Development of SOFC Interconnects and Coatings

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Presentation Outline

- Objectives
- Background
  - AISI 441
  - Spinel coatings for steel interconnects
- Results:
  - Performance of Ce-modified MnCo spinel-coated AISI 441
  - Effect of alloy surface treatments
  - Optimization of Ce-modified MnCo spinel coatings
  - Alternative coating compositions
- Conclusions
- Future Work
- Acknowledgements

Objectives

- Global 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
- Specific Objectives
  - Improved understanding of performance of Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ spinel coatings on AISI 441 steel
    - ASR, oxidation behavior, scale adhesion at 800 and 850ºC
  - Evaluation of alloy surface treatments
    - Collaborations with Allegheny Ludlum and NETL-Albany
  - Optimization of Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ spinel coatings
    - Ultrasonic spray process; effect of coating thickness
  - Evaluation of cost reduction approaches
    - Reduced Co content to lower coating cost
    - Metallic precursors

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

Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ Spinel Coatings

- 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

$$CTE_{Mn_{1.5}Co_{1.5}O_4} \cong 11\times10^{-6}K^{-1}, 20-800^{o}C$$

- Chemically compatible with contact pastes, cathodes
- Cr-free composition
- CeO_2 inclusions improve scale adhesion of alloy substrate (rare earth effect)

Coating Provides:

Reduced Cr volatility from steel

Improved scale adhesion

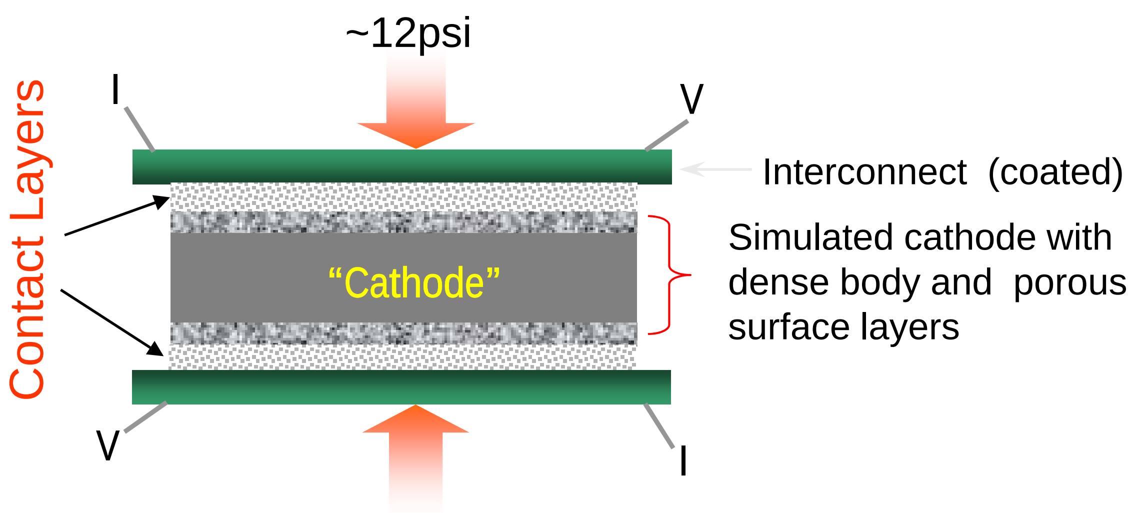
Reduced oxidation rate of alloy:

k_p (g^2/cm^4-s)	800ºC	850ºC
Ce-MC coated 441	2×10^{-14}	1×10^{-13}
Bare 441	5×10^{-14}	3×10^{-13}

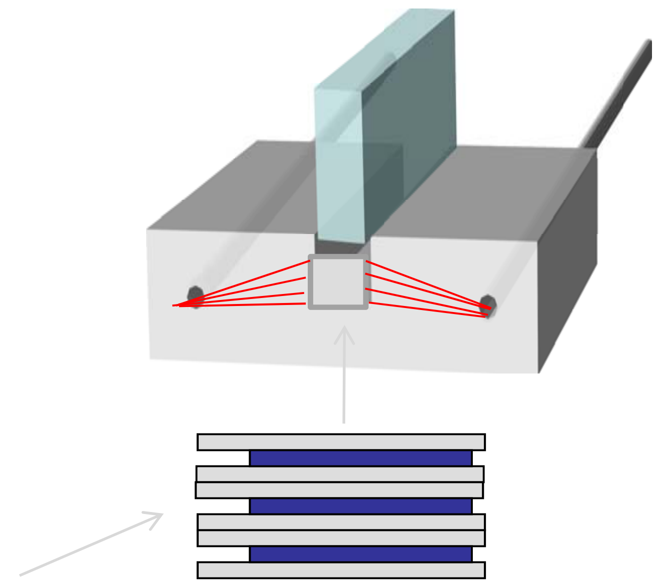
Performance of Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ spinel coatings on AISI 441 steel

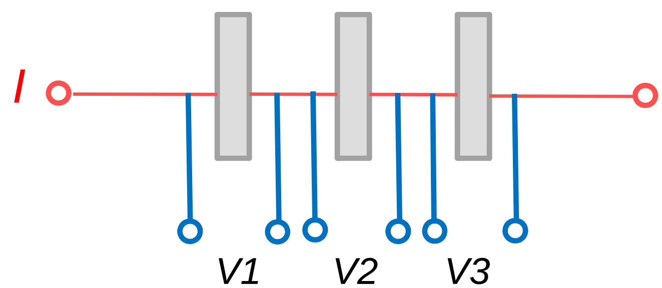
Area Specific Resistance (ASR) Measurements

$$ASR_{cathode-interconnect} = \Phi(scale, contact material, coatings)$$



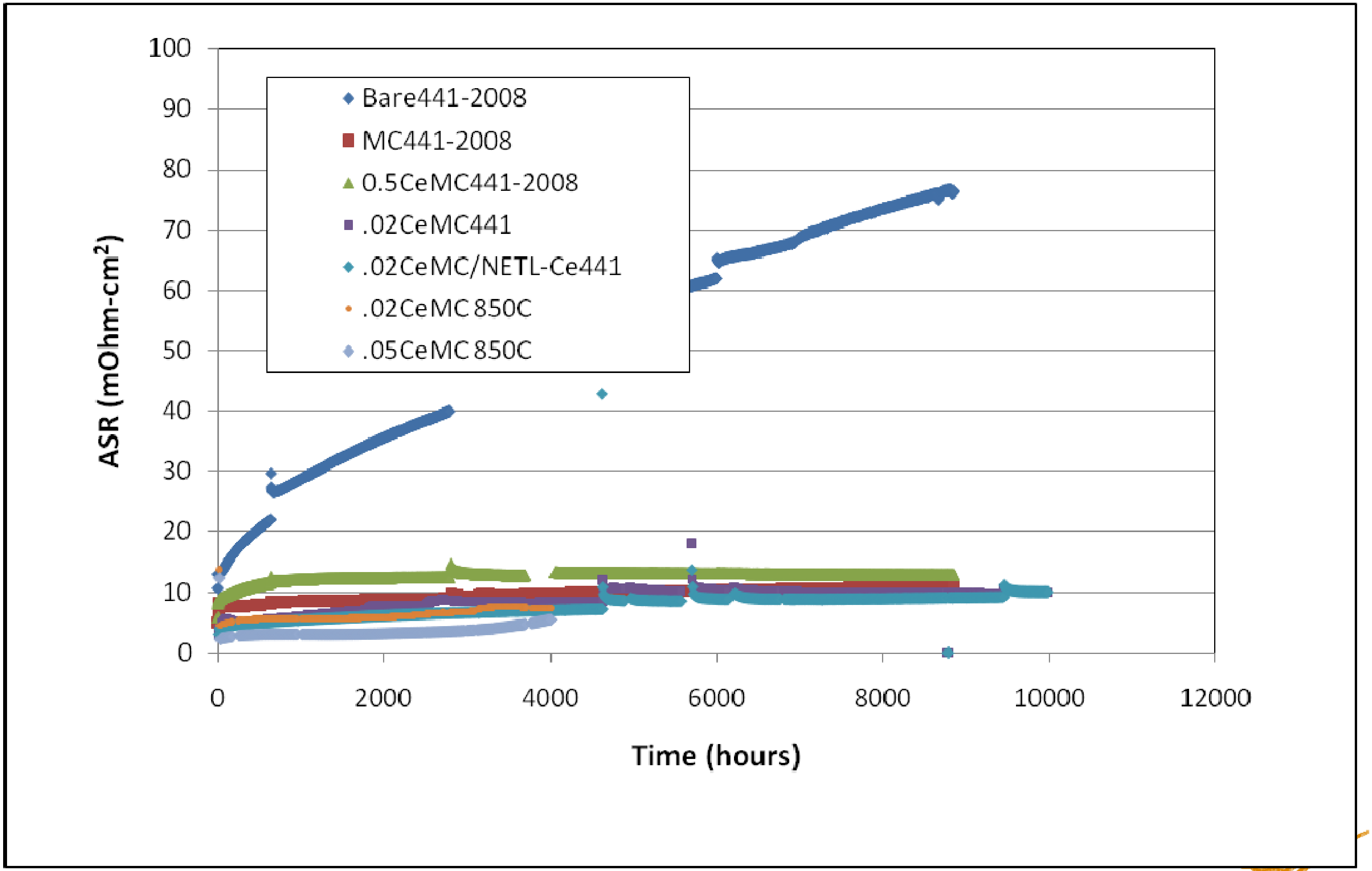
Current Density: 0.5A.cm^{-2}





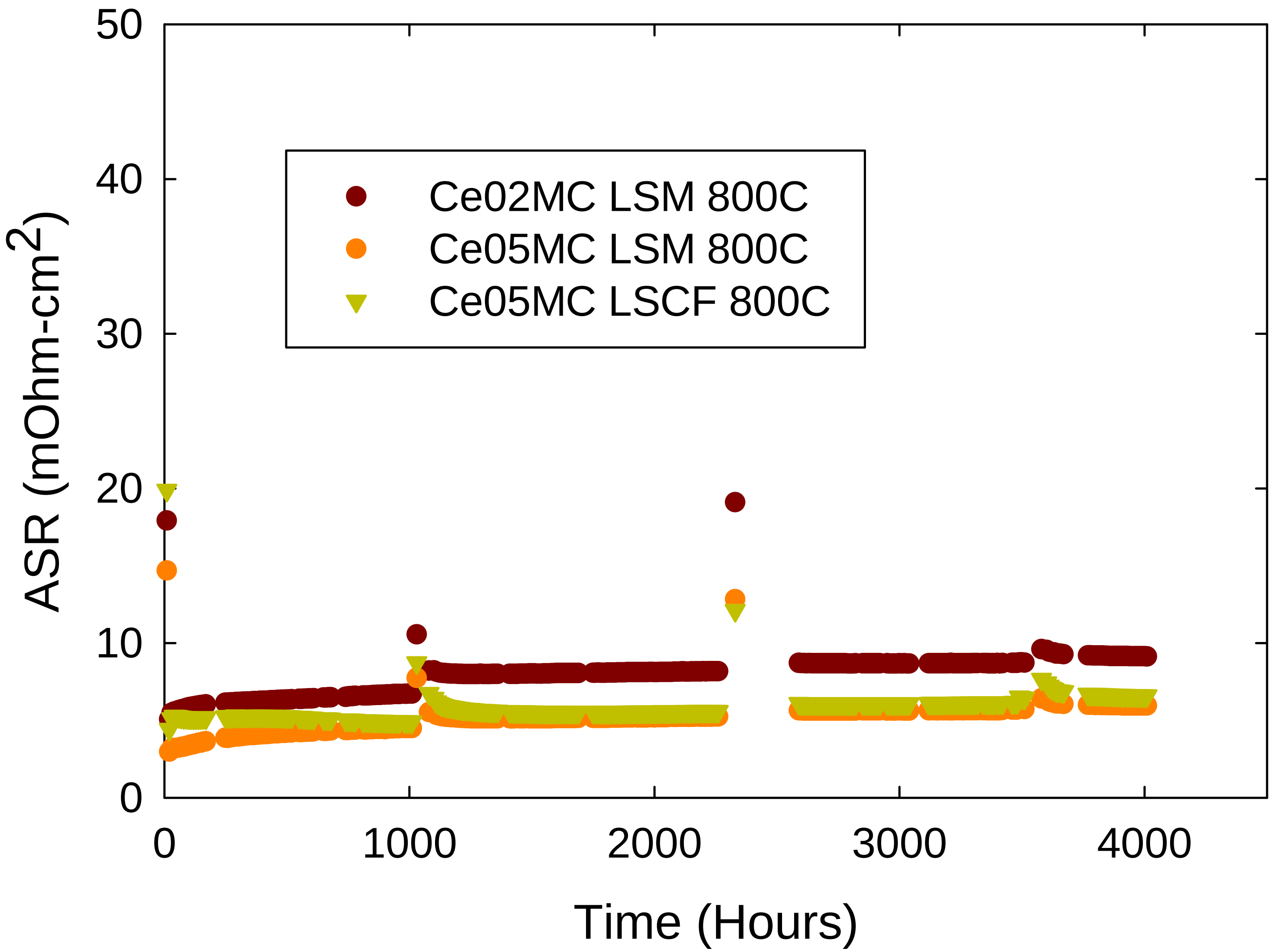
ASR Stack (3 sets)

Long-Term ASR measurements: 800 and 850ºC

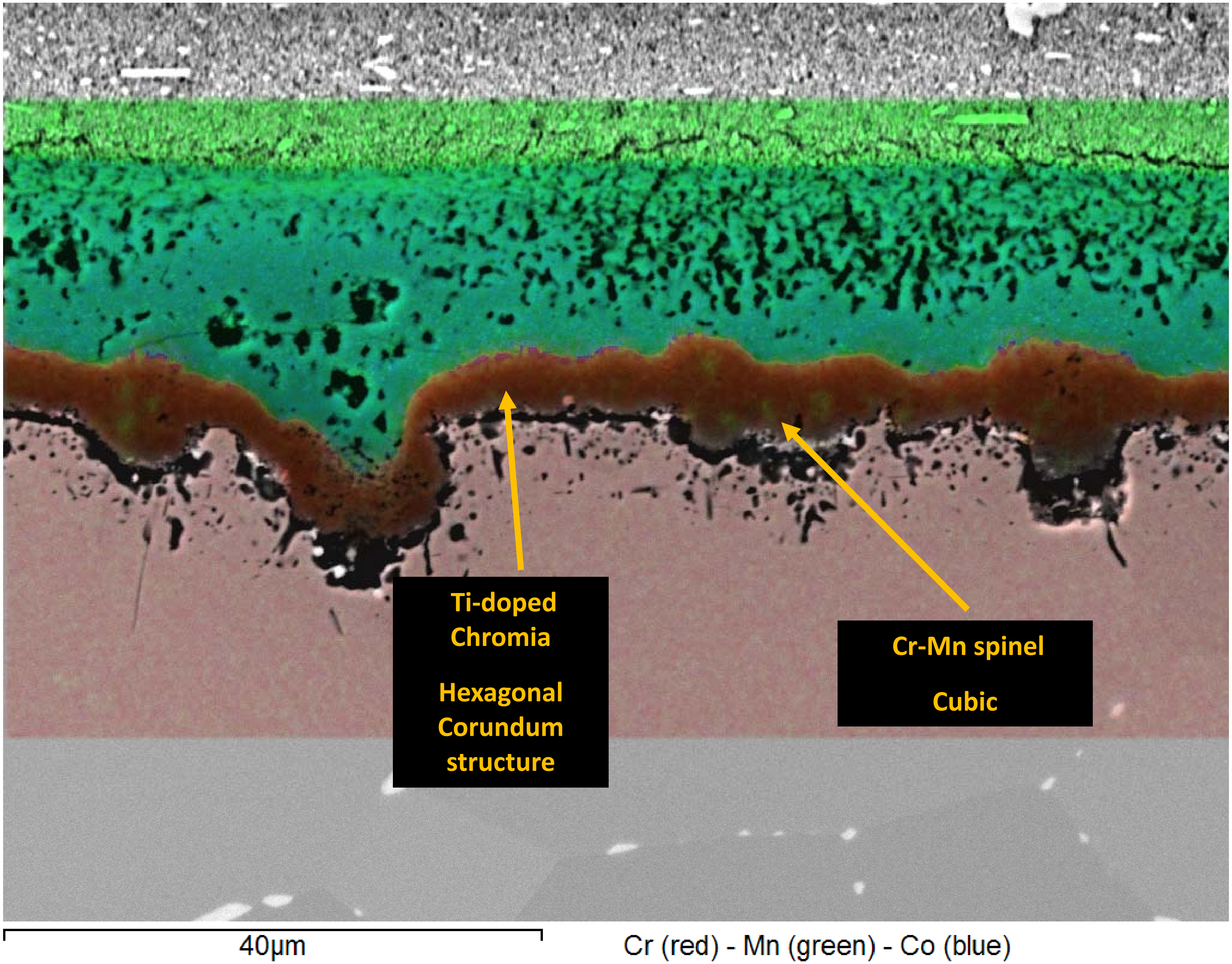


800ºC except where noted.

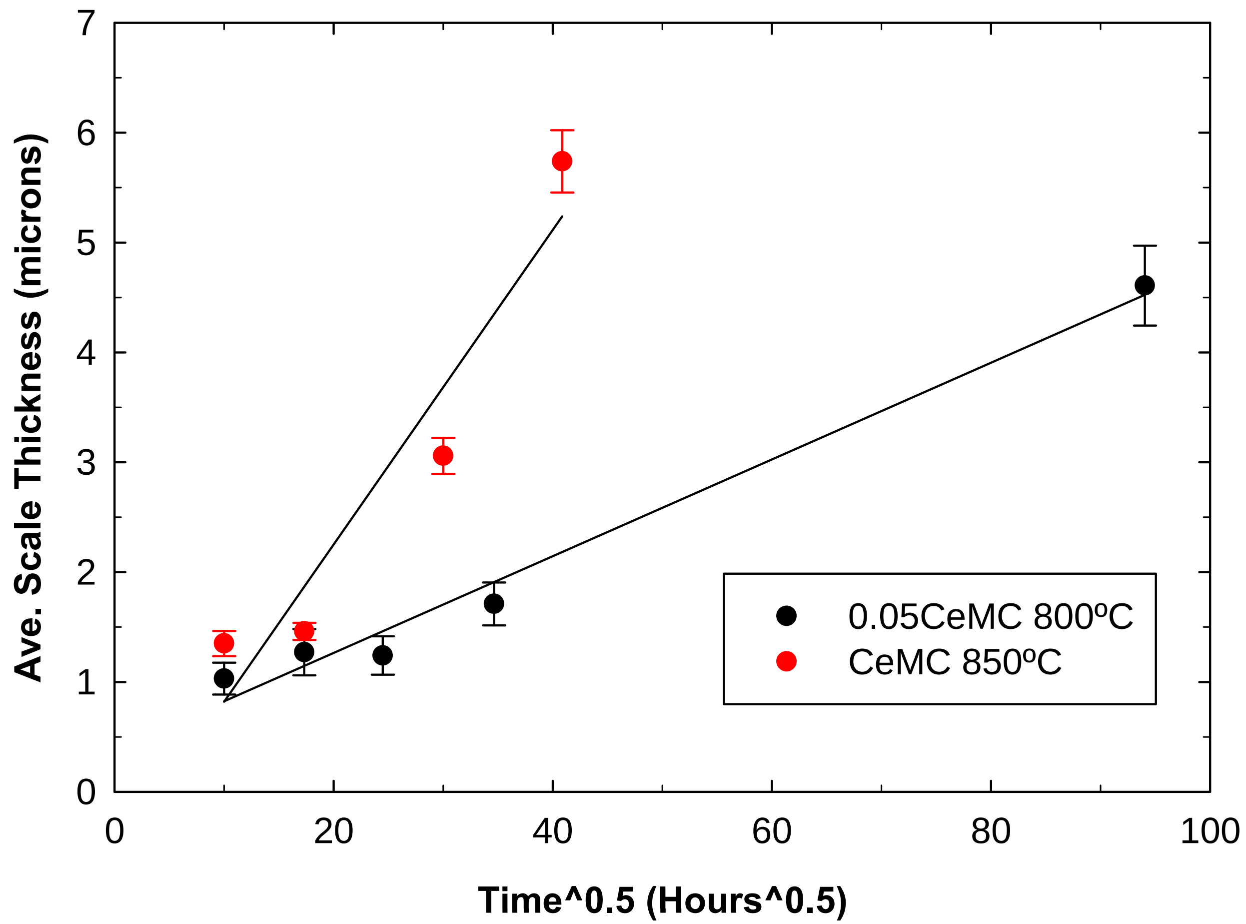
ASR Testing including Thermal Cycling



SEM/EDS/EBSD Analysis



Effects of Temperature on Scale Growth and Adhesion



Spallation observed (scale/alloy interface) after 1670 hours at 850ºC

No evidence of spallation in long term ASR test (no thermal cycling)

Effect of Surface-Treatment on Oxidation Behavior of Spinel-coated 441

- 800ºC
  - Allegheny Ludlum: Mill Reference, De-siliconized, Surface blasted, Surface ground, Temper rolled
  - NETL Albany: Ce surface treatment
  - All coated with Ce-MnCo spinel, heat-treated in air at 800ºC for up to 10,000 hours
    - As expected, no spallation after 2000 hours

Surface Treatment	Ave. Scale Thickness
Mill Reference (1200 grit)	2.23 ± 0.17
De-siliconized	1.71 ± 0.14
Surface ground	3.83 ± 0.97
Surface blasted	3.27 ± 0.40
Temper rolled	1.55 ± 0.18
Ce Treatment	3.27 ± 0.68

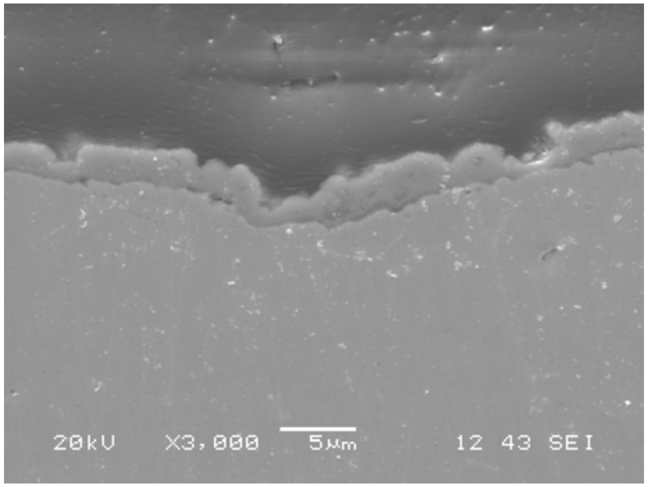
Effect of Surface-Treatment on Oxidation Behavior of Spinel-coated 441 (continued)

- 850ºC
  - As-received 441 w/ Ce-MC spinel coating
    - Typically observe spallation at scale/alloy interface after 1000 - 1500 hours
  - NETL-Albany Ce surface treatment
    - No spallation observed on uncoated, surface treated coupons after 5100 hours, possibly due to enhanced RE effect from higher Ce level at surface
    - Testing of spinel-coated coupons in progress
  - Shot-peened 441 (Metal Improvement Co.)
    - No spallation observed on uncoated coupons after 2500 hours or on coated coupons after 2000 hours
    - Testing of spinel-coated coupons in progress
  - Allegheny Ludlum surface treatments w/ spinel coating
    - To be initiated in near future
- Post-test analysis:
  - Evaluate scale adhesion
    - Visual inspection for spallation
    - Indentation for quantification of interfacial strength to allow for prediction of interconnect lifetime

Optimization of Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ spinel coatings

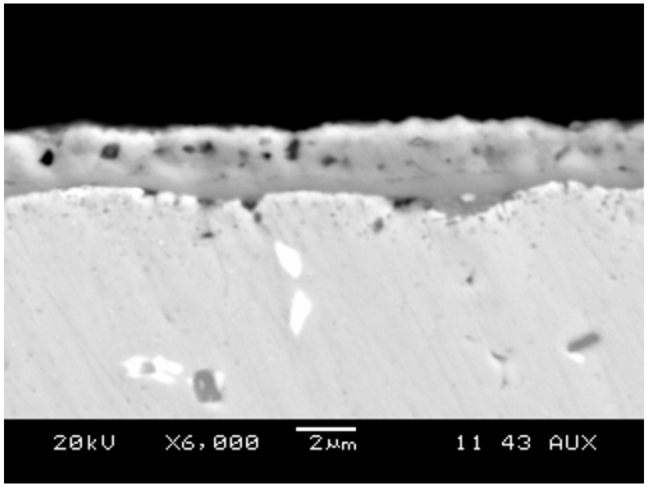
Ultrasonic spray coating: Optimization of Spray Parameters

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



Wide Mode

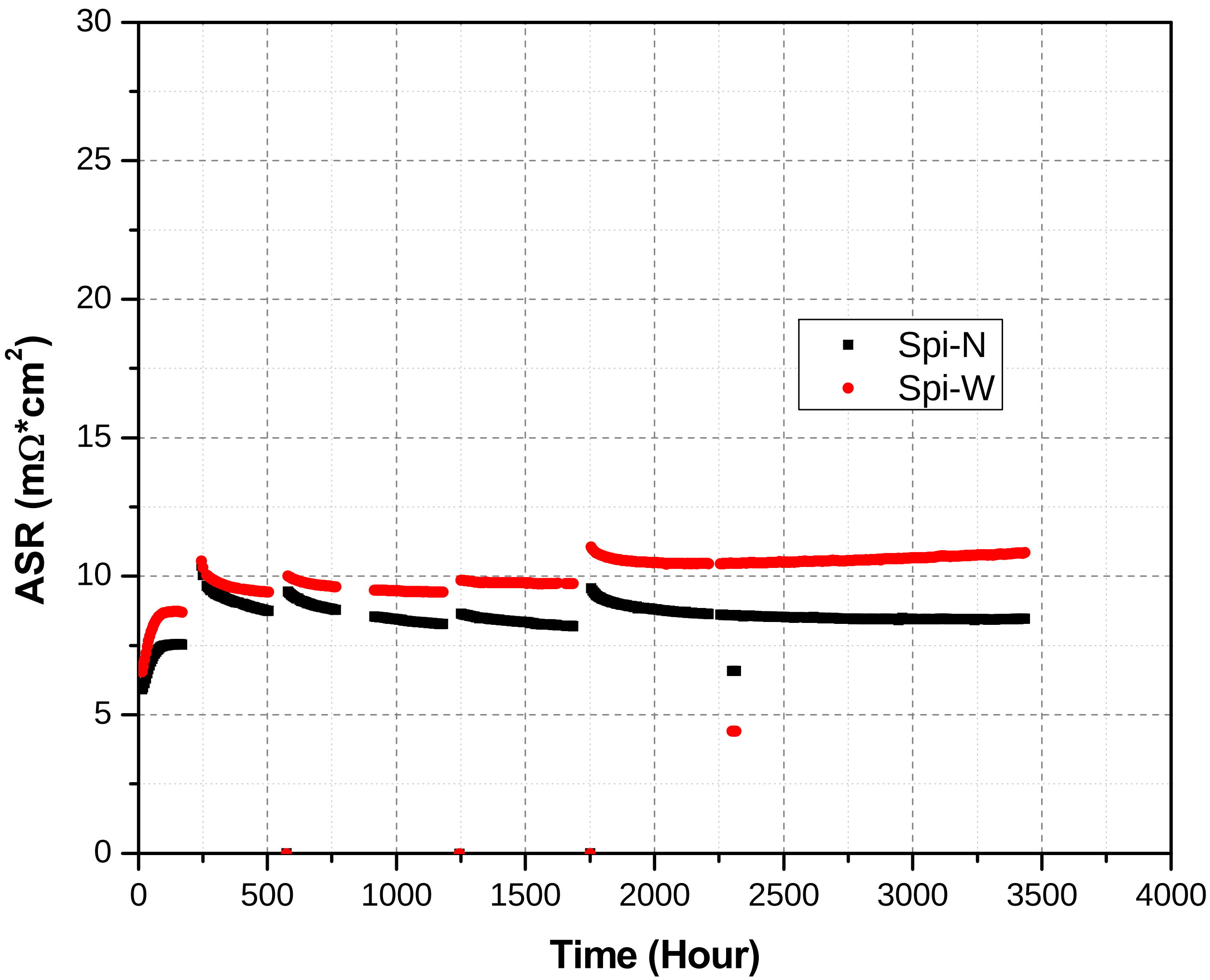
Viscosity : 5cp
Coating speed : 100mm/sec
Head height : 35mm
Ink feeding rate : 1ml/sec
Air flow rate : 30ml/sec



Narrow Mode

Viscosity : 5cp
Coating speed : 100mm/sec
Head height : 15mm
Ink feeding rate : 0.5ml/sec
Air flow rate : 40ml/sec

Ultrasonic Spray Coatings: ASR Results/800ºC



Ultrasonic spray process currently used for aluminization and spinel coating of interconnects/frames for PNNL's single/multiple stack fixture testing

Optimization of Ce-MC Spinel Coatings

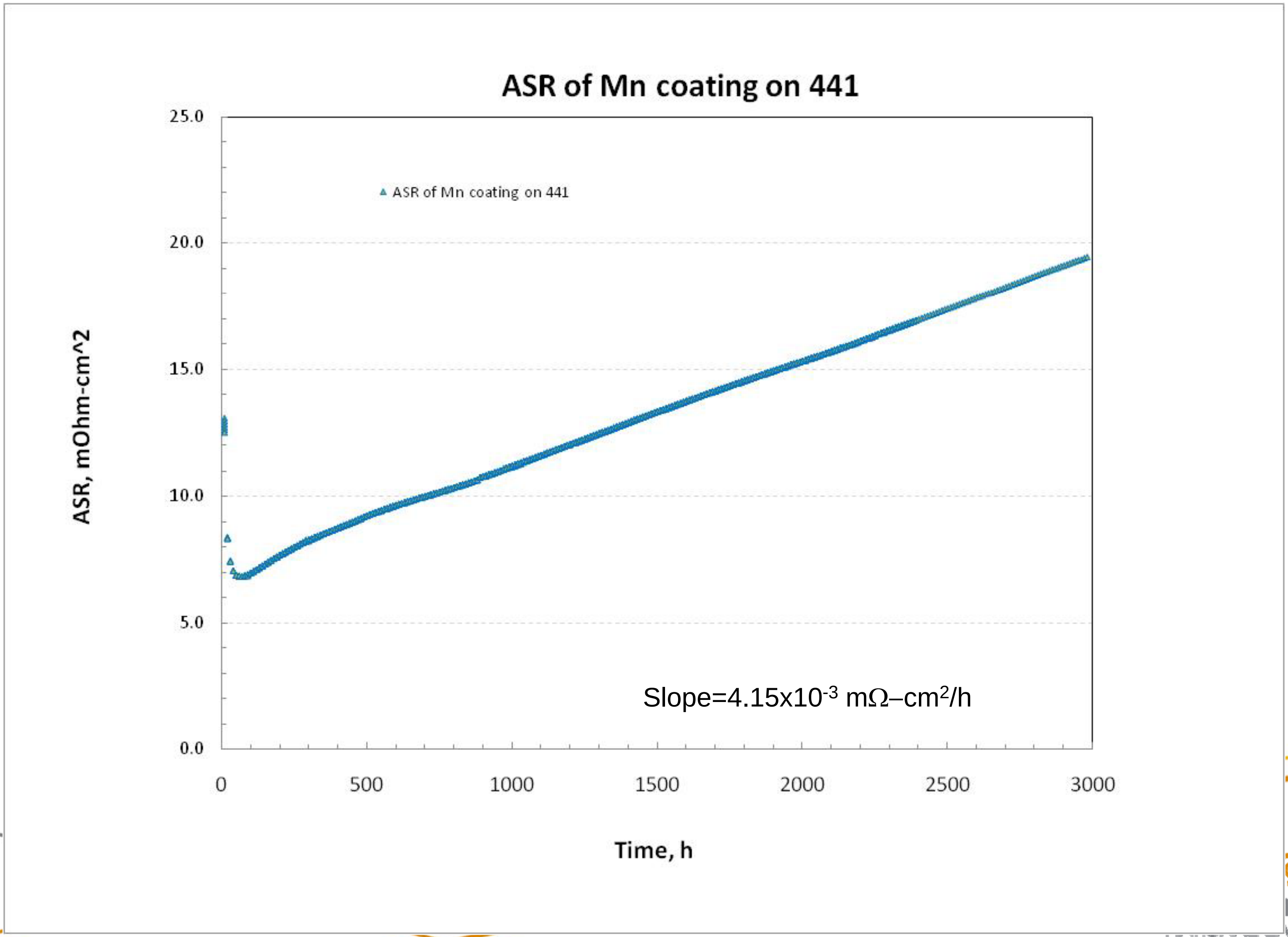
- Adaptation of ultrasonic spray process to Ce-modified spinel powder
  - Extension of previous optimization of fabrication process for unmodified spinel

- Effect of coating thickness on oxidation resistance of AISI 441
  - Two studies in progress: Sprayed coatings, Screen-printed coatings
    - ~5, 10, 20 microns thick
    - Oxidation for 2000 hours

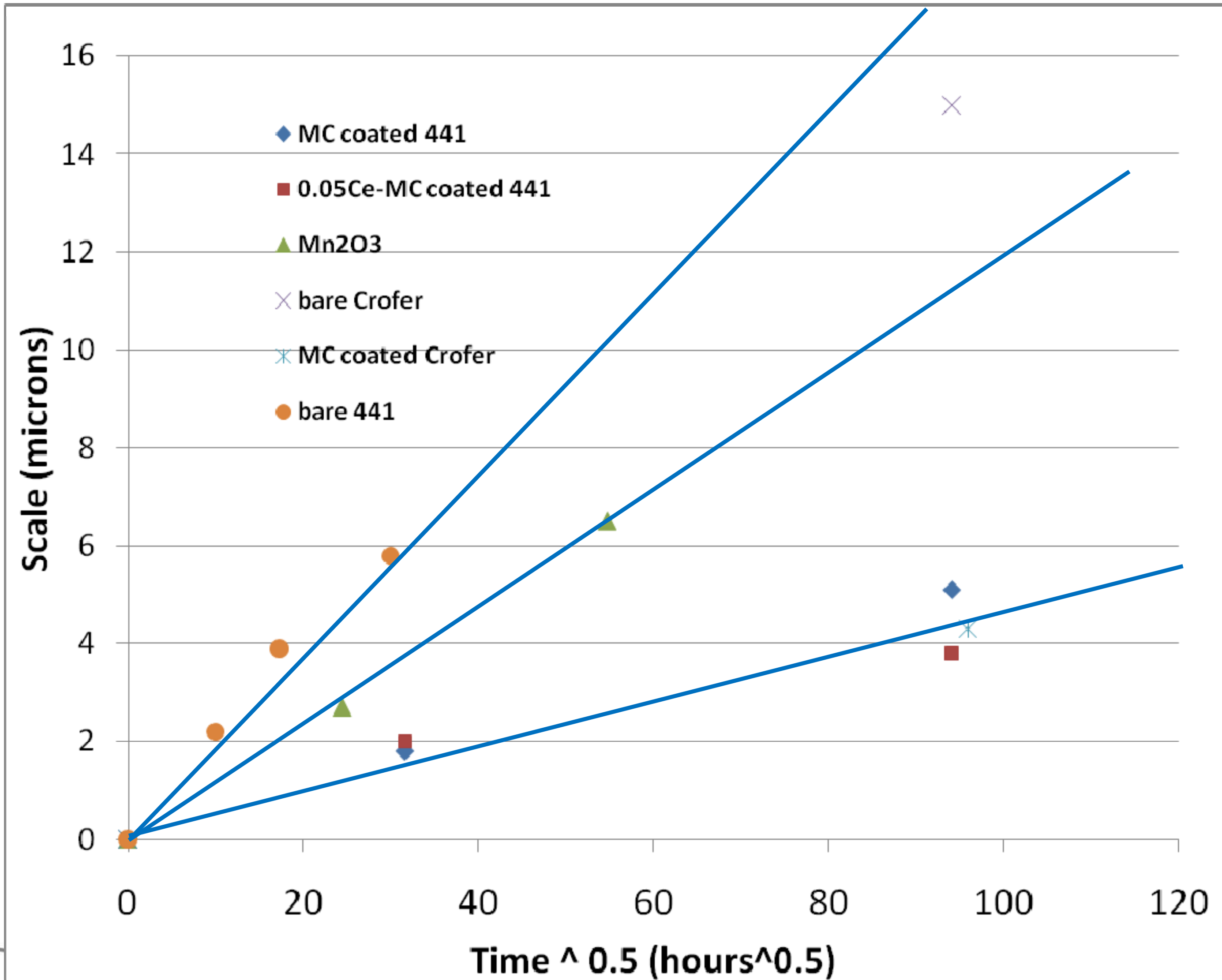
Alternative Interconnect Coating Compositions

- Reduce Co content to reduce coating cost
  - Mn oxide (Cobalt-free)
  - Mn-Co oxide coatings: Reduced Co content relative to $(Mn_{0.5}Co_{0.5})_3O_4$

Initial Study: ASR of Mn oxide coated 441 at 800^{o}C



Oxide scale thickness as f(time)



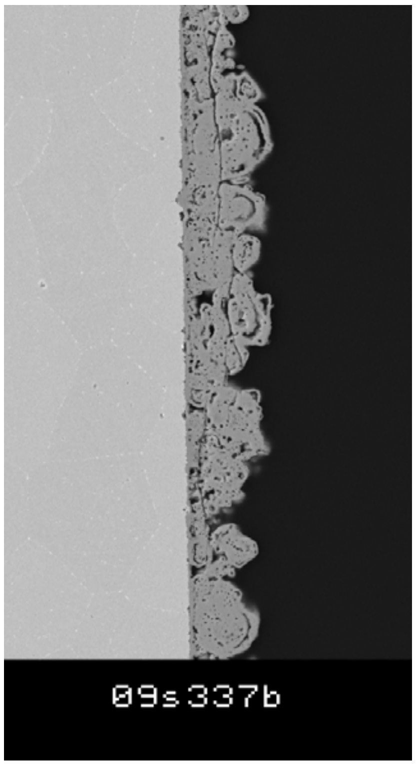
Rapid scale growth under Mn oxide coating: Intrinsic or bad microstructure?

Optimization of Mn oxide Protective Coatings on AISI 441

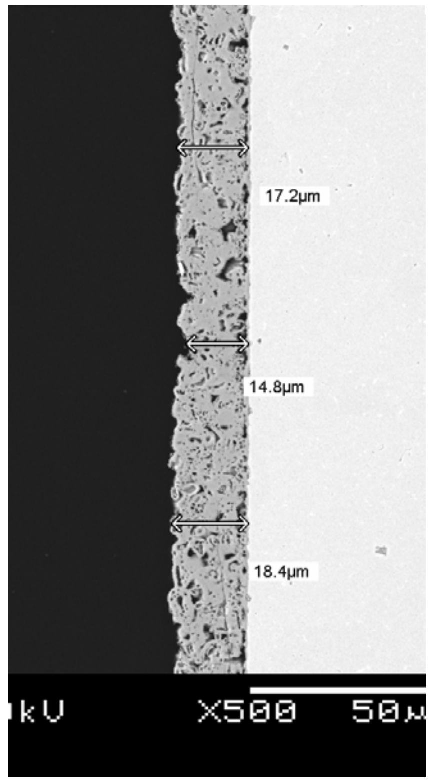
- Densification study of Mn oxide coatings prepared from Mn powder
  - Effect of particle size distribution
  - Effect of binder system and binder/solids ratio
- Optimization via SEM analysis
- Evaluation via electrical resistance testing (ASR)

Effect of particle size
SEM of Mn oxide coating on AISI 441

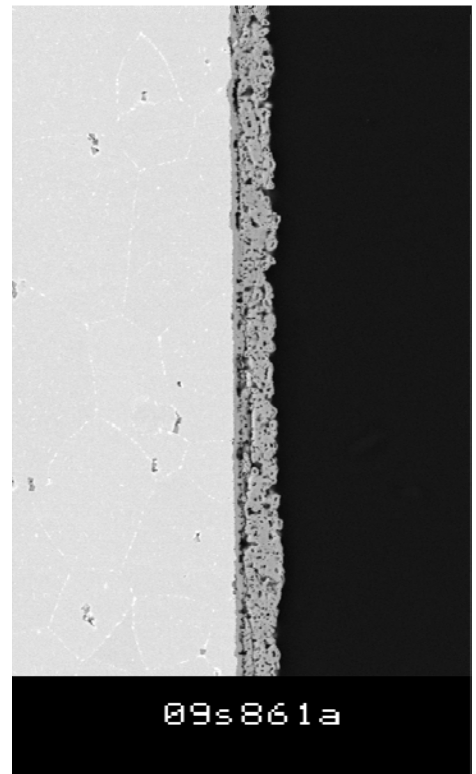
As received powder, <10um



milled powder, <5um



milled powder,<3um



The coatings prepared using Mn powder with smaller particle size showed more uniform surface

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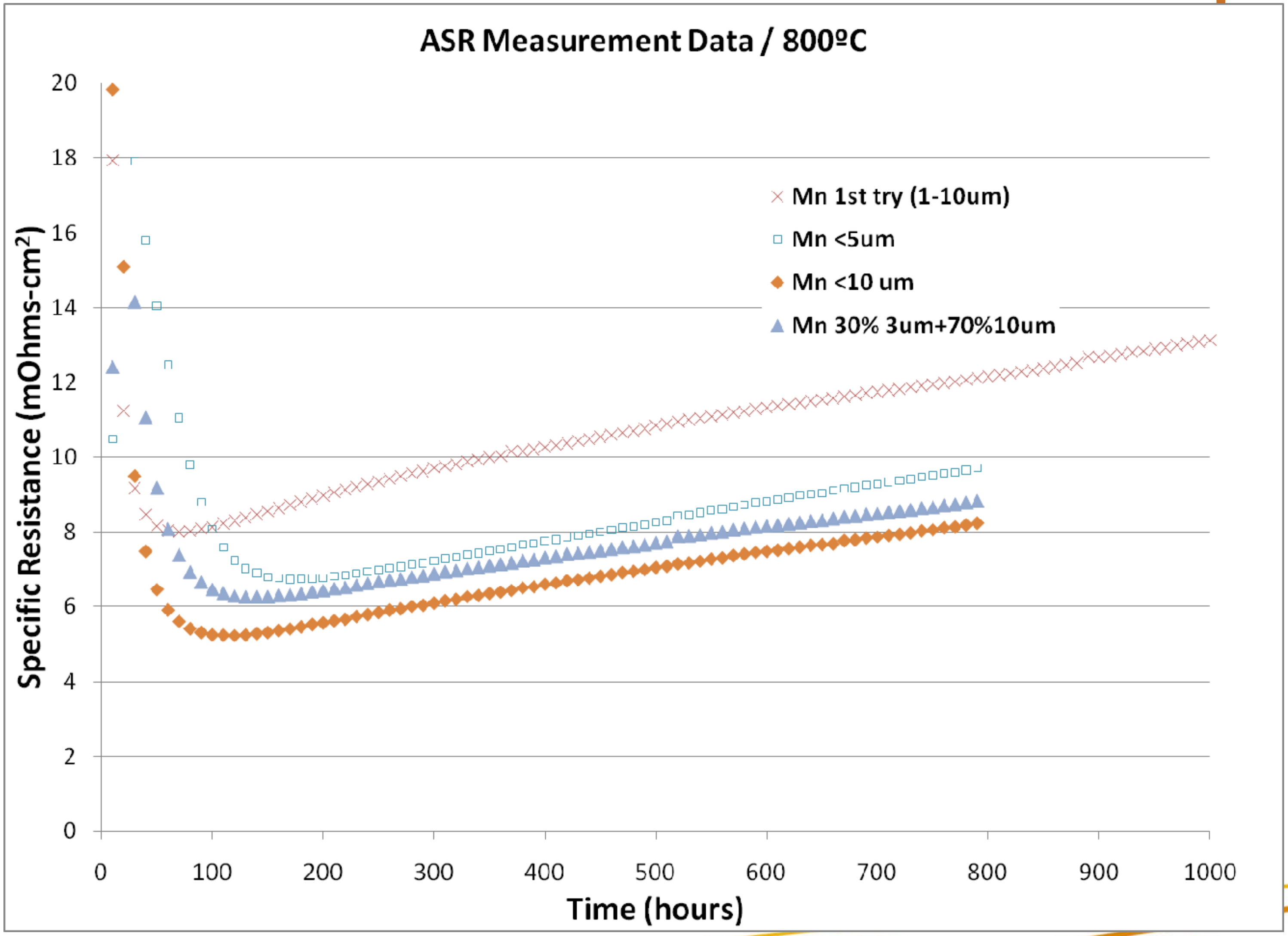
ASR Evaluation of Mn Coated 441 Samples



ASR increased linearly with time on oxidation even though the improved Mn oxide coatings appeared to be gas tight.

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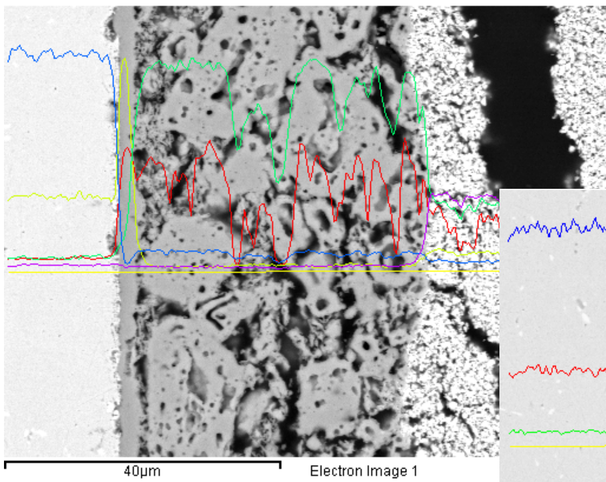
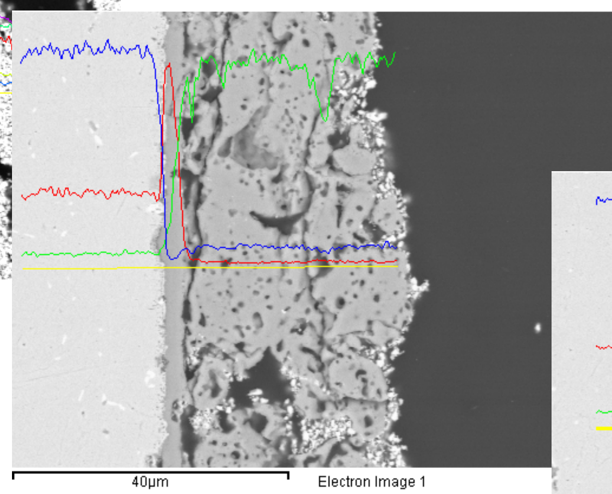
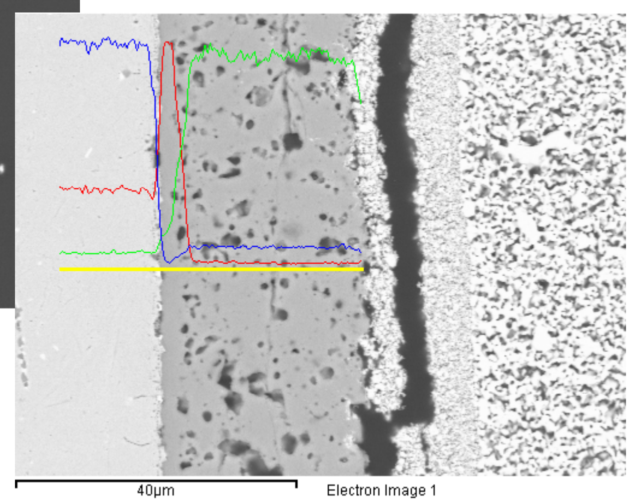
Cross-section SEM Images of Mn Coated 441 after ASR Measurement



Mn < 5μm



Mn <10μm



Composition from SEM

Mixed Mn powder (30% <3μm+70%10μm)

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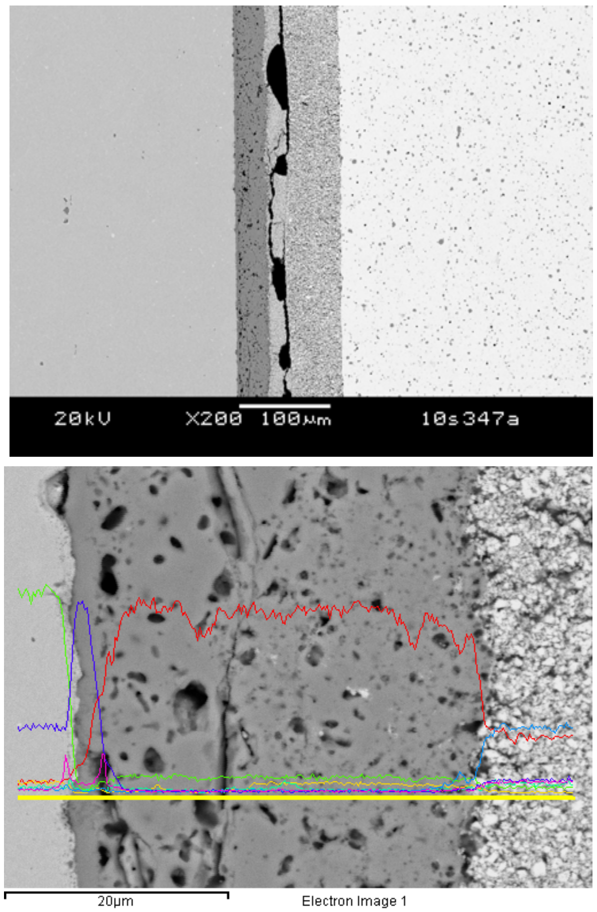
Alternative Mn-Co oxide coatings:

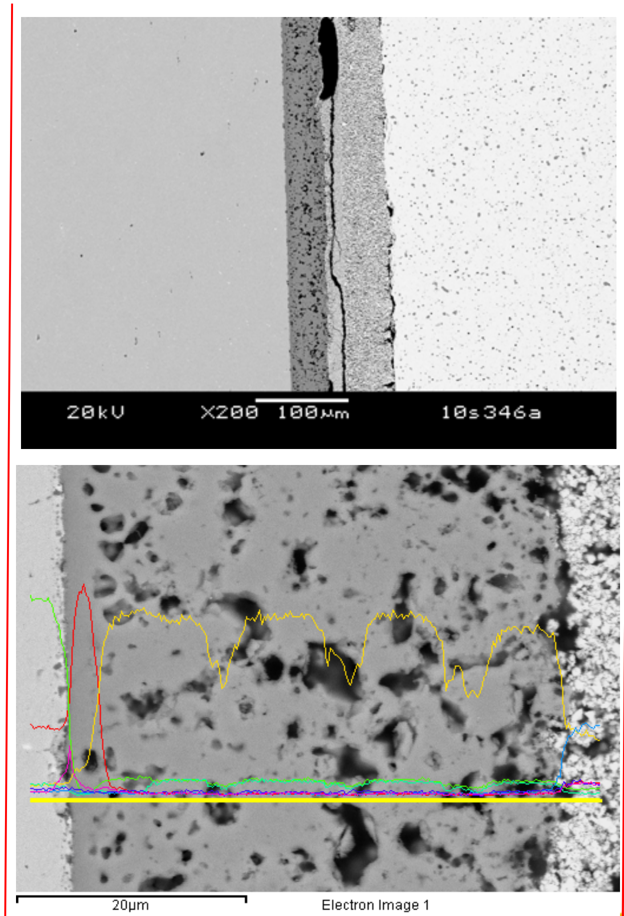
Reduced Co content relative to $(Mn_{0.5}Co_{0.5})_3O_4$

SEM Images of Mn-Co Oxide Coated 441

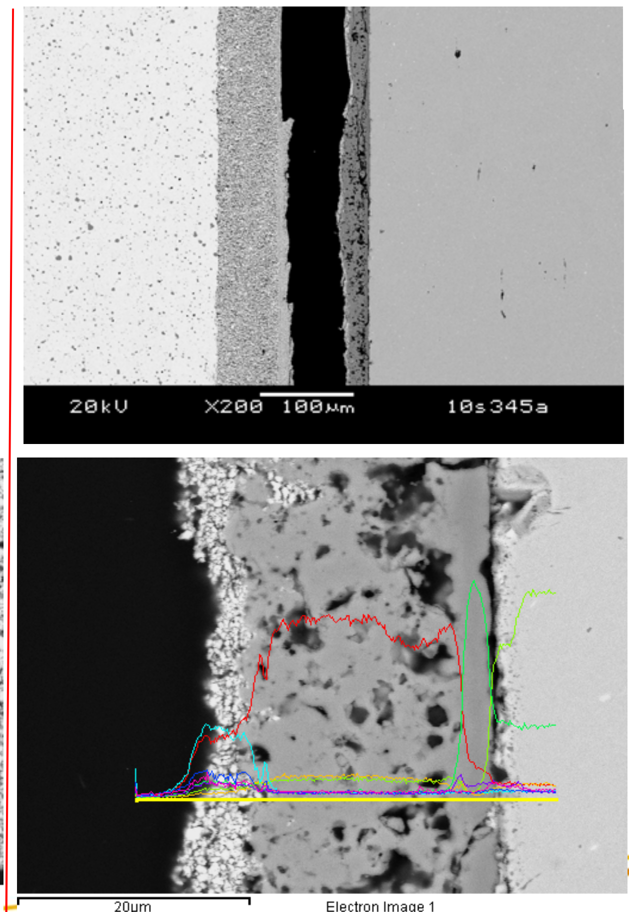
(after ASR measurements at 800°C for ~500hrs)



Mn20Co1 (33µm)



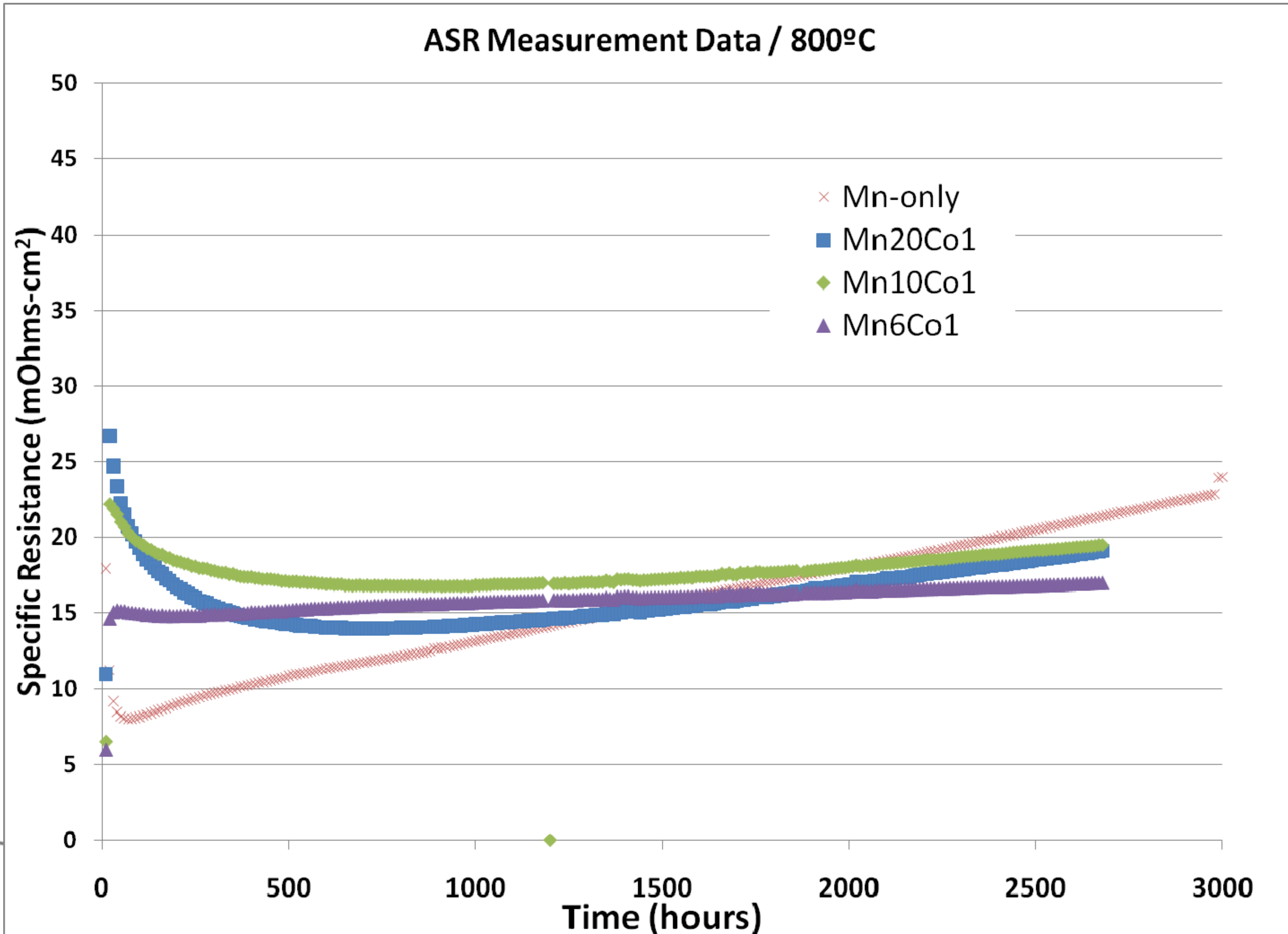
Mn10Co1 (41µm)



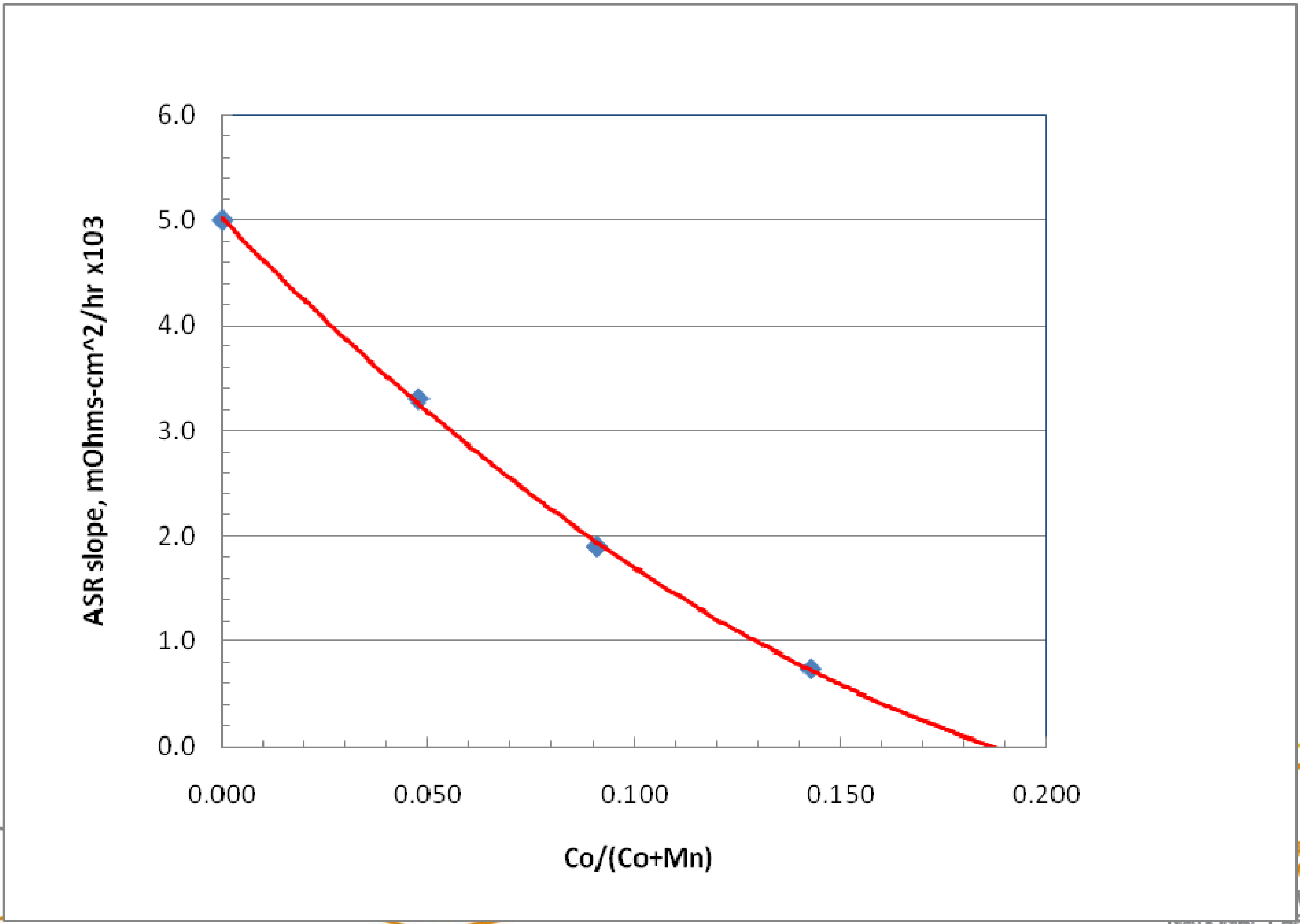
Mn6Co1 (18µm)

Prepared from metal precursors according to listed molar ratios

ASR of Reduced Cobalt Coatings



Effect of Co Content on Rate of ASR Increase



Summary

- MnCo spinel coatings on AISI 441 exhibit excellent long-term performance at 800ºC
- At 850ºC, MnCo spinel coatings exhibit low, stable ASR obtained after 4,000 hours
  - Scale adhesion issues observed at 850ºC
  - Additional studies/approaches, including alloy surface treatments, are in progress
- Ultrasonic spray process for application of MnCo spinel coatings has been optimized
- MnCo oxide coatings with substantially reduced Co content appear to be promising approach for reducing coating cost
  - Mn oxide coatings did not provide low, stable ASR

Future Work

- Continue to evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 steel
  - Evaluate at 800 and 850ºC
  - Long-term evaluation in stack test fixture
- Evaluate effect of alloy surface treatments on oxidation and spallation resistance of Ce-MC coated 441
- Optimize thickness, and automated ultrasonic spray process, for Ce-modified spinel coatings
- Reduce cost of protective coatings through elimination of reducing heat treatment and/or minimization or elimination of Co content

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