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Computational Modeling and Assessment of Nanocoatings for USC Boilers

DE-FC26-07NT43096
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Outline

- Project background, technology, and approach
- Coating selection
- Initial results
- Processing changes & research
- Current results

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Background

- Typical boiler wastage rates:
  - Subcritical – 20 mils (0.5mm)/year
  - Supercritical – 40-100 mils (1.0-2.5mm)/year
- Corrosion rates tend to increase with increasing temperatures.
- Higher operating metal temperature of supercritical boiler tubes tend to increase corrosion rates by 2-5X

Equivalent Availability Loss from Boiler Tube Failures in U.S. is 2.5-3.0%

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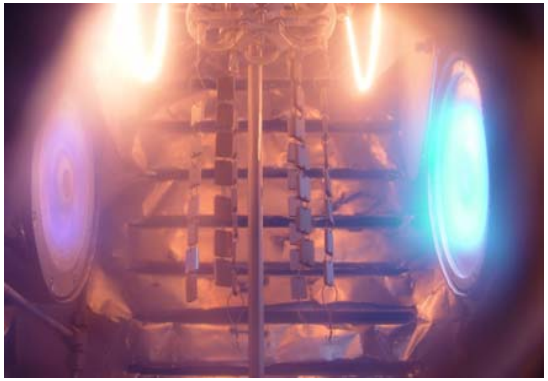
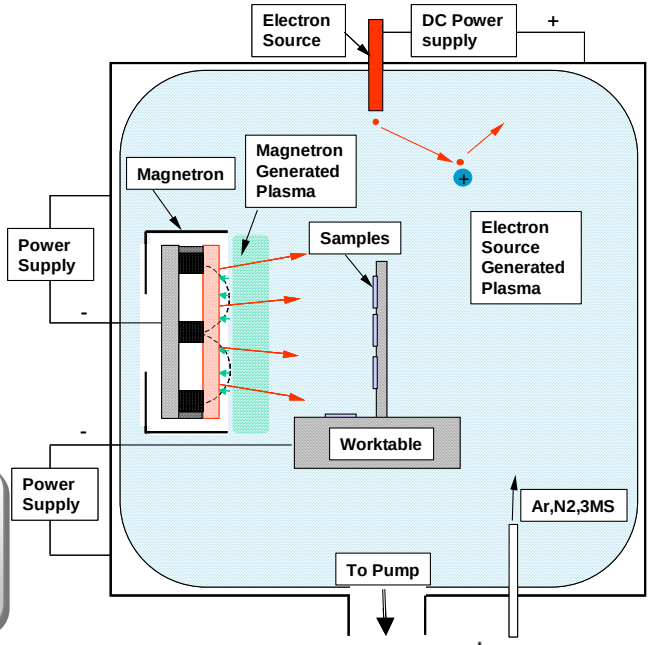
Background: Physical Vapor Deposition (PVD) and Plasma Enhanced Magnetron Sputtering (PEMS)

Distinct advantages of the process:

- *Ion sputter cleaning* is used to fully remove surface contaminants
- Plasma generated during the coating stage fills the entire chamber and *greatly increases the current density to a substrate*
- *Used to produce nanostructured coatings (grain size <100nm)*



1m x 1m x 1m Vacuum Chamber (SwRI)



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PEMS Technology is well advanced and being used for erosion & wear applications

- Nanocomposite & single phase coating
  - Up to 80 μm in thickness; 2-5μm for cutting tools & 20-80 μm for erosion resistant applications
  - TiSiCN, ZrSiCN, TiN, ZrN, CrN, etc.
- Equipment includes: end-mills, gear shapers and hobs, airfoils, valve stems

Malcomized Inconel 901 steam turbine valve stem prior to field-trial installation with a TiSiCN Nanocoating produced by PEMS process

Military turbine blade airfoils coated with PEMS

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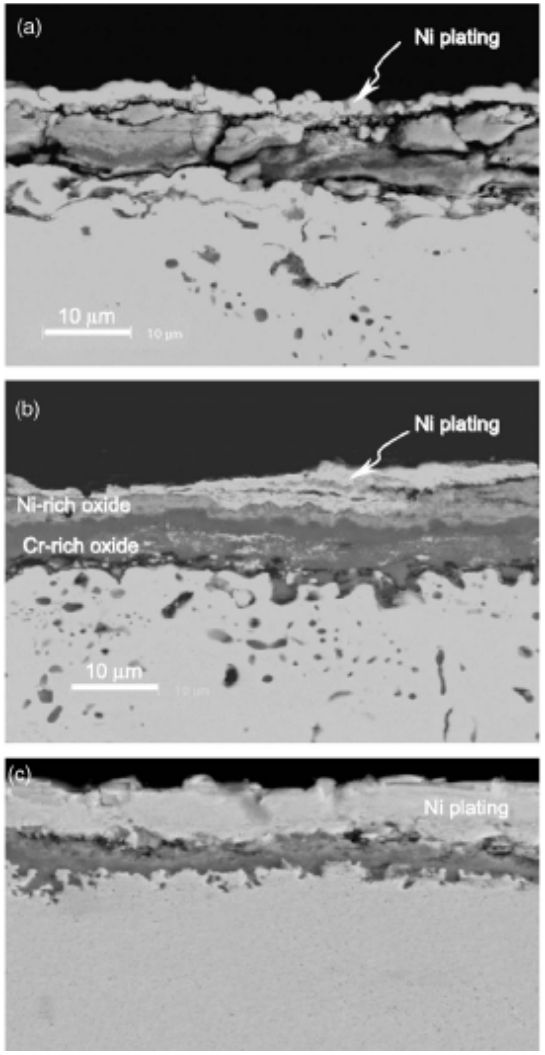
Why evaluate nanocoatings for boiler fireside corrosion?

Nanostructure lowers the Cr requirement

- Ni-10% conventional coating was severely corroded (no continuous chromia scale!)
- Continuous chromia scale was formed under the Ni-rich oxide in Ni-20% Cr coating - showed minor internal sulfidation
- Nanostructured Ni-11% coating showed continuous chromia scale (no sulfidation)



Ni-10% Cr Conventional

Ni-20% Cr Conventional

Ni-11% Cr Nanostructure

K2SO4-20%NaCl-10K2SO4 @ 700°C for 50 hrs

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DOE Nanocoatings Project Objectives (DE-FC26-07NT43096)

- Develop/demonstrate *nano-structured coatings* using computational modeling methods to improve corrosion/ erosion performance of tubing in USC boiler applications.

- Improve the reliability/availability of USC fossil-fired boilers and oxy-fuel advanced combustion systems by developing advanced nano-stuctured coatings:
  1. optimized utilizing science-based computational methodologies
  2. validated via experimental verification and testing in simulated boiler environments

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Project Tasks – Project Completion June 2011

- Task 1: Computational Modeling of MCrAl Systems (100%)
- Task 2: Establishment of Baseline Coating Data (100%)
- Task 3: Processing Advanced MCrAl Nanocoatings (95%)
- Task 4: Fire-Side Corrosion Testing (90%)
- Task 5: Computational Modeling & Validation (95%)
- Task 6: Project Management & Reporting (95%)

- Reports:
  - Task 1&2 Technical Report Published
  - Task 3 Technical Report Published (first iterations)
  - Task 4 Technical Report Published (first iterations)
  - Task 5 Technical Report – In progress
  - Final Report - June 2011 (includes Task 3&4 results for optimized coatings)

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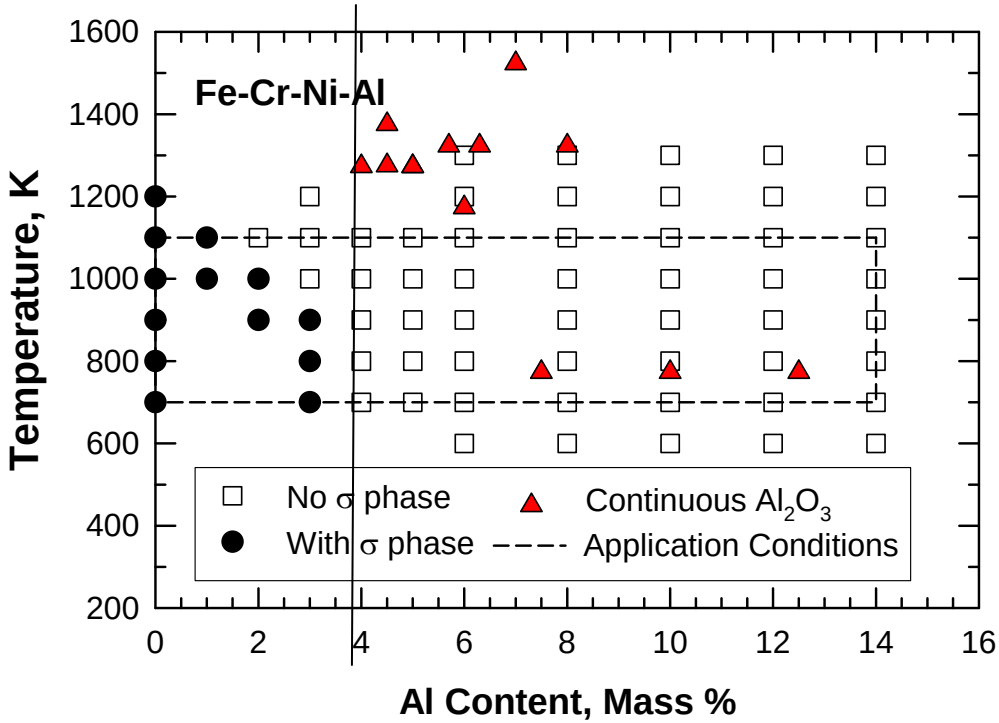
Task 1- Computional Modeling Of MCrAl Composition Selection

- Completed computations of FeNiCrAlx phase diagrams
- Developed grain growth, sintering and diffusion models
- Determined interface toughness

- Al additions suppress sigma phase formation, while Mo and Co promotes.
- 4-5%Al is required to form a continuous Alumina scale and to suppress sigma.

- To ensure sufficient Al source, 10% Al (min) is selected.



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Candidate Nanocoatings for Evaluation

Model Recommendation

- Coating composition: Fe-30/40Ni-25Cr-10Al
  - A patent disclosure was filed on the composition

Four Candidate Nanocoating Compositions Selected For Evaluation

Iron base coatings

- 310 + Al (Fe-25Cr-20Ni-10Al)
- Haynes 120+Al (Fe-37Ni-25Cr-10Al)

Nickel base coating

- Haynes 160+Al (Ni-29Cr-28Cr-3Si-10Al)

Cobalt base coating

- Haynes 188+Al (Co-22Ni-22Cr-14W-10Al)

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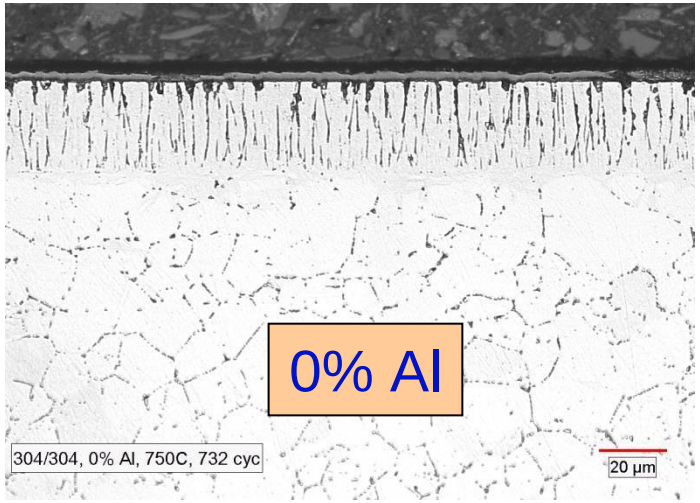
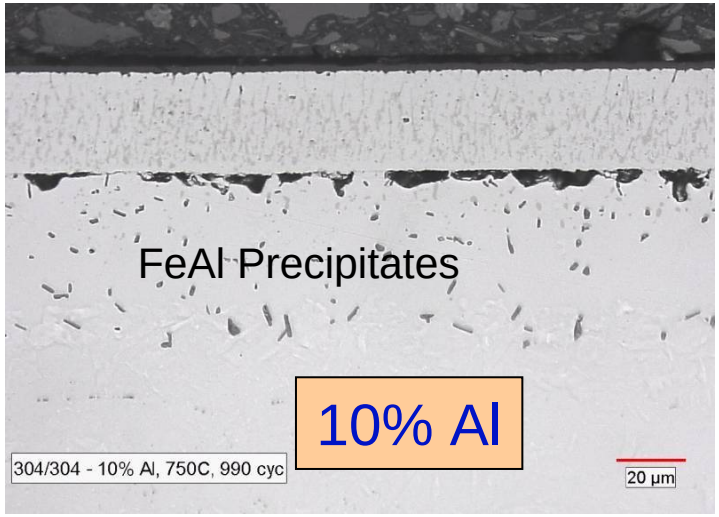
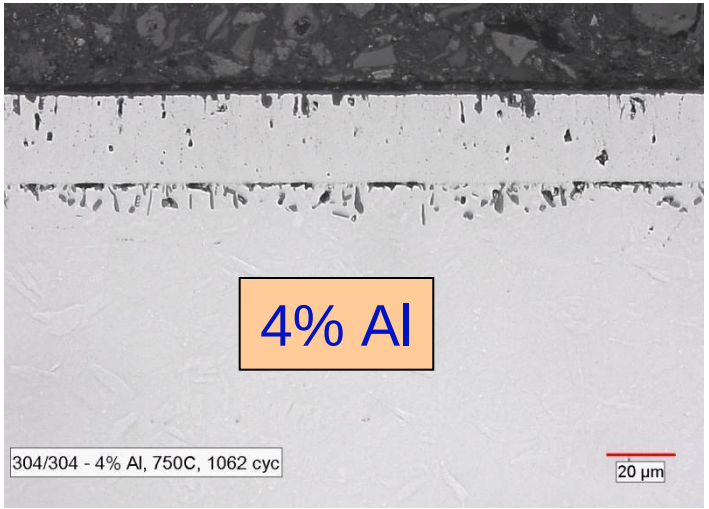
Task 2. Baseline Coating Oxidation Characterization -- Fe-18Cr-8Ni-xAl





After 990 cycles @750ºC



1). The protective oxide layer

- 0% Al coating Cr_2O_3
- 4 and 10%Al coatings Al_2O_3

2). **Inward diffusion of Al led to formation of inter-diffusion zone with FeAl particles**

3). Al content in the coating dropped from 10% to 3.7% after 990Cycles

Interdiffusion of Al is a concern

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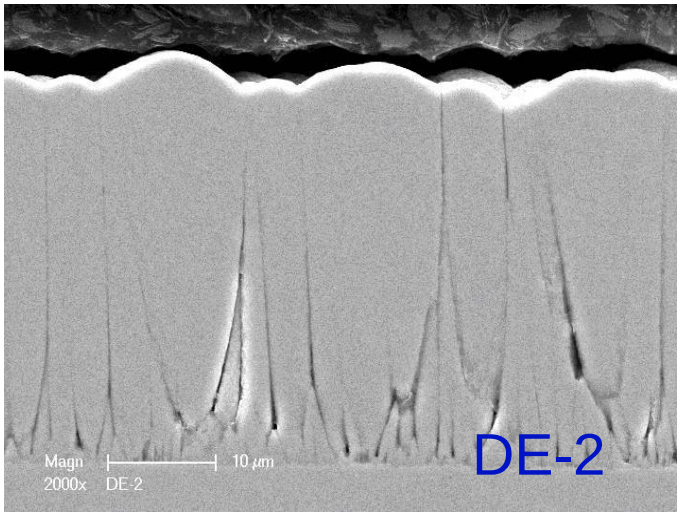
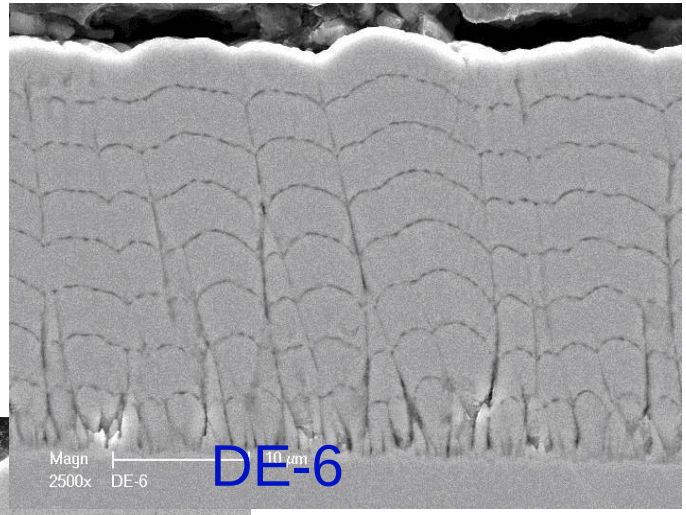
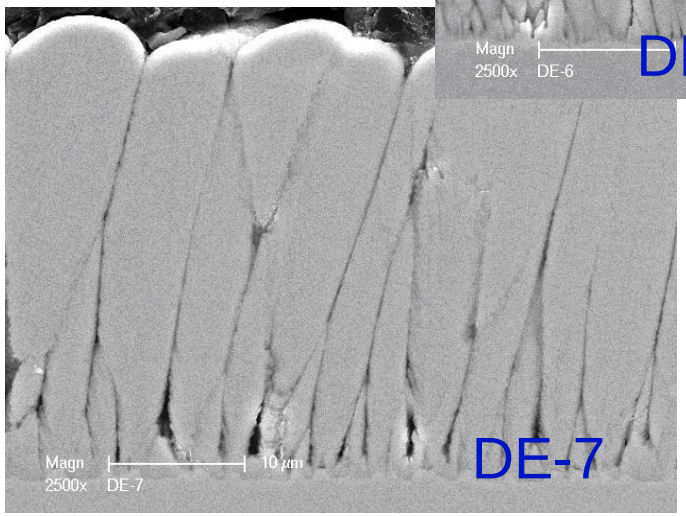
Task 3 - Processing of Advanced NanoCoatings -Metallographic Examination of Initial Trials

Result: Columnur Grain Nanocoating Microstructures



2000X





Non-optimum coating conditions

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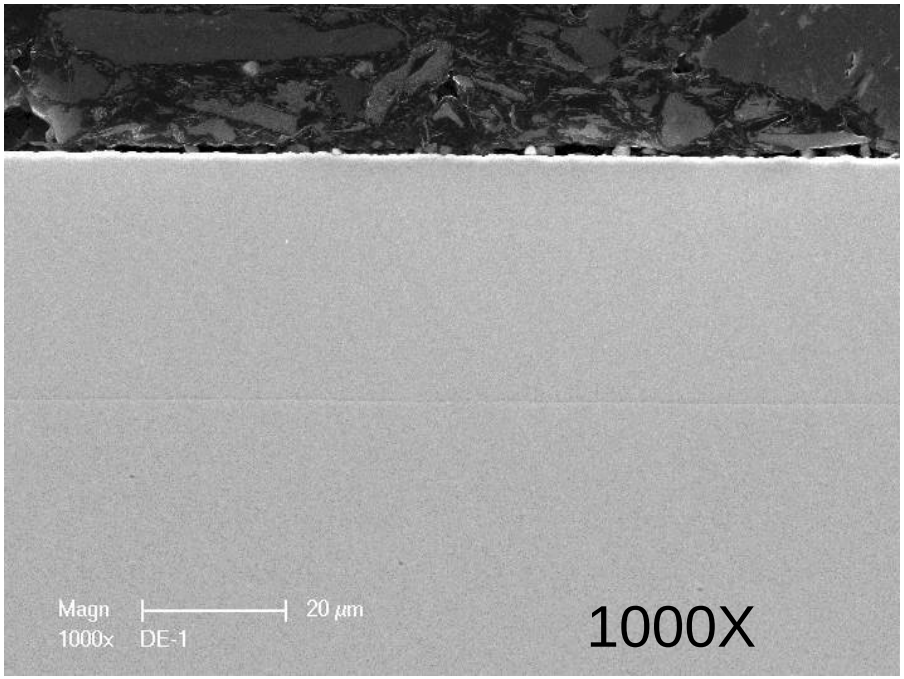
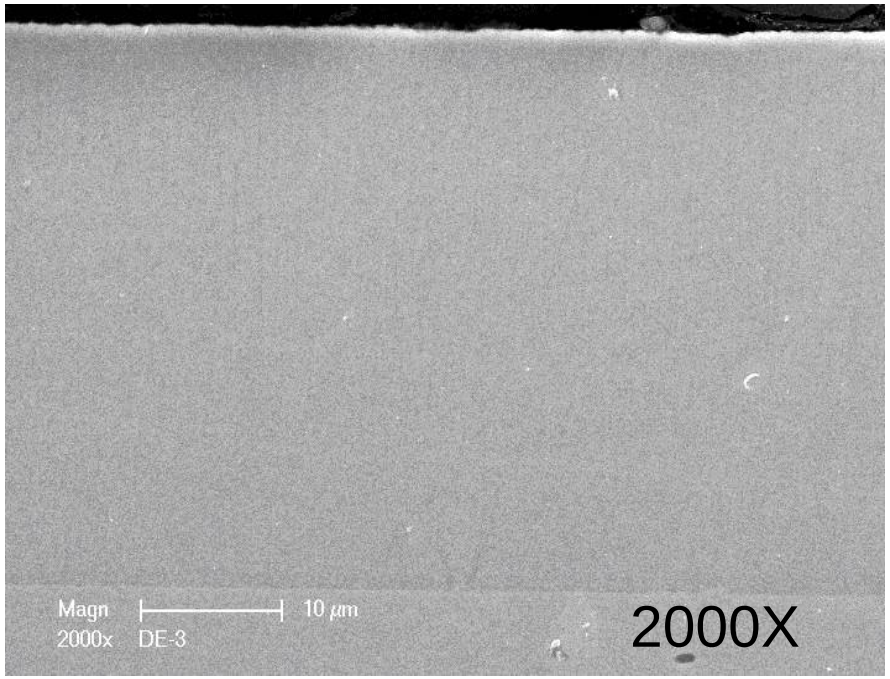
Task 3 - Processing of Advanced NanoCoatings -Metallographic Examination of Initial Trials

Result: Dense Nanocoating Microstructures



DE-1



DE-3

DE-1 and DE-3 exhibited good toughness and showed no coating delamination

Optimum conditions chosen for initial corrosion testing

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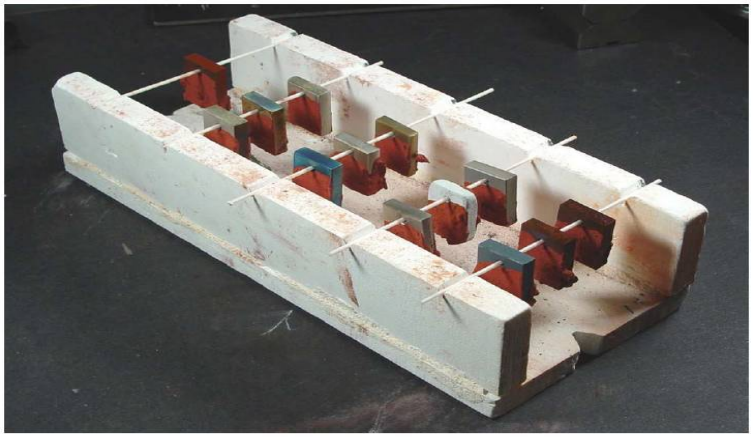
Task 4 - Corrosion Testing -Testing Conditions (FW)



Waterwall Testing

- 850ºF (454ºC), 975ºF (524ºC), and 1100ºF (593ºC)
- 40 percent FeS and 0.2 percent chlorides (same as U.S. DOE/OCDO A-USC program)

Superheater/Reheater Testing

- 1100ºF (593ºC), 1300ºF (704ºC), and 1500ºF (816ºC).
- 5 percent alkali sulfates (same as U.S. DOE/OCDO A-USC program)
- simulate Eastern bituminous coal compositions.

• Perform 1000hr tests (at 100hr intervals).

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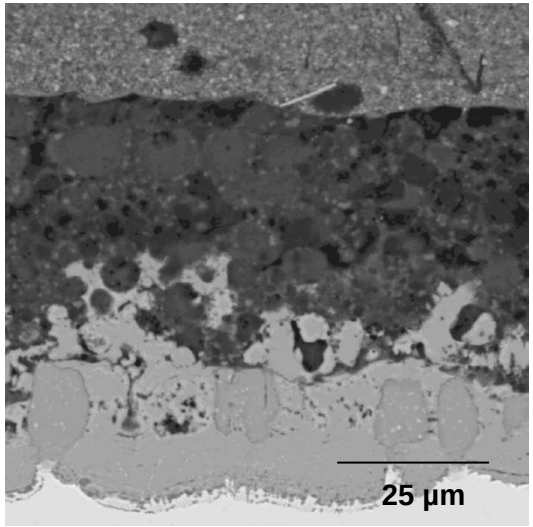
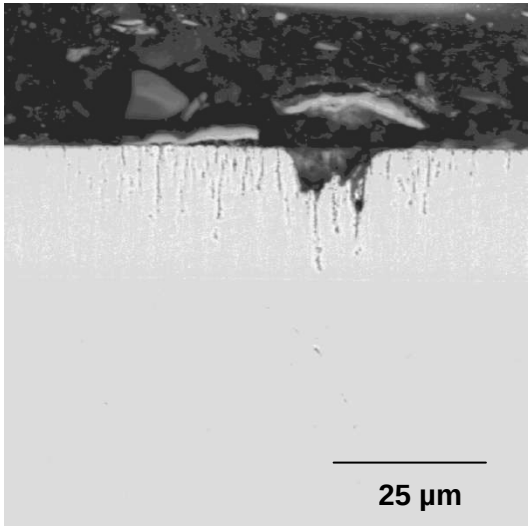
Microscopic: Waterwall – 1000hr, 975°F (Initial trials)

Phosphorus-containing coating

(Commercial coating)



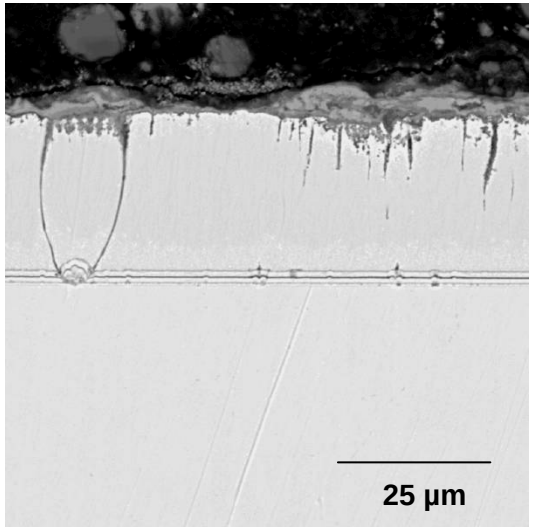


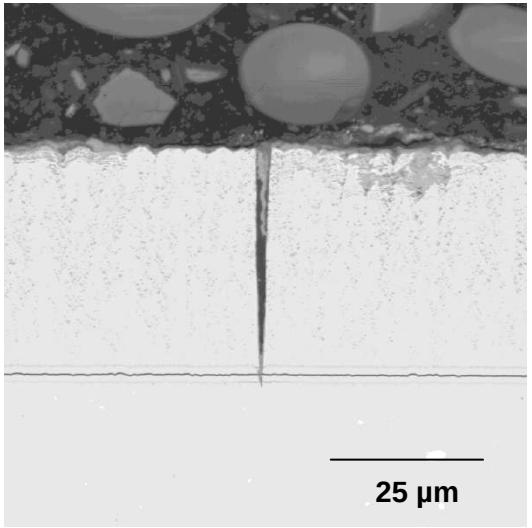
Nickel nano-coating

Commercial coating did not provide protection

Nanocoatings showed 'bulk' protective behavior but corrosion penetrated defects

Iron nano-coating





Cobalt nano-coating

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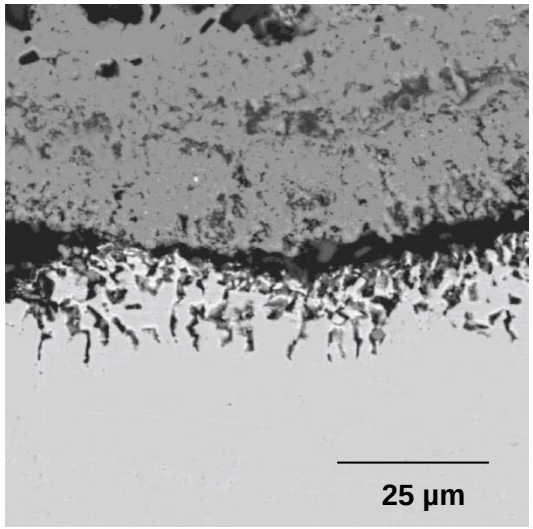
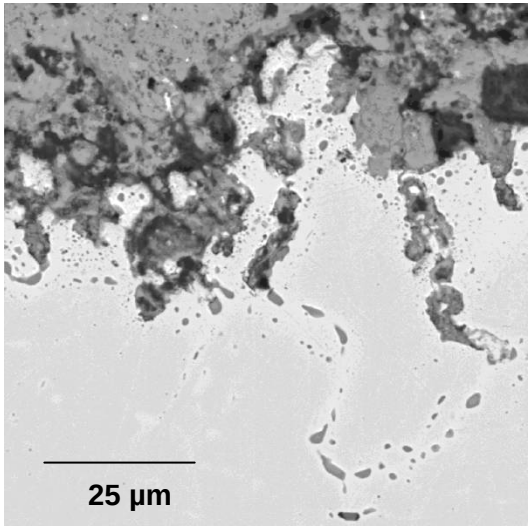
Microscopic: SH/RH – 1000hr, 1300°F (Initial trials)

Phosphorus-containing coating

(commercial coating)



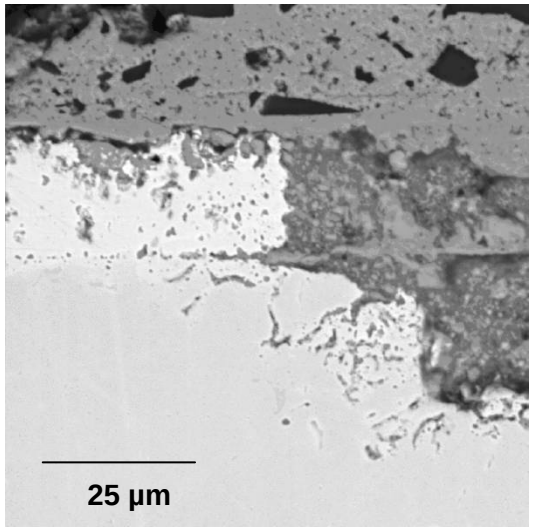


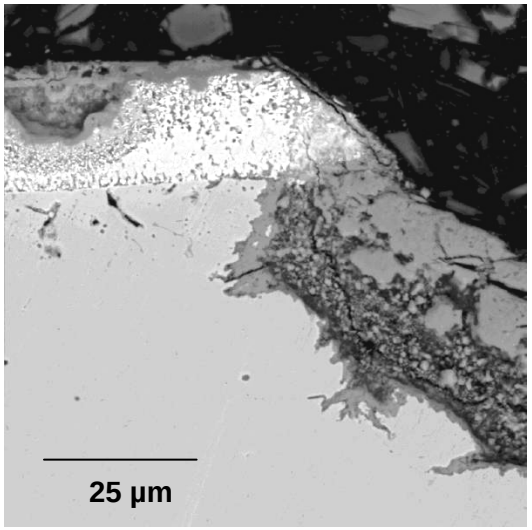
Nickel nanocoating

Commercial coating did not provide protection

Nanocoatings did not perform well due to coating defects

Iron nanocoating





Cobalt nanocoating

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Waterwall Conditions
Initial Coating Results (Foster Wheeler Tests)

Commercial Nanocoatings

- Provided little-to-no protection
- Significant penetration of oxide and sulfide species noted
- Interconnected network of cracks allowed for penetration

DOE Nanocoatings (Poor quality coatings)

- Cracking/spallation generally noted in coatings w/Al
- Generally resisted “bulk” coating corrosion
- Scatted penetration of oxide and sulfide species noted @ columnar grain boundaries and defect sites

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SH/RH Conditions
Initial Coating Results (Foster Wheeler Tests)

Commercial Nanocoatings

- Displayed very poor resistance to corrosion
- No evidence of coating apparent following exposure

DOE Nanocoatings with defects

- Severe corrosion was noted on all nanocoating materials
  - Complete consumption of the coating and subsequent wastage to the substrate material
  - Degradation generally increased with test temperature
- Some nanocoatings were not stable at high temperatures
  - Interdiffusion between coating and substrate

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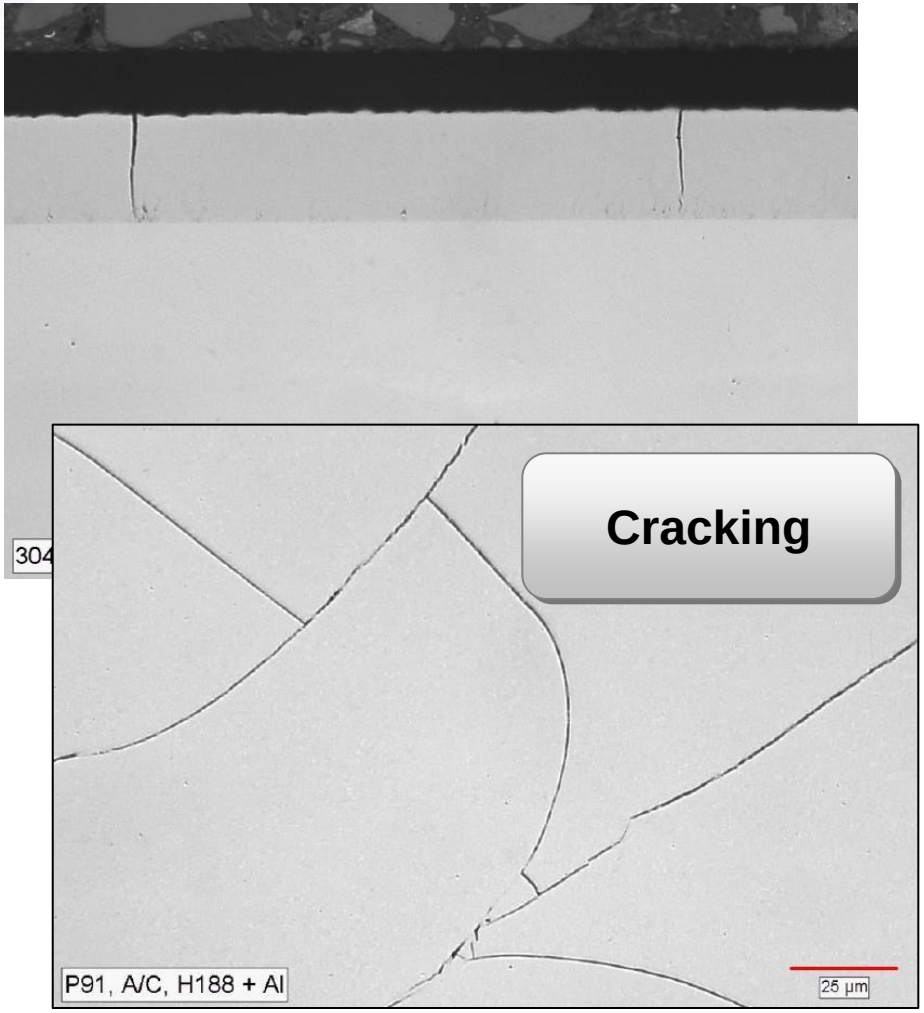
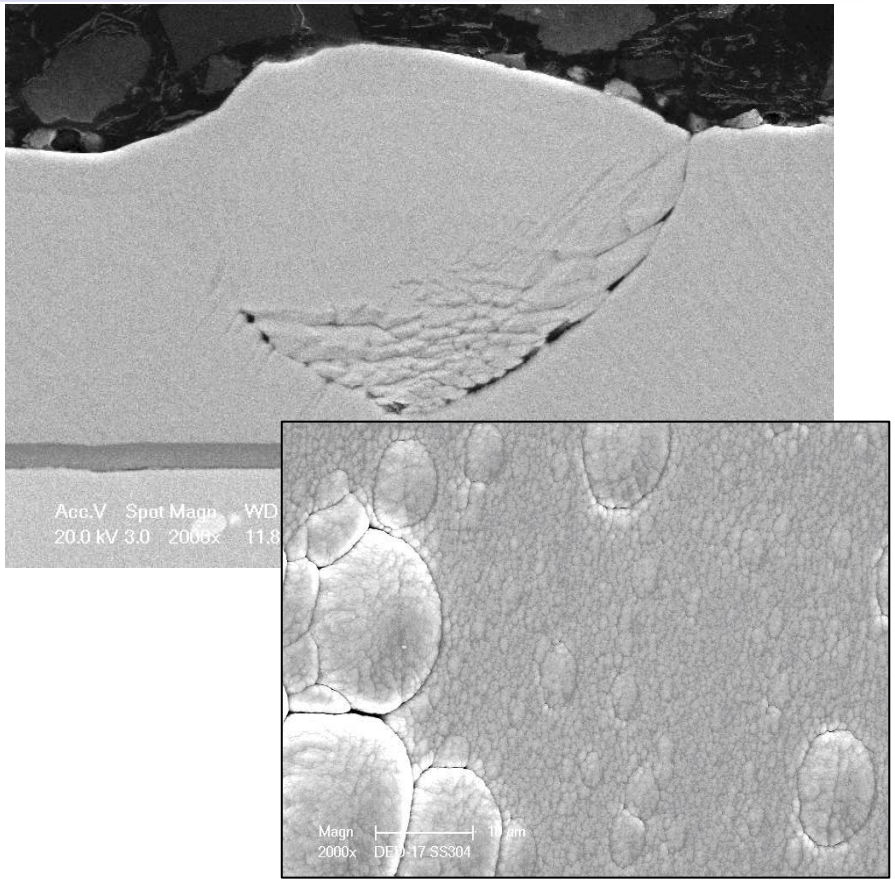
Coating defects ‘short-circuit’ potentially good corrosion behavior



Cracking



Cauliflower Defects

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Initial Task 3 & 4 Results: Two major concerns

1. Interdiffusion into substrate
   - Cyclic oxidation tests at superheater conditions showed Al diffused out of coating & precipitates in substrate materials
   - Fireside corrosion tests at superheater conditions found similar results
2. Coating quality and reproducibility
   - Defects compromised coatings at waterwall conditions despite good ‘bulk’ behavior
   - Coatings at superheater conditions were consumed
   - Defects included both cracking & cauliflower-type defects

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Research plan to address initial results

1. Interdiffusion into substrate
   - *Develop an interdiffusion barrier layer*
     - **Successful with thin TiN interlayer**
2. Coating quality and reproducibility
   - *Processing conditions*
     - Cracking was eliminated
     - Cauliflower defects persisted
   - *High Power Impulse Magnetron Sputtering*
     - Eliminated cracking but had very poor adhesion
   - *Pulsed DC power supply (Colorado School of Mines)*
     - **Best results, no cracking, minimized cauliflower defects, no through-thickness defects (with intermittent Ar-cleaning)**

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Task 3 - Processing of NanoCoatings
Second Iterations: Reduce Interdiffusion

- Diffusion barrier interlayer coatings considered
  - AlN, TiN, and TiSiCN
  - TiN/AlN and TiSiCN/AlN

- After application of interlayer, nanocoatings were applied and conducted cyclic oxidation testing:
  - Ni-20Cr-10Al-coated Haynes samples
    - 2100 thermal cycles (750°C, 1010°C)
  - Fe-18Cr-8Ni-10Al-coated 304SS samples
    - 1051 thermal cycles (750°C)

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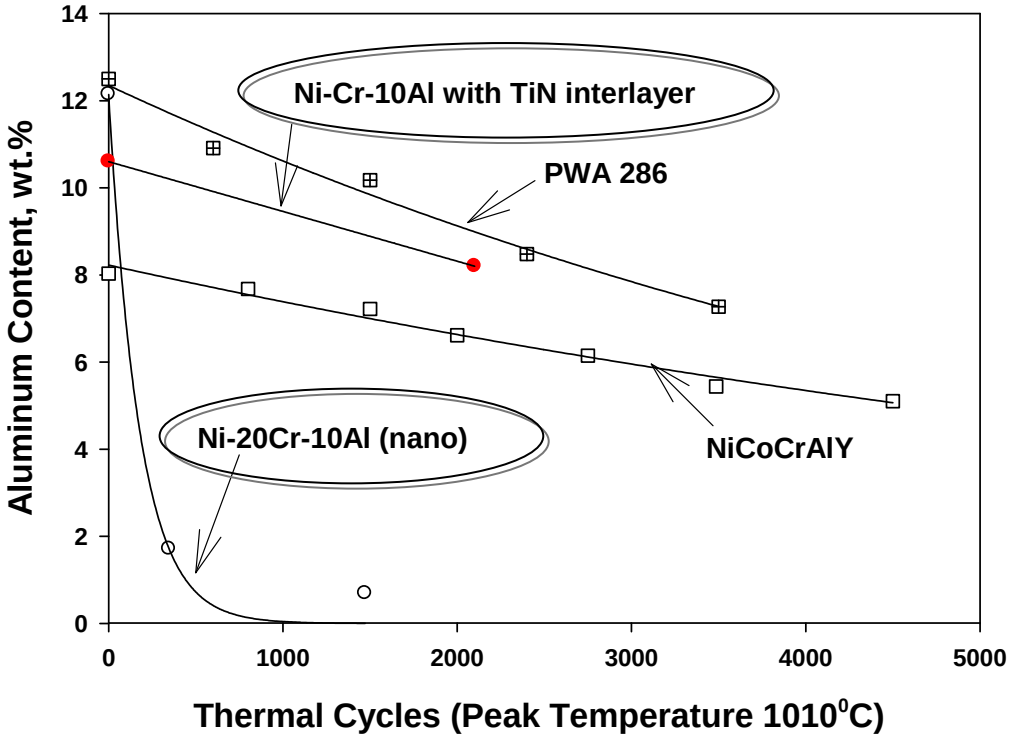
Thermal cycling shows TiN interlayer is an effective barrier to Al Depletion in nanocoatings



Interlayer is very effective at slowing Al consumption (accelerated test conditions)

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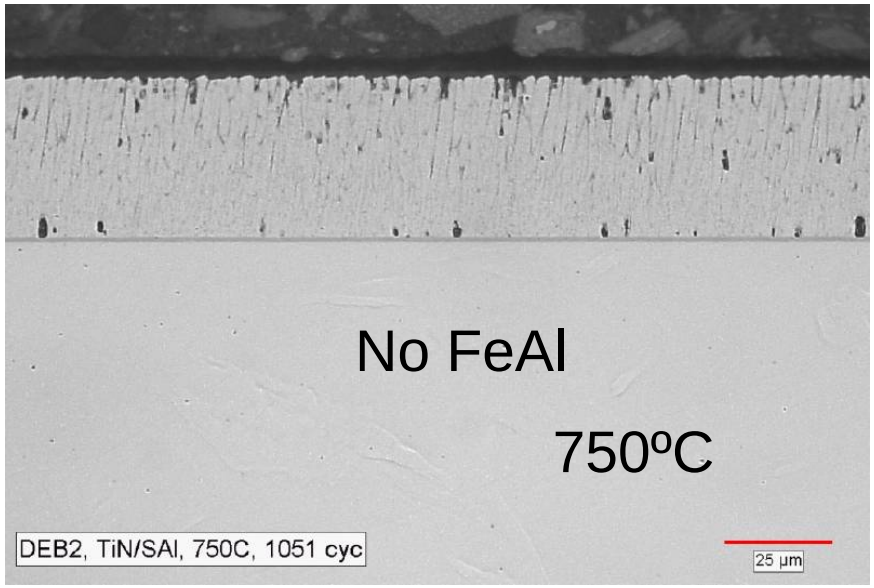
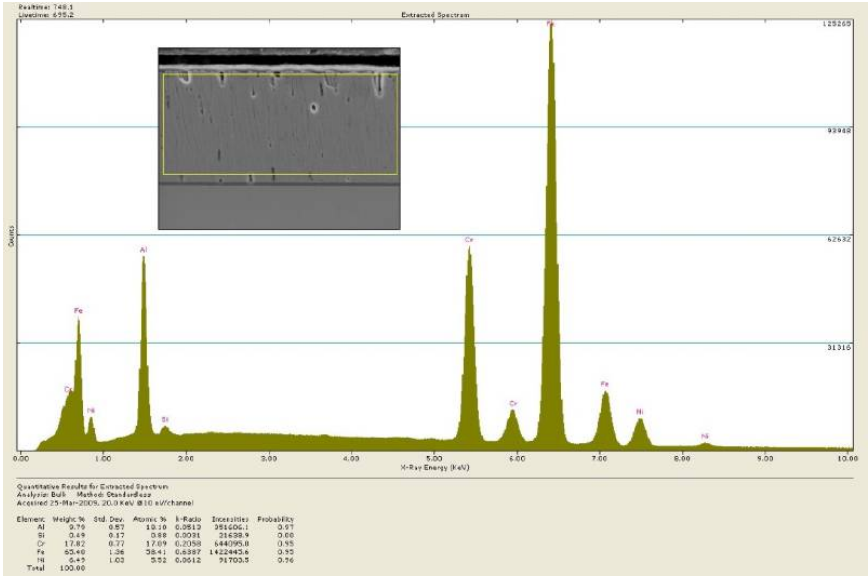
Effectiveness of TiN Interlayer Barrier Coating – Microstructural results

Fe-18Cr-8Ni-10Al coating over TiN Coated 304SS after 1051 cycles





Al remained at approx. same range >>10% to 9.8 wt%

- **TiN interlayer is intact**
- **No inward diffusion of Al into 304SS**
- **Interlayer is effective**

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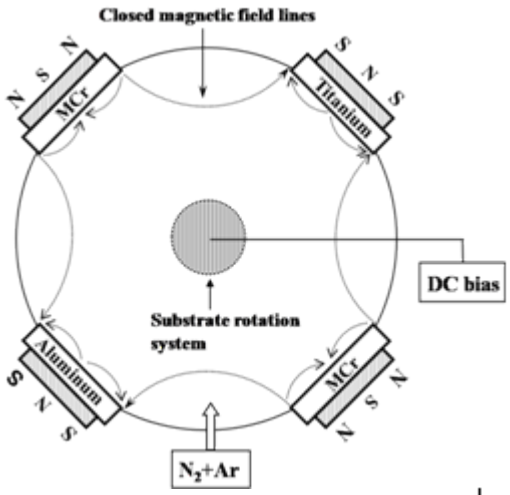
Second processing iterations: Pulsed DC Magnetron Sputtering

- Pulsed DC power supply (Colorado School of Mines)
- Deposited 6-8 µm thick H160+Al coating on 304SS using Pulsed DC with 1kw and 1.5kw power
- Deposited ~30 µm thick H160+Al coating on 304SS and Haynes 230
- Coated samples were destructively examined



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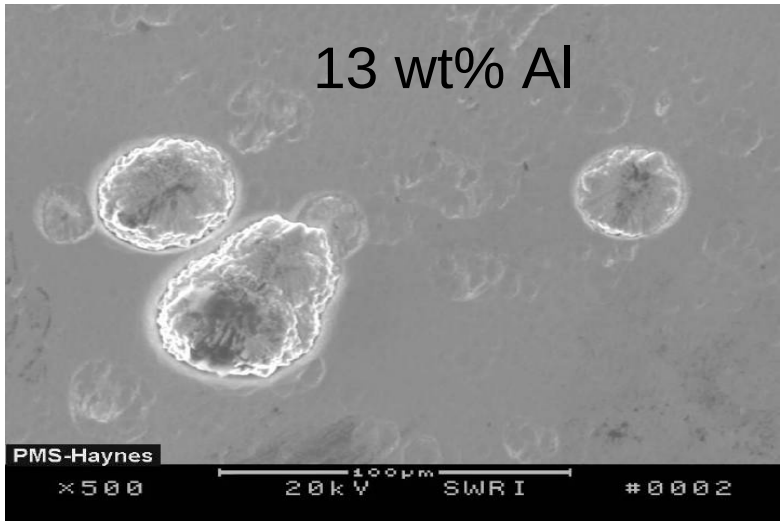
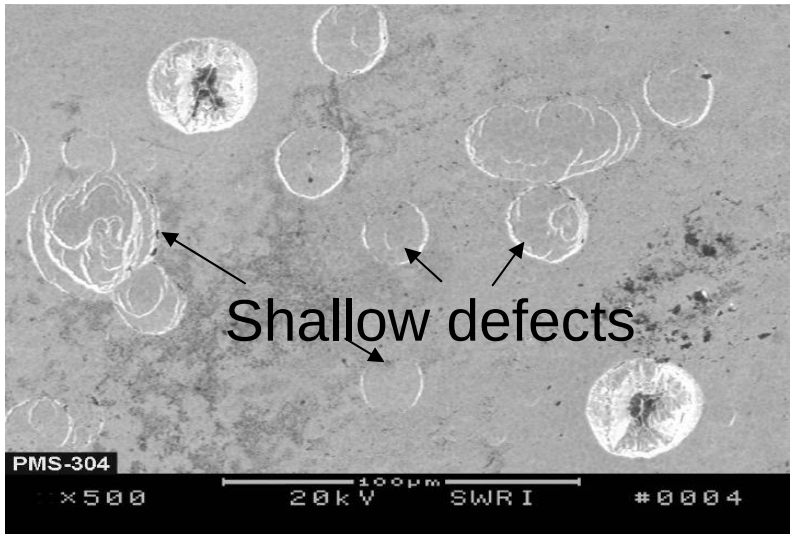
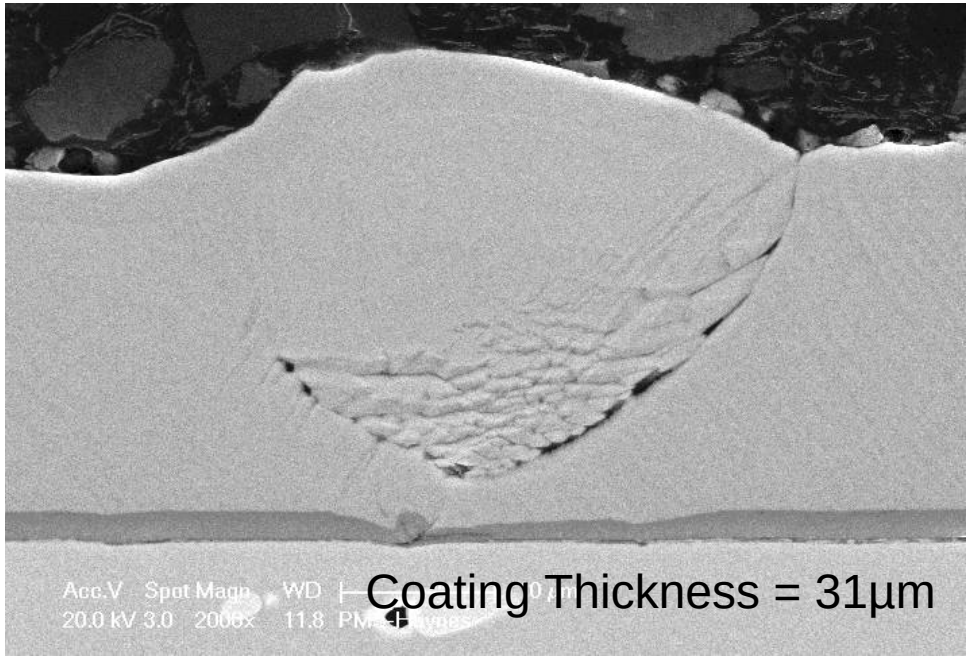
Pulsed DC Magnetron Sputtering Trials







No cracking, few cauliflower defects were shallow

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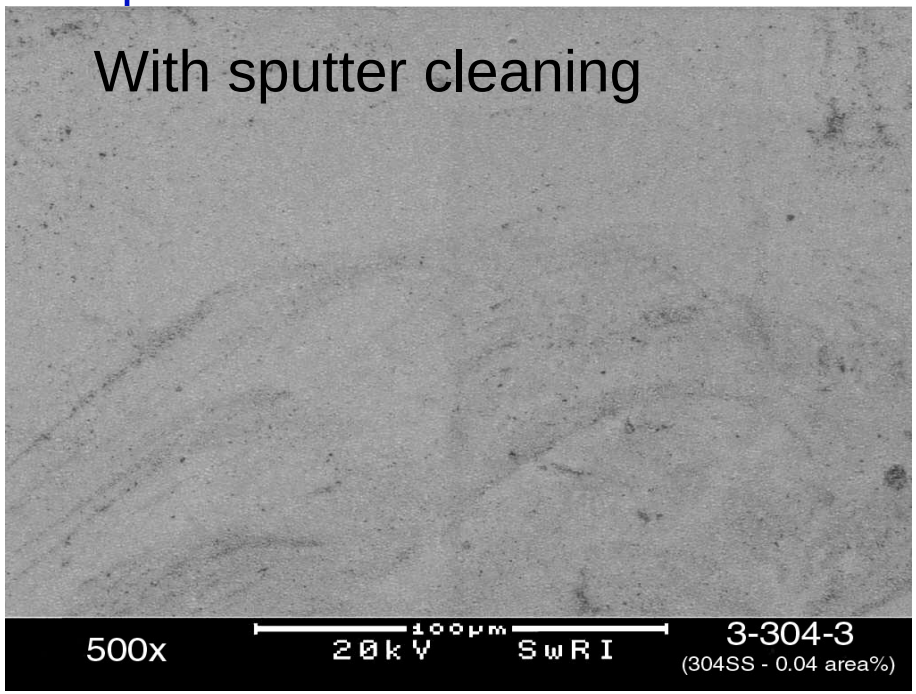
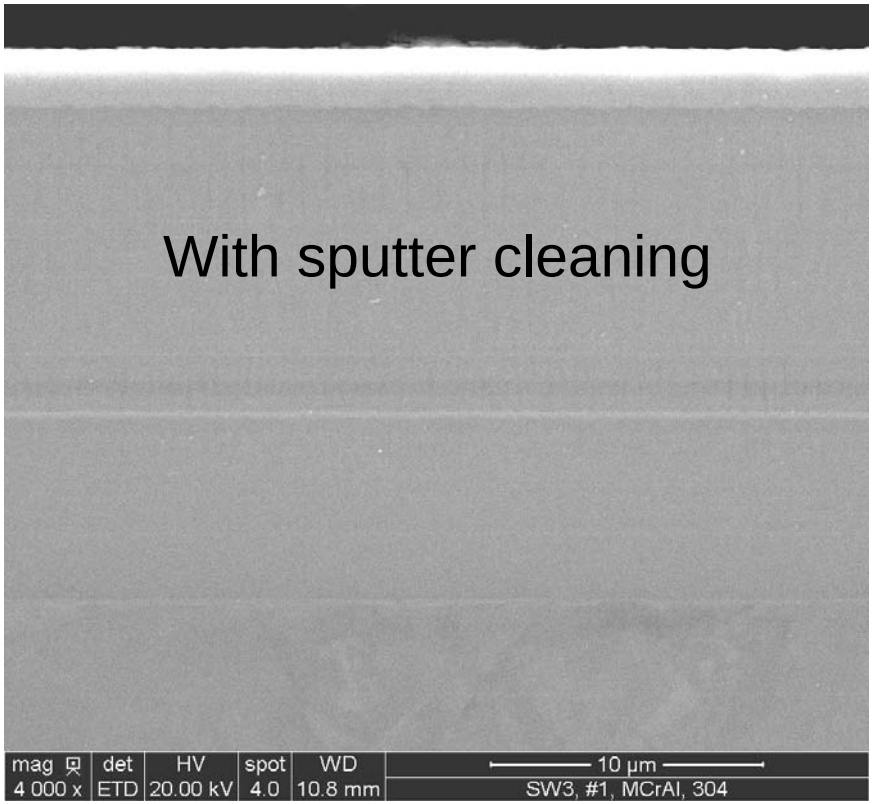
Pulsed DC Magnetron Sputtering
Process optimization for thick coatings

Coating Quality Improvement of thick coatings

- Sputter cleaning (plasma etching) at predetermined intervals





Good coating quality achieved with minimal defects

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Pulsed DC Magnetron Sputtering -Coating Quality variability Trials

- Multiple coating deposition trials were conducted
- Four trails with plasma etching at predetermined intervals On 304 and Haynes samples (without TiN interlayer)
- Two trails with plasma etching at predetermined intervals on TiN coated 304 and Haynes samples
- Four trails for deposition of multilayer MCrAl/Al coating on 304 and Haynes samples

Need to ensure reproducibility of coatings

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Pulsed DC Magnetron Sputtering -Coating Quality Variability Results

- The quality of the coatings deposited in **10 trials** on multiple samples was excellent
- In all cases chemical composition was consistent
- The grain size of the coating deposited on multiple samples varied form **4 to 8 nm**.
- Coatings were free from cracking and delamination
- The maximum area fraction of defects among samples
  - **0.30%** (Single layer coating with no TiN interlayer)
  - **1.2%** (Single layer coating with TiN interlayer)
  - **0.6%** (Multilayer coating)

The process is repeatable and ready for corrosion testing

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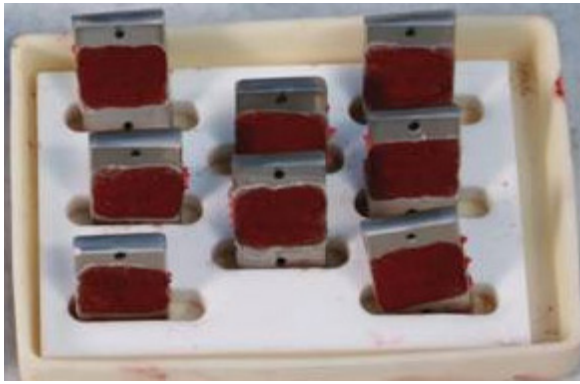
Task 4 - Corrosion Testing
Pulsed DC Optimized Repeatable Coatings

Superheater/Reheater Screening Tests
(No flowing gas)

- 1100ºF (593ºC), 1300ºF (704ºC), and 1500ºF (816ºC).
- simulated Eastern bituminous coal ash compositions.
- Good results → final tests initiated



Superheater/Reheater Testing at 1500ºF (816ºC)

- 5 % alkali sulfates (same as A-USC program & earlier tests)
- simulate Eastern bituminous coal ash compositions.
- 7.5% alkali sulfates (same as A-USC program)
- simulate Midwestern bituminous coal ash compositions
- Flowing Simulated Flue Gas

  71% N, 15% CO_2, and 0.25 % SO2

- Perform 1000hr tests (at 100hr intervals inspection and recoating the ash deposit)

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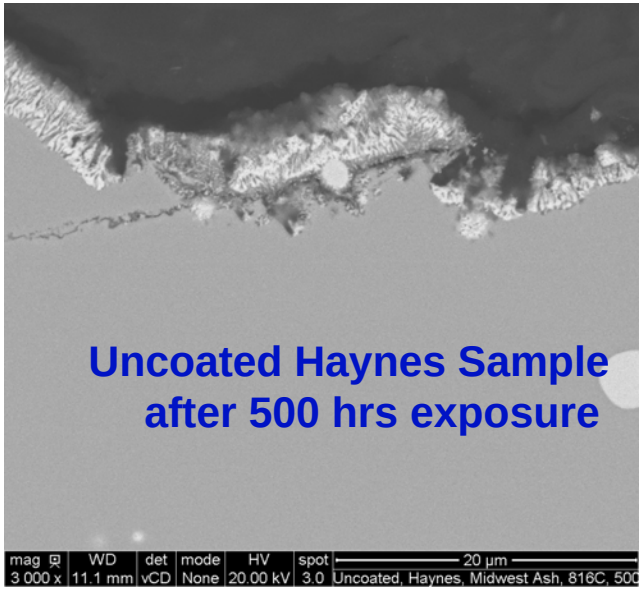
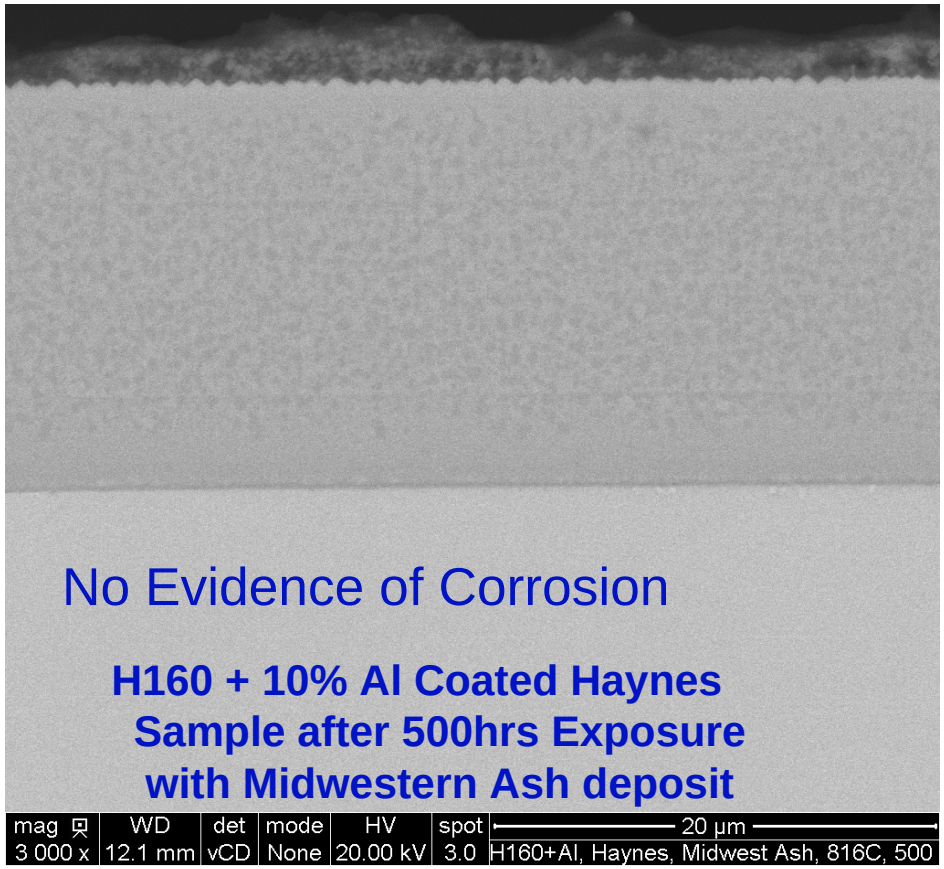
Corrosion Results after 500hrs (of 1000hrs)
Superheater/Reheater Condition (Flowing gas)





Promising Corrosion Results

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Conclusions (To Date)

- For long-term term durability, nanocoatings should contain ~10%Al.
  - A continuous, Al-rich protective oxide scale can be achieved with Al content as low as 3 wt.%.
- Four (4) nanocoatings were selected using computational thermodynamics.
- Good cyclic oxidation performance exhibited for baseline nanocoatings (Fe-18Cr-8Ni-xAl, Ni-20Cr-xAl)
- Oxidation and Al_2O_3 Scale Spallation are **not** issues
- Pulsed DC sputtered coatings were almost free from cauliflower type defects and cracks
- Initial results show the defect-free optimized (second iteration) coatings exhibited good fire-side corrosion resistance

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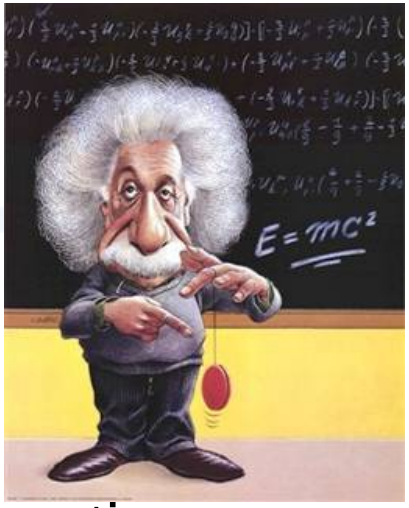
Project successes (To Date)



Major Concerns Addressed

1. Aluminum Consumption (solved)
   - A TiN diffusion barrier layer slowed Al consumption rate dramatically.
2. Coating Quality Issues (solved)
   - Pulsed DC Magnetron Sputtering
     Process with intermittent plasma cleaning produced high quality coating

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To do

- Complete 1000 hour fireside corrosion testing and analysis
- Complete Task 5 report
- Begin and complete Final Report including new processing (Task 3) and corrosion (Task 4) results
- Complete project (June 2011)

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