Graphene - Corrosion Protection Behaviour

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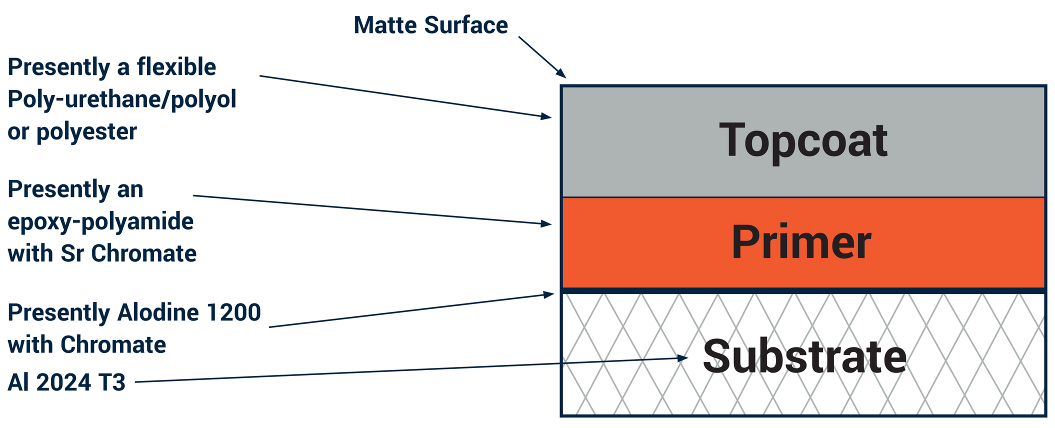
Abstract

This study explores the corrosion resistance characteristics of graphene coatings on metallic substrates from both the literature and a collaborative exploratory pilot program with the Defence Science Technology (DST) Group.
A variety of methods are available to deposit graphene or graphene-rich coatings onto metallic substrates. An increase in corrosion protection performance up to 1.5 orders of magnitude has been reported.
The pilot study on 2024-T3 aluminium alloy (aerospace material) provided mixed corrosion protection performance. It is thought the quality of the graphene coating was the cause for this poor performance.

Introduction

- The Australian Defence Forces manages an ageing aircraft fleet.
- Corrosion rectification is a significant sustainment cost $AUD245M/yr
- High demand is placed by the aerospace industry on the coating system used to protect aircraft components. The coating system provides:
  - protection against the environment,
  - improved adhesion,
  - visual aesthetics and
  - specialised functions such as low visibility or stealth.

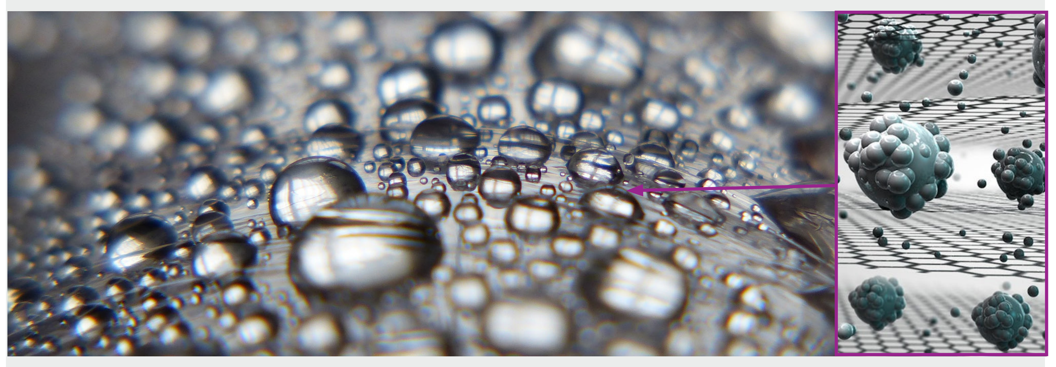


Schematic of components of an aircraft coating system

Work Health and Safety concerns with the current corrosion protection systems which rely on chromates or cadmium for protection. Graphene has emerged as a material that may provide a less hazardous option in affording corrosion protection to materials.

Graphene as a Corrosion Barrier

Graphene combines strength and ductility, and possesses the attributes of toughness, impermeability to gases and salts and hydrophobicity. Furthermore, its excellent electrical conductivity and high surface area properties serves it well as a barrier to retard corrosion.



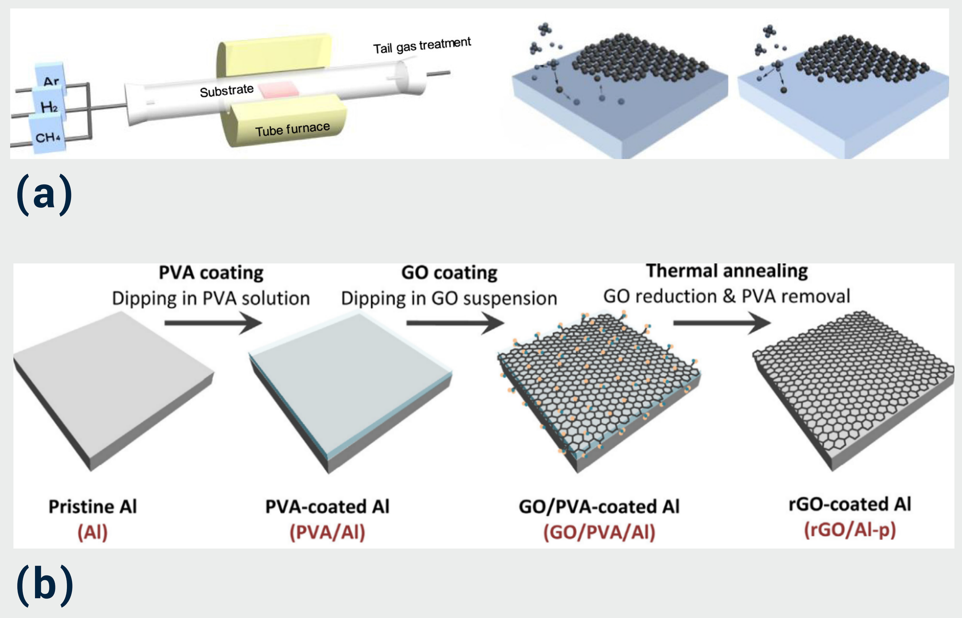
Benefits of graphene and graphene-composites for corrosion protection arise principally from reduced permeation to oxygen and water.
Properties being explored in this study deal with the ability of graphene to act as an ionic barrier and its nobility towards reaction with the environment.

Graphene Deposition Characteristics

Processes to deposit graphene are many and varied in type.

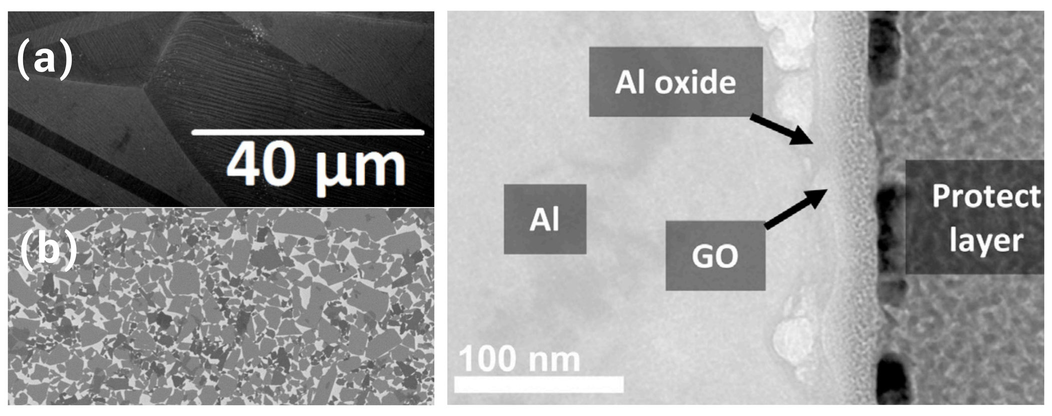
Method	Properties
Chemical Vapour Deposition	– Decomposition of methane to produce carbon – Monolayer or bilayer graphene – High quality graphene coatings – High processing costs; Temperatures > 1000°C – Low yields to acquire a continuous graphene film – Limitations on substrate materials (not AA)
Hybrid	– Two-step process – Graphene grown on a Cu foil by the CVD method; sealed with polypyrrole – Considered a 'sandwich coating'
Graphene Oxide Solution Method	– Oxidised graphene (oxidising graphite powder with sulfuric acid, hydrogen peroxide & potassium permanganate) – GO is hydrophilic – Simple deposition of GO films onto substrates. – Referred to as "graphene paint' or 'dip coating'
Sol-Gel Method	– Incorporation of GO or inorganic nanoparticles
Epoxy Resin Method	– Graphene-nano-platelets (GNP) (2µm diameter) – Various GNP used (0.1 to 0.7 per cent by wt) – Incorporation involves dispersion of GNP in a mixture of epoxy resin and acetone solvent (2:1) through sonication – Solvent removed by vacuum in the final step

Deposition Method Schematics



Schematic of the (a) CVD Process and the (b) GO solution Process

Morphology

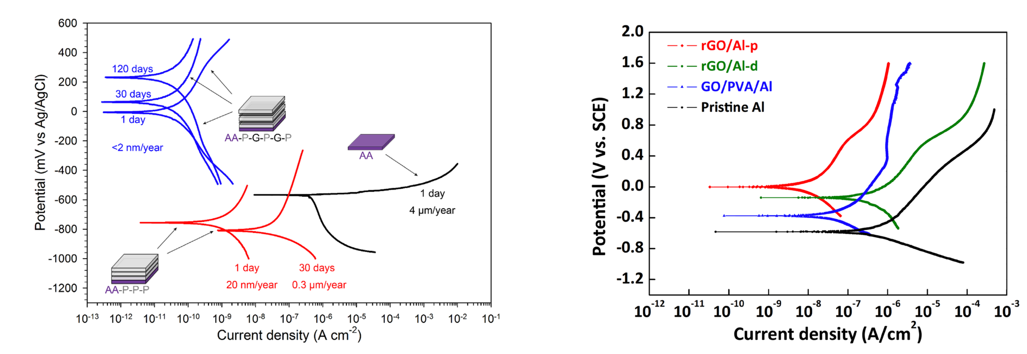


Images of (a) CVD coating and (b) a GO coating

Aluminium directly coated by GO showing frequent pores between Al oxide and GO

Current State of Knowledge

Corrosion Protection performance dependant on both deposition process and substrate material.
Single-layered graphene on Cu (CVD) increased the corrosion resistance by 1.5 orders of magnitude. Electrochemical characterisation showed anodic and cathodic current densities reducing by almost two orders of magnitude.
Hybrid coatings (two single layers of CVD graphene sandwiched by three layers of polyvinyl butyral) provided complete corrosion protection of a aluminium alloy up to 2880 hrs of exposure in seawater
Corrosion resistance of the aluminium coated in GO was three orders of magnitude higher than the uncoated specimens. (increase in E_{corr} and reduction in corrosion current (i_{corr}). Epoxy resin incorporated with graphene on a Zn demonstrated good anti-corrosion properties at graphene concentrations from 0.1 to 0.7 % wt.



Electrochemical Studies of graphene coatings

Sample	E_{corr}, mV vs SCE	I_{corr}, A/cm^2
Pristine Al	-581	6.2×10^{-7}
GO/PVA/Al	-376	2.6×10^{-8}
rGO/Al-p	-0.5	3.0×10^{-9}
rGO/Al-d	-140	7.6×10^{-8}

Corrosion potential and corrosion current density obtained from potentiodynamic measurements for various samples

Results from the Literature (not exhaustive) with respect to Corrosion Resistance (CR) is shown below. Various methods using graphene coatings on Aluminium Alloys (AA) have been successfully trialled. The use of graphene to protect materials from corrosion is promising.

Substrate	Method	CR ⇓	CR ⇑
Ni	CVD	1	-
Cu	CVD	7	2
Fe	CVD	2	-
AA	CVD (T)	1	-
AA	GO	8	1
AA	Sol Gel	5	-
AA	Epoxy Resin	4	-

Overview of Corrosion Results from the Literature

Pilot Program

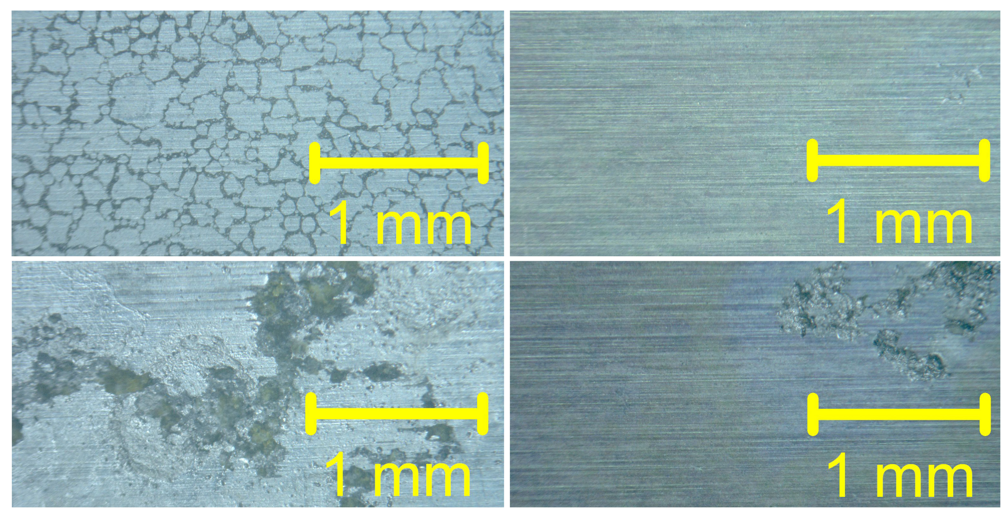
Participants: DST Group, Imagine IM, QQ (UK) and University of Surrey
Material: AA2024-T3 - Bare, Chromate Conversion Coating (CCC), 4 graphene 'mixes'

Modified Salt-spray used (ASTM-B117 and ASTM-G85):
- 1.5 % salt spray @ 35°C – 1 min
- Humid atmosphere @ 35°C – 11 hr, 59 min
- Dry atmosphere @ 50°C – 8 hrs
- Dry atmosphere @ 35°C – 4 hrs

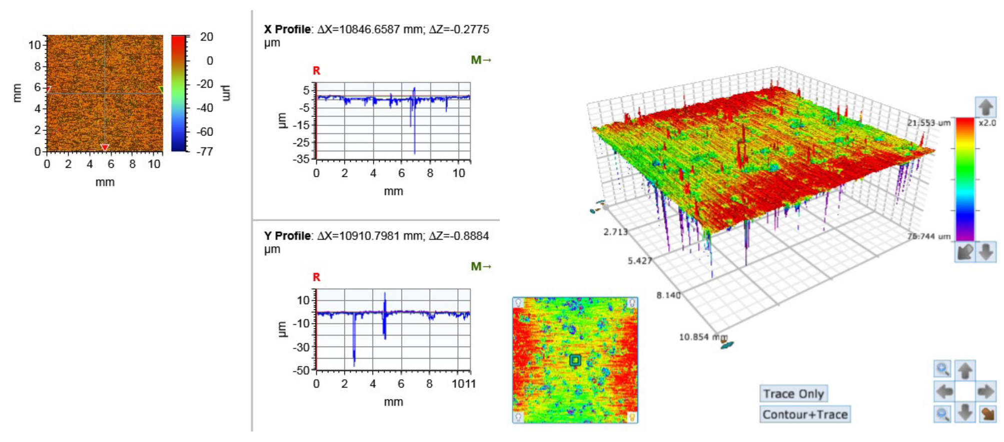
Exposure up to 1344 hrs
ASTM Performance requirement is:
- 672 hrs without corrosion (films)
- 2000 hrs without corrosion (coatings)

Results

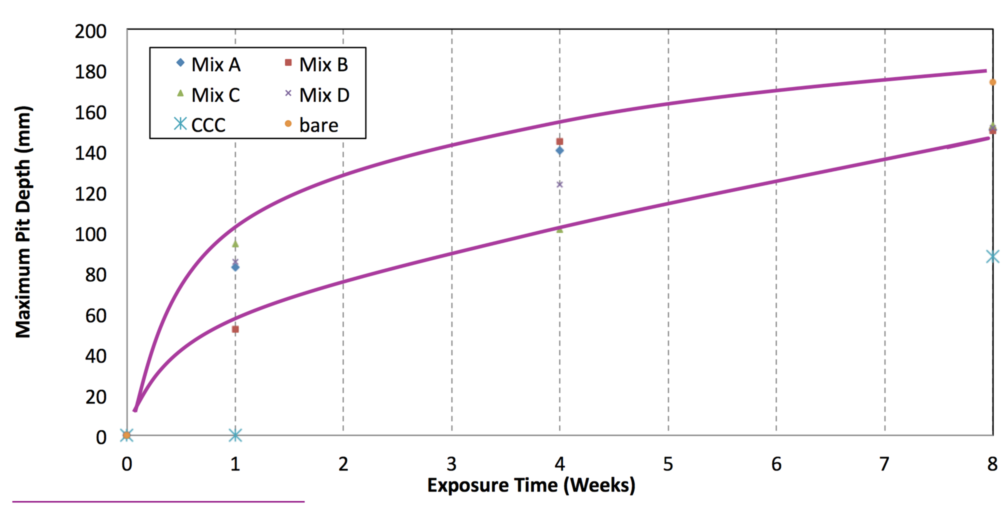
- Corrosion on graphene coated coupons after 144 hrs (cf 24 hrs - bare)
- Segregation of metallics at grain boundaries (preferential corrosion attack)
- Visual inspection revealed
  - areas with GO coverage – minimal corrosion
  - areas with poor GO coverage – pitting corrosion
- Corrosion pitting on the CCC coupons after 1344 weeks
- Maximum pit depth followed a power law relationship



Graphene coated and CCC specimens (0 and 1244 hrs)



Overview of Metrology Pit Depth Measurement Process.



Maximum Pit Depth Profiles

Conclusions

- A variety of methods can be used to deposit graphene on metallic surfaces.
- Graphene coatings have shown the ability to provide corrosion protection of metallic materials of over an order of magnitude.
- Corrosion testing of graphene coatings on aluminium alloys have focussed on GO, sol gels and its incorporation in epoxy resins.
- CVD not applicable to AA (small concentration of graphitic materials creates a galvanic couple between the anodic substrate and cathodic graphene)
- Pilot program produced mixed results. Poor performance in areas where graphene coverage was incomplete; protection in areas where adequate.
- Defence typically operate older aircraft and corrosion is the primary cause of structural non-conformances and maintenance burden on airframes. In addition to cost benefits, graphene coatings have the added advantage in providing an environmentally friendly alternative to chromates.

Future Work

- Tailoring of coating with graphene manufacturers.
- Additional Electrochemical testing to understand corrosion mechanics
- Characterisation of the graphene coating (SEM, XPS, Raman Spectroscopy
- Trial program on a redundant/ tertiary structural component.

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