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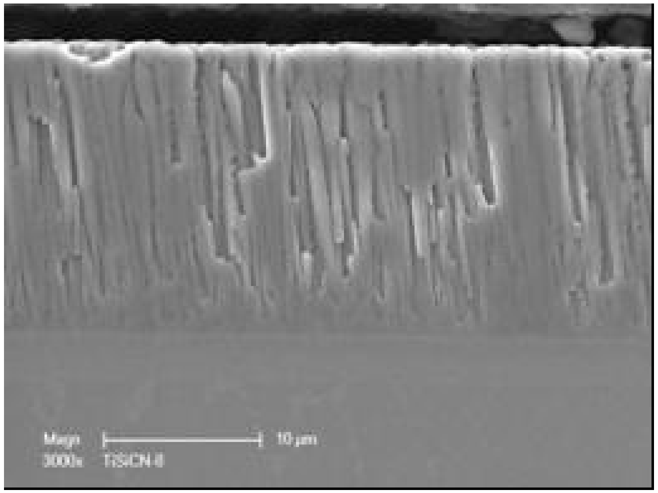


# Computational Modeling and Assessment of Nanocoatings for USC Boilers

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# Background

- Fireside corrosion of boiler waterwalls continues to be the #1 issue resulting in forced outages and boiler unavailability for “conventional” coal-fired fossil boiler power plants.

Equivalent Availability Loss from Boiler Tube Failures in US is 2.5-3.0%

# Background
# --Annual Corrosion Costs

| Corrosion Problem | O&M Corrosion Cost $ Millions | Depreciation Corrosion Cost $ Millions | Total Corrosion Cost $ Millions |
|---|---|---|---|
| **Waterside/Steamside Corrosion of Boiler Tubes** | 916.0 | 228.4 | 1,144.4 |
| Turbine CF & SCC | 458.0 | 142.8 | 600.8 |
| Oxide Particle Erosion of Turbines | 274.8 | 85.7 | 360.5 |
| Heat Exchanger Corrosion | 274.8 | 85.7 | 360.5 |
| **Fireside Corrosion of Waterwall Tubes** | 183.2 | 142.8 | 326.0 |
| Generator Clip to Strand Corrosion | 183.2 | 28.6 | 211.8 |
| Copper Deposition in Turbines | 91.6 | 57.1 | 148.7 |
| **Fireside Corrosion of SH & RH tubes** | 91.6 | 57.1 | 148.7 |

Source: Syrett, et al. Low Temperature Corrosion, EPRI





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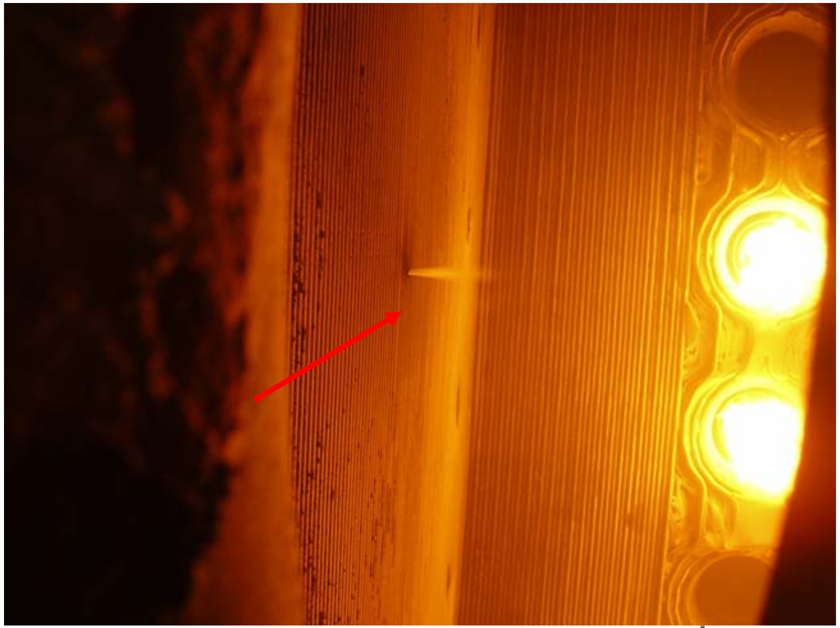
# Background

- Typical boiler wastage rates are:
  - 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



# Background

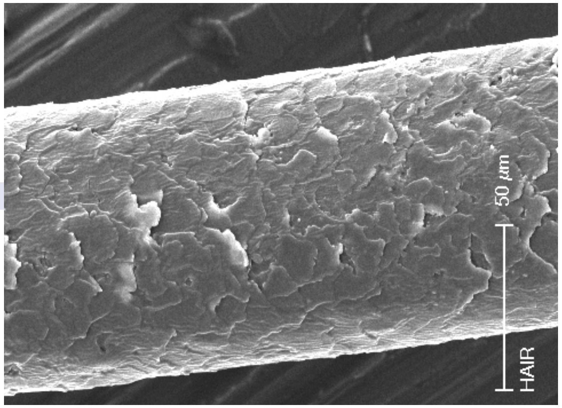
- USC boiler metal temperatures will approach 1400F (760C).
  - Accelerated corrosion rates are anticipated at these temperatures
- Alloys such as P91, Super 304H (austenitic SS), and Alloy 230 (nickel-based) alloys will be required.
- Advanced austenitic SS typically exhibit poor sulfidization or coal ash resistance.
  - Reliable sulfidization and oxidation resistant nanocoatings are required for improved durability of USC boiler tubes.

# DOE Nanocoatings Project Objectives

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

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

# What is a Nanocoating?



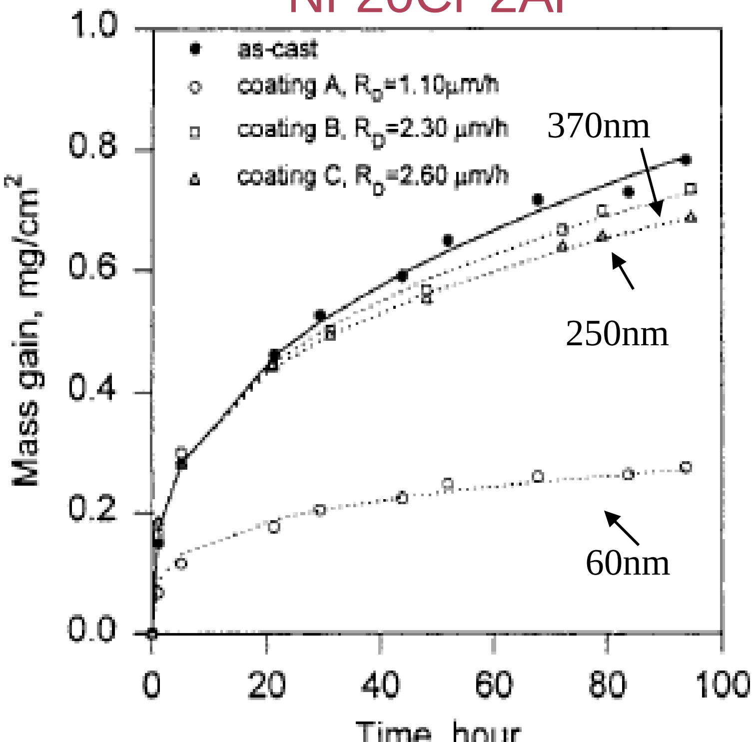

**Human Hair = 85µm = 85000nm**

Nanocrystalline materials/coatings:

- Single or multi-phase
- Grain size <100 nm (1nm = 10 Angstroms)
- Interfaces cover significant portion of the microstructure
- Dense
- Very hard and tough
- Offer excellent corrosion/oxidation/erosion properties compared to conventional materials/coatings

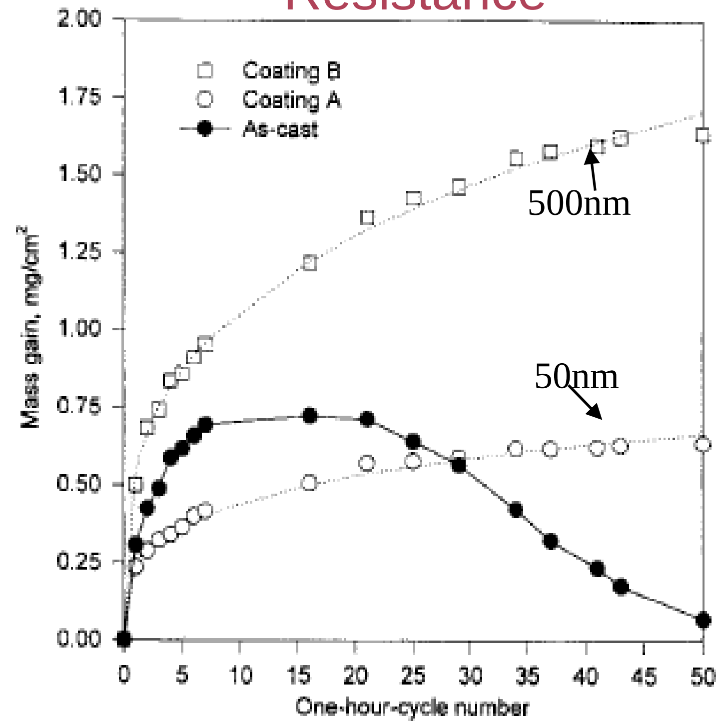
# Oxidation Behavior of Nanocoatings
## --@ 1000°C (1832°F)

Effect of Grain Size
Ni-20Cr-2Al




Lower oxidation kinetics

Spallation Resistance




Improved scale spallation resistance

Similar results were reported for CoCrAlY/FeNiCrAl microcrystalline coatings

1) Gao et al., *Advanced Materials,* 2001, 13, pp. 1001, 2) Liu et al., *Oxidation of Metals*, 1999, 51, pp. 403, and 3) Wang et al., *Oxidation of Metals,* 1996, 45, pp. 39





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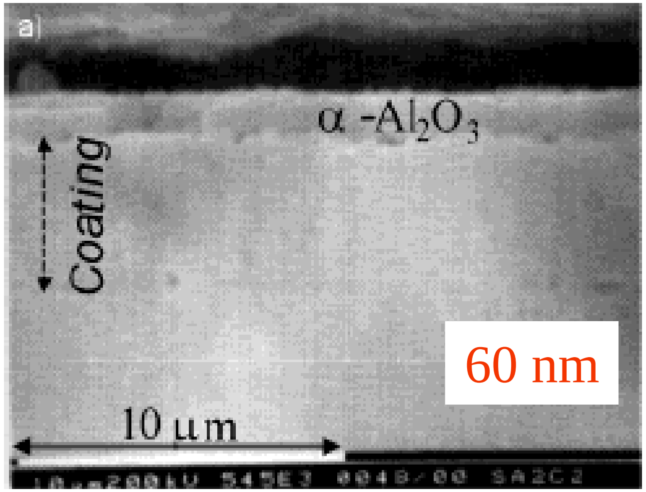
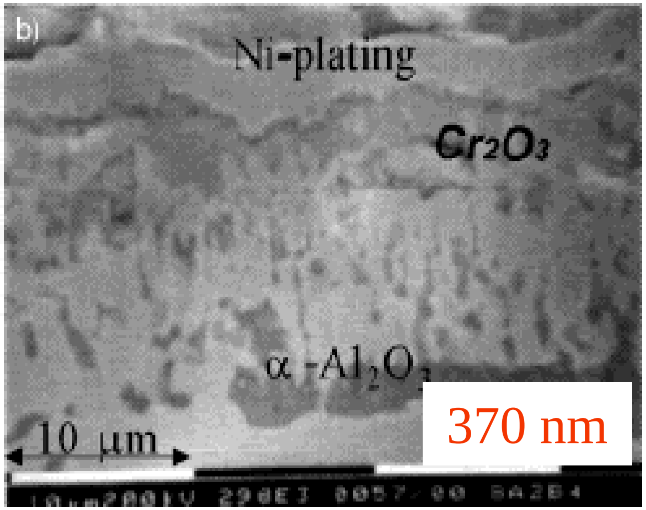
# Finer Grain Size Promotes Formation of Stable Alumina Scale

- Coating Ni-20Cr-2 Al
- Exposed @ 1000°C for 100 hrs
- Fine grained coating (60nm) exhibited continuous protective alumina scale
- Coarse grained coating severely oxidized




Finer grain size lowers minimum Al requirement!

**This would increase life by 3 to 4X**

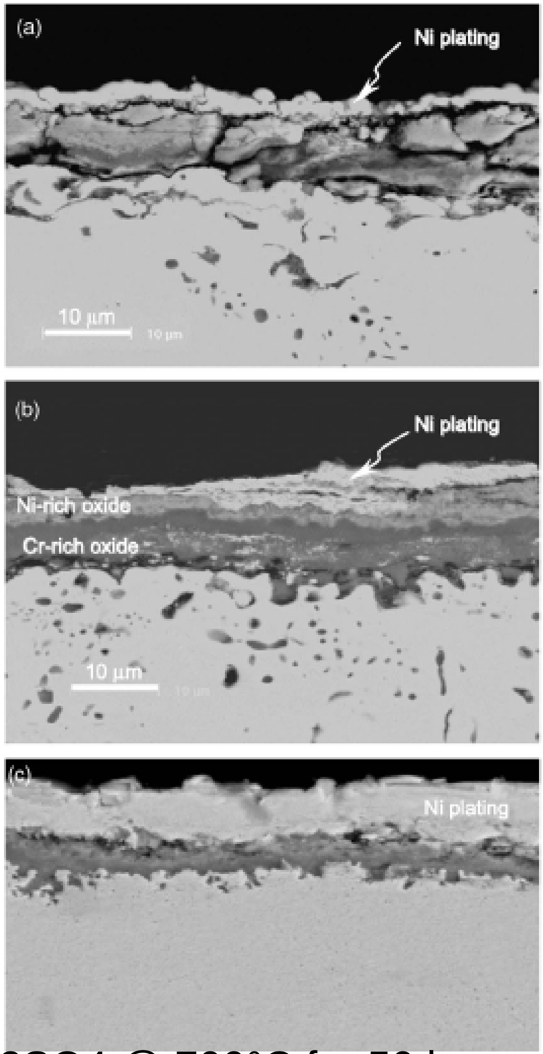
Gao et al., Nano and Microcrystal Coatings, *Advanced Materials,* 2001, 13, pp. 1001

# Corrosion Resistance of Nanocoatings

## --Finer grain size also 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

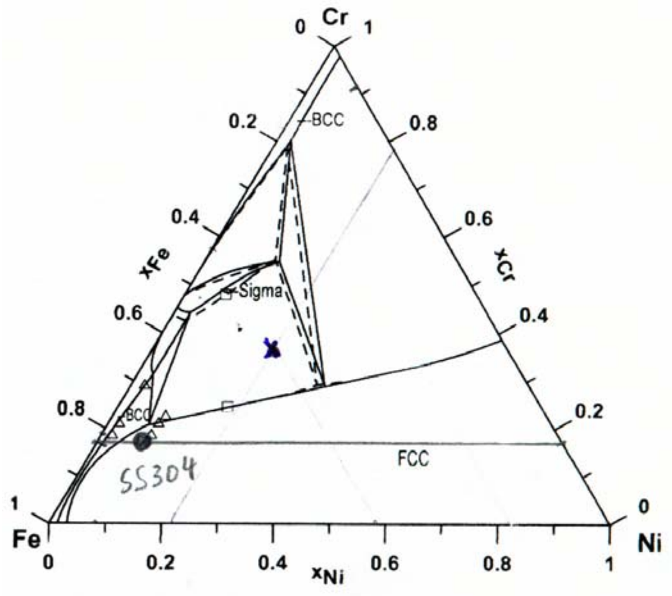
Ni-20% Cr Conventional

Ni-11% Cr Nanostructure

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

# Project Tasks

- Task 1: Computational Modeling of MCrAl Systems
- Task 2: Establishment of Baseline Coating Data
- Task 3: Process Advanced MCrAl Nanocoatings
- Task 4: Fire-Side Corrosion Testing
- Task 5: Computational Modeling & Validation
- Task 6: Mockup Demonstration
- Task 7: Project Management & Reporting



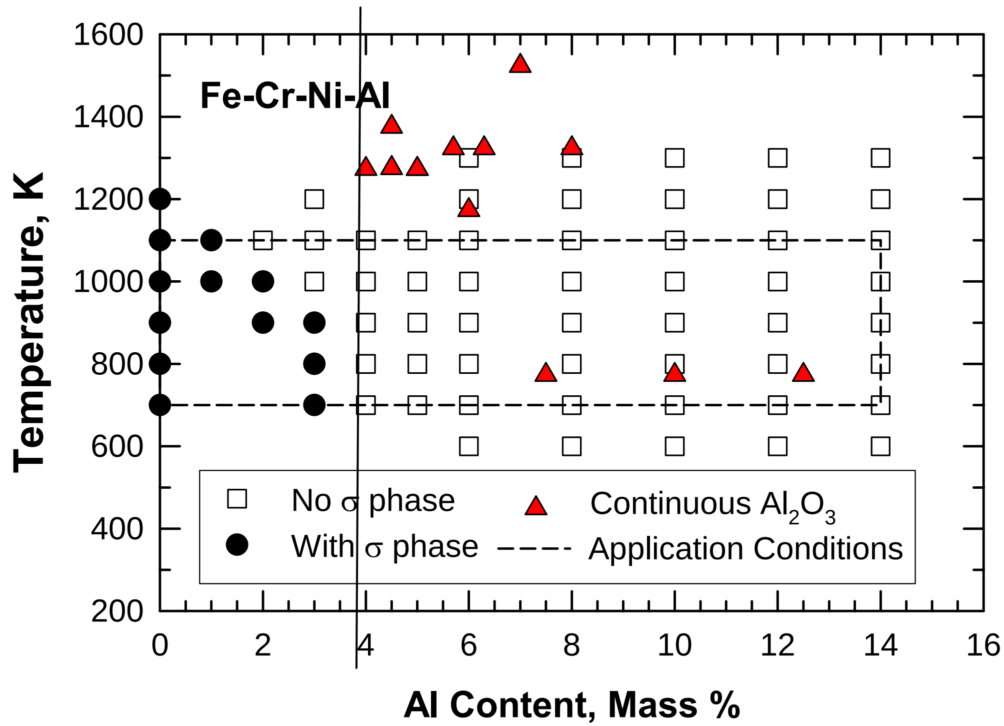

# Task 1: Computational Modeling of MCrAl Systems

**--completed**

**Objective: Select potential MCrAl nanostructured coating compositions using computational modeling**

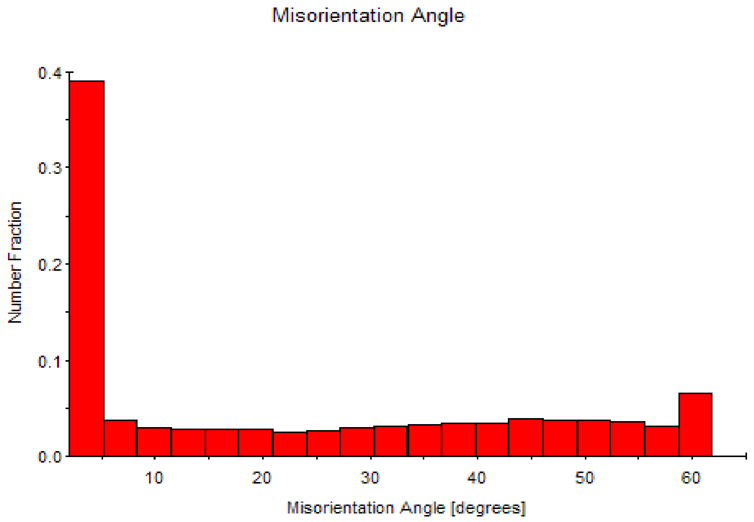
# Task 1- Computional Modeling Of MCrAl Composition Selection

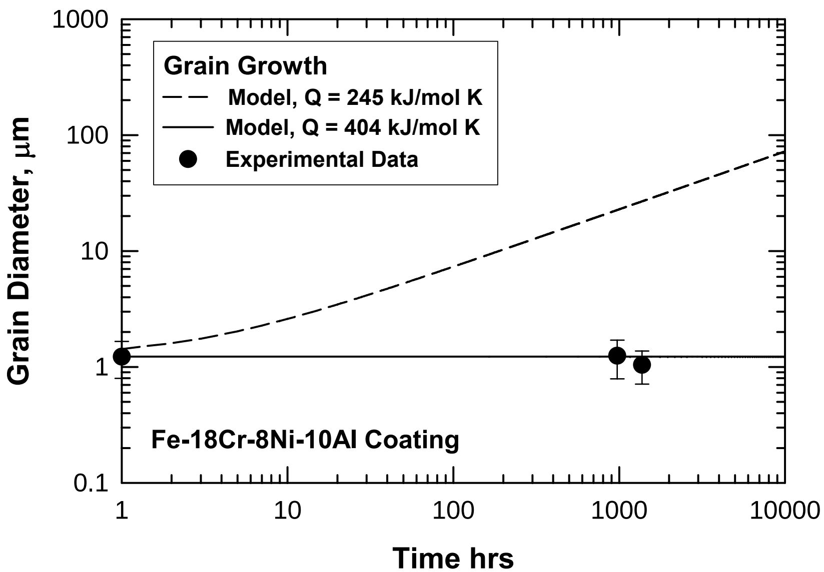
- Completed computations of FeNiCrAlx phase diagrams
- Al additions suppress sigma phase formation, while Mo and Co promotes.
- 4-5%Al is required to form a continuous Alumina scale.
- To ensure sufficient Al source, 10% Al is selected.
- Suggested nano-coating systems for evaluation:
  - 310 +10%Al
  - 310 +30-35Ni +10%Al
  - Fe-35-40Ni-25Cr-10%Al



# Task 1 - Computational Modeling --Grain Growth Modeling

- Grain growth model results showed that the presence of high concentration low angle boundaries in the coating prevents grain growth
- Thermal exposure at 750ºC leads to sintering
- Coating/interface toughness was determined
- The sputtered coatings exhibited good toughness
- Indentation testing showed no coating delamination





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# Candidate Nanocoatings for Evaluation

## Model Recommendation

- Coating composition: Fe-25Cr- 30/40Ni-10 Al

## Candidate Nanocoatings Selected For Evaluation

- 310 + Al (Fe-25Cr-20Ni-10Al)
- Haynes 120+Al (Fe-37Ni-25Cr-Al)
- Haynes 160+Al (Ni-29Cr-28Cr-3Si-Al)
- Haynes 188+Al (Co-22Ni-22Cr-14W-10Al)

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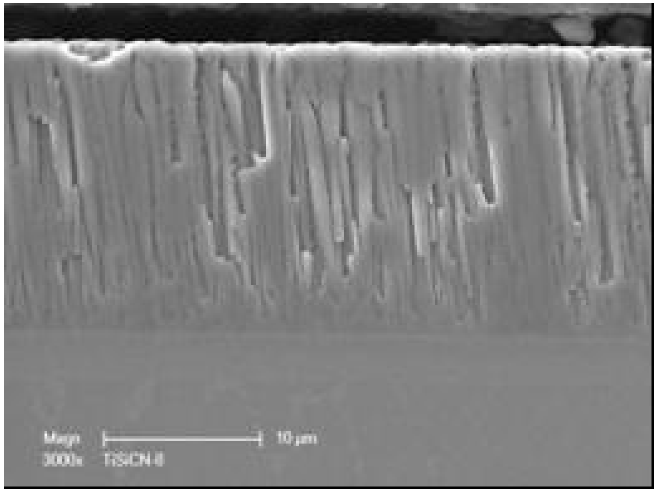


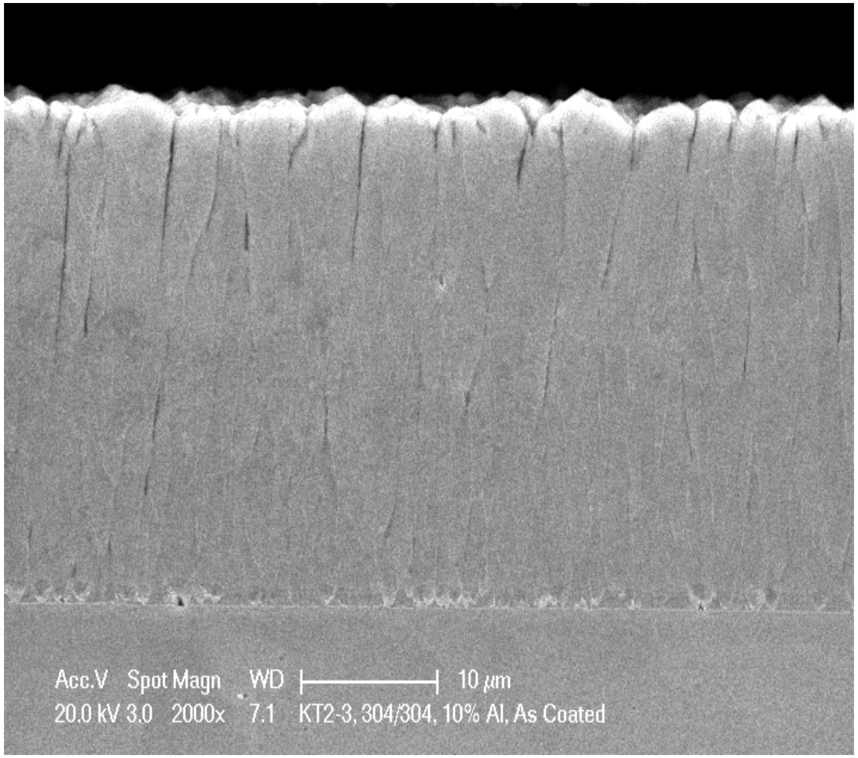

# Task 2: Establishment of Baseline Coating Data

**--completed**

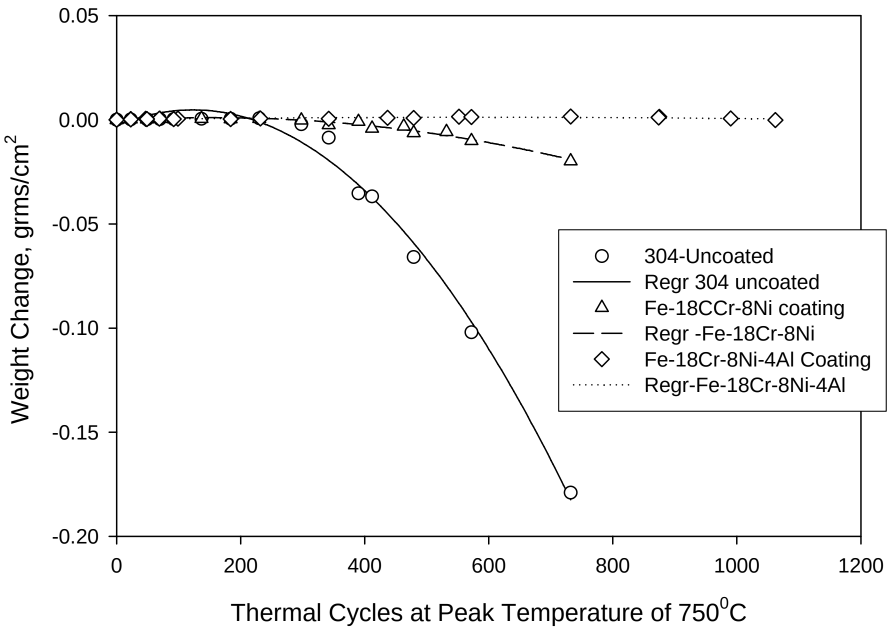
**Objective: Evaluate conventional- and available vendor nanocoatings to assess properties**

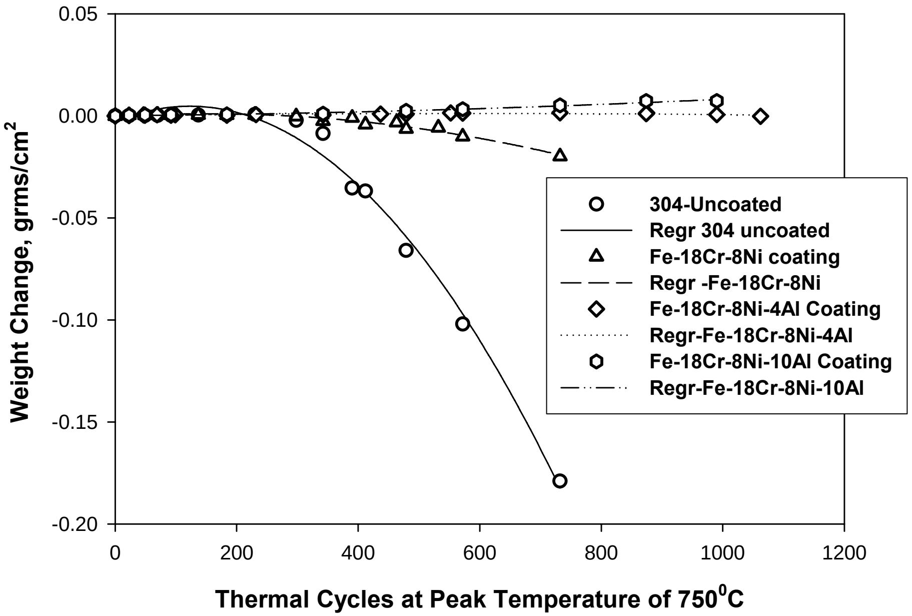
# Task 2. Establishment of Baseline Coating Data

- Fe-18Cr-8Ni-xAl Nano-coatings were deposited on 304SS and P91 samples
- Ni-20Cr-xAl Nano-coatings were deposited on Haynes 230 and P91 samples
- Long term cyclic oxidation tests were conducted on the coated samples



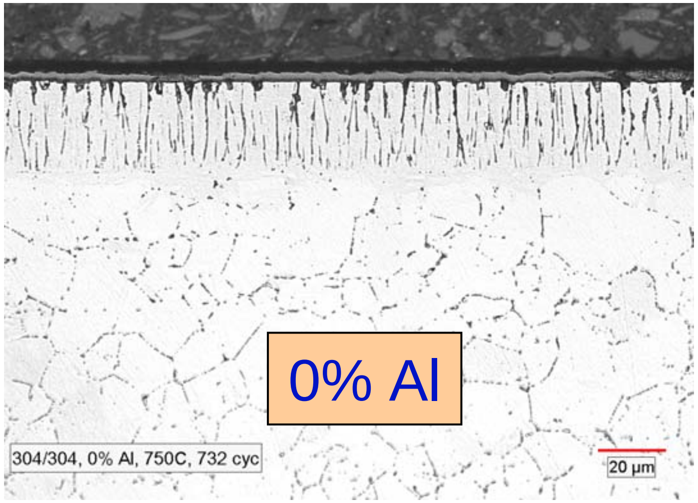
# Task 2. Baseline Coating Data
# --Cyclic Oxidation Behavior of Fe-18Cr-8Ni-xAl Coatings

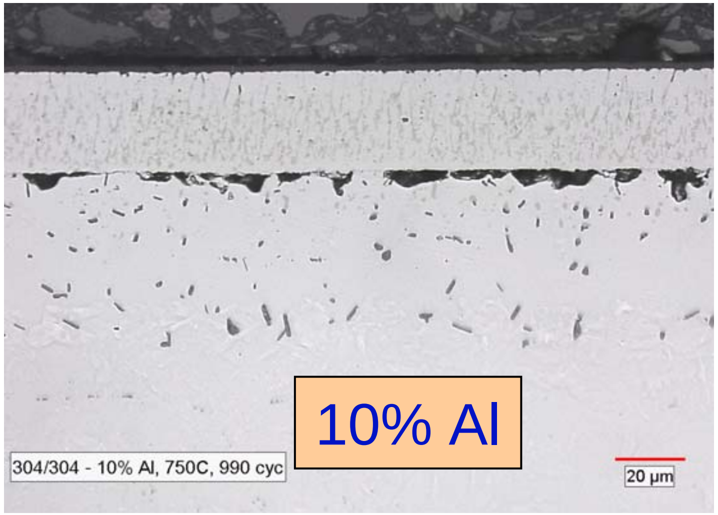


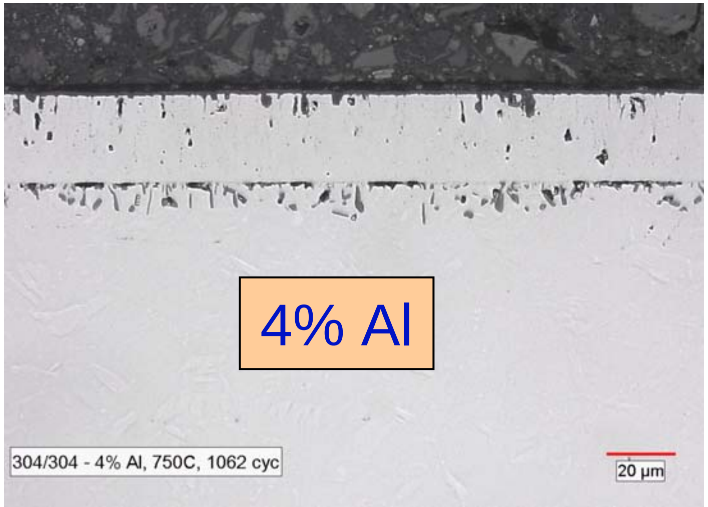




- Fe-18Cr-8Ni-xAl Nano-Coating Improved Oxidation Resistance By 2X.
- The Addition Of Al Improved
  - Oxide-Scale Spallation Resistance
  - And Oxidation Resistance

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




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

3). 10% Al coating was free from internal oxidation

4). Inward diffusion of Al led to formation of inter-diffusion zone





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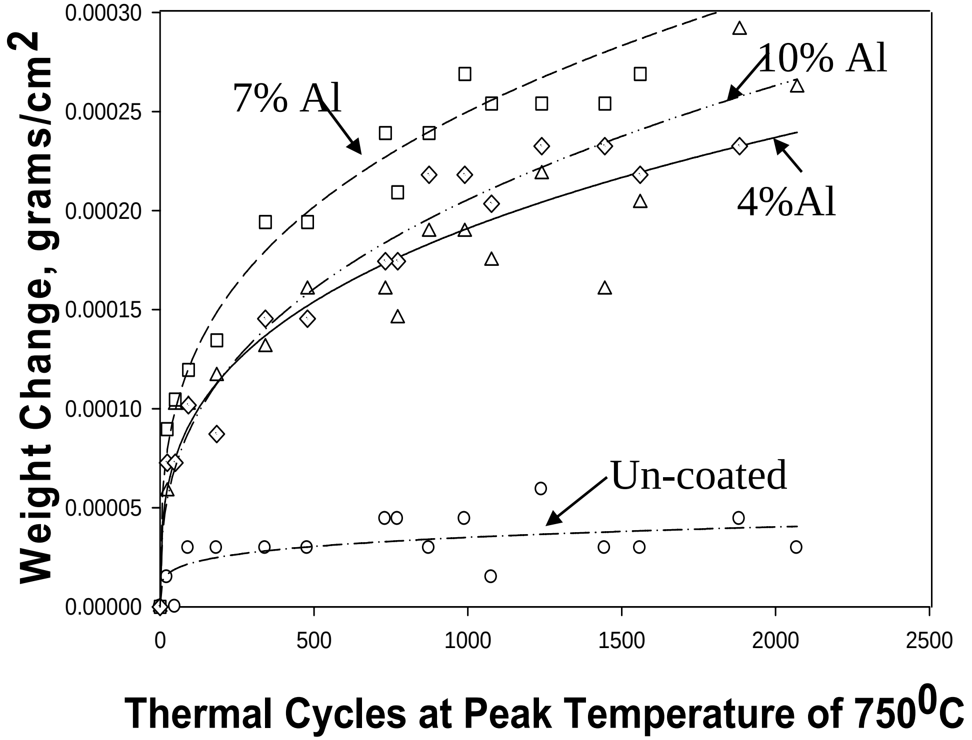
# Task 2. Baseline Coating Data --Cyclic Oxidation Behavior of Ni-20Cr-xAl Nanocoated and Uncoated Samples at 750ºC

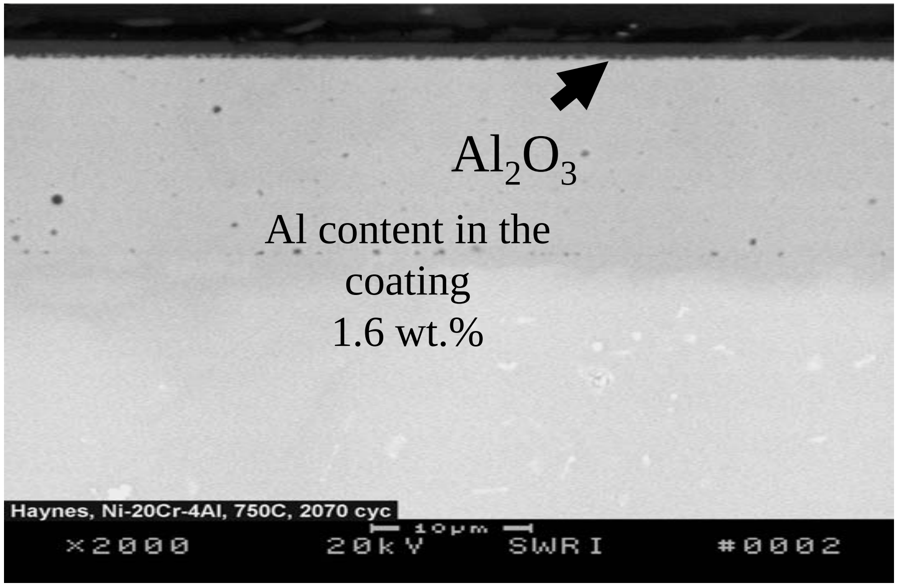
Continuous mass gain of the coated samples indicates the outward growth of oxide scale

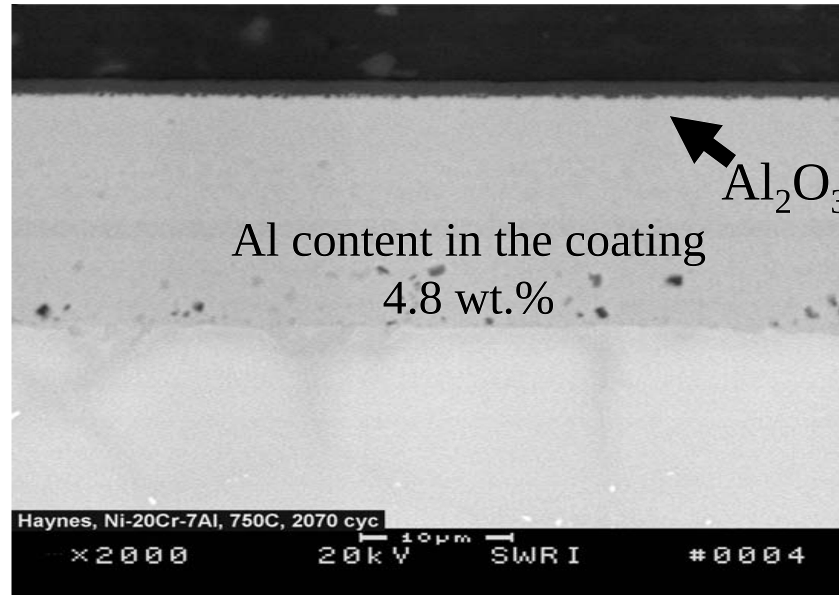
Scale is highly resistant to spallation

Haynes 230 may not need a coating at 750C

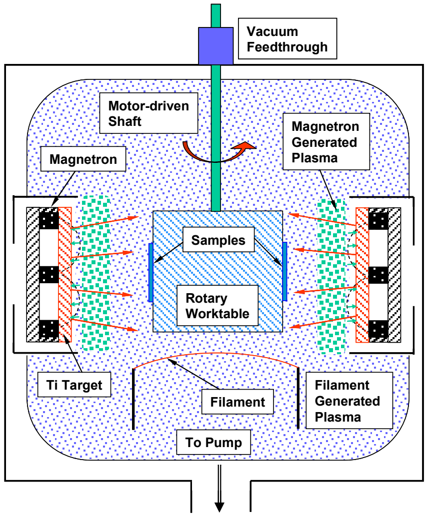


# Task 2. Baseline Coating Data
# --Oxide Scale on Ni-20Cr-xAl NanoCoating After Exposure at 750°C




- Protective external oxide scale is dense, free from cracks
- Highly 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
- The coating with 4% Al may not be durable for long-term service
- Established need for at least 7% Al for long-term durability

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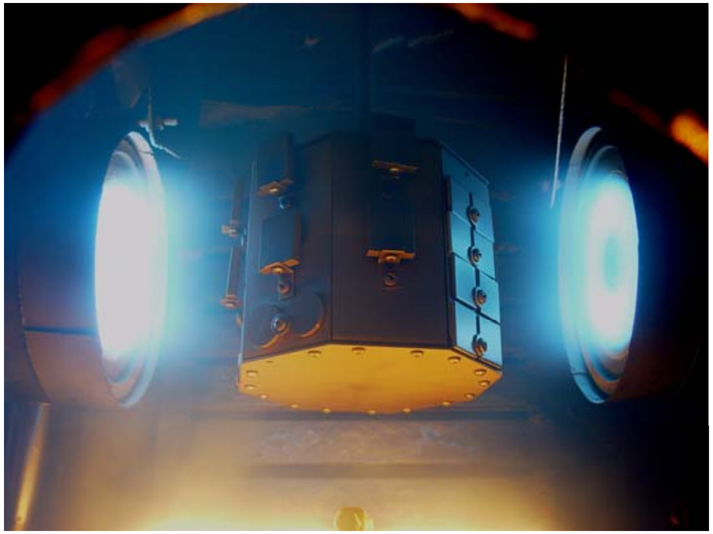
# Task 3: Processing of Advanced NanoCoatings

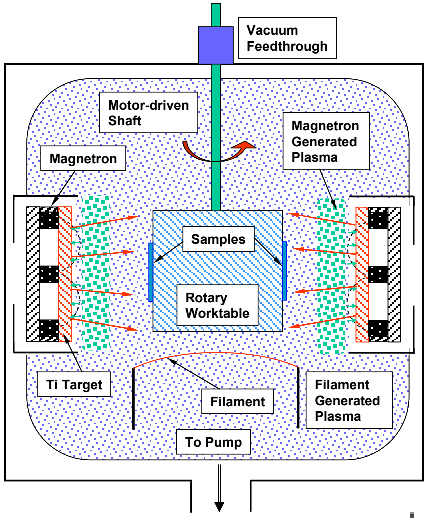
## --in progress

**Objective: Apply advanced nanocoatings on USC substrates and evaluate properties**

# Task 3 - Processing of Advanced NanoCoatings

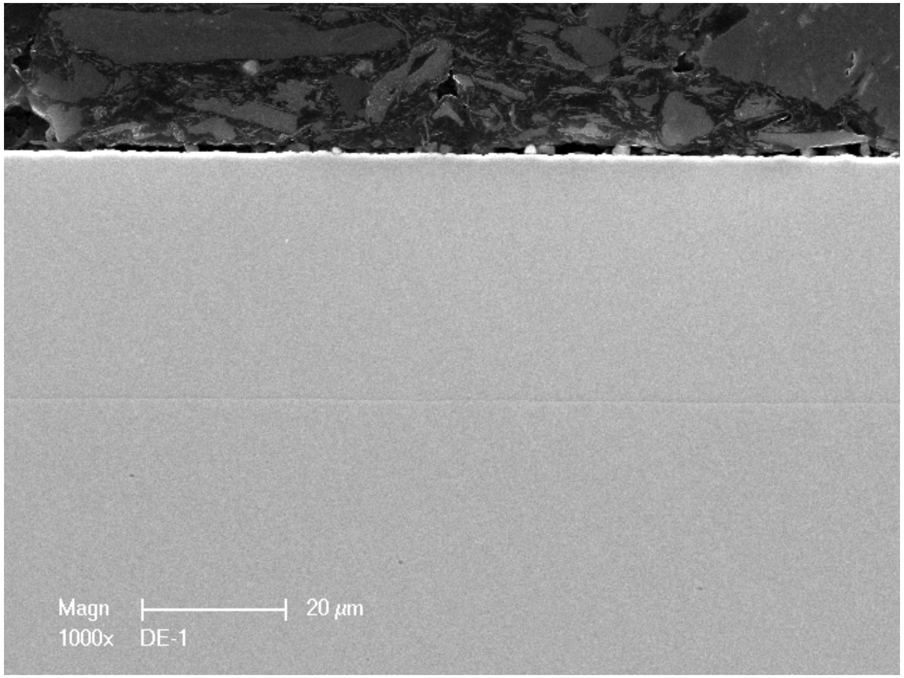
- Plasma Enahanced Magnetron Sputtering
- Process optimization study was conducted to improve the density of the coating
  - power applied to targets and bias voltage were varied
- Several trial coatings: 304+10Al, 310+10Al and Ni-20-10Al were deposited
- Coated samples were destructively examined



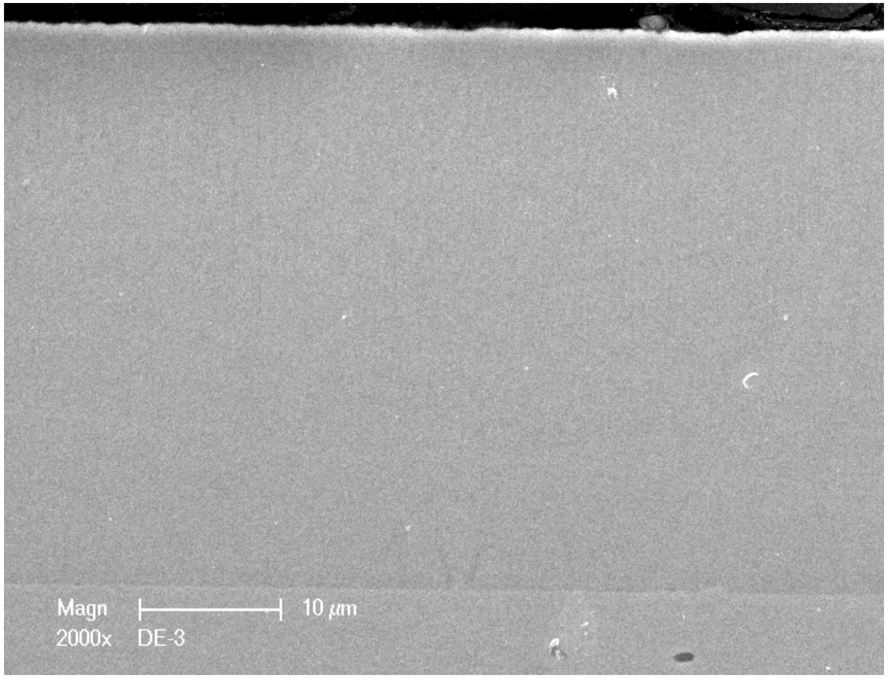


# Task 3 - Processing of Advanced NanoCoatings --Metallographic Examination

## Result: Dense Nanocoating Microstructures




1000X

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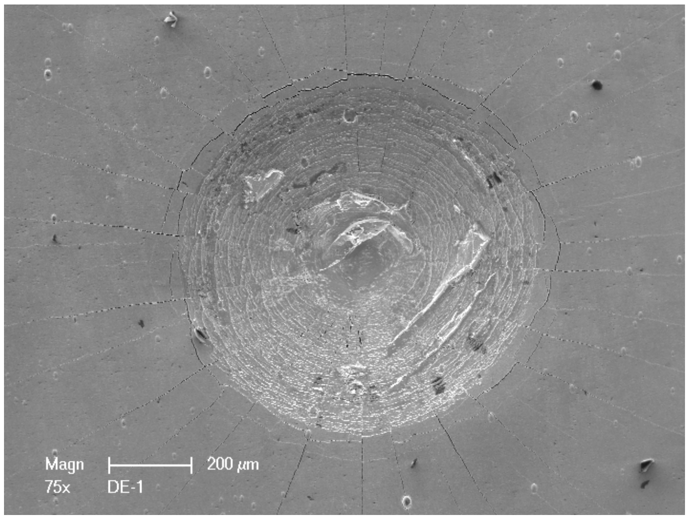
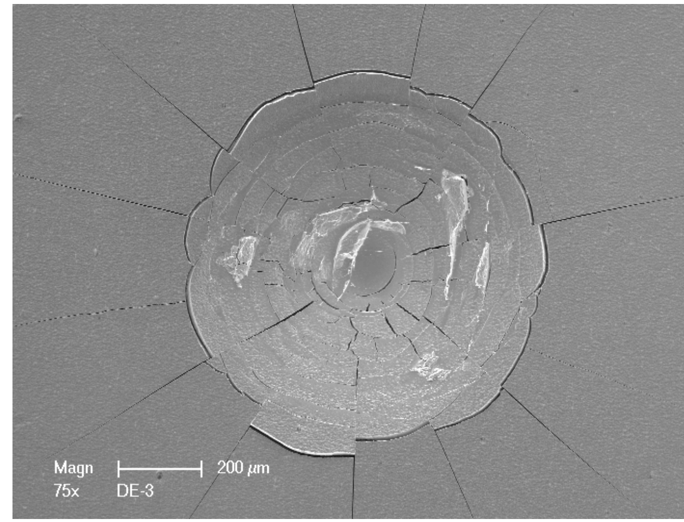
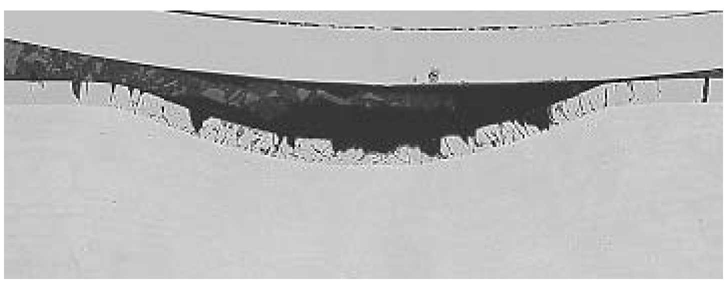
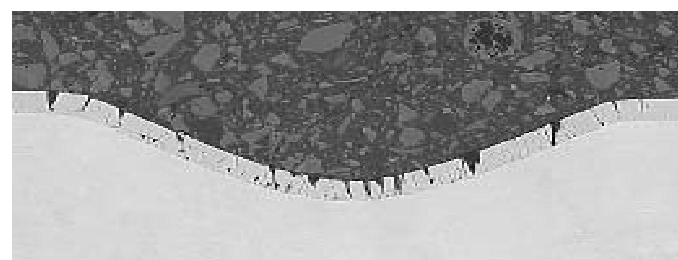
# Task 3 - Processing of Advanced NanoCoatings -- Coating Adhesion Results





**No coating delamination,**
**DE 3 parameters were selected**

# Task 3 - Processing of Advanced NanoCoatings -- Selection of Process

- Process parameters of DE 3 produced good quality coating
- Four advanced coatings (next slide) were deposited on P91, 304 SS and Haynes 230 samples for corrosion testing using DE 3 parameters

Concerns:

- ✓ Accelerated Al consumption rate
- ✓ Repeatability of Coating Quality
- ✓ Coating Cracking

# Task 3 - Processing of Advanced NanoCoatings

- Four advanced coatings were deposited:
  - 310 + Al (Fe-25Cr-20Ni-10Al)
  - Haynes 120+Al (Fe-37Ni-25Cr-Al)
  - Haynes 160+Al (Ni-29Cr-28Cr-3Si-Al)
  - Haynes 188+Al (Co-22Ni-22Cr-14W-10Al)

- Coated P91, 304SS and Haynes 230 samples were shipped to Foster Wheeler for Corrosion Testing
- Process optimization trials for depositing interlayer and advanced coatings are in progress



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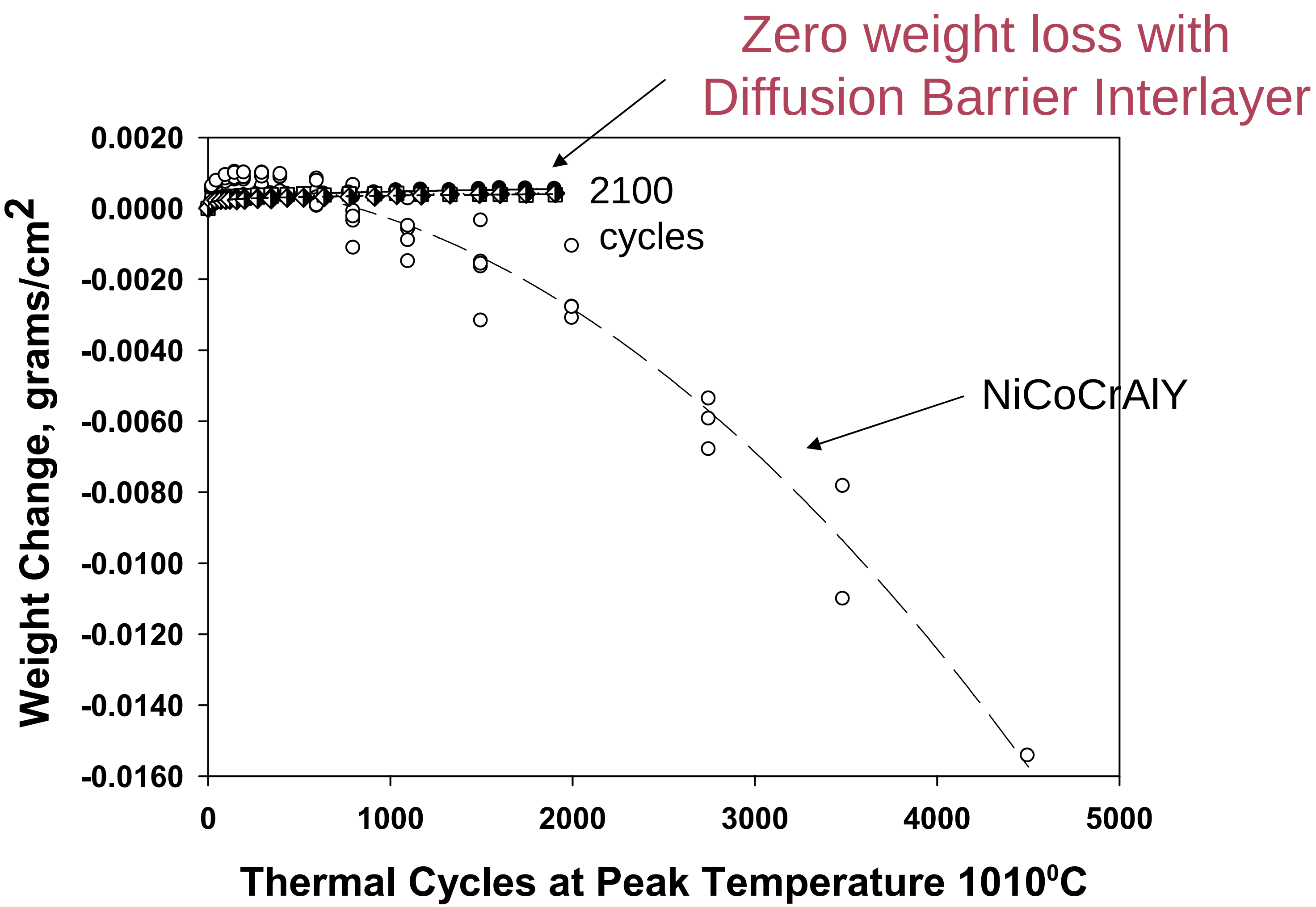
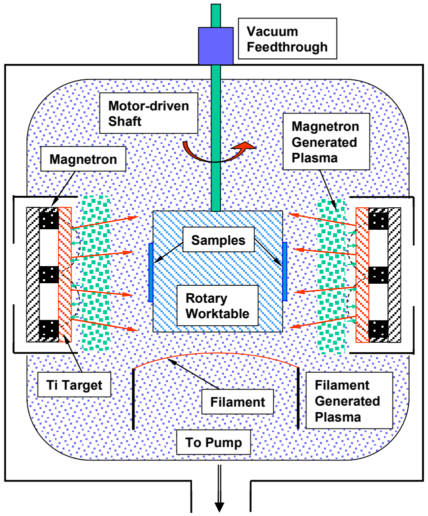
# Task 3 - Processing of Advanced --Comparison of Nanocoatings with Conventional Plasma-Sprayed NiCoCrAlY



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# Task 4: Fireside Corrosion Testing

## --in progress

**Objective: Conduct accelerated fireside corrosion tests**

# Task 4 - Corrosion Testing

- In addition to the 4 newly developed test nanocoatings, two vendors supplied nanocoatings for corrosion testing:
  - N-TECH Inc.
  - NanoSteel

# Task 4 - Corrosion Testing --Testing Conditions

## Waterwall Testing

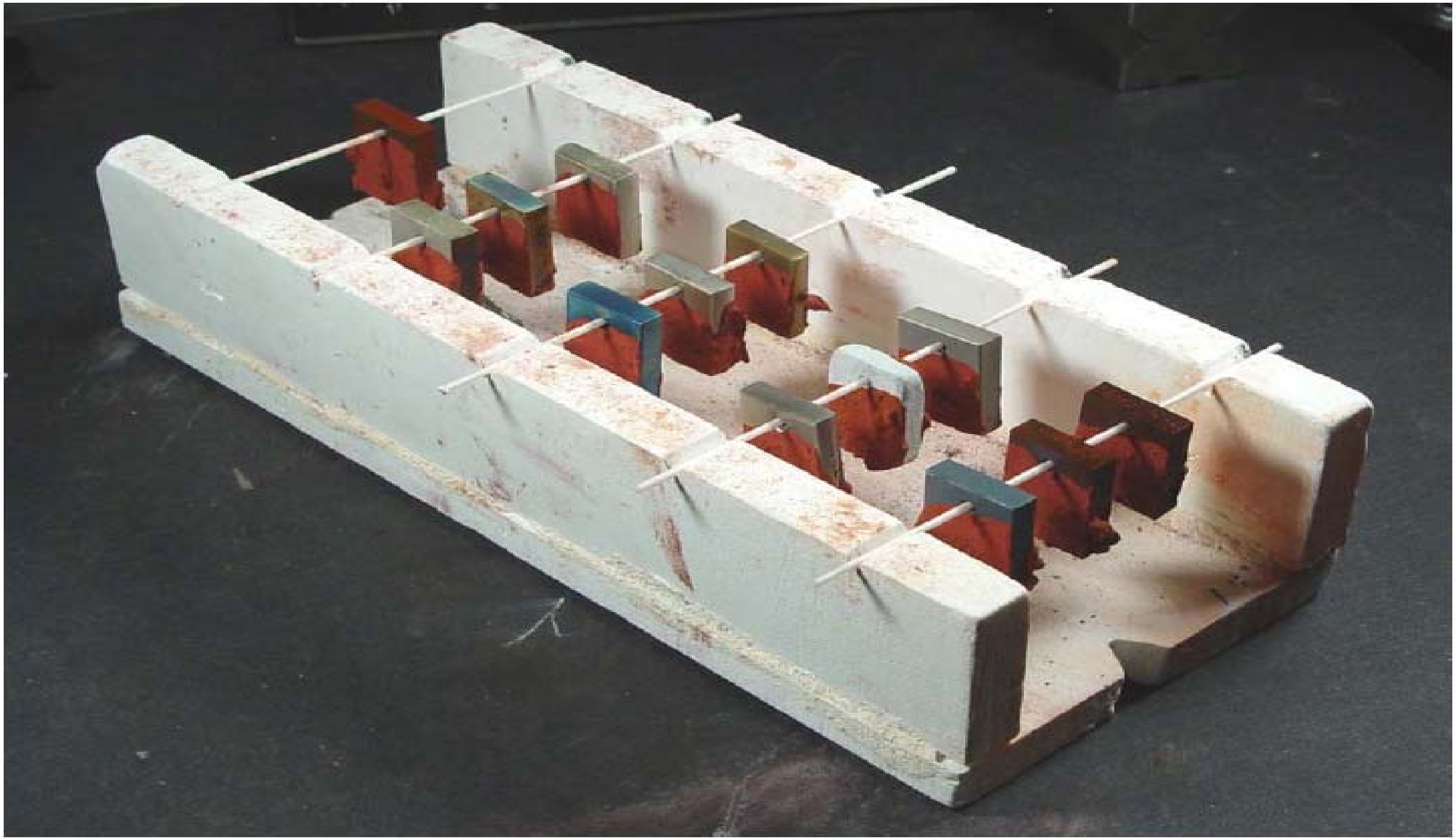
– 850F (454C), 975F (524C), and 1100F (593C)
– 40 percent FeS and 0.2 percent chlorides (same as USC program)

## Superheater/Reheater Testing

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

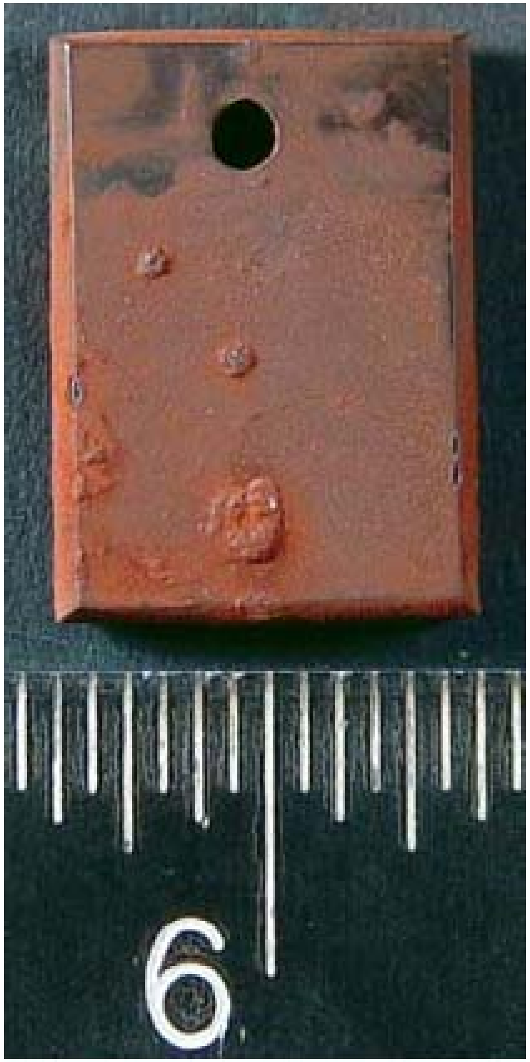
- Perform 1000hr tests (at 100hr intervals).

# Task 4 - Corrosion Testing
# -- Following first 100hrs of testing



Waterwall Test Rack at 850F (100 hrs)

# Task 4 - Corrosion Testing
# -- Following 500hrs of testing




- A few nanocoatings still in good shape after 500hrs exposure.
- Many samples exhibited some level of blistering.
  - Suggests coating processing issues.
- Metallography just starting
- Will require recoating (process improvement warranted) and additional corrosion testing.

# Conclusions To Date

- For long-term term durability, nano-coatings should contain ~10%Al.
  - A continuous, Al-rich protective oxide scale can be achieved with this level of aluminum.
- 4 nanocoatings selected using computational thermodynamics.
- Good cyclic oxidation performance exhibited for baseline nanocoatings (Fe-18Cr-8Ni-xAl, Ni-20Cr-xAl)
- Early nanocoatings corrosion results suggest processing concerns—more work to do!
- A diffusion barrier layer slows Al consumption rate dramatically.

# What's Next

- Complete fire-side corrosion testing (1000 hr) of nanocoatings at Foster-Wheeler (Task 4)
- Repeat coating processing trials (Task 3) and additional corrosion work.
- Validate computational model (Task 5)
- Nanocoating mockup demonstration (Task 6)

# Together…Shaping the Future of Electricity