Advanced Metallic Interconnect Development

Z. Gary Yang, Gordon Xia,
Prabhakar Singh, Jeff Stevenson

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Interconnect Development

Objectives:

- Develop cost-effective, optimized materials and coatings for intermediate temperature SOFC interconnect and interconnect/electrode interface applications.
- Identify and understand degradation processes in interconnects and at their interfaces.

Approaches:

- **Evaluation of conventional and newly developed alloys (chemical, electrical, mechanical properties, cost).**
- **Investigation and understanding of degradations in bulk alloy interconnects and at their interfaces under SOFC operating conditions.**
- **Materials development**
  - **Surface modification**
  - **Bulk modification or alloy development**
  - **Cathode/interconnect interfaces**

Focus Areas & Progress

- Study of Ni-based alloys.
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces

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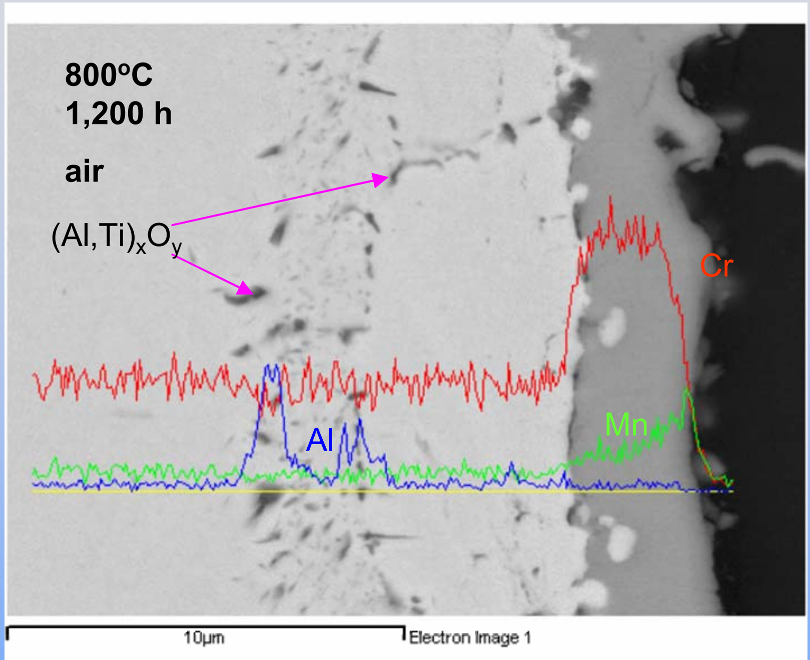
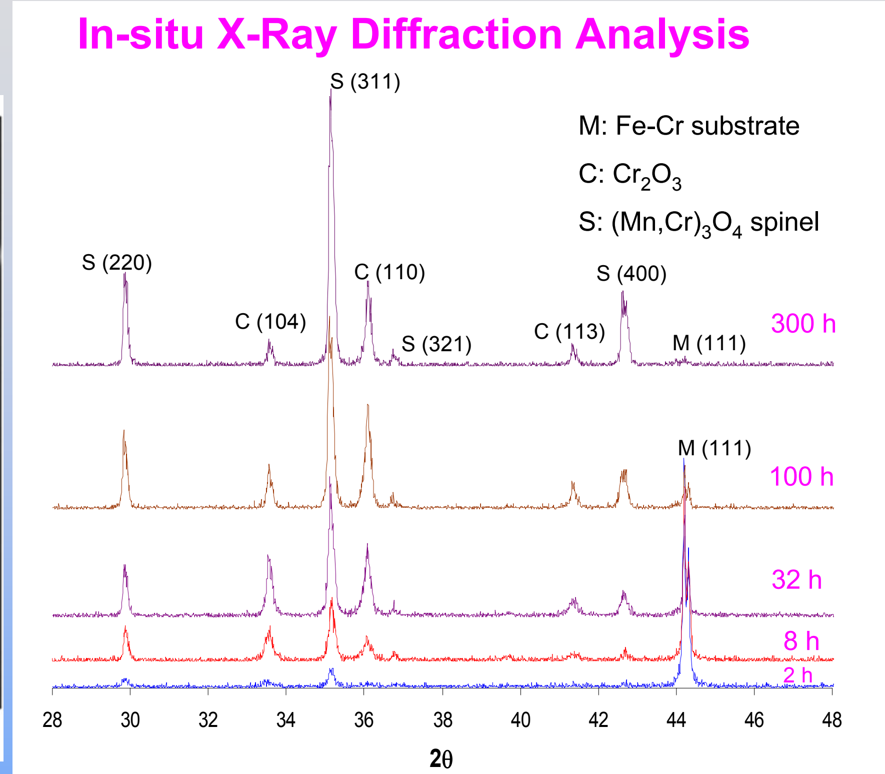
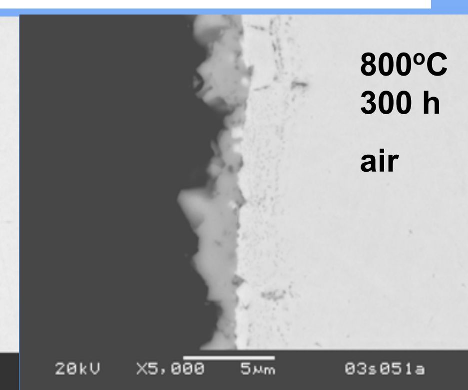
Ferritic Stainless Steels: Status and Issues

Crofer22 APU





- Scale volatility;
- Long term oxidation resistance under SOFC operating conditions;
- Life time scale electrical properties;
- Mechanical/thermomechanical stability.



Study and Evaluation of Ni-Based Alloys

Alloys[a]	Nominal composition, wt%													
	Ni	Cr	Fe	Co	C	Mn	Si	Mo	W	C_b	Ti	Al	B	V	Others
Haynes242	Bal	8.0	2.0[b]	2.5[b]	0.03[b]	0.8[b]	0.8[b]	25.0	--	--	--	0.5[b]	0.006[b]	--	0.5[b] Cu
LTES700	Bal	12.0						18.0			1.1	0.9			
Hastelloy C-4	Bal	16.0	3.0[b]	2.0[b]	0.01[b]	1.0[b]	0.08[b]	16.0	--	--	0.70	--	--	--	
Hastelloy S	Bal	16.0	3.0[b]	2.0[b]	0.02[b]	0.5	0.4	15.0	1.0[b]	--	--	0.25	0.015[b]	--	0.02La
Haynes230	Bal	22.0	3.0[b]	5.0[b]	0.10	0.5	0.4	2.0	14.0	--	--	0.3	0.015	--	--

Haynes242, C, S, and 230 were developed by Haynes International; LTES700 by Mitsubishi Heavy Industries.

Why Ni-based Alloys?

- Excellent oxidation resistance, super high temperature strength, and good manufacturability.
- Formation of NiO top scale as potential Cr stopping layer.
- CTE can be modified through alloying.
- Scale can be potentially engineered for improved electrical conductivity.

Questions

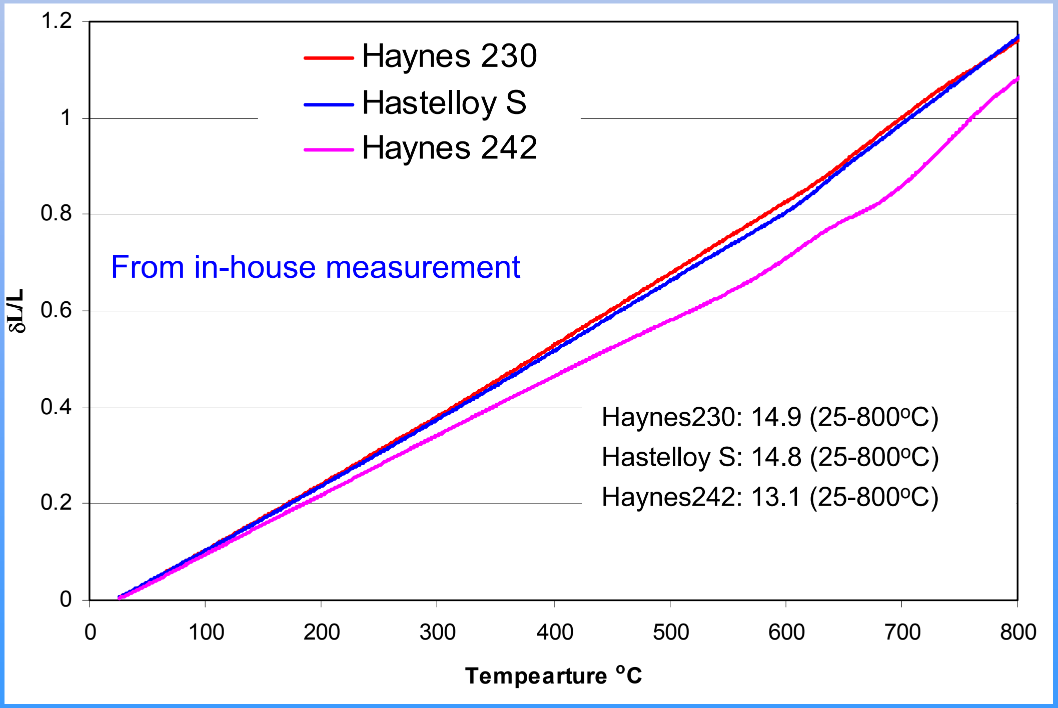
- Can the required combination of properties be found in a single alloy composition?
- Cost?

Low CTE Ni-Based Alloys

- Traditional Ni-based alloys have a CTE of 15.0~19.0 μm/m.K^{-1} (RT~800^{o}C). A relatively low CTE of 13.0~14.5 μm/m.K^{-1} (RT~800^{o}C) can be achieved via alloying.
- Mo, W, Ti and Al reduce CTE of Ni-based alloys; while Cr, Ta+Nb and Co increase it;
- Cr concentration has to be relatively low in these alloys.

$$\alpha = 13.87 + 7.28\,x10^{-2}\,Cr + 3.75\,x10^{-2}(Ta + 1.95\,Nb) + 1.98\,x10^{-2}\,Co - 1.84\,x10^{-2}\,Al - 7.95\,x10^{-2}\,W - 8.24\,x10^{-2}\,Mo - 1.63\,x10^{-1}\,Ti$$

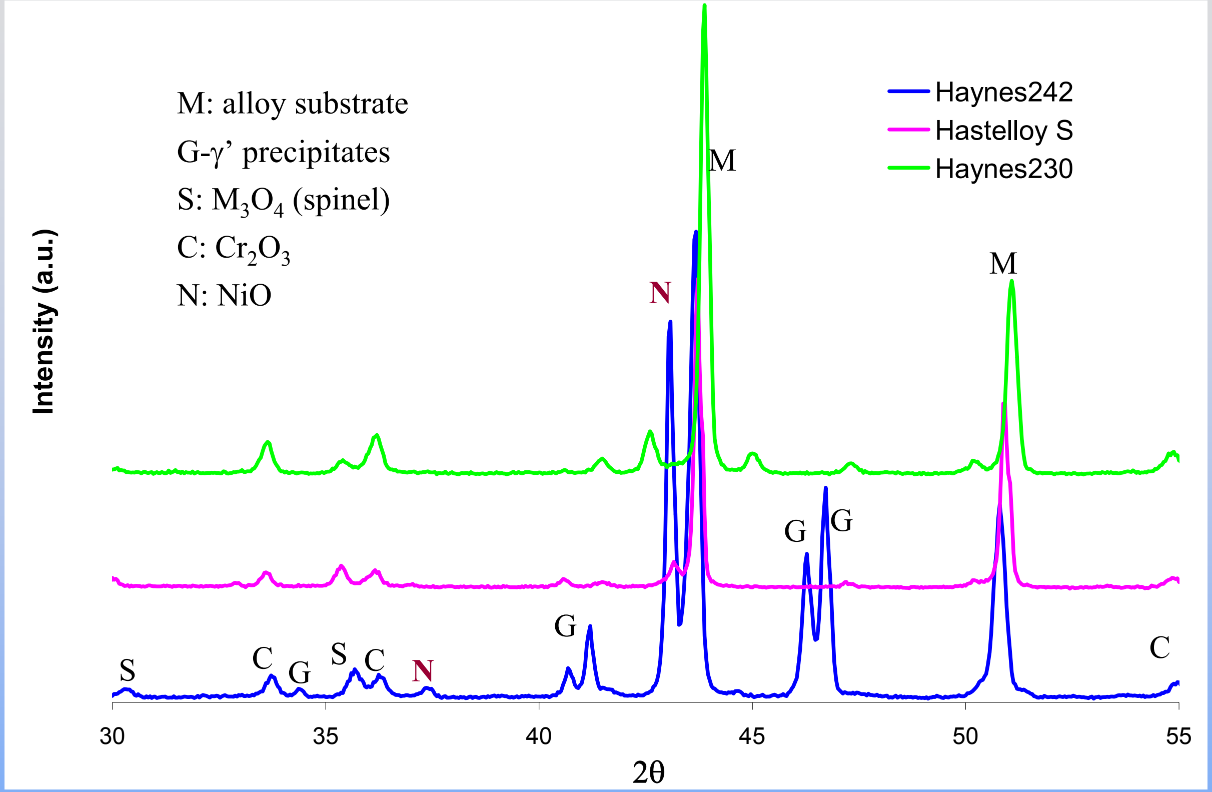
Yamamoto, et al.

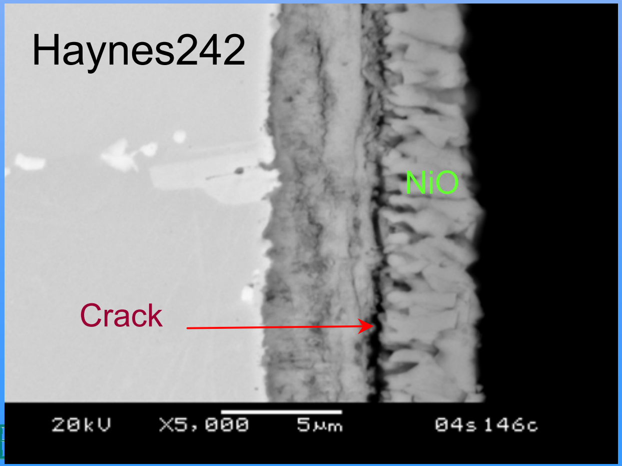


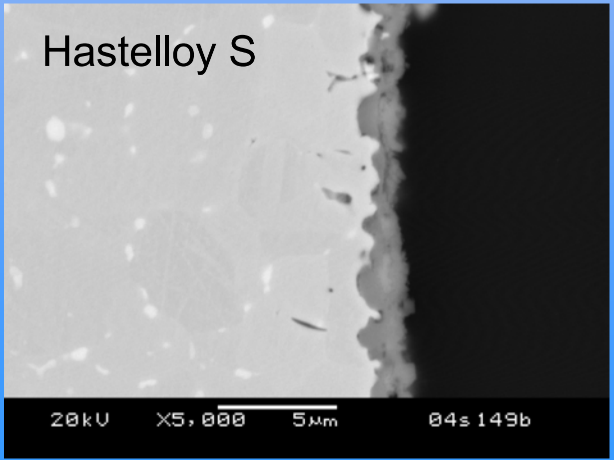
Alloys	TEC×10^{-6}.K^{-1} (from manufacturers)
Crofer22 APU	12.2 RT-760ºC
Haynes242	12.2-13.9 20-540-760ºC
LTES700	13.6 RT-760ºC
Hastelloy C-4	13.3-14.4 20-540-760ºC
Hastelloy S	13.3-14.4 20-540-760ºC
Haynes 230	15.2 25-800ºC

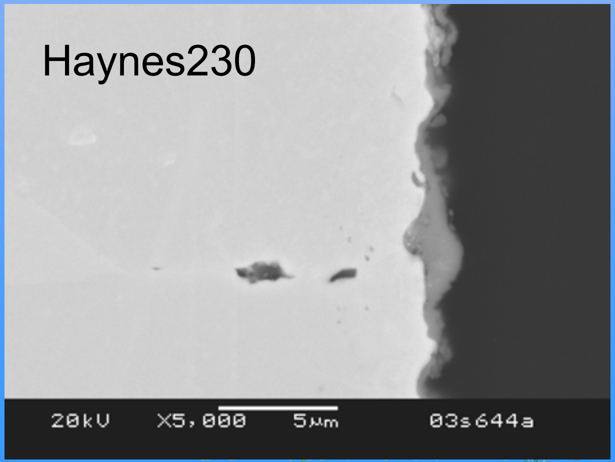
Scale Structure and Composition

After oxidation at 800°C for 300 hours in moist **AIR**.

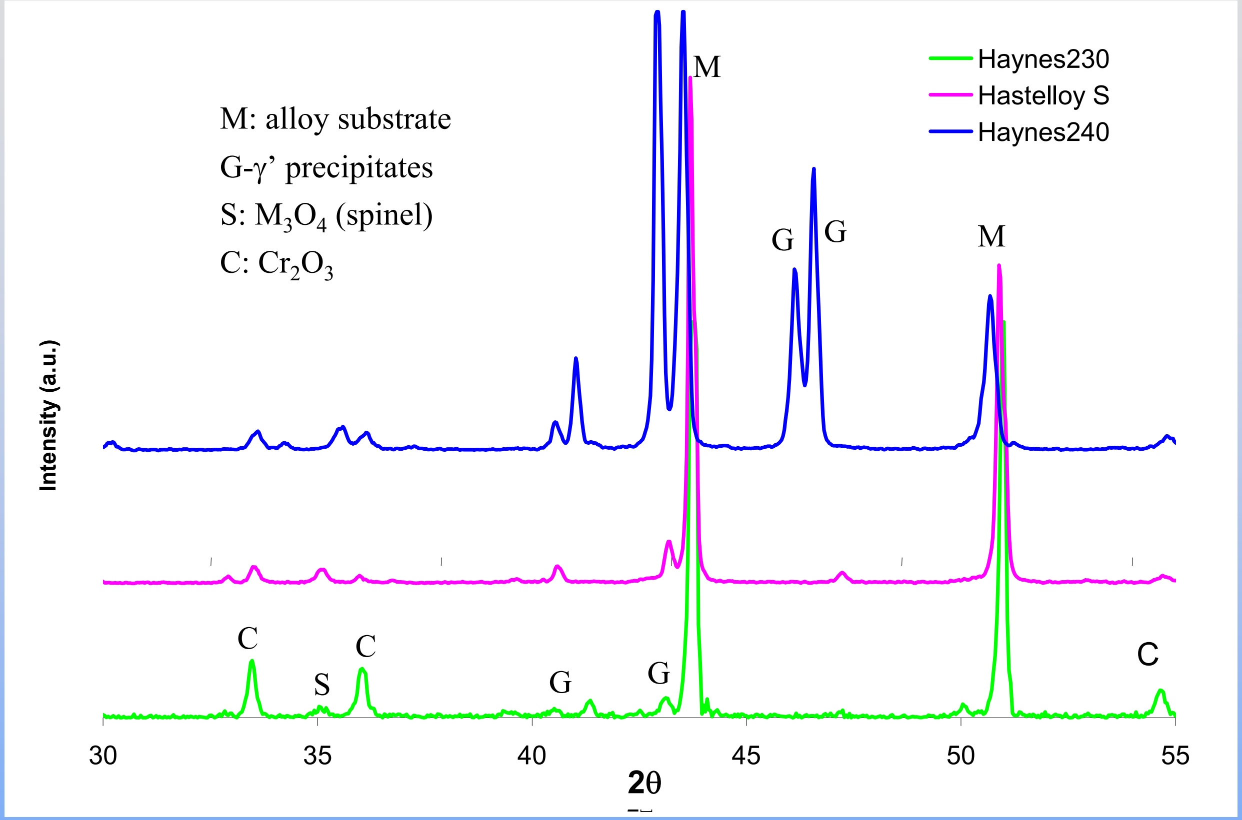




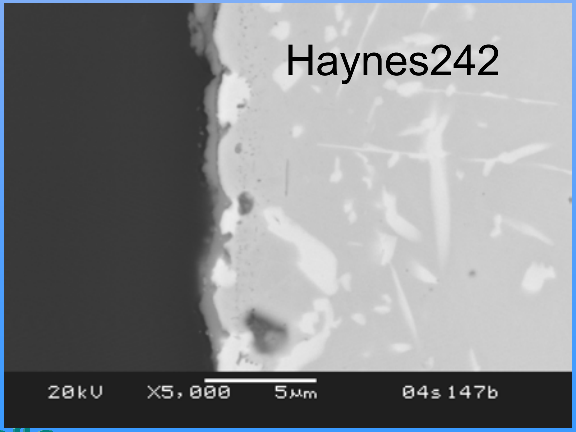


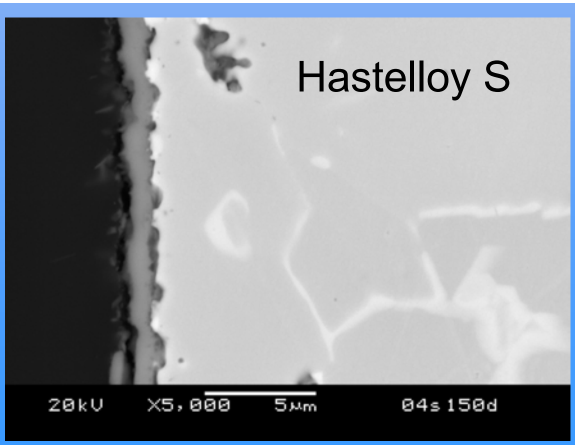


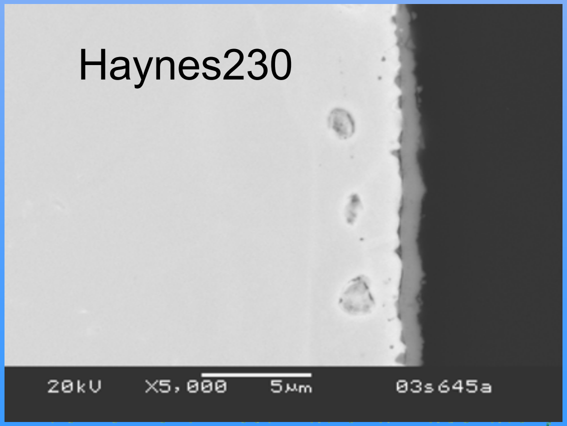
Scale Structure and Composition



After oxidation at 800°C for 300 hours in moist **HYDROGEN**.

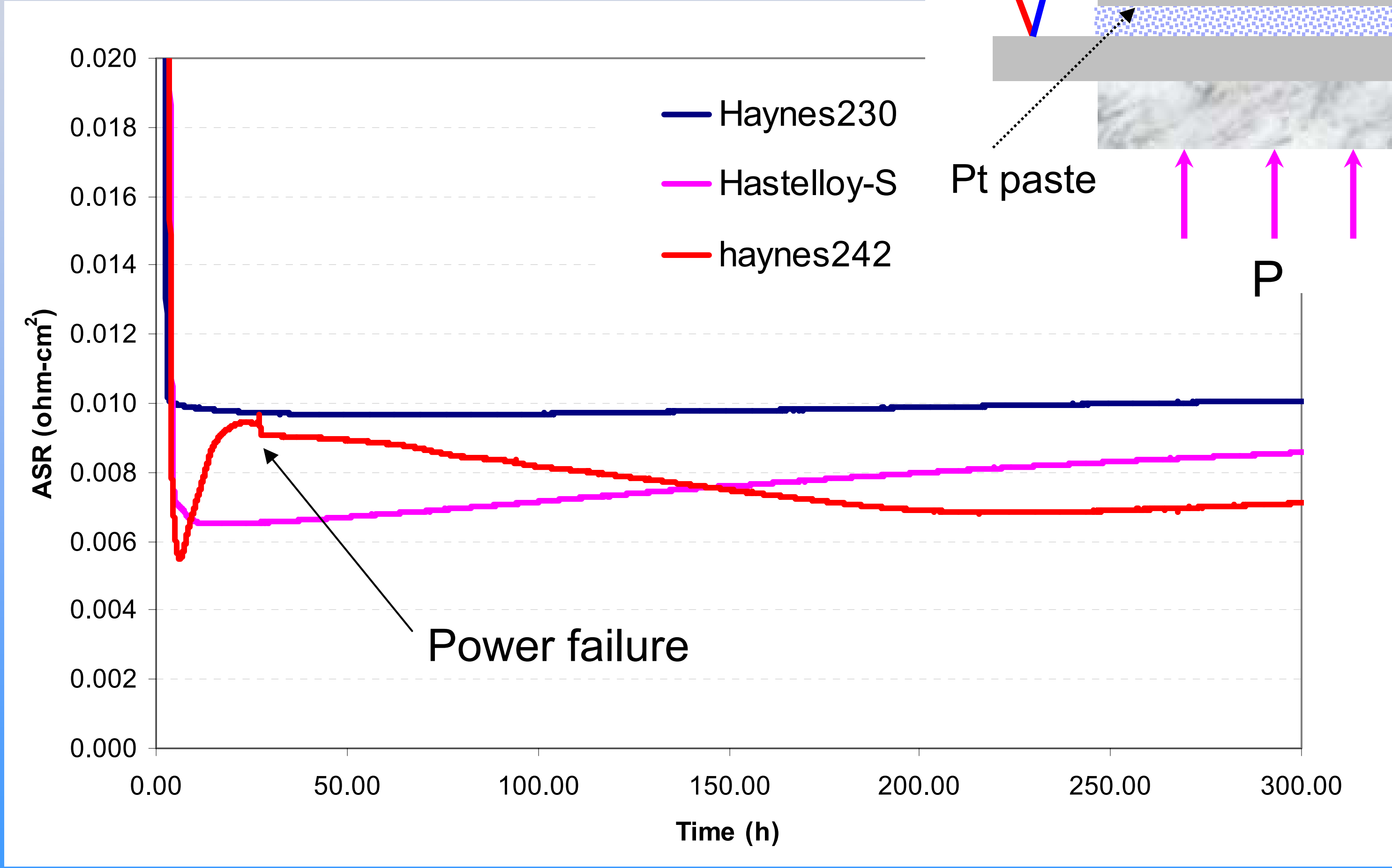


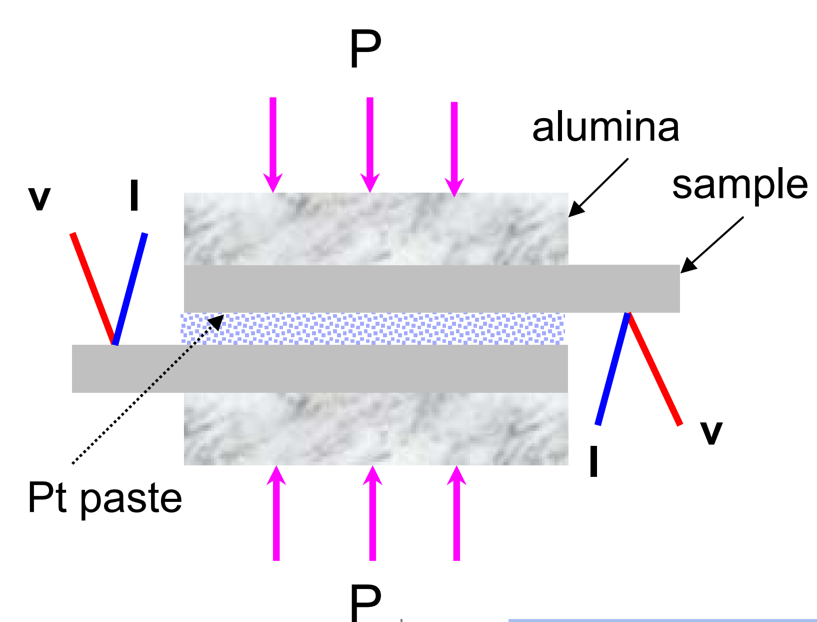




Scale ASR

The measurement was carried out at 800ºC in moist air.





Summary

Ferritic Stainless Steels

- The newly developed FSS demonstrates reduced scale volatility, good CTE matching, reduced scaled resistance, and improved surface compatibility with sealing glasses.
- There is however a need for further improvement in long term scale chemical, electrical, and mechanical stability (for temperatures >700^{o}C).

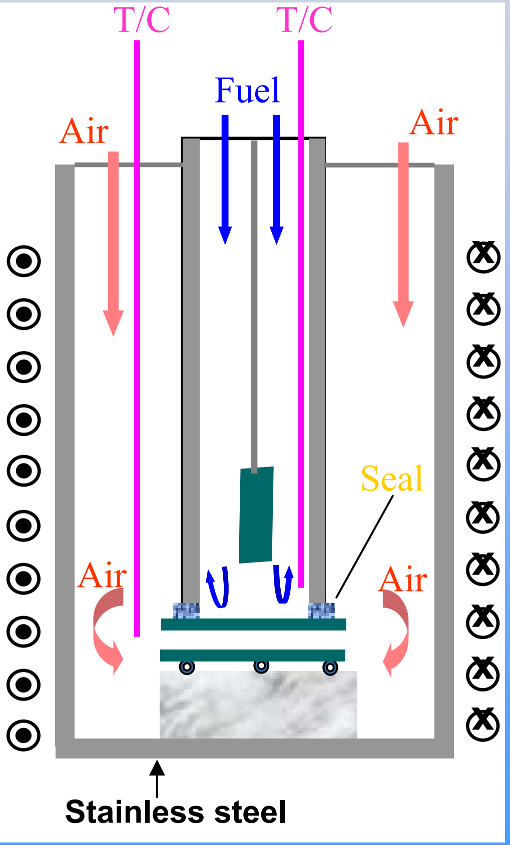
Ni-Based Alloys

- CTE of Ni-based alloys can be adjusted to a relatively low value via lowering Cr% and adding metal elements such as W, Mo, etc.
- The decreased Cr% may however raises concerns over the oxidation resistance of an alloy in cathode environment; The heavy alloying also creates nonlinearity in the CTE curve.
- A scale with a NiO outer-layer can be formed on low Cr% Ni-alloys in cathode-side environment, but its suitability as an electrically conductive protective layer is questionable.

Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces

Oxidation Behavior of Alloys under Interconnect Dual Exposures



Motivation:

- Oxidation study has been a common area of interest, but typically under single atmosphere exposure.
- Dual exposures are commonly found in SOFC stacks and BOP, as well as other systems.
- Understanding helps develop robust materials.

Materials studied:

NiBS { Haynes 230-22%Cr, Hastelloy S-17%Cr, Haynes 242-8%Cr }

FeSS { E-brite-27%Cr, Crofer22-22%Cr, AISI430-17%Cr }

Variables:

- Alloy composition
- Isothermal vs. cycling
- Moisture

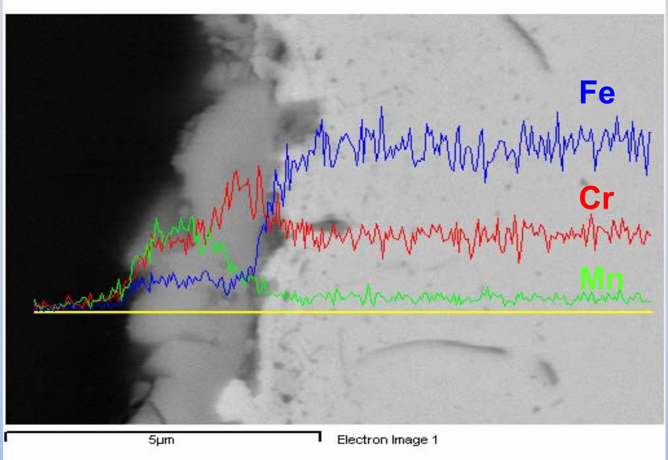
Anomalous Oxidation of FSS under Interconnect Dual Exposures: A Summary

The DUAL exposures lead to an anomalous oxidation behavior of ferritic stainless steels under the SOFC interconnect dual exposure conditions;

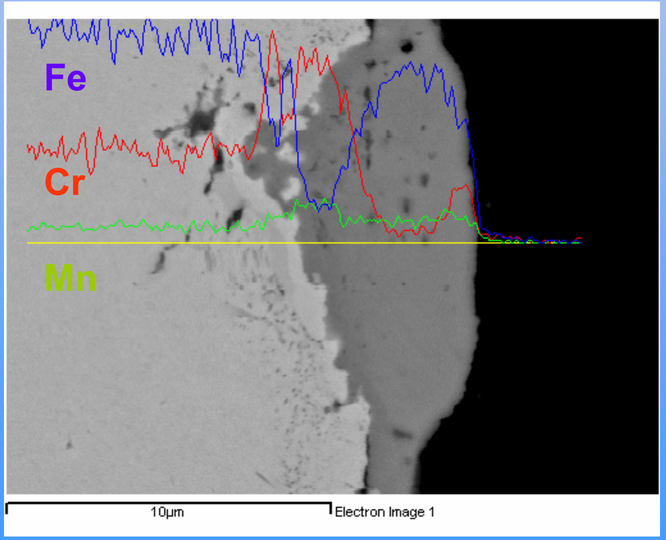
The anomalous oxidation behavior appears to be caused by hydrogen diffusion from the fuel side to the airside of alloy interconnects.

- For 430 with 17% Cr, dual exposures enhanced the iron transport in the scale on the airside, leading to hematite formation and localized attack;
- Fro Crofer22 (22% Cr), Fe enrichment was found in the spinel layer after isothermal oxidation; thermal cycling resulted in the hematite nodule formation and localized attack;
- For ferritic stainless steels with enough chromium, e.g. E-brite (27% Cr), the accelerated iron transport and iron oxide formation are inhibited, though differences in scale microstructure and morphology are observed

Airside of Crofer22 APU



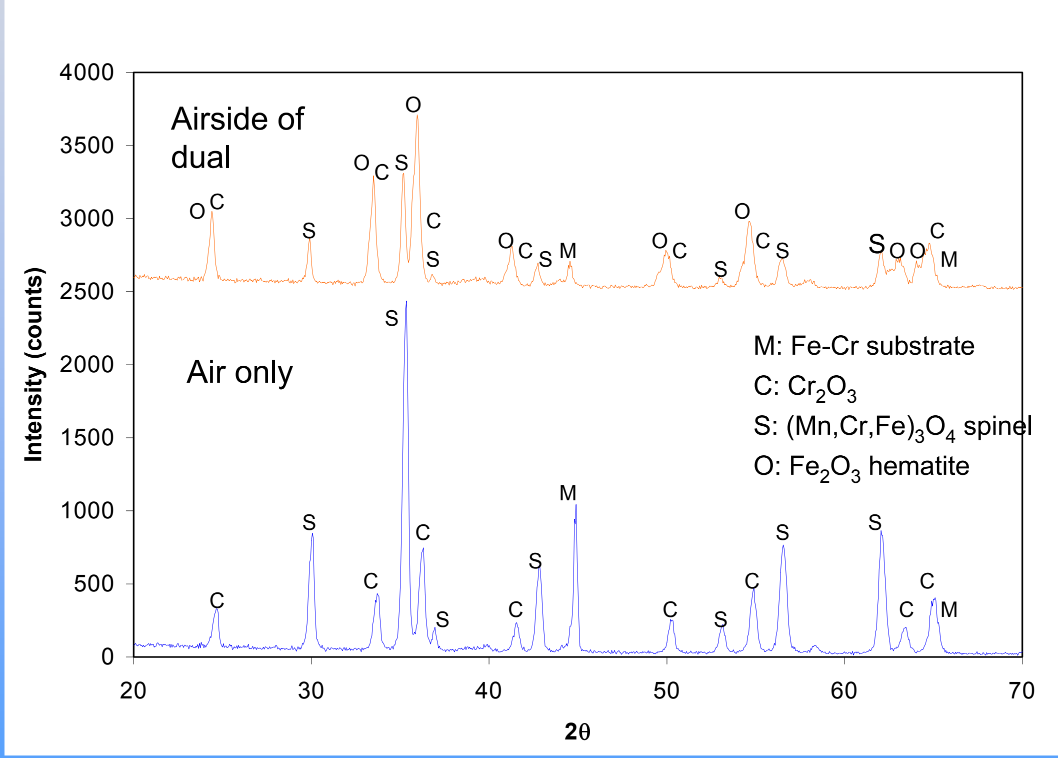
Isothermal: 800°C, 300h



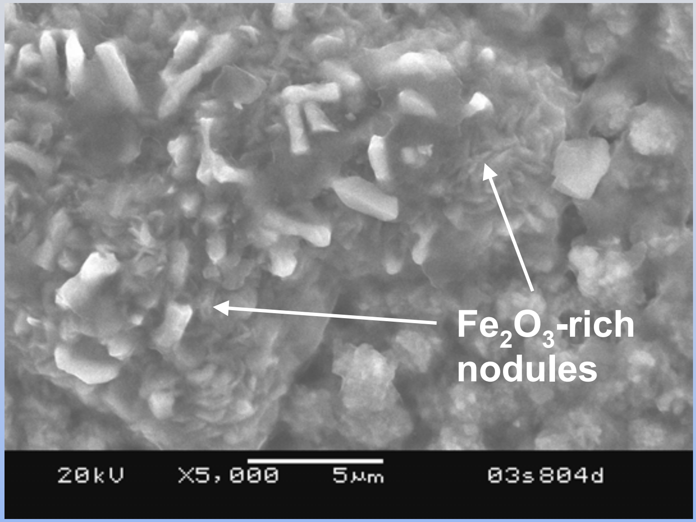
Thermal cycling: 800°C, 3x100h

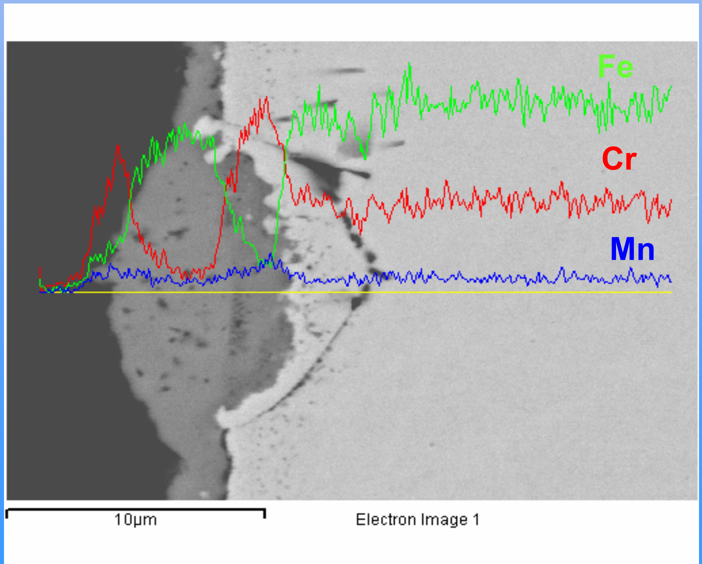
Crofer22 APU: Effects of Moisture

Grown on the coupon in moist (3%H_2O) air only and on the airside of the coupon that was ISOTHERMALLY heat-treated at 800°C, 300 hours.



Airside of dual exposures

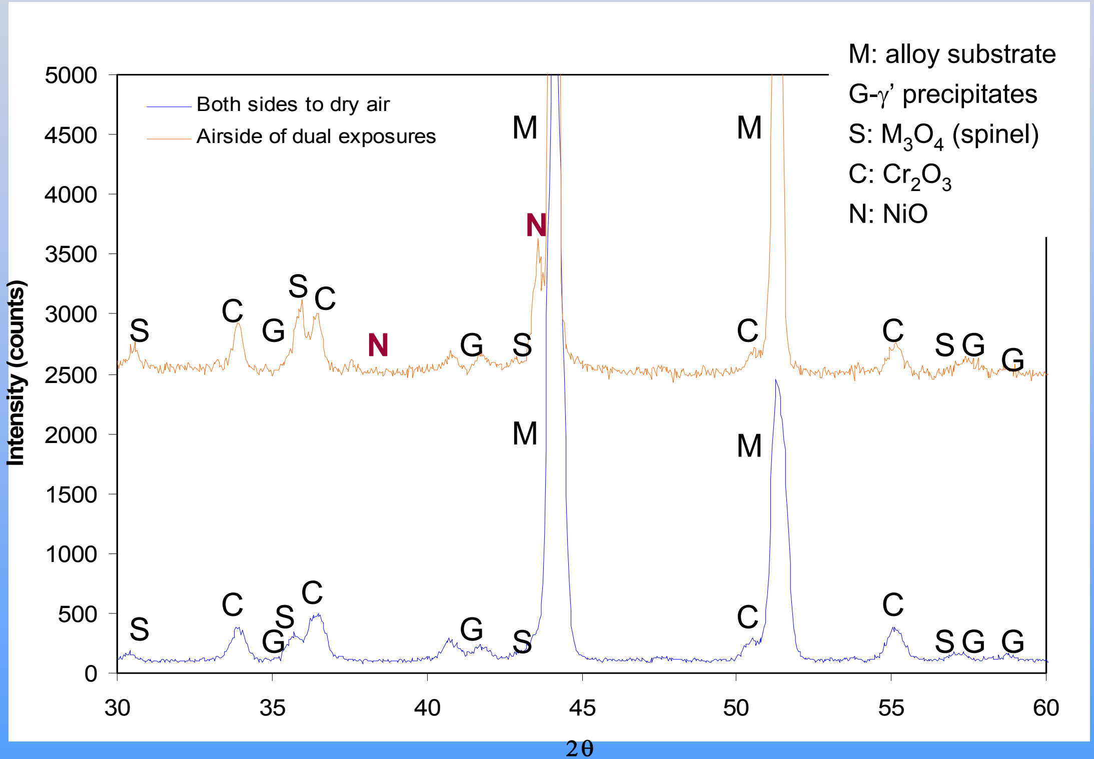




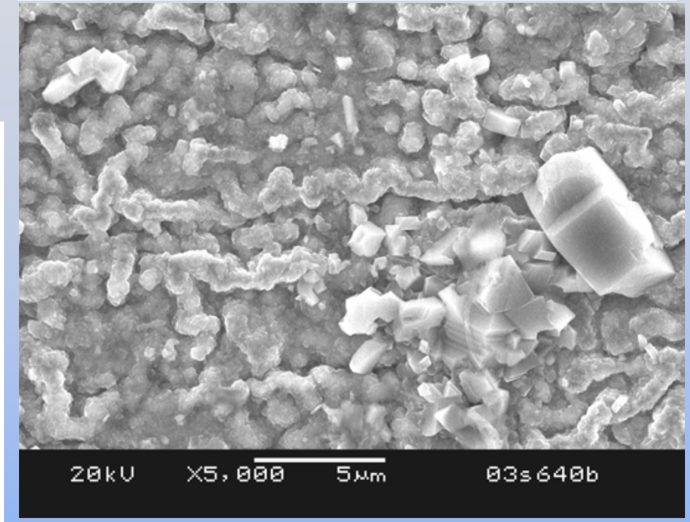
Presence of moisture accelerated the anomalous oxidation.

Haynes230: Oxidation Behavior

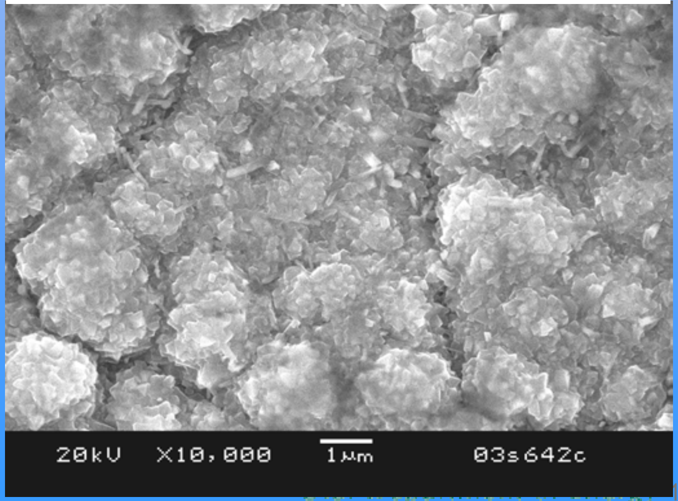
Grown on the coupon in air only (ambient air) and on the airside of the coupon that was isothermally heat-treated at 800°C, 300 hours.



Air exposure at both sides

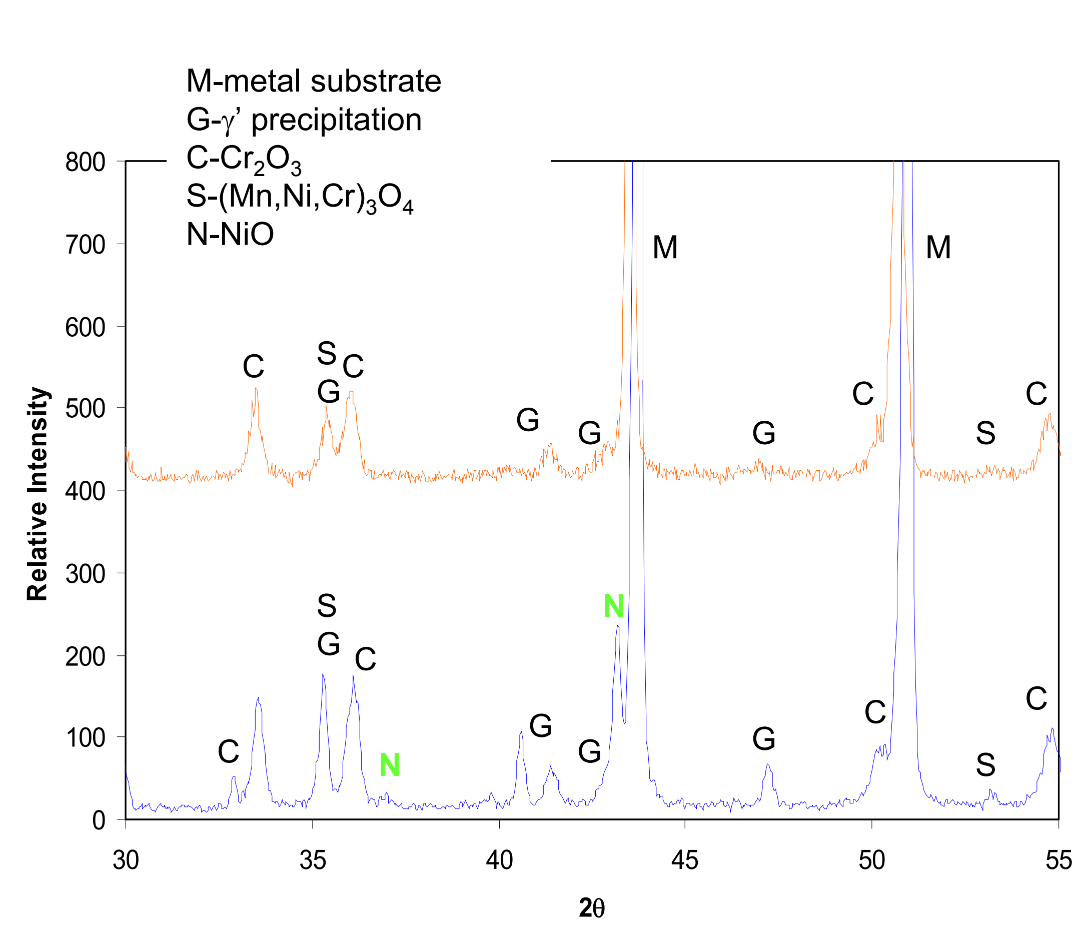


Airside of dual exposures

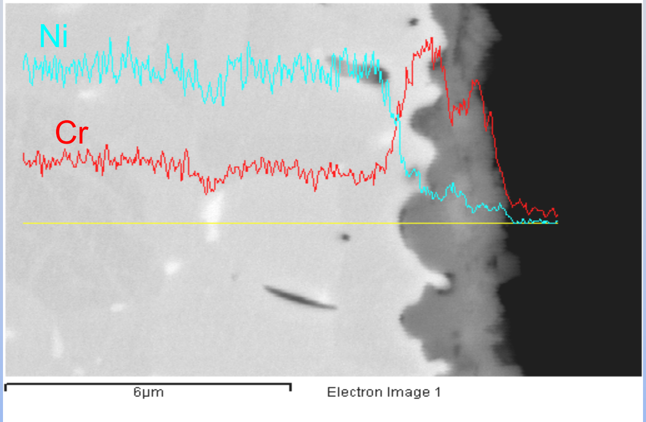


Hastelloy S: Oxidation Behavior

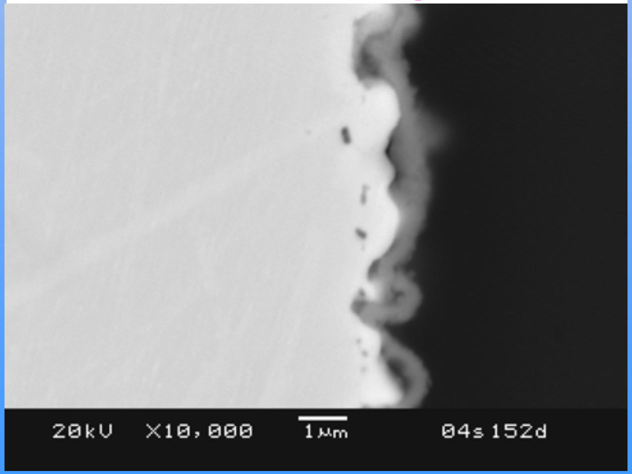
Grown on the coupon in air only and on the airside of the coupon that was isothermally heat-treated at 800°C, 300 hours.



Air exposure at both sides

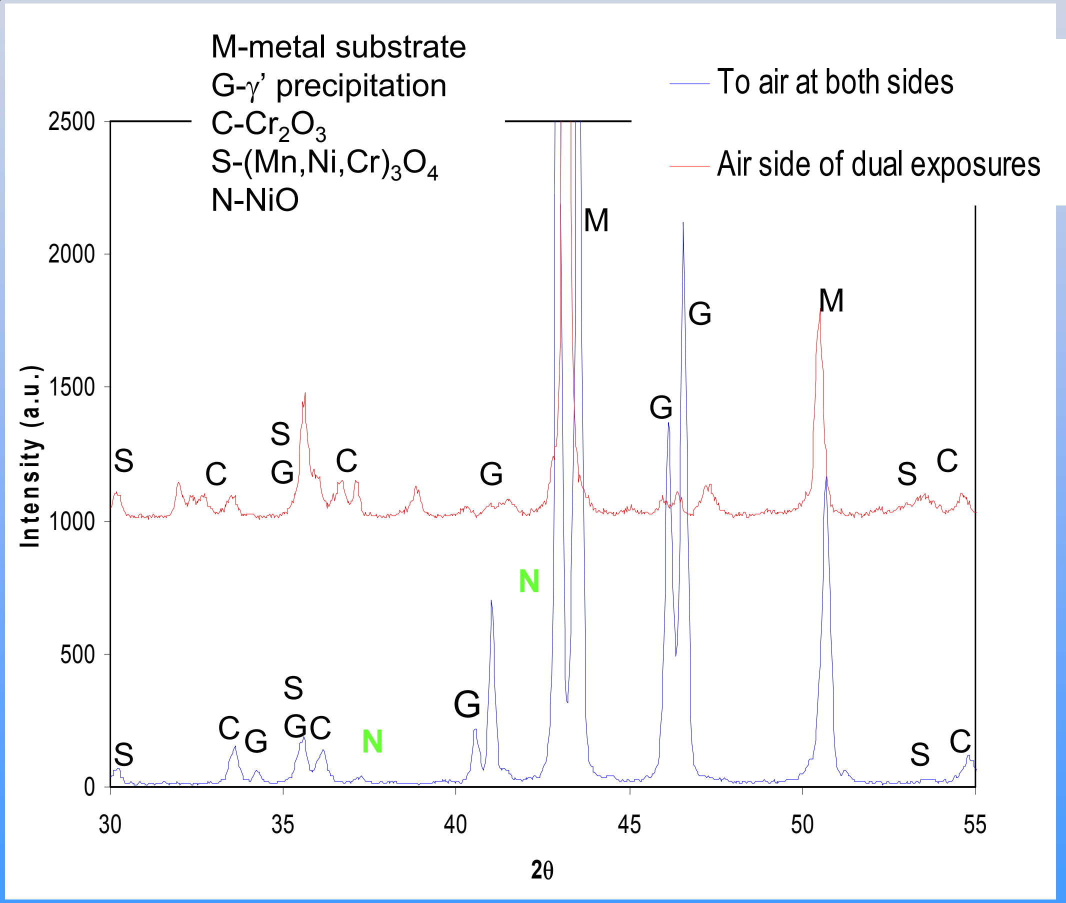


Airside of dual exposures

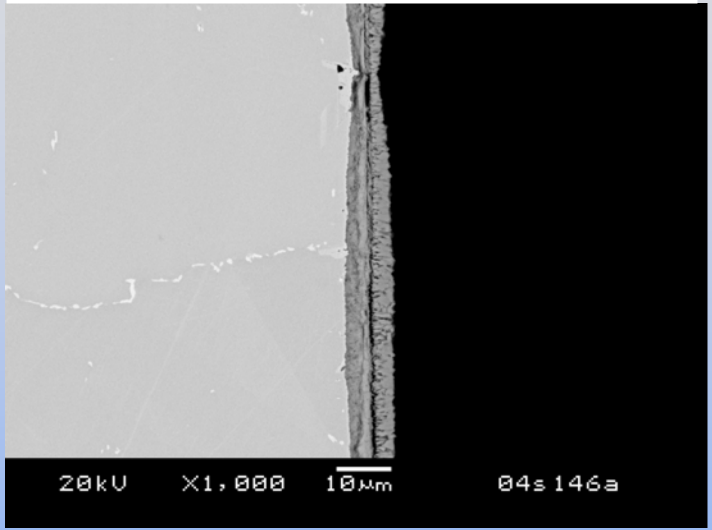


Haynes242: Oxidation Behavior

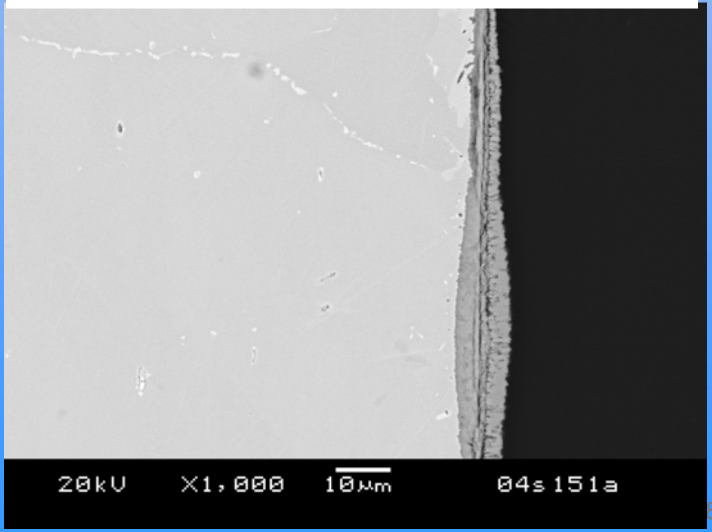
Grown on the coupon in air only and on the airside of the coupon that was isothermally heat-treated at 800°C, 300 hours.



Air exposure at both sides



Airside of dual exposures



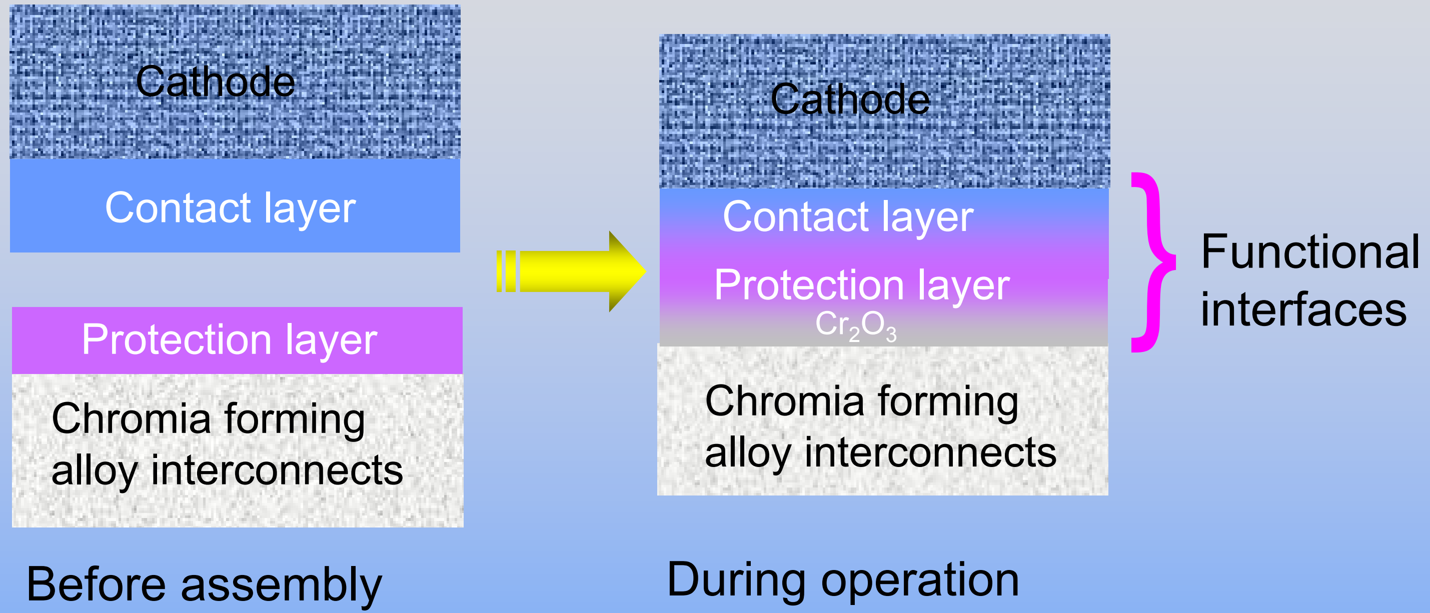
Summary

- For **ferritic stainless steels** with relatively low chromium levels (22% or less), dual exposure enhances the iron transport in scale on the airside, leading to hematite formation and localized attack.
- The presence of moisture enhances the anomalous oxidation, leading to localized attack.
- For **Ni-based alloys**, dual atmosphere exposure tends to reduce NiO formation, and to facilitate the formation of a uniform chromia/spinel dominated scale.

Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces

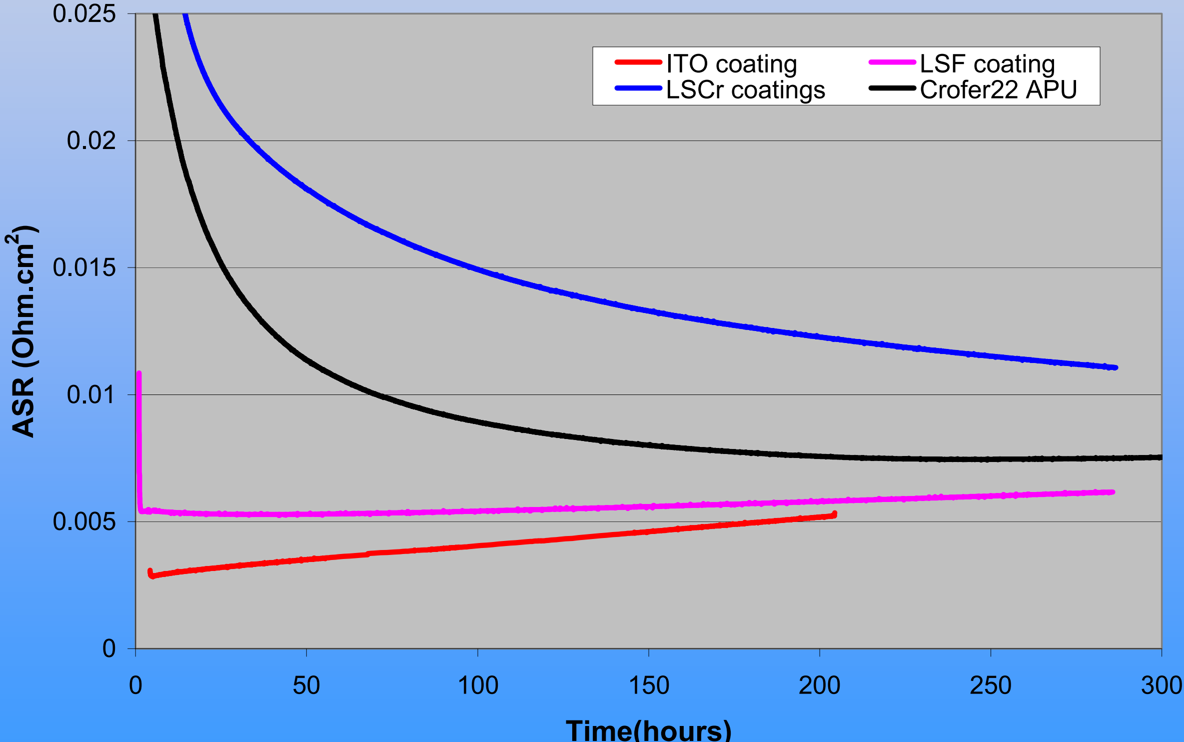
Cathode-Side Functional Interfaces

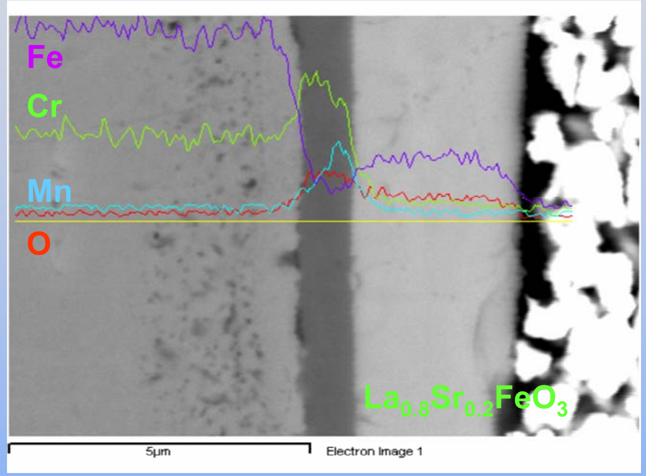


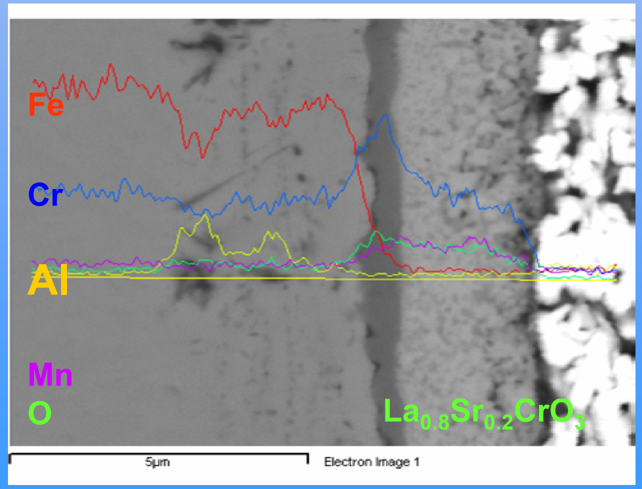
- **Protection layer acts as a mass barrier to mitigate or prevent Cr migration via both gas transport and solid state reactions, as well as to decrease electrical contact resistance. The subsequently grown chromia sub-scale serves as cation and anion transport barrier, protecting the alloy interconnect.**
- **Contact layer promotes contact between cathodes and interconnects, and helps minimize interfacial resistance and power loss.**

Provskite Coatings as Protection Layers

- The provskite coatings decrease electrical resistance and mitigate or prevent Cr migration;
- The growth rate of the chromia beneath the coatings and the eventual scale depends on the ionic conductivity of coatings.
- Long term stability needs to be further studied.







Both bare and coated samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.

Thermal Grown Spinel Protection Layer

Concept

As prepared

Ms_3O_4 spinel

Chromia forming alloy interconnects

During operation

Ms_3O_4 spinel

Cr_2O_3

Chromia forming alloy interconnects

- The protection layer is intended to be thermally grown.

Approach

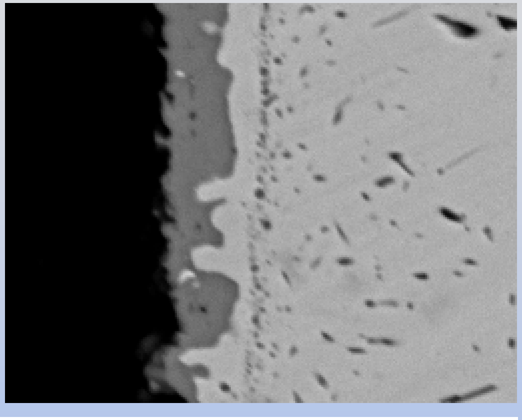
Solution coating, PVD, CVD or EC plating of spinel formation metals.

Growth of a thin spinel layer via reactions during a heat treatment in an optimized environment

Formation of a spinel-chromia functional scale on interconnects during subsequent oxidation or SOFC operations.

Growth of $(Mn,Co)_3O_4$ on Crofer22 APU

Current focus is on thermally grown spinels which contain no Cr and/or are more stable than $(Cr,Mn)_3O_4$.



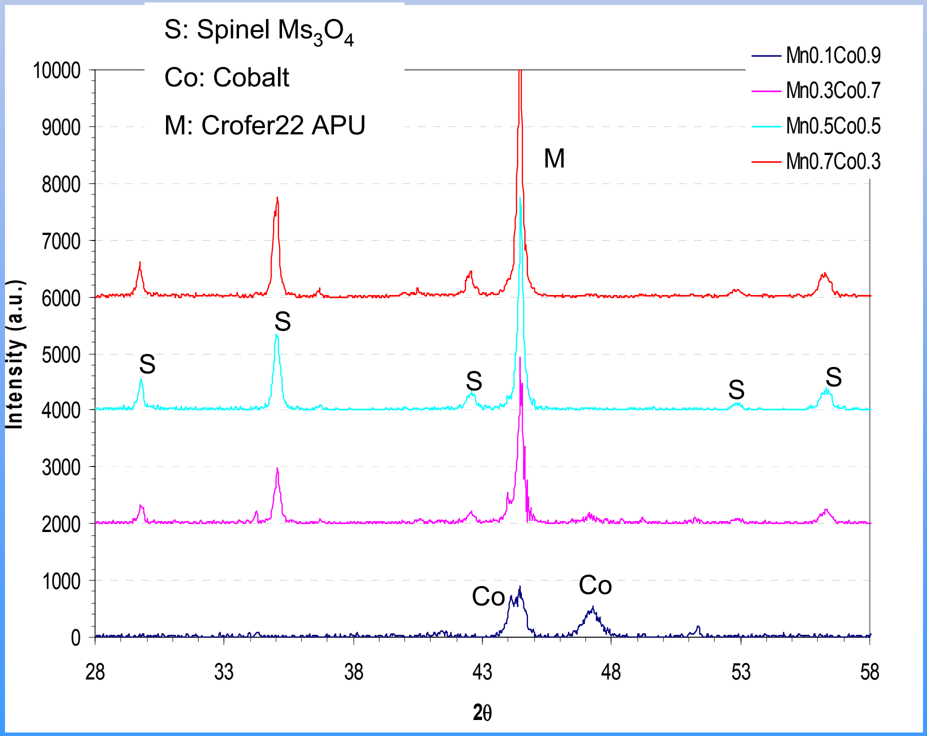
$MnCO_3+Co_3O_4$ Slurry coating

↓

Heat treating in $2.75H_2+Ar$ at 950ºC for 24 hours.

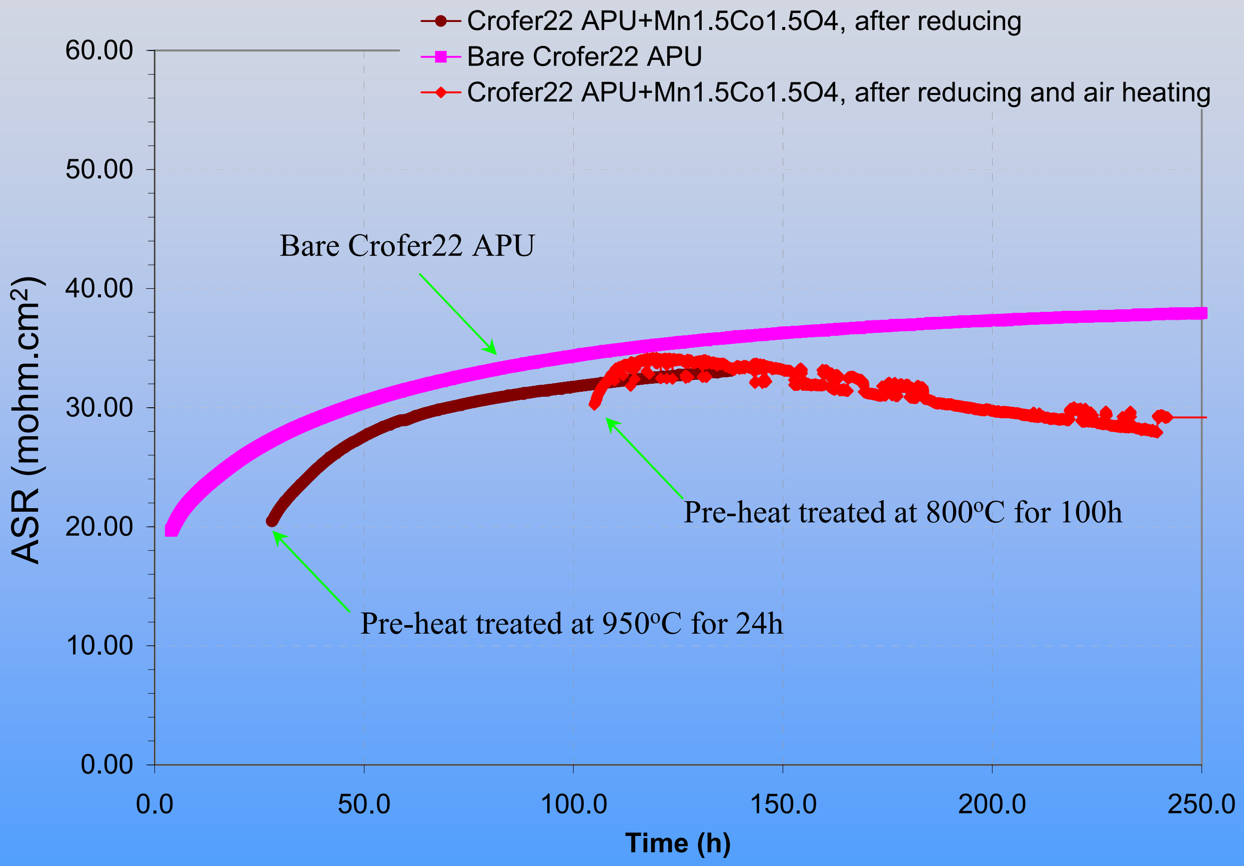
↓

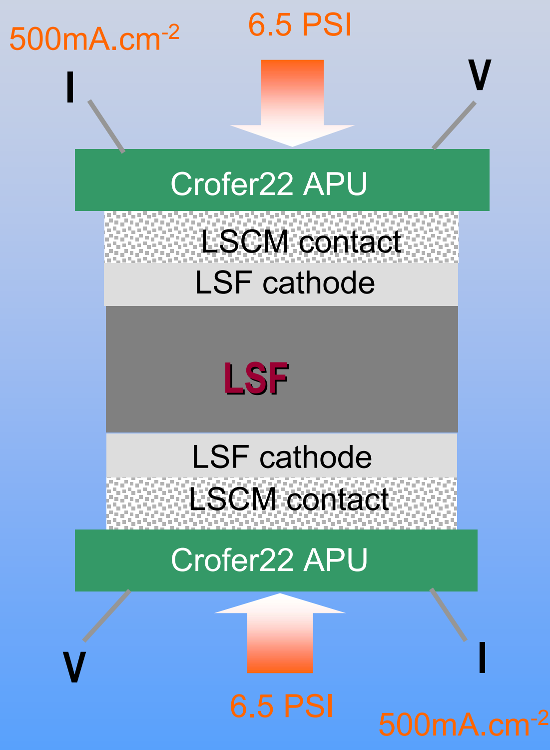
Oxidation in oxidizing environment



Interfacial ASR of Crofer22 APU Grown with Spinel Protection Layers

The $(Mn,Co)_3O_4$ spinel protection layer on Crofer22 APU minimizes the interfacial resistance when $(La_{0.8}Sr_{0.2})Co_{0.5}Mn_{0.5}O_3$ used as a electrical contact.





$$ASR_{cathode/interconnect} = \Phi(scale, contacts, reactions)$$

Summary

- Continuous, thin spinel protection layer can be thermally grown on chromia forming alloys during optimized pre-heat treating; the spinel protection layer is intended to help minimize volatilization of Cr vapor species and the interfacial electrical resistance.
- Preliminary work on Co/Mn spinel layers indicates low interfacial electrical resistance.
- Mitigation of Cr volatility to be verified experimentally.

Future Work:

Study oxidation behavior under dual exposures

- Mechanistic understanding: Interaction and transport of H/H^+ at the metal/oxide interface and in the oxide scale; their effects on defect structure, transport properties, scale growth.
- Study effects of dual exposure on scale electrical conductivity.
- Oxidation behavior of alloys under the reforming gas/air dual exposures.

Investigate and develop cathode-side functional interfaces

- Spinel protection layers: Continue to screen and search for spinels that compatible to candidate alloys and more thermochemically stable than $(Mn,Cr)_3O_4$; optimize processing and materials composition.
- Electrical contact layers: Continue to study the interactions between conductive oxides and candidate alloys; investigate the interfacial ASR and optimize the composition for a minimized interfacial resistance.

Develop and investigate cladded composite-structure interconnects

- Continue to the proof of concept investigation.
- Study interdiffusion and predict life via modeling.
- Optimize structure and compositions.

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