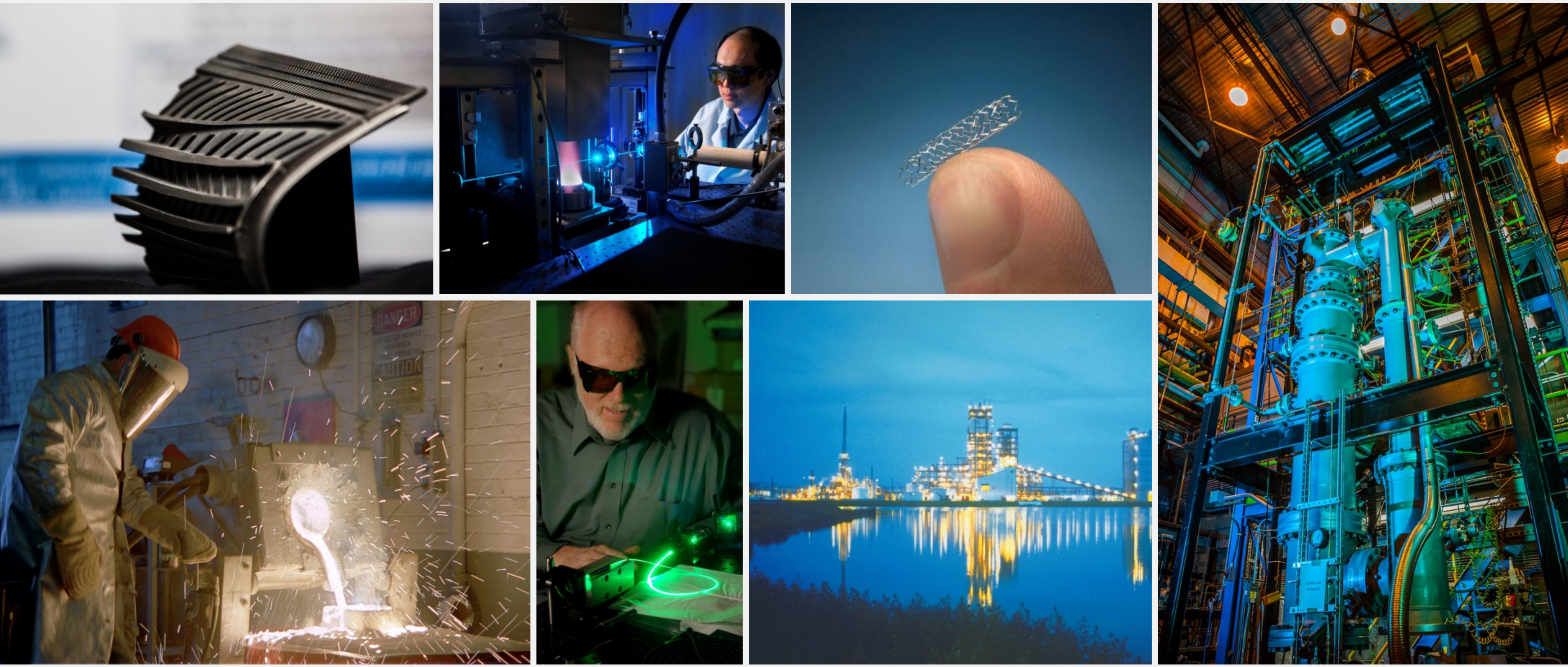
Driving Innovation ♦ Delivering Results



High-Temperature Corrosion of Diffusion Bonded Ni-Based Superalloys in CO_2

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U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

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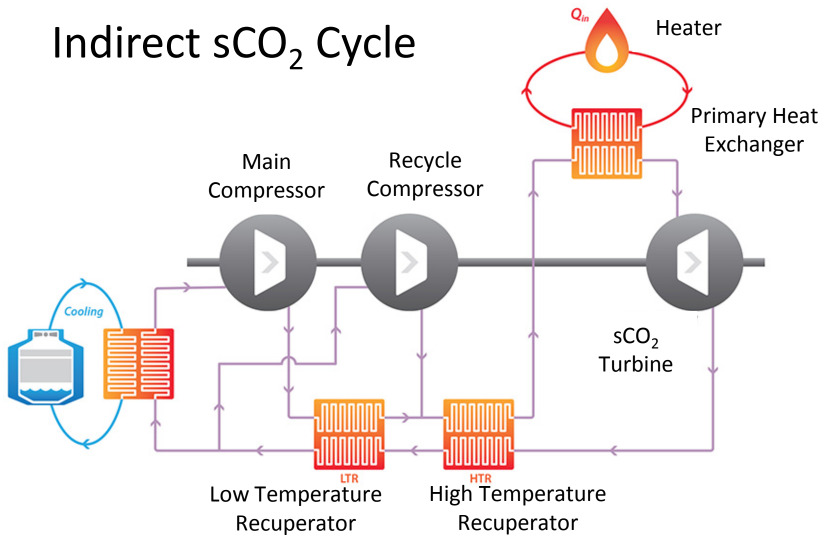
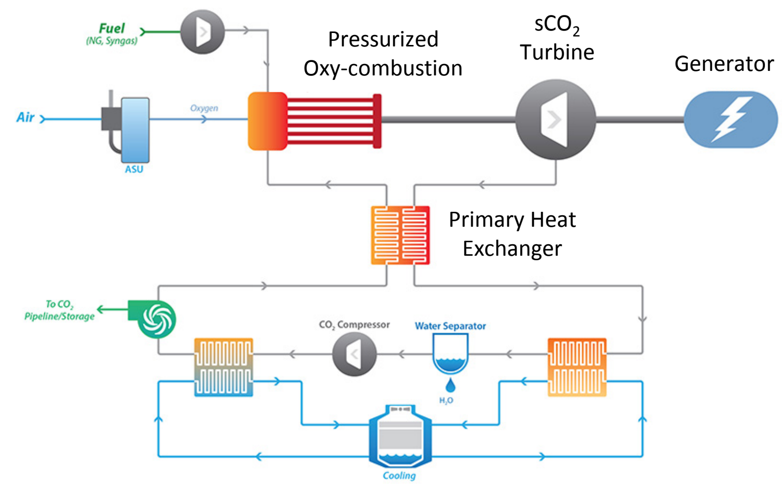
Supercritical CO_2 Power Cycles

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
Indirect	Turbine	650-750	20-30	550-650	8-10
Indirect	HX	550-650	8-10	100-200	8-10
Direct	Combustor	750	20-30	1150	20-30
Direct	Turbine	1150	20-30	800	3-8
Direct	HX	800	3-8	100	3-8

Essentially pure CO_2

CO_2 with combustion products including H_2O, O_2, and SO_2

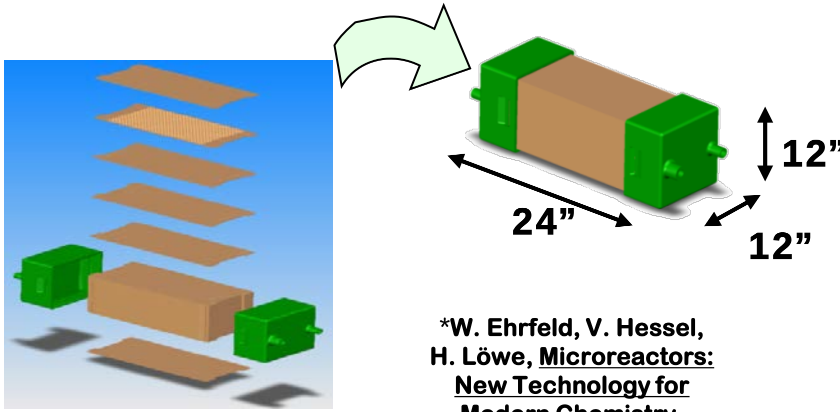
Compact Heat Exchangers

- **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

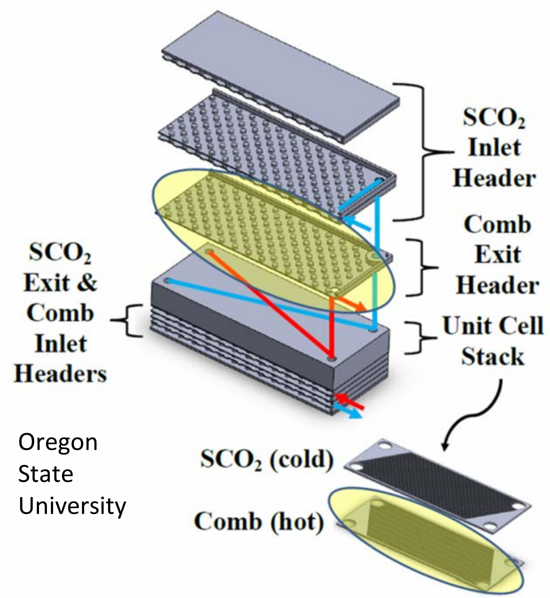
Typical Microchannel HX Fabrication Process

Microlamination-

1. **Pattern microscale flow paths into laminae using a variety of methods (etching, micromachining, laser cutting, EDM, others)**
2. **Bond these laminae using a variety of methods (diffusion bonding, laser welding, brazing, others). For sCO_2, diffusion bonding and brazing are the most robust approaches**



*W. Ehrfeld, V. Hessel, H. Löwe, Microreactors: New Technology for Modern Chemistry, Wiley-VCH, 2000.

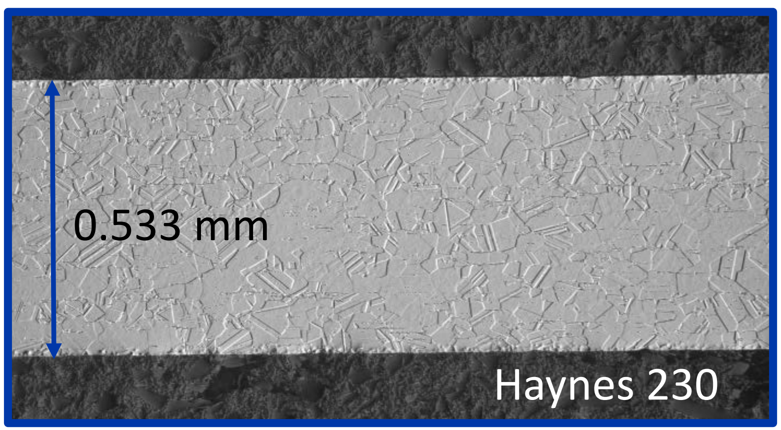


Oregon State University

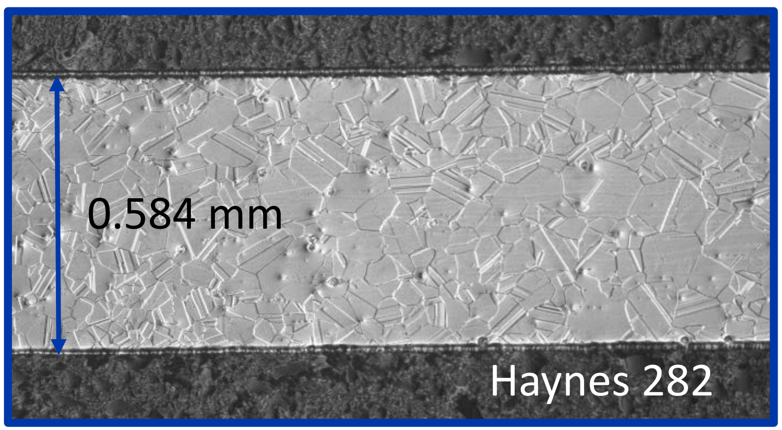
Materials

Nominal chemical composition (weight %) of materials used in this study (Haynes 230 and Haynes 282)												
	Ni	Cr	W	Ti	Mo	Fe	Co	Mn	Si	Al	C	B
H230	57	22	14	--	2	3*	5*	0.5	0.4	0.3	0.10	0.015*
H282	57	19.5	--	2.1	8.5	1.5*	10	0.3*	0.15*	1.5	0.06	0.005

* = maximum



Solid-solution strengthened
Cold rolled and 1232 °C solution annealed sheet



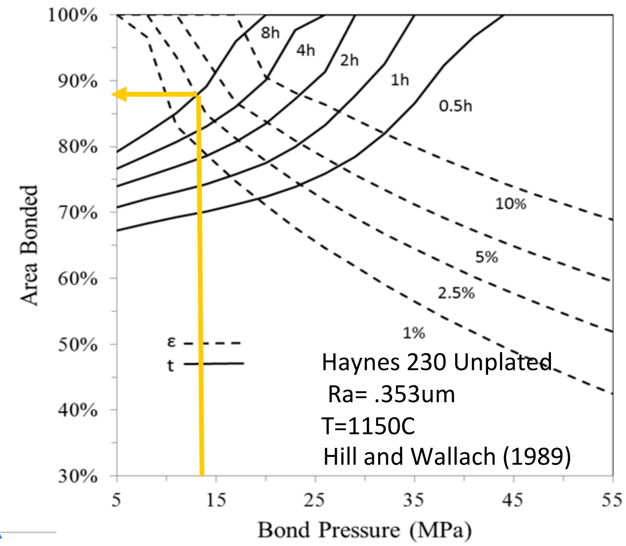
Precipitation strengthened
1149 °C solution annealed sheet

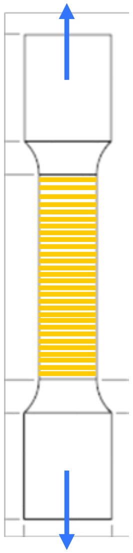
Diffusion Bonding

- Sheets were water-jet cut into shims
- 100 shims were bonded together in each stack
- All shims were reverse current etched and cleaned with acetone
- Some stacks used shims plated with electroless nickel, 2 - 4 μm thick
- Some shims contained pin-fin microfeatures identical to those used in a heat exchanger
- All shims were thoroughly cleaned by hand and in an ultrasonic acetone bath for 15 minutes immediately before bonding

Diffusion Bonding

- Shim stacks were held in a fixture during bonding and pressure was applied only after the temperature ramped up to the desired value
- The hot press vacuum was maintained at approximately 5 x 10^{-6} torr (0.0007 Pa)
- 1150°C for 8 hours at 12.7 MPa
- After bonding, each stack was machined to produce 6 tensile specimens using wire EDM and a CNC lathe
- After bonding, H230 experienced approximately 4.1% strain (2.5% predicted by model)
- H282 without Ni plating did not bond well

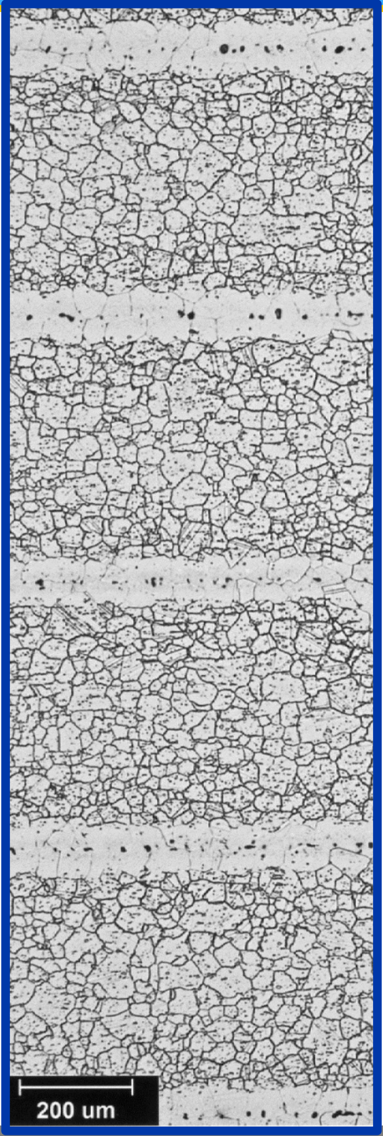




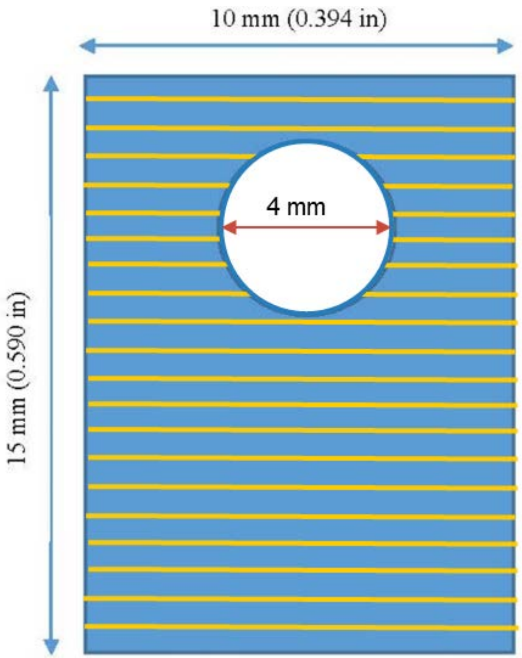
Wednesday – March 30th
8:50 am
Session: Heat Exchangers III
Salon A

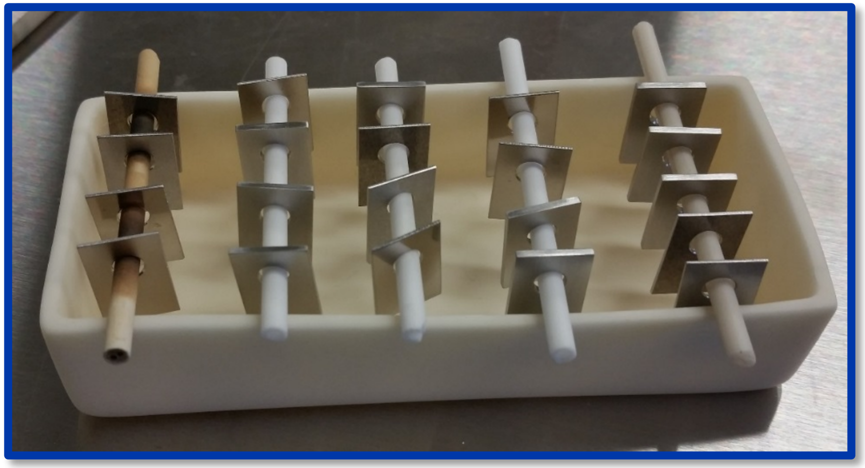
Diffusion Bonding

- **Diffusion bonding is the "weak link" in the fabrication process**
- **Sharp edges in the architecture lead to locations of high stress concentration in the mechanical design simulations**
- **We need information on**
  - The parameters for diffusion bonding (T, P, t) for these superalloys
  - The strength of the diffusion bond
  - Whether the high stress concentration predicted by the mechanical design simulations is indeed a problem or not.
  - Corrosion behavior of diffusion bonded regions in sCO_2



Oxidation tests





Characterization

Mass Change

XRD

SEM

Gas: 1 bar CO_2 (99.999% purity)

Gas flow rate: 0.032 kg/h

Temperature: 700°C

Duration: 500 h

24 h purging with CO_2 before heating

- **Unlike in sH_2O, there is no evidence of increased oxidation rates at high pressure in sCO_2**

Thursday – March 31st
9:00 am
Session: Materials I
Salon C

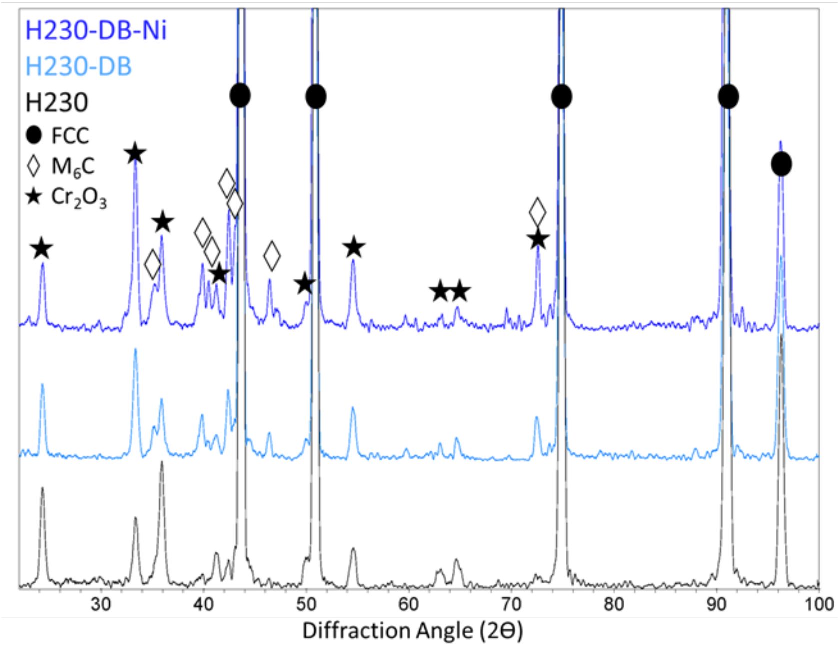
Oxidation Results

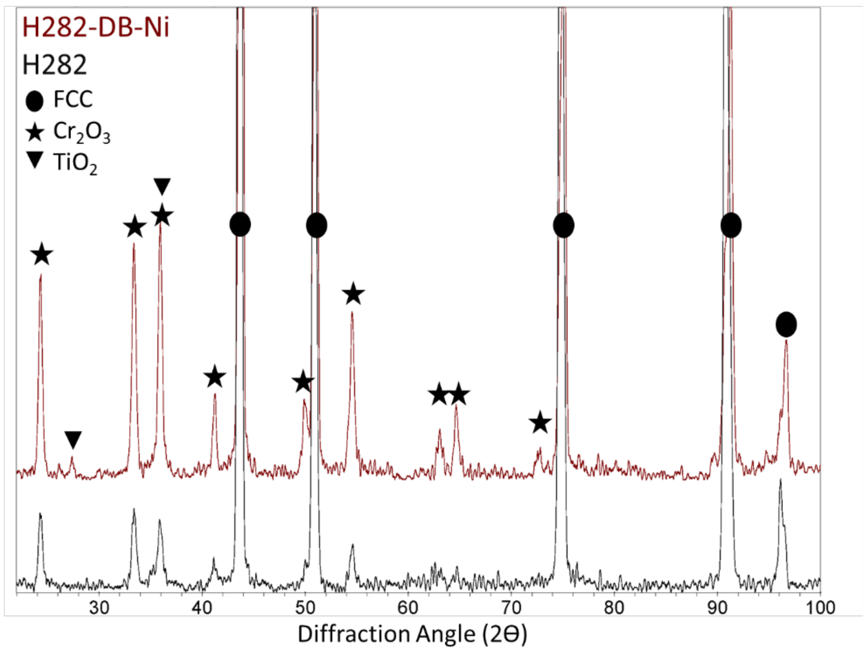
Mass changes as a result of the CO_2 exposure at 700°C for 500 h. Averages and standard deviations are from three coupons for each condition.		
	Average mass change (mg/cm^2)	**Standard deviation (mg/cm^2)**
H230	**0.077**	**0.012**
H230-DB	**0.115**	**0.013**
H230-DB-Ni	**0.112**	**0.005**
H282	**0.038**	**0.022**
H282-DB-Ni	**0.236**	**0.008**

H230: Minor mass change increase

H282: More significant mass change increase

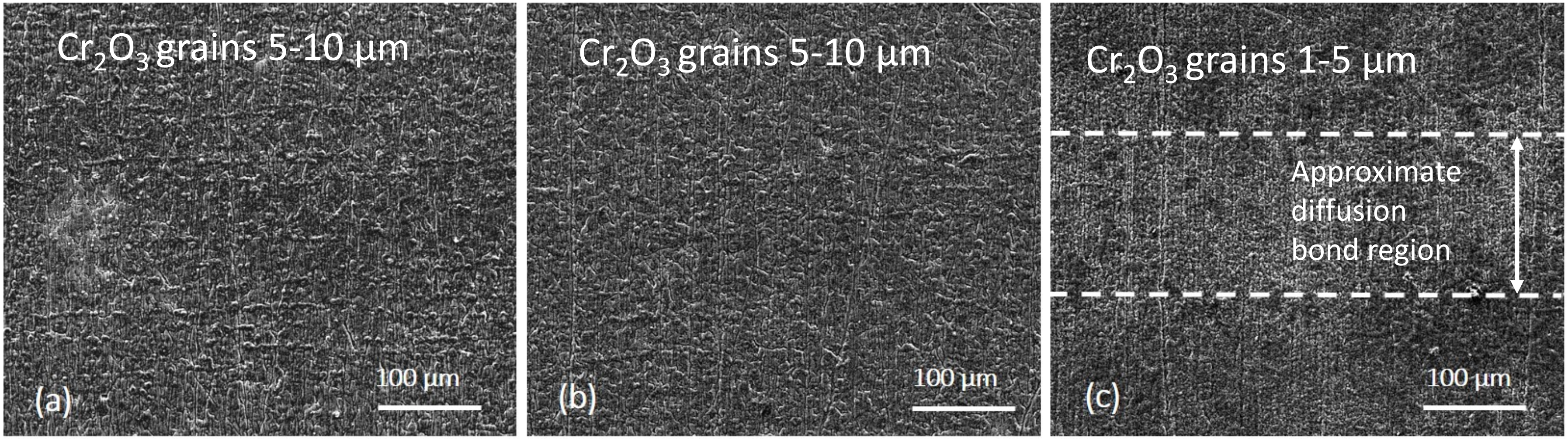
XRD on the Oxidized Samples





XRD signal from both oxide scale and underlying alloy
Chromia oxide scales form on both alloys
H230 contains W and Mo rich M_6C carbides
H282 contains γ' precipitates, $Ni_3(Al,Ti)$, but was not detected by XRD

SEM on the surface of oxidized samples

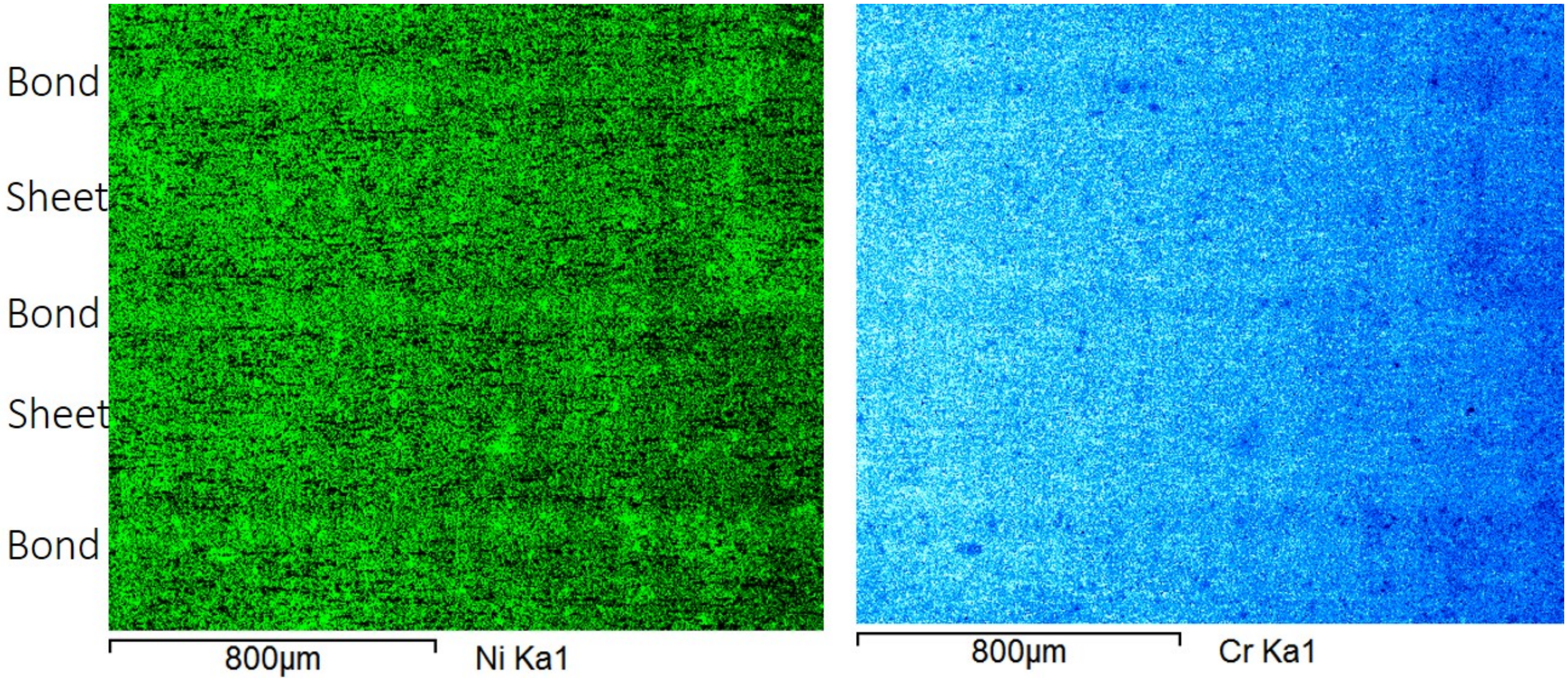


H230-DB-Ni H230-DB H282-DB-Ni

Dense, fine-grained, oxide scales
No observed differences in H230 between bond and non-bond areas
Some contrast differences in H282 in and near bond areas

Secondary Electron Images

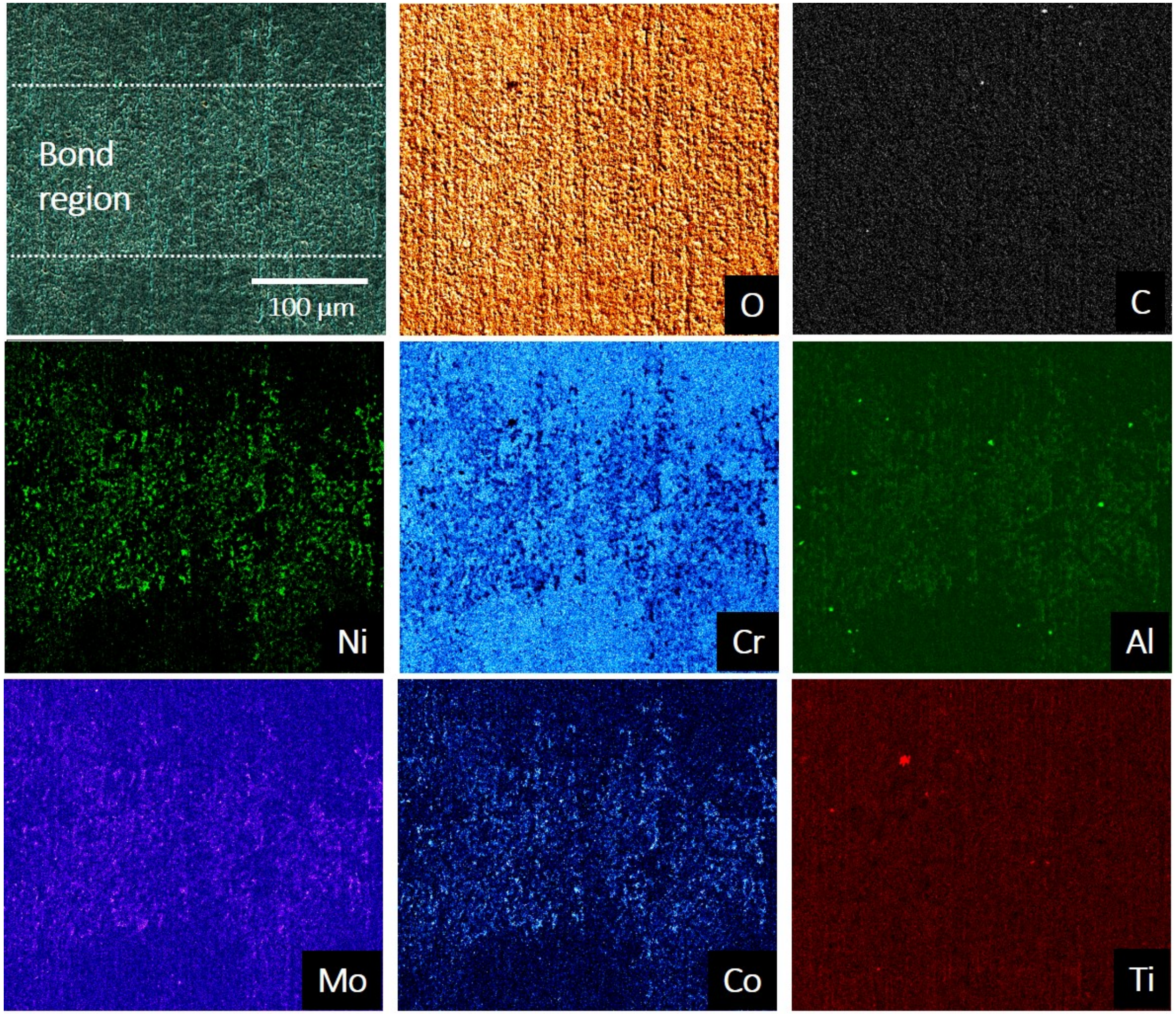
SEM on the surface of oxidized samples – H230-DB-Ni



Slight Ni enrichment and Cr depletion were detected using x-ray elemental mapping on the bond regions of the H230-DB-Ni. The other elements did not show a detectable variation.

Ni plating was 2-4 µm (4-8 µm total for each bond), so bond area reflects diffusion zone

SEM on the surface of oxidized samples – H282-DB-Ni

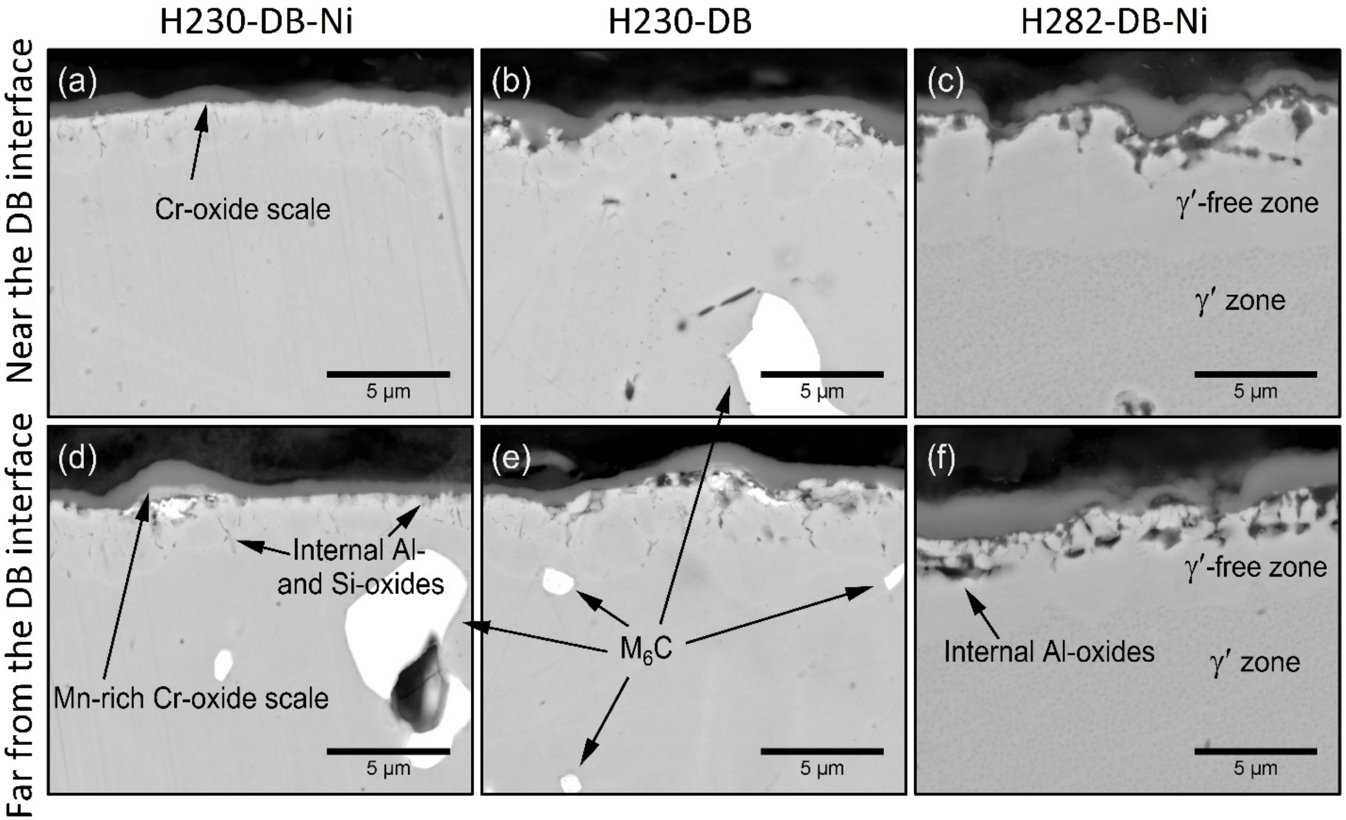


Elemental X-ray maps acquired on one of the bond regions of the H282-DB-Ni coupon after the 500 h CO_2 exposure at 700°C.

Enrichment of Ni, Al, Mo, Co in the bond region

Lower Cr in bond region

SEM on the cross-sections of oxidized samples



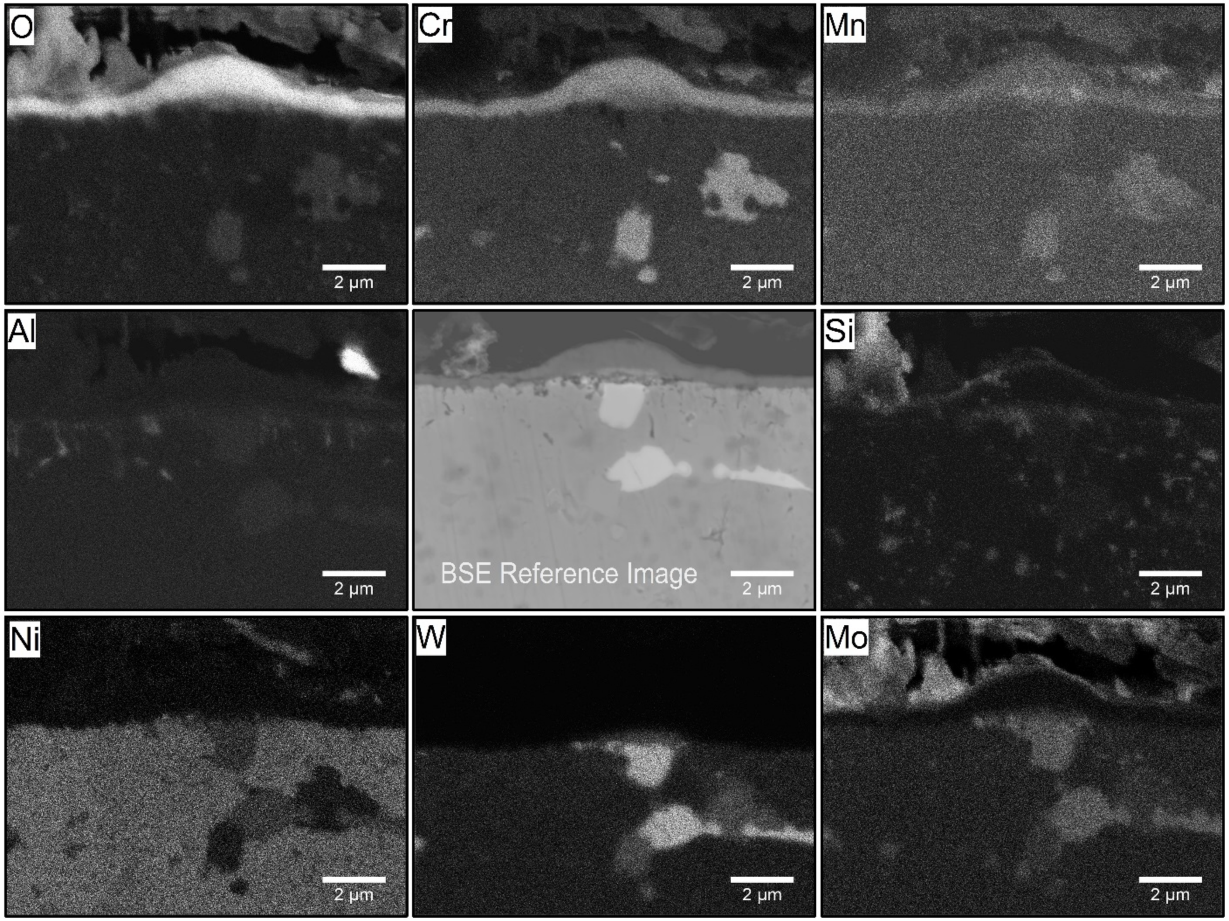
No significant difference between bond regions and away from bond regions

More internal oxidation in H282, resulting from higher Al and Ti levels

γ’ loss in H282 below the internal oxidation layer

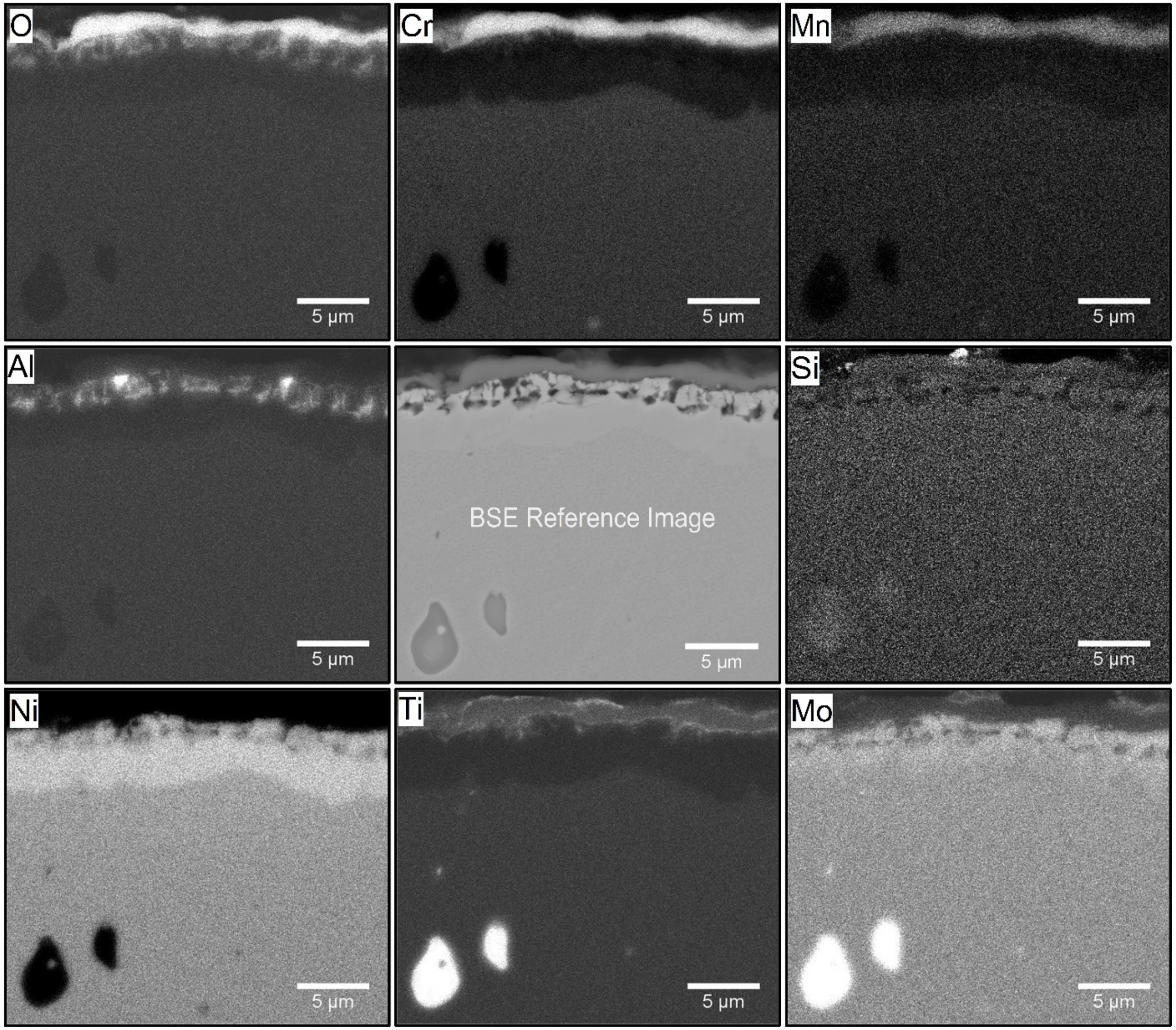
Back-Scattered Electron Images

SEM on the cross-sections of oxidized samples – H230-DB-Ni



X-ray maps of select elements for H230-DB-Ni far from the DB interface. W and Si were acquired in WDS mode and all other elements were collected in EDS mode.

SEM on the cross-sections of oxidized samples – H282-DB-Ni



X-ray (EDS) maps of select elements for H282-DB-Ni far from the DB interface

Summary

- As determined after a 500 h exposure to CO_2 at 700°C, diffusion bonding was not detrimental to the oxidation resistance of the H230. The diffusion bond regions of H230 did not exhibit an accelerated oxidation.
- Diffusion bonding of H282 resulted in increased mass gains during oxidation. However, a chromia scale was still formed, and overall oxidation rates were still low.

Future Symposium

Materials Degradation in Supercritical CO_2 Power Cycles

Materials Science and Technology (MS&T) Conference

October 23-27, 2016

Salt Lake City, Utah

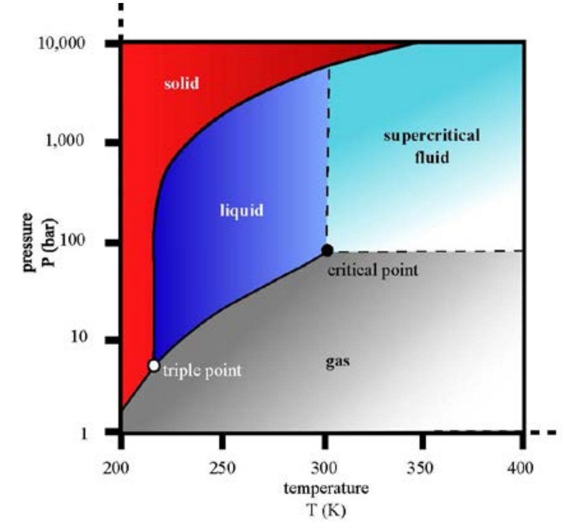
Abstracts are due on March 31, 2016

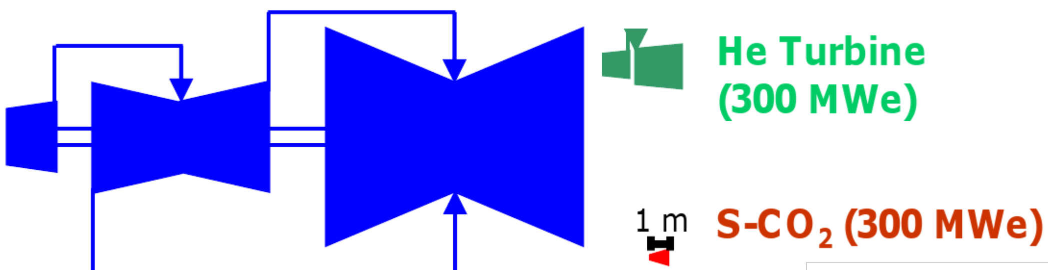
and can be submitted on ProgramMaster :

http://www.programmaster.org/PM/PM.nsf/Home?OpenForm&ParentUNID=F9FD0D2AAFA2D29285257D86004BE7A3

Supercritical CO_2 Power Cycles

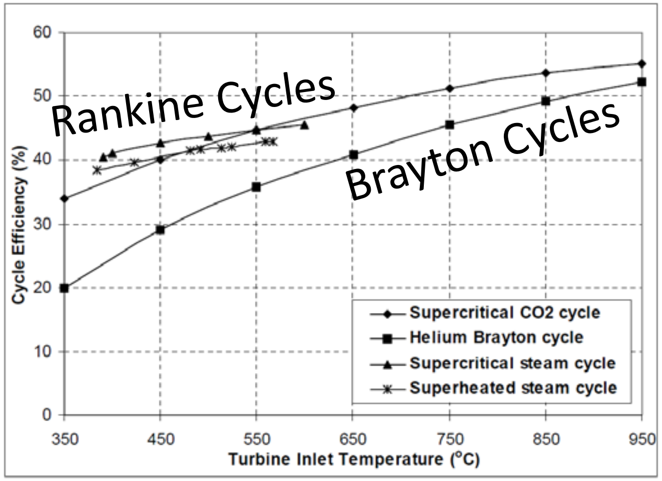
Properties of sCO2 Cycles	Impact
No phase change (Brayton Cycle)	Higher efficiency
Recompression near liquid densities	Higher efficiency
High heat recuperation	Higher efficiency Large HX footprint
Compact turbo machinery	Lower capital cost
Simple configurations	Lower capital cost
Dry/reduced water cooling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





Steam Turbine (250 MWe)

S. A. Wright, "OVERVIEW OF SUPERCRITICAL CO2 POWER CYCLE DEVELOPMENT AT SANDIA NATIONAL LABORATORIES," in *2011 University Turbine Systems Research Workshop*, Columbus, Ohio, 2011.



M. J. Driscoll, "Optimized, Competitive Supercritical-CO2 Cycle GFR for Gen IV Service," MIT-GFR-045, 2008.