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

DE-FE0024120, P.O.P. 10/01/14-09/30/17

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NETL 2017 Project Review Meeting for Crosscutting Research, Gasification Systems, and Rare Earth Elements Research Portfolios
March 20, 2017 (Pittsburg, PA USA)

Vito Cedro, NETL Project Manager

Project Goals and Objectives

- Predict the oxidation/corrosion performance of structural alloys in high-temperature high-pressure sCO_2 via laboratory testing
- Combine laboratory corrosion data with 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

Milestone Description	Completion Date
Task 1.0 - Updated Project Management Plan	10/29/2014
Task 1.0 - Kickoff Meeting	11/24/2014
Task 2.0 – Identify materials and impurities for supercritical CO_2 testing and complete initial machining of samples	3/31/2015
Task 3.1 – Assemble corrosion test rig and conduct a 300 hour test at 650-700°C	5/11/2015
Task 3.2 – Complete tests to support final decision on CO_2 composition for remaining testing	8/31/15
Task 3.3 – Complete 700C-1000 hour test	11/30/15
Task 3.3 – Complete 650C-1000 hour test	2/27/2016
Task 3.3 – Complete 750C-1000 hour test	5/10/2016
Task 3.5 – Complete long-term 5000-hour confirmatory testing	In Progress
Task 4.0 – Produce table of oxidation/corrosion rates in supercritical CO_2	1/31/16
Task 5.0 Customize ORNL exfoliation model for current alloys and lab scale pin geometries	3/31/2016
Task 5.0 Complete exfoliation modeling for standard geometries and produce data for preliminary alloy selection	In progress

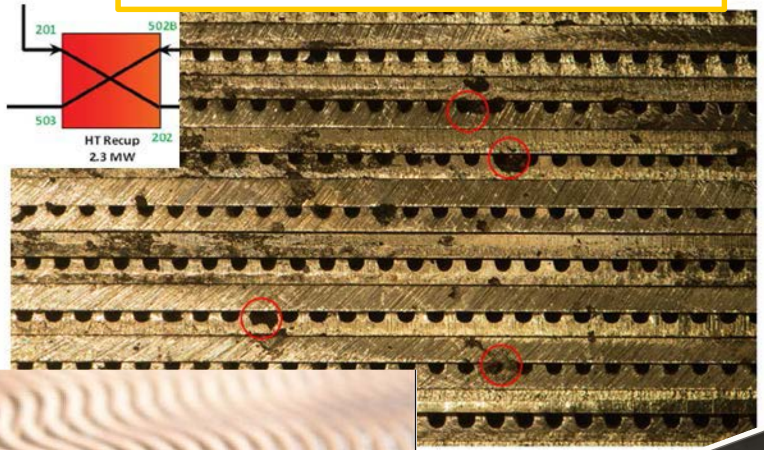
Outline

- Motivation for the Research
- Team Assembled, Plan, and Defining Test Conditions & Materials
- Experimental Approach
- Results and Ongoing Characterization
- Modeling Approach to Aid Alloy Selection
- Ongoing Research

Technology Challenges for sCO_2 Power Cycles: Heat Exchangers (HX)

- Expensive HX required: ~40% of plant cost
- Small, thin channels
- Large surface areas
- Materials considerations: thermal fatigue, creep (thin sections), brazing/diffusion bonding, corrosion/oxidation/carburization
- **Corrosion concerns:**
  - 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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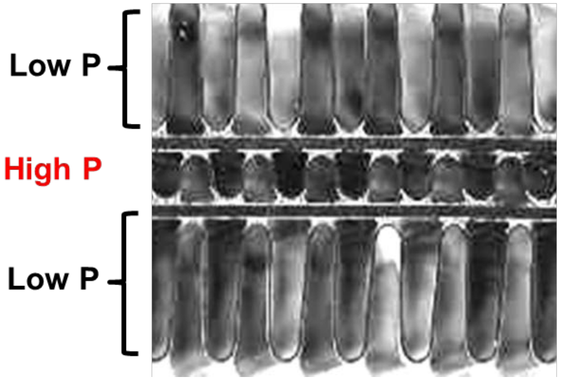
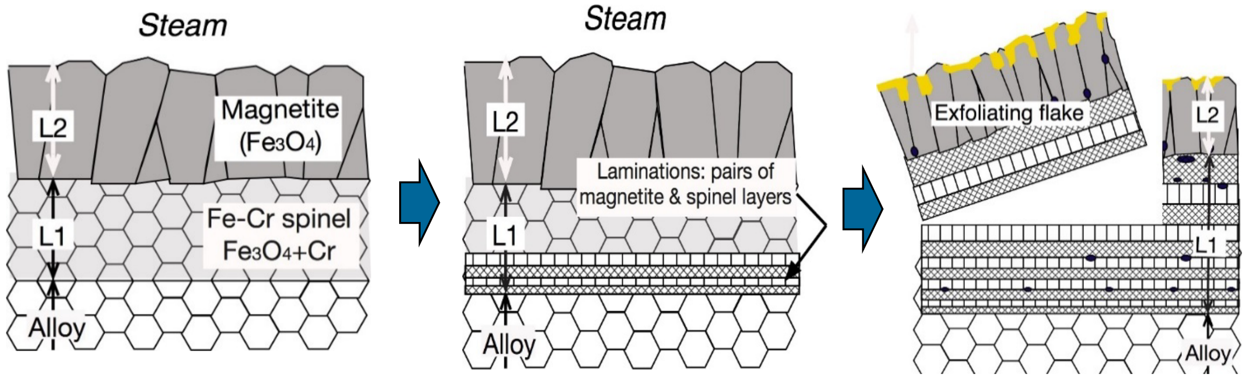
Potential Oxidation/Corrosion Failure Modes: sCO2 Heat Exchangers (HX)

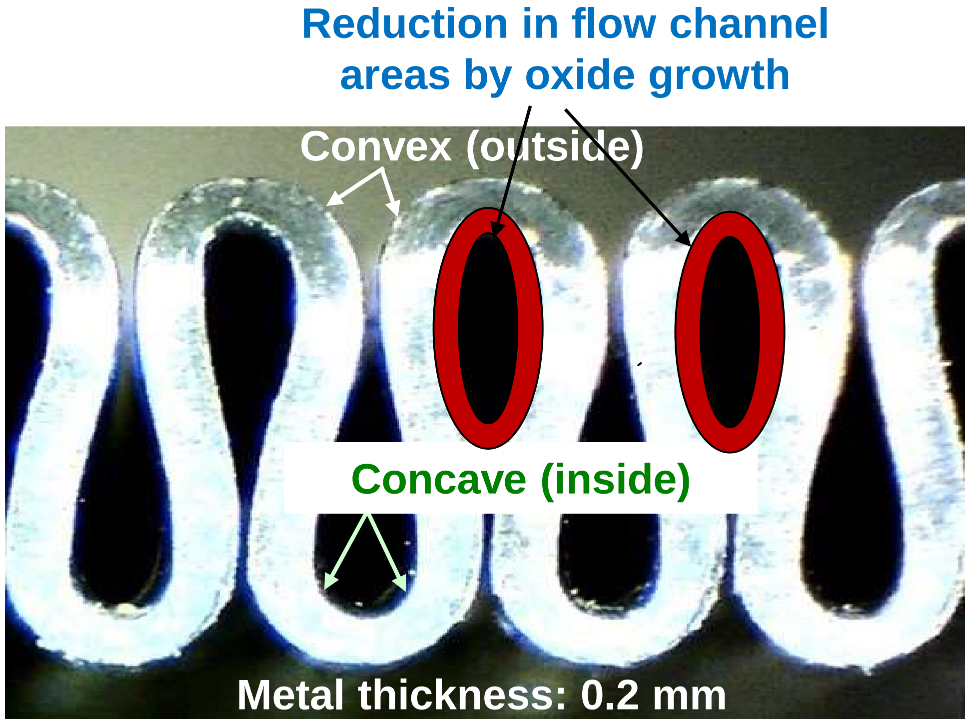
Note: Depends on HX Design (channel size, material thickness, materials of construction)





EPRI Suggested Sequence for Exfoliation of Ferritic Steels in Steam

1. **Loss of flow channel** area from scale formation
2. **Depletion of chromium** causing rapid acceleration of oxidation (Breakaway)
   - **Consumption of Cr** due to small reservoir of Cr in thin materials
   - **Carburization** reducing Cr near surface
3. **Exfoliation** causing channel blockage



Mass gain data are not enough: thickness kinetics, scale morphology, microstructure, & modeling

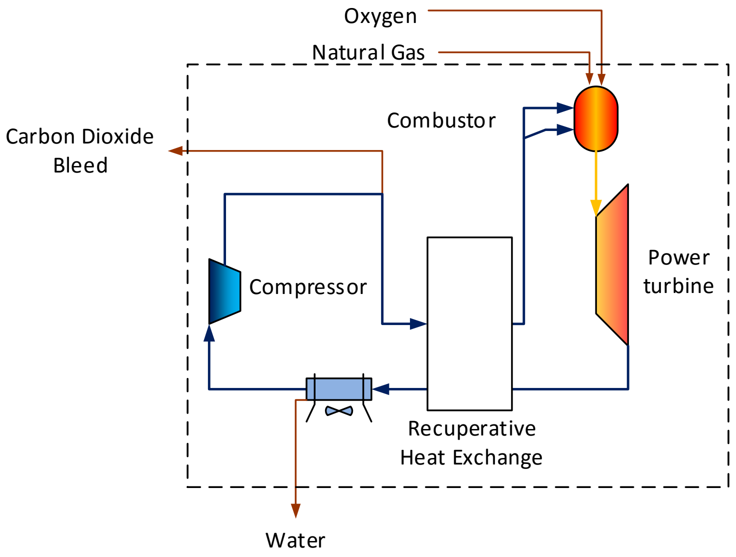
Project Team and Project Structure

- **EPRI** (Lead project, survey vendors, source materials, determine test conditions through cycle analysis, integrate experimental results, analyze data, perform limited characterization)
  - John Shingledecker (Principle Investigator)
  - David Thimsen
  - Steve Kung
  - *Facilities: materials, machining, characterization*
- **DNV-GL** (Testing and measurements)
  - Brett Tossey
  - *Facilities: sCO_2 testing, corrosion measurements, materials characterization*
- **WrightHT** (Comparisons with steam behavior, support modeling approaches)
  - Ian Wright
- **Oak Ridge National Laboratory** (Modeling)
  - Adrian Sabau

- Task 1.0 – Project Management and Planning
- Task 2.0 – Materials Selection, Production of Specimens, and Selection of Impurities in sCO2 Fluid
  - 2.1: Select Materials
  - 2.2: Produce Test Specimens
  - 2.3: Select Types & Concentrations of Impurities in the sCO2 Fluid
- Task 3.0 – Laboratory Oxidation/Corrosion Testing and Analysis of Exposed Test Specimens
  - 3.1: Assemble & Shake-Down of sCO2 Oxidation/Corrosion Test Rig
  - 3.2: Evaluate Impurities in sCO2 Fluid
  - 3.3: Perform High Pressure Oxidation/Corrosion Tests
  - 3.4: Characterize and Analyze Exposed Test Specimens
  - 3.5: Perform Model Validation Tests
- Task 4.0 – Evaluation of Oxidation Kinetics & Compare w/Steam
- Task 5.0 –Computational Model of Oxidation/Corrosion in sCO2
  - 5.1 – Develop a Physical Properties Database
  - 5.2 – Develop the Computational Model Framework
  - 5.3: Input Oxidation Kinetics and Perform an Isothermal Analysis
  - 5.4: Model Performance of Standard Heat Exchanger Geometries

Realistic sCO_2 conditions for semi-open Allam cycles

- **Survey of industry and current studies**
  - 700ºC 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)



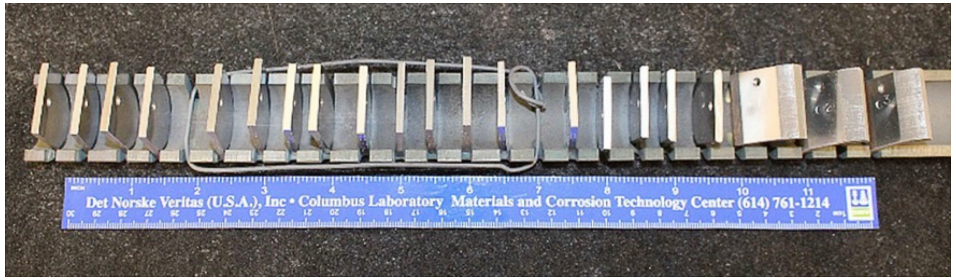
Species	Composition (mol%)		
	Methane	Cooled raw coal syngas	Oxygen
CH_4	100	1.0	
CO		39.0	
H_2		28.3	
CO_2		8.0	
H_2O		20.0	
N_2+Ar		2.0	0.5
H2S		0.9	
HCl		0.02	
O_2			99.5
LHV	912 BTU/scf	218 BTU/scf	

Component	Composition (mol%)			
	Methane		Cooled Raw Coal Syngas	
Fuel Stream	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	4	1	1
HCl				20 ppm
SO_2				1,000 ppm

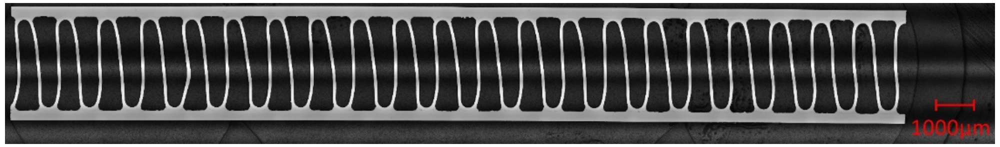
O_2 = 3.6 vol%, H_2O = 5.3 vol%

Scope of Laboratory sCO_2 Corrosion Tests

- Conditions
  - 650-750°C, 200 bar
  - sCO_2
    - Commercially pure CO_2
    - Simulated open cycle with impurities (O_2 + H_2O) from NG



Material Class	Alloys Selected		
Ferritic steels	Gr. 91 (8-9Cr)	VM12 (11-12Cr)	Crofer22H (22Cr)
Austenitic stainless	304H (18Cr)	HR3C (25Cr)	
Nickel-based	617 (20Cr, solid sol'n)	740H (25Cr, ppt. strengthened)	



- Exposures
  - 300 hours (Gr 91, 304H, 740H), 700°C
  - 1,000 hours (all 7 alloys), 650, 700, and 750°C
  - 5,000 hours (all 7 alloys + component samples), 700°C

- Materials of interest
  - Commercially available
  - Code approved or Industrially relevant
  - Focus on economics

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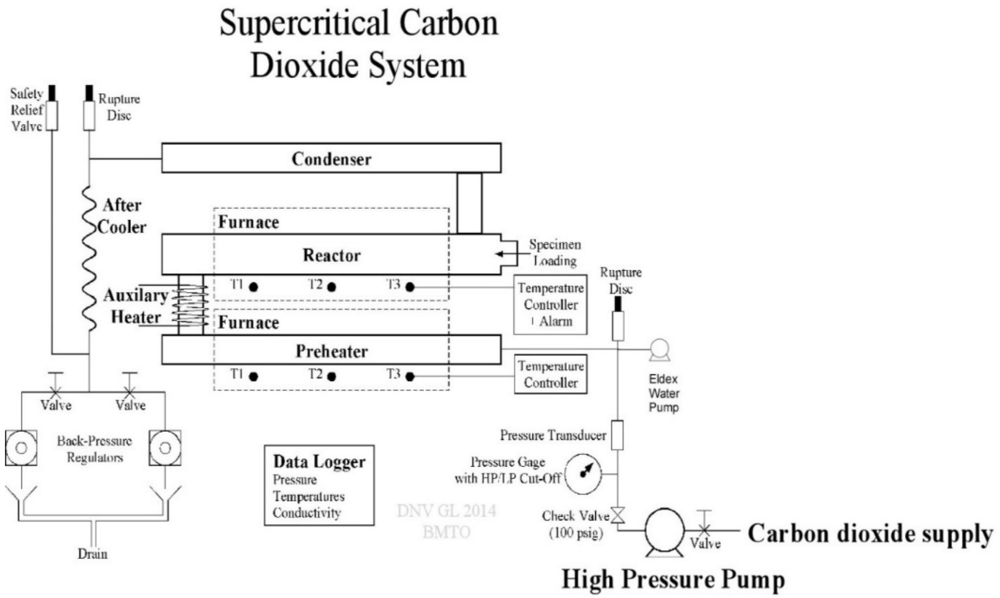
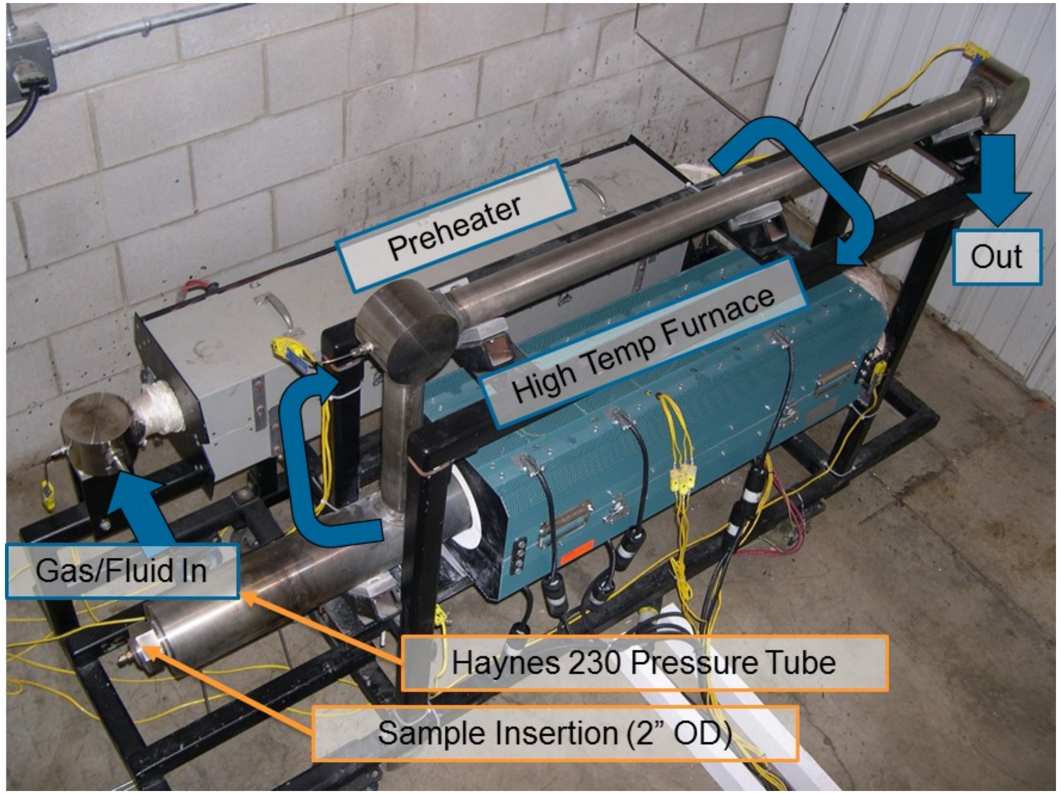
Laboratory Testing Facility (DNV-GL)

- High temperature and pressure (600-750^{o}C, 200 bar)
- Existing test facility modified for sCO_2 with safety features
- Capable of introducing impurities (O_2, H_2O)
- Shake-down (300hr) tests with Gr. 91, 304, and 740H showed similar mass gains to other studies for pure sCO_2





Gas Volume: 4.41 liters

Refresh Rate: static, with occasional replenishment

Temperatures: preheat at 454^{o}C. exit at 149^{o}C

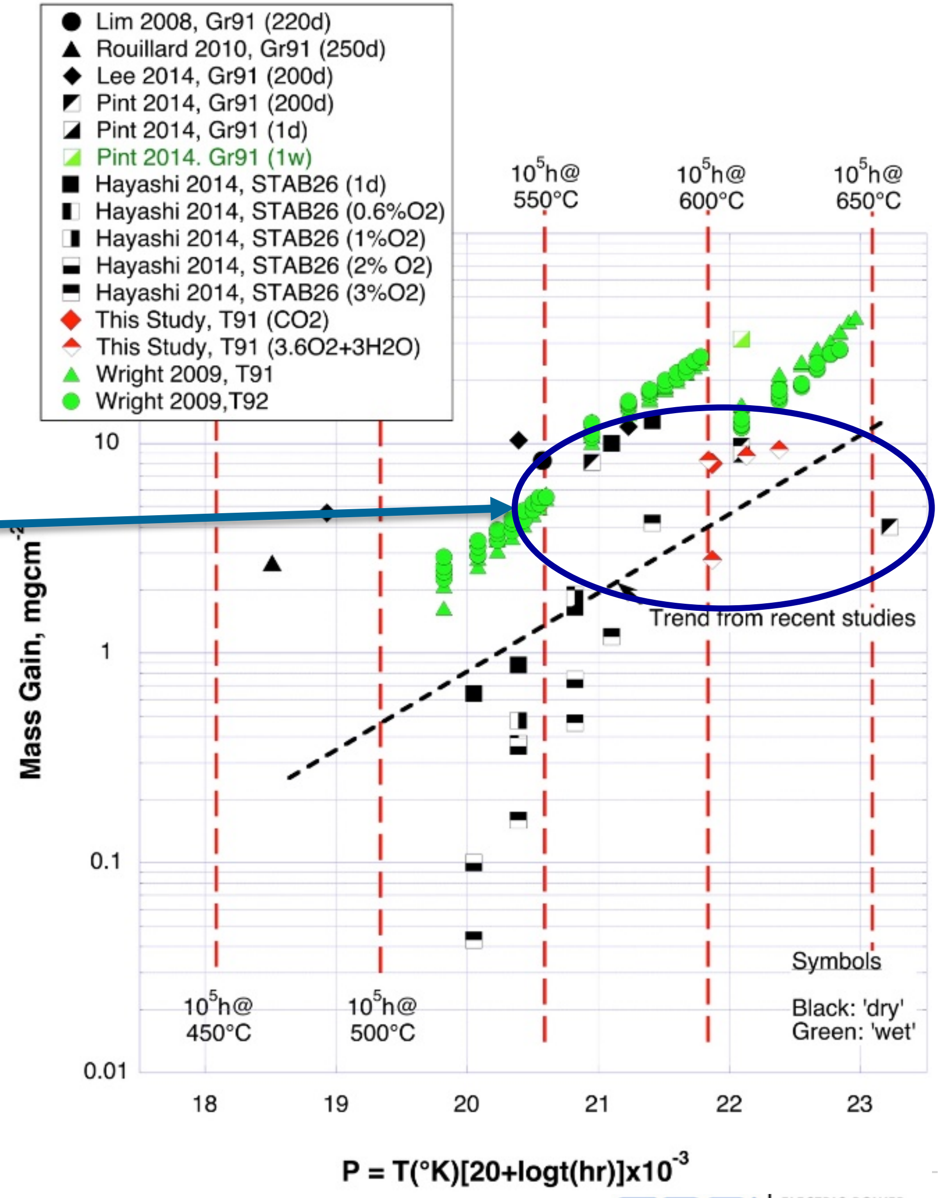
Large volume compared to sample area

Solubility of H2O in sCO2 at ~130°C = 0.5: up to 50% reduction in H2O on samples

Shake-Down Tests and Comparison of mass gain in sCO_2 and steam

- Mass gain results from 300-hour tests at 700ºC and 200 bar are similar to those in steam and sCO_2 from other studies
- **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



Mass gain data from current project are consistent with assembled literature steam data

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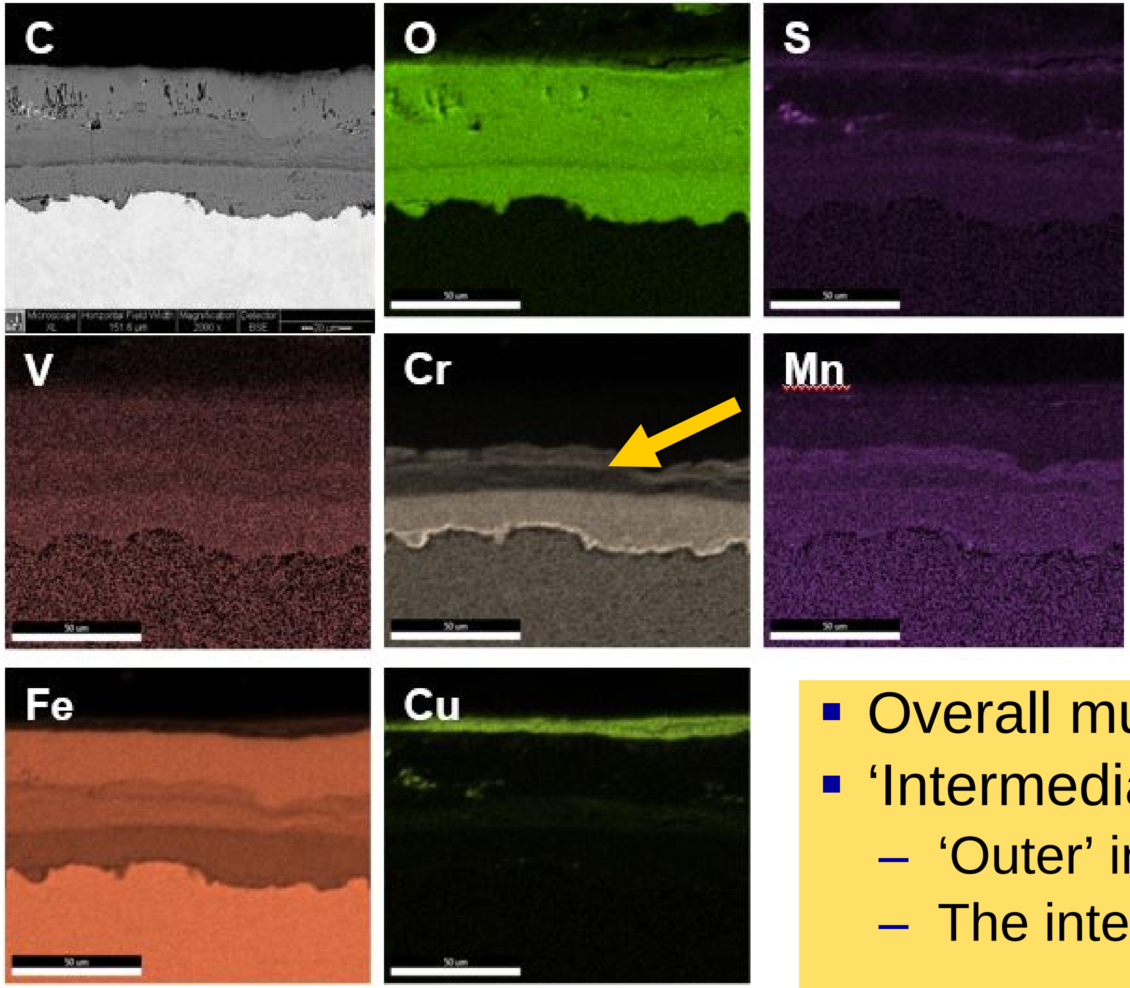
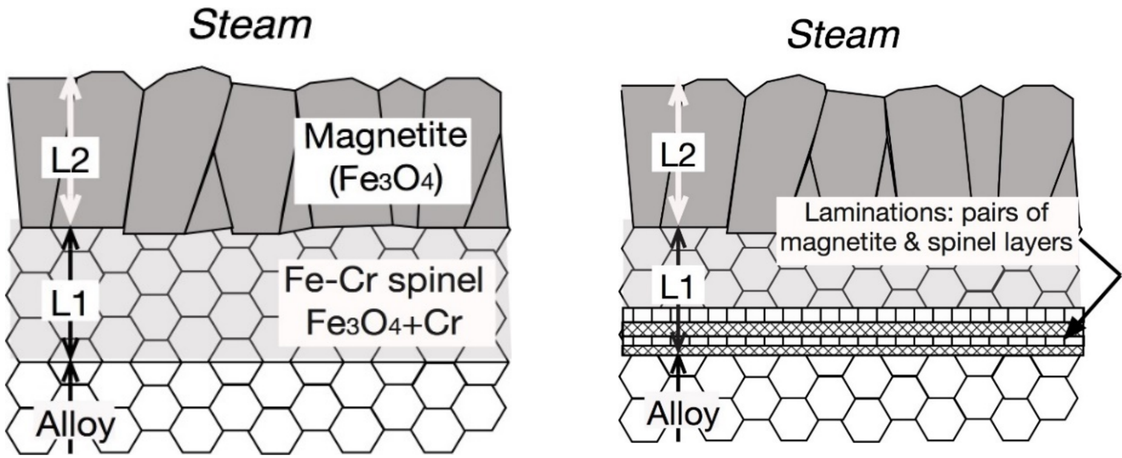
Oxide Morphology of Grade 91 after 300 hour test in pure CO_2 at 200 bar, 700ºC

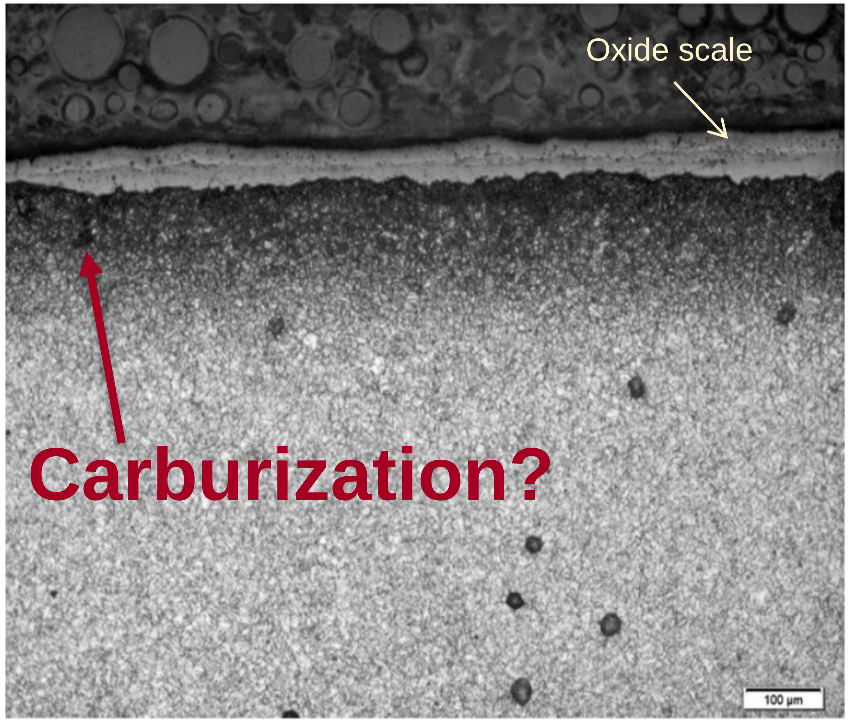




- Overall multi-layered scale structure, but
- ‘Intermediate layers’ present between expected L1 & L2
  - ‘Outer’ intermediate layer contains Cr (level lower than in L1)
  - The intermediate layers not found on other alloys tested

Gr 91 suggesting carburization after only 300 hours in pure sCO_2 at 200 bar and 700ºC

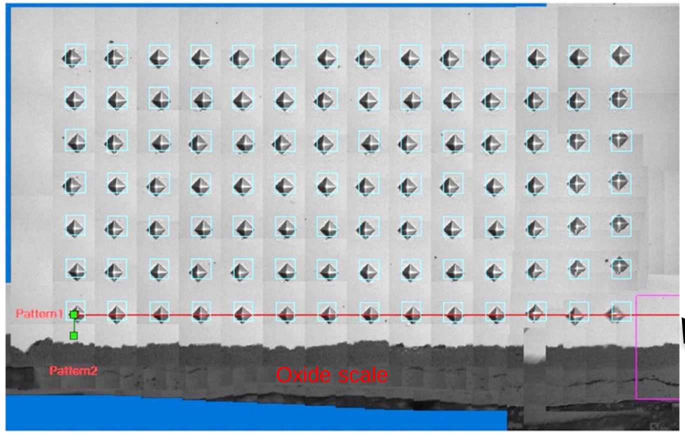
- Decoration of etched Gr 91 microstructure
- Initial spot hardness measurements for carburization inconclusive
- More detailed characterization performed



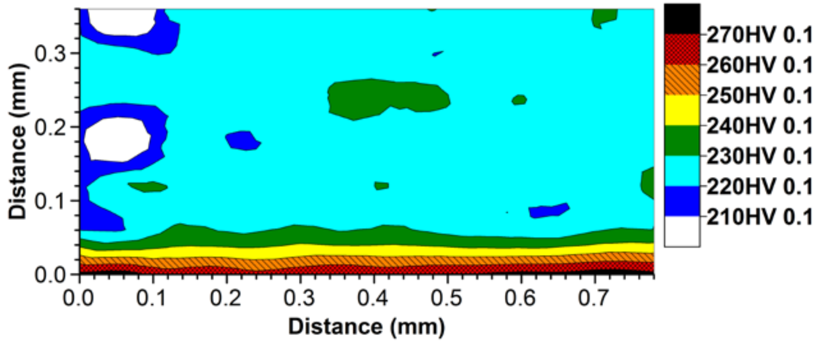
Hardness Profiles on Gr 91 after 300 hour test in pure and impure sCO_2 at 200 bar and 700ºC

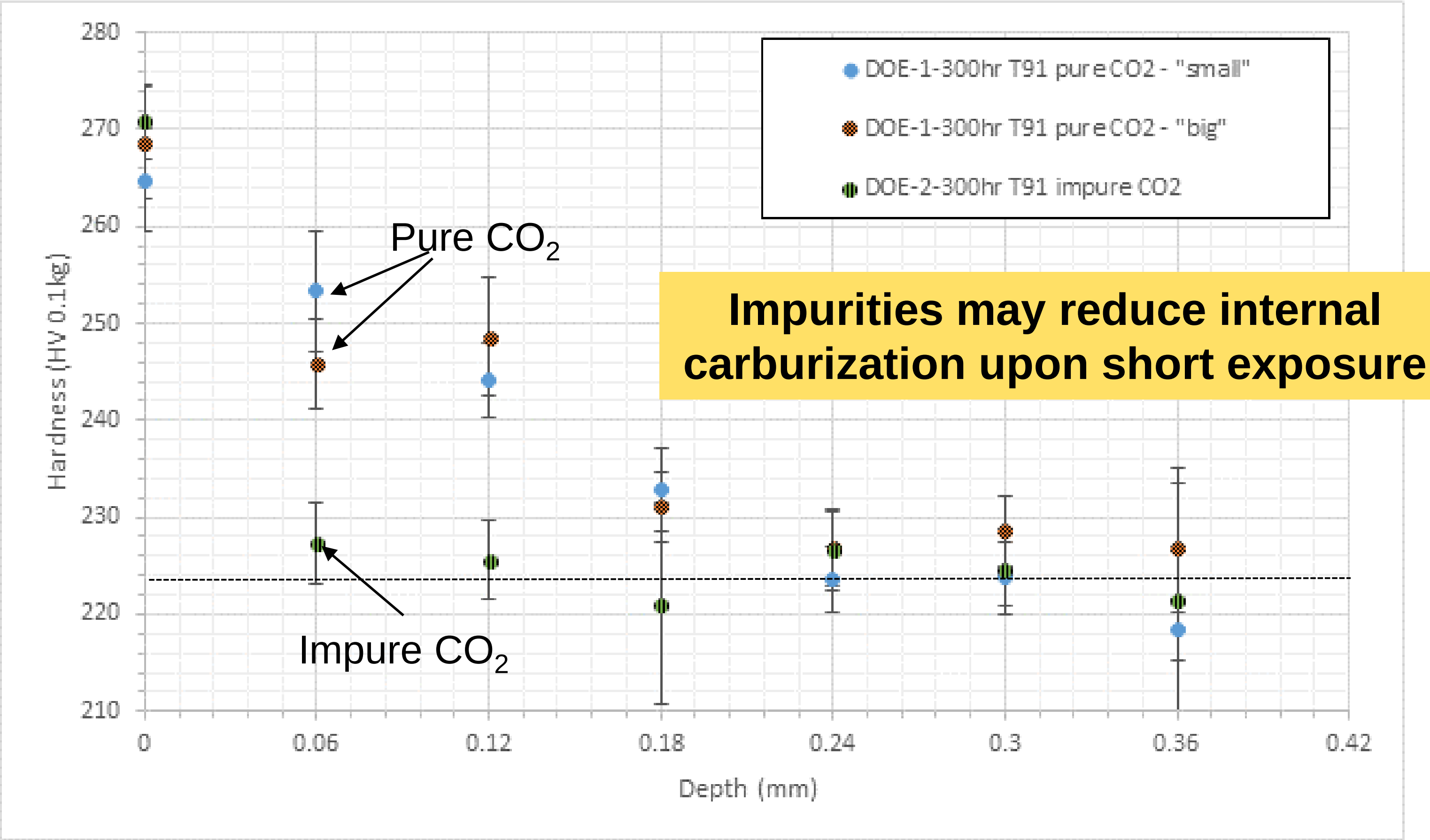
Experimental Approach

Hardness Map: 14x7=98indents



Metal-Oxide Interface





Impurities may reduce internal carburization upon short exposure

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

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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	Mass gains and thickness complete, final SEM analysis
	650°C-1,000hr-Impure	Complete	
	750°C-1,000hr-Impure	Complete	
Long-Term (Validate Models and test unique geometries)	700°C-5,000hr-Impure *Includes actual commercial HX components from OEMs*	1,000hr **Complete** 3,500hr **Complete** 5,000 hr **Ongoing(April)**	Started

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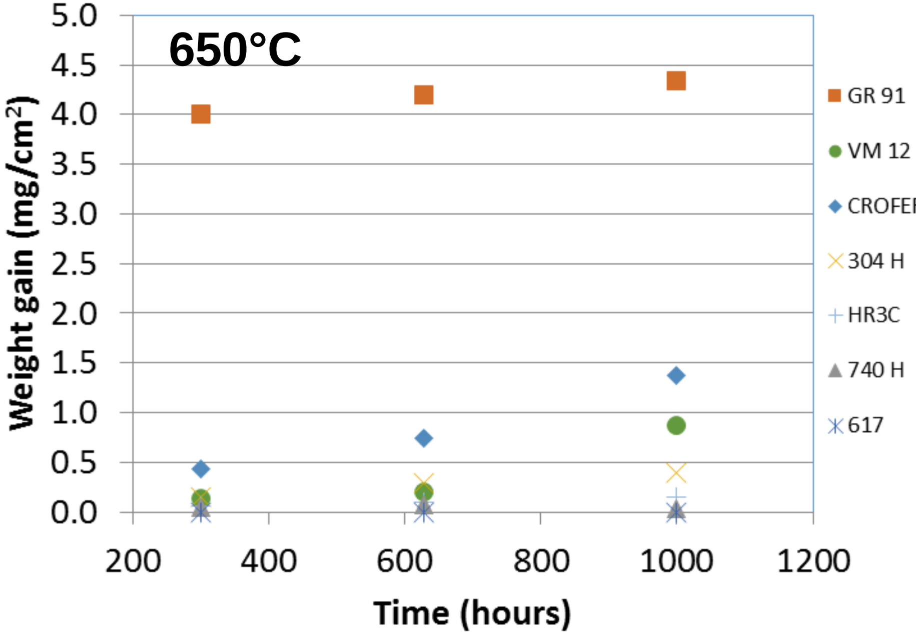
Weight Gain



8.4%Cr

11.2%Cr

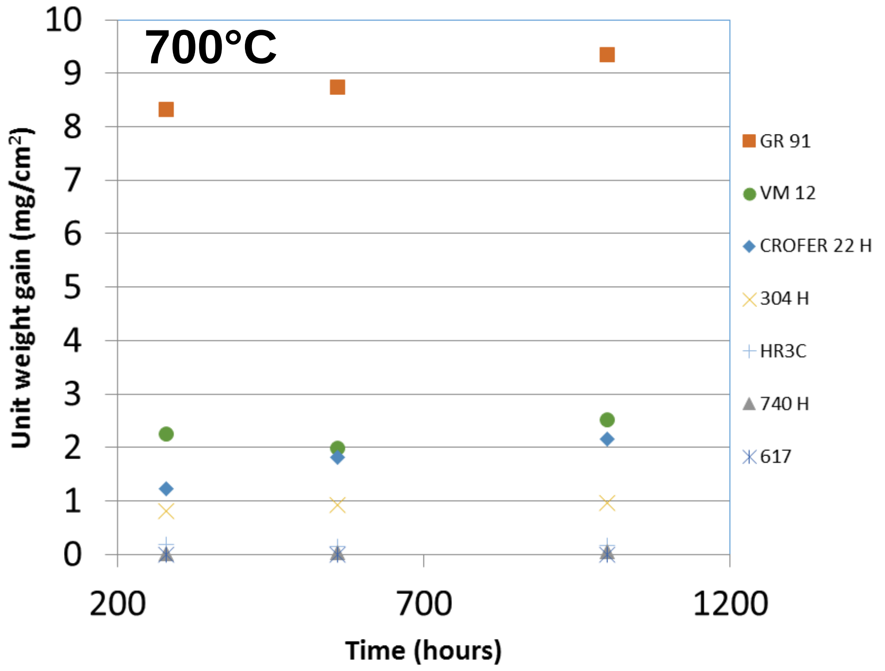
22.7%Cr

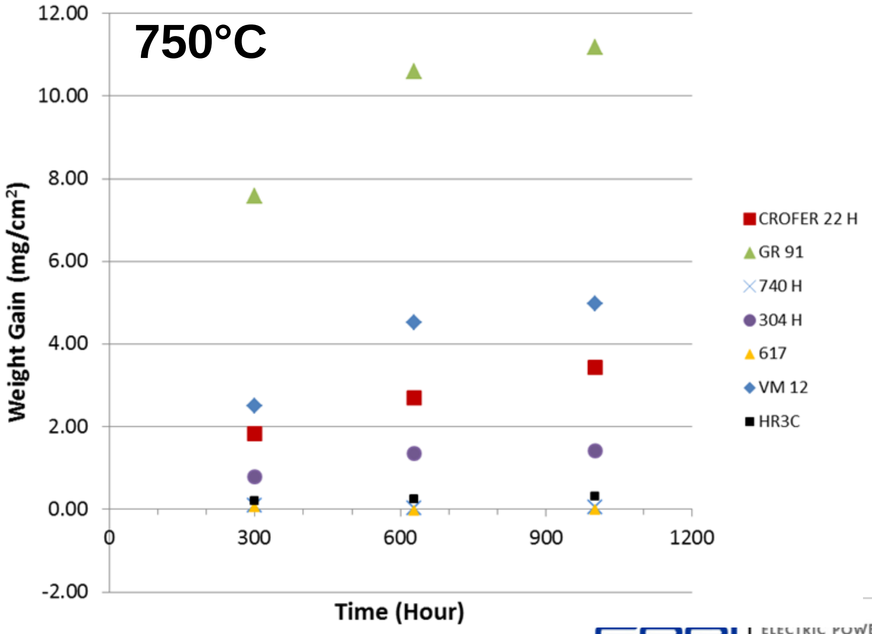
18.4%Cr-8.1%Ni

25.1%Cr-19.9%Ni

24.5%Cr-Ni

22.2%Cr-Ni





- Gr91>VM12/Crofer22H>304H>HR3C/740H/617
- 1000hrs: no clear change in oxidation rate (mass gain) – need to do longer term tests

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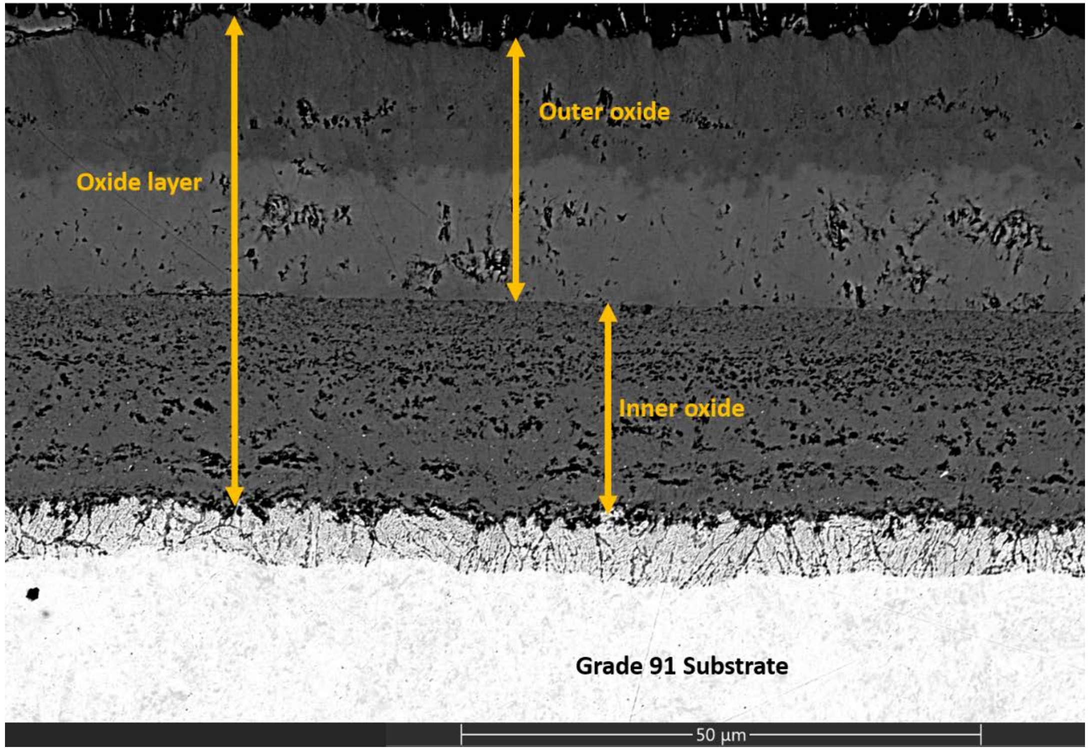
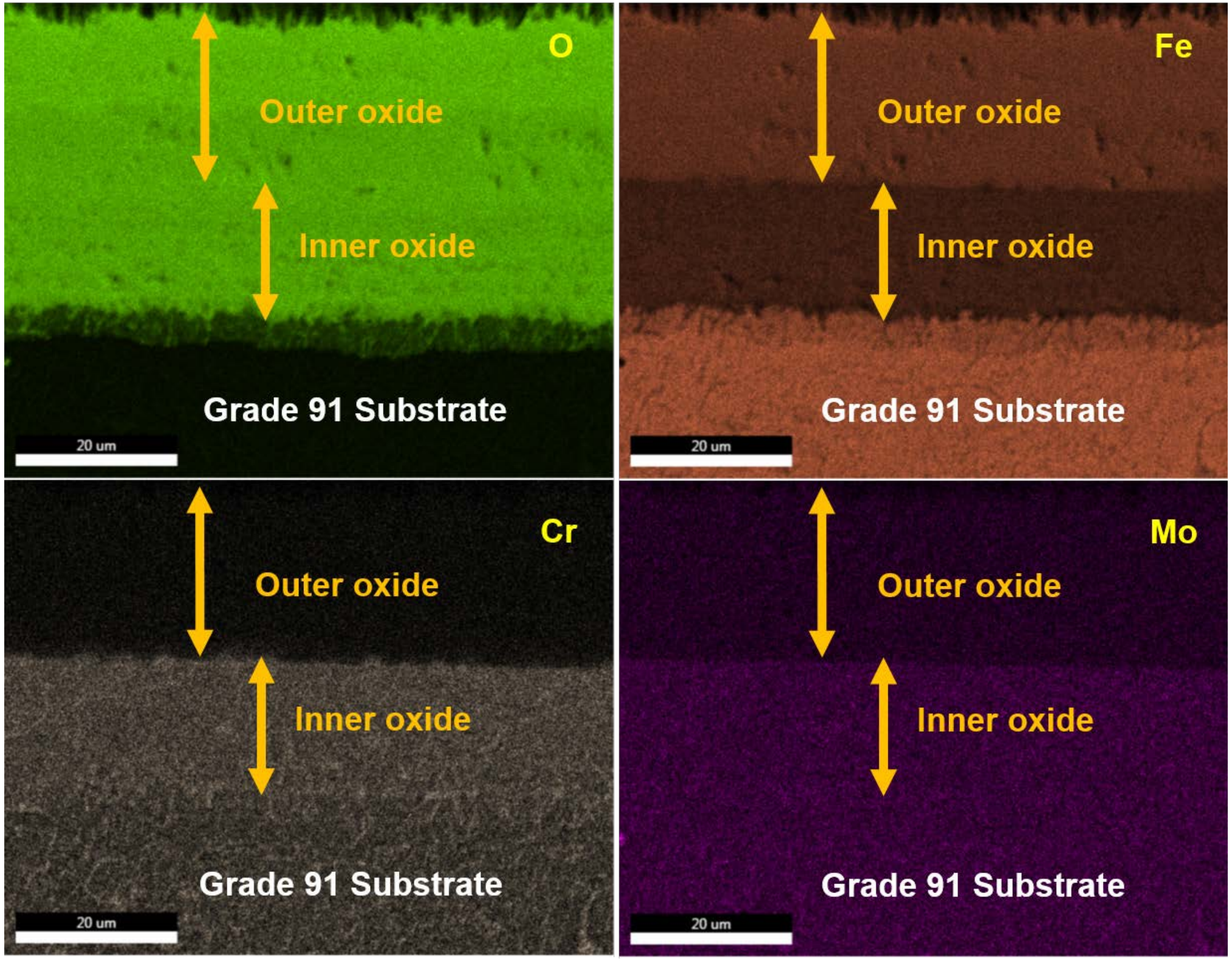
Comparison of scale morphology for Grade 91 and 304H

1,000 hours in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar and 700ºC



Grade 91



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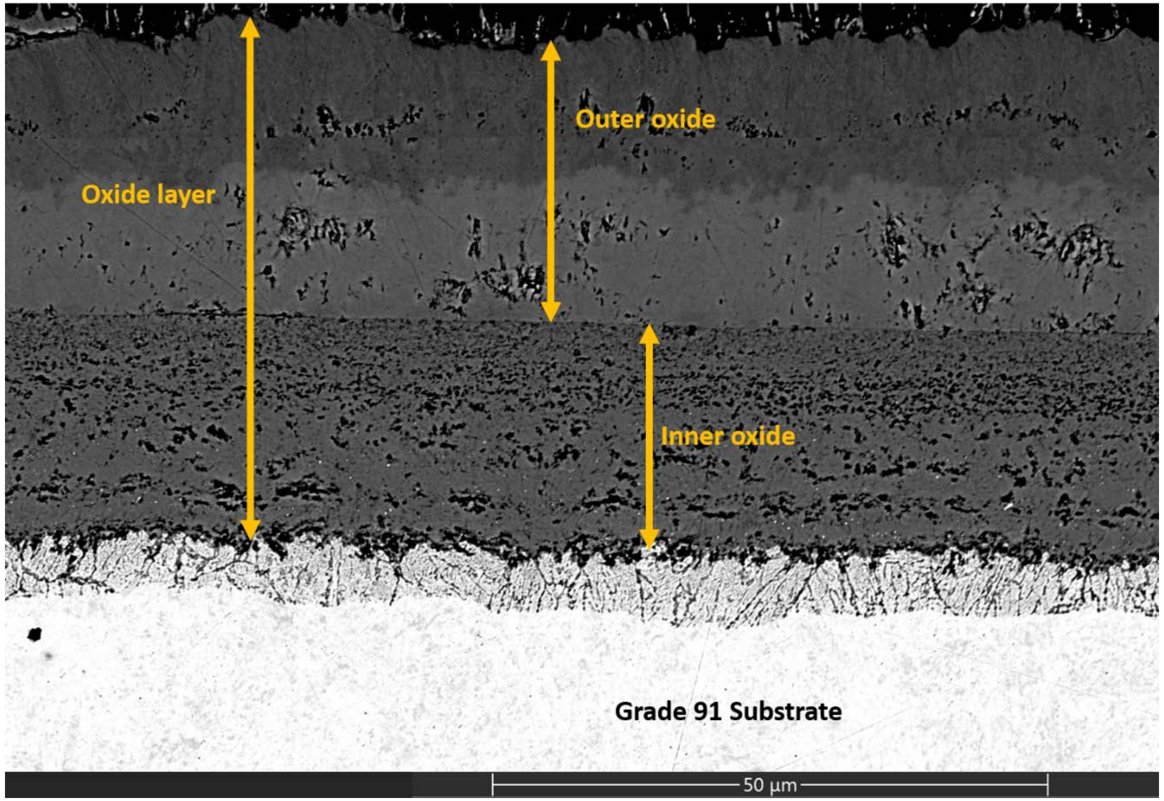

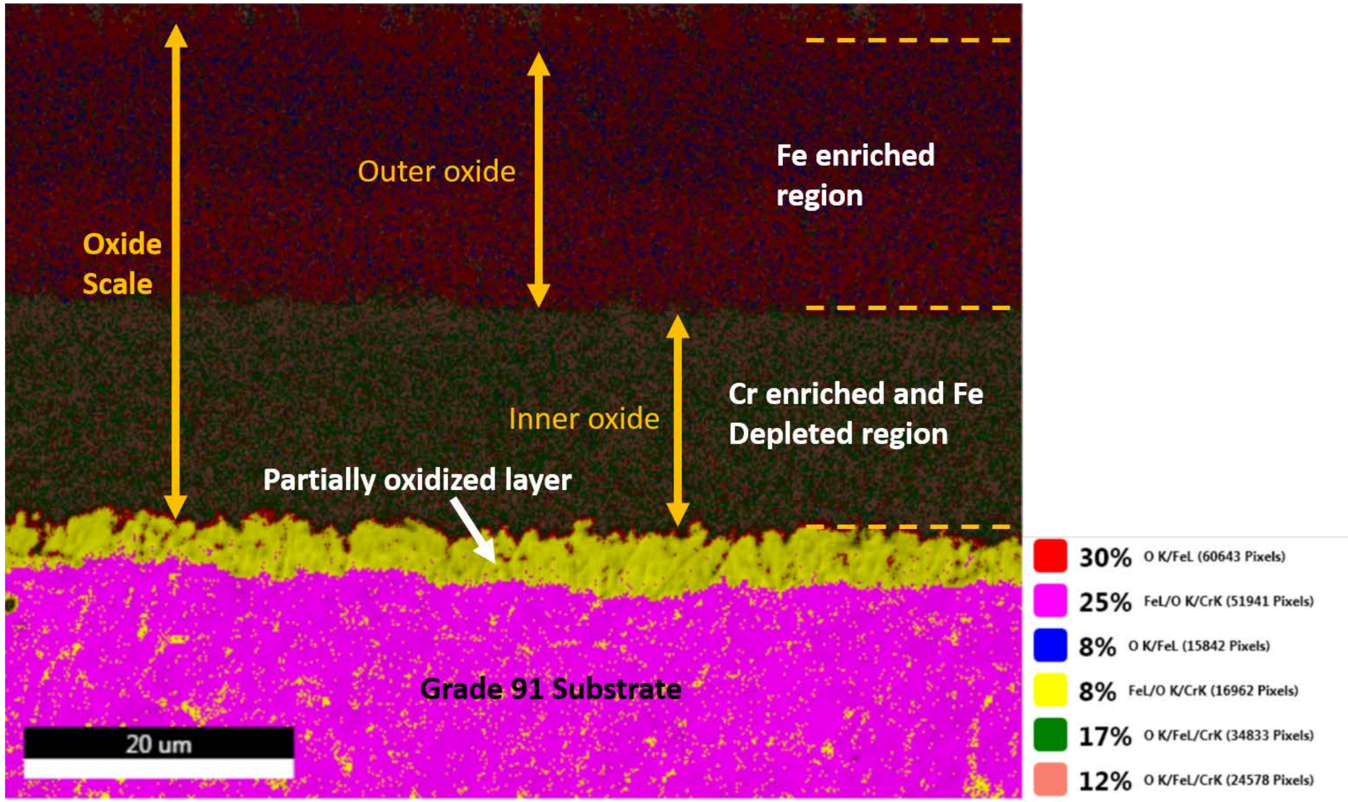

Grade 91

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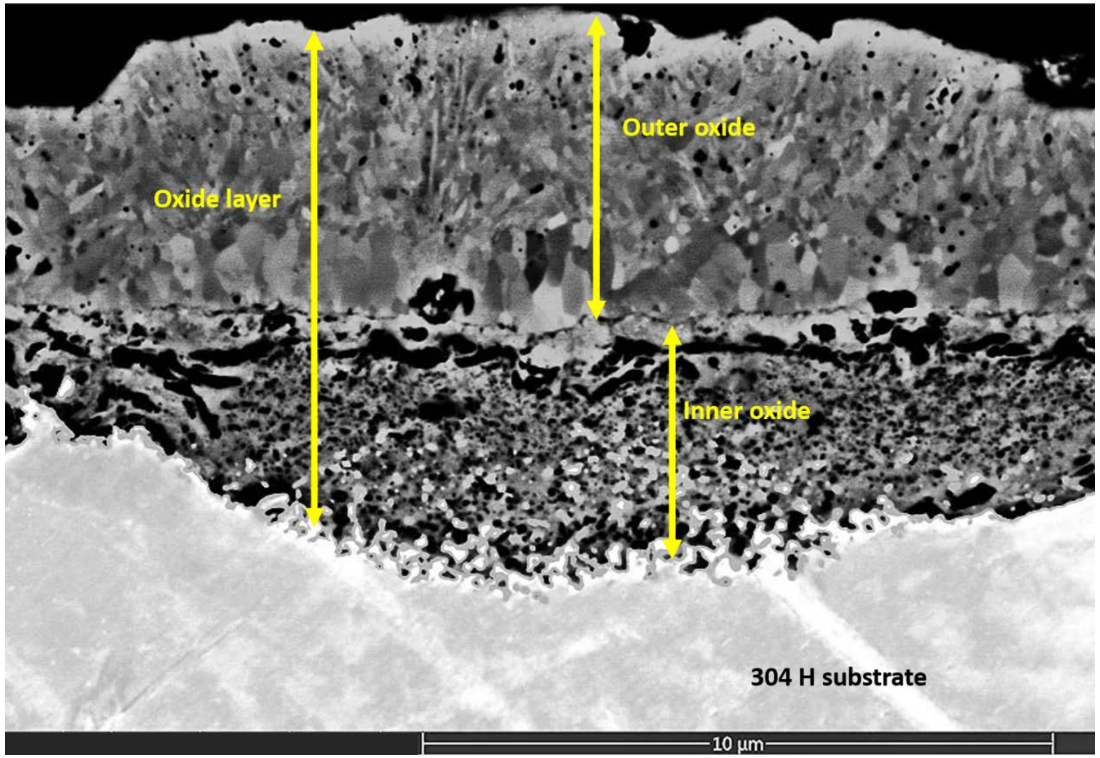
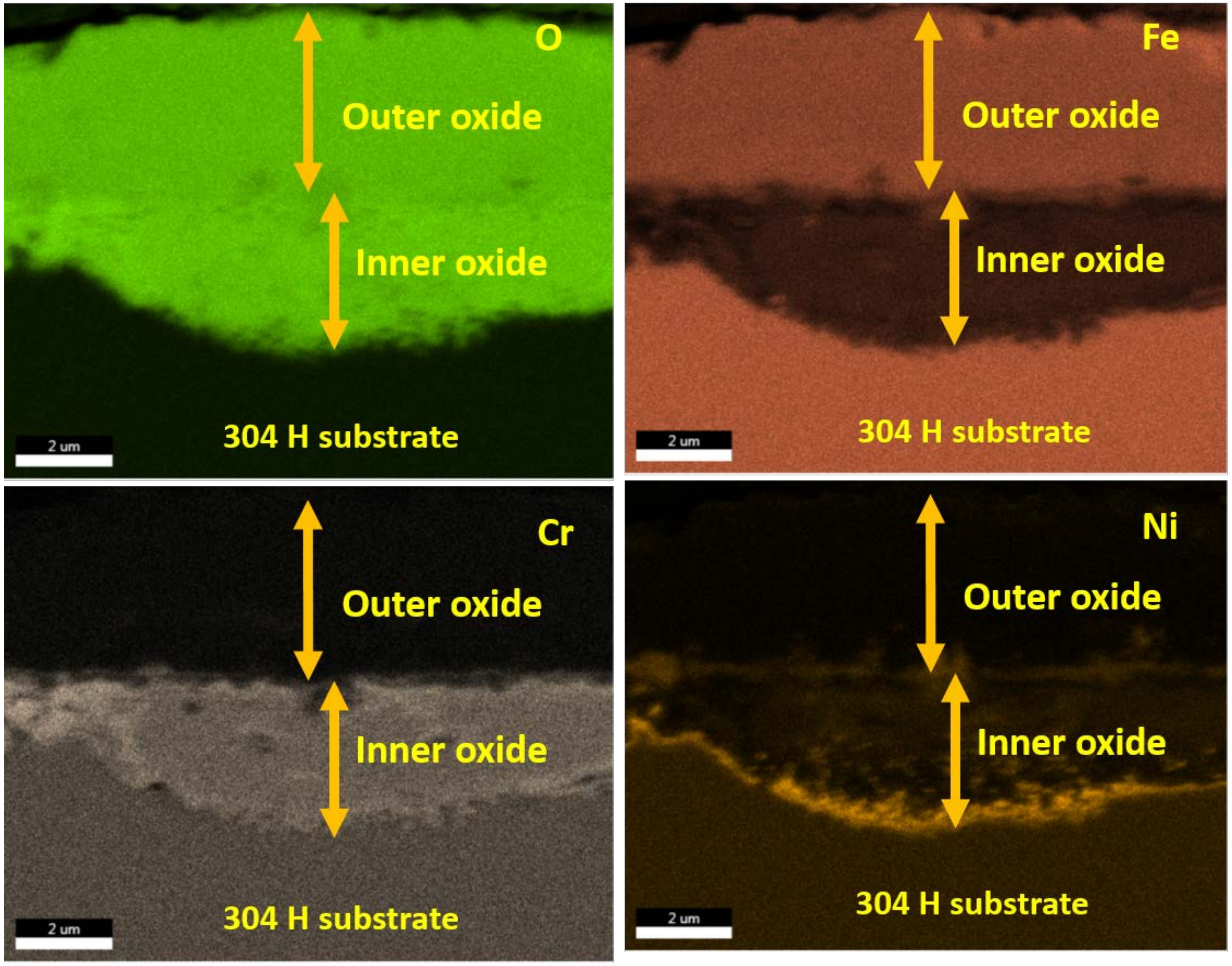


304H



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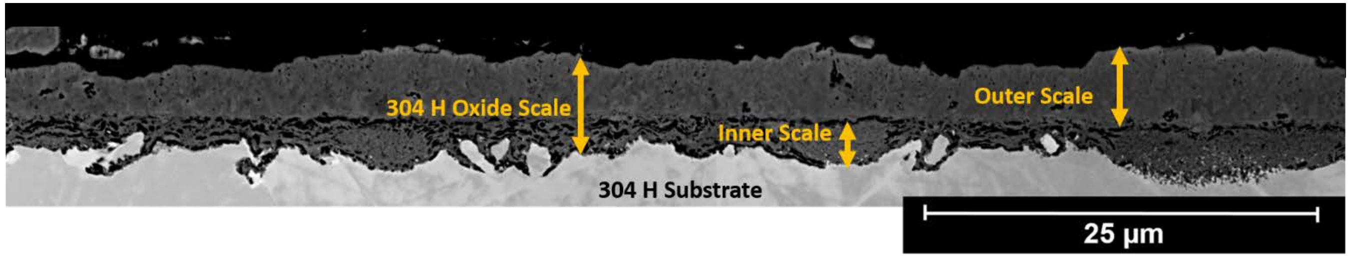
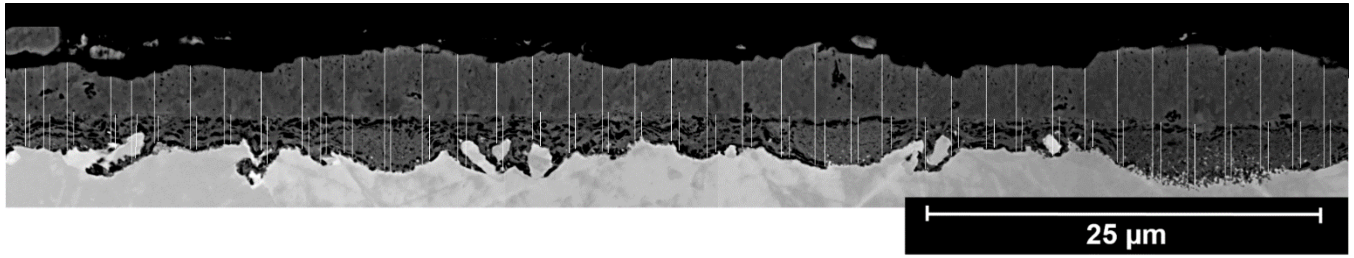
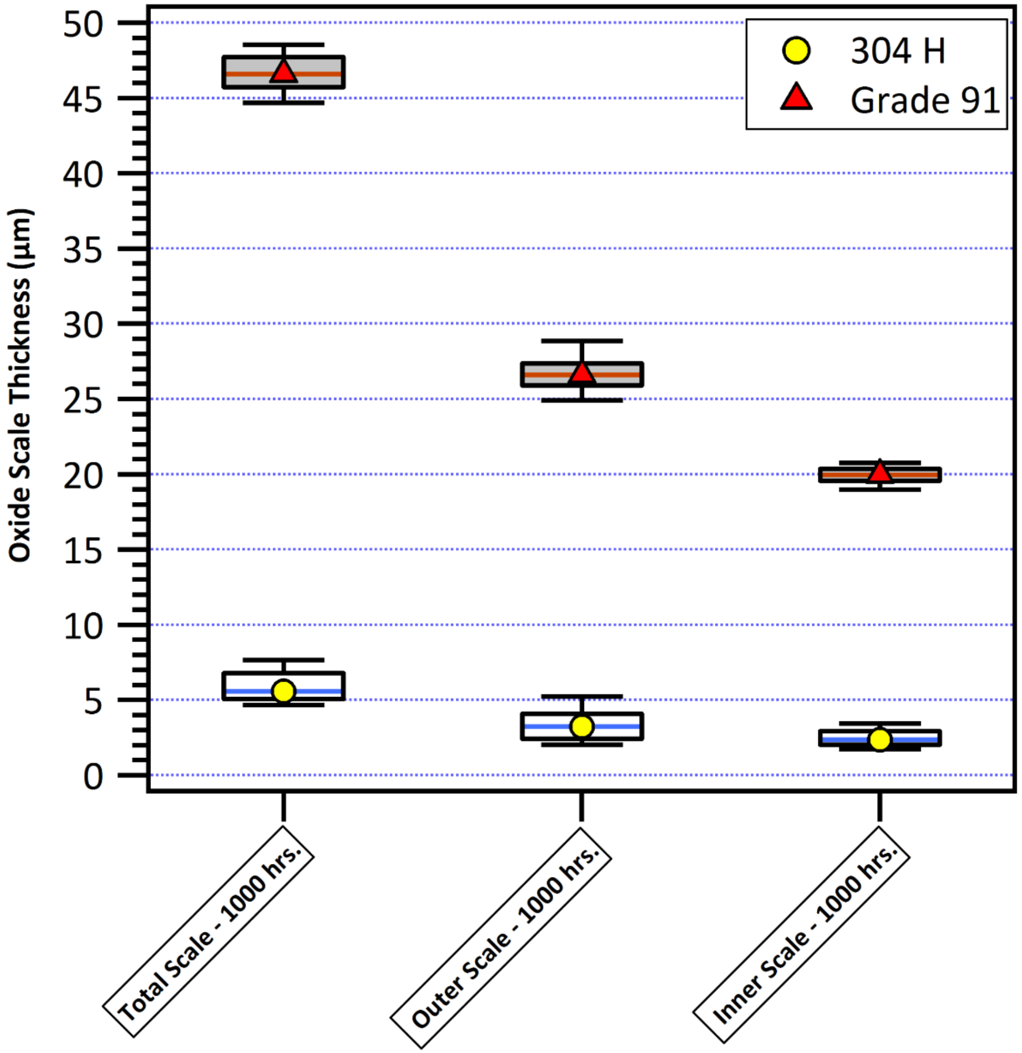
Comparison of scale thickness for Grade 91 and 304H

1,000 hours in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar and 700ºC

- Statistical measurements of thickness (Optical and/or SEM)
- Differences in inner (L1) and outer oxide (L2) thickness







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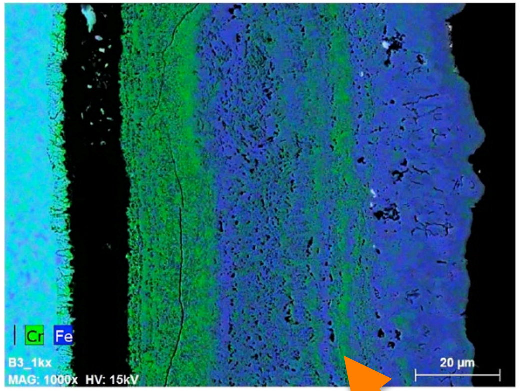
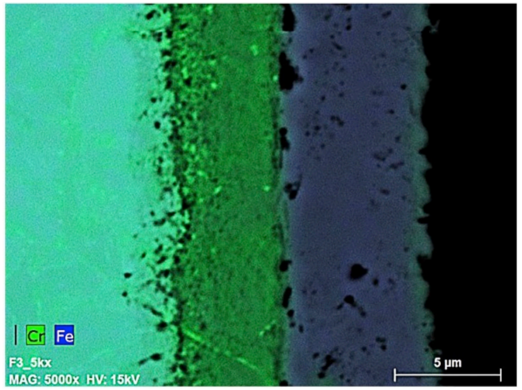
Comparison of scale morphology for ferritics and 304H

1,000 hours in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar and 700°C

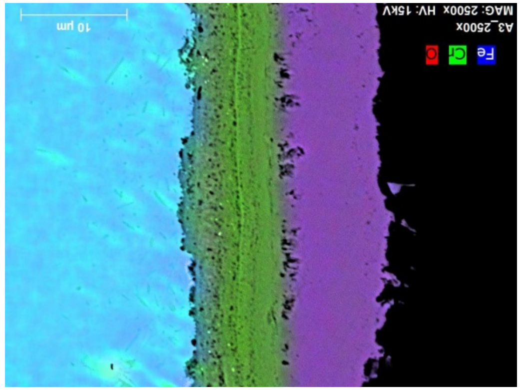
EDS Fe-Cr or Fe-Cr-O Maps Overlayed on SEM Images



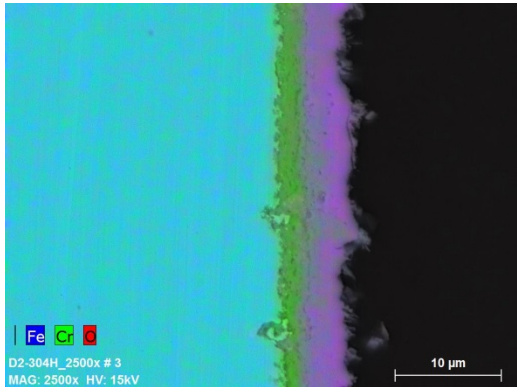
Gr 91 (8.4%Cr)



VM12 (11.2%Cr)



Crofer 22H (22.7%Cr)



304 Stainless Steel: 18.4%Cr-18.1%Ni

- Outer oxides are Fe-based
  - Gr. 91 continued to show intermediate layer(s) with Cr & Fe striations after 1000 hours
  - 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

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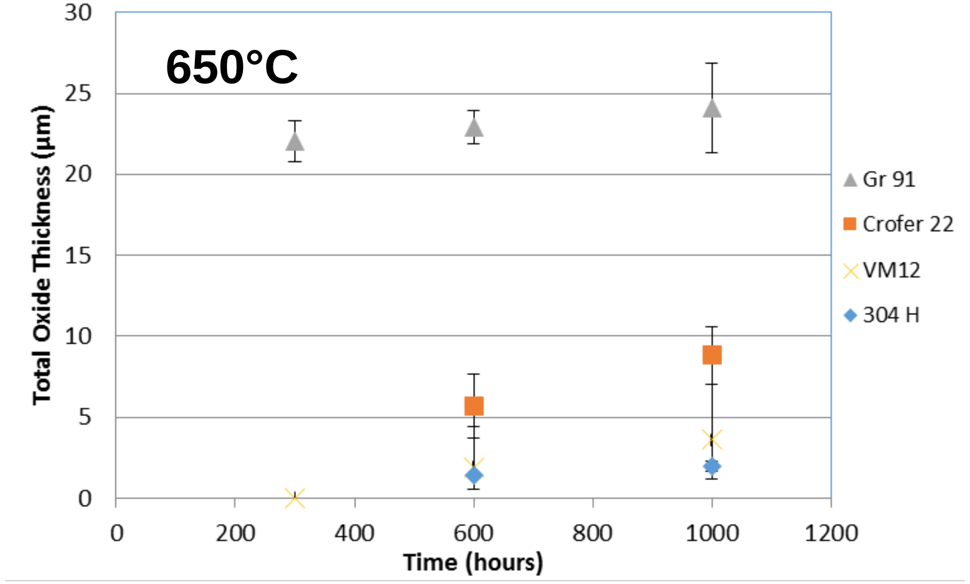
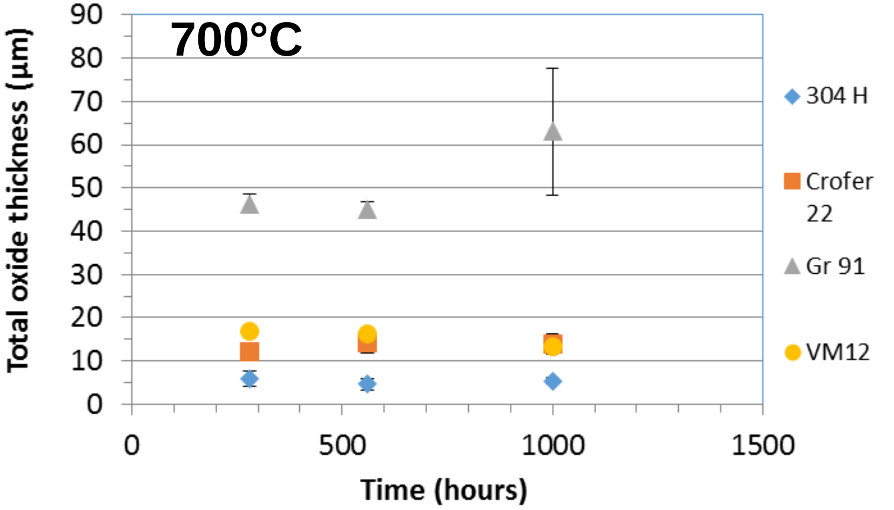
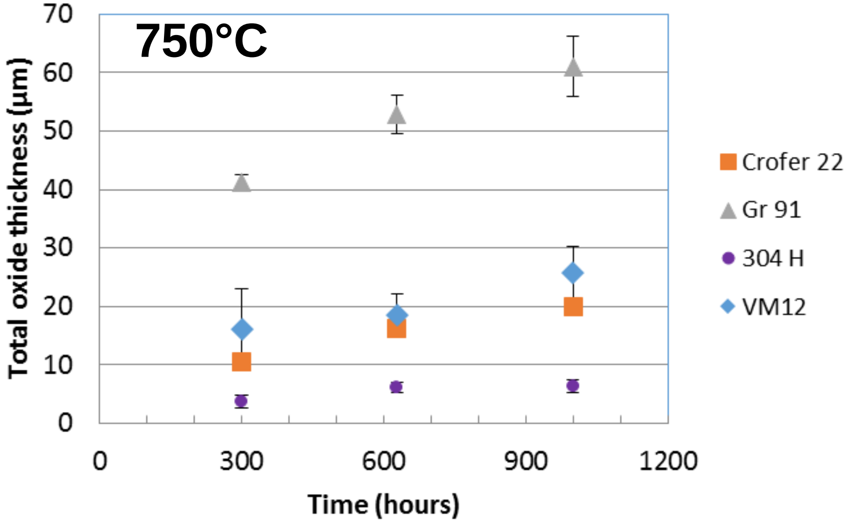
Comparison of Total Oxide Thicknesses

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







- Inner, Outer, and Total Oxide thickness measured
- Lower Cr alloys show more variation in thickness
- HR3C and Nickel-based could not be measured optically

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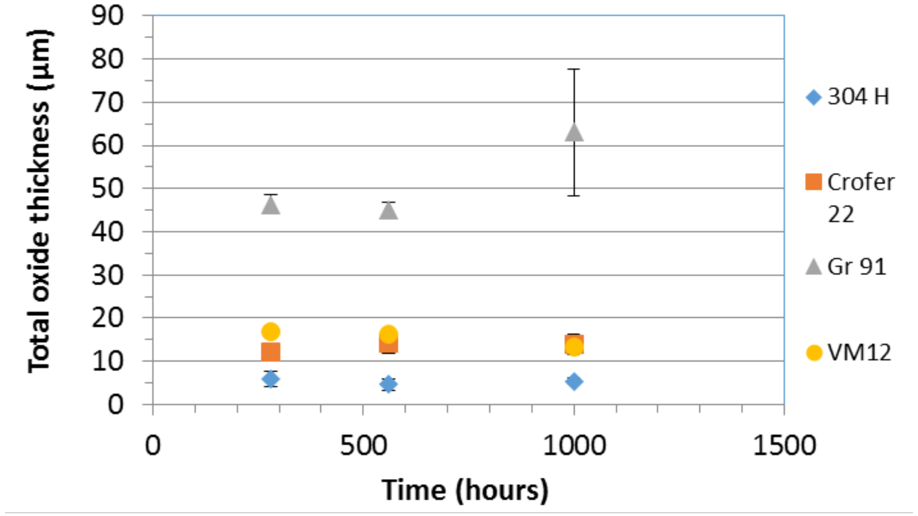
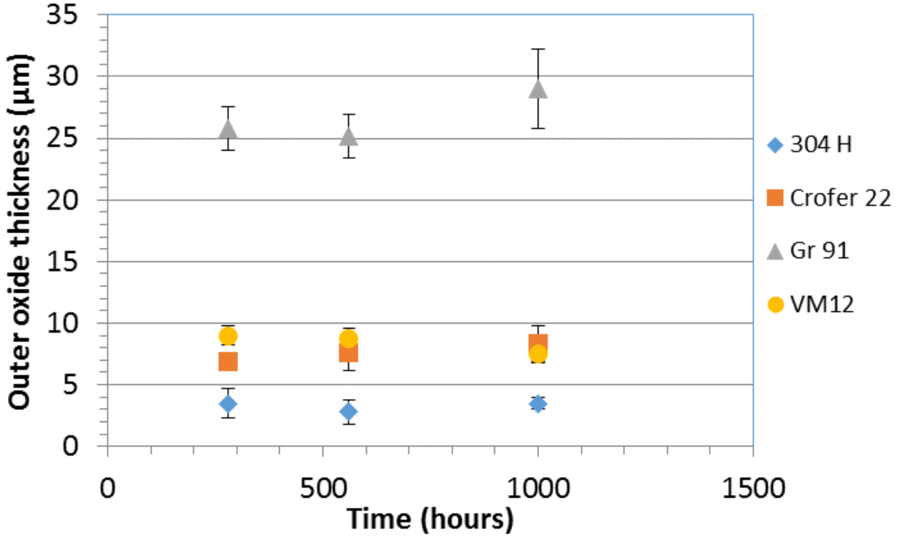
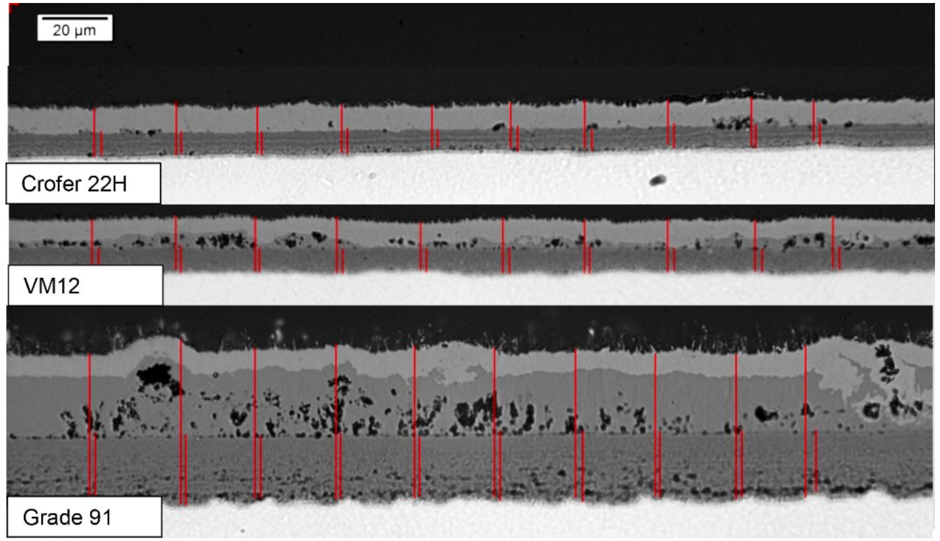
Comparison of scale thickness for ferritics and 304H

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



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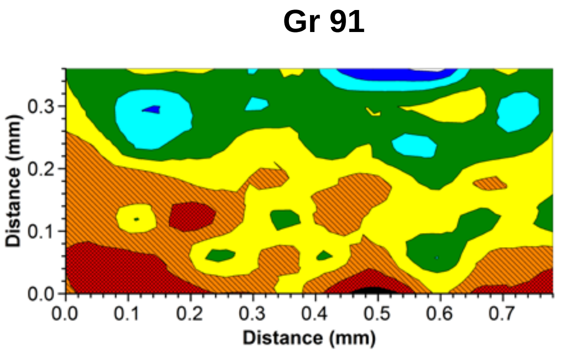
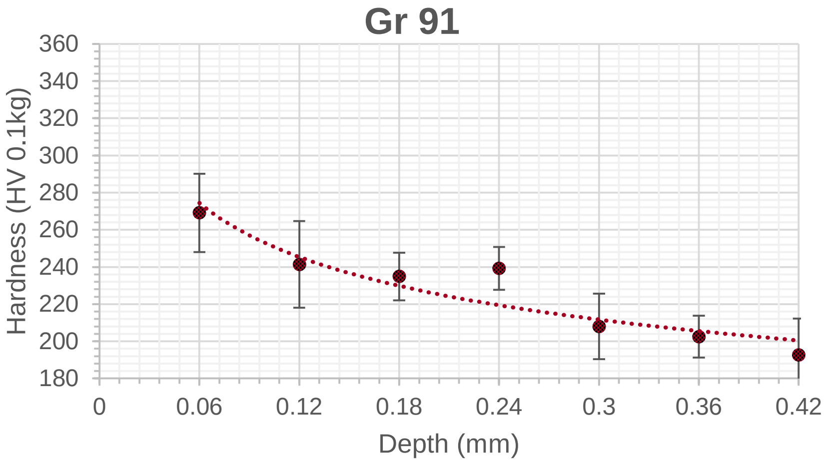
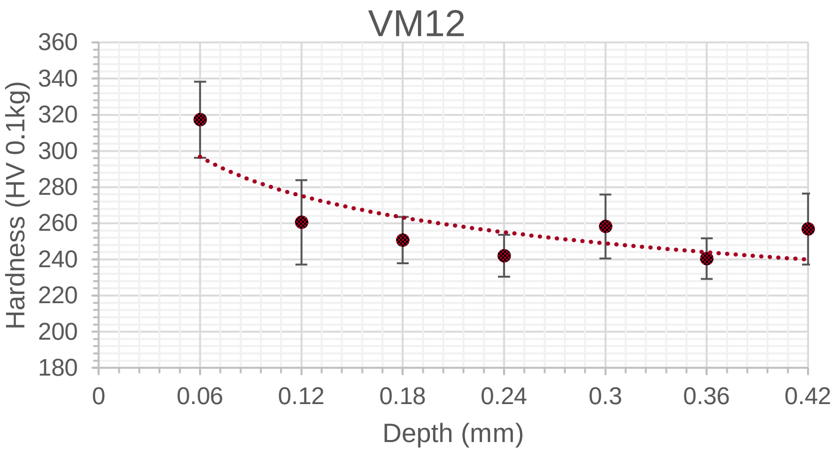
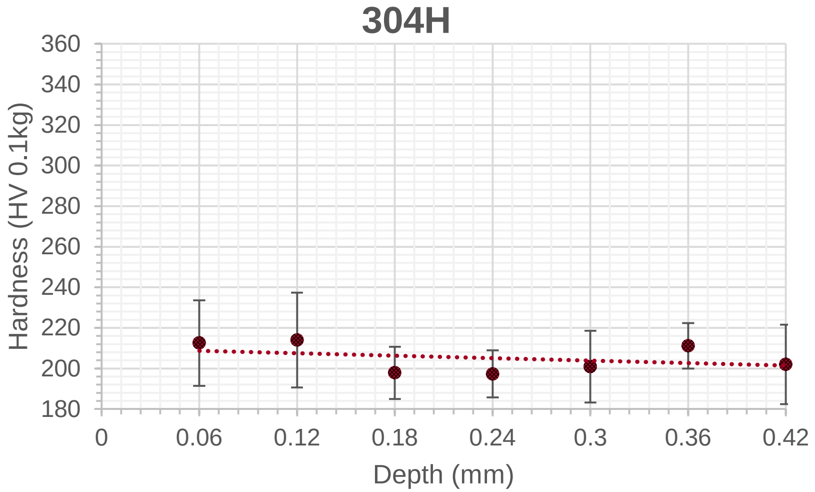
Hardness on Gr 91, VM12 and 304H after 1000-hour test in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar and 700ºC



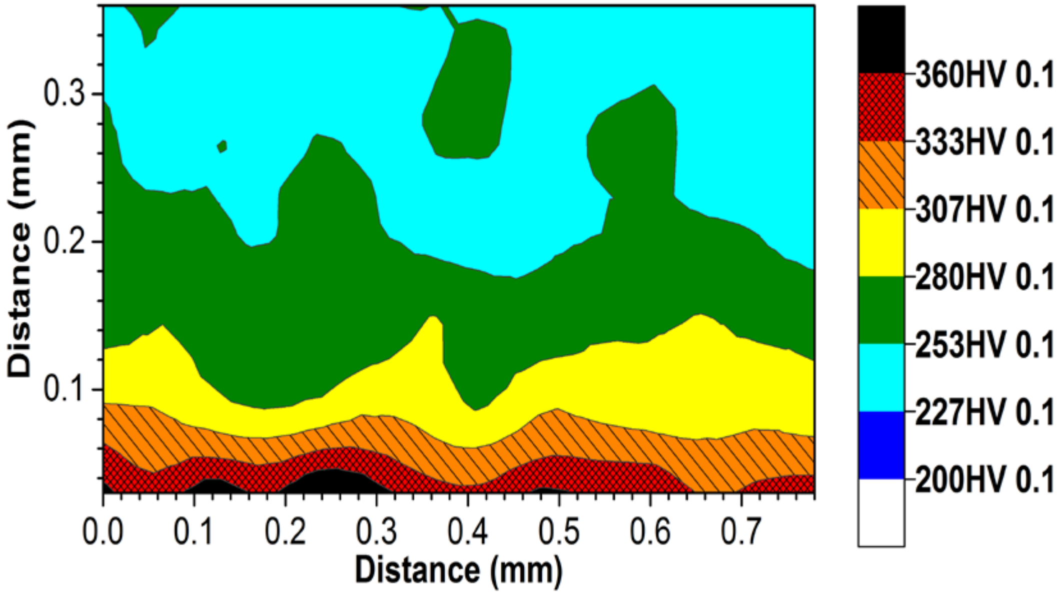


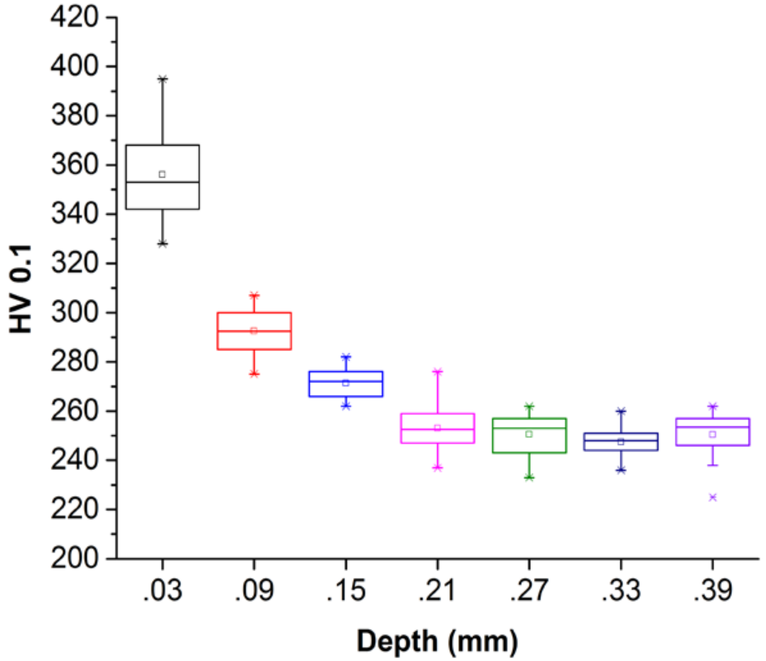




- **Ferritic Gr 91 and VM12 exhibit increased hardness near surface**
- **Hardness in 304H stainless steel flattens out after 1000 hours**
- **Ni-base alloys show no sign of carburization**

Hardness on HR3C after 1000-hour test in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar and 700°C





Carburization suggested in HR3C (25Cr-20Ni) despite low mass gain
- Likely due to high Cr content (relatively to Ni content) for carbide formation
- More microstructural investigations planned

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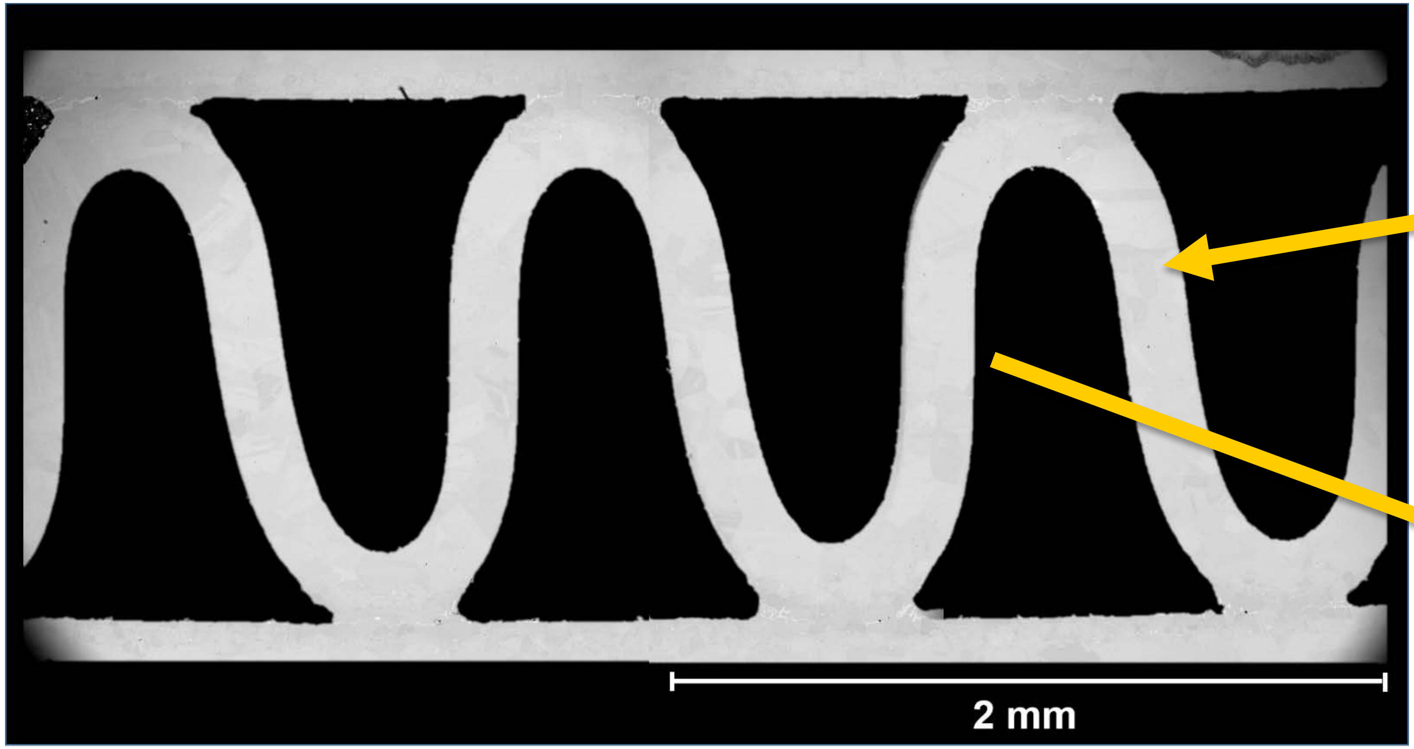
Long-term tests: Characterization Ongoing

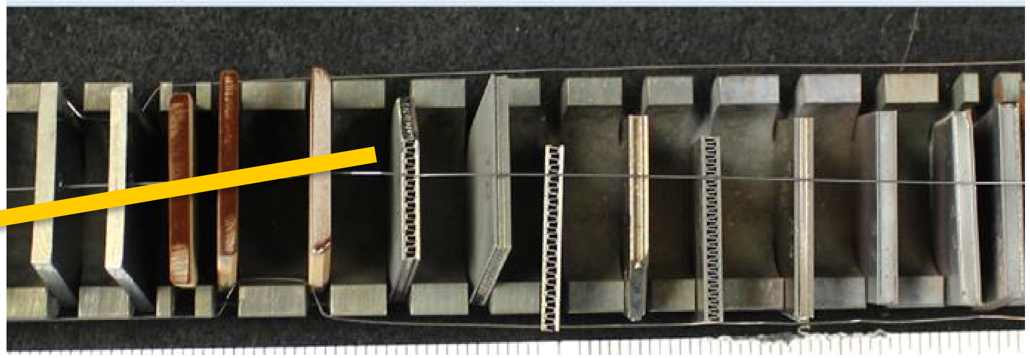
Unit weight gains of alloys after exposure to impure sCO_2 containing 3.6 vol.% O_2 and 5.3 vol.% H_2O at 700°C (in mg/cm^2)

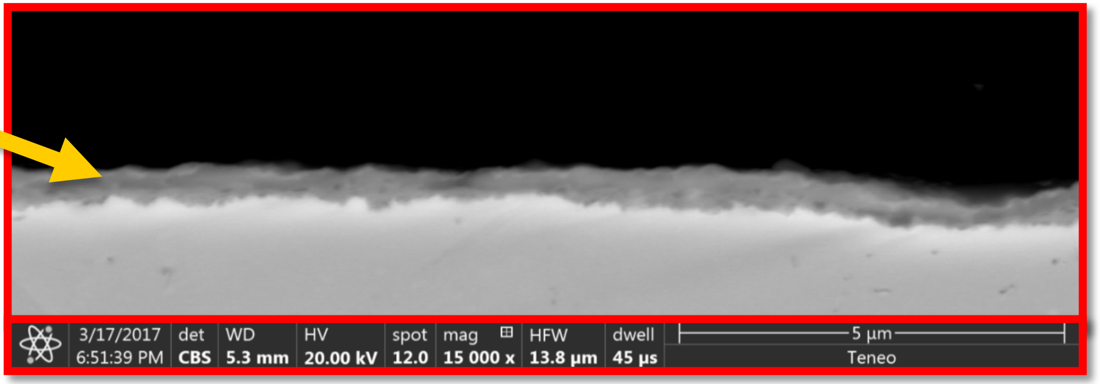
Alloy Name	1000 Hours *	1,000 hours	3,500 hours	5,000 hours
Gr 91	9.34	8.86	13.94	
VM 12	2.51	3.36	7.20	
Crofer 22	2.16	1.88	3.52	
304H	0.96	0.78	1.66	
HR3C	0.16	0.07	0.15	
740H	0.05	0.05	0.02	
617	0	0	0	

***Data extracted from the previous 1000-hour test in impure sCO_2**

Ongoing Characterization: Subcomponents







Inconel 625: 3,500hrs Impure sCO2 Exposure

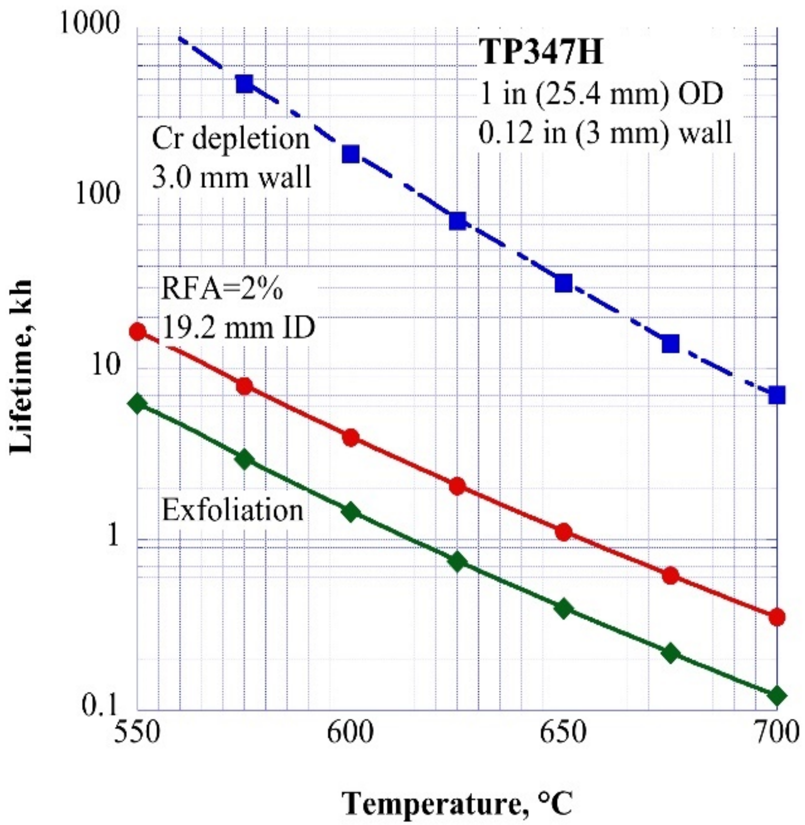
- Subcomponent Materials in Test: 625, 230, 304/304L, 347H, FeCrAl

Outline

- Motivation for the Research
- Team Assembled, Plan, and Defining Test Conditions & Materials
- Experimental Approach
- Results and Ongoing Characterization
- Modeling Approach to Aid Alloy Selection
- Ongoing Research

Current Modeling Research

Evaluation of Failure Criteria for Standard Boiler Superheater



Results show #1 Concern is Exfoliation

-Cr depletion is not a concern
- Carburization not considered
- Reduction in Flow Area (RFA) is low

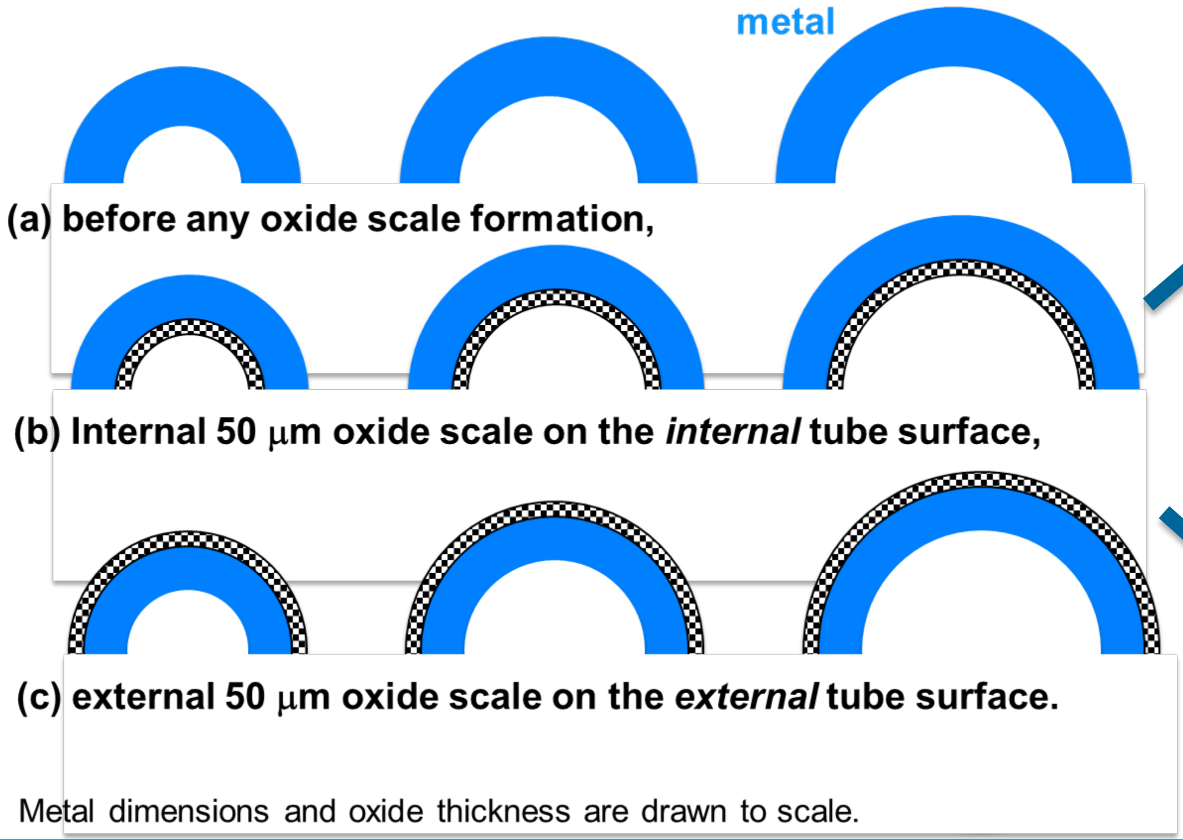
Differences of sCO2 HX compared to Boiler Tubes

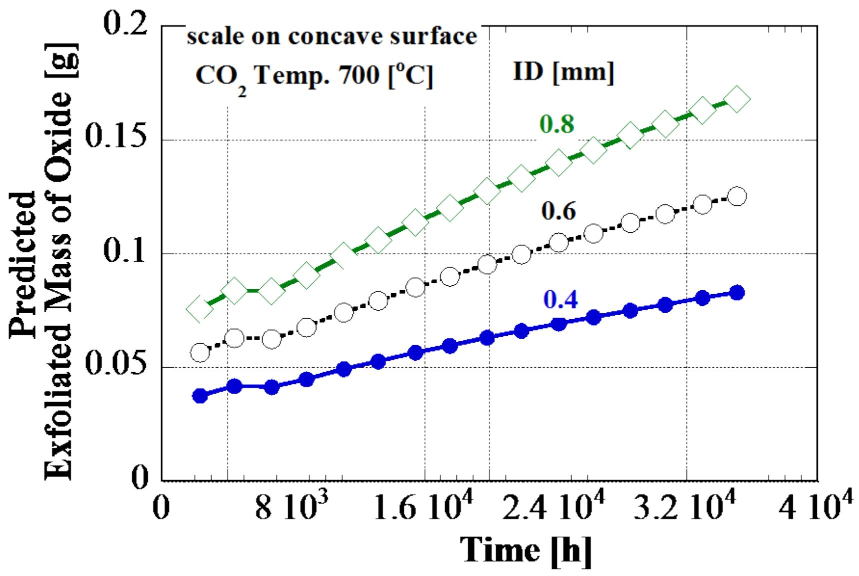
Fluid/Size/Property	sCO_2 channels	Steam tubes
Channel shape	Variable curvature	Circular
Oxide growth location	Inside channel (concave) Outside channel (convex)	Inside channel (concave)
Metal thickness [mm]	0.2	7 to 10
Internal Hydraulic Diameter [mm]	*0.2 to 0.4	20 to 30
Channel length [mm]	500 to 1,000	20,000 to 25,000
Ratio channel length to ID radius	1,200 to 5,000	600 to 1,200
Number of 90º or 180º bends per channel	**none	1
Location of possible blockage	Tube exit	bends
Shape of blockage	Horizontal,or in the bend at channel exit	Horizontal, or Inclined in bends

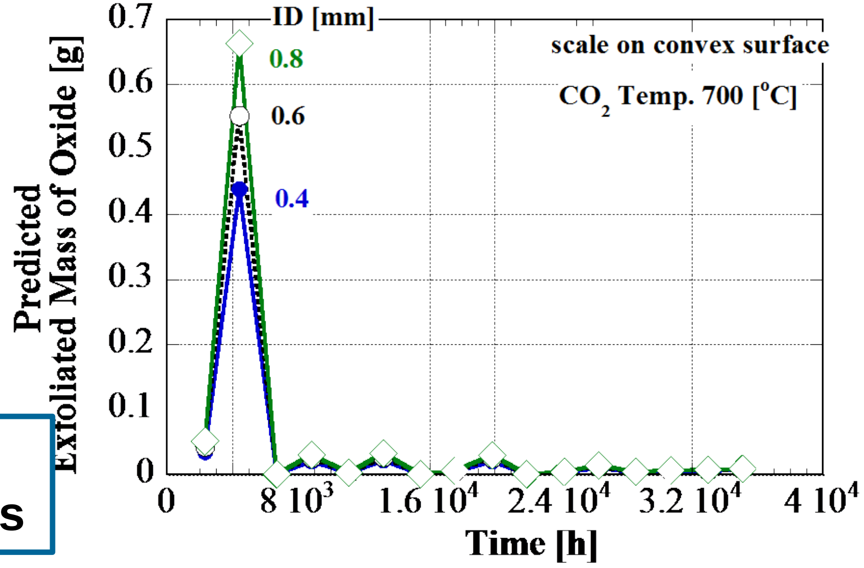
*ID radius of curvature 0.2 to 0.6 [mm]
**Bend at channel exit in the current design

<u>Developing similar basis for sCO2 HX</u>

Addressing Potential for Exfoliation in HX Using EPRI-ORNL Approach for Steam







exfoliated mass exhibits different evolution in time for the oxide grown on convex surfaces from those grown on concave surfaces

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- and 1000-hour laboratory tests with and without impurities completed
  - 1,000-hour tests were performed at 200 bar and 650, 700, and 750°C
  - 5000-hour test in progress at 700ºC and 200 bar
- Although mass gains for alloys in sCO_2 and steam appear similar, some differences in scale morphology on Gr.91
- Carburization appears more severe in pure sCO_2 than impure conditions (short-term)
- Both ferritic and austenitic stainless steels appear susceptible to carburization
- Nickel-base alloys did not suffer carburization (after 1000 hours)
- Effect of sCO_2 and geometry on oxidation to be evaluated through modeling

Next Steps

- Complete 5,000 hours exposures
- Scale thickness kinetic equations and comparisons to steam for modeling
- Evaluation of subcomponent geometries
- Evaluation of carburization (additional methods to verify hardness approach) and microstructures
  - GD-OES on a few selected samples
- Comparison of different failure modes for each material
- Final report

- *Follow-on work (potential): introduce additional impurities for transformational fossil-fired systems (Sulfur, etc.)*

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Back-Up: H_2O in sCO_2

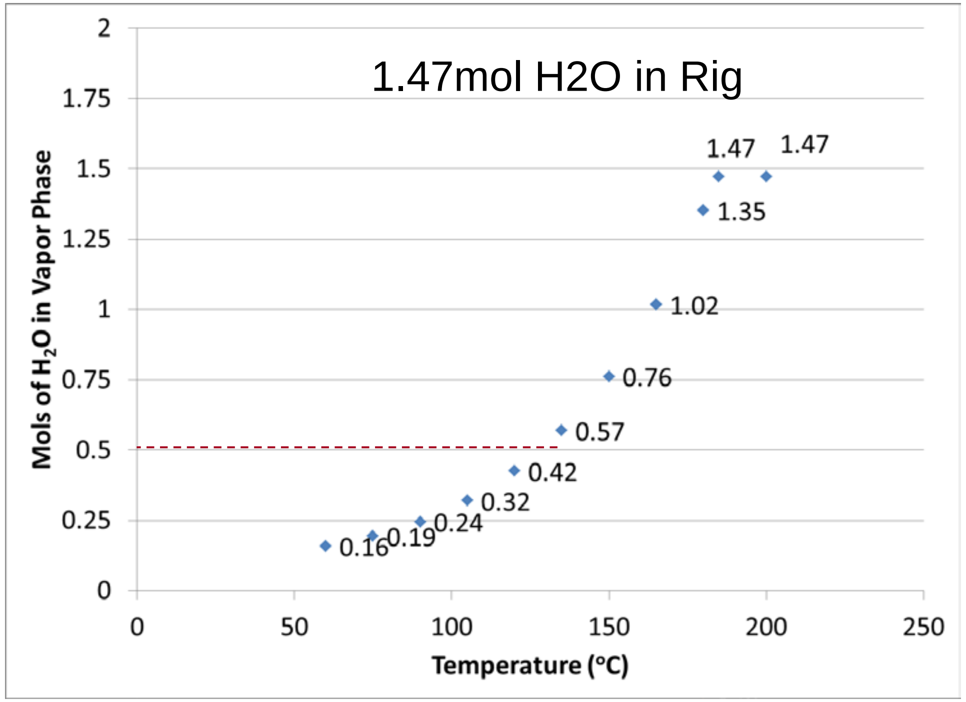

Figure 3.2.1 - OLI model results showing the solubility of 5.3 vol.% water in impure sCO_2 containing 3.6 vol.% oxygen.

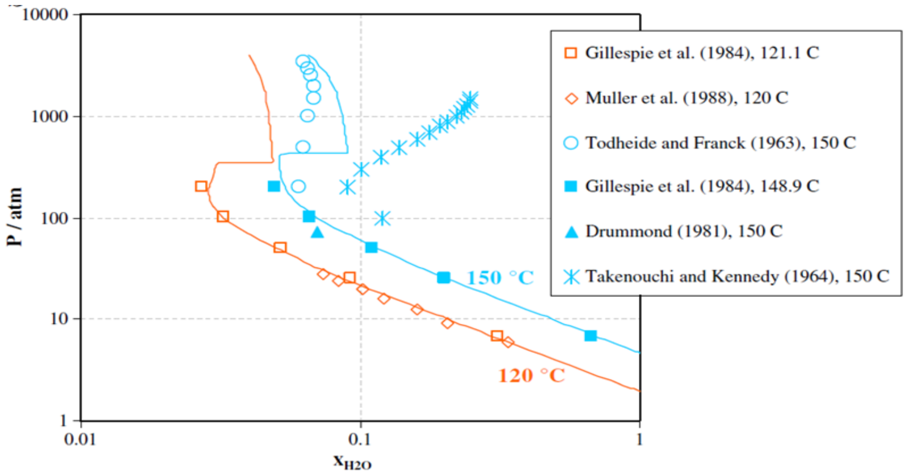

Figure 3.2.2 - Modelling results and experimental results reported by R.D. Springer et al. [1] for the solubility of water in supercritical carbon dioxide at 150 and 120 degrees Celsius.

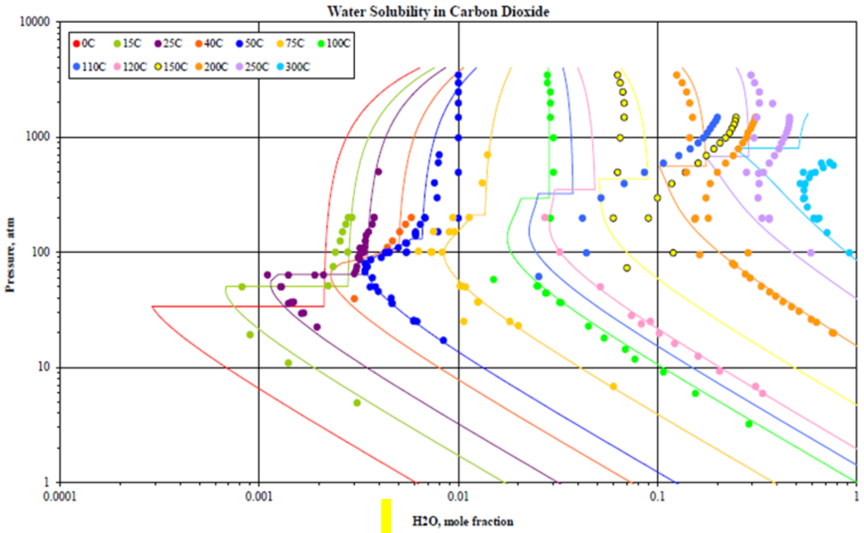

Figure 3.2.3 - Modeling and experimental results summarized by R.D. Springer, et. al. [1] for the solubility of water in sCO_2 at different temperatures.

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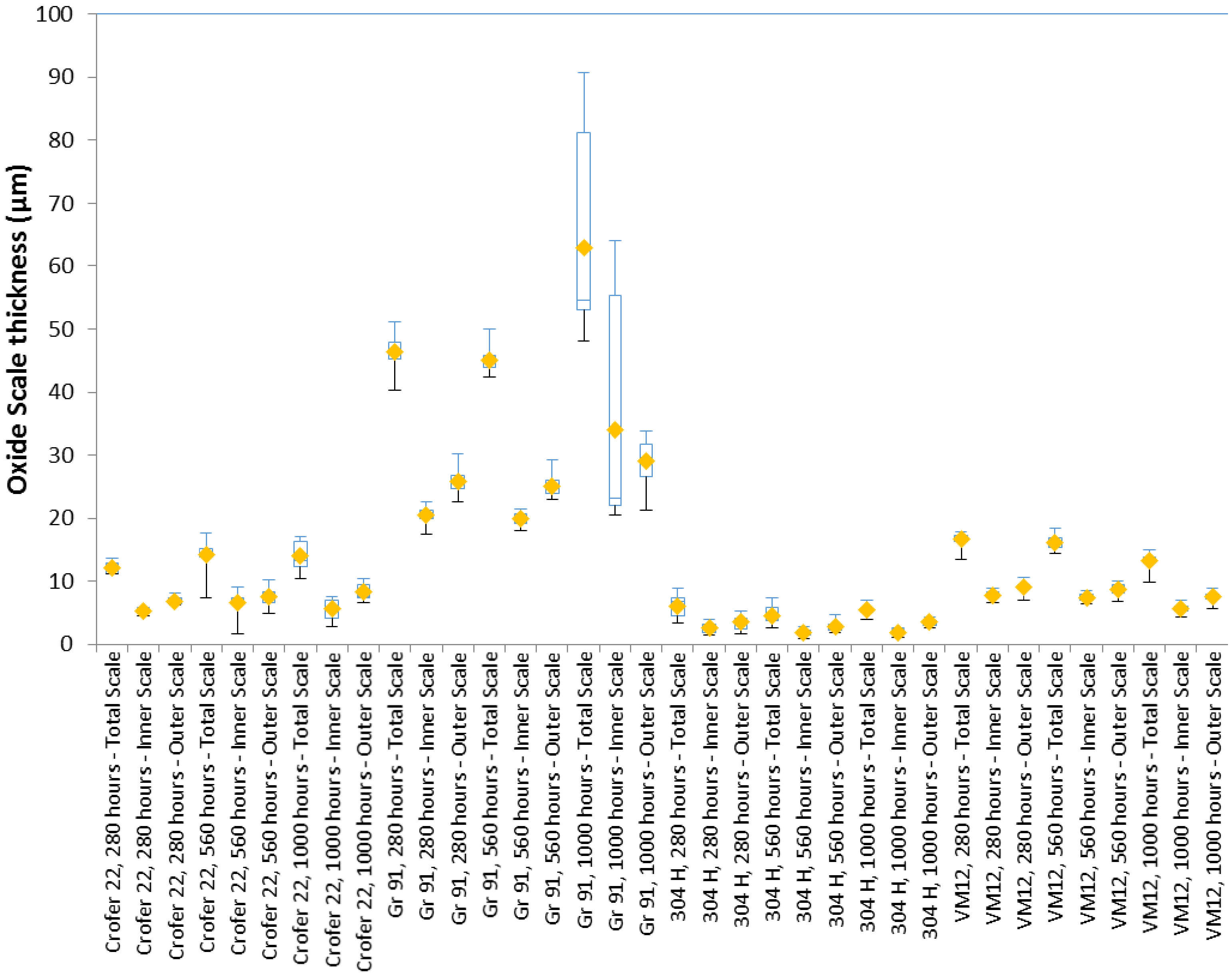
Statistical Box Plot: 700C Impure Tests

- Inner, Outer, and Total Oxide Thickness
- Box and wisker plot



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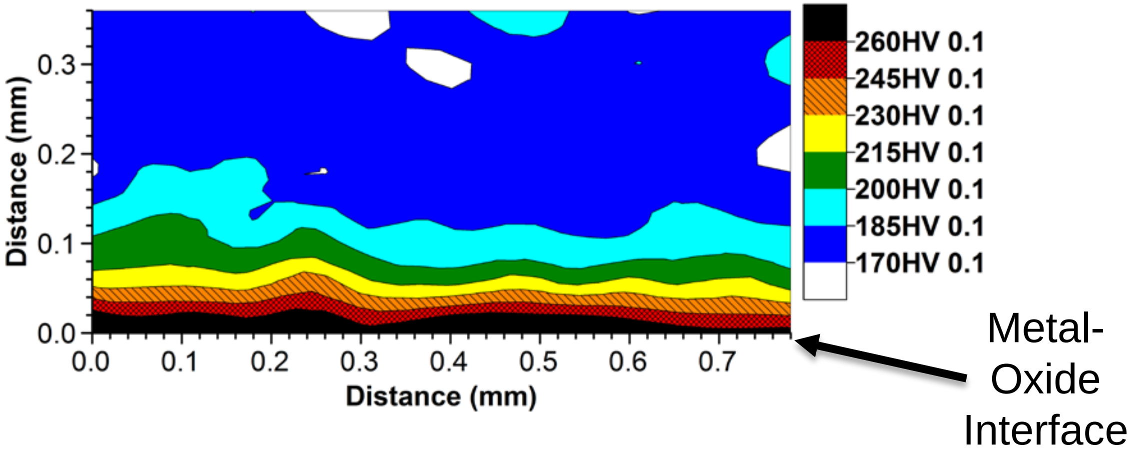
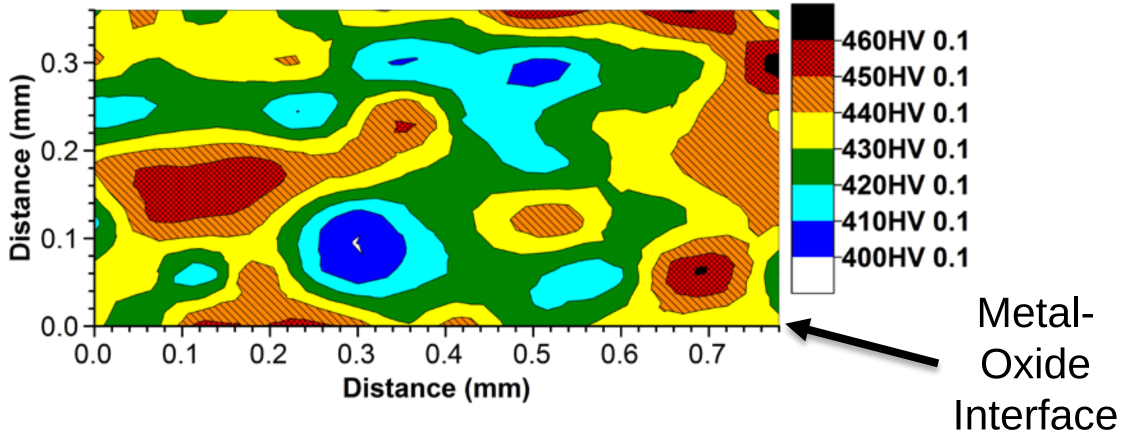
Hardness on 304H and 740H after 300-hour test in impure sCO_2 (3.6% O_2, 5.3% H_2O) at 200 bar and 700ºC

Stainless Steel 304H

304H shows some hardness increase after 300 hours



Nickel-Base Alloy 740H



740H exhibits good resistance to carburization in sCO_2