DE-FE0027947

MINIMIZING CR-EVAPORATION FROM BALANCE OF PLANT COMPONENTS BY UTILIZING COST-EFFECTIVE ALUMINA-FORMING AUSTENITIC STEELS

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Background - SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
    - Grain growth
    - Coarsening of the particles
    - Surface re-construction
- Strontium segregation related issues

$$2Sr_{La}^{'} + V_{O,LSCF}^{\bullet\bullet} + 2O_{O}^{x} \leftrightarrow 2SrO(s)$$

- Chemical reaction with YSZ electrolyte.

$$La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s) \qquad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s)$$

- **Poisoning of the cathode** (e.g. by CO_2, **chromium species** etc.)

$$SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \qquad SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$$

$$2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g)$$

Cr_2O_3 Related Degradations

- Cr poisoning of SOFC Cathode

$$Cr_2O_3(s) + 1.5O_2(g) = 2CrO_3(g)$$

$$Cr_2O_3(s) + 1.5O_2(g) + 2H_2O(g) = 2CrO_2(OH)_2(g)$$

- Reactions with other components

$$2Cr_2O_3(s) + 4BaO(s) + 3O_2(g) = 4BaCrO_4(s)$$

$$CrO_2(OH)_2(g) + BaO(s) = BaCrO_4(s) + H_2O(g)$$

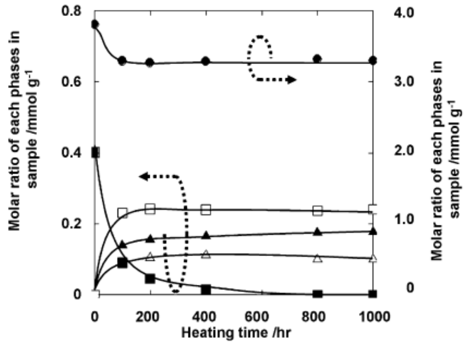
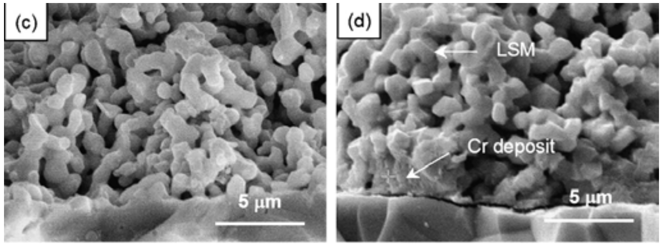
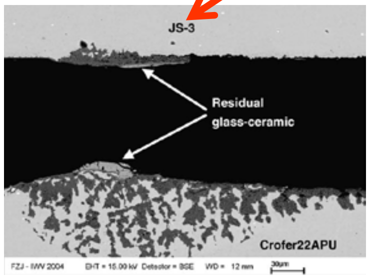


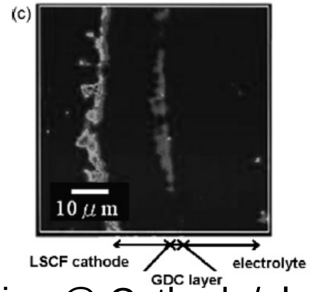
Fig. 4. Molar ratio of phases in LSCF–Cr_2O_3 mixture during heating at 1073 K for 0–1000 h: (●) LSCF, (■) Cr_2O_3, (□) $SrCrO_4$, (▲) $CoCr_2O_4$ spinel, (△) $(Fe,Cr)_2O_3$.



J. Power Sources 162 (2006) 1043–1052



J. Power Sources 152 (2005) 156–167

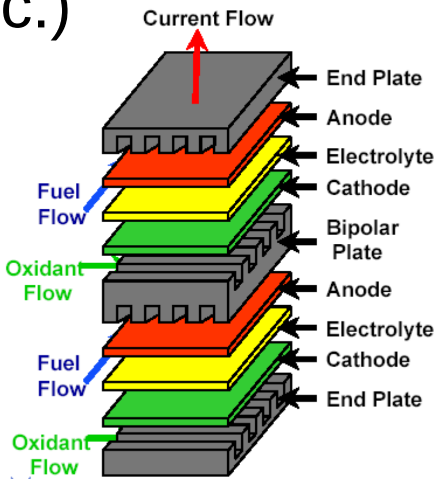


Cr-distribution @ Cathode/electrolyte Interface

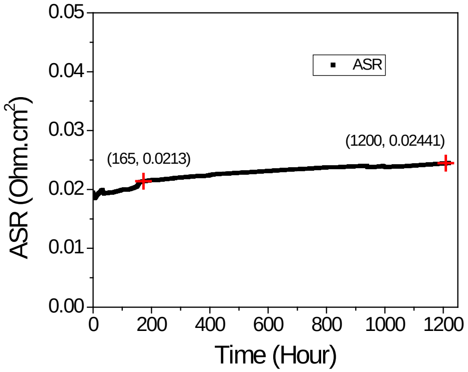
- **Cr Sources: Interconnect and BOP**

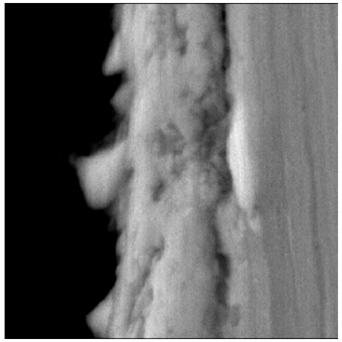
SOFC Interconnect Coatings

- Various Spinel Coatings (Mn-Co, Mn-Cu, etc.)
- PVD, CVD, Spray, Electroplating, EPD



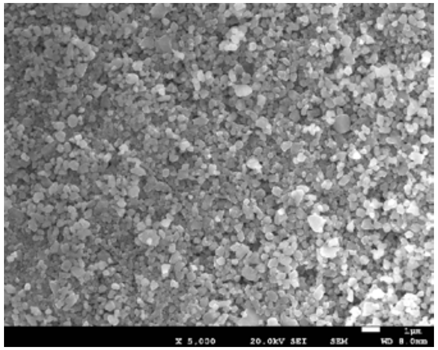
Electro plating Mn-Co

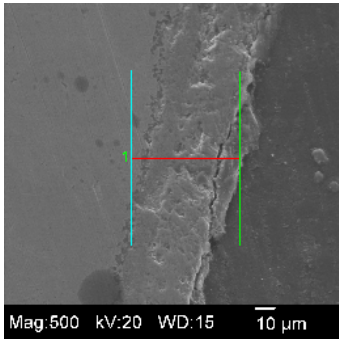




J. Wu, C. Johnson, Y. Jiang, R. Gemmen, **X. Liu***, *Electrochimica Acta (2008) 793-800*

EPD Mn-Co spinel





Hui Zhang, Zhaolin Zhan, **Xingbo Liu**, *JPS 196 (2011) 8041-8047*

Coating impedes degradation of SOFCs

Researchers at West Virginia University have put their heads together with scientists from the Department of Energy's National Energy Technology Laboratory. The result of this collaboration has been the development of a new manganese-cobalt coating for solid oxide fuel cell interconnects.

The new process uses an electroplating technique that reportedly does not harm the environment, and offers significant advantages in terms of cost and ease of operations over other coating methods, the researchers say. Extensive on-cell testing has demonstrated considerable improvement of SOFC degradation compared to uncoated interconnects, the researchers contend.

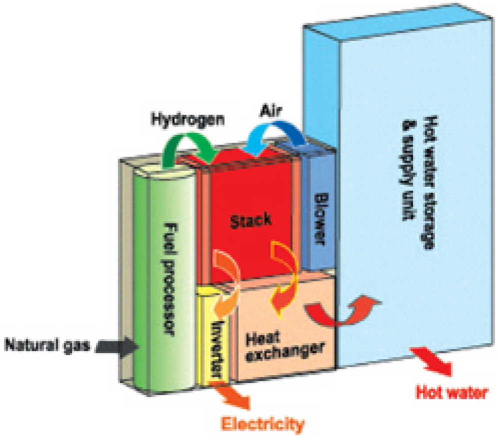
The team has published its research findings in two peer-reviewed journals, and a patent disclosure of the process also has been filed. In addition, team members report exceptionally positive feedback from the report on the coating presented at the 2008 MS&T Conference last October.

Recent results during on-cell testing showed considerable improvement of SOFC degradation with this coating method as compared with uncoated interconnects. Further improvements are anticipated as optimized plating variables are identified. (Visit: http://netl.doe.gov) ■

Junwei Wu, a Ph.D. student at West Virginia University, demonstrates environmentally friendly electroplating for SOFC interconnects.

Project Technical Approaches

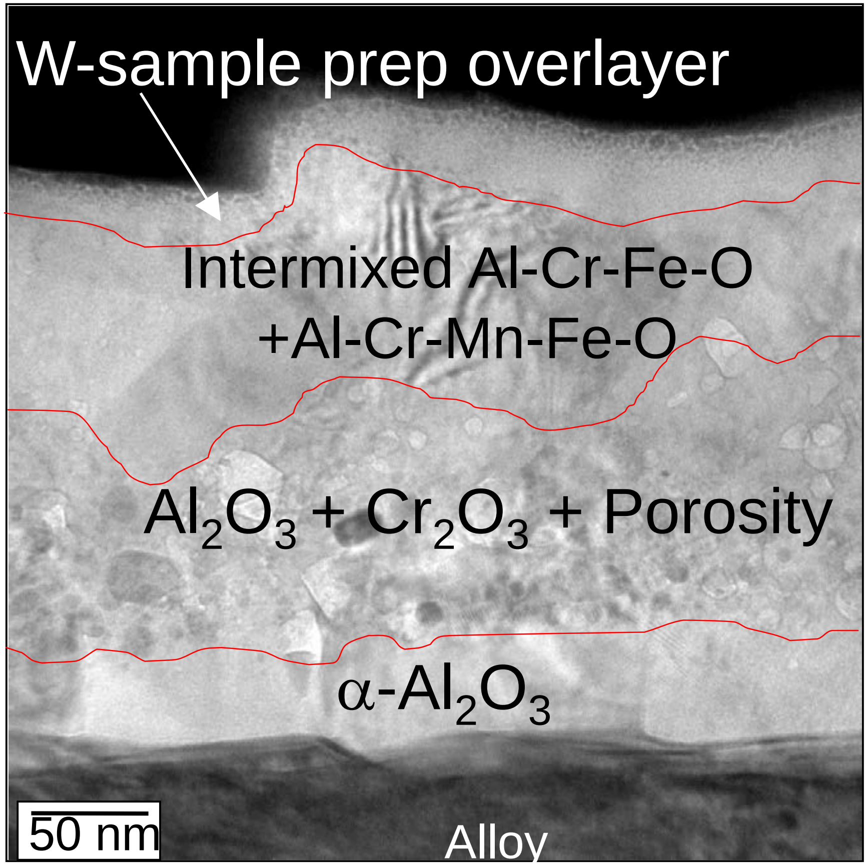
Developing Cost-Effective Alumina Forming Austenitic Stainless Steels (AFA), to replace Austenitic Stainless Steel 316L and Ni-base Superalloy Inconel 625, for Key **Balance of Plant (BOP) components**, to minimize Cr-Poisoning of SOFC Cathode



Compression Plate in BOP

AFA Form Transient Al-Rich Oxide Overlying Inner, Columnar a-Al_2O_3

TEM of HTUPS 4 After 1000 h at 800°C in Air + 10% Water Vapor



- α-Al_2O_3 the source of the excellent oxidation resistance
- Occasional transient nodules 0.5-5 μm thick, some Nb-oxide also detected

Project Objectives – Phase I

- Develop and utilize cost-effective alumina forming austenitic steels (AFAs) for balance of plant (BOP) components and pipes in solid oxide fuel cell (SOFC) systems to minimize the Cr-poisoning and improve system stability;

- Systematically investigate the influence of the operation condition, i.e., temperature and moisture, on the oxidation and Cr-release from the AFA steels, and their effects on the degradation of SOFC performance

- Prepare for Phase II of the project, in which we will manufacture and test the related BOP components in industrial SOFC systems

Materials Design

Multiple AFA Grades Under Study for Balance of Cost, Processability, Cr-Evaporation, and Oxidation

•Two temperature regimes of interest: 700-800° C and 900-950° C
 -temperature targets vary with component and SOFC manufacturer

•Upper-temperature oxidation limit for AFA composition dependent
 -≤ 850° C: Fe-25Ni-14Cr-(3-3.5)Al-(1-2.5)Nb-(0.1-0.2C) *base
 -900-1000° C: Fe-(25-35)Ni-(15-18)Cr-4Al-(1-2.5)Nb-(0.1-0.2C) *base ± Hf, Y, Zr

•Cost and ease of processing varies with alloy content
 -higher Ni, Nb, and Hf, Y, Zr increases cost
 -Zr lower cost than Hf, easier processing

*Minor additions of Mn, Si, Mo, W, B, etc. also used in some AFA compositions

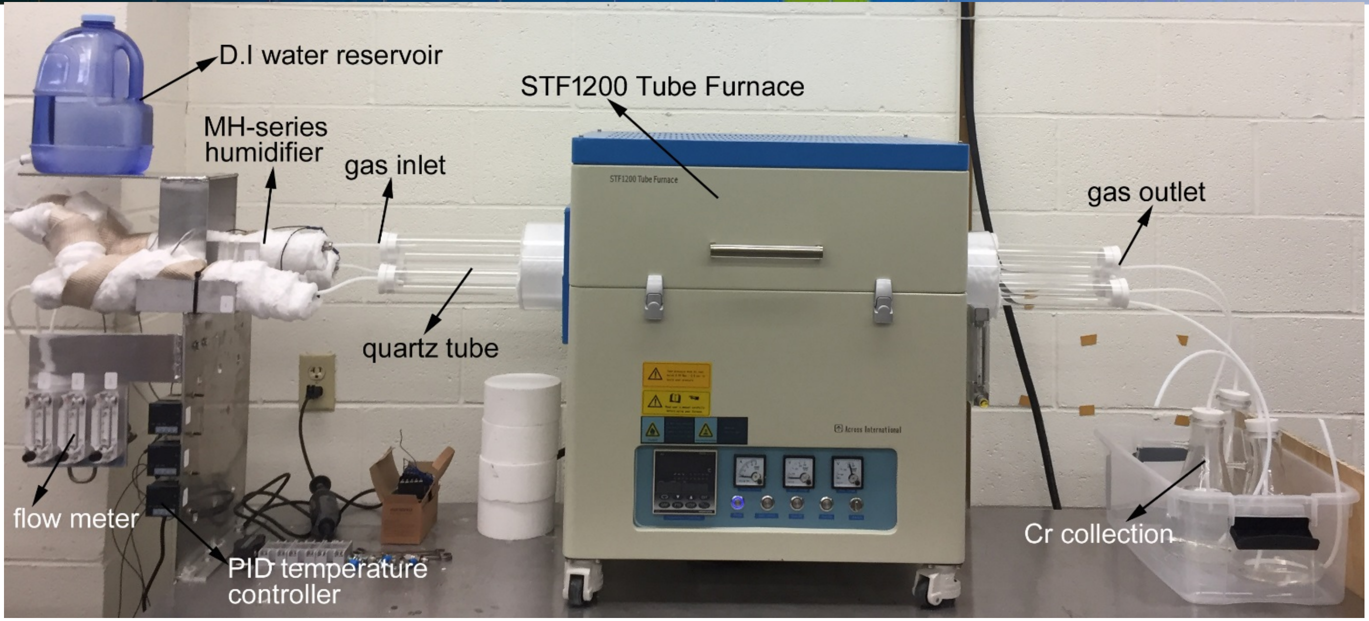
Material Compositions

Alloy	Fe	**Ni**	**Cr**	**Al**	**Nb**	Mn	Si	Mo	W	**C**	B	**other**
AFA for ≤ 800°C use												
MOD 2 OCD	51	**25**	**14**	**4**	**1**	2	0.15	2	0	**0.15**	0.01	0.5Cu
OC5	51	**25**	**14**	**3**	**1**	2	0.15	2	1	**0.1**	0.01	0.5Cu
OC4	49	**25**	**14**	**3.5**	**2.5**	2	0.15	2	1	**0.1**	0.01	0.5Cu
AFA for ≥ 850°C use												
OCF	49	**25**	**14**	**4**	**2.5**	2	0.15	2	1	**0.2**	0.01	0.5Cu
OC11	49	**25**	**15**	**4**	**2.5**	2	0.15	2	0	**0.1**	0.01	0.5Cu **Hf, Y**
35Ni	39	**35**	**18**	**3.5**	**1**	2	0.15	0	0	**0.15**	0.01	0.5Cu **Hf, Y**
Benchmark commercial Cr_2O_3-forming alloys												
310S	53	20	25	0	0	2	0.75	0.75	0	0.08	0	0.5Cu
625	5	61	22	0.2	3	0.4	0.25	8		0.04	0	0.2Ti

🟨 Rare element additive; 🟪 Benchmark samples;

- *Alloy compositions confirmed by bulk chemical analysis.*

Experimental set up and Test Matrix

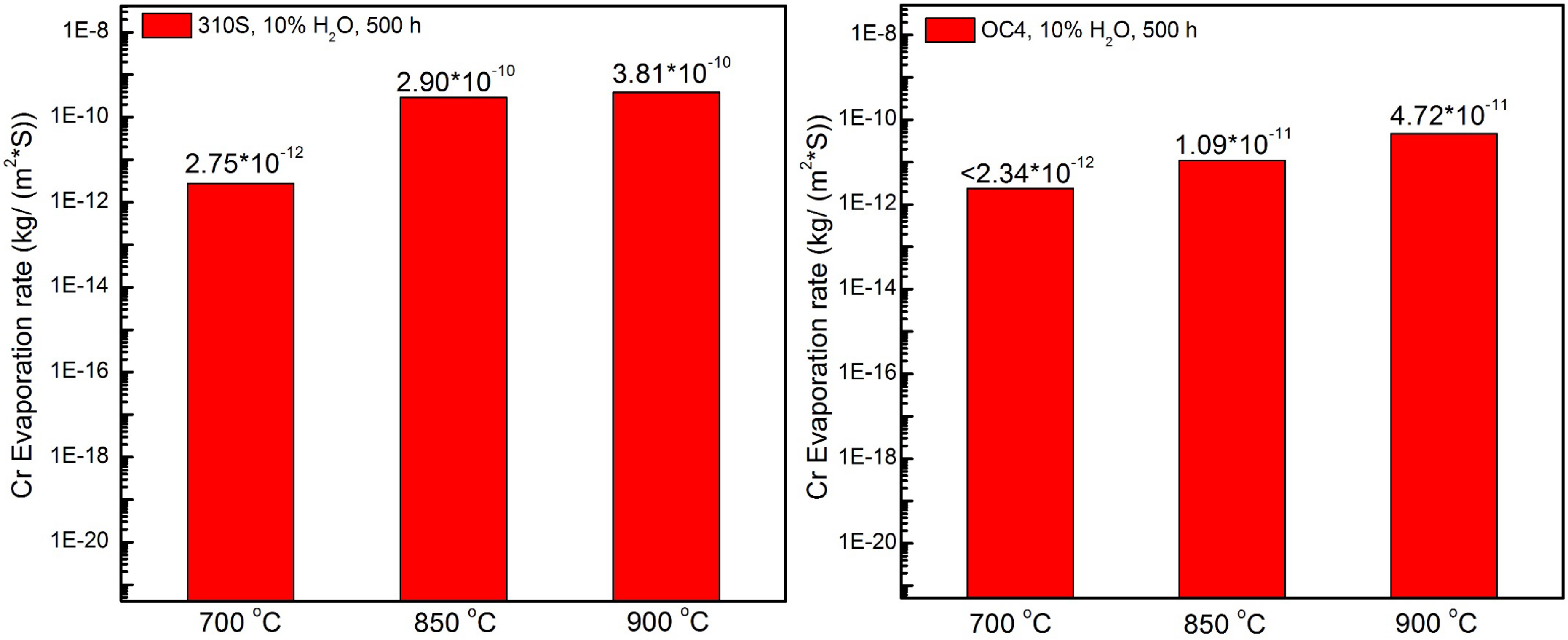


Sample size:
25 mm×20 mm×1 mm, polished up to 800 grit before use.

Fresh sample test:10% H_2O, 500 hours								
Sample	**OC4**	**OC5**	**OCF**	**310S**	**New 35 Ni**	**OC-11**	**MOD 2 OC-D**	**Alloy 625**
700 °C*	√	√	√	√	–	–	√	√
850 °C	√	in process	in process	√			—	in process
900 °C	√	—	√	√	√	√	—	√

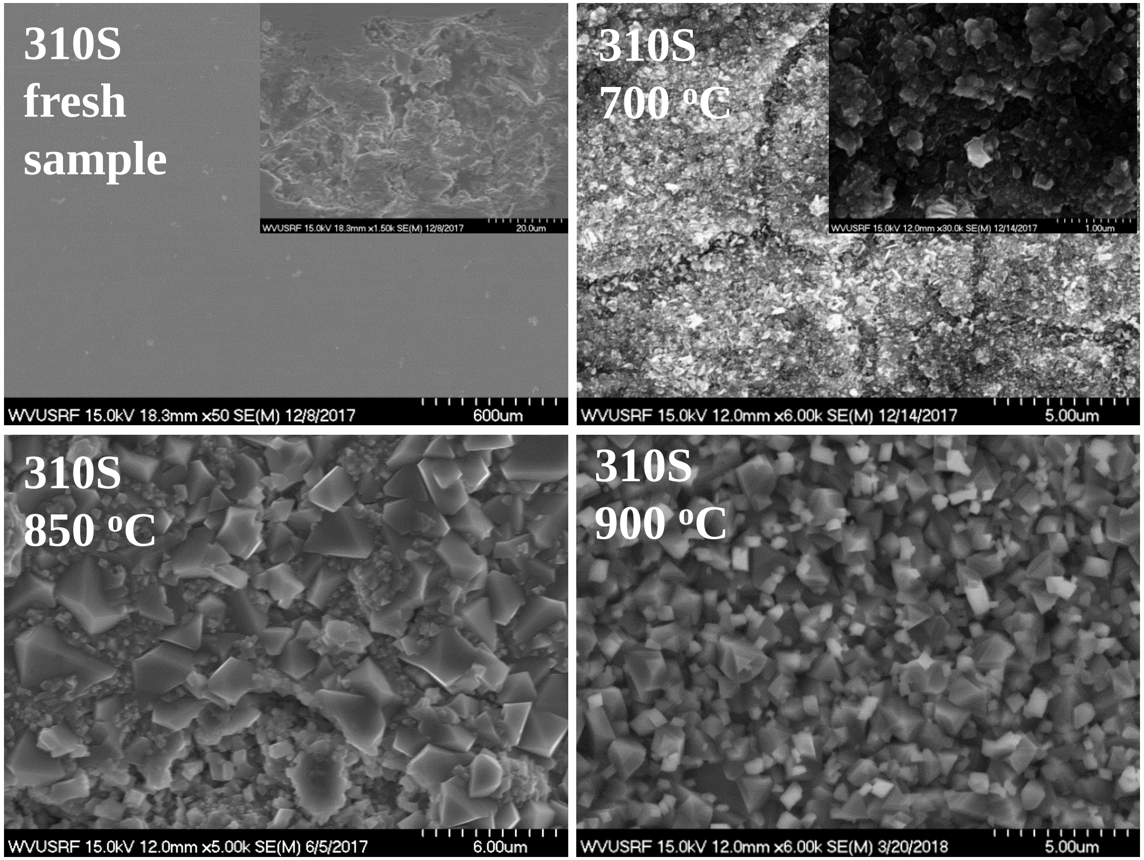
*Note: at 700°C, the Cr release was below the detection limit for the AFA alloys and Ni-base alloy 625 control.

Effect of Temperature on the Cr-Evaporation



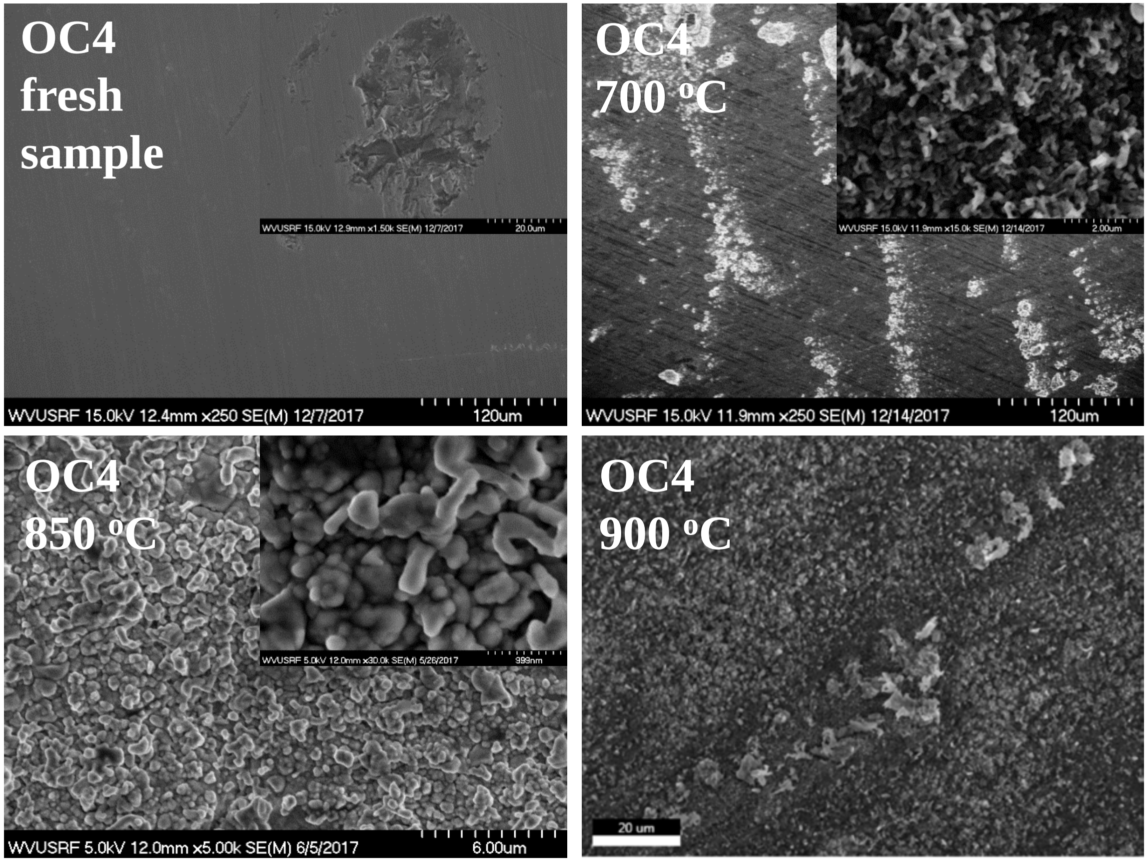
- ➢ Cr evaporation rate increased with the increase of temperature.
- ➢ The Cr release rate keeps relatively stable after 850 °C;

Effect of Temperature on the Cr-Evaporation



Microstructure vs. Temperature for 310S

Effect of Temperature on the Cr-Evaporation



OC4
fresh
sample

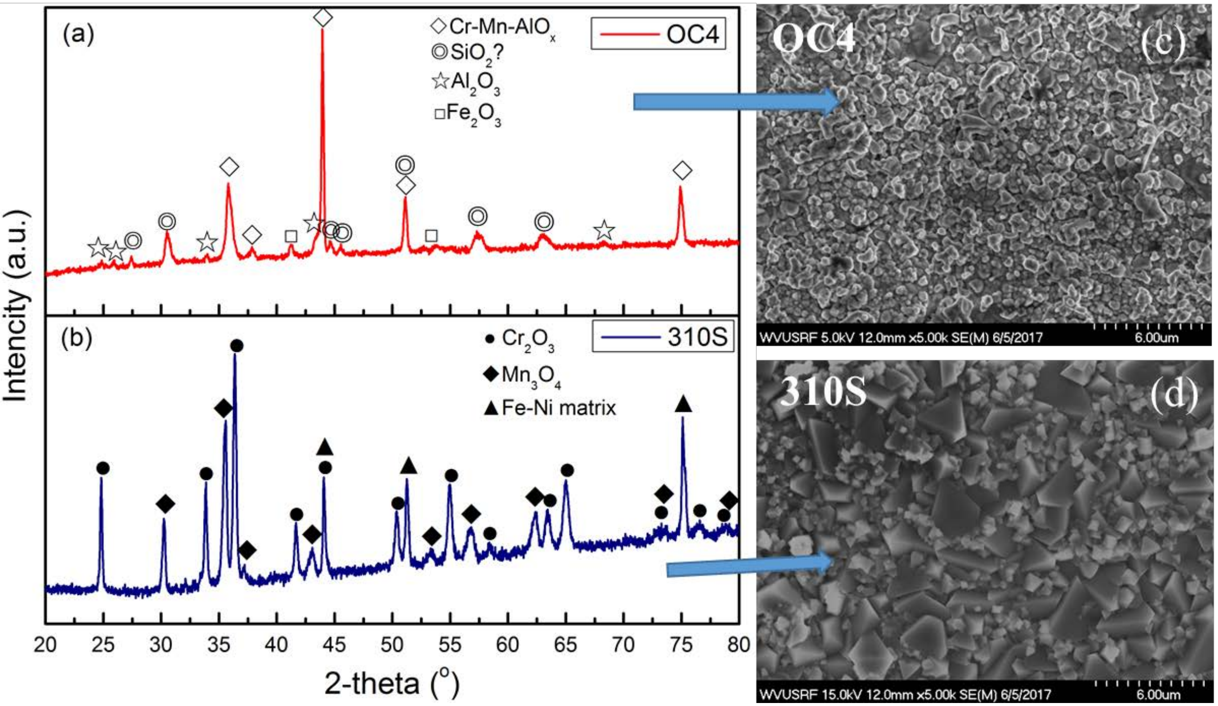
OC4
700 ºC

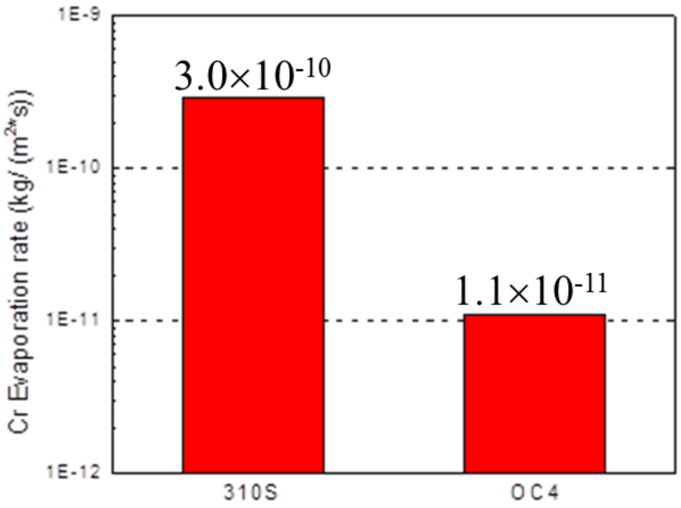
OC4
850 ºC

OC4
900 ºC

Microstructure vs. Temperature for OC4

Effect of Alloy Composition on the Cr-Evaporation



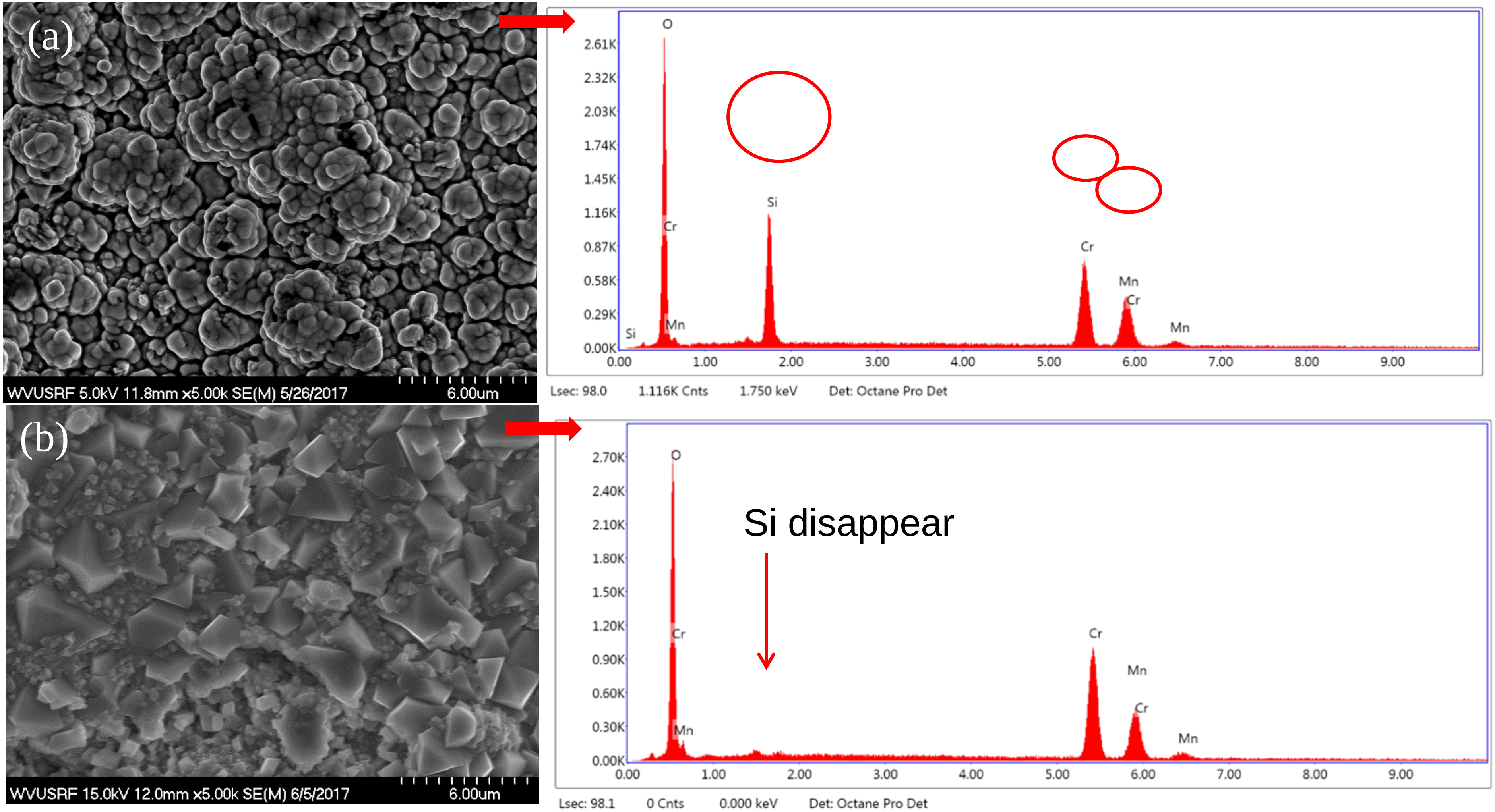


Cr evaporation rates of 310S and OC4

XRD of the corrosion films.

310s vs. OC4, at 850 ^{o}C, 10% H_2O 500 h.

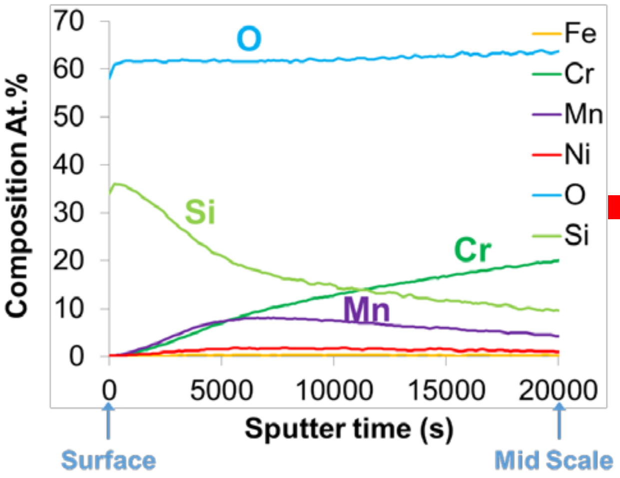
SEM and EDS Analysis for the Surface of 310S

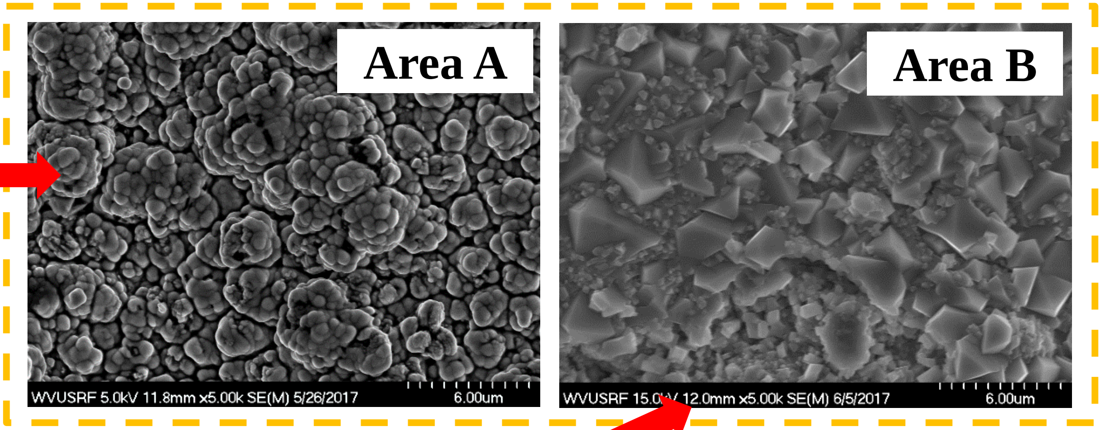


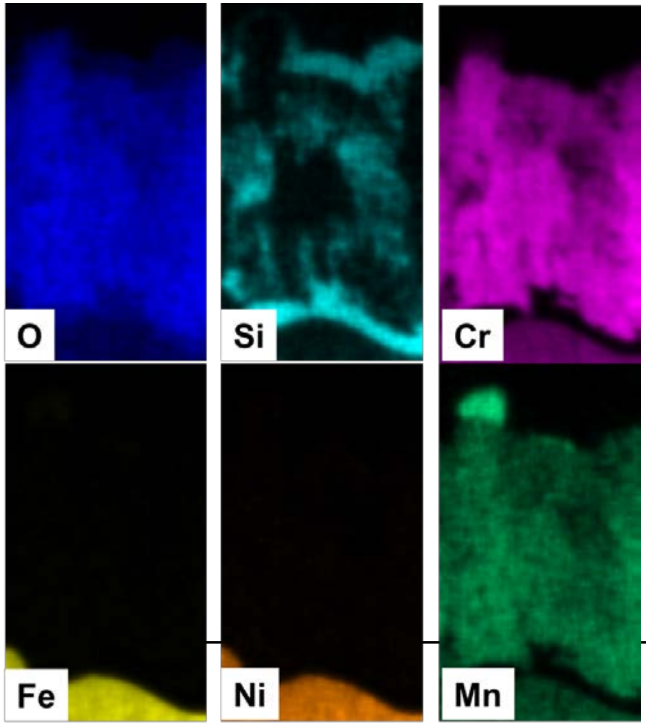
Si disappear

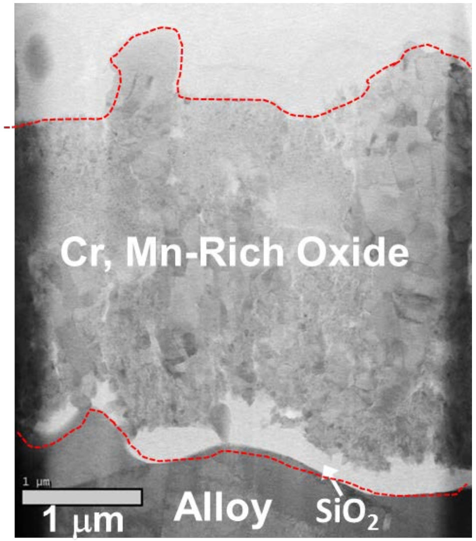
Different area SEM images for **310S** after 850 ^{o}C for 500 hours in air with 10% water vapor and EDS spectrums.

Cross section of 310S: STEM-EDX mapping and XPS depth profiling by ORNL





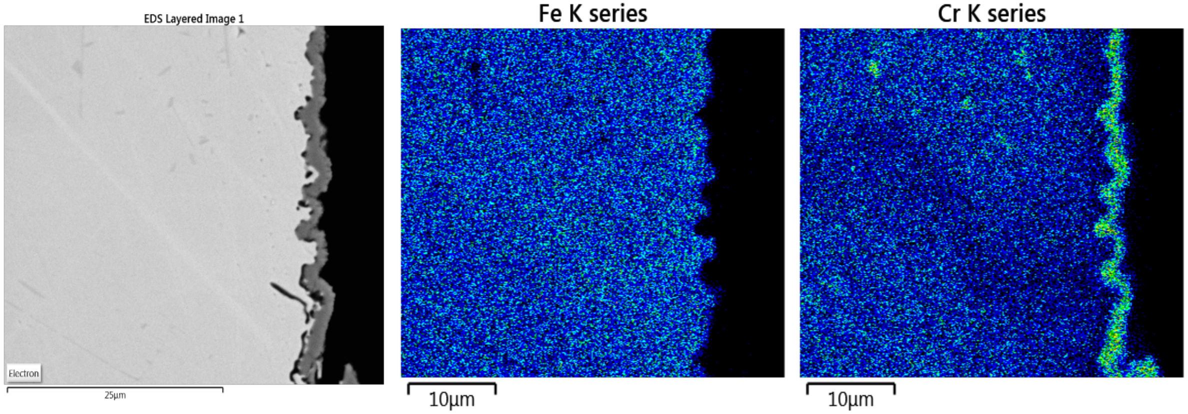


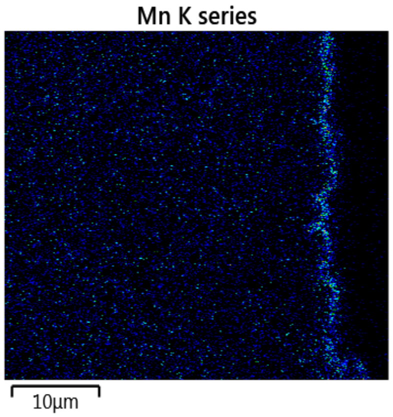


XPS depth profiling might be corresponding to the area A, while the STEM element mapping corresponding to the area B. This indicates the corrosion film is not uniformly covered on the surface. Some areas are not covered with Cr-rich oxide.

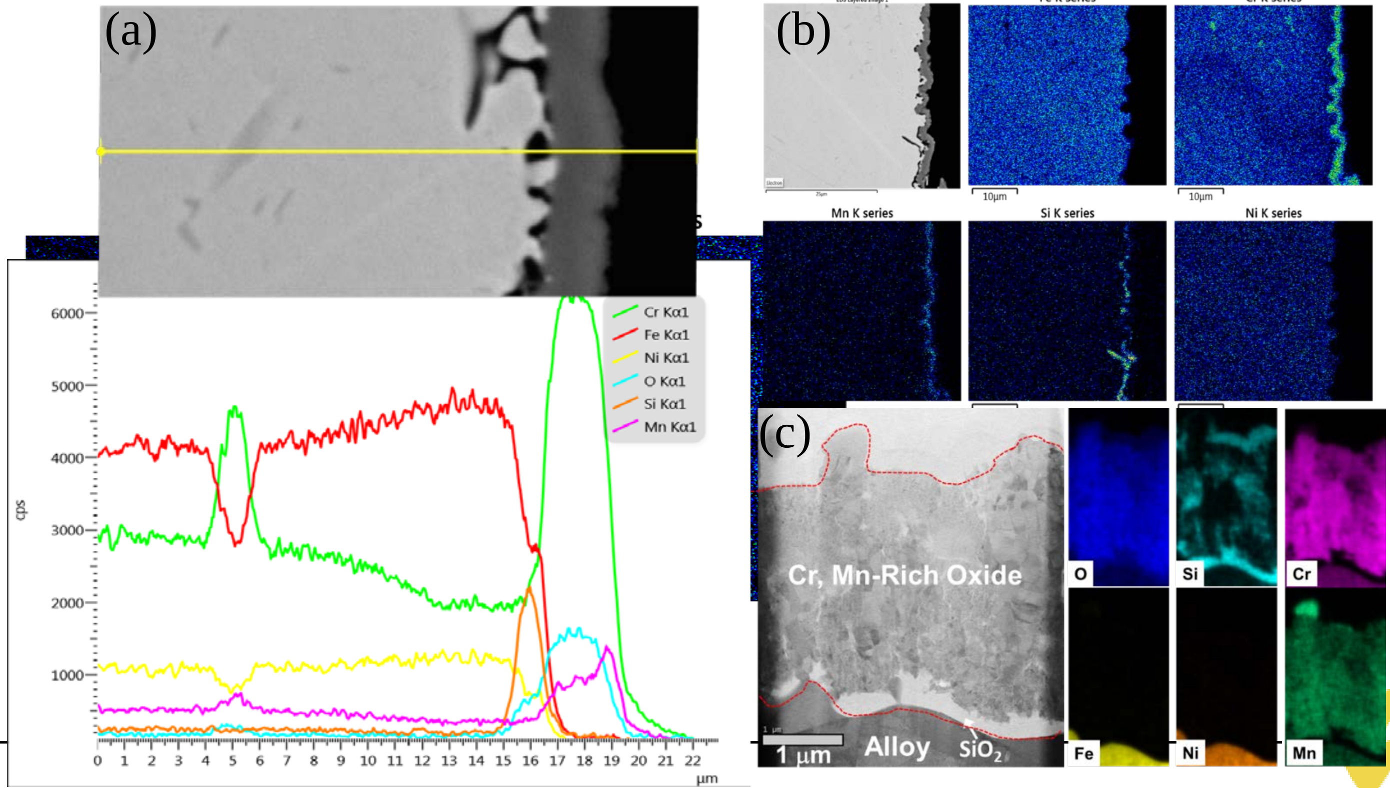
STEM Cross-Section

Cross Section of 310S: Analyzed by *FuelCell Energy*



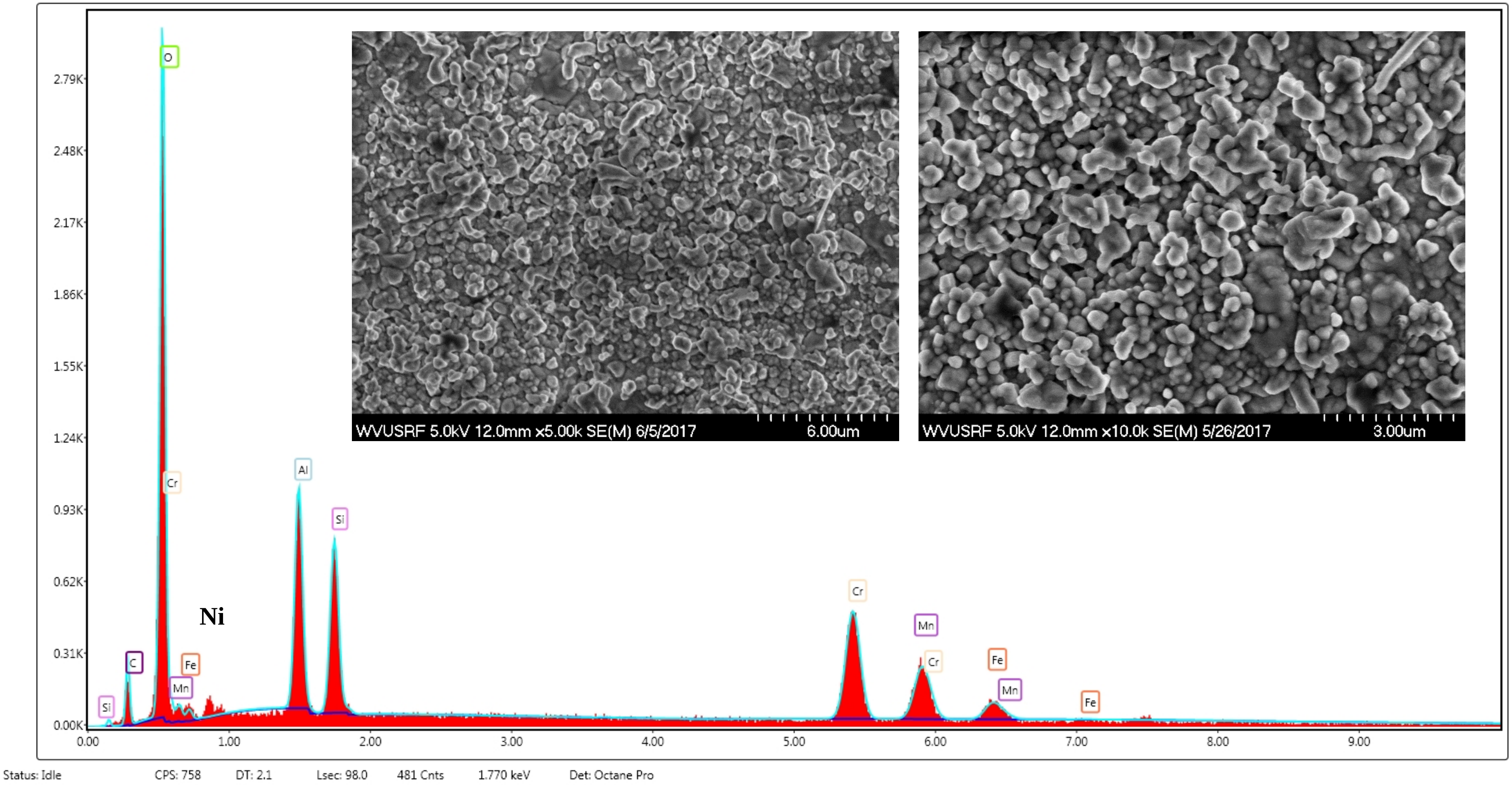


Coincides with our results that Si-containing layer is underneath the crystal Cr_2O_3 layer.



Notes: before crystal Cr_2O_3 layer forming on the top of the corrosion scale, the surface is rich of Si-containing composition.

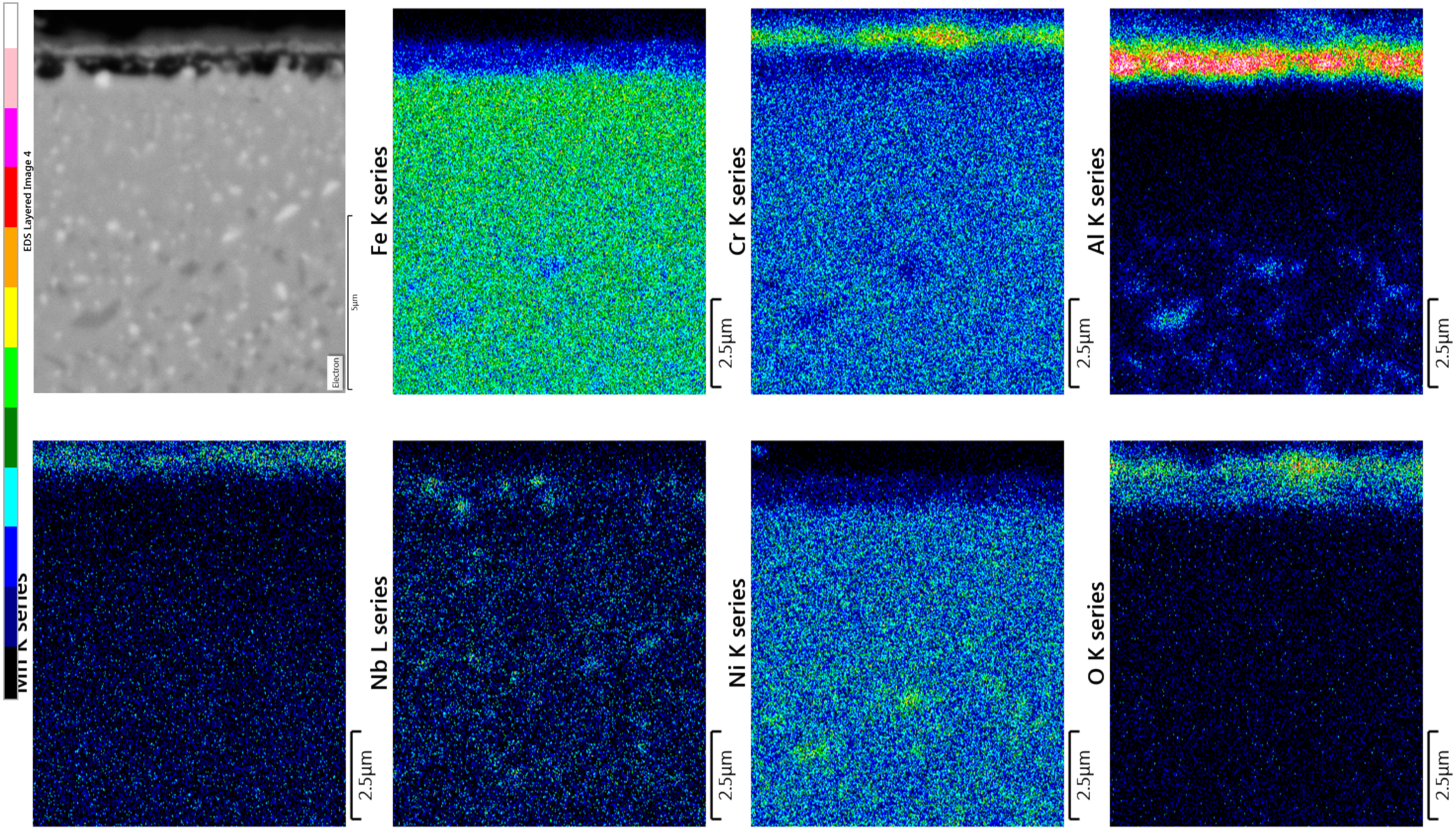
SEM and EDS Analysis for the surface of OC4



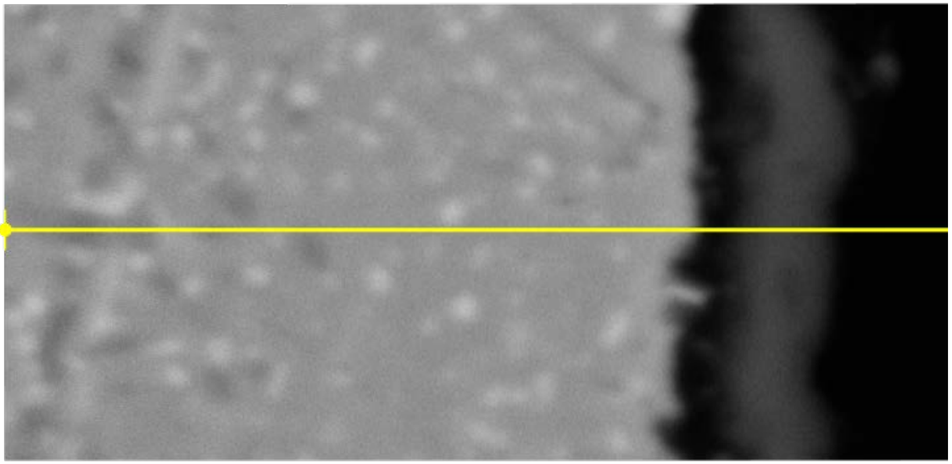
Status: Idle CPS: 758 DT: 2.1 Lsec: 98.0 481 Cnts 1.770 keV Det: Octane Pro

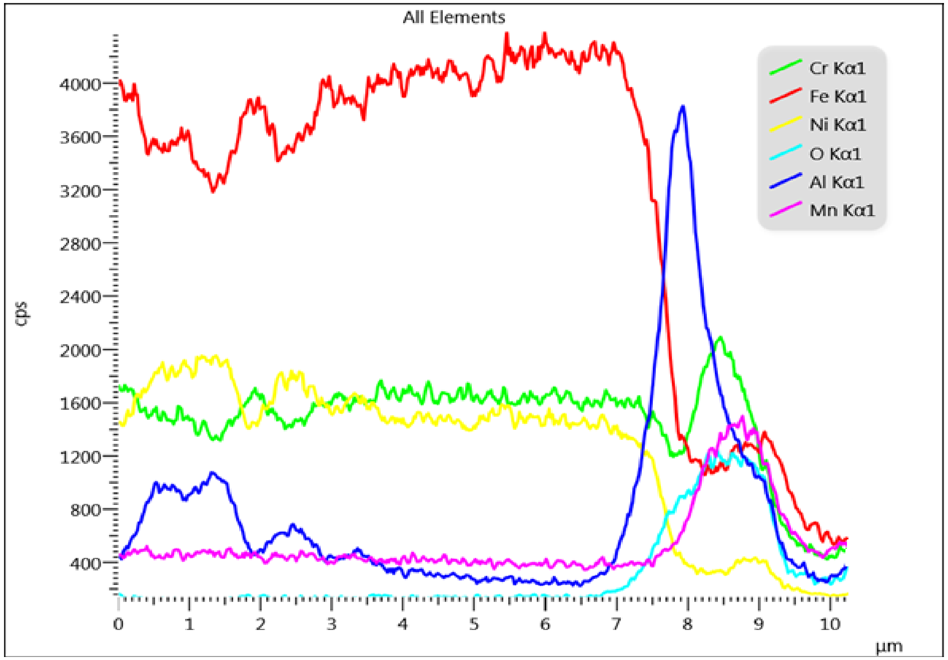
SEM images for **OC4** after 850 ^{o}C for 500 hours in air with 10% water vapor and EDS spectrums.

OC4 Cross Section: Analyzed by *FuelCell Energy*

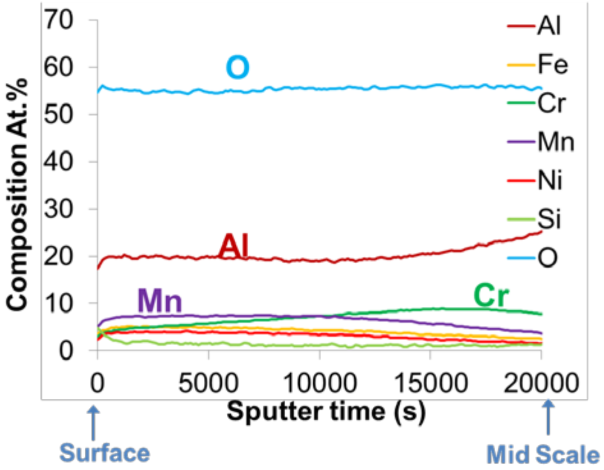


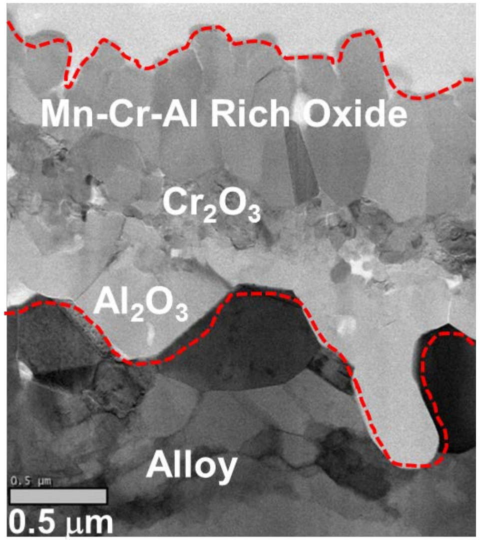
OC4 Cross Section: line scan by *FuelCell Energy*

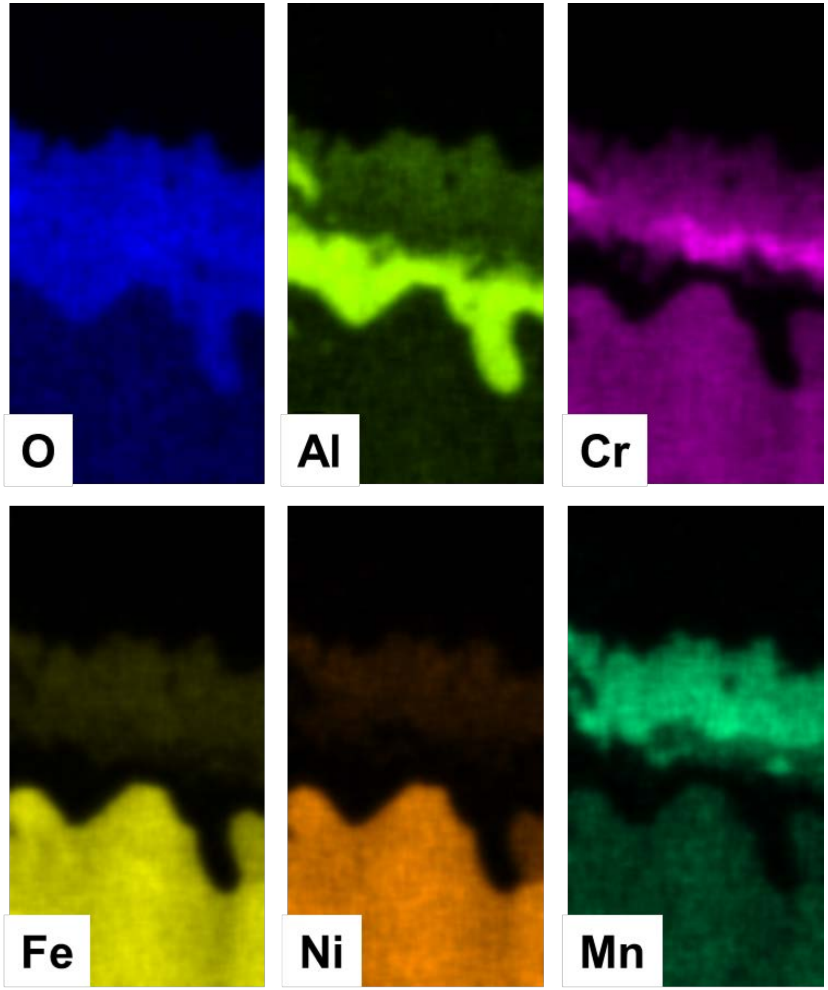




Cross Section of OC4: STEM-EDX Mapping and XPS Depth Profiling by ORNL



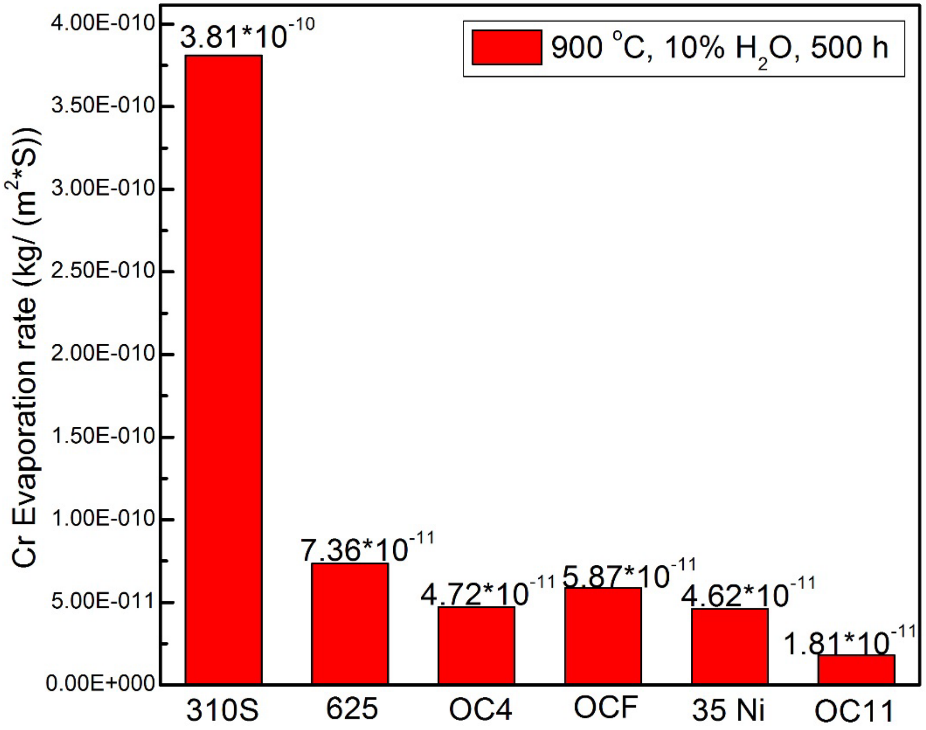




Multi-Layer scale formed on AFA OC-4 after 500 h at ~850°C in Air + 10% H_2O.

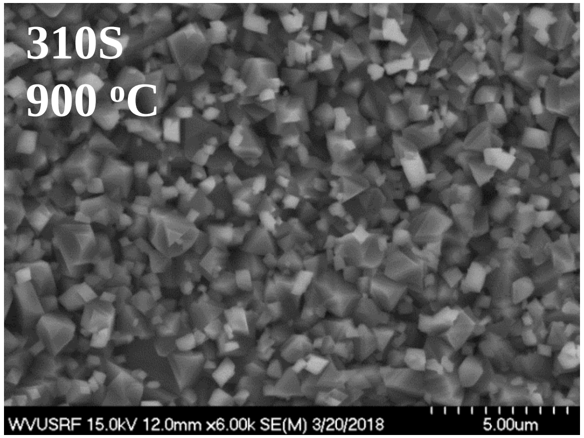
- Continuous inner Al_2O_3
- Duplex transient scale of middle Cr_2O_3 rich + outer Mn-Cr-Al oxide
- Cr release rate decrease with time after transient cut off by Al_2O_3?

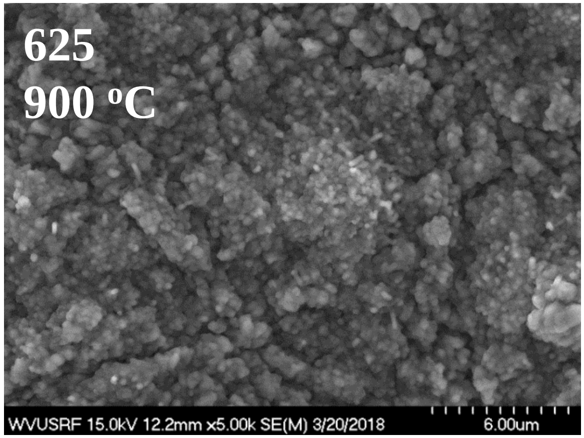
AFAs vs. Chromia-forming 310S and Ni-base Alloy 625 at 900 ^{o}C, 10% H_2O 500 h.

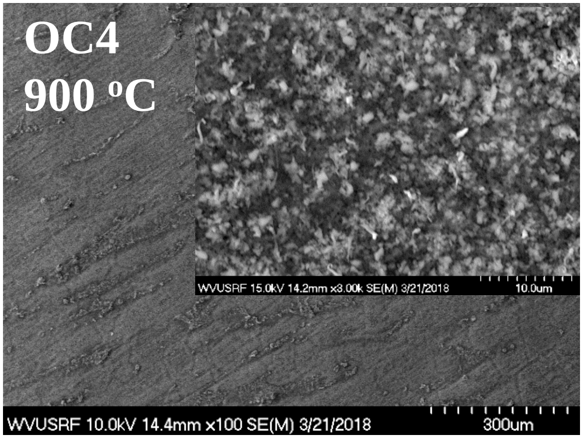


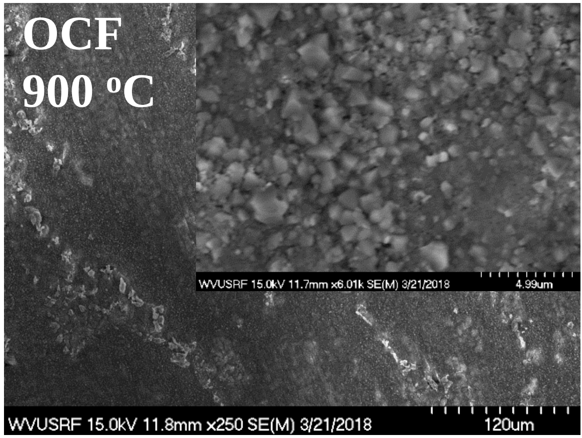
- •Little difference among AFA alloys at 900° C (all “good”, especially for OC11)
- •AFA significantly lower oxidation than Cr_2O_3 forming 310S.

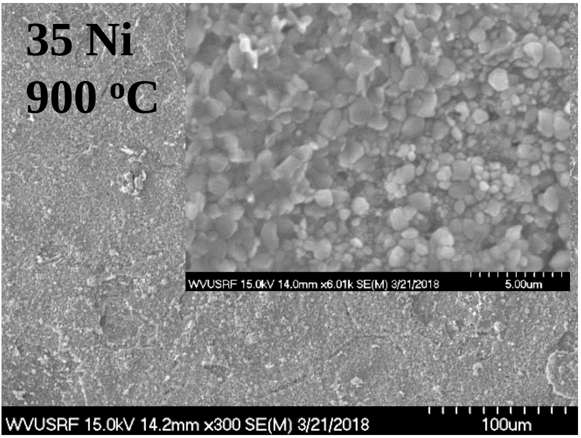
AFAs vs. Chromia-forming 310S and Ni-base Alloy 625 at 900 °C, 10% H_2O 500 h.

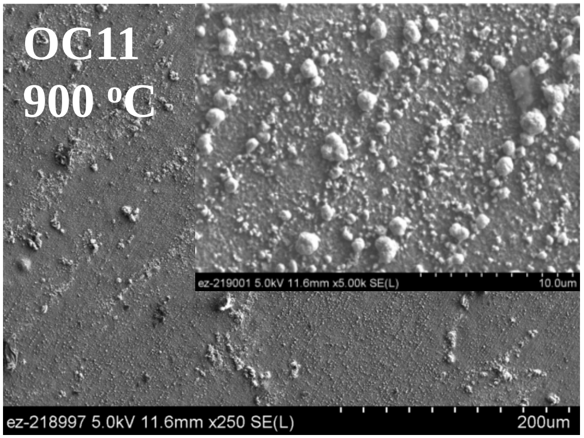








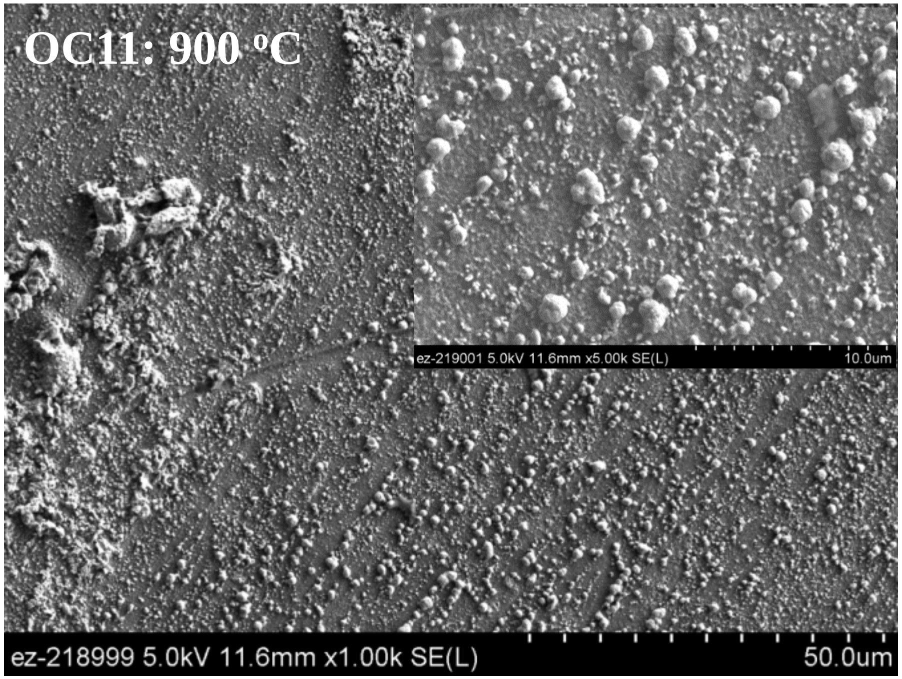




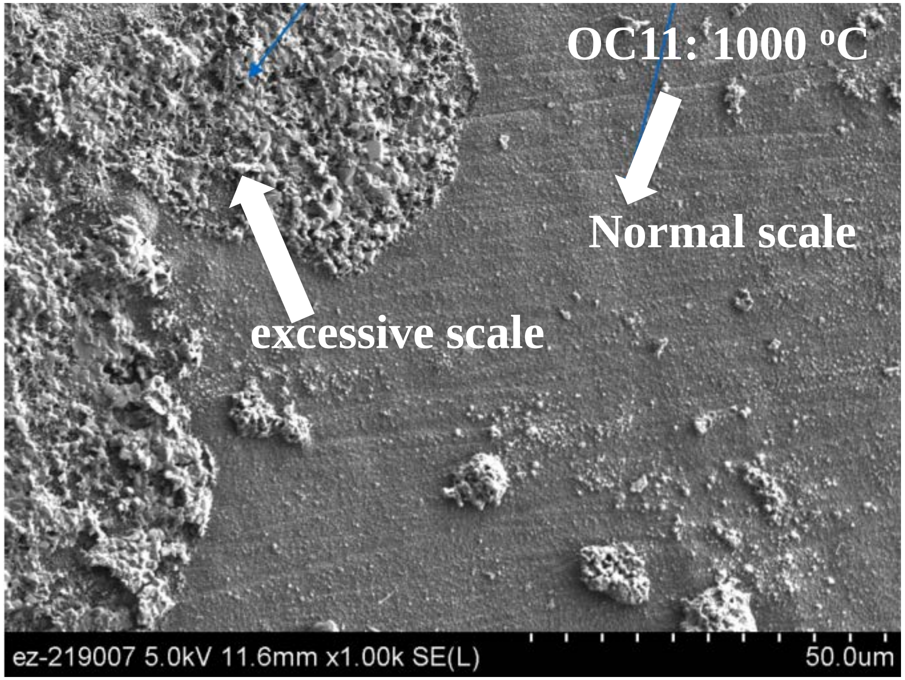
Fe-(25-35)Ni-(15-18)Cr-4Al-(1-2.5)Nb-(0.1-0.2C) base + rare element (**Hf and Y**) show highest resistance for Cr evaporation.

OC11 at Higher Temperature

OC11 (rare elements additive) show the lowest Cr evaporation rate. Thus was further investigated and characterized in detail.



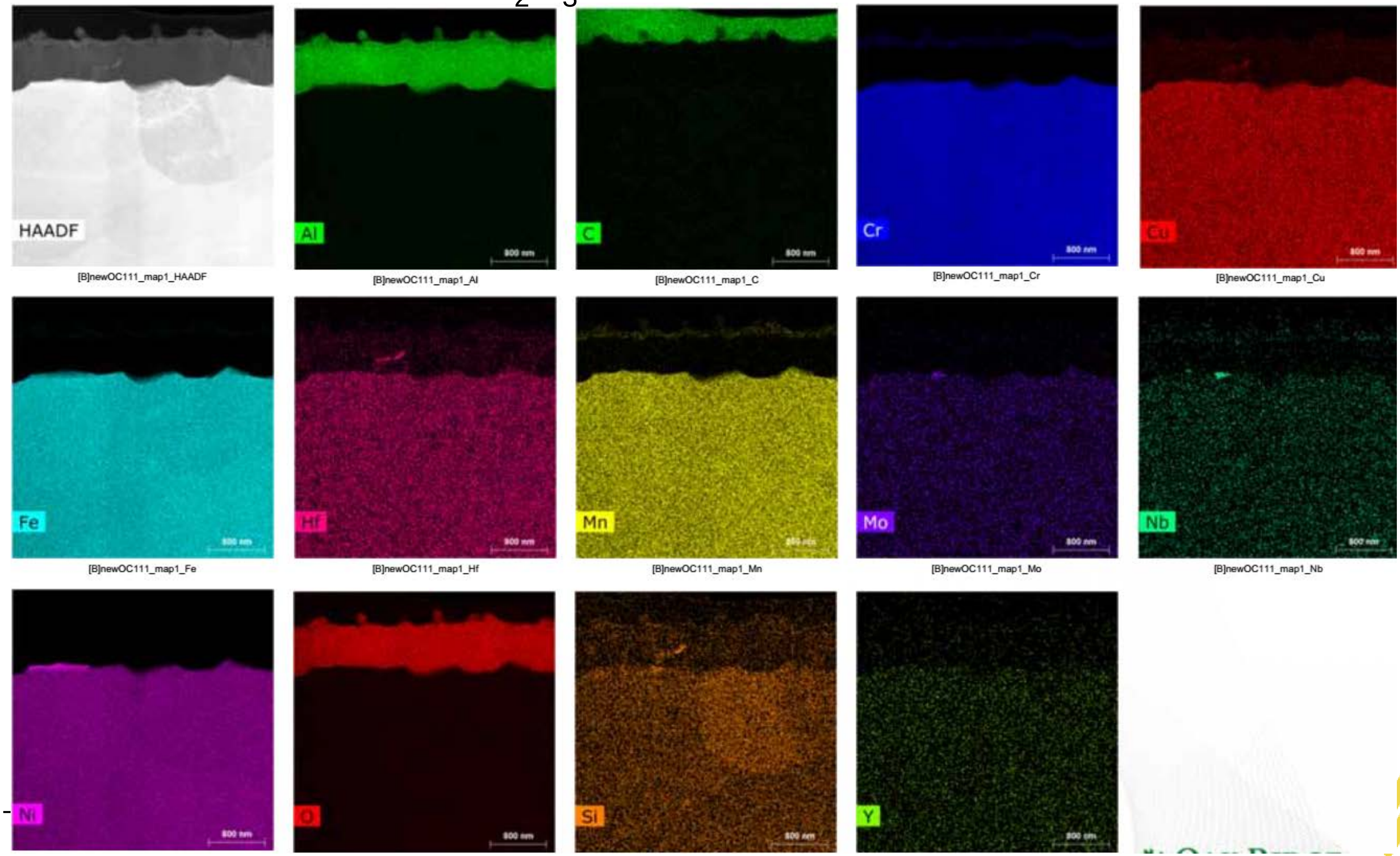
OC11-1: 900 ºC, 1000 h 10% H_2O



OC11: 1000 ºC, 1000 h 10% H_2O

STEM and EDX mapping for OC11-1 Tested at 900 ºC for 1000 h in 10% H_2O

- Minor Cr, Fe, Mn in transient ; Nb enrich at transient/Al_2O_3
- Hf enrich at columnar Al_2O_3

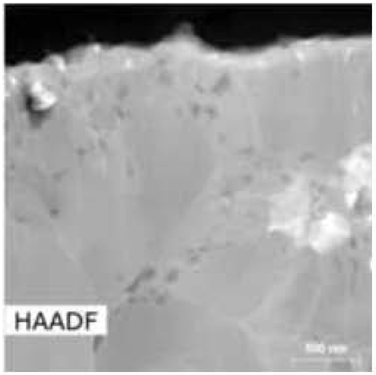


[B]newOC111_map1_HAADF [B]newOC111_map1_Al [B]newOC111_map1_C [B]newOC111_map1_Cr [B]newOC111_map1_Cu

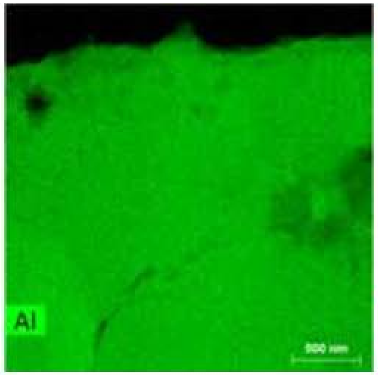
[B]newOC111_map1_Fe [B]newOC111_map1_Hf [B]newOC111_map1_Mn [B]newOC111_map1_Mo [B]newOC111_map1_Nb

STEM and EDX mapping for OC11 Tested at 1000 °C for 1000 h in 10% H_2O

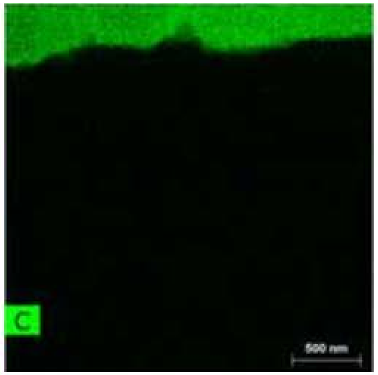
Surface and cross-section of *excessive scale*.



[C]OC11_map2_HAADF



[C]OC11_map2_Al



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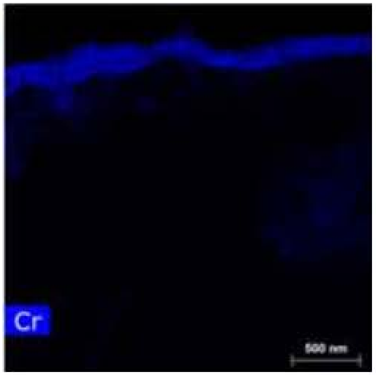

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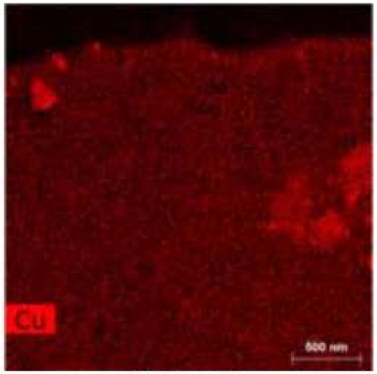

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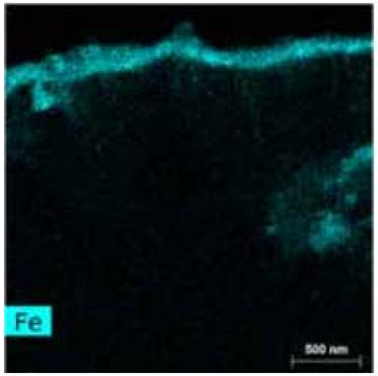

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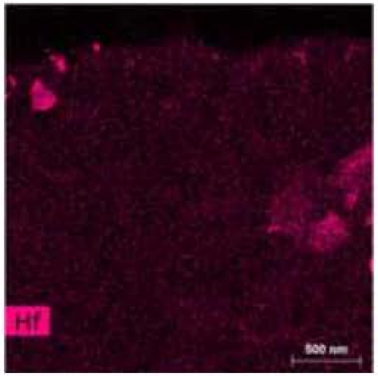

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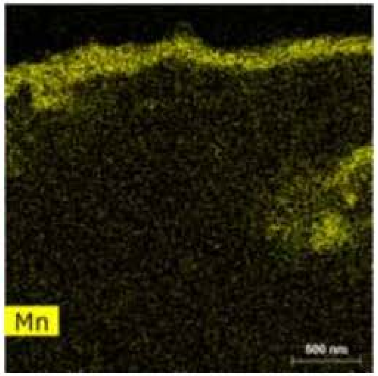

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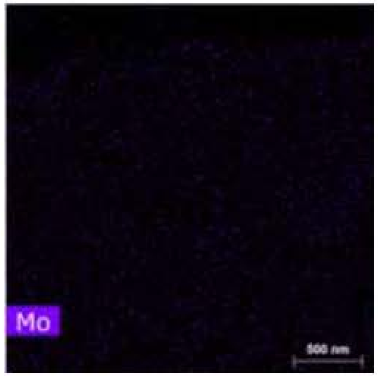

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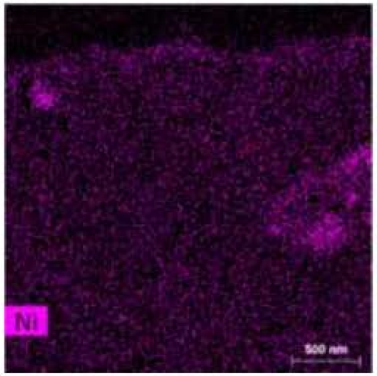

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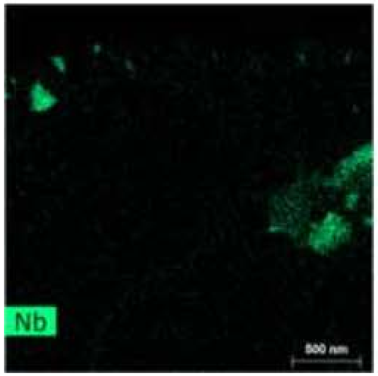
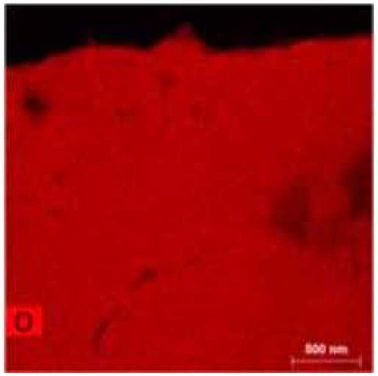
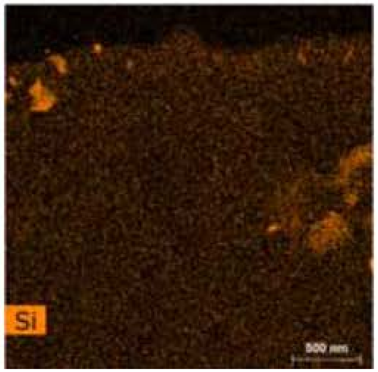
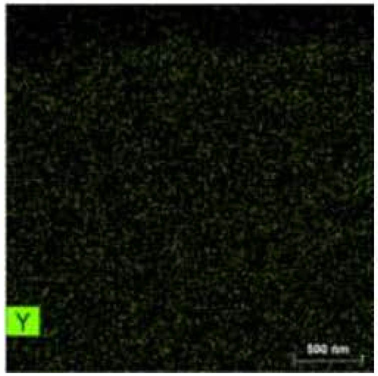
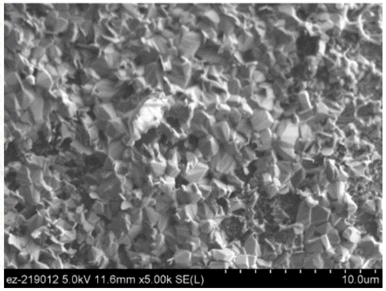






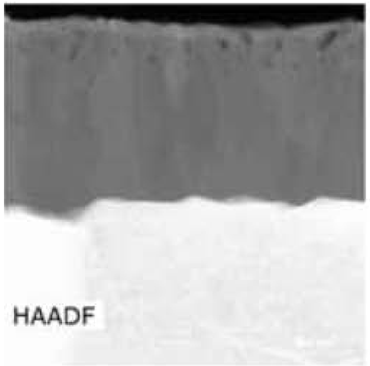


surface of excessive scale



STEM and EDX mapping for OC11 tested at 1000 ºC for 1000 h in 10% H_2O

Surface and cross-section of *normal scale*.



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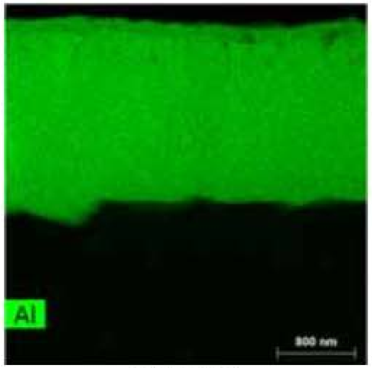

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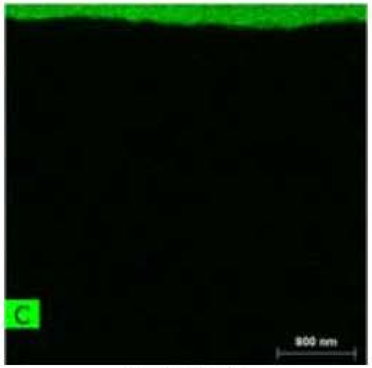

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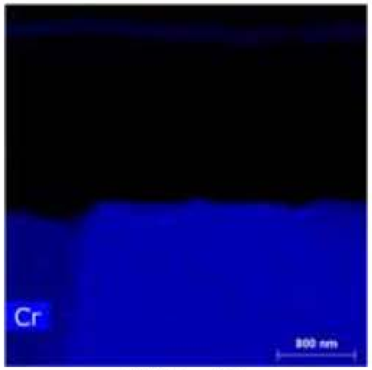

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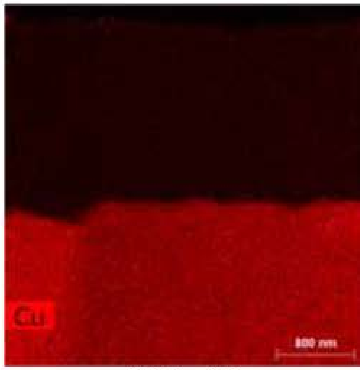
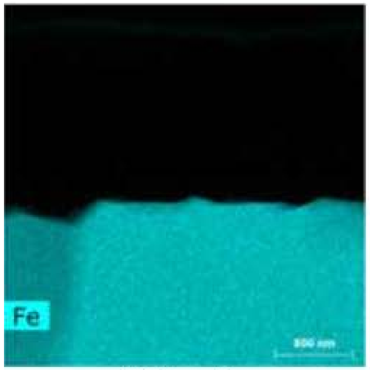


[C]OC11_map3_Cu



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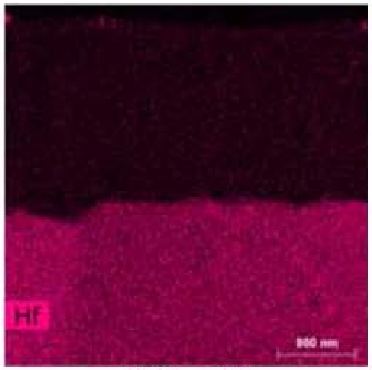

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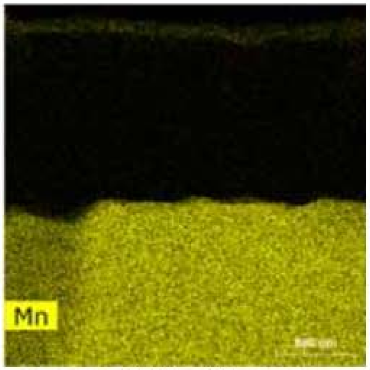

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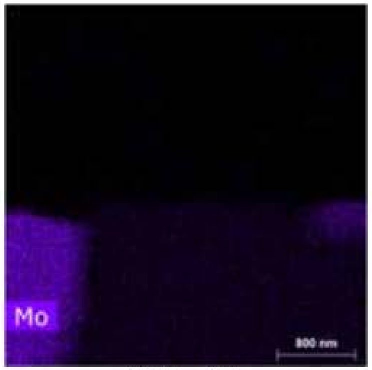

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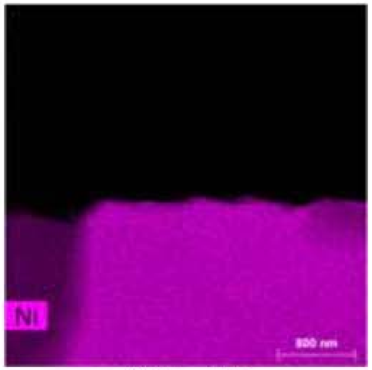

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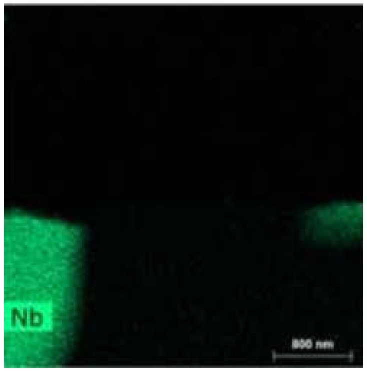
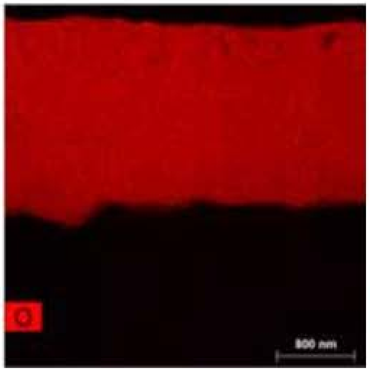
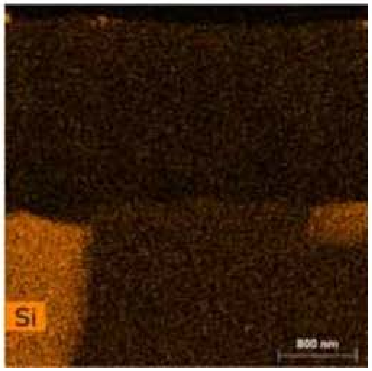
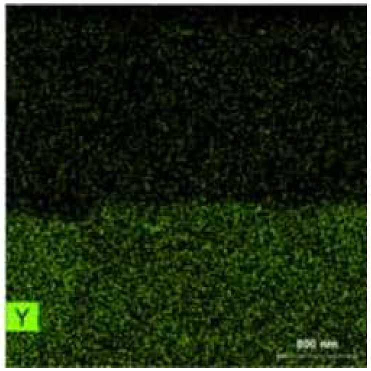
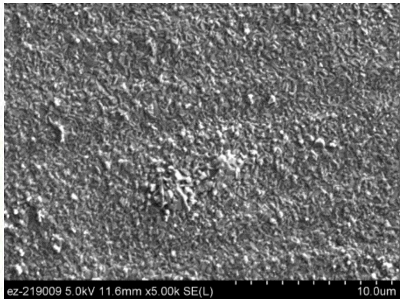




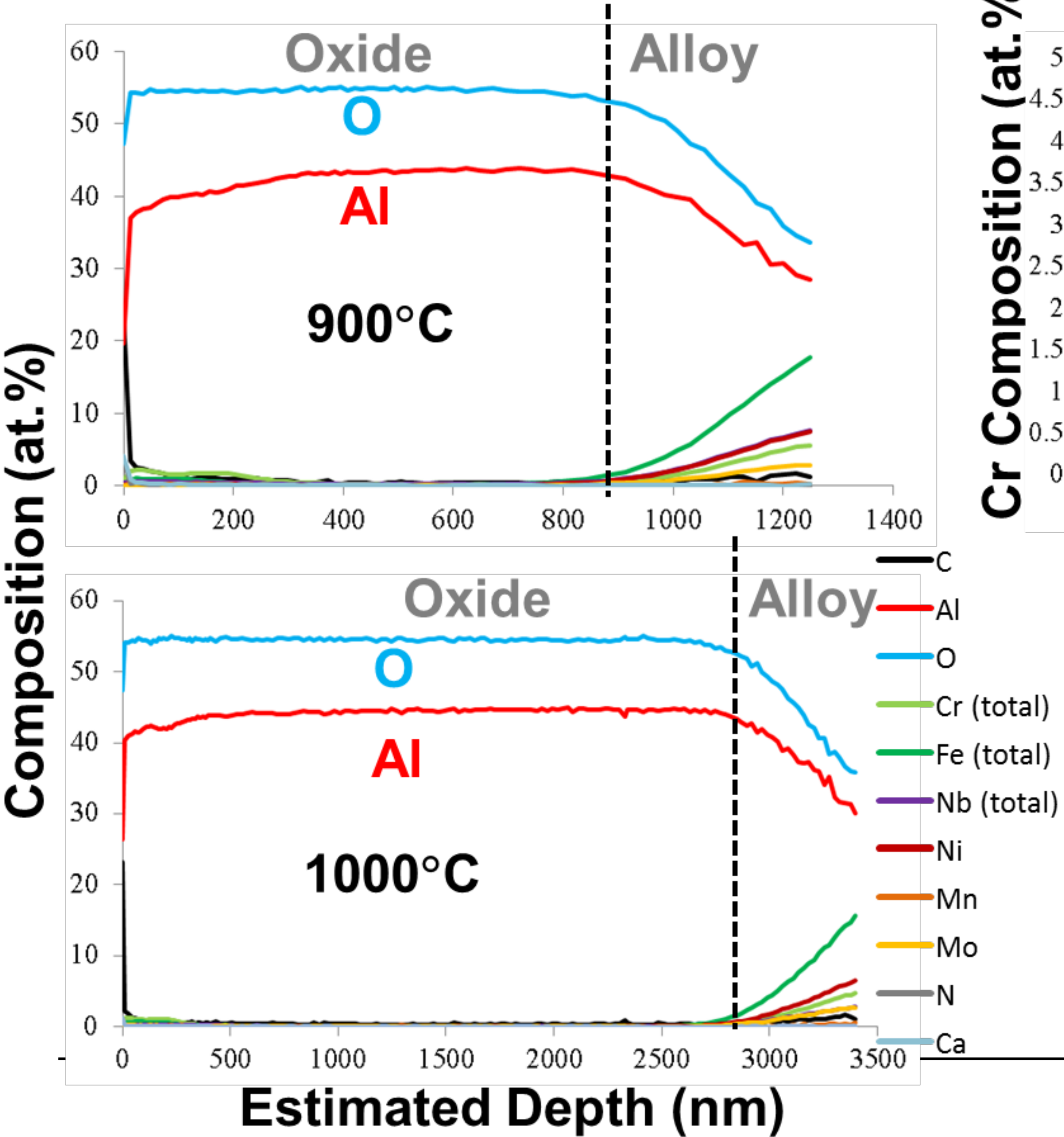


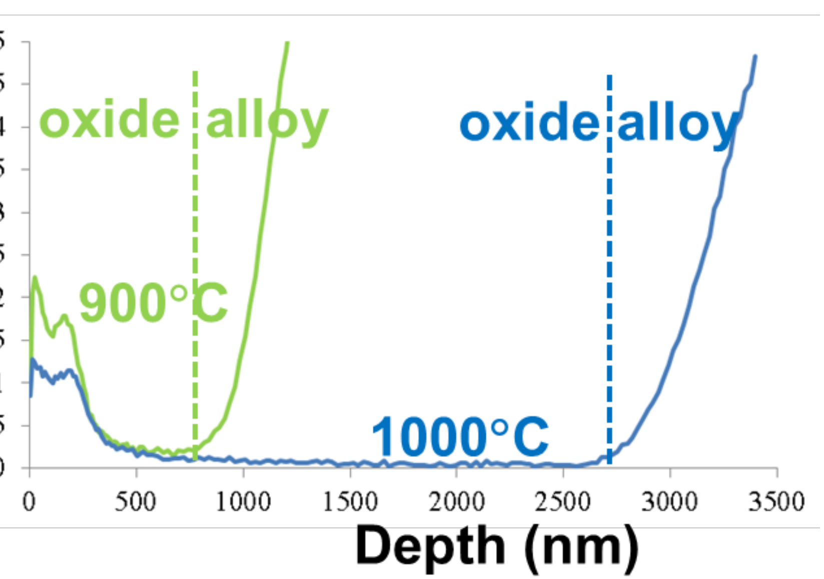


surface of normal scale



XPS Shows Al-rich Oxide on OC11 25Ni + Hf, Y AFA after 1000 h in Air with 10% H_2O

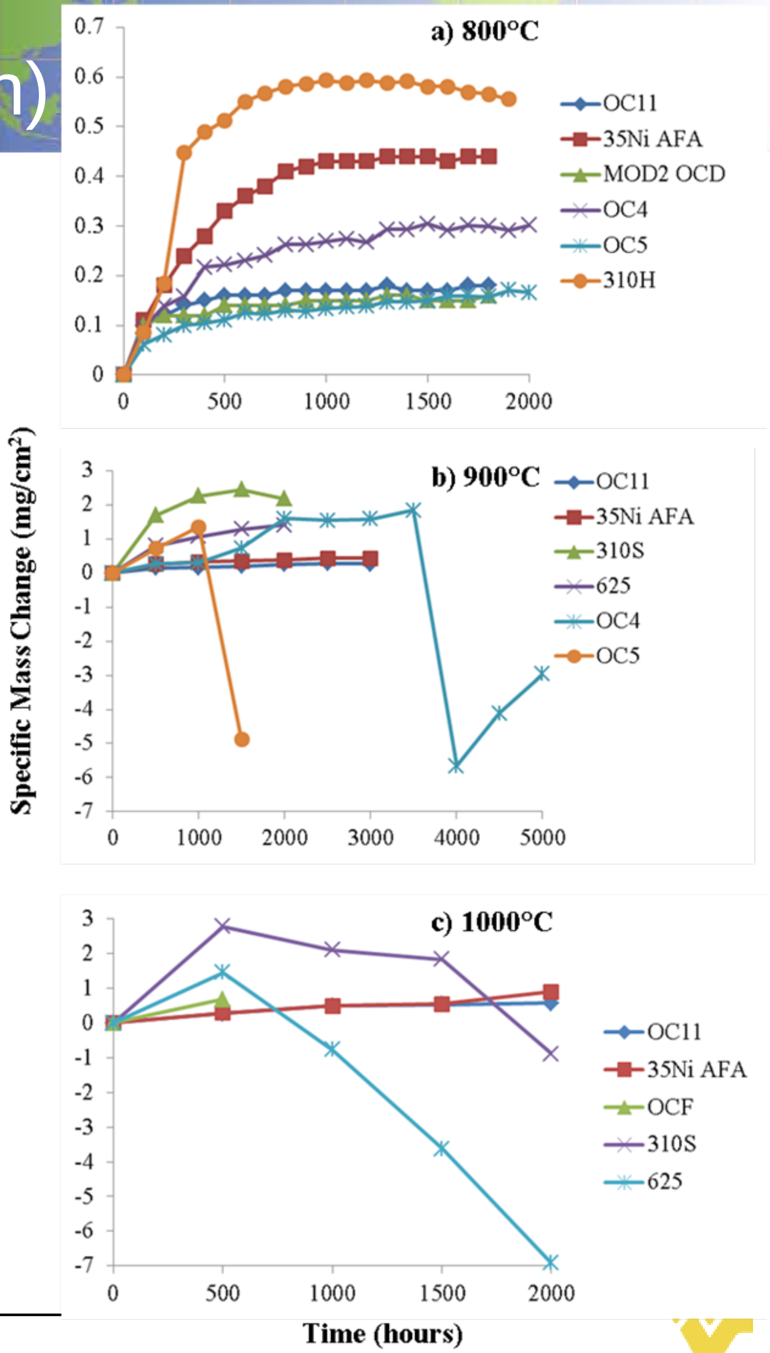




- Al_2O_3 base oxide scale with only a few % Cr at outer surface
- XPS averaged over 400 micron spot

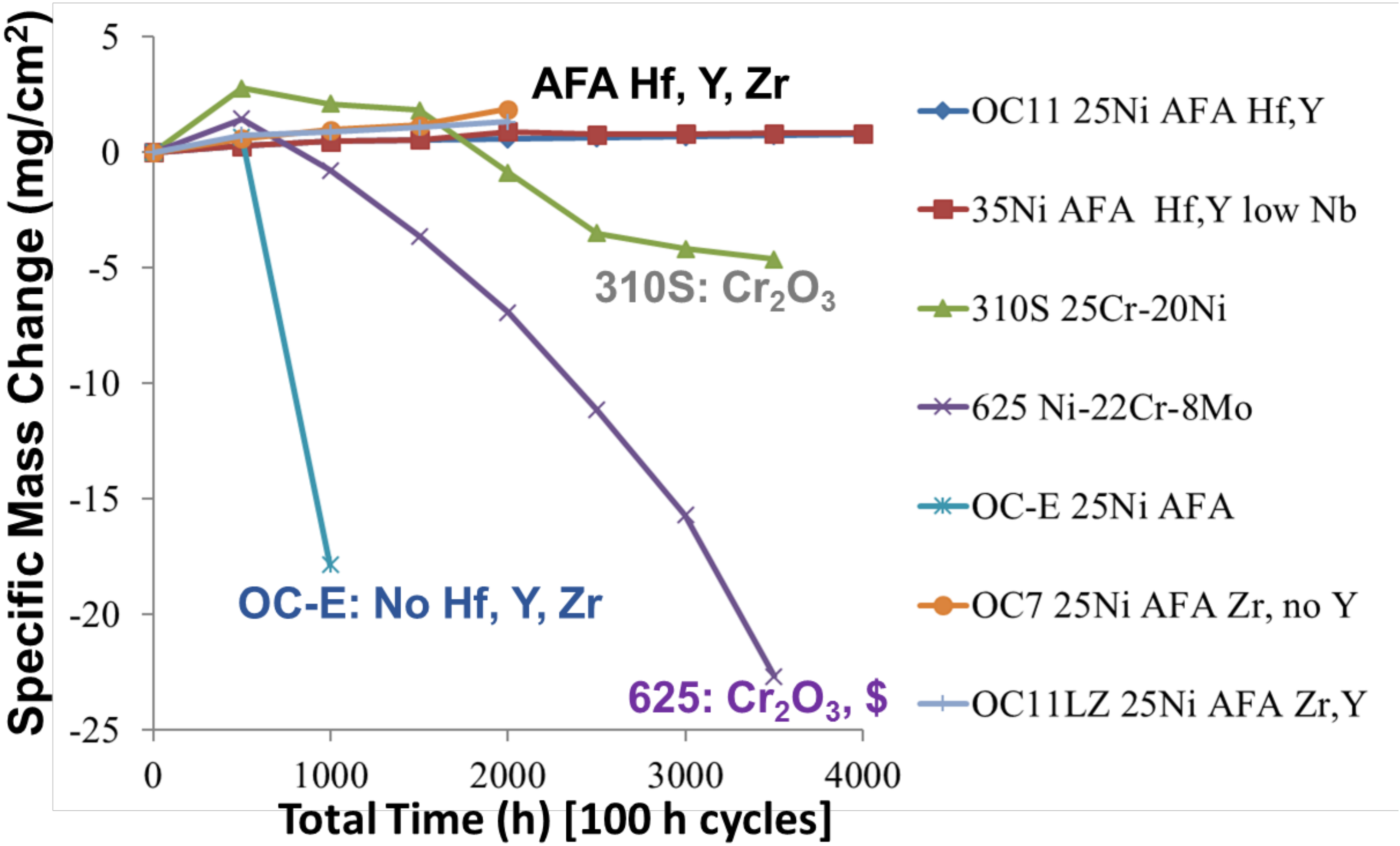
Oxidation kinetics (mass evolution)

- ➢ Low oxidation rates were exhibited by the AFA alloys at 800 ºC, whereas Cr-forming 310S stainless steel exhibited higher oxidation behavior;
- ➢ At 900 ºC, the OC11 and 35Ni AFA alloys exhibited significantly lower Cr evaporation rate than 310S and 625. AFA alloys OC4 and OC5 transitioned to scale spallation and mass loss.
- ➢ At 1000 ºC, the 310S and 625 transitioned to scale spallation and mass loss, whereas the OC11 and 35Ni AFA alloys exhibited low rates of oxidation consistent with protective alumina scale formation.
- ➢ AFA alloys exhibited significantly greater oxidation resistance than the Cr-forming 310 and 625 alloys in air + H_2O environments of interest for SOFC’s.



Oxidation Kinetics Analysis for the Cr-Evaporation

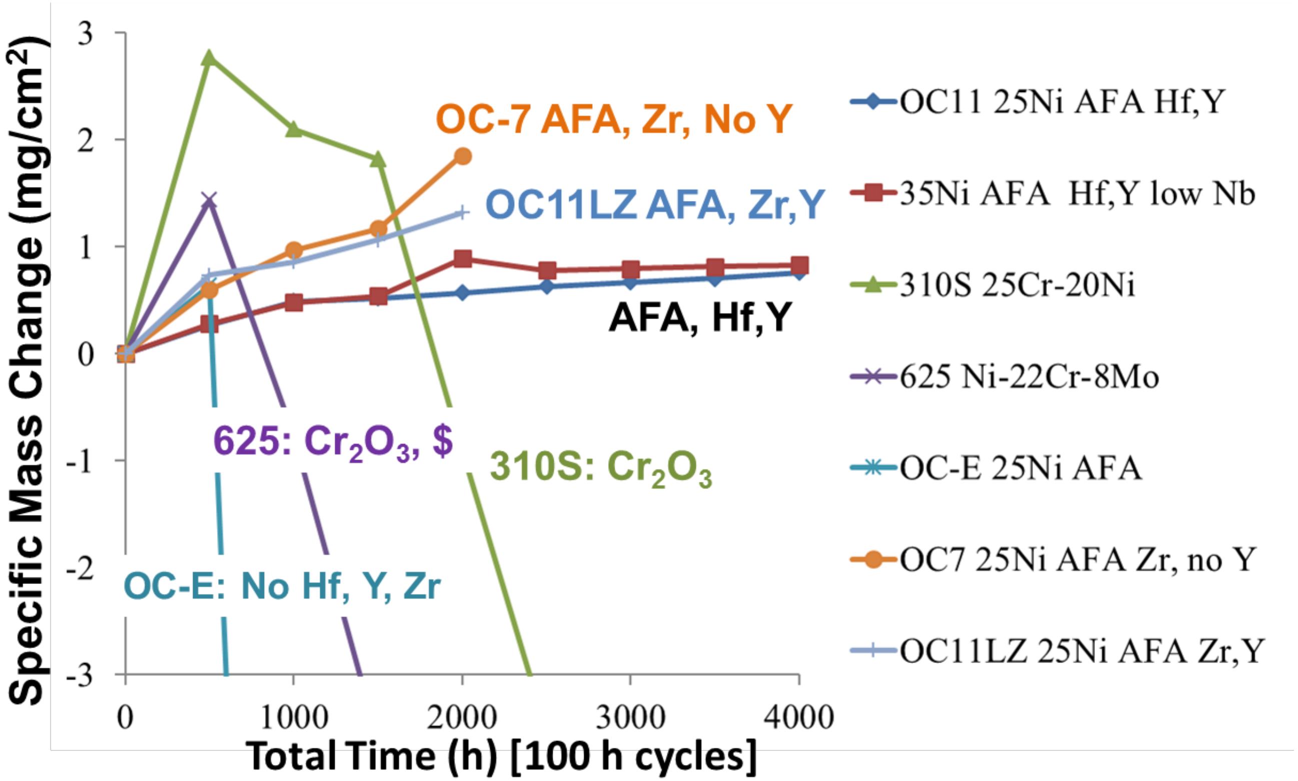
25Ni AFA with Hf, Y, Zr Show Promising Oxidation Behavior at 1000 ° C in Air + 10% H_2O



- Oxide scale spallation by Cr_2O_3 formers 625 and 310S
- AFA without Hf, Y, Zr do not form protective Al_2O_3 at 1000° C

Oxidation Kinetics Analysis for the Cr-Evaporation

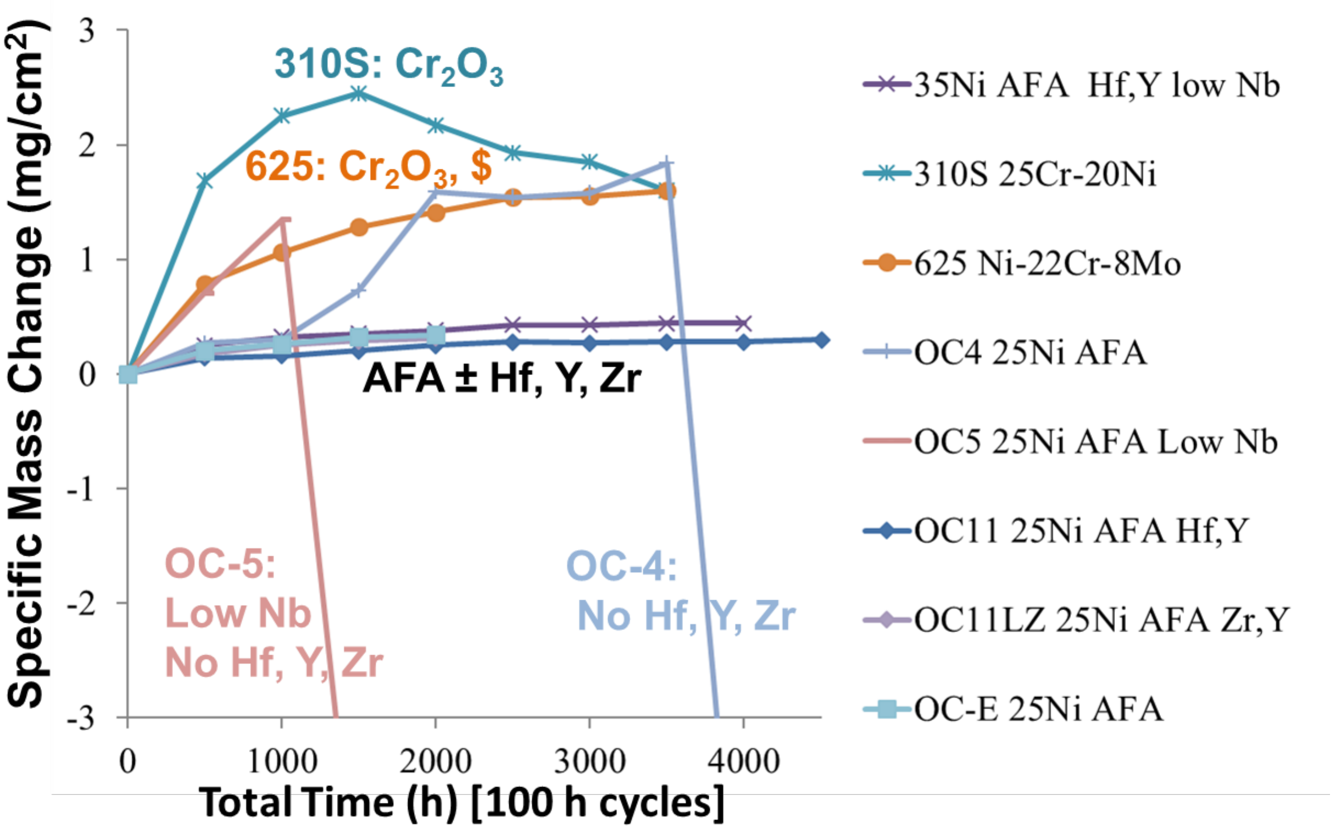
25Ni AFA with Lower Cost Zr Shows Promising Oxidation Behavior at 1000° C in Air + 10% H_2O



- Co-optimization for cost and performance in progress
    - ➢ likely can use Zr instead of Hf (Hf better but differences appear small)
    - ➢ determination if can drop Y for oxidation ≤ 950-1000° C in progress

Oxidation Kinetics Analysis for the Cr-Evaporation

25Ni AFA with Zr Matches Hf AFA Alloy Oxidation Behavior at 900° C in Air + 10% H_2O

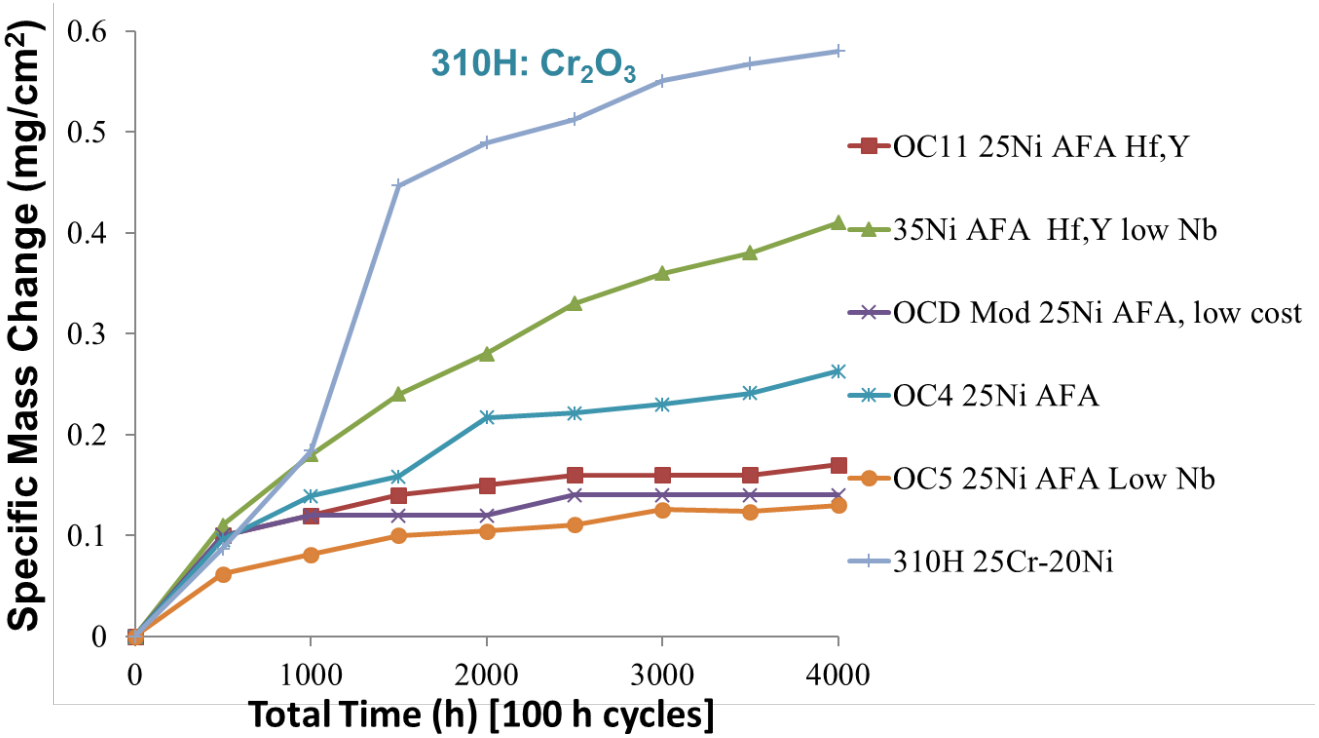


- •Hf, Y, Zr -free OC-E grade (higher Al, Cr) also shows promise at 900° C

- •AFA significantly slower oxidation than Cr_2O_3 forming 625 and 310S

Oxidation Kinetics Analysis for the Cr-Evaporation

Hf, Y, Zr and Higher Nb Not Needed for 25Ni AFA at 800° C in Air + 10% H_2O



- Slow oxidation among AFA alloys at 800° C (all "good", differences minor)
- AFA significantly slower oxidation than Cr_2O_3 forming 310H

Conclusions – Phase I

- The 6 evaluated AFA alloy variations exhibited superior oxidation resistance to benchmark chromia-forming alloys at 800-1000°C in the simulated SOFC BOP environment of air + 10% H_2O for 2000-3000 hours accumulated (testing ongoing).

- Significantly reduced Cr release rates were observed in 500 hour testing from 700-900°C; with, for example, a nearly 30x Cr release rate reduction for AFA alloy OC4 at 850°C compared to benchmark Cr_2O_3-forming 310S stainless steel.

Sample	OC4	OC5	OCF	New 35 Ni	OC-11	MOD 2 OC-D	310S	Alloy 625
700 °C	$< 2.34 \times 10^{-12}$	$< 2.14 \times 10^{-12}$	$< 2.16 \times 10^{-12}$	—	—	$< 2.14 \times 10^{-12}$	2.75×10^{-12}	$< 2.20 \times 10^{-12}$
850 °C	1.09×10^{-11}	In progress	In progress	*	*	—	2.9×10^{-10}	In progress
900 °C	4.72×10^{-11}	—	5.87×10^{-11}	4.62×10^{-11}	1.81×10^{-11}	—	3.81×10^{-10}	7.36×10^{-11}

Future (Ongoing) Work – Phase II

- Begin optimization and down-select of 2 grades of AFA alloys for SOFC BOP testing :
  - 1 grade for ≤ 800°C operation
  - 1 more highly-alloyed grade for 850-950°C operation.
- Long-Term Cr-release Testing to understand the kinetics
- On-cell testing to understand the degradation of cells as function of Cr
- Working with Industrial Partners (Bloom Energy & Fuel Cell Energy) on manufacturing and testing AFA components in industrial environments

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Acknowledgement

- **NETL-SOFC Team**: Shailesh Vora, Heather Guedenfeld, Joel Stoffa, Jason Lewis etc.

- **Co-PIs:** Mike Brady (Oak Ridge National Lab),
  Hussein Ghezel-Ayagh, Ali Torabi (FCE)

- **Industrial Partner:** Samuel Kernion (Carpenter)

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