Thoughts on sCO_2 materials

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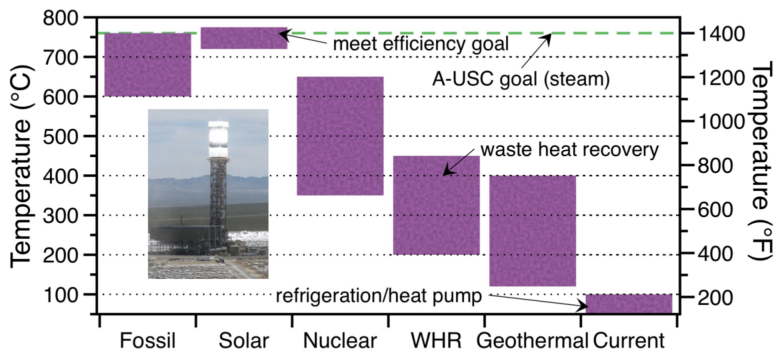
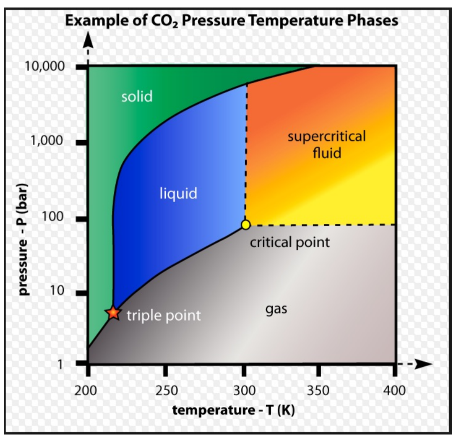
US DOE Fossil Energy & C Mgmt FWPs (2013-2023)

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**

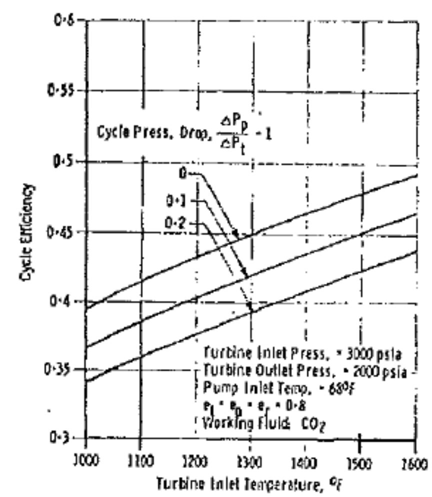
Concerns:

Limited operation experience

Supply chain for new cycle

Cost: Ni-based alloys

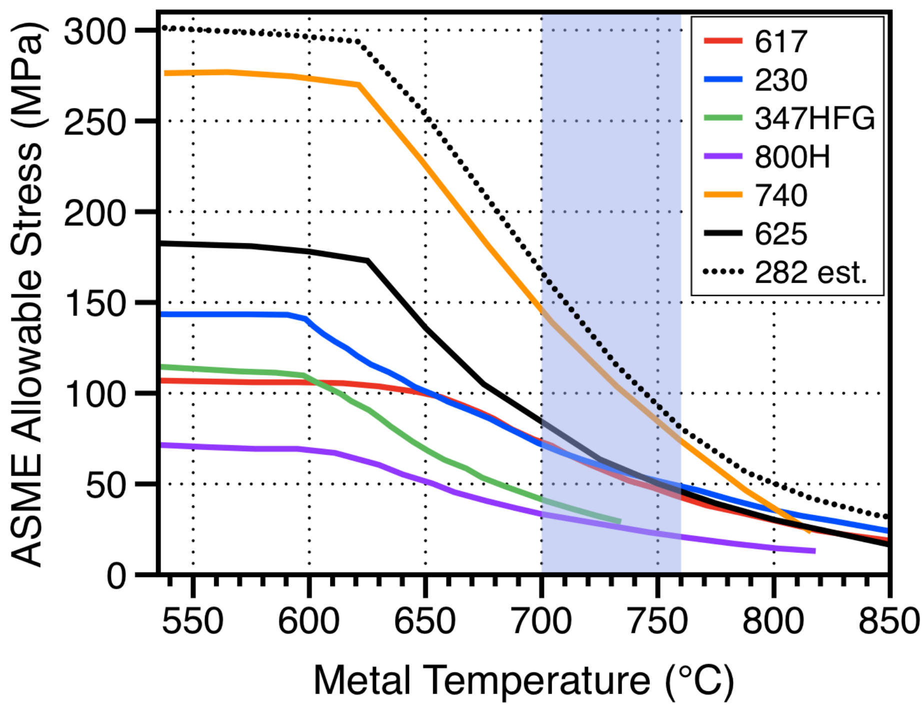
Interest in >700°C for high efficiency

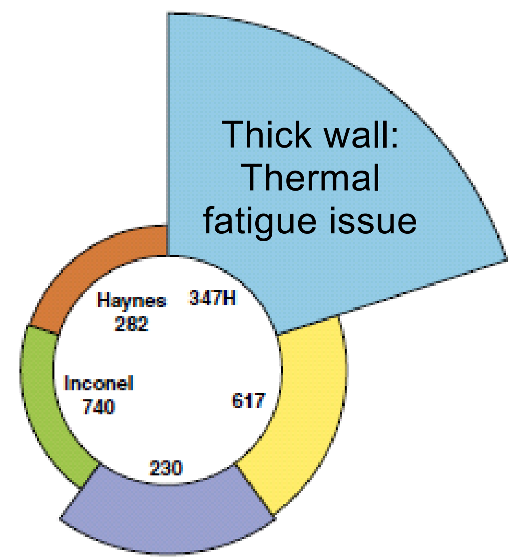


Feher, 1965

50% sCO_2 eff @ >720°C

700°-750°C sCO_2 cycles: materials are available
Benefit of DOE Fossil A-USC (Steam) Consortium work





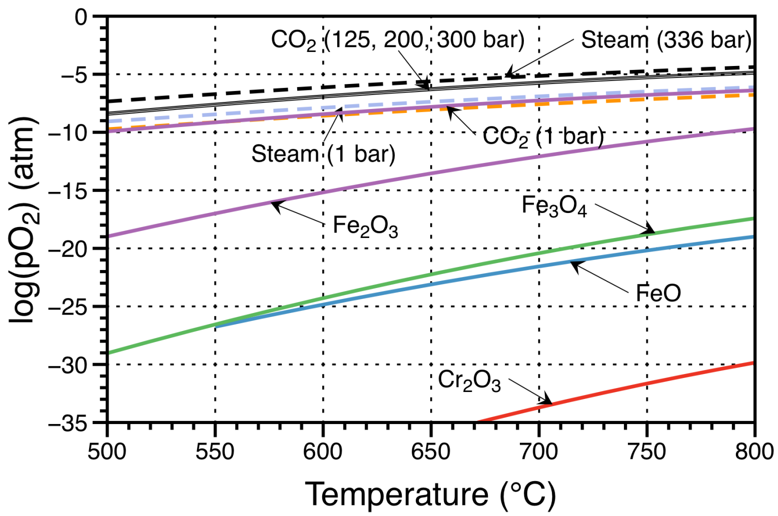
Shingledecker ~2011

Precipitation-strengthened Ni-base alloys 740H and 282 advantageous above 700°C

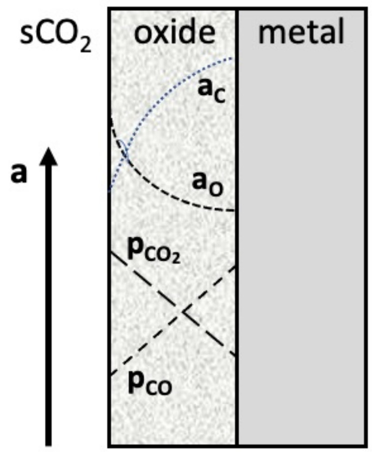
ORNL assisted with both code cases

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

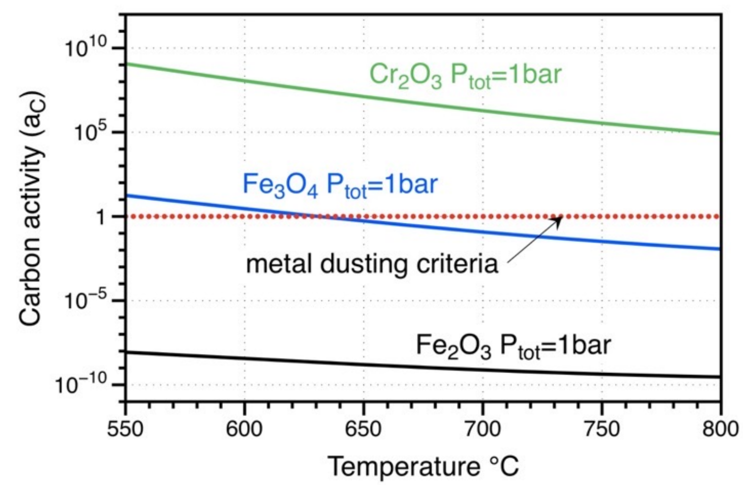
Factsage calculations:



All of our favorite oxides are stable!



Young et al., 2011



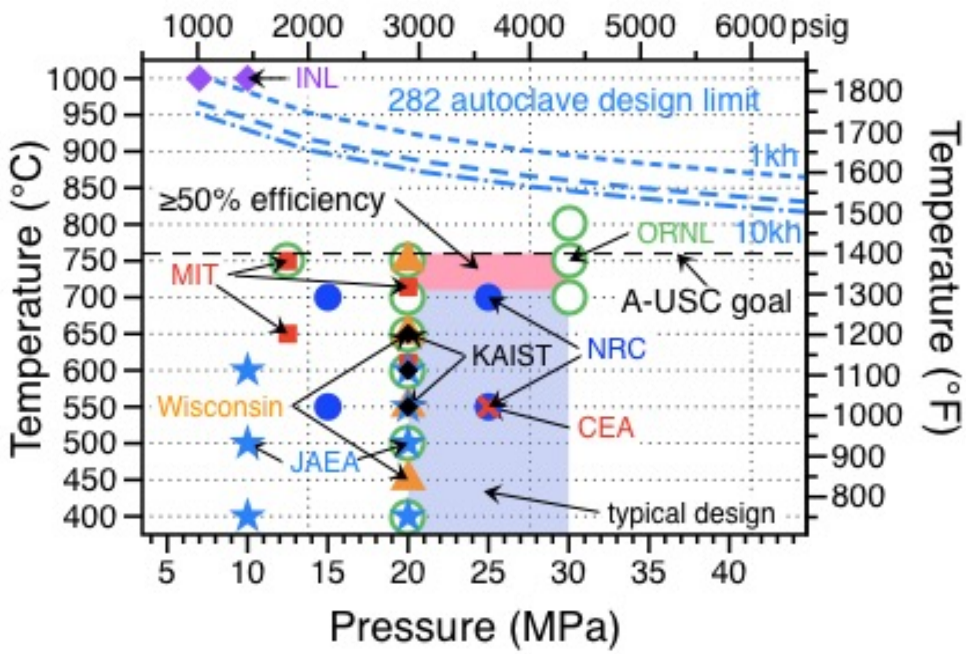
$2CO(g) = C(s) + CO_2(g)$ $CO_2(g) = 0.5O_2 + CO(g)$

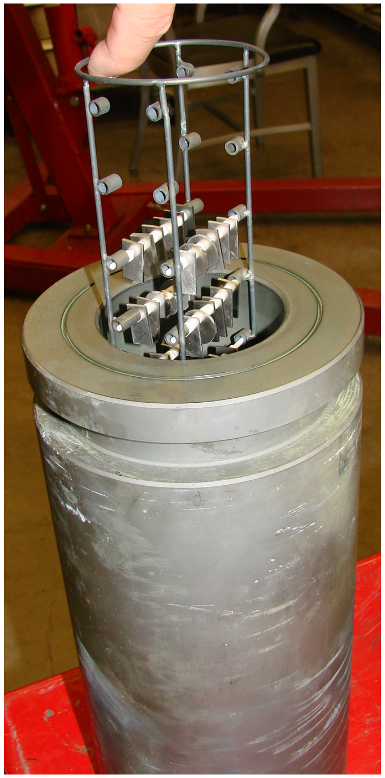
High carbon activity at P_{total} = 1 bar (What is $P_{interface}$?)

General conclusion: internal carburization concern for Fe-based alloys

Autoclaves can simulate sCO_2: T, P and O_2/H_2O impurities Generally finding low reaction rates for Ni-based alloys

Wide range of conditions investigated





ORNL

Alloy 282

Autoclave

From Pint and Brese, Chapter 4 High Temperature Materials
in *Fundamentals and Applications of Supercritical Carbon Dioxide (2017)*

Oxford modeled CO_2 lifetime in UK gas-cooled reactors
But results are not relevant for low impurity sCO_2

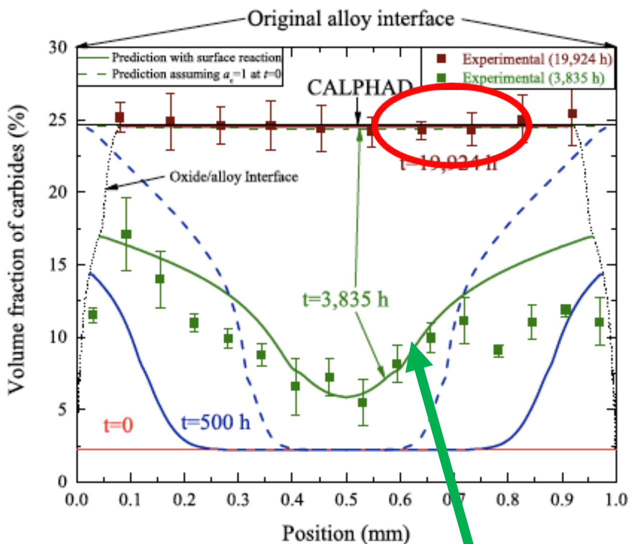
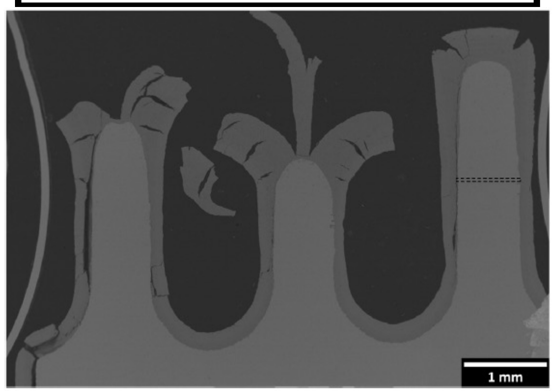


Fig. 8. Predicted profiles of volume fraction of carbides for a 1 mm fin exposed to experimental gas conditions at 600 °C at 0, 500 h, 3835 h and 19924 h, in comparison with measurements corresponding to black box marked in Fig. 1(b); simulations were conducted by 1D-DiCTra as described in § 3.2 treating migration of oxide/alloy interface and non-steady state carburisation with $\alpha_{\mu C} = 1.2 \times 10^{-12}$ mol m s^{-1} J^{-1} (solid lines) or fixed $a_C = 1$ at the oxide/alloy interface (dashed lines).

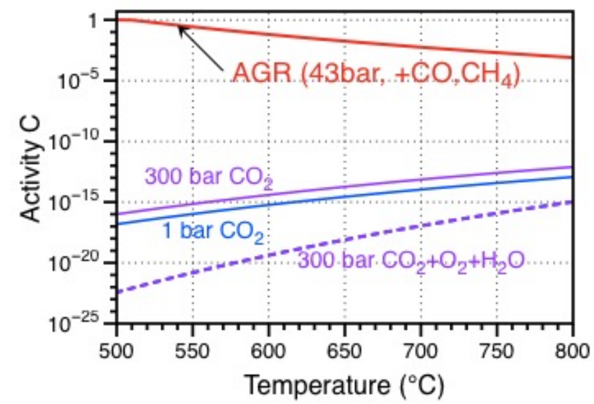
Gong, Young…Reed, Acta Mater. 2017



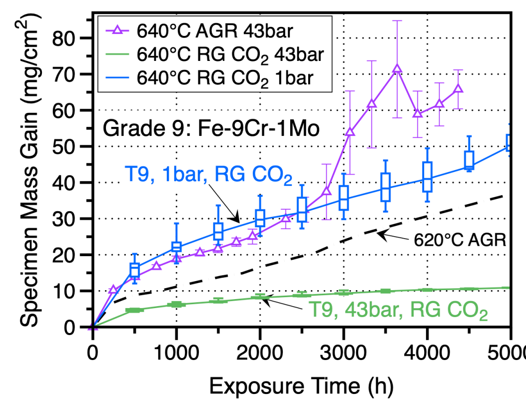
Grade 9 steel fins:
Fe-9Cr-1Mo

Experimental data (80-200 kh!) 580°-640°C:
Cr tied up as carbides

#1 AGR CO_2 is very different



#2 RG CO_2: no breakaway



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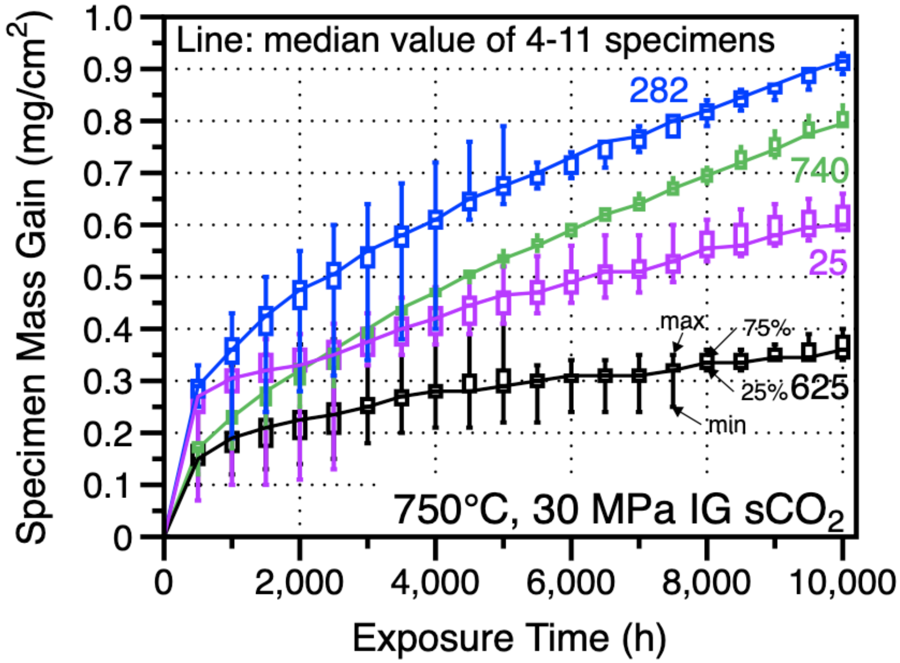
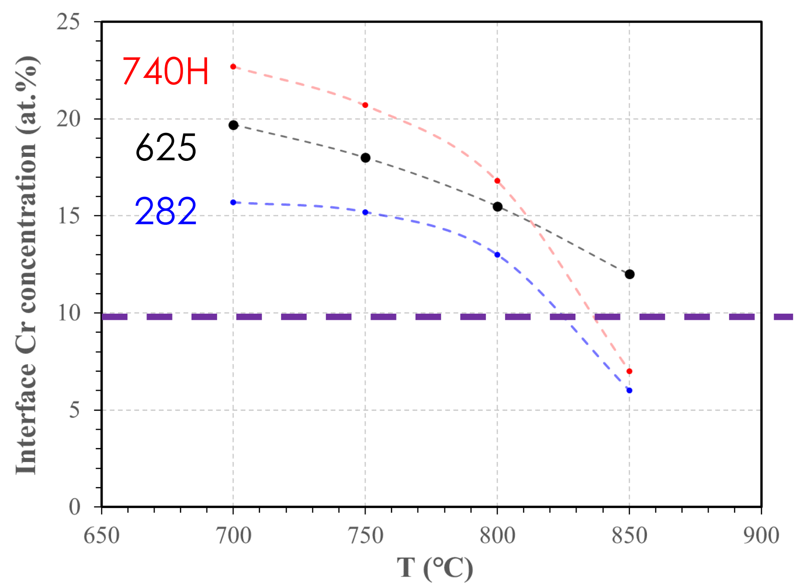
sCO_2 lifetime models developed using FE and SETO datasets

SETO dataset: 10,000 h at 750°C/300 bar in IG sCO_2



Pint et al., Oxid. Met. 2020

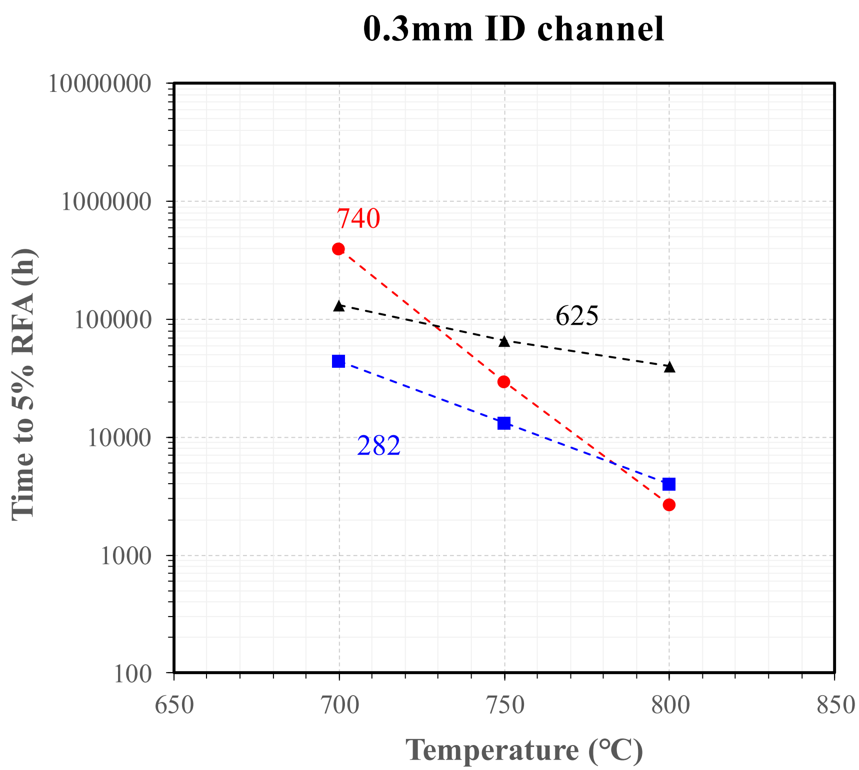
Pillai: Predicted Cr interface concentration after 100,000 h

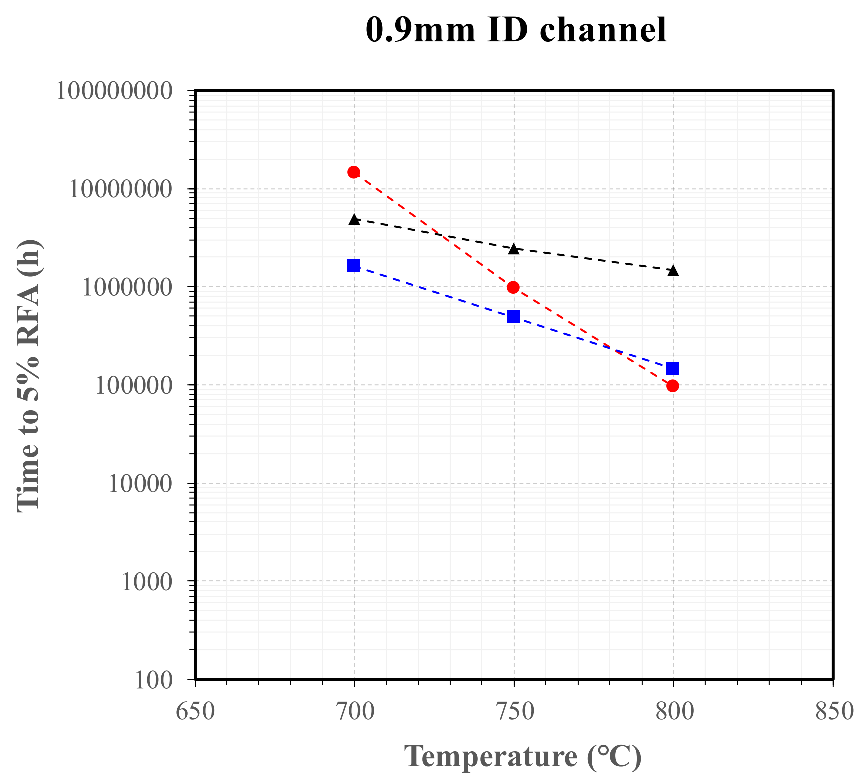


Failure criteria: Cr content drops to 10% at the metal-oxide interface

Failure mode II. Reduction in flow area (RFA) due to oxidation

RFA> 5% considered critical [Kung 2018 (EPRI)]





- **0.3mm channel is predicted to be an issue for all alloys**
- **0.9mm channel is predicted to be safe for all alloys up to 800°C**

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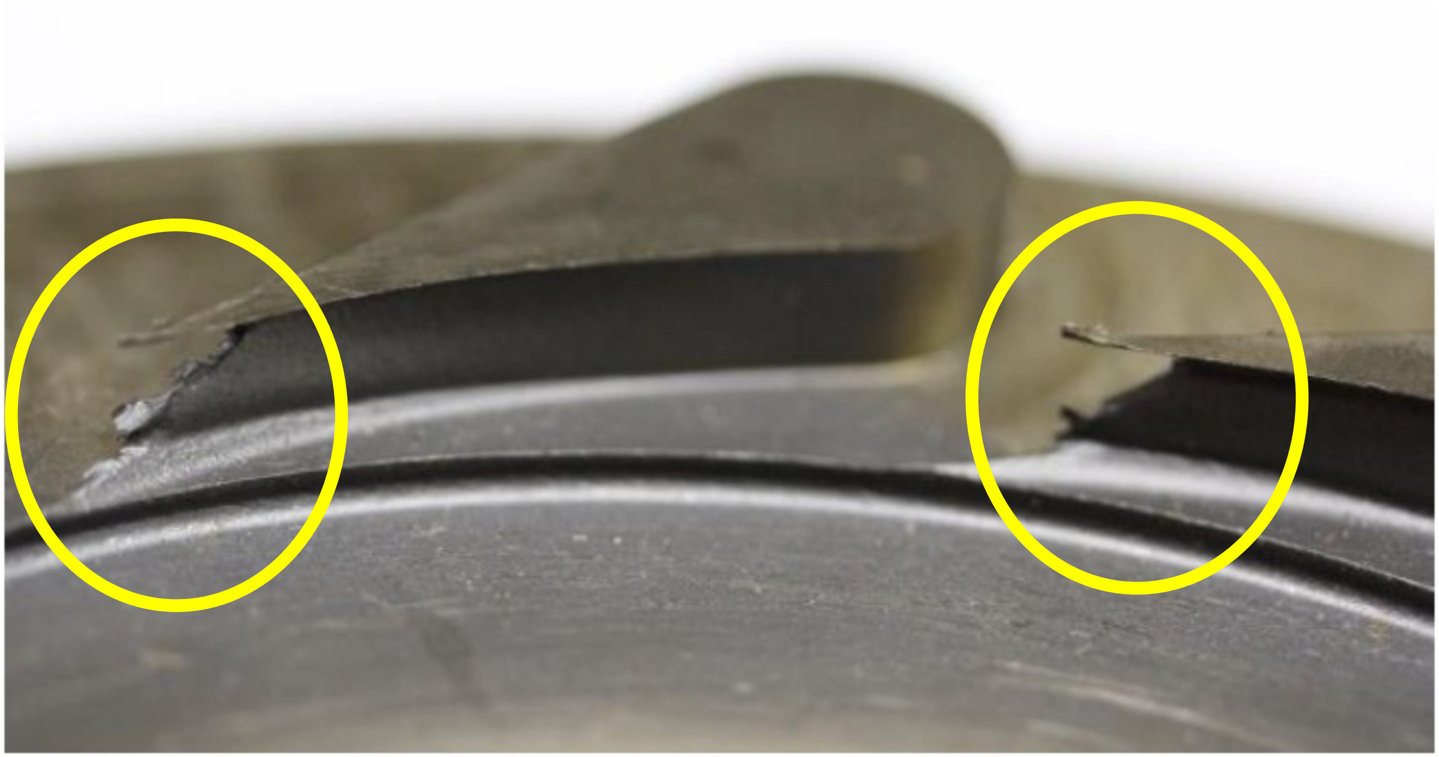
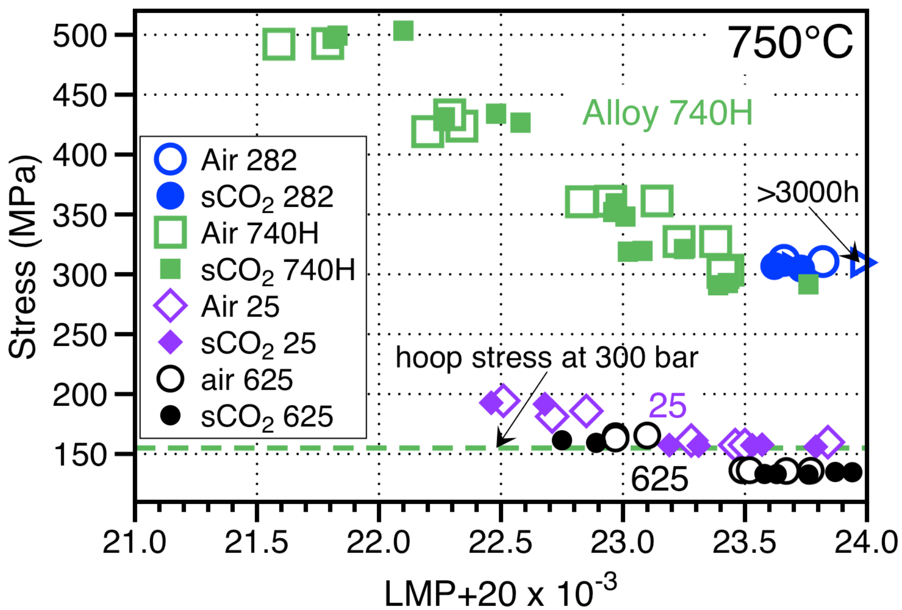
Erosion (by fluid or particles?) not going to be investigated in autoclaves

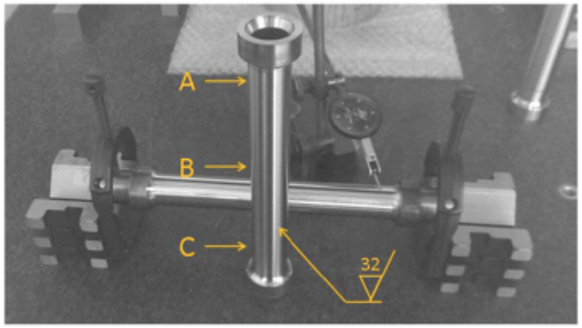


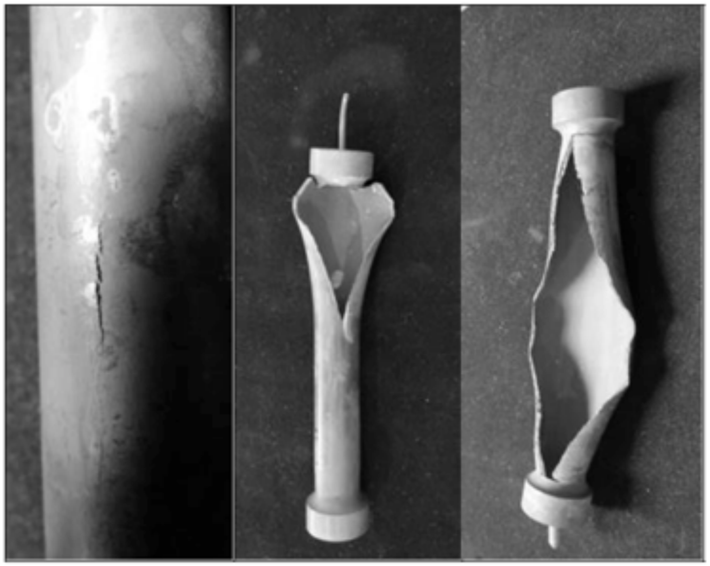
From Fleming et al. Sandia National Laboratory report, 2014

SETO: creep rupture testing of tubes at 750° showed no difference between sCO2 and pressurized air



LMP = T(in K) (20 + log(time in h))





Closed symbol: sCO_2 (open: air)

740/282 show much higher strength

One 282 specimen did not fail

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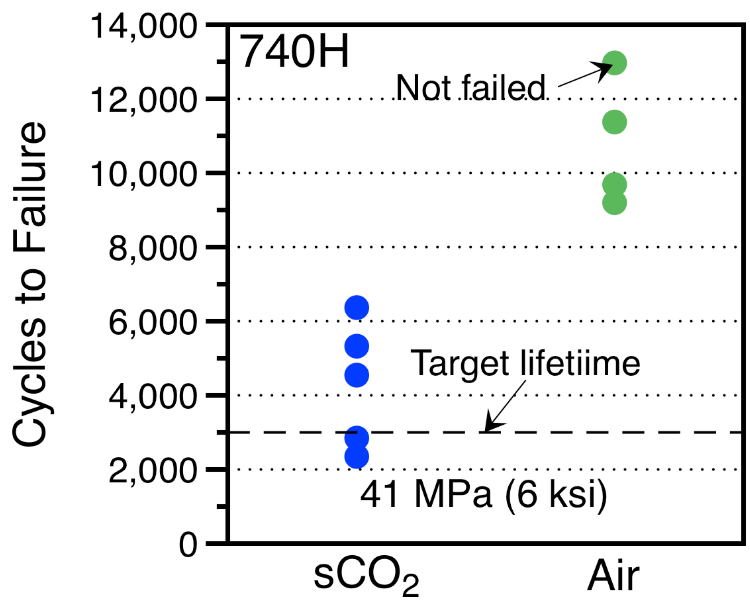
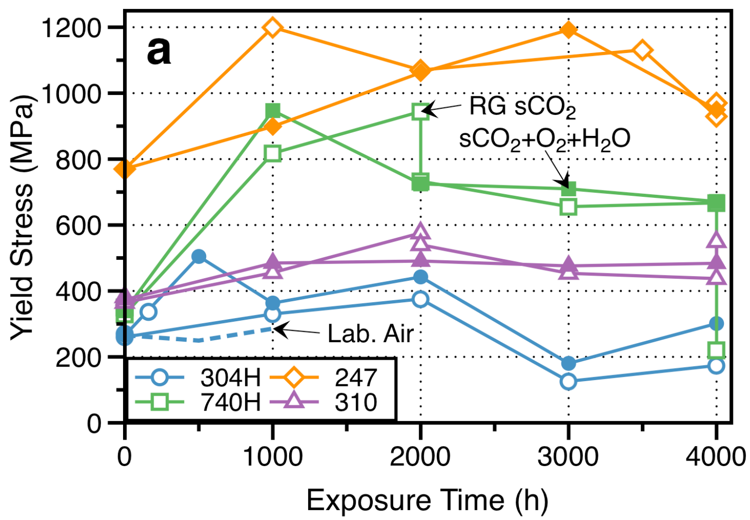
SETO Phase 3: creep-fatigue testing of 740H tubes at 750°C Difference in lifetime between sCO_2 and pressurized air

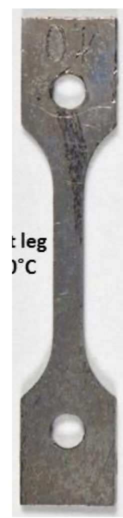


- Cycle: 8min hold at 41 MPa followed by depressurizing
- Each group stopped with one specimen not failed
- Began testing 625 specimens but none failed by end of project
- Work performed by Brayton Energy (Jim Nash, et al.)

Mechanical properties may be better to assess effect of sCO_2 on steels: example 25°C elongation of 304H
FY19(20?) evaluation of steels at 450°-650°C will

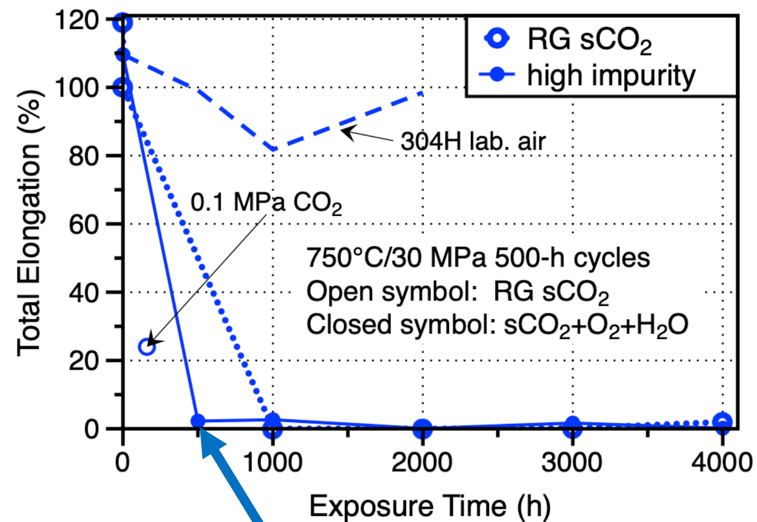
Yield strength of 4 alloys:





25mm dogbone

Post-exposure elongation of 304H:

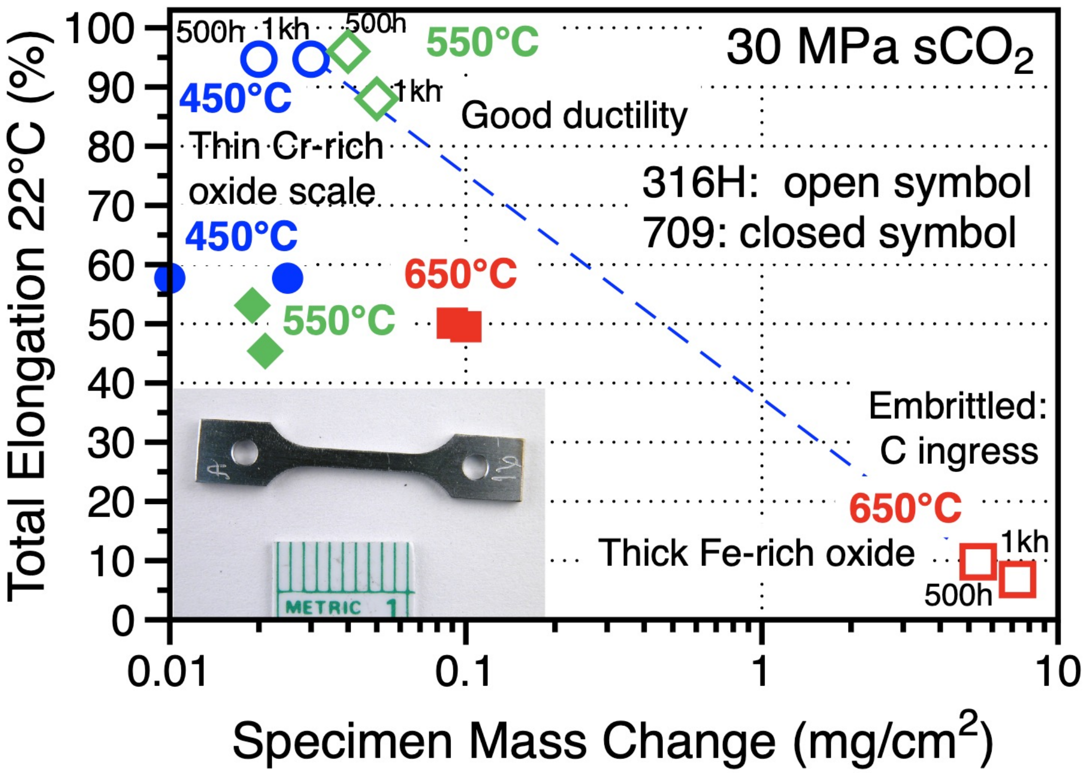


304H: large drop in sCO_2 due to internal carburization

Pint, et al., Materials and Corrosion, 2019

No impurities: combination of mass change and ductility to illustrate issue with 316H at 650°C (709 not affected)

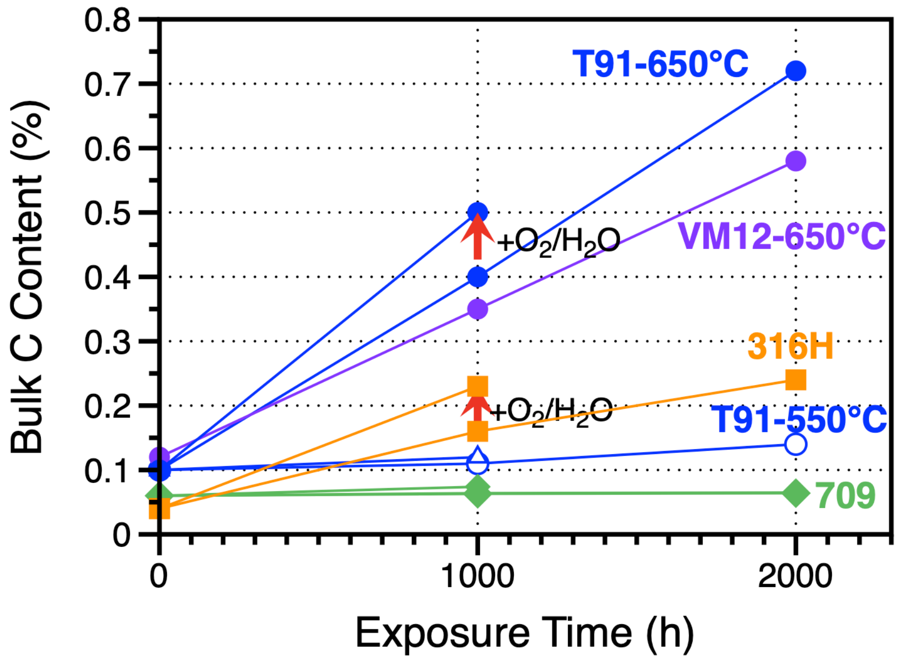
High ductility & low mass gain



500h & 1000 h measurements for each stainless steel

Low ductility & high mass gain

Bulk C measurements: Fe-rich oxides allow C ingress



RG sCO_2: No impurities

- 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

Supercritical CO_2 Allam cycle: first clean fossil energy?

NetPower 25MWe test facility (Texas)

Exelon, Toshiba, CB&I, 8Rivers Capital: $140m

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

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

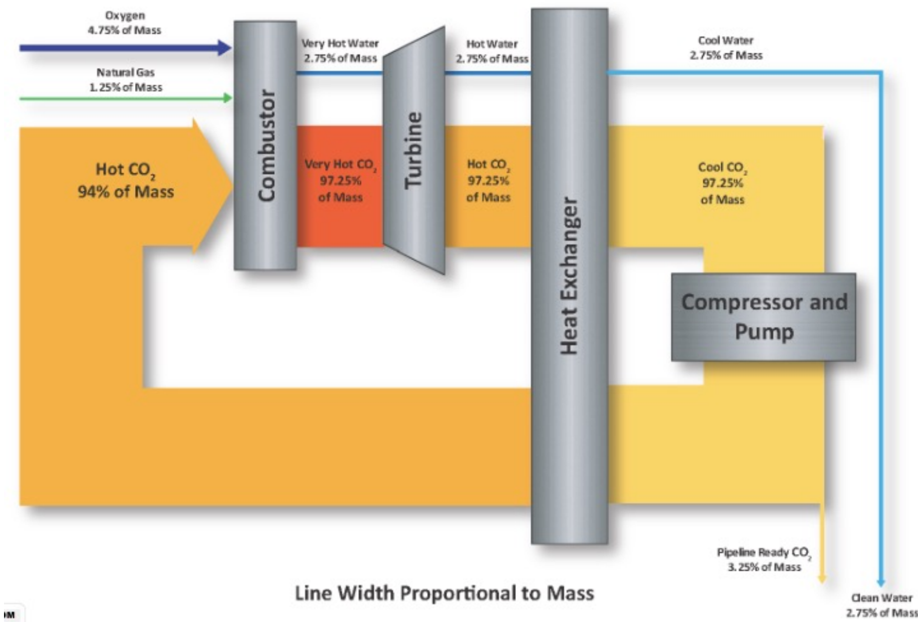
May 2018: announced first firing
November 2021: 1st grid power

Material challenges:

Combustor: 1150°C (!?!) (now 900°C)

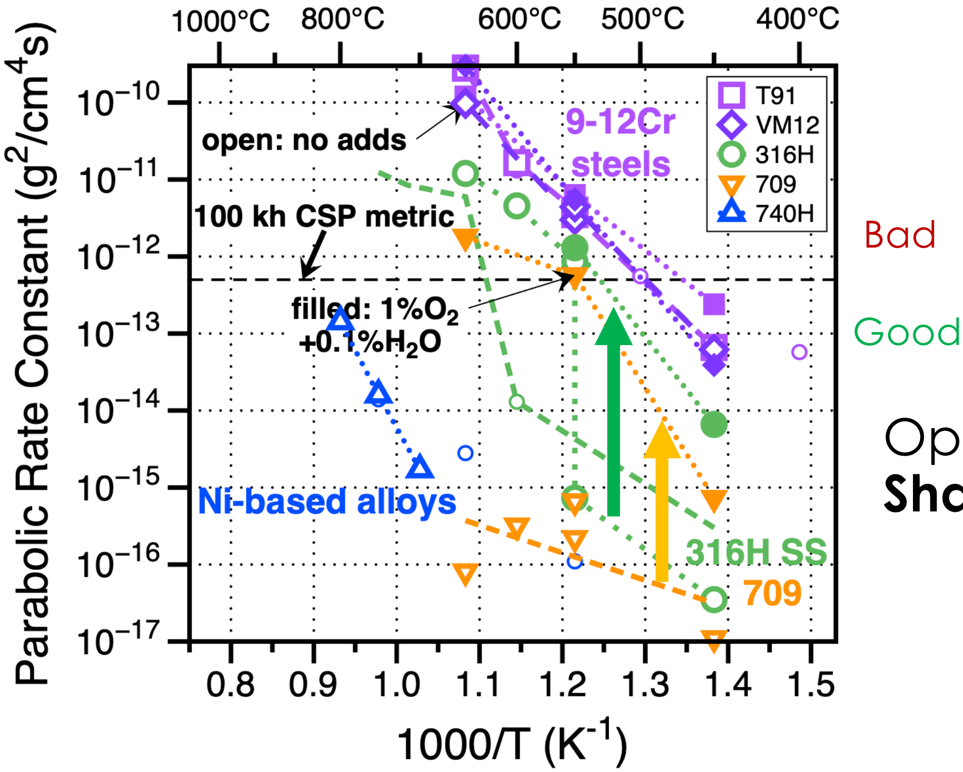
Turbine exit: 750°C/300 bar

Combustion impurities: O_2, H_2O, SO_2



Burning natural gas in sCO_2 creates impurities…what is the effect?

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

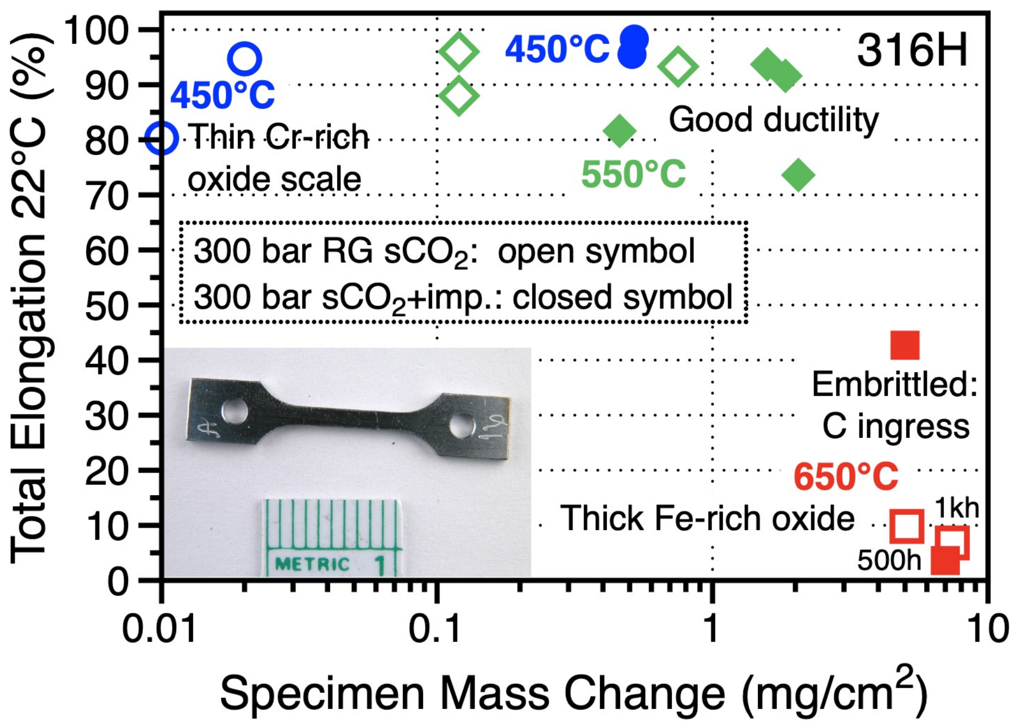
- no change for Gr91 and VM12
- higher rates for 316H and 709

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

With impurities: 316H not significantly embrittled at 550°C Similar embrittlement at 650°C

High ductility & low mass gain



500h & 1000 h measurements for 316H

Open symbol: RG sCO_2
Closed symbol: $sCO_2+O_2+H_2O$

Low ductility & high mass gain

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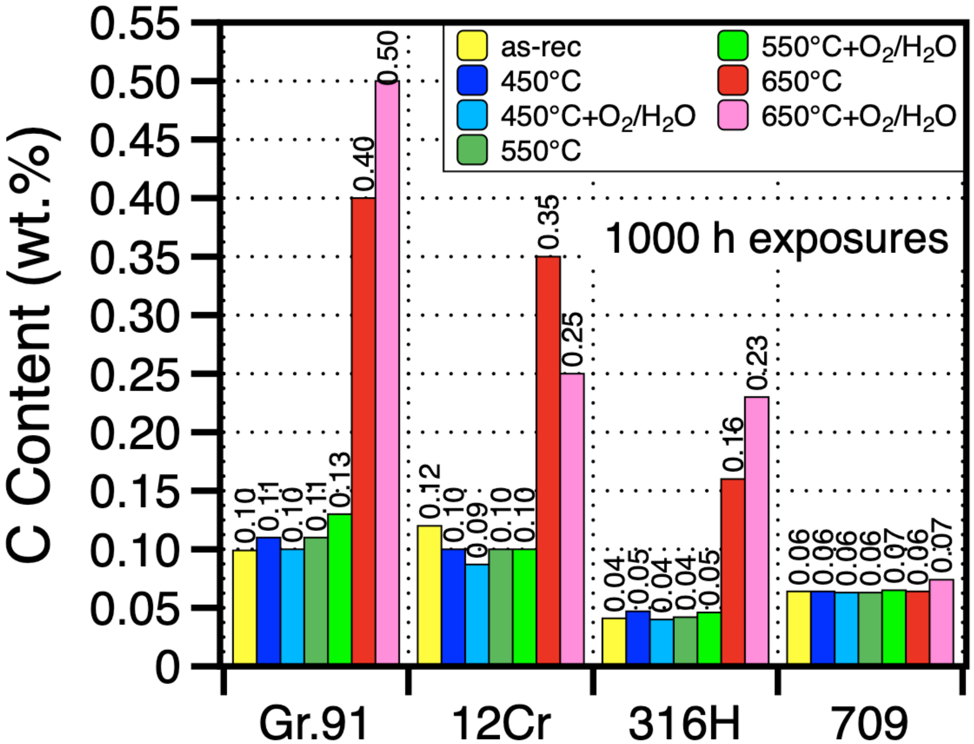
650°C: increased C ingress with impurities (limited change in bulk C at lower temperatures)

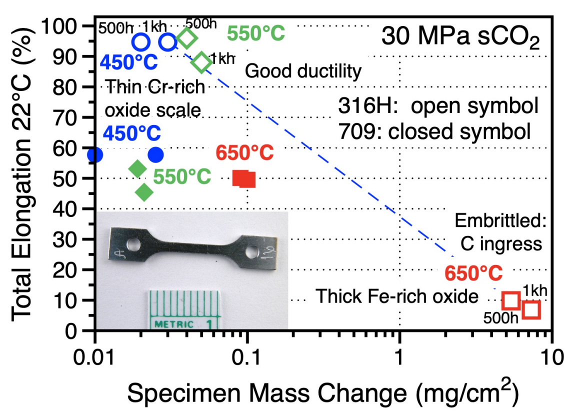


Determined by combustion analysis

sCO_2 compatibility: broad range of conditions considered

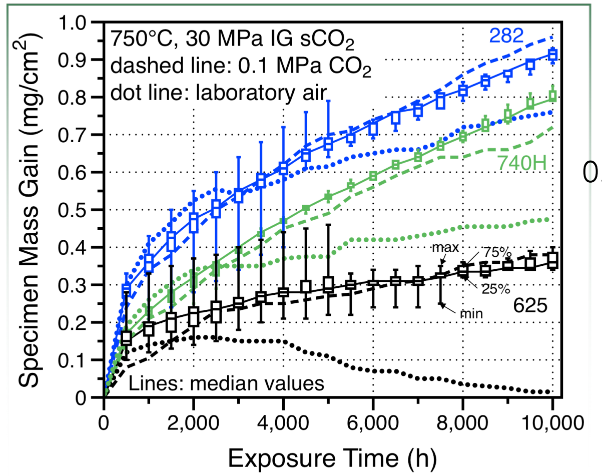
400°-650°C: concern about steel carburization

- 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

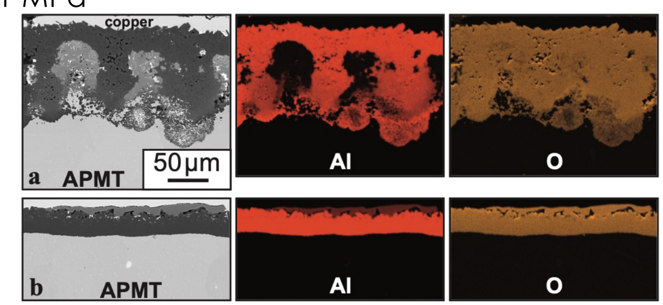
- No issues for Ni-based alloys
  - Low C solubility, protective Cr_2O_3 formation
- Similar rates for air, CO_2 and sCO_2
  - **Little or no P effect @ 750°C**



>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

Materials summary

- Highest temperatures (700°-750°C) appear achievable
  - Low C solubility in Ni-based alloys may be key to compatibility
- Above 800°C will be a challenge
- Where can lower cost steels be used?
  - Concern about carburization and breakaway oxidation
  - What corrosion allowance to use for austenitics and ferritics?
  - Various coating concepts are being explored
- Is erosion the real problem?
  - Fluid or debris? Is exfoliation of reaction products an issue?
- Mechanical properties of thin-walled components (fatigue debit?)