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

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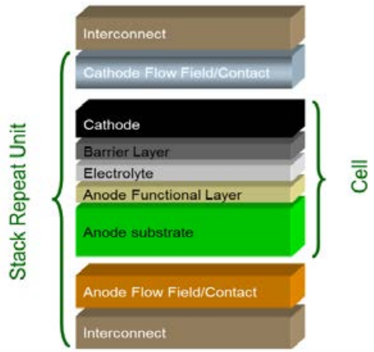
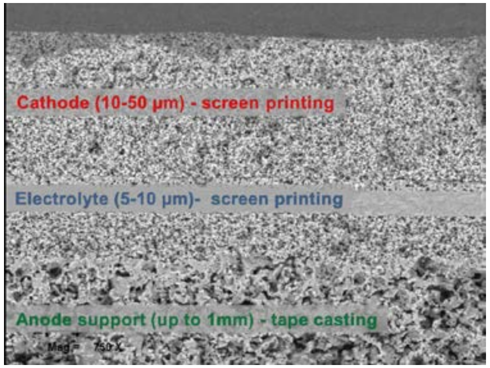
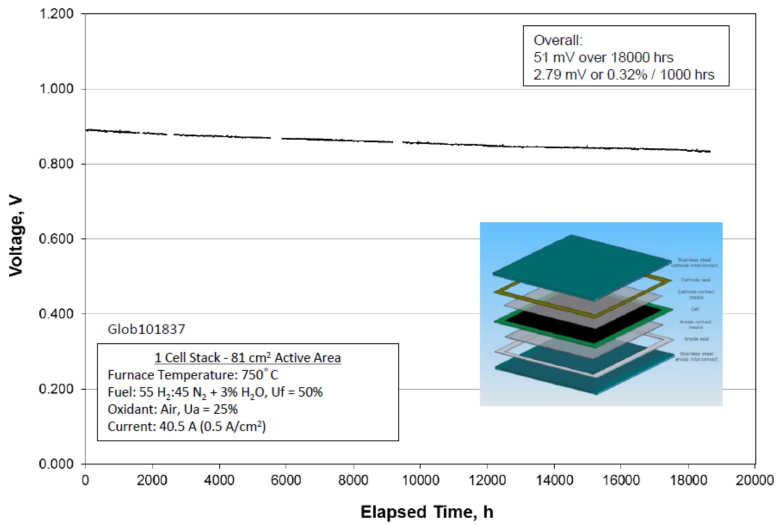
Outline

- Background & Motivation
- Technical Approach
- Project Objective & Structure
- Project Schedule & Achievement
- Summary to Day
- Moving Forward

Background - SOFC Stacks & Long-term Degradation







Component	Materials	Thickness	Porosity	Process
Anode	Ni/YSZ	0.3 - 1 mm	~ 40%	Tape casting
Electrolyte	YSZ	5 - 10 µm	< 5%	Screen printing
Cathode	Conducting ceramic	10 - 50 µm	~ 30%	Screen printing

➡ Long-term cell endurance was verified in >2 years of operation with a 0.32%/1000h performance degradation

* NETL 2015 SOFC Workshop – FCE Presentation

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

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

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

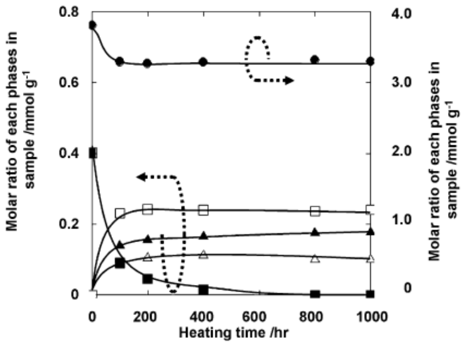
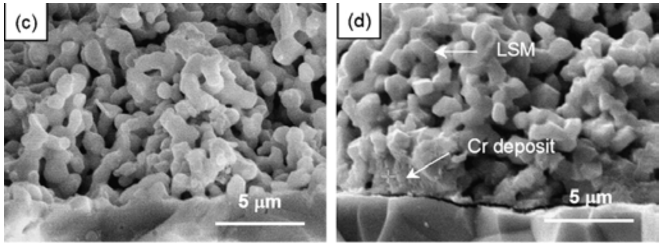
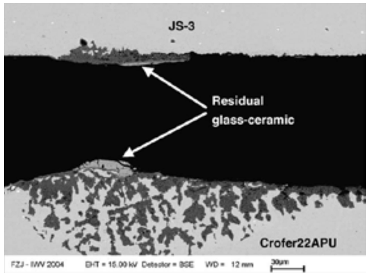


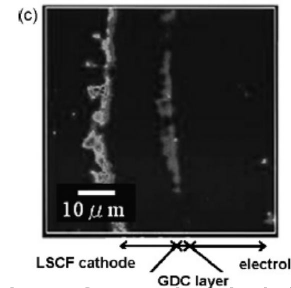
Fig. 4. Molar ratio of phases in LSCF–Cr_2O_3 mixture during heating at 1073 K for 0–1000 h: (●) LSCF, (■) Cr_2O_3, (□) $SrCrO_4$, (▲) $CoCr_2O_4$ spinel, (△) $(Fe,Cr)_2O_3$.



J. Power Sources 162 (2006) 1043–1052



J. Power Sources 152 (2005) 156–167

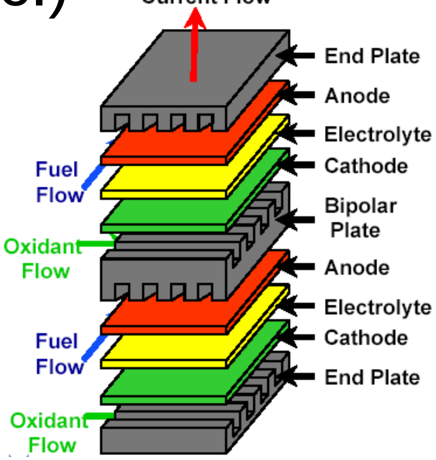


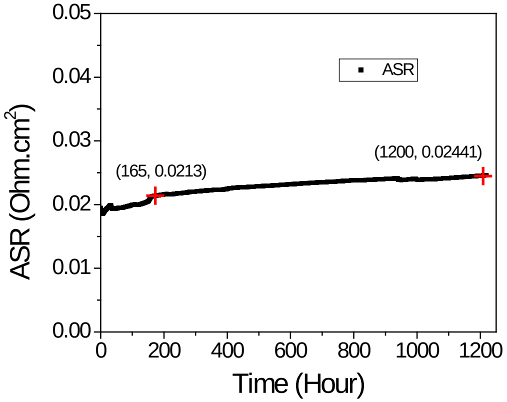
Cr-distribution @ Cathode/electrolyte Interface

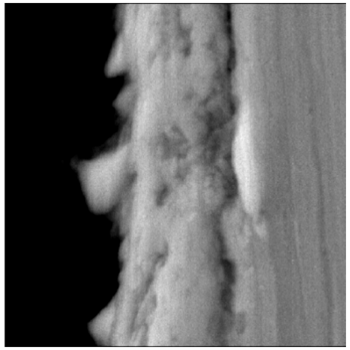
- **Cr Sources: Interconnect and BOP**

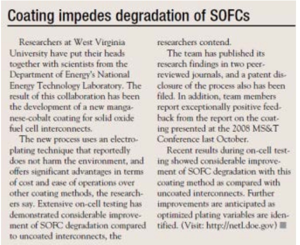
SOFC Interconnect Coatings

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









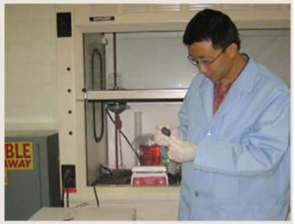
Coating impedes degradation of SOFCs

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.

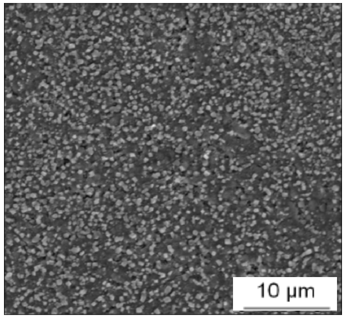
The new process uses an electroplating technique that reportedly does not harm the environment, and offers significant advantages in terms of cost and ease of operations over other coating methods, the researchers say. Extensive on-cell testing has demonstrated considerable improvement of SOFC degradation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

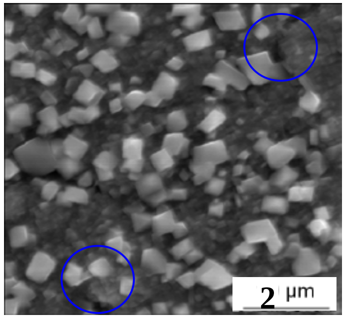
The team has published its research findings in two peer-reviewed journals, and a patent disclosure of the process also has been filed. In addition, team members report exceptionally positive feedback from the report on the coating presented at the 2008 MS&T Conference last October.

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)



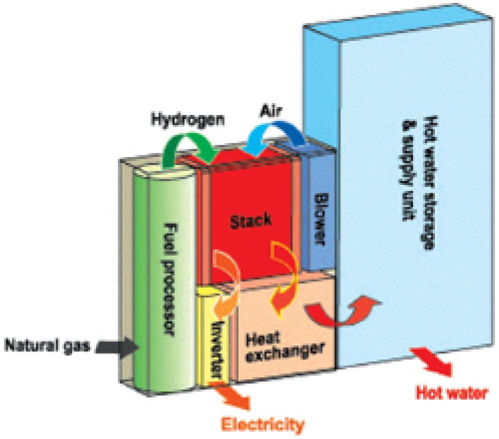
Junwei Wu, a Ph.D. student at West Virginia University, demonstrates environmentally friendly electroplating for SOFC interconnects.





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

Stainless Steels with Higher-Temperature Capability Needed

- Driver: Increased efficiencies with higher operating temperatures in power generation and chemical process systems.

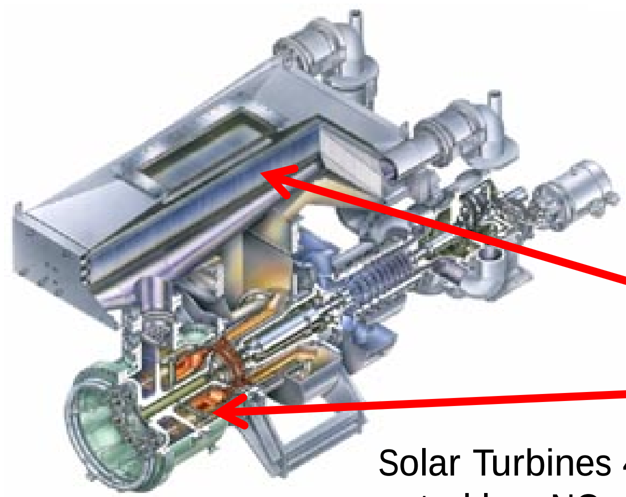
- Key issues are creep and oxidation resistance.

  - Significant gains have been made in recent years for improved creep resistance via nano MX precipitate control (M = Nb, Ti, V; X = C, N).

  - Stainless steels rely on Cr_2O_3 scales for protection from high-temperature oxidation.
    -Limited in many industrial environments (water vapor, C, S)
    -Most frequent solution is coating: costly, not always feasible

- **Approach: Al_2O_3-forming austenitic stainless steels**
  -background and potential advantages
- **Current alloy status for microstructure, mechanical properties, and oxidation resistance**

Initial target(s)



Recuperator, Casing

Solar Turbines 4.6 MW Mercury 50 recuperated low NO_x gas turbine engine

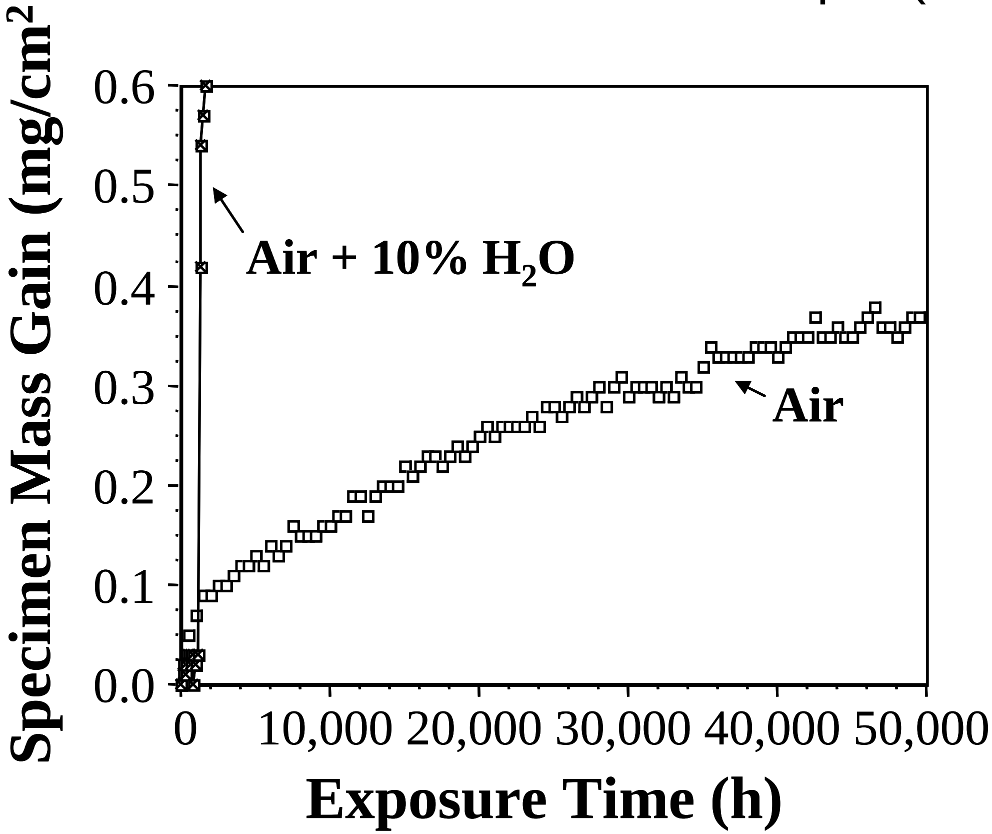
Fossil Power Steam Turbine, Boiler Tubing

HMN-Series (High-, Intermediate- and Low-Pressure) Steam Turbine for Combined-Cycle and Steam Power Plants

➢ Tubing in chemical/process industry, etc. also targeted.

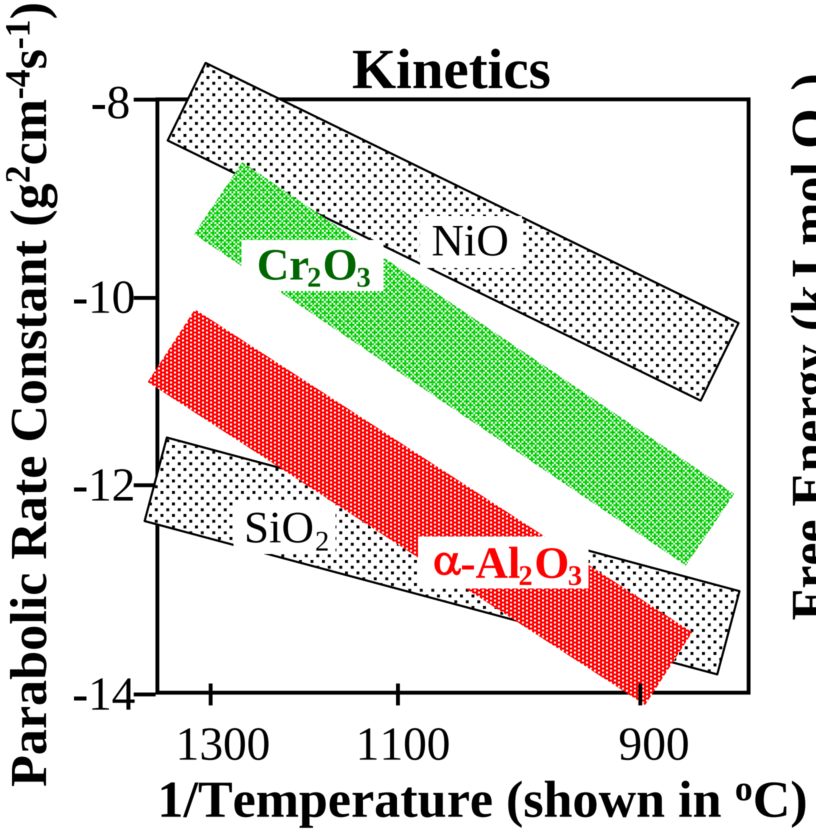
Cr_2O_3-Formers Suffer Accelerated Attack in Water-Vapor Environments

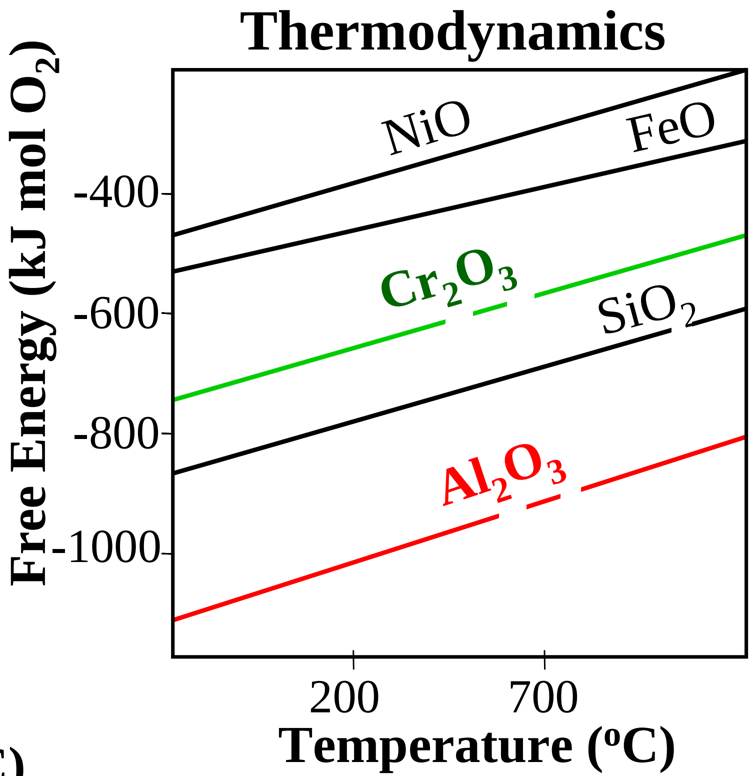
Oxidation Data for 347 Stainless Steel Foil (Fe-18Cr-11Ni base) at 650°C in Air and Air + 10% Water Vapor (Pint et al.)



- Susceptibility from Cr-oxide volatility in H_2O and enhanced internal oxidation
- Particularly important for thin components such as heat exchangers

Al_2O_3 Scales Offer Superior Protection in Many Industrially-Relevant Environments





- Al_2O_3 has lower growth rate/more thermo. Stability in oxygen than Cr_2O_3
- Al_2O_3 highly stable in water vapor
- Al_2O_3 generally (not always) better resistance to carburization and sulfidation

Few Available Options for Al_2O_3-Forming Alloys

•FeCrAl Alloys: Open body-centered cubic structure is weak

-Not suitable for most structural uses above ~500°C

•Ni-Base Alloys/Superalloys: too costly

-5 to 10 times greater cost than stainless steels

-limited to niche applications with ultrahigh performance needs

•Typically use Al_2O_3-forming coatings or surface treatments

-increases cost

-not feasible for many components/applications

Challenge of Alumina-forming Austenitic (AFA) Stainless Steel Alloys

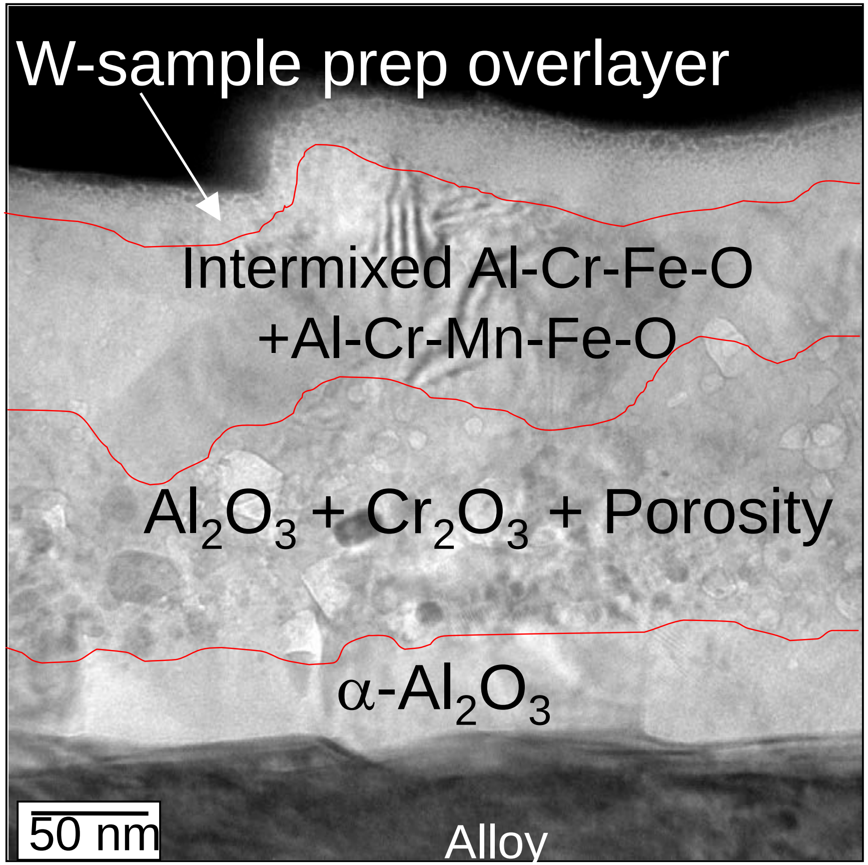
- Numerous attempts over the past ~30 years (e.g. McGurty et al. alloys from the 1970-80's, also Japanese, European, and Russian efforts)

- Problem: Al additions are a major complication for strengthening
  - strong BCC stabilizer/delta-ferrite formation (weak)
  - interferes with N additions for strengthening

- Want to use as little Al as possible to gain oxidation benefit
  - keep austenitic matrix for high-temperature strength
  - introduce second-phase (intermetallics/carbides) for precipitate strengthening

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

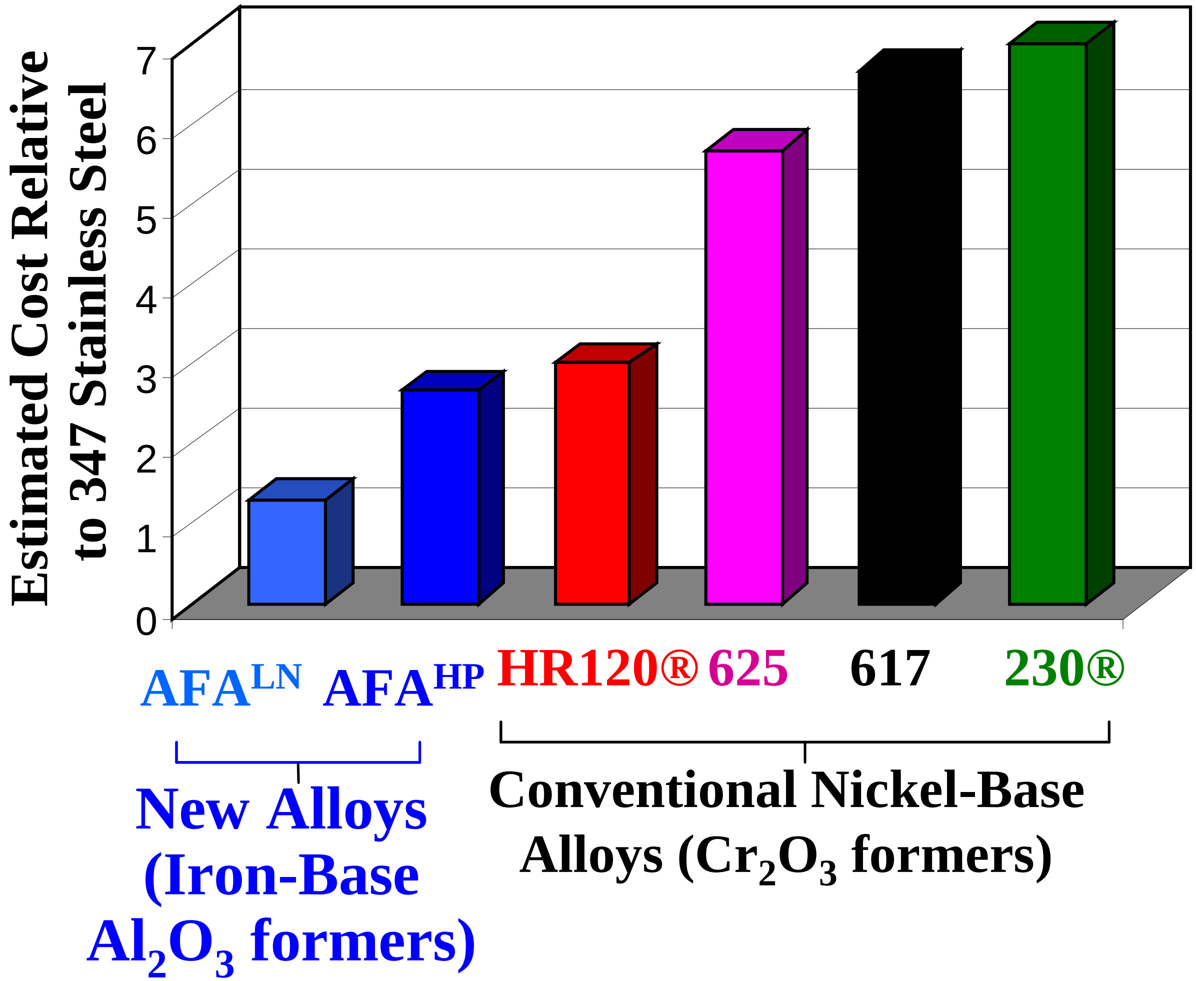


- α-Al_2O_3 the source of the excellent oxidation resistance
- Occasional transient nodules 0.5-5 μm thick, some Nb-oxide also detected

AFA is a Family of Alloys

- Three different grades of AFA series (wrought alloys)
  - **AFA Grade**: Fe- (14-15)Cr-(2.5-4)Al-(**20-25**)**Ni**-(**1-3**)**Nb** wt.% base
    - *~750-950 ° C temperature limit for Al_2O_3 formation*
    - *higher temperature ranges need higher Ni and Nb + rare earth additions*
    - *MC and $M_{23}C_6$ strengthening*
  - **Low Nickel AFA[LN] :** Fe-14Cr-2.5Al-**12Ni**-0.6Nb-**5Mn**-3Cu wt.% base
    - *~ 650-700 ° C temperature limit for Al_2O_3 formation*
    - *$M_{23}C_6$ strengthening*
  - **High Creep resistance γ'-Ni_3Al strengthened AFA**: Fe-(14-19)Cr-(2.5-3.5)Al-(**30-35**)**Ni**-3Nb + wt.% base
    - *~750-850 ° C temperature limit for Al_2O_3 formation*
- Cast AFA: *Cast version of AFA alloys*

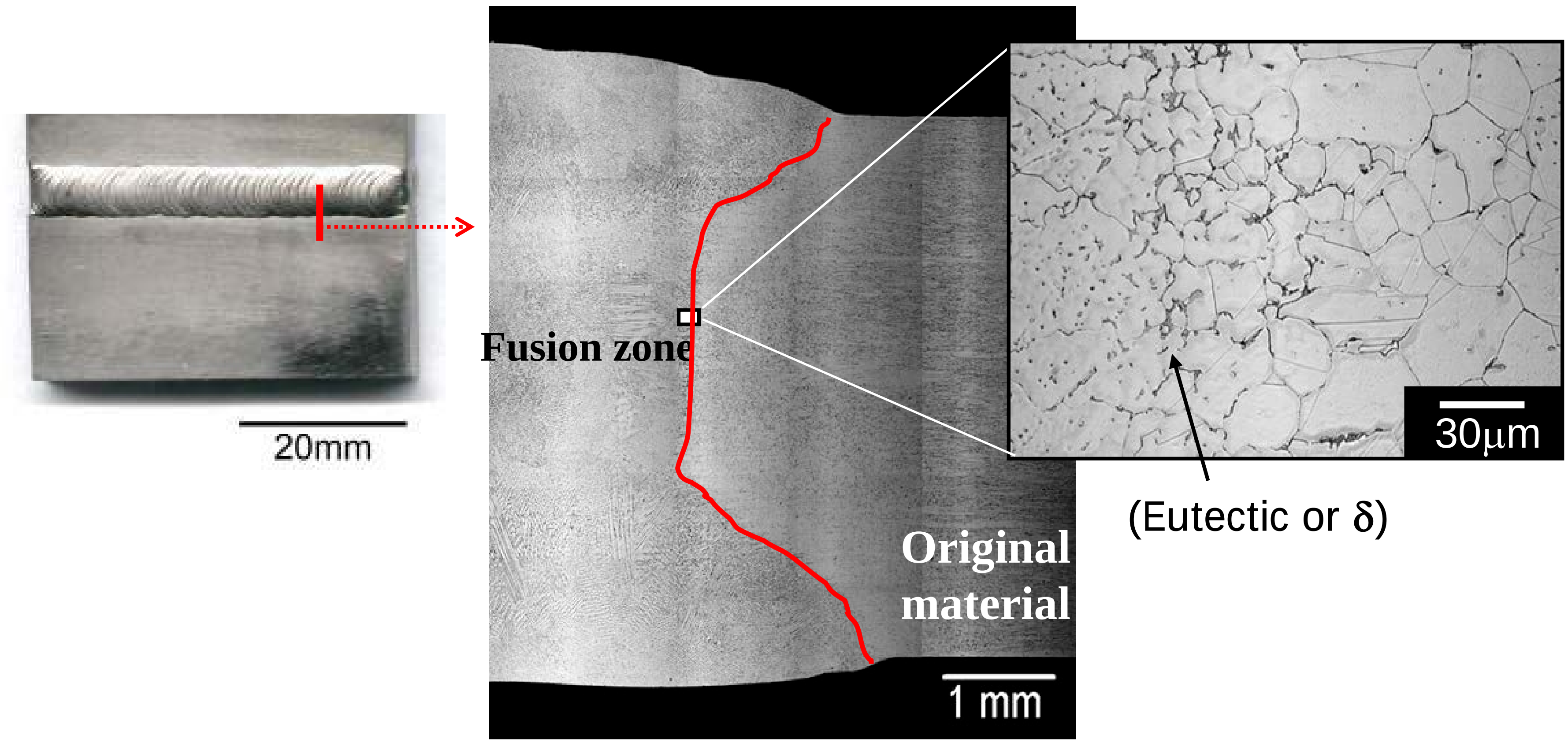
AFA Lower Raw Material Cost to High-Ni Austenitics/Ni-Base Alloys



AFA Alloys Appear to be Readily Welded (limited data)

Gas Tungsten Arc Weld

(used same alloy as a filler material)



- No cracking at fusion/heat-affected zones

AFA Highlights

Creep-Resistant, Al2O3-Forming Austenitic Stainless Steels
Y. Yamamoto, *et al.*
Science **316**, 433 (2007);
DOI: 10.1126/science.1137711

AFA Steel team: Alan Liby, Alexander DeTrana, Mike Brady, Yukinori Yamamoto; Michael Santella, Joseph Marasco, Bruce Pint, Craig Blue

Creep-Resistant, Al_2O_3-Forming Austenitic Stainless Steels

Y. Yamamoto,* M. P. Brady, Z. P. Lu, P. J. Maziasz, C. T. Liu, B. A. Pint, K. L. More, H. M. Meyer, E. A. Payzant

A family of inexpensive, Al_2O_3-forming, high–creep strength austenitic stainless steels has been developed. The alloys are based on Fe-20Ni-14Cr-2.5Al weight percent, with strengthening achieved through nanodispersions of NbC. These alloys offer the potential to substantially increase the operating temperatures of structural components and can be used under the aggressive oxidizing conditions encountered in energy-conversion systems. Protective Al_2O_3 scale formation was achieved with smaller amounts of aluminum in austenitic alloys than previously used, provided that the titanium and vanadium alloying additions frequently used for strengthening were eliminated. The smaller amounts of aluminum permitted stabilization of the austenitic matrix structure and made it possible to obtain excellent creep resistance. Creep-rupture lifetime exceeding 2000 hours at 750°C and 100 megapascals in air, and resistance to oxidation in air with 10% water vapor at 650° and 800°C, were demonstrated.

2011 R&D 100

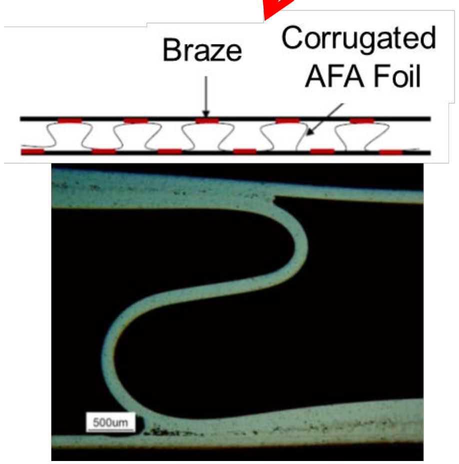
ORNL's AFA licensed to Carpenter Technology Corp.

AFA Commercialization:
OC4 (14Cr-3.5Al-25Ni-2.5Nb) Products

Carpenter 10,000lb AFA heat (VIM/VAR)

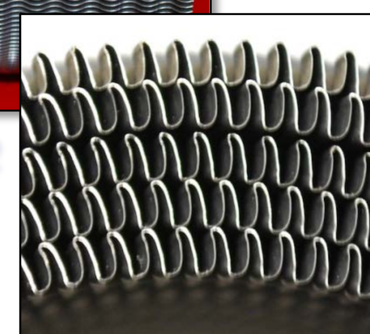
Elgiloy 8" wide, 300 lb, 3.2 mil coil for Capstone

350 lb wire coil
Elgiloy to Capstone



UTRC 6 mil foil subscale brazed heat exchanger (foil by Elgiloy)

15" wide, 4 mil AFA foil for **Solar Turbines** recuperator (Metalwerks 2000lb heat, Haynes, Somers, Elgiloy)



Capstone folded 8" wide 3.2 mil Foil

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

Project Team Information

PI - Xingbo Liu

- Program Management
- Cr-release Measurement
- On-Cell Testing
- Phase II Preparation

Co-PI - Mike Brady

- AFA Development
- Oxidation Measurement

Co-PI - Hossein Ghezel-Ayagh
Alireza Torabi

- Cr-release Measurement
- Phase II Preparation

Industrial Partner – Samuel Kernion

- AFA Manufacturing

Project Timeline

I.D.	Task	Year 1				Year 2	
		Q1	Q2	Q3	Q4	Q5	Q6
1.0	Project Management	■ ◆	■	■	■	■	■
2.0	Developing & Manufacturing AFAs						
2.1	AFA Development	■	■	■	■		
2.2	Microstructure Characterizations		■		■		
3.0	Oxidation and Cr Evaporation in Simulated SOFC Environments						
3.1	Oxidation Kinetics			■		■	
3.2	Scale characterization			■		■	
3.3	Cr Evaporation Evaluation			■		■ ◆	
3.4	Contributions of partial pressure of different Cr species				■		■
4.0	Investigation on Cr-poisoning of SOFC in associate with BOP Alloys						
4.1	Assembly of SOFCs with BOP Alloys				■		
4.2	Electrochemical Investigations				■	■ ◆	
4.3	Post-Mortem Analyses					■	■
5.0	Phase II preparation						■ ◆

Note: ◆ = Decision Points

Materials and Experimental Set up

	Fe	Cr	Mn	Ni	Cu	Al	Si	Nb	V	Ti	Mo	W	C
310 stainless steel	Bal.	25	2	20			0.75				0.75		0.08
OC 11	Bal.	15	2	25	0.5	4	0.15	2.5	0.05	0.05	2	0	0.1
New 35Ni	Bal.	18	2	35	0.5	3.5	0.15	1	0.05	0.05	0	0	0.15
Mod OC-D	Bal.	14	2	25	0.5	4	0.15	1	0.05	0.05	2	0	0.15
OC5	Bal.	14		25	0.5	3	0.15	1			2	1	0.1
OC4	Bal.	14		25	0.5	3.5	0.15	2.5			2	1	0.1
OCF	Bal.	14	2	25	0.5	4	0.15	2.5			2	1	0.2

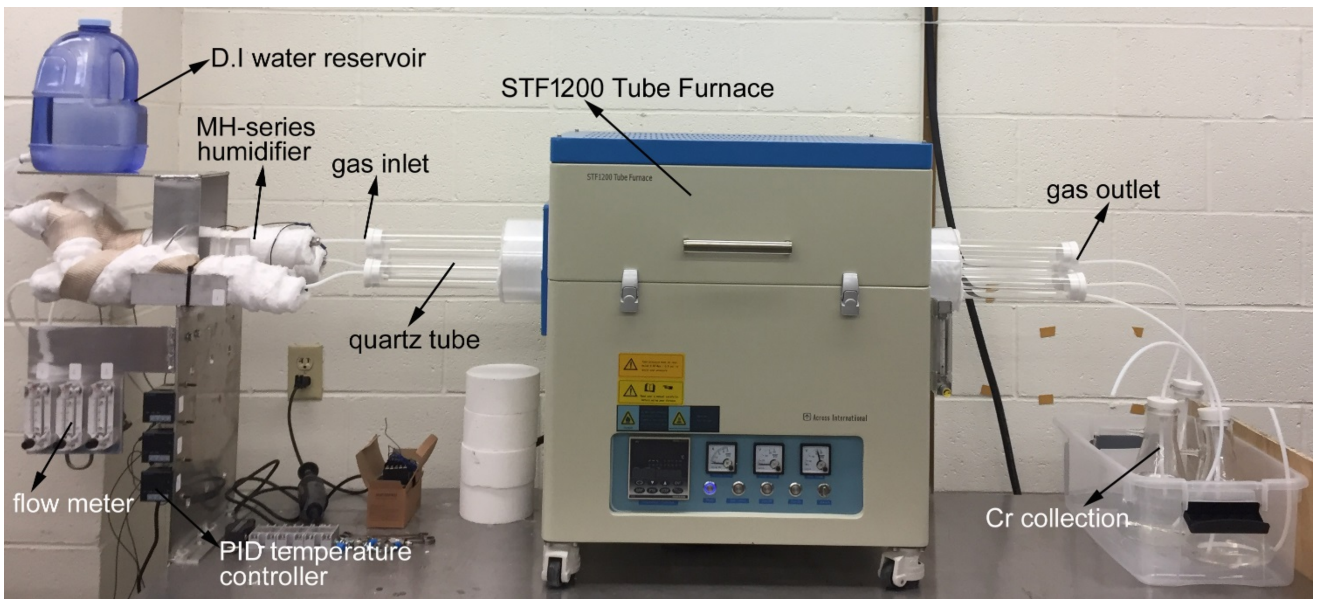


Figure 1 Cr volatility test apparatus.

Test conditions:

- 10% H_2O;
- 850 ^{o}C;
- 500 h;

Sample size:

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

Cr-Release Measurement

Table 2 Cr analysis for 310S and OC4 @ WVU.

Analyte		Cr	Volume
Unit		mg/L	mL
Analysis Date		4/4/17	-
Method Detection Limit	Matrix	**0.006**	-
OC4 (2 samples in one quartz tube)	water	0.02	1070
310S (2 samples in one quartz tube)	water	0.009	1110
Clean solution for the 310S quartz tube	water	4.044	138

Table 3 Cr evaporation rate tested by *FCE*.

Sample	Surface area	Mass before	Mass after	Mass gain	time	Cr, ICP	Cr, rate
	cm^2	g	g	%	h	mg	$kg.m^{-2}.s^{-1}$
OC-4	31.112	9.0336	9.0385	0.0542	504	0.339	5.999E-11
310S	34.226	10.6525	10.6595	0.0657	502	3.19	5.157E-10

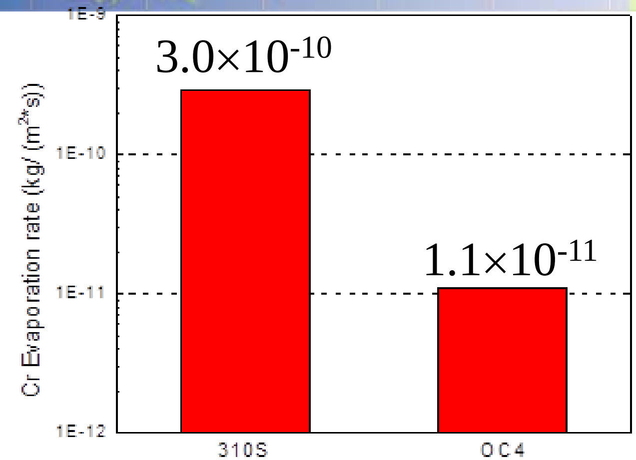


Figure 2 Cr evaporation rates of 310S and OC4 at 850 °C for 500 hours in air with 10% water vapor.

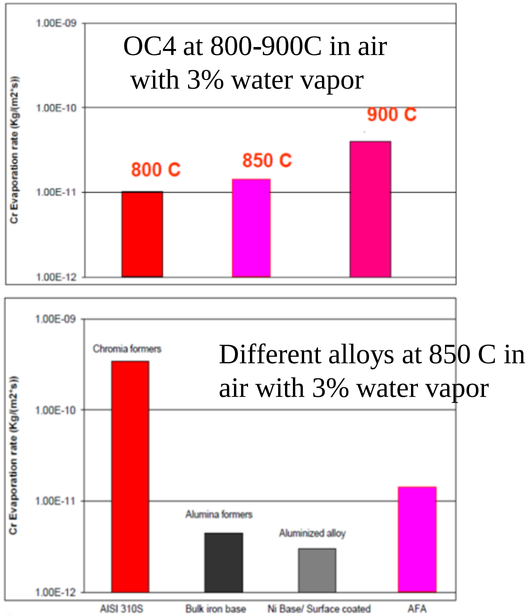
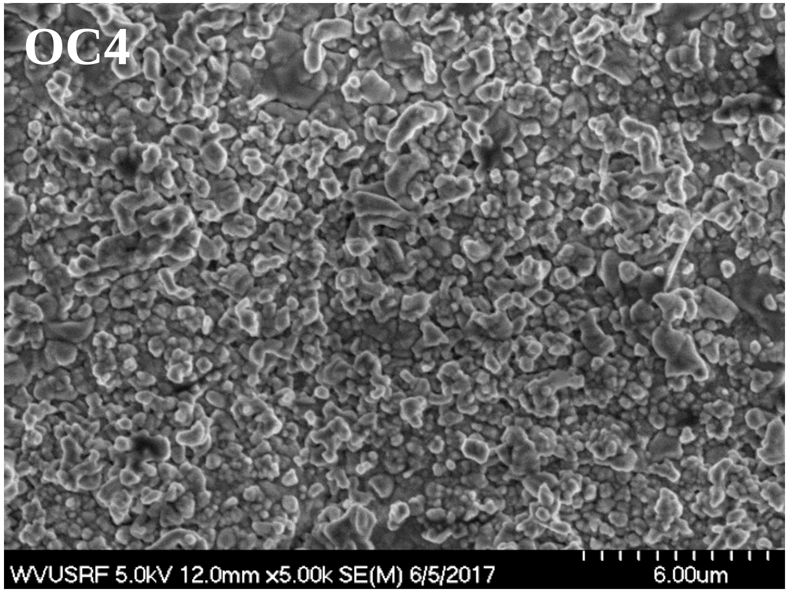
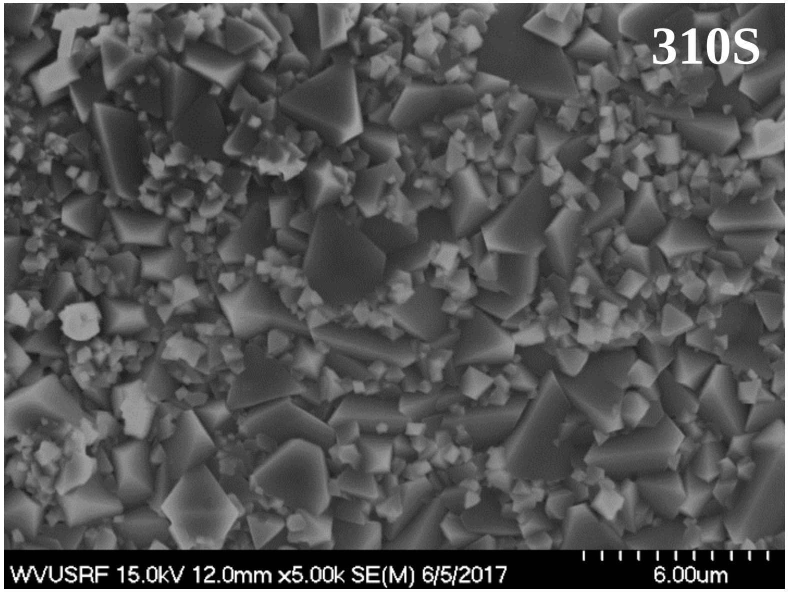


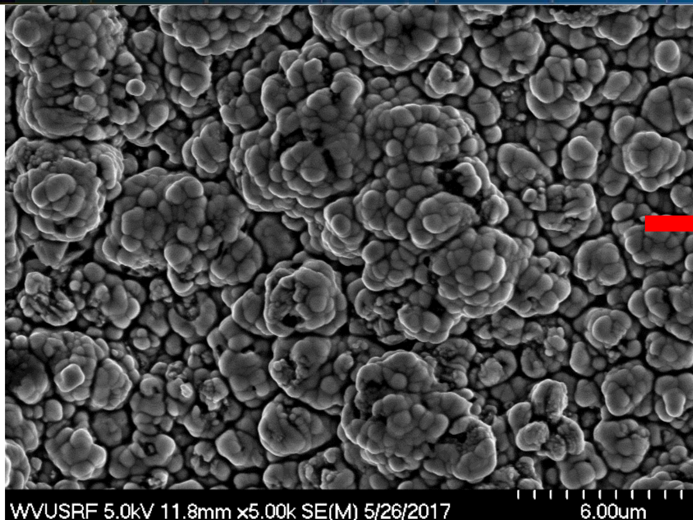
Figure 3 (a) Cr evaporation rates of AFA OC4 and relative competing alloys reported by ORNL.

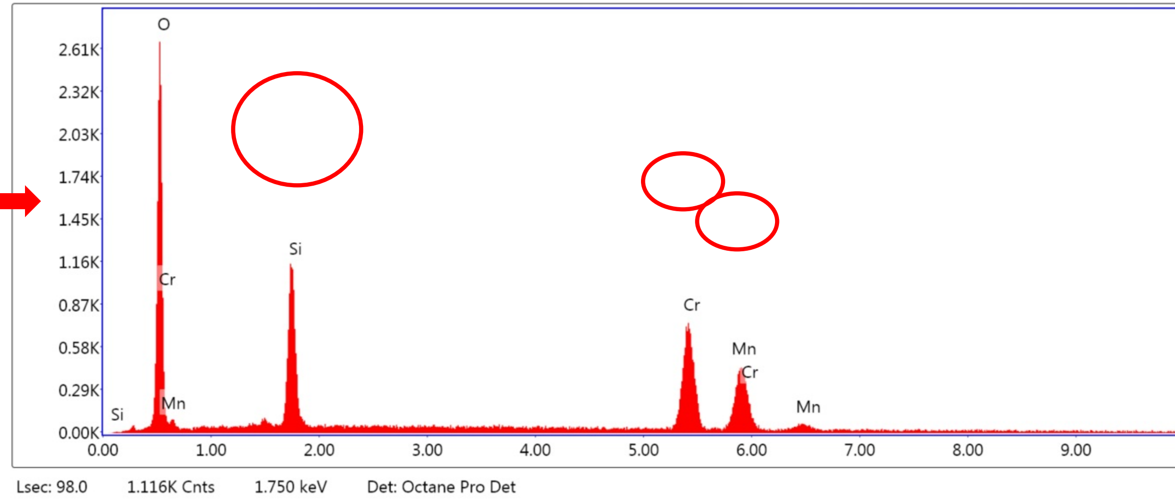
Corrosion Products Analysis by *WVU*

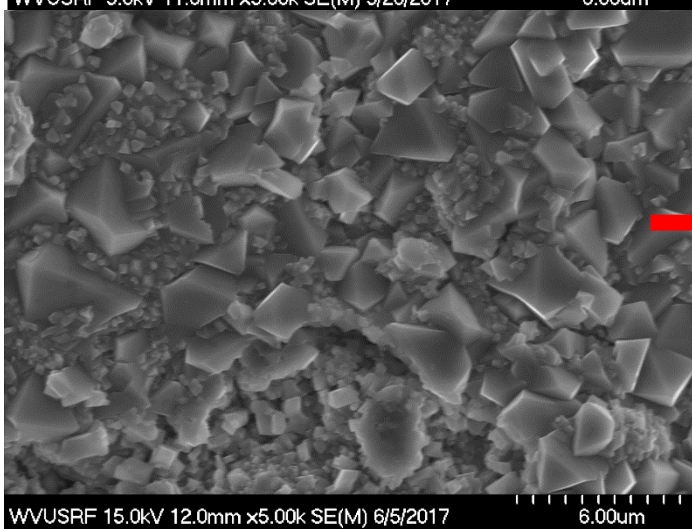


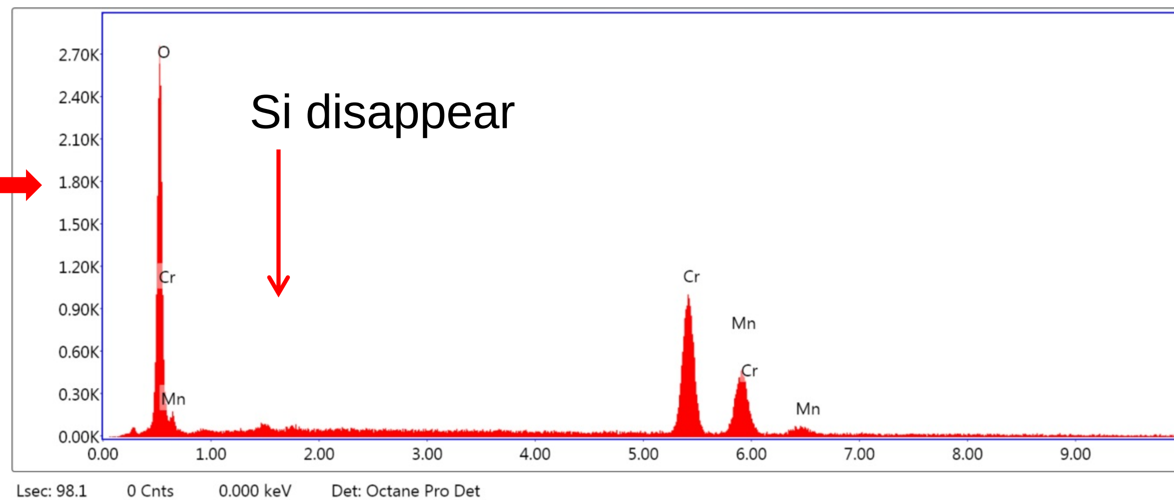


SEM and EDS analysis for the surface of 310S

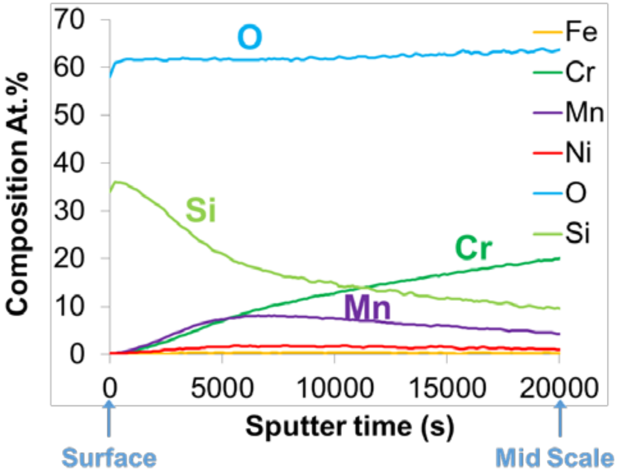


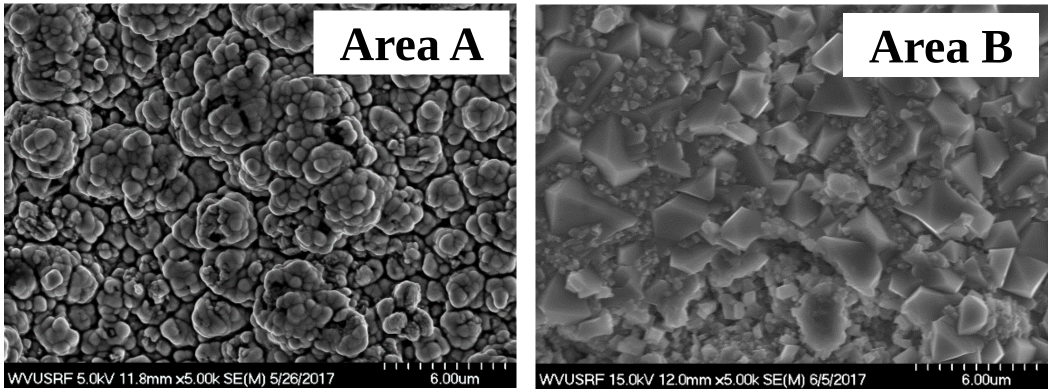


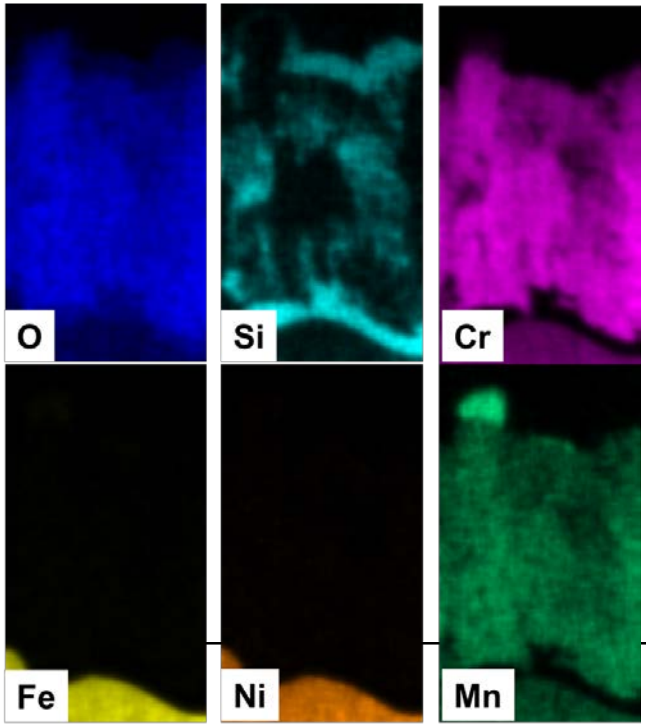


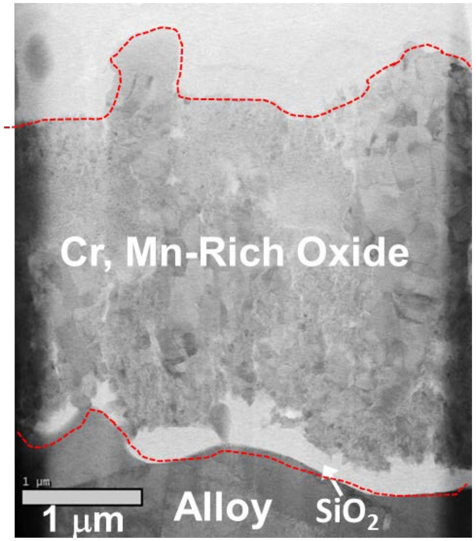


Cross section of 310S: STEM-EDX mapping and XPS depth profiling by ORNL





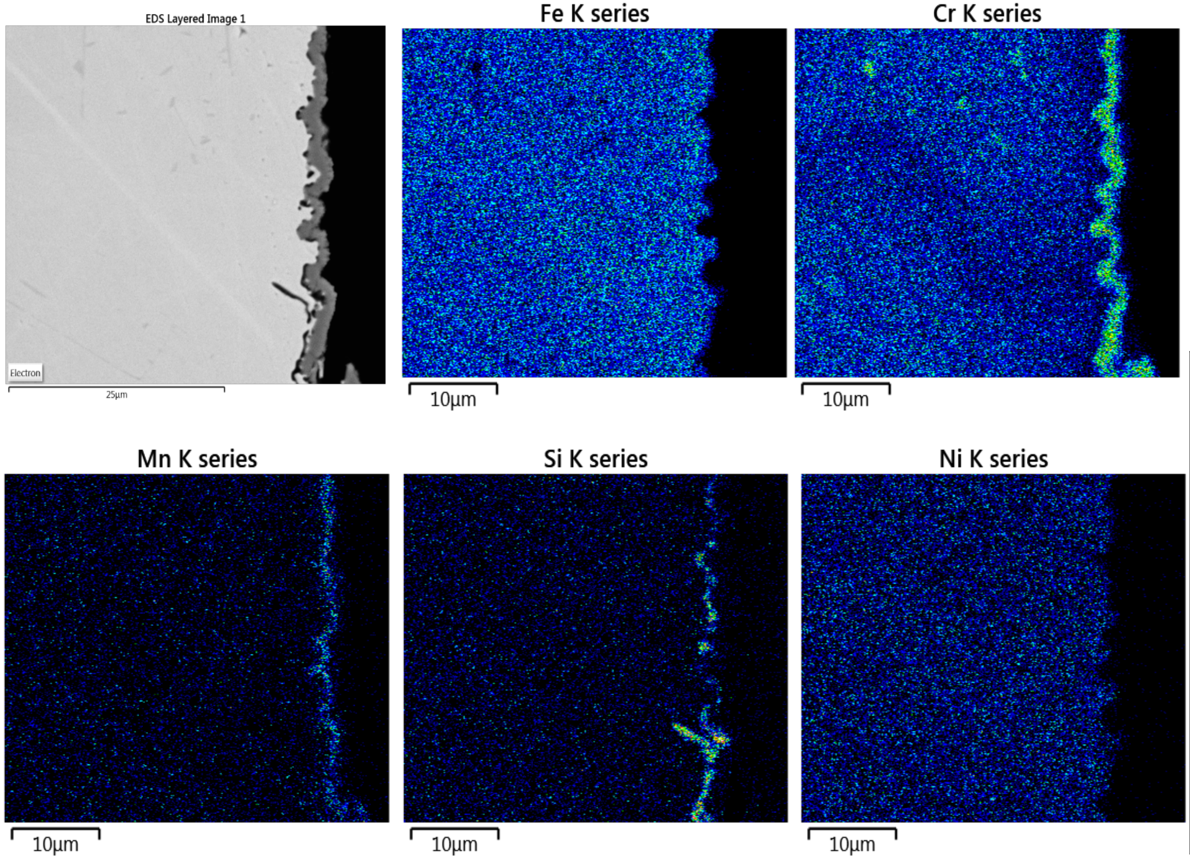


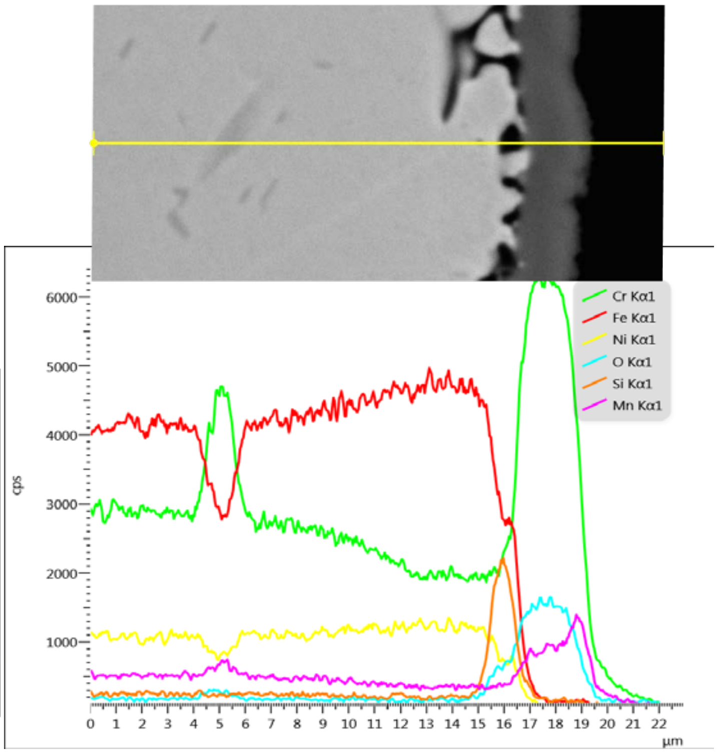


STEM Cross-Section

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.

Cross section of 310S: EDS map by *FCE*





Coincides with WVU & ORNL results that Si-containing layer is underneath the crystal Cr_2O_3 layer.

SEM and EDS analysis for the surface of OC4 @ WVU

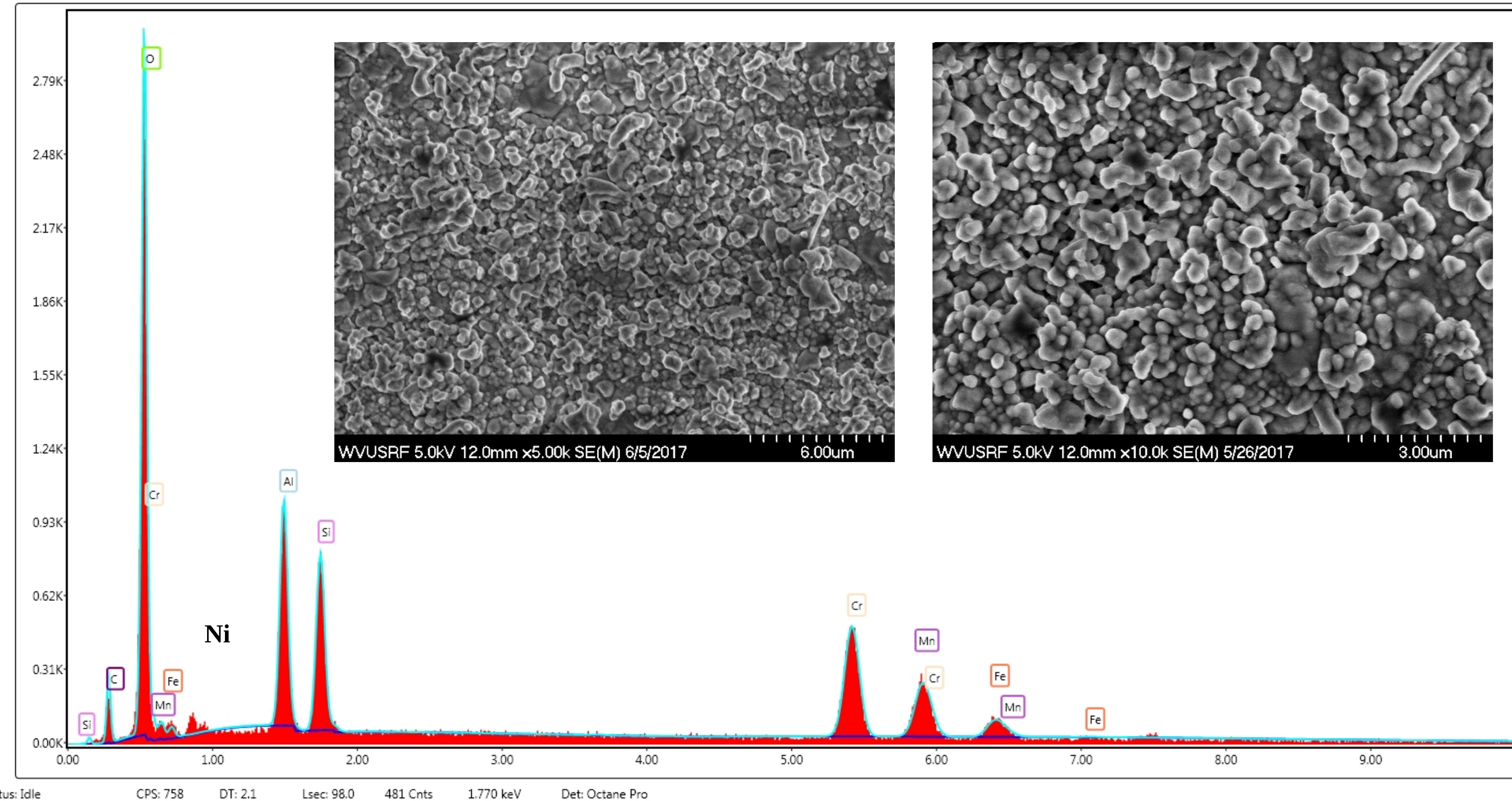
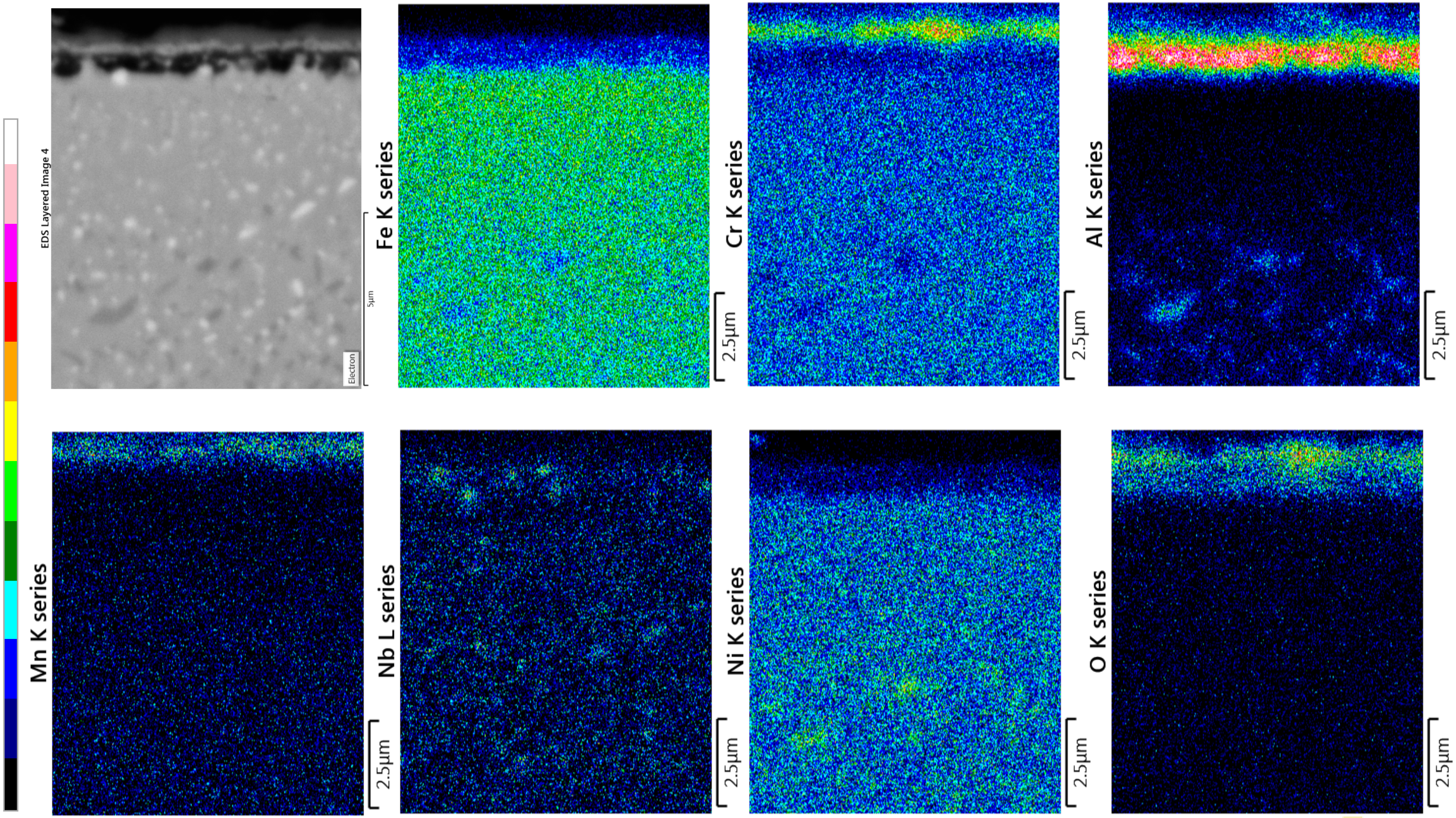
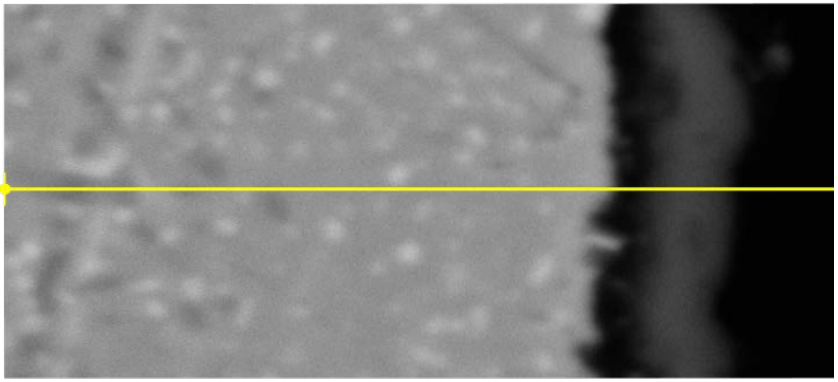


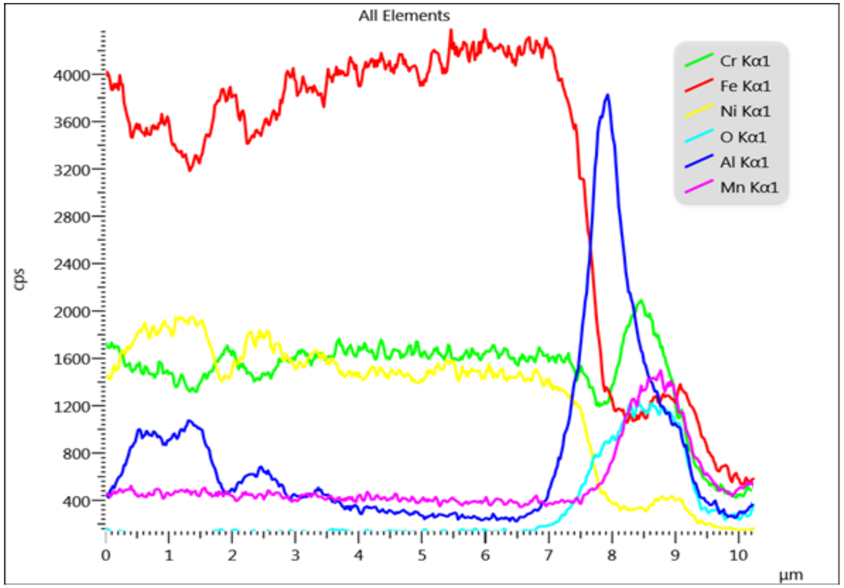
Figure 5 SEM images for **OC4** after 850 ^{o}C for 500 hours in air with 10% water vapor and EDS spectrums.

SEM Cross-section of OC4 – EDS Mapping *by FCE*

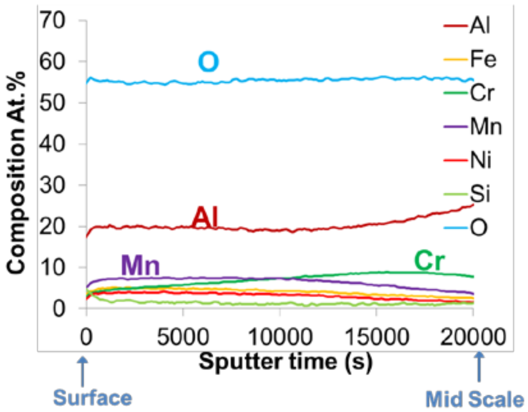


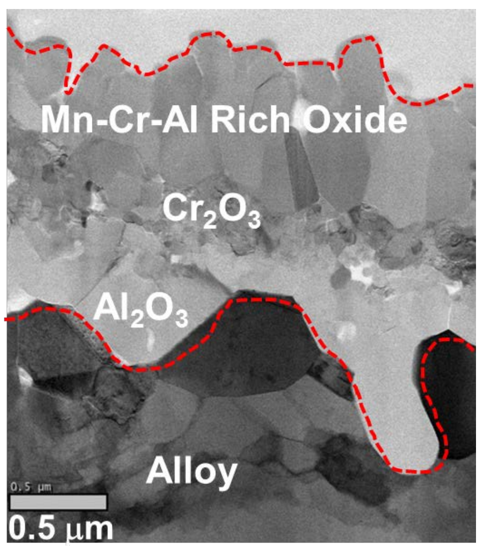
SEM Cross-section of OC4 – Line-Scan *by FCE*

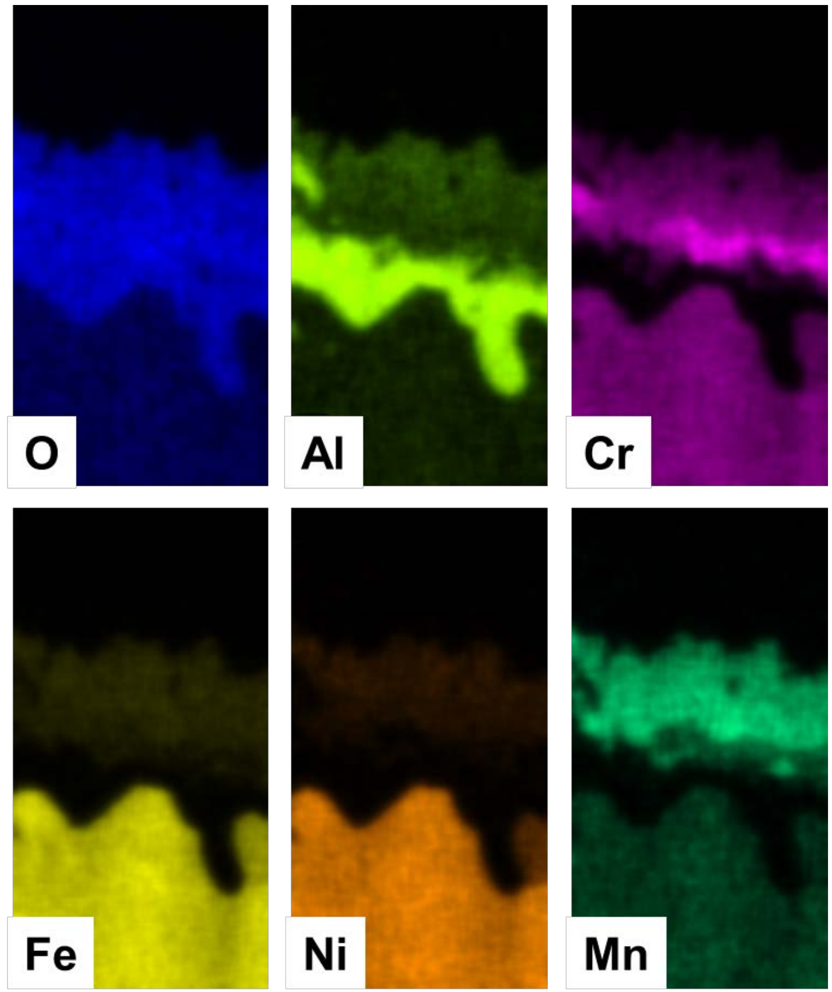




Cross section of OC4: STEM-EDX mapping and XPS depth profiling by ORNL



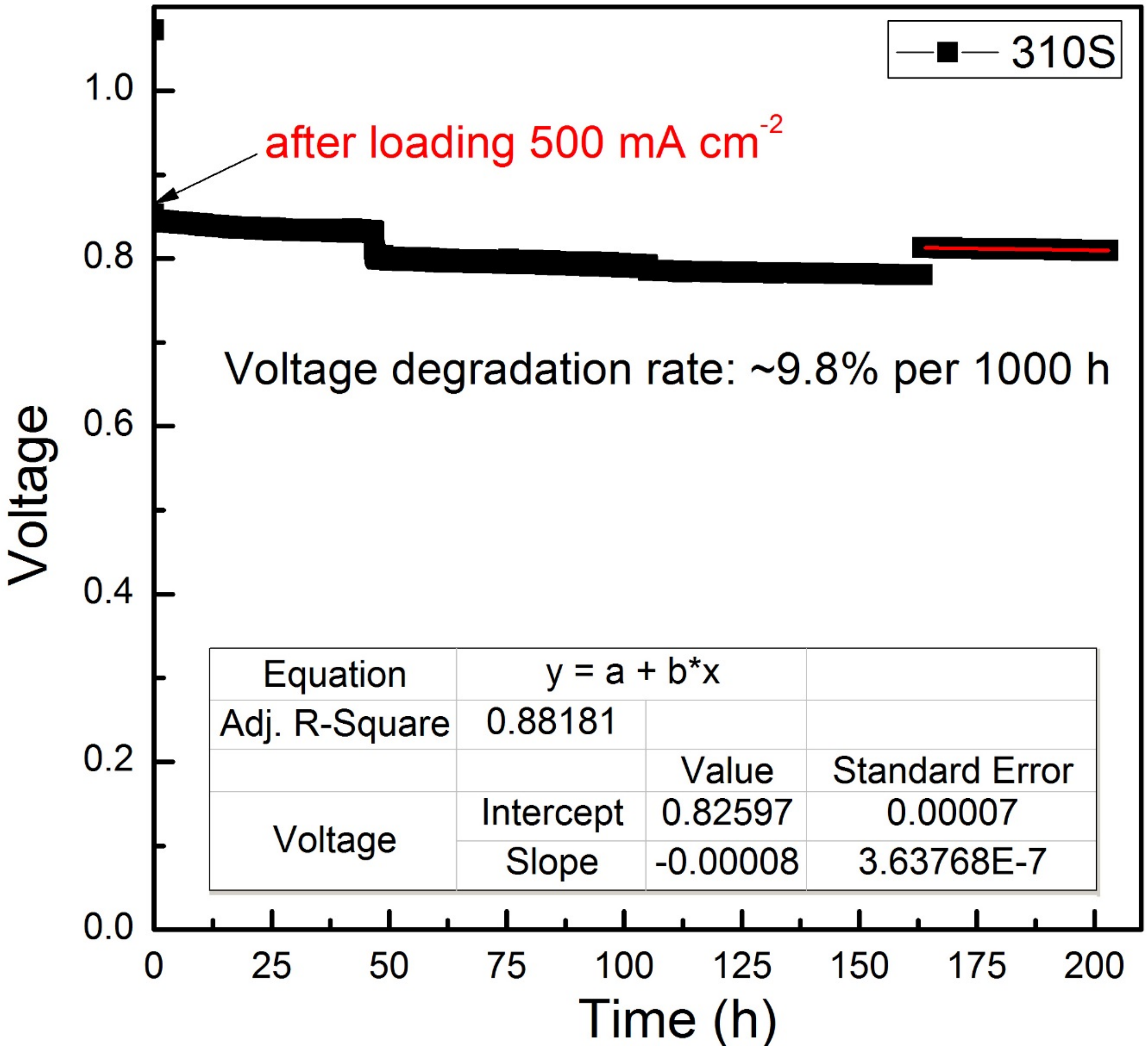




Multi-Layer scale formed on AFA OC-4 after 500 h at ~850°C in Air + 10% H_2O.

- 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?

SOFC Performance



Equation	y = a + b*x		
Adj. R-Square	0.88181		
		Value	Standard Error
Voltage	Intercept	0.82597	0.00007
	Slope	-0.00008	3.63768E-7

Summary to Day

OC4 AFA shows significant advantages in terms of both improving Corrosion resistance and reducing Cr-release

- OC4 Scale is half of that of 310S SS
- Cr-release rate is 10-30 times lower than that of 310SS
- Both Cr-Mn-Al Oxide top layer and Al_2O_3 sub-scale offers much improved protection and Cr-blocking

Moving Forward

- **Alloy Development**
  - Higher temperature alloys (~900C)
  - Pre-Oxidation
  - Surface Aluminization

- **On-Cell Testing to Confirm the improvement of Cell Stability**

- **Preparation for Phase II**

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

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