The Effect of Temperature on the sCO_2 Compatibility of Conventional Structural Alloys

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M. Stephens, T. Lowe - specimen preparation/handling

T. Jordan - metallography

ORNL craft workers

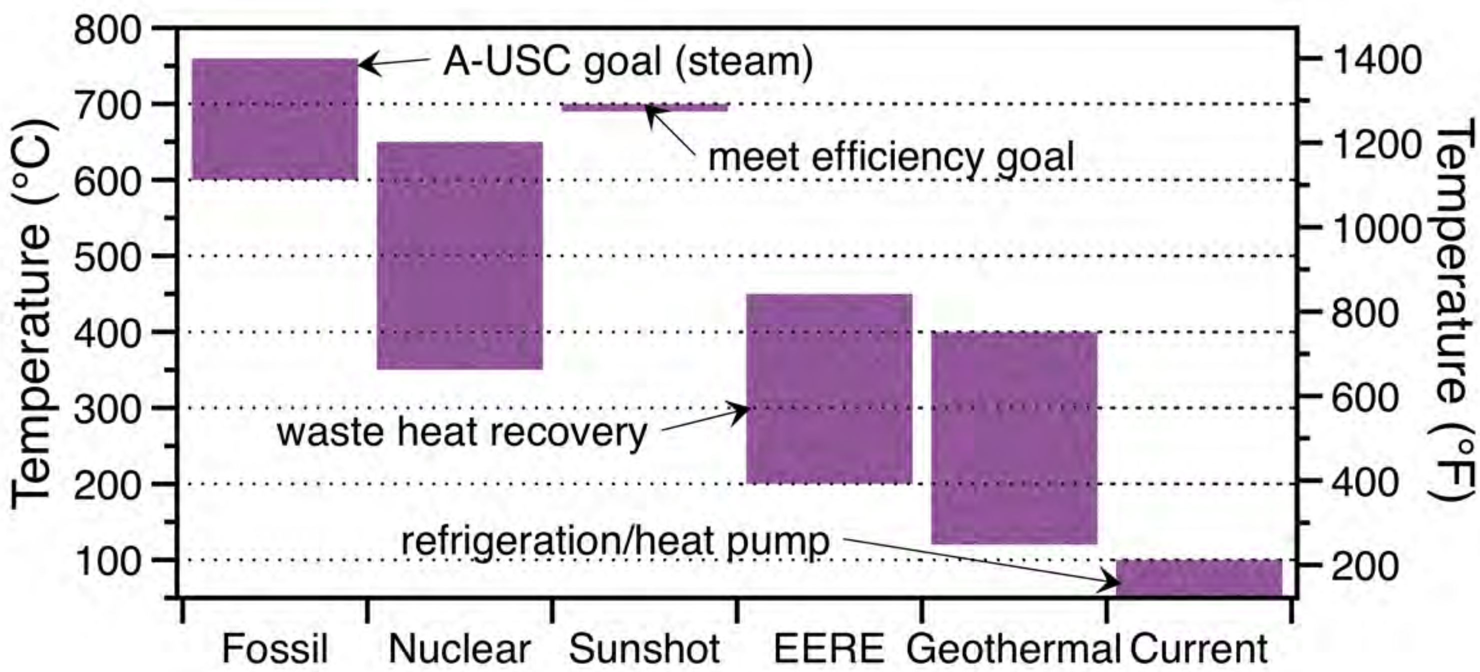
Alloy coupons:

- Haynes International
- Special Metals
- Allegheny-Ludlum
- Sumitomo Metals
- Sandvik (Kanthal)
- Capstone Turbines
- Siemens
- Plansee

Research sponsored by: U. S. Department of Energy, Office of Coal and Power R&D, Office of Fossil Energy

Different temperature targets

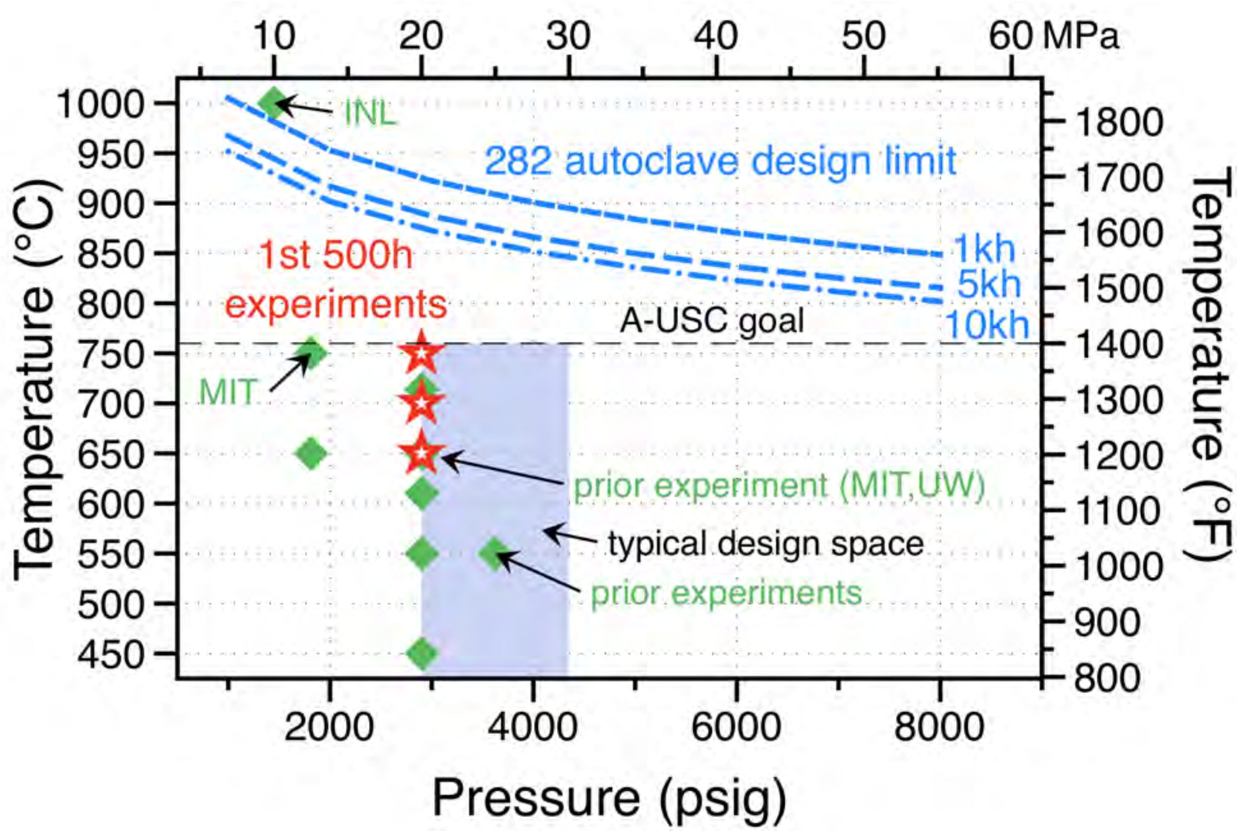
- Uncertainty about ranges for sCO_2 applications
- Fossil energy interest for power generation
  coal/natural gas: replace steam with closed cycle
- At the highest temperatures, little data available



Temperature effect investigated

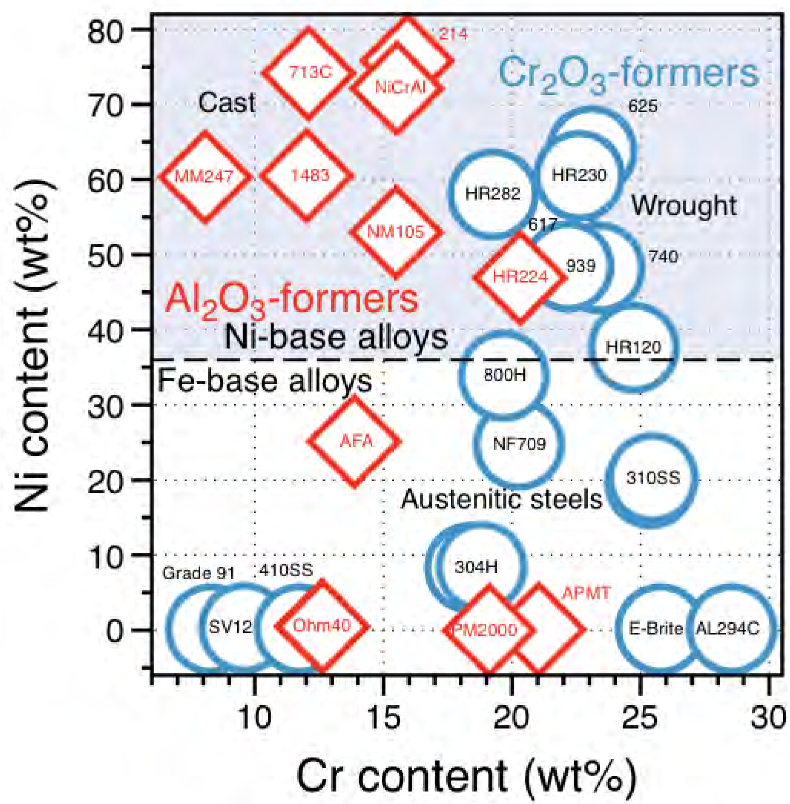
- Varied temperature at 20MPa: 650°-750°C
- Three 500h isothermal experiments
- Second: effect of pressure (FY15)

1200°-1380°F



Range of alloys exposed

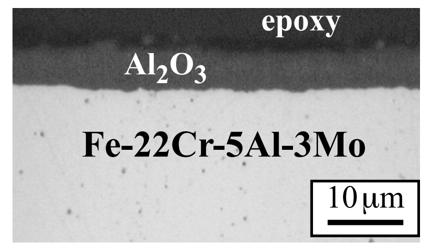
- ~30 alloy coupons exposed plus SiC ceramic



1200°C steam exposures:

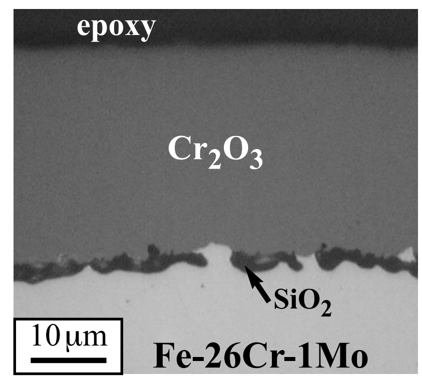
Alumina-former:

48 h



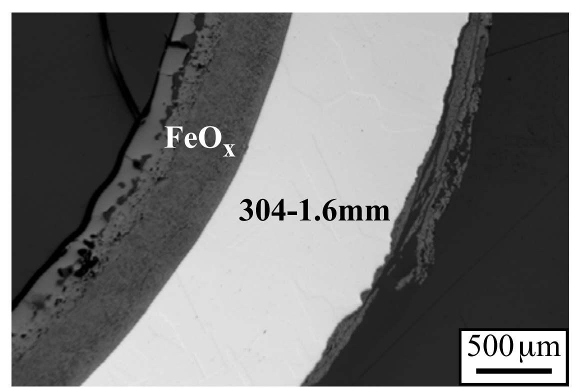
Chromia-former:

48 h



Non-protective iron oxide:
Type 304L stainless steel

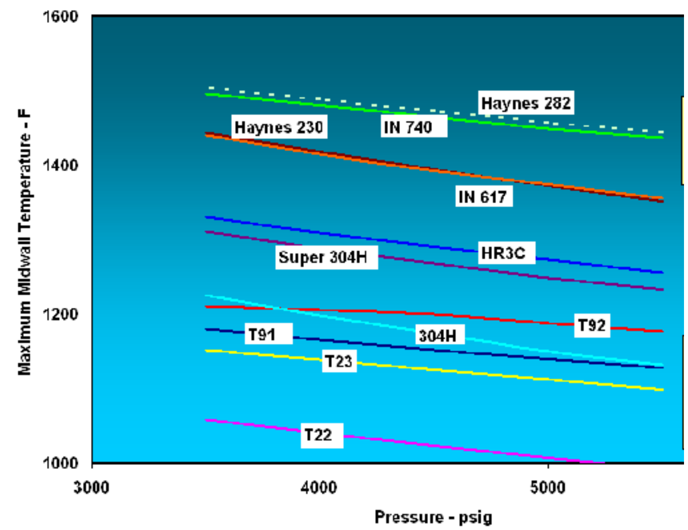
2 h

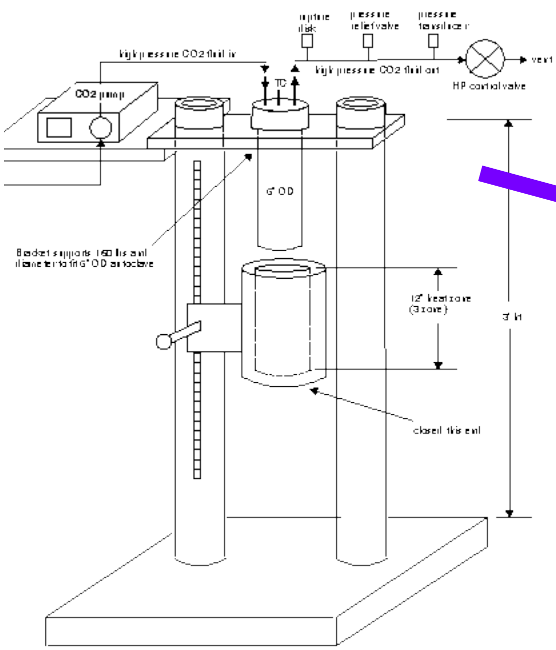


ORNL sCO_2 rig finished in May

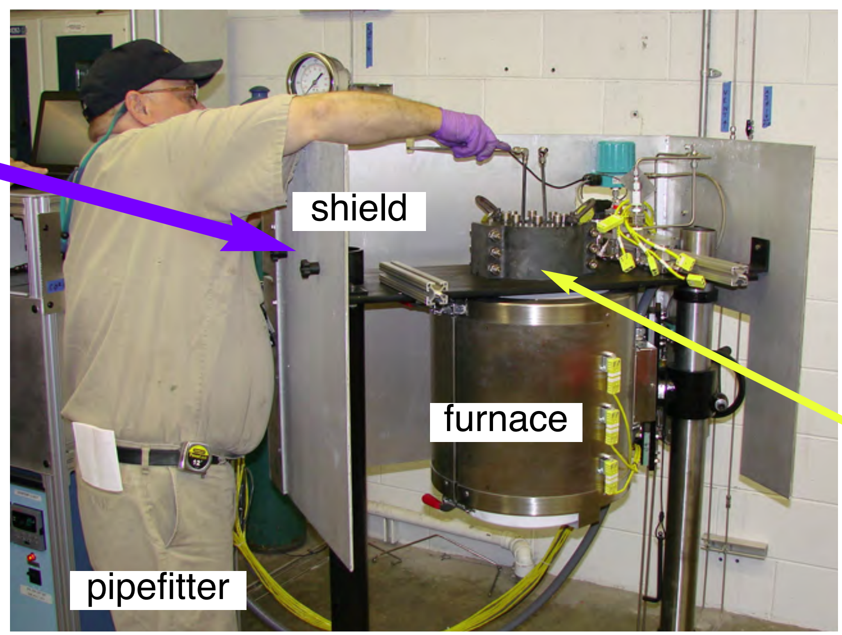
- ORNL design (team: 100+ years of experience)

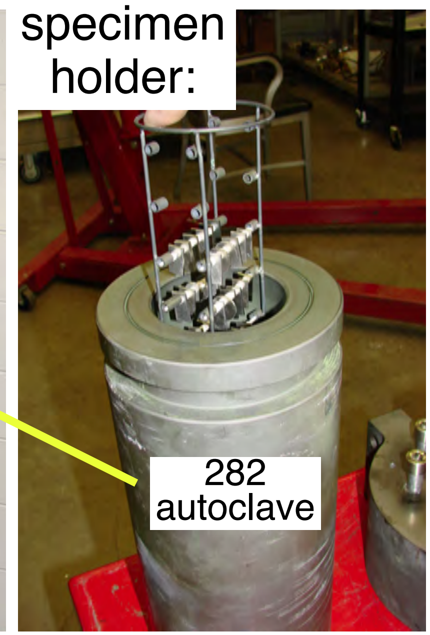
- HR282 6” diameter autoclave





ORNL sCO_2 rig:

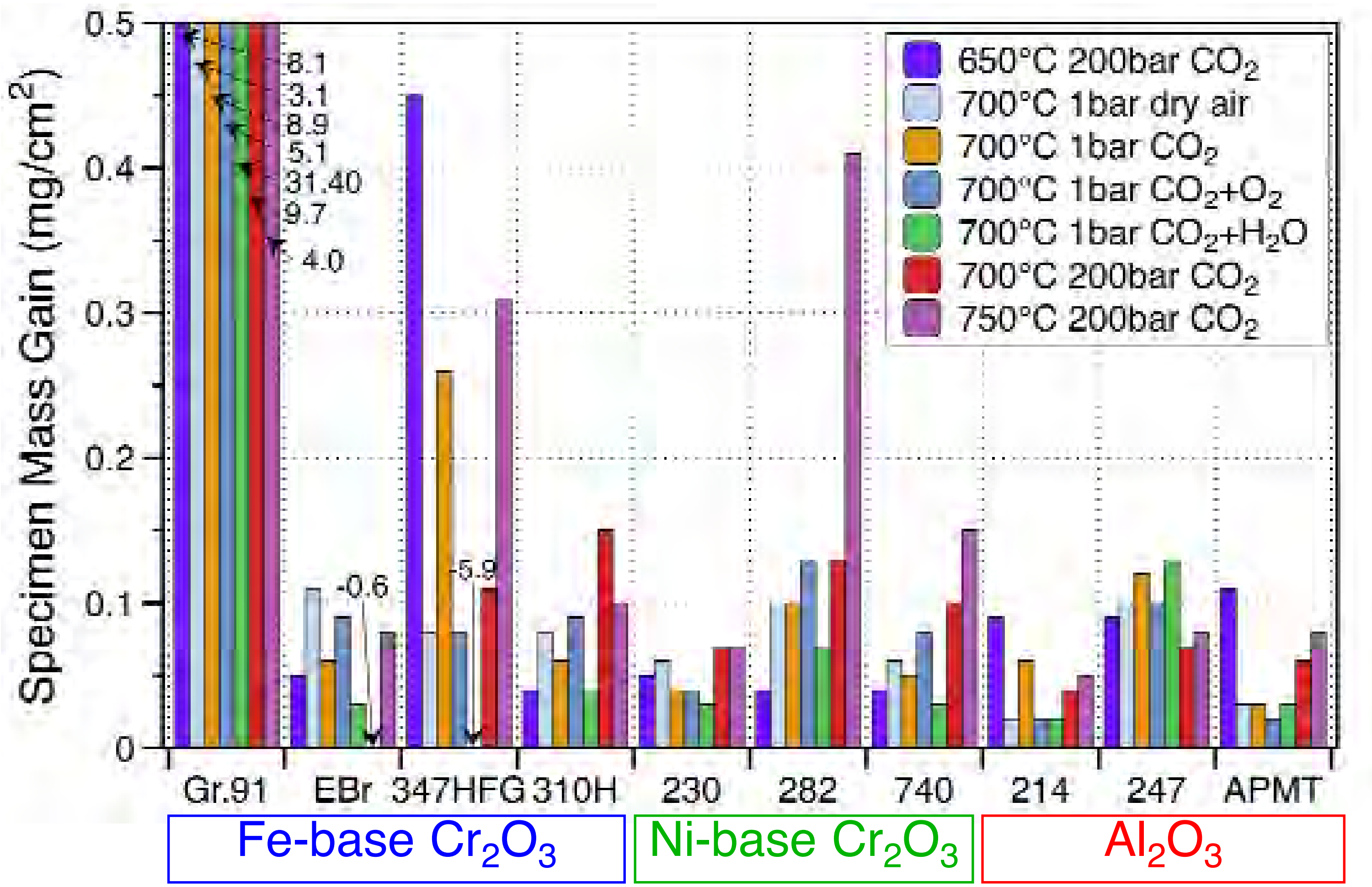




Baseline created at 700°C 1bar

10 representative alloys were focus of metallography

1bar: dry air, CO_2, CO_2+0.15O_2, CO_2+10%H_2O



0.1 mg/cm^2 ~ 0.5 μm surface oxide

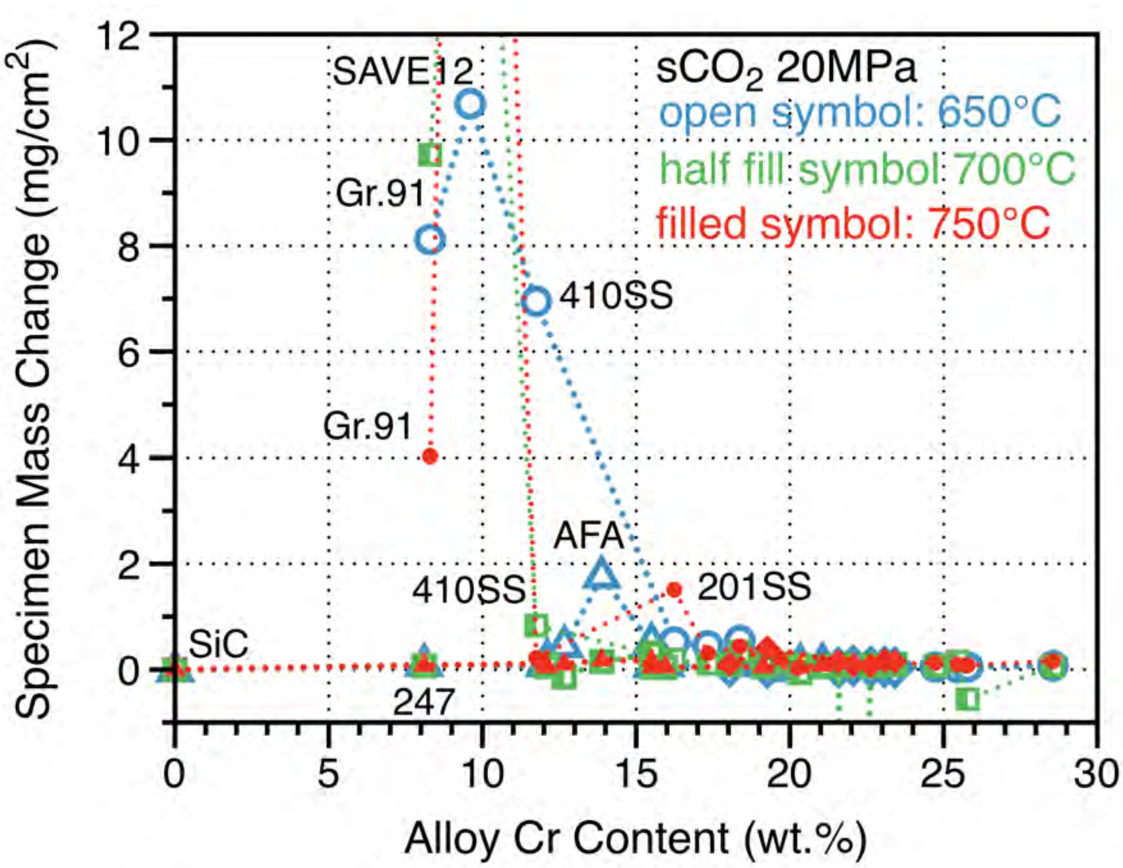
10 mg/cm^2 ~ 50 μm (2 mils)

200bar mass change by %Cr

Many alloys exhibited a low mass gain at 650°-750°C

Low Cr steels were heavily attacked

18-25%Cr alloys performed similarly



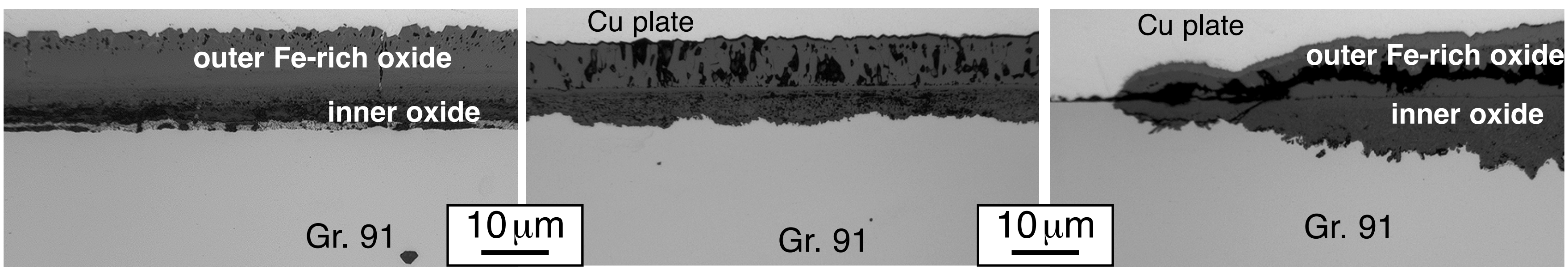
Typical Fe-rich oxide on Gr.91

Similar oxide forms in dry air at 700°C, steam, etc.

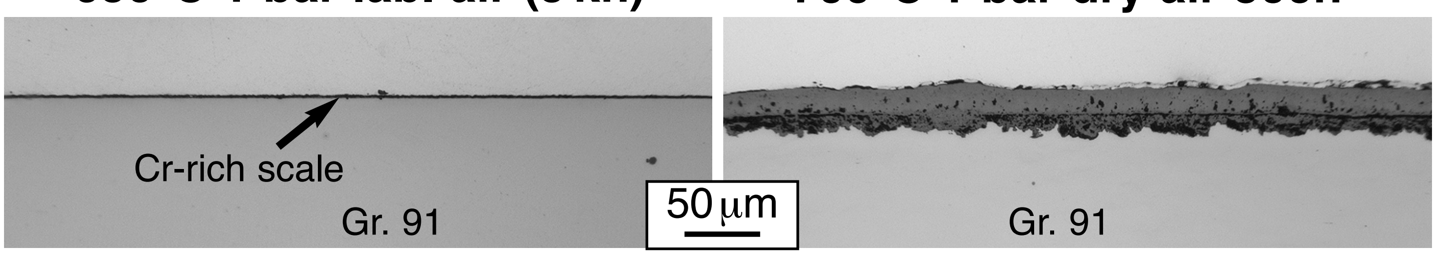
- Outer Fe_2O_3/Fe_3O_4 layer
- Inner $(Fe,Cr)_3O_4$ layer

Rather than thin-protective Cr-rich scale (650°C,air)

650°C 200 bar CO_2 **700°C 200 bar CO_2** **700°C 1 bar CO_2**



650°C 1 bar lab. air (5 kh) **700°C 1 bar dry air 500h**



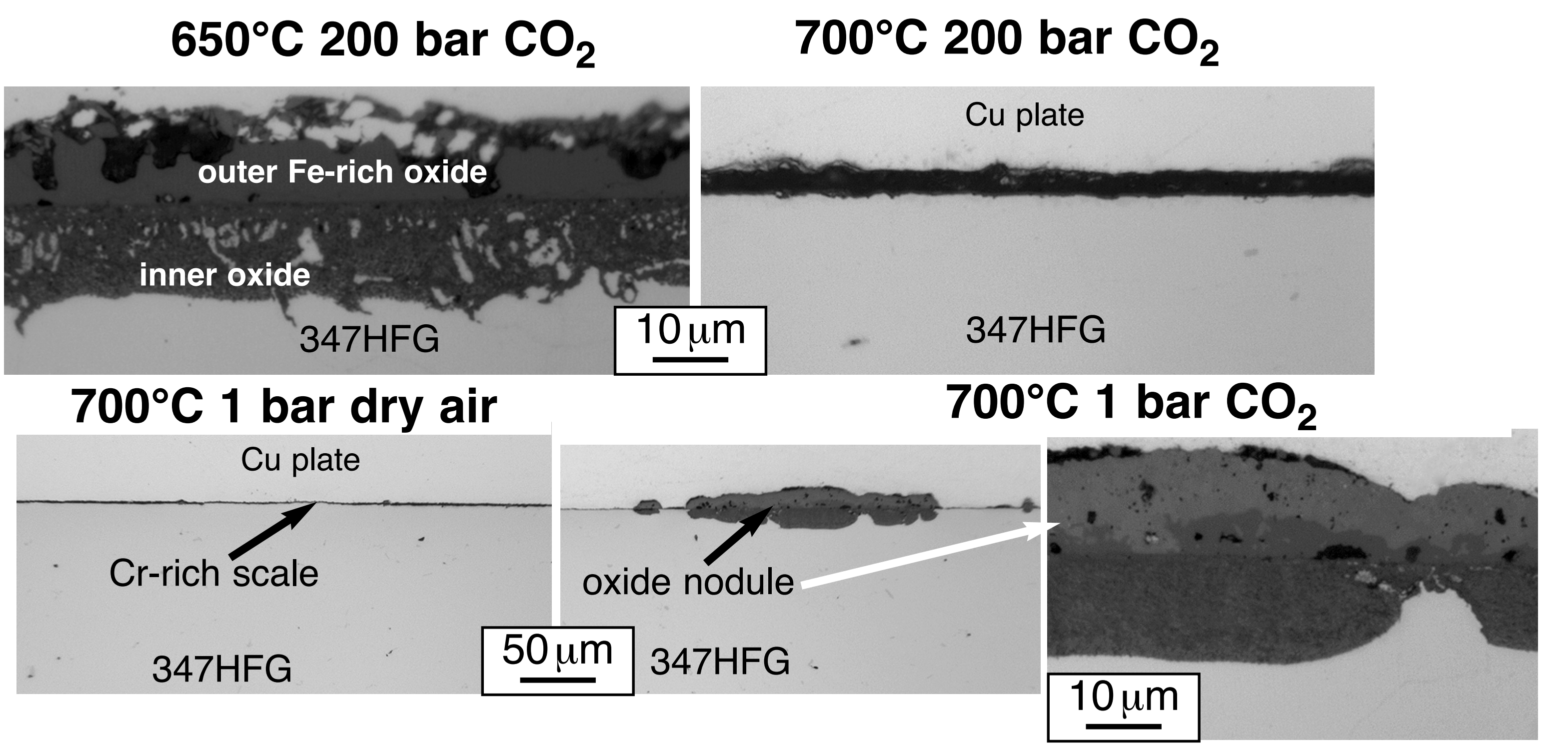
Grade 91: Fe-9Cr-1Mo

light microscopy of polished cross-sections

347HFG, 700°C: more protective

Thick duplex oxide formed at 650°C in sCO_2

Only a few nodules formed at 700°C



347HFG (fine grain) Fe-18Cr-9Ni<1Nb

light microscopy of polished cross-sections

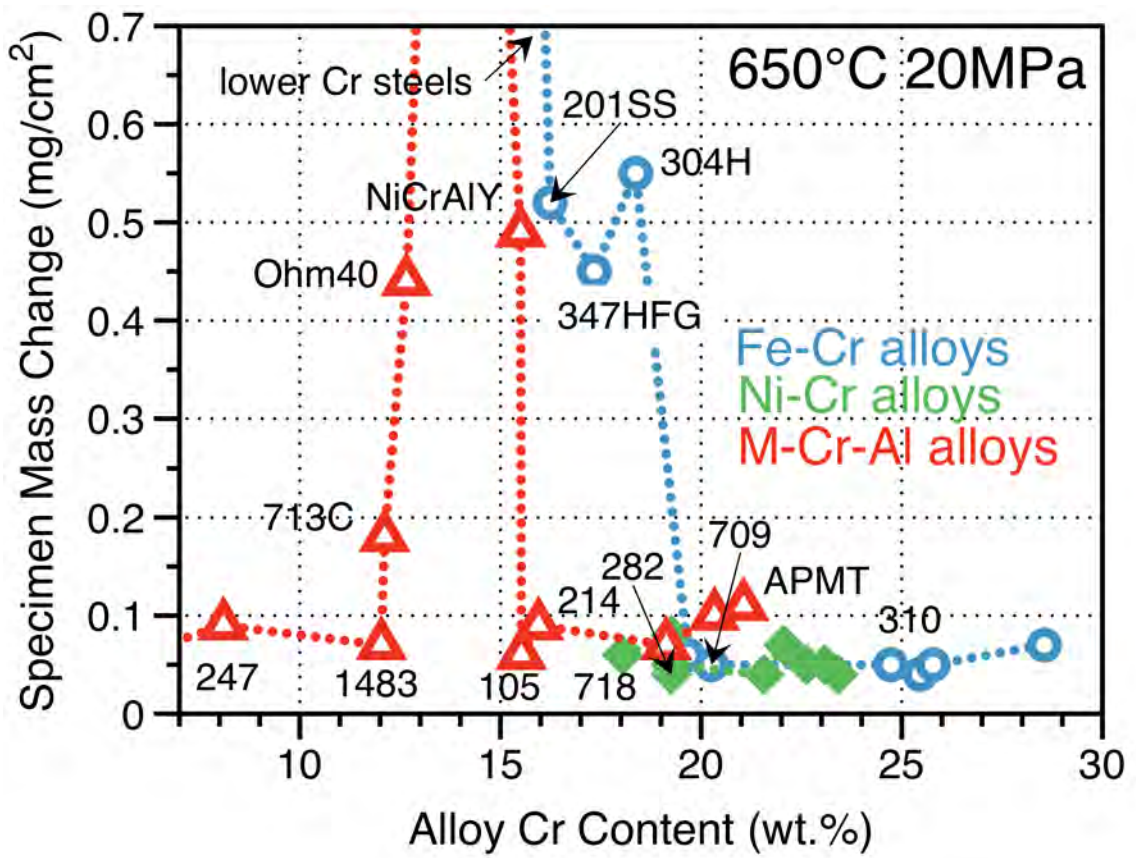
650°C sCO_2: hard to form Al_2O_3

Higher mass gain for alumina-forming alloys

- Some unable to form alumina

Low mass gain for all Ni-Cr alloys

Low mass gain for >20%Cr Fe-base alloys

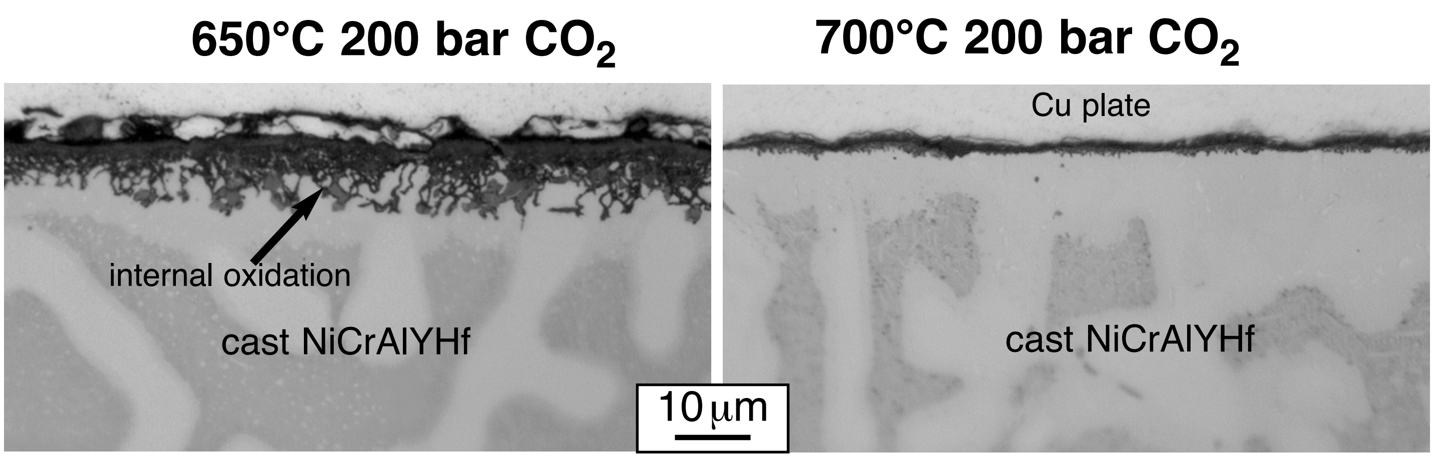


Model superalloy coating example

650°C - not protective as expected

700°C - thinner scale

Faster Al transport in alloy at higher temperature



Cast Ni-15Cr-12Al+Y,Hf

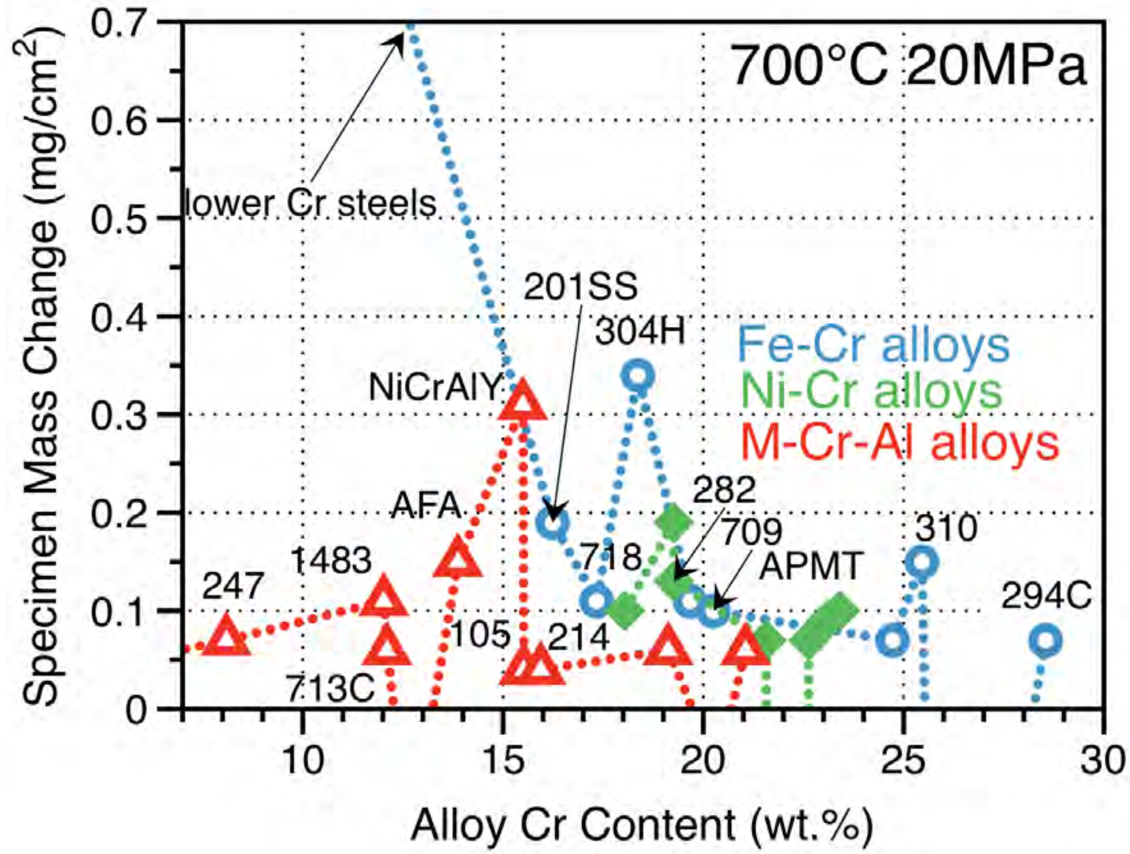
light microscopy of polished cross-sections

700°C sCO_2: better Al_2O_3

Low mass gain for many specimens

Lower mass gain for some alumina-forming alloys

A few specimens lost mass (?)

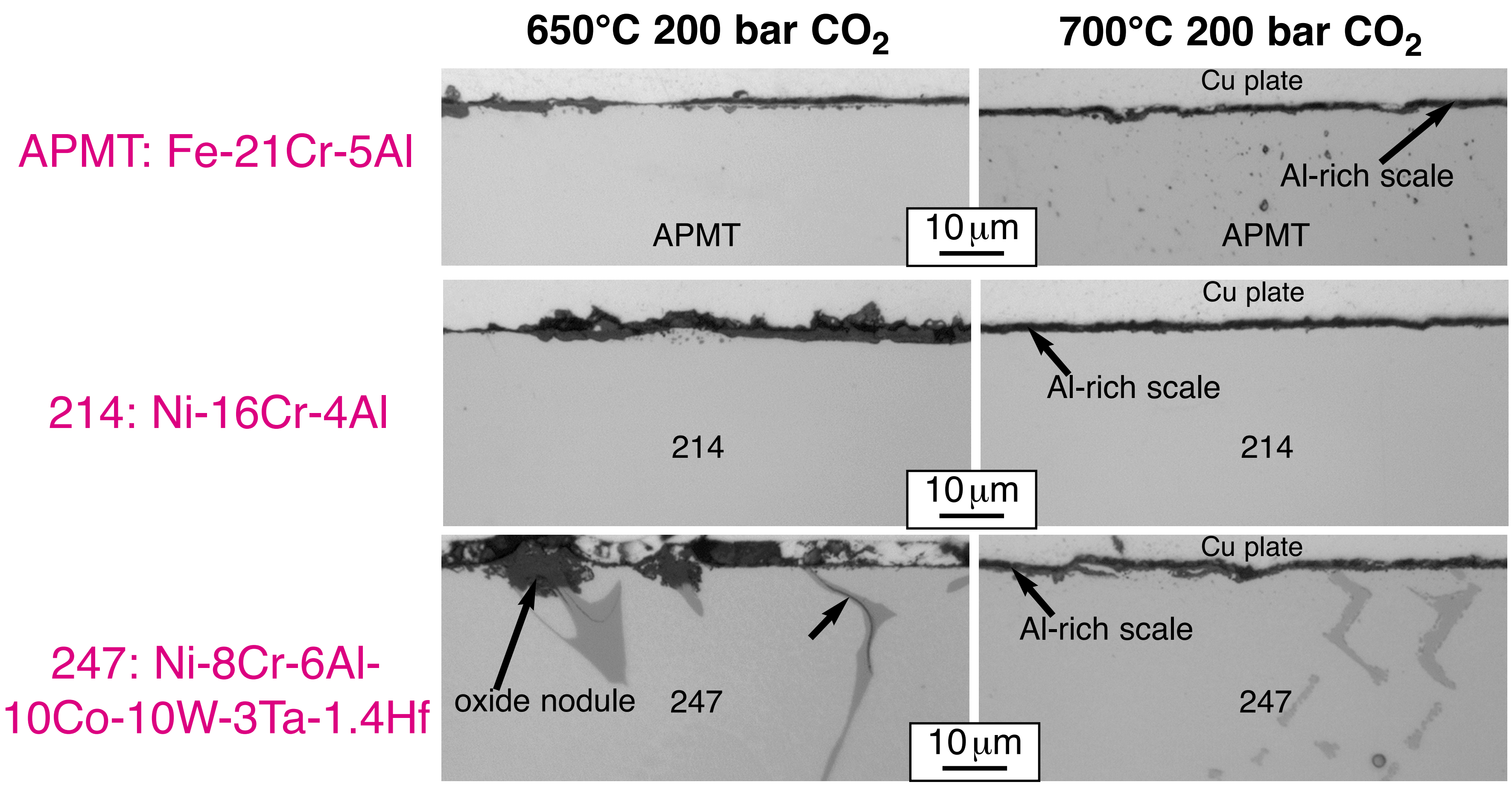


Thinner Al_2O_3 at 700°C

Confirms the higher mass gains at 650°C

700°C: All alumina-forming alloys performed better

CM247 superalloy - 1%Hf no strong C reaction

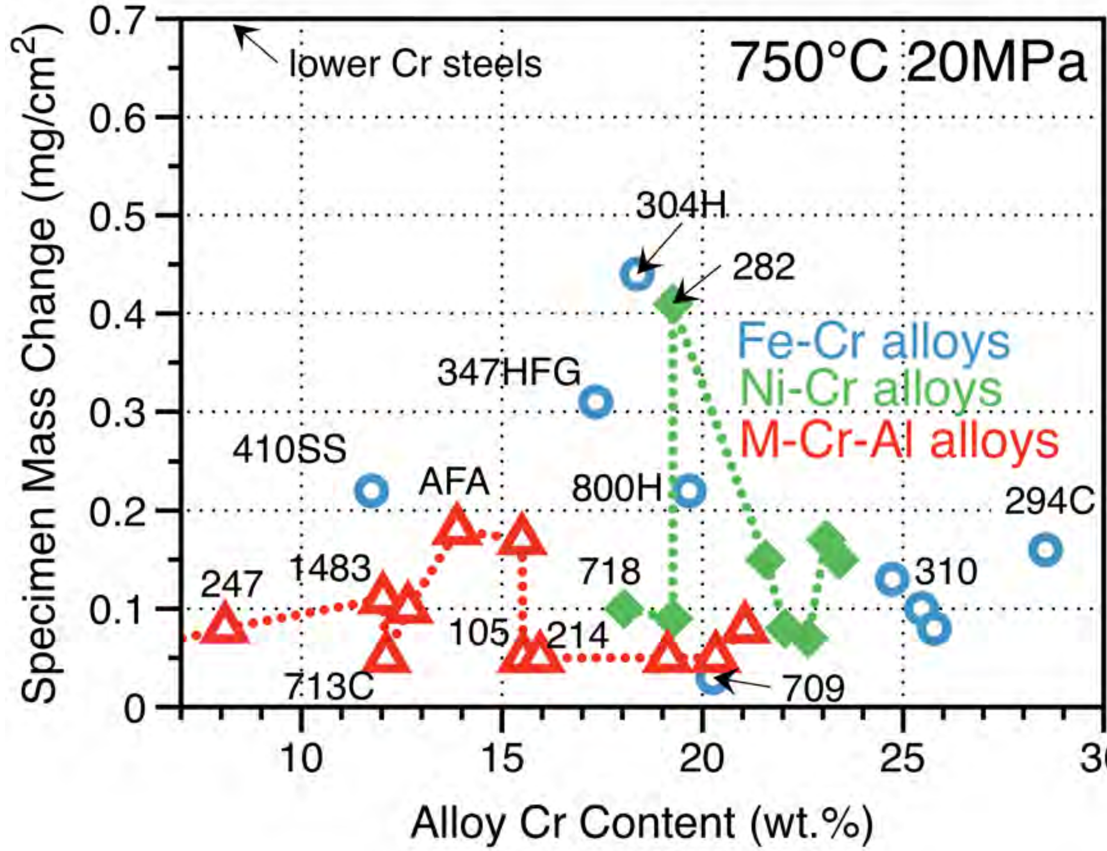


light microscopy of polished cross-sections

Similar trends at 750°C

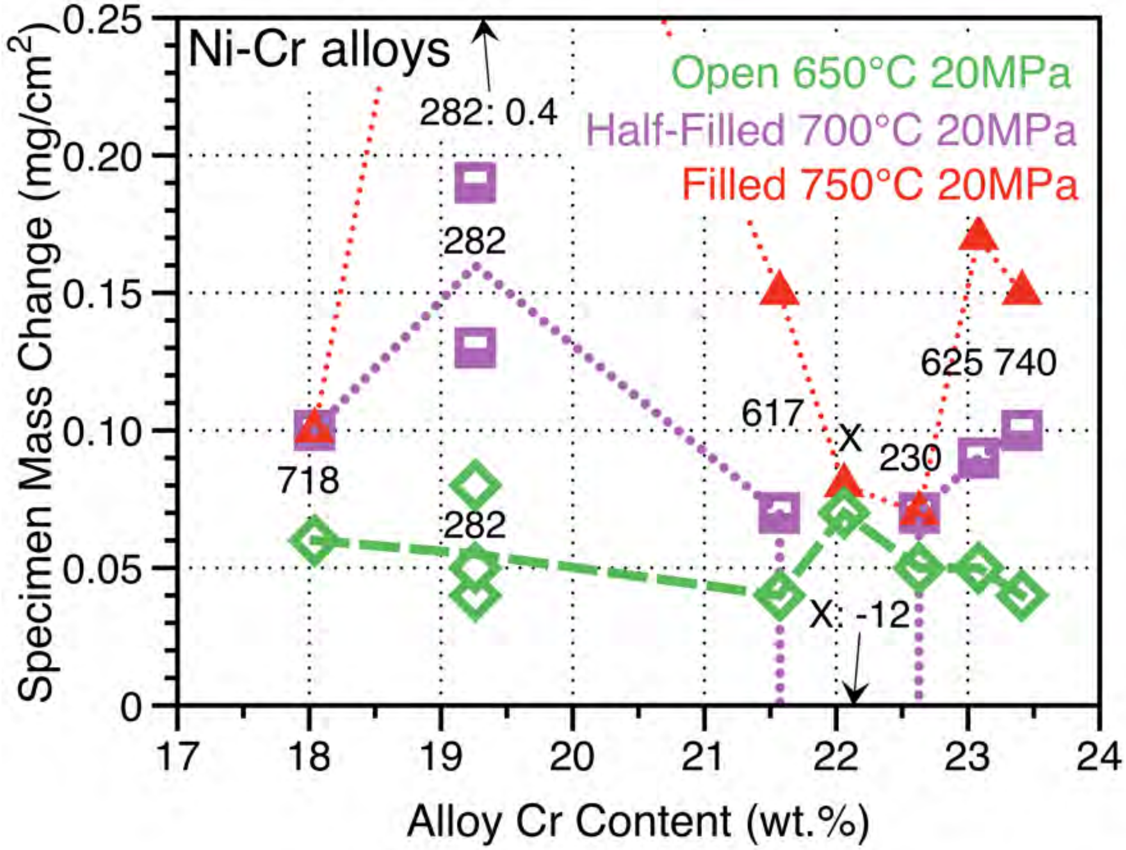
Alumina-forming alloys typically lower than chromia-forming alloys

Higher mass gain for alloy 282 specimen



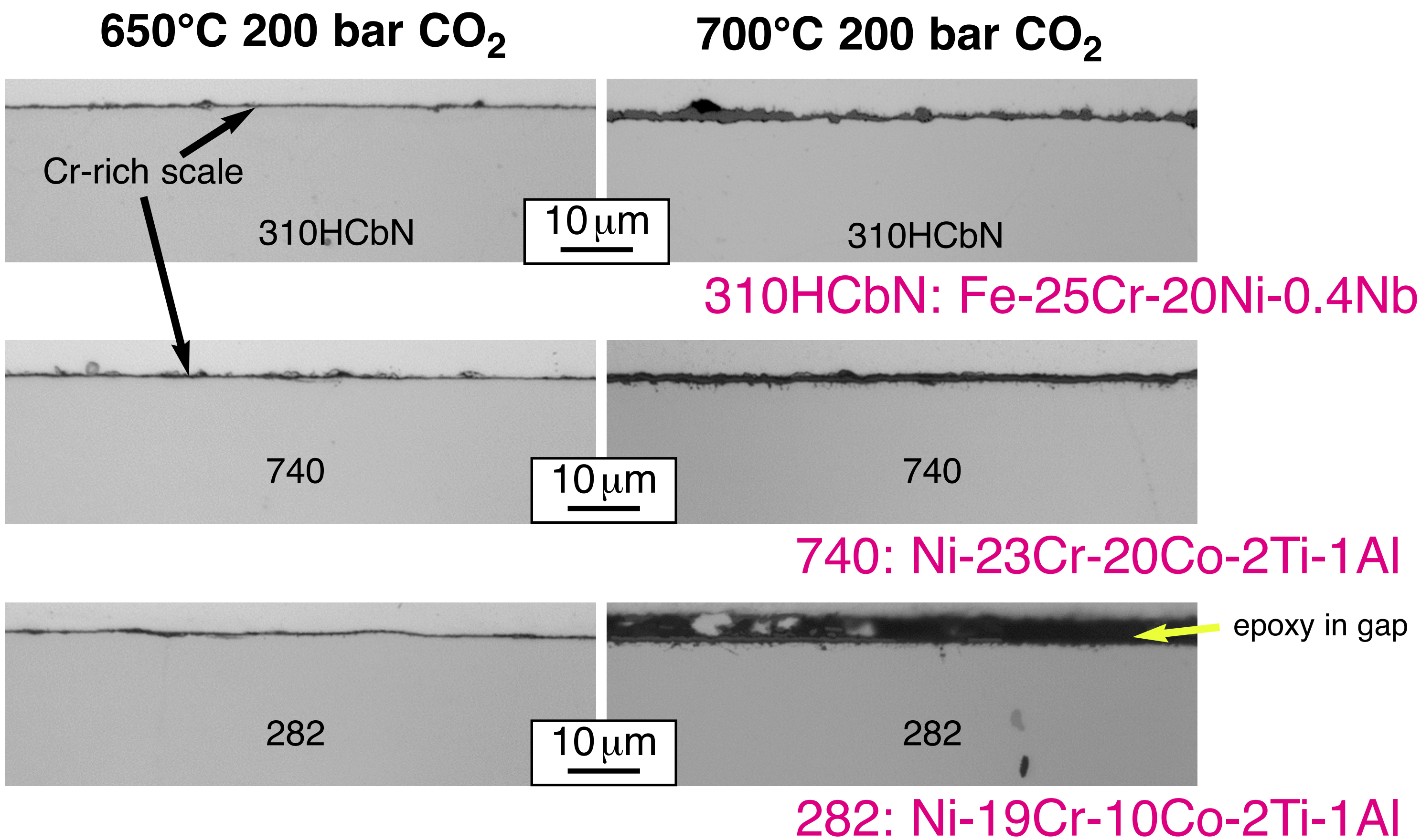
Ni-Cr alloys similar behavior

Increasing mass gain with increasing temperature
A few odd results (mass loss for alloy X at 700°C)



Thicker Cr_2O_3 at 700°C

As expected, higher temperature leads to thicker reaction product



light microscopy of polished cross-sections

Thoughts

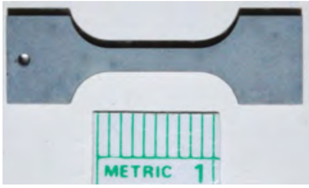
More characterization needed of current results
- Better understand some unusual results

Concern:
- Degradation by C penetration through Cr_2O_3
  - (McCoy 1965 at 1bar)
- Need to evaluate longer times + ex-situ ductility
- Al_2O_3 thought to be better barrier to C ingress
  - Pre-oxidation may assist in Al_2O_3 formation

Future work

Next work: effect of pressure, lower temperatures

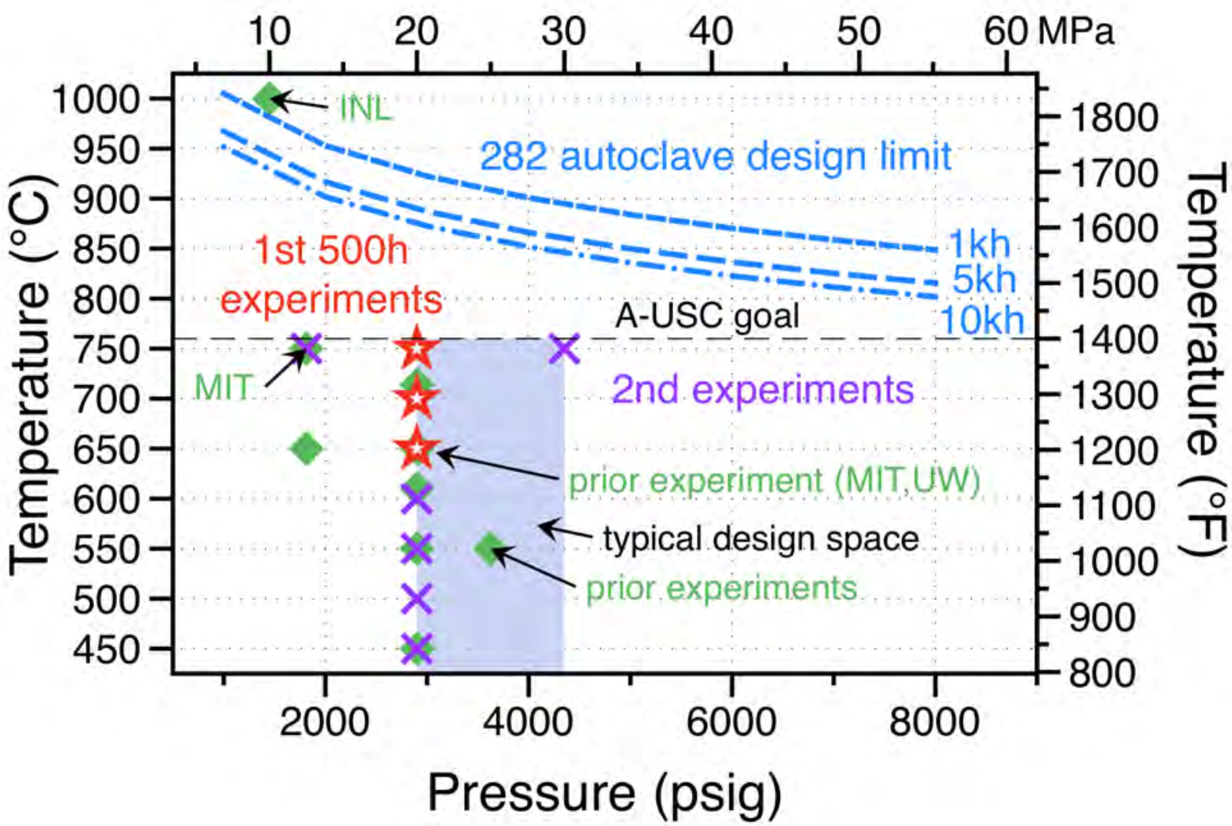
effect on ex-situ mechanical properties:



2015

Second rig for impurity effects (measure in + out)

1 bar results for CO_2+O_2 or H_2O: minor effects



Summary

Completed three 500h tests at 200 bar CO_2

- 650°-750°C (1200°-1380°F)
- Higher temperatures of interest for fossil energy
- Wide range of alloys exposed
- Companion 1bar tests at 700°C

Similar to other studies:

- Typical FeCr and FeCrNi alloys form thick scales
- Higher alloyed FeCr + NiCr alloys formed thin protective scales

Also:

- Alumina-forming alloys more protective >650°C
- At 500h, pressure effect (1 vs 200bar) minimal