Characterization of Oxide Scale Structures on Alloys Exposed to Open-Fired sCO2 Power Cycles

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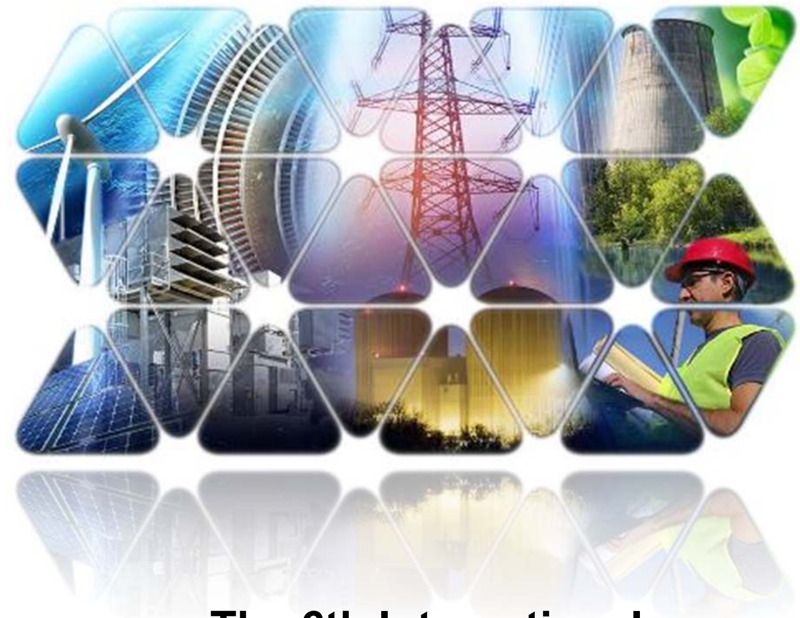


The 6th International Supercritical CO_2 Power Cycles Symposium

29 March 2018, Pittsburgh, PA

Recent Project on Predicting Oxidation Behavior of Structural Alloys in sCO_2

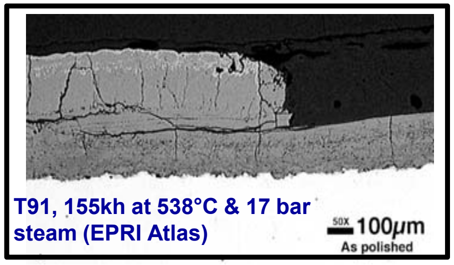
- Overall Objectives
  - *predict the oxidation/corrosion performance of structural alloys in high-temperature high-pressure supercritical CO_2 (sCO_2)*
  - *combine laboratory testing & computational modeling, incorporating unique attributes of sCO_2 heat exchangers and recuperators, to accomplish this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

Ian Wright, Steven Kung, and John Shingledecker, *Predicting the Oxidation/Corrosion Performance of Structural Alloys in Supercritical CO2*. United States: N. p., 2017. Web. doi:10.2172/1415286.

Potential Issues Due to Oxidation

Scale Growth

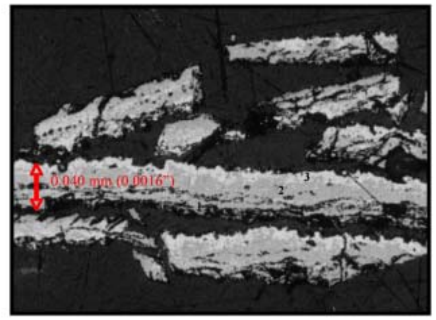
Oxidation kinetics influenced by alloy and working parameters



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

Scale Failure

- Evolution of scale morphology
- Development of stress/ strain

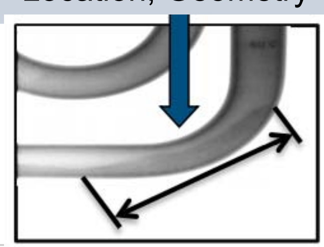


Scale loss (exfoliation)

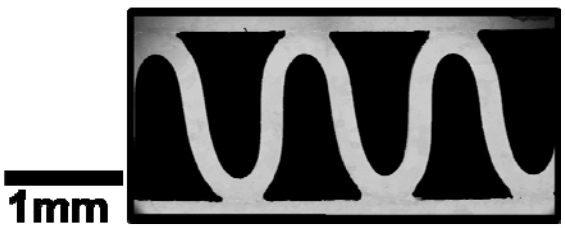
Criteria for scale separation

Formation of Deposits and Blockage

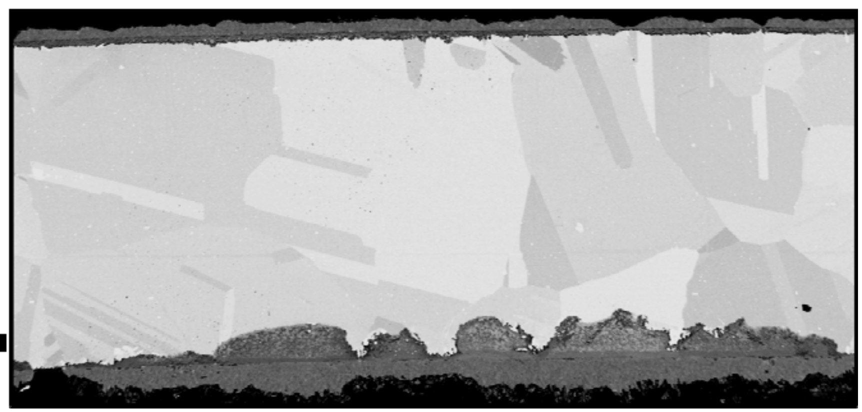
- Size, Packing
- Location, Geometry



Thin and intricate shapes



347H, 5000h at 700°C in sCO_2 - 3.6% O_2-5.3% H_2O at 200 bar



100 μm

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Scope of Laboratory sCO_2 Oxidation Tests

- **Conditions**
  - 650-750°C, 200 bar
    - sCO_2 (Commercial purity)
    - simulated semi-open cycle impurities (O_2 + H_2O)

O_2 = 3.6 vol%, H_2O = 5.3 vol%

- **Materials**
  - Commercially available
  - Code approved/industry relevant
  - Focus on economics

Material Class	Alloys Selected		
Ferritic steels	**Gr 91** (8-9Cr)	**VM12** (11-12Cr)	**Crofer 22H** (20Cr)
Austenitic stainless	**TP304H** (18Cr)	**HR3C** (25Cr)	**TP347H** (18Cr-9Ni-Nb-C)
Nickel-based	**IN617** (20Cr, solid soln. stren.)	**IN740H** (25Cr, ppt. stren.)	

- **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 8 alloys)
  - 1 x 5,000-h test in CO_2 + impurities, 700°C, 200 bar (all 8 alloys)

S. Kung, "Corrosion of Heat Exchanger Alloys in Open-Fired sCO2 Power Cycles", 6th International Supercritical CO2 Power Cycles Symposium, Pittsburgh, Pennsylvania, March 27 – 29, 2018 (This conference)

Information Needed For sCO_2 Oxidation/Exfoliation Model

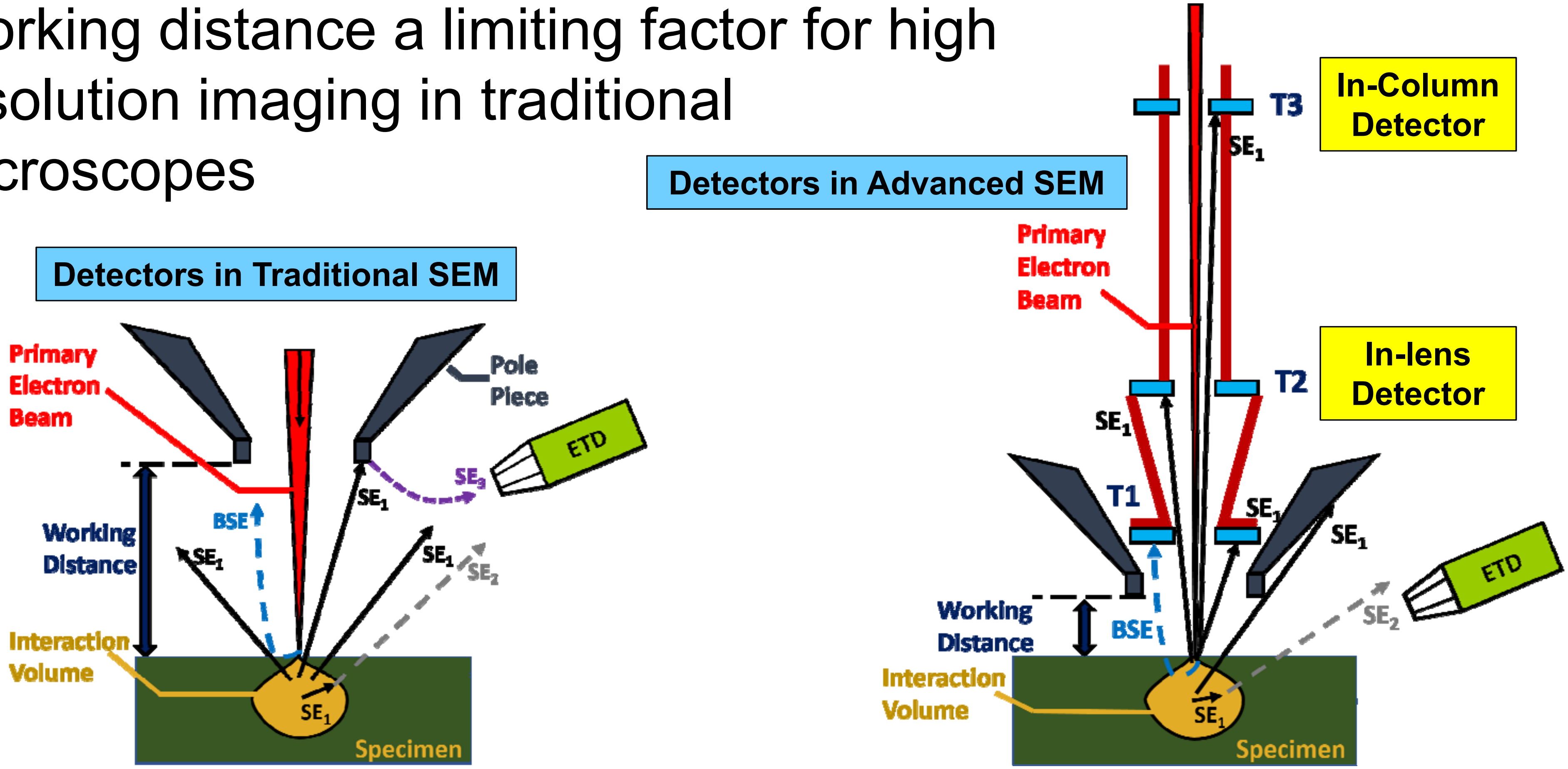
- **Oxidation rates as a function of oxide <u>thickness</u> vs. *t* and *T***
  - for oxide thickness: $d^2 = 2.k_p.t$, where: $k_p = Ae^{-Q/RT}$, or $\ln k_p = A–Q/RT$
  - Q from slope of an Arrhenius plot
  - ***mass-based oxidation data are of limited value***
    - both oxidation and carburization lead to 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

Approach for Characterization of Scale Morphology and Quantification of Scale Thickness

- Scanning electron microscope based imaging of oxide scale
  - Low working distance, and optimization of beam parameters for high resolution imaging
  - Continuous imaging along the edge of the sample capture more information regarding oxide morphology
- Meticulous measurements of oxide scales
  - Careful measurement practice to capture variation in thickness of oxide scales

A Note on Recent Advances in SEM Technology

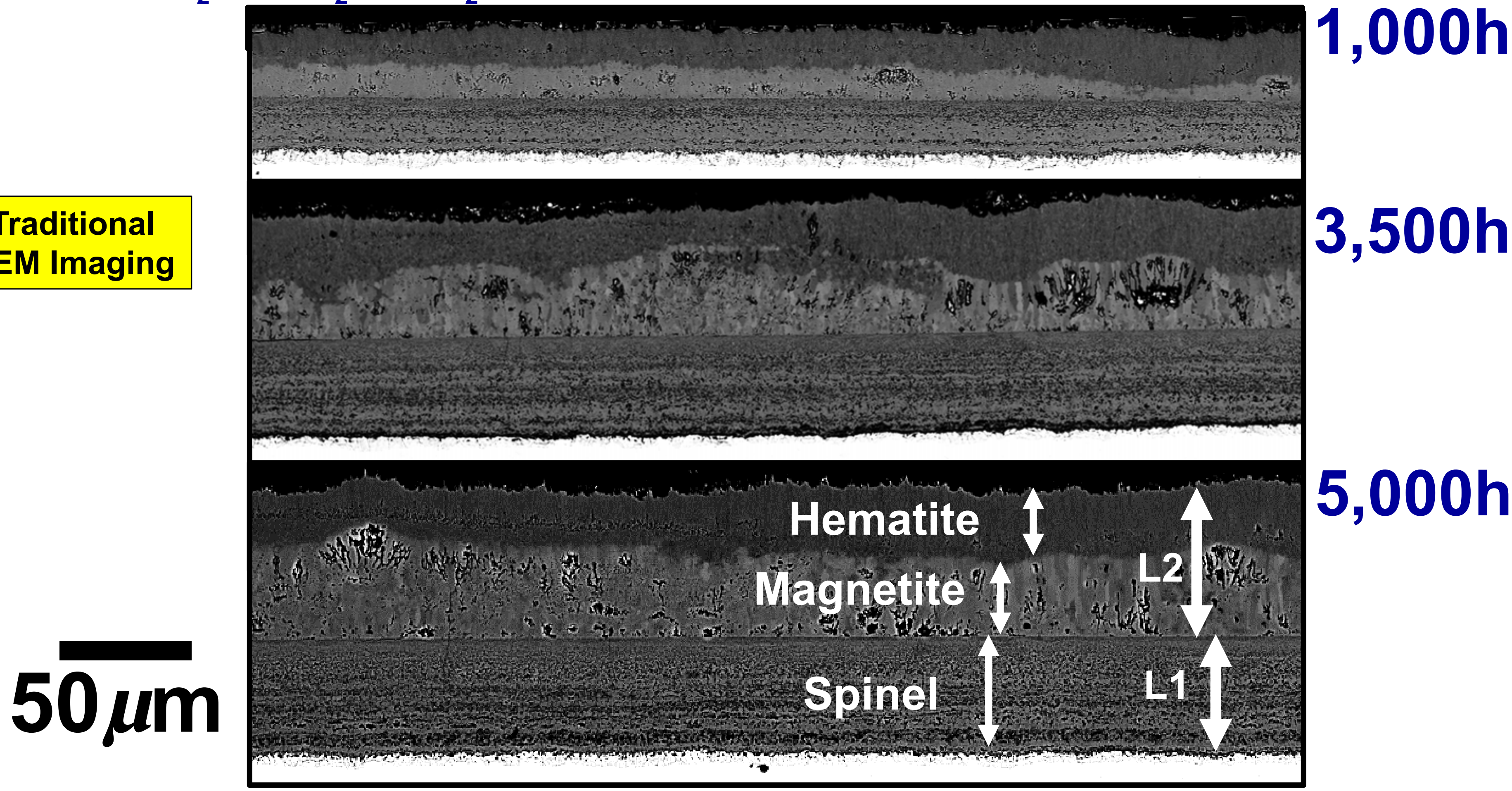
- Working distance a limiting factor for high resolution imaging in traditional microscopes



Morphology of Grade 91 Oxide Scale

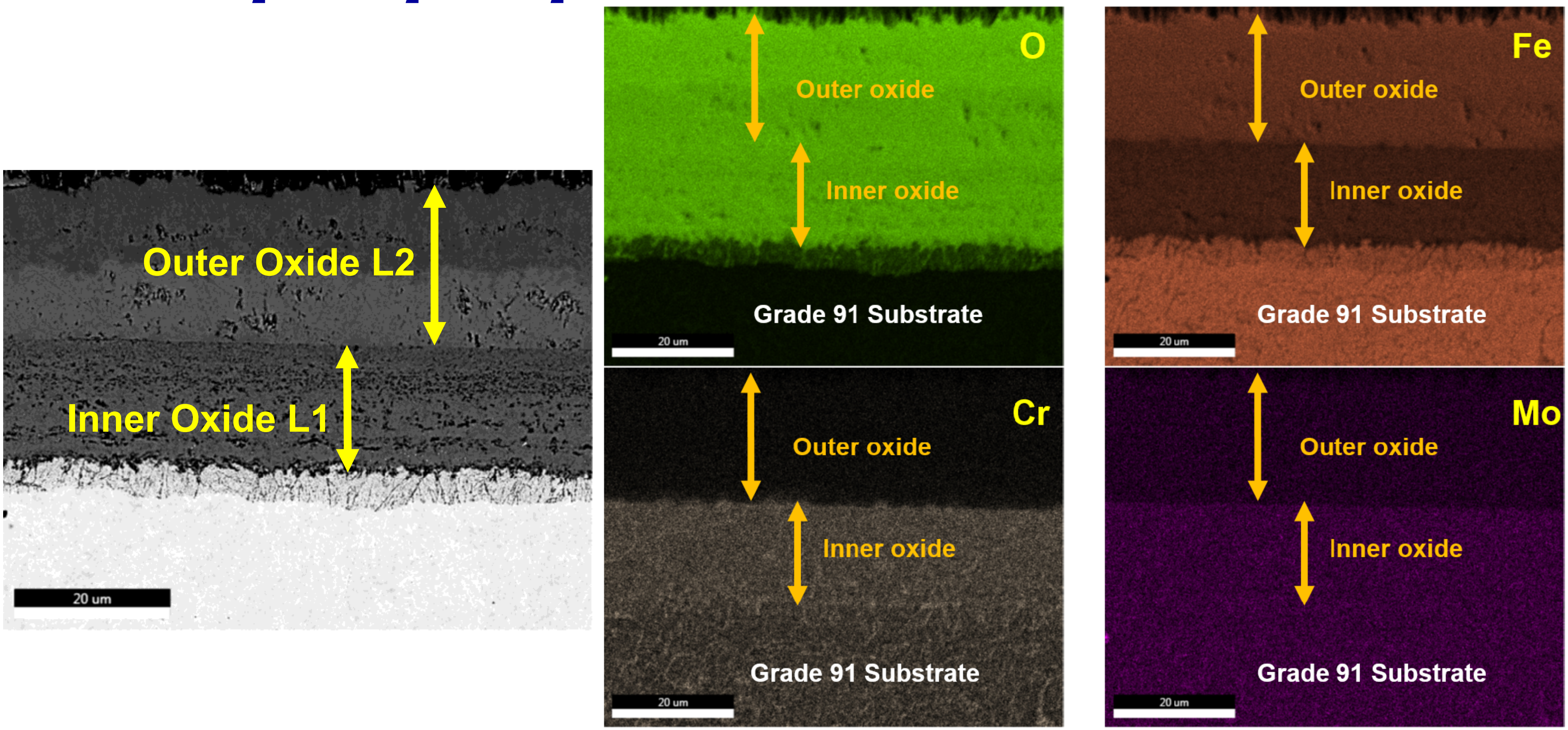
700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar

Traditional SEM Imaging



Distribution of Alloying Elements at Grade 91 Oxide Scale

700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar



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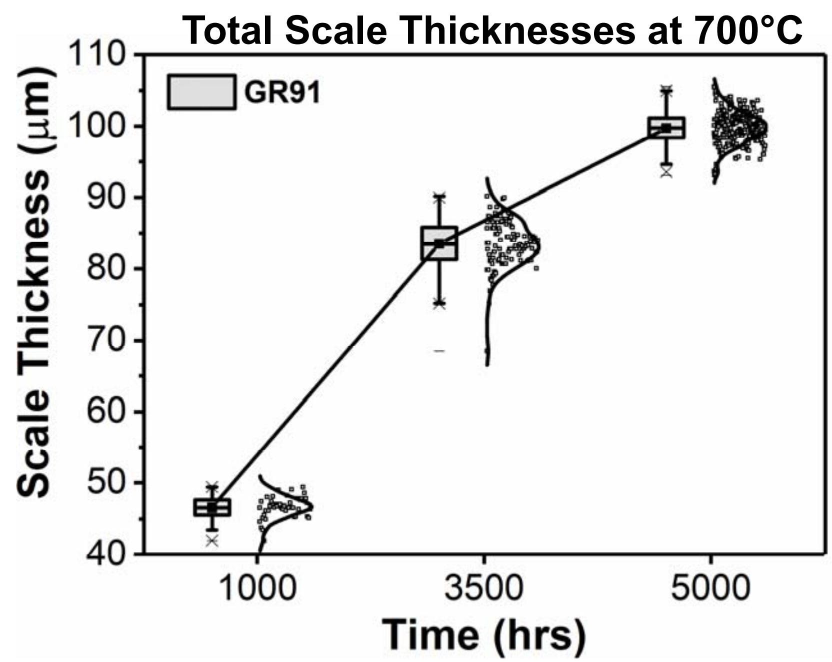
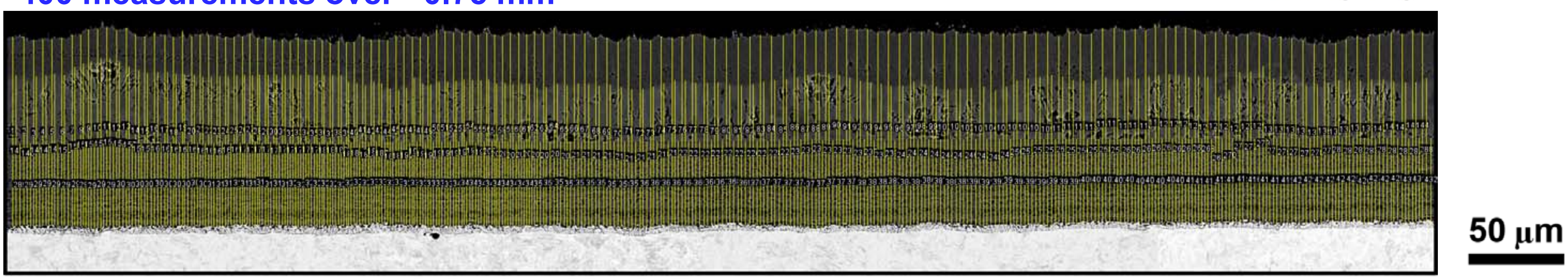
Variation in Thickness of Oxide Scale in Gr 91,

700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar

- Variation in thickness of oxide scale shown in box normal plots
- Total scale thicknesses shown for simplicity
- Individual oxide layers were identified, and their thicknesses also measured



400 measurements over ~0.75 mm



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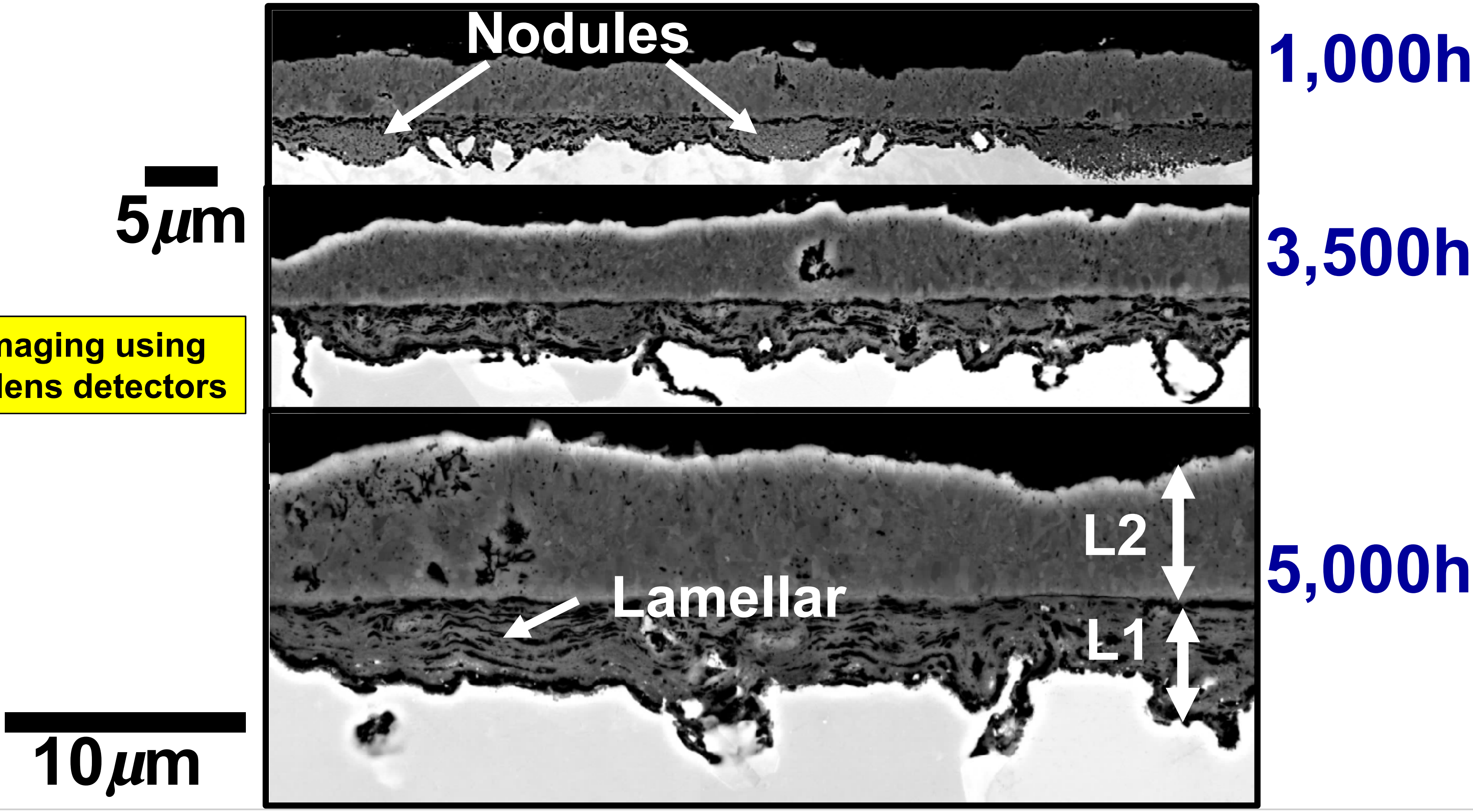
Morphology of 304H Oxide Scale

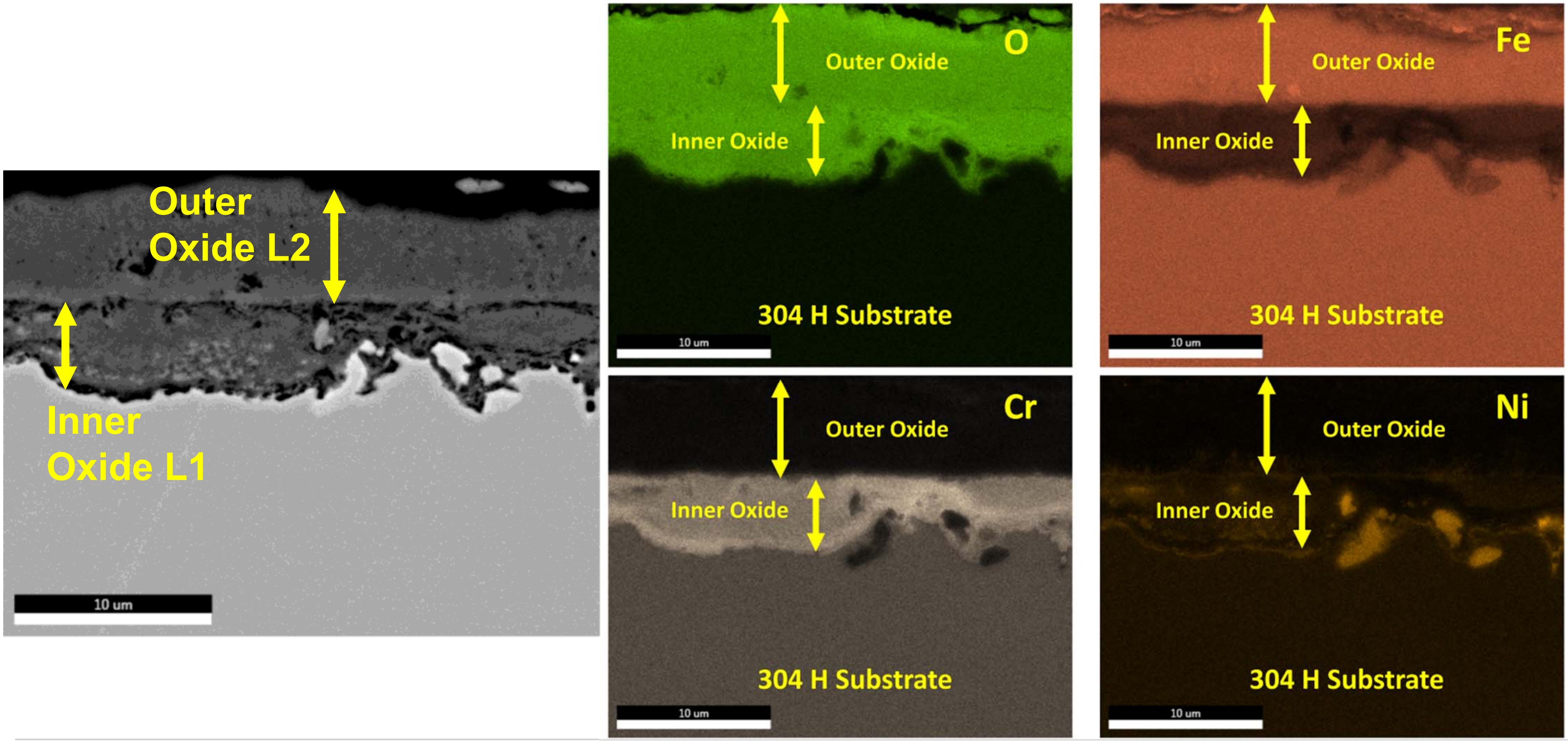
700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar



Imaging using in-lens detectors

Distribution of Alloying Elements at 304H Oxide Scale

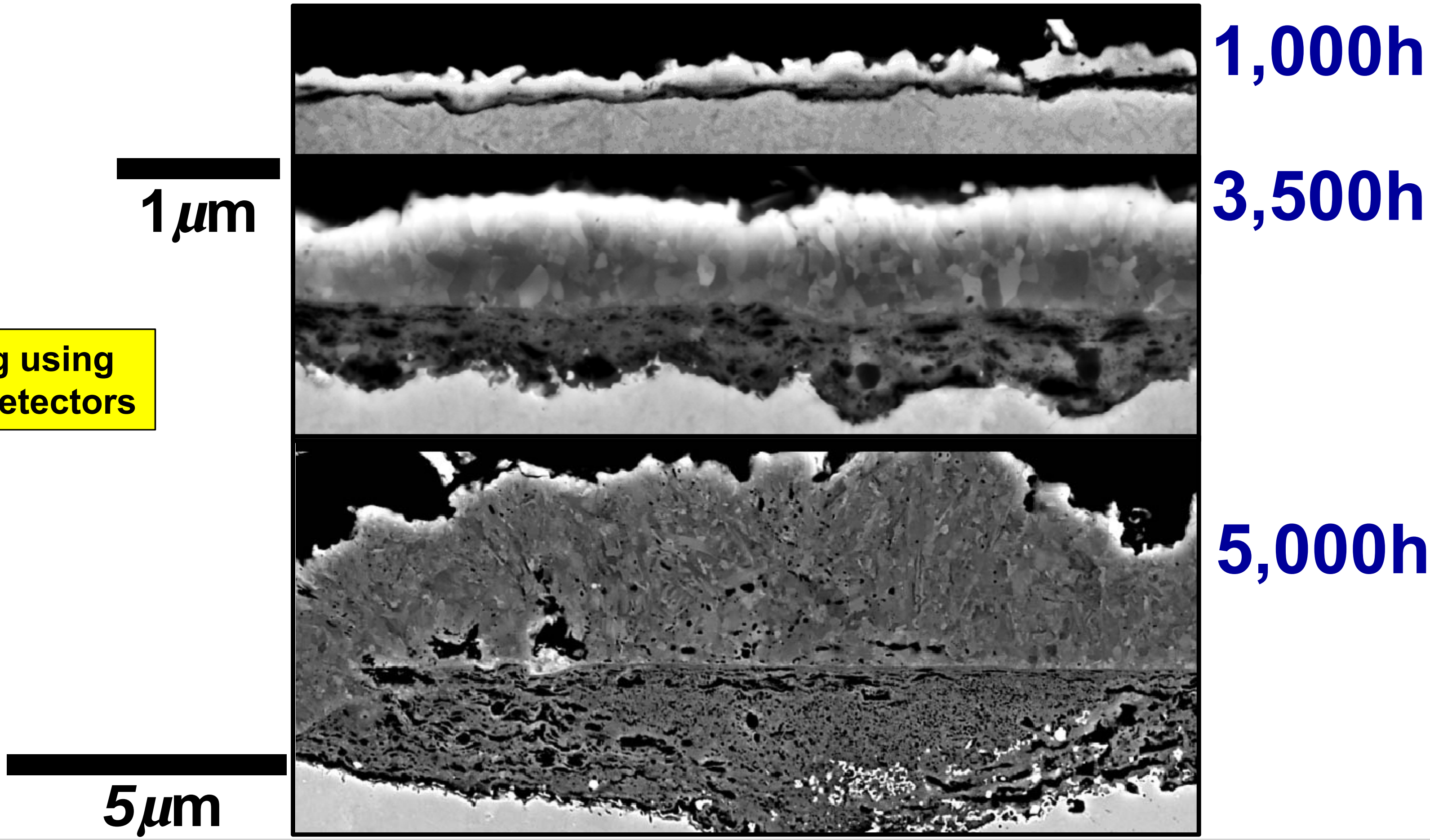
700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar



Morphology of 347H Oxide Scale

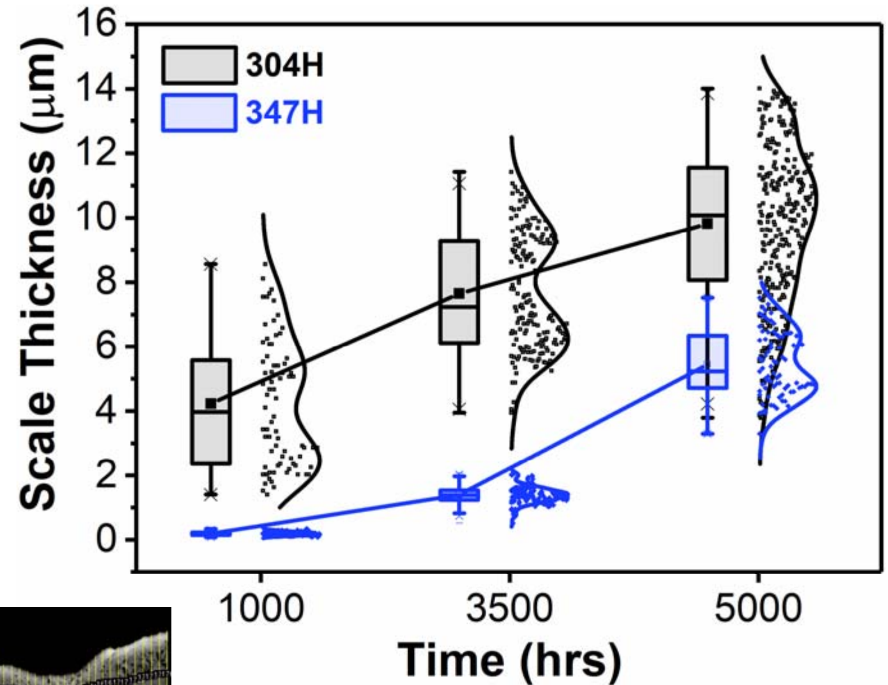
700°C in sCO_2-3.6% O_2-5.3% H_2O at 200 bar

Imaging using in-lens detectors

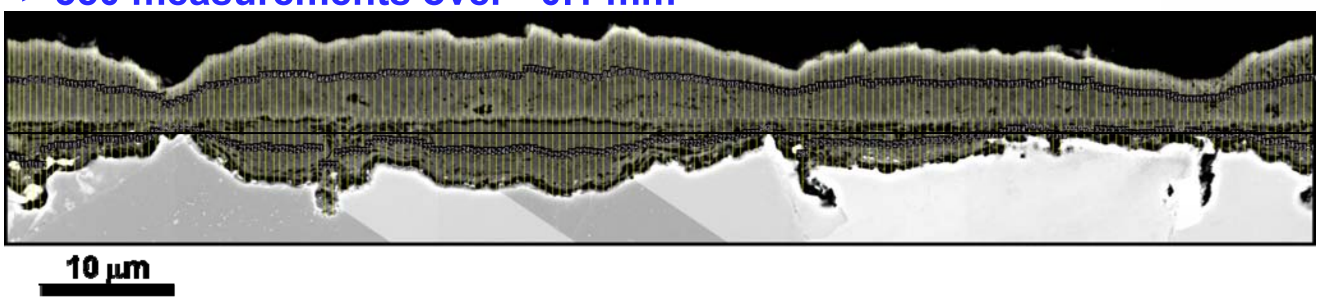


Comparison of 304H and 347H Oxide Scale Growth

- 347H exhibits relatively thin oxide layer after 1000 hrs. and 3500 hrs.
- Although less than thickness of 304H oxide, rapid change in scale thickness noted after 3500 hrs.
- Bimodal distribution due to non-uniform thickness of inner layer (L1)



> 350 measurements over ~0.1 mm



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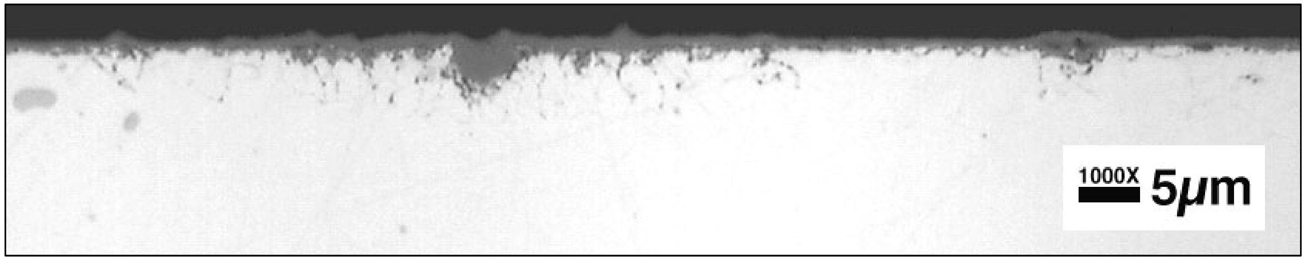
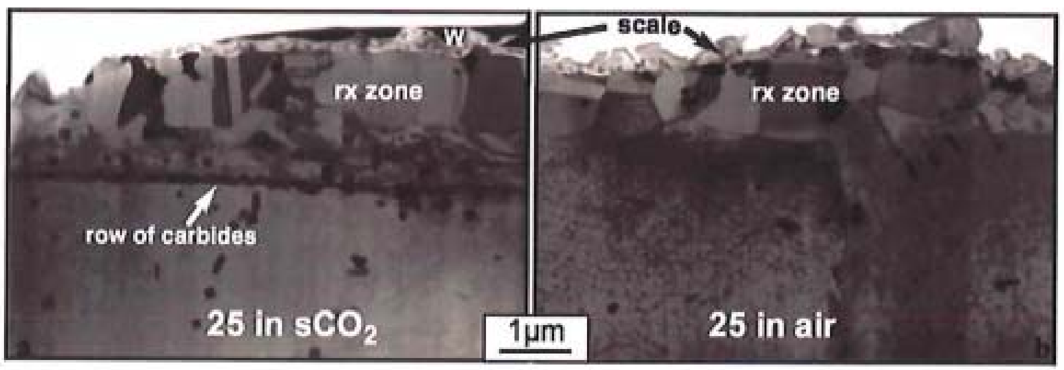
Thin Scales on HT Alloys Complicate Thickness Measurements

- Max power of optical microscopy produces marginal resolution



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

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



B. A. Pint *et al.* (2017)

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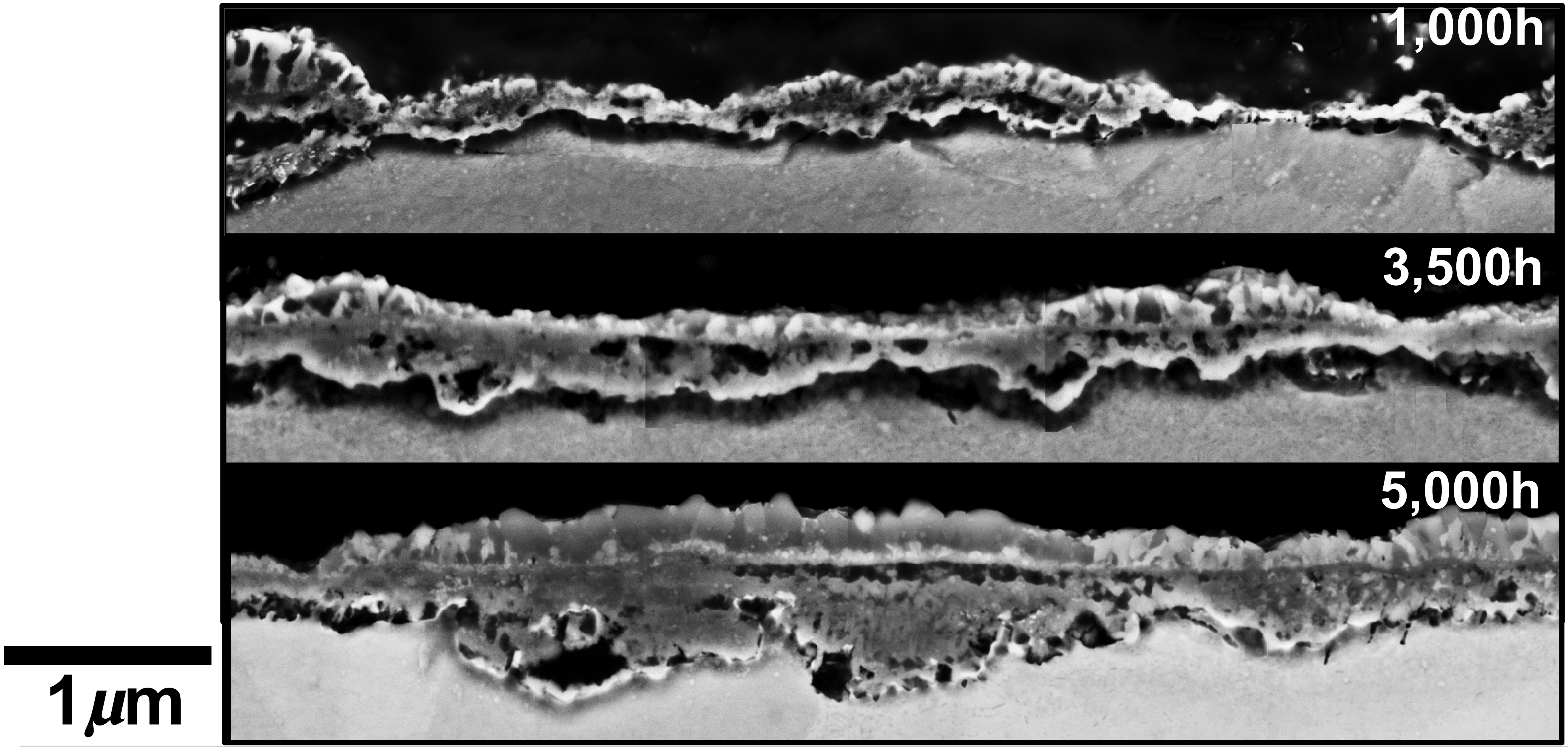
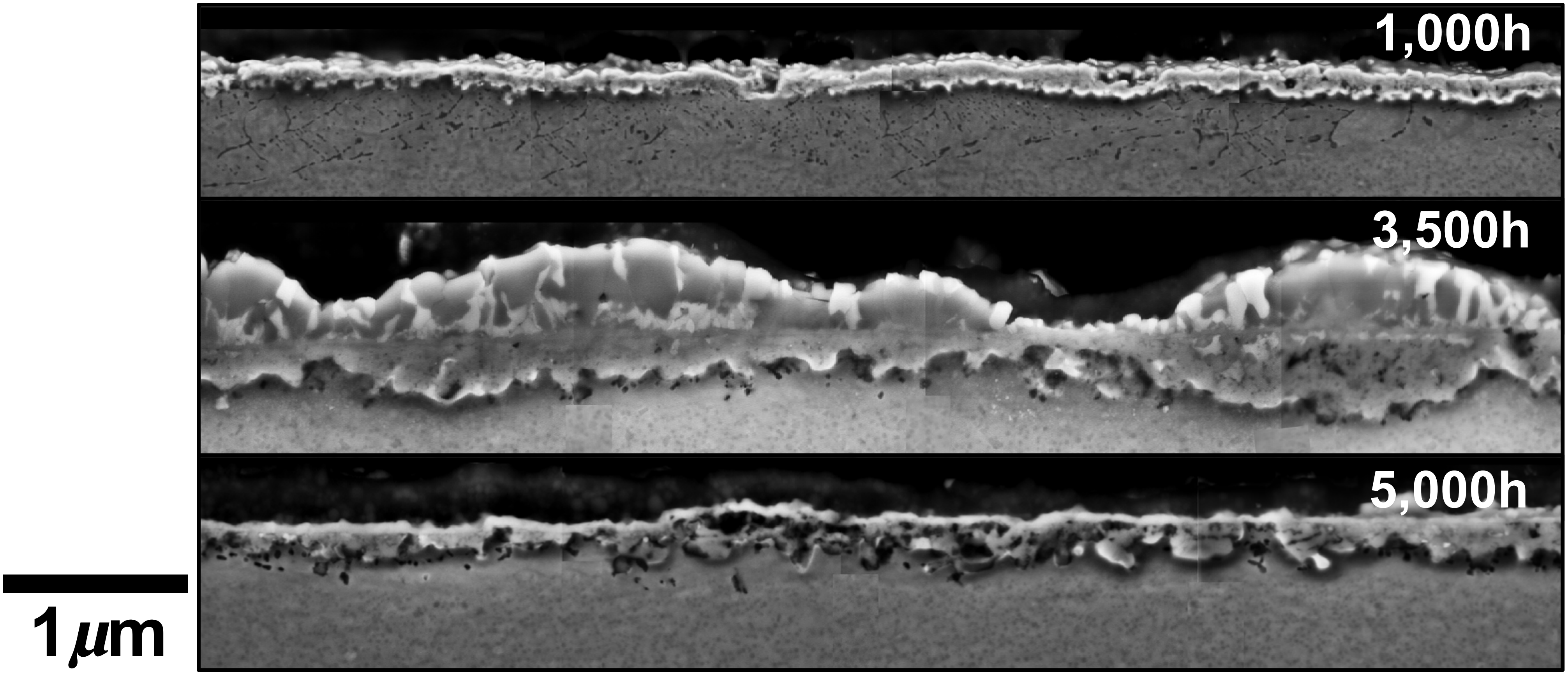
Morphology of IN617 Oxide Scale

700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar



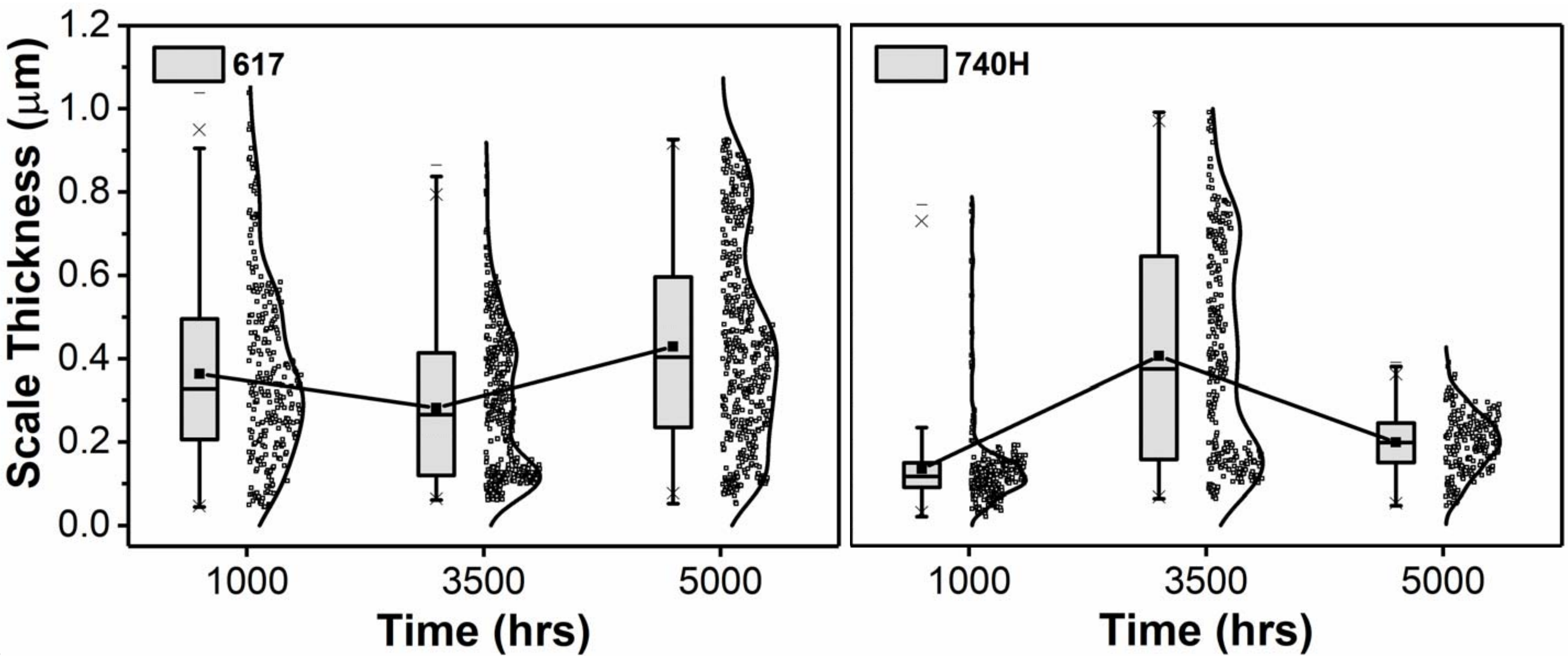
Morphology of IN740H Oxide Scale

700°C in sCO_2 -3.6% O_2-5.3% H_2O at 200 bar



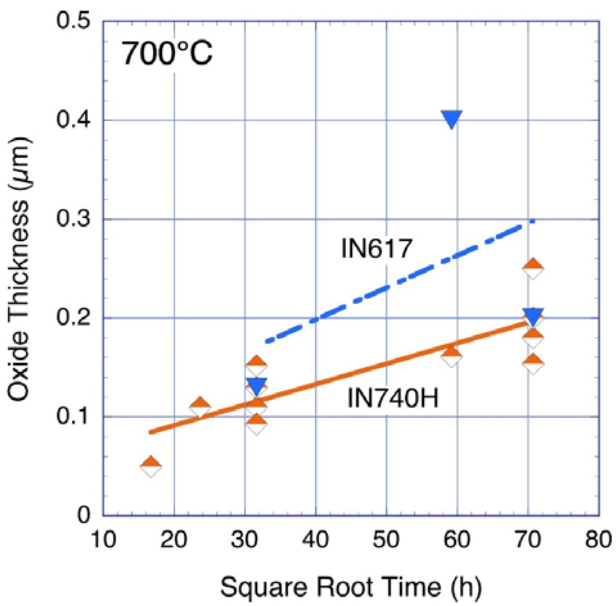
Comparison of IN617 and IN740H Oxide Scale Growth

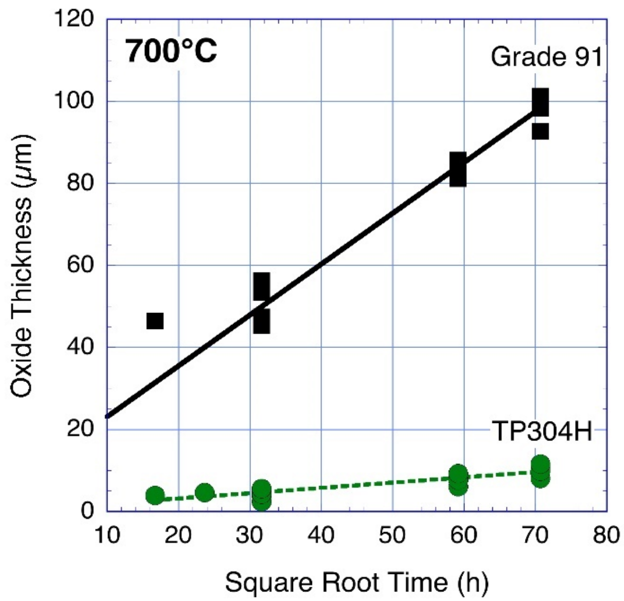
- Both alloys exhibited non-uniform oxide scales
- Significant variation in scale thickness in 617 after all three test durations



Measurement of Scale Thicknesses of HT Alloys:

- Quality of data for IN740H ≈ matches those for ferritic and austenitic steels
- k_p value for IN740H at 700°C appears reasonable
- BUT, results at 700°C only: insufficient to determine Arrhenius Constants





Alloy	k_p (µm²/h)	R^2
Gr91	6.3×10^{-1}	0.96
TP304H	6.7×10^{-3}	0.71
IN740H	2.2×10^{-6}	0.71

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Summary – Characterization Results

- Grade 91 displayed uniform three-layered oxide scale, with a lamellar inner oxide layer similar to scales in high-pressure steam
- Austenitic stainless steel alloys displayed duplex oxide scale structure
  - inner oxide was non-uniform with irregular lamellar structure,
  - outer oxide was uniform with columnar grains.
- Rate of oxide growth on TP347H was markedly lower than TP304H for similar exposure duration and conditions.
- Scales formed on the two nickel based alloys (IN617 and IN740H) were less than 1µm at all tested durations
- Significant variation in measured thickness of the total oxide scale due to very thin nature and complex morphology of oxide scale formed on the four austenitic alloys.

Summary –Characterization Procedure

- Morphology and thickness of oxide scales was determined using a new-generation of high-resolution scanning electron microscope with in-lens and in-column detectors
- **Work highlights the advantage of such high-resolution electron microscopes over other imaging techniques such as STEM, in obtaining information from a larger field of view, while not compromising on image resolution**
- Oxide scale measurement techniques developed with an aim of capturing variability in the oxide scale thickness and morphology.

Acknowledgement

DOE
Funding# DE-FE0024120

Together…Shaping the Future of Electricity

Materials Related Challenges in sCO2 - HX Components

- Supercritical CO_2 based power cycles are an attractive for HR systems
- Material related challenges need to be addressed
  - 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.