Effect of Impurities on Supercritical Carbon Dioxide (Steels at 450°-650°C)

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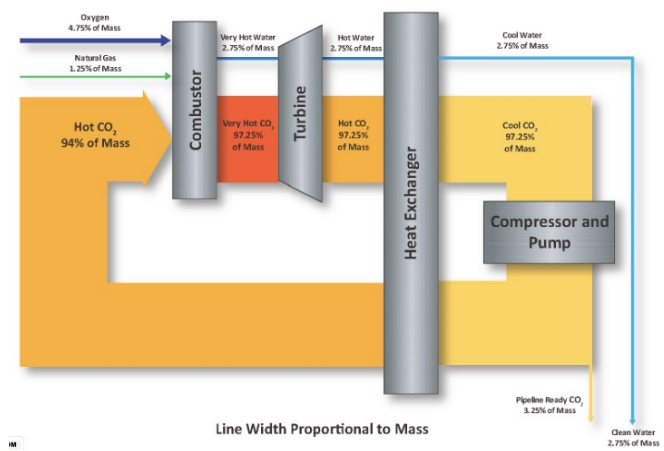
Supercritical CO_2 is moving towards commercialization

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

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

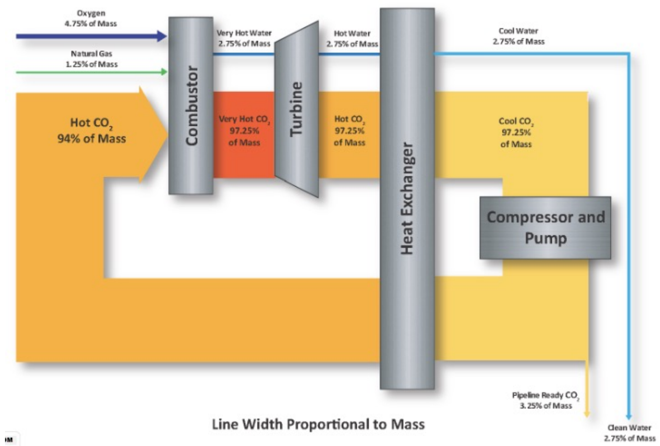


11/17/2021: NetPower 25MW component demonstration plant in Laporte, TX

Supercritical CO_2 is moving towards commercialization

8 Rivers Unveils 560 MW of Allam Cycle Gas-Fired Projects for Colorado, Illinois

8 Rivers Capital, inventor of a novel supercritical carbon dioxide (CO_2) cycle, plans to begin operating a 280-MW NET Power natural gas-fired plant within the Southern Ute Indian Reservation in southwest Colorado by 2025. The company on April 15 also said it will team with agricultural and processing firm Archer-Daniels-Midlands Co. (ADM) to locate a 280-MW NET Power facility in Decatur, Illinois.



sCO_2+
~0.1%H_2O
~1%O_2 + add

sCO_2+
~3%H_2O
~1%O_2

The first clean fossil energy: integrated CO_2 capture

BUT, burning natural gas in sCO_2 creates impurities…

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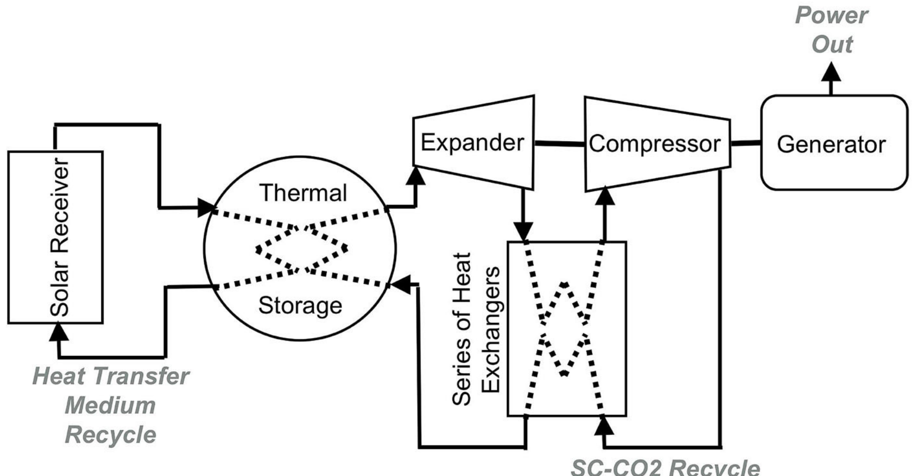
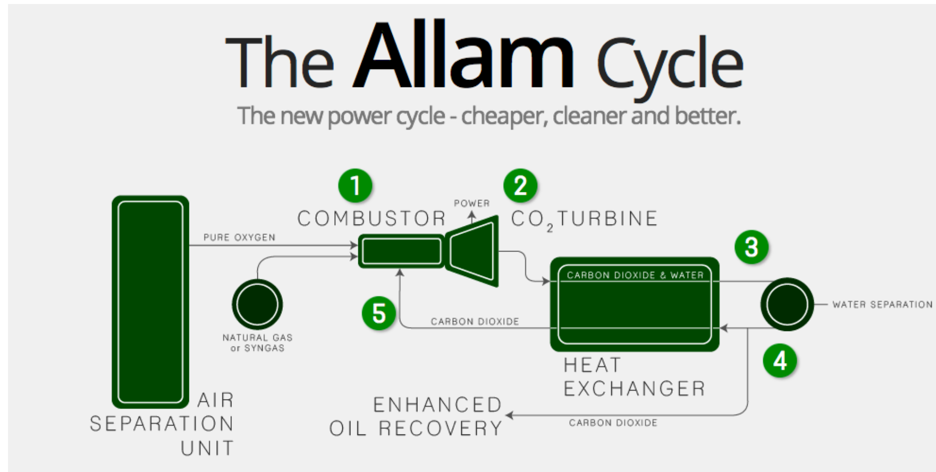
Impurities differ in indirect- & direct-fired sCO_2 cycles
(i.e. closed vs. open)

Closed cycle:
"pure" CO_2 100-300 bar



Fossil: 2013-2015 general study
Solar: 2015-2018 700°-800°C
Fossil: 2019-21 Cermets 1000+°C
ARPA-E: 2019-22: ≥800°C HX

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



Fossil: 2015-2018 750°C
Fossil: 2020-2022 steel project

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National Laboratory

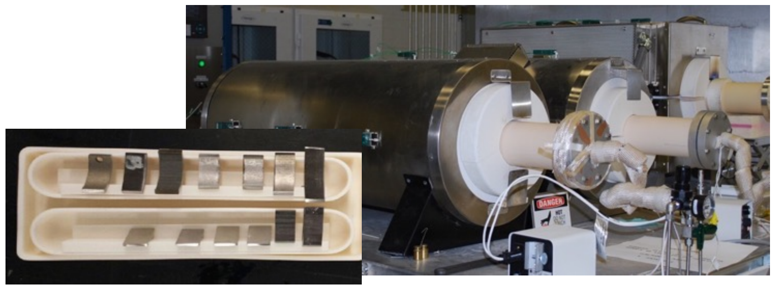
CO_2 compatibility evaluated three ways at 400°-1200°C

Autoclave: 300 bar sCO_2
500-h cycles (400°-800°C)

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: above 800°C
500-h cycles, 1-43 bar CO_2

Studies at 1-43 bar

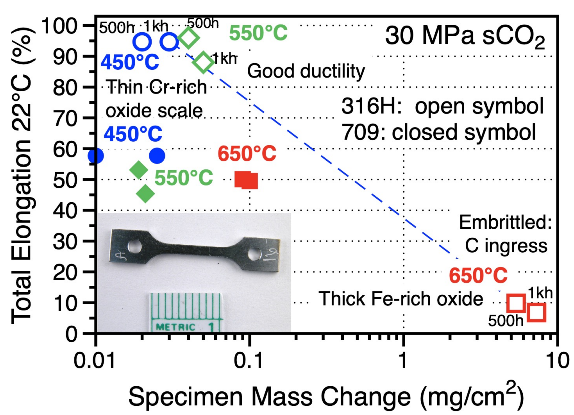
Baseline of research grade (RG) CO_2: ≤ 5 ppm H_2O and ≤ 5 ppm O_2

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

sCO_2 compatibility: broad range of conditions considered

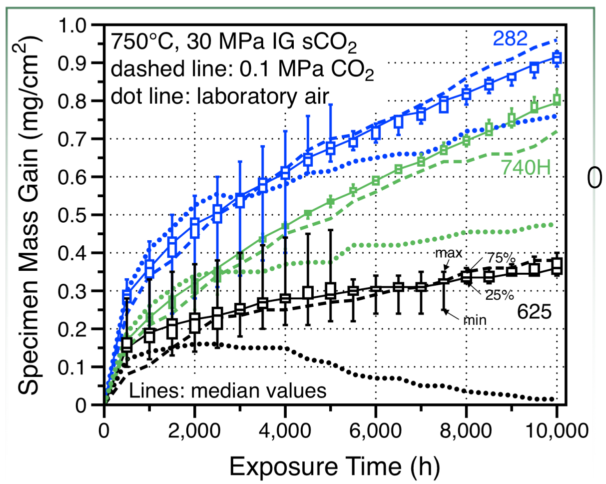
400°-650°C: concern about steel carburization

- Well-known issue from CO_2-cooled reactors
  - Grade 9 steel current issue
- 550°-600°C transition temperature for normal austenitic steels



650°-800°C: Ni-based alloys

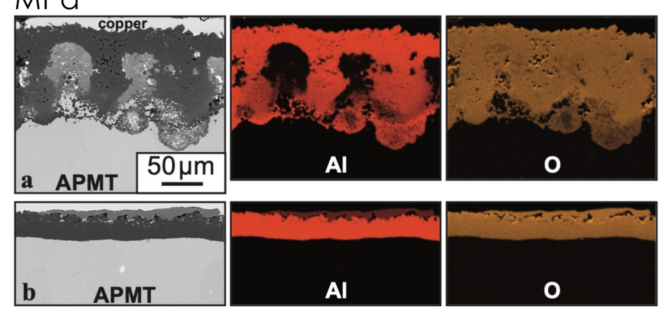
- No issues for Ni-based alloys
  - Low C solubility, protective Cr_2O_3 formation
- Similar rates for air, CO_2 and sCO_2
  - **no P effect**



>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



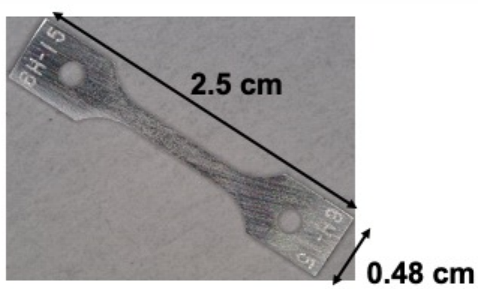
2 MPa CO_2

ORNL steel project started in August 2019

Initial test matrix is complete

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

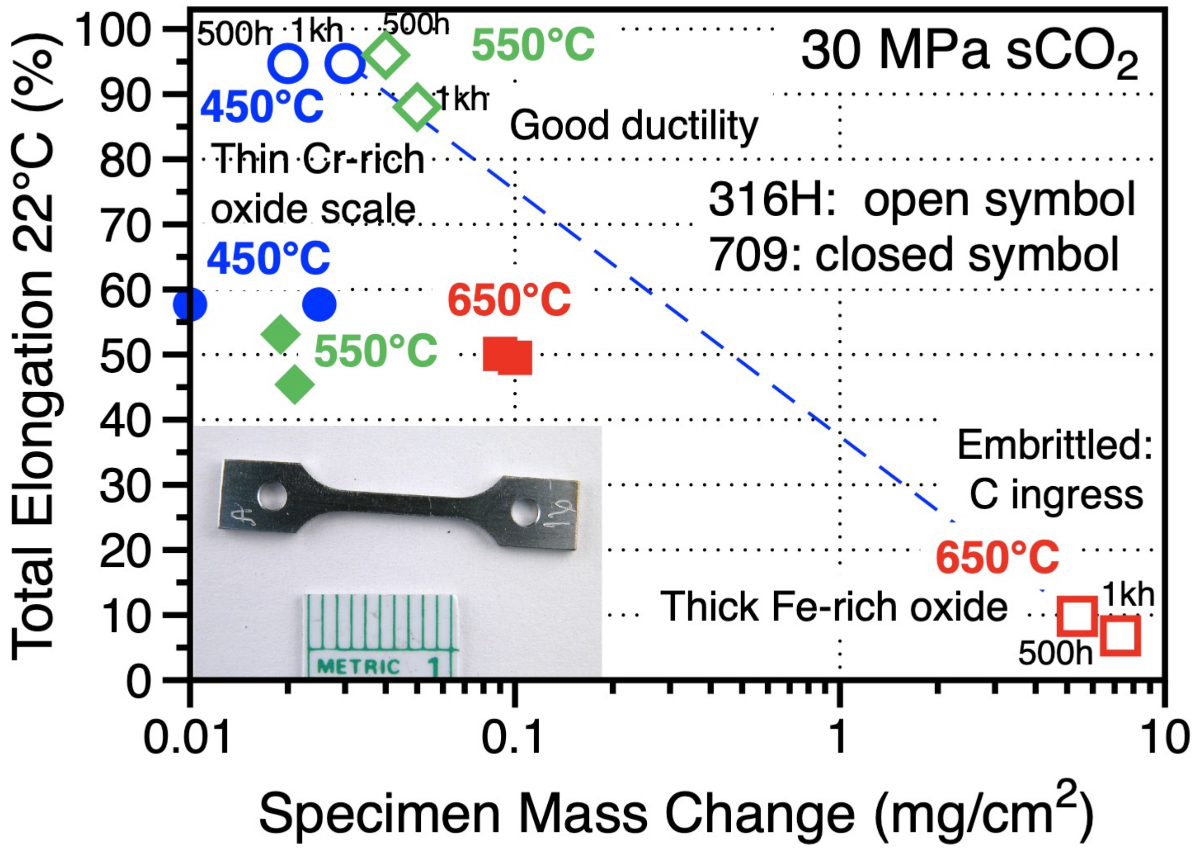
Focus on four steels

- 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 & without impurities (open vs. closed cycle)

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

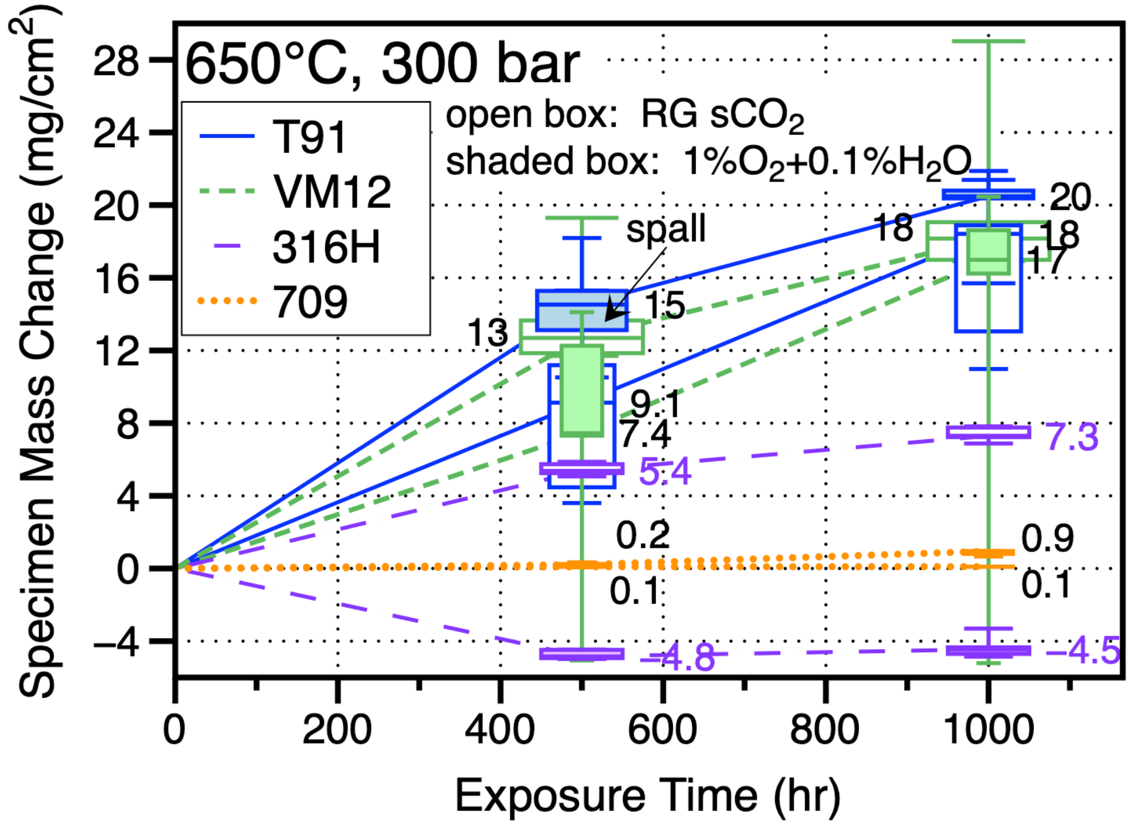
Pure sCO_2: Cr_2O_3 scale prevents C ingress



- 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

Pint, 2021, ECS Interfaces

Adding impurities caused accelerated attack in SS:



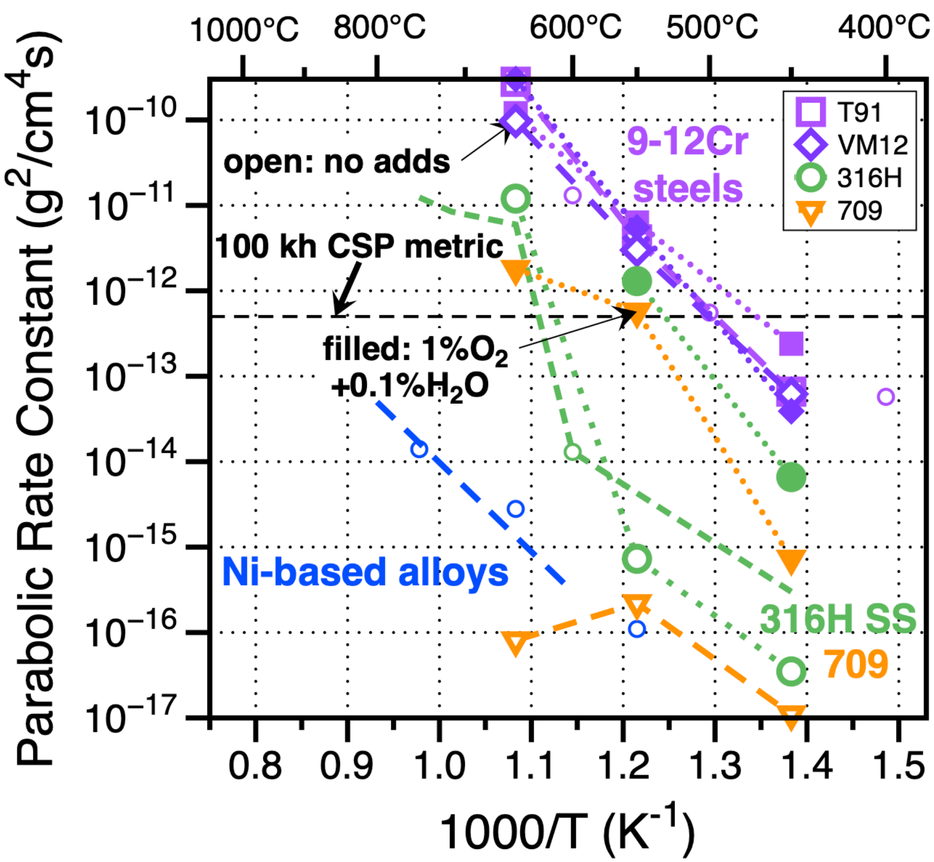
Minor changes for 9-12Cr steels: Thick scales in all cases

Increase for 709

Spallation for 316H

sCO_2+1%O_2-0.1%H_2O per NetPower

Matrix complete: Acceleration evident for 316H and 709



Bad

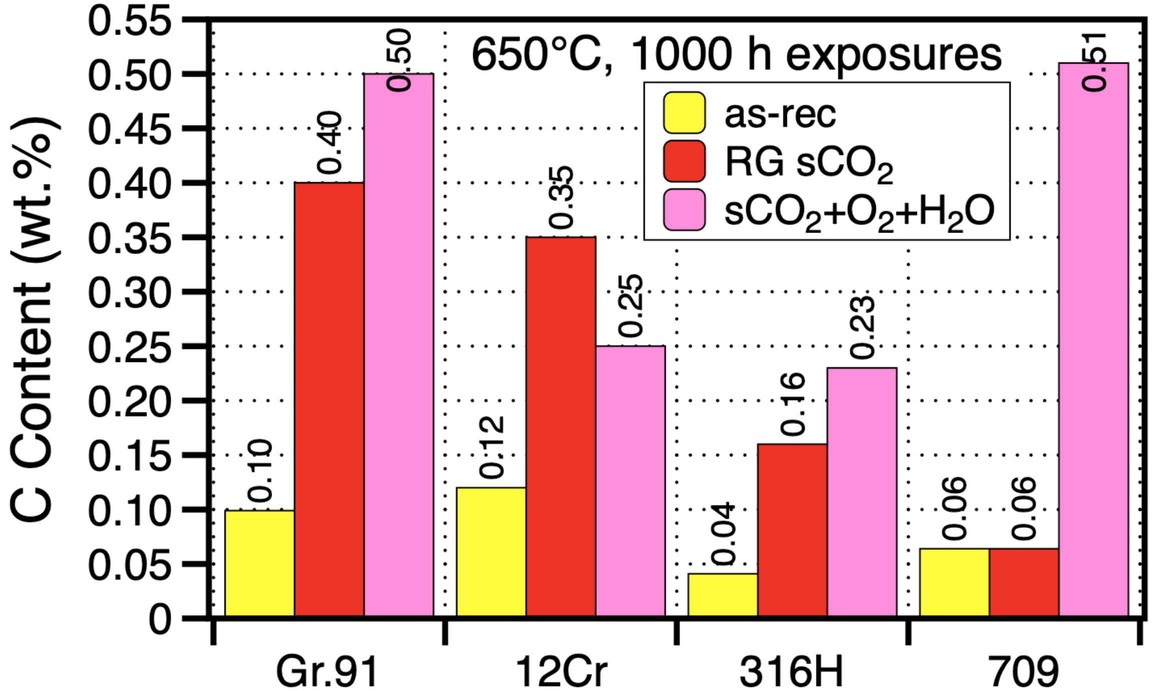
Good

316H and 709 rates above the metric at 550°C

- Longer exposures may be needed to obtain more accurate steady-state rates in this environment
- **What about 600°C?**
- What about coatings?
- **Can we do better than k_p metric assessment?**

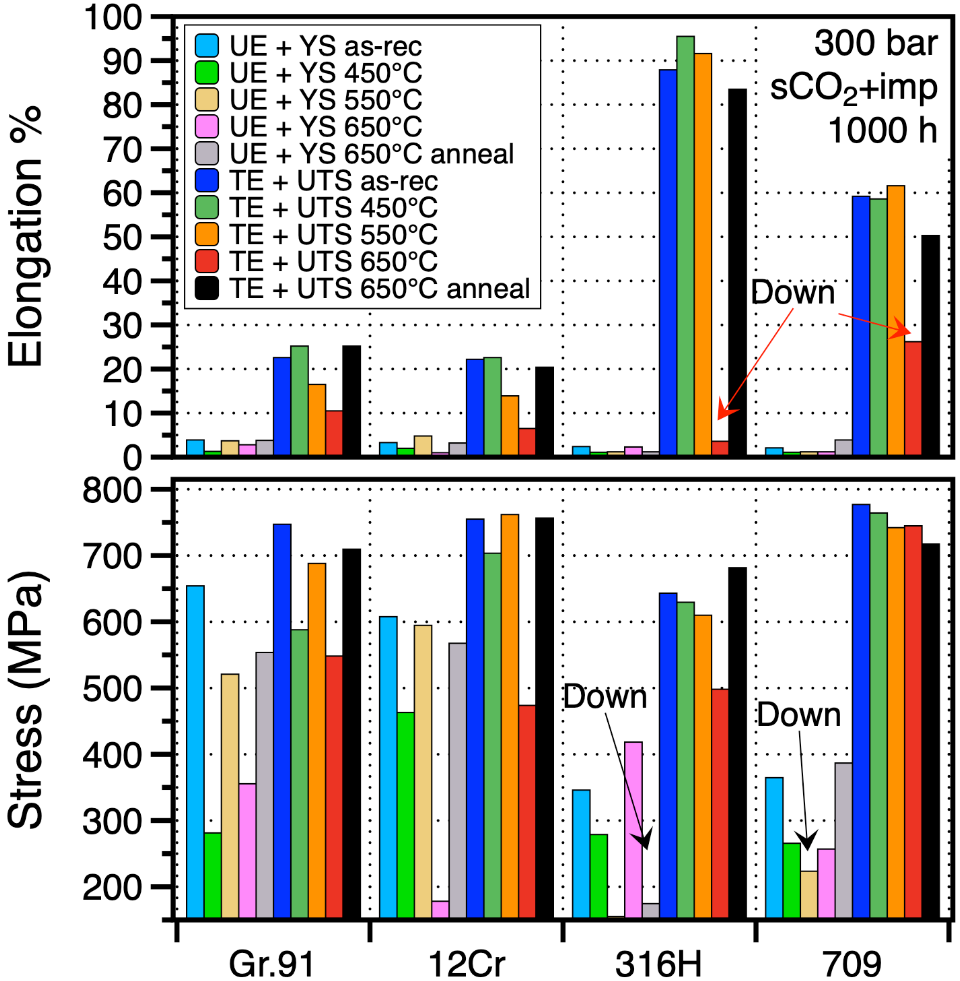
Increased C ingress with impurities

Determined by combustion analysis (bulk measurements)

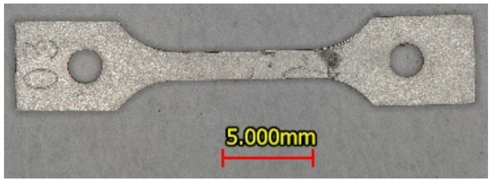


Need to repeat 709 measurement

25°C tensile properties with impurities: similar effect on all

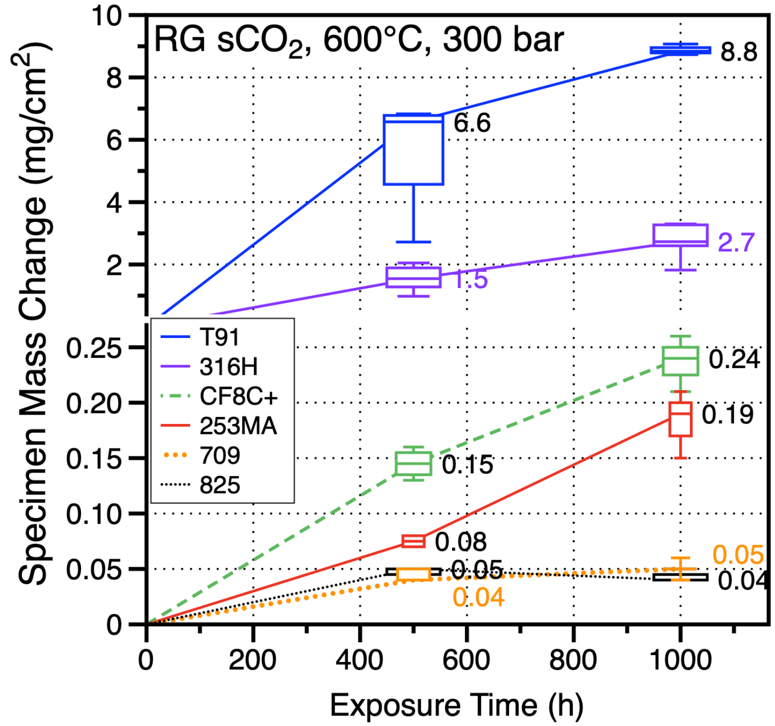


All steels show loss in ductility after 650°C sCO_2+imp compared to 650°C Ar anneal



sCO_2 600°C: one more RG sCO_2 experiment

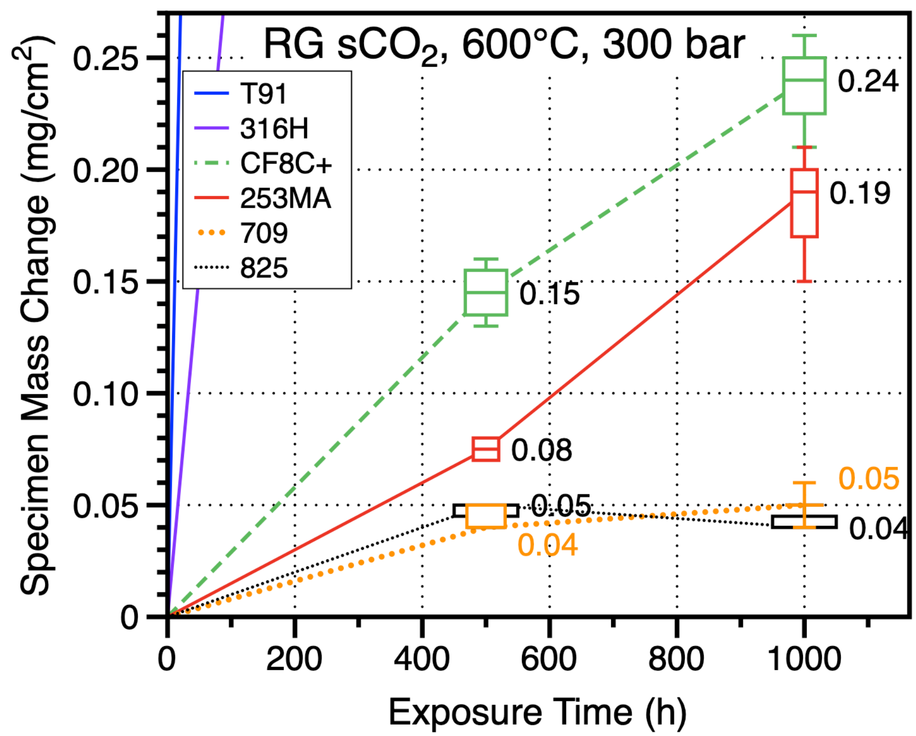
- Previously 450, 550 and 650°C
  - 30 MPa, RG CO_2
  - Fill in gap + add new materials
    - 825: industry interest
    - 253MA: suggestion at NACE 2021
    - CF8C-Plus: code case in progress
- Mass change: 1st indications
  - 4-6 specimens of each alloy
  - Box plot: median value shown
  - Higher mass gain: Fe-rich oxide
  - 709+825 showed low mass gain
  - 253MA+CF8C-Plus: accelerating mass gain = FeO_x nodules…



- 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

sCO_2 600°C: 2021 explored some additional candidates

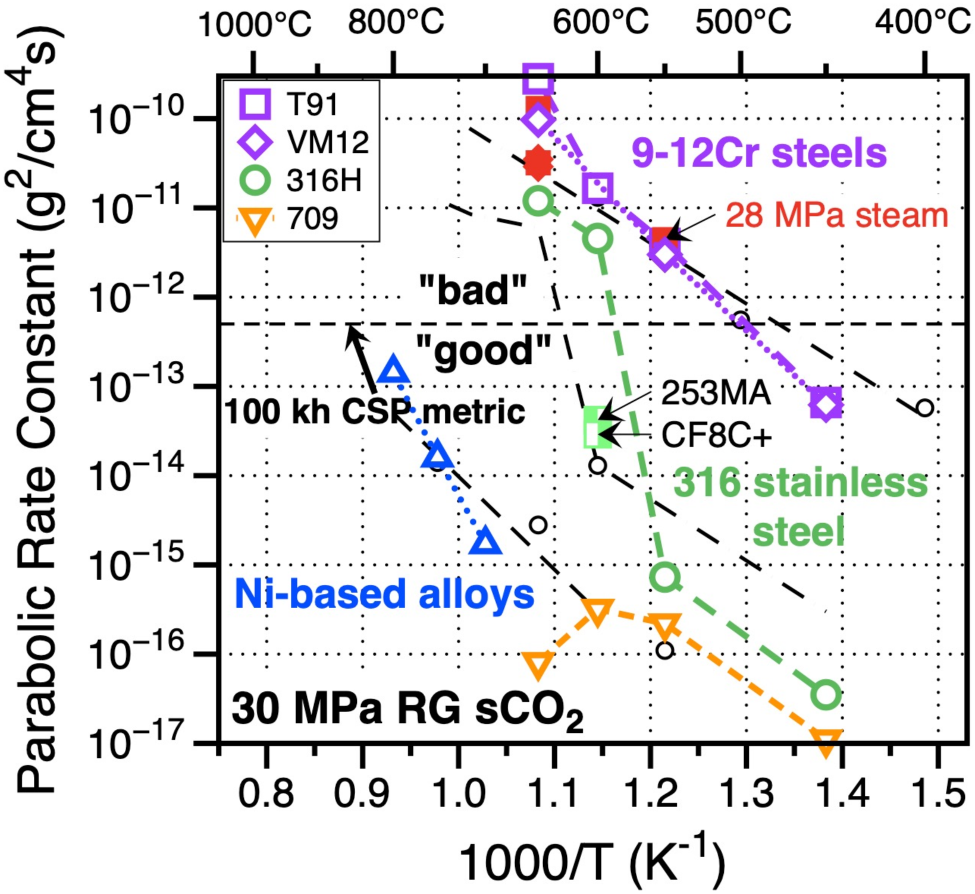
- 550°-600°C critical temperature
  - 30 MPa, RG CO_2
  - 4-6 specimens of each alloy
- Ni-based alloy 825 (Ni-31Fe-23Cr)
  - Small mass change (as expected)
  - Similar to advanced austenitic 709 (Fe-20Cr-25Ni)
- 253MA: higher Cr, Si + Ce/La
  - accelerating mass gain = FeO_x nodules...
- CF8C-Plus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



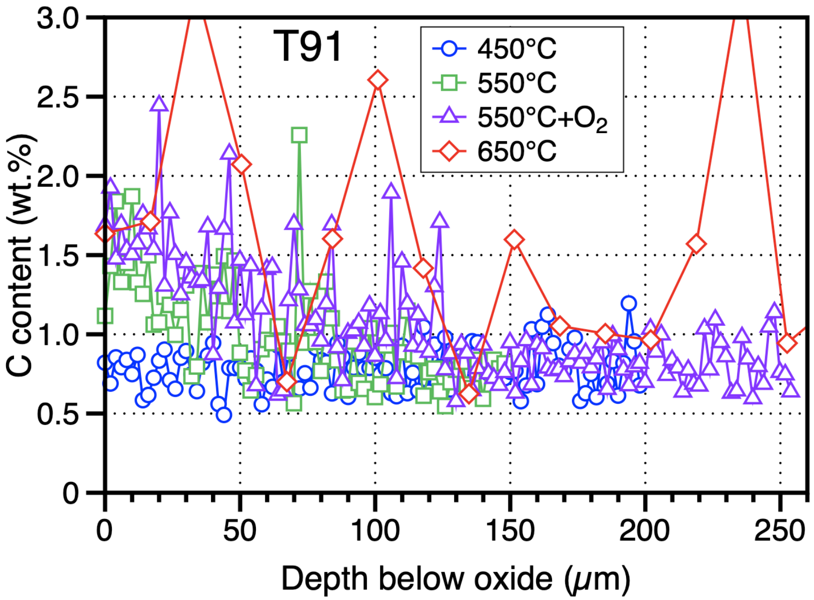
- **825**: 40Ni-31Fe-23Cr-3Mo-1.7Cu-1Ti-0.5Mn-0.3Si
- **CF8C-Plus**: Fe-12.5Ni-19.5Cr-**4Mn**-0.7Nb-0.7Si-0.5Cu-0.3Mo-0.25N (ASTM spec.)
- **253MA**: 65Fe-11Ni-21Cr-1.5Si-0.7Mn-0.3Mo0.15N-0.03Ce-0.01La

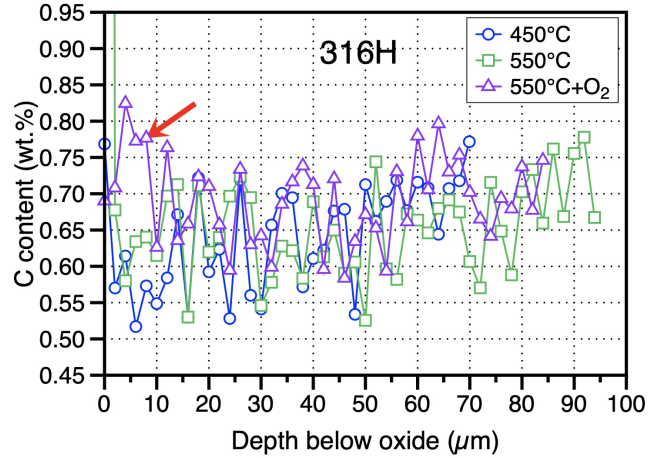
Rate from 2 data points provides a comparison

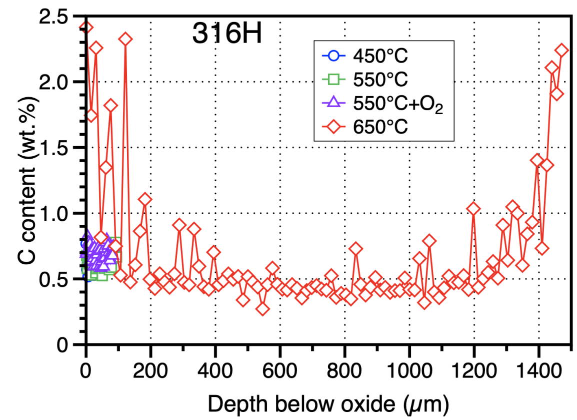
- T91: in line with sCO_2 + sH_2O
- 316H: faster than literature
  - Due to heating in sCO_2?
- 709: low as measurable
  - 20Cr/25Ni: value of higher Ni
    - 310SS: 25Cr/20Ni, much weaker
- 253MA/CF8C+: some benefit
  - Looking for cheaper than 709
- 825: 0.01mg/cm² mass loss
  - Average of 3-4 specimens



EPMA: measurements of C ingress for modeling

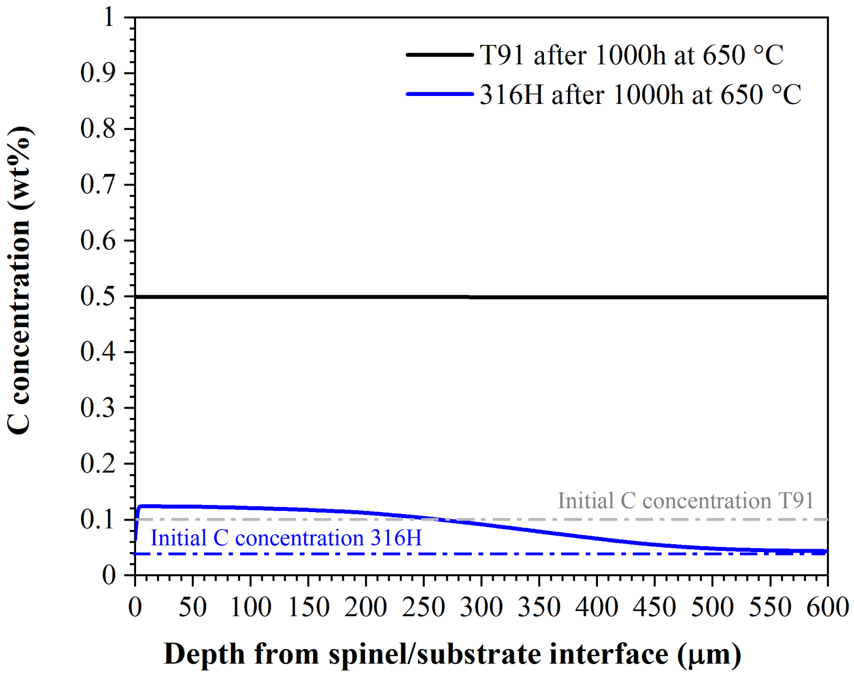


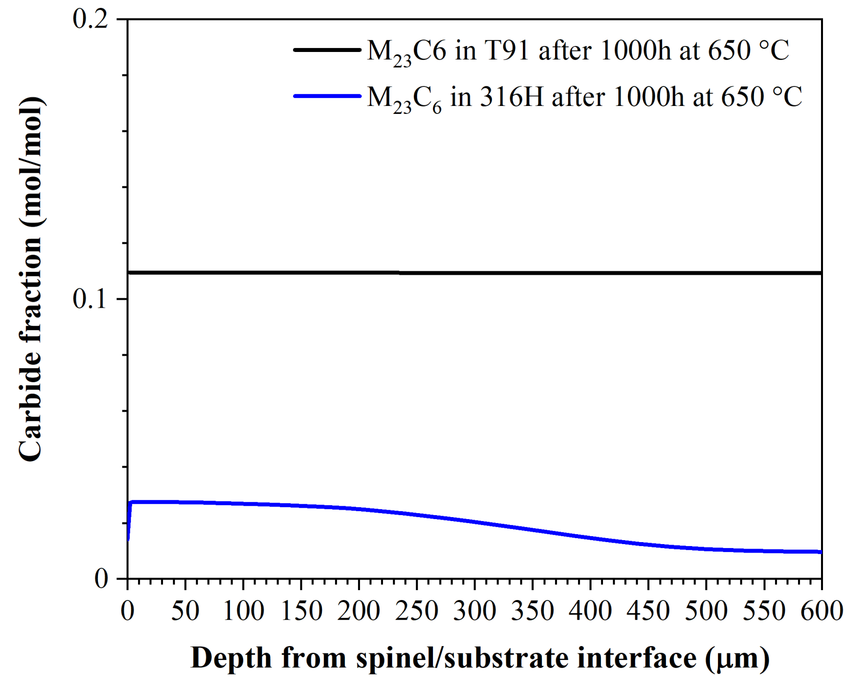




- Massive C uptake at 650°C for both alloys
- Very little uptake at 450°C for both alloys
- Collecting more EPMA data to feed modeling task
- GDOES now operational: beginning measurements

Initial steel modeling (Pillai): Calculated average C profiles and carbide fraction

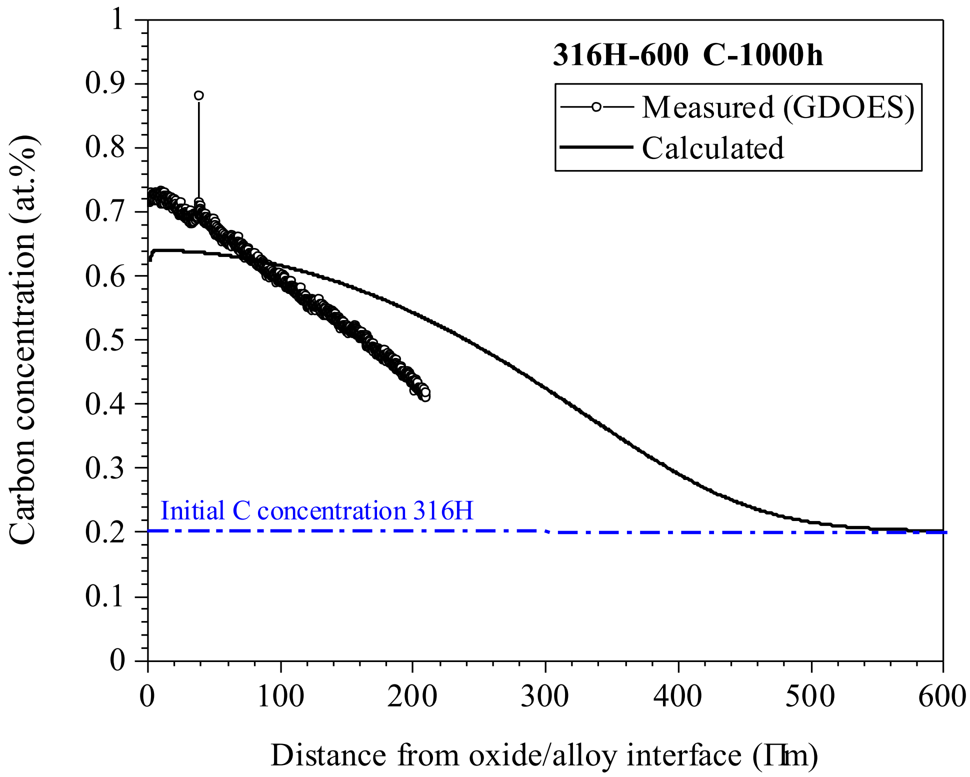




Goal: predict 100,000 kh C ingress as a function of temperature for T91 and 316H

Collecting C profiles using GDOES at 450°-650°C

GDOES: Glow discharge optical emission spectroscopy

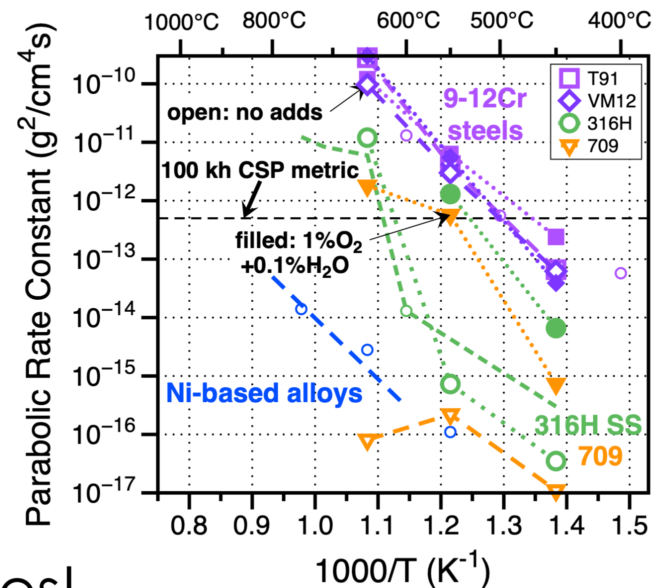


GDOES C profiles
(in progress)
- Effect of temperature
- Effect of impurities
- 316H/709 comparison

Last task is to complete modeling work

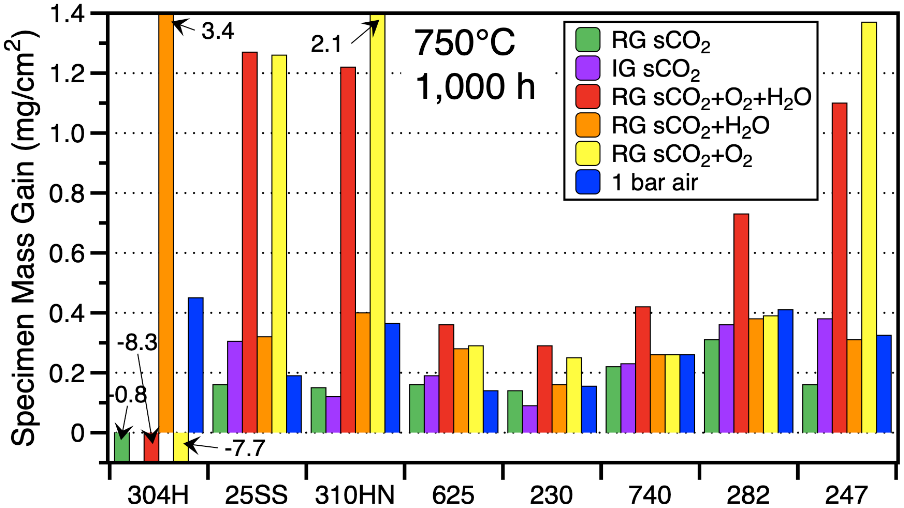
Summary: sCO_2 is a challenging environment for steels

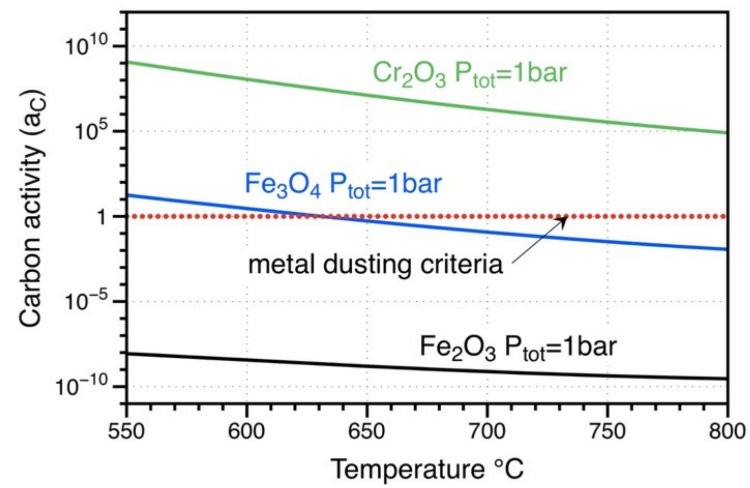
- At 650°-800°C, Ni-based alloys appear compatible
- Steels have problem forming protective scales:
  - 9-12%Cr may be limited to ~500°C
    - Fe-rich oxide formation observed in sCO_2
  - 316H at 600°-650°C in RG sCO_2
    - Carbon ingress + embrittlement
  - 709 formed Cr-rich oxide in all cases
    - Longer times at 650°C?
    - 310HCbN/alloy 25: no C ingress at 750°C
    - Accelerated attack at 650°C with impurities



- All of these steels are affected by impurities!

Backups





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