Understanding Protective Film Formation by Magnesium Alloys in Automotive Applications

Co-P.I.'s M.P. Brady and K.A. Unocic
Oak Ridge National Laboratory

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Contacts: bradymp@ornl.gov; unocicka@ornl.gov

Overview: New Project

Timeline

- Project start: Feb. 2012
- Project end: Sept. 2015
- ~30 Percent complete

Budget

- Total project funding
  - $1350k DOE share
  - $210k In-Kind (MENA)
- $450k received in FY12
- $300k in FY13

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 (MENA)
- Project Lead: Oak Ridge National Lab

Relevance: 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

- Mg alloys need to enable recycling, low cost joining, and corrosion resistance for successful implementation
  - Must achieve this with reduction or elimination of rare earth additions

- 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
  - Focus on how alloy additions to Mg effect structure, chemistry and protectiveness of film formation (bare alloys and converison coatings)

Strategy: New Advanced Characterization Techniques to Elucidate Film Formation

- Film formation on bare Mg alloys and conversion coatings are 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 to ambient films on Mg
  - Cross-section transmission electron microscopy
  - Tracer studies with tagged O and H species
  - Small angle neutron scattering
  - Combine with surface chemistry + electrochemical techniques

Strategy: Focus on how alloy chemistry and exposure affect surface film structure, chemistry, and protectiveness

- Start with AZ31B and E717: Represents two major 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**: ZEK 100 type with Mg-(0.7-1.3)Zn + Nd, Zr wt.%
  - **CP + UHP Mg**: three 9's and six 9's purity for control purposes
  - **Conversion coated** AZ31B and Elektron 717 (selected by MENA)

- Aqueous Environments ± Salt
  - Immersion in ambient distilled ionized (DI) water 4 to 48 h
  - Immersion in ambient distilled ionized (DI) water + salt 4 to 48 h
  - Electrochemical studies in DI water saturated with $Mg(OH)_2$ ± salt

Project FY12/FY13 Milestones Devoted to Characterization Technique Development

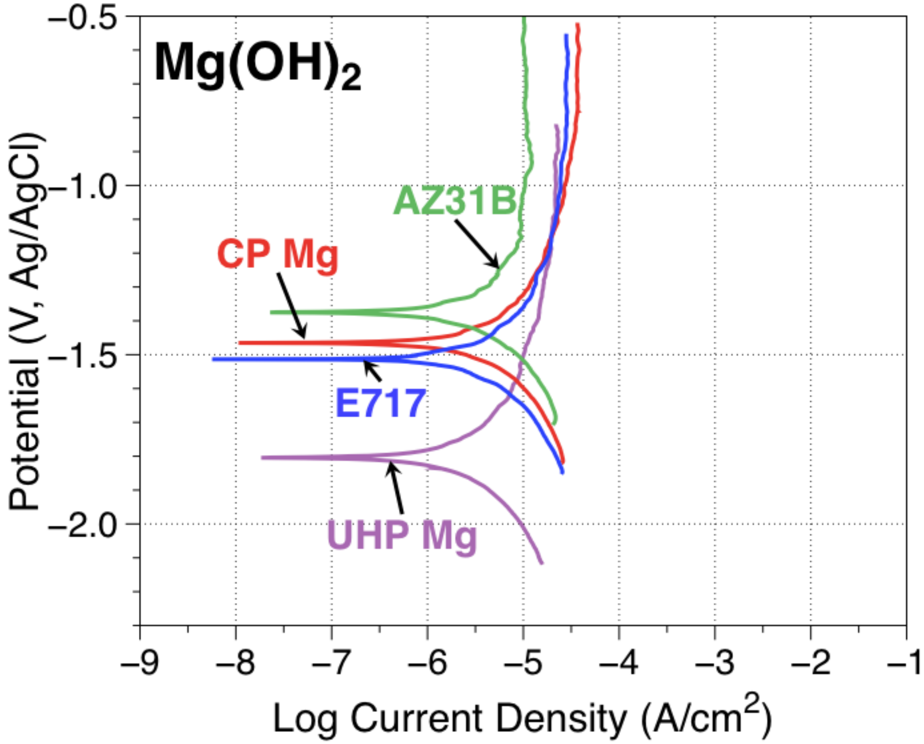
FY 2012: Sample technique development for focused ion beam (FiB) cross-section transmission electron microscopy (TEM) of Mg surface films. (September 2012). **MET**

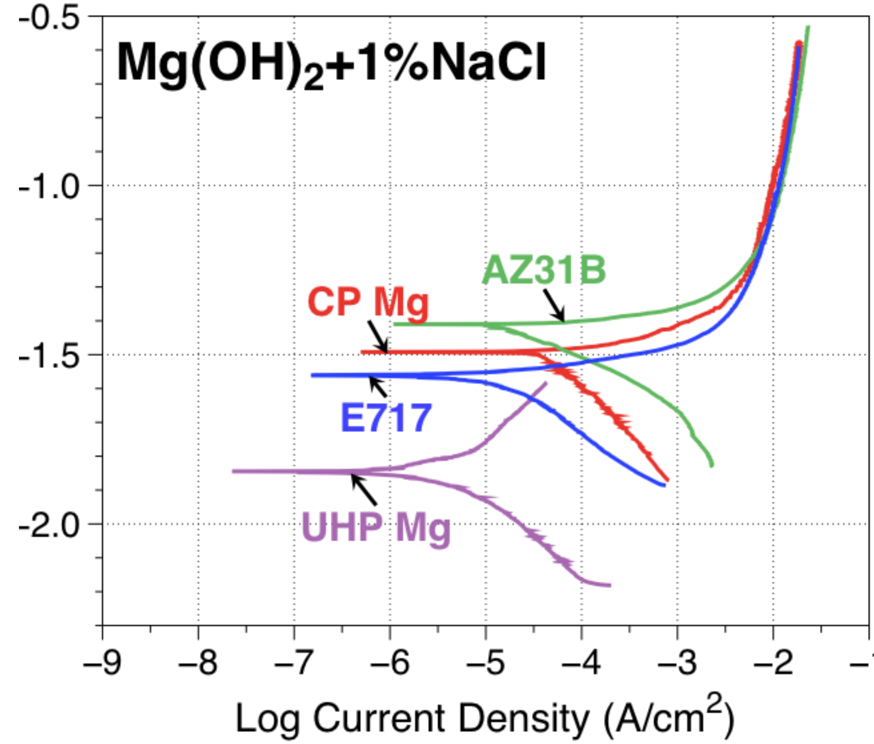
FY 2013: Determine feasibility to perform isotopic tracer studies (^{18}O, ^{2}H) to understand growth mechanism of surface films formed on Mg alloys. Go/No go decision for this experimental approach. (**August 31, 2013**) **On-Track**

FY 2013: Submit at least one journal article on magnesium alloy film growth based on down selected advanced characterization technique findings (**September 30, 2013**) **On-Track**

FY 2014/2015 Milestone metrics involve additional journal article submissions per DOE direction to focus on gaining improved understanding of Mg corrosion and widely disseminating findings

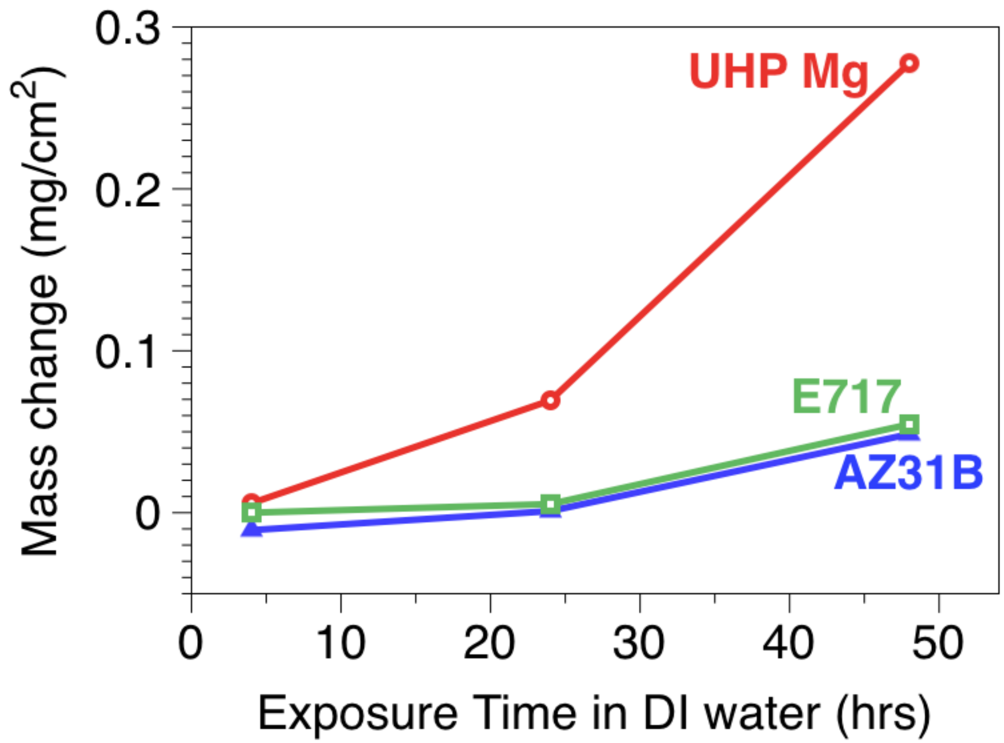
Corrosion Overview in $Mg(OH)_2$ Saturated Water With and Without NaCl





- Lower cathodic currents for UHP Mg due to high purity/absence of second phase precipitates in matrix
- Lower alloy content in E717 yields behavior closer to UHP Mg than AZ31B
- Increased currents/decreased corrosion resistance with salt

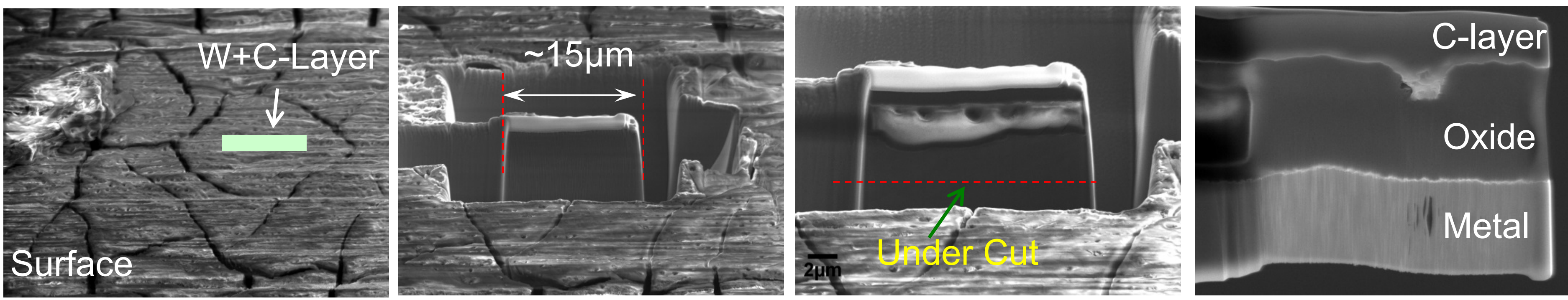
Similar Low Mass Gain for E717 and AZ31B on Immersion in Room-Temperature DI Water



- Highest mass gain for UHP Mg
- Uptick in mass gain rate for all 3 alloys between 24 and 48 h immersion
- TEM cross-sections performed at 4, 24, and 48 h water immersion to understand film growth trends (future work repeat with water + NaCl)

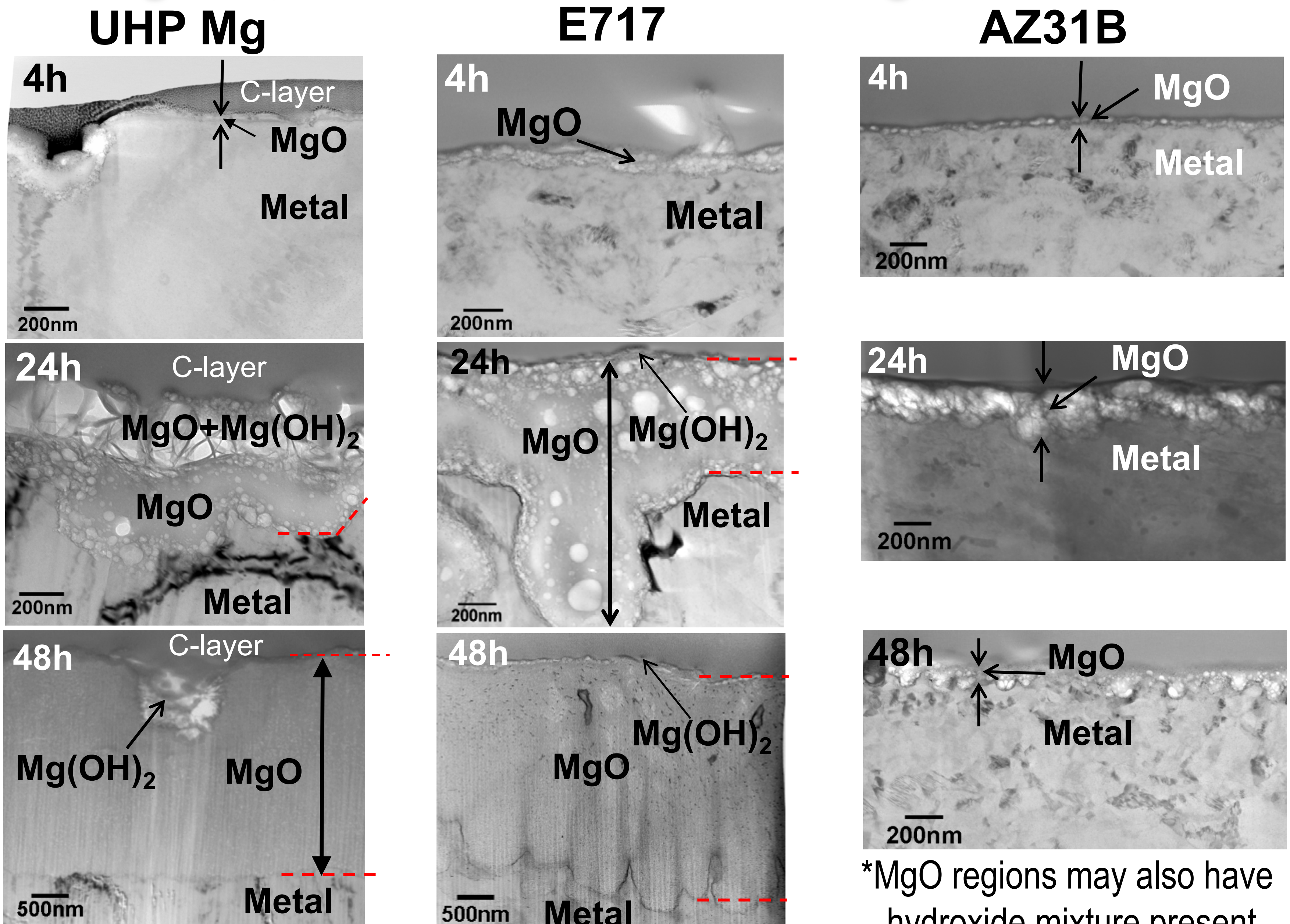
Preparation Techniques Successfully Developed for Cross-Section TEM

Preparation Technique via **F**ocused **I**on **B**eam Milling (FiB)



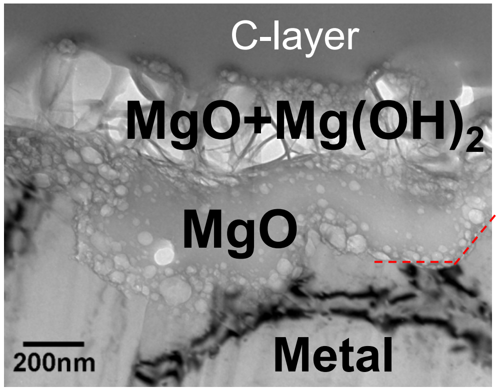
- Deposited W+C overlayer to protect film integrity during milling
- Can target specific local regions of interest for analysis
- Cross-section region lifted out and available for advanced characterization

Irregular, Thick Films on UHP Mg, E717 in Water



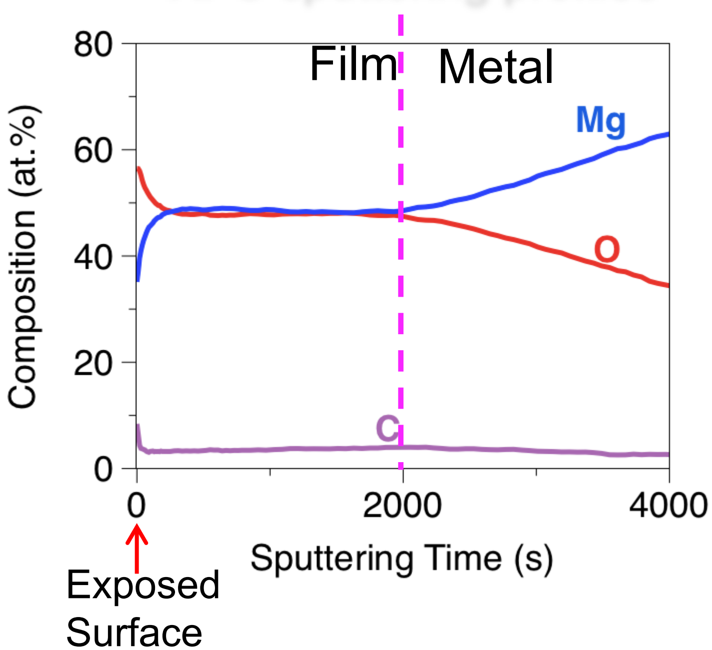
*MgO regions may also have hydroxide mixture present

24h Water UHP Mg: XPS+SIMS+TEM Suggests Film is Primarily MgO+H with $Mg(OH)_2$ at Surface

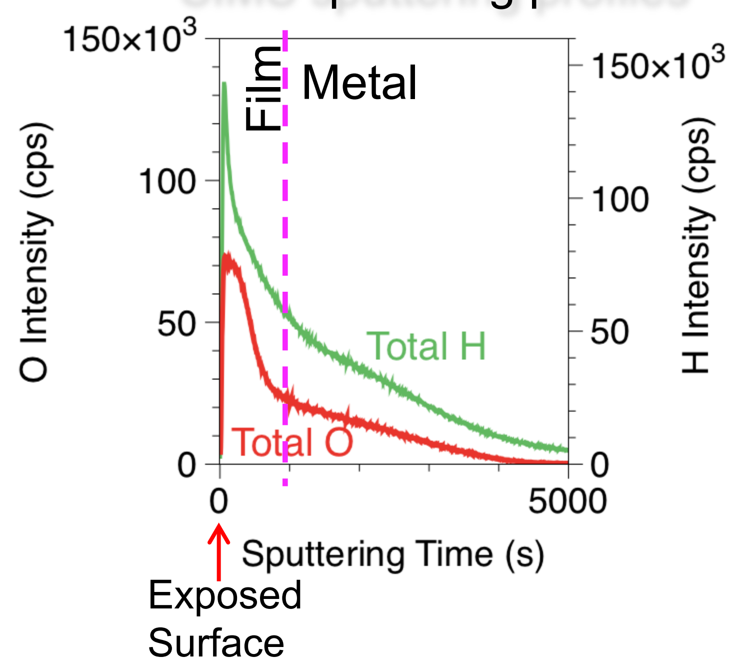


- Film is irregular thickness, film/metal interface in XPS + SIMS not sharp
- XPS shows some hydroxide near surface and small carbonate signal
- SIMS shows H in MgO regions and H penetration into metal, some O into metal?

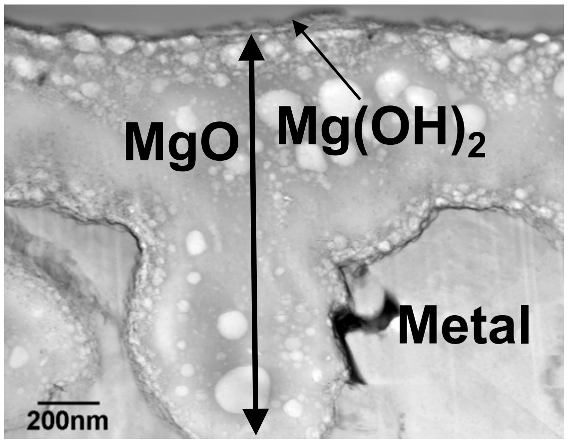
XPS sputtering profiles



SIMS sputtering profiles

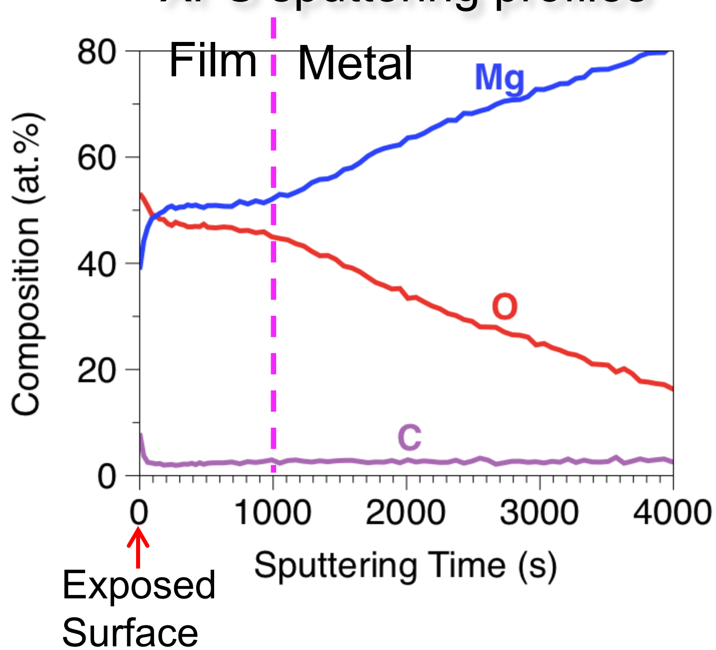


24h Water E717: XPS+SIMS+TEM Suggests Film is Primarily MgO+H with $Mg(OH)_2$ at Surface

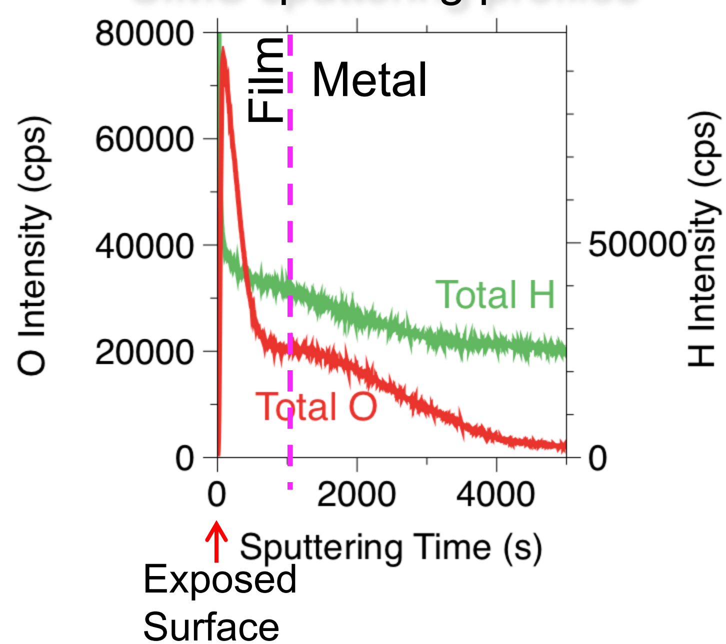


- Film similar (thinner) to UHP Mg: irregular thickness, film/metal interface not sharp
- XPS shows some hydroxide near surface and small carbonate signal
- SIMS shows H in MgO regions and <u>extensive H penetration into metal</u>, some O into metal?

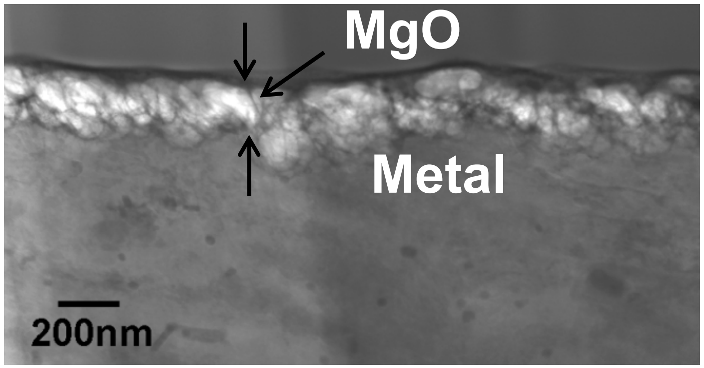
XPS sputtering profiles



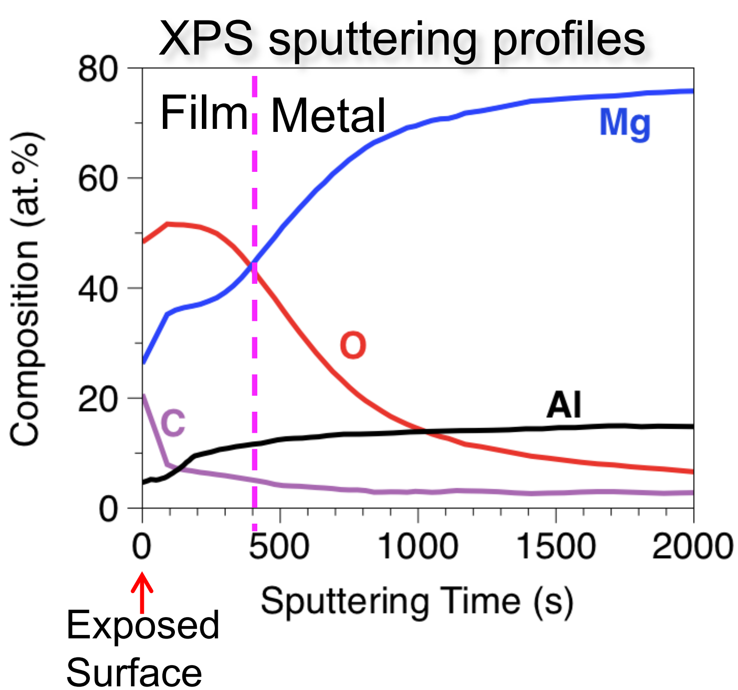
SIMS sputtering profiles

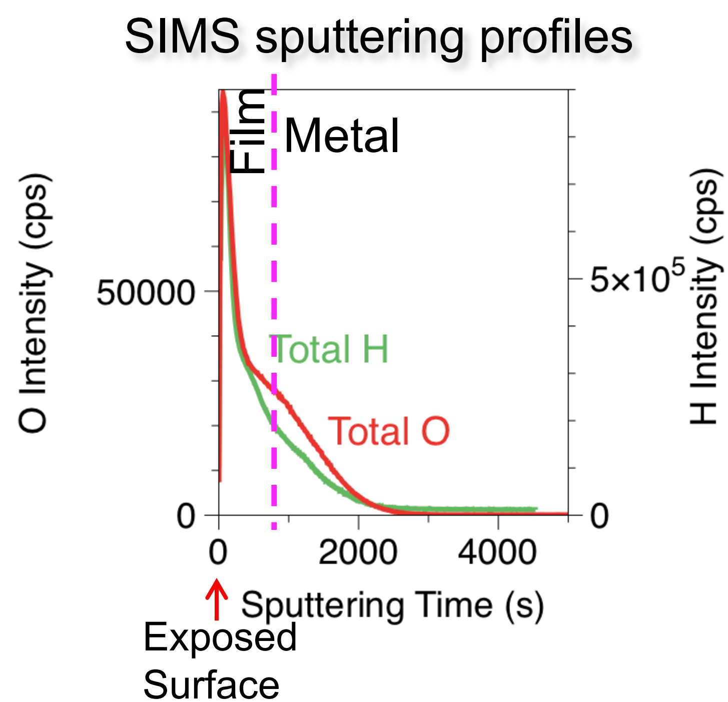


24h Water AZ31B: XPS+SIMS+TEM Suggests Thin MgO + $Mg(OH)_2$ Film



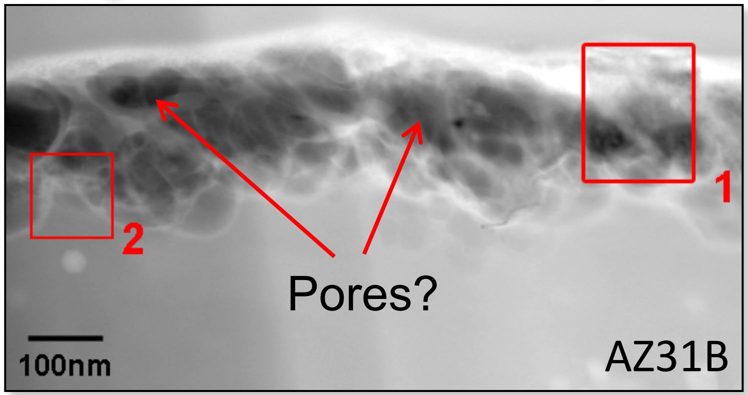
- Film far thinner than on UHP Mg and E717
- XPS shows some hydroxide near surface, small carbonate signal, Al in inner film
- SIMS shows H/O track together (mixed oxide + hydroxide?), H,O penetration into metal



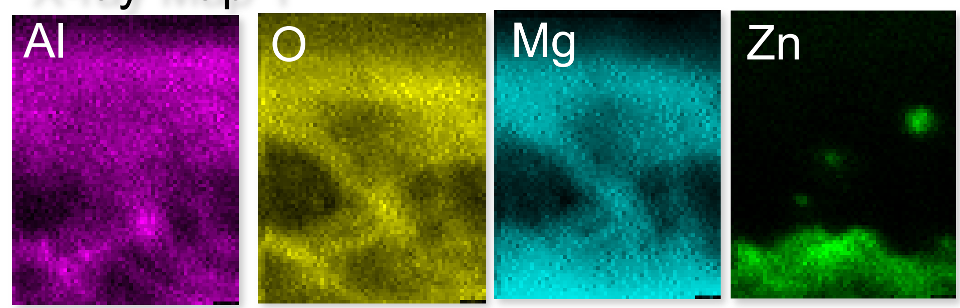


24h Water AZ31B: Thin Film Enriched With Al and Zn Near Metal/Film Interface

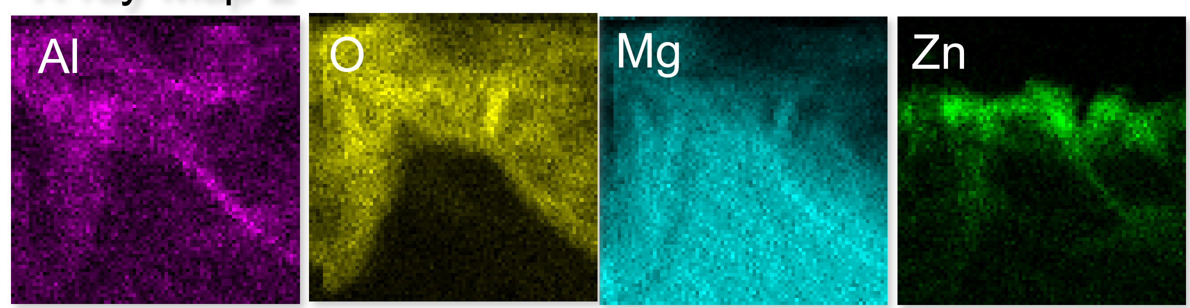
High Angle Annular Dark Field (HAADF) Image



X-ray Map 1

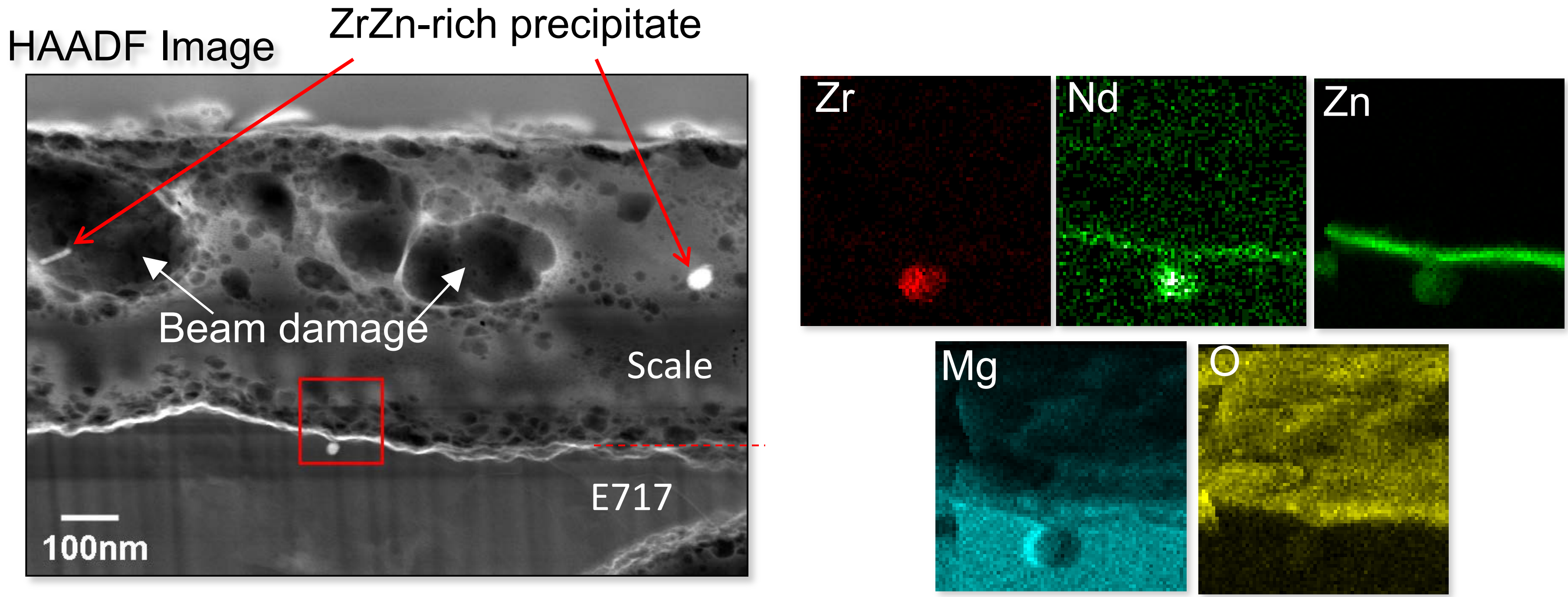


X-ray Map 2



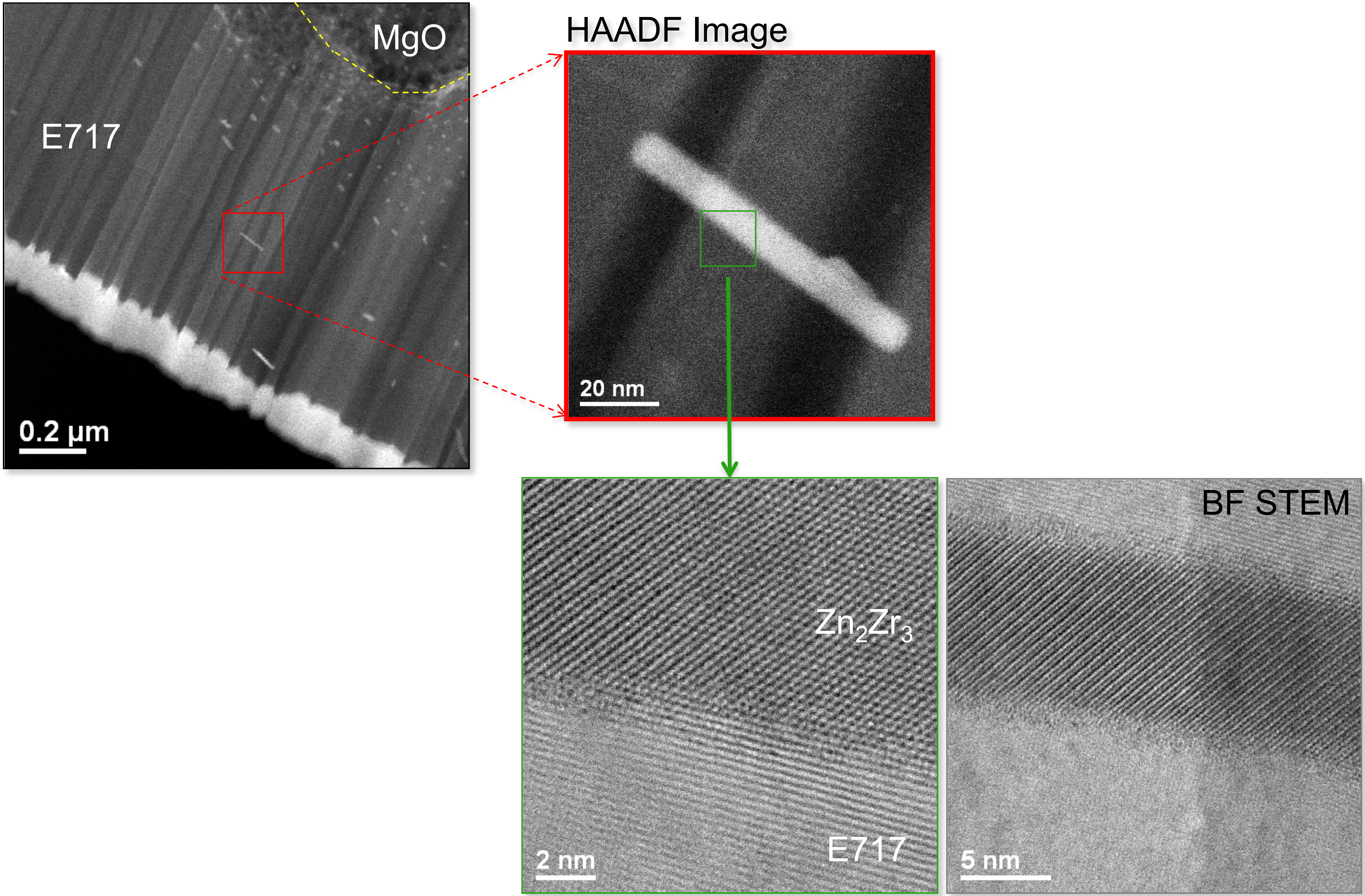
- Zn enrichment at metal/film interface
- Al present in the inner film (source of thinner film?)
- Zn precipitates present in the film

24h Water E717: Metal/Film Interface Enriched with Nd and Zn

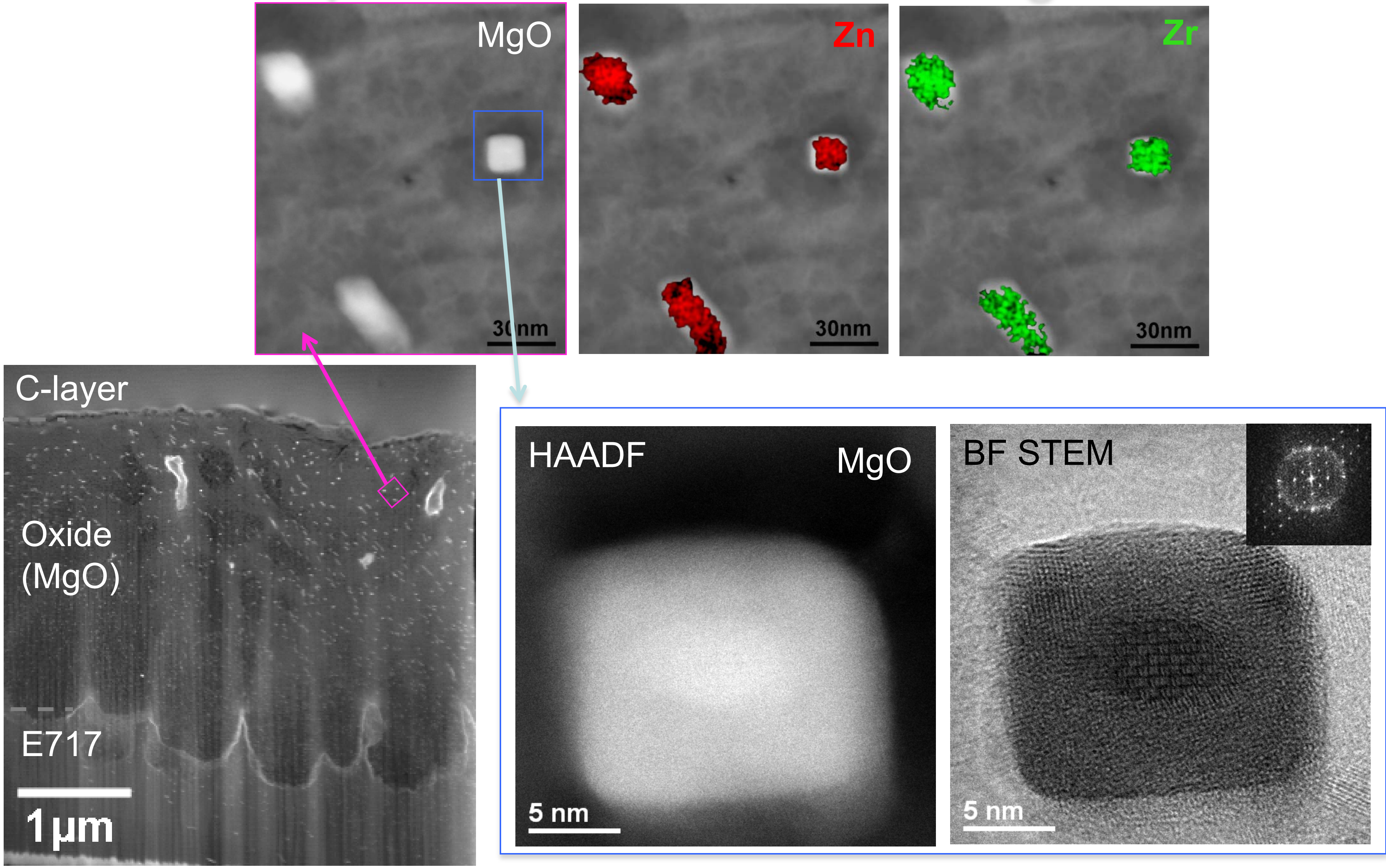


- Zn enrichment at metal/film interface (similar to AZ31B)
- Nd enrichment at metal/film interface
- ZnZr-rich precipitates: investigate with probe corrected microscope
- Beam damage artifact induced porosity: small angle neutron scattering to determine degree of actual nanoporosity in film

48h Water E717: Zn_2Zr_3 Nano Precipitate in Alloy

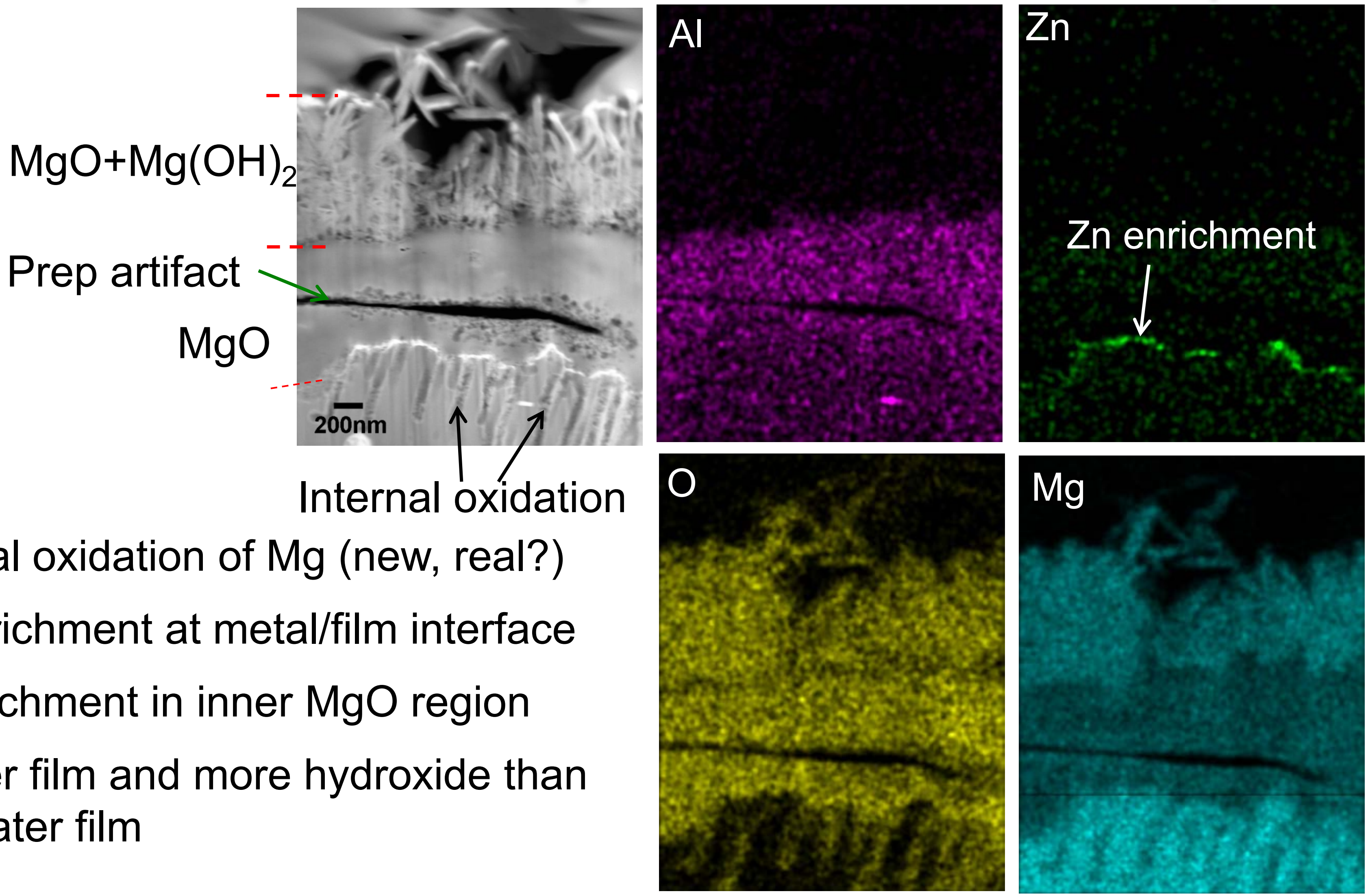


48h Water E717: Zn_2Zr_3 Nano Precipitate Incorporated into Inward Growing Film



24h, 5 Wt.% NaCl in Water AZ31B: Thick Film with Possible Internal Oxidation at Metal/Film Interface

Preliminary TEM Film Section and EDS Maps



- Internal oxidation of Mg (new, real?)
- Zn enrichment at metal/film interface
- Al enrichment in inner MgO region
- Thicker film and more hydroxide than 24 h water film

Collaboration and Coordination With other Institutions

- Bruce Davis of Magnesium Elektron North America

  -In-kind cost share partner for manufacture of model and commercial alloys, conversion coatings ($210k planned total cost share)

  -Ongoing role with experimental planning and interpretation

  -Partner in joint user proposal for neutron scattering studies (details follow)

- Mostafa Fayek, Canada Research Chair in Isotope & Environmental Geochemistry

  -SIMS analysis for tracer studies of Mg film growth mechanism (unique capabilities and expertise from geochemical systems)

  -Longtime collaborator with ORNL geochemistry and materials science

Future Work

• Baseline water film formation for UHP Mg, E717, AZ31B established with TEM and XPS. Remainder of **FY 13**:

-Water film growth SIMS tracer study in progress w/ $^{1}H_2{}^{18}O$ and $^{2}H_2{}^{16}O$

- MENA + ORNL High Flux Isotope Reactor user time in May for small angle neutron scattering to assess film nanoporosity

  i) bare E717 and AZ31B

  ii) conversion coated E717 and AZ31B: alodine 5200 (epoxy base); Surtec 650 and Metalast TCP-HF (trivalent Cr-salt base)

  iii) as received and after 24 h water immersion

• Test matrix will expand to include model Mg+ X alloys to better understand differing behavior of E717 and AZ31B

• **FY14** work will move to include film formation in water + salt

Summary: Planned Milestone Journal Publications On-Track

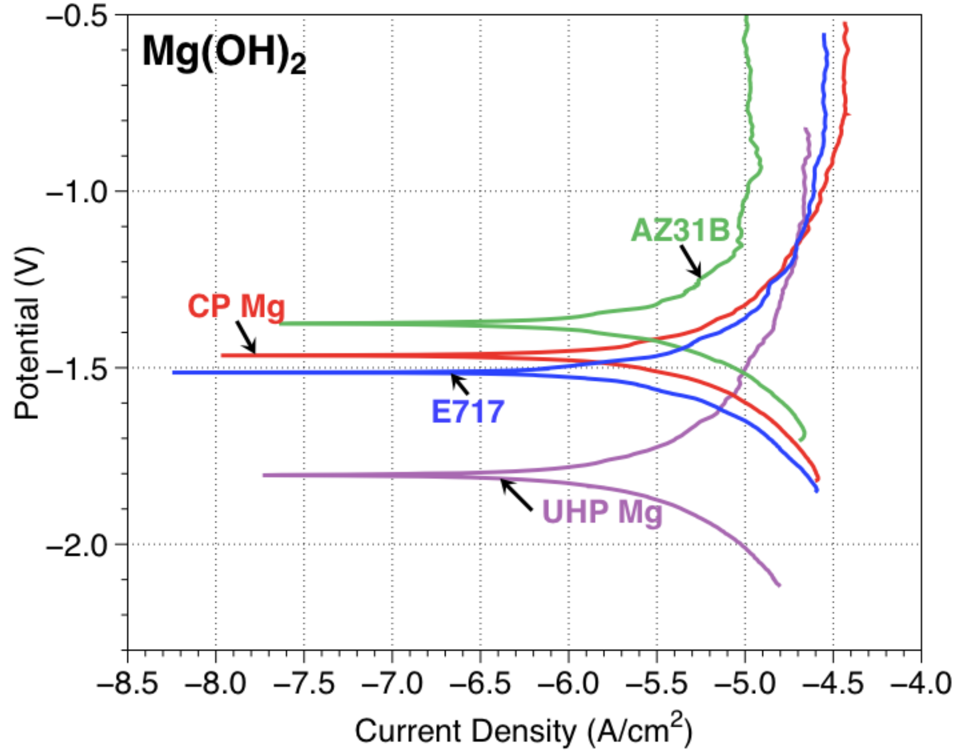
- Preparation techniques established for cross-section TEM of surface films formed on Mg
- Baseline studies of film formation in water for UHP Mg, E717, and AZ31B using TEM + XPS + SIMS nearly completed
  - -Films consisted primarily of H-enriched MgO, with surface regions also containing $Mg(OH)_2$ and carbonate
- Films significantly affected by alloying and exposure times
  - -AZ31B (thinnest): Al enriched at inner MgO, Zn at metal/film interface
  - -E717: Zn and Nd at metal/film interface. Inward growth incorporates nano Zn_2Zr_3 precipitates from alloy into film
- SIMS data suggest penetration of H and O into metal under film formed in water
  - -extensive H penetration in E717 (related to Zr, Nd addition?)

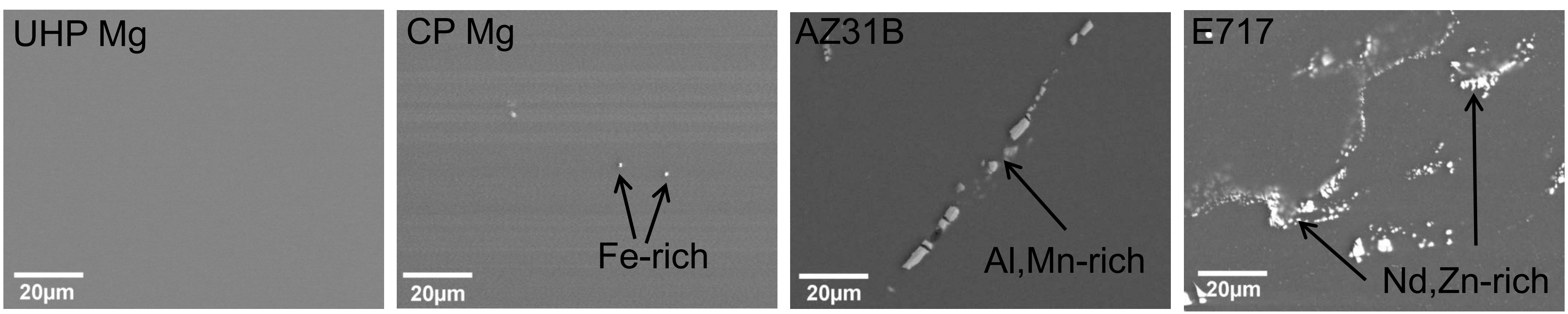
Technical Back-Up Slides

Collaboration and Coordination

- Bruce Davis of Magnesium Elektron North America
  - -In-kind cost share for model and commercial alloys, conversion coatings
  - -Ongoing role with experimental planning and interpretation
- Mostafa Fayek, Canada Research Chair in Isotope & Environmental Geochemistry: SIMS + Isotopic tracers
- Multi-Disciplinary ORNL Team (Brady + Unocic Co-PI's)
  - -M.P. Brady/J.R. Keiser: metallurgy + high-temperature oxidation
  - -K.A. Unocic: microscopy and corrosion background
  - -H. Elsentriecy: post-doc fellow, electrochemistry and Mg coatings
  - -H.M. Meyer III: surface chemist
  - -L. Anovitz: geochemistry (includes Mg-O-H systems)
  - -G. Rother: geochemistry and neutron scattering
  - -G. Muralidhardan: metallurgy, processing, and neutron scattering
  - -G. Song: New hire at ORNL, Mg corrosion and electrochemistry

Change in OCP due to Presence of 2nd Phases

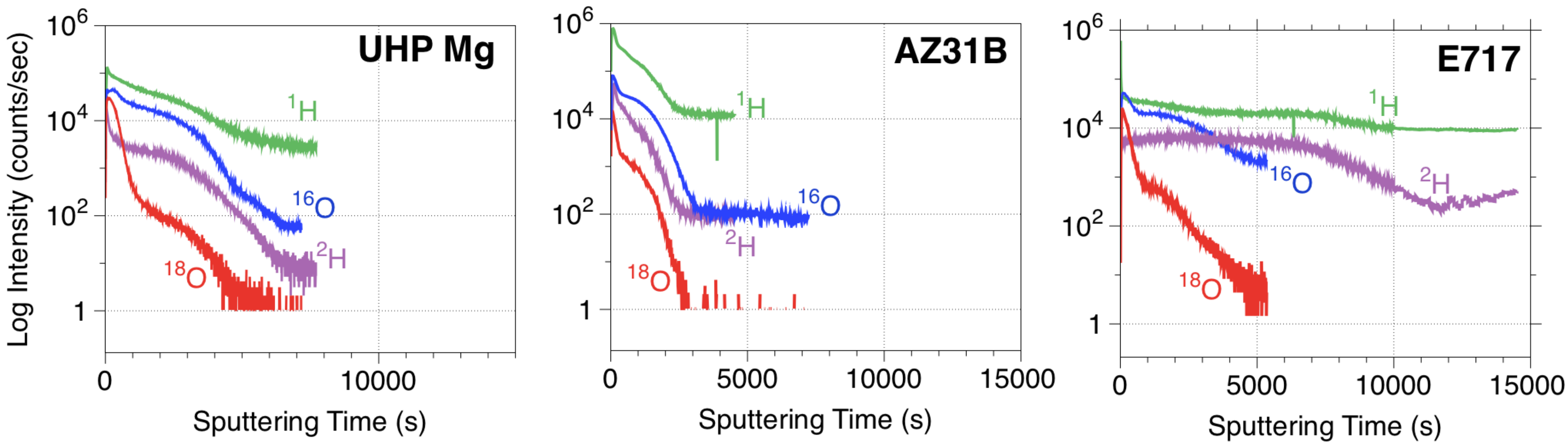




- Current density instead of OCP - reliable criteria parameter
- No significant difference in corrosion behavior in Mg(OH)$_2$ exposure

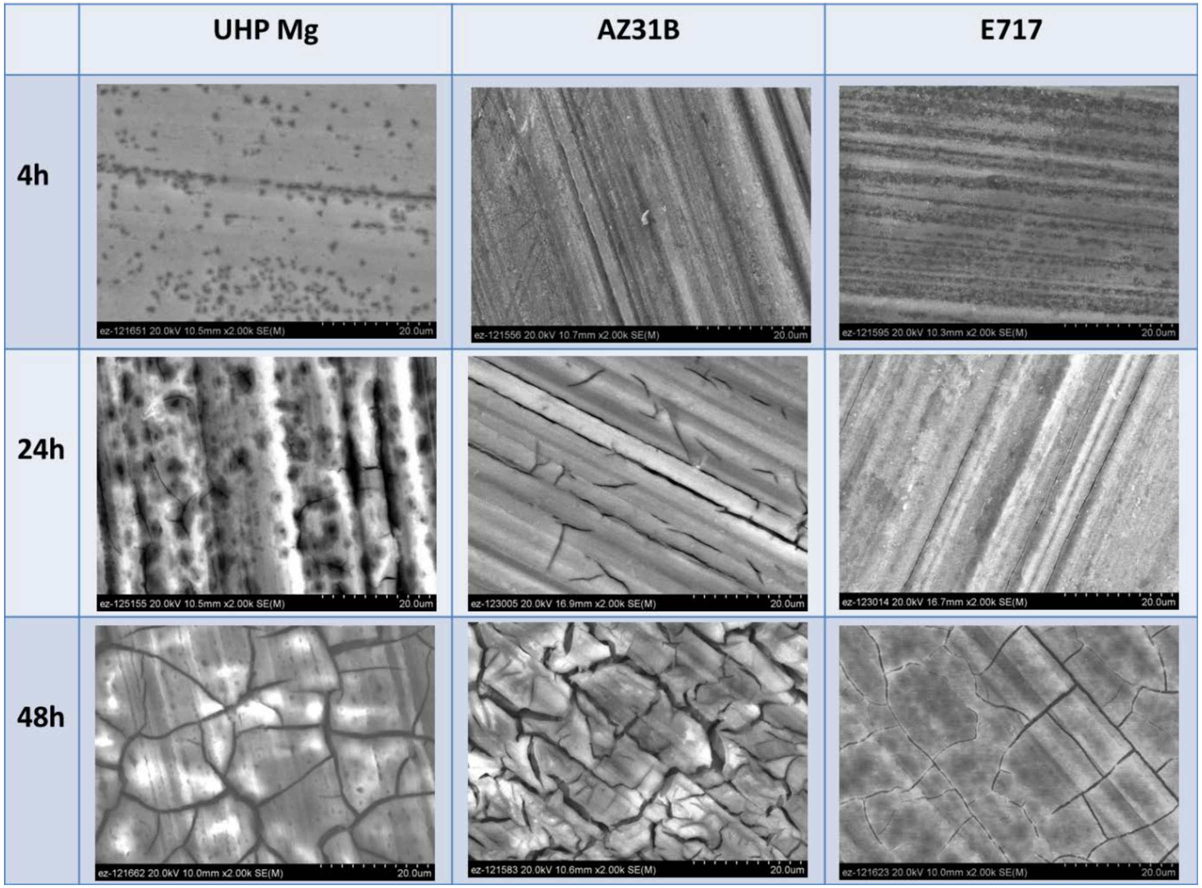
Preliminary Tracer Data Suggests Inward Film Growth and Significant H Penetration

Tracer Film Growth: 4 h immersion in ^{18}O water + 20 h in ^{2}H water (D_2O)



- Data suggests inward growth of surface film
- H penetrates far greater than O - suggests H in metal under film
- Extensive H penetration in Elek 717 - possibly RE effects (Nd, Zr)?

Surface SEM Analysis of Films Formed in Water Immersion



Surface cracking observed after 24 to 48 h of water immersion

i) volume increase from MgO → $Mg(OH)_2$?
ii) volume decrease from Mg→ MgO?
iii) dehydration? (cracks also observed optically so not caused by SEM vacuum)