Effect of Impurities on Supercritical Carbon Dioxide Compatibility (FWP-FEAA144)

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2023 Gordon Research Conference on High Temperature Corrosion

- July 16-21, 2023
- Colby Sawyer College
  - New London, NH
- You're all invited to attend
- For students and early career:
  - Gordon Research Seminar 7/15-16

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Acknowledgments

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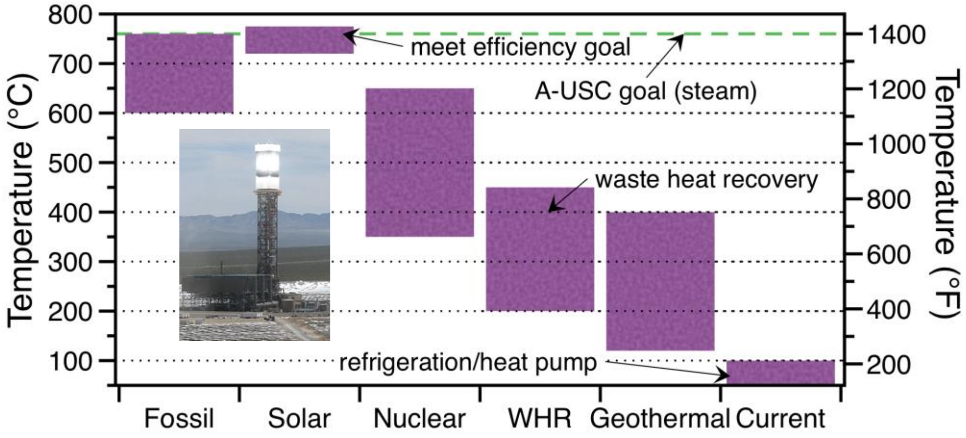
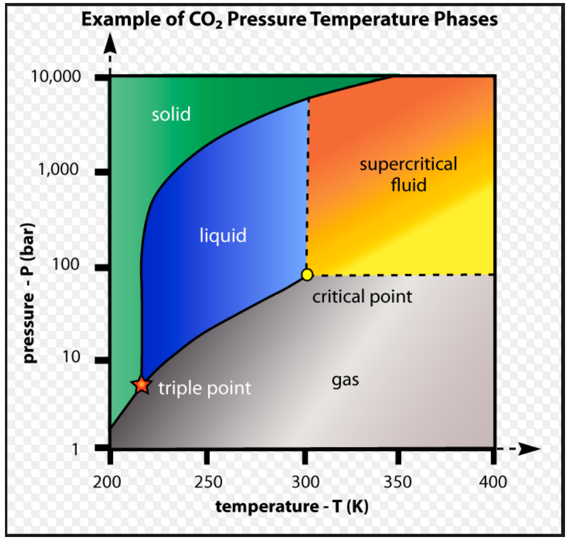
  - Tenaris
  - EPRI
  - Sam Sham, INL (US heat, alloy 709)

sCO_2 cycles are of wide interest: goal is to commercialize!

Supercritical CO_2 applications



sCO_2 has many unique & attractive aspects

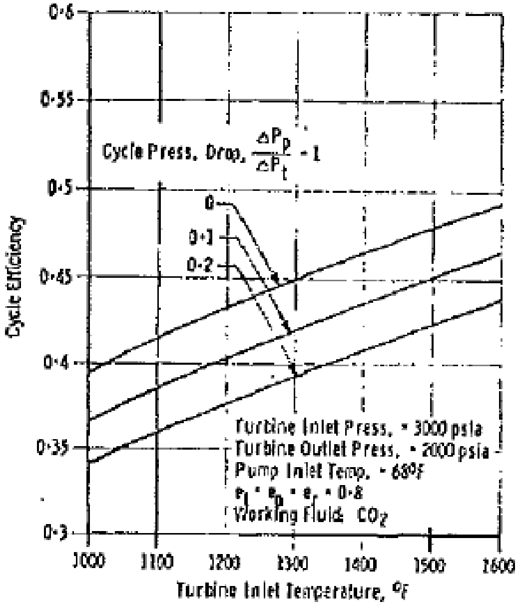


- Low critical point (31°C/7.4 MPa)
- High, liquid-like density
- Flexible, small turbomachinery

Lots of potential

What will help de-risk the technology?

Interest in >700°C for high efficiency



Feher, 1965

50% sCO_2 eff @ >720°C

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Supercritical CO_2 Allam cycle: first clean fossil energy?

NetPower 25MWe test facility (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

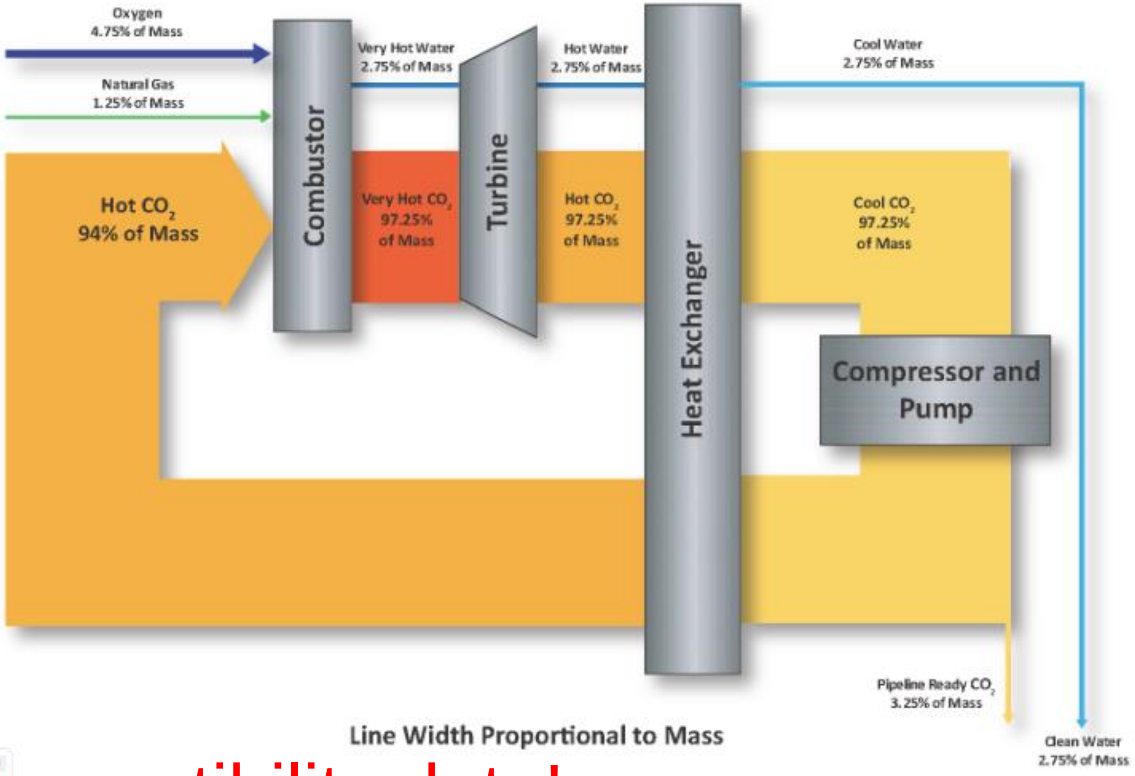
November 2021: plant connected to grid (announced plans for 280MW)

Material challenges:

Combustor: 1150°C (!?!) (now 900°C)

Turbine exit: 750°C/300 bar

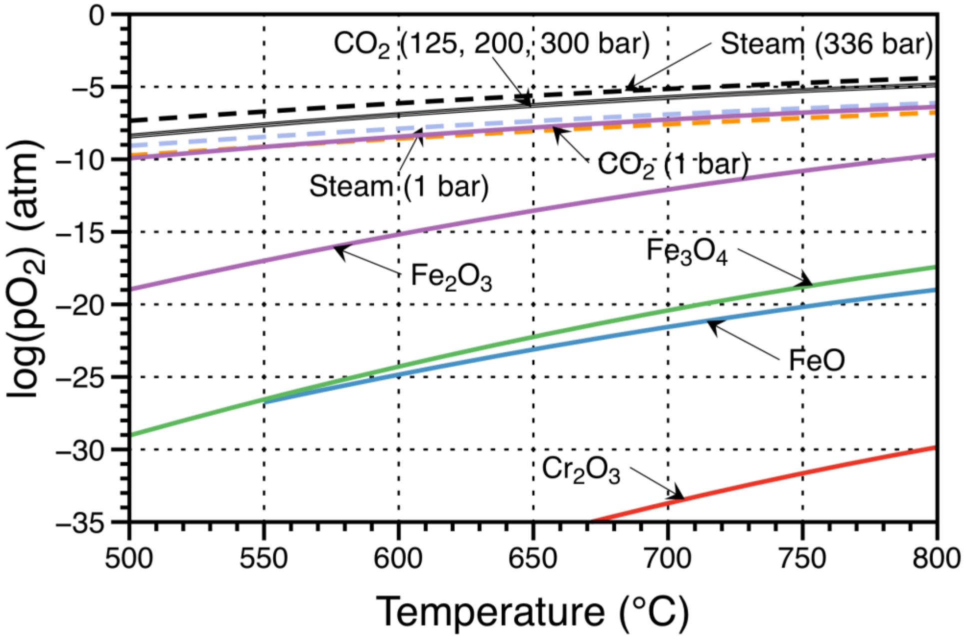
Combustion impurities: O_2, H_2O, SO_2?



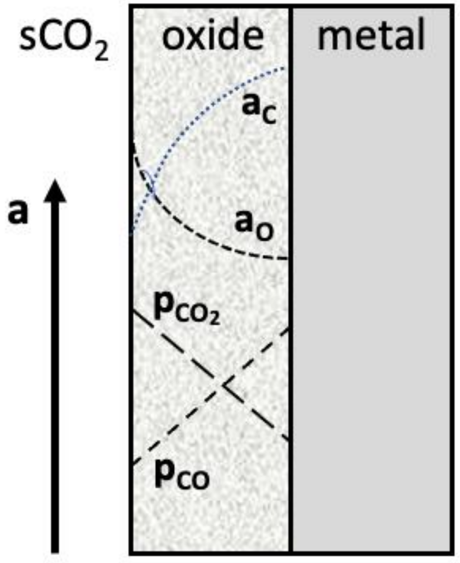
Moving forward with limited compatibility data!
As audacious as Eddystone in 1960

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

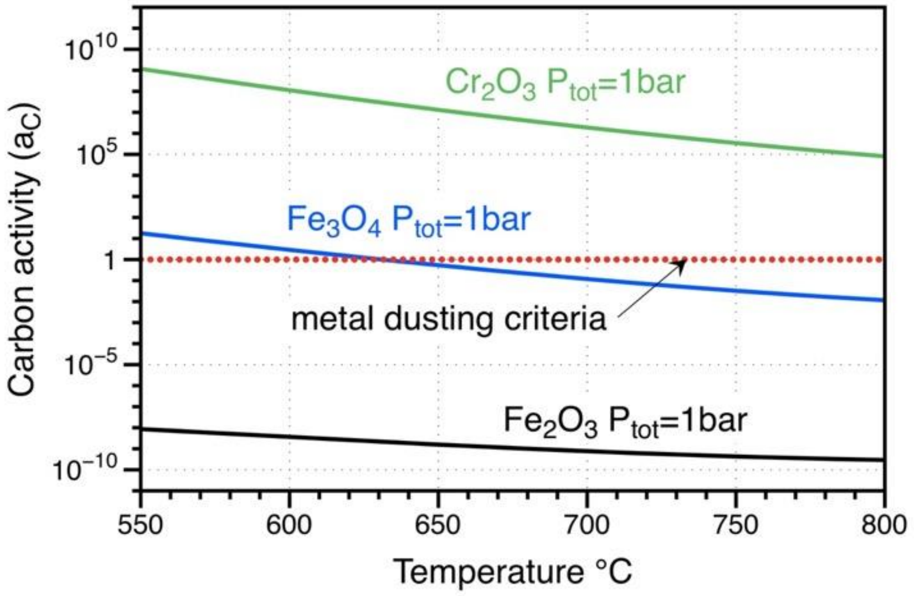
Factsage calculations:



All of our favorite oxides are stable!



Young et al., 2011



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

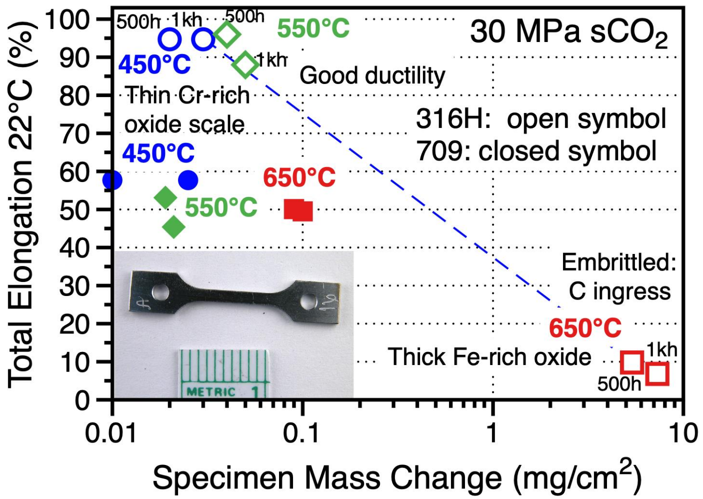
High carbon activity at P_{total} = 1 bar (What is $P_{interface}$?)

General conclusion: internal carburization concern for Fe-based alloys

sCO_2 compatibility: broad range of conditions considered

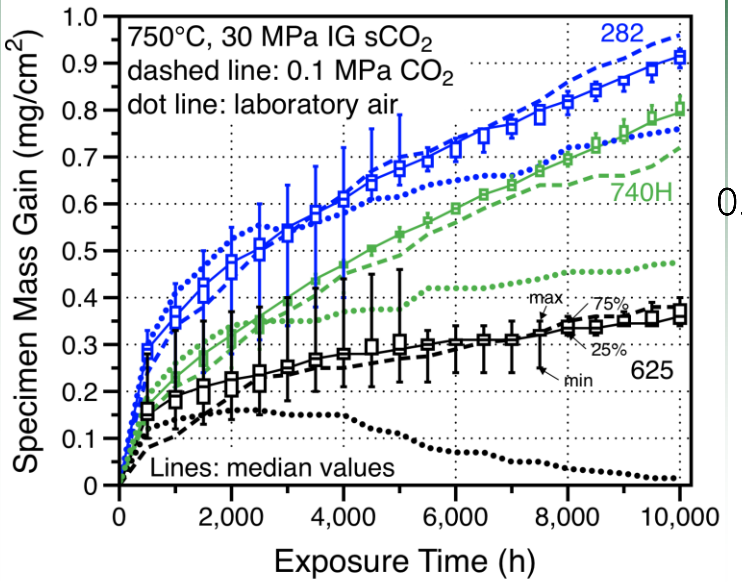
400°-650°C: concern about steel carburization

- 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

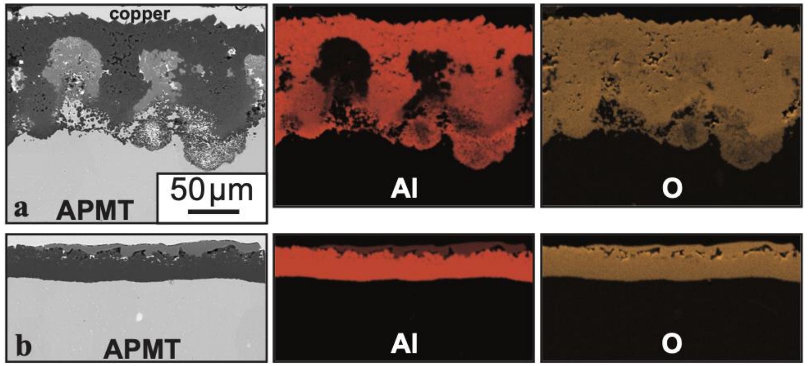
- No issues for Ni-based alloys
  - Low C solubility, protective Cr_2O_3 formation
- Similar rates for air, CO_2 and sCO_2
  - **Little or no P effect @ 750°C**



>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



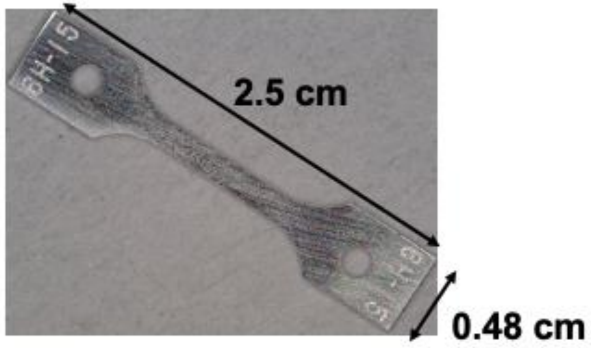
2 MPa CO_2

ORNL steel project started in August 2019 (paused in 2021)

Test matrix & progress

Temperature	RG sCO_2	$+1\%O_2+0.1\%H_2O$
450°C (842°F)	2000 h	1000 h
550°C (1022°F)	2000 h	1000 h
650°C (1202°F)	1000 h	1000 h

Autoclave: 300 bar sCO_2
500-h cycles



SS-3 dogbone tensile

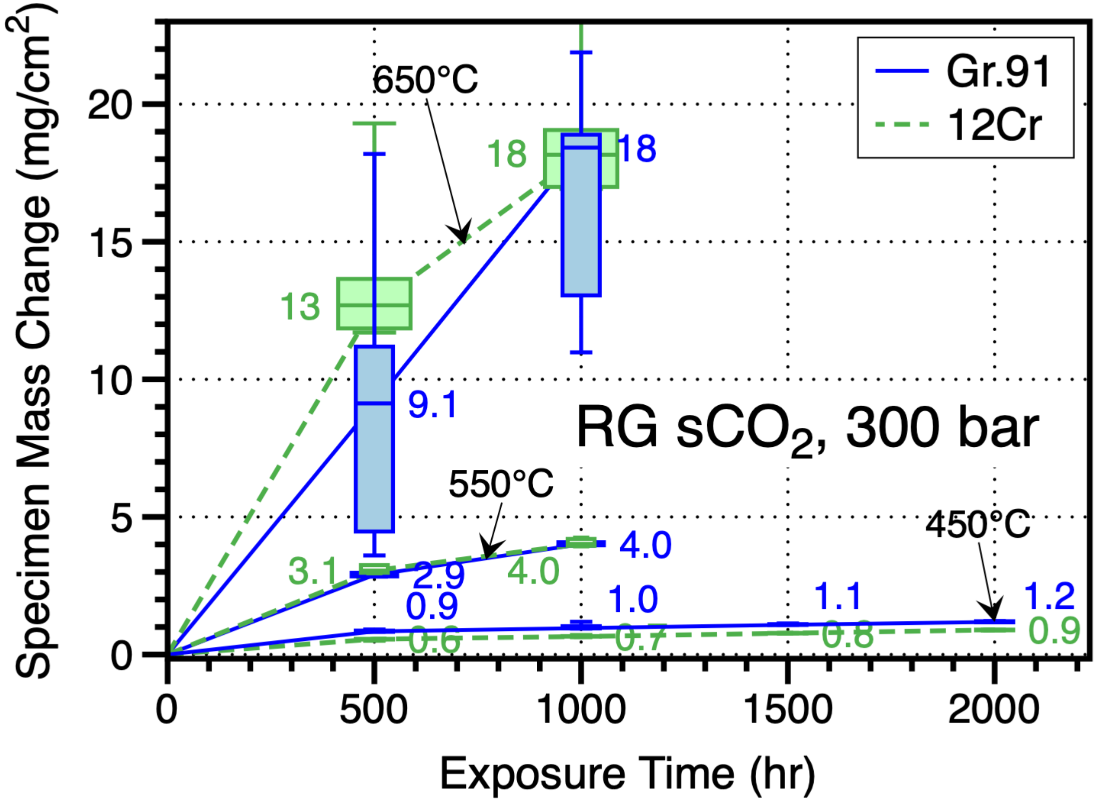
~5 cm^2 alloy coupons + tensile specimens

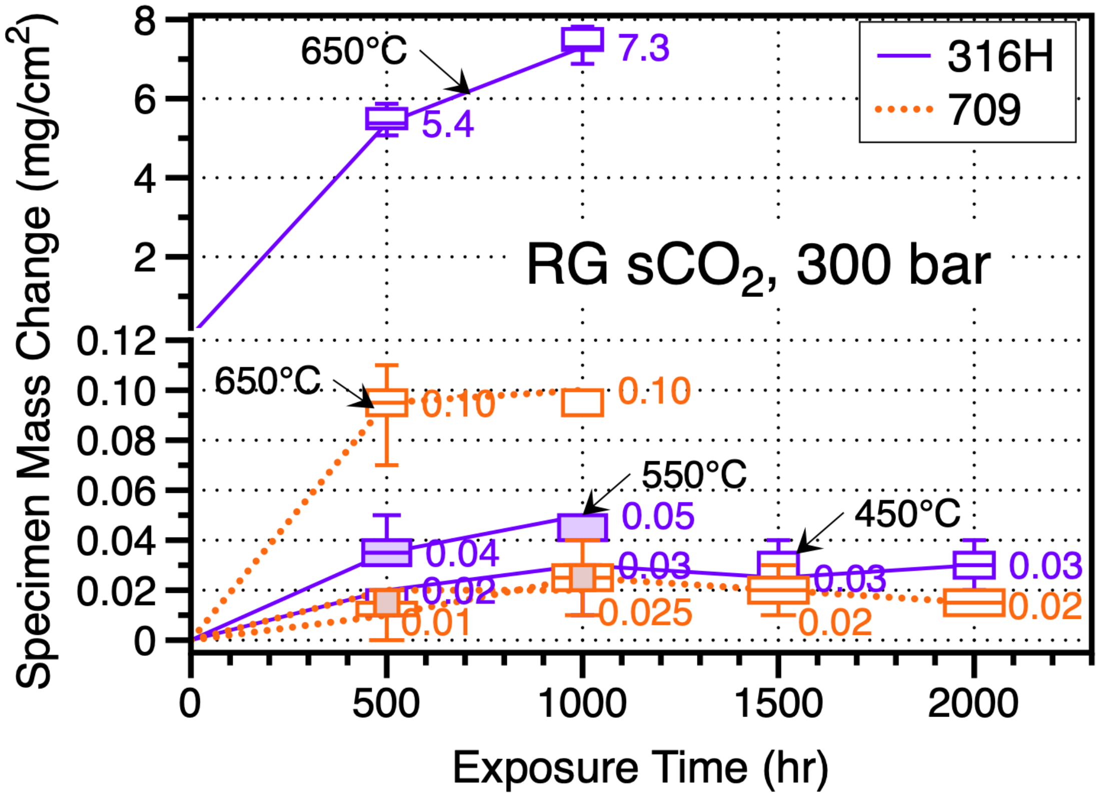
- Four primary alloys in test matrix
  - T91 (9Cr-1Mo)
  - VM12 (~11Cr)
  - 316H (conventional stainless steel)
  - (NF)709 (advanced austenitic, 20Cr-25Ni+Nb)
- 10 specimens of each alloy: starting point
- With and without impurities (open vs. closed)

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
709	S31025	20.1	25.2	0.9	0.4	.06	.15	1.5Mo,0.2Nb

Baseline of research grade (RG) CO_2: $\leq$ 5 ppm H_2O and $\leq$ 5 ppm O_2

Mass change of 5-6 specimens in RG sCO_2 plotted

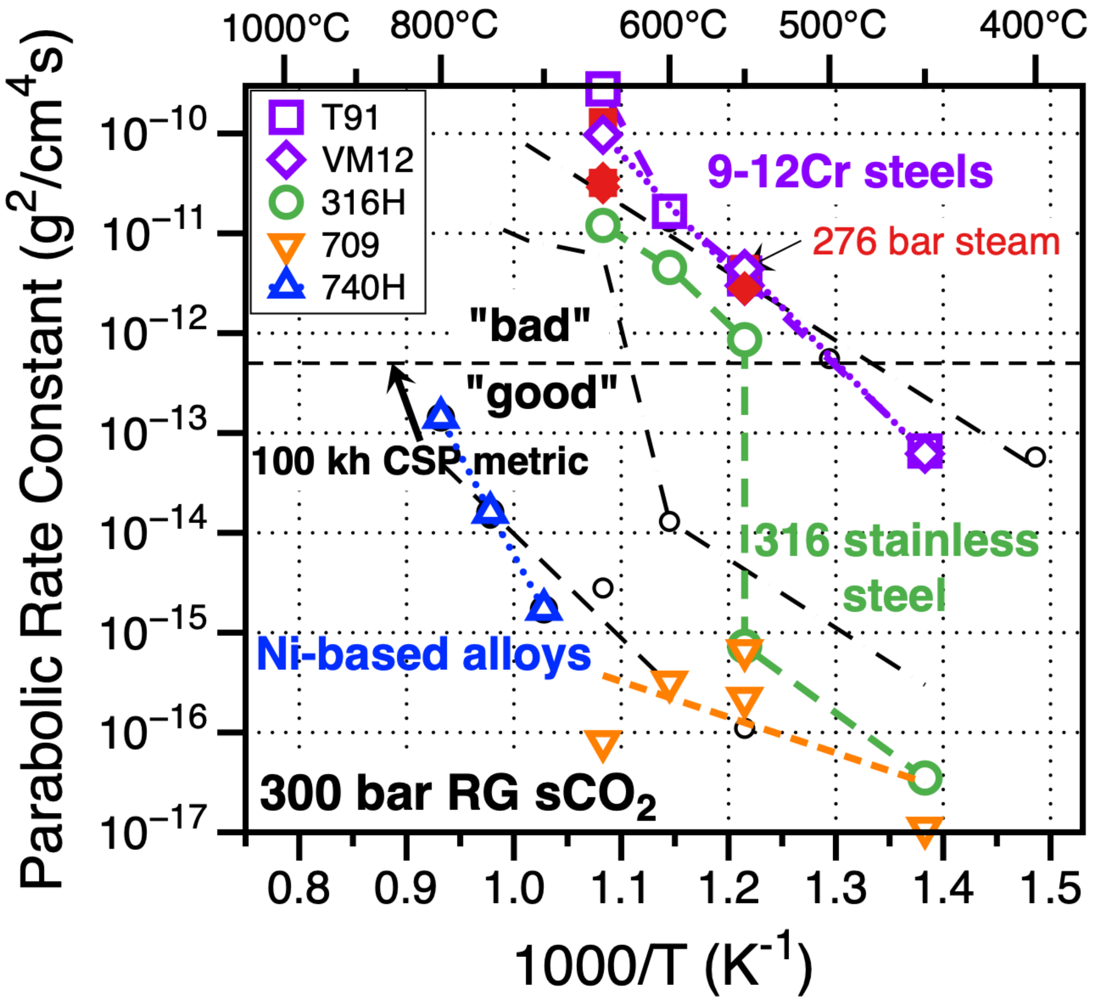




- One specimen of each alloy removed at 500 h for metallography
- High mass gains for 9-12%Cr steels in all cases
- Low mass gains for FCC steels except 316H at 650°C
  - Ran 450°C experiment to 2,000 h for improved assessment

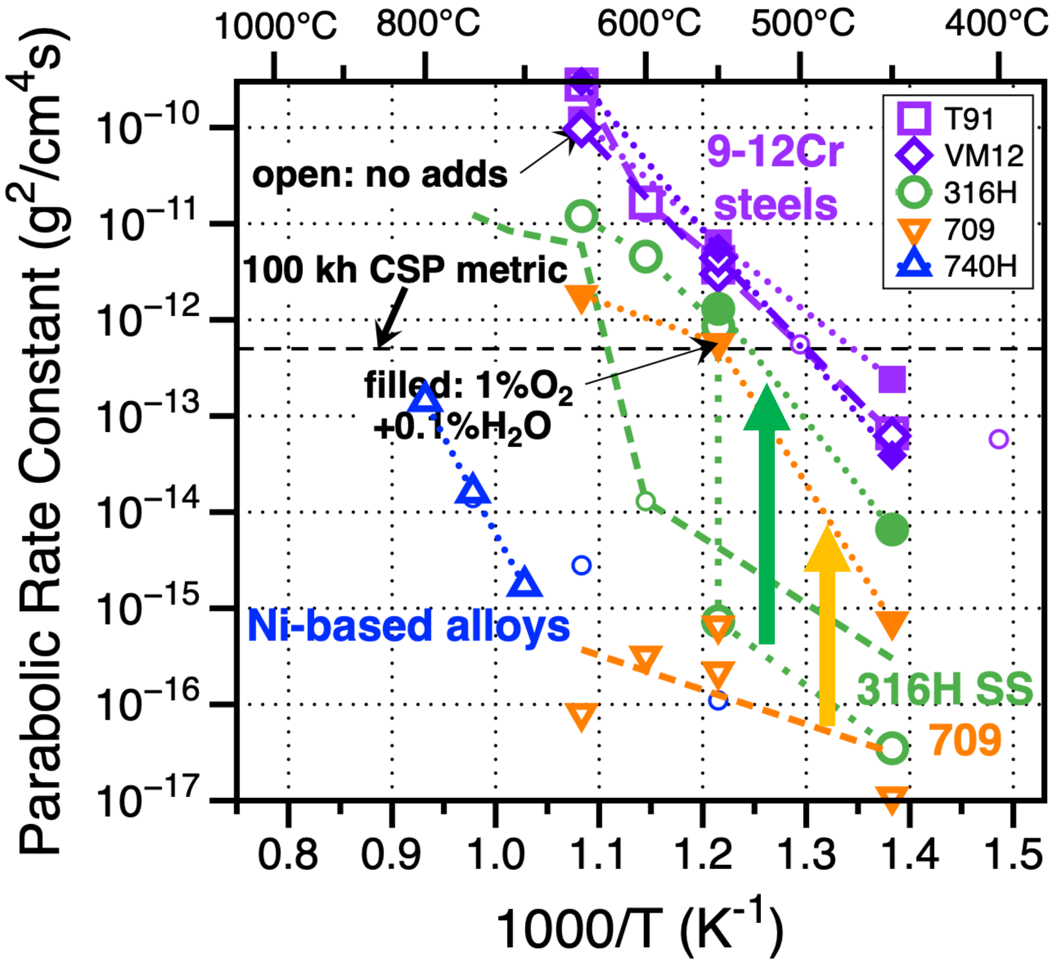
Measured rates in sCO_2 consistent with the literature

- Metric developed for Solar CSP
  - Slow rate = OK for 100kh life
- Ni-based alloys all "good"
  - Lifetime model: ≤ 800°C = 100kh
- **Steel limitations**
  - Ferritic-martensitic alloys <500°C
  - Austenitic alloys <600°C
    - Obvious jump in kinetics
  - Advanced austenitics (709), better
    - Value in 20-25%Cr, 20-25%Ni
    - Low values hard to measure



9-12Cr steels have similar rates in 276 bar steam

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



Open symbol: RG sCO_2

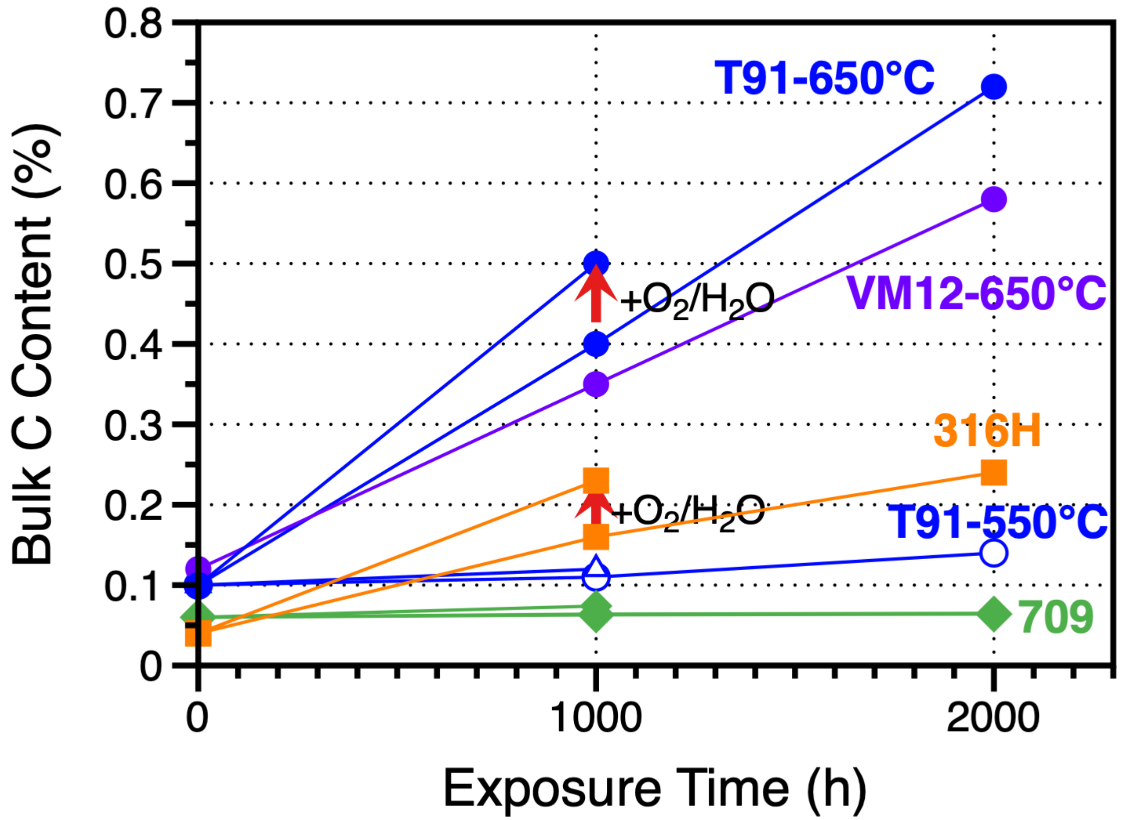
Shaded: RG sCO_2 + $1\%O_2$ + $0.1\%H_2O$

- 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

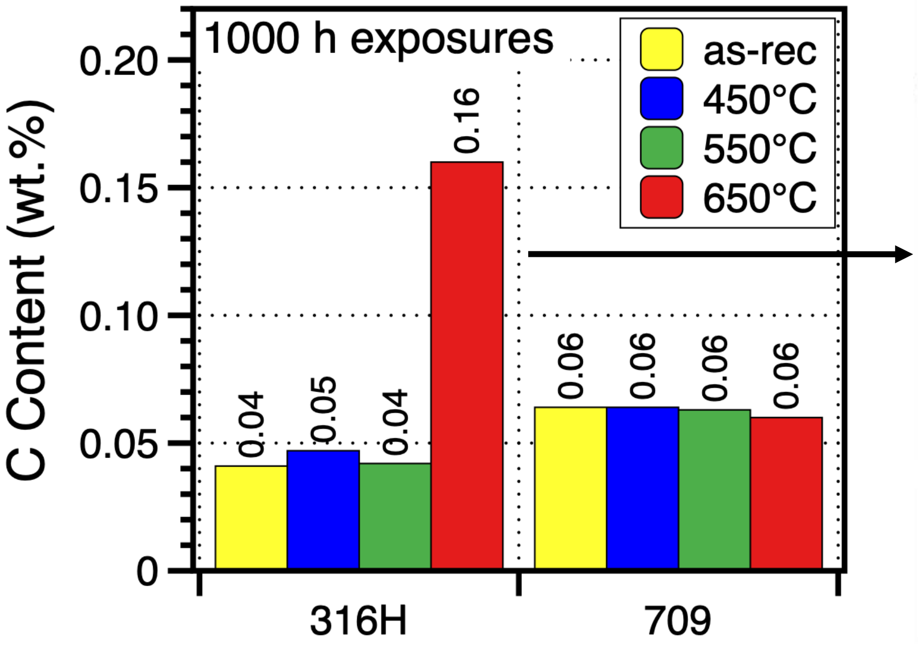
Bulk C measurements: Fe-rich oxides allow C ingress

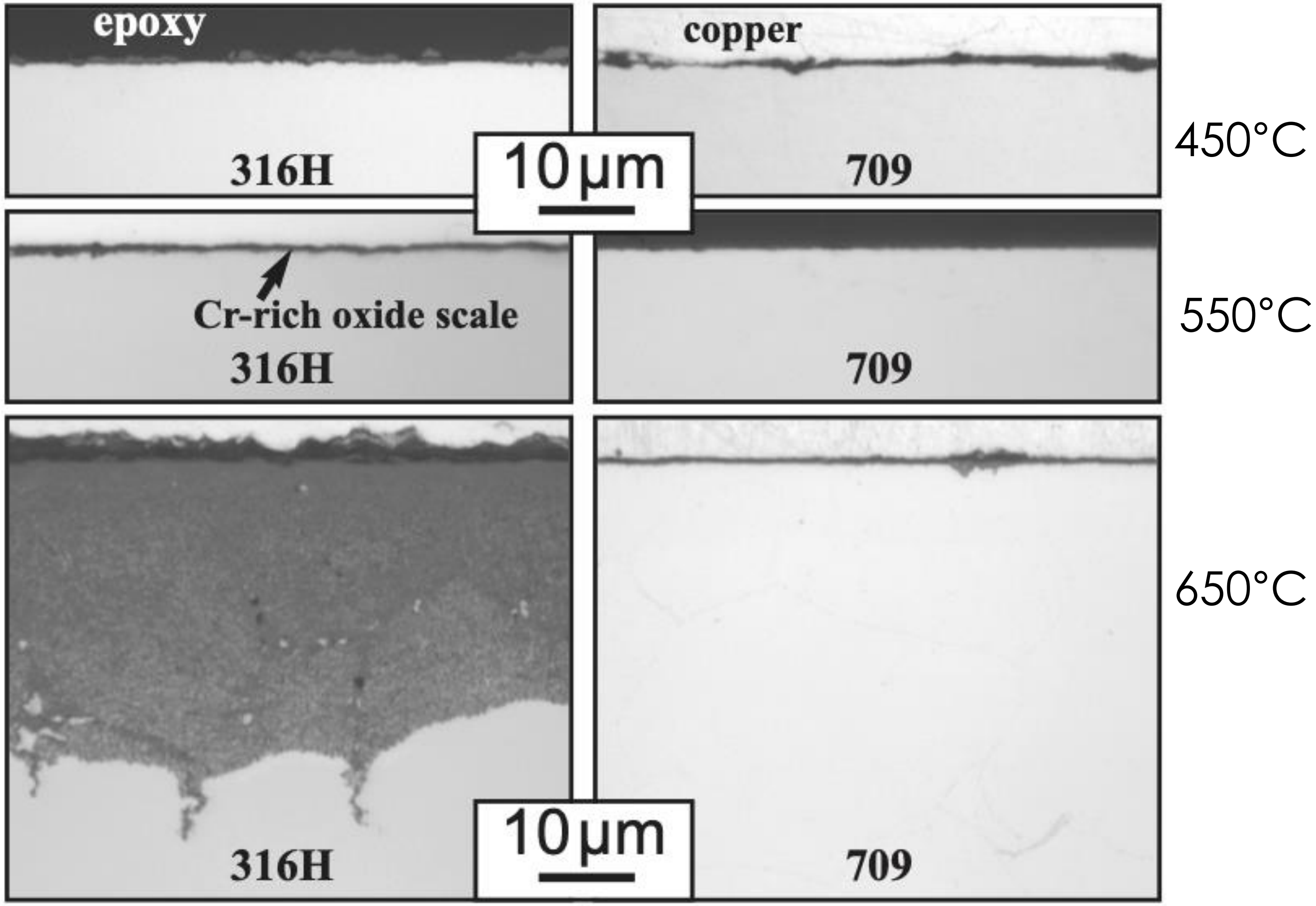


- Measurements by combustion analysis, increasing with time
- Focus on 650°C results, less ingress at 600° and 550°C
- sCO_2 impurities tend to increase C ingress

709 (20Cr/25Ni): resistant to C ingress 1000h up to 650°C
316H at 650°C: thick Fe-rich oxide + C ingress + embrittlement

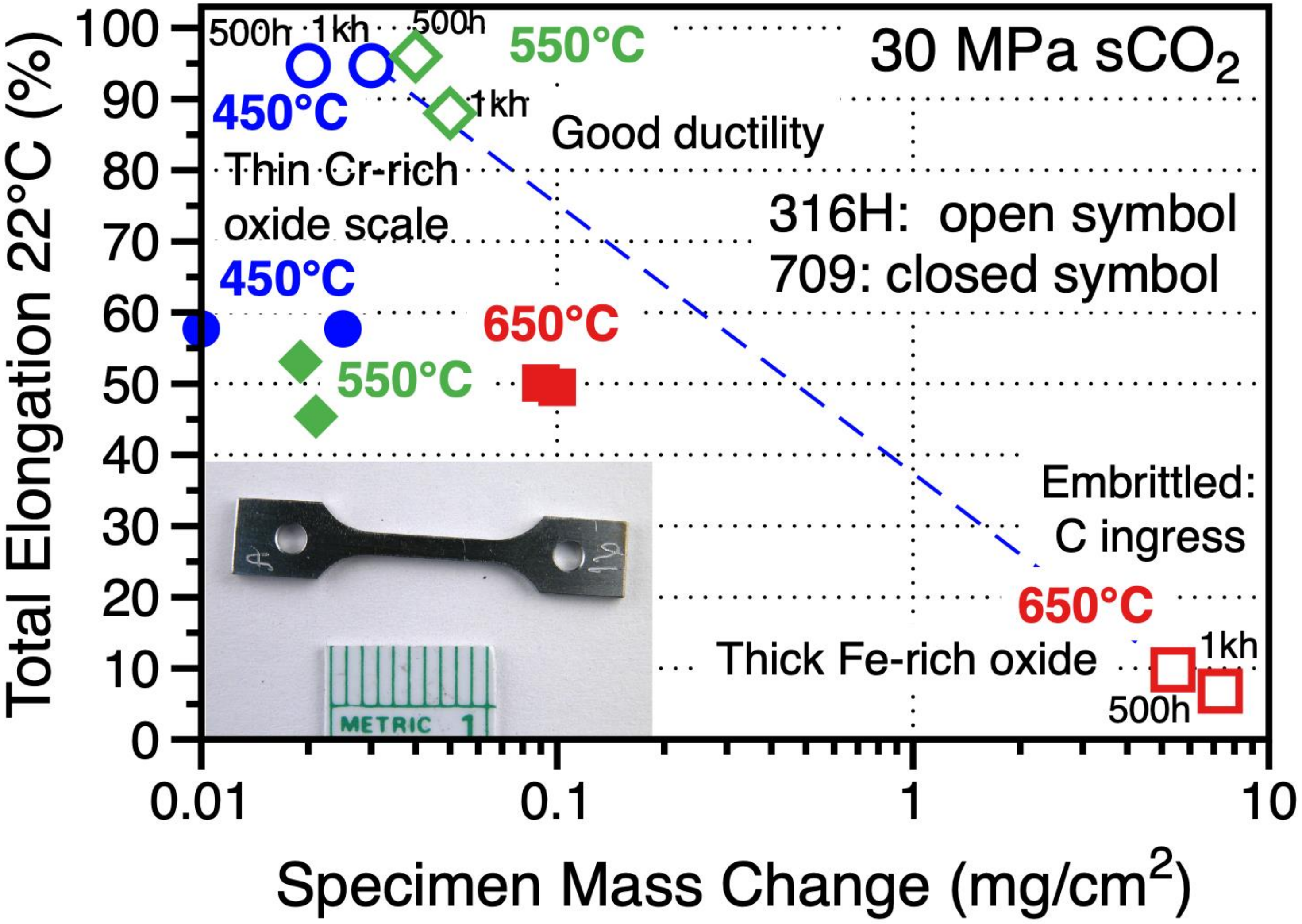
Results for RG CO_2, 30MPa
- No impurities





1000 h at each condition

Pure sCO_2: Cr_2O_3 scale prevents C ingress



- 25mm long dogbone specimens
- 316H (16Cr-10Ni)
  - Cr-rich oxides = low mass gain + good ductility
  - Fe-rich oxides = high mass gain + embrittlement
- 709 (20Cr-25Ni):
  - no loss in ductility in this experiment

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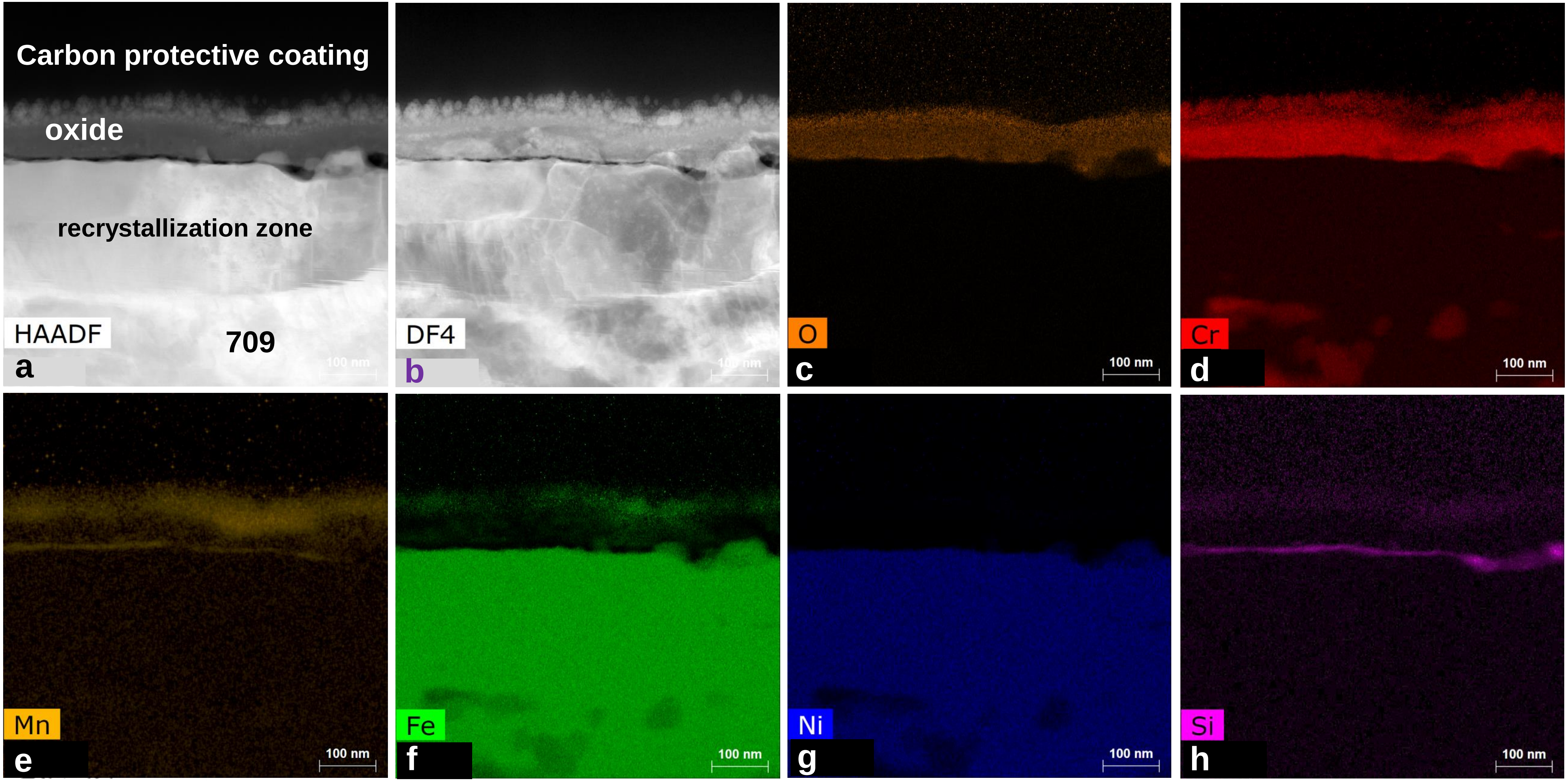
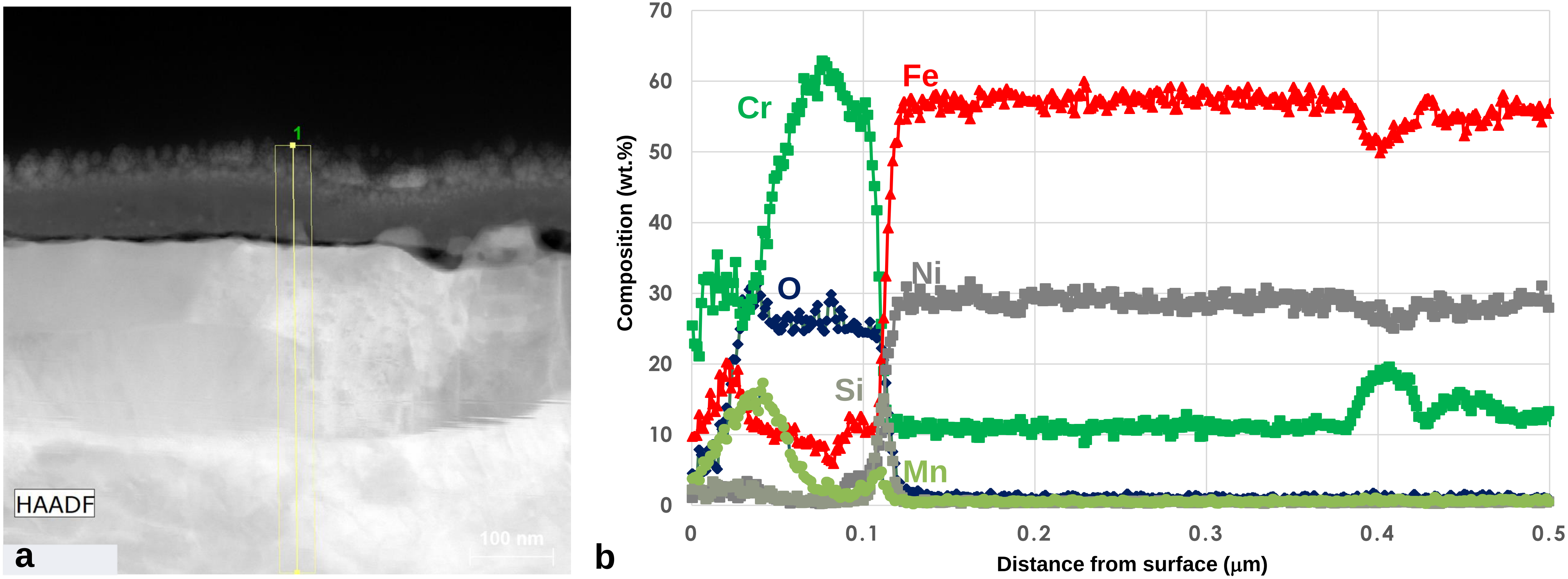
709/air, 650°C/1000 h: Talos EDS maps of scale, looks “normal”



709/air, 650°C/1000 h: Talos EDS line profile of Cr-rich scale

- Small region shows Cr depletion near surface



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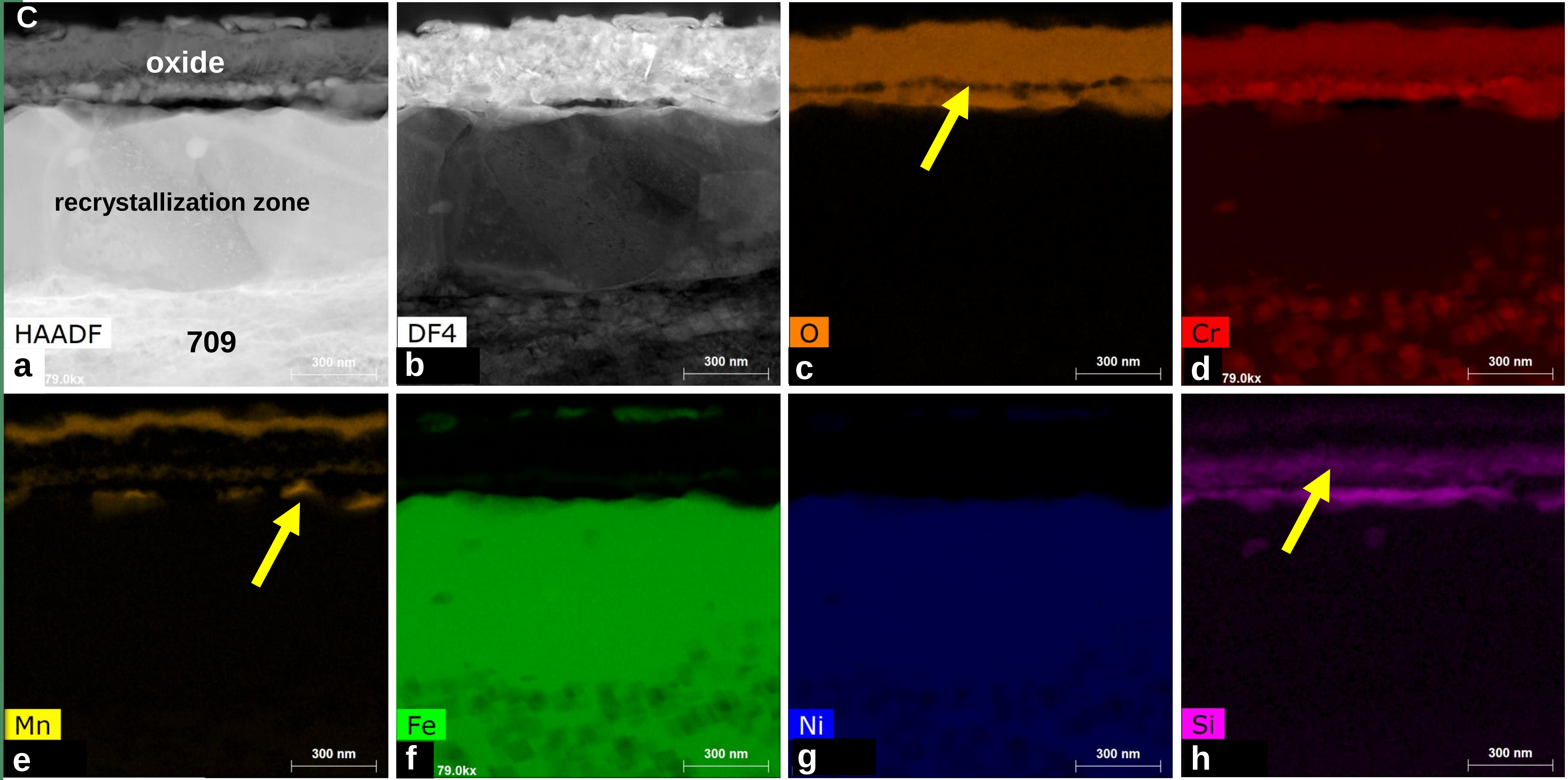
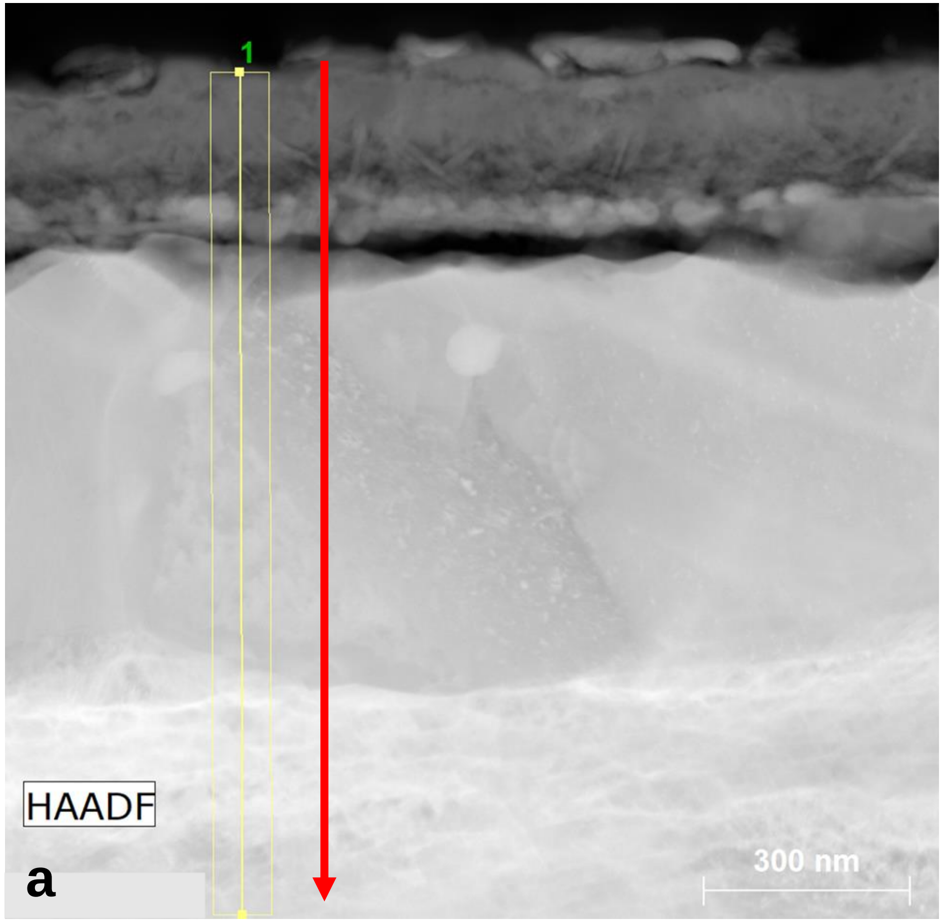
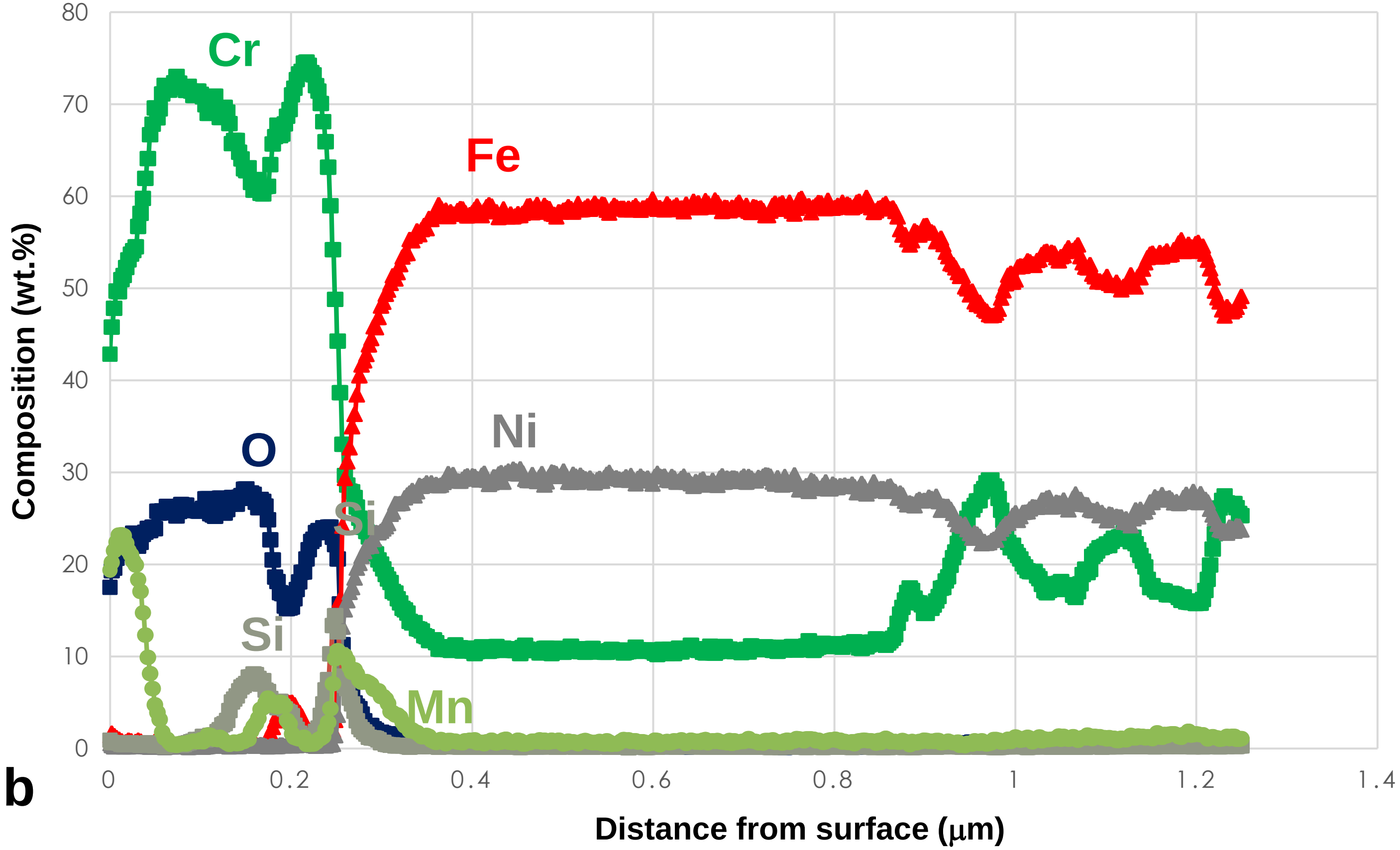
709/sCO_2, 650°C/1000 h: Talos EDS maps of thicker multi-layer scale

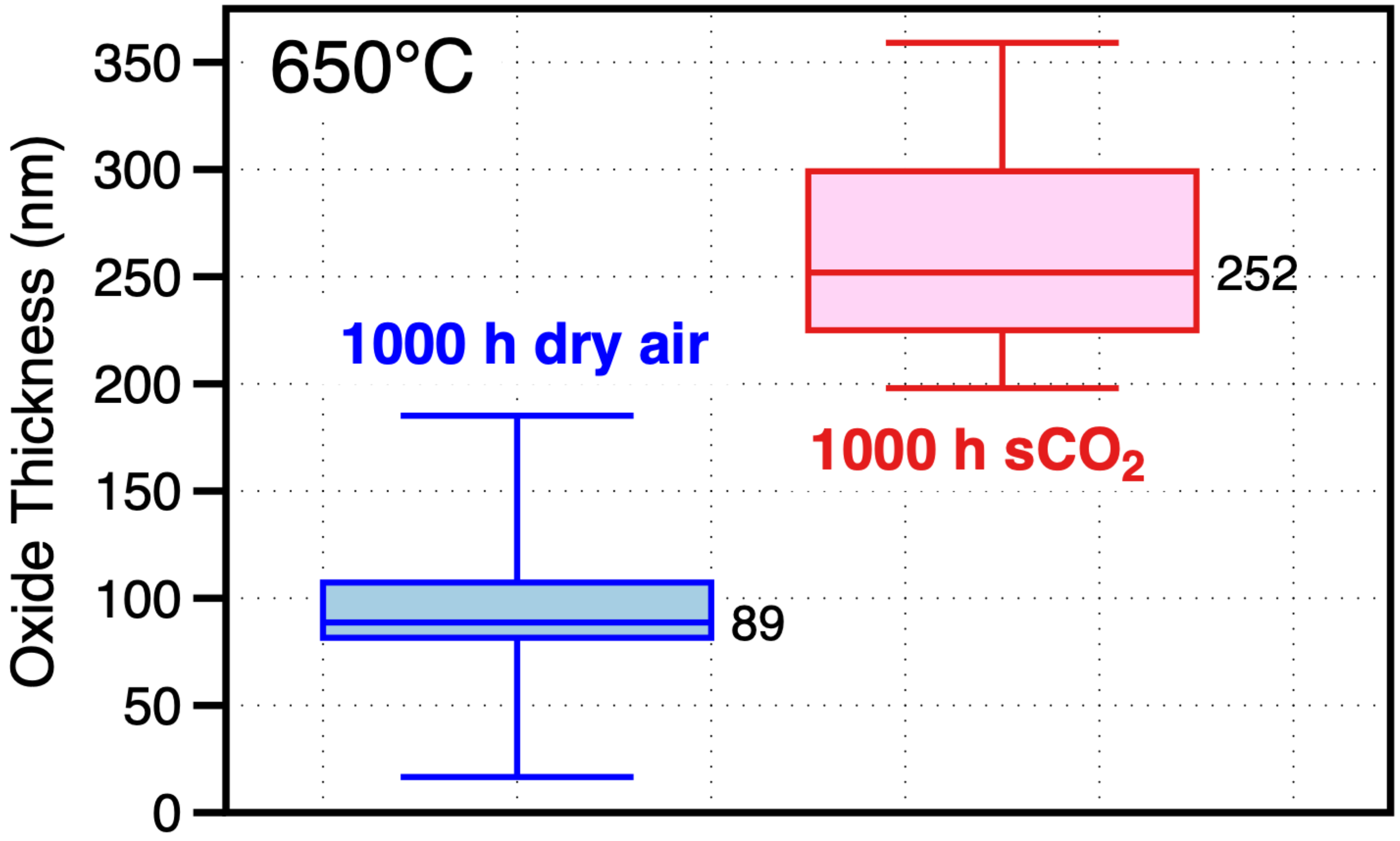


709/sCO_2, 650°C/1000 h: Talos EDS line profile of multi-layer scale





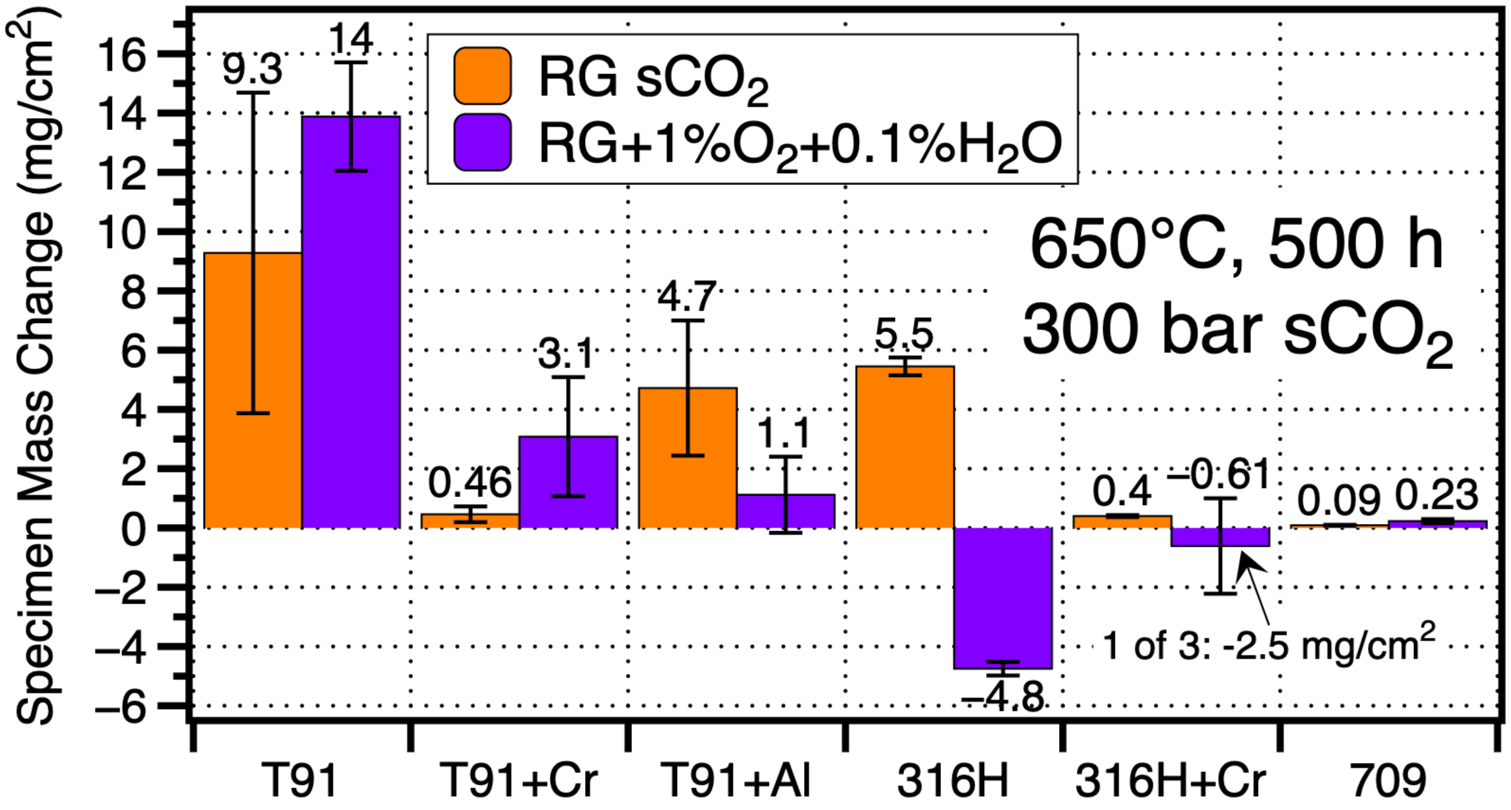
Scale formed in sCO_2 was much thicker



Median values shown

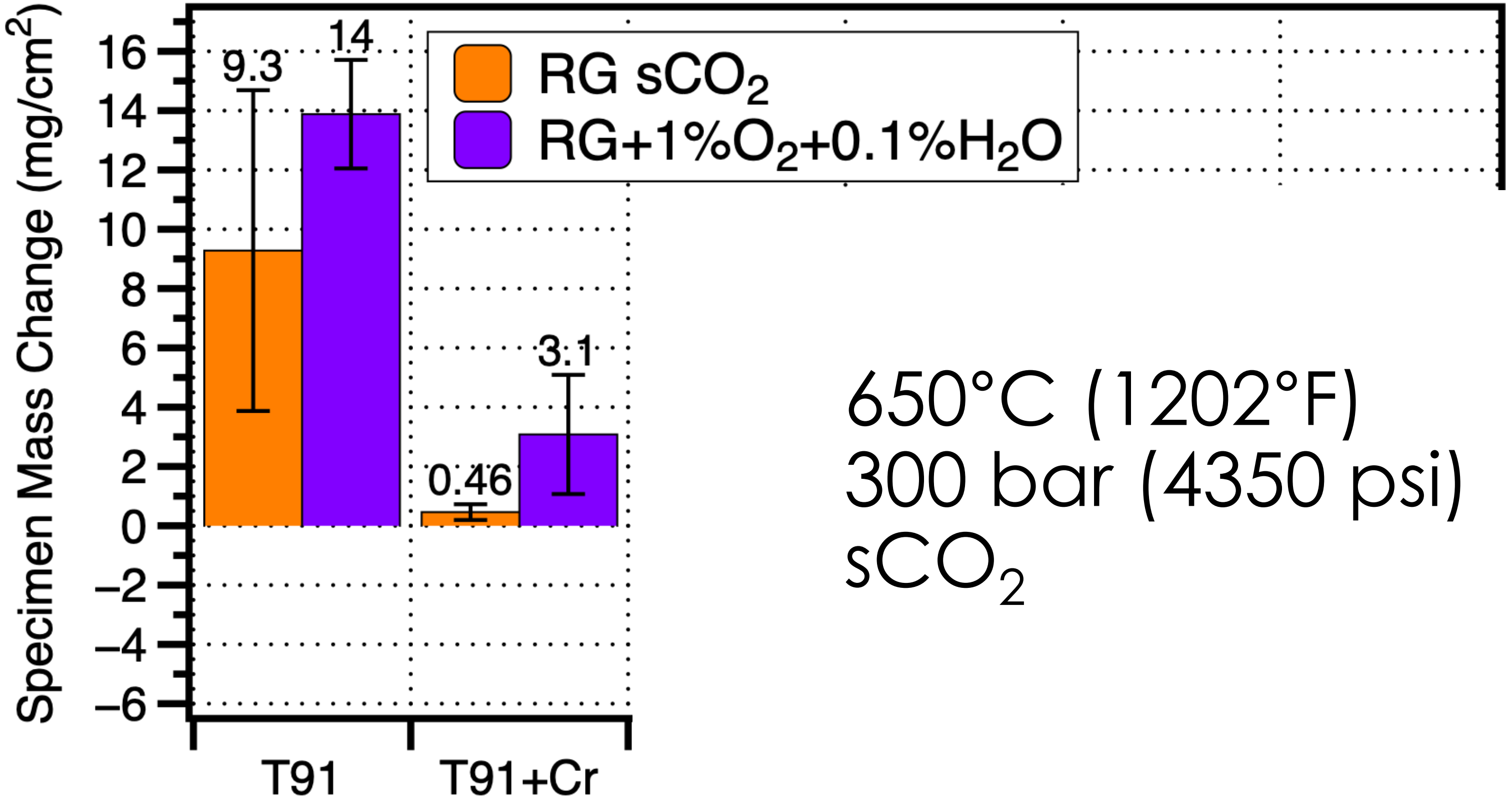
Automated image analysis: >1200 measurements from all TEM images

3 Coatings: initial sCO_2 testing at 650°C ± O_2/H_2O



- T91 + 316H: pack Cr coating
- T91: pack Al coating
- Some benefit from coatings but less effective with impurities

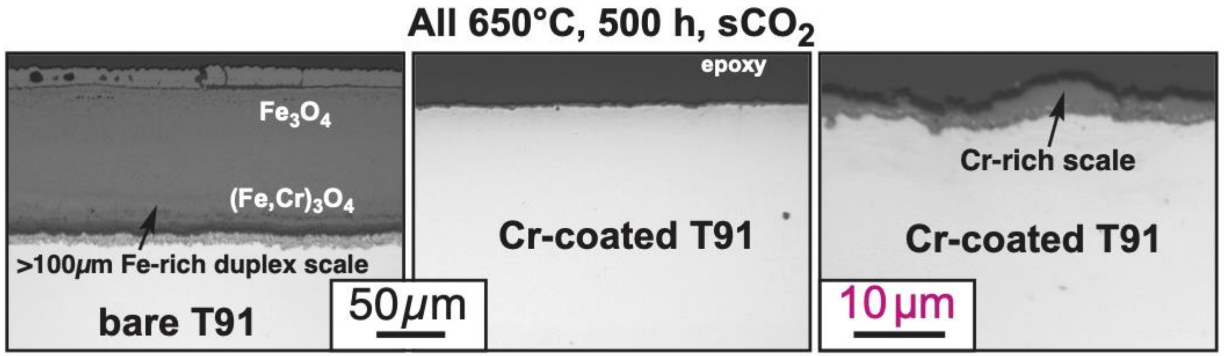
3 coatings: initial sCO_2 testing at 650°C ± O_2/H_2O

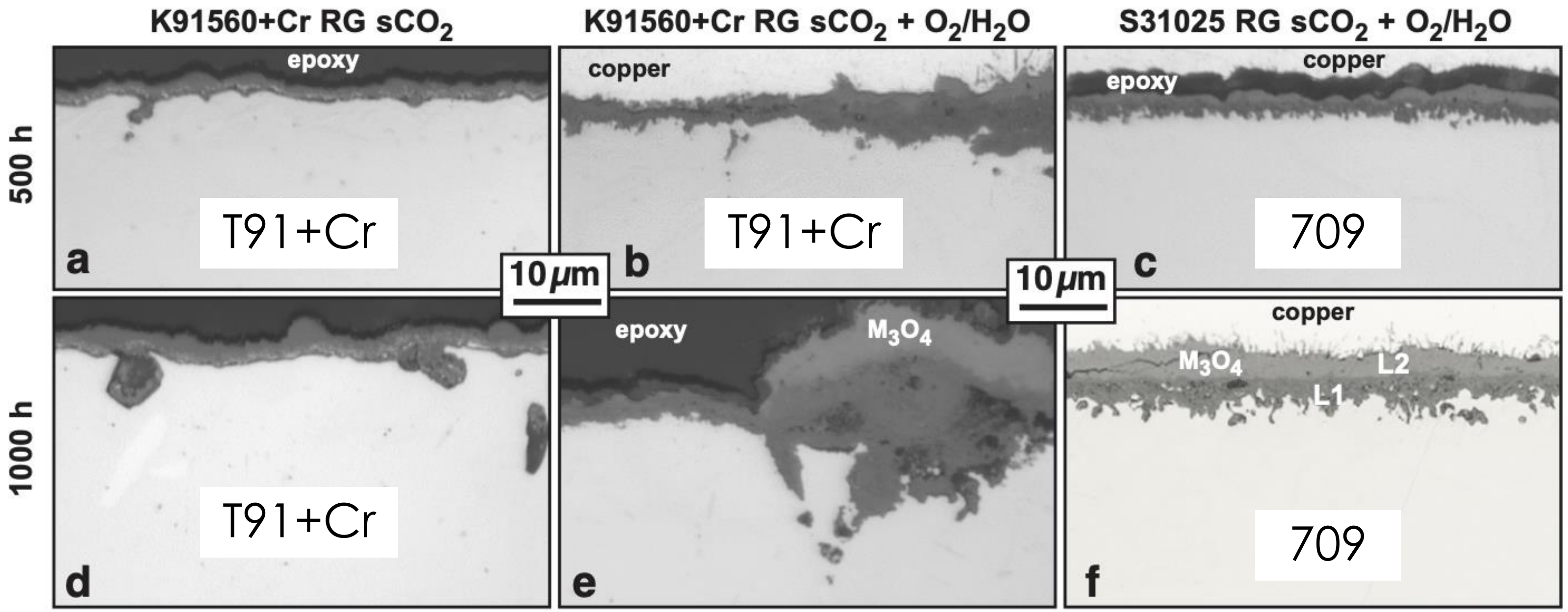


650°C (1202°F)
300 bar (4350 psi)
sCO_2

- High mass gains for uncoated 9Cr steel: variable due to spallation
- Low mass gain in RG sCO_2 increased with impurities

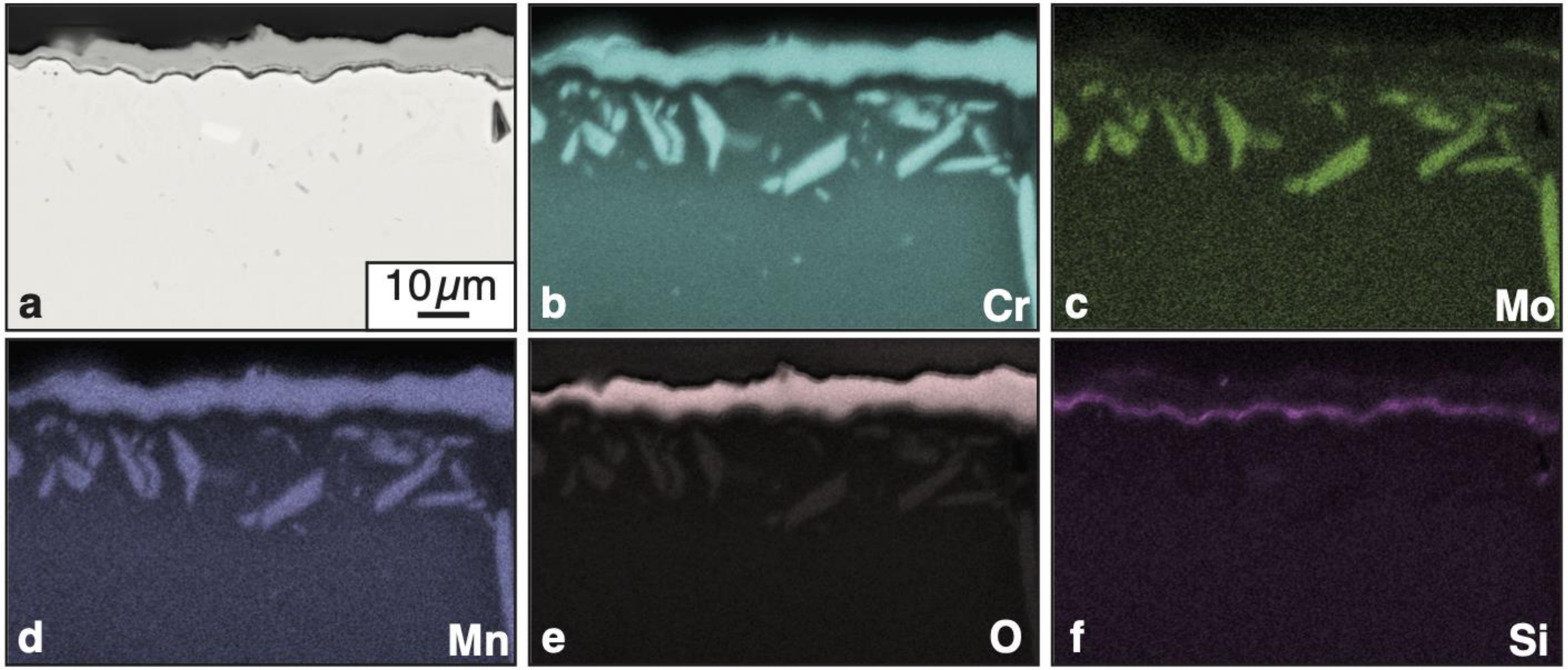
Cr coating on T91 more effective in RG sCO_2

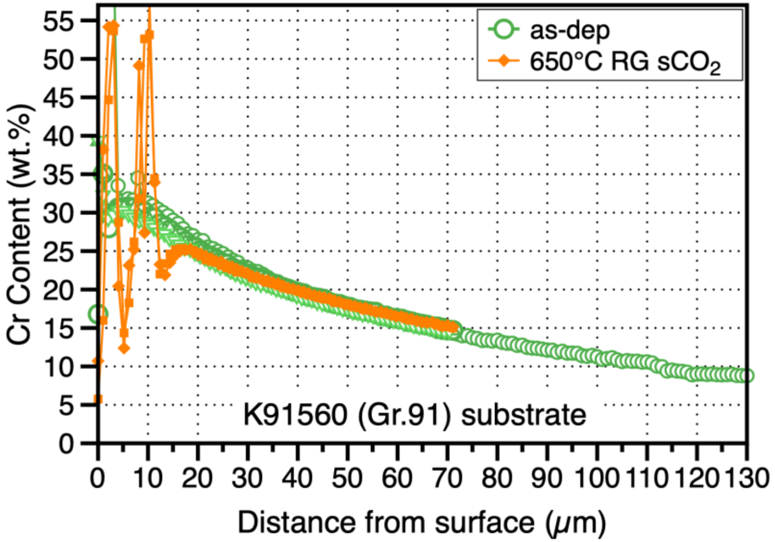




- Thin scale formed in RG sCO_2 : not thick Fe-rich oxide
- Oxide nodules formed with O_2/H_2O additions

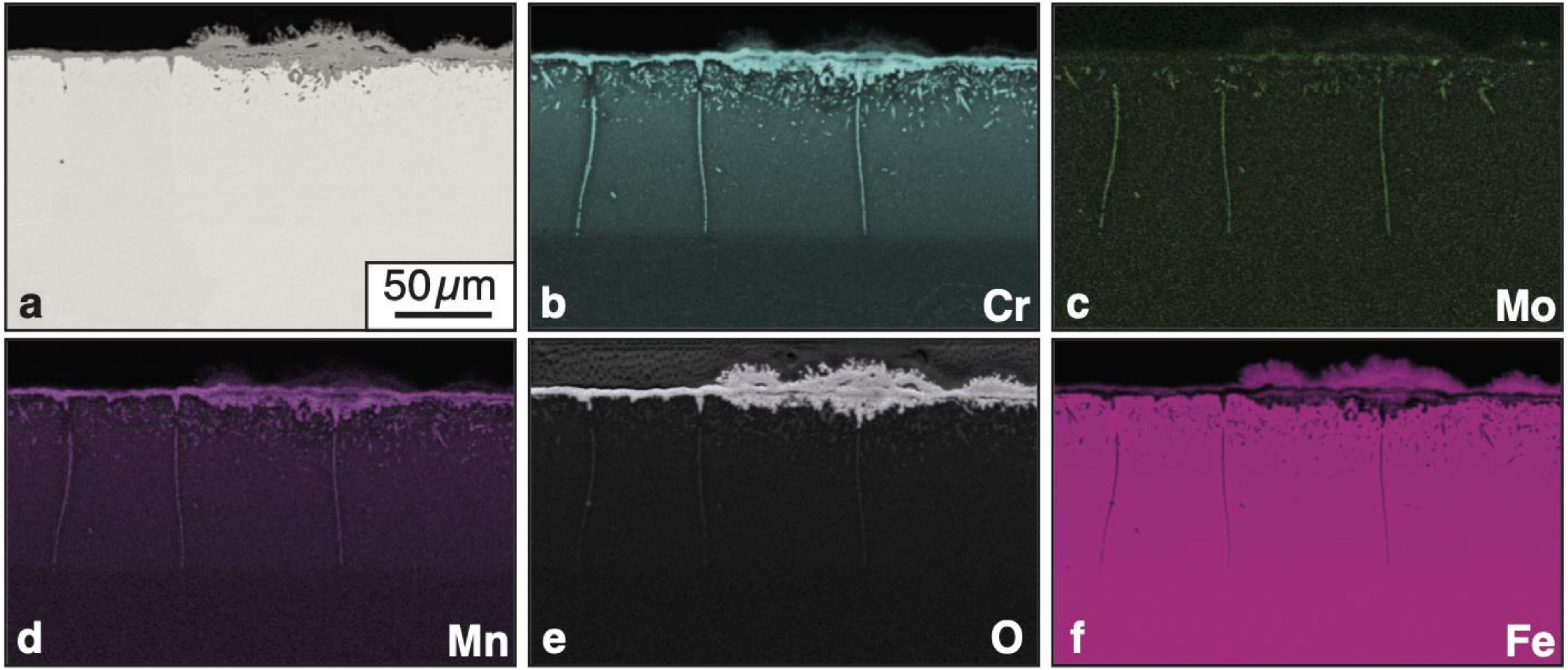
Precipitates in coating after 1,000 h at 650°C in RG sCO_2





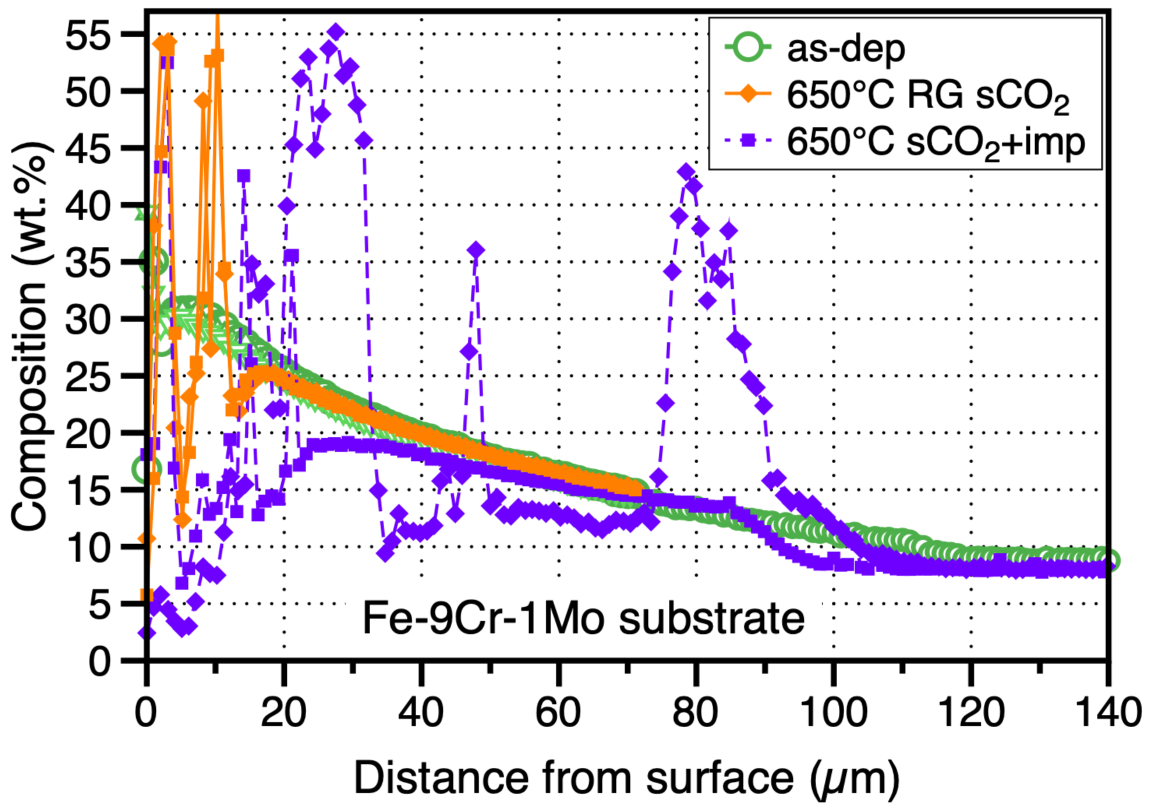
- Coating ~110 μm thick
- Confirmed carbide precipitates by EPMA

sCO_2 with impurities: 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

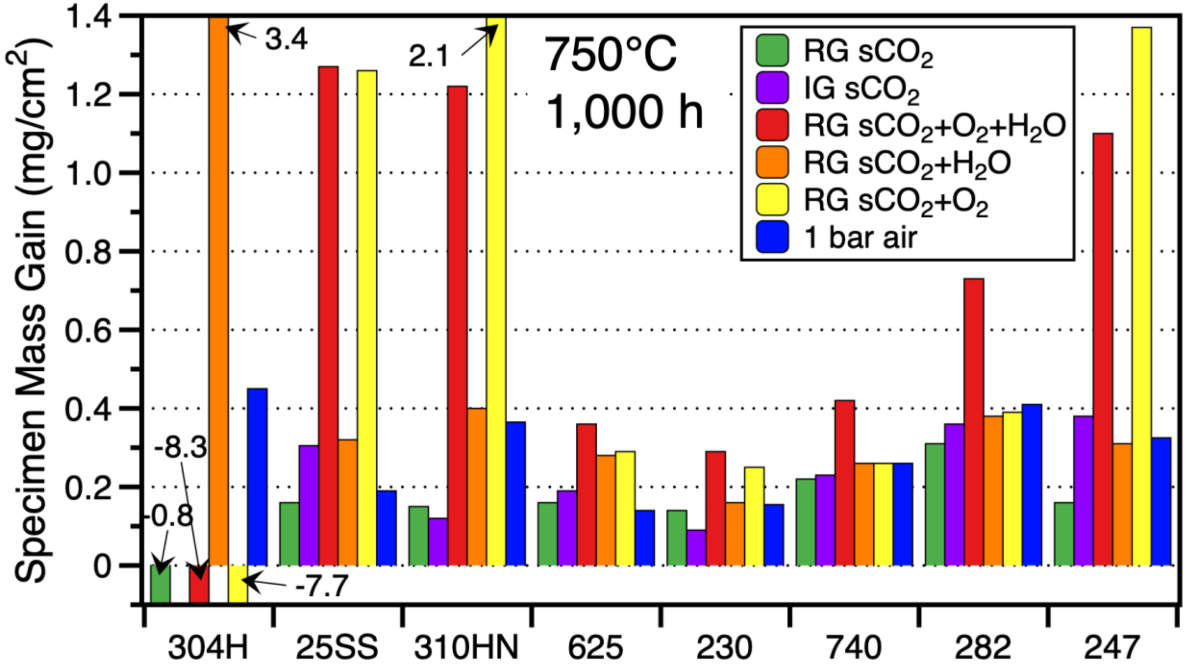


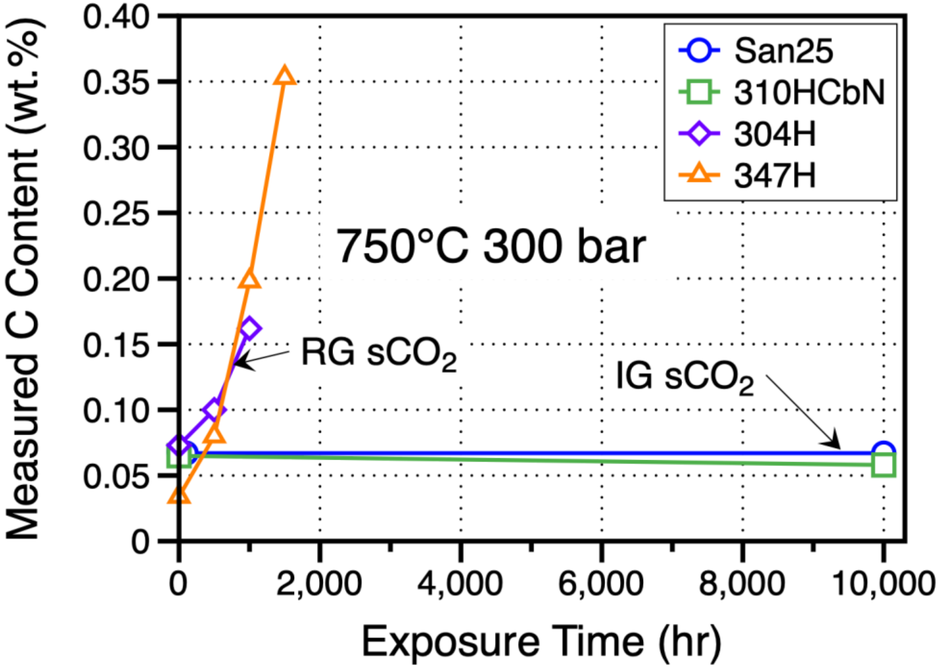
- 1000 h/650°C: higher Cr consumption with impurities
- 650°C: temperature too high for ~110 μm thick Cr pack coating
- Next: testing at 550°C

Summary: sCO_2 is a challenging environment

- At 650°-800°C, Ni-based alloys appear compatible
- Steels degrading at 550°-650°C in sCO_2
  - 9-12%Cr steels may be limited to ~500°C
    - Fe-rich oxide formation observed in sCO_2 similar to sH_2O
    - 550°C and higher issue with C ingress
  - 316H at 600°-650°C in RG sCO_2
    - Carbon ingress + embrittlement
  - 709 formed Cr-rich oxide in all cases
    - Thicker, more complex scale forms in sCO_2
    - Could scale break down at longer times?
  - Increased attack when O_2 and H_2O impurities in sCO_2
- Opportunity for coatings?
  - Pack Cr and Al coatings evaluated on T91 and 316H at 650°C
    - Cr on T91: reduced mass gain but internal carbides observed in sCO_2
    - Lower temperature (550°C) sCO_2 evaluations in progress

Questions?





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

All 650°C, 500 h, sCO_2