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

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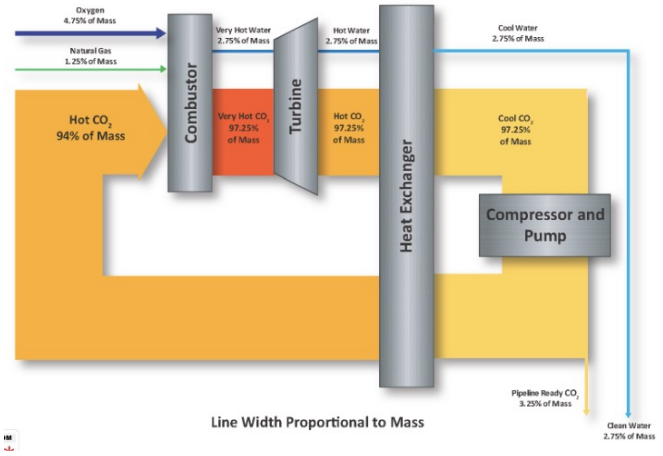
Disclaimer:

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.



The first clean fossil energy: integrated CO_2 capture

BUT, burning natural gas in sCO_2 creates impurities…

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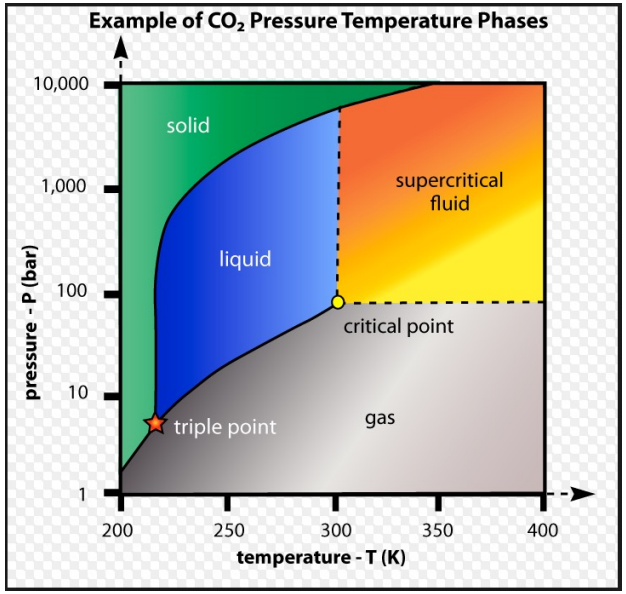
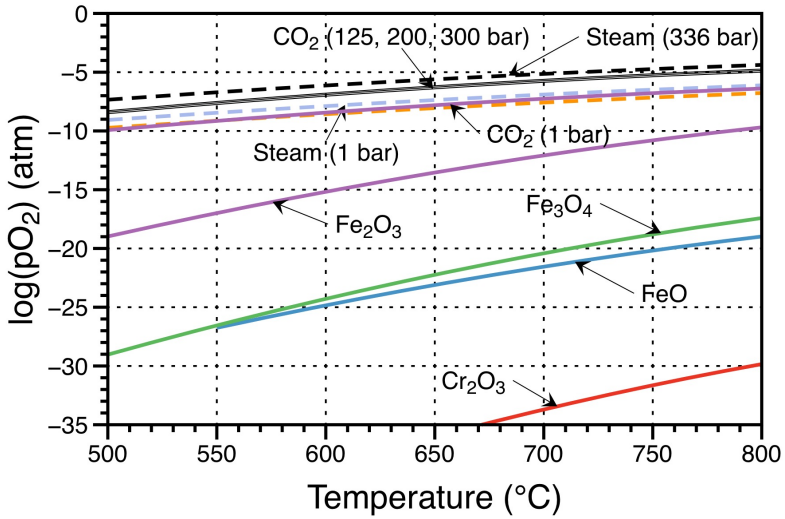
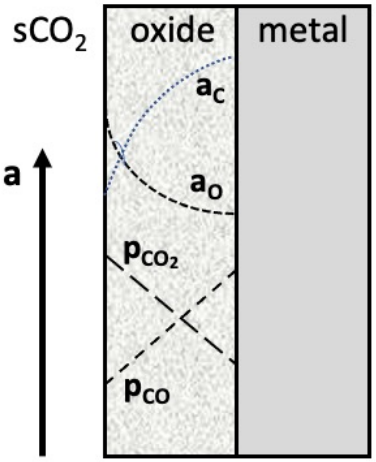
Without impurities, there is a carburization concern in sCO_2



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

Factsage calculations





Young et al., 2011

Ni-based alloys: OK in sCO_2

But cost is a concern:

Where can steels be used?

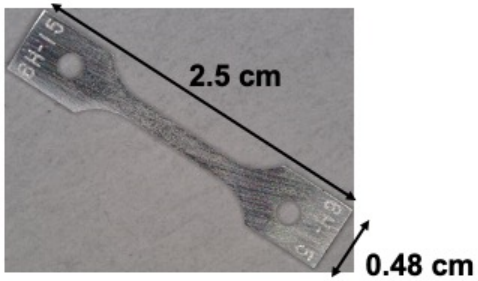
New metrics focus on internal carburization

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

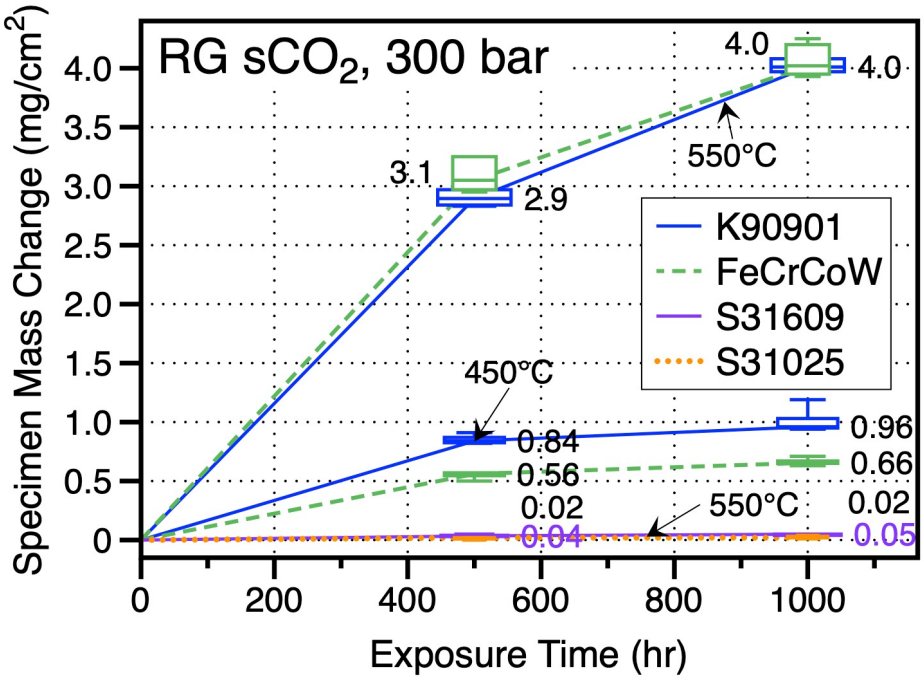
Focus on four steels

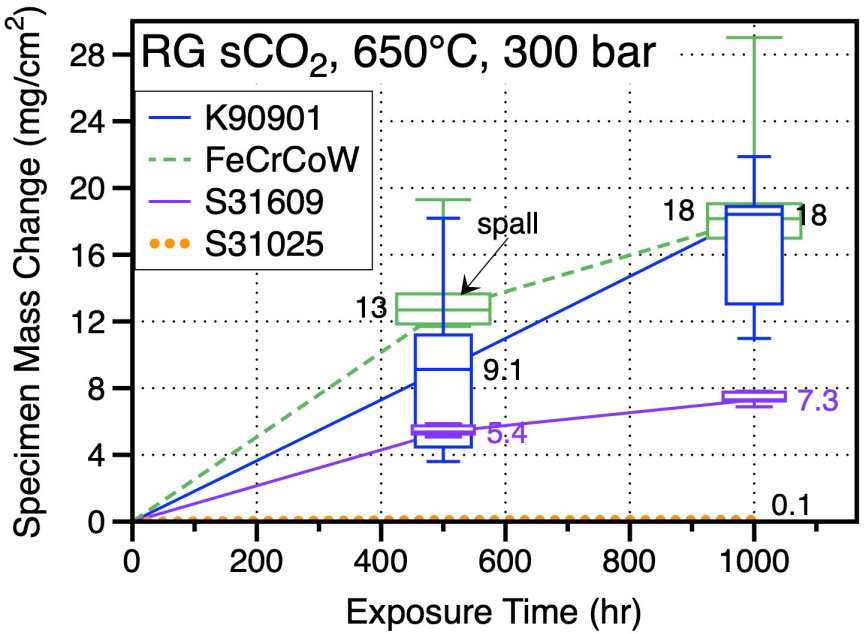
- Four primary alloys in test matrix
  - T91 (9Cr-1Mo)
  - VM12 (~11Cr)
  - 316H (conventional stainless steel)
  - NF709 (advanced austenitic, 20Cr-25Ni+Nb)
- 10 specimens of each alloy
- With & without impurities (open vs. closed cycle)

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

Mass change of 5-6 specimens in RG sCO_2 plotted

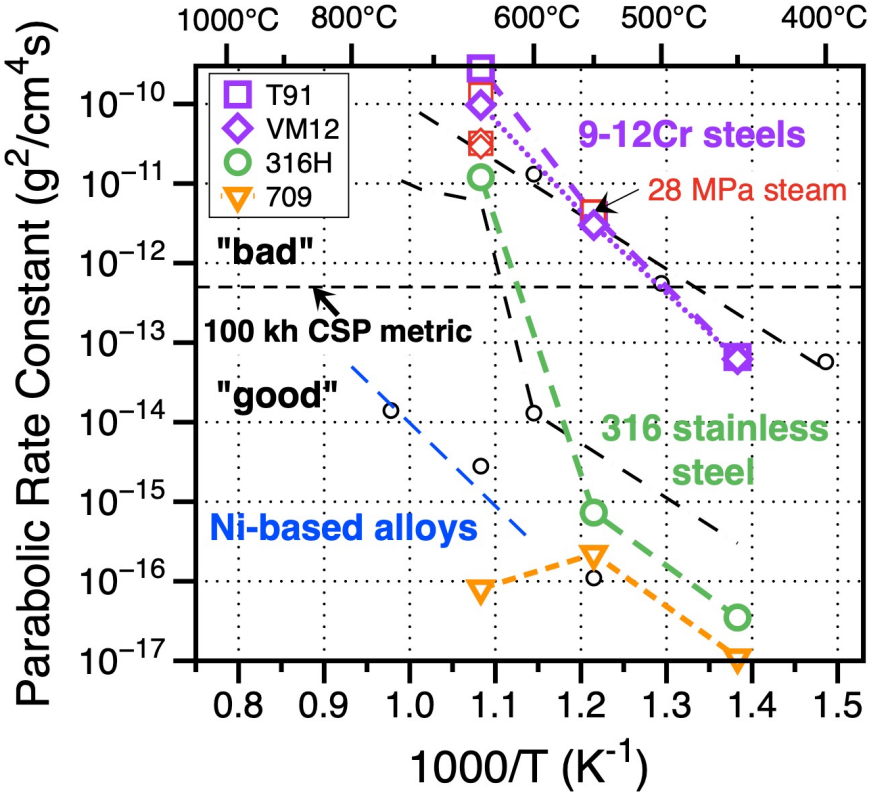




- One specimen of each alloy removed at 500 h for metallography
- High mass gains for 9-12%Cr steels in all cases
- Low mass gains for FCC steels except 316H at 650°C

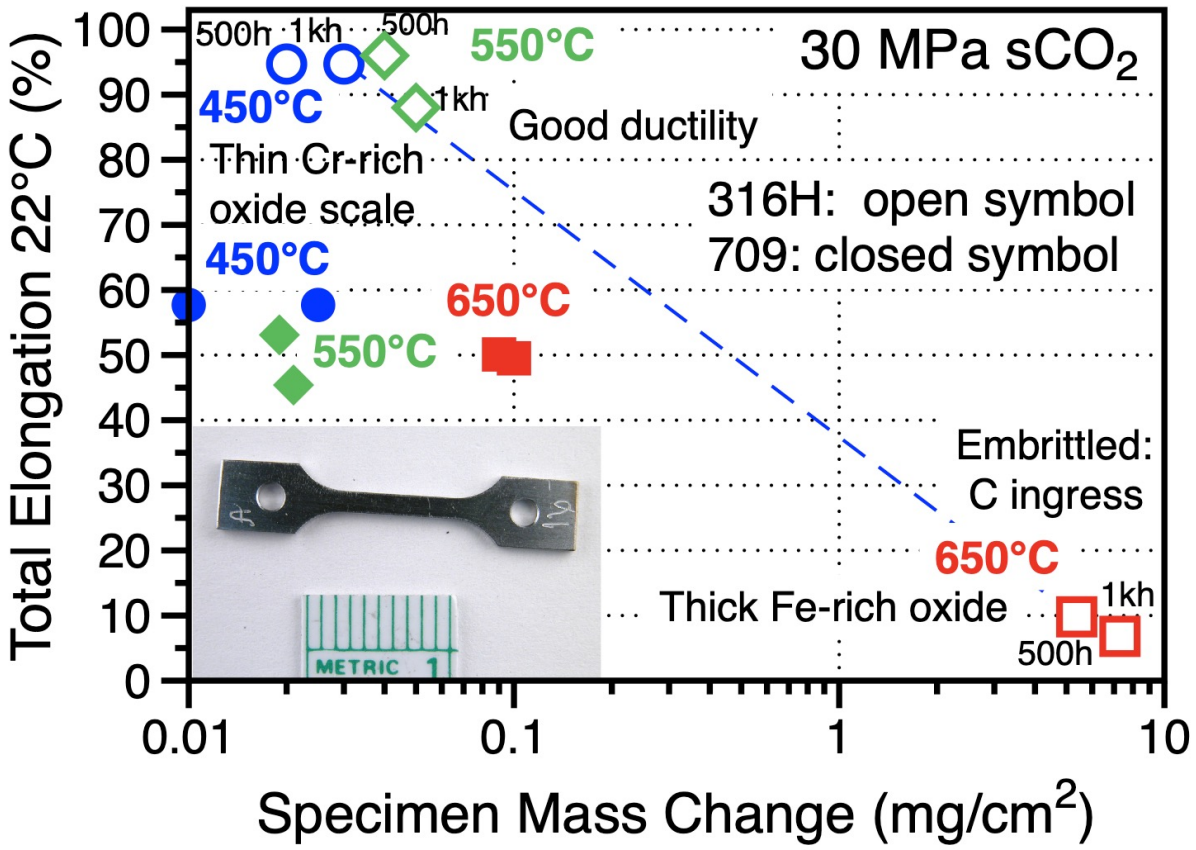
Measured rates in sCO_2 consistent with the literature

- 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



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

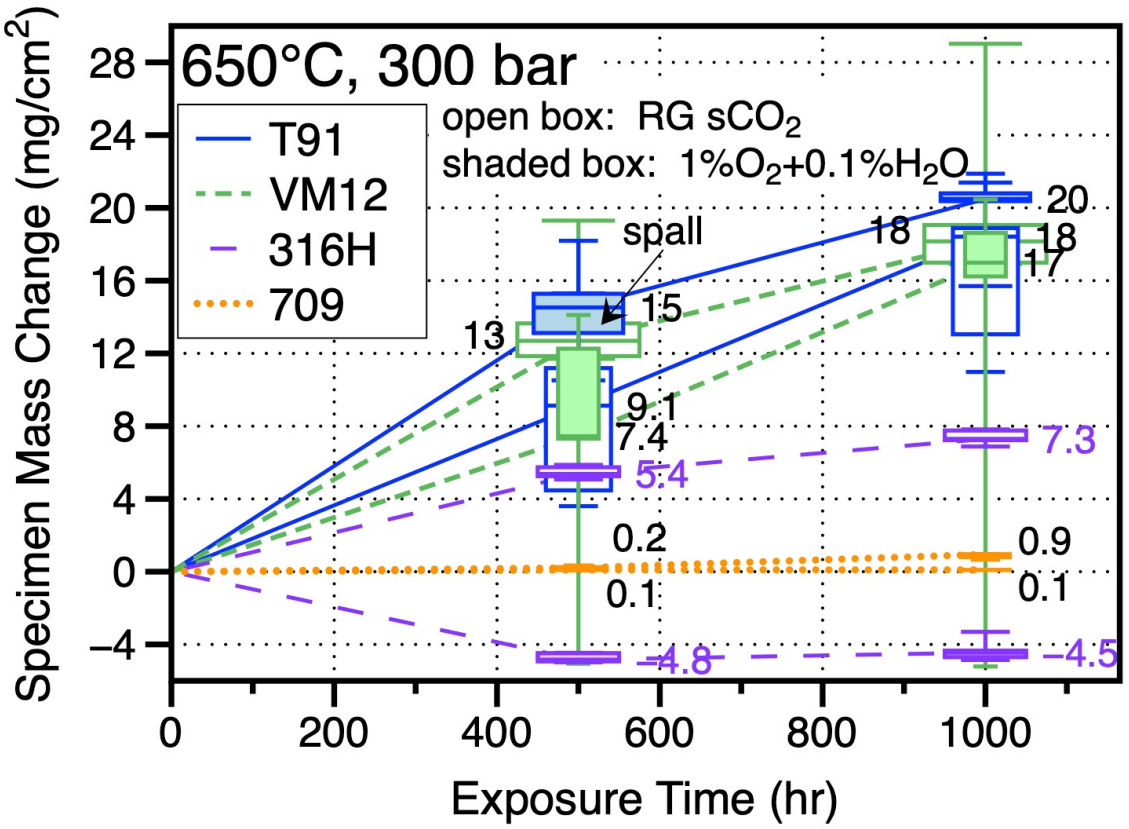
New metric #1: post-exposure room temperature ductility



- 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, in press

Adding impurities caused accelerated attack in SS:



Minor changes for 9-12Cr steels

Increase for 709

Spallation for 316H

sCO_2+1%O_2-0.1%H_2O per NetPower

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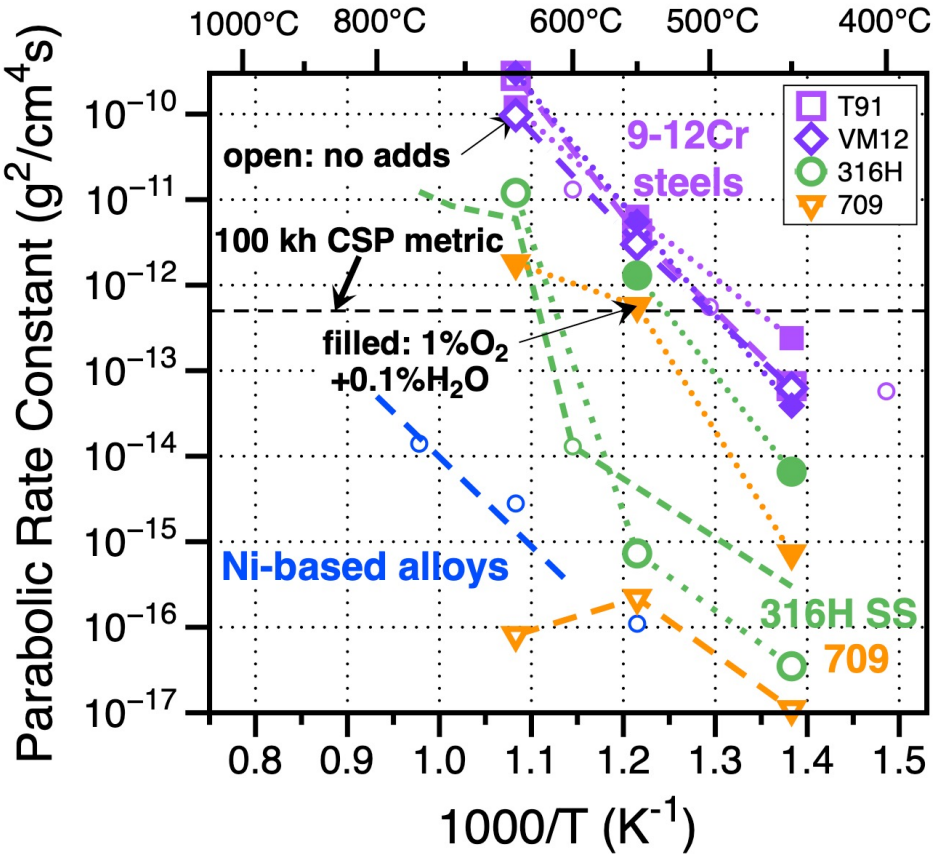
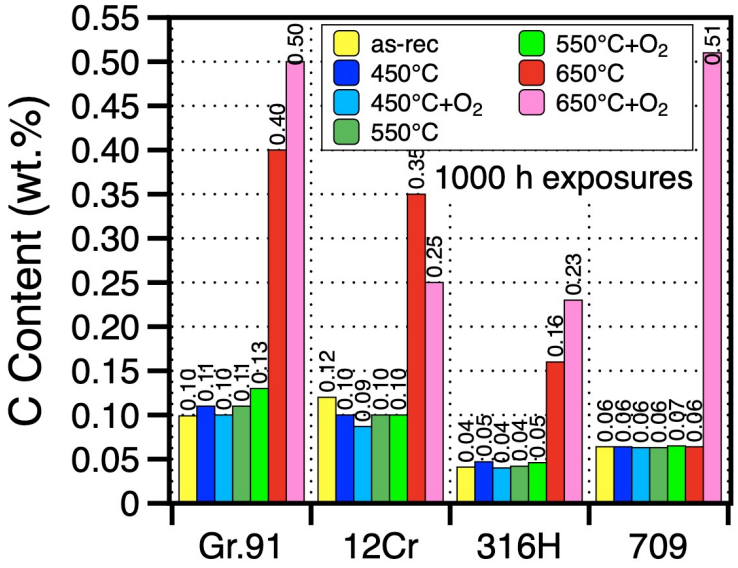
Acceleration evident for 316H and 709 (20Cr-25Ni)

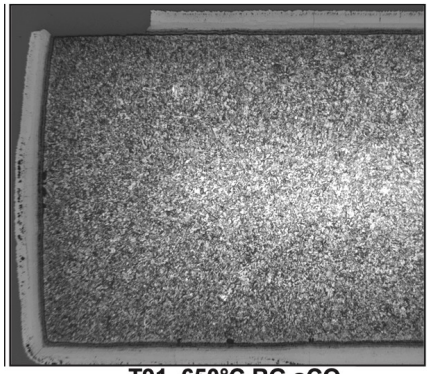


316H and 709 rates above the metric at 550°C

⇢ Longer exposures may be needed to obtain more accurate steady-state rates in this environment

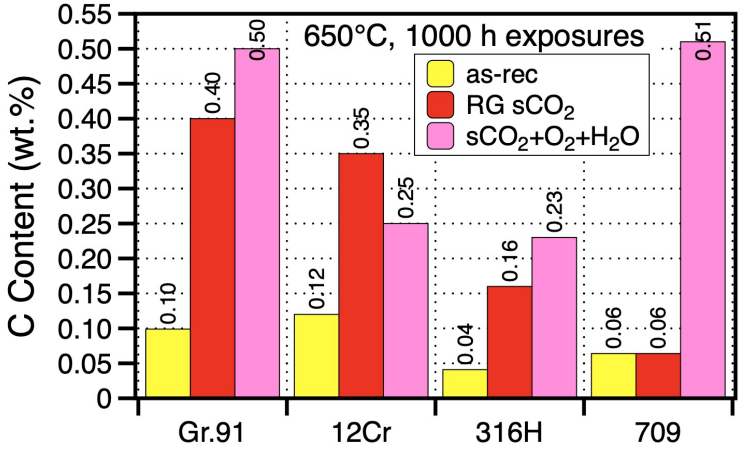
New metric #2: Bulk C measurements after exposure





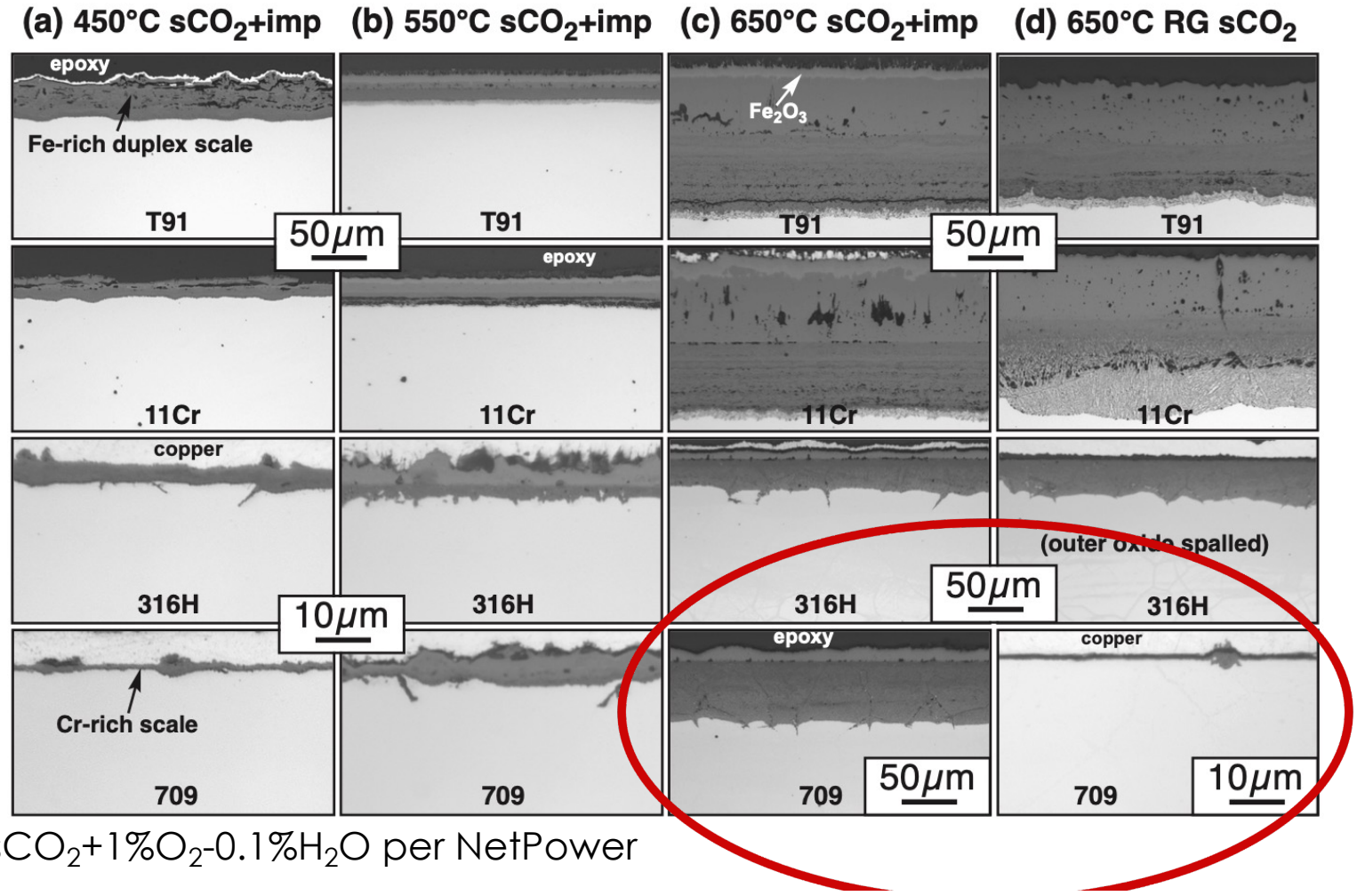
T91, 650°C RG sCO_2

C increase detectable mainly at 650°C



650°C: most materials showed higher C uptake with impurities in sCO_2 : less protective scales

Light microscopy: just getting started on characterization



sCO_2+1%O_2-0.1%H_2O per NetPower

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 650°C in RG sCO_2
    - Carbon ingress + embrittlement
    - **What about 600°C?**
  - 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!