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
  - Ceramic interconnect materials
- Summary
- Future Work
- Acknowledgements

Objectives

- Global Objectives
  - Develop cost-effective, optimized materials and fabrication approaches for SOFC interconnects
  - Identify, understand, and mitigate degradation processes in SOFC interconnects
- Specific Objectives
  - Improved understanding of performance and long-term stability of AISI 441 steel coated with Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ spinel coating
    - ASR, oxidation behavior, scale adhesion at 800 and 850ºC
    - Stack fixture testing
  - 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

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)
- Reaction-sintering process developed at PNNL increases coating density at low processing temperatures

Coating provides:

Reduced Cr volatility from steel

Improved scale adhesion

Reduced oxidation rate of alloy:

k_p $(g^2/cm^4\text{-}s)$	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

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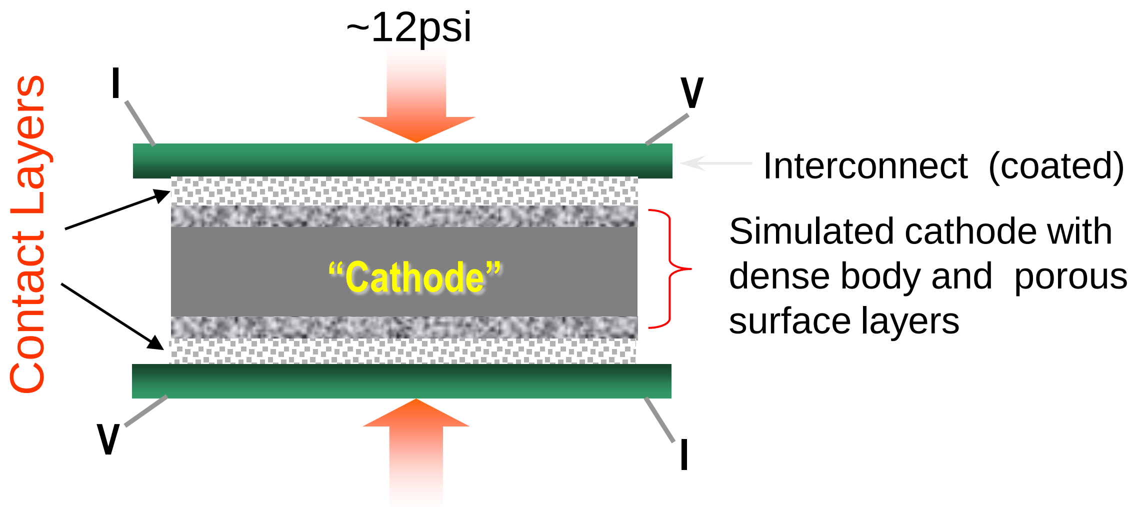
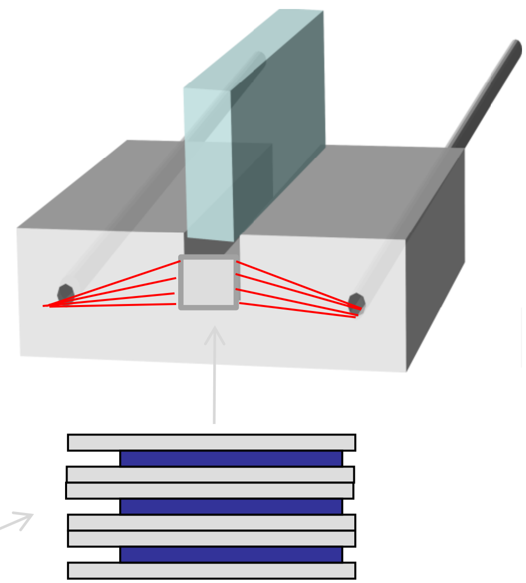
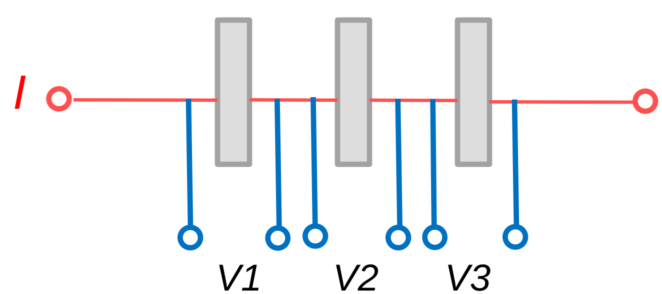
Area Specific Resistance (ASR) Measurements

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



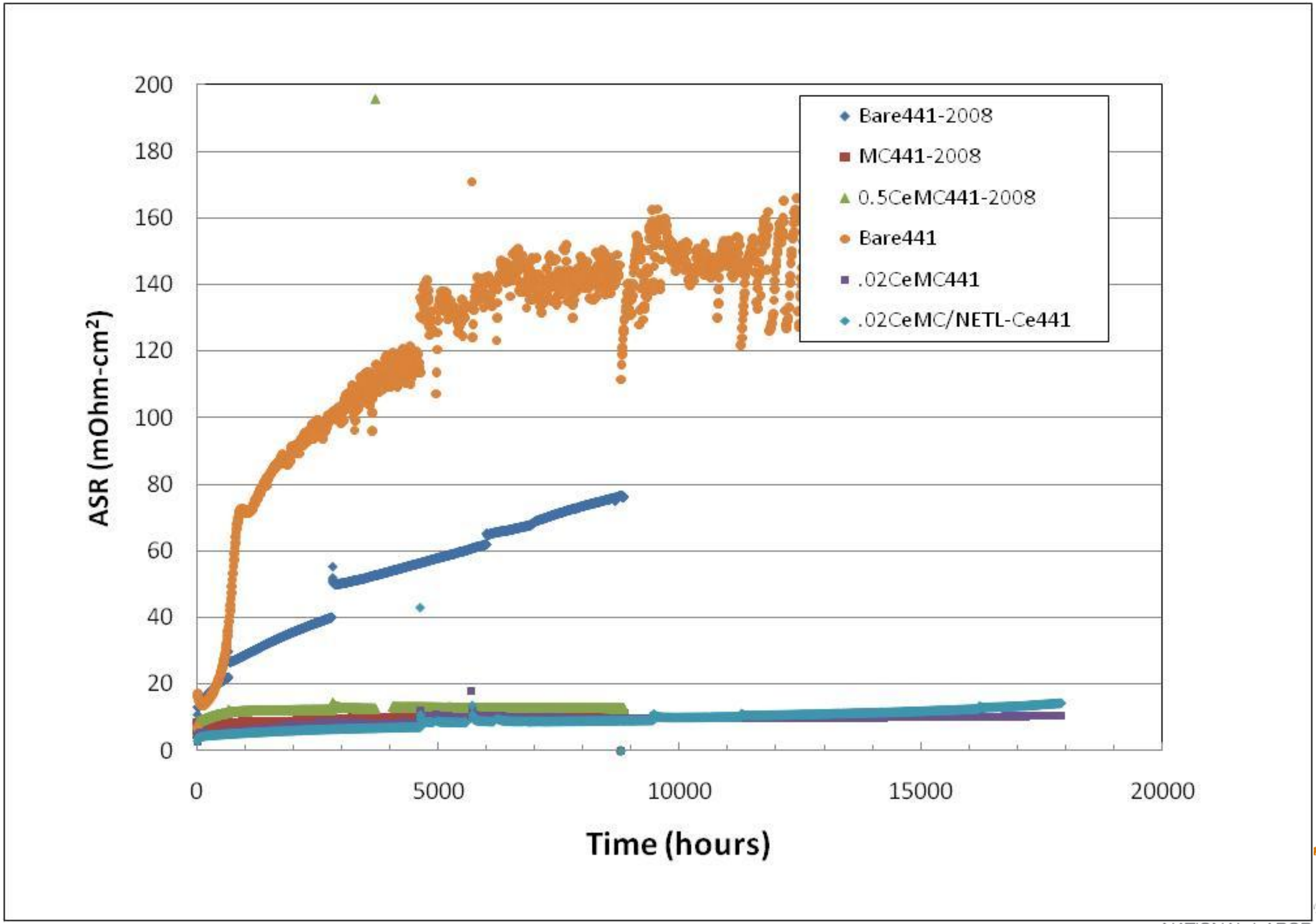
Current Density:
$0.5 A.cm^{-2}$



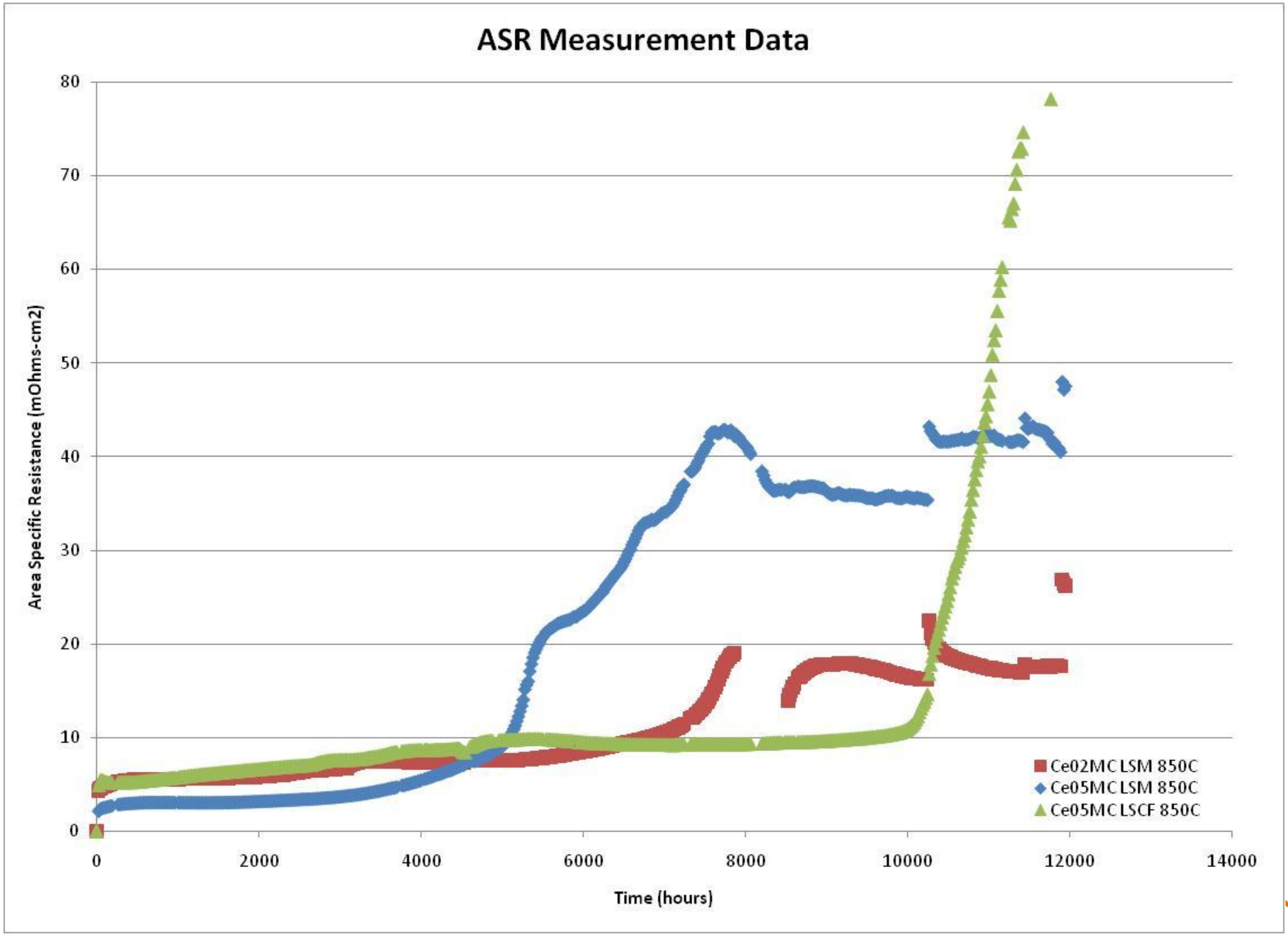


ASR Stack (3 sets)

Long-Term ASR measurements: 800ºC



Long-Term ASR measurements: 850ºC



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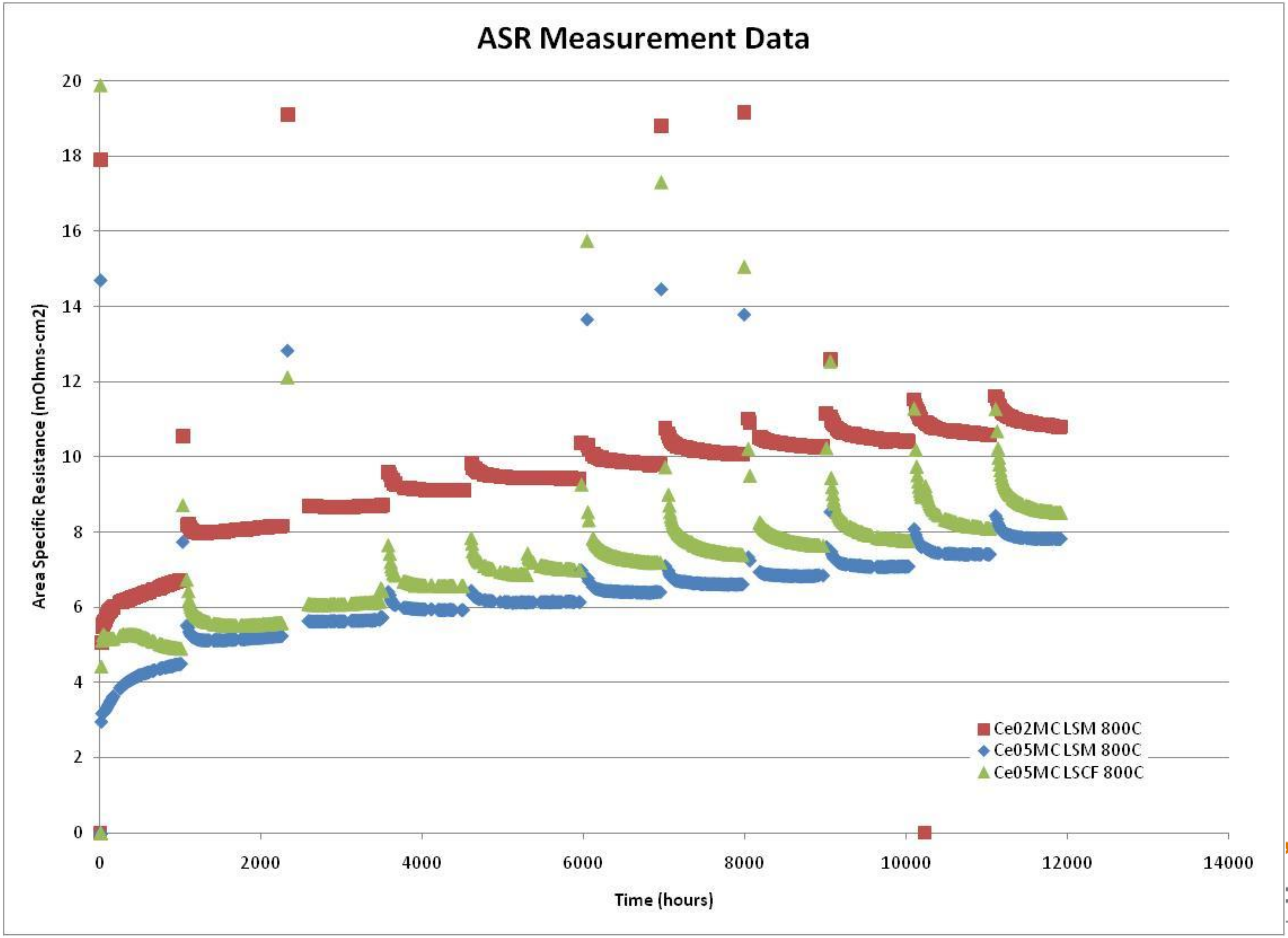
Long-term testing at 800ºC w/ deep thermal cycle every ~1000 hours



Surface Modifications to AISI 441

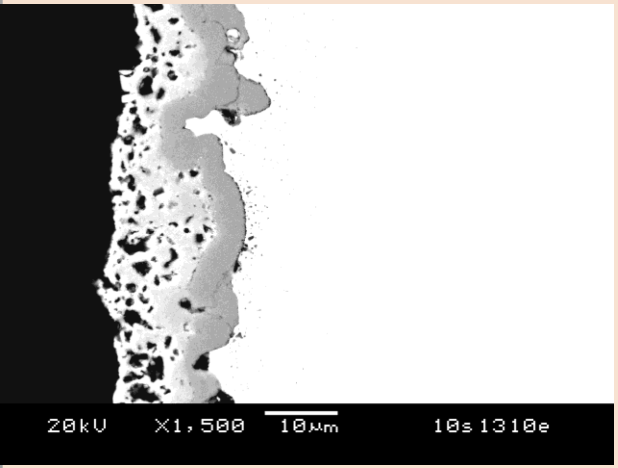
- Goal: Improve long-term scale adhesion under spinel coating
- Provided by Allegheny Ludlum:
  - 1. Mill reference (as would be provided to a customer without any additional modifications)
  - 2. Desiliconized (treatment to sequester silicon from the near surface of the sheet; an alternative to decreasing Si content of alloy)
  - 3. Surface blasted (abrasion/peening resulting in surface deformation)
  - 4. Surface ground (rough surface abrasion resulting in surface deformation)
  - 5. Temper rolled (cold rolling process resulting in through-thickness deformation)
- 0.020” thick coupons coated with Ce-MnCo spinel, heat-treated in air at 800 or 850ºC; 16 coupons for each condition

- Study is in progress
  - Interim report was sent to SECA industry representatives in February, 2011

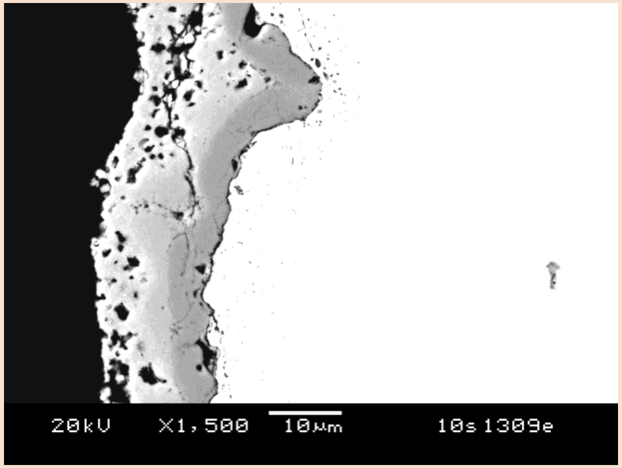
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441 (800ºC)

- 2000 hours
  - No spallation
- 4000 hours
  - Spallation observed on 1 mill reference coupon
- 6000 hours
  - Spallation on all except 1 one of the mill reference coupons, also 1 desiliconized coupon
  - De-bonding at scale/alloy interface observed in mounted temper-rolled coupon
- 8000 hours
  - Last of the mill reference coupons spalled, others were OK
- 10000 hours
  - No further spallation

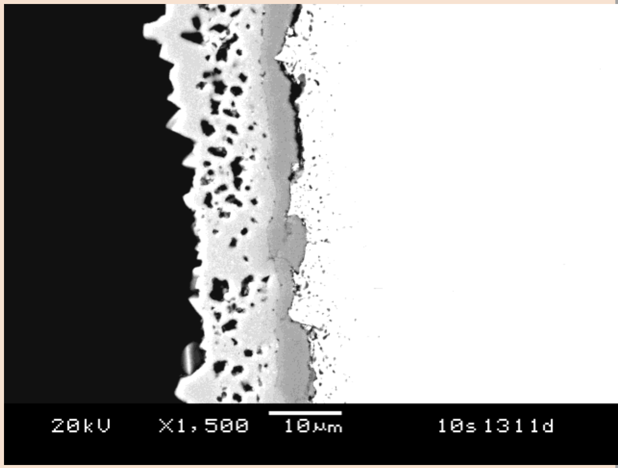
6000 h, 800ºC in air



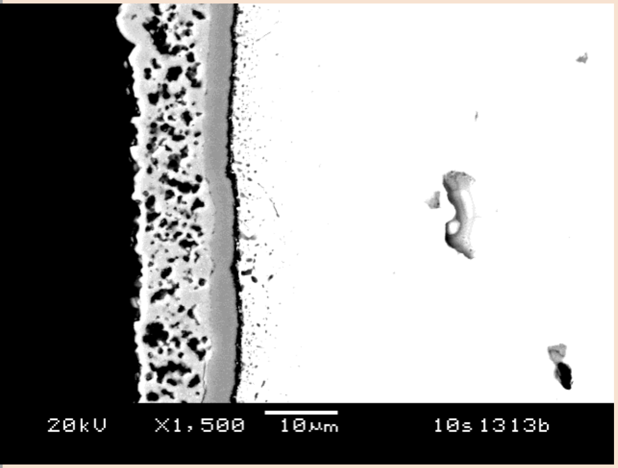
Surface Blast



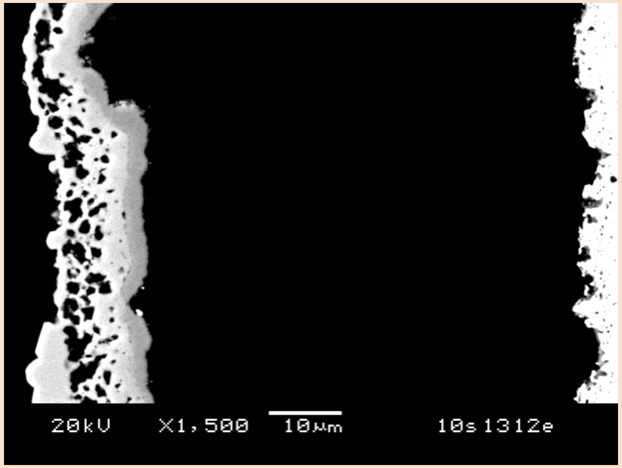
Surface Grind



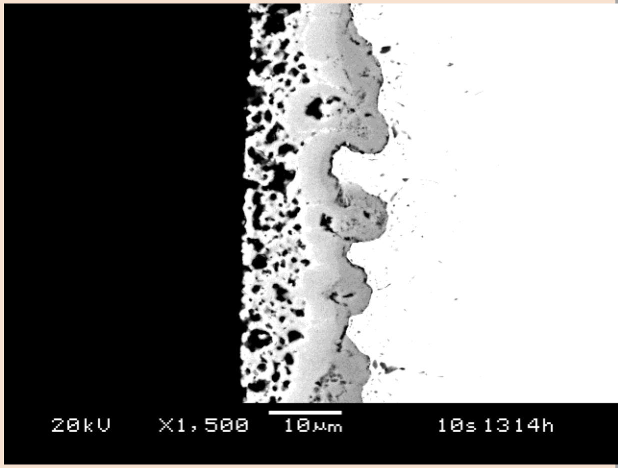
Desiliconized



Mill Reference (note: most of scale spalled after cooling)

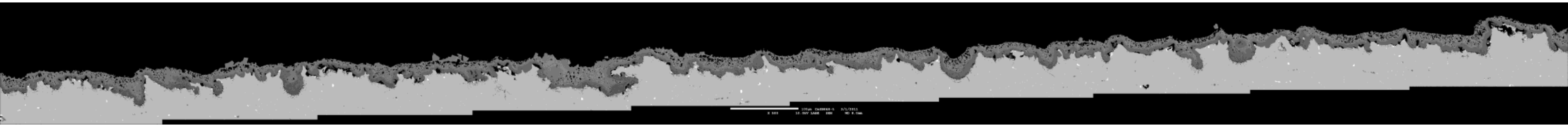


Cold Rolled (note: scale debonded during mounting)

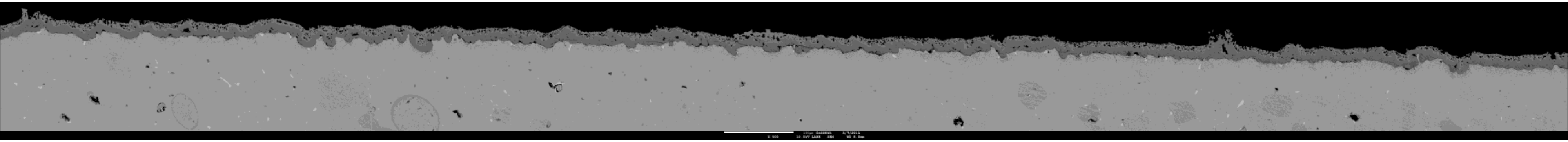


NETL-Albany Ce treatment

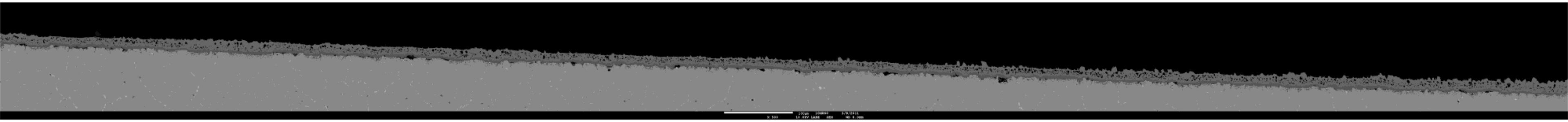
6000 h, 800ºC in Air



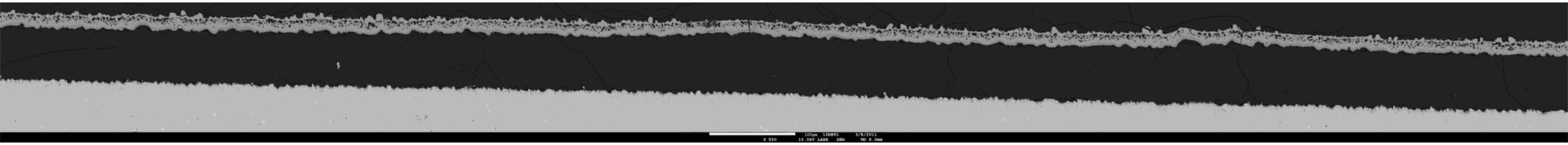
- Surface Blast



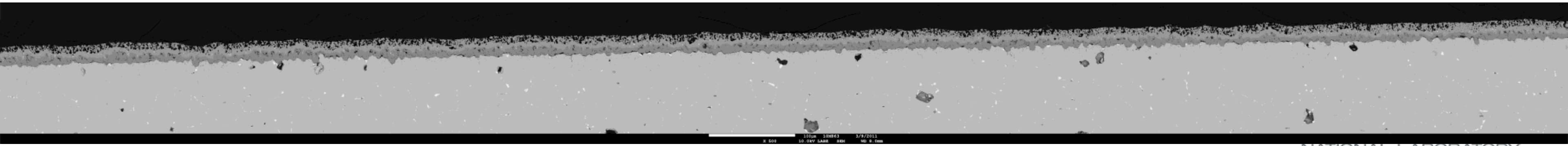
- Surface Ground



- De-siliconized

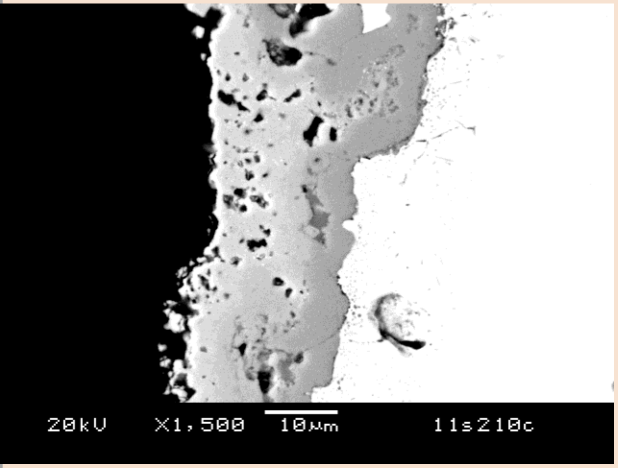


- 50% Cold Rolled

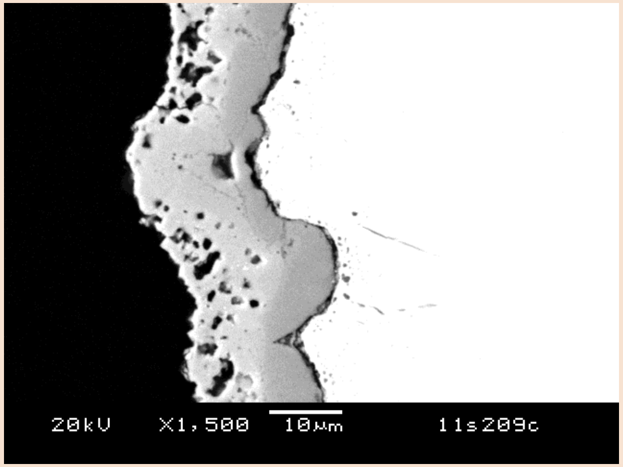


- NETL-Albany Ce treatment

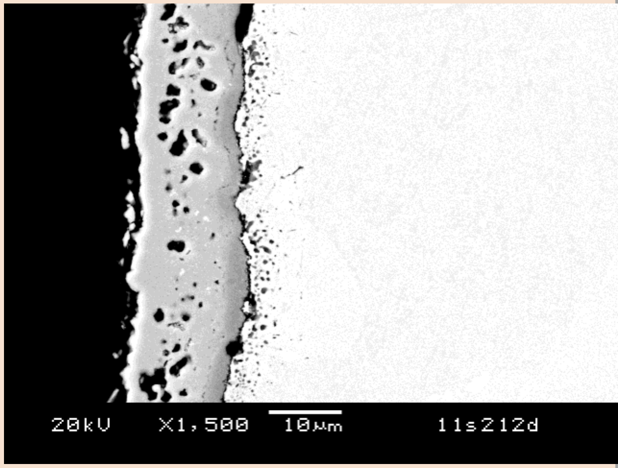
8000 h, 800ºC in air



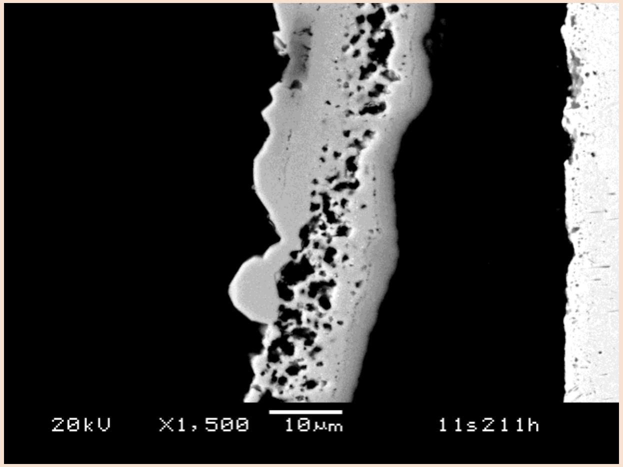
Surface Blast



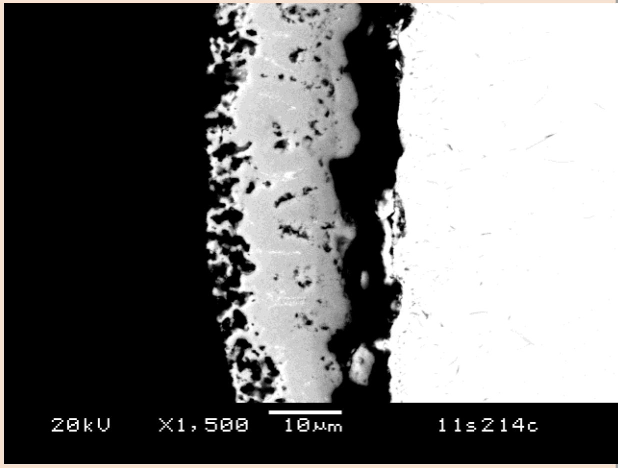
Surface Grind



Desiliconized

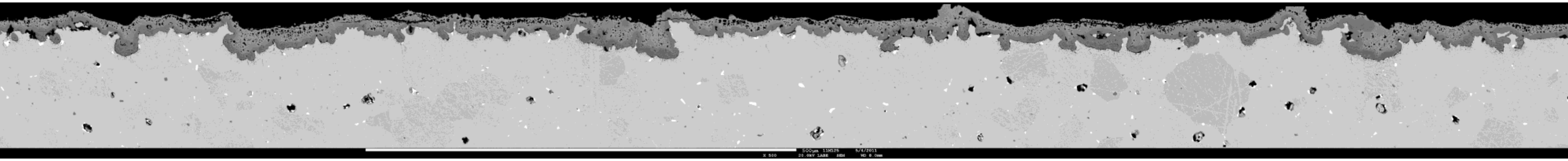


Cold Rolled (note: scale debonded during mounting)

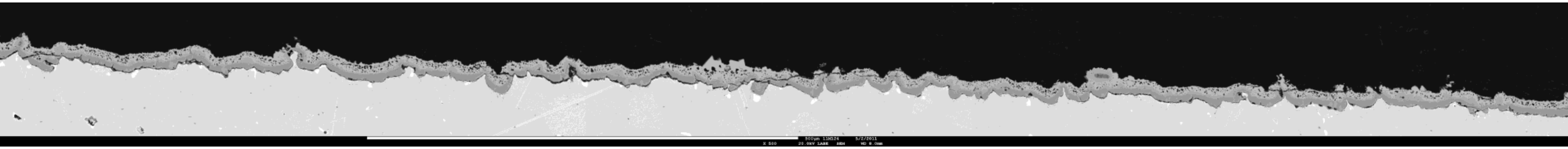


NETL-Albany Ce treatment

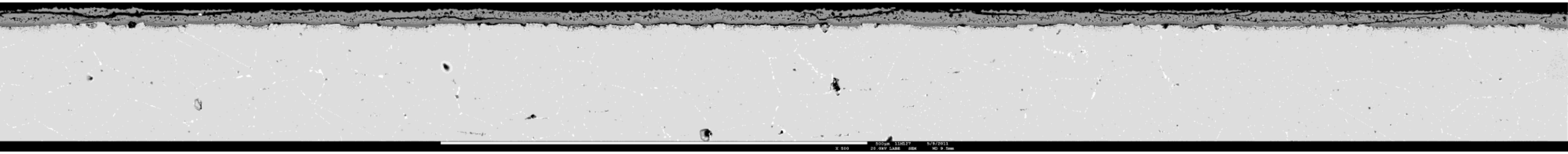
8000 h, 800ºC in Air



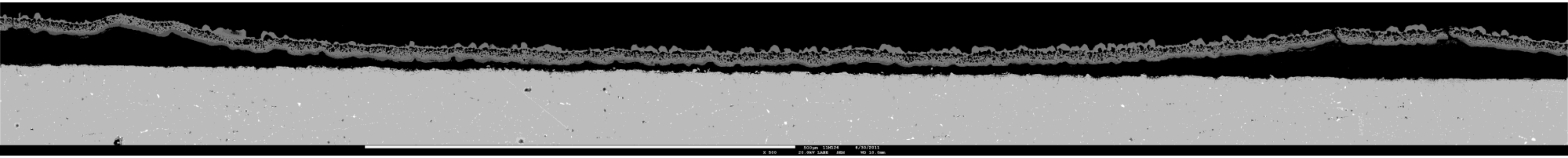
- Surface Blast



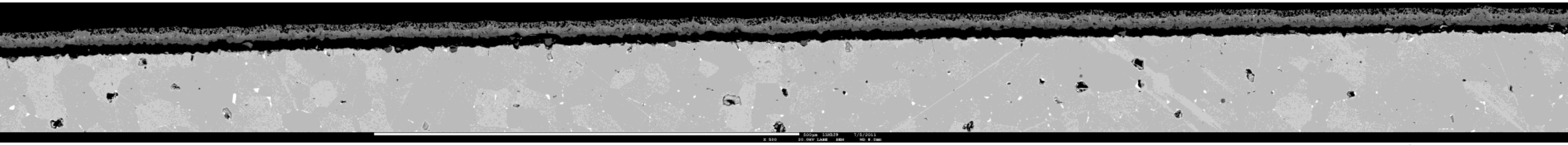
- Surface Ground



- De-siliconized



- 50% Cold Rolled



- NETL-Albany Ce treatment

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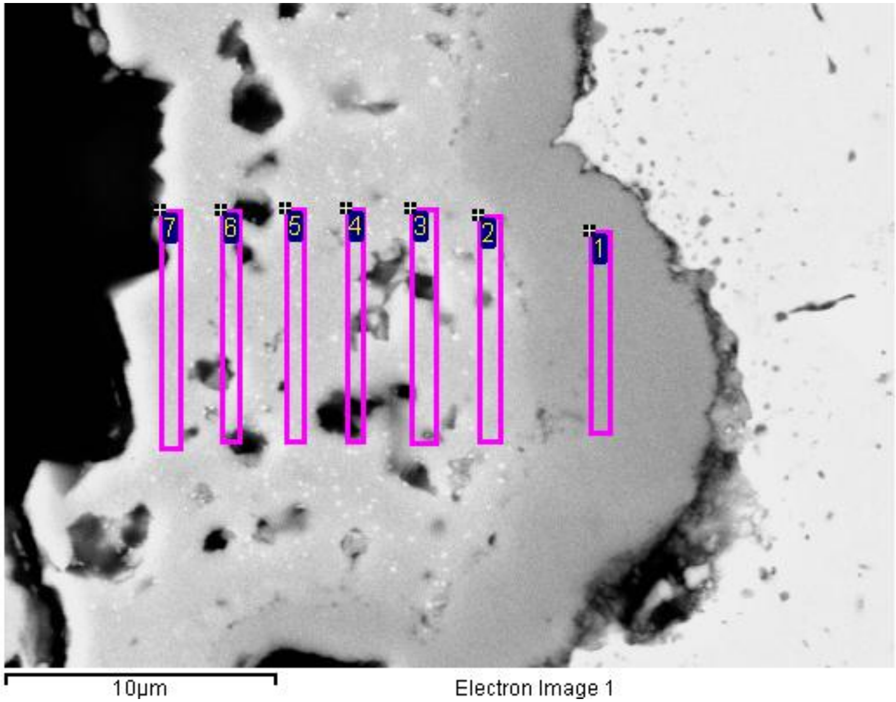
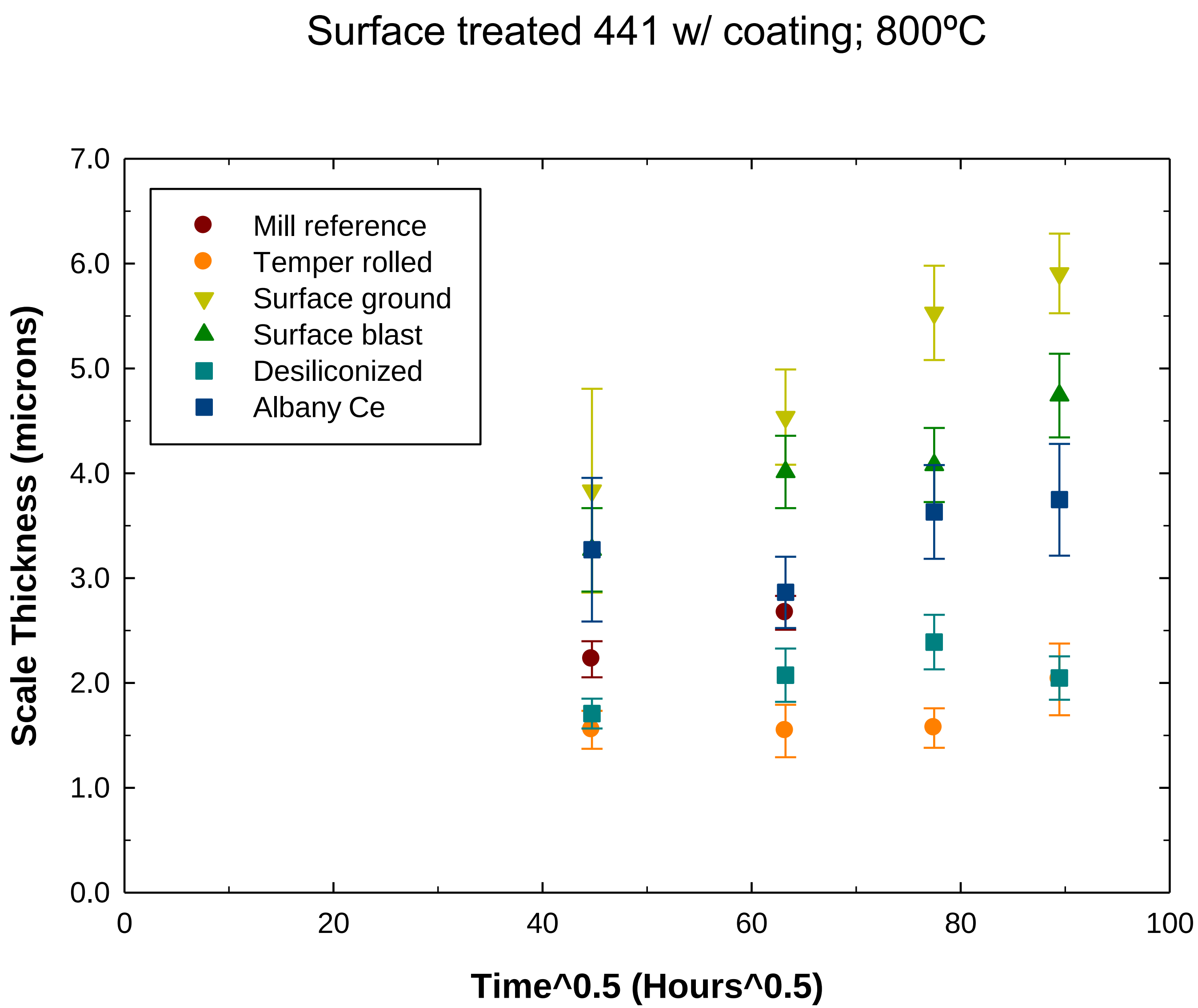
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 8,000 hours, 800ºC, air



Spectrum	O	Ti	Cr	Mn	Fe	Co	Ce
1	65.53	0.97	33.21		0.28		
2	62.01	0.57	11.04	11.68	2.01	12.69	
3	60.52	0.89	1.69	18.83	2.97	15.11	
4	58.62	0.75	1.38	19.96	3.18	15.78	0.34
5	61.77	0.69	1.18	18.32	3.06	14.66	0.32
6	60.39	0.65	1.27	19.31	3.07	15.04	0.26
7	62.33	0.60	1.60	17.80	2.98	14.69	
Max.	65.53	0.97	33.21	19.96	3.18	15.78	0.34
Min.	58.62	0.57	1.18	11.68	0.28	12.69	0.26

Atomic%

Surface Treated 441 w/coating; 800ºC



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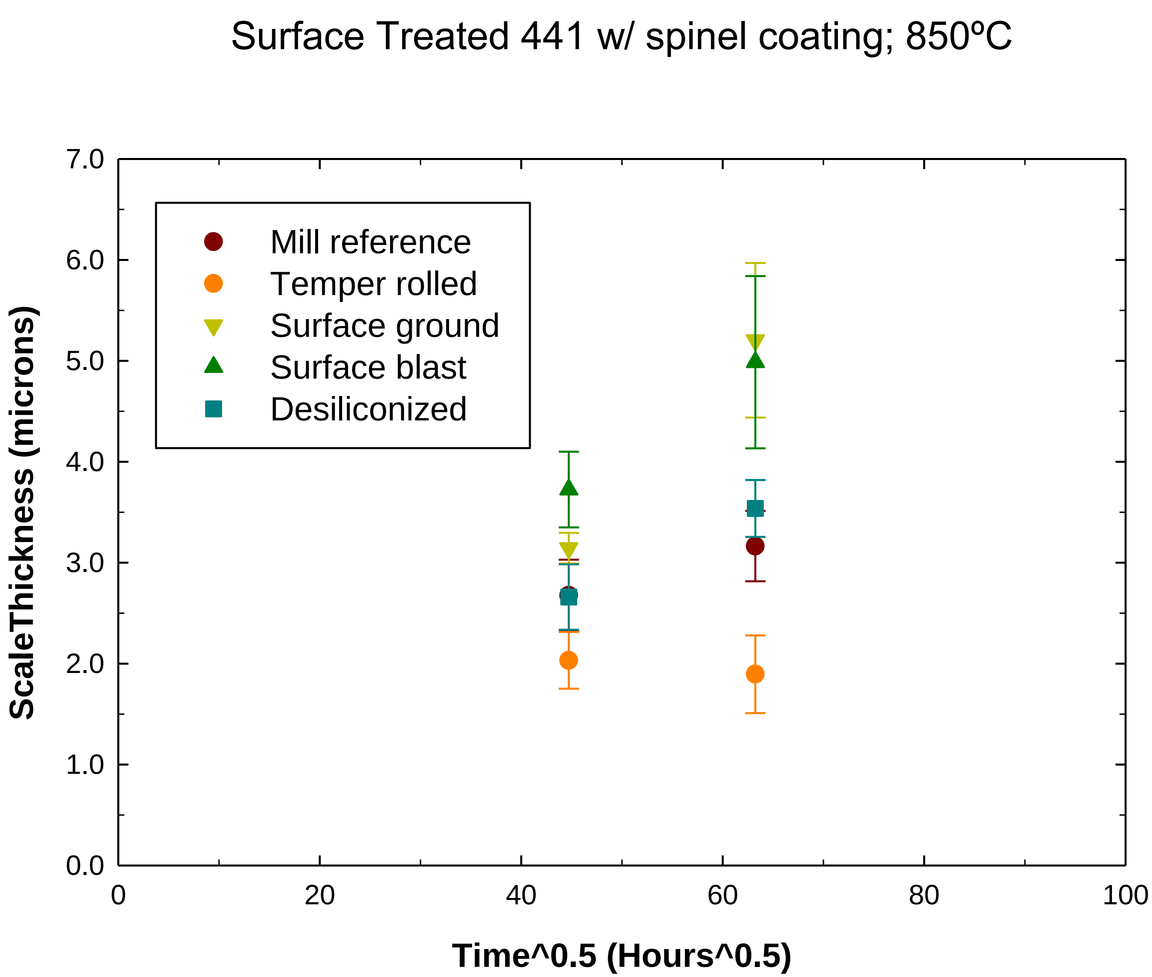
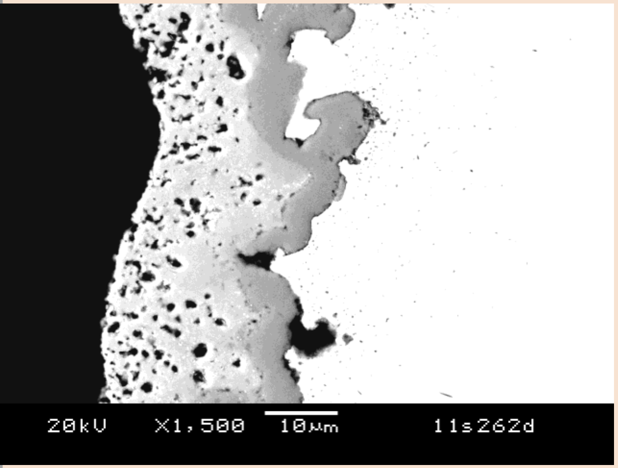
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441 (850ºC)

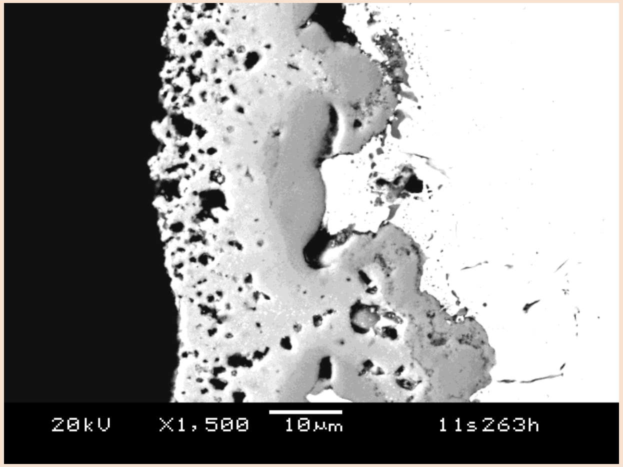
- 2000 hours
  - No spallation
- 4000 hours
  - No spallation
- Reached 6000 hours on July 20



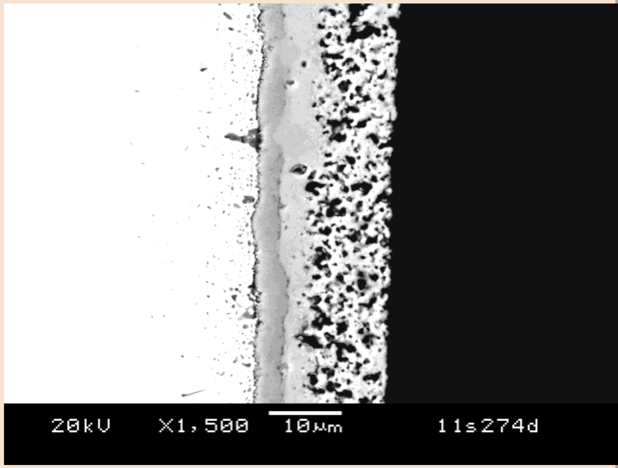
4000 h, 850ºC in air



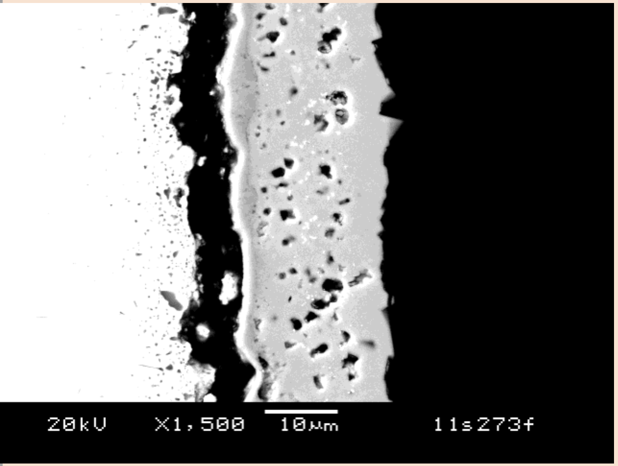
Surface Blast



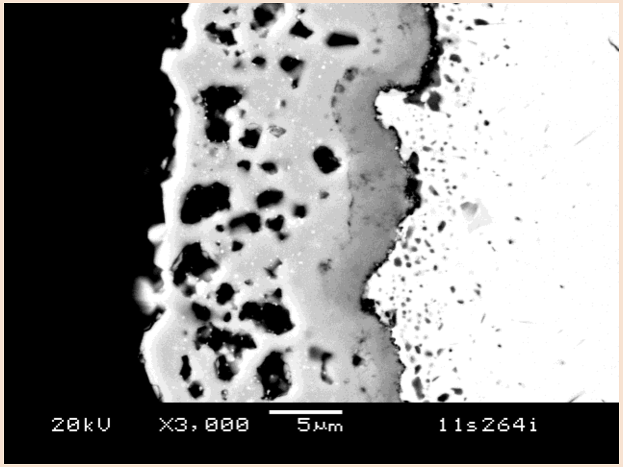
Surface Grind



Desiliconized

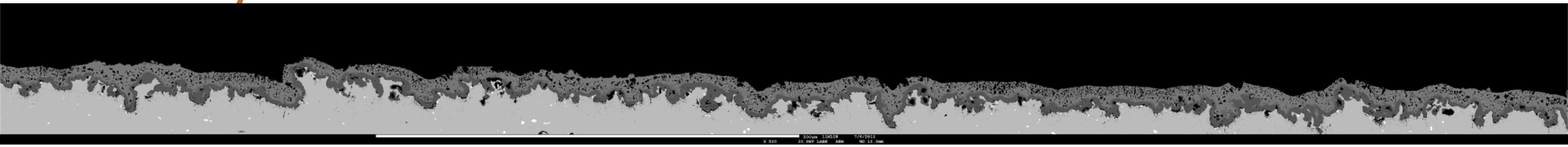


Mill Reference

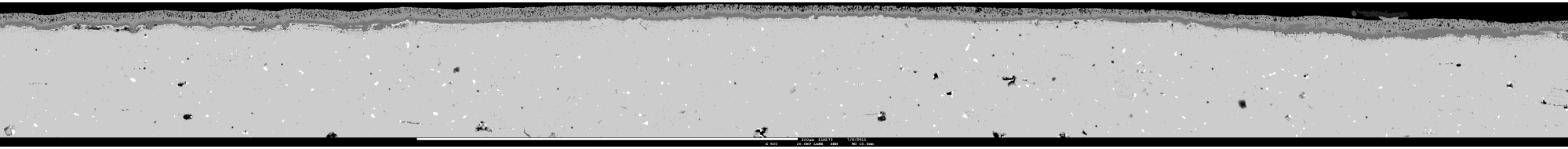


Cold Rolled – higher mag

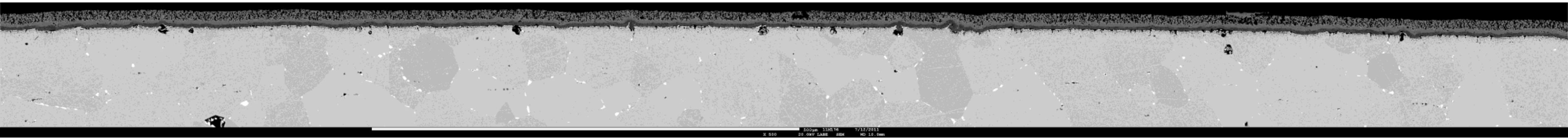
4000 h, 850ºC in Air



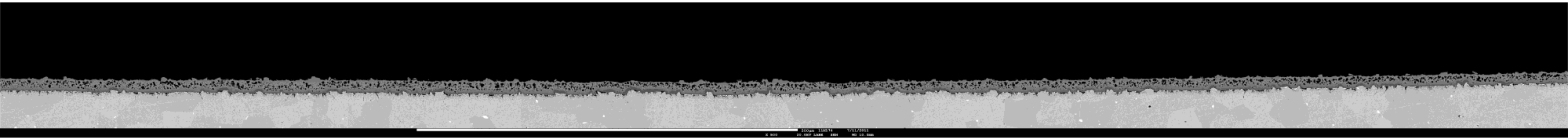
- Surface Blast



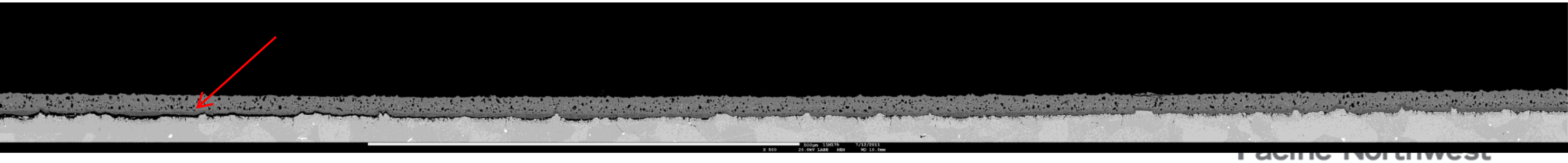
- Surface Ground



- De-siliconized

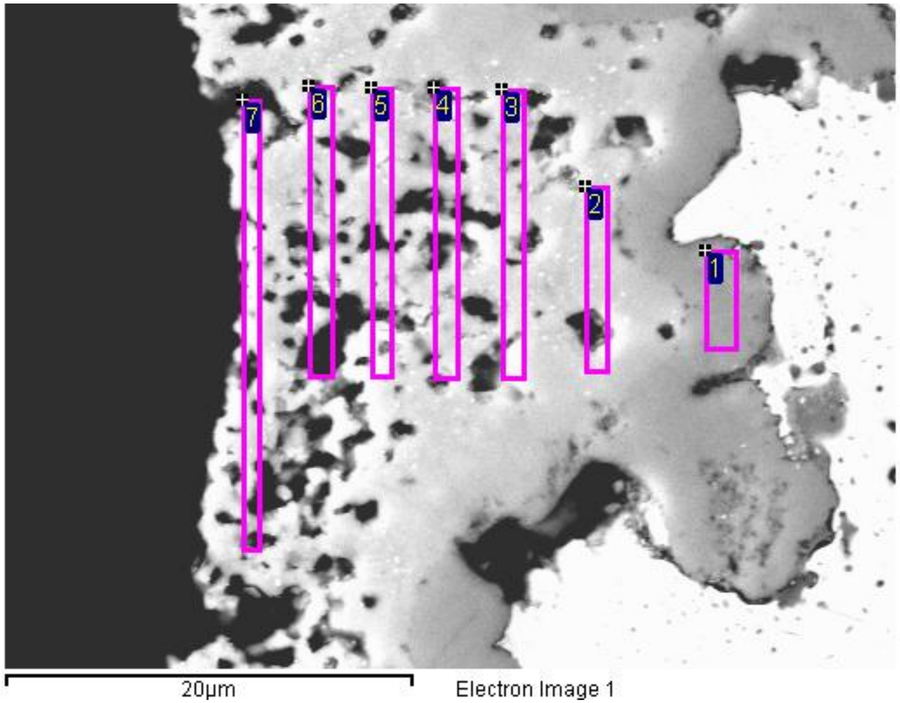


- 50% Cold Rolled



- Mill Reference

Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 4,000 hours, 850ºC, air



Spectrum	O	Si	Ti	Cr	Mn	Fe	Co	Ce
1	65.18	0.28	0.36	31.71	1.67	0.60	0.20	
2	60.64	0.22	0.21	4.33	17.44	1.62	15.54	
3	61.17	0.43	0.23	1.33	18.88	1.81	15.88	0.25
4	59.31	0.30	0.18	1.30	20.22	1.68	16.68	0.33
5	60.74			1.02	19.71	1.76	16.46	0.31
6	57.96			1.17	21.16	1.67	17.61	0.43
7	60.30	0.28		1.14	19.59	1.57	16.83	0.29
Max.	65.18	0.43	0.36	31.71	21.16	1.81	17.61	0.43
Min.	57.96	0.22	0.18	1.02	1.67	0.60	0.20	0.25

Atomic%

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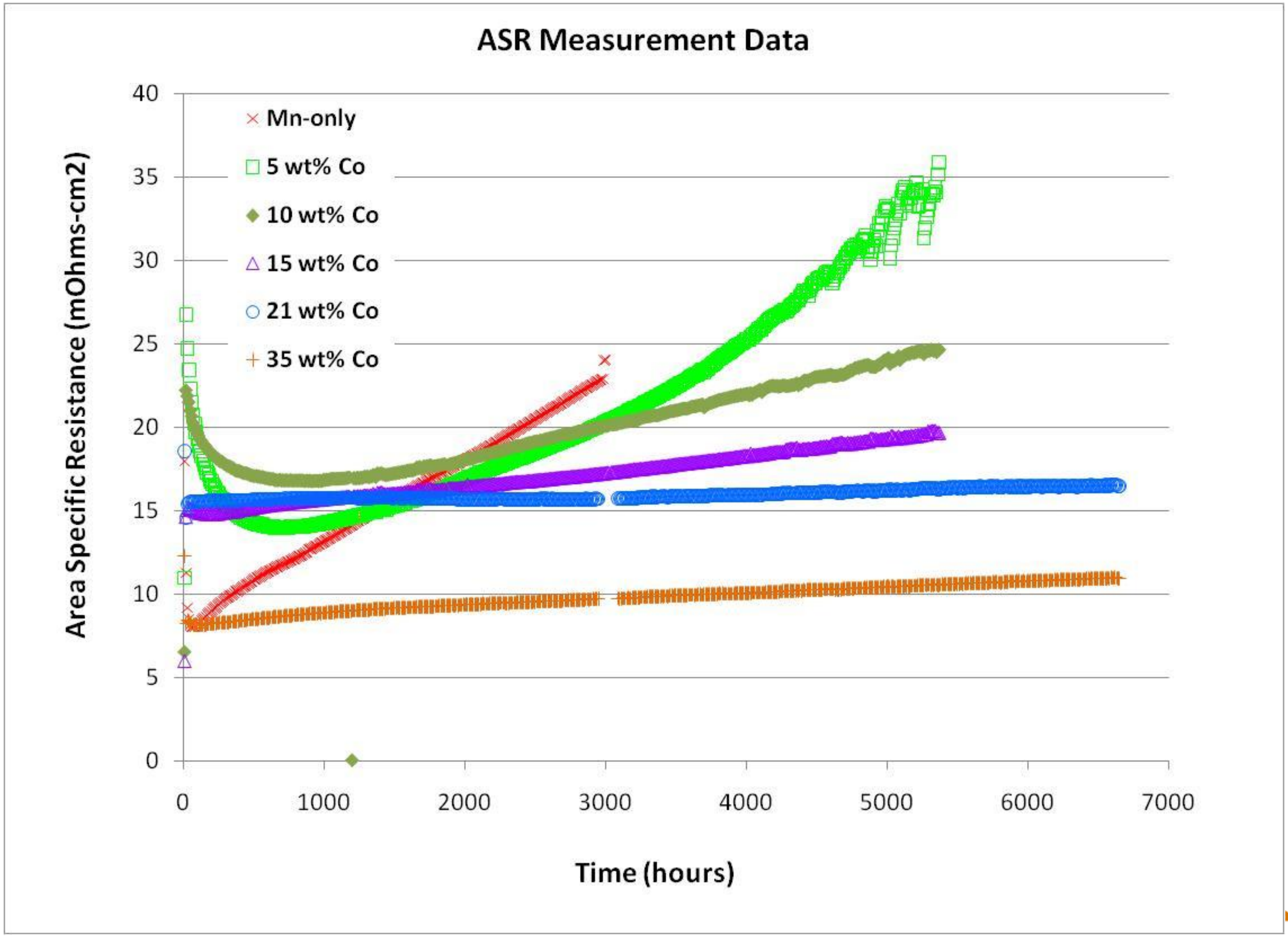
Optimization of Ce-MC Spinel Coatings

- Adaptation of ultrasonic spray process to Ce-modified spinel powder
  - Extension of previous optimization of fabrication process for unmodified spinel
  - Reference J.P. Choi et al., Poster Presentation, 2011 SECA Workshop

- 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

ASR Results for Reduced Co Content in Mn-Co Oxides on AISI441



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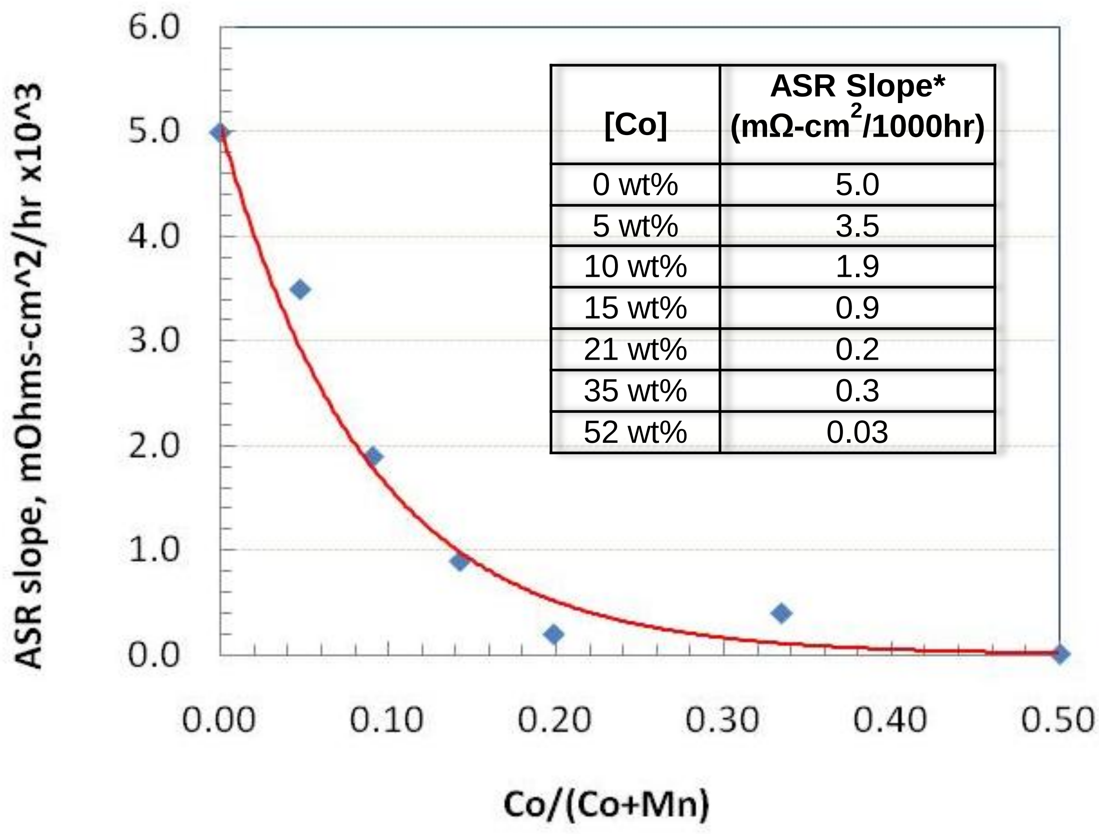
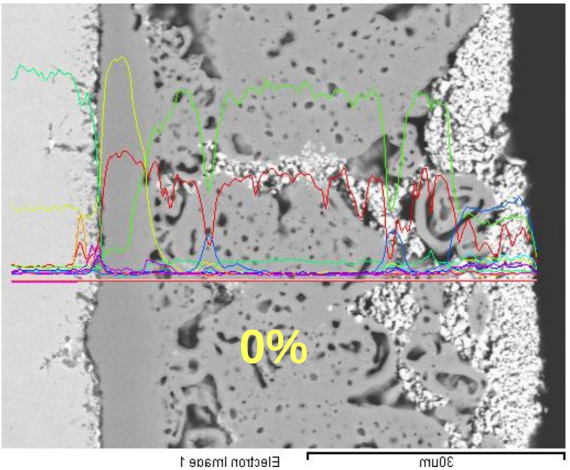
Alternative Coating Compositions

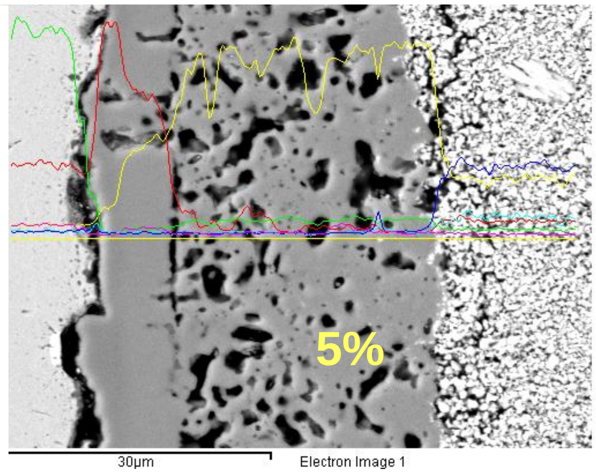
- Goal: Reduce Co content to reduce coating cost
  - Current preferred composition: $(Mn_{0.5}Co_{0.5})_3O_4$
- $(Mn_{1-x}Co_x)_3O_4$; $0.0 \le x \le 0.5$
  - x = 0 (Mn oxide)
    - Even after optimization of coating density, did not obtain stable ASR
  - $0.05 \le x \le 0.5$
    - Strong dependence of ASR rate of increase on Co content

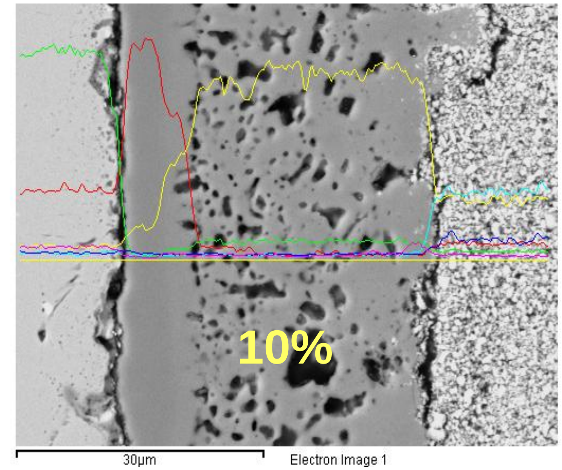


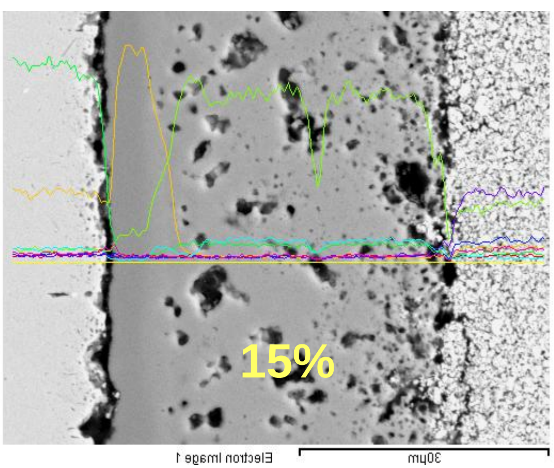
[Co]	ASR Slope* ($m\Omega\text{-}cm^2/1000hr$)
0 wt%	5.0
5 wt%	3.5
10 wt%	1.9
15 wt%	0.9
21 wt%	0.2
35 wt%	0.3
52 wt%	0.03

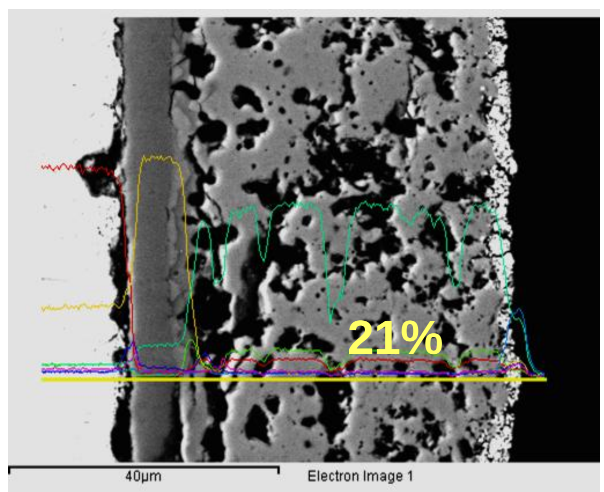
SEM Images of $Mn_{3-x}Co_xO_4$ Protection Coatings on AISI441 after ASR Tests

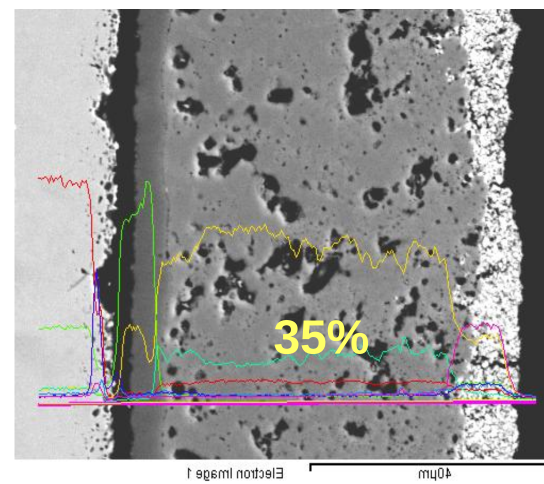












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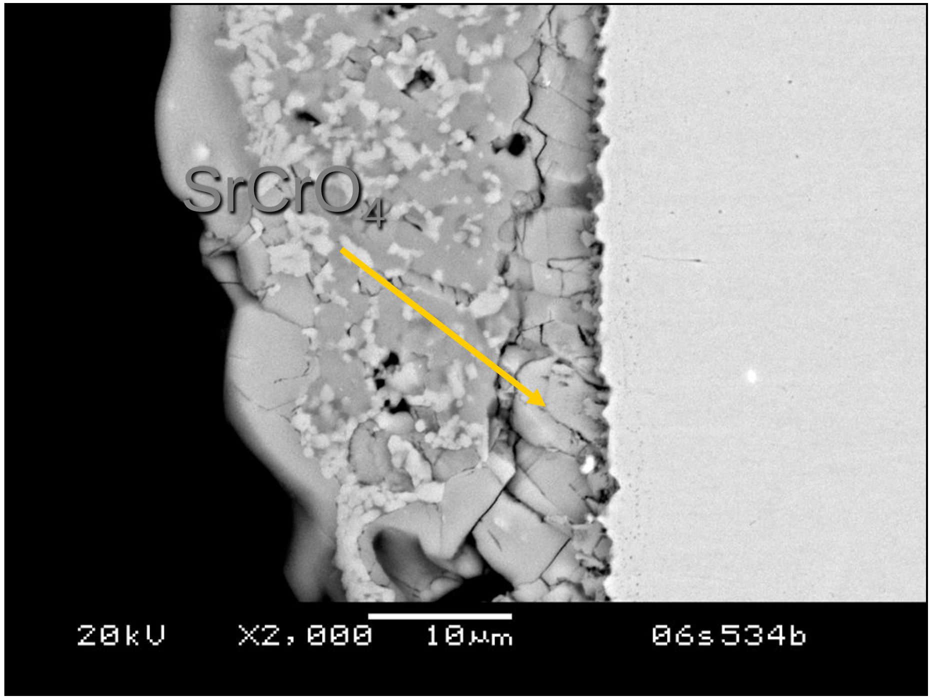
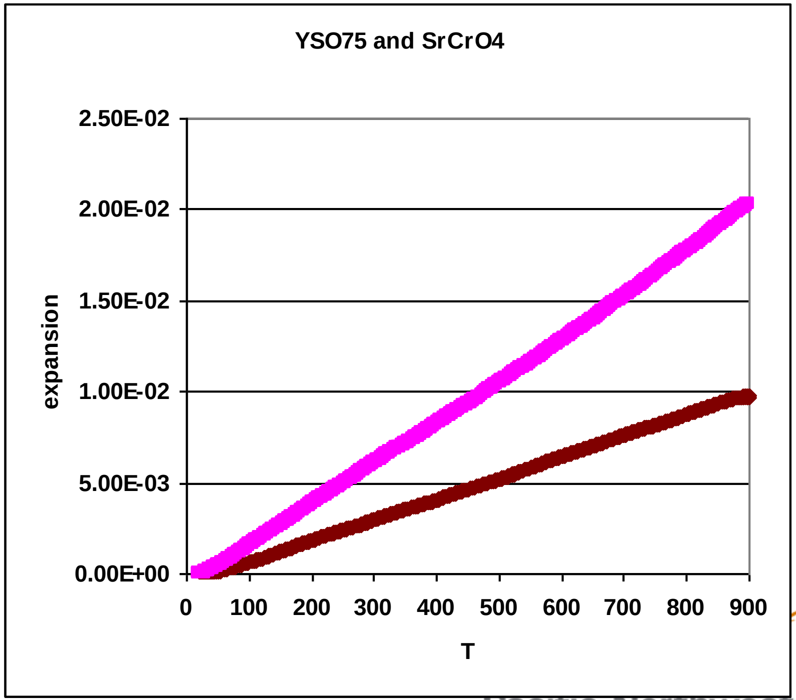
Reactive Air Aluminization

- Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., $SrCrO_4$), which degrade interfacial strength
- Cr volatility from alloys can poison cathodes
- Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects
  - Aluminum powder slurry-based process, 1000ºC heat treatment in air





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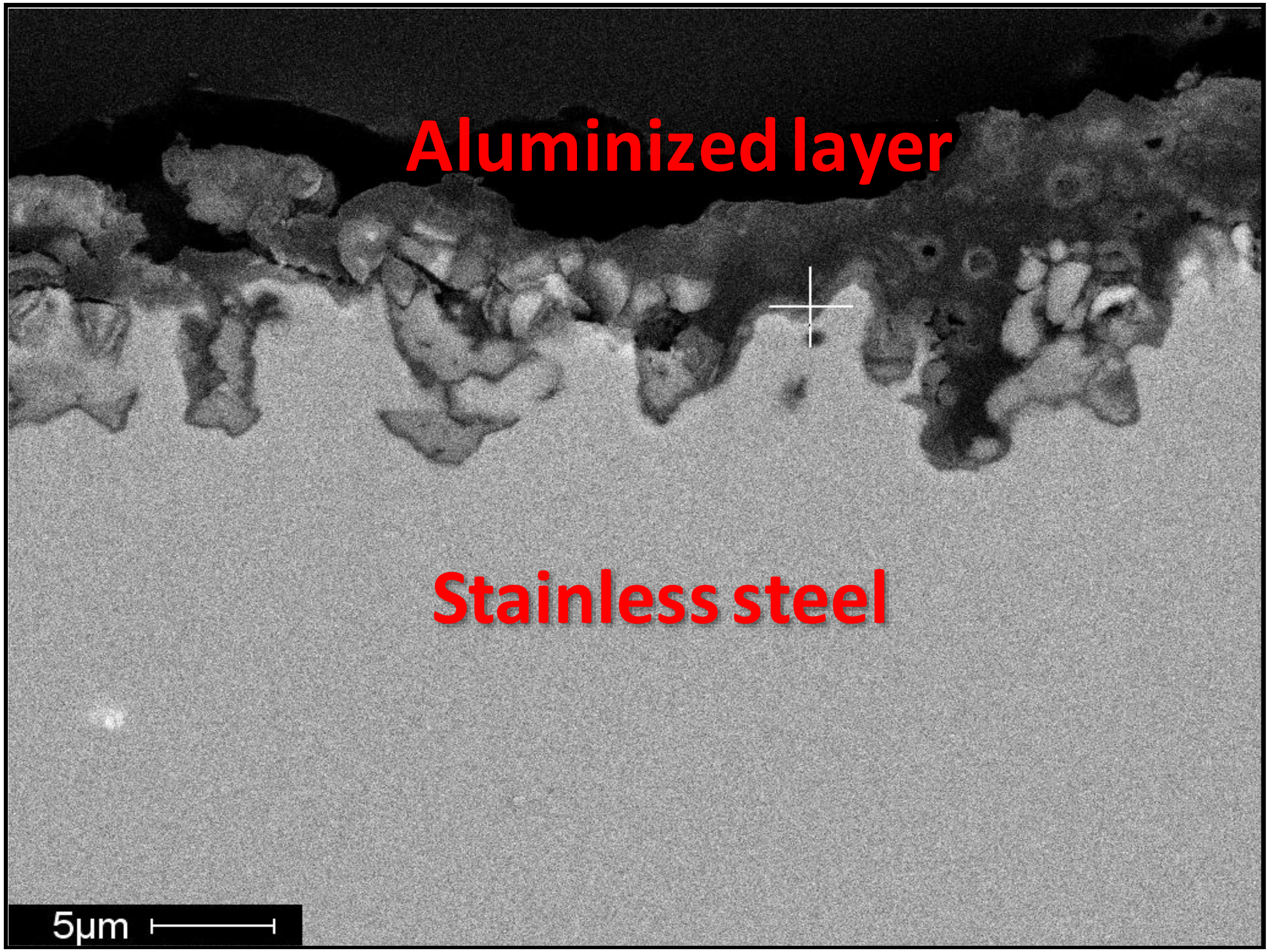
Reactive Air Aluminization

Cross sectional SEM analysis: 1000 C, 1 h oxidative heat treatment



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Ceramic Interconnects for SOFC

- Doped yttrium chromite is being optimized for SOFC with operating temperature >850ºC
  - Ca on A-site; Co, Ni, and/or Cu on B-site
  - Electrical conductivity, CTE, ionic transference number comparable to standard material (doped lanthanum chromite)
  - Improved sinterability, reduced chemical expansion, and lower reactivity (e.g., zirconate formation) relative to lanthanum chromite

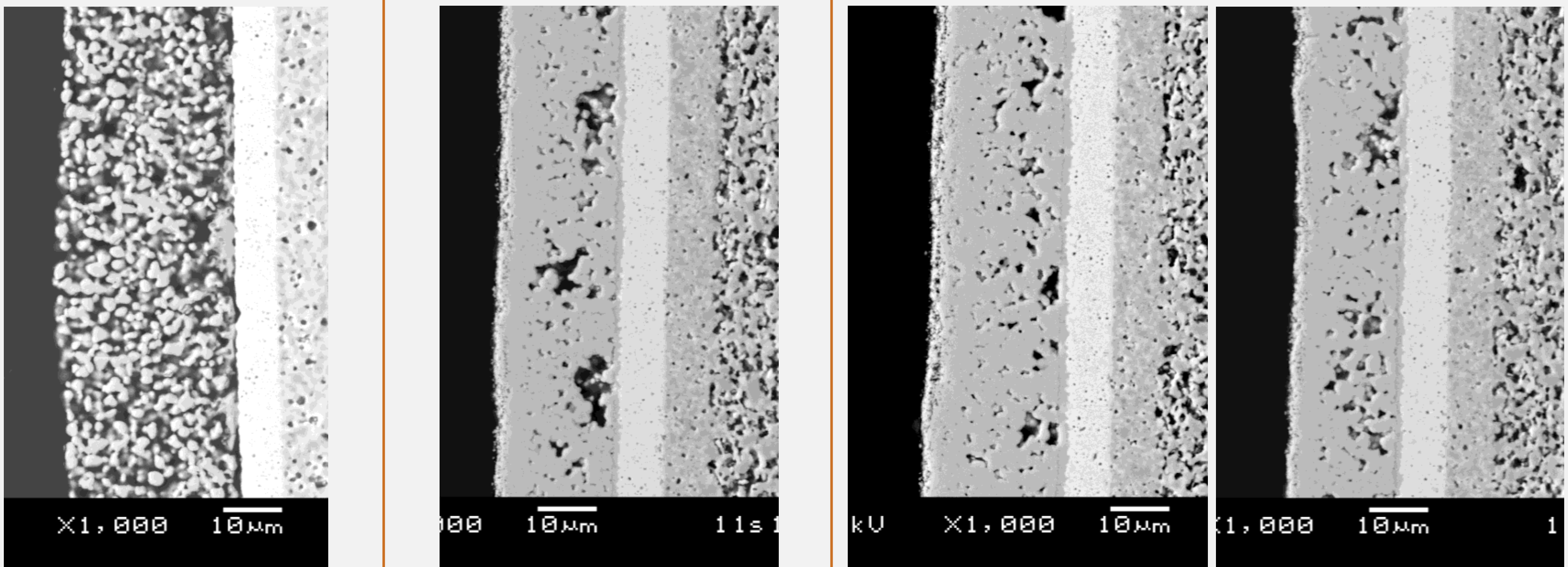
- **Electrical Conductivity**
  - **Electronic, Ionic**
- **Sintering Behavior**
- **Stability toward Reduction**
  - **Chemical Expansion**
- **Thermal Expansion**
- **Chemical Reactivity**

→

- **A-Site: 20% Ca**
- **B-site: 10% Co, 4% Ni, 1% Cu**

  - Current emphasis on improving densification under constrained sintering and co-sintering conditions

Increased density through infiltration process



No Infiltration	50 vol.% Ethanol 1300°C after S.P. 1300°C after Infiltration	50 vol.% Ethanol 1200°C after Screen Printing 1300°C after Infiltration

- **Reference: K.J. Yoon et al., Poster Presentation, 2011 SECA Workshop**

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Summary

- AISI 441 w/ Ce-modified MnCo spinel coatings exhibits low, stable ASR in long-term testing
  - Less than 12 mΩ-cm^2 after ~ 2 years at 800ºC in air
- Surface-modified AISI 441 w/ Ce-modified MnCo spinel coatings exhibit improved long-term spallation resistance
  - 10,000 hours at 800ºC (tests in progress)
  - 4,000 hours at 850ºC (tests in progress)
- Based on ASR tests, effectiveness of Mn-Co spinel coatings decreases with decreasing Co content, especially for Co/(Co+Mn) < 0.20
- Optimization of ultrasonic spray process for application of Ce-modified MnCo spinel coatings is in progress

Future Work

- Continue to evaluate long-term stability and electrical performance of surface modified Ce-MC spinel-coated 441 steel
  - Parametric investigation of surface treatment options
  - Evaluation at 800 and 850ºC
  - Long-term evaluation in stack test fixture
- Optimize thickness, and automated ultrasonic spray fabrication process, for Ce-modified spinel coatings
- Reduce cost of protective coatings through minimization or elimination of Co content
- Develop fabrication approaches for sintering of Cr-based perovskite interconnects under constrained/co-sintered conditions.

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