SECA Core Technology Program R&D at PNNL

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Richland, WA 99352

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13th Annual SECA Workshop

Pittsburgh, PA

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Objective

- Provide R&D support to SECA program
  - Development/evaluation of improved materials and fabrication processes for SOFC cells and stacks
  - Improved understanding of performance degradation mechanisms
  - Development/implementation of modeling tools to facilitate cell and stack design and optimization
  - Technology transfer to industry teams

Technology Transfer Process

- **<u>First step:</u>** Testing and characterization at sub-stack level
  - Materials Characterization
    - XRD, SEM, EDS, TEM, XPS, TGA, DSC, PSA, dilatometry, electrical conductivity, single & dual atmosphere oxidation
  - Multiple Component Tests
    - Button cell testing
    - ASR testing of interconnect/cathode contact/cathode structures
    - Electrical testing and leak testing of seal/interconnect and cell/seal/interconnect structures

- **<u>Second step</u>:** Testing under realistic "stack-like" conditions to bridge the gap between small-scale tests (e.g., button cells) and SECA industry team stacks

Technology Transfer Process

- SECA CTP Stack Test Fixture
  - Advantages:
    - Can evaluate/validate new materials and fabrication processes under more realistic conditions
    - Larger cell size than button cells (50mm x 50mm)
    - Complete stack functionality (cell, cell frame, seals, interconnects, electrical contact materials)
  - Challenges:
    - Increased complexity (and cost) of assembly, co-fabrication of seals and electrical contact materials
    - Multiple components & phenomena, so results can be more difficult to interpret
  - Note: PNNL has transferred fixture design and test protocols to other SECA CTP participants (NETL, U. Conn.)

- **Final step:**
  - **Delivery of topical reports**
  - **Delivery of materials to SECA industry teams for in-house evaluation**

Scope of Work

- **Determined through consultation with NETL program management and SECA industry teams**
  - Increased communication with industry teams in past year

- **Current areas of emphasis**
  - SOFC interconnects
    - Alloys and coatings for IT-SOFC, Ceramic interconnects
  - Seals for SOFC stacks
    - Devitrifying glass seals, Compliant glass seals
  - Cathode materials and interactions
    - In-situ XRD characterization, Effects of humidity
  - Anode materials and interactions
    - Effects of high fuel utilization, Mitigation of sulfur poisoning
  - Modeling
    - 2D and 3D modeling tools to assist in cell/stack design
    - Modeling of cell/stack degradation processes

Seal Development

- **<u>Devitrifying Glass Seals</u>**
  - A series of devitrifying glass seals with sealing temperatures between 825 and 1000ºC have been developed.
    - Good CTE match to other components
    - Rapid stabilization of dimensions and microstructure due to devitrification
    - Good bonding to YSZ and interconnects (with aluminization of steel surface)
      - Reactive air aluminization process developed at PNNL
  - **Current work focused on improved wetting/flow behavior at sealing temperatures ≥ 950ºC**
- **<u>"Compliant" glass seals</u> also under development**
    - **Collaboration with ORNL**
    - **Potential advantages: reduction of thermal stresses, self-healing behavior**
    - **Potential challenges: crystallization, reactivity, and containment**

- **Poster Presentation**
  - **Glass Seal Development at Pacific Northwest National Laboratory**

Cathodes

- Current Priorities:
  - Investigating degradation mechanisms
    - *In-situ* high temperature XRD of operating LSCF cathodes
    - 700, 750, and 800ºC
  - Effects of air humidity on cell performance
    - LSCF and LSM/YSZ cathodes
    - Dry air vs. 3%H_2O
- Poster Presentations
  - Effects of Humidity in Cathode Air on LSM-YSZ Cathodes
  - Extended Duration (1000 h) In-situ XRD of Operating LSCF Cathodes

Anodes

- **Effects of high steam content (high fuel utilization) on Ni-YSZ anodes**
  - Test anode-supported button cells with Ni/YSZ anodes and LSM/YSZ cathodes
  - Test conditions
    - 700ºC, 800ºC, 900ºC
    - Constant current corresponding to 0.7 or 0.8 V
    - Fuel is a simulated coal gas
    - Fuel humidity corresponding to various fuel utilizations achieved by adding oxygen
    - Include “control” cells held at low fuel utilization
  - **Ac and dc electrochemical measurements of each cell**
  - **Monitor temperature of each individual cell**
  - **Post-test characterization using SEM/EDS, TEM, and EBSD**

- **Poster Presentation**
  - **Durability of Nickel/Zirconia Anodes in SOFCs at High Fuel Utilization**

Alloy Interconnects and Protective Coatings

- Primary emphasis is on AISI 441 w/ Ce-modified MnCo spinel (MC) protective coating. Current activities:
  - Long-term evaluation of oxidation resistance and electrical performance
  - Effects of alloy surface treatments on oxidation behavior, spallation resistance are under investigation (collaboration with Allegheny Ludlum)
  - Optimization of ultrasonic spray fabrication process: coating uniformity and thickness
    - **Poster presentation**
      - **The Effect of Spinel Coating Thickness on SOFC Interconnect Resistance**

- Investigation of alternative coating compositions (e.g., oxides with reduced Co content, aluminization)

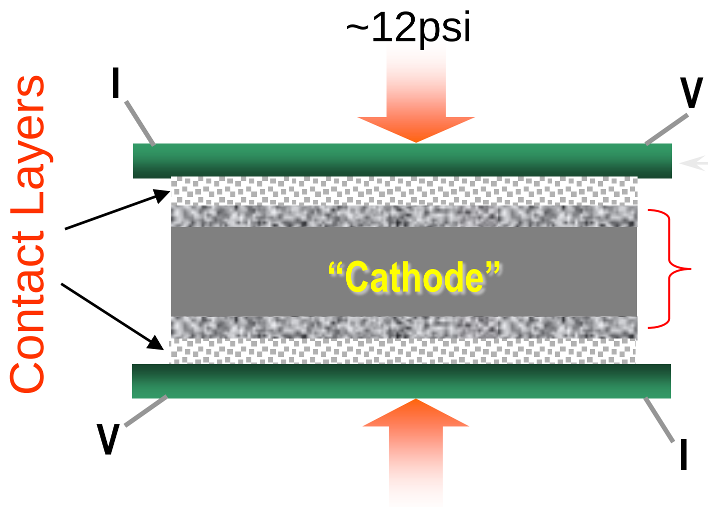
Low-cost Alloy-based Interconnects

- **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
  - 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)
- **Interconnect Coating: Ce-modified $(Mn_{0.5}Co_{0.5})_3O_4$ Spinel**
  - High electrical conductivity (~60 S/cm), good CTE match (~11 ppm/K)
  - Ceria inclusions improve oxide scale adherence
  - Coating improves oxidation resistance and mitigates Cr volatility

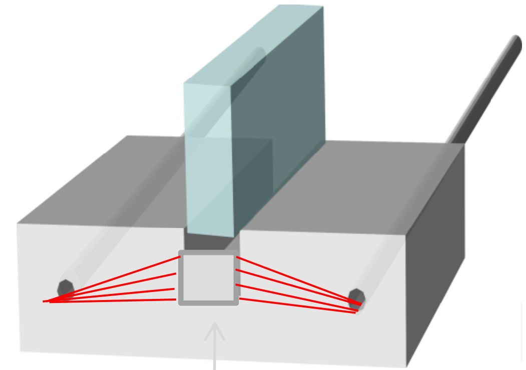
k_p (g^2/cm^4-s)	800ºC	850ºC
Ce-MC coated 441	2×10^{-14}	1×10^{-13}
Bare 441	5×10^{-14}	3×10^{-13}

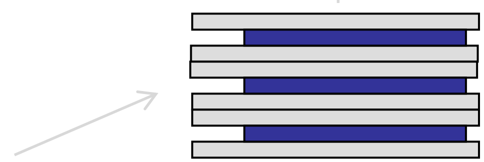
Area Specific Resistance (ASR) Measurements

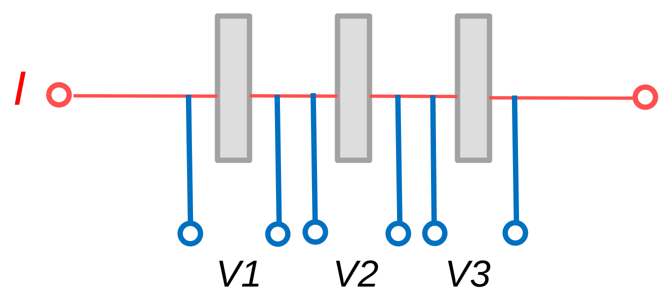
$$ASR_{cathode-interconnect} = \Phi(scale, contact material, coatings)$$



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







ASR Stack (3 sets)

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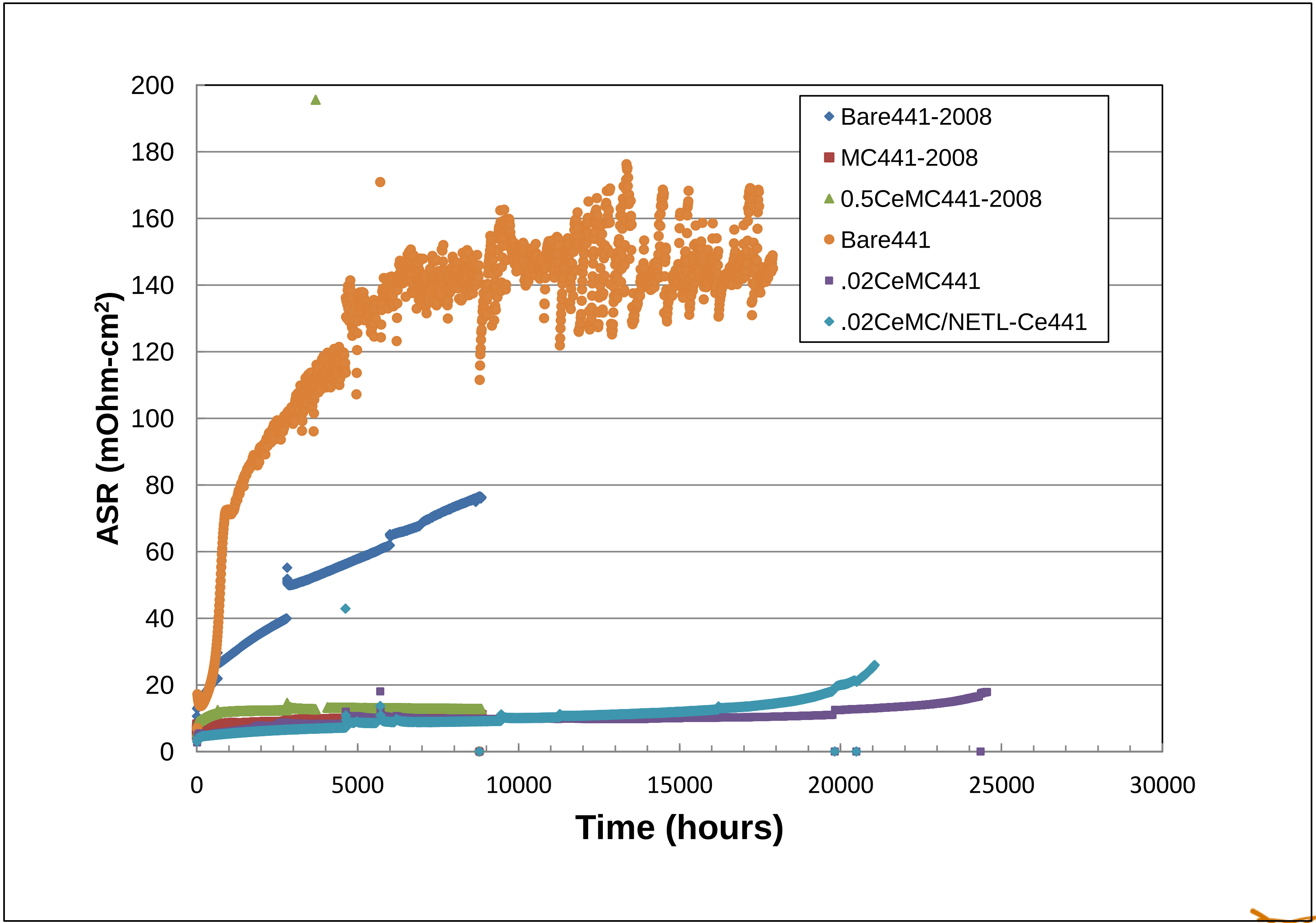
Long-Term ASR measurements: 800ºC



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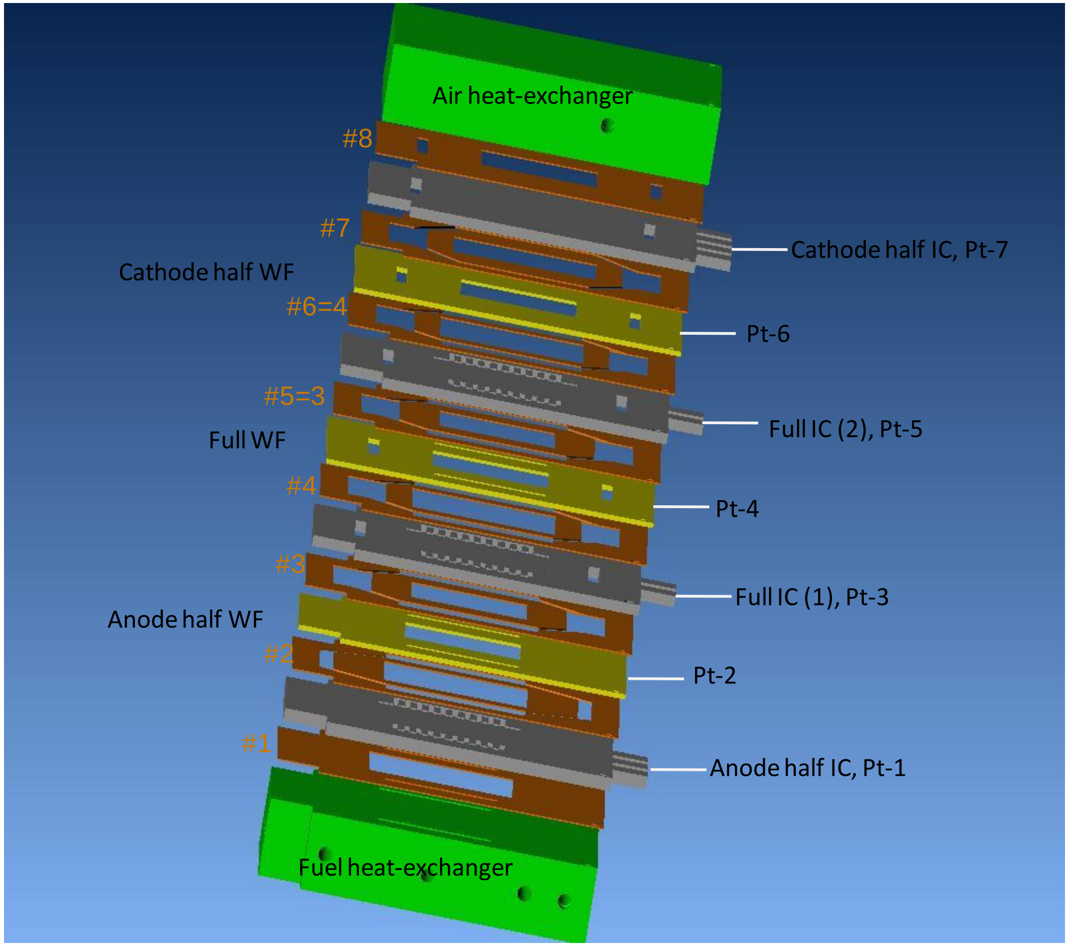
Long-term testing of Ce-MC spinel-coated AISI 441

- 6,000 hour test under stack-like conditions (SECA CTP stack test fixture)
- 800ºC; air vs. moist H_2/N_2



Poster Presentation: "Recent Progress in SOFC Stack Test Fixture Development and Materials Validation at PNNL"

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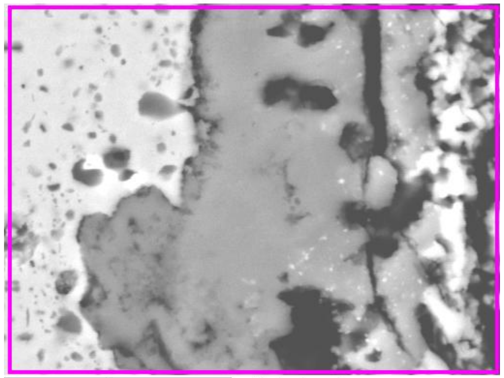
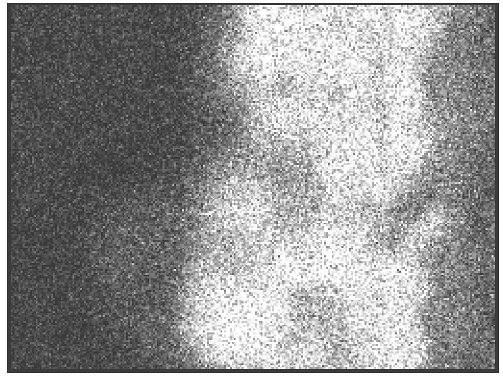
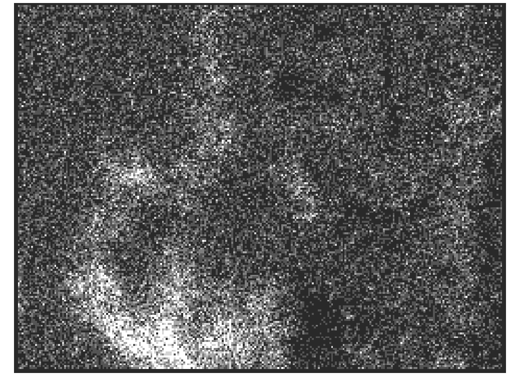
Spinel-coated cathode IC and LSM contact interface



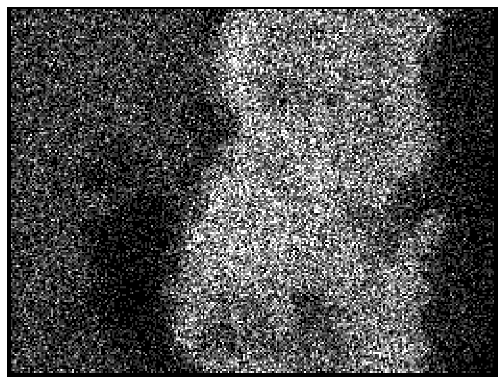
Electron Image 1



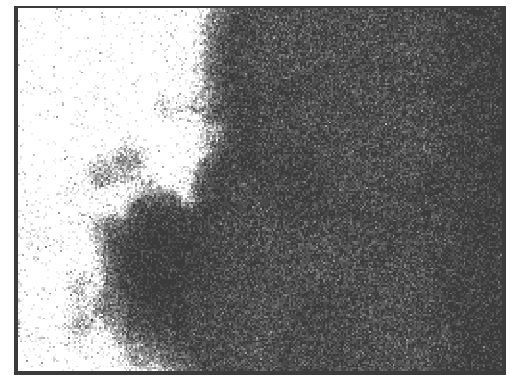
Mn Ka1



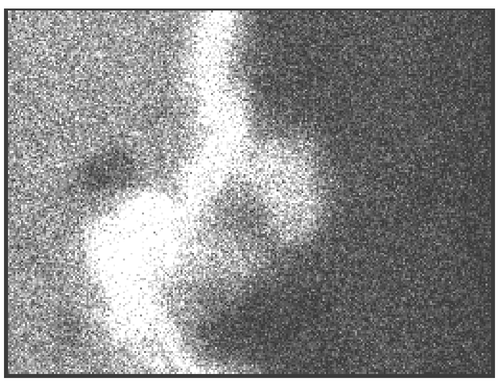
Si Ka1



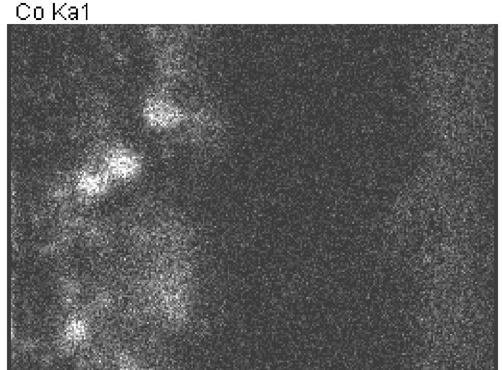
Co Ka1



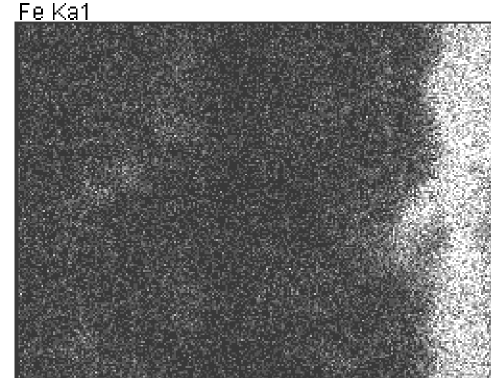
Fe Ka1



Cr Ka1

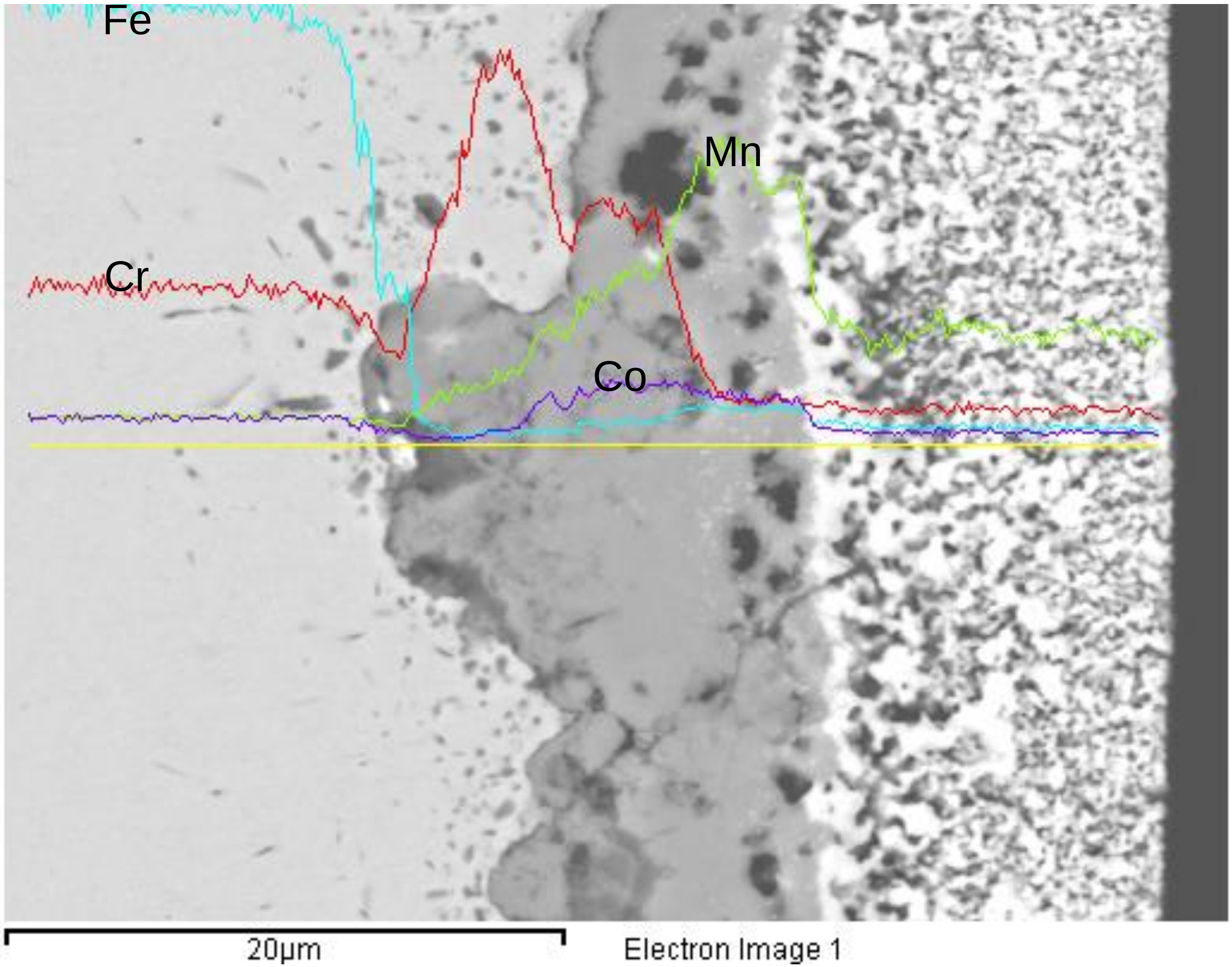


Ti Ka1

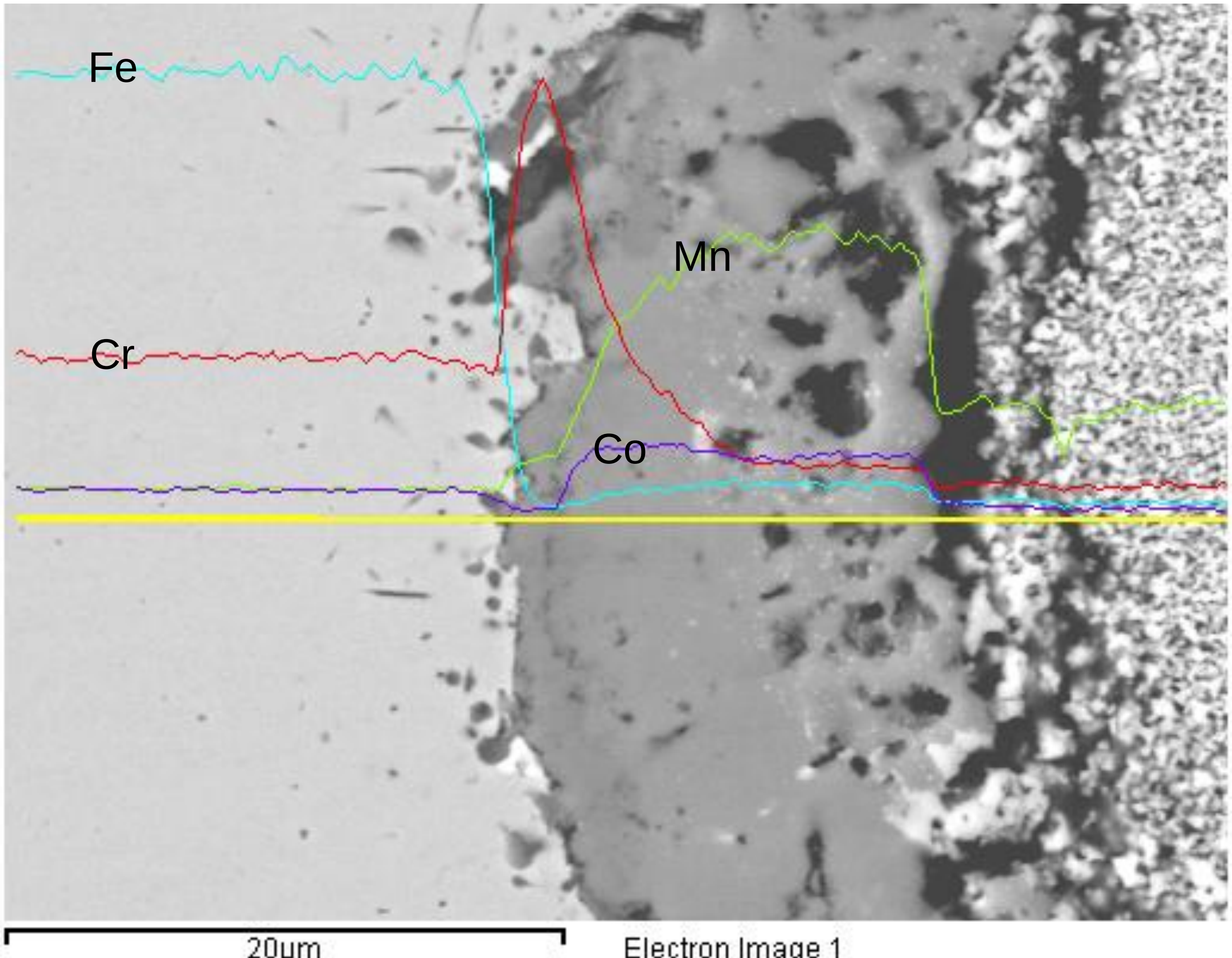


La La1

Spinel-coated cathode IC and LSM contact interface



Spinel-coated cathode IC and LSM contact interface



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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

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

Time (h)	Mill Reference (1200 grit)		Temper Rolled		De-siliconized		Surface Grind		Surface Blast	
	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding
2000										
4000	X									
6000	X			C	X					
8000	X			C						
10000	XX			C						
12000	XX						X	L		
14000	XX					L				
16000	XX									
18000	XX									

X - spallation on at least one coupon
XX - no unspalled coupons left in study
C - complete de-bonding of scale of SEM/EDS sample
L - localized de-bonding of scale of SEM/EDS sample

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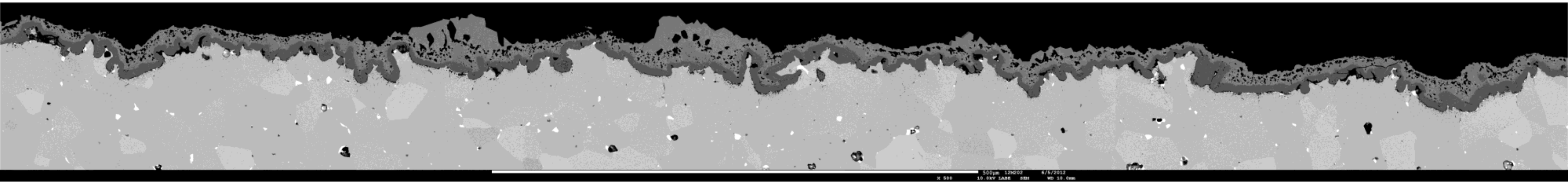
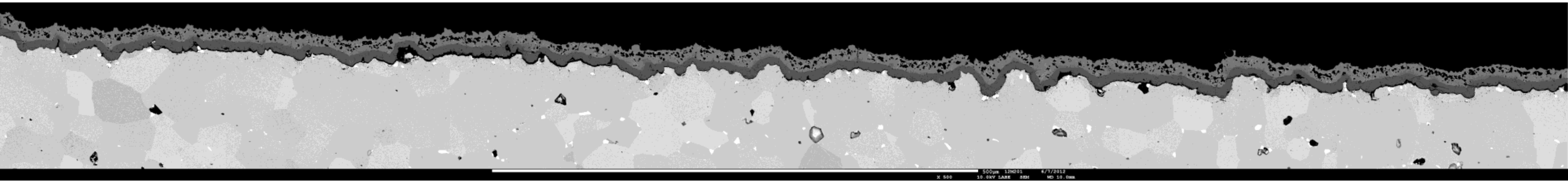
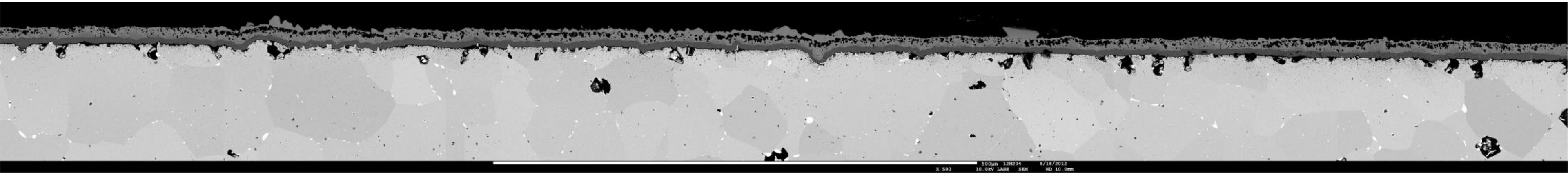
18000 h, 800ºC in Air



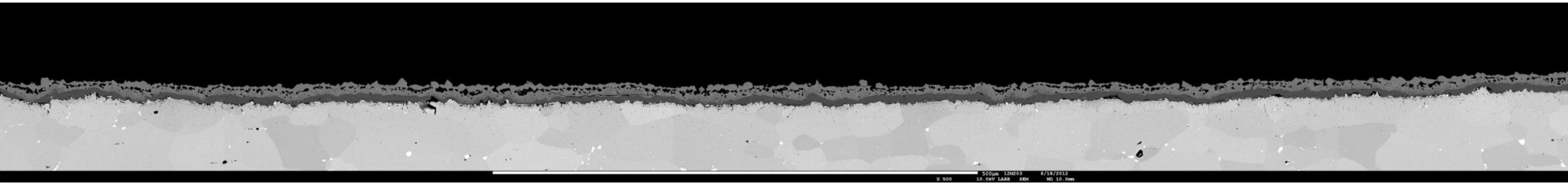
- Surface Blast



- Surface Ground

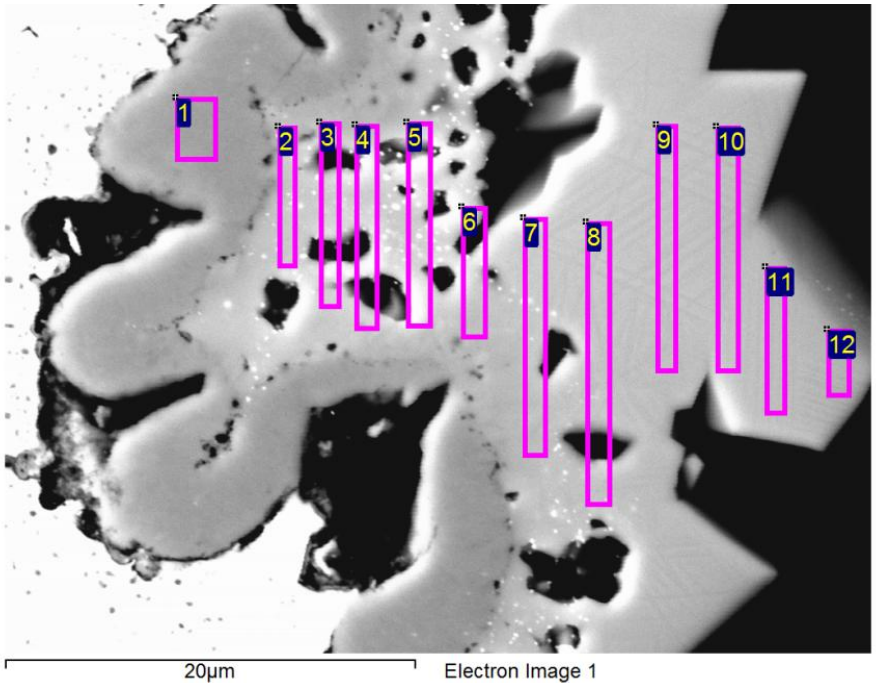


- De-siliconized



- 50% Cold Rolled

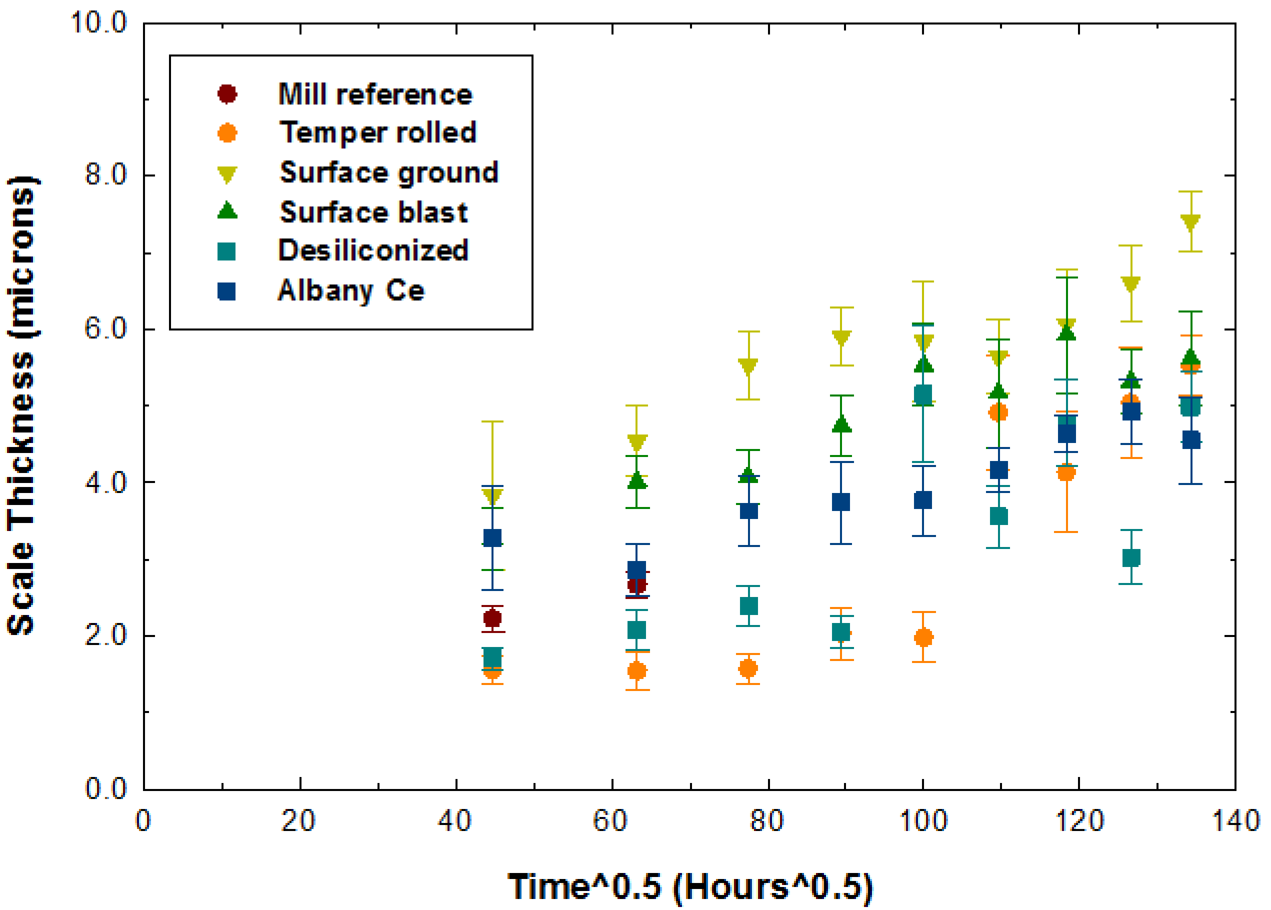
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 18,000 hours, 800ºC, air



Spectrum	O	Si	Ti	**Cr**	Mn	Fe	Co	Ce
1	66.15		0.25	**32.66**	0.69	0.26		
2	60.09		0.37	**9.57**	14.46	3.36	12.15	
3	57.78		0.47	**5.55**	18.04	4.10	13.68	0.38
4	58.25		0.41	**4.64**	18.37	4.10	13.82	0.41
5	60.12		0.33	**4.15**	17.51	4.09	13.47	0.34
6	59.95		0.26	**4.87**	17.40	3.97	13.55	
7	60.56		0.19	**4.59**	17.33	3.95	13.38	
8	59.99	0.28	0.23	**2.39**	19.27	4.38	13.47	
9	59.43		0.21	**2.14**	19.83	4.52	13.86	
10	59.12			**3.26**	19.26	4.40	13.96	
11	58.84			**4.06**	18.75	4.33	14.03	
12	58.75			**4.19**	18.74	4.28	14.04	

Atomic%

Surface Treated AISI 441 w/ Ce-modificed MnCo spinel coating; 800ºC



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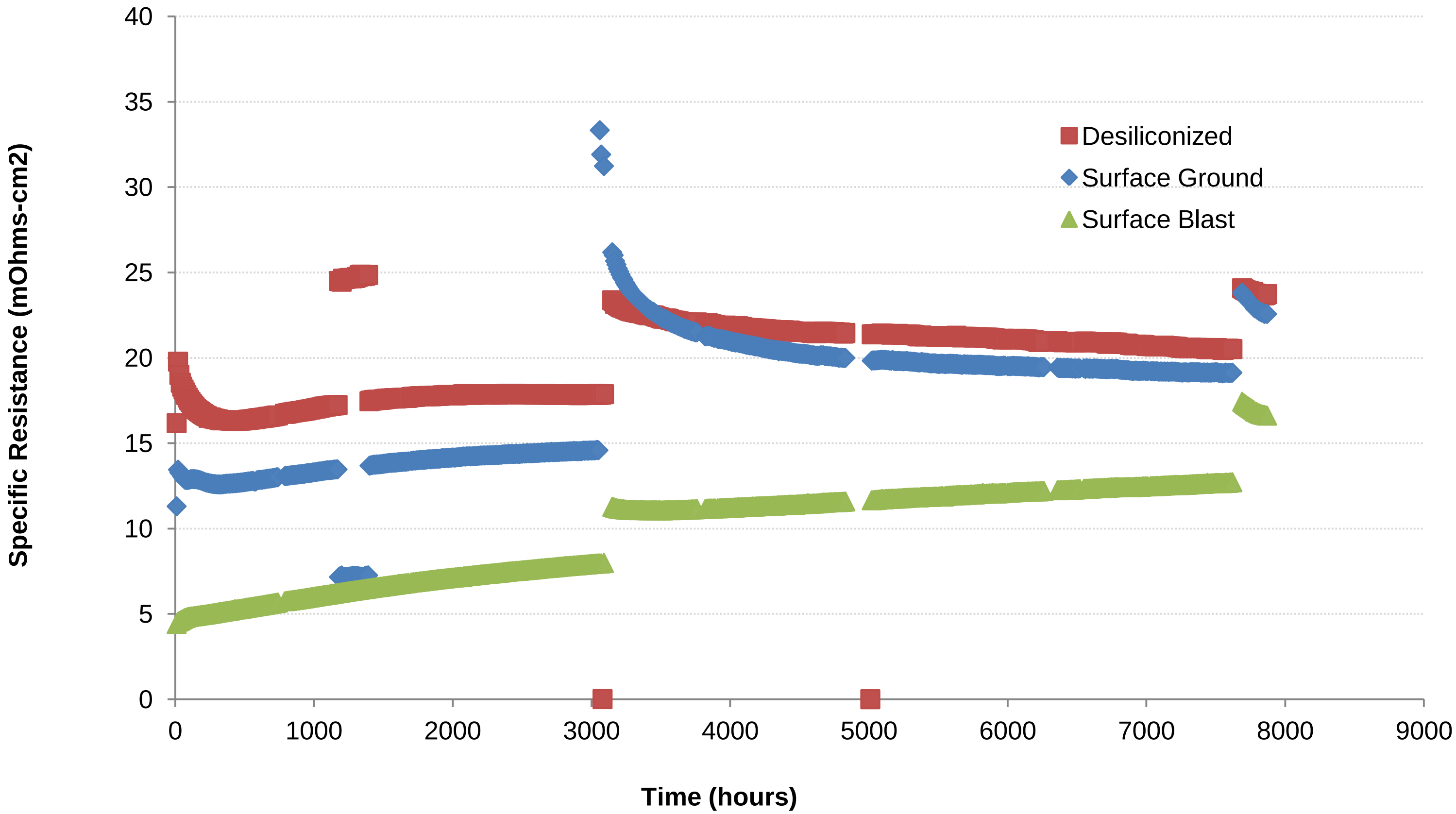
ASR Results for Surface Treated AISI441

(LSCF cathode and contact, Ce-MC 441)



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

Time (h)	Mill Reference (1200 grit)		Temper Rolled		De-siliconized		Surface Grind		Surface Blast	
	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding
2000										
4000										
6000		C								
8000		C				C				
10000	X		X			C				
12000	X		X		X					#

X - spallation on at least one coupon
XX - no unspalled coupons left in study
C - complete de-bonding of scale of SEM/EDS sample
L - localized de-bonding of scale of SEM/EDS sample
- coupon not removed for analysis due to limited # of coupons

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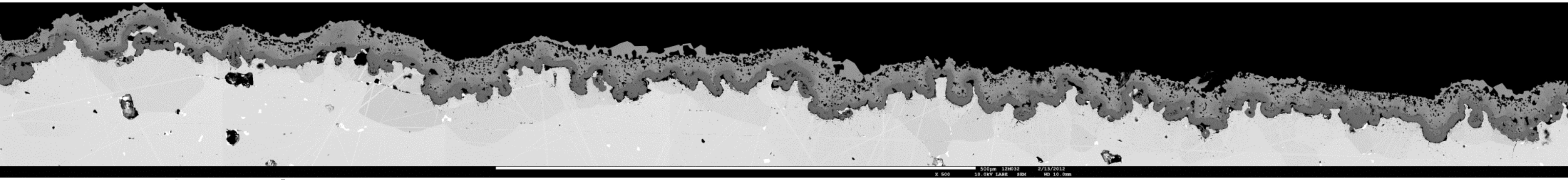
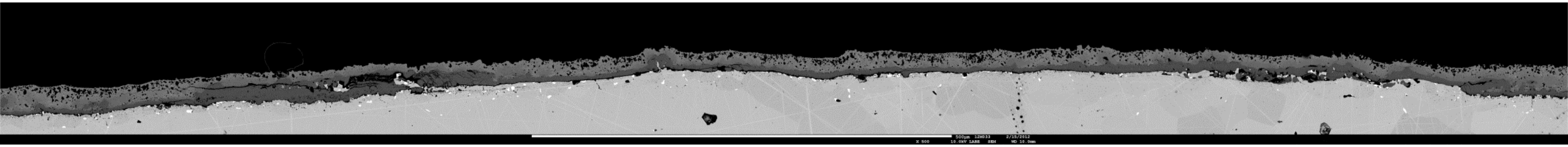
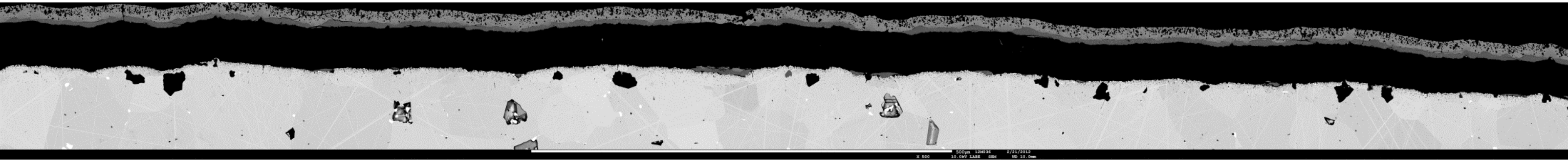
10000 h, 850ºC in Air



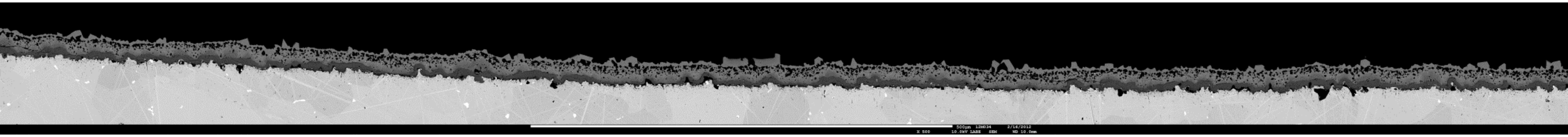
- Surface Blast



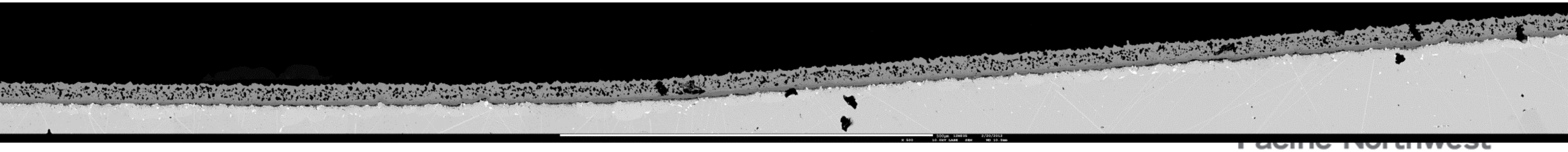
- Surface Ground



- De-siliconized

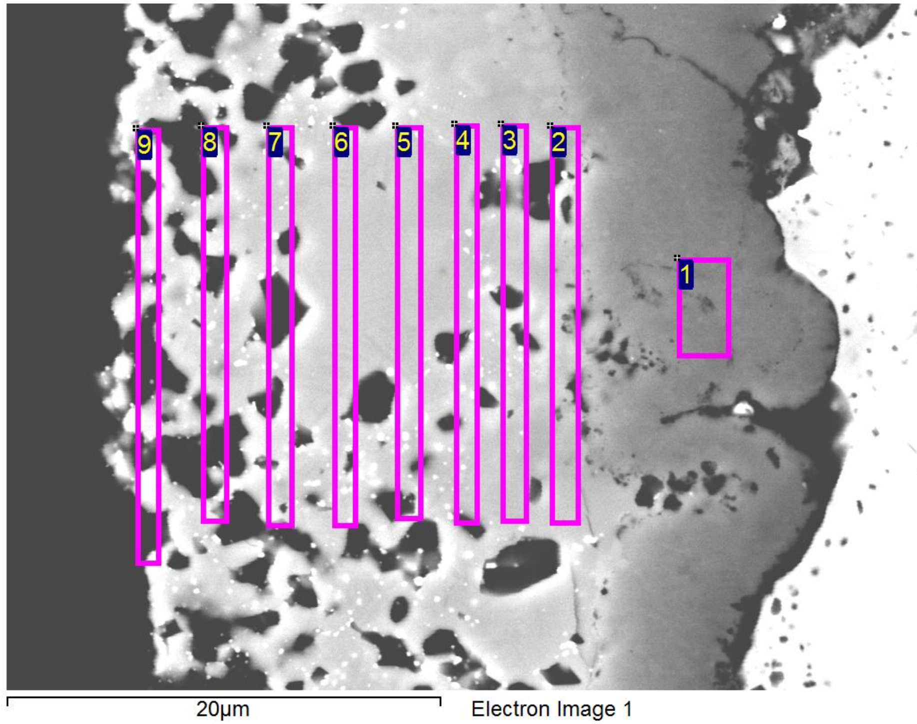


- 50% Cold Rolled



- Mill Reference (1200 grit)

Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 10,000 hours, 850ºC, air



Spectrum	In stats.	O	Si	Ti	**Cr**	Mn	Fe	Co	Ce
1	Yes	64.99	0.49	0.78	**33.58**		0.16		
2	Yes	63.67	0.96	0.22	**16.91**	7.61	0.86	9.77	
3	Yes	62.05	1.01	0.27	**8.28**	14.05	1.75	12.59	
4	Yes	62.12	0.71	0.32	**5.67**	16.17	1.87	12.85	0.30
5	Yes	62.19		0.31	**5.68**	16.47	1.91	13.20	0.24
6	Yes	62.18		0.31	**4.67**	17.43	1.83	13.58	
7	Yes	59.57	0.71	0.31	**3.75**	19.06	2.11	14.15	0.34
8	Yes	59.72		0.32	**3.49**	19.39	2.14	14.59	0.36
9	Yes	58.86		0.26	**3.69**	19.48	2.27	14.95	0.50
Max.		64.99	1.01	0.78	33.58	19.48	2.27	14.95	0.50
Min.		58.86	0.49	0.22	3.49	7.61	0.16	9.77	0.24

Atomic%

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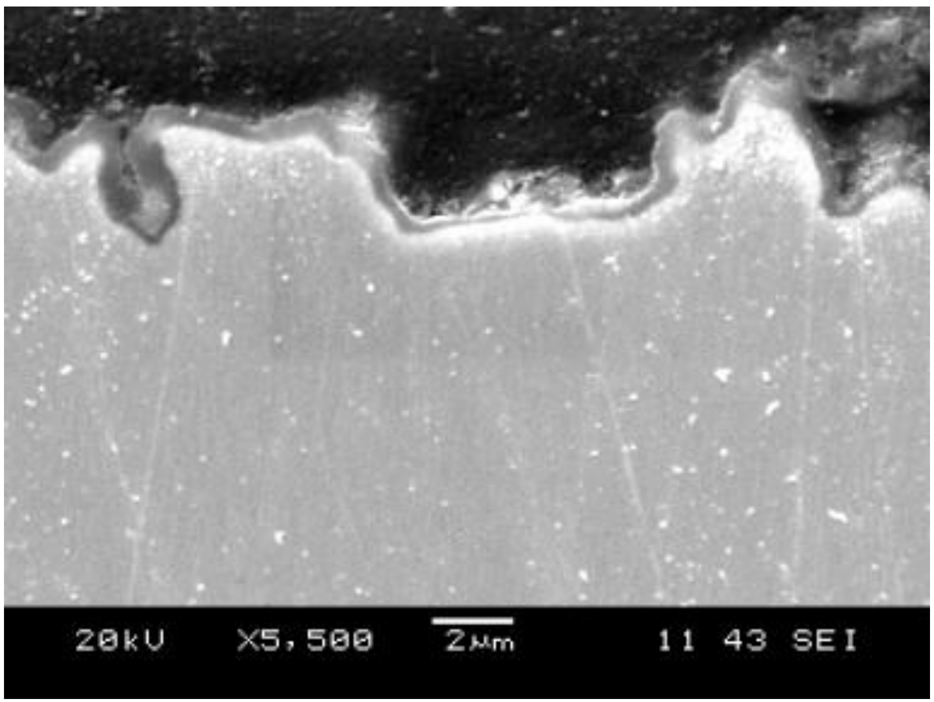
Reactive Air Aluminization (RAA)

•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 and BOP components



Report on RAA distributed to industry teams in October, 2011

Samples aluminized and delivered to industry teams for evaluation

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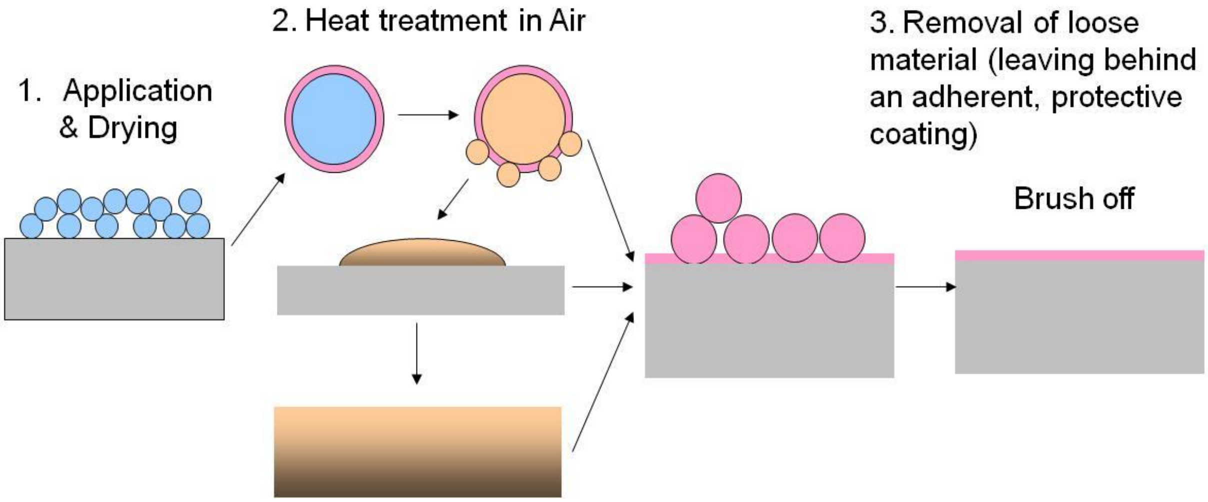
Reactive Air Aluminizing



- Aluminum powder slurry-based process
- Heat treatment in air
  - 3ºC/min to 1000ºC
  - 1 hour dwell at 1000ºC
  - 3ºC/min cooldown

Perovskite Interconnects

- Candidate Compositions
  - Yttrium chromite
    - More stable towards water and YSZ than lanthanum chromite
    - **$Y_{0.8}Ca_{0.2}Cr_{0.9}Ni_{0.1}O_3$**
      - CTE = 11 ppm/K
      - Conductivity in reducing atm: ~5 S/cm
      - Low chemical expansion: 0.06 at 900ºC
  - Lanthanum chromite
    - **$La_{0.78}Sr_{0.2}CrO_3$**
      - CTE = 11.1 ppm/K
      - Low chemical expansion: 0.07 at 900ºC
      - More stable towards reduction (no Ni, Co, or Cu)?
- Previously demonstrated densification under constrained conditions
  - Multiple liquid infiltrations/heat treatments required
- Two current approaches to enhance sintering under constrained conditions
  - Both involve formation of final perovskite phase during sintering process
    - Reaction sintering approach (enthalpy of reaction)
    - Sintering aid approach (liquid phase assistance + enthalpy of reaction)

Summary

- AISI 441 w/ Ce-modified MnCo spinel coatings exhibits low, stable ASR in long-term testing
  - Less than 20 mΩ-cm^2 after 25,000 hours at 800ºC in air
- Surface-modified AISI 441 w/ Ce-modified MnCo spinel coatings exhibits improved long-term spallation resistance
  - 18,000 hours at 800ºC (tests in progress)
  - 12,000 hours at 850ºC (tests in progress)

- Future work:
  - Continue long-term testing of surface-modified AISI 441
  - Quantify relationship between surface morphology and oxidation resistance/scale adhesion
    - Prediction/Extension of IC lifetime

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