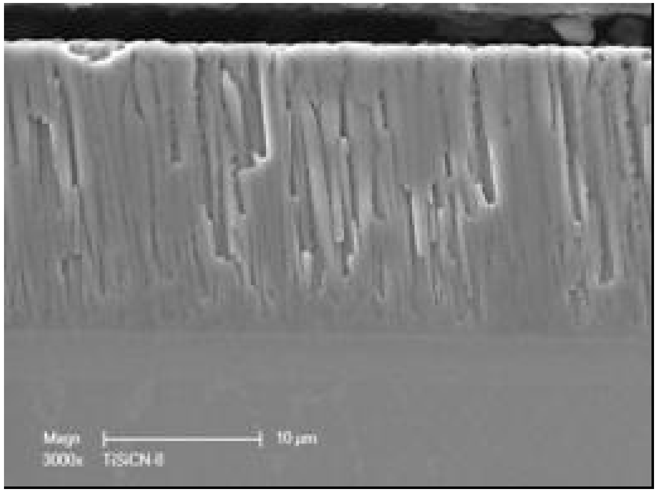

Computational Modeling and Assessment of Nanocoatings for USC Boilers

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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
--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

Background

- The introduction of No_x emission controls with staged burner systems has increased wastage rates to as much as 120 mils (3 mm) per year.
  - Reducing environment produced by low No_x combustion process.

Photographs of waterwall and a cross-section of tubes showing the extent of corrosion and wall thickness wastage

Background

- Corrosion deposits on sub- and supercritical boiler WWs contain predominantly iron sulfide (FeS) and alkali chlorides which are deposited under reducing conditions.
- Under such conditions, the protective oxide scale Fe_3O_4 will not form on the WW tubes, and promotes the formation of the less protective FeS –rich scale.
- The formation of FeS and other deposits will lead to pronounced corrosion under oxidizing or reducing environments.
  - Source of corrosion is the formation of alkali iron tri-sulfates on the tube surfaces

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
- Advanced alloys such as P91, Super 304H (austenitic SS), and Alloy 230 (nickel-based) alloys will be required.
- Higher corrosion resistance is exhibited for advanced austenitics and nickel-based alloys over ferritic alloys under sub- and supercritical conditions.
- 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.

Background

- EPRI recently completed a year-long project in early 2007 that included a *State of Knowledge Review of Nanostructured Coatings for Boiler Tube Applications (1014805)*
- Key Objectives of the Project were to:
  - To review currently available boiler tube coatings and field application methods
  - To perform an in-depth review of nanostructured coatings
  - To assess the potential for protection of boiler tubes by nanostructured coatings

Background

Key SOK Review Results--Nanocoatings

- Containing Cr and/or Al are much more resistant to both oxidation and corrosion than conventional coatings with the same compositions.
- Exhibit much slower reaction kinetics with high temperature environments which stem from the rapid establishment of thin, impervious, thermally grown oxides (TGOs) at the nanocoating surfaces (ie., they selectively oxidize).
- Are difficult to apply by conventional “powder” type processes due to transport through feeder/liner.

Background

Key SOK Review Results--Nanocoatings

- The promotion of selective oxidation by nanocrystalline grains is attributable to short-circuit diffusion of Al and Cr though the grain boundaries.
- For the same reason, nanostructured coatings require only about one-quarter the Al or Cr content needed in conventional coatings to establish thin, continuous, protective TGOs.
- TGOs on nanostructured coatings are more adherent and resistant to spalling than oxide scales on conventional coatings
- Nanostructured coatings are more resistant to spalling and better bonded to substrates than conventional coatings.

Background

Key SOK Review Results--Nanocoatings

- Unresolved Issues
  - Cr_2O_3 vs Al_2O_3 Scales--which is better?
  - Compositional Requirements for Long-term protection
  - Thickness requirements
  - Ranking of Nanostructured Coatings
  - Coefficients of Thermal Expansion
  - Corrosion
  - Erosion-Corrosion

Work Led To DOE Project Award --DE-FC26-07NT43096

Computational Modeling and Assessment of Nanocoatings for Ultrasupercritical Boilers

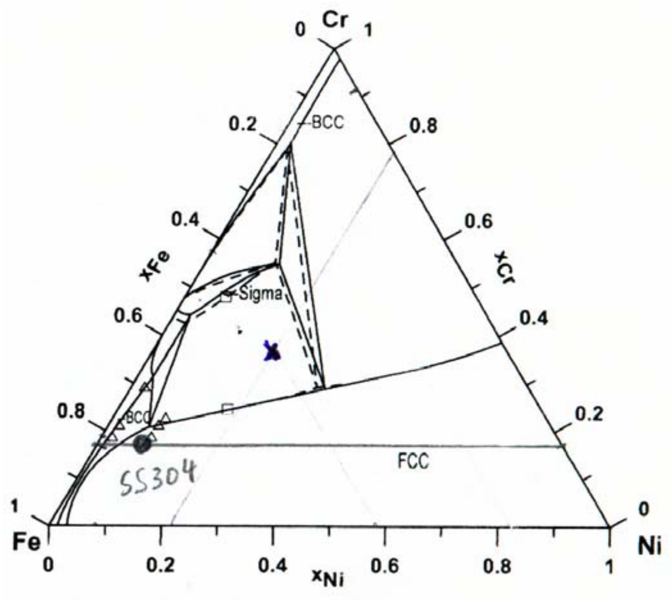
- Initiated in August 2007
- 3-year effort
- EPRI, SWRI, Foster-Wheeler, Applied Films

Current DOE Nanocoatings Project Objectives

1. To develop and demonstrate nano-structured coatings using computational modeling methods that will significantly improve both corrosion and erosion performance of tubing in USC boiler applications.
2. To improve the reliability and availability of USC fossil-fired boilers and oxy-fuel advanced combustion systems by developing advanced nano-stuctured coatings.
   - Coatings will be optimized utilizing science-based computational methodologies and validated via experimental verification and testing in simulated boiler environments using 3 different coal conditions and temperatures.

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



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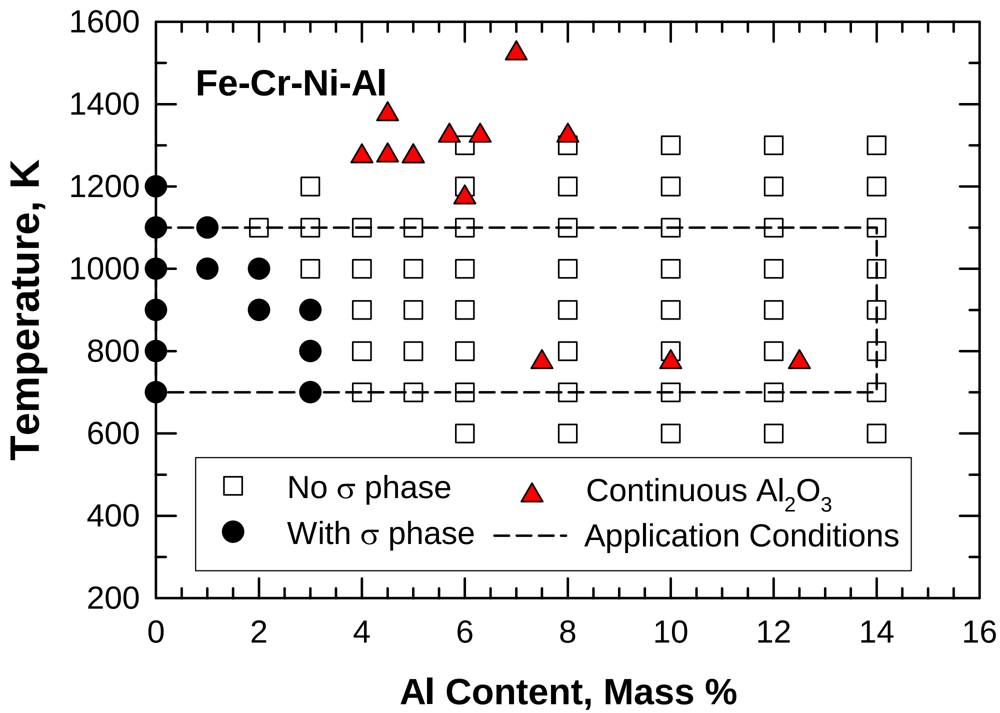
Task 1: Computational Modeling of MCrAl Systems

Task 1- Computational Modeling Objectives

- Potential Fe-Cr-Ni-Al nanostructured coating compositions were selected through computational modeling methods.
- The approach was to design and optimize the compositions of Fe-Cr-Ni-Al system to produce stable nanostructured coatings that form a protective, continuous scale of alumina or chromia.
- Define the minimum Al content for continuous alumina formation, Cr content for continuous chromia formation, and coating compositions without sigma phase formation.

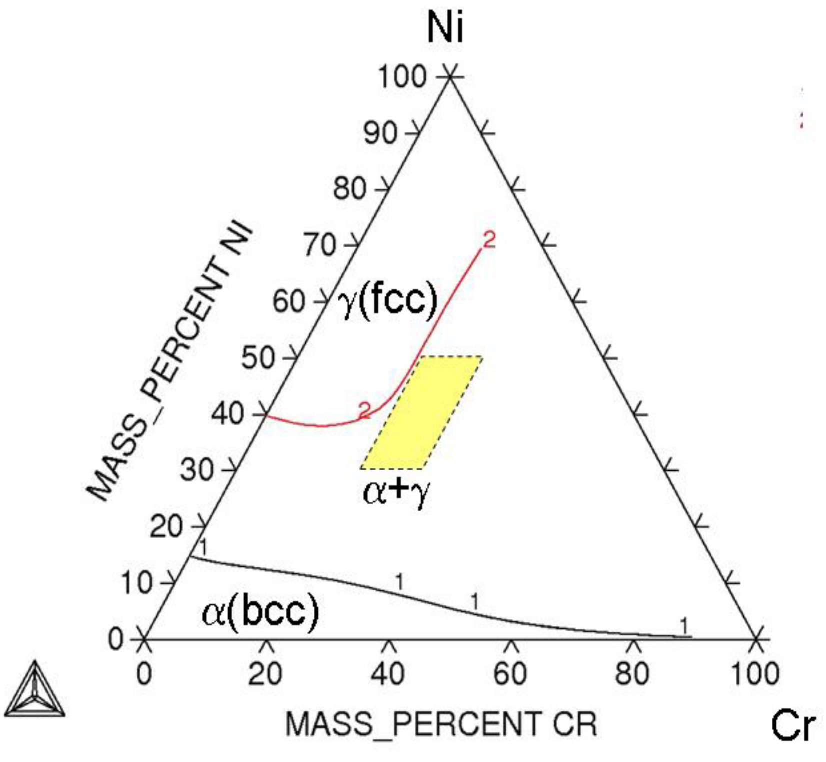
Task 1- Computional Modeling Of MCrAl Composition Selection -- Progress

- 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.
- Al additions stabilize BCC – accelerates inward diffusion of Al and Cr.



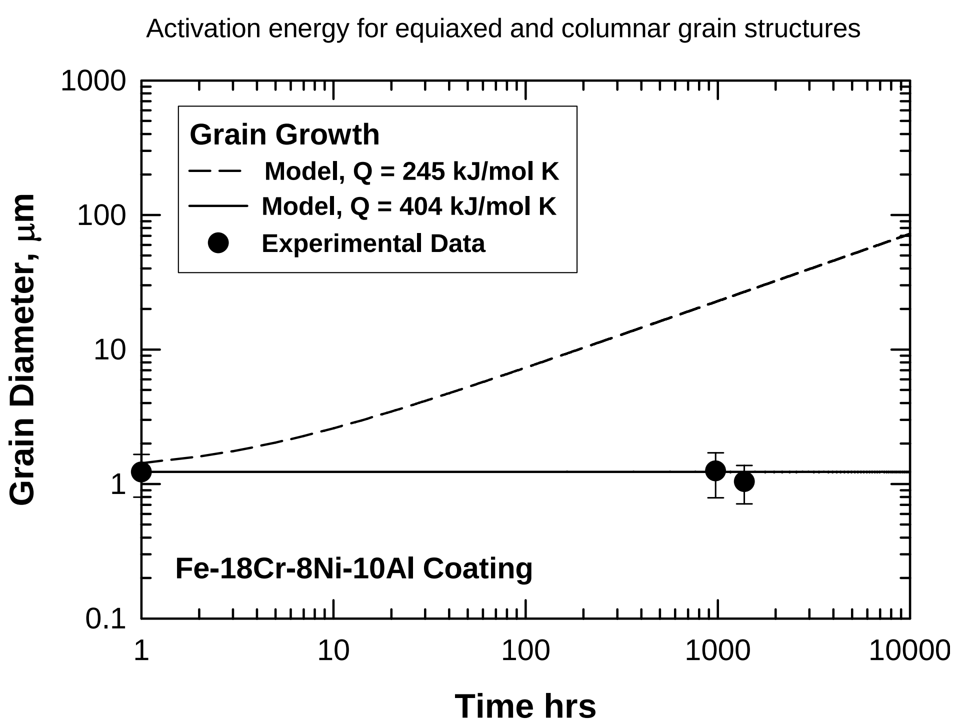
Task 1- Computional Modeling --Effect of Nickel on FCC/BCC

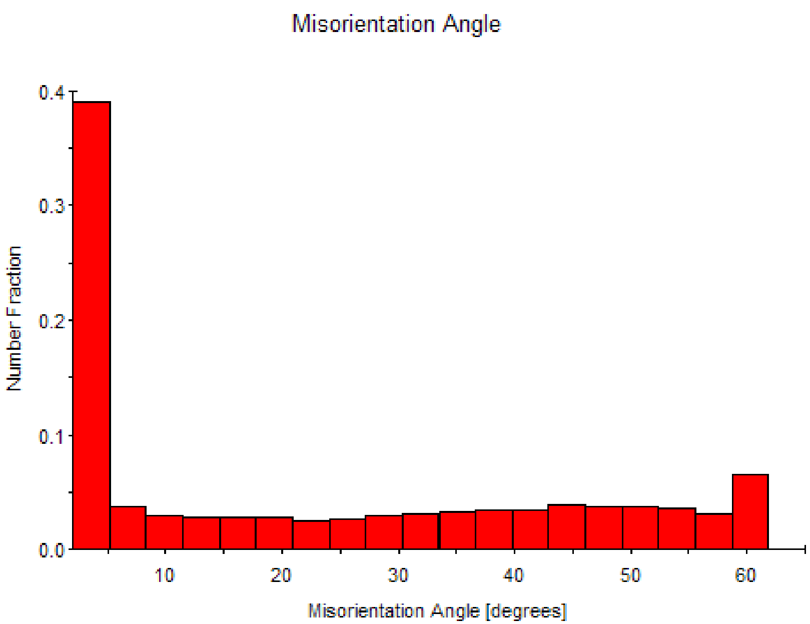
- Higher Ni is required to stabilize FCC to lower inward Al/Cr diffusion into the substrate
- Modeling results suggested the addition of 30-40%Ni (with 10%Al) helps to form FCC phase at the coating/substrate interface
- Suggested nano-coating systems for evaluation:
  - 310 +10%Al
  - 310 -30-35Ni +10Al
  - 35Fe-40Ni-25Cr,
  - 35Fe-40Ni-25Cr-10Al



Task 1 - Computational Modeling --Grain Growth Modeling

- Grain growth model results showed that the nano-crystalline grains are stable at 750ºC
- Grain stability is attributed to the presence of high concentration of low-angle boundaries in the nano-coating.





Task 1 - Computational Modeling --Sintering Modeling

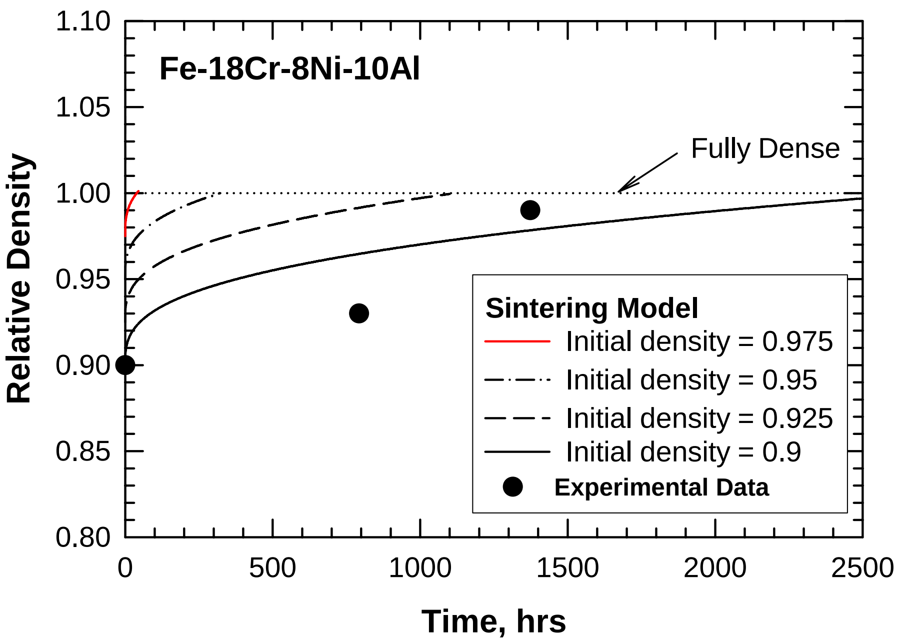
- An existing sintering model was utilized to compute the linear shrinkage rate (DL/L):

$$\frac{\Delta L}{L} = \left(\frac{15a^4}{r^4} \frac{D\gamma}{kT} \right)^{1/3} t^{1/3}$$

- Relative density was computed as a function of time for Fe-Cr-Ni-Al nanocoatings

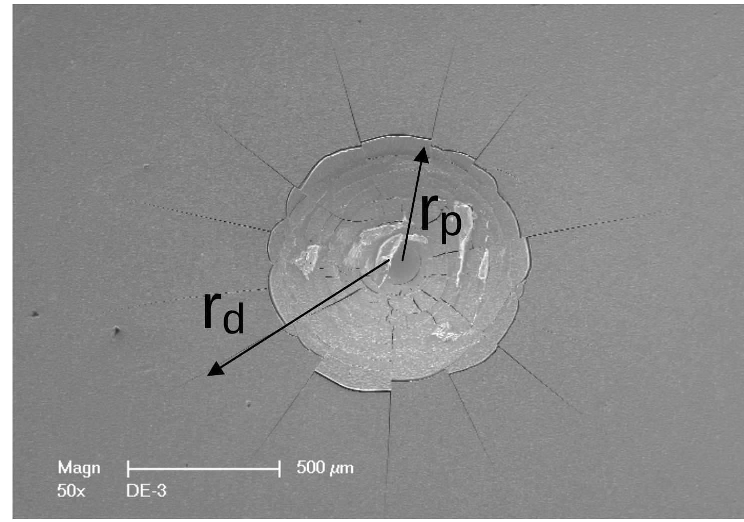
- Initial density of the as-deposited coating must be >98% for sintering to take place in couple of hours

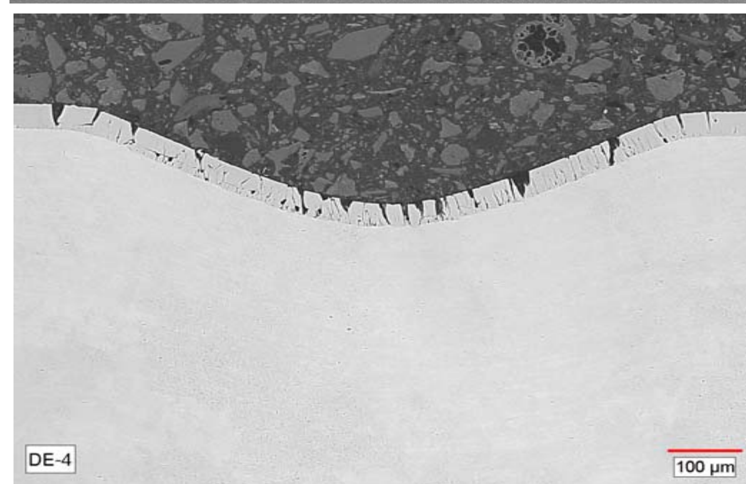
- Thermal exposure at 750ºC leads to sintering

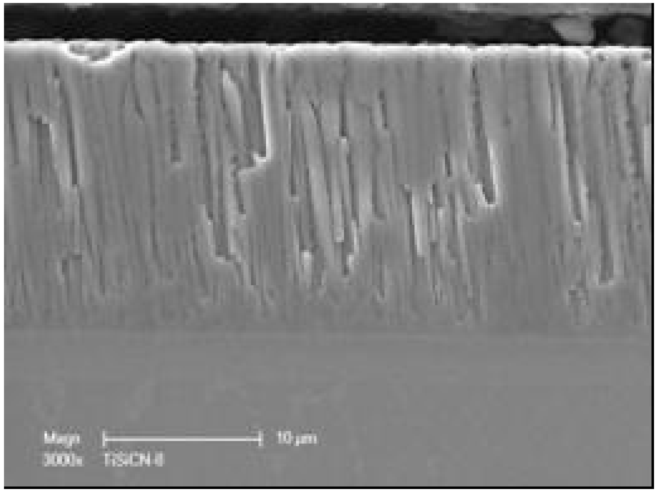


Task 1 - Computational Modeling --Toughness Modeling

- Indentation resulted in the formation of a circular indent of radius r_p and a debonded zone of radius r_d
- Ratio of r_d and r_p is used to compute toughness
- The sputtered coatings exhibited good toughness.
- Indentation testing showed no nano-coating delamination







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Task 2: Establishment of Baseline Coating Data

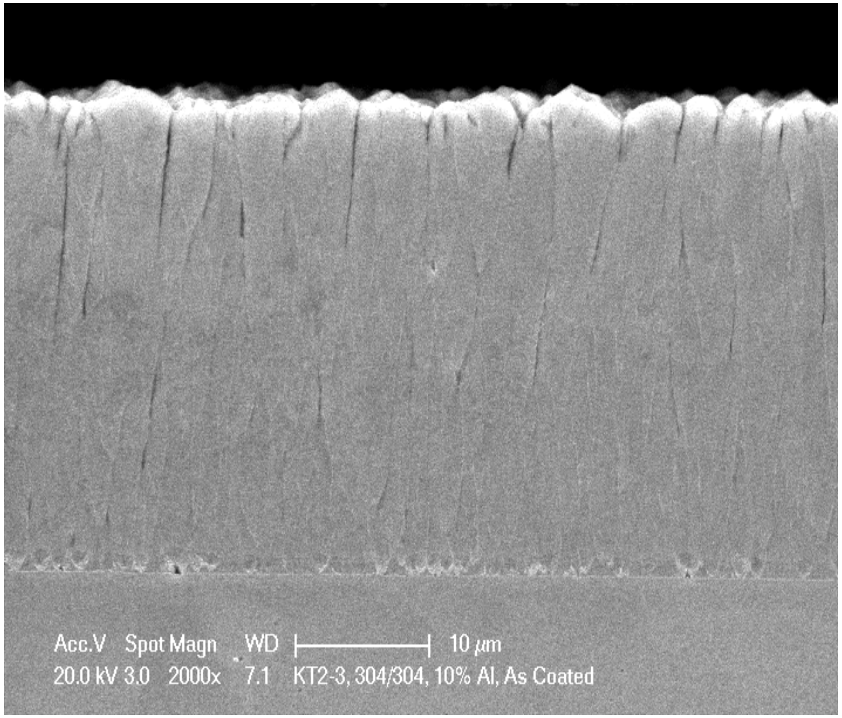
Task 2. Baseline Coating Data --Objectives

- To Generate Baseline Data For Conventional Coatings And Existing Nano-coatings For Comparison With The Advanced Nano-structured Coatings Properties

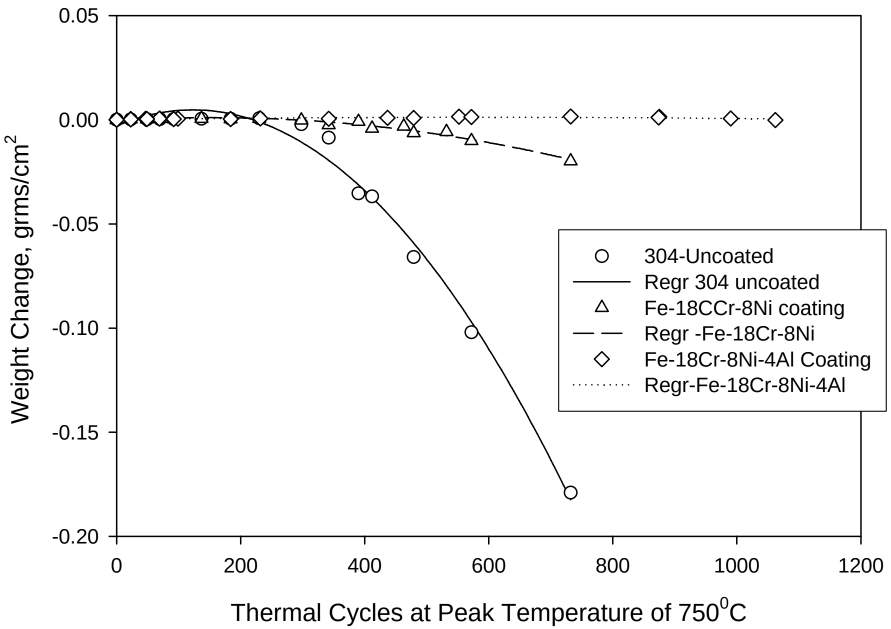
- Baseline Data Will Be Established For Both Conventional And Currently Available Nano Coatings (InfraMet) And Fe-Ni-Cr-Al/ Ni-Cr-Al (Nano Coatings Produced By SWRI).

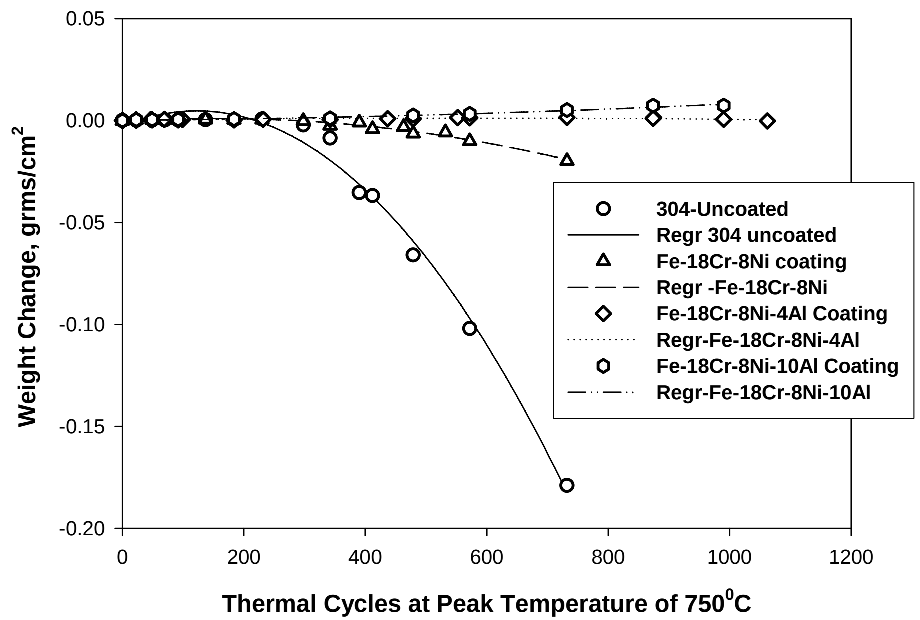
Task 2. Establishment of Baseline Coating Data--Progress

- Fe-18Cr-8Ni (304)+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



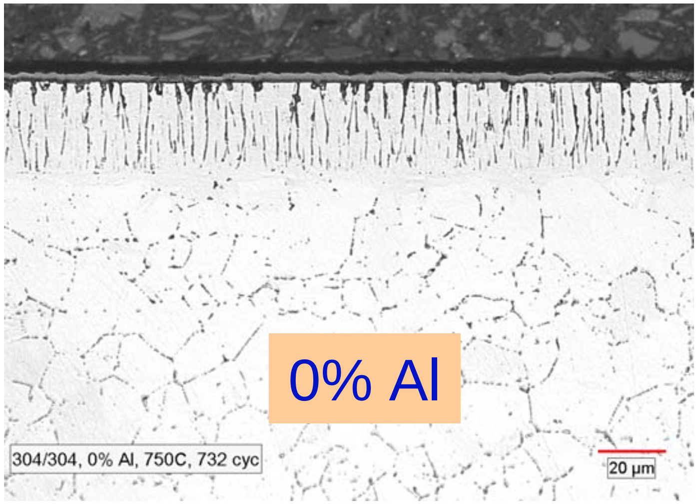
Task 2. Baseline Coating Data
--Cyclic Oxidation Behavior of Fe-Ni-Cr (304)-xAl Coatings

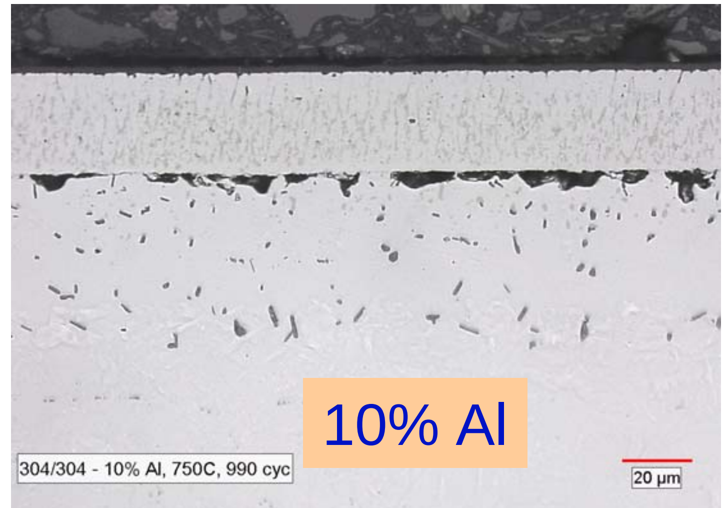


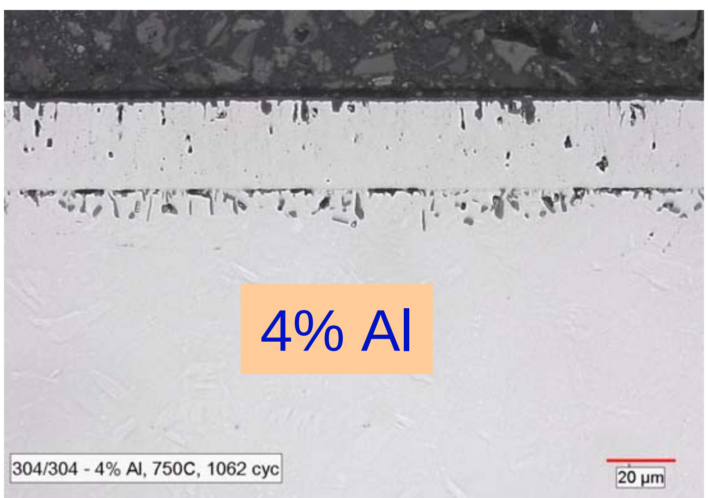


- 304SS Nano-Coating Improved Oxidation Resistance By 2X.
- The Addition Of Al Improved
  - Oxide-Scale Spallation Resistance
  - Oxidation Resistance

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

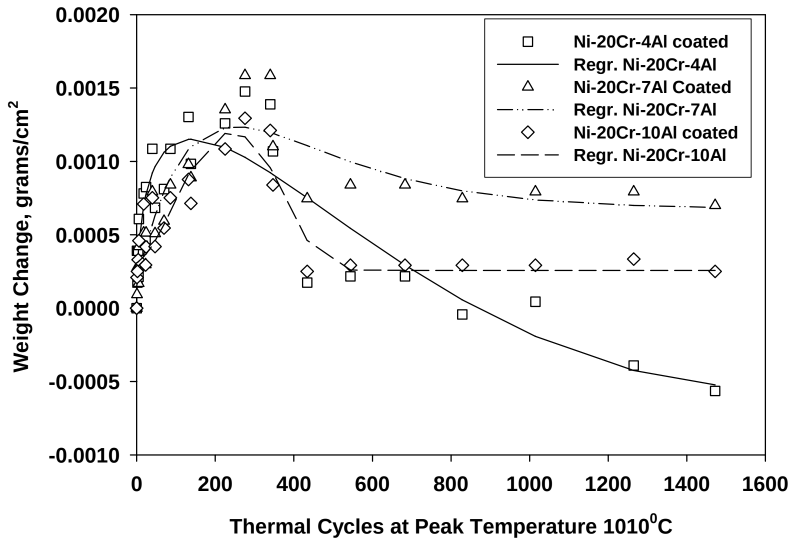
2). 4% Al coating was oxidized

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

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

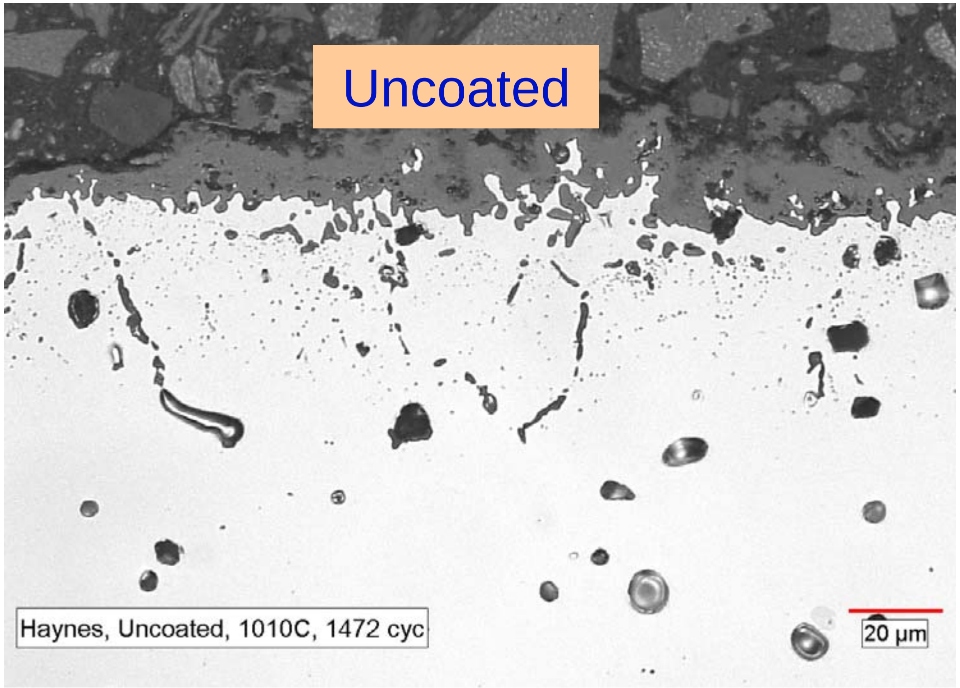
Task 2. Baseline Coating Data -- Cyclic oxidation behavior of Ni-20Cr-xAL

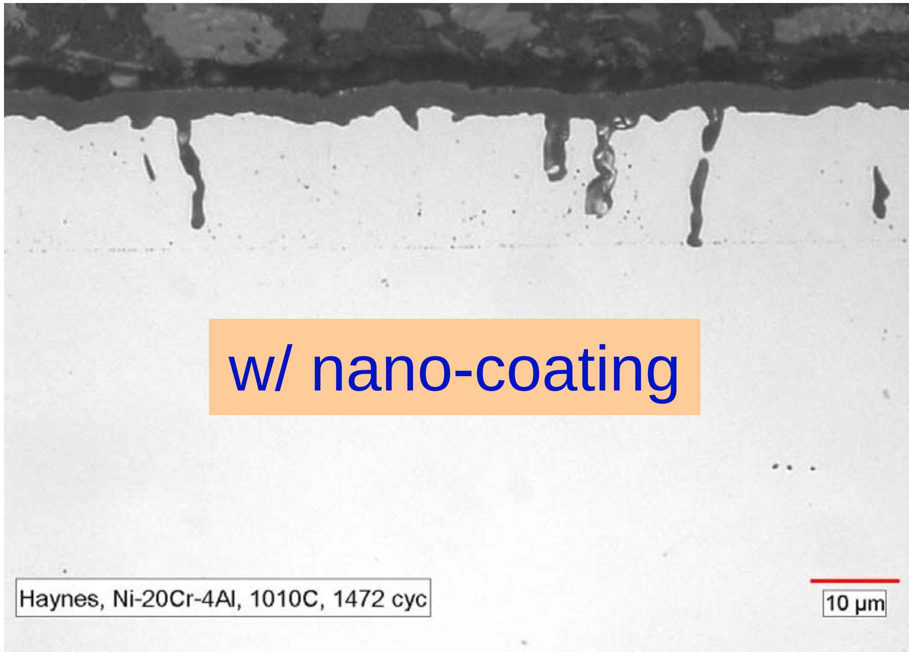
- Cyclic oxidation tests on Ni-Cr-Al coated Haynes 230 specimens were performed at two peak temperatures-- 750C and 1010C
- P91 coated specimens were tested at peak a temperature of 750C
- At 750C, continuous increase in wt was seen for both uncoated and coated P91 and 230 specimens
- At 1010C, the coated 230 specimens performed significantly better



Coated and Uncoated Haynes 230

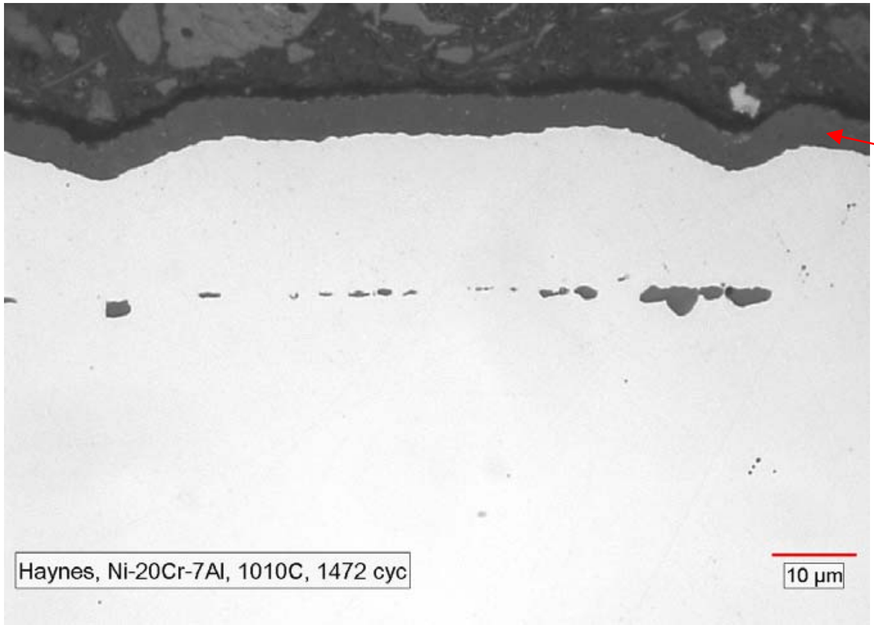
Task 2. BaseLine Coating Data
-- Coating Oxidation Characterization
Ni-20Cr-xAl on Haynes 230



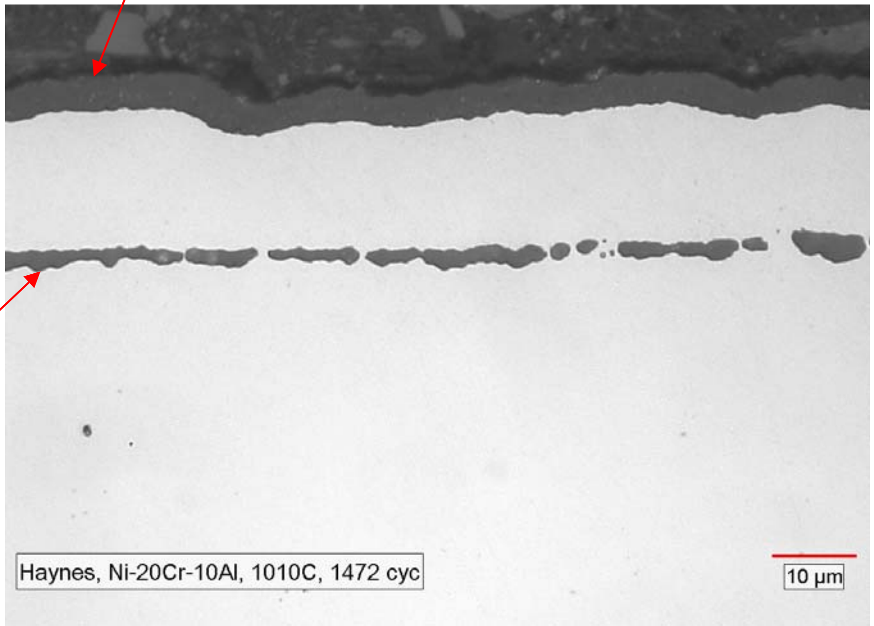


Nanocoating improves the oxidation resistance at 1010C

Task 2. Baseline Coating Data
-- Coating Oxidation Characterization
Ni-20Cr-xAl on Haynes 230

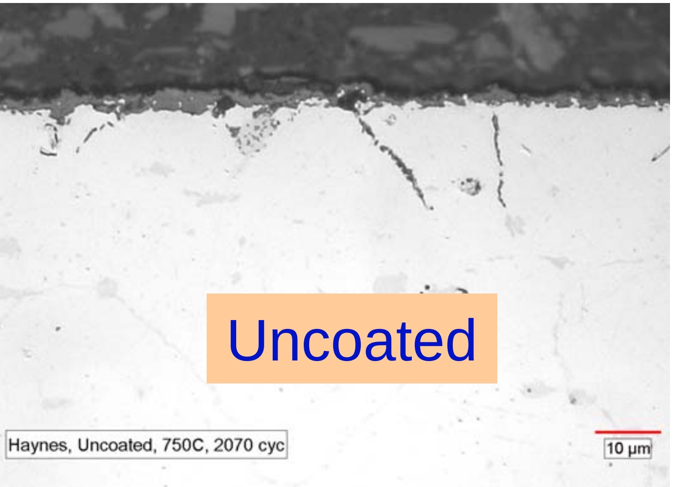


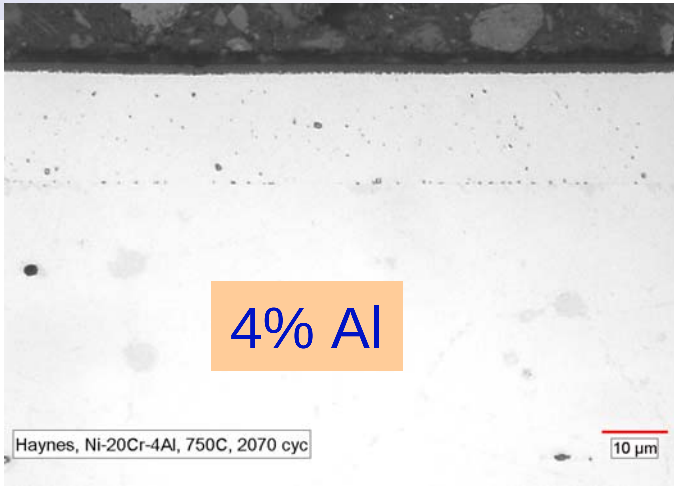
Al_2O_3



Al–rich precipitate observed along the Coating-Substrate Interface

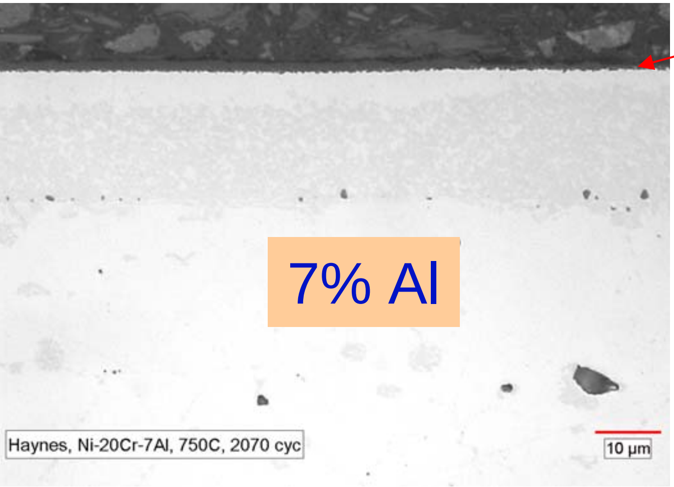
Task 2. Baseline Coating Data -- Oxidation of Uncoated and Ni-20Cr-xAl Coated Samples @ 750C

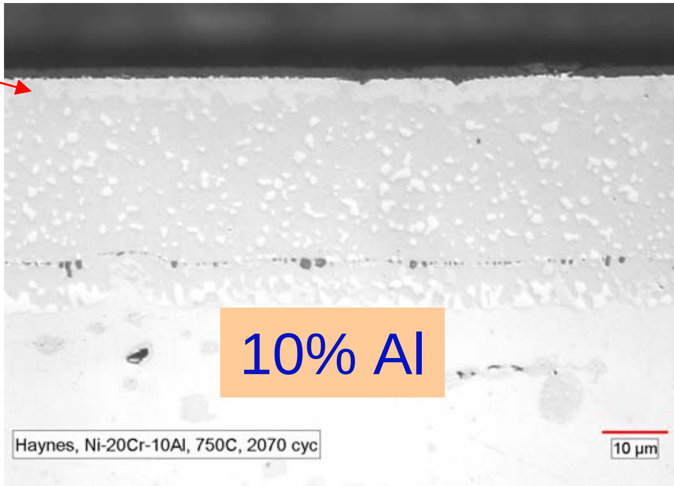




Coating is in Good condition

Protective Scale: Al_2O_3





Conclusions To Date

- *Grain Growth Modeling*
  - Suggests Columnar-Grained Structure Nano-coatings Are Stable
- *Sintering Modeling*
  - Determined Initial Relative Density Of The As-processed Coating Must Be Greater Than 98% To Achieve Full Density In <2 Days Of Thermal Exposure At 750°C.
- Fe-Cr-Ni-Al Nanocoatings Exhibit High Interface Toughness.

Conclusions To Date

- *Inter-Diffusion Modeling*
  - Indicated That Inward Diffusion Results In Moderate-to-Substantial Al and Cr Losses From The Coating Into The Substrate During Thermal Exposure At 750C.

- *Inter-Diffusion Computation*
  - Suggested Certain Fe-Cr-Ni-Al Nanocoatings Form a Diffusion Barrier Layer At The Coating/Substrate Interface.

Conclusions To Date

- Un-coated 304SS and Haynes 230 exhibited evidence of internal oxidation after cyclic oxidation testing
- The sputtered Fe-18Cr-8Ni-xAL and Ni-20Cr-xAl nano-coatings exhibited improved oxide scale *spallation resistance* compared the uncoated specimens.
- The nano-coatings containing 4%Al showed evidence of internal oxidation along the columnar grain boundaries
- For long-term term durability, nano-coatings containing ~10%Al are recommended

Conclusions To Date

- A continuous Al-rich protective oxide scale was observed on the coating outer surface. Coatings containing 10%Al were in good condition
- Thermal exposure led to precipitation of:
  - aluminides in the inter-diffusion zone in the 304SS
  - an Al-rich phase along the coating/substrate interface in the Ni-based alloy.
- Thermal exposure led to rapid loss of Al content in Ni-20Cr-xAl coatings due to inward and outward diffusion.

What's Next

- Baseline nano-coatings and the newly developed nanocoatings will be applied to substrates and exposed to accelerated corrosion testing (1000 hr) at Foster-Wheeler.
  - Testing will include 3 North American coal blends and 3 different temperatures

Questions/Discussion
?????