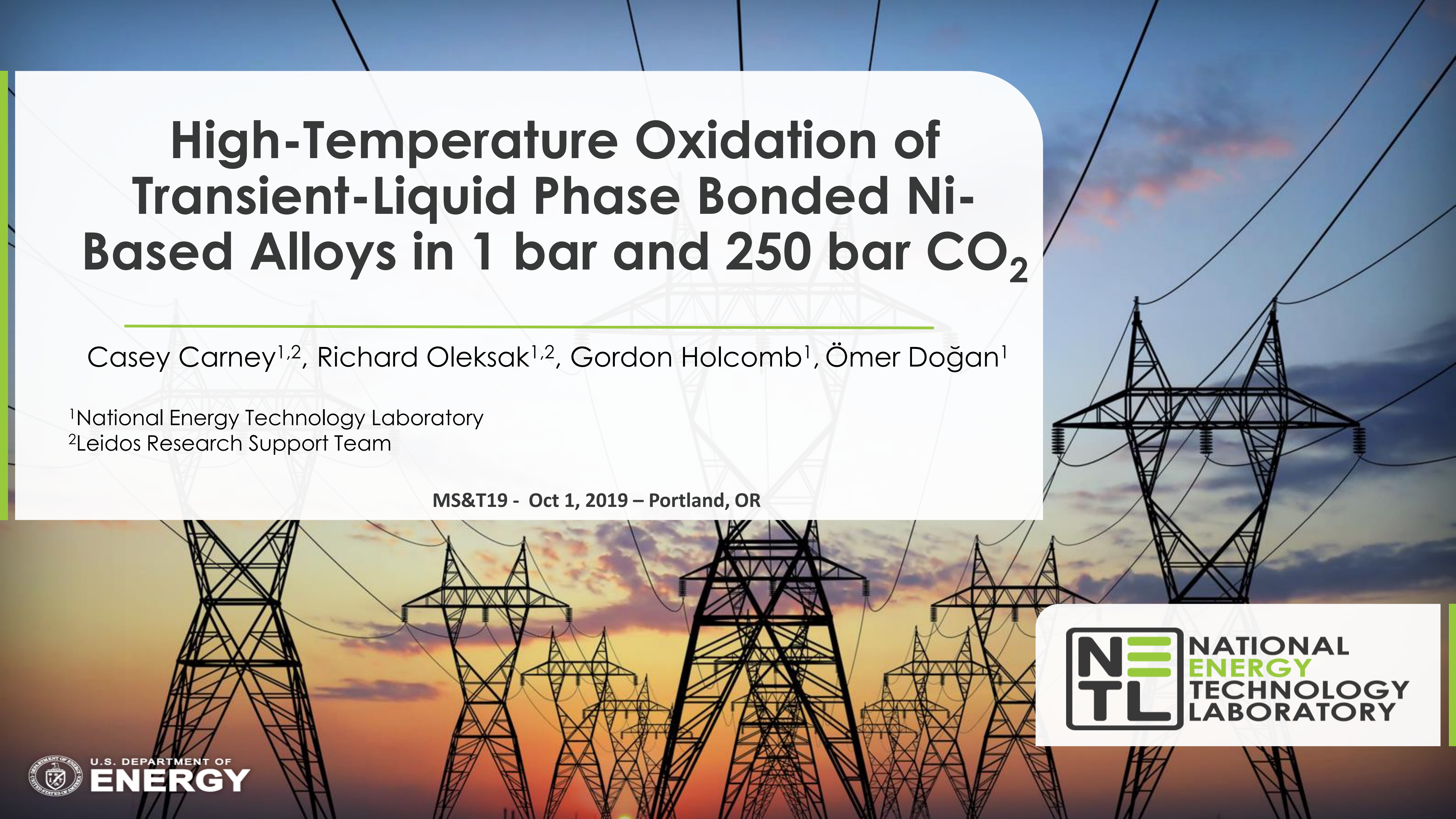

High-Temperature Oxidation of Transient-Liquid Phase Bonded Ni-Based Alloys in 1 bar and 250 bar CO_2

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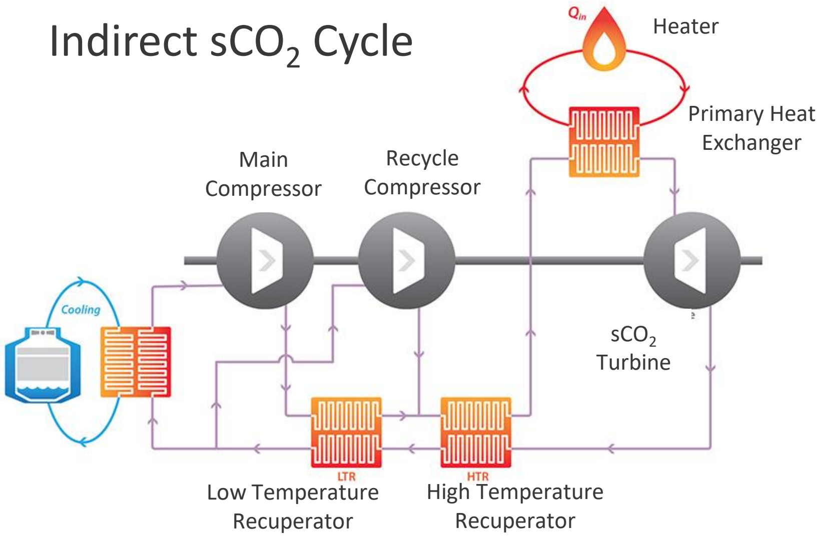
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

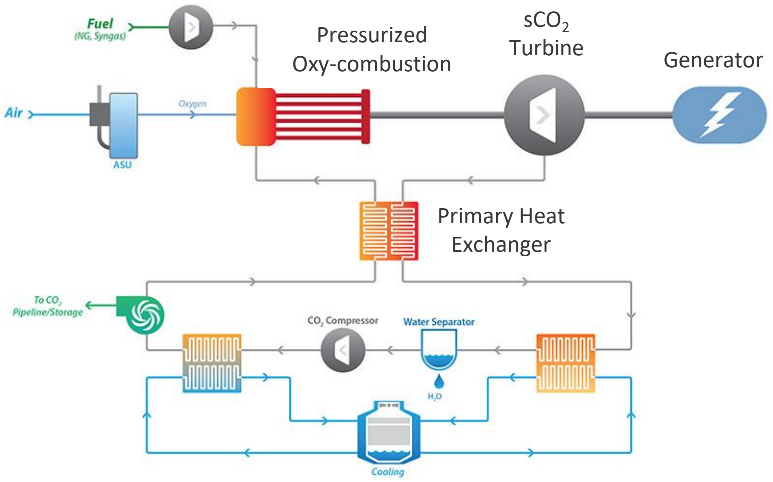
Supercritical CO_2 Power Cycles

Indirect sCO_2 Cycle



- Widely proposed for Concentrated Solar and Nuclear Energy due to their relatively narrow temperature range requirements
- The split recuperator allows a portion of the high pressure sCO_2 to bypass the LTR to balance its heat duty and improve efficiency
- For Fossil Energy applications, consideration must be given to use the significant thermal energy remaining in the combustion flue gas after passing through the PHX

Direct sCO_2 Cycle

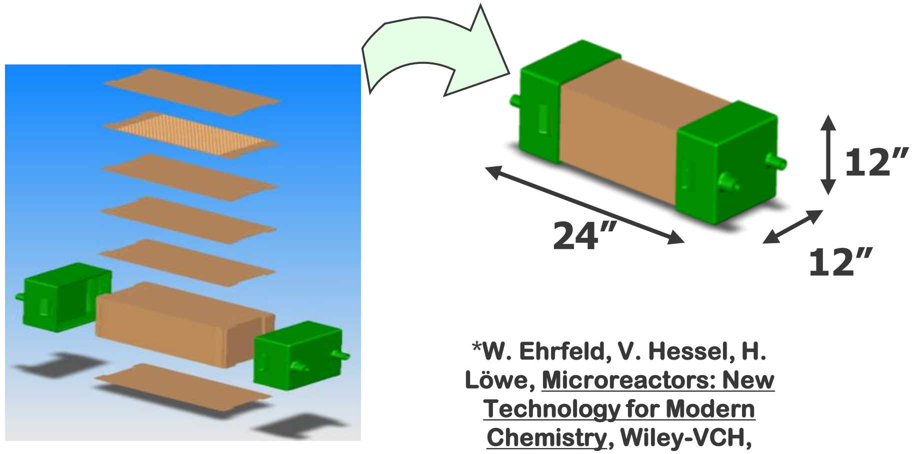


- Oxycombustion using O_2 instead of air to burn fuel
- More akin to gas turbines (indirect cycles more akin to steam turbines)
- Higher turbine inlet temperatures and thus higher efficiencies
- High pressure sCO_2 output allows for CO_2 transport and sequestration
- Working fluid not pure CO_2, but contains other combustion products including H_2O

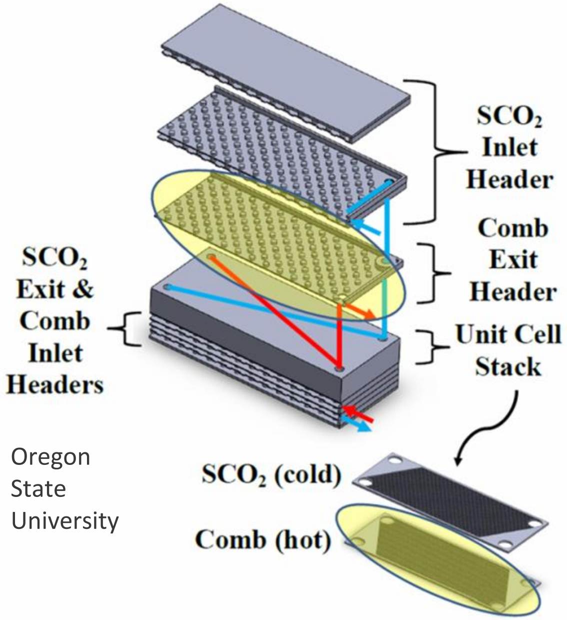
Typical Microchannel HX Fabrication Process

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 seems to be the most robust approach
3. Transient Liquid Phase (TLP) bonding used for this study
    - Shims coated with lower melting point Ni-P layer to facilitate bonding



*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)

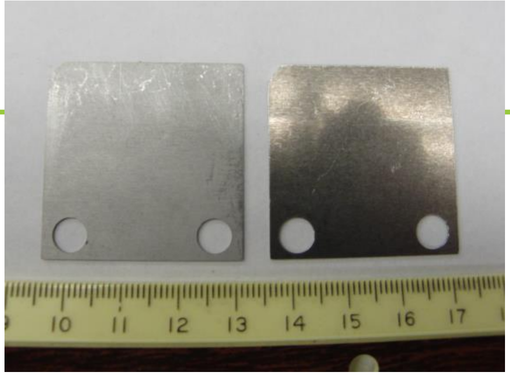
	Ni	Cr	W	Ti	Mo	Fe	Co	Mn	Si	Al	C	B
H230	57	22	14	--	2	3*	5*	0.5	0.4	0.3	0.10	0.015*
H282	57	19.5	--	2.1	8.5	1.5*	10	0.3*	0.15*	1.5	0.06	0.005

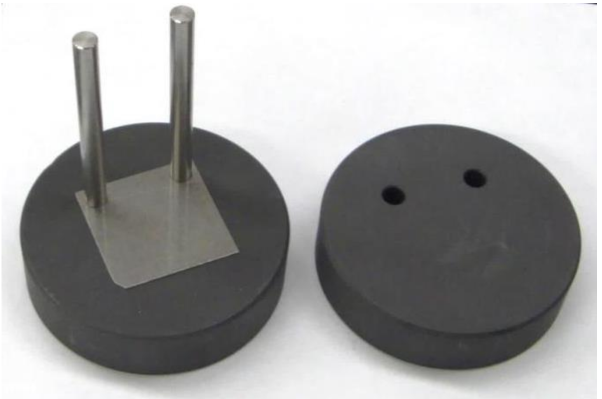
* = maximum

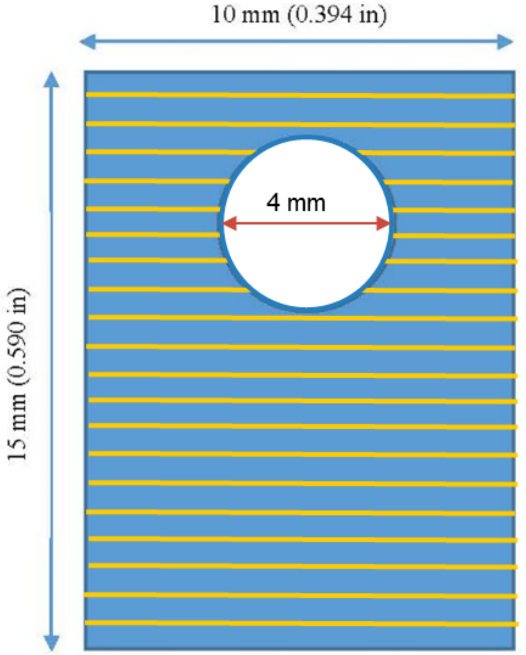
Sheet Thickness
H230 sheet: 0.533 mm
H282 sheet: 0.584 mm

TLP 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
- Shims plated with electroless nickel, 2 - 4 µm thick
- All shims were thoroughly cleaned by hand and in an ultrasonic acetone bath for 15 minutes immediately before 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 ~5 x 10^{-6} torr (0.0007 Pa)
- Annealing stacks at 1150°C, 12.7 MPa
  - 250 bar exposures → 8 hours (Ni-12P interlayer)
  - 1 bar exposures → 4 hours (Ni-6P interlayer)

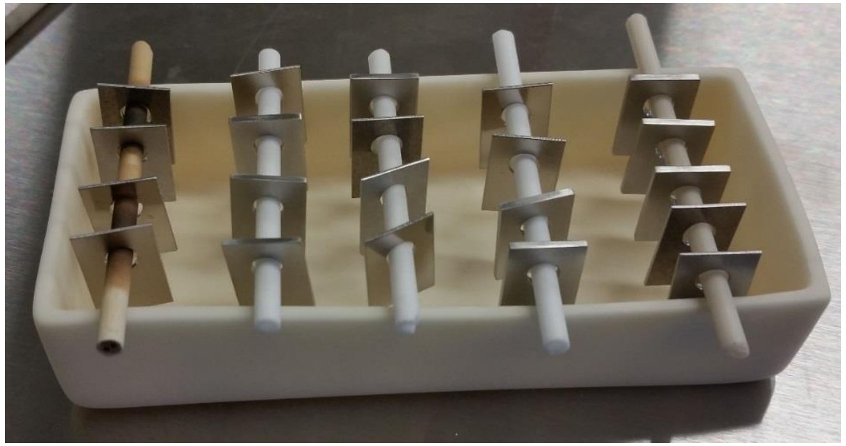






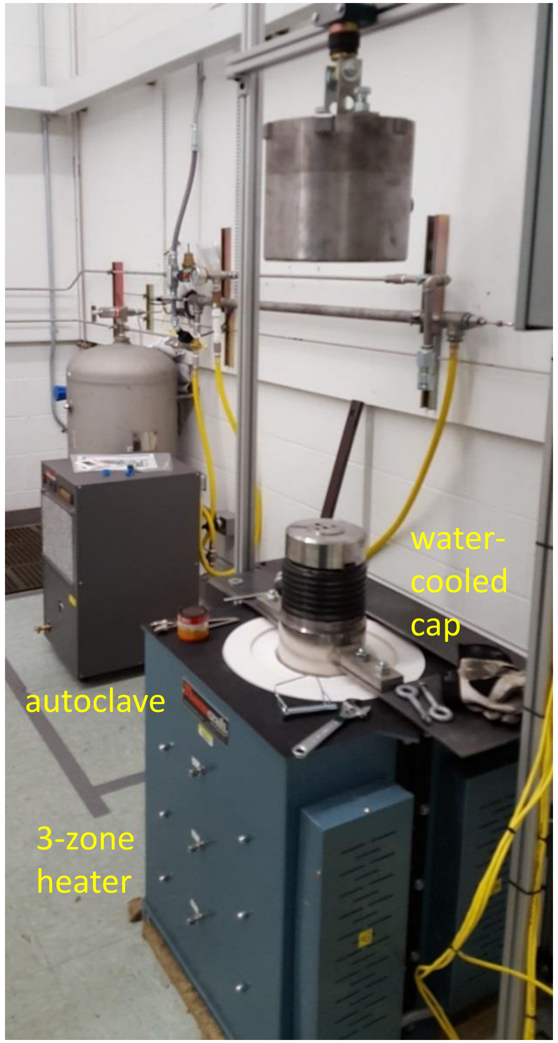
Oxidation Exposures (1 bar)

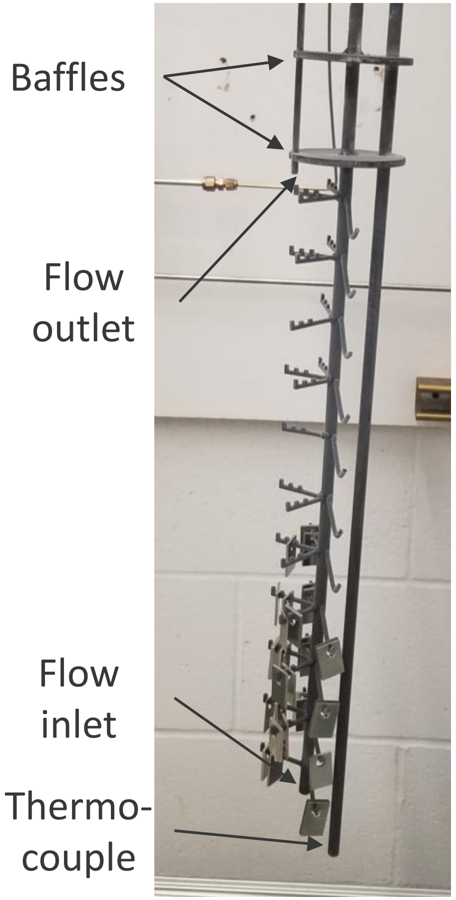
- Three zone furnace control for a flat temperature zone where samples are located
- Gas: 1 bar CO_2 (99.999% purity)
- Gas flow rate: 0.032 kg/h
- Temperature: 700 °C
- Duration: 2500 h (500 h increments)
- 14 h purging with CO_2 before heating
  - 6 h dwell at 350 °C to fully desorb oxygen from system
- Oxygen monitored with downstream inline sensor
  - Oxygen levels at 2-11 ppm
- Three replicates of each sample
  - Removal at 500, 1500, and 4000 h



Oxidation Exposures (250 bar)

- Flow controlled with a high pressure pump
- Pressure controlled with a back pressure regulator
- ASME rated to 800°C/277 bar
- Autoclave body made of H230
- Three zone furnace control for a flat temperature zone where samples are located
- Gas: 250 bar CO_2 (99.999% purity)
- Gas flow rate: 0.14 kg/h
- Temperature: 720 °C
- Duration: 1500 h (500 h increments)
- 10 cycles Ar backfill purging before heating
- Three replicates of each sample
  - Removal at 500 and 1500 h



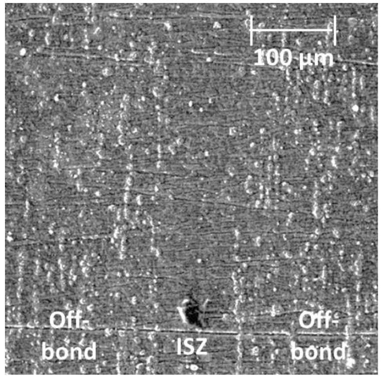


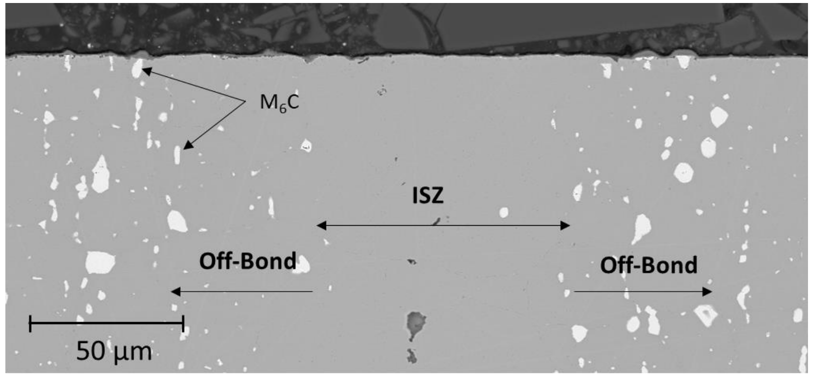
Isothermally Solidified Zone (ISZ)

1 bar, 500 h

H230

Surface

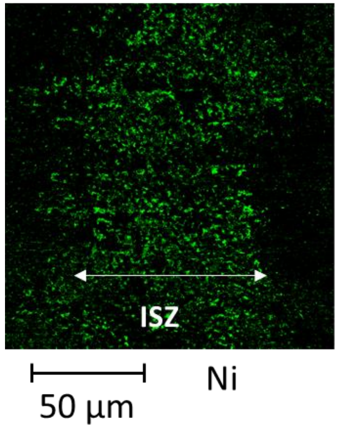




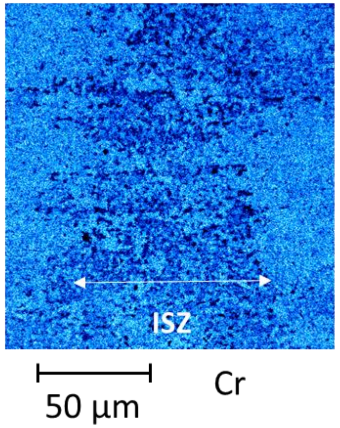
Carbide free within ISZ

H282

Ni-rich, Cr poor within ISZ

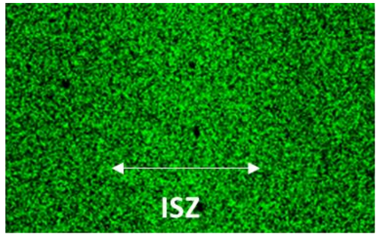


Ni

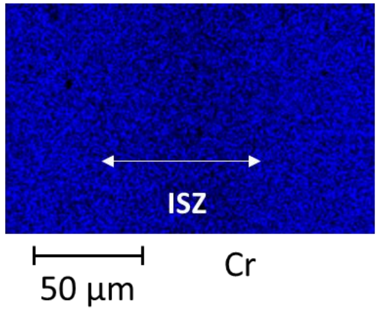


Cr

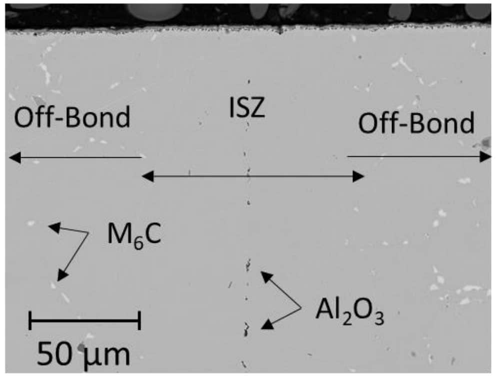
Surface



Ni



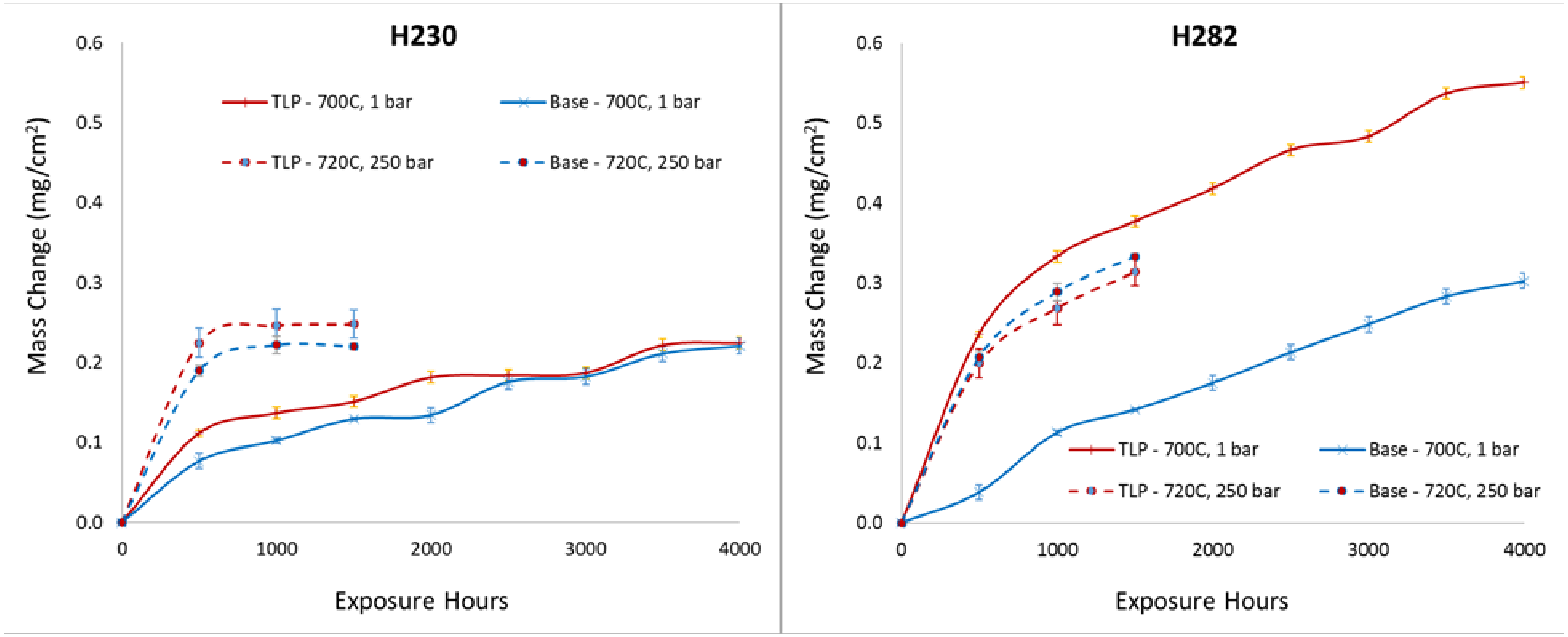
Cr



ISZ not fully homogenized during TLP bonding process (both alloys)

Doesn’t appear to affect overall oxidation

Mass Change Results



- XRD confirms oxide is predominantly Cr_2O_3, with small spinel amounts
- Most oxide growth in initial 500-1000 h, followed by steady oxide formation
- Slight pressure effect on mass gain
- H282 1 bar TLP mass gains unexpectedly high

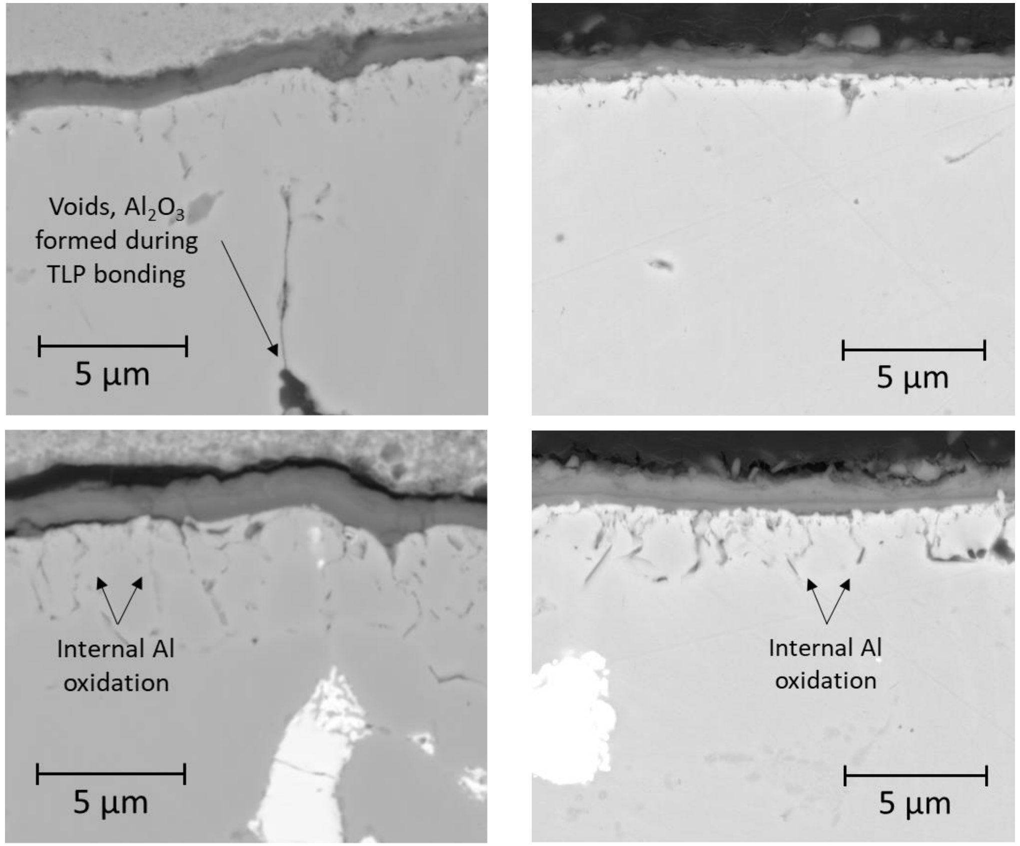
TLP Microstructure

Internal Al oxidation leads to more H282 oxidation
(than H230)

ISZ

Off-bond

H230

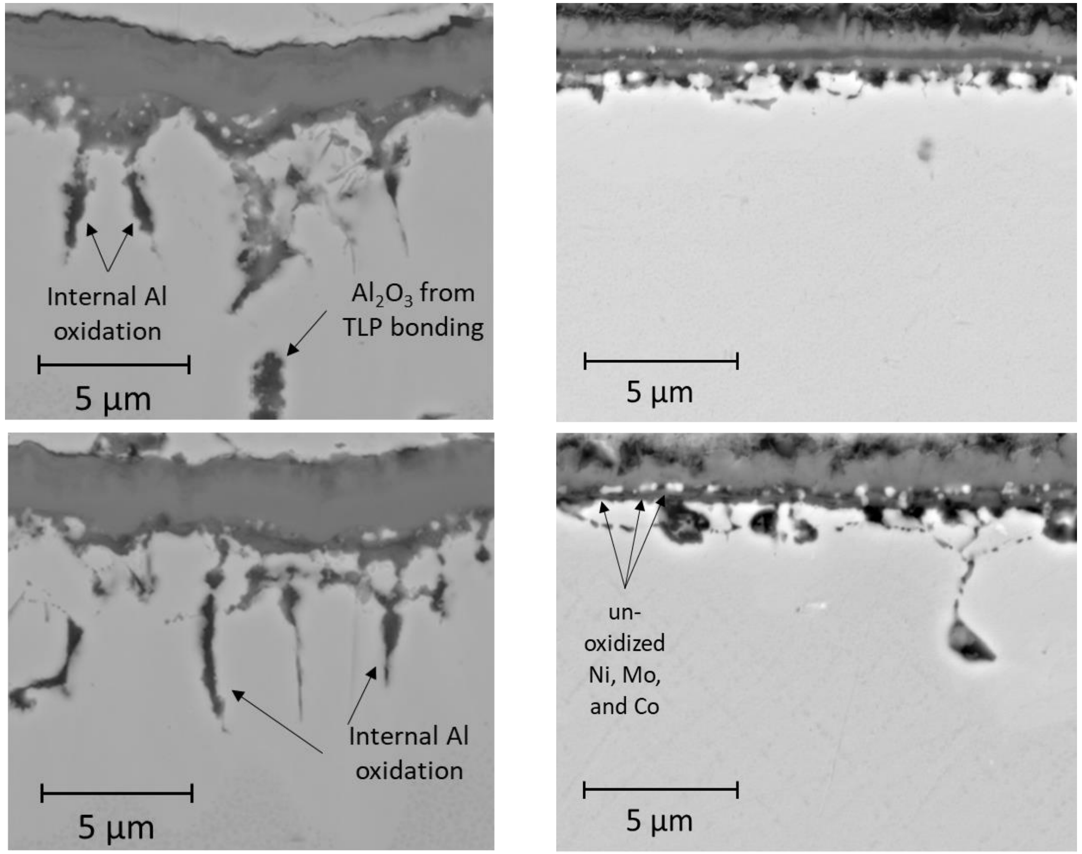


1 bar, 4000 h

250 bar, 1500 h

Similar oxide scales
Increased internal oxidation off-bond

H282

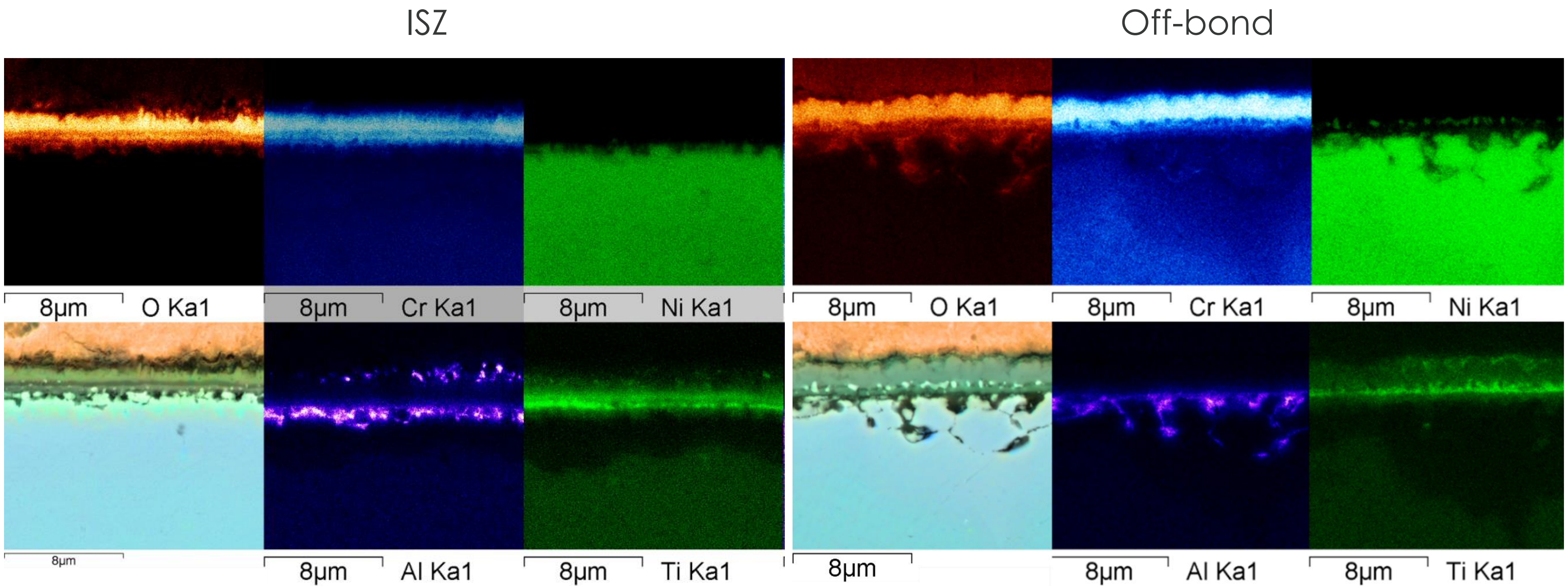


1 bar, 4000 h

250 bar, 1500 h

These metallic structures generally not found at 1 bar or within the ISZ

H282 TLP Microstructure, 250 bar



- Predominantly chromia oxide layer
- Gamma prime free, Cr/Ti/Al depleted sub-oxide region
- Off-bond regions not significantly different
  - Oxide layers appear equivalent for both
  - Exception is unreacted Ni-rich phase in lower oxide
  - These areas also contain deeper gamma prime free zones and increased internal oxidation

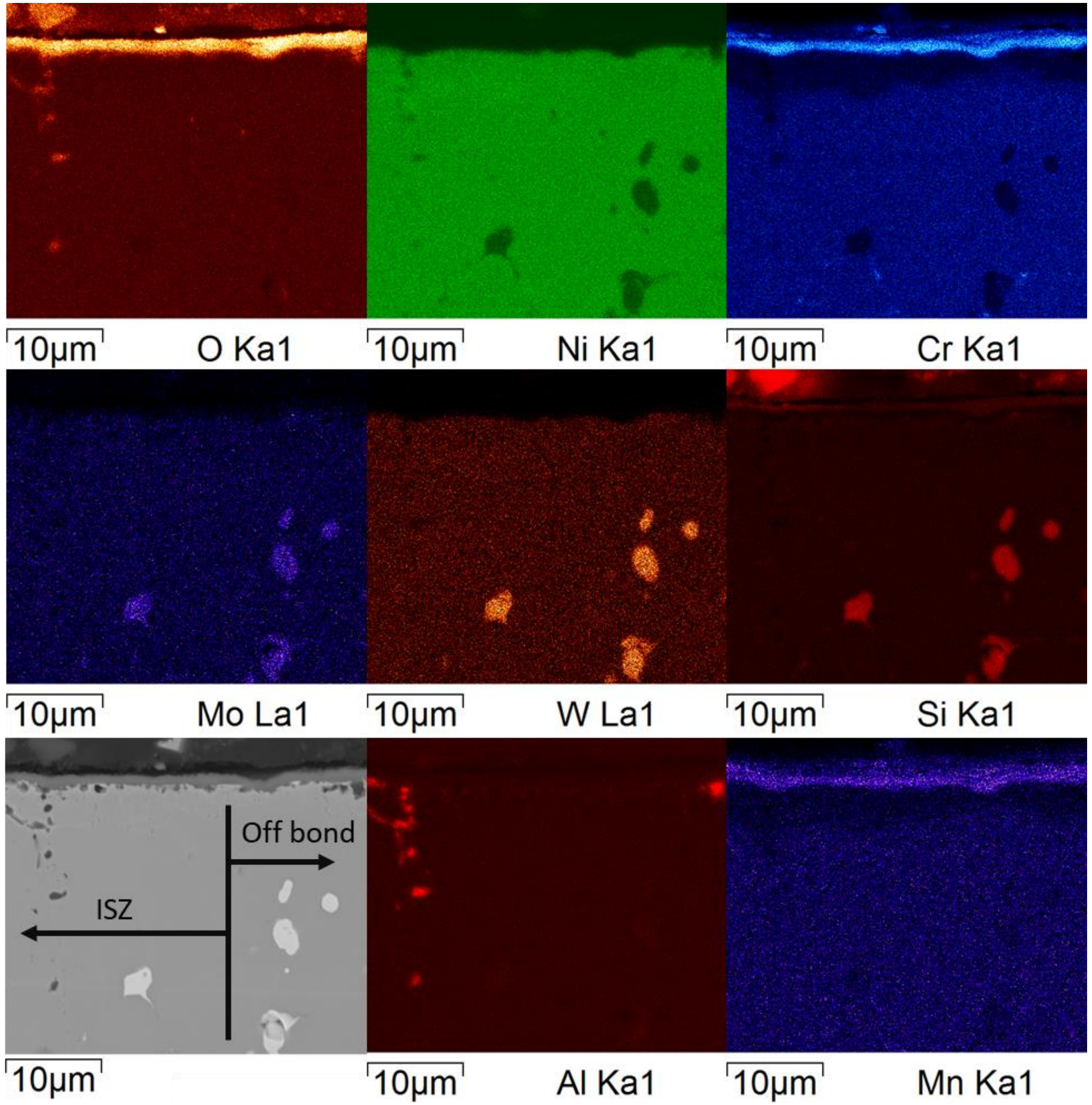
H230 TLP Microstructure

1 bar, 1500 h

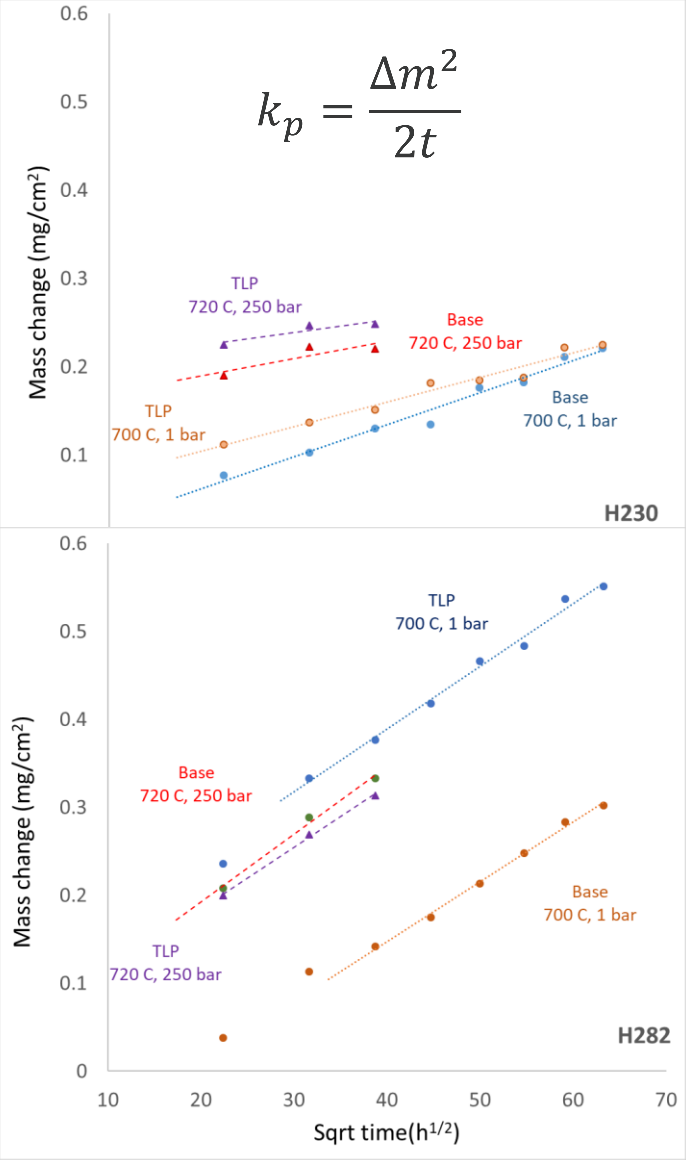
Alumina found along bond line deposited during TLP process

Carbides less likely to be found within ISZ

ISZ not fully homogenized, but still no observable oxide difference between ISZ and off-bond regions



Diffusion Controlled → Parabolic Kinetics



$$k_p = \frac{\Delta m^2}{2t}$$

- **Linear regions of plot indicate diffusion controlled kinetics**
- **All samples obey parabolic kinetics after 500-1000 h oxide buildup phase**
  - Slope is parabolic rate constant (k_p)
  - More negative log k_p = slower reaction
- **Slight slowing of continued oxidation with increased pressure**
- **H282 little difference between base and TLP**
- **H230 slightly decreased oxidation for TLP**
- **H282 more oxidation than H230**
  - Increased Al, Ti composition

H230 Samples	log Kp	H282 Samples	log Kp
Base - 700 °C, 1 bar	-14.7	Base - 700 °C, 1 bar	-14.2
TLP - 700 °C, 1 bar	-15.0	TLP - 700 °C, 1 bar	-14.1
Base - 720 °C, 250 bar	-15.5 (-15.3)	Base - 720 °C, 250 bar	-14.3 (-14.1)
TLP - 720 °C, 250 bar	-15.8 (-15.5)	TLP - 720 °C, 250 bar	-14.4 (-14.2)

*Arrhenius behavior used to adjust 720 °C log k_p values to 700 °C equivalent for comparison

Summary

- All H230/H282 TLP samples exhibited excellent corrosion resistance in high purity CO_2 at 1 bar/700 °C/4000 h and 250 bar/720 °C/1500 h
- Little difference in overall mass gain between base alloy and TLP
  - 1 bar H282 TLP the exception
- TLP bonds did not fully homogenize, but overall oxidation protection was minimally affected
  - Locally around the TLP bonds and bulk
- All samples obeyed parabolic kinetics after initial oxide buildup phase of 500-1000 h, indicating a diffusion controlled process
- Higher pressure increased the initial oxidation step, but then resulted in slight reduction of continued oxidation rates
- A few minor morphological/compositional differences at higher pressure

Acknowledgement & Disclaimer

Acknowledgement

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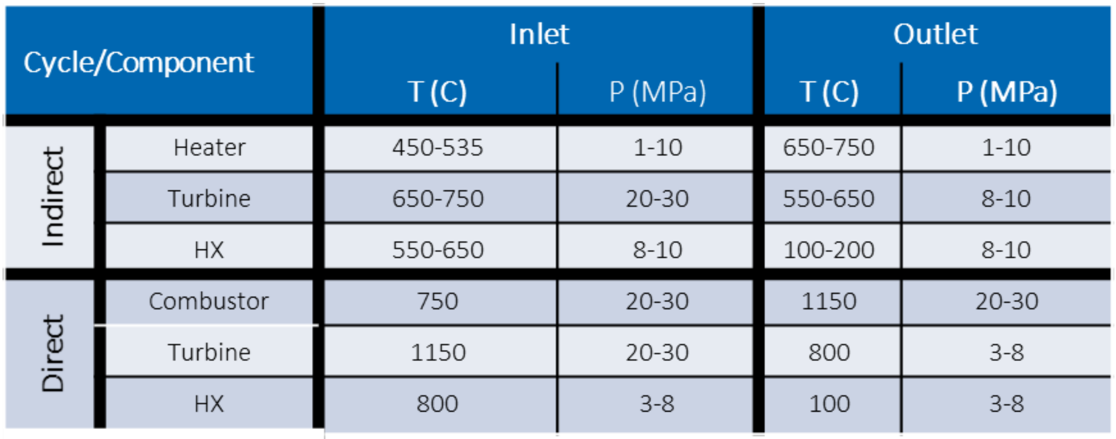
Extra if needed



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 H_2O and SO_2