The Effect of Impurities on Oxidation in Supercritical CO_2 at 750°C

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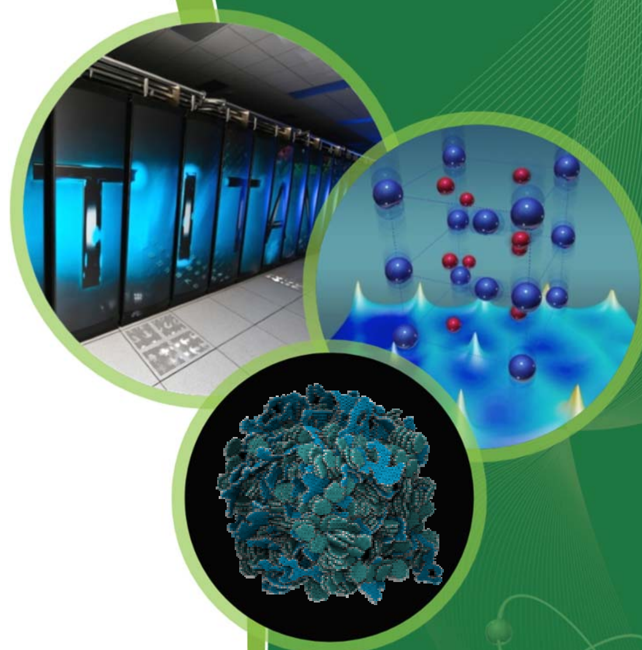

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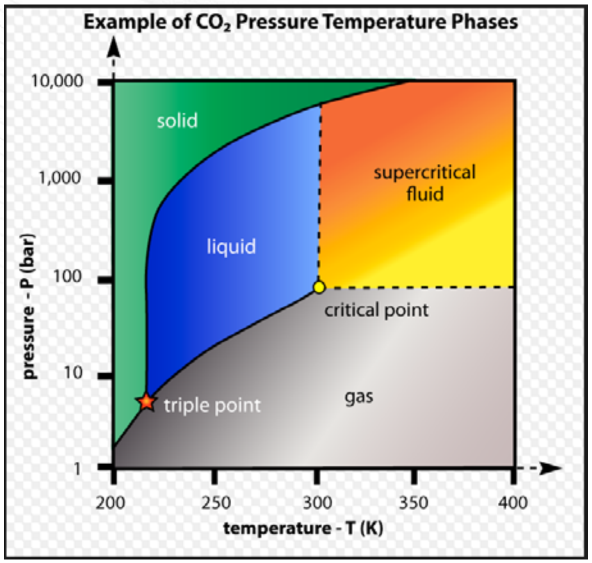
Acknowledgments

- Funding from DOE Solar Energy Technology Office
  - SunShot Initiative, SuNLaMP award number DE-EE0001556
- Funding from DOE Fossil Energy Program
  - Vito Cedro (NETL) project monitor, Regis Conrad (DOE) program manager
- GDOES, Michael Lance
- TEM, Kinga Unocic
- ORNL technicians
  - Mike Howell
  - Mike Stephens
  - Tracie Lowe (SEM/ImageJ)
  - George Garner
  - Tyson Jordan

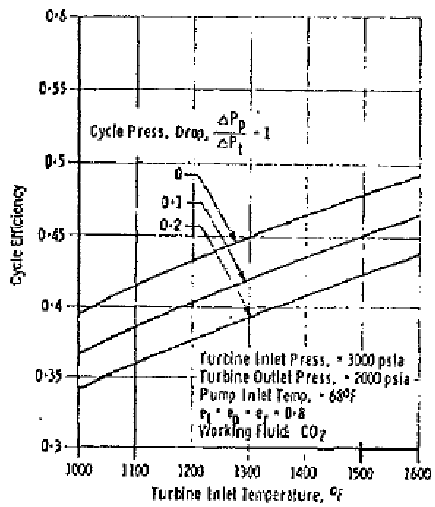
Supercritical CO_2 (sCO_2) has high efficiency potential for several power generation applications



- High density
  - Like a liquid
- Flexible
  - small turbomachinery

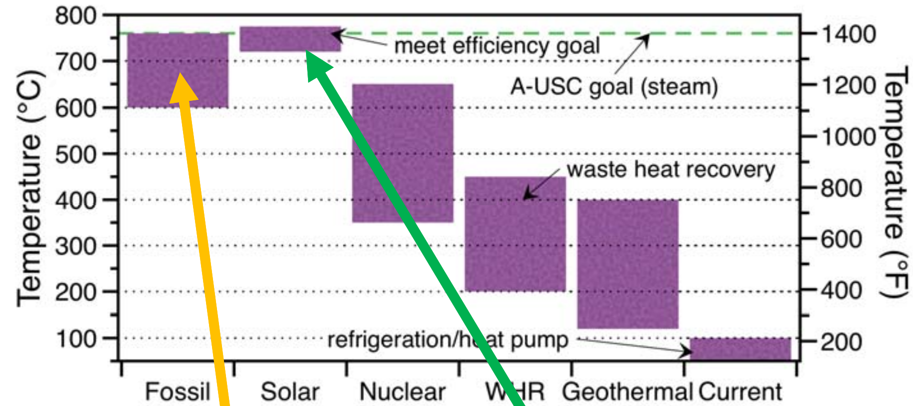
Critical Point: 31°C, 74 bar

50% eff @ >720°C



Feher, 1965

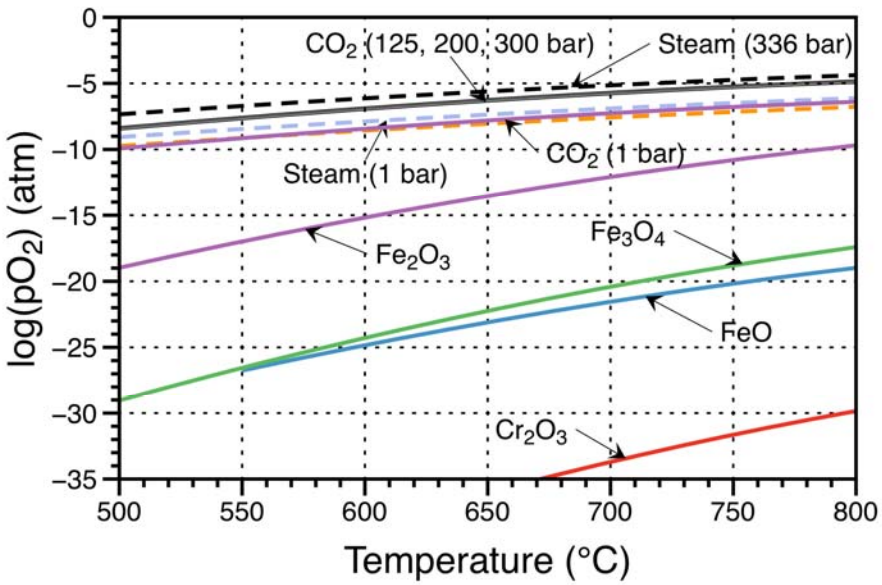
Temperature range estimates for various applications



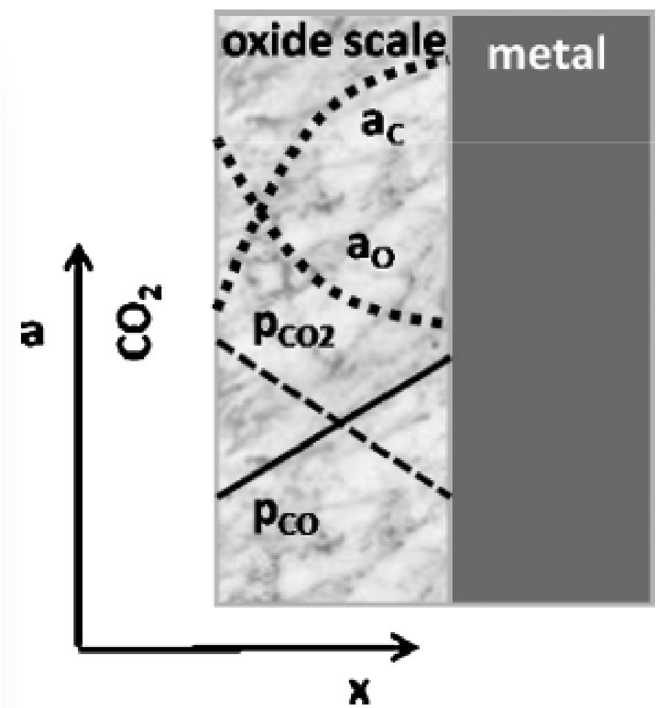
Fossil bottoming cycle

National Laboratory

Thermodynamics: Oxygen levels similar in steam/CO_2 Concern about high C activity at m-o interface



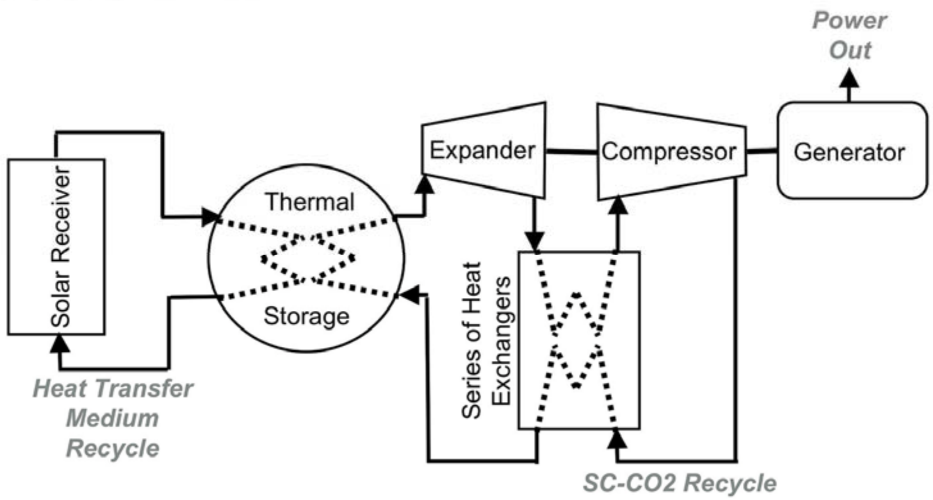
Factsage calculations



From Young et al. 2011
Also Fujii and Muessner, 1967

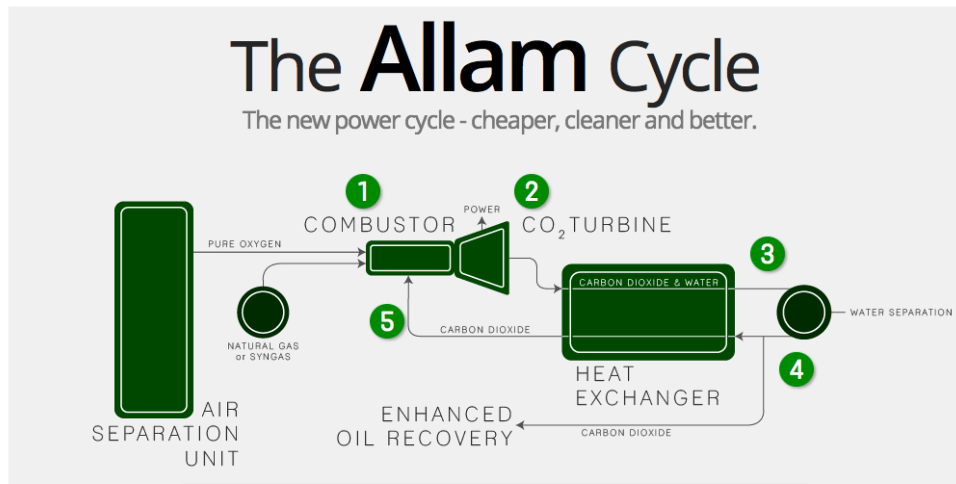
Indirect- vs. direct-fired sCO_2 systems (i.e. closed vs. open)

Closed cycle (indirect-fired):
"pure" CO_2 100-300 bar



DOE SunShot funding

Open cycle (direct-fired):
sCO_2 + impurities (O_2,H_2O…)



DOE Fossil Energy funding

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Supercritical CO_2 Allam cycle: first clean fossil energy?

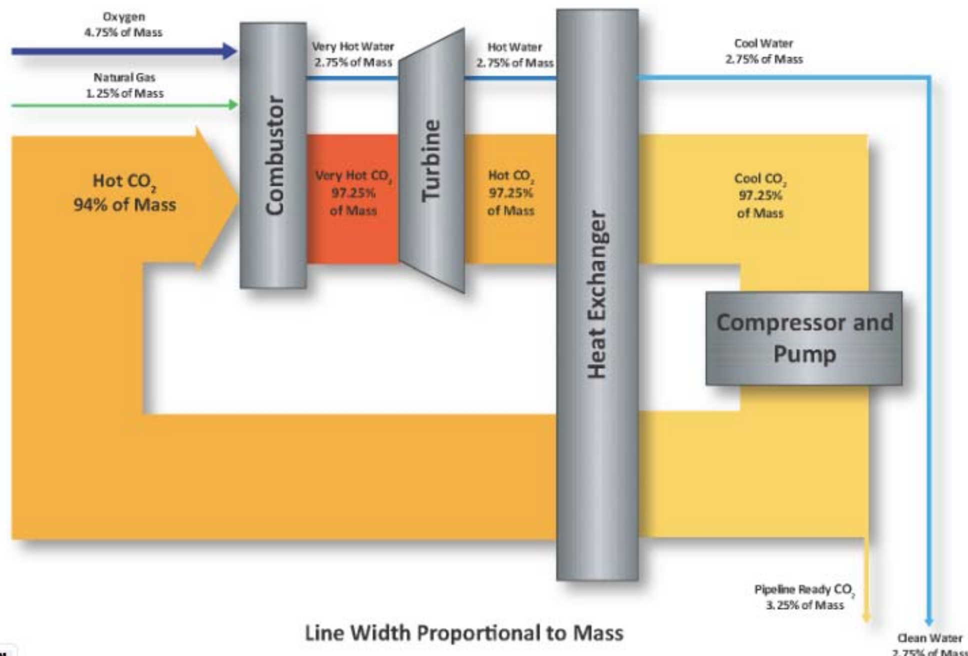
NetPower 25 MWe demo plant (Texas)

Exelon, Toshiba, CB&I, 8Rivers Capital: $140m

The prototype NET Power plant near Houston, Texas, is testing an emission-free technology designed to compete with conventional fossil power. CHICAGO BRIDGE & IRON

Reported 95+% complete

Material challenges:
Combustor: 1150°C (!?!)
Turbine exit: 750°C/300 bar



Moving forward with limited compatibility data!
As audacious as Eddystone in 1960

Project goal is to study O_2+H_2O effects on sCO_2 compatibility

- Conflicting literature on effect of impurities (U.Wisc., EPRI)
- BUT, we can't easily pump impurities into flowing sCO_2 fluid
- 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 (2014-15)
2) Compare 1 & 300 bar: industrial vs. research grade CO_2 vs. lab air
   - Test matrix nearly complete, creating a baseline for understanding #5
3) **Study 1 & 25 bar RG CO_2 vs. CO_2+10%H_2O vs. CO_2+10%H_2O+0.1%SO_2**
   - **500 h exposures completed at 700° and 800°C**
4) Study 1 & 43 bar RG CO_2 at 640°C to compare to gas-cooled reactors
5) **Constructed rig for 300 bar/750°C testing with 1%O2+0.25%H_2O**
   - First experiment completed in February

Two sCO_2 projects at ORNL

DOE Fossil Energy

- 750°C/300 bar: 500-h cycles
- Focus on impurity effects for direct-fire
  - Baseline research grade (RG) CO_2
  - New autoclave with controlled O_2+H_2O
- Alloys
  - 310HCbN (HR3C, Fe-base SS)
  - 617
  - 230
  - MarM247 (Al_2O_3-forming superalloy)
  - Haynes 282 (Heat #1)
  - 740H, Special Metals

DOE SunShot (CSP)

- 750°C/300 bar: 500-h cycles
  - Including 750°C/1 bar, 10-h cycles
- Focus on industrial grade (IG) CO_2
  - Indirect fired (closed loop)
- Alloys
  - Sanicro 25 (Fe-base SS)
  - 625
  - 740H, Special Metals
  - Haynes 282 (Heat #2)

Cooperative test matrix:

	Air	RG CO_2	IG CO_2	FE: CO_2+O_2/H_2O
1 bar	5,000 h	5,000 h	4,000 h	——
300 bar	——	4,500 h	5,000 h	500 h

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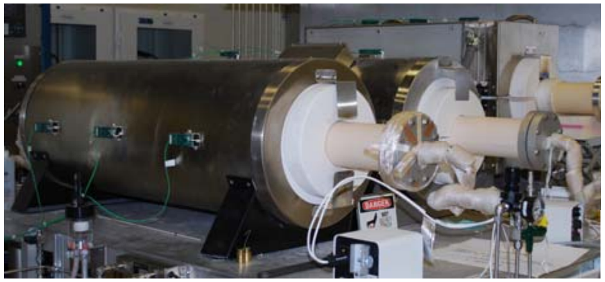
CO_2 compatibility evaluated three ways at 700°-800°C

Autoclave: 300 bar sCO_2
500-h cycles

Correct temperature and pressure

Tube furnace: 1 bar CO_2
500-h cycles



Same cycle frequency as autoclave

"Keiser" rig:
500-h cycles, 1-43 bar CO_2

Study impurities at 1-43 bar

Baseline of research grade (RG) CO_2: ≤ 5 ppm H_2O and ≤ 5 ppm O_2
industrial grade (IG) CO_2: 18±16 ppm H_2O and ≤ 32 ppm O_2

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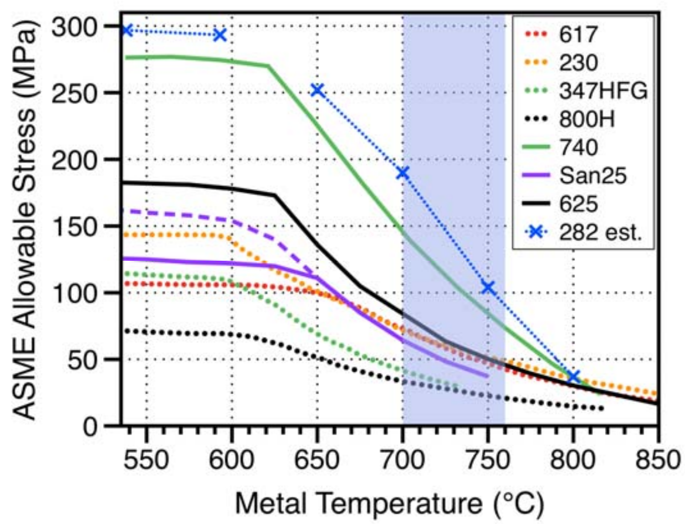
Four alloys selected for SunShot study

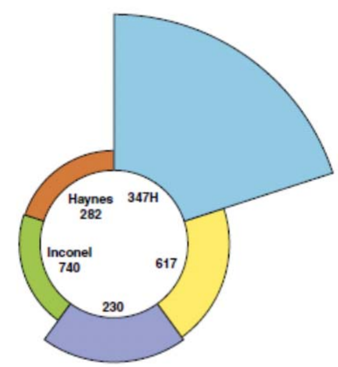
- Composition analyzed by ICP-OES and combustion analyses

Alloy	Fe	Ni	Cr	Al	Co	Mo	Nb	Ti	Mn	Si	Other
Sanicro 25 (Sandvik)	42.6	25.4	22.3	0.03	1.5	0.2	0.5	0.02	0.5	0.2	3.5W, 3.0Cu, 0.2N 0.068 C
Haynes 282 (Haynes International)	0.2	57.1	19.6	1.6	10.6	8.6	<	2.2	0.02	0.04	0.059 C (< is less than 0.02)
Inconel 740H (Special Metals)	0.1	49.7	24.5	1.4	20.6	0.3	1.5	1.4	0.3	0.2	0.027 C
625 (industry selection)	4.0	61.0	21.7	0.12	0.1	8.8	3.5	0.2	0.2	0.2	0.06W,0.09Cu,0.016C

ASME Boiler & Pressure Vessel Code allowables:

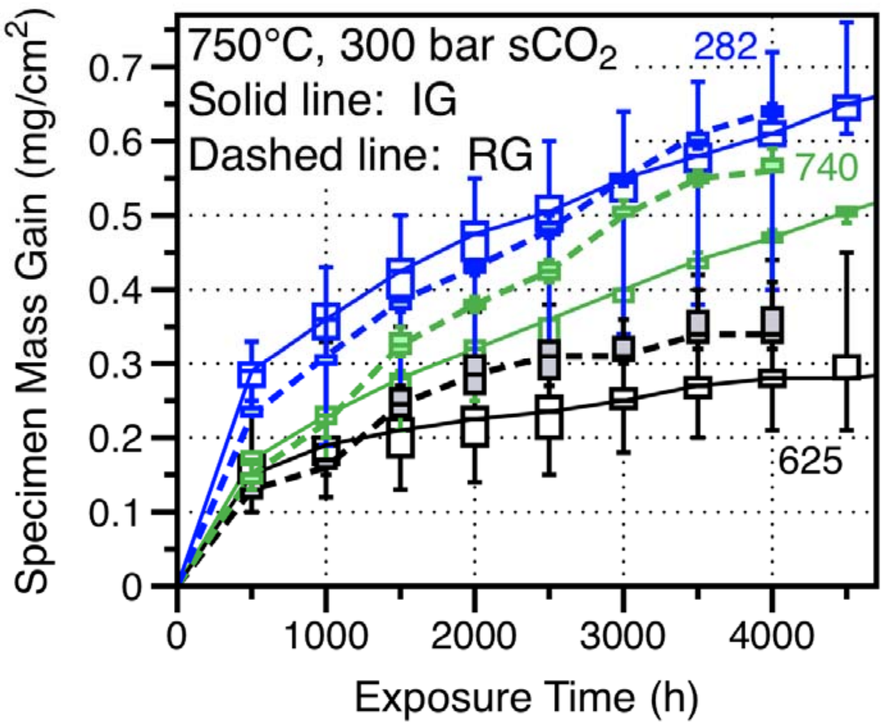
Precipitation-strengthened (γ´) Ni-base alloys

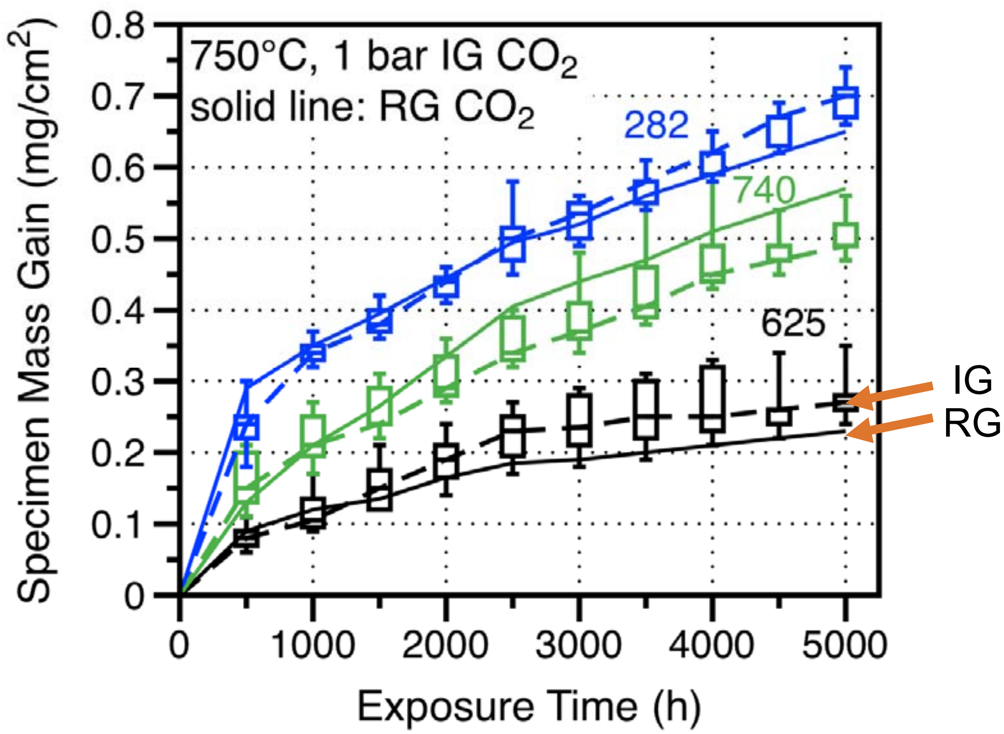




Shingledecker ~2011

No major differences in mass change at 750°C between IG and RG CO_2 at 300 and 1 bar





Line: median values **Box: 25-75%** **Whiskers: min./max.**

5-10 specimens per condition

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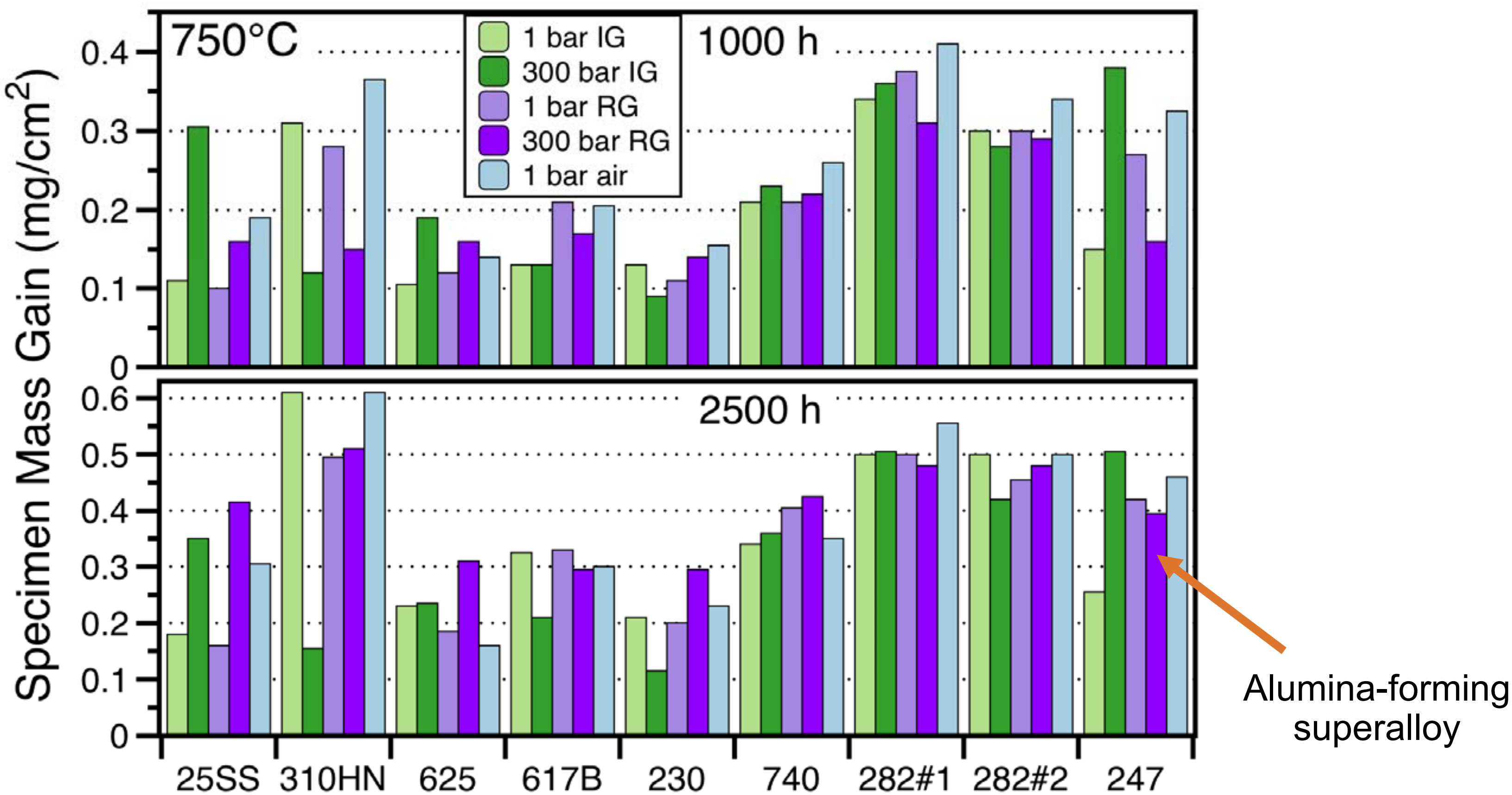
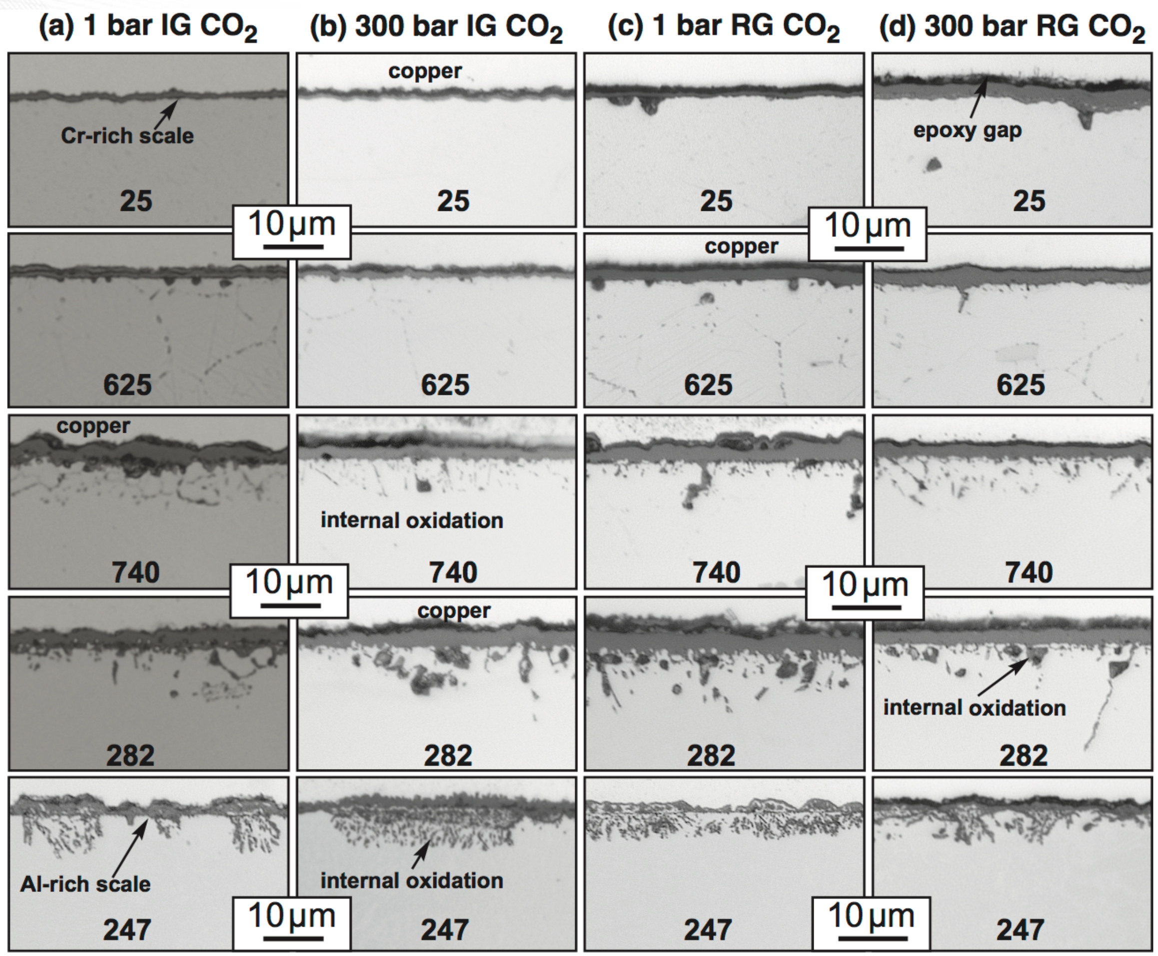
All conditions: not much different from lab. air exposure



Fe-based alloys show largest variations

Minor differences observed after 2,500 h exposures at 750°C



Fe-22Cr-25Ni-4W-3Cu
Lower-cost steel

Ni-22Cr-9Mo-4Nb-0.1Al-0.2Ti

Ni-25Cr-20Co-2Nb-1.4Al-1.4Ti

Ni-20Cr-10Co-9Mo-1.6Al-2.2Ti

Ni-8Cr-10Co-10W-6Al-1Ti-3Ta-1Hf
Al_2O_3-forming superalloy

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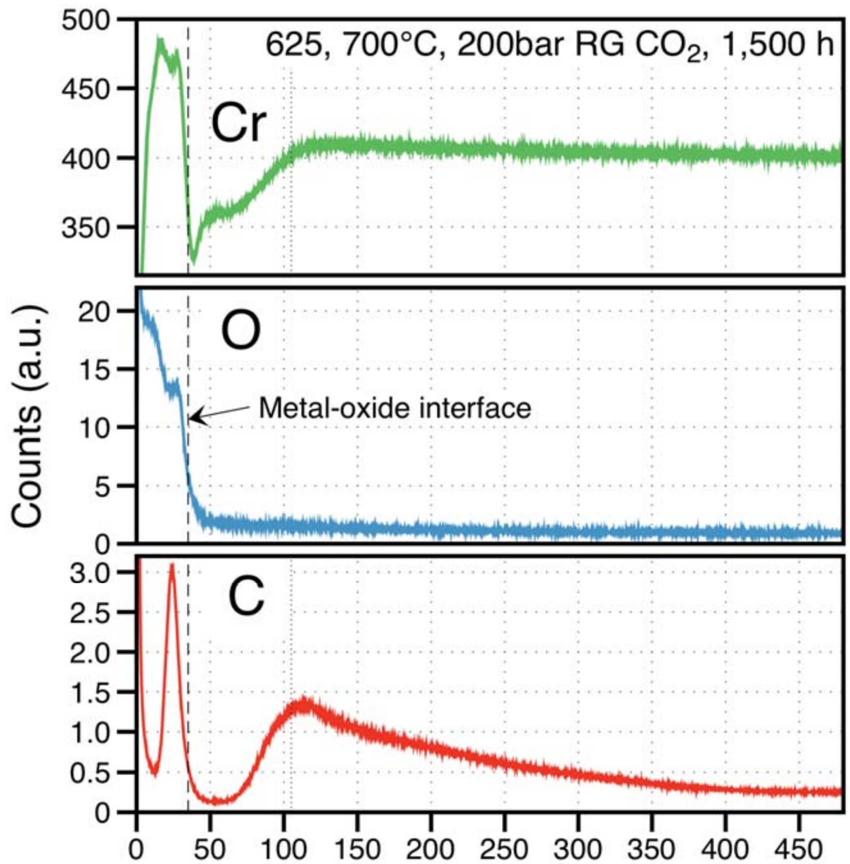
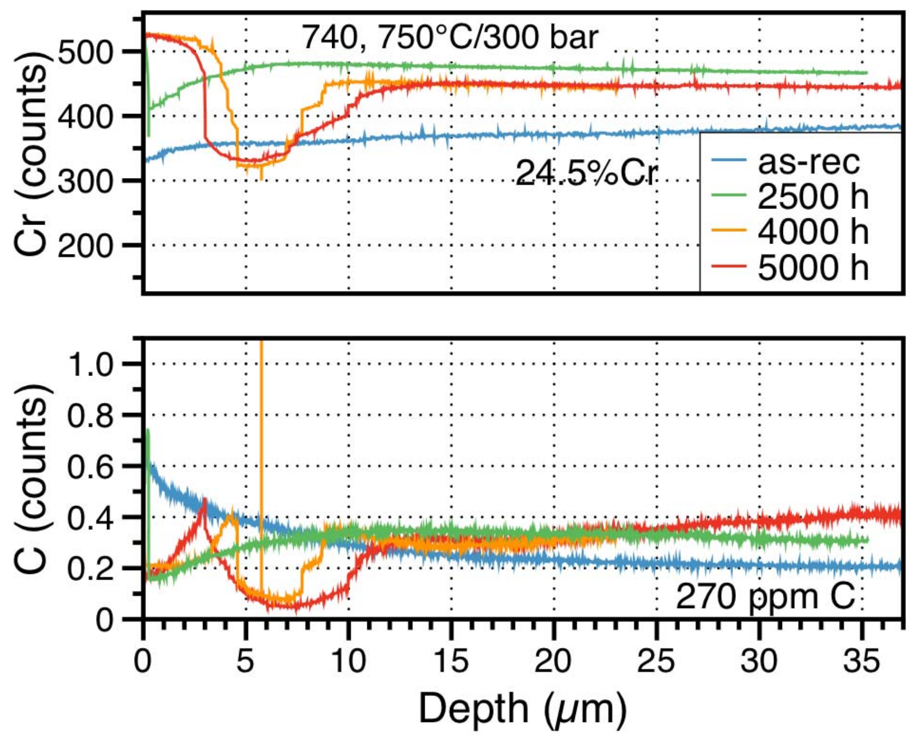
GDOES can detect C ingress (when it occurs)

GDOES: glow discharge, optical emission spectroscopy

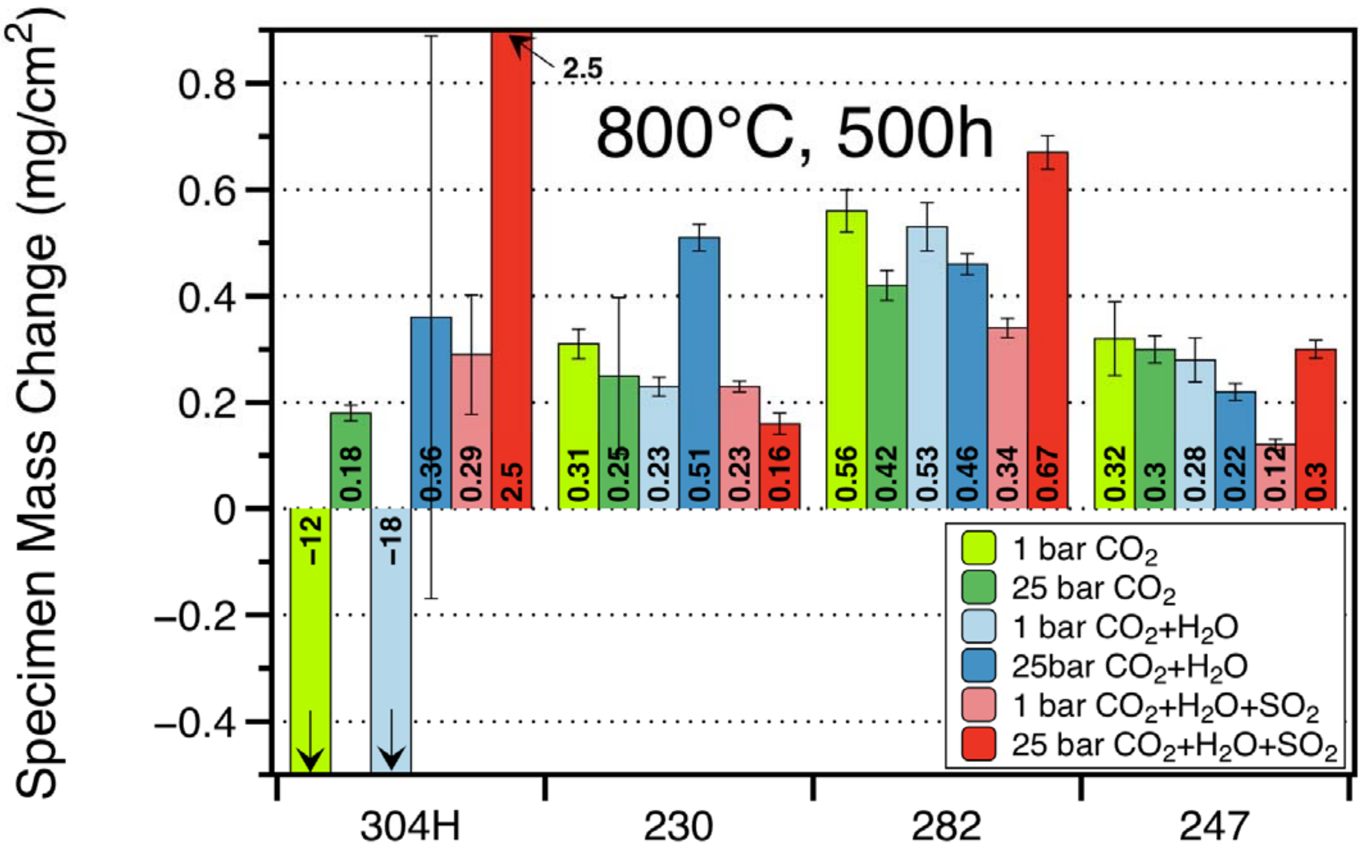


No C detected in 740H at 750°C/300 bar



Michael Lance (ORNL) presentation tomorrow

Effect of impurities and pressure (NACE Corrosion 2018)
800°C 500h: strong variations for 304H (steel “canary”)



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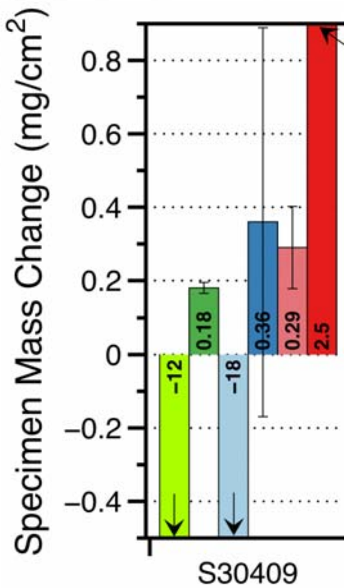
800°C light microscopy: strong variations observed for 304H

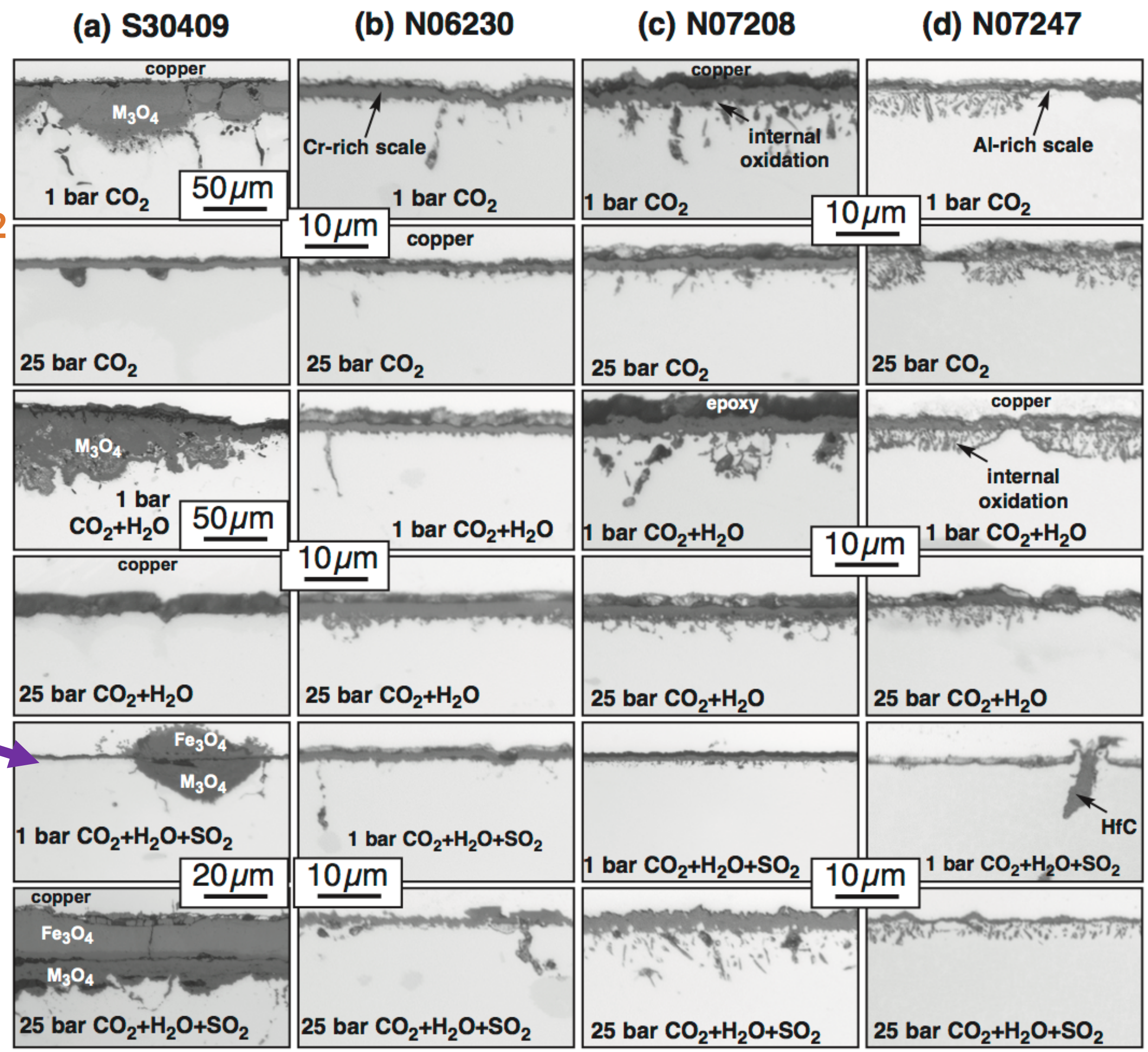


RG CO_2

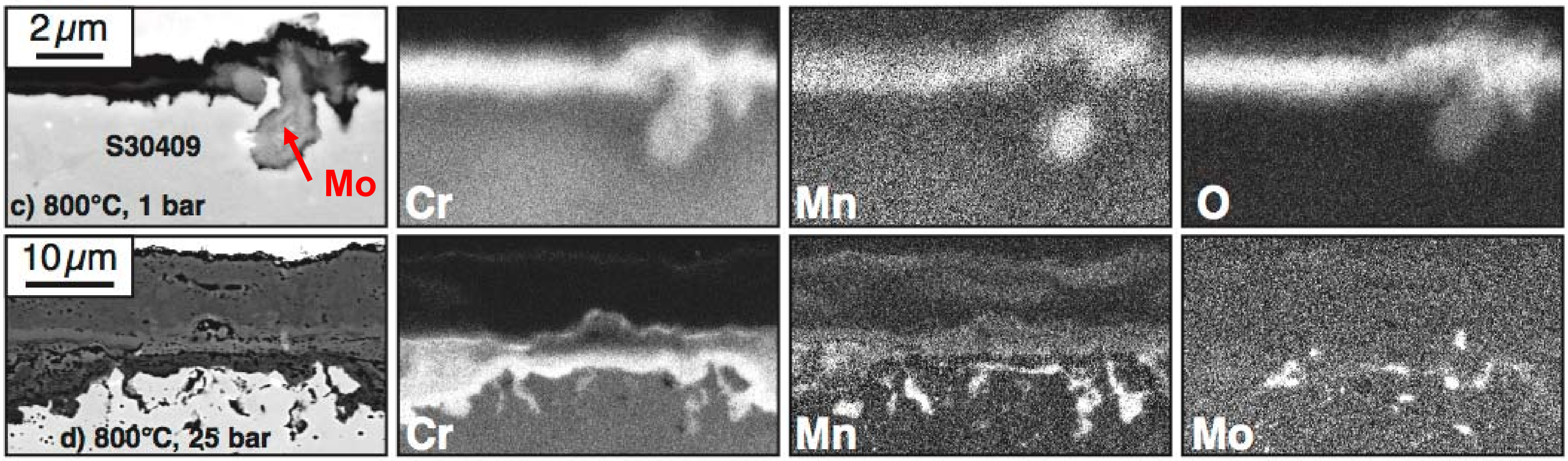
+10%H_2O

Almost Protective!

+10%H_2O
+0.1%SO_2



SEM/EDX 304H: w/SO_2 at 1 bar formed thin protective scale (no good S maps)



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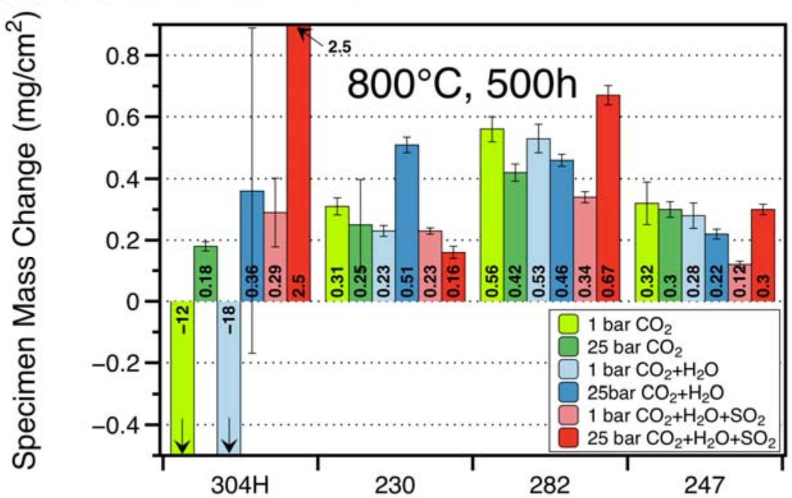
800°C light microscopy: variations observed with pressure and SO_2

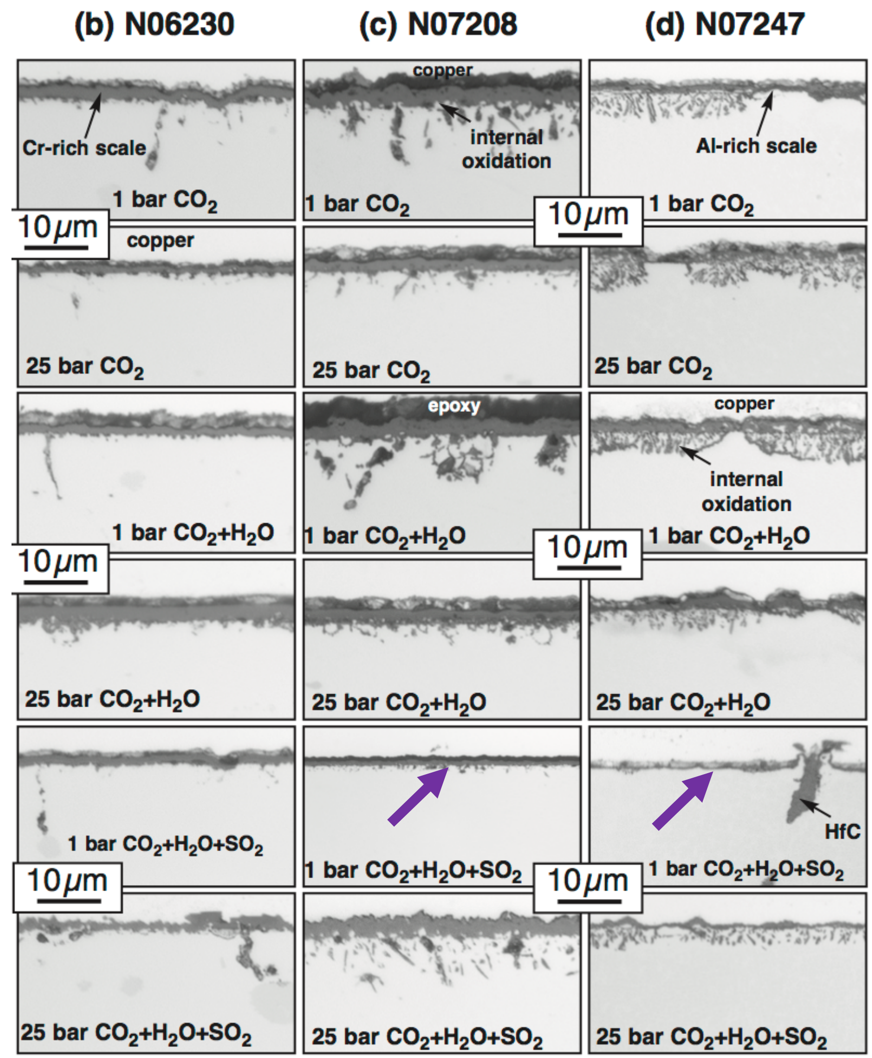


RG CO_2

+10%H_2O

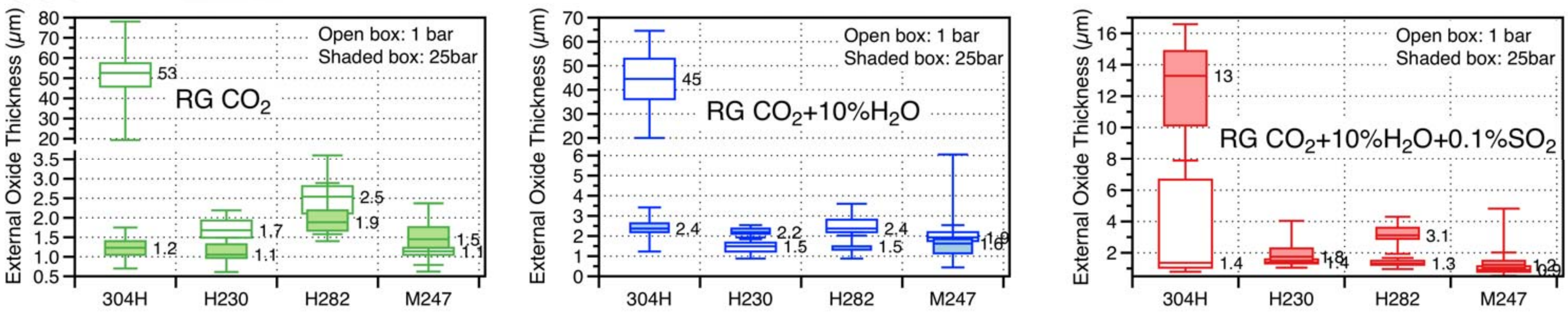
Minimal IO

+10%H_2O
+0.1%SO_2



800°C Scale Quantification: thinner scale at 25 bar (in some cases)

~30 measurements per condition



Does higher P promote a denser (fewer voids/cracks) scale?
Except with SO_2: inhibits C/OH effects at 1 bar
25 bar increases p_{S_2} resulting in a negative effect

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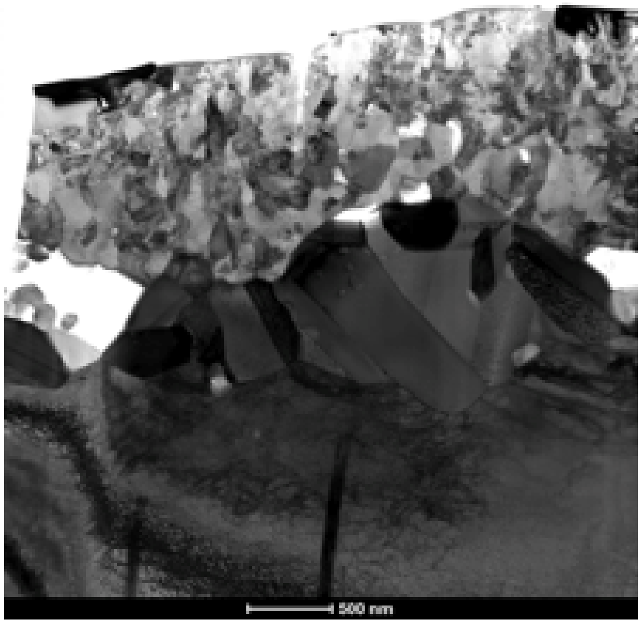
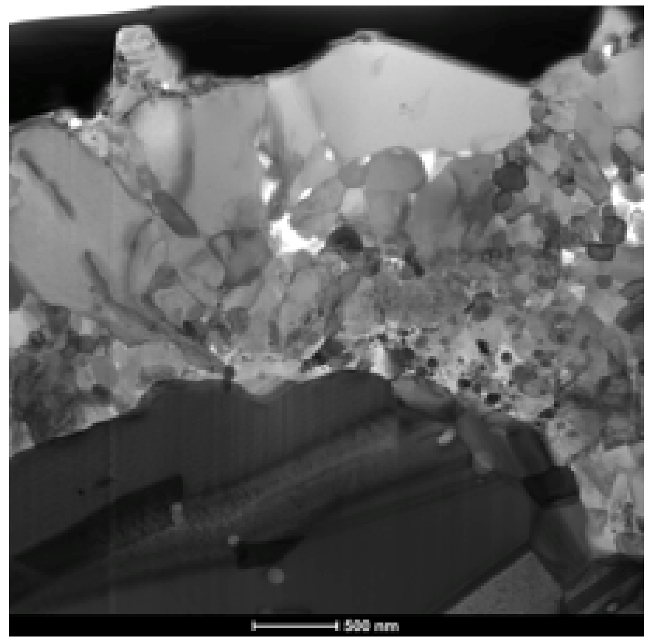
TEM used to study porosity in scale formed on alloy 625 at 750°C

IG CO_2 1 bar, 5,000 h

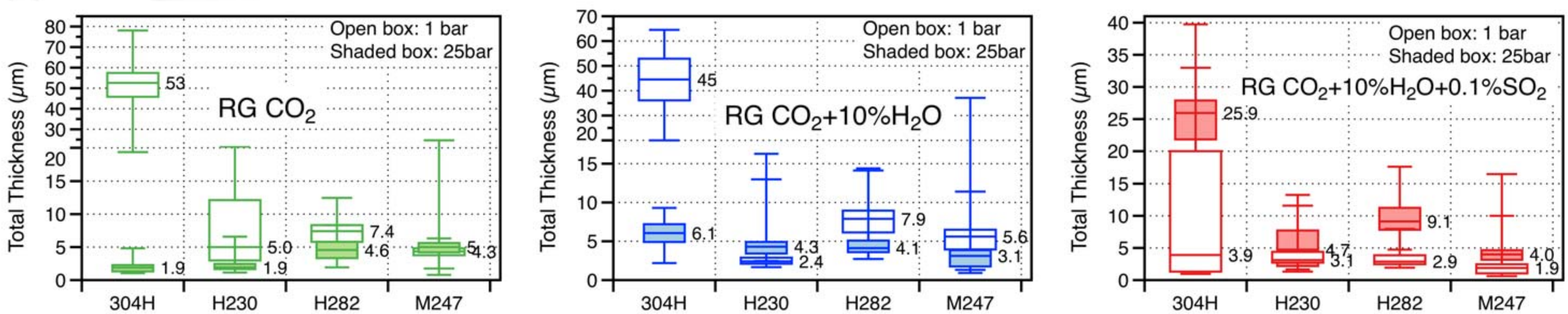


IG CO_2 300 bar, 5,000 h



Thin scales observed with less (?) porosity in sCO_2

800°C Total Reaction (including internal oxidation): reduced in 25 bar except with 0.1%SO_2



0.1%SO_2 1 bar: inhibited negative CO_2/H_2O effect, especially for 304H

- Similar result for Young (CO_2+H_2O) and Quadakkers (H_2O) on Fe-Cr
- Like SO_2 poisoning of metal dusting

0.1%SO_2 25 bar: sulfidation attack with 25X higher p_{S_2}

Oxford CO_2 lifetime model for UK gas-cooled reactors We need to determine relevance to industrial grade sCO_2

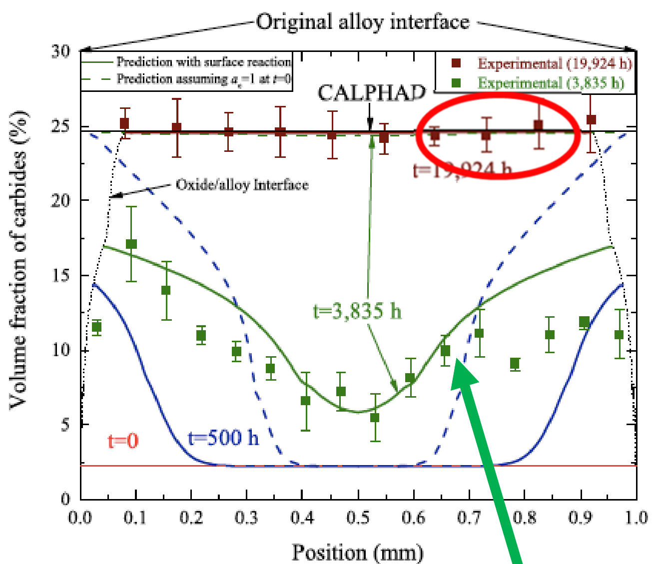
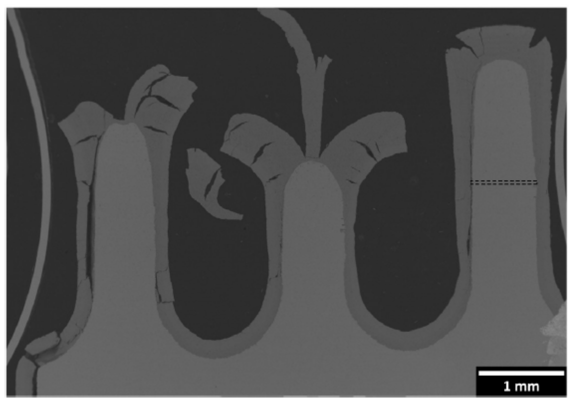


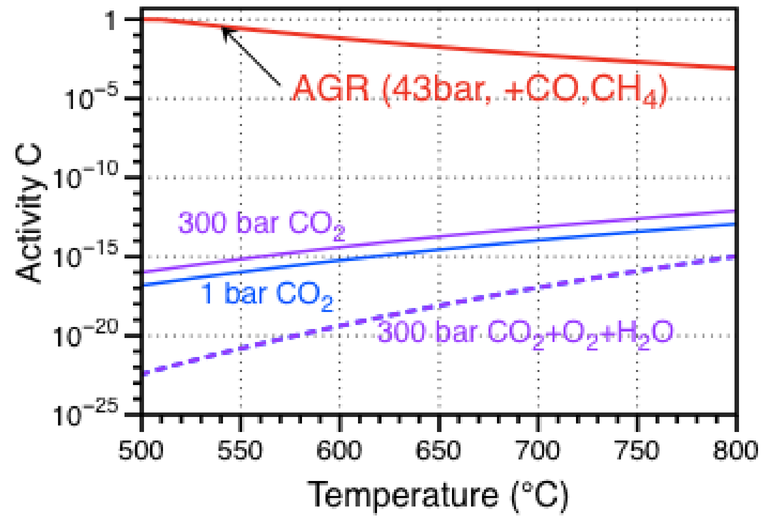
Fig. 8. Predicted profiles of volume fraction of carbides for a 1 mm fin exposed to experimental gas conditions at 600 °C at 0, 500 h, 3835 h and 19924 h in comparison with measurements corresponding to black box marked in Fig. 1(b); simulations were conducted by 1D-DiCTra as described in § 3.2 treating migration of oxide/alloy interface and non-steady state carburisation with $\alpha_{\mu C} = 1.2 \times 10^{-12}$ mol m^{-1} J^{-1} (solid lines) or fixed $a_C = 1$ at the oxide/alloy interface (dashed lines).

Gong,Young...Reed, Acta Mater. 2017



Grade 9 steel fins: Fe-9Cr-1Mo

But the 600 psi CO_2 in AGR is very carburizing



Experimental data (80-200 kh!) 580°-640°C: Cr tied up as carbides

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Initial results show less mass gain in RG CO_2

Gong et al. 2017 Figure 3:

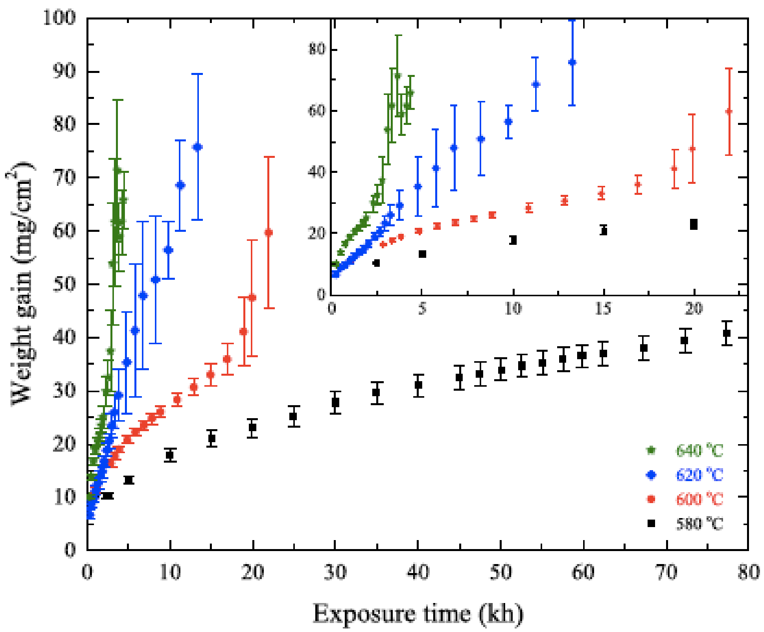
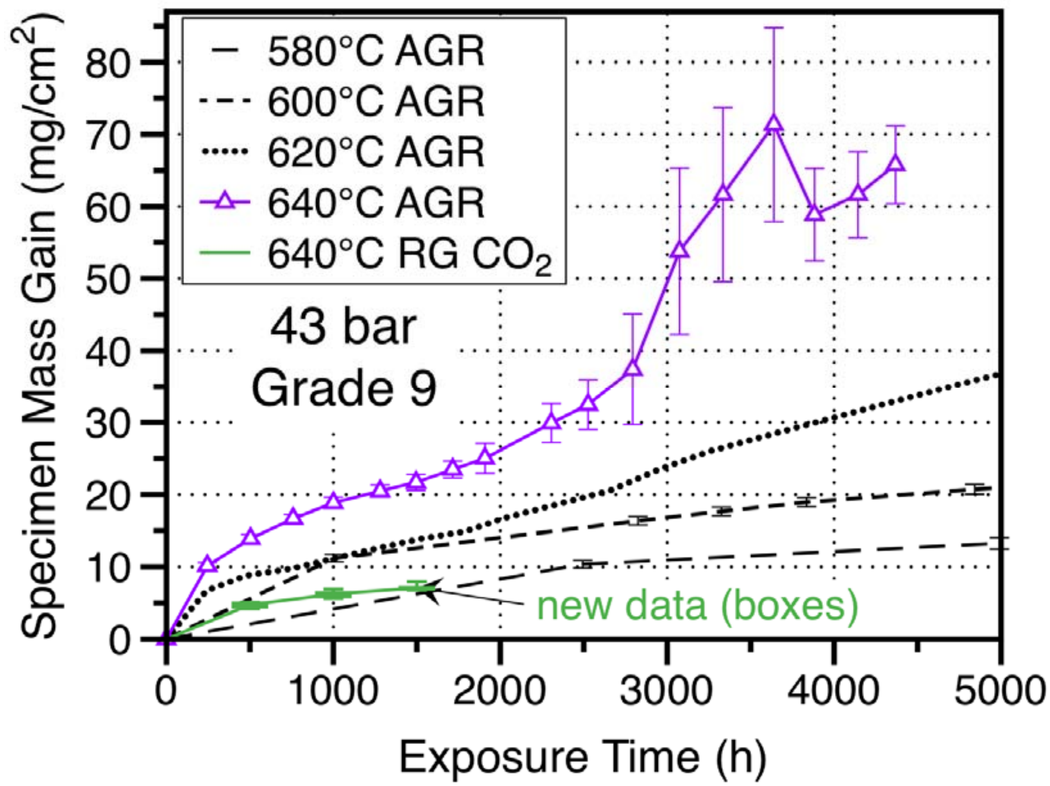
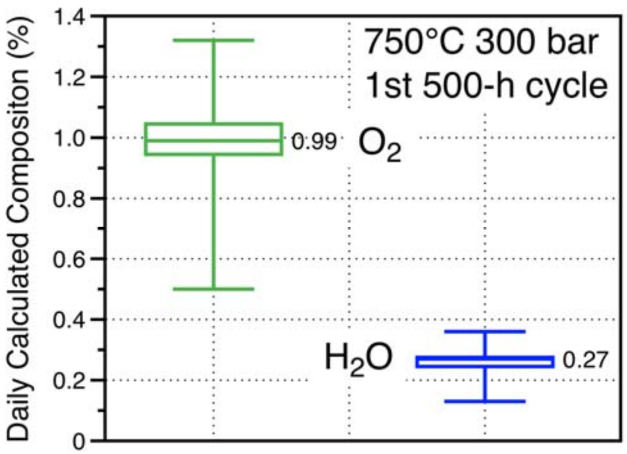


Fig. 3. Weight gain changes of experimental samples exposed at 580 °C (black), 600 °C (red), 620 °C (blue) and 640 °C (green) with gas compositions of 100 vppm H_2, 300 vppm CH_4, 1 vol% CO, 300 vppm H_2O and balance CO_2 at gas pressure of 600 psig (42.38 bar); one stand deviation from repeated tests is used to evaluate uncertainties. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

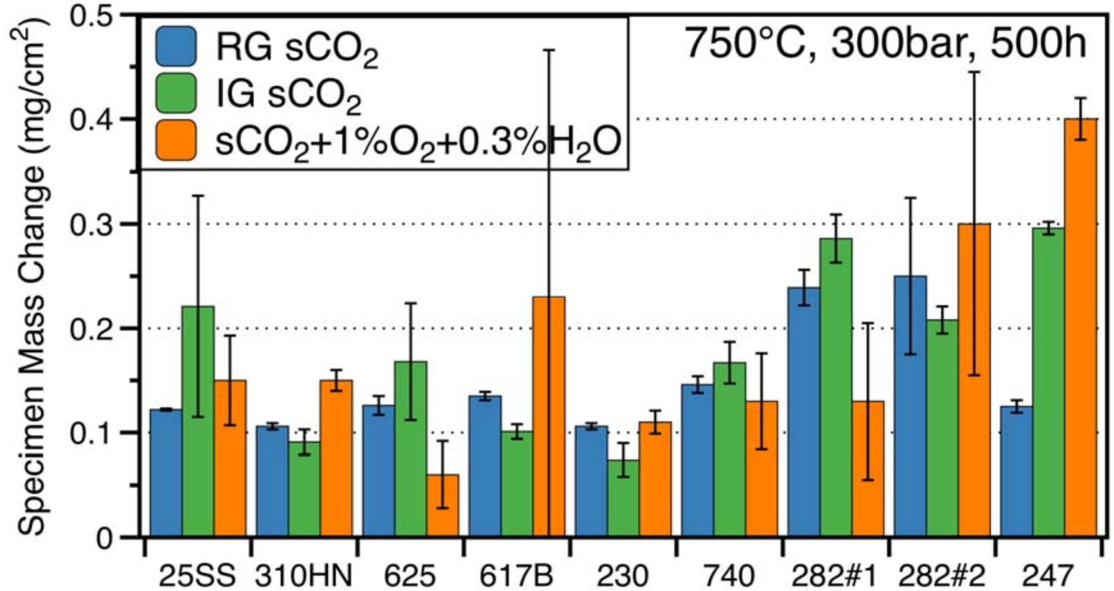


Thanks to EDF, Y. Gong and R. Reed for providing mass change data

First 300 bar impurity data obtained
New rig completed first cycle in February 2018
Second cycle completed March 27



Goal: $1\%O_2+0.25\%H_2O$
(industry suggestion)
Not easy to control at 300 bar



Average of 3 specimens in first experiment

No plans to add SO_2 to autoclave

Summary: impurity and pressure effects

- Want to study impurities in sCO_2 for direct-fired clean energy concept at 750°C
  - Several studies at 1, 25 and 300 bar while waiting for 300 bar $sCO_2+H_2O+O_2$ autoclave tests
  - Comparison of industrial and research grade CO_2 at 1 and 300 bar
    - Symposium paper
  - Effect of H_2O and 0.1%SO_2 at 1 and 25 bar
    - Corrosion 2018 paper
  - 43 bar test to compare to extensive UK reactor database
  - Initial results at 300 bar sCO_2+1%O_2+0.25%H_2O
- Minor effects comparing IG and RG sCO_2
  - Similar mass gains in laboratory air
- Low SO_2 levels may be acceptable in sCO_2
  - More work needed to understand supercritical conditions
  - Beneficial "poisoning" effects of SO_2 may disappear at high pressure (S level set by coal)
- Current hypotheses
  - Higher P = denser, more protective scale
    - More characterization of thin scales required
  - SO_2 suppresses C & OH effects (Young & Quadakkers): can we take advantage?

My hero was rich and famous, long before the era of type and hype

"When I want to discover something, I begin by reading up everything that has been done along that line in the past - that's what all these books in the library are for. I see what has been accomplished at great labor and expense in the past. I gather data of many thousands of experiments as a starting point, and then I make thousands more."

- Thomas Alva Edison

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Four alloys selected for this study

- Composition analyzed by ICP-OES and combustion analyses

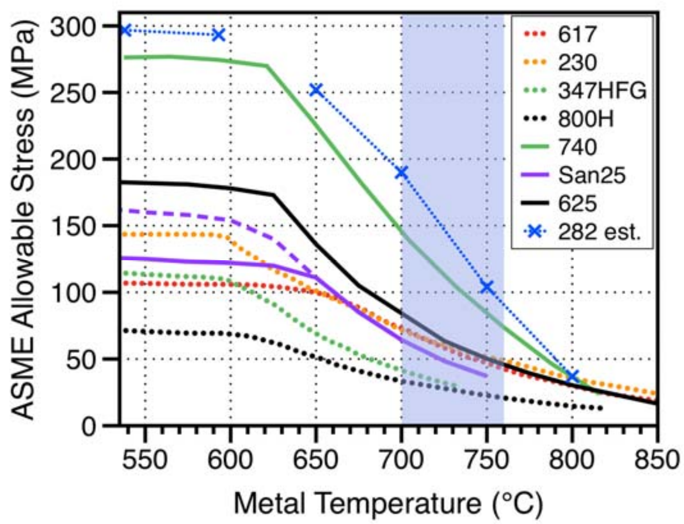
Alloy	Fe	Ni	Cr	Al	Co	Mo	Ti	Mn	Si	C	Other	
304H	70.4	8.4	18.4		0.1	0.3		1.6	0.3	0.06	0.4Cu,0.07N	steel “canary”
230	1.0	60.0	21.6	0.4	0.2	1.2		0.5	0.4	0.10	14.6W, 0.02La	solid-solution
Haynes 282	0.2	58.0	19.3	1.5	10.0	8.3	2.2	0.07	0.06	0.06		γ´- strengthened
MarM247	0.1	59.5	8.5	5.7	9.8	0.7	1.0	<	0.03	0.16	9.9W,3.1Ta,1.4Hf	turbomachinery

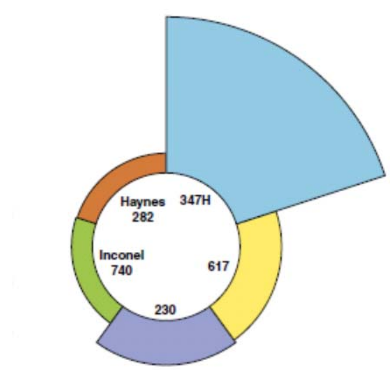
(< is less than 0.02)

Al_2O_3-former

ASME Boiler & Pressure Vessel Code allowables:

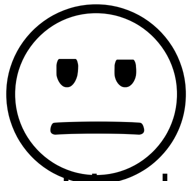
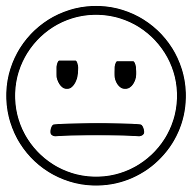
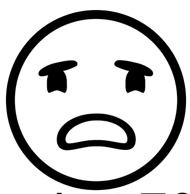
Precipitation-strengthened (γ´) Ni-base alloys

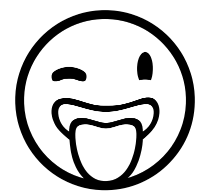




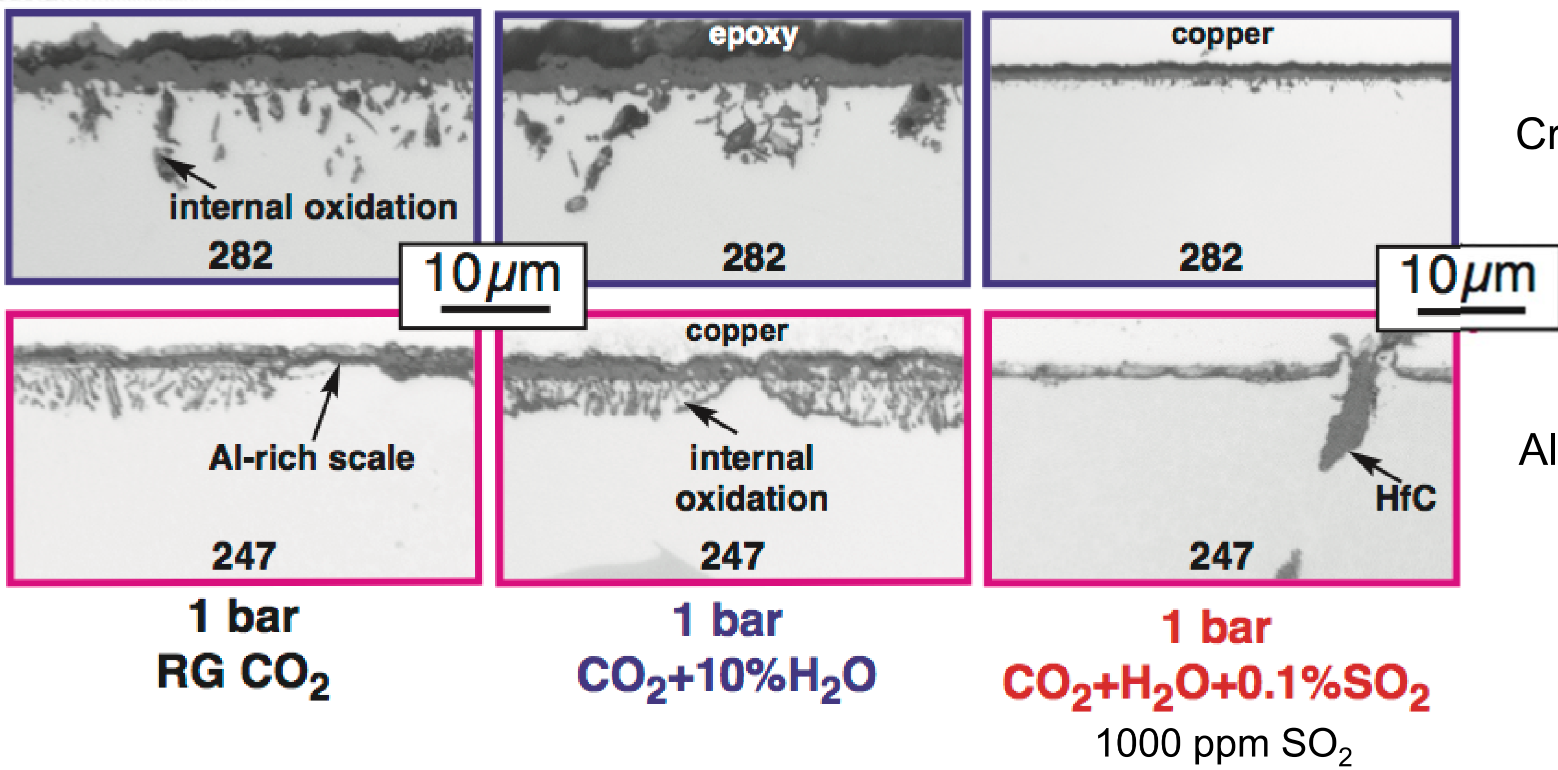
Shingledecker ~2011

Many variables can be considered

- Temperature 
  - Cr_2O_3 better C barrier at higher T (?)
  - Steels more T limited than in steam
- Pressure 
  - No strong effect of increasing P
- Thermal cycling 
  - Stainless steel attacked at 700°-750°C

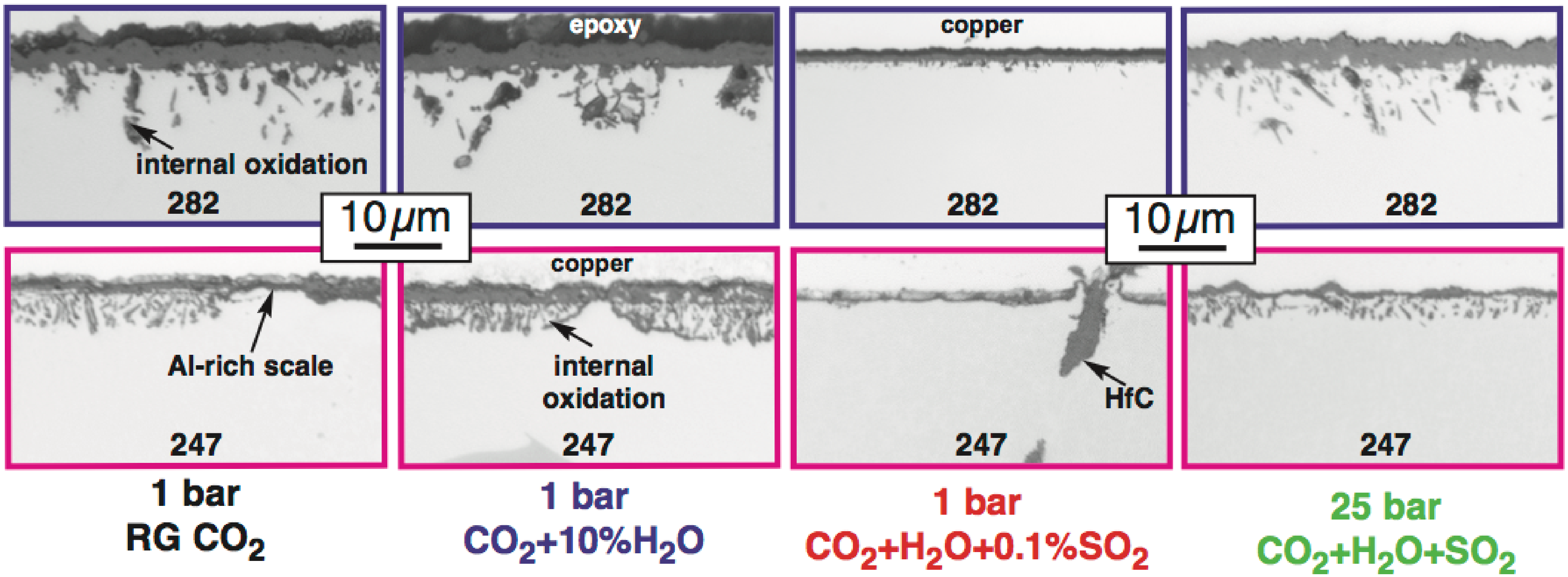
- Oxygen 
  - ORNL & UW different results
- H_2O 
  - Negative, especially for steels
- CO
  - UW 1%CO results
- SO_2 
  - Complicated…

500h at 800°C: SO_2 suppressed internal oxidation at 1 bar



Similar results for SO_2 reported by Young (UNSW) and Quadakkers (Jülich)

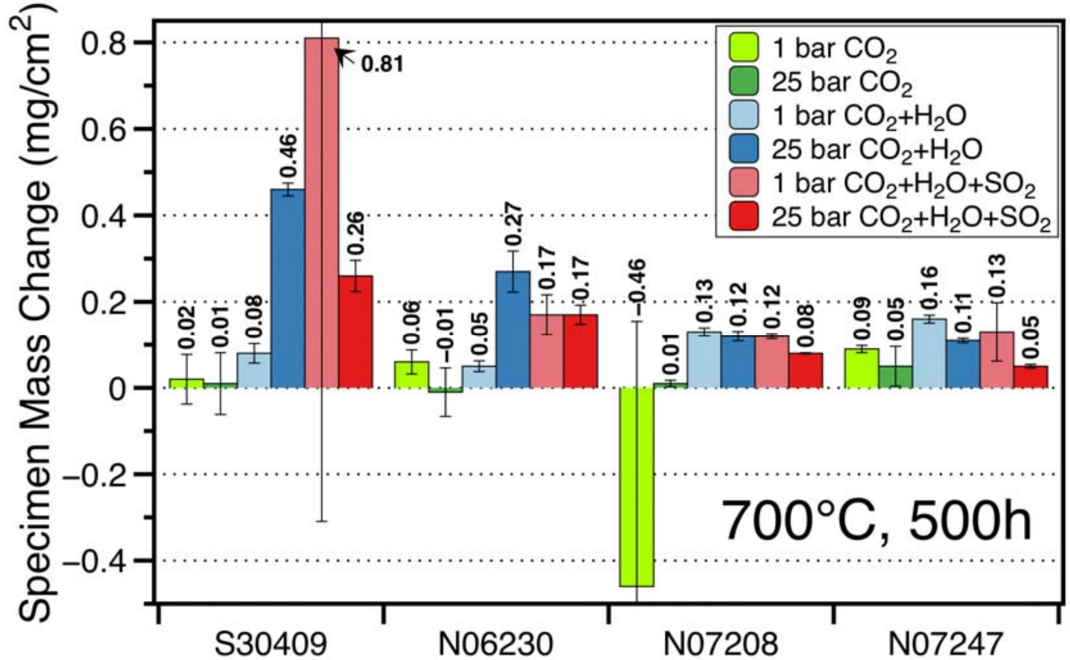
500h at 800°C: at 25 bar, 0.1%SO_2 resulted in more attack



Haynes 282: Ni-20Cr-11Co-9Mo-1.6Al-2.2Ti

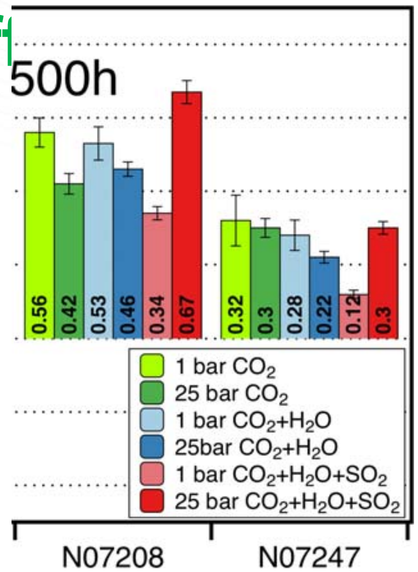
MarM247 superalloy: Ni-9Cr-10Co-1Mo-6Al-1Ta-3Ta-1.4Hf

700°C 500h: mainly small mass changes



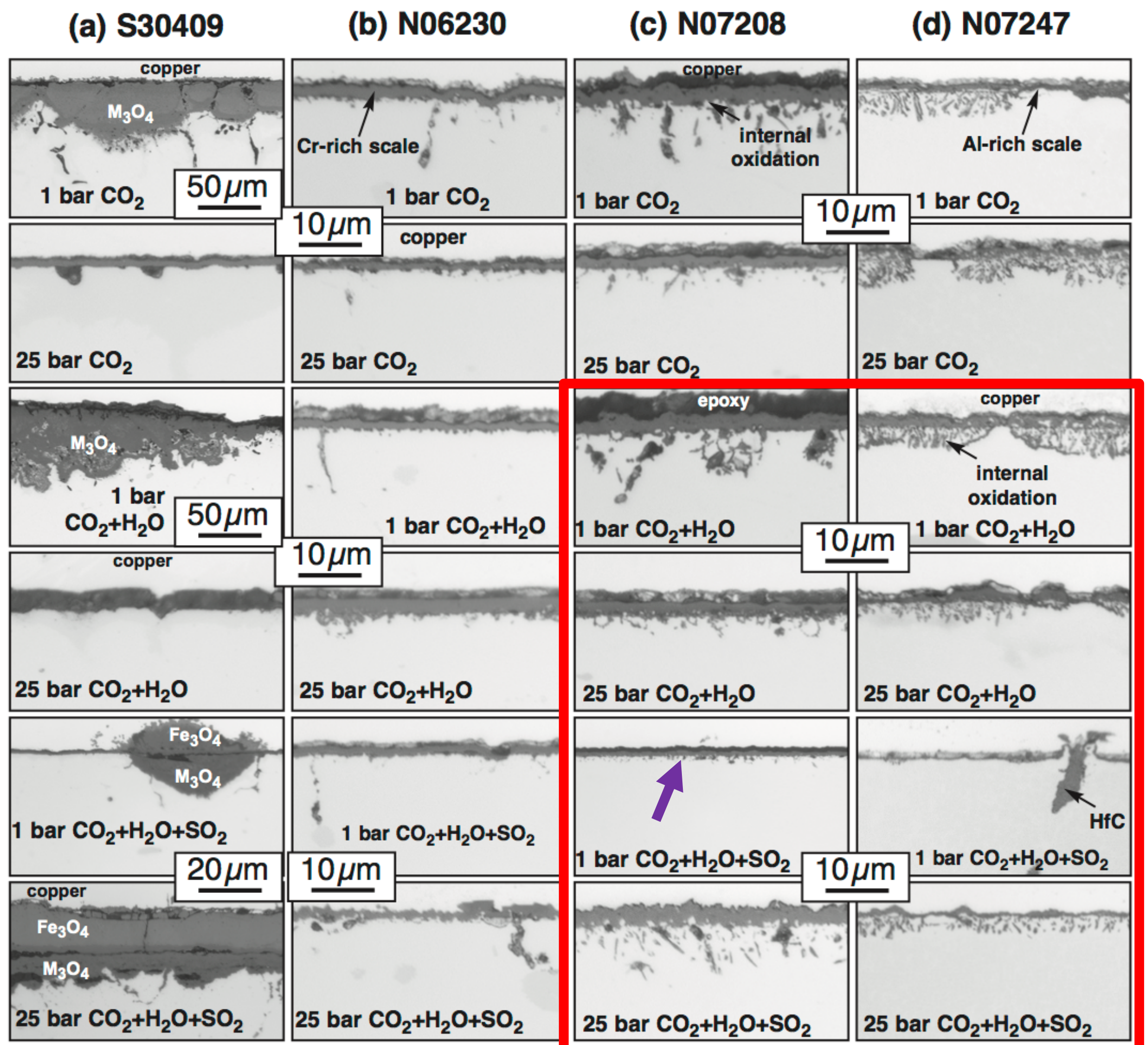
Average mass change for three specimens: whiskers show a standard deviation

800°C light microscopy: 25 bar: less internal attack +SO_2: opposite P eff



+10%H_2O

+10%H_2O
+0.1%SO_2



National Laboratory

Similar observation with 600°C ORNL study for staged pressurized oxy-combustion (SPOC):

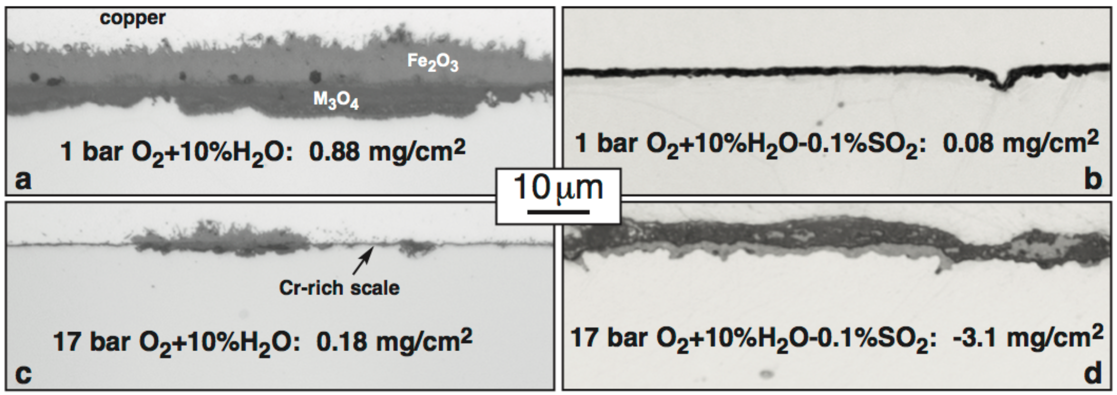


Figure 5: Light microscopy of S30409 specimens exposed at 600°C for 500 h in two environments and two pressures.

No CO_2 in this study

O_2-10%H_2O: reduced attack at 17 bar compared to 1 bar

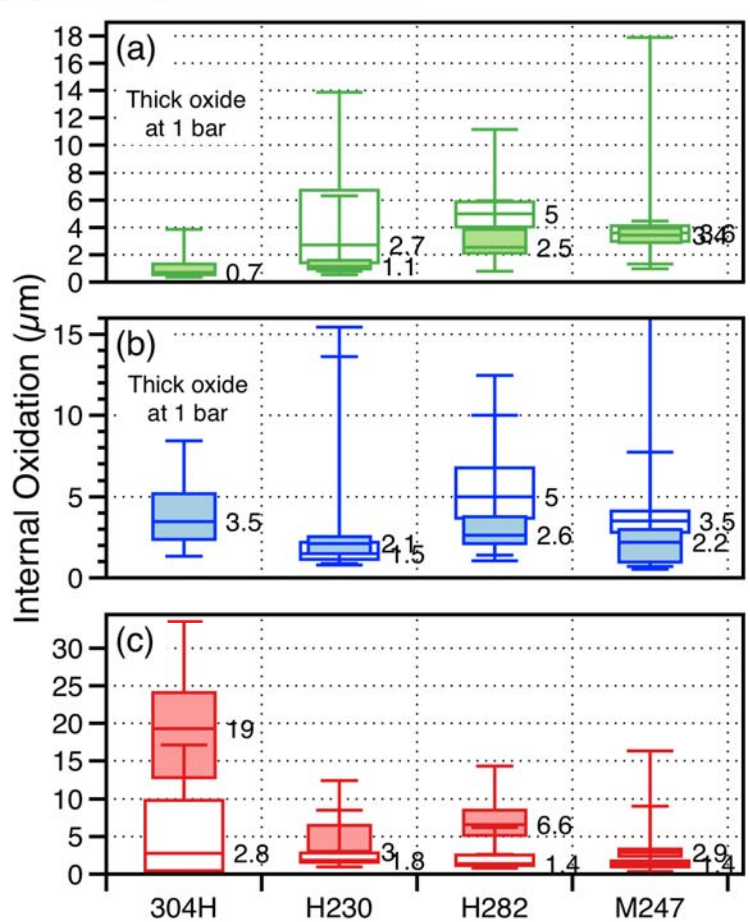
0.1%SO_2 1 bar: inhibited negative CO_2/H_2O effect (protective scale)

Similar result for Young (CO_2+H_2O) and Quadakkers (H_2O)

0.1%SO_2 17 bar: sulfidation attack with 17X higher p_{S_2}

OAK RIDGE National Laboratory

800°C internal oxidation: lower at 25 bar except with SO_2



- Hypotheses
  - Higher P = denser scale
  - SO_2 suppresses C and OH effects (Young)
- How affect depth of internal oxidation?
  - Young also reported SiO_2 formation with SO_2
- Is this a lasting benefit?
  - only 500 h exposure