Enhanced High Temperature Corrosion Resistance in Advanced Fossil Energy Systems by Nano-Passive Layer Formation

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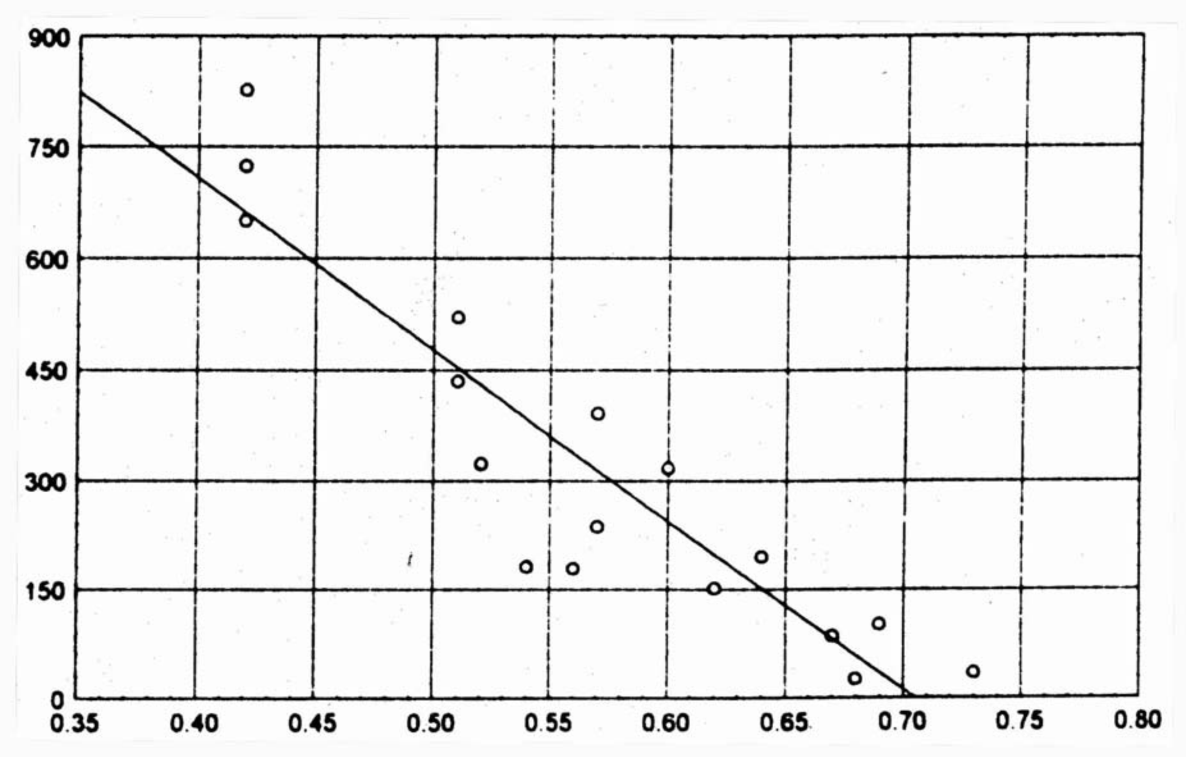
Fossil Energy Environments

- New Clean Air Acts require reduction of harmful NO_x compounds in exhaust gases
- Fuel rich gas is utilized to reduce emission of NO_x compounds
- Change in combustion parameters increases the amount of sulfur present in the exhaust gas



H_2S (ppm)

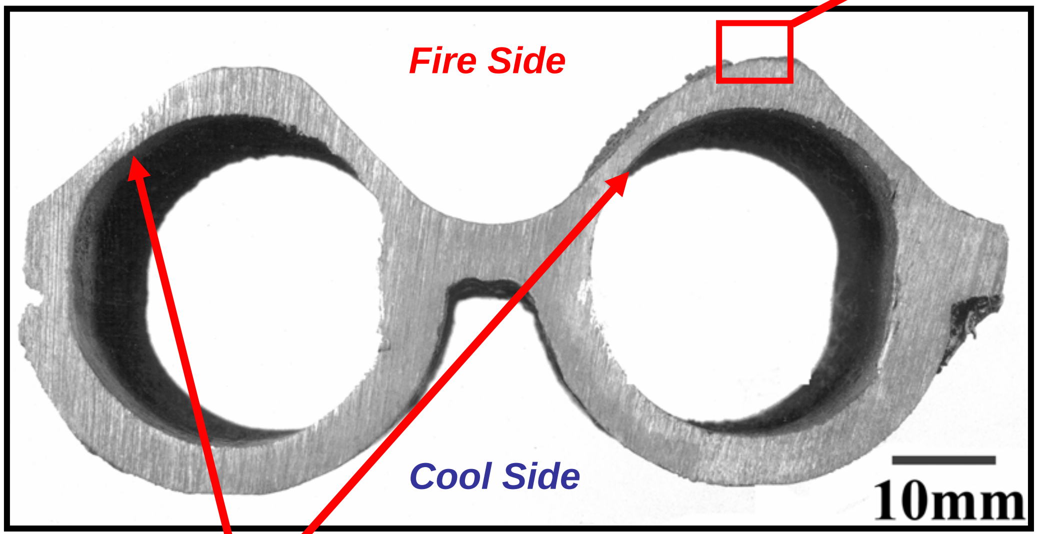
Economizer NO_x (lbs/MMBtu)

Staged Combustion Creates More Reducing Environment

Gabrielson and Kramer, *Joint Power Generation Conference (1996)*

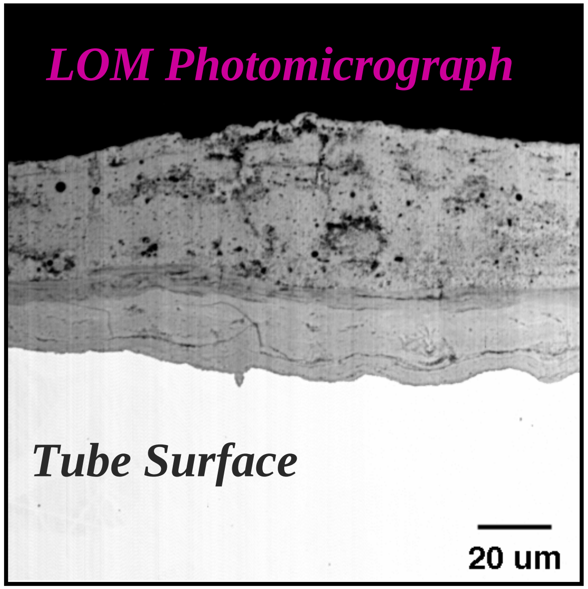
Typical Failure of Waterwall Tube After Six Months of Service

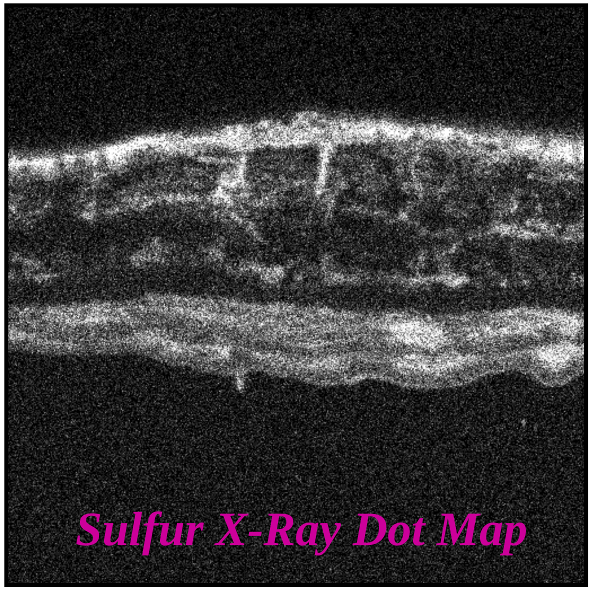
Tube acquired 23 years of service prior to installation of Low NO_x burners



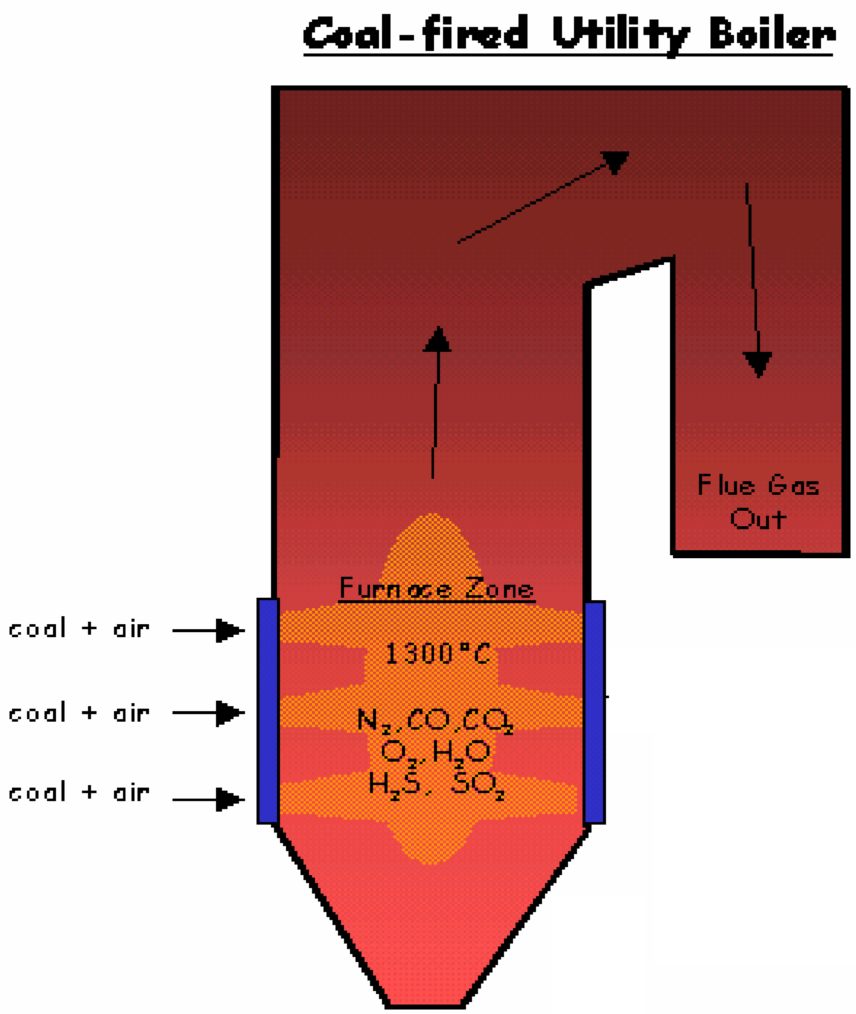
Excessive Wall Thinning

(Corrosion/Erosion Mechanism)



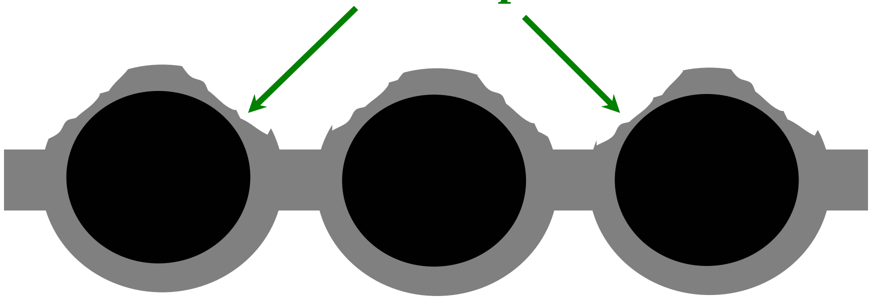


Weld Overlay Coatings for Waterwall Protection



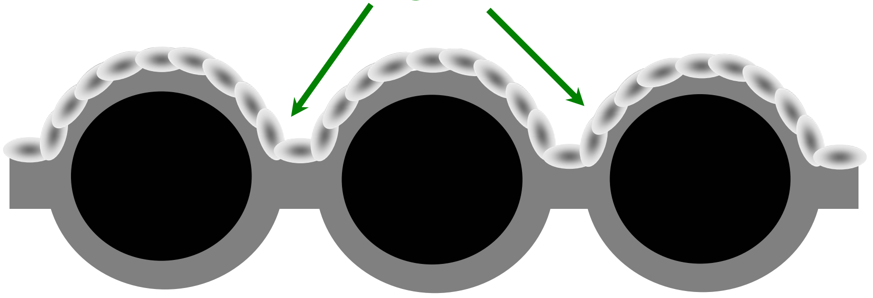
Exposed Uncoated Tubes

Excessive Wall Thinning Leads to Rupture



Weld Overlay Tubes

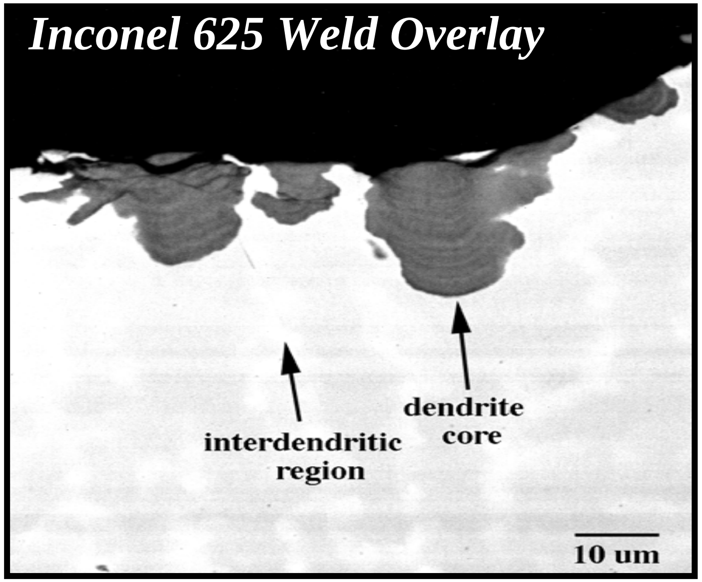
Corrosion Resistant Material Deposited onto Existing Boiler Tubes



Fe-Al Based Alloys as Weld Overlay Coatings

Problems with Austenitic Overlays:

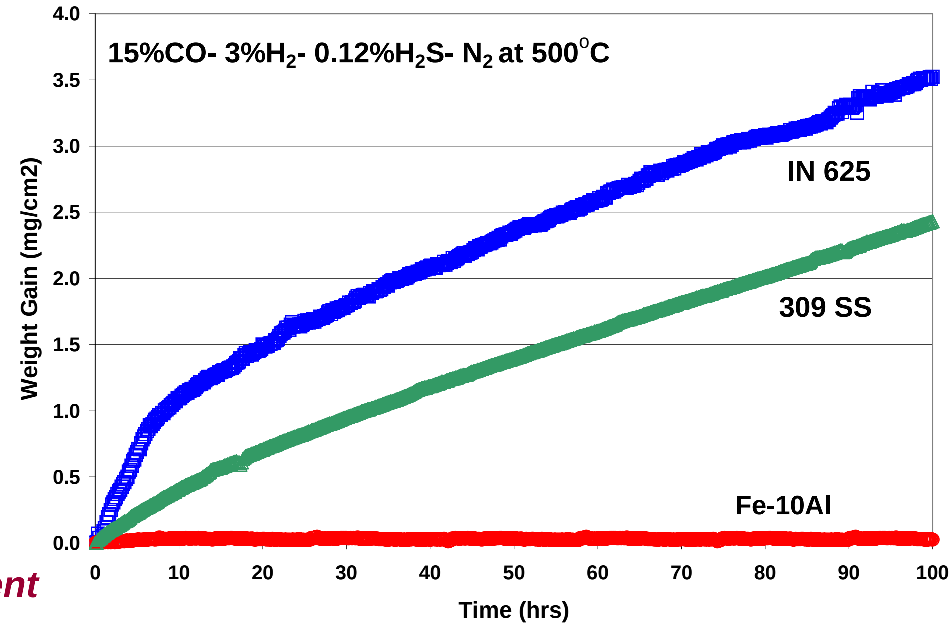
- Expensive: $15-$30/lb
- Exhibit microsegregation and preferential corrosion
- Susceptible to circumferential cracking



Preferential Attack due to Microsegregation

Advantage of Fe-Al Weld Overlays:

- Low cost: ~ $5/lb
- No microsegregation
- Excellent corrosion resistance in sulfur bearing environments

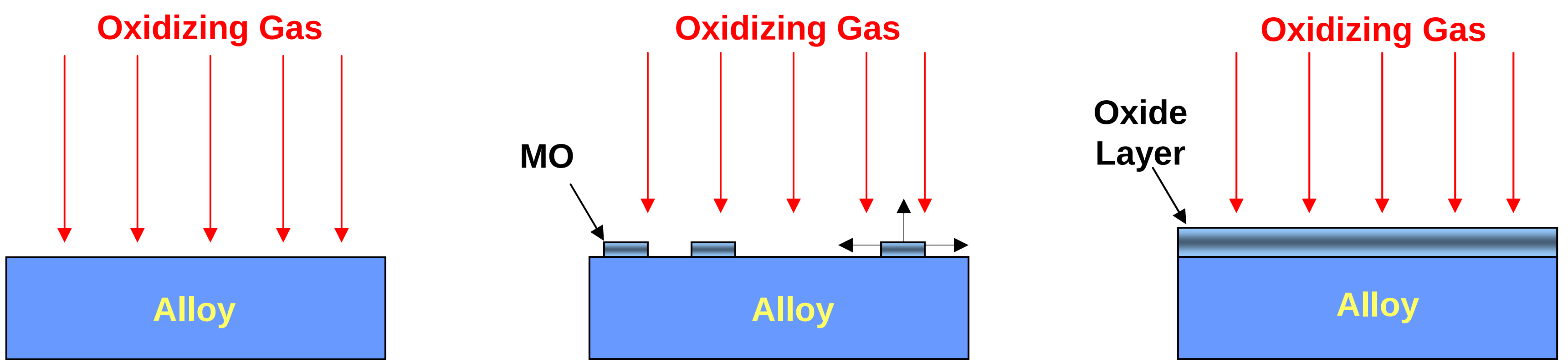


Sulfidizing Environment

Corrosion Resistance with Oxide Layers

Formation and Maintenance of Protective Oxide Layer Provides Weld Overlay Coatings with Corrosion Protection

$$M(s) + \frac{1}{2}O_2(g) \rightarrow MO(s)$$



1. Oxygen containing gas comes in contact with alloy and adsorbs to surface
2. Oxide particles (MO) nucleate and grow both vertically and laterally along surface
3. Protective oxide layer prevents metal and corrosive gas from direct contact

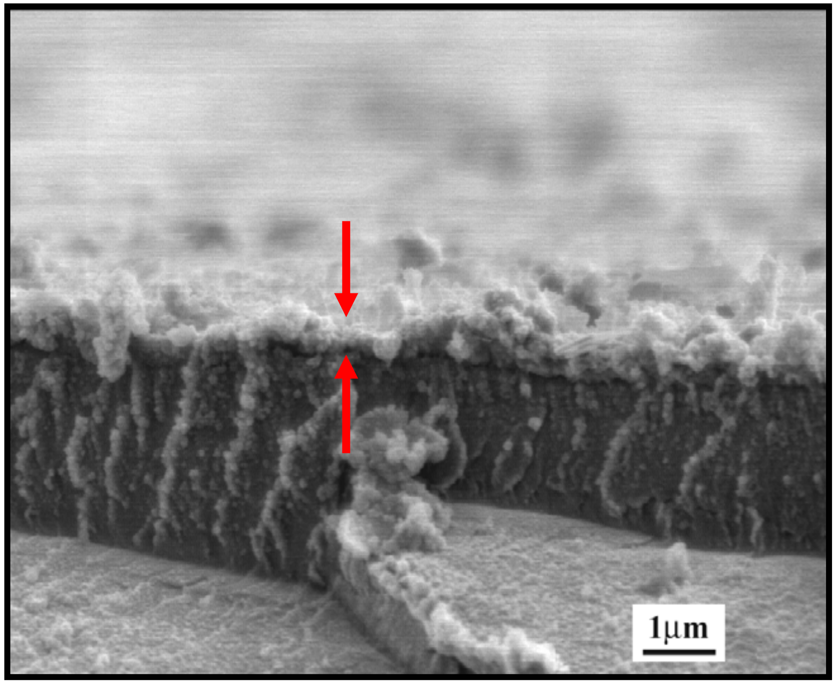
Doychak, *Intermet. Comp., Vol. 1 (1994)*

Scale Observed at Low pO_2

- Thin protective scale formed under wide range of pO_2
- Layer is sub-micron regardless of amount of O_2 and S_2
- Composition of layer not determined

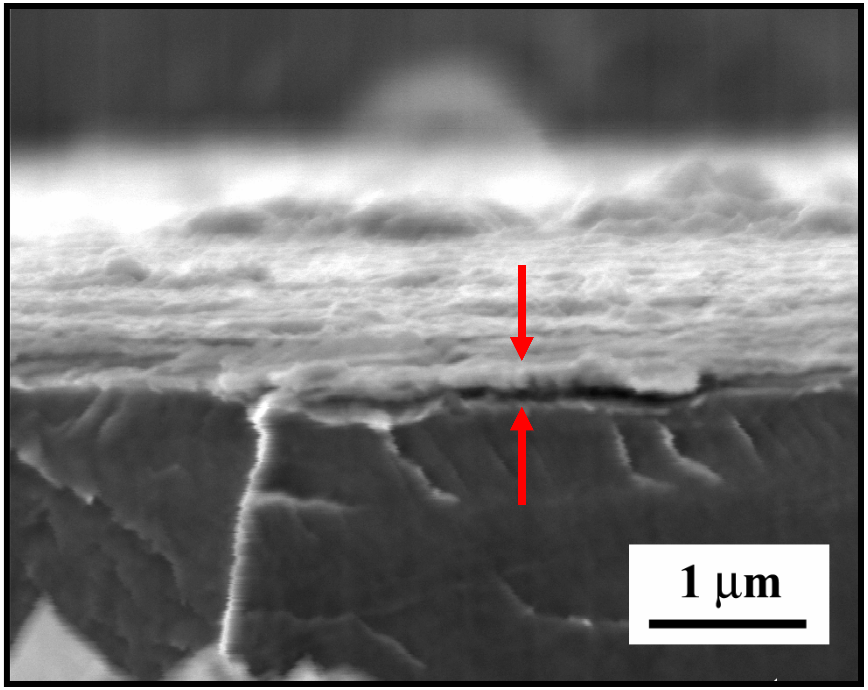
Sulfidizing Environment

$[pO_2 \cong 10^{-28}, pS_2 \cong 10^{-6}]$



Oxidizing Environment

$[pO_2 \cong 10^{-2}, pS_2 \cong 10^{-46}]$



Binary Fe-Al Critical Alloying Content

Purely Oxidizing Environments

Binary Fe-Al Alloys

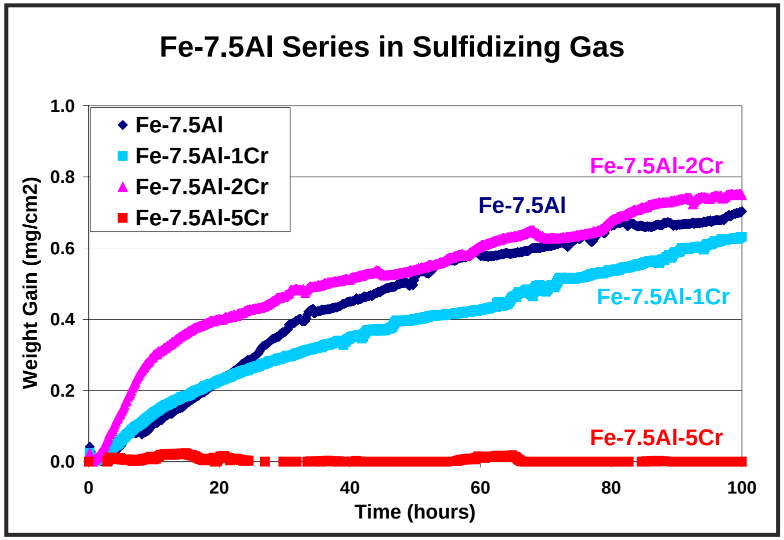
Source	Temperature (°C)	wt% Al	at% Al
Tomaszewski and Wallwork, *Rev. High-Temp. Mater, (1978)*	600	12.0	22
Boggs, *J. Electrochem. Soc, (1971)*	600	10.0	19
Wallwork and McGirr, *(1975)*	800	7.8	15
Tomaszewski and Wallwork, *Oxid. Met. (1983)*	800	7.5	14
Saegusa, *Corrosion (1966)*	1000	5.0	10

Critical Al concentrations of 10-12 wt% reported at temperatures near reported boiler tube temperatures

Corrosion Resistance of Fe-Al-Cr Alloys

<u>Sulfidizing Environment</u>

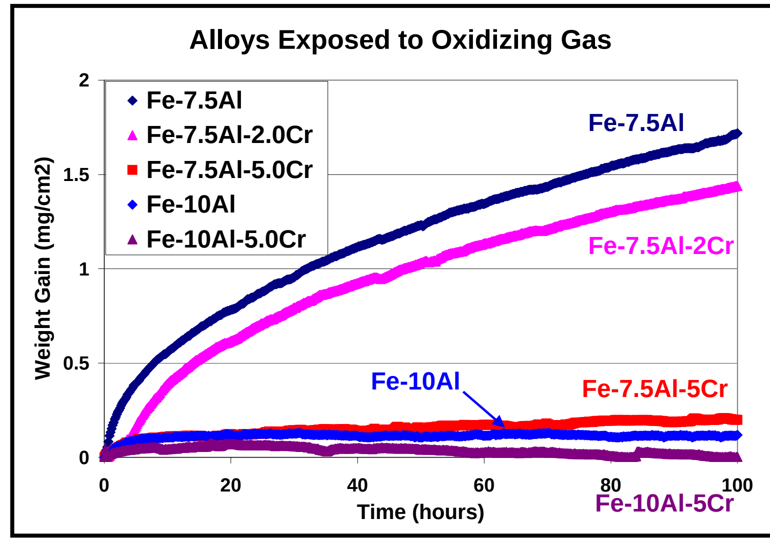
15%CO-3%H_2-0.12%H_2S-N_2



Alloys containing 10wt%Al and 0-5wt%Cr were protective

<u>Oxidizing Environment</u>

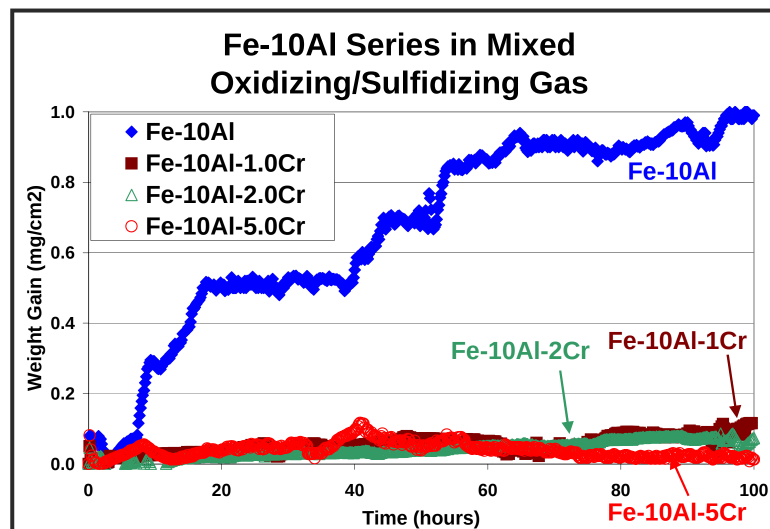
2%O_2-15%CO_2-6%H_2O-0.12%SO_2-N_2



<u>Mixed Environment</u>

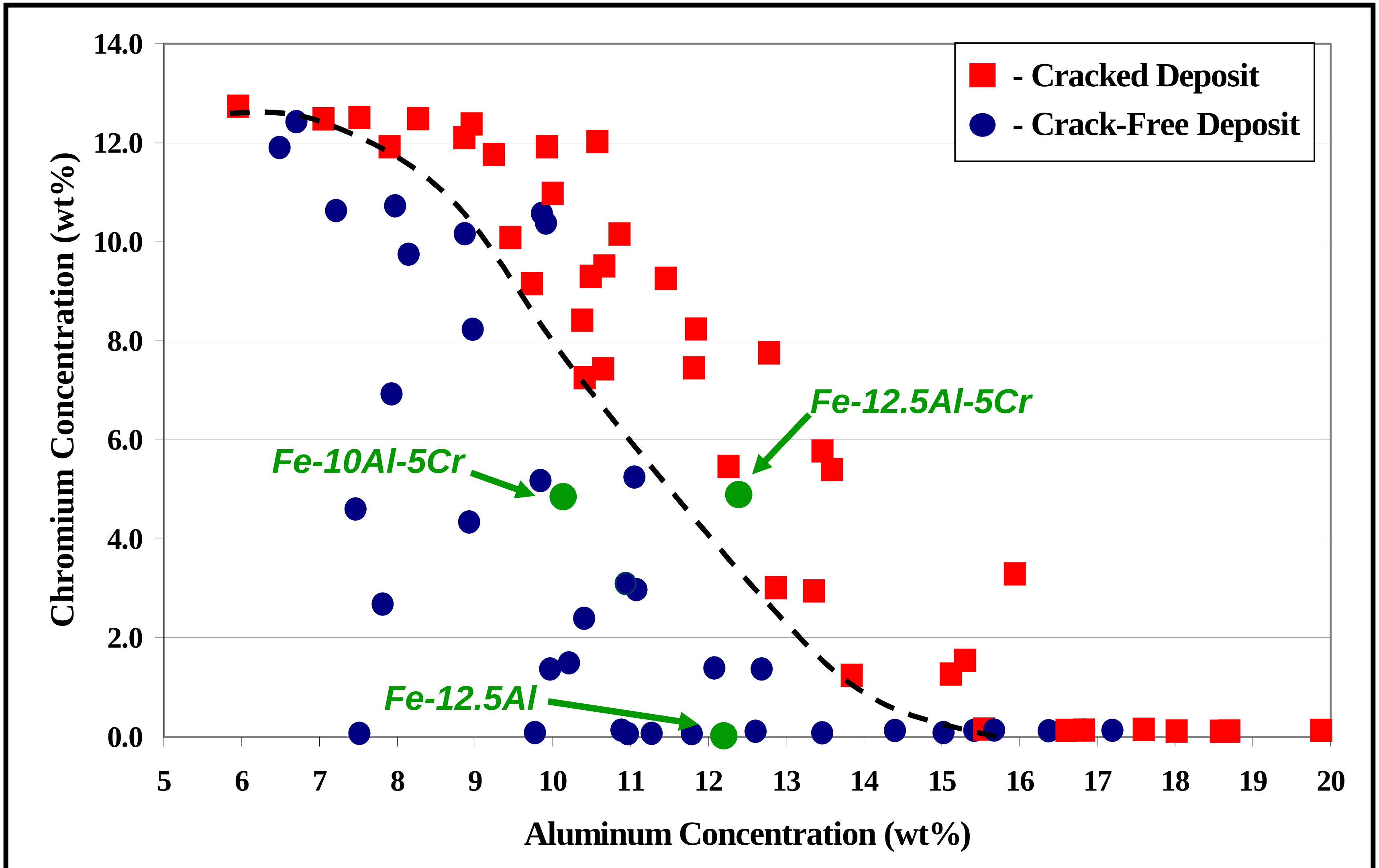
10%CO-5%CO_2-2%H_2O-0.12%H_2S-N_2

Alloys containing 7.5wt%Al and 0-5wt%Cr were <u>not</u> protective



Overlay Alloys Must Be Weldable

- TIG study determined weldability of Fe-Al-Cr alloys



Research Objective

Develop an understanding of passive layer formation and breakdown at intermediate temperatures on FeAlCr alloys in a simulated fossil fuel environment.

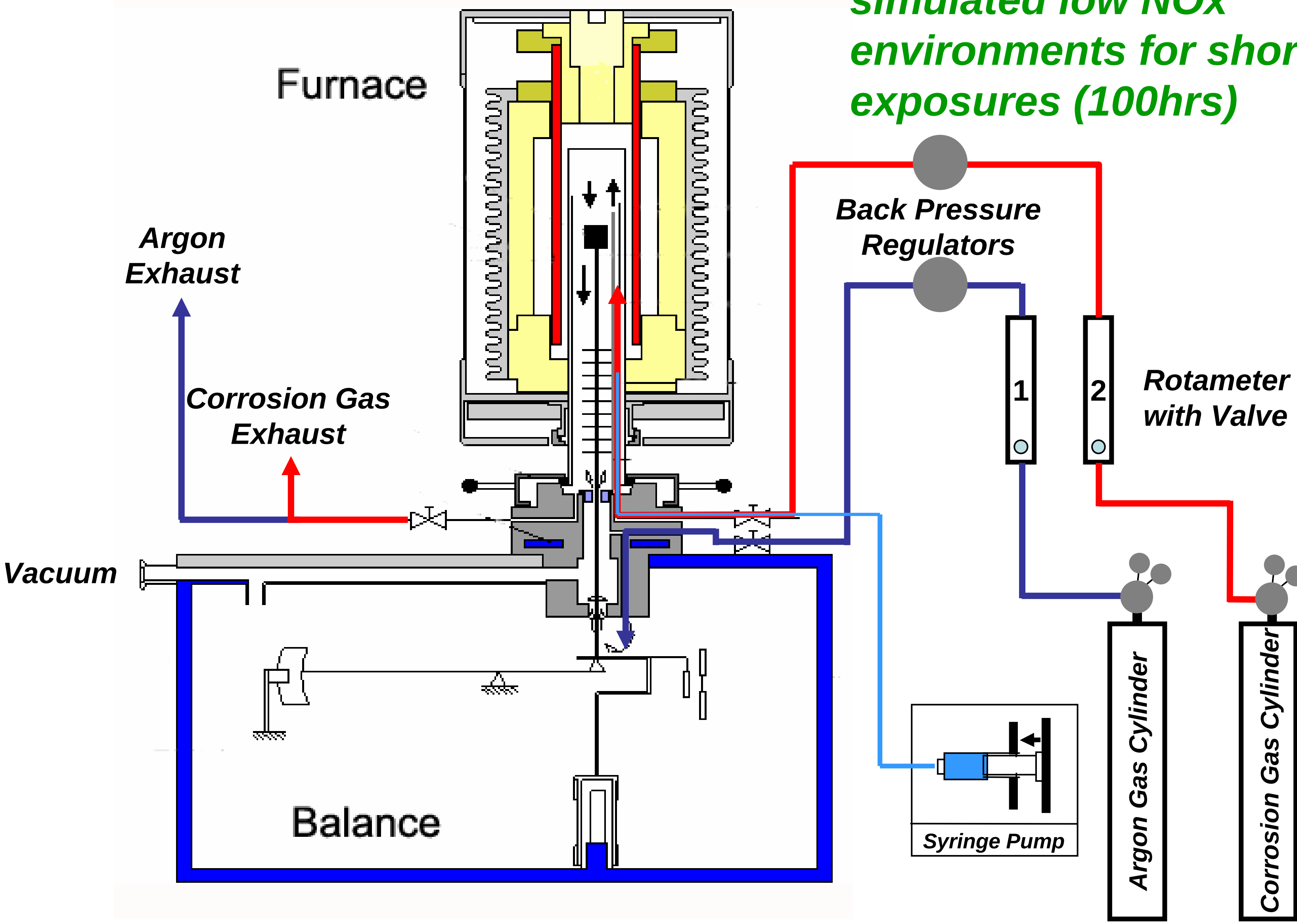
Research Approach

1. ***Study the corrosion response of model coatings in low NO_x gases.***
2. ***Characterize the microstructure, nano-chemistry and growth rate of passive layer***
3. ***Develop lifetime prediction model for coatings based on above data***

Thermogravimetric Analyzer

- Netzsch 409 STA

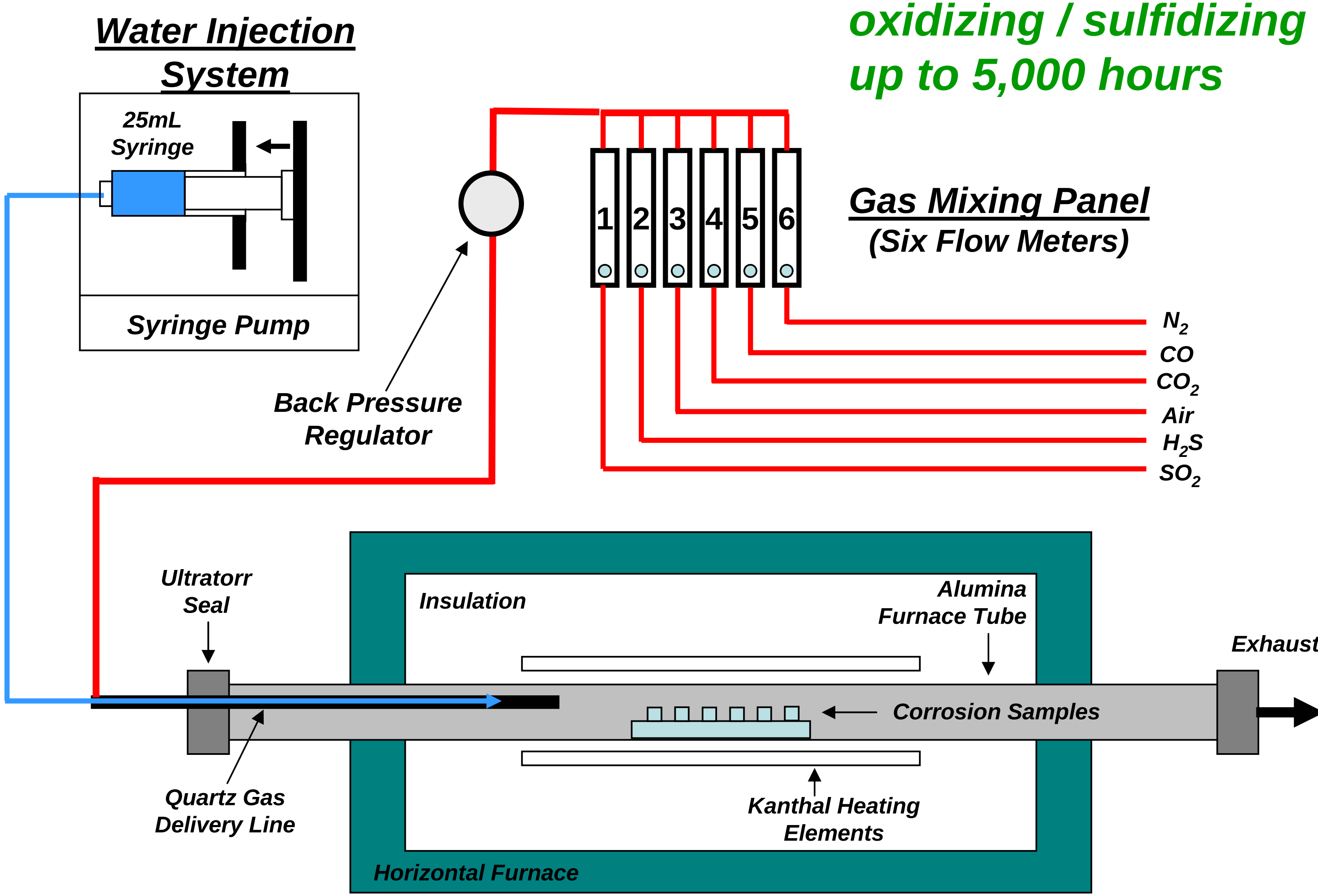
→ Generation of kinetic data in simulated low NOx environments for short term exposures (100hrs)



Long Term Corrosion Tests

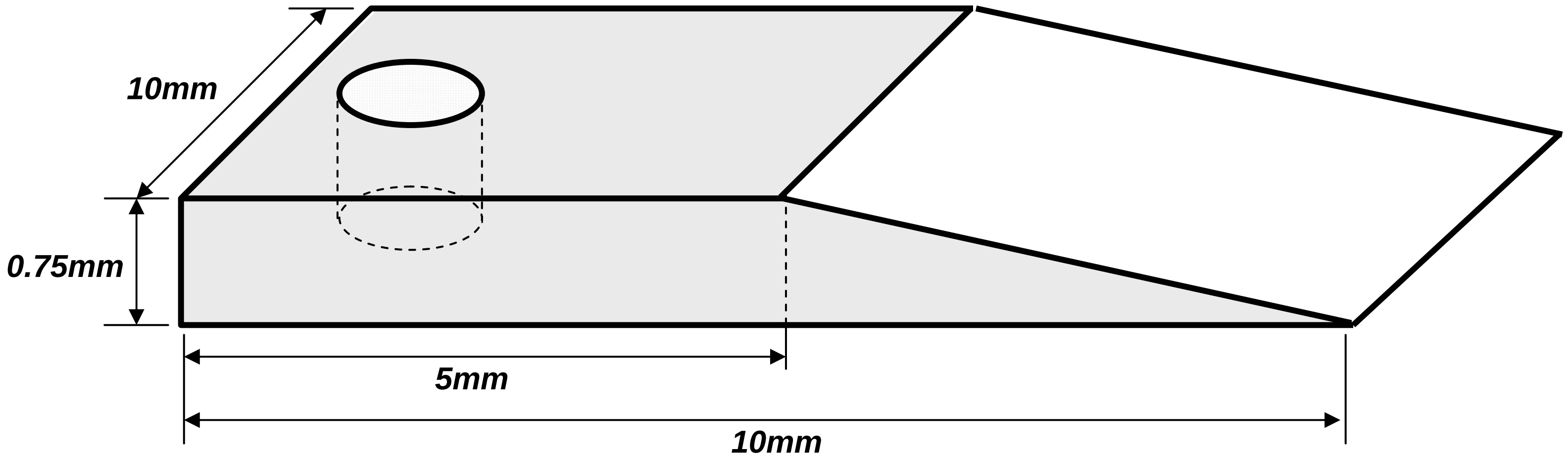
- Horizontal tube furnaces modified to create simulated low NO_x environments

→ Exposures at 500°C in mixed oxidizing / sulfidizing gas for up to 5,000 hours



Long Term Corrosion Test Coupons

- *Traditional coupon shape is square, approximately 1cm x 1cm x 1mm*
- *Thin foil samples are useful for alloy depletion studies*
  - *Difficult to prepare*
  - *Complete destruction of coupon can occur if too thin or test duration is too long*
  - *Corrosion behavior of thin foils may not be representative of bulk corrosion behavior*
- *New wedge-shaped test coupon allows for testing in bulk condition and in thin region to examine alloy depletion*

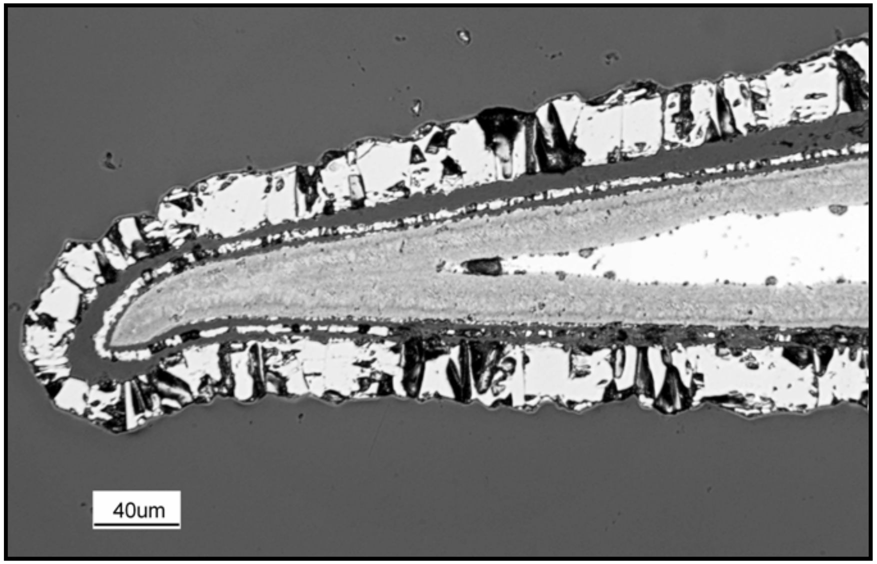


Validity Check of Wedge Shaped Sample

- *Three coupons of same alloy composition (Fe-7.5Al-5Cr) exposed in mixed oxidizing / sulfidizing gas at 500°C, 100hrs*
  - *One square sample, two wedge samples*
- *Normalized weight gains between square and wedge coupons very similar (within 0.0085g/cm^2)*
- *Similar corrosion scale observed on both square and wedge samples*

Square Sample

Wedge Sample



Corrosion Exposure Tests

- **Short Term Exposures**
  - Thermogravimetric analyzers
  - Sulfidizing gas, Oxidizing gas, mixed oxidizing / sulfidizing gas
  - Temperatures of 500, 600, 700, 800°C
  - 100hrs

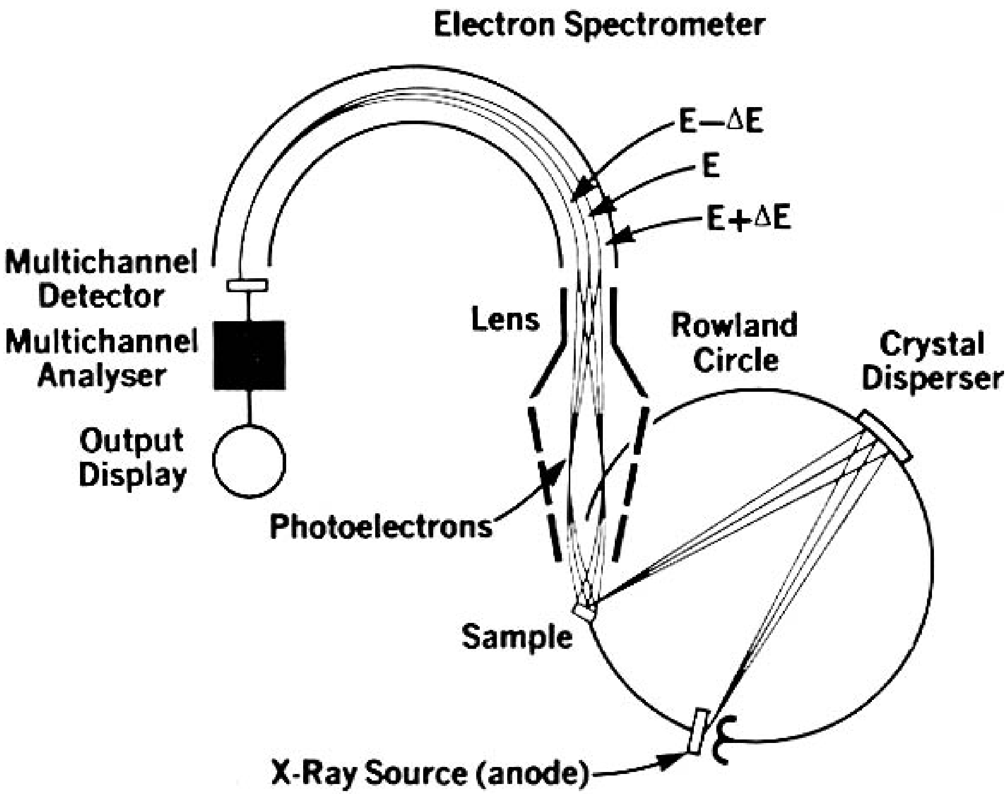
  → Kinetic data for range of environments, temperatures

- **Long Term Exposures**
  - Horizontal tube furnaces
  - Mixed oxidizing / sulfidizing gas
  - 500°C only
  - Durations of 100, 250, 500, 1000, 2000, 5000hrs

  → Long term depletion of alloy elements

X-ray Photoelectron Spectroscopy

- *Surface sensitive technique (x-rays in, electrons out)*
- *Scienta ESCA 300 with monochromatic Al Kα X-rays*
- *Heated stage capable of >600°C*



In-Situ Oxidation Experiments:

Sample inserted into analysis chamber, pumped to UHV

Ar-sputtered to clean metal surface (for some experiments)

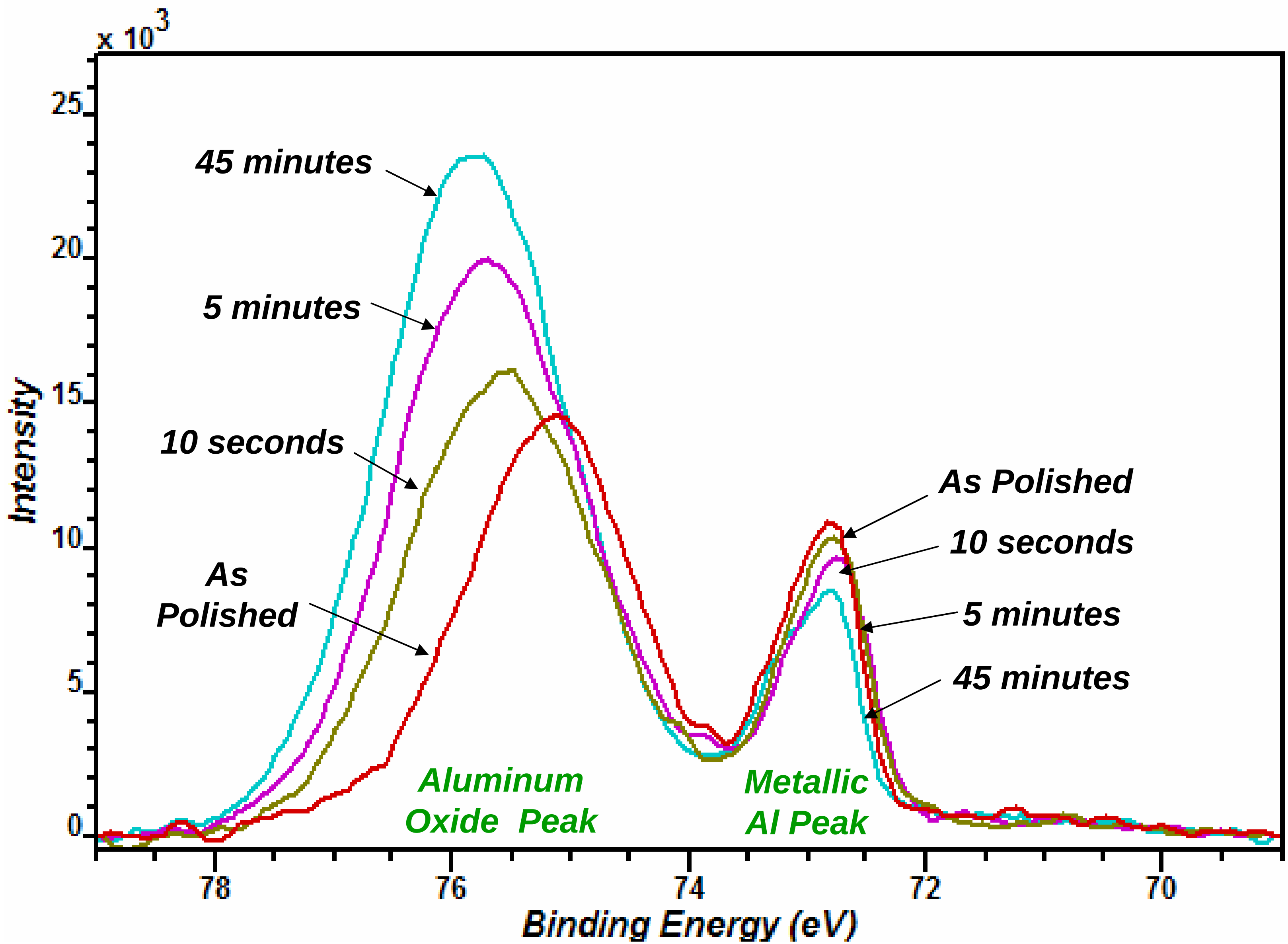
Heated to 500°C, oxygen permitted to the analysis chamber ($3x10^{-7}$ torr) for various times

Surface composition analyzed

Briggs, D. & Seah, M.P., *Practical Surface Analysis, (1983), p57*

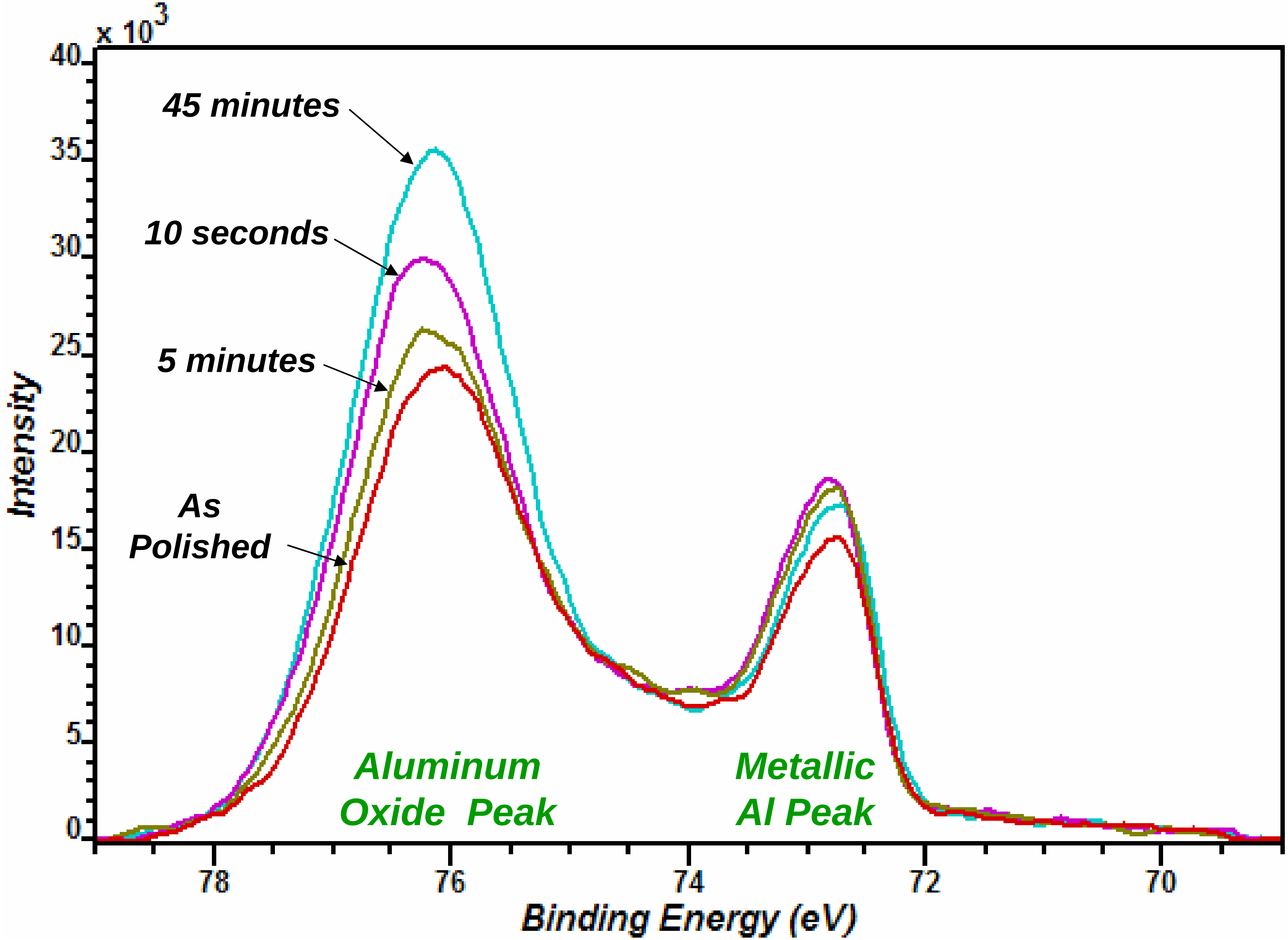
In-Situ Oxidation of As-Polished Fe-12.5Al

500°C, Pure Oxygen, Chamber Pressure of $3x10^{-7}$



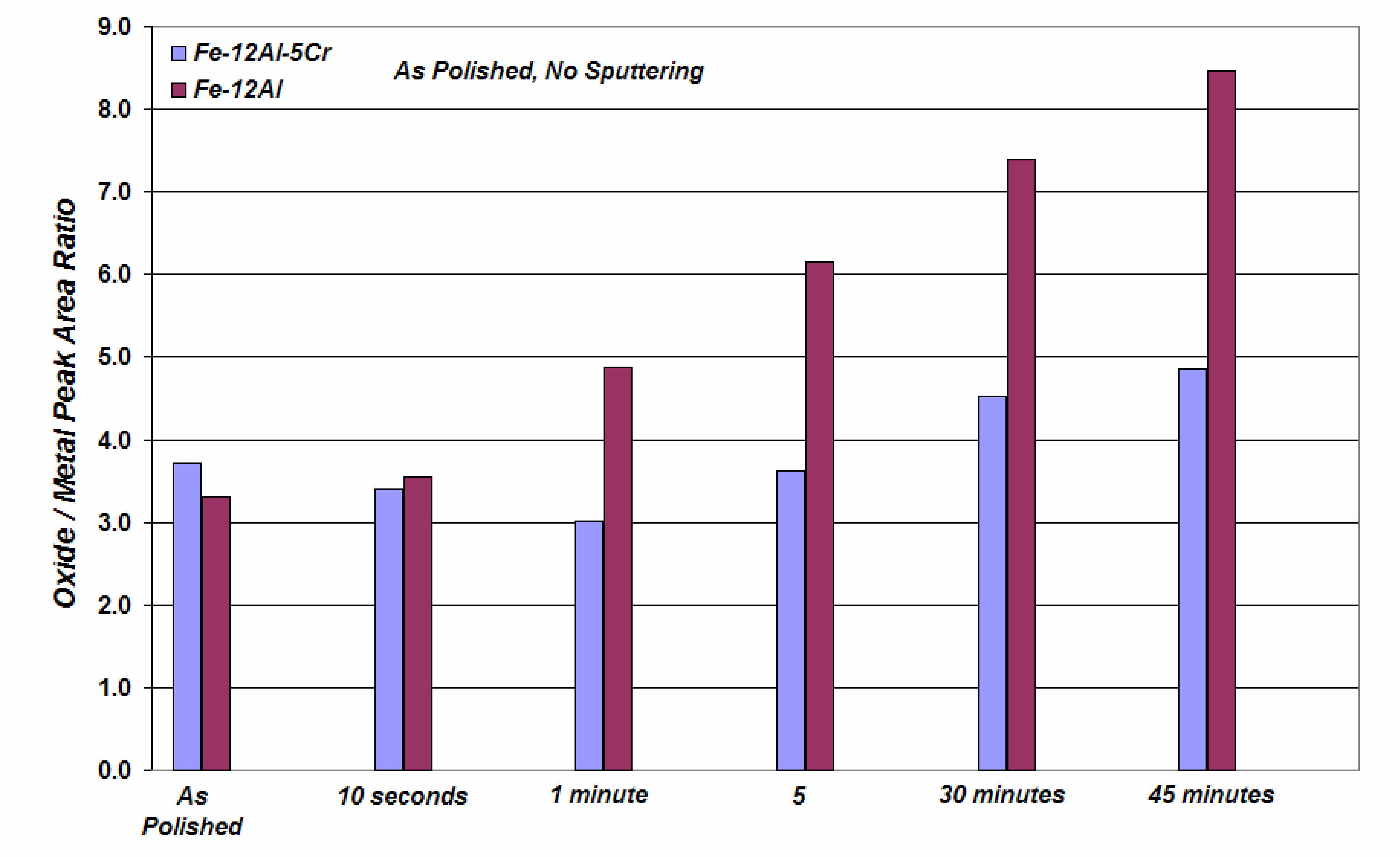
In-Situ Oxidation of As-Polished Fe-12.5Al-5Cr

500°C, Pure Oxygen, Chamber Pressure of $3x10^{-7}$



Oxide to Metal Peak Area Ratio – Polished

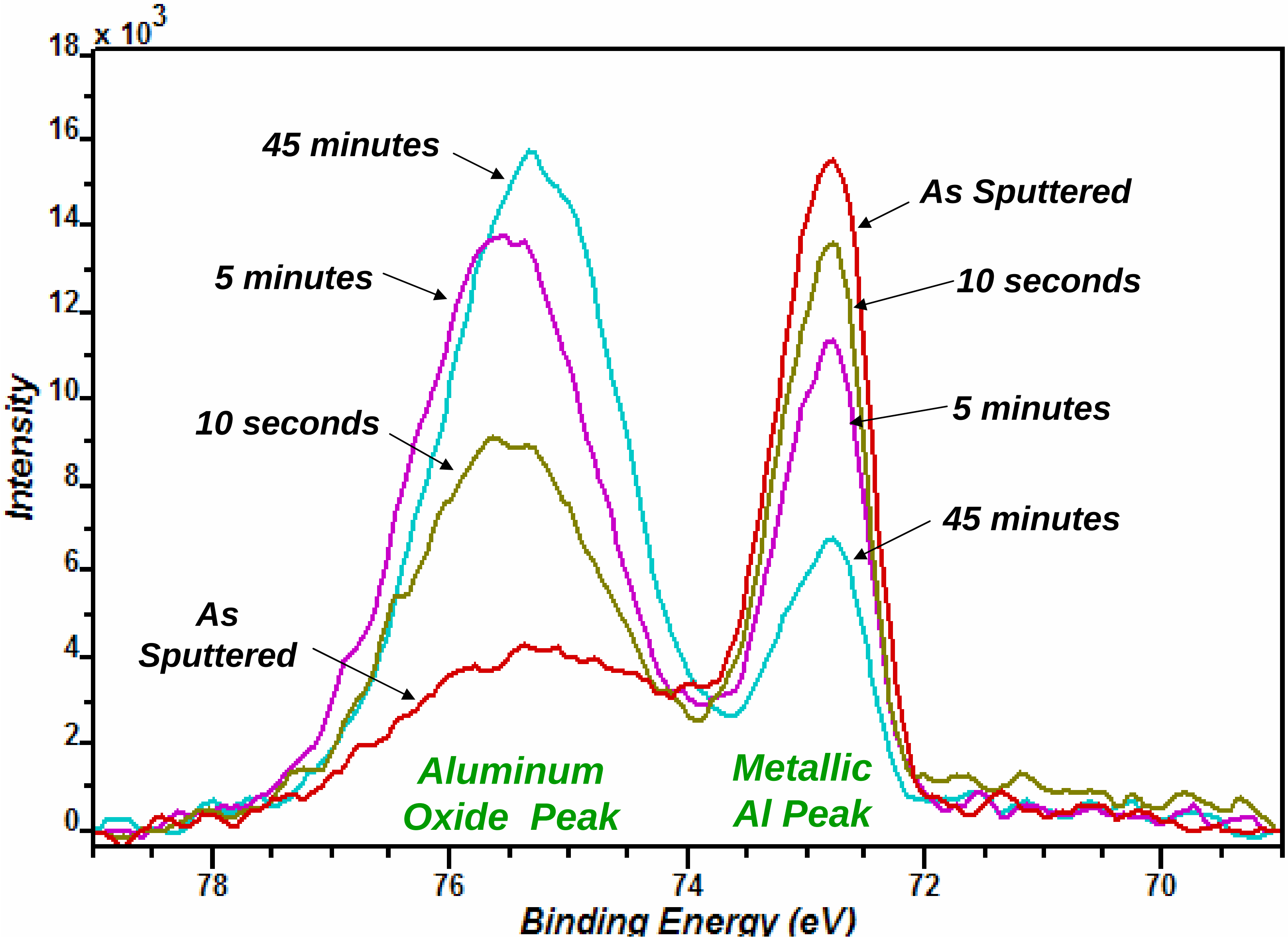
Samples in as polished condition (same prep as corrosion tests)



→ Chromium addition slows formation of aluminum oxides

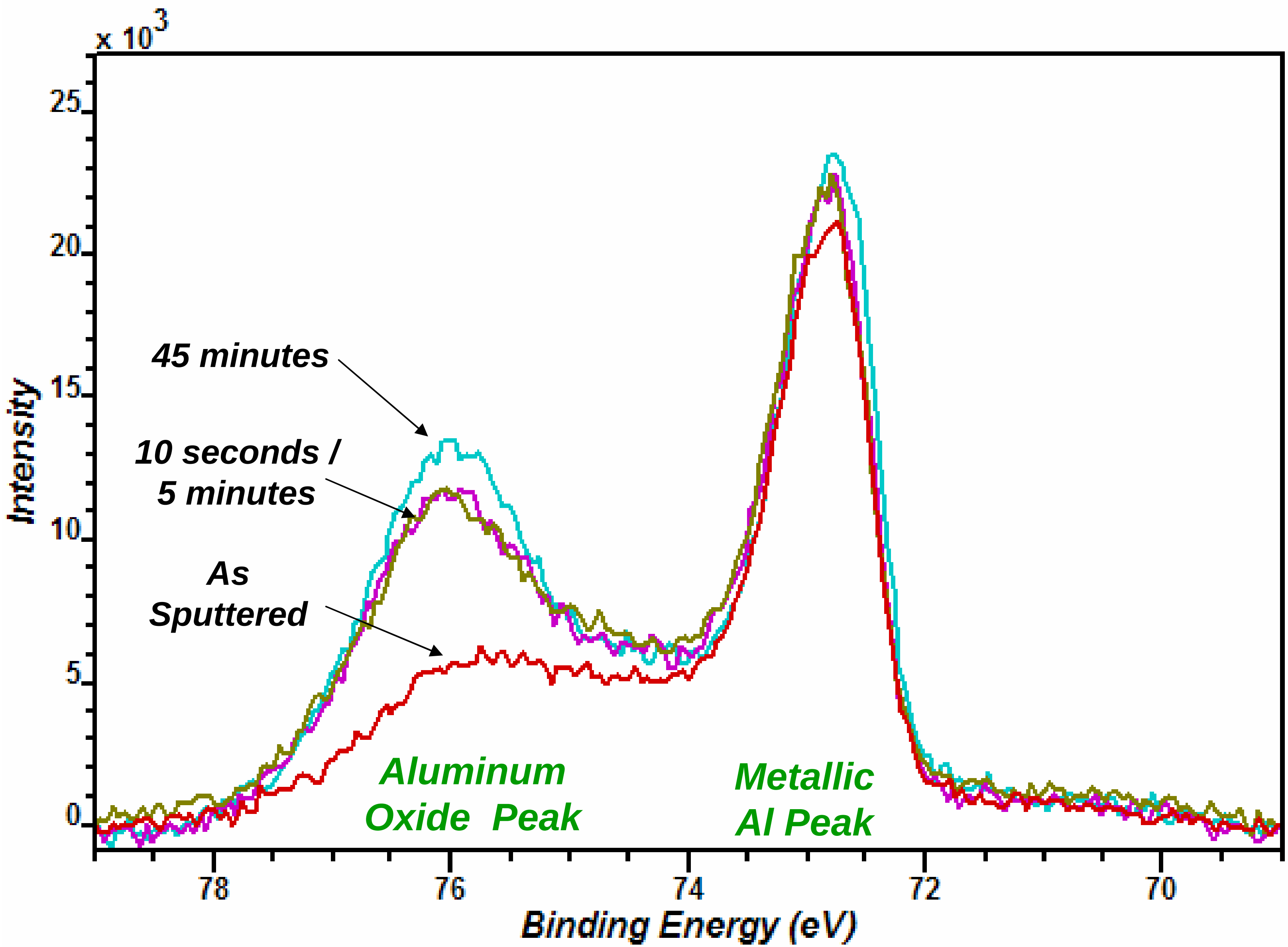
In-Situ Oxidation of As-Sputtered Fe-12.5Al

500°C, Pure Oxygen, Chamber Pressure of $3x10^{-7}$



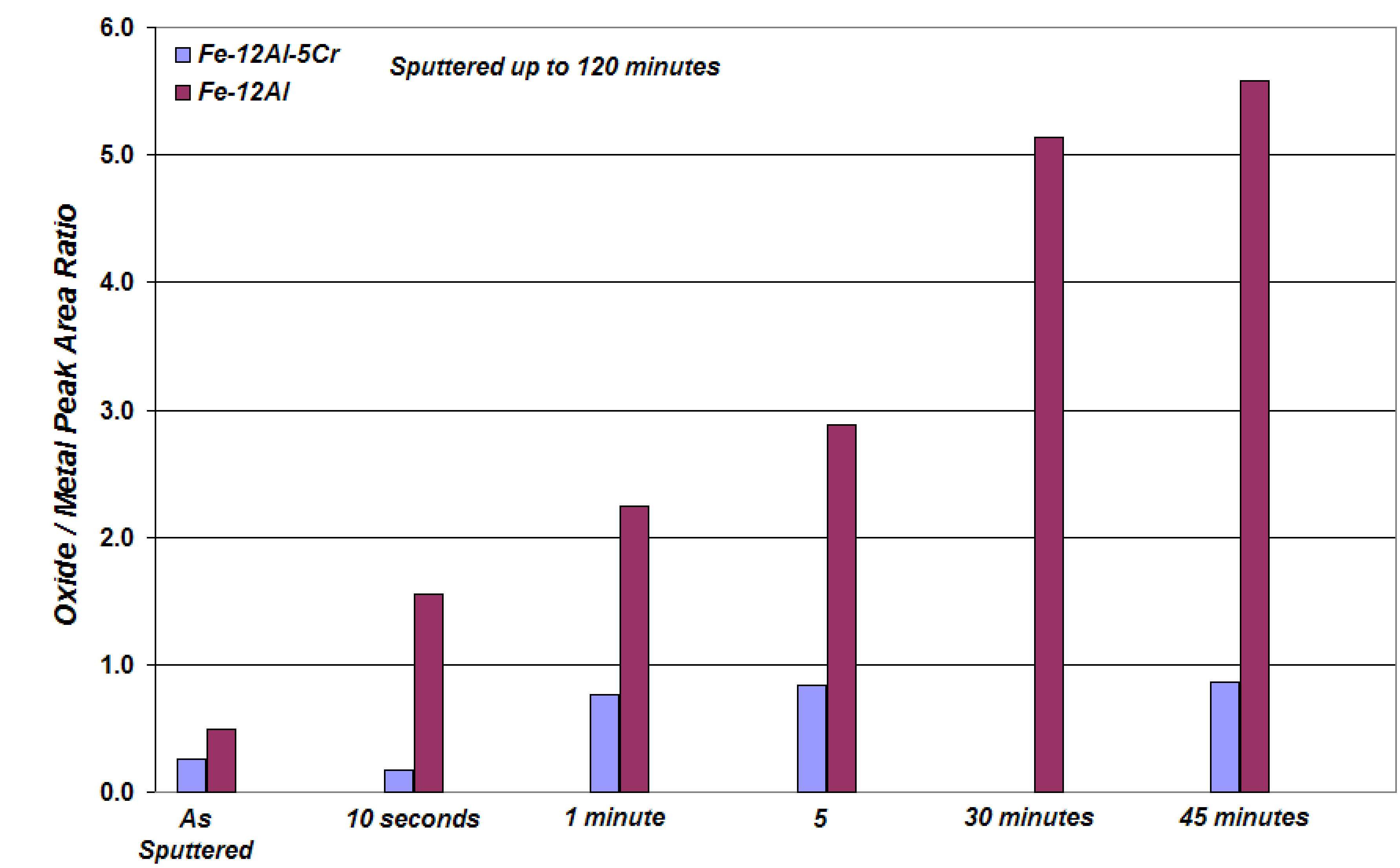
In-Situ Oxidation of As-Sputtered Fe-12.5Al-5Cr

500°C, Pure Oxygen, Chamber Pressure of $3x10^{-7}$



Oxide to Metal Peak Area Ratio - Sputtered

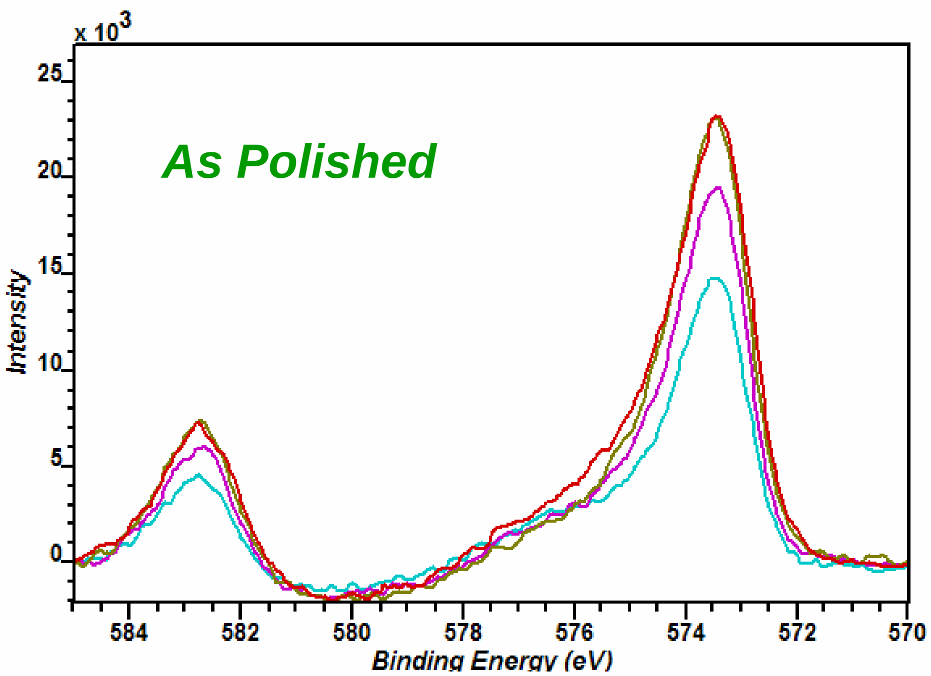
Samples sputtered to remove surface oxides prior to oxidation

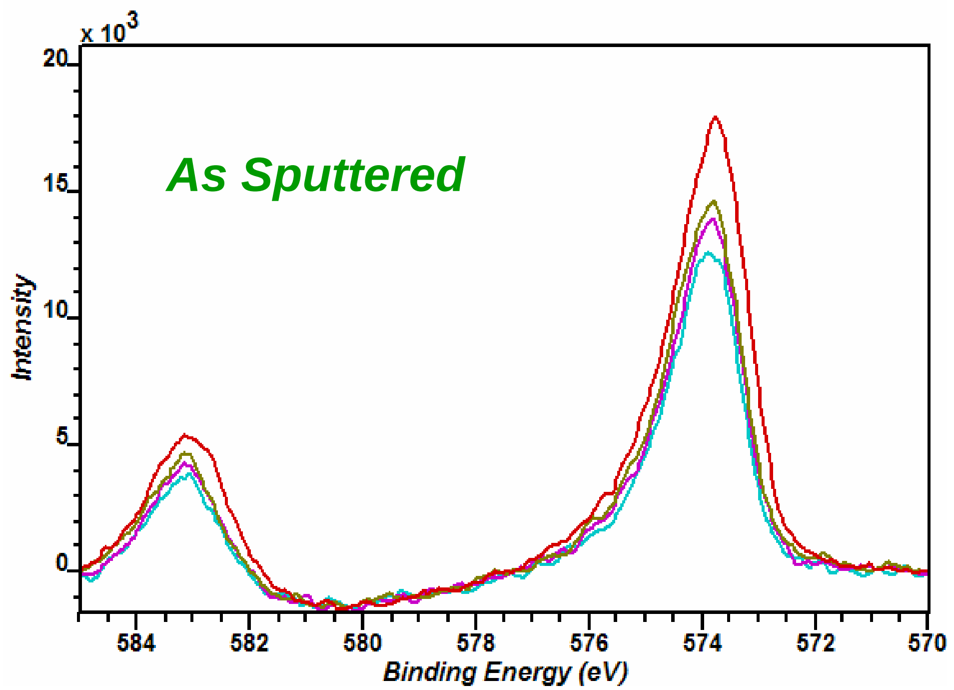


→ Chromium addition slows formation of aluminum oxides

Change in Chromium Peak During Oxidation

- *Shape of chromium 2p peaks does not change during oxidation, for either as polished or as sputtered condition*
- *Indicates that independent chromium oxide is not forming*
- *Requires further analysis to determine what role chromium is playing*

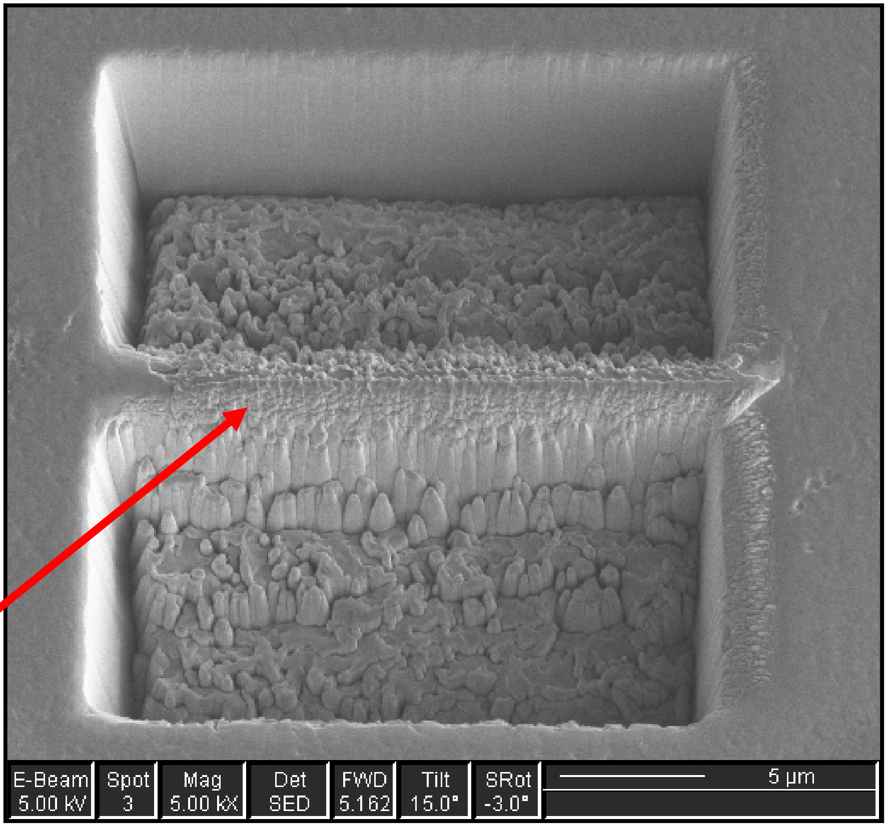




Corrosion Scale Analysis

- Corrosion scale will be analyzed using variety of electron microscopy techniques
  - SEM, TEM, STEM
  - Structure, chemistry
- Electron microscopy sample preparation will be performed using focused ion beam

Electron-transparent sample can be removed from specific location using FIB technique



Rough-milled Fe-12.5Al coupon

Summary

- ***Corrosion resistant and weldable Fe-Al-Cr alloy compositions have previously been identified***
- ***Current research focuses on determining properties of oxide layer, developing lifetime prediction model***
- ***Short and long term corrosion exposures will test corrosion resistance for variety or times, temperatures, environments***
- ***XPS experiments allow for in-situ study of oxidation, provide accurate data about surface***
- ***Analysis of corrosion scale will provide information about scale composition, overlay lifetime***

Summary

- ***Corrosion equipment has been modified for simulated low NO_x testing, testing has begun***
- ***Initial XPS experiments indicate that chromium slows the oxidation of aluminum***
  - ***Specific role of chromium needs to be elucidated***

Future Work

- ***Continued corrosion exposure testing***
- ***Analysis of corrosion scale morphology and chemistry***
- ***Development of lifetime prediction model based on alloy depletion during corrosion tests***
- ***Further experimentation on XPS***
  - ***Low angle studies to determine morphology of initial oxides***
  - ***Oxidation to longer times / at different temperatures***

Acknowledgements

- U.S. Department of Energy
- National Energy Technology Laboratory

Questions?