Identifying Cost-effective Steels for Direct-Fired sCO_2 Power Cycles

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Acknowledgements

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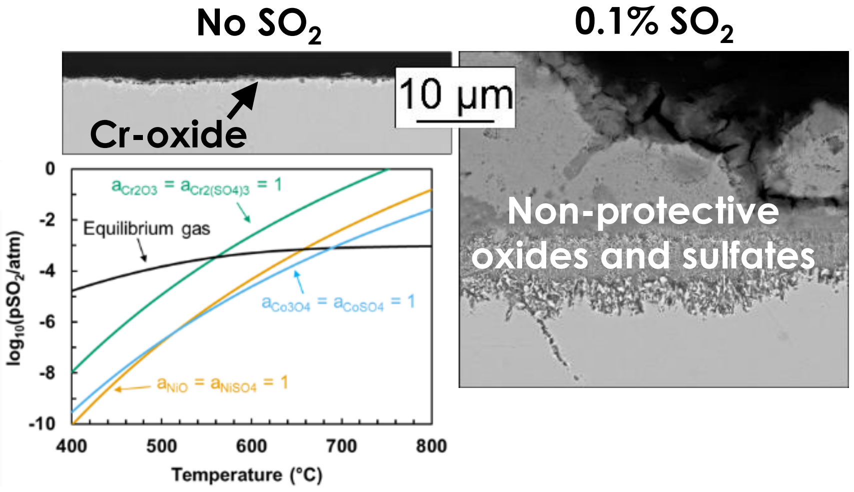
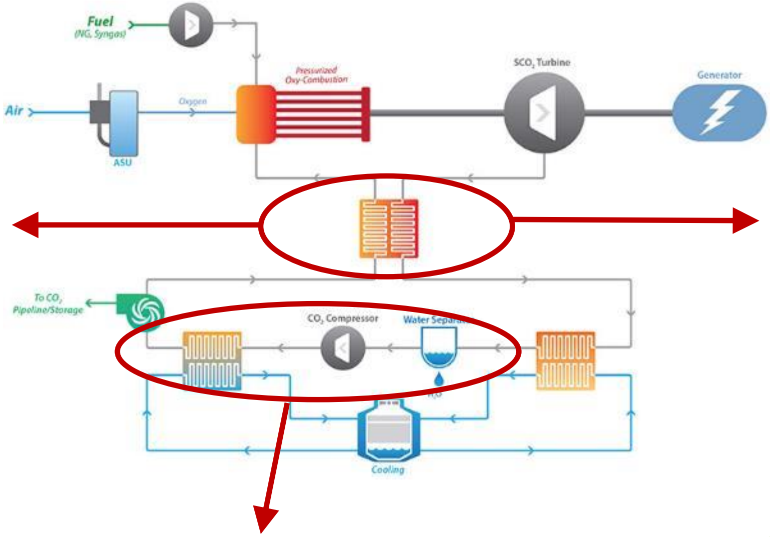
Disclaimer

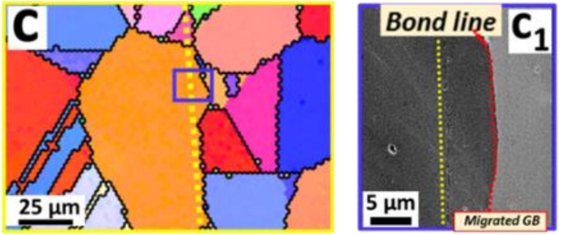
Overview of sCO_2 Materials Research at NETL

HIGH-TEMPERATURE OXIDATION OF ALLOYS

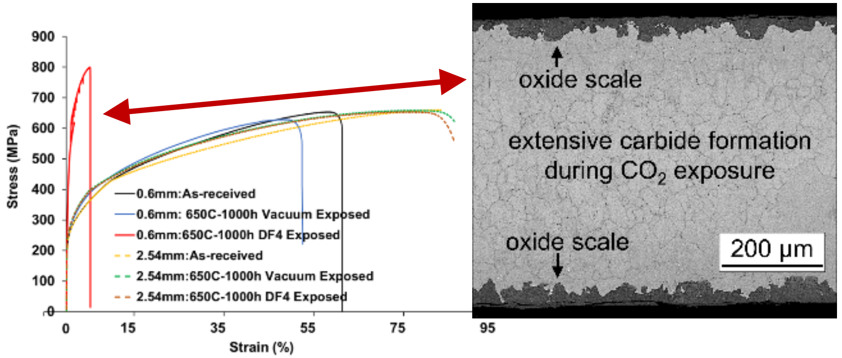




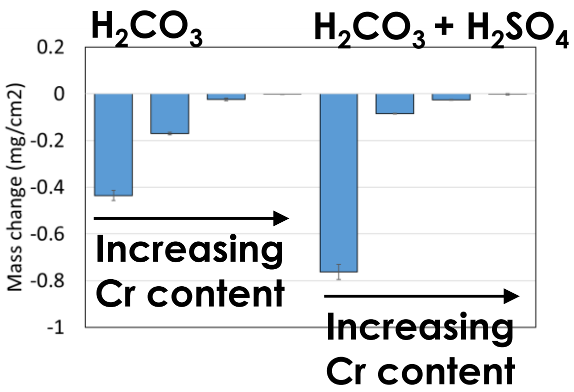
FABRICATION OF COMPACT HEAT EXCHANGERS



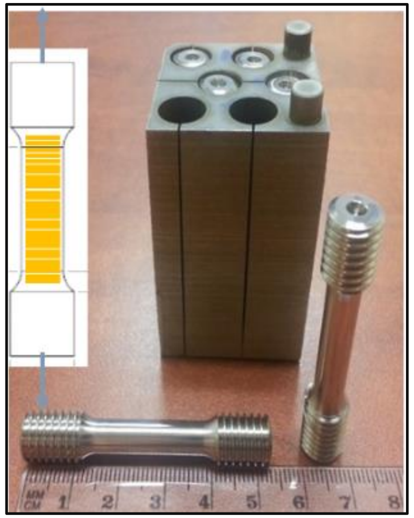
LINKING OXIDATION BEHAVIOR AND MECHANICAL DEGRADATION

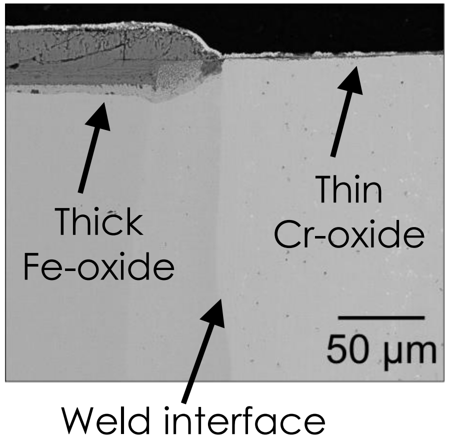


LOW-TEMPERATURE CORROSION OF ALLOYS



OXIDATION AND MECHANICAL PERFORMANCE OF JOINED STRUCTURES

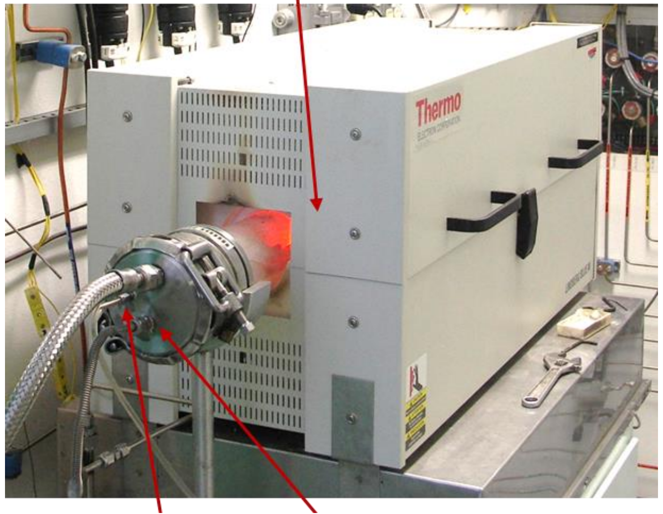




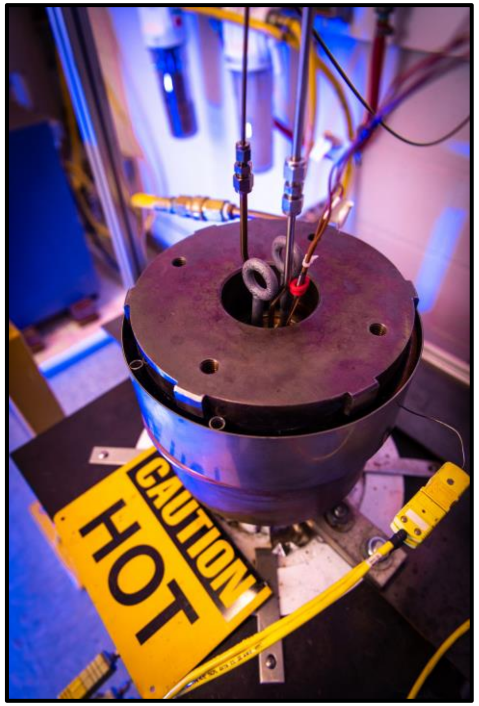
Simulating sCO_2 Power Cycle Environments at NETL

A Multifaceted Approach to Understand Alloy Degradation Behavior

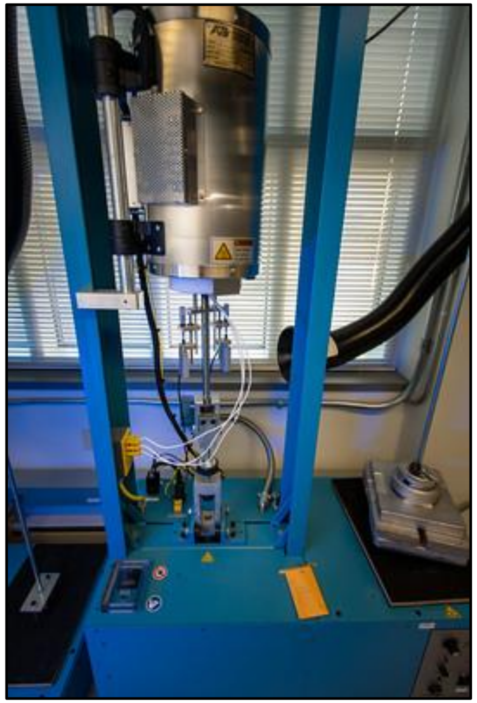
Tube furnace



High pressure flowing autoclave



Mechanical testing



Closely simulating sCO_2 power cycles is challenging:

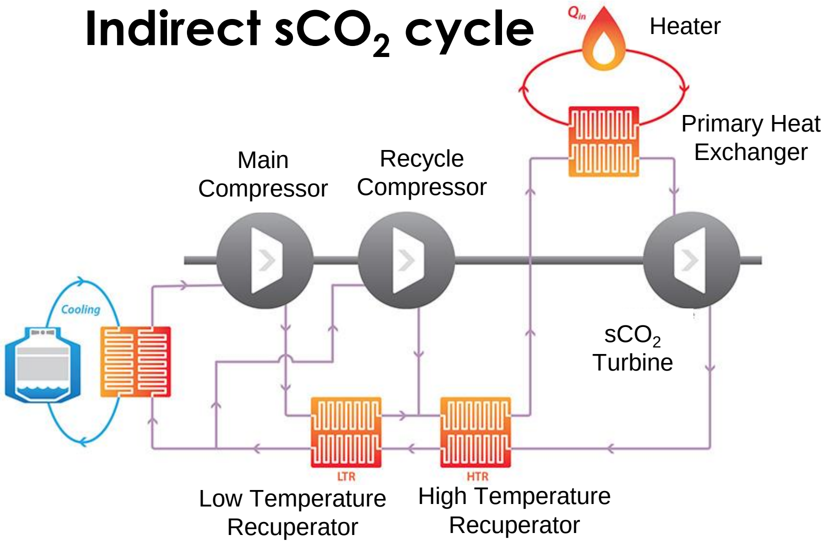
- High temperatures
- High pressures/stresses
- High flowrates
- Impurities in the CO_2

We have used different experiments to understand the effects of many of these variables to enable predictions of material performance in real sCO_2 power systems

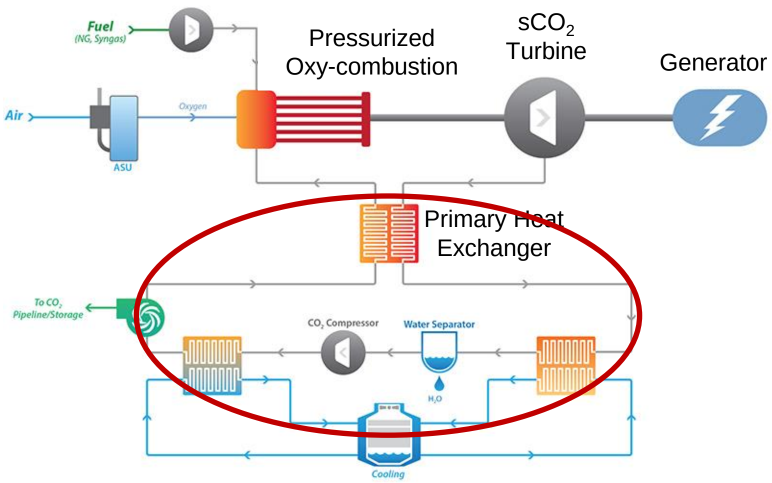
Direct-fired sCO$_2$ Cycles Generate Harsh Environments

Defining Anticipated Operating Conditions

Indirect sCO$_2$ cycle



Direct sCO$_2$ cycle



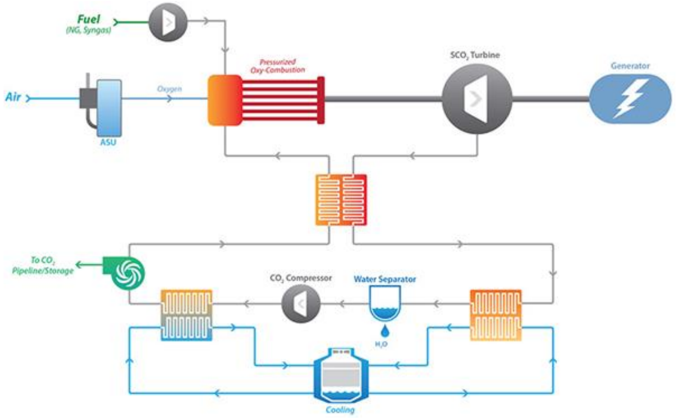
Cycle Type	Component	Inlet		Outlet		Fluid components
		T (°C)	P (MPa)	T (°C)	P (MPa)	
Indirect	Heater	450-535	1-10	650-750	1-10	High purity CO$_2$
	Turbine	650-750	20-30	550-650	8-10	
	HX	550-650	8-10	100-200	8-10	
Direct	Combustor	750	20-30	1150	20-30	CO$_2$ containing impurities (H$_2$O, O$_2$, SO$_2$, etc.)
	Turbine	1150	20-30	800	3-8	
	HX	800	3-8	100	3-8	

- Direct-fired cycle = semi-open loop of impure CO$_2$
- This work focuses on components seeing temperatures from ≈50 to 550 °C

Summary of Steel Testing Conditions

Simulating Intermediate-to-low Temperature Components in Direct-fired Cycles

Test Name	T (°C)	P (MPa)	Composition	Phase	Component Being Simulated
aCO_2	450	0.1	99.999% CO_2	Gas	Intermediate Temperature HX of Indirect Cycle
DF4	450	0.1	95%CO_2, 4%H_2O, 1%O_2	Gas	Intermediate Temperature HX of Natural Gas-Fired Direct Cycle
DF4S	450	0.1	95%CO_2, 4%H_2O, 1%O_2, 0.1%SO_2	Gas	Intermediate Temperature HX of Coal Syngas-Fired Direct Cycle
sDF4	550	20	95%CO_2, 4%H_2O, 1%O_2	Supercritical Fluid	Intermediate Temperature HX of Natural Gas-Fired Direct Cycle
Carbonic Acid	50	8	H_2O containing 0.05 mM H_2CO_3 and 1 mM O_2	Aqueous	Low Temperature HX and Water Separator of Natural Gas-Fired Direct Cycle
Carbonic/ Sulfuric Acid	50	8	H_2O containing 0.05 mM H_2CO_3, 0.5 mM H_2SO_4, 1 mM O_2	Aqueous	Low Temperature HX and Water Separator of Coal Syngas-Fired Direct Cycle

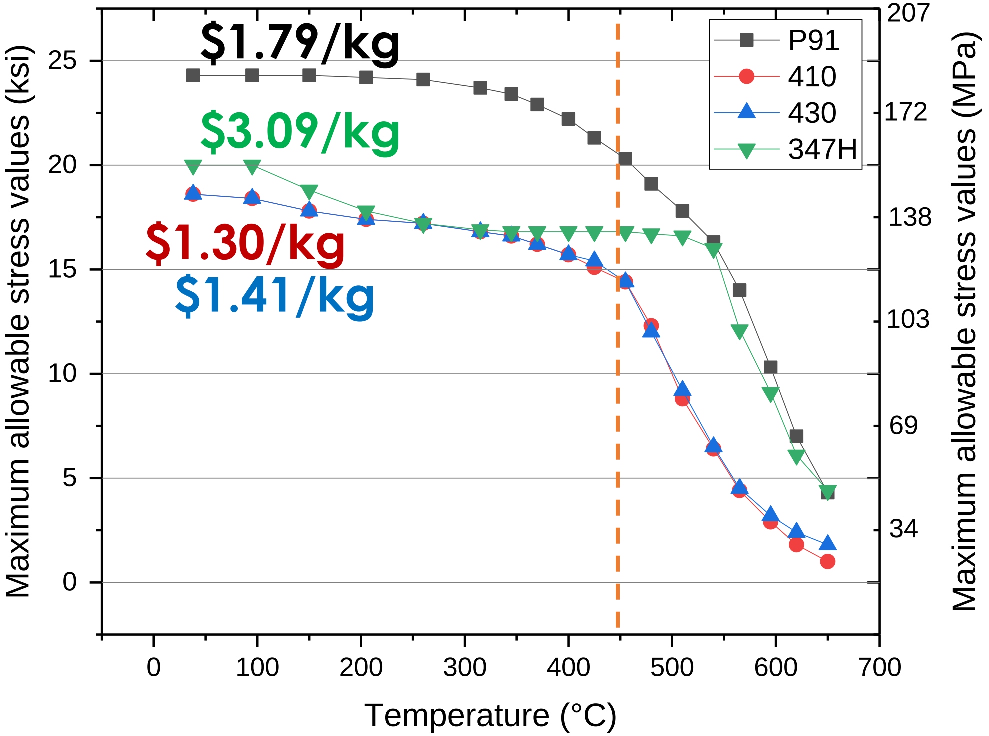


- Several exposure tests were used to simulate conditions relevant to direct-fired cycles:
- Atmospheric pressure testing with/without impurities at 450 °C
- High pressure (supercritical) testing with impurities at 550 °C
- Low temperature (50 °C) testing in acidic environments

Candidate Steels Used for Testing

Trade-off of Performance and Cost

	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
	JMP3	83.2	-	9.6	-	-	-	-	-	-	-	-	-
	JMP4	82.7	-	10.1	-	-	-	-	-	-	-	-	-
	SAVE 12	82.8	-	10.5	2.9	-	2.9	-	0.2	-	0.5	0.07	0.1
	409	86.8	0.3	11.5	0.03	0.02	-	0.1	0.4	0.2	0.4	0.01	0.08
	410	86.9	0.4	11.8	-	0.04	-	0.01	0.4	-	0.4	-	0.1
	420	86.0	0.4	12.4	0.02	0.09	0.02	0.05	0.3	0.01	0.5	0.01	0.2
	416	85.5	0.3	12.5	0.02	0.2	0.01	0.01	0.2	0.01	1.1	0.01	0.1
	L80	85.7	0.3	13.1	0.02	-	0.02	0.01	0.2	0.01	0.4	0.01	0.2
	430	82.5	0.3	16.3	-	0.05	-	-	0.4	-	0.4	-	0.04
	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
	309H	62.9	12.2	22.3	0.2	0.4	-	0.01	0.3	0.01	1.6	-	0.06
	310S	53.5	19.1	25.0	0.2	0.09	-	0.02	0.4	-	1.4	0.01	0.04



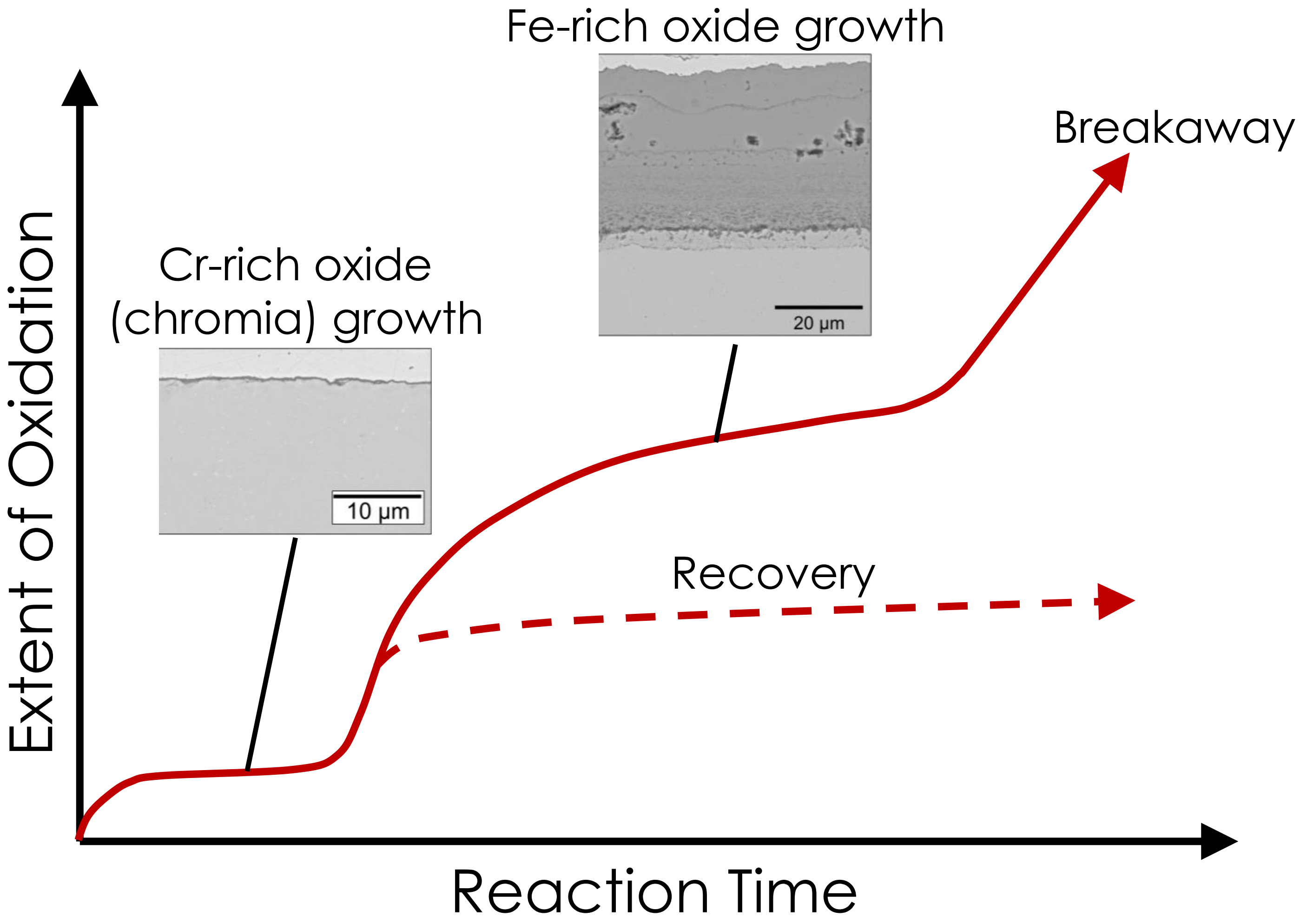

Exposure samples

Important considerations include:

- Strength (max-use temperature)
- Cr content (environmental resistance)
- Ni content ($)

Oxidation Regimes of Fe-Cr Steels in Hot CO_2

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

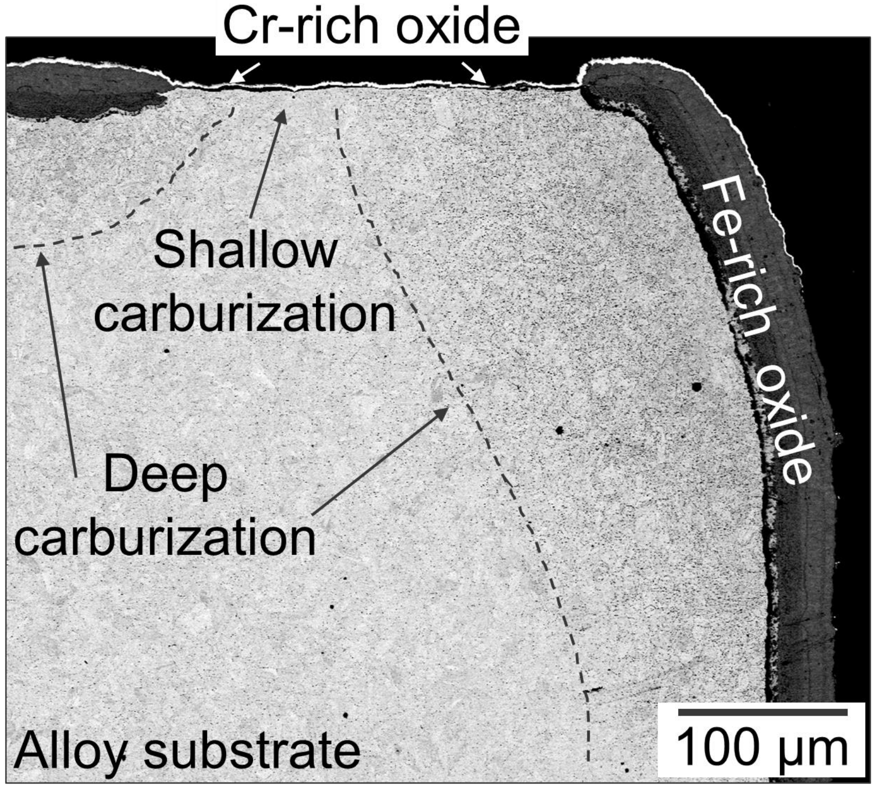


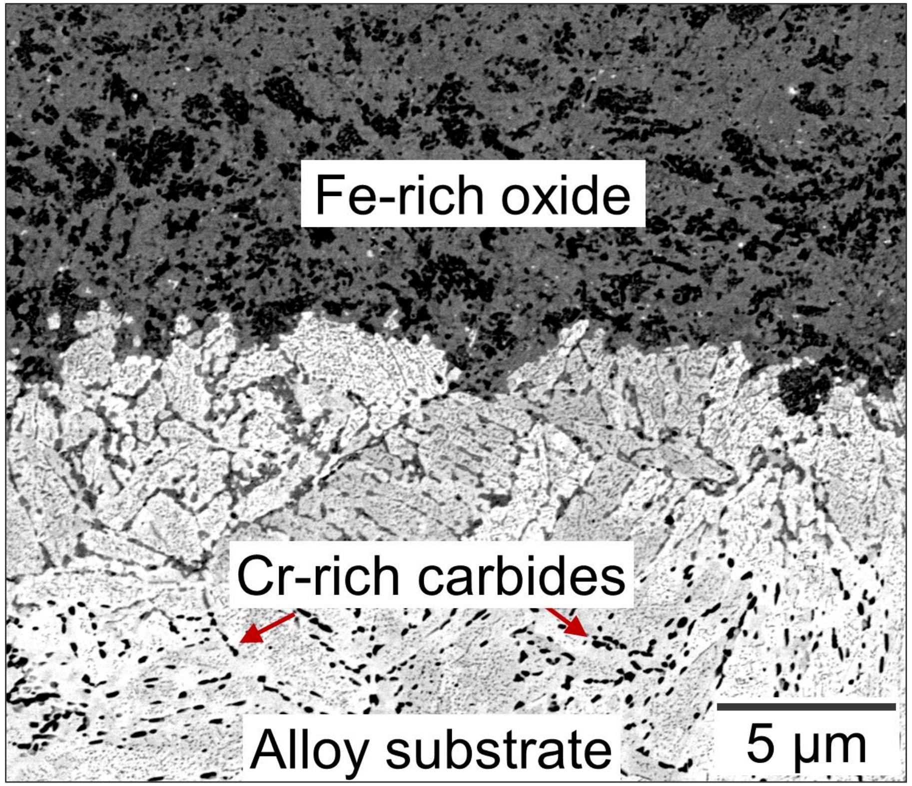
- Chromia-forming steels are typical candidates for sCO_2 power cycles
- Understanding the factors (temperature, impurities, pressure, …) that affect the formation and stability of chromia scales is important for successful materials selection

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

Fe-rich Oxide Scales Are Not "Protective"

Grade 91 (9 wt% Cr) Steel Exposed to CO_2 at 550 °C and 1 atm for 1,500 Hours



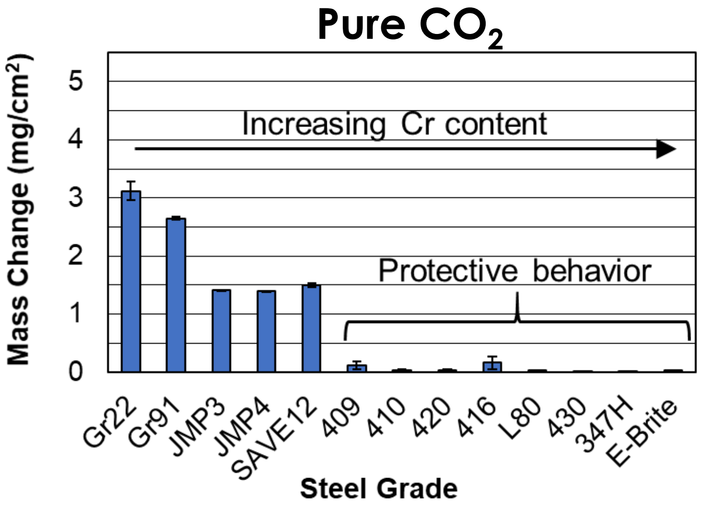


- Fe-oxide grows much faster than Cr-oxide and is significantly more permeable to carbon
- Carbon diffuses into the steel, depletes metallic Cr (reducing long-term oxidation resistance) and compromises mechanical properties

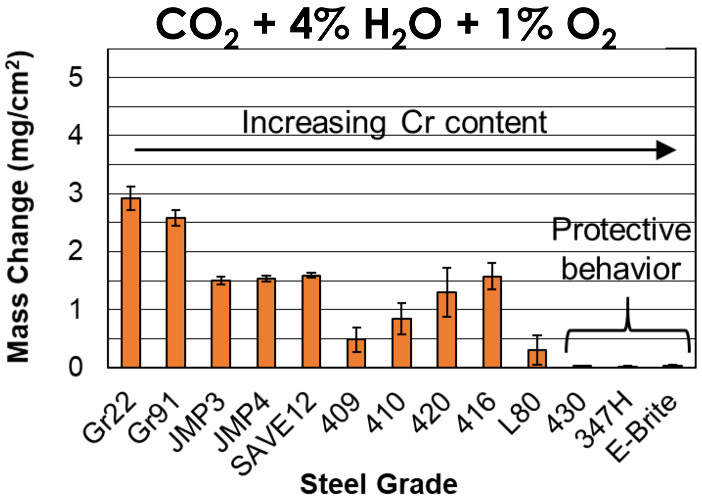
R.P. Oleksak, G.R. Holcomb, C.S. Carney, L. Teeter, O.N. Dogan, "Effect of surface finish on high-temperature oxidation of steels in CO2, supercritical CO2, and air," Oxidation of Metals **92** (2019).

Effect of Impurities on Steel Oxidation

Atmospheric Pressure Testing in CO_2-rich gases at 450 °C

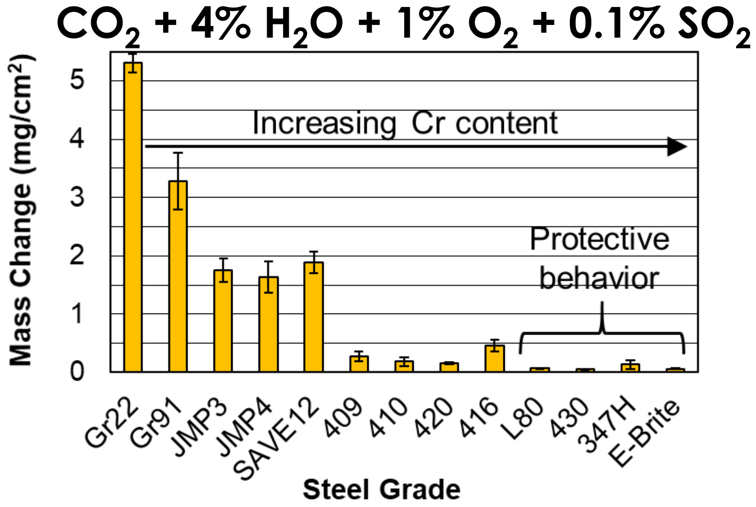


Pure CO_2

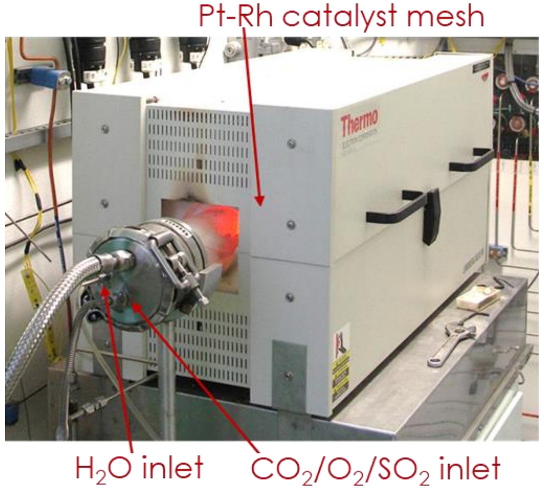


CO_2 + 4% H_2O + 1% O_2

- Clear transition from high to low mass gains in pure CO_2 when steel contains ≥11.5 wt% Cr
- Adding 4% H_2O, 1% O_2, 0.1% SO_2 increases this value to ≥16.3 wt% Cr (without SO_2) and ≥13.1 wt% Cr (with SO_2)

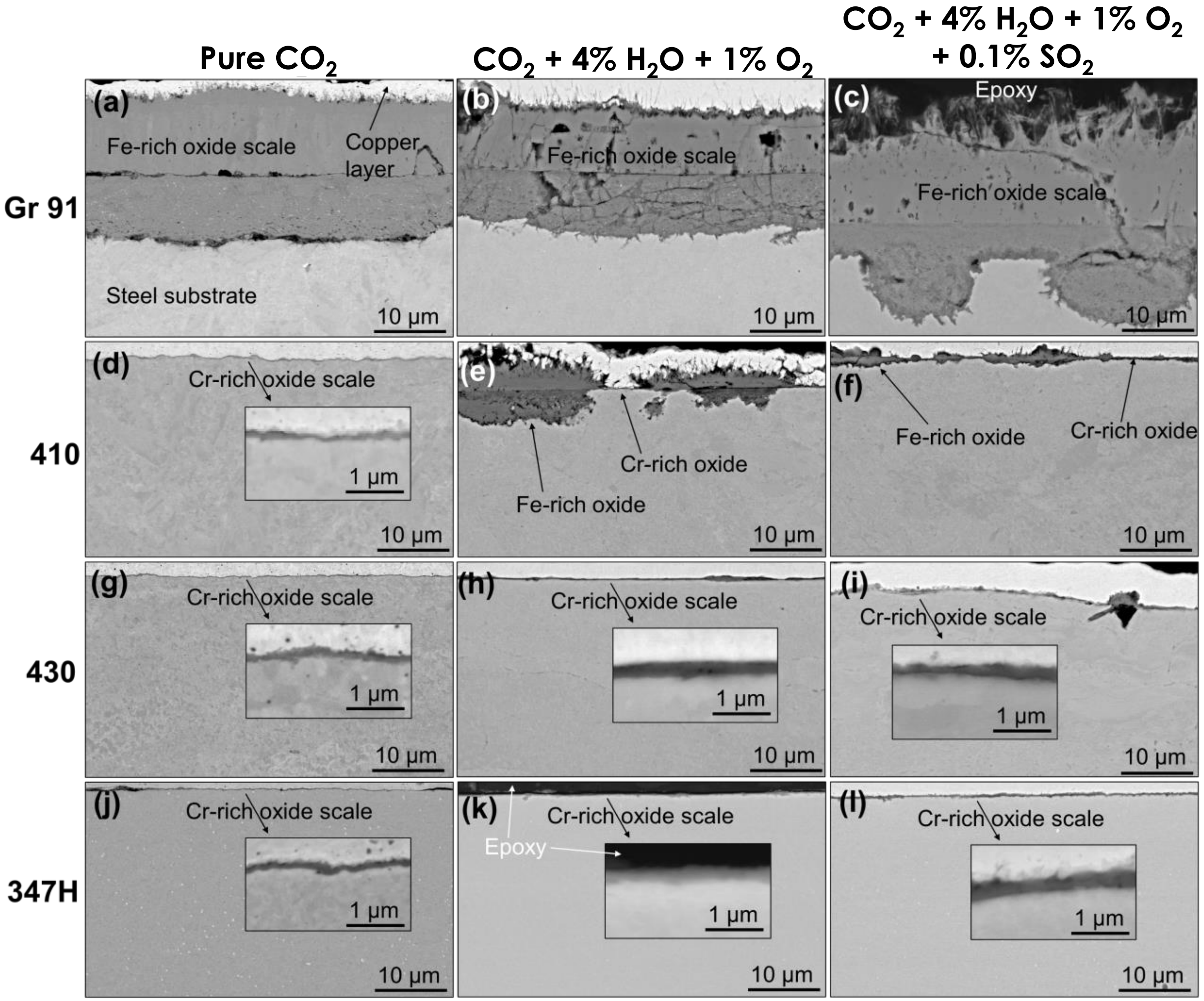


CO_2 + 4% H_2O + 1% O_2 + 0.1% SO_2



Visualizing Oxide Scales

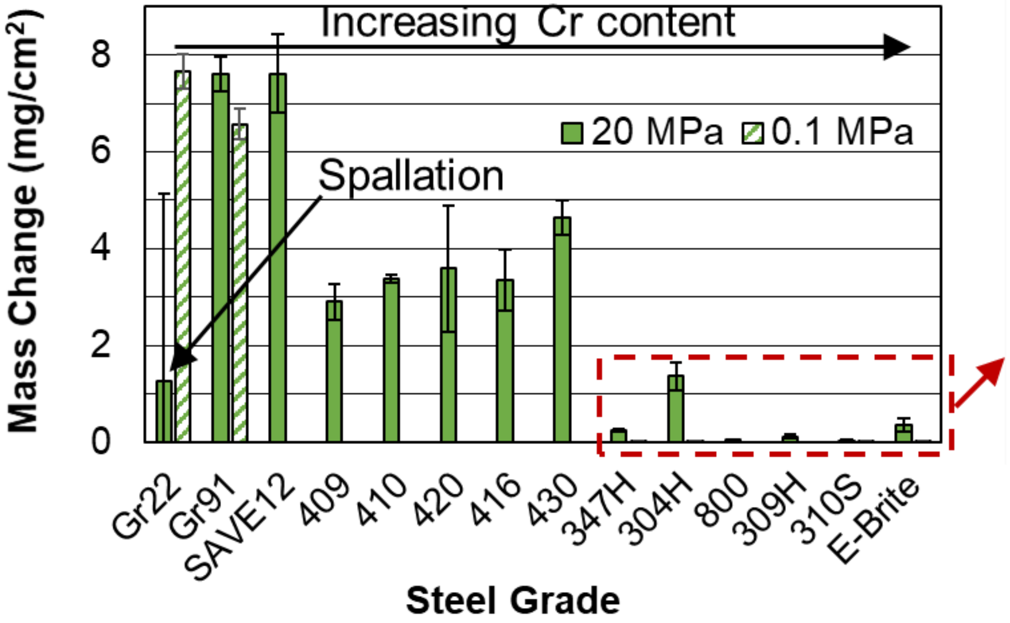
Cross-sectional SEM of Steels After Atmospheric Pressure Testing in CO_2-rich gases at 450 °C

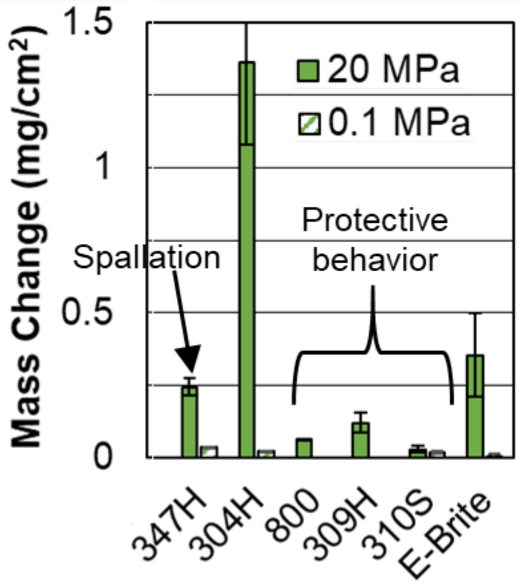


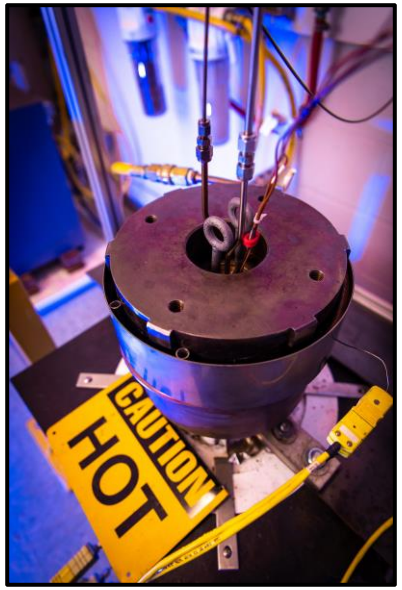
- SEM confirms the oxide scales expected from mass gains:
  - Low mass gains = thin Cr-oxide
  - High mass gains = thick Fe-oxide
- More Cr is required to form Cr-oxide when 4% H_2O and 1% O_2 impurities are present in the gas
- 0.1% SO_2 slightly improves the situation at 450 °C (reduced Fe-oxide formation for “borderline” Cr-oxide formers)
- 430 (16Cr-0.3Ni steel) shows similar performance as 347H (18Cr-10Ni steel)

Combined Effect of Impurities and Pressure

High Pressure (Supercritical) Testing in CO_2 + 4% H_2O + 1% O_2 at 550 °C and 20 MPa







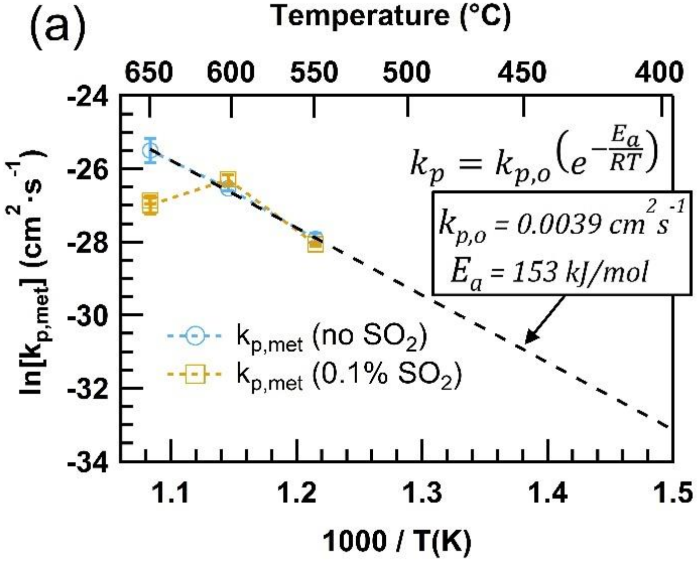
- Comparison to prior atmospheric-pressure testing at 550 °C shows a strong (negative) effect of pressure

- Only steels with ≥19.9 wt% Cr appear protective. Sample characterization is planned to better understand this behavior

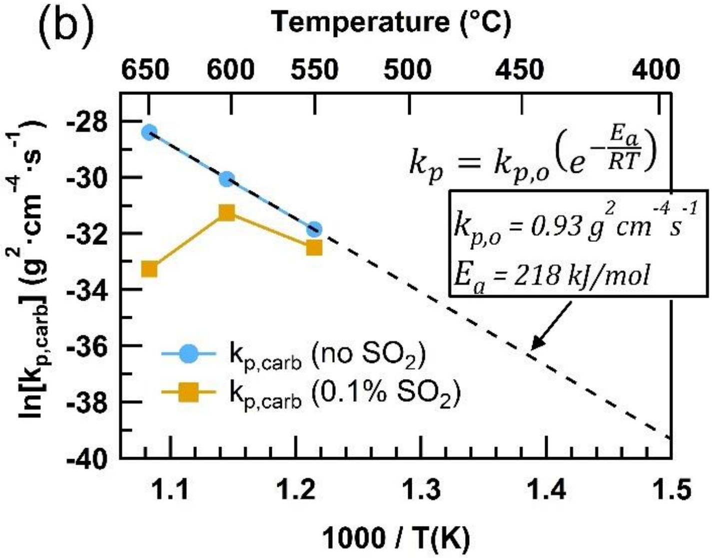
Establishing Temperature-dependence of Degradation

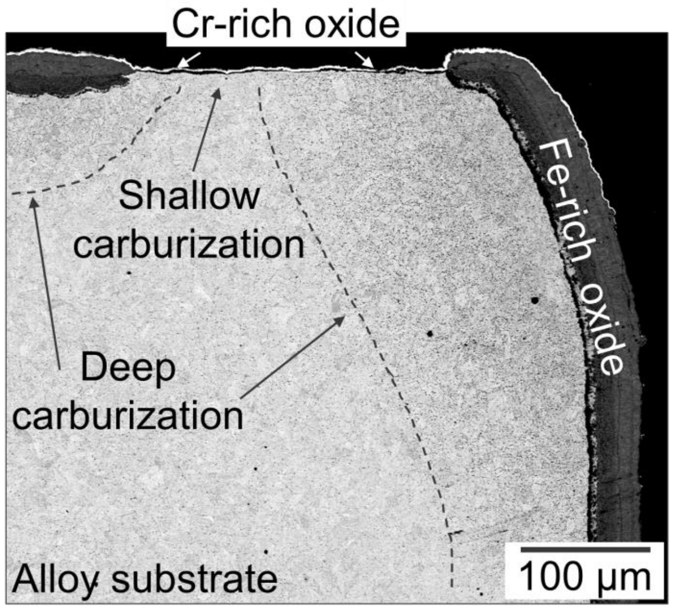
Grade 91 Steel Tested in CO_2 + 4% H_2O + 1% O_2 (+ 0.1% SO_2) at 550, 600, 650 °C and 0.1 MPa

Oxidation (Metal Recession)



Carburization (Total C Uptake)



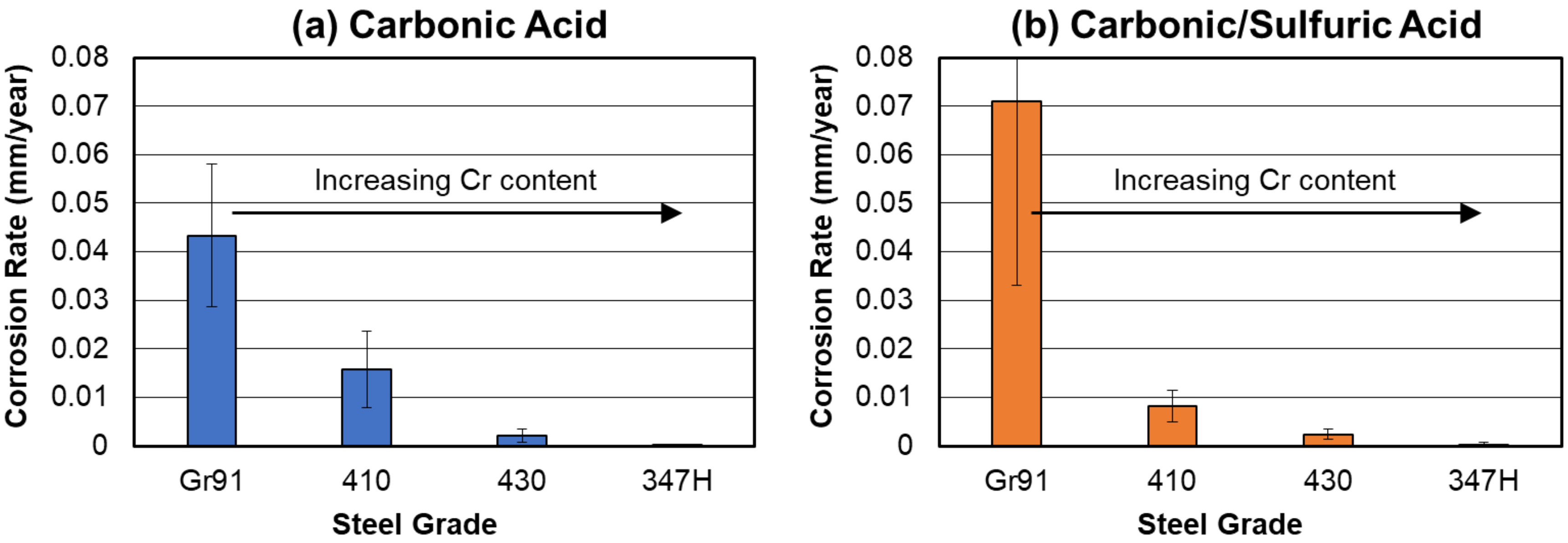


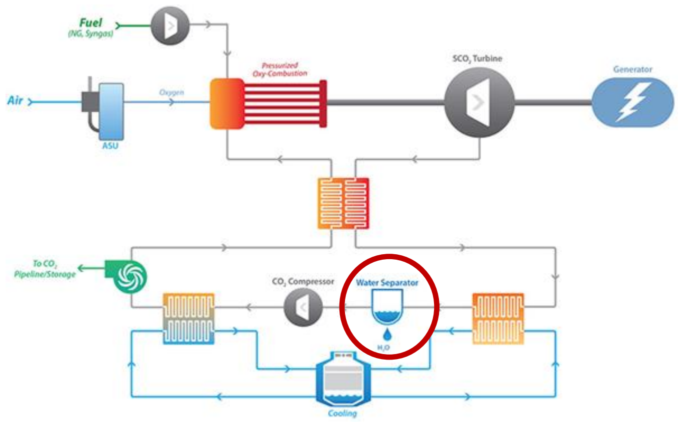
- In the natural gas-fired (SO_2-free) case both oxidation (metal recession) and carburization (total carbon uptake by the steel) follow a clear temperature dependence
- This information is useful for establishing a maximum use temperature for a given steel and component geometry

R.P. Oleksak, J.H. Tylczak, O.N. Dogan, “Temperature-dependence of oxidation and carburization of Grade 91 steel in CO2 containing impurities,” Corrosion Science **198** (2022).

Steel Performance in Low-T Aqueous Environments

Corrosion behavior in carbonic and carbonic/sulfuric acid at 50 °C and 8 MPa





- Corrosion rates show a clear dependence on Cr content of the steel
- Minimal difference in corrosion rates with/without dilute sulfuric acid additions
- 430 (16Cr-0.3Ni steel) shows corrosion rates similar to 347H (18Cr-10Ni steel)

Summary and Conclusions

- For the past six years, NETL has been evaluating materials in sCO_2 power cycle environments. One recent focus is identifying cost-effective steels that can be used at low/intermediate temperatures
- Impurities (H_2O, O_2, SO_2) and pressure both affect the critical Cr content needed to form a protective oxide scale, which is required at high temperatures (>450 °C)
- At lower temperatures Cr-oxide formation may not be required—In this case understanding temperature-dependence of degradation rates can help to establish max-use temperatures
- 400-series steels with high Cr content (e.g., 430) may represent a cost-effective alternative to 18Cr-10Ni steels (e.g., 316, 347) up to their max-use temperatures (≈450 °C), including in low-T aqueous environments
- At somewhat higher temperatures (≈550 °C) austenitic steels with high Cr and relatively low Ni (e.g., 309) may represent an optimal trade-off of performance and cost

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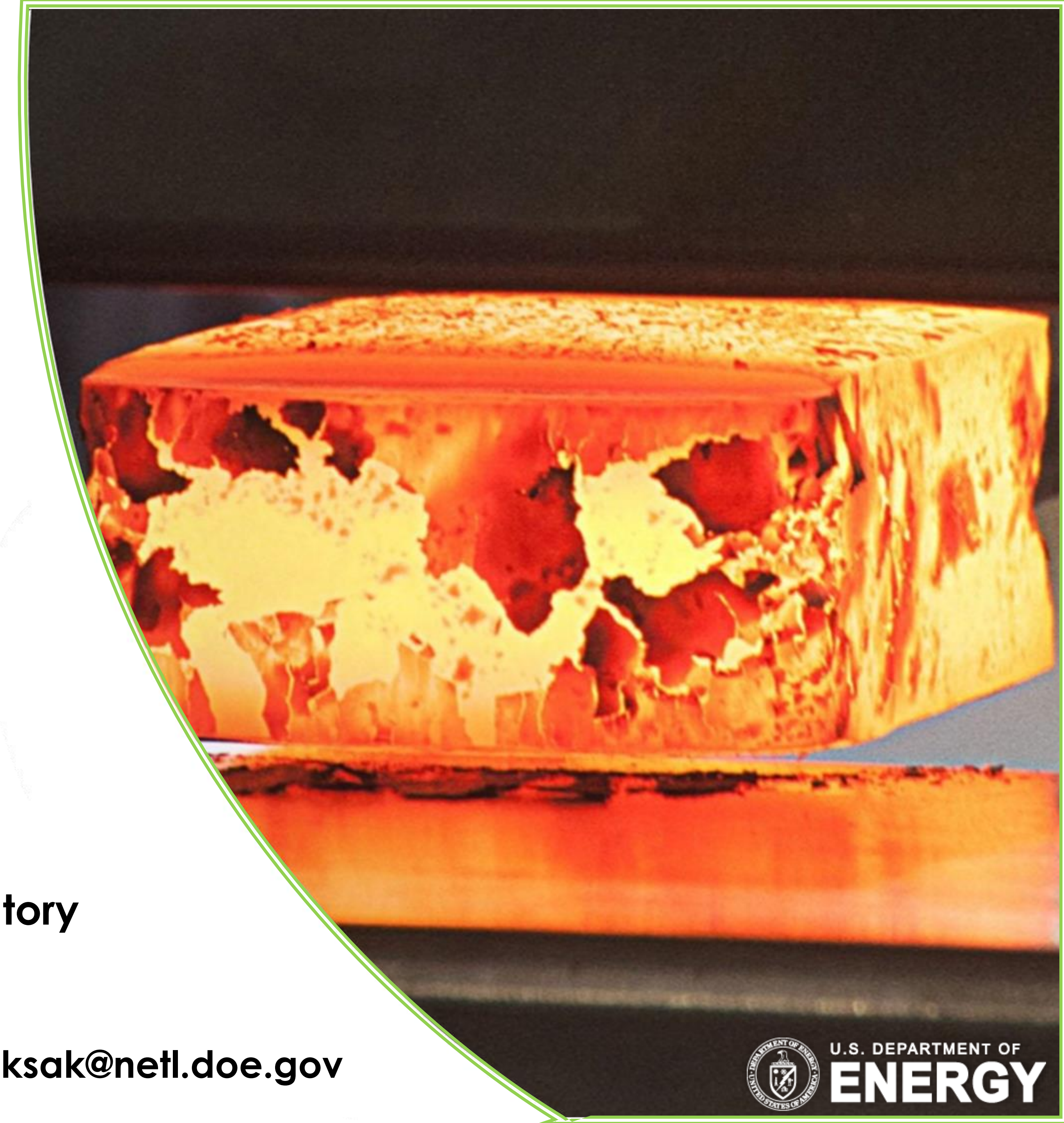

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