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

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J. Hammer, S. Laney, F. Pettit, & G. Meier
Department of Materials Science & Engineering
University of Pittsburgh

N. Dhanaraj & J. Beuth
Department of Mechanical Engineering
Carnegie Mellon University

SECA Annual Workshop and Core Technology Program Peer Review

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University of Pittsburgh

Carnegie Mellon

PROJECT STRUCTURE

NETL

Dr. Lane Wilson	Technical Monitor
Dr. Chris Johnson	NETL Fellowship Mentor

University of Pittsburgh

Prof. Frederick. S. Pettit	Co-principal Investigator
Prof. Gerald. H. Meier	Co-principal Investigator
Ms. Julie Hammer	Graduate Student
Mr. Scot Laney	NETL Partnership Fellow
Ms. Mary Birch	Senior Project Student

Carnegie Mellon University

Prof. Jack L. Beuth	Co-principal Investigator
Ms. Nandhini Dhanaraj	Graduate Student

Completed

Ms. Kelly Coyne	B.S. Engineering Phys.
Ms. Carrie Davis	B. S. Materials Science
Mr. Wesley Jackson	B. S. Materials Science

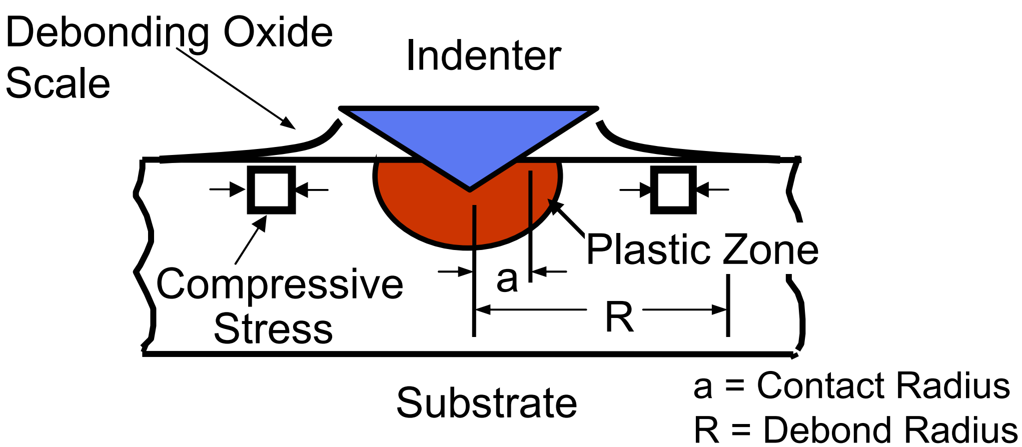
PROGRAM FOCUS
TASK I: Mechanism-Based Evaluation Procedures (Chromia-Forming Alloys)

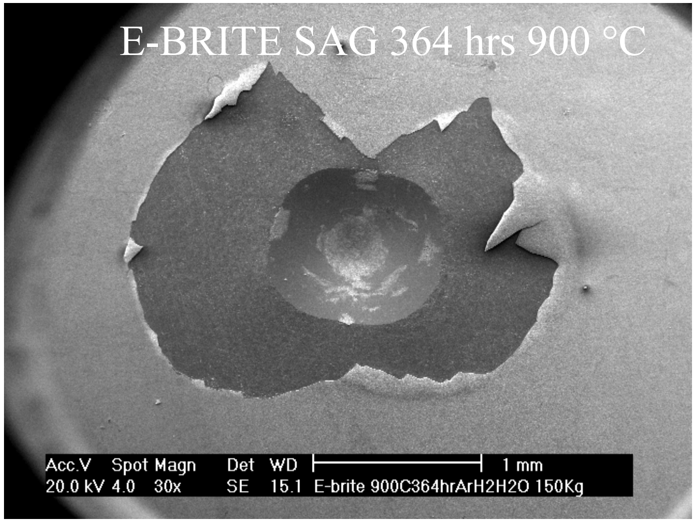
- Characterization of Exposed Fuel Cell Interfaces
- Growth Rates of Chromia Scales on Cr and Ferritic Alloys
- Adhesion of Chromia Scales
- Oxide Evaporation
- Complex Atmosphere Testing

*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





Key Issues: What leads to spallation: scale thickening, stress changes or changes at the interface?

Can we quickly evaluate alloy systems without testing to the time for spontaneous spallation?

PROGRAM FOCUS
TASK III: Alternative Material Choices

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

- Control of Growth Rate and Conductivity of Simple Oxides (e. g. CoO, NiO)
- 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

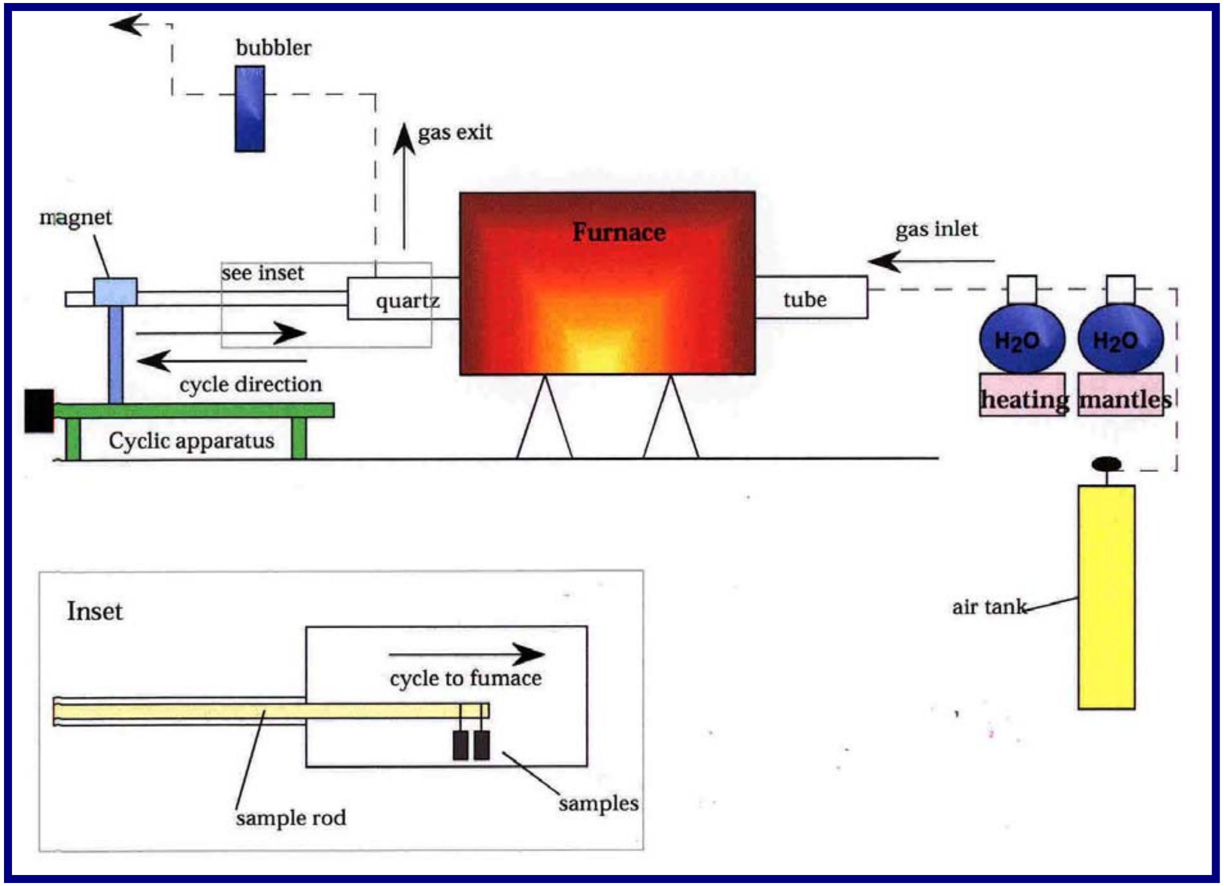
Alloys

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

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)

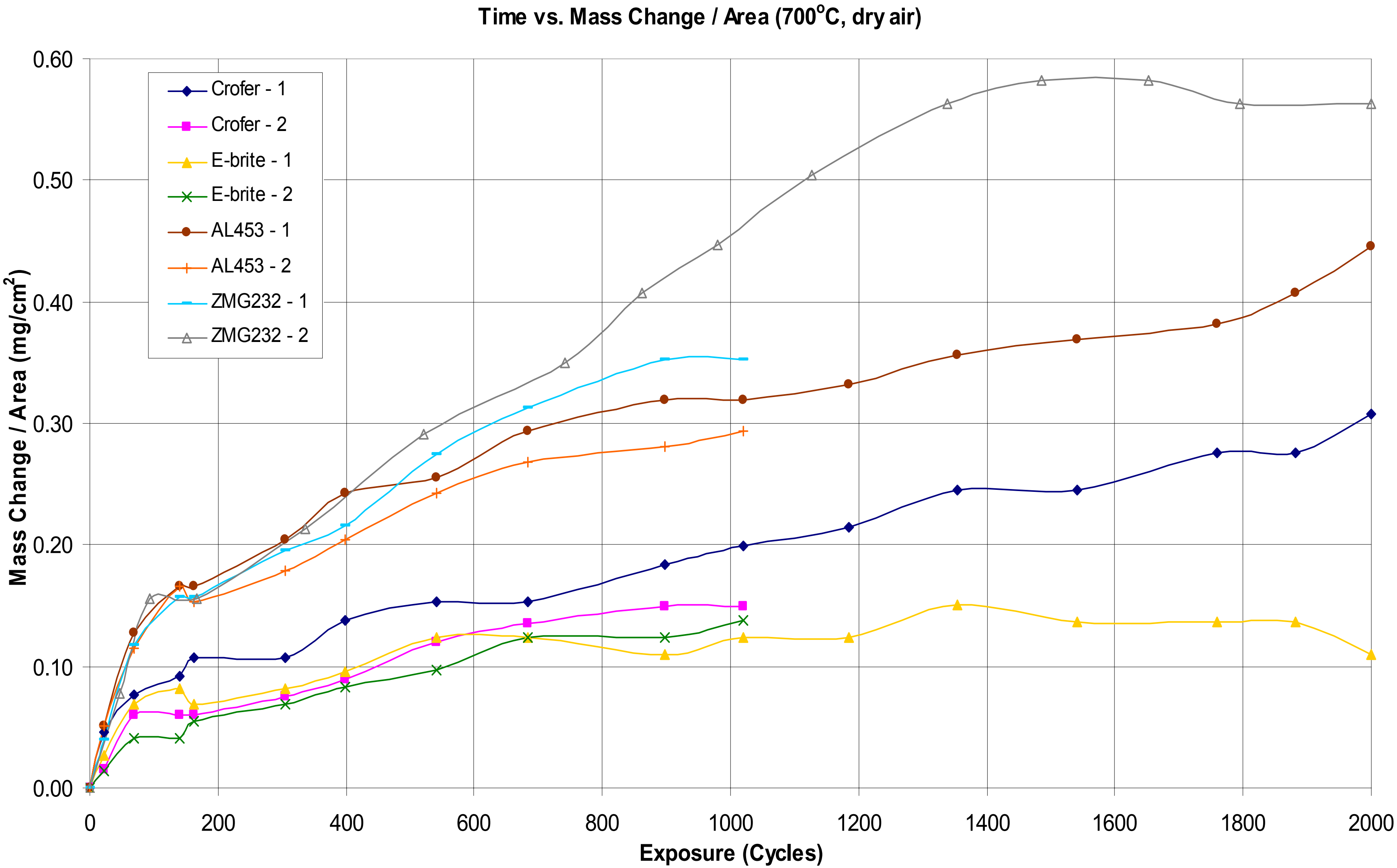
TASK I: RESULTS
Diagram of Apparatus



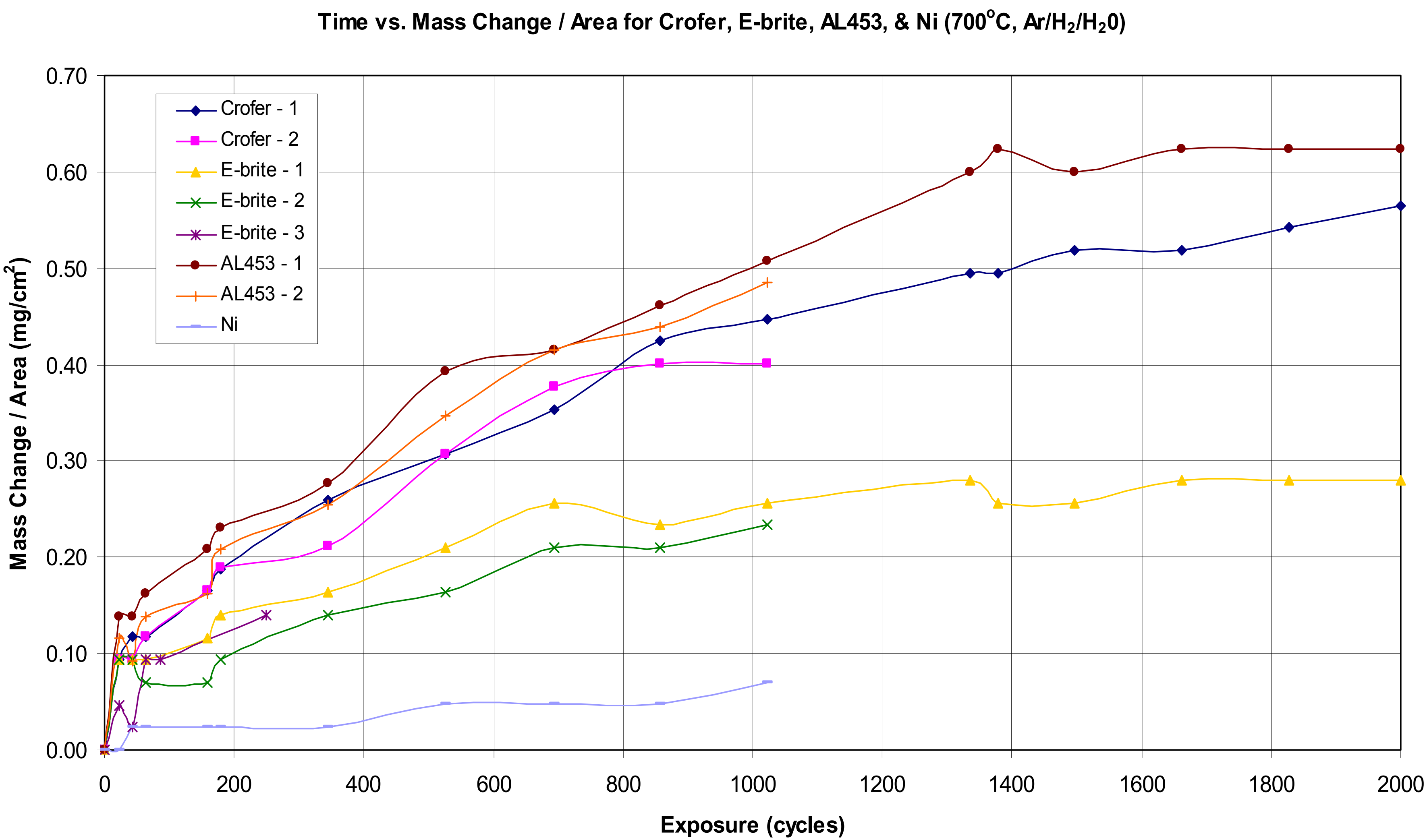
Previous Results

- Oxidation in wet air produced the most severe degradation at 900˚C (accelerated chromia growth on Crofer and AL453 and increased spallation from E-brite).
- ASR correlated with oxide thickness.
- Thin specimens deform under oxidation-induced stresses.

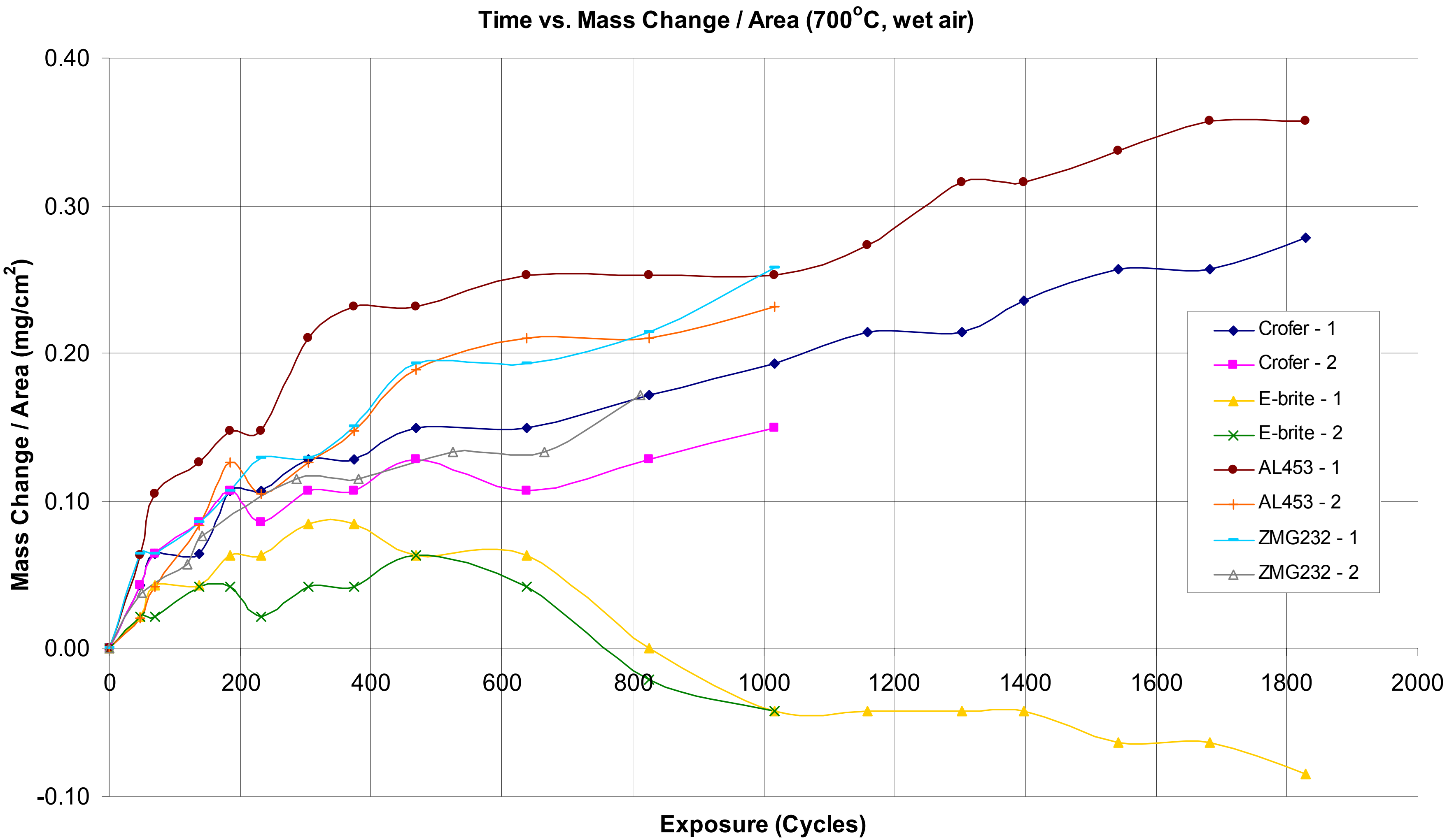
TASK I: RESULTS
Dry Air Exposures – 700°C



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



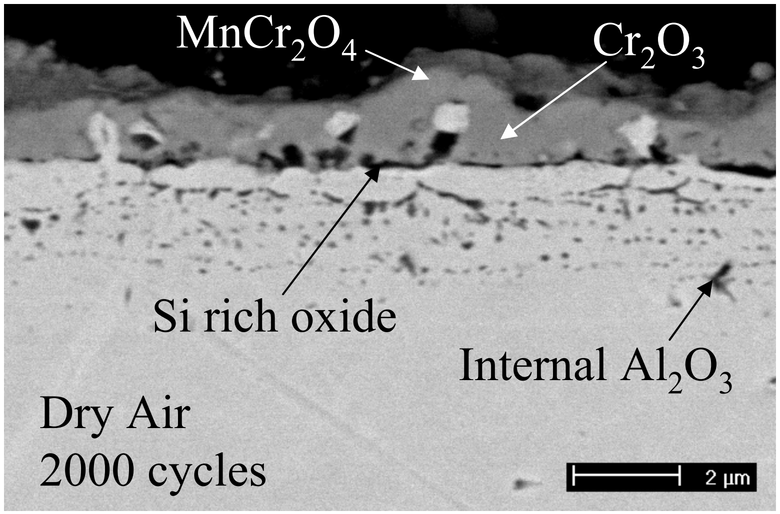
TASK I: RESULTS
Wet Air (0.1 atm H_2O) Exposures - 700°C

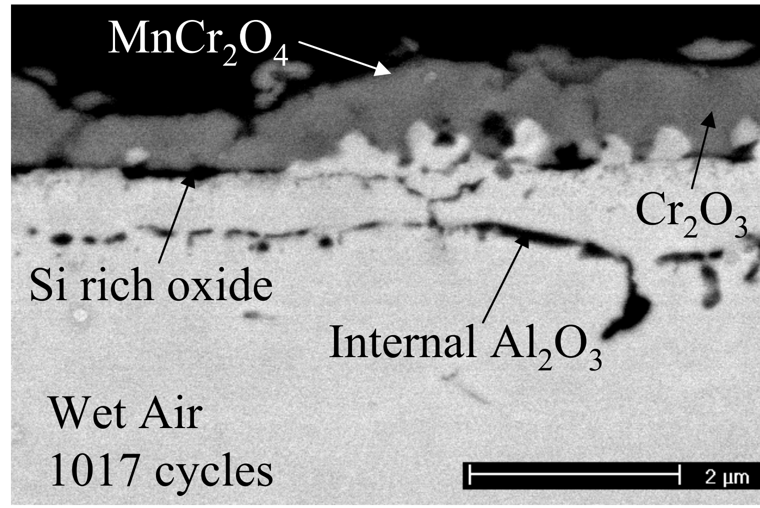


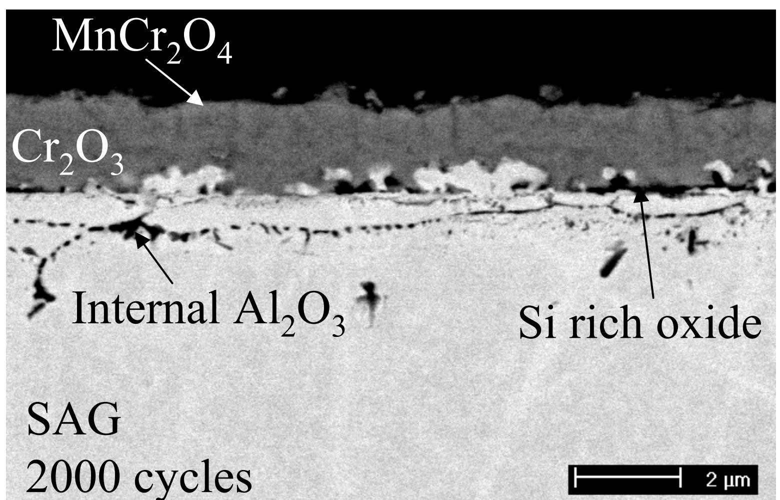
TASK I: RESULTS

Microstructural and Phase Identification

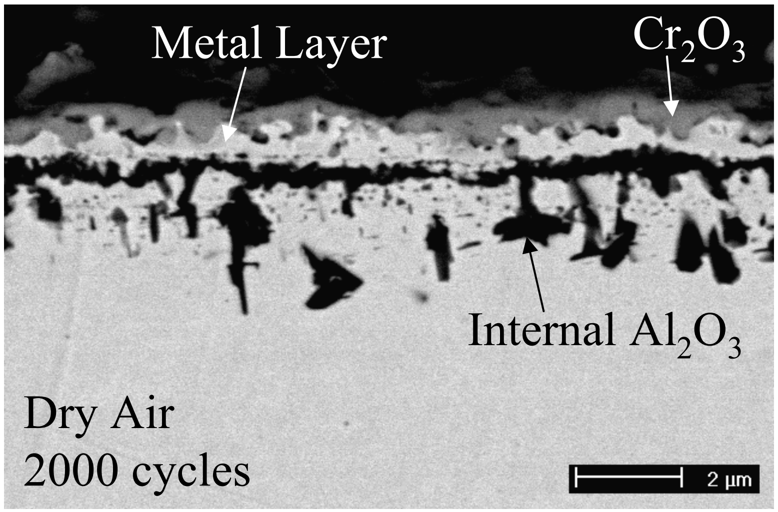
Crofer 700^{o}C

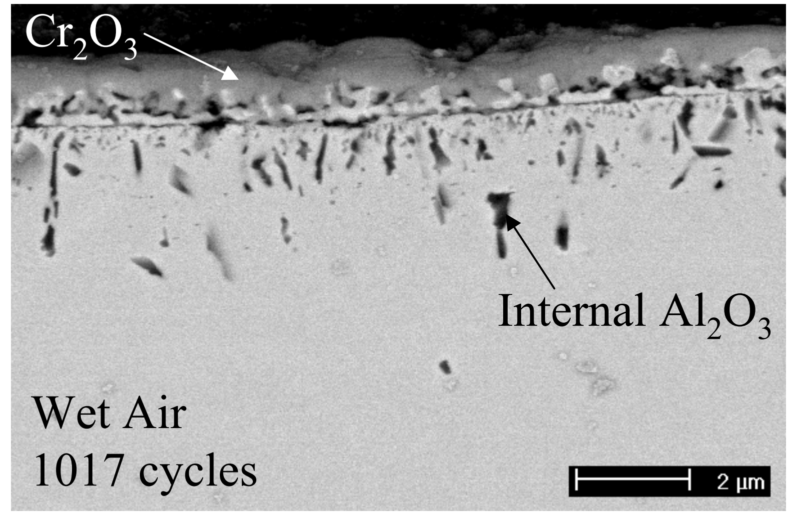


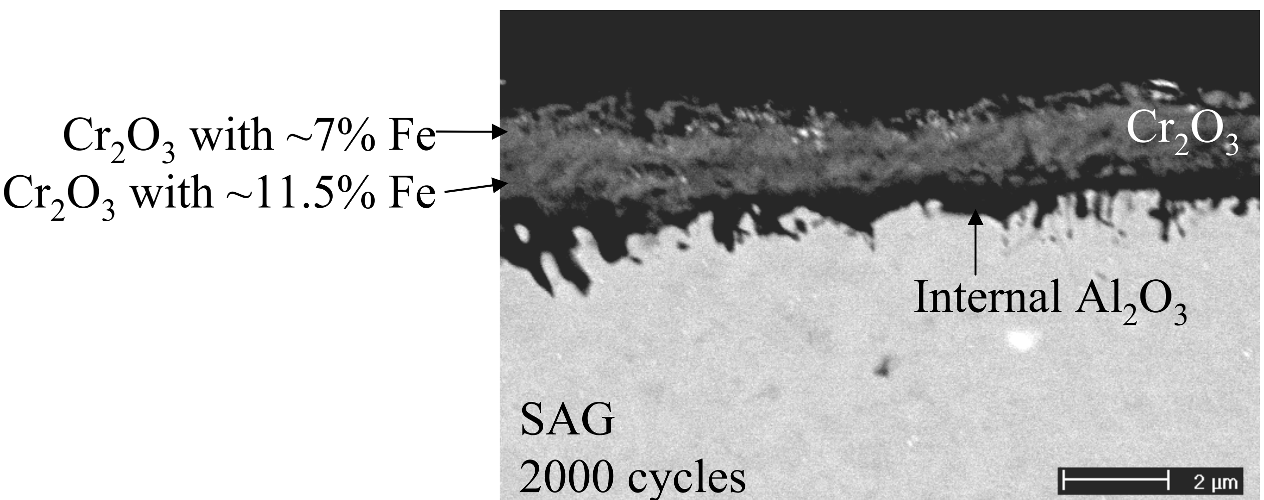




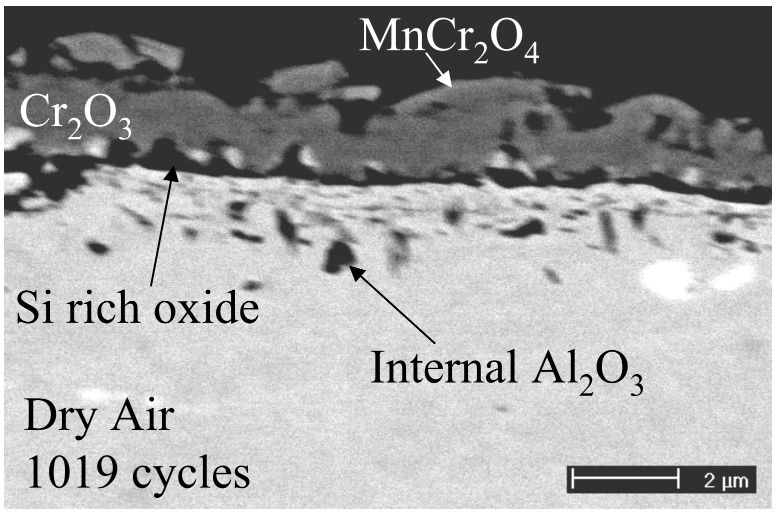
TASK I: RESULTS
Microstructural and Phase Identification
AL453 700°C

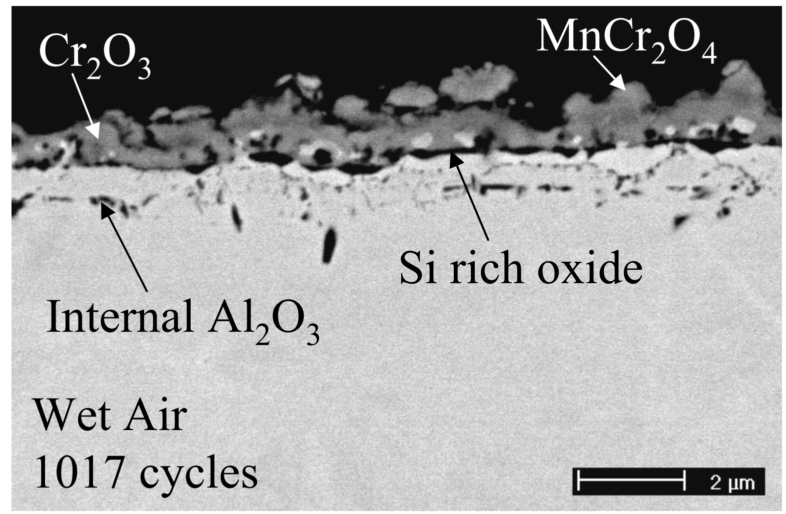






TASK I: RESULTS
Microstructural and Phase Identification
ZMG232 700°C

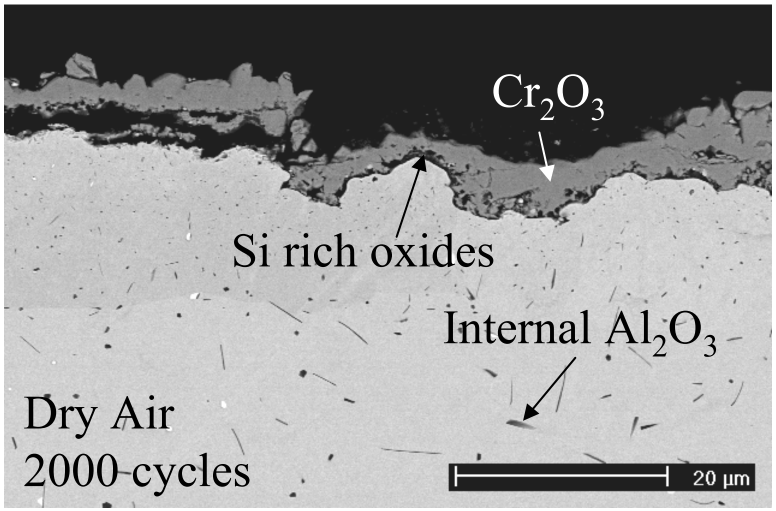


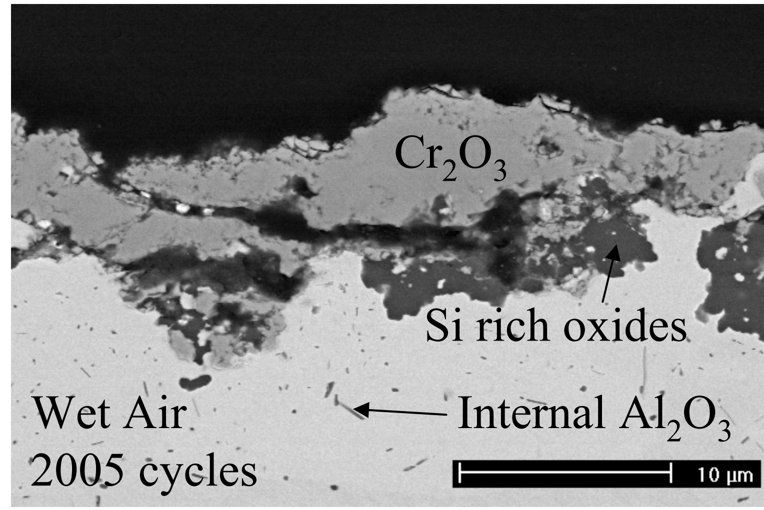


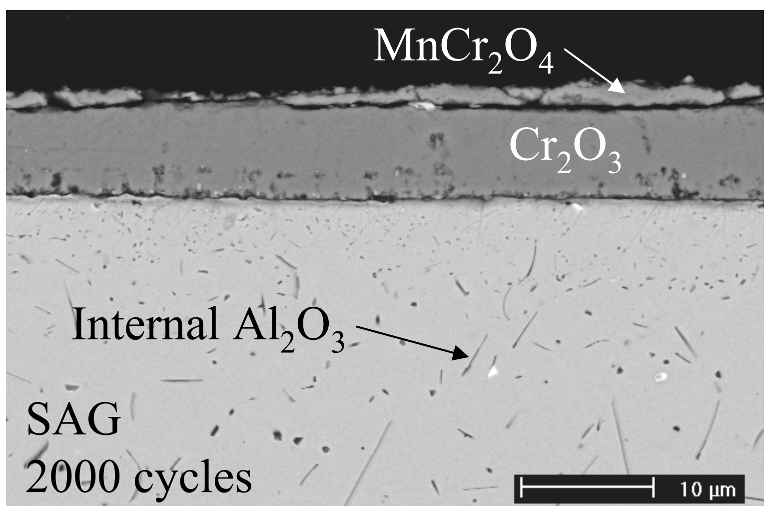
TASK I: RESULTS

Microstructural and Phase Identification

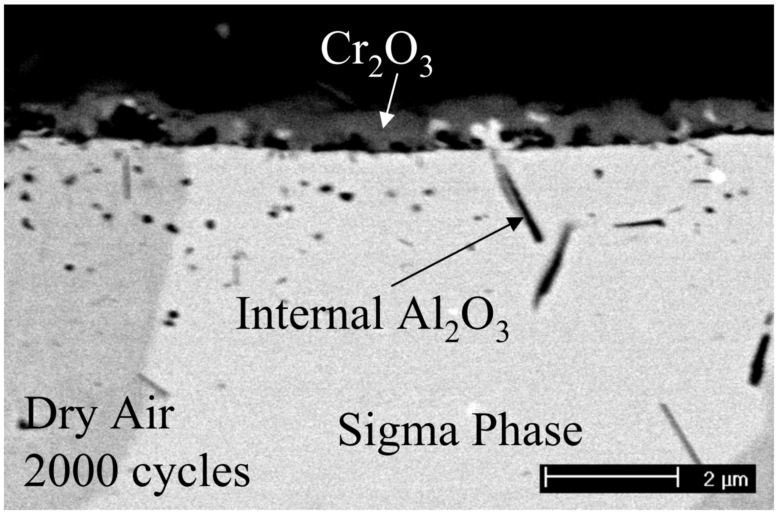
E-brite 900°C

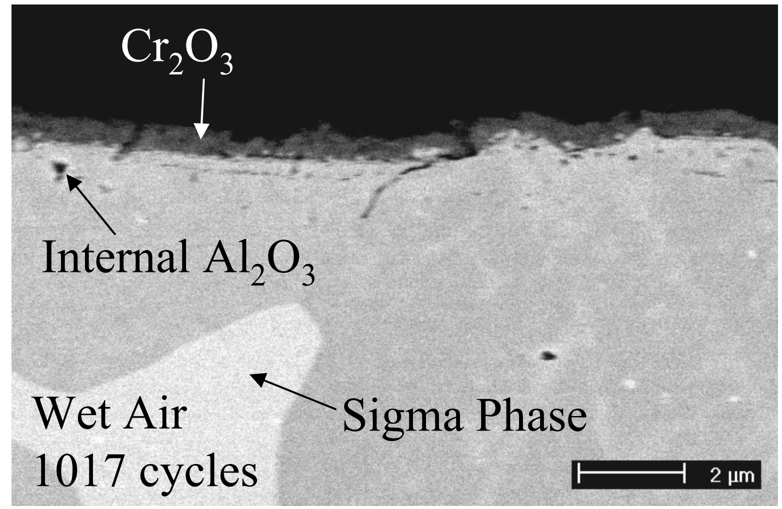


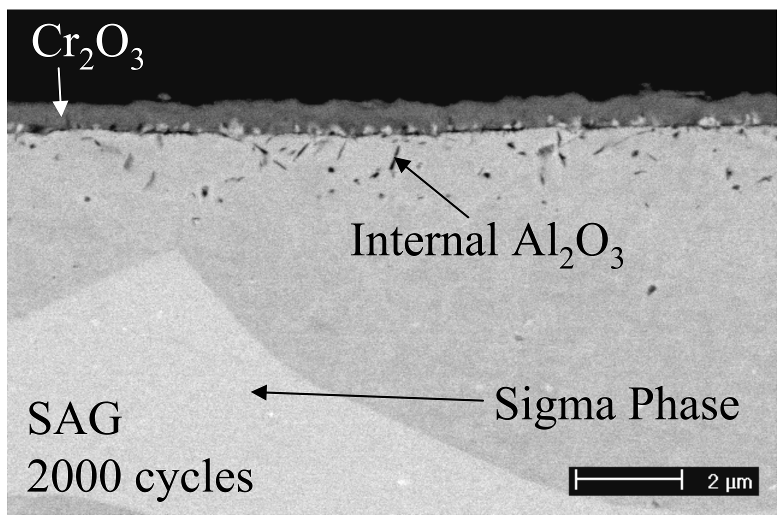




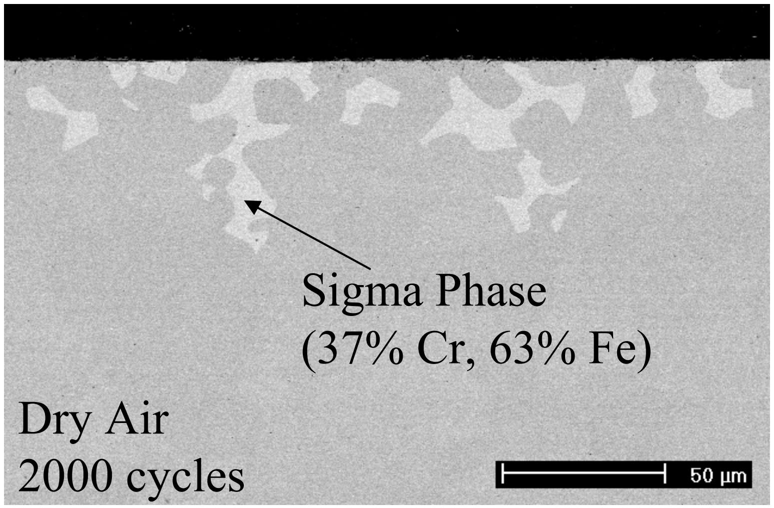
TASK I: RESULTS
Microstructural and Phase Identification
E-brite 700°C

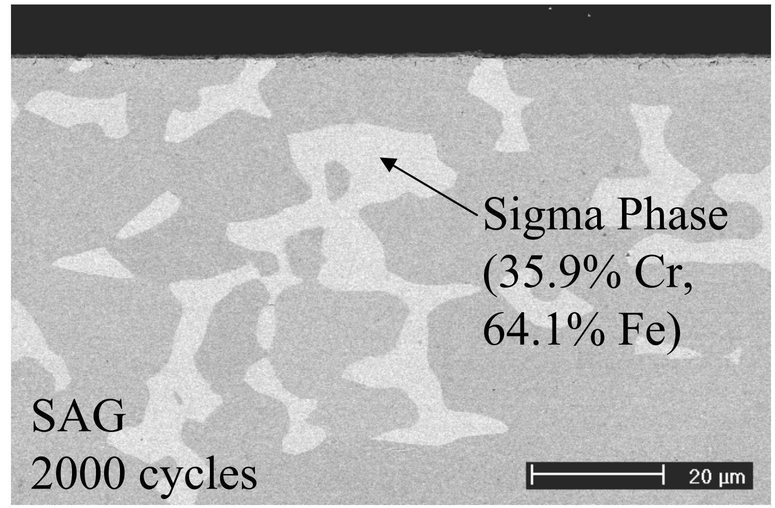


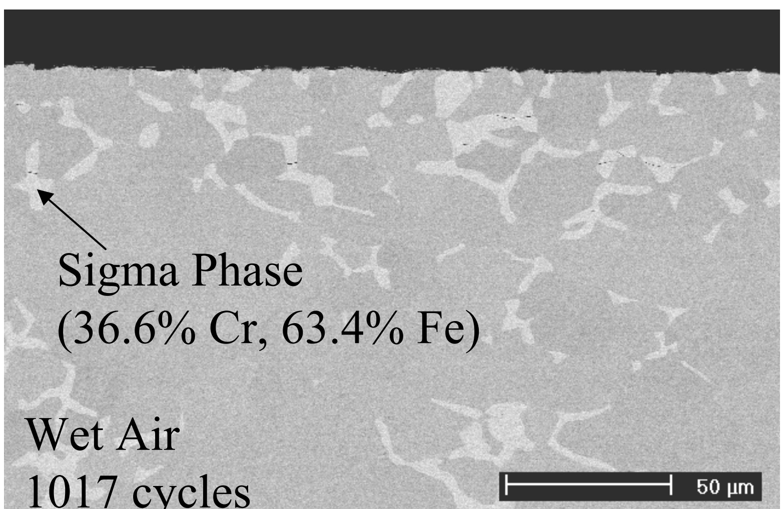


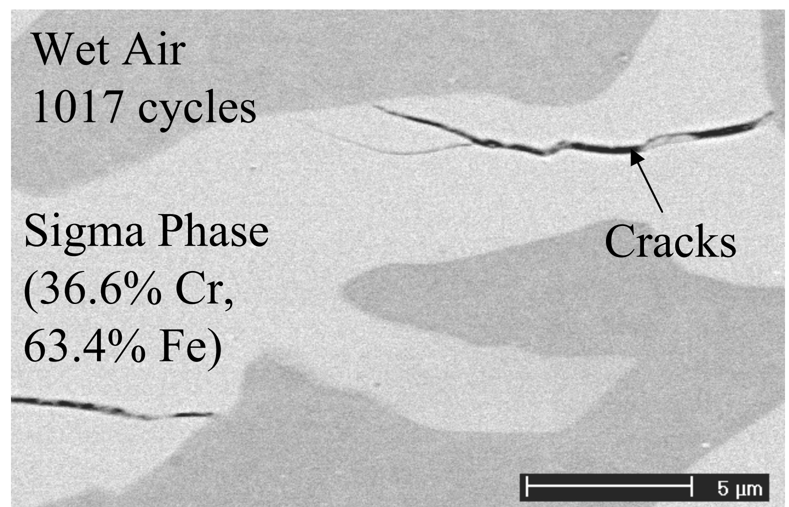


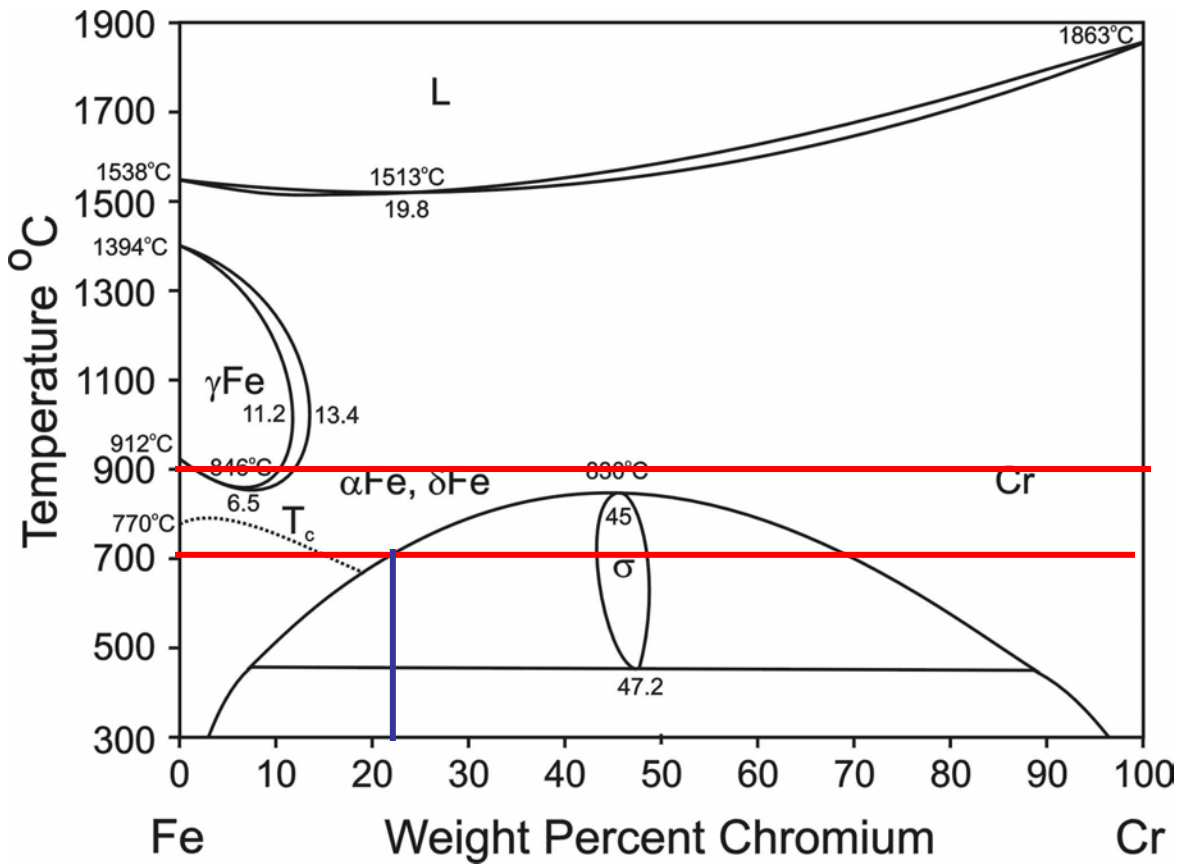
TASK I: RESULTS
Sigma Phase in E-brite at 700°C







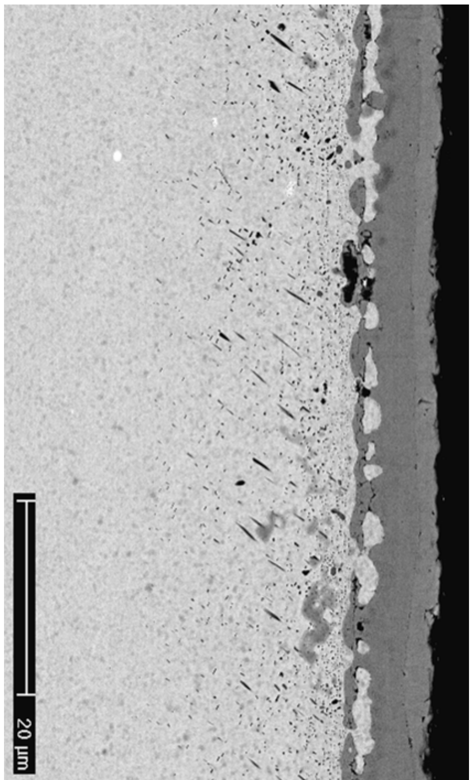




1900
1700
1500
1300
1100
900
700
500
300
Temperature °C
1863°C
L
1538°C
1513°C
19.8
1394°C
γFe
11.2
13.4
912°C
846°C
830°C
αFe, δFe
Cr
6.5
770°C
T_c
45
σ
47.2
0
10
20
30
40
50
60
70
80
90
100
Fe
Weight Percent Chromium
Cr

Chromia Evaporation

Crofer



$MnCr_2O_4$

$$Cr_2O_3(s) + \tfrac{3}{2}O_2(g) = 2CrO_3(g)$$

$$p_{CrO_3} = K^{\frac{1}{2}} a_{cr_2O_3}^{\frac{1}{2}} p_{O_2}^{\frac{3}{4}}$$

$$MnO(s) + Cr_2O_3(s) = MnCr_2O_4(s)$$

$$\Delta G^o_{1100K} \approx -89KJ/mole$$

Chromia Saturation $a_{Cr_2O_3} = 1$ $p_{CrO_3} = 4x10^{-11}\,atm$

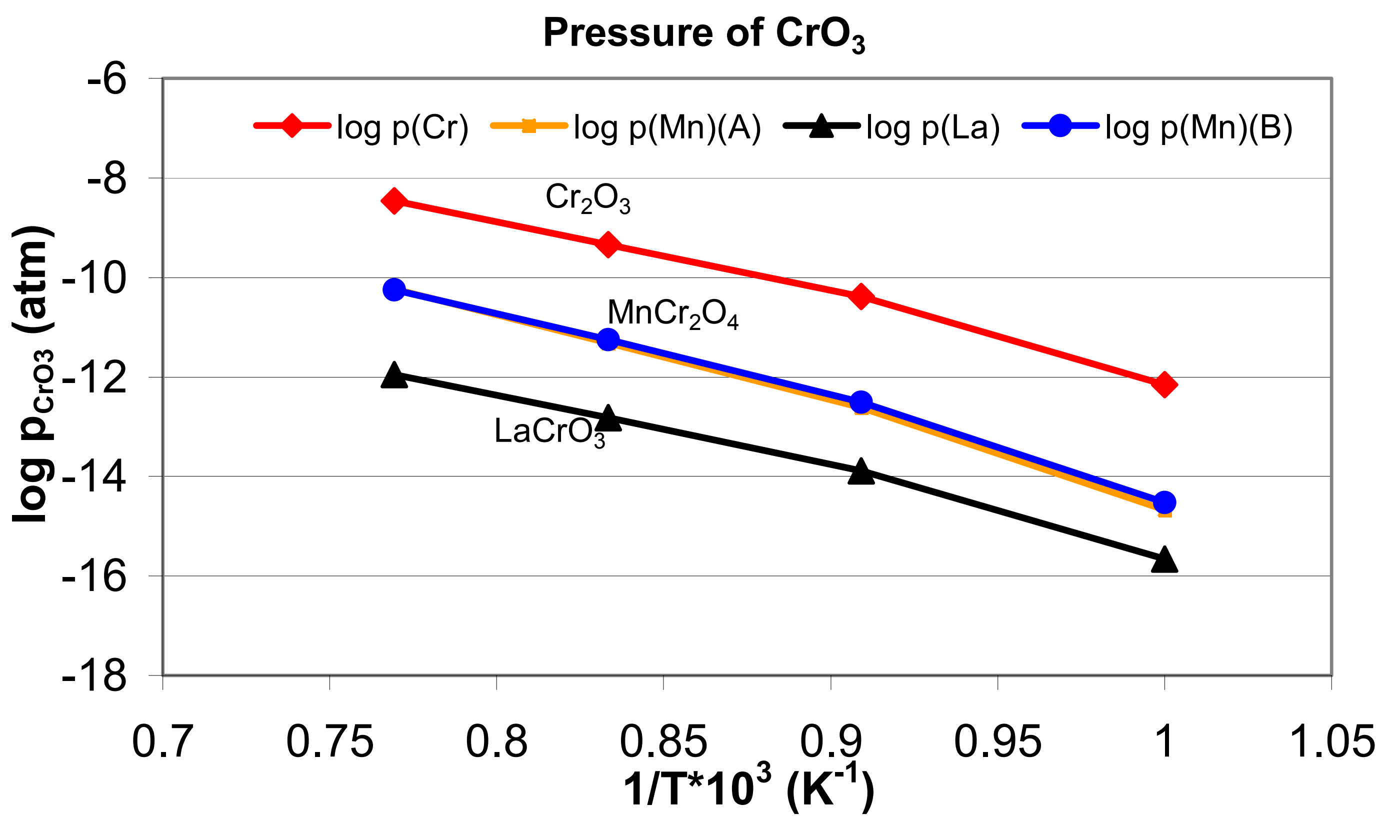
MnO Saturation

$a_{Cr_2O_3} = 6x10^{-5}$ $p_{CrO_3} = 3x10^{-13}\,atm$

$LaCrO_3$ (Activity data from Hilpert et al)

$a_{Cr_2O_3} = 10^{-7}$ $p_{CrO_3} = 1x10^{-14}\,atm$

Partial pressures of CrO_3 in Equilibrium with Cr_2O_3, MnO-saturated $MnCr_2O_4$, and $LaCrO_3$

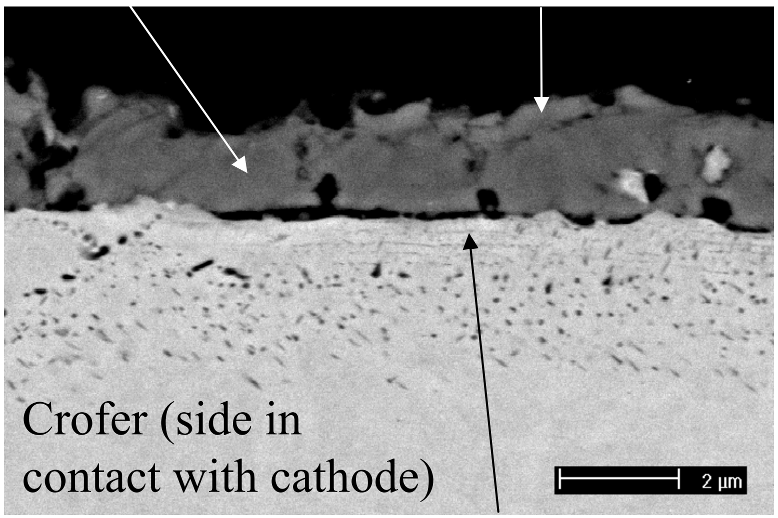


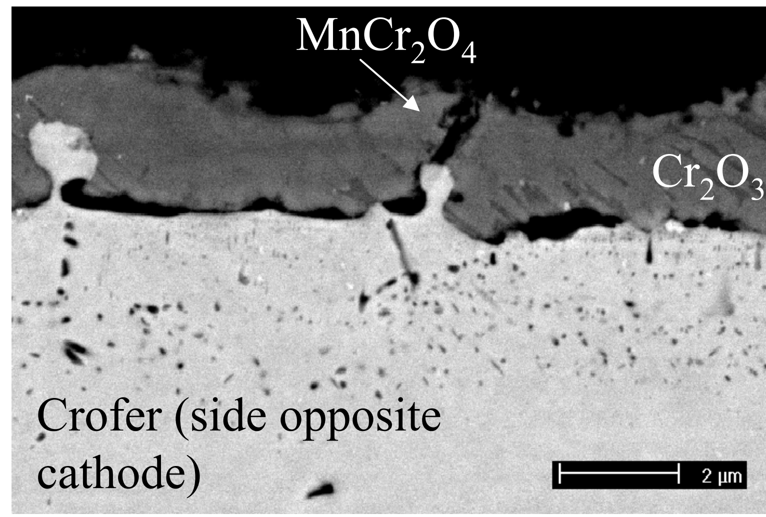
Note: **similar reductions would be achieved in the pressure of $CrO_2(OH)_2$**

Crofer oxidized in contact with $LaSrMnO_4$ (cathode) for 88hrs at 900^{o}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

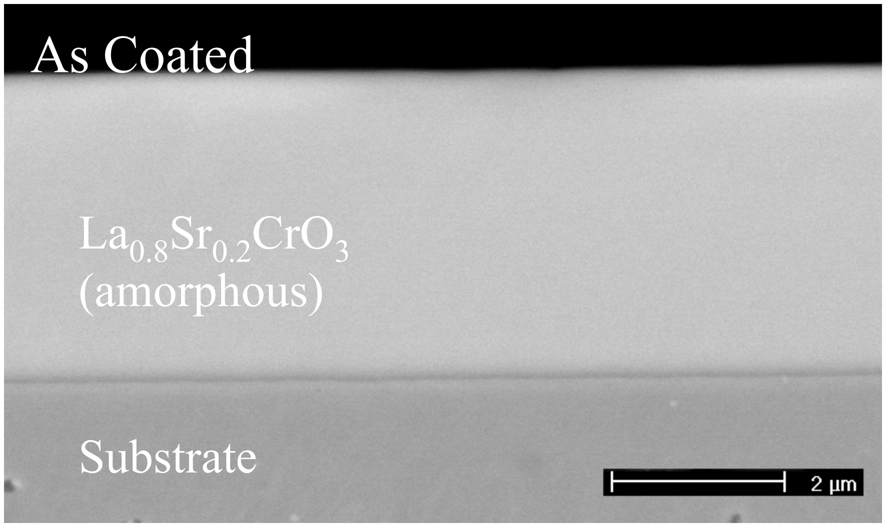


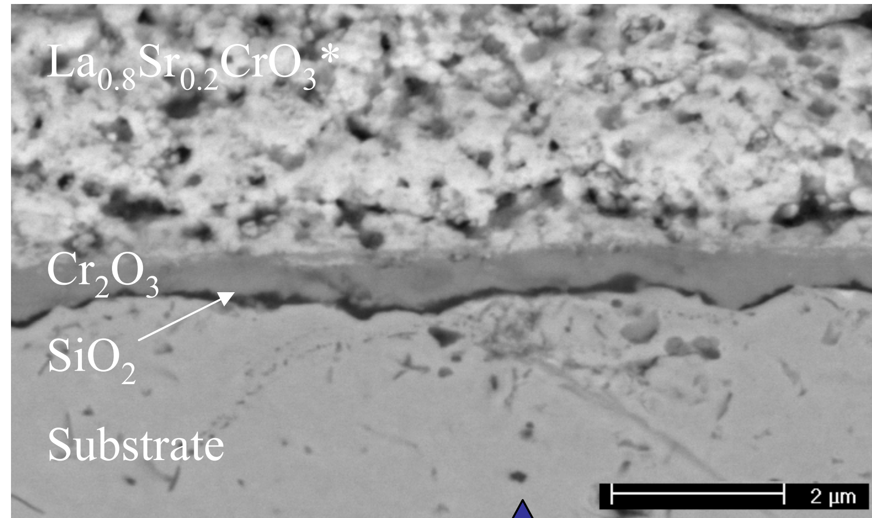


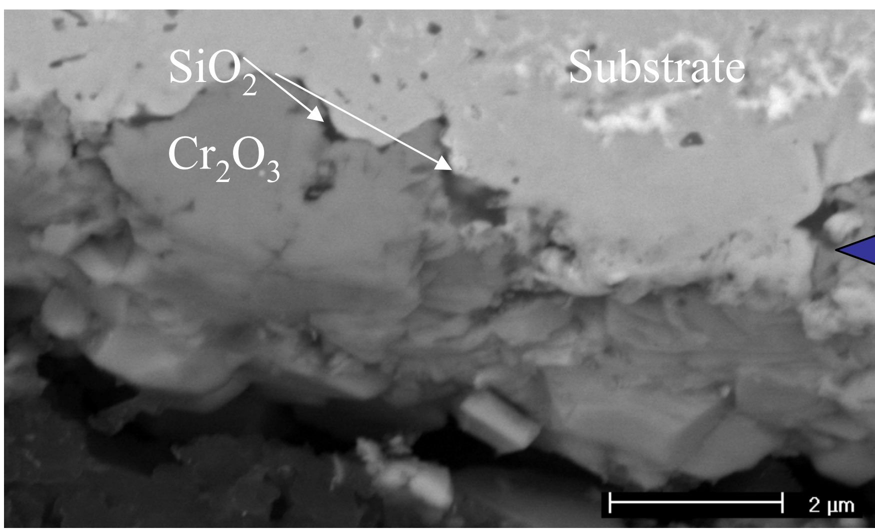
~74.9% Fe
~20% Cr
~2.2% La
~2% Mn
~0.9% Sr

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

$La_{0.8}Sr_{0.2}CrO_3$ Coated E-Brite (~5µm thick)







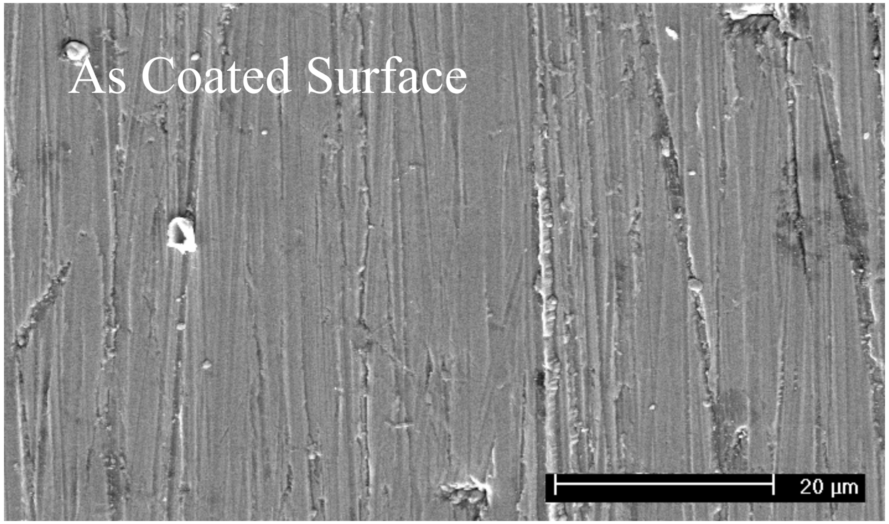
Coated side

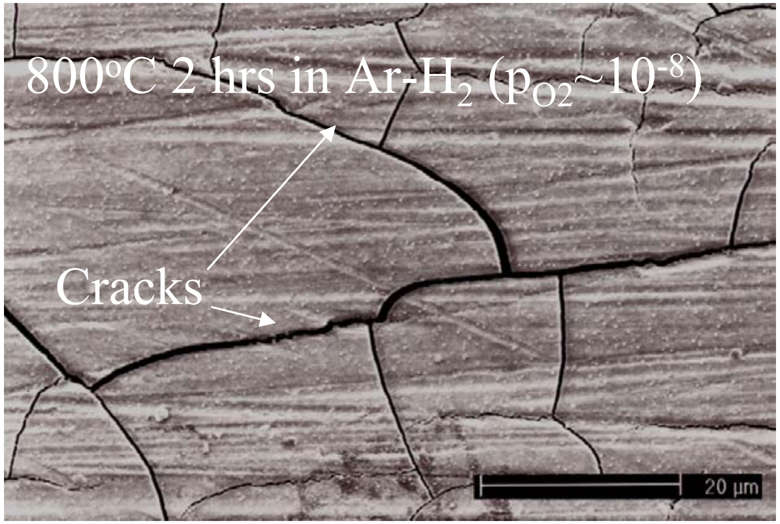
Uncoated side

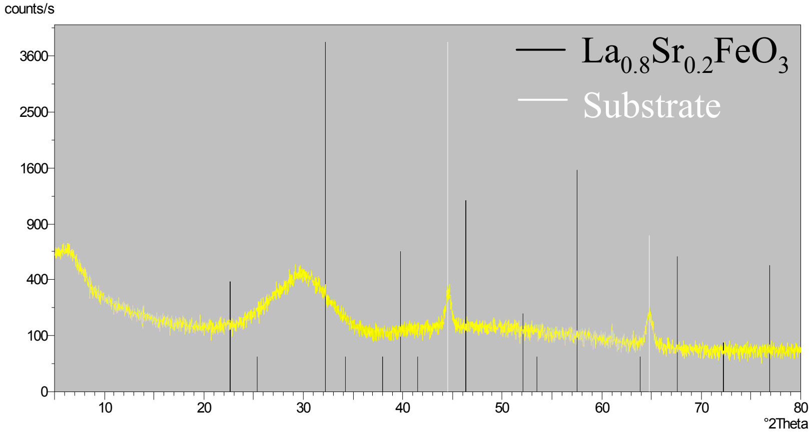
100 hrs Isothermal, 900^{o}C in Dry Air

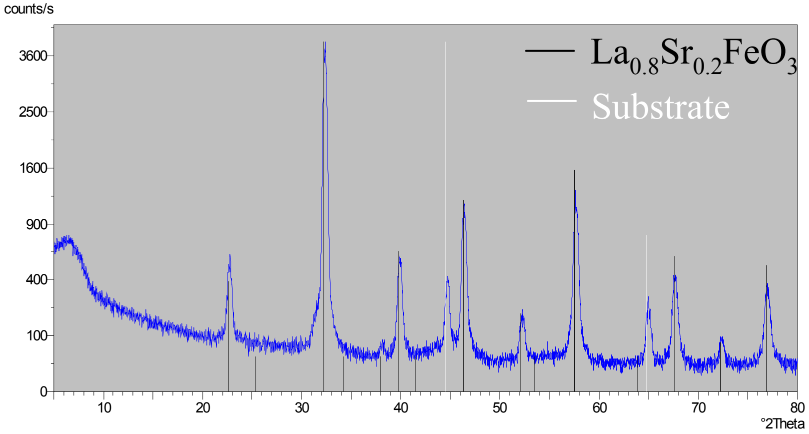
***Coating is porous due to a phase transformation during devitrification**

$La_{0.8}Sr_{0.2}FeO_3$ Coated E-Brite (~5μm thick)

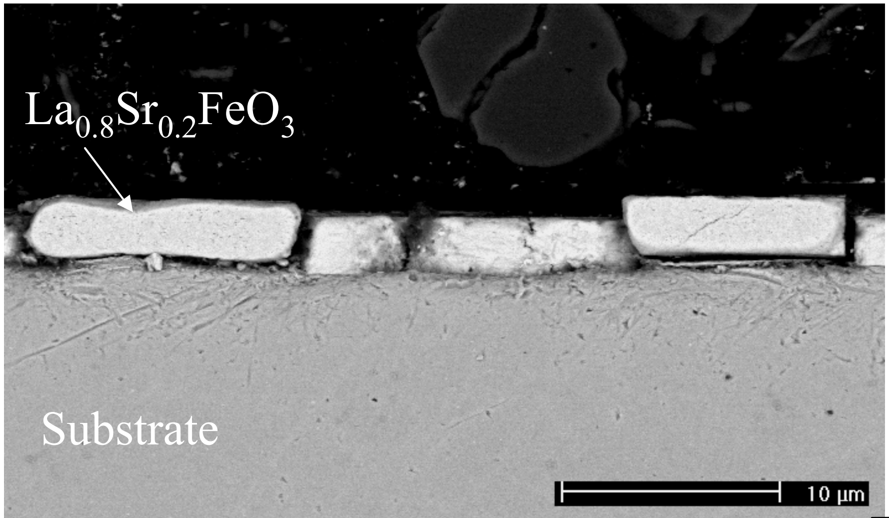


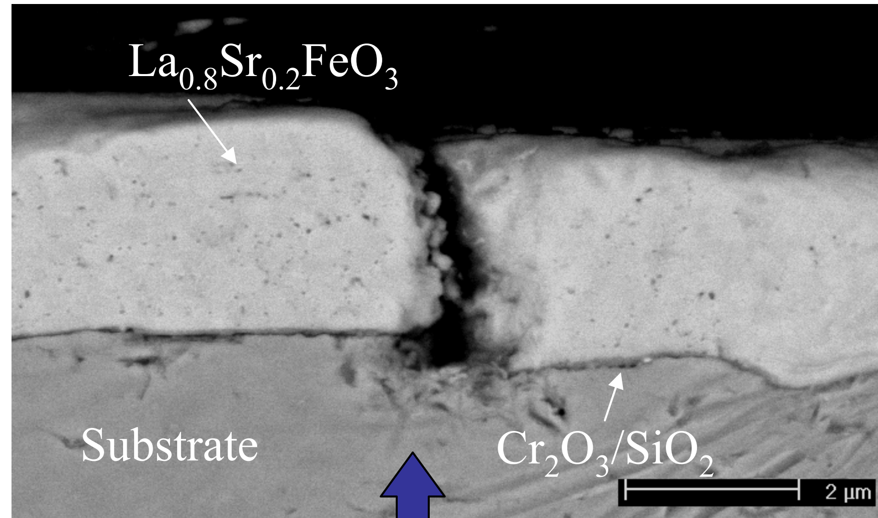


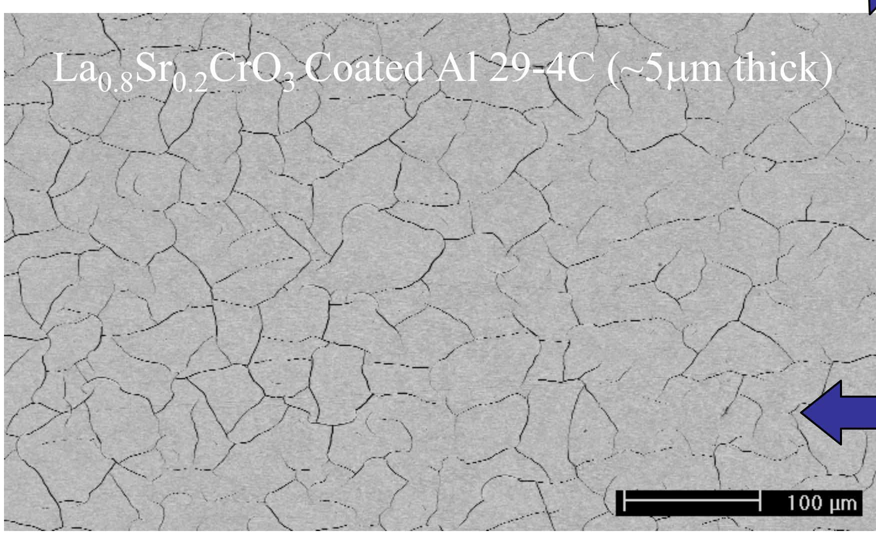




$La_{0.8}Sr_{0.2}FeO_3$ Coated E-Brite (~5μm thick)







Cross sections show the coating to be much more dense, but also confirms the cracks seen from the surface

Chromite coating cracked as well after same exposure conditions

Task I Summary

- Oxidation morphologies were similar at 700 and 900^{o}C.
- $MnCr_2O_4$ is more stable than other transition metal chromates.
- Measurable interaction between Crofer and cathode material.
- Sigma-phase was observed to form in the higher Cr content alloys at 700˚C.
- Chromia growth reduced under chromite coating.
- Chromite and ferrite coatings cracked during devitrification.

TASK I: FUTURE WORK
Work Planned for Next Twelve Months

- 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)
- Study the kinetics of sigma-phase formation.
- Investigate Effects of Simultaneous Exposure to Cathode and Anode Gases
- Continue Study of Effects of Coatings (Chromite) on Chromia Growth and Evaporation

TASK II SUMMARY

- Indentation Has Been Used to Induce Spallation in Vapor- and SAG-Exposed E-BRITE and in Coated Specimens
- Initial Observations and Fracture Calculations are Consistent with Observations
- Ability to Predict Spallation Behavior at Early Times is Key as Testing Temperatures are Reduced

TASK II: FUTURE WORK

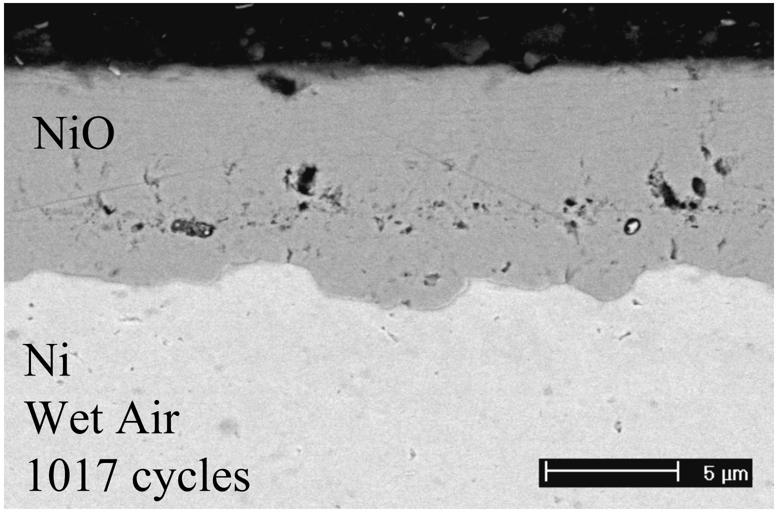
Work Planned for Next Twelve Months

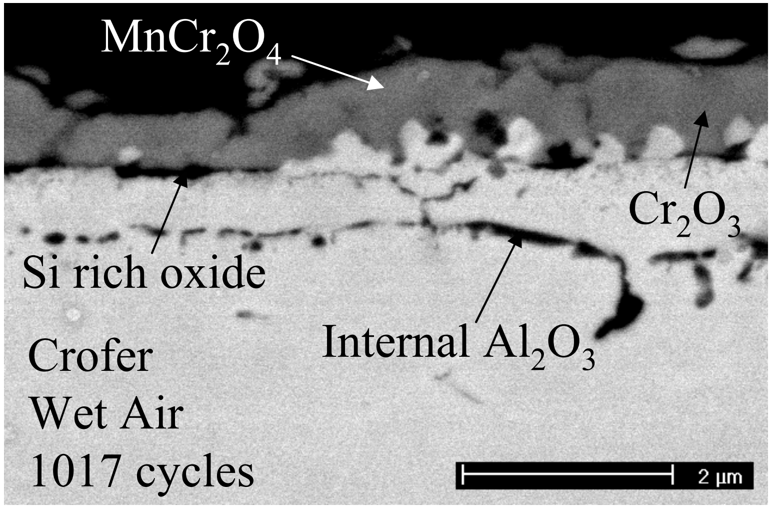
- Extend Modeling of Indentation of E-BRITE to Other Substrate Systems
- Incorporate Oxide Thickness and XRD Stress Measurements into Models: Identify Mechanisms Leading to Spallation
- Indentation Tests on E-BRITE for Longer Exposures at 900° C in Wet Air and Simulated Anode Gas
- Indentation Tests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

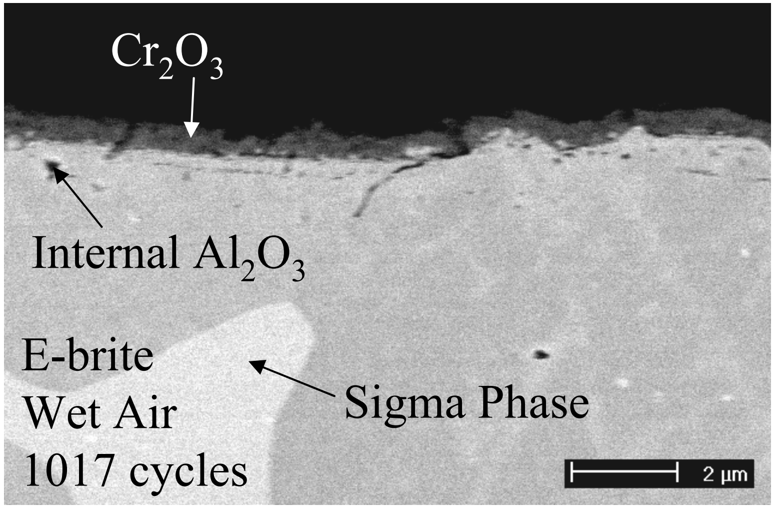
TASK III: RESULTS

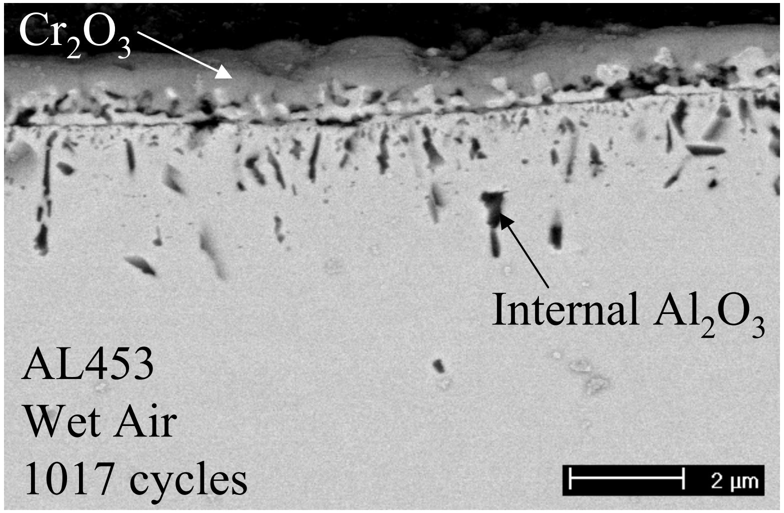
Comparison of oxide thickness for NiO and Cr_2O_3 -700˚C

Estimated ASR is approximately the same for Ni and Crofer after oxidation

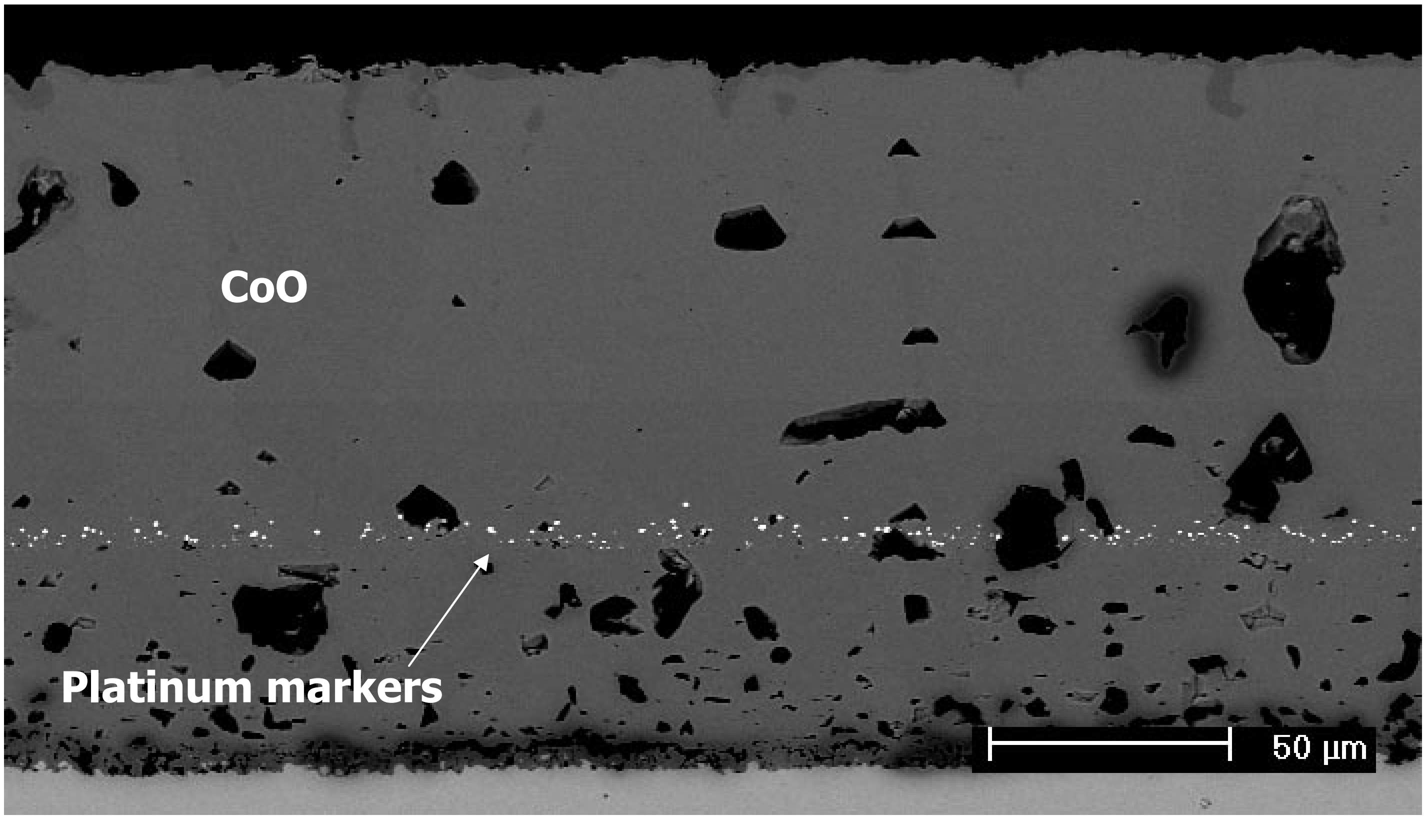






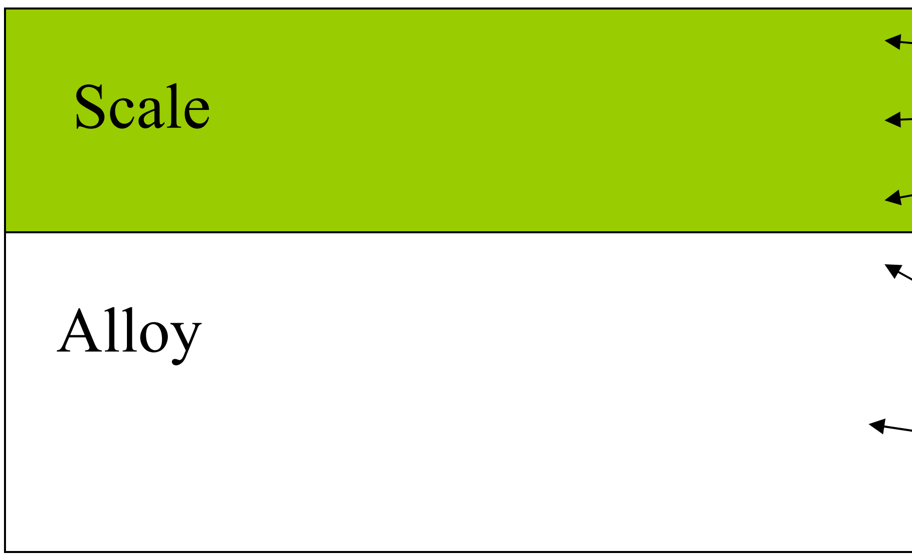


Task III: TYPICAL RESULTS
Co-8 wt% Cu - 900ºC Dry Air - 28 hours



Pt markers observed above scale/alloy interface

Copper Concentrations 125 hr exposure

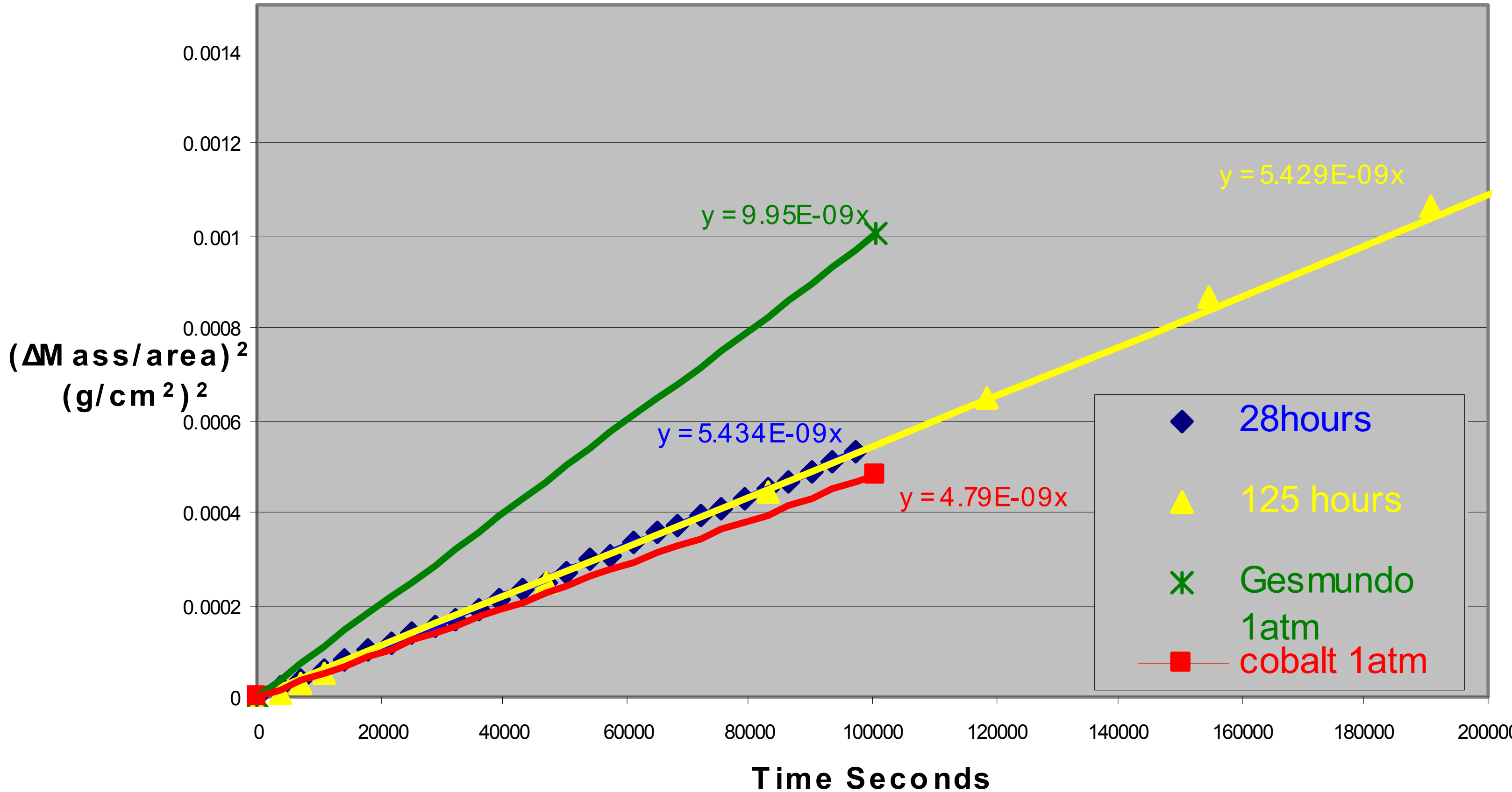


Copper to Cobalt ratio		Position
12.51	±1.06	5 µm from gas/scale interface
7.01	±0.95	midway through scale
2.55	±1.05	5 µm above scale/alloy interface

Copper Concentration		Position
6.38%	±0.83%	5 µm below scale/alloy interface
8.40%	±1.17%	midway through alloy

Note significant "uphill diffusion" of Cu in CoO.

Parabolic Rate Constants at 900ºC



Summary: **Cu was successfully doped into CoO but growth rate was not decreased.**

TASK III: PRELIMINARY RESULTS
Alternative Material Choices

- This Task involves a theoretical evaluation of alternate metallic materials which have properties superior to the ferritic alloys.
- CoO scales have been successfully doped with Cu from an alloy but growth rate was not decreased

TASK II: FUTURE WORK
Work Planned for Next Twelve Months

- Work on doping of CoO and NiO by alloying will continue focussing on growth rate and conductivity.
- The most promising materials will be fabricated and tested.

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.

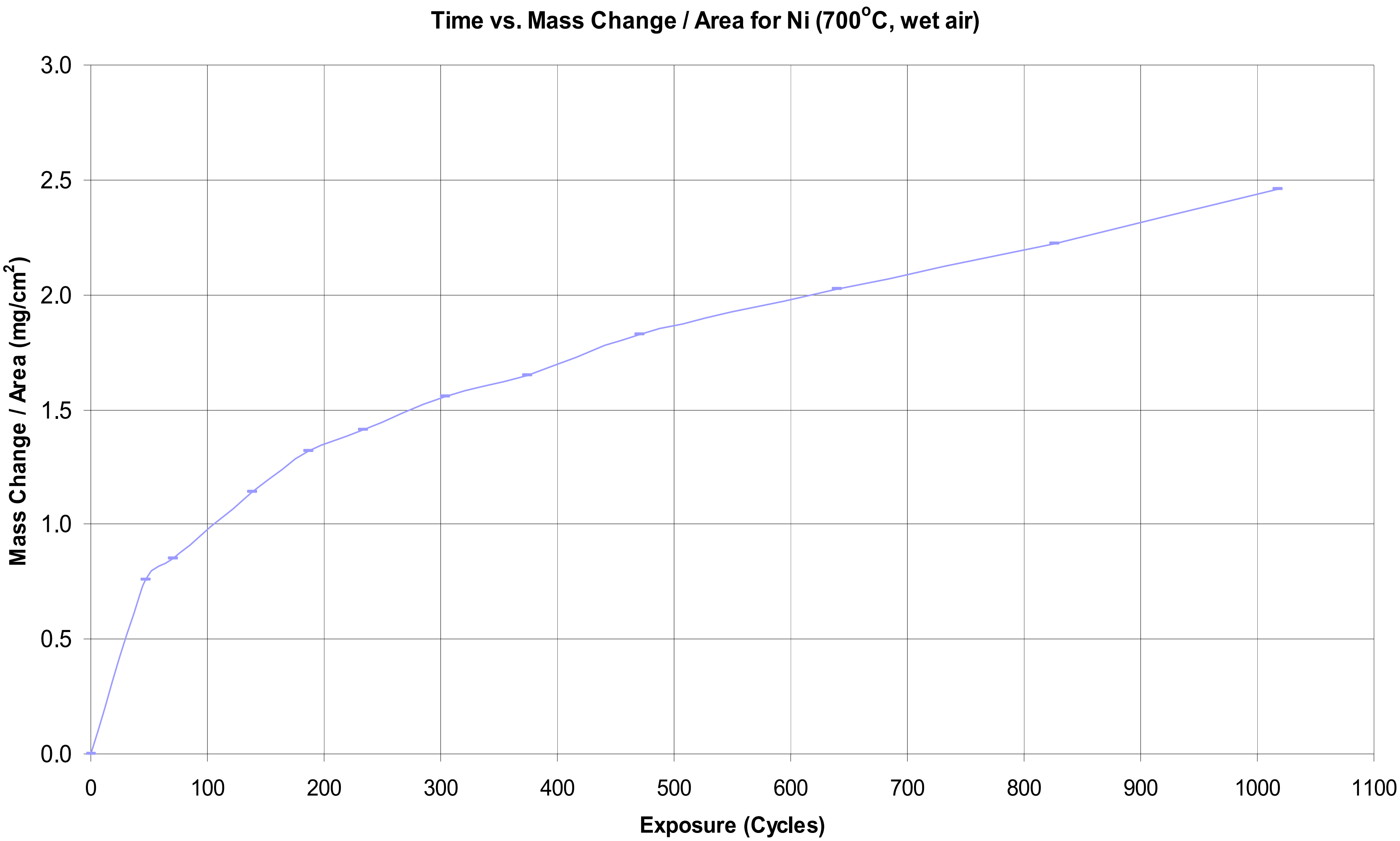
COLLABORATION

Collaboration, advice, and support from the following organizations is gratefully acknowledged:

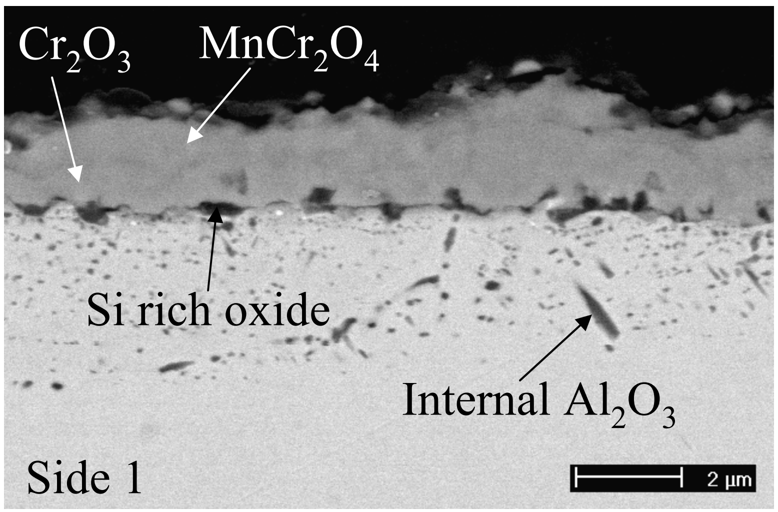
- PNNL (P. Singh, G. Yang)
- NETL Morgantown (C. Johnson, L. Wilson, G. Richards)

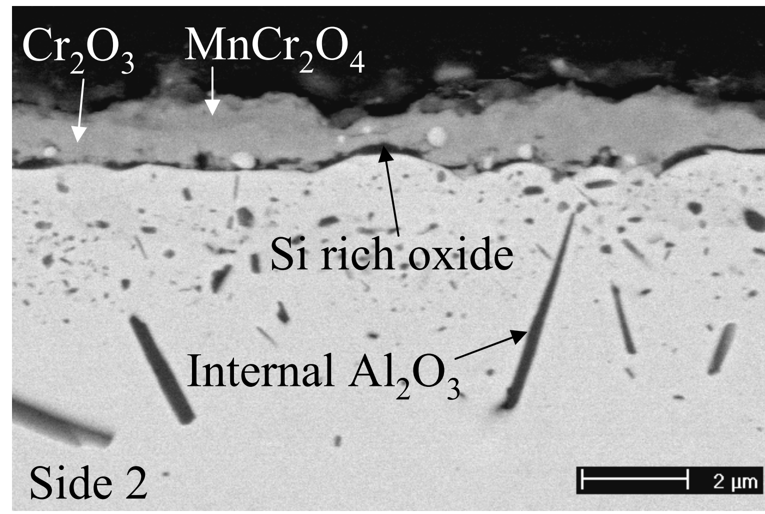
We would welcome the opportunity to collaborate with other branches of the National Laboratories and Industry.

TASK I: RESULTS
Wet Air (0.1 atm H_2O) Exposures (for Ni) - 700°C

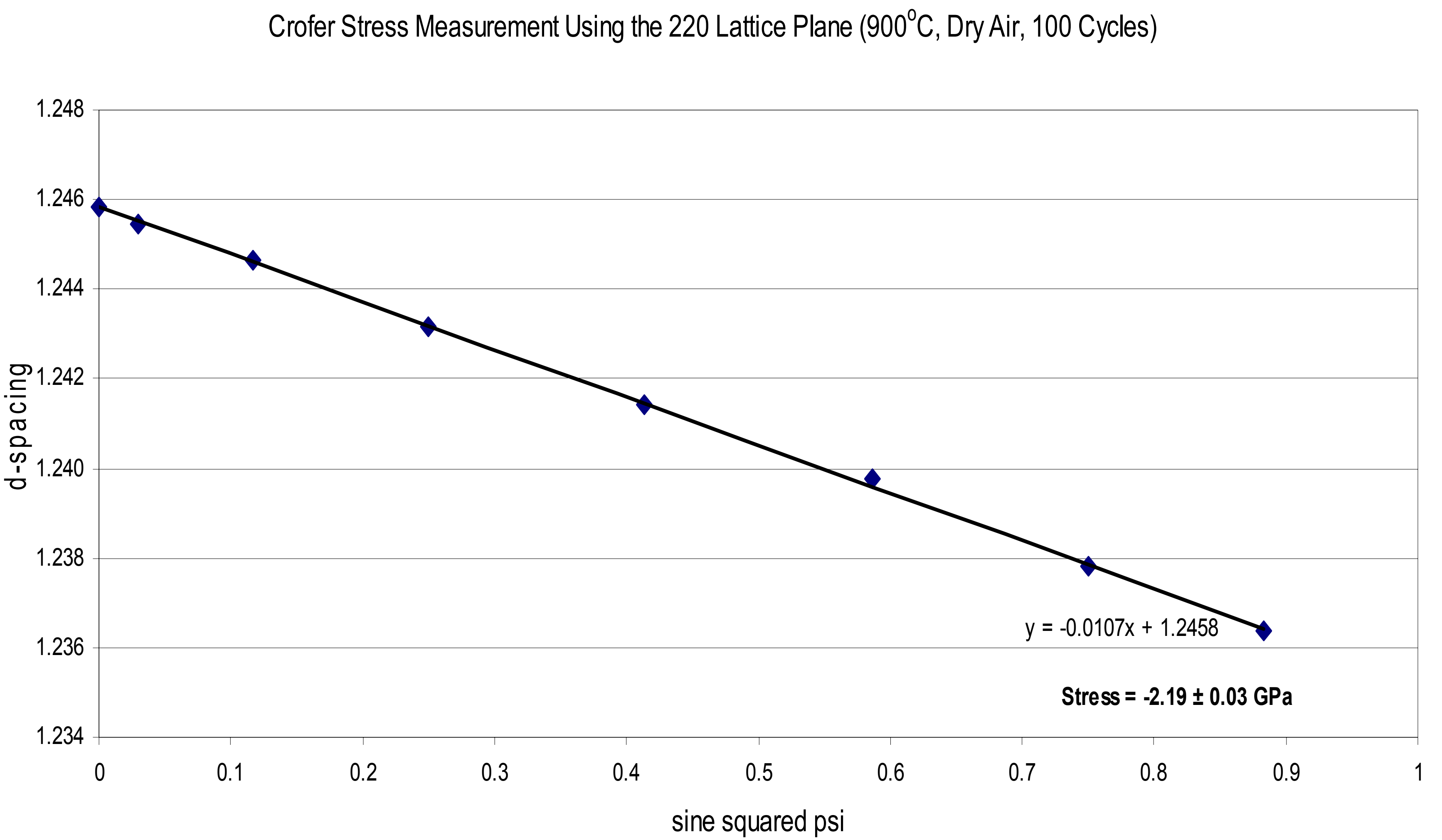


TASK I: RESULTS
Dual Atmosphere Conditions
800^{o}C, 3 cycles, 100 hours per cycle



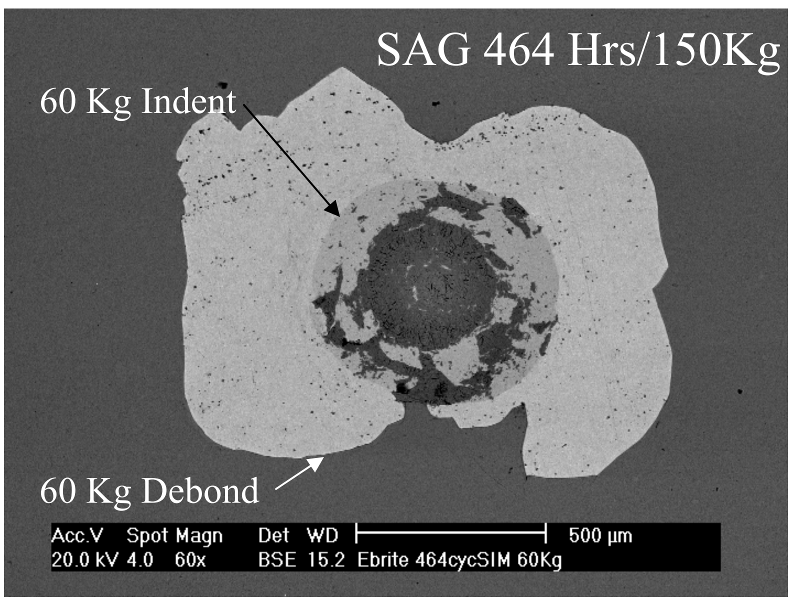


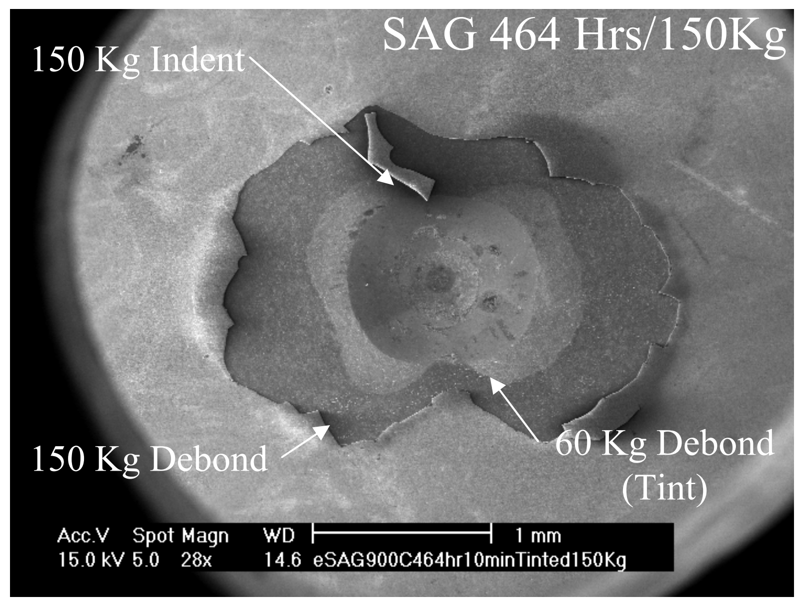
TYPICAL RESULTS
TASK II: THERMOMECHANICAL BEHAVIOR
Stress Measurements with 220 Lattice Plane – 900°C, Dry Air



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 $t_{oxide} = 2\mu m$ Yields: $G_c = 34\ J/m^2$