Advanced Interconnect Development at PNNL

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Presentation Outline

- Objectives/Approach
- Background
  - AISI 441
  - Spinel coatings for steel interconnects
- Results:
  - Performance of MnCo spinel-coated 441
  - Optimization of MnCo spinel coatings
  - Alternative coating compositions
- Conclusions
- Future Work
- Acknowledgements

Objectives and Approach

- Objectives
  - Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature alloy-based SOFC interconnects
  - Identify, understand, and mitigate degradation processes in alloy-based interconnects
- Approach
  - Materials and process development
    - Collaboration with ATI Allegheny Ludlum and NETL
    - Emphasis on AISI 441 as alloy substrate
      - Modified alloys also being evaluated
    - Mn-Co spinel and other coatings for cathode-side protection
  - Synthesis of coating materials, Fabrication of coatings
  - Characterization of candidate materials
    - Oxidation tests (including dual atmospheres – air vs. fuel)
    - Area-specific resistance (ASR) tests
    - CTE
    - Alloy, scale, and coatings chemistry via XRD, SEM, EDS, TEM, etc.

Candidate Interconnect Alloy: AISI 441

- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
  - No vacuum processing required
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO_2 layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

Typical Analysis:

Designation	Cr	Mn	Ni	C	Al	Si	P	S	Ti	Nb	La
AISI 441	18	0.35	0.30	0.01	0.05	0.34	0.023	0.002	0.22	0.50	
AISI 430	16-18	≤1.0		≤0.12		≤1.0	≤0.04	≤0.03			
Crofer 22 APU	23.0	0.4-0.8		0.030	≤0.02	≤0.02	0.02	0.050	≤0.2		0.04-0.20

Sources: Allegheny Technologies, Inc.; Thyssen Krupp

Properties of $(Mn_{0.5}Co_{0.5})_3O_4$ Spinel

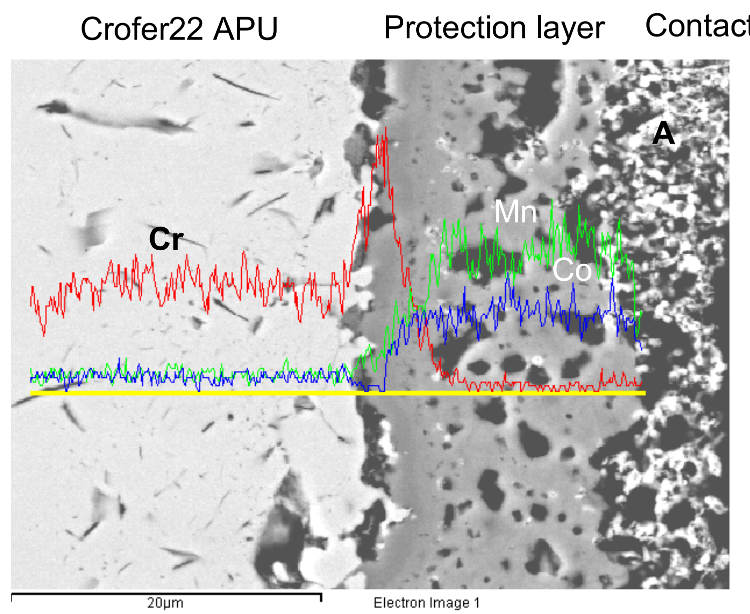
- High electrical conductivity
  ~60 S/cm at 800ºC

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

- Good CTE match to FSS and anode-supported cells

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

- Chemically compatible with contact pastes, cathodes
- Cr-free composition
- Tested with several FSS (Crofer22APU, 430, Ebrite, 441)



•6 month thermal cycle test (800ºC)
•Negligible Cr transport into coating
•Reduced oxidation rate of alloy

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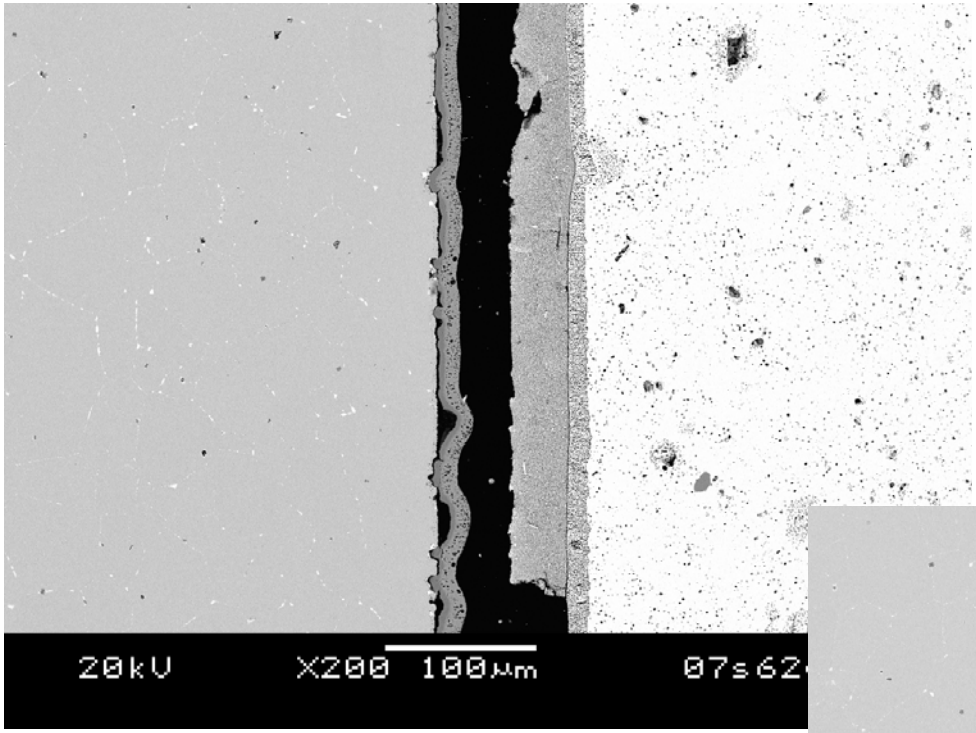
Ce-modified Mn-Co Spinel

- Rare earth (RE) additions (e.g., Ce, La) to alloys is well-established means of improving scale adherence
- NETL-Albany: Ce surface treatment leads to improved oxidation resistance, lower ASR
- PNNL: Ce-modified Mn-Co spinel coatings improve scale adherence on AISI 441
  - Simple modification – Ce nitrate included in glycine/nitrate precursor
  - Provides
    - Previously established benefits of MnCo spinel coating (improved oxidation resistance, lower ASR, Cr volatility mitigation)
    - Benefits of rare earth effect without need for RE additions to alloy

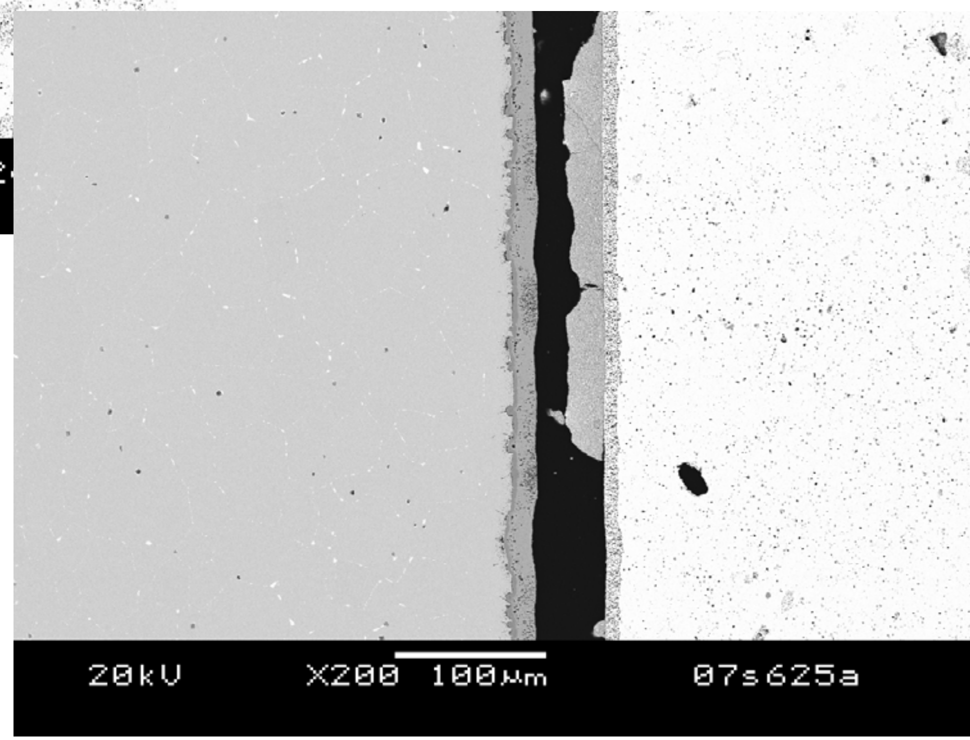
Improved Scale Adherence with Ce-MC Coatings



MC coated 441

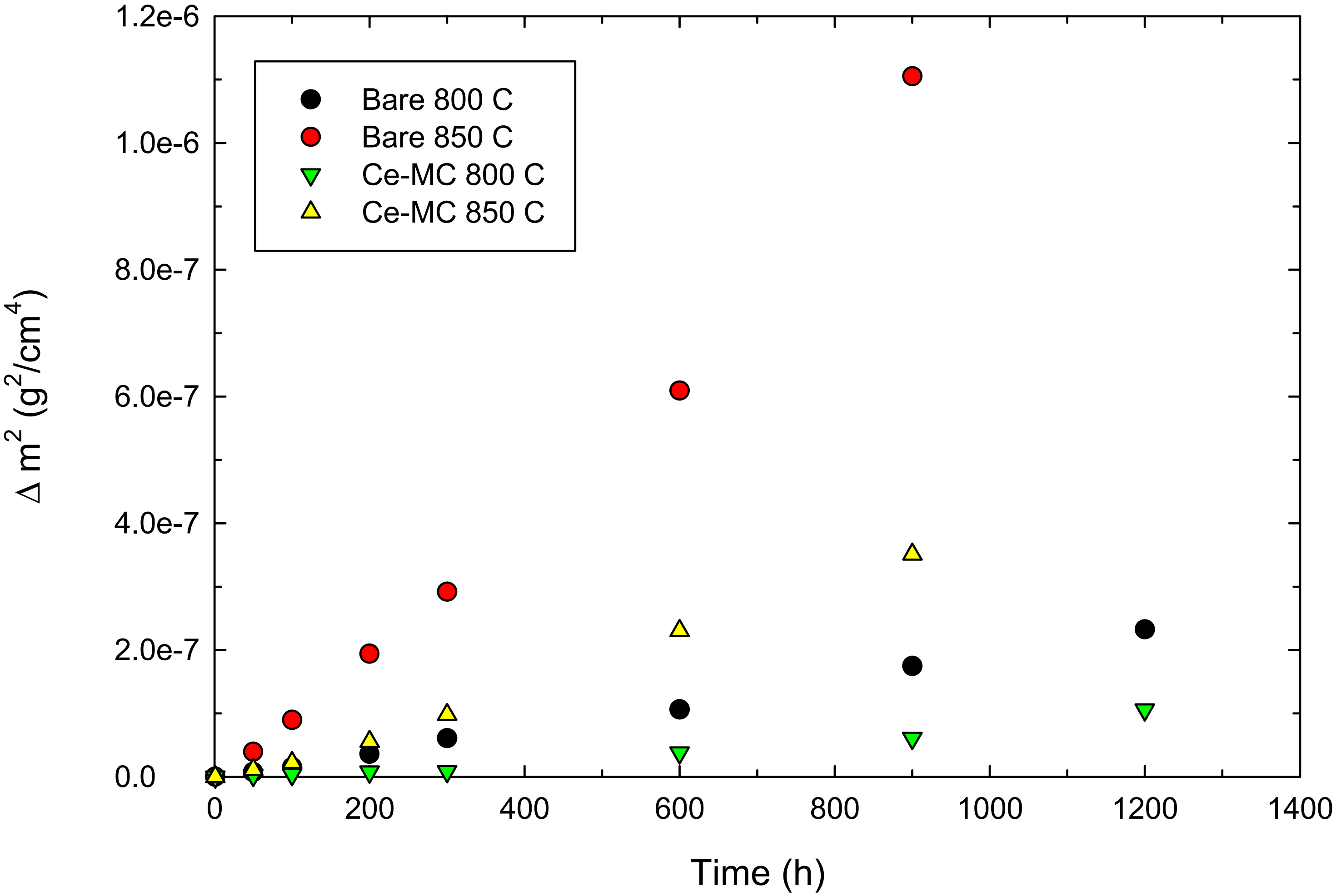
After 700 h, 850ºC ASR measurement (similar results at 800ºC)

Ce-MC coated 441

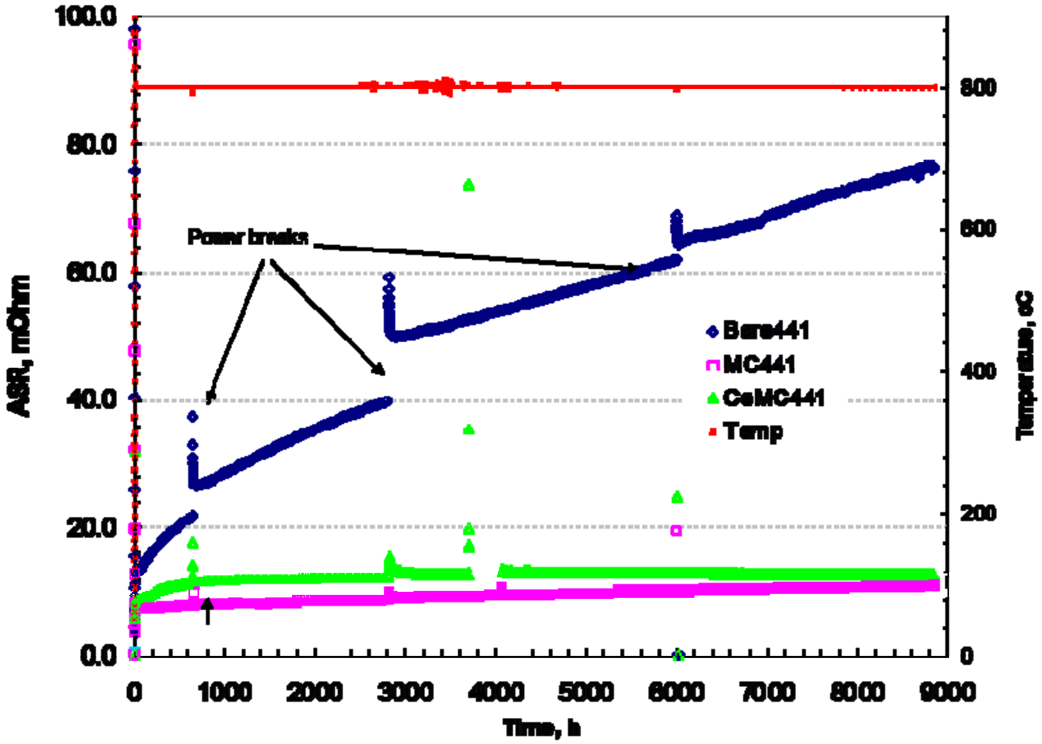


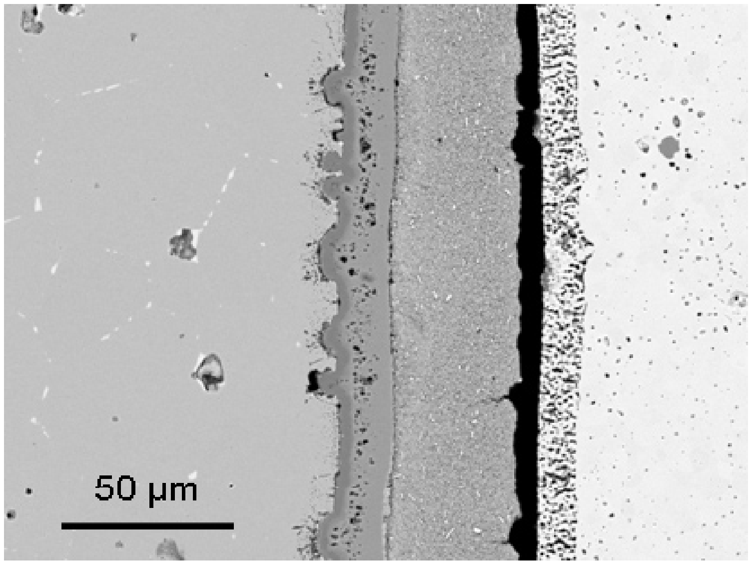
Ce-MC coating:
$Ce_{0.05}Mn_{1.475}Co_{1.475}O_4$

Oxidation Kinetics of AISI 441: Bare vs. Ce-MnCo Spinel Coated



Electrical Testing of 441





- Scale growth rates: Bare > MC coated > Ce-MC coated
- Ce altered interface morphology: smooth scale/metal interface for MC 441, rough interface for Ce-MC 441

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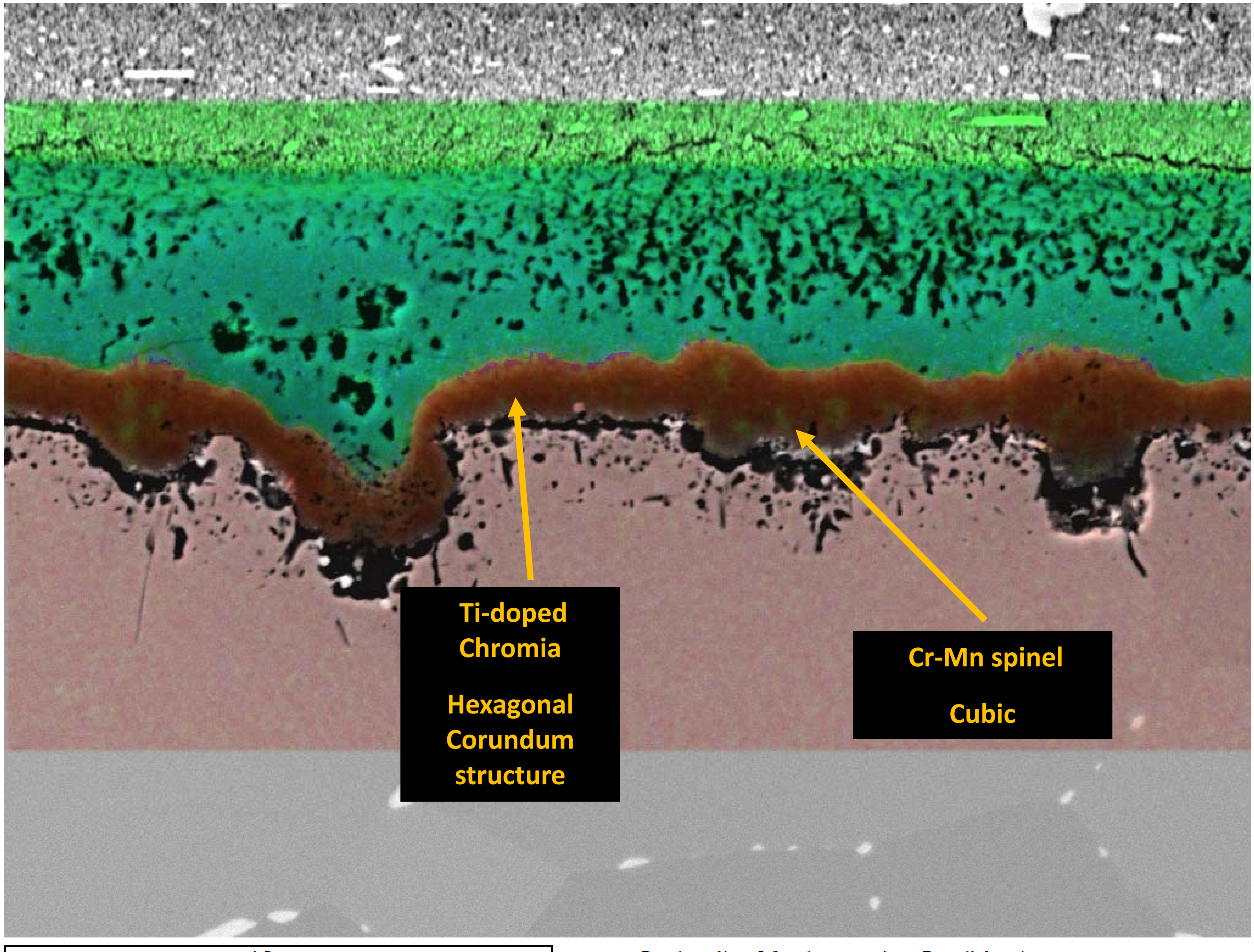
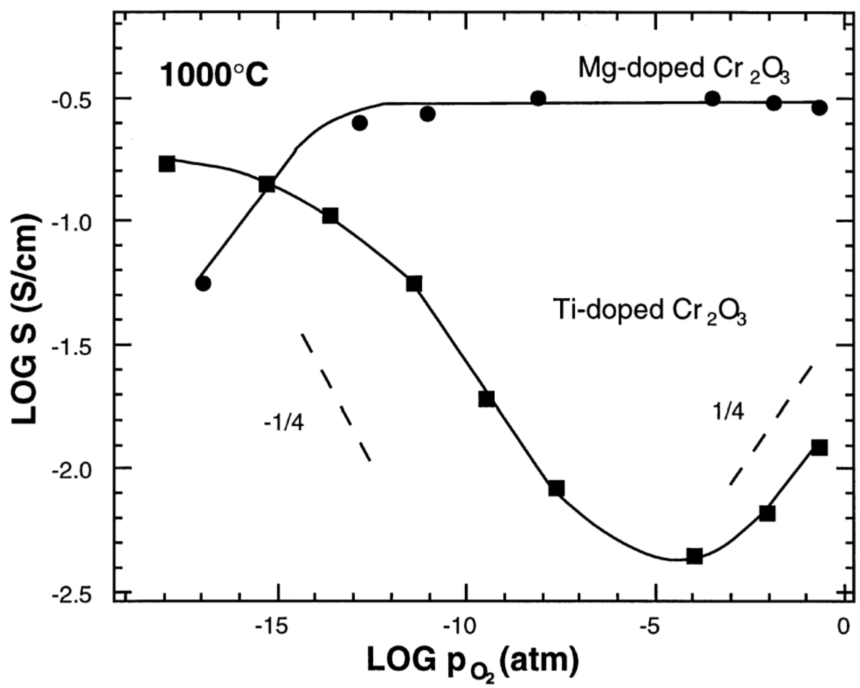
SEM/EDS/EBSD Analysis



Cr (red) - Mn (green) - Co (blue)

Effect of Ti doping on Conductivity of Cr_2O_3

$$TiO_2 = Ti_{Cr}^{\bullet} + \frac{3}{2}O_o + e' + \frac{1}{4}O_2(g)$$



Holt & Kofstad, Solid State Ionics 117 (1999) 21

Porous Contact Material
Coating
Scale
Alloy

← a_{O2} = ~$10^{-0.7}$ atm

← a_{O2} = ? atm

← a_{O2} = ~10^{-28} atm

For conductivity of 0.1 S/cm and scale thickness of 6 microns, calculated ASR = 6 mOhm-cm^2

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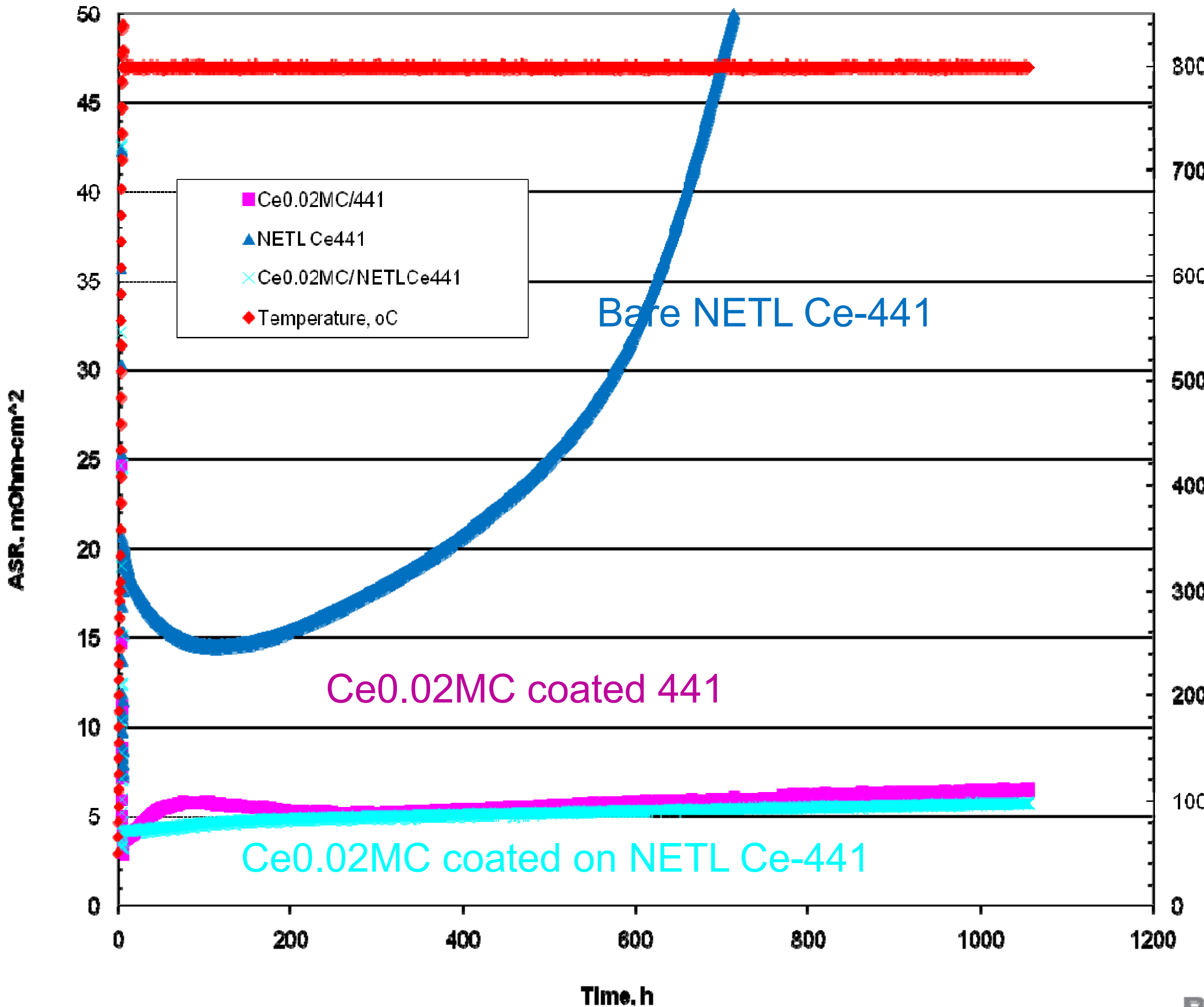
ASR testing of AISI 441:
0.02Ce-MnCo spinel, NETL-Albany Ce surface treatment



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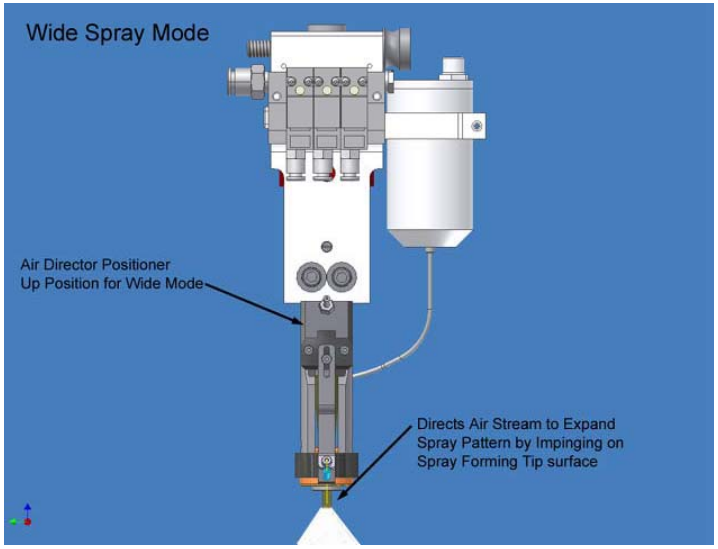
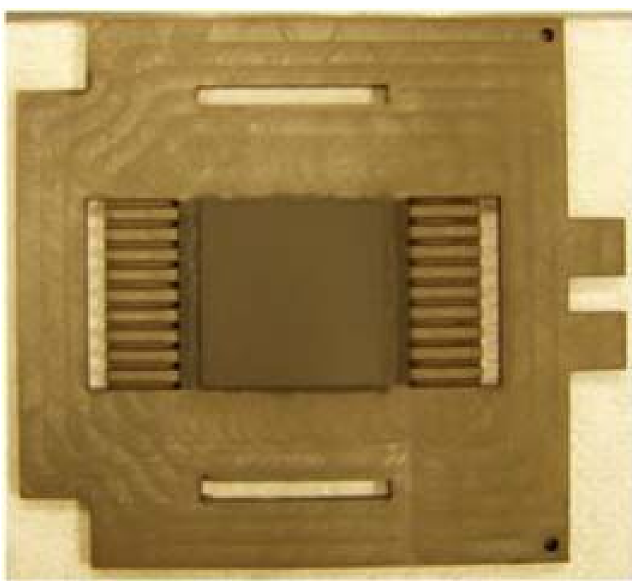
Optimization of Ce-MnCo spinel coatings

Parameters	Value	Comments
Calcination Temp.	900^{o}C	key parameter
Particle Size	<1mm	attrition -milled
Binder to Powder Ratio	0.6:1	may vary with binder type
Coating Drying Temp.	<60^{o}C	better results with slow drying
Reducing atmosphere	2.7% H_2, wet	gas passing through a water bubbler
Reducing Temp. and Time	850^{o}C, 4h	at least 650^{o}C
Pre-oxidation Temp.	950^{o}C, 0.5h	match with sealing temperature

Ultrasonic spray-based fabrication of Ce-MnCo spinel coatings: Preliminary Results



Coating speed	: 80mm/sec
Head height	: 35mm
Coating mode	: Wide mode
Ink feeding rate	: 1.5ml/sec
Air flow rate	: 50ml/sec



Ultrasonic spray-based fabrication: Process Optimization

Design Of Experiment (DOE) Optimization
Taguchi, Grey-Taguchi method and ANOVA (Analysis of Variance)

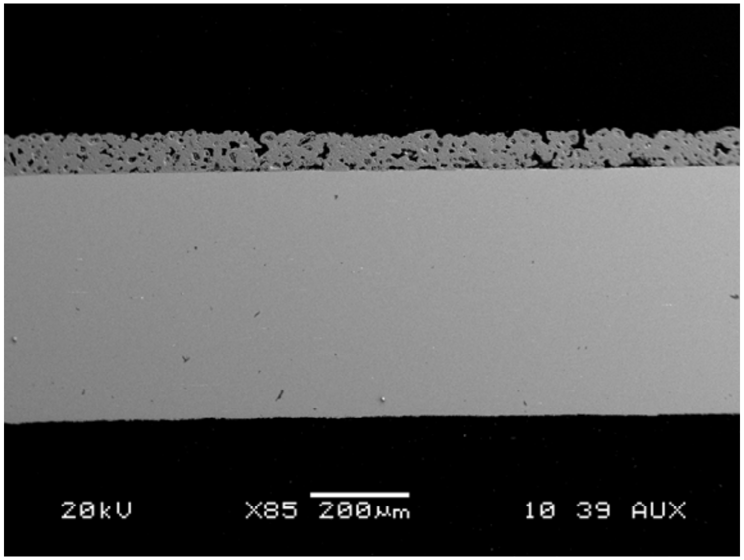
Points of reference: Coating thickness, pore area per unit area and the amount of material used

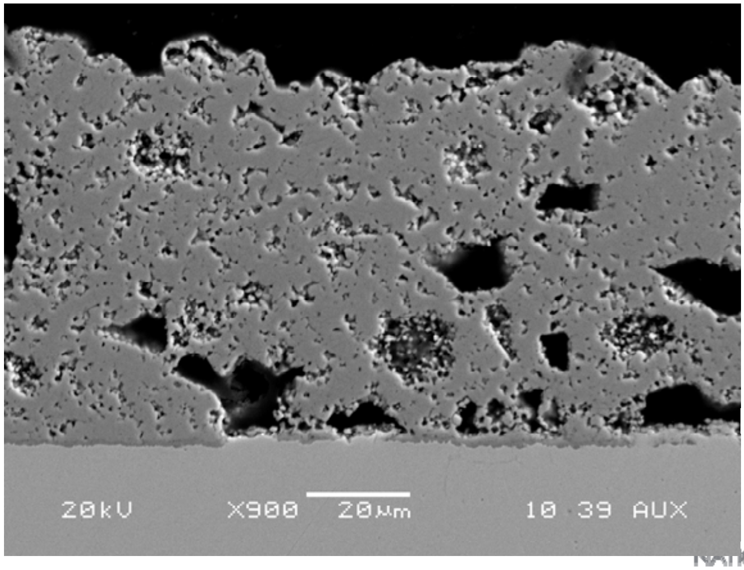
Two different mode : 1. Wide mode
2. Narrow mode

Factors	level1	level2	level3	level4
Viscosity	37 cP	17 cP	9 cP	5 cP
Coating speed	40mm/sec	60mm/sec	80mm/sec	100mm/sec
Head height	15mm	25mm	35mm	45mm
Ink feeding rate	0.5ml/sec	1ml/sec	1.5ml/sec	2ml/sec
Air flow rate	30ml/sec	40ml/sec	50ml/sec	60ml/sec

Elimination of Reducing Atmosphere Heat Treatment for MnCo Spinel Coatings

- Standard fabrication approach requires heat treatment in reducing atmosphere followed by oxidative heat treatment.
- Use of metallic precursor powders (Mn, Co) eliminates reducing heat treatment, and thus reduces coating cost.
- Compatible with reactive air aluminization (RAA) of sealing surfaces of the interconnect
- Preliminary results:





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Solid-State Sintering

- **Conventional Sintering**
  - Thermodynamics
    - Driving Force: Decrease in surface free energy, E_S
    - $S_A = 4\pi r^2 N = 3V_m/r$; $E_S = 3\gamma V_m/r$
    - Assume $\gamma = 1$ J/m², r = 1µm, $V_m = 2.5\times10^{-5}$ m³: **E_S = 75 J/mole.** (Rahaman, "Ceramic Processing and Sintering," Dekker)
  - Kinetics
    - Diffusion-based process, so thermally activated: $D \propto Exp(-E_a/kT)$
    - Thermal Energy obtained from furnace
    - Assuming $E_a = 1.5$ eV, $D_{1400°C}/D_{900°} \approx 80$
- **Pressure Sintering**
  - Driving Force: Externally applied pressure, P_a, during heating
  - Assume 30 MPa pressure: $W = P_a V_m$ = **750 J/mole**
- **Reaction Sintering**
  - Driving Force provided by decrease in energy accompanying chemical reaction
  - Challenges in controlling microstructure due to simultaneous processes (chemical reaction/sintering)

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Reaction-Assisted Sintering of Spinels

- Reaction-Assisted Sintering
  - Both Thermal and Chemical Energy available to enhance densification rate
  - Example (data for MnCo spinel not available):
    - $Co(s) + 2\ FeO(s) + O_2(g) = CoFe_2O_4$
    - **$\Delta H_r(900°C) = -547$ kJ/mol**
    - Adiabatic Temperature: ~3600ºC

  - Less advantage with all-oxide precursors:
    - $CoO(s) + 2\ FeO(s) + 0.5O_2(g) = CoFe_2O_4$
    - $\Delta H_r(900°C) = -314$ kJ/mol
  - **Greater advantage with all-metallic precursors:**
    - $Co(s) + 2\ Fe(s) + 2O_2(g) = CoFe_2O_4$
    - **$\Delta H_r(900°C) = -1077$ kJ/mol**

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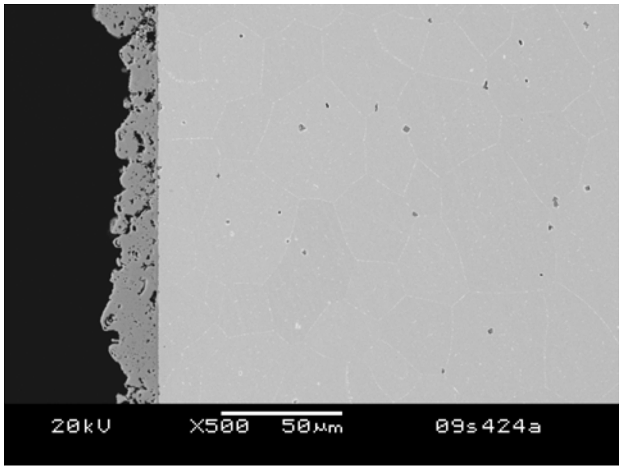
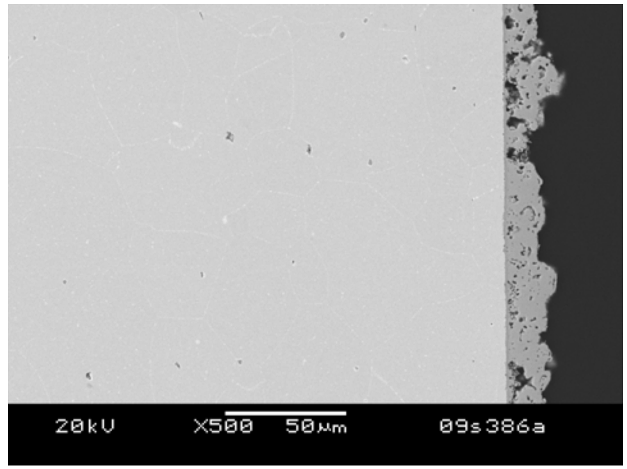
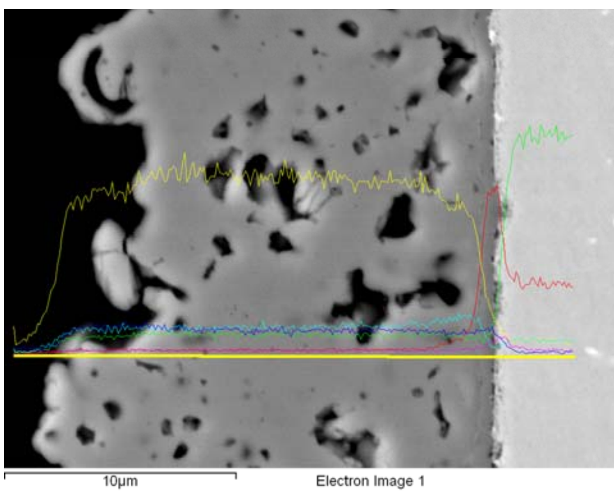
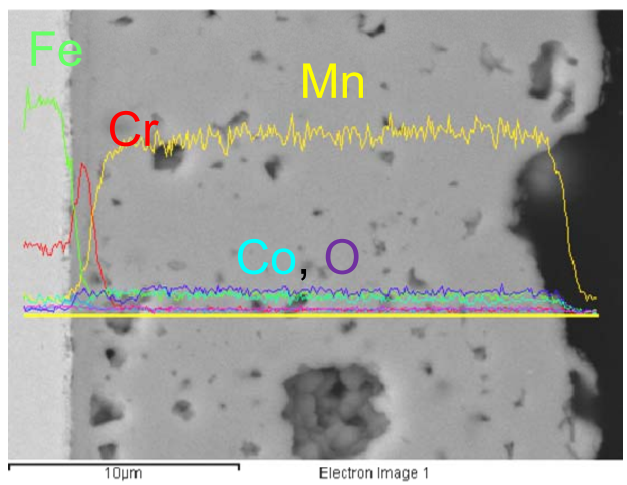
Alternative Interconnect Coating Compositions





Emphasis on reduction / elimination of Co, to reduce coating cost





Mn4Co1

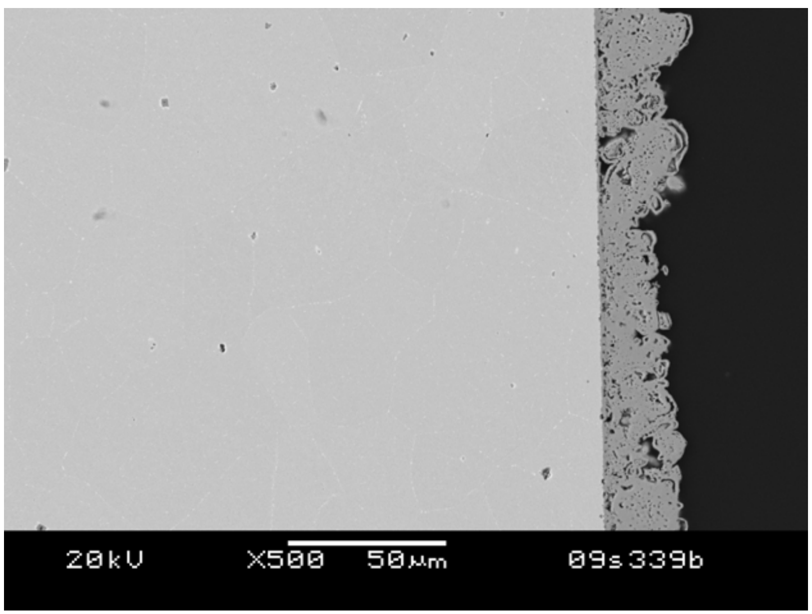
Mn3Co1

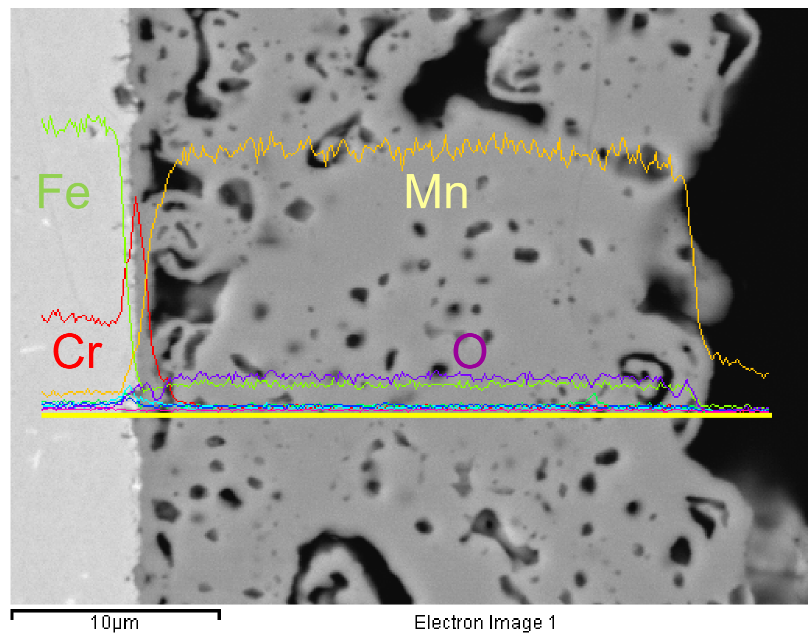
MnCo with reduced Co content ←

800ºC in air, 24 hours

Alternative Interconnect Coating Compositions

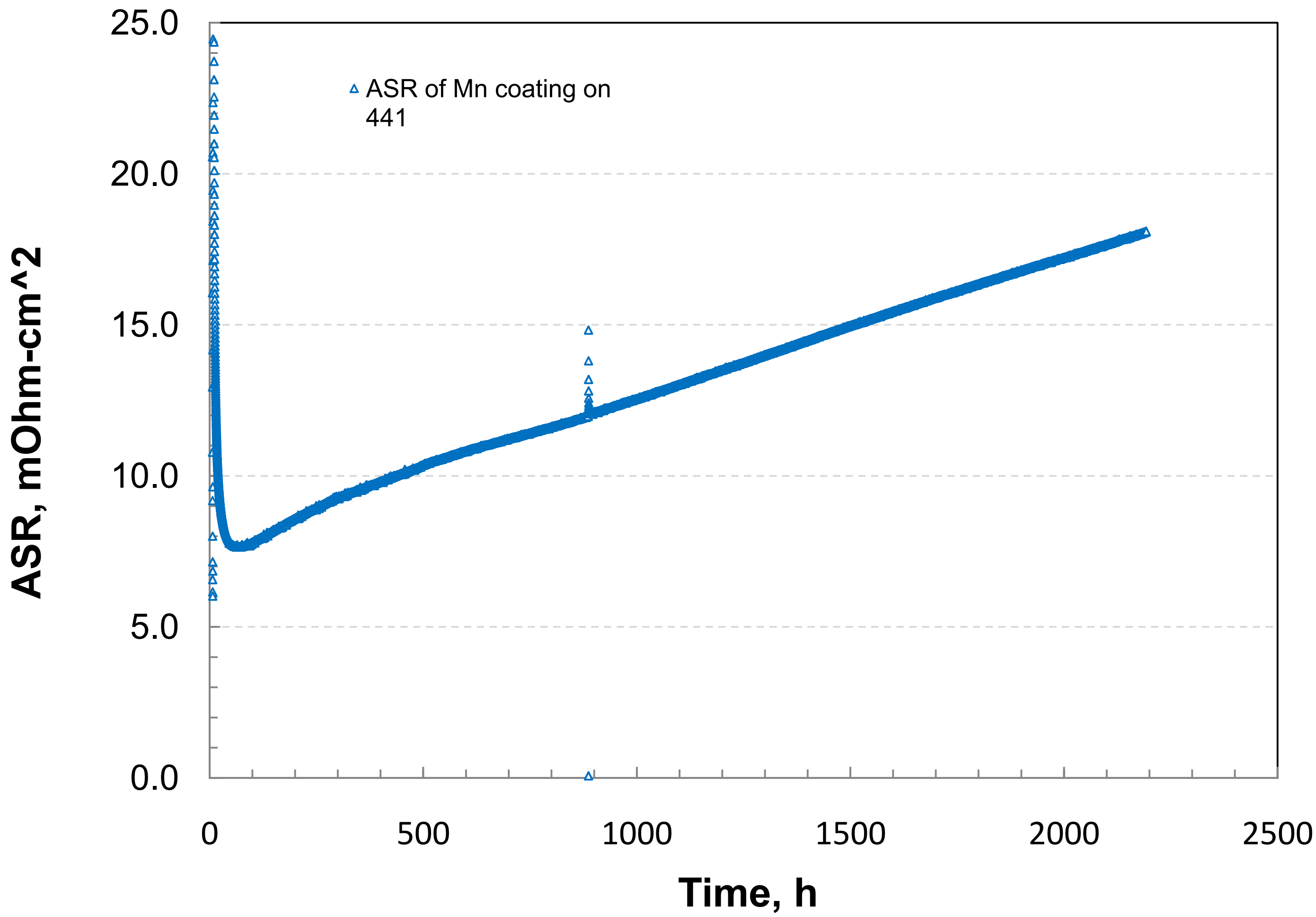
- Mn only precursor (Cobalt-free)
- Mn oxide coating prepared from Mn powder:





Heat treatment: 800ºC in air for 24 hours

ASR of Mn Coated 441 at 800°C



- Post-test analysis will be performed to determine cause of ASR increase
- Other compositions are under investigation

Conclusions

- AISI 441 exhibits promising alloy chemistry for SOFC interconnect applications
  - Expensive refining processes not required, so cost is reduced
- Ce-modified MnCo spinel coatings exhibit the benefits of original MnCo coatings, and also provide improved scale adherence and lower scale growth rate
- Ultrasonic spray-based fabrication process appears promising
  - DOE matrix of optimization trials in progress
- Cost-reduction approaches are under investigation
  - Elimination of need for preliminary reducing atmosphere heat treatment
  - Reduction or elimination of Co content

Future Work

- Evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 steel, including dual atmosphere (w/ simulated coal gas fuel) and thermal cyclic conditions.
- Optimize automated ultrasonic spray process for coating of larger, shaped parts.
- Reduce cost of protective coatings through elimination of reducing heat treatment and/or minimization or elimination of Co content

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