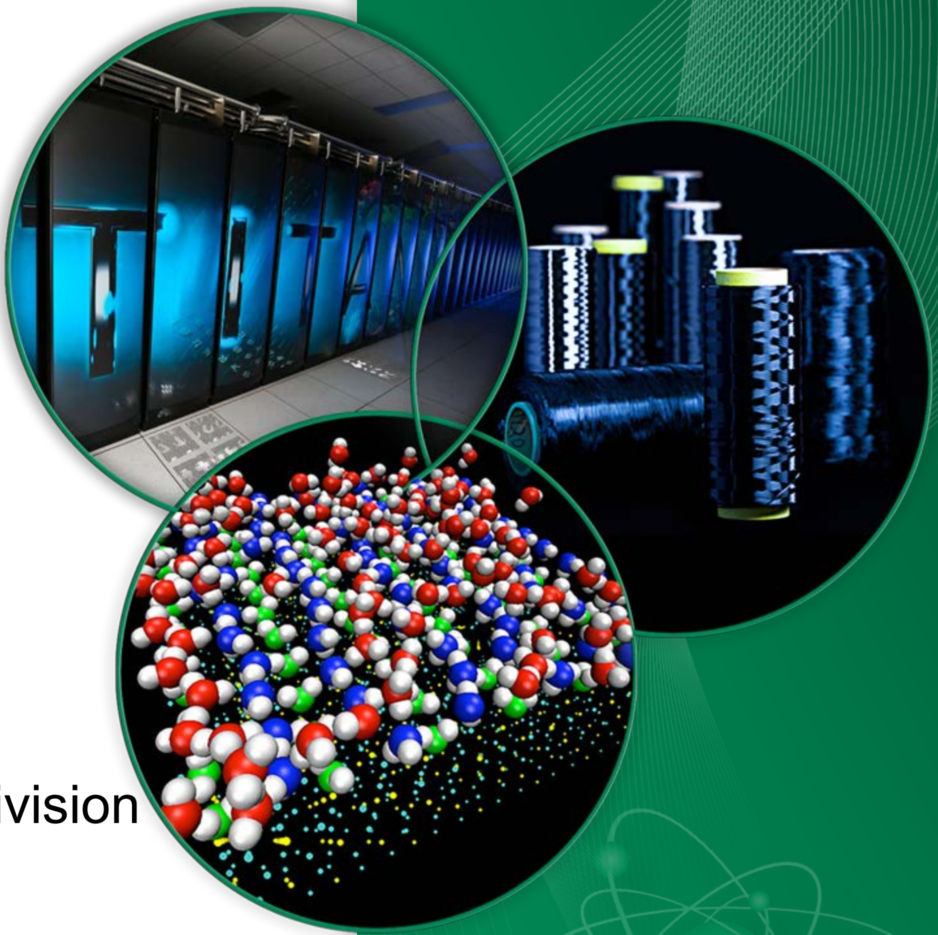
Understanding Protective Film Formation on Magnesium Alloys in Automotive Applications



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Overview: Project

Timeline

- Project start: Feb. 2012
- Project end: Sept. 2015
- ~85 Percent complete

Budget

- Total project funding
  - –$1550k DOE share
  - –$210k In-Kind (MENA)
- $450k received in FY14
- $350k in FY15
  (ORNL PI cost per year ~ $450k)

Barriers

- Barriers addressed
  - Lightweight Materials Barrier H: Maintenance, Repair, and Recycling
  - Lightweight Materials Barrier C: Performance (corrosion resistance)
  - 50% vehicle body/chasis weight reduction target will require low-cost, corrosion-resistant Mg alloys

Partners

- Magnesium Elektron North America
- U. Manitoba (collaborator)
- Henkel Corp. (new FY15 collaborator)
- McMaster U. (expanded FY 15 collab.)
- New FY 15 Interactions: Magna International and McGill U.

Relevance and Objective: Develop Scientific Foundation for Mg Alloys w/ Improved Corrosion Resistance

- Mg and carbon fiber have the highest potential to achieve targeted 50% weight reduction in vehicle body and chassis
- Poor corrosion resistance is a major challenge to achieve widespread adoption of Mg alloys in vehicle applications
- Film formation and corrosion of Mg is highly complex
  - Improved scientific understanding needed to provide the basis to develop more corrosion-resistant Mg alloys and coatings
- **Objective**: Delineate how alloy additions to Mg affect structure, chemistry and protectiveness of film formation (bare alloys and coatings)

Approach/Strategy: New Characterization Techniques to Elucidate Film Formation

- Film formation on bare Mg alloys and coatings are one key to corrosion resistance
- Near-ambient films on Mg relatively thick
  - Tens of nanometers to microns as opposed to thin (< 10nm) films formed on stainless steels, Al, etc.
  - Shares characteristics with films more often observed for heat-resistant alloys in high-temperature oxidation and corrosion
- Apply new characterization techniques from high-temperature oxidation community to ambient films on Mg
  - Cross-section transmission electron microscopy (TEM)
  - Isotopic film growth mechanism tracer studies with D_2O and $H_2{}^{18}O$
  - Small angle neutron scattering (SANS) of Mg film structure/nanoporosity
  - Combine with established surface chemistry + electrochemical approaches

Strategy: How Alloy Chemistry and Exposure Affect Film Structure and Protectiveness

- Demonstrate new characterization techniques and insights for aqueous film formation ± salt
  - Goal is not corrosion rate assessments, such data already available
  - Short term (4-48 h) exposure studies + multiple technique characterization to understand initial film structure, chemistry, and growth mechanism
  - Complement with electrochemical studies
- In-depth focus on AZ31B and E717: Represents two major vehicle relevant Mg alloy classes (both near-single phase)
  - **AZ31B**: Mg-(2.5-3.5)Al-(0.7-1.3)Zn-(0.2-1)Mn wt.%
  - **Elektron 717**: ZE10A type with Mg-(0.7-1.3)Zn-0.25Zr-(<0.5)Nd wt.%

    (succssful warm forming of door panels from E717, Niu et al., Magna-Cosma, Thermec 2013)
  - Pure Mg and model alloys as controls to understand alloying effects
- Compare film formation on bare vs. coated AZ31B and E717
  - Bonderite® 5200 and Surtec® 650 ± BASF Cathoguard® 525 E-coat
  - State-of-the-Art Henkel Bonderite® Electro-Ceramic Coating

Milestones: Focus on New Film Characterization Techniques and Findings Dissemination

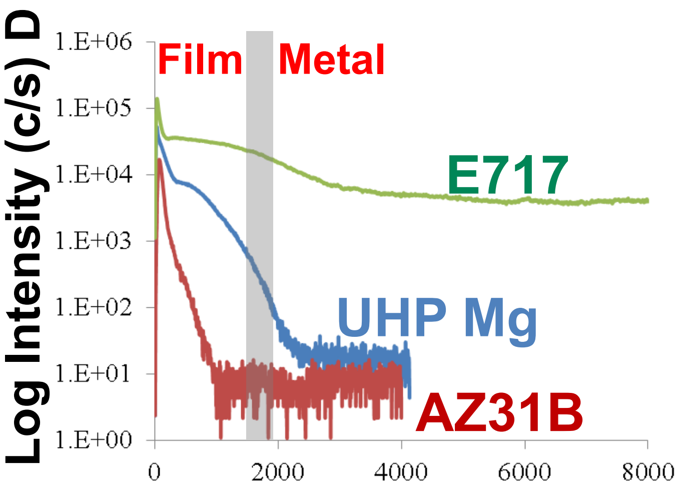
- ✓ **FY 2014** Measure nanoscale porosity and/or H species incorporation into Mg corrosion products by small angle neutron scattering (12/31/2013): **Go Decision**
- ✓ **FY 2014** Complete baseline isotopic tracer study of film growth in water (3/31/14): **Met- paper published**
- ✓ **FY 2014** Determine feasibility of 3D Mg corrosion atomic scale film chemistry by atom probe tomography (6/30/14): **No go decision**
- ✓ **FY 2014** Submit paper on advanced characterization study of salt species effects on surface film (9/30/2014): **Met-paper published**
- ✓ **FY 2015** Go/No Go for Mg film tracer study in salt solution (12/31/14): **Met/Go**
- ✓ **FY 2015** Submit paper on tracer study of elevated temperature oxidation/film growth of UHP Mg, AZ31B, and E717 in air with water vapor (3/31/14): **Met**
- ✓ **FY 2015** Complete polarization study of coated AZ31B and E717 in salt solution (6/30/15): **On Track**
- ✓ **FY 2015** Submit paper on advanced characterization findings for coated AZ31B and E717 alloys (9/30/15): **On Track**

Progress: Highlight FY15 Tracer Studies + Coating Characterization Efforts

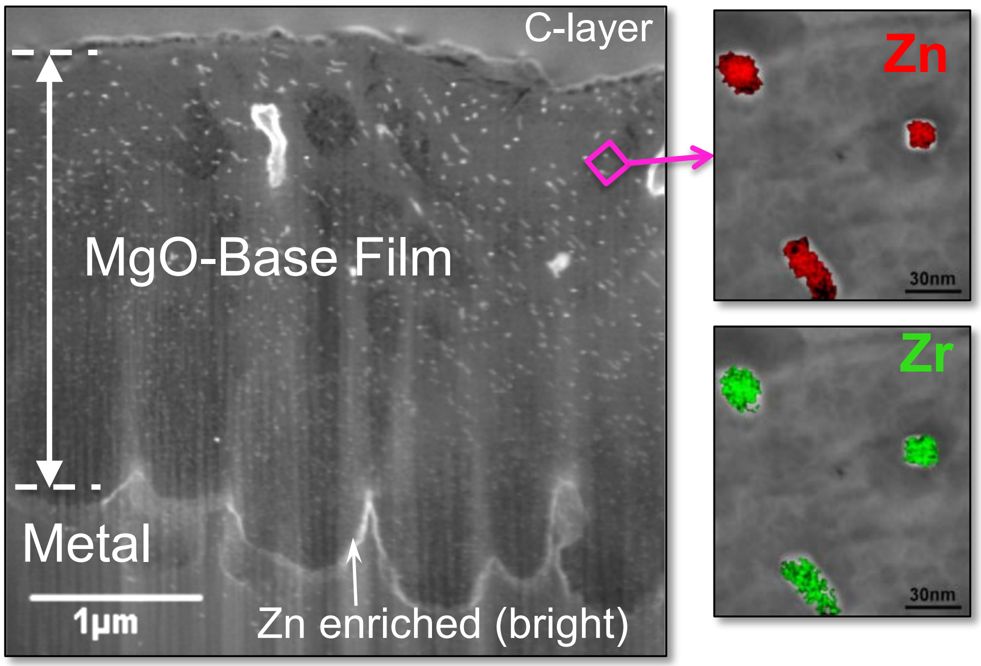
- Builds on Previous Years Findings for E717 and AZ31B
  - -bare alloy → coated (included alloy chemistry, structure, ambient films)
  - -aqueous immersion → water vapor → salt solutions
- Small angle neutron scattering (SANS) of film breakdown in salt solutions: completed FY14/FY15 (see extra slides)
- Film growth tracer studies with $D_2{}^{16}O$, $H_2{}^{18}O$ and SIMS profiling
  - -aqueous immersion completed FY14 (not presented here)
  - -elevated-temperature water vapor completed FY15 (see extra slides)
  - -aqueous alloy composition/H uptake studies in-progress FY15
  - -salt solution tracer studies in-progress FY15 (see extra slides)
- Coatings: How alloy affects coating formed (coating as film growth)
  - -SANS studies of nanoposity FY15 in-progress (not presented here)
  - -EIS/polarization studies FY15 in-progress (see extra slides)
  - -TEM cross-sections of as-coated structures in-progress FY15

FY14: E717 Showed Unexpected Features in Initial Aqueous Film Formation Tracer Study

SIMS/Tracer D Data
4 h in D_2O Water

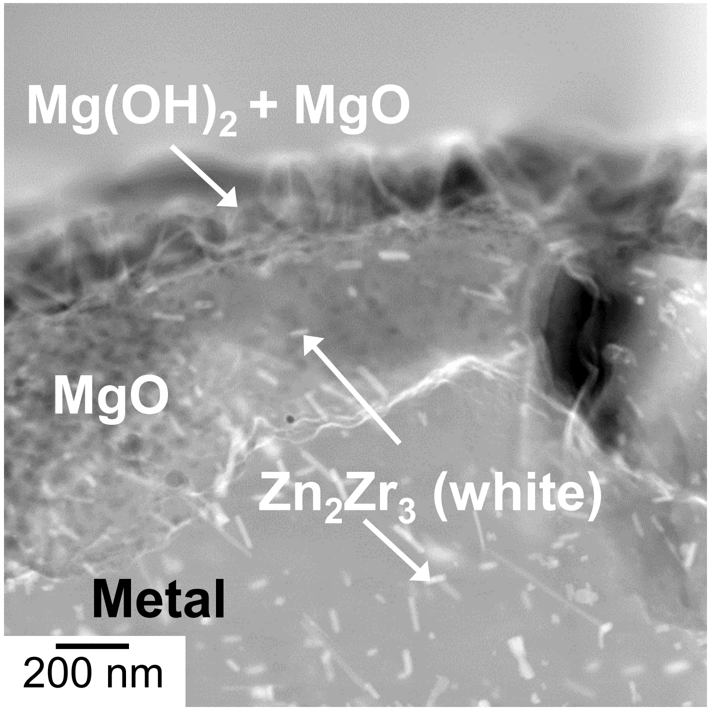


STEM Cross-Section of E717: 48h in H_2O



- Extensive hydrogen (D) penetration through film into underlying alloy for E717
- Inward-growing E717 MgO film incorporated nano Zn_2Zr_3 particles from underlying alloy: short circuit path for D into alloy? Nd also play a role?
- As-cast model alloys based on E717 studied in FY15: Mg-Zr, Mg-Zr-Zn, Mg-Zr-Nd, Mg-Zr-Zn-Nd, etc. to better understand

FY15: STEM Cross-Section of Cast Mg-Zn-Zr-Nd After 24 h in H_2O Similar to Wrought E717 Film

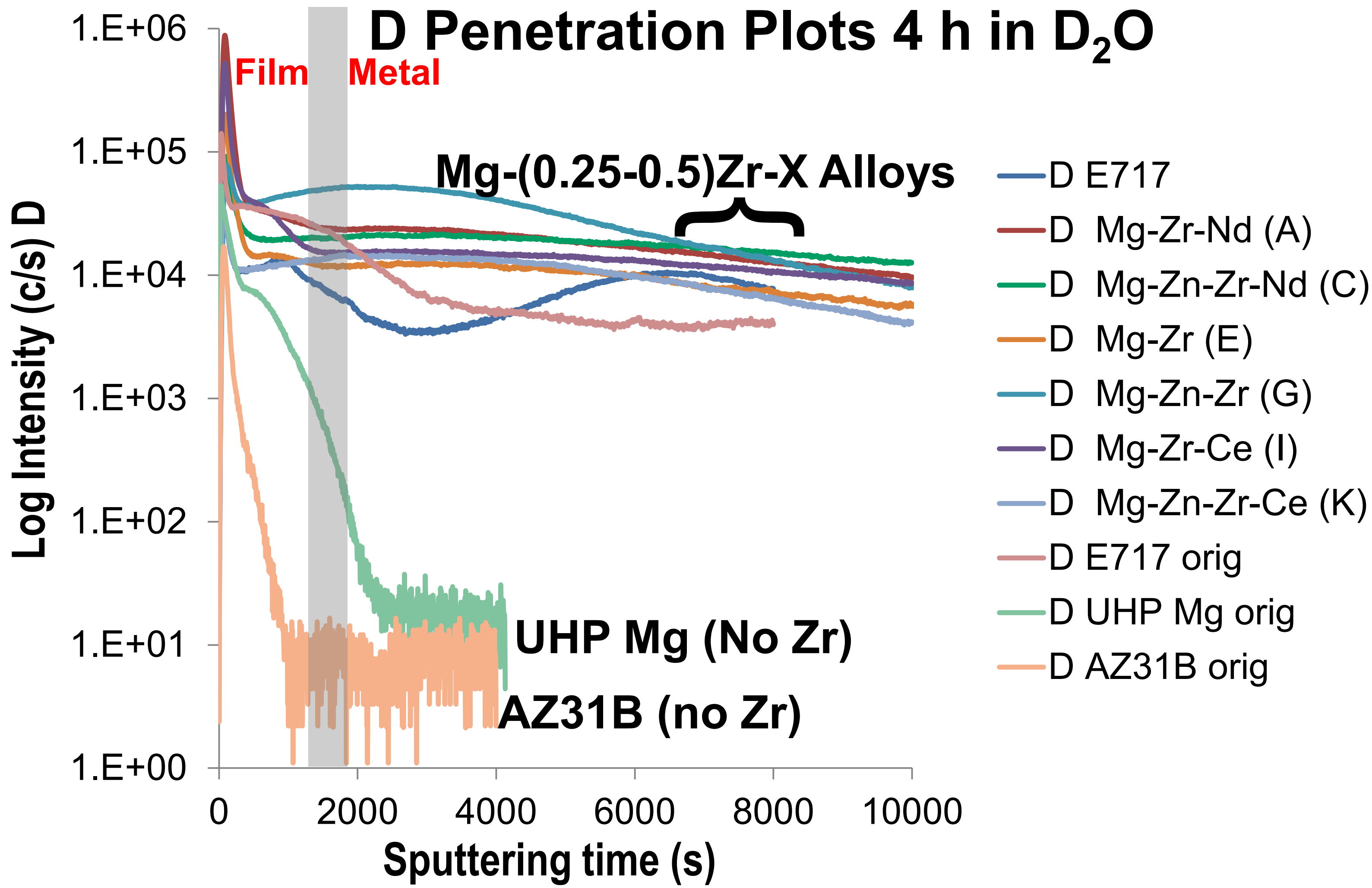


Cast Model Alloy Set via MENA (all have Zr to keep Fe < 50 ppm)

Mg-0.4Zr-0.3Nd
Mg-0.9Zn-0.4Zr-0.3Nd
Mg-0.5Zr
Mg-1Zn-0.5Zr
Mg-0.4Zr-0.4Ce
Mg-1Zn-0.4Zr-0.3Ce

- Cast model Mg-Zn-Zr-Nd alloy exhibited similar film structure and 2nd phase particles (albeit coarser) to that formed on wrought E717
- Cast model alloy set can be used to study alloy addition effects in E717
  - -E717 important alloy class, warm-formed door panels
  - -Zr or rare earths enhances H uptake? Possible issue for SCC or H embrittle?

Initial Tracer Data for 4 h D_2O Exposure Suggests Zr Enhances Hydrogen Uptake by Mg in Water

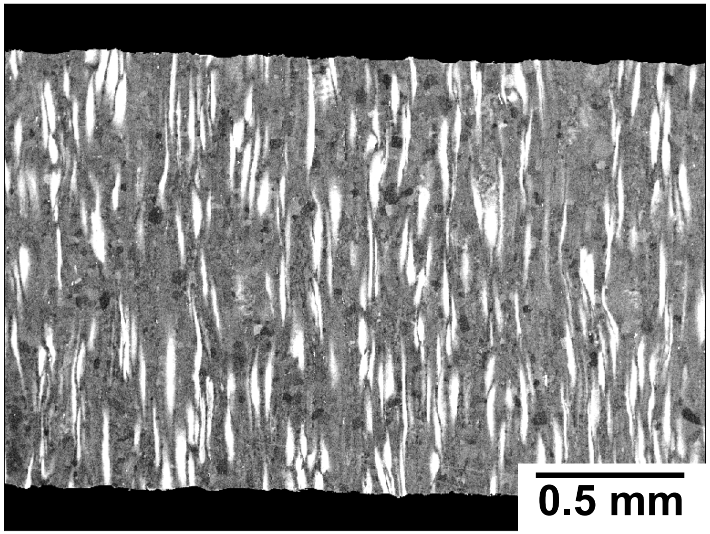


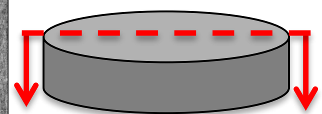
- Zr typically added as alloy grain refiner, getter for Fe impurities

Focusing on Model Cast Binary Mg-Zr/Nd Alloys to Understand and I.D. Enhanced H Uptake Paths

Backscatter Images of As-Cast Mg-Zr Sample Cross-sections

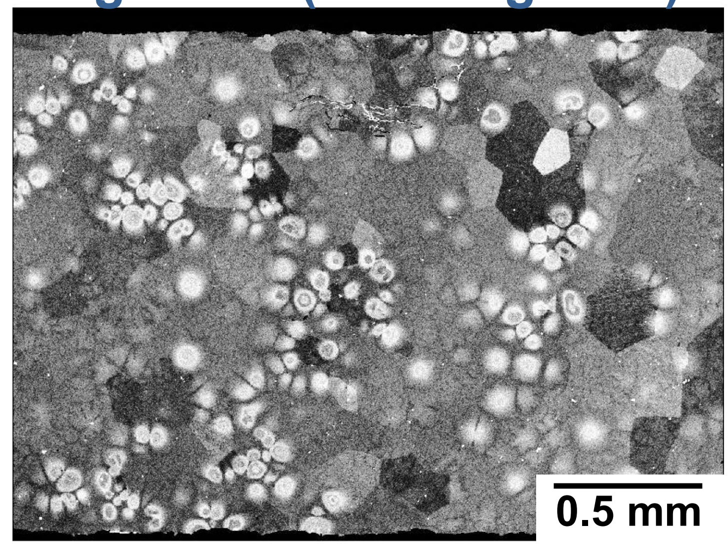
Mg-0.5 Zr (fine grains)





White Regions Zr-enriched

Mg-0.2 Zr (coarse grains)



•Additional SIMS/tracer D_2O exposures, XPS, and TEM in progress for Mg-0.5Zr, Mg-0.2Zr, Mg-0.2Nd (no Zr), and commercial purity/high purity Mg

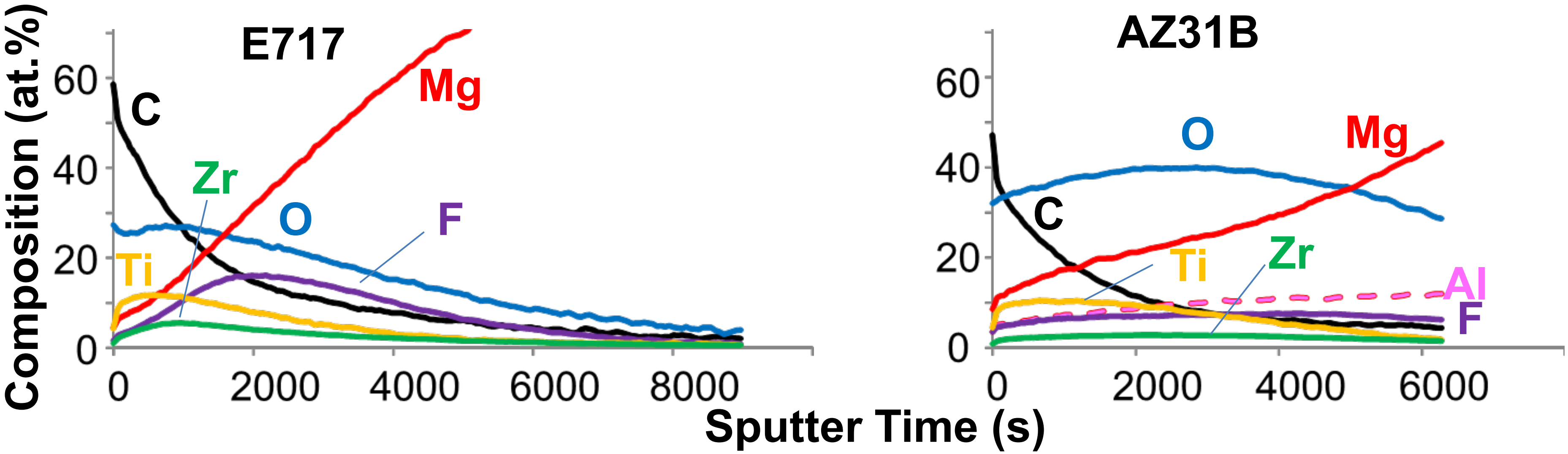
•Is there a threshold Zr level below which enhanced H uptake minimized?
- -do rare earths also impact enhanced H uptake? Impurities (e.g. Fe)?
- -alternative additions to Zr for grain refining, Fe impurity removal, etc?

FY15: Extensive Coating Characterization Focus

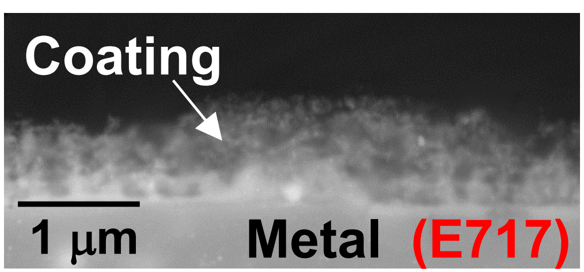
- Focus on how substrate alloy affects coating structure/chemistry on AZ31B and E717 (view coating as film growth process)
  - -as conversion coated Bonderite® 5200 (Cr free) and Surtec® 650 (Cr^{+3})
  - -conversion coat + BASF Cathoguard® 525 E-coat (vendor via MENA)
  - -Henkel Bonderite® Electro-Ceramic coatings (via Henkel)
- Detailed as-coated characterization to provide understanding to guide modified alloy design/coating processing for better protection
- Polarization and electrochemical impedance spectroscopy for bare/coated AZ31B and E717 in support of effort (see extra slides)
  - -not being done as engineering corrosion assessment (no top coat or paint)
  - -relate coating chemistry and structure to NaCl solution interactions/attack
- MENA Cast E717-based model alloy set sent to McMaster and Henkel for Electro-Ceramic coating/corrosion studies (bare and coated) E717 bare alloy/coating work at ORNL will serve as baseline control

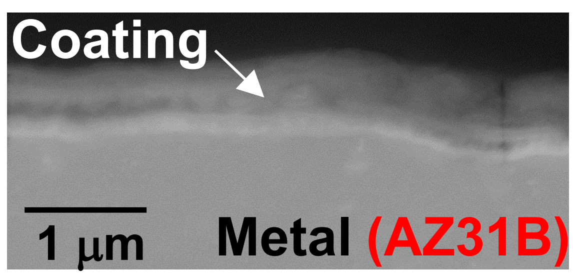
Differences As-Conversion Coated Bonderite® 5200 on AZ31B vs. E717

XPS Sputter Profiles Through Coatings Into Metal (~2 at.% N, not shown)



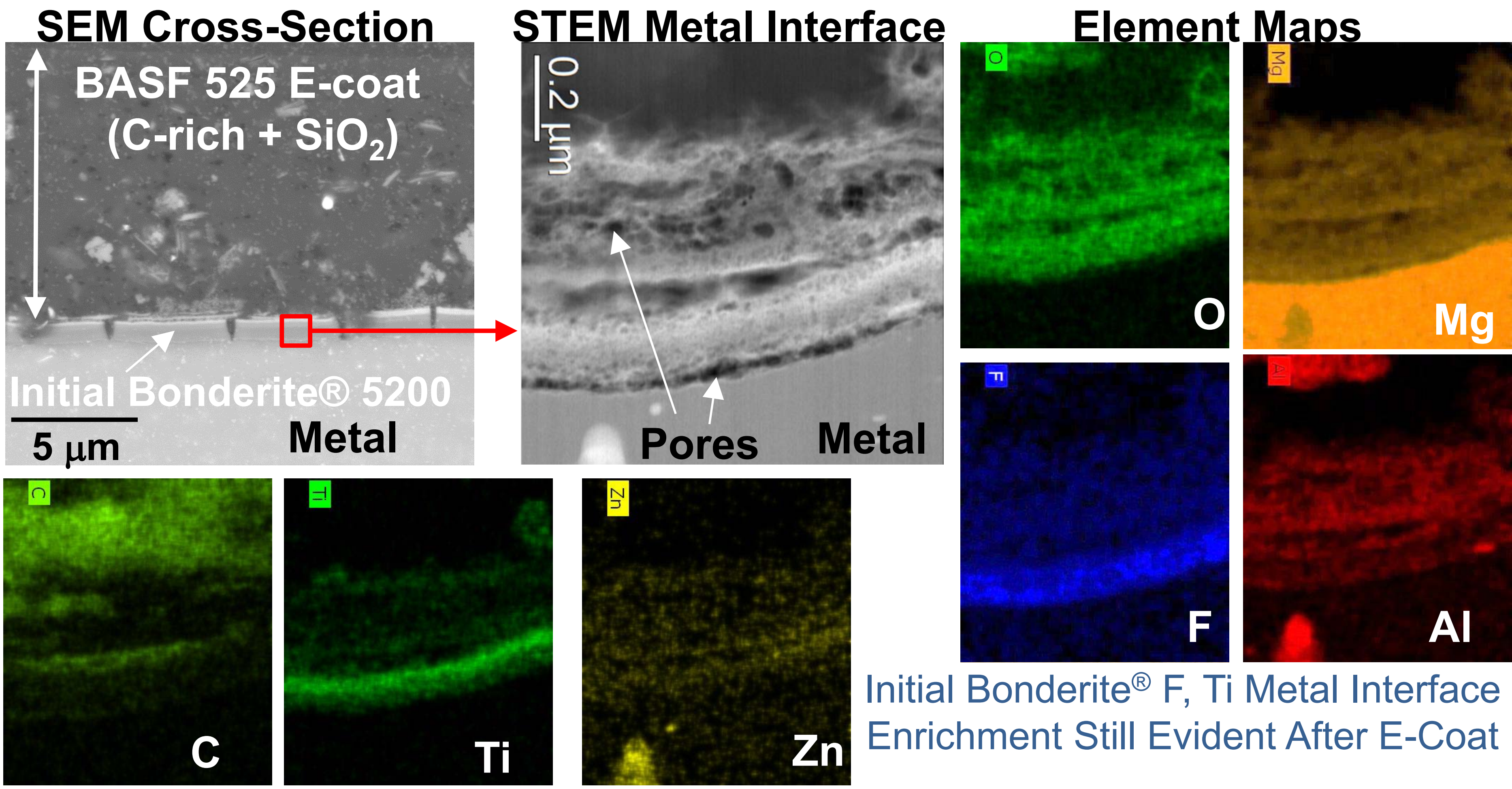
SEM Cross-Sections As-Conversion Coated





- Complex Mg-C-O-F-Ti-Zr-N film (E717 more porous?)
- Al from AZ31B, and higher Zr from E717 in coating

Porous Metal-Coating Interface on AZ31B With Bonderite® 5200 + BASF E-Coat

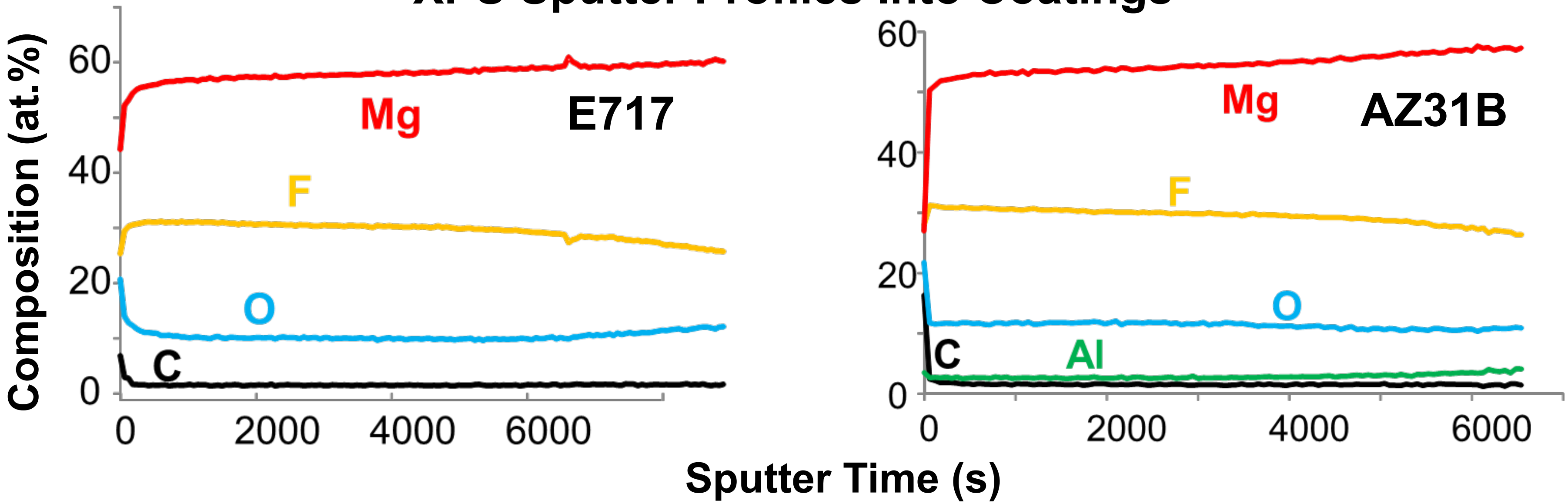


Initial Bonderite® F, Ti Metal Interface Enrichment Still Evident After E-Coat

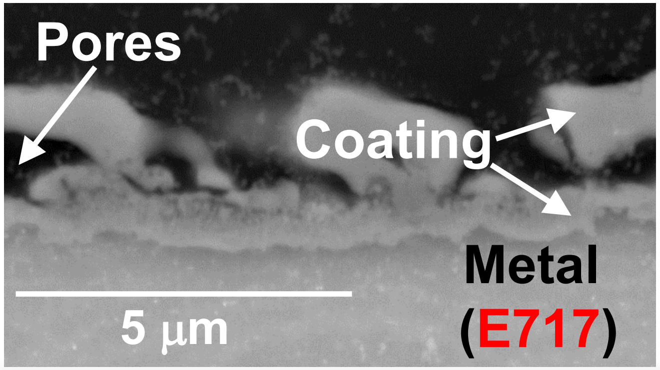
- After E-coat + Bonderite®, more porosity at metal interface than Bonderite® only?
- Porous layer contains Al/Zn from AZ31B and C from E-coat (affects protection?)

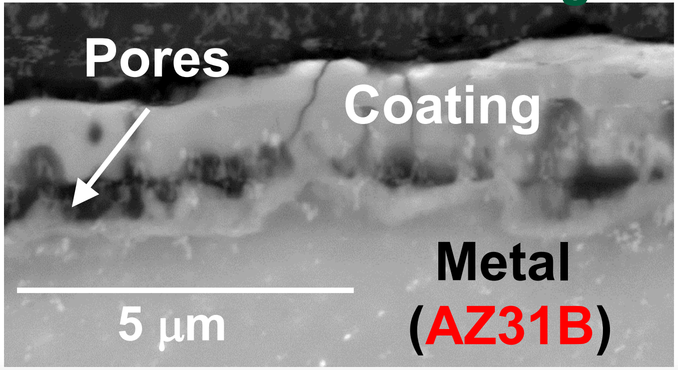
Bonderite® Electro-Ceramic Coatings Yield Uniform MgF_2+O on Both E717 and AZ31B

XPS Sputter Profiles Into Coatings



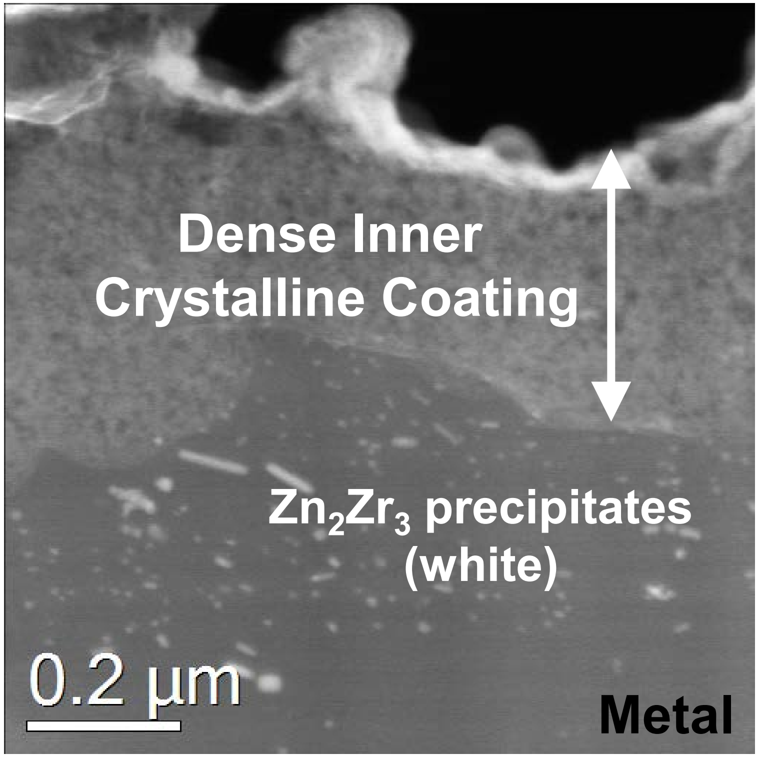
SEM Cross-Sections of Electro Ceramic Coatings

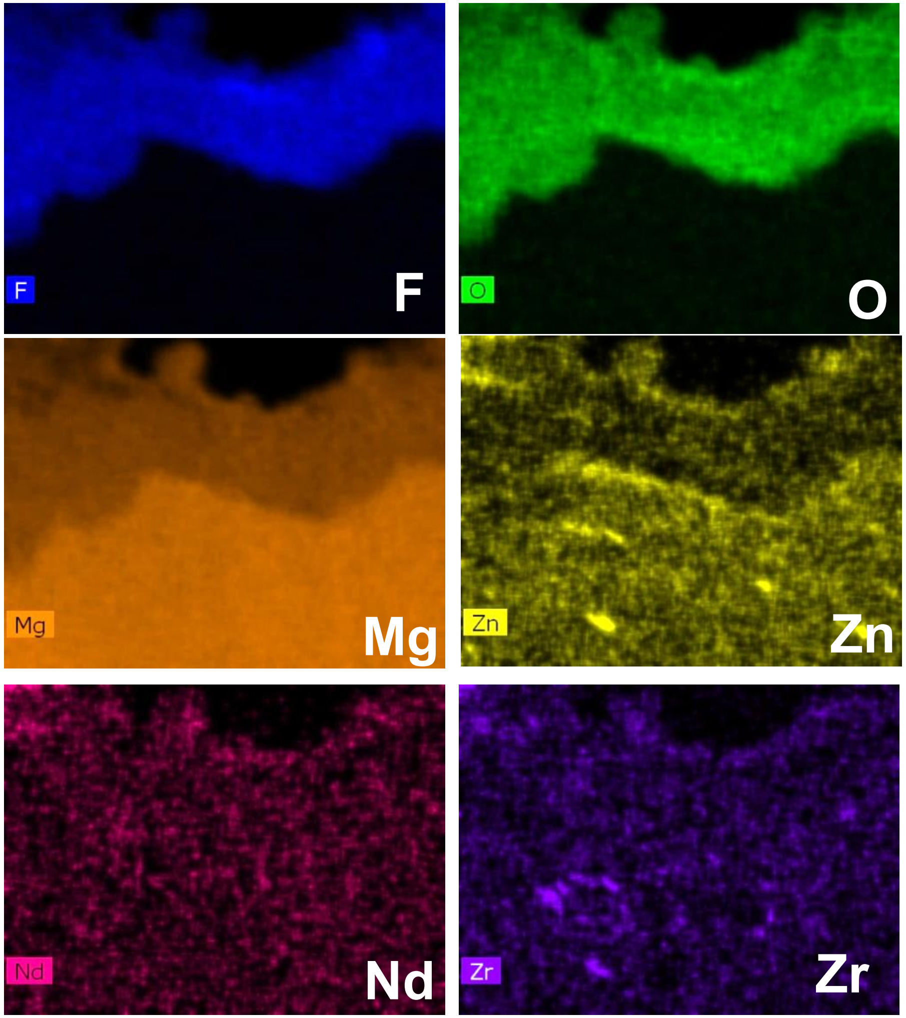




- Continuous 200 nm inner coating layer
- Pores middle/ outer coating-more for E717? (SANS planned)

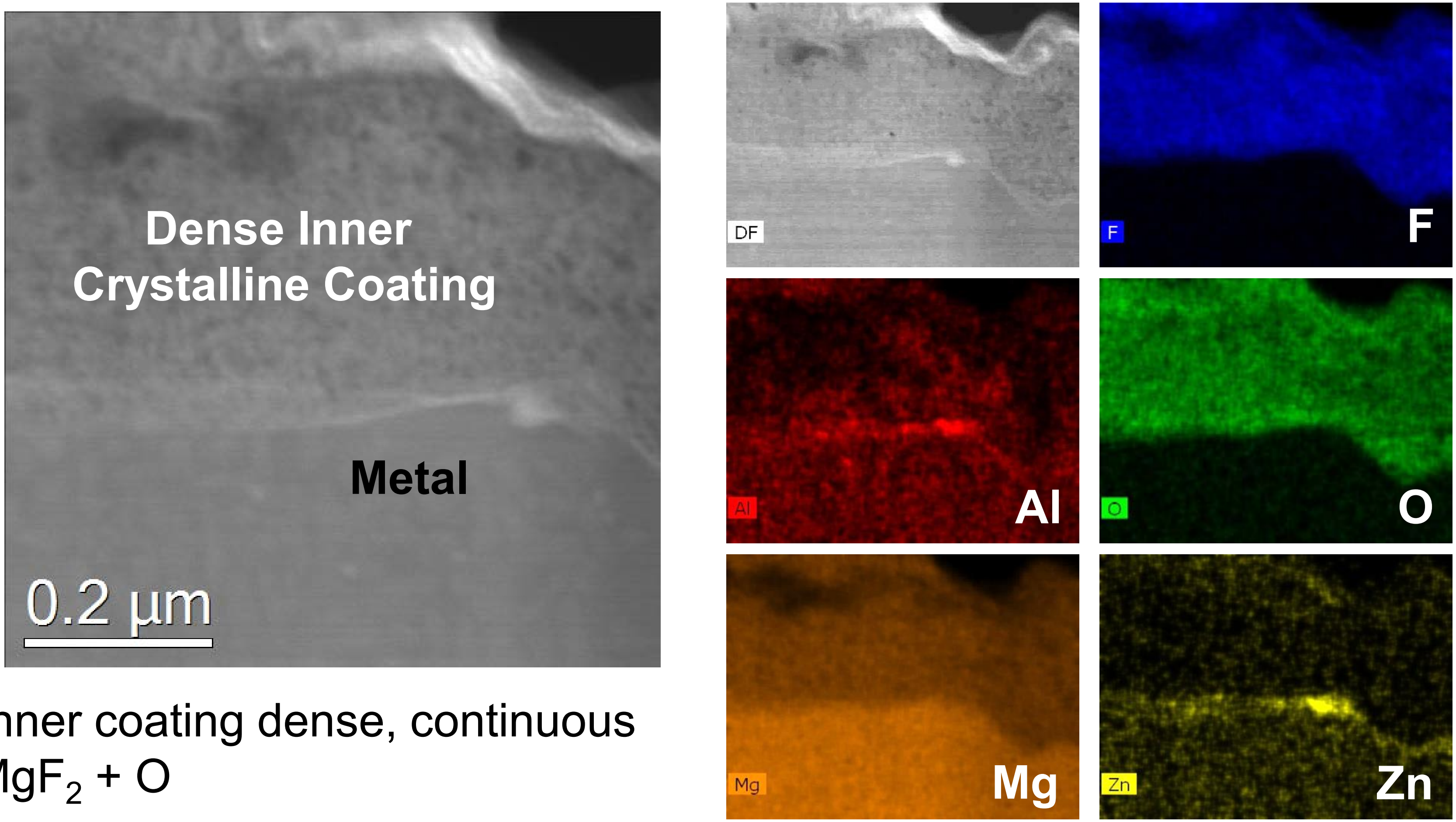
STEM Cross-Section of Bonderite® Electro-Ceramic on E717: Dense Inner Coating





- Inner coating dense, continuous MgF_2 + O
- Zn_2Zr_3 precipitates not captured in film (outward growth mode?)

STEM Cross-Section of Bonderite® Electro-Ceramic on AZ31B: Local Al Enrichment



- Inner coating dense, continuous MgF_2 + O
- Some incorporation of Al in coating from substrate, Al/Zn enrichment at metal interface

Response to Reviewer Comments

Request collaborations/interactions beyond MENA, U. Manitoba, McMaster U.
Formal collaboration with McMaster and Henkel Corp added in FY15 (electro-ceramic coatings). Interactions with Magna also added in FY15. Magna interest in enhanced H uptake in Zr + rare earth Mg alloys relative to H embrittlement of rivets used for sheet Mg joining. New Magna-McGill U.-ORNL interactions on Zr-free, Mg-Nd-Zn-Ca-rare earth model alloys for future H uptake study.

Need more emphasis on findings impact and dissemination to industry
Due to time and review format constraints we can only highlight limited aspects of our results. This is also a basic science project building on previous years efforts to achieve understanding and relevance. The linking of Zr in Mg alloys to enhanced H uptake is a new finding that may have implications for rivet joining, SCC, H embrittlement etc., which may be addressed by modified alloy design (e.g. reduce Zr levels).

Characterization efforts for coatings should help provide basis to modify alloy or coating processing to enhance protectiveness. New techniques developed by this effort (e.g. tracer studies, SANS, etc) can also then be applied by industry/university to address other aspects of Mg corrosion. We have expanded collaborations, and are widely publishing findings .

Suggests linkage with modeling community? Project budget limited, but thermodynamic modeling of Mg-Zr-H system added in FY15 to better understand H uptake results

Collaboration/Coordination with Other Institutions

- **Bruce Davis, Kris Kitchen Magnesium Elektron North America**
  - Supply model and commercial alloys for study, conversion/e-coatings
- **Mostafa Fayek, University of Manitoba**
  - SIMS analysis for tracer studies of Mg film growth mechanism (unique expertise from relevant geochemistry, e.g. Brucite $Mg(OH)_2$)
- **Joey Kish, McMaster University**
  - Collaboration for E717-based cast model alloy set (bare and coated) coordinated study w/ Henkel Corp.
- **John Kukalis, Bruce Goodreau, Omar Abu Shanab, Henkel Corp.**
  - electro-ceramic coatings
- **Tim Skszek, Magna International**
  - Discussions on ORNL H uptake findings, industrial perspective for Mg alloys
- **Stephen Yue, McGill University**
  - Planned coordinated studies with McGill Mg-Nd-Ca-Zn sheet manufacturability study by ORNL for H uptake, film growth, and coating study of this alloy set

Future Work: Project Ends Sept 2015

- Complete and publish coating characterization study TEM, XPS, SANS: as-coated structures on AZ31B and E717 (conversion, e-coat, electro-ceramic) + electrochemical behavior in salt solutions
- Complete and publish SIMS/Tracer and TEM study of AZ31B, E717, and UHP Mg film growth mechanism in salt solutions (see extra slides)
- Complete and publish aqueous H uptake study for Mg-Zr and related cast model alloys
- Support McMaster/Henkel bare and Electro-Ceramic coated E717-based cast model alloy set study
- Proposed new project to build on current AZ31B and E717 results for film, H uptake, and coating studies to include:
  - -McGill Mg-Nd-Ca-Zn alloy set (no Zr): aide design of formable sheet product with improved corrosion resistance and/or coating formation
  - -Study of WE43, AZ91 Mg alloys of interest for housings, cradles, etc. Also provides comparison with E717/AZ31B (higher rare earth/Al levels)

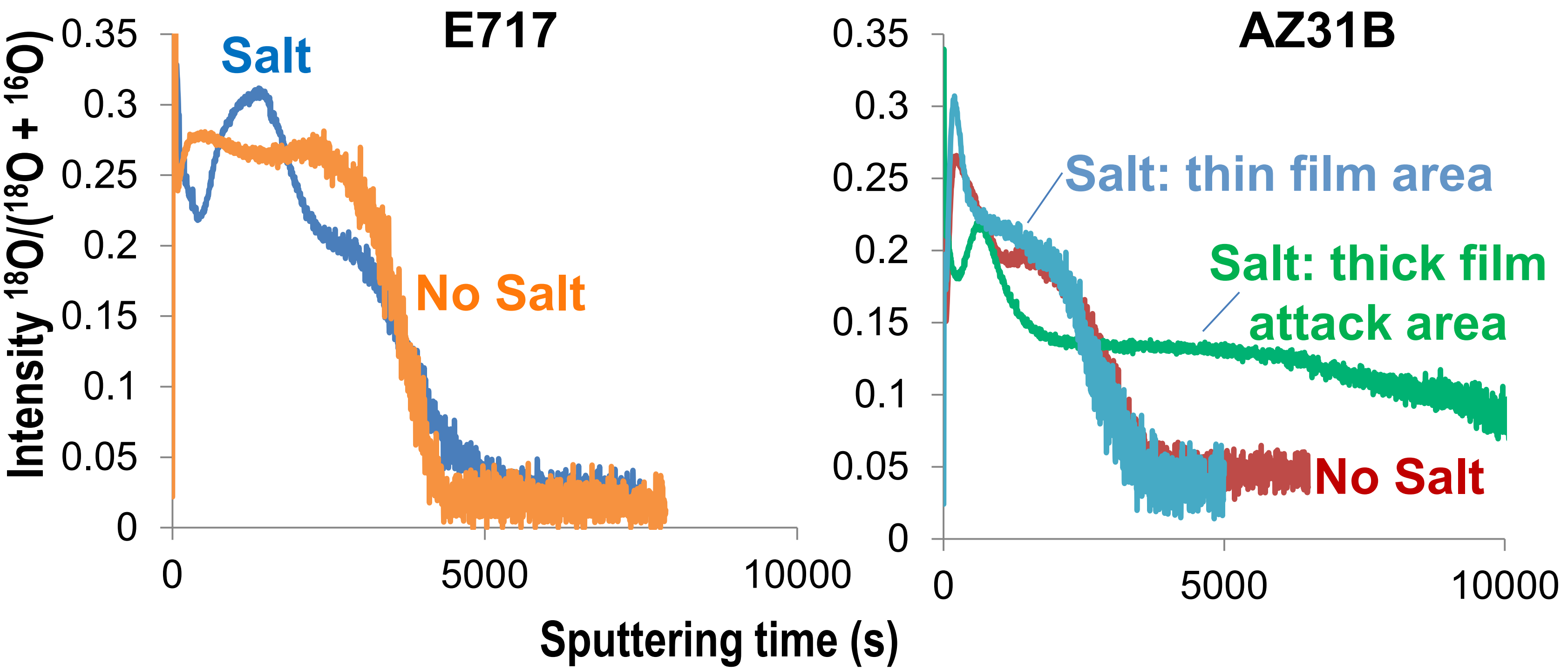
Summary

- ✓ Project has successfully demonstrated advanced characterization methods new to Mg corrosion for improved understanding of film formation to aide future Mg alloy and coating optimization
  - -extensive industrial and academic input and collaboration
- ✓ Isotopic tracer method has revealed aqueous film growth mechanisms and unexpected enhanced H uptake phenomena as a function of Mg alloy composition
- ✓ Advanced characterization methods are revealing chemistry and morphology differences that may impact coating protectiveness as a function of coating method and substrate alloy composition

Technical Back-Up Slides

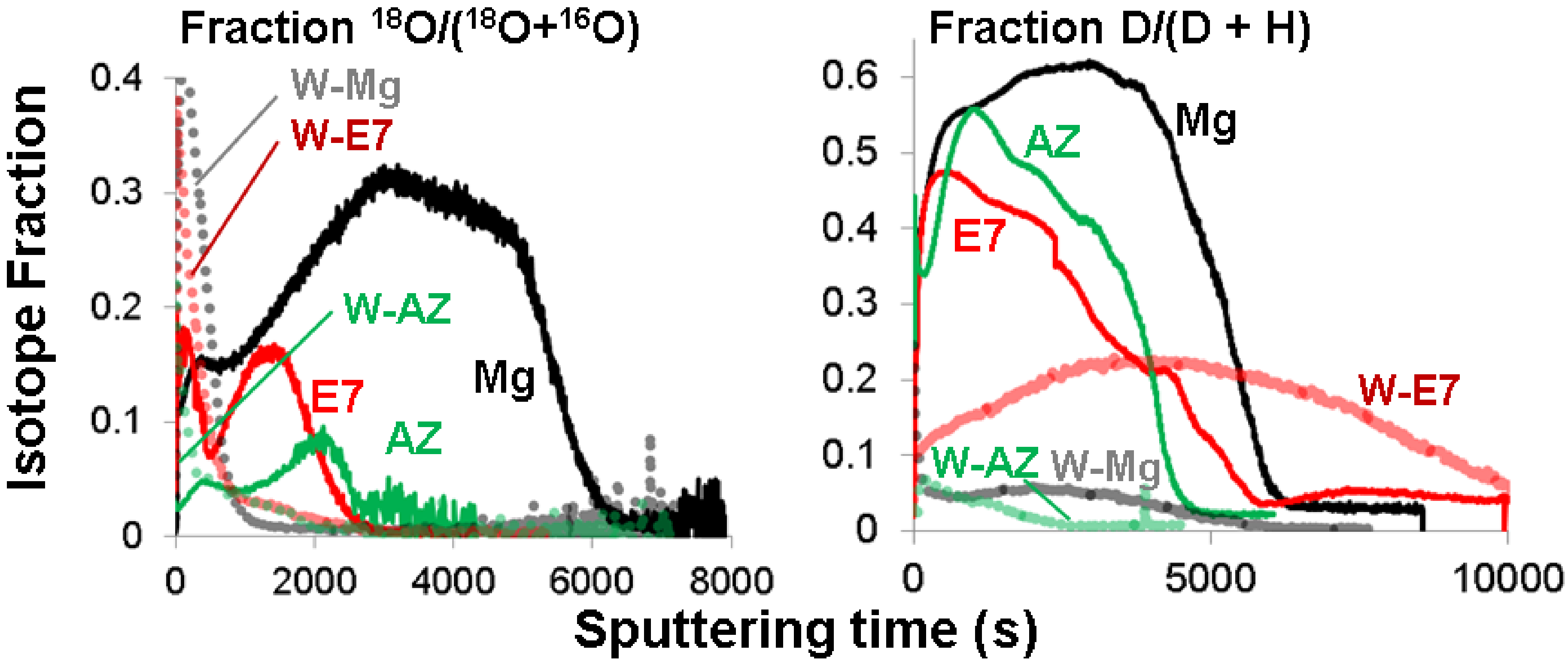
Sequential $D_2{}^{16}O$ + $H_2{}^{18}O$ + Salt Tracer Studies Show Enhanced Outward Film Growth Mechanism

Oxygen Fraction Plots (4h $D_2{}^{16}O$ + 20 h $H_2{}^{18}O$ ± 0.01%NaCl)



- Intermediate peaks in O fraction when 0.01% NaCl added for $H_2{}^{18}O$ step indicates shift from O inward growth in water to mixed inward/outward growth
- Preliminary D fraction data with NaCl in progress: behavior for E717 different than AZ31B and UHP Mg

SIMS Tracer Study in 85°C Air + Water Vapor Shows Shift to Outward Film Growth Relative to Ambient Aqueous Water Immersion



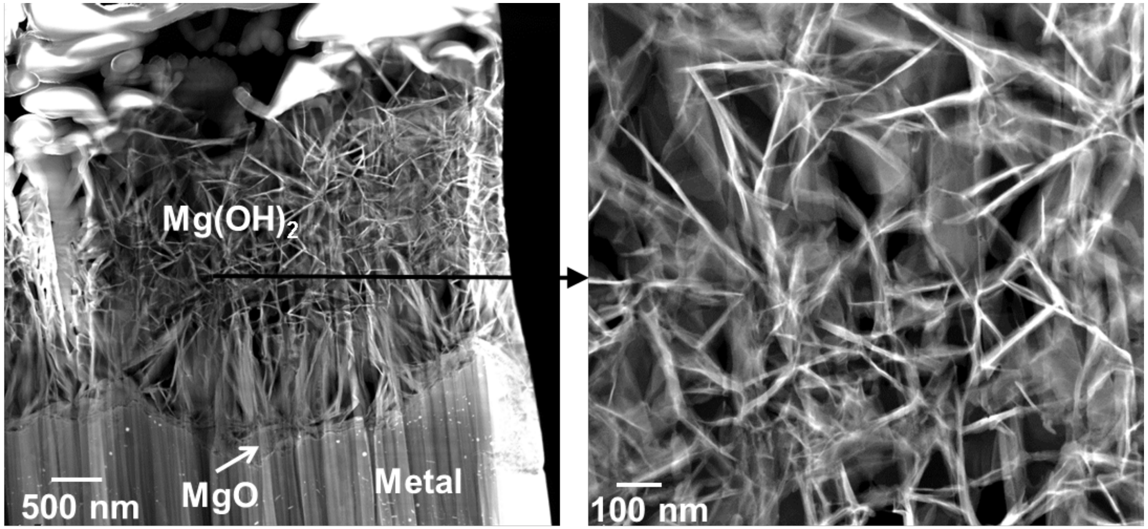
2-step tracer: 4 h $D_2{}^{16}O$ + 20 h $H_2{}^{18}O$

-immersed in water at room-temperature "W" for AZ31B (AZ), E717 (E7), Mg

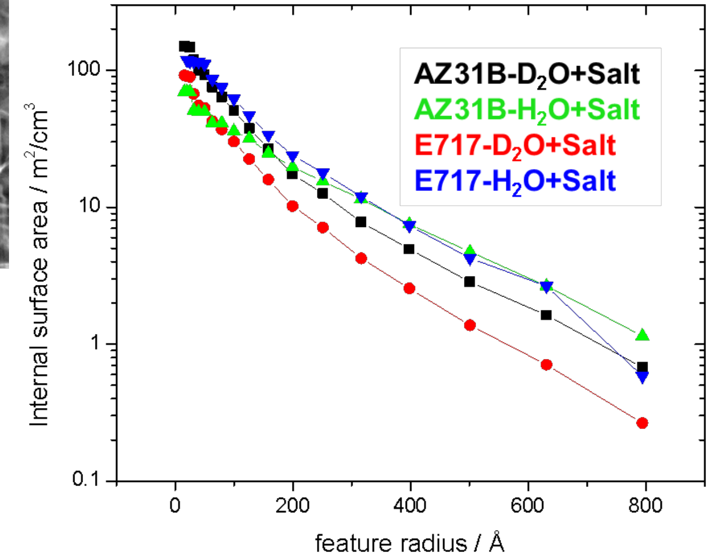
-oxidized at 85°C in air with water vapor source of $D_2{}^{16}O$ and $H_2{}^{18}O$

Small Angle Neutron Scattering (SANS) Sensitive to NaCl Solution Breakdown of Mg Films, Rapid Formation of Nanoporous $Mg(OH)_2$

Cross-Section TEM Typical 24 h exposure in 5 wt% NaCl Solution for AZ31B and E717 (shown below)



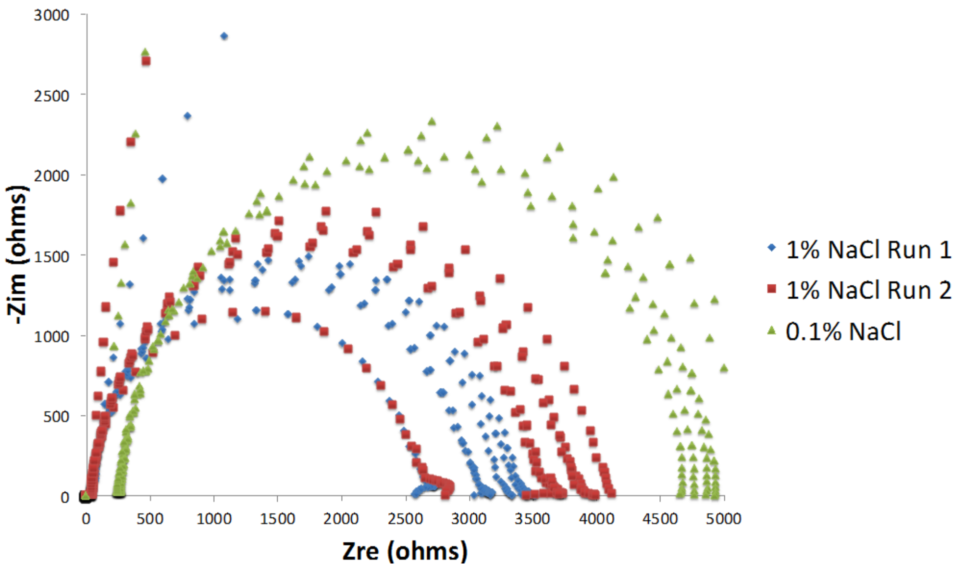
Analyzed SANS Data: $Mg(OH)_2$ Surface Area of 100 m^2/cm^3 (40 m^2/g, very high surface area)

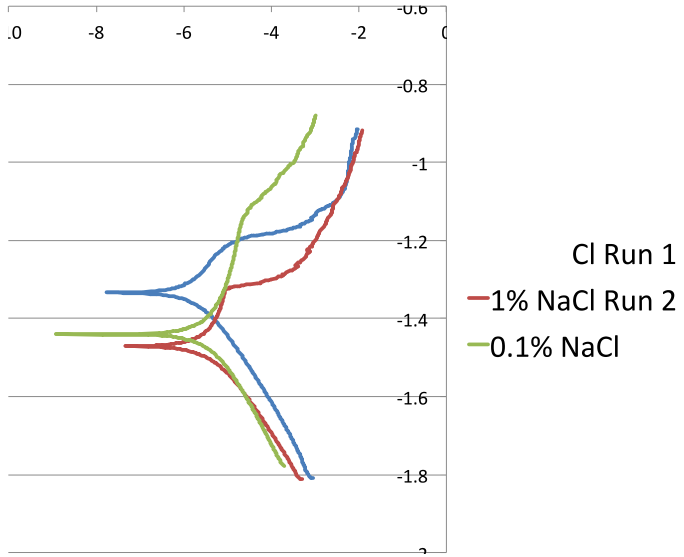


- "Film Breakdown and Nano-Porous $Mg(OH)_2$ Formation from Corrosion of Magnesium Alloys in Salt Solutions, MP Brady, G Rother, LM Anovitz, KC Littrell, KA Unocic, HH Elsentriecy, G-L Song, JK Thomson, NC Gallego, B Davis, Journal of The Electrochemical Society 162 (4), C140-C149 (2015)

Example Impedance Spectroscopy/Polarization Data of Coatings in Saturated $Mg(OH)_2$ + NaCl

Bonderite® Electro-Ceramic Coating on E717





Coated 15 mm diameter Test Sample

NOT AN ENGINEERING COATING CORROSION RESISTANCE STUDY
-No Top Coat Used
-Correlating with coating structure/chemistry

Run 1: 1 wt.% NaCl **Run 2: 1 wt.% NaCl** **Run 1: 0.1 wt.% NaCl**

FY14: Example TEM of As-Conversion Coated Surface (Compare Before/After E-Coat)

As-Coated Bonderite® 5200 on E717