FEAA150
Steamside Oxidation Issues in Current Coal-Fired Boilers

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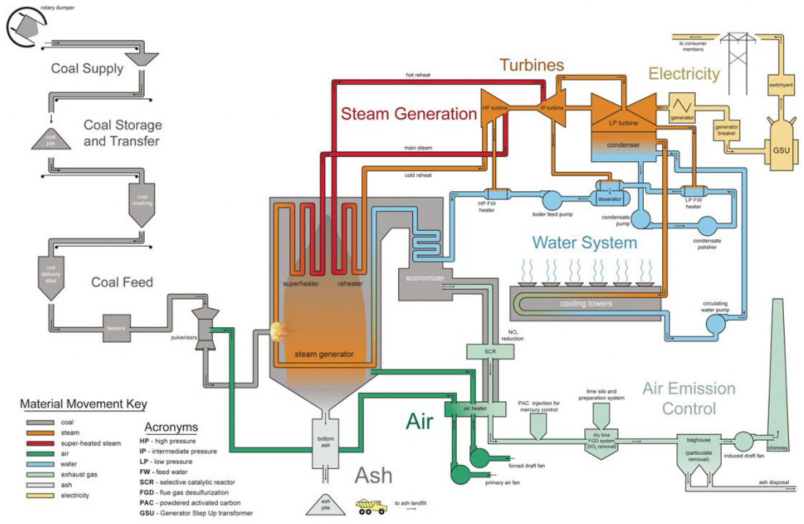
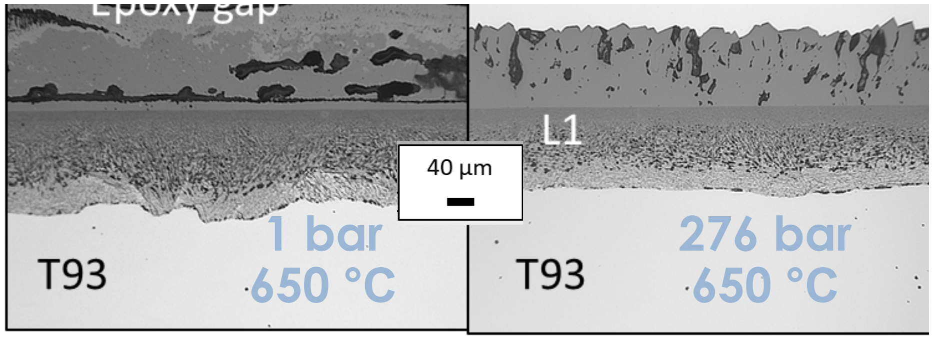
- B. Johnston, M. Stephens, A. Willoughby — oxidation experiments
- T. Lowe — SEM, image analysis
- V. Cox, T. Jordan — metallography
- S. Raiman — Design of water loop
- Materials — EPRI, TENARIS

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

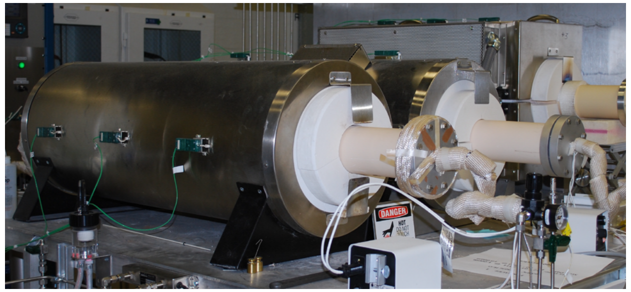


Clear impact of pressure on

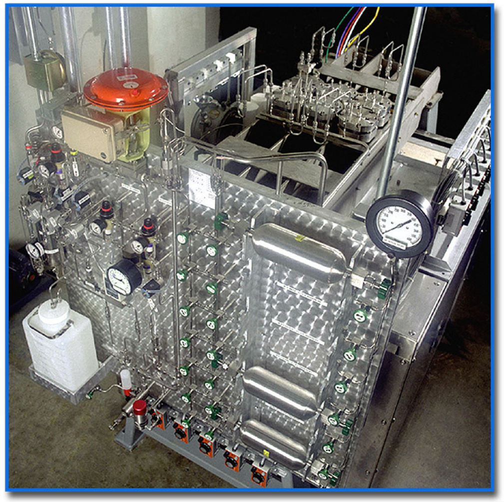


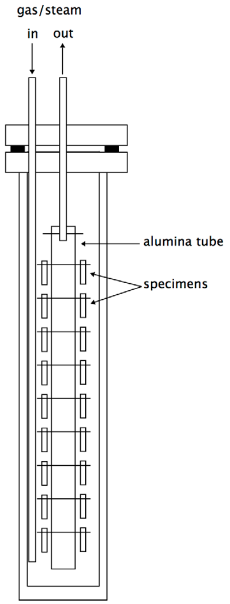
Alloy	Fe	Cr	Ni
T93	83.7	8.9	0.1

Tube furnace: 1 bar
500-h cycles



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





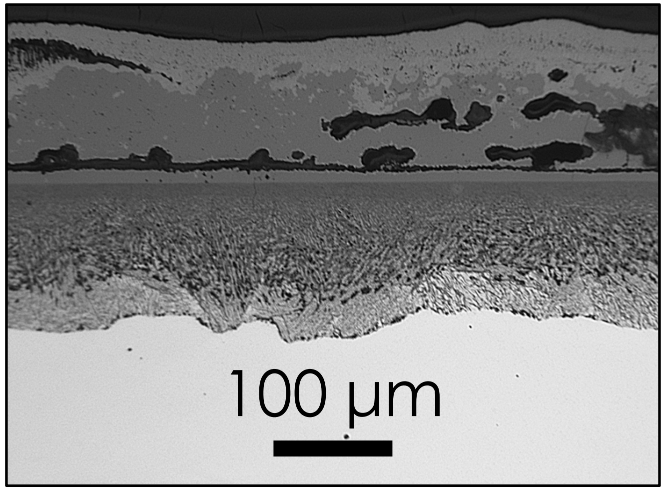
Water loop

Autoclave: 275 bar water
500-h cycles

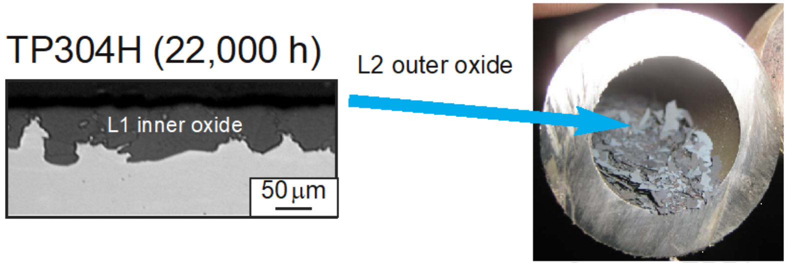
Controlled water chemistry
pH and O_2

What is the continued 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,

Overall goal of FEAA150 (in cooperation with EPRI)

- Evaluate the effect of additives (ammonia, hydrazine, filming chemicals) on growth, adhesion and microstructure of oxide scales grown on representative ferritic-martensitic and austenitic steels during exposure in ultra-supercritical steam conditions

Experimental program (prioritized based on EPRI's guidance and reduced funding)

Temperature	650 °C
Pressure	276 bar
Atmosphere	100% steam
Treatment	➢ Oxygenated Treatment, OT (200 ppb dissolved O_2) - **completed** ➢ All Volatile Treatment-Reducing, AVT-R (<5 ppb dissolved O_2) - **completed**
Additions	Ammonia, Hydrazine, film forming products (amines)
Time	up to 1000h (500h-cycle)
Specimens	20 x 12 x 1.5mm coupons
Materials	Ferritic-martensitic, austenitic, advanced austenitic

Focus of this presentation

- Comparison of oxidation behavior of representative ferritic-martensitic and austenitic steels exposed in three different water chemistries
  - Phase I: Oxygenated Treatment, OT (Dissolved oxygen ~100 ppb): Ammonia additions
  - Phase I: Oxidizing All Volatile Treatment, AVT-O (Dissolved oxygen <10 ppb): Ammonia additions
  - **Current phase:**
    Reducing All Volatile Treatment, AVT-R (Dissolved oxygen <5 ppb): Ammonia + hydrazine additions

- Key approaches

– **Gravimetry:**	measured mass change
– **Thicknesses of oxide layers:**	automated image analyses of micrographs
– **Oxide morphology:**	light optical and electron microscopy
– **Oxide compositions:**	electron and wavelength dispersive spectroscopy
– **Oxide structure:**	Raman spectroscopy

Combined additions of ammonia and hydrazine to emulate reducing all volatile treatment (AVT-R) conditions

Investigated materials
(Measured composition in wt.%, C and Ni in wppm)

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
VM12	83.3	**11.5**	0.4	0.4	1.6	0.4	0.42	0.08	1200	360
THOR	87.6	**10.7**	0.1	0.5	-	0.4	0.18	0.04	980	420
304H	70.4	**18.4**	8.4	0.3	0.02	1.6	0.26	0.4	600	660
Su304H	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

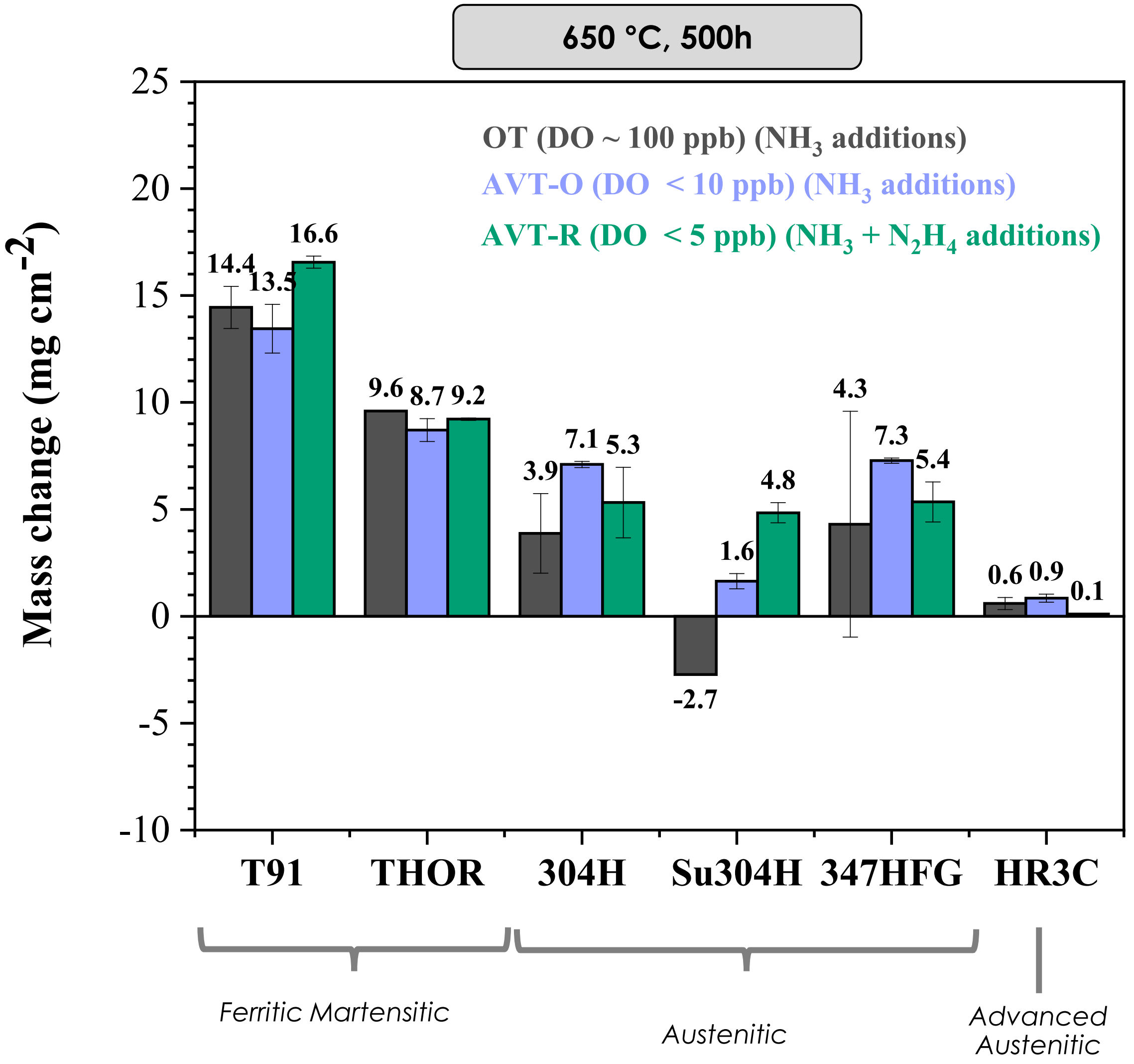
- *Inductively coupled plasma optical emission spectroscopy (ICP-OES) for Fe, Cr, Ni, Mo, W, Mn and Si*
- *Combustion analyses for C*
- *Inert gas fusion for N*

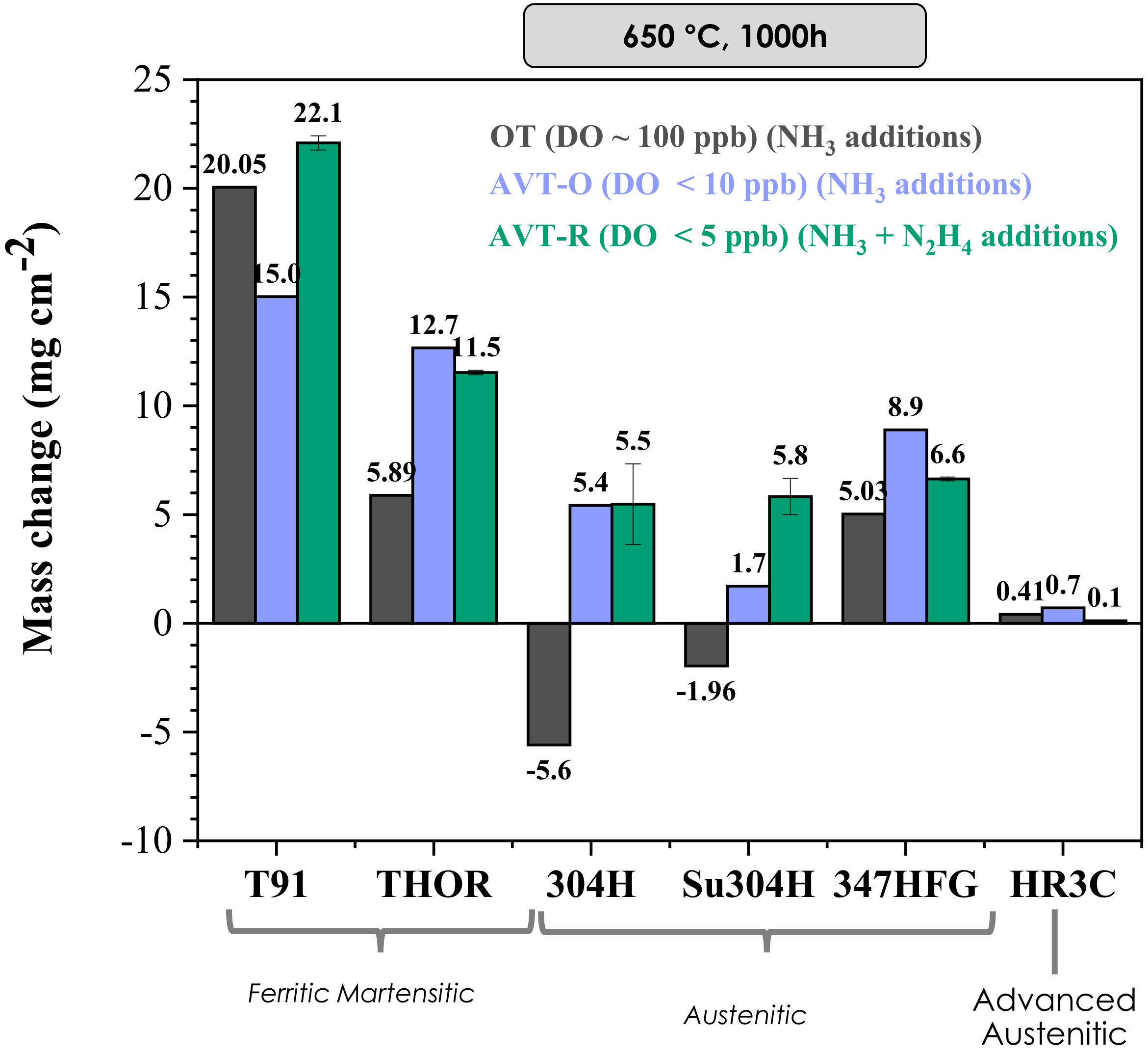
Water loop

Specimen holder

Temperature	Dissolved Oxygen	Additives	Pressure	pH	Time
650°C	max. 1 ppb	1.5 ppm NH_3 + 20 ppm N_2H_4	276 bar	9.3-9.5	1000h (2 500h-cycles)

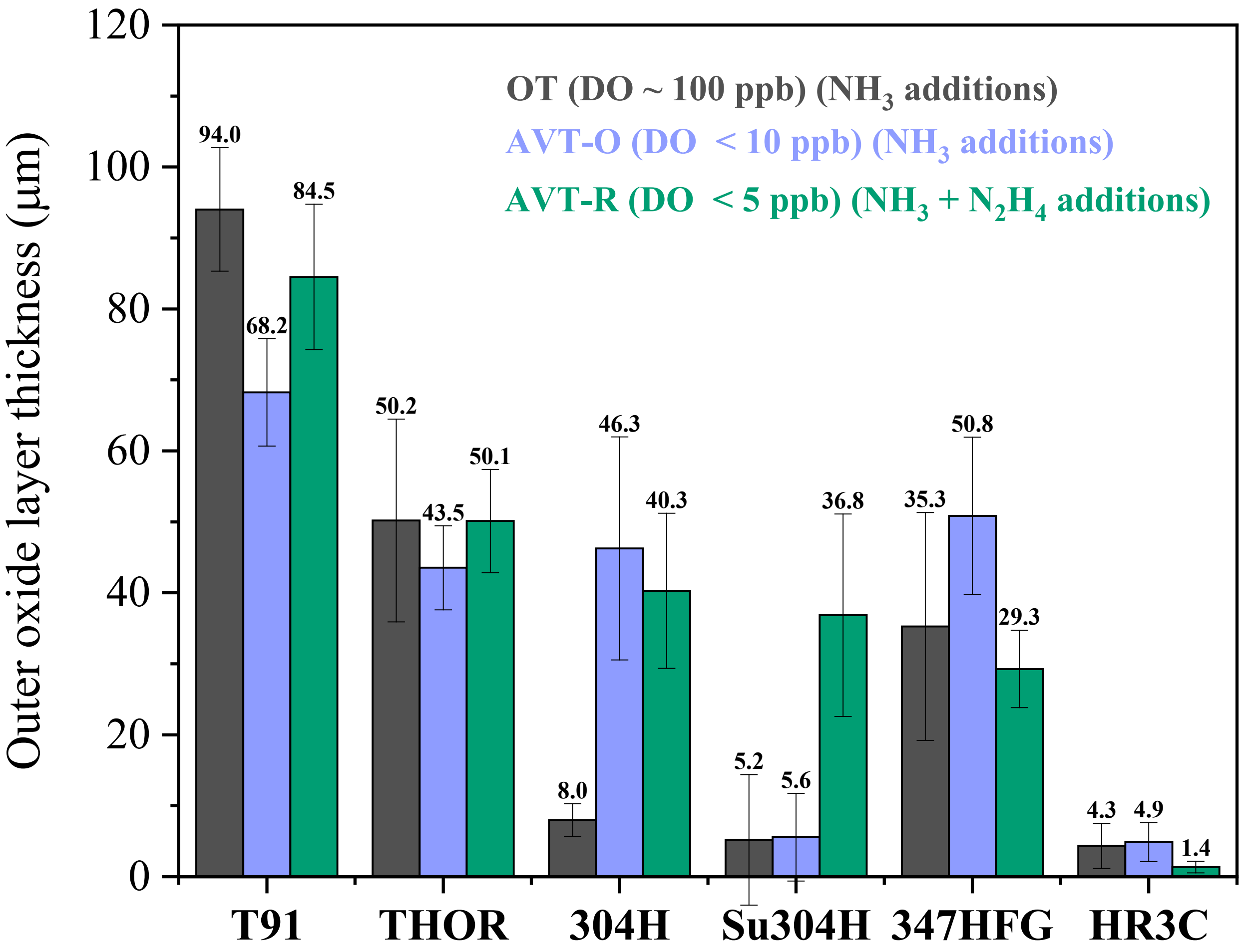
Lower mass gains under AVT-R conditions for the high Cr containing austenitic steels

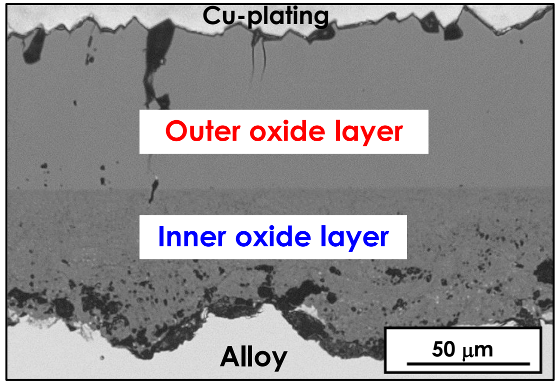




- Significant mass loss observed for the austenitic steels 304H, Su304H, 347HFG under OT conditions after 500 and 1000h

Thicker outer oxide layers and significant spallation of the outer layers on the austenitic steels under OT conditions after 1000h at 650°C (276 bar)



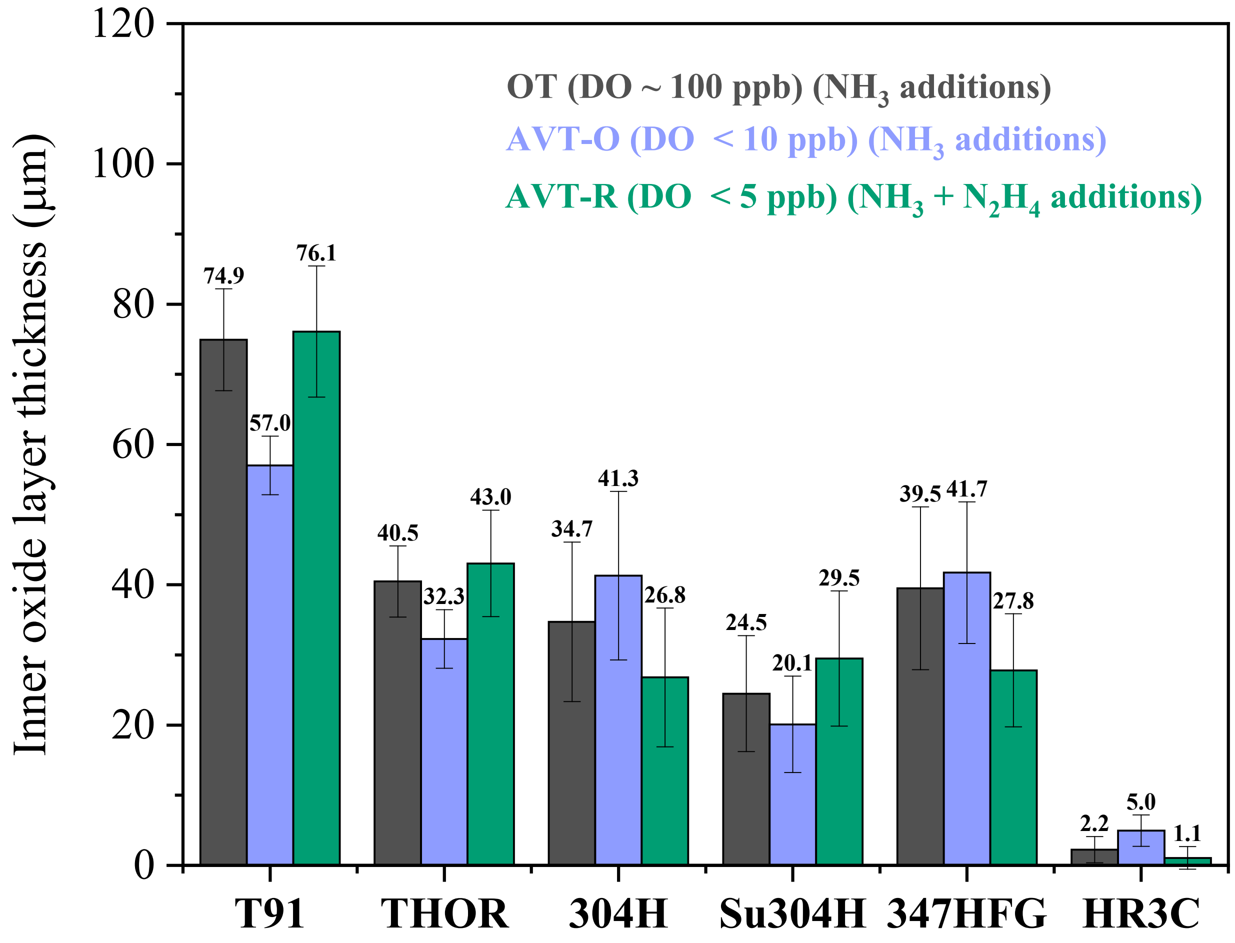


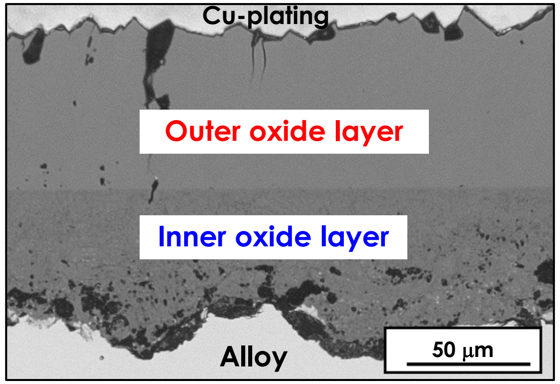
Comparison of oxide layer thickness

T91 THOR	**OT > AVT-R > AVT-O**
304H Su304H* 347HFG	**AVT-O > AVT-R**

**Spalled outer layers on Su304H both under OT and AVT-O conditions*

Thicker inner oxide layers on the FM steels but thinner on the austenitic steels under AVT-R conditions after 1000h at 650°C (276 bar)





Comparison of oxide layer thickness

T91 THOR	OT ≈ AVT-R > AVT-O
304H 347HFG HR3C	AVT-O > OT > AVT-R

**Spalled outer layers on Su304H both under OT and AVT-O conditions*

- Detailed characterization results will focus on T91, THOR and 347HFG

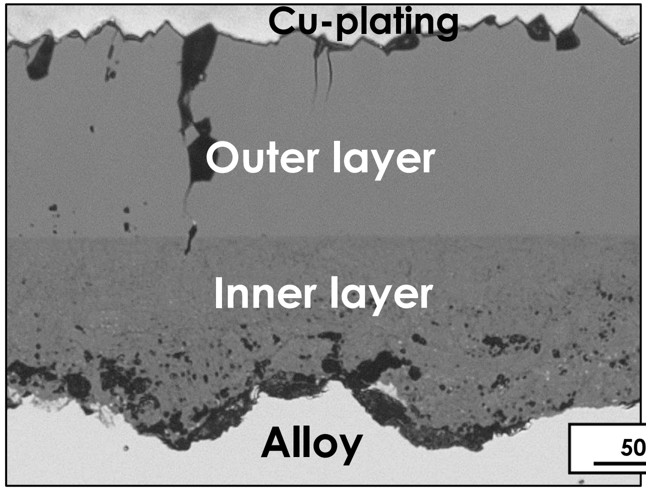
A less porous outer oxide layer was observed after 1000h under AVT-R conditions on T91 (Fe-8.6 wt.% Cr)

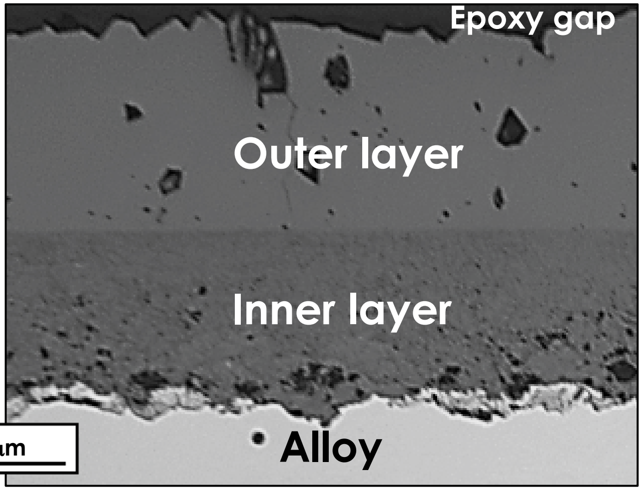
OT: DO ~100ppb

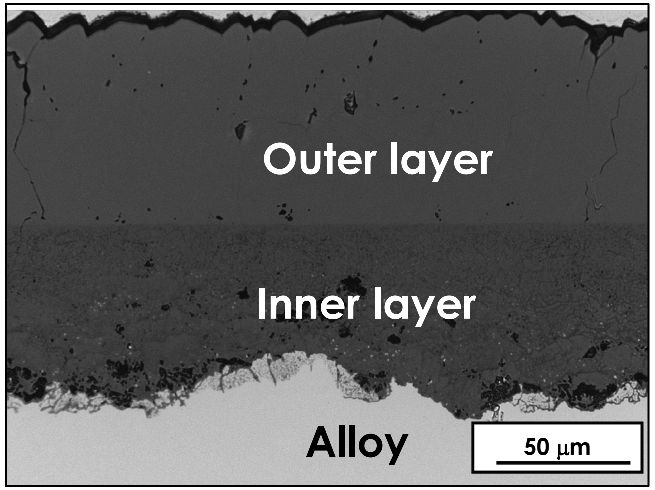
AVT-O: DO < 10 ppb

AVT-R: DO < 5 ppb

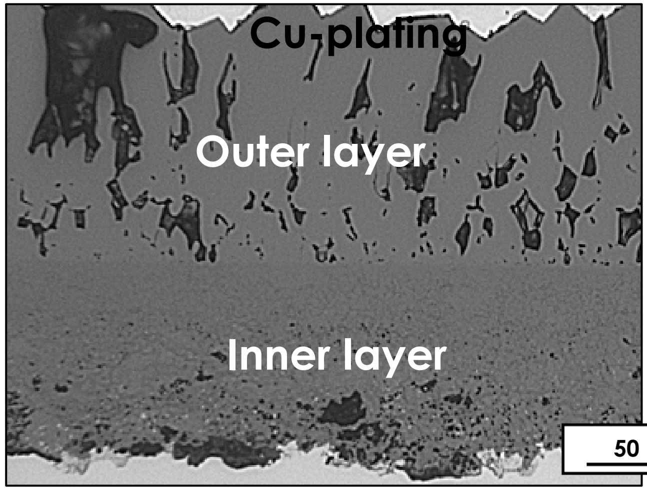
650°C 500h

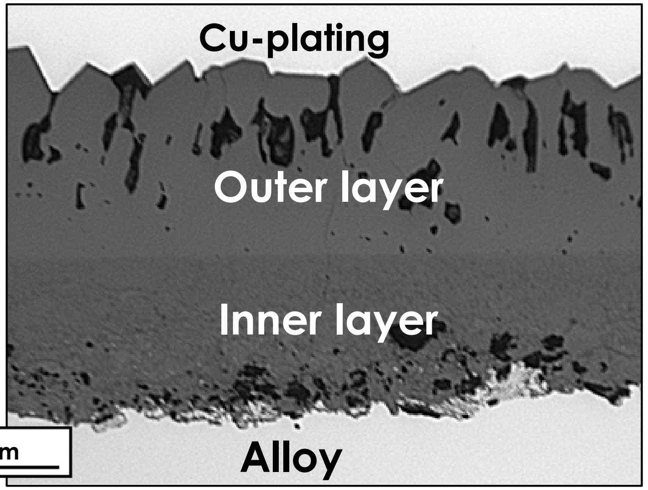


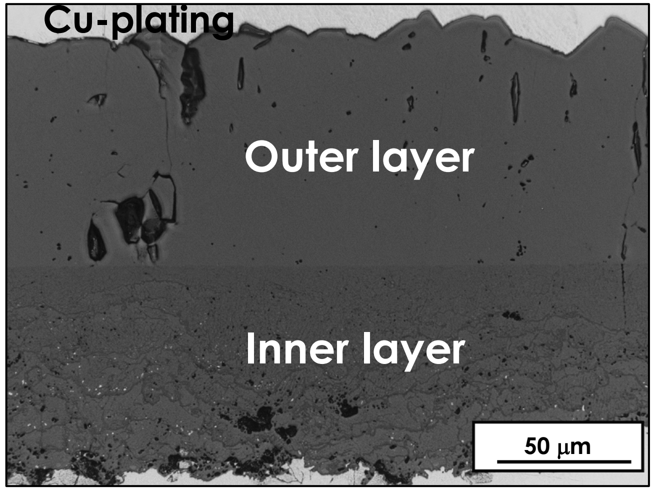




650°C 1000h







On the higher Cr-containing THOR (Fe-10.7 wt.% Cr):

Outer oxide layer spalled after 500h and almost detached from the inner oxide layer after 1000h under OT conditions

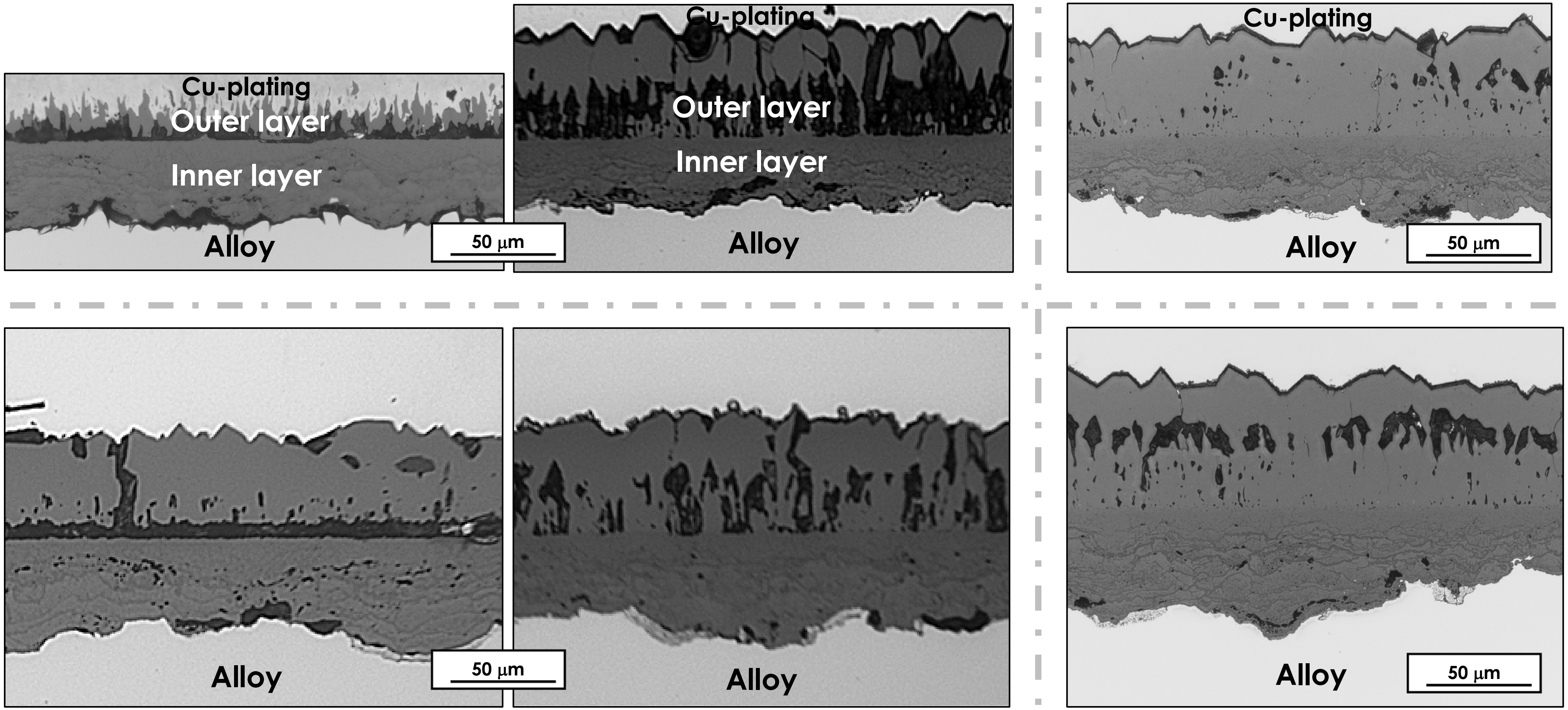
OT: DO ~100ppb

AVT-O: DO < 10 ppb

AVT-R: DO < 5 ppb

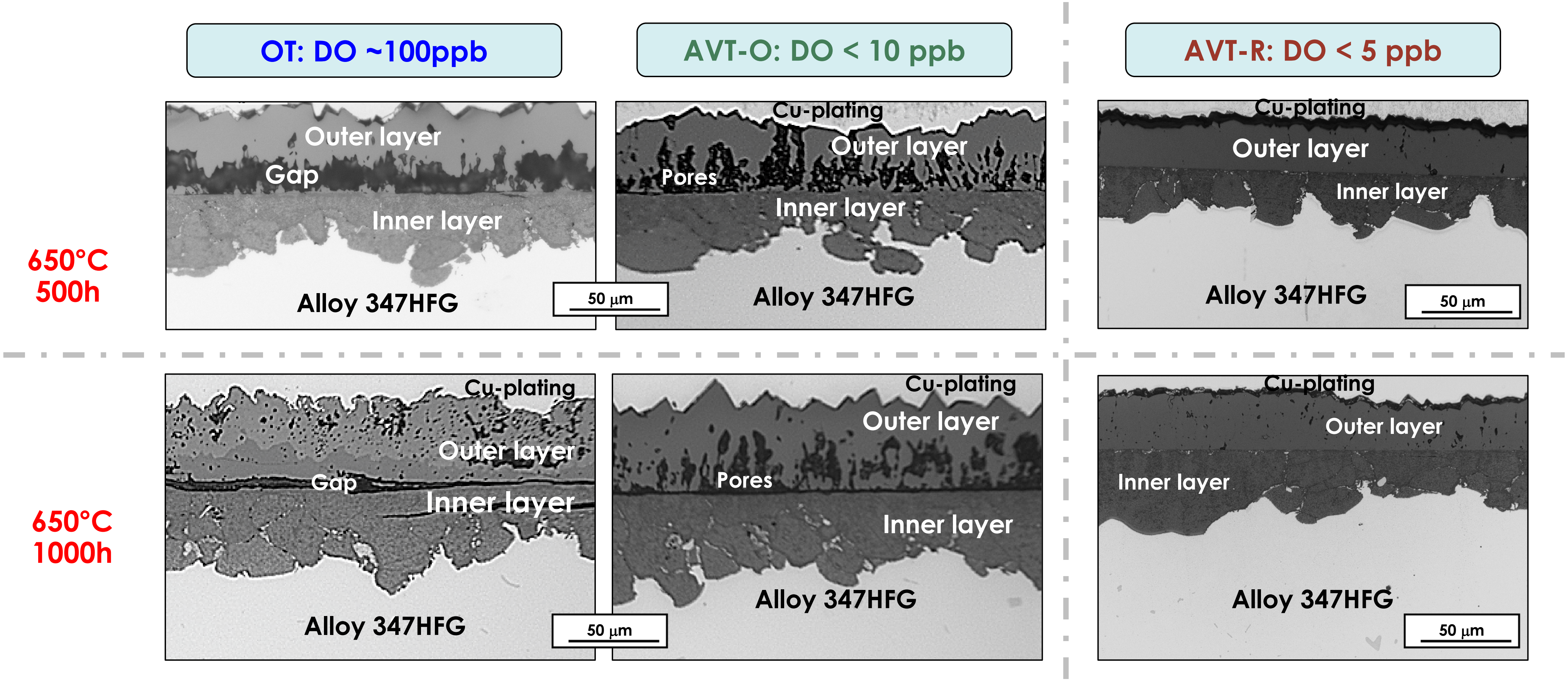
650°C 500h

650°C 1000h



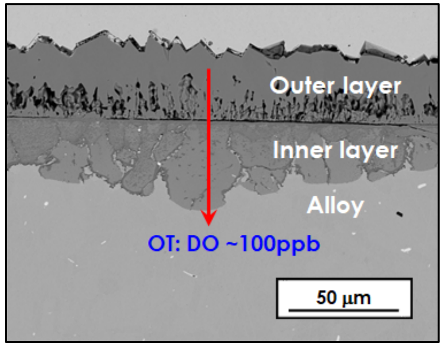
On the austenitic 347HFG (Fe-18.6Cr-11.8Ni wt.%):

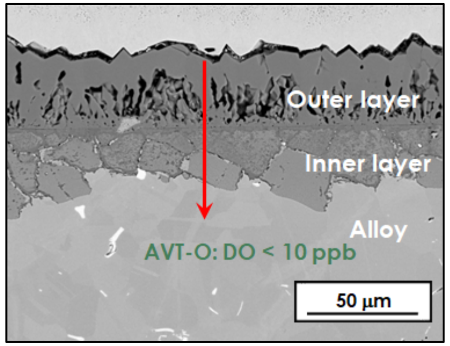
- **Outer oxide layer considerably less porous under AVT-R conditions**
- **Detached outer layer allows formation of hematite at the gas\oxide interface after 1000h**

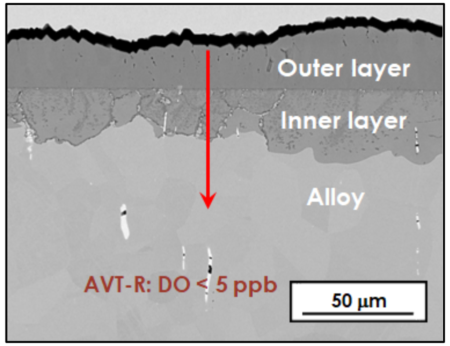


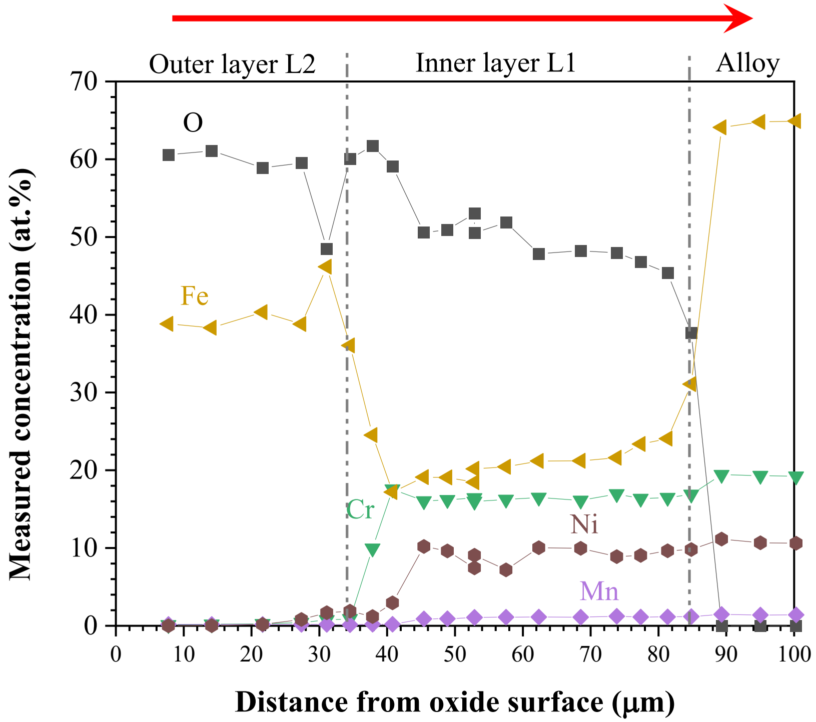
➢ Additional characterization work focused on 347HFG

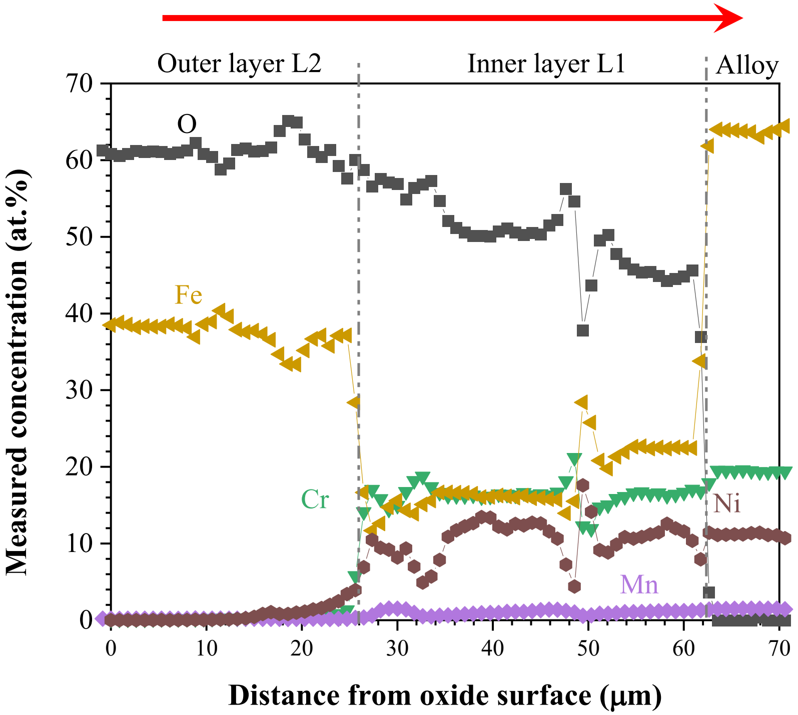
Lower O contents were measured (wavelength dispersive spectroscopy) in the inner oxide layer on 347HFG under AVT-R conditions (500h at at 650°C, 276 bar)

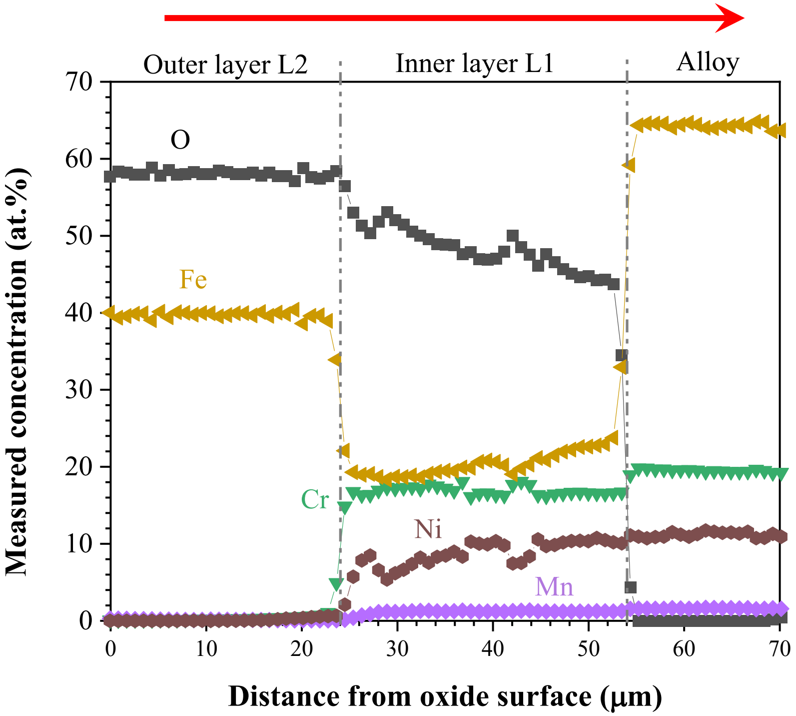






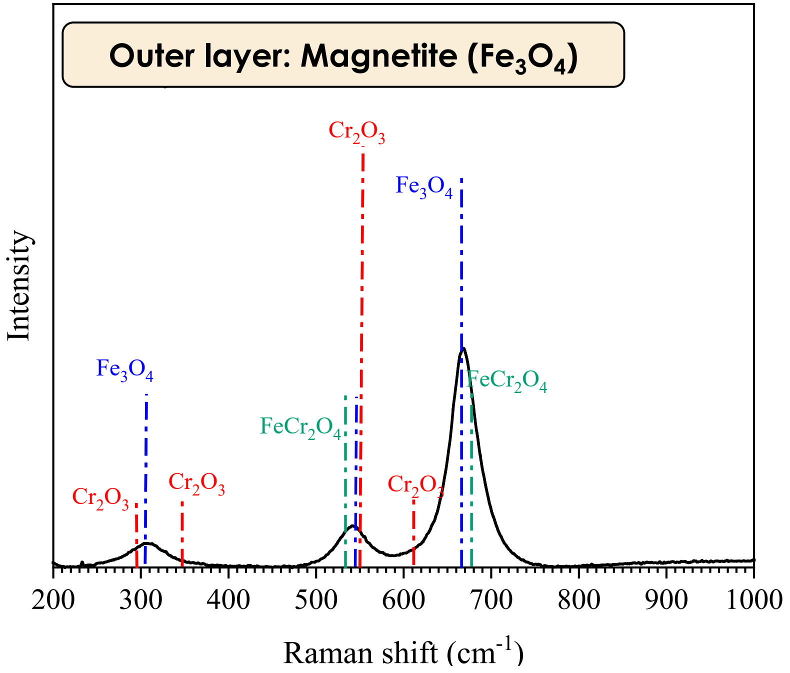


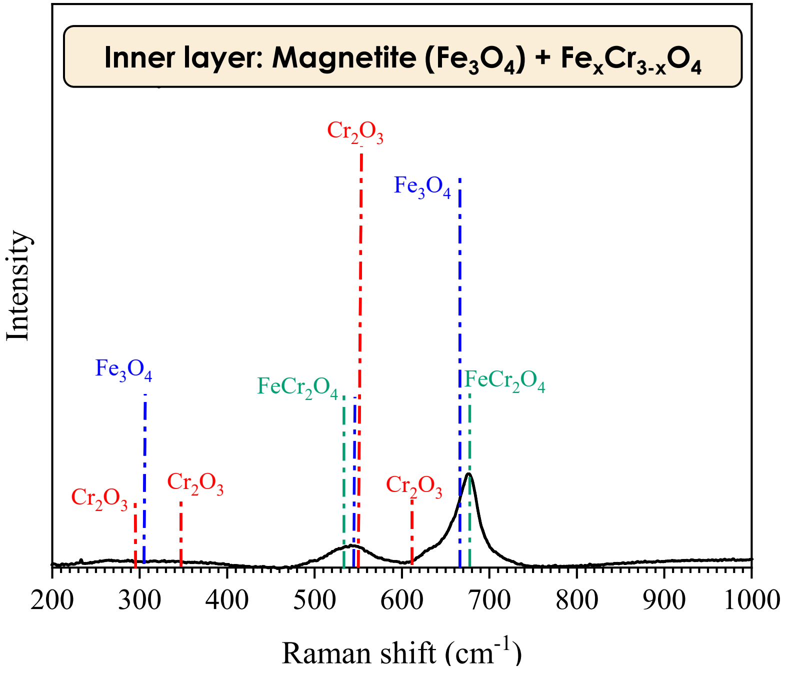


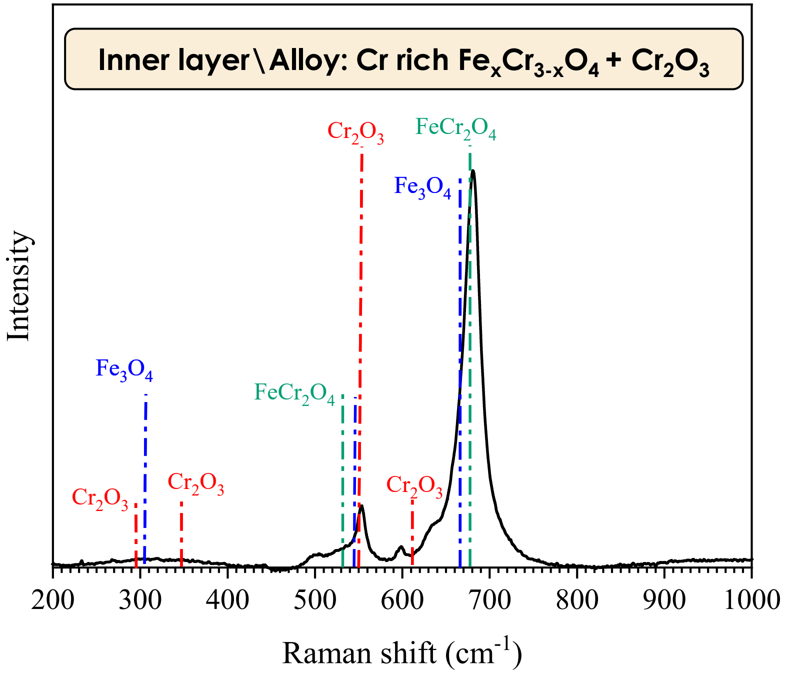


Qualitatively similar oxide structures were identified with Raman spectroscopy for 347HFG exposed for 500h in OT, AVT-O and AVT-R conditions

347HFG, AVT-R, 500h at 650°C, 276 bar


Outer layer: Magnetite (Fe_3O_4)

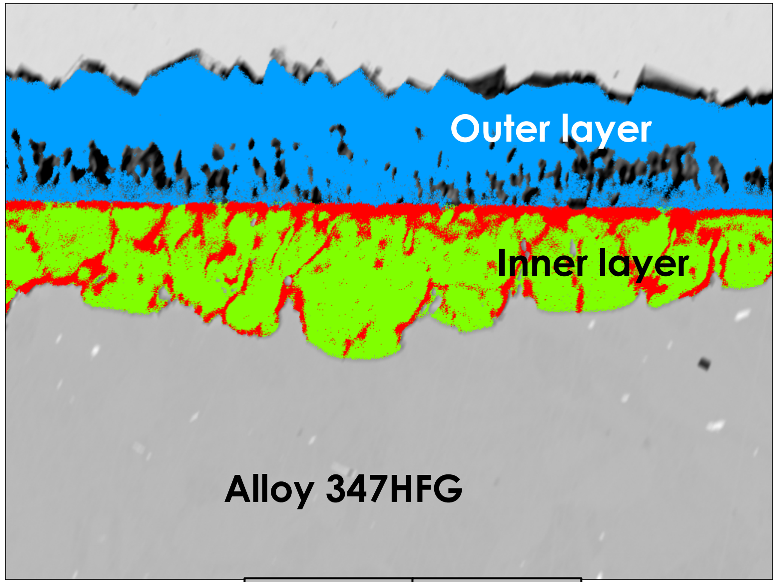

Inner layer: Magnetite (Fe_3O_4) + $Fe_xCr_{3-x}O_4$


Inner layer\Alloy: Cr rich $Fe_xCr_{3-x}O_4$ + Cr_2O_3

- Close proximity of the Raman spectra for Fe_3O_4 and $Fe_xCr_{3-x}O4$ spinel did not allow an unequivocal distinction between the different oxides
- An evident difference in the distribution of the different oxides in the inner oxide layers between OT, AVT-O and AVT-R could not be ascertained

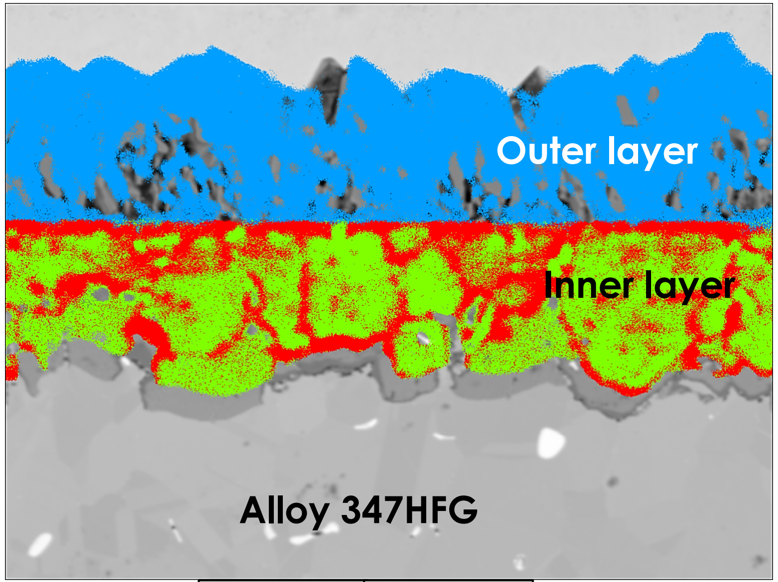
Measured average compositions (EDS) and fractions of the oxide phases confirm the presence of an Fe-rich spinel primarily at the outer/inner oxide layer interface of 347HFG under AVT-R conditions (650 °C, 500h)

OT: DO ~100ppb



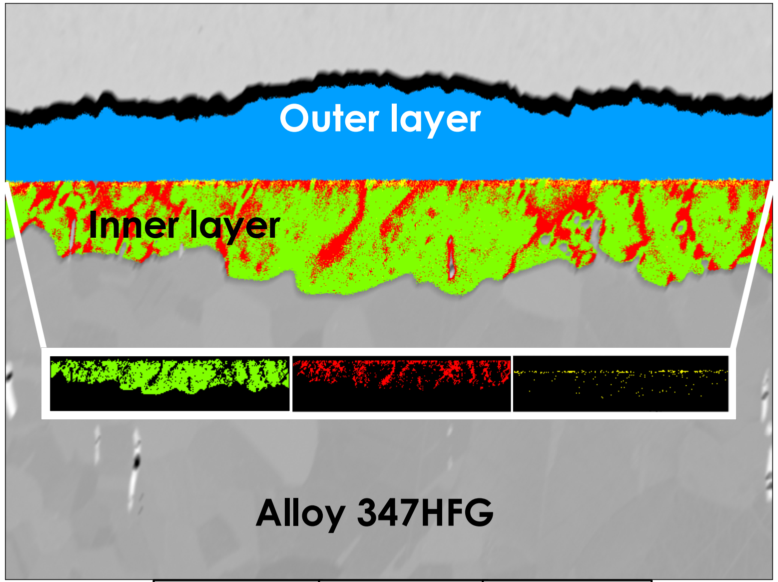
Oxide fractions	62%	38%

AVT-O: DO < 10 ppb



51%	49%

AVT-R: DO < 5 ppb



60%	36%	4%

Measured (EDS) oxide compositions in at.%

	Fe	Cr	Ni	O
Outer layer	44.6	0.5	0.5	53.1
Inner layer	22.4	18.9	10.8	44.3
	20.1	19.9	5	51.8

Fe	Cr	Ni	O
44.9	0.4	0.4	53.1
21.4	18.8	11.3	44.7
20.9	20.4	5.8	49.9

Fe	Cr	Ni	O
46	0.6	0.1	52.7
23.1	19.4	11.1	43.4
20.8	20.6	6.9	48.7
26.2	16.2	6.8	49.3

Summary

- Considerably less defective outer oxide layers under AVT-R conditions for all tested alloys
- Minimal spallation of the outer oxide layers on austenitic steels under AVT-R conditions
- Qualitatively similar distribution of the oxides for 347HFG under OT, AVT-O and AVT-R test conditions
    - Outer layer: Magnetite
    - Inner layer: Magnetite + FeCrNi-spinel
    - Inner layer\alloy interface ; Cr-rich FeCrNi-spinel
- Fe-rich FeCrNi-spinel was observed at the outer/inner oxide layer interface and at oxide grain boundaries in the inner layer for 347HFG after 500h at 650 °C in AVT-R conditions

Disclaimer