

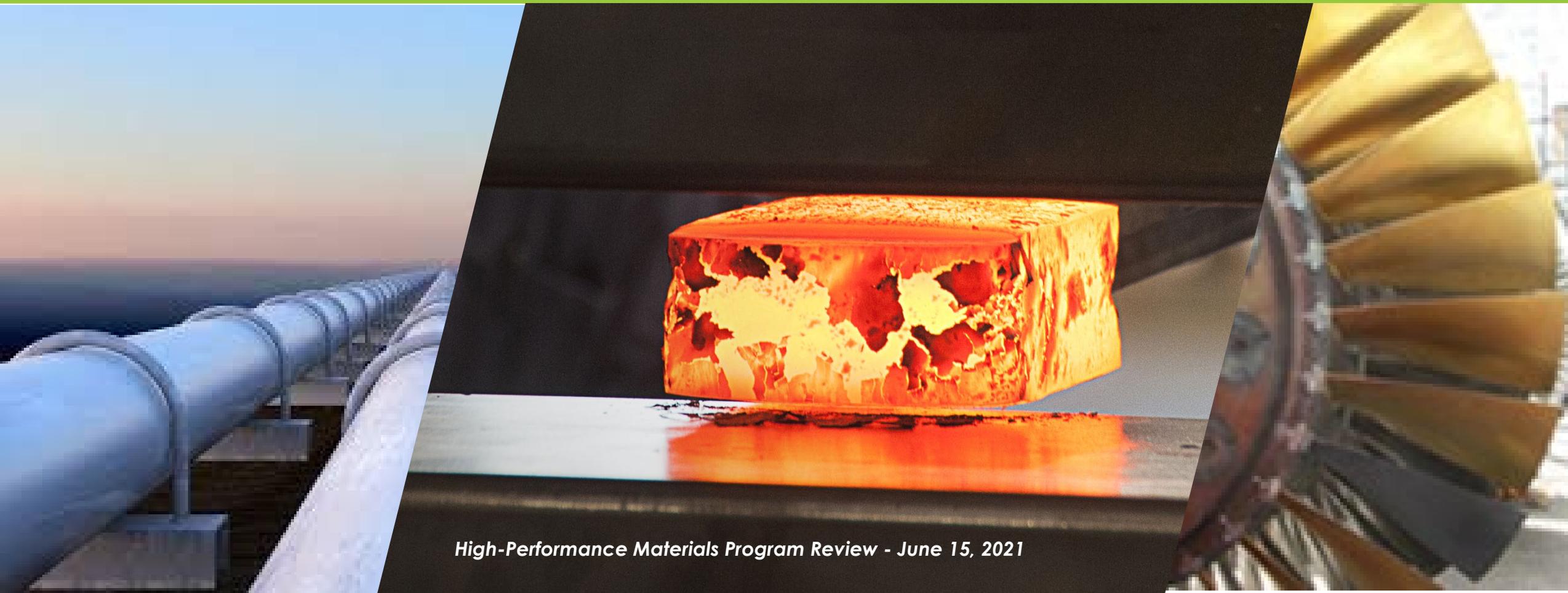
Materials Performance in sCO₂ Power Cycles



Advanced Alloy Development FWP Task 12

Ömer Doğan

Research and Innovation Center



High-Performance Materials Program Review - June 15, 2021

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Authors and Acknowledgements



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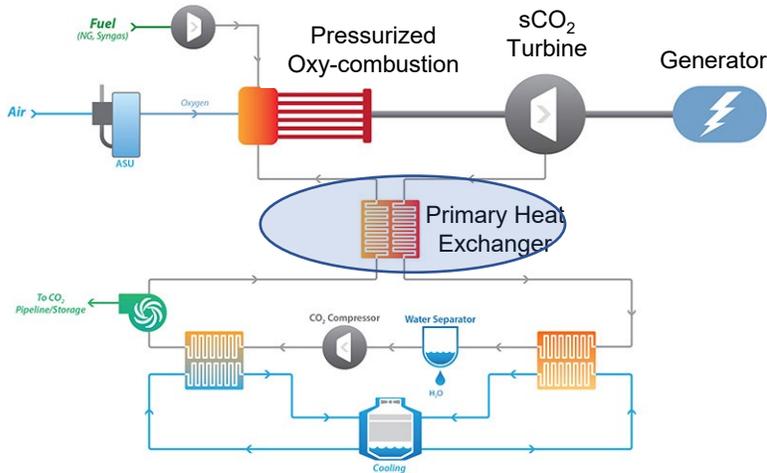
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Supercritical CO₂ Power Cycles

Direct-fired sCO₂ cycle



Materials are enablers for deployment of sCO₂ power cycles

Materials Challenges in sCO₂ power cycles:

- Materials perform in harsh environments (High T, P, and complex chemistry)
- Lack of data for materials performance
- Availability of cost-effective materials
- Manufacturing processes for components are not established for advanced materials

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

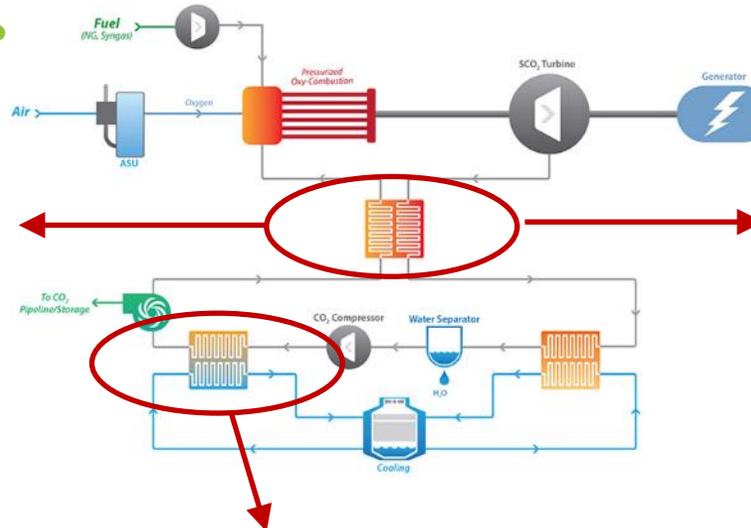
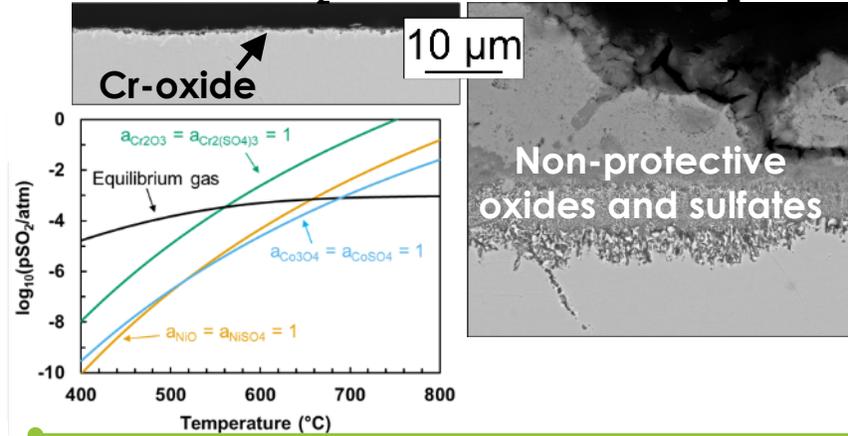
Materials Performance in Supercritical CO₂ Power Cycles

HIGH-TEMPERATURE OXIDATION OF STEELS AND SUPERALLOYS

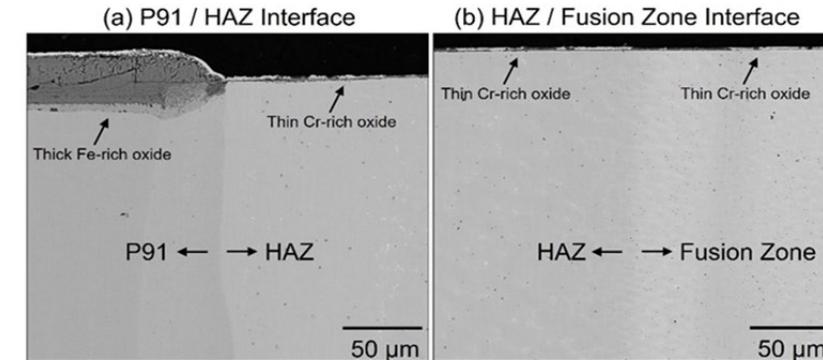
Effects of impurities and pressure

No SO₂

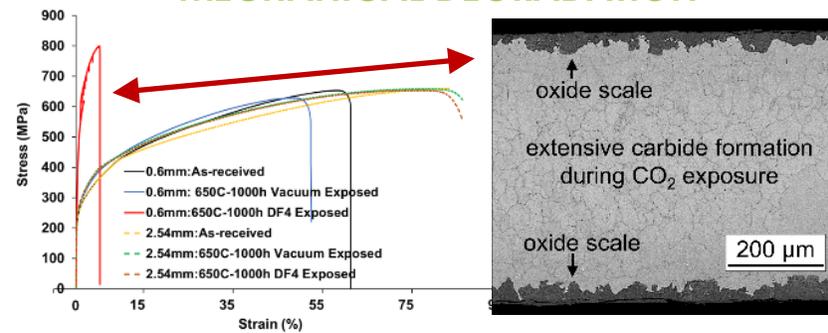
0.1% SO₂



JOINING

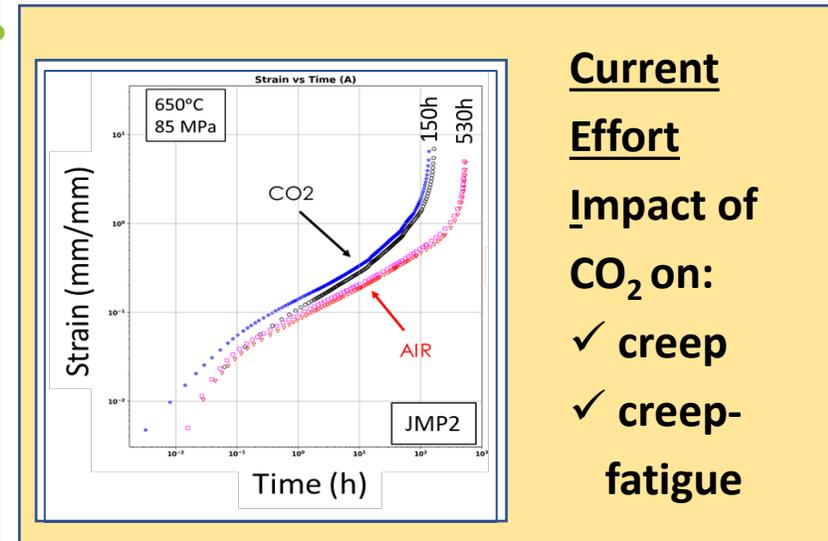
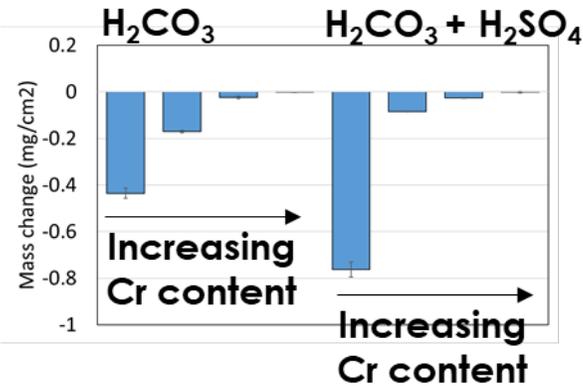


LINKING OXIDATION BEHAVIOR AND MECHANICAL DEGRADATION



LOW-TEMPERATURE CORROSION

Identifying low-cost steels resistant to acidic condensates



Current

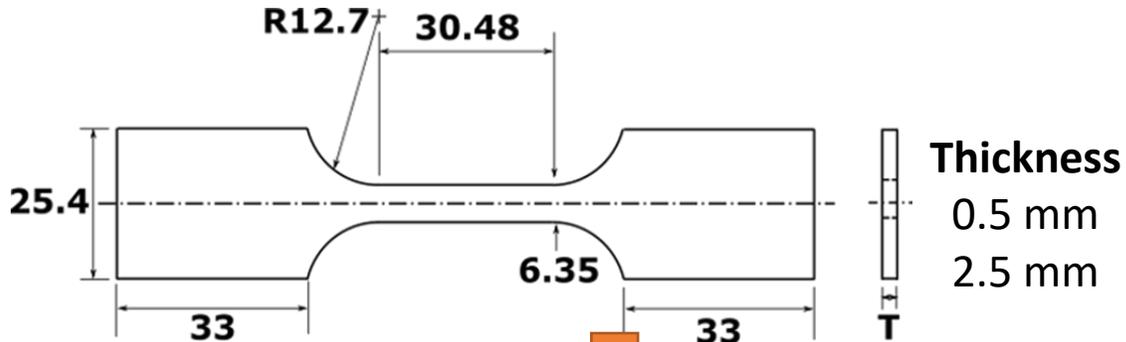
Effort

Impact of

CO₂ on:

- ✓ creep
- ✓ creep-fatigue

Effect of Direct sCO₂ Conditions on Mechanical Performance of 9 Cr Steels



As-received
Normalized at 1038C for 4 h
Tempered at 788C for 1.5h

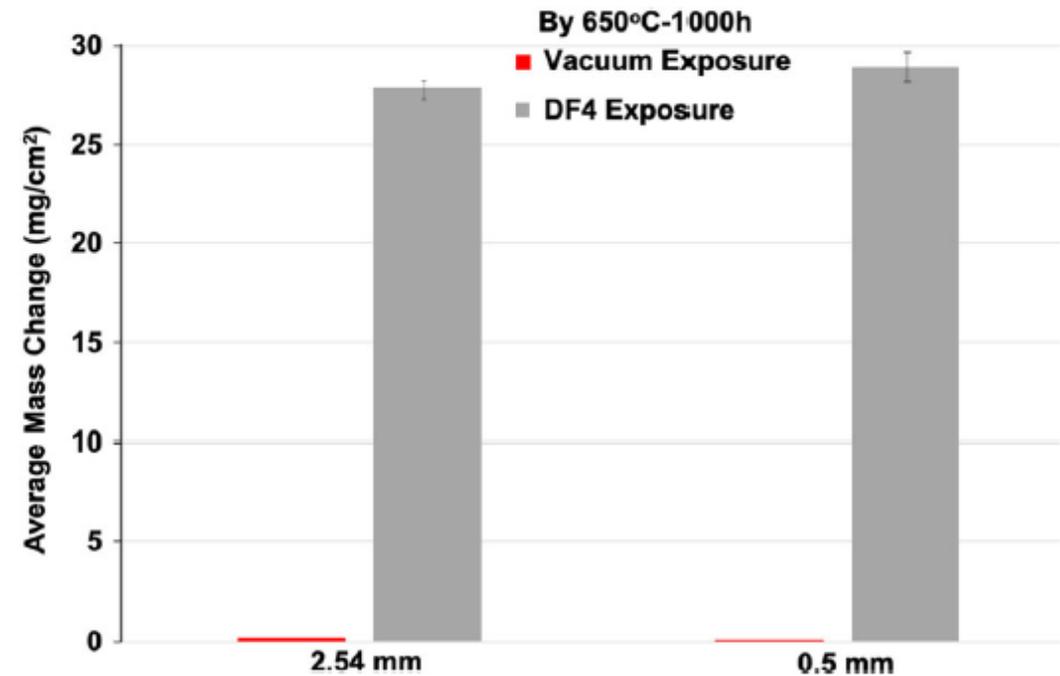
DF4 Exposure
1 bar flowing gas (95%CO₂+4%H₂O+1%O₂) at 650°C for 1000 hours

Vacuum Exposure
at 650°C for 1000 hours

Tensile testing
Room temperature
Strain rate of 4x10⁻⁵ s⁻¹

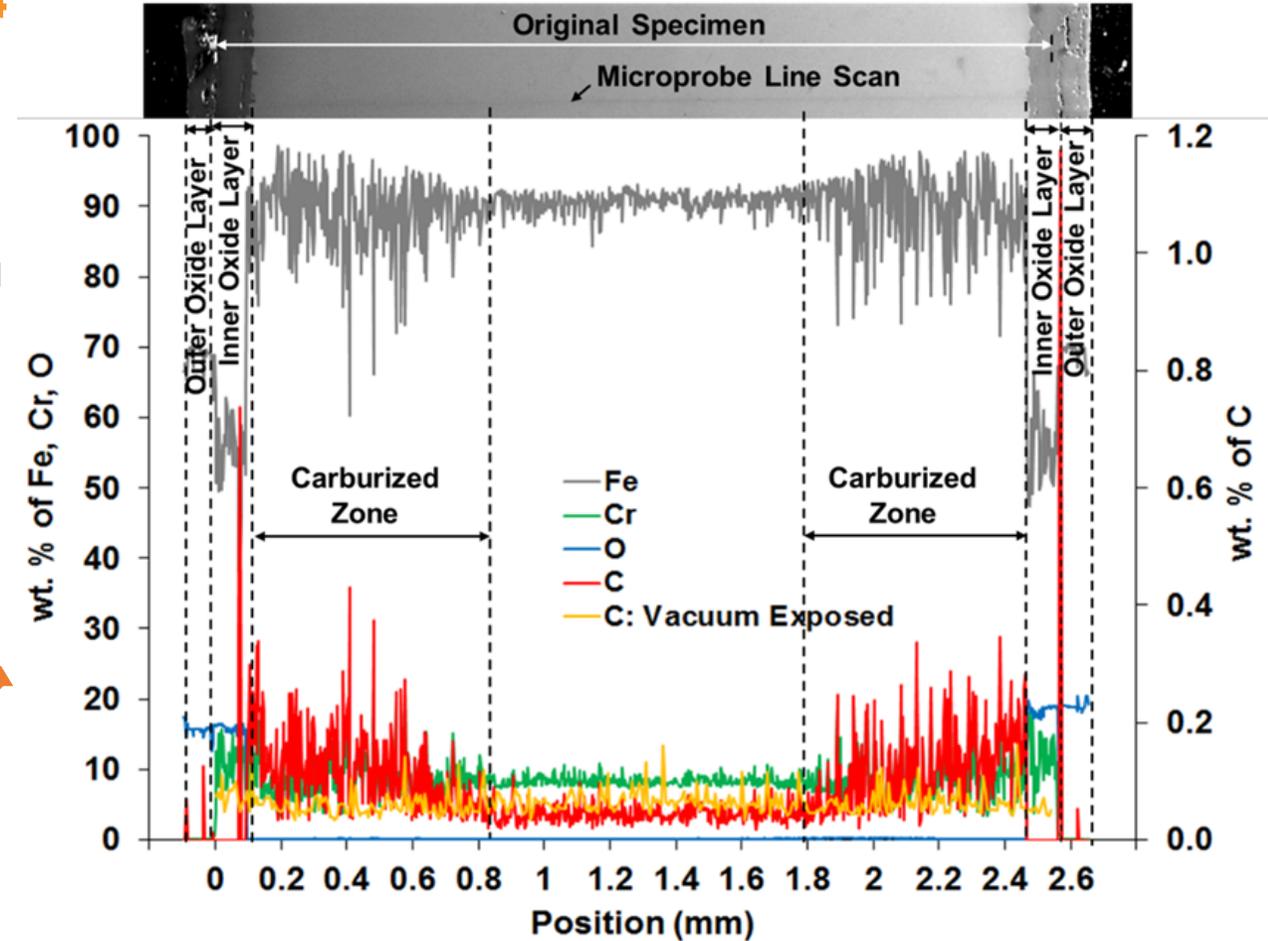
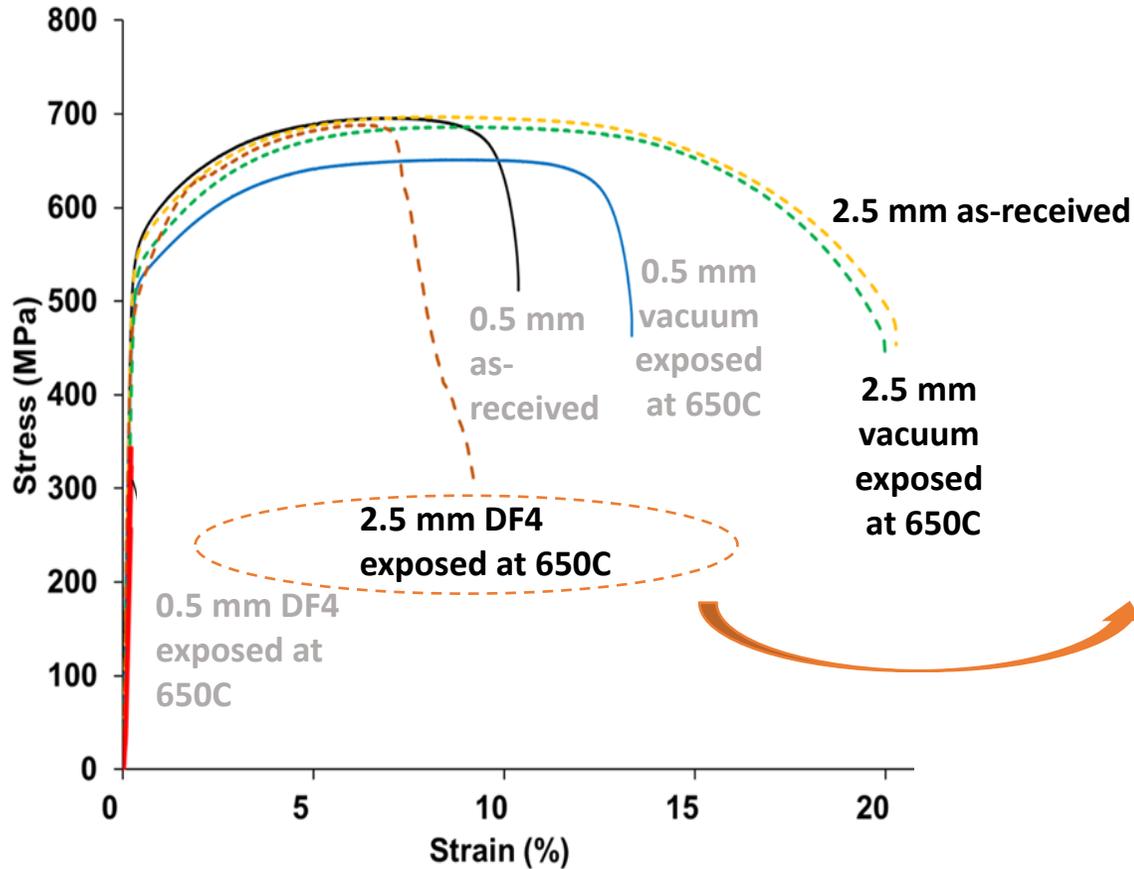
Grade 91

Fe	Cr	C	Mn	Mo	Ni	V	Si	Nb	N
Bal.	8.37	0.09	0.45	0.90	0.09	0.22	0.33	0.07	0.05



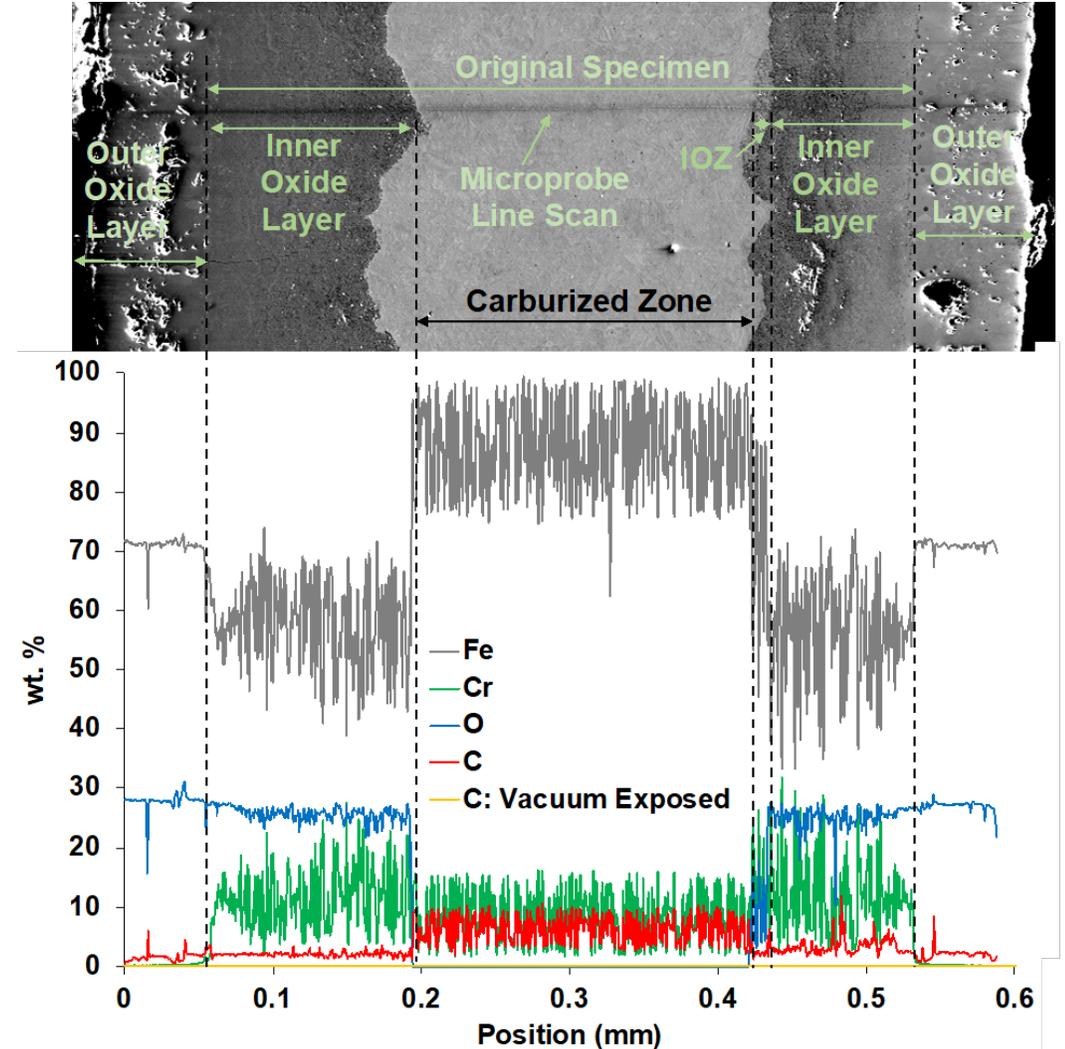
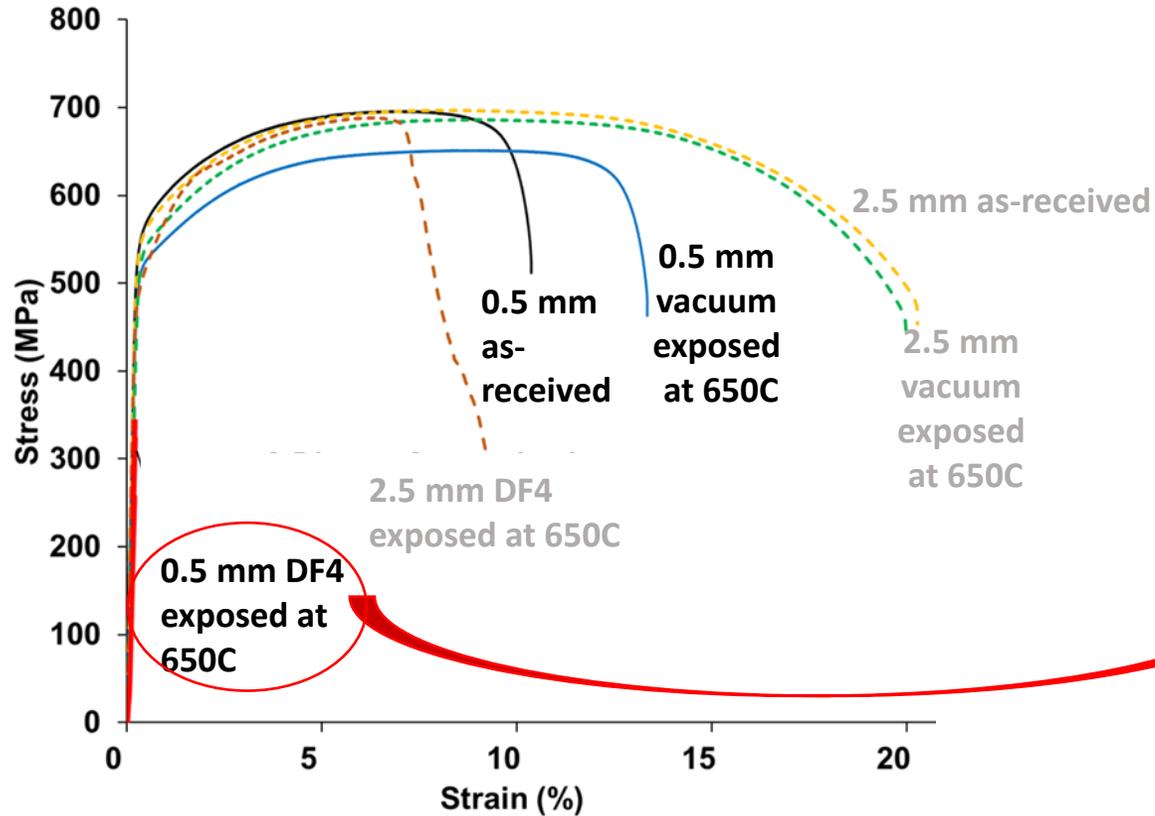
Effect of Direct sCO₂ Conditions on Mechanical Performance of 9 Cr Steels

2.5 mm thick specimen after exposure to DF4



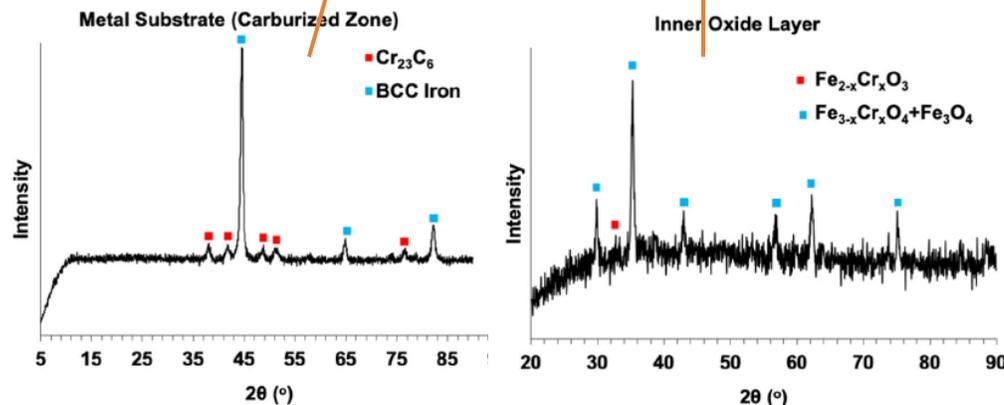
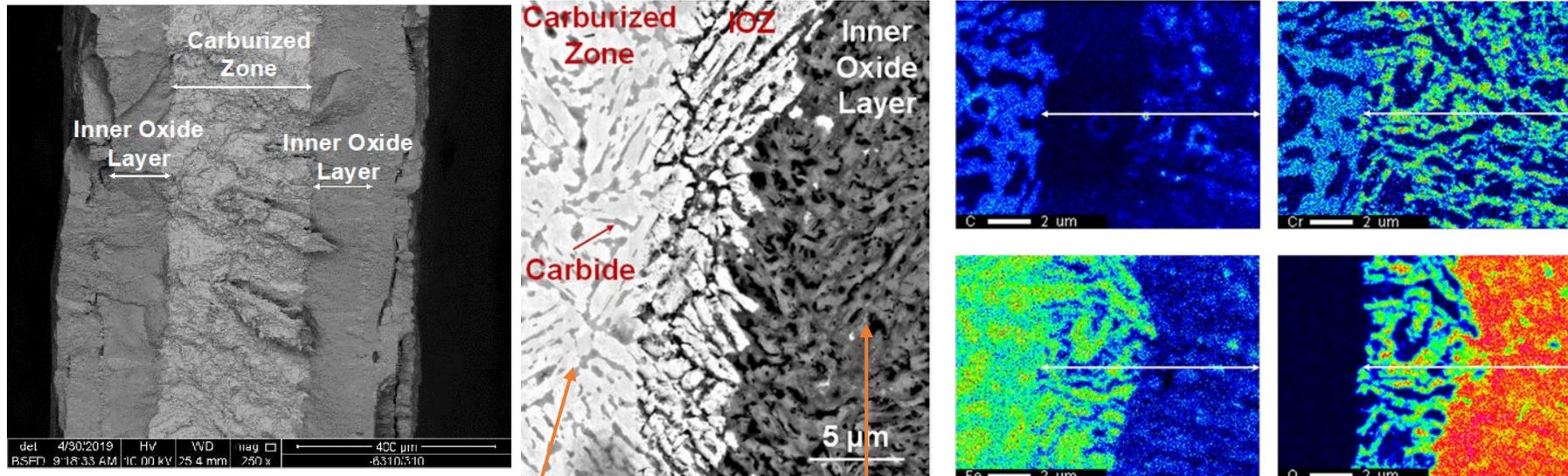
Effect of Direct sCO₂ Conditions on Mechanical Performance of 9 Cr Steels

0.5 mm thick specimen after exposure to DF4



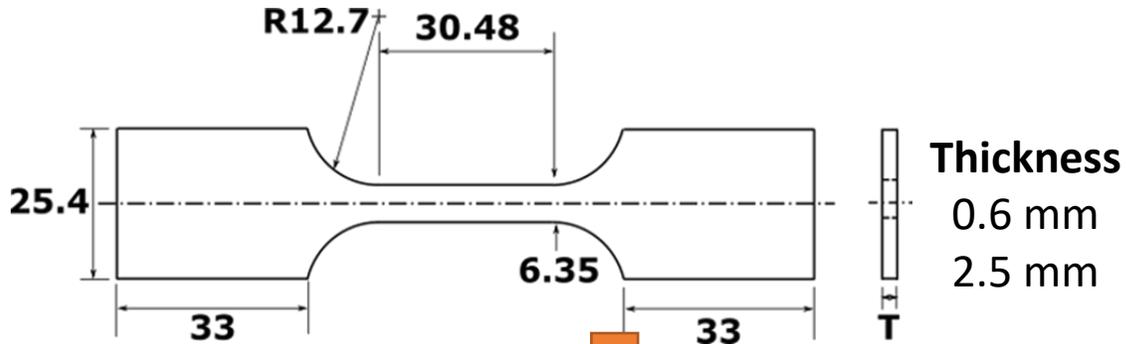
Effect of Direct sCO₂ Conditions on Mechanical Performance of 9 Cr Steels

0.5 mm thick specimen after exposure to DF4



- Duplex oxide scale formation
- CO₂ transport to the oxide-metal interface
- Oxidation of Cr and Fe and C deposition at the oxide-metal interface
- Diffusion of C into the metal and formation of Cr rich carbides (M₂₃C₆)
- Growth of inner oxide into the alloy
- Conversion of Cr rich carbides to Cr-rich oxides
- C liberation and diffusion further into the alloy
- C saturation and deposition of C in the oxide scale
- Breakaway oxidation

Effect of Direct sCO₂ Conditions on Mechanical Performance of Austenitic Steels



As-received
Annealed at
1065C

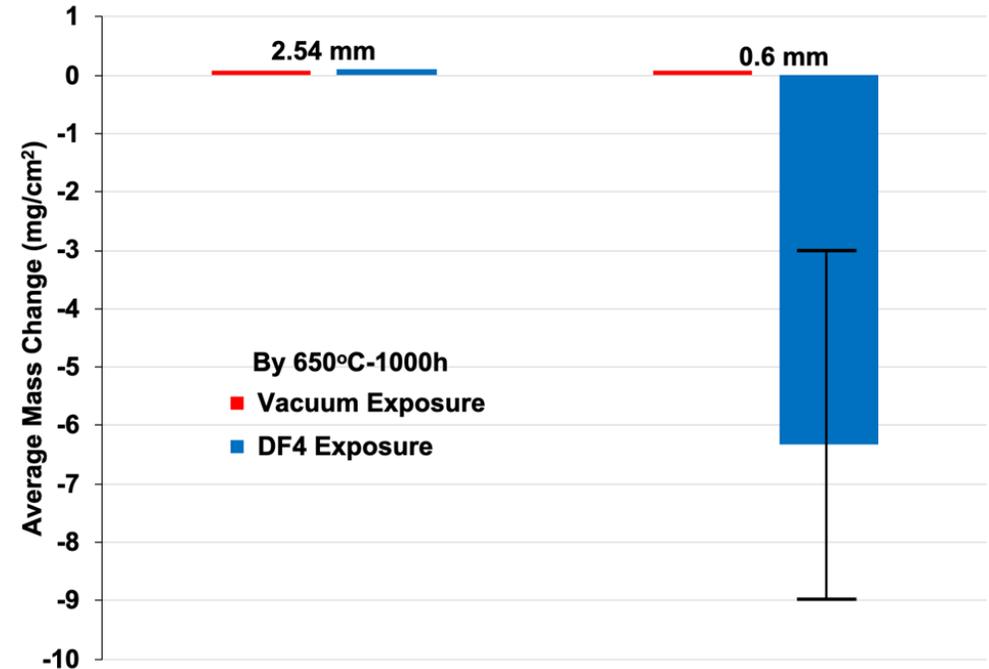
DF4 Exposure
1 bar flowing gas
(95%CO₂+4%H₂O+1%O₂)
at 650°C for 1000 hours

Vacuum Exposure
at 650°C for
1000 hours

Tensile testing
Room temperature
Strain rate of 4x10⁻⁵ s⁻¹

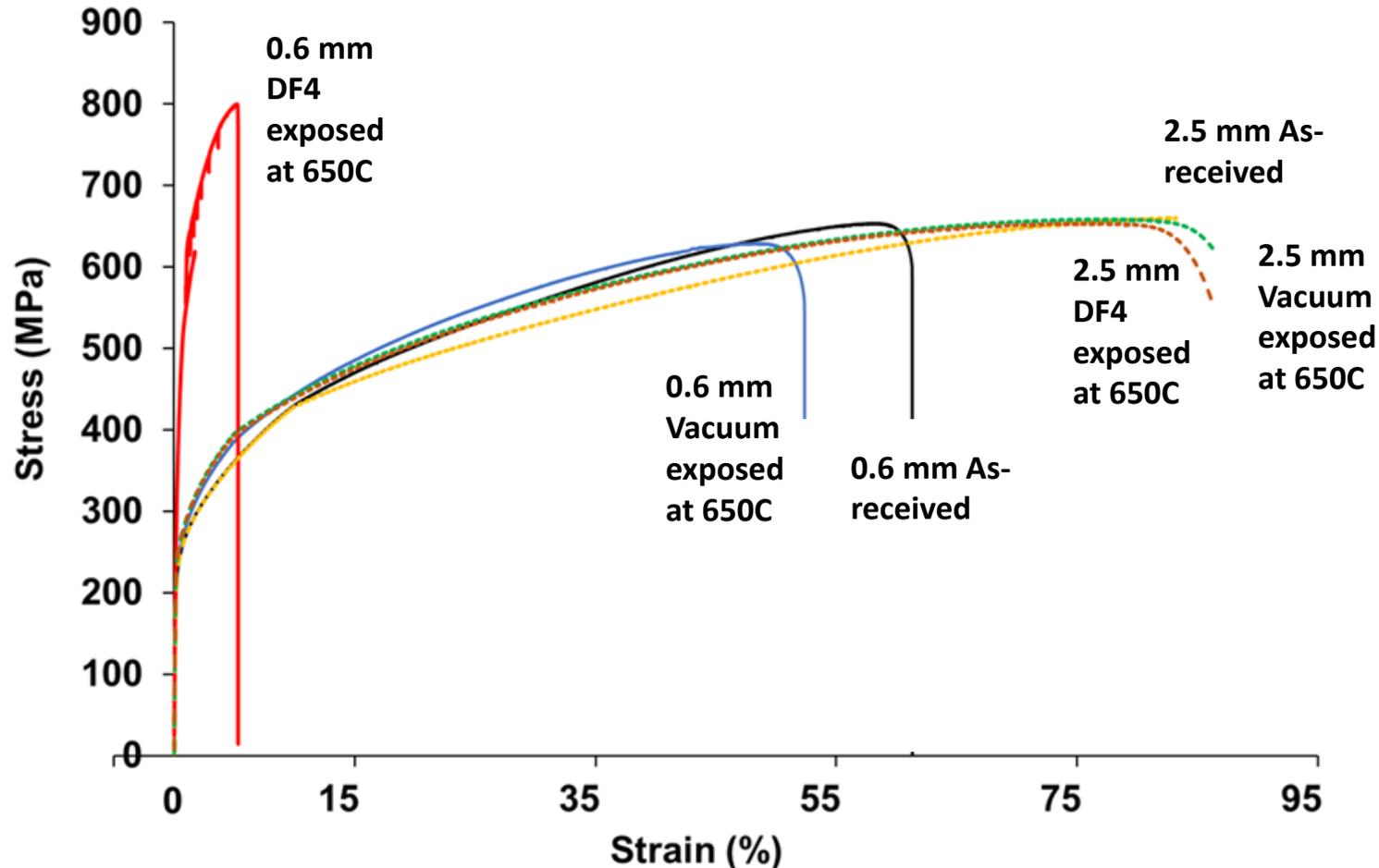
347H

Fe	Cr	Ni	Mn	Si	Nb	Cu	Co	Mo	C
Bal.	17.3	9.0	1.5	0.4	0.6	0.4	0.2	0.4	0.05



Effect of Direct sCO₂ Conditions on Mechanical Performance of Austenitic Steels

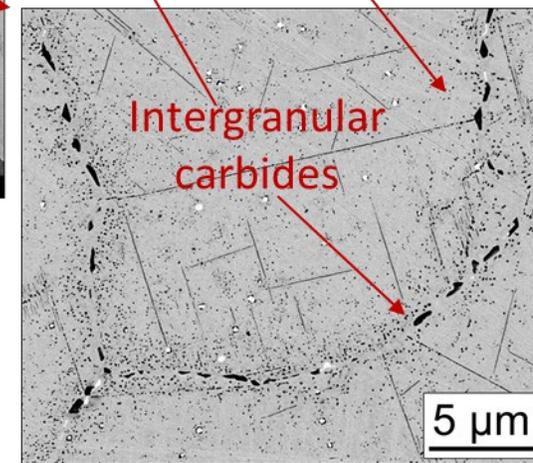
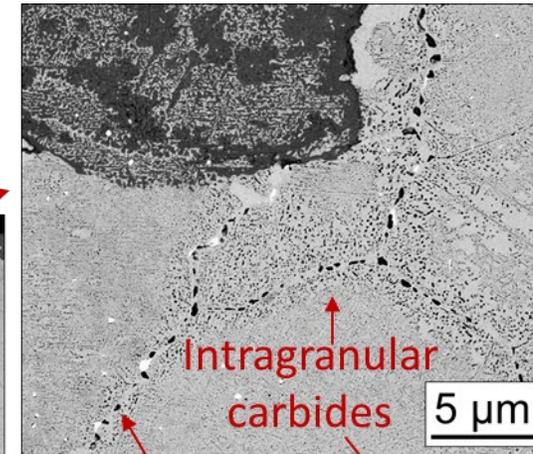
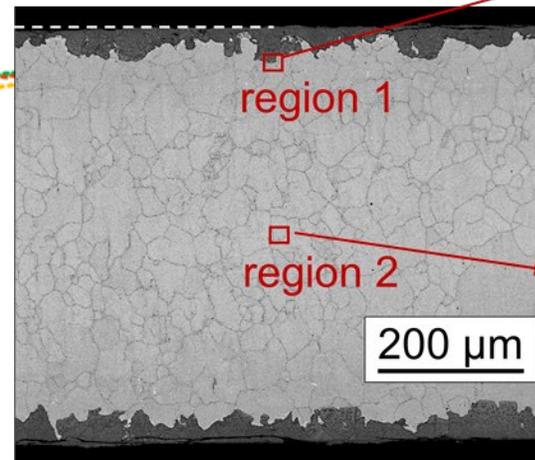
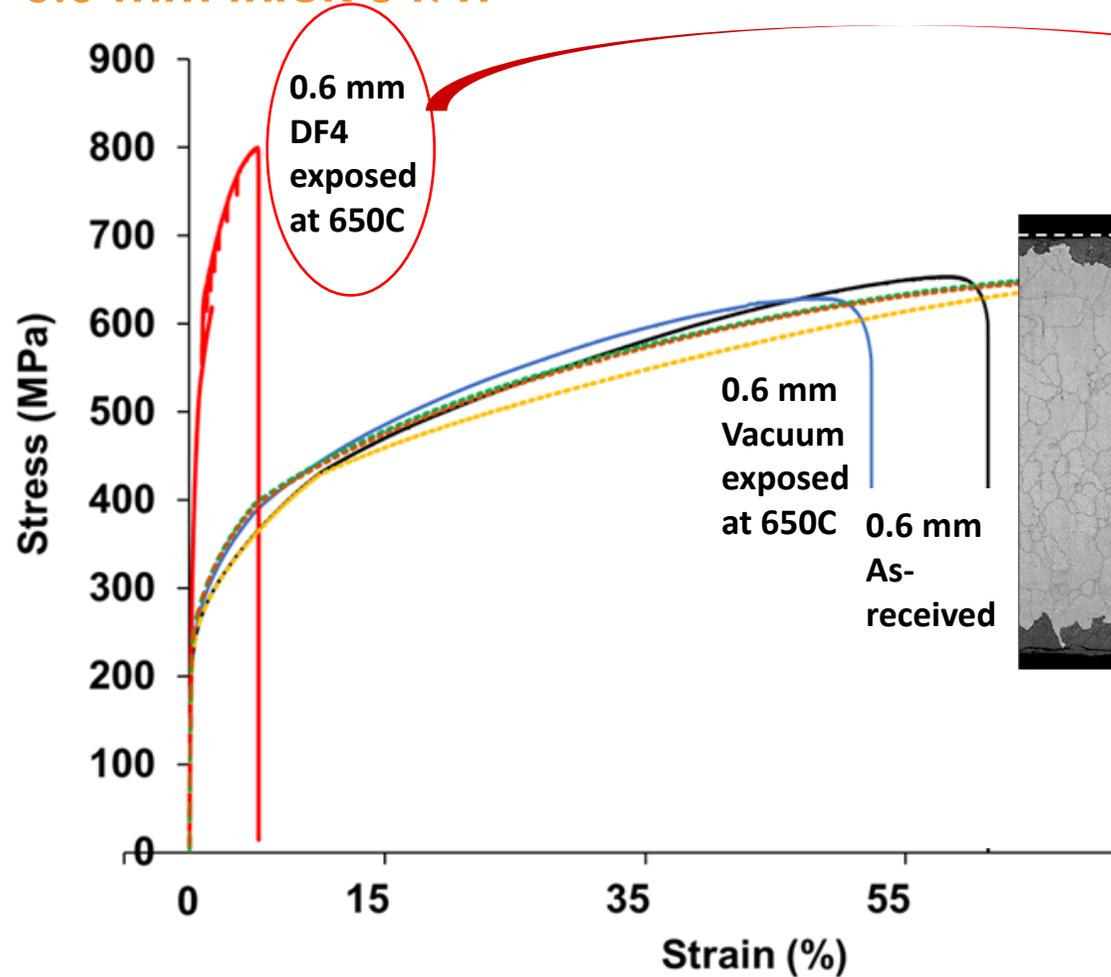
347H



- 2.5 mm thick 347H formed a protective chromia scale, resulting in no mechanical degradation.
- **0.6 mm thick 347H failed to form chromia, resulting in extensive carburization and embrittlement.**

Effect of Direct sCO₂ Conditions on Mechanical Performance of Austenitic Steels

0.6 mm thick 347H

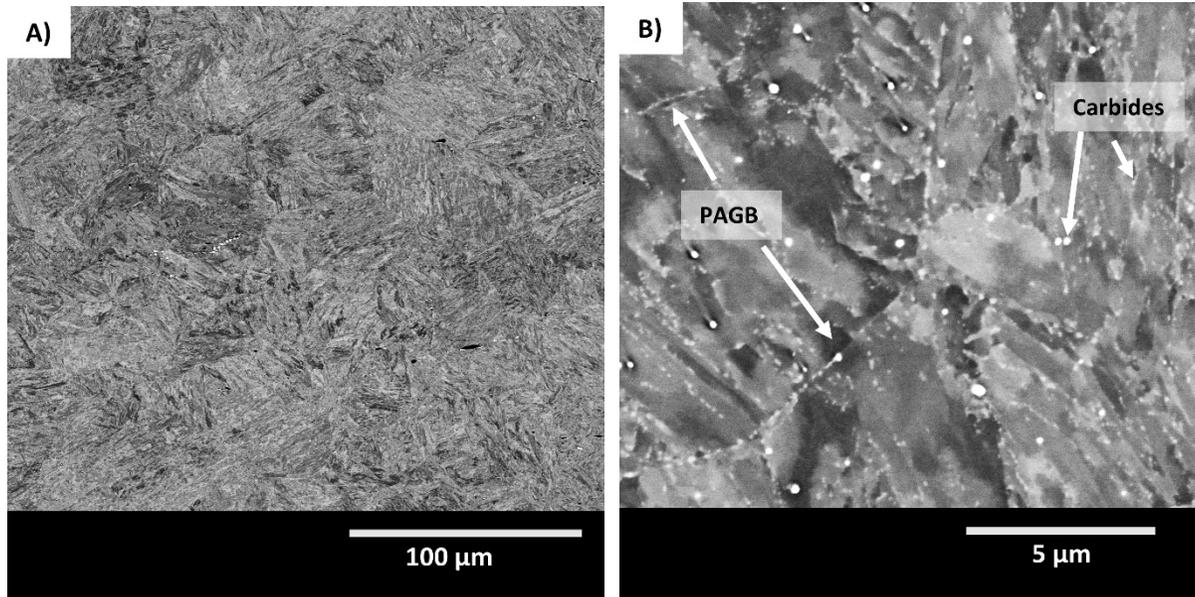
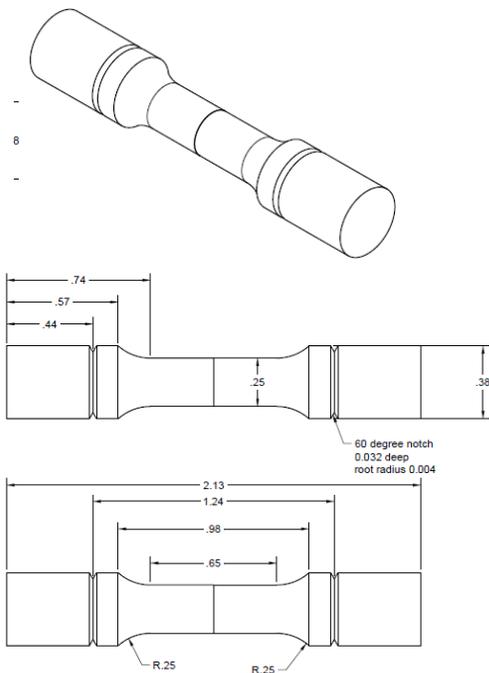


- Steels containing less than 18%Cr cannot be used in thin wall applications (compact heat exchangers) for direct sCO₂ power cycles.
- Higher Cr steels will need to be tested.

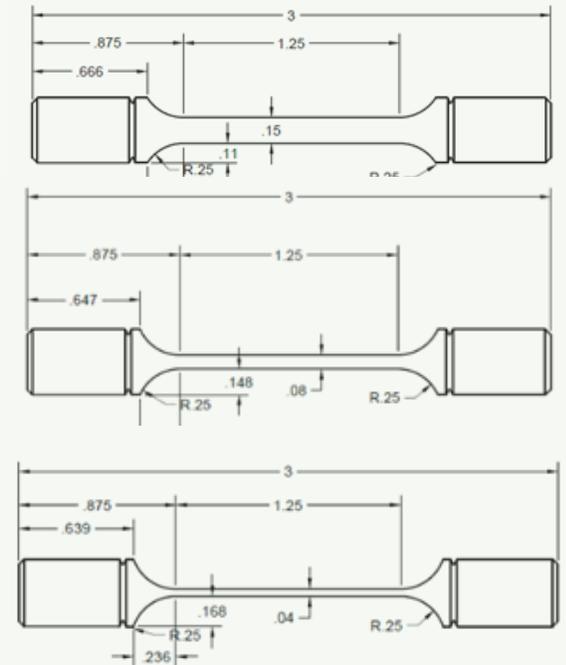
Environmental Creep Testing of Steels in CO₂

MARBN

Fe	Cr	Co	W	Mn	Ta	V	Ni	Mo	Nb	C	N	B
Bal.	9.08	2.93	2.90	0.51	0.35	0.20	0.18	0.10	0.06	0.15	0.02	0.01

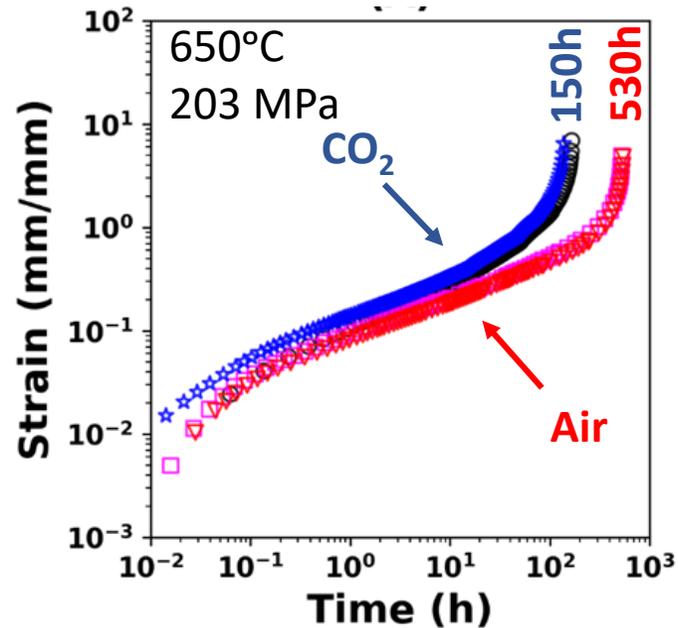


347H SS specimens with three thicknesses are being tested in air and CO₂

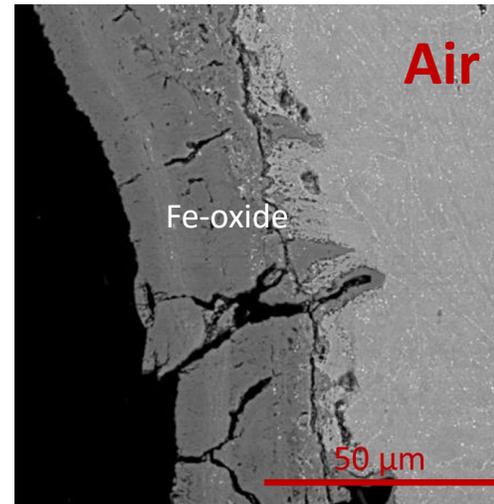
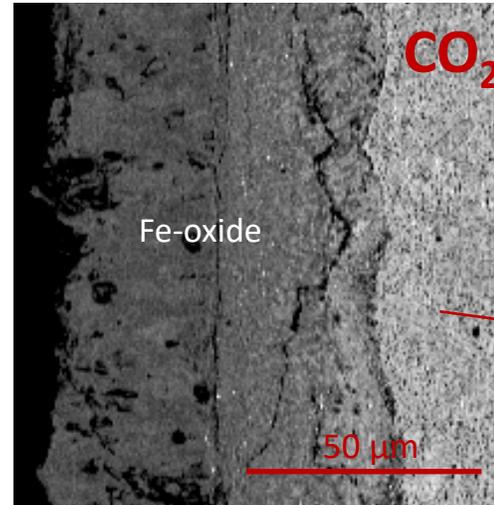


Environmental Creep Testing of Steels in CO₂

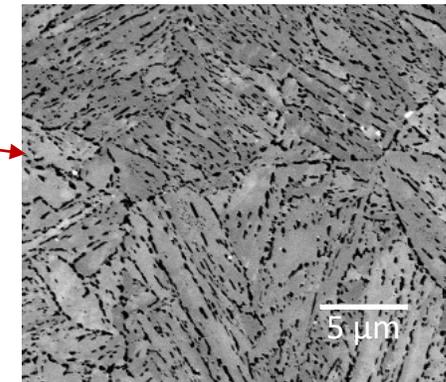
MARBN Ferritic-Martensitic 9Cr steel



Reduced creep life in CO₂ relative to air at 650 °C



Steel carburization in CO₂ enables crack propagation via carbide network



Task 12 Milestones and Recent Publications



Milestones

03/31/2022	Determine the effect of environment on the creep behavior of thin-section components of Fe alloys in sCO ₂ power cycles.
03/31/2022	Identify an alloy that is at least 30% less expensive than 18Cr-10Ni grades (e.g., 347H) and shows comparable oxidation performance in sCO ₂ power cycle environments at temperatures ≤ 450°C.

- [Effect of Specimen Thickness on the Degradation of Mechanical Properties of Ferritic-Martensitic P91 Steel by Direct-fired Supercritical CO₂ Power Cycle Environment](#), S.R. Akanda, R.P. Oleksak, R. Repukaiti, K.A. Rozman, Ö.N. Doğan, *Metall Mater Trans A* (2021) 52 (1) 82-93. <https://doi.org/10.1007/s11661-020-06065-9>.
- [High-Temperature Oxidation of Transient-Liquid Phase Bonded Ni-Based Alloys in 1 bar and 250 bar Carbon Dioxide](#), C.S. Carney, R.P. Oleksak, M. Kapoor, G.R. Holcomb, , Ö.N. Doğan, *Materials at High Temperatures* (2020) 37 (6) 445-461. <https://doi.org/10.1080/09603409.2020.1818046>.
- [Tensile Deformation Behavior of a Dissimilar Metal Weldment of P91 and 347H Steels](#), S.A. Akanda, R.W. Wheeler, K.A. Rozman, J. Rider, Ö.N. Doğan, M.L. Young, J.A. Hawk, *Strain* (2020) <https://doi.org/10.1111/str.12366>.
- [Temperature-Dependence of Corrosion of Ni-Based Superalloys in Hot CO₂-Rich Gases Containing SO₂ Impurities](#), R.P. Oleksak, J.H. Tylczak, G.R. Holcomb, Ö.N. Doğan, *JOM* (2020).
- [High temperature oxidation of steels in CO₂ containing impurities](#), R.P. Oleksak, J.H. Tylczak, G.R. Holcomb, Ö.N. Doğan, *Corrosion Science* (2020).

Status and Summary

- Ni alloys demonstrate good corrosion properties in direct sCO₂ environment; however, identifying steels that can work at appropriate temperature range is important for cost reduction. So far, our work on steels shows that:
 - Steels containing >12 wt% Cr perform well in direct sCO₂ environments.
 - 9Cr steels perform poorly in direct sCO₂ conditions due to high rates of oxidation and carburization, resulting in severe embrittlement.
 - Steels containing less than 18% Cr (such as 347H, 316) likely cannot be used in thin wall applications (compact heat exchangers) for direct sCO₂ power cycles. Higher Cr steels will need to be tested.
 - Reduced creep life of 9Cr steels in CO₂ was demonstrated in environmental creep test setup.