Computational Modeling and Assessment of Nanocoatings for USC Boilers

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Outline

- Project Objectives
- Background
- Modeling of Advanced MCrAl Nanocoatings
- Processing Advanced Nanocoatings
  - Quality Issues
  - Al Consumption
- Fireside Corrosion Testing
- Conclusions

DOE Nanocoatings Project Objectives

- 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

Goals Align with DOE Objectives

- Advanced materials for NZE power plants.
- Computational methods

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 US is 2.5-3.0%

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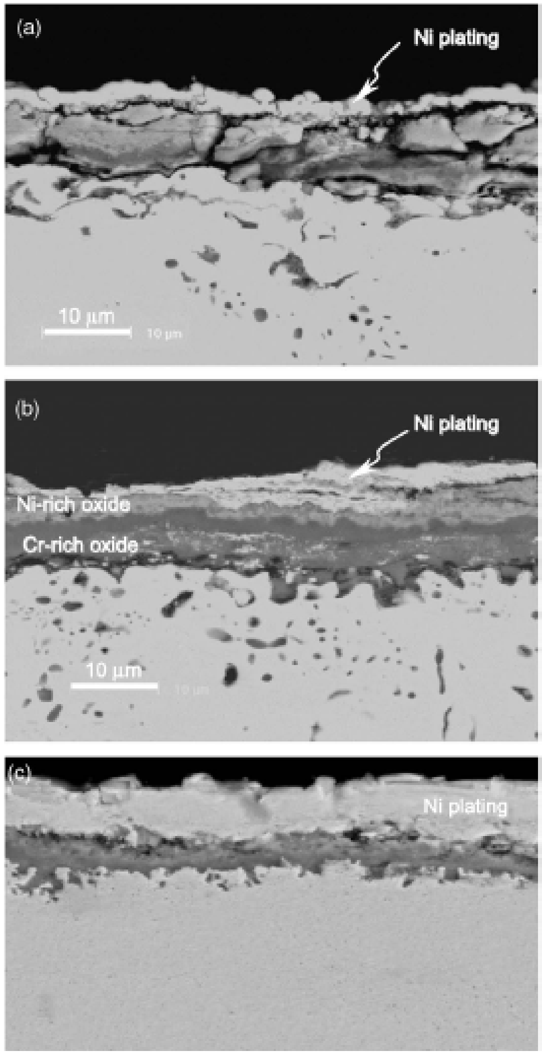
Background--Corrosion Resistance of Nanocoatings

--Finer grain size lowers minimum Cr requirement!!

For corrosion resistance formation of chromia scale is crucial.
--Typically 20% Cr is required for protective scale formation

- 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

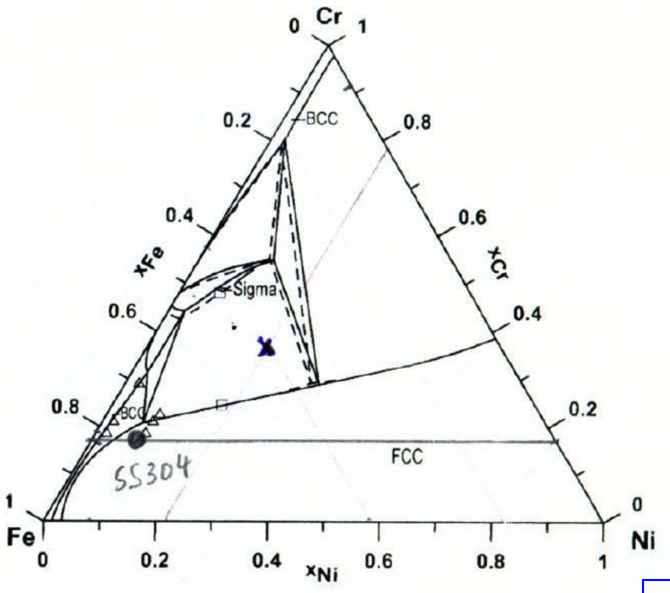
Ni-20% Cr Conventional

Ni-11% Cr Nanostructure

K_2SO_4-20%NaCl-$10K_2SO_4$ @ 700°C for 50 hrs

Project Tasks & Milestones

- Task 1: Computational Modeling of MCrAl Systems (06/2008)
- Task 2: Establishment of Baseline Coating Data (06/2008)
- Task 3: Processing Advanced MCrAl Nanocoatings (80%)
- Task 4: Fire-Side Corrosion Testing (03/2009)
- Task 5: Computational Modeling & Validation (40%)
- Task 6: Mockup Demonstration (delayed)
- Task 7: Project Management & Reporting (80%)
- Completion by end of 2010



Task 1: Computational Modeling of MCrAl Systems

--completed

Objective: Select potential MCrAl nanostructured coating compositions using computational modeling

Task 1- Computational Modeling Of MCrAl --Composition Selection

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

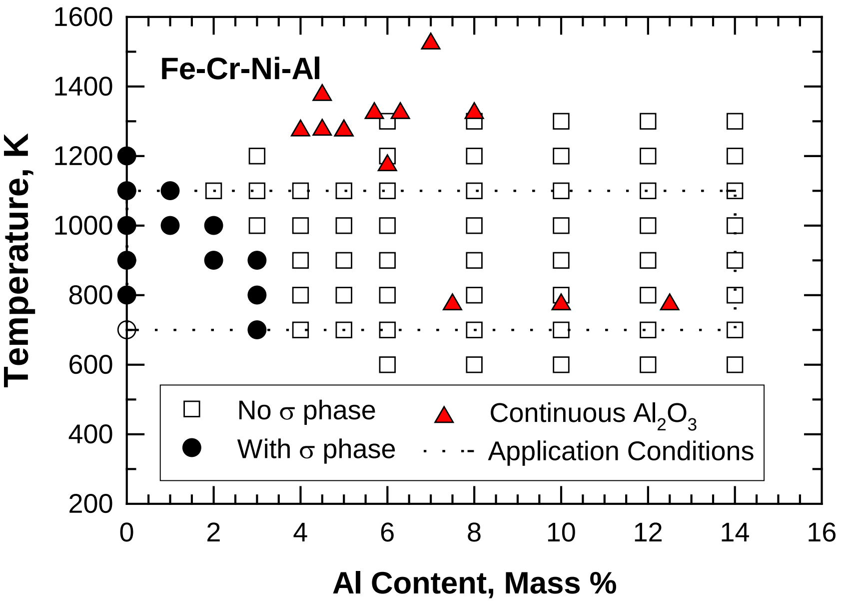
- 310 + Al (Fe-25Cr-20Ni-10Al)
- Haynes 120+Al (Fe-37Ni-25Cr-10Al)

Nickel base coating

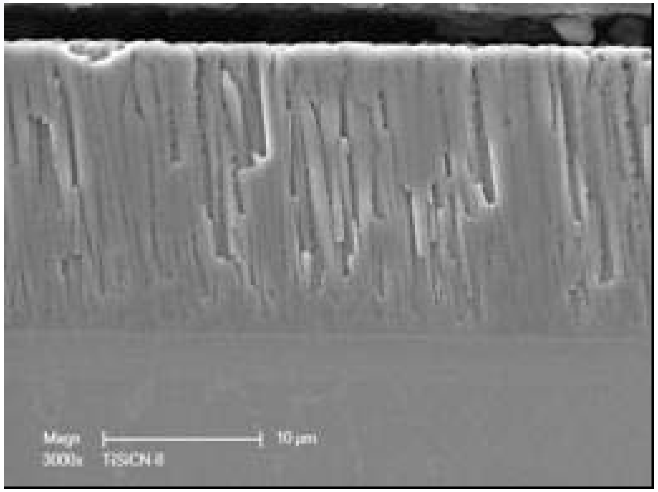
- Haynes 160+Al (Ni-29Co-28Cr-3Si-10Al)

Cobalt base coating

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



- Computations based on FeNiCrAlx
- Developed phase diagrams; then grain growth, sintering, diffusion models, and interface toughness

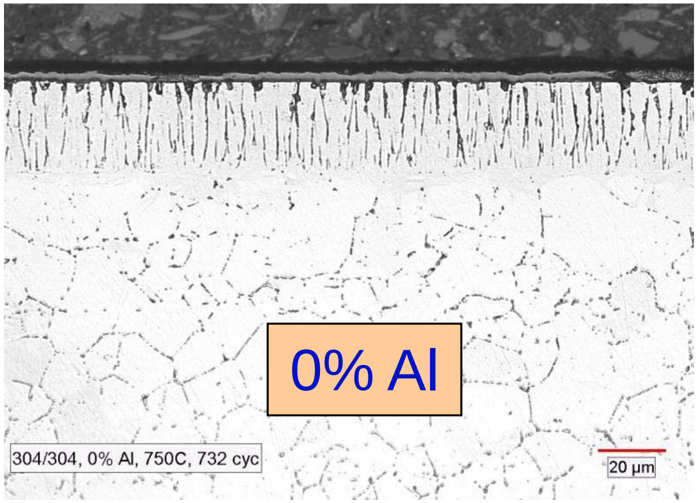


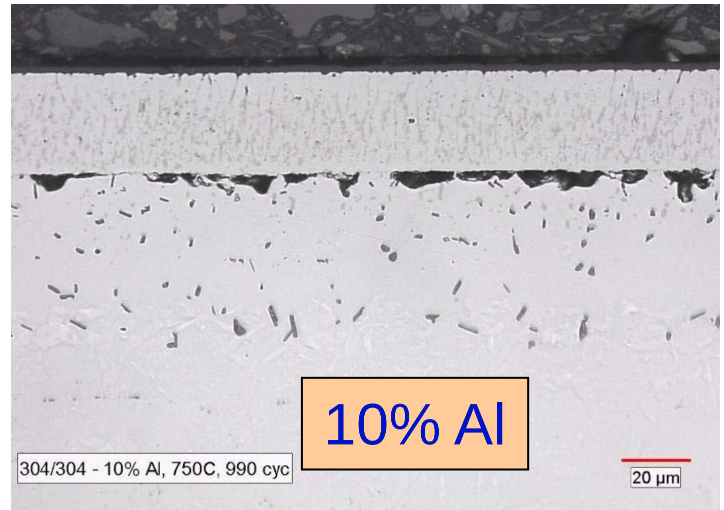
Task 2: Establishment of Baseline Coating Data

--completed

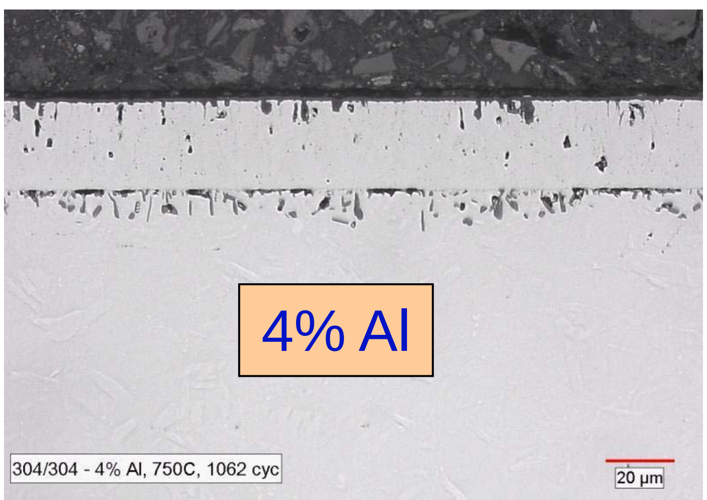
Objective: Evaluate conventional coatings and available vendor nanocoatings to assess properties

Task 2. Baseline Coating Oxidation Characterization -- Fe-18Cr-8Ni-xAl and Ni-20Cr-xAl (not shown)





After 990 cycles @750ºC



1). The protective oxide layer
- 0% Al coating Cr_2O_3
- 4 and 10%Al coatings Al_2O_3

2). 4% Al coating was oxidized slightly
3). 10% Al coating free from internal oxidation
4). Inward diffusion of Al led to formation of inter-diffusion zone with FeAl particles
5). Al content in the coating dropped from 10% to 3.7% after 990Cycles

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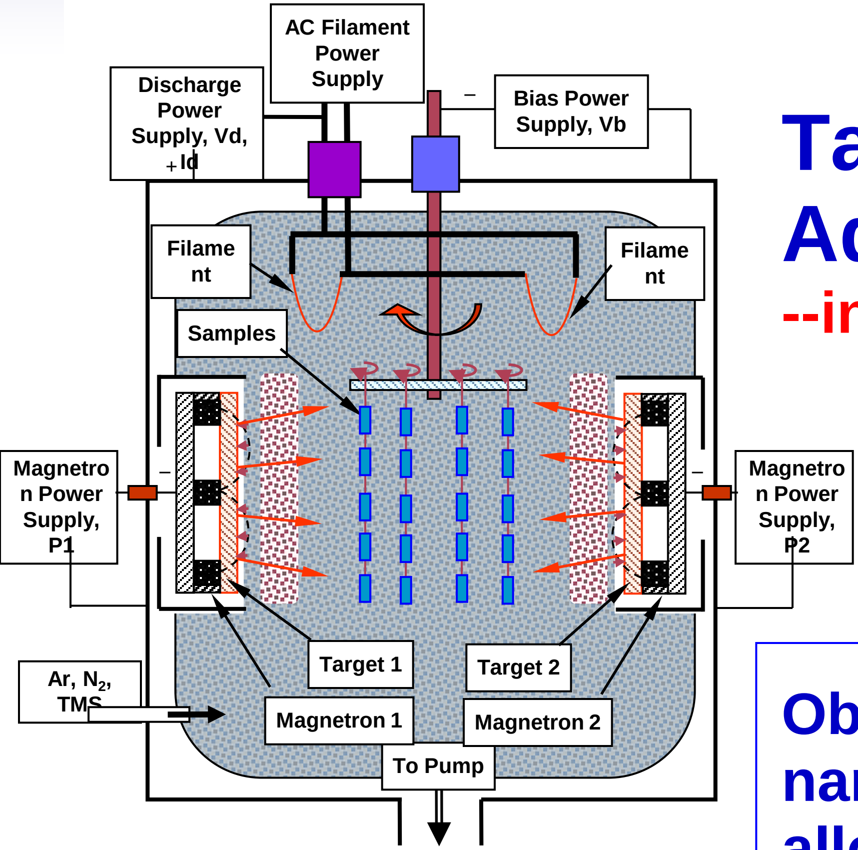


Task 3: Processing of Advanced NanoCoatings

--in progress

Objective: Apply advanced nanocoatings on USC substrate alloys and evaluate properties

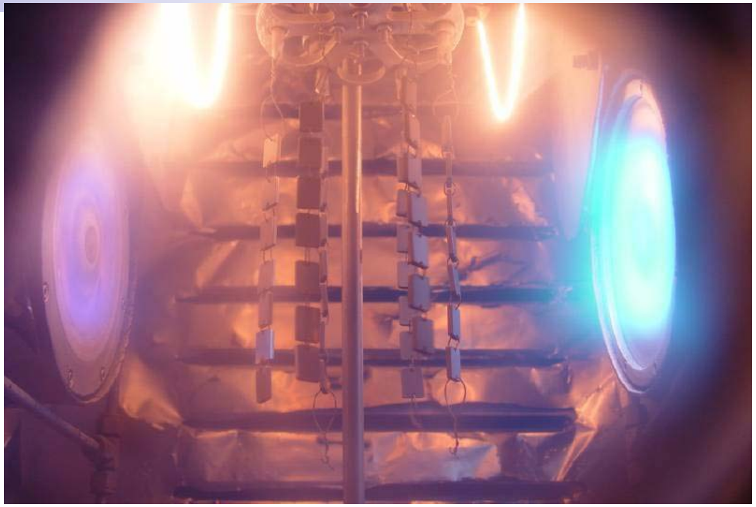
Task 3 - Processing of Advanced NanoCoatings

Four Plasma-Enhanced Magnetron Sputtering Units Evaluated

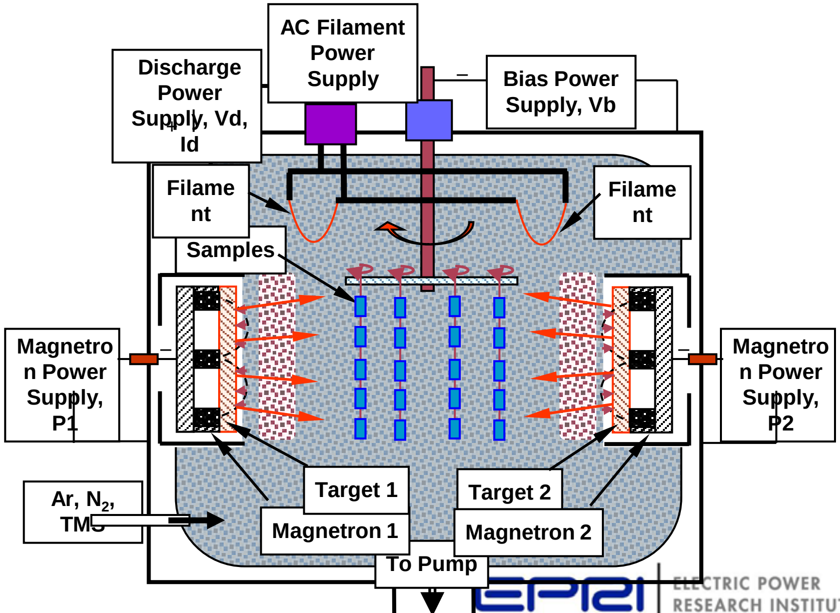
- PEMS—2 Magnetrons
- High Power Impulse Magnetron Sputtering
- Large PEMS Chamber ($1M^3$)–4 Magnetrons
- Pulsed DC Powered PEMS (Colorado School of Mines)

- Employed 4 Nanocoatings defined in Task 2 for Processing Characterization
  - 2 Iron-based, 1 nickel-based, and 1 cobalt-based
  - Applied on 304 SS, P91 and Haynes 230 substrates

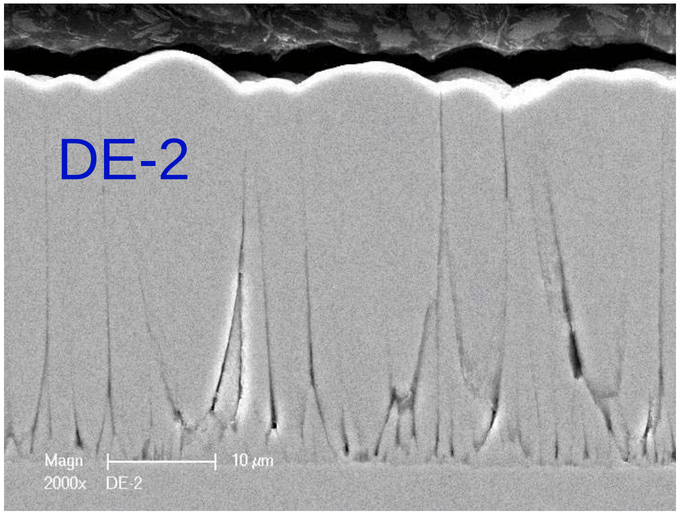
Task 3 - Processing of Advanced NanoCoatings
1. PEMS--2 Magnetrons

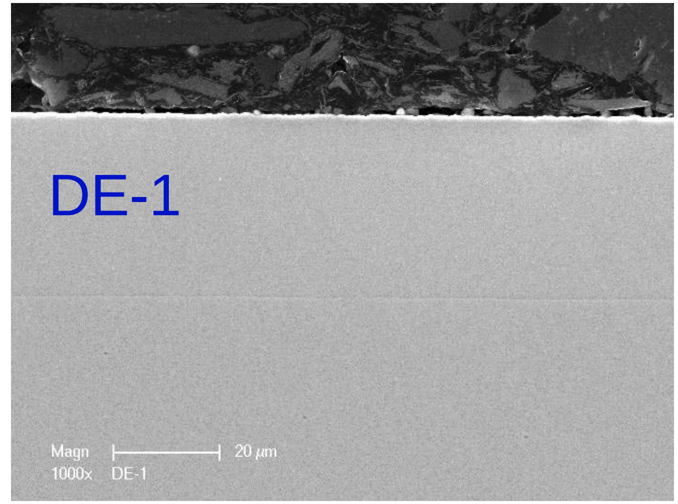


- Process optimization study conducted to improve the consistency of the coating
  - power applied to targets and bias voltage were varied
- Several trial nanocoatings: 304+10Al, 310+10Al and Ni-20-10Al deposited
- Coated samples were destructively examined

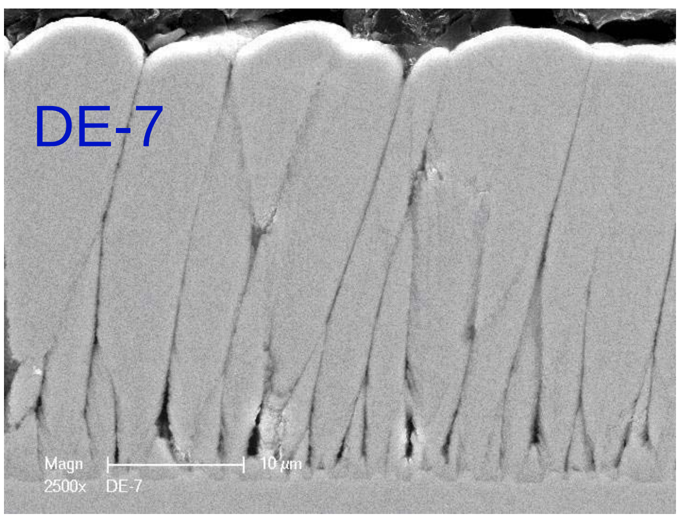


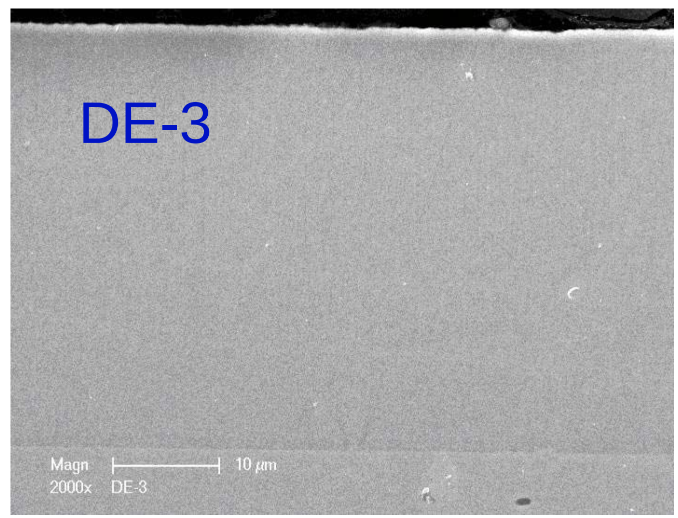
Task 3 - Processing of Advanced NanoCoatings --Metallographic Examination





2000X





Columnar Grains

Dense Structure

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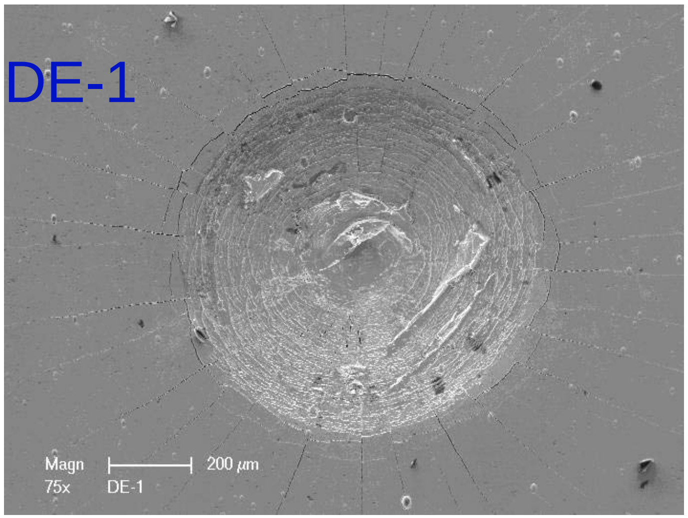
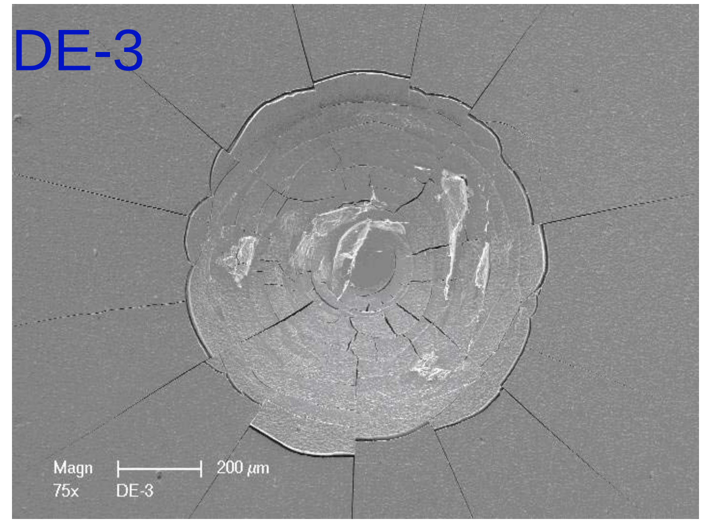
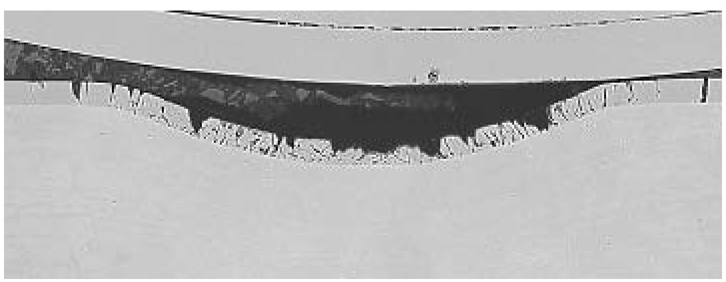
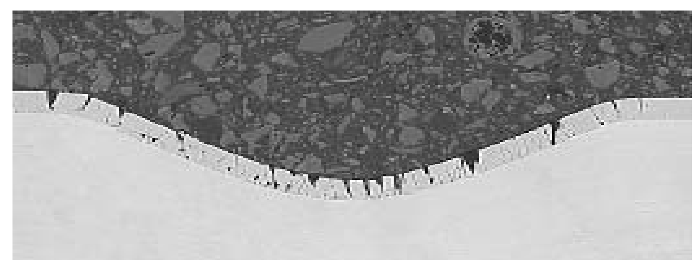
Task 3 - Processing of Advanced NanoCoatings -- Coating Adhesion Results



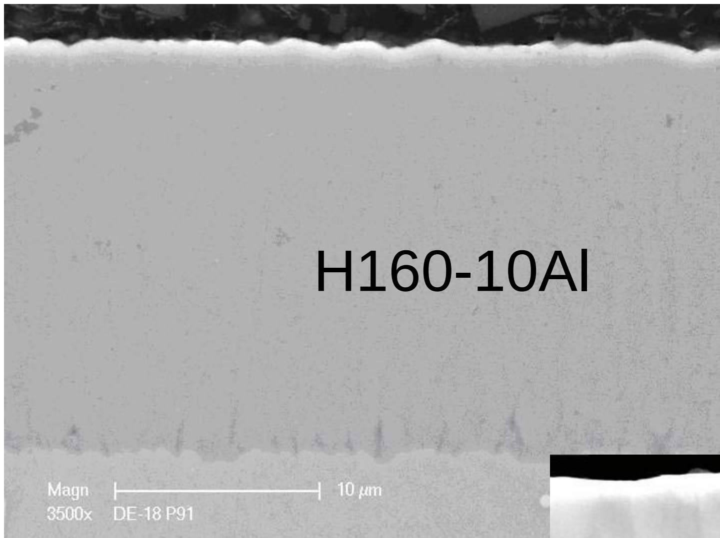






- **DE-1 and DE-3 exhibited good toughness**
- **Showed no coating delamination**

Task 3 - Processing of Advanced NanoCoatings --Coatings Microstructures



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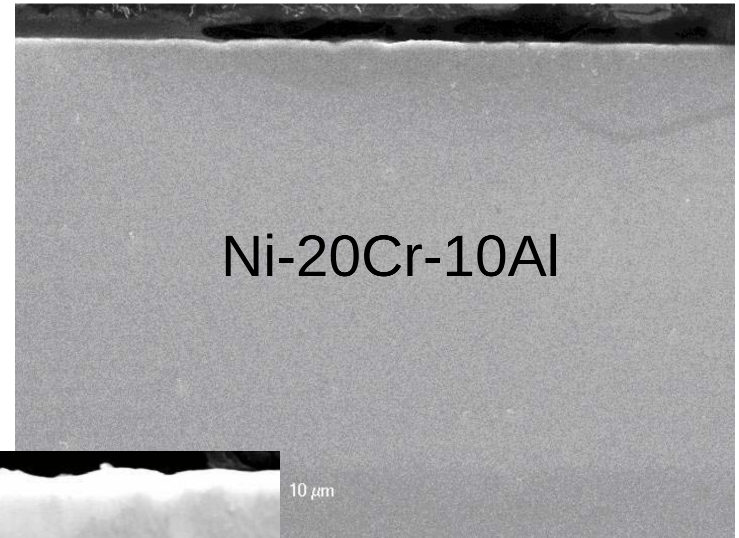

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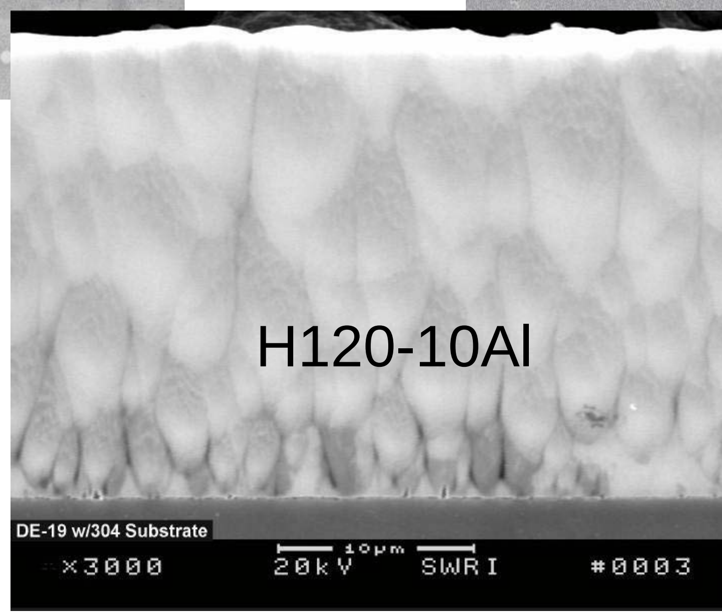

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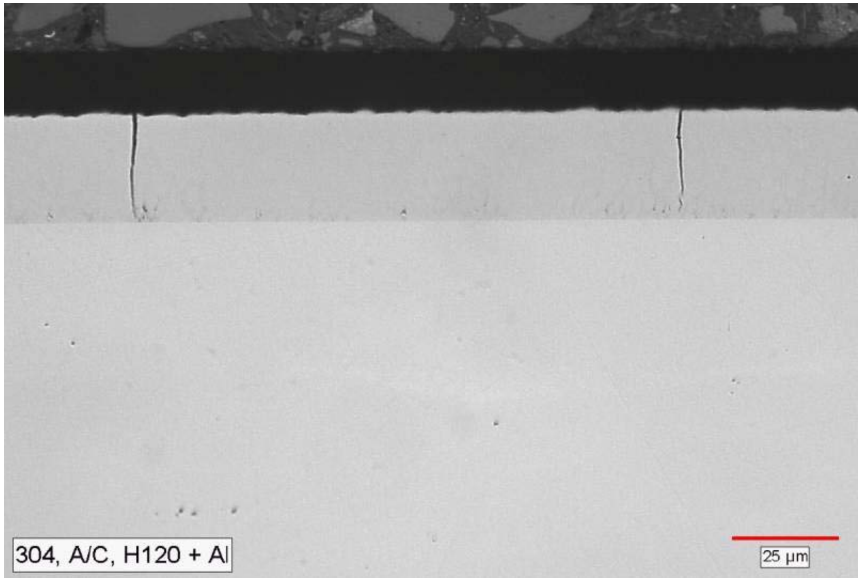
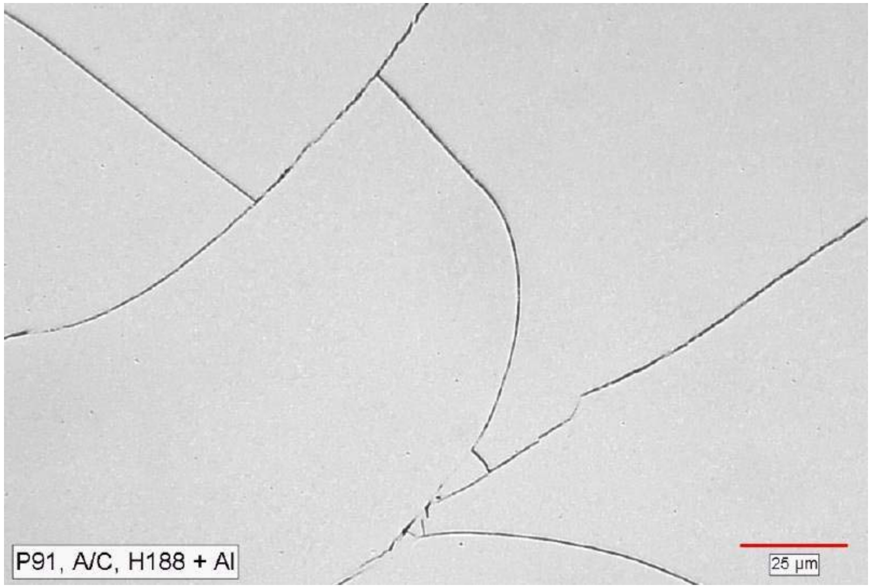
3 Nanocoatings Applied using Optimized Parameters

Task 3 - Processing of Advanced NanoCoatings --Coating Cracking and Major Concerns





Major Concerns To Address:

- Coating Quality Issues
- Aluminum Consumption

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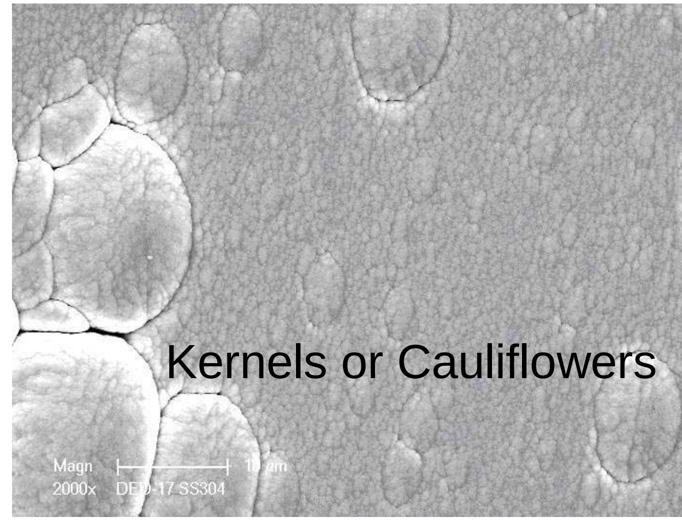
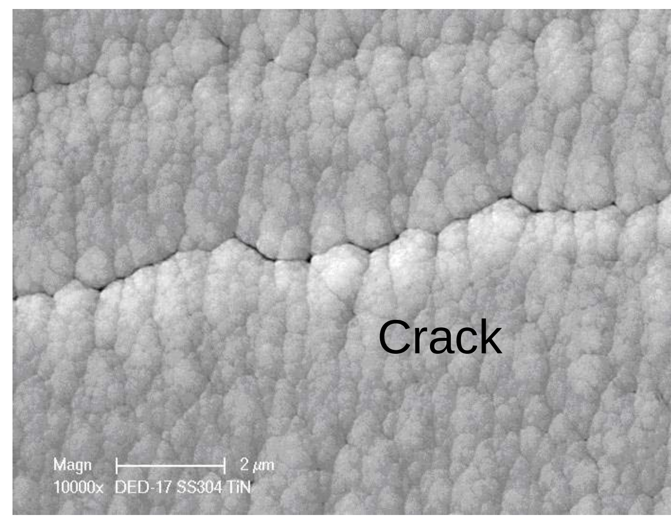
Task 3 - Processing of NanoCoatings --Process Optimization- Quality Issues

- Several nanocoating trials:
  - Fine-tuned DE-1 and DE-3 parameters & process conditions
  - Increased pre-coating sputtering (cleaning) time
  - Stress relieving the samples

- Visual examination showed a few crack-free samples.
  - These samples were sent for corrosion tests
- Metallographic examination revealed coating defects kernels, cracks etc.



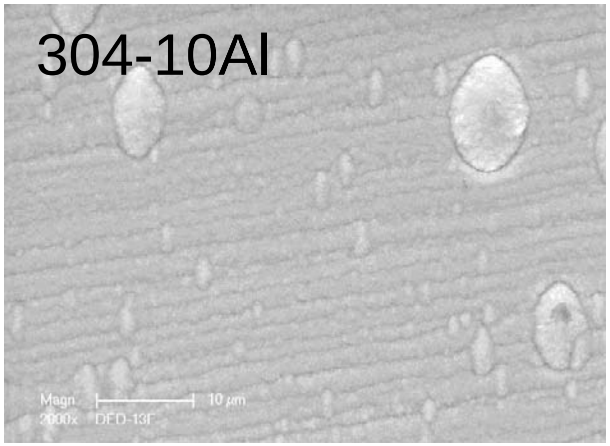


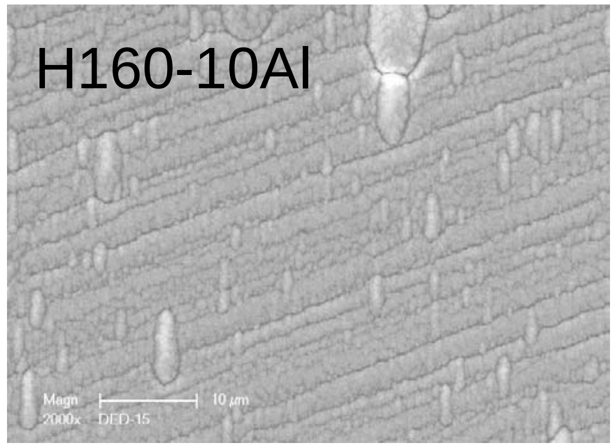
Task 3 - Processing of NanoCoatings
2. High Power Impulse Magnetron Sputtering

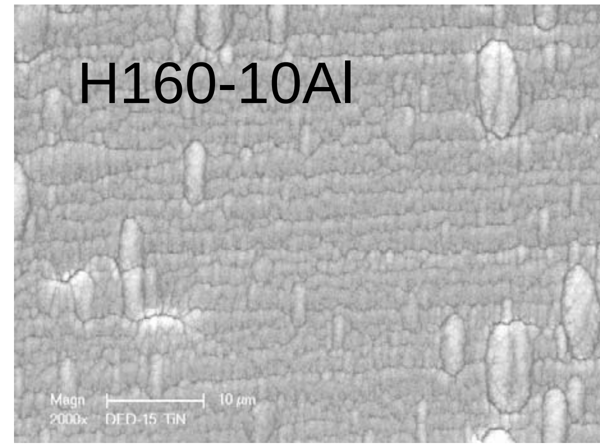
- *High Power Impulse Magnetron Sputtering* (HIPIMS) recently used to produce dense coatings
- Several coating trails were conducted to produce dense, crack free coatings
- After optimizing the process variables, H120-10Al, H160-10Al, and H188-10Al coatings were applied
  - V, I, target power (variables)
  - Employed AlN and TiN/AlN diffusion barrier layers
  - The coatings were dense and crack-free
  - Exhibited poor adhesion unfortunately

Task 3 - Processing of NanoCoatings
--HIPIMS Process Optimization-Microstructure

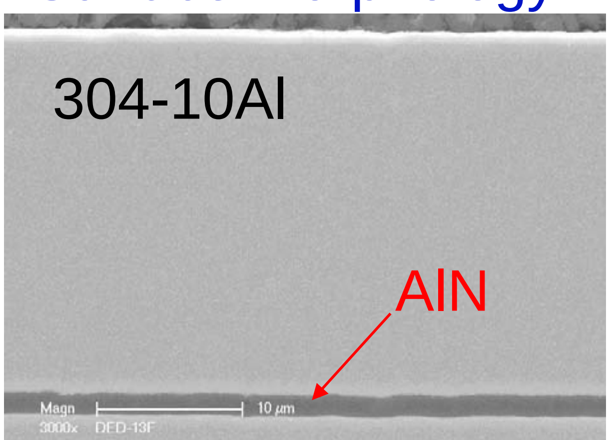
Coatings are dense and exhibited no cracks

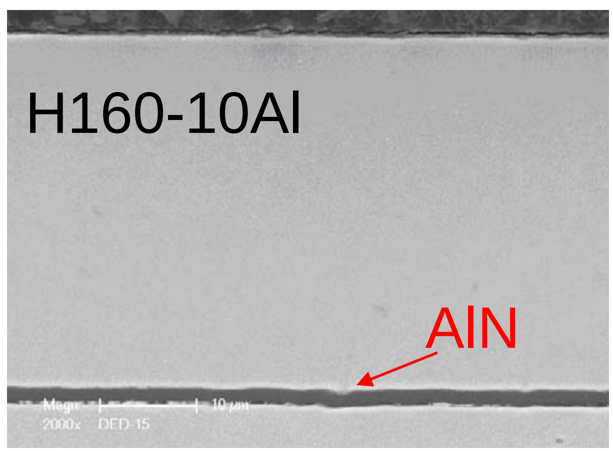


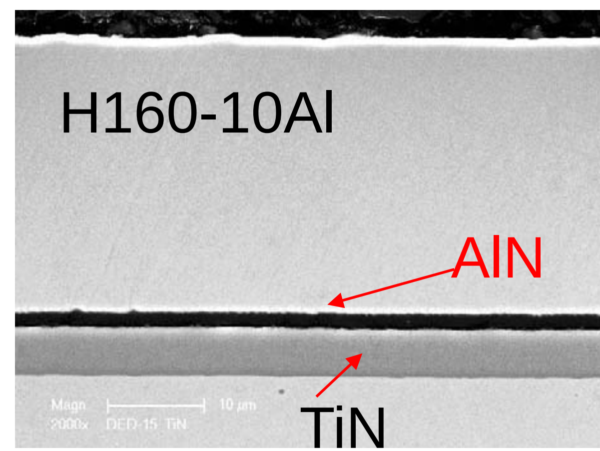




Surface Morphology







Cross Section

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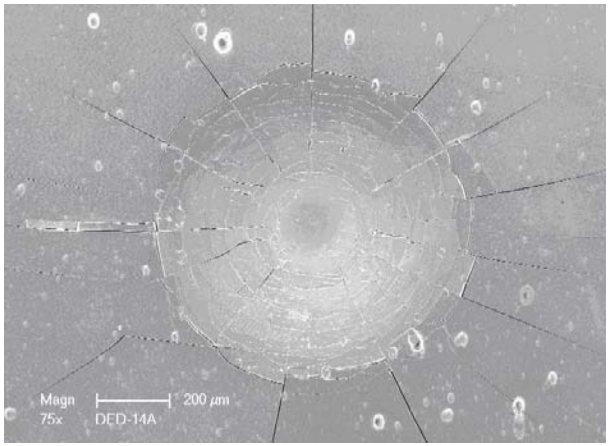
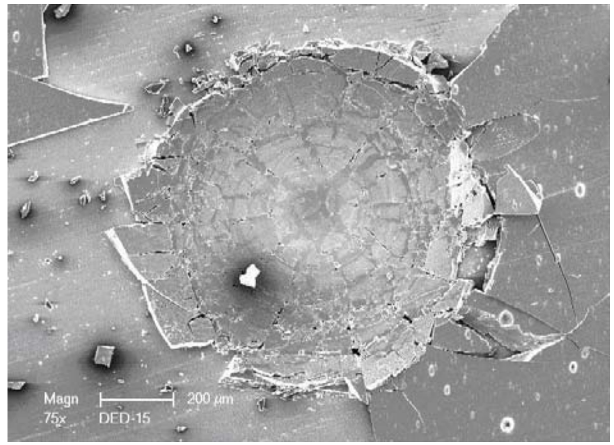
Task 3 - Processing of NanoCoatings --HIPIMS Process Optimization- Coating Adhesion

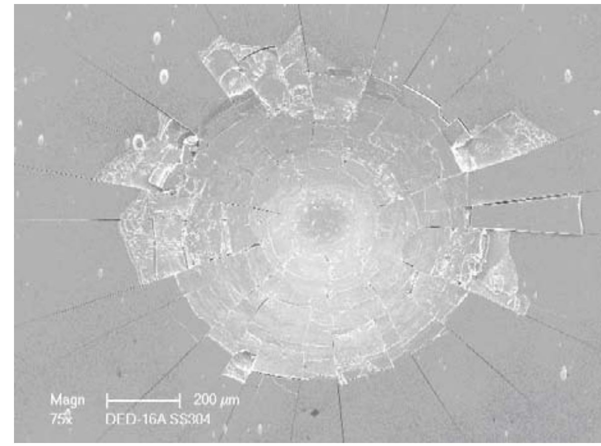
Poor adhesion & brittle



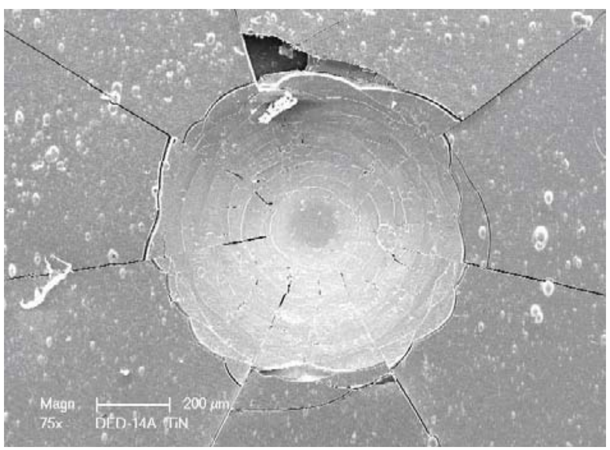
H120+10Al on AlN



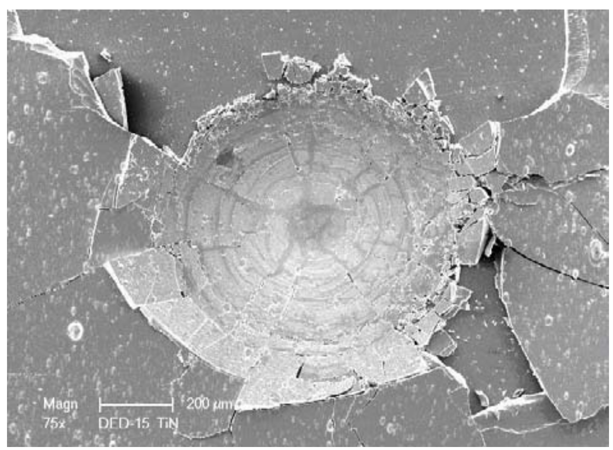
H160+10Al on AlN



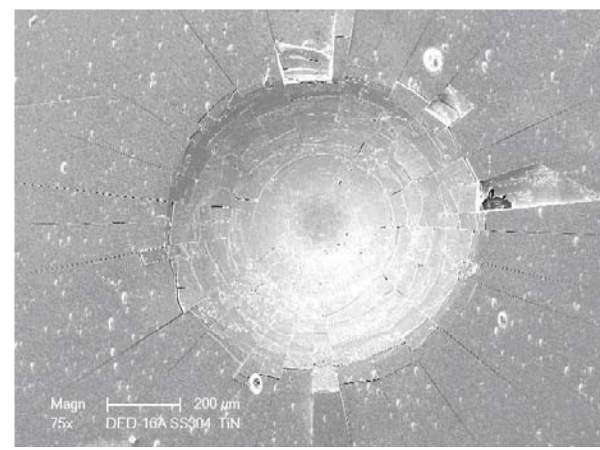
H188+10Al on AlN



H120+10Al on TiN/AlN

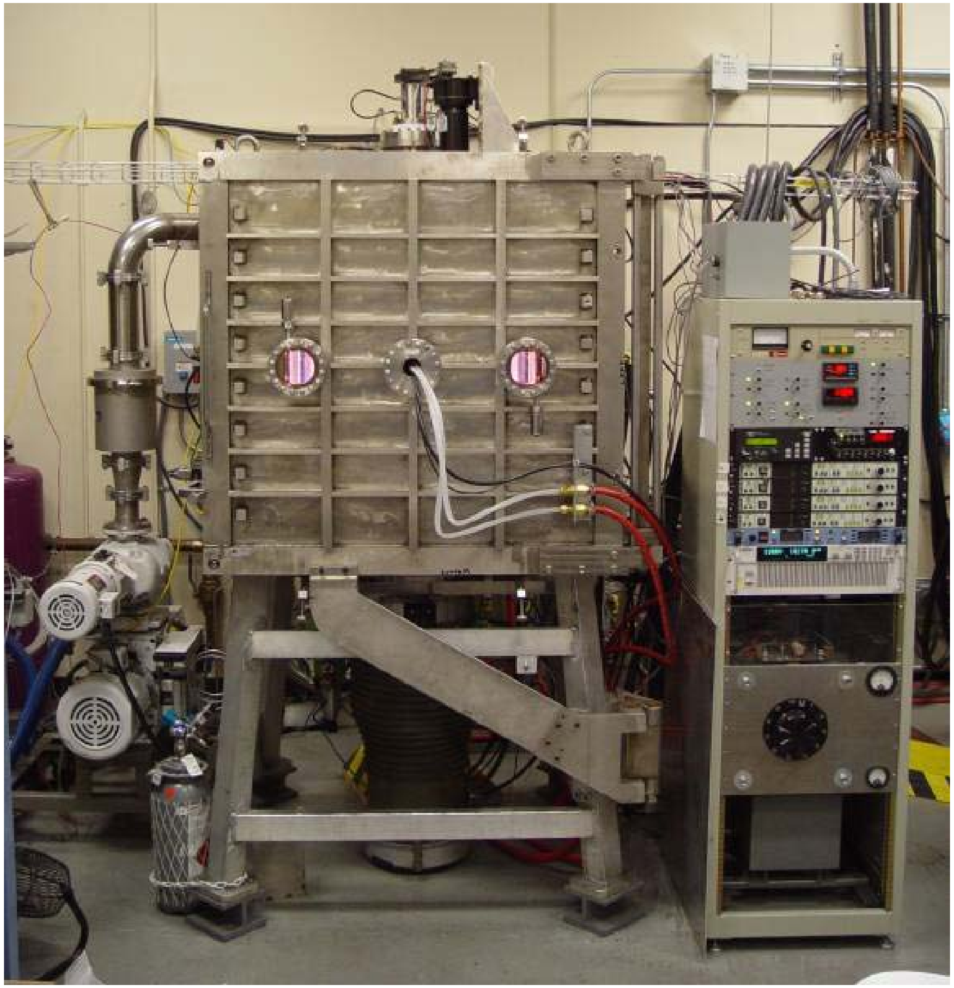


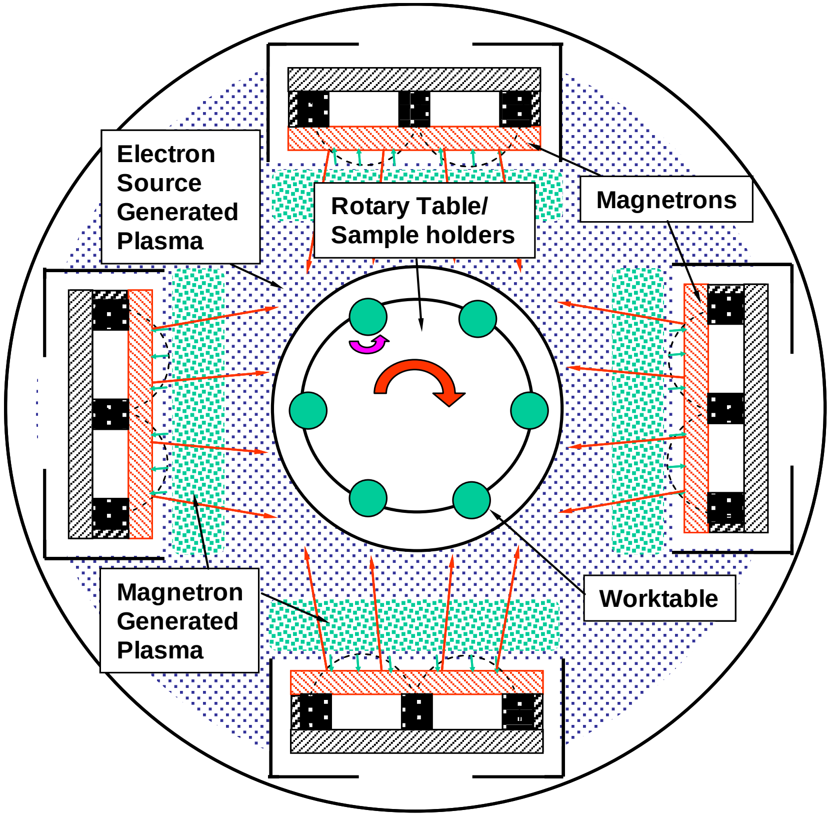
H160+10Al on TiN/AlN



H188+10Al on TiN/AlN

Task 3 - Processing of NanoCoatings
3. Large PEMS w/ 4 Magnetrons

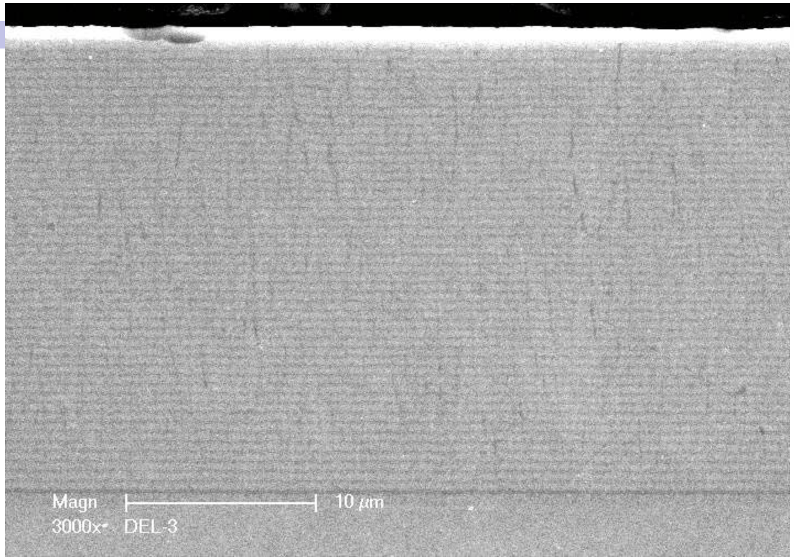


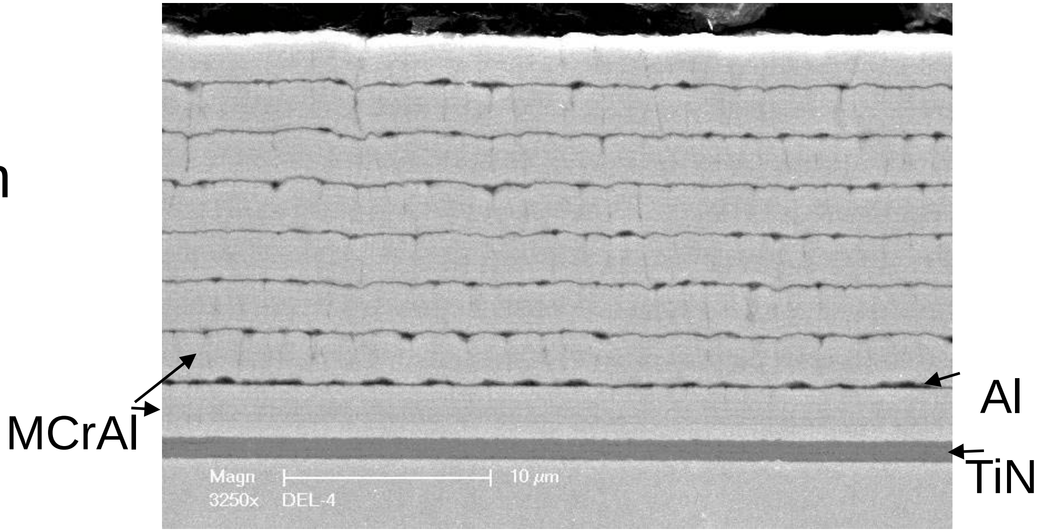


1 m3 Cube with Four Magnetrons

Task 3 - Processing of NanoCoatings
3. Large PEMS w/ 4 Magnetrons

- Conducted 20+ Coating Trials
- Varied Process Variables for 5 target materials (304, 310, Ni-20Cr, H120 and H160)
  - Sputter cleaning time
  - Magnetron Power, bias and discharge currents
  - Single or multi-layer MCrAl/Al Coatings
- Produced dense coatings with fine, discontinuous lamellar structure
- Selected the best process parameters





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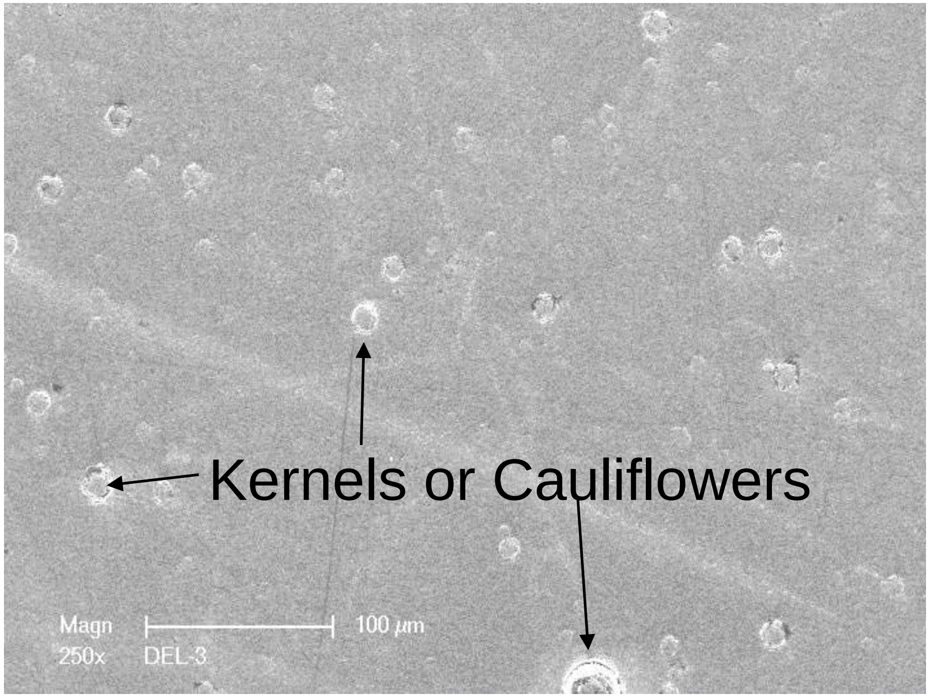
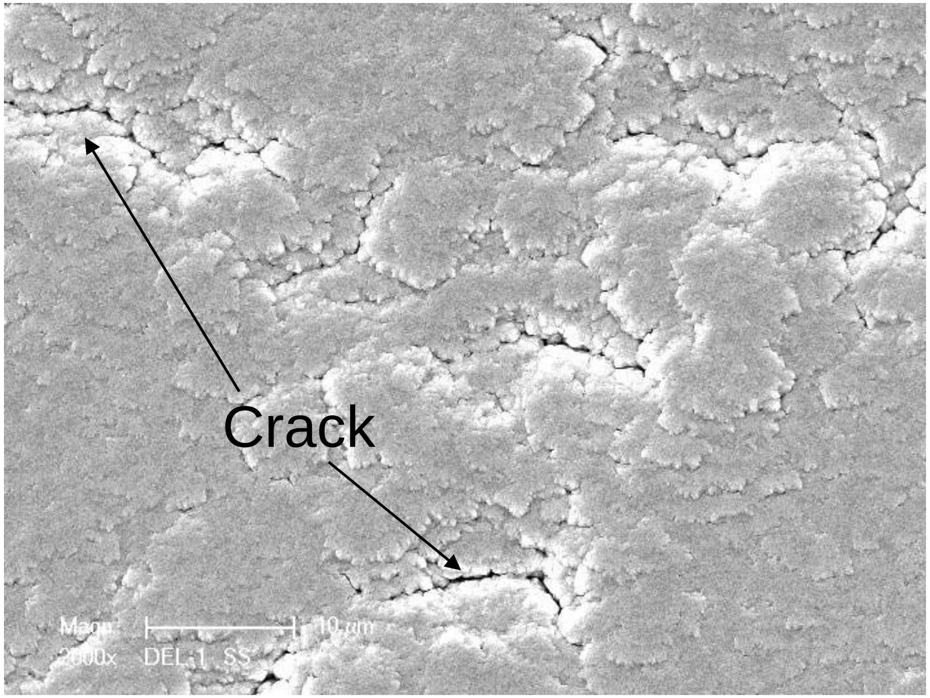
Coating Development Using Large PEMS -- Coating Quality





Still coatings exhibited kernels or cauliflowers and fine cracks

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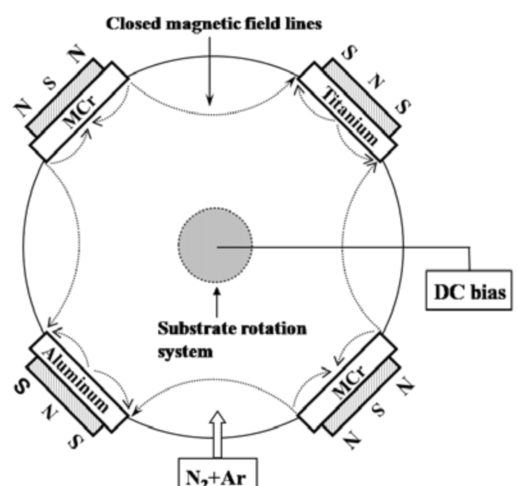
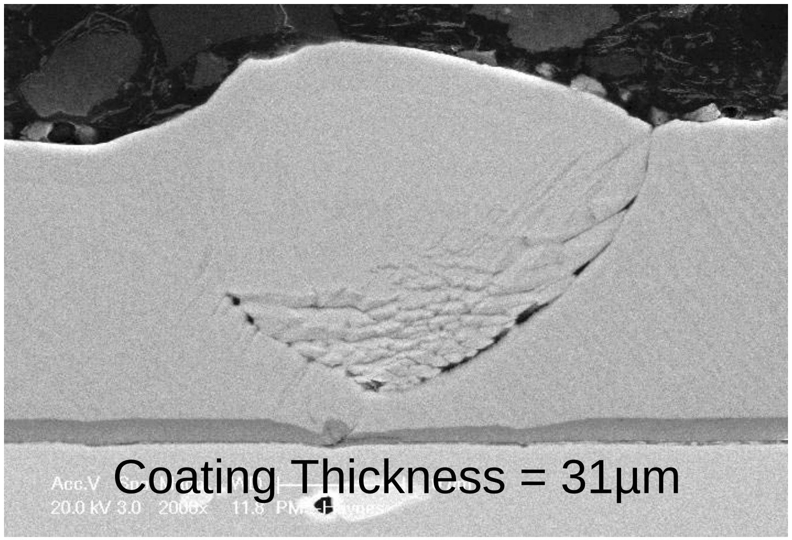
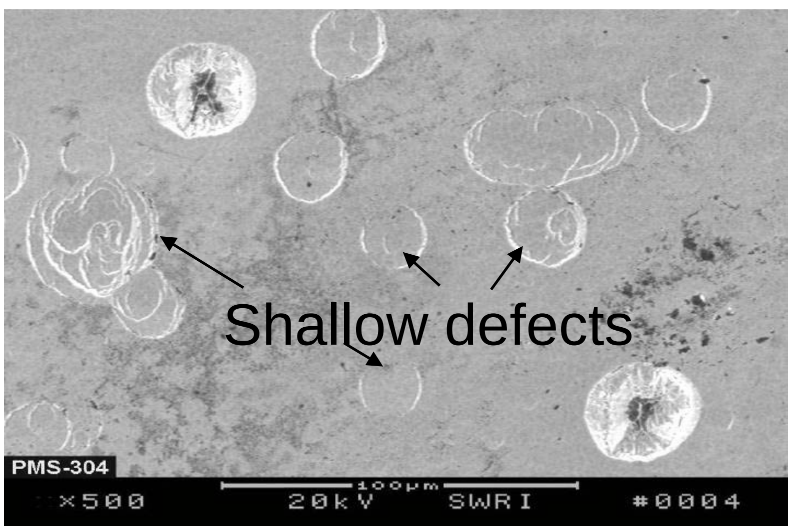
Task 3 - Processing of NanoCoatings
4. Pulsed DC Magnetron Sputtering

- Contacted Colorado School of Mines for coating deposition using Pulsed DC power supply
- 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



Pulsed DC Magnetron Sputtering – Thick Coatings





Coating Quality Improvement Plans—continuing

- Thick coating deposition with sputter cleaning at predetermined intervals
- Deposition of multilayer MCrAl/Al coating

- No Cracks
- Still a few cauliflower defects

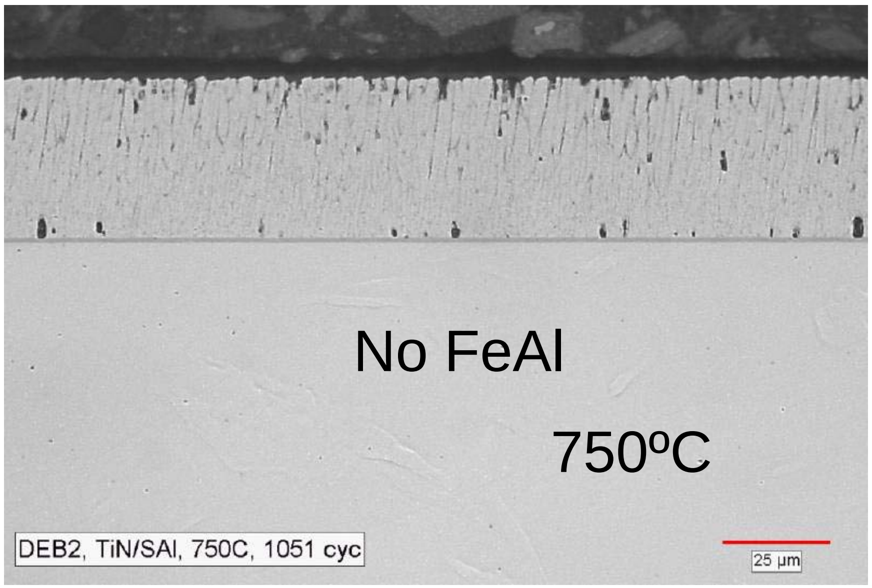
Task 3 - Processing of NanoCoatings
--Reducing Al Consumption

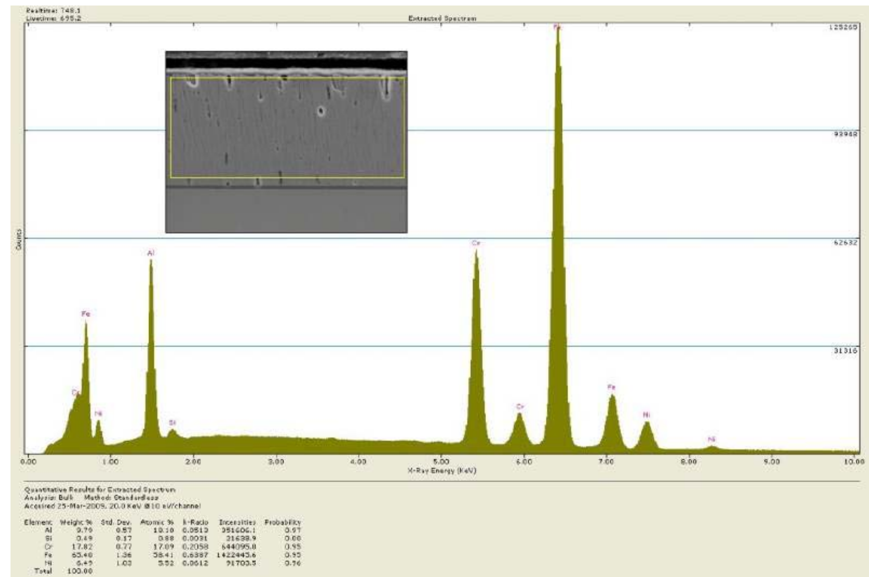
- Diffusion barrier interlayer coatings considered
  - AlN, TiN, and TiSiCN
  - TiN/AlN and TiSiCN/AlN

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

Task 3 - Processing of NanoCoatings --TiN Interlayer Barrier Coating

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

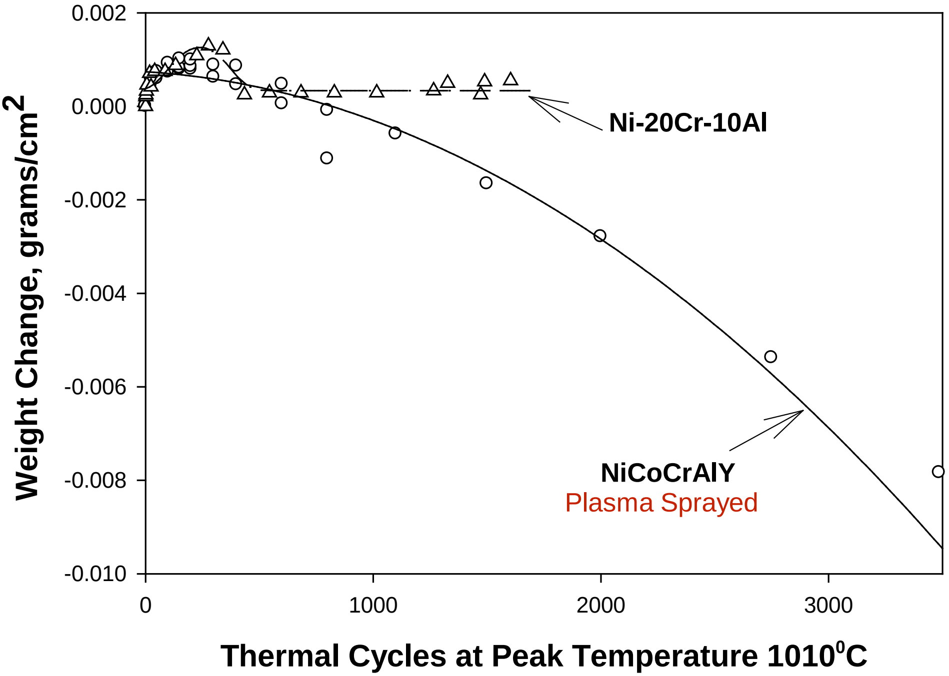


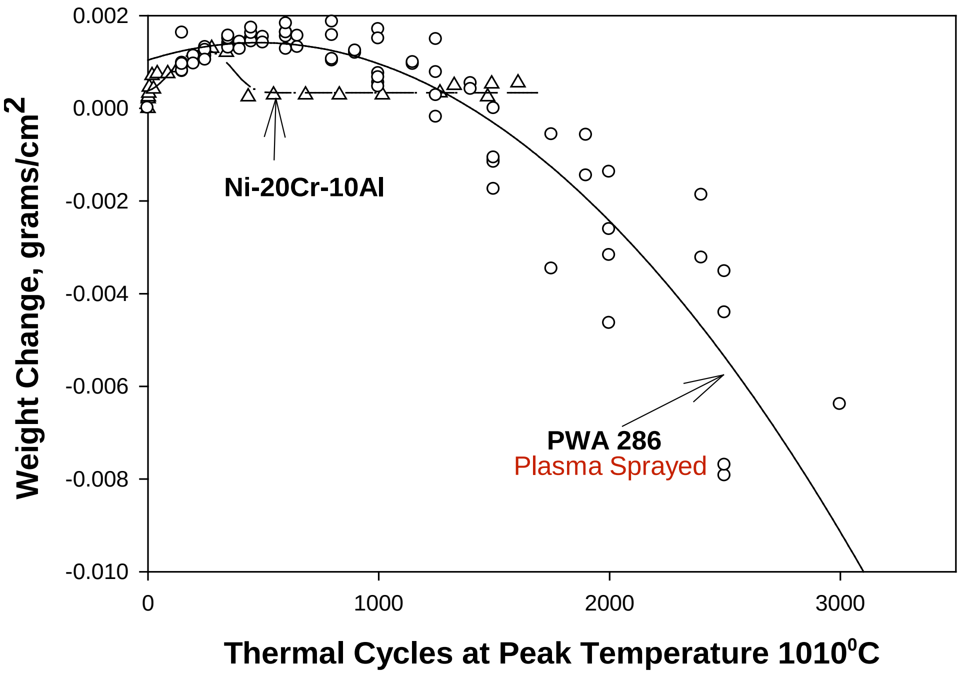


- TiN interlayer is intact
- No inward diffusion of Al into 304SS
- Interlayer is very effective

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

Comparison Oxidation Resistance of Nanocoating Ni-20Cr-10Al and Plasma-Sprayed NiCoCrAlY & PWA 286



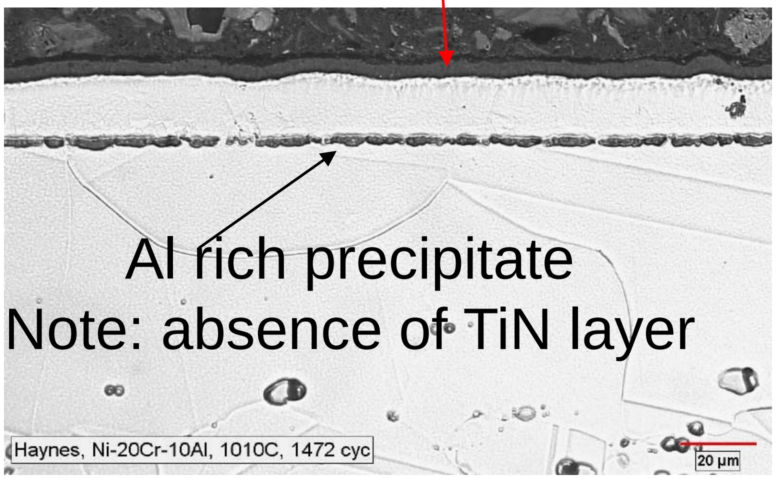


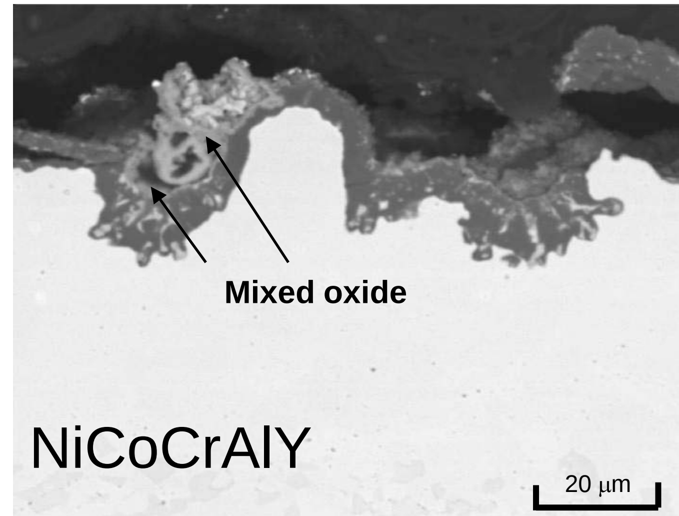
Oxide scale on nanocoating showed almost no evidence of spallation

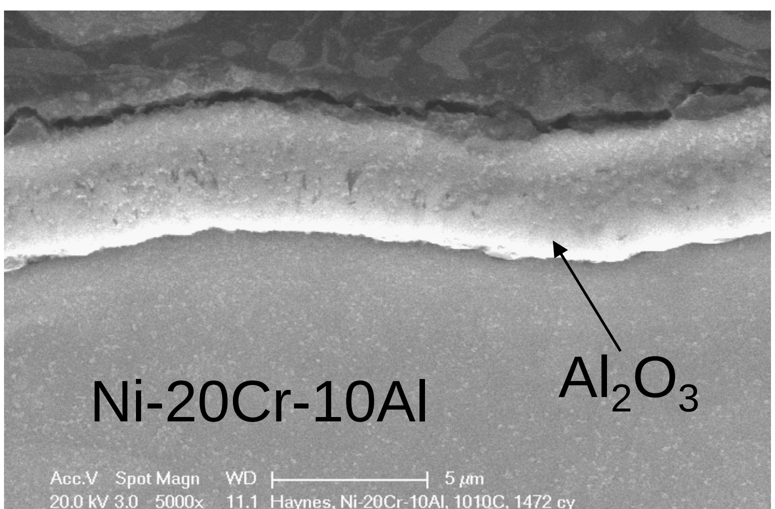
Comparison Coating Degradation of Nanocoating Ni-20Cr-10Al and Plasma-Sprayed PWA 286

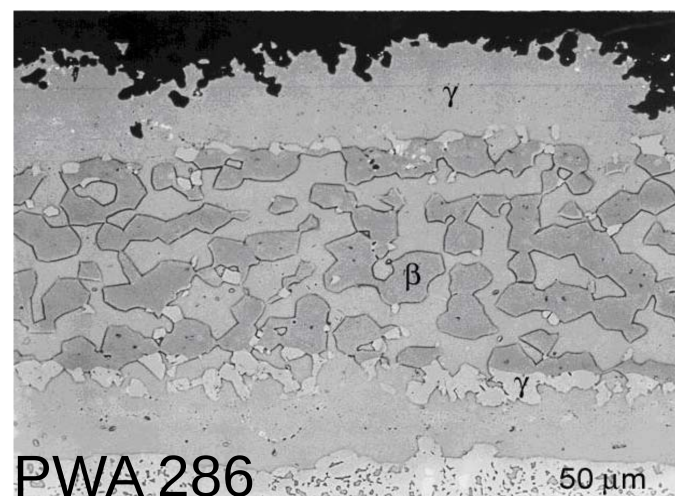
1500 cycles at 1010ºC

Continuous Al_2O_3

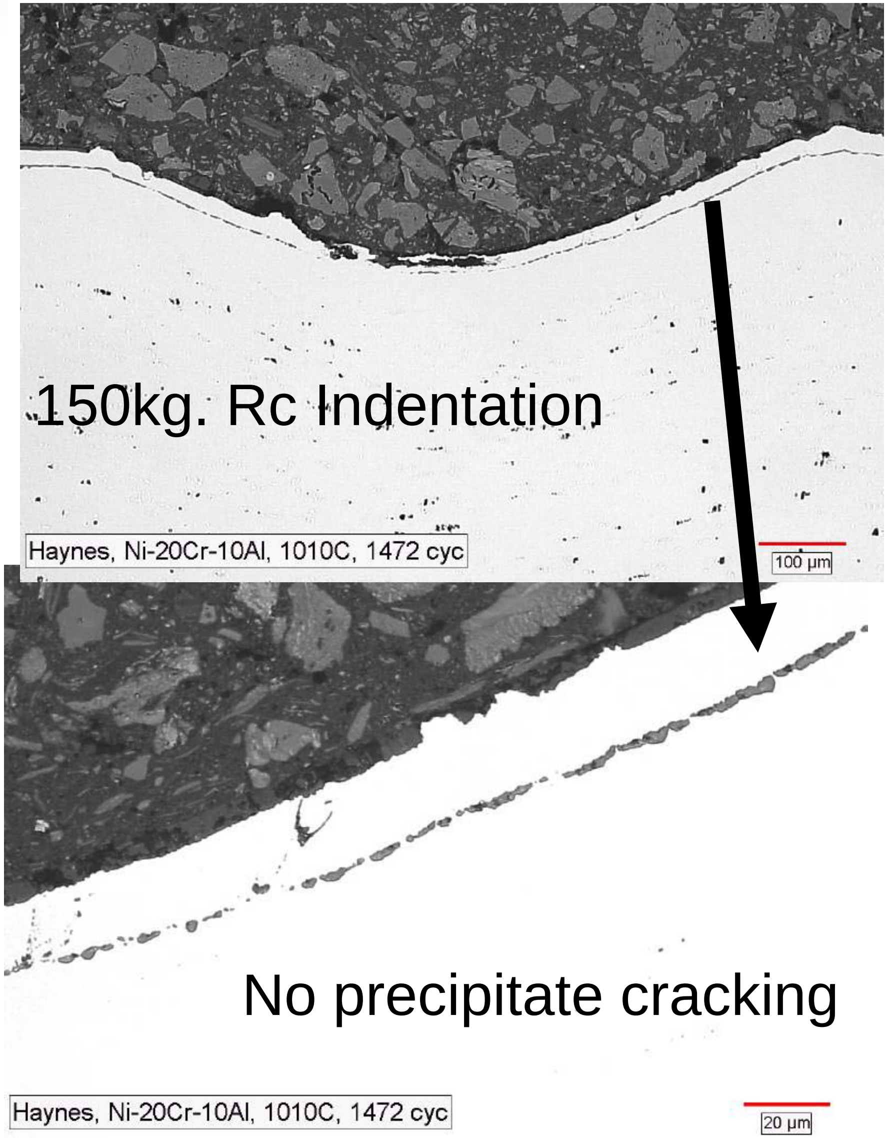


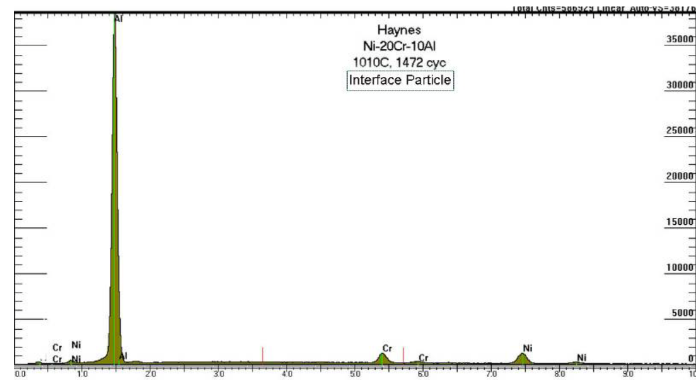






Ni-20Cr-10Al nanocoating degradation-Ductile interface Al-rich precipitate

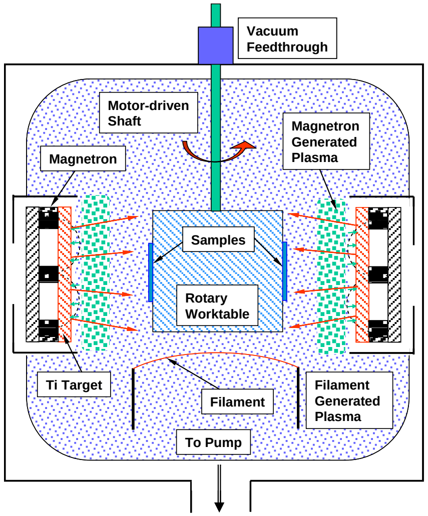




Al rich interface precipitate

- Nanocoating exhibited better oxidation Resistance than MCrAlY and PWA 286 at 1010ºC
- Oxidation is not a concern for these coatings at USC boiler operating temperatures

A patent disclosure was filed

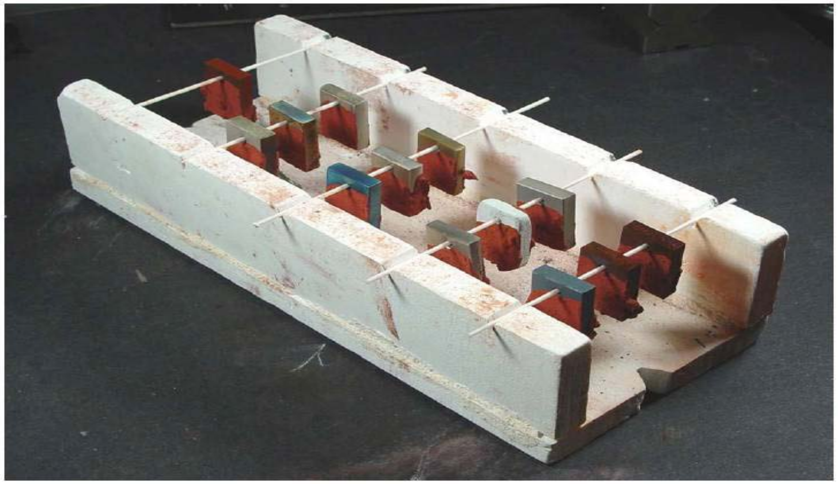


Task 4: Fireside Corrosion Testing

--completed original scope

Objective: Conduct accelerated fireside corrosion tests

Task 4 - Corrosion Testing --Testing Conditions



Waterwall Testing

- 850ºF (454ºC), 975ºF (524ºC), and 1100ºF (593ºC)
- 40 percent FeS and 0.2 percent chlorides (same as USC program)

Superheater/Reheater Testing

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

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

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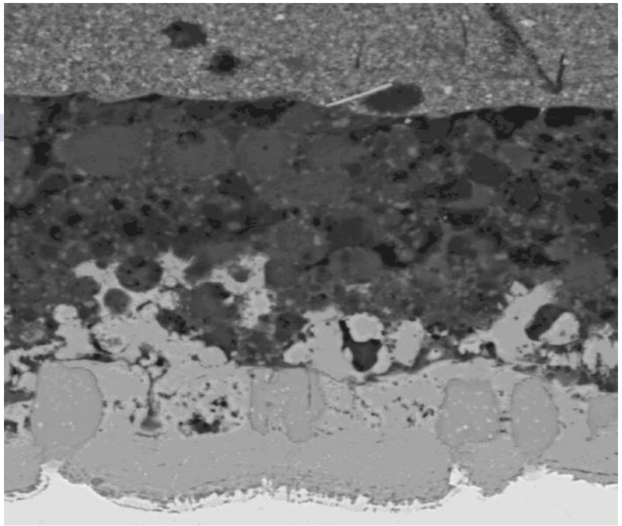
Waterwall Conditions --Results

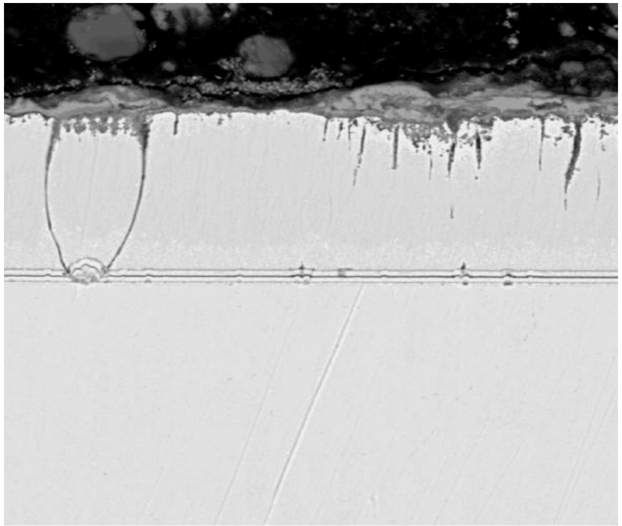
Commercial Nanocoatings

- Relatively porous; provided little protection
- Significant penetration of oxide & sulfide species
- Interconnected network of cracks allowed for penetration

DOE Nanocoatings

- Cracking/spallation generally noted
- Generally resisted "bulk" coating corrosion (some level of protection)
- Scattered penetration of oxide and sulfide species noted @ columnar grain boundaries and defect sites





Waterwall – 1000hr, 975°F

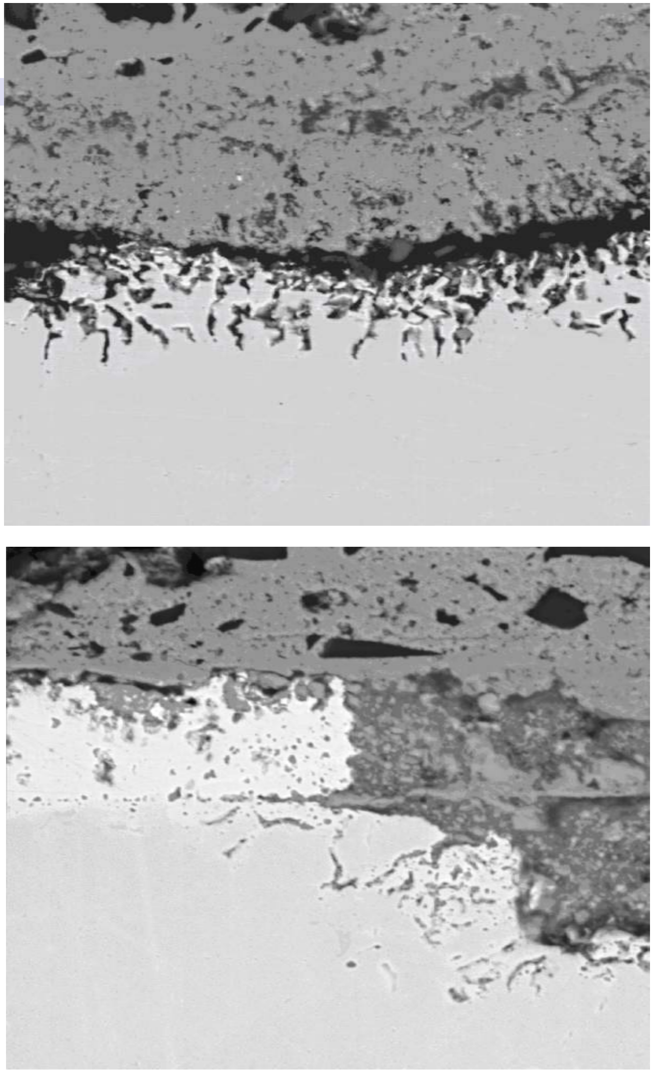
SH/RH Conditions --Results

Commercial Nanocoatings

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

DOE Nanocoatings

- Complete consumption of the coating and subsequent wastage
  - Degradation generally increased with test temperature
- Some nanocoatings were unstable at high temperatures
  - Interdiffusion between coating and substrate

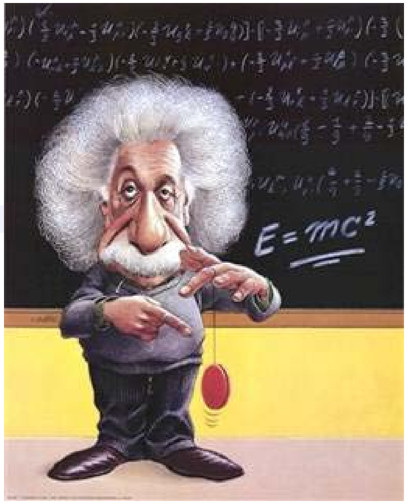


SH/RH – 1000hr, 1300°F

Conclusions To Date (1)

- For long-term term durability, nanocoatings should contain ~10%Al.
  - A continuous, Al-rich protective oxide scale can be achieved with this level of aluminum.
- Four (4) nanocoatings selected using computational thermodynamics, other models.
- Good cyclic oxidation performance exhibited for baseline nanocoatings (Fe-18Cr-8Ni-xAl, Ni-20Cr-xAl)
- Poor fire-side corrosion observed
  - Due to penetration of oxides and sulfides & cracking
- Nanocoatings did provide some protection for WW applications, but cracking ultimately resulted in failure.

Conclusions To Date (2)



Major Concerns Addressed

1. Coating Quality Issues (under investigation)
   - Cauliflowers (kernels) still evident
   - Cracking issues appear to be solved

2. Aluminum Consumption (solved)
   - A TiN diffusion barrier layer slows Al consumption rate dramatically.
   - Oxidation and Spallation are <u>not</u> issues (compared to plasma-sprayed PWA286 & NiCoCrAlY)

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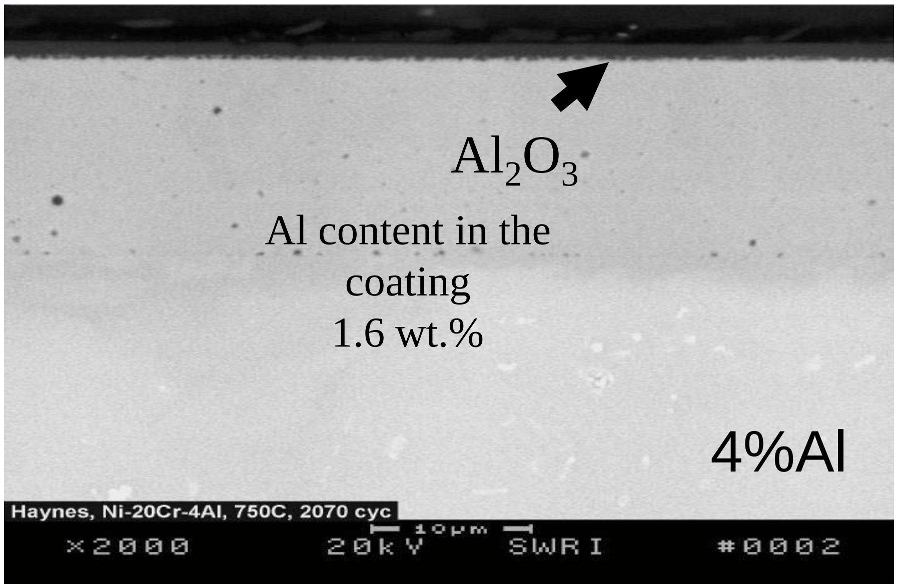
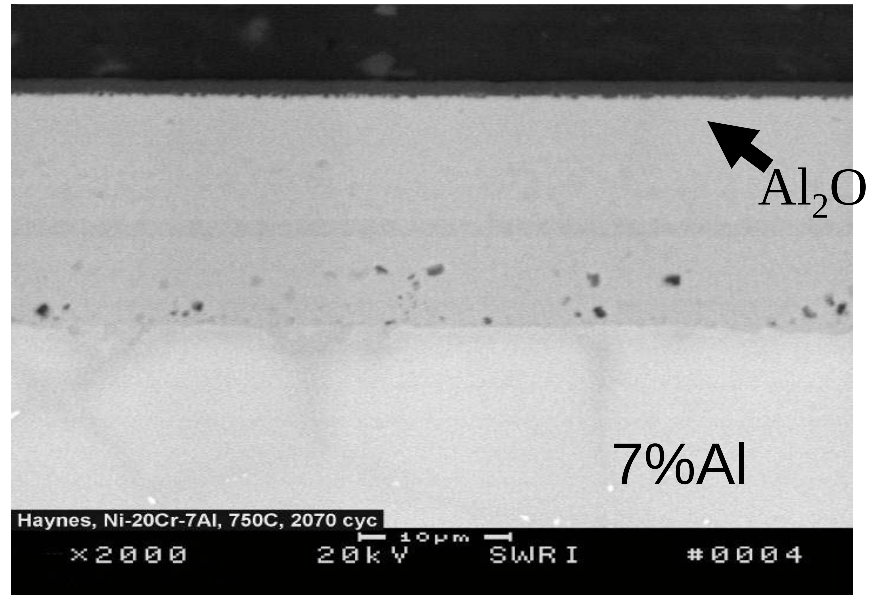
Task 2. Baseline Coating Oxidation Characterization -- Ni-20Cr-xAl





After 2070 cycles at 750ºC

- Protective external oxide scale is dense, free from cracks
- Resistant to spallation and coating is free from internal oxidation
- Continuous mass gain is due to outward growth of the scale
- Al consumption rate is high
- Established need for at least 7% Al for long-term durability

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