FEAA150
Steamside Oxidation Issues in Current Coal-Fired Boilers

R. Pillai, B.A. Pint
R&D Staff, Corrosion Science and Technology
Oak Ridge National Laboratory, Oak Ridge, TN USA

NETL Program manager: Michael Fasouletos
Collaborators: EPRI

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

Research was sponsored by U.S. Department of Energy
Office of Fossil Energy

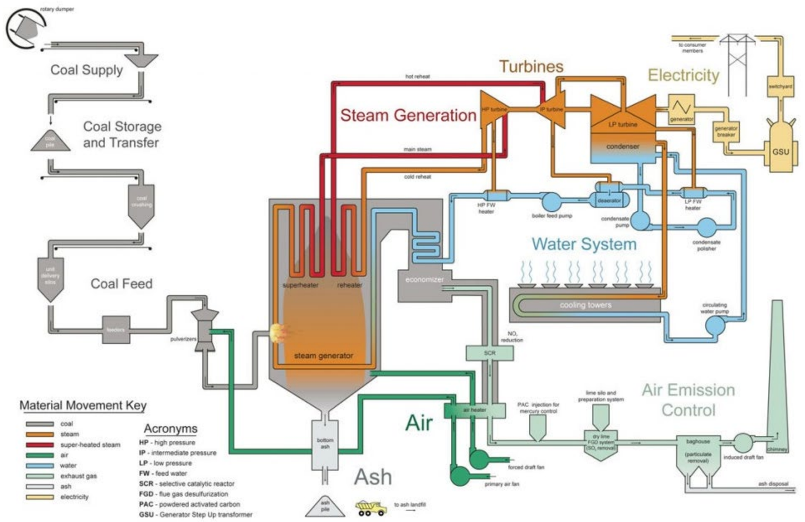
Acknowledgements

- DOE Office of Fossil Energy — Funding
- B. Johnston, M. Stephens, A. Willoughby — oxidation experiments
- T. Lowe — SEM, image analysis
- M. Gussev — Tensile testing in the SEM
- T. Watkins — Residual stress measurements
- V. Cox, T. Jordan — metallography
- S. Raiman — Design of water loop
- Materials — EPRI

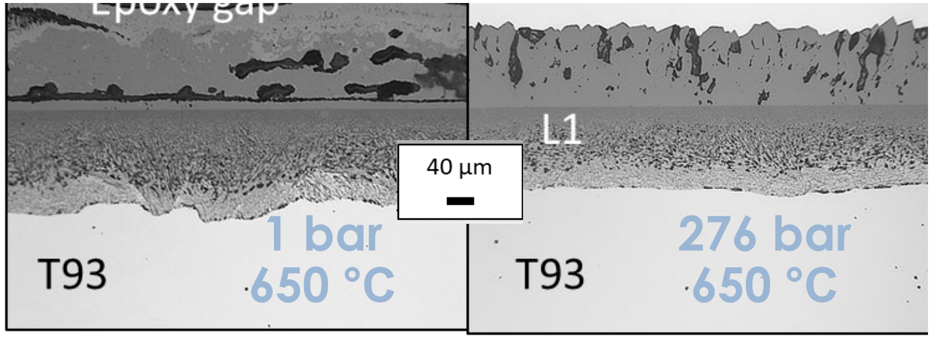
Disclaimer

- This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

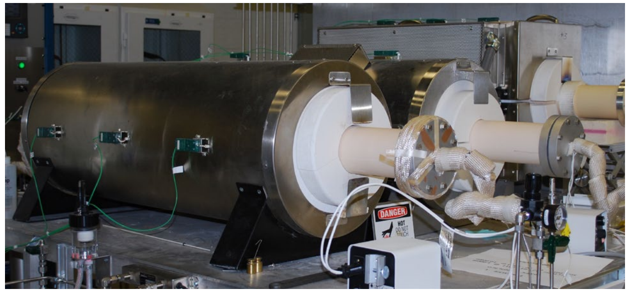
Need to test materials in realistic USC conditions motivated development of the water loop at ORNL



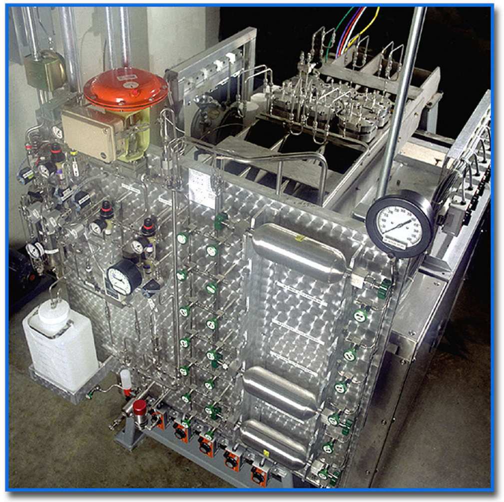
Clear impact of pressure

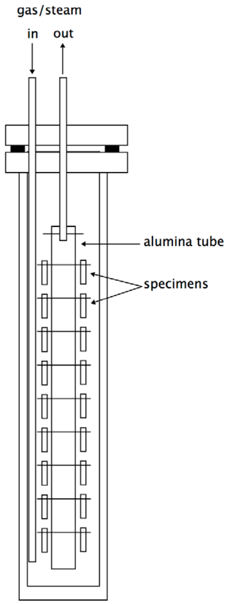


Tube furnace: 1 bar
500-h cycles



"Keiser" rig:
500-h cycles
1-43 bar





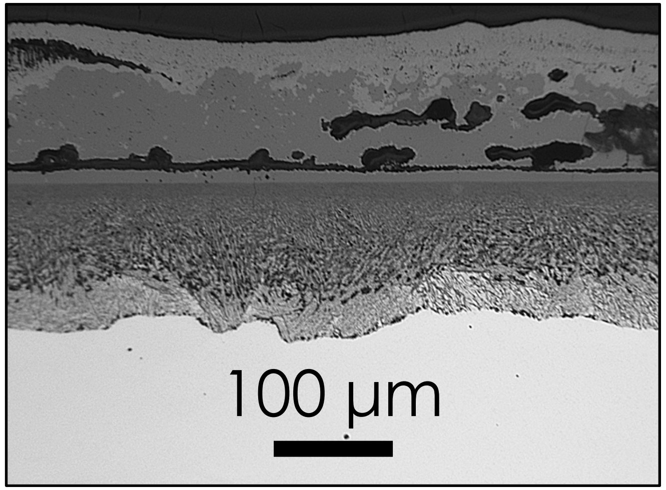
Water loop

Autoclave: 275 bar water
500-h cycles

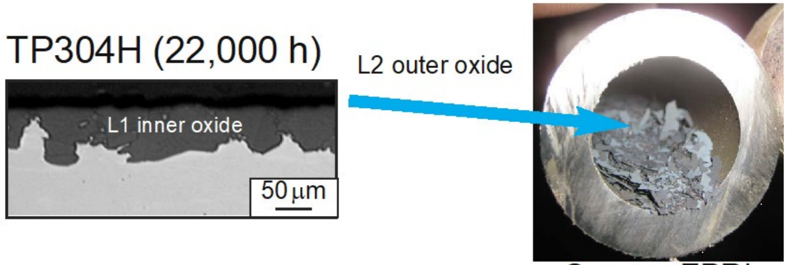
Controlled water chemistry
pH and O_2

What is the importance of steamside oxidation studies?

Thick Fe-rich (fast growing) scales



Spalled oxide scales cause pipe blockage



Source: EPRI

- **Oxide exfoliation is still a concern**
  - Pipe blockages
  - Downstream corrosion of steam turbines due to exfoliated scales
- Employing high Cr austenitic steels does not completely alleviate the problem (CTE mismatch)
- Need to understand role of film-forming products (oxygen scavengers) on oxide growth and adhesion
- Lack of predictive models that will incorporate important real-world parameters such as
  - water chemistry,
  - oxide growth and exfoliation and
  - quantitative description of oxide scale adhesion for current coal-fired boiler systems,

Open questions from previous project phase led to the current project

- Currently inconclusive impact of dissolved oxygen content on oxidation behavior
- Influence of film-forming products
- Scale spallation mechanisms
- Predictive capability (lifetime model)
- Role of coatings (chromizing) – collaboration with ATC-CES
  FEAA364: Presentation by Jeff Henry on June 15@10:50 in the Session: Materials Characterization, Modeling, Existing Fleet, and Alloy Development

Goals of FEAA150 (in cooperation with EPRI) started in Sept. 2019

Investigated materials (in wt.% except C and N in ppmw)

Alloy	Fe	Cr	Ni	Mo	W	Mn	Si	Cu	C	N
G91	88.8	**8.6**	0.3	0.9	-	0.5	0.35	0.1	990	450
G93	83.7	**8.9**	0.1	0.04	3.1	0.5	0.23	0.02	920	100
THOR	87.6	**10.7**	0.1	0.5	-	0.4	0.18	0.04	980	420
VM12	83.3	**11.5**	0.4	0.4	1.6	0.4	0.42	0.08	1200	360
304H	70.4	**18.4**	8.4	0.3	-	1.6	0.26	0.4	600	660
S304H	68.0	**19.0**	8.9	0.1	0.02	0.4	0.13	2.9	760	1090
347HFG	66.0	**18.6**	11.8	0.2	0.02	1.5	0.39	0.17	910	550
HR3C	51.0	**25.7**	20.4	0.07	0.01	1.2	0.36	0.07	650	2530

Temperature: 550, 650 °C

Pressure: 276 bar

Atmosphere: 100% steam

Treatment:
OT (100ppb O_2), AVT (<10 ppb O_2)

Additions:
Ammonia, Hydrazine, film forming products (amines)

Time: up to 1000h

Specimens:
20x12x1.5mm coupons, quarter tube specimens

- **Continue characterization efforts to evaluate role of water chemistry**
- **Evaluate the influence of film-forming products (amines) on the oxidation behavior**
- **Quantify adhesion of oxide scales**
  (a singular consistent and repeatable measurement method is missing in literature)
- **Evaluate role of surface modifications (e.g., coatings) in high-pressure steam oxidation tests**
- **Enhance the existing exfoliation model, previously developed (Sabau, Wright et al.), by incorporating quantified adhesion energies**

Combining experiments, advanced characterization and modeling to achieve project goals

Experiments

Water loop

Specimen holder in autoclave

- 275 bar water, 500-h cycles, 550-650°C
- Ferritic-martensitic and austenitic steels
- Controlled water chemistry: OT (100ppb O2), AVT (<10 ppb O2)
- Additions: Ammonia, Hydrazine, Film forming products

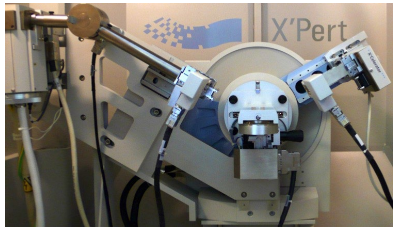
Characterization

Electron microscopy + Electron Backscatter diffraction

Tensile testing in Electron microscope

Raman spectroscopy

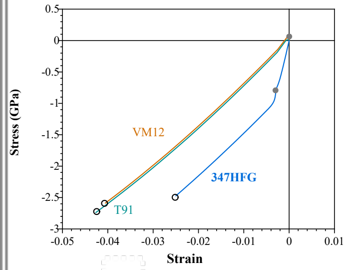
XRD

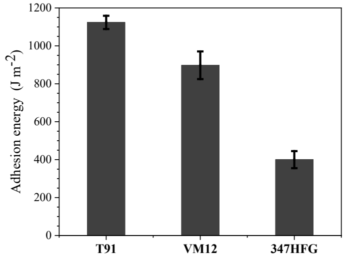


- Oxide scale composition
- Oxide scale morphology
- Residual stress measurement
- Oxide adhesion
- Compositional changes
- Phase transformations

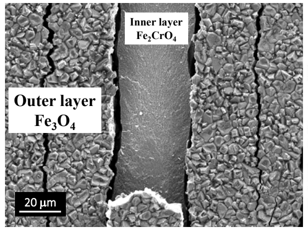
Physics-based modeling

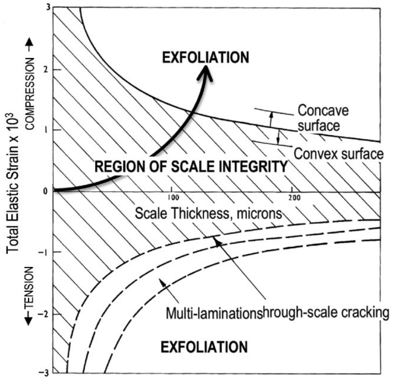
Calculate adhesion of oxide scales





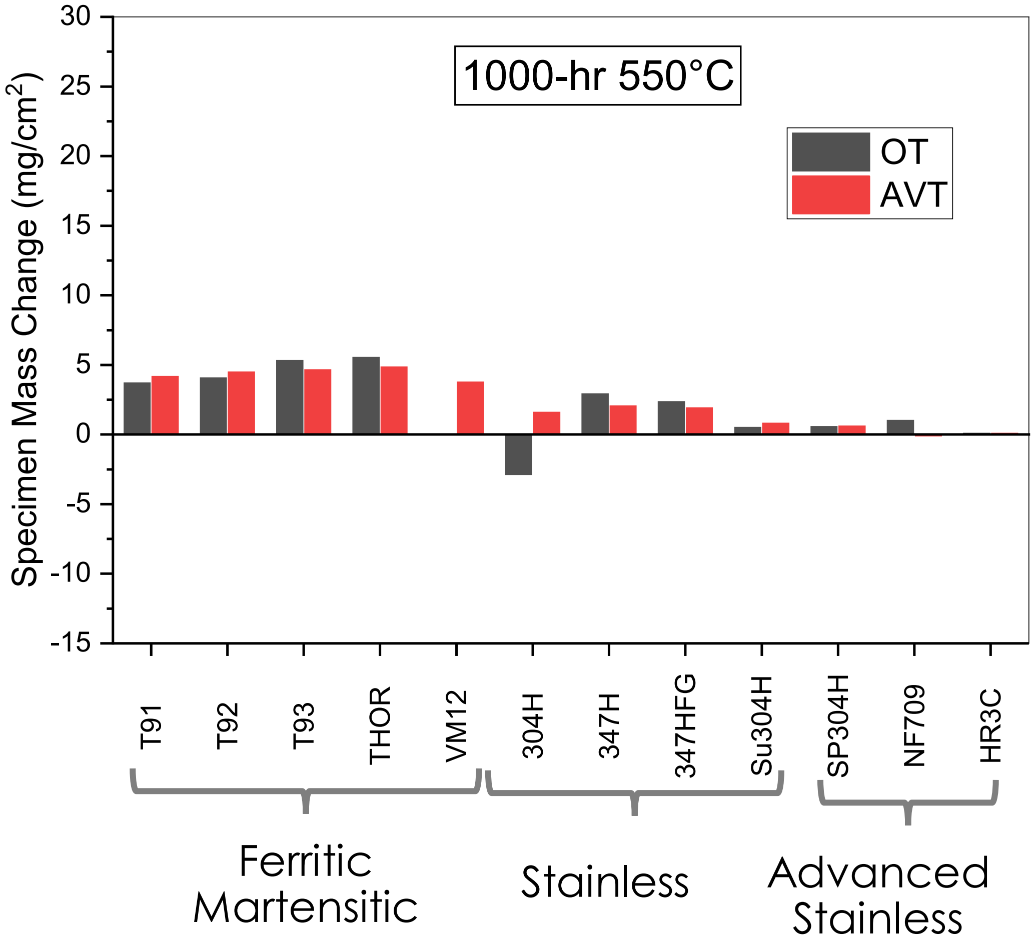
Predict integrity of external oxide scales

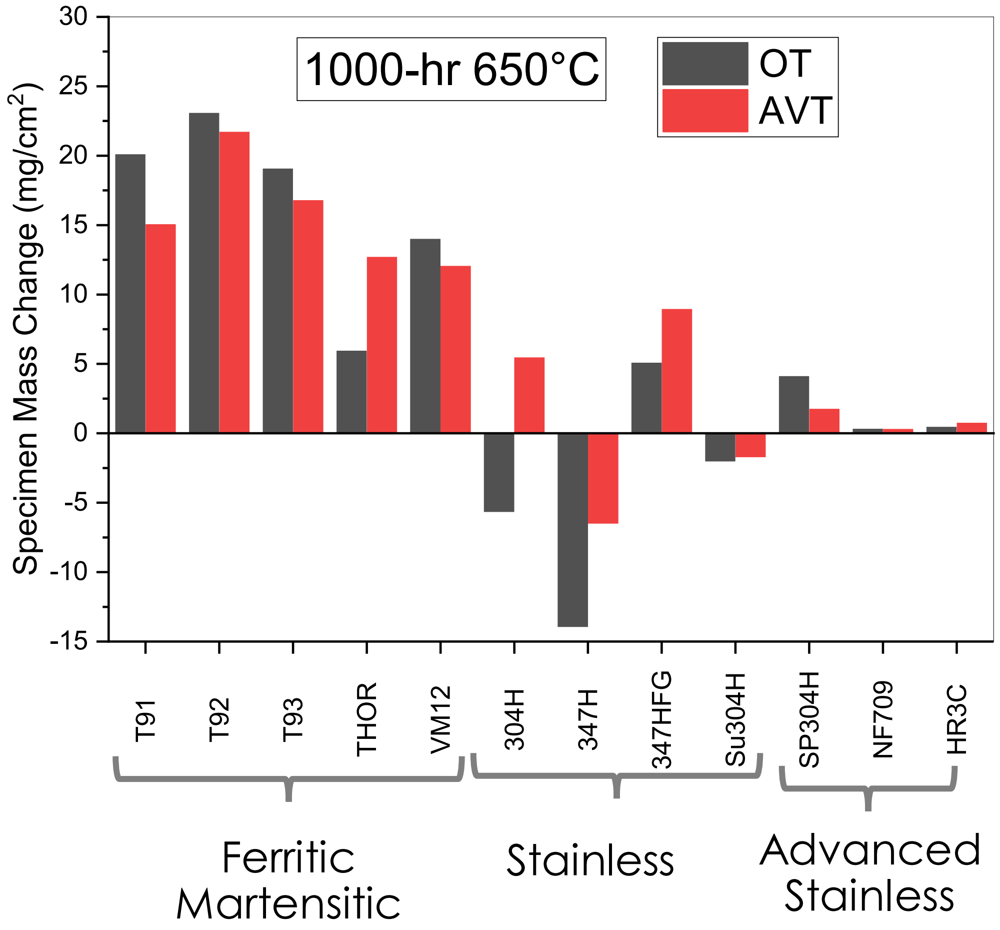




- Predict oxide spallation
- Integrate physics-based features
- Lifetime predictions (time to non-protective oxidation behavior)

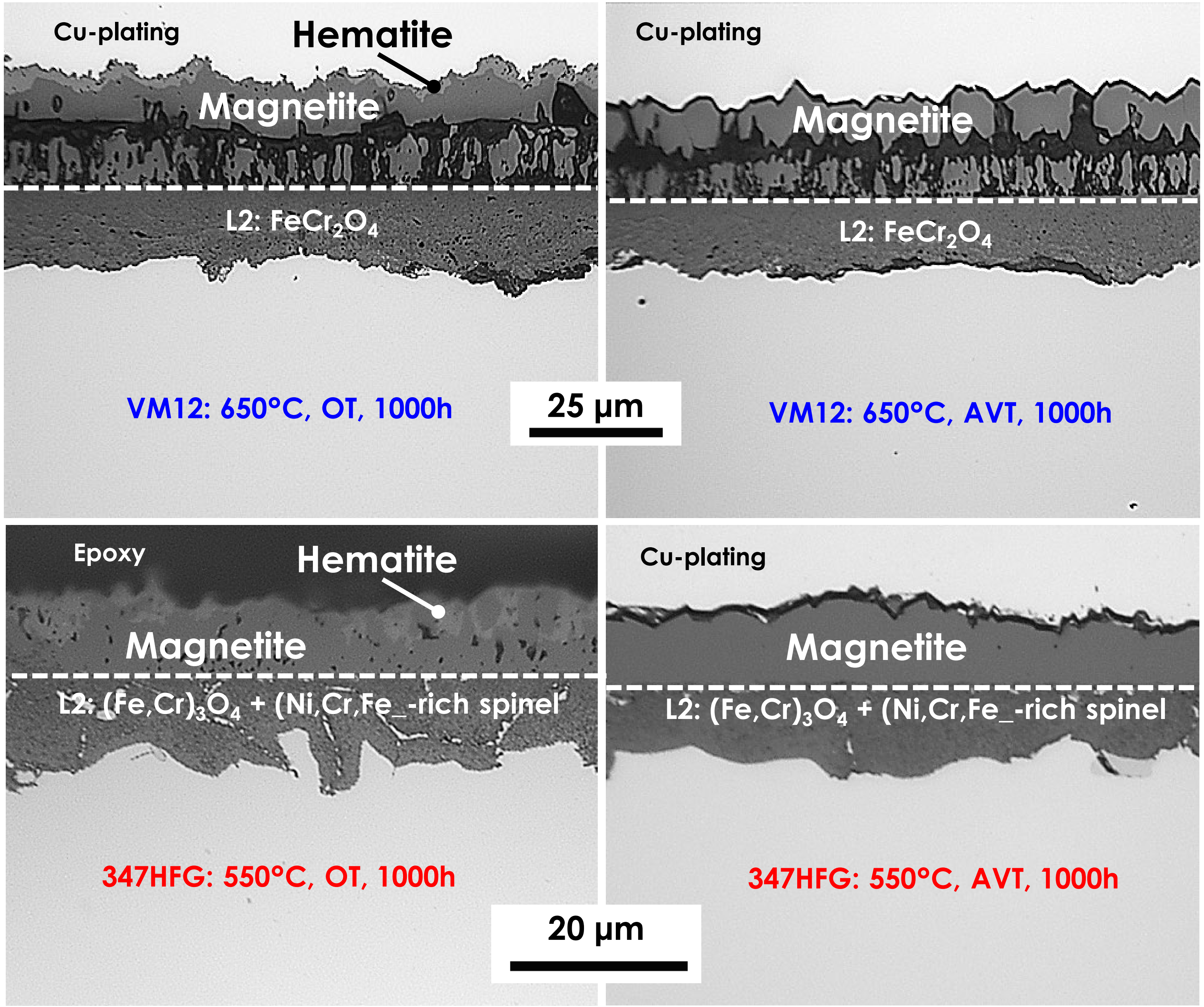
One of the goals of the previous project phase (ended 2019) was to evaluate the influence of water chemistry on steam oxidation behavior





- Clear difference going from low Cr to high Cr alloys
- Mass change shows no clear impact of dissolve oxygen contents OT (~100 ppb) and AVT (< 10 ppb)

A closer look did show differences of dissolved oxygen contents

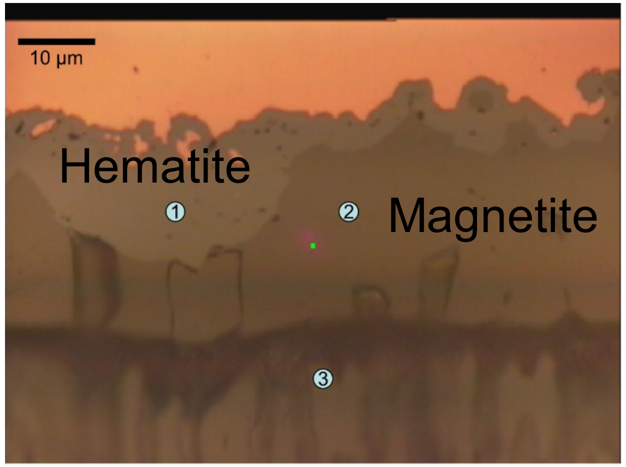


- Outer oxide layer composed of hematite (Fe_2O_3) + magnetite (Fe_3O_4) under **OT conditions** for both **VM12** (**650°C, 1000h**) and **347HFG (550°C, 1000h)**

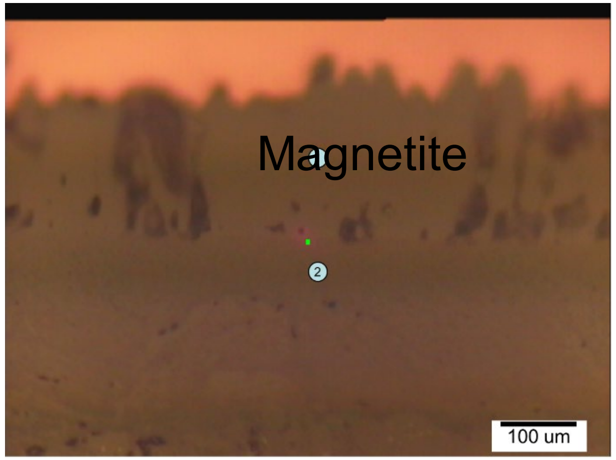
Detailed characterization (Raman spectroscopy) was performed to further confirm the presence of hematite at the steam\oxide interface

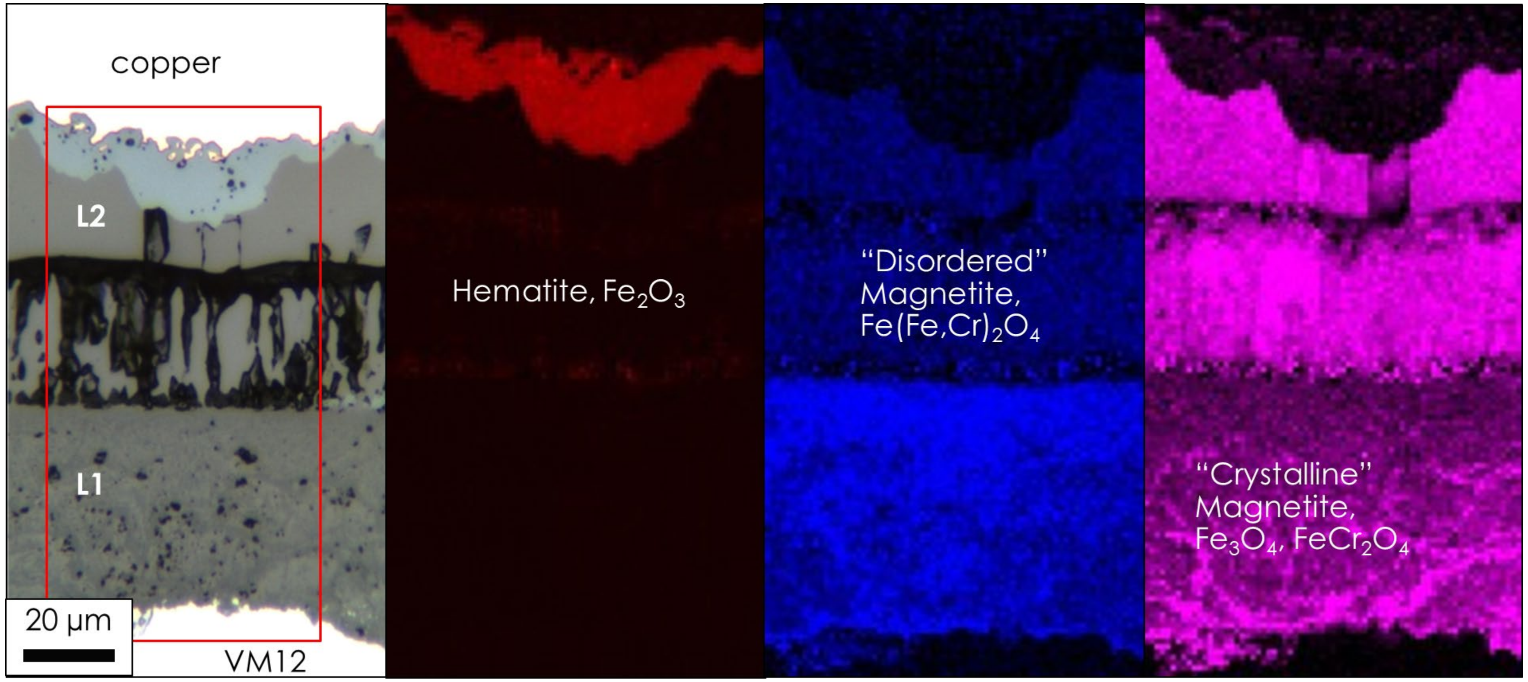
VM12 1000-hr, 650°C, 276 bar

OT



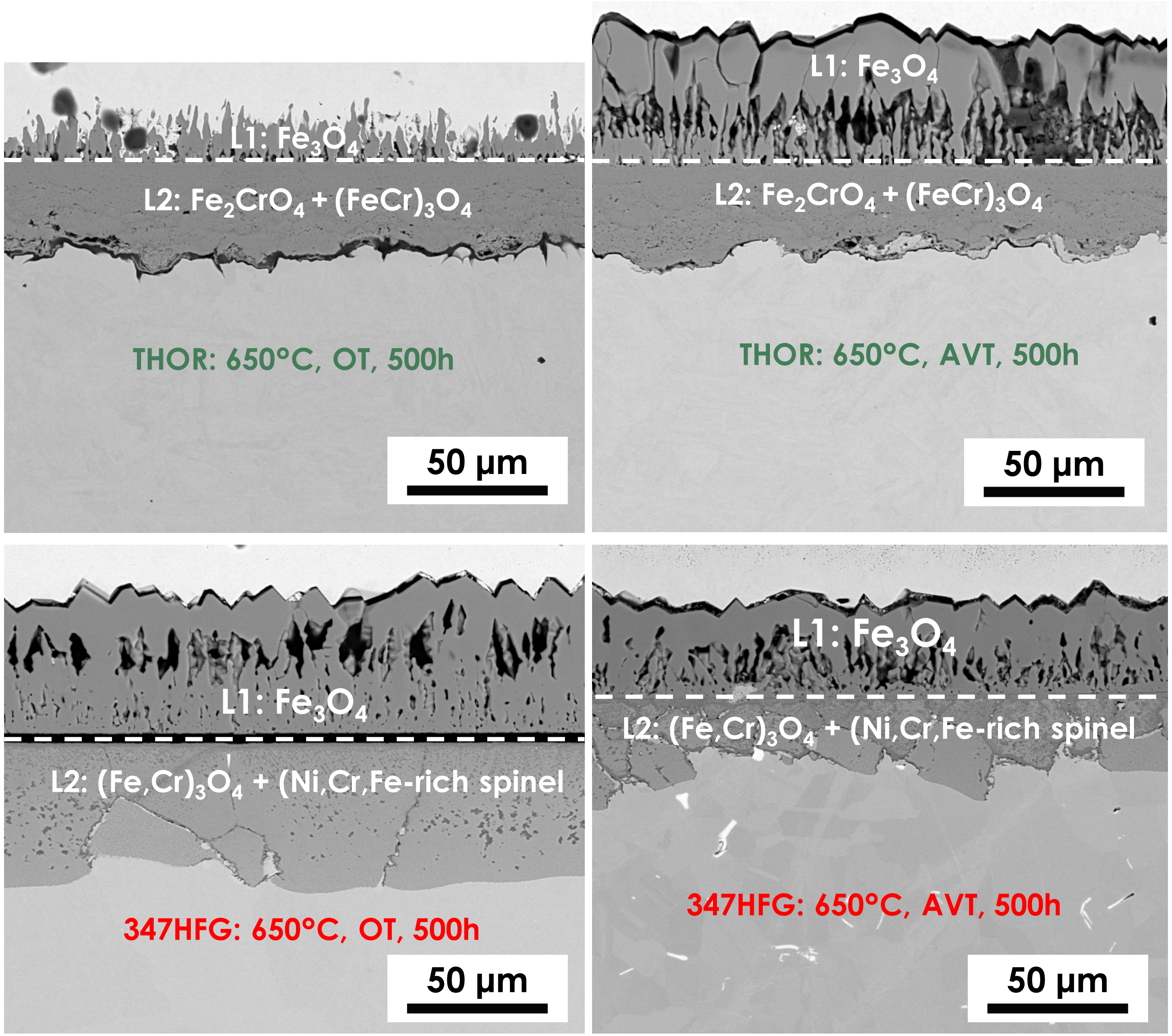
AVT





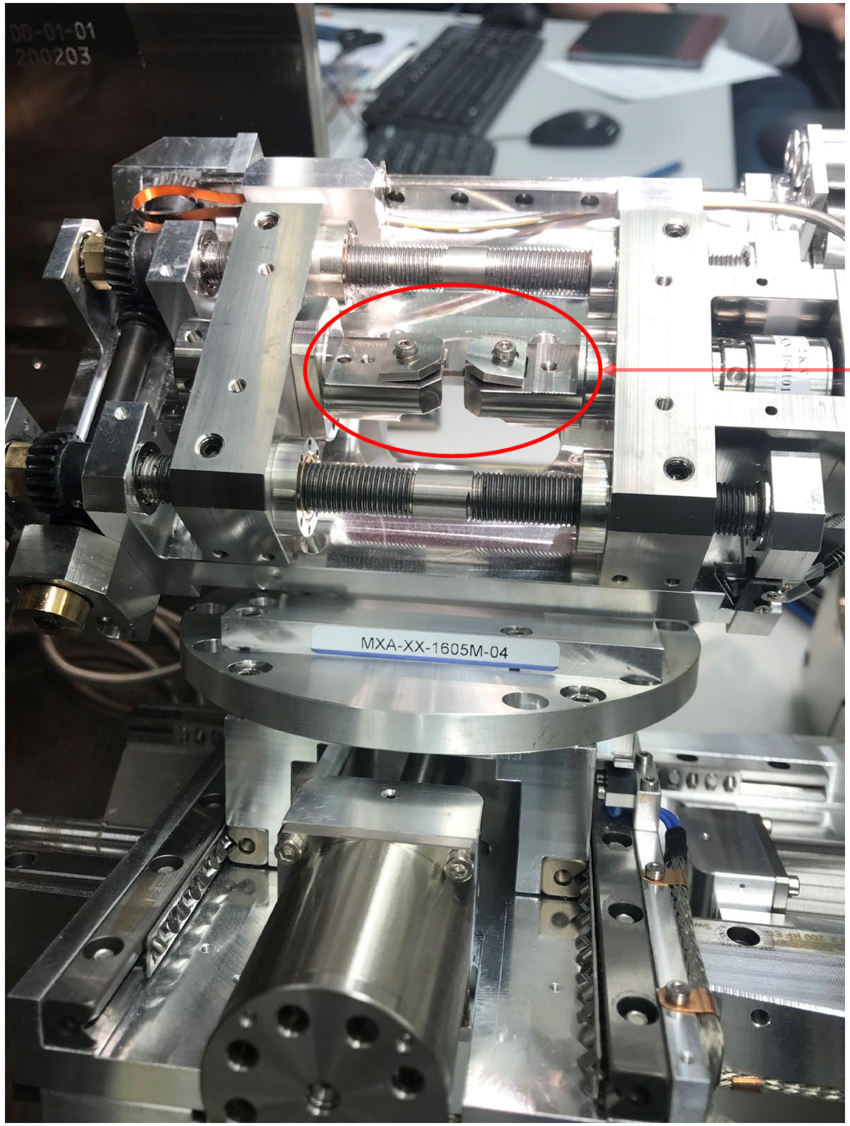
- Raman map of the OT samples shows layer of hematite at surface only
- Outer layer: Disordered magnetite
- Inner layer: Crystalline magnetite + $FeCr_2O_4$

Better adherence of oxide scales in some cases under AVT conditions at 650°C



- Outer oxide scales spalled under **OT conditions** for both **THOR** and **347HFG** after **1000h at 650°C**

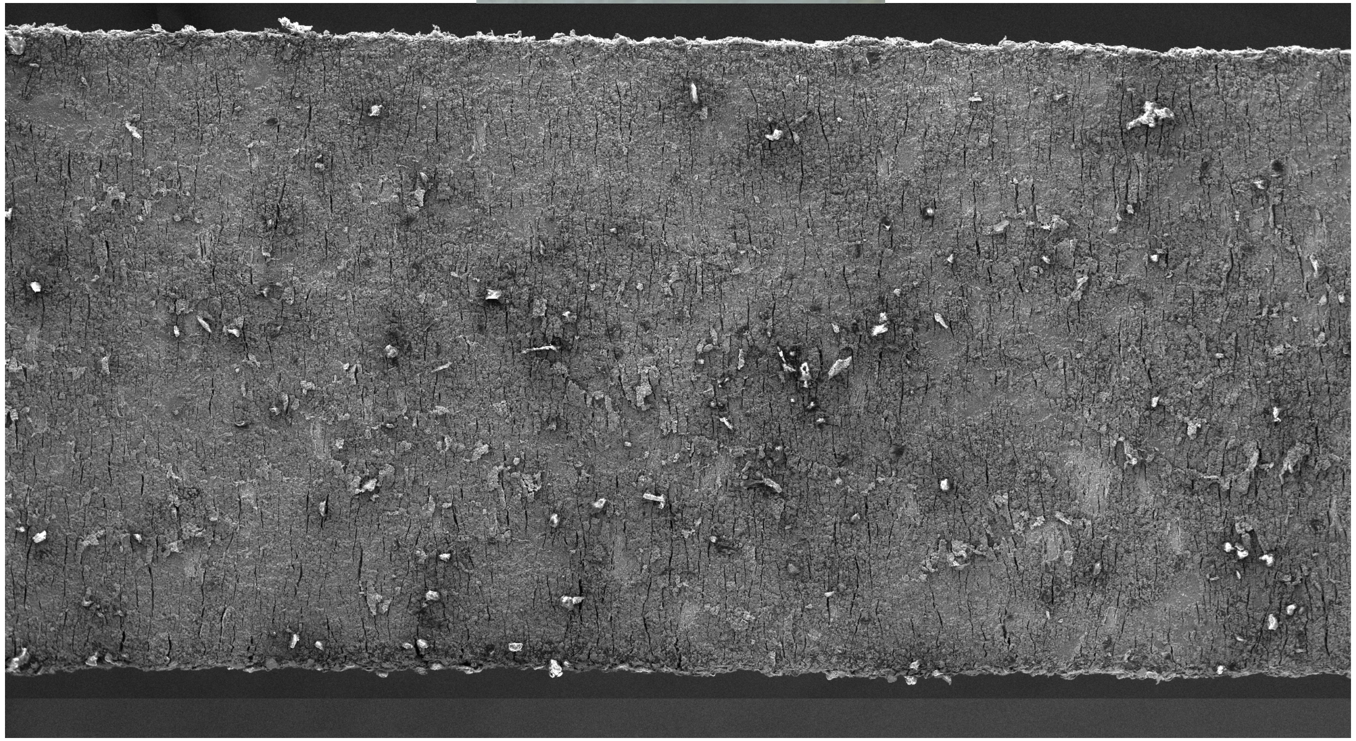
Identified reliable method to quantify oxide adhesion strength of oxide scales grown in steam on ferritic-martensitic and austenitic steels



- Oxidized sample is cut to specific shape
- Sample is placed in tensile frame
- Tensile frame put in SEM chamber
- Load is applied in steps
- Imaging done at each step
- Key points are initial cracking and spallation

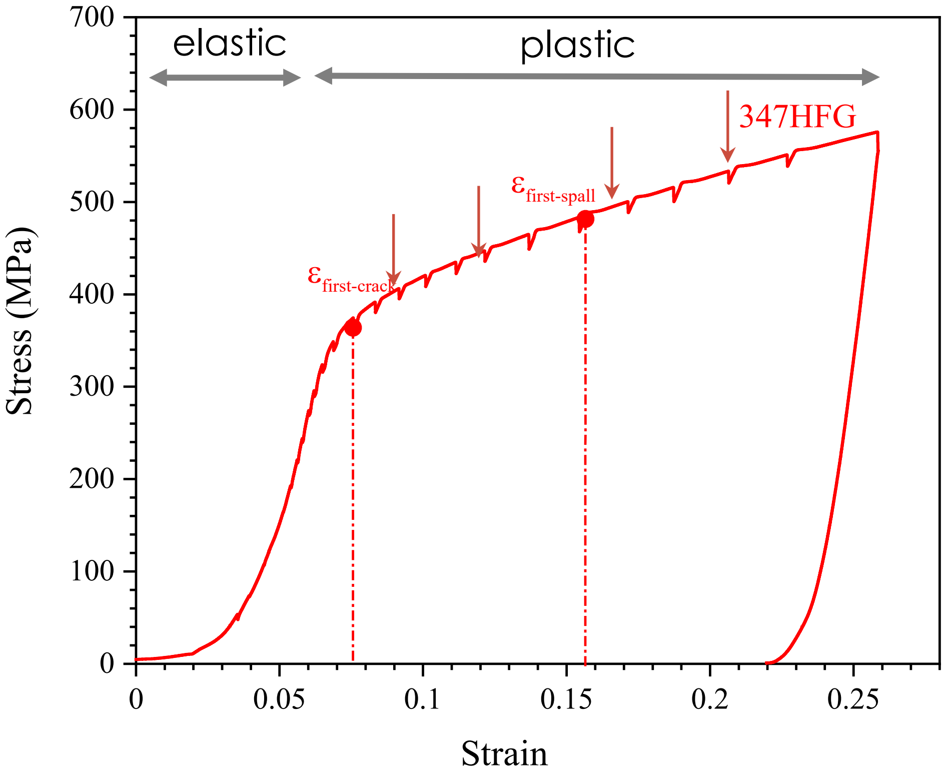
Pillai et al., Mat. & Corr., 2021

Time evolution behavior of specimen surface with increasing strain



500 μm

Measured stress strain in the alloy

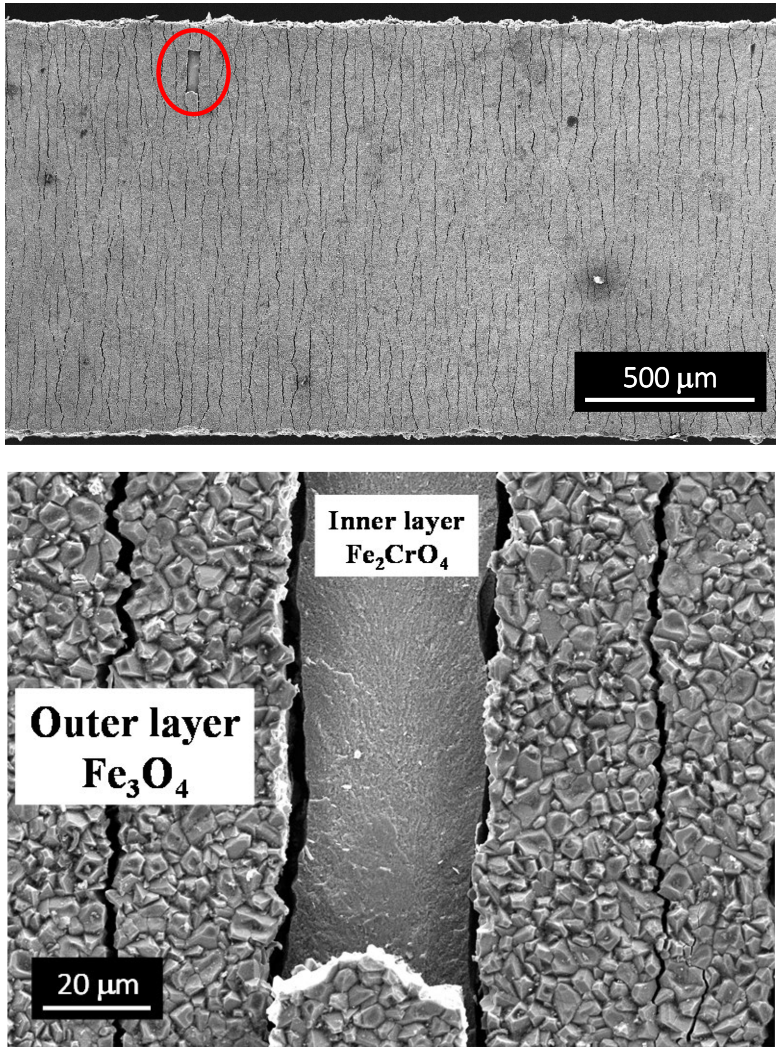


347HFG 550°C, 1000h, OT, 276 bar

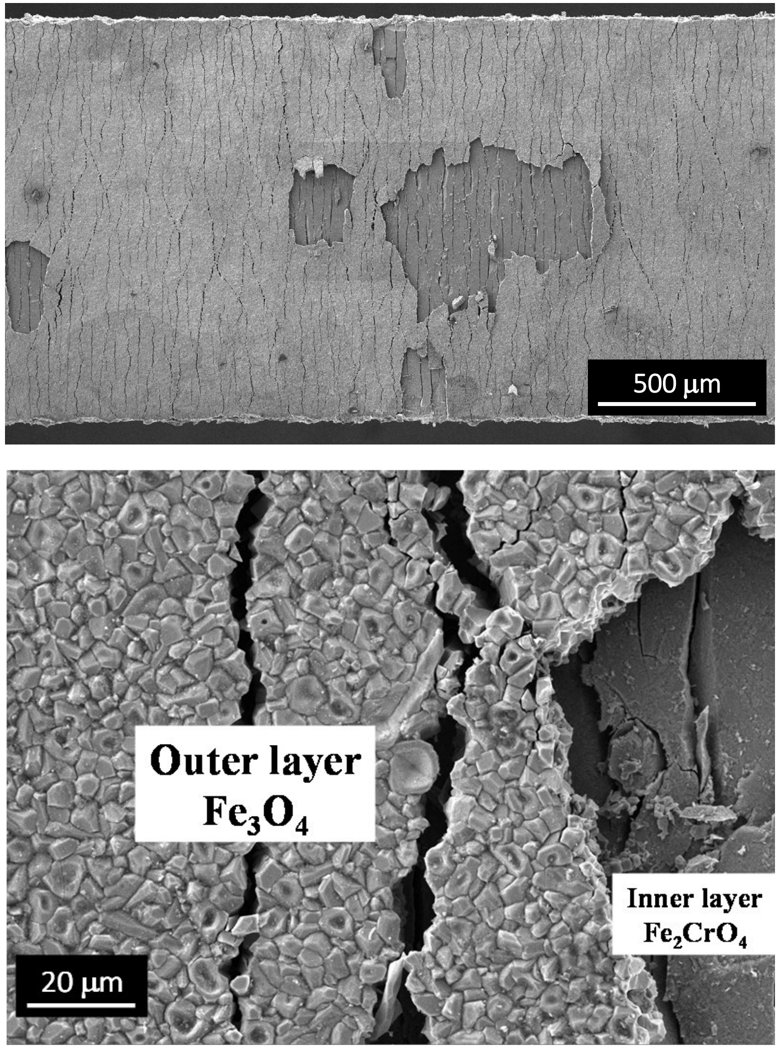
- Images recorded at chosen loading intervals
- EDS elemental mapping performed at cracking and spallation events

Oxide failure location for all alloys at the inner/outer oxide interface after 1000h at 550°C in 276 bar OT (~ 100 ppb O_2) steam

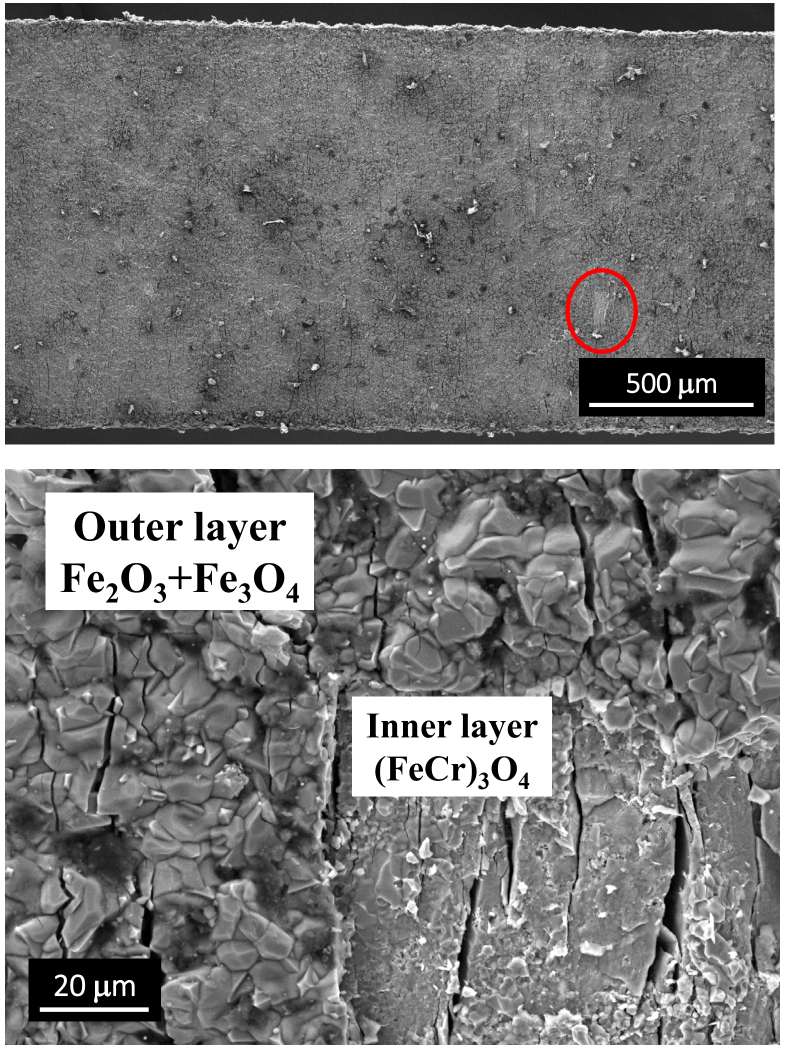
T91



VM12



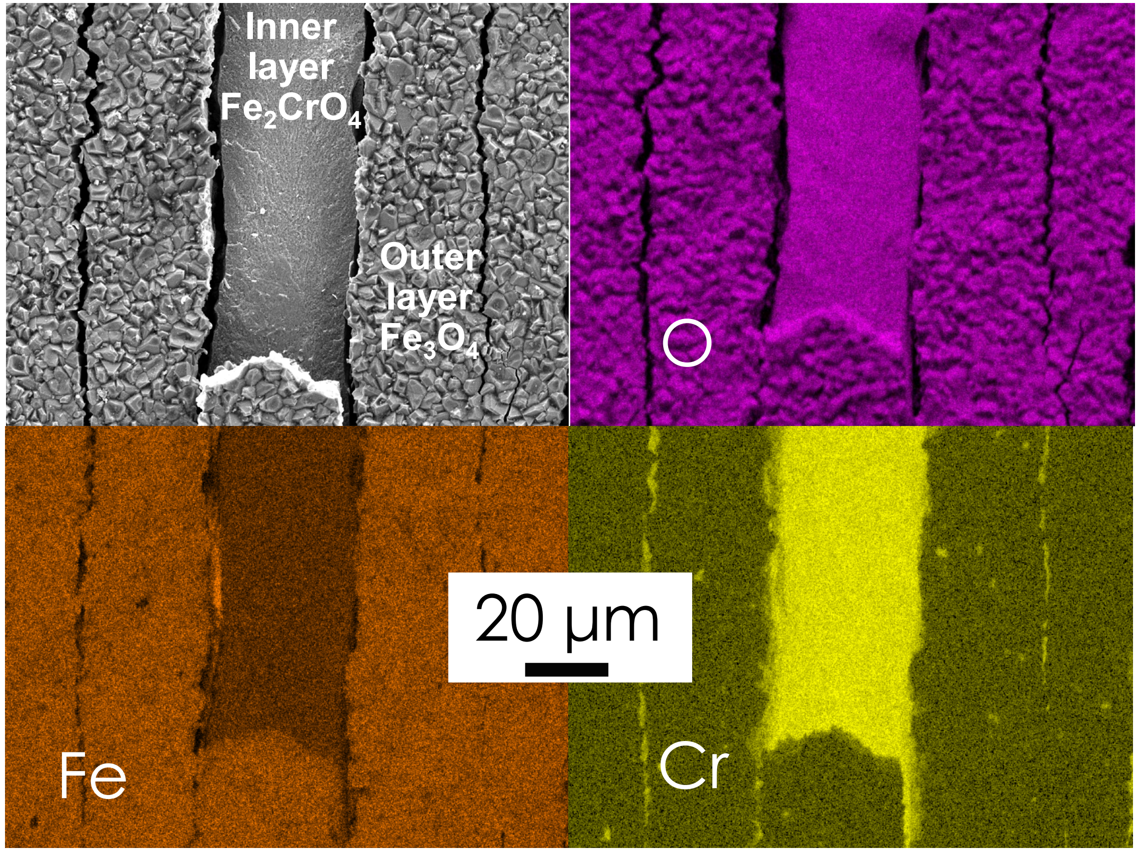
347HFG



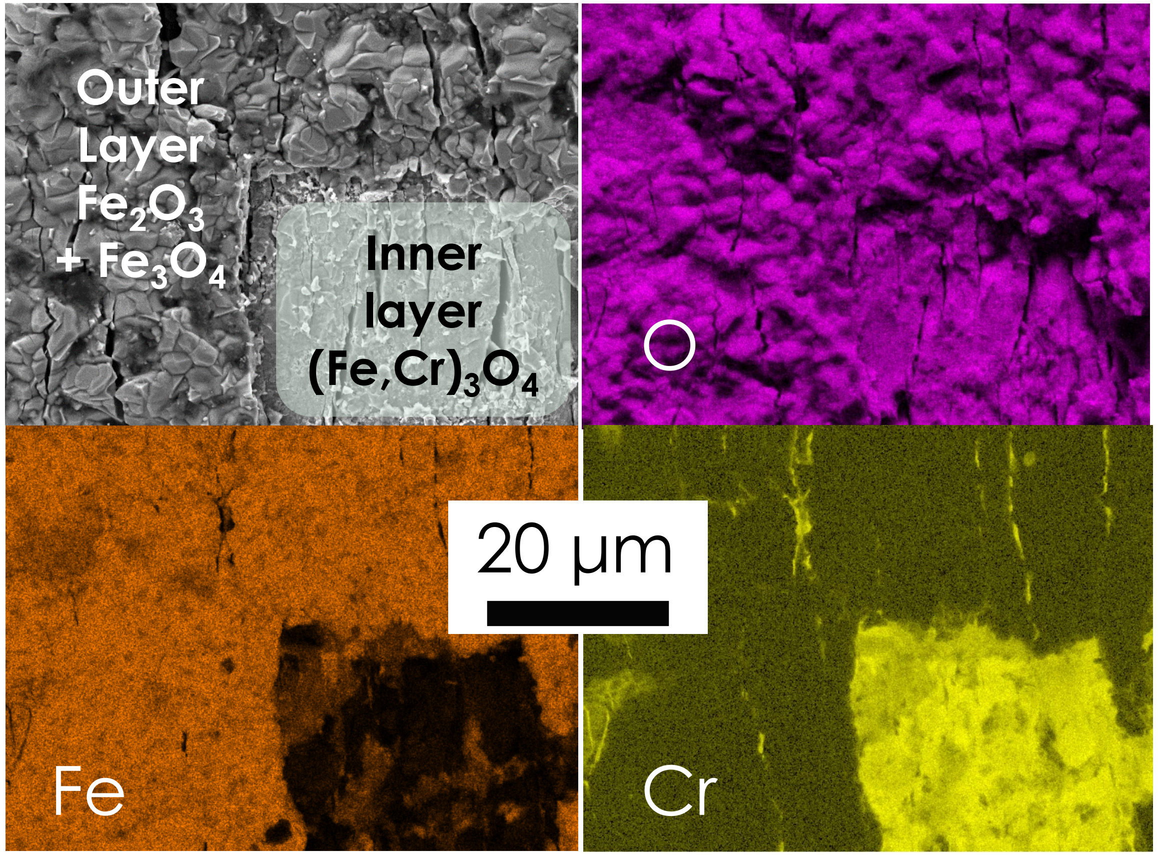
Pillai et al., Mat. & Corr., 2021

EDS elemental maps and oxide compositions measured at spalled locations further confirm failure location for all alloys at the inner/outer oxide interface after 1000h at 550°C in 276 bar OT (~ 100 ppb O_2) steam

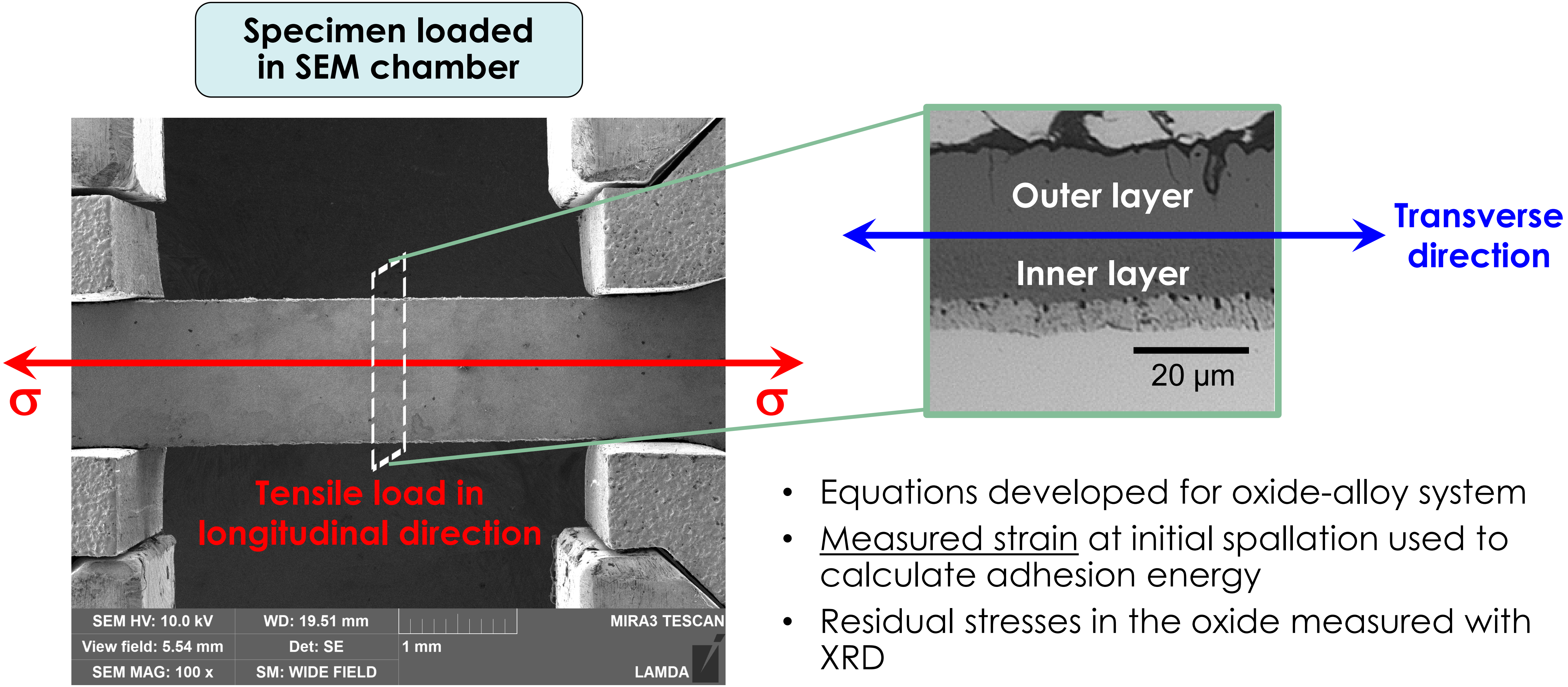
T91



347HFG



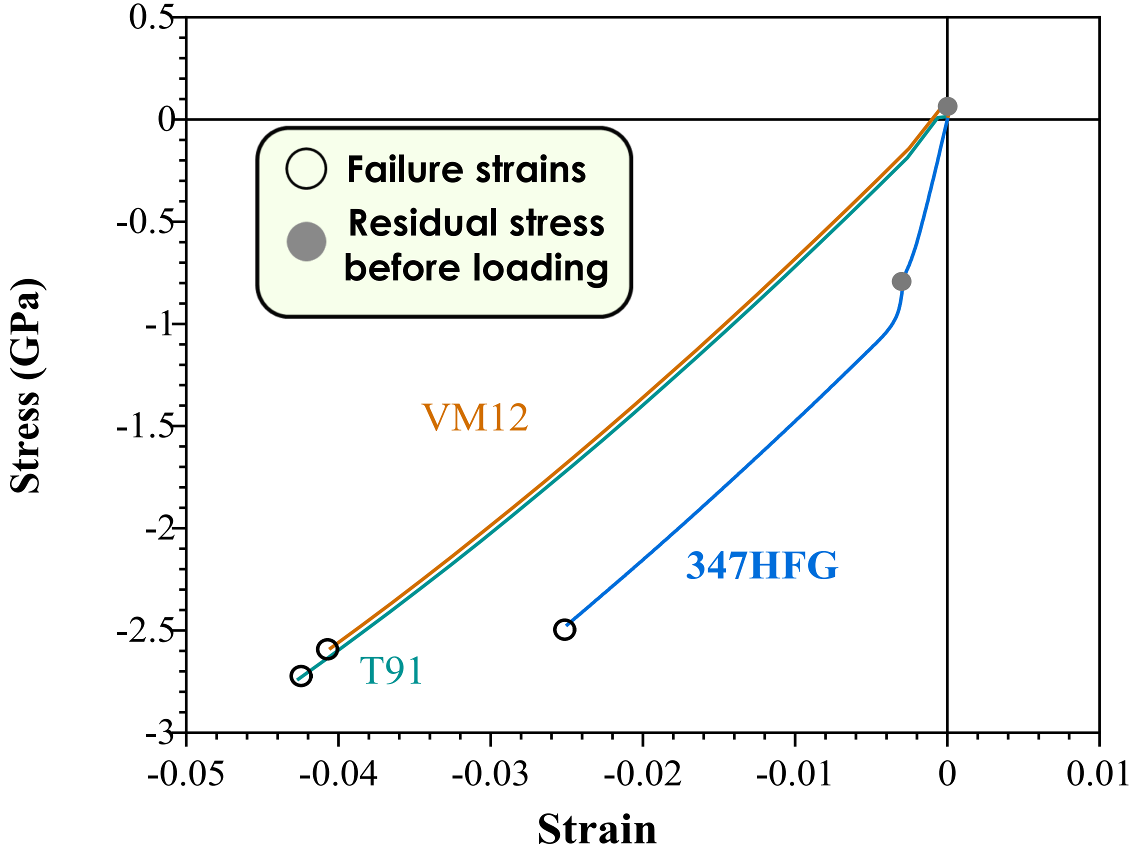
Stresses calculated in the metal and oxide in longitudinal and transverse directions assuming elastic oxide behavior



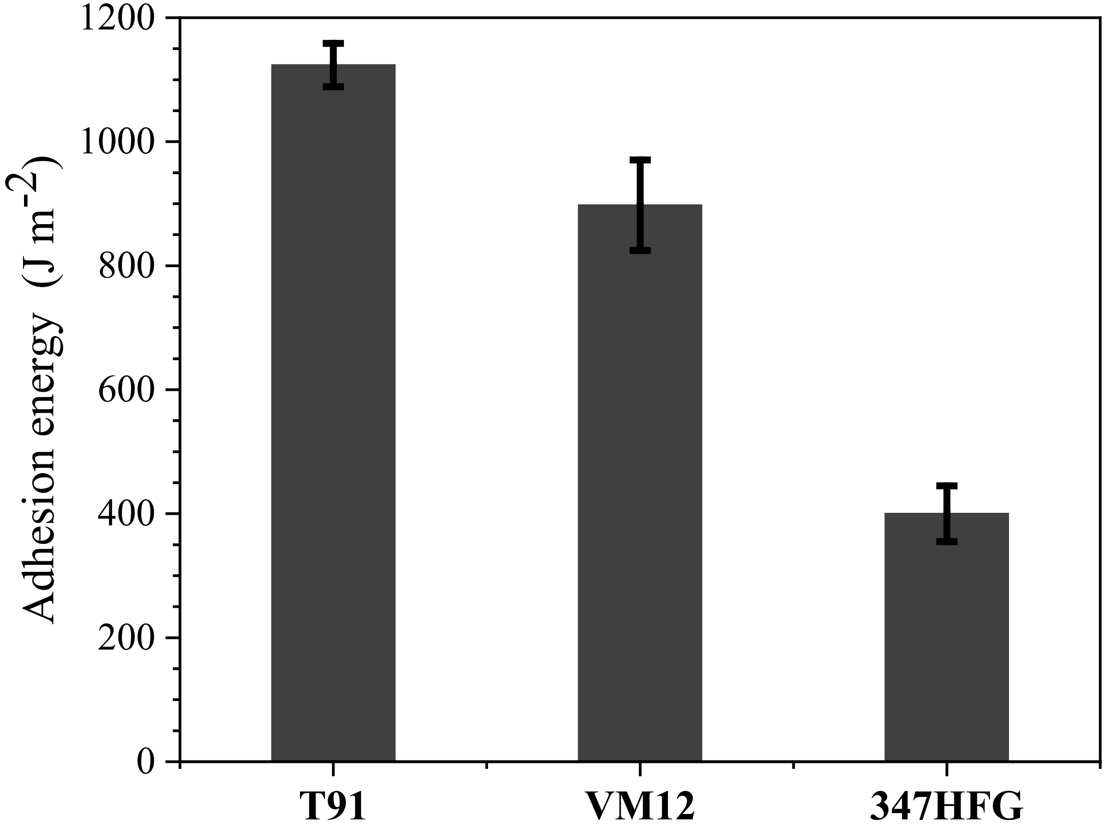
- Equations developed for oxide-alloy system
- Measured strain at initial spallation used to calculate adhesion energy
- Residual stresses in the oxide measured with XRD

Stresses in the transverse direction in the outer oxide layer will most likely contribute to the spallation of this layer during cooling after 1000h at 550°C in 276 bar OT (~ 100 ppb O_2) steam

Calculated stress-strain in the outer oxide layer

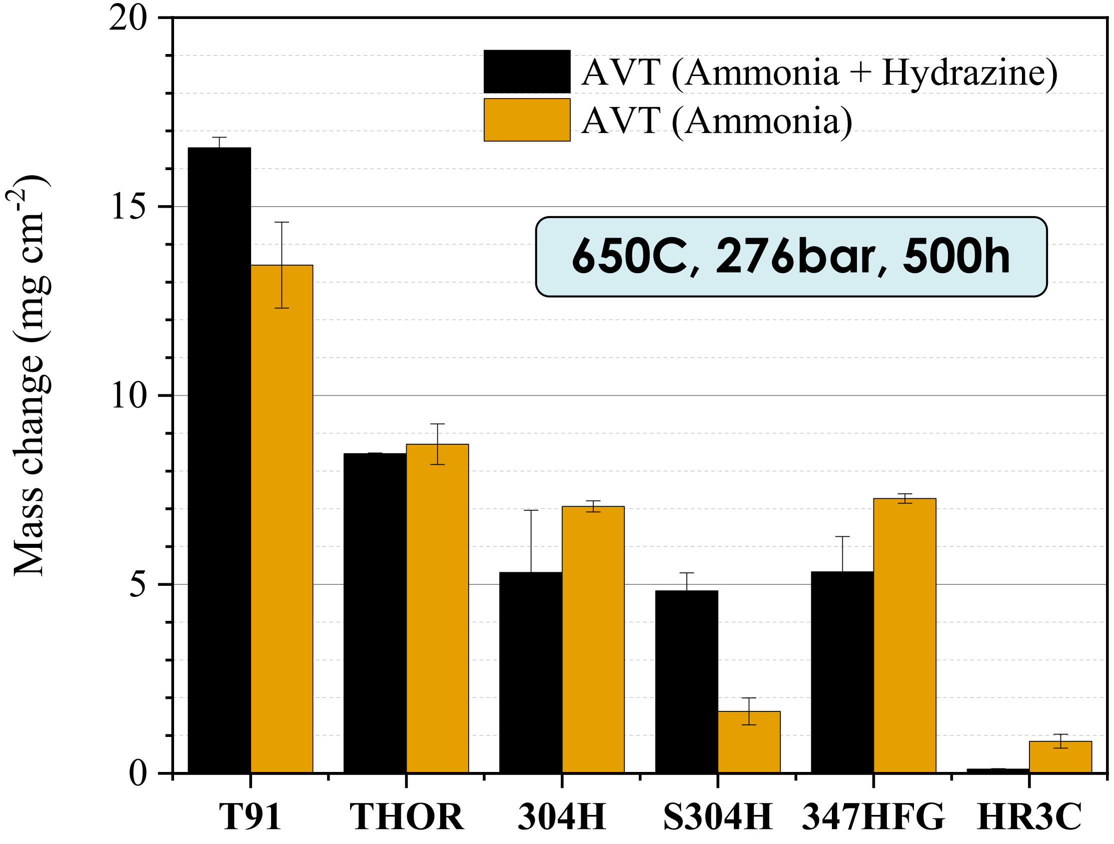


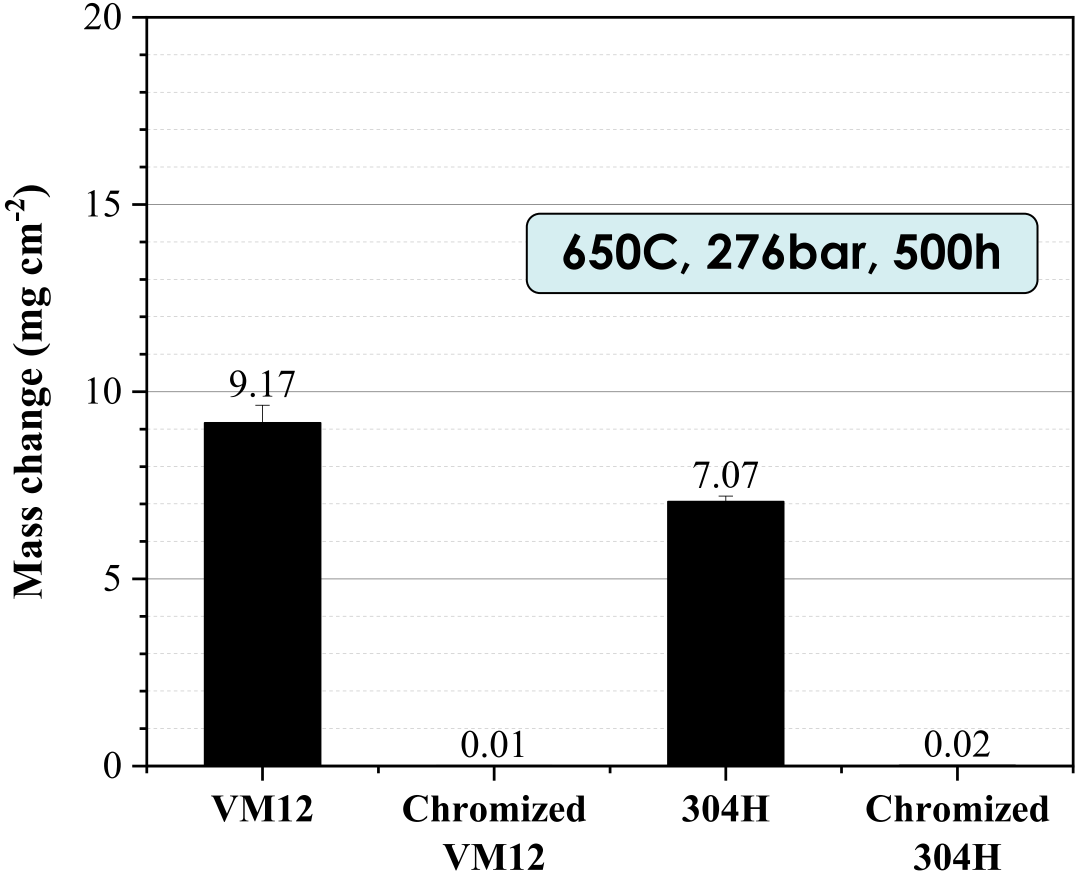
Calculated adhesion energies between outer and inner oxide layer



- Lowest adhesion energies predicted for the oxide-alloy interface on 347HFG and corresponds well to experimental observations for oxide adherence on austenitic steels

Continuing experiments to evaluate role of water chemistry on oxidation behavior by simultaneous additions of hydrazine and ammonia





- Comparison of measured mass change with previous test with only ammonia additions after 500h shows varying influence on ferritic-martensitic and austenitic steels
- Ongoing microstructural characterization to identify key differences in oxide composition and morphology
- Massive reduction in mass gain with chromized specimens (FEAA364)

Future work highlights

- Continue experimental program
- Evaluate the influence of film-forming products on the oxidation behavior
- Assess performance of coated materials (chromized specimens) in high-pressure steam oxidation tests
- Quantify oxide adhesion energies for exposures in AVT-R conditions
- Compare oxide adherence between OT and AVT conditions
- Incorporate quantified oxide adhesion energies in the oxide exfoliation model developed earlier at ORNL (Adrian Sabau)
- Develop a realistic lifetime prediction of currently employed materials under a range of partial and full-load duty cycles