The Mitigation of Galvanic Corrosion between Mechanically Coupled Aluminum and Carbon-Fiber Reinforced Polymer Matrix Composites

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In a quest to reduce weight and improve performance, aluminum (Al) alloys have been used in conjunction with lightweight materials such as carbon-fiber reinforced (CFR) polymer-matrix composites (PMCs) in a multitude of applications such as defense, aerospace, automotive and civil-infrastructure industries.

The major objective of this research was on devising corrosion control strategies for couples of 6061-T6 aluminum (Al) that were mechanically fastened to carbon-fiber reinforced (CFR) PMCs using Ti-6Al-4V bolts.

The CFR PMCs were fabricated from epoxy-matrix prepregs reinforced with graphite (conductive) fibers.*

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Galvanic Corrosion Problems

- The mechanical contact of CFR PMCs (which serves as cathode) with Al alloys (which serves as anode) can result in galvanic corrosion of the Al alloys in a corrosive environment.

**Oxygen reduction on the PMC enhances galvanic corrosion:**

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^- \]

- The pH at the interface was monitored by placing the couples in a 3.15 wt% sodium chloride (NaCl) gel (made with Agar) containing a universal pH indicator.

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**Diagram:**

- Hydrolysis of metal cations produces solvated protons that acidify the crevice.
- Chlorides migrate into the crevice due to excess protons.
- Oxygen reduction on the PMC enhances galvanic corrosion.
- The entire region around CFR PMC became more alkaline due to the hydroxyl (OH⁻) ions generated on the cathode as a result of oxygen reduction.
A three-pronged, corrosion-control strategy was investigated for the 6061-T6 Al and PMC couples:

1. Application of a hybrid ceramic-polymer (or ceramer) coating called SiloXel* on the 6061-T6 Al surface to attenuate galvanic corrosion at the interface with CFR PMC\(^1\).

2. Galvanically decouple the 6061-T6 Al from the CFR PMC using insulating layers of various lengths (skirt) for a multitude of salt loading and humidity levels\(^2\).

3. Use hydrophobic coating on the insulative skirts to enhance the decoupling effect for mechanically-coupled 6061-T6 Al and CFR PMCs\(^3\).

*Developed at the University of Hawaii by Dr. Atul Tiwari of the Hawaii Corrosion Laboratory, Department of Mechanical Engineering.


\(^2\)Raghu Srinivasan and Lloyd Hihara, “Corrosion Protection of Interfaces Between Aluminum and Mechanically-Coupled Polymer Matrix Composites (PMCs)”, ECS 2013, October 2013, San Francisco, California.

Ceramer Coatings on Aluminum

- The galvanic corrosion on uncoated 6061-T6 Al that was coupled to the CFR PMC was observed in regions that were inside and outside of the Al-CFR PMC interface when exposed to an aggressive marine environment (Marine Corps Base of Hawaii (MCBH)) for 12 months.

- The chloride deposition on the couples created a salt bridge from the CFR PMC to the Al coupon that extended beyond the perimeter of the CFR PMC.

- The salt bridge created a continuous ionic path from the cathodic CFR PMC to the anodic 6061-T6 Al coupon, which resulted in galvanic corrosion on the uncoated Al surface outside the interface region.

*Video Image Enhanced Evaluation of Weathering
On the coated Al coupons, the SiloXel coatings restricted the formation of the salt bridge to a tighter, well-defined perimeter around the PMC; hence, the galvanic corrosion on the coated 6061-T6 Al was limited closer to the interface region as compared to the uncoated coupon.

However, at the MCBH, although the SiloXel coating reduced the breadth of corrosion from interface, it induced trenching around the perimeter of the CFR PMC.

Hence, the SiloXel coating on aluminum is not sufficient to attenuate galvanic corrosion.
A typical method used to mitigate galvanic corrosion when bolting Al to CFR PMCs is to insert an insulating layer (G-10 fiberglass or E-glass–reinforced PMC) between the members.

Although the direct contact between the aluminum and CFR PMC is eliminated, the aluminum and the CFR PMC could still be galvanically coupled through the Ti fastener.

Galvanic corrosion can occur if the electrolyte bridges over the insulating layer, as shown in the specimens below.
Current flowing between the two electrically connected materials is governed by Ohm’s Law: $E=IR$.

$$IR = E_c - E_a = I_{Galv}R = i_{Galv}A_{anode}R$$

- $i_{Galv}$ is galvanic current density
- $A_{anode}$ is anode area

Hence, $i_{Galv}$ is dependent on the magnitude of the value of $IR$, where $i_{Galv1}$ corresponds to $IR_1$, and $i_{Galv2}$ corresponds to $IR_2$, and so forth.

The magnitude of $i_{Galv}$ between the CFR PMC and 6061-T6 Al is at a maximum when the $IR$ loss between anode and cathode is zero, and decreases as the $IR$ in the galvanic circuit increases.
Hence, $I_{Galv}$ can be attenuated by increasing the $IR$ between the anode and cathode. The resistance $R$ that is responsible for the $IR$ loss resides in the electronic and ionic components of the galvanic circuit.

\[ \sum R = R_a + R_c + R_m + R_s \]

- $R_a$, $R_c$ and $R_m$ are the materials property of 6061-T6 Al, CFR PMR, and the Ti fastener (fixed resistance).
- The sum of resistances of the electronic components ($R_a$, $R_c$, and $R_m$) is much lower than the ionic resistance of the solution $R_s$.
- For atmospheric exposure, the ionic resistance of the solution $R_s$ will be a function of the salt layer that bridges the anode and cathode.
- Resistance of the solution ($R_s$) can be controlled by adjusting the salt spray and by extending the insulating skirt to various lengths.
The ionic resistance $R_s$ of the salt layer will be estimated assuming that it forms a continuous, uniform, and moist layer on top of the insulating skirt.

The resistance $R_s$ of the salt layer is dependent on the resistivity of the salt layer $\rho$, the length of the skirt $l_s$, the width of the skirt $w$, and the thickness $t$ of the salt layer:

$$ R_s = \frac{\rho l_s}{wt} $$

The resistivity $\rho$ is the reciprocal of the conductivity ($K$), which can be written as:

$$ \rho = \frac{1}{K} = \frac{1}{F \sum Z_j \mu_j C_j} $$

Model Development

$$ Z_j = Z_{Na^+} = Z_{Cl^-} = Z = 1 \quad \text{and} \quad C_{Na^+} = C_{Cl^-} = C $$
Model Development

\[ R_s = \frac{l_s}{Fwt \sum Z_j \mu_j C_j} = \frac{l_s}{FwtZC \sum \mu_j} \]

\[ \sum \mu_j = \mu_{Na^+} + \mu_{Cl^-} \]

- The concentration \( C \) is the moles of NaCl, \( n \), present on the skirt divided by the volume of the electrolyte, which is the width of the skirt, \( w \), times the length of the skirt, \( l_s \), times the thickness of the electrolyte layer, \( t \).

- The moles of NaCl, \( n \), on the skirt can also be written as the mass of NaCl, \( m \), on the skirt divided by the atomic weight of NaCl, \( W_{NaCl} \):

\[ C = \frac{n}{twl_s} = \frac{m}{W_{NaCl}twl_s} \]

This conveniently eliminates the term for the thickness of the salt layer, \( t \), which is not trivial to measure.

*Mobility values of Na\(^+\) and Cl\(^-\), which are equal to 5.193 \times 10^{-4} \text{ and } 7.912 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}, \text{ respectively}
In our specimen configuration, the skirt width, \( w \), is also equal to the width of the 6061-T6 Al anode, \( w \).

Rearranging and substituting the terms \( m/(wl_s) \) with \( m' \), which is denoted as the salt loading per unit area [g/cm\(^2\)] gives

\[
IR = i_{Galv}A_{anode}R = i_{Galv} \frac{LWL_s^2}{FZm} \sum \mu_j
\]

The logarithmic form of this Equation is given as

\[
\log IR = \log (i_{Galv}) + \log \left( \frac{LWL_s^2}{FZ\sum \mu_j} \frac{l_s}{m'} \right)
\]

To decrease \( i_{Galv} \), the IR drop must be increased by increasing the \( l_s/m' \).

The value of \( i_{Galv} \) is, thus, a function of the \( l_s/m' \).
The salt loading density (m’) on the G-10 fiber glass were determined by 15 seconds spray of different chloride solutions.
Humidity ZRA Experiment

Experimental Procedure

• The galvanic corrosion rates for couples with different insulating-skirt lengths were to be monitored at 30°C and various relative humidity over a period of up to 3 days using the zero resistance ammeter (ZRA) technique.

• The couples were sprayed with different concentrations of salt solutions.

Humidity ZRA Chamber (view from top)

• Area of the anode (6061-T6 Al) and the area of the cathode (CFR PMC) were kept consistent for all the samples.

• The carbon fiber orientation (90°) on the exposed CFR PMC samples were similar to the polarization electrodes.
Each curve is an average of at least 3 experiments.
For 0 inch Skirt Length

- The highest steady state galvanic current ($I_{\text{Galv}}$) were observed for high chloride concentration (>10000 ppm) treatments and they were comparable.

- The steady state galvanic current ($I_{\text{Galv}}$) for 1000 ppm Cl$^-$ treatment and 100 ppm Cl$^-$ treatments were lower than high chloride concentration (>10000 ppm) treatments.

- The steady state galvanic current ($I_{\text{Galv}}$) for 0 and 10 ppm Cl$^-$ concentration were zero as the ionic conductivity of the solution is nearly zero.

- The steady state galvanic current ($I_{\text{Galv}}$) decreased as the length of the skirt increased for 20000, 10000, 1000, and 100 ppm Cl$^-$ treatments.
Insulating Layer of Various Skirt Lengths

- Experimental data from humidity galvanic experiments were used to plot galvanic corrosion rate ($i_{\text{Galv}}$) vs skirt length-to-salt loading ratio ($l_s/m'$).
- These plots can be used to determine the proper skirt length for different environments (based on different salt loading) to limit galvanic corrosion to a specified value.
Insulating Layer of Various Skirt Lengths

- To suppress $i_{\text{Galv}}$ between 6061-T6 Al and the CFR PMC to a specified acceptable value, the corresponding IR loss must be achieved by obtaining the appropriate skirt length, $l_s$, for a given salt loading, $m'$. Skirt lengths needed to limit $i_{\text{galv}}$ to $6 \times 10^{-6}$ A/cm² (normal corrosion rate) as a function of salt loading at an aggressive marine environment such as MCBH ($m'=3.7$ g m⁻²day⁻¹).

<table>
<thead>
<tr>
<th>Days of Salt Buildup at MCBH</th>
<th>Salt Loading (g/m²)</th>
<th>Log salt Loading (g/cm²)</th>
<th>Skirt length (cm)</th>
<th>Skirt length (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>37</td>
<td>-2.43</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>30</td>
<td>111</td>
<td>-1.95</td>
<td>2.1</td>
<td>0.8</td>
</tr>
<tr>
<td>60</td>
<td>222</td>
<td>-1.65</td>
<td>4.2</td>
<td>1.7</td>
</tr>
<tr>
<td>120</td>
<td>444</td>
<td>-1.35</td>
<td>8.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Skirt lengths needed to limit $i_{\text{galv}}$ to $6 \times 10^{-6}$ A/cm² as a function of salt loading at a mild-moderate marine environment such as Coconut Island ($m'= 0.14$ g m⁻²day⁻¹).

<table>
<thead>
<tr>
<th>Days of Salt Buildup at Coconut Island</th>
<th>Salt Loading (g/m²)</th>
<th>Log salt Loading (g/cm²)</th>
<th>Skirt length (cm)</th>
<th>Skirt length (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.4</td>
<td>-3.85</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
<td>4.1</td>
<td>-3.38</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>60</td>
<td>8.2</td>
<td>-3.08</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>120</td>
<td>16.4</td>
<td>-2.77</td>
<td>0.32</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Assuming that the salt accumulation would be washed off every few days due to rain
• Visual observation at the interface of 6061-T6 Al and G10 fiberglass for the $7.58 \times 10^{-4} \text{ g/cm}^2$ salt loading showed excessive corrosion damage for 0 cm skirt length when compared to longer skirt lengths.

• The corrosion damage was attenuated at the interface for longer skirt lengths.
The deposition of salts on the insulative skirt, however, can create a continuous ionically-conductive electrolyte film that can bridge the CFR PMC and Al, thus reducing the effectiveness of the skirt.

In this present study, hydrophobic coatings were used on the insulating skirt to attenuate galvanic corrosion by breaking up the continuous electrolyte film.

Short Skirt Vs Long Skirt (Humidity Chamber Experiments)

- The galvanic corrosion rates for couples with different insulating-skirt lengths coated with Siloxel were monitored at 30° C and 90% RH over a period of up to 3 days.
- The galvanic currents ($I_{\text{Galv}}$) between the CFR PMC and 6061-T6 Al were recorded every 15 seconds for 3 days.
- The couples were sprayed with different concentrations of salt solutions.

Schematic CFR PMC/6061-T6 Al couples

Actual CFR PMC/6061-T6 Al couples
Humidity chamber (view from top)
20000 ppm spray (Day 1)
The hydrophobic Siloxel coating reduced the steady-state galvanic currents for short skirts (i.e., lengths of 0.25 and 0.5 in) by 6 orders of magnitude compared to the uncoated skirts.

The galvanic currents for the uncoated skirts gradually decreased as the skirt length increased; whereas, those for SiloXel-coated skirts reach a minima at approximately 0.25 in.

For the following conditions, the steady state galvanic current dropped to zero and could not be plotted on the log scale: a) 8 inch SiloXel-coated skirt for all of chloride levels b) all SiloXel-coated skirts for chloride levels < 1000 ppm, and c) for uncoated skirts for chlorides levels <100.
If the water droplets from the salt spray were larger than approximately the length of the insulating skirt, the hydrophobic nature of the coatings on the skirt aided capillary forces in pulling the electrolyte to the CFR PMC and/or 6061-T6 Al border, thus breaking the continuity of the ionic path.
Outdoor Exposure

• To study the effectiveness (due to capillary wicking) of shorter skirt lengths at outdoor exposure, Siloxel coatings on 0.25 and 0.5 inch long insulating skirts were compared for outdoor exposure.

• Siloxel* and Epoxy# were selected to be used as hydrophobic skirt coatings for outdoor exposure on 0.5 inch long insulating skirts.

• The galvanic current between CFR-PMC and 6061-T6 Al couples with no coatings on the insulative skirt (0.5 inch long) were also monitored as a control.

• CFR PMC/Al galvanic couples with 0.5 inch insulating skirts (with either the Siloxel or Epoxy coatings, or no coatings) were exposed at rain forest (Manoa) and severe marine (MCBH) environments for 72 days.

• The galvanic currents ($I_{Galv}$) between the CFR PMC and 6061-T6 Al were recorded every 5 minutes for 72 days.

* Developed at the University of Hawaii by Dr. Atul Tiwari of the Hawaii Corrosion Laboratory, Department of Mechanical Engineering.
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Experimental Procedure

- The CFR PMC/Al galvanic specimens at the severe marine site (MCBH) were exposed in two conditions: sheltered and unsheltered.
- The sheltered specimens were subjected to significant salt build up; whereas, the unsheltered specimens were subjected to the periodic cleansing effects of rain.

### Weather Data (72 day Exposure)

<table>
<thead>
<tr>
<th>Test Sites</th>
<th>Average Temperature (°C)</th>
<th>Average Humidity (%RH)</th>
<th>Rainfall (mm)</th>
<th>Average Chloride Deposition rate (mg/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCBH</td>
<td>24.8</td>
<td>73.8</td>
<td>50.8</td>
<td>3047.1</td>
</tr>
<tr>
<td>Manoa</td>
<td>21.9</td>
<td>81.0</td>
<td>753.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Experimental Procedure

• The contact angle of the coating on the insulating skirt material was measured before and after exposure to the outdoor test sites to study the effects of hydrophobicity on galvanic currents.
  – Hydrophobicity of the insulating skirt were determined by measuring the contact angle for wetting using KSV instrument’s CAM 200 program.
  – Contact angles were measured using ultrapure 18.1 MΩ-cm water droplets in static mode at ambient temperature.
  – The wetting angles were calculated using the Young/Laplace curve fitting method.
  – The reported contact angle is an average of ten drops and each drop has left and right side wetting angle.
Results and Discussion

Short Skirt Length (0.25 inch) vs Long Skirt Length (0.5 inch) for Siloxel Coatings

- The capillary-wicking effects that reduced the galvanic current for Siloxel-coated skirts with shorter lengths (in the laboratory humidity-chamber experiments) were not observed in outdoor exposure.
In outdoor field environments, since natural salt particles (on the order of a few microns) are deposited on the substrate (and not sprayed in solution as in the laboratory experiments), the capillary-wicking mechanism does not have a chance to operate in the absence of substantial rain.
Results and Discussion

Short Skirt Length (0.25 inch) vs Long Skirt Length (0.5 inch) for Siloxel Coatings

Short Skirt Length (0.25 inch)

Long Skirt Length (0.50 inch)
Results and Discussion

Sheltered Vs Unsheltered Specimens at MCBH

- For the uncoated insulated skirt specimens, the galvanic-current density for the sheltered specimens were consistently higher than that of the unsheltered specimens.

- The steady rise in the galvanic-current density was likely due to the buildup of salt deposits.

- The lower galvanic-current density for the unsheltered condition could be due to the cleansing effect of rain.

Specimen with 0.5 in Skirt Length (No coatings)
Epoxy coatings on the insulating skirt showed greater attenuation of the galvanic corrosion rate compared to the Siloxel coating.

The galvanic corrosion rates for the specimens with the Siloxel-coated skirts were actually higher than that of the uncoated skirts.

The epoxy matrix of the G10 fiber glass substrate degraded due to exposure to sunlight causing the Siloxel coating (only several microns thick) to debond and crack.
Results and Discussion

Unsheltered Specimens (MCBH)

- The visual appearance of Siloxel-coated and uncoated G10 are similar, showing exposed glass fibers.

- This compromised the hydrophobic nature of the Siloxel coatings.

- The much thicker epoxy coatings retained integrity for the duration of the test.
Results and Discussion

Unsheltered Specimens (MCBH)

- The morphology of the Siloxel-coated G10 was similar to that of the uncoated G10.
- Siloxel-coated G10 degraded over time and galvanic corrosion rates were similar to that of uncoated G10, as discussed earlier.

* Scale bar is 200 microns and applies to all the SEM pictures.
Results and Discussion
Unsheltered Specimens (MCBH)
Epoxy Coatings

- The epoxy coating showed initial signs of cracking, but its thickness preserved its overall integrity.

* - Scale bar is 200 microns and applies to all the SEM pictures.
Results and Discussion

Contact Angle (Before and After Exposure)

- The Siloxel coating had the highest (92.5°) initial contact angle.

- In the unsheltered condition at MCBH, the contact angle of the Siloxel coating reduced to approximately ½ (48.7°) of the initial value.

- This indicated that the Siloxel-coated G10 degraded and lost its hydrophobic nature; hence, the galvanic corrosion rates were the highest.

- The contact angle of the epoxy coating for the unsheltered specimens at MCBH were similar before-and-after exposure.

- The epoxy coating retained the highest contact angle after exposure; hence, the galvanic corrosion rates were lowest.
Results and Discussion

Contact Angle (Before and After Exposure)

- The sheltered specimens at MCBH were not exposed to direct sunlight; hence, the Siloxel coating on G10 retained its high contact angle.

- Although the contact angle on Siloxel coatings for the unsheltered specimens at Manoa decreased, the contact angle was slightly higher compared to that of the epoxy coating.
Results and Discussion

- For the sheltered specimens at MCBH and unsheltered specimens at Manoa, the Siloxel-coated skirt was the most effective in attenuating the galvanic-corrosion rate when compared to the epoxy-coated and uncoated skirts.
- Due to much higher salt-deposition rates at MCBH, the galvanic corrosion rates at MCBH were at least two orders of magnitude higher than that at Manoa.
Results and Discussion

Sheltered Specimens (MCBH)
- no coatings
- Epoxy
- Siloxel coatings

Unsheltered Specimens (Manoa)
- no coatings
- Epoxy
- Siloxel coatings
A model was developed to experimentally analyze the galvanic corrosion mechanism of the CFR PMC and 60061-T6 Al and were used to develop a model linking the galvanic corrosion rate ($i_{\text{Galv}}$) to salt loading $m'$, the ohmic loss increases as the skirt length ($l_s$) increases.

The ohmic loss is expressed as a function of $m'$ and $l_s$ and it is given by:

$$\log IR = \log (i_{\text{Galv}}) + \log \left( \frac{L W_{\text{NaCl}} l_s}{F Z \sum \mu_j} m' \right)$$

- where $i_{\text{Galv}}$ is the galvanic corrosion rate, $L$ is exposed anode length, $W_{\text{NaCl}}$ is the atomic weight of NaCl, $F$ is Faraday’s constant, $Z$ is the magnitude of charge on the ionic species, and $\mu_j$ [cm$^2$ sec$^{-1}$ V$^{-1}$] is the mobility of species $j$. 

Summary
• The ohmic loss depends on the ionic conductivity of the electrolyte film or salt layer that bridges the anode and cathode that forms on the insulating skirt.

• The parameters that affect the ionic conductivity of this film are salt loading ($m'$) of various Cl$^-$ concentrations, and various lengths of insulating skirt ($l_s$).

• Galvanic corrosion can be mitigated by increasing the ohmic loss (IR loss) between Al (anode) and CFR PMC (cathode), which can be achieved by lengthening the insulating skirt and the polarization behaviors of the anode and cathode.

Summary

Galvanic corrosion can be mitigated by increasing the ohmic loss (IR loss) between Al (anode) and CFR PMC (cathode), which can be achieved by lengthening the insulating skirt and the polarization behaviors of the anode and cathode.
• Shorter skirt lengths (i.e., 0.25 inch) with a hydrophobic coating was shown to be most effective in attenuating galvanic corrosion based on the capillary effect if the water droplets were larger from the salt spray.

• However, if small particles of salt aerosols (few microns in size) are deposited during outdoor exposure, it is possible that a continuous ionic path could form prior to deliquescent droplets agglomerating, rendering low IR loss.
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