Alloy Performance in Supercritical CO_2 Environments: Effects of sCO_2 Exposure

FWP 1022406 –Advanced Alloy Development
Period of performance: 10/1/2016 – 9/30/2017

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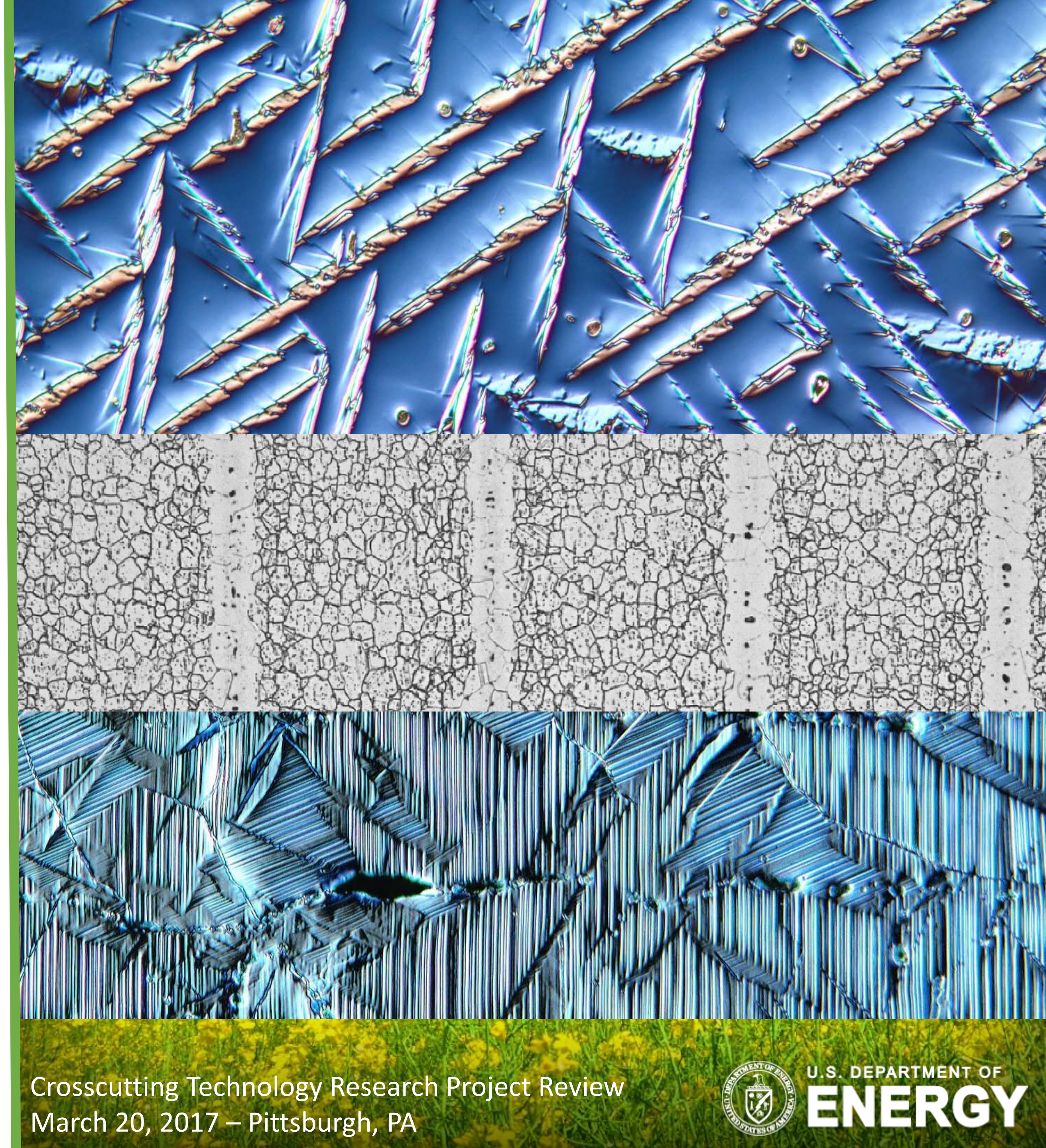
NATIONAL ENERGY TECHNOLOGY LABORATORY



Crosscutting Technology Research Project Review
March 20, 2017 – Pittsburgh, PA

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Project Goals and Objectives

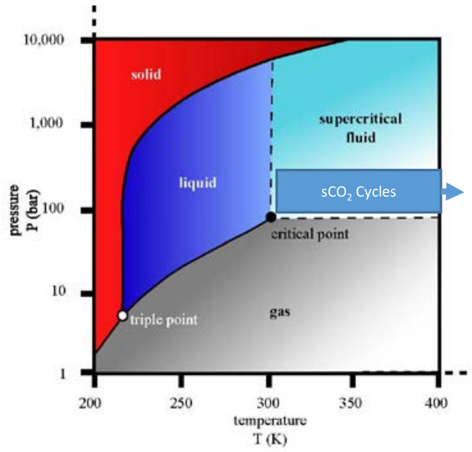
- **Accelerating commercialization of supercritical carbon dioxide power cycle technology by evaluating the performance of appropriate materials in sCO_2 power cycle environments.**
- **Milestones**
  - M1.17.5.A - Completed initial set of ex-situ FCGR experiments for alloys (H282, IN625 and 347H) exposed to sCO_2, sH_2O, ambient CO_2 at 730°C. - 09/30/2017
- **Deliverables**
  - Technical report (either presentation or publication) on low temperature corrosion behavior. - 03/31/2017
  - Technical report (either presentation or publication) on fatigue crack growth rate after exposure to sCO_2. - 06/30/2017
  - Technical report (either presentation or publication) on comparative performance. - 09/30/2017

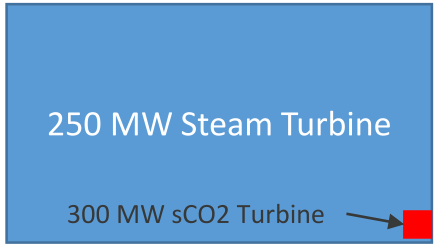
Outline

- **Supercritical CO_2 power cycles**
- **Corrosion of advanced alloys in direct sCO_2 power cycle environments (Task 5.1)**
  - High-temperature oxidation
  - Low-temperature corrosion
- **High-temperature oxidation of advanced alloys in indirect sCO_2 power cycles (Task 5.1)**
- **Mechanical property – environment interactions (Task 5.2)**
  - Effect of sCO_2 on fatigue crack growth

Supercritical CO_2 Power Cycles

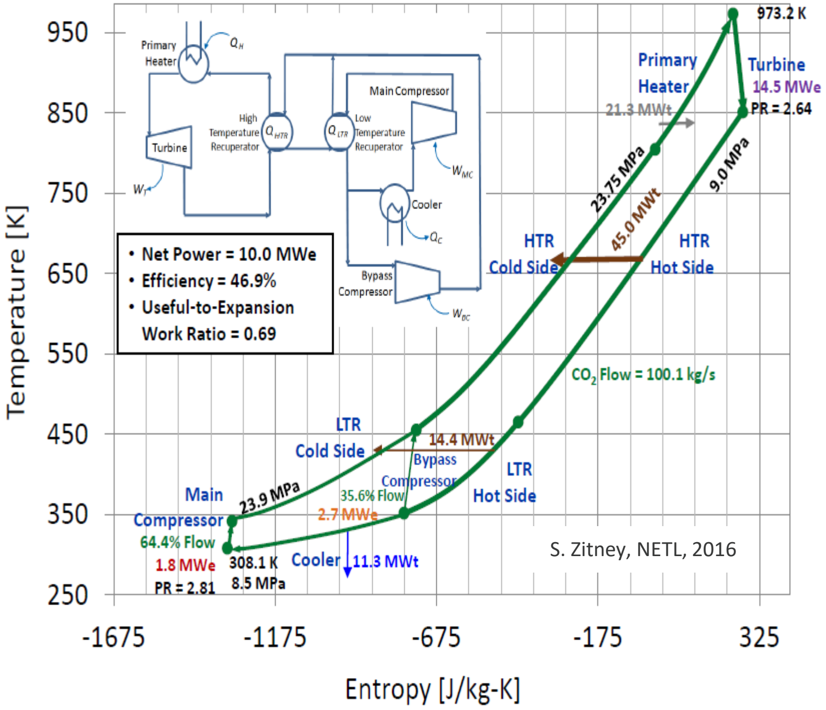
Properties of sCO2 Cycles	Impact
No phase change (Brayton Cycle)	Higher efficiency
Recompression near liquid densities	Higher efficiency
High heat recuperation	Higher efficiency
Compact turbo machinery	Lower capital cost
Simple configurations	Lower capital cost
Dry/reduced water cooling	Lower environmental impact
Storage ready CO_2 in direct cycles	Lower environmental impact





250 MW Steam Turbine

300 MW sCO2 Turbine



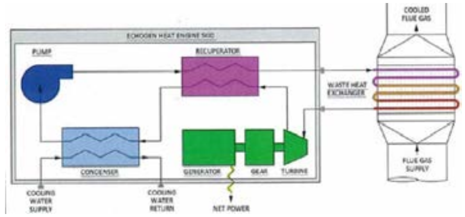
- Net Power = 10.0 MWe
- Efficiency = 46.9%
- Useful-to-Expansion Work Ratio = 0.69

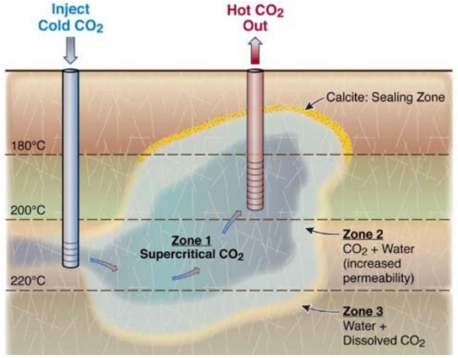
S. Zitney, NETL, 2016

Supercritical CO_2 Power Cycles

Application	Size [MWe]	Temperature [°C]	Pressure [MPa]
Nuclear (NE)	10 – 300	350 – 700	20 – 35
Fossil Fuel (FE) (Indirect heating)	300 – 600	550 – 900	15 – 35
Fossil Fuel (FE) (Direct heating)	300 – 600	1100 – 1500	35
Concentrating Solar Power (EERE)	10 – 100	500 – 1000	35
Shipboard Propulsion	<10 – 10	200 – 300	15 – 25
Waste Heat Recovery (FE)	1 – 10	< 230 – 650	15 – 35
Geothermal (EERE)	1 – 50	100 – 300	15

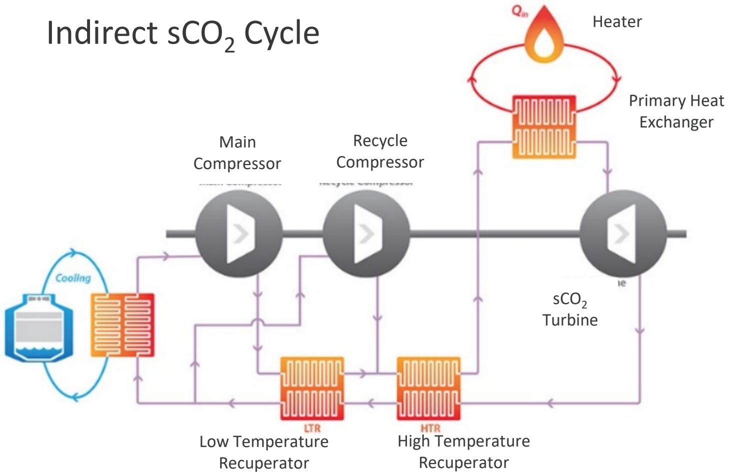
(Ref. sCO_2 Power Cycle Technology Roadmapping Workshop, February 2013, SwRI San Antonio, TX)



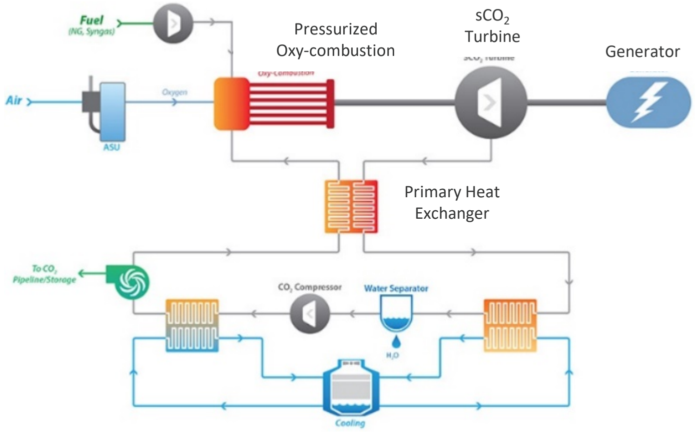


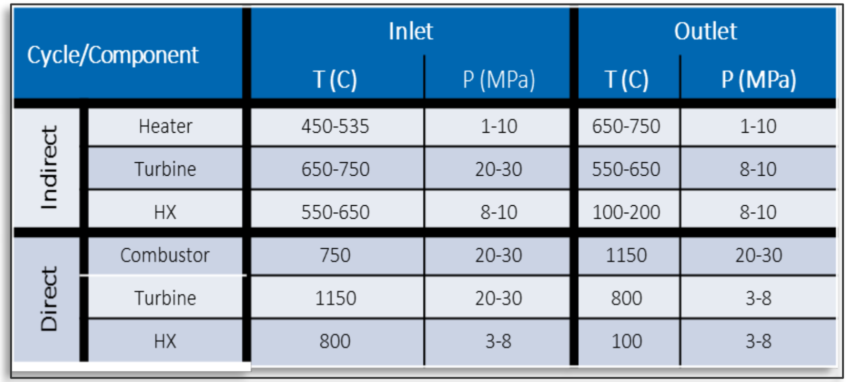
Supercritical CO_2 Power Cycles

Indirect sCO_2 Cycle



Direct sCO_2 Cycle



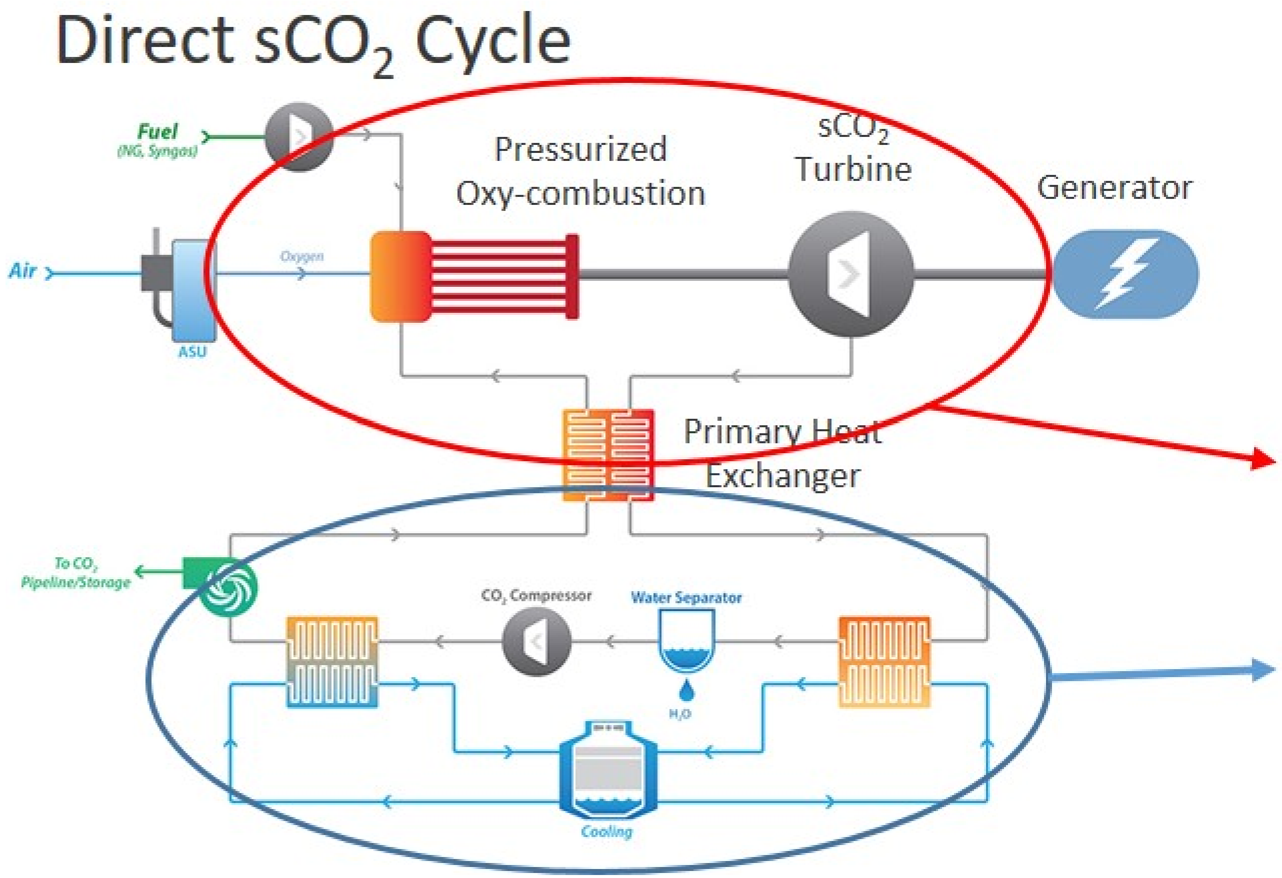


Cycle/Component		Inlet		Outlet	
		T (C)	P (MPa)	T (C)	P (MPa)
Indirect	Heater	450-535	1-10	650-750	1-10
	Turbine	650-750	20-30	550-650	8-10
	HX	550-650	8-10	100-200	8-10
Direct	Combustor	750	20-30	1150	20-30
	Turbine	1150	20-30	800	3-8
	HX	800	3-8	100	3-8

Essentially pure CO_2

CO_2 with combustion products including O_2, H_2O and SO_2

Corrosion in Direct sCO_2 Power Cycles


Direct sCO_2 Cycle

Working Fluid

95% CO_2

4% H_2O

1% O_2

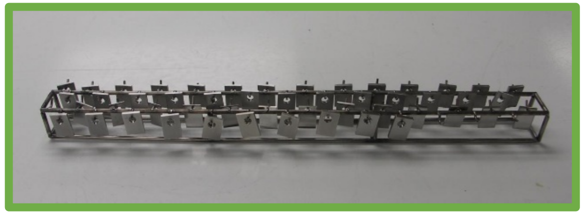
SO_2

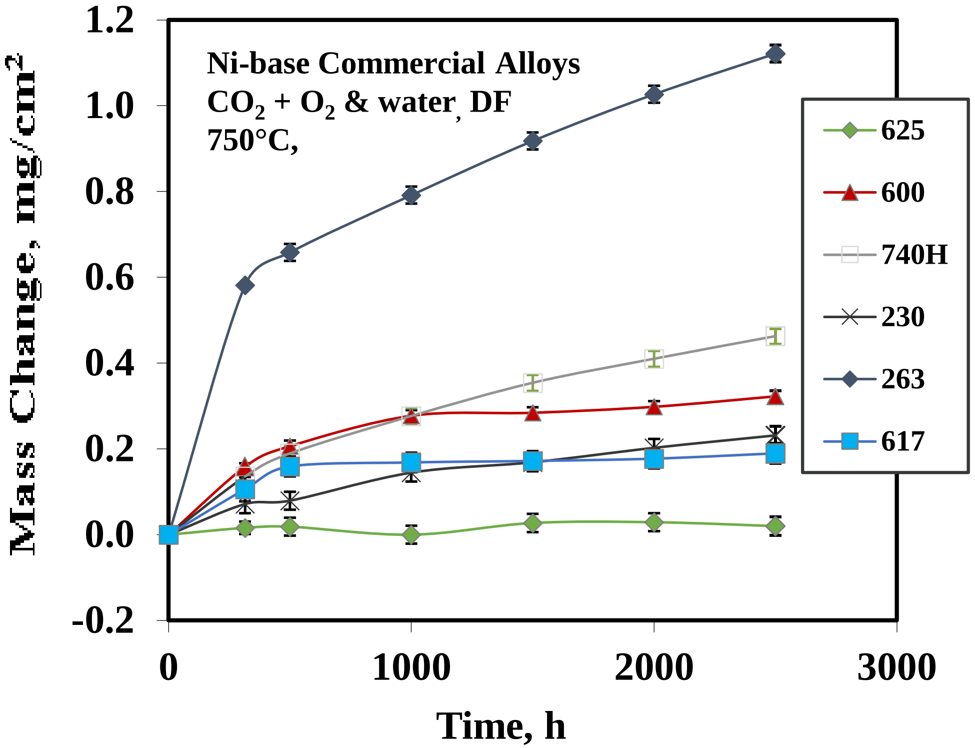
HCl

High-T Oxidation

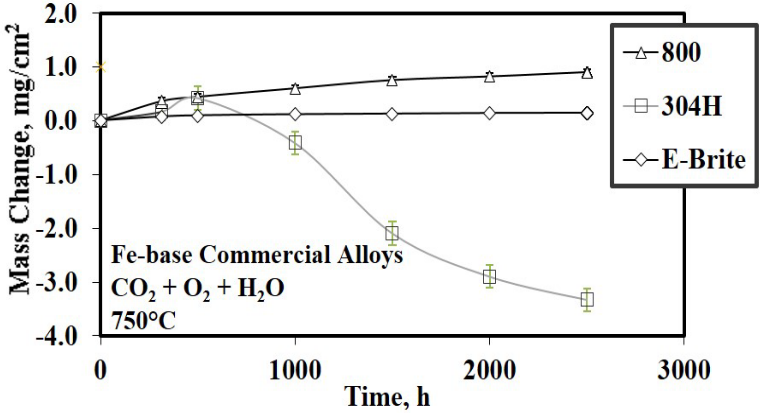
Low-T Corrosion

High-Temperature Corrosion in Direct sCO_2 Power Cycles

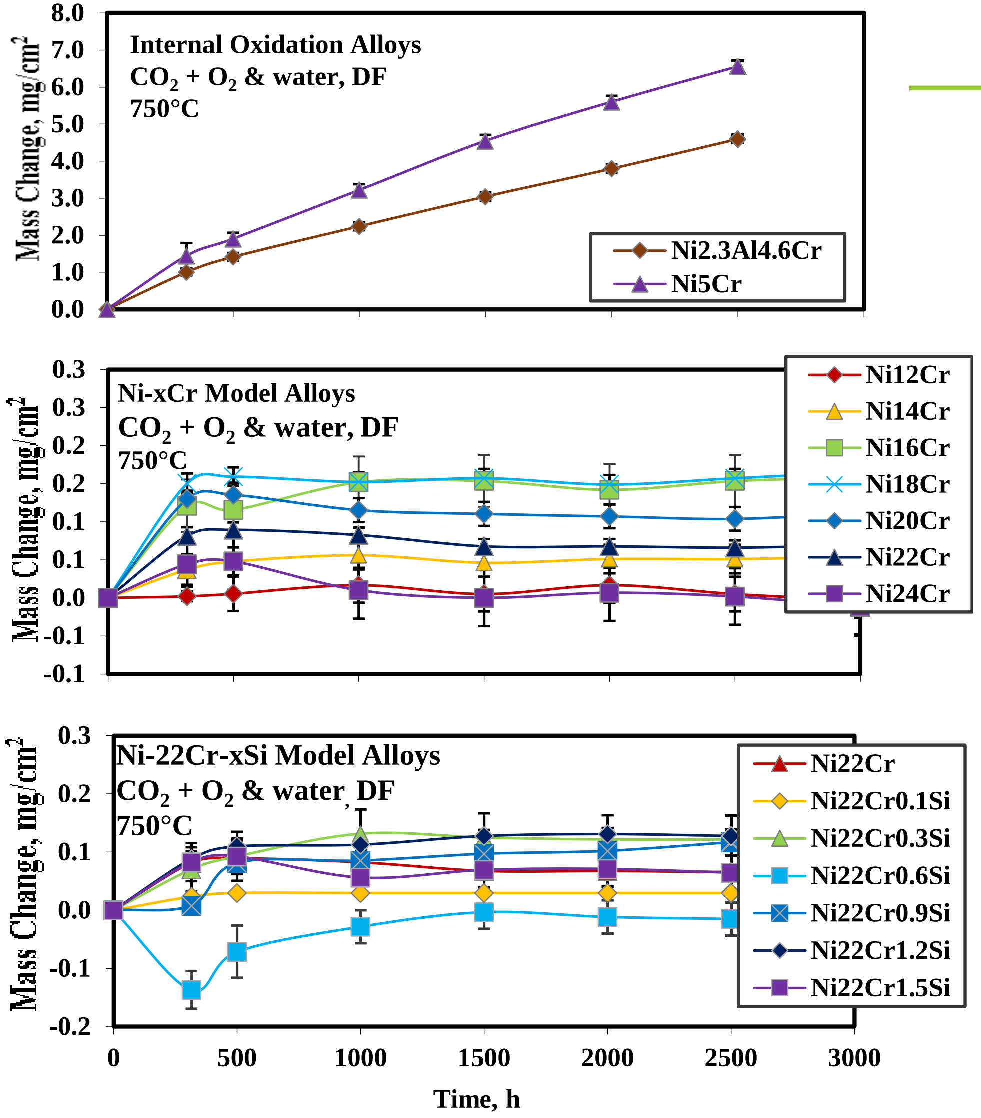




- Conditions
  - 750 °C
  - 1 bar
  - Gas
    - 69 vol % CO_2
    - 1 % O_2
    - 30 % H_2O
  - 500 h exposures
    - (Currently at 3000 h)



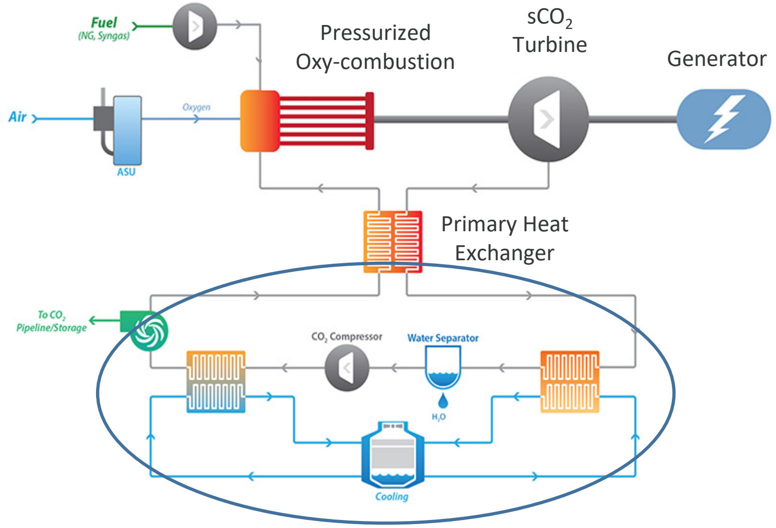
High-Temperature Corrosion in Direct sCO_2 Power Cycles



- **Ongoing work at ambient pressure**
  - Alloy response to SO_2 in CO_2
  - 750 °C for Ni based alloys, 650 °C for Fe based alloys.
  - New gas composition
    - 95 % CO_2
    - 1 % O_2
    - 4 % Water
    - With and without 1000 ppm SO_2

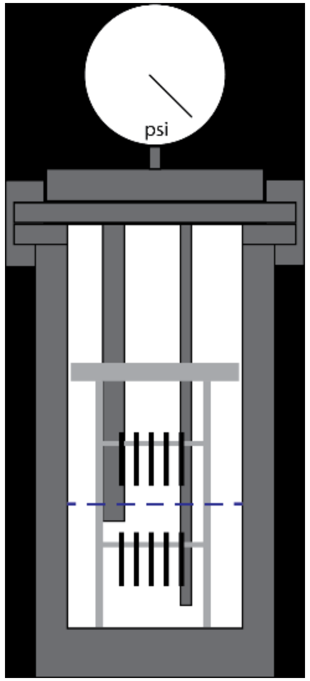
- **Summer**
  - Tests in Supercritical CO_2 + H_2O

Low-Temperature Corrosion in Direct sCO_2 Power Cycles



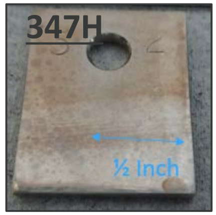
- Influence of liquid H_2O saturated with CO_2 on the corrosion of 347H, 316, and P91 at 50°C
- Effect of condensation transient on corrosion during shut down

- Autoclave experiments
  - Materials selection
  - Effects of condensation on corrosion behavior [shut down]
- Electrochemical tests
  - Mechanisms of corrosion due to condensation during shut down [general corrosion or/and localized corrosion]



Autoclaves and samples rack design

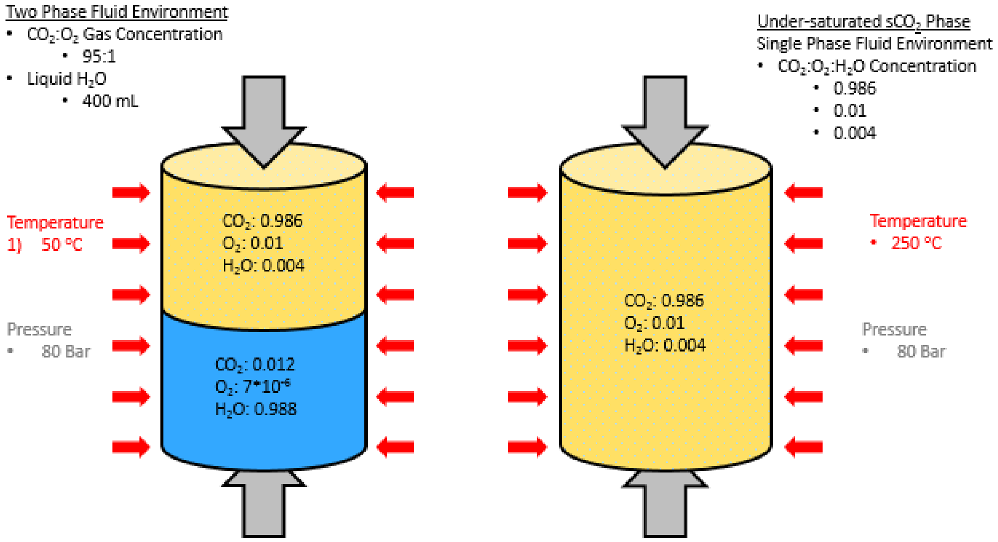
Electrochemical Test Setup



Collaborator:
8Rivers
Capital
(Net Power)

Low-Temperature Corrosion in Direct sCO_2 Cycles

Autoclave Tests



Two Phase Fluid Environment
- CO_2:O_2 Gas Concentration
  - 95:1
- Liquid H_2O
  - 400 mL

Temperature
1) 50 °C

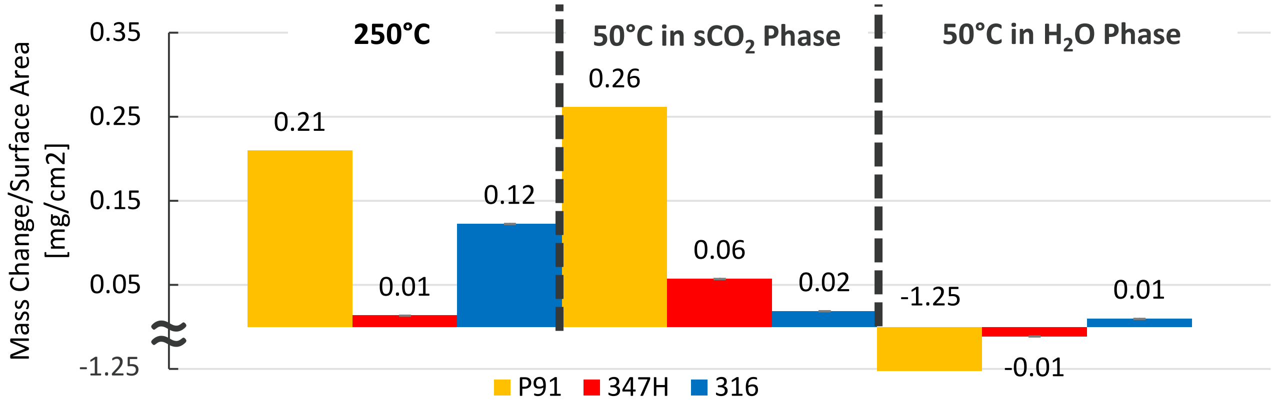
Pressure
- 80 Bar

Under-saturated sCO_2 Phase
Single Phase Fluid Environment
- CO_2:O_2:H_2O Concentration
  - 0.986
  - 0.01
  - 0.004

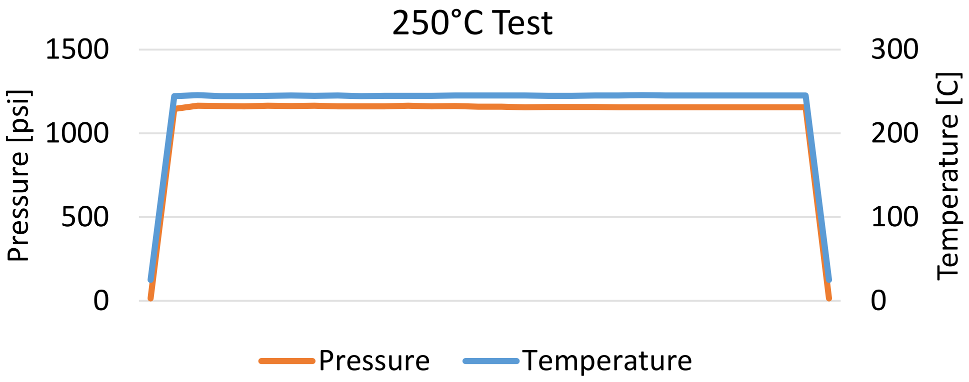
Temperature
- 250 °C

Pressure
- 80 Bar

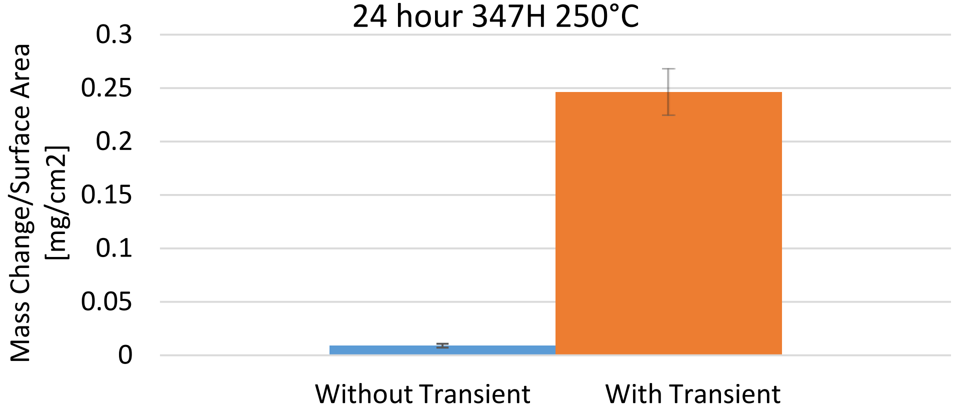
Constant Mole Fraction at 50°C and 250°C



Mass Change of the Constant Mole Fraction Experiments after 500 h



P-T-t Diagram

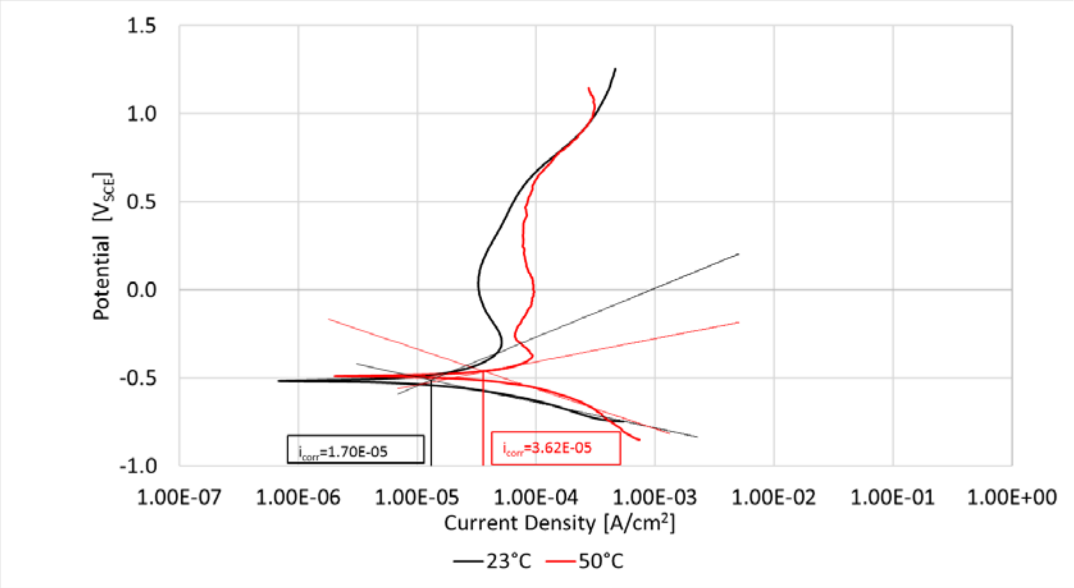


Influence of Condensation Transient

Low-Temperature Corrosion in Direct sCO_2 Cycles

Electrochemical Tests

- **Materials and conditions**
  - Materials: 347H Austenitic stainless steel, P91 Martensitic-ferritic steel
  - Environment: Carbonic acid [bubbling CO_2 into DI water]
  - Temperature: 23°C, 50°C
  - Ambient pressure
  - Test types:
    - pH measurement
    - Open circuit potential
    - Polarization resistance
    - Potentiodynamic scan
    - Cyclic voltammetry scan
    - Potentiostatic scan
- **Post electrochemical test**
  - XRD/SEM/XPS



Potentiodynamic Polarization Scan, 347H, Scan Rate 5 mV/s

$$CR = K_1 \frac{i_{cor}}{\rho} EW$$

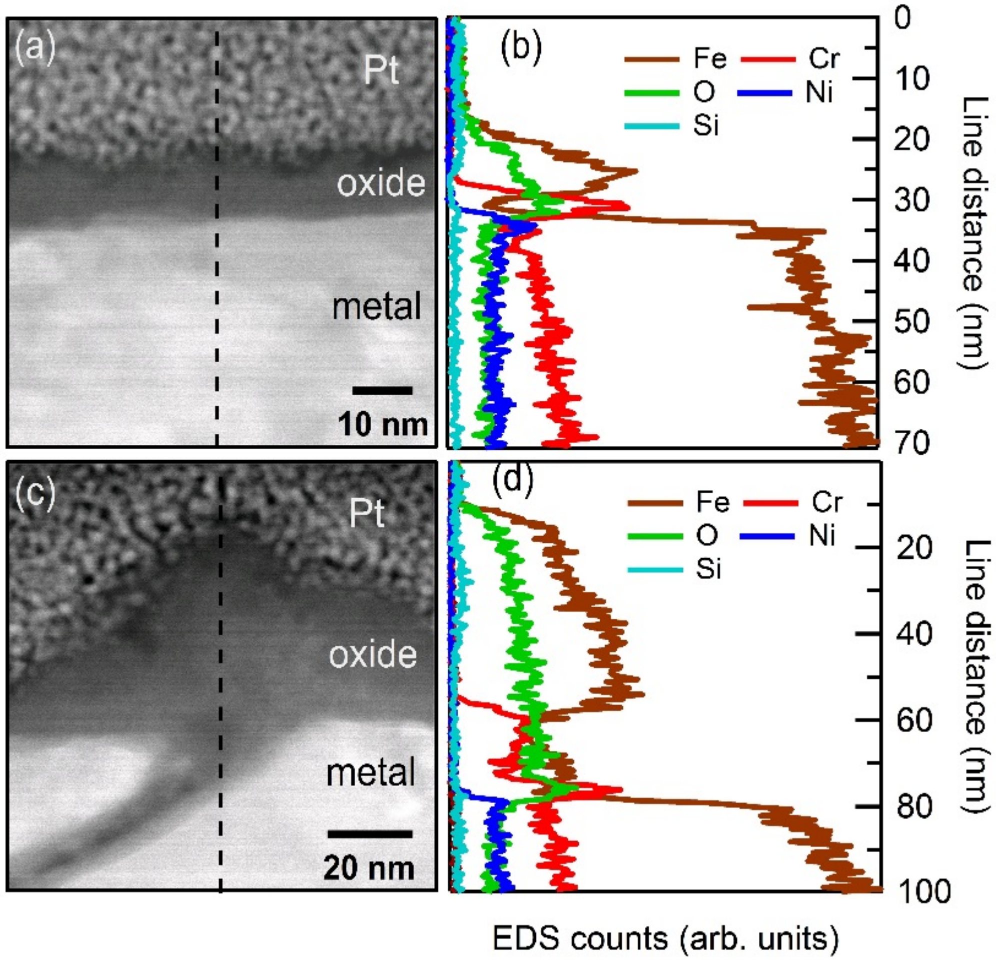
K= 0.00327

ρ = 7.96 g/cm^3

Equivalent Weight = 26.53

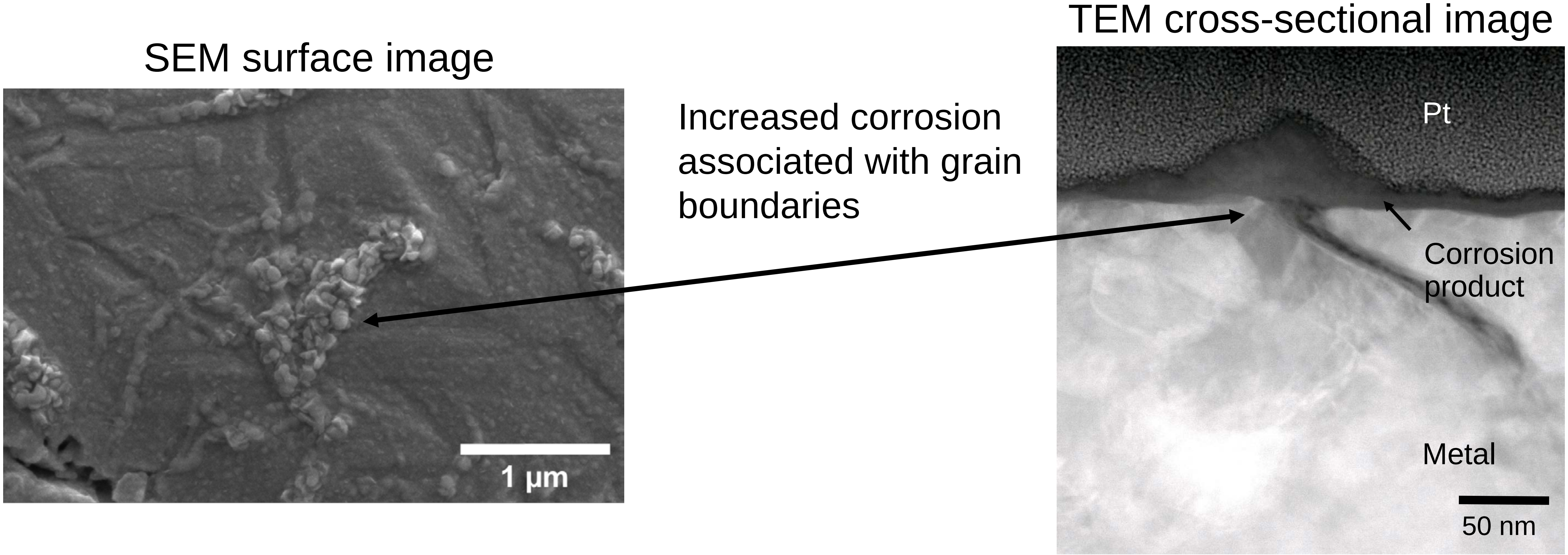
Temperature	E_{corr} [V]	i_{corr} [A/cm^2]	Estimated Corrosion Rate [mm/year]
23°C	-0.48	1.70E-05	0.19
50°C	-0.47	3.62E-05	0.39

347H exposed to 250 °C sCO_2 direct cycle environment without condensation transient



- Good corrosion resistance observed (negligible mass change).
- TEM analysis reveals an Fe-rich oxide layer forms under these conditions.
- Increased oxide thickness is observed above grain boundaries.

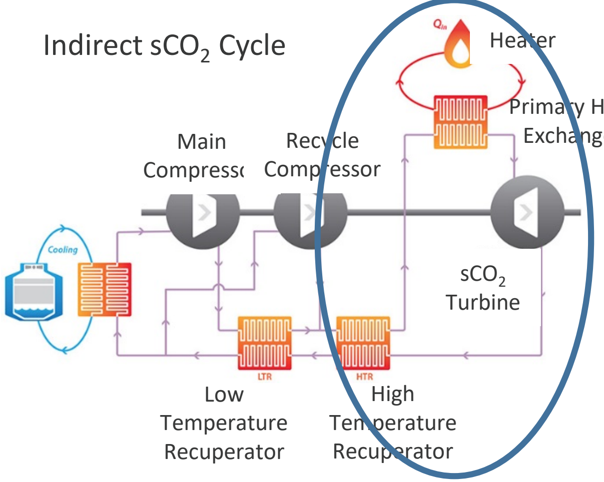
347H exposed to 250 °C sCO_2 direct cycle environment without condensation transient

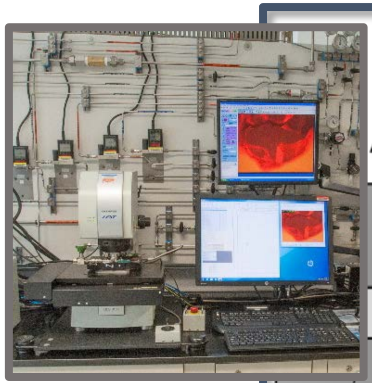


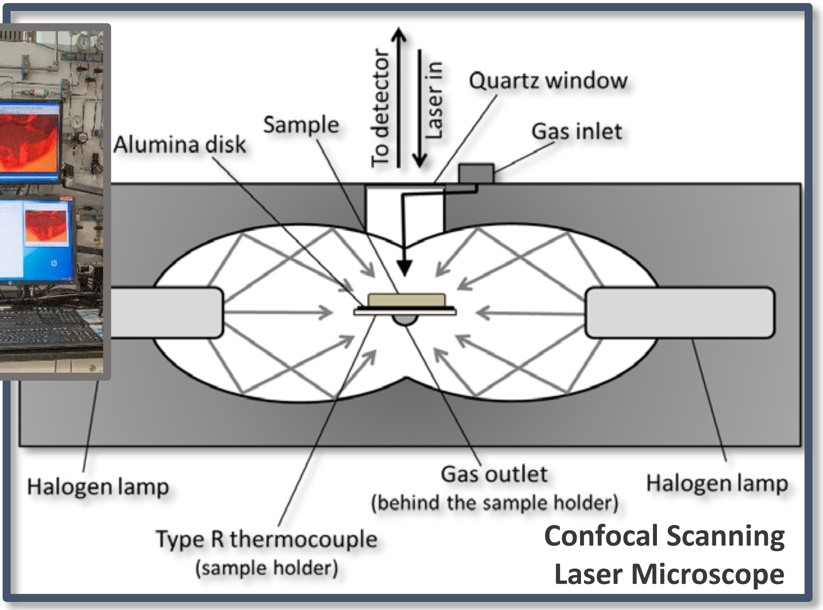
Increased corrosion associated with grain boundaries

Structural transformations incurred during surface finishing play an important role on the corrosion resistance of the alloy.

High-Temperature Oxidation Indirect sCO_2 Cycles

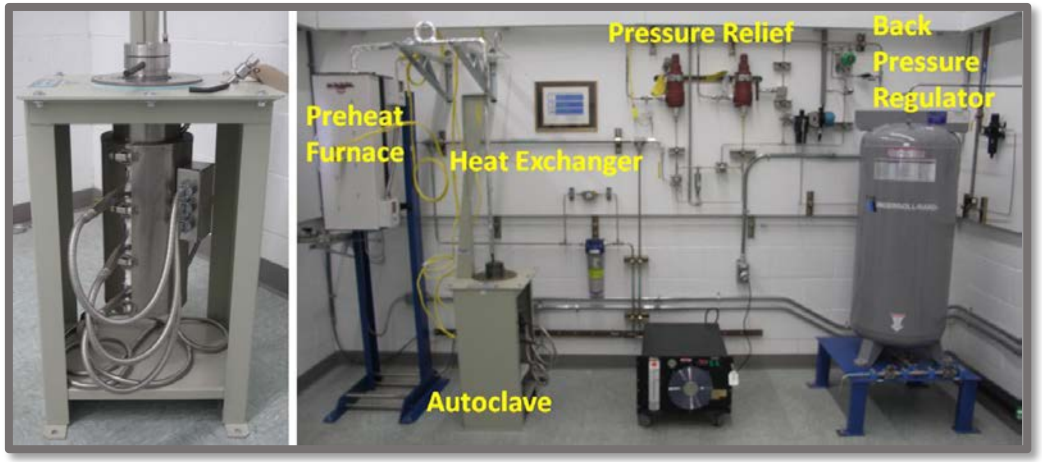






Confocal Scanning Laser Microscope

Tube furnaces for ambient pressure exposures



USC Steam Autoclave

Flow controlled with a high pressure pump

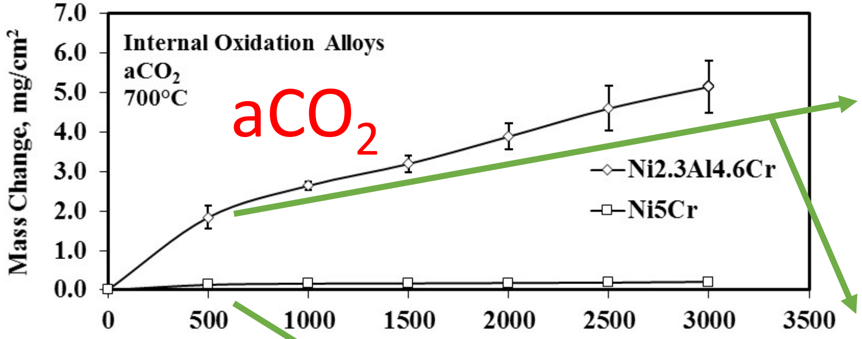
Pressure controlled with a back pressure regulator

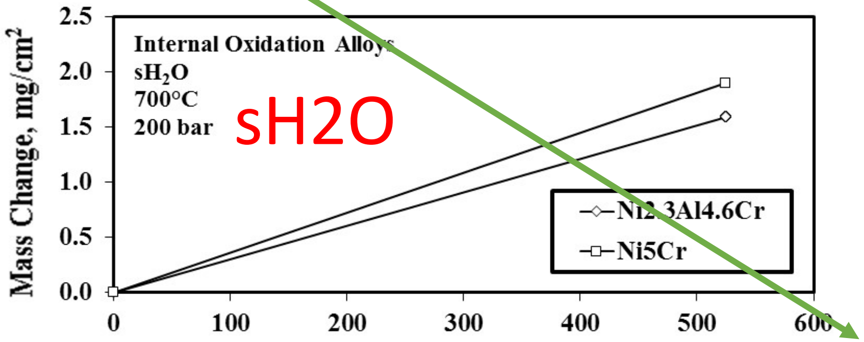
ASME dual rated to 704°C/346 bar and 760°C/228 bar

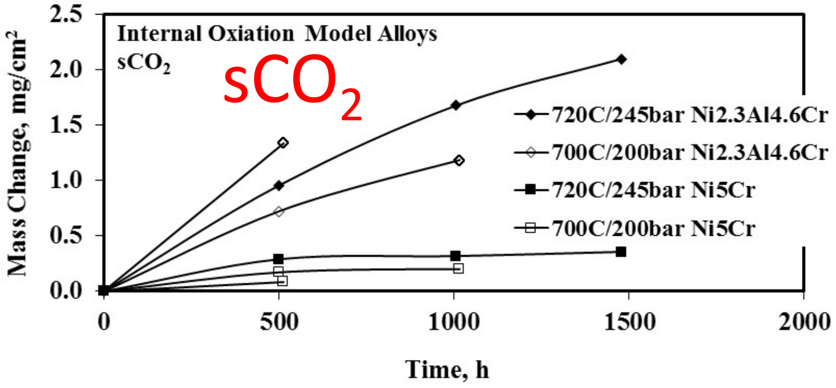
Autoclave body made of Alloy 230

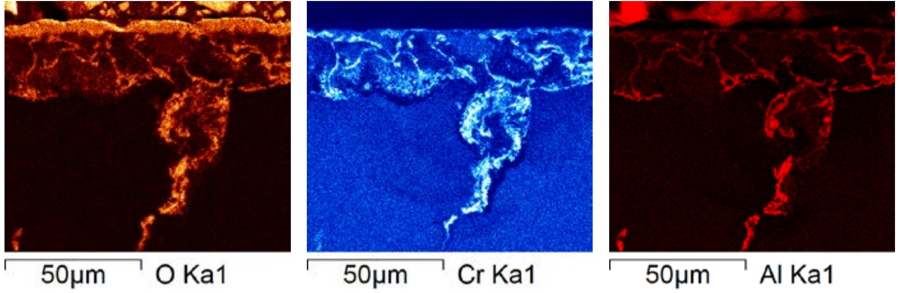
CO_2 Autoclave designed for 275 bar CO_2 at 800°C. Capable of injecting H_2O as an impurity.

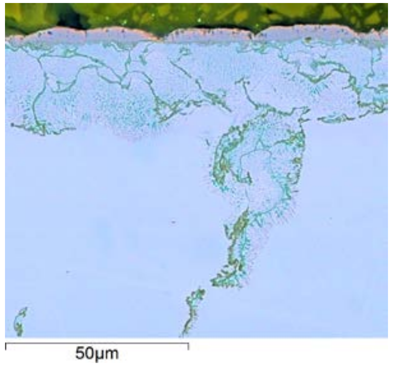
Indirect Cycles—Low Cr Alloys











Ni2.3Al4.6Cr in aCO_2 & sH_2O

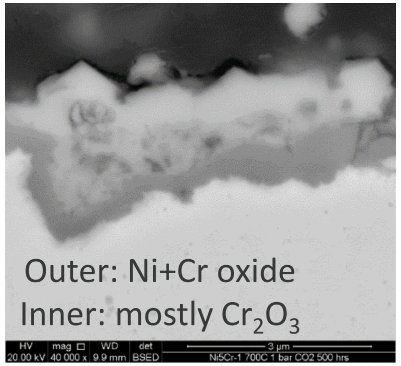
- Internal oxidation of Al & Cr

Ni5Cr in aCO_2

- Mostly a thin oxide scale

sCO_2

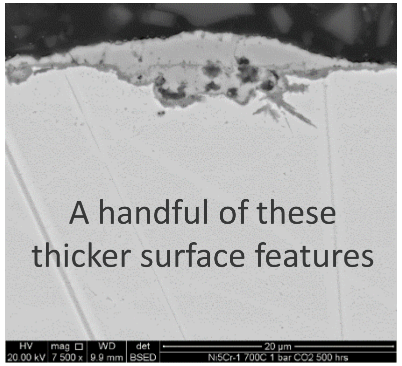
- Ni2.3Al4.6 less Δmass than aCO_2
- Ni5Cr more Δmass than aCO_2



Outer: Ni+Cr oxide

Inner: mostly Cr_2O_3

3 µm

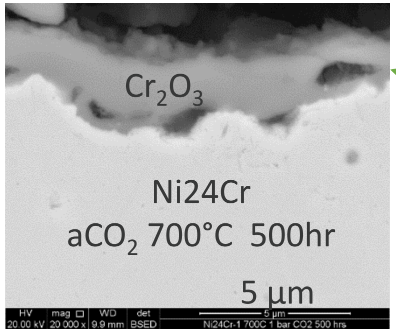


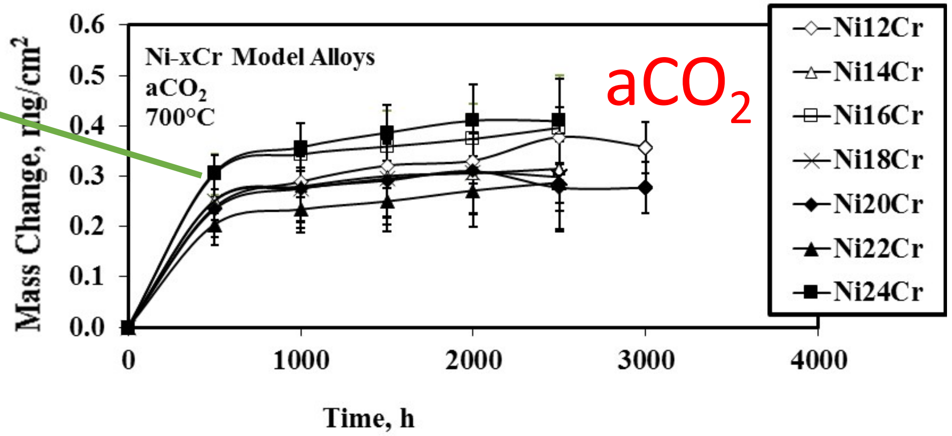
A handful of these thicker surface features

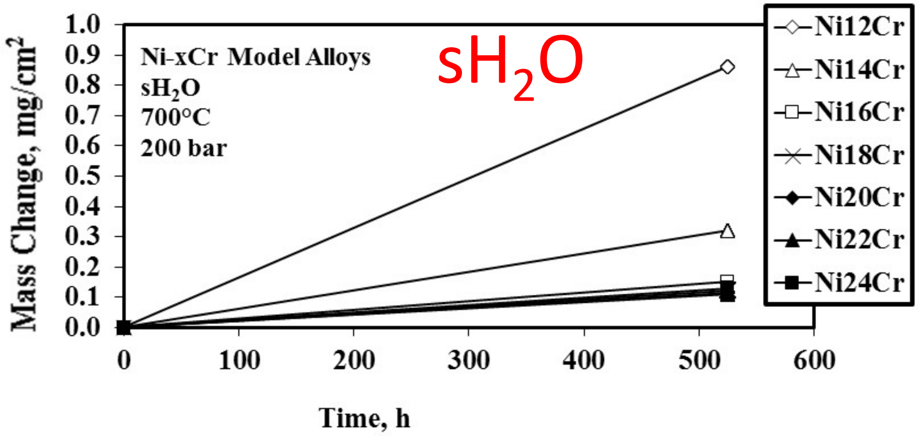
20 µm

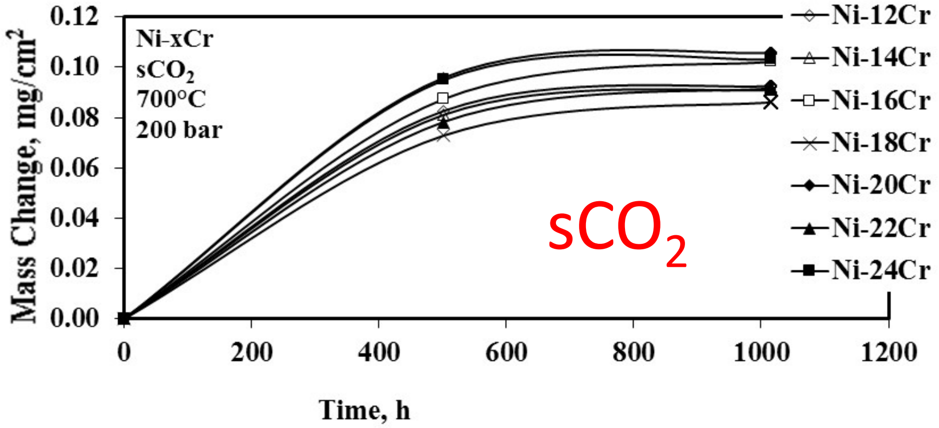
Indirect Cycles — Ni-xCr Alloys (12-24Cr)

- Protective behavior in CO_2 environments
- Chromia scales
- Most mass gain in aCO_2



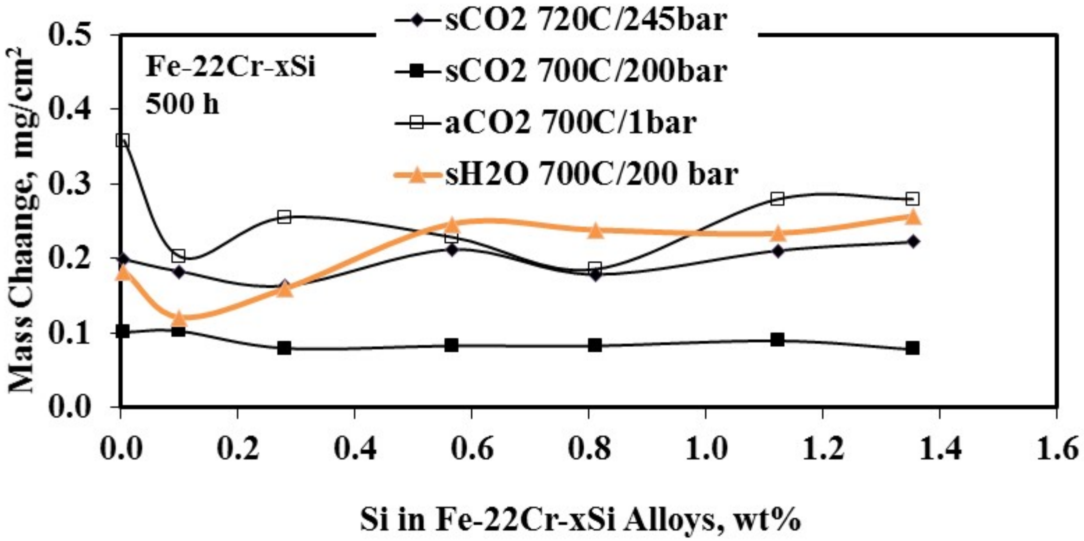


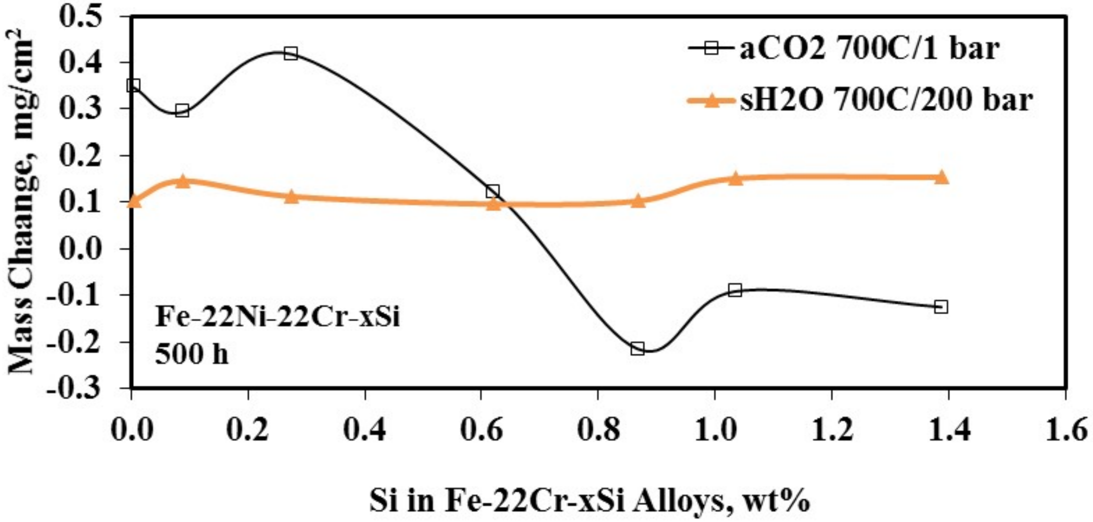




Indirect Cycles
Fe-22Cr-xSi and Fe-22Ni-22Cr-xSi Model Alloys

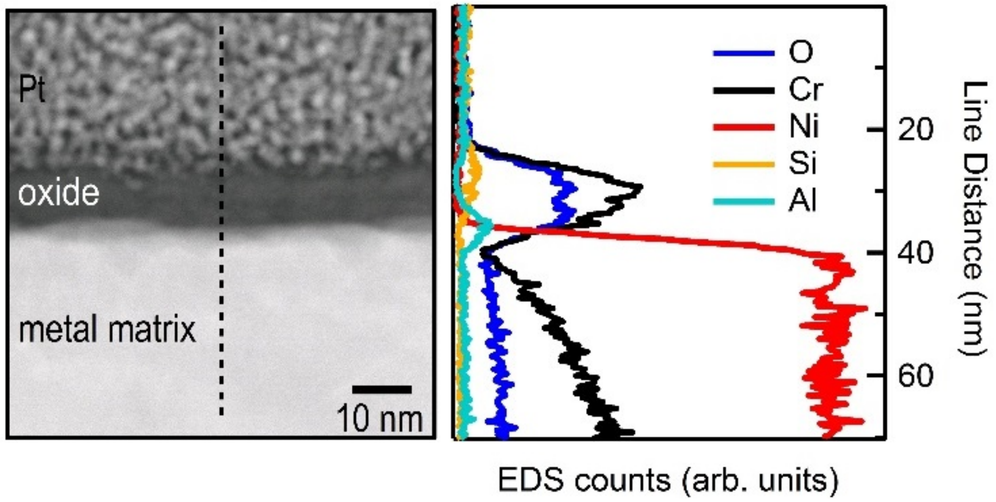
- Small mass gains in all 3 environments
- No clear trends with Si



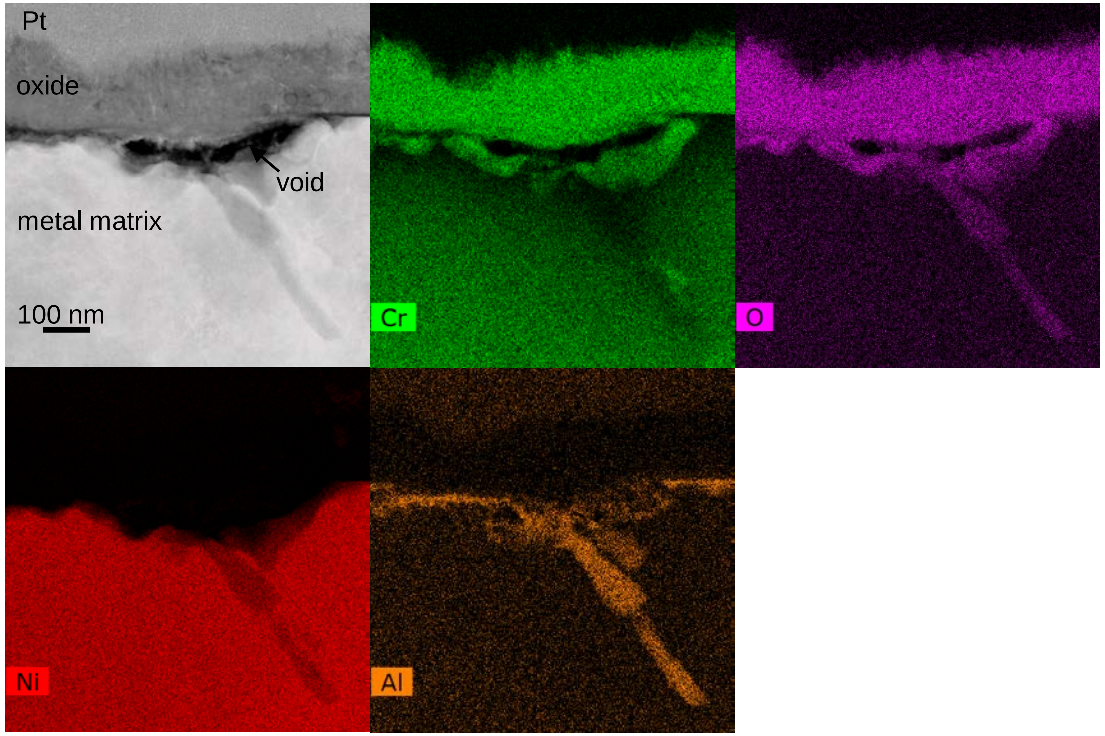


Alloy 617 early-stage oxidation results

t = 5 min



t = 100 h

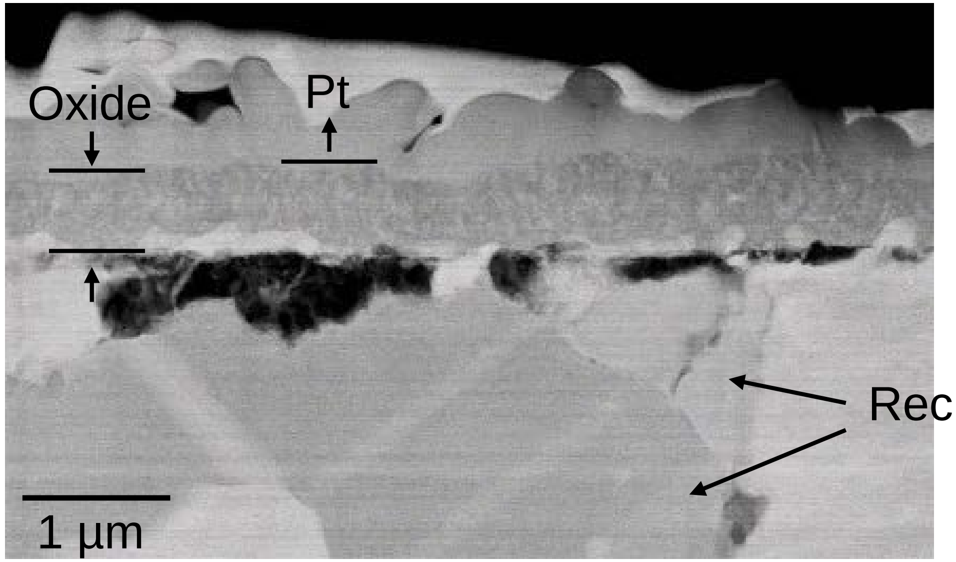


For a typical commercial Ni superalloy (617), a thin protective chromia scale forms after only 5 min exposure to 700 °C 0.1 MPa CO_2.

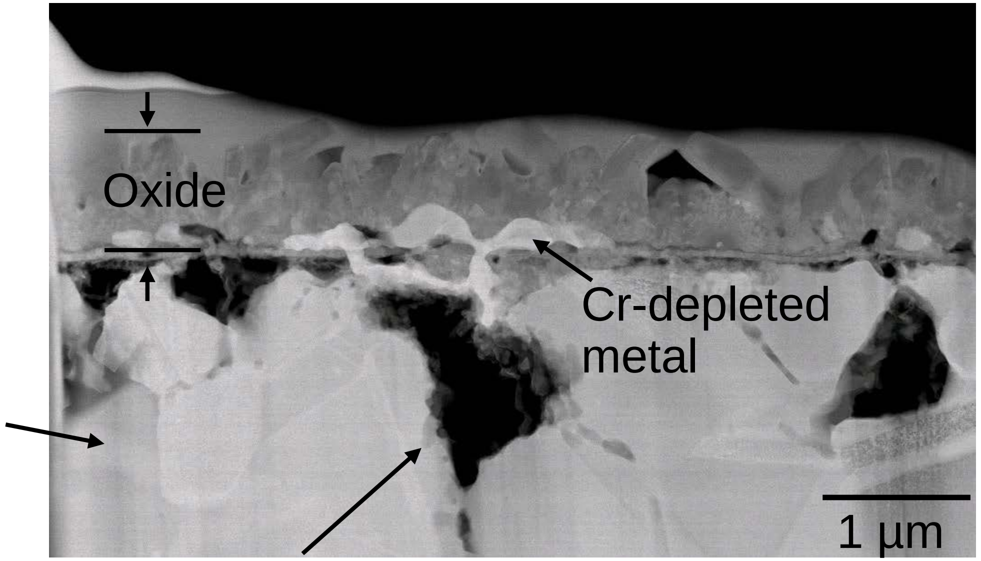
After 100 h exposure the protective chromia scale thickens. Voids are observed at the oxide/metal interface. These voids are highly correlated with internal oxidation of Al, and likely play an important role in long-term oxidation resistance.

Alloy 617 - Atmospheric vs. Supercritical CO_2

0.1 MPa, 700 °C, 500 h



20 MPa, 700 ° C, 500 h

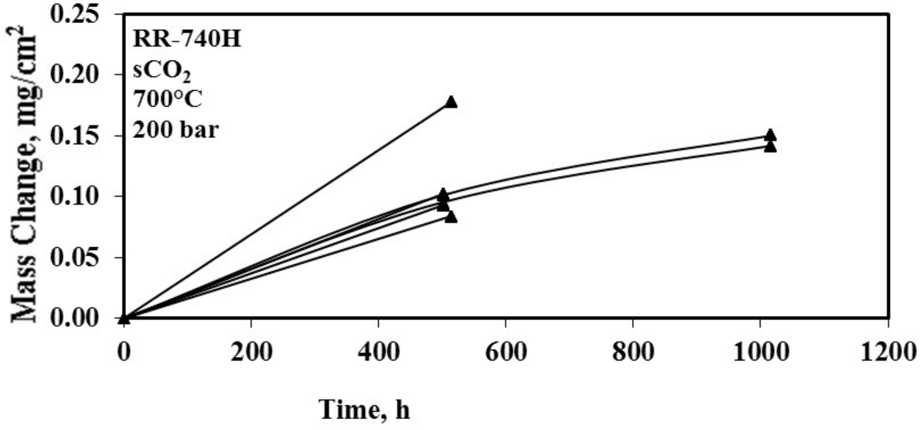


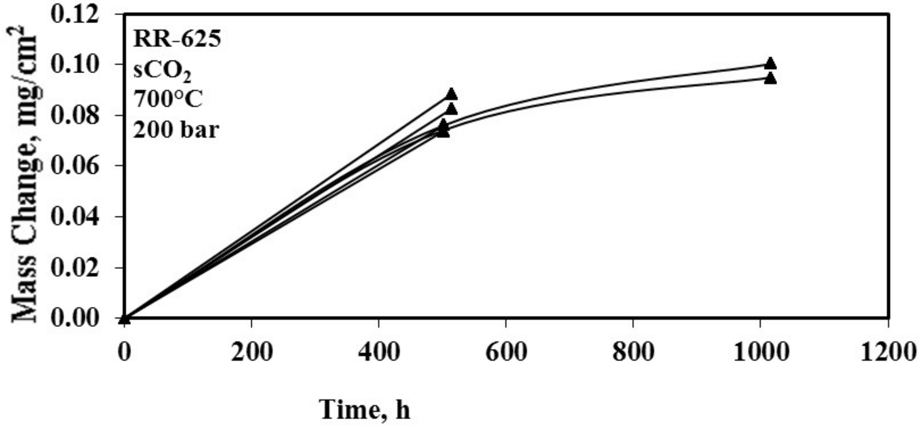
20 MPa (supercritical) exposure is controlled by similar processes as 0.1 MPa (atmospheric) exposure, but proceeds to a larger extent.

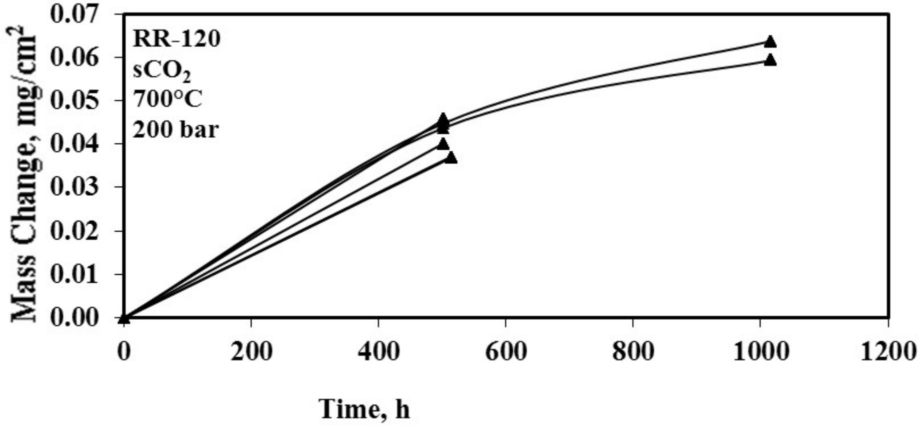
- 20-30% thicker oxide layer.
- More extensive sub-surface effects including voiding and recrystallization.
- Increased inward oxide growth (note Cr-depleted metal that is incorporated into the oxide layer).

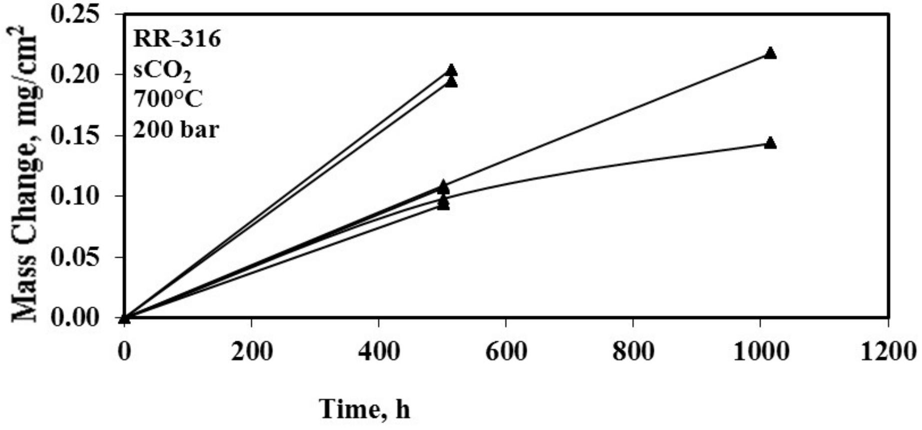
Round Robin Test Program

Update on 700°C exposures in 200 bar sCO$_2$ at NETL









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Korea Adv Inst of S&T
Oak Ridge NL
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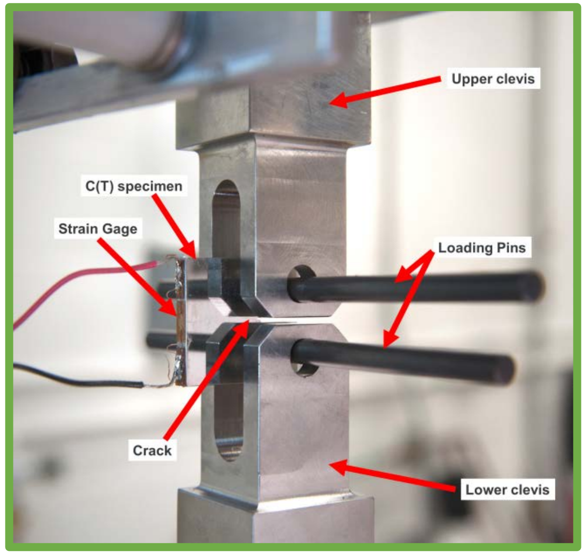
NETL
CSIRO

Mechanical Behavior of Materials in sCO_2 Power Cycles



Presence of cracks can significantly reduce life of structural components

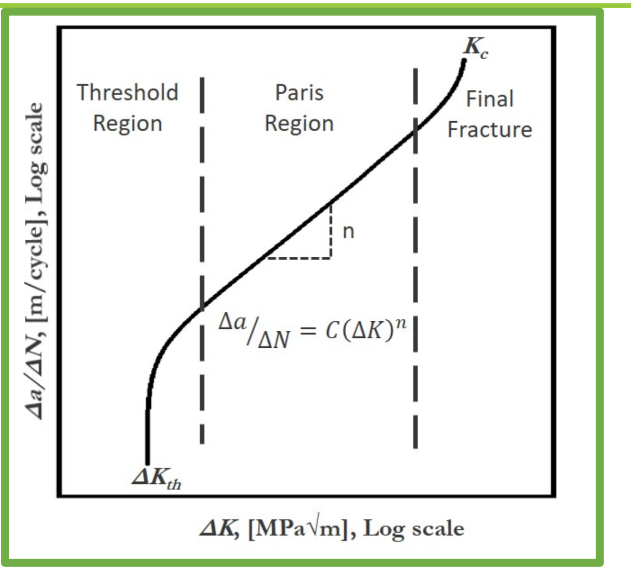
To estimate the lifetime of cracked parts, linear elastic fracture mechanics (LEFM) methods are employed

For LEFM analysis one typically needs the following information

Stress intensity factor, *K*

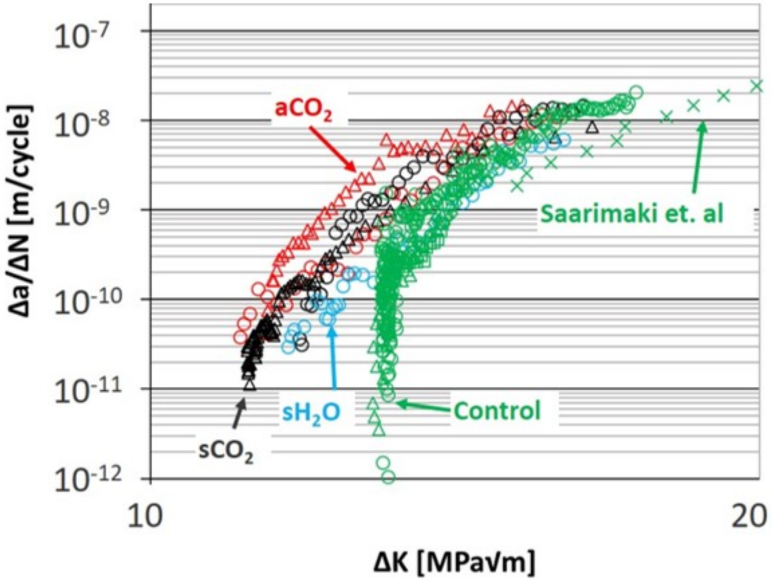
Crack velocity, *Δa/ΔN*

Initial crack size, a_i



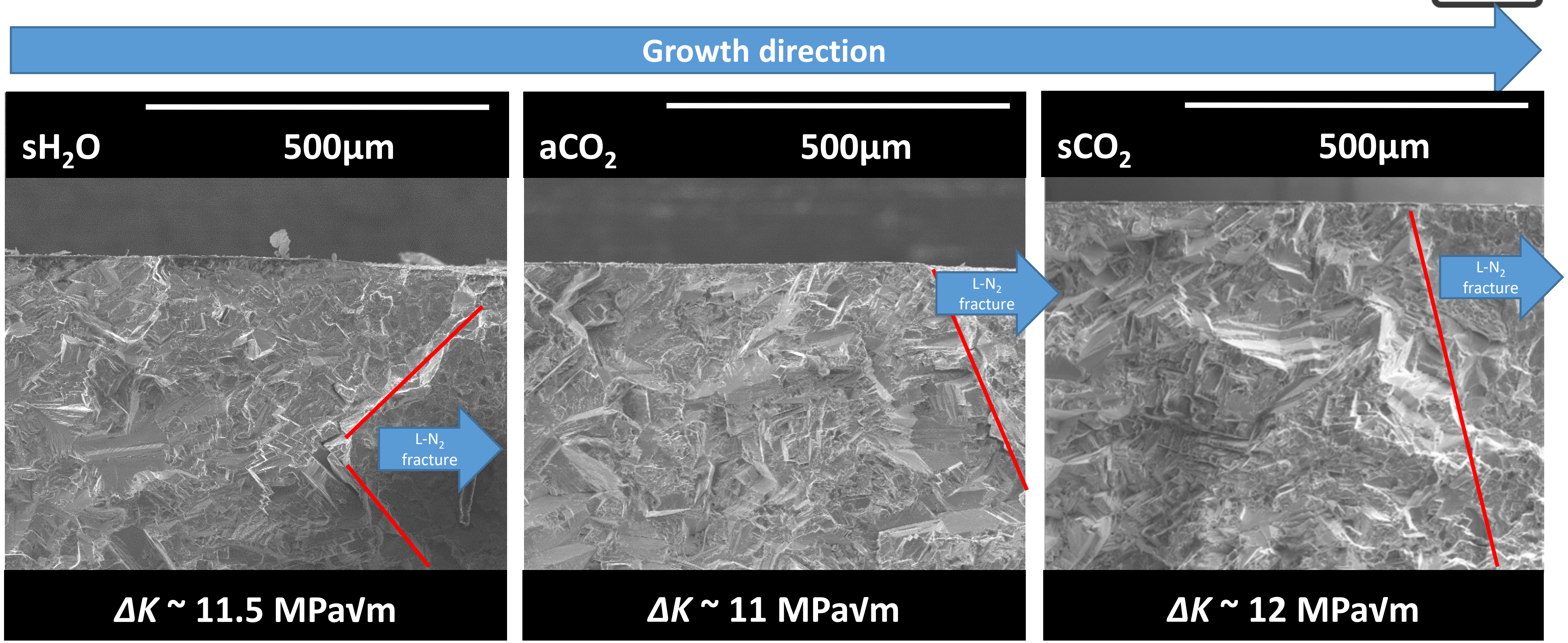
Mechanical testing of candidate materials: Demonstrating and quantifying effect of sCO_2 environment on mechanical properties

Fatigue crack growth rate of Alloy 282 was measured after exposing the test specimens to supercritical CO_2, CO_2, and supercritical H_2O at 730°C. The specimens exposed to sCO_2 and CO_2 showed faster fatigue crack growth rates especially at lower stress intensities.



Fracture Surfaces

Experimental results

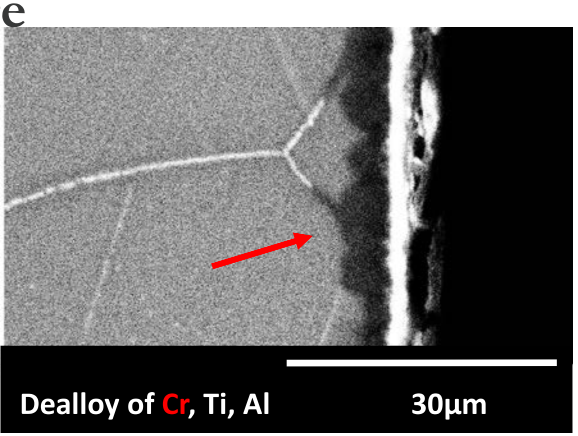


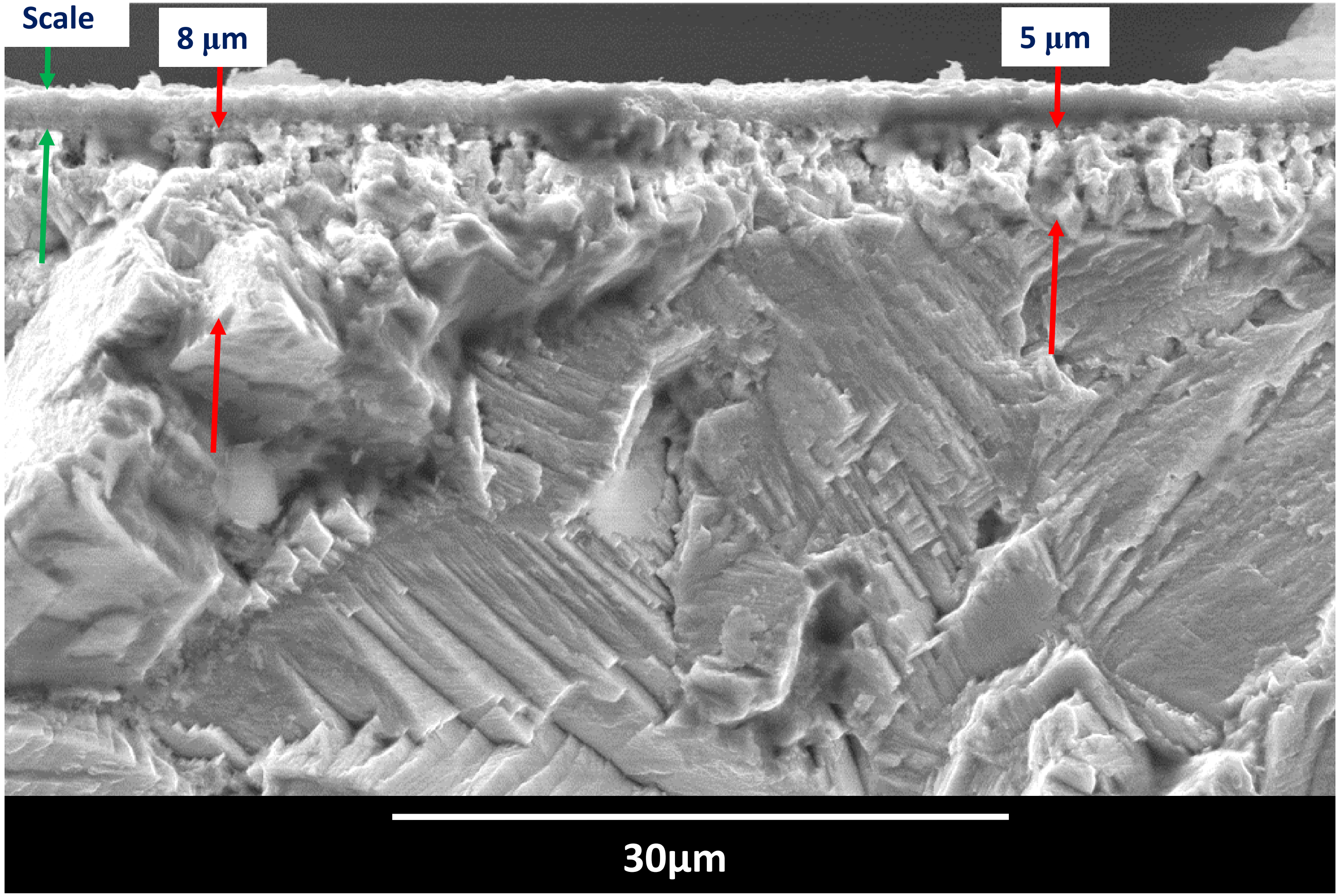
- **Fracture surfaces show signs of stage one crack growth independent of exposure environment**
  - Stage one crack growth is typical of threshold crack growth
  - Observed by planer features intersecting on crystallographic slip planes (slip band cracking)

Fracture Surfaces

At Higher Magnifications

- Featured: aCO_2 sample
- Change in fracture morphology near surface
- Possible "Intergranular cracking"
- Consistent depth with depleted zone
- "Intergranular cracking" does not appear to affect crack propagation as depth is consistent with the oxidation damage

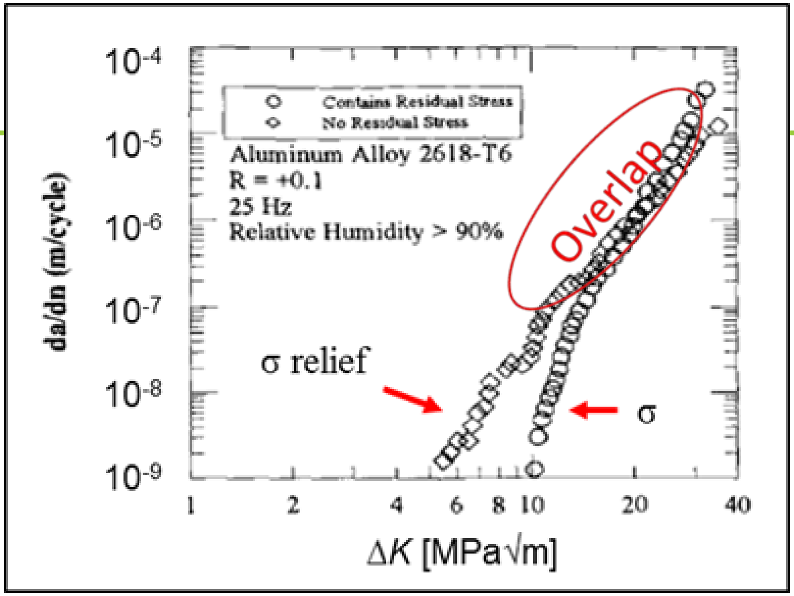




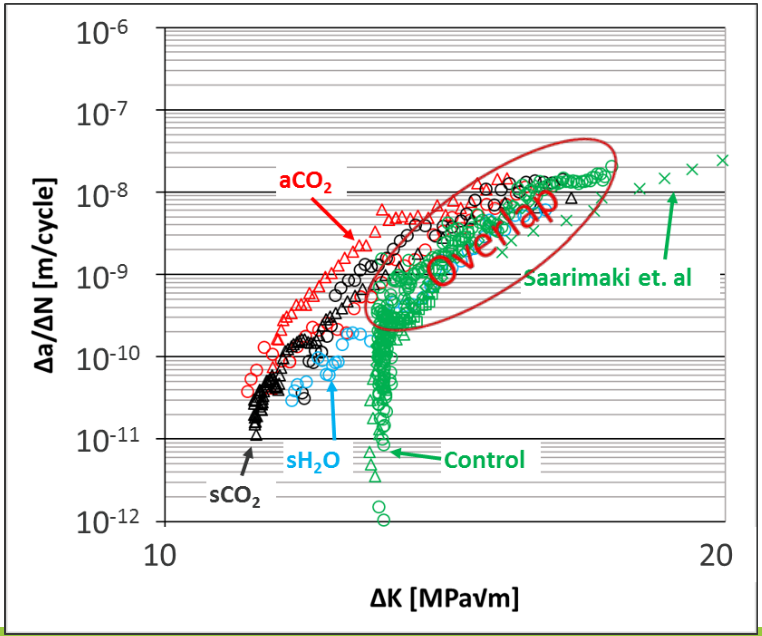
Analysis

Possible explanation of effect

- **Compact tension specimens particularly sensitive to residual stress**
  - Small sample size (W=0.78 inch/20mm) more sensitive
- **Residual stress acts to increases threshold stress intensity range [Bush et al. 2000]**
- **One could argue 500 hr at 730°C acts as stress anneal**
- **Mitigated residual stress by:**
  - Precracked to a/w > 0.28
  - $\Delta K_{initial}$ selected to be >110% of $\Delta K_{precrack}$
- **Overlap of FCG rates from $18 < \Delta K < 14$ MPa√m and deviation of threshold ΔK values <14 MPa√m is consistent with residual stress effect observed by Bush et al.**
- **Vacuum exposure planned to determine if effect is due to the exposures or related to a stress anneal**



Adapted from Bush, et al. (2000)



- **Plan to test effect of environmental exposures on:**
  - IN625
  - IN740
  - 347H
- **High load ratios**
- **Vacuum test**
- **In-situ mechanical tests in CO_2 environmental chamber**

Summary

- **Corrosion - Direct sCO_2 Cycles**
  - Influence of liquid H_2O saturated with CO_2 on the corrosion of 347H, 316, and P91 at 50◦C
  - Confirmed effect of condensation transient on corrosion during shut down
  - Precipitation strengthened Ni alloys (263, 740H) demonstrated higher oxidation rates compared to the solution strengthened Ni alloys (230, 625, 600, 617) at 750°C in $CO_2+H_2O+O_2$
- **Oxidation - Indirect sCO_2 Cycles**
  - Variation in Cr content (5-24 mass %) in model Ni alloys exposed to CO_2 at 700°C did not affect the oxidation behavior up to 3000 hours.
  - Based on the early observations (500 h) on the Fe-Ni-Cr model alloys, oxidation rate did not have a clear relationship with Si content of the alloys in CO_2.
- **Fatigue crack growth in alloy 282 was measured after exposing the specimens to sCO_2, sH_2O, and aCO_2. All exposed specimens showed faster crack growth rates compared to the control samples especially at low stress intensities.**