SECA Core Technology Program R&D at PNNL: Overview

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Pacific Northwest National Laboratory
Richland, WA 99354

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14th Annual SECA Workshop

Pittsburgh, PA

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Objective

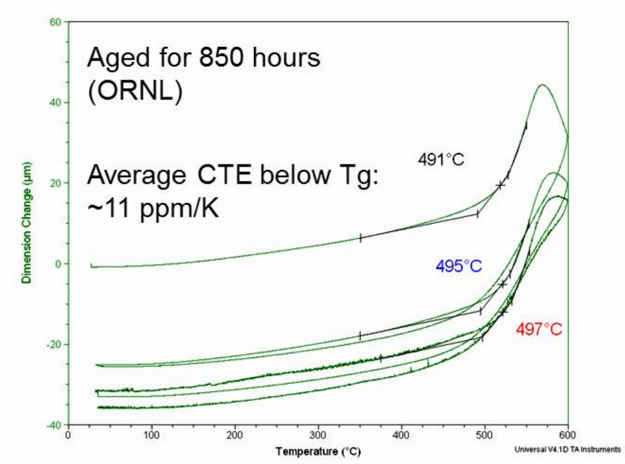
- **Provide R&D support to SECA program**
  - **From SECA Program Mission statement: "Increase reliability, robustness, and durability of cell and stack technology"**
  - Development/evaluation of improved materials and fabrication processes for SOFC cells and stacks
  - Improved understanding of performance degradation mechanisms
  - Development/implementation of modeling tools to facilitate cell and stack design and optimization
  - <u>Technology transfer</u> to industry teams
    - **Stack test fixture validation**
    - **Topical reports**, journal articles
    - **Semi-annual one-on-one reviews**, SECA Workshop
    - **Provide materials, software for evaluation/implementation by industry teams**

Scope of Work

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

- **Current areas of emphasis (combined experimental/modeling approach)**
  - SOFC interconnects
    - Alloys and coatings for IT-SOFC interconnects
  - Seals for SOFC stacks
    - Compliant glass-based seals
  - Cathode materials and interactions
    - Effects of humidity; In-situ XRD characterization
  - Anode materials and interactions
    - Effects of high fuel utilization; Mitigation of sulfur poisoning
  - Cell/stack design
    - 2D and 3D modeling tools to assist in cell/stack design
    - **Poster Presentation: ROM Tool for SOFC Modeling (Brian Koeppel)**
    - **Oral Presentation: Modeling Tools for SOFC Design and Analysis (Brian Koeppel)**

Seals for SOFC Stacks

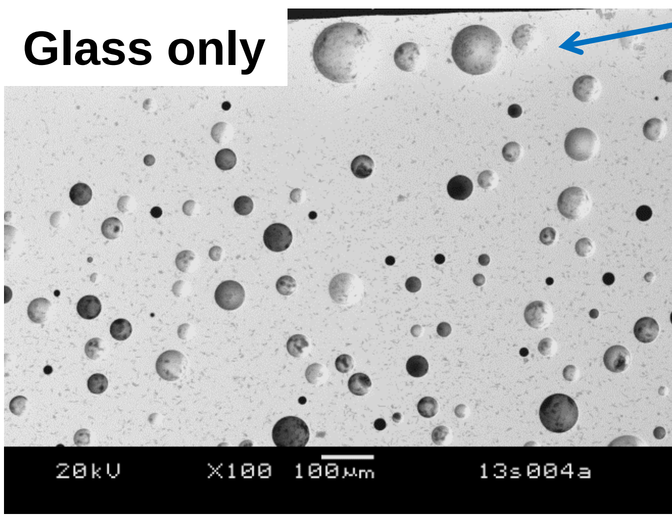


- Primary Challenge
  - Reliability during thermal cycling (high residual stresses)
- Approach (collaboration with ORNL)
  - "Compliant glass" based seals: Glass exhibits low Tg and relatively low viscosity at operating temperature, resulting in mitigation of mechanical stresses during operation and thermal cycling. Potential for self-healing of cycling-related damage.
  - ORNL is primarily responsible for materials properties characterization, while PNNL has primary responsibility for modeling and seal test activities.
    - Evaluate thermal, mechanical, and chemical <u>sealing glass properties</u> (including glass-based composites).
    - Design and test <u>compliant glass-based seals</u> to evaluate seal performance in terms of leakage, mechanical stability, and reactivity (e.g., interactions with adjacent materials, electrode poisoning due to volatilization and deposition of glass constituents).
    - Develop <u>compliant glass constitutive models</u> to simulate thermal stresses, seal damage evolution, and healing behavior during stack operation.

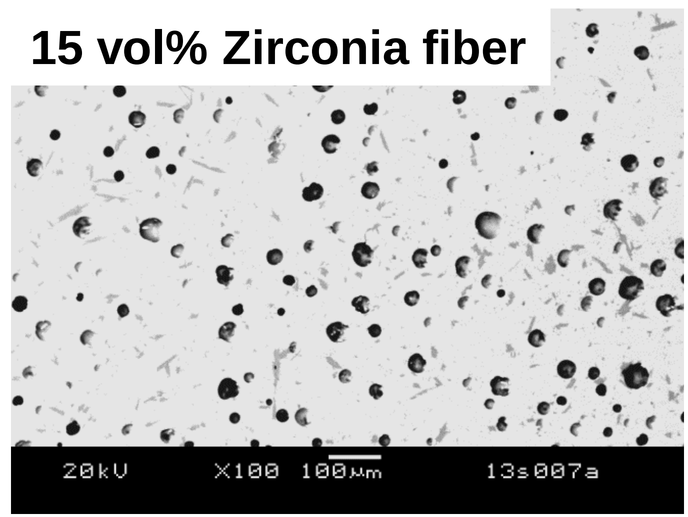
Compliant Glass-based Seals

- Status (completed work)
  - Measurement of thermo-physical and mechanical properties (viscosity, CTE, elastic constants, crystallization rate; 15,000 hours)
  - Assessment of electrical, microstructural, and chemical stability
    - High electrical resistance maintained with aluminized steel components
    - Some de-vitrification observed; controlled by limited amount of Ba and Al in glass
    - Minimal volatilization over stack lifetime
    - Potential issues associated with pore coarsening/void formation

Glass only



15 vol% Zirconia fiber

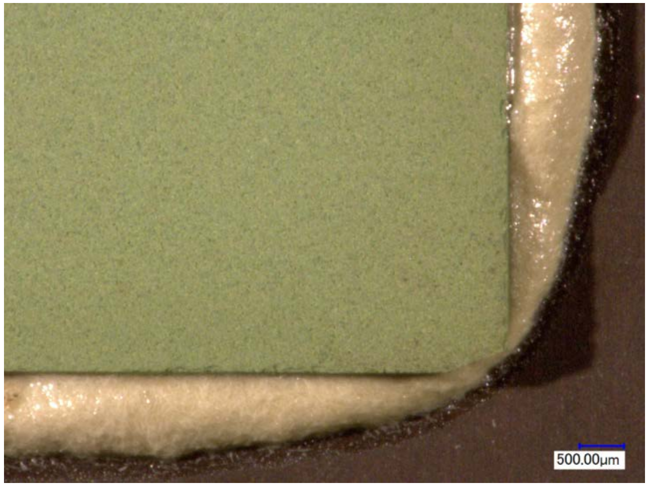


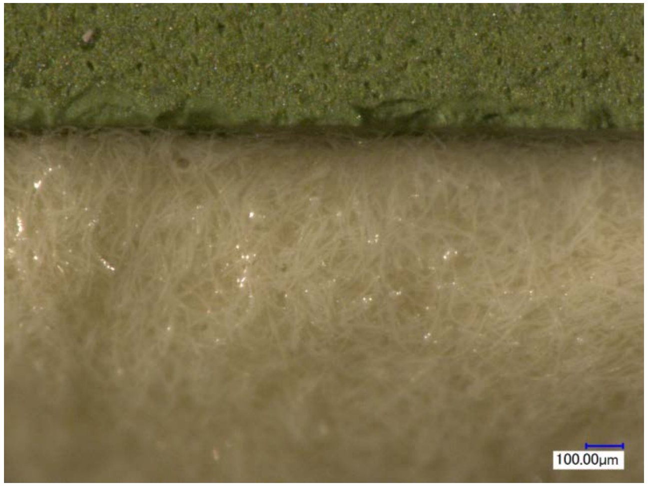
Aged 800ºC, 250 hours

Compliant Glass-based Seals

- Ongoing/Future work
  - Inclusion of fillers (zirconia fibers, particles) to modify viscosity, control porosity and displacement
  - Optimization of seal design and fabrication techniques
  - Long-term evaluation of seals in seal test fixture and stack test fixture
  - Modeling of microstructural, thermophysical, and mechanical behavior
    - Self-healing behavior
    - Simulation of seal performance in stacks
- Preliminary assessment in seal test fixture:

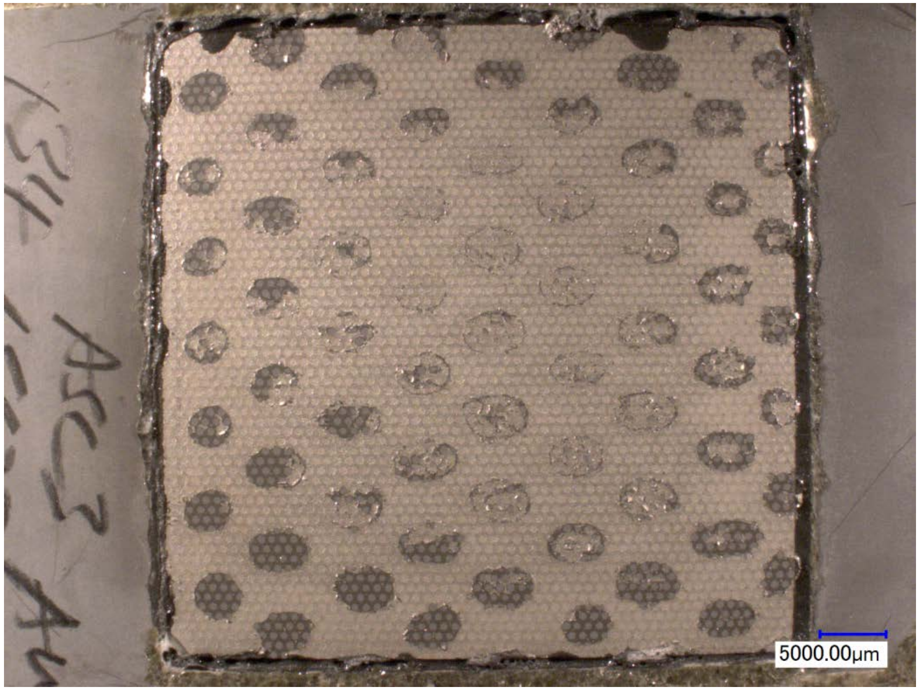
12 deep thermal cycles (RT to 800ºC)

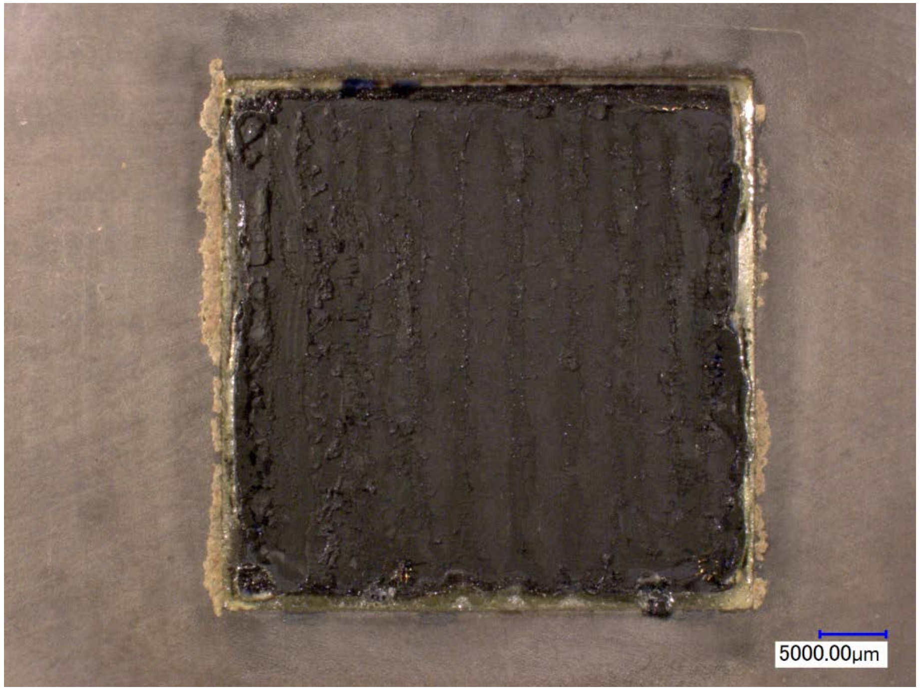




Preliminary evaluation of compliant glass seal: ~1300h, 800ºC, 3 thermal cycles

- No cross-bubbling at room temperature
- No discoloration on either cathode and anode side
- No iso-propanol penetration along sealing edges or through cell





- Long-term evaluation in stack test fixture is in progress
  - Poster:
    Compliant Glass Seal Development at Pacific Northwest National Laboratory (Matt Chou; collaboration with ORNL)

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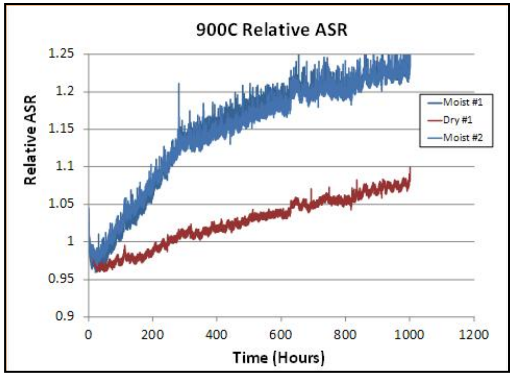
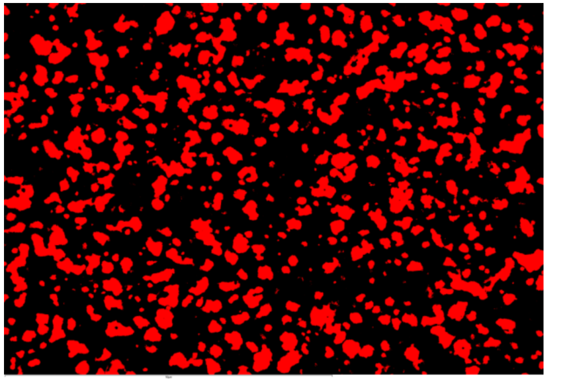
Cathodes

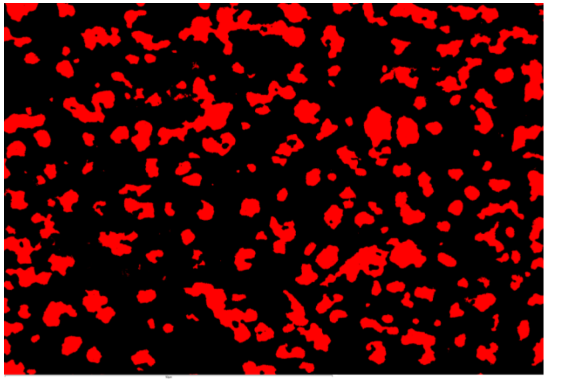


- Primary Challenges
  - Long-term stability
  - Effects of contaminants
- Approach
  - Emphasis on effects of humidity in cathode air stream on cell performance
    - Button cell tests (including high temperature XRD) at varying temperatures and humidity levels
    - Modeling to develop improved understanding of cathode reactions and degradation mechanisms
  - **Leveraging activities/results with other SECA Core Program cathode researchers**
- Status
  - 1000 hour cell tests completed on LSCF and LSM-20/YSZ; performance trends identified
- Ongoing / Future activities
  - Tests in progress on LSM-0 (LM) and LSM-5
  - High temperature XRD on working cathodes: Effect of humidity on LSM/YSZ cathodes
  - Modeling of kinetics, thermodynamics, and possible reactions with LSM-20
- Posters:
  - **LSM-20/YSZ Cathode Response to Elevated Steam Content in 500-1000 h Tests (John Hardy; collaboration with NETL)**
  - **In-Operando XRD of Anode-Supported LSCF Cathodes at 700 – 800°C for 1000 h (John Hardy)**

Anodes

- Primary Challenges
  - Long-term microstructural stability in high water environments
  - Effects of contaminants
- Approach
  - Emphasis on effects of high fuel utilization (high water content) on Ni-YSZ anode performance
    - Cell and coupon tests at varying temperatures and water levels
    - Fuel is simulated clean coal gas
  - Mitigation of sulfur poisoning





- Ongoing / Future activities
  - Microstructural changes (Ni coarsening) observed at 900 and 1000°C at high fuel water contents; tests and analysis in progress
  - Attempting to correlate anode electrochemical performance with microstructural changes
- Poster:
  - **Stability of Nickel in Ni/Zirconia Electrodes at High Steam Concentrations (Olga Marina)**

SOFC Interconnects & Coatings

- Primary Challenges
  - Cr volatility (cathode poisoning)
  - Increasing electrical resistance
  - Scale de-bonding/spallation

- Approach
  - Low cost ferritic stainless steel interconnects with protective coatings (MnCo spinel, aluminization)
  - Experimental: Oxidation testing, ASR testing, stack fixture testing, micro/nano indentation
  - Modeling: Finite element-based modeling tools utilizing experimentally obtained strength data to determine spallation mechanisms and predict interconnect lifetime

- Posters
  - **Recent Progress of SOFC Materials Validation in a Generic Stack Fixture at Pacific Northwest National Laboratory (Matt Chou)**
  - **Novel Interconnect Spinel Coating Process for Planar SOFC Stacks (Jung Pyung Choi)**
  - **Interconnect Lifetime Prediction from Interfacial Indentation (Brian Koeppel)**

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}

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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)

- Oxidation testing of 0.02” thick, MnCo spinel-coated coupons at 800 and 850ºC

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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	XX		C				L		
12000	XX	XX					X	L		
14000	XX	XX				L				
16000	XX	XX								
18000	XX	XX								
20000	XX	XX				L	X	L		
22000	XX	XX		#		#	X	#		#
24000	XX	XX		#		#		#		#
26000	XX	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
- coupon not removed for analysis due to limited # of coupons remaining

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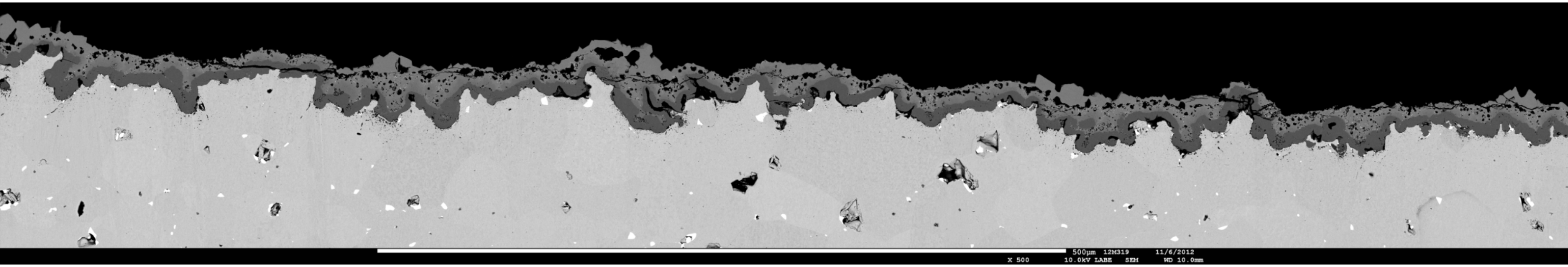
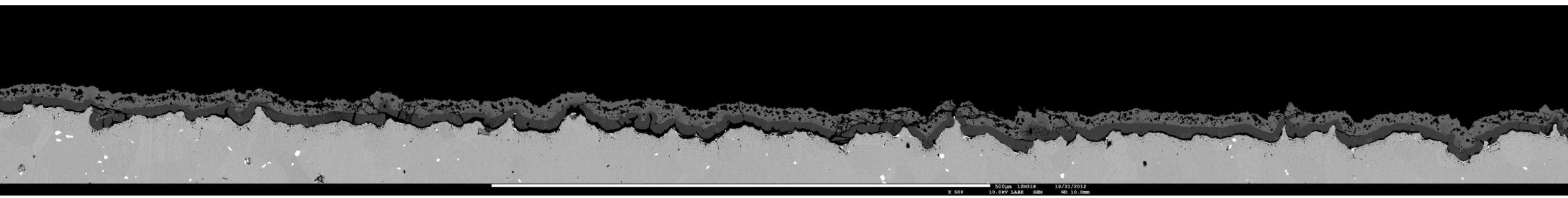
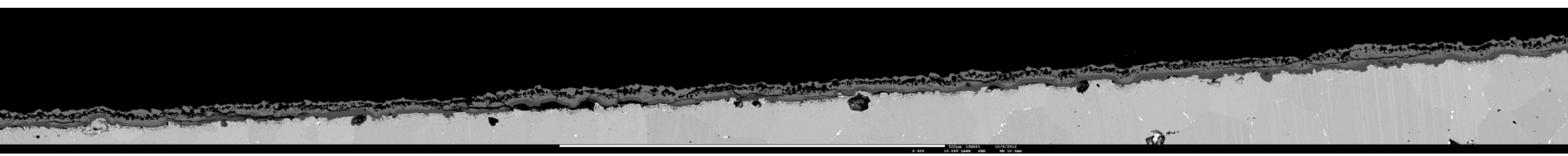
20000 h, 800ºC in Air



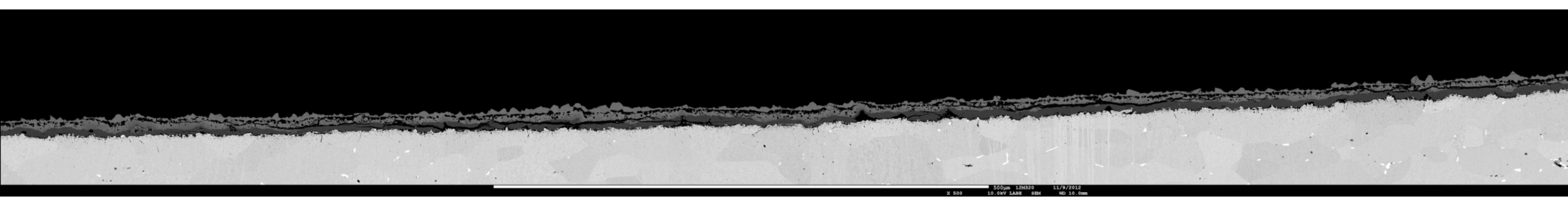
- Surface Blast



- Surface Ground

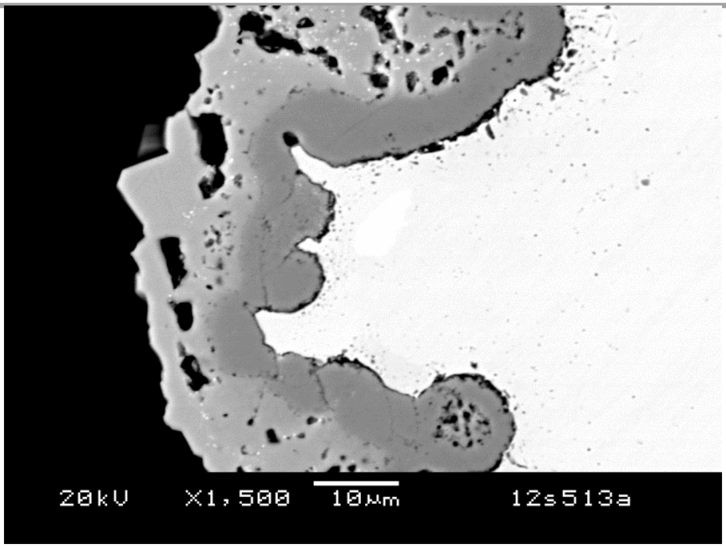


- De-siliconized

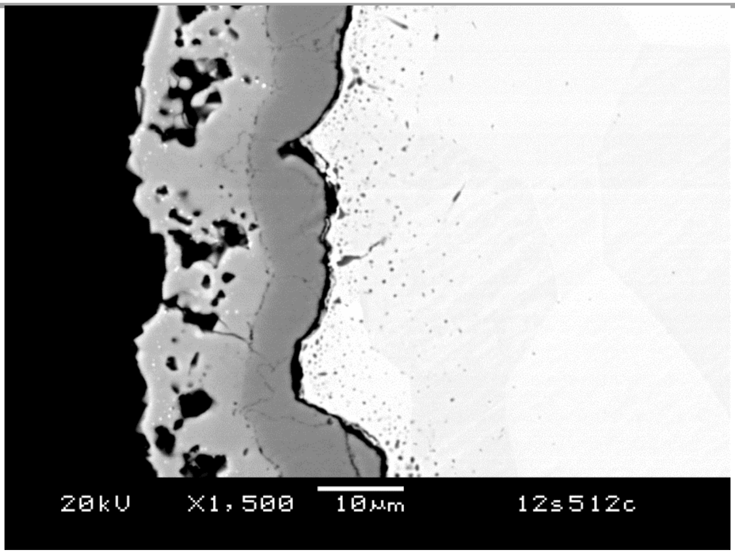


- 50% Cold Rolled

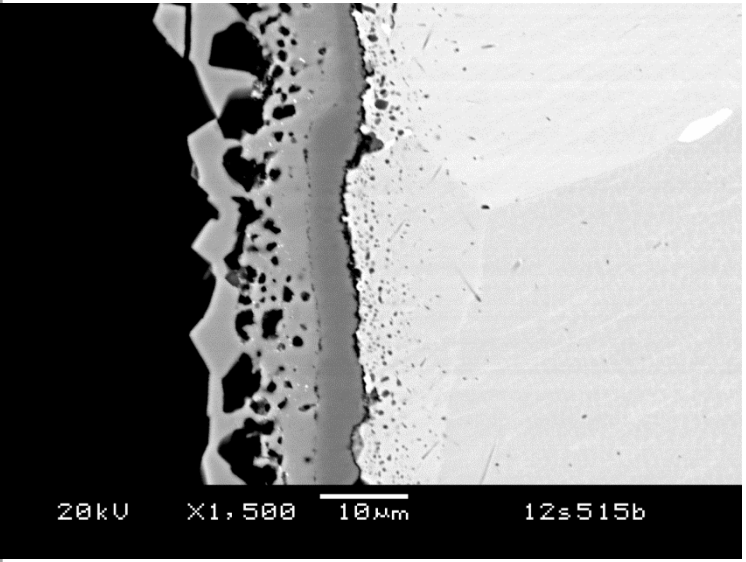
20000 h, 800ºC in air



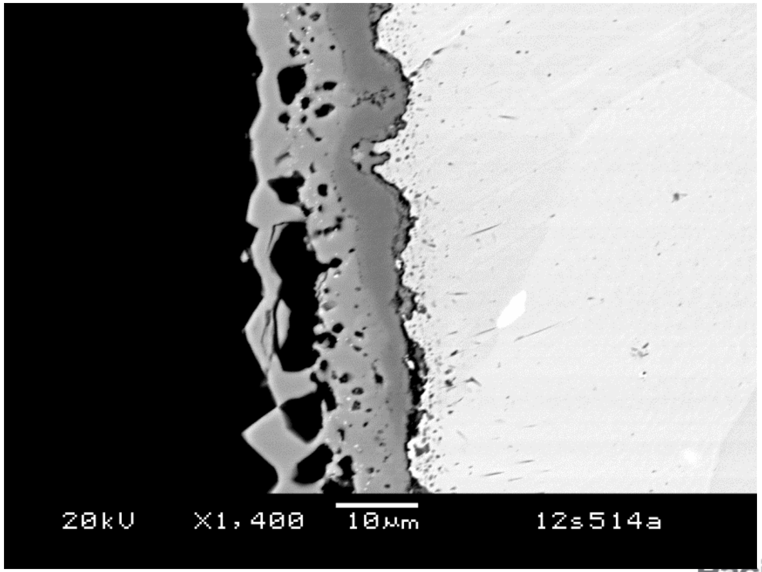
Surface Blast



Surface Grind

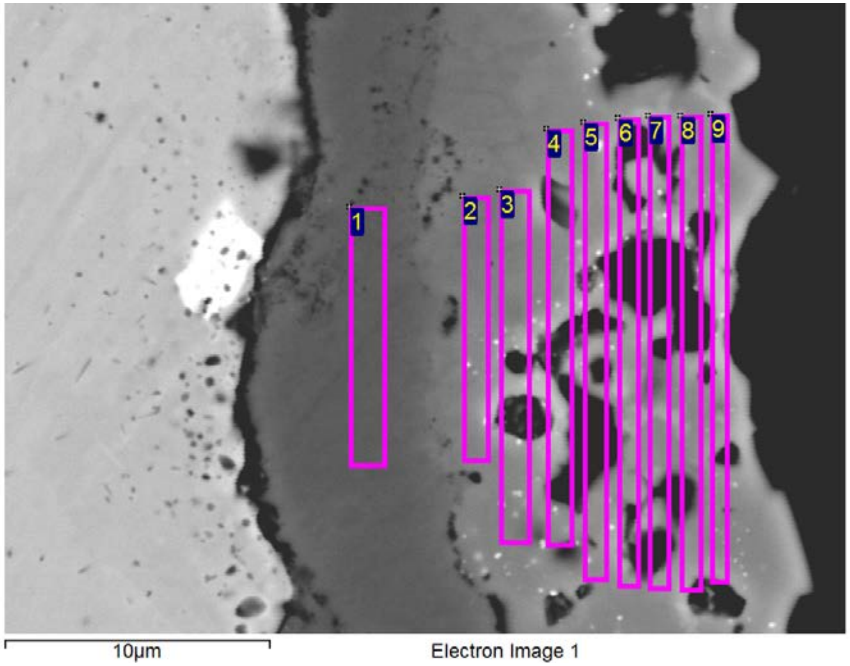


Desiliconized



Cold Rolled

Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 20,000 hours, 800ºC, air



Spectrum	O	Si	Ti	Cr	Mn	Fe	Co	Ce
1	63.90	0.27	0.27	**35.38**		0.17		
2	61.16		0.27	**13.42**	11.65	1.90	11.59	
3	60.33	0.30	0.43	**7.72**	15.94	2.78	12.22	0.28
4	59.42		0.50	**5.52**	18.42	2.99	13.15	
5	57.68	0.60	0.51	**5.25**	19.30	3.09	13.28	0.29
6	58.89	0.68	0.44	**5.07**	18.84	2.81	12.78	0.48
7	57.05	0.75	0.48	**5.28**	19.79	2.87	13.21	0.56
8	57.30	0.41	0.49	**5.37**	19.59	2.96	13.53	0.36
9	61.84	0.42	0.43	**4.61**	17.30	2.67	12.50	0.24

Atomic%

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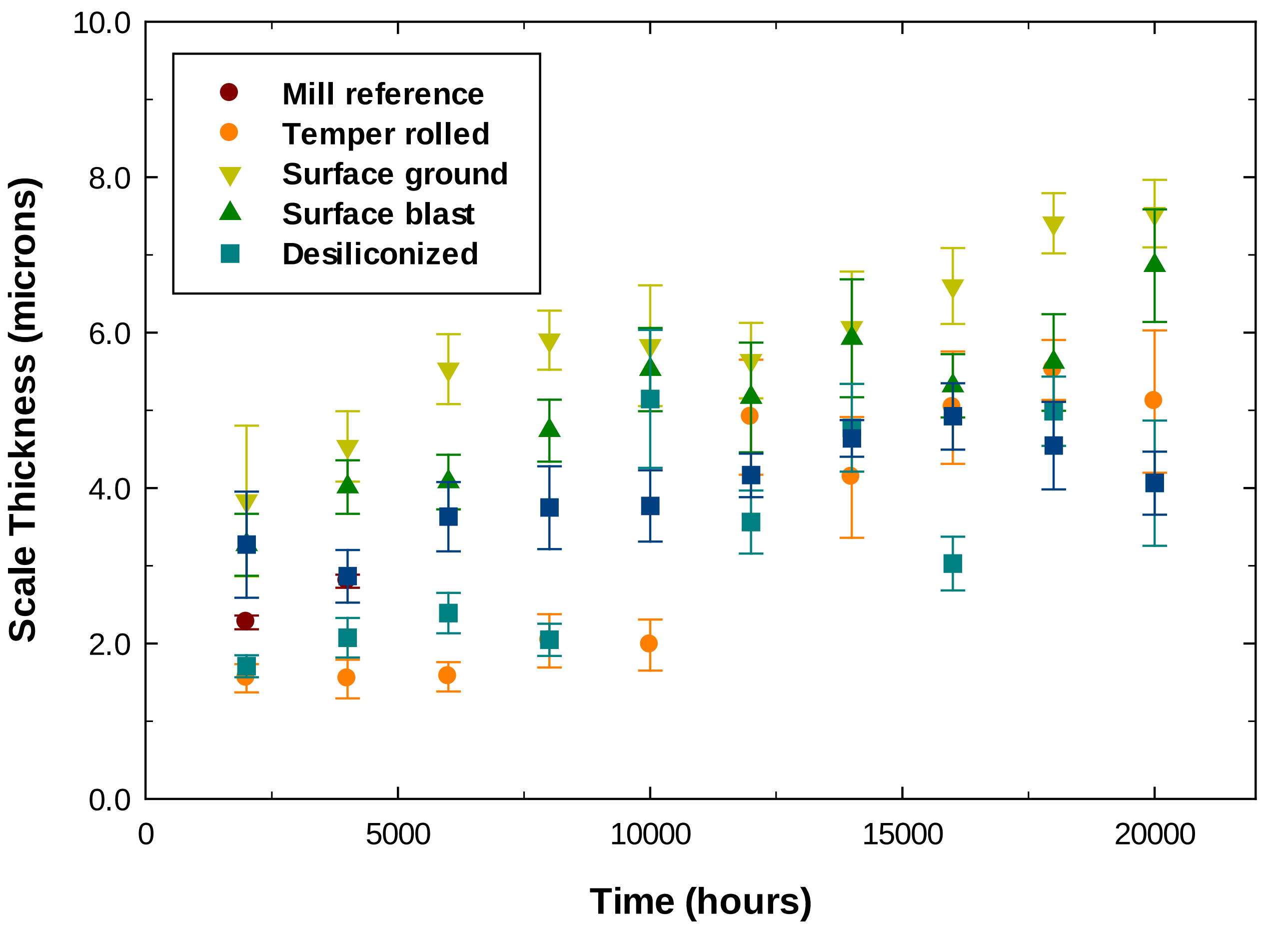
Surface Treated 441 w/coating; 800ºC



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		L								
6000		C								
8000		C				C				
10000	X		X			C				
12000	X		X		X	C				#
14000	X		X		X	L				#
16000	XX	XX		#		#		#		#
18000	XX	XX		#		#		#		#
20000	XX	XX			XX	XX				
22000	XX	XX		#	XX	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
- coupon not removed for analysis due to limited # of coupons remaining

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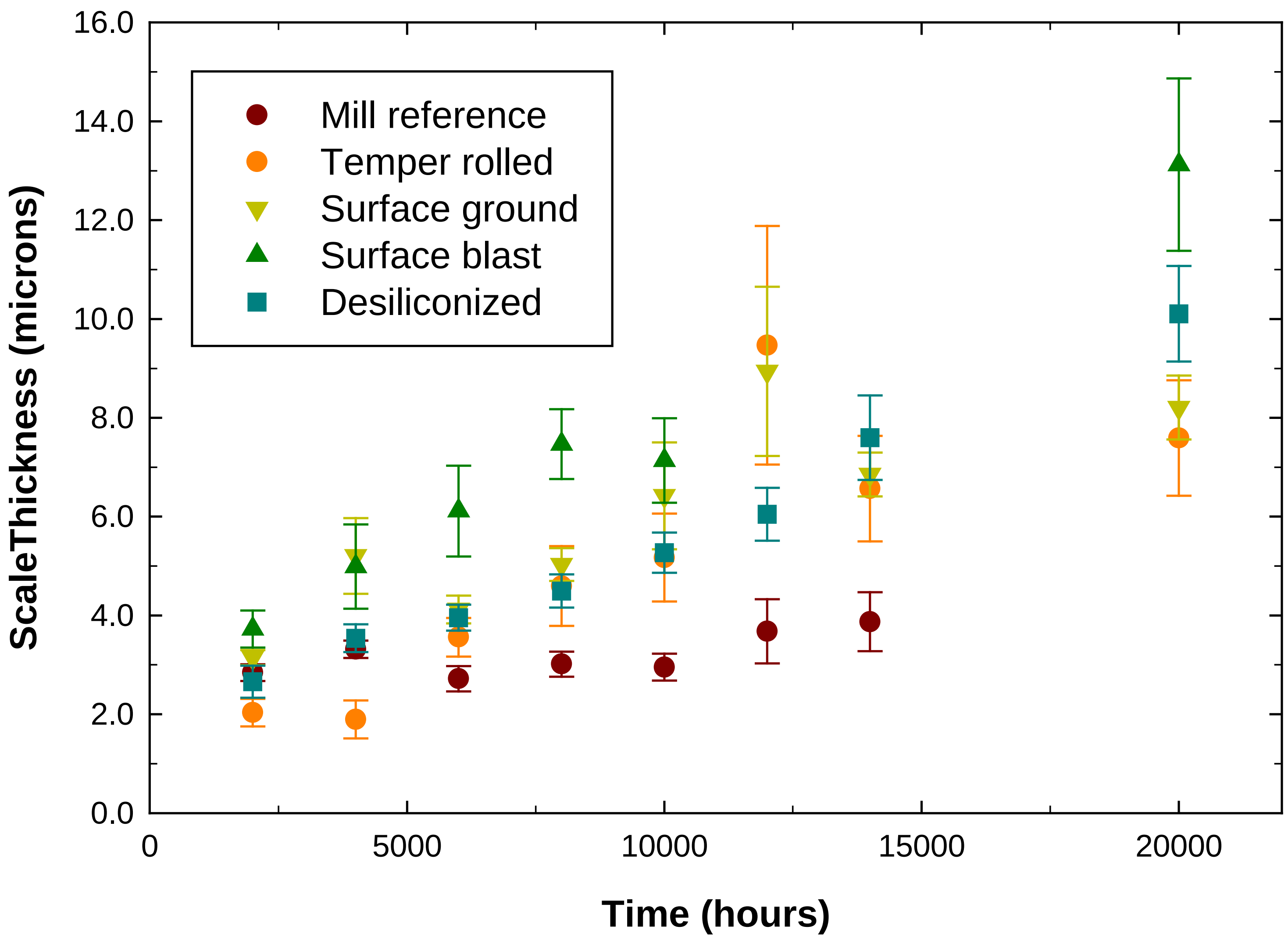
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 850ºC



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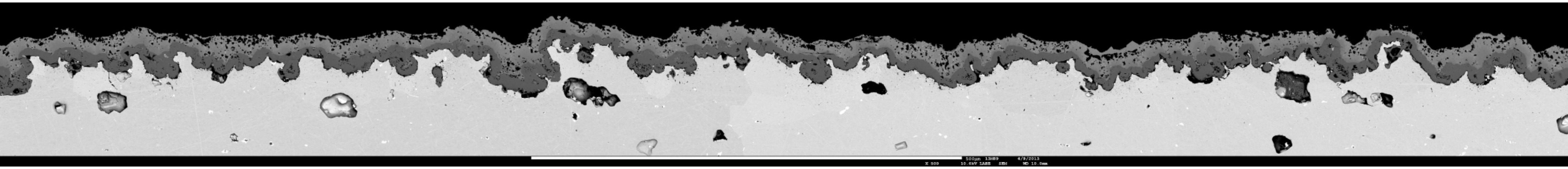
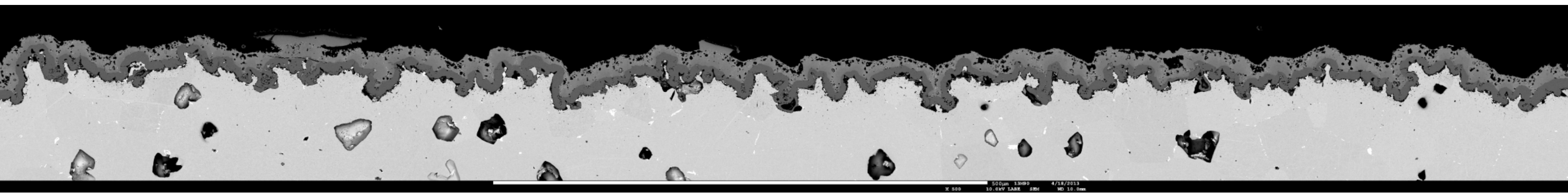
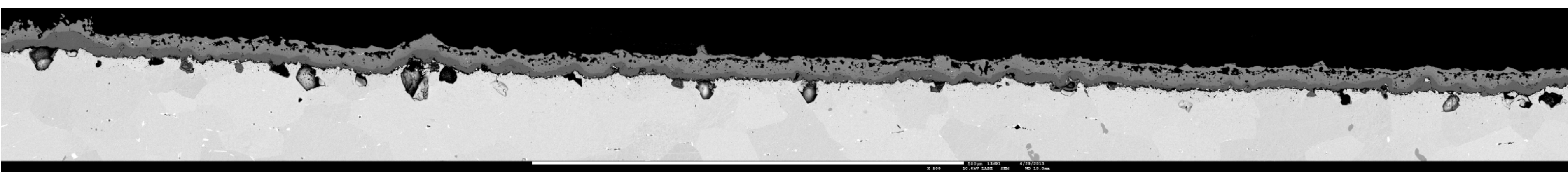
20000 h, 850ºC in Air



- Surface Blast



- Surface Ground



- 50% Cold Rolled

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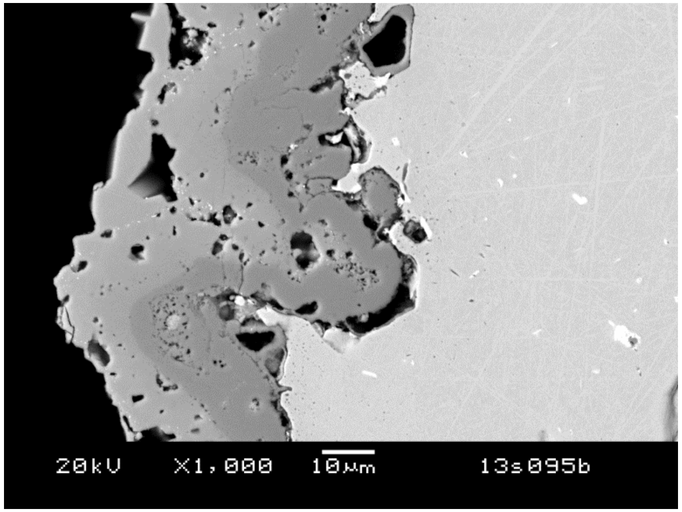
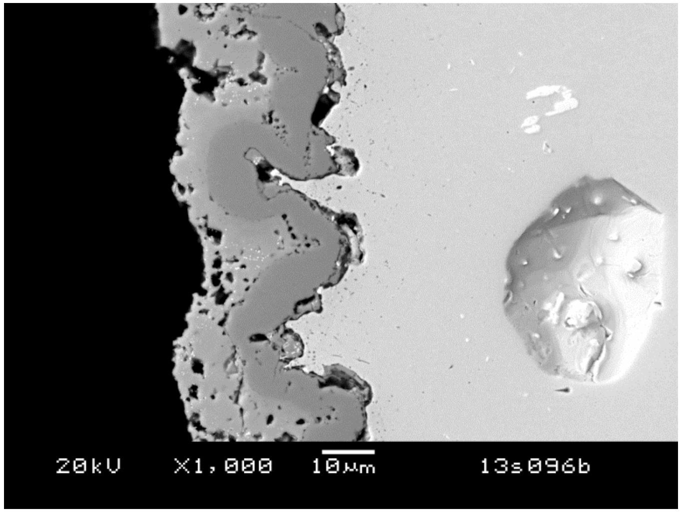
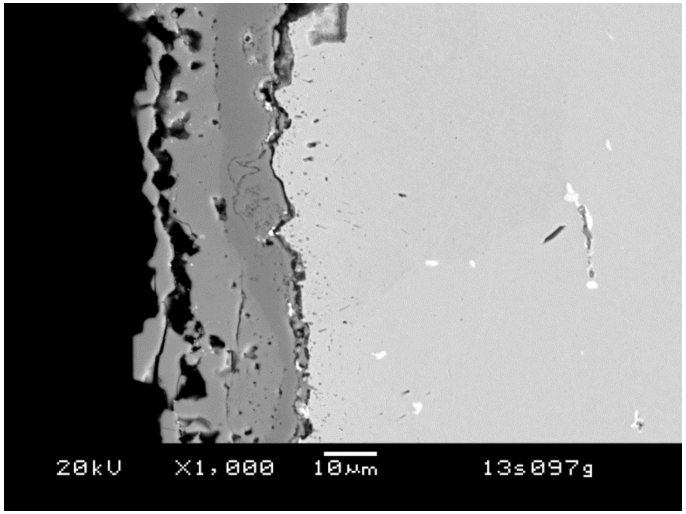
20,000 h; 850ºC in air



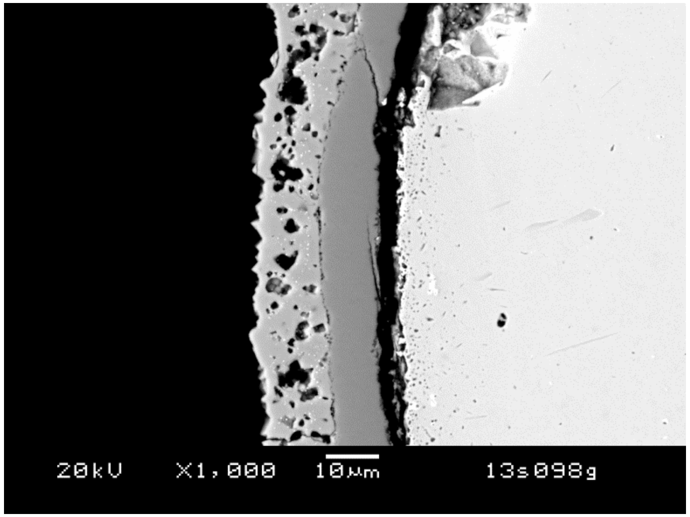
Surface Blast



Surface Grind

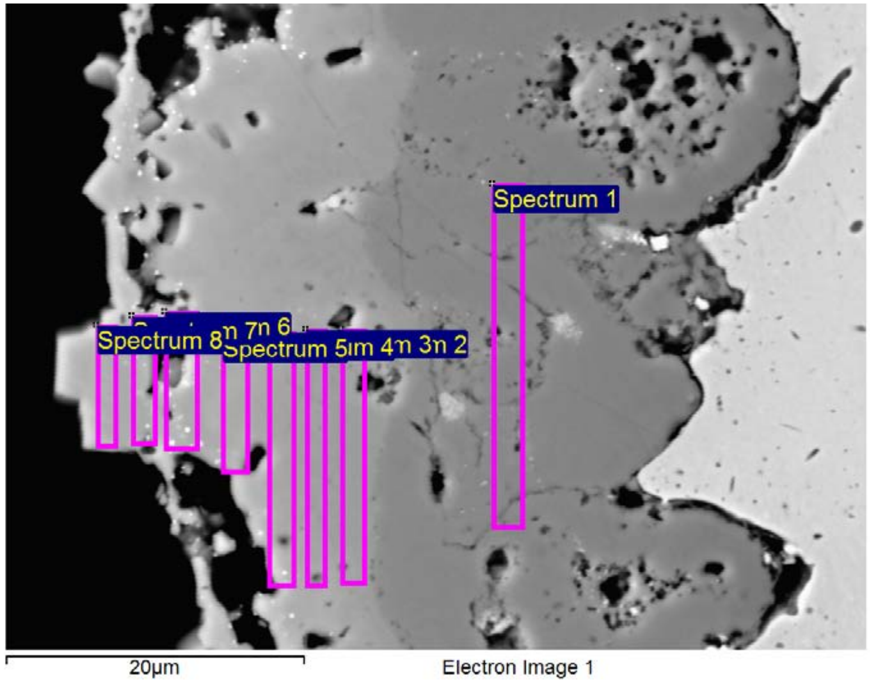


Cold Rolled



Desiliconized

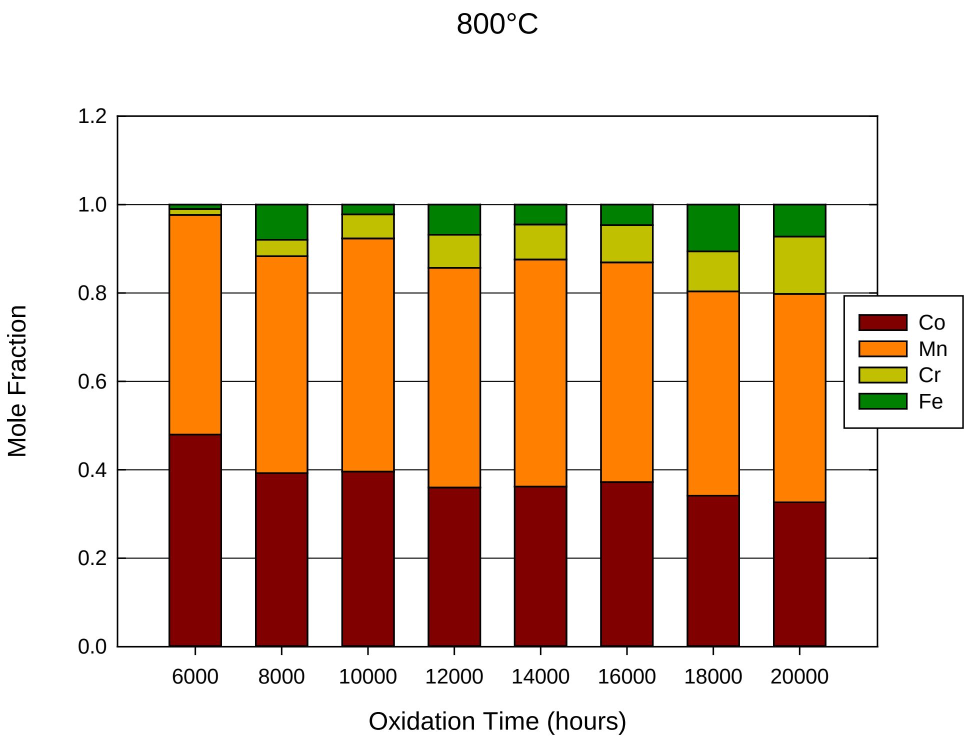
Surface Blast AISI 441 w/ Ce-modified MnCo Spinel coating: 20,000 hours, 850ºC, air

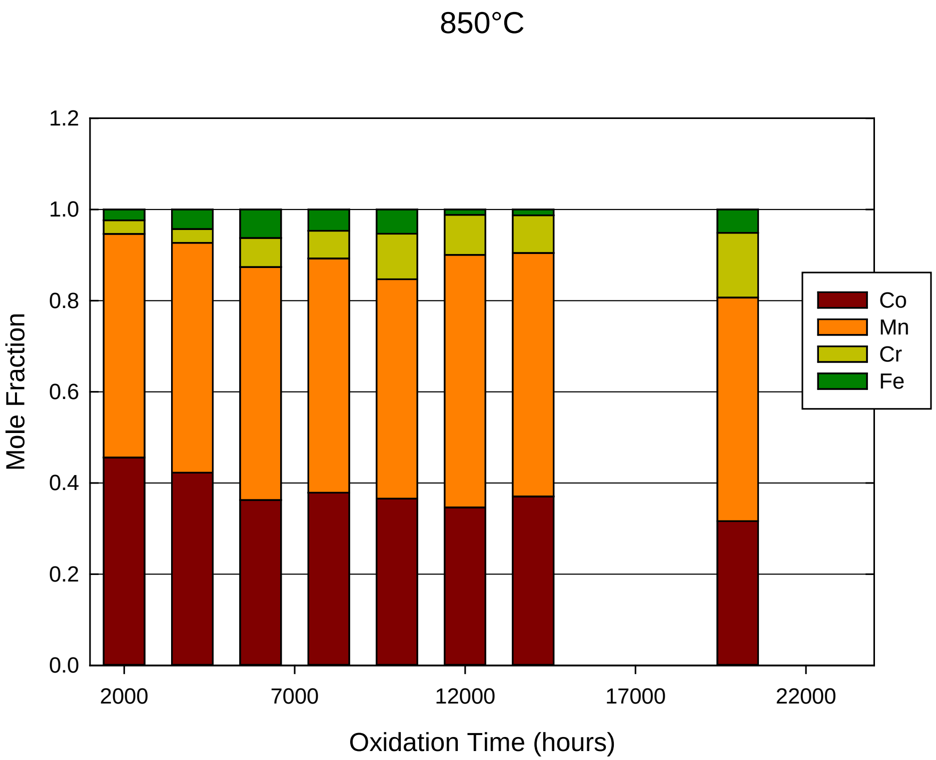


Spectrum	O	Si	Ti	Cr	Mn	Fe	Co	Ce
Spectrum 1	64.28	0.37	0.49	**33.34**	0.81	0.72		
Spectrum 2	61.76			**22.71**	5.20	0.47	9.85	
Spectrum 3	61.38		0.11	**18.50**	8.31	0.91	10.77	
Spectrum 4	61.11	0.25	0.15	**13.08**	12.05	1.38	11.99	
Spectrum 5	61.29		0.23	**6.50**	17.96	1.89	12.11	
Spectrum 6	60.03		0.23	**6.36**	17.72	1.96	13.11	0.59
Spectrum 7	60.85		0.23	**5.12**	19.42	1.98	12.15	0.23
Spectrum 8	62.27		0.23	**3.82**	20.34	2.06	11.28	

Atomic%

Spinel composition (metals basis)





Surface blast coupons, except 850C, 12000 and 14000h are surface grind

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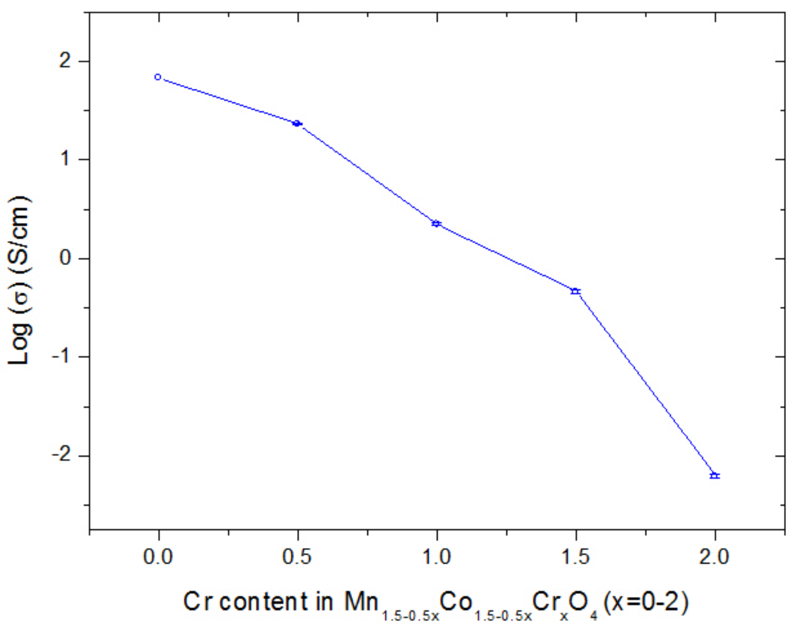
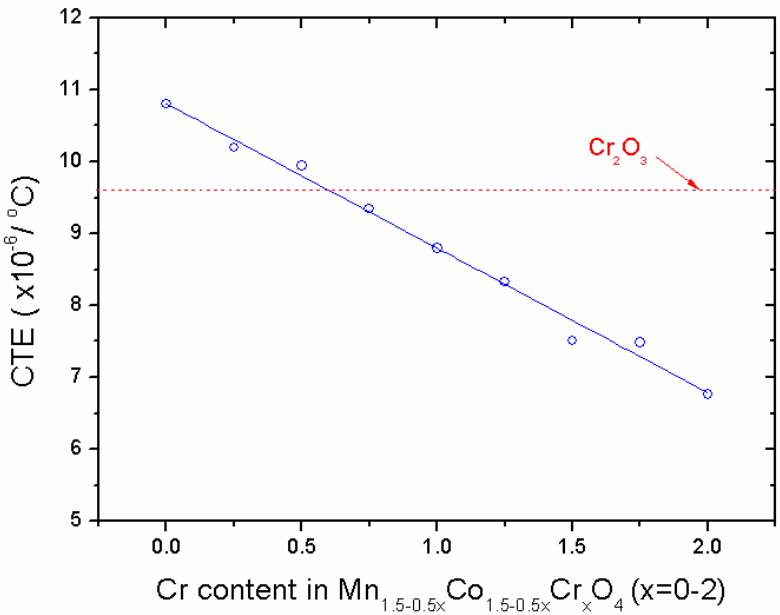
Effect of Cr on spinel electrical conductivity and CTE



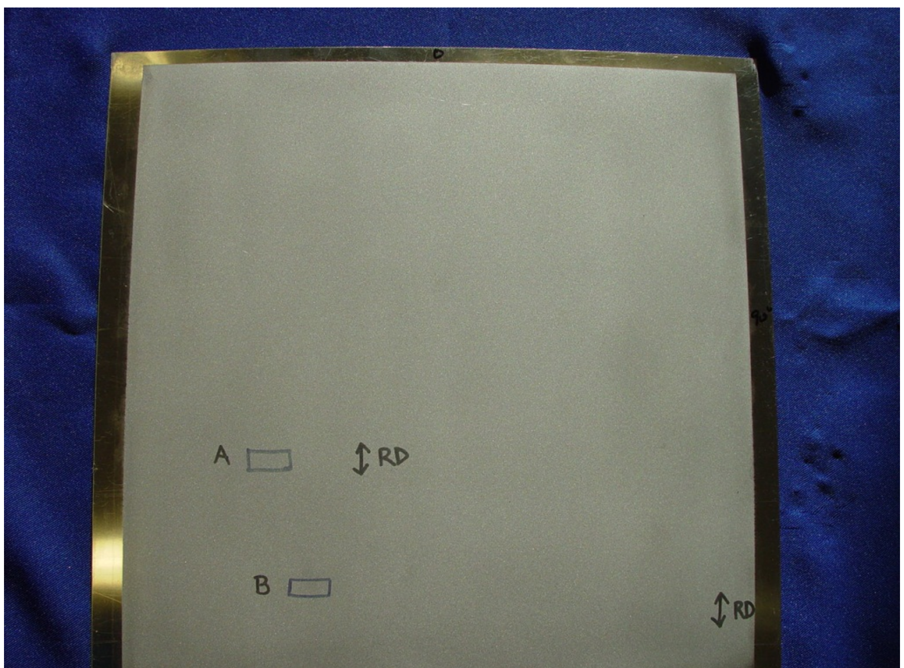


Source: Liu, Fergus, and Cruz, J. Am. Ceram. Soc., <u>96</u>, 1841 (2013)

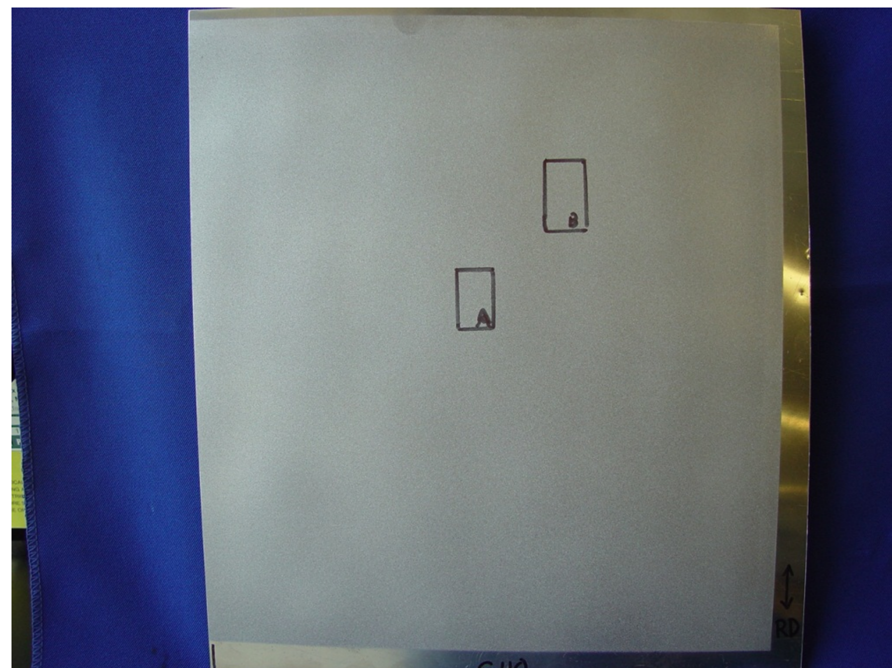
Optimization of Surface Blast Surface Modification

- 441 samples (0.5 mm) were prepared via surface grit blasting to further quantify and understand the effects of surface morphology on oxidation/ spallation behavior
  - Grit size was varied to evaluate two distinctively different processed surfaces (G80 vs. G40)
  - Long-term oxidation testing in progress

Grit size: G80 (0.125-0.425 mm)



Grit size: G40 (0.300-1.00 mm)



Summary

- PNNL is using experimental and computational methodologies to support SECA Industry Team SOFC development.
- Interconnects
  - Spinel-coated, surface-modified AISI 441 exhibits improved long-term scale spallation resistance compared to coated, unmodified AISI 441.
    - Surface blast appears to be most promising surface treatment
      - 26,000 hours at 800ºC (tests in progress)
      - 22,000 hours at 850ºC (tests in progress)
      - Topical Report delivered to SECA Industry Teams (January 2013)
- Cathodes
  - Cell test results indicate that effects of moisture (3% water) on degradation rate become more severe with decreasing temperature for both LSCF and LSM/YSZ cathodes.
- Anodes
  - Microstructural changes (Ni coarsening) observed at 900 and 1000°C at high fuel water contents.
- Compliant Seals
  - Preliminary results indicate excellent isothermal performance (>1000 hours) and stability towards thermal cycling

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- NETL: Shailesh Vora, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz
- ATI Allegheny Ludlum: Matt Bender
- ORNL: Edgar Lara-Curzio
- PNNL: Shelley Carlson, Nat Saenz, Dan Edwards, Clyde Chamberlin, and Alan Schemer-Kohrn

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