Advanced Interconnect Development at PNNL

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Presentation Outline

- Conclusions
- Objectives/Approach
- Background
- Results:
  - Oxidation behavior of AISI 441
  - Performance of Spinel-coated 441
- Future Work
- Conclusions
- Acknowledgements

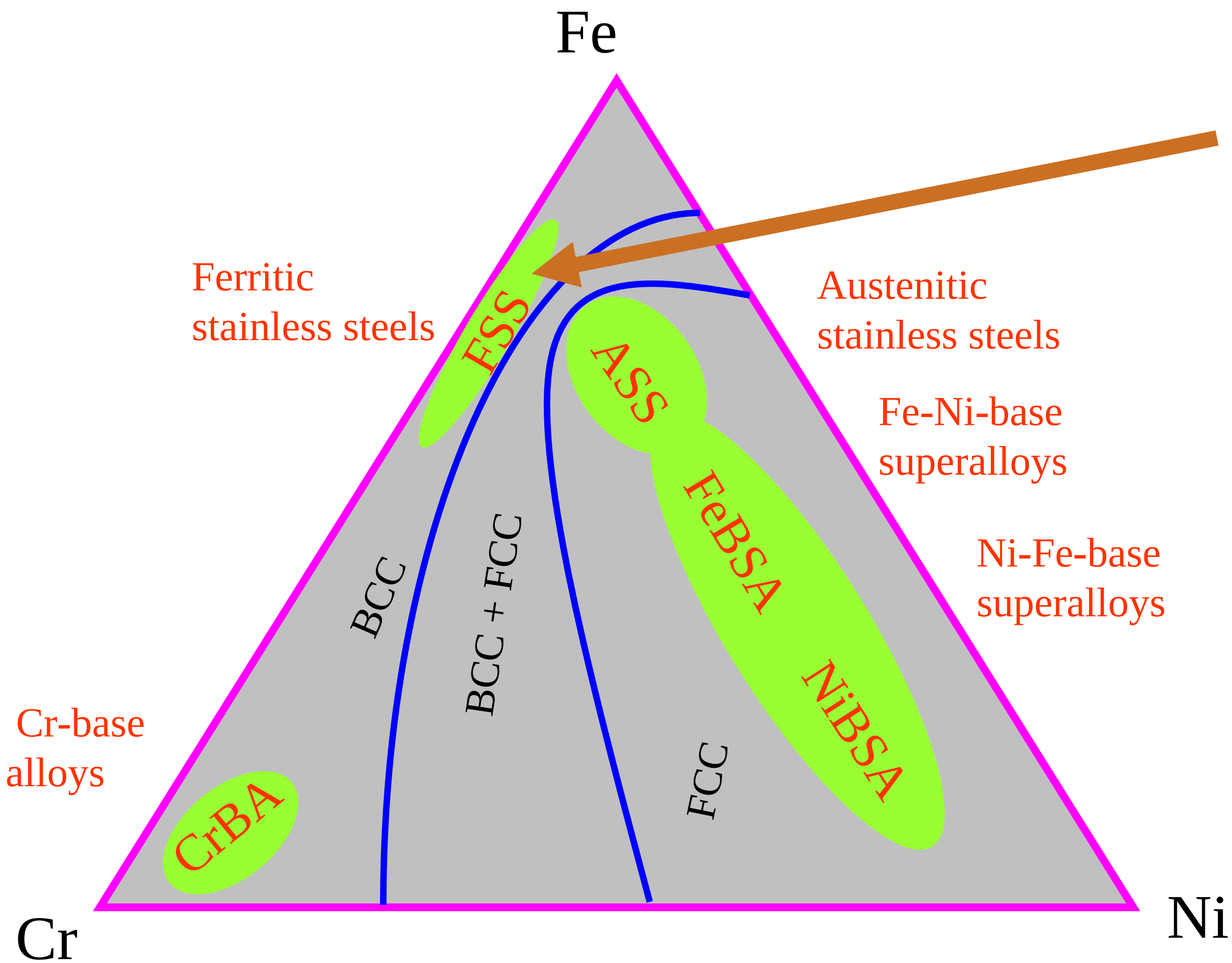
Conclusions/Accomplishments

- AISI 441 exhibits promising alloy chemistry
  - Expensive refining processes not required, so cost is reduced
  - Nb/Ti additions promote desirable Laves phase precipitation, leading to lower electrical resistance (and higher mechanical strength)
- Limitations identified through oxidation testing:
  - Poor scale adherence due to lack of rare earth additions
  - As with other FSS, protective coating is required due to inadequate intrinsic oxidation resistance, and Cr volatility
- Ce-modified MnCo spinel coatings exhibit the benefits of original MnCo coatings, but also result in improved scale adherence, presumably due to the rare earth (RE) effect (usually achieved through RE additions to base alloy)

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 Allegheny Technologies, Inc. and NETL
    - Emphasis on AISI 441 as alloy substrate
      - Modified alloys also being evaluated
    - Mn-Co spinel coatings for cathode-side protection
  - Characterization of candidate materials
    - Oxidation tests (including dual atmospheres – air vs. fuel)
    - ASR tests
    - CTE
    - Alloy, scale, and coatings chemistry via XRD, SEM, EDS, TEM, etc.

Alloy-based Interconnects: Background



Emphasis on "Chromia-forming" Ferritic Stainless Steels, because:

- CTE match
- Conductive, protective oxide scale
- Low cost
- Ease of fabrication

Also: Co-base superalloys

Candidate Interconnect Alloy: AISI 441

- Manufactured via conventional (inexpensive) 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

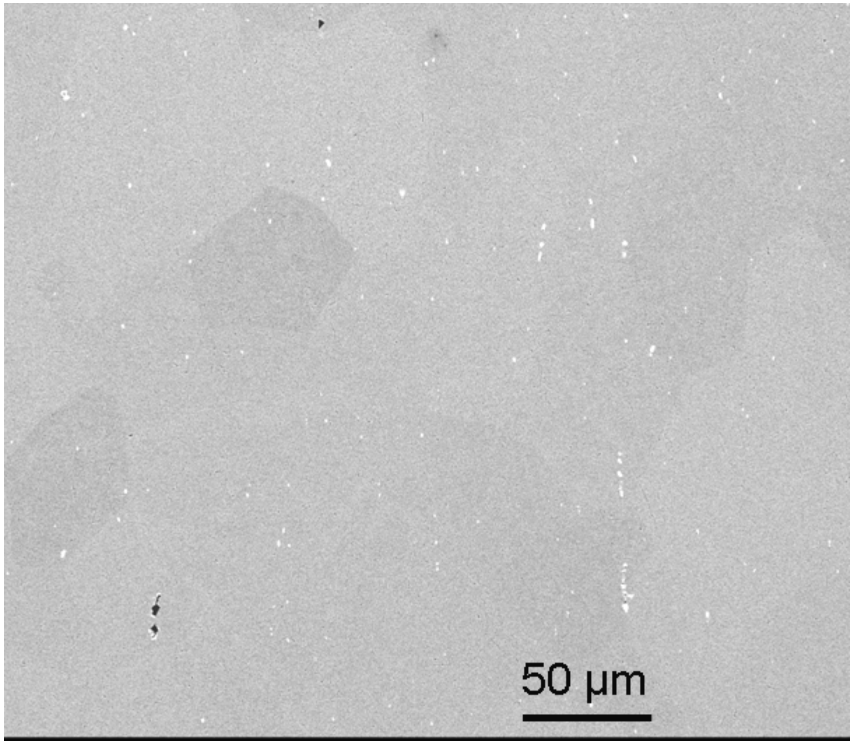
Typical Analysis:

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

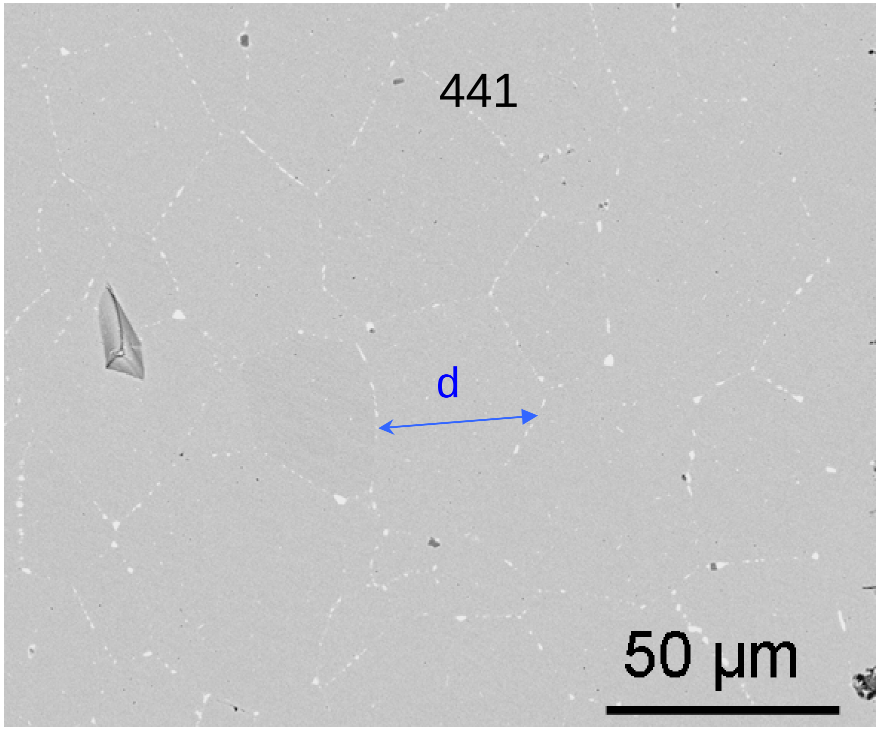
Sources: Allegheny Technologies, Inc.; Thyssen Krupp

Microstructural Evolution in 441

As-received



After 300 hrs oxidation in air at 800°C



- Second phase (Laves phase) randomly distributed in the alloy grains
- Intergranular precipitates decorate grain boundaries after oxidation
- No obvious grain growth during oxidation

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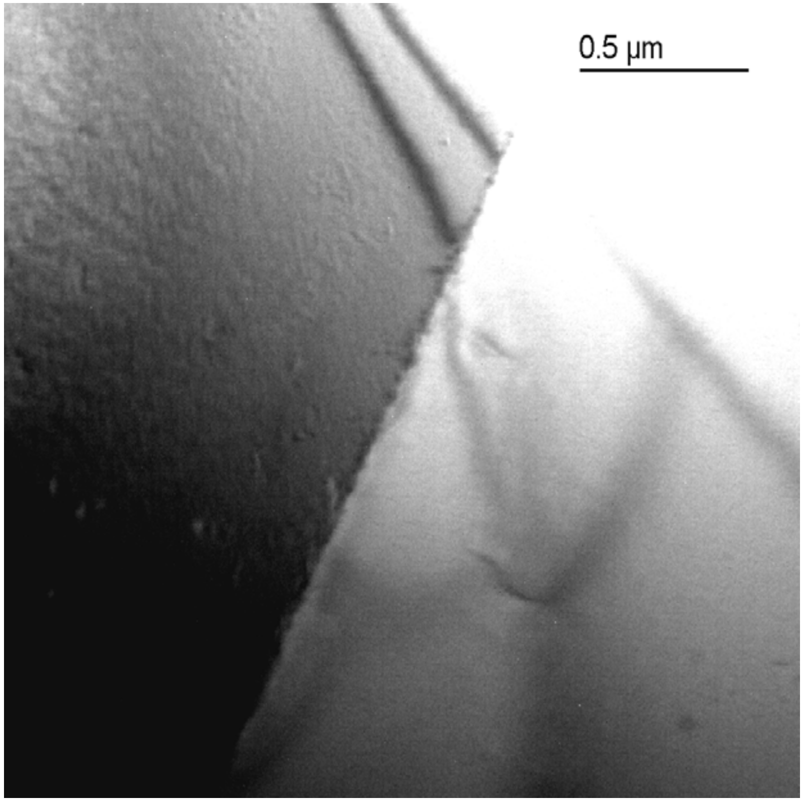
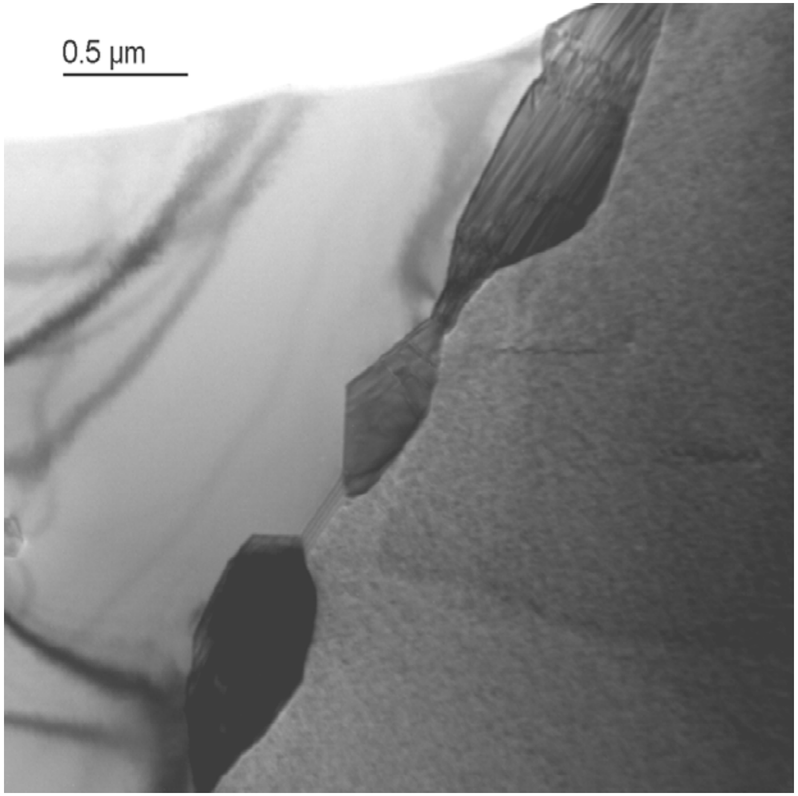
TEM Analysis of 441

As received



After 300 hrs oxidation in air at 800^{o}C



- As received: clean grain boundaries
- After oxidation, Laves phase precipitated along grain boundaries
  - Laves phase enriched in Ti, Nb, and Si

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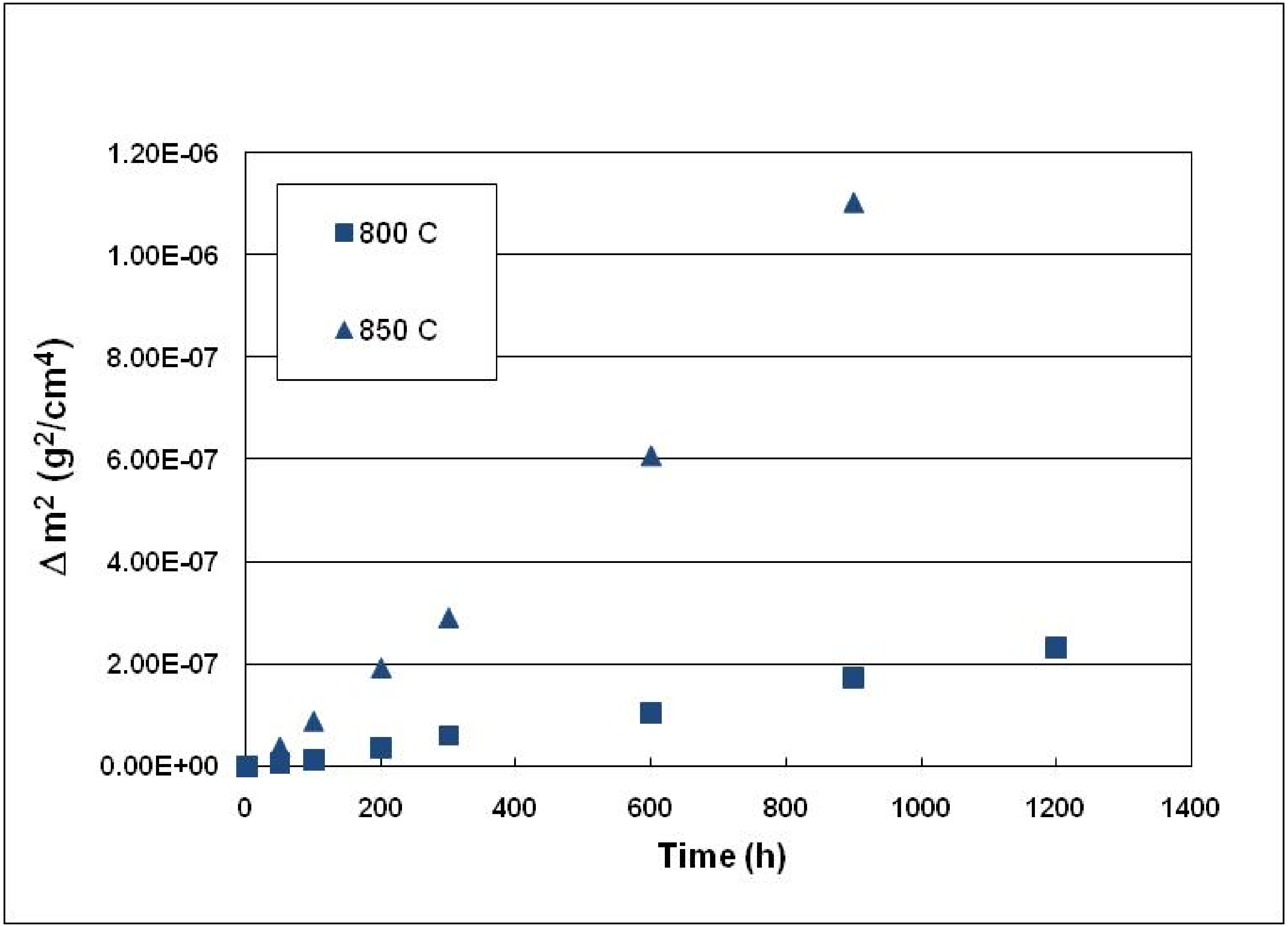
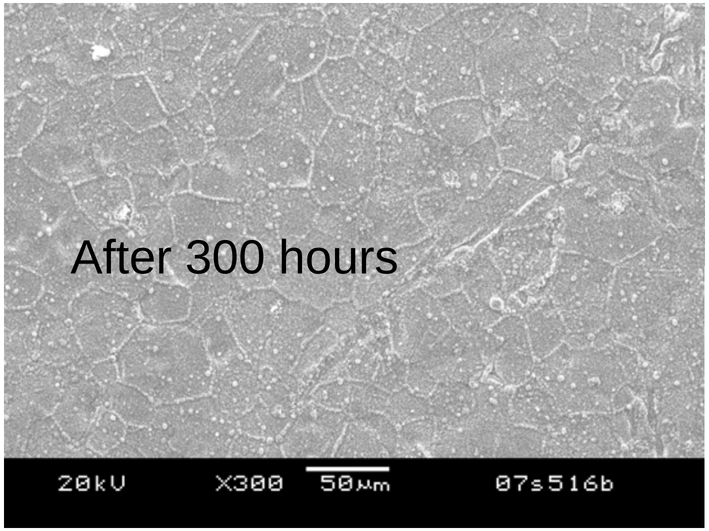
Oxidation Kinetics of AISI 441

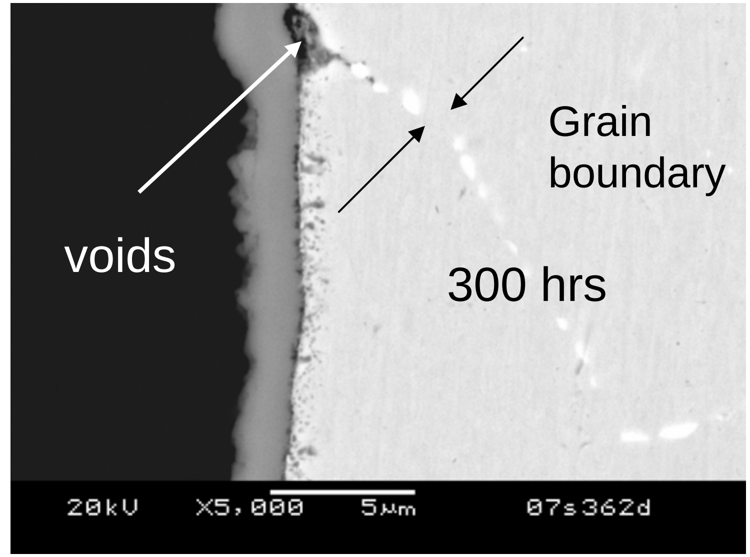


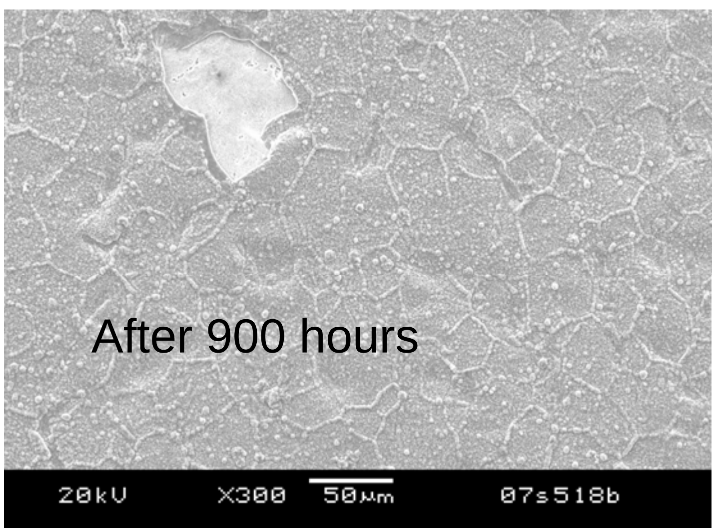
Approximately parabolic growth:
K(800) ~ 5 x 10^{-14} g^2/cm^4-sec

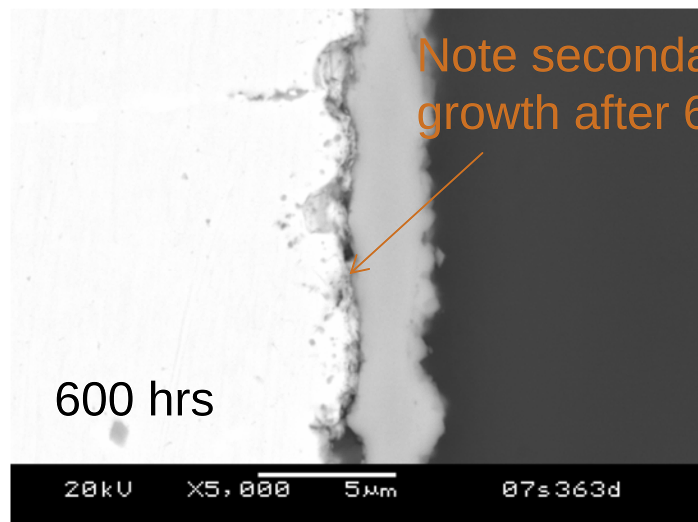
Issue: Weak Scale Adherence

Oxidized at 800^{o}C in air









Note secondary scale growth after 600 hours.

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

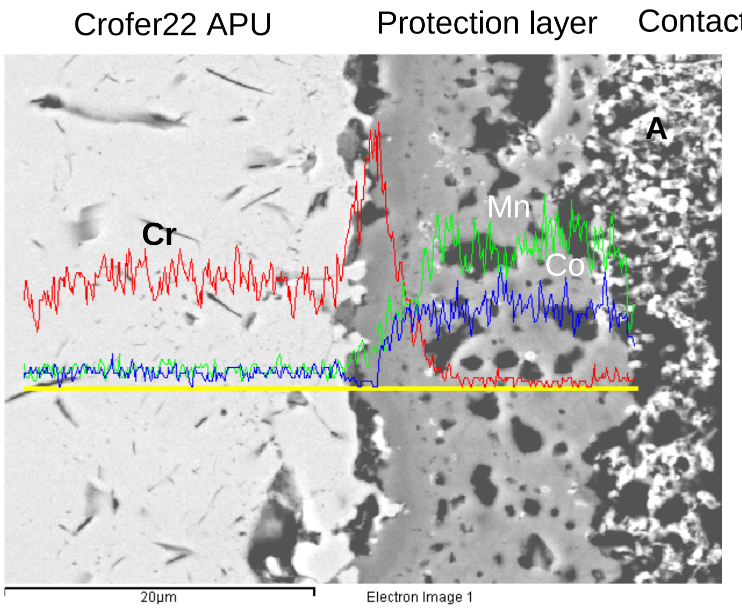
- High electrical conductivity
  ~60 S/cm at 800ºC

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

- Good CTE match to FSS and anode-supported cells

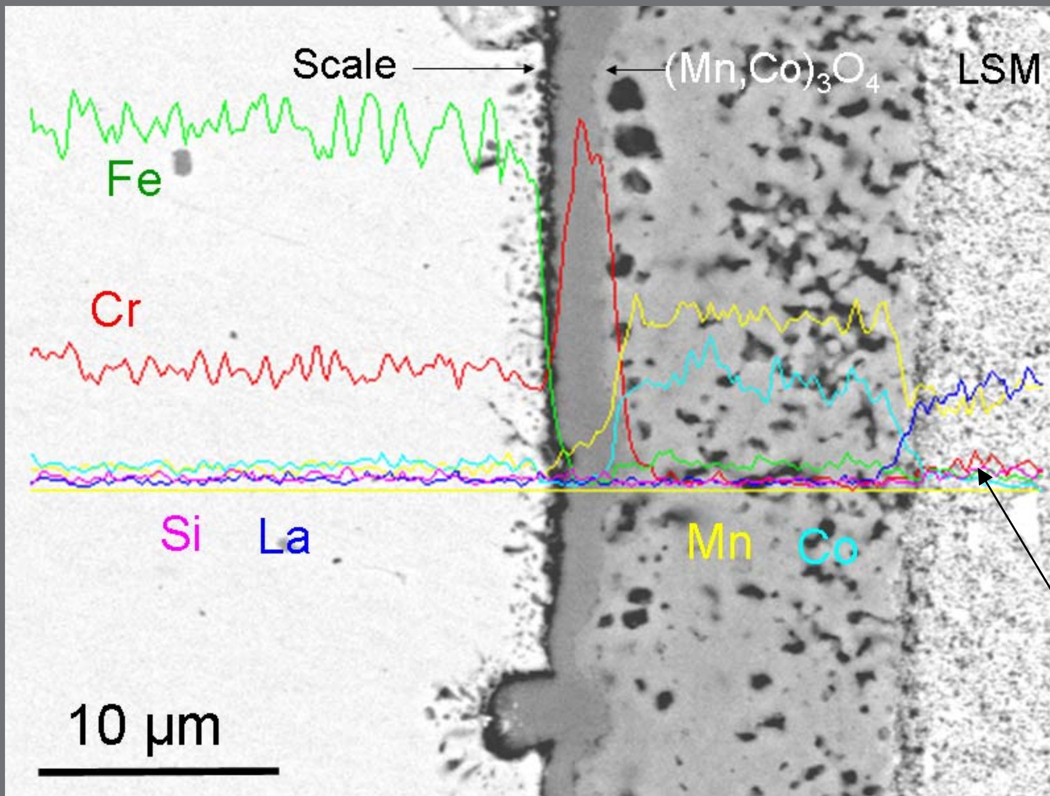
$$CTE_{Mn_{1.5}Co_{1.5}O_4} = 11.5\times10^{-6}K^{-1}, 20-800^{o}C$$

- 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

MC Spinel-Coated AISI 441



- ASR Test: 1000 hours at 800ºC in air.
- Note Fe migration into the spinel protection layers, presumably due to lower Cr (18%), but no Cr transport into coating. Fe migration not observed for Crofer22APU.
- No silica layer formation at alloy/scale interface, as observed with AISI 430.

Probably La overlap rather than Cr

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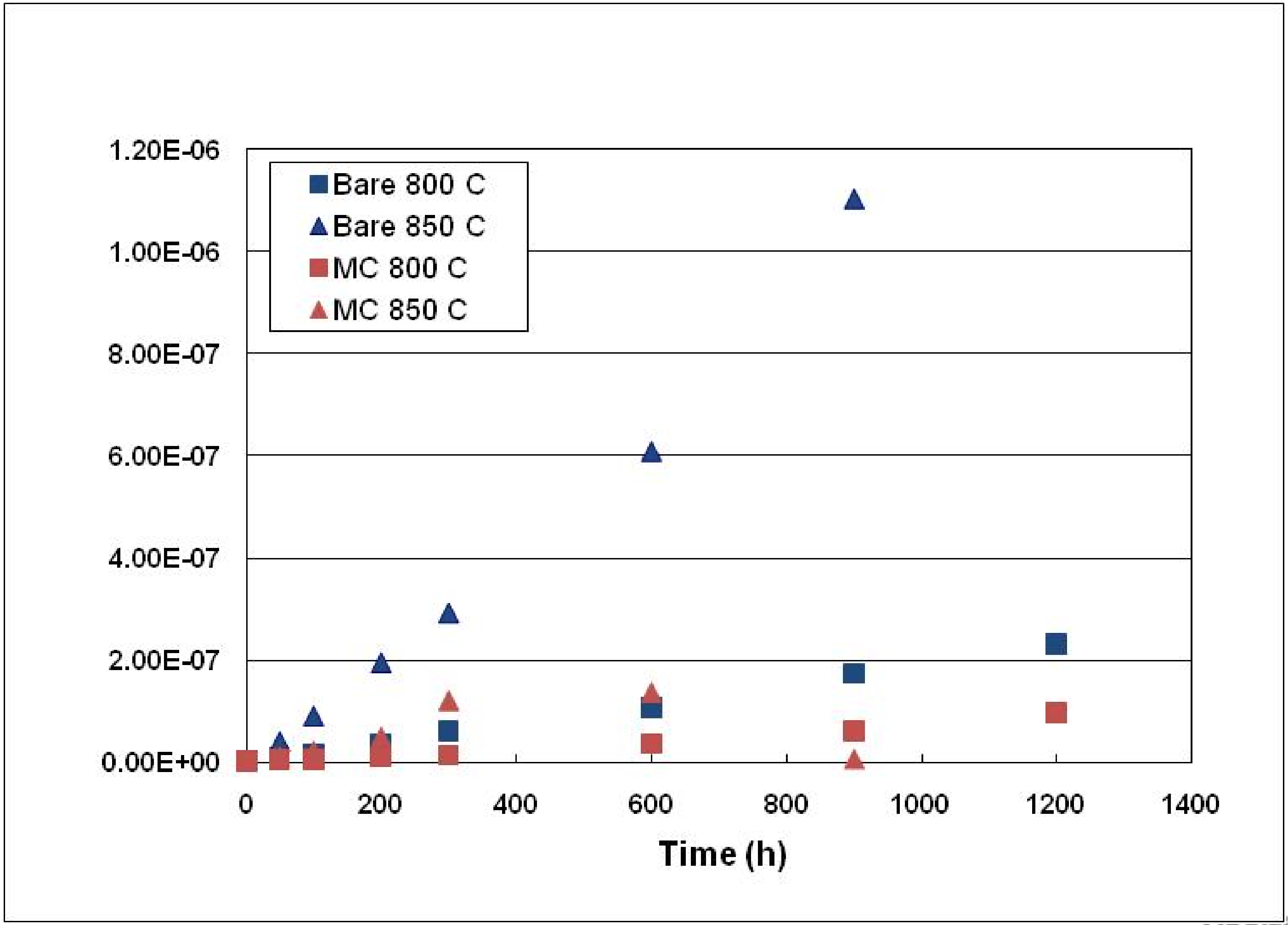
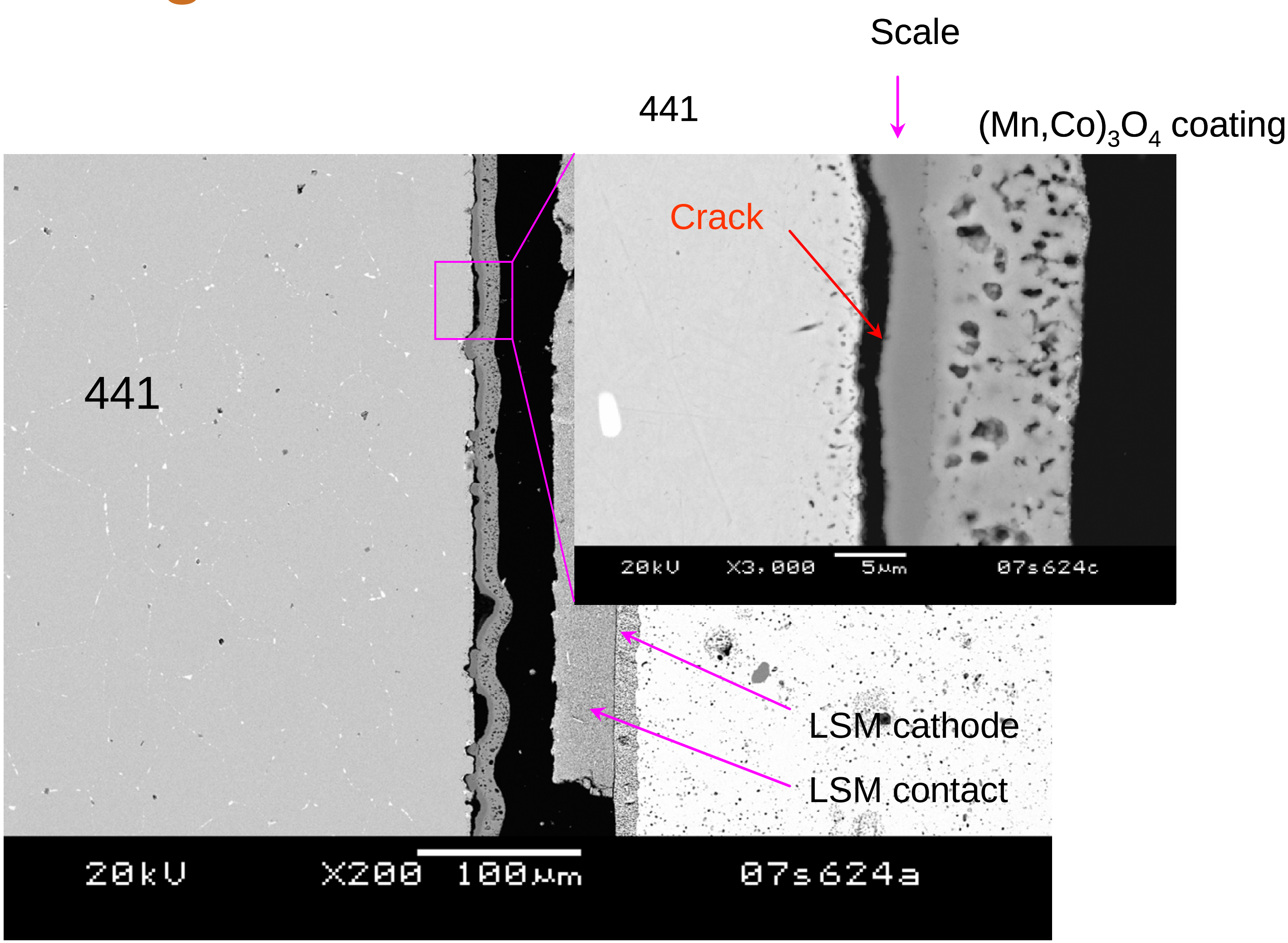
Oxidation Kinetics of AISI 441: Bare and MC Spinel Coated



Poor adhesion of scale under MC spinel coating



700 h, 850°C ASR measurement

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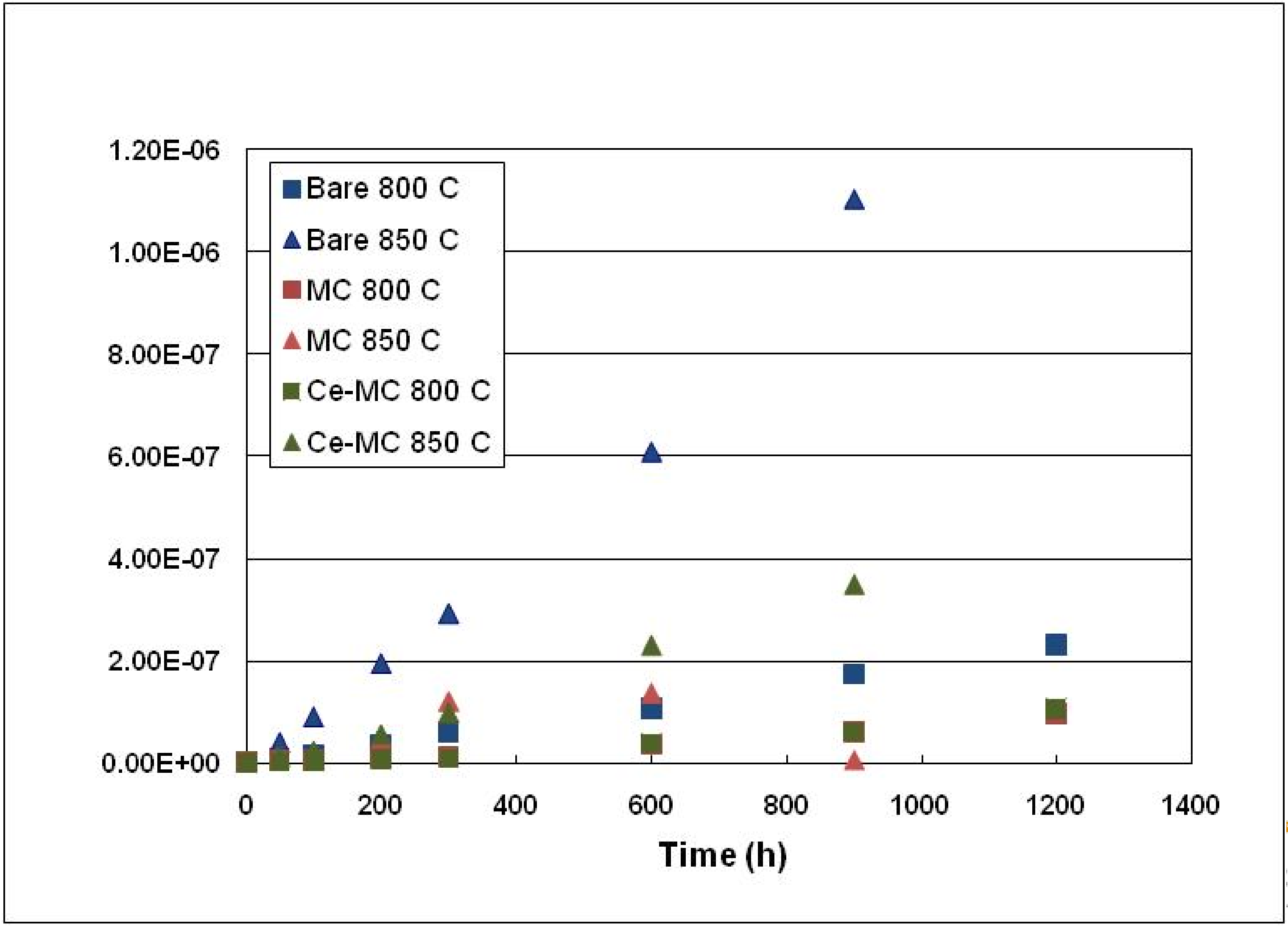
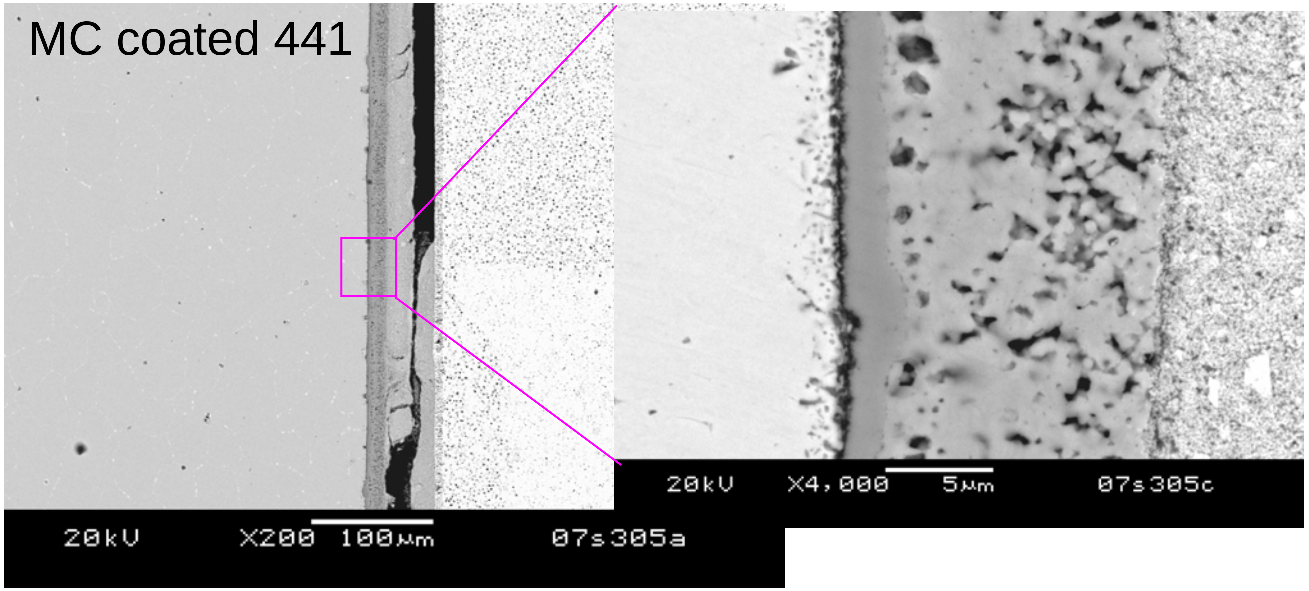
Ce-modified Mn-Co Spinel

- Motivation:
  - Rare earth (RE) additions (e.g., Ce, La) to alloys - well-established means of improving scale adherence
    - Crofer22APU has La addition; AISI 441 has no RE additions
  - NETL-Albany: Ce surface treatment leads to improved oxidation resistance, lower ASR
  - PNNL: Ce-modified Mn-Co spinel ($Ce_{0.05}Mn_{1.475}Co_{1.475}O_4$) coatings appear promising for improving scale adherence
    - Simple modification – Ce nitrate included in glycine/nitrate precursor
    - May provide
      - Established benefits of MC spinel coating (improved oxidation resistance, lower ASR, Cr volatility mitigation)
      - Benefits of rare earth effect without need for RE additions to alloy

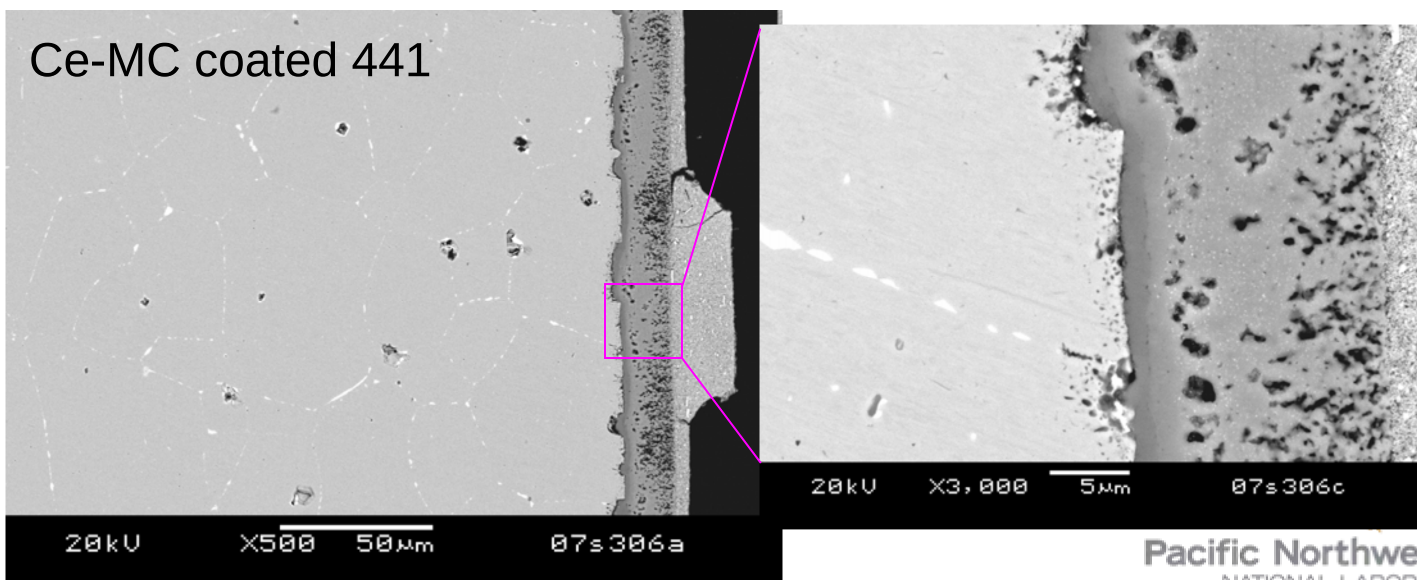
Oxidation Kinetics of AISI 441: Bare, MC Spinel Coated, and Ce-MC Spinel Coated



Improved Scale Adherence with Ce-MC Coatings



After 1,000 h, $800^{o}C$ ASR measurement



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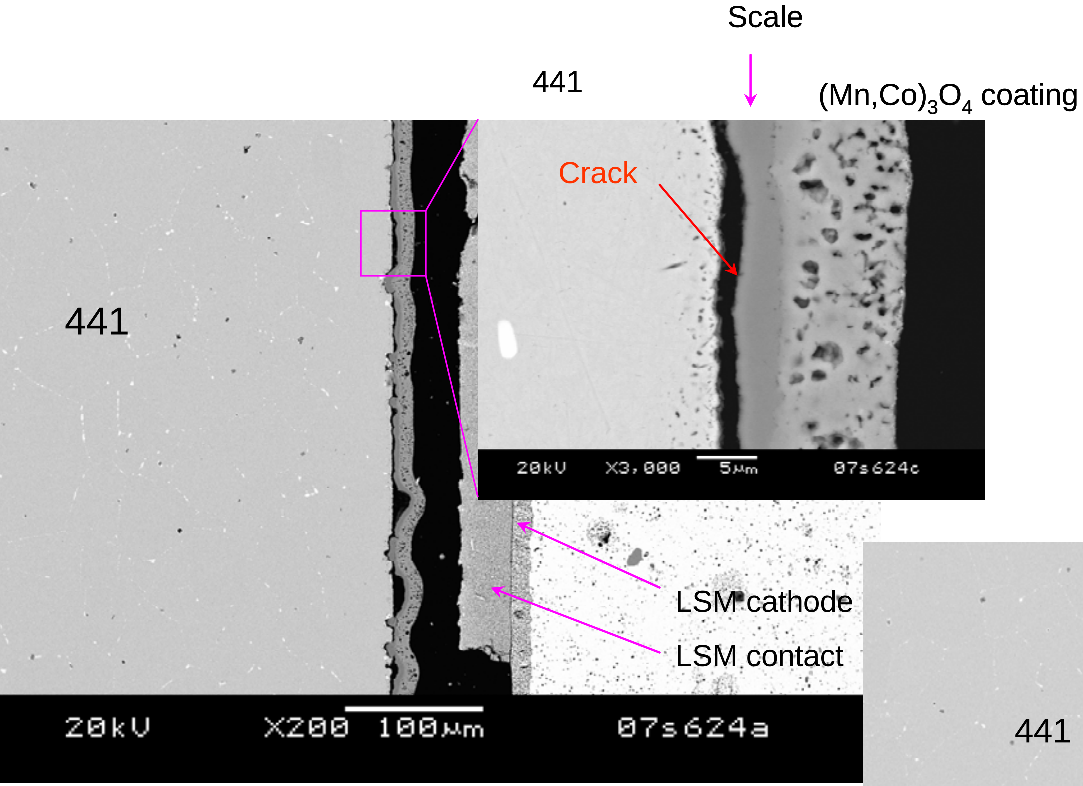
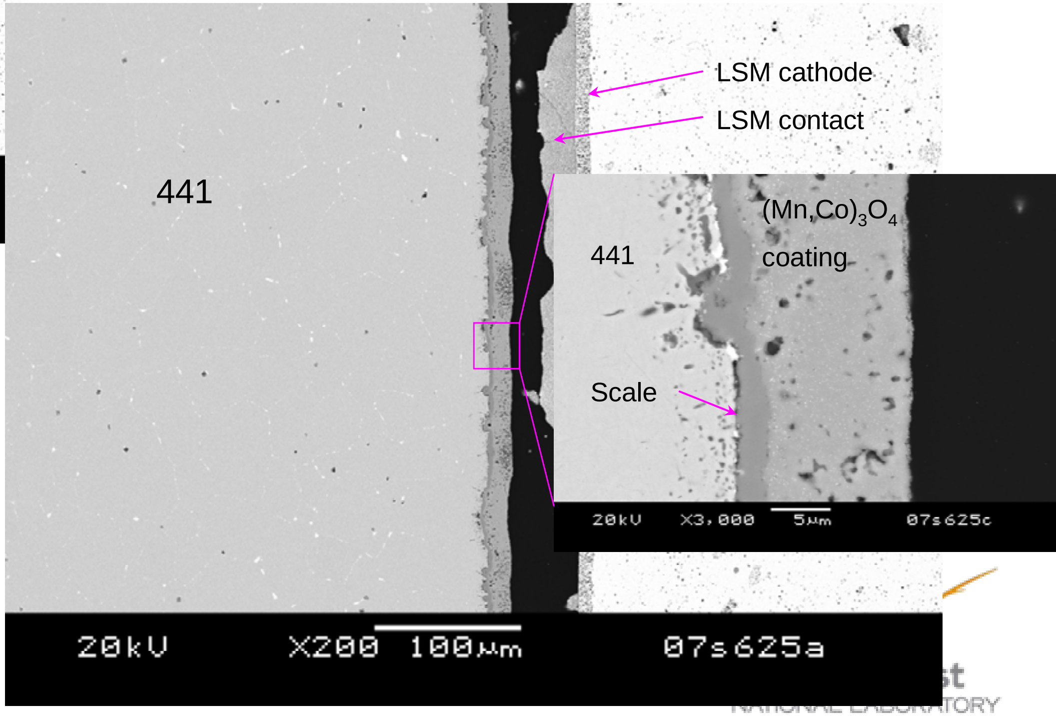


MC coated 441

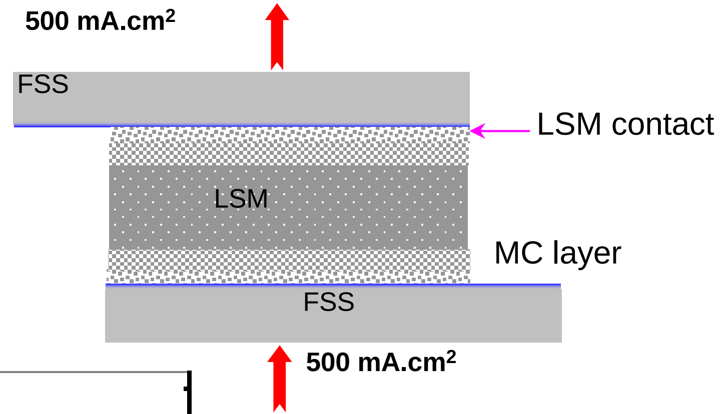
After 700 h, 850ºC ASR measurement (similar results at 800ºC)

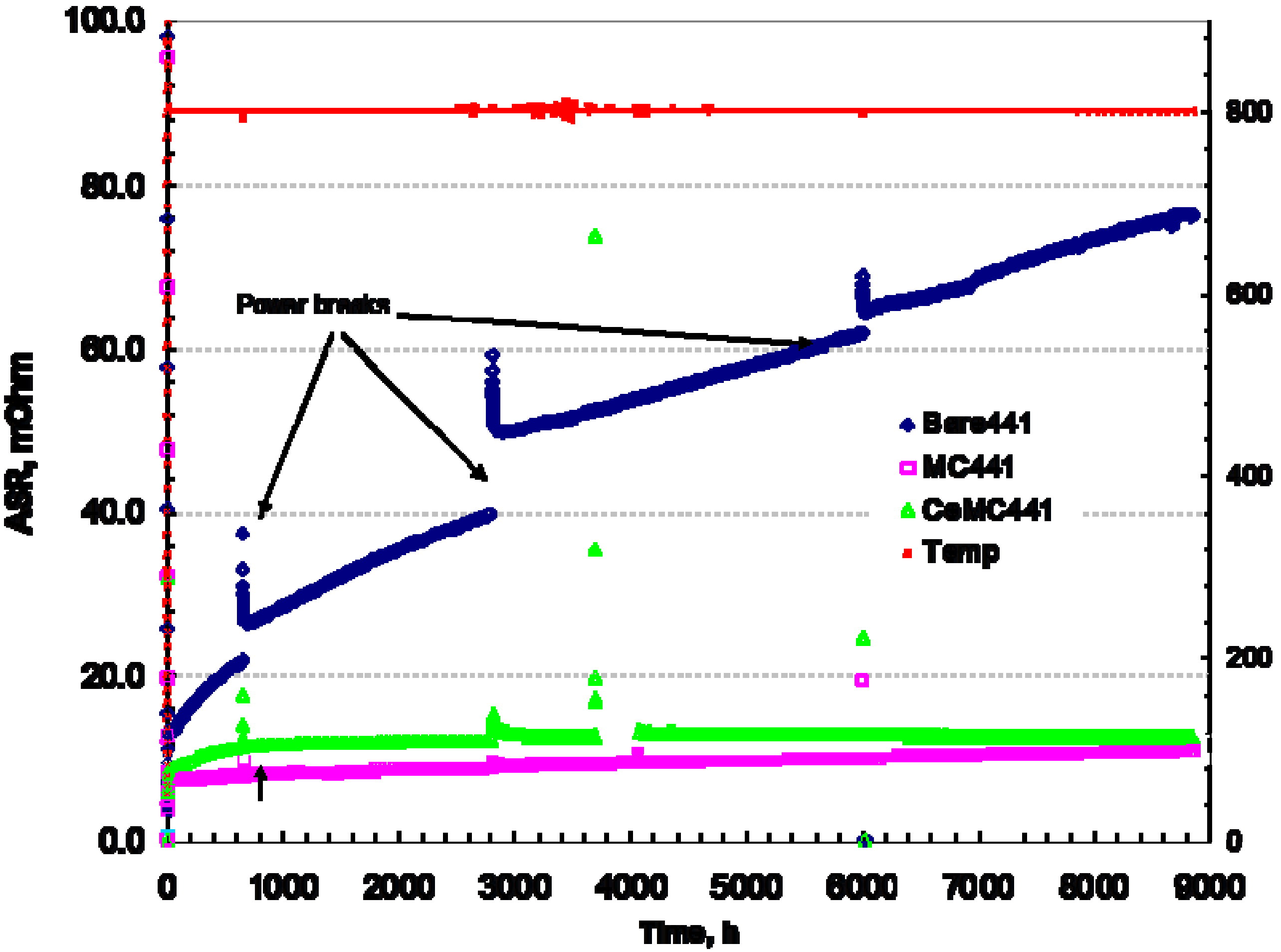
Ce-MC coated 441



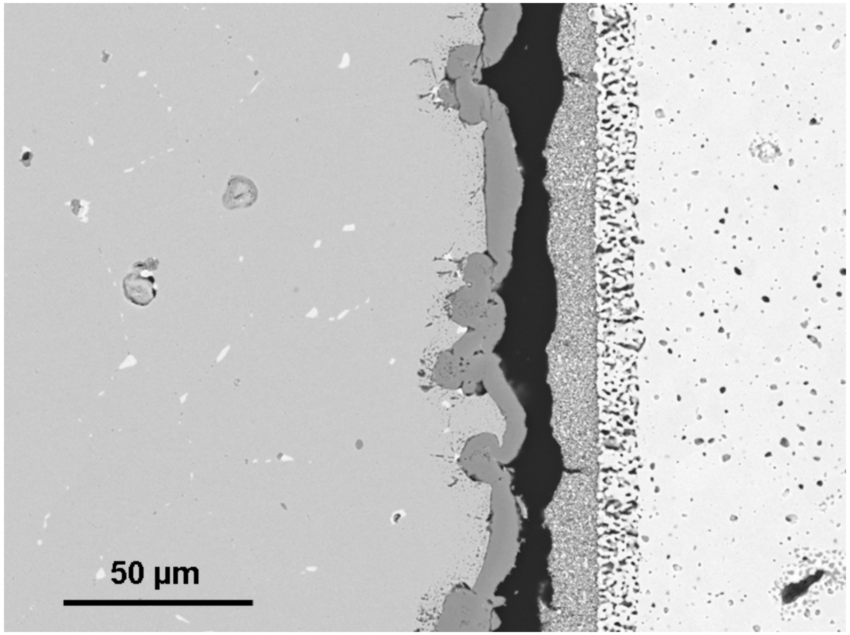
Ce-MC coating:
$Ce_{0.05}Mn_{1.475}Co_{1.475}O_4$

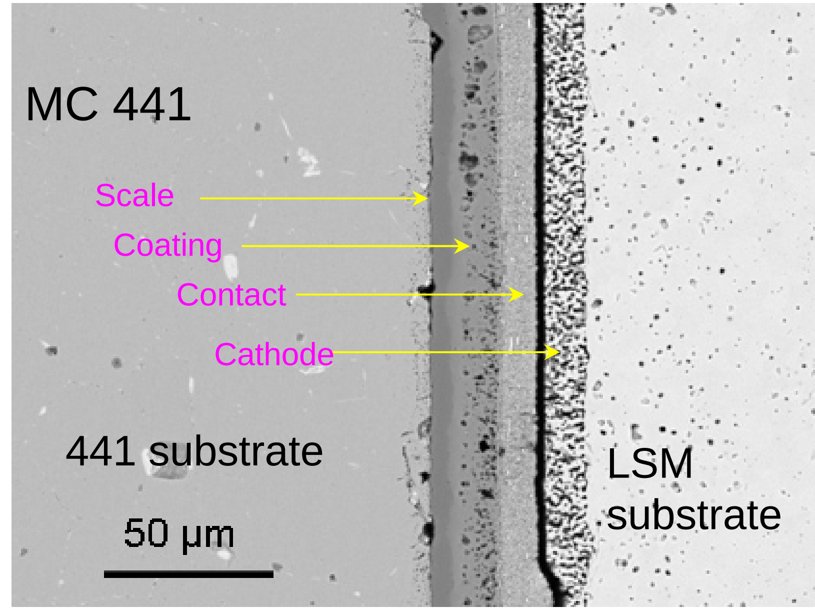
Electrical Testing of 441

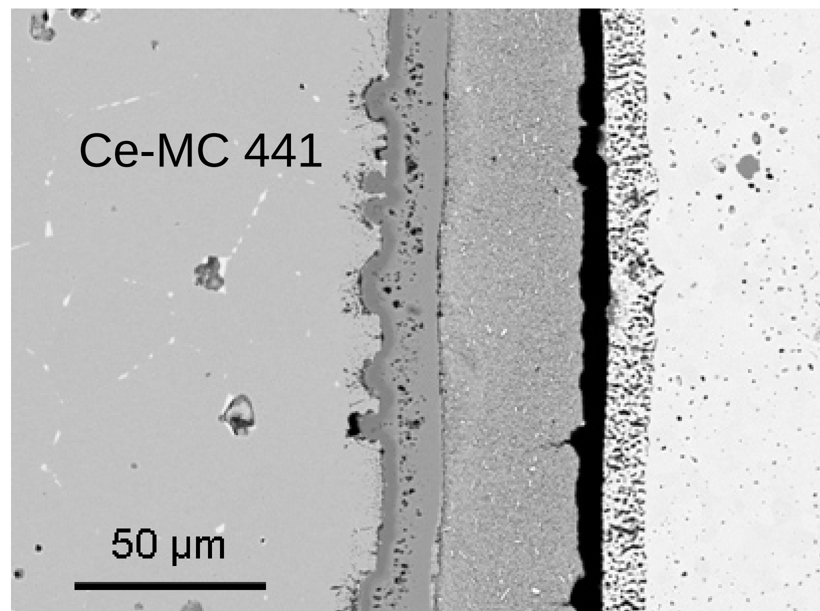




SEM Analysis on 1 year ASR Test

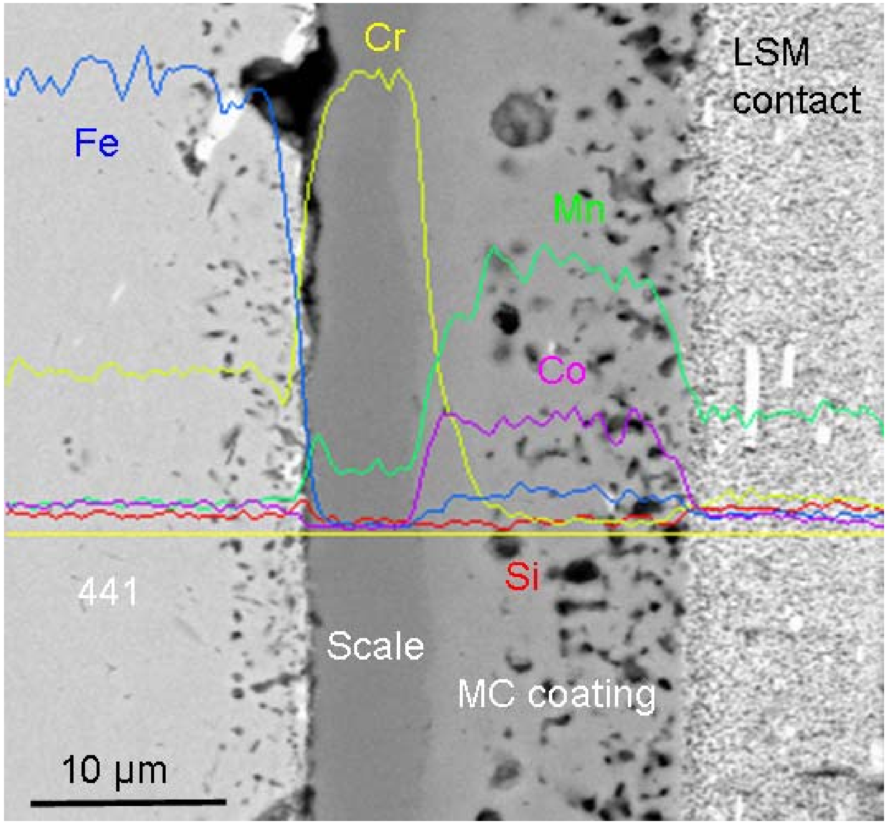


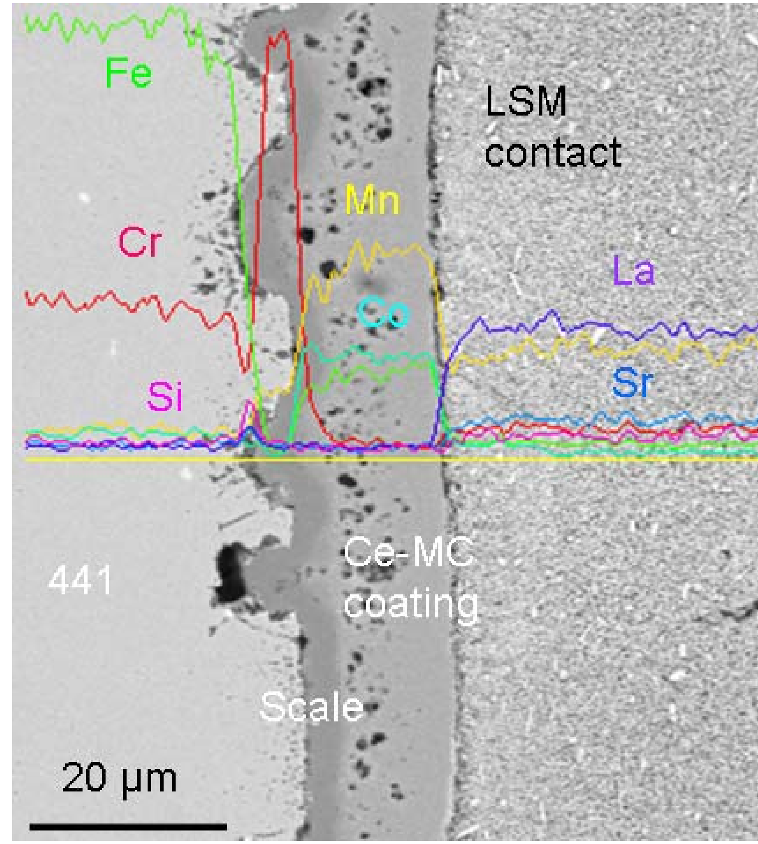




- ❑ No detachment along scale/steel interfaces; Spallation was observed on bare 441 surface (not shown).
- ❑ Scale growth rates: Bare > MC > Ce-MC
- ❑ Ce altered interface morphology: smooth scale/metal interface for MC 441, rough interface for Ce-MC 441 (also for bare, possibly due to the La in contact material)

SEM Analysis on 1 year ASR Test

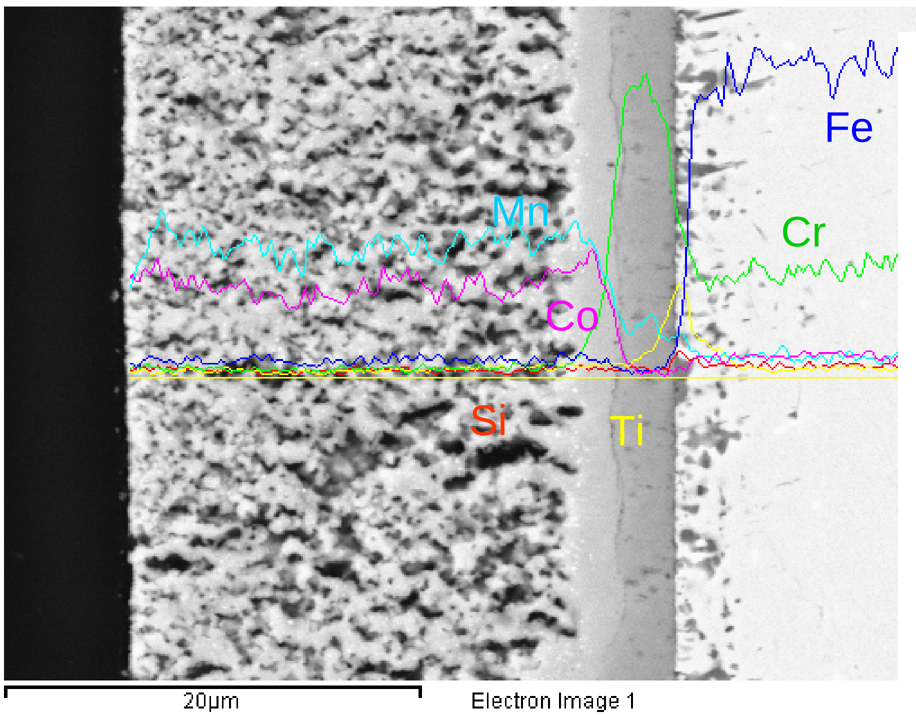




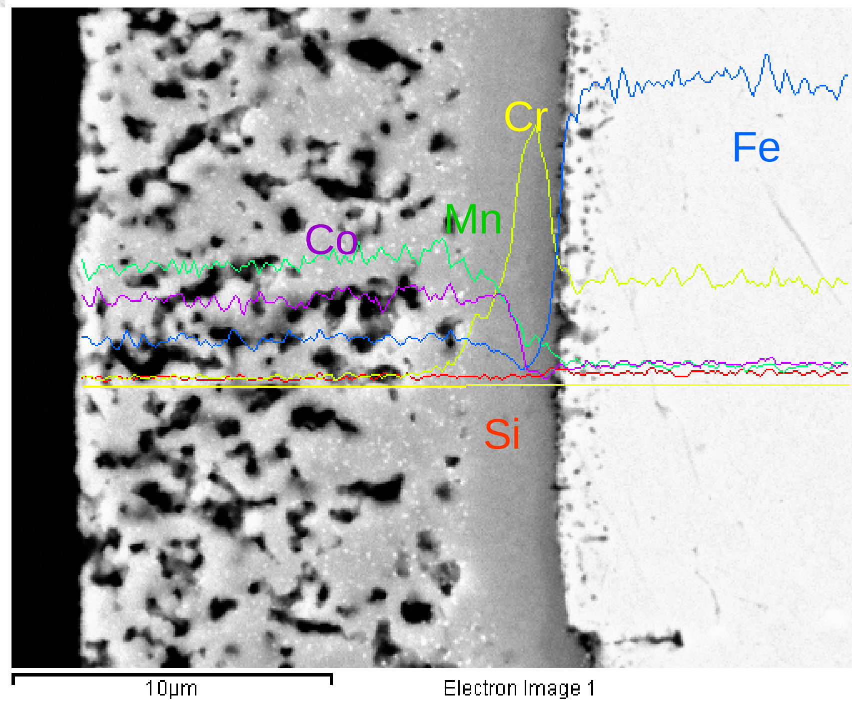
- No Cr-penetration into MC or Ce-MC protection layers, as confirmed by EDS point and area analyses.
- Some Fe transport into the MC or Ce-Mc protection layers.
- EDS analyses found neither Cr nor Fe in LSM contact (apparent increase in Cr profile in contact is due to spectra overlap of Cr and La).

Dual Exposure Testing of Ce-MC Spinel-Coated AISI 441

- Moist air vs. moist hydrogen, 1000 hours, 800ºC
- Air only exposure: Effective barrier only to Cr, but not Fe.
- Air side of dual exposure: Inhibited Fe transport may have caused reduced sintering activity of the Ce-MC coating on the airside; no nodule formation; good scale adherence



Airside of the sample that was exposed to air at one side and moisture hydrogen at the other



The sample that was exposed to air at both sides

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Conclusions

- AISI 441 exhibits promising alloy chemistry
  - Expensive refining processes not required, so cost is reduced
  - Nb/Ti additions promote desirable Laves phase precipitation, leading to lower electrical resistance (and higher mechanical strength)
- Limitations identified through oxidation testing:
  - Poor scale adherence due to lack of rare earth additions
  - As with other FSS, protective coating is required due to inadequate intrinsic oxidation resistance, and Cr volatility
- Ce-modified MnCo spinel coatings exhibit the benefits of original MnCo coatings, but also result in improved scale adherence, presumably due to the rare earth (RE) effect (usually achieved through RE additions to base alloy)

Future Work

- Evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 under dual atmosphere (w/ simulated coal gas fuel) and thermal cyclic conditions.
- Optimize RE-modified MC coatings (composition, fabrication procedures) on Fe-Cr-Nb-Ti steels.
  - Composition: La as alternative to Ce, reduction in Co content
  - Fabrication: Optimize heat treatment conditions (reducing, oxidizing) for improved density; Develop automated spray process for larger, shaped parts.
- Investigate oxidation and corrosion at anode-side, in particular in a coal gas environment, and, if required, develop protective solutions for long-term stability.

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