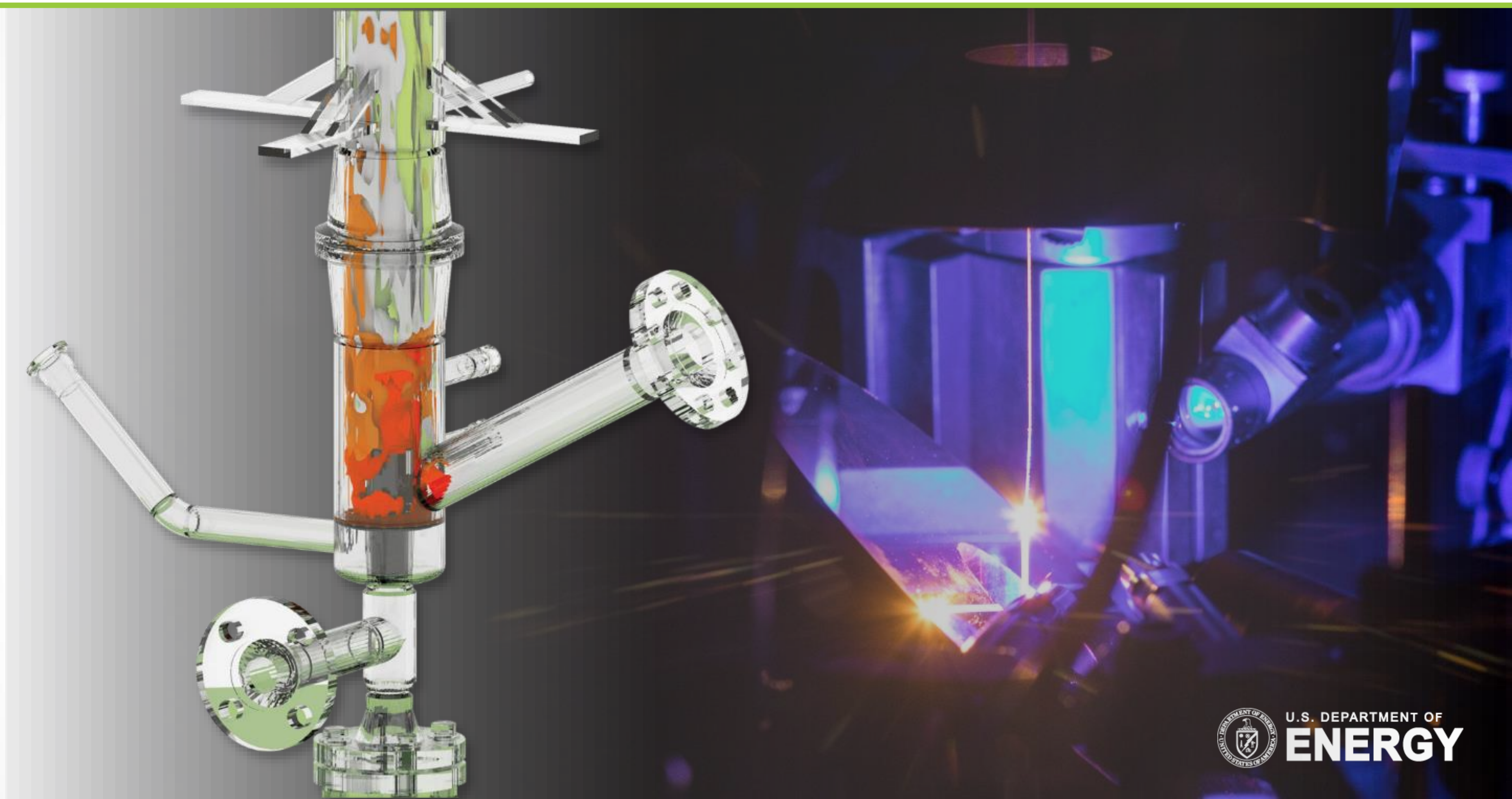
The Effect of Pressure on the Oxidation of Steels in Direct-Fired Supercritical CO_2 Power Cycle Environments

Casey S. Carney
NETL Support Contractor



MS&T 2022 – Pittsburgh, PA
Oct. 11, 2022

U.S. DEPARTMENT OF ENERGY

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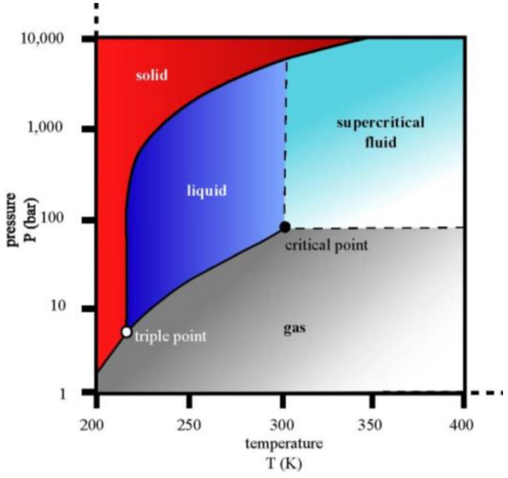
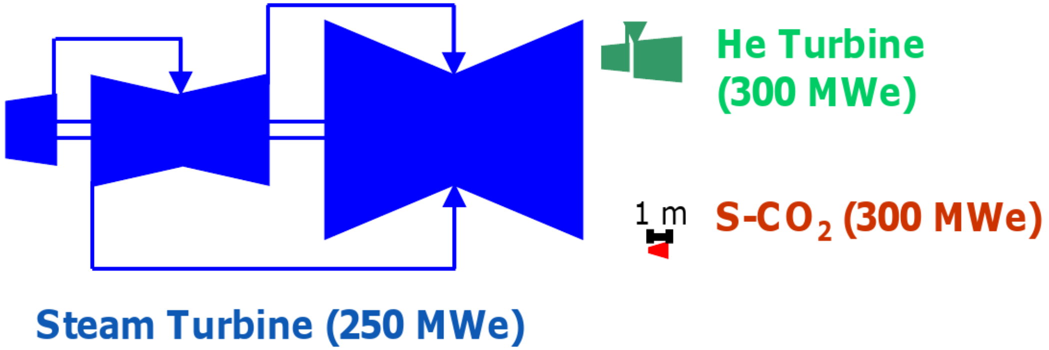
Supercritical CO_2 Power Cycles

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





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

- sCO_2 as working fluid for turbine generators
- Higher efficiency
  - Shorter heat diffusion lengths in fluid
- Smaller size
  - Less space and materials (expensive superalloys)
  - Simpler configuration
- Modular design
  - Expandable to large power plants
- Higher heat recuperation makes heat exchangers an integral part of the sCO2 cycles

Materials Considerations

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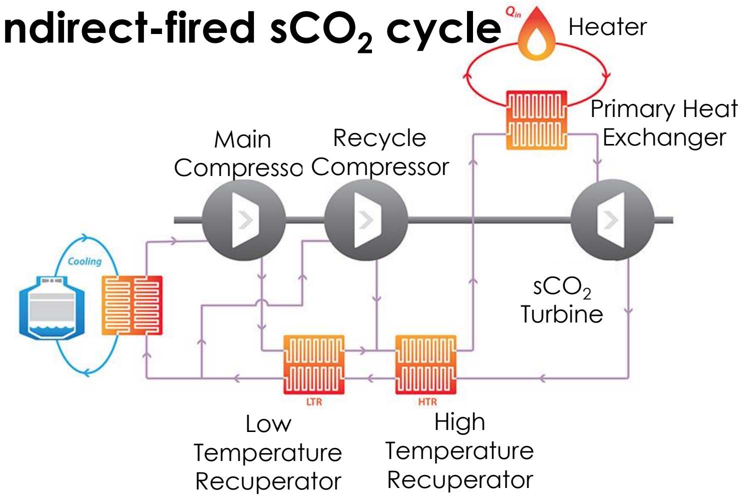
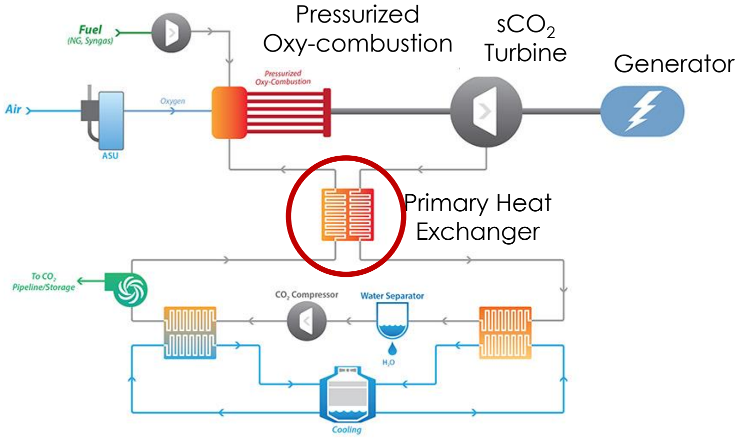
Indirect-fired sCO_2 cycle

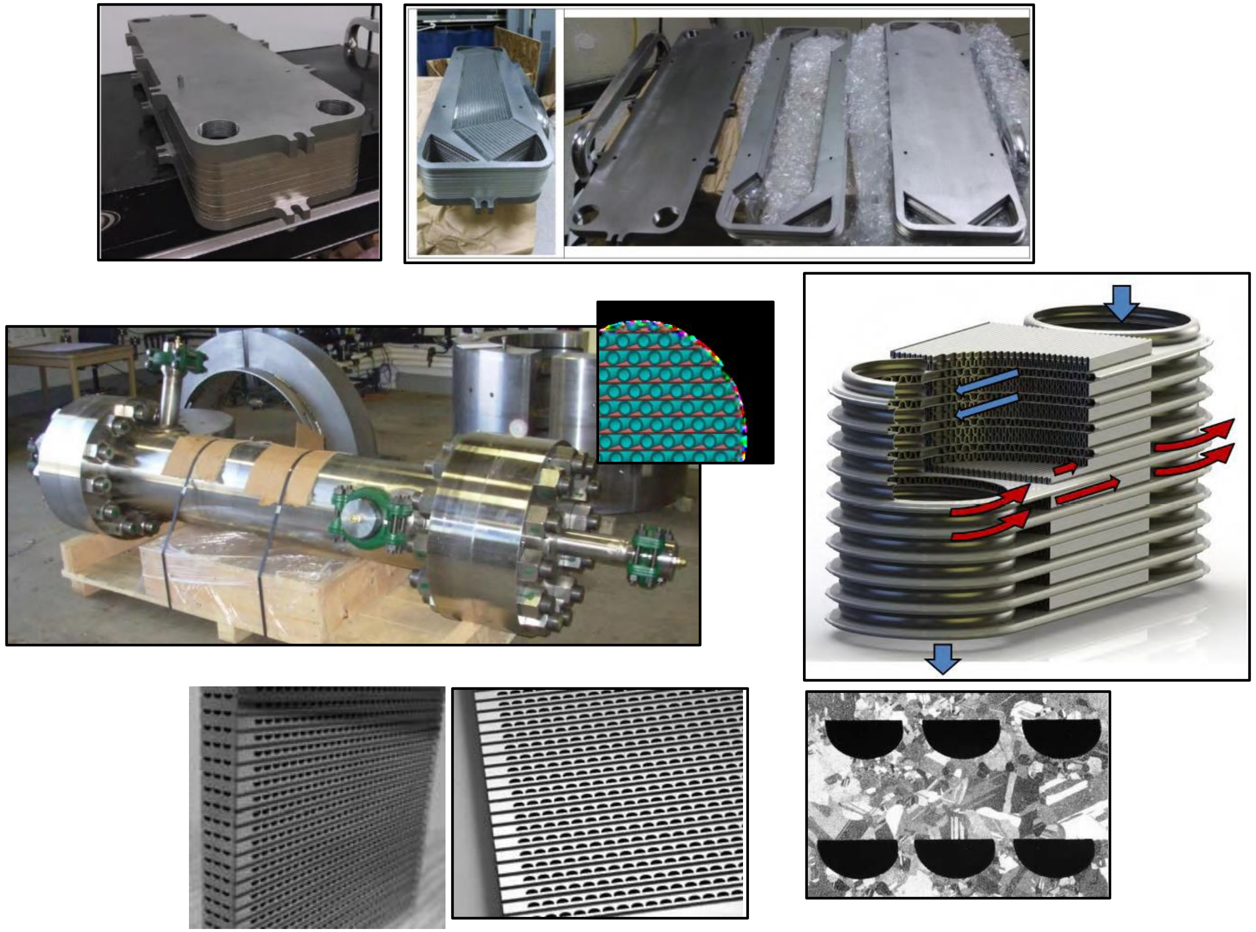


Direct-fired sCO_2 cycle



Cycle Type	Component	Inlet T (°C)	Inlet P (MPa)	Outlet T (°C)	Outlet P (MPa)	Fluid components
Indirect	Heater	450-535	1-10	650-750	1-10	High purity CO_2
	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	CO_2 containing H_2O, O_2, and other impurities based on fuel (e.g., SO_2)
	Turbine	1150	20-30	800	3-8	
	HX	800	3-8	100	3-8	

Compact (Microchannel) Heat Exchangers for sCO_2 Power Cycles



High efficiency

- Short diffusion lengths for heat transfer in the fluid

Small size

- Requires less material (expensive superalloys)

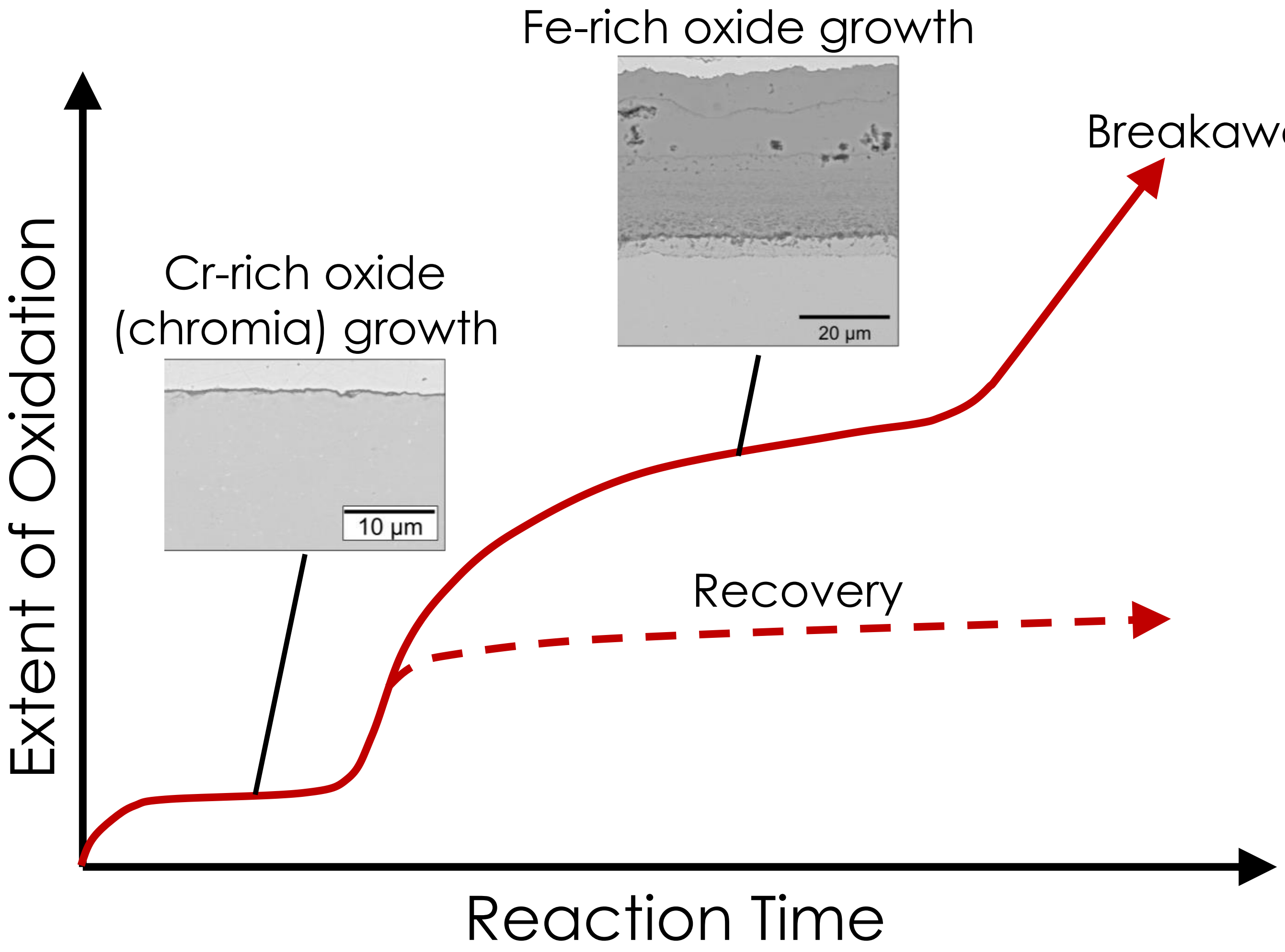
Modular design

- Expandable to large power plants

Thin metal sections present unique challenges for long-term oxidation.

Oxidation Regimes of Fe-Cr Steels

At High Temperatures, Cr-oxide is Required for Environmental Compatibility



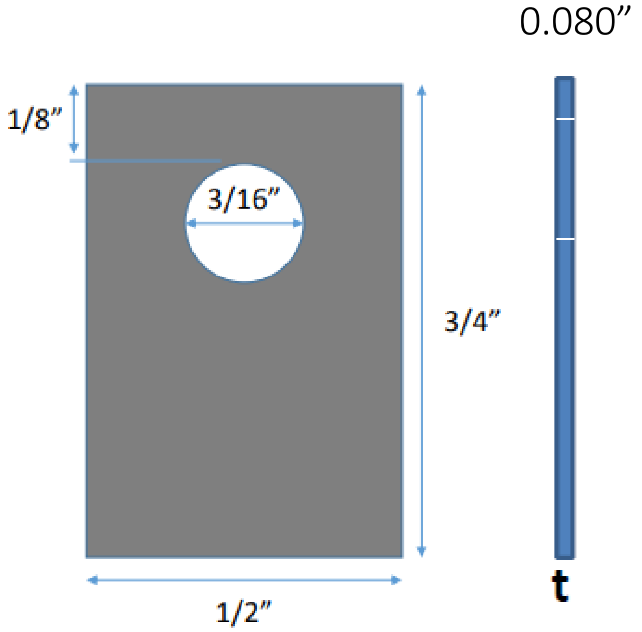
- Chromia-forming Fe-based and Ni-based alloys are leading candidates for sCO_2 power cycles
- Understanding factors that affect the formation and stability of chromia scales is important for successful materials selection

R.P. Oleksak, F. Rouillard, "Materials performance in CO_2 and supercritical CO_2" in Comprehensive Nuclear Materials 2nd edition, Elsevier (2020).

Materials

	Alloy	Fe	Ni	Cr	Co	Mo	W	Al	Si	Ti	Mn	Nb	C
Ferritic/ Martensitic Steels	Grade 22	95.5	0.2	2.3	-	0.9	-	0.03	0.2	-	0.5	-	0.1
	Grade 91	89.3	0.09	8.4	-	0.9	-	0.01	0.3	-	0.5	0.07	0.09
	E-Brite	71.6	0.2	26.5	0.02	1.0	-	0.1	0.3	-	0.04	0.1	0.01
Austenitic Steels	347H	70.1	9.0	17.3	0.1	0.4	-	-	0.3	-	1.9	0.5	0.05
	304H	70.6	8.3	18.7	0.2	0.1	0.01	0.01	0.4	-	1.1	0.01	0.07
	800	44.2	32.7	19.9	0.07	0.2	-	0.4	0.5	0.5	0.9	0.05	0.1
	309	60.5	13.5	23	-	-	-	-	.75	-	2.0	-	0.2
	310S	53.5	19.1	25.0	0.2	0.09	-	0.02	0.4	-	1.4	0.01	0.04

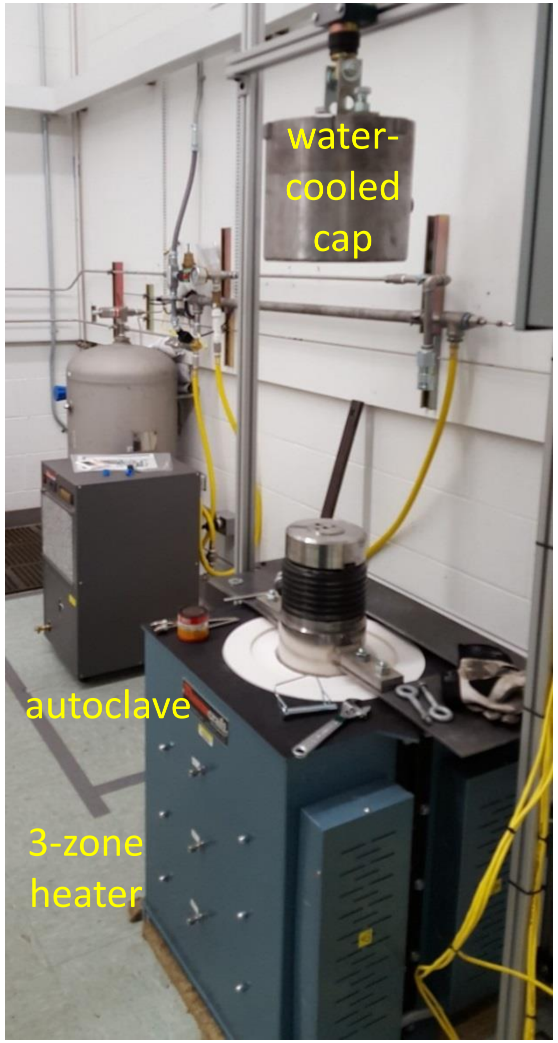
Increasing Cr content

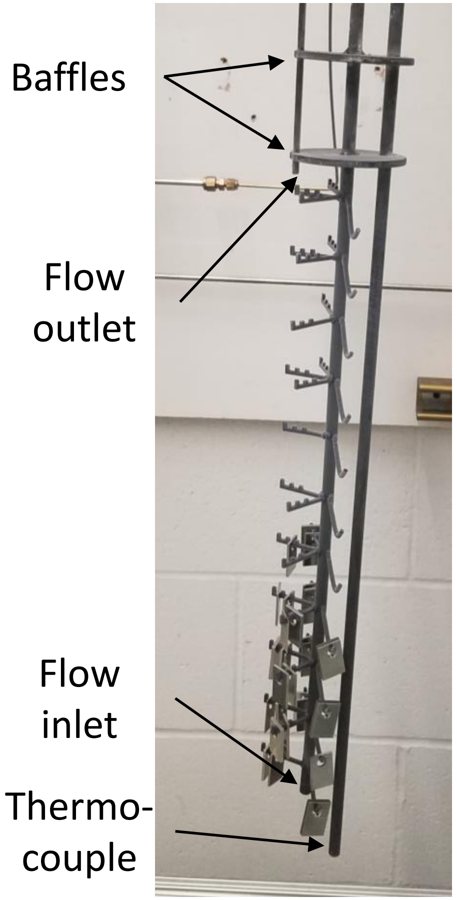


Commercially available alloy samples coupons were exposed to direct-fired conditions at 1 bar and 200 bar

Oxidation Exposures (200 bar)

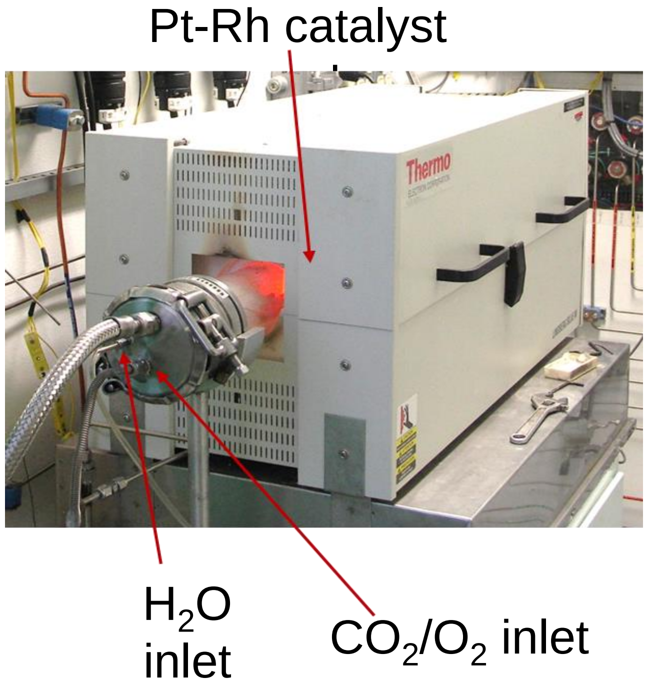
- Flow controlled with two high-pressure liquid pumps (CO_2, H_2O) and a pneumatically driven booster pump (O_2/Ar)
- Pressure controlled with a back pressure regulator
- Autoclave body made of H230
- Three zone furnace control for a flat temperature hot zone
- Fluid environment
  - 550 °C, 20 MPa
  - CO_2 (99.999% purity), 2.16 g/min
  - H_2O (DI, aerated), 0.037 g/min
  - 20 % O_2 in Ar (99.999% purity), 0.099 g/min
- Duration: 2,500 h (500-h increments)
- 10 cycles Ar backfill purging before heating
- Three replicates of each alloy

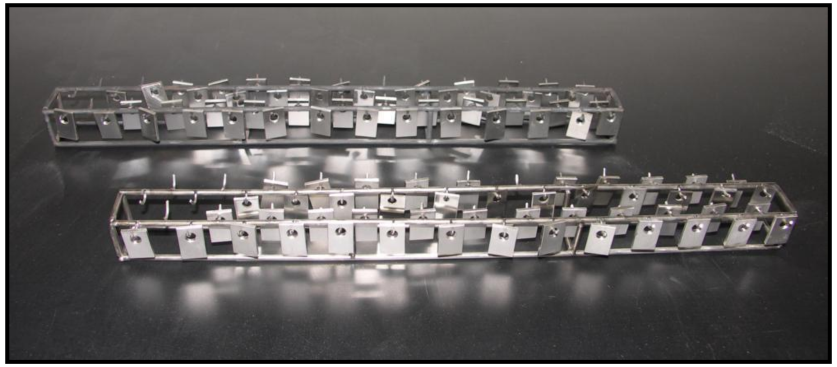




Oxidation Exposures (1 bar)

- Three zone furnace control for a flat temperature zone
- Gas: 0.1 MPa CO_2 (99.999% purity)
- Gas flow rate: 0.032 kg/h
- DI water injected via liquid pump
- Temperature: 550 °C
- Duration: 2,500/3,000 h (500-h increments)
- Three replicates of each alloy
- Overnight CO_2 purge flow before heating

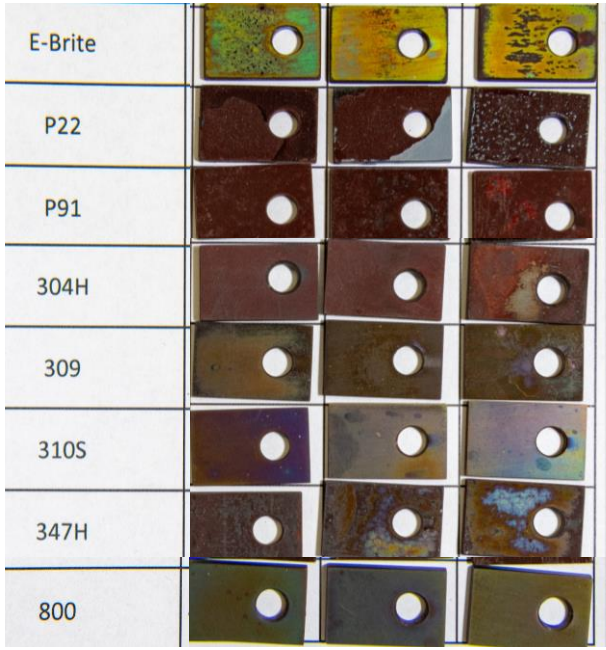




Surface Oxidation Appearances

1 bar (includes other alloys)

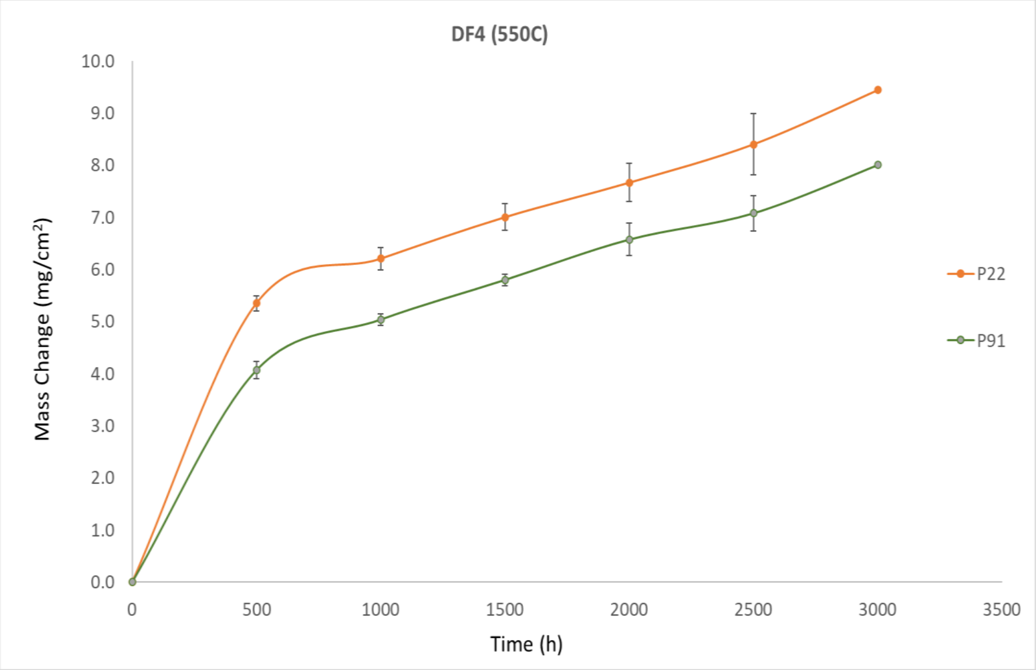
200 bar



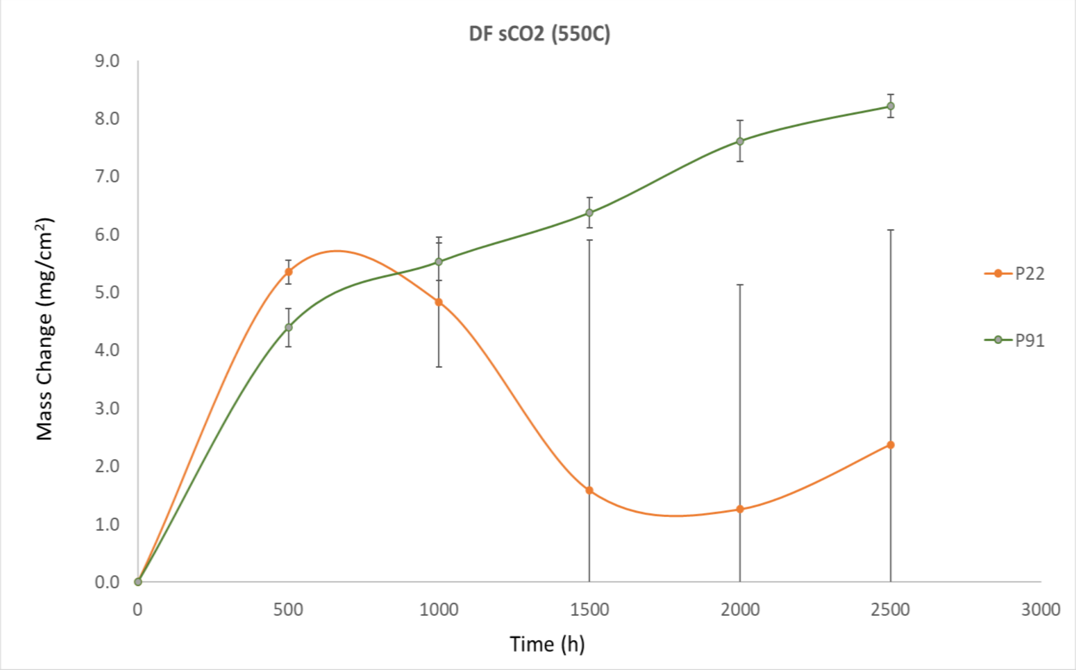
- Negligible visible oxide scale and variation between alloys at 1 bar
- Increased surface deposition observable at 200 bar
  - Evidence of spallation for P22, 304H, and 347H

Pressure Effect on Ferritic Steels

1 bar



200 bar



- P91 → similar mass gains at both pressures
- P22 → similar early mass gains, followed by indication of spallation at 200 bar

Oxidation of P91 Ferritic Steel

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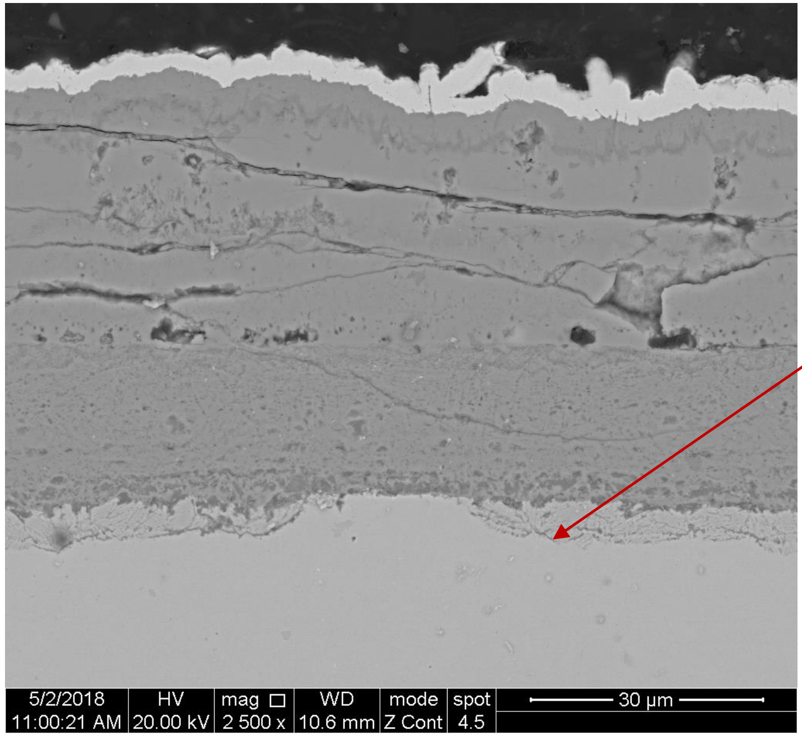
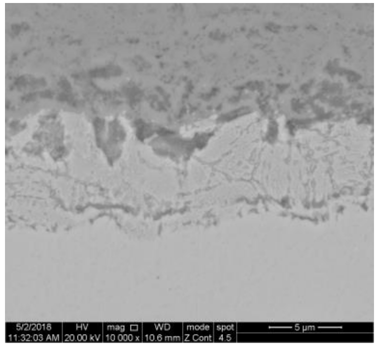
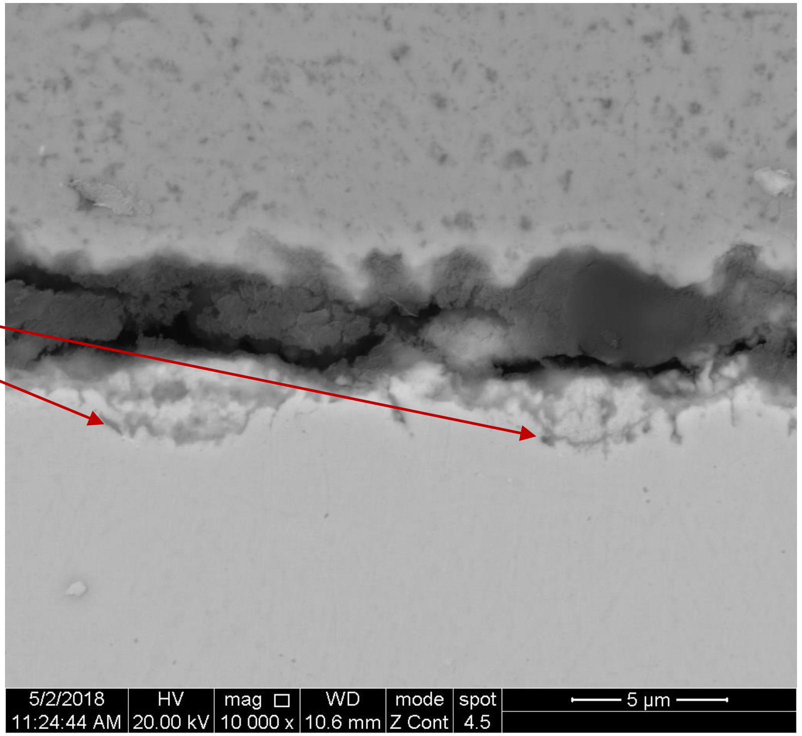
1 bar



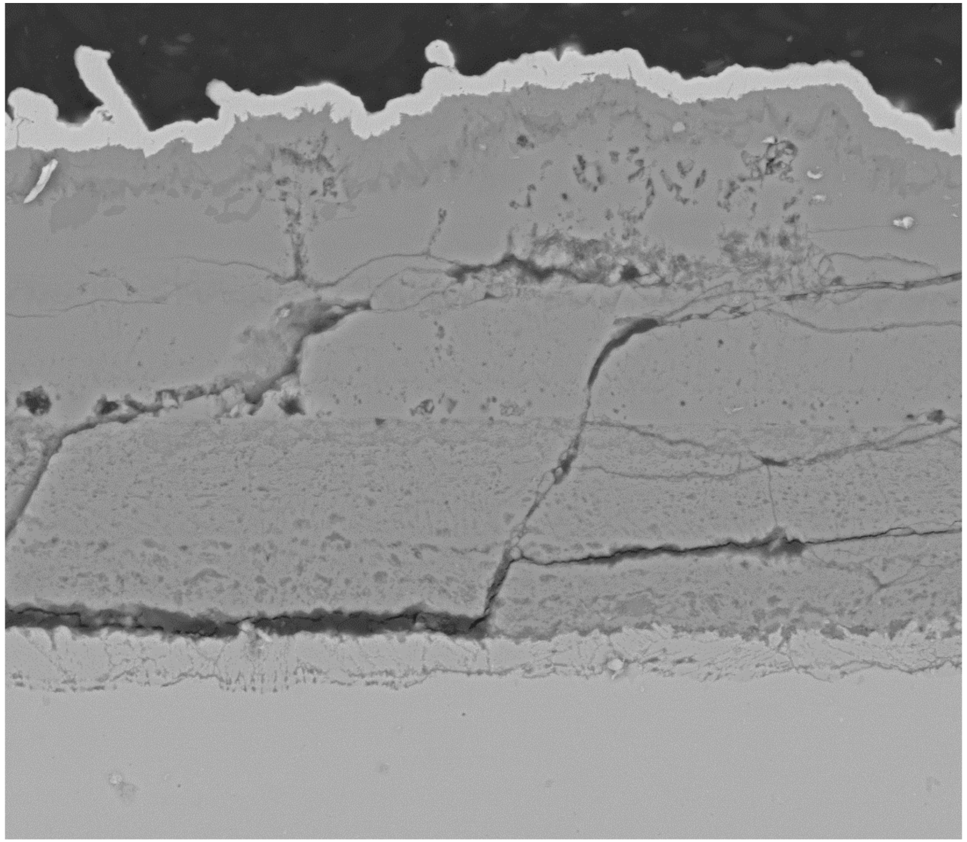
- Duplex oxide formation
  - Fe growth outward
  - Cr growth inward
- Periodic, small internal oxidation phase
  - At the oxide-metal interface



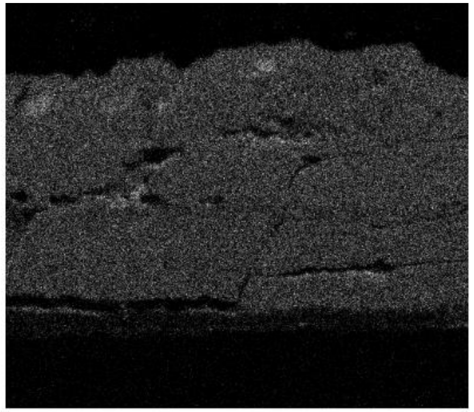


Elemental Mapping of P91 Ferritic Steel

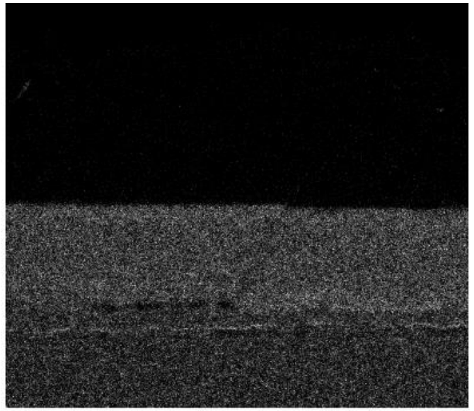
1 bar



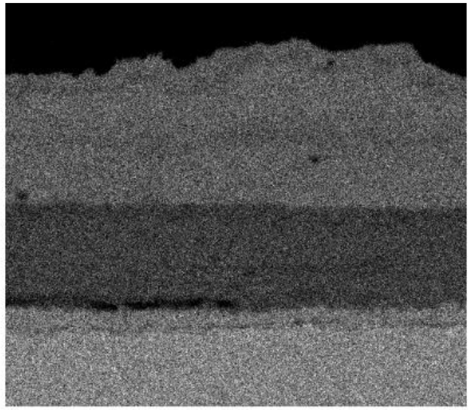
50µm Electron Image 1



O Ka1



Cr Ka1

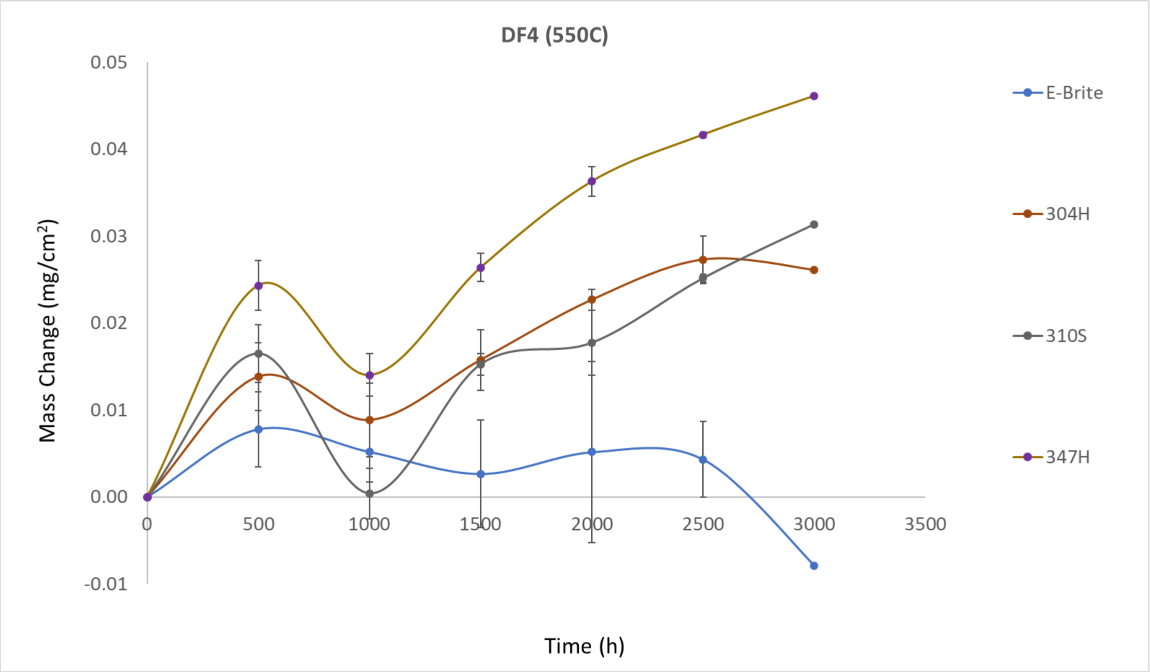


Fe Ka1

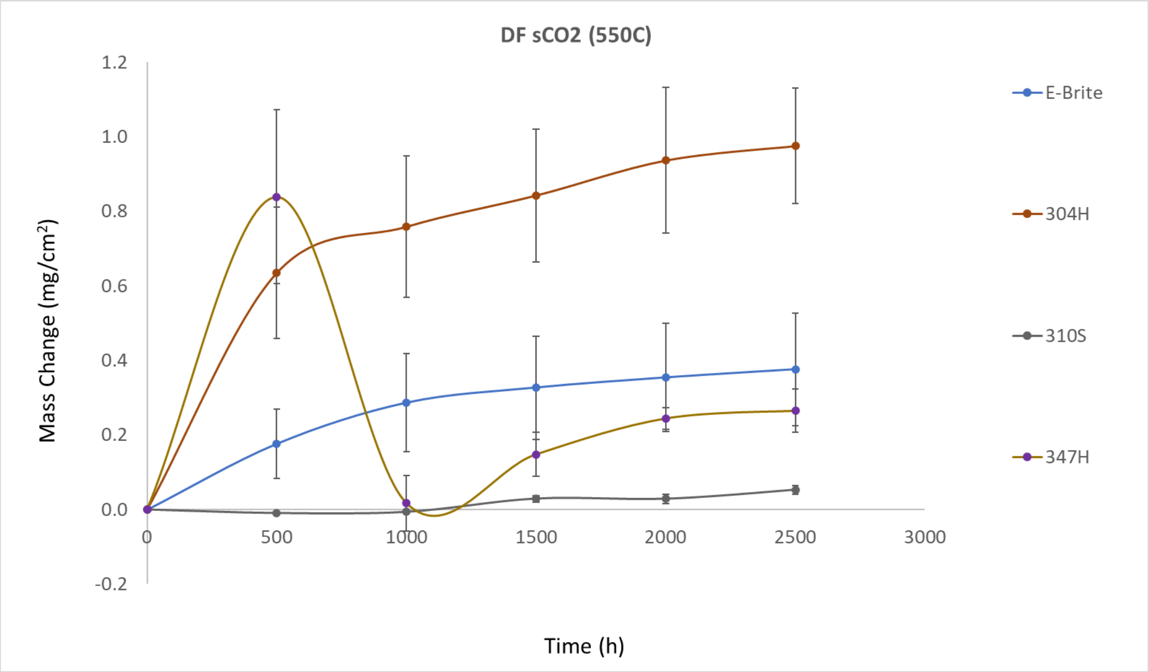
- Internal oxidation phase at interface appears Fe rich
- Thin Cr layer at the interface low boundary

Pressure Effect on Austenitic Steels

1 bar



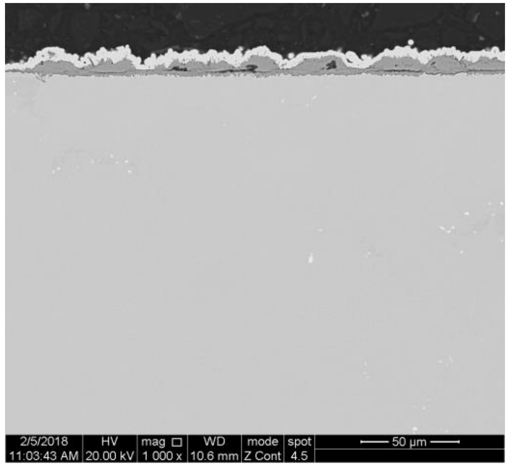
200 bar



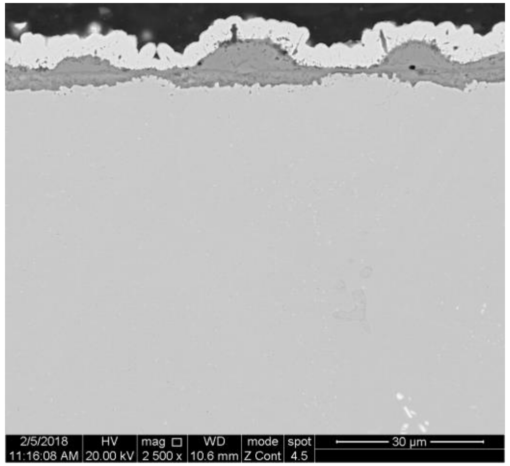
- Mass gains negligible at 1 bar, much higher at elevated pressure for all alloys except 310S (highest Cr content)
- Definite spallation for 347H at high pressure

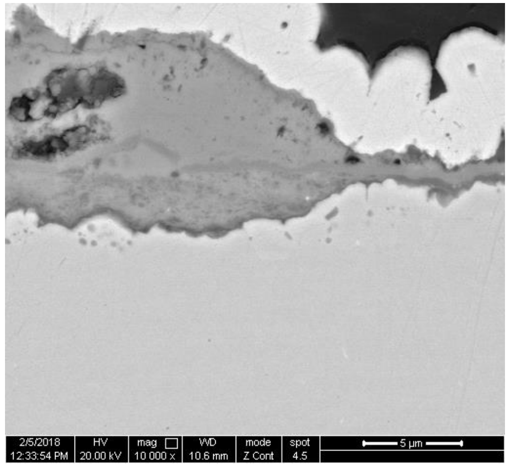
347H Oxidation

1 bar



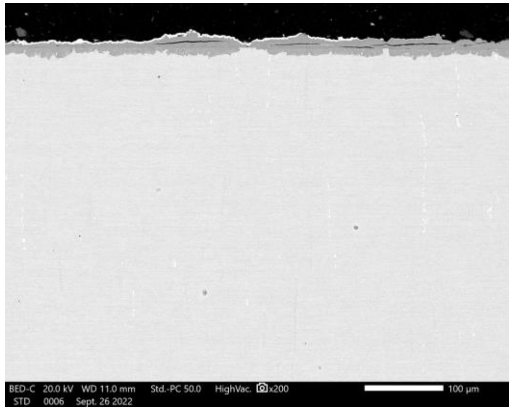
- Somewhat regular surface nodule formation
  - Appear to have duplex oxide structure
- Much thinner scales than for 200 bar
  - Compare mag scales

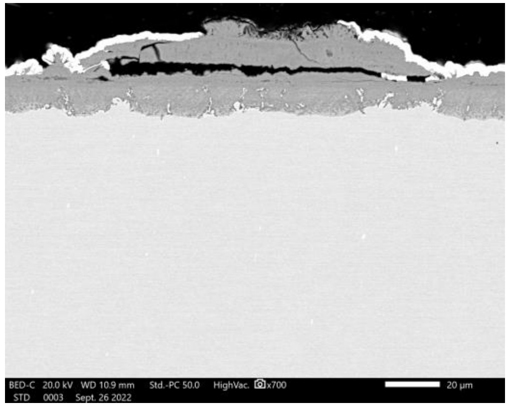


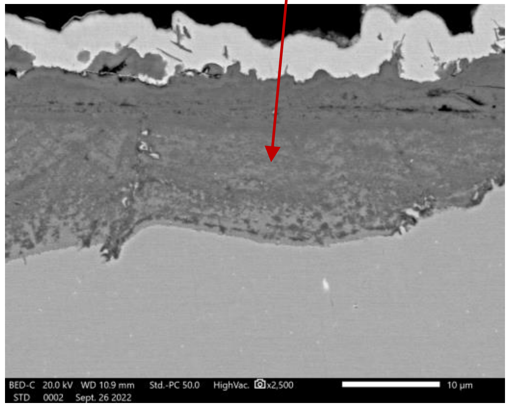


200 bar

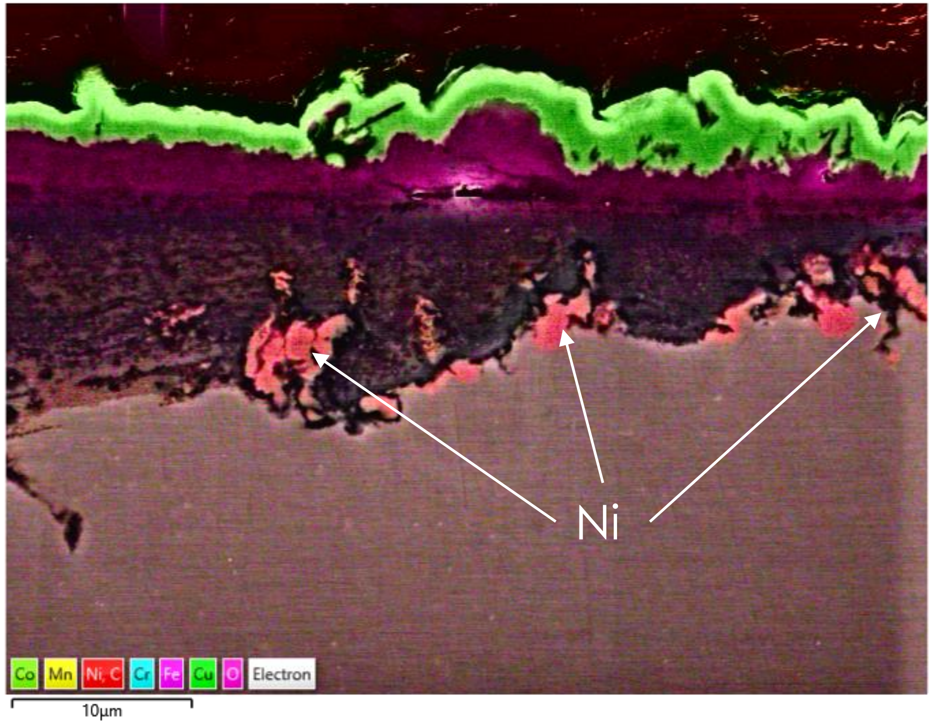
- Nodule formation not as frequent
- Much thicker scales
- Duplex oxide
  - Some phase mixing for inner oxide





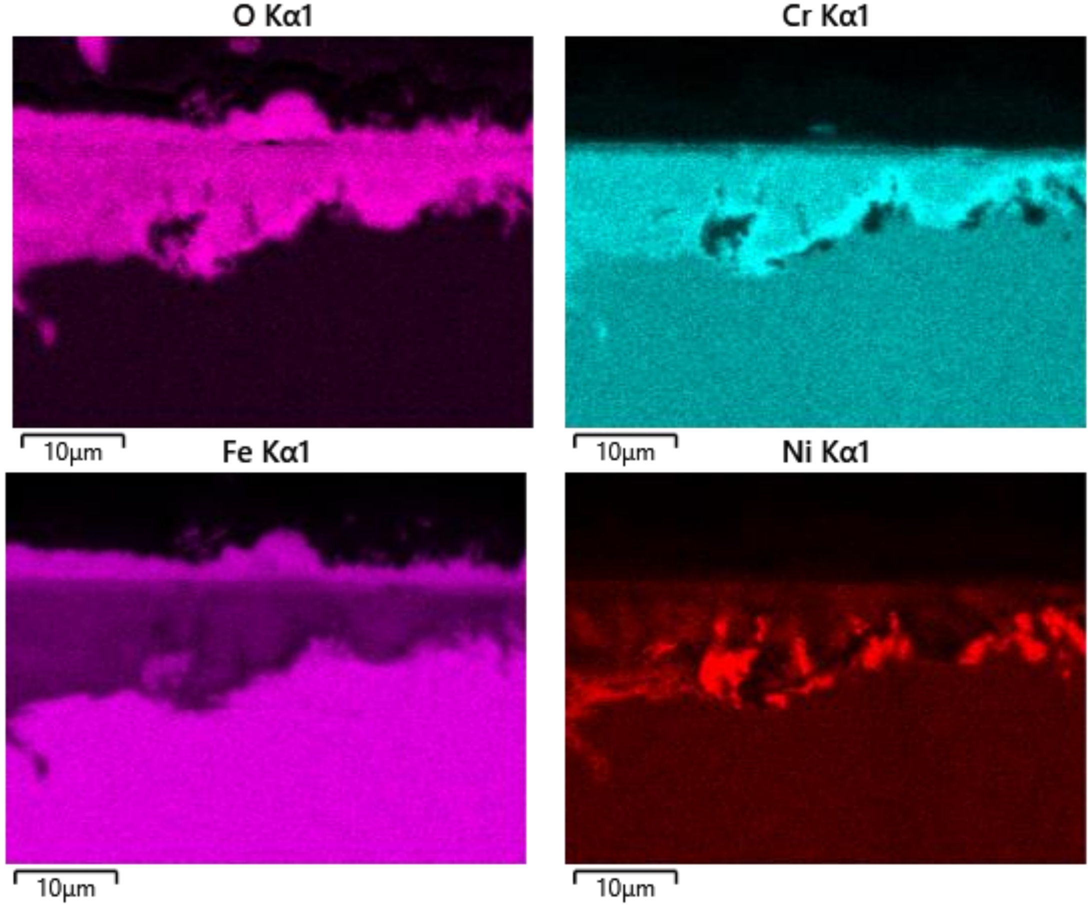


347H High Pressure Oxidation



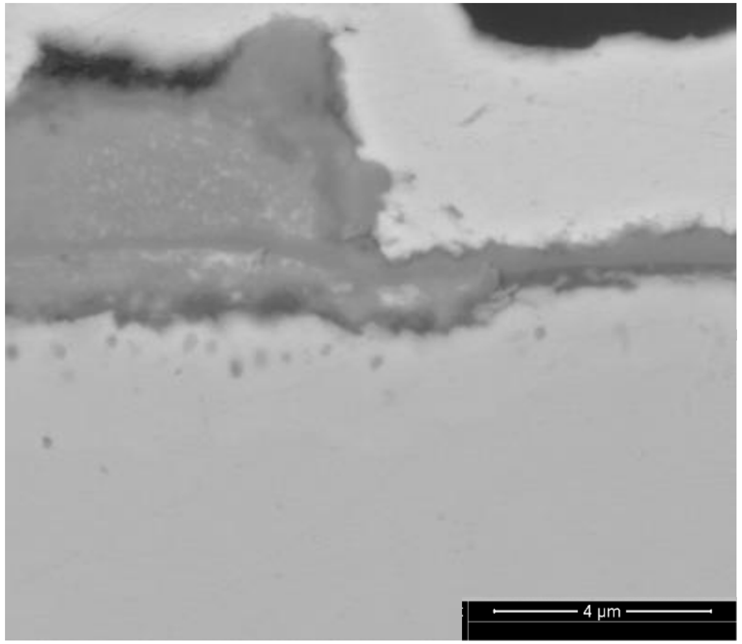
- Small, outward growing Fe-rich oxide phase
  - Periodic nodule formation
- Larger, inward growing Cr-rich phase
  - Oxide depth irregular
- Metallic Ni regions collected near the oxide-metal interface

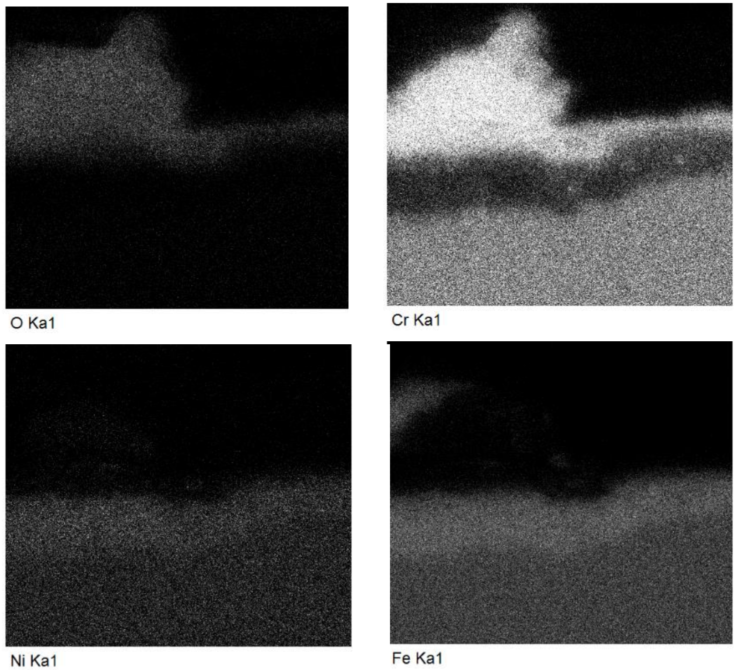
200 bar

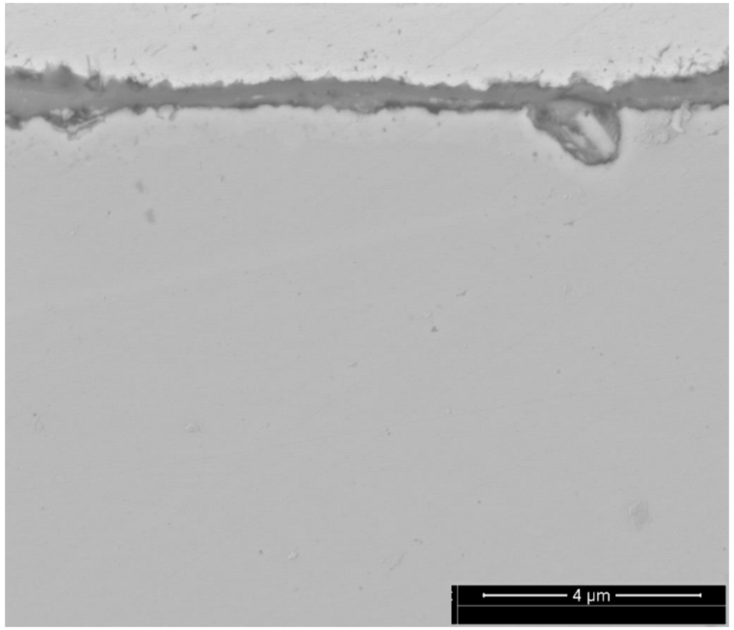


310 Oxidation

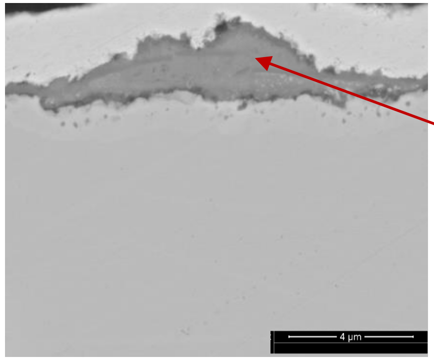
1 bar







- Protective Cr-rich outer oxide layer
  - Occasional nodules/humps still Cr-rich
- Inner oxide layer is Fe-rich
  - Potentially internal oxidation layer



- Oxide layer is mostly uniform
  - Nodule formation is rare

Conclusions

- Ferritic Steels
  - No protective oxide layer formed at 1 or 200 bar
  - Increased pressure had little effect on P22, but increased pressure induced spallation for P22
  - Thin Cr phase observed at the metal-oxide interface for P91

- Austenitic Steels
  - Protective oxide scales developed for all steels at 1 bar
    - Inner Fe-rich oxide phase formed in 310S
  - At 200 bar
    - 310S → minimal effect
    - E-Brite, 304H → protective scales developed, but total mass gains still higher
    - 347H → increase in mass gain and spallation inducement
      - Metallic Ni phases found at the oxide-metal interface
      - Thicker oxide scales, but more infrequent surface nodule formation

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