Long Term Corrosion Protection Performance and Activity of Graphene-Based Epoxy Coating Systems for Aluminium and its Alloys

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Introduction
Introduction

Graphene’s two-dimensional structure in the nanoplatelet form results in materials with:

• very high aspect ratio
• high surface area

These materials are particularly suited for use as multi-functional additives in paints and coatings.

The proposed mechanism by which graphene delivers anti-corrosion performance is a combination of physico-chemical process restricting uptake of water (combined with oxygen and salt) and electro-chemical activity.
The Protection of Self-Passivating Metals

- Passivating metals readily form a stable and unreactive surface coating
  - Protection from further corrosion
- Under certain conditions of pH and oxygen concentration, passivation of passivating metals will proceed
- Outside of such conditions passivation will not occur
- The passivation layer may start to break down
- Unprotected aluminium will corrode
The Protection of Self-Passivating Metals

- Traditionally, self-passivating metals have been protected from corrosion through anodization and alloying.
- Anti-corrosive inhibitive coatings may also be applied to aluminium surfaces.
- The active constituents of such coatings are typically marginally water soluble and produce active species which inhibit the ongoing corrosion of the metallic substrate.
- Active constituents include chromates but other species such as phosphates, molybdates, nitrates, borates and silicates are also used.
- The selection of active constituents is increasingly subject to regulatory pressures due to increased concerns for the environment and health and safety.
Aluminium in contact with carbon materials could exhibit galvanic corrosion
  - Depending on how material is encapsulated

Graphene has been demonstrated to be electrically conductive
  - Current density is 1,000,000 times greater than copper

When dispersed into a matrix, graphene nano-platelets offer significantly reduced conductivity
  - Levels below the percolation threshold required to achieving any meaningful conductivity

Graphene incorporated into a coating may offer the possibility of a dual functionality on aluminium
  - Improved barrier performance
  - Promotion of self-passivation
AGM Graphene Nano Platelets

**Reduced graphene oxide (RGO)**
- Composed of mixture of nanoplatelet type sheets
- Excellent barrier properties
- Moderate density and surface area gives high loading levels in most matrices
- Typically 10% in dispersion for further dilution in final formulation
- Resistivity – 50,000 Ω.m

**Graphene**
- Very thin, crumpled sheets. (of 5-15 atomic layers)
- Very low density and high surface area, enabling enhanced corrosion
- Typical loading levels 0.5-1% by weight in dispersion for further dilution in final formulation
- Resistivity – 0.0037 Ω.m

AGM supplies its graphenes in dispersion format
Objectives

Initial work has shown an increase corrosion protection performance using graphene-based coatings with relatively low GNP loadings (down to 0.003 wt.%) 

We seek to understand the mechanism behind such improvements in the corrosion protection of aluminium through the use of simple graphene-containing epoxy clears
Experimental
Test Program

Prohesion/Salt Spray Testing
- ASTM G85 annex 5 (prohesion) for a period of up to 4000 hours
- Panels were assessed at 500 hour intervals for signs of blistering, corrosion, and corrosion creep in accordance with ISO4628

Electro-chemical AC Impedance Spectroscopy (EIS)
- Demonstrate the improvement of the barrier properties through the addition of graphene to organic coatings
- Assess the impact of graphene within organic coatings on the rate of passivation of aluminium

Potentiodynamic Polarisation Technique
- Assess the impact of graphene within organic coatings on the rate of passivation of aluminium
Electro-chemical Testing

- Measurements recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer
- The test area of the working electrode was 14.6 cm$^2$ and run using a 3.5 wt% NaCl electrolyte
- For EIS, an AC voltage of 10 mV was applied across the samples, with a zero volt DC bias, over a frequency range of 1 MHz to 0.05 Hz
- For potentiodynamic tests, a potential of ±250 mV from the open circuit potential (500 mV sweep) was applied at a scan rate of 0.5 mV/second
Testing of Scribed Coatings

- Scribed samples were studied in addition to unscribed samples
- Scribing offers an immediate study of the bare metal substrate in contact with electrolyte and functional coating (triple phase boundary)
- To identify any electrochemical influence imparted by the graphene
- Provides the opportunity to observe changes prior to the lengthy breakdown/degradation of the functional coating
Coating Formulation

- Various loadings of GNPs were incorporated into an epoxy resin system
- Resin only clears and not fully formulated products
- Typical GNP Loadings for enhanced barrier properties are 0.1 – 0.5 wt.%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Epoxy System (wt.%)</th>
<th>RGO (wt.%)</th>
<th>Graphene (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Epoxy Blank)</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>99.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>99.97</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>99.997</td>
<td>0.003</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>99.9</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>99.97</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td>7</td>
<td>99.997</td>
<td>0</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Panel Preparation

- Aluminium 5005 panels of dimensions 150 x 100 x 2mm
- Panels were degreased using acetone prior to coating application
- Coatings were applied using a conventional gravity-fed spray gun
  - DFTs 40-60 µm
- All panels were allowed to cure for a period of 7 days at 23°C (+/-2°C).
Results
Prohesion/Salt Spray Testing

- 4000 hours prohesion testing
- No obvious signs of corrosion were noted in any of the graphene-incorporated epoxy samples
- Graphene loadings as low as 0.003 wt.% (barrier type effect from the graphene nanoplatelets expected to be relatively low)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of Corrosion</th>
<th>Area (%)</th>
<th>Blistering</th>
<th>Adhesion to substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Blank</td>
<td>Ri 5</td>
<td>40-50</td>
<td>-</td>
<td>Delamination</td>
</tr>
<tr>
<td>0.003 wt.% Graphene</td>
<td>Ri 0</td>
<td>0</td>
<td>-</td>
<td>Good</td>
</tr>
<tr>
<td>0.03 wt.% Graphene</td>
<td>Ri 0</td>
<td>0</td>
<td>-</td>
<td>Good</td>
</tr>
<tr>
<td>0.003 wt.% RGO</td>
<td>Ri 0</td>
<td>0</td>
<td>-</td>
<td>Good</td>
</tr>
<tr>
<td>0.03 wt.% RGO</td>
<td>Ri 0</td>
<td>0</td>
<td>-</td>
<td>Good</td>
</tr>
</tbody>
</table>
EIS results

Bode plots post 60 hours immersion

- Difference in impedance between steel and aluminium due to presence of passivation layer
- Increased barrier performance seen with all coated samples
- An order of magnitude improvement in barrier performance over the blank coating is seen for the graphene sample
EIS Equivalent Circuit Modelling

**Initial Immersion, T = 0**
(high impedance coating)

- Solution resistance
- Coating
- Metal Substrate

**Short term**

- Solution resistance
- Coating
- Metal Substrate
- $\text{H}_2\text{O}$ uptake (capacitance)
- Pore formation (pore resistance)

**Longer term or scribed coating**

- Solution resistance
- Coating
- Metal Substrate
- Polarisation Resistance
- Double layer capacitance

Coating Degradation

Coating Properties

Interfacial Properties

www.appliedgraphenematerials.com
## EIS Equivalent Circuit Modelling

<table>
<thead>
<tr>
<th>Circuit element</th>
<th>Epoxy blank</th>
<th>0.003 wt.% Graphene</th>
<th>0.03 wt.% Graphene</th>
<th>0.1 wt.% A Graphene</th>
<th>0.003 wt.% RGO</th>
<th>0.03 wt.% RGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution resistance, $R_{\text{soln}}$ (Ω)</td>
<td>22.97</td>
<td>23.62</td>
<td>17.27</td>
<td>21.35</td>
<td>21.13</td>
<td>32.10</td>
</tr>
<tr>
<td>Double layer capacitance, $C_{\text{cor}}$ (F/cm$^2$)</td>
<td>8.97 x 10$^{-9}$</td>
<td>7.23 x 10$^{-11}$</td>
<td>5.48 x 10$^{-11}$</td>
<td>3.26 x 10$^{-12}$</td>
<td>1.70 x 10$^{-8}$</td>
<td>3.34 x 10$^{-9}$</td>
</tr>
<tr>
<td>Corrosion resistance, $R_{\text{cor}}$ (Ω.cm$^2$)</td>
<td>6.29 x 10$^5$</td>
<td>4.38 x 10$^6$</td>
<td>7.37 x 10$^6$</td>
<td>3.34 x 10$^7$</td>
<td>7.45 x 10$^5$</td>
<td>4.20 x 10$^5$</td>
</tr>
</tbody>
</table>

- Similar values for solution resistance indicative of good data fit
- The epoxy blank sample shows a relatively high double layer capacitance and low corrosion resistance (normal passivation of aluminium)
- The double layer capacitance is seen to decrease with the addition of Graphene as low as 0.003 wt.% (likely greater passivation)
- Graphene addition appears to increase corrosion resistance – 2 orders of magnitude for the 0.1 wt.% sample with a smaller increase as low as 0.003 wt.%
- Again suggests Graphene is acting to increase the rate of passivation within the scribed region
- Graphene can act as both a barrier and also increases rate of passivation
- RGO appears to make no difference to corrosion resistance and double layer capacitance
  - No real impact on the rate of passivation of aluminium
  - Appears to act mostly as a barrier material
Potentiodynamic Polarisation Scans

- Beyond the Tafel regions, when an extended potential range is applied, additional useful features may be observed in the polarisation data.

- One such feature is the passivation potential:
  - As the applied potential increases above this value, a decrease in the measured current density is observed until a low, passive current density is achieved.
  - The point at which the current density undergoes no change with an increase in applied potential (passive region).

- Beyond this point, if the applied potential permits, and is sufficiently positive, the current rapidly increases: the breakaway potential. For aluminium alloys, this breakaway potential may be due to a localised breakdown in passivity (pitting).
Potentiodynamic Polarisation Scans

0.03 wt.% Graphene (Unscribed)
- No direct access to the metal surface
- No passivation occurring
- Relatively high Tafel constant
- Coating acting as a barrier

0.03 wt.% Graphene (Scribed)
- Direct access to the metal surface
- Onset of passivation observed at \(~+18\) mV from the corrosion potential
- Relatively low Tafel constant – high anodic reaction
Potentiodynamic Polarisation Scans

0.03 wt.% RGO (Scribed & Unscribed)

- Almost identical plots for scribed and unscribed samples
- Passivation onset does not appear in the RGO samples
- RGO, of lower conductivity, is performing more as a physical barrier than controlling corrosion by accelerated passivation
Summary

- During prohesion testing, all graphene incorporated samples significantly outperformed the epoxy blank control.
- EIS has shown that graphene incorporated at 0.1 wt.% offers a greater barrier performance than the blank control.
- Fitting of equivalent circuits models to the EIS data has shown an increase in corrosion resistance where RGO samples showed no change from the control.
- Potentiodynamic testing has shown an onset of passivation in the more conductive graphene samples.
- Suggests graphene is acting to increase the rate of passivation of the metal surface, acting in a catalytic manner.
Potential Applications

- Low build primers – extension of lifetime
- In combination with anodised metals
- In combination with other forms of conversion coating