Defining Temperature Limitations for Steels in sCO_2 Applications

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Acknowledgments

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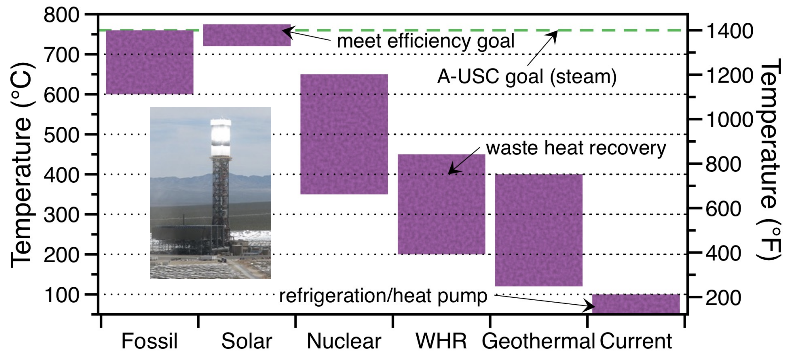
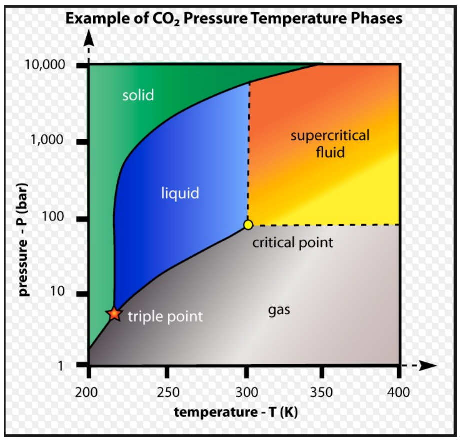
- M. Howell (retired), B. Johnston — oxidation experiments
- T. Lowe — SEM, image analysis
- V. Cox — metallography
- Special thanks for alloys:
  - Tenaris (T91)
  - EPRI (VM12)
  - Sam Sham, INL (709 NE code case material)

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

Supercritical CO_2 applications



sCO_2 has many unique & attractive aspects



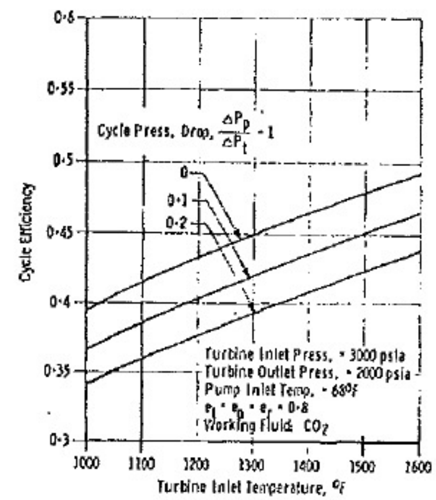
- **Low critical point (31°C/7.4 MPa)**
- **High, liquid-like density**
- **Flexible, small turbomachinery**

Cost is a concern:

Ni-based alloys: OK in sCO_2

Where can steels be used?

Interest in >700°C for high efficiency

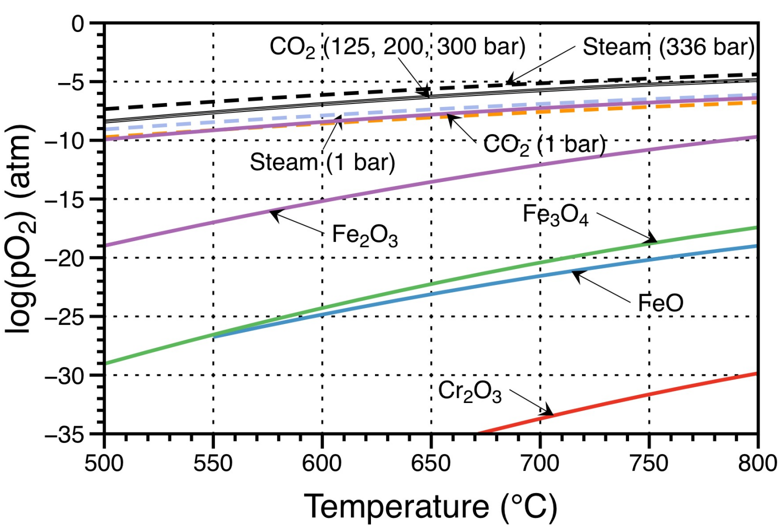


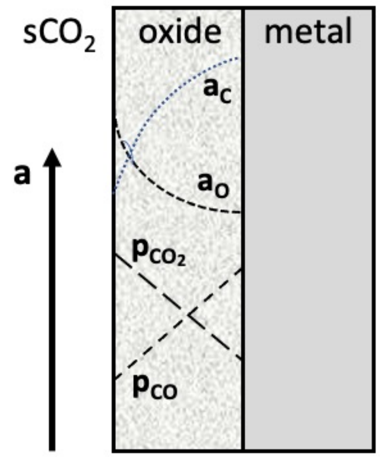
Feher, 1965

50% sCO_2 eff @ >720°C

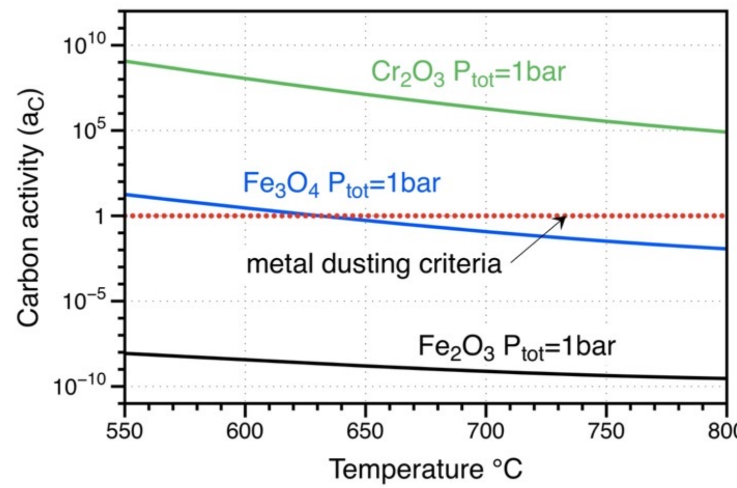
Thermodynamics: Oxygen levels similar in steam/CO_2 Concern about high C activity at m-o interface

Factsage calculations





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

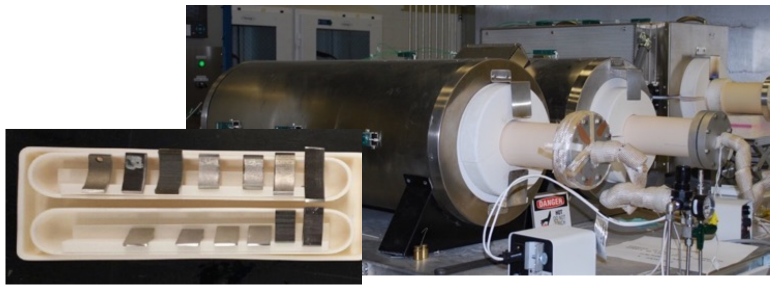
sCO_2 compatibility focused on steels at 450°-650°C in RG CO_2

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

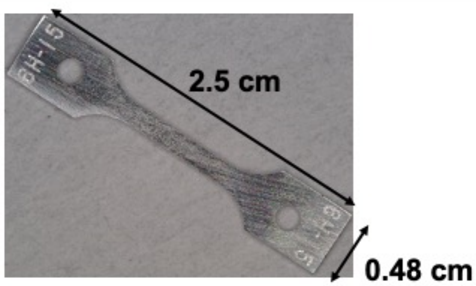
ORNL steel project started in August 2019

Test matrix & progress

Temperature	RG sCO_2	$+1\%O_2+0.1\%H_2O$
450°C (842°F)	2,000 h	1000 h
550°C (1022°F)	2,000 h	1000 h
650°C (1202°F)	1000 h	1000 h

Not for today

Autoclave: 300 bar sCO_2
500-h cycles



SS-3 dogbone tensile

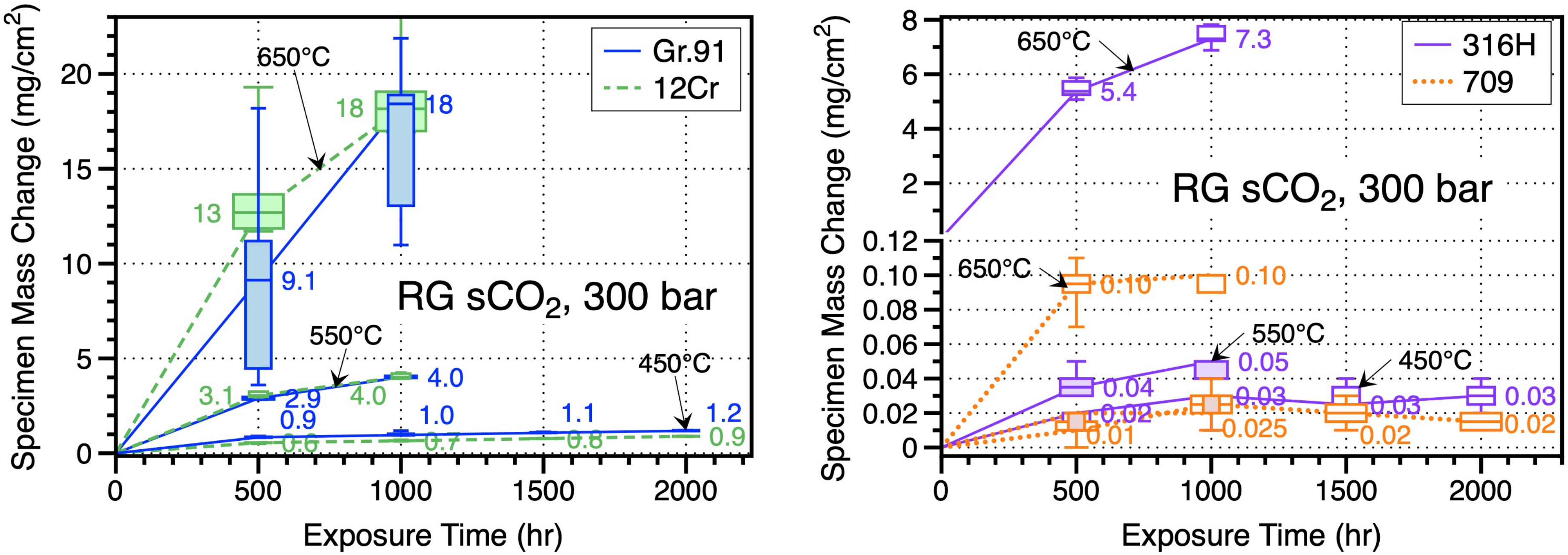
~5 cm^2 alloy coupons + tensile specimens

- Four primary alloys in test matrix
  - T91 (9Cr-1Mo)
  - VM12 (~11Cr)
  - 316H (conventional stainless steel)
  - NF709 (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

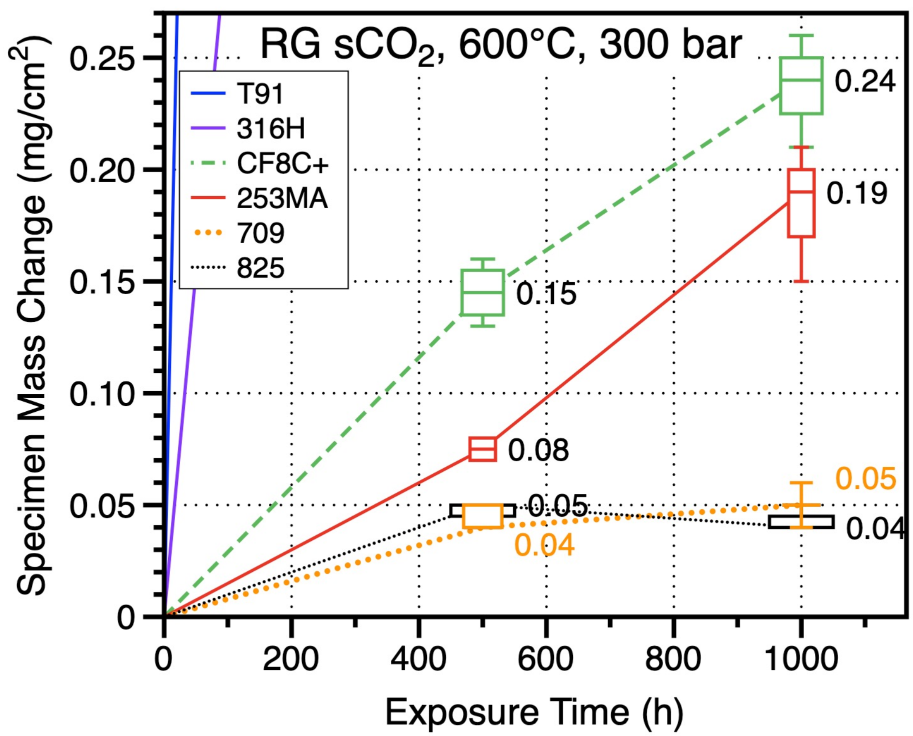
Mass change of 5-6 specimens in RG sCO_2 plotted



- 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

sCO_2 600°C: 2021 explored some additional candidates

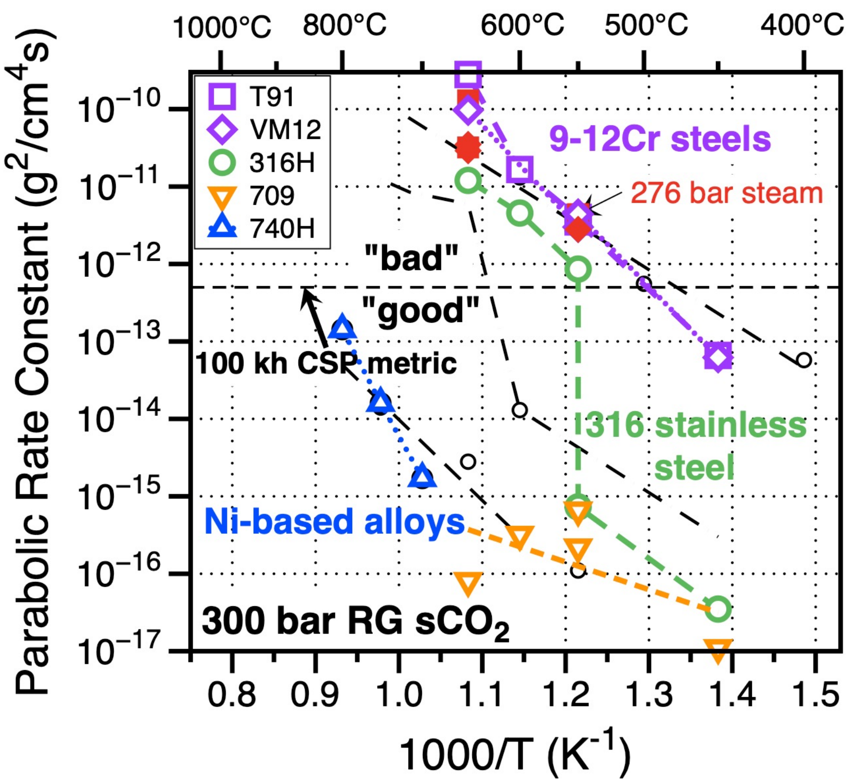
- 550°-600°C critical temperature
  - 30 MPa, RG CO_2
  - 4-6 specimens of each alloy
- Ni-based alloy 825 (Ni-31Fe-23Cr)
  - Small mass change (as expected)
  - Similar to advanced austenitic 709 (Fe-20Cr-25Ni)
- 253MA: higher Cr, Si + Ce/La
  - accelerating mass gain = FeO_x nodules…
- CF8C-Plus (cast 347): high Mn
  - Higher strength version of CF8C
  - Also accelerating mass gain



- **825**: 40Ni-31Fe-23Cr-3Mo-1.7Cu-1Ti-0.5Mn-0.3Si
- **CF8C-Plus**: Fe-12.5Ni-19.5Cr-**4Mn**-0.7Nb-0.7Si-0.5Cu-0.3Mo-0.25N (ASTM spec.)
- **253MA**: 65Fe-11Ni-21Cr-1.5Si-0.7Mn-0.3Mo0.15N-0.03Ce-0.01La

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, better
    - Value in 20-25%Cr, 20-25%Ni
    - Low values hard to measure



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

Scales on 9-12Cr steels after 1,000 h exposures at each temperature

- Fe-rich oxide in each case
  - Classic two-layer structure
    - Fe_3O_4 with low pO_2 in sCO_2
  - Internal oxidation zone
- Little benefit of higher Cr content in VM12 under these conditions

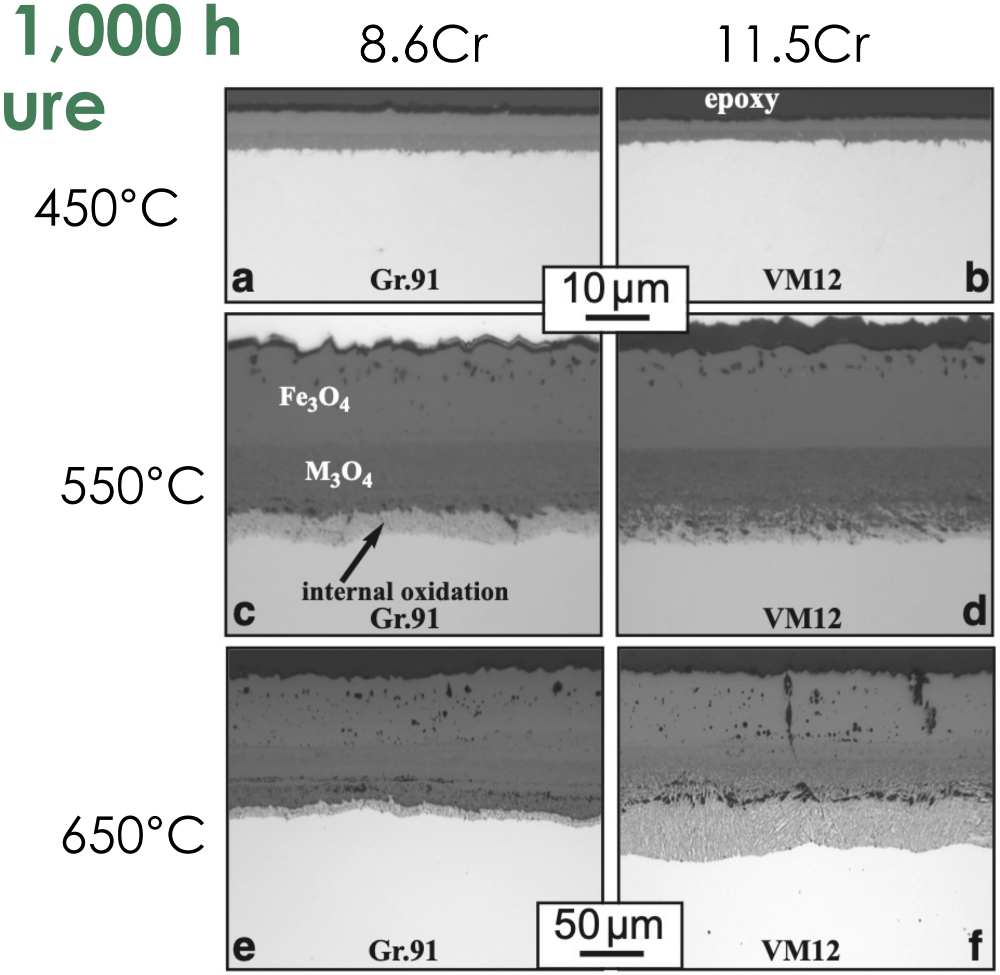


Figure 3. Light microscopy of polished cross-sections of (a,c,e) Gr.91 and (b,d,f) VM12 after 1000 h in RG sCO_2 at (a,b) 450°C, (c,d) 550°C and (e,f) 650°C.

Light microscopy

Scales on stainless steels after 1,000 h exposures at each temperature

- Cr-rich oxides in 5 of 6 cases
  - Thin, protective: difficult to image using light microscopy
- Fe-rich oxide for 316H at 650°C
  - Two-layer structure, but only inner layer was retained
- Strong benefit of increasing the Cr/Ni content in alloy 709
  - You get what you pay for!

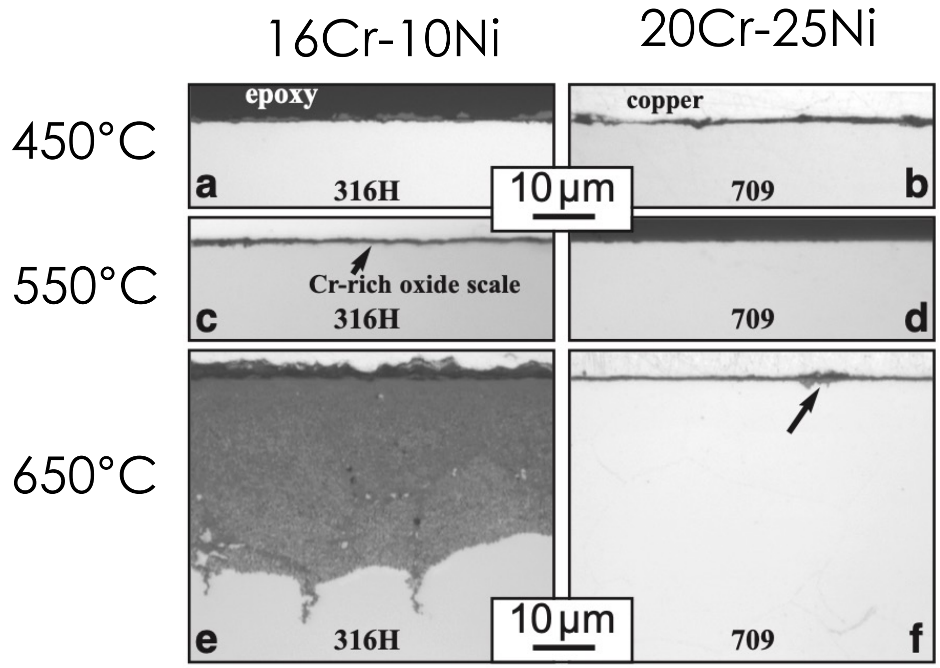


Figure 4. Light microscopy of polished cross-sections of (a,c,e) 316H and (b,d,f) 709 after 1000 h in RG sCO_2 at (a,b) 450°C, (c,d) 550°C and (e,f) 650°C.

Light microscopy

Scales on stainless steels after 1,000 h exposures at each temperature

- Cr-rich oxides in 5 of 6 cases
  - Thin, protective
  - Cr depletion beneath scale
  - Nodules primarily Cr-rich
- Fe-rich oxide for 316H at 650°C
  - Two-layer structure, but only inner layer was retained
- Strong benefit of increasing the Cr/Ni content in alloy 709

709: 20Cr-25Ni 650°C

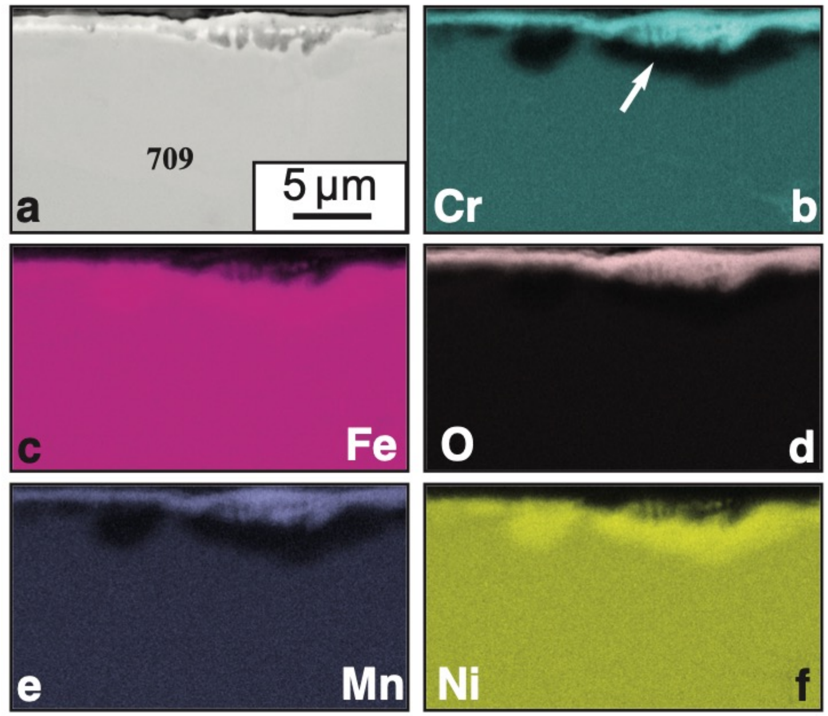


Figure 7. (a) SEM secondary electron image of 709 after 1000 h at 650°C in RG sCO_2 and (b-f) EDX maps of the same region.

Scanning electron microscopy/EDX maps

Scales on stainless steels after 1,000 h exposures at each temperature

- Cr-rich oxides in 5 of 6 cases
  - Thin, protective
- Fe-rich oxide for 316H at 650°C
  - Two-layer structure, but only inner layer was retained
  - Cr-rich oxide at metal-oxide interface with Cr depletion
  - Perhaps Ni metal incorporated
- Strong benefit of increasing the Cr/Ni content in alloy 709

316H: 16Cr-10Ni 650°C

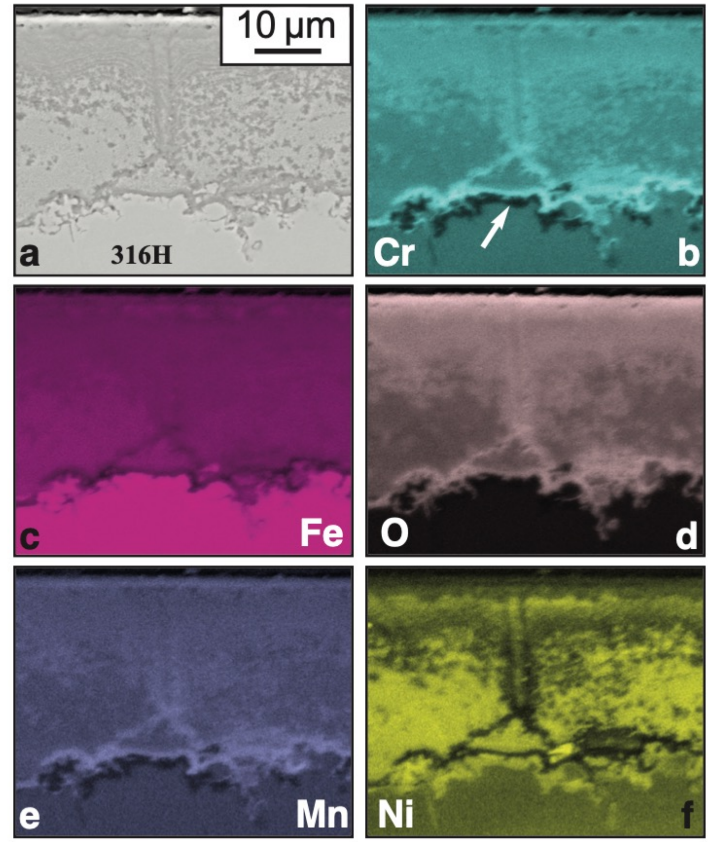
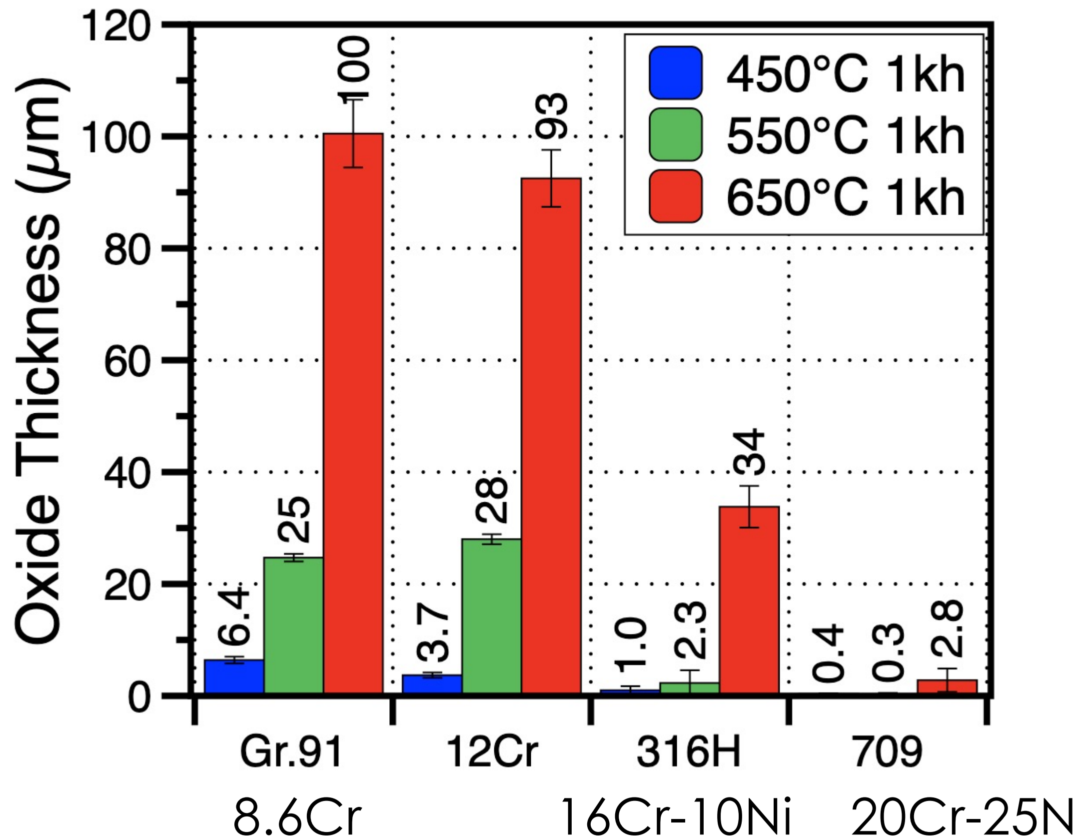


Figure 6. (a) SEM secondary electron image of the inner scale formed on 316H after 1000 h at 650°C in sCO_2 and (b-f) EDX maps of the same region.

Scanning electron microscopy/EDX maps

Oxide thickness after 1,000 h exposures at each temperature

- Consistent with mass change data
- Large increase for 316H at 650°C
  - ~50% of oxide spalled!



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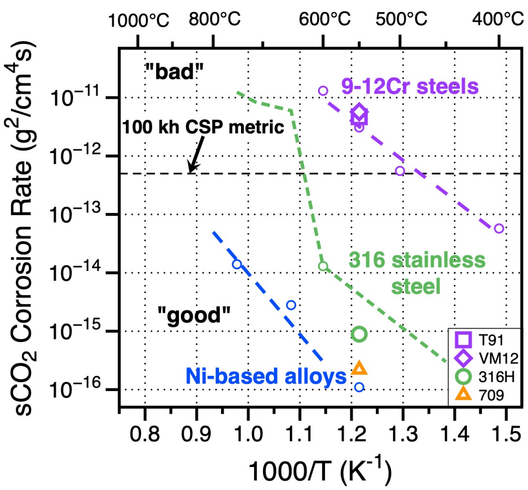
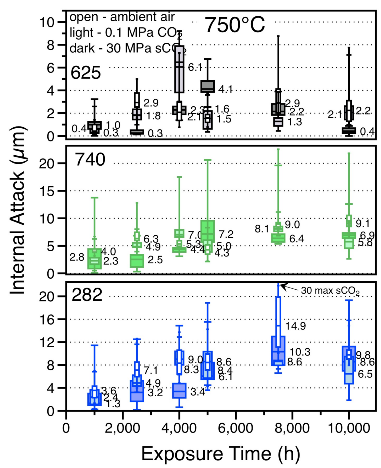
Do we need new metrics for steel sCO_2 compatibility?

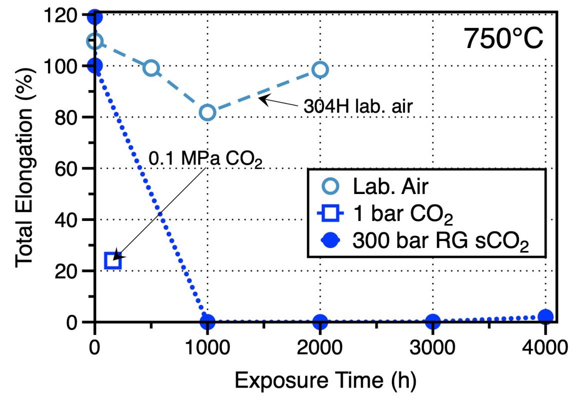
Current metrics: Mass change/rate constants/oxide thickness





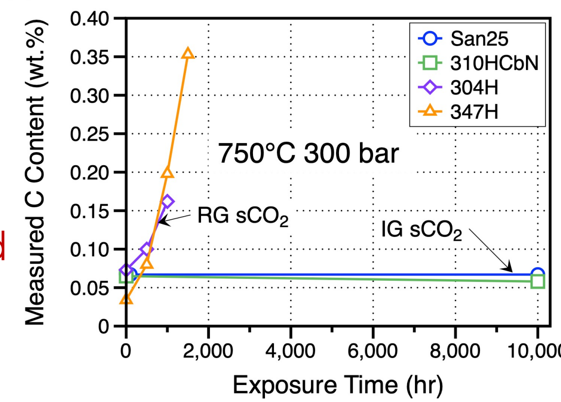
How useful is this information in materials selection?

New metrics: C uptake & retained ductility

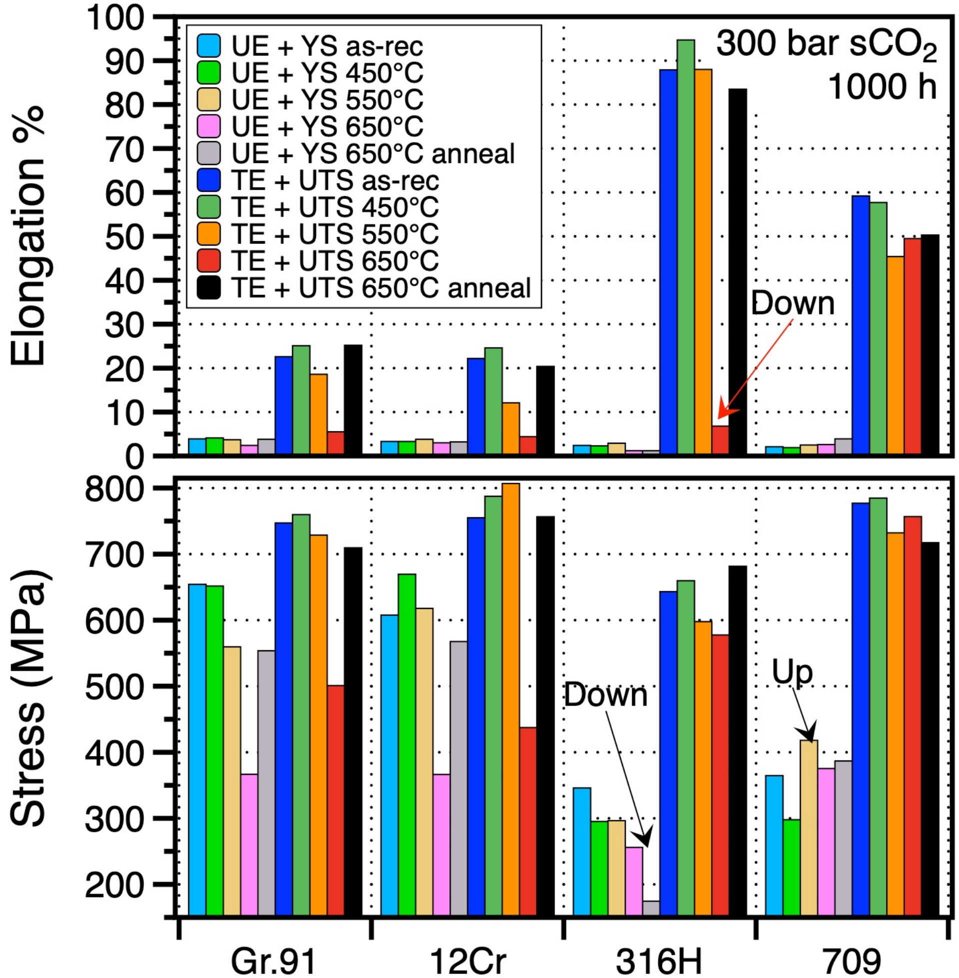


304H stainless: embrittled in CO_2 not in air at 750°C

750°C: High C uptake for 304H/347H Not for advanced austenitics



Room temperature tensile properties: 650°C/316H impact

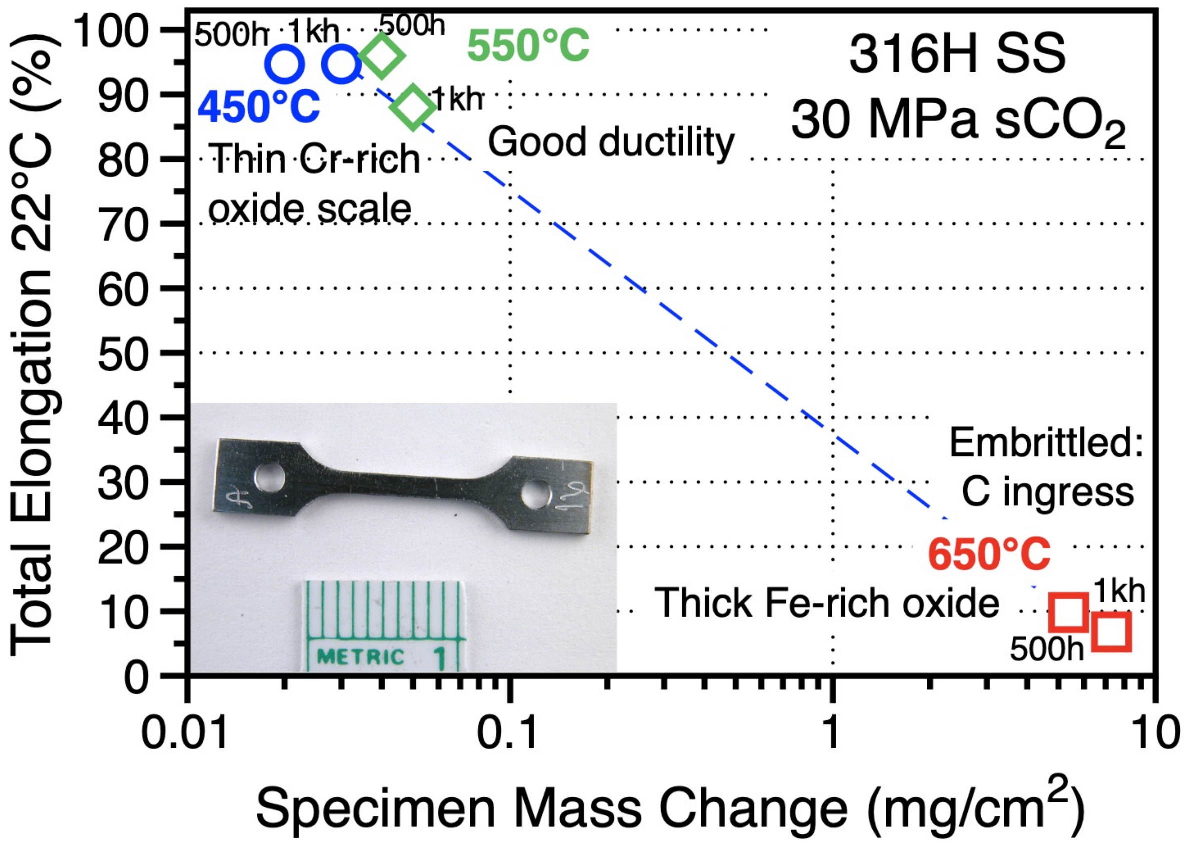


316H/650°C:
- Drop in ductility
- Increase in YS
- Consistent with C ingress

FS/650°C: also degraded

650°C anneal: minor loss in ductility

Room temperature tensile properties: 650°C/316H impact

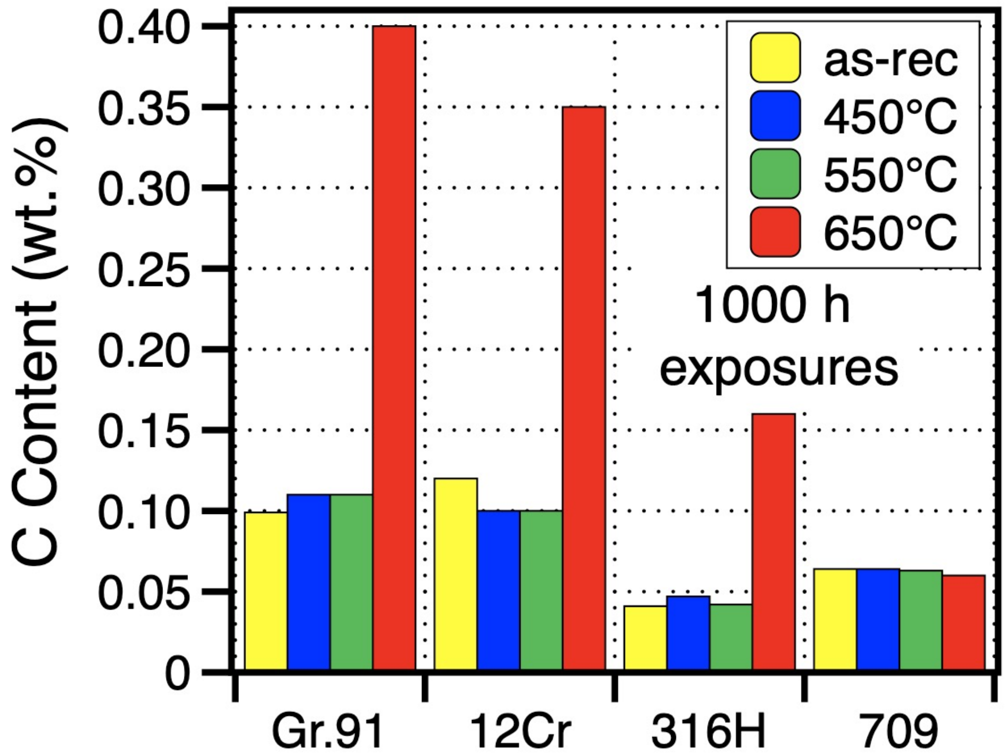


Low mass gain =
Cr-rich oxide
= high ductility
(prevented C ingress?)

High mass gain =
Fe-rich oxide
= low ductility

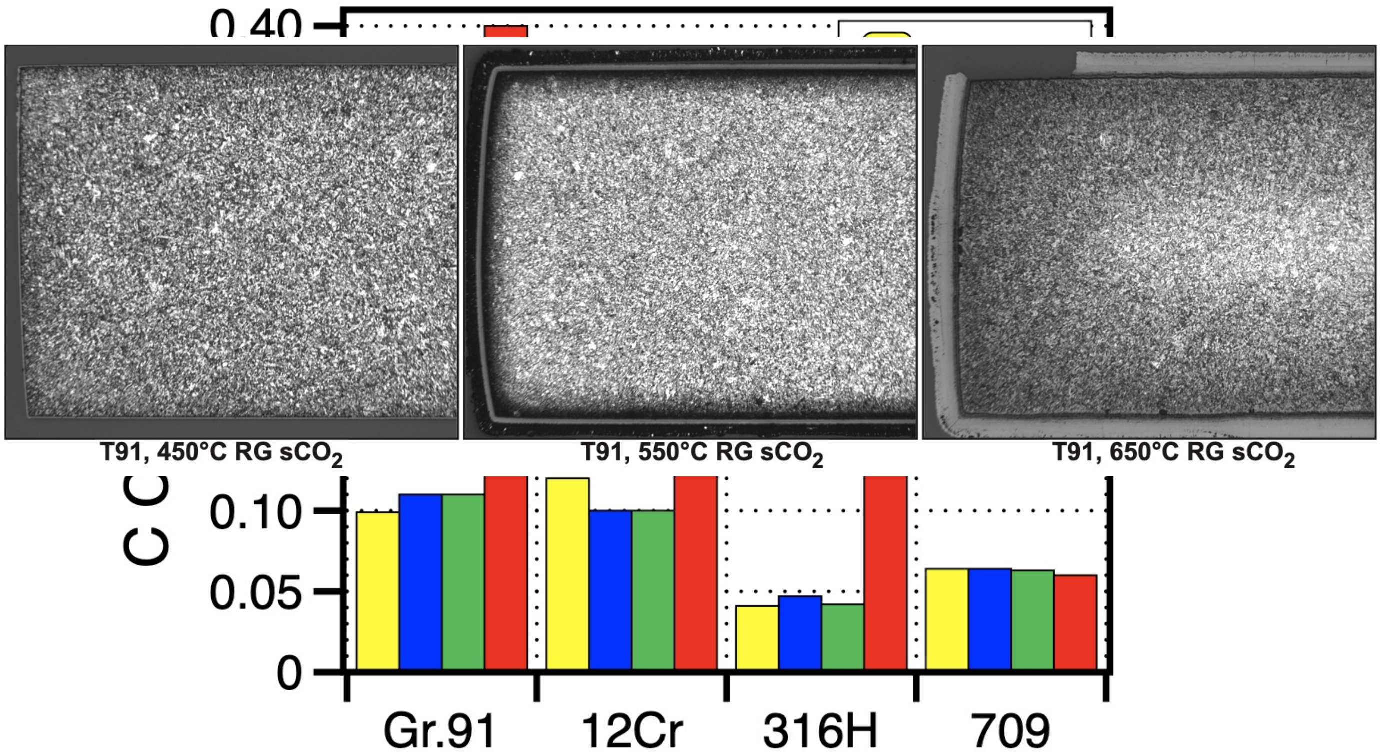
Due to C ingress?

Bulk C content: major C increase at 650°C for 3 steels



650°C: thick Fe-rich oxides allowed C ingress
550°C: longer exposures needed

Bulk C content: major C increase at 650°C for 3 steels

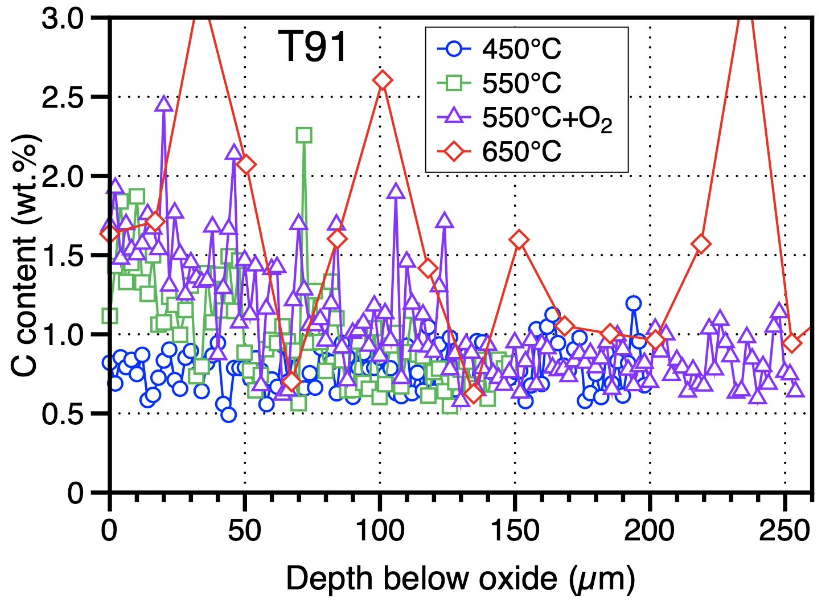


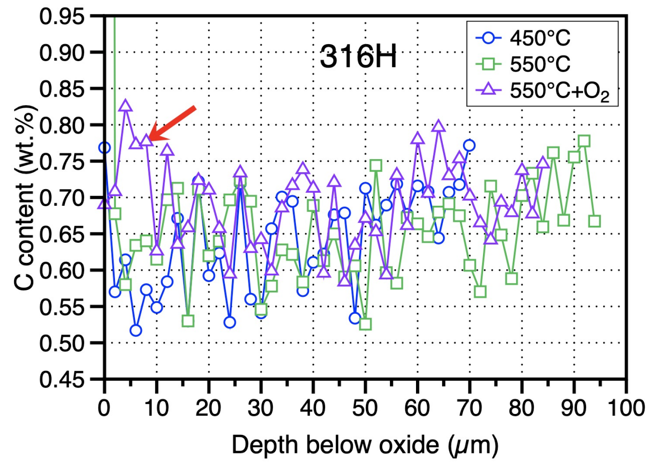
Aqua regia etch

(1.5mm thick specimens)

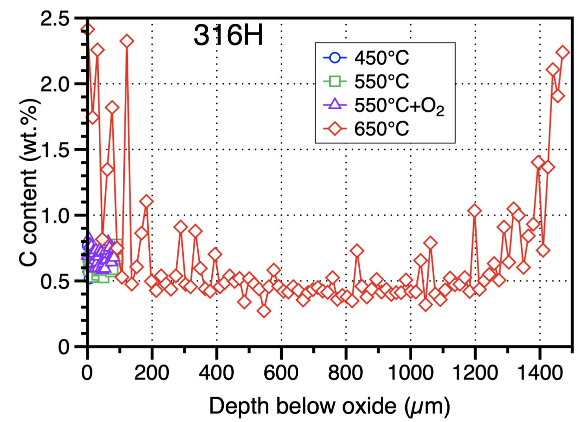
650°C: thick Fe-rich oxides allowed C ingress
550°C: longer exposures needed

EPMA: measurements of C ingress for modeling

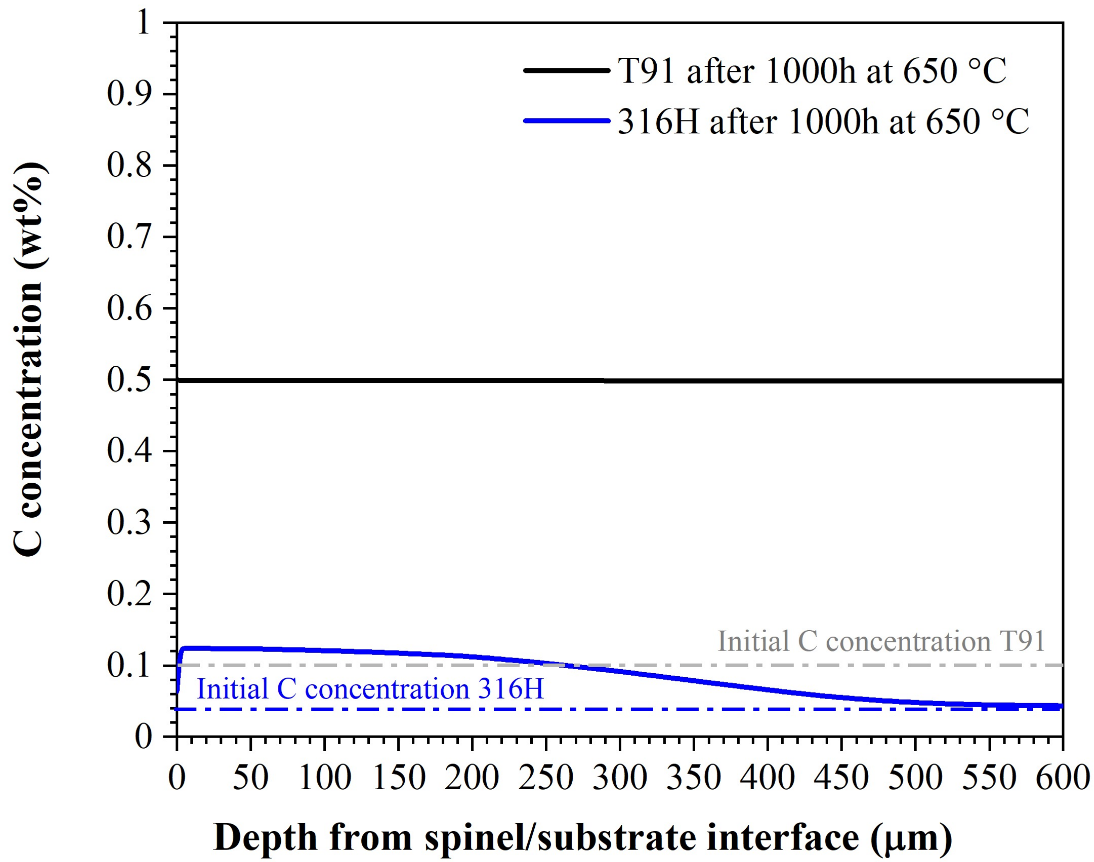




- Confirmed massive C uptake at 650°C for T91/316H
- Very little uptake at 450°C for both alloys
- Gradient observed at 550°C
- Collecting more EPMA data to feed modeling task

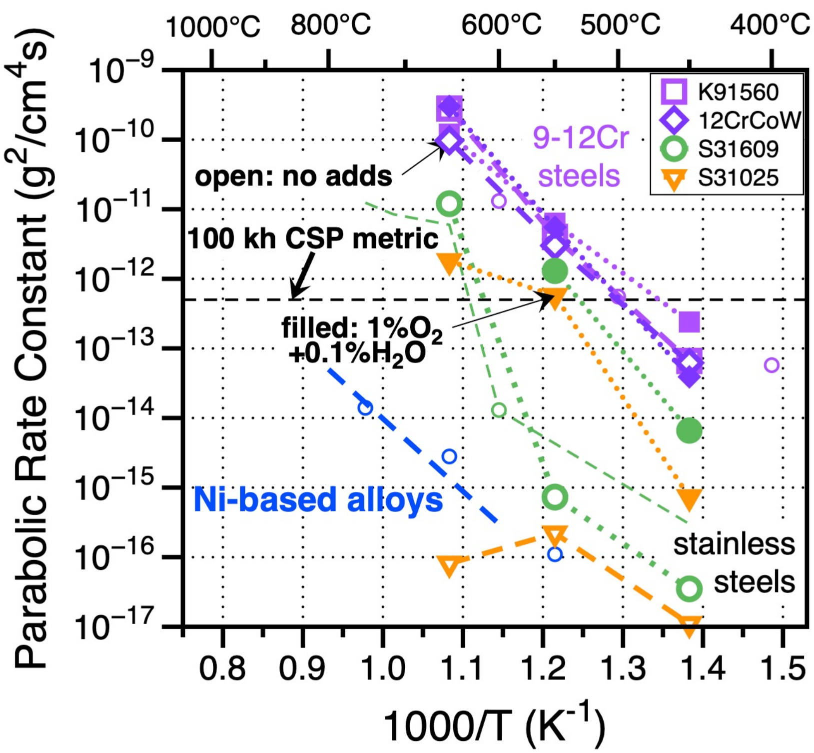


Initial steel modeling: Calculated average C profiles



Goal: predict 100,000 kh C ingress as a function of temperature for T91 and 316H

NACE 2022: Addition of 1%O_2+0.1%H_2O: accelerates all !



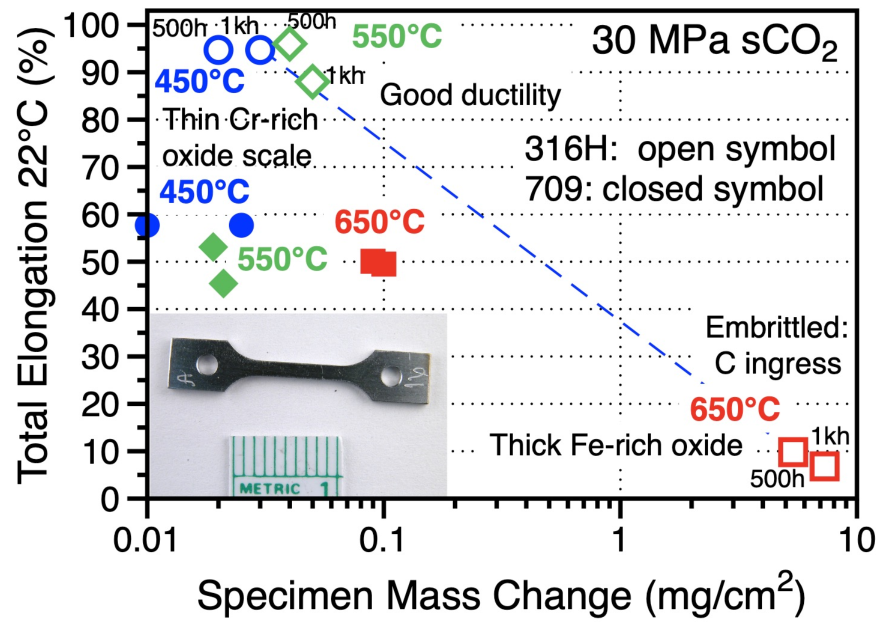
Open symbol: RG sCO_2
Filled: RG sCO_2 + 1%O_2 + 0.1%H_2O
All 300 bar

2019: Ni-based alloys 2-5X rate increase
with impurities at 750°C

Based on CSP (solar) metric: all limited to <550°C with impurities
9-12Cr steels: high rates with or without impurities
Rates for 709 (20Cr/25Ni): may not reflect steady state at 1000 h

Summary: sCO_2 is a challenging environment

- At 650°-800°C, Ni-based alloys appear compatible
- Steels have problem forming protective scales:
  - 9-12%Cr all conditions 450°-650°C
    - Fe-rich oxide formation observed in sCO_2
    - These steels form Cr-rich scale in air
  - 316H at 650°C in RG sCO_2
    - Carbon ingress + embrittlement
  - 709 formed Cr-rich oxide in all cases
    - Longer times at 650°C?
    - 310HCbN/alloy 25: no C ingress at 750°C
  - With O_2 impurities: all have problems!



Thank you!

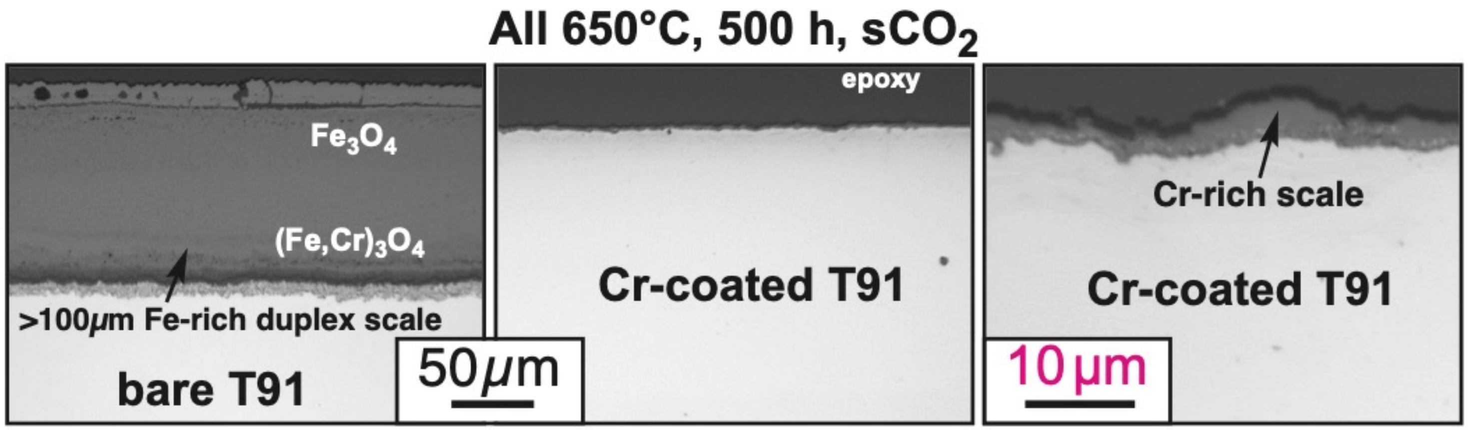


Table 1

Alloy chemical compositions (weight %)$^{(1)}$

Alloy	UNS#	Fe	Cr	Ni	Mo	Mn	Si	C	S(ppm)	Other
Gr.91	K90901	88.8	8.6	0.3	0.9	0.46	0.35	0.10	6	0.2V,0.06Nb,0.045N
12CrCoW		83.3	11.5	0.4	0.4	0.38	0.42	0.12	3	1.6W,1.5Co,0.2V,0.04N
316H	S31609	69.5	16.3	10.0	2.0	0.84	0.46	0.041	6	0.3Cu,0.3Co,0.04N
709	S31025	51.3	20.1	25.2	1.5	0.89	0.41	0.064	3	0.2Nb,0.06Cu,0.15N

(1) measured by inductively coupled plasma analysis and combustion analysis
< indicates below the detectability limit of <0.01%