A systematic multiscale modeling and experimental approach to understand corrosion at grain boundaries in magnesium alloys

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Project ID: LM095
• Why Use Magnesium
  – Lightweight to replace heavy engine parts
  – High stiffness to weight ratio
  – High strength to weight ratio
  – Excellent castability and damping capacity
  – Easily corroded in the presence of salt-water

• Why ICME and Multiscale Modeling
  – Reduce product development time
  – Reduce product costs through innovation in material, product, and process designs
  – Reduce the number of costly large systems scale experiments
  – Increase product quality and performance by providing more accurate predictions of response to design loads
  – Help develop new materials
Multiscale Corrosion Modeling

Bridge 1 = Surface Energy, Cohesive Energy, Electrochemical Potential
- Atomistics - MD
- Nanoscale - Electronics Principles (DFT)

Bridge 2 = Microstructural features
- Macroscale
- Mesoscale - Butler-Volmer

Bridge 3 = Anodic, cathodic reactions

Bridge 4 = Particle interactions
- Macroscale

Bridge 5 = Elastic Moduli, valence, Alloy formation energy, H₂O dissociation energy, H atom adsorption energy

Bridge 6 = Nanoscale Mg Dissolution, Hydrogen evolution

Bridge 7 = Anodic/cathodic reaction

Bridge 8 = Pit Nucleation

Bridge 9 = Pit growth, Pit coalescence

Bridge 10 = Material Model

10-100 µm

100’s Nm
Multiscale Corrosion Internal State Variable (ISV) model

Effect: Macroscopic Corrosion Damage (Electrochemical Potential, Hydrogen Evolution Rate, Anodic Dissolution Rate)

**Step 1:**
Downscaling Requirements
- Nanoscale anodic and cathodic reactions and surface reaction kinetics affected by doping elements

_Cause:_ uncertainties (determined by simulations at lower length scale)

**Step 2:** Simulation at NanoScale (DFT) and Atomics scale (MD)
- Effect of doping on surface stability
- Adsorption energies of molecules relevant to corrosion
- Identify the role of cathodic impurities (elements) vs cathodic precipitates (phases)
- Water dissociation reactions
- Mg dissolution reactions
- Hydrogen evolution reactions

**Step 3:**
Upscaling Results
- Microstructure
- Hydrogen volume
- Magnesium loss (volume)
- Equation Trends for anodic and cathodic reactions
• Macroscale Corrosion Damage Framework
• Mesoscale Corrosion Modeling
• Nanoscale Corrosion Simulation
• Experiment Calibration
• Application and Implementation
What is an Internal State Variable (ISV) ?

- Uniquely defines the Helmholtz (or Gibbs) free energy of a system undergoing an irreversible process
- Describes the internal structure rearrangement with the associated length scales
- Selection is arbitrary, but the rate equations are physically motivated (microstructural morphology) and strongly influence the history of the material and can be garnered from lower length scale arguments
Kinetics of Plasticity-Damage-Corrosion Framework

- Corrosion Damage

Macroscopic observation examples of the (a) general, (b) pitting, and (c) intergranular damage mechanisms on specimen surfaces (Alvarez et al., 2010)

\[
\phi_c = \phi_{gc} + \phi_{pc} + \phi_{ic} \\
\dot{\phi}_{total} = \dot{\phi}_{gc} + \dot{\phi}_{pc} + \dot{\phi}_{ic} \\
\phi_{pc} = \eta_p \nu_p c_p \\
\dot{\phi}_{pc} = \eta_p \nu_p c_p + \eta_p \dot{\nu}_p c_p + \eta_p \nu_p \dot{c}_p
\]

Macroscale-Mesoscale Bridge Information

Macroscale: Internal State Variable Theory

\[ \dot{\phi}_{total} = \dot{\phi}_{gc} + \dot{\phi}_{pc} + \dot{\phi}_{ic} \]
\[ \dot{\phi}_{gc} = \frac{C_1 M}{Fz} (C_2 - \phi_{gc}) \]
\[ \dot{\phi}_{pc} = \dot{\eta}_p \psi_p c_p + \eta_p \psi_p \dot{c}_p \]
\[ \dot{\phi}_{ic} = \begin{cases} C_{15} (C_{16} - \phi_{ic}) \left( \frac{MO}{MO_0} \right)^{z_{ic}} & \text{if } t < t_c \\ C_{17} (C_{18} + \phi_{ic}) \left( \frac{MO}{MO_0} \right)^{z_{ic}} & \text{if } t \geq t_c \end{cases} \]

Mesoscale: Butler-Volmer Equation

\[ I = A \cdot j_0 \cdot \left\{ \exp \left[ \frac{\alpha_a nF}{RT} (E - E_{eq}) \right] - \exp \left[ -\frac{\alpha_c nF}{RT} (E - E_{eq}) \right] \right\} \]

- \( I \): electrode current
- \( A \): electrode active surface area
- \( J \): electrode current density
- \( E \): electrode potential
- \( E_{eq} \): equilibrium potential
- \( \alpha_a \): anodic charge transfer coefficient
- \( \alpha_c \): cathodic charge transfer coefficient
Outline

- Macroscale Corrosion Damage Framework
- Mesoscale Corrosion Modeling
- Nanoscale Corrosion Simulations
- Experiment Calibration
- Application and Implementation
Mesoscale Modeling/Simulations

\[ I = A \cdot j_0 \cdot \left\{ \exp \left[ \frac{\alpha_a nF}{RT} (E - E_{eq}) \right] - \exp \left[ - \frac{\alpha_c nF}{RT} (E - E_{eq}) \right] \right\} \]

- \( I \): electrode current
- \( A \): electrode active surface area
- \( j \): electrode current density
- \( E_{eq} \): equilibrium potential
- \( E \): electrode potential

\[ 2\text{H}_2\text{O}_{\text{ads}} + 2e^- \rightarrow 2\text{OH}_{\text{ads}} + \text{H}_2 \]

- \( \alpha_c \): cathodic charge transfer coefficient

\[ \text{Mg} \rightarrow \text{Mg}^{+2} + 2e^- \]

- \( \alpha_a \): anodic charge transfer coefficient

\( a_c = f(\text{second phase number density, second phase particle size, second phase nearest neighbor distance, matrix composition, solution type (water, salt water, etc.), and hydrogen evolution}) \)

\( a_a = f(\text{second phase number density, second phase particle size, second phase nearest neighbor distance, matrix composition, solution type (water, salt water, etc.), and magnesium dissolution rate}) \)
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Mesoscale-Nanoscale Bridge Information

Mesoscale: Butler-Volmer Equation

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- \( I \): electrode current
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- \( \alpha_c \): cathodic charge transfer coefficient
- \( \alpha_a \): anodic charge transfer coefficient

Nanoscale: Kohn-Sham Equations

\[ E[\rho] = T_s[\rho] + \int d\mathbf{r} \ v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + V_H[\rho] + E_{xc}[\rho] \]

\[ T_s[\rho] = \sum_{i=1}^{N} \int d\mathbf{r} \ \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2\right) \phi_i(\mathbf{r}). \]

\[ V_H = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \ \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \]

\[ v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \]

\[ E = \sum_i \epsilon_i - V_H[\rho] + E_{xc}[\rho] - \int \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) d\mathbf{r} \]
Background: Atomistic Framework

Oxide layer protection: Previous DFT investigation

- DFT Calculated Grain Boundary and bulk doping of MgO developed previously
- Rare-earth doping improve oxide layer stability
- Grain boundary segregated of species that bound water strongly are favorable
- Aggressive species interaction with oxide layer underway

Anodic dissolution and galvanic coupling to cathodic precipitates

- Anodic and cathodic reactions for corrosion progression in Mg-X alloys
- Alloying elements and surface reaction kinetics
- Connection to microstructure and cathodic precipitate distribution
- Multiscale connection to experiments and ISV model

Corrosion Reactions in Mg-Alloys

- Overall Reaction can be expressed as: \( \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \)

- Contributing half-cell reactions
  - Anodic: Oxidation reaction
    \( \text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \)
  - Cathodic: Reduction reaction
    \( 2\text{H}_2\text{O}_{ads} + 2\text{e}^- \rightarrow 2\text{OH}_{ads} + \text{H}_2 \)
    \( \text{Mg}^{2+} + 2\text{OH} \rightarrow \text{Mg(OH)}_2 \)
  - Corrosion product
    \( \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \)

- Alloying elements Mg-X (X=Ca, Al, Mn, Fe, Zn, As..) change cathodic/anodic reactions

- Alloying element and segregation change MgO ↔ Mg(OH)_2 dissolution/precipitation/transport kinetics
Kohn-Sham Eqtns used in Density Functional Theory (DFT) Calculations

- Overall Reactions calculated using DFT methods on Mg(001) slab surface
- Alloying elements Mg-X (X=Ca,Al,Mn,Fe,Zn,As..) compared
- Focus on Mg-Al results for establishing understanding and baseline of corrosion rates
- Identify the role of cathodic sites (elements) vs cathodic precipitates (phases)

Less Al in preferred compared to higher Al% in terms of alloy formation energy

\[ E_{\text{mixing}} = \left( E_{\text{total}} - n_{\text{Mg}} E_{\text{Mg(bulk)}} - n_{\text{Al}} E_{\text{Al(bulk)}} \right) / (n_{\text{Mg}} + n_{\text{Al}}) \]

Energy of Mg-Al Bulk System with Al at Different Concentrations

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e^- \\
2\text{H}_2\text{O}_{\text{ads}} + 2e^- & \rightarrow 2\text{OH}_{\text{ads}} + \text{H}_2 \\
\text{Mg}^{2+} + 2\text{OH} & \rightarrow \text{Mg(OH)}_2 \\
\text{MgO} + \text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2
\end{align*}
\]
DFT Calculations for Water Dissociation Reactions

Show that as the %AL Increases the Barrier Energy Decreases

- Water transports through the MgO/Mg(OH)$_2$ layer and reacts with Mg-alloy matrix
- Al in-solution of Mg matrix and Mg$_{17}$Al$_{12}$ phase are investigated

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{ad}$, $H_2O$ (eV)</th>
<th>$E_{ad}$,H (eV)</th>
<th>$E_{ad}$,OH (eV)</th>
<th>$\Delta H_{Rxn}$ (eV)</th>
<th>$E_{Barrier}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg</td>
<td>-0.43</td>
<td>-2.38</td>
<td>-4.95</td>
<td>-1.09*</td>
<td>0.65</td>
</tr>
<tr>
<td>Mg-1Al</td>
<td>-0.50</td>
<td>-2.45</td>
<td>-5.01</td>
<td>-1.16</td>
<td>0.64</td>
</tr>
<tr>
<td>Mg-2Al</td>
<td>-0.54</td>
<td>-2.40</td>
<td>-5.10</td>
<td>-1.15</td>
<td>0.64</td>
</tr>
<tr>
<td>Mg$<em>{17}$Al$</em>{12}$</td>
<td>-0.66</td>
<td>-2.52</td>
<td>-5.14</td>
<td>-1.20</td>
<td>0.62</td>
</tr>
</tbody>
</table>

$\Delta H_{correction}$: -0.17 $\Delta G_{correction}$: -0.04

Barrier of H$_2$O dissociation more favorable for beta-phase Mg$_{17}$Al$_{12}$

H$_2$O/OH binds strongly but H adsorption shows trend reversal at higher Al concentration
Mg-X Alloys: Impurity Promotes Water Dissociation Reactions

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{\text{ads}, \text{H}_2\text{O}}$ (eV)</th>
<th>$E_{\text{ads}, \text{H}}$ (eV)</th>
<th>$E_{\text{ads}, \text{OH}}$ (eV)</th>
<th>$\Delta H_{\text{Rxn}}$ (eV)</th>
</tr>
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<td>-0.43</td>
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<td>-1.09</td>
</tr>
<tr>
<td>Mg-Al</td>
<td>-0.50</td>
<td>-2.45</td>
<td>-5.01</td>
<td>-1.16</td>
</tr>
<tr>
<td>Mg-Zn</td>
<td>-0.51</td>
<td>-2.44</td>
<td>-5.04</td>
<td>-1.17</td>
</tr>
<tr>
<td>Mg-Ca</td>
<td>-0.74</td>
<td>-2.66</td>
<td>-5.19</td>
<td>-1.30</td>
</tr>
<tr>
<td>Mg-Mn</td>
<td>-0.45</td>
<td>-2.63</td>
<td>-4.95</td>
<td>-1.33</td>
</tr>
<tr>
<td>Mg-Fe</td>
<td>-0.47</td>
<td>-2.68</td>
<td>-4.98</td>
<td>-1.38</td>
</tr>
</tbody>
</table>

In general cathodic impurities promote water dissociation but also increase H adsorption.
Mg-X Alloys: Mg Dissolution Reactions

Defect formation energy is important since anodic dissolution is first step for metal loss and Mg(OH)$_2$ precipitation. Reaction happens at two interfaces:

- On the MgO/Mg(OH)$_2$ interface
- At the metal layer/oxide/hydroxide layer – Mg(0001) used a guide for the trends

Barrier layer in Mg is ineffective – thus, anodic dissolution trend is determined by dissolution at the grain boundaries and from flat surfaces.
**Mg-Al Corrosion: H₂ Evolution Reaction Trend**

Cathodic Rxn’s followed

\[ \text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H}_{\text{ads}} \]

\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \]

**Reaction barrier (rate) depend on H atom adsorption energy**

- **Mg**: \( E_{\text{ads}} = -2.38 \text{ eV} \)
- **Mg-1Al**: \( E_{\text{ads}} = -2.45 \text{ eV} \)
- **Mg-2Al**: \( E_{\text{ads}} = -2.40 \text{ eV} \)
- **Mg\textsubscript{17}Al\textsubscript{12}**: \( E_{\text{ads}} = -2.52 \text{ eV} \)

**The final H₂ evolution rate near cathodic Al-sites and Mg\textsubscript{17}Al\textsubscript{12} decrease – Less corrosion as seen in experiments**
For Mg-2% Al alloy, no second phase was formed, dendritic arm region and grain boundaries have higher aluminum intensity.

For Mg-6% Al alloy, Mg$_{17}$Al$_{12}$ phase was formed, the second phase mainly distributed along grain boundaries and dendritic arm region.

<table>
<thead>
<tr>
<th>Materials</th>
<th>grain size (um)</th>
<th>particle size (um)</th>
<th>Particle Number density (mm$^2$)</th>
<th>NND (um)</th>
<th>Particle type</th>
<th>Matrix type</th>
<th>Mean area of second phase particle (um$^2$)</th>
<th>Second phase particle area fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-2% Al</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-6% Al</td>
<td>161.25</td>
<td>5.6</td>
<td>1434</td>
<td>13.172</td>
<td>M$<em>{17}$Al$</em>{12}$</td>
<td>saturated Al</td>
<td>31.368</td>
<td>4.494%</td>
</tr>
</tbody>
</table>
Outline

- Corrosion Damage Framework
- Mesoscale Corrosion Modeling
- Nanoscale Corrosion Simulation
- Experiment Calibration
- Application and Implementation
General Corrosion Model Calibration

\[
\dot{\phi}_{total} = \dot{\phi}_{gc} + \dot{\phi}_{pc} + \dot{\phi}_{ic}
\]

General corrosion refers to corrosion dominated by uniform thinning that proceeds without appreciable localized attack.

\[
\dot{\phi}_{gc} = \frac{C_1 M}{F \xi} (C_2 - \phi_{gc})
\]

\[
C_1 = 10 \xi^2 + 70 \xi - 250 \quad C_2 = 47 \xi^{-0.075}
\]

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow
\]

Faraday’s Law of electrolysis summarizes mass loss based on the total electric charge of the substance.

\( m \) – mass

\( F \) – Faraday constant

\( M \) – the molar mass of the substance

\( z \) – the valence number of ions

\( \xi \) – Al percentage in the materials
Pitting Corrosion-Nucleation Calibration

\[ \dot{\phi}_{pc} = \dot{\eta}_p \nu_p c_p + \eta_p \dot{\nu}_p c_p + \eta_p \nu_p \dot{c}_p \]

The nucleation term is defined as the number density/unit area

\[ \dot{\eta} = \begin{cases} C_3 (C_4 - \eta) & \text{if } t < t_{critical} \\ C_5 (C_6 - \eta) & \text{if } t \geq t_{critical} \end{cases} \]

\[ t_{critical} = 1.1437 e^{0.05253 \xi} \]

\[ C_3 = 0.17 \ln(\xi) + 0.5344 \quad C_4 = 128.57 \xi + 1607.1 \]

\[ C_5 = -0.0016 \xi + 0.0593 \quad C_6 = 741.88 \xi^{0.1513} \]

where \( C_3, C_4, C_5, C_6 \) are material parameters, that are related to material’s Al percentage, \( \xi \), in this study, and as a function of second phase/particle volume fraction, particle size, temperature, pH level. \( t_{critical} \) is the transition time from pit nucleation dominated to pit coalescence or general corrosion dominated.
Pitting Corrosion-Growth Calibration

\[
\dot{\phi}_{pc} = \dot{\eta}_p \nu_p c_p + \eta_p \dot{\nu}_p c_p + \eta_p \nu_p \dot{c}_p
\]

The growth term signifies the pit area at which pits are growing across the surface.

\[
\dot{v}_p = \begin{cases} 
C_7(C_8 - A) & \text{if } t < t_{\text{critical}} \\
C_9(C_{10} + A) & \text{if } t \geq t_{\text{critical}}
\end{cases}
\]

\[
C_7 = 0.0425e^{0.3214\xi}
\]

\[
C_8 = 253.25\xi + 1533.7
\]

\[
C_9 = 0.0038\xi^2 - 0.0099\xi + 0.0012
\]

\[
C_{10} = 1.2499\xi^2 - 0.4996\xi - 1
\]

where \(C_7, C_8, C_9, C_{10}\) are material parameters that relate to Al percentage in the materials, also are as a function of temperature, pH level, and materials microstructural characteristics.

\(A\) is the average in-plane pit area on the specimen surfaces, please notice that \(A\) can also be the average pit volume if you measured pit volume instead of in-plane pit area.
Pitting Corrosion-Coalescence Calibration

\[ \dot{\phi}_{pc} = \dot{\eta}_p \nu_p c_p + \eta_p \dot{\nu}_p c_p + \eta_p \nu_p \dot{c}_p \]

The coalescence rate can be directly related to the nearest neighbor distance of two pits on the surface

\[ N\dot{N}D = \begin{cases} C_{11}(C_{12}-NND) & \text{if } t < t_c \\ C_{13}(C_{14}-NND) & \text{if } t \geq t_c \end{cases} \]

\[ \dot{c}_p = \frac{k_e q_1 q_2}{\varepsilon_0 \pi (N\dot{N}D(t))^4} \]

- \( k_e \) is the proportionality constant = \( 8.987 \times 10 \) Nm\(^2\)/C\(^2\)
- \( q_1 \) and \( q_2 \) are point charges
- \( \varepsilon_0 \) is the electric constant = \( 8.854 \times 10^{-12} \) F/m
- \( NND \) is the separation distance between pits
- \( \dot{c}_p \) is the coalescence rate

Coulomb’s Law and Maxwell’s stress both represent an electrostatic interaction between two charged particles with respect to the force on the body.
Intergranular Corrosion Calibration

\[
\dot{\phi}_{\text{total}} = \dot{\phi}_{gc} + \dot{\phi}_{pc} + \dot{\phi}_{ic}
\]

Intergranular corrosion takes place when the corrosion rate of the grain-boundary areas of an alloy exceeds that of the grain interiors.

\[
\begin{align*}
\dot{\phi}_{ic} &= \begin{cases} 
C_{15}(C_{16} - \phi_{ic}) \left( \frac{MO}{MO_0} \right)^{z_{ic}} & \text{if } t < t_c \\
C_{17}(C_{18} + \phi_{ic}) \left( \frac{MO}{MO_0} \right)^{z_{ic}} & \text{if } t \geq t_c
\end{cases}
\end{align*}
\]

Form of localized corrosion caused by precipitates and segregation leading to the formation of microgalvanic cells, \( \left( \frac{MO}{MO_0} \right)^{Z_{ic}} \) is a misorientation factor that represents galvanic cells formed, \( C_{15}, C_{16}, C_{17}, C_{18} \) are material parameters.
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Application-Casted Mg alloys in 3.5 wt.% NaCl solution Environment

- **General Corrosion**

- **Pit nucleation**

- **Pit Growth**
Summary

Preliminary Conclusion

• Developed a fully coupled ISV model that captures the corrosion damage evolution for magnesium alloys
• Bridged information passage from different length scale
• Completed corrosion calibration experiments for Mg-Al alloys
• Qualitative agreement with DFT that pure Mg H-evolution is greater compared to Mg-Al
• Anodic dissolution of Mg-X can be organized with respect to the baseline with Mg-Ca seems least reactive towards H-evolution according to DFT

Next Steps

• Implementation of model to Mg-Zn magnesium alloys
• Mg-Zn magnesium alloys model calibration
• Connect the limiting current density at different overpotentials to include galvanic effects where, overpotential \( (\varepsilon_V - \varepsilon_{o,V}) \) and H-coverage ratios \( (\theta_H/\theta_H^0) \) obtained from DFT are related below in a Butler-Volmer form

\[
i_k = i_{o,k} \left\{ \frac{\theta_H^0}{\theta_H^0} \exp \left[ \frac{\alpha F}{RT} (\varepsilon_V - \varepsilon_{o,V}) \right] - \frac{1 - \theta_H^0}{1 - \theta_H^0} \exp \left[ -\frac{(1 - \alpha) F}{RT} (\varepsilon_V - \varepsilon_{o,V}) \right] \right\}
\]