Coated and Uncoated Steel Compatibility in Supercritical CO_2 at 450°-650°C

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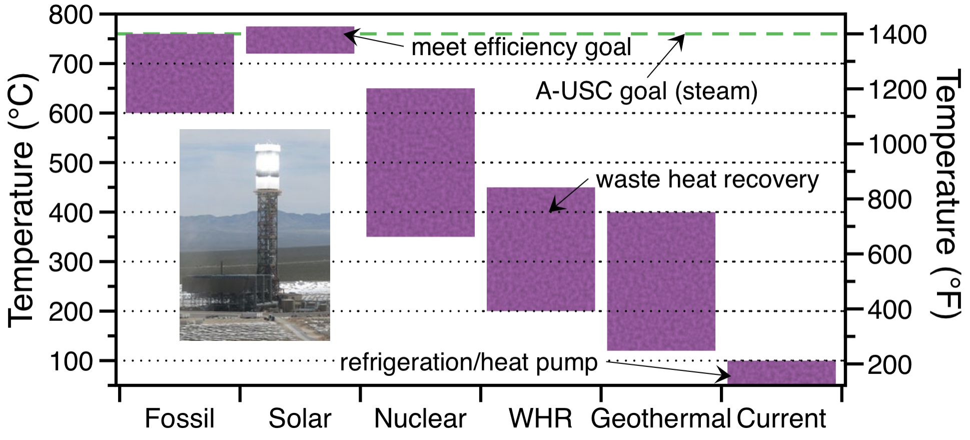
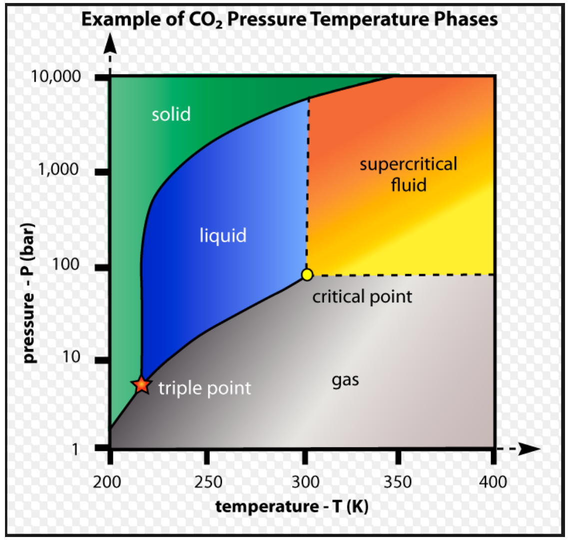
  - Tenaris, T91
  - EPRI, VM12
  - Sam Sham, INL (US heat, alloy 709)

Most questions over 10 years were about steels & coatings!

Supercritical CO_2 applications



sCO_2 has many unique & attractive aspects



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

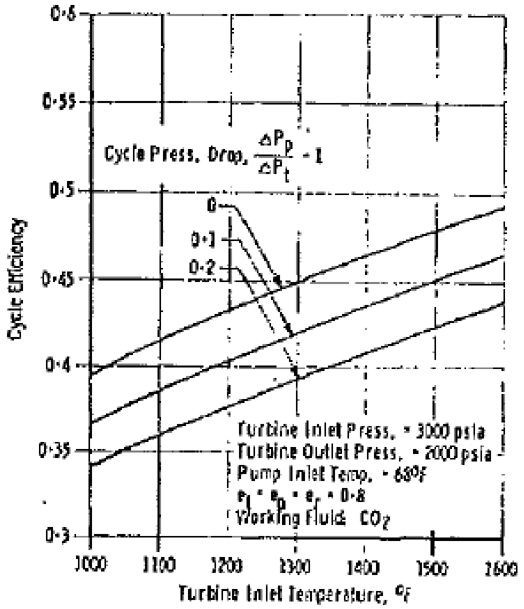
Cost is a concern:

Ni-based alloys: OK in sCO_2

Where can steels be used?

Can we coat them?

Interest in >700°C for high efficiency



Feher, 1965

50% sCO_2 eff @ >720°C

Supercritical CO_2 Allam cycle: first clean fossil energy?

NetPower 25MWe test facility (Texas)

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

CO2-free natural gas? CCS project powers grid for first time

By Carlos Anchondo, Edward Klump | 11/17/2021 07:07 AM EST

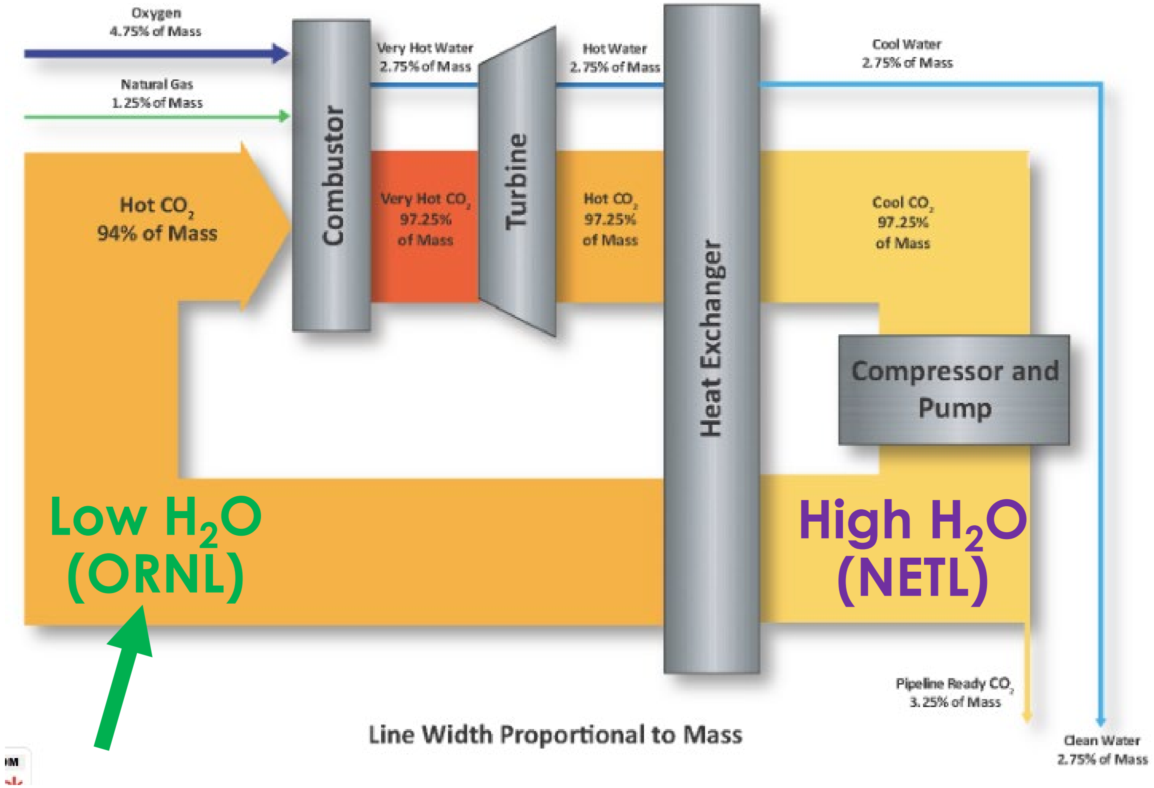
May 2018: announced first firing
November 2021: 1st grid power

Material challenges:

Combustor: **900°C**

Turbine exit: 750°C/300 bar

Combustion impurities: O_2, H_2O, SO_2

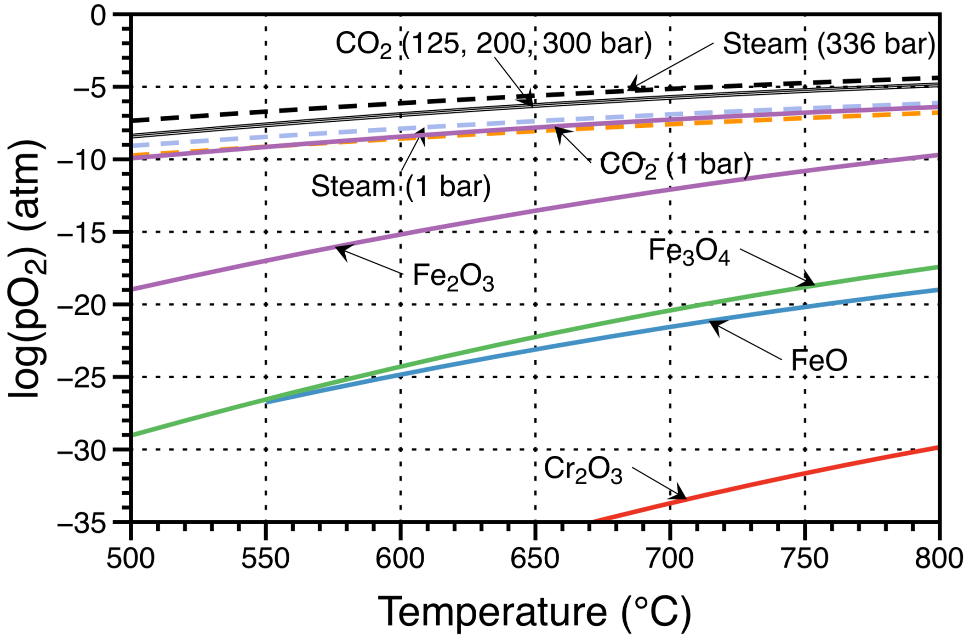


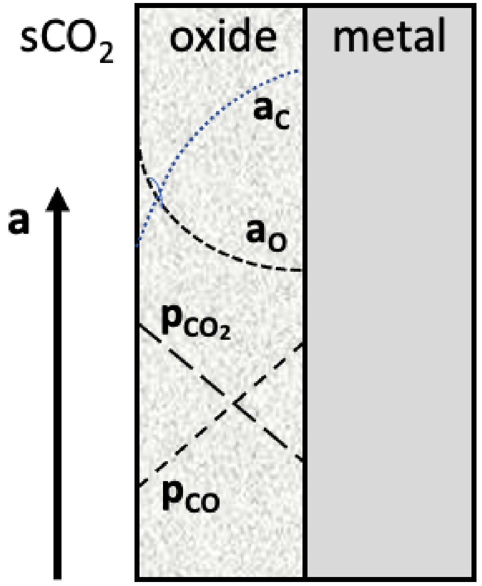
Burning natural gas in sCO_2 creates impurities…what is effect?

Thermodynamics: Oxygen levels similar in steam/CO_2

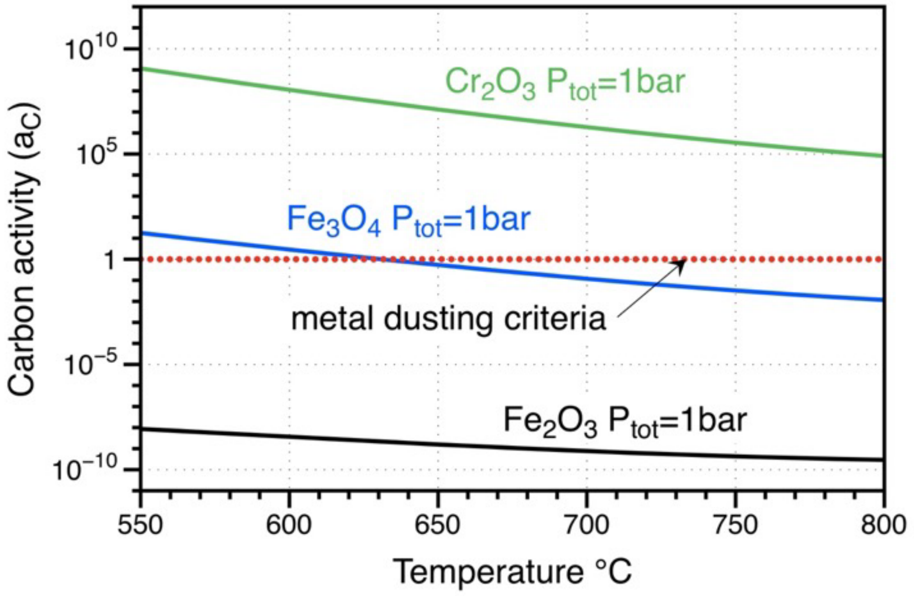
Concern about high C activity at m-o interface

Factsage calculations





After Young, et al., 2011



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

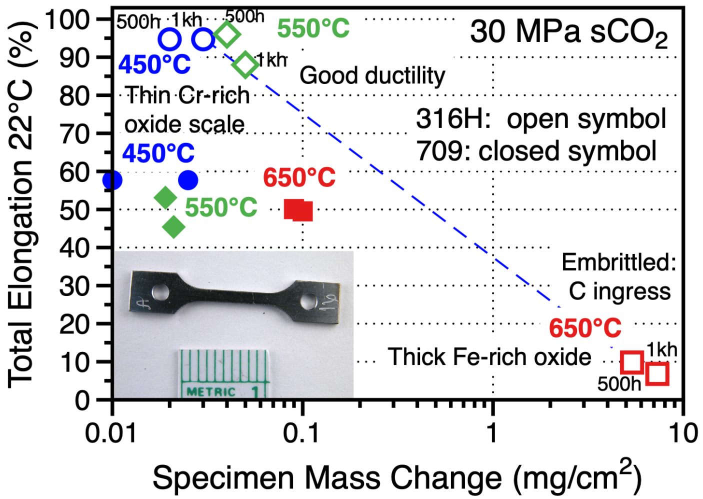
High carbon activity at P_{total} = 1 bar (What is $P_{interface}$?)

General conclusion: internal carburization concern for Fe-based alloys

sCO_2 compatibility: broad range of conditions considered

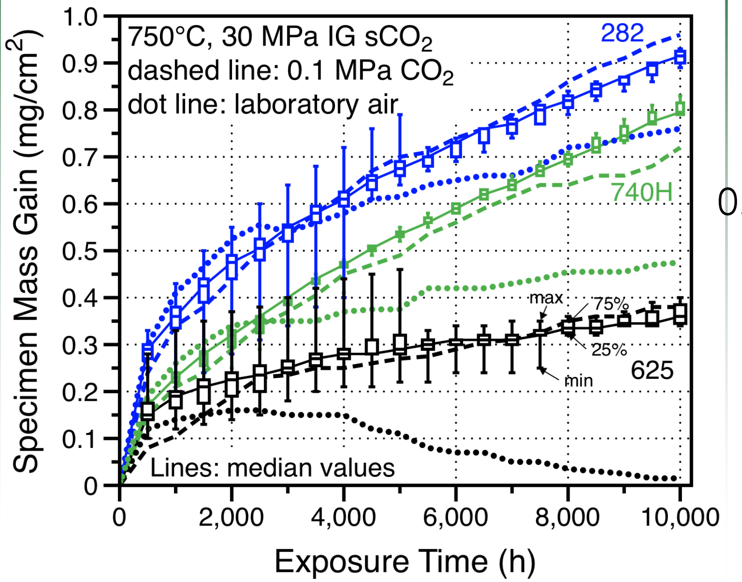
400°-650°C: concern about steel carburization

- Well-known issue from CO_2-cooled reactors
  – Grade 9 steel current issue
- 550°-600°C transition temperature for normal austenitic steels
- **Key to low-cost technology**



650°-800°C: Ni-based alloys

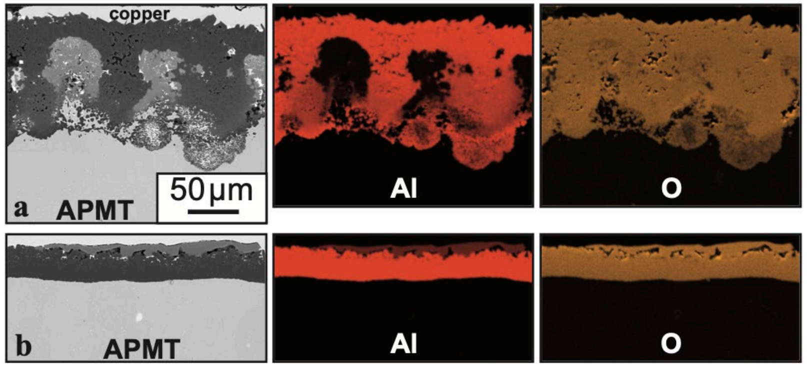
- No issues for Ni-based alloys
  – Low C solubility, protective Cr_2O_3 formation
- Similar rates for air, CO_2 and sCO_2
  – **Little or no P effect @ 750°C**



>800°C: challenging for superalloys/cermets/FeCrAl

- Initial results at 0.1 & 2 MPa
  – **Subcritical P effect observed**
- Mo/W cermets need coating
- Accelerated attack of Ni-based superalloys
- SiC promising, but not $MoSi_2$
- FeCrAl attacked at 1200°C
  – Al_2O_3 supposed protective?

0.1 MPa



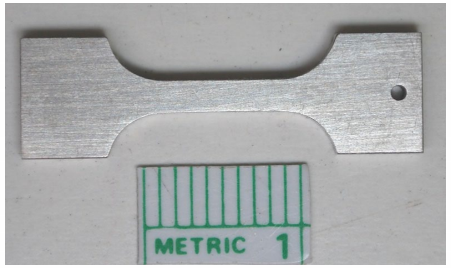
2 MPa CO_2

ORNL steel project started in August 2019

Test matrix & progress

Temperature	RG sCO_2	$+1\%O_2+0.1\%H_2O$
450°C (842°F)	**2,000 h**	1,000 h
550°C (1022°F)	**2,000 h**	1,000 h
650°C (1202°F)	**2,000 h**	1,500 h

Autoclave: 300 bar sCO_2
500-h cycles



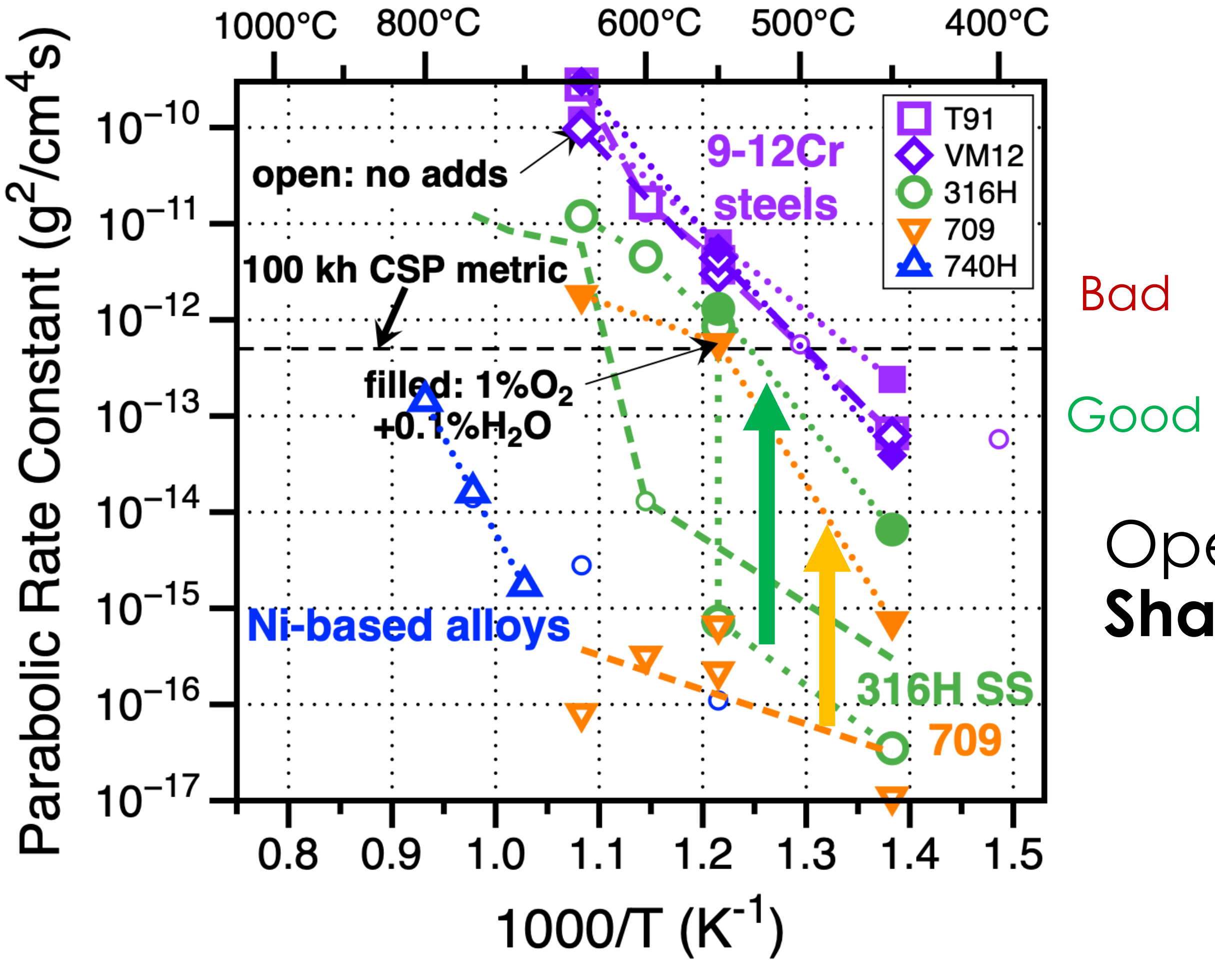
~5 cm^2 alloy coupons + tensile specimens

- Four primary alloys in test matrix
  - T91: Fe-9Cr-1Mo, creep strength enhanced steel
  - VM12: Fe~12Cr-Co-W
  - 316H: conventional stainless steel
  - 709: advanced austenitic, 20Cr-25Ni+Nb
- 10 specimens of each alloy
- With and without impurities (open vs. closed)

Alloy	UNS	Cr	Ni	Mn	Si	C	N	Other
Gr.91	K90901	**8.6**	0.3	0.5	0.4	.10	.05	0.9Mo,0.2V
VM12	12CrCoW	**11.5**	0.4	0.4	0.4	.12	.04	1.6W,1.5Co
316H	S31609	**16.3**	**10.0**	0.8	0.5	.04	.04	2.0Mo,0.3Co
NF709	S31025	**20.1**	**25.2**	0.9	0.4	.06	.15	1.5Mo,0.2Nb

Baseline of research grade (RG) CO_2: ≤ 5 ppm H_2O and ≤ 5 ppm O_2

Addition of $1\%O_2+0.1\%H_2O$: accelerates SS mass gains!



Performance metric from CSP

Open symbol: RG sCO_2

Shaded: RG sCO_2 + $1\%O_2$ + $0.1\%H_2O$

- no change for Gr91 and VM12
- higher rates for 316H and 709

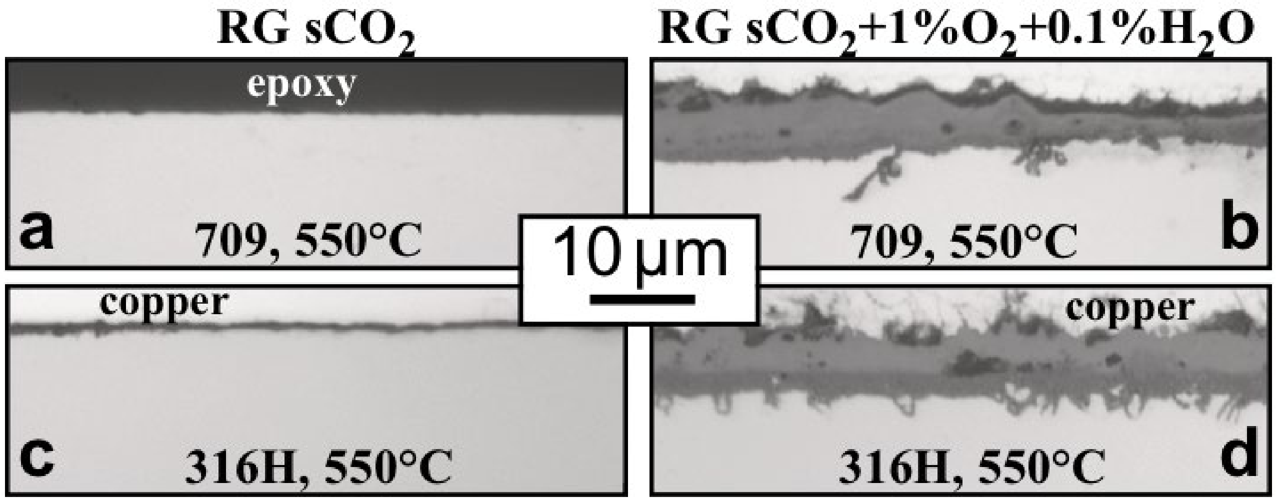
Based on CSP (solar) metric: all limited to <550°C with impurities

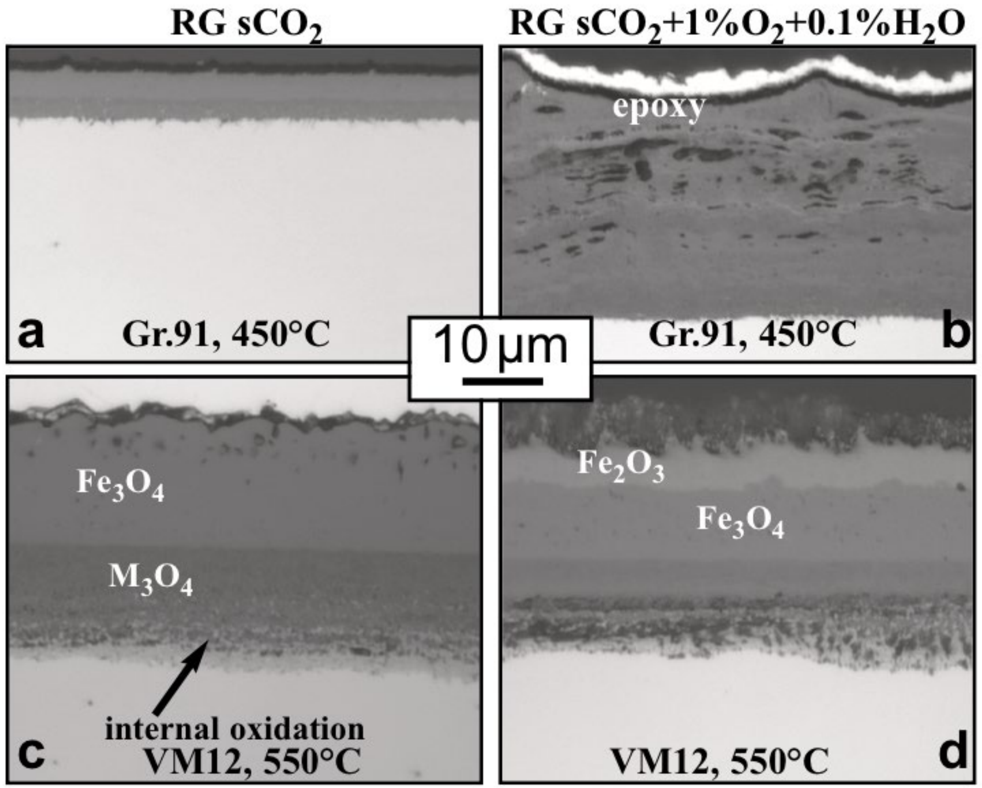
Rates for 709 (UNS S31025): may not reflect steady state at 1000 h

Similar T91 rates in steam. Are we really concerned about rates?

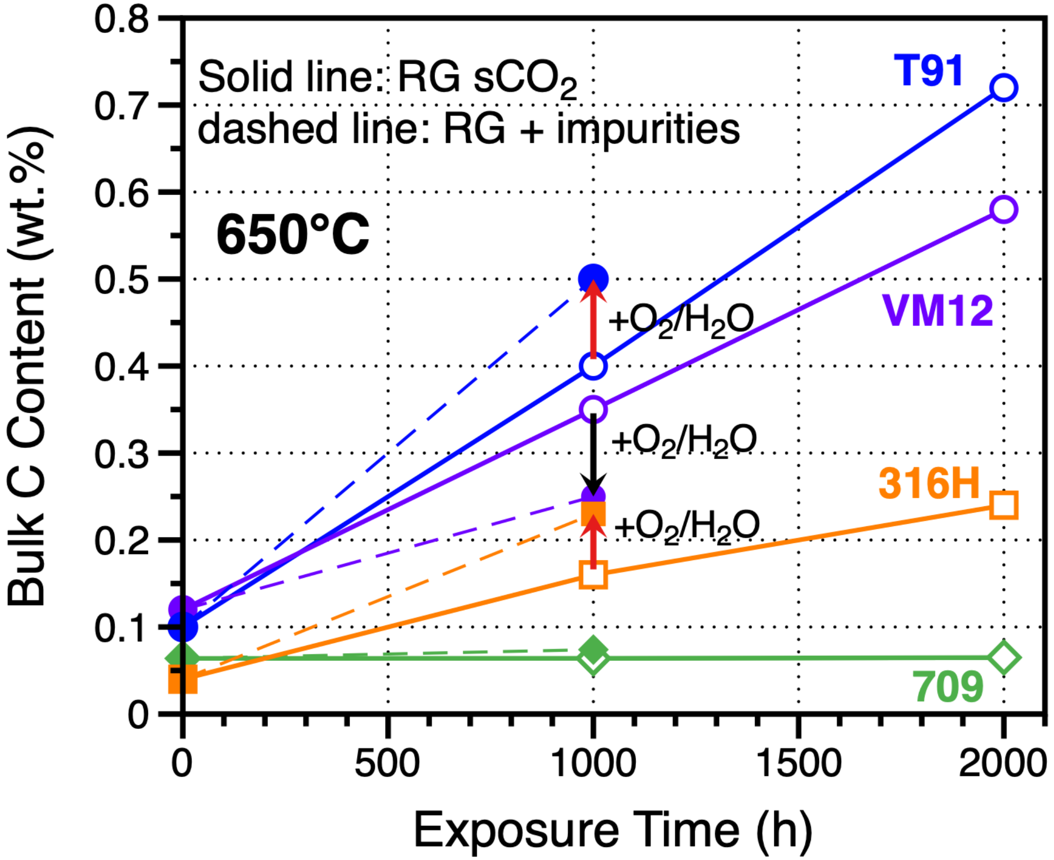
SS: faster attack with O_2/H_2O
FeCr: Fe_2O_3 formation

- Stainless steel (316/709)
  - RG sCO_2 : thin Cr-rich scale
    - Good C barrier
  - Impurities: duplex scale
    - Common with steels
    - Now is C ingress possible?
- 9-12Cr steels
  - 450°C: increased T91 attack
  - 550°-650°C
    - Clear duplex scale in both cases
    - With 1%O_2 form Fe_2O_3 layer
  - VM12: no benefit of higher Cr content after 1,000 h





Bulk C measurements: Fe-rich oxides allow C ingress



RG sCO_2: No impurities open symbols

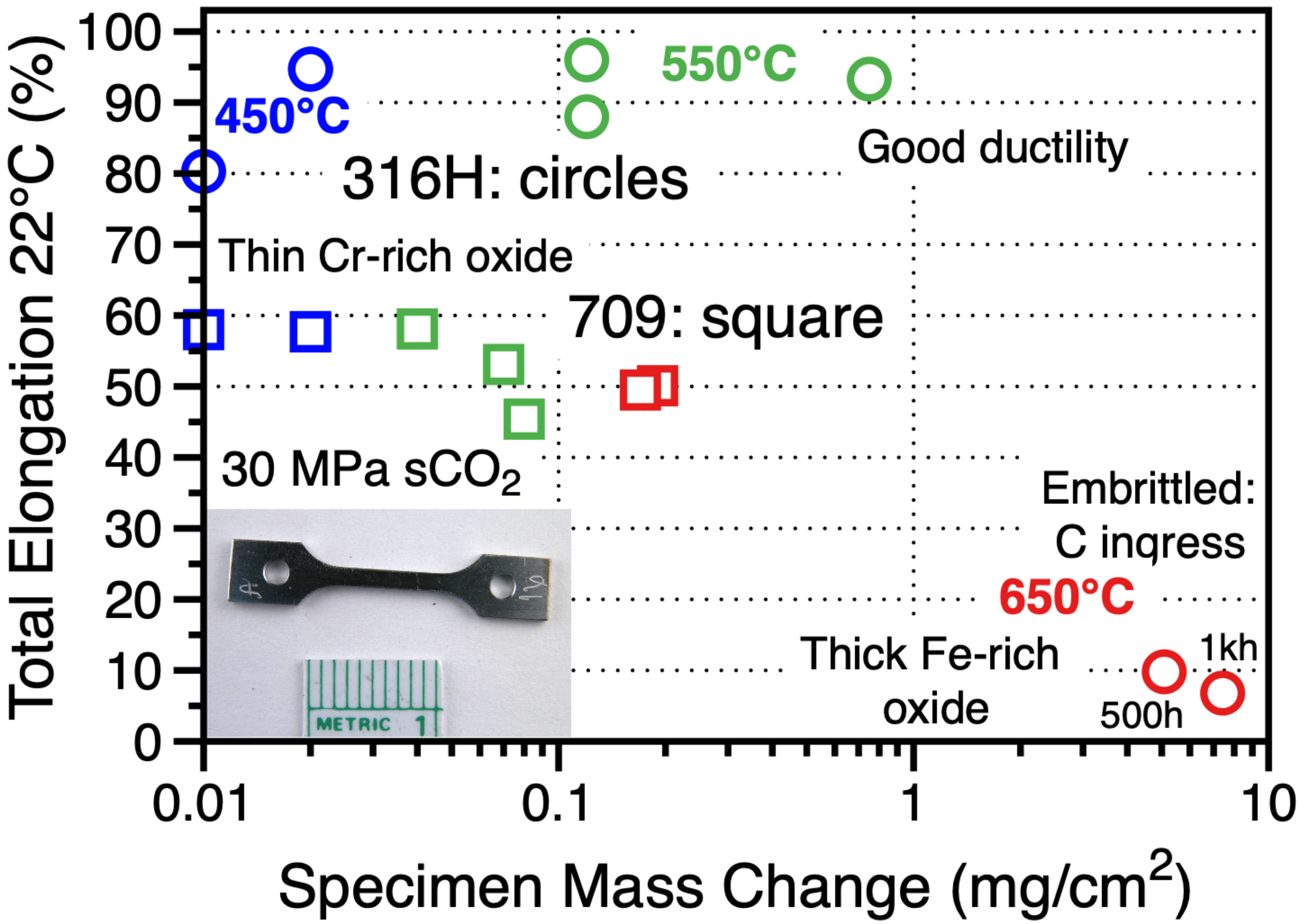
O_2/H_2O add: closed symbols

Relatively unaffected

- Measurements by combustion analysis, increasing with time
- Focus on 650°C results, less ingress at 600° and 550°C
- sCO_2 impurities tend to increase C ingress (but not all cases)

RG sCO_2: combination of mass change & 25°C ductility to illustrate issue with 316H at 650°C (709 not affected)

High ductility & low mass gain



500h & 1000 h measurements for each stainless steel

Low ductility & high mass gain

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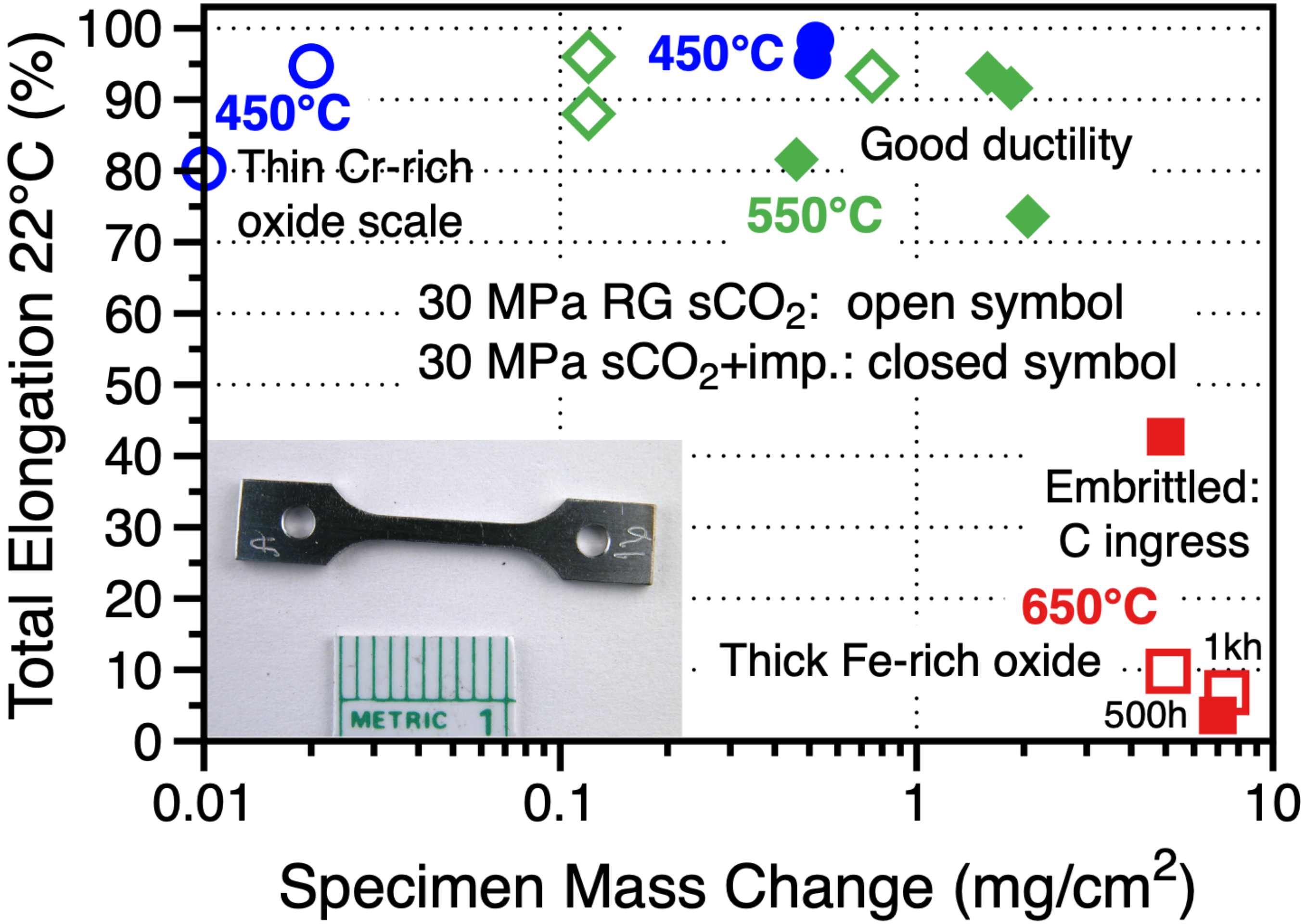
316H: not much change in 25°C ductility with impurities More mass gain, similar embrittlement at 650°C

High ductility & low mass gain

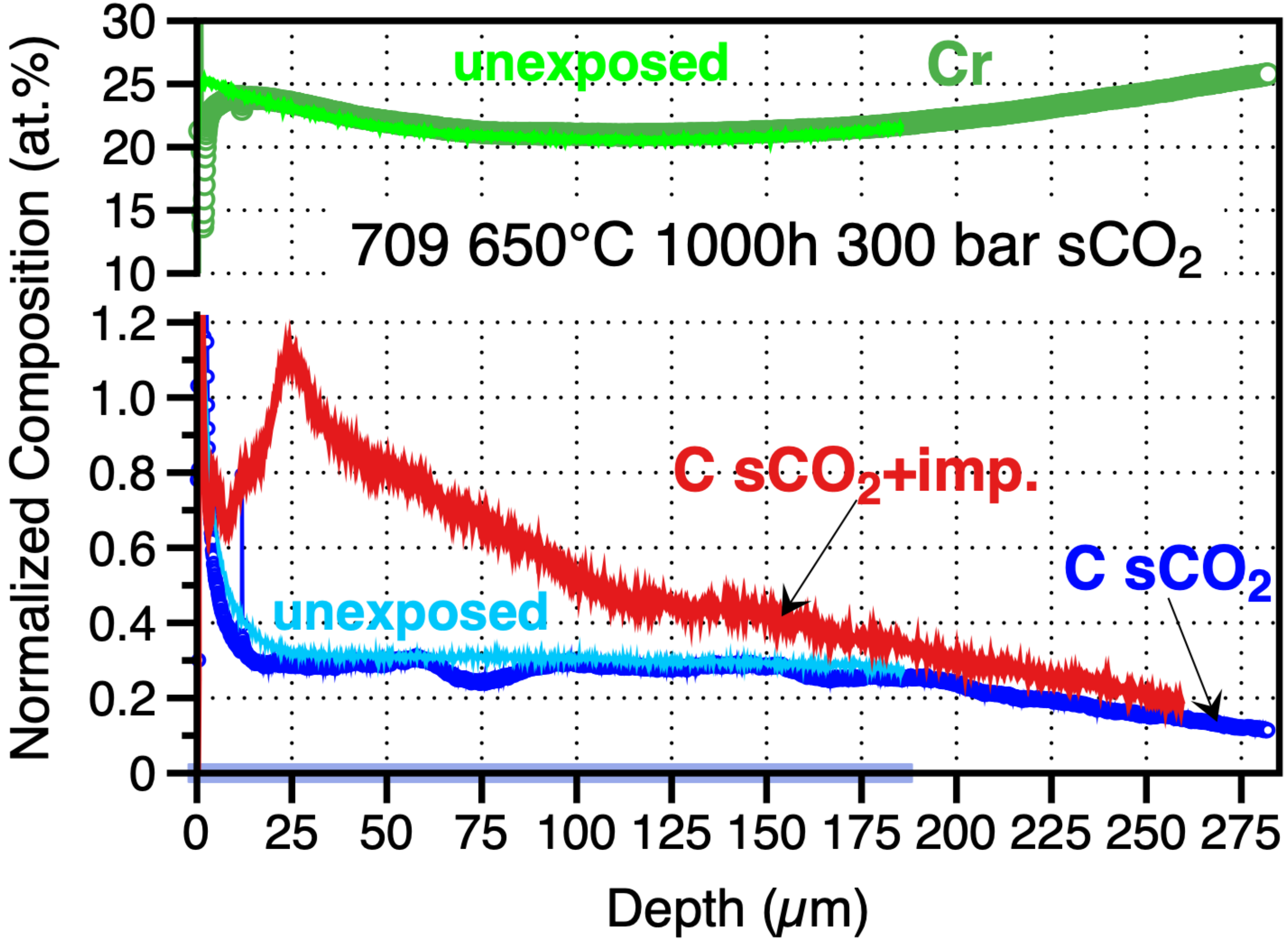


500h & 1000 h measurements for 316H

Low ductility & high mass gain

GDOES of 709 specimens after 1000 h

GDOES: Glow discharge optical emission spectroscopy

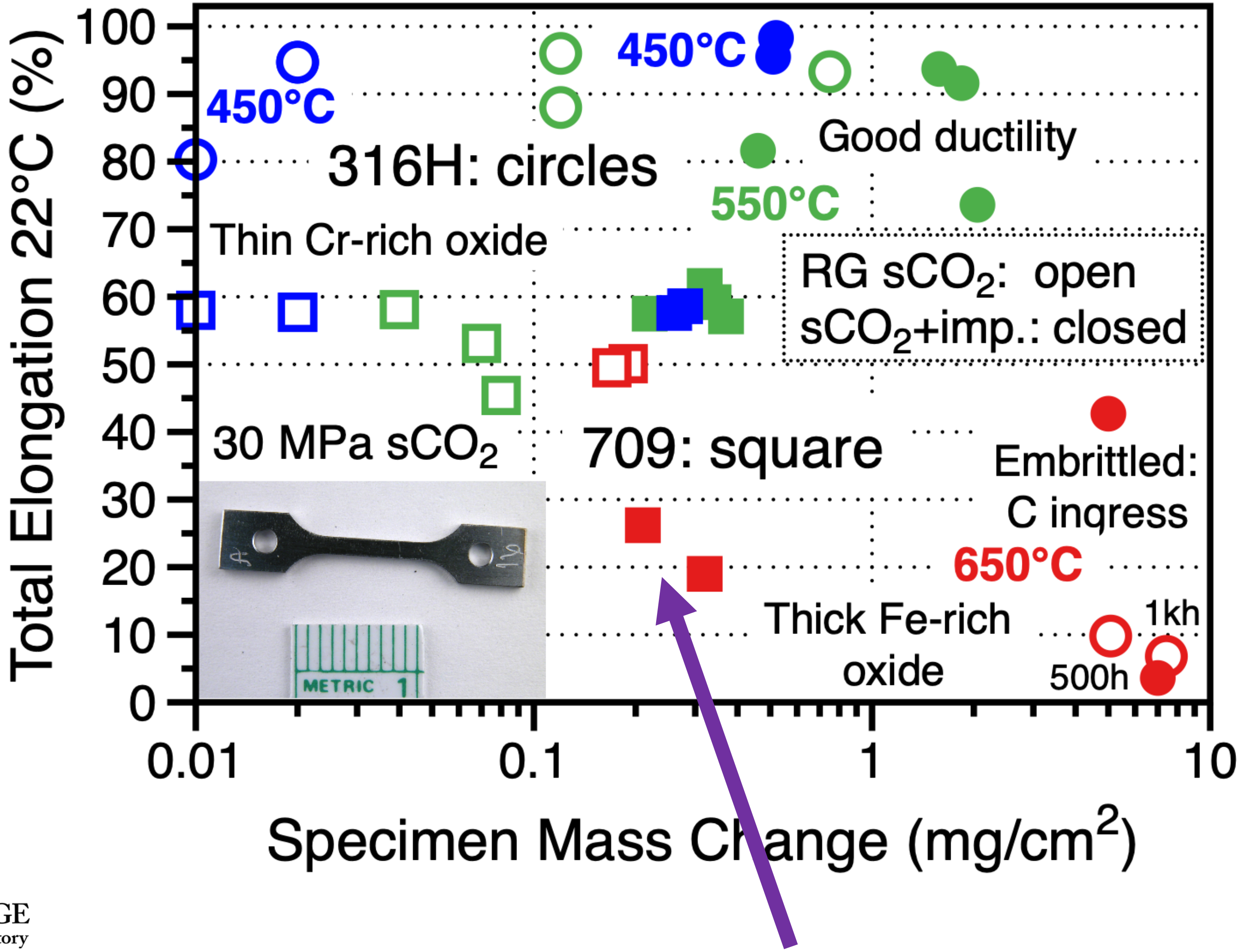


650°C: more C ingress with impurities

GDOES: signal normalized based on starting measured composition

709 showed drop in 25°C ductility at 650°C with the addition of O_2/H_2O impurities

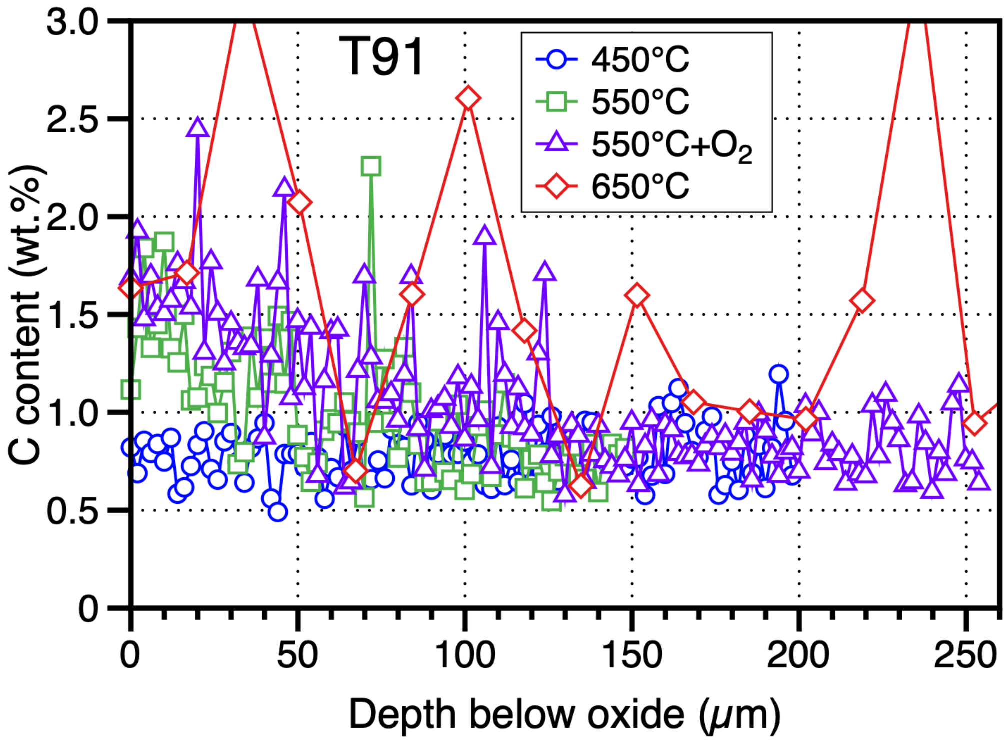
High ductility & low mass gain

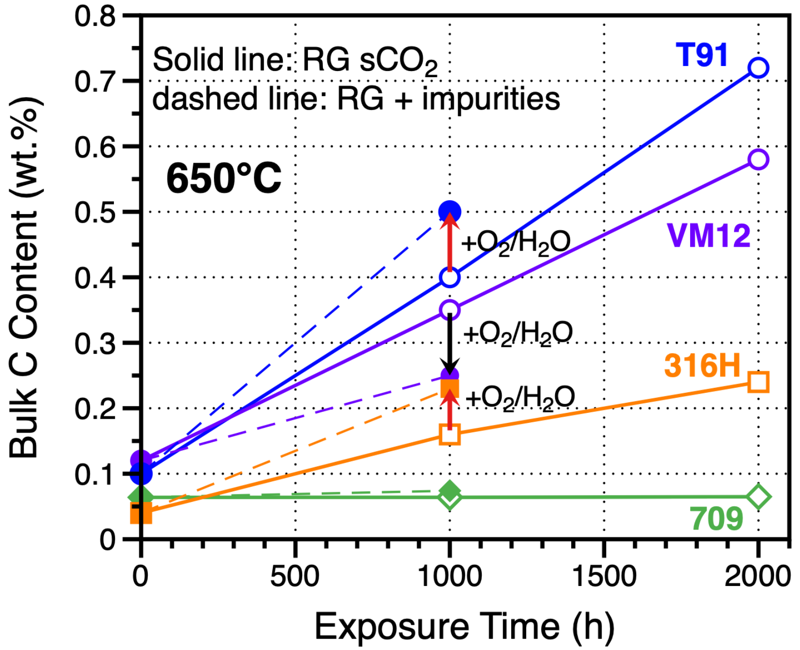


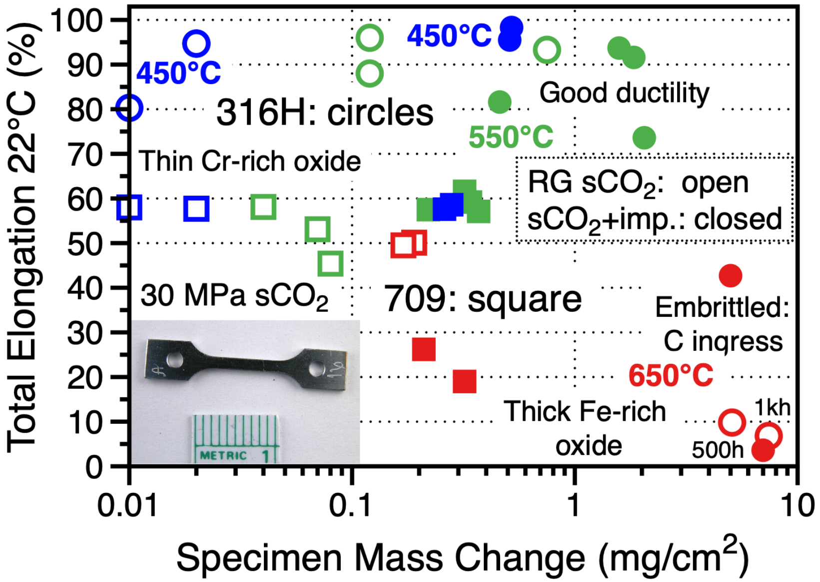
500h & 1000 h measurements for each stainless steel

Low ductility & high mass gain

Observed massive internal carburization of steels

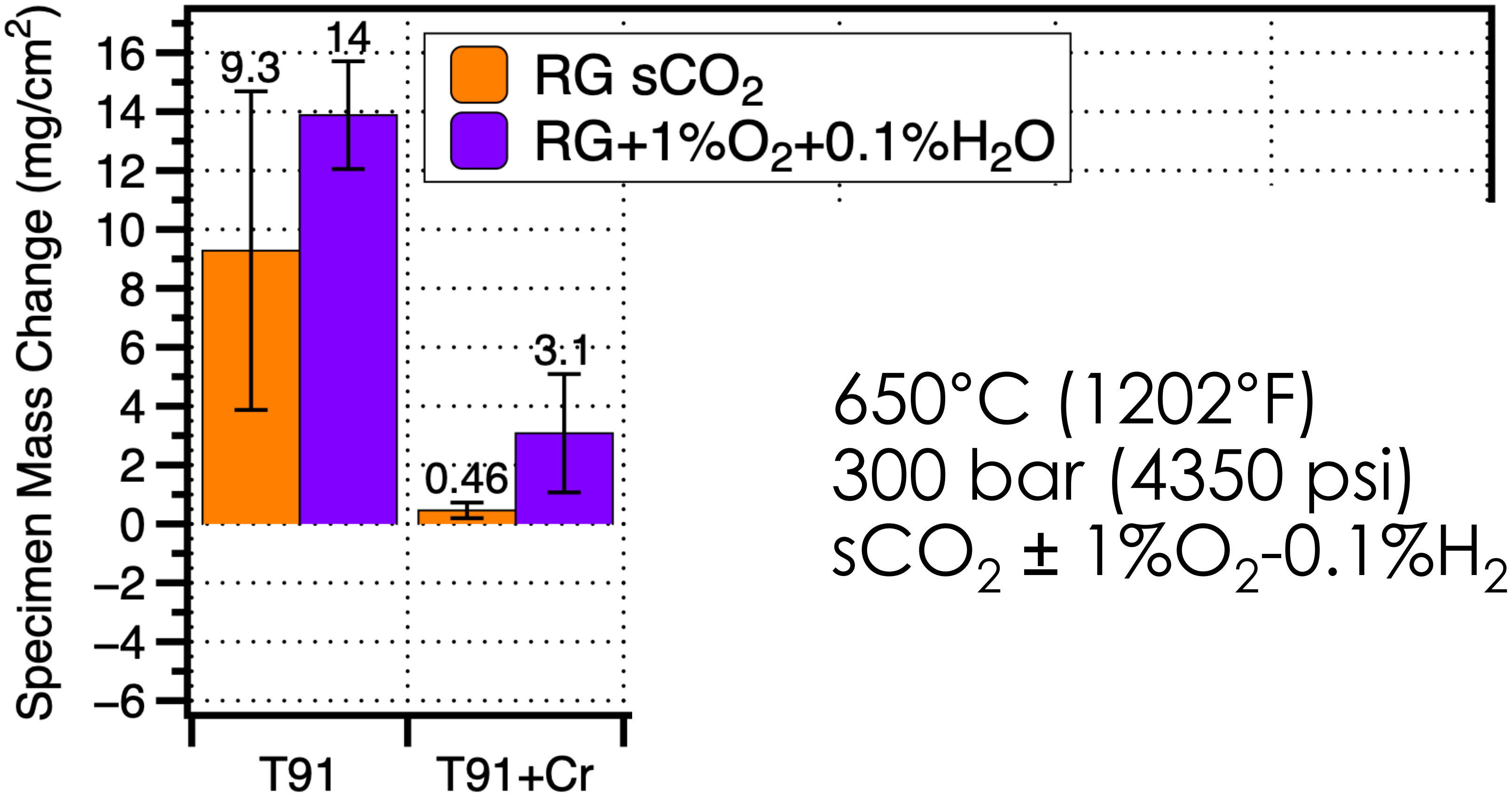






- T91: Fe-9Cr-1Mo
- 316H: Fe-16Cr-10Ni
- Massive C uptake at 650°C for both alloys
  - Reflected in bulk C measurements
  - And loss of room temperature ductility
- **Can coatings help inhibit C uptake?**

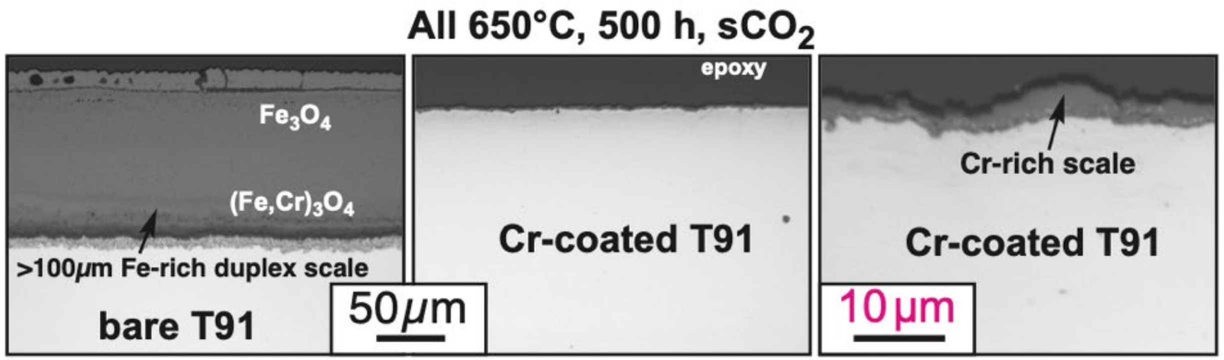
Initial sCO_2 testing at 650°C ± O_2/H_2O with pack Cr coating

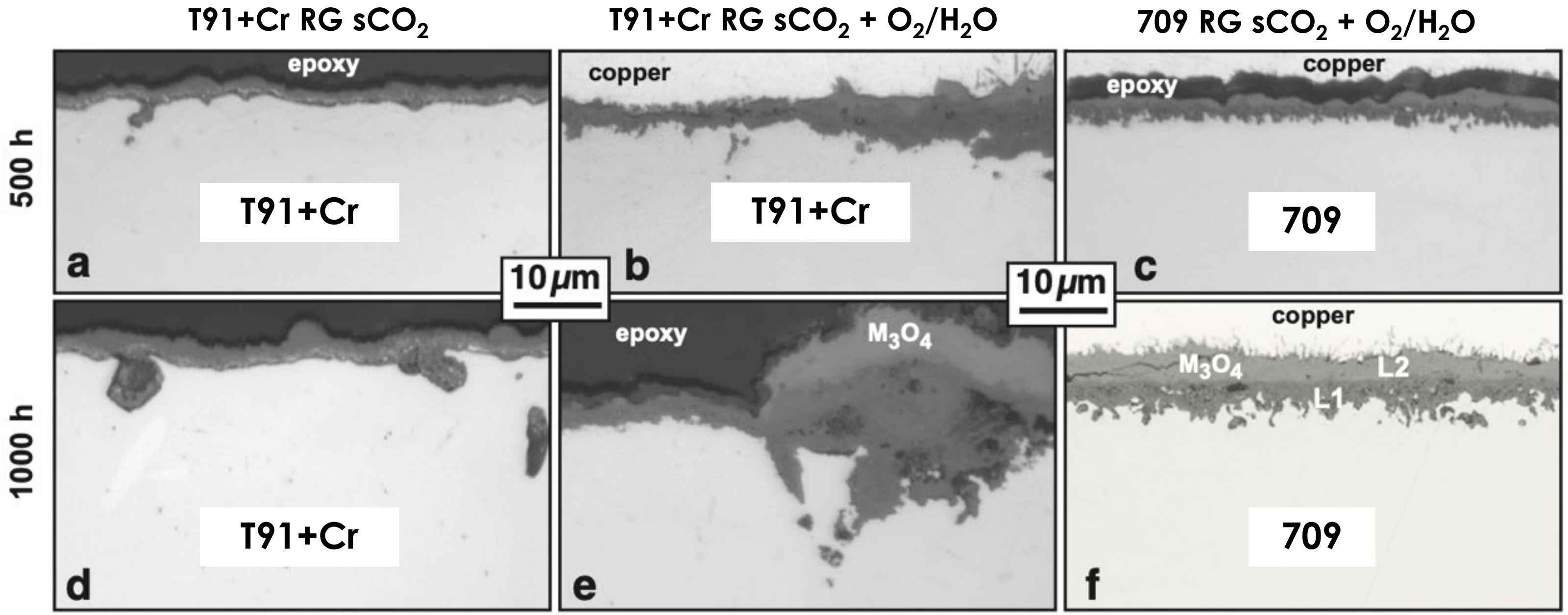


650°C (1202°F)
300 bar (4350 psi)
sCO_2 ± 1%O_2-0.1%H_2O

- Pack Cr coating by industrial partner: no details available
- High mass gains for uncoated 9Cr steel: variable due to spallation
- Low mass gain in RG sCO_2 but mass gain increased with impurities

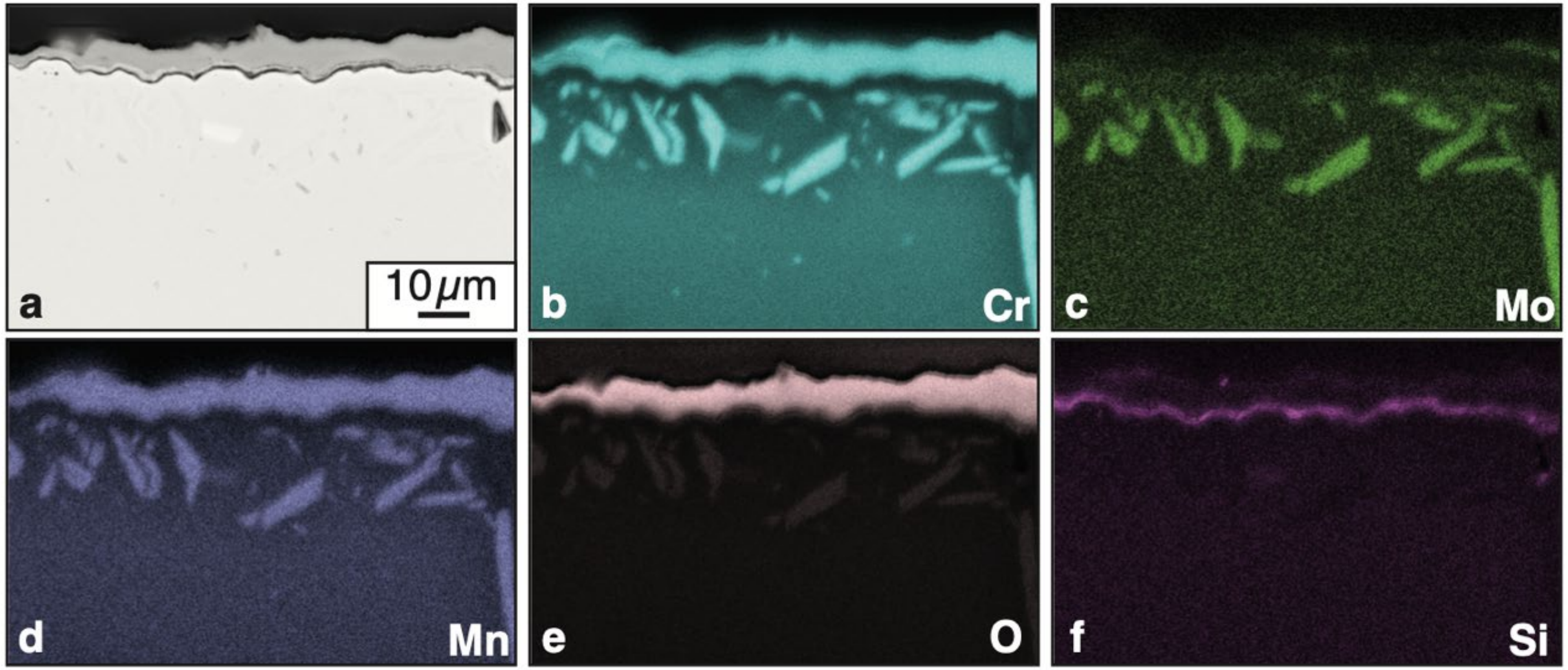
Cr coating on T91 more effective in RG sCO_2

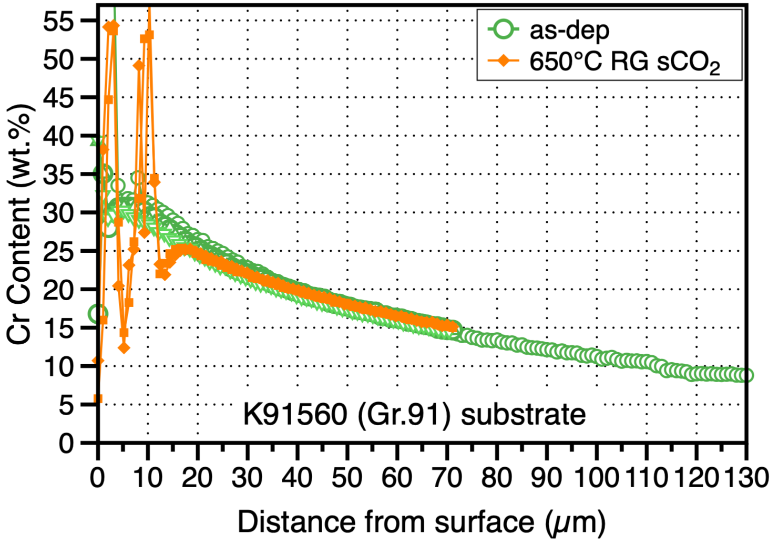




- Thin scale formed in RG sCO_2 : not thick Fe-rich oxide
- Oxide nodules formed with O_2/H_2O additions

Precipitates in coating after 1,000 h at 650°C in RG sCO_2

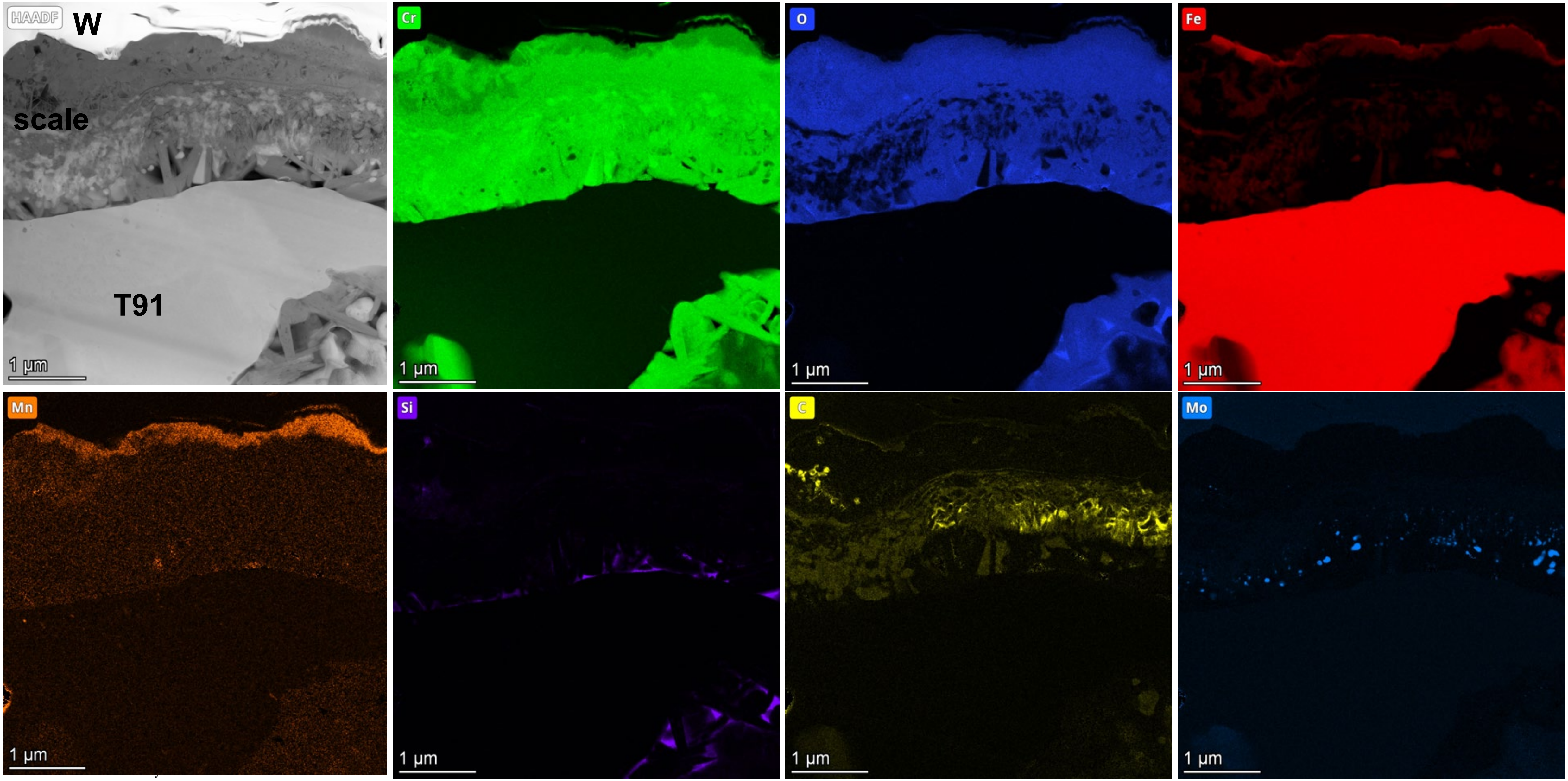




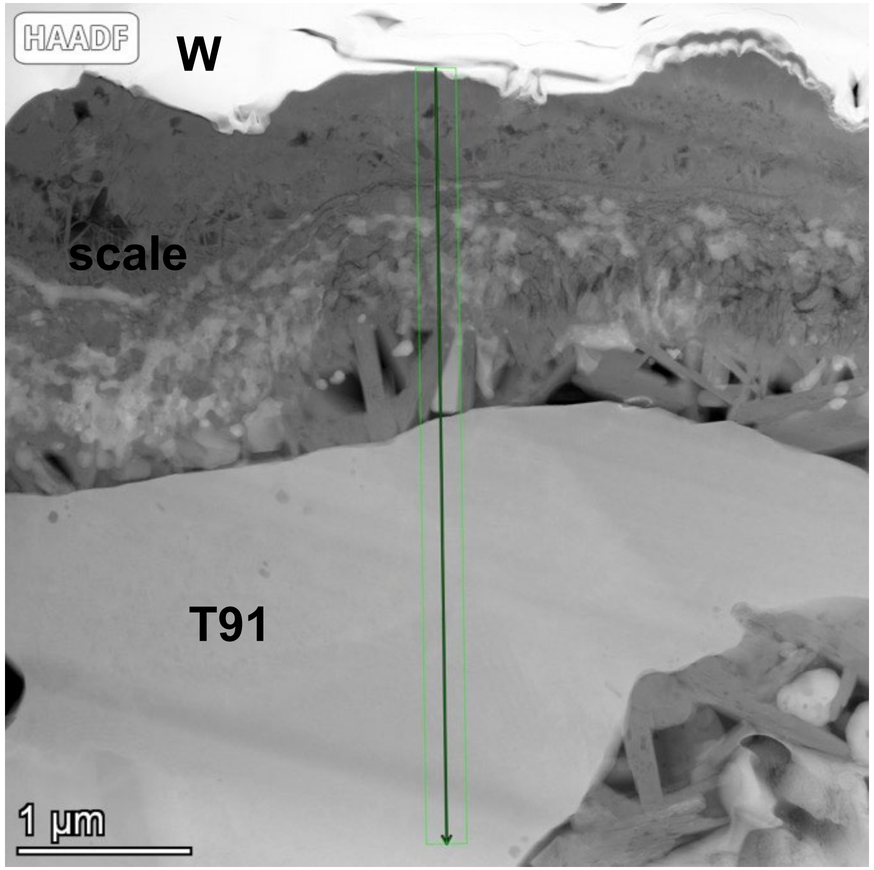
SEM/EDS Cr profile in T91

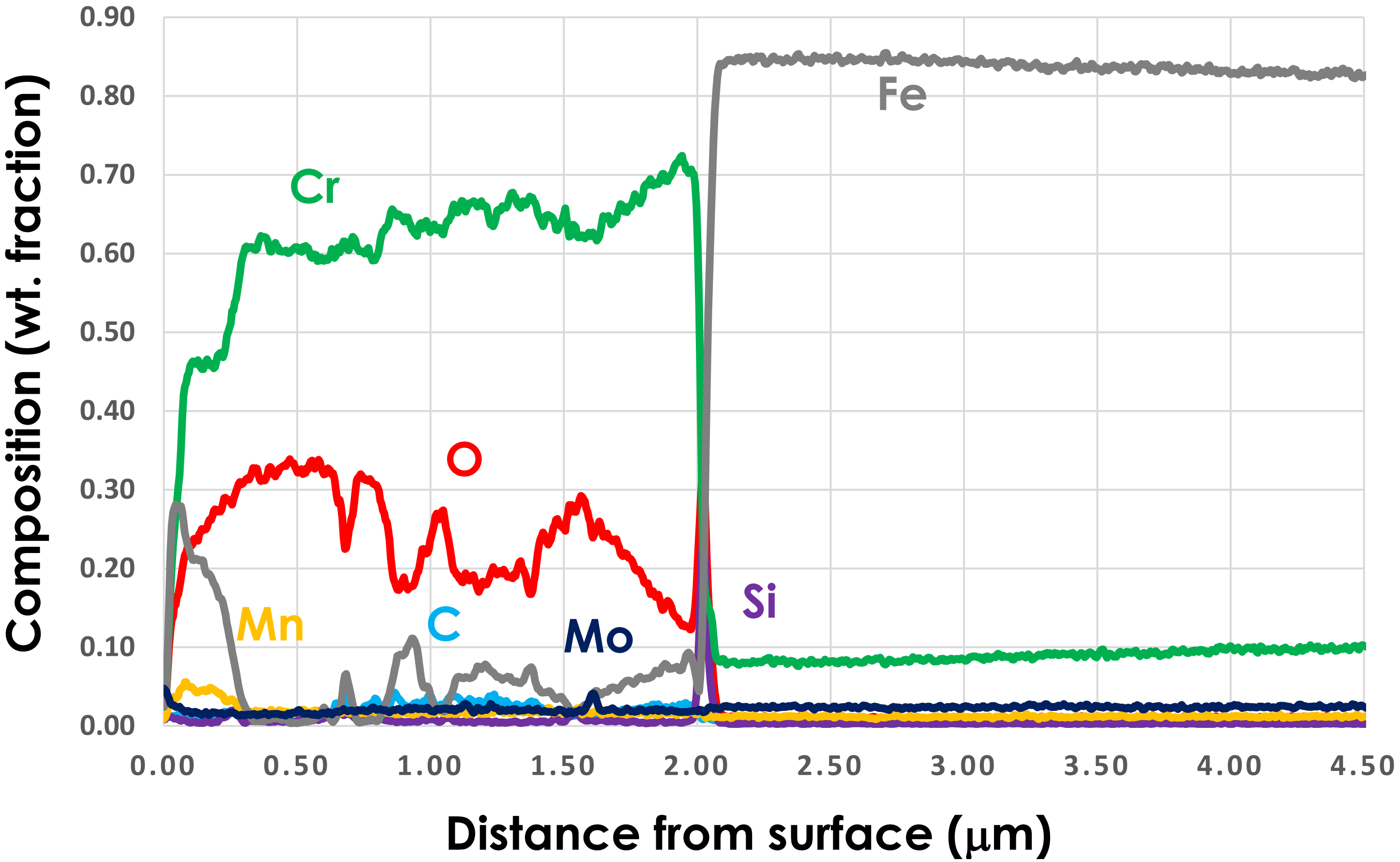
- Coating ~110 μm thick
- Confirmed carbide precipitates by EPMA

STEM/EDS of T91+Cr 1kh/650°C sCO_2: C in Cr_2O_3



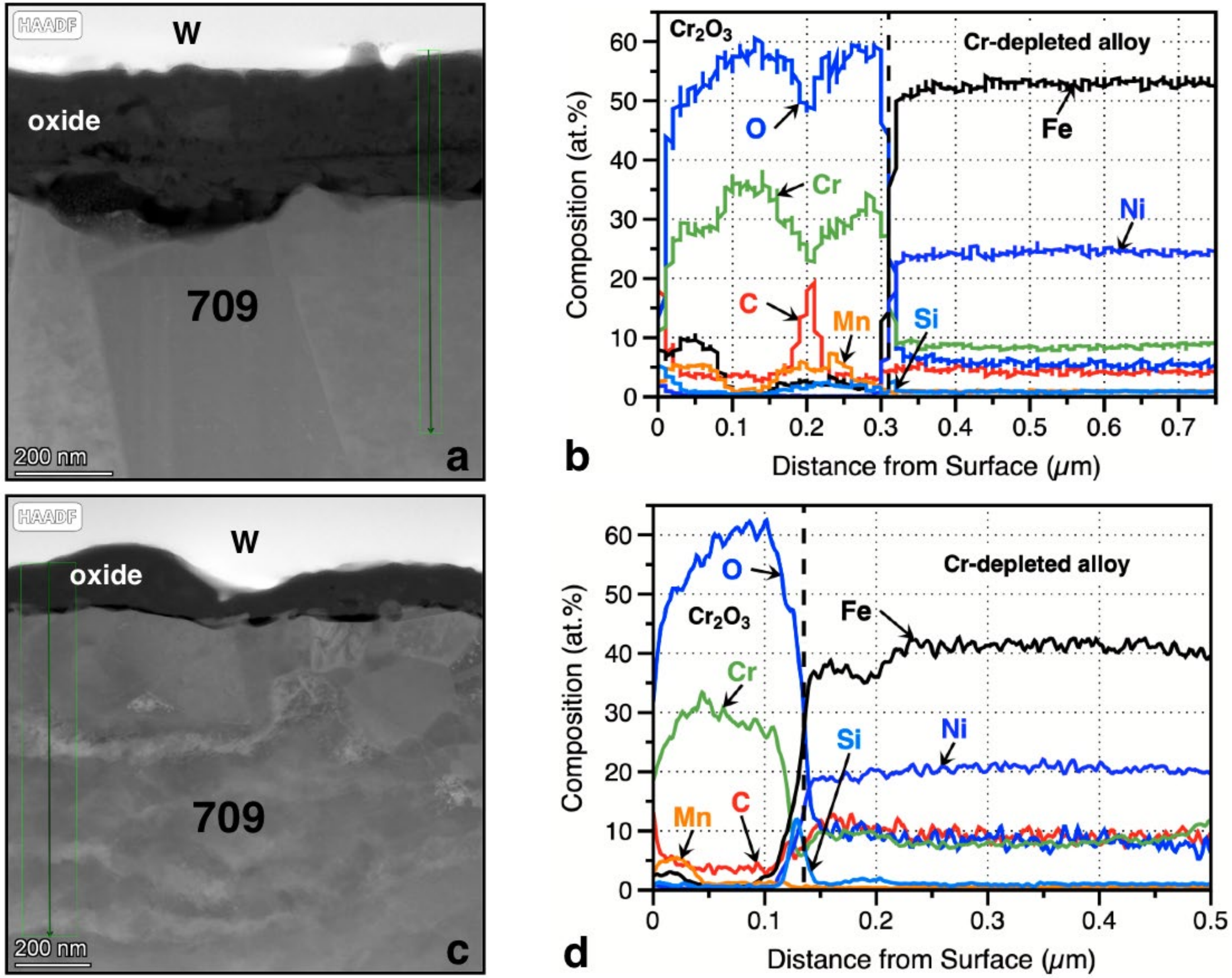
STEM/EDS of T91+Cr 1kh/650°C sCO_2: C and Mo in Cr_2O_3





- Unusual area with oxidized precipitate under scale
  - <10%Cr left in coating at interface
- C and Mo within inner scale
- Fe and Mn in outer scale

709 500h: thicker complex scale at 300 bar, not 1 bar CO_2

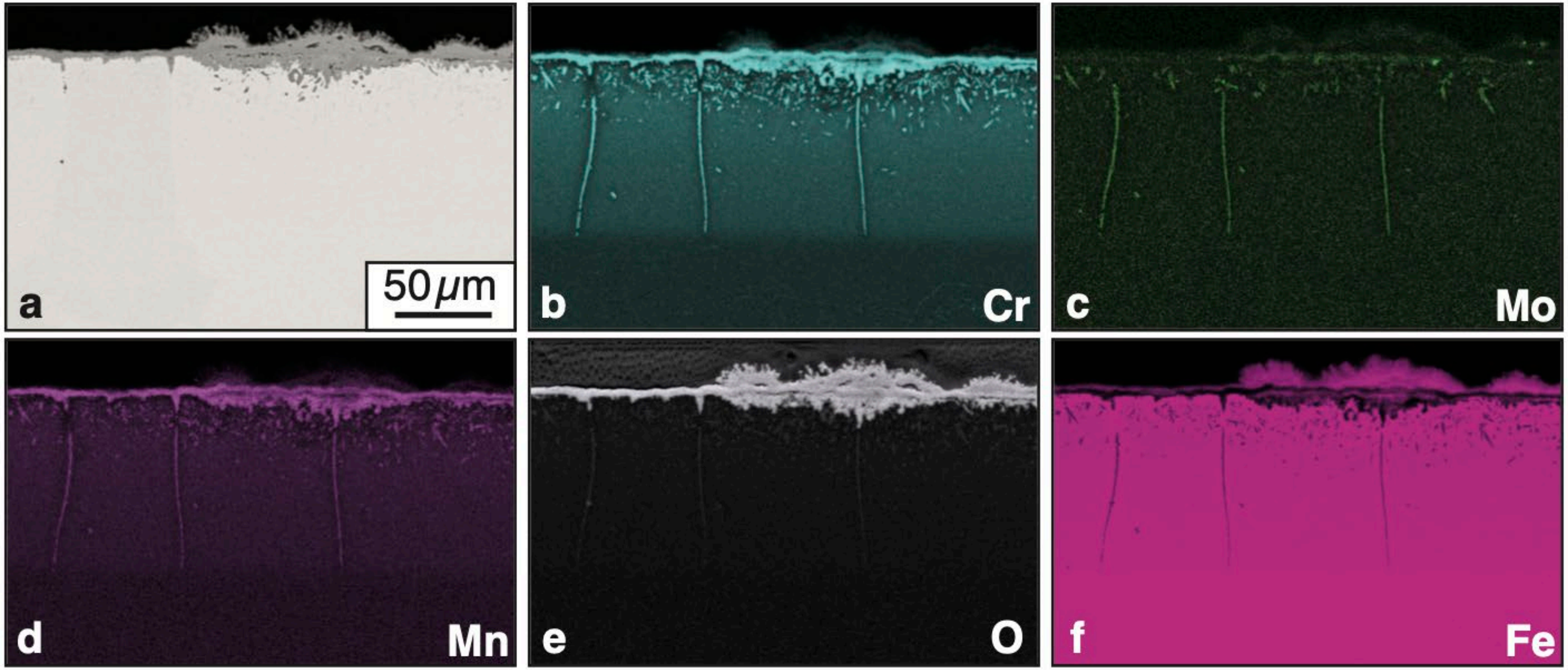


300 bar sCO_2

1 bar CO_2

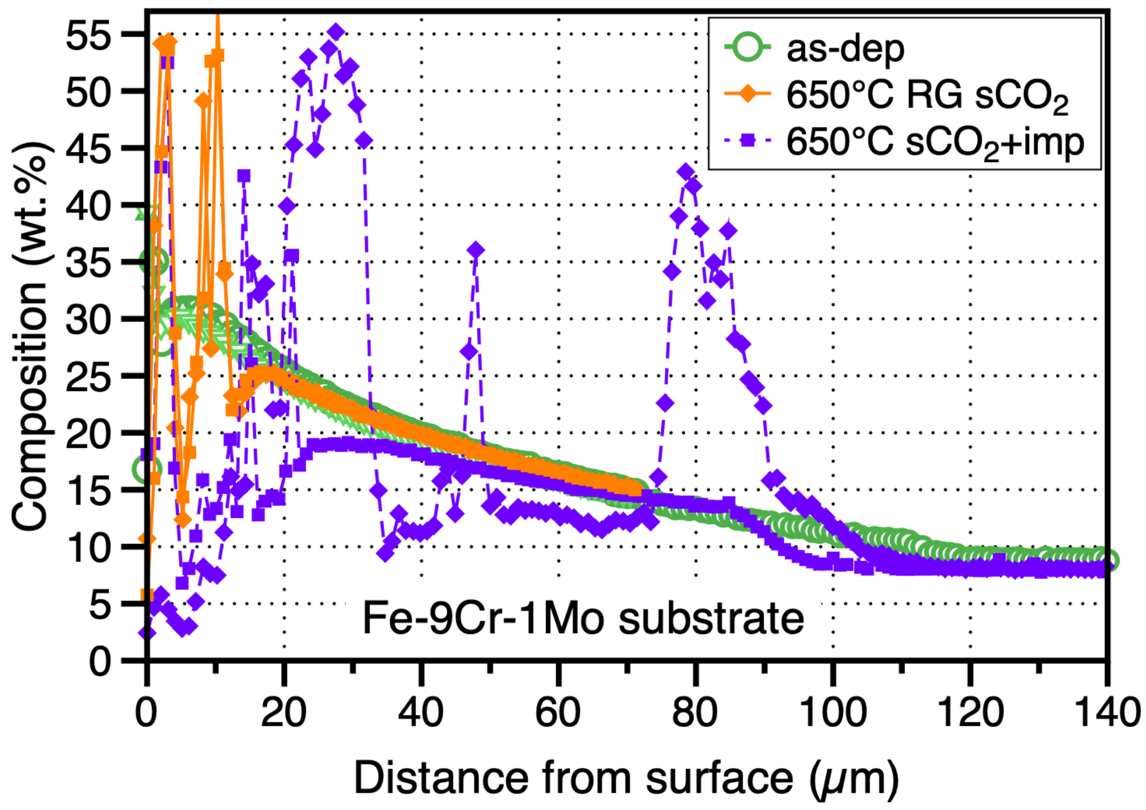
Heating to 650°C in sCO_2 may be an issue

T91+Cr, sCO_2 w/O_2+H_2O: forming Fe-rich oxide nodules



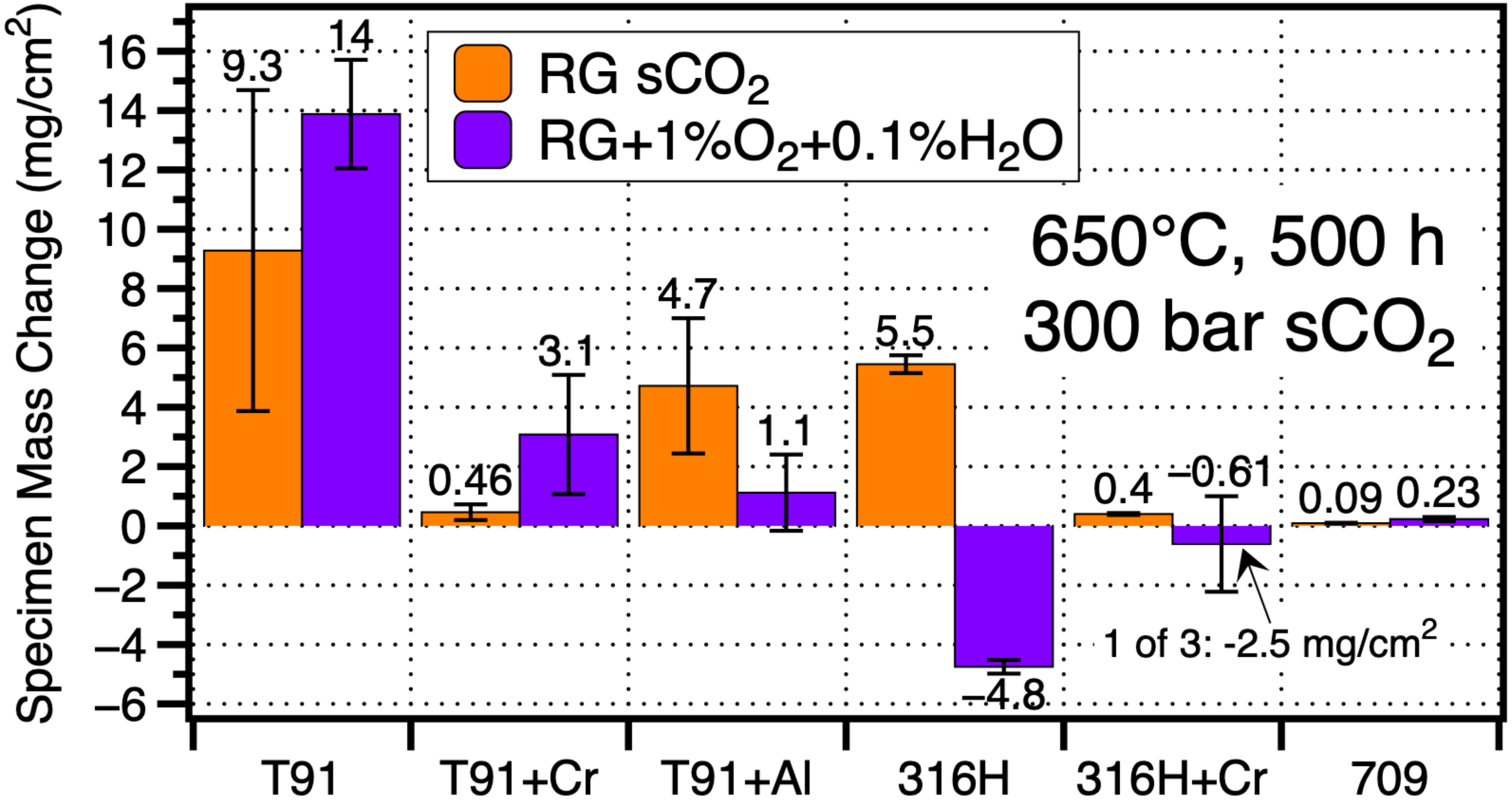
- Unable to form protective Cr-rich oxide with 1%O_2+0.1%H_2O
- Cr-rich precipitates also formed beneath scale after 1000 h

sCO_2 with impurities: significant Cr consumption



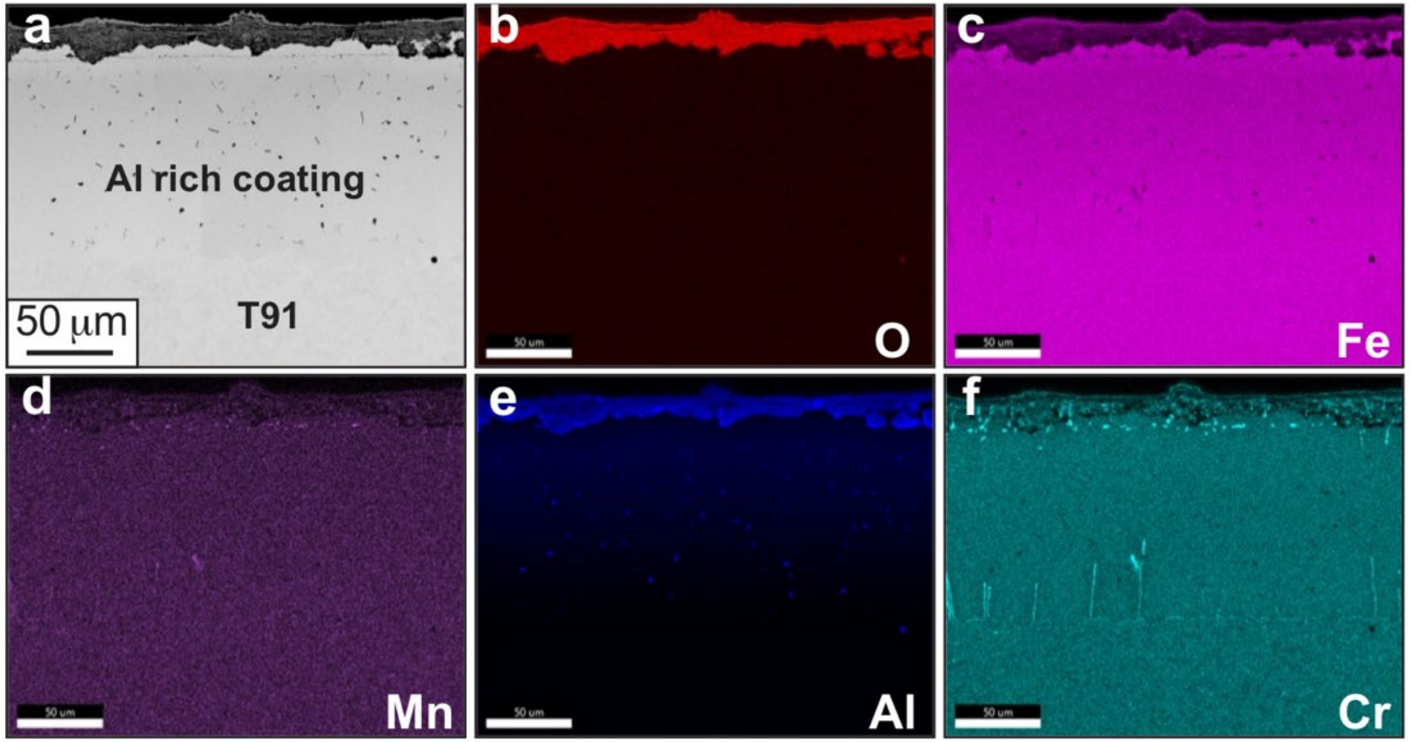
- 1000 h/650°C: higher Cr consumption with impurities
- 650°C: temperature too high for ~110 μm thick Cr pack coating

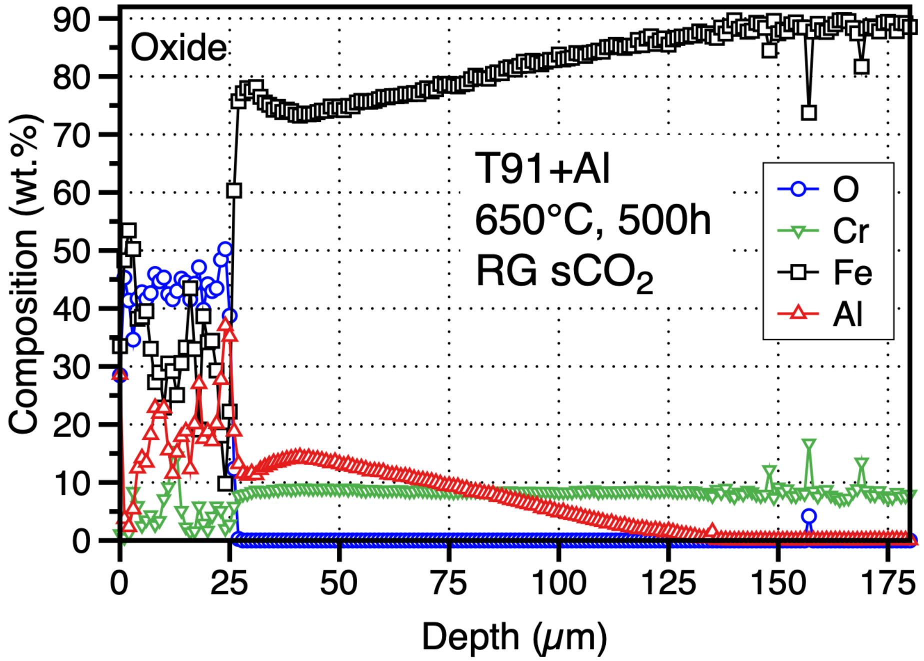
Second batch of pack coatings tested at 650°C



- Al at TTU: 30min at 1050°C, 20wt.%Cr-10%Al+2%NH_4Cl+78%Al_2O_3
- Pack aluminizing T91 did not work as well as Cr in RG sCO_2
- Pack chromizing 316H effective in RG sCO_2 at 650°C

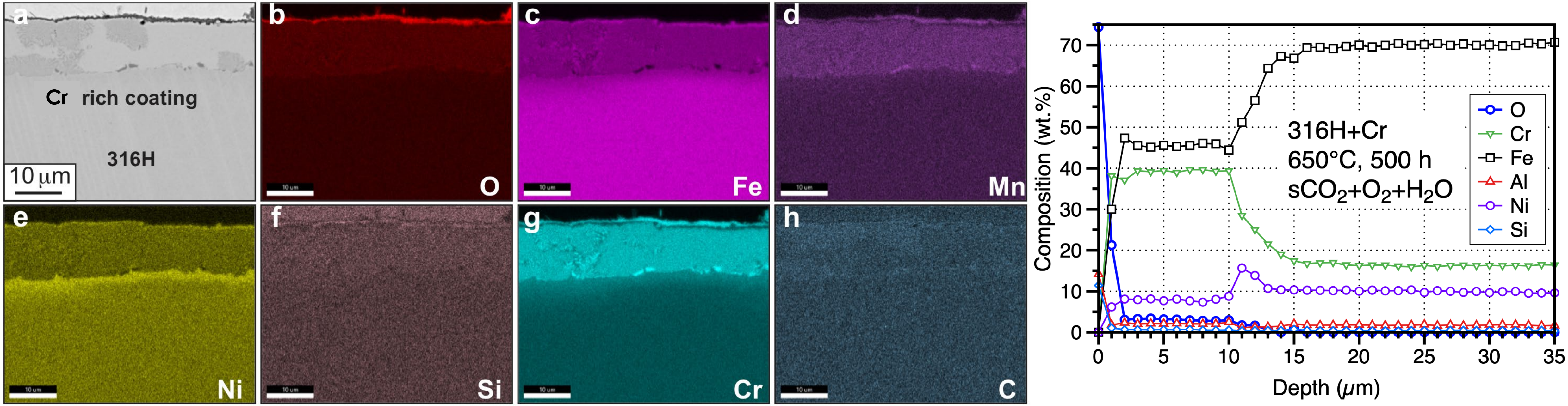
T91: Pack aluminide formed mixed Al-Fe oxide at 650°C





- Targeted low ~20wt%Al coating with good CTE mismatch with T91
- High mass gain due to mixed Fe-Al oxide formation
  - 650°C is low temperature for selective Al oxidation
  - High Al coating may perform better

Chromized 316H: thin Cr-rich scale formed + precipitates

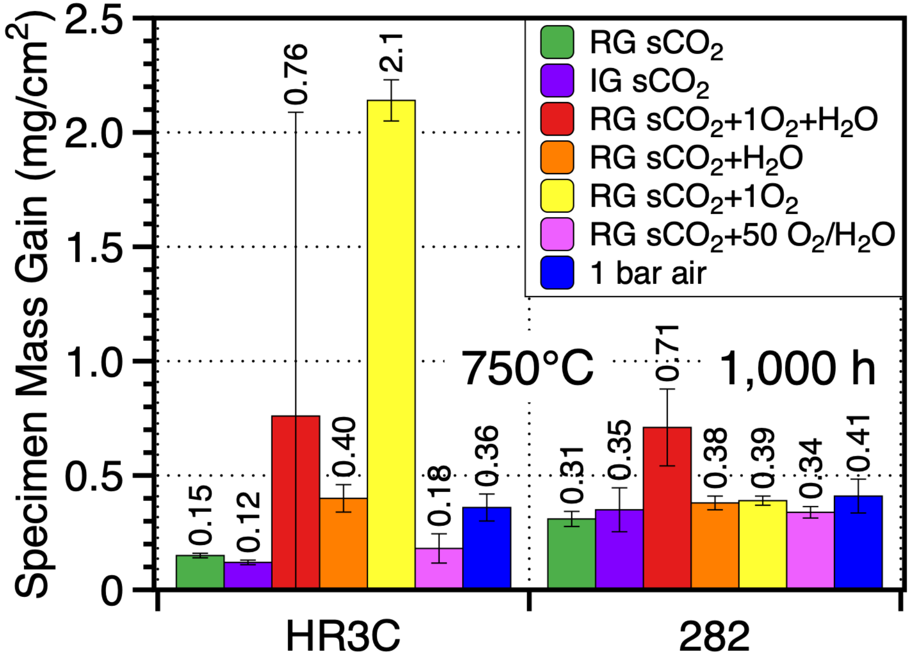


- Thinner coating formed on FCC 316H substrate
  - Again, coating made by company, no details on process
- Beneficial effect in RG sCO_2 at 650°C after 1,000 h
  - But Cr-rich precipitates are concerning for small Cr reservoir in coating

Summary: sCO_2 is a challenging environment

- All steels degrading at 550°-650°C in sCO_2
  - Increased attack when O_2 and H_2O impurities in sCO_2
  - Increased C uptake for Fe-rich oxides (vs. Cr-rich oxides)
    - Observed decrease in 25°C ductility for 316H in sCO_2 and 709 with impurities
- Opportunity for coatings?
  - Pack Cr and Al coatings evaluated on T91 and 316H
    - Processing (coating thickness + heat treatment) needs to be optimized
  - Cr-rich pack coating beneficial at 650°C
    - Thicker coating tested on T91 compared to 316H
    - Reduced mass gain in sCO_2 but internal carbides observed
    - With impurities at 650°C: significant Cr consumption after only 1000 h
  - Pack aluminized T91 (~20 wt.% peak Al)
    - Not forming a thin Al-rich scale on surface after 500 h at 650°C
- Longer exposures needed at lower temperatures (550°C)

Thank you!



RG sCO_2+1%O_2+0.25%H_2O or +0.25%H_2O or +1%O_2

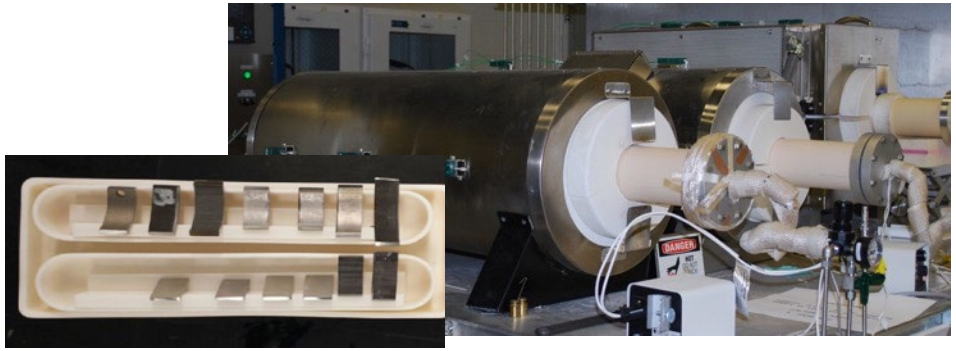
sCO_2 compatibility focused on steels at 450°-650°C

Autoclave: 300 bar sCO_2
500-h cycles

Correct temperature and pressure

4-5 cm^2 alloy coupons

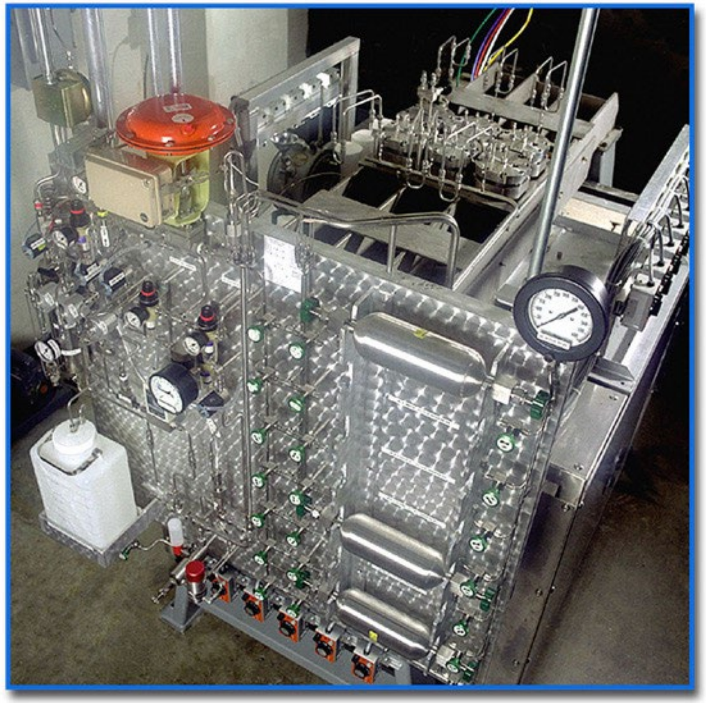
Tube furnace: 1 bar CO_2
500-h cycles



Same cycle frequency as autoclave

Box furnace:
Lab. Air
500-h cycles
(baseline)

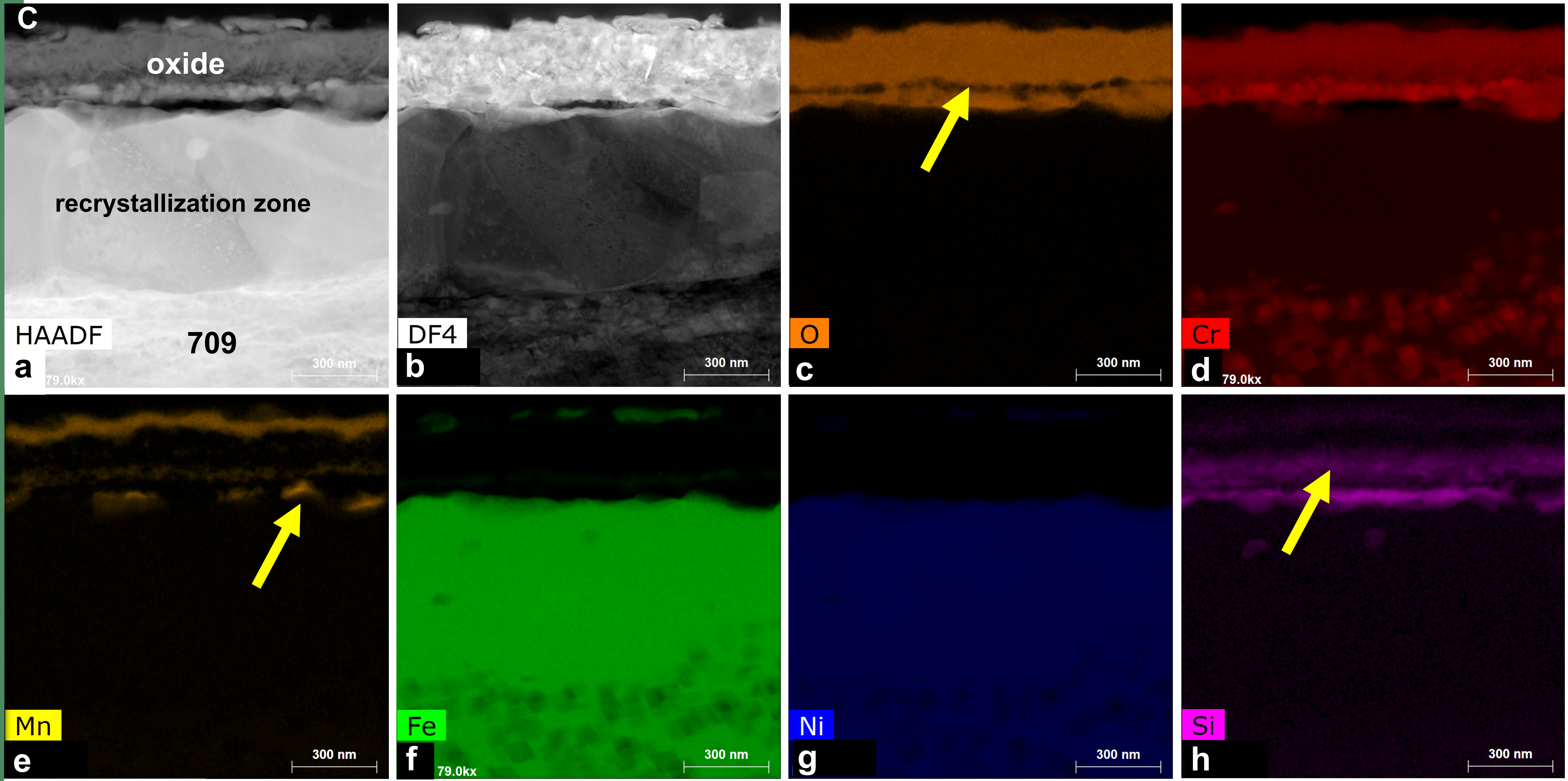
"Keiser" rig:
500-h cycles, 1-43 bar CO_2



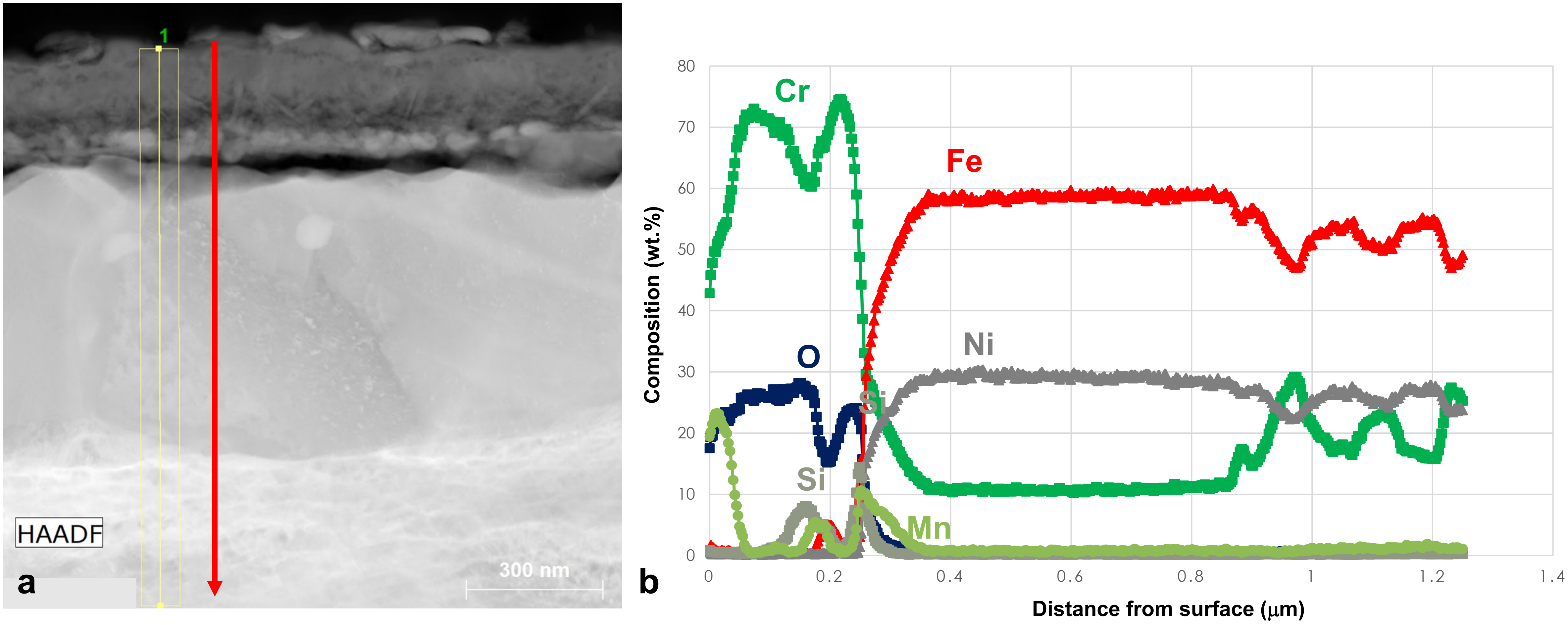
Studies at 800°-1200°C

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

709/sCO_2, 650°C/1000 h: Talos EDS maps of thicker multi-layer scale



709/sCO_2, 650°C/1000 h: Talos EDS line profile of multi-layer scale



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