FEM based studies of a Mg/Al hybrid component joint regarding corrosion prediction

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## Comsol History

<table>
<thead>
<tr>
<th>Year</th>
<th>Reference</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2013</strong></td>
<td>S. Klink, D. Höche, F. La Mantia, W. Schuhmann; FEM modelling of a coaxial three-electrode test cell for electrochemical impedance spectroscopy in lithium ion batteries, Journal of Power Sources, Vol. 240: 273-280, 2013</td>
<td><img src="image6.png" alt="Image" /></td>
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<tr>
<td></td>
<td>D. Höche and J. Isakovic; Mikrogalvanische Korrosion am Magnesium-Aluminium System - Detaillierte elektrochemische Einblicke mittels FEM - Simulationen, Chemie Ingenieur Technik, online, 2013.</td>
<td><img src="image7.png" alt="Image" /></td>
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<tr>
<td></td>
<td>D. Höche; Towards the simulation based design of Mg/Al hybrid component joints in terms of corrosion prevention, Proceedings EuroCORR, Estoril, 2013.</td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Corrosion in multi-material design

- galvanic corrosion (AA, Mg, Steel, CFK)
- under paint corrosion
- crevice corrosion (gap, edge, scratch)
- localised corrosion / filiform corrosion

Anti-corrosive lightweight design needs:

- Constructive corrosion protection
  - component selection (non-metallic)
  - avoiding galvanic contacts
  - spacer distances etc.
- Active corrosion protection
  - optimized coating systems (hybrid)
  - superior pre-treatments
- Corrosion resistant materials / alloys
Aims of simulation action

Application on engineering tasks

→ Assisting engineers in Multi-Material-Design (combination of different materials) under corrosion protection aspects
→ Corrosion prediction for Multi-Material-Joints (welds, rivets, clinches) = minimising the need of corrosion protection action (coatings, etc.)
→ Tailoring of various properties like spacing distances

Most common advantages

→ Reduction of development expenses and periods
→ Improved planning ability due to tailored properties
→ Simulation based safeguarding of corrosion protection action

Objective:

Computer-Aided Engineering (CAE) in terms of corrosion protection
Anti-corrosive simulation based design

1. Challenge ➞ the model development chain

**Joining technology**
- welds (FSW, Laser, arc) clinches, rivets, adhesive
- selfpierce punch rivet

**Geometry**
- sheets, casts, crevices, spacers, exposed area
- 2 sheets and a rivet

**Materials M1, M2, Mx**
- bulk materials, AA, Mg alloys, steels, CFK...
- bulk Mg and Al sheet, Al rivet

**Surface state**
- bare, cleaned, etched, conversion coated, top coat
- bare

**Environmental Exposure**
- liquid couluum, thin film, flow, splashes
- thin film

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**scientific aspects**

- materials state (as received)
- scratches, artefacts
- Impurities

- galvanic corrosion
- crevices
- under paint corrosion

- electrical properties (conductivity)
- electrochemical response

- interface chemistry
- Faraday reaction
- passivation, layer growth

- ion concentration, pH
- conductivity
- transport mechanism

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Chose the **correct** interdisciplinary approach including the correct physics / chemistry

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Self-pierce punch rivet model problem (Al in Mg)

Geometry setup:

- use symmetries
- reduce to “active” domains

- Try to figure out **all** aspects → develop the model starting with most “weighted” issue.
- Keep it **as easy as possible** (checking requirements in context to limitations and assumptions)
Most „weighted“ problem

Galvanic couples in Mg based engineering

[Diagram showing standard potentials and overpotentials]
General rules – galvanic couples

- **ratio of cathode area to anode area / area rule**
- galvanic corrosion will **become more severe** over time once it is initiated.
- affected zone can be relatively large and galvanic corrosion may be caused by a **remote cathode metal** (spacing aspects).
- **avoid** that the anode is **electrically connected** to the cathode (not possible).
- relative positions of electrodes → corrosion products from the Mg anode can be transferred to the cathode, corrosion could be slightly reduced through an **“alkalisation effect”**. (being simulated)
- Corrosion products from the cathode on the Mg surface (e.g. by convection) leading to a **“passivation” or “poisoning” effect**, which could either slightly, ameliorates or deteriorates the galvanic corrosion. (very important)
- A **“shortcut” effect** can be caused by the accumulation of corrosion products → accelerating galvanic corrosion unexpectedly at a remote area.

Mathematical approach

Nernst:

\[
\frac{\partial c_i}{\partial t} + \nabla \left( -D_i \nabla c_i - z_i u_{\text{mob}} F c_i \nabla U_{\text{el}} \right) + \mathbf{u} \cdot \nabla c_i = R_{i,\text{tot}}
\]

Faraday:

water autoprotolysis

\[
H_2O \leftrightarrow H^+ + OH^-
\]

\[
R_{\text{oh}} = R_{\text{H}^+} = k_f - k_b (c_{H^+} c_{OH^-})
\]

\[
j_{\text{el}} = F \sum z_i N_i
\]

\[
i_{\text{el}} = -\sigma \cdot \nabla U
\]

• moving interface
• Mg(OH)\textsubscript{2} precipitation
• anodic dissolusion

Specimens:
(to be extended)

<table>
<thead>
<tr>
<th>species</th>
<th>(\text{Mg}^{2+})</th>
<th>(\text{OH}^-)</th>
<th>(\text{H}^+)</th>
<th>(\text{Na}^+)</th>
<th>(\text{Cl}^-)</th>
<th>(\text{O}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D \text{ [m}^2\text{/s}] \times 10^{-9})</td>
<td>0.71</td>
<td>5.27</td>
<td>9.31</td>
<td>1.33</td>
<td>5.27</td>
<td>1.98</td>
</tr>
<tr>
<td>(C_0 \text{ [mol/m}^3)</td>
<td>0</td>
<td>(10^{-4})</td>
<td>(10^{-4})</td>
<td>42</td>
<td>42</td>
<td>0.233</td>
</tr>
</tbody>
</table>
Mathematical approach

to be used: (in 4.2a)

- Tertiary Current Distribution, Nernst-Planck Interface
  - modified boundary conditions (weak form) to include the reduced flux due to layer growth
- Surface Reactions Interface
- Deformed Geometry and Moving Mesh Interface (ALE)
- Mathematics Interface
  - 3 ODE’s for surface coverage, layer thickness and porosity
Boundary conditions – electrode response

<p>| | |</p>
<table>
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<td>anodic:</td>
<td>Mg dissolution</td>
</tr>
<tr>
<td></td>
<td>$Mg \rightarrow Mg^{2+} + 2e^-$</td>
</tr>
<tr>
<td>cathodic:</td>
<td>oxygen reduction</td>
</tr>
<tr>
<td></td>
<td>$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$</td>
</tr>
<tr>
<td></td>
<td>$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$</td>
</tr>
<tr>
<td>global reaction:</td>
<td>$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2$</td>
</tr>
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</table>

\[ i_{\text{anode}} = (1 - \theta + \varepsilon \theta) \cdot i_0 \left( e^{\left( \frac{zα_Fη}{RT} \right)} - e^{\left( -\frac{zα_Fη}{RT} \right)} \right) \]

\[ i_{\text{cathode}} = (1 - \theta + \varepsilon \theta) \cdot \frac{i_0 e^{\left( \frac{zα_Fη}{RT} \right)}}{1 - \left( \frac{i_0}{i_d} \right) \left[ 1 - i_0 e^{\left( -\frac{zα_Fη}{RT} \right)} \right]} + (1 - \theta + \varepsilon \theta) \cdot i_0 H \cdot 10^{\left( \frac{η_0}{β} \right)} \]

\[ \rightarrow \text{Tafel does not work} \]

\[ \rightarrow \text{self induced corrosion layer growth} \]

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Boundary conditions – surface coverage

Surface coverage θ:

\[
\frac{d\theta}{dt} = -\frac{1}{l(1-\varepsilon)} \left( \frac{R_{\text{Mg}^{2+}}M_{\text{Mg(OH)}_2}}{\rho_{\text{Mg(OH)}_2}} \right) R_{\text{Mg}^{2+}} = -(1 - \theta) k_{\text{Mg(OH)}_2} \left( c_{\text{Mg}^{2+}} c_{\text{OH}^-}^2 - K_{\text{Mg(OH)}_2} \right)
\]

Reduced flux:

\[
n \cdot (N_{\text{total}} - N_{\text{eff}})_i = n \cdot N_{\text{i-red}} = D_i \left( \theta - \frac{\theta}{N_M} \right) \left( -\nabla c_i - \frac{z_i F}{RT} c_i \nabla U_{\text{el}} \right)
\]

Interface velocity:

\[
u_{\text{total}} \cdot n = -\frac{M}{zF \rho} i_{\text{Mg}}(\theta) + u_{\text{layer}}\ 
\text{with } u_{\text{layer}} = \frac{R_{\text{Mg(OH)}_2} M_{\text{Mg(OH)}_2}}{(1 - \varepsilon) \rho_{\text{Mg(OH)}_2}}
\]

anodic dissolution
deposit growth
Assumptions and limitations

- Al is non-corroding (anodic branch is neglected)
- dilute solution theory is applicable
- precipitates do not dissolve
- hydroxide formation occurs at the interface
- limited number of chemical specimens and reaction products
- non-technical alloys
- without localised effects (pitting / Cl⁻)
- …..
Results – checking the model

\[ R_{\text{film}}(t) \approx \text{const} \frac{l(t)}{\sigma_{\text{eff}}(t)} = \text{const} \frac{l(t)}{\sigma(t)s^n \varepsilon^2} \]

\( \theta > 0 \) at \( t=0 \) (native layer)

\( Z'' \) vs. \( Z' \)

Mg in 0.1% NaCl

Electrolyte

Porous deposit

Double layer

*stirring

92 h

96 h

0 h

Expected shape

\( R_{\text{dl}} \)

\( R_{\text{por}} \)

\( CPE_{1} \)

\( CPE_{2} \)

\( l(t) \) [m]

\[ l(t) \] according to the simulation

\( \sigma \approx \varepsilon \)
Results – Geometry aspects

*first results without reducing flux:*

e.g. different head shape:

minimizing the corrosion current density:

Mixed potential:

- "alkalisation effect"

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Results – Possible studies

• Aspects of galvanic corrosion can be predicted
• Environmental exposure modelling still needs to be setup
• Surface treatments and coatings have to be tackled separately
Need of further extensions

- addition of further chemical specimens
- improved layer model including the MgO aspects
- predicting localised corrosion issues
- correlation to functionality (e.g. strength, stiffness)
- Al activity has to be taken into account especially at high pH values (>12 hydroxide species)
- .....
Results and issues of the model study

**beside** the previous explained aspects by Song et.al:

- sharp edges and gradients should be avoided due to local “critical” increases in the current density arising in discontinues anodic “dissolution” currents
- the relative position of the cathode should be “below” the anode to force precipitation of chemical products → decrease in the cathodic current
- \( \theta=1 \) for a non-porous structure would stop corrosion → **the engineer should try to find an alloy system achieving** \((1- \theta + \theta \varepsilon) \rightarrow 0\)

**Modelling issues:**

- physical and chemical correct time depended boundary conditions
- capacitive double layer, layer growth is still to strong, convective effects
- pH and conductivity variations / migration
- re - dissolution effects
Summary

- Simulations can assist the design regarding corrosion protection
- Chose of the model depends on requirements (careful)
- Simplified parameter studies are possible and can save experimental effort
- Many process parameters still have to be implemented
- The whole simulation based design approach requires interdisciplinary working and should be tackled in modules

there is still much to do

Thank you