SOFC Interconnects & Coatings

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Objectives and Approach

- Objectives
  - Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature SOFC interconnect and interconnect/electrode interface applications
  - Identify and understand degradation processes in interconnects and interconnect/electrode interfaces
- Approach
  - Materials and process development
    - **Surface modification (Focus of today's presentation)**
    - Interconnect/electrode contact materials
    - Alloy development
  - Characterization of candidate materials
    - Oxidation tests (including dual atmospheres – air vs. moist hydrogen; air vs. simulated reformate), ASR tests, CTE, alloy and scale chemistry via XRD, SEM, EDS, TEM, etc.

Spinel Protective Coatings: Background

- Goal: Cost-effective protective coatings which improve alloy oxidation resistance, mitigate Cr volatility, and minimize contact resistance
- Previous Accomplishments:
  - Studied structure and properties of compositions in $(Mn,Co)_3O_4$ system; selected $(Mn_{1.5}Co_{1.5})_3O_4$
  - Developed slurry-based fabrication process for fabricating $(Mn,Cr)_3O_4$ spinel coatings onto FSS interconnects
  - Evaluated performance of coated alloys: oxidation, ASR, coating/alloy interactions
- **FY06 Accomplishments:**
  - **Investigated performance/stability of spinel-coated alloys under SOFC exposure conditions (dual atmosphere)**
  - **Performed long-term (> 1 year) oxidation tests on coated/uncoated FSS**
  - **Optimized slurry-based fabrication approach**

Conclusions

- $Mn_{1.5}Co_{1.5}O_4$ spinel protective coatings are effective in reducing oxide scale growth kinetics and Cr volatility of Cr-containing ferritic stainless steels
- Spinel-coated Crofer22APU (22-23% Cr, low Si) demonstrates long-term (>1 year) structural, thermo-mechanical, and electrical stability
- No iron oxide nodule formation or other localized attack observed in coated Crofer22APU under dual exposure conditions
- Spinel-coated AISI 430 (17% Cr, 0.5% Si) exhibits significant Fe diffusion into coating, and high ASR due to silica subscale formation
- Slurry-based fabrication method has been improved; better control of microstructure and thickness
- Alternative electroplating-based approaches under investigation

Properties of $(Mn_{1.5}Co_{1.5})_3O_4$ Spinel

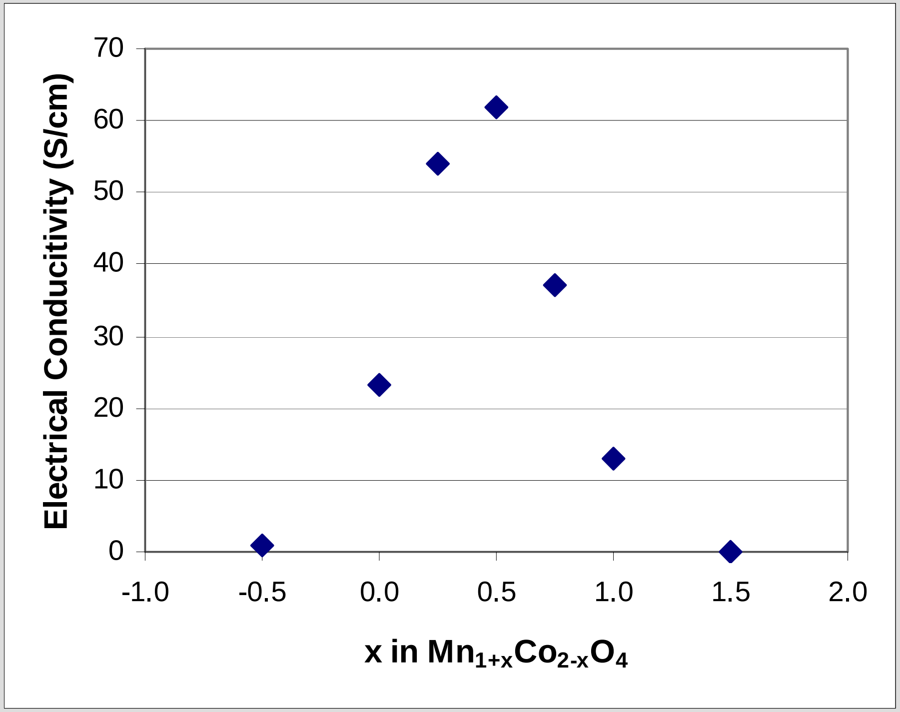
- High electrical conductivity
  ~60 S/cm at 800ºC

$$\sigma_{Mn_{1.5}Co_{1.5}O_4} = 10^{3\sim4}\sigma_{Cr_2O_3}$$

- Good CTE match to FSS and anode-supported cells

$$CTE_{Mn_{1.5}Co_{1.5}O_4} = 11.5\times10^{-6}K^{-1}, 20-800^oC$$

- Chemically compatible with contact pastes, cathodes
- Cr-free composition



Fabrication of $(Mn,Co)_3O_4$ Spinel Protection Layers

Slurry-Based Process

Preparation of materials and slurry

↓

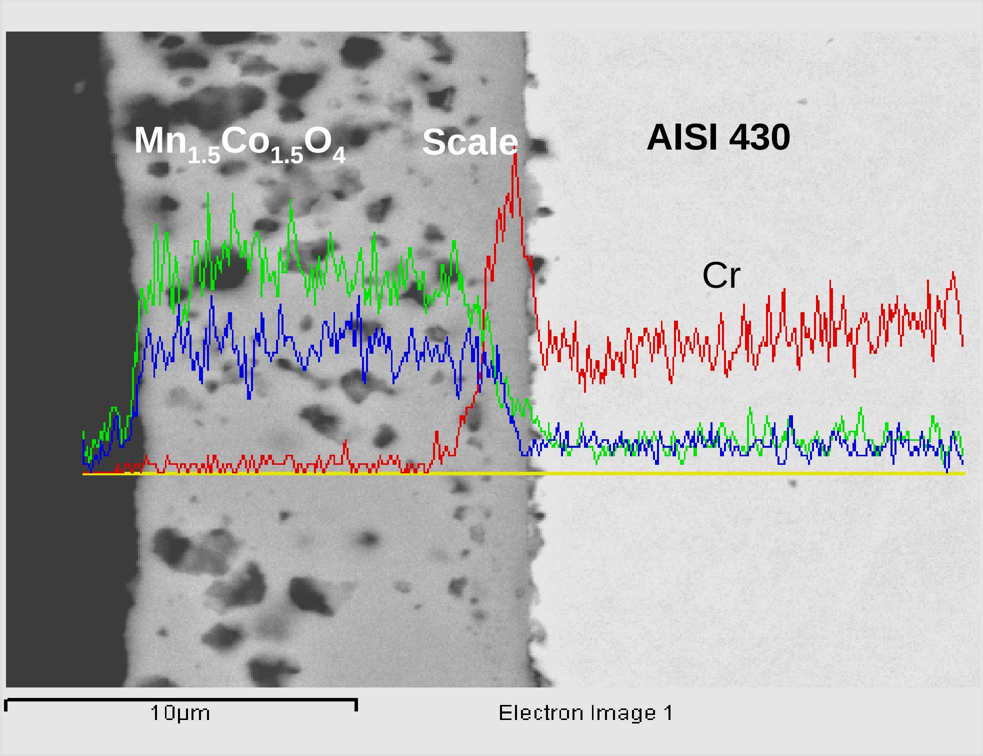
Spray- or dip- coating

↓

Heat treatment in reducing environment (4 hr, 800ºC)

↓

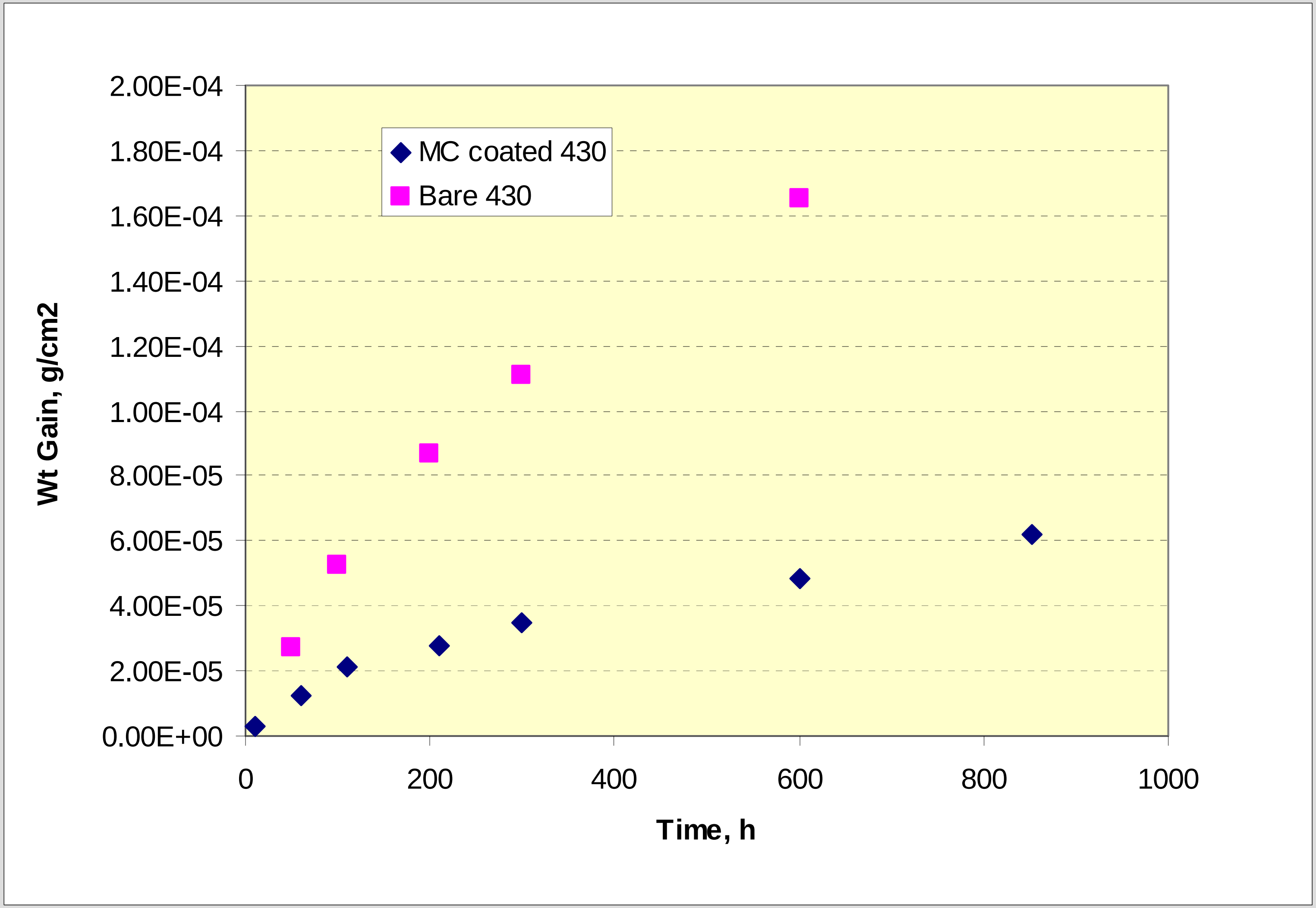
Oxidation in air (800ºC - Pre-oxidation or in-stack)



$$4Mn_{1.5}Co_{1.5}O_4 \Rightarrow 6Co + 6MnO + 5O_2$$

$$6Co + 6MnO + 5O_2 \Rightarrow 4Mn_{1.5}Co_{1.5}O_4$$

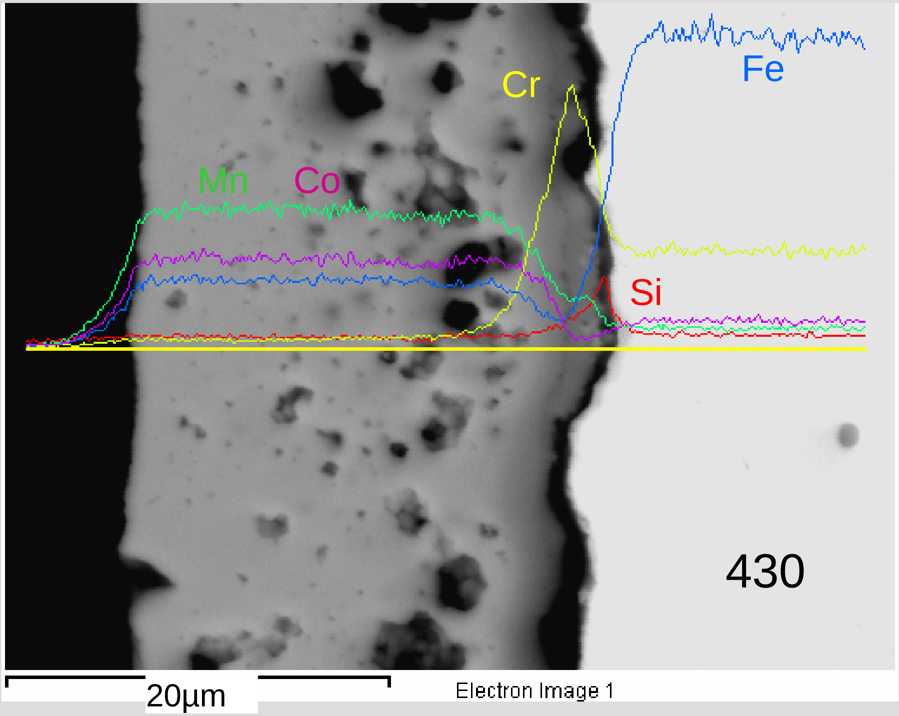
Effect of Coating on Scale Growth



800ºC in air

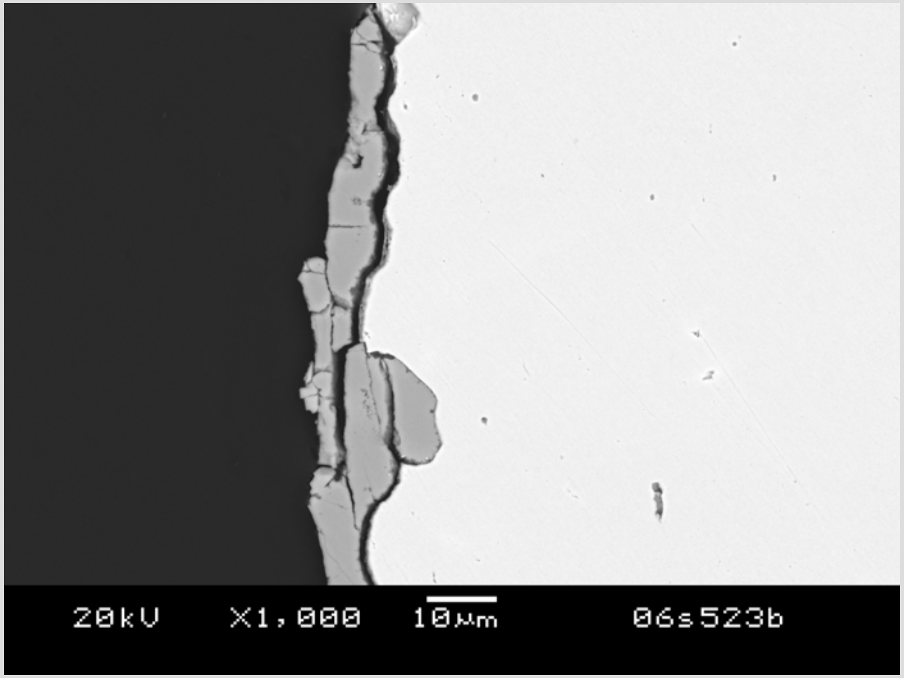
Long-Term Test of AISI 430

Coated



800°C - 9,200 h - air

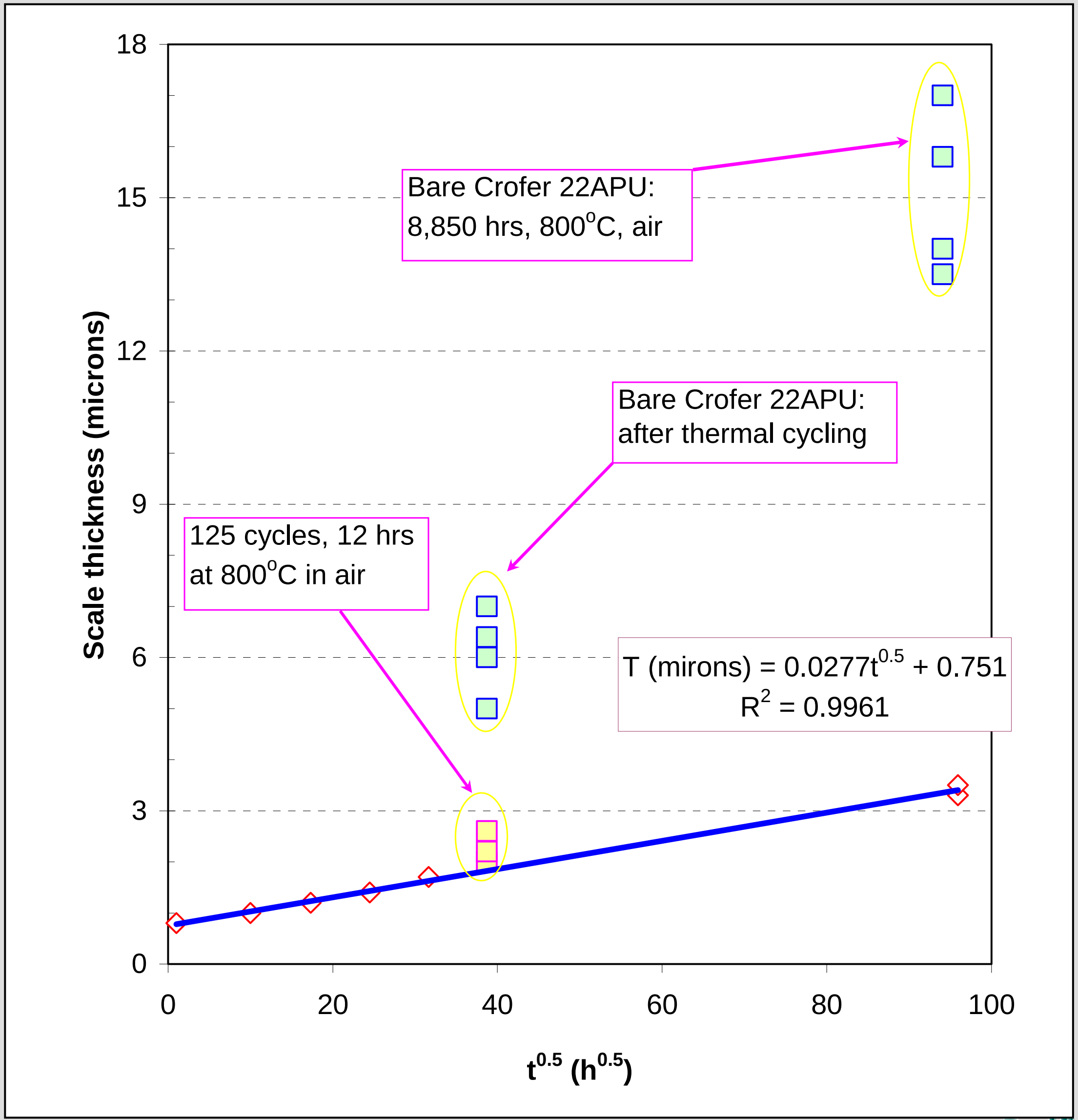
Uncoated



800°C – 8,850 h - air

Note ~10% Fe in coating

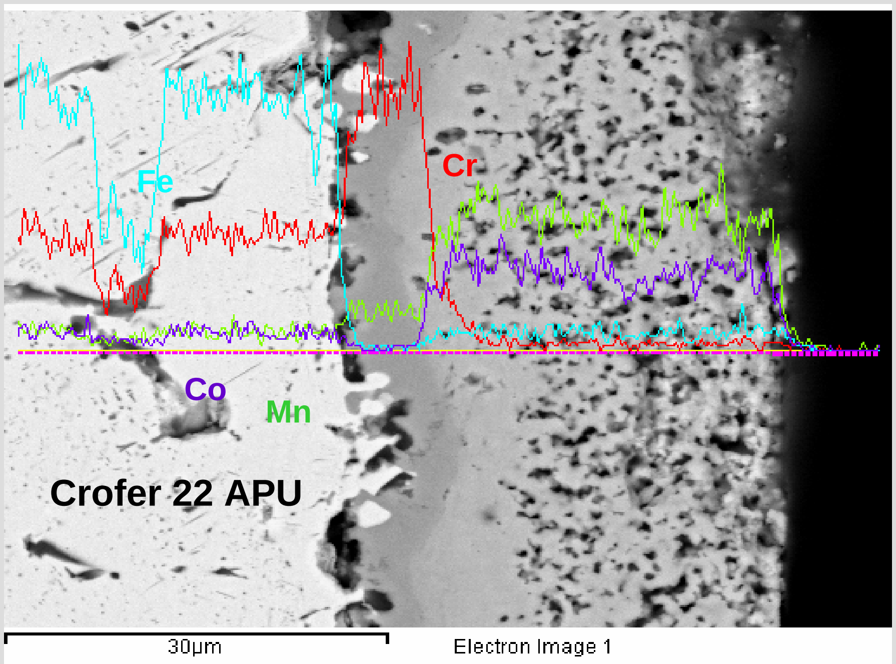
Effect of Coating on Crofer22APU Scale Growth



Long-Term Oxidation Behavior of Crofer22 APU

Coated

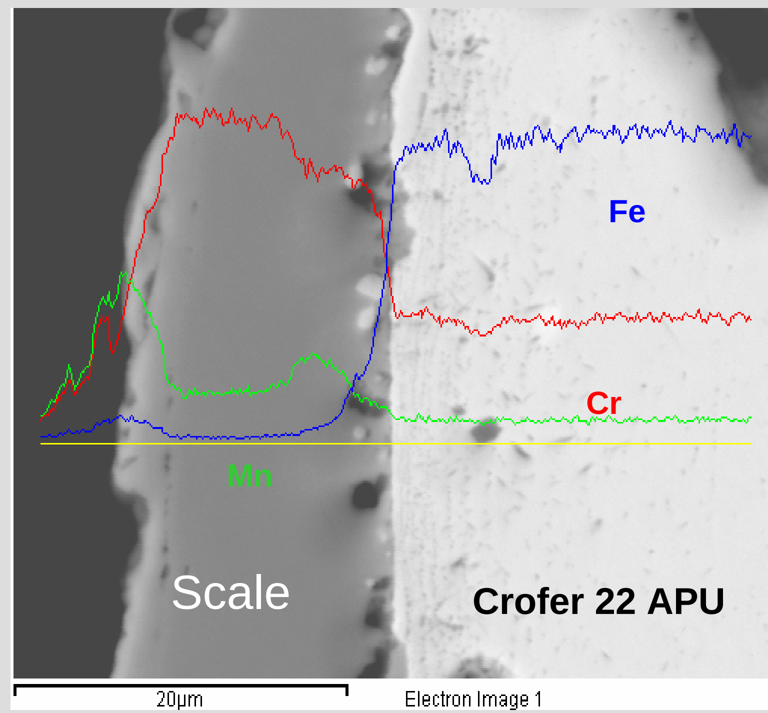
~ 4 µm scale



$800^{o}C$ - 9,200 h - air

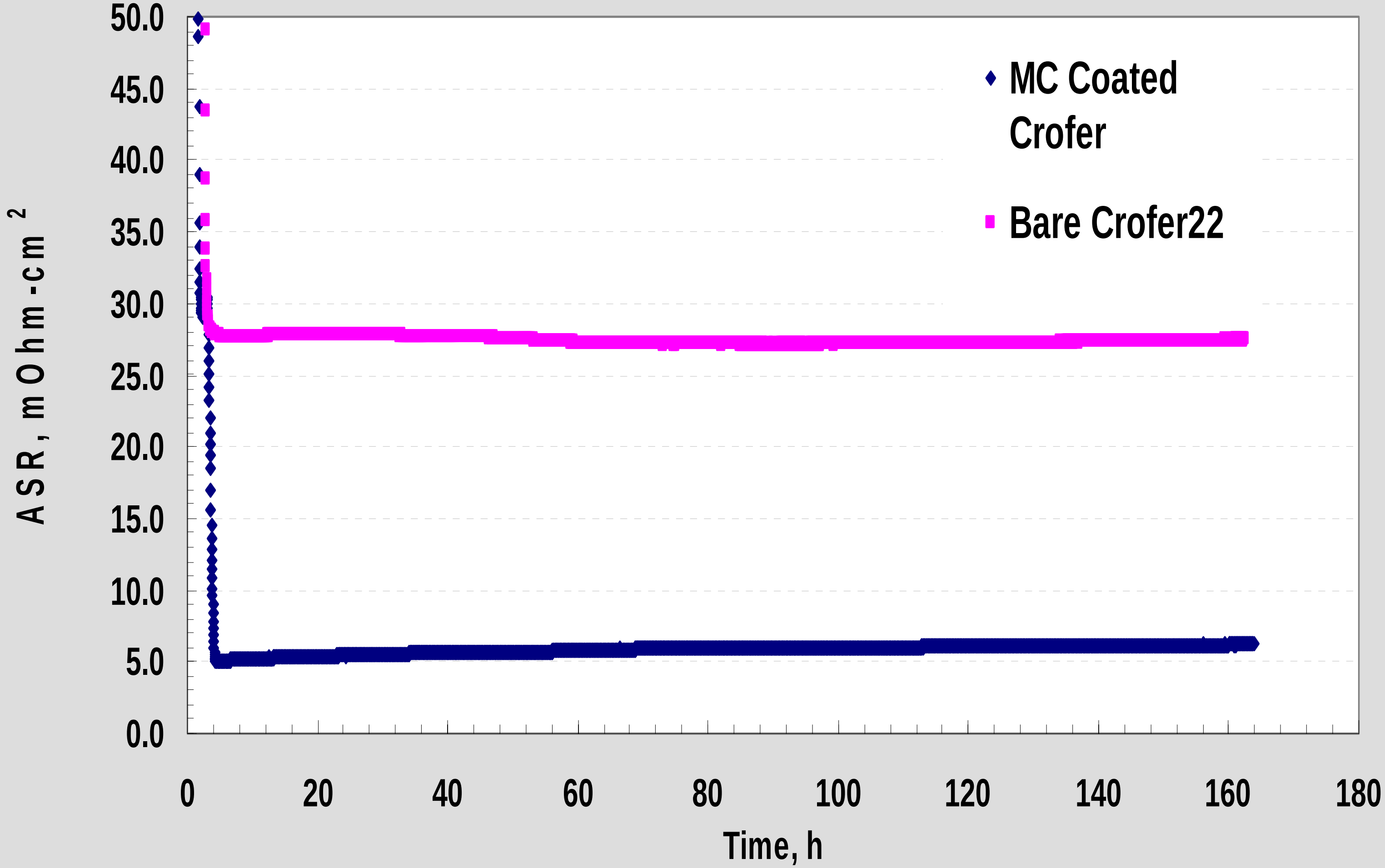
Uncoated

~ 14 µm scale

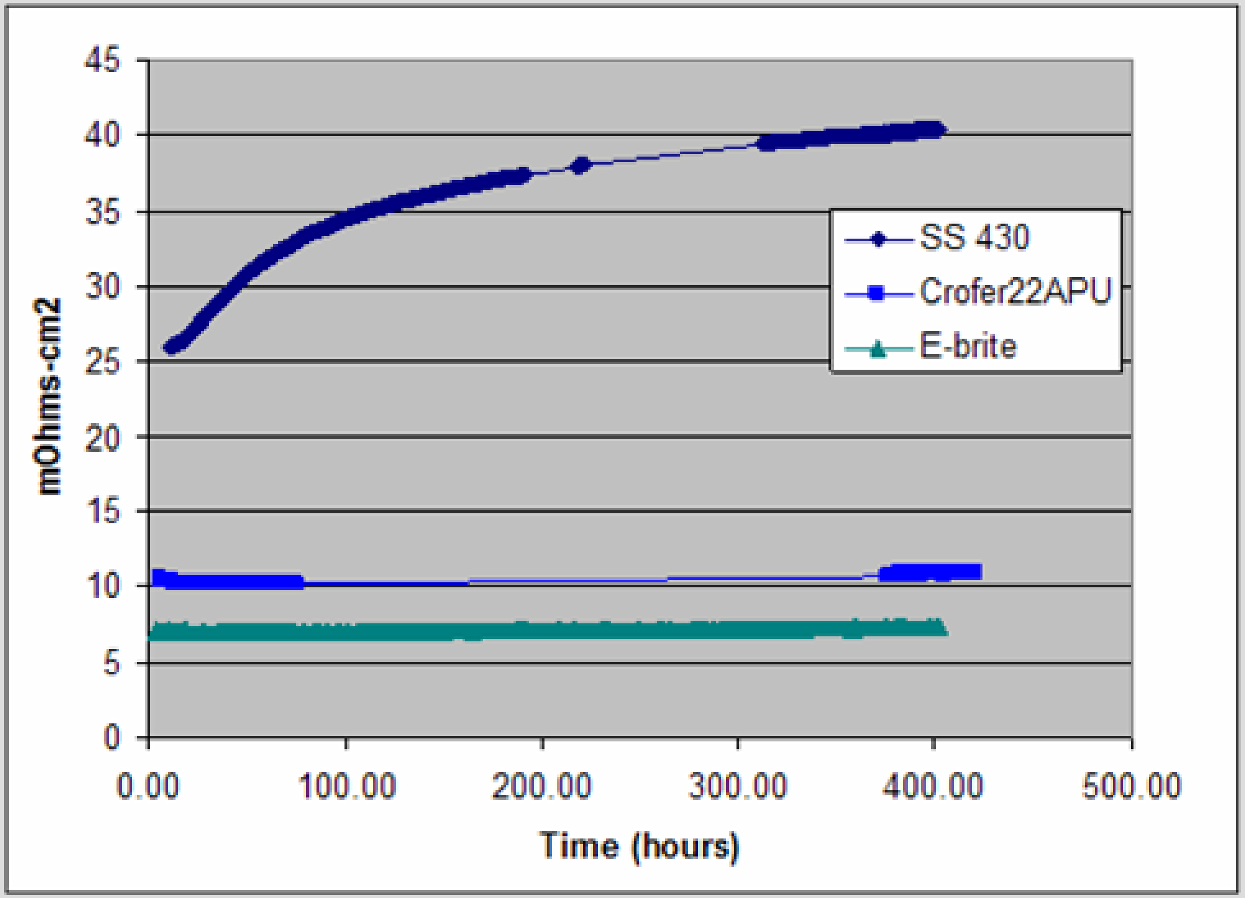


$800^{o}C$ – 8,850 h - air

Electrical Resistance after Long-Term Oxidation Test

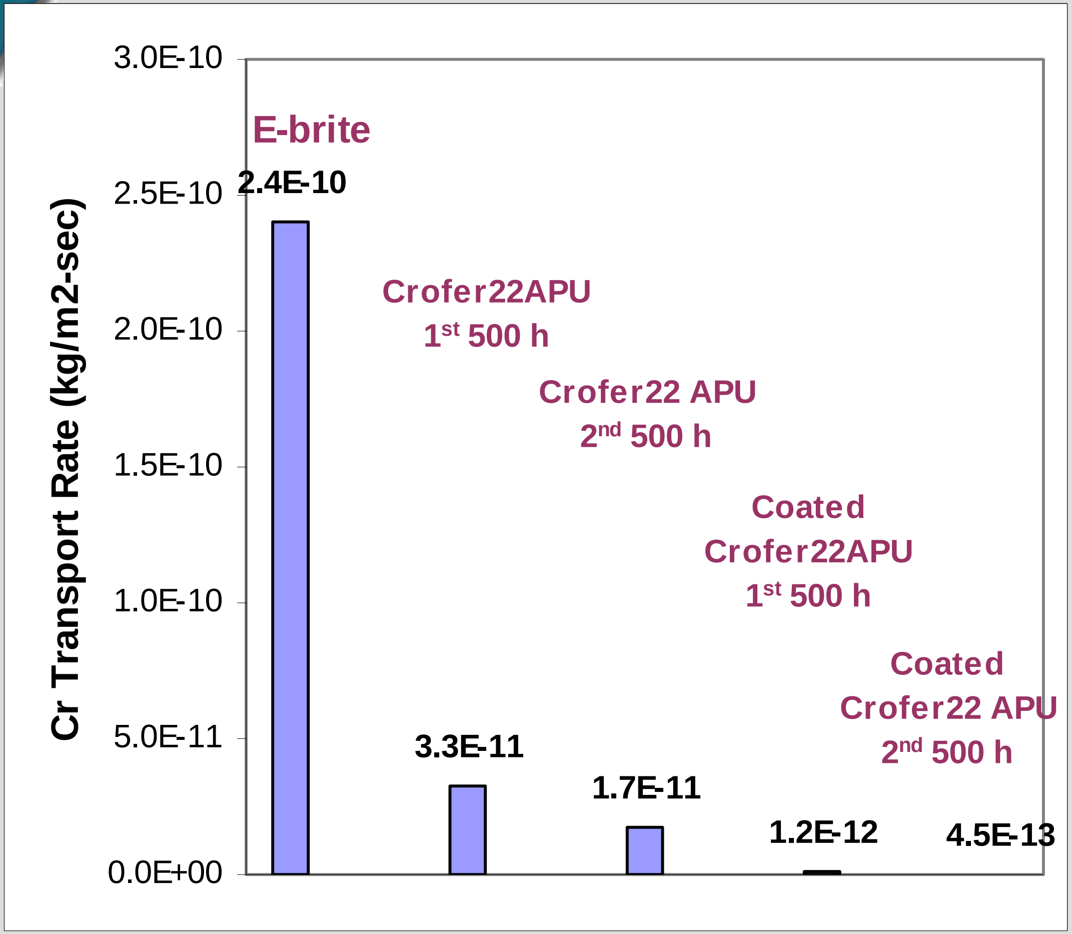


Electrical Resistance of Spinel-Coated AISI 430



Results demonstrate need for low Si content in alloy; AISI 430 has ~0.5wt% Si

Cr Volatility Experiments

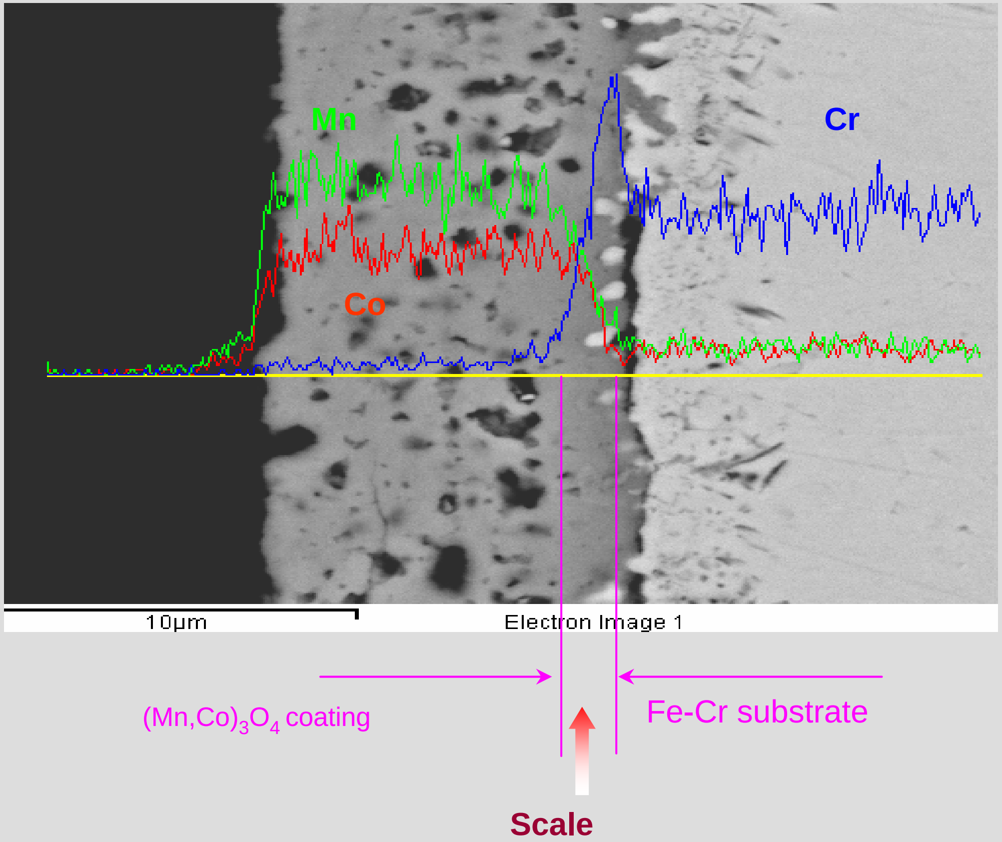


Transpiration measurements were carried out at 800ºC in air with ~3%H_2O

Cr release of coated Crofer22APU was <4% of Cr release of uncoated Crofer22APU

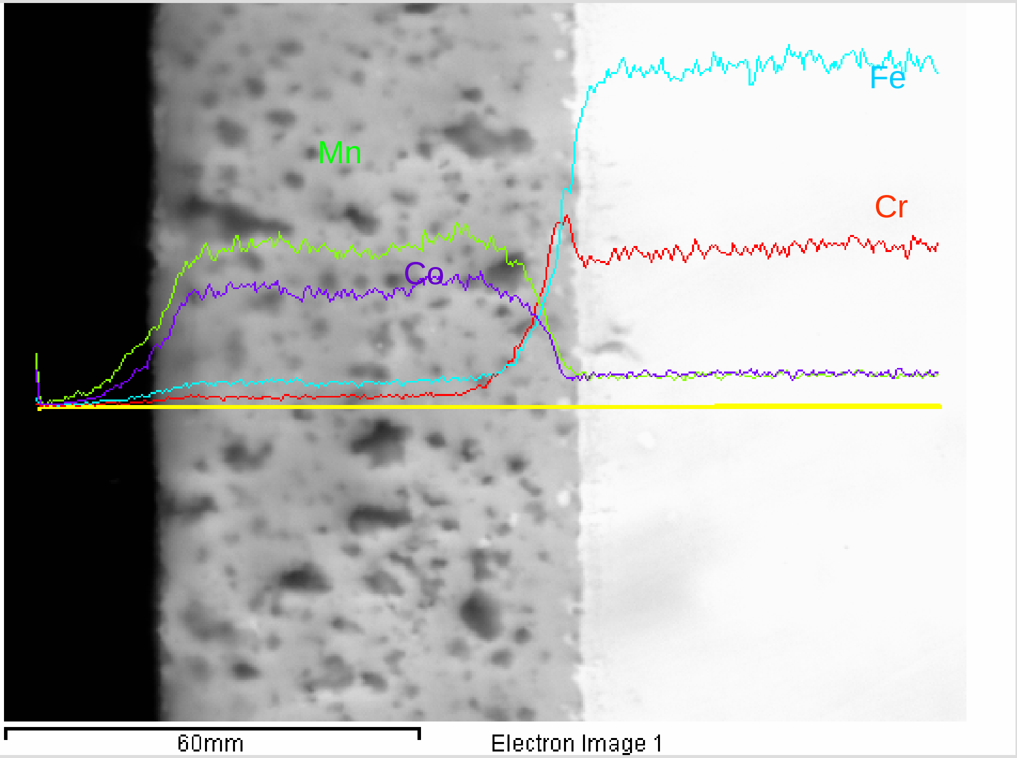
Performance & Stability under Dual Atmosphere Exposure: *Isothermal Test*

- $Mn_{1.5}Co_{1.5}MnO_4$ coating on Crofer22APU; pre-reduced at 800ºC for 4 hours
- **Tested isothermally at 800ºC / 1000 hours**
- Air (~3%H_2O) vs. Hydrogen (~3%H_2O)
- SEM/EDS: ~2 wt%Fe in coating; no Fe_2O_3 nodule formation or other localized attack



Performance & Stability under Dual Atmosphere Exposure: *Thermal Cyclic Test*

- **60 microns thick** $Mn_{1.5}Co_{1.5}MnO_4$ coating on Crofer22APU; pre-reduced at 800ºC for 4 hours; pre-oxidized at 800ºC for 24 hours
- **110 thermal cycles: 8 hours at 800ºC, 5ºC/min**
- Total test duration: 2100 hours
- Air (~3%H_2O) vs. hydrogen (~3%H_2O)
- SEM/EDS: ~2 wt%Fe in coating; no Fe_2O_3 nodule formation or other localized attack

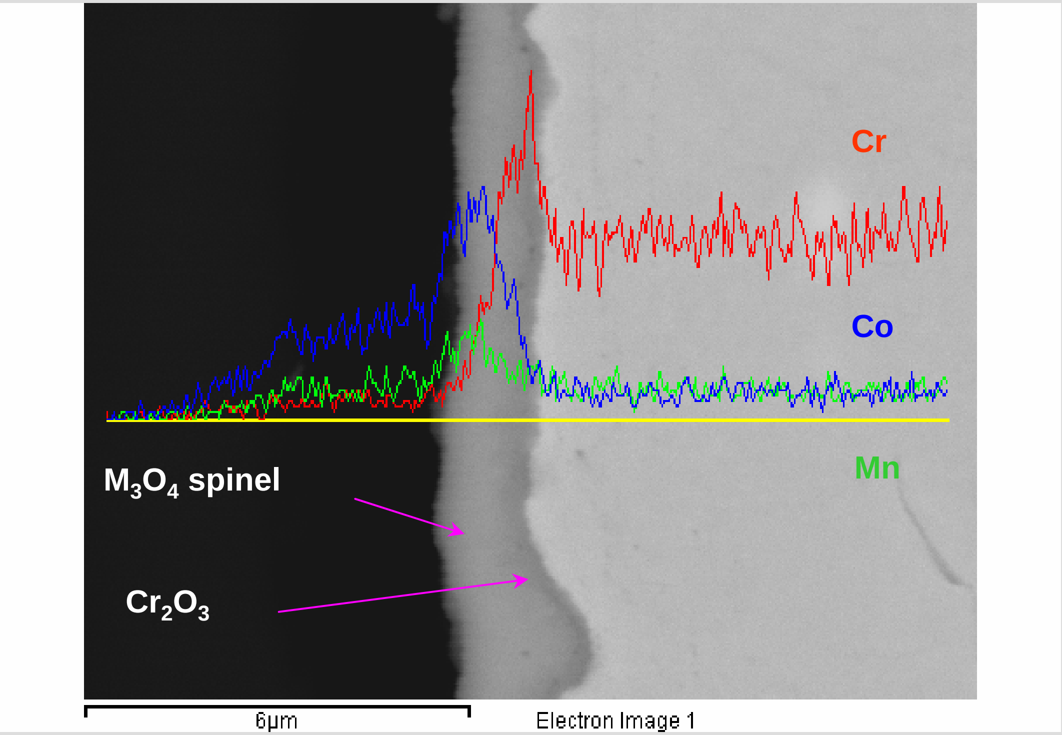


Optimization of Spinel Coating Process

- Transitioning from Solvent-based to Aqueous Slurry System
  - Environmentally friendly; compatible with spray-coating, dip-coating process
- Improved control of coating thickness
  - ~2-20 microns via optimization of slurry viscosity and spray parameters
- Reducing atmosphere heat treatment
  - Typically 800ºC, but XRD indicates ~650ºC is sufficient
  - Typically 4 hours, but TGA, XRD indicate 1 hour is sufficient
- Investigating elimination of reducing heat treatment via combined slurry/solution-infiltration approach

Growth of Spinel Protection Layers via Oxidation of Co layer on Crofer

- Possible Fabrication Route: Electroplating of Co (or Co+Mn) followed by oxidative heat treatment
- Proof-of-concept via sputtering of Co
- EDS/XRD indicate Mn-Co spinel above chromia layer
- Thickness: ~2 microns (thinner than slurry-based coatings)
- Electroplated samples received and under evaluation



800ºC; 100 hours; air

Future Work

- Final optimization of slurry-based coating process
  - Elimination of reducing heat treatment?
- Evaluate viability of electroplating approaches
  - Composition, microstructure, performance
- Investigate alternative coating compositions
  - Eliminate Co?
- Assess effects of air/reformed fuel dual atmospheres on performance of interconnect alloys
- Develop improved interconnect/electrode interfaces
  - Reaction-sintered interconnect/cathode contact materials for improved conductivity and strength

Conclusions

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