Materials and Manufacturing for Supercritical CO_2 Power Cycles

FWP 1022406 –Advanced Alloy Development

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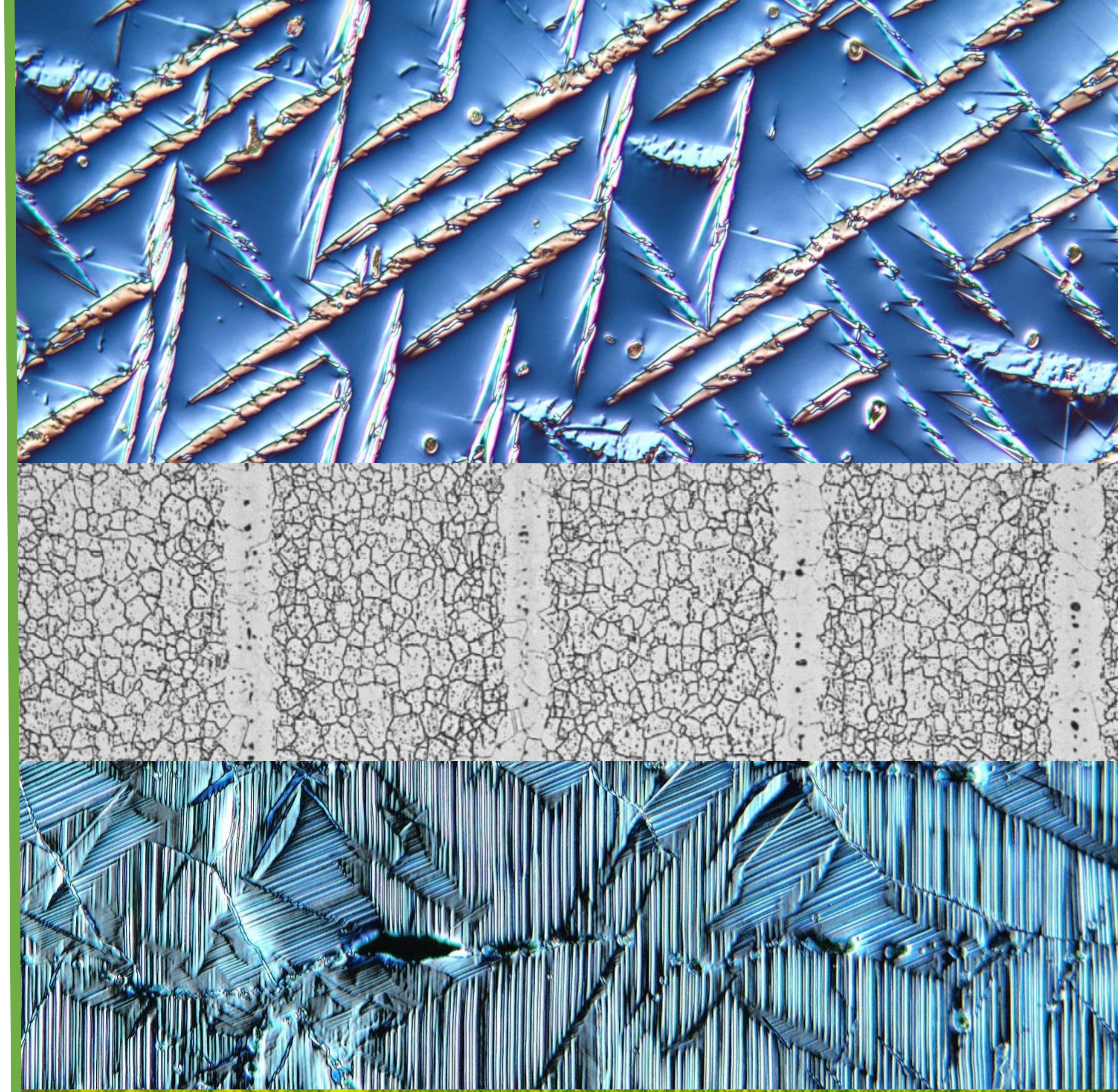

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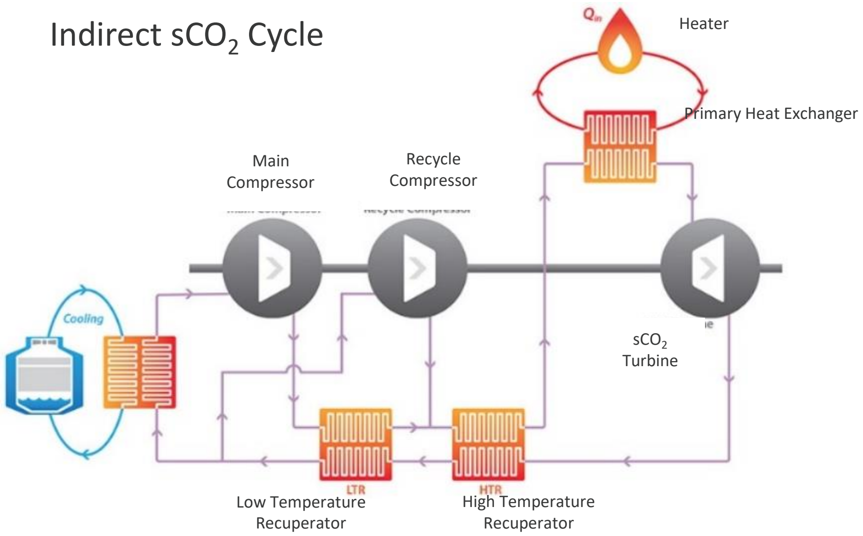
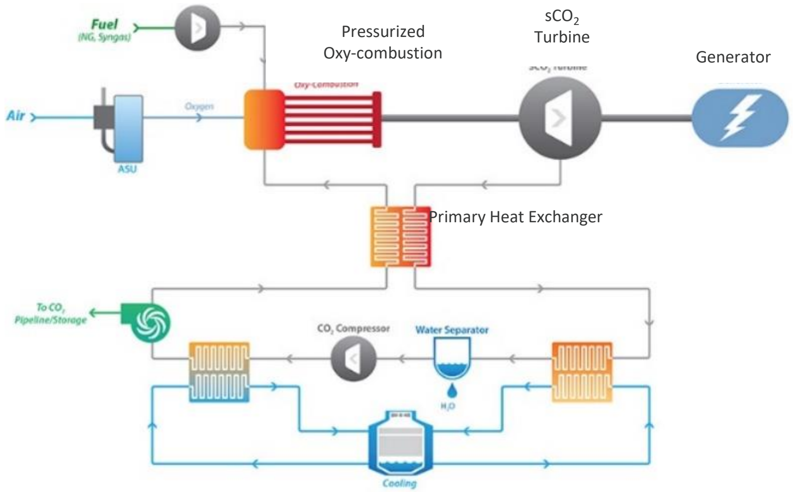
Supercritical CO_2 Power Cycles

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

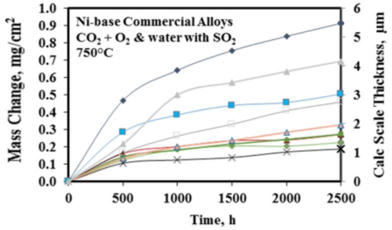
Essentially pure CO_2

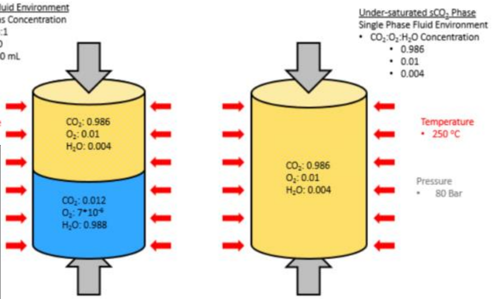
CO_2 with combustion products including O_2, H_2O and SO_2

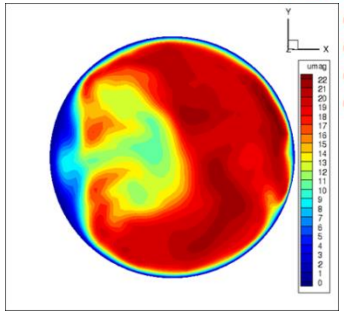
Supercritical CO_2 Power Cycles

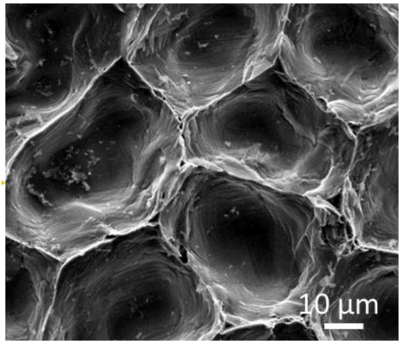
Materials Research at NETL

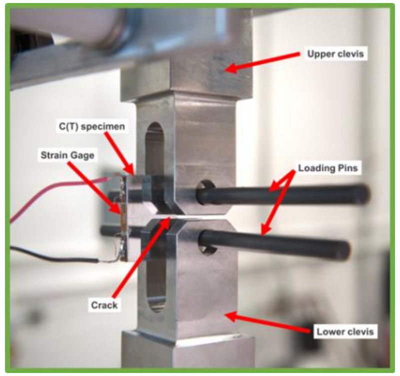
- High-temperature oxidation in direct sCO_2 power cycles
- Low-temperature corrosion in direct sCO_2 power cycles
- Effect of sCO_2 cycle environments on mechanical properties
- Erosion in components of sCO_2 power cycles
- Materials issues in manufacturing compact heat exchangers
- Mechanical and chemical stability of joined materials in sCO_2
- Additive manufacturing of heat exchangers with new geometries





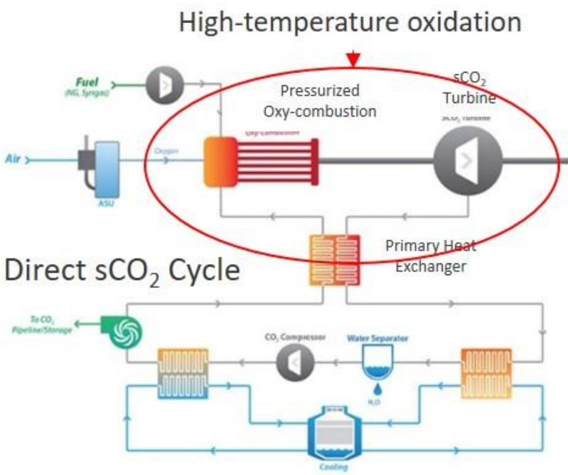


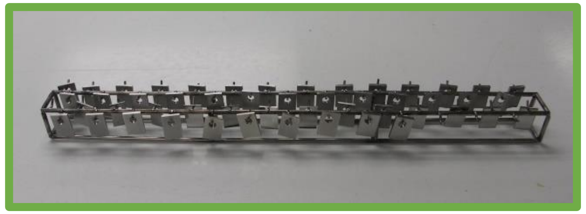




High-Temperature Oxidation in Direct sCO_2 Power Cycles

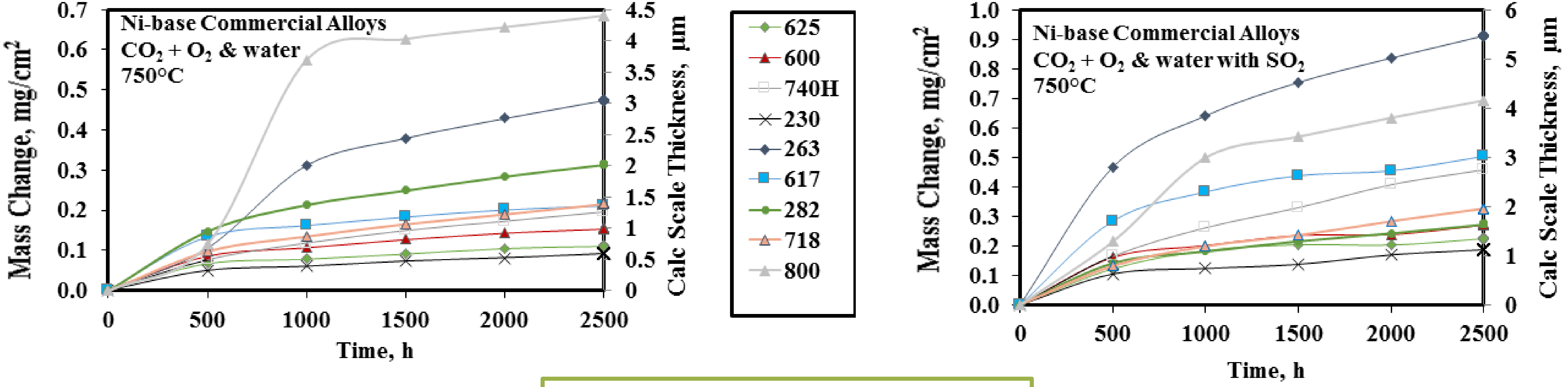
- **Importance**
  - Corrosion resistance of available structural materials need to be determined to built demonstration and future commercial sCO_2 power plants in a cost effective way.
- **Scope**
  - Evaluating A-USC alloys (both Ni-based and Fe-based) for their high-temperature oxidation performance in direct sCO_2 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 sCO_2 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 sCO_2+H_2O+O_2 will begin in Q1.
  - Oxidation rates of the exposed alloys (1 bar and 200 bar) will be reported.
  - Oxidation mechanisms of the exposed alloys will be defined.





R.P. Oleksak, et al.., *Corrosion Science* (2017), http://dx.doi.org/10.1016/j.corsci.2017.06.005)

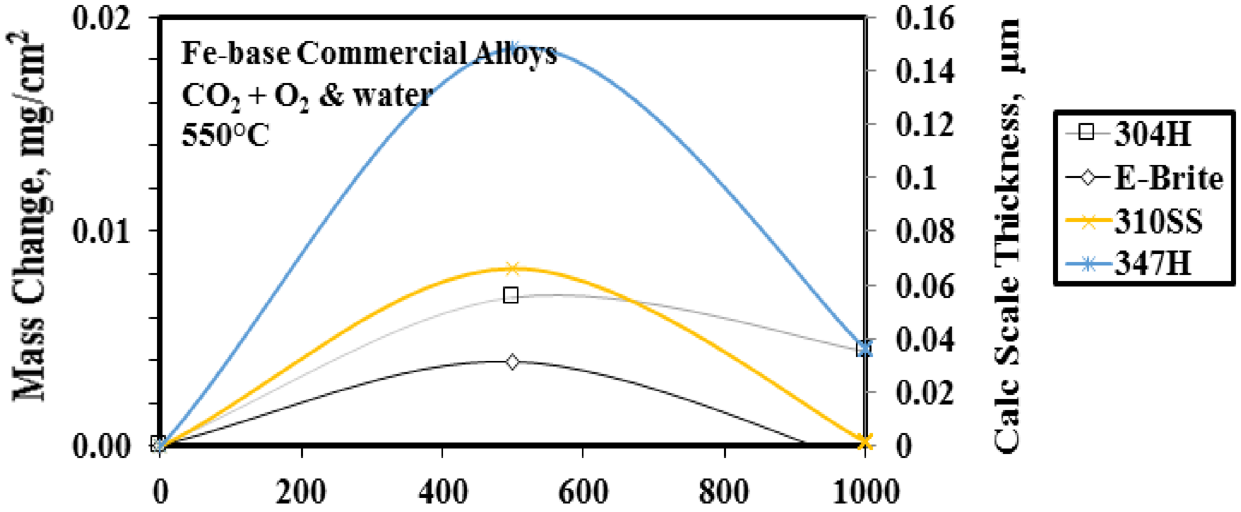
High-Temperature Oxidation in Direct sCO_2 Power Cycles

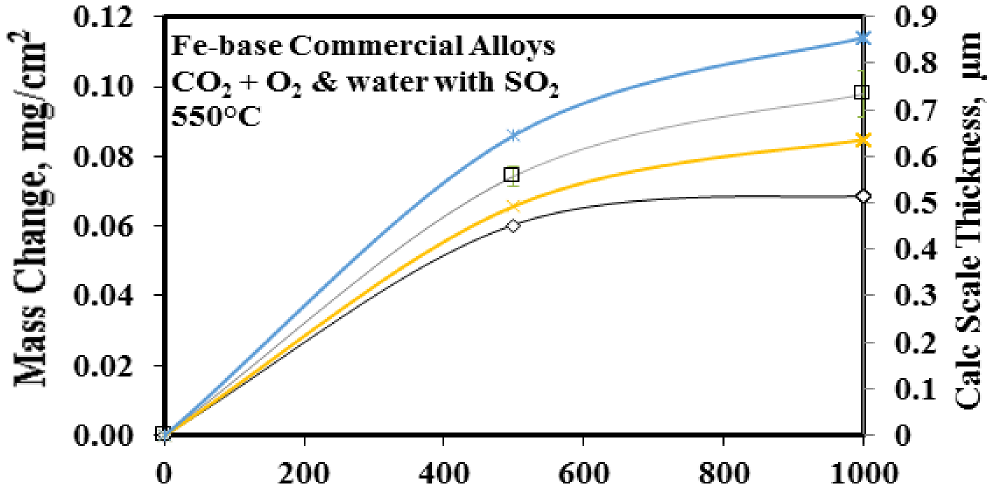


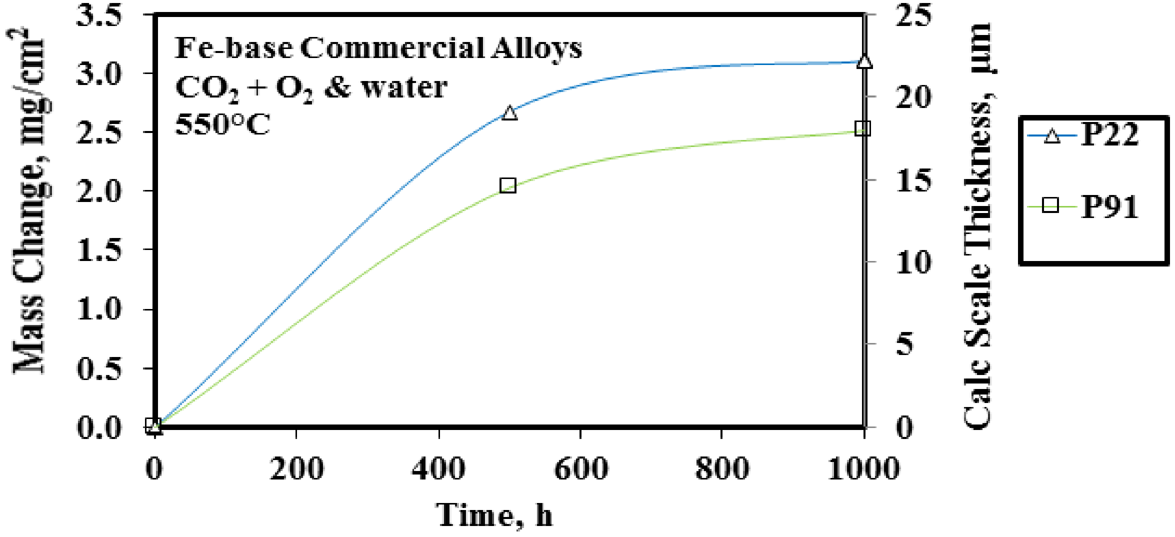
Oxidation tests
CO_2 + 4% H_2O + 1% O_2 (+ 0.1% SO_2)
1 bar
750°C

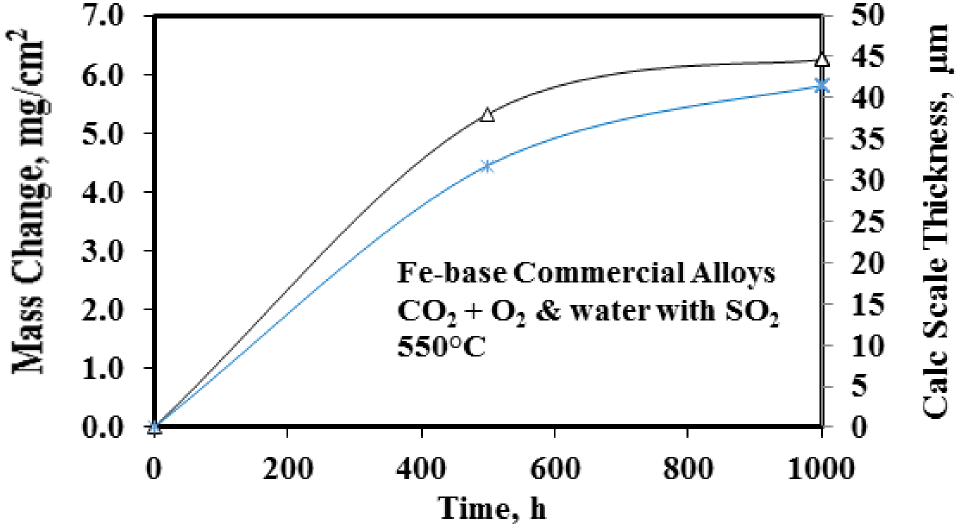
- Oxidation rates of Ni alloys are higher in direct sCO_2 cycle environments
- Addition of SO_2 to the gas mix increases the oxidation rates

High-Temperature Oxidation in Direct sCO_2 Power Cycles







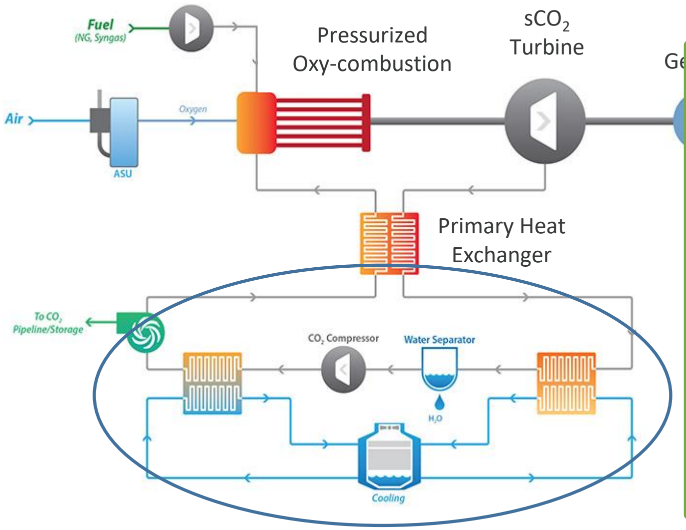


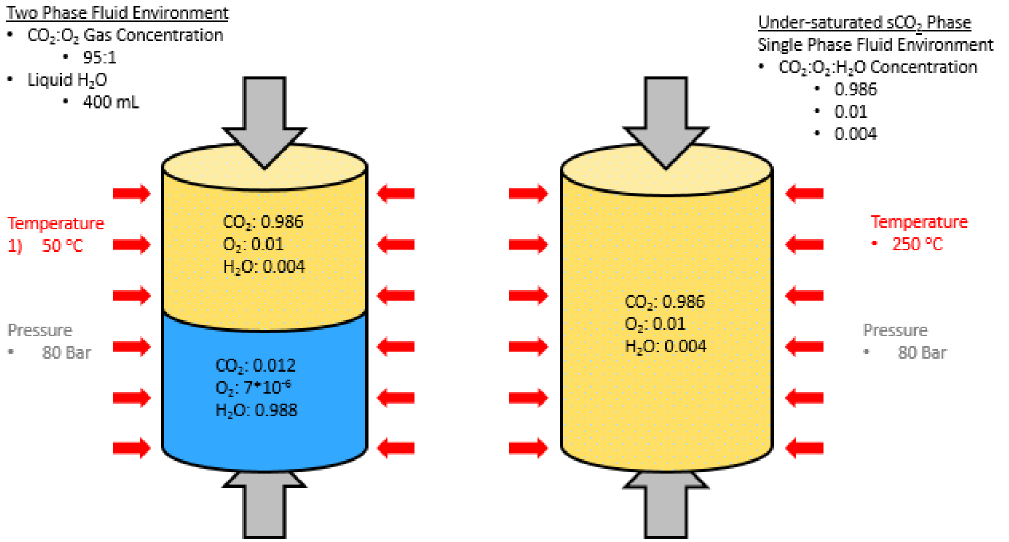
High-Temperature Oxidation in Direct sCO_2 Power Cycles

- Direct cycle environments are more corrosive than indirect cycles
- Materials in coal-fired direct cycles will face more corrosion issues compared to those in the natural gas–fired cycles
- Based on short-term data, Ni alloys (230, 625, 282, 740H) at 750°C and austenitic stainless steels (304H, 347H, and 310S) at 550°C perform well in SO_2 containing direct cycle environments.

Low-Temperature Corrosion in Direct sCO_2 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 CO_2 (Carbonic acid).
- **Progress to Date**
  - A series of autoclave coupon exposure tests simulating the environment of low-temperature recuperators and coolers in a direct sCO_2 cycle power plant have been performed
  - Due to high corrosion rates of Grade 91 steel in water saturated with CO_2, it is concluded that unlike in the steam cycles, lower Cr steels are not suitable for low-temperature components of direct sCO_2 cycle plants. 347H performed well in the same environment.
- **FY18 Expected Accomplishments**
  - In coal-fired direct sCO_2 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.





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

Temperature
1) 50 °C

Pressure
- 80 Bar

CO_2: 0.986
O_2: 0.01
H_2O: 0.004

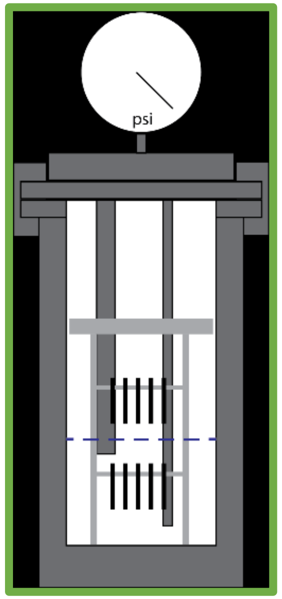
CO_2: 0.012
O_2: $7*10^{-6}$
H_2O: 0.988

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

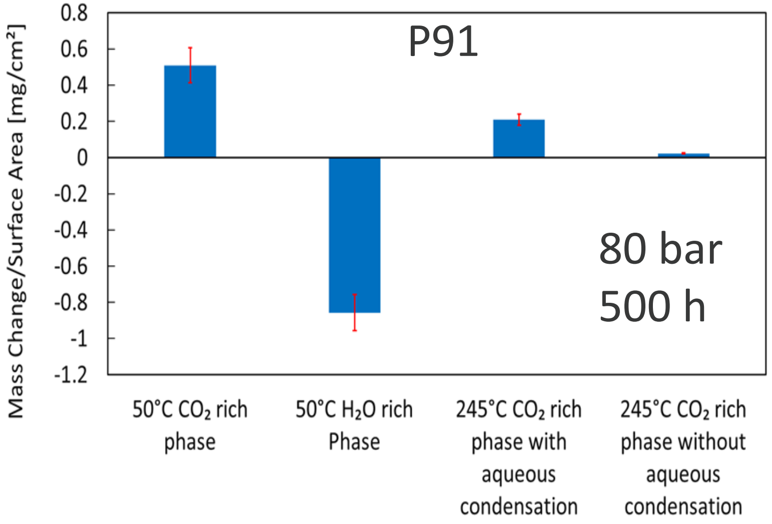
Pressure
- 80 Bar

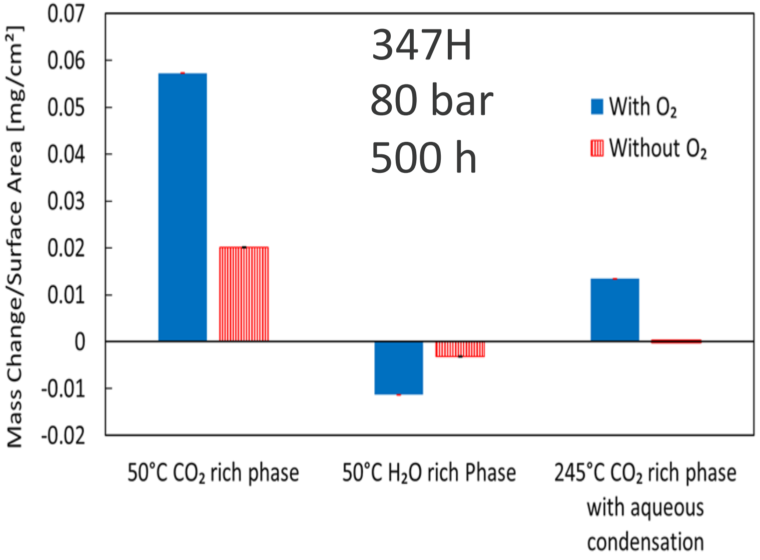
CO_2: 0.986
O_2: 0.01
H_2O: 0.004



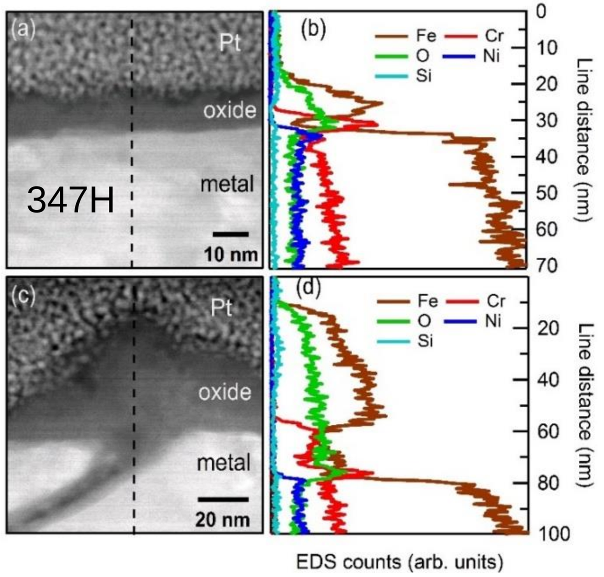
Low-Temperature Corrosion in Direct sCO_2 Power Cycles

Autoclave Tests





- Inexpensive alloys such as P22 and P91 may not be an option for the low-temperature components in direct sCO_2 cycles due to condensation of water saturated with CO_2.
- More expensive austenitic stainless steels work well for this application.
- It is expected that condensation of H_2SO_4 might cause severe corrosion at intermediate temperatures in coal-fired direct sCO_2 systems without pre-combustion sulfur removal.



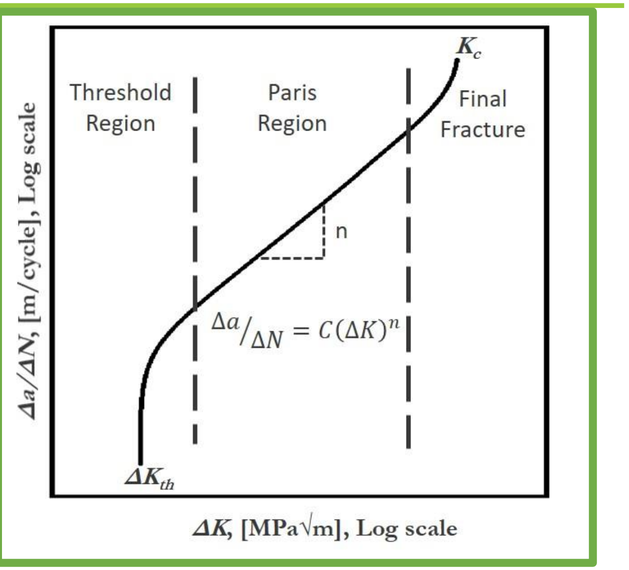
347H

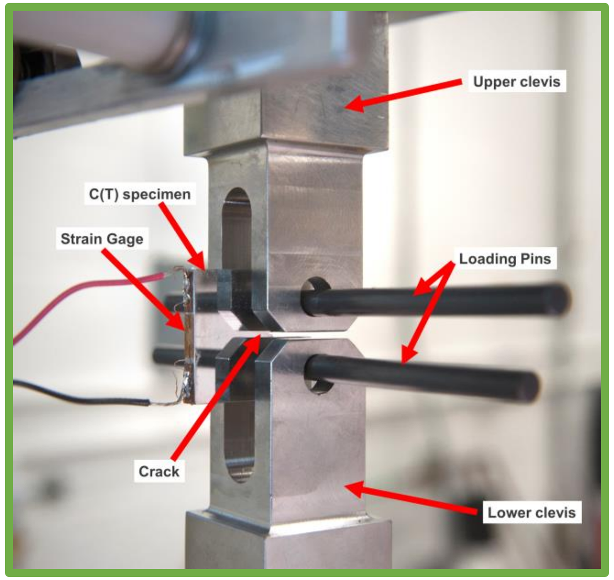
- Good corrosion resistance observed (negligible mass change).
- TEM analysis reveals an Fe-rich oxide layer forms under these conditions.
- Increased oxide thickness is observed above grain boundaries.

L. Teeter, et al, Electrochemical Society Transactions, 72 (17) 137-148 (2016).
R. Repukaiti, et al., Electrochemical Society Transactions, in press (2017).

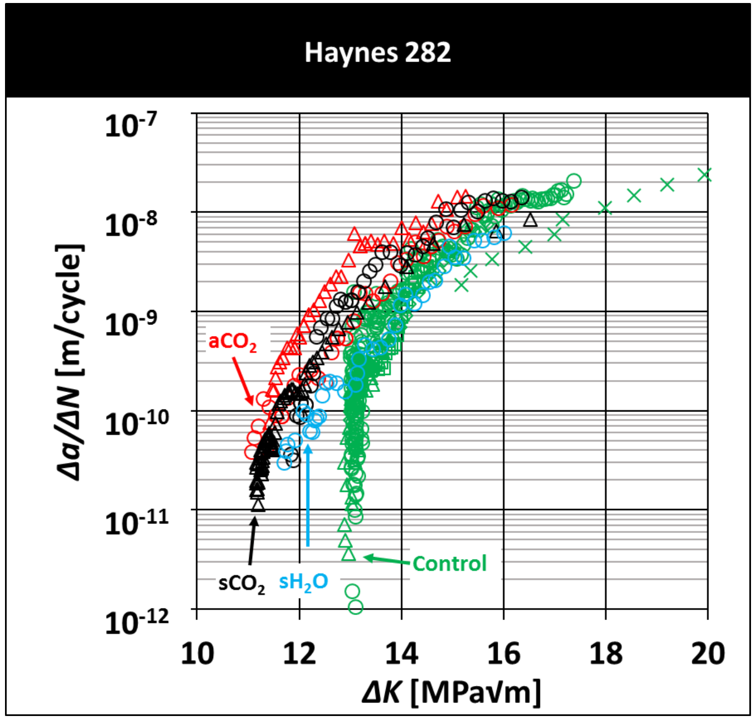
Effect of sCO_2 Cycle Environments on Mechanical Properties

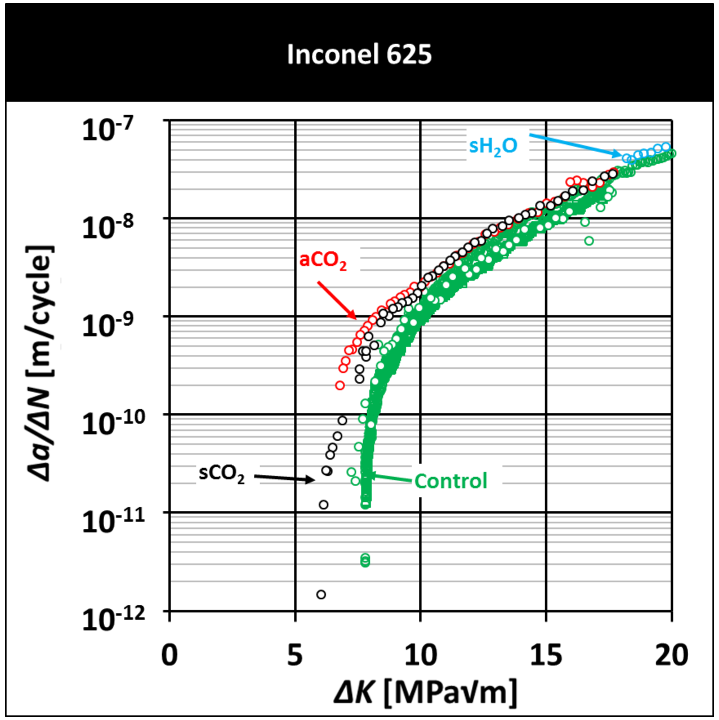
- **Importance**
  - Presence of micro cracks in structural materials can significantly reduce fatigue life of components. The lifetime of a part containing cracks can be estimated using linear elastic fracture mechanics (LEFM) methods. These methods require data on stress intensity factor (K), crack growth rate (Δa/ΔN), and initial crack size (a) for a given material. The environment can affect the fatigue crack growth rate (FCGR).
- **Scope**
  - Effect of sCO2 exposures on the fatigue crack growth rate of A-USC alloys is determined.
- **Progress to date**
  - FCGR of Haynes 282 and IN625 were measured after the samples were exposed to sCO_2, CO_2, and sH_2O at 730°C for 500 hours.
  - Fractography of the tested samples were performed to delineate the effect of environment on the FCGR.
- **FY18 Expected Accomplishments**
  - 347H stainless steel and IN 740H samples will be tested.





Effect of sCO_2 Cycle Environments on Mechanical Properties





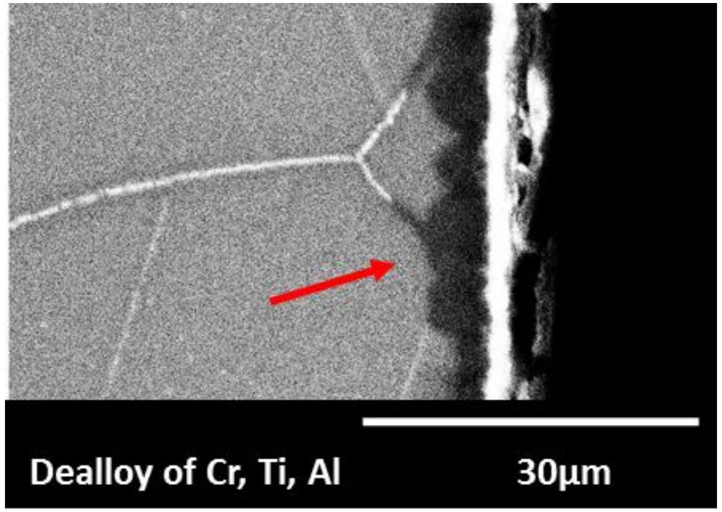
- Tested the effect of prior exposure on threshold *ΔK*
    - Exposures at 730°C for 500 hours
        - Supercritical CO_2 and H_2O at 200 Bar
        - CO_2 at 1 Bar

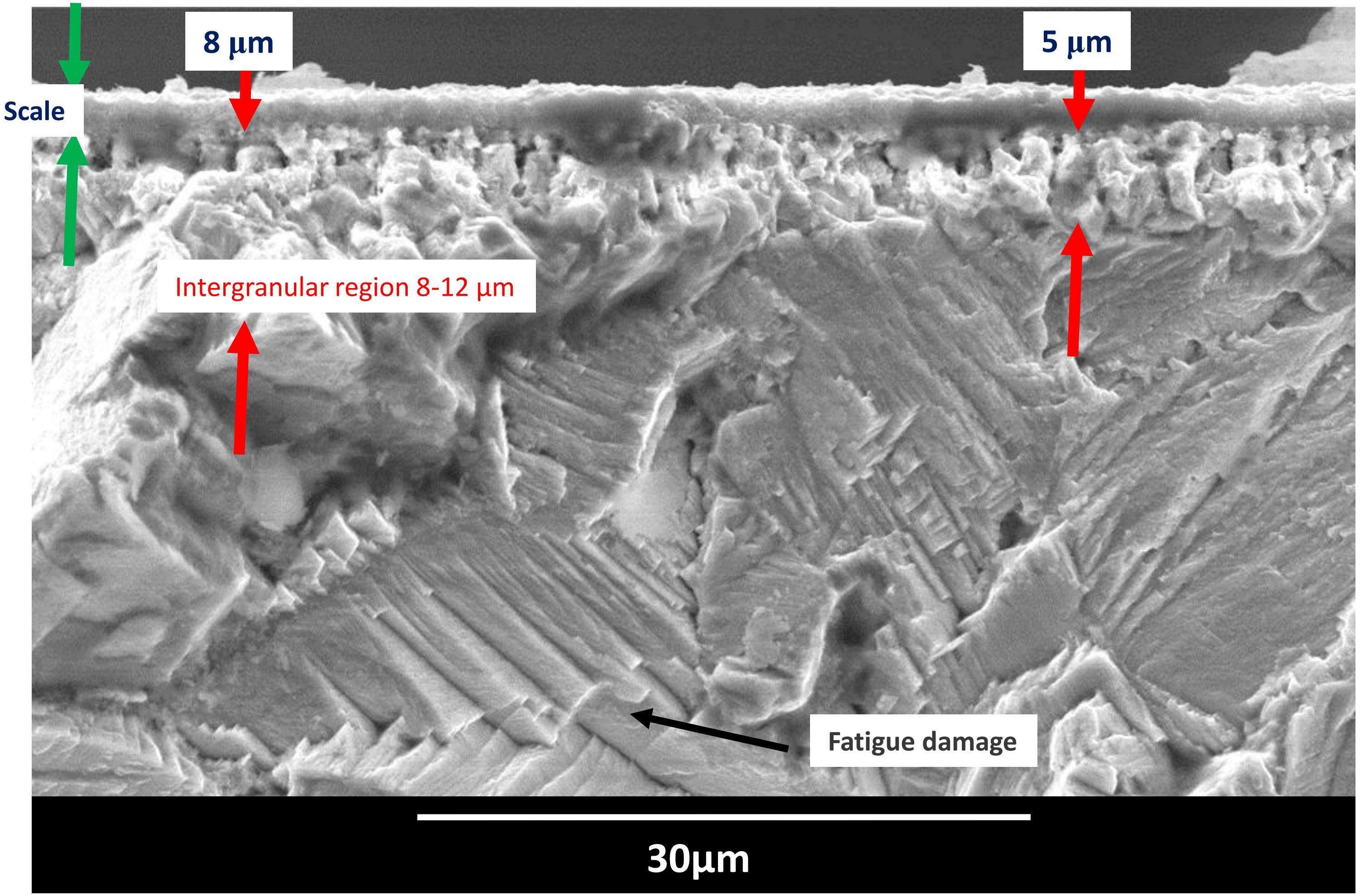
- Apparent reduction in ΔK_{th} with high temperature gas exposure
- Increase in threshold *Δa/ΔN* for CO_2 exposed samples
- Repeatable effect
    - Multiple samples
    - Multiple labs (OSU / NETL)

Effect of sCO_2 Cycle Environments on Mechanical Properties

Fracture Surface of Haynes 282

- Featured: 1 bar CO_2 sample
- Change in fracture morphology near surface for H282
- Intergranular path consistent depth with depleted zone
- Does not appear to affect crack propagation as depth is consistent with the oxidation damage

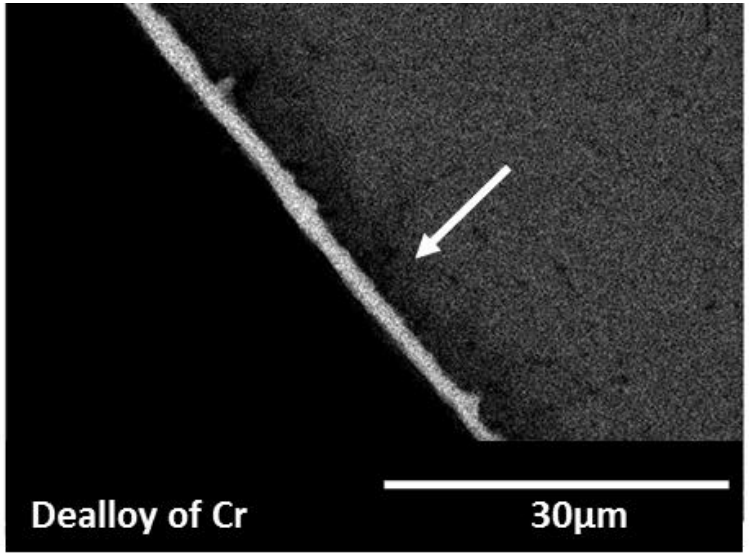


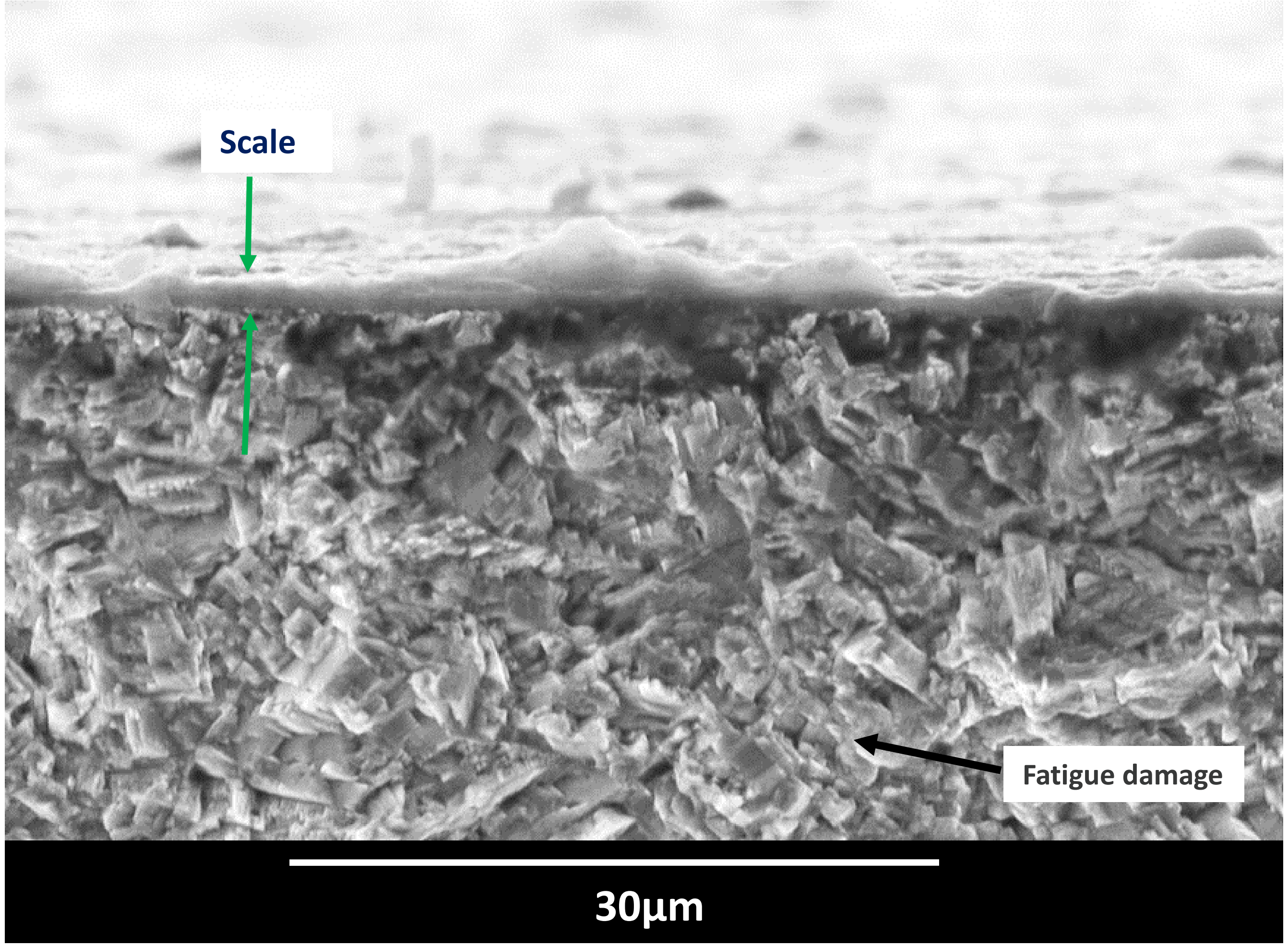


Effect of sCO_2 Cycle Environments on Mechanical Properties

Fracture Surface of Inconel 625

- Featured: Supercritical CO_2 sample
- No change in fatigue morphology in IN625 sample near surface



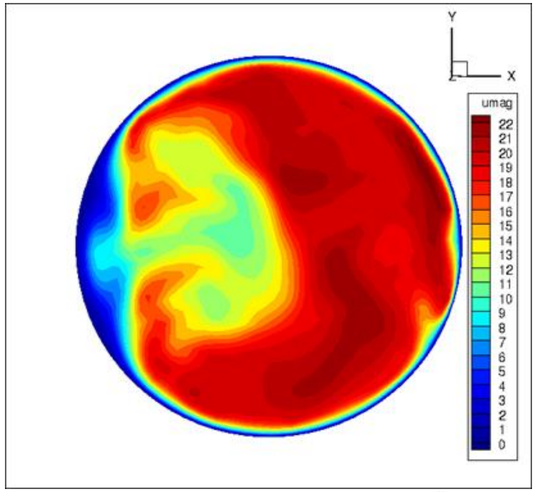


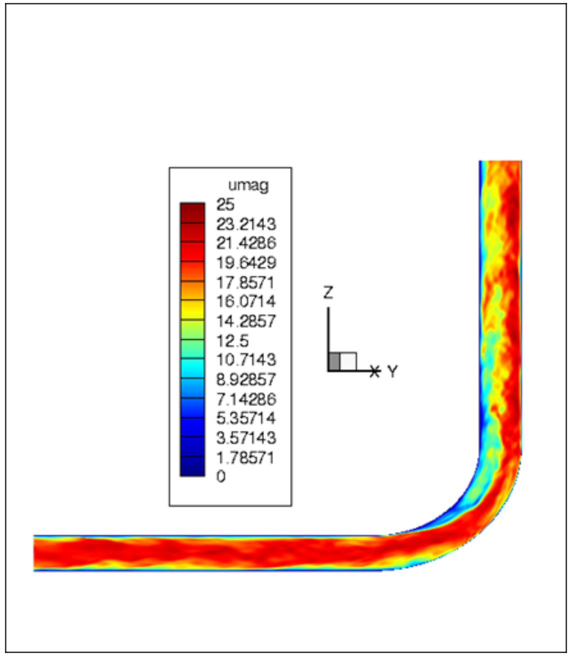
Erosion in Components of sCO_2 Cycles

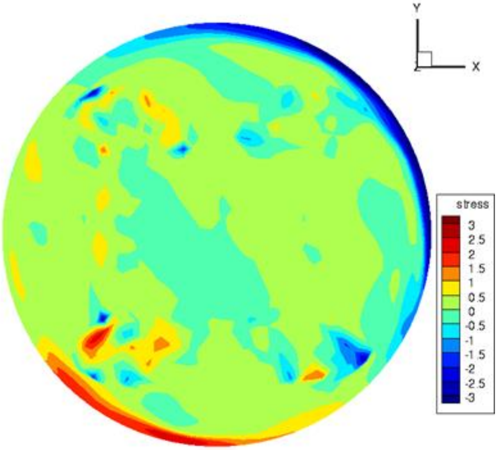
- **Importance**
  - This work will establish:
    - Whether erosion a significant potential problem in sCO_2 power cycles
    - An understanding of erosion mechanism
    - A guidance for an experimental work which might be implemented if erosion is shown to be a problem.
- **Scope**
  - Large eddy simulations 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**
  - Include effect of heat transfer in the simulations
  - Begin a finite element model to study effect of oscillating shear stresses on the pipe wall material.

Erosion of turbine nozzle in sCO_2 test loop

D. Fleming, Sandia Report SAND2014-15546



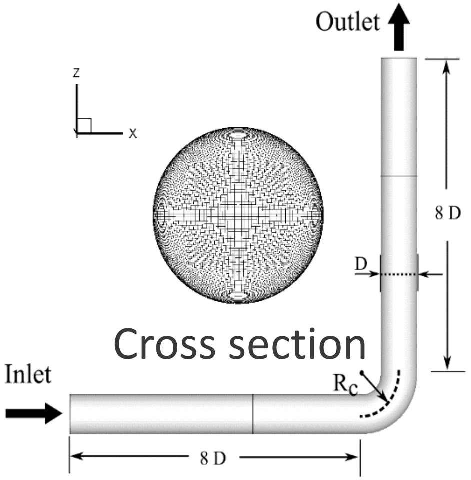




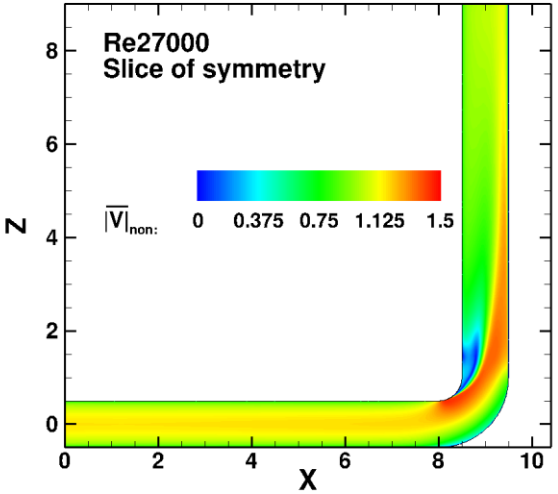
S.V. Apte, Ö.N. Doğan, C. Ghodke, Proceedings of The 5th International Symposium on Supercritical CO2 Power Cycles, March 28-31, 2016, San Antonio, Texas

Erosion in Components of sCO_2 Cycles

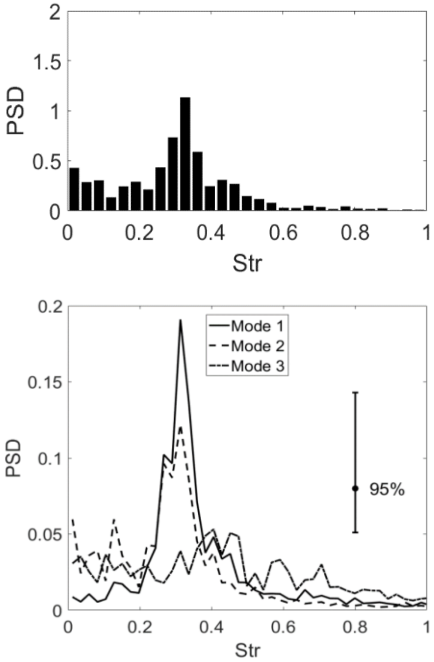
- Large-eddy simulation (LES) is implemented using a highly validated, efficient and predictive solver, which is fully parallel and uses finite volume method.



Geometry and cross section of the pipe



Time averaged velocity along the pipe on the center slice

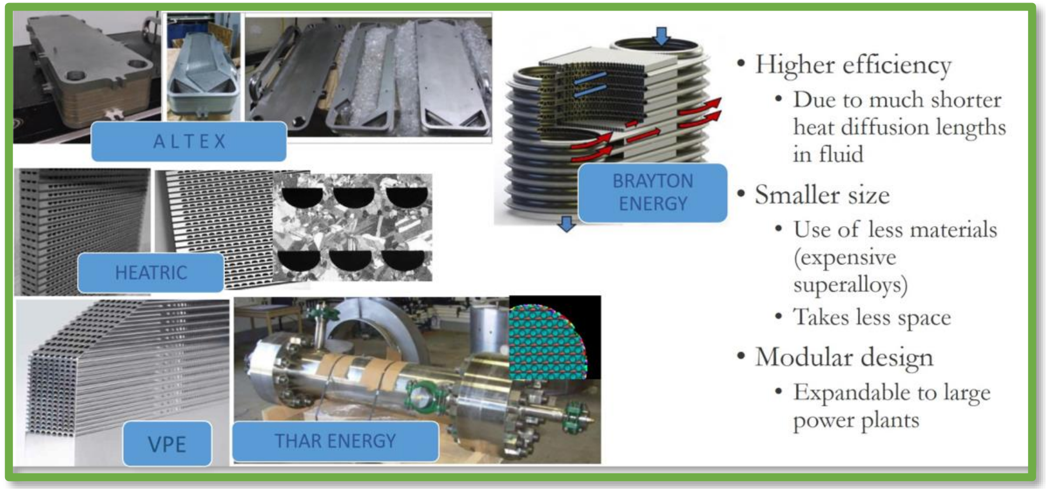


Spectra of shear force (up) and secondary flow patterns (down), indicating they are highly correlated.

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.

Materials Issues in Manufacturing Compact Heat Exchangers

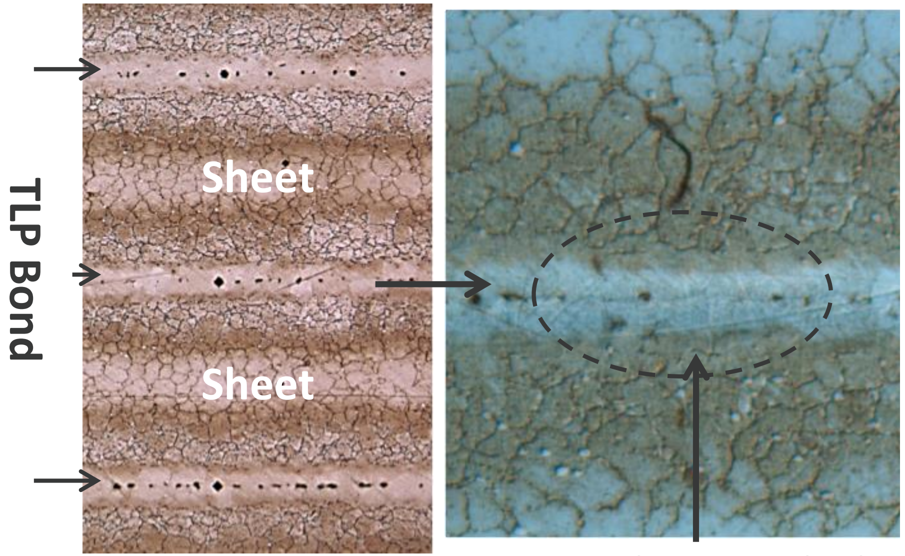
- **Importance**
  - sCO_2 cycle conditions necessitate the use of higher temperature materials (in many cases, state-of-the-art Ni-based alloys) in manufacturing compact heat exchangers. The goal of this task is to enable manufacturing of microchannel heat exchangers for sCO_2 cycles by developing surface preparation and bonding techniques for Ni-based alloys.
- **Scope**
  - In this task, process parameters for effective transient liquid phase bonding of Haynes 230, Haynes 282, Inconel 740H Ni-based alloys are investigated. Scope of this work includes determining process parameters for surface preparation, melt depressant alloy plating, bonding, and post bonding heat treatment.
- **Progress to Date**
  - Diffusion bonded stacks of Haynes 230 and Haynes 282 were produced. Their mechanical strength and oxidation behavior in sCO_2 cycle environments were evaluated.
- **FY18 Expected Accomplishments**
  - Diffusion bonding of Inconel 740H will be investigated. Diffusion bonded stacks will be produced and their performance will be determined.
  - High-temperature oxidation behavior of diffusion bonded Haynes 230 and 282 will be evaluated in direct sCO2 environments.



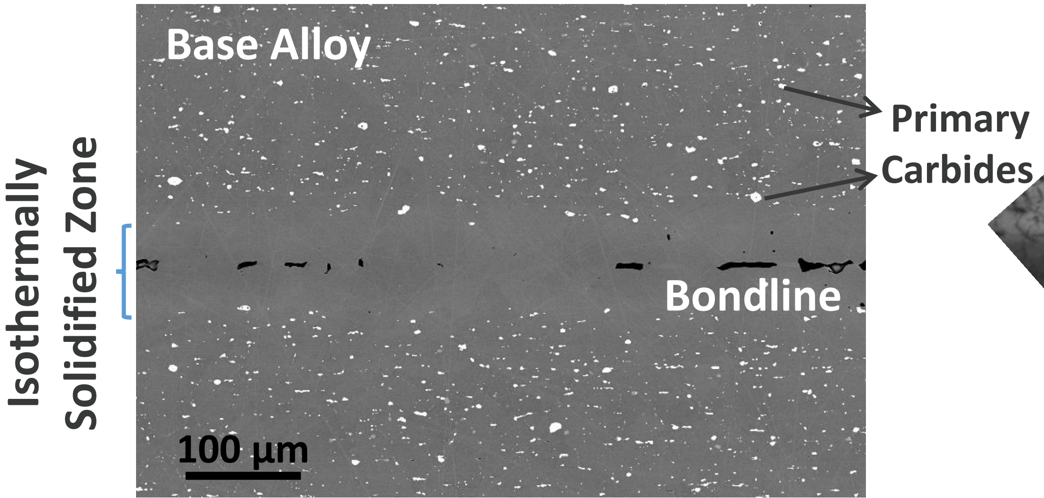
- Higher efficiency
  - Due to much shorter heat diffusion lengths in fluid
- Smaller size
  - Use of less materials (expensive superalloys)
  - Takes less space
- Modular design
  - Expandable to large power plants

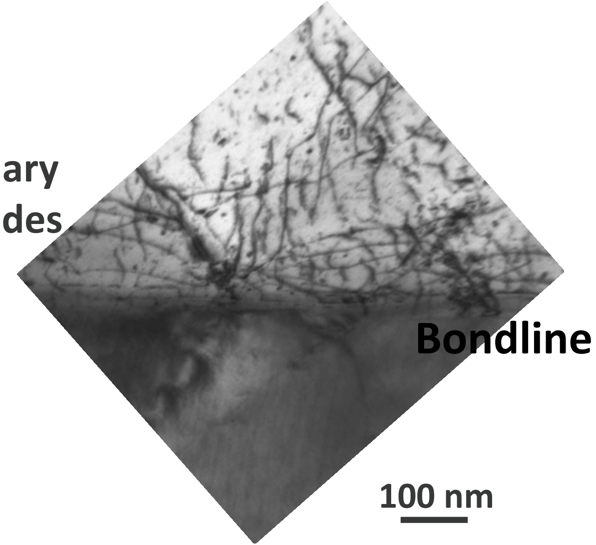
Materials Issues in Manufacturing Compact Heat Exchangers

Diffusion (TLP) Bonding of Alloy H230

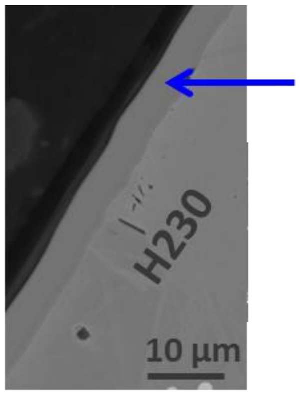


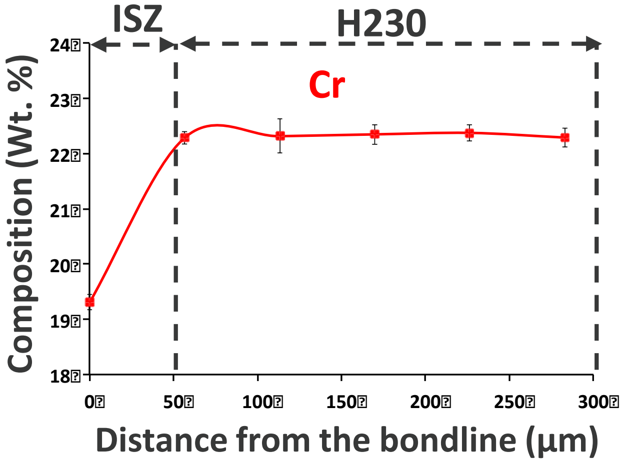
Grain growth across the bond

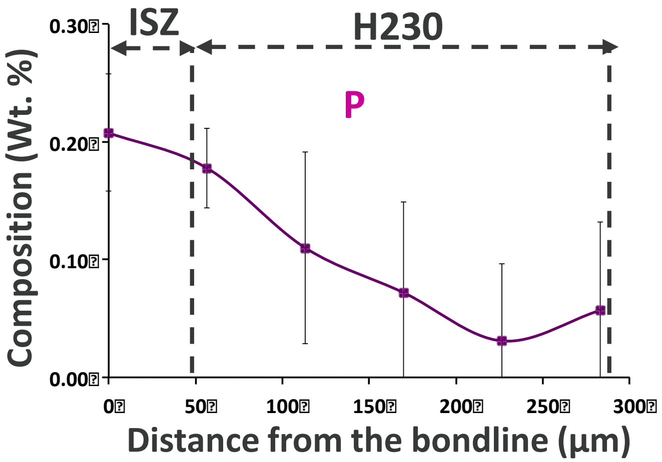




No nanoscale phase near the bondline





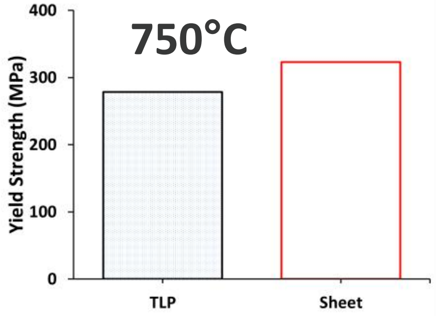


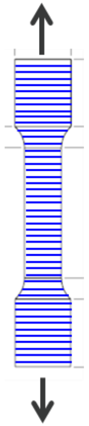
- **Cr important for oxidation resistance - Slight reduction in Cr near the bondline**
- **P should be as low as possible to avoid formation of brittle phases - P is ~0.2 wt. % near the bondline**

M. Kapoor, et al., Mat. & Met. Trans. A, (2017) 48, 3343

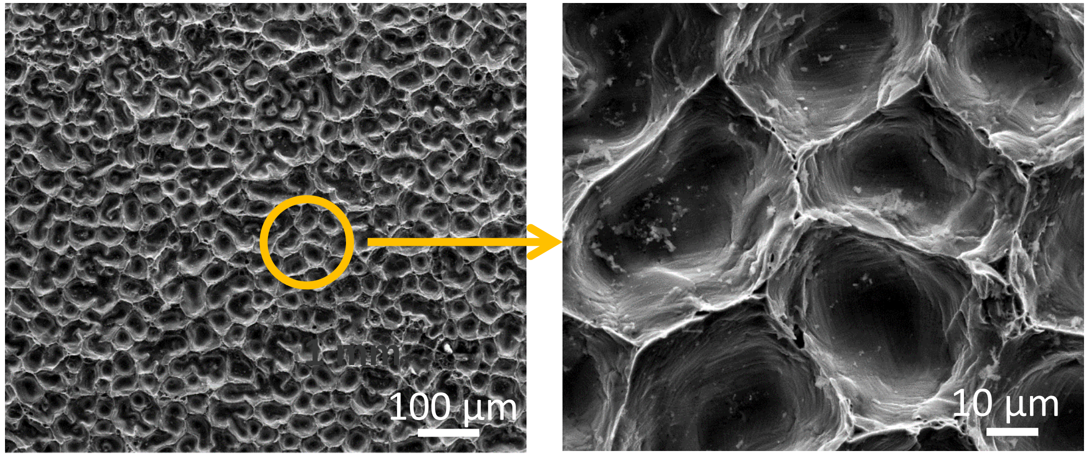
Materials Issues in Manufacturing Compact Heat Exchangers

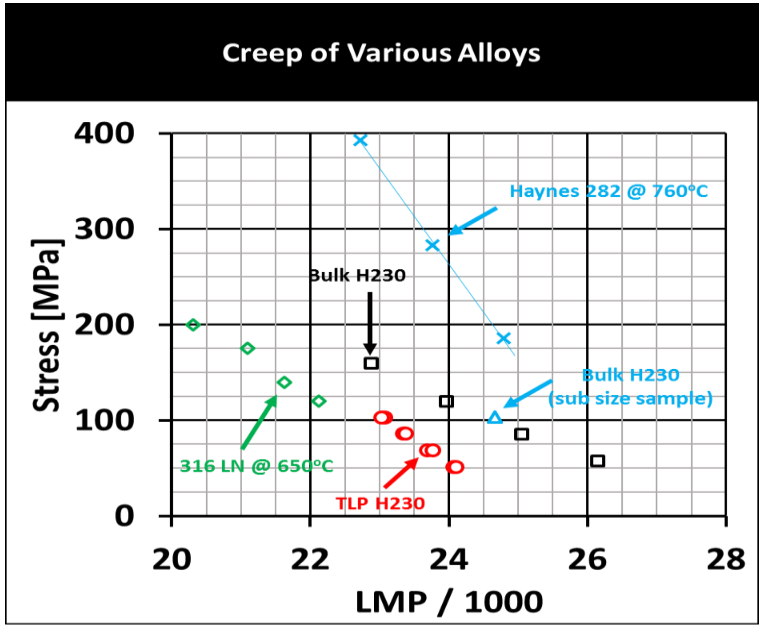
Mechanical Properties of TLP Bonded H230

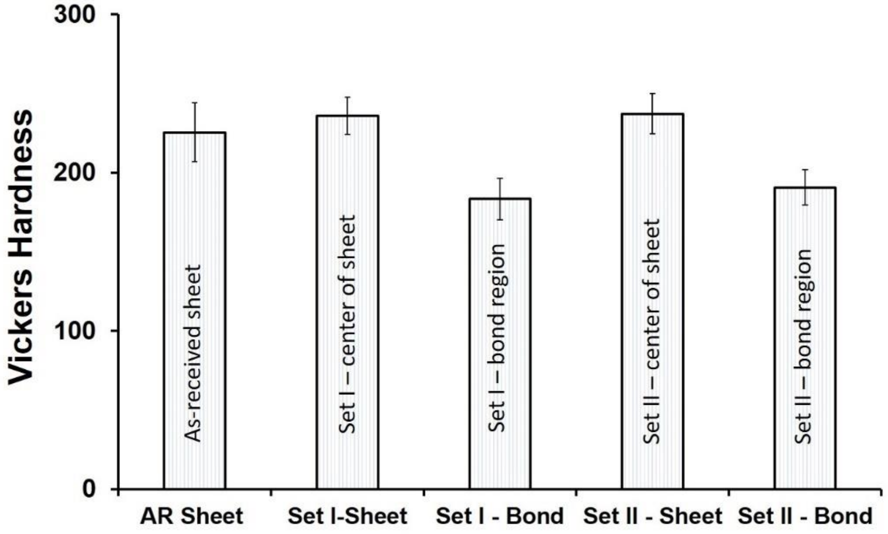




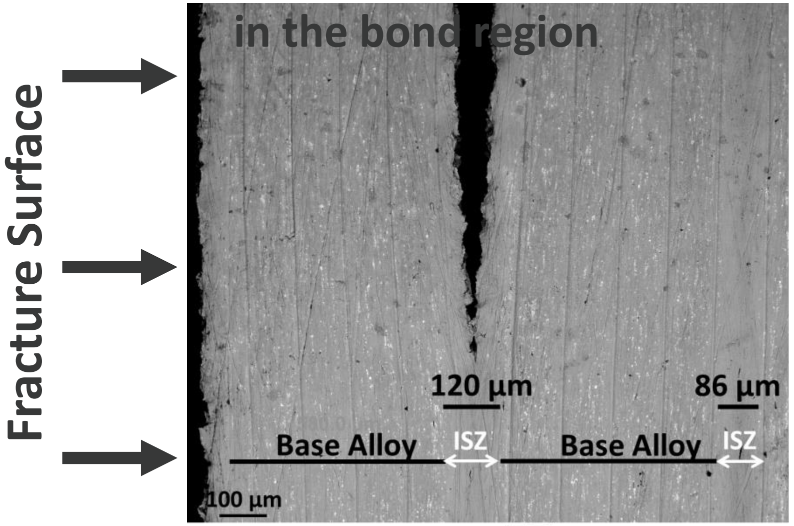
Ductile fracture through the bond region





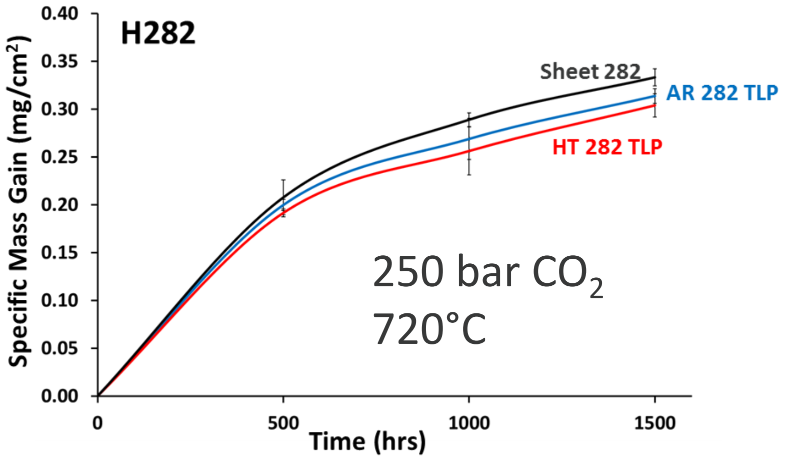


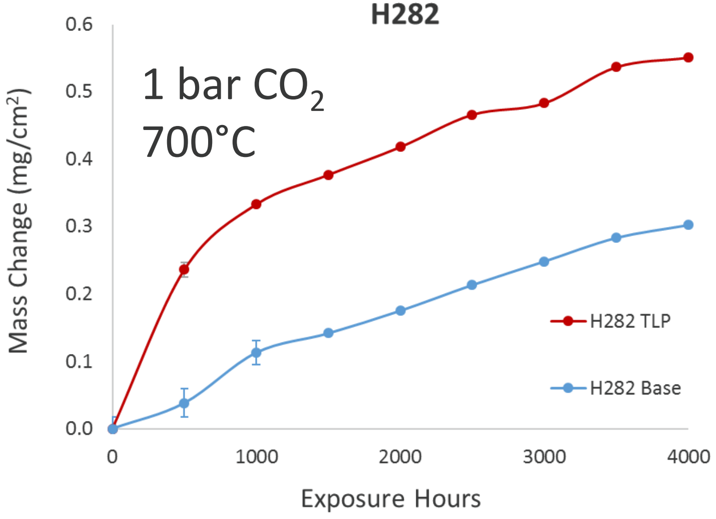
Plastic strain is constrained in the bond region

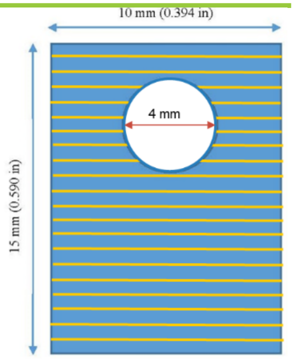


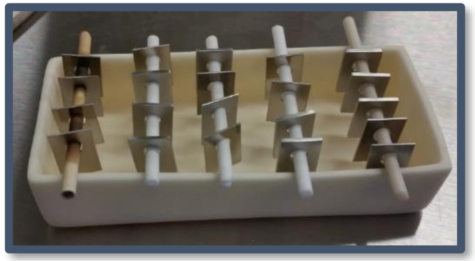
Materials Issues in Manufacturing Compact Heat Exchangers

High-Temperature Oxidation of Diffusion Bonded Ni Alloys



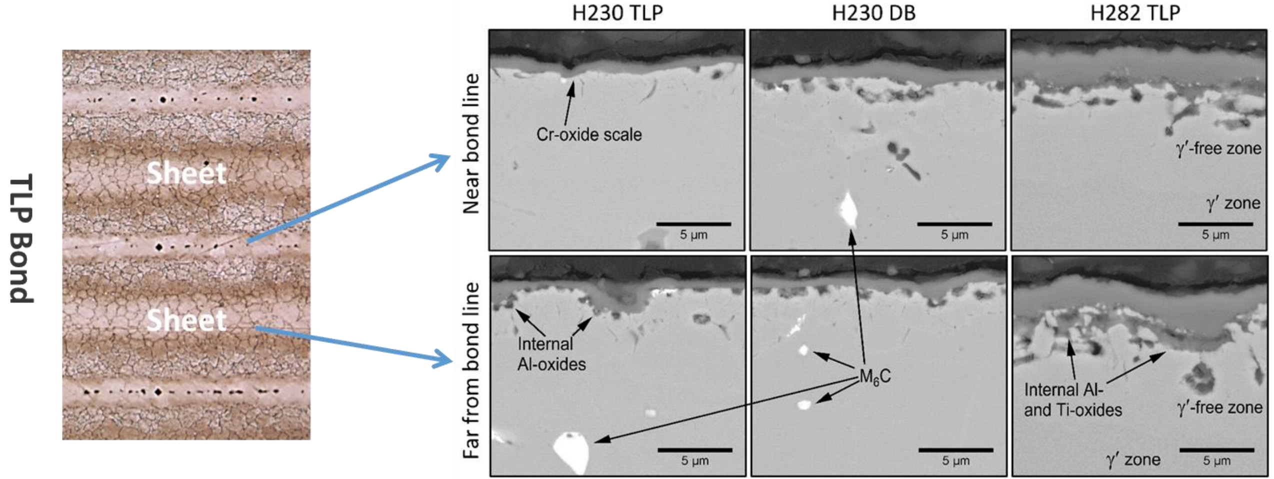






- Thin, protective Cr-rich oxide layers are formed for H230 and H282 during exposure to 1 bar CO_2 at 700 °C
- Internal oxidation of Al leads to a sub-surface layer depleted of γ’ phase in H282.
- No difference in oxidation resistance is observed near/far from the bond layer for either alloy.

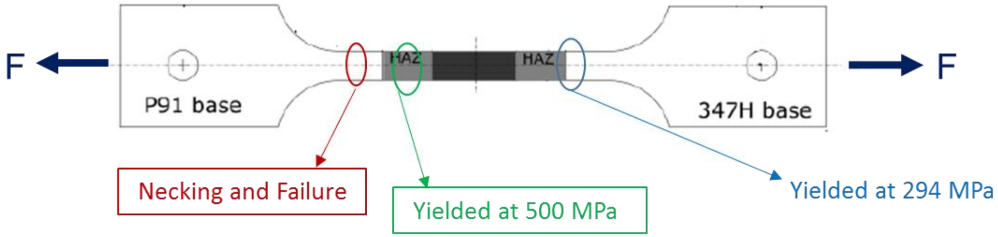
- Haynes 230 layers were successfully diffusion bonded.
- Mechanical properties (yield, creep, low-cycle fatigue) of the bonded structures were lower compared to the base material but acceptable for the application.
- High-temperature oxidation resistance of the bonded structures was as good as the base material.



Ö.N. Doğan, et al., The 5th International Symposium on Supercritical CO2 Power Cycles, March 28-31, 2016, San Antonio, TX

Mechanical and Chemical Stability of Welded Alloys in sCO_2

- **Importance**
  - High-temperature components (piping, recuperators, turbines) in sCO_2 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 sCO_2 environments.
- **Scope**
  - Effect of sCO_2 on the welded structures will be investigated and documented. The investigation involves making the joined structures, exposing them to sCO_2, 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 sCO_2 on welded regions is being investigated on P91-347H dissimilar metal weld.
- **FY18 Expected Accomplishments**
  - More similar and dissimilar metal welds exposed to sCO_2 will be evaluated.

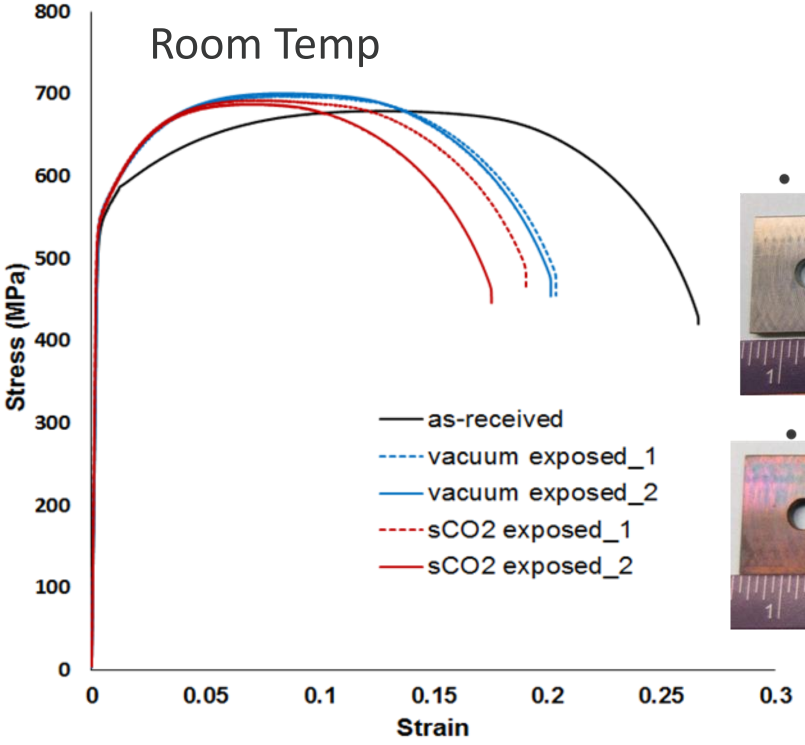


At Edison Welding Institute (EWI)

By Gas Tungsten Arc Welding (GTAW).

With Post Weld Heat Treatment.

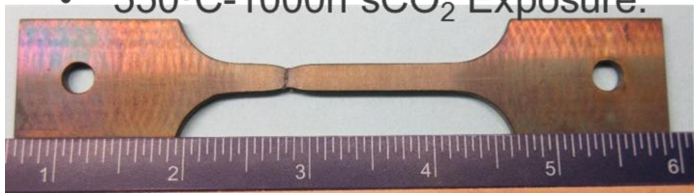
Mechanical and Chemical Stability of Welded Alloys in sCO$_2$

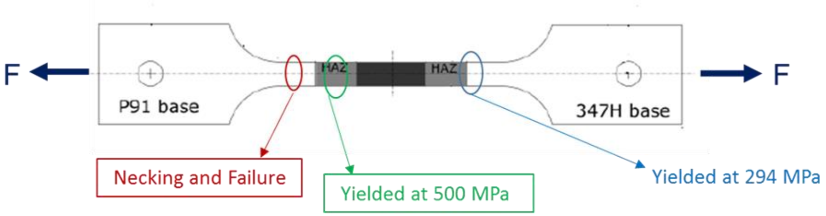


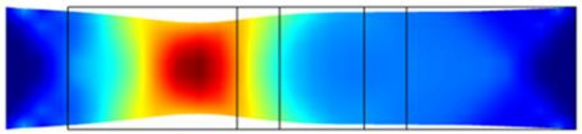
P91 Base Metal

- 550°C-1000h Vacuum Exposure.

- 550°C-1000h sCO$_2$ Exposure.

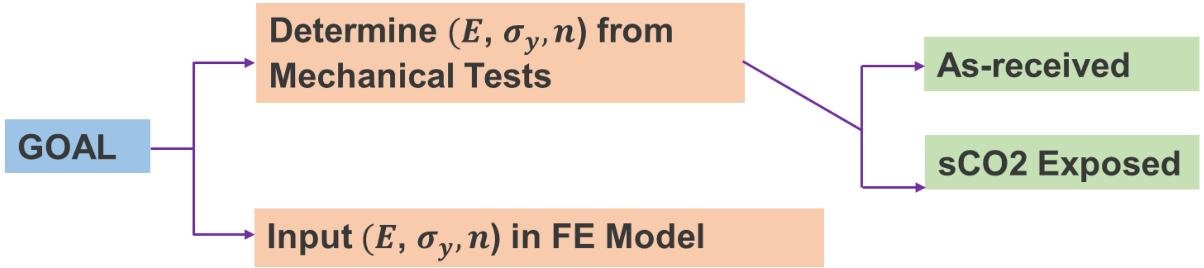






Effective Plastic-strain distribution

Condition	E (GPa)	$\sigma_{y,0.2}$ (MPa)	σ_{UTS} (MPa)	n	Elongation (%)
As-Received	202.08	540.03	679.10	0.1025	23.3
Vacuum Exposed	218.21	557.59	699.16	0.1166	21.2
sCO2 Exposed	257.16	552.87	690.01	0.1131	20.2



GOAL

Determine (E, σ_y, n) from Mechanical Tests

As-received

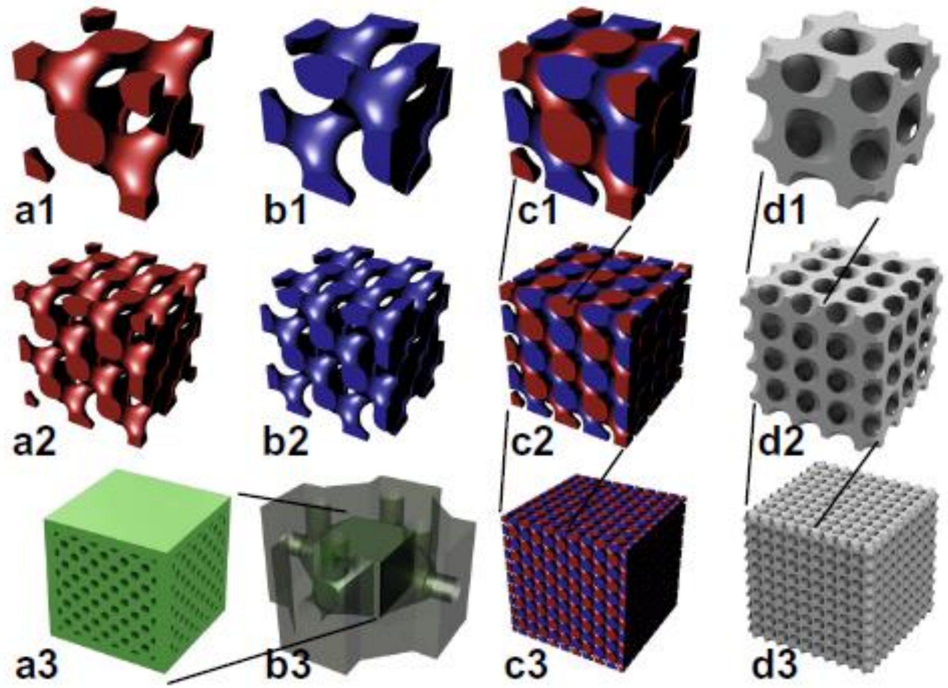
sCO2 Exposed

Input (E, σ_y, n) in FE Model

Additive manufacturing of heat exchangers with new geometries

- **Importance**
  - This subtask will develop a heat exchanger for supercritical CO_2-based (sCO_2) power cycles with radically improved material efficiency and heat exchange effectiveness than current technologies. The project will combine additive manufacturing of high-temperature superalloys with new geometries based on triply-periodic minimal-surfaces (gyroid)) to create a new class of heat exchangers.
- **Scope**
  - In collaboration with Lawrence Livermore National Laboratory (LLNL), this subtask will produce optimized structures through additive manufacturing of metal superalloys, starting from small coupons through the production of heat exchanger modules. Using the powder bed fusion (PBF) process, we will investigate processing—property relationships for each candidate alloy
- **FY18 Expected Accomplishments**
  - Print and evaluate (microstructure and mechanical properties) test coupons of target alloys and then print and evaluate a refined, second generation of coupons for the most promising alloy

T. Femmer et al. / Chemical Engineering Journal 273 (2015) 438–445



Lawrence Livermore National Laboratory

Supercritical CO_2 Power Cycles

Materials Research at NETL

- High-temperature oxidation in direct sCO_2 power cycles
- Low-temperature corrosion in direct sCO_2 power cycles
- Effect of sCO_2 cycle environments on mechanical properties
- Erosion in components of sCO_2 power cycles
- Materials issues in manufacturing compact heat exchangers
- Mechanical and chemical stability of joined materials in sCO_2
- Additive manufacturing of heat exchangers with new geometries