Advanced Materials Issues for Supercritical CO_2 Cycles FEAA123 (2016 – 2018)

Bruce Pint

Corrosion Science & Technology Group
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156 USA

Presentation for 2019 Crosscutting Research Project Review Meeting
April 9, 2019

Acknowledgments

- J. Keiser, M. Howell, M. Stephens — oxidation experiments
- T. Lowe — SEM, image analysis
- T. Jordan — metallography
- K. Unocic — TEM
- Special thanks for alloys:
  - Haynes International
  - Special Metals
  - ATI
  - Sandvik
  - Capstone Turbine

Project is studying materials issues relevant to direct-fired supercritical CO_2 cycles

- Goals and Objectives
  - Address materials issues for scaling up direct-fired sCO_2 Brayton cycles to higher temperatures for increased efficiency and larger size for commercial power generation
- Milestones
  - FY16
    - Data analysis on effect of temperature on reaction rates (6/16, complete)
    - 1 and 25 bar testing at three different impurity levels (8/17, complete)
    - Complete construction of test rig capable of studying impurity effects in sCO2 (9/17, complete)
  - FY17
    - Complete analysis of reaction products as a function of temperature, pressure, etc. (12/17, complete)
    - Complete 500h exposures at three different impurity levels in 300 bar sCO_2 (2/18, complete)
    - Complete 2,500 h of cumulative exposure in sCO_2 with a high H_2O content (6/18, complete)
  - FY18
    - Compare 2,500 h sCO_2 reaction products formed with and without O_2 and H_2O (9/18, complete)
    - Complete 5,000h with a high H_2O content to quantify reaction rate effects (12/18, complete)
    - Complete a time series of 25°C tensile properties at 750°C/300 bar w/o impurities (12/18, complete)

Supercritical CO_2 Allam cycle: first clean fossil energy?

NetPower 25MWe 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

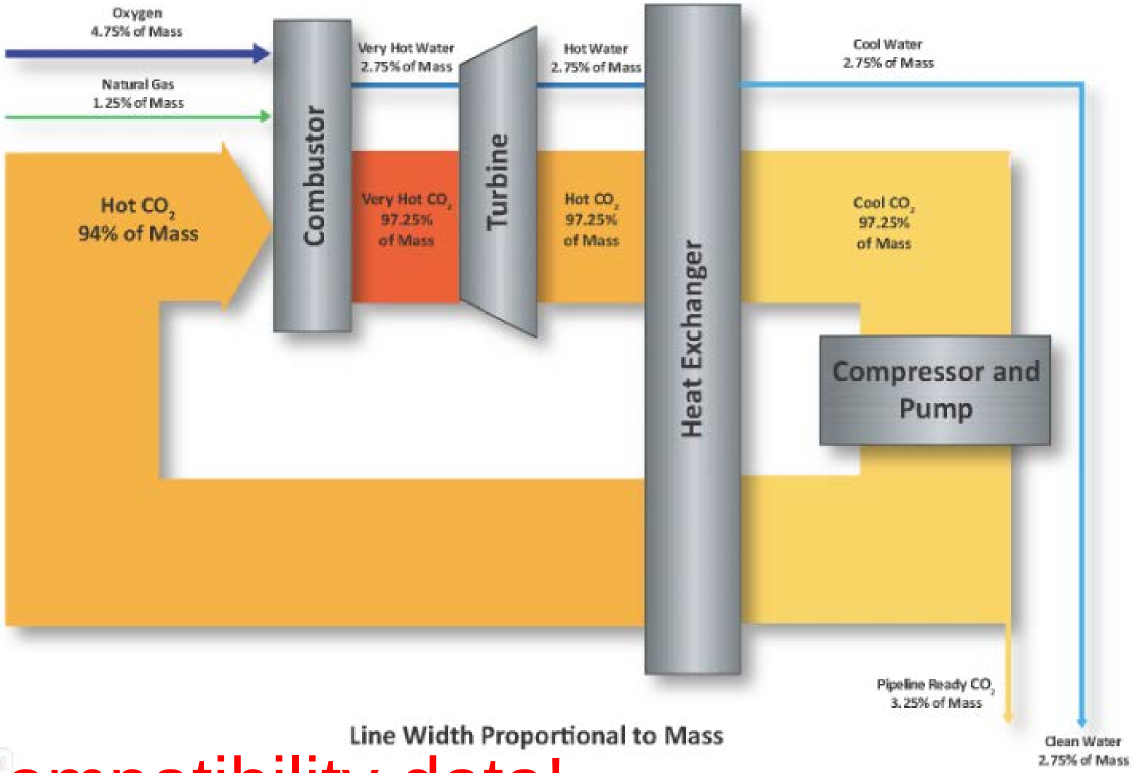
May 2018: announced first firing

Material challenges:

Combustor: 1150°C (!?!)

Turbine exit: 750°C/300 bar

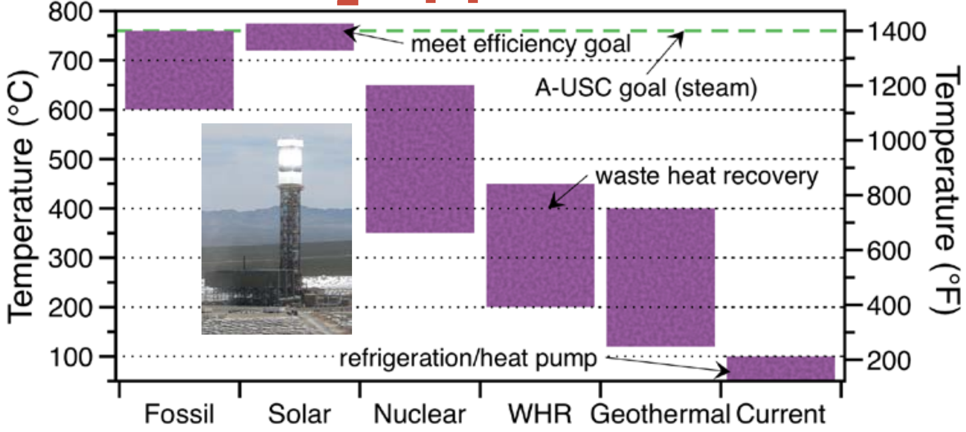
Combustion impurities: O_2, H_2O, SO_2

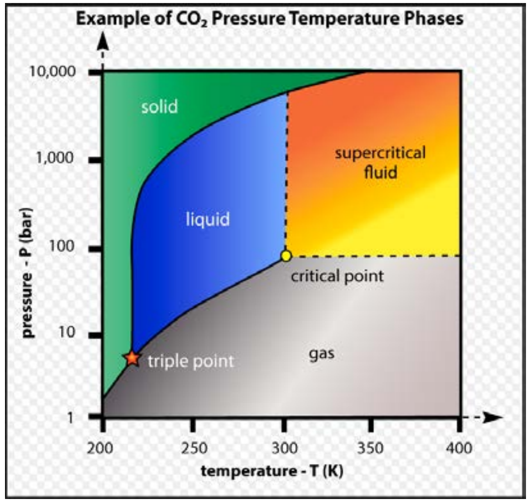


Moving forward with limited compatibility data!
As audacious as Eddystone in 1960

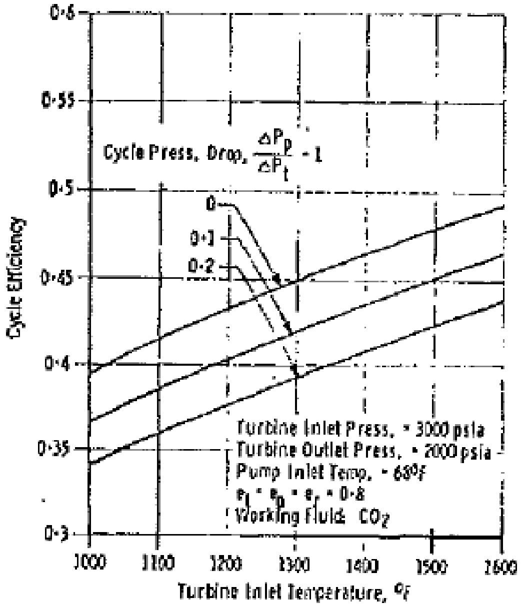
Fossil/Solar focus on >700°C for high efficiency sCO_2

sCO_2 applications





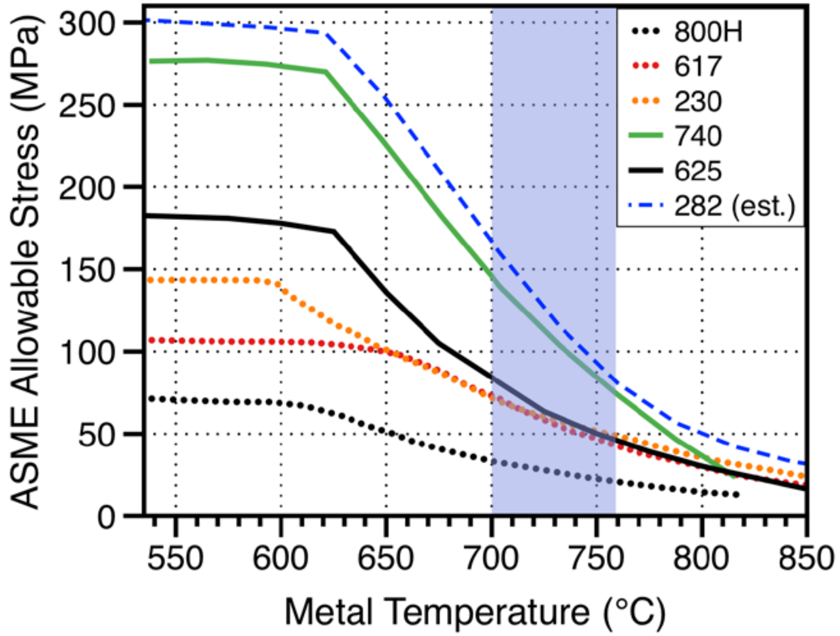
- **Low critical point (31°C/7.4 MPa)**
- **High, liquid-like density**
- **Flexible, small turbomachinery**



Feher, 1965

50% sCO_2 eff @ >720°C

>700°C: favors precipitation-strengthened **Ni-based alloys**



740/282 above 700°C

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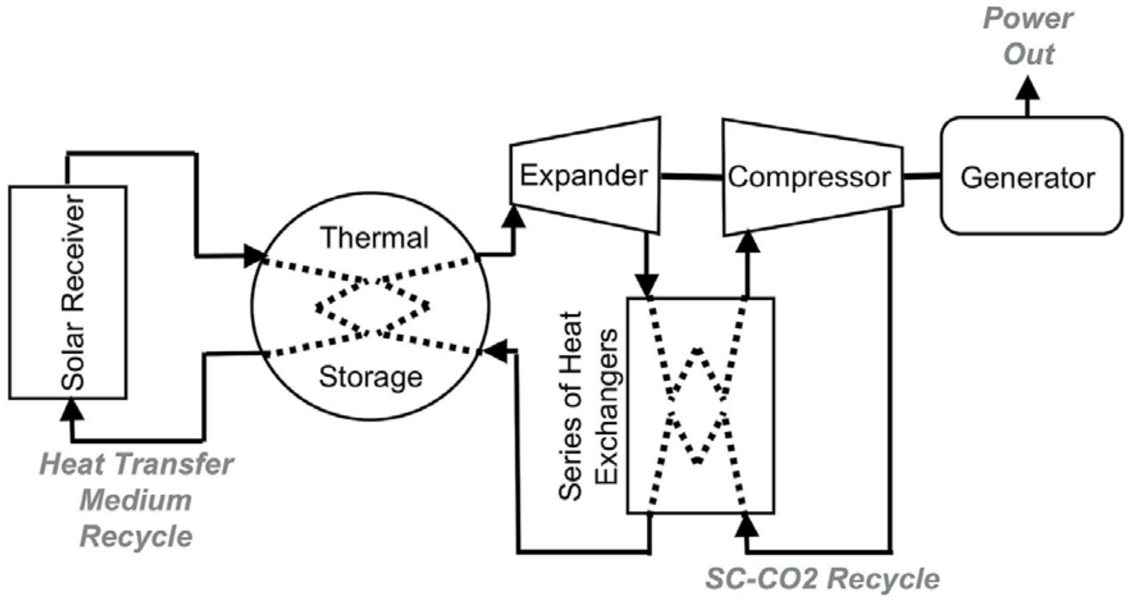
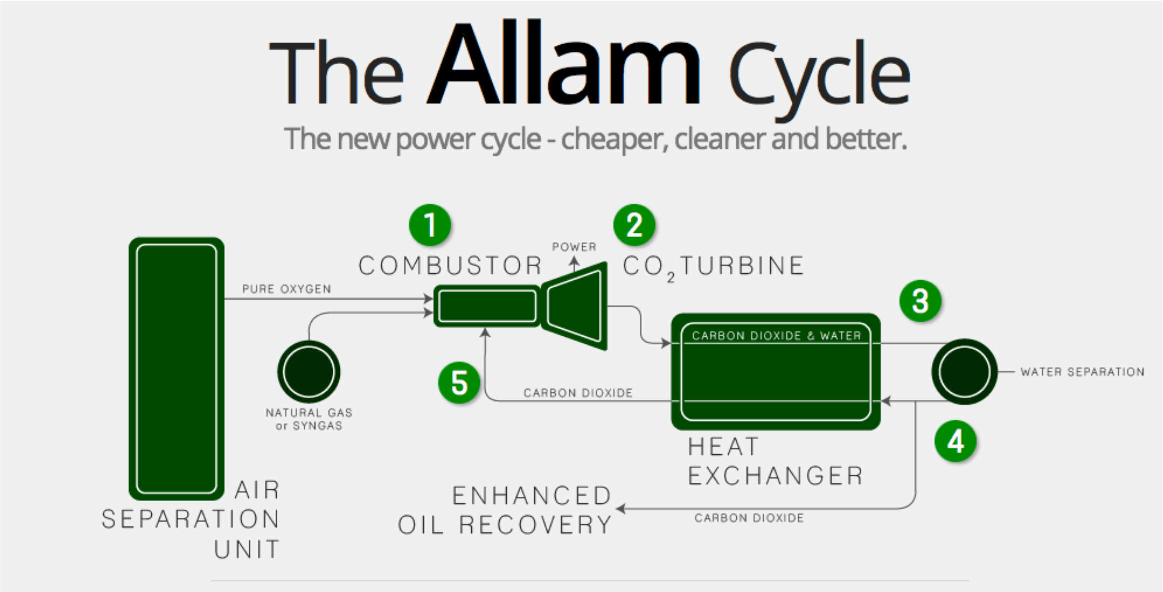
Indirect- vs. direct-fired sCO_2 systems
(i.e. closed vs. open)

Closed cycle:
"pure" CO_2 100-300 bar

Open cycle:
sCO_2 + impurities (O_2,H_2O...)





DOE SunShot funding

DOE Fossil Energy funding

Two sCO_2 projects completing at ORNL

DOE Fossil Energy (2015-2018)

- 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
  - 247 (Al_2O_3-forming superalloy)
  - 282 (Heat #1)
  - 740

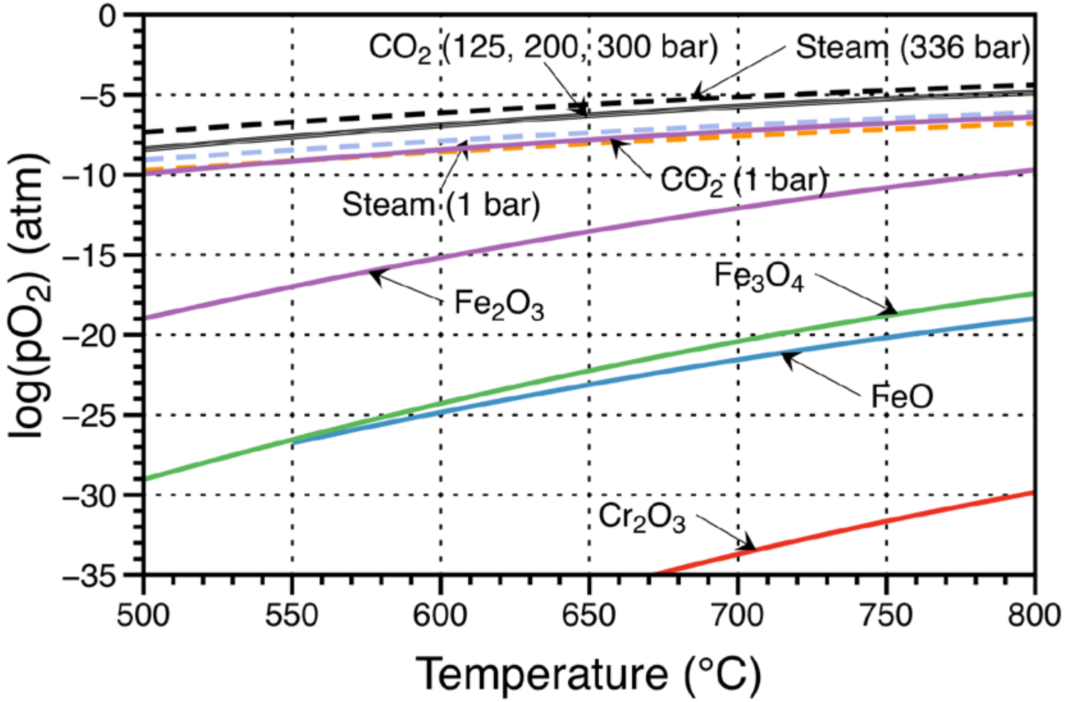
DOE SunShot (CSP) (2015-2018)

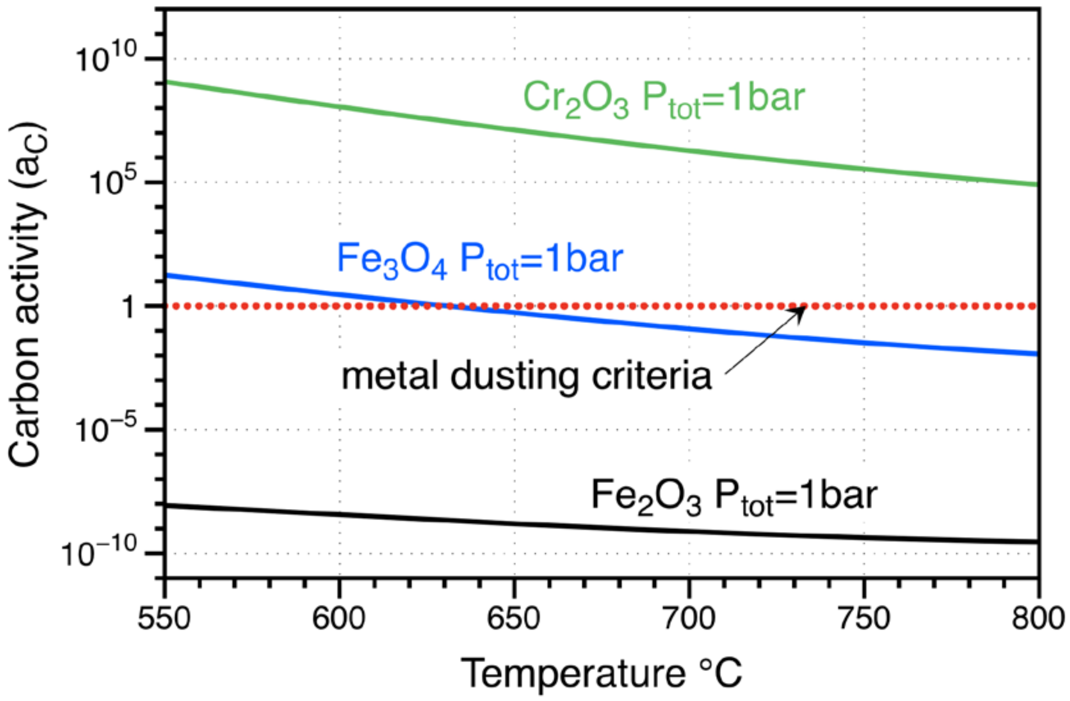
- 750°C/300 bar: 500-h cycles
  - Including 750°C/1 bar, 10-h cycles
- Focus on industrial grade (IG) CO_2
  - Indirect fired (closed loop)
- Alloys
  - Alloy 25 (Fe-base SS Sanicro 25)
  - 625
  - 740
  - 282 (Heat #2)

Cooperative test matrix:

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

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





Factsage calculations

$2CO(g) = C(s) + CO_2(g)$ $CO_2(g) = 0.5O_2 + CO(g)$

High carbon activity at P_{total} = 1 bar

What is $P_{interface}$?

Range of alloys have been evaluated

	Ni	Cr	Fe	Co	Refractories	Ti	Al	S	Other
Grade 91	0.1	8.3	90	0.01	0.9Mo,0.1Nb	<0.01	<0.01	10	0.03Cu,0.3Mn,0.1Si,0.3V
304H	8.4	18	70	0.1	0.3Mo,0.01Nb	<0.01	<0.01	29	0.4Cu,1.6Mn,0.3Si,0.07N
25	25	22	**43**	1.5	3.5W,.5Nb,.2Mo	0.02	0.03	8	3.0Cu, 0.5Mn, 0.2Si, 0.2N
310HCbN	20	25	**51**	0.3	0.1Mo,0.4Nb	0.01	<0.01	<10	0.1Cu,1.2Mn,0.3Si,0.3N
230	**61**	**23**	**2**	**0.1**	**1Mo, 12W**	**0.01**	**0.3**	**9**	**0.02La**
625	**61**	**22**	**4**	**0.1**	**9Mo, 4Nb**	**0.2**	**0.1**	**<10**	**0.2Si,0.1Mn,0.02C**
617	54	22	1	13	9Mo, 1Nb	0.3	1.1	<3	
740	**48**	**23**	**2**	**20**	**0.3Mo, 2Nb**	**2.0**	**0.8**	**<10**	**0.5Si,0.3Mn,0.03C**
282	**58**	**19**	**0.2**	**10**	**8Mo**	**2.2**	**1.5**	**<1**	**0.1Si,0.1Mn,0.06C**
247	60	8	0.03	10	10W,3Ta,1Mo	1.1	**5.3**	<1	1.3Hf,0.14C

Compositions measured using ICP-OES and combustion analyses

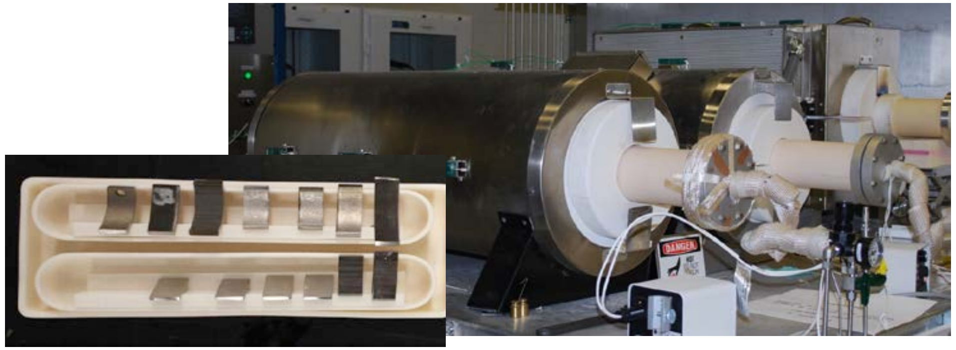
CO_2 compatibility evaluated several ways at 700°-800°C

Autoclave: 300 bar sCO_2
500-h cycles

Correct temperature and pressure

4-5 cm^2 alloy coupons

Tube furnace: 1 bar CO_2
500-h cycles



Same cycle frequency as autoclave

Baseline:
Box furnace:
Lab. Air
500-h cycles

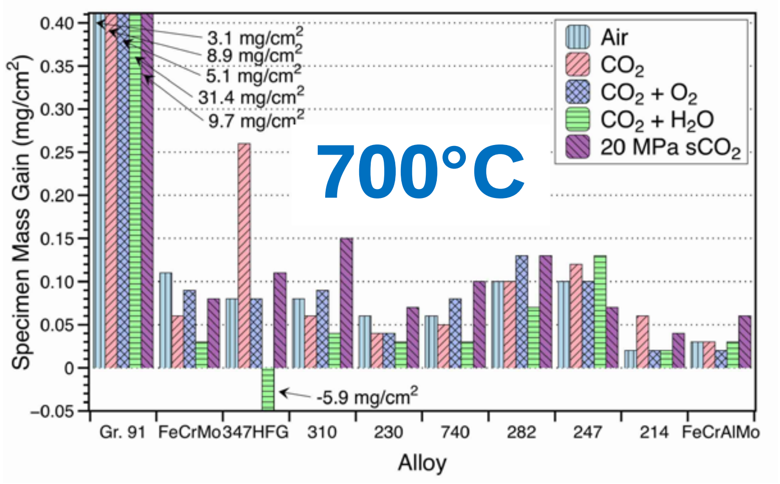
Previously:
"Keiser" rig:
500-h cycles, 1-43 bar CO_2

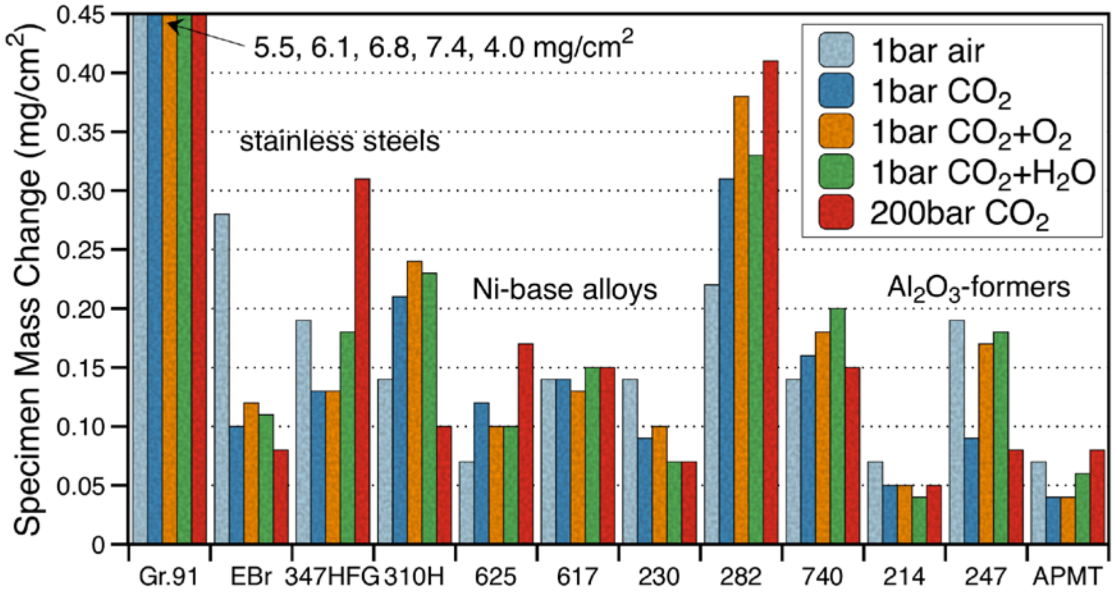
Study impurities at 1-43 bar

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

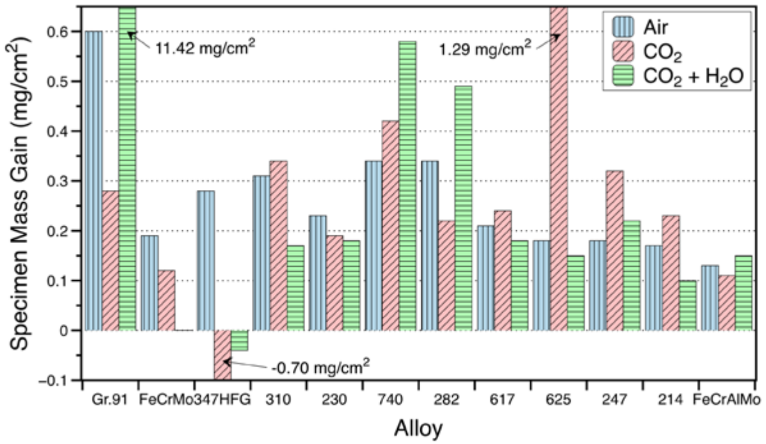
Impurities (2015): 1atm, many alloys (1 of each)

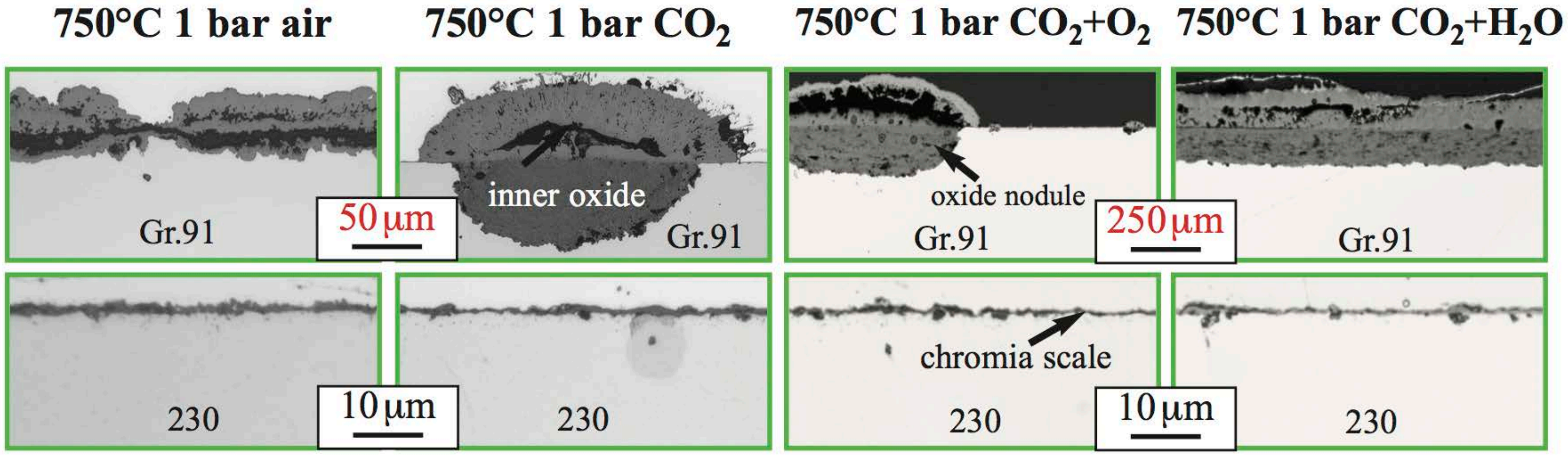
700°C





800°C





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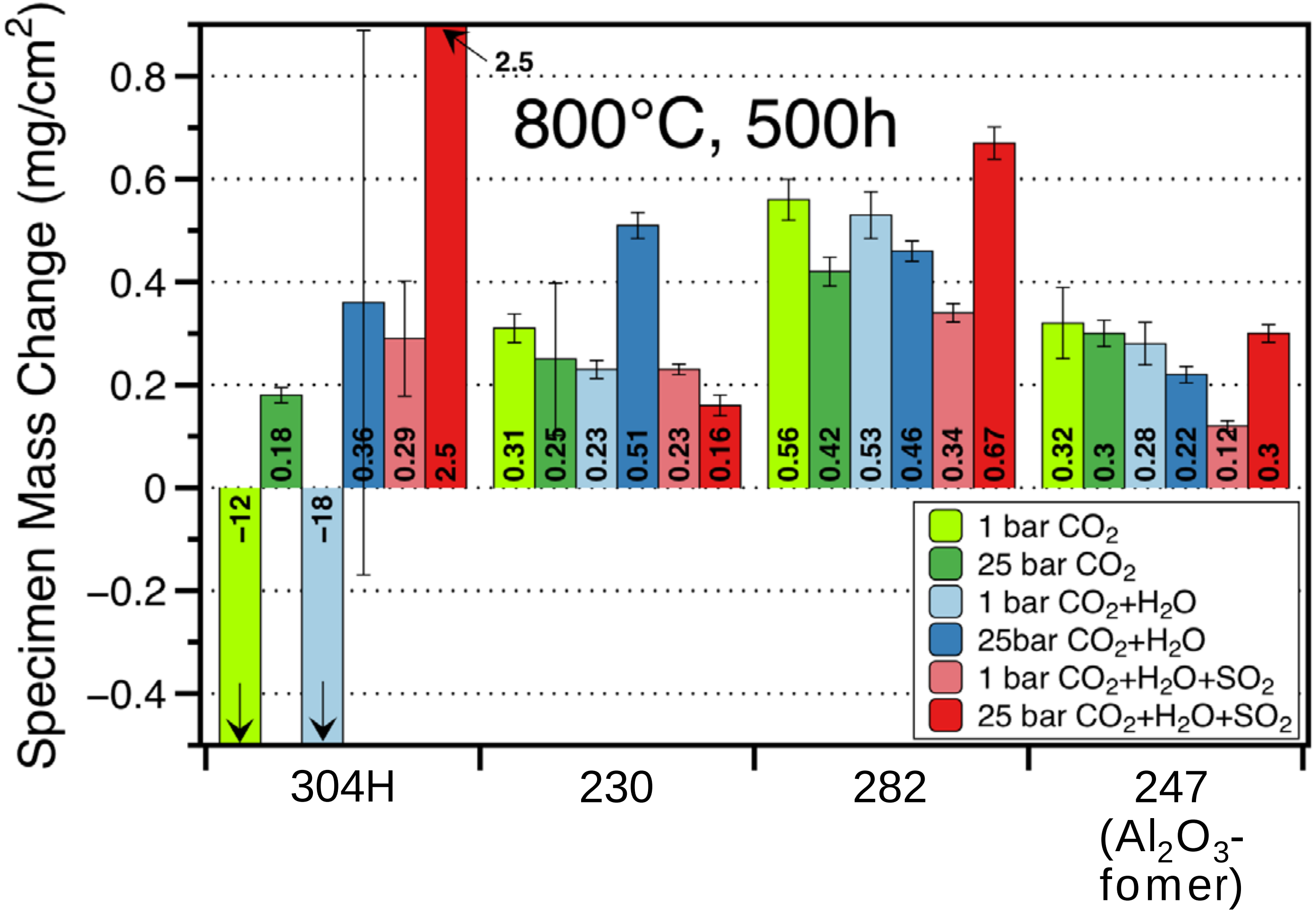
Impurities (2017): fewer alloys (3 of each), 1 and 25 bar



Two alloy 230 reaction tubes:

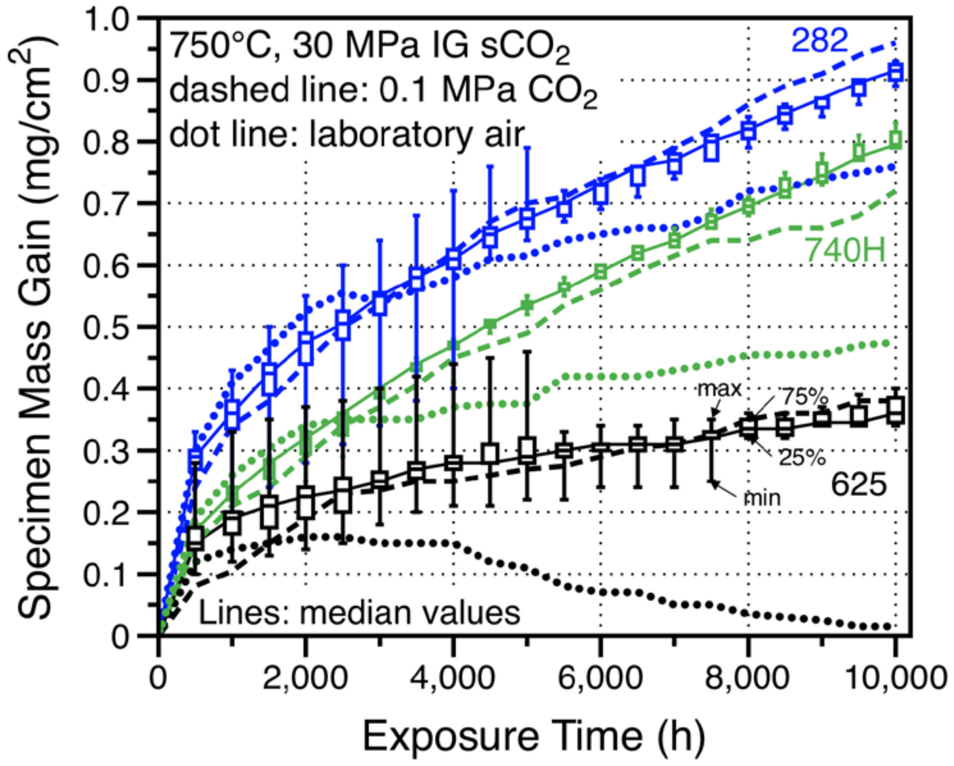
Pressure: 1 and 25 bar

Gas: RG CO_2
CO_2+10%H_2O
CO_2+10%H_2O+0.1%SO_2

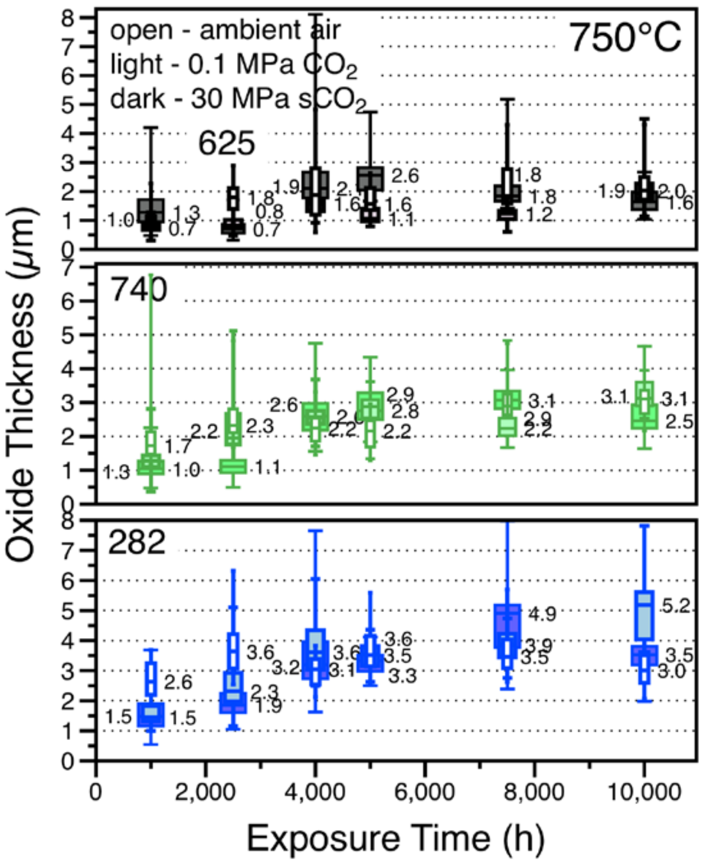
Pint, Brese, Keiser, NACE Corrosion 2018 C2018-11199

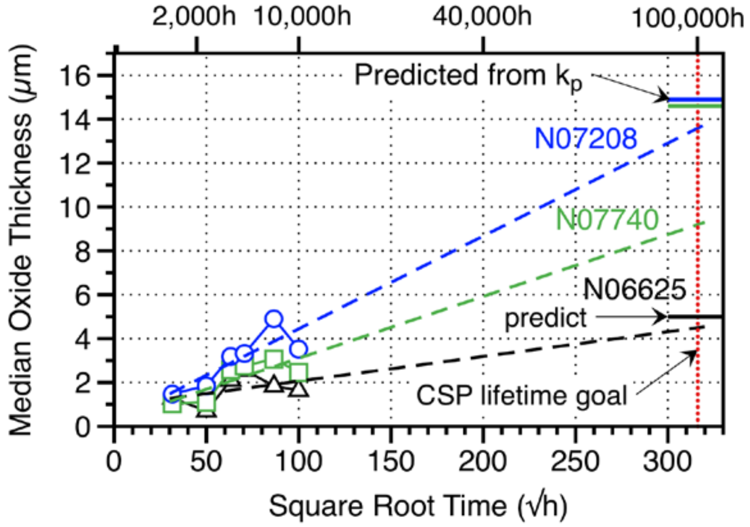
CSP: completed 10,000 h exposures for lifetime model

500-h cycles: three different environments



Quantification of scale thickness in three environments:

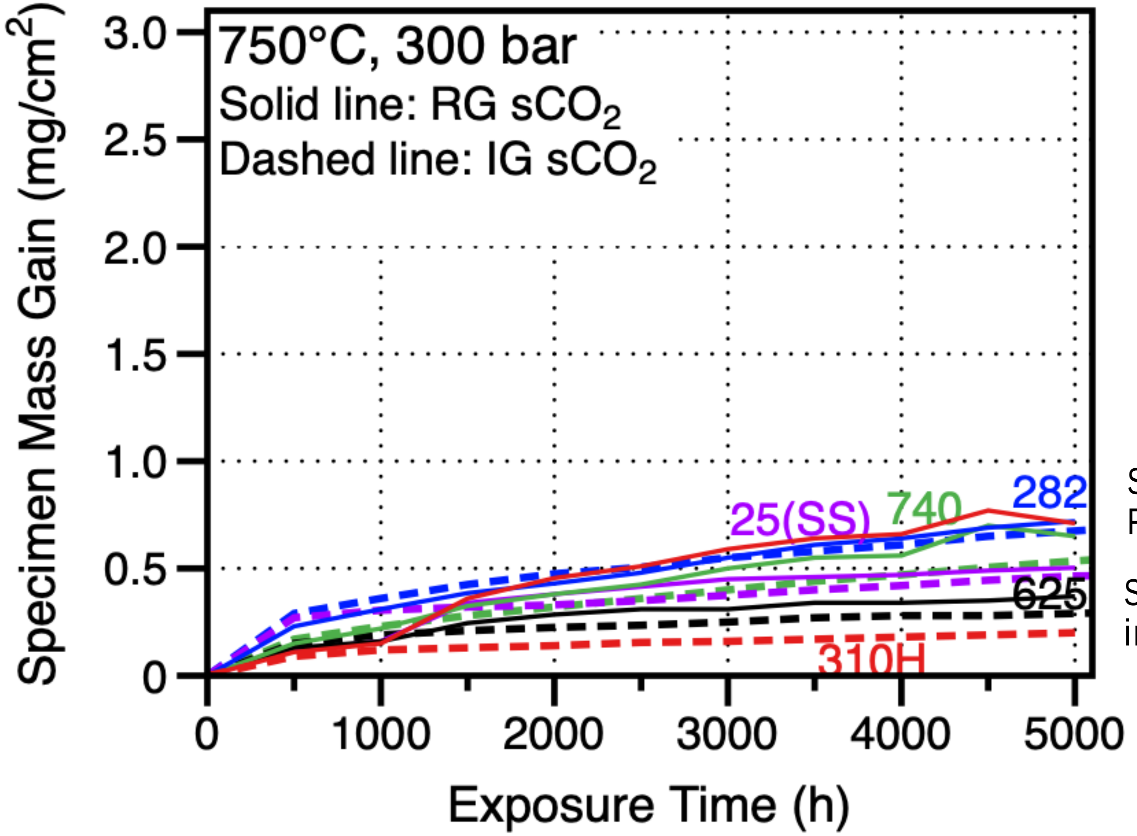




Extrapolation sCO_2 to 100,000 h

Pint, Keiser, NACE Corrosion 2019 C2019-12750

2016-2017: baseline performance in RG and IG sCO2

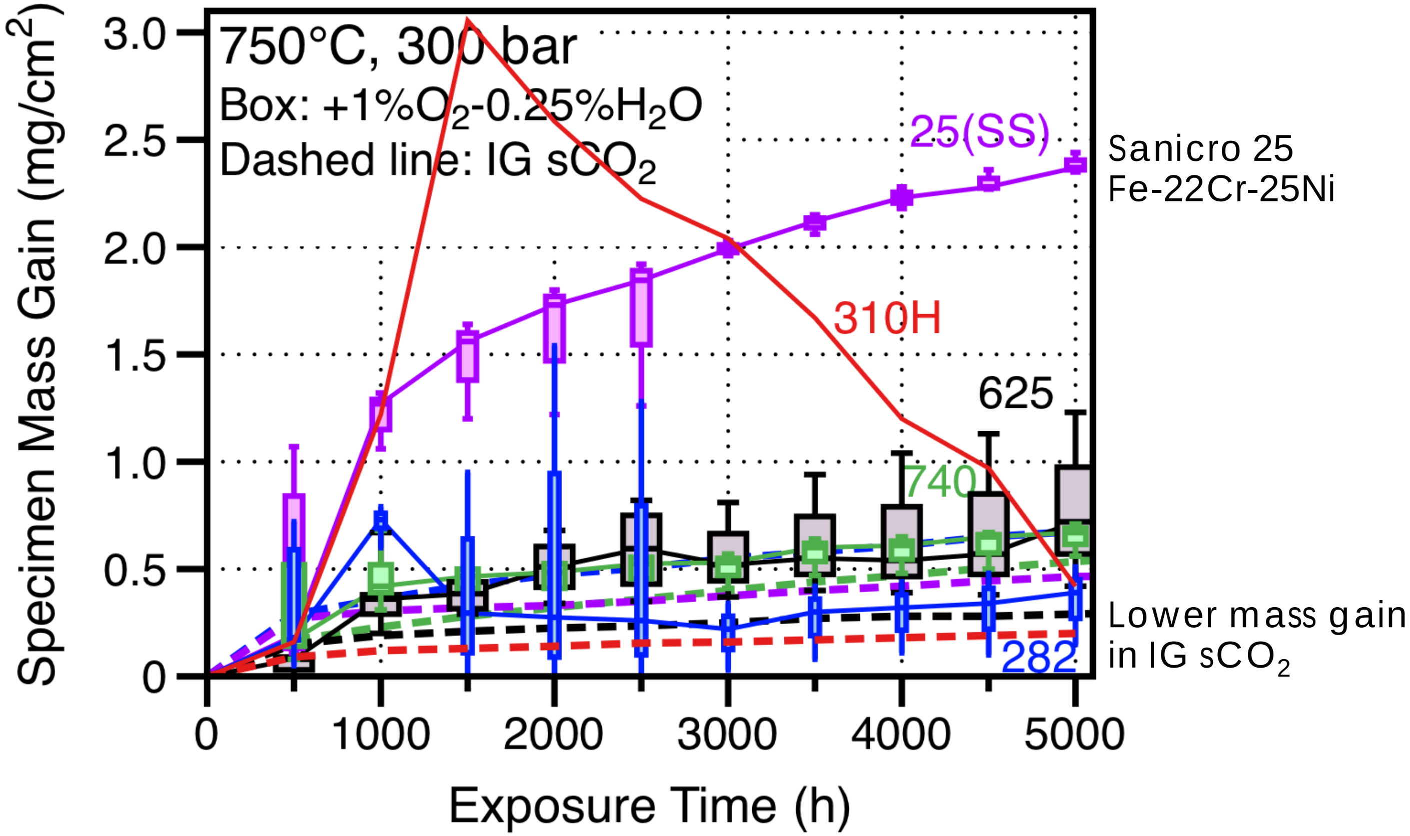


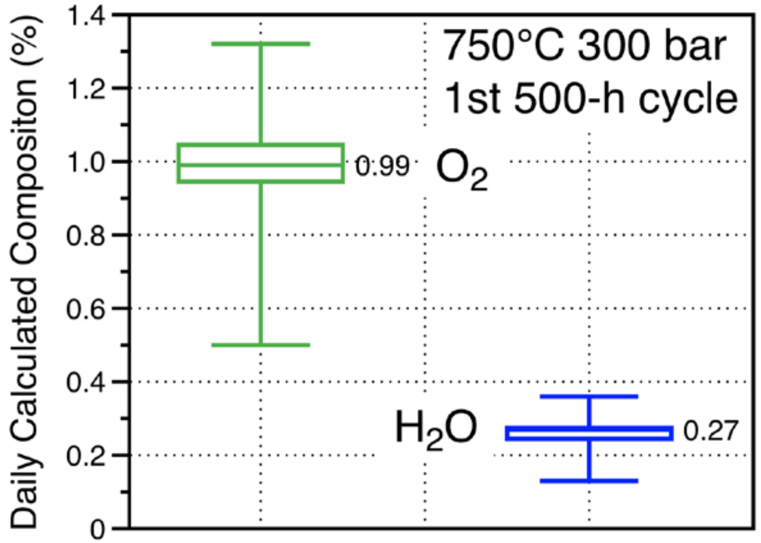
Sanicro 25
Fe-22Cr-25Ni

Similar mass gain
in RG & IG sCO_2

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

2018: finally completed multi-pump 300 bar autoclave
Clearly see an effect of impurities

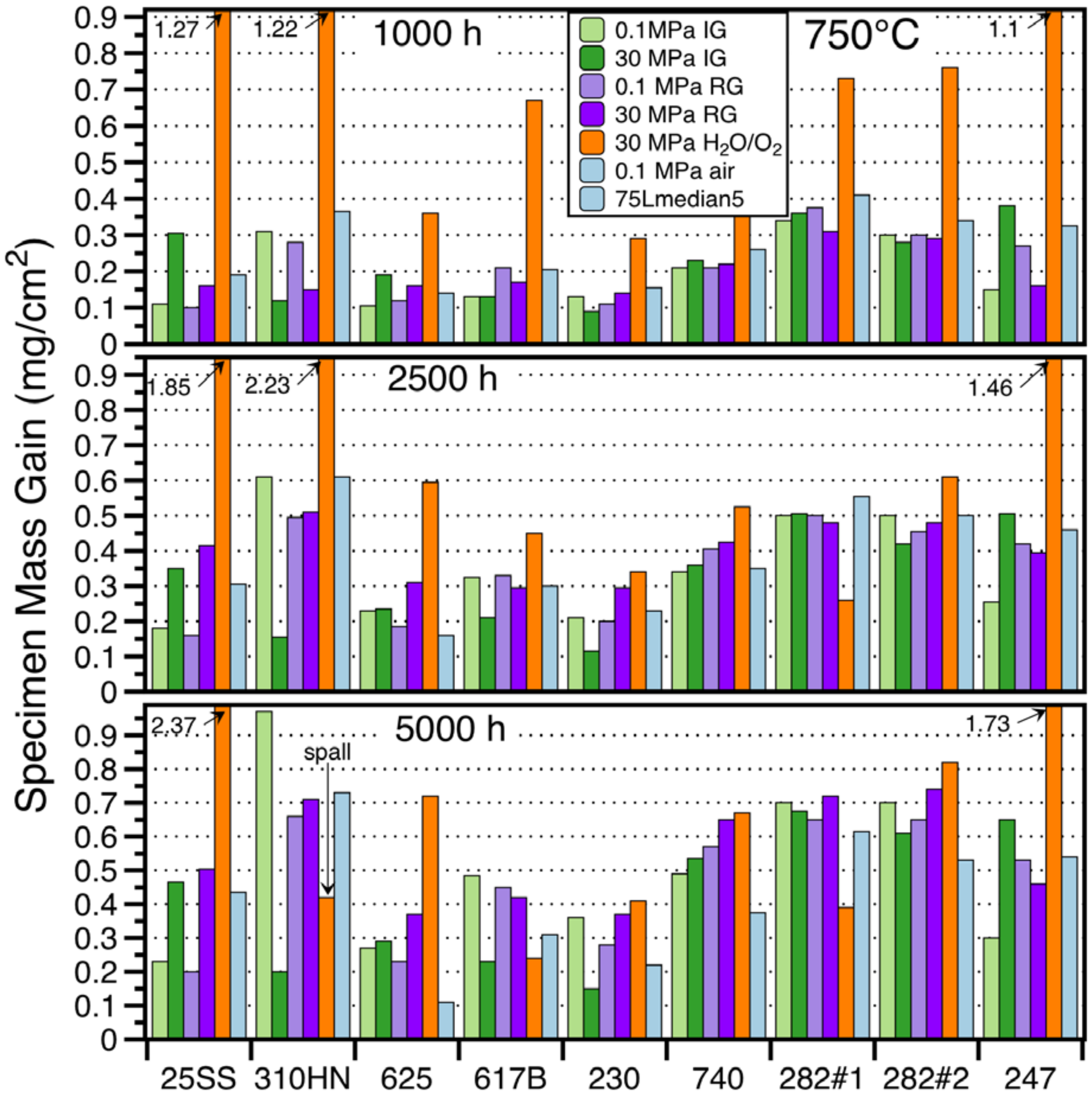




Goal: 1%O_2+0.25%H_2O
(industry suggestion)
Not easy to control at 300 bar

Industrial grade (IG) CO_2: 18±16 ppm H_2O and ≤ 32 ppm O_2

Summary: impurities caused a higher mass gain



RG CO_2 + 1%O_2 + 0.25% H_2O

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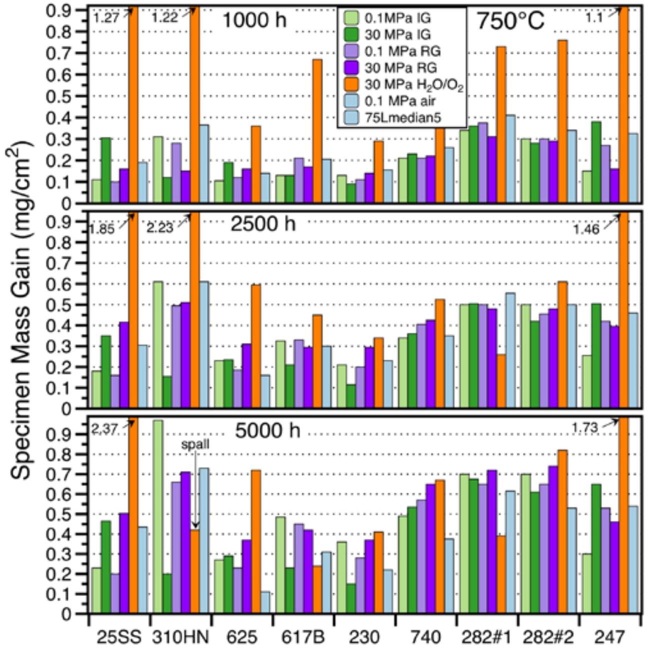
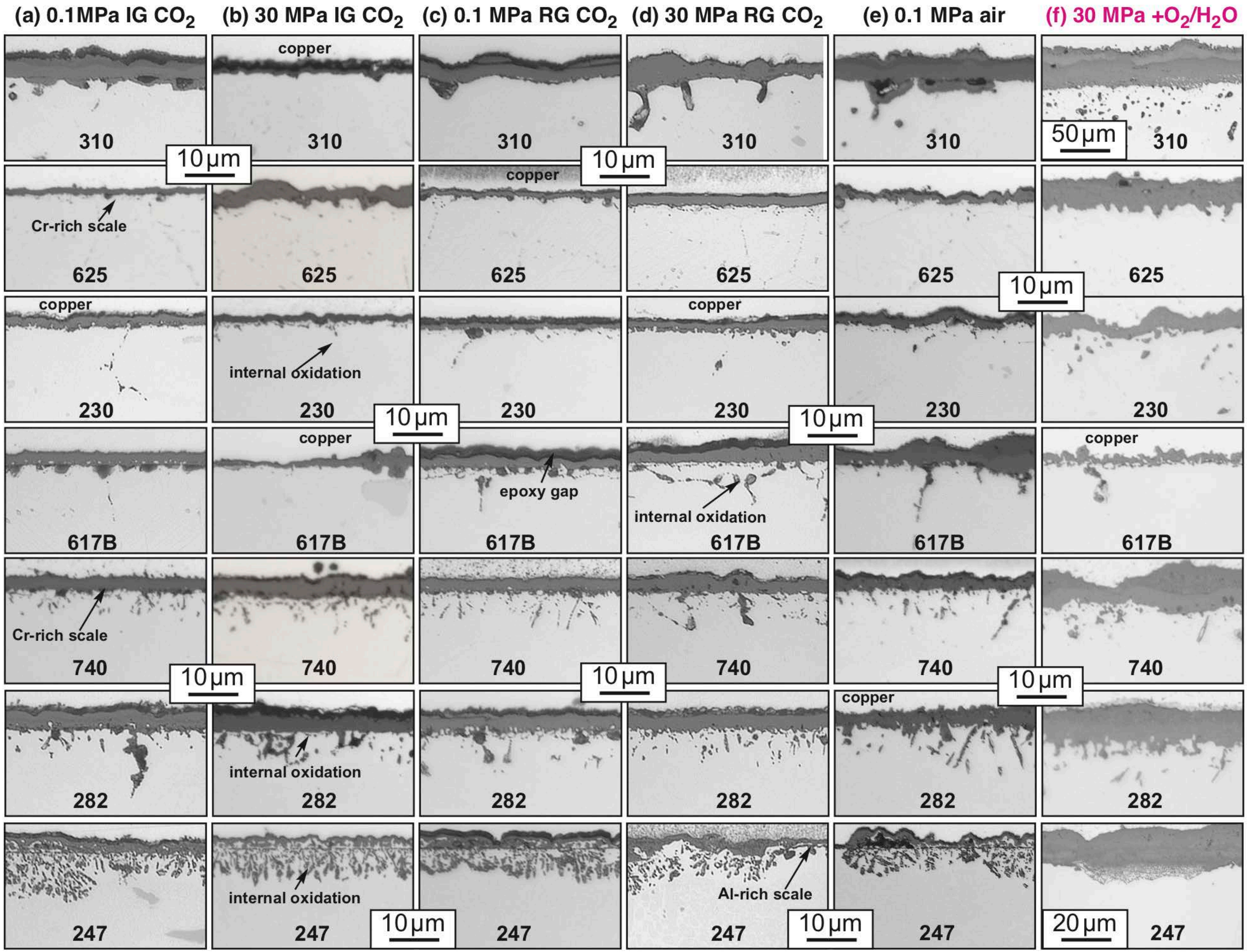
Metallography consistent with mass change





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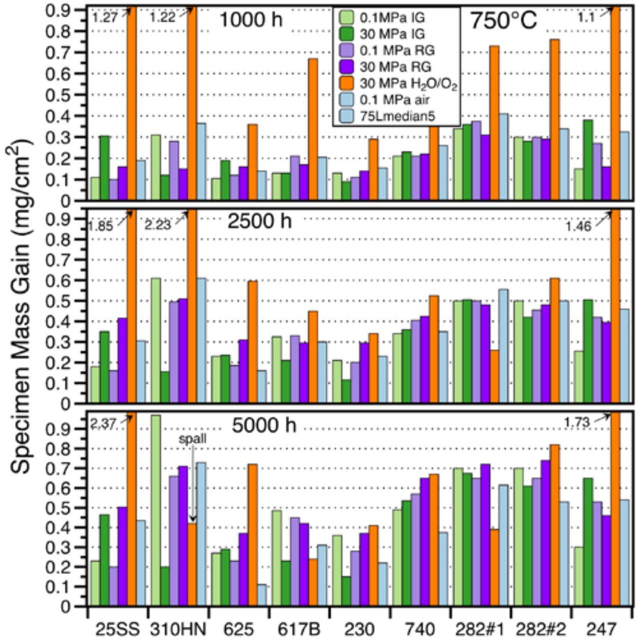
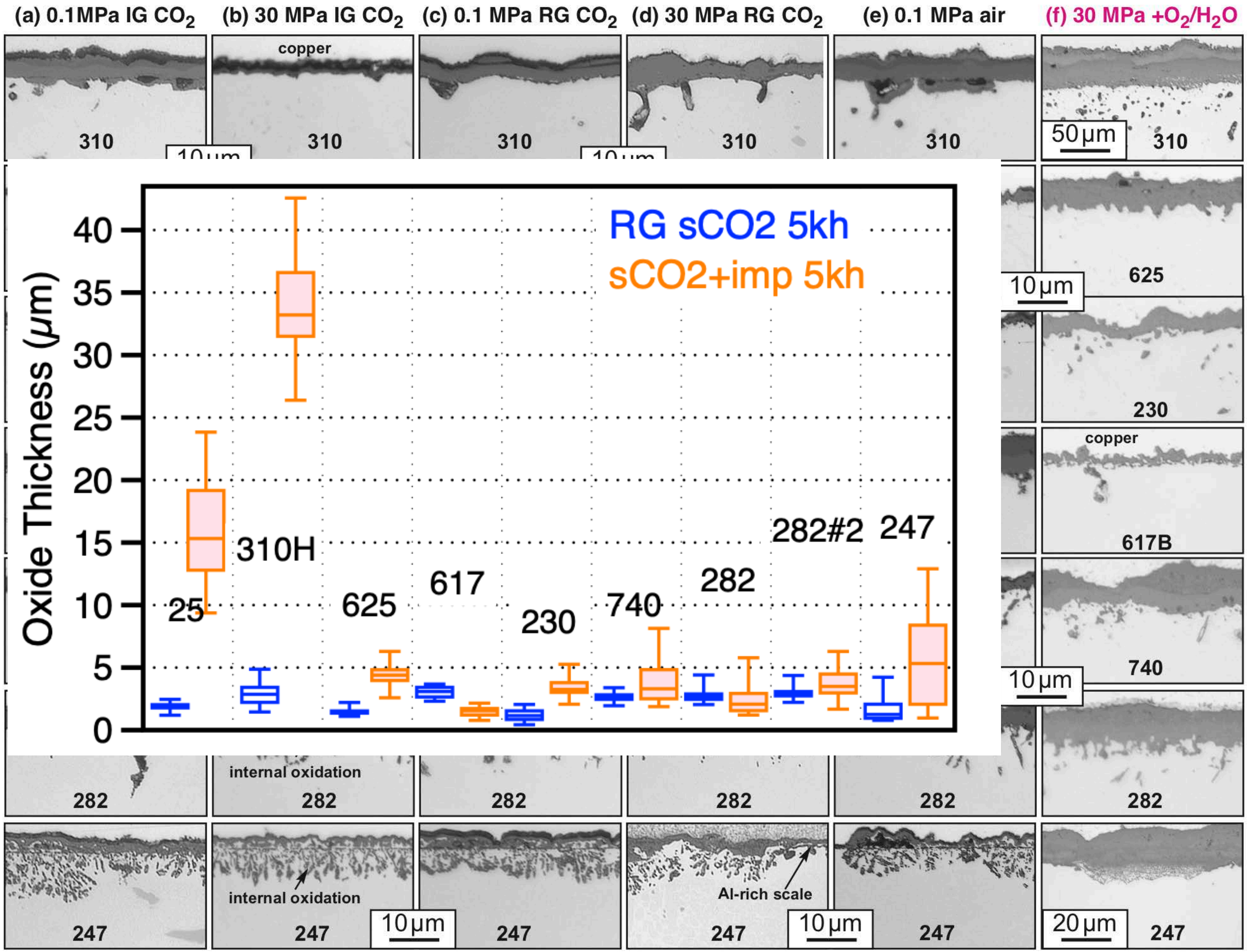
Fe-based alloys: strongest effect





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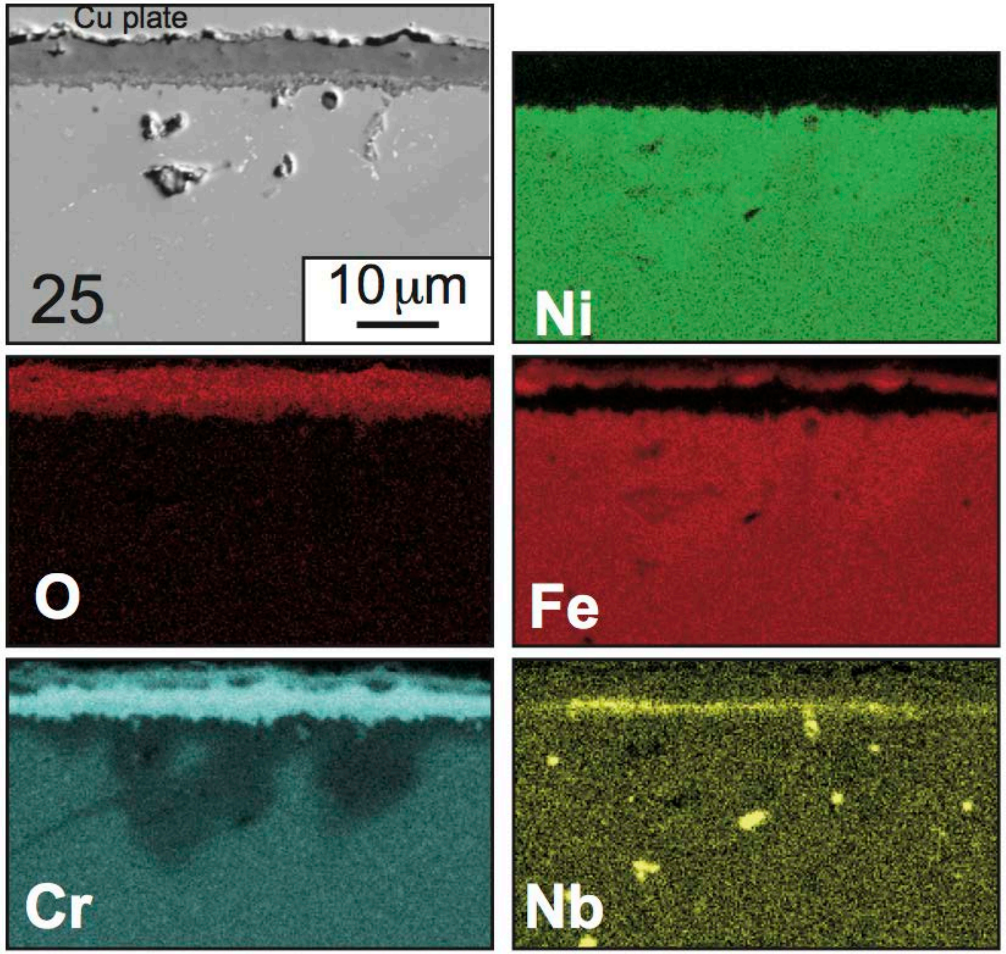
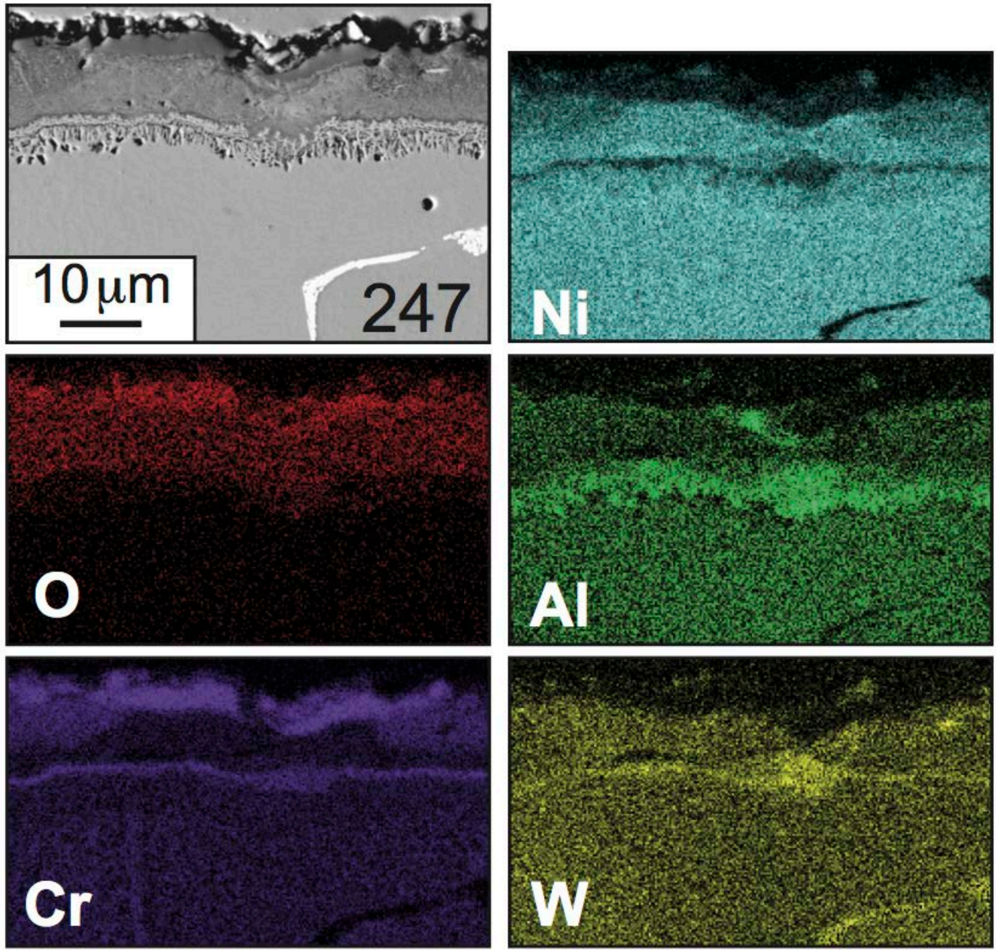
SEM/EDS: Fe/Ni-rich oxide forming with impurities





1000 h at 750°C, 300 bar sCO_2+1%O_2+0.25%H_2O

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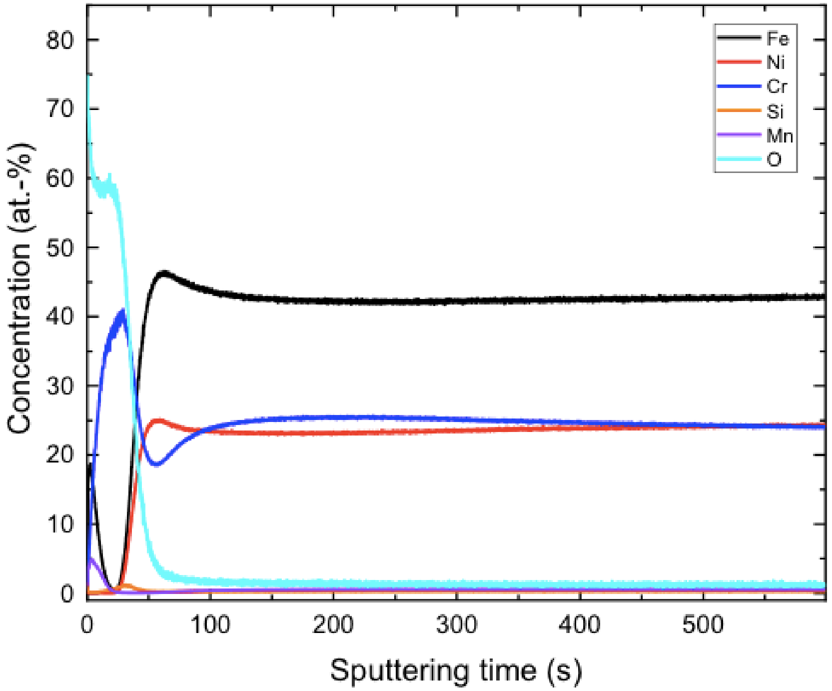
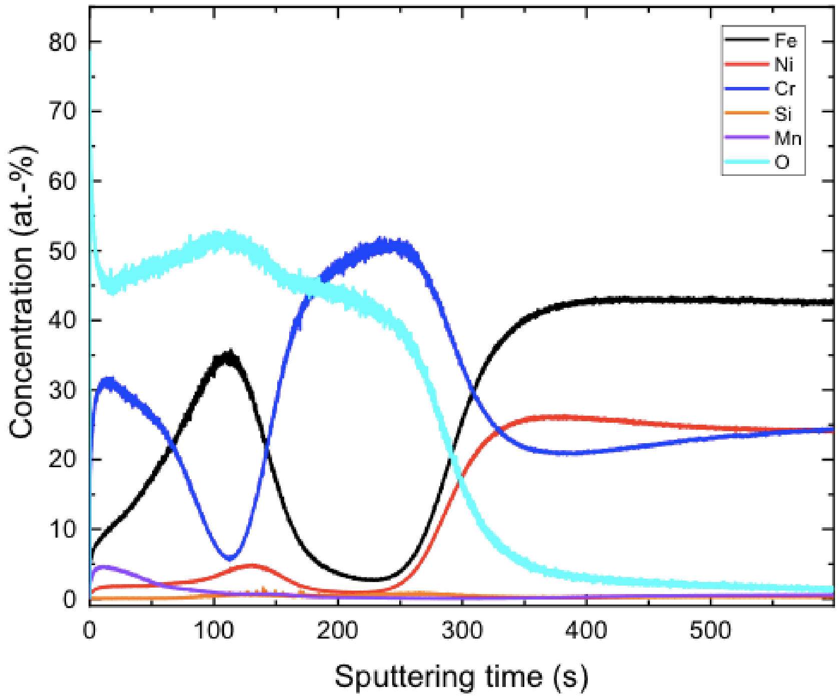
GDOES: very different oxide forming on 25: (Fe-22Cr-25Ni)

RG sCO_2



sCO_2+1%O_2+0.25%H_2O

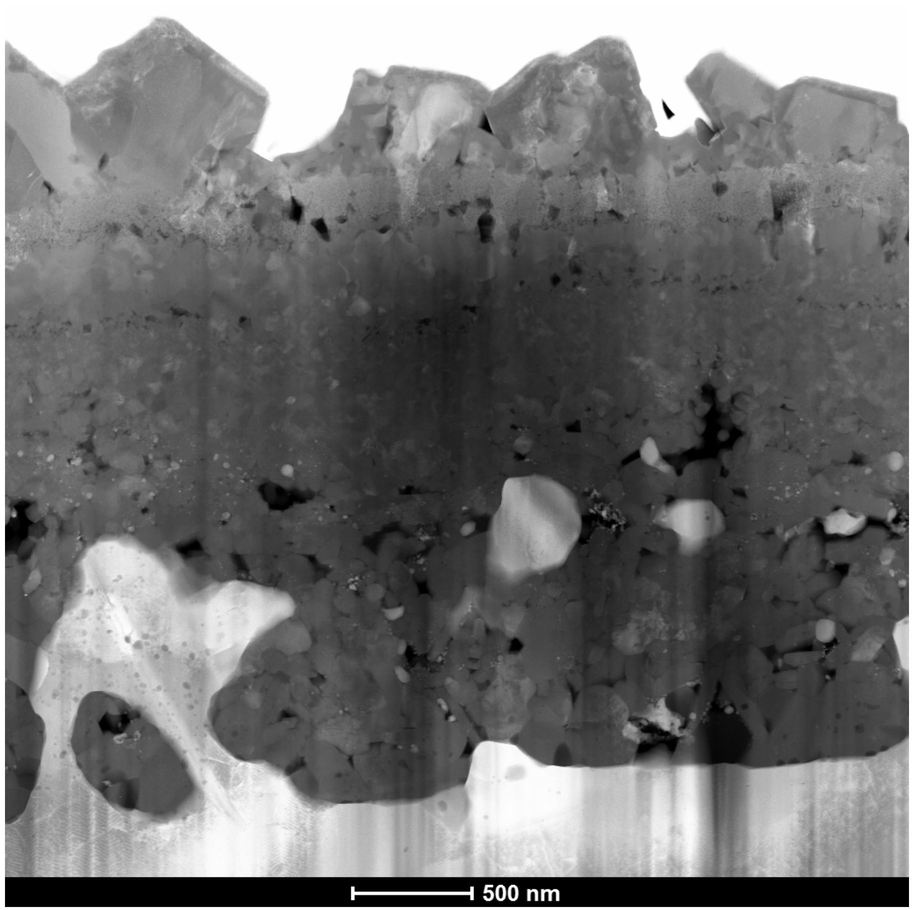


1000 h at 750°C, 300 bar

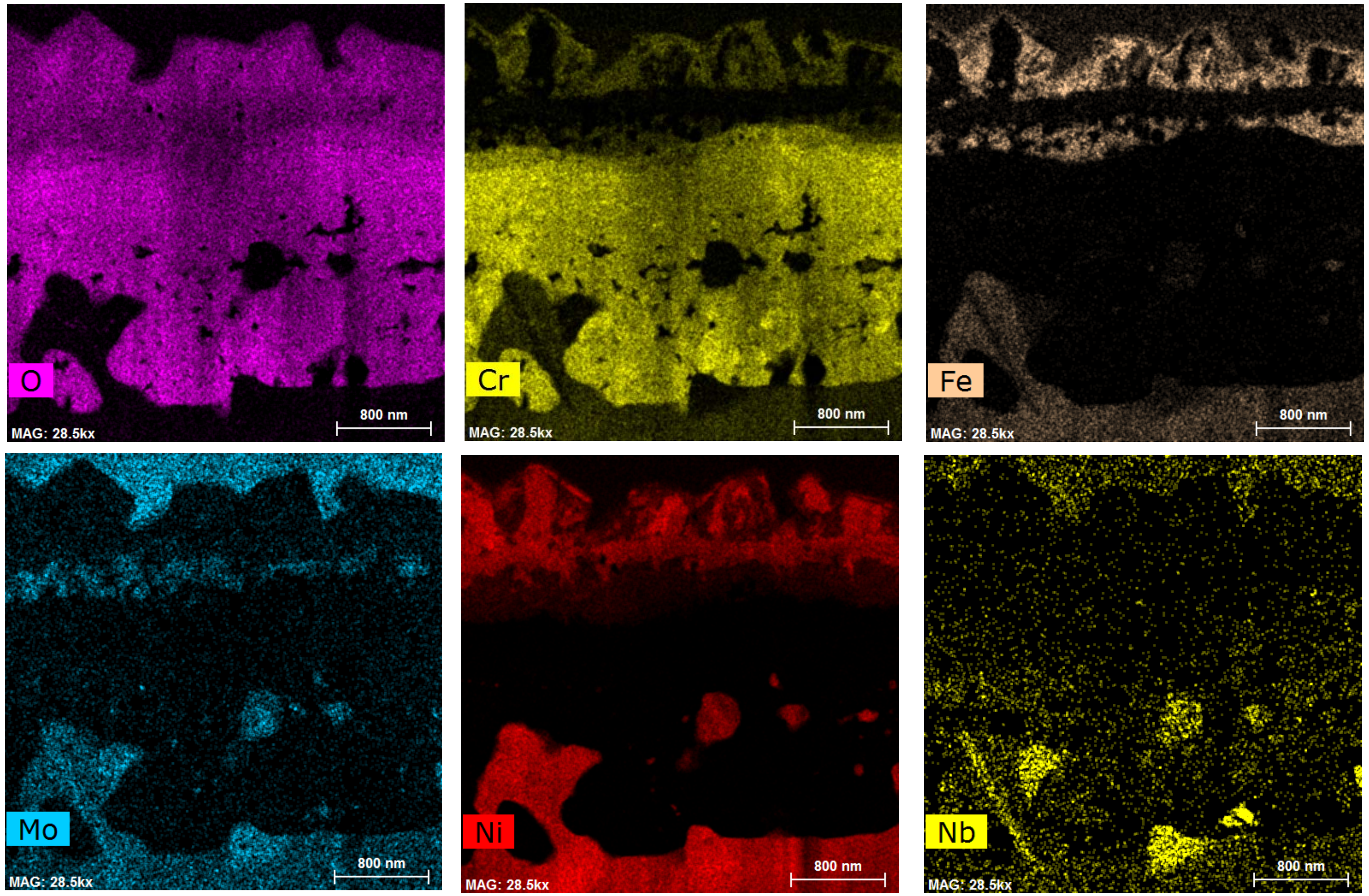
Glow discharge optical emission spectroscopy

625 (NiCr) 1000h STEM: unusually thick Cr-rich oxide layer

STEM annular dark field image



Scanning transmission electron microscopy



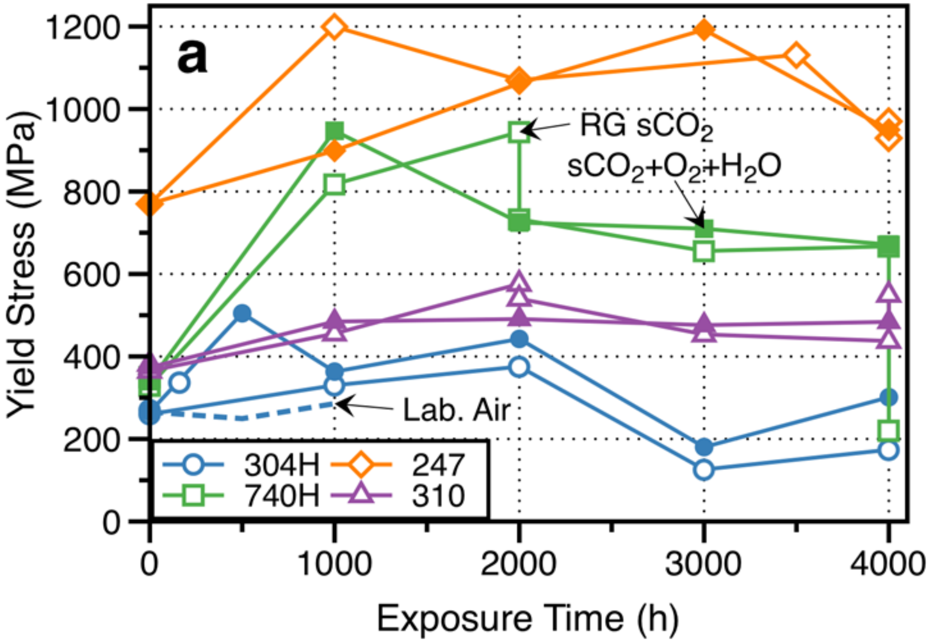
Scale thickness 3.70±44µm

1000 h at 750°C, 300 bar $sCO_2+1\%O_2+0.25\%H_2O$

Measuring 25°C tensile properties suggests future strategy: Post 750°C exposure shows drop in ductility

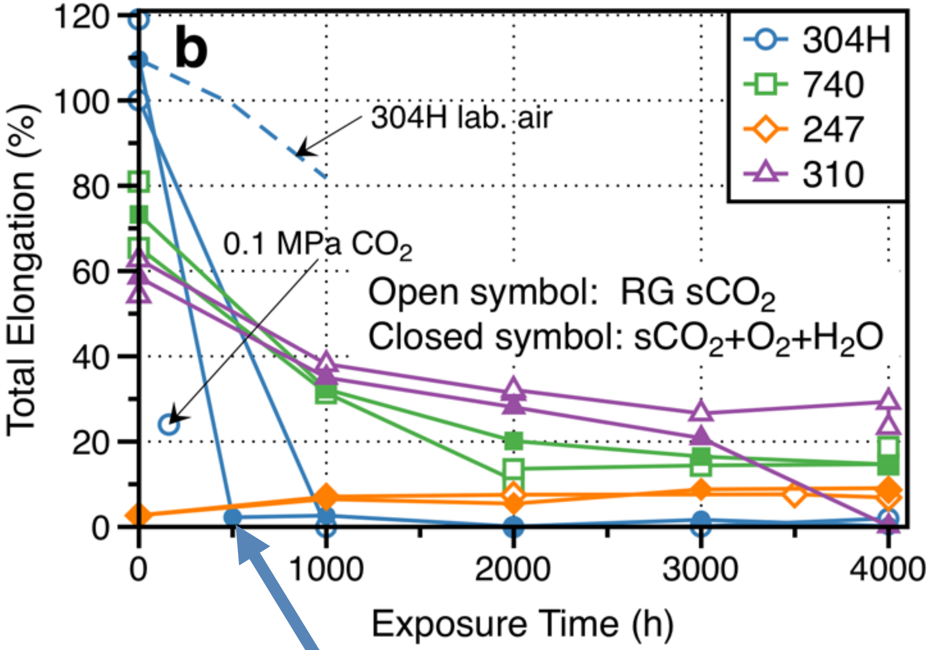
Method to quantify degradation of steels at 450°-650°C (?)

Yield strength



25mm dogbone

Elongation:



304H: large drop in sCO_2

310: also degrading, w/o impurities

Pint, et al., Materials and Corrosion, 2019, on-line

Project is concluding having achieved its goals

- Developed new experimental equipment for studying impurity effects on structural materials at up to 750°C/300 bar
- Results indicate that there is a negative effect of impurities, more so for Fe-based alloys than Ni-based alloys
- Room temperature tensile data suggests a simple route to quantify sCO_2 impact on mechanical properties of steels exposed at lower temperatures

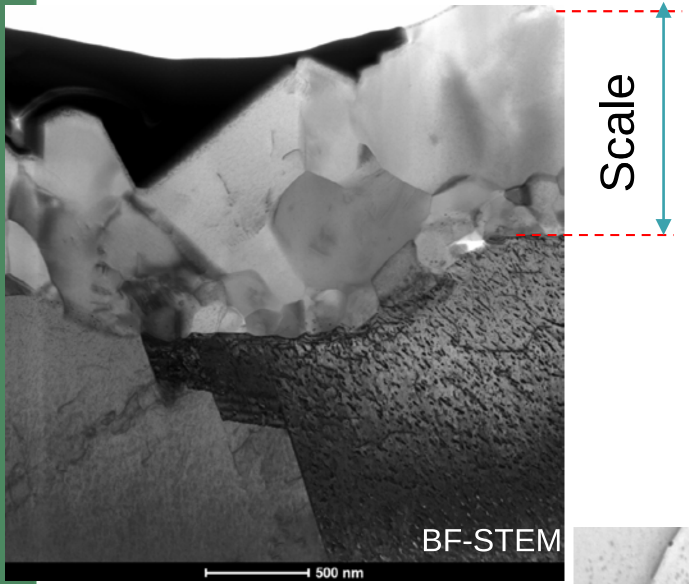
Industrial collaborations

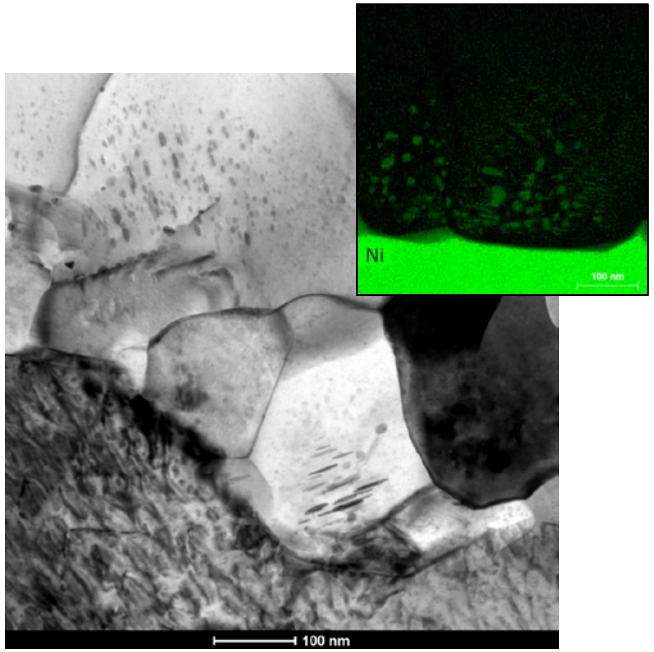
- All major US alloy manufacturers
- Conference calls conducted with HX, sCO_2 community (CSP project)
- Feedback from 8 Rivers/NetPower on impurity levels of interest
- Public presentations (TMS, MS&T, EFC workshop, NACE, EU sCO_2)

Backups

FE project studying model Ni-22Cr alloy specimens

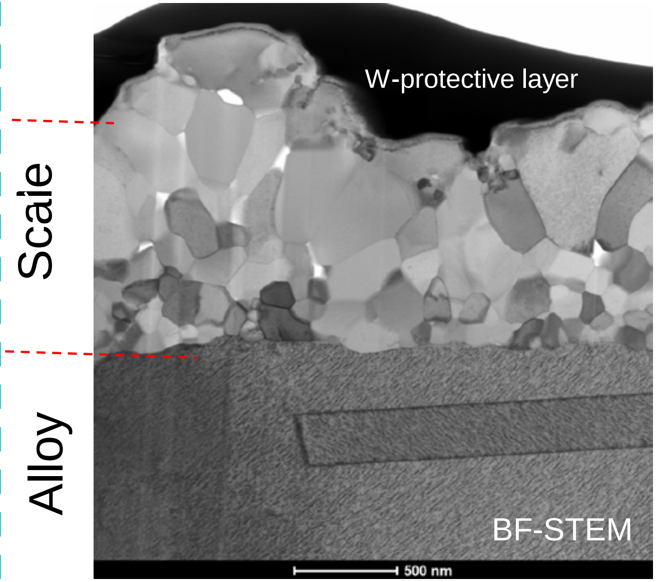
750°C, Air, 1000h



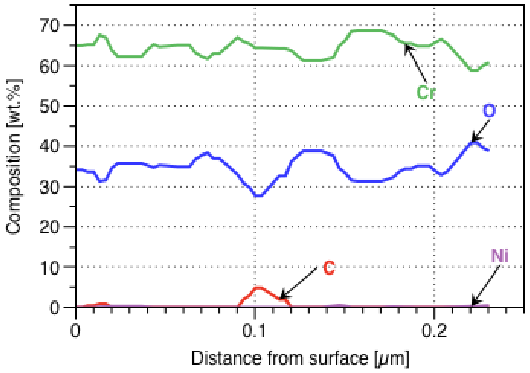


Air only: Metallic Ni particles in scale near substrate interface

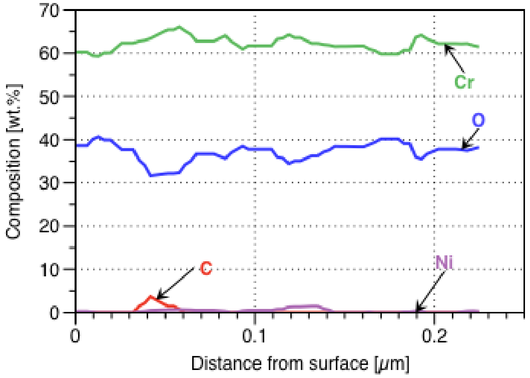
750°C, 300 bar sCO_2, 1000h

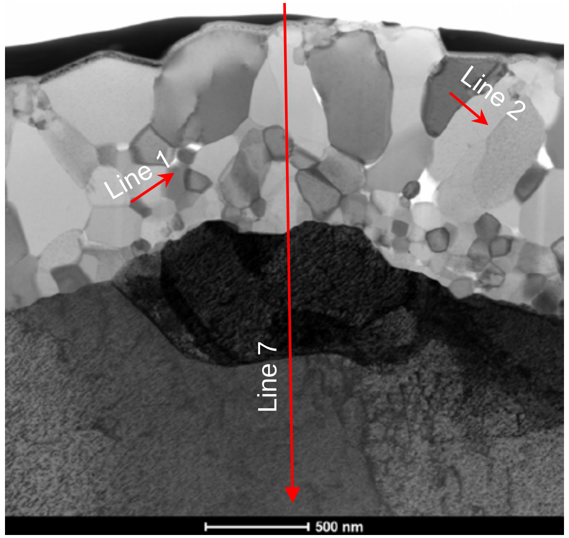


EDS Line 2



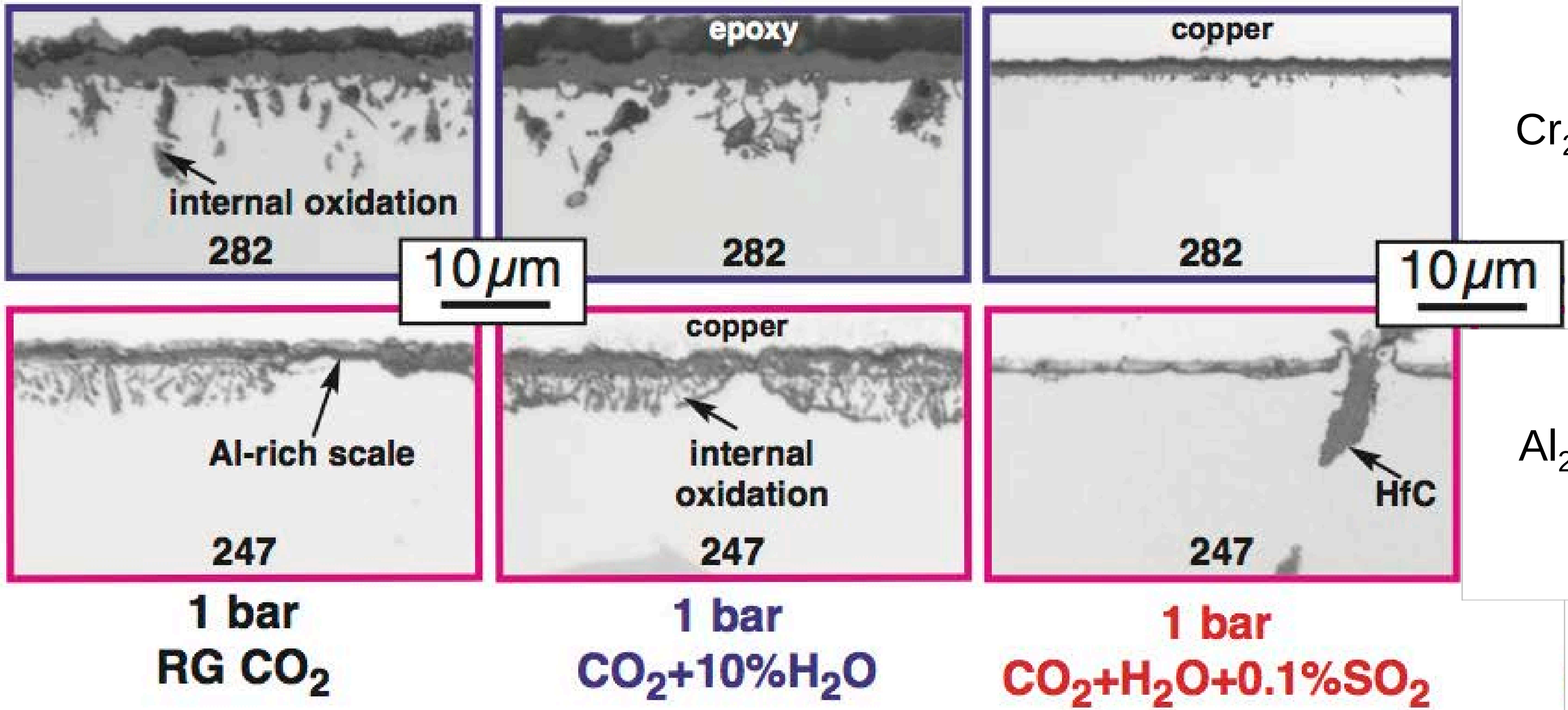
EDS Line 1





C on oxide grain boundaries

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



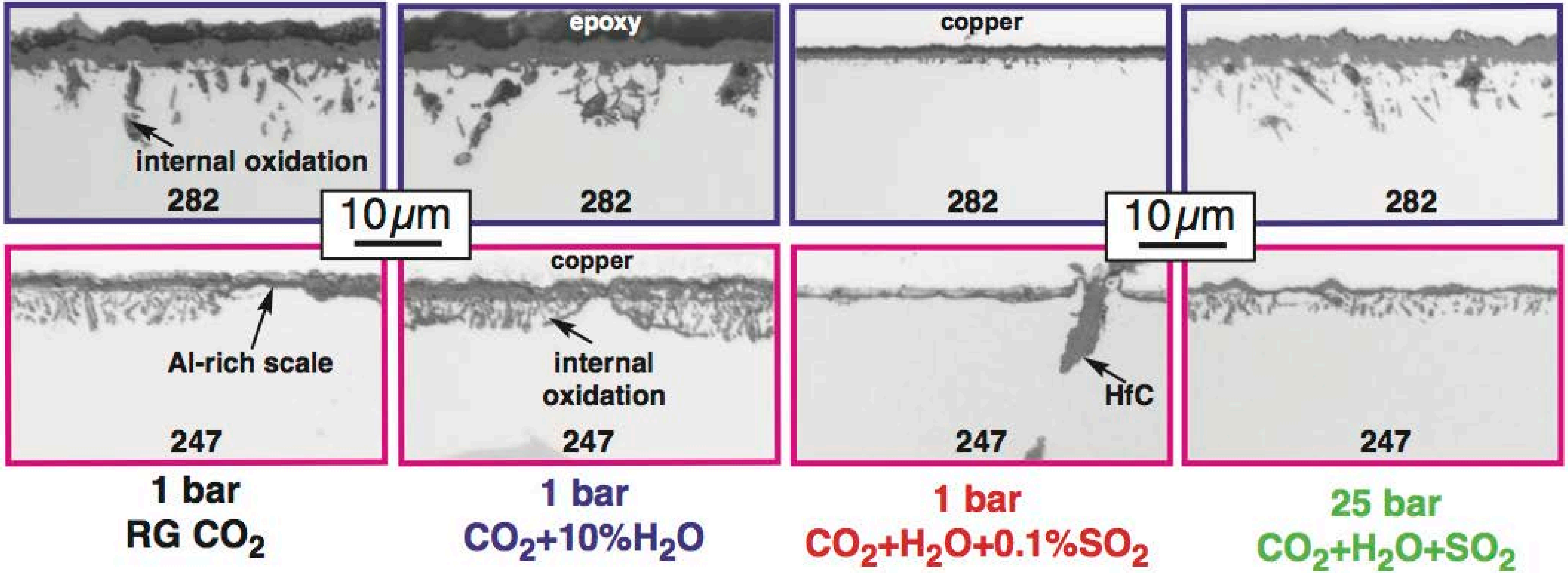
Cr_2O_3-former

Al_2O_3-former

$10\%H_2O+1000$ ppm SO_2

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



10%H_2O+1000 ppm SO_2 10%H_2O+1000 ppm SO_2

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

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

NACE 2018 paper

Success warrants continued work to answer more q's

- Complete characterization and publications in early 2019
  - Mount 5,000 h specimens, etching, TEM, EPMA, etc.
- New FWP to focus on:
  - Mechanistic understanding of O_2/H_2O effects with $^{18}O/H_2{}^{18}O$ tracers
    - Separate O_2 and H_2O effects
  - **Focus on steels at lower temperatures: technology enabler**
    - #1 question from industry is "where can I use T91?": cheaper and strong vs. fear
    - Provide input to alloy designers on effect of Cr/Ni in Fe-Cr-Ni alloys
    - Use 25mm tensile bars to assess sCO_2 effect on strength & ductility
  - Surface modifications to improve steel performance (as warranted)
    - Shot peening
    - Coatings
  - Creep assessment of thin-walled material at 750°C (282/740/etc.)
  - Model lifetime as a function of temperature/HX dimensions/heat transfer