

Advanced Alloys in Supercritical CO₂ Power Cycles

FWP 1022406 –Advanced Alloy Development

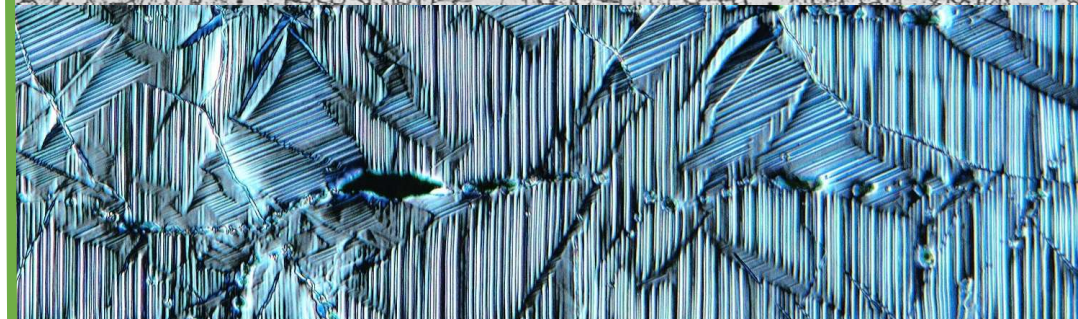
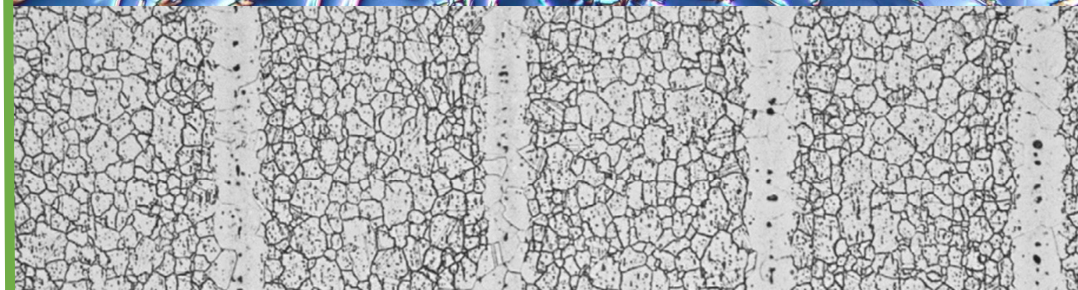
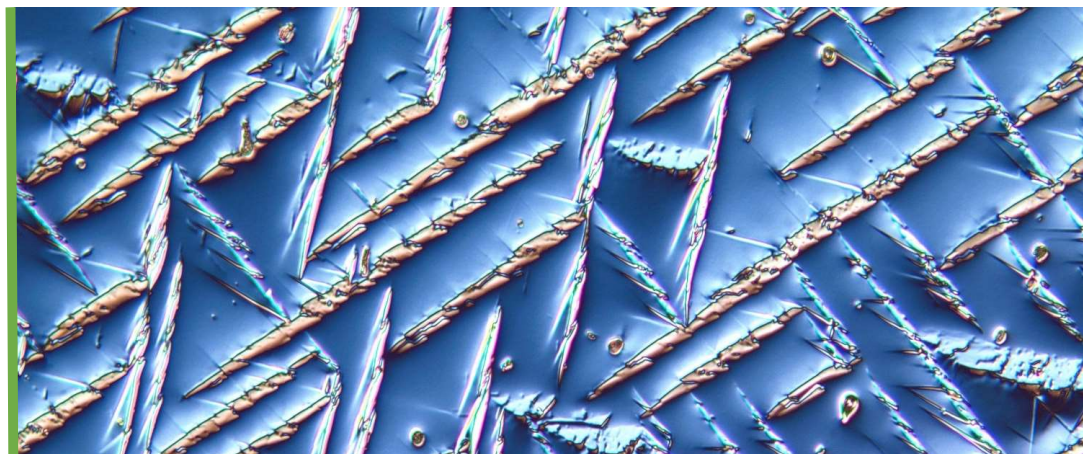
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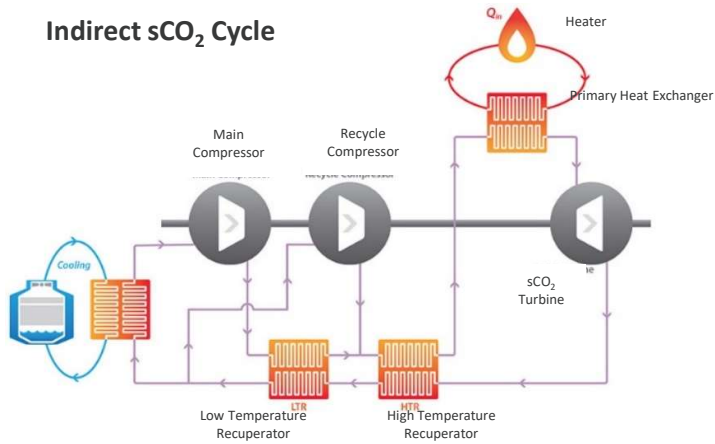
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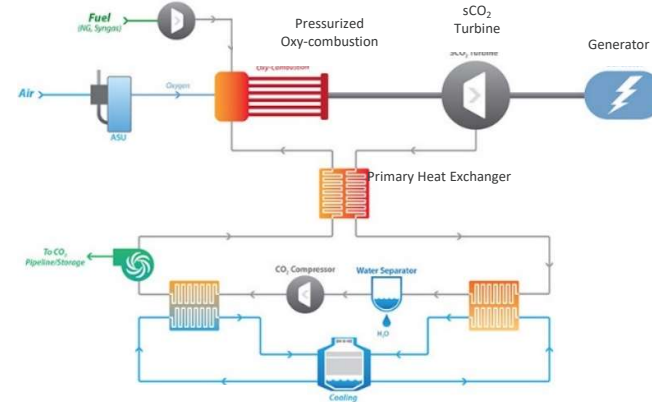
Supercritical CO₂ Power Cycles



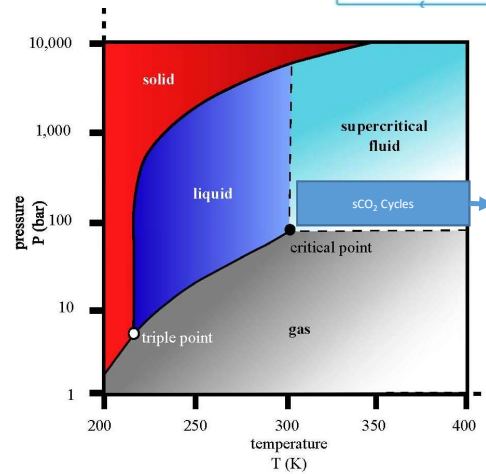
Indirect sCO₂ Cycle



Direct sCO₂ Cycle



Properties of sCO ₂ 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

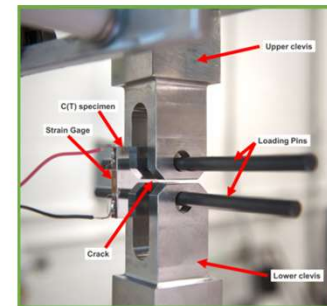
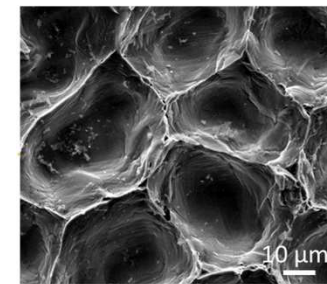
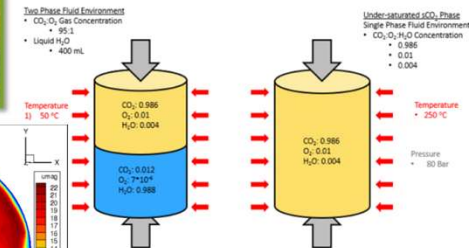
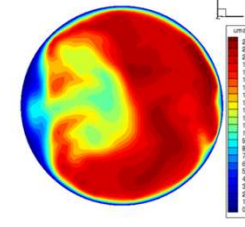
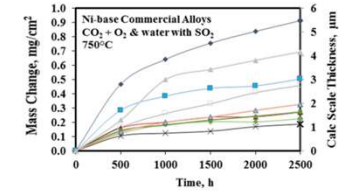


250 MW Steam Turbine
300 MW sCO₂ Turbine

Supercritical CO₂ Power Cycles

Materials Research at NETL

- High-temperature oxidation in direct sCO₂ power cycles
- Low-temperature corrosion in direct sCO₂ power cycles
- Effect of sCO₂ cycle environments on mechanical properties
- Erosion in components of sCO₂ power cycles
- Materials issues in manufacturing compact heat exchangers
- Mechanical and chemical stability of joined materials in sCO₂
- Additive manufacturing of heat exchangers with new geometries



High-Temperature Oxidation in Direct sCO₂ Power Cycles

• Importance

- Corrosion resistance of available structural materials need to be determined to built demonstration and future commercial sCO₂ power plants in a cost effective way.

• Scope

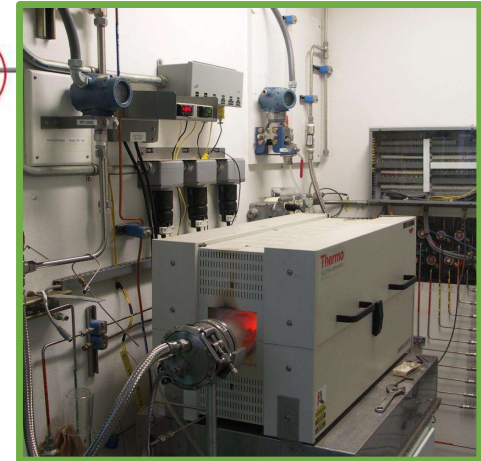
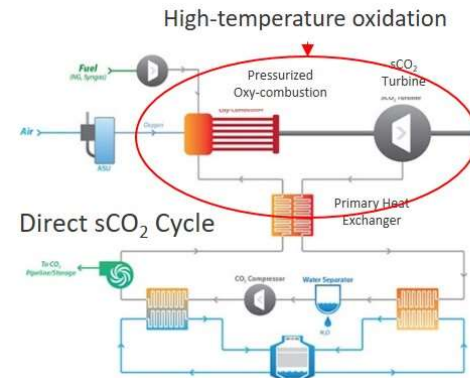
- Evaluating A-USC alloys (both Ni-based and Fe-based) for their high-temperature oxidation performance in direct sCO₂ power cycle environments

• Progress to Date

- Ni alloys (740H, 282, 625, 617, 230, 600, 718) and steels (347H, 304H, 310S, P91, P22) were tested at 750°C and 550°C, respectively, in atmospheres (1 bar) simulating natural gas-fired and coal-fired direct sCO₂ power cycles.
- Model alloys (Ni-xCr, Fe-22Cr-xSi, Fe-22Ni-22Cr-xSi, Fe-Cr-xSi) were also exposed in the direct cycle environments to study the effect of alloying elements (Cr and Si) on oxidation.

• FY18 Expected Accomplishments

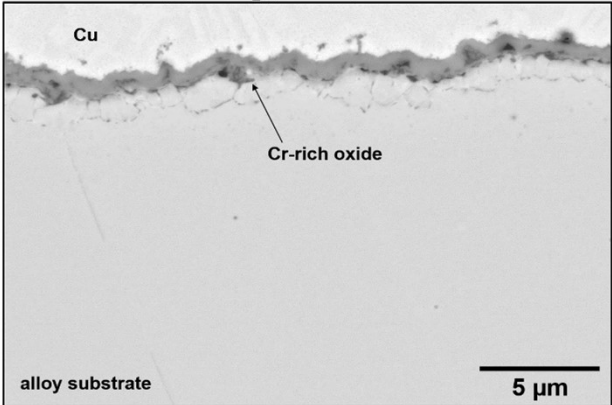
- High-pressure (~200 bar), high-temperature (>700°C) oxidation tests in sCO₂+H₂O+O₂ will begin.
- Oxidation rates of the exposed alloys (1 bar and 200 bar) will be reported.
- Oxidation mechanisms of the exposed alloys will be defined.



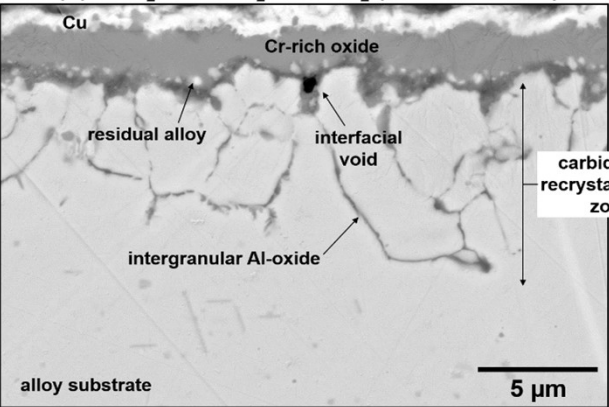
High-Temperature Oxidation in Direct sCO₂ Power Cycles

740H

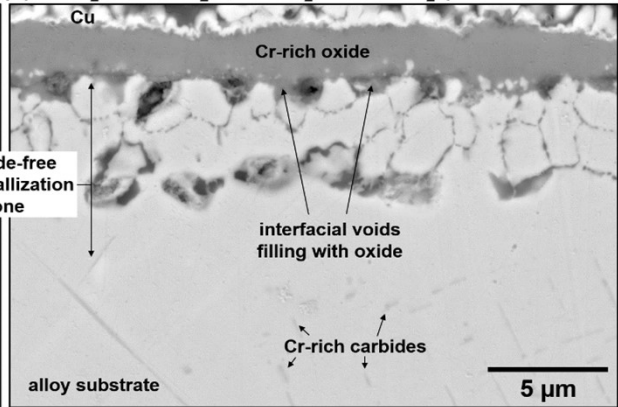
(a) sCO₂ (700 °C, 1500 h)



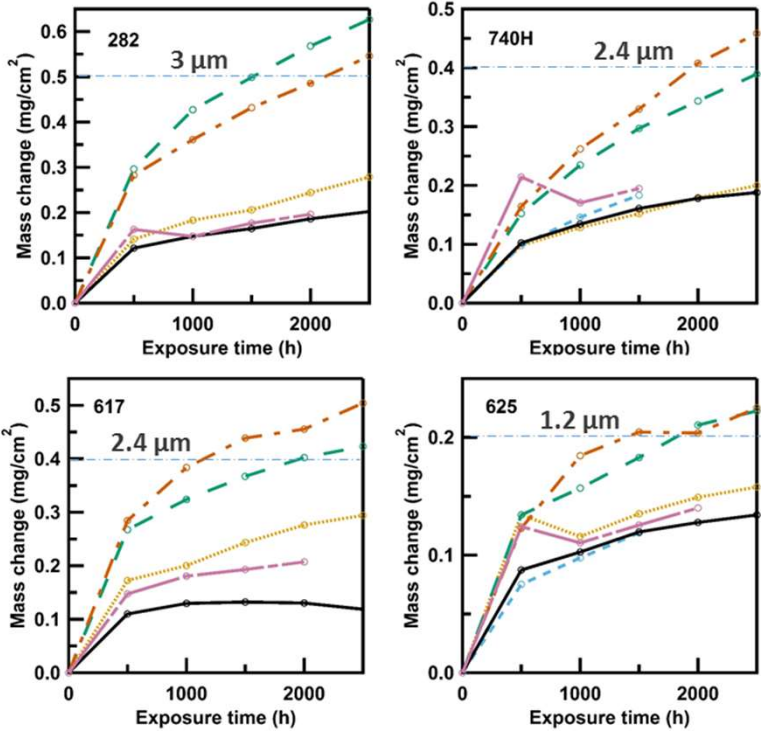
(b) aCO₂ w/ 4% H₂O, 1% O₂ (750 °C, 2500 h)



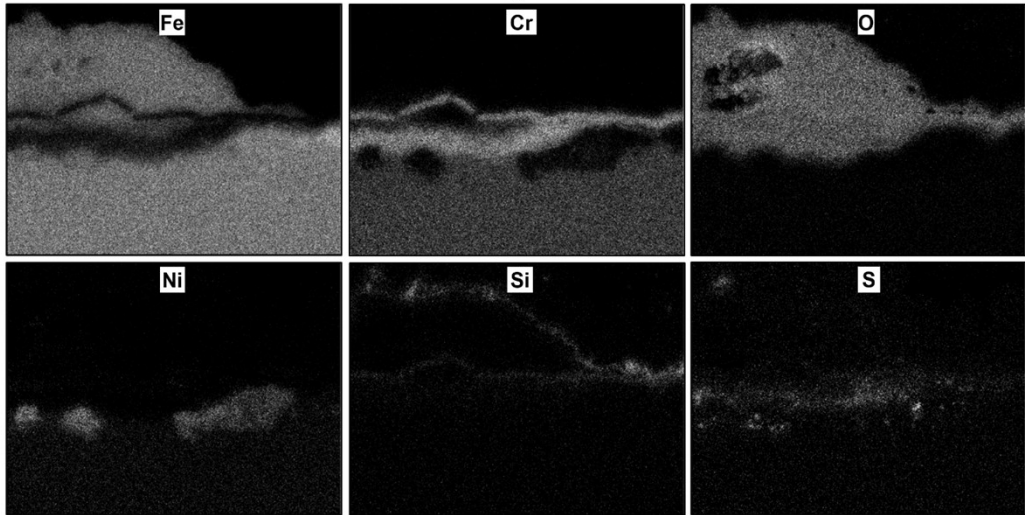
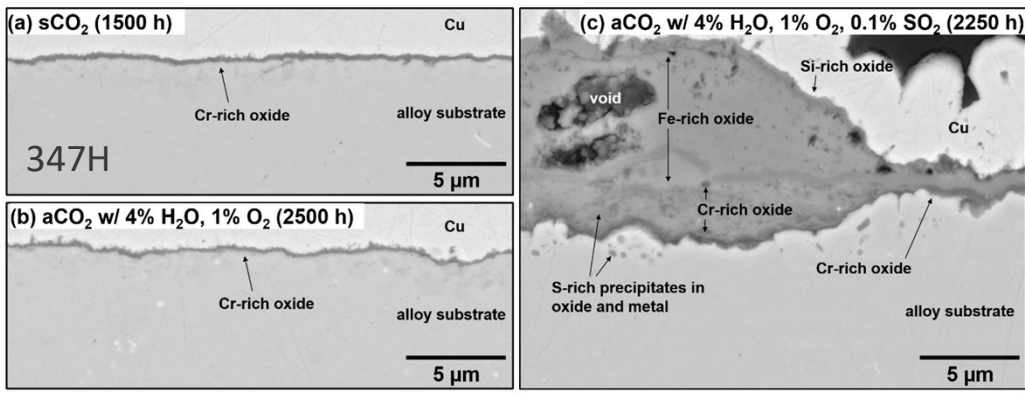
(c) aCO₂ w/ 4% H₂O, 1% O₂, 0.1% SO₂ (750 °C, 2500 h)



- aCO₂ (700 °C)
- sCO₂ (700 °C)
- air (700 °C)
- DF = aCO₂ w/ 4% H₂O, 1% O₂ (750 °C)
- DFS = aCO₂ w/ 4% H₂O, 1% O₂, 0.1% SO₂ (750 °C)
- sH₂O (700 °C)

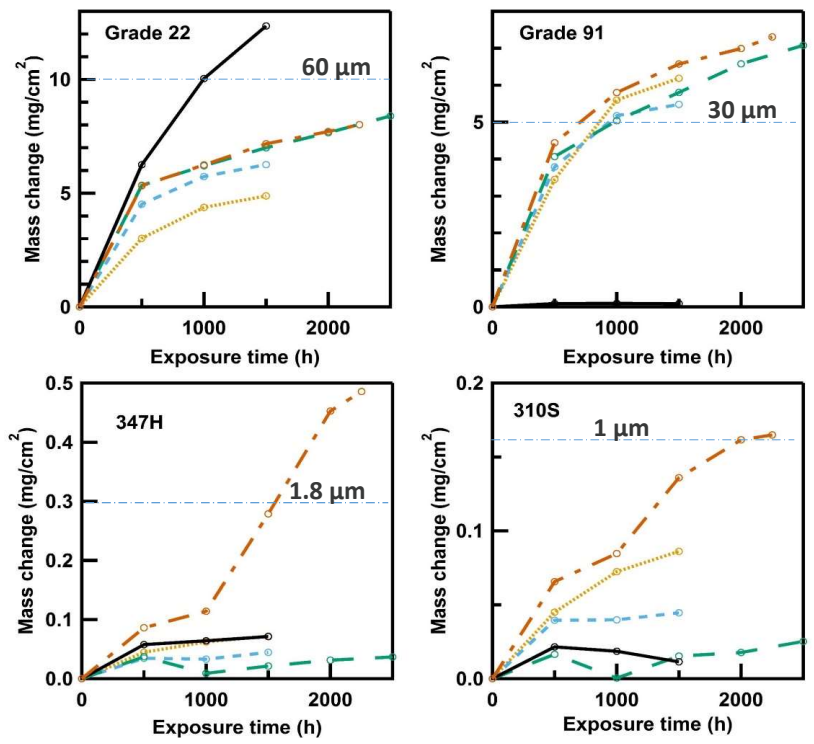


High-Temperature Oxidation in Direct sCO₂ Power Cycles



T = 550 °C

- aCO₂ (yellow dotted line)
- sCO₂ (blue dashed line)
- air (black solid line)
- DF = aCO₂ w/ 4% H₂O, 1% O₂ (green dashed line)
- DFS = aCO₂ w/ 4% H₂O, 1% O₂, 0.1% SO₂ (orange dashed line)



Summary – High-Temperature Oxidation in Direct sCO₂ Power Cycle Conditions



- Fe and Ni based alloys were exposed to conditions intended to simulate the direct fired sCO₂ cycles
- Tests included gas streams (CO₂+H₂O+O₂) with and without SO₂ additions
- No sulfur effect was observed on Ni alloys. Some sulfur compounds were observed on stainless steels
- Ni based solution strengthened alloys generally showed less mass gain than the age hardenable alloys

Low-Temperature Corrosion in Direct sCO₂ Power Cycles

• Importance

- Low-temperature components of the 25 MW Net Power demonstration plant (natural gas-fired direct cycle) is being built using an austenitic stainless steel. This task investigates whether a lower Cr (less expensive) steel could be used instead.

• Scope

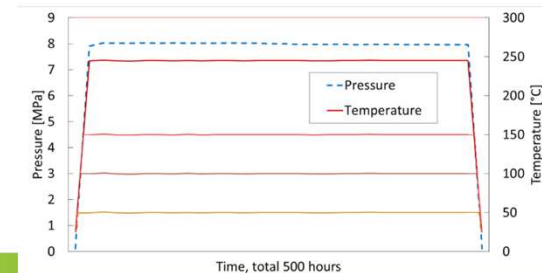
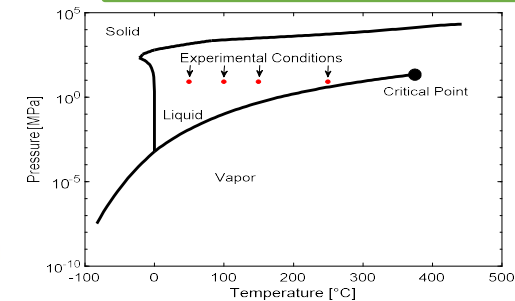
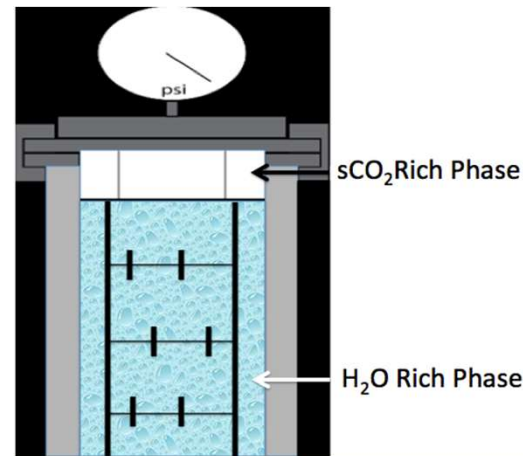
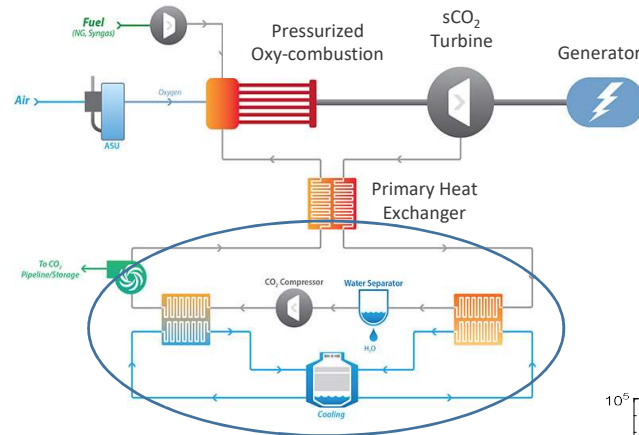
- An experimental investigation of corrosion resistance of Grade 91 and 347H steels in condensed water saturated with CO₂ (Carbonic acid).

• Progress to Date

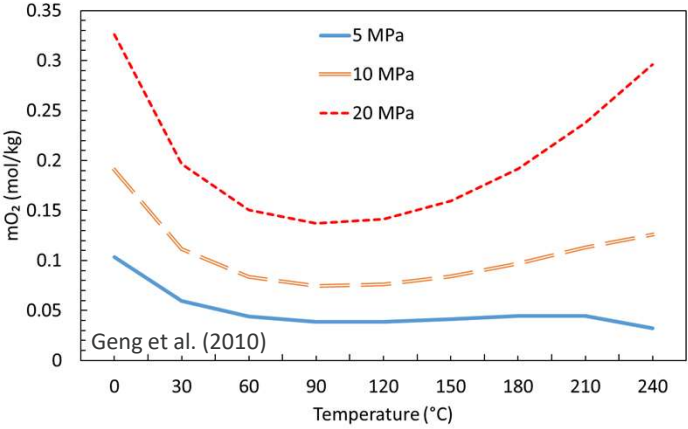
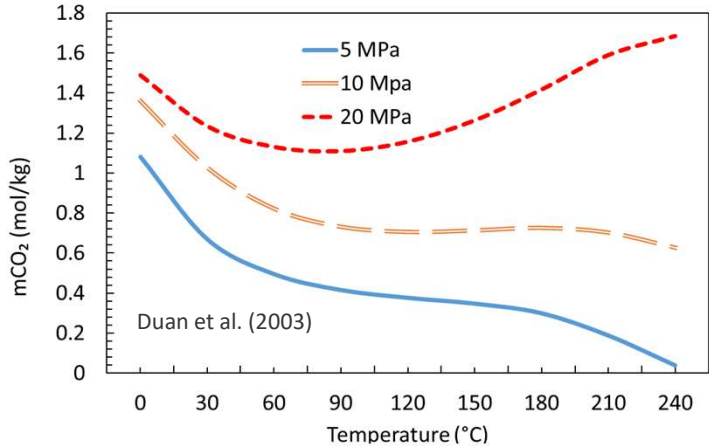
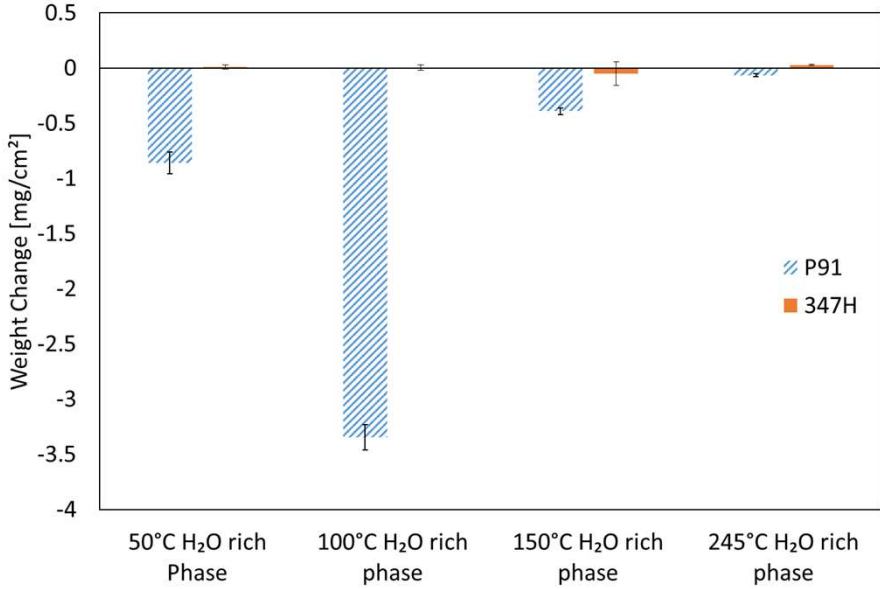
- A series of autoclave coupon exposure tests simulating the environment of low-temperature recuperators and coolers in a direct sCO₂ cycle power plant have been performed
- Due to high corrosion rates of Grade 91 steel in water saturated with CO₂, it is concluded that unlike in the steam cycles, lower Cr steels are not suitable for low-temperature components of direct sCO₂ cycle plants. 347H performed well in the same environment.

• FY18 Expected Accomplishments

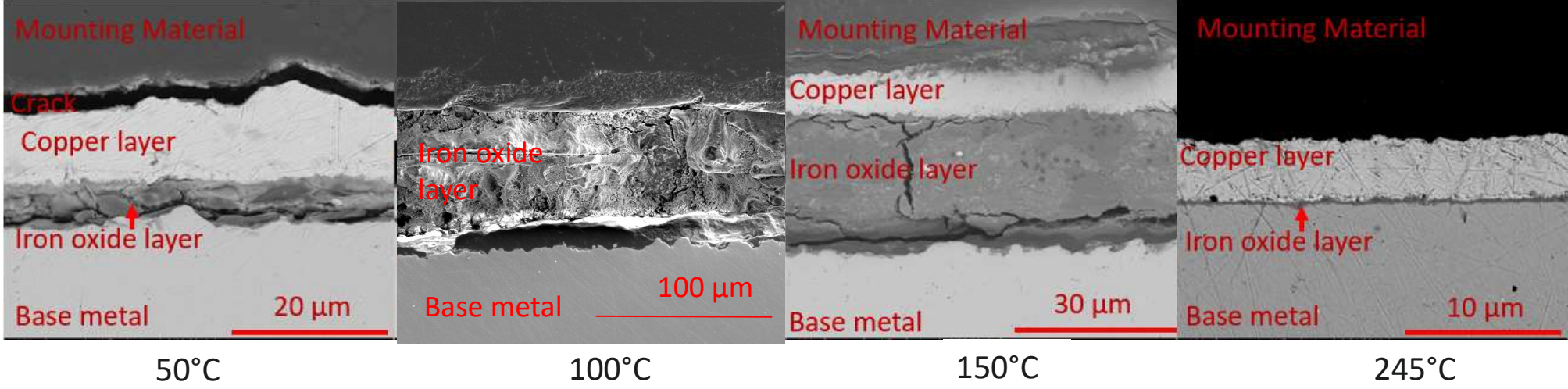
- In coal-fired direct sCO₂ cycle power plants without pre-combustion sulfur removal, sulfuric acid can condense in the cooler parts of recuperator. Corrosion of stainless steels due to sulfuric acid condensation will be investigated.



Low-Temperature Corrosion in Direct sCO₂ Power Cycles



Low-Temperature Corrosion in Direct sCO₂ Power Cycles



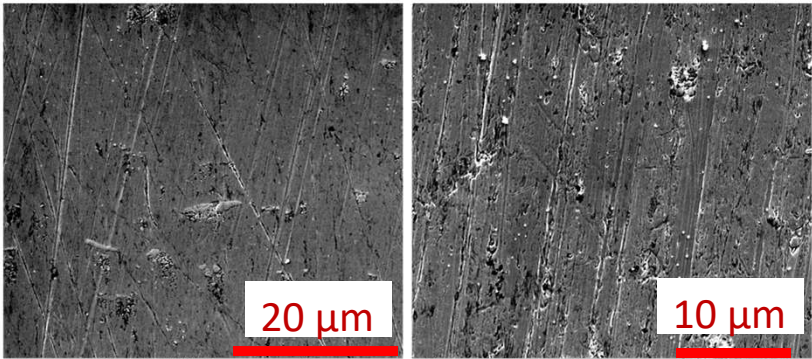
50°C	100°C	150°C	245°C
Fe ₂ O ₃	Fe ₂ O ₃	Fe ₂ O ₃	Fe ₂ O ₃
FeO(OH)	Fe ₃ O ₄	Fe ₃ O ₄	Fe ₃ O ₄
Fe ₃ O ₄			

XRD Analysis of P91 Corrosion Products

Low-Temperature Corrosion in Direct sCO₂ Power Cycles

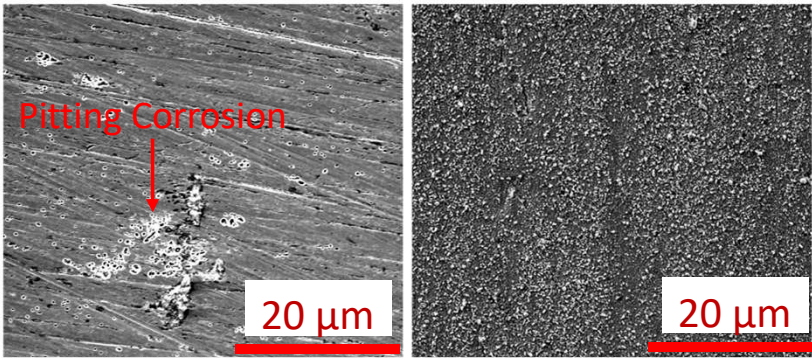


347H Stainless Steel



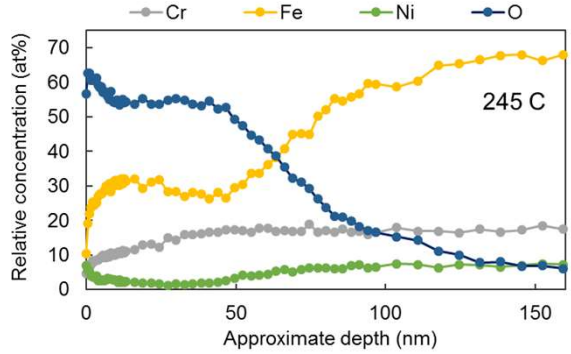
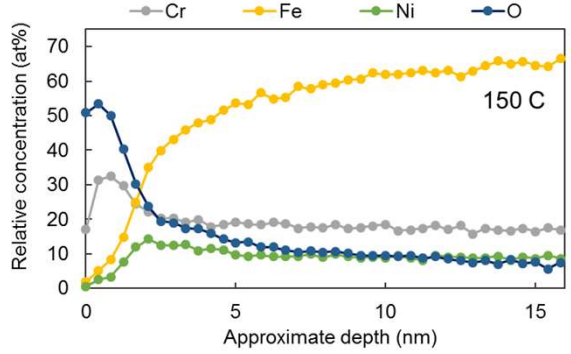
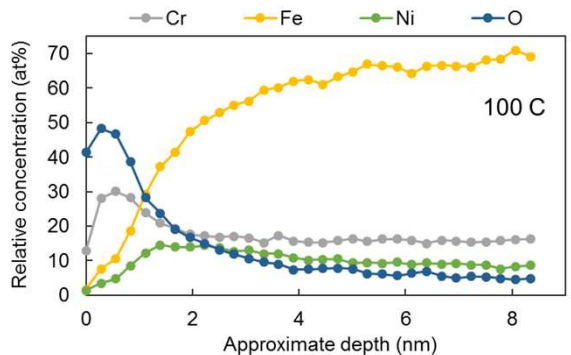
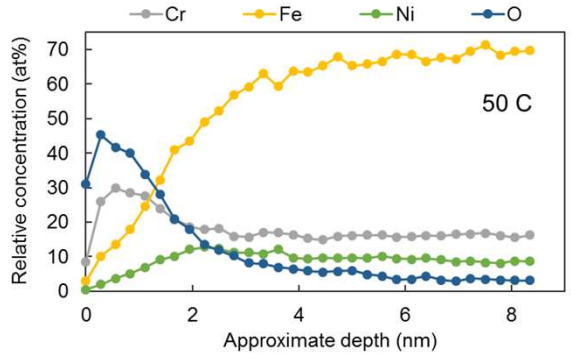
50°C

100°C



150°C

245°C



Summary – Low-Temperature Corrosion



- Residual corrosion products on the Grade 91 coupons were identified as Fe_2O_3 and Fe_3O_4 , while 347H coupons showed minimal mass change and very thin passive layers.
- Lower Cr steels such as Grade 91 may not be suitable for the low / intermediate temperature components in the direct sCO_2 power cycles.
- We will evaluate higher Cr steels that are less costly than austenitic stainless steels.

Erosion in Components of sCO₂ Cycles

- **Importance**

- This work will establish:
 - Whether erosion might be a significant problem in sCO₂ power cycles
 - An understanding of erosion mechanism
 - A guidance for an experimental work which might be implemented if erosion is shown to be a problem.

- **Scope**

- Large eddy simulations are performed at different Reynolds numbers to determine magnitude of oscillating shear stresses and the effect of heat transfer in a 90 degree bend pipe in order to identify the potential causes of the erosion.

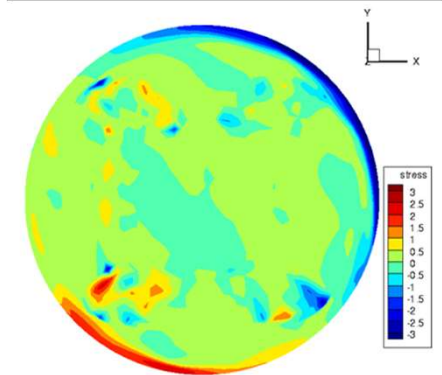
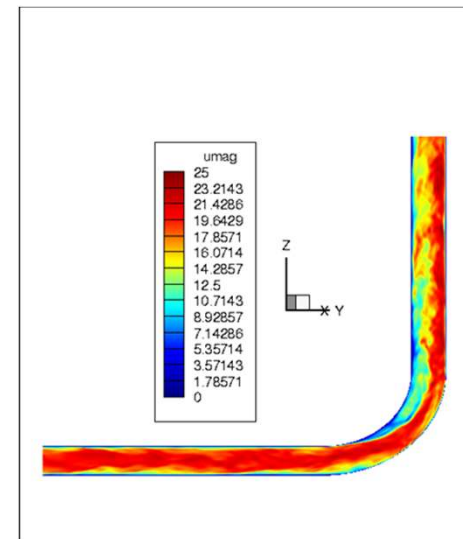
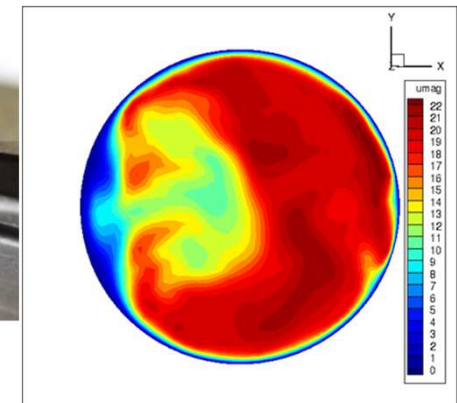
- **Progress to date**

- Oscillating shear stresses on pipe wall were investigated for Reynolds numbers of 5000, 27,000, 45,000, 70,000 and 95,000.

- **FY18 Expected Accomplishments**

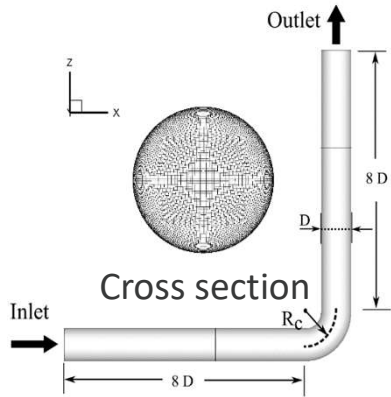
- Begin a finite element model to study effect of oscillating shear stresses on the pipe wall material.
- Introduce hard particles into the sCO₂ flow and examine their effect on the component walls.

Erosion of turbine nozzle in sCO₂ test loop

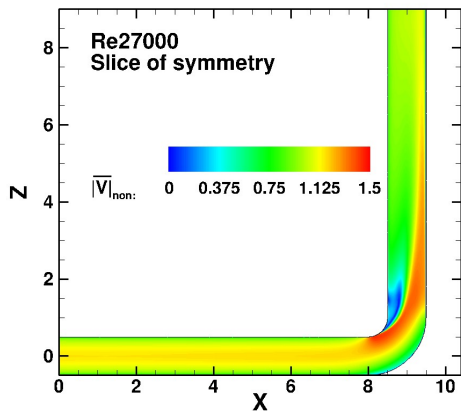


Erosion in Components of sCO₂ Cycles

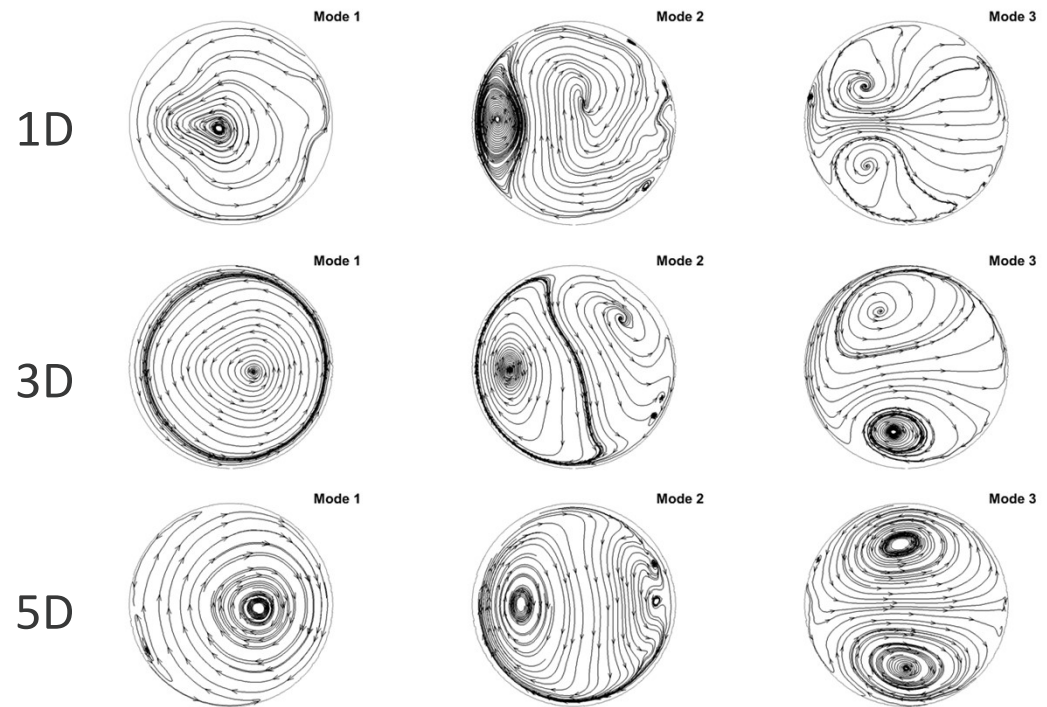
- Large-eddy simulation (LES) is implemented using a highly validated, efficient and predictive solver, which is fully parallel and uses finite volume method.



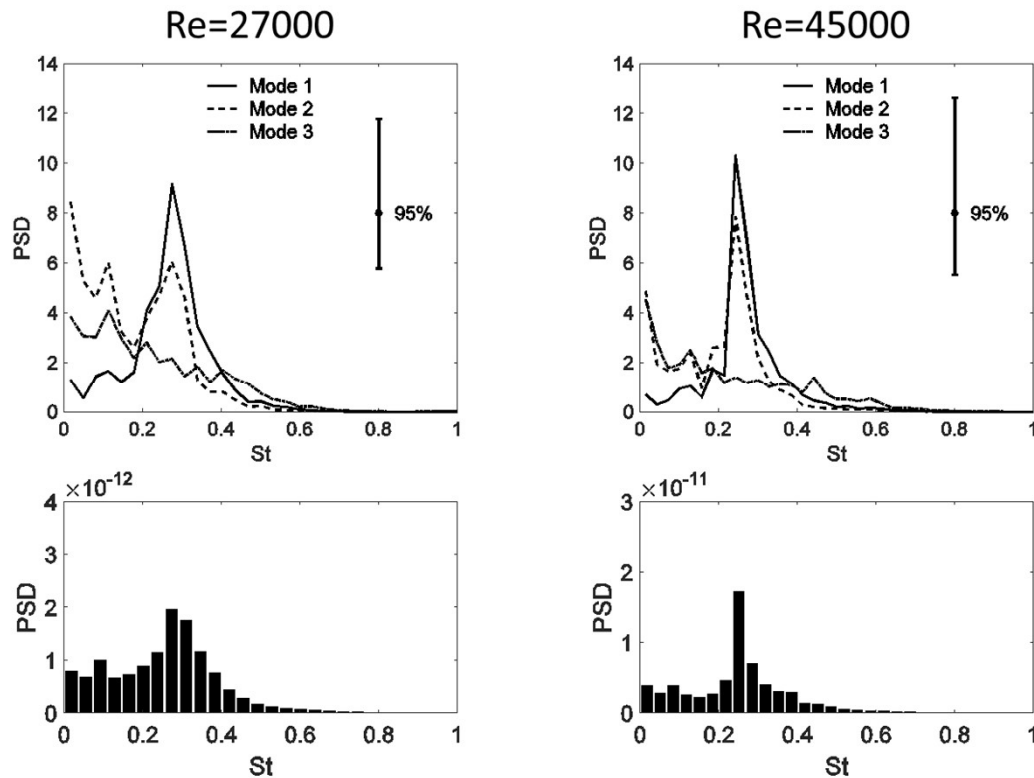
Geometry and cross section of the pipe



- Mean streamwise velocity becomes higher at the inner wall at 30 degree angle;
- At 90 degree, the maximum velocity shifts towards the outer wall.



Erosion in Components of sCO₂ Cycles

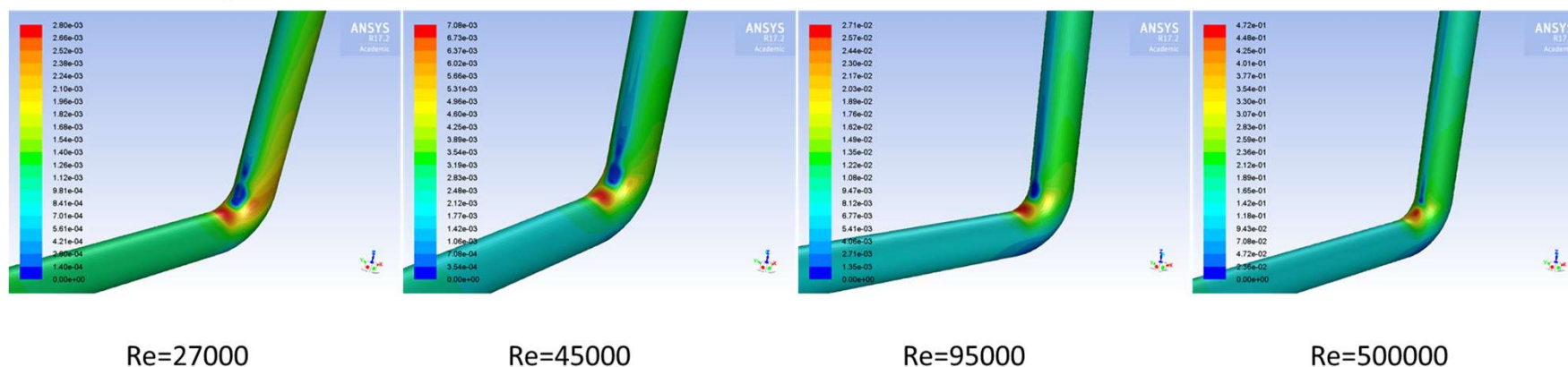


Spectra of shear stress (down) and secondary flow patterns (up), indicating they are highly correlated.

The oscillation of the secondary flow patterns directly causes the oscillation of the shear forces, which could possibly result in the erosion on the pipe surface.

Estimation of the shear force for the real sCO₂ power plant

- In the real sCO₂ power cycle pipe lines, the Reynolds number can go as high as about 15 million. It is necessary to estimate the magnitude of the oscillating shear force on the wall to see if it can actually cause the erosion;
- For such high Reynolds number flows, the computational costs for LES would be enormous. As a result, RANS model is used to estimate the mean value of the shear forces.



- Although more detailed analysis is needed, the shear force at Re=15M is likely to be responsible for the breakdown of the oxide scale on the inner surface of the pipe, causing the erosion.

Summary – Erosion in sCO₂ Power Cycle Components

- Performed large-eddy simulations for turbulent flows through pipe bends a range of Reynolds numbers between 5000 and 100,000;
- Swirl switching phenomenon was observed downstream of the bend for $Re = 27,000$. Similar phenomenon is expected for higher Re cases;
- The swirl switching is highly correlated with the shear force on the wall. This has the potential to cause fatigue and erosion of oxide scale on pipe wall;
- Effect of hard particles entrained in sCO₂ flow will also be investigated.

Mechanical and Chemical Stability of Welded Alloys in sCO₂

- **Importance**

- High-temperature components (piping, recuperators, turbines) in sCO₂ cycles are typically joined together by welding. Although the goal is to form a monolithic structure, depending on the alloy composition and microstructure, the interface region (weld, heat affected zone) of the joined structure usually have a microstructure different from the parent alloy. This can be a source of mechanical and/or chemical instability for the structure in the sCO₂ environments.

- **Scope**

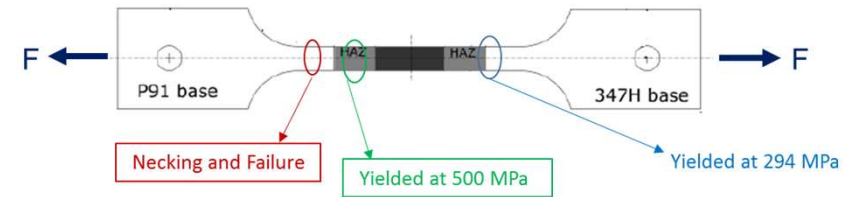
- Effect of sCO₂ on the welded structures will be investigated and documented. The investigation involves making the joined structures, exposing them to sCO₂, evaluating their properties, and modeling the mechanical behavior.

- **Progress to Date**

- Ten (10) similar and dissimilar metal welds (8"x6"x1" plates) were produced by GTAW.
- Mechanical behavior (tensile, indentation) of welded structures is being modeled.
- Effect of sCO₂ on welded regions is being investigated on P91-347H dissimilar metal weld.

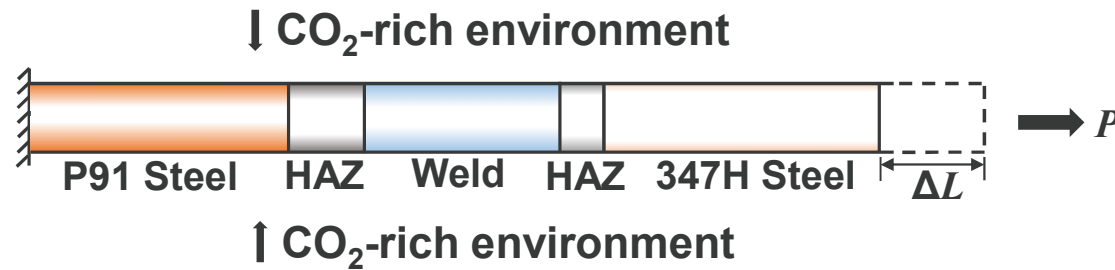
- **FY18 Expected Accomplishments**

- More similar and dissimilar metal welds exposed to sCO₂ will be evaluated.

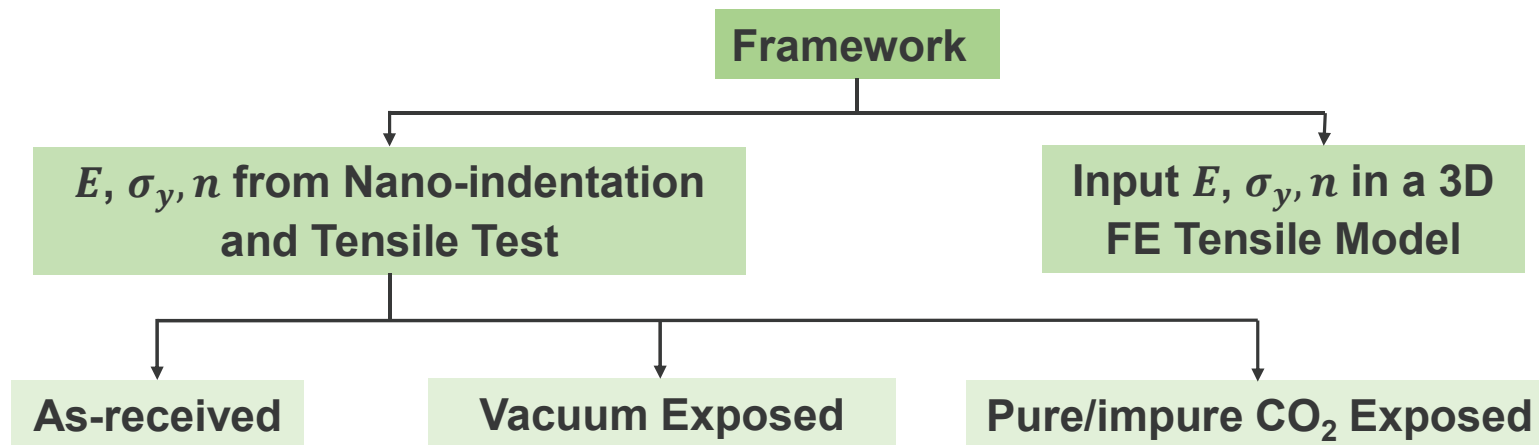


At Edison Welding Institute (EWI)
By Gas Tungsten Arc Welding (GTAW).
With Post Weld Heat Treatment.

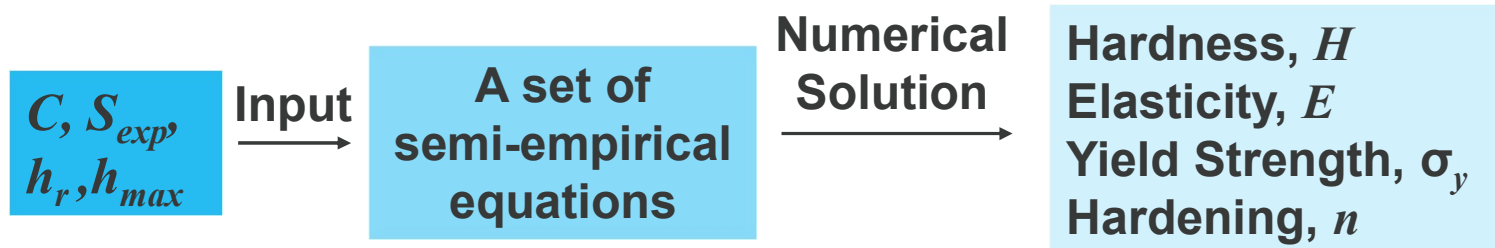
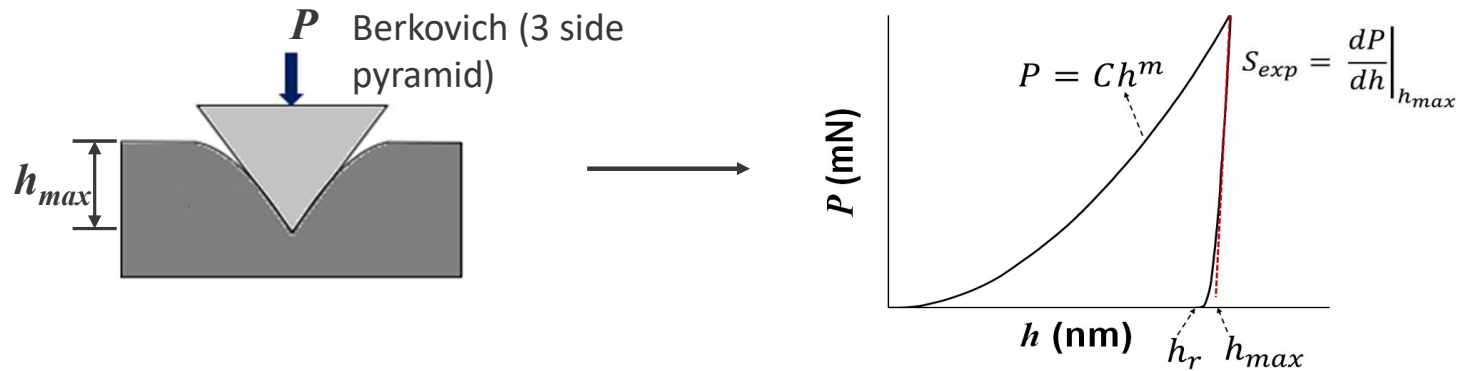
Performance of welds under load



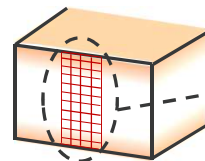
GOAL : *Development a framework to study the effect of environment on the global deformation behavior of dissimilar metal-welds.*



Nano-indentation Test

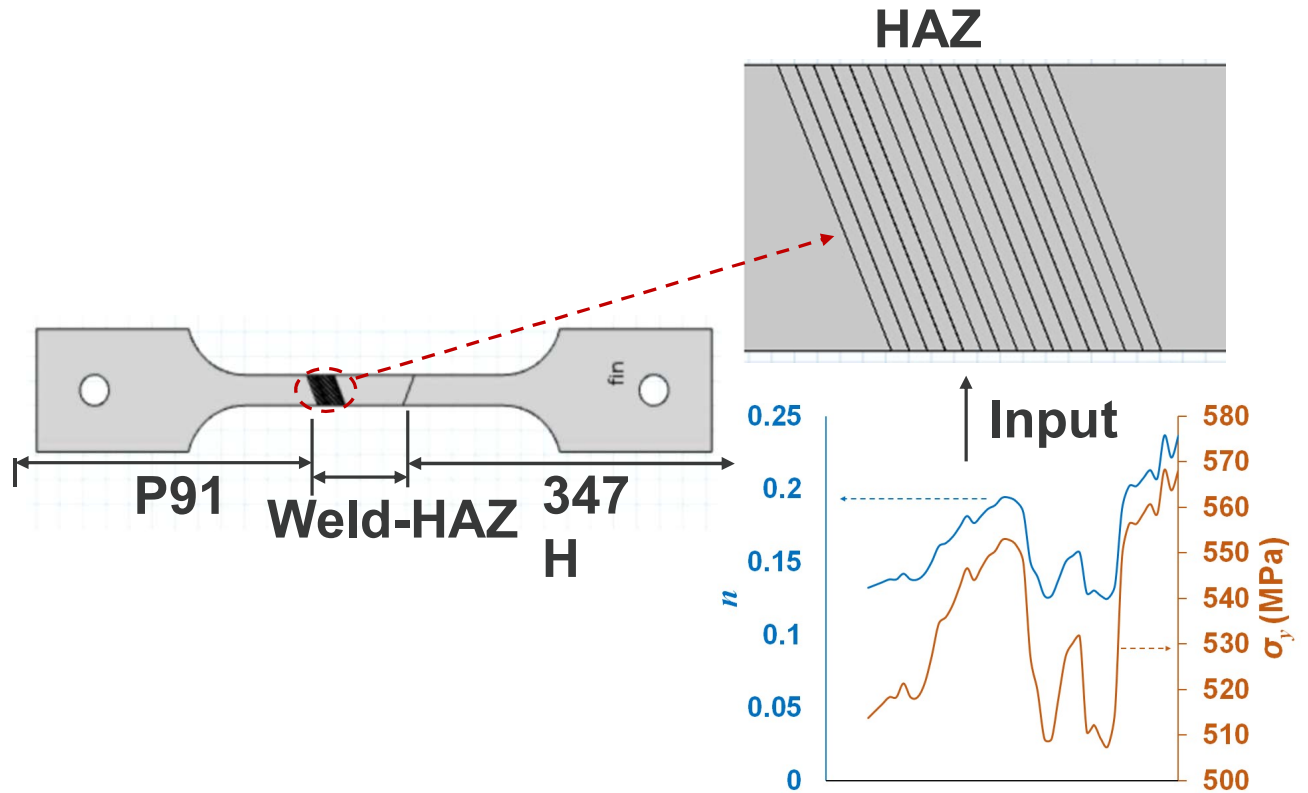
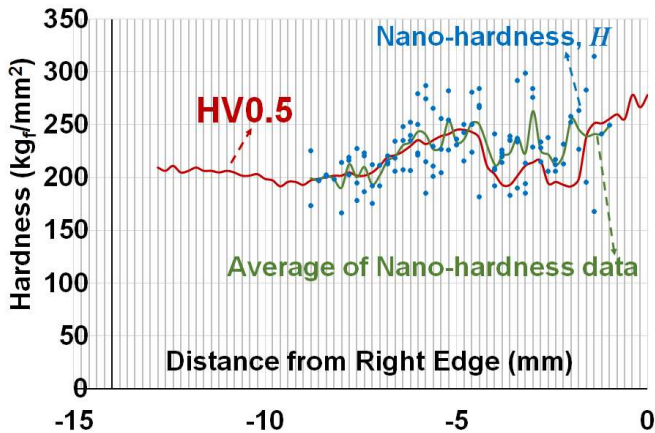
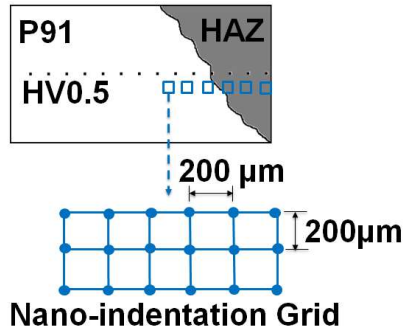


Advantage: Can capture the local mechanical property.



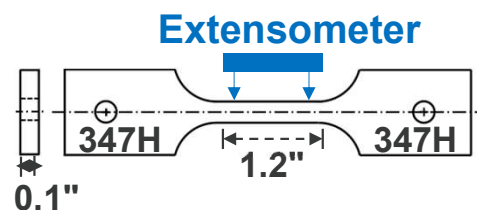
Nano-indentation Test Grid on carburized cross-section.

Nano-indentation Test to Capture the Mechanical Properties of HAZ

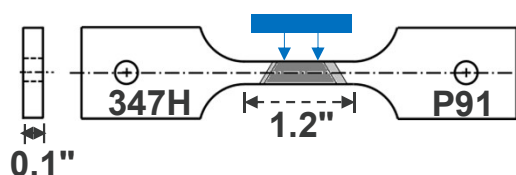


Obtained from Nano-indentation Test

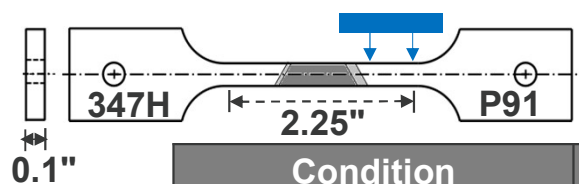
Room Temperature Tensile Test Results



Condition	E (GPa)	n	σ_y (MPa)
As-Received	217.94 \pm 39.02	0.391 \pm 0.0066	232.92 \pm 4.92
CO ₂ +4%H ₂ O+1%O ₂ , 650C-1000h Exposed	193.31 \pm 9.67	0.3628 \pm 0.0041	256.68 \pm 5.41



Condition	E (GPa)	n	σ_y (MPa)
As-Received	186.26 \pm 24.79	0.114 \pm 0.03	491.19 \pm 20.68
CO ₂ +4%H ₂ O+1%O ₂ , 650C-1000h Exposed	176.76 \pm 0.488	0.1589 \pm 0.0336	587.84 \pm 4.42

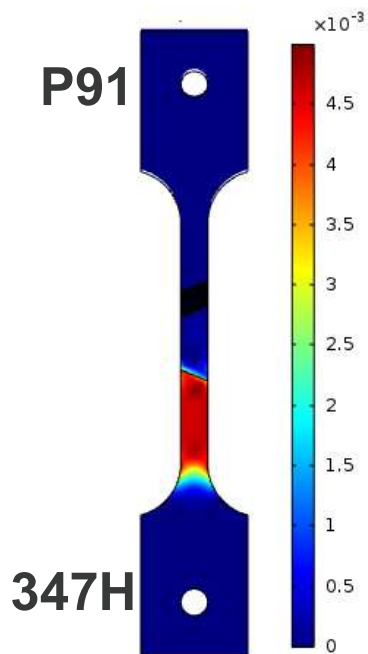


Condition	E (GPa)	n	σ_y (MPa)	% Area Reduction	Failure Location
As-Received	249.03 \pm 4.32	0.125 \pm 0.0023	488.93 \pm 4.18	66.3 \pm 5.93	P91
CO ₂ +4%H ₂ O+1%O ₂ , 650C-1000h Exposed	167.73 \pm 16.79	0.1616 \pm 0.0036	406.16 \pm 2.80	38 \pm 9.3	P91

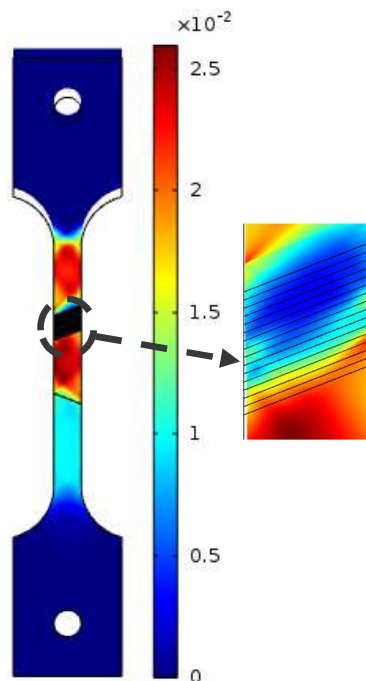
FE Simulation Results of P91-347H Weld Couple

Plastic Strain Distribution at:

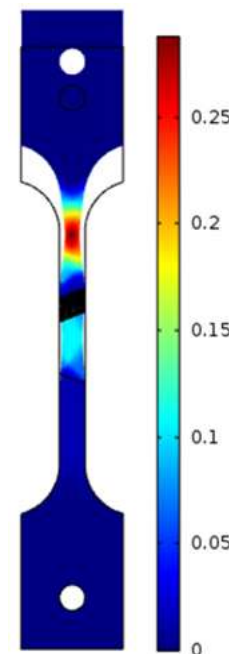
$\Delta = 0.3 \text{ mm}$



$\Delta = 1.1 \text{ mm}$

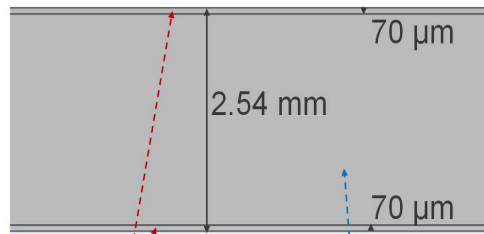
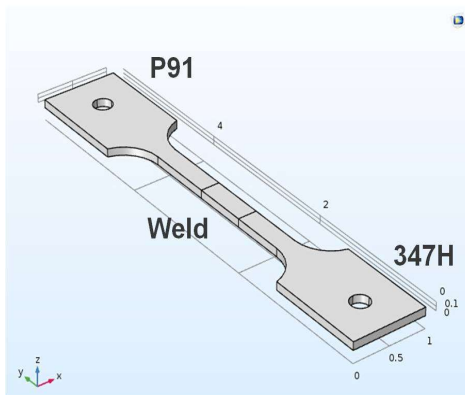


$\Delta = 4.5 \text{ mm}$



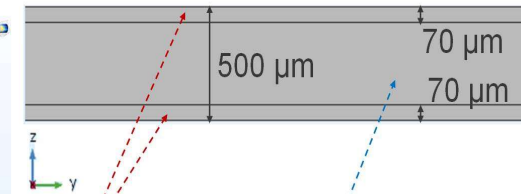
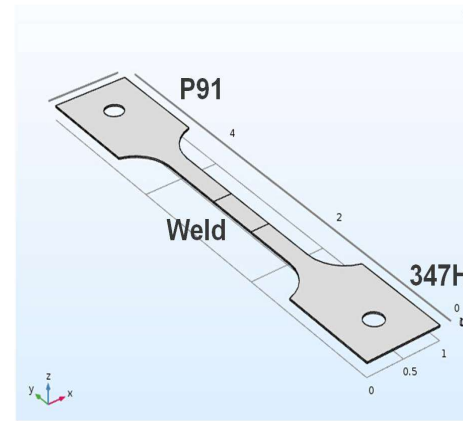
Failure location is on P91 from both FE simulation and tensile test.

FE Simulation of Surface Modified P91-347H Weld Couple



P91:
 $E = 167.63 \text{ GPa}$
 $\sigma_y = 550 \text{ MPa}$
 $n = 0.2$
Weld:
 $E = 176.76 \text{ GPa}$
 $\sigma_y = 530 \text{ MPa}$
 $n = 0.15$

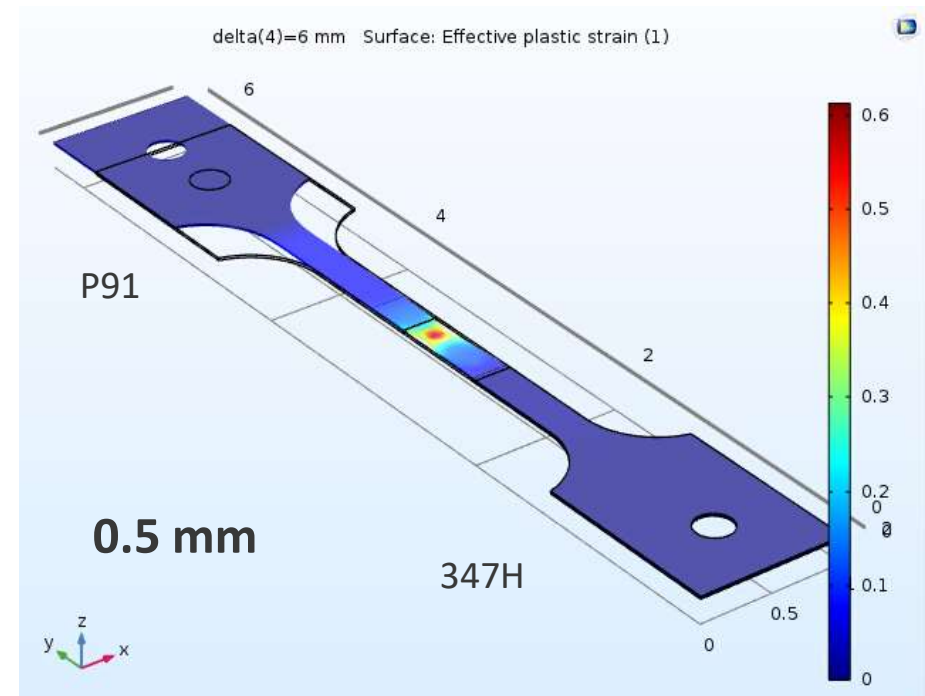
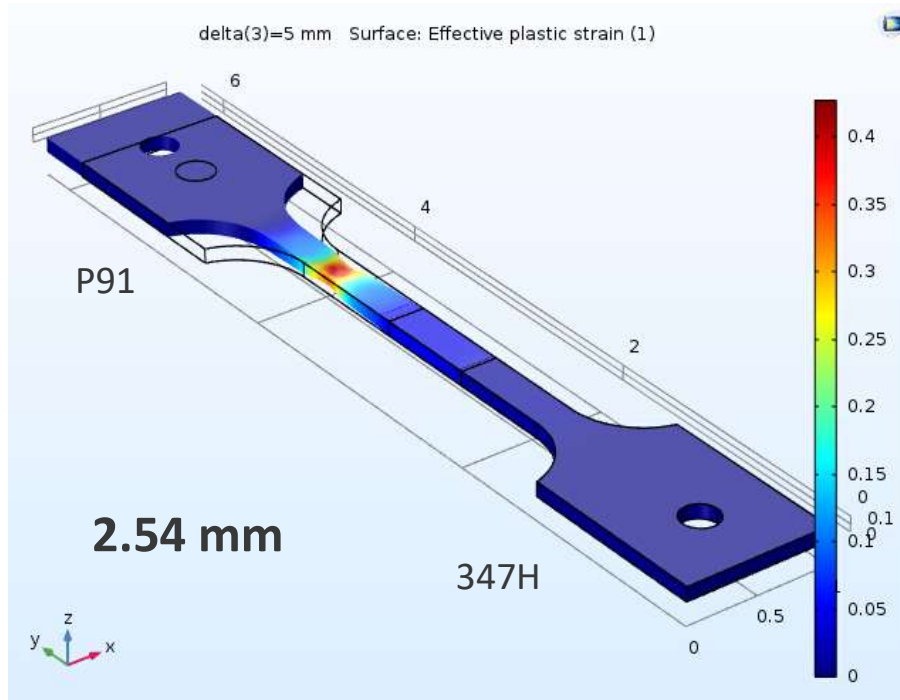
P91:
 $E = 249.03 \text{ GPa}$
 $\sigma_y = 488.93 \text{ MPa}$
 $n = 0.105$
Weld:
 $E = 168.73 \text{ GPa}$
 $\sigma_y = 476.56 \text{ MPa}$
 $n = 0.136$



P91:
 $E = 167.63 \text{ GPa}$
 $\sigma_y = 550 \text{ MPa}$
 $n = 0.2$
Weld:
 $E = 176.76 \text{ GPa}$
 $\sigma_y = 530 \text{ MPa}$
 $n = 0.15$

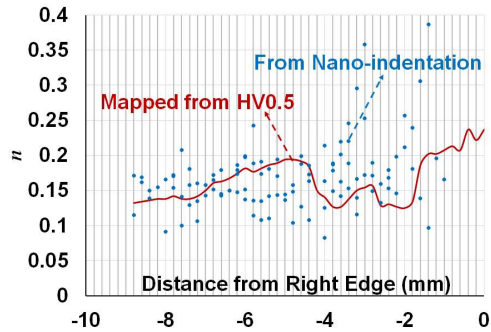
P91:
 $E = 249.03 \text{ GPa}$
 $\sigma_y = 488.93 \text{ MPa}$
 $n = 0.105$
Weld:
 $E = 168.73 \text{ GPa}$
 $\sigma_y = 476.56 \text{ MPa}$
 $n = 0.136$

FE Simulation of Surface Modified P91-347H Weld Couple

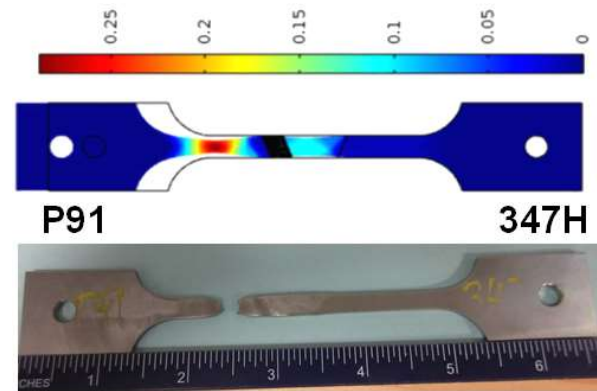


3D FE Simulation suggests that thin sheet specimen of 500 μm may behave differently than thick specimen of 2.54 mm (0.1") due to internal carburization.

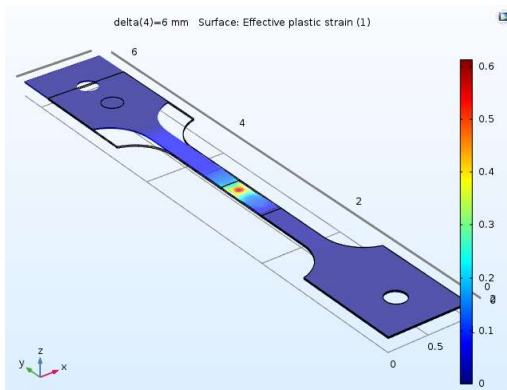
Summary – sCO₂ Effect on Dissimilar Metal Welds



As-received HAZ-P91 property variation is captured by nano-indentation.



2D FE Simulation predicts failure location successfully.



3D FE Simulation suggests that thin sheet specimens may behave differently than thick specimens under tensile load due to corrosion/carburization.

Supercritical CO₂ Power Cycles

Materials Research at NETL

- High-temperature oxidation in direct sCO₂ power cycles
- Low-temperature corrosion in direct sCO₂ power cycles
- Effect of sCO₂ cycle environments on mechanical properties
- Erosion in components of sCO₂ power cycles
- Materials issues in manufacturing compact heat exchangers
- Mechanical and chemical stability of joined materials in sCO₂
- Additive manufacturing of heat exchangers with new geometries

