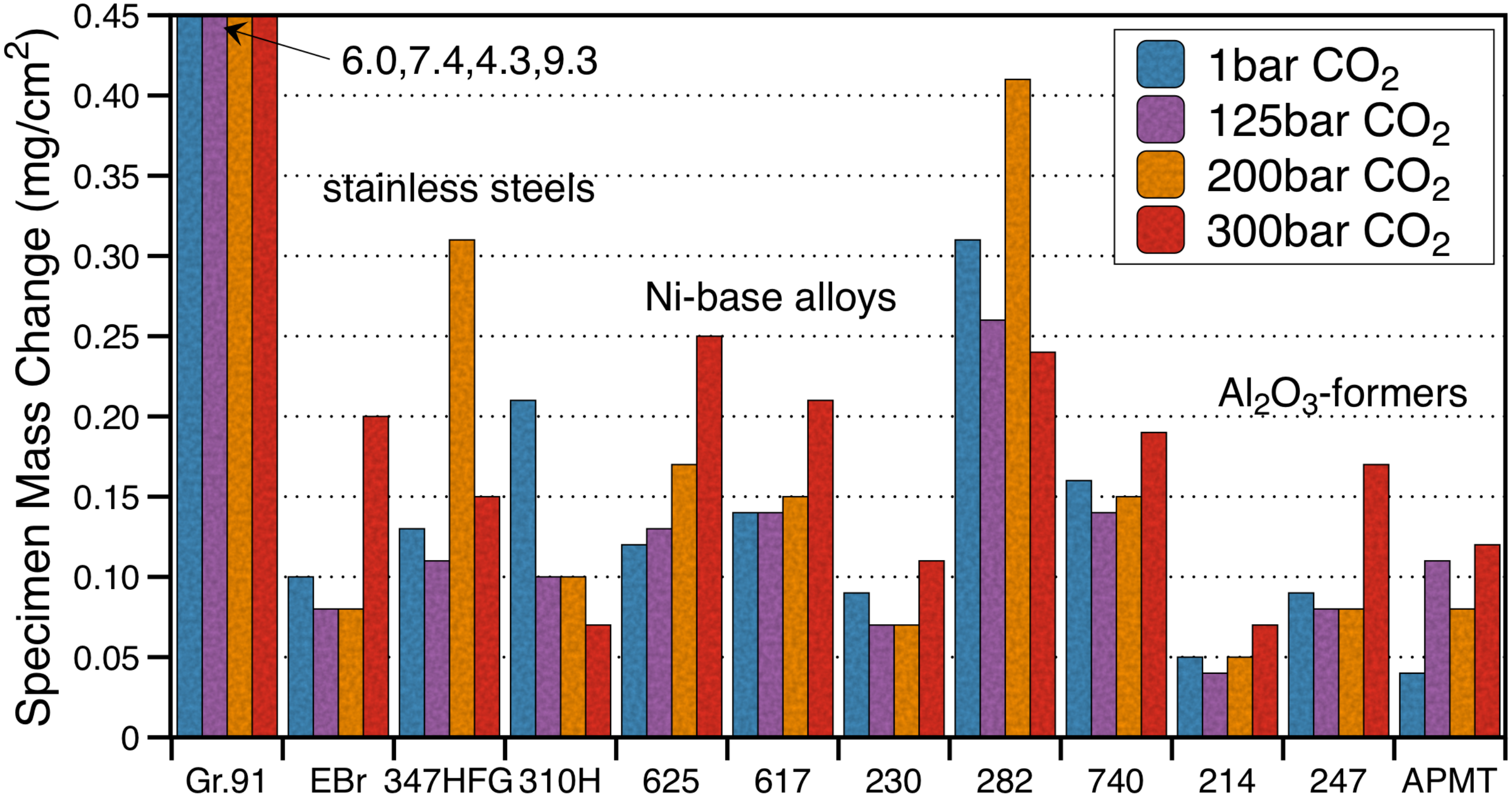
Higher mass gain for alloy 282 specimen



Little effect of pressure observed

500h exposures at 750°C

Core group of 12 alloys evaluated



All 500h tests

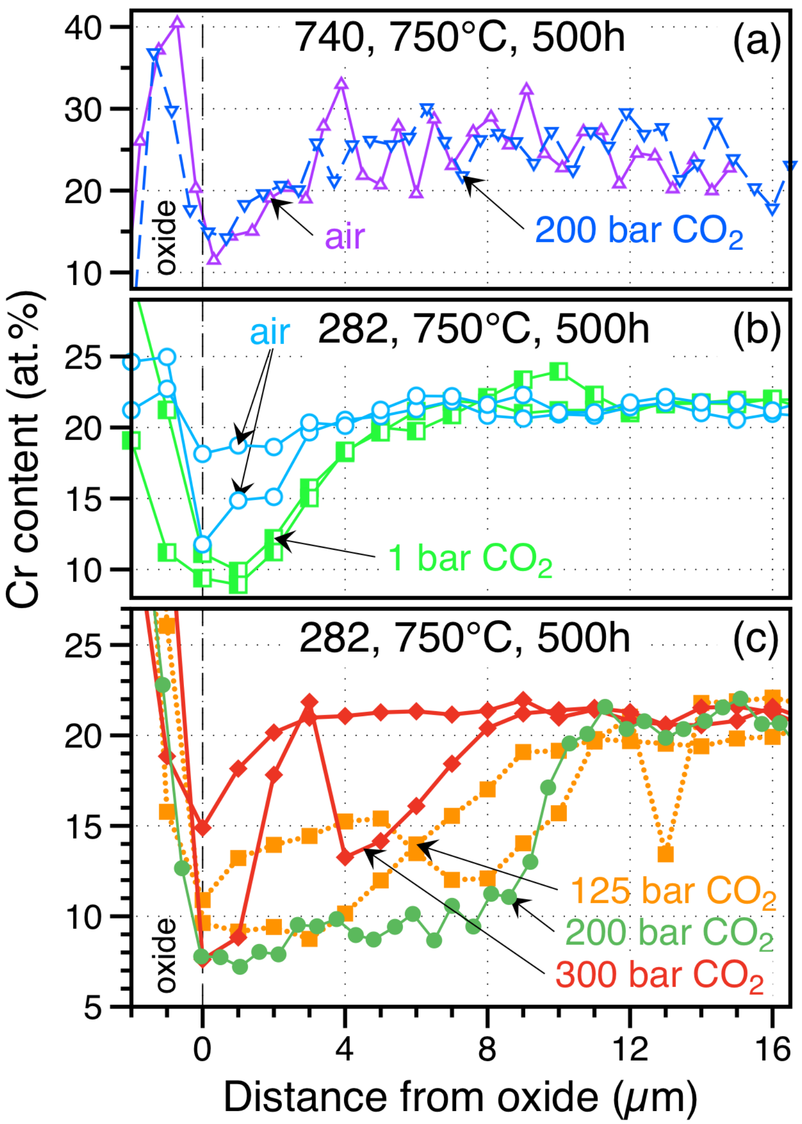
Fe-base Cr_2O_3 | Ni-base Cr_2O_3 | Al_2O_3

0.1 mg/cm^2 ~ 0.5 μm surface oxide

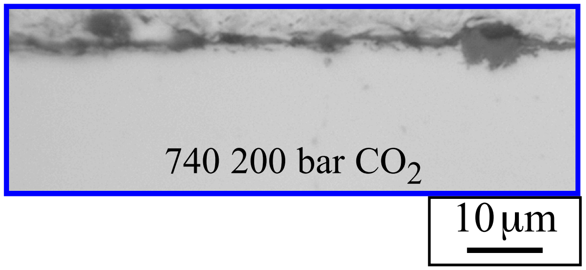
10 mg/cm^2 ~ 50 μm (2 mils)

282: deeper Cr depletion in sCO_2(?)

EPMA depth profiles beneath scale at 750°C

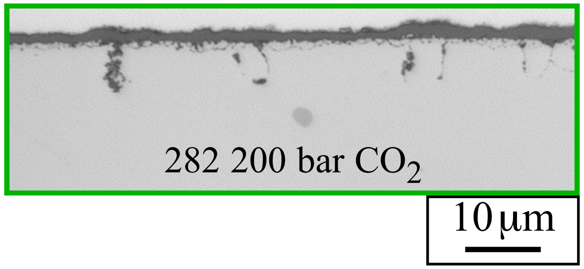


1 bar air vs. 200bar CO_2



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

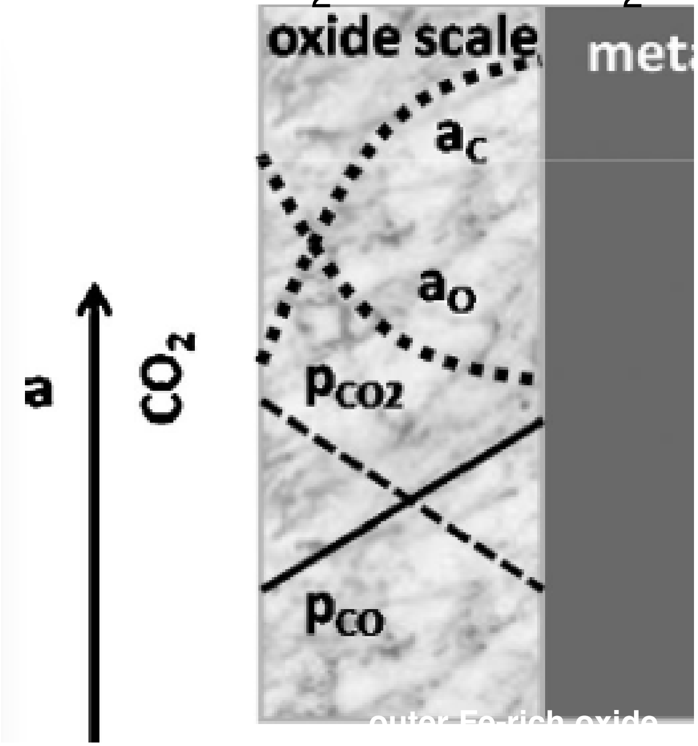
282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti



Looking for internal carburization

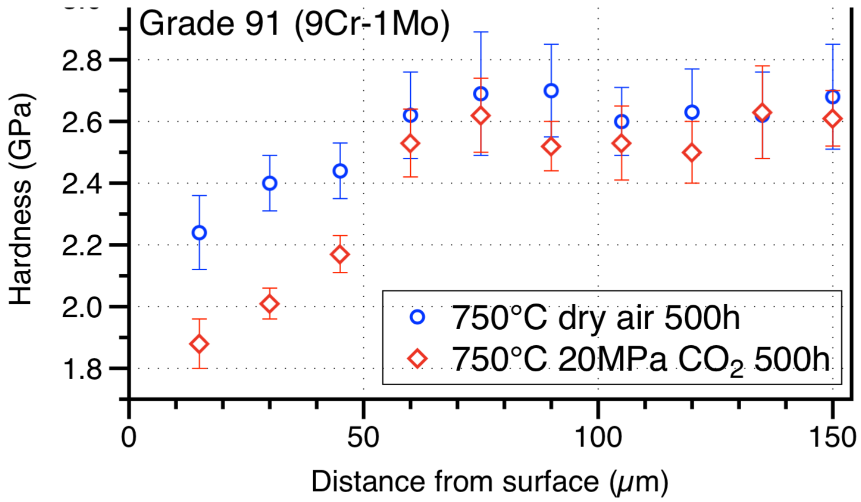
High a_c predicted, McCoy (1965) observed in 1bar CO_2

$CO_2 = CO + 1/2O_2$

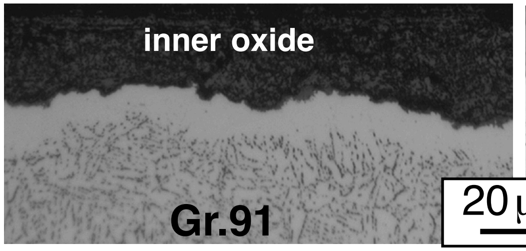


from Young, et al. 2011

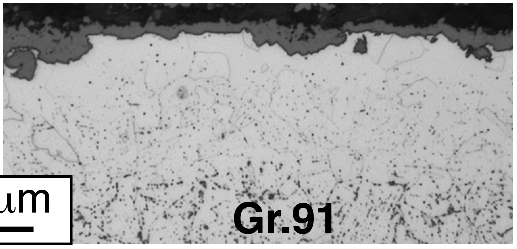
microhardness of Gr.91



700°C 1 bar dry air

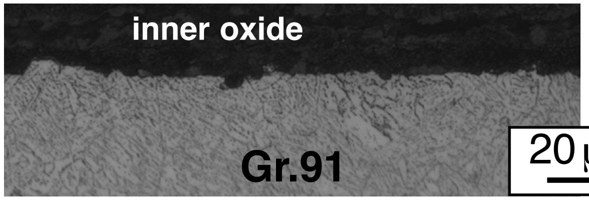


750°C 1 bar dry air

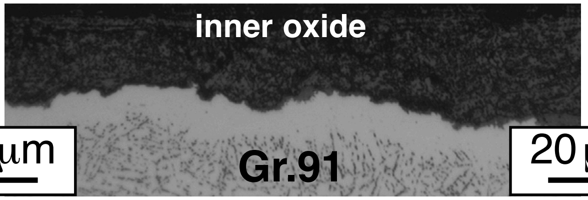


oxalic acid etch

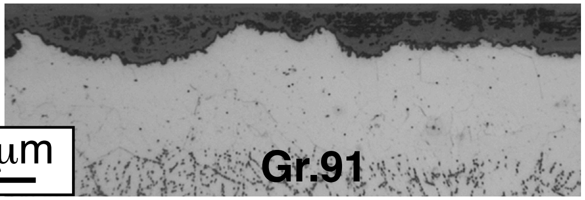
650°C 200 bar CO_2



700°C 200 bar CO_2



750°C 300 bar CO_2



Typical Fe-rich oxide on Gr.91

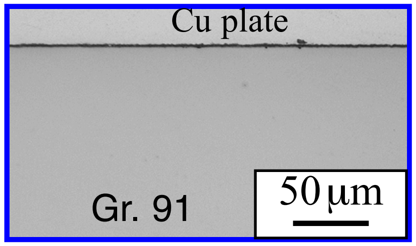
However, inner/outer ratio appears to change with P

Outer Fe_2O_3/Fe_3O_4 layer

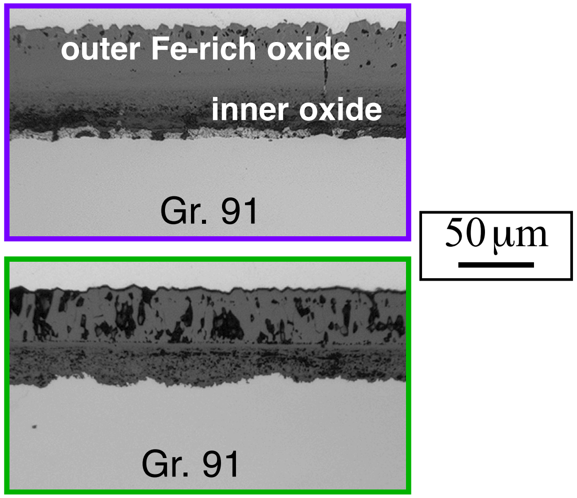
Inner $(Fe,Cr)_3O_4$ layer

Grade 91: Fe-9Cr-1Mo

Some thin-protective Cr-rich scale at 1bar



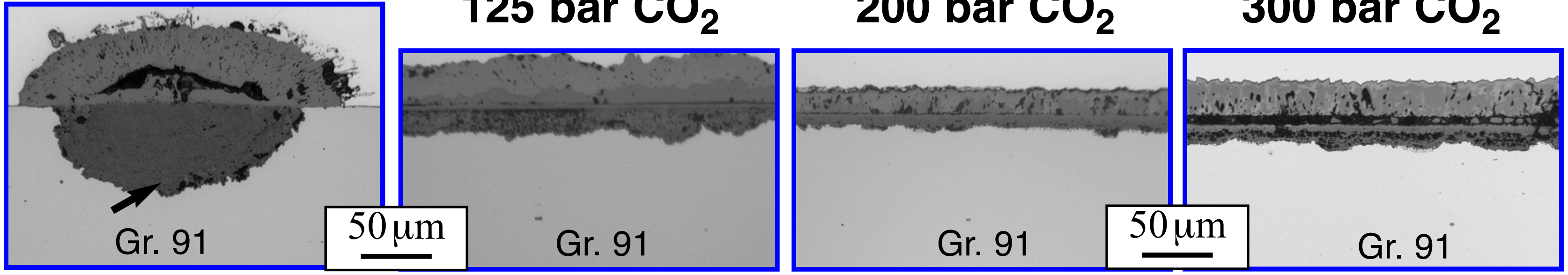
650°C 1 bar lab. air (5 kh)



650°C 200 bar

700°C 200 bar

750°C



1 bar CO_2

125 bar CO_2

200 bar CO_2

300 bar CO_2

light microscopy of polished cross-sections

347HFG: protective at 750°C

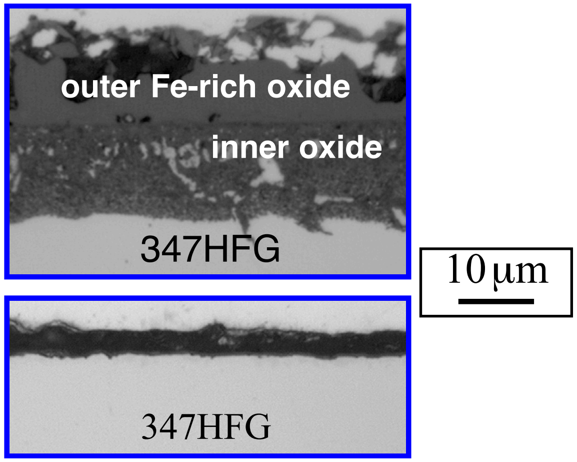
Thick duplex oxide formed at 650°C in sCO_2

Only a few nodules formed at 700°-750°C
- faster Cr diffusion in alloy can affect behavior
- could change after longer exposures

347HFG (fine grain):
18.6Cr-11.8Ni-0.8Nb

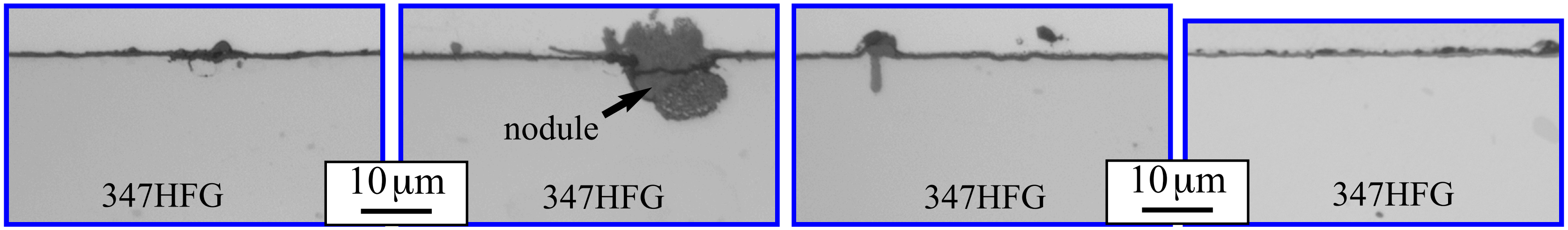
650°C
200 bar

700°C
200 bar



750°C

1 bar CO_2 | **125 bar CO_2** | **200 bar CO_2** | **300 bar CO_2**



light microscopy of polished cross-sections

Hf-rich carbide oxidized in sCO_2

EPMA shows carbide transformed to oxide at 750°C

247: Ni-8Cr-6Al-10Co-10W-3Ta-1.4Hf