Anomalous Oxidation of Ferritic Stainless Steels under Air//Hydrogen Fuel Dual Environments

Z. Gary Yang, Dean M. Paxton, Prabhakar Singh,
J.W. Stevenson, M.S. Walker, Gordon Xia

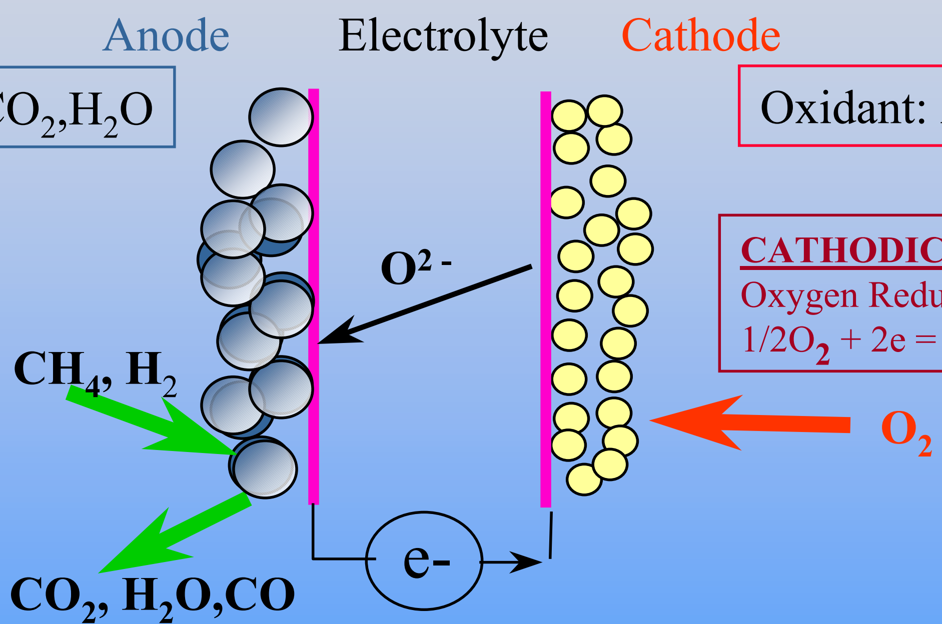
Presented at 134rd TMS Annual Meeting at San Francisco, February 15, 2005

Solid Oxide Fuel Cell Operation

Electrochemical and Reformation Processes

Fuel: CH_4,H_2,CO,CO_2,H_2O

Oxidant: Air, O_2



ANODIC REACTION

Electrochemical Oxidation:

$H_2+O^{2-} = H_2O + 2e$

$CO+O^{2-} = CO^{2} + 2e$

Steam reforming:

$CH_4+H_2O = CO + 3H_2$

Shift Reaction:

$CO+H_2O = CO_2 + H_2$

CATHODIC REACTION

Oxygen Reduction

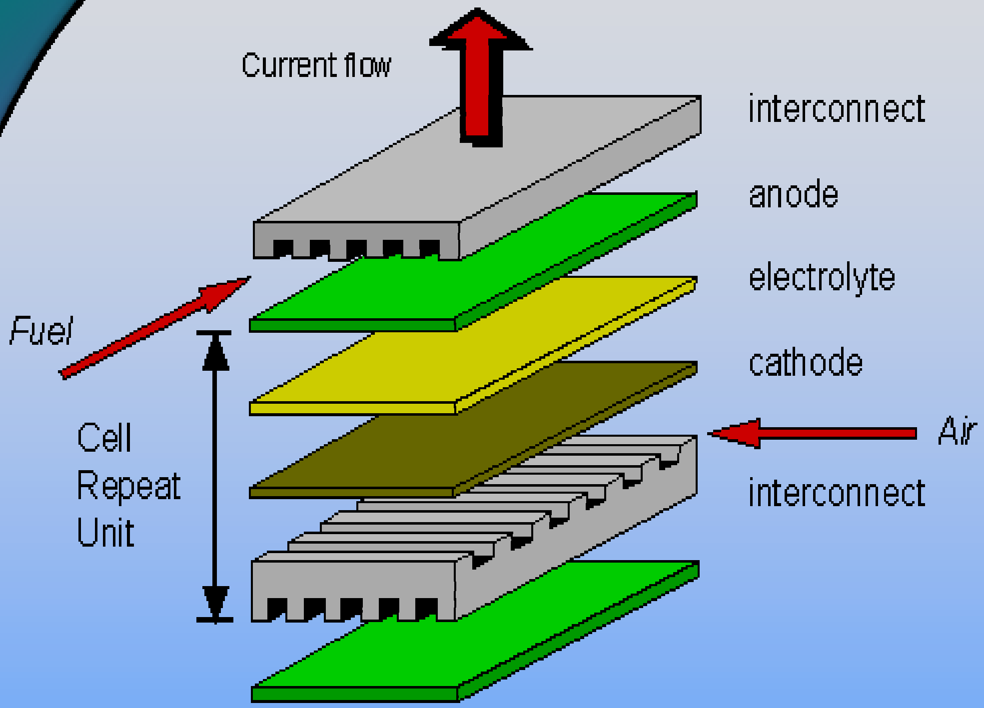
$1/2O_2 + 2e = O2-$

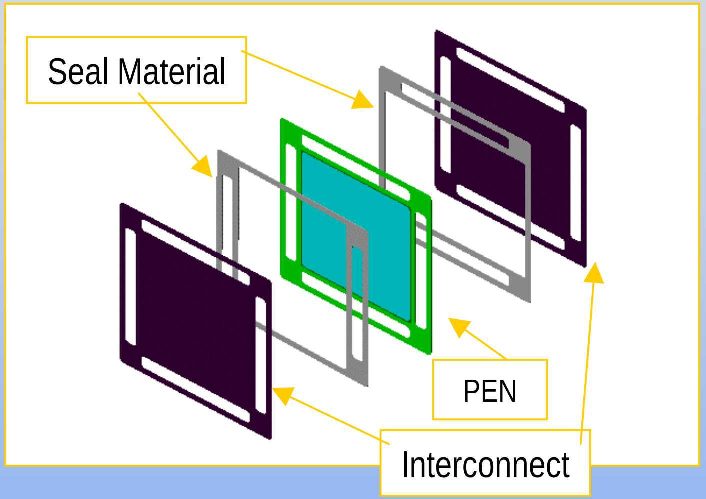
OVERALL CELL REACTION

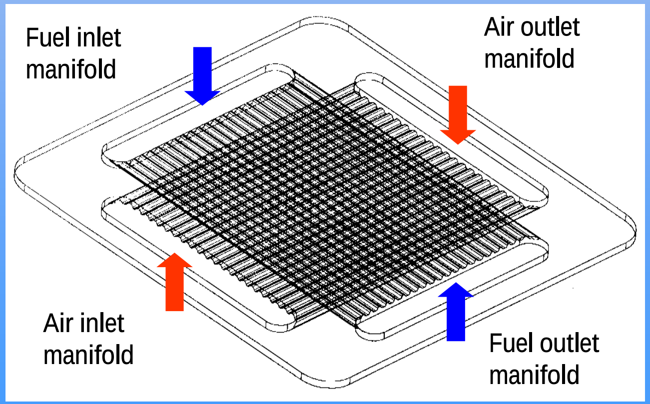
$H_2+1/2O_2 = H_2O$

$CO+1/2O_2 = CO_2$

Planar Solid Oxide Fuel Cells



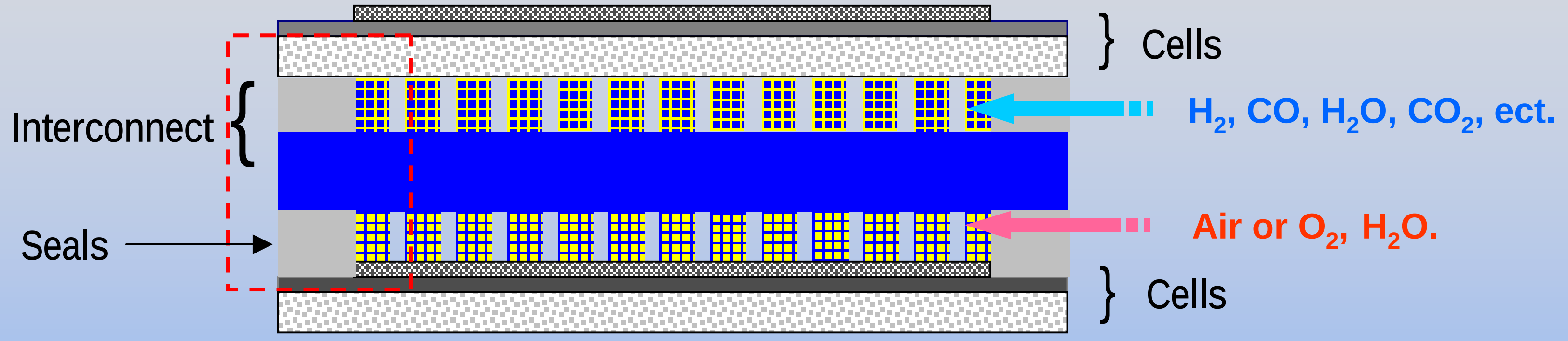




Repeat Components

Oxidation resistance alloy interconnects have been used in planar SOFC systems

Interconnect: Functions & Exposure Conditions



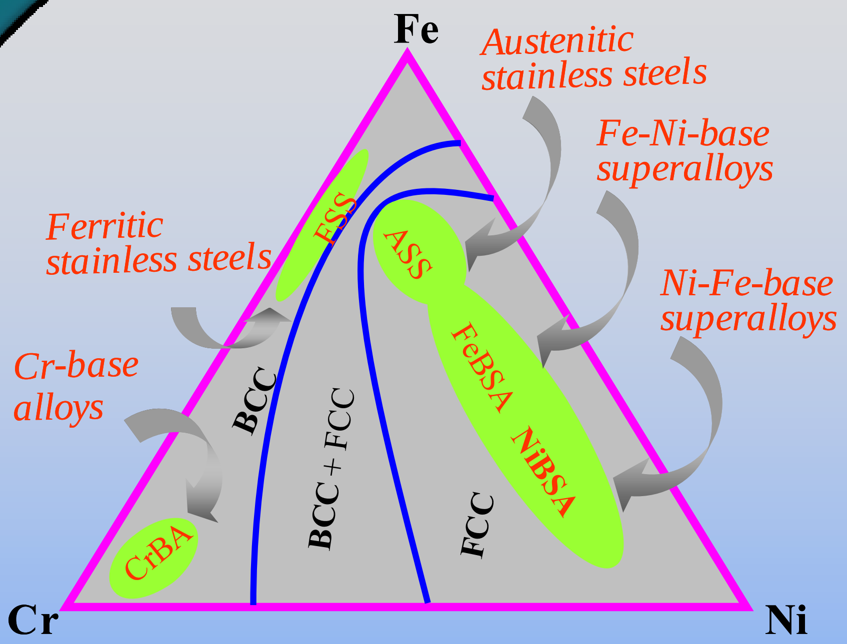
Functions

1) Acts as physical barrier, hermetically separating fuel and oxidant.
2) Acts as a low resistant electrical conduit over life time of the device.
3) Provides mechanical support and stability to the stacks.

Exposure conditions

1. Simultaneously exposed to oxidizing gas at anode side and fuel gas at anode side.
2. Compliant seal/metal interface.
3. Electrical contact/metal interface.
4. Ambient/metal interface.

Metallic Candidates



Overall, heat resistant alloys could be potential candidates, including

- Ferritic stainless steels
- Austenitic stainless steels
- Fe-Ni-base superalloys
- Ni-Fe-base superalloys
- Cr-base alloys

Plus

- Co-base superalloys

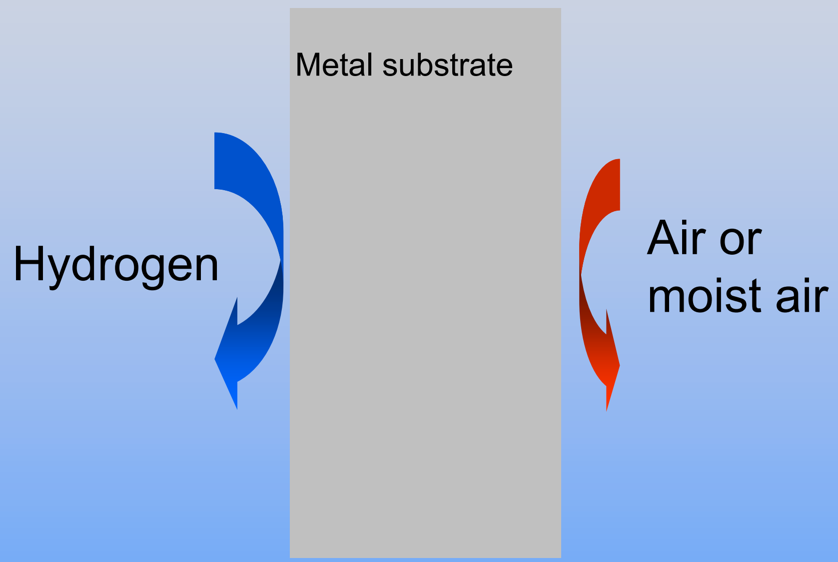
Alloys	Matrix structure	TEC $\times 10^{-6}.K^{-1}$	Oxidation resistance	Mechanical strengths	Manufactur-ability	Cost
CrBA	BCC	11.0-12.5 (RT-800°C)	Good	High	Difficult	Very expensive
FSS	BCC	11.5-14.0 (RT-800°C)	Good	Low	Fairly readily	Inexpensive
ASS	FCC	18.0-20.0 (RT-800°C)	Good	Fairly high	Readily	Inexpensive
FeBSA	FCC	15.0-20.0 (RT-800°C)	Good	High	Readily	Fairly expensive
NiBSA	FCC	14.0-19.0 (RT-800°C)	Good	High	Readily	Expensive

Ferritic stainless steels offer a combination of good CTE matching and manufacturability, as well as being cost-effective.

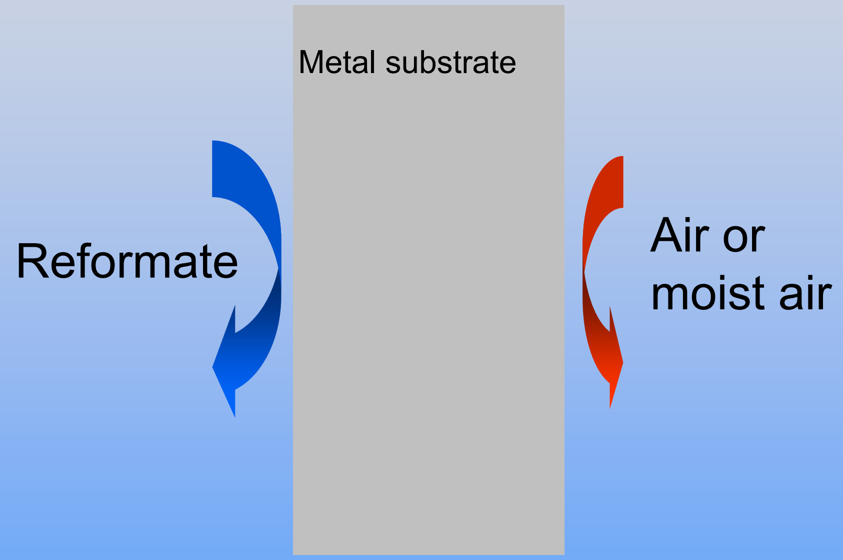
Motivation

- Oxidation has been a common area of interest and widely studied in the past century.
- But the studies were typically carried out in a single exposure.
- The oxidation behavior under "simultaneous" dual exposures is indeed unclear.
- Understanding helps develop robust materials and improve reliability and durability of components such as interconnects that function under dual exposures.

Interconnect "Dual" Exposures

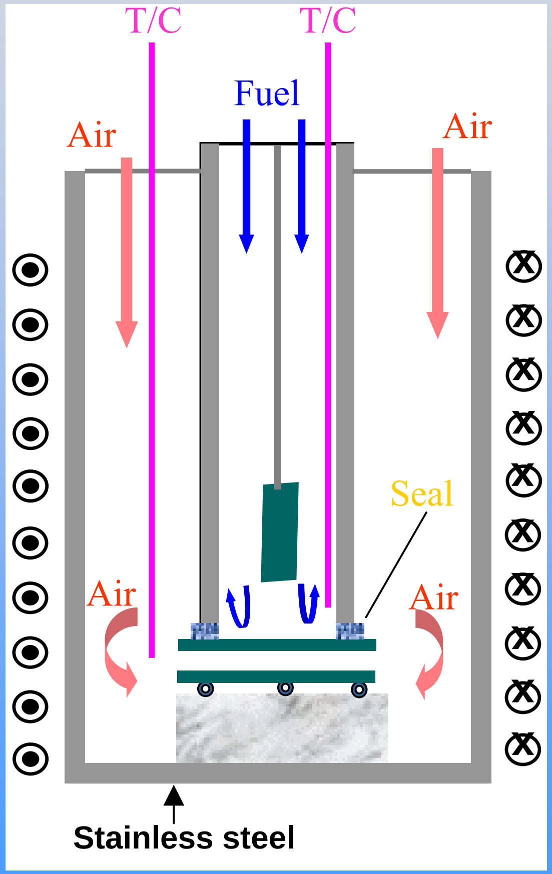


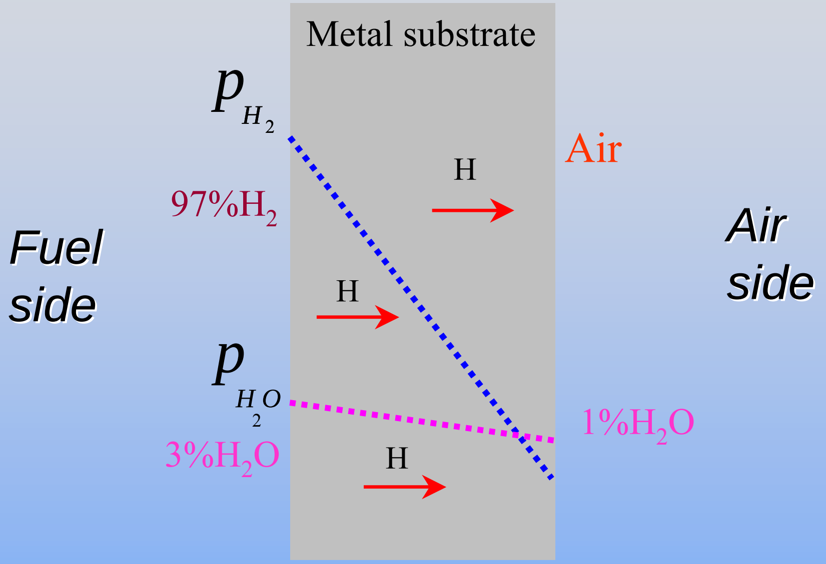
H_2//Air



Reformate//Air

Oxidation Study under H_2//Air Dual Exposures



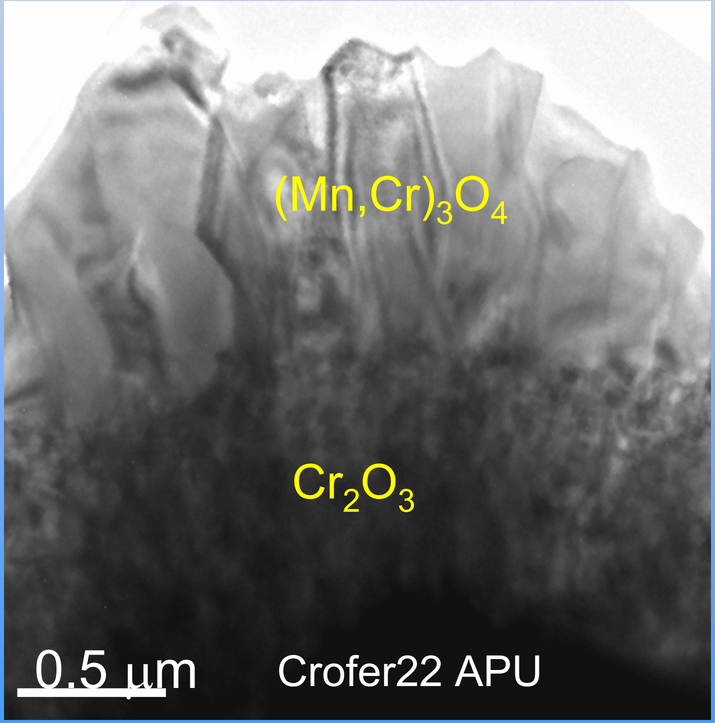


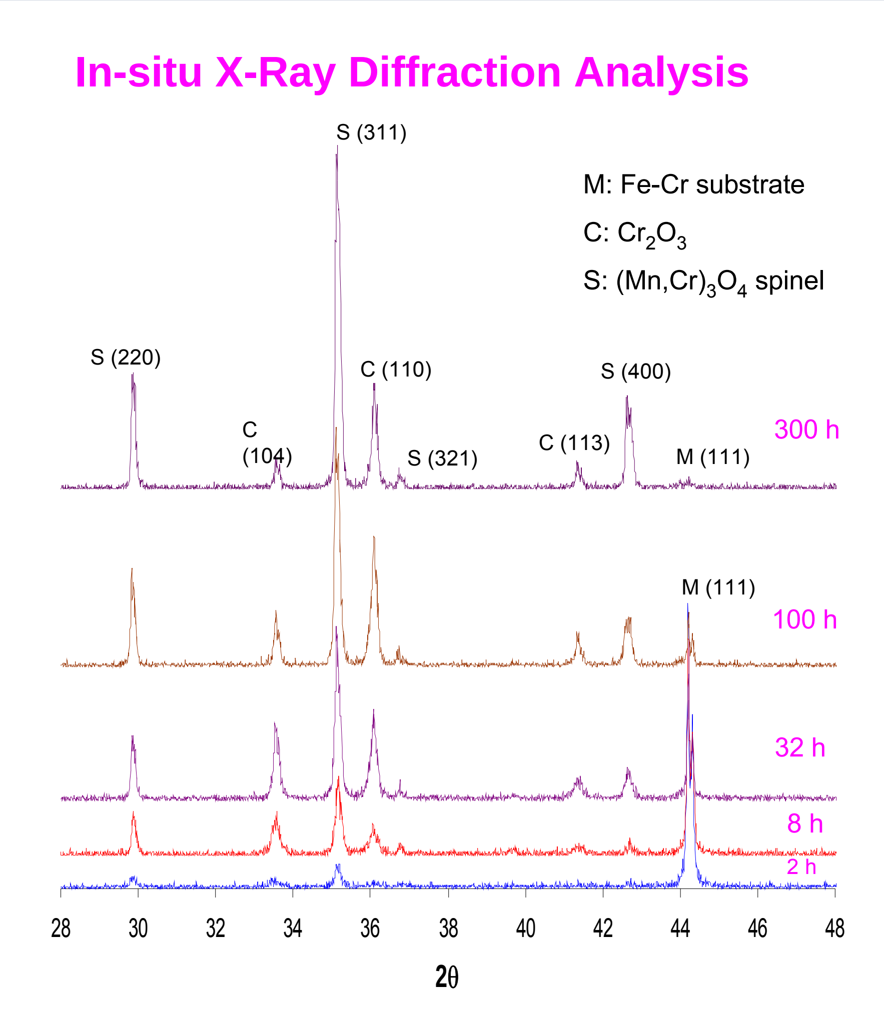
Variables:

- Alloy composition
  - E-brite-27%Cr
  - Crofer22-22%Cr
  - AISI430-17%Cr
- Water vapor effects
- Thermal history: isothermal vs. cycling

Crofer22 APU: Scale Growth in Air Only

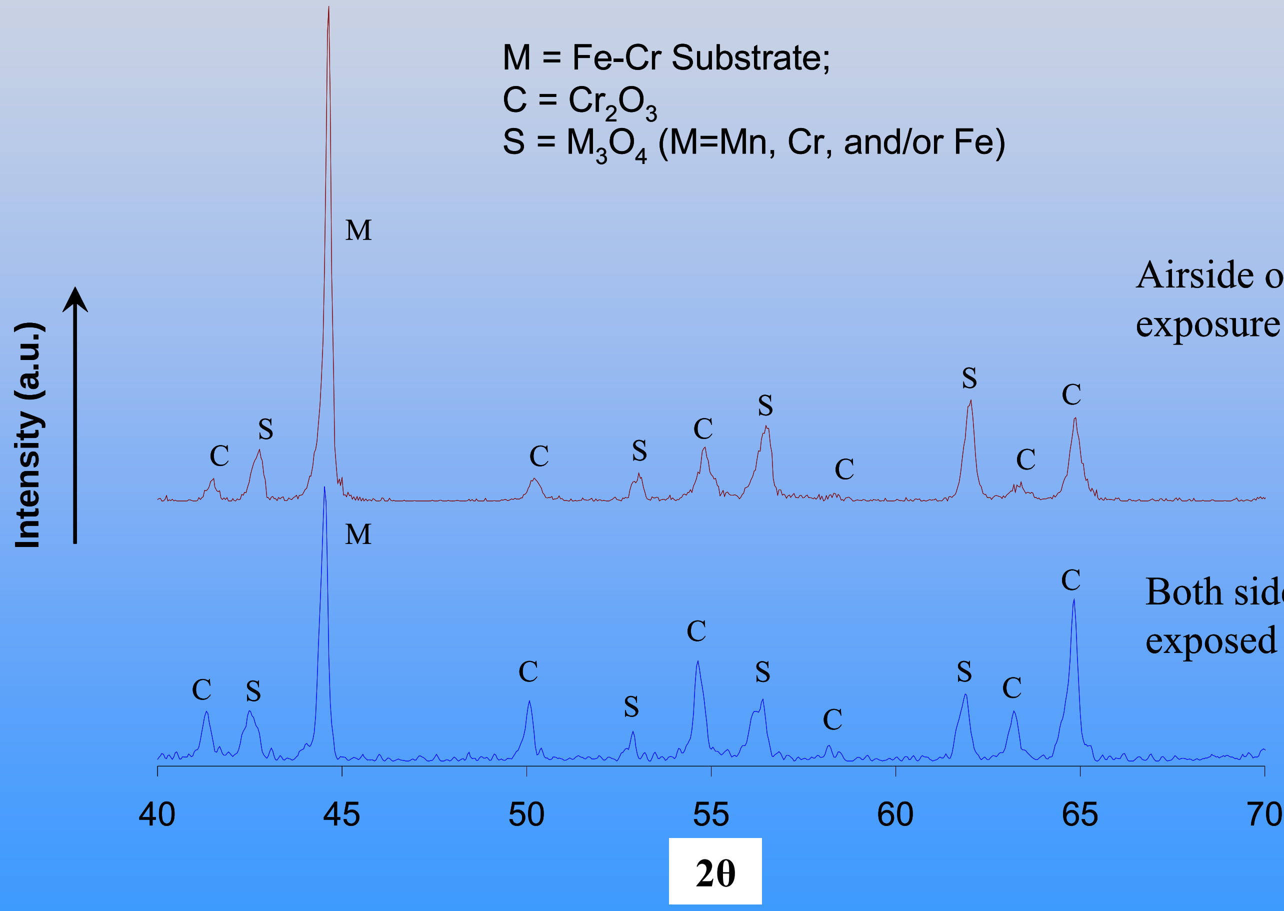
Crofer22 APU is characterized by formation of a unique scale that is comprised of course, column-grown $(Mn,Cr)_3O_4$ toper layer and a fine, granular Cr_2O_3-rich sub-layer.





Crofer22 APU (22%Cr): Structure of Scales

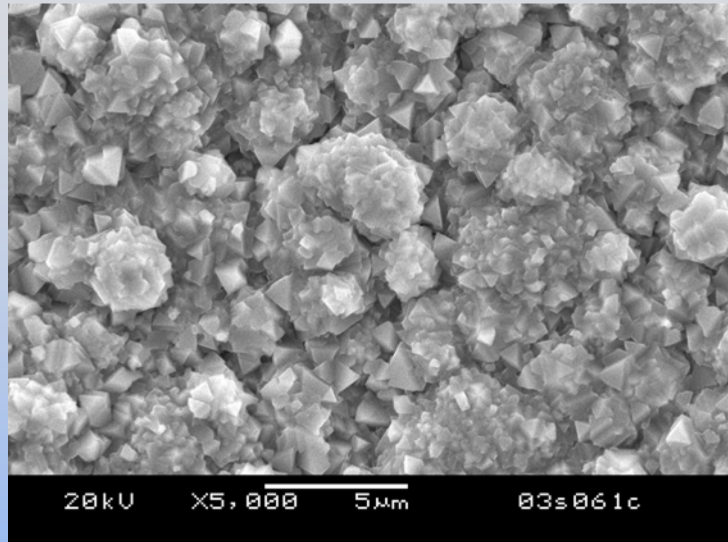
Grown on the coupon in air only and at the airside of the coupon that was ISOTHERMALLY heat-treated at 800°C, 300 hours.

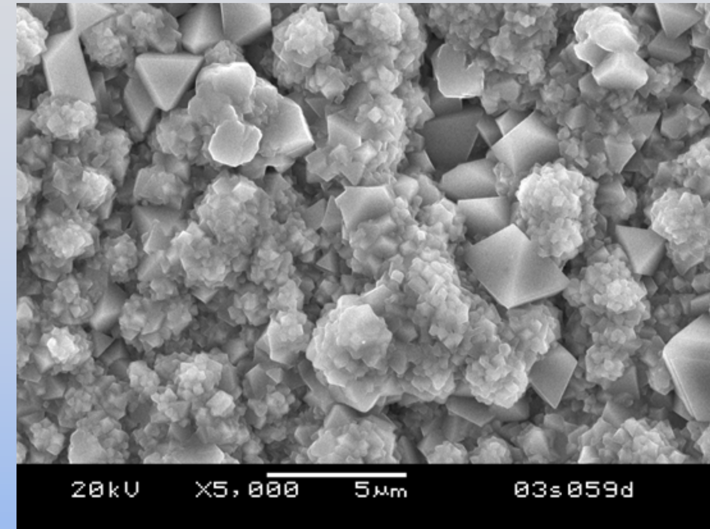


Crofer22 APU: Scale Microstructures

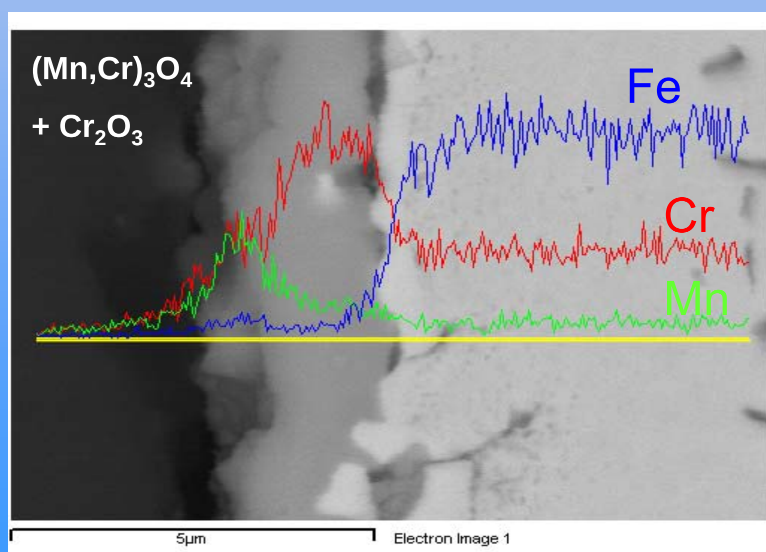
Air exposure at both sides | **Air-side of dual test**

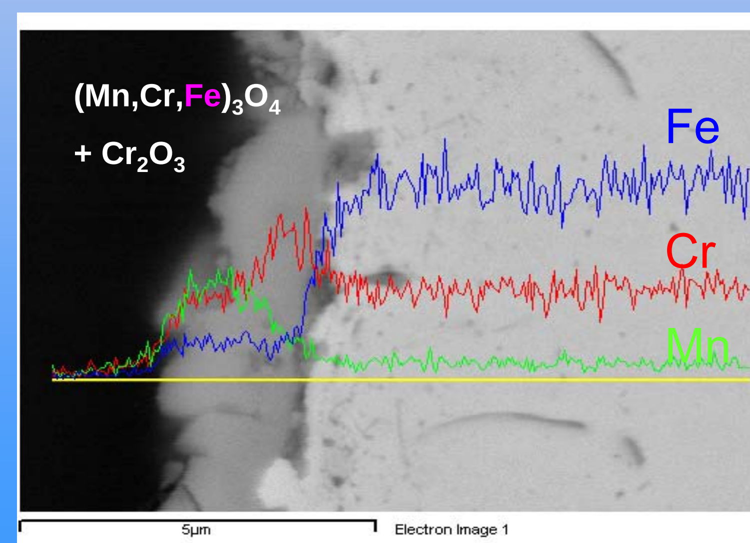
Surface microstructures





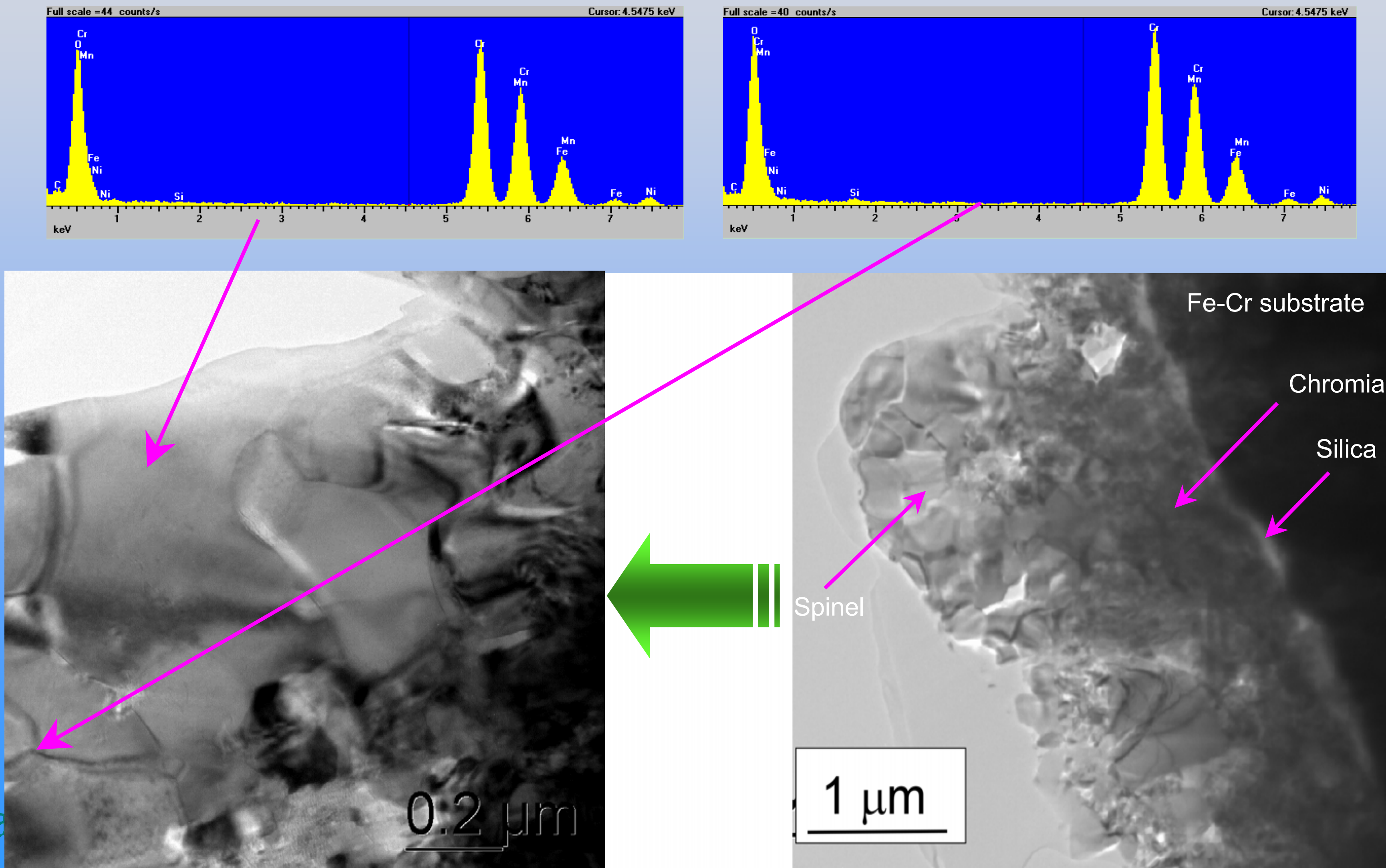
Cross-sections





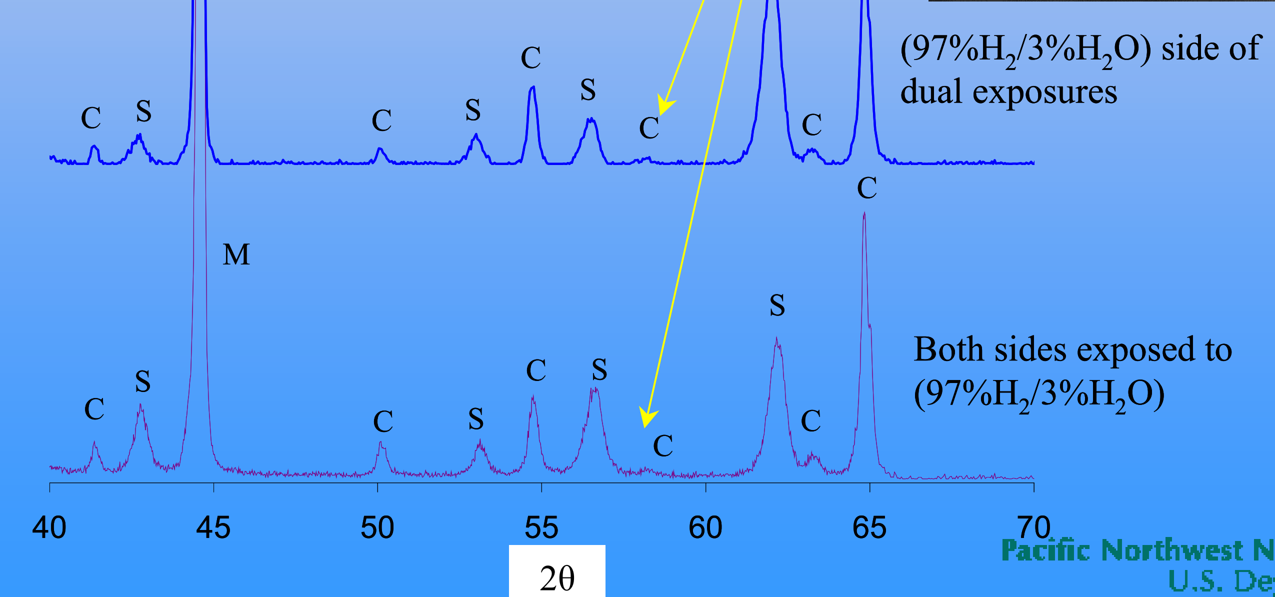
Scale Growth on Airside

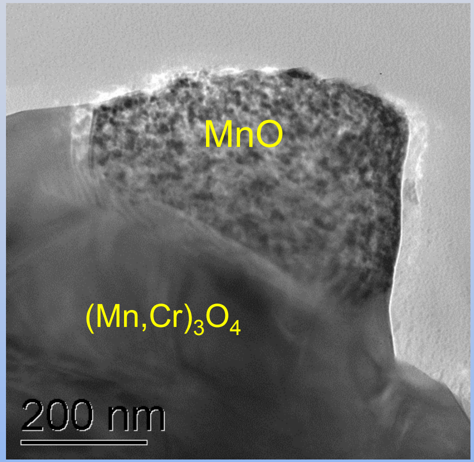
Fe enrichment found both in $(Mn,Cr,Fe)_3O_4$ grains and at grain boundaries.



Crofer22 APU (22%Cr): Structure of Scales

Grown on the coupon in fuel (H_2+3%H_2O) only and at the fuel side of the coupon that was ISOTHERMALLY heat-treated at 800°C, 300 hours.

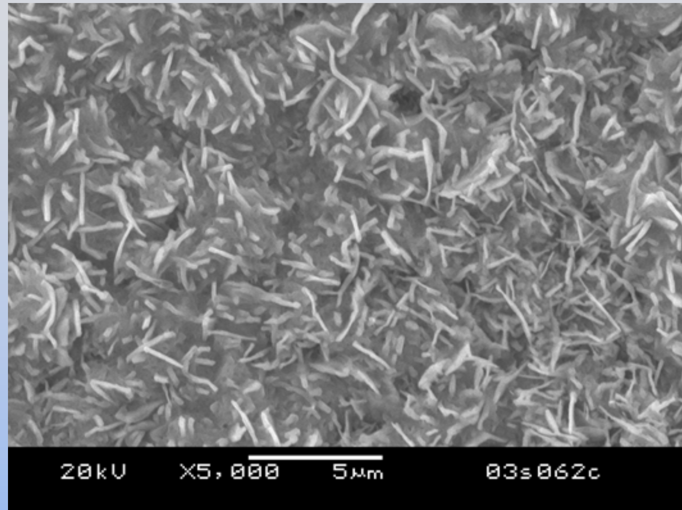


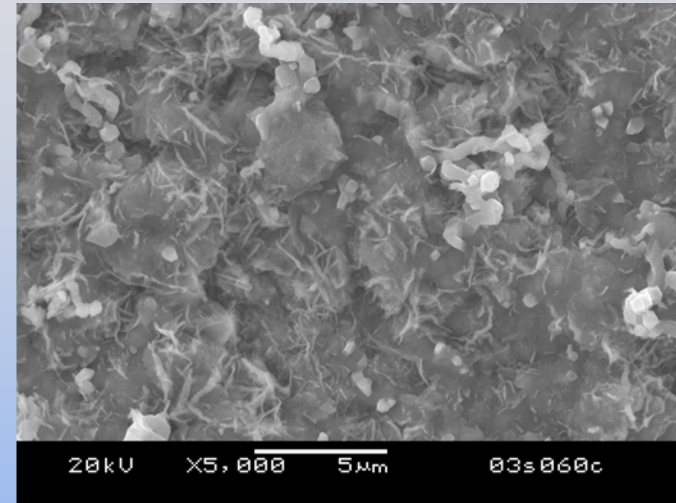


Crofer22 APU: Scale Microstructures

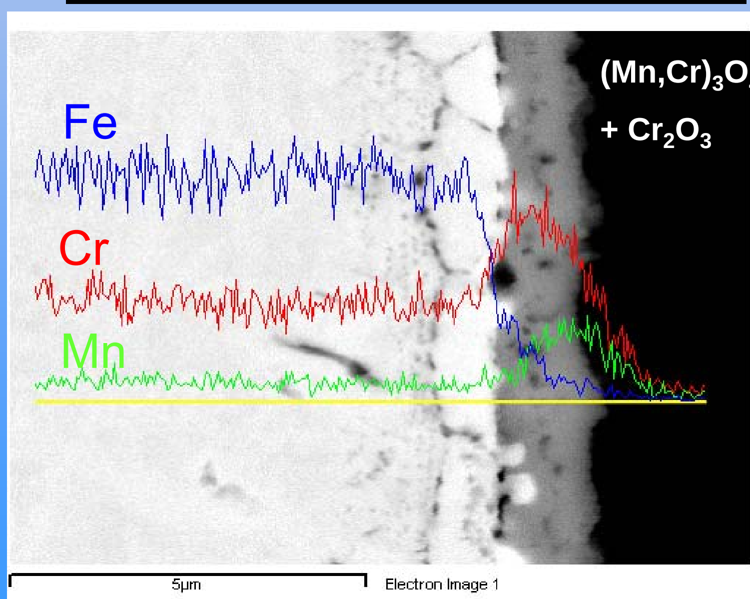
Fuel exposure at both sides | Fuel side of dual test

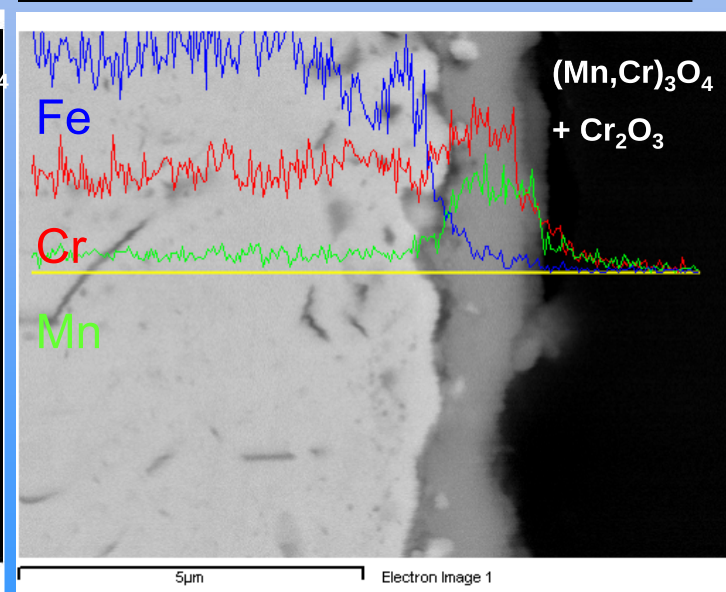
Surface microstructures





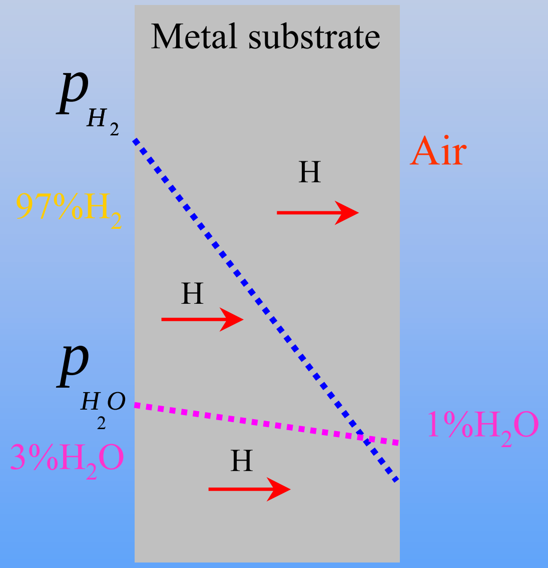
Cross-sections

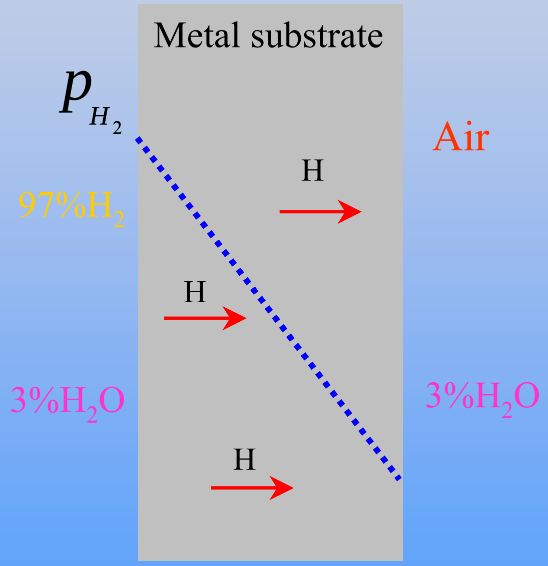




Effects of Water Vapor

Ambient air was replaced by moist air, increasing water content from 1% to 3%.

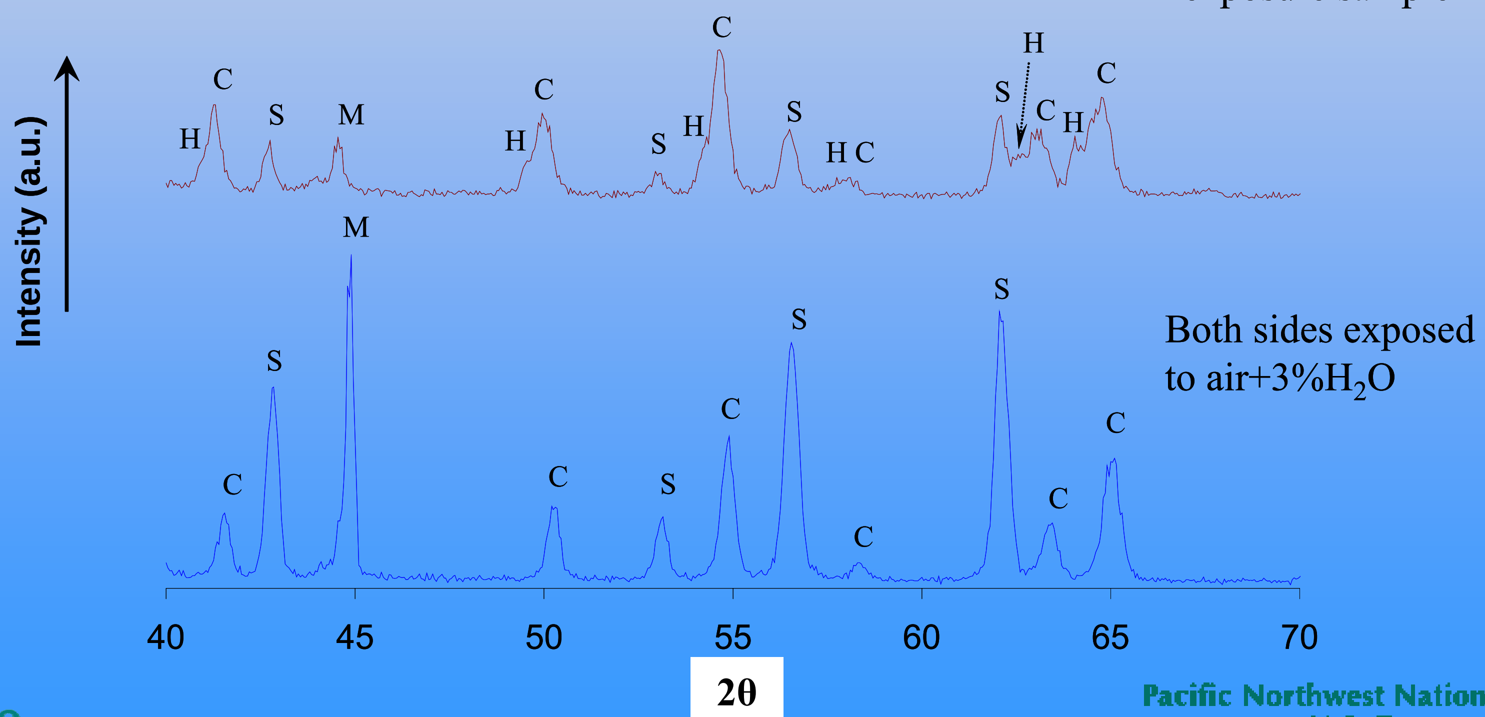




Crofer22 APU: Effects of Water Vapor

Grown on the **Crofer22 APU** coupon in air (3% H_2O) only and at the airside of the coupon that was heat-treated at 800°C, three cycles with each cycle of 100 hours.

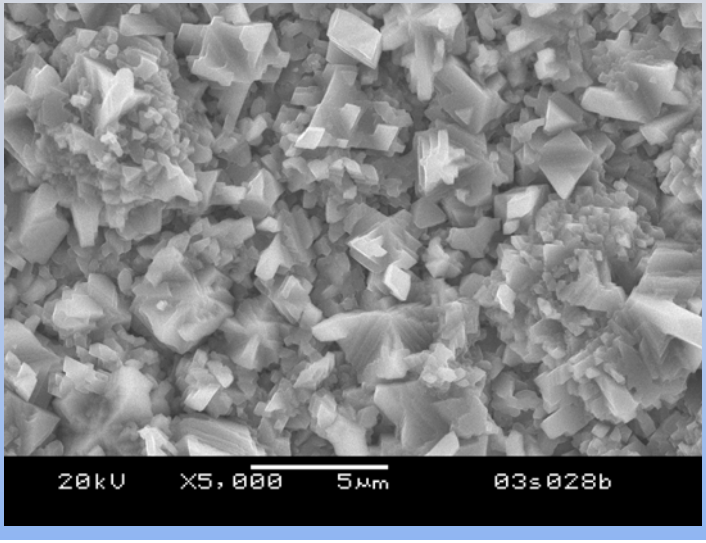
M = Fe-Cr Substrate; C = Cr_2O_3
S = M_3O_4 (M=Mn, Cr, and/or Fe); H = α-Fe_2O_3



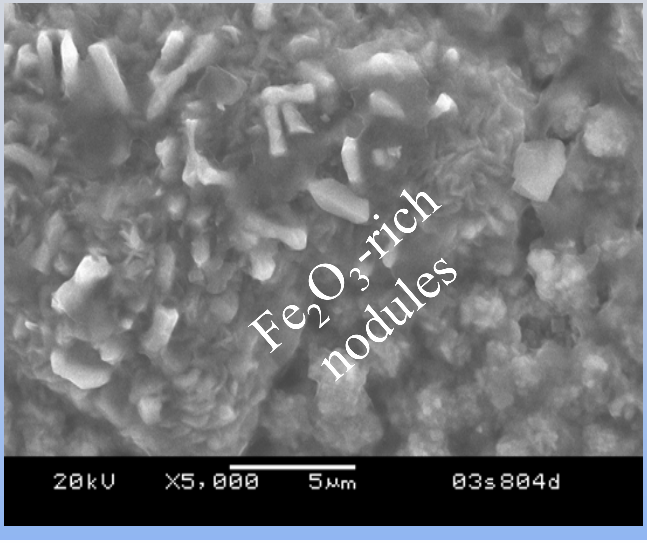
Crofer 22 APU: Effects of Water Vapor

Surface microstructures

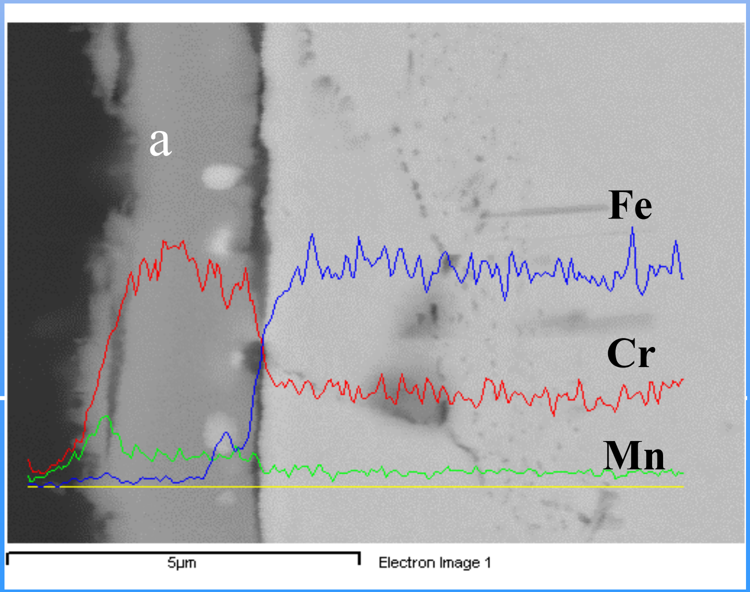
To air+3% H_2O at both sides.

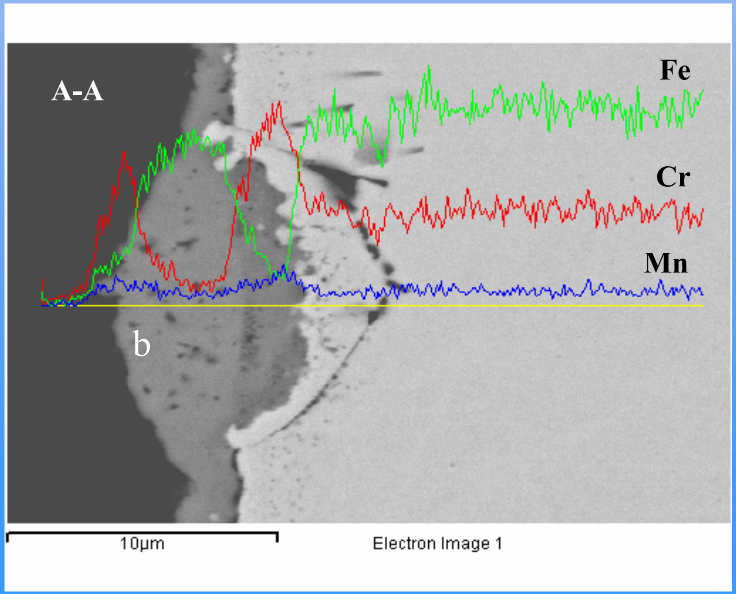


(Air+3% H_2O) side of dual exposures.



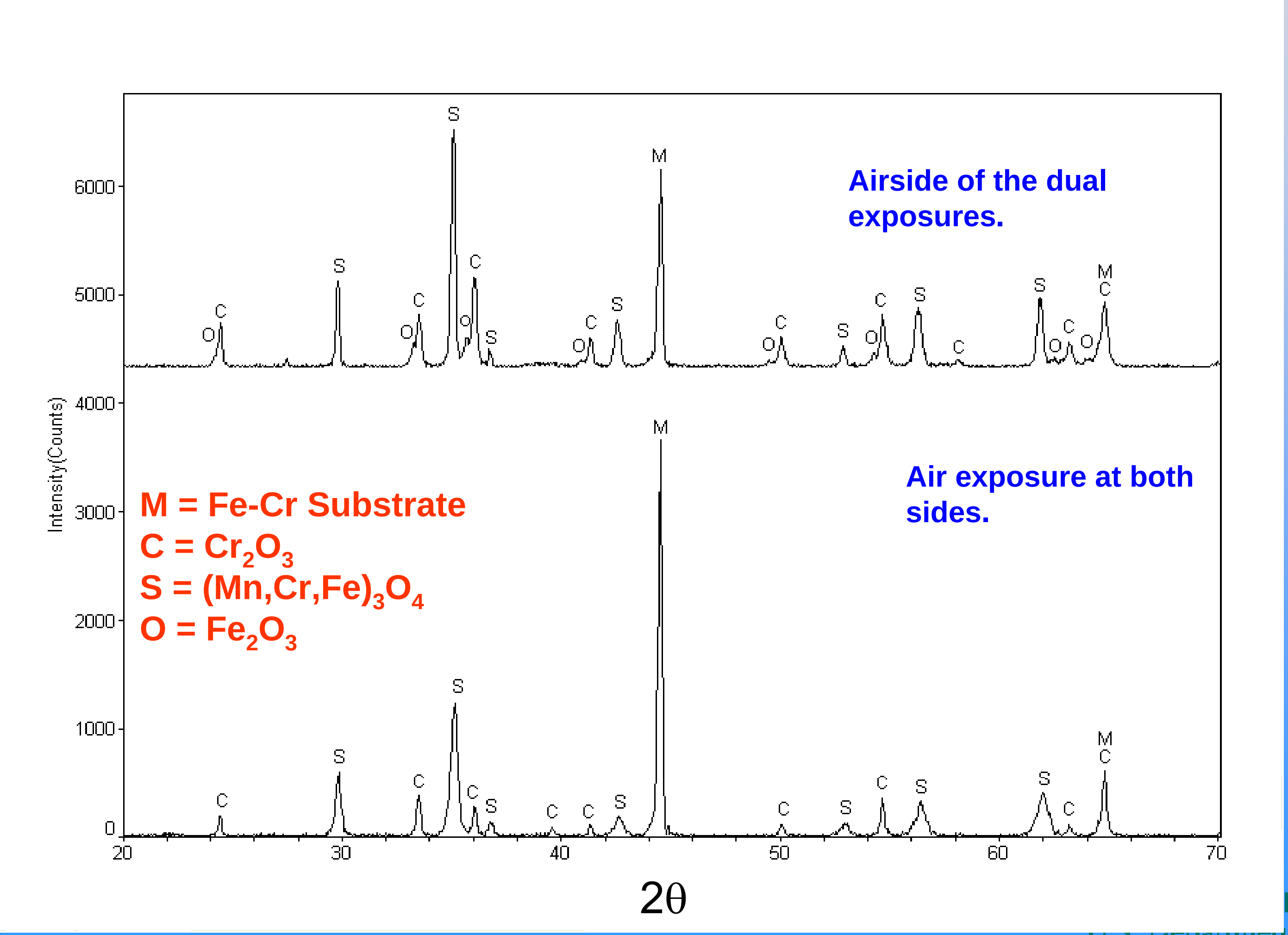
Cross-sections





Crofer22 APU: Effects of Thermal Cycling

Grown on the **Crofer22 APU** coupon in air only and at the airside of the coupon that was heat-treated at 800°C, three cycles with each cycle of 100 hours.

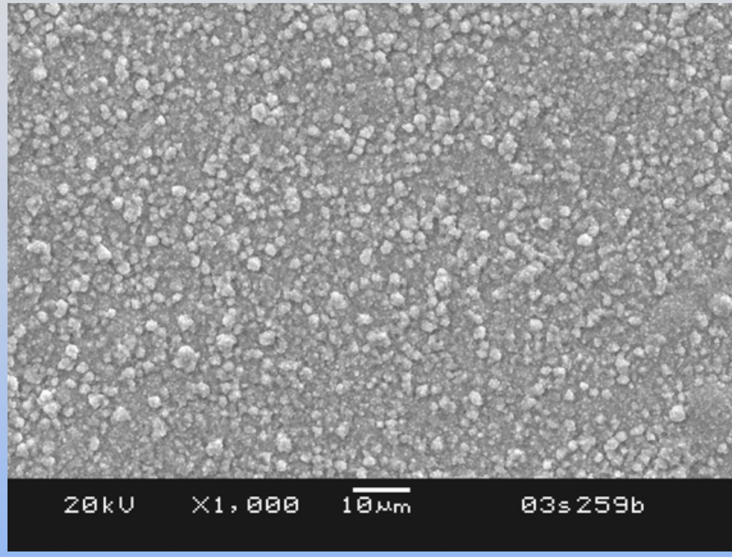


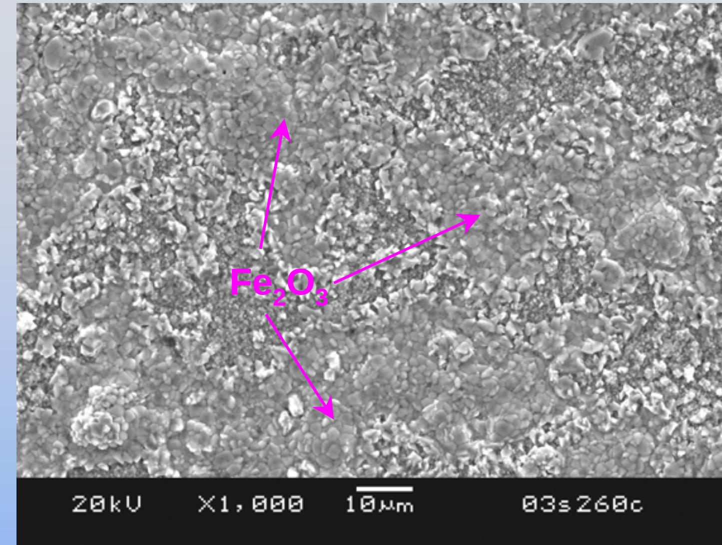
Crofer22 APU: Effects of Thermal Cycling

To air at both sides

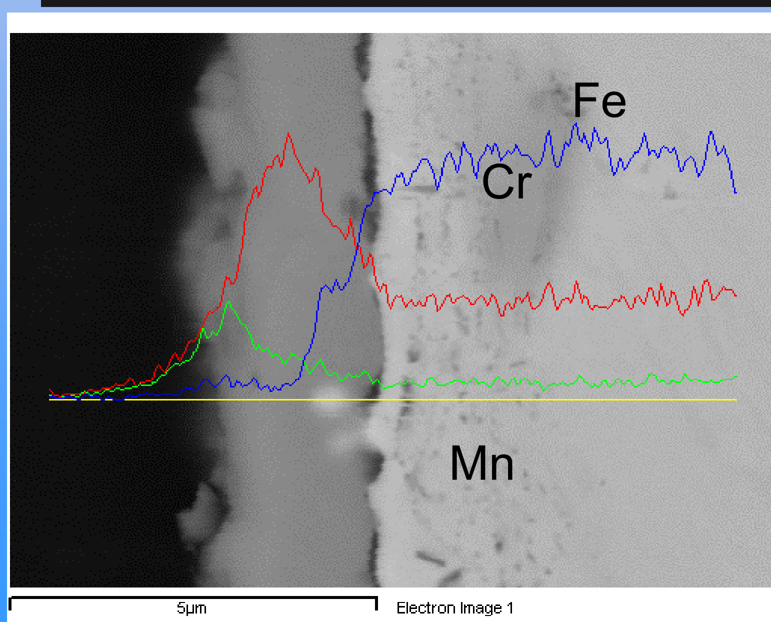
Airside of dual exposures

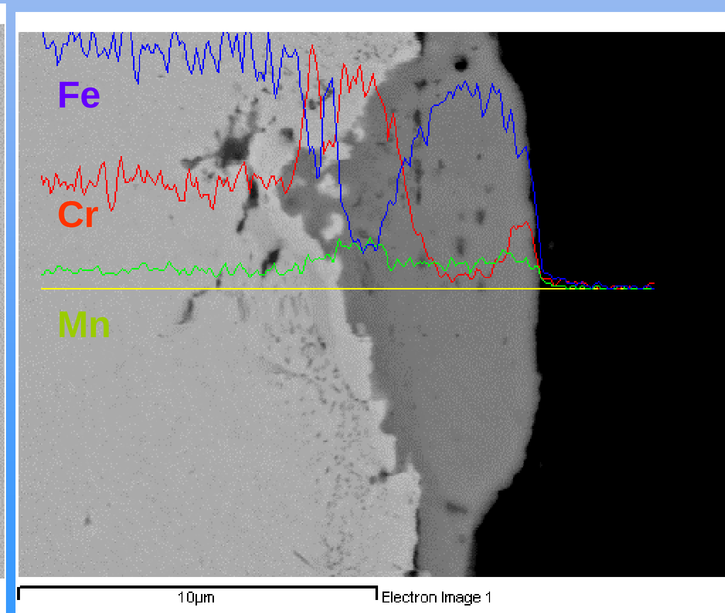
Surface microstructures





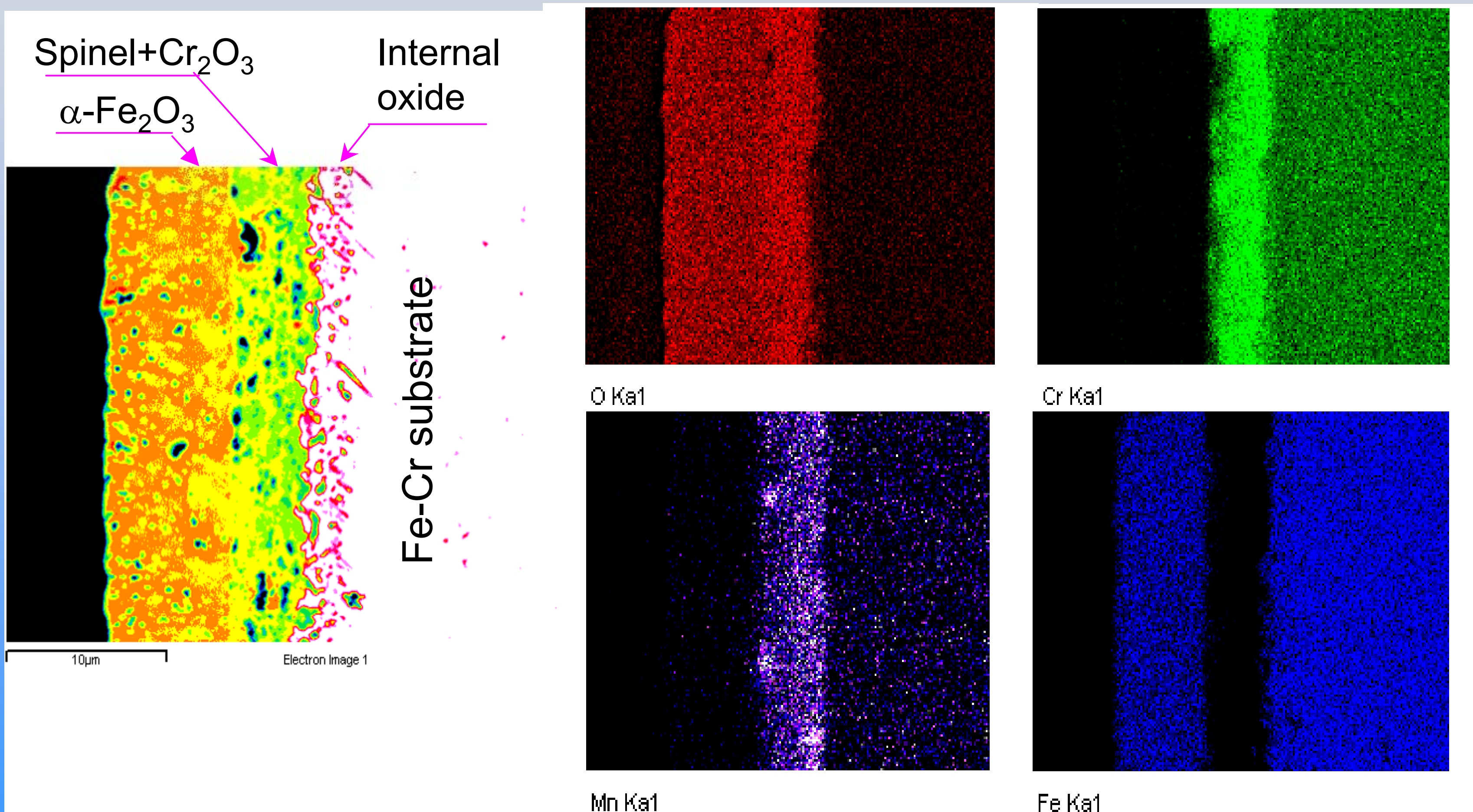
Cross-sections





Crofer22 APU: Effects of Temperature

Grown on the airside of the **Crofer22 APU** that was heat-treated under the hydrogen/air dual exposures at 850°C for 300 hours.



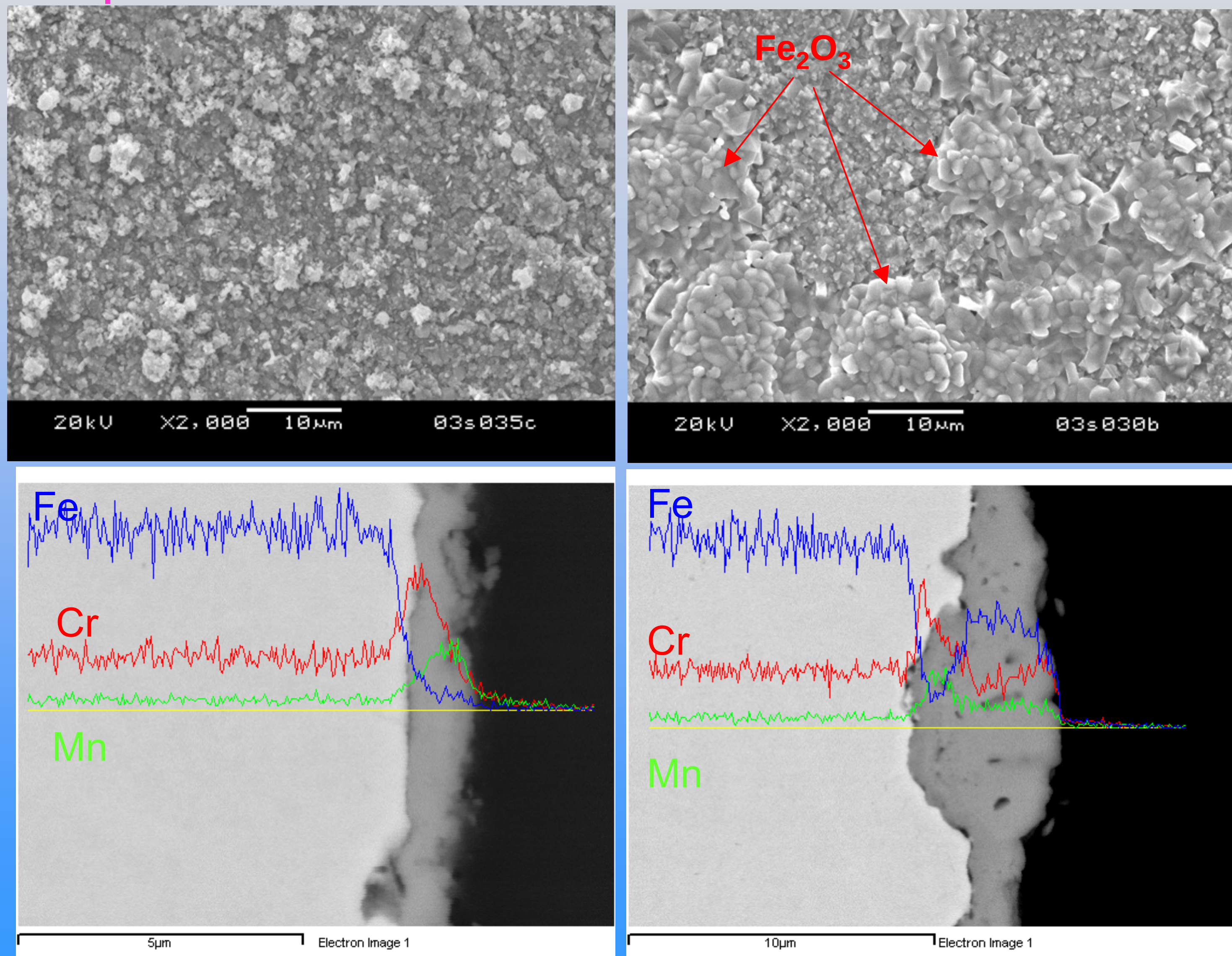
Effects of Cr%: AISI430 (17% Cr)

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

Air exposure at both sides | **Air-side of dual test**

Surface microstructures

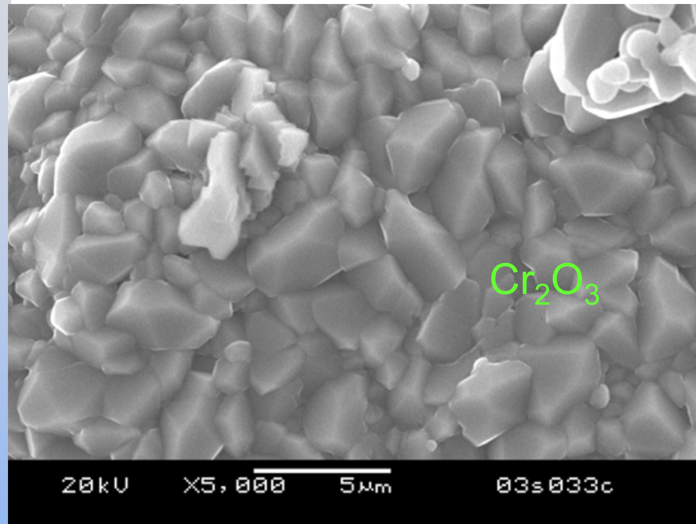
Cross-sections



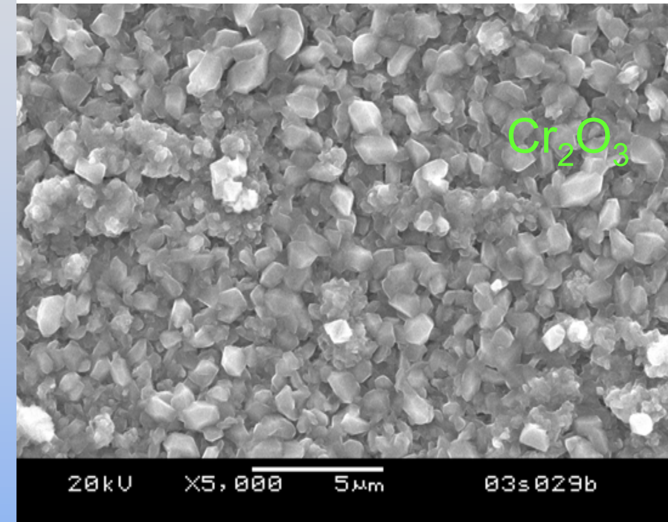
Effects of Cr%: E-brite (27% Cr)

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

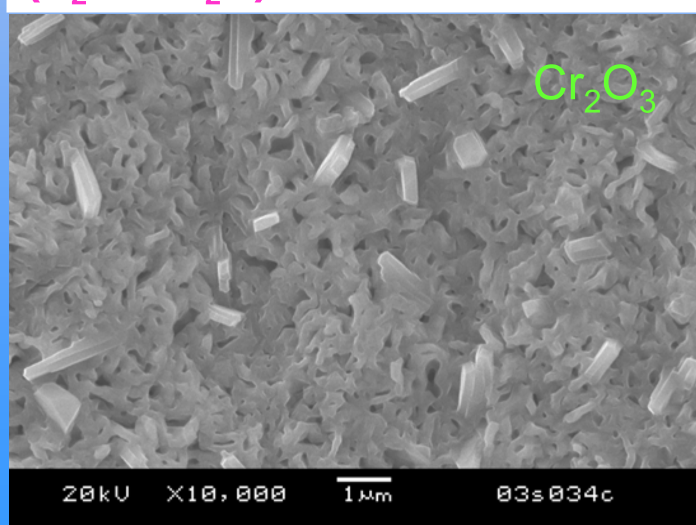
Air exposure at both sides



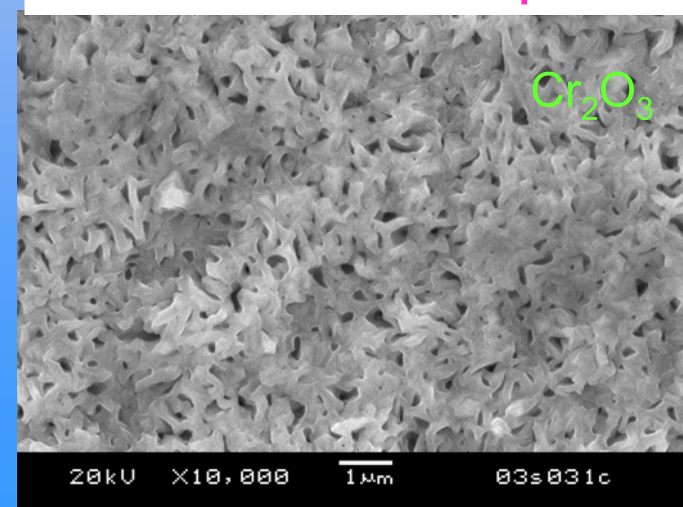
Air side of dual atmospheres



(H_2+3%H_2O) at both sides



Fuel side of dual atmospheres

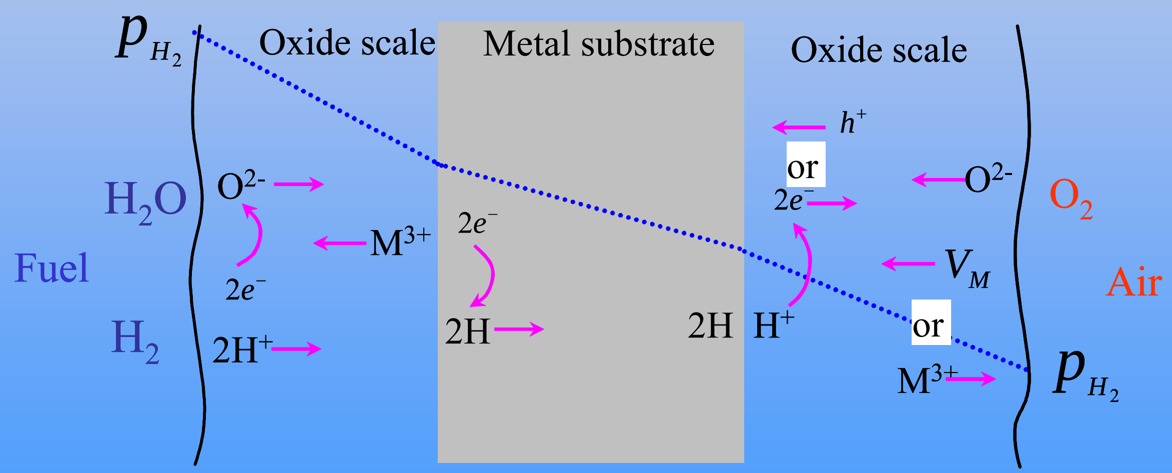


Mechanism ?

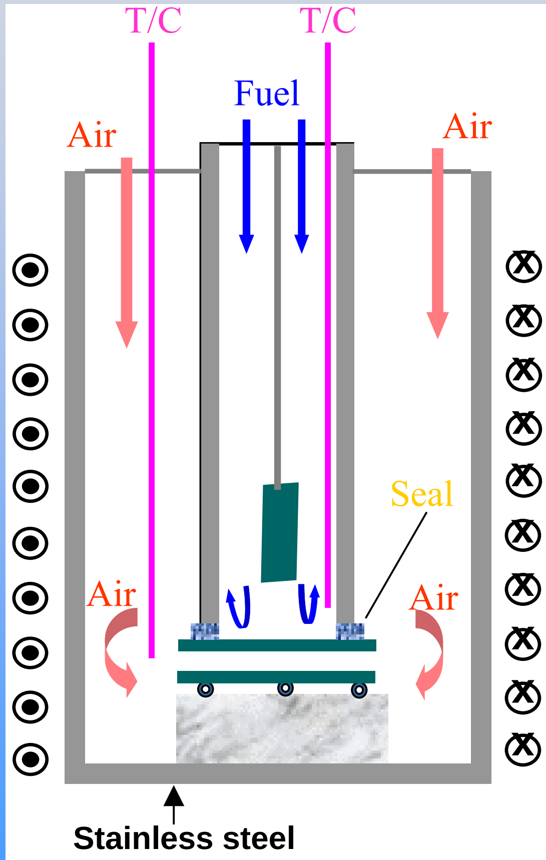
H/H$^+$ Induced Anomalous Oxidation

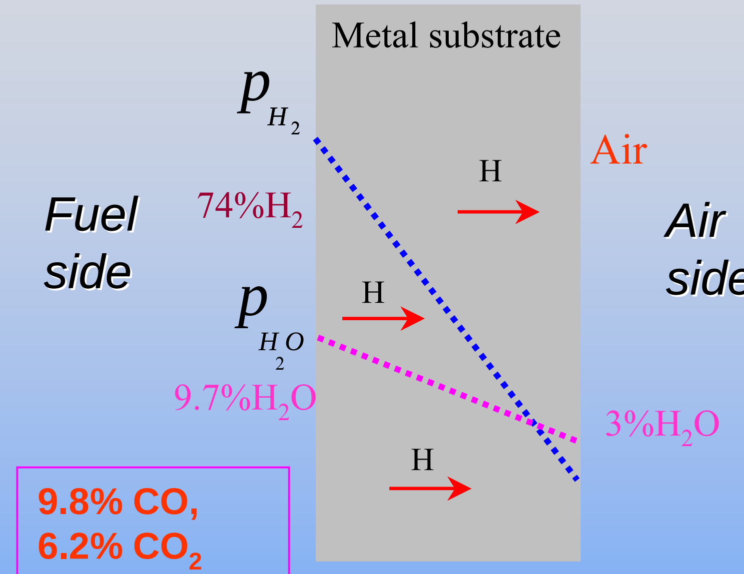
$$H + O_O^{\times} + h^{\bullet} = (OH)_O^{\bullet}$$

$$[h^{\bullet}] + [(OH)_O^{\bullet}] = 3[V_M''']$$



Oxidation Study under Reformate||Air Dual Exposures

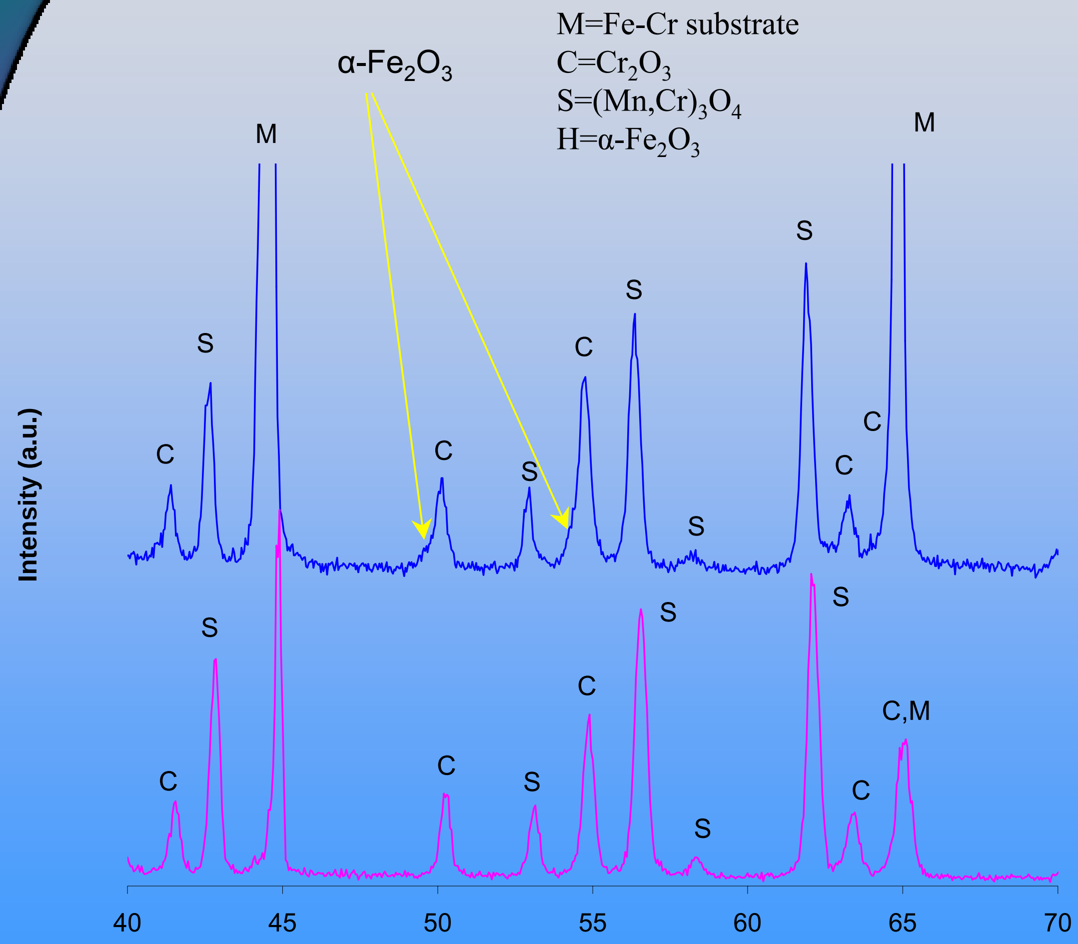




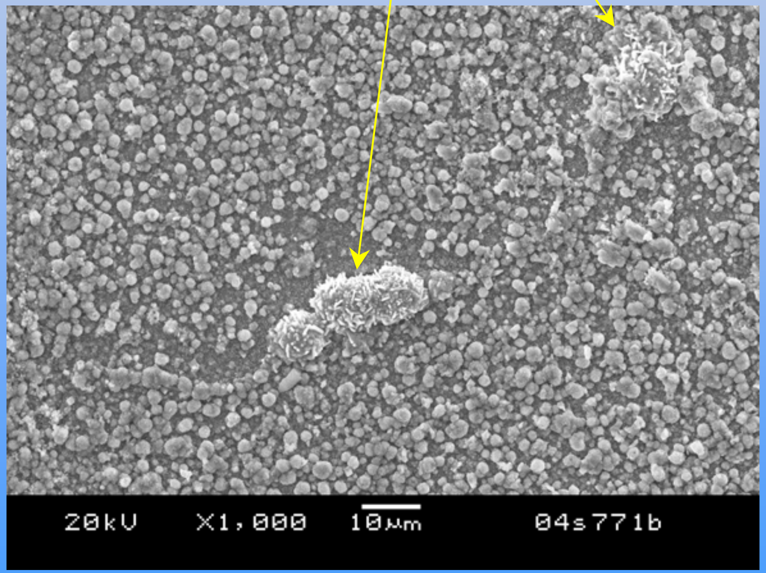
Materials studied:

- Alloy composition
  - E-brite-27%Cr
  - Crofer22-22%Cr
  - AISI430-17%Cr

Oxidation Behavior at Airside



Nucleation of Fe-rich nodules

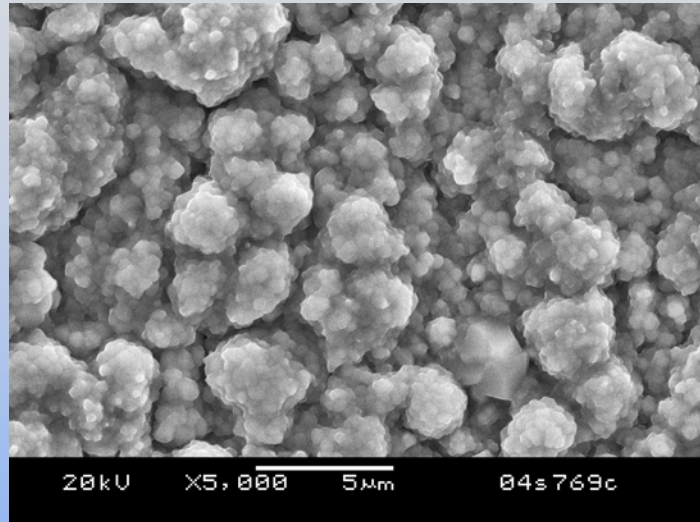


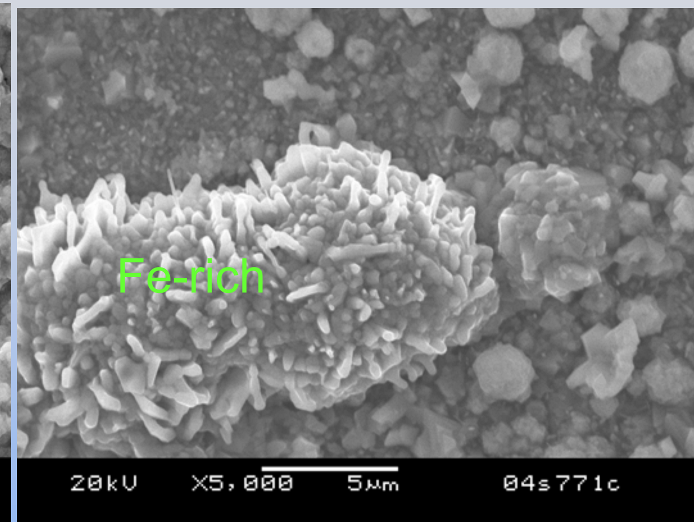
Oxidation Behavior: Air Only vs. Dual

Air exposure at both sides

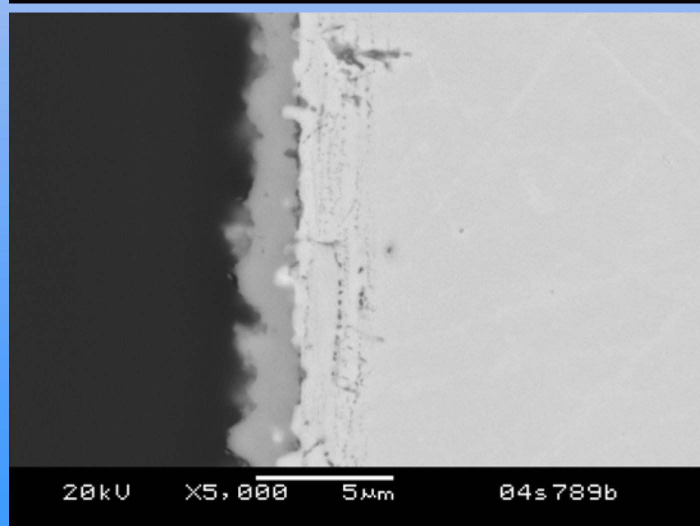
Airside of dual exposures

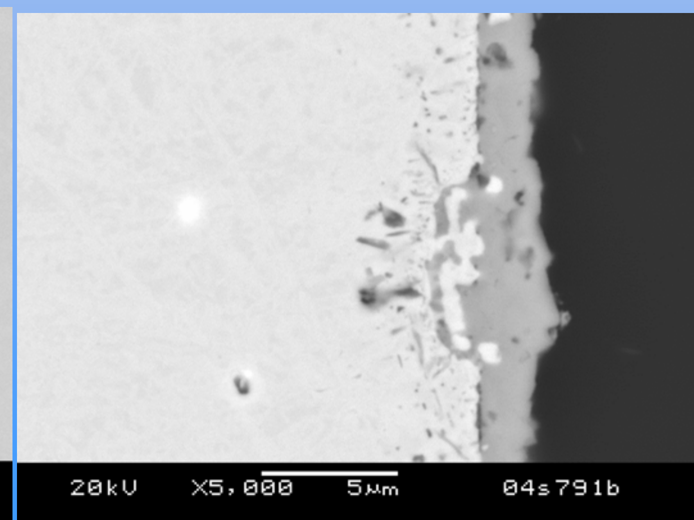
Surface microstructures



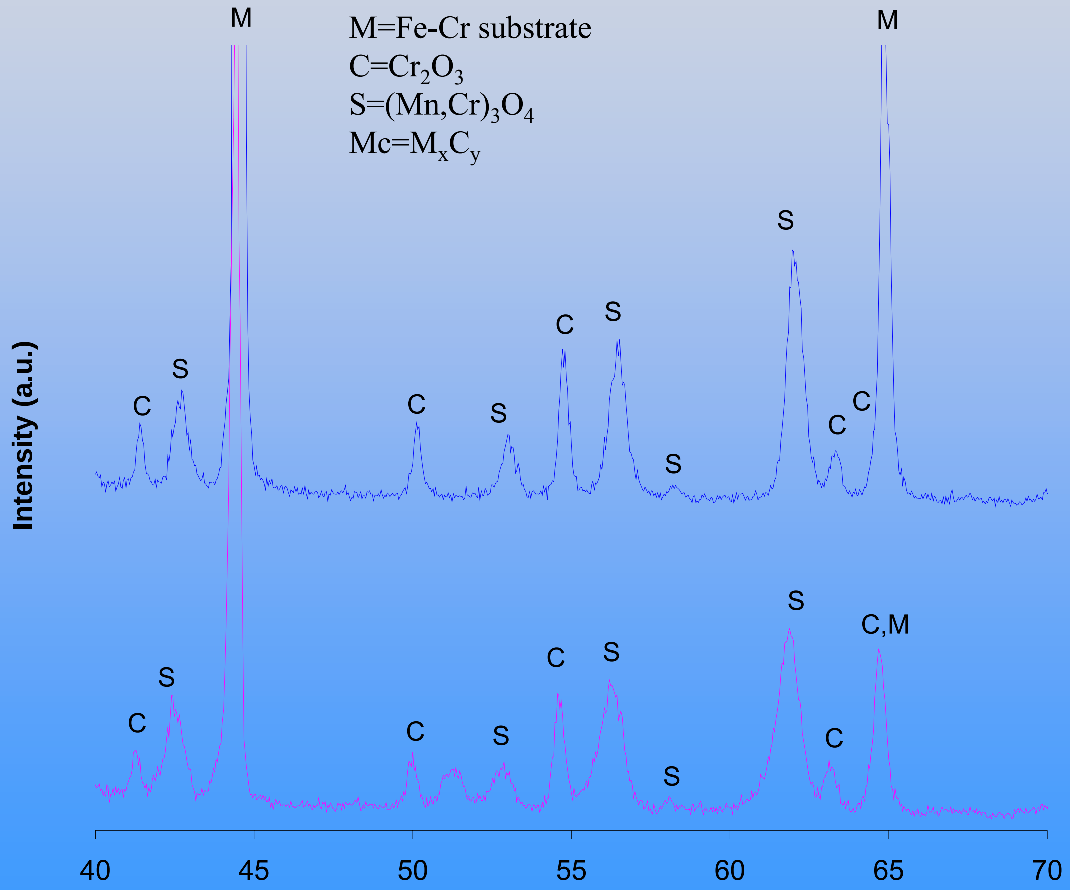


Cross-sections

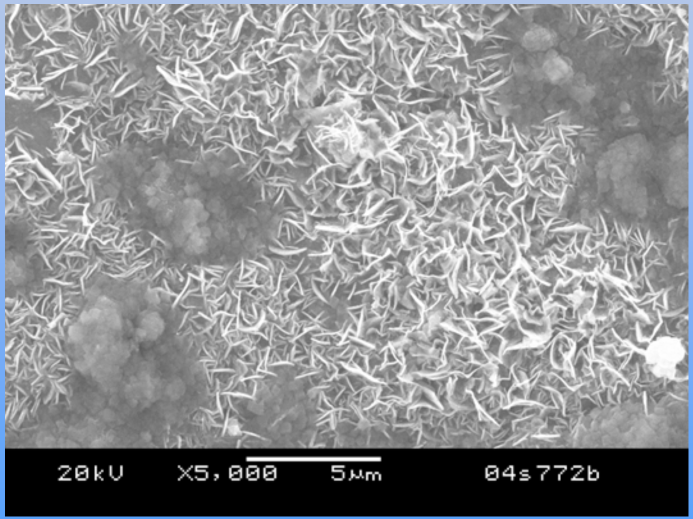




Scale Growth at Fuel Side



Mc=M_xC_y ?



Battelle

Conclusions

The DUAL exposures lead to an anomalous oxidation behavior of high temperature oxidation resistant alloys under the SOFC interconnect dual exposure conditions:

❖ For ferritic stainless steels particularly with relative low Cr%, dual exposures enhance the iron transport in the scale on the airside, leading to hematite formation and localized attack;

❖ Thermal cycling further accelerates the iron oxide formation and attack;

❖ Under the reformate||air dual exposures, hydrogen and water gradient across Crofer22 APU enhance the anomalous oxidation at the airside of the metal.

❖ Further study needs to clarify the effects of carbon potential at the fuel side.

Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy's Solid-State Energy Conversion Alliance (SECA) Core Technology Program - Wayne Surdoval, Program Coordinator.
- The authors wish to thank Wayne Surdoval, Lane Wilson, Travis Shultz and Don Collins (NETL) for their helpful discussions regarding this work.
- Metallographic preparation and SEM: Jim Coleman, Shelley Carlson, Nat Saenz.