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

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- T. Lowe — SEM, image analysis
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  - Tenaris
  - EPRI
  - Sam Sham, INL (US heat, alloy 709)

Supercritical CO_2 Allam cycle has been demonstrated!

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

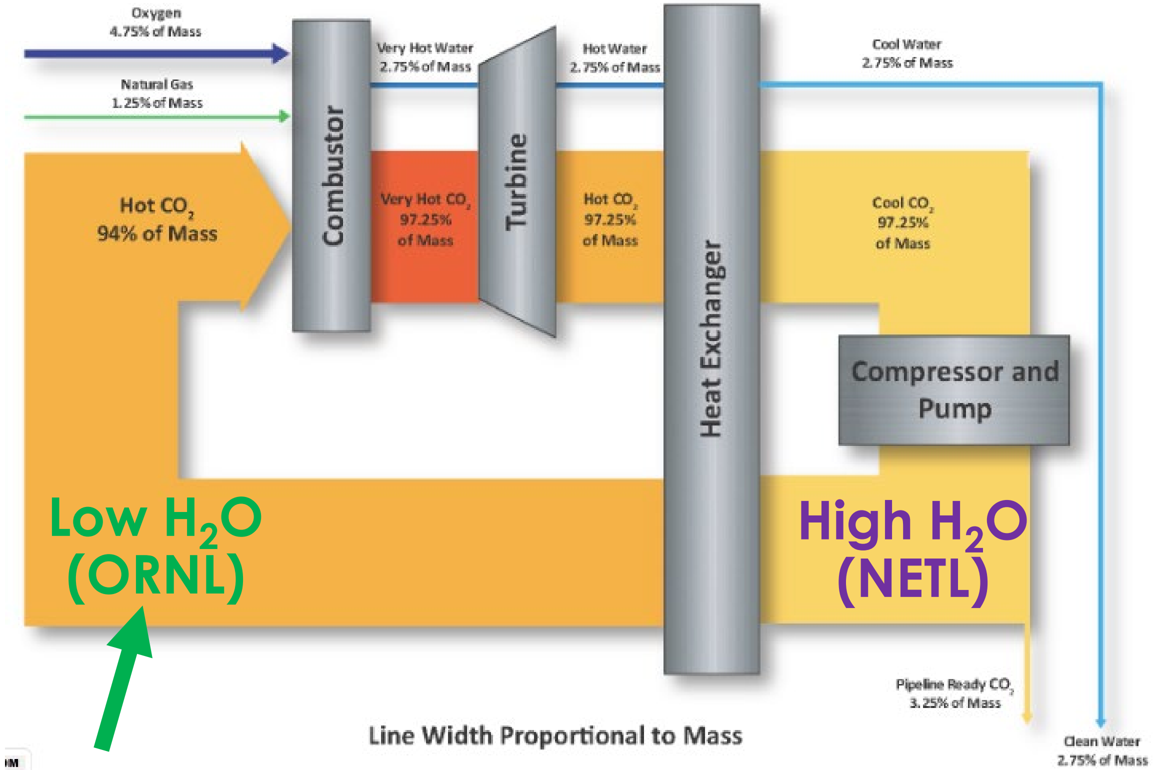
November 2021: plant connected to grid (announced plans for 280MW)

Material challenges:

Combustor: 900°C (initially 1100°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?

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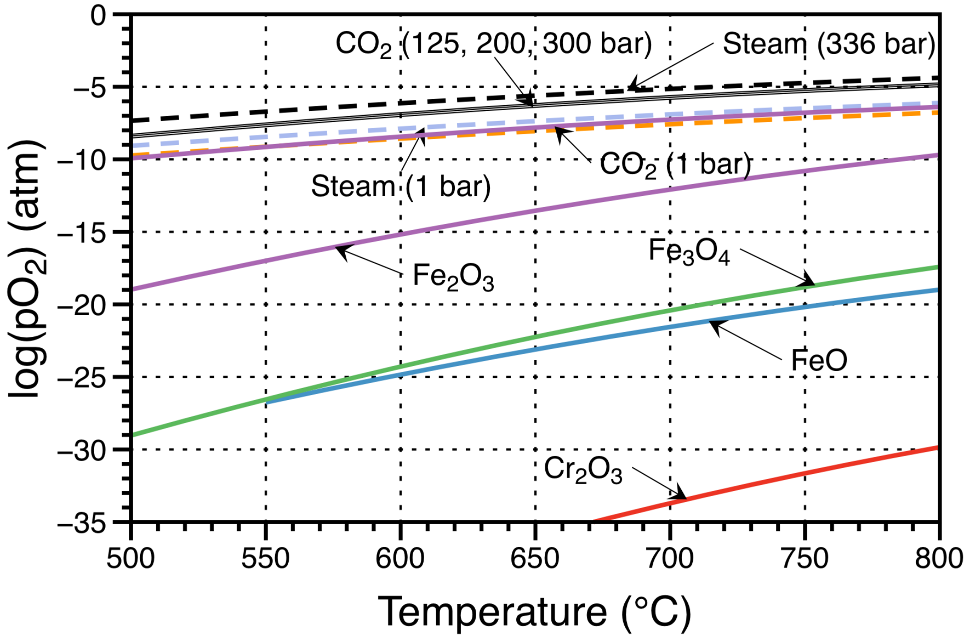
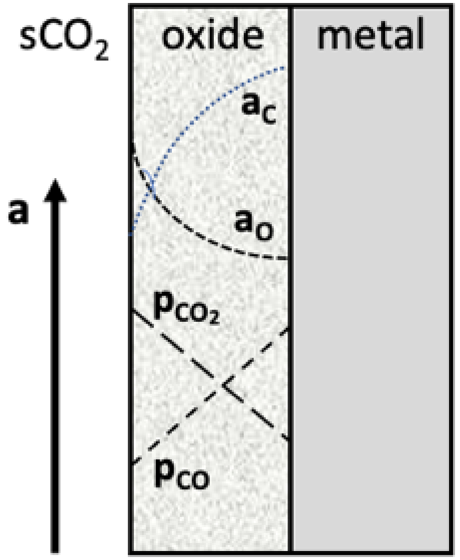
Thermodynamics: Oxygen levels similar in steam/CO_2
Concern about high C activity at m-o interface: not "inert"

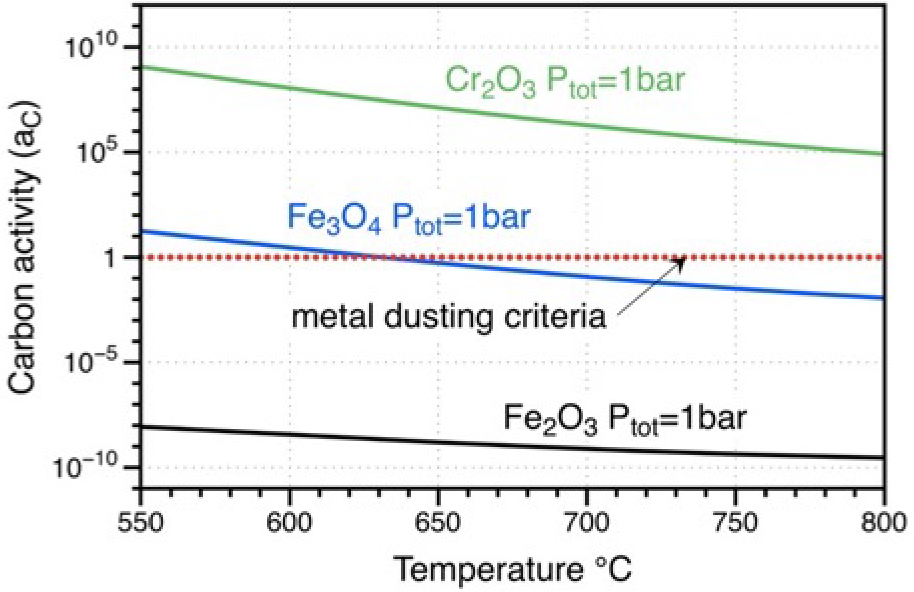
Factsage calculations:



All of our favorite oxides are stable!



Young et al., 2011



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

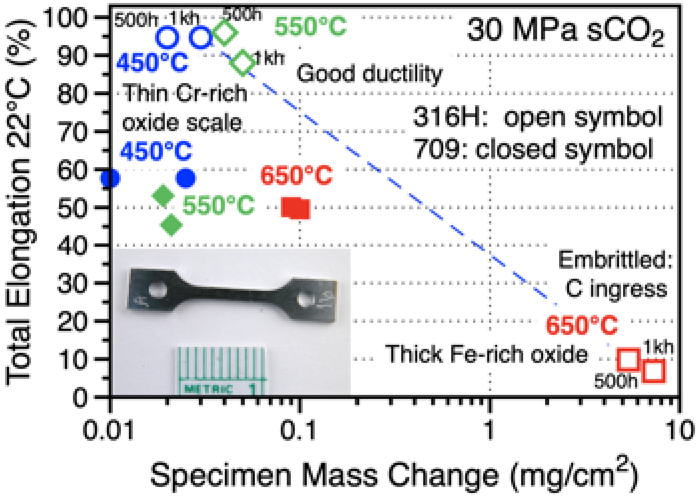
High carbon activity at P_{total} = 1 bar (What is $P_{interface}$?)

General conclusion: internal carburization concern for Fe-based alloys

sCO_2 compatibility: broad range of conditions considered

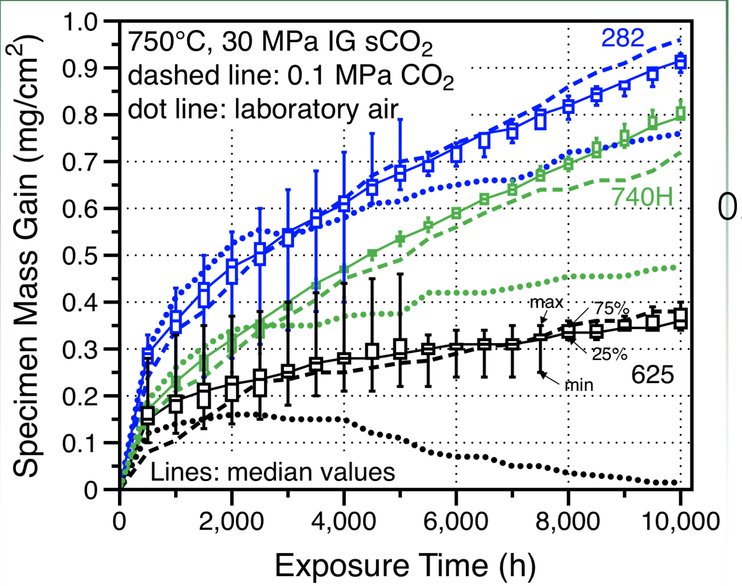
400°-650°C: concern about steel carburization

- 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

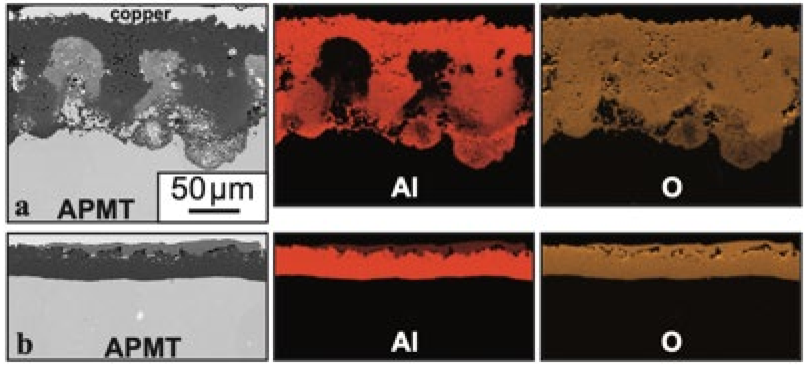
- No issues for Ni-based alloys
  - Low C solubility, protective Cr_2O_3 formation
- Similar rates for air, CO_2 and sCO_2
  - **Little or no P effect @ 750°C**



>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

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ORNL sCO_2 project wrapping up in 2024 (originally 2023)

- Focus on 4 steels
  - BCC: 9Cr (G91), 12Cr (VM12)
  - FCC: 316H (16Cr-10Ni), 709 (20Cr-25Ni)
- Completed tasks
  - Reaction kinetics with and without impurities (1%O_2+0.1%H_2O)
    - Degraded protective Cr-rich oxide on 316H and 709
  - Evaluated 3 pack cementation coatings: G91+Cr, G91+Al, 316H+Cr
    - Cr: internal carburization observed in both alloys, less protective in sCO_2+O_2+H_2O
    - Al: ~20wt.%Al not sufficient to form protective Al-rich oxide in sCO_2 at 600°/650°C
- Tasks wrapping up
  - Creep testing Ni-base alloy foils (sCO_2 HX application)
    - Foils can show decreased strength compared to bulk material
    - More strongly affected by environment (example 1000 h 800°C air+10%H_2O)
  - Modeling C ingress
    - Determine maximum use temperature for steels to avoid C embrittlement

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

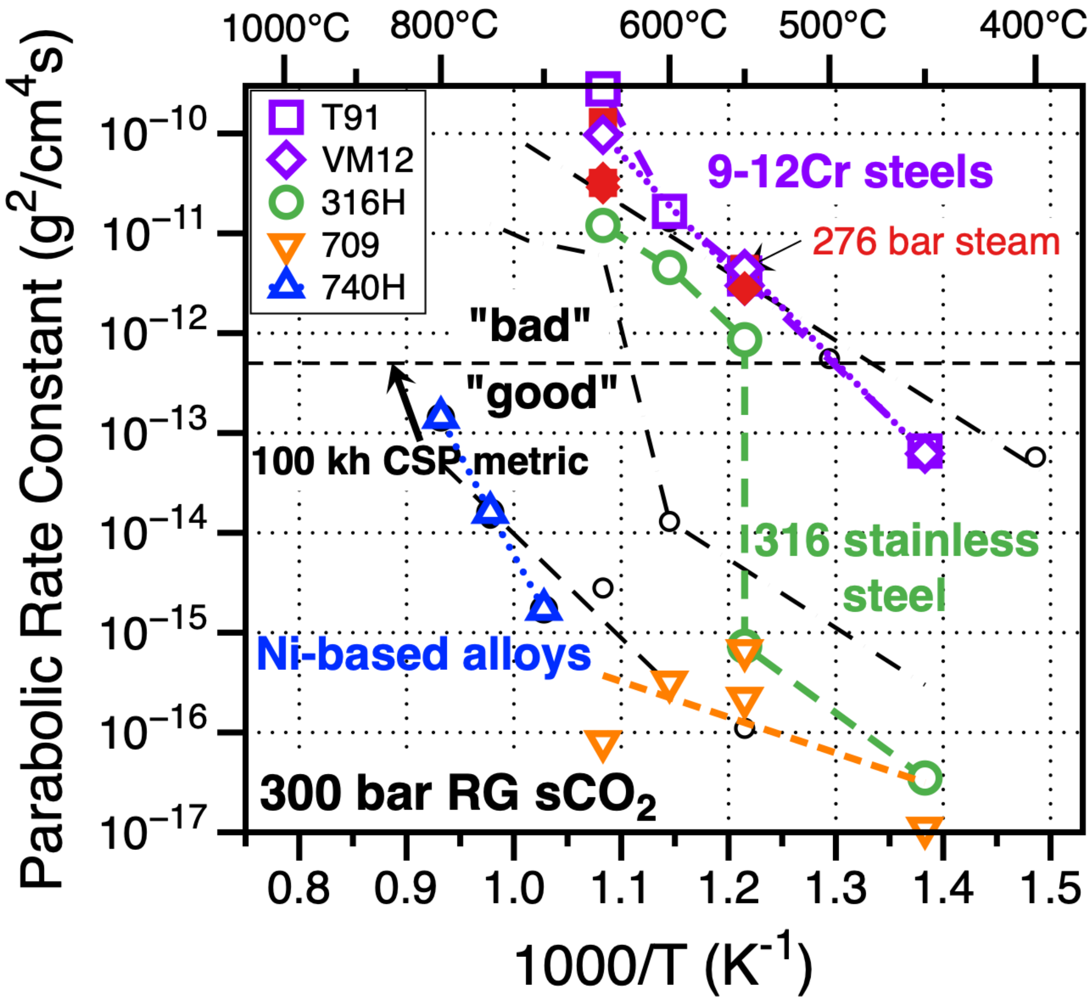
- Four primary alloys in test matrix
  - T91: Fe-9Cr-1Mo, creep strength enhanced steel
  - VM12: Fe~12Cr-Co-W
  - 316H: conventional stainless steel
  - 709: advanced austenitic, 20Cr-25Ni+Nb
- 10 specimens of each alloy
- With and without impurities (open vs. closed)

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

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

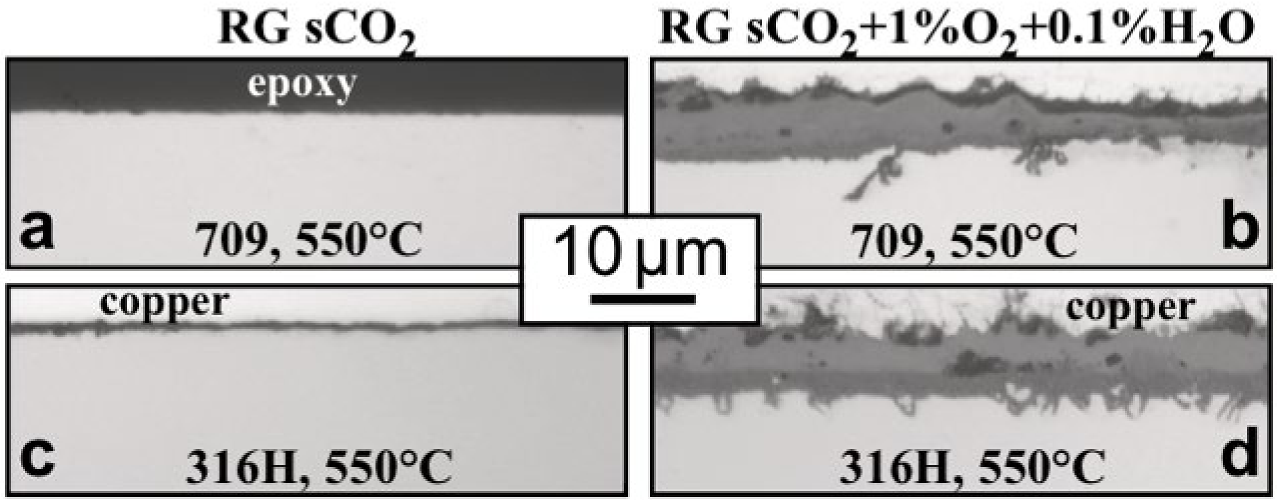


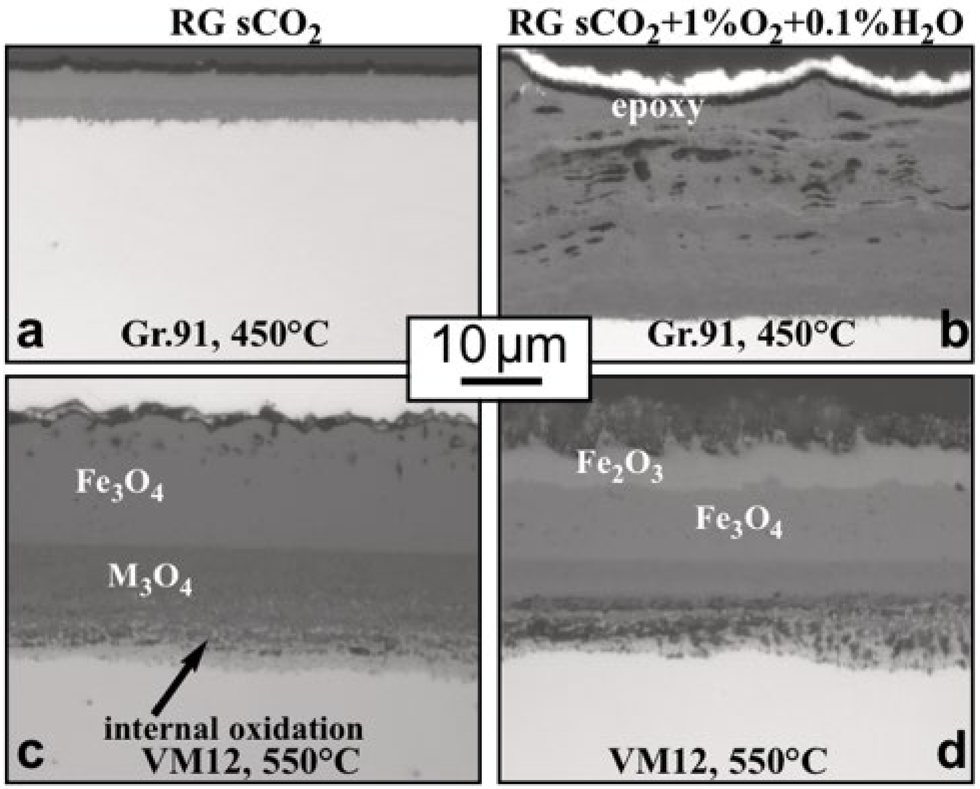
9-12Cr steels have similar rates in 276 bar steam

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

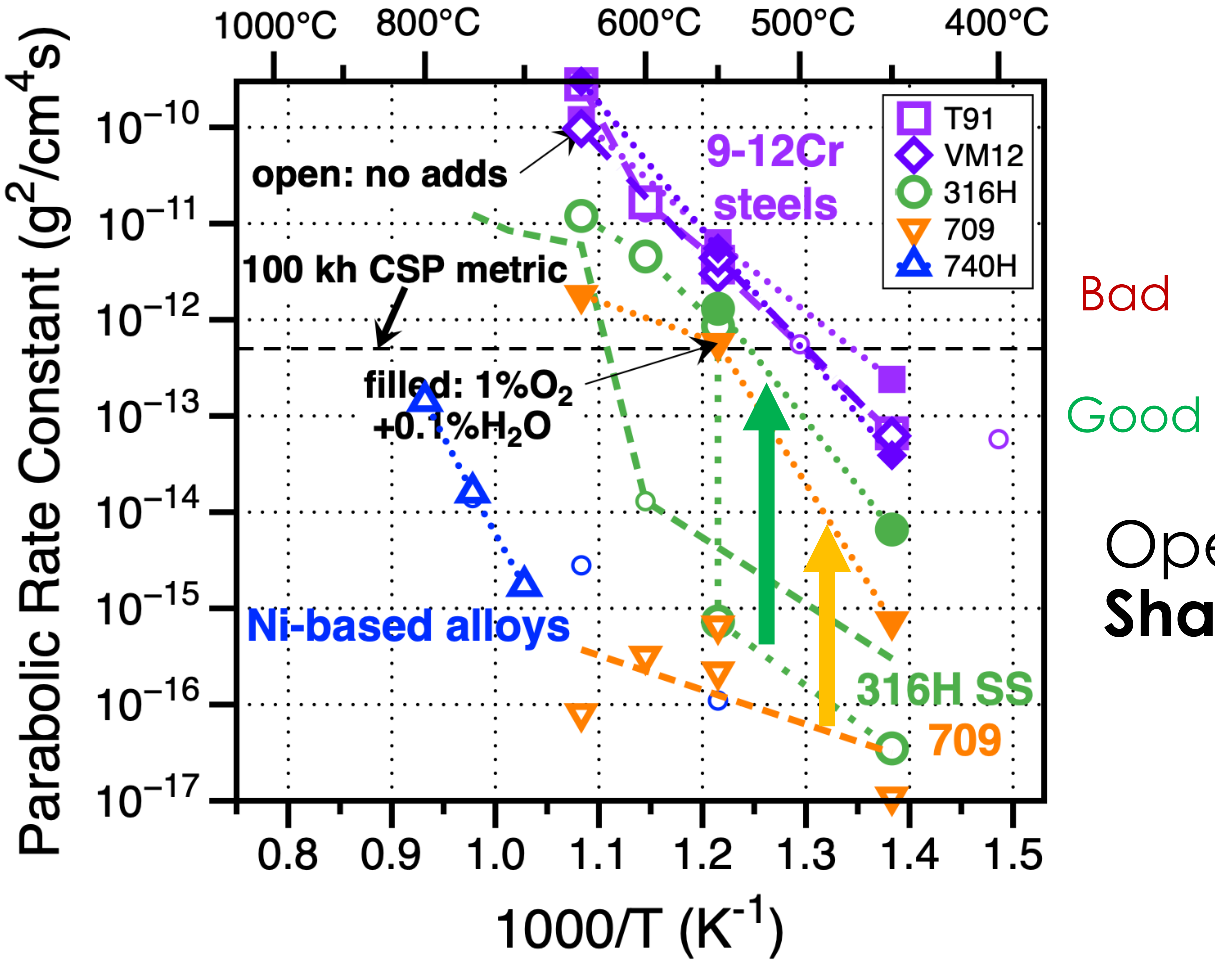
- Stainless steel (316/709)
  - RG sCO_2 : thin Cr-rich scale
    - Good C barrier
  - Impurities: duplex scale
    - Common with steels
    - Now is C ingress possible?

- 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





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

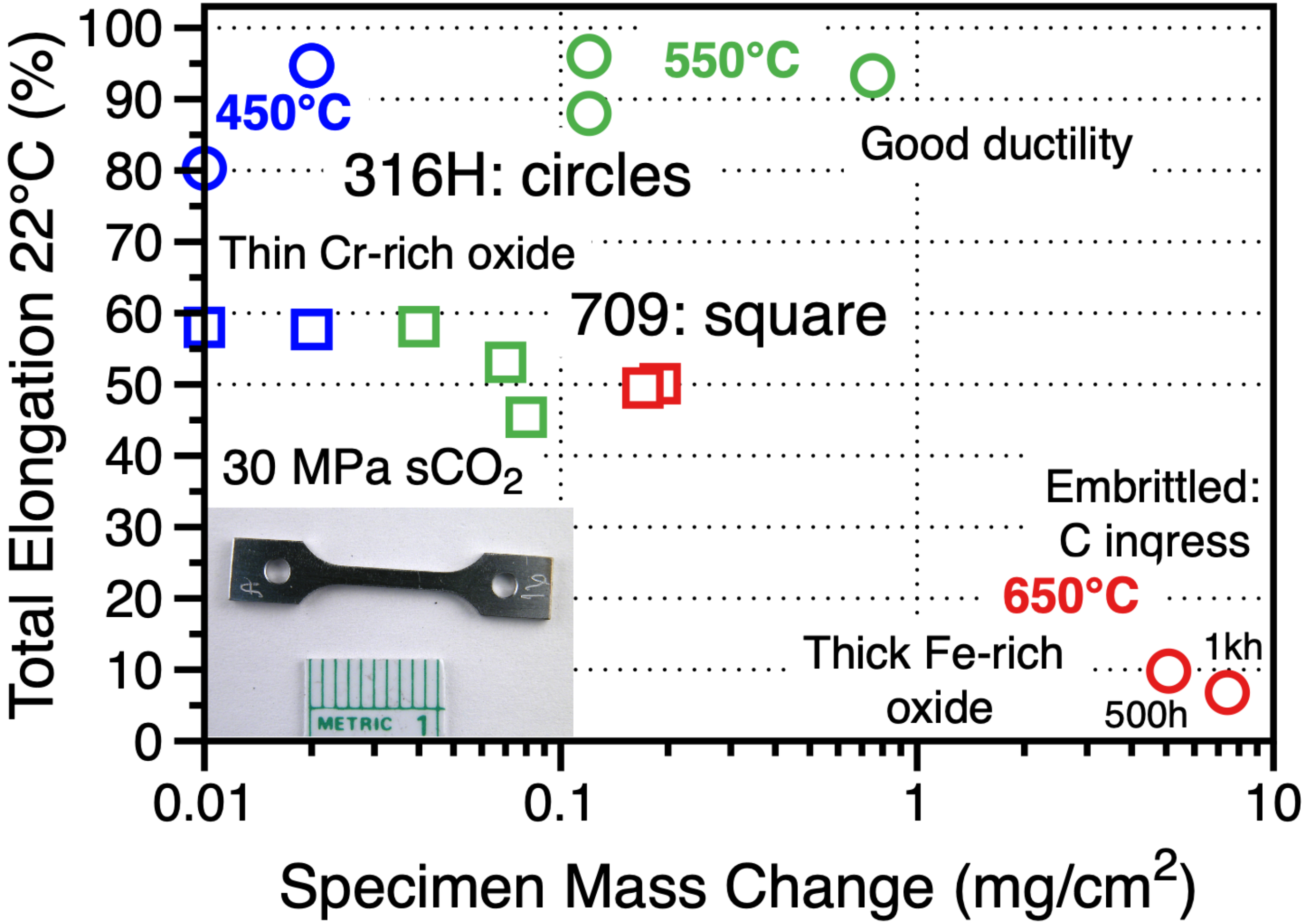
Based on CSP (solar) metric: all limited to <550°C with impurities

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

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

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

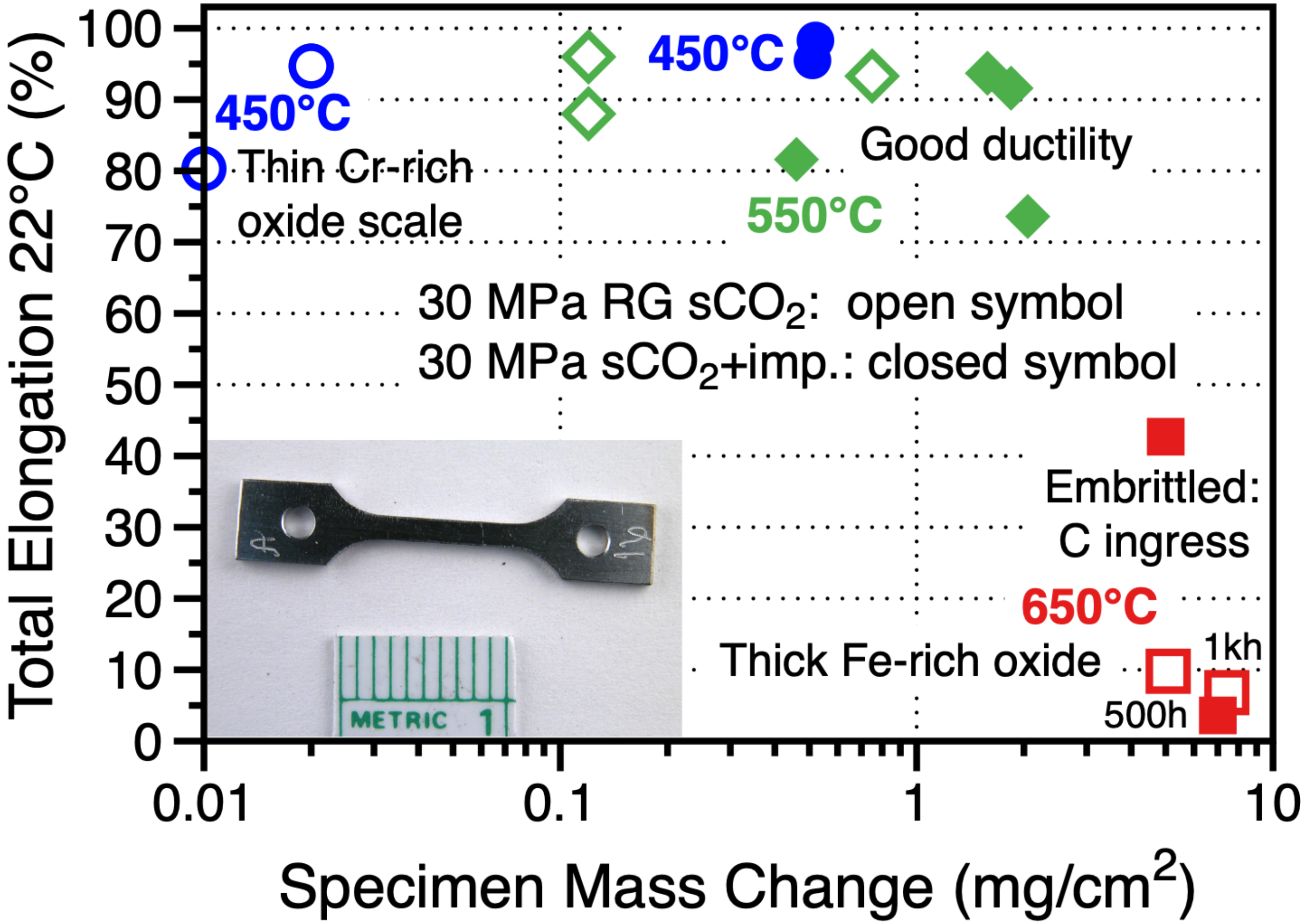


500h & 1000 h measurements for each stainless steel

Low ductility & high mass gain

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

High ductility & low mass gain

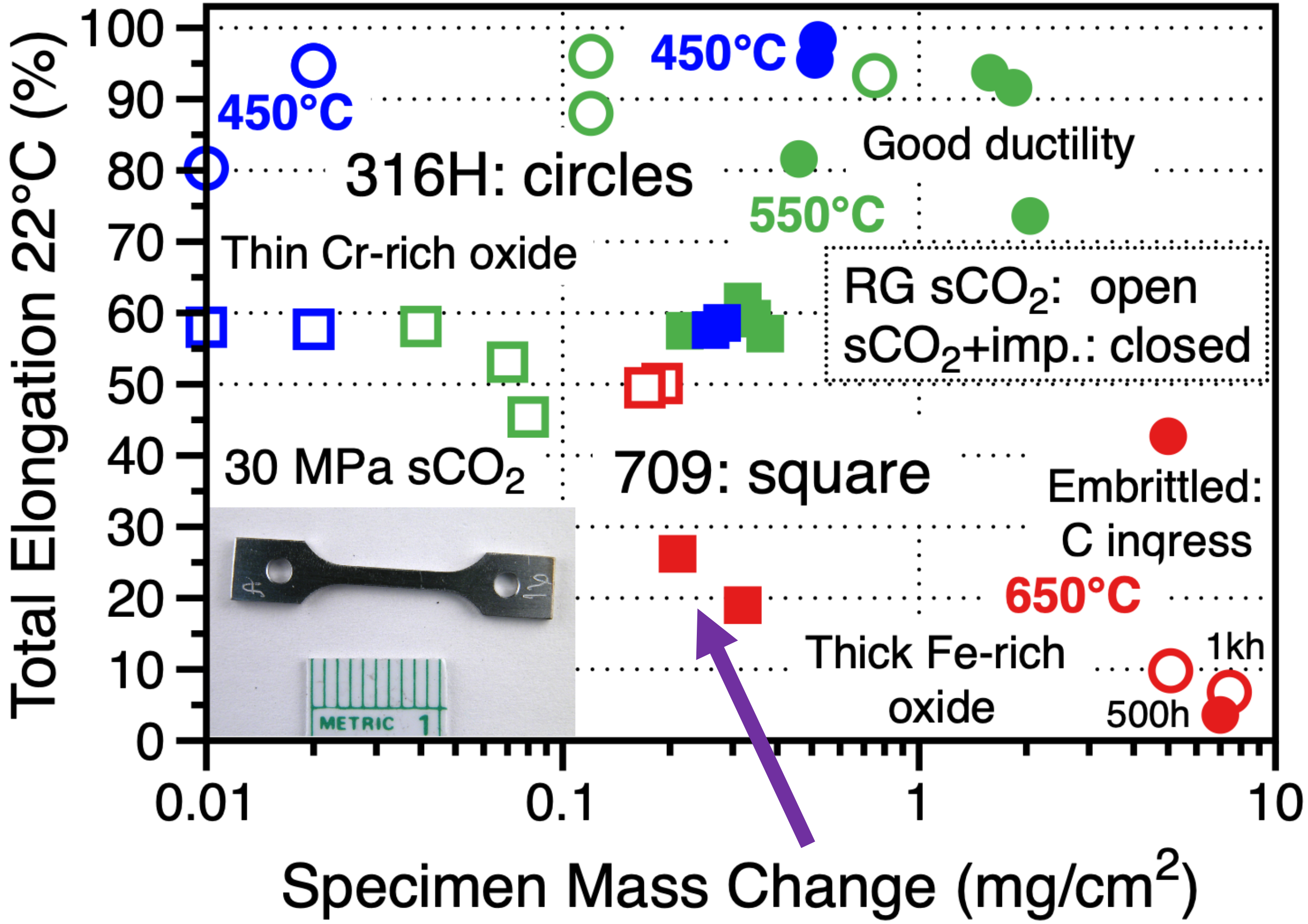


500h & 1000 h measurements for 316H

Low ductility & high mass gain

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

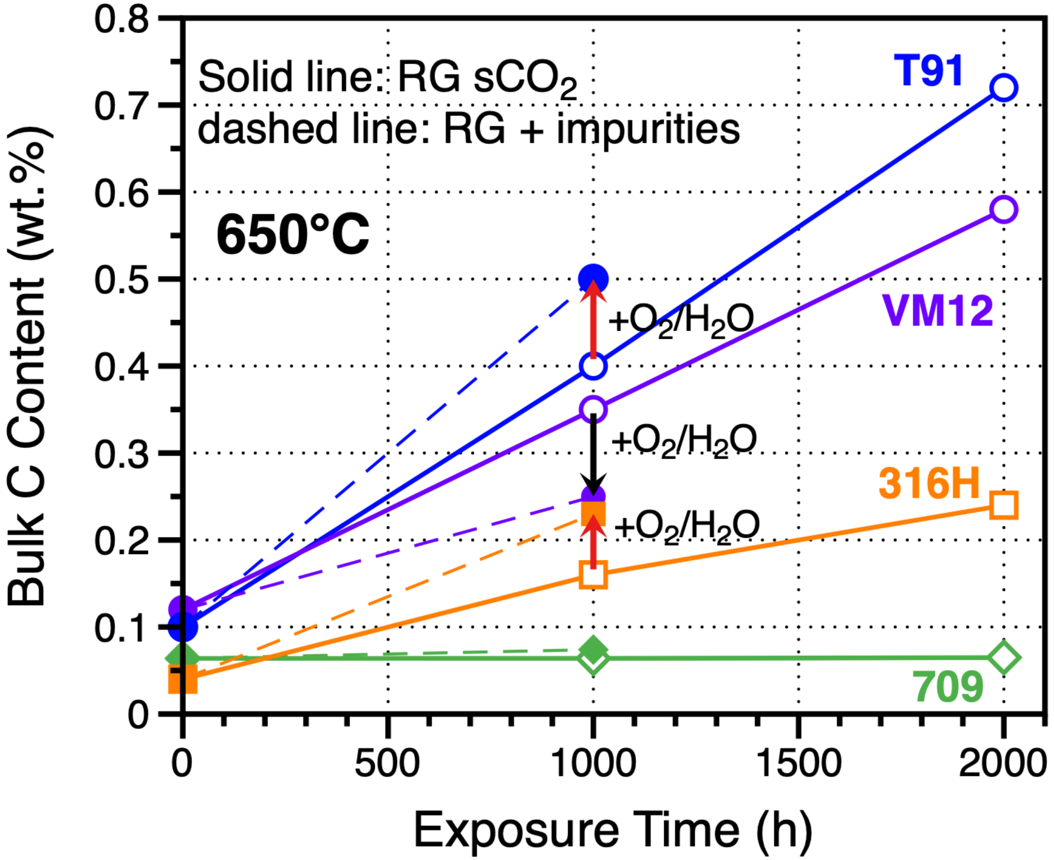
High ductility & low mass gain



500h & 1000 h measurements for each stainless steel

Low ductility & high mass gain

Bulk C measurements: Fe-rich oxides allow C ingress



RG sCO_2: No impurities open symbols

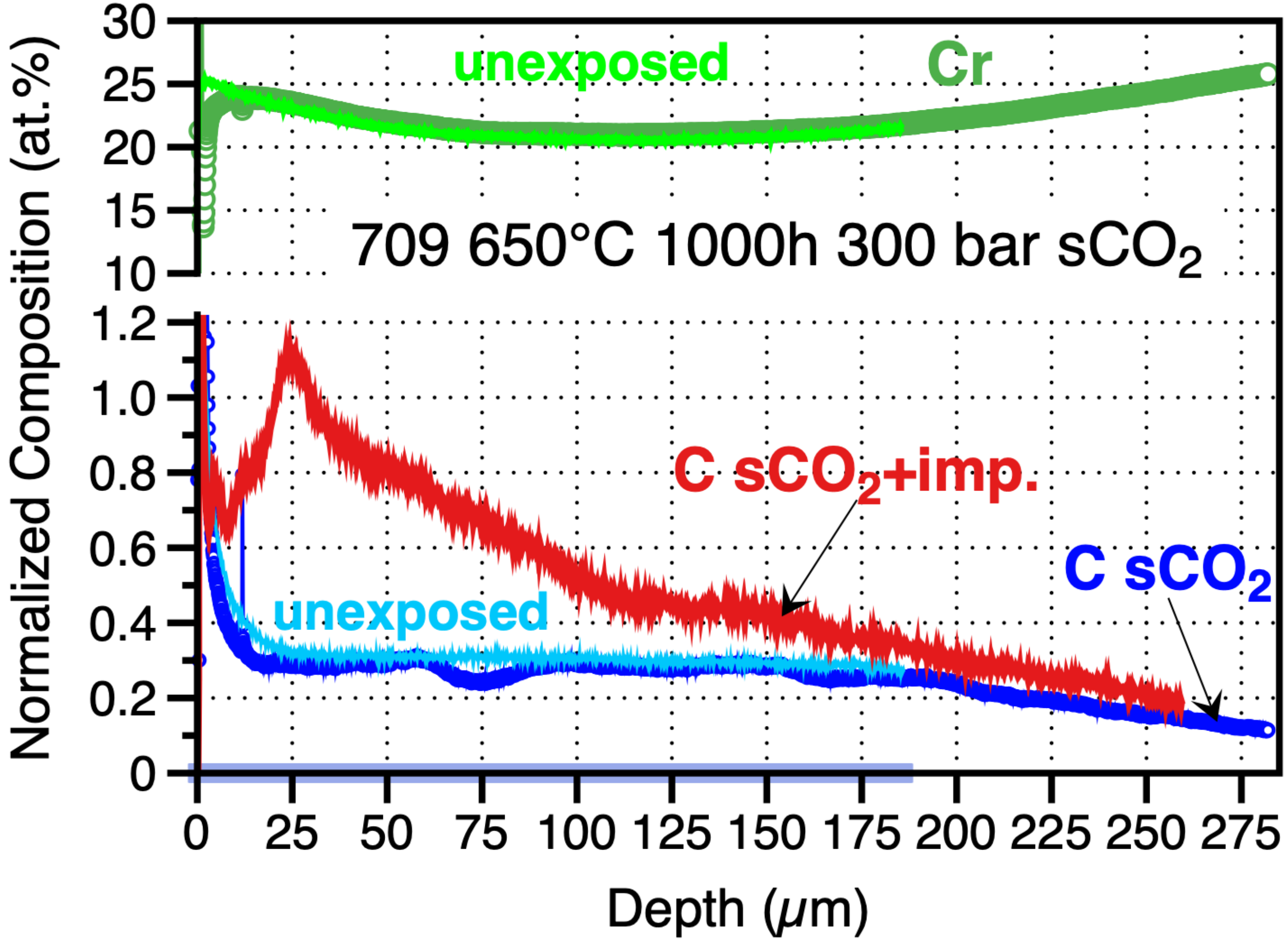
O_2/H_2O add: closed symbols

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)

GDOES of 709 specimens after 1000 h

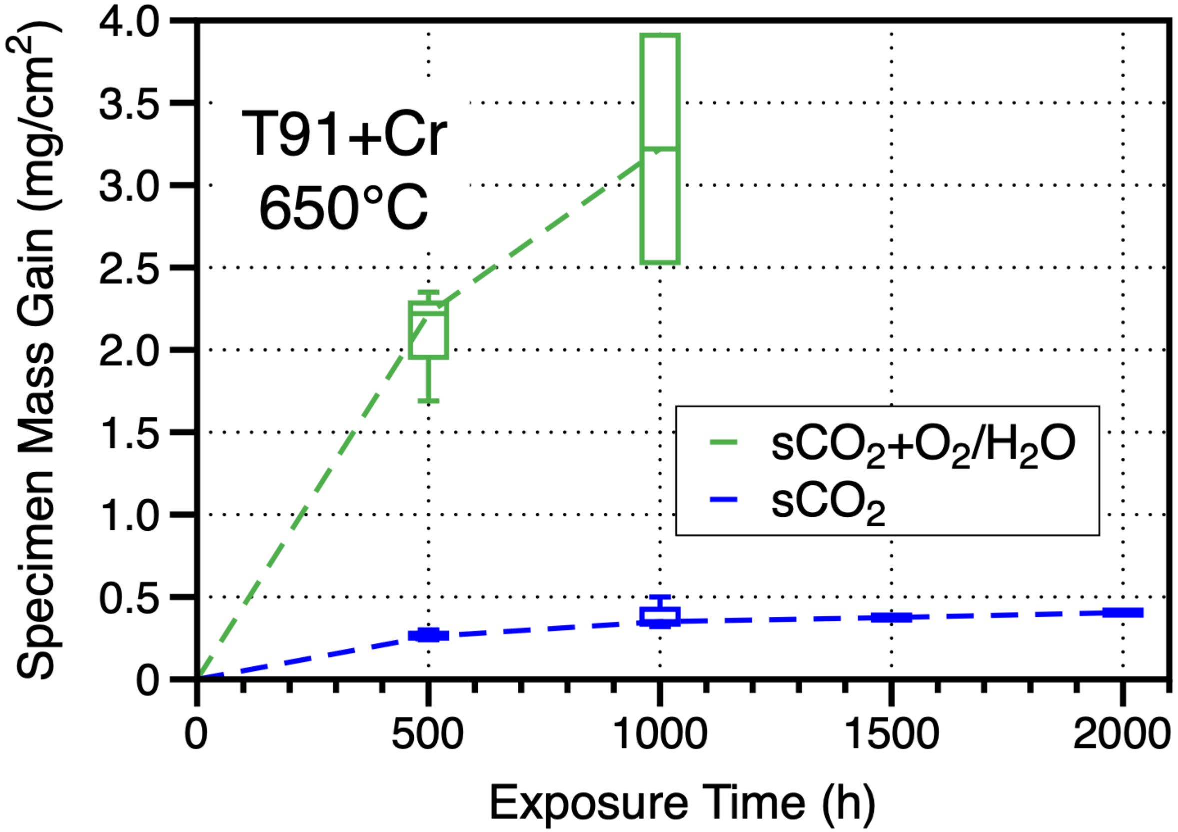
GDOES: Glow discharge optical emission spectroscopy



650°C: more C ingress with impurities

GDOES: signal normalized based on starting measured composition

Proprietary Cr pack coatings on Gr.91 tested at 650°C

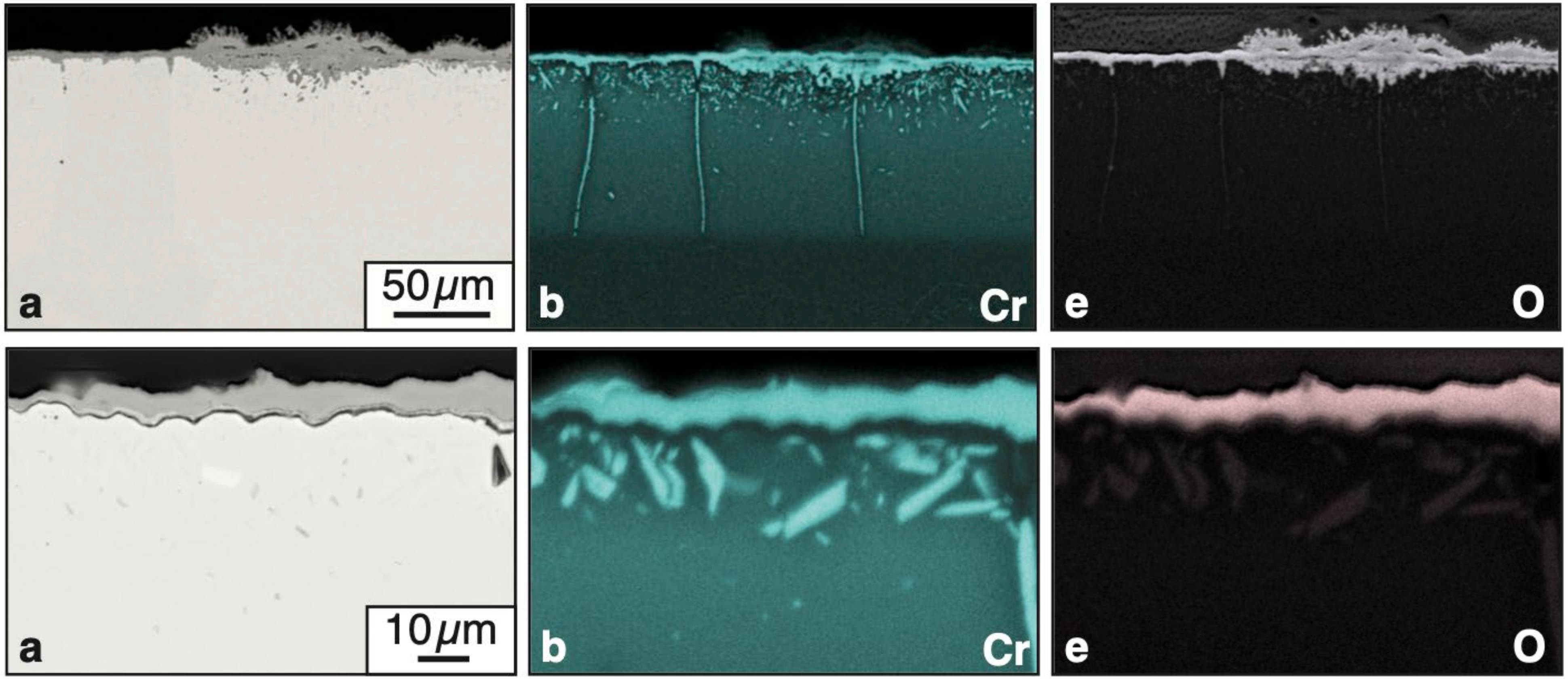


- Four specimens tested at each condition
- Low mass gain maintained in RG sCO_2 to 2000 h (2 specimens)
- Much higher mass gain in sCO_2 with 1%O_2-0.1%H_2O

SEM EDS: coating performance not promising

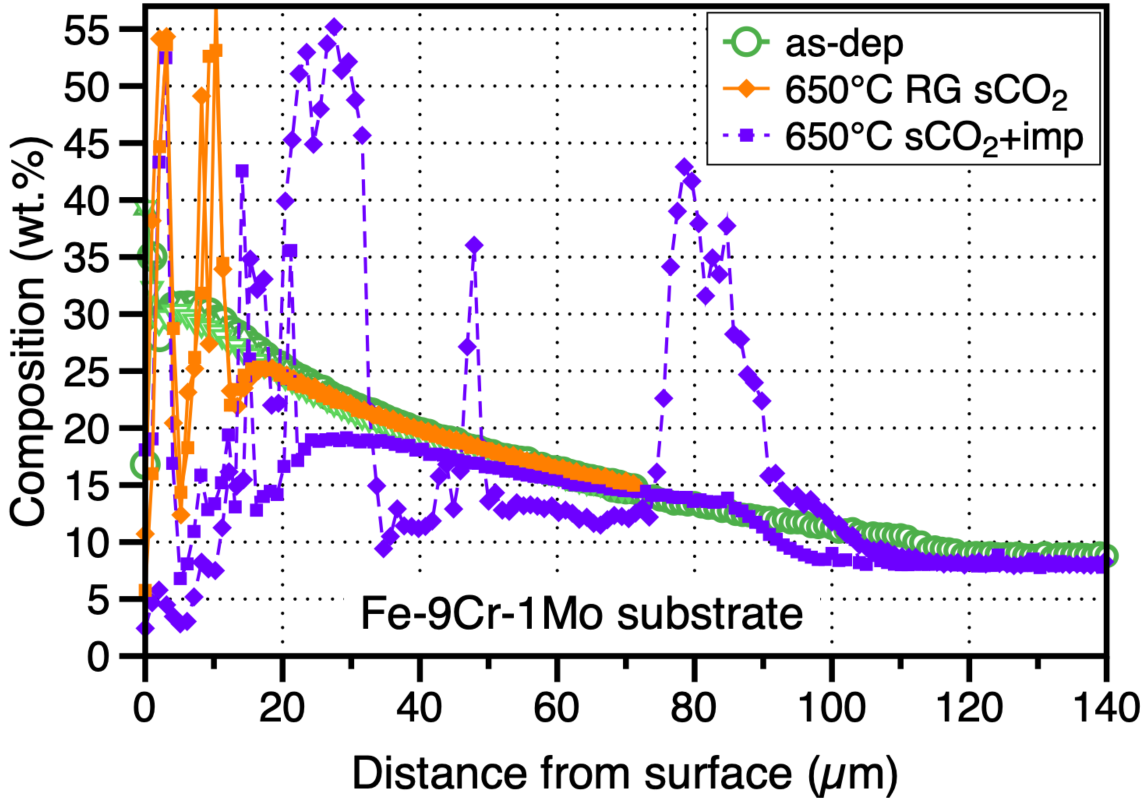
RG sCO_2
+1%O_2
+0.1%H_2O

RG sCO_2
No impurities



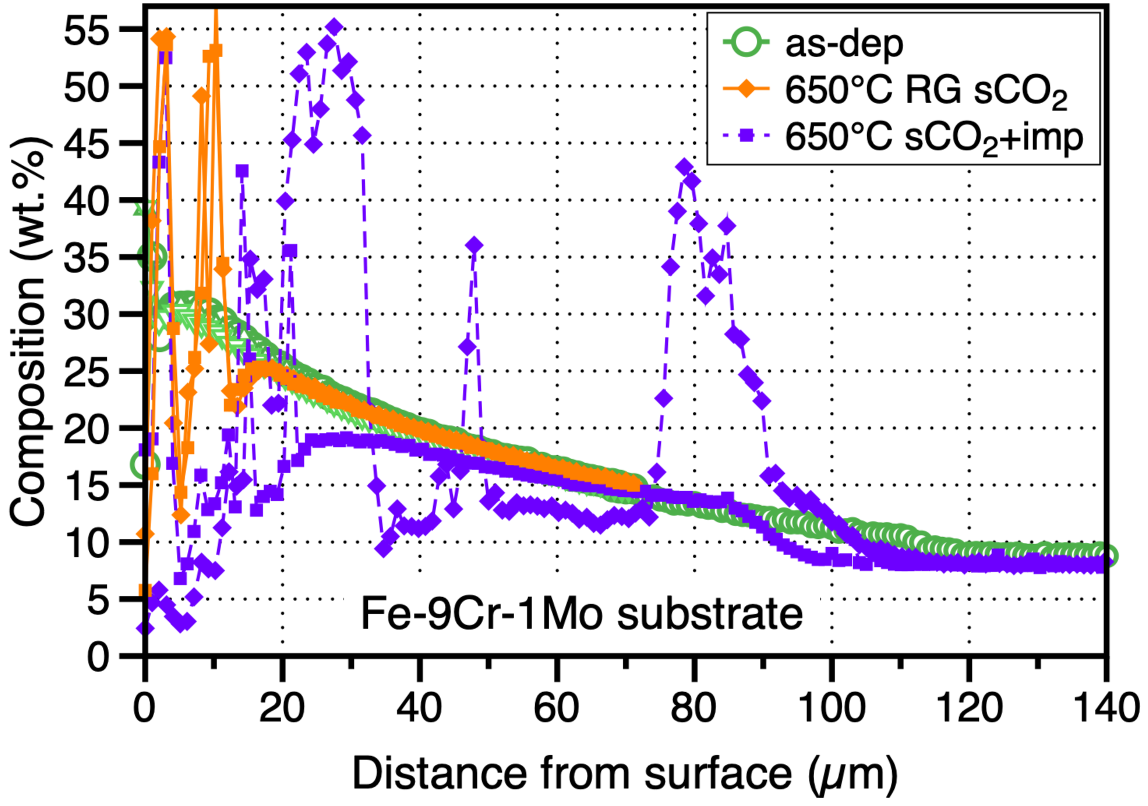
- Unable to form protective Cr-rich oxide with 1%O_2+0.1%H_2O
- Cr-rich precipitates in coating (carbides by EPMA)

sCO_2 ± impurities: significant Cr consumption by C or O

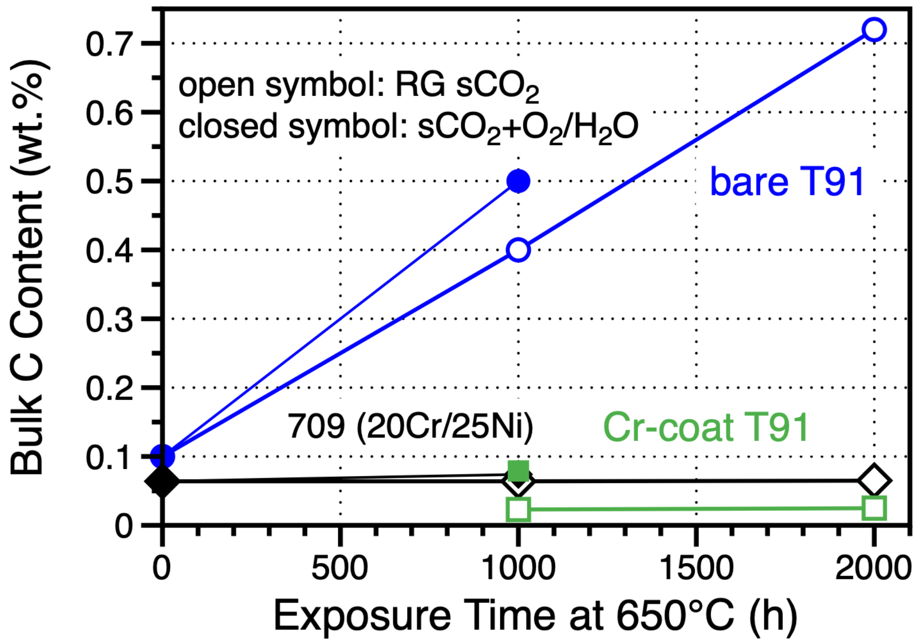


- 1000 h/650°C: higher Cr consumption with impurities
- 650°C: temperature too high for ~110 μm thick Cr pack coating

sCO_2 ± impurities: significant Cr consumption by C or O

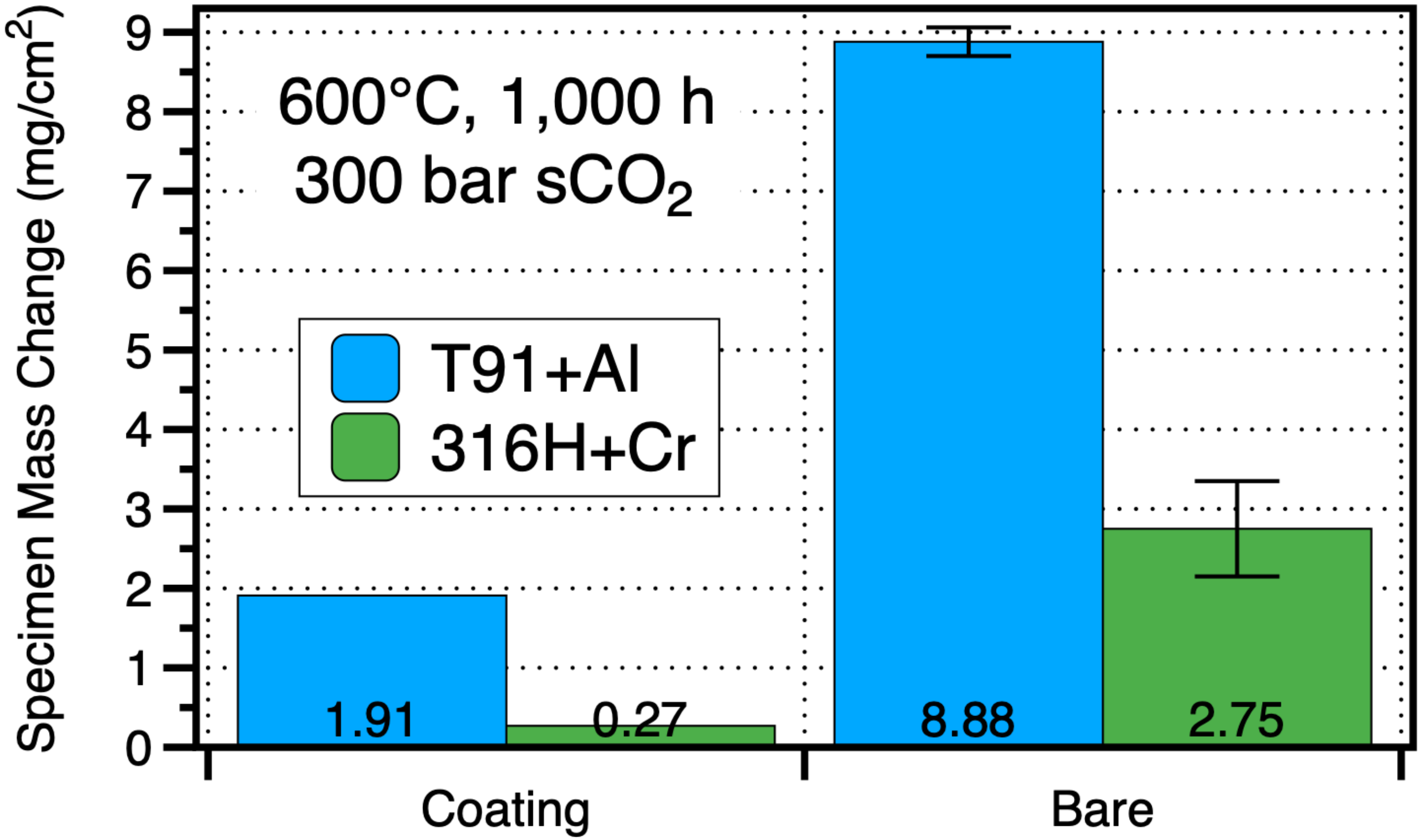


But coating blocked C!



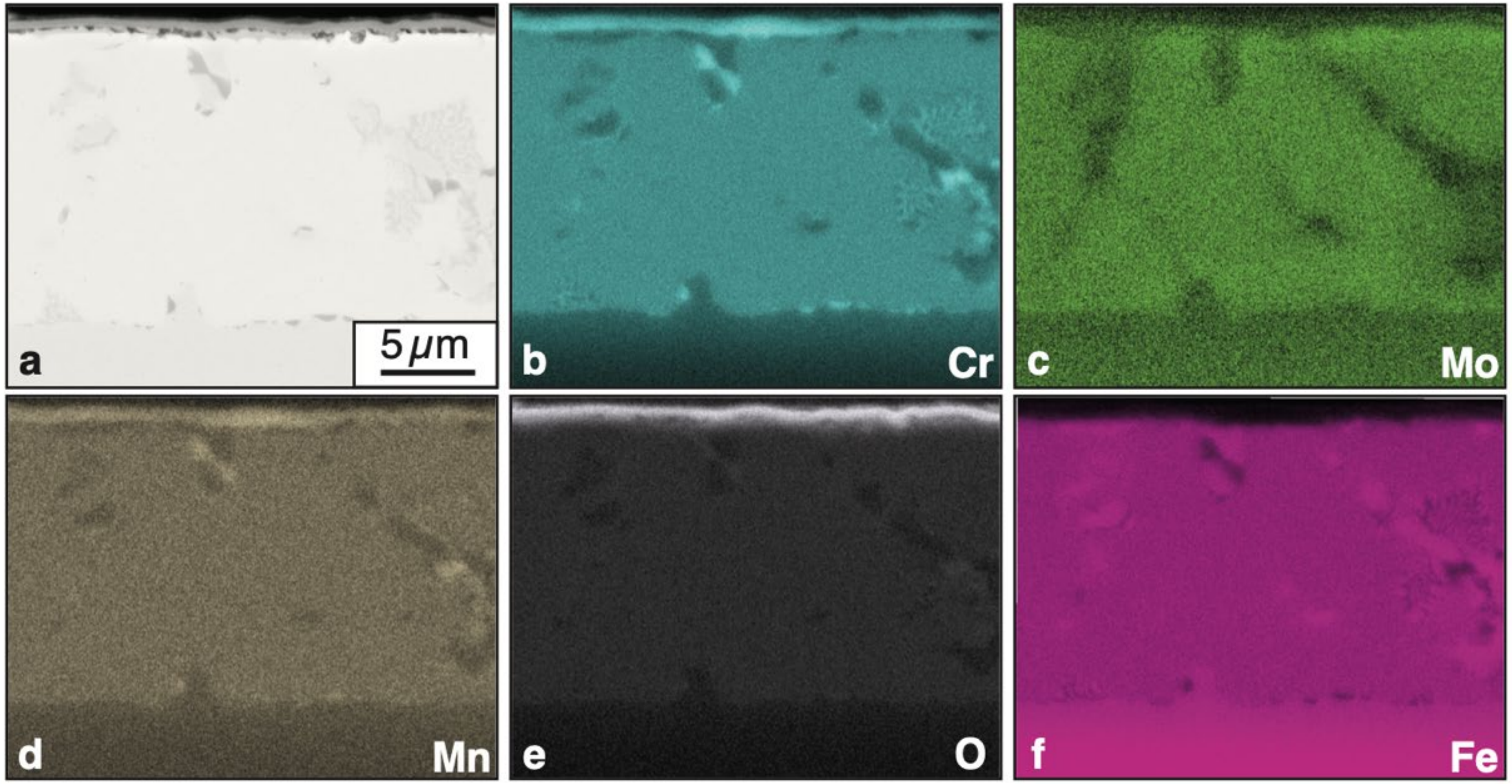
- 1000 h/650°C: higher Cr consumption with impurities
- 650°C: temperature too high for ~110 μm thick Cr pack coating

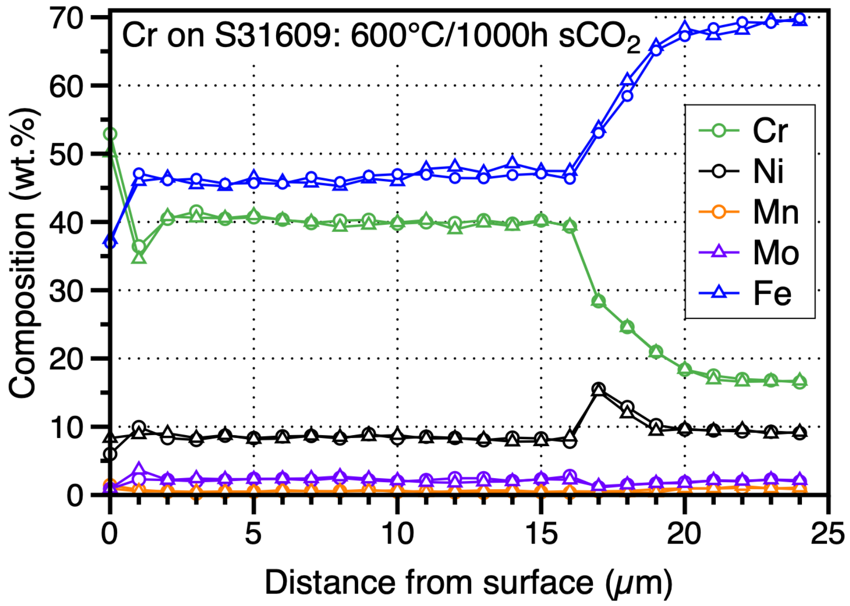
2nd batch of pack coatings also tested at 600°C in sCO_2



- Cr on 316H: similar benefit as on T91
- Aluminized T91: mass gain not consistent with Al_2O_3 formation
  - Even more difficult for selective oxidation at 600°C

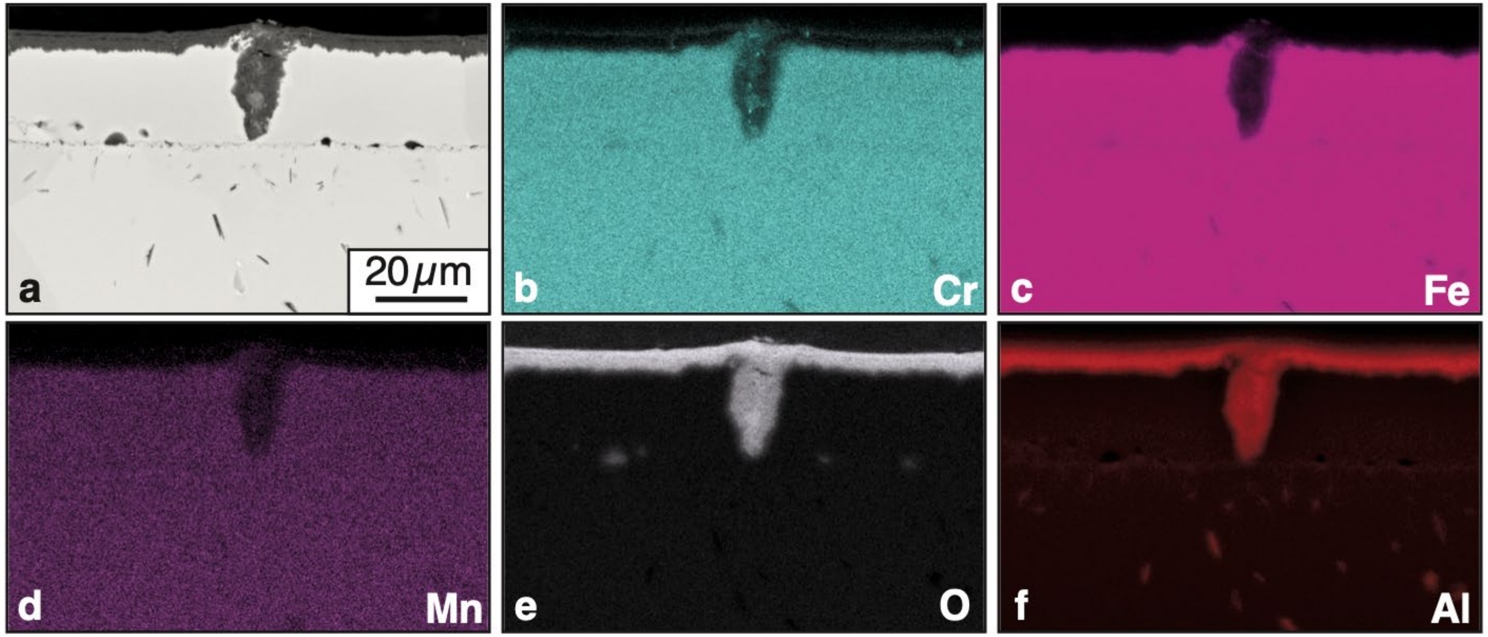
Chromized 316H: thin Cr-rich scale formed + precipitates

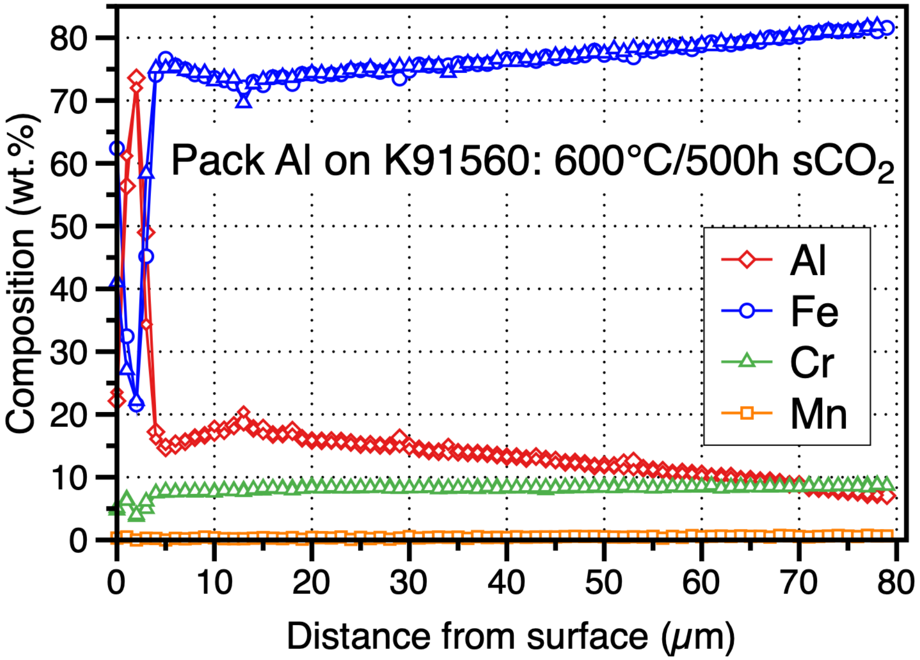




- Thinner coating formed on FCC 316H substrate
  - Again, coating made by company, no details on process
- Beneficial effect in RG sCO_2 at 600°C after 1,000 h

Aluminized Gr.91: thick oxide after 500 h



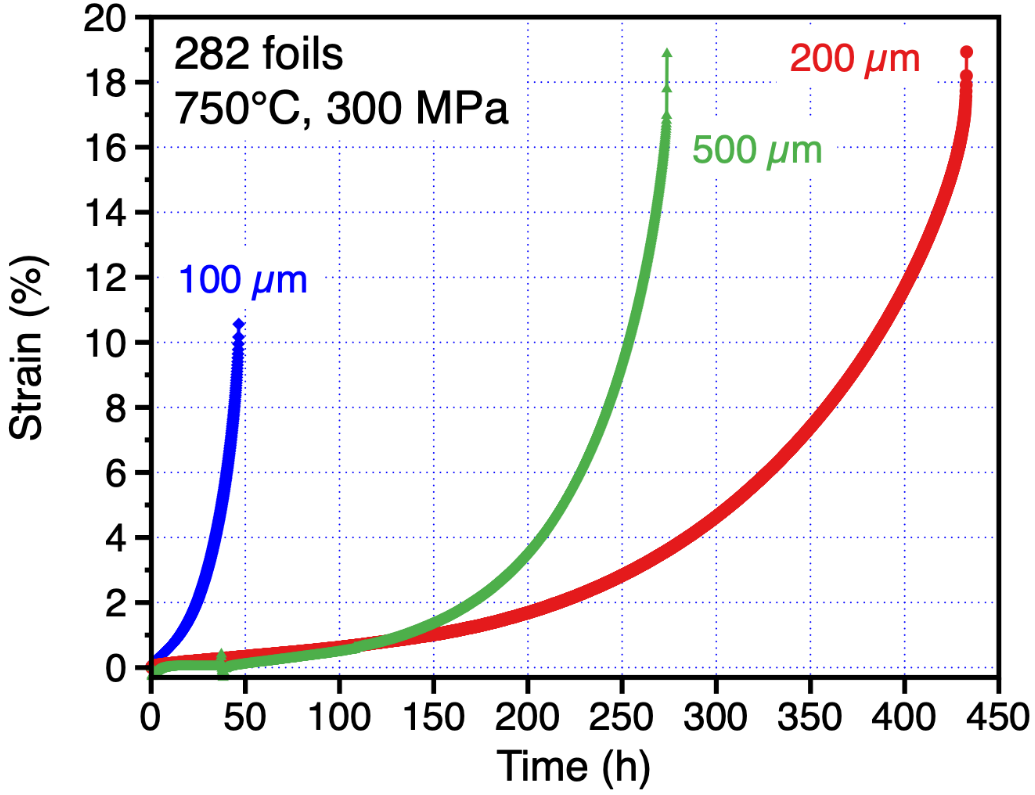


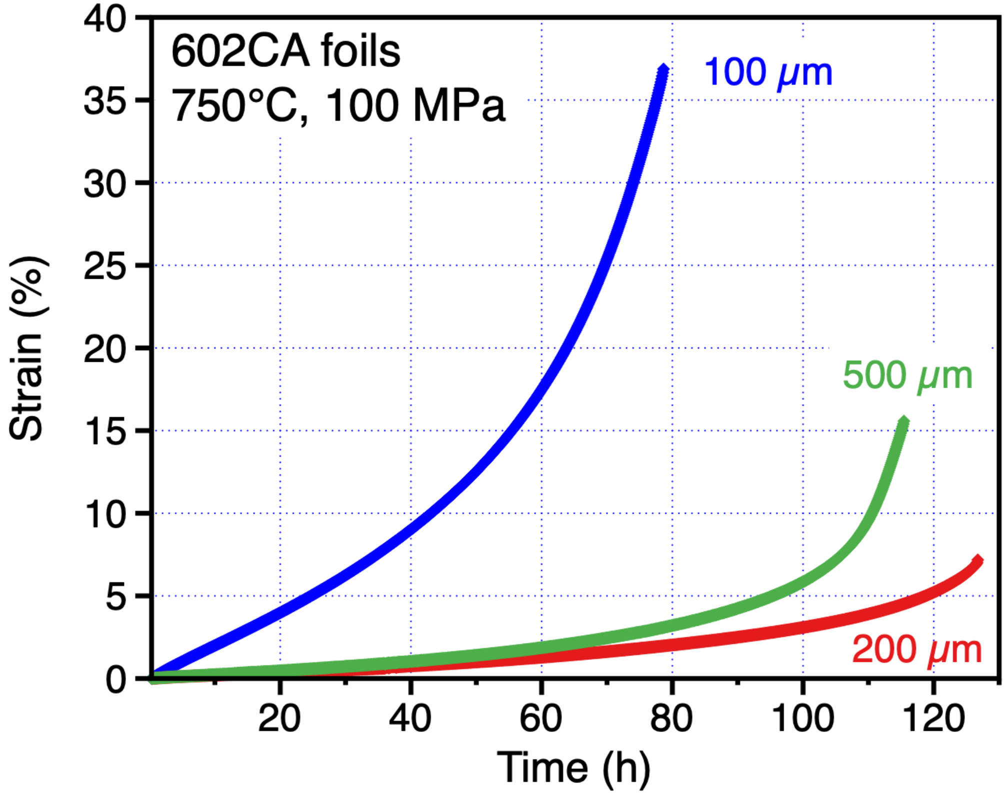
- ~100 μm thick Al diffusion profile into substrate
- Surface oxide Al-rich but thicker than expected after 500 h at 600°C in sCO_2

Thin walled heat exchanger: reduced 750°C creep lifetime for 282 and 602CA foils

282: Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti-0.06C
602CA: Ni-25Cr-9Fe-2.4Al-0.2Ti-0.2C

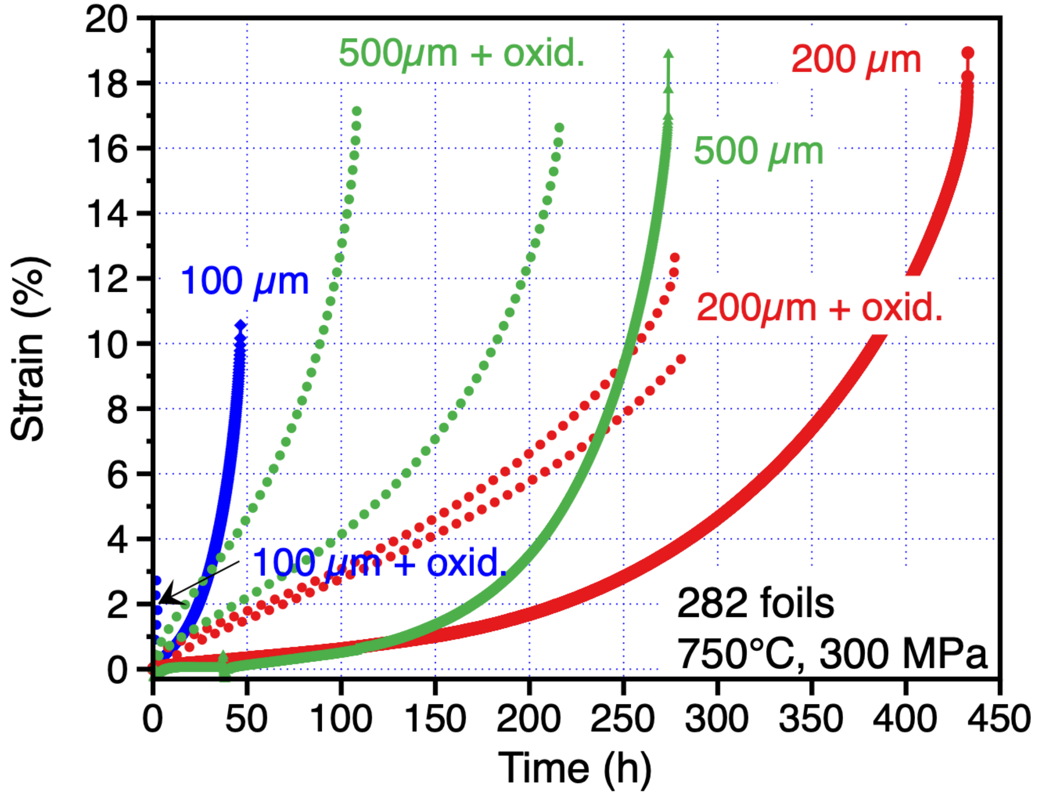
Expected lifetime for wrought = ~1500h





- Lower stress (100 MPa) for weaker 602CA material
- Lowest lifetime for 100μm foils as expected
- But 500μm foil exhibited shorter life than 200μm!

Does corrosion affect foil lifetime? Yes!
Foil creep specimens exposed 1,000 h at 800°C in wet air



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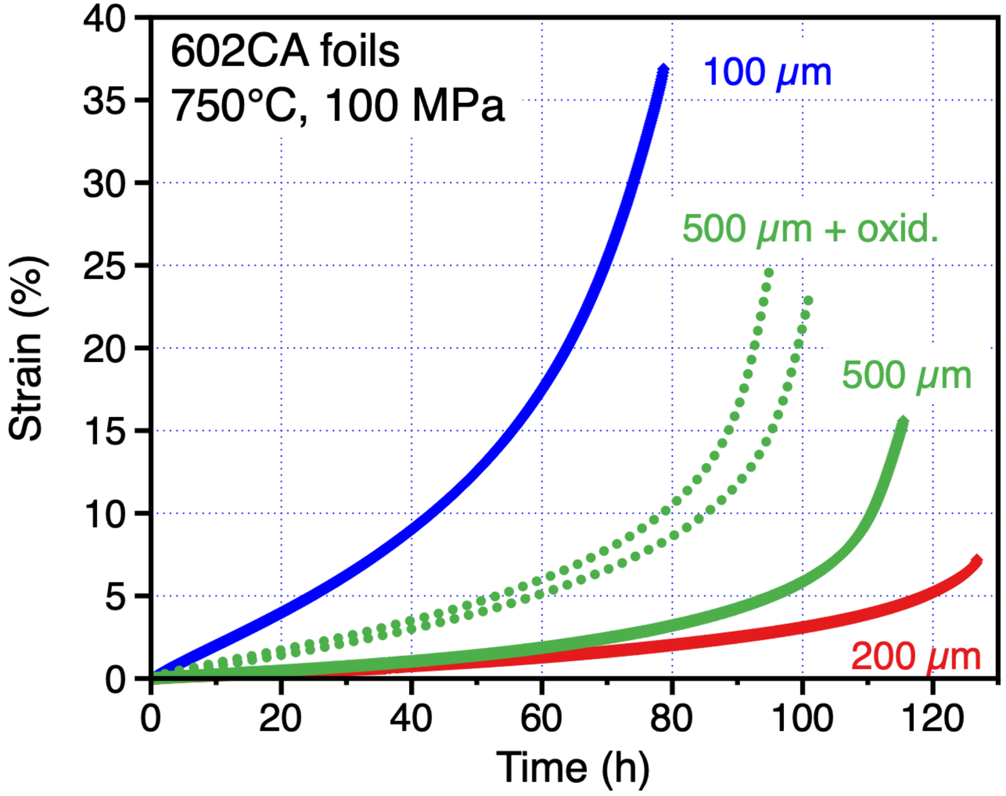
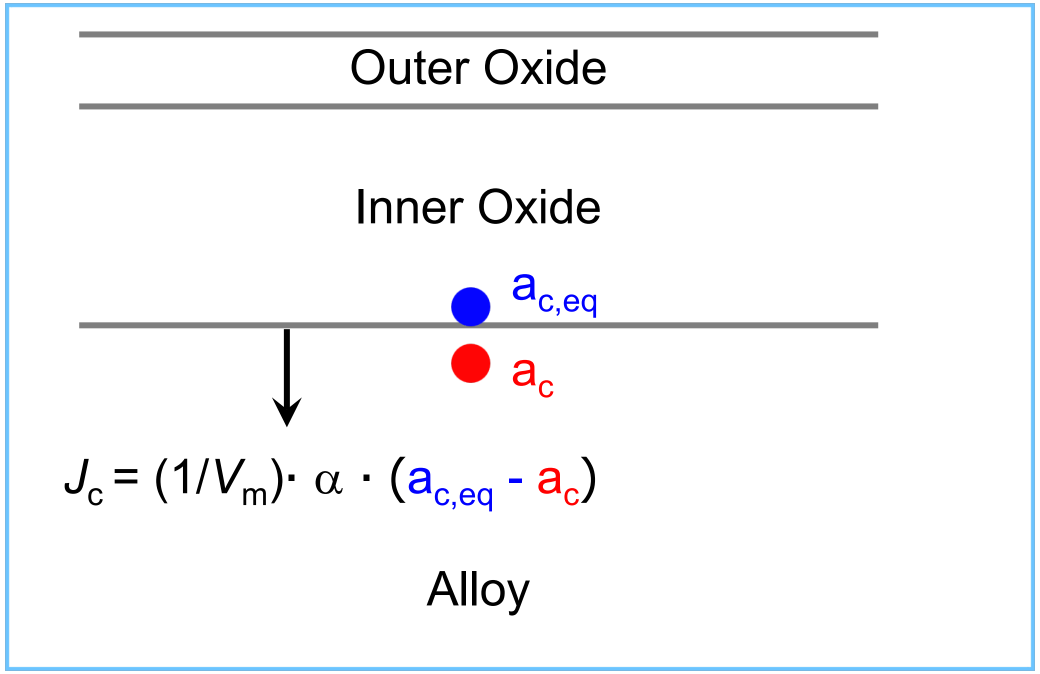
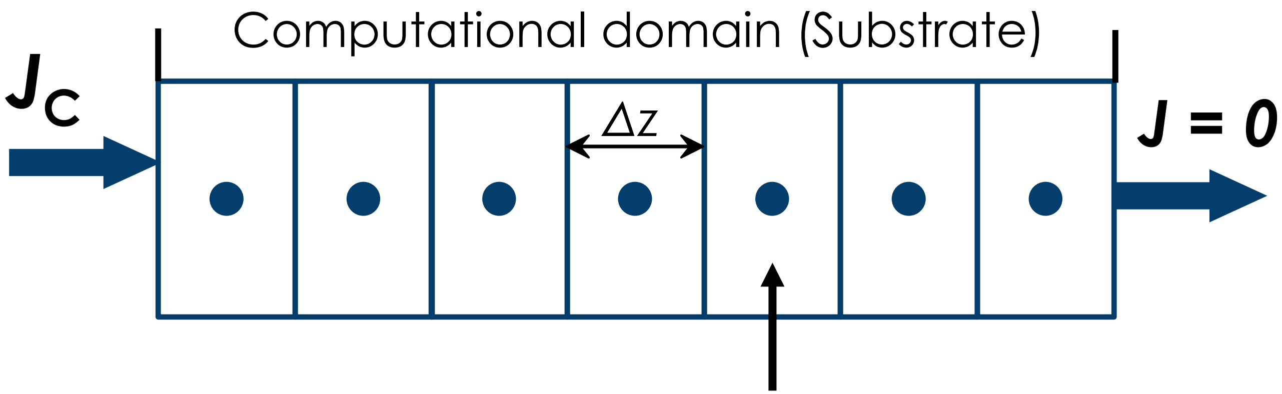


282: Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti-0.06C
602CA: Ni-25Cr-9Fe-2.4Al-0.2Ti-0.2C

- Post-test characterization in progress
- 282: internal Al + Ti oxidation reduces γ´ strengthening
- 602CA: Cr oxidation impacts carbide strengthening

One-dimensional Physics-based Modeling approach

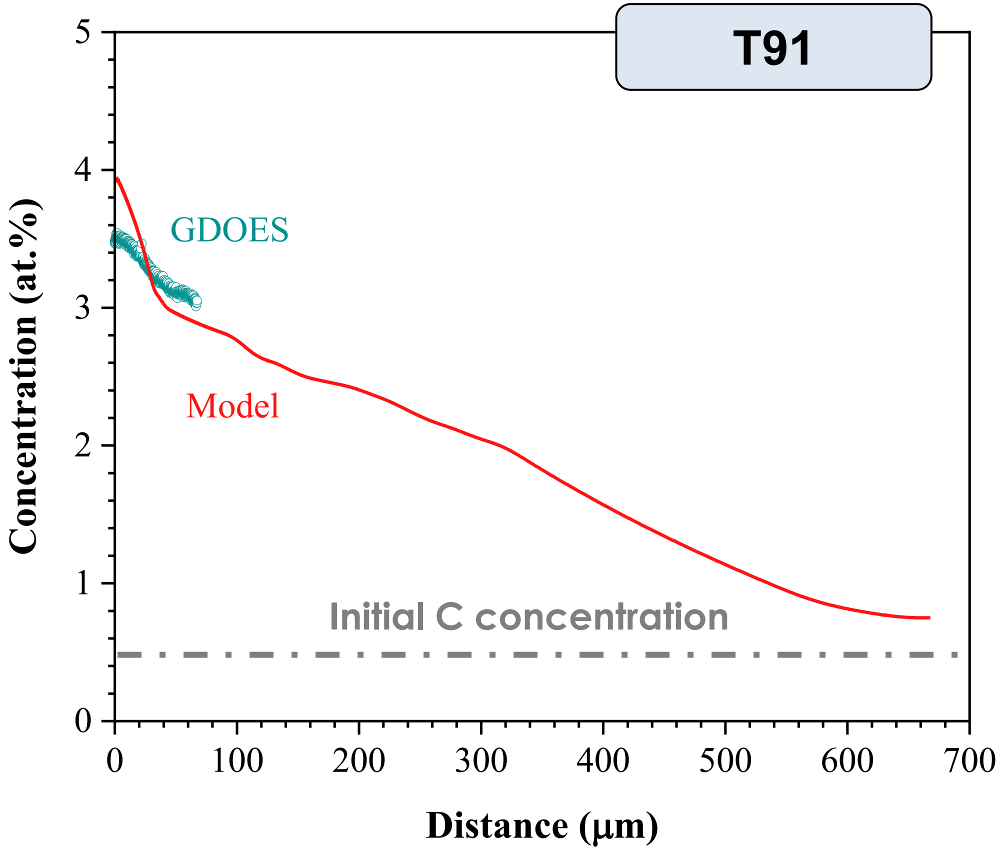


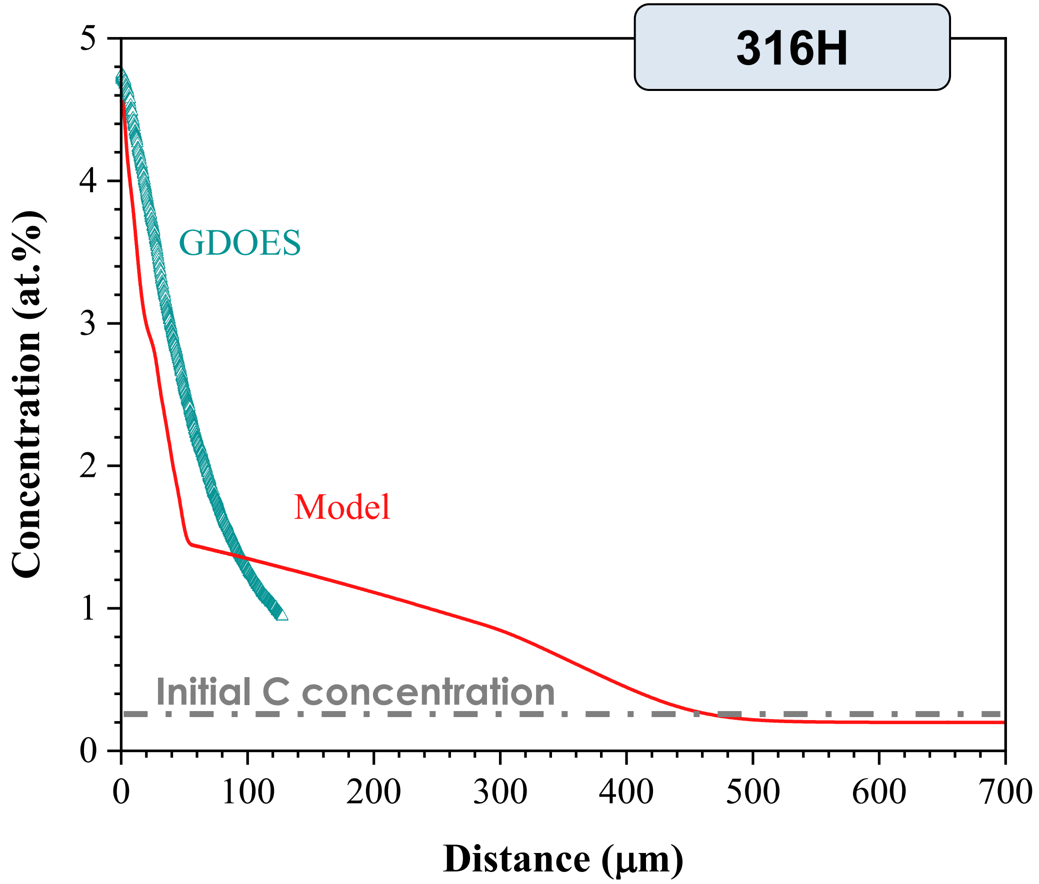


- **Calculation of element fluxes**
- **Calculation of phase equilibria**

- α is mass transfer coefficient
- Assumed $a_{c,eq} = 1$ while a_c is carbon activity in the alloy at the oxide-alloy interface
- Use of independent thermodynamic-kinetic data (Thermo-Calc)
- Empirical description of grain boundaries (e.g., accelerated diffusion)
- Consideration of relevant elements & phases in commercial high temperature alloys and coating systems
- Thermodynamic calculations on multiple cores
  - 30,000h simulation of multicomponent-multiphase alloys in < 1 week

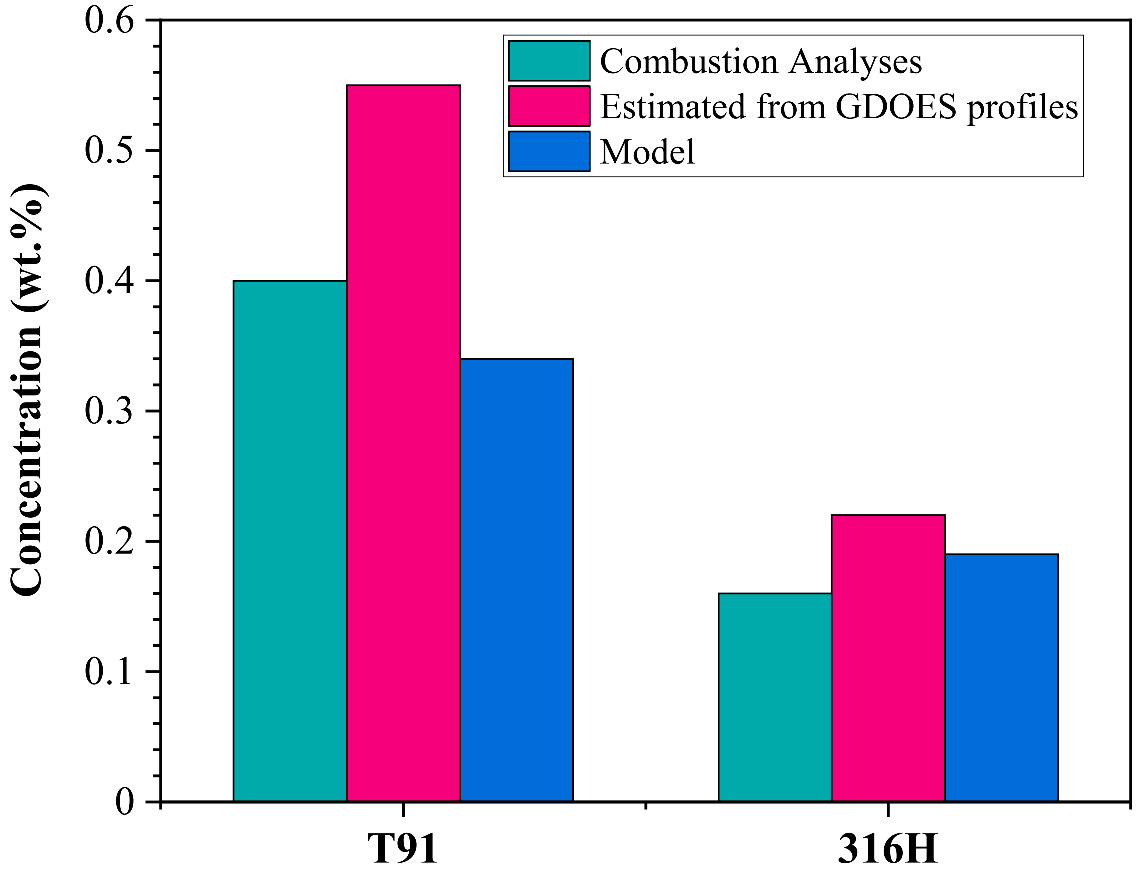
Model qualitatively predicted the observed differences in carburization behaviors between T91 and 316H after 1000 h at 650 °C in sCO_2





- **Almost complete carburization expected for a 1.5 mm T91 specimen**
- **About 0.4 mm carburization depth predicted for 316H**

Good agreement between the measured and predicted C-uptake for T91 and 316H after 1000h at 650 °C in sCO_2 (without impurities)

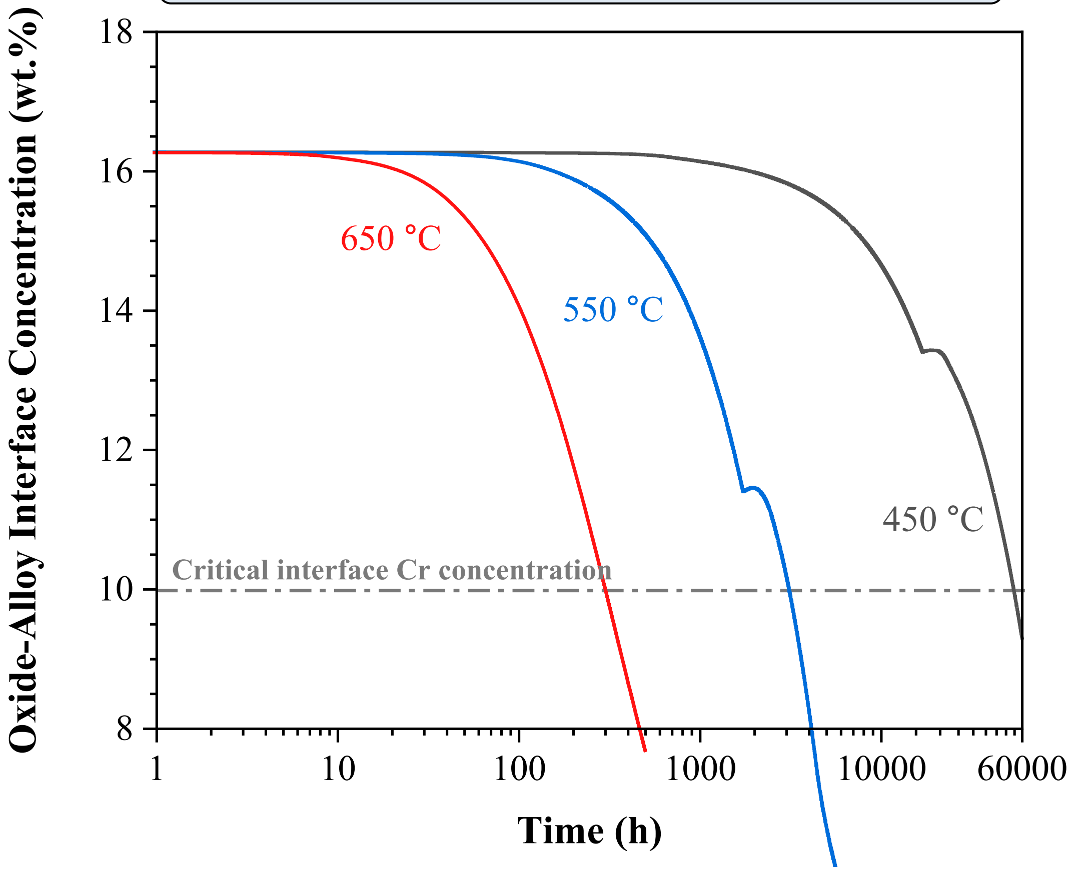


- ➢ **Linear extrapolation of GDOES profile from measurement depth to specimen center is most likely resulting in overestimation of C uptake**

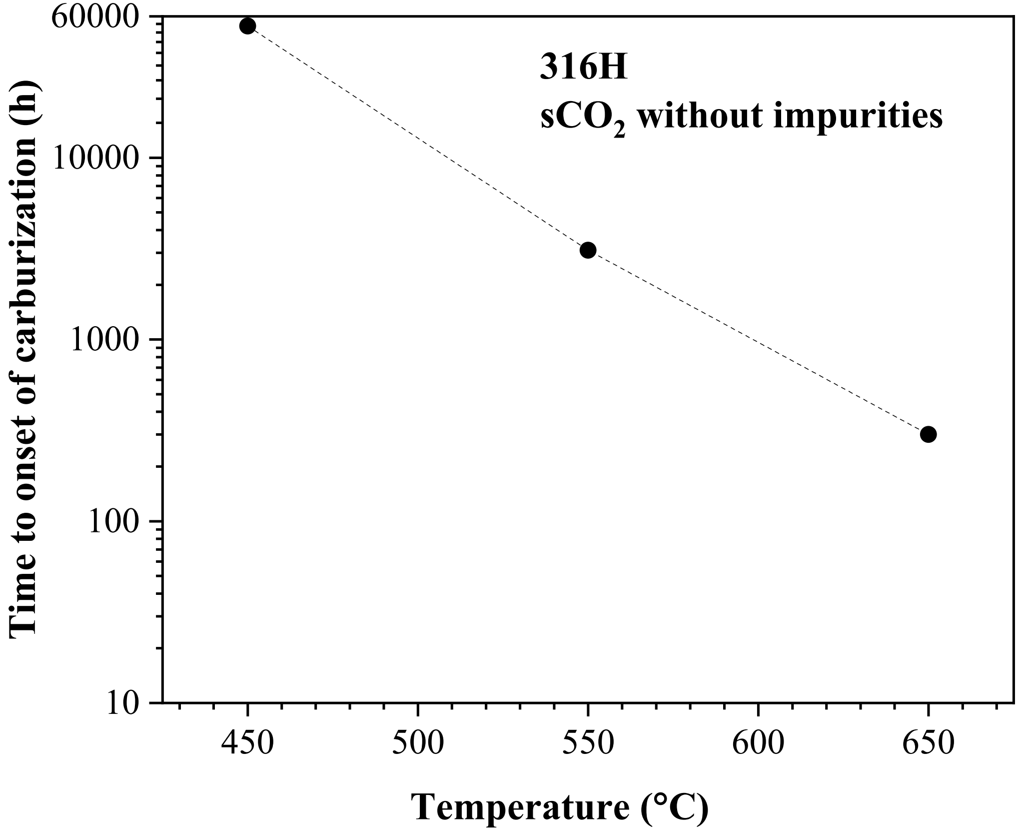
How long can 316H provide carburization resistance at lower temperatures?

Conservative estimates*: 316H predicted to resist carburization for up to 60,000 h at 450 °C and 3100 h at 550 °C

Time to breakdown of protective oxidation



Time to onset of carburization

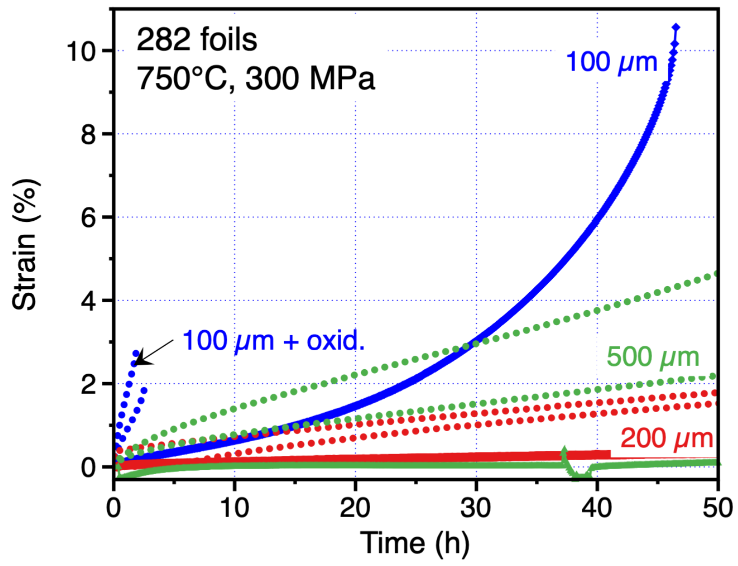


- *Time to start forming Fe-rich oxides when C ingress can begin
- After C ingress begins, next stage is to model time to impacting mechanical properties
- Strong need for model validation

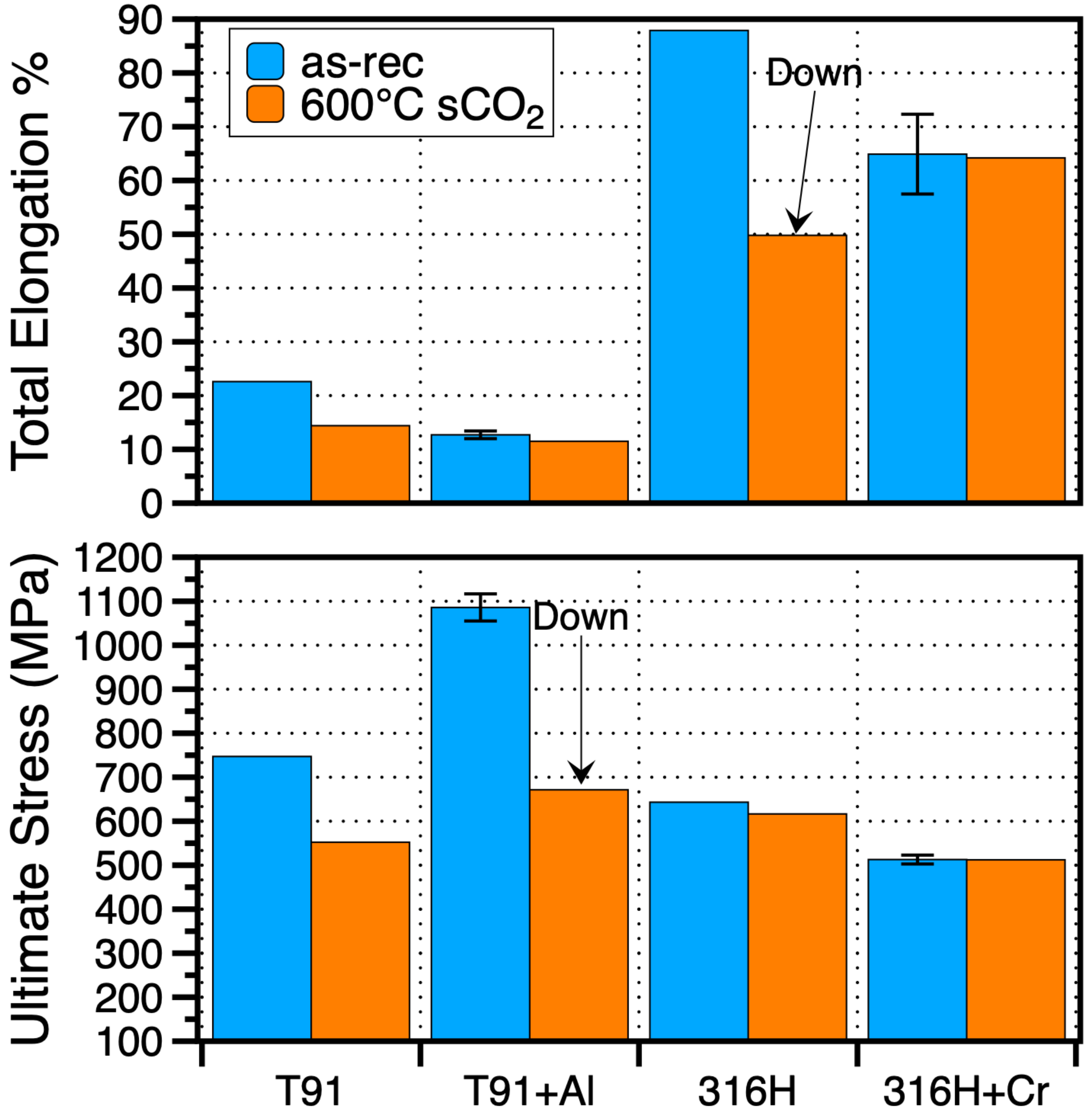
Summary: sCO_2 is a challenging environment

- Steels degrading at 550°-650°C in 300 bar sCO_2
  - Increased attack when O_2 and H_2O impurities in sCO_2
  - Even 709 (20Cr-25Ni) showed signs of embrittlement at 650°C with O_2+H_2O
- Opportunity for coatings?
  - Pack Cr and Al coatings evaluated on T91 and 316H at 650°C in sCO_2
    - Cr on T91: reduced mass gain but internal carbides + less protective with O_2+H_2O
  - Initial exposure at 600°C in sCO_2
    - Al on T91: ~20wt.% Al not sufficient to form protective Al-rich oxide
- At 650°-800°C, Ni-based alloys appear compatible
  - Thin wall HX: creep testing 100-500 μm foils of 282 and 602CA in air:
  - Reduced lifetime especially for 100 μm foils
  - Further degradation when oxidized (800°C in wet air to accelerate effect)

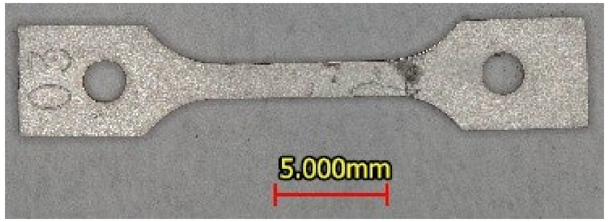
Questions?


282 foils
750°C, 300 MPa
100 µm
100 µm + oxid.
500 µm
200 µm
Strain (%)
Time (h)
0
2
4
6
8
10
0
10
20
30
40
50

Post-600°C sCO_2 exposure room temperature tensile testing



- 0.015/min strain rate
- **T91 HT: ~1050°C + ~700°C temper**
- Pack aluminized T91
  - Reduced ductility as coated
  - Drop in UTS vs. as-coated
  - 1050°C pack affected properties
    - Similar to normalization (temper in sCO_2)
- Cr-coated 316H
  - Lower properties after coating
  - No ductility loss after 600°C sCO_2



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