Predicting the Oxidation/Corrosion Performance of Structural Alloys in Supercritical CO_2

DE-FE0024120

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2016 Crosscutting Research & Rare Earth Elements Portfolios Review

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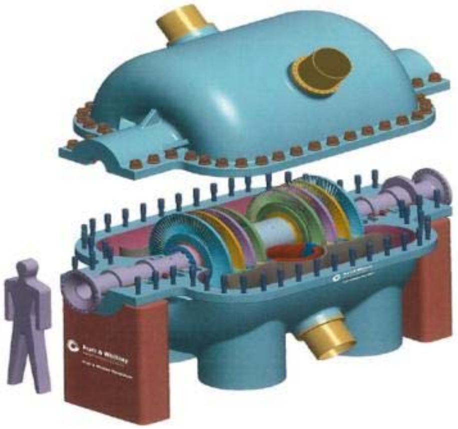
Project Objectives

- Overall Objective
  - Predict the oxidation/corrosion performance of structural alloys in high-temperature high-pressure supercritical CO_2 (sCO_2)
  - Combine laboratory testing & computational modeling including unique attributes of sCO_2 heat exchangers to accomplish this goal
- Materials for sCO_2 help enable US DOE program goals for Future Transformational Power Systems



sCO_2 Power Turbine (676 MW)

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Some configurations of the sCO_2 Brayton power cycle might achieve ***100% carbon dioxide capture and zero emissions of conventional pollutants*** *with little or no efficiency or capacity penalty.*

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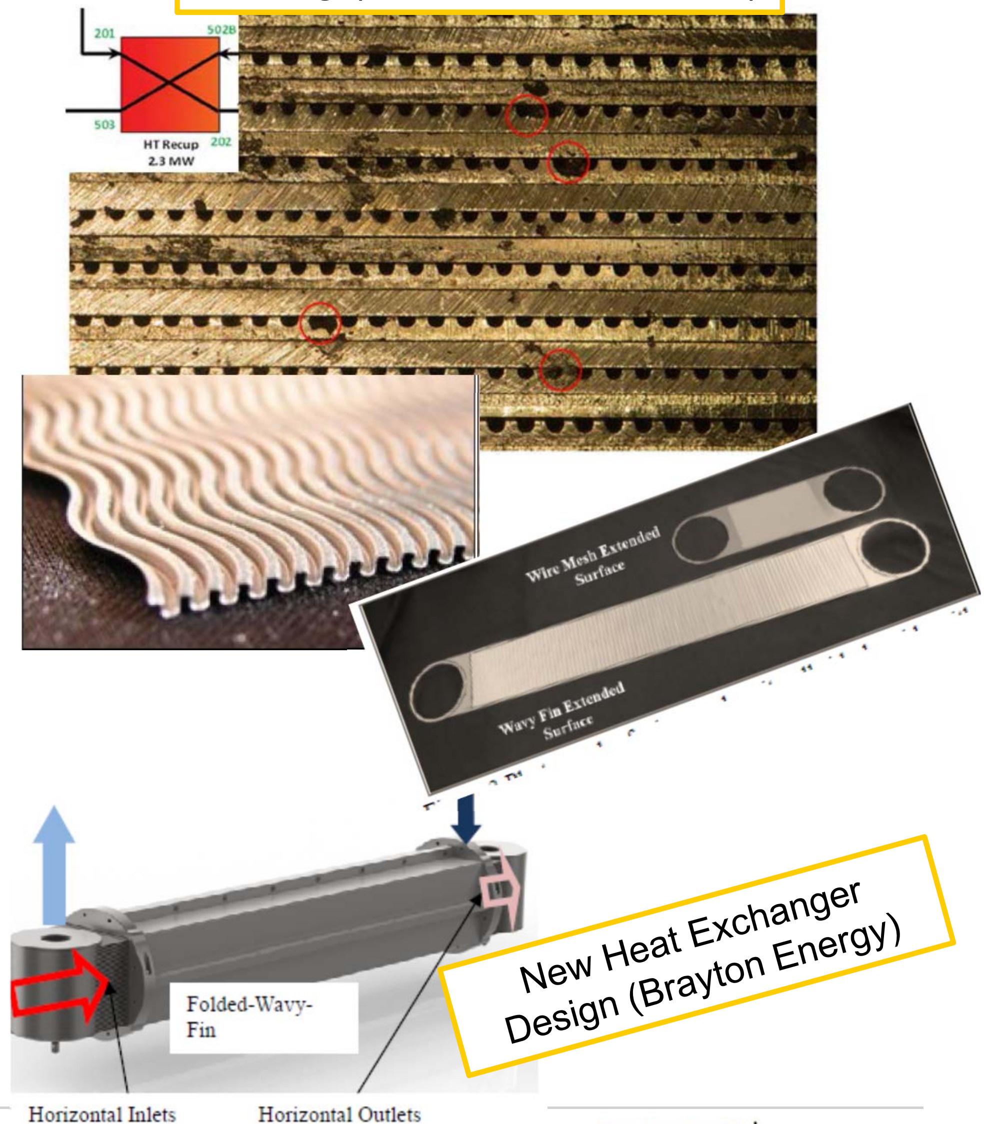
Technology Challenges for sCO_2

- Expensive HX: '40% of plant cost'
- Small channels
- Large surface areas
- Materials considerations: thermal fatigue, creep (thin sections), brazing/diffusion bonding, corrosion/oxidation/carburi-zation
- **Corrosion:**
  - Closed cycle = build-up of impurities
  - **Open cycle = combustion products**
  - Long-term performance, pluggage, blockage, etc.

Compact Heat Exchanger Fouling (Sandia National Lab)



New Heat Exchanger Design (Brayton Energy)

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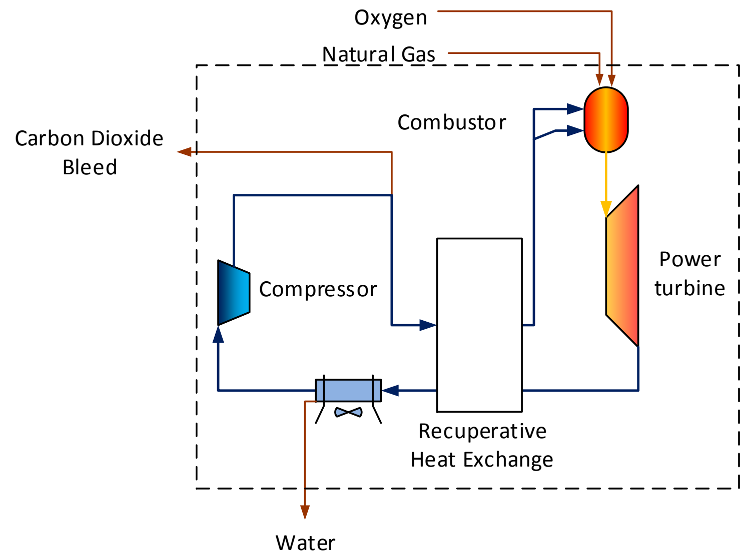
Realistic sCO_2 conditions for semi-open Allam cycles

- **Survey of industry and current studies**
  - 700°C likely maximum temperature in heat-exchangers
- **Evaluation of impurities for nearest-term 'open/direct-fired cycle' – Allam Cycle**
  - H_2O, O_2, N_2, Ar, NO_x, SO_x, HCl
  - Mass-balance calculations for methane and cooled, raw syngas (checked against thermodynamic calculations)



Species	Composition (mol%)		
	Methane	Cooled raw coal syngas	Oxygen
CH_4	100	1.0	
CO		39.0	
H_2		28.3	
CO_2		8.0	
H_2O		20.0	
N_2+Ar		2.0	0.5
H2S		0.9	
HCl		0.02	
O_2			99.5
LHV	912 BTU/scf	218 BTU/scf	

Component	Composition (mol%)			
Fuel Stream	Methane		Cooled Raw Coal Syngas	
	Combustor Inlet	Turbine Inlet	Combustor inlet	Turbine Inlet
CO_2	95	90	90	85
H_2O	250 ppm	5	250 ppm	5
N_2+Ar	1	1	9	9
O_2	4	3.6	1	1
HCl				100 ppm
SO_2				1,000 ppm

O_2 = 3.6 vol%, H_2O = 5.3 vol%

Scope of Laboratory sCO_2 Corrosion Tests

- Conditions
  - 650-750°C, 200 bar
  - sCO_2
    - Commercially pure
    - Simulated open cycle with impurities (O_2 + H_2O) from NG
- Materials
  - Commercially available
  - Code approved or Industrially relevant
  - Focus on economics
- Exposures
  - 300 hours (Gr 91, 304H, 740H), 700°C
  - 1,000 hours (all 7 alloys), 3 temperatures
  - ≥3,000 hours (all 7 alloys), 1 temperature

Material Class	Alloys Selected		
Ferritic steels	Gr. 91 (8-9Cr)	VM12 (11-12Cr)	Crofer 22H (22Cr)
Austenitic stainless	304H (18Cr)	HR3C (25Cr)	
Nickel-based	617 (20Cr, solid soln)	740H (25Cr, ppt. strengthnd)	

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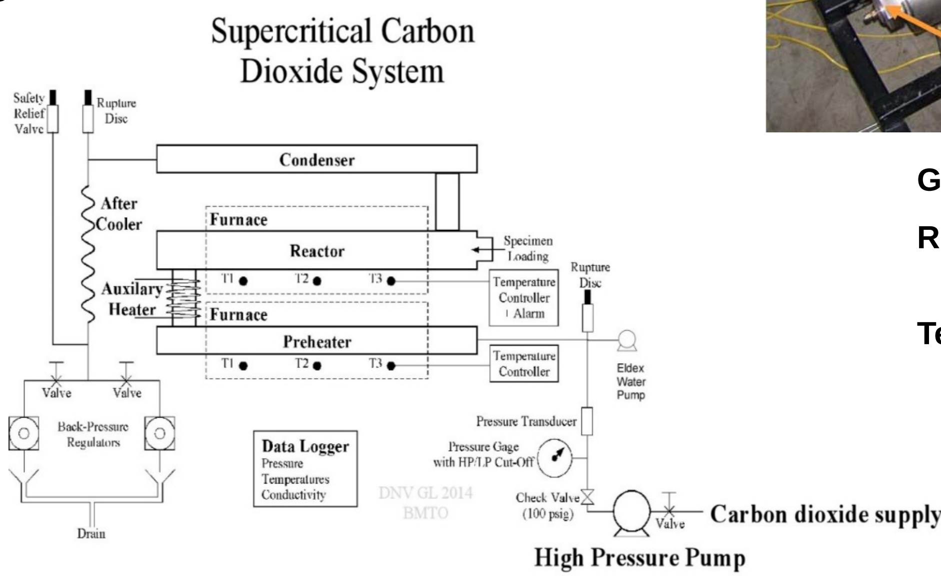
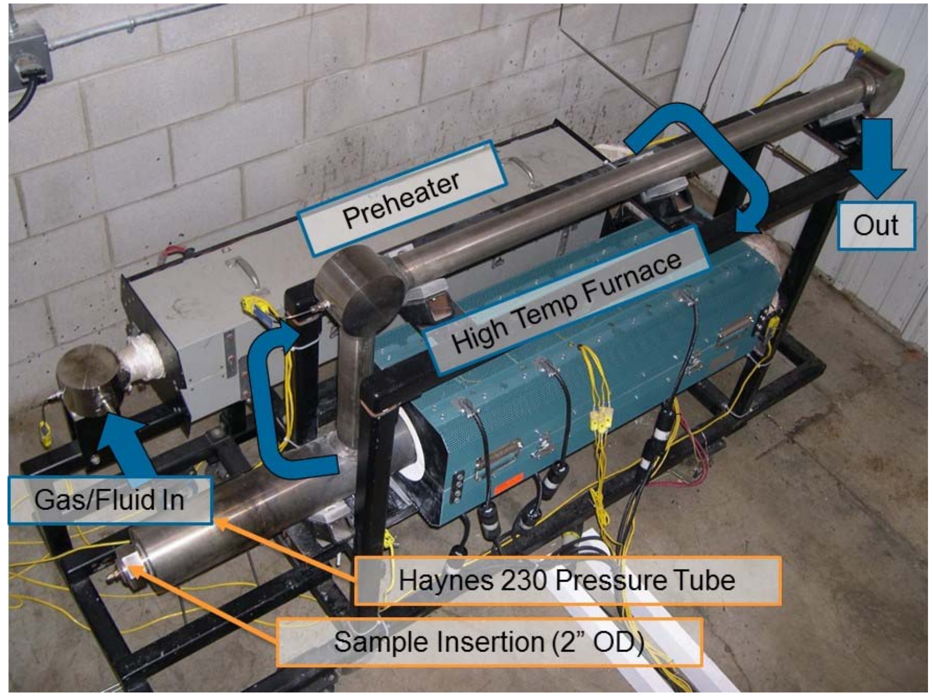
Compositions of alloys investigated

	T91	VM12	Crofer 22H	304H	HR3C	617	740H
Al	0.01	0.01	0.01	<0.01	0.01	1.13	1.33
B	0.002	0.004	<0.001	0.001	0.001	0.002	0.001
Ce	-	-	-	<0.01	<0.01	<0.01	<0.01
Ca	<0.01	<0.01	<0.01	-	-	-	-
Co	0.02	1.47	0.02	0.22	0.08	11.44	20.28
Cr	8.39	11.2	22.71	18.42	25.13	22.19	24.53
Cu	0.09	0.08	0.01	0.18	0.03	0.03	0.01
Fe	-	-	-	70.33	52.39	1.55	0.12
La	<0.01	<0.01	0.06	-	-	-	-
Mn	0.44	0.39	0.43	1.8	1.19	0.09	0.26
Mo	0.93	0.36	0.01	0.22	0.1	9.5	0.32
Nb	0.06	0.03	0.5	0.01	0.44	0.06	1.49
Ni	0.13	0.36	0.26	8.13	19.85	53.31	50.04
P	0.014	0.015	0.018	0.028	0.015	<0.002	<0.002
Si	0.24	0.41	0.29	0.48	0.4	0.08	0.15
Sn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ta	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ti	<0.01	<0.01	0.08	<0.01	<0.01	0.35	1.36
V	0.18	0.2	0.02	0.05	0.05	0.03	0.01
W	0.15	1.6	1.9	0.01	<0.01	0.13	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
As	0.0038	0.0029	0.0019	0.0025	0.0021	0.0002	<0.0001
Bi	<0.00001	<0.00001	<0.00001	0.0008	0.00006	0.00007	0.00017
Pb	0.00005	<0.00001	0.00007	-	-	-	-
Sb	0.00077	0.00041	0.0001	-	-	-	-
C	0.08	0.12	0.004	0.043	0.066	0.091	0.024
S	0.001	0.001	0.002	0.002	0.001	<0.001	0.002
O	0.0032	0.0037	0.0032	0.0032	0.0016	0.0005	0.0006
N	0.0447	0.0359	0.017	0.0604	0.238	0.0065	0.004

Laboratory Testing Facility (DNV-GL)

- High temperature and pressure (600-750°C, 200 bar)
- Existing test facility modified for sCO_2 to ensure safety
- Introduction of impurities
  (O_2, H_2O)
- **300-hour tests in sCO_2 with and without impurities completed successfully at 700°C**
- **Two 1000-hour tests completed at 650 and 700°C**





Gas Volume: 4.41 liters

Refresh Rate: static, with occasional replenishment

Temperatures: preheat 454°C. exit 149°C

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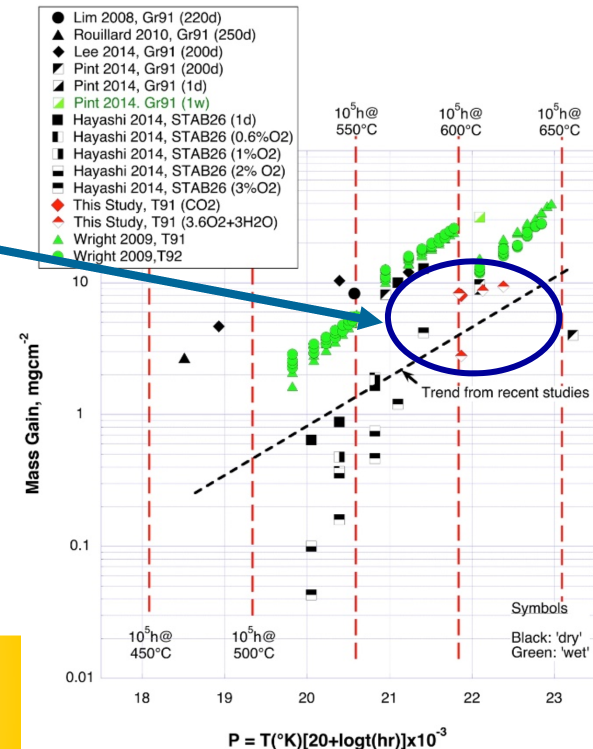
Comparison of Mass gain in sCO_2 and steam

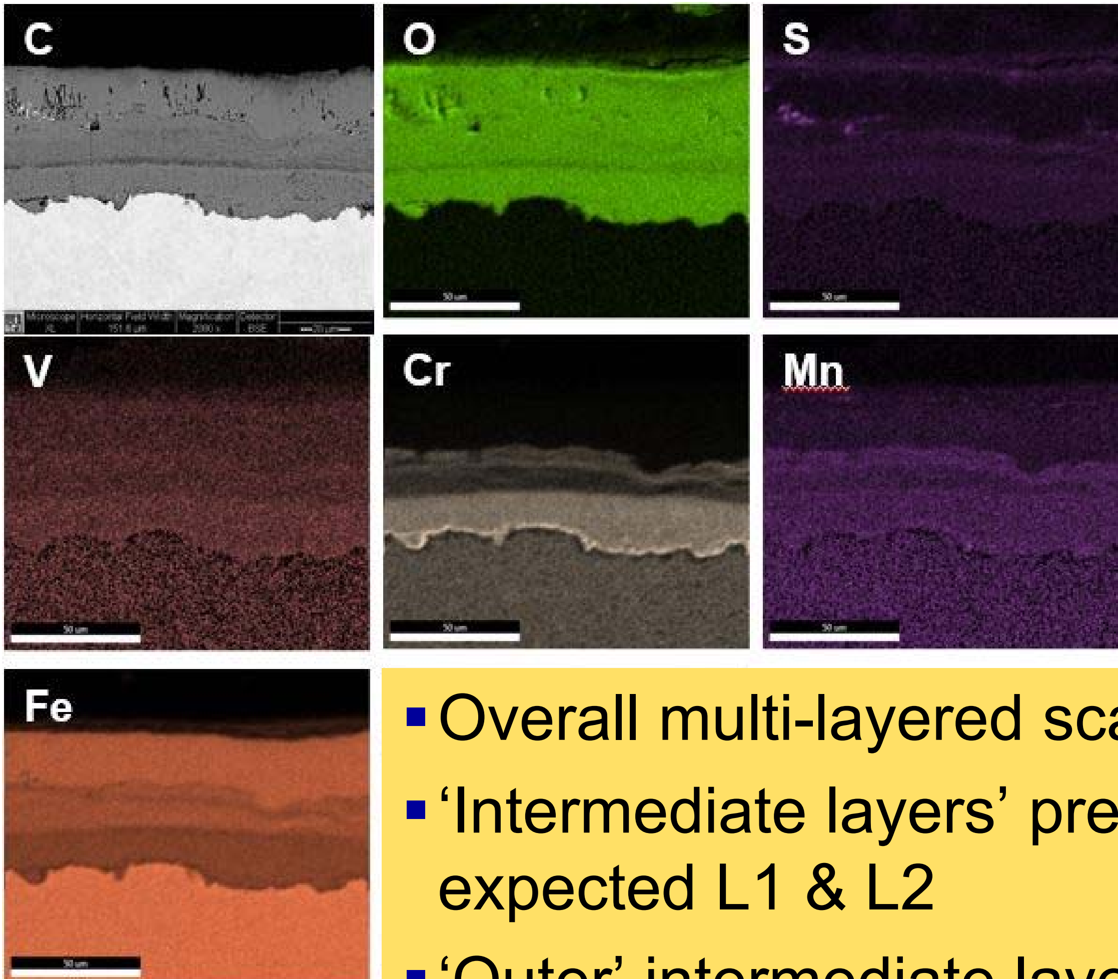
- Results from 300-hour test in pure sCO_2, 700°C, 200 bar Mass gains are similar to results in steam and other studies in sCO_2
- **However, mass gain is not useful for evaluating oxide morphology and propensity for exfoliation**

Sample ID	Sample #	Weight gain	
		mg	mg/cm²
T91	1	124.57	7.66
	2	143.47	8.82
	3	124.17	7.63
TP304H	1	4.53	0.28
	2	2.77	0.17
	3	3.97	0.24
740	1	3.13	0.19
	2	3.47	0.21
	3	3.80	0.23



300-hr mass gain data are consistent with assembled literature steam data

Oxide Morphology of Grade 91 after 300 hour test in pure CO_2 at 200 bar, 700ºC



- Overall multi-layered scale structure, but
- 'Intermediate layers' present between expected L1 & L2
- 'Outer' intermediate layer contains Cr (level lower than in L1)

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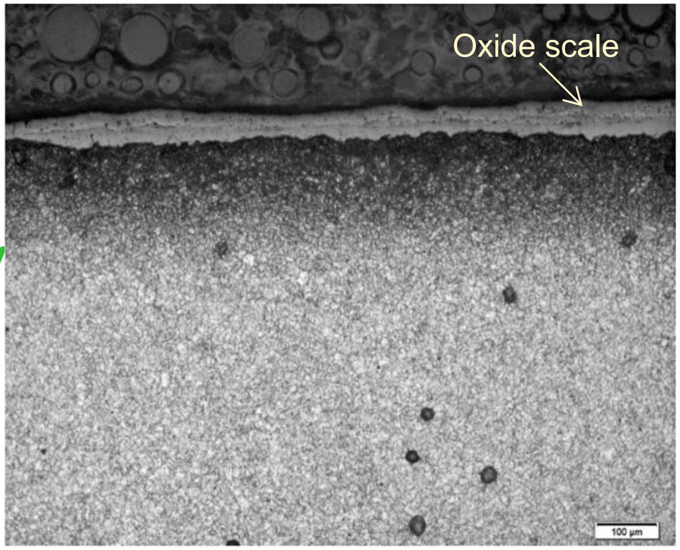
Surface decoration on Gr 91 after 300 hour in pure sCO_2 at 200 bar, 700°C

- Decoration of etched Gr 91 microstructure
- Initial spot hardness measurements for carburization inconclusive
- More detailed characterization performed

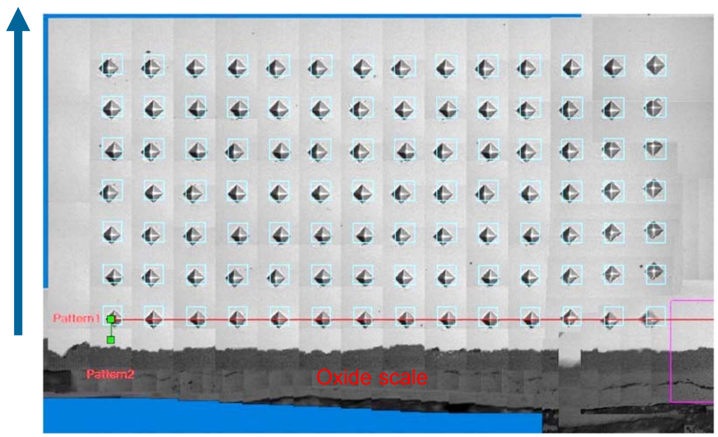
Hardness Spot Checks

Depth (microns)	Hardness (Vickers)
625	224
417	234
271	251
167	321
83	297

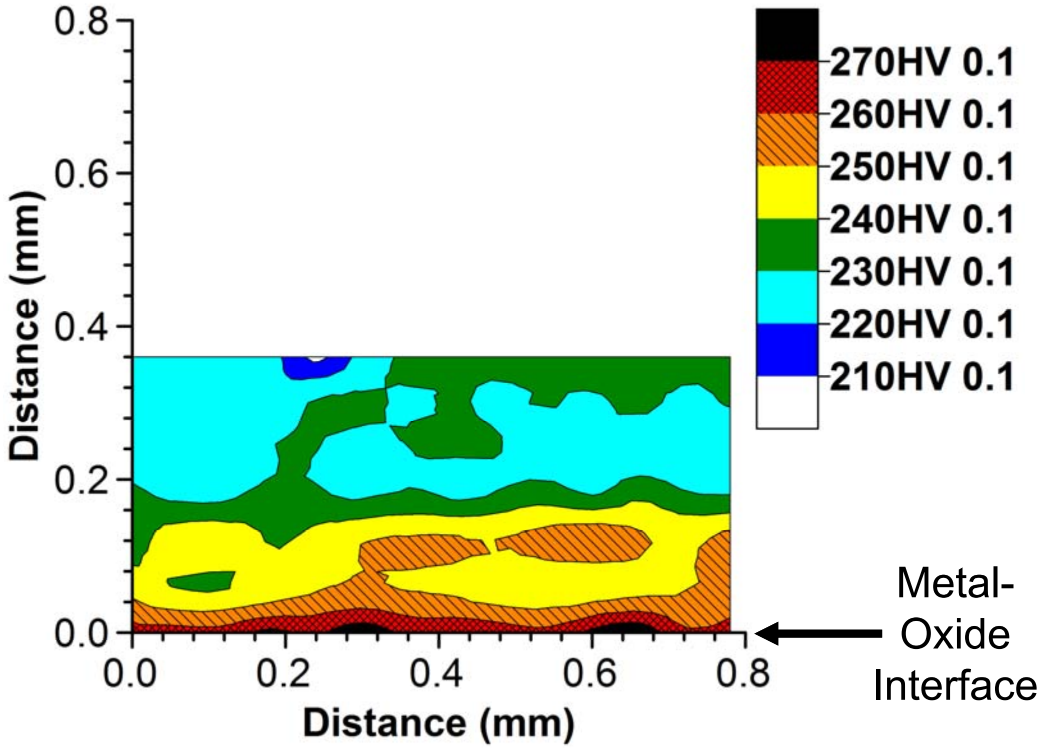


Carburization on Gr 91 evident from micro-hardness measurements in pure sCO_2 after 300 hour at 200 bar, 700^{o}C

Depth into alloy



Hardness Map: 14x7=98indents



Automated hardness map shows hardening near-surface region

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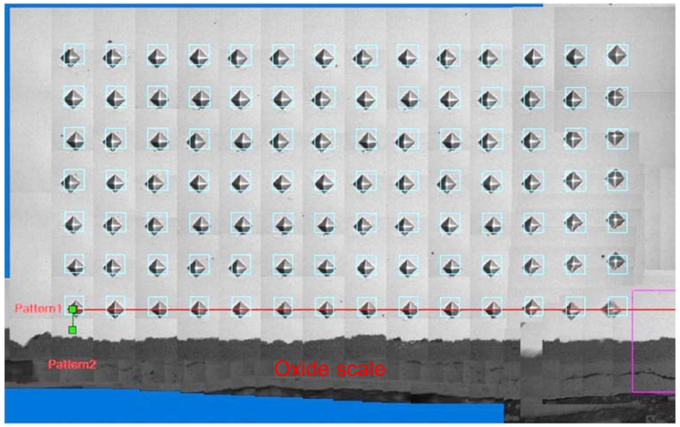
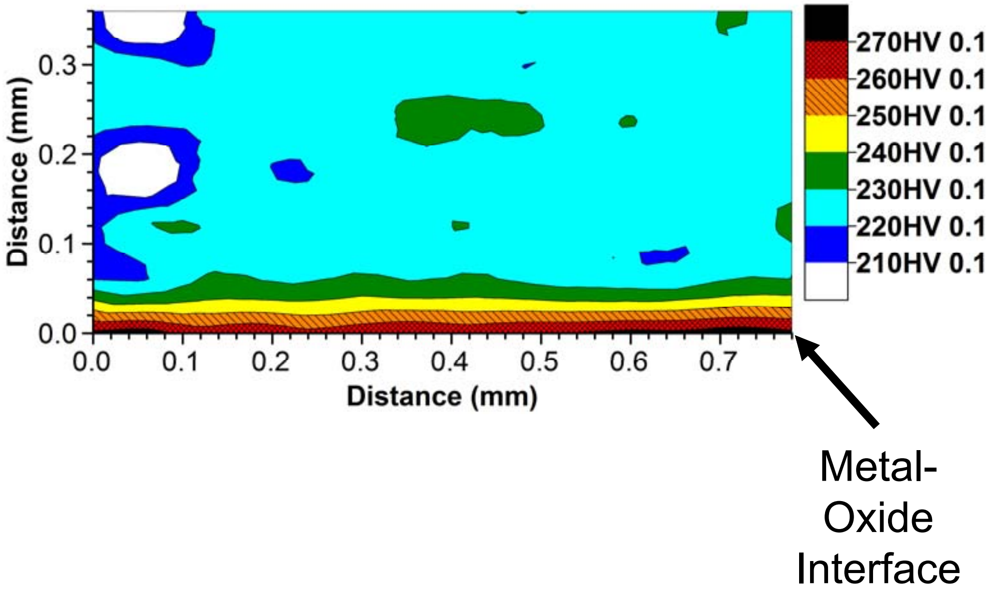
Hardness on Gr 91 after 300 hour test in <u>impure</u> sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar, 700ºC





Behavior appears to have some dependence on impurity content of sCO_2

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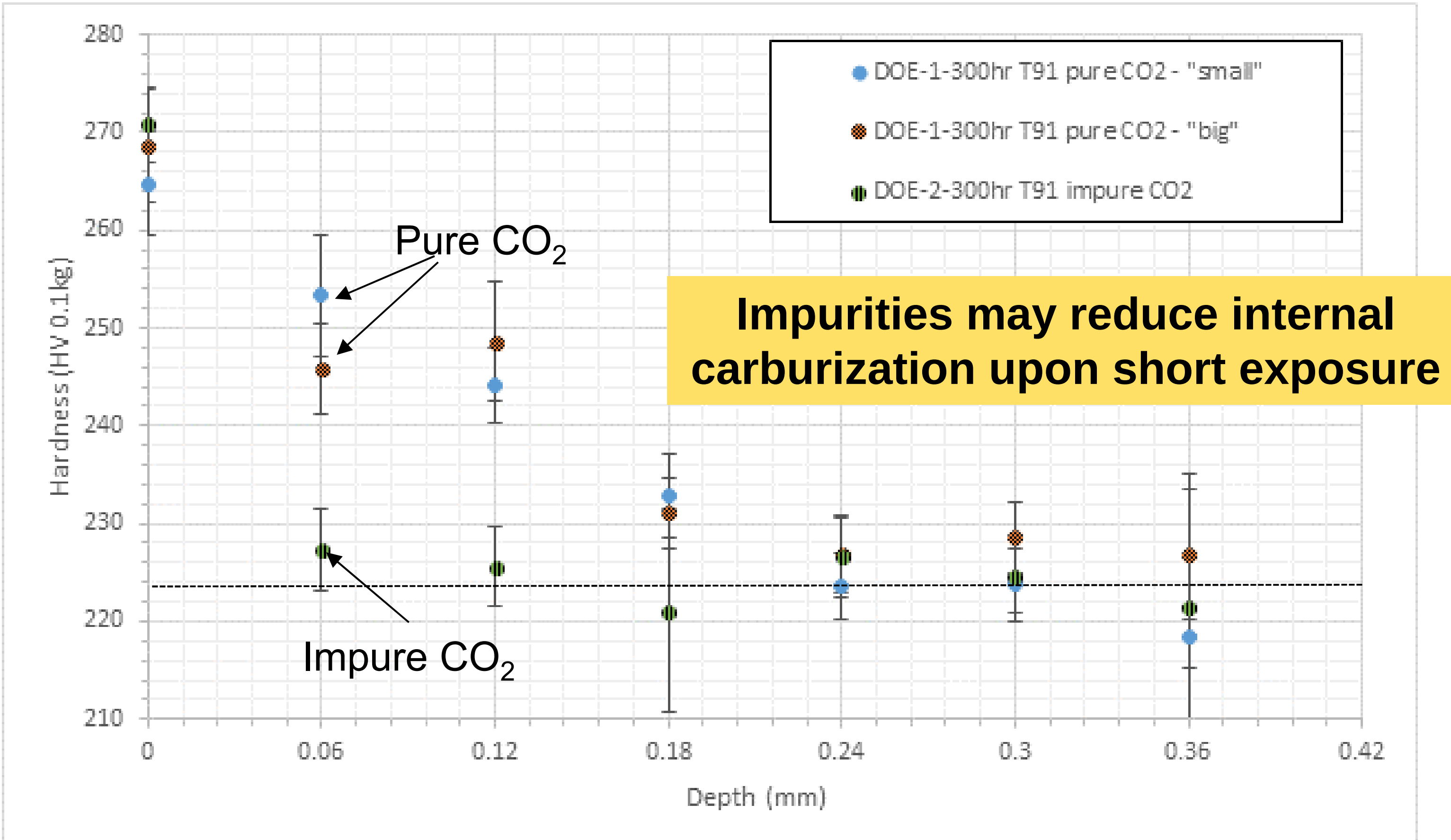
Hardness Profiles on Gr 91 after 300 hour test in pure and impure sCO_2 at 200 bar, 700°C

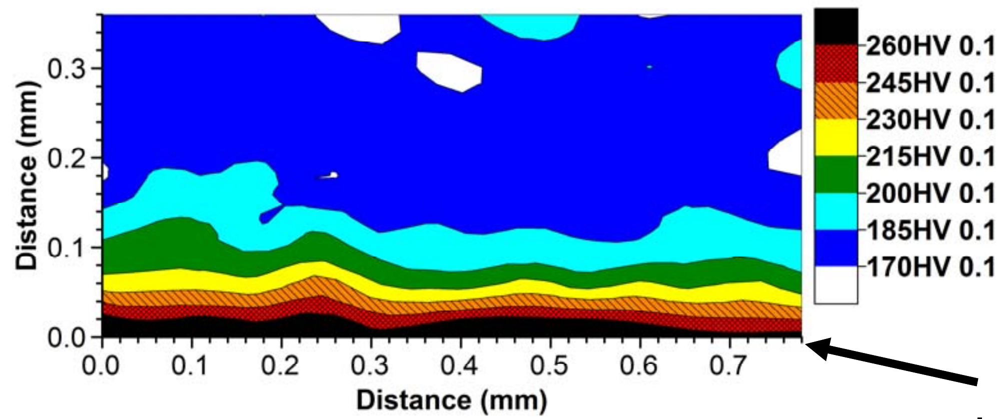


- Carburization depth >200 µm after 300 hours
- Would it lead to early breakaway corrosion?

Hardness on 304H and 740H after 300-hour test in <u>impure</u> sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar, 700°C

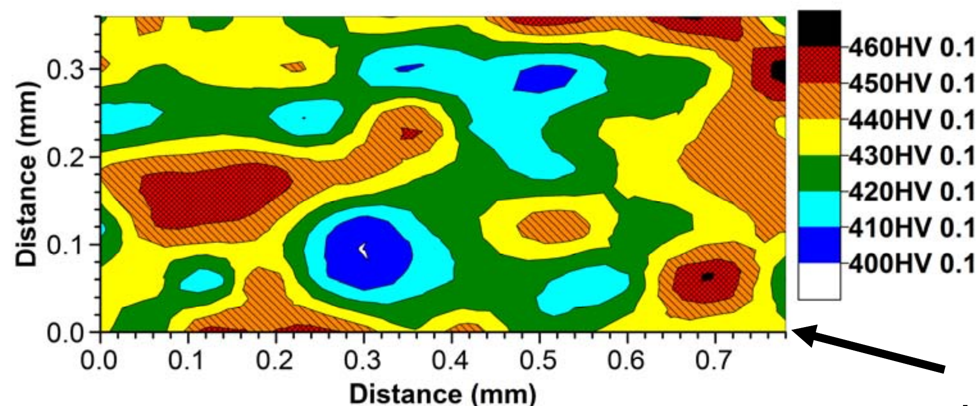
Stainless Steel 304H

304H shows some hardness increase near the alloy surface – need to evaluate further (sample prep, carburization, other)



Metal-Oxide Interface

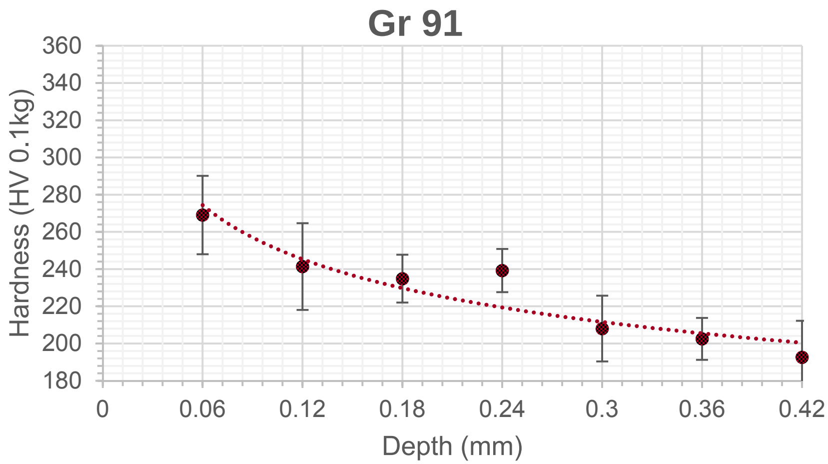
Nickel-Base Alloy 740H

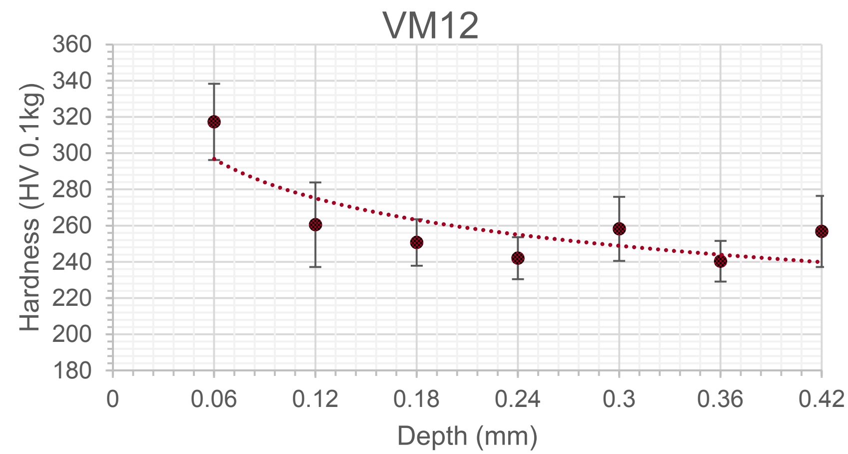


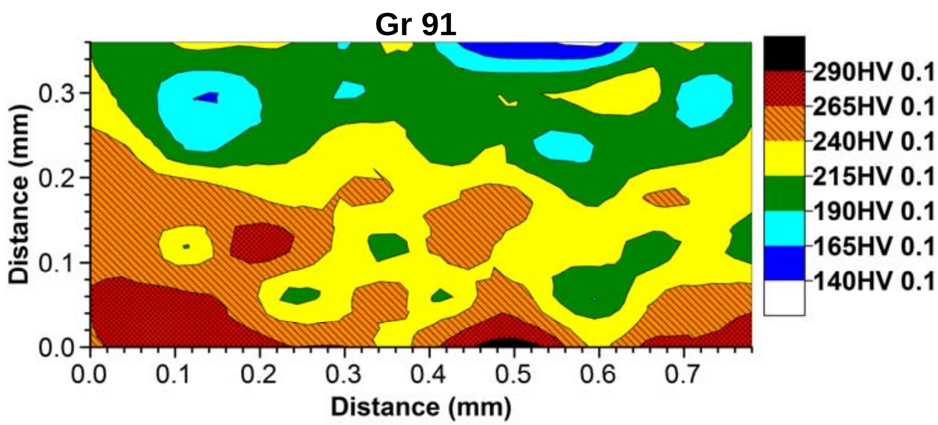
Metal-Oxide Interface

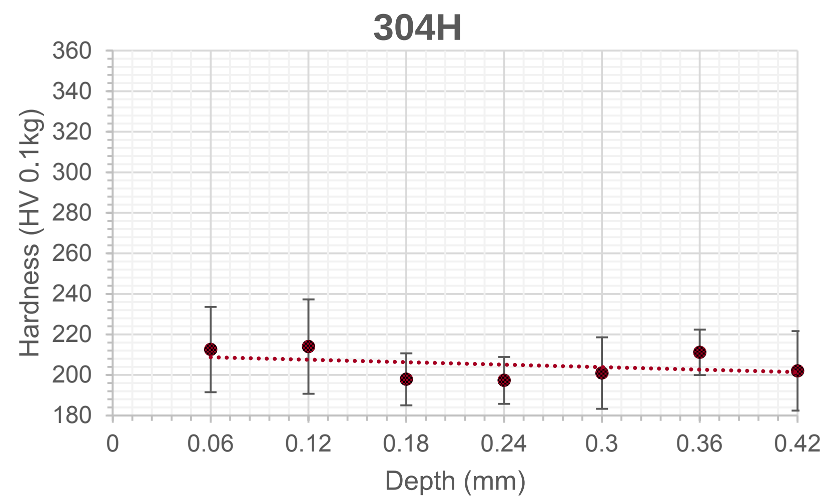
740H shows no evidence of change in surface hardness with sCO_2 exposure

Hardness on Gr 91, VM12 and 304H after 1000-hour test in <u>impure</u> sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar, 700°C









- Ferritic Gr 91 and VM12 exhibit increased hardness near surface
- Stainless steel and Ni-base alloys show no (or negligible) sign of carburization

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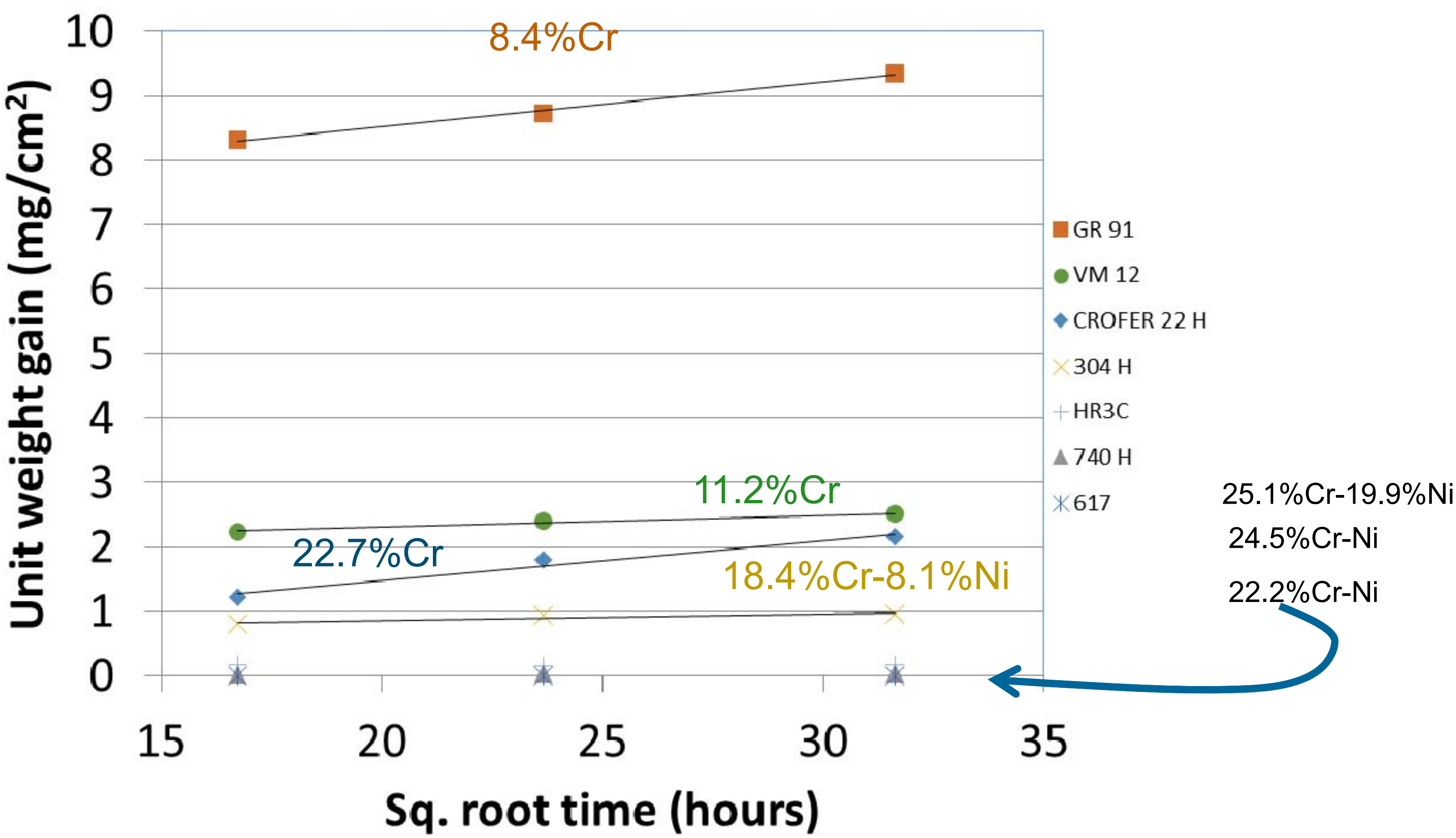
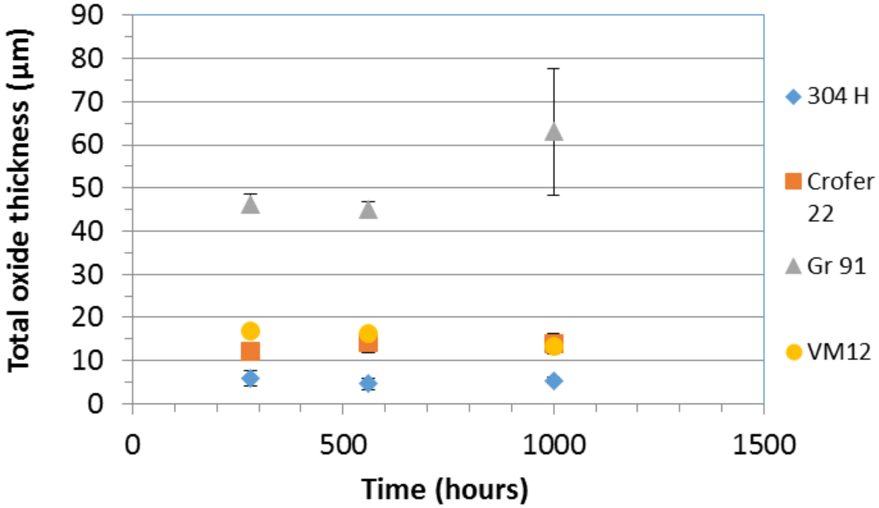
Mass Gain from 1000-hour test in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar, 700°C

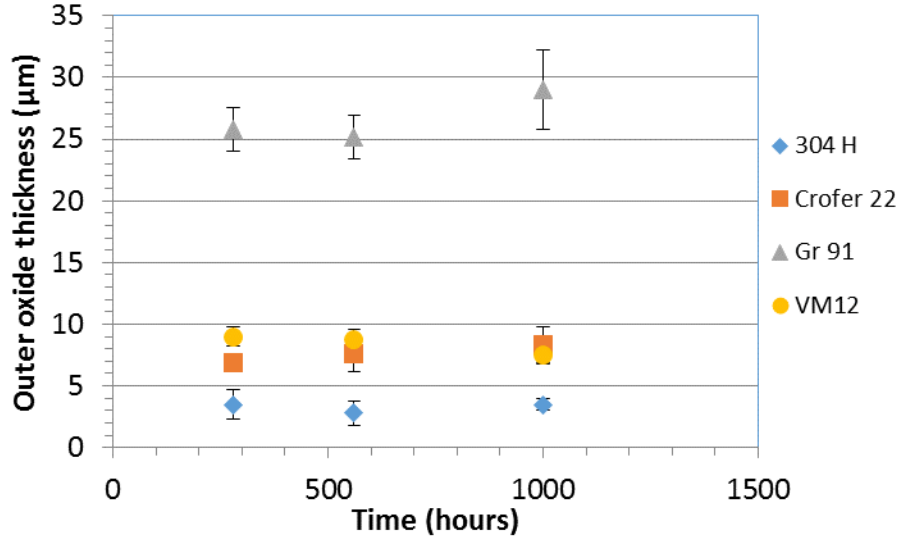


- Mass gains trend with alloy chromium content for Fe-based alloys
- 304H stainless steel has higher mass gain than HR3C
- Mass gains for HR3C, 617, and 740H are low and comparable

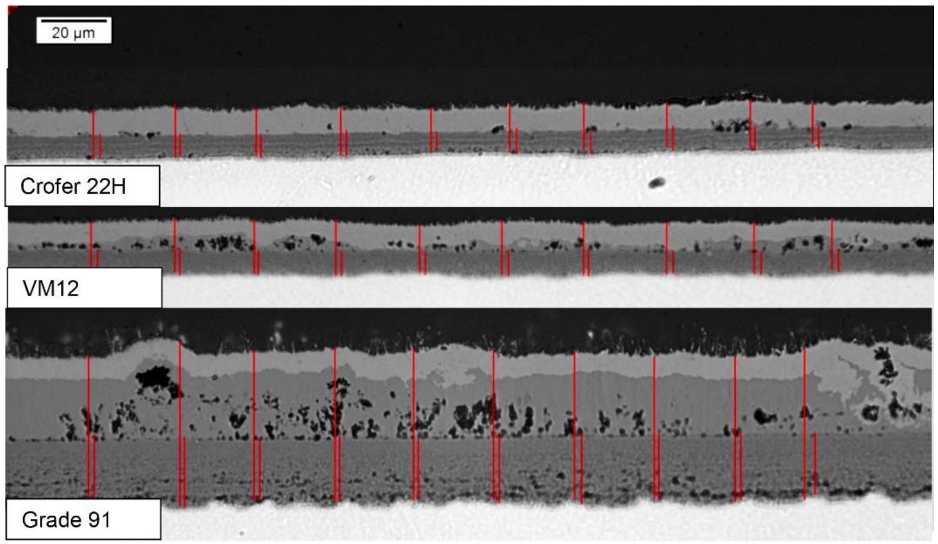
Comparison of scale thickness for ferritics and 304H

1,000-hour test in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar, 700°C





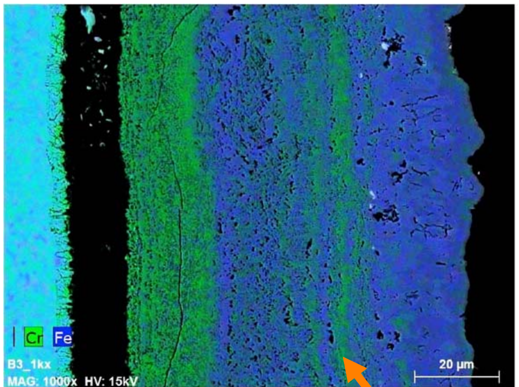
- All ferritic alloys form duplex scale structure at 700°C, even with ~23%Cr
- No exfoliation observed (yet)
  - EPRI models for steam predict exfoliation from Gr.91 at 200 to 400 microns total oxide thickness



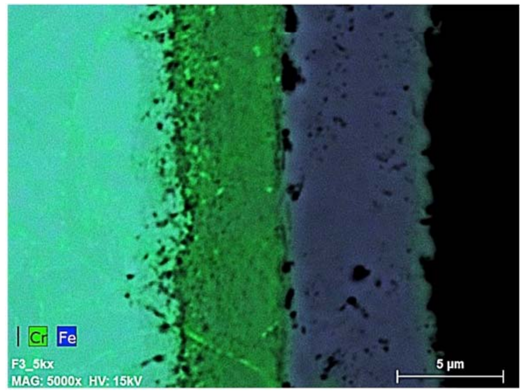
Comparison of scale morphology for ferritics and 304H

1,000-hour test in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar, 700^{o}C

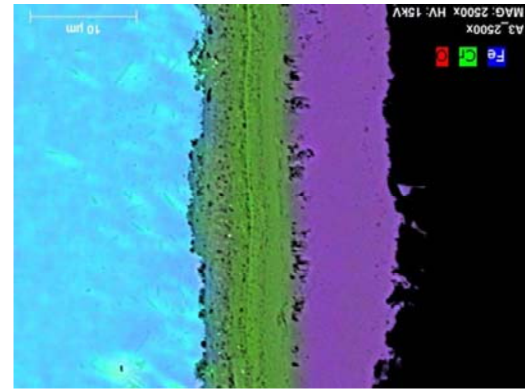
EDS Fe-Cr or Fe-Cr-O Maps Overlayed on SEM Images



Gr 91 (8.4%Cr)

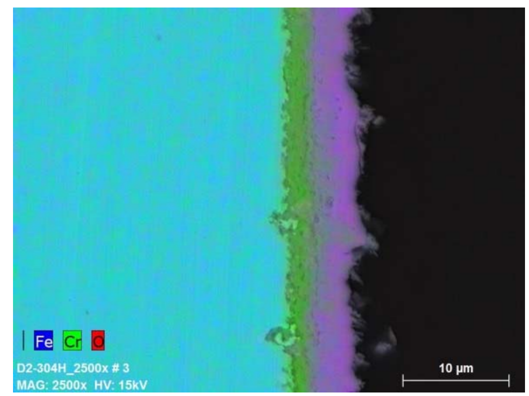


VM12 (11.2%Cr)



Crofer 22H (22.7%Cr)

- Outer oxides are Fe-based
  - Gr. 91 continued to show intermediate layer(s) showing Cr & Fe striations
  - With exception of Gr. 91, oxide morphologies appear similar to those in steam
- No exfoliation observed, but
  - outer Fe-oxide (L2) growing on all alloys suggests eventual exfoliation
  - Voids already forming on L1/L2 interfaces on ferritic alloys--these are typical locations for scale failure



304 Stainless Steel:
18.4%Cr-18.1%Ni

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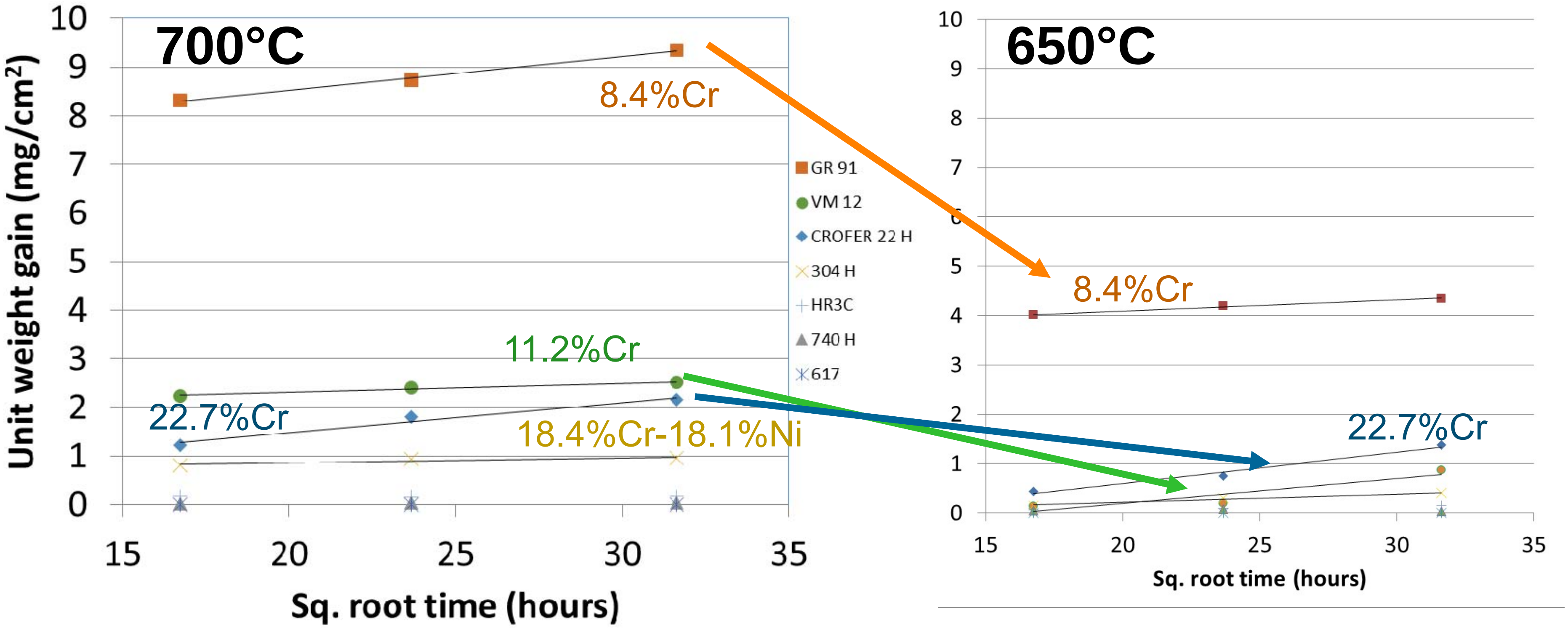
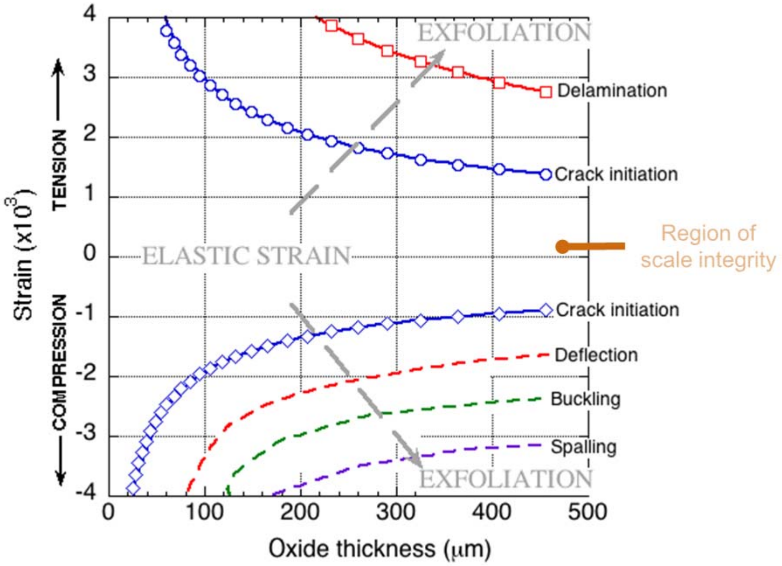
Recent Data: Mass gain from 1000-hour test in impure sCO_2 ($3.6\% O_2$, $5.3\% H_2O$) at 200 bar, 700°C versus 650°C

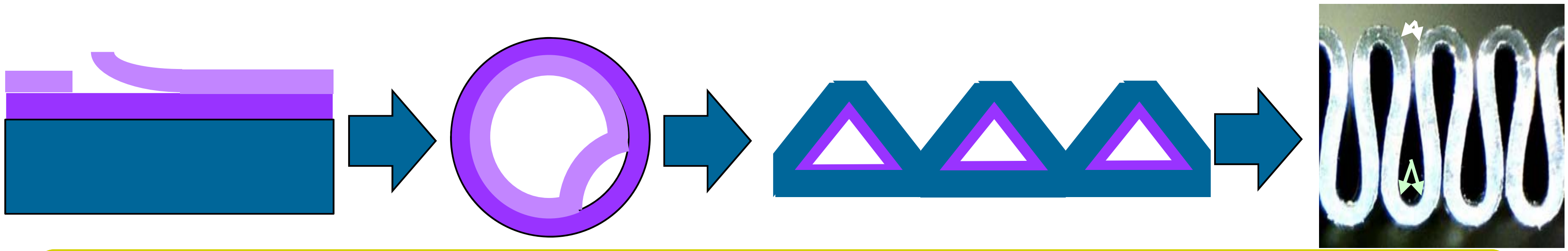


- Similar trends at 650°C to 700°C
  - Weight gain reduced by ½ with 50°C reduction in temperature
  - VM12 and Crofer 22H ranking inconsistent between tests
  - Oxide scales being characterized

Unique modeling consideration for oxide growth and exfoliation in small channel heat-exchangers

- Lab studies: isothermal oxide growth on flat coupons
- Real world: heat-flux, stress from complex geometries
- Modeling:
  - EPRI-developed strain trajectory approach for steam tubes
  - Properties of sCO_2 and alloys collected
  - **Discussion with OEMs on convex vs. concave surfaces – need to develop a generic modeling approach**





Complex HX Design envisioned for sCO_2 Brayton cycles

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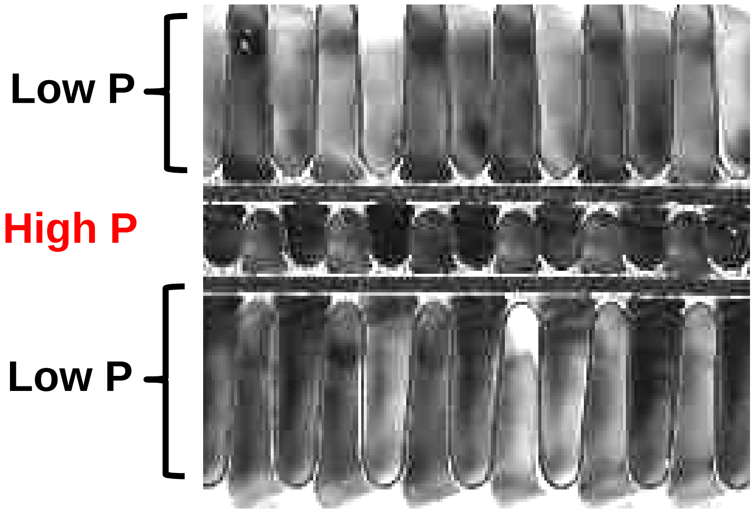
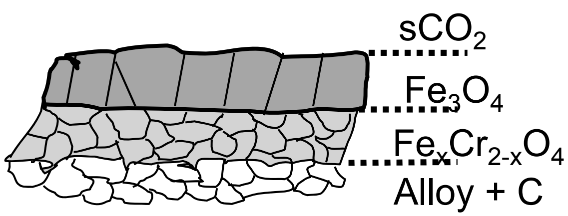
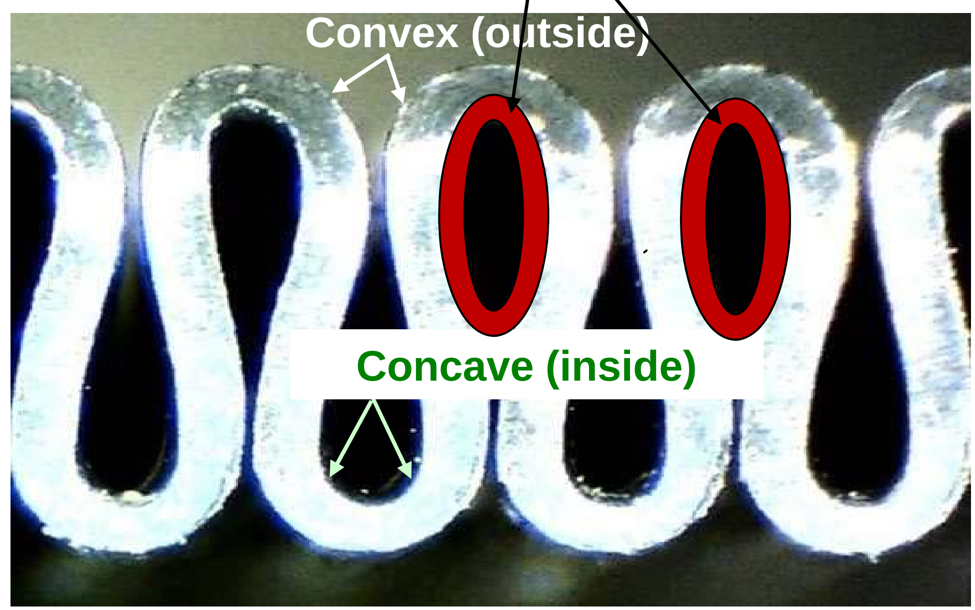
Loss of flow channel areas from scale formation





Maximum allowable thickness of the total oxide scale limited by:
- **Metal thickness**
- **Channel opening**

Reduction in flow channel areas by oxide growth



Metal thickness: 0.2 mm

Oxidation and carburization may significantly impact on HX efficiency and mechanical integrity

Project Test Matrix Progress

Description (Purpose)	Conditions	Test Status	Characterization
Rig Commissioning	Temperature monitoring & pressure	Complete	100%
Short-term (compare to literature, impurity introduction)	700°C-300hr-Pure	Complete	100%
	700°C-300hr-Impure	Complete	100%
Test Program (develop oxide thickness kinetics and propensity for exfoliation)	700°C-1,000hr-Impure	Complete	Ongoing: ~300, 700, 1,000hr: mass gain, oxide thickness, morphology
	650°C-1,000hr-Impure	Complete	
	750°C-1,000hr-Impure	Ongoing	
Long-Term (Validate Models and test unique geometries)	700°C-3,000+hr-Impure	Discussions with vendors to test actual components	

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Summary

- First project to address oxidation in open sCO_2 Allam cycle
  - Impurity concentrations have been determined via mass balance and thermodynamic calculations
- A new test rig assembled, and 300-hour laboratory tests with and without impurities completed
  - 1,000-hour tests are progressing at 650-750°C
- Although mass gains for alloys in sCO_2 and steam are similar, some differences in scale morphology on Gr.91
  - Intermediate layer between L1 & L2 with Cr striations
  - Carburization identified on ferritics using hardness mapping; appears more severe in pure sCO_2
- Effect of sCO_2 and geometry on oxidation to be evaluated through modeling

Acknowledgements

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Project Manager: Vito Cedro

Together…Shaping the Future of Electricity