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

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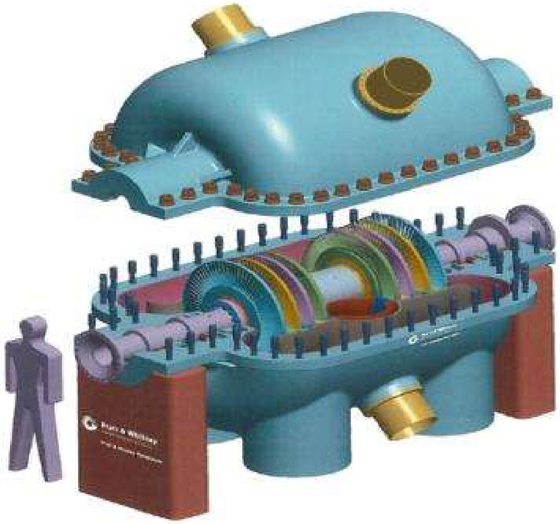
Project objectives

- Overall Objectives
  - *predict the oxidation/corrosion performance of structural alloys in high-temperature high-pressure supercritical CO_2 (sCO_2)*
  - *combine laboratory testing & computational modeling, incorporating unique attributes of sCO_2 heat exchangers and recuperators, to accomplish this goal*
- Identify materials to help enable U.S. DOE Program Goals for future sCO_2 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.*

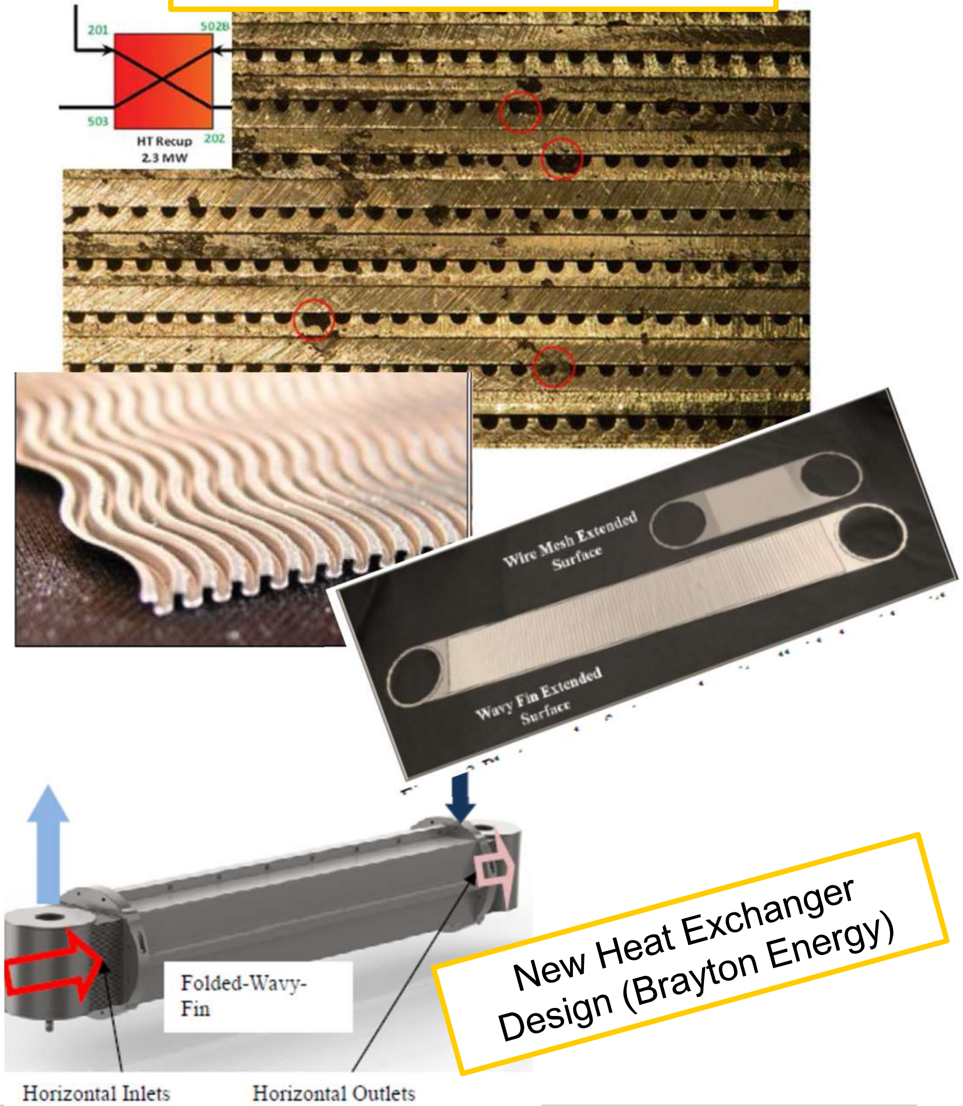
Technology Challenges for sCO_2

- HX Expensive: about 40% of the plant cost
- Unique designs
  - – *small channels*
  - – *large surface areas*
- Materials considerations
  - – *thermal fatigue, creep (thin sections)*
  - – *brazing/diffusion bonding*
  - – *corrosion/oxidation/carburization*

Corrosion/Oxidation

- Closed cycle = build-up of impurities
- **Open cycle = combustion products**
- Long-term performance, pluggage, blockage, etc.

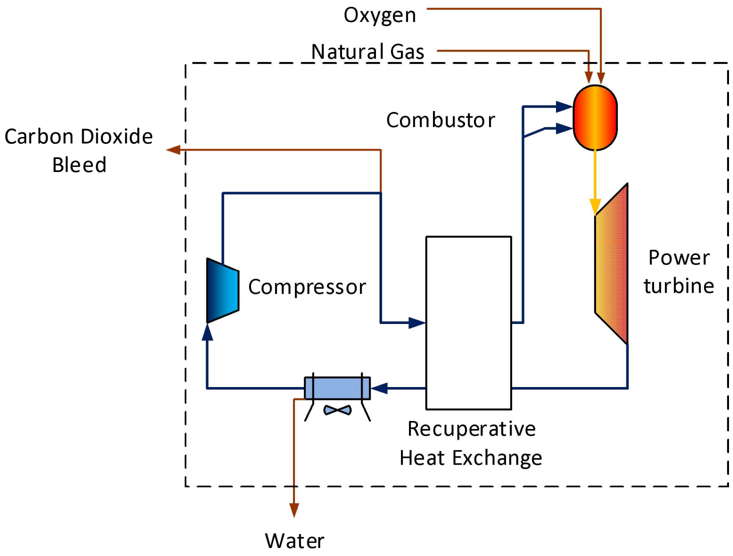
Compact Heat Exchanger Fouling (Sandia National Lab)



New Heat Exchanger Design (Brayton Energy)

Realistic sCO_2 conditions for (open) Allam cycles

- **Survey of industry and current studies**
  - *700°C likely maximum temperature in heat-exchangers*
- **Evaluation of impurities for near-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	2 ppm	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	5.3	250 ppm	5
N_2+Ar	1	1	9	9
O_2	3.8	3.6	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*
    - commercial purity
    - simulated semi-open cycle impurities (O_2 + H_2O)

Material Class	Alloys Selected		
Ferritic steels	**Gr 91** (8-9Cr)	**VM12** (11-12Cr)	**Crofer 22H** (20Cr)
Austenitic stainless	**TP304H** (18Cr)	**HR3C** (25Cr)	
Nickel-based	**IN617** (20Cr, solid soln. strengthened)	**IN740H** (25Cr, ppt. strengthened)	

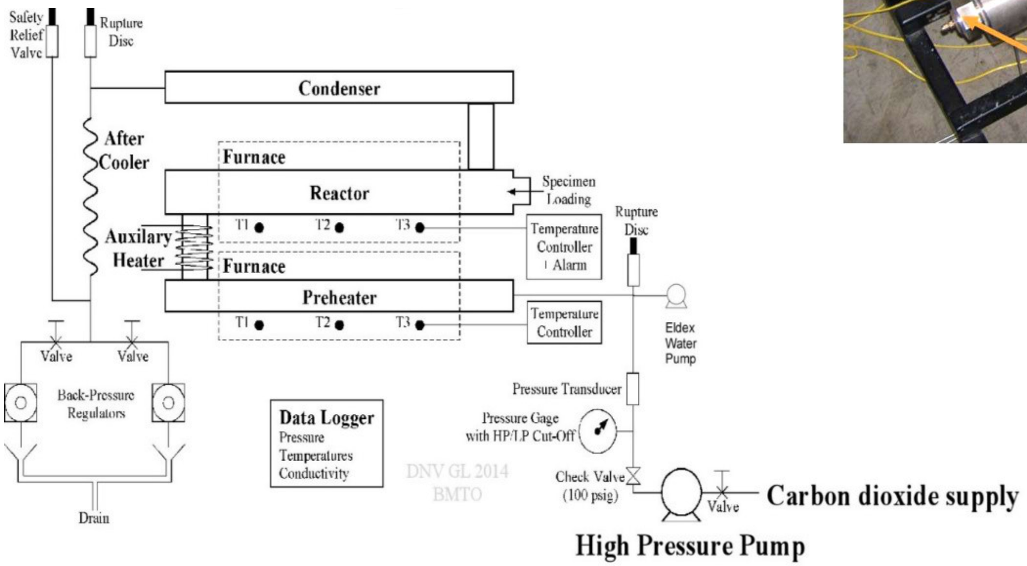
- Materials
  - *commercially available*
  - *Code approved/industry relevant*
  - *focus on economics*

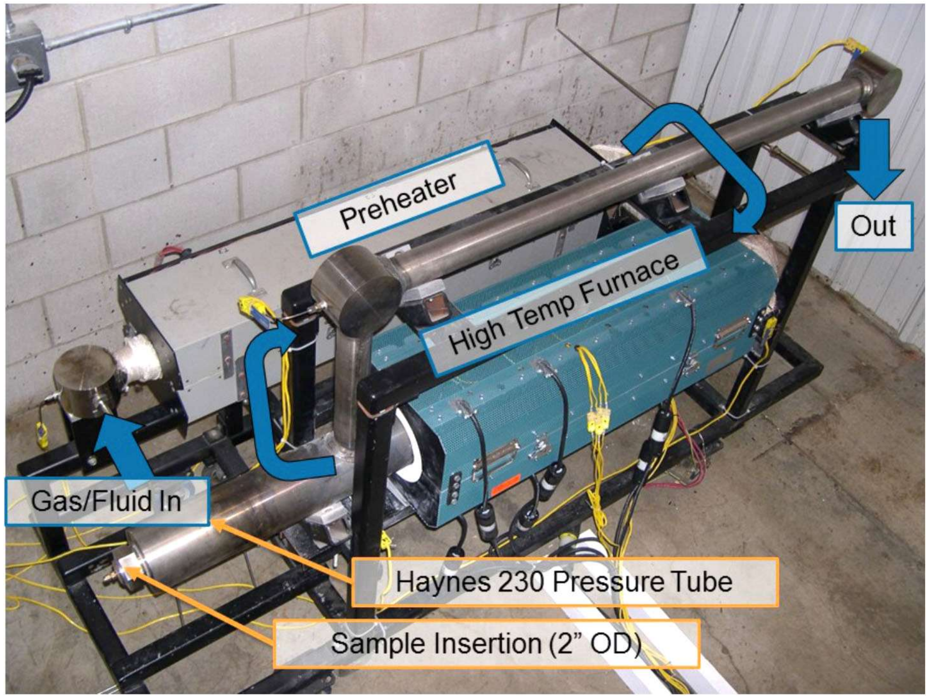
- Exposures
  - *2 x 300-h shakedown tests in CO_2 ± impurities, 700°C, 200 bar (Gr91, TP304H, IN740H)*
  - *3 x 1,000-h tests in CO_2 + impurities, 650, 700, 750°C, 200 bar (all 7 alloys)*
  - *1 x 5,000-h test in CO_2 + impurities, 700°C, 200 bar (all 7 alloys), with scheduled sample retrievals*

Laboratory testing facility

- Existing test facility modified for sCO_2 to ensure safety
- 650-750°C, 200 bar
- Introduction of impurities

  ($3.6\ O_2$, $5.3\ H_2O$ mol%)
- 5,000-h test in sCO_2 with impurities completed successfully





Gas Volume: 4.41 liters

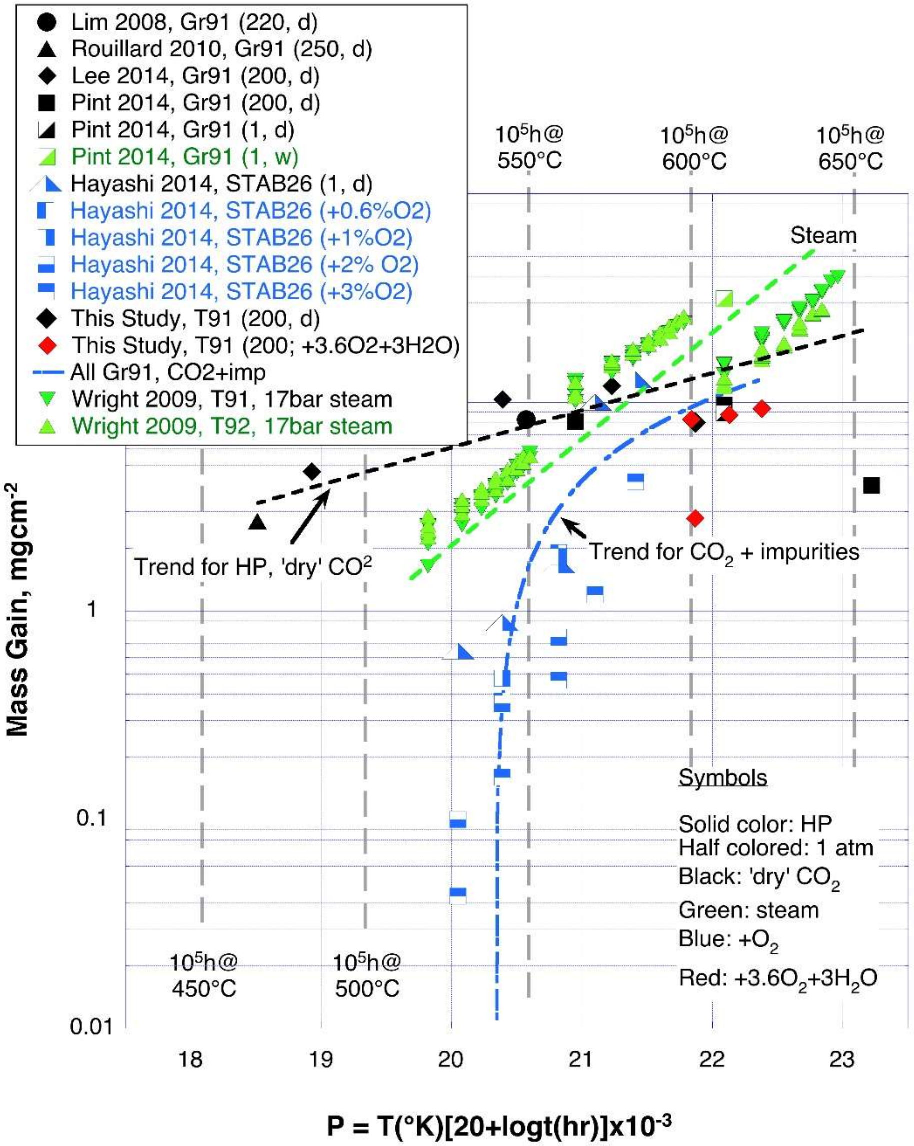
Refresh Rate: static, with occasional replenishment

Temperatures: preheat 454°C. exit 149°C

Information needed for development of sCO_2 Exfoliation Model

- Oxidation rates as a function of oxide thickness vs. *t* and *T*
  - *for oxide thickness:* $d^2 = 2.k_p.t$, *where:* $k_p = Ae^{-Q/RT}$, *or* $\ln k_p = A - Q/RT$
  - *Q from slope of an Arrhenius plot*
  - *mass-based oxidation data are of limited value*
    - both oxidation and carburization lead to to weight gain
    - weight gain cannot be easily converted to thickness
    - but, bulk of literature data rely on mass gain
    - nevertheless, mass gain data are useful for comparisons of available data, for examining trends, etc.
- Morphological data
  - *needed to infer modes of scale failure*
  - *current EPRI Exfoliation Model is based on morphologies formed in steam*
    - hence, importance of understanding similarities/differences in sCO_2
  - *for HT alloys, adequate characterization of very thin scales is problematic*

Ferritic steels: Available mass gain data in sCO_2 and steam



- Pure CO_2
  - *mass gain ±higher than in steam at lower values of Larson-Miller parameter (P)*
- Impure CO_2
  - *significantly lower mass gains than in pure CO_2 at lower values of P*
- Expect similar morphologies in sCO_2 & steam?
  - *only after higher T, longer t?*

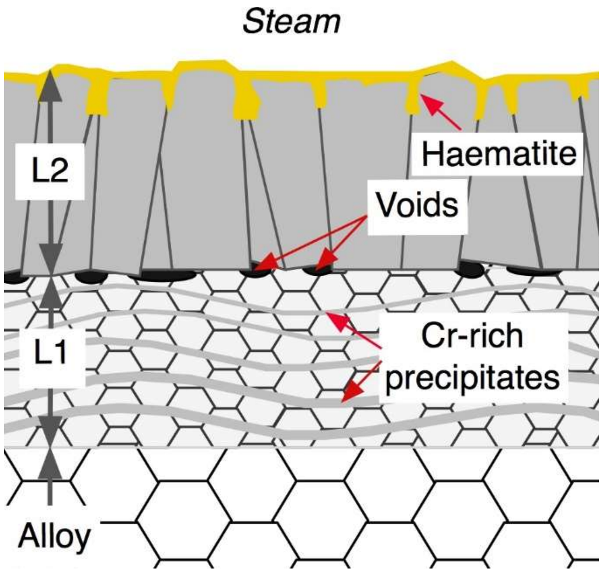
Potential differences in scale morphologies on ferritic steels from sCO_2 compared to HP steam?

- Steam oxidation: different scale morphologies than in *air*
  - *$H_2O = O^{-2} + 2H^+$: mobility of all 3 in scales*
  - *for ferritic (& austenitic steels), typically 2-layered scales: Fe-Cr spinel (inner, L1), magnetite (outer, L2)*

Schematic representation:

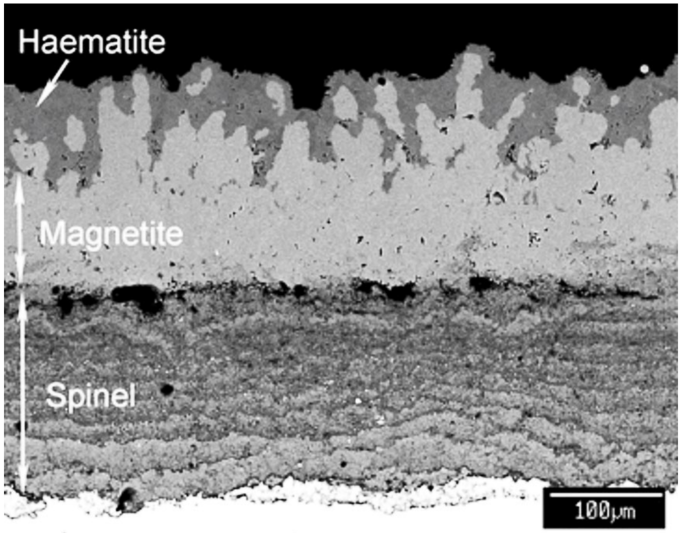
cross section of fully-developed scale

on T91 in HP steam (EPRI Atlas) ➔

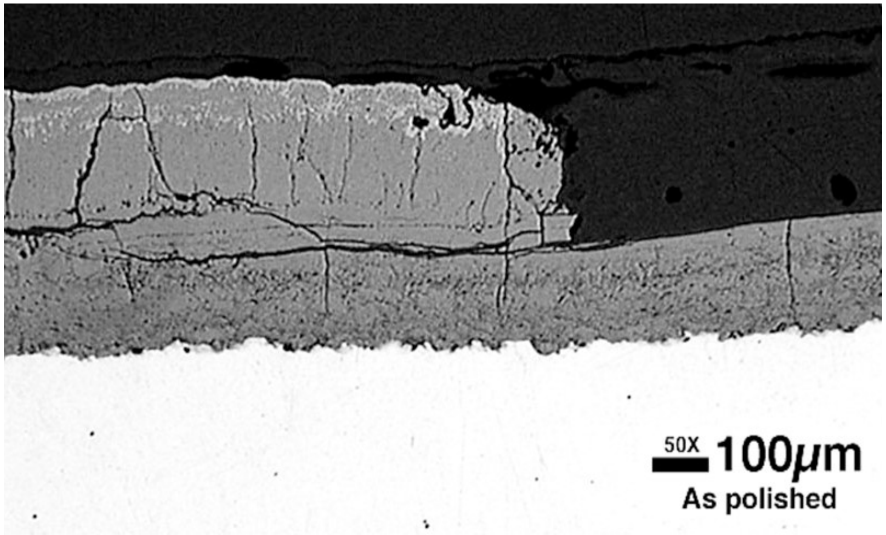


- CO_2 oxidation involves: $CO_2 = O^{-2} + CO^{+2}$
  - *similar oxidation process to steam (i.e. similar scale morphologies)*
  - *but, carburization could occur*

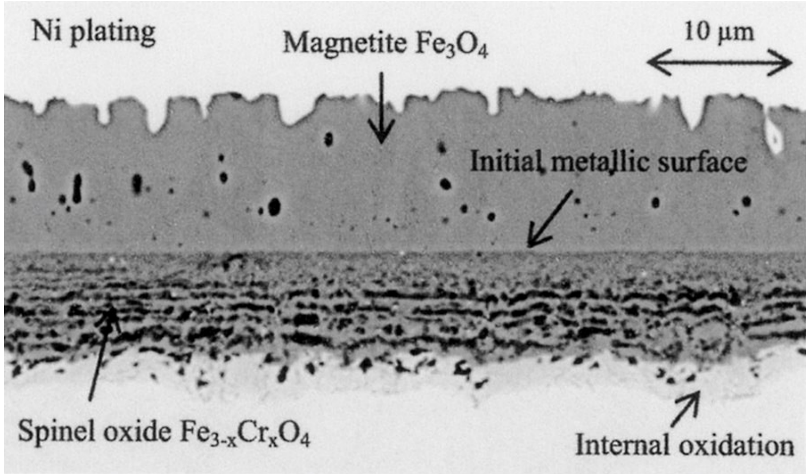
Typical scale morphologies associated with ferritic steels



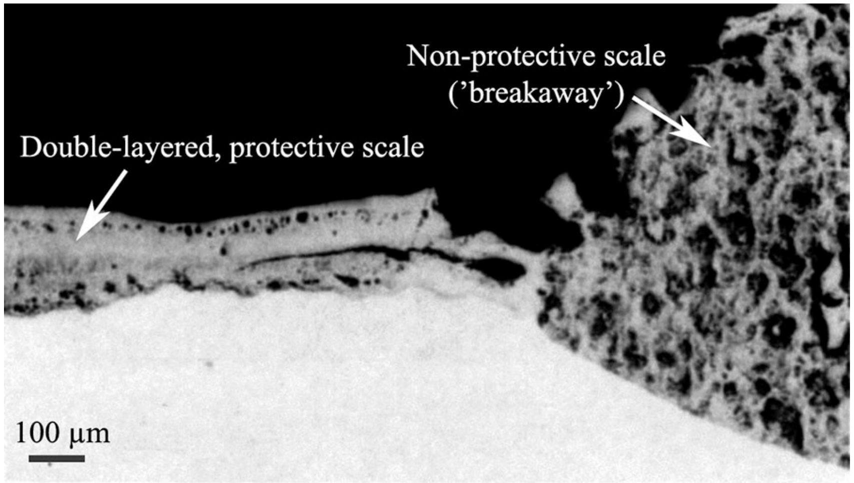
T91, 64kh at 566°C & 138 bar steam (EPRI Atlas)



T91, 155kh at 538°C & 17 bar steam (EPRI Atlas)



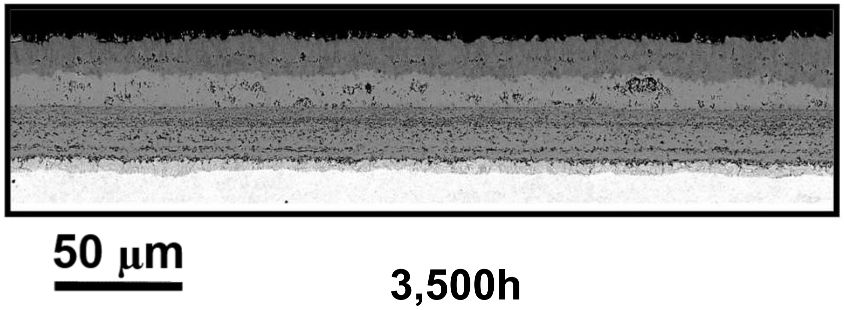
T91, ≈300h at 550°C & 250 bar CO_2 (Rouillard, 2010)



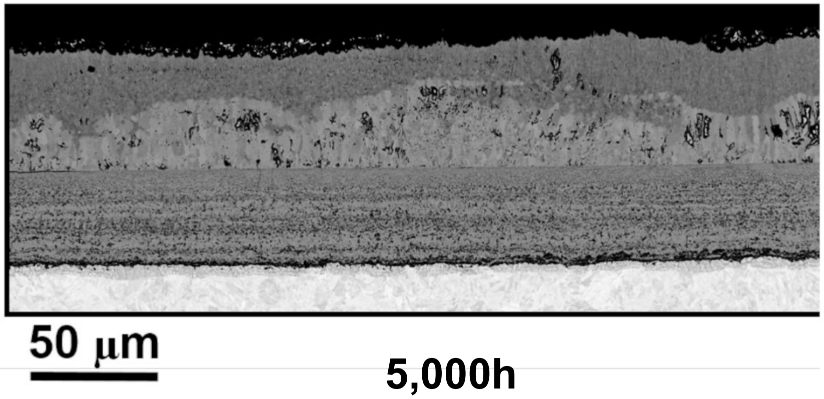
Fe-9Cr, ≤9kh at 550°C & 40 bar (imp) CO_2 (Harrison, 1974)

New results: Gr 91, 700°C in sCO_2 +3.6% O_2, 5.3% H_2O at 200 bar

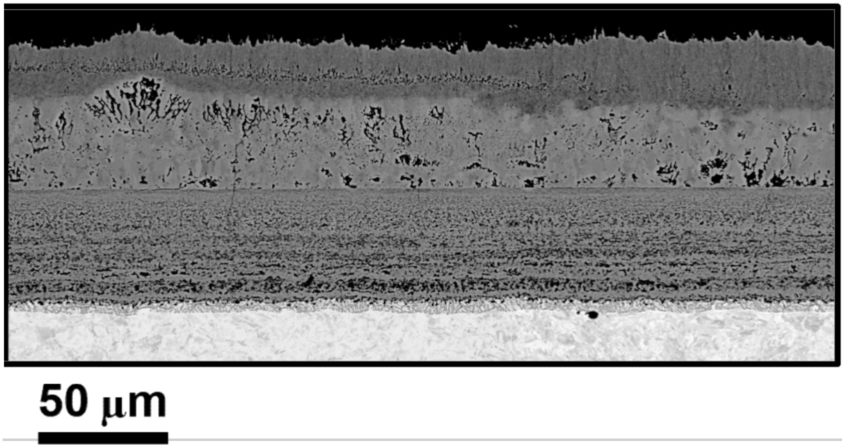
1,000h



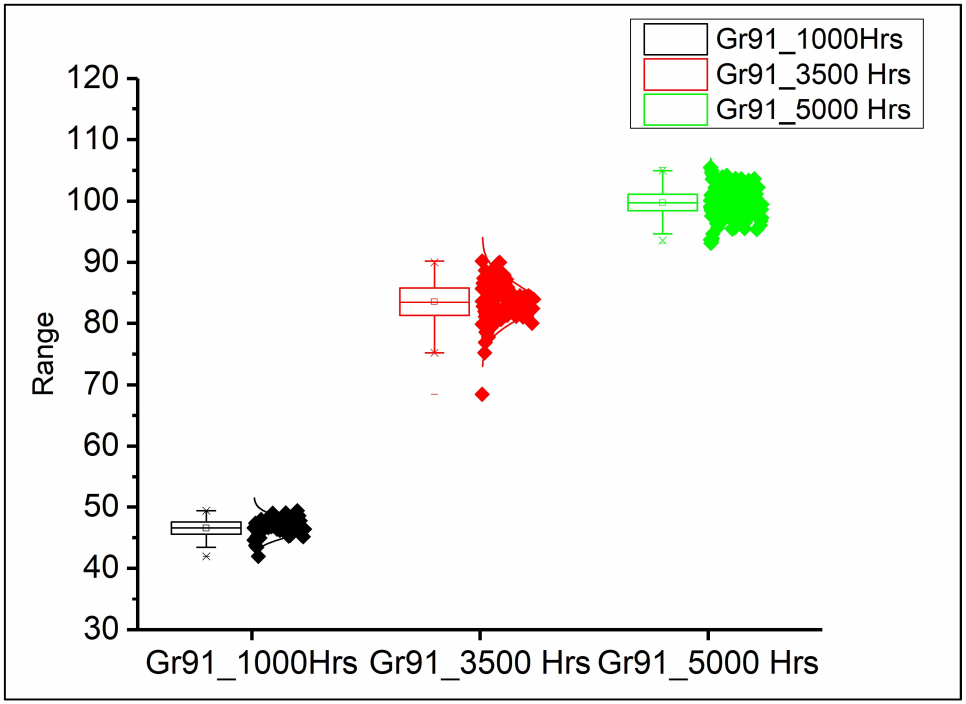
3,500h



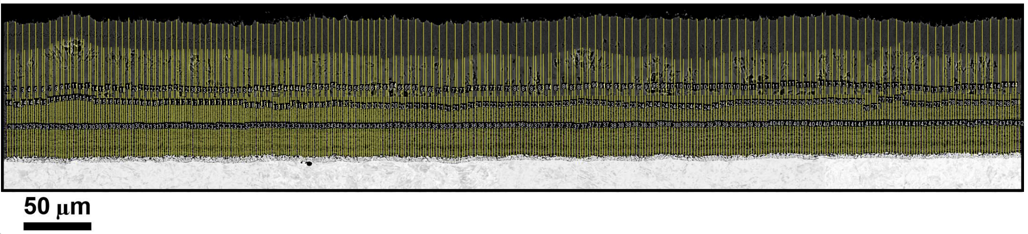
5,000h



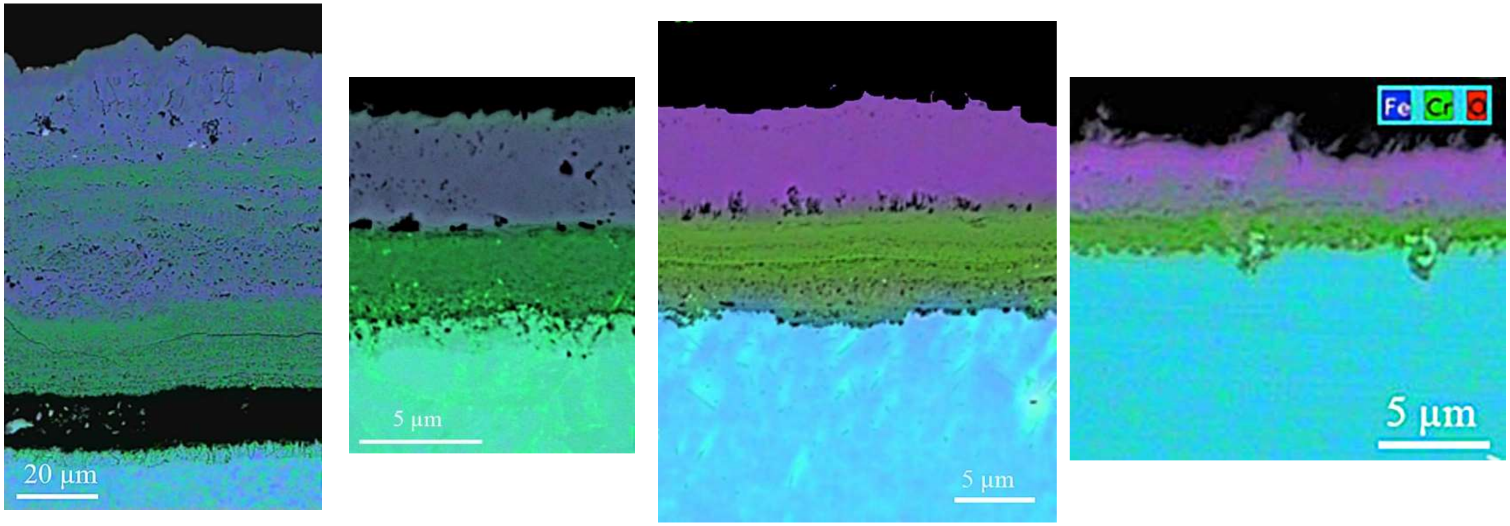
Total Scale Thicknesses at 700°C



- Total scale thicknesses shown for simplicity
- Individual oxide layers were identified, and their thicknesses also measured



Scale morphologies after 1,000h in CO_2 +3.6% O_2, 5.3% H_2O at 700°C and 200 bar – similar to those formed in steam



Gr91 **VM12** **Crofer 22H** **TP304H**

EDS Maps for Fe, Ni, Cr & O Overlaid on SEM Images

- Overall, similar structures to those in steam
  - *voids associated with exfoliation are present in usual locations*
- Some differences in apparent structure of inner layer (L1)
  - *Gr91 shows layer(s) intermediate between L1 and L2 with Cr & Fe striations*
  - *some differences in extent and structure of 'IOZ' at alloy-L1 interface*

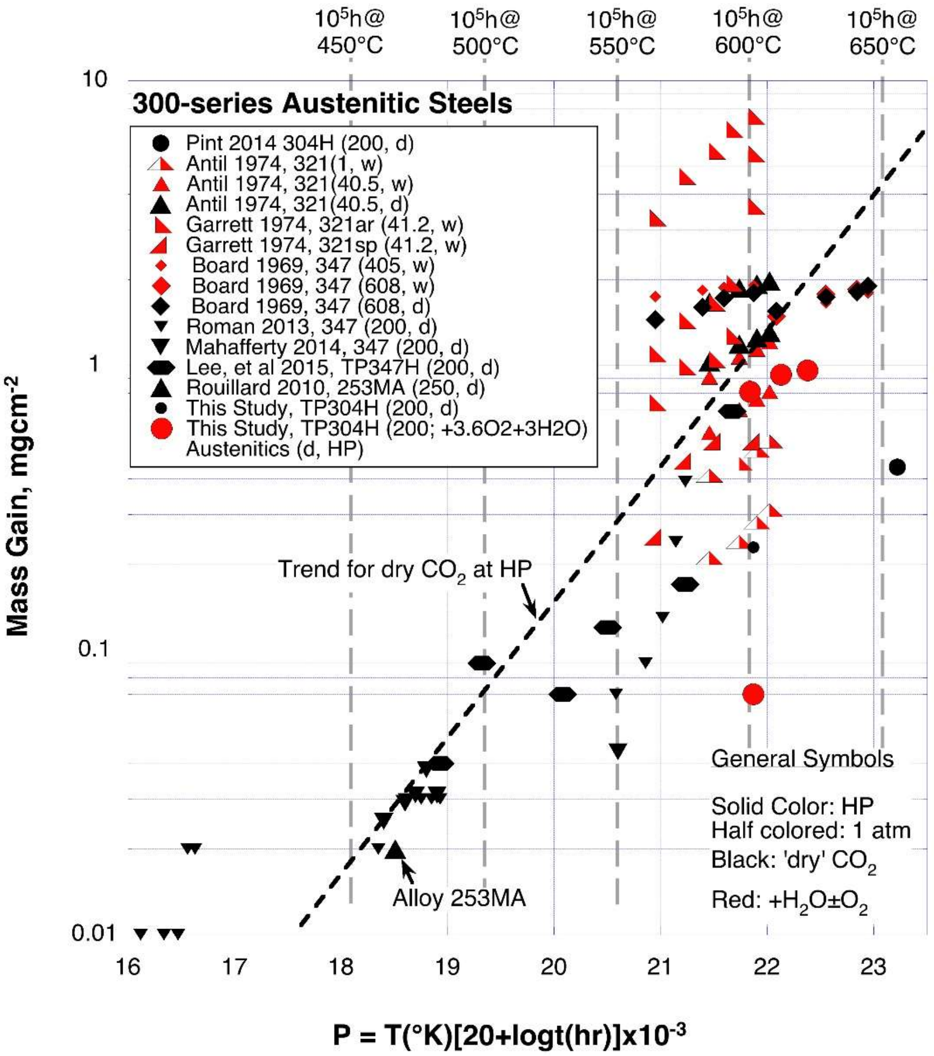
Effects of impurities in sCO_2 on austenitic stainless steels?

- No real trend for pure vs. impure CO_2

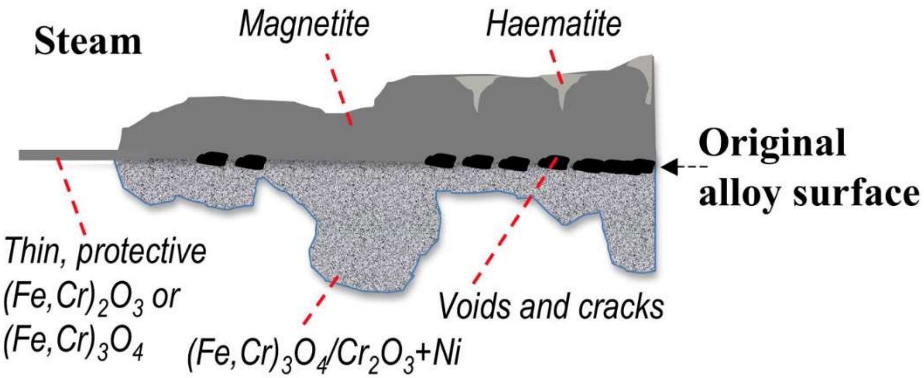
  -or for HP vs. 1 atm

  -or vs. HP steam (not shown)

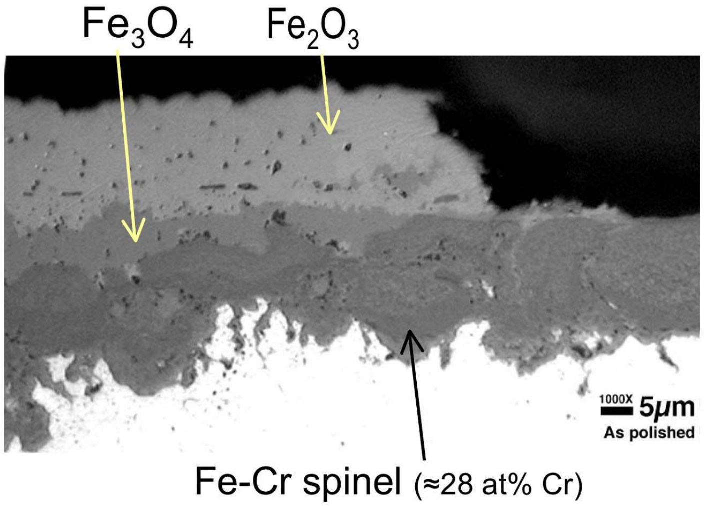
- Expect similar morphologies in CO_2, sCO_2, ±most impurities, and HP steam



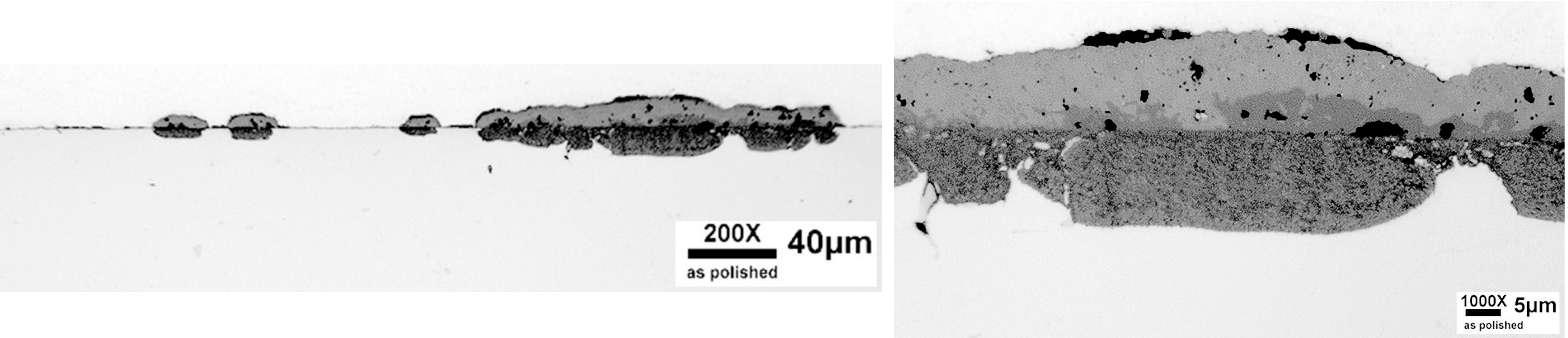
Scale morphologies observed on austenitic stainless steels



Main features of scale in HP steam (Wright & Dooley, 2011)

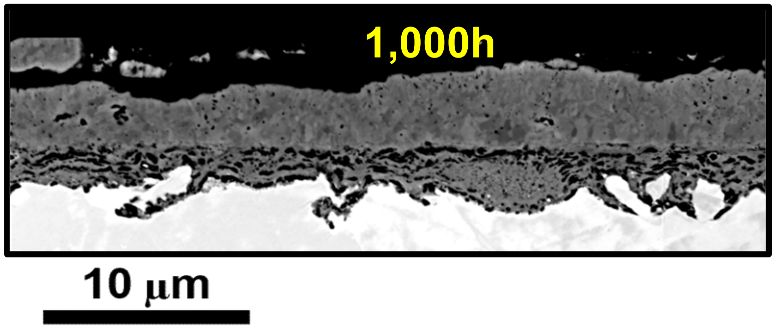


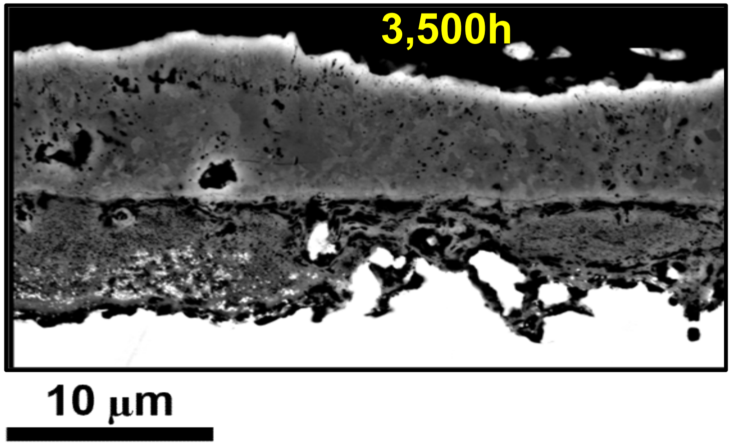
TP347HFG, 11kh at 670°C & 251 bar steam (EPRI Atlas)

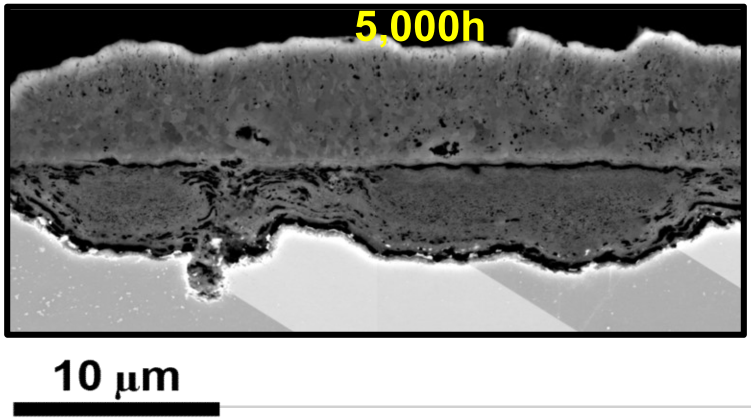


TP347HFG, 500h at 700°C & 200 bar CO_2 (Pint & Keiser, 2014)

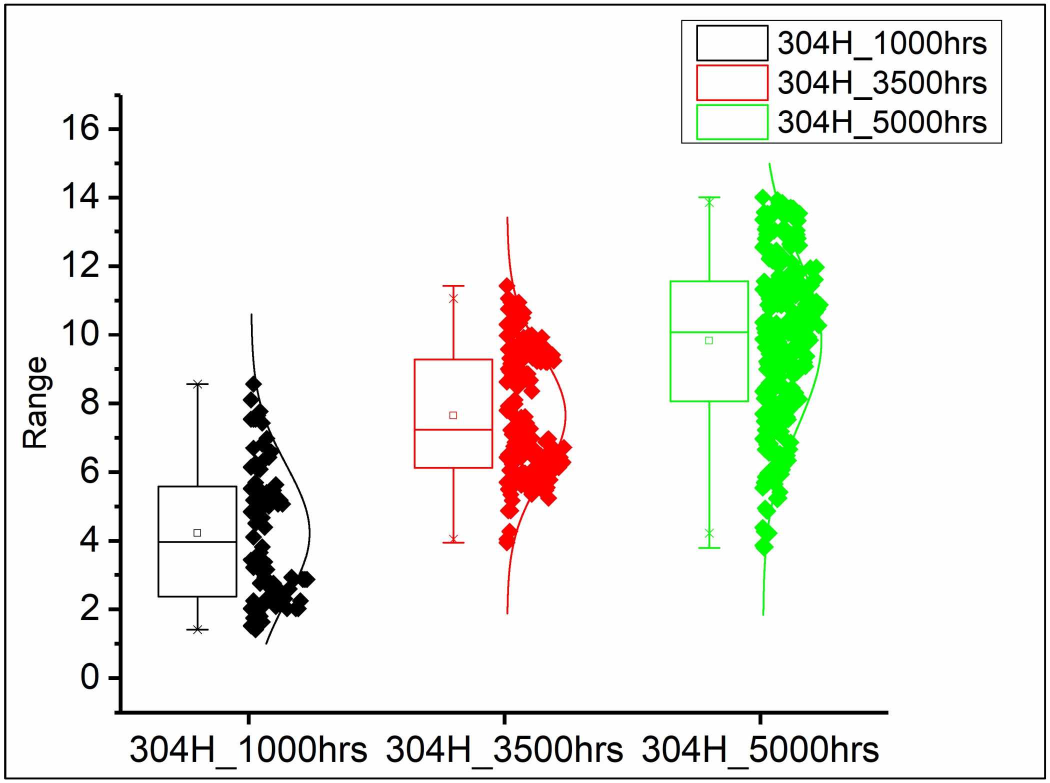
New results: TP304H, 700°C in CO_2 +3.6% O_2, 5.3% H_2O at 200 bar



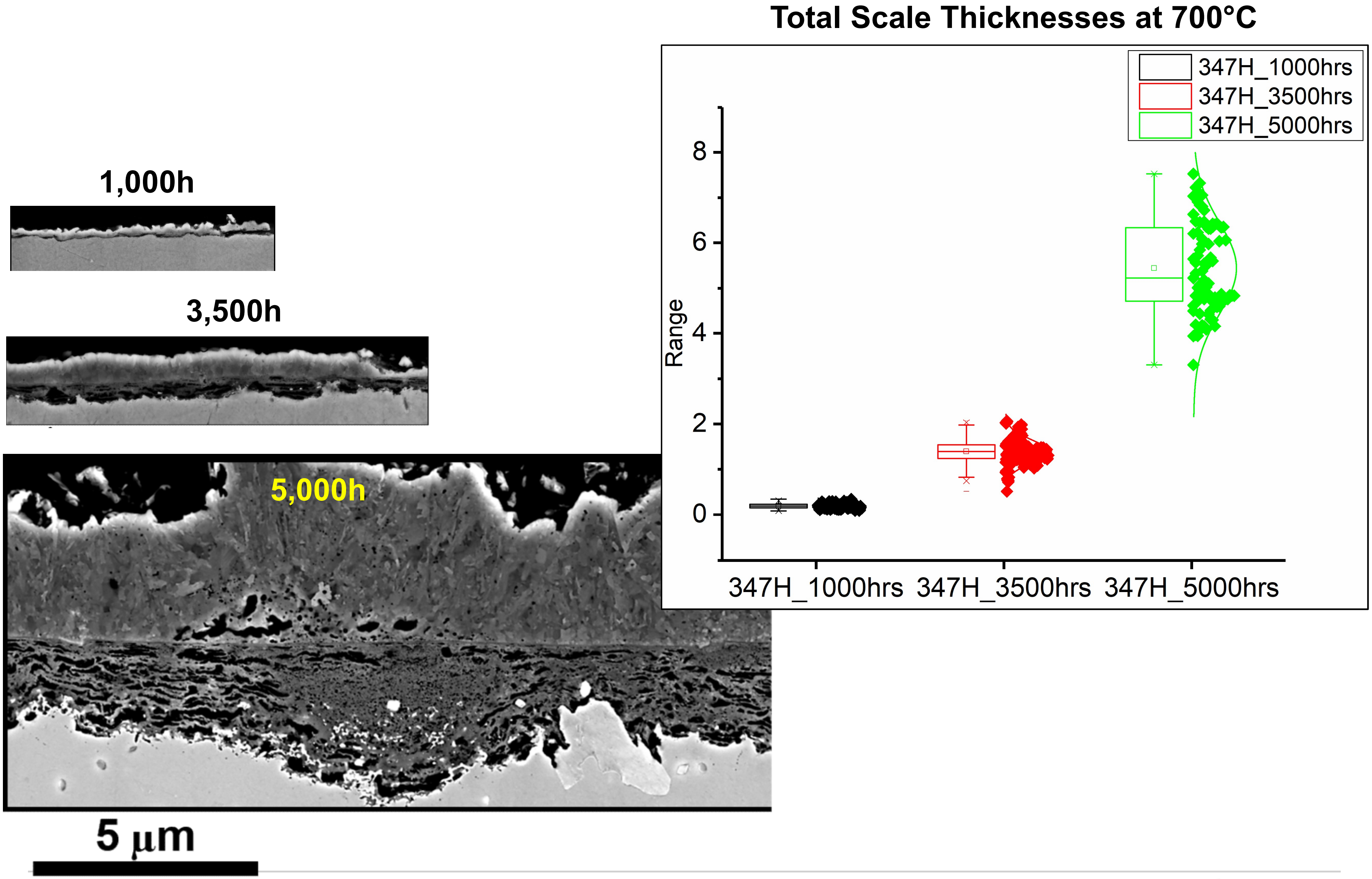




Total Scale Thicknesses at 700°C



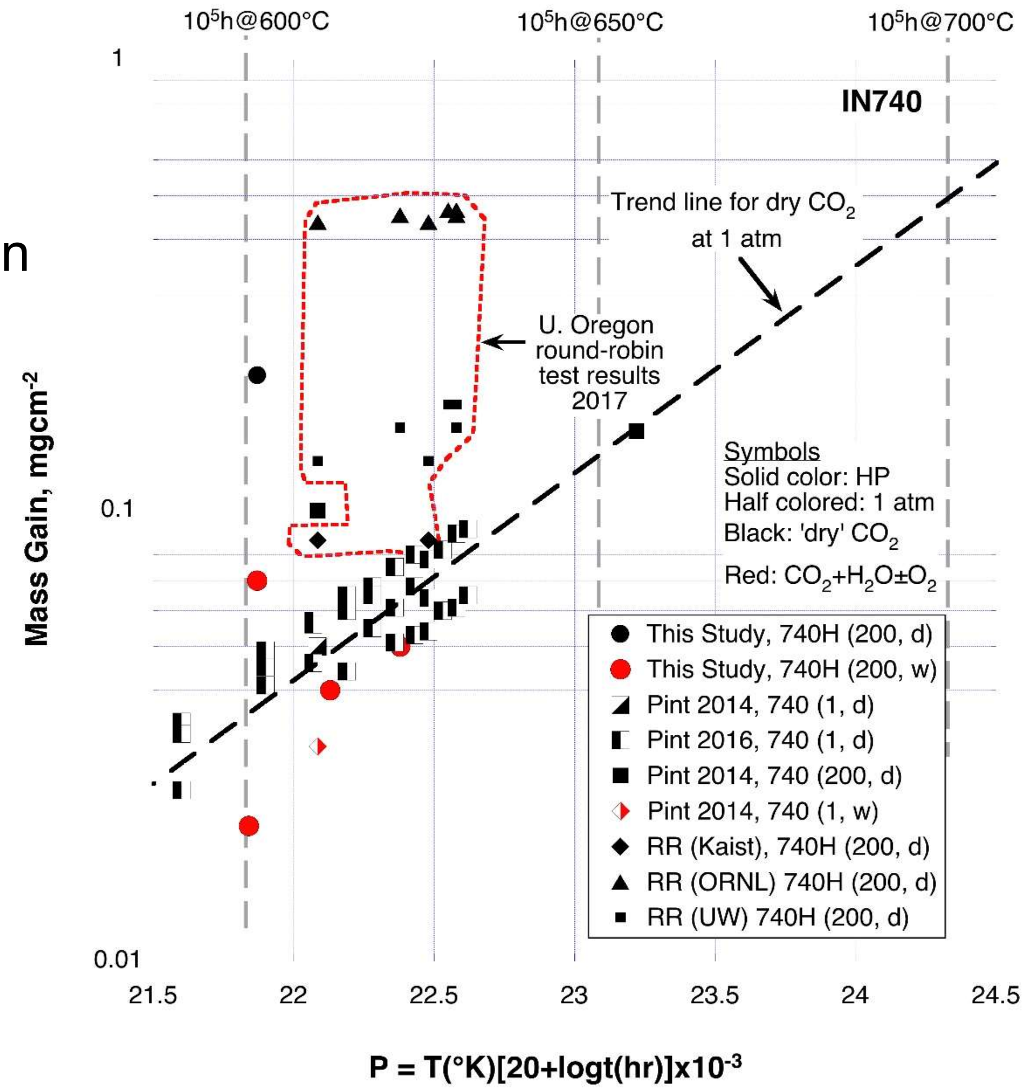
New results: TP347H – initially protective scale


Total Scale Thicknesses at 700°C

Effects of Impurities in sCO_2 on IN740H?

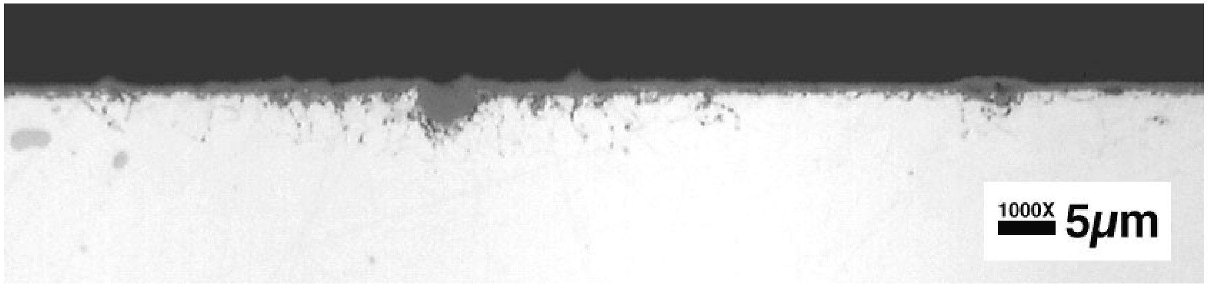
- So far, no obvious effects of impurities in CO_2 on weight gain
- More data are needed

EPRI supplied samples to all sCO_2 Round Robin testing laboratories and provides technical input



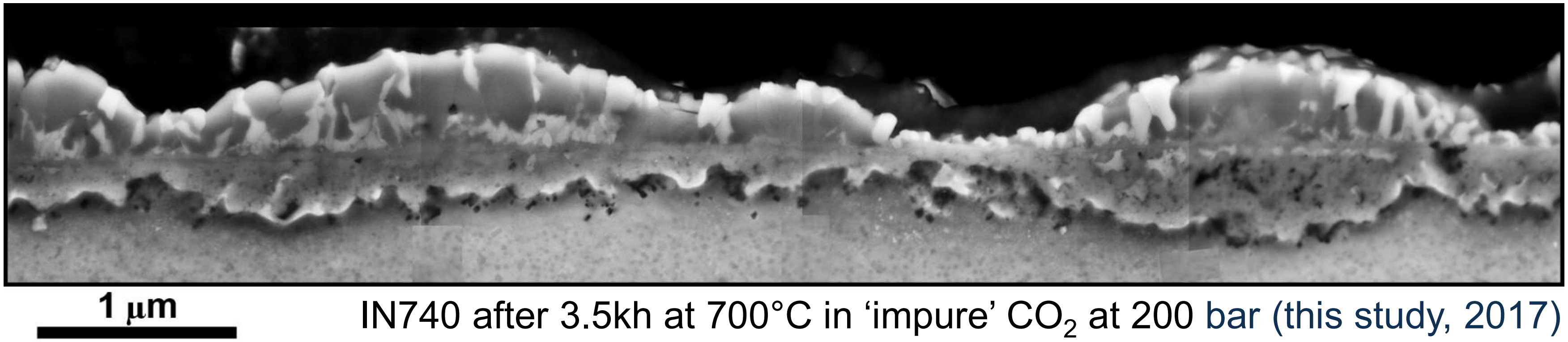
Thin scales on HT alloys complicate thickness measurements

- Max power of optical microscopy produces marginal resolution



IN740 after 4kh at 700°C in steam at 17 bar (Wright, 2009)

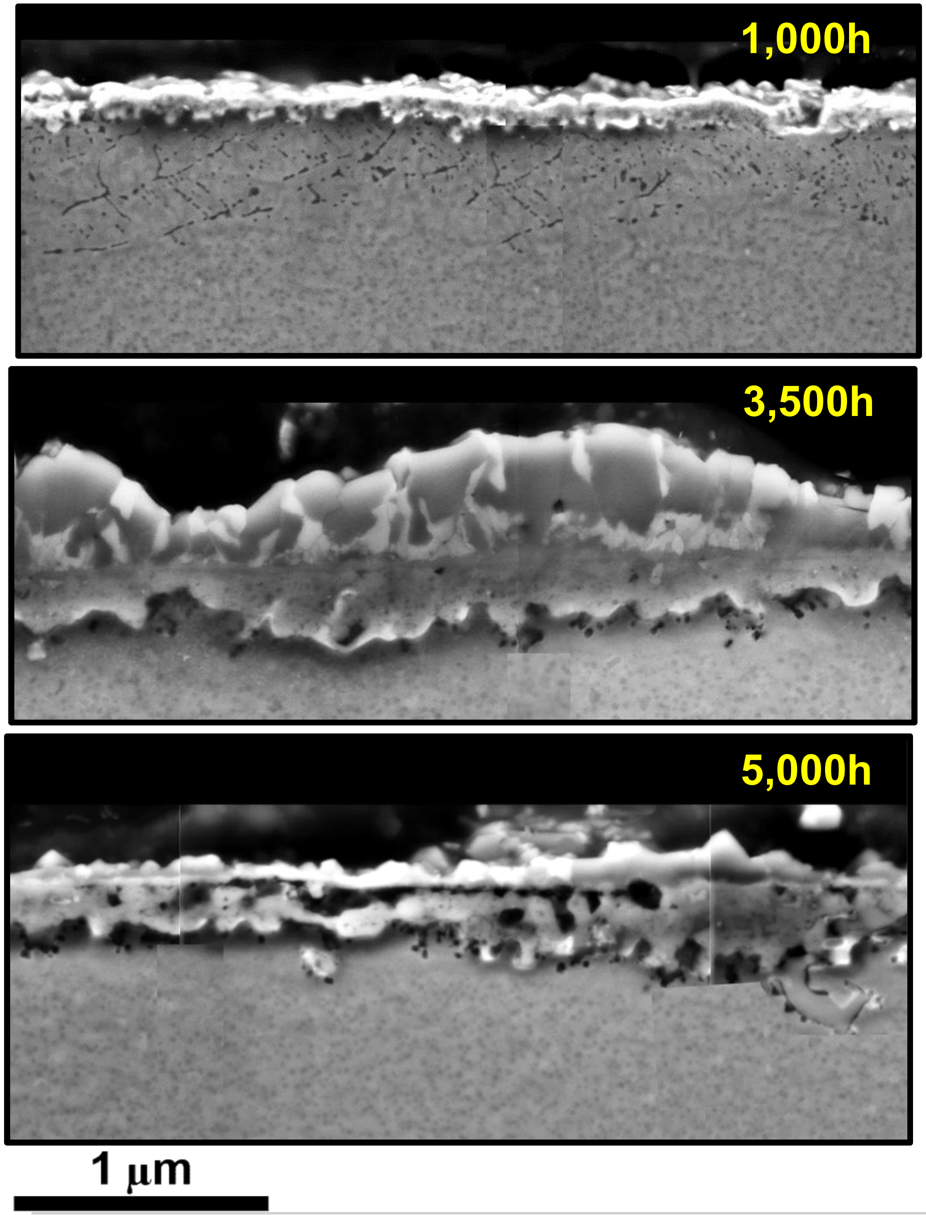
- New SEM/BSE/EDS/EBSD techniques explored by EPRI



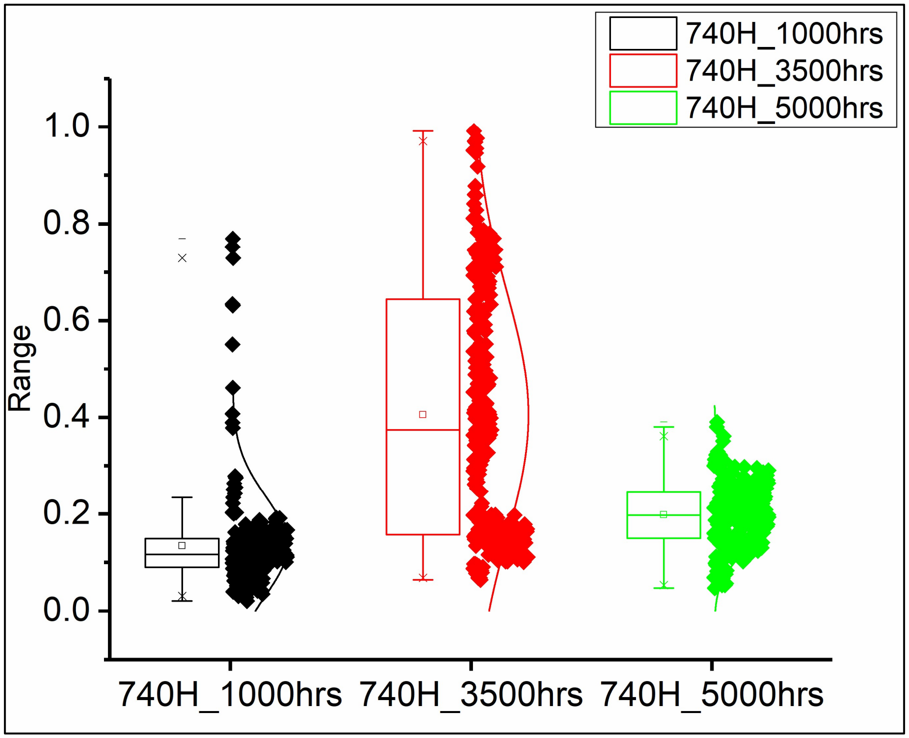
IN740 after 3.5kh at 700°C in 'impure' CO_2 at 200 bar (this study, 2017)

FIB-STEM offers better resolution, but it is time consuming and limited in area

New results: IN740H, 700°C, CO_2 +3.6% O_2, 5.3% H_2O at 200 bar

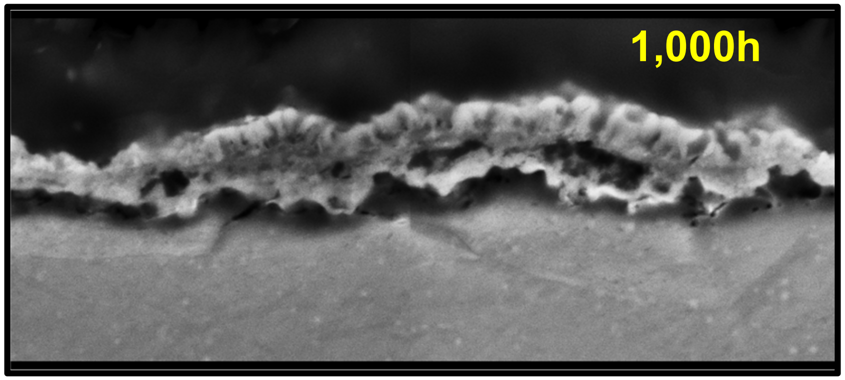


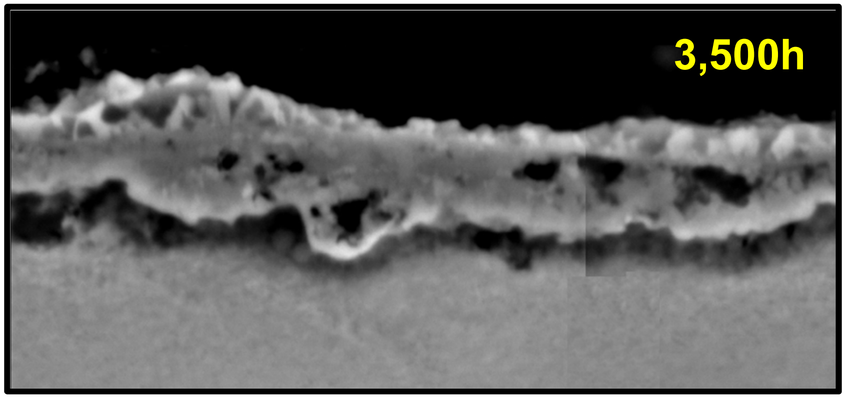
Total Scale Thicknesses at 700°C

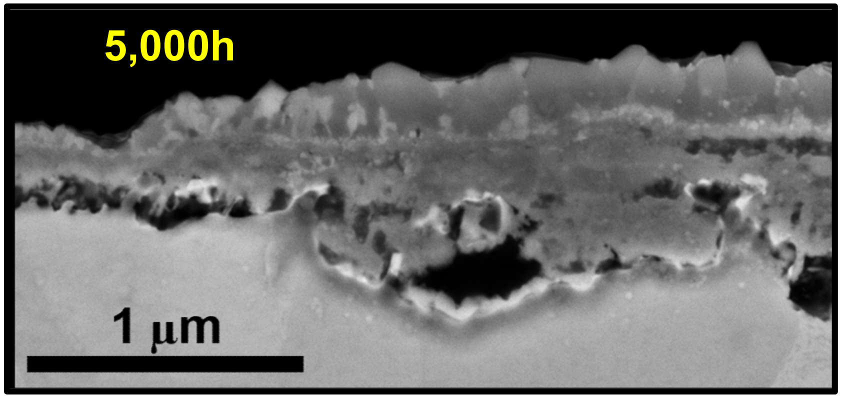


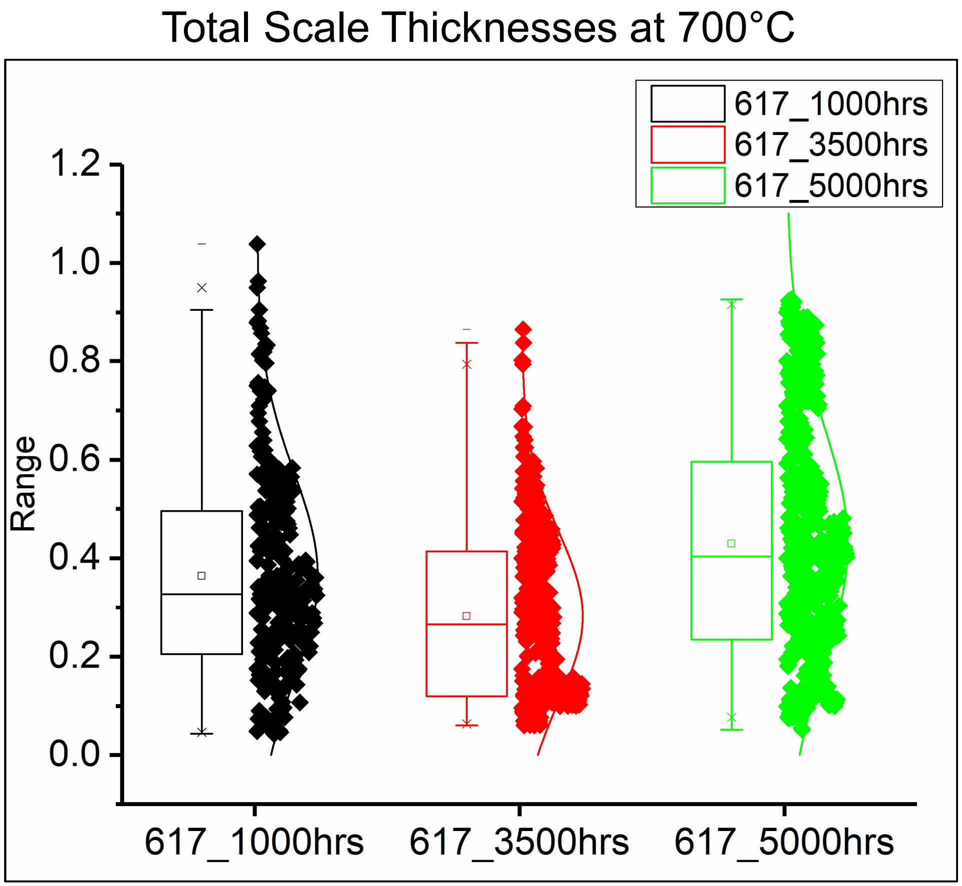
Thin, non-uniform scale clearly evident on 740H surface

New results: IN617, 700°C in CO_2 +3.6% O_2, 5.3% H_2O at 200 bar



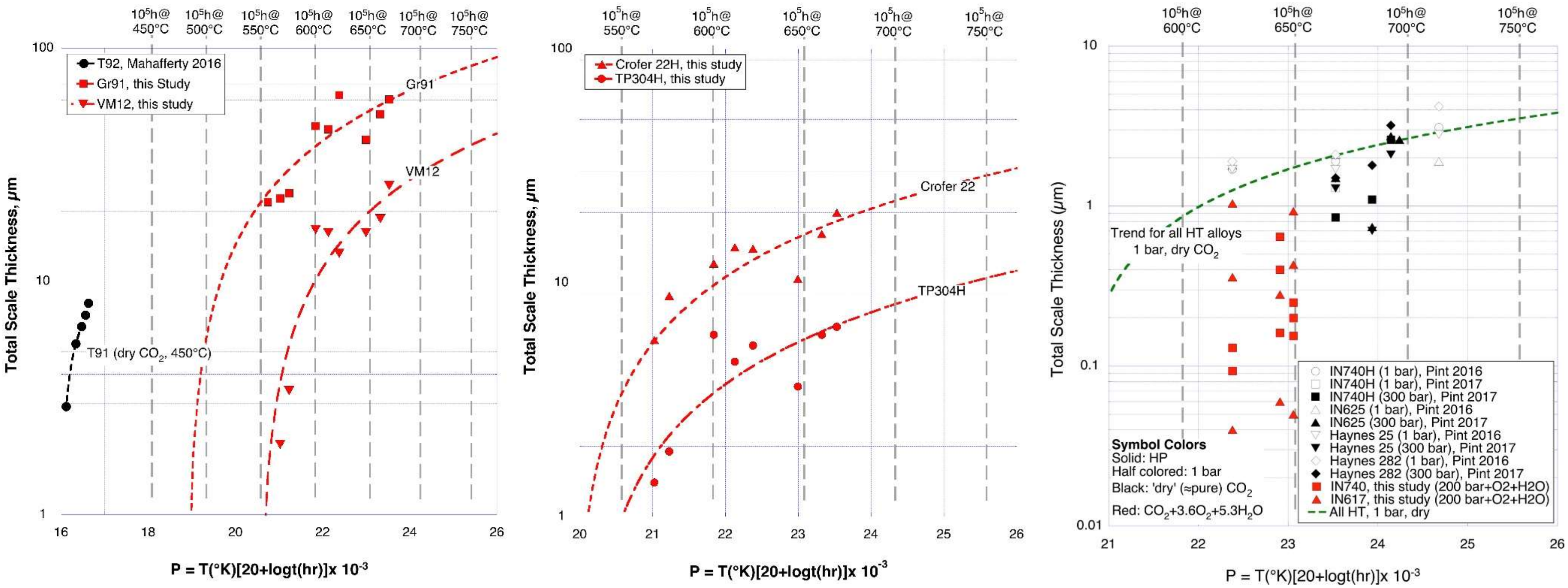





Total Scale Thicknesses at 700°C

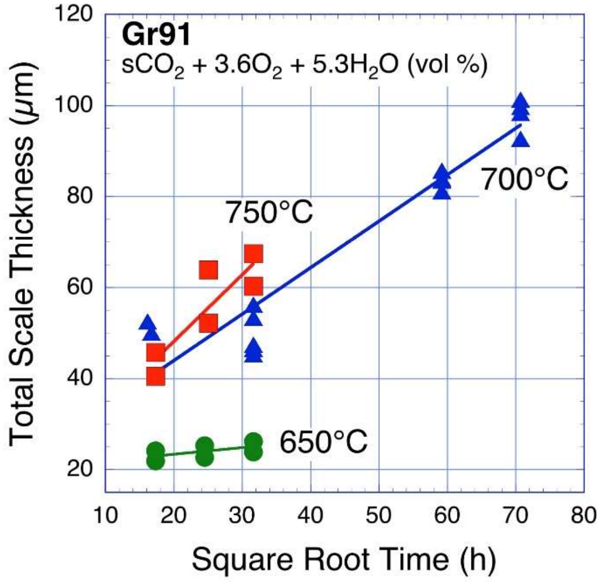
Resulting oxidation kinetics available for use to modify EPRI Exfoliation Model (?)

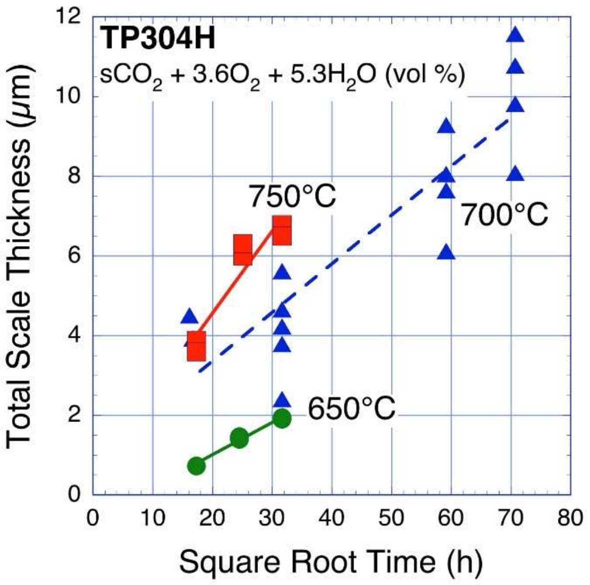
- Considerations:
  - *caution in using ‘literature’ data due to apparent influence of oxidizing impurities*
  - *new data appear mostly consistent, but are limited to results at 3 temperatures*
- However, data for HT alloys show considerable scattering
  - *augment measured thicknesses with converted mass-gain results?*

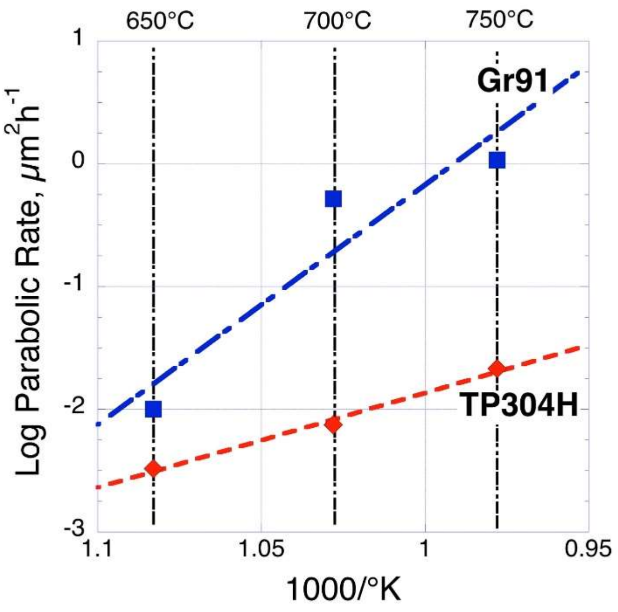


Examples of resulting oxidation kinetics data (this study)

- Parabolic rate constants readily calculated from thickness data for ferritic and austenitic steels





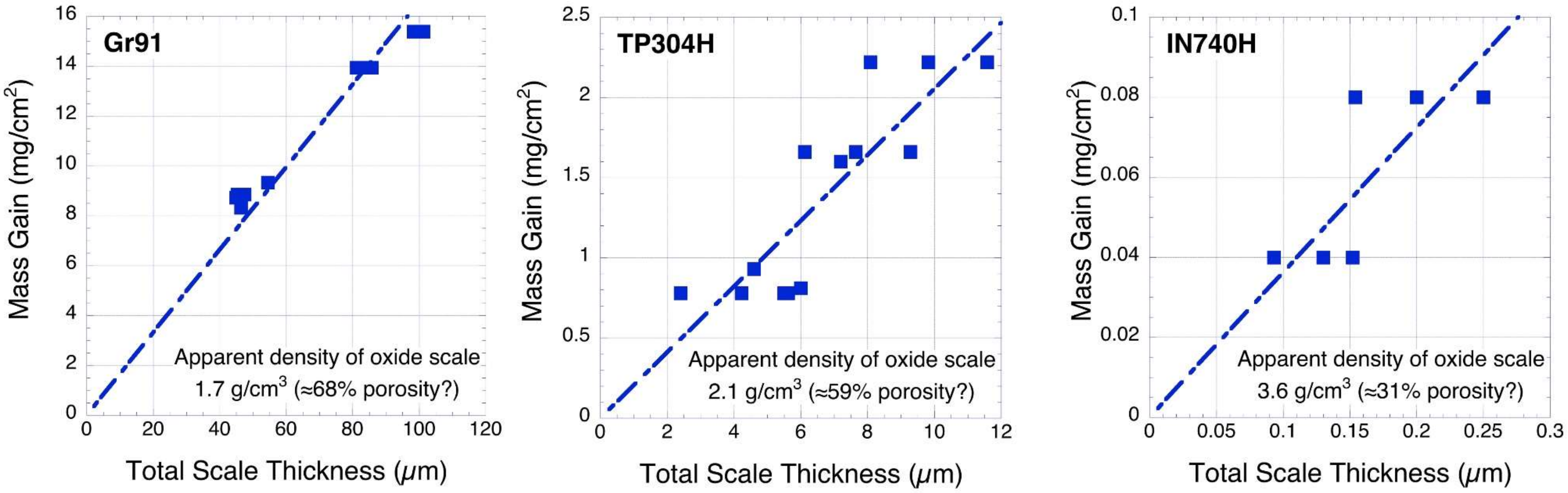


- Derived algorithms appear reasonable

Alloy	T Range (°C)	A (µm²/h)	Q (kJ/mole)
Gr91	650-750	2.3×10^{19}	-374
TP304H	650-750	7.6×10^{5}	-148

Work in progress:
Extraction of consistent kinetics for HT alloys

- Augmentation of thickness measurements with thicknesses derived from mass gain?



Apparent density of oxide scale 1.7 g/cm^3 (≈68% porosity?)

Apparent density of oxide scale 2.1 g/cm^3 (≈59% porosity?)

Apparent density of oxide scale 3.6 g/cm^3 (≈31% porosity?)

Data for 700°C up to 5,000h. Compared with 30% porosity in T92 at 650°C in steam (Knodler & Ennis, 2001)

  - *suggested densities of scales appear to be low*

    e.g., porosity of scale on Gr91≈ 68% (vs. 30% for T92 in steam)

  - *few matching scale thickness-mass gain measurements for IN740H, IN617*

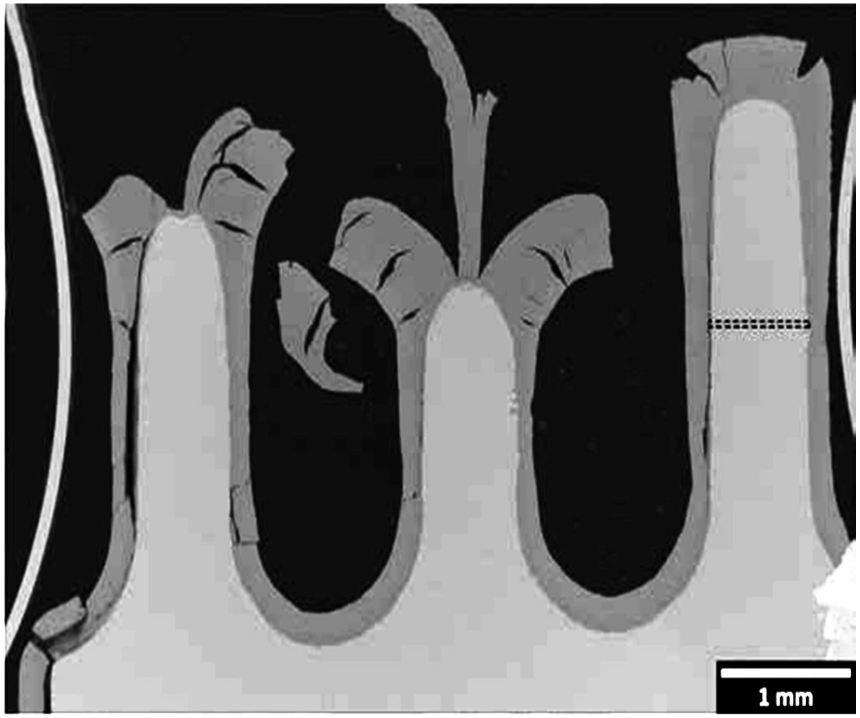
- Or, possible incorporation of oxidation kinetics for reliable chromia-forming alloys measured in HT steam (such as PMCr)?

Expected signs of C participation?

- Ferritic steels
  - *UK research (1970s) identified breakaway oxidation phenomenon under AGR conditions*
- Austenitic steels
  - *C pick-up observed only in initial stages, or when duplex scales present (or after exfoliation)*
- Chromia scales are known to be excellent barriers to C ingress
  - *confirmed by recent observations at 550-750°C, to 200 bar (Pint, ORNL)*
- High-Cr Ni-based (HT) alloys likely to be resistant to C pickup
  - *equally applicable to solid solution and precipitation-strengthened Ni-based candidate alloys?*

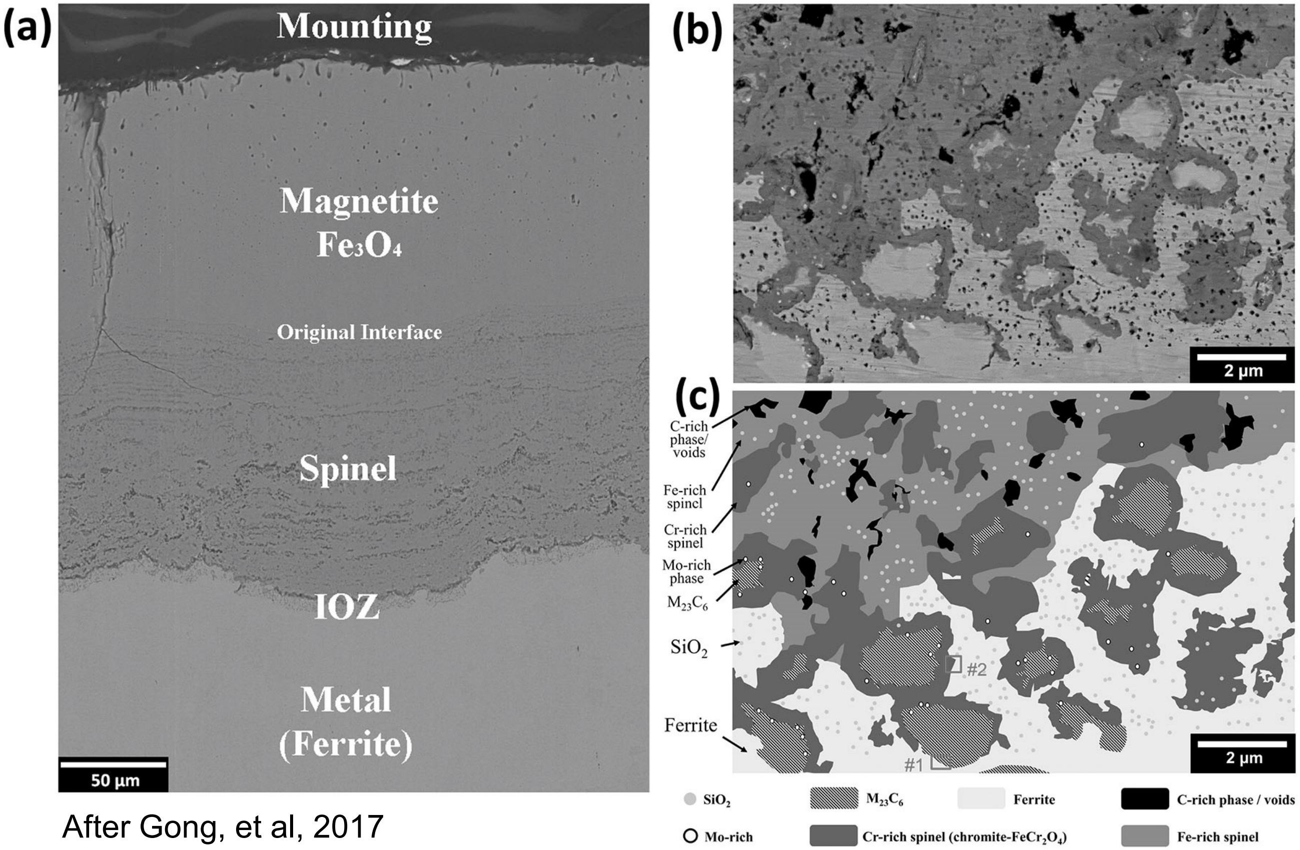
Observed effects of C on oxidation of 9Cr ferritic steel

- AGR testing showed accelerated oxidation of 9Cr steels in (impure) CO_2:
  - *CO_2 containing 1 vol% CO-300 ppmv H_2O-300 ppmv CH_4-100 ppmv H_2 at 40 bar*
  - *breakaway oxidation > 580°C, ≥20 kh*
  - *C saturation model for breakaway criteria*
- However, not much information on scale morphologies
  - *measured alloy C volume fraction vs. t, T*



9Cr -1Mo finned SH tube, 20kh at 600°C in 42 bar CO_2 (Gong et al, 2017)

Fe-9Cr-1Mo at transition to breakaway (RH fin in previous slide)



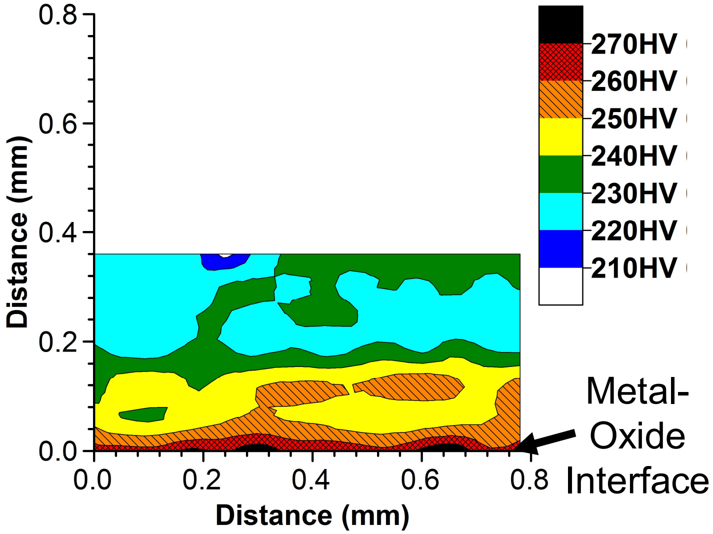
After Gong, et al, 2017

a) Morphology of main scale indistinguishable from those in steam

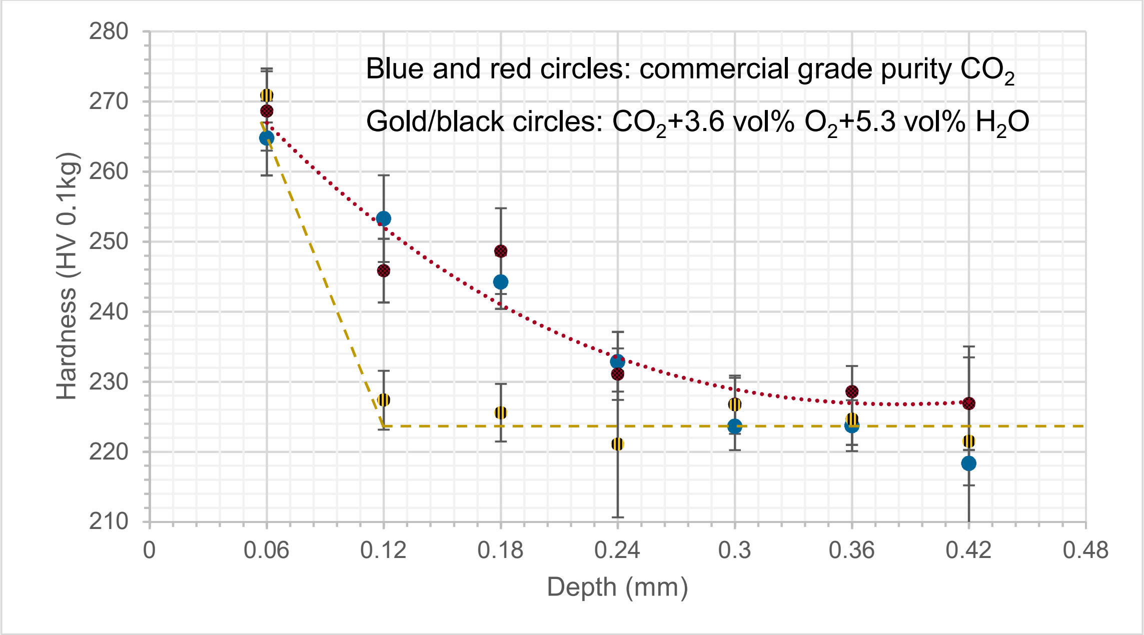
b) IOZ shows fine, distributed carbides

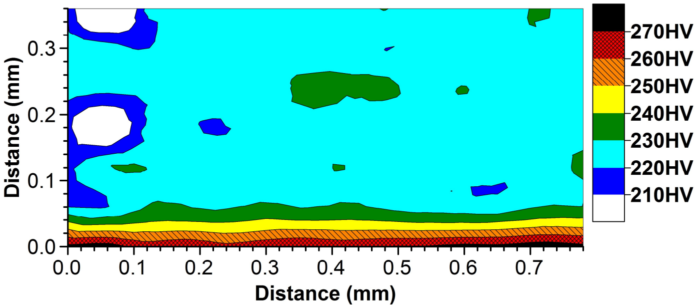
c) Alloy substrate was saturated with C: large, blocky $M_{23}C_6$, and $M_2(C,N)$ needles

This study: Gr91 had greater depth of hardening in CG purity than CO_2 +3.6% O_2, 5.3% H_2O at 200 bar after 300h at 700°C



Commercial-grade purity CO_2



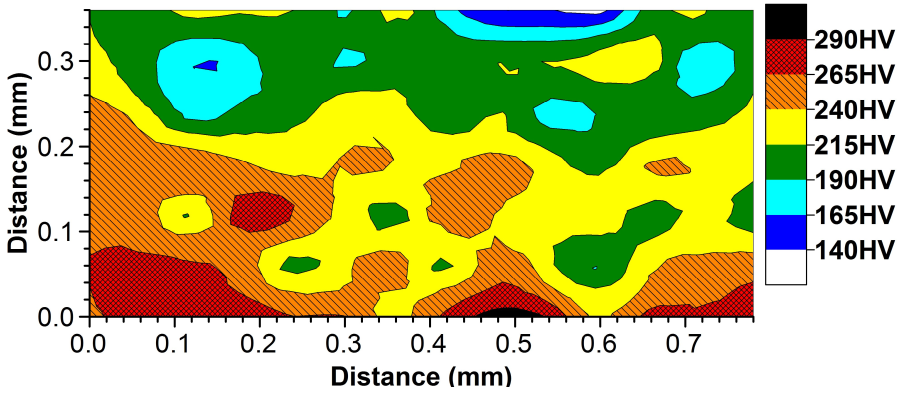


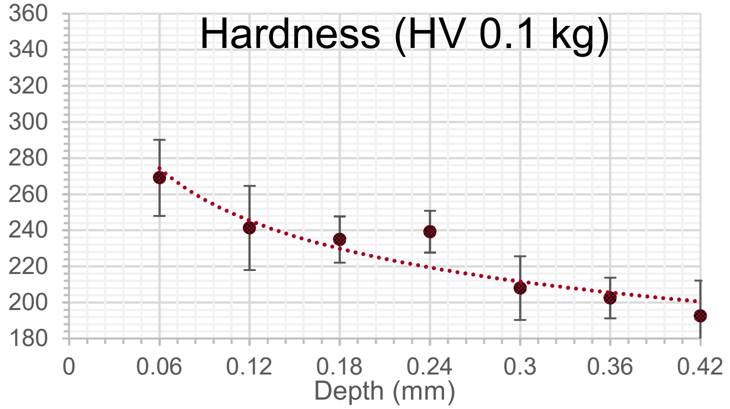
CO_2+3.6 vol% O_2+5.3 vol% H_2O

- Hardness maps from arrays of 7 x 14 indentations
- Alloy-oxide interface at y = 0.0 (bottom of map)
- Oxidizing impurities appear to retard hardening

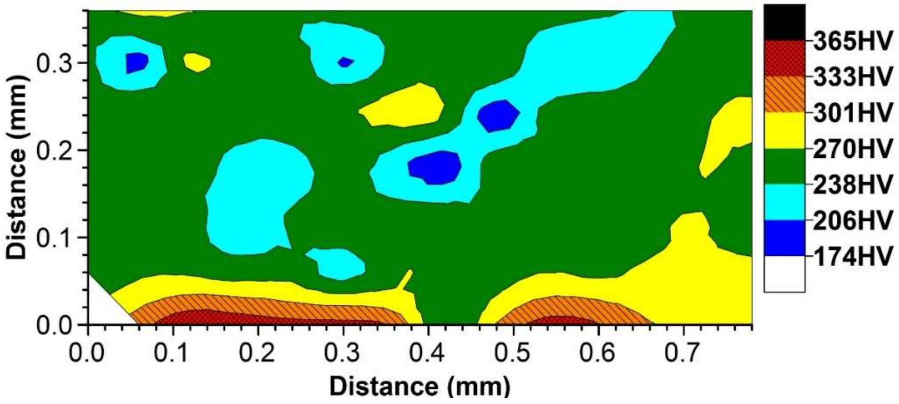
Ferritic Steels: 1,000h at 700°C in CO_2 +3.6% O_2, 5.3% H_2O at 200 bar

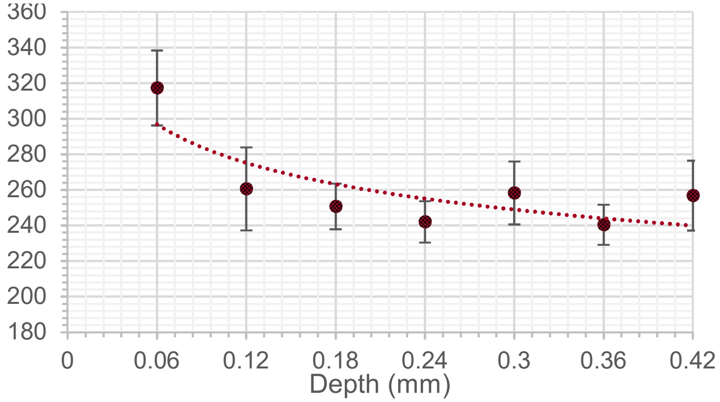
Gr91



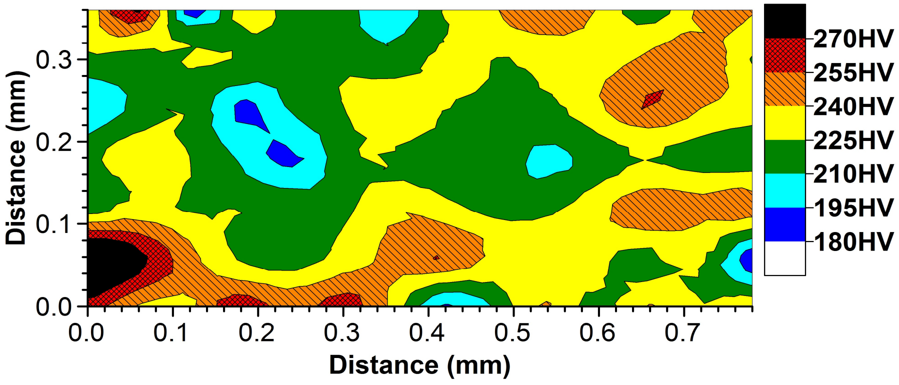


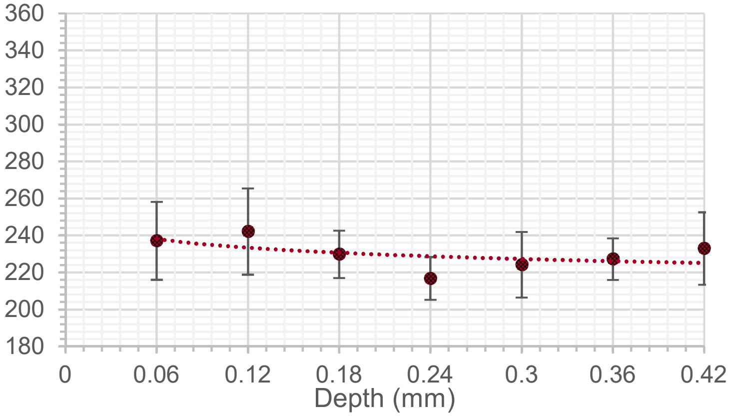
VM12





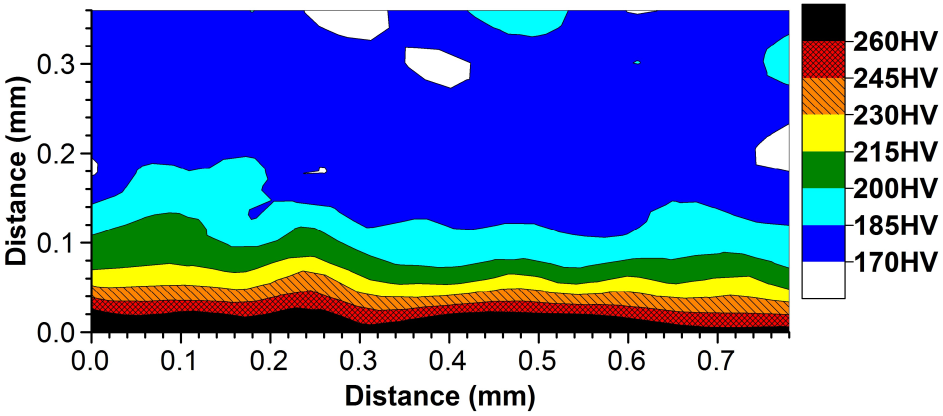
Crofer 22H

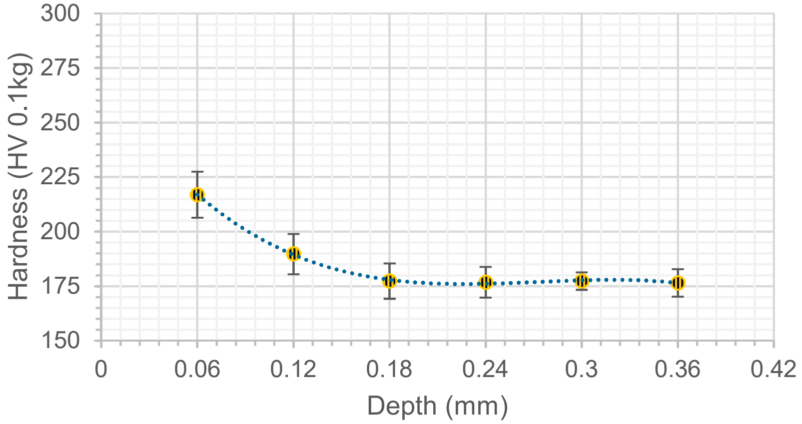




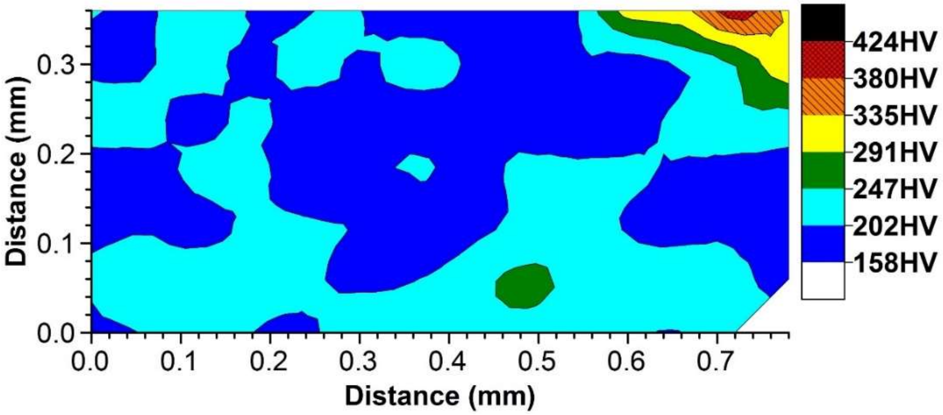
Anomalous Hardness Changes in TP304H after exposure at 700°C to CO_2 containing 3.6 vol% O_2, 5.3 vol% H_2O at 200 bar?

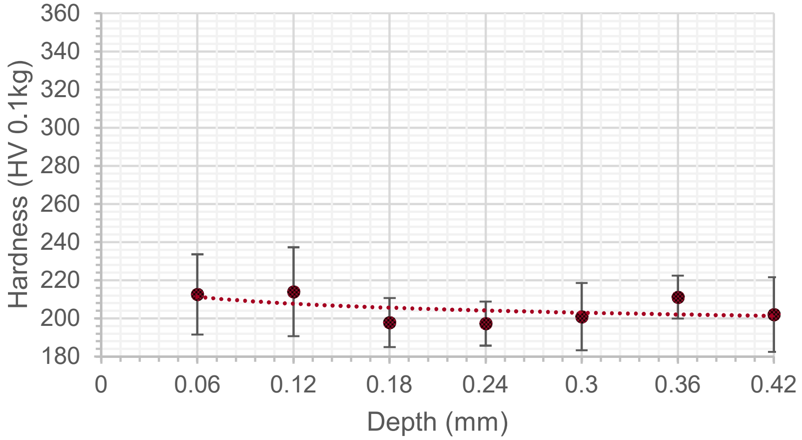
- 300h: significant but highly-localized near-surface hardening





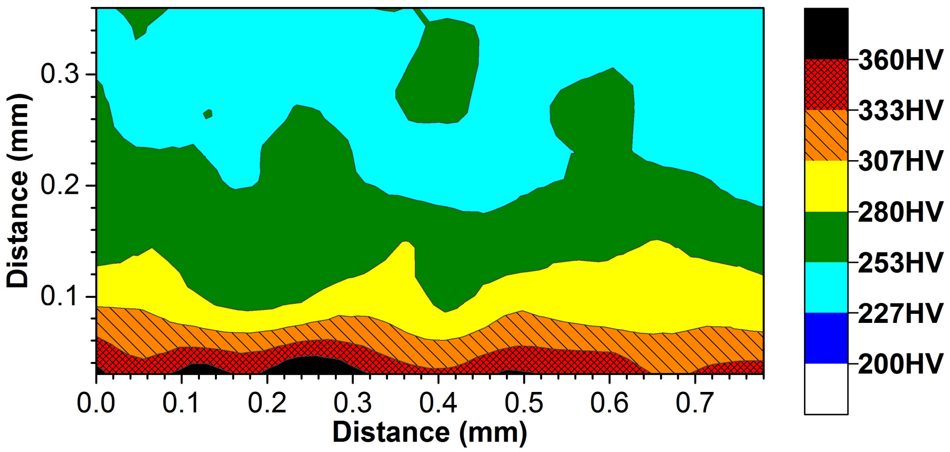
- 1,000h: no apparent increase in hardness

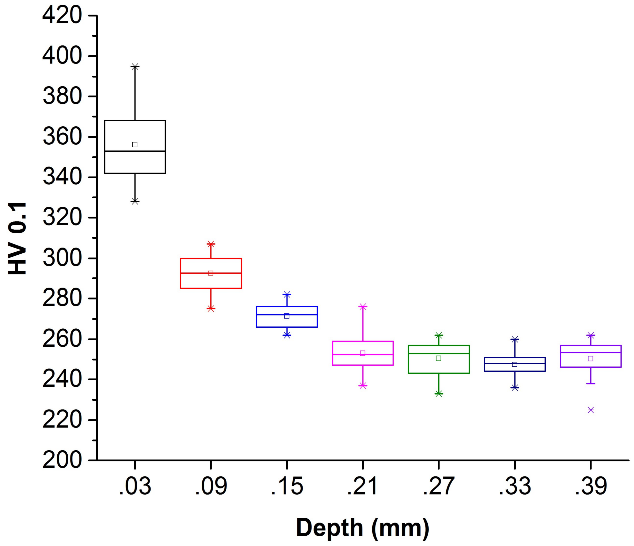




Hardness changes in HT alloys after exposure for 1,000h at 700°C to CO_2 containing 3.6 vol% O_2, 5.3 vol% H_2O at 200 bar

HR3C





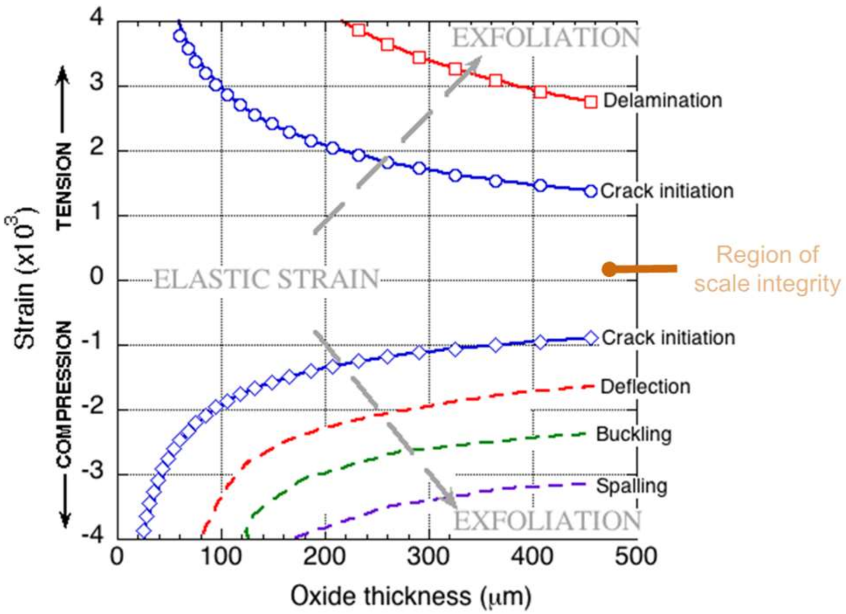
- Significant hardening to a relatively uniform depth of 150-200 μm
- Surprising, since HR3C is expected to form a protective chromia scale
- Could be associated with cold work from surface preparation ?

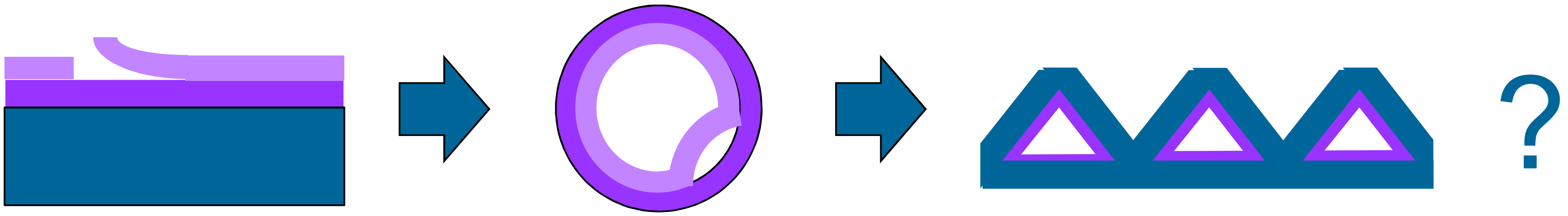
IN617 and IN740H

- Micro-hardness measurements did not reveal any evidence of carburization.

Exfoliation Model to address unique influences of oxide growth on service life of small-channel heat-exchangers

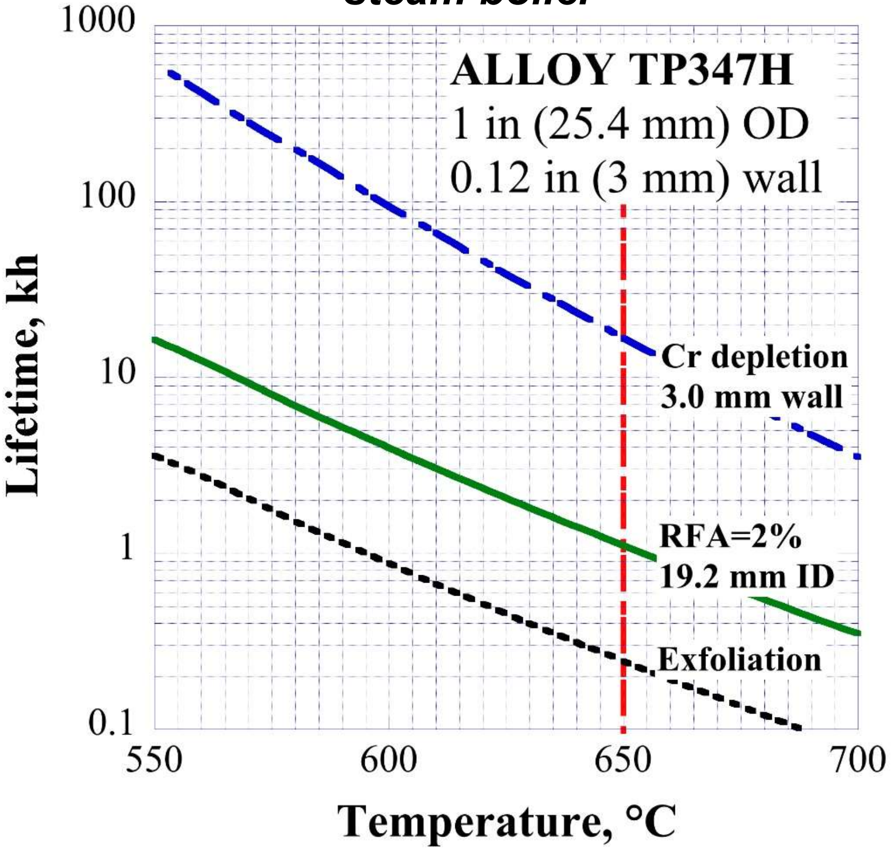
- Lab studies: isothermal oxide growth on small flat coupons
- Real world: heat-flux, stress from complex geometries
- Modeling:
  - EPRI-developed strain trajectory approach for steam tubes
  - Properties of sCO_2 and alloys collected
  - **Discussion with vendors on convex vs. concave surfaces – need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





Proposed Overall Summary of Results

Example for SH tube in conventional steam boiler



- Actual examples that illustrate lifetime issues related to oxide growth
- Use critical dimensions from sCO_2 HX designs; all seven alloys
- Lifetime criteria used:
  1) *ΔP due to oxide thickening*
  2) *t to breakaway due to Cr consumption*
  3) *t to reach critical scale thickness for exfoliation*
- Possible further criterion:
  4) *t for wall thickness to be thinned to unsafe level (strength criteria?)*

Summary

- First project to address oxidation in semi-open Allam cycle sCO_2 conditions
  - *impurity concentrations determined via mass balance and thermodynamic calculations*
  - *a new test rig was assembled and laboratory tests to 5,000h with and without impurities completed*
- Oxidation rates in sCO_2
  - *appear consistent, with similarities to those in HP steam*
  - *possibly slower when oxidizing impurities are present in* sCO_2
  - *no systematic effect of total pressure*
- Scale morphologies
  - *nominally followed expectations from steam, with some potential influences of C*
- Surface hardening
  - *identified in Gr 91 and VM12; more severe in 'pure'* sCO_2
  - *also in TP304H & HR3C, although behavior of TP304H appeared anomalous*
  - *none found in Ni-base alloys*
- Evaluation of impact of scale growth in sCO_2 on service lifetimes for compact heat exchanger designs in progress - built on existing EPRI Oxide Exfoliation Model

Acknowledgements / Team

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