FUNDAMENTAL STUDIES OF THE DURABILITY OF MATERIALS FOR INTERCONNECTS IN SOLID OXIDE FUEL CELLS

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PROJECT STRUCTURE

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Ms. Kelly Coyne	B.S. Engineering Phys.

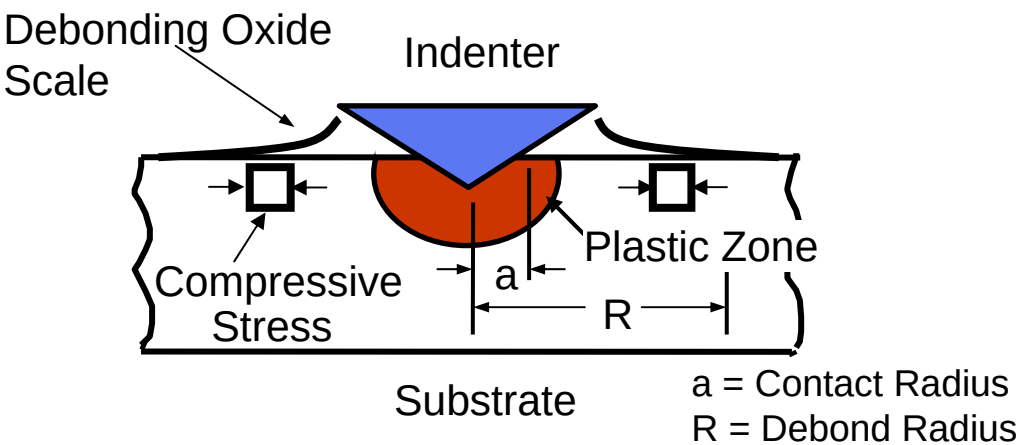
PROGRAM FOCUS
TASK I: Mechanism-Based Evaluation Procedures (Chromia-Forming Alloys)

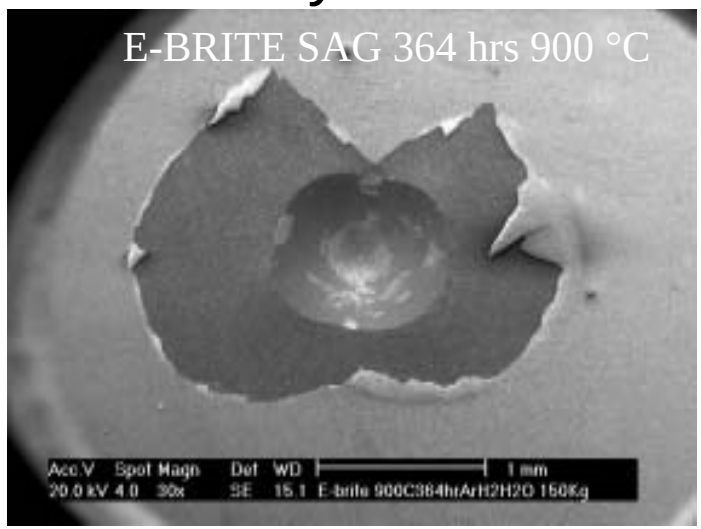
- Characterization of Exposed Fuel Cell Interfaces
- Growth Rates of Chromia Scales on Cr and Ferritic Alloys
- Adhesion of Chromia Scales
- Oxide Evaporation
- Complex Atmosphere Testing

Note: An important theme which cuts across Tasks I and II is the establishment of ***accelerated testing protocols****.*

PROGRAM FOCUS; TASK II
FUNDAMENTAL ASPECTS OF THERMOMECHANICAL BEHAVIOR

- XRD Stress Measurements (Chromia Films)
- Indentation Testing of Interface Adhesion
- Indentation Test Fracture Mechanics Analysis





Note: An important theme which cuts across Tasks I and II is the establishment of ***accelerated testing protocols****.*

PROGRAM FOCUS
TASK III: Alternative Material Choices

This Task involves theoretical analysis of possible alternative metallic interconnect schemes including:

- Ni and dispersion-strengthened Ni
- Low CTE Alloys Based on Fe-Ni (Invar)
- Bi-layer Alloys

The most promising systems will be evaluated experimentally with regard to durability and oxide conductivity

TASK I: RESULTS
Oxidation of Ferritic Alloys

Alloys

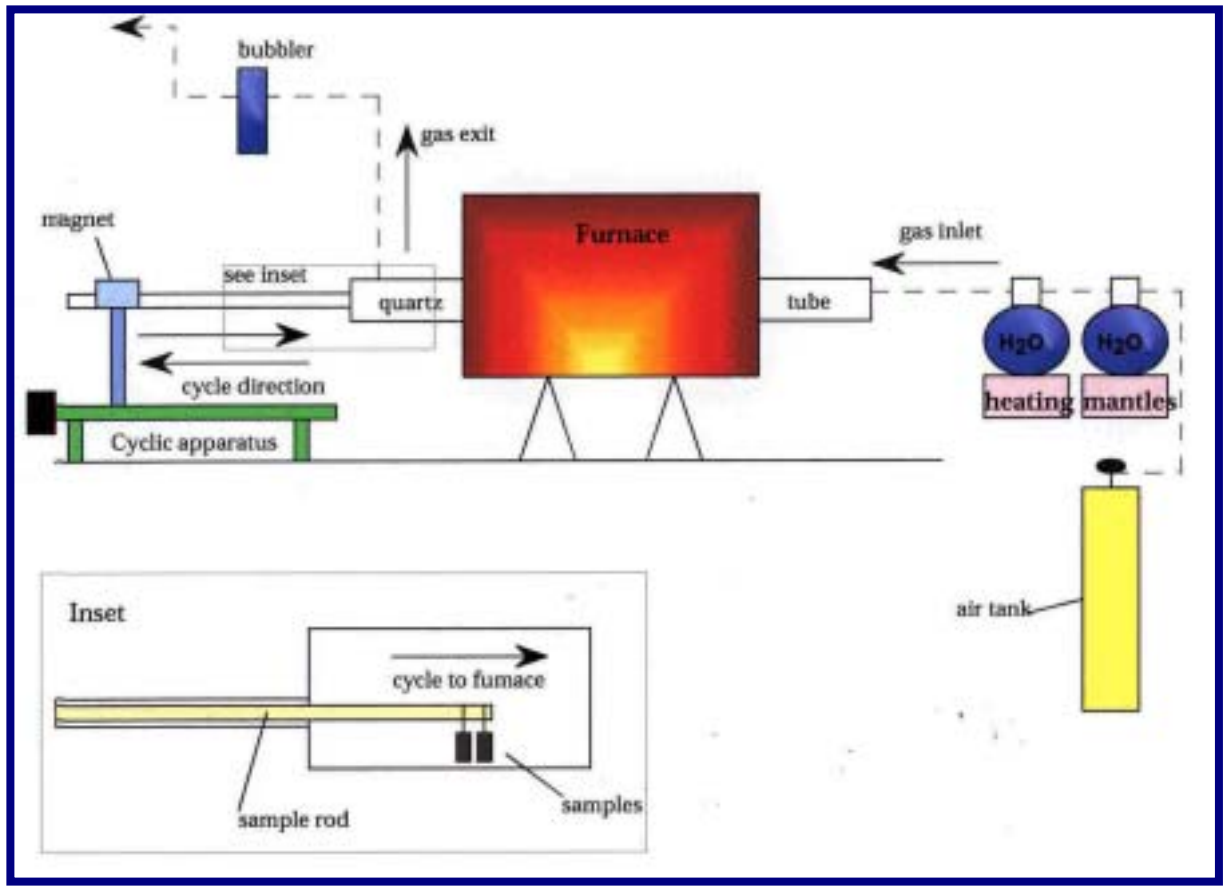
- E-BRITE (26 Cr-1 Mo)
- AL 453 (22 Cr + Ce/La)
- Crofer
- ZMG232

Exposure Conditions

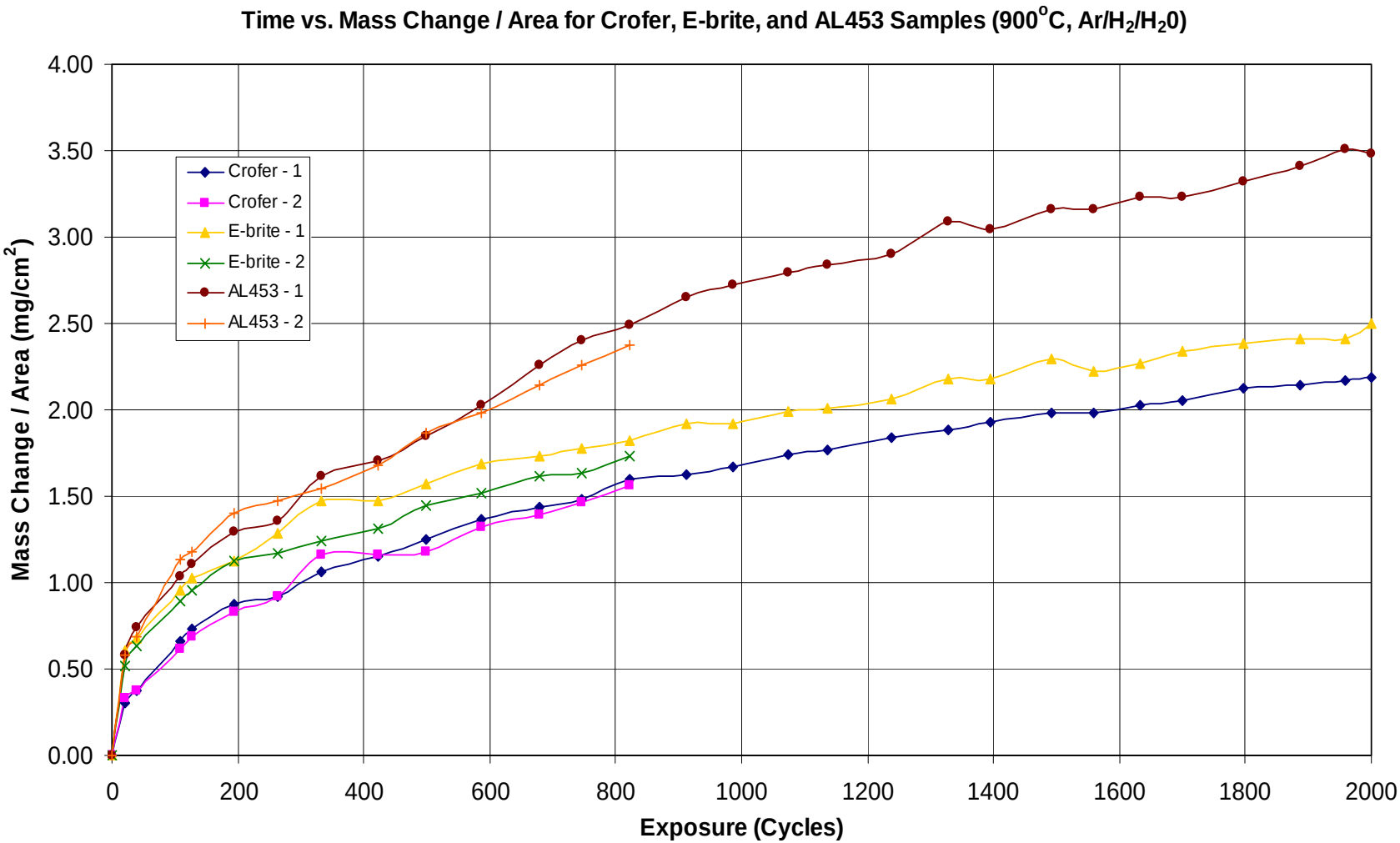
- T = 700°C, 900°C
- One-Hour Cycles
- Atmospheres
  - Dry Air (SCG)
  - Air + 0.1 atm H_2O
  - $Ar/H_2/H_2O$ (SAG)

    (p_{O2} = 10^{-20} atm at 700°C and 10^{-17} atm at 900°C)

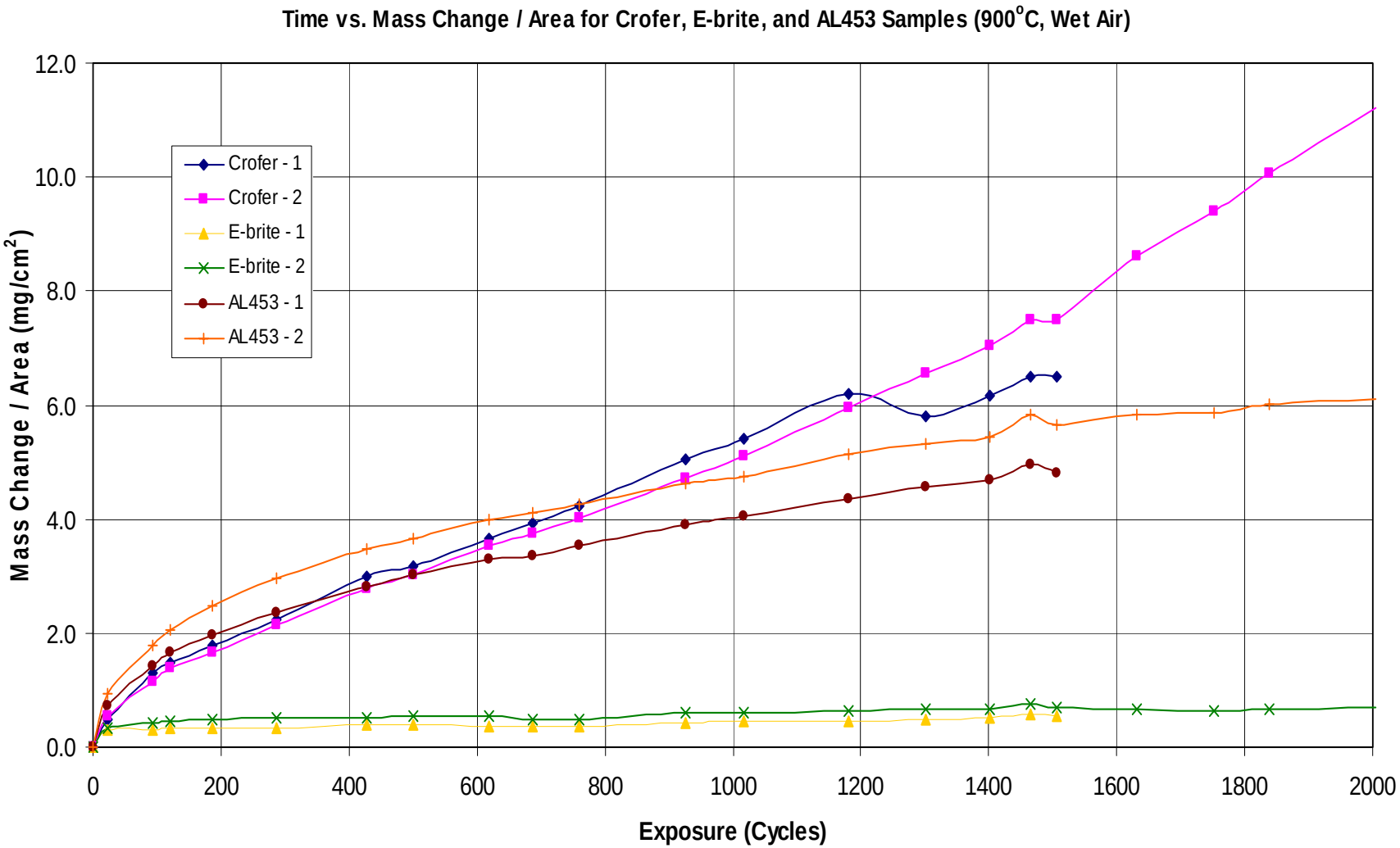
TASK I: RESULTS
Diagram of Apparatus



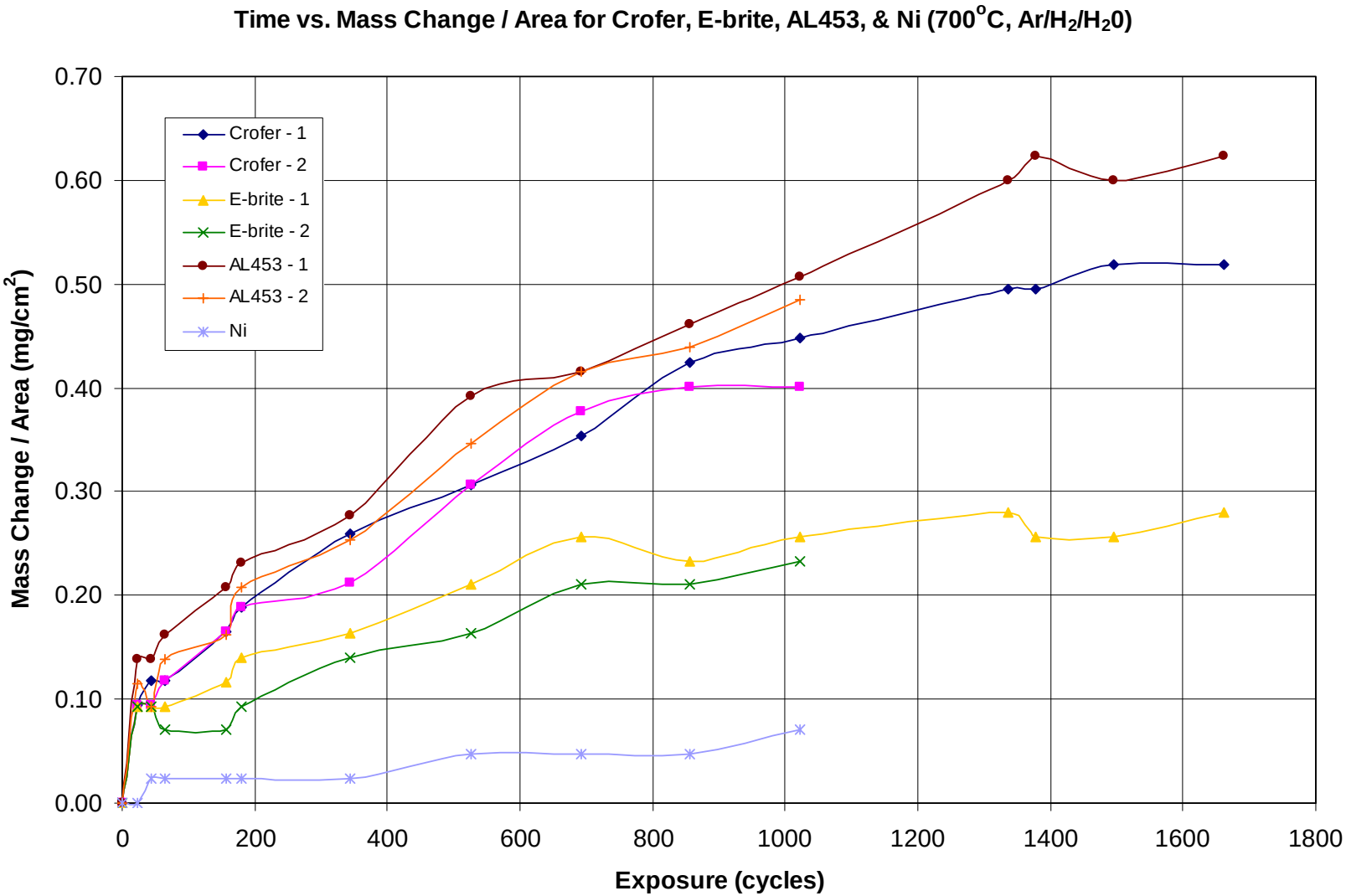
TASK I: RESULTS
Simulated Anode Gas (Ar-4%H_2, H_2O) Exposures – 900°C



TASK I: RESULTS
Wet Air (0.1 atm H_2O) Exposures - 900°C



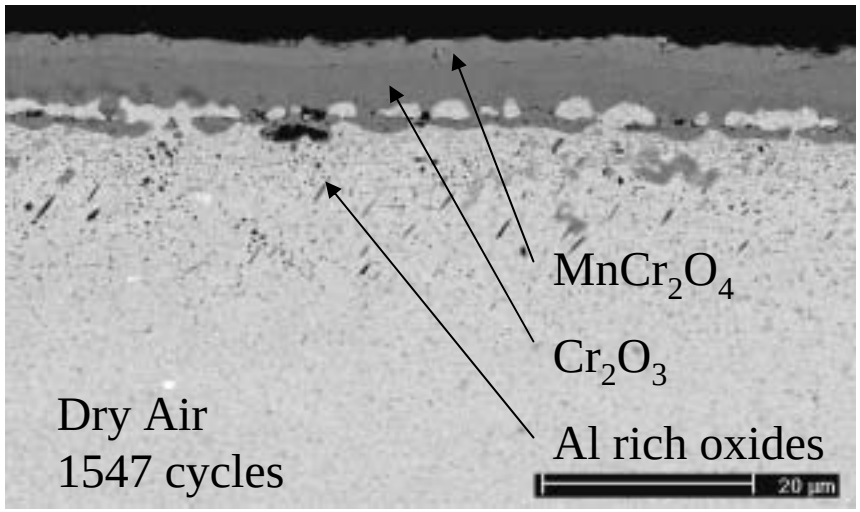
TASK I: RESULTS
Simulated Anode Gas (Ar-4%H_2, H_2O) Exposures – 700°C

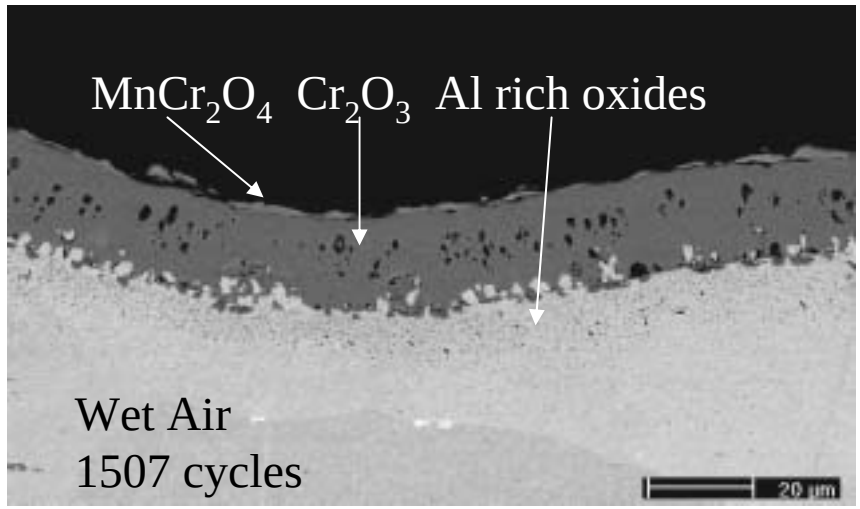


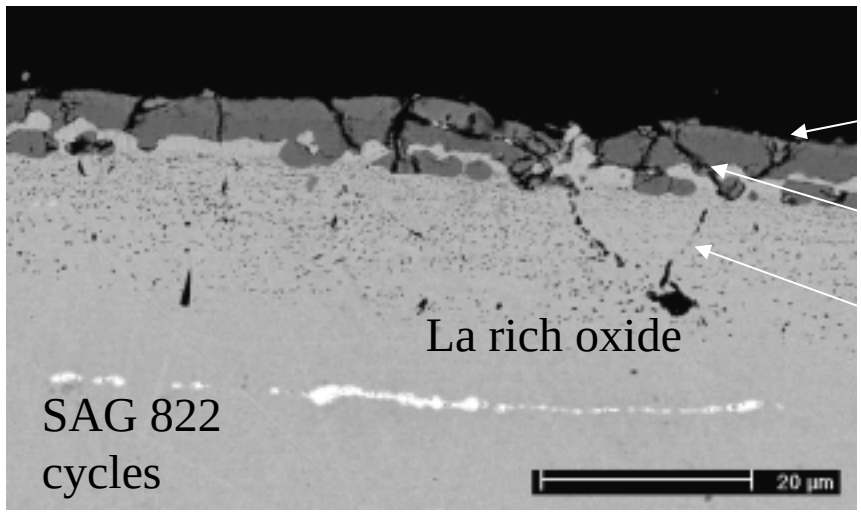
TASK I: RESULTS

Microstructural and Phase Identification

Crofer 900°C





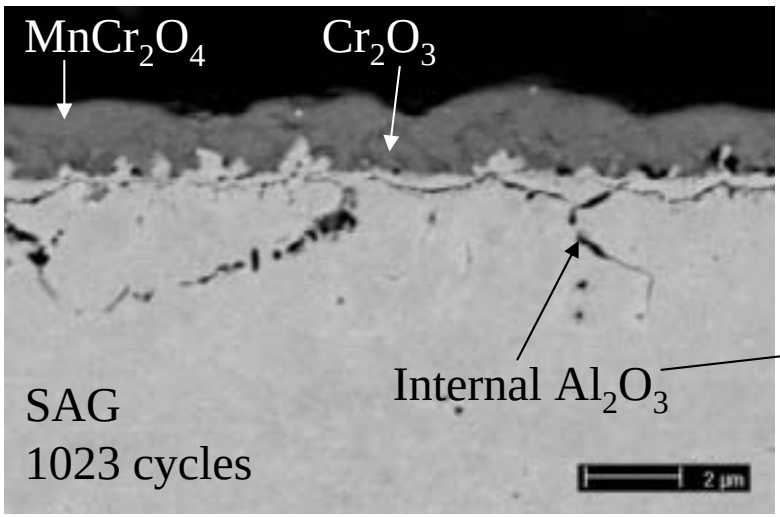


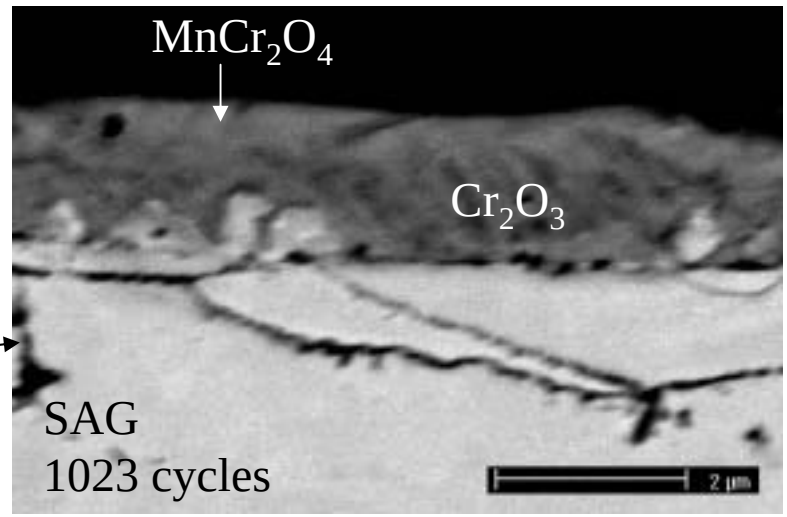
$MnCr_2O_4$

Cr_2O_3

Al rich oxides

TASK I: RESULTS
Microstructural and Phase Identification
Crofer 700°C





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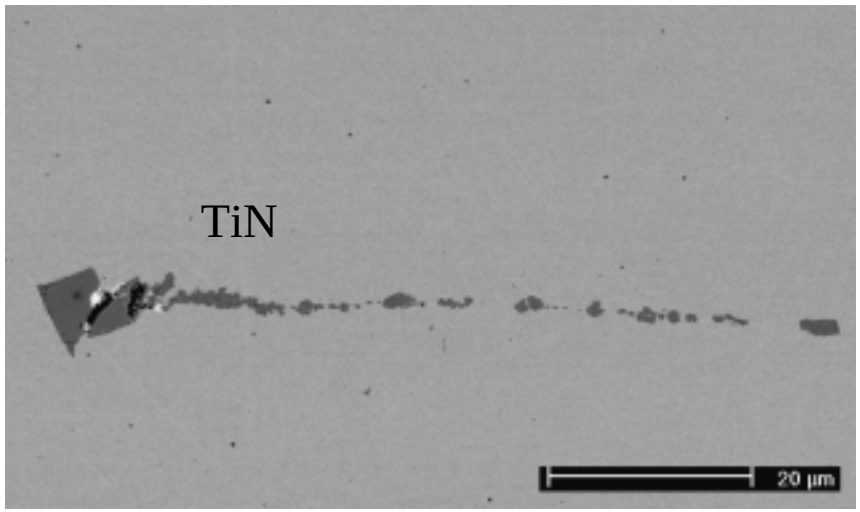
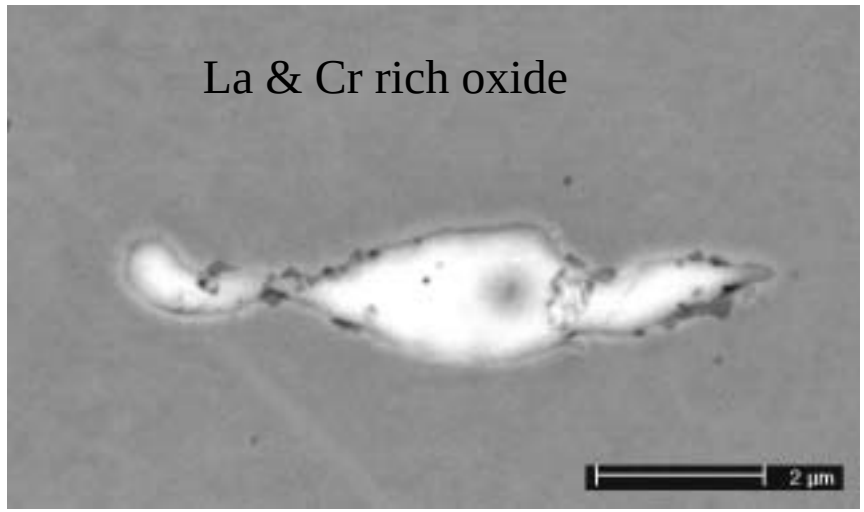
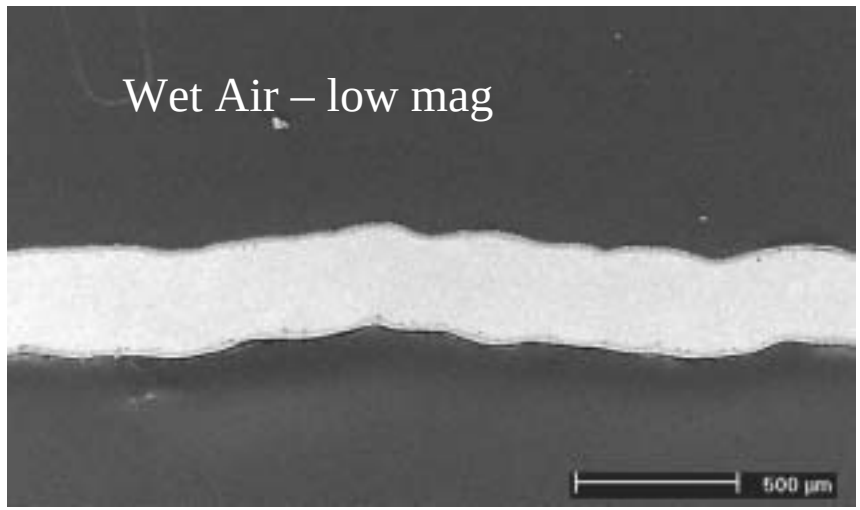
Microstructural and Phase Identification
Crofer 900°C



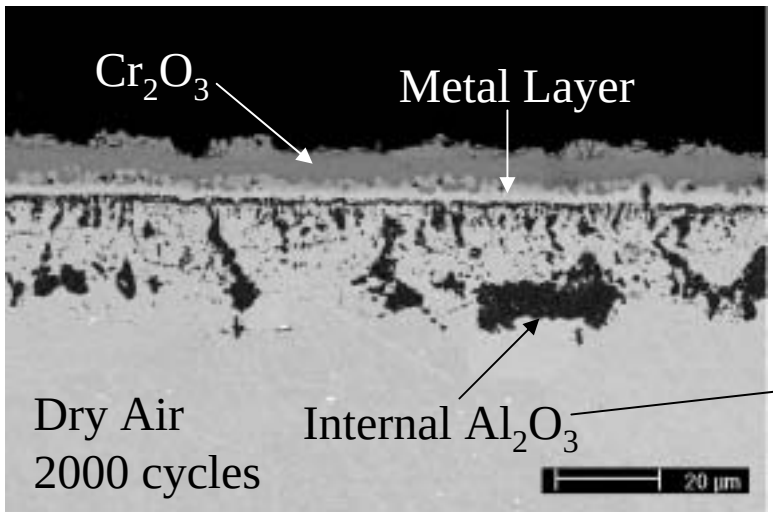


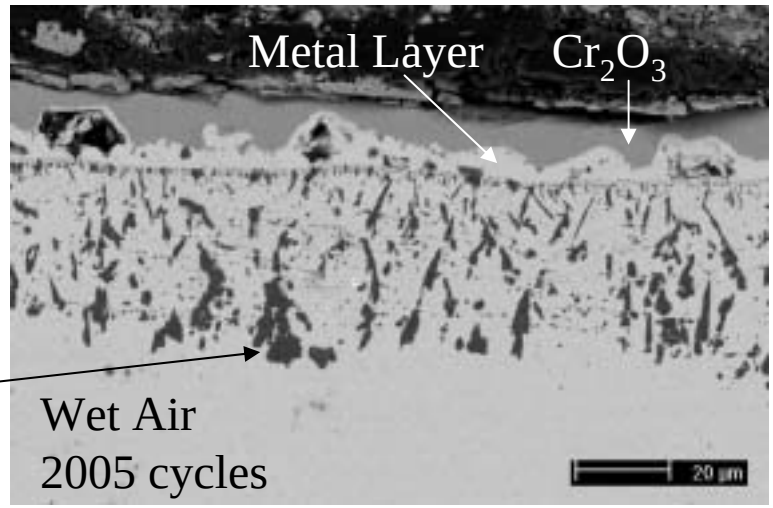


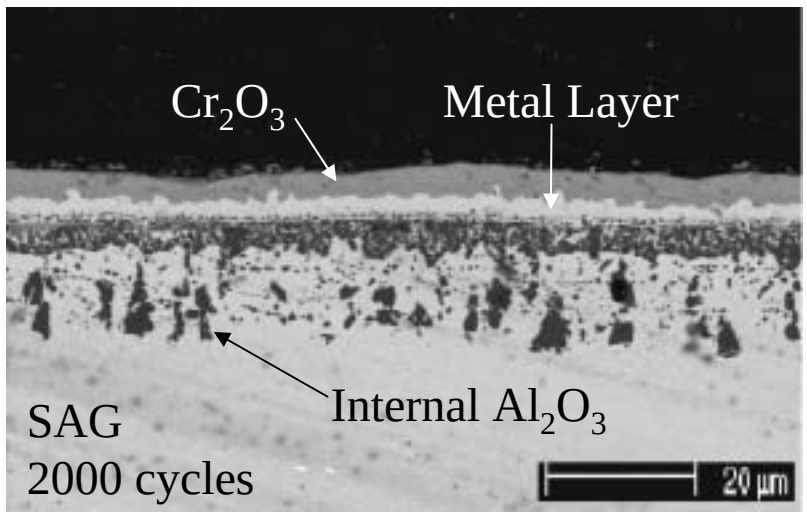
TASK I: RESULTS

Microstructural and Phase Identification

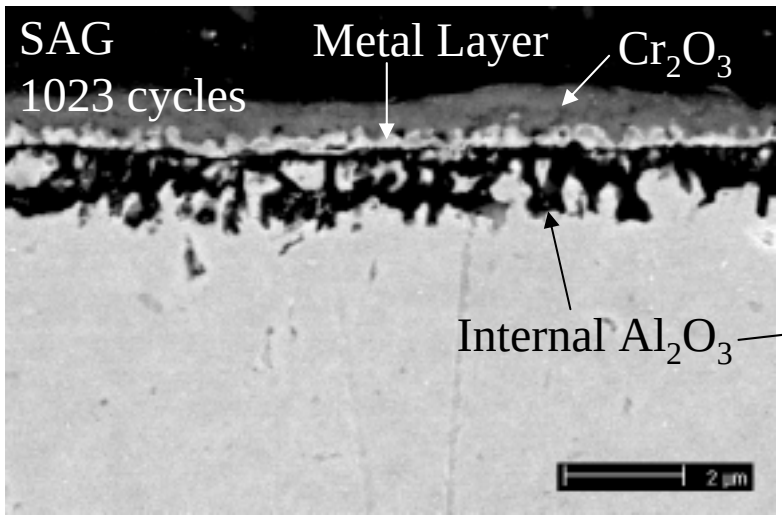
AL453 900°C

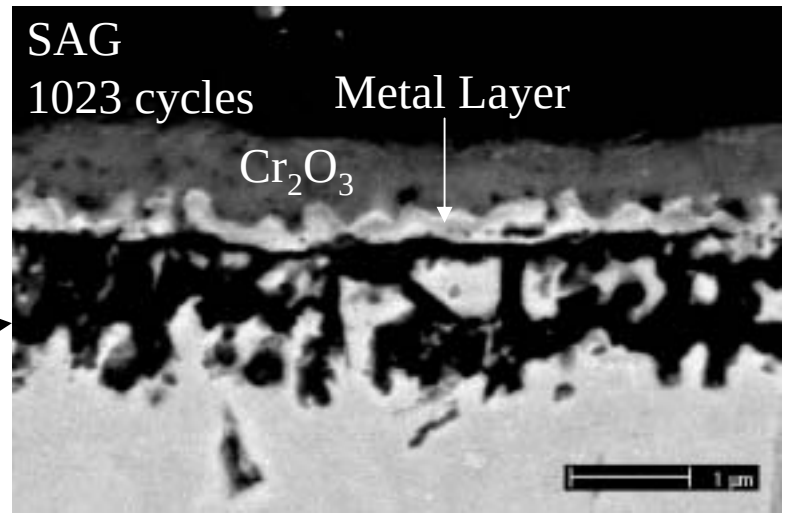




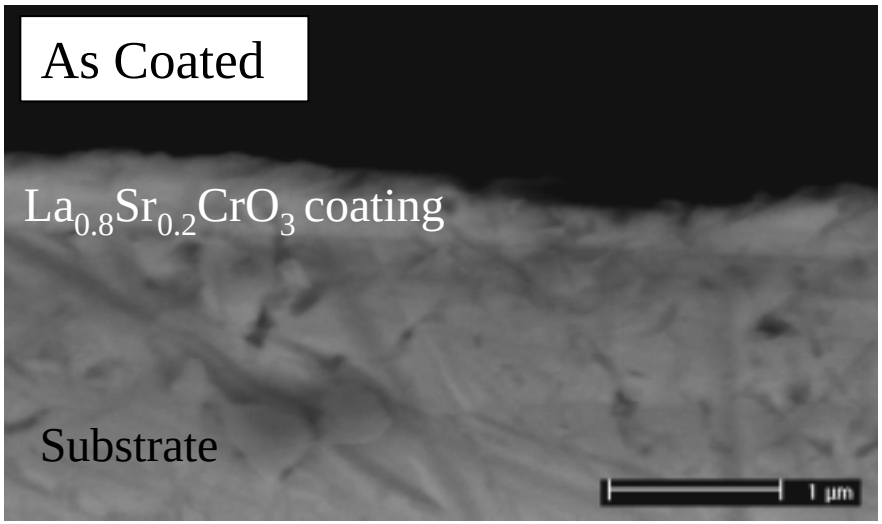


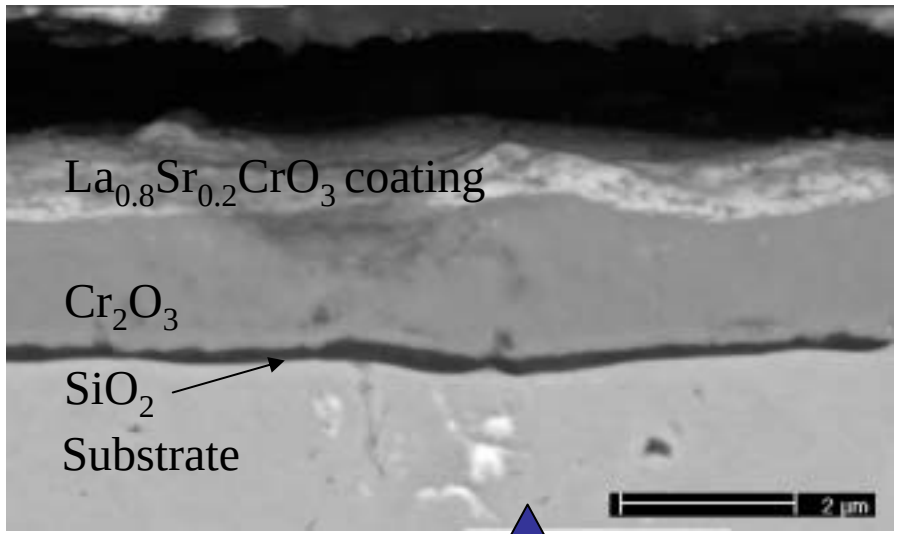
TASK I: RESULTS
Microstructural and Phase Identification
AL453 700°C

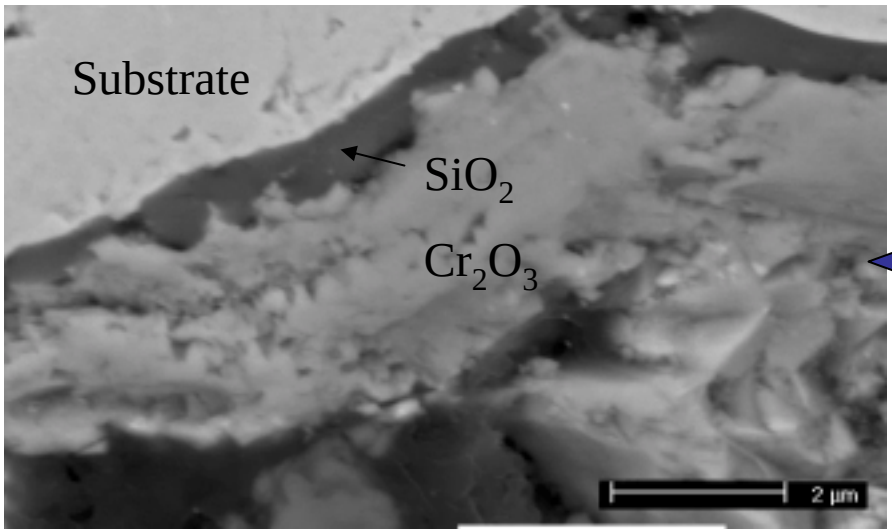




$LaCrO_3$ Coated T446 Stainless Steel (~0.5µm thick)







Coated side

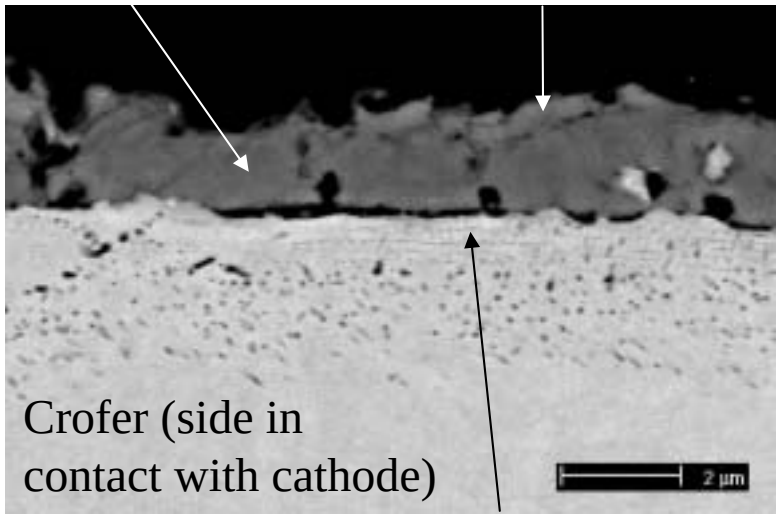
Uncoated side

100 hrs Isothermal, 900°C in Dry Air

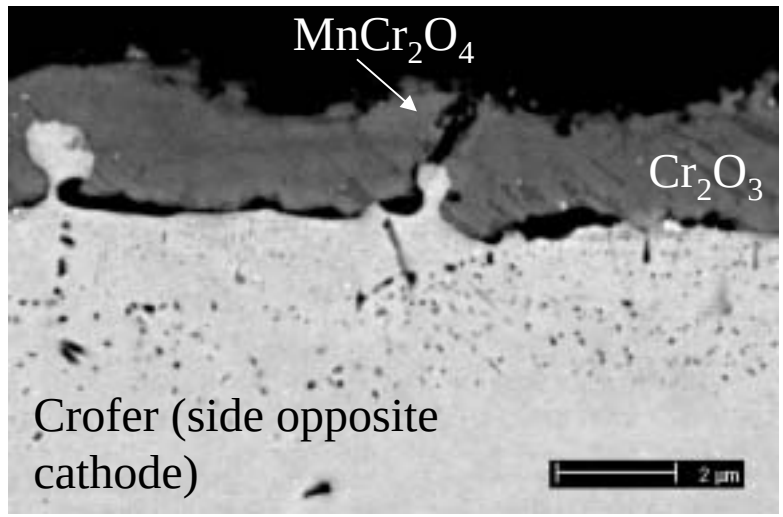
Crofer oxidized in contact with $LaSrMnO_4$ (cathode) for 88hrs at 900°C in air + 0.1atm H_2O

Cr_2O_3 with ~2% Sr, ~4% La, and ~4.7% Mn

$MnCr_2O_4$ with ~1.5% Sr and ~2.6% La



~74.9% Fe
~20% Cr
~2.2% La
~2% Mn
~0.9% Sr



After exposure, the cathode contained ~0.9% Cr and ~1.8% Al

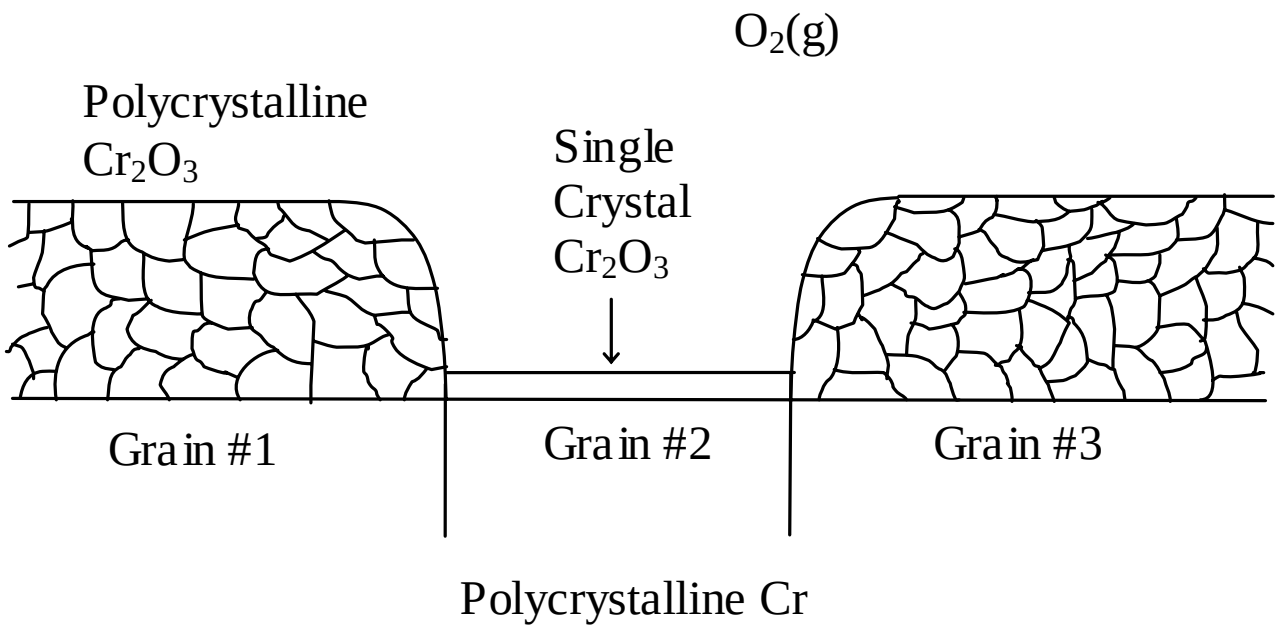
Oxidation Summary

- Oxidation in wet air produced the most severe degradation (accelerated chromia growth on Crofer and AL453 and increased spallation from E-brite).
- Oxidation morphologies were similar at 700 and 900^{o}C.
- ASR correlated with oxide thickness.
- Thin specimens deform under oxidation-induced stresses.
- Measurable interaction between Crofer and cathode material.
- Chromia growth reduced under chromite coating.

TASK I: FUTURE WORK
Work Planned for Next Six Months

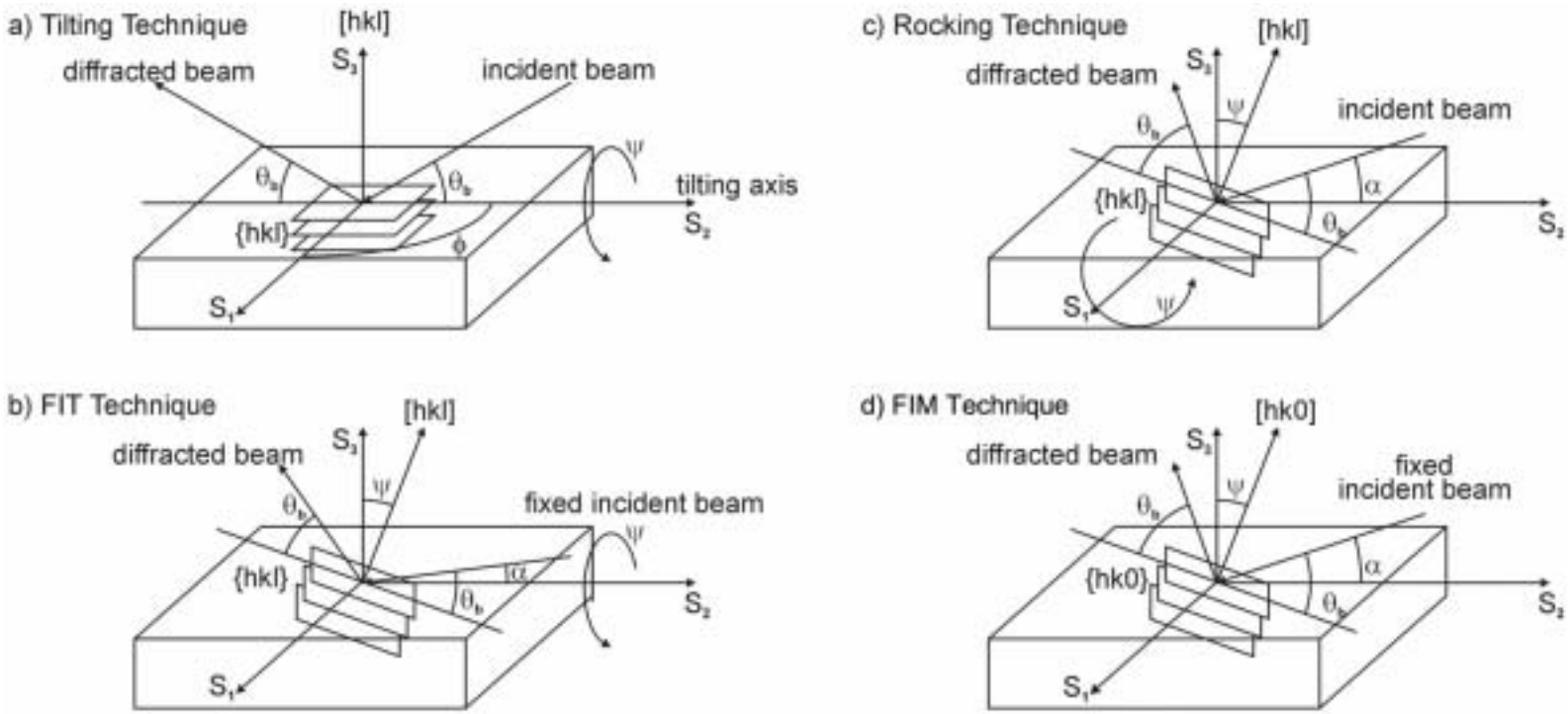
- Complete Cyclic Oxidation Experiments at 700°C.
- Continue Conductivity Measurements on Scales
- Continue Study of Effect of Contact with Anode and Cathode Materials
- Experiments to Decrease Chromia Growth Rate (Reactive Elements, Elimination of Grain Boundaries in Chromia)
- Investigate Effects of Simultaneous Exposure to Cathode and Anode Gases
- Continue Study of Effects of Coatings (Chromite) on Chromia Growth and Evaporation

Oxidation of Chromia-forming Alloys



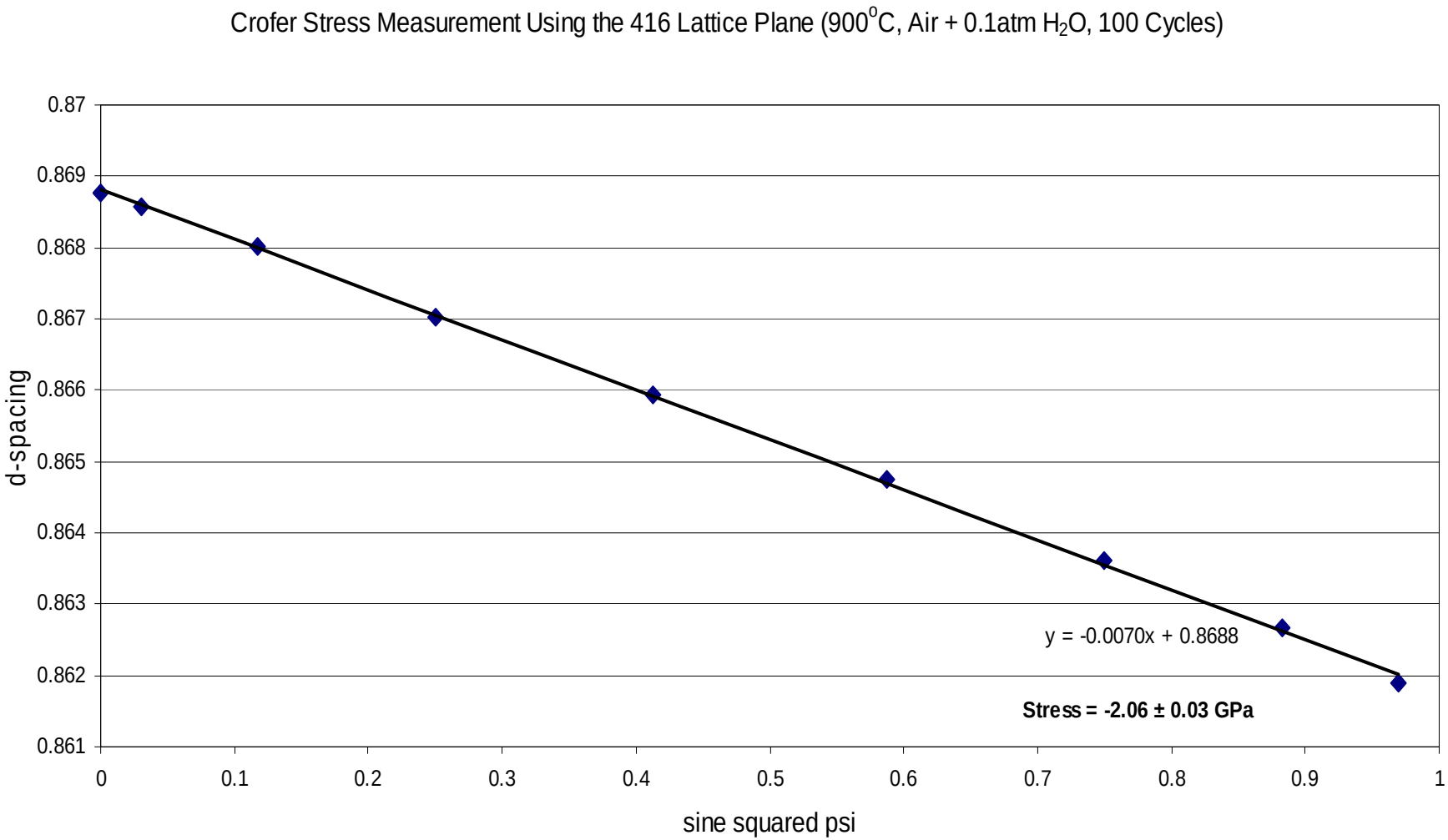
Caplan and Sproule, Oxid. Of Metals, 1975

TASK II: THERMOMECHANICAL BEHAVIOR
XRD Techniques



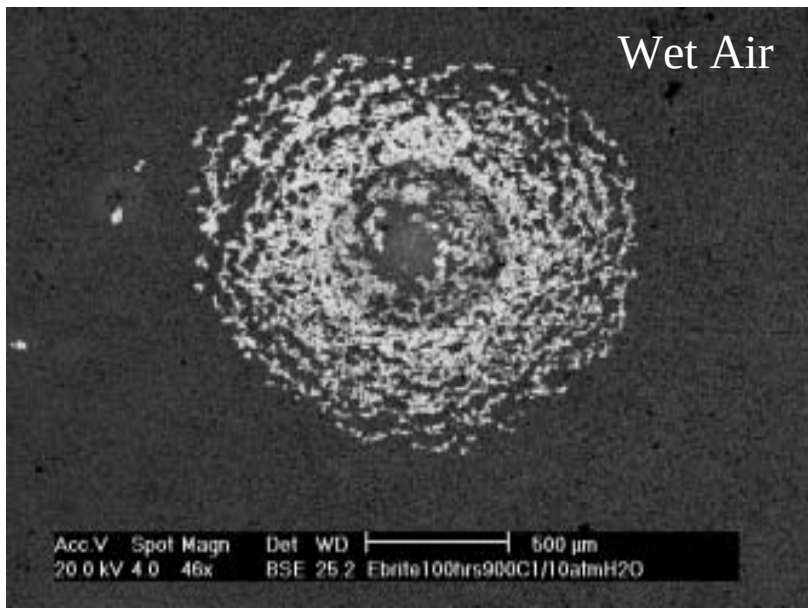
$$\varepsilon_\Psi = \frac{d_\Psi - d_0}{d_0} = \tfrac{1}{2} s_2(hkl)\sigma_o \sin^2\psi + 2s_1(hkl)\sigma_o$$

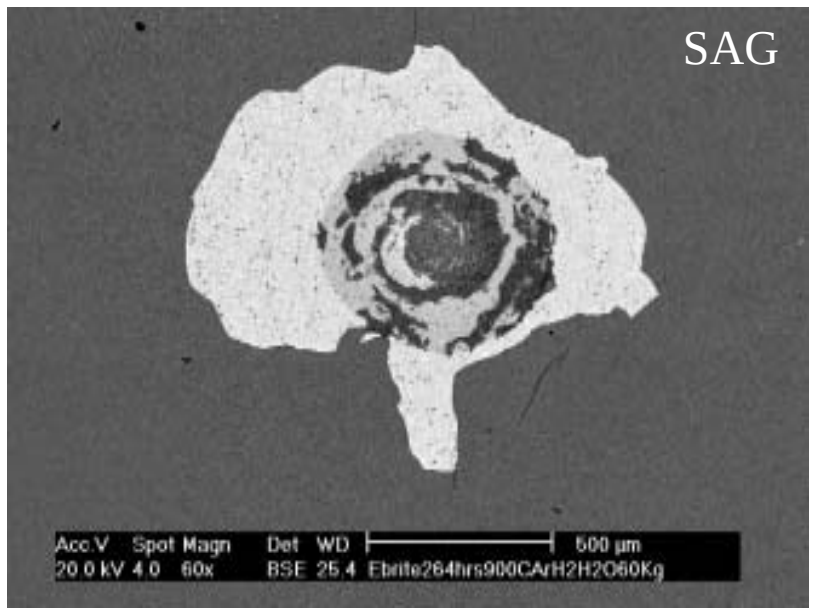
RESULTS
TASK II: THERMOMECHANICAL BEHAVIOR
Stress Measurements with 416 Lattice Plane – 900°C, Wet Air



TASK II: THERMOMECHANICAL BEHAVIOR
INDENTATION TESTING OF EXPOSED E-BRITE

- Significant Difference Seen in Wet Air vs. Simulated Anode Gas Exposures at 900°C *at Early Times (100-264 hrs)*
- Consistent with *Long-Term* TGA Results
- Wet Air Specimens Show a Non-Uniform Toughness, with Density of Debonding Decreasing with Radial Distance
- SAG Specimens Show a Peeling of Intact Chromia Scale – Due to Thicker Scale and/or Poorer Adhesion

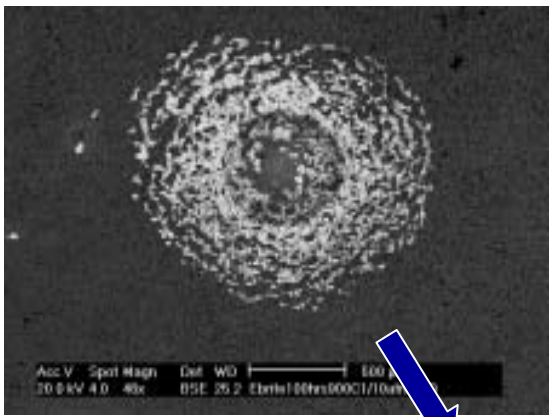




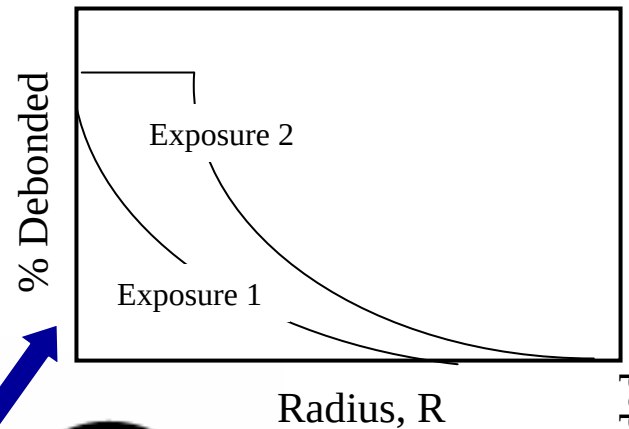
TASK II: THERMOMECHANICAL BEHAVIOR

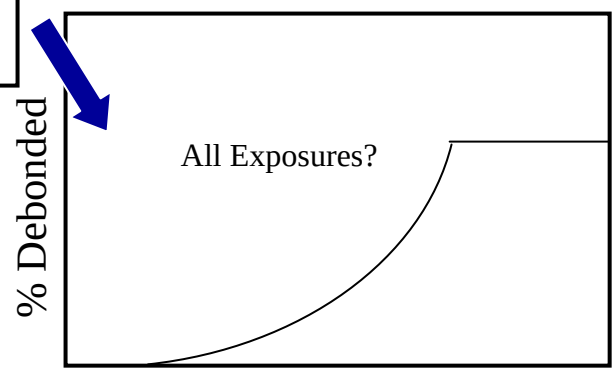
APPROACH FOR ANALYZING WET AIR SPECIMENS

- Use Image Analysis to Quantify the Percentage of Debonded Scale vs. Radius
- Use Energy Release Rate vs. Radius from Fracture Models to Plot Percentage of Debonded Scale vs. Energy Release Rate: *G Calculation Includes Measured Oxide Stress and Thickness Changes*
- See Whether Debond Percentage vs. Energy Release Rate (Distribution of Interfacial Toughness) Changes with Exposure



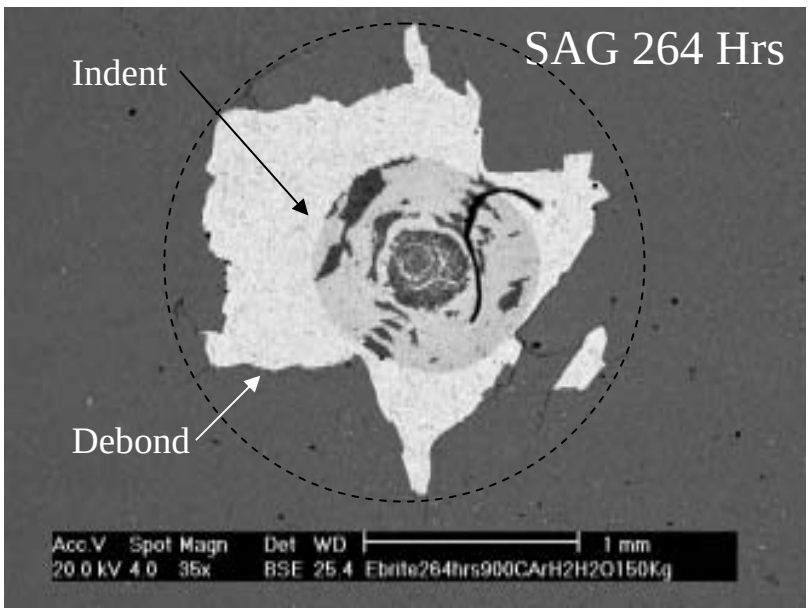
Debond Density in Rings About Indent

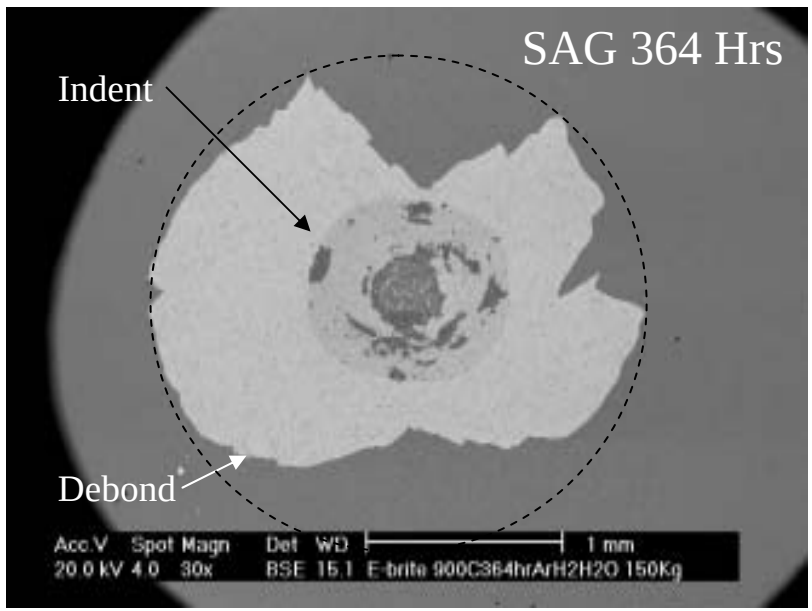




TASK II: THERMOMECHANICAL BEHAVIOR
SAG SPECIMEN TOUGHNESS ESTIMATES

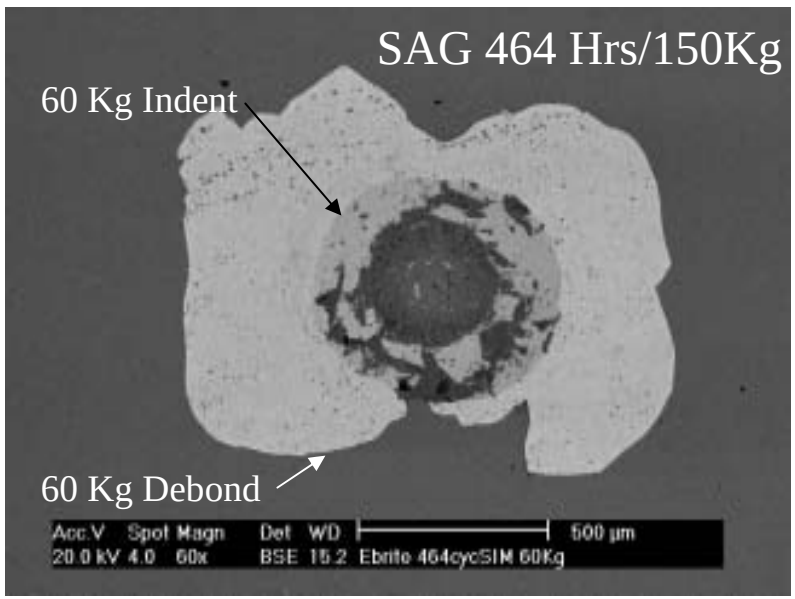
- Debond Size Appears to Increase from 264 to 364 Hours of Exposure at 900°C (though Debond Size is Not Changed at 464 Hours)
- Debond Size Could be Due to Increased Scale Thickness or Loss of Adhesion (Qualitative Trends Agree with Oxide Scale Growth Data)
- Indentation Model Results Coupled with Oxide Thickness and XRD Residual Stress Measurements will Yield Interfacial Toughness Values and Mechanisms Leading to Spallation

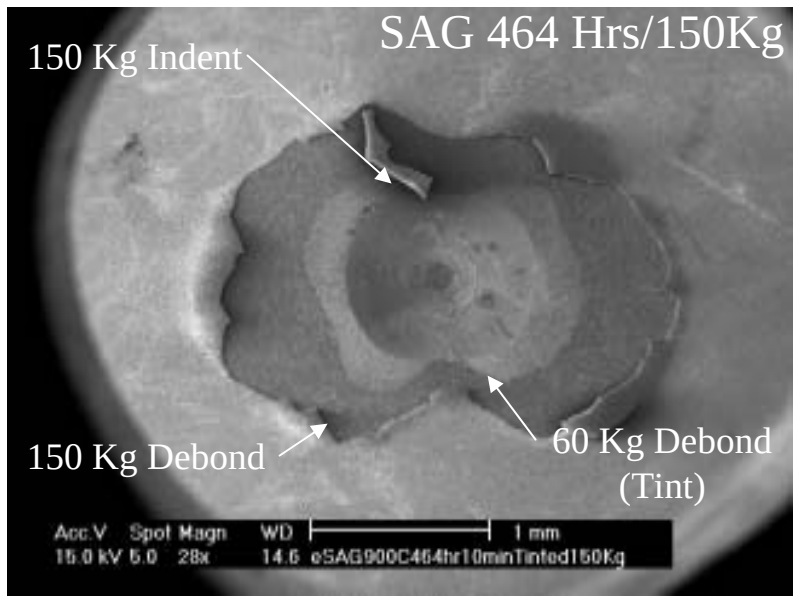




TASK II: THERMOMECHANICAL BEHAVIOR
USE OF TINTING TO VIEW SAG SPECIMEN DEBONDS

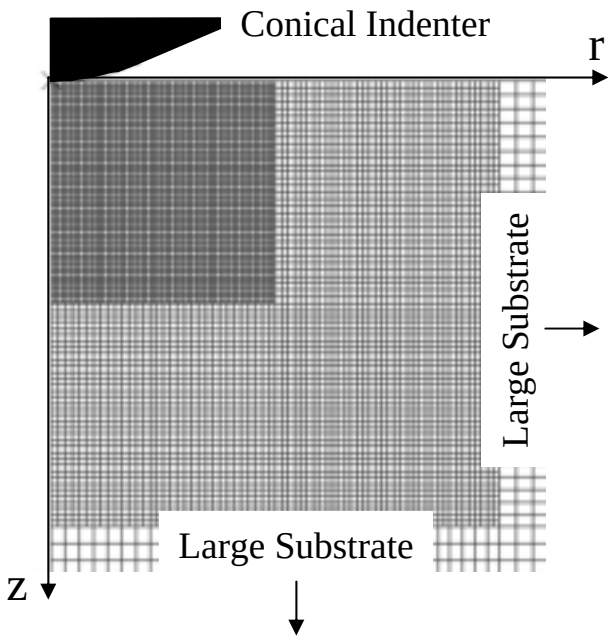
- Two Indents after 464 Hours at 900°C
- 60kg Indent, 10min at 700°C (tint), 150kg Indent (Mechanics Analysis Shows Increased Load Only Increases the Size Scale of the Damage)
- Tinting allows Clear Visualization of Debond Size at 60kg
- Visual Extent of Debonding Roughly Equals Actual Extent of Debonding

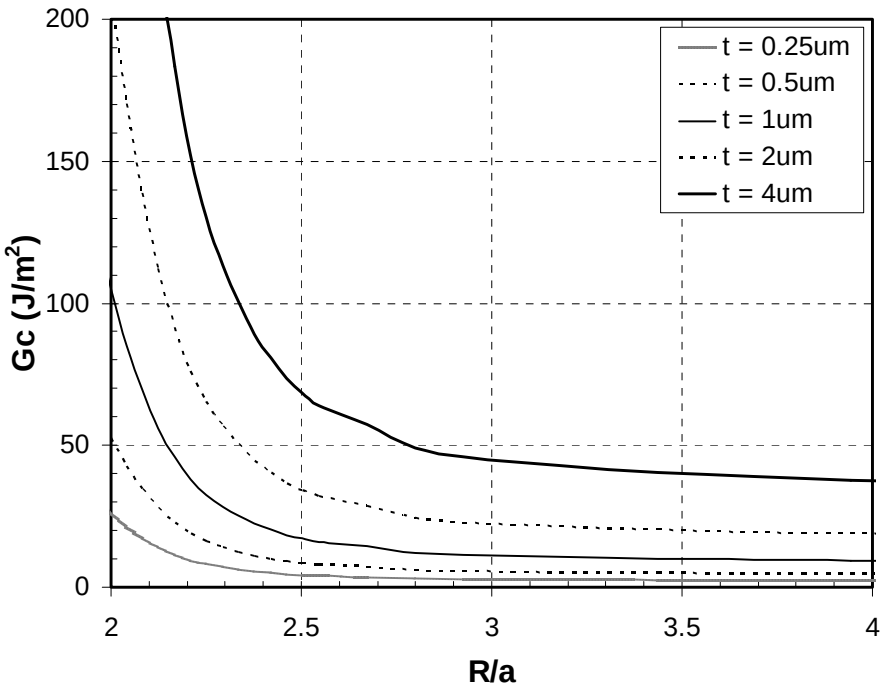




TASK II: THERMOMECHANICAL BEHAVIOR
SAG SPECIMEN INDENT FRACTURE MODELING

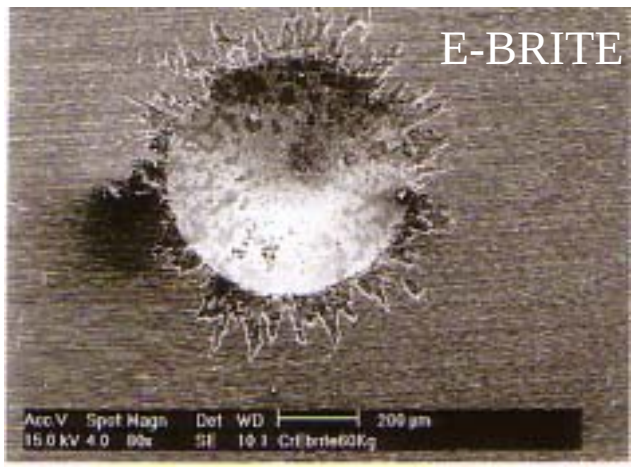
- Finite Element Model of the Indent Problem: Substrate Strains Transferred to the Chromia Scale
- Fracture Mechanics Formulas Estimate G_c vs. Normalized Debond Radius (Residual Stress of -2.22 GPa in Chromia Scale)
- R/a = 2.5 and t_{oxide} = 2μm Yields: G_c = 34 J/m^2

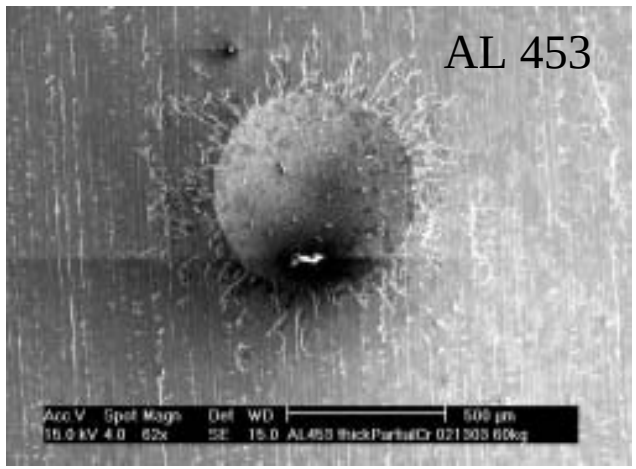


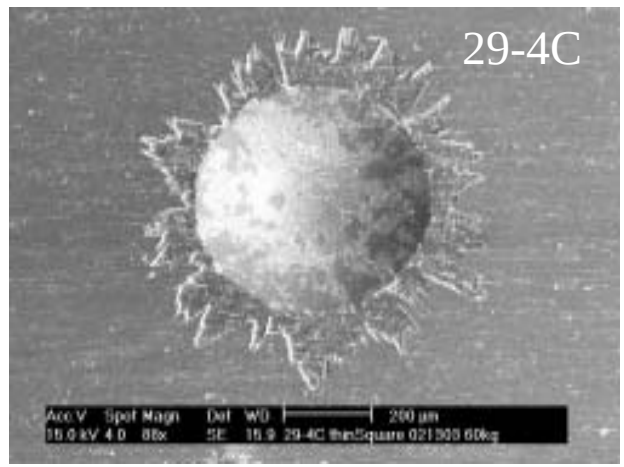


TASK II: THERMOMECHANICAL BEHAVIOR
AS-PROCESSED CHROMITE COATED SPECIMENS

- Specimens of $La_{0.8}Sr_{0.2}CrO_3$ on E-BRITE, AL 453 and AL 29-4C , Indented Before Exposure (from PNNL)
- Coating can Add to the Stored Energy Driving Chromia Spallation
- All 3 Substrate Systems Show Indent-Induced Spallation (Confined to the Near-Indent Region)

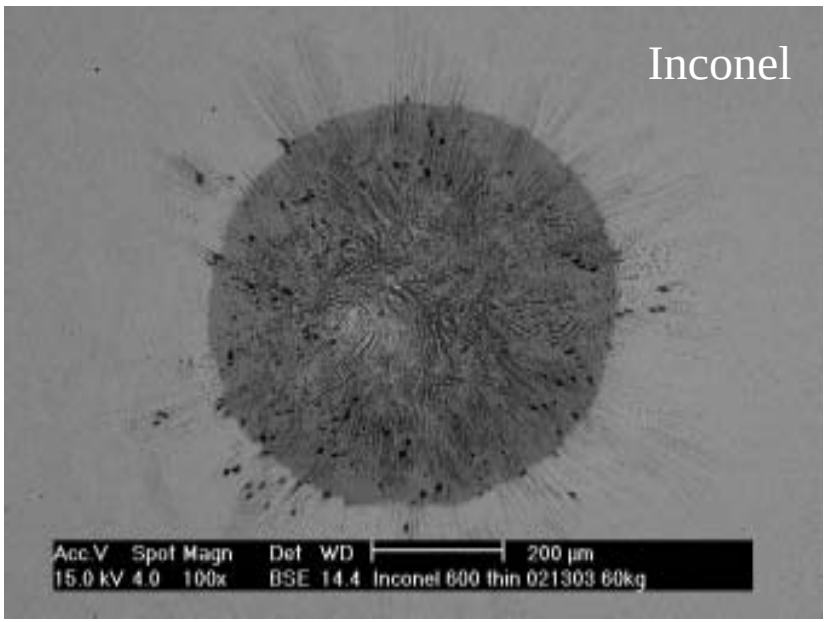


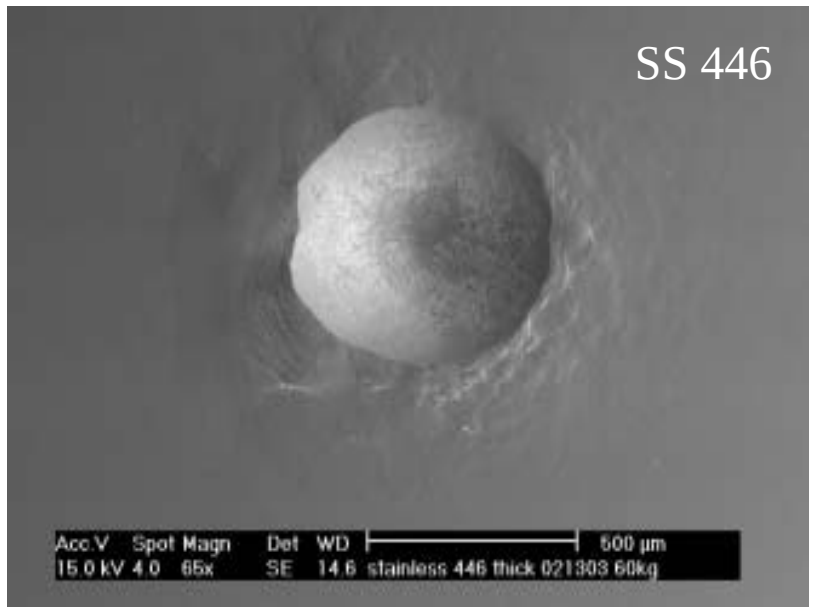




TASK II: THERMOMECHANICAL BEHAVIOR
AS-PROCESSED CHROMITE COATED SPECIMENS

- $LaCrO_3$ Coating on Inconel and SS 446
- NETL and Drexel Providing Specimens, Coating Properties
- Spallation is not Seen, but Radial Cracking Seen for Inconel
- Lack of Debonding Likely due to Very Thin Coating

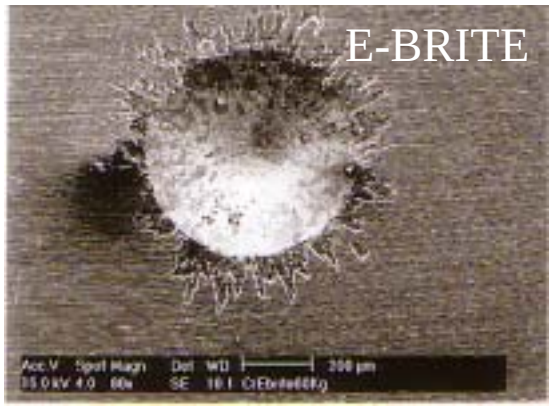




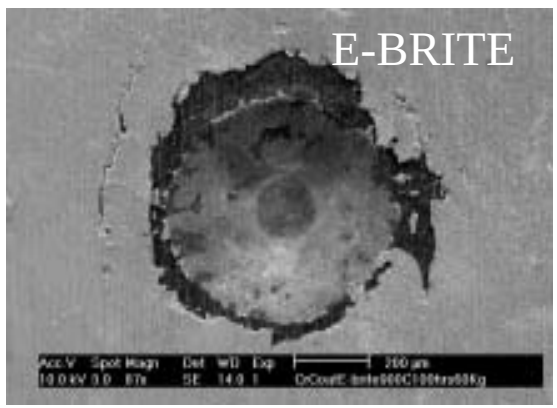
TASK II: THERMOMECHANICAL BEHAVIOR
EXPOSED CHROMITE COATED SPECIMENS

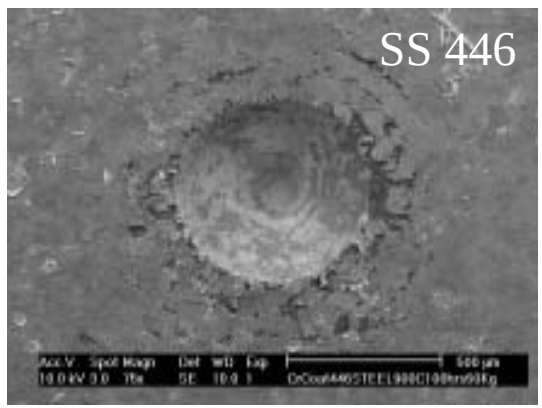
- $La_{0.8}Sr_{0.2}CrO_3$ on E-BRITE (PNNL) and $LaCrO_3$ on SS 446 (Drexel/NETL)
- Debonding More Extensive for $La_{0.8}Sr_{0.2}CrO_3$ and Now Occurs for $LaCrO_3$
- Chromia Scale has Formed Under Both Coatings; Debonding at Chromia/Metal Interface

As Processed:



Exposed 100hr 900°C:





TASK II

WORK PLANNED FOR NEXT SIX MONTHS

- Extend Modeling of Indentation of E-BRITE to Other Substrate Systems
- Incorporate Oxide Thickness and XRD Stress Measurements into Models: Identify Mechanisms Leading to Spallation
- Indentation Tests on E-BRITE for Longer Exposures at 900° C in Wet Air and Simulated Anode Gas
- Indentation Tests on Specimens Exposed at 700° C
- Study of Adherence of Exposed Coated Specimens

TASK III: RESULTS
Alternative Material Choices

- This Task involves a theoretical evaluation of alternate metallic materials which have properties superior to the ferritic alloys.
- The most promising materials will be fabricated and tested in Phase II.

SUMMARY AND CONCLUSIONS

The aim of this project is to evaluate the chemical and thermomechanical stability of ferritic alloys in the fuel cell environment.

The understanding gained will be used to attempt to optimize the properties of the ferritic alloys.

A parallel study is evaluating the potential use of alternate metallic materials as interconnects.