Multilayer sol–gel coatings for corrosion protection of magnesium

A.L.K. Tan\textsuperscript{a,*}, A.M. Soutar\textsuperscript{a}, I.F. Annergren\textsuperscript{a}, Y.N. Liu\textsuperscript{b}

\textsuperscript{a}Singapore Institute of Manufacturing Technology, 71 Nanyang Drive Singapore 638075, Singapore
\textsuperscript{b}School of Materials Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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Abstract

Magnesium, although valuable, is reactive and requires protection before it can be used in many applications. This study evaluates the corrosion protection of Mg by multilayer coatings. The coatings consist of an anodised layer and one or two sol–gel layers. Potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion properties of these coatings. A porous anodised Mg oxide layer is employed as an intermediate layer, which enhances the adhesion of sol–gel layers. Sol–gel layers provide corrosion protection by physically sealing pores in the anodised layer and acting as a barrier. Defects and porosity in the coatings are the main causes of corrosion, allowing diffusion paths for corrosive species to reach the metal surface, where they can initiate corrosion. The multilayer approach is found to significantly improve the corrosion resistance of Mg by reducing levels of porosity.

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1. Introduction

Magnesium is abundant in the earth crust [1] and has many useful properties that are suitable for a number of applications. It has a high strength-to-weight ratio, allowing a significant decrease in the weight of components without sacrificing structural strength [2]. Magnesium also has high thermal conductivity, high damping characteristics, good machinability and is easily recycled [3]. Its electromagnetic shielding properties have led to its use in electronic applications [3]. However, magnesium and its alloys are highly susceptible to corrosion, and this has limited its useful applications [4,5].

One way to provide corrosion protection is to coat the surface to physically prevent contact with the environment. Sol–gel coatings have been reported to provide corrosion protection to metals [6,7]. However, it is not possible to apply sol–gel coatings directly to the magnesium surface, as it would react with the coating solution, leading to poor adhesion of the layer and subsequent corrosion of the metal.

It has been reported that the presence of an anodised layer substantially improves the adhesion of subsequently applied sol–gel coatings [8,9], which provide corrosion protection by physically sealing pores in the anodised layer and acting as a barrier layer [6]. Unfortunately, pores and defects in the sol–gel layer provide paths for electrolyte to diffuse through the coating and corrode the substrate. Although increasing the coating thickness can improve the barrier layer and reduce the likelihood of corrosive species diffusing across it, thicker layers are prone to cracking when the critical thickness of the coating is exceeded. One alternative is to apply multiple thinner layers to increase corrosion resistance.

This study examines a multilayer approach to provide corrosion protection to magnesium substrates. Electrochemical techniques have been employed to characterise the corrosion properties of these coatings.

2. Methodology

2.1. Coating of Mg

Magnesium substrates (AZ91D) with dimensions of 10×6×1 cm were polished, degreased in an alkaline solution and finally etched before anodising. Anodising
was conducted at room temperature for 15 min using direct
current in a solution of 2.44 M NaAlO₂ and 3 M NaOH,
with a rectangular grid of stainless steel serving as the
cathode.

3-Methacryloxypropyl trimethoxysilane (MEMO; Aldrich, 99.7%, 19.8 g), 3-mercaptopropyl trimethoxysilane (TPTMS; Aldrich, 95%, 0.8 g) and ethanol (GR, 11.0 g) were mixed together and stirred. Water-based colloidal silica (9 g) was added dropwise. The mixture was allowed to hydrolyse before an oligomer (6.8 g) and a photoinitiator (2-hydroxyl-2-methylpropiophenone, 2.0 g) were added. The sol was diluted with alcohol to produce an appropriate viscosity for deposition by spraying.

Sol–gel coatings were applied to the anodised magnesium by spraying. By changing the number of passes that the spray gun made over the substrate (one, two, three or five times), the thickness of the coatings was varied. Coated samples were first UV cured before a thermal cure at 150 °C for 30 min was carried out.

2.2. Electrochemical measurements

For potentiodynamic measurements and electrochemical impedance spectroscopy (EIS), an electrochemical interface SI 1287 and an Impedance/Gain-Phase Analyser SI 1260 from Solartron Group, England, were used in combination. The test cell used was a critical pitting test cell from Gamry Instruments, USA, with an active area of 0.90 cm². A thre electrode system was used, consisting of a calomel reference electrode, a graphite counter electrode and the sample under test as the working electrode. The electrolyte employed was 3% w/w sodium chloride solution. Samples were allowed to stabilise at their open circuit potential for 30 min before the measurements were started. EIS was then performed with a superimposed AC potential of 30 mV and with the DC potential fixed at the corrosion potential. Measurements were conducted in the frequency range of 10⁻⁴–10⁻² Hz.

After the EIS measurements, the samples were potentiodynamically polarised cathodically −0.20 V from the open circuit potential. Thereafter, the sample was polarised anodically. A scan rate of 0.5 mV/s was used during polarisation.

3. Results and discussion

3.1. Potentiodynamic polarisation

Polarisation of the anodised Mg layer showed no passive region. The sample exhibited an open circuit potential of −1.60 V, indicating that the response was from Mg and that the anodised layer did not function as an effective barrier against the electrolyte. Fig. 1 shows the surface of an anodised layer, illustrating that the anodised layer is highly porous. Pores are measured to be about 1 μm in diameter. The highly porous layer permits the penetration of electrolyte to the Mg surface and allows corrosion to proceed.
Although the corrosion resistance of the anodised layer is poor, it promotes adhesion by mechanical interlocking with subsequently applied sol–gel layers [8,9]. Fig. 2 shows a cross-sectional view of the anodised Mg with a single layer of sol–gel coating, illustrating that the sol–gel layer fuses with the anodised layer.

Results from the polarisation measurements conducted on a sample coated with a single-pass sol–gel coating are illustrated in Fig. 3. Samples exhibited a small passive potential range, in which the current was low and stable. However, at 2.55 V, there was a rapid increase in current density, indicating that pitting of the coating was initiated. The existence of the passive region is due to the sol–gel layer that seals pores in the anodised layer, inhibiting electrolyte diffusion to the Mg surface. However, the sol–gel layer still has defects, and when the polarisation becomes too positive, pitting occurs.

When thicker single layers were applied, the pitting potential increased. Fig. 4 shows the polarisation diagram for a three-pass single-layer coating. Coatings exhibited a larger passive region, probably due to the fact that the coating was thicker (21–23 μm), and provided a more...
effective physical barrier against corrosive attack as compared with the thinner one-pass single-layer coating (6–10 µm). Pitting was initiated at 12.52 V, due mainly to the defects and pores that exist in the sol–gel layer, and which provide pathways for electrolyte diffusion.

When the number of spray passes was further increased to five, the thickness of the sol–gel was increased to 54–57 µm. Polarisation measurements of five-pass single-layer coatings exhibited an open circuit potential of −0.8 V, implying that the sol–gel layer is sufficiently dense and defect-free that the response is only related to the sol–gel layer. Upon polarisation, the coating exhibited passive behaviour throughout the polarisation range, and no pitting occurred up to the scan limit of 14 V (Fig. 5a). When the measurement was conducted on an area with a visible defect, the current density remained low and no breakthrough could be detected on the forward anodic scan. However, pitting occurred in the cathodic scan at a potential of 5.54 V. This occurred because the potential was probably wearing down the region with the defect during the forward scan and the coating was finally worn down and breakthrough occurred in the defect region during the cathodic scan (Fig. 5b).

Polarisation studies for all single-layer coatings show that failure occurred, even for layers as thick as 54–57 µm, since defects are unavoidable. Another approach is needed to overcome this problem, instead of merely spraying thicker coatings, which brings about other problems such as cracking, when the critical layer thickness is exceeded.

Double-layer coatings were obtained by spraying two layers of two passes each. The first layer was UV cured prior to the application of the second. The thickness of each layer was about 15 µm. Polarisation measurements conducted on areas with and without visible defects showed that samples remained passive up to the scan limit of 14 V, with no evidence of pitting detected. Fig. 6 shows the polarisation diagram for a two-pass double-layer coating on an area with visible defects. A cross-sectional view of the coating (Fig. 7) shows that the bottom sol–gel layer binds with the anodised layer and the two sol–gel layers merge well with each other.

The increased corrosion protection is assumed to be due to the additional layer of sol–gel layer, which covers pores and/or defects in the bottom layer and prevents the bottom layer from being exposed directly to the corrosive electrolyte. There is a low probability that defects produced in individual layers are connected with each other and electrolyte is thus not able to penetrate to the metal surface and start a localised attack. In addition, applying a further layer increases the thickness of the barrier coating, which serves as a better protective coating without running into problems like cracking. However, good adhesion properties between the layers must also be ensured to prevent the electrolyte from diffusing between the layers.

3.2. Electrochemical impedance spectroscopy

Fig. 8 shows bode diagrams for Mg, anodised Mg and the sol–gel coatings. The impedance of the Mg substrate is in the range of $10^2 \Omega$ at low frequencies. In the same frequency range, the impedance of the anodised layer is increased to the range of $10^3 \Omega$. Coating the anodised substrate with sol–gel layers increases the impedance further by at least three orders of magnitude. The impedance of the single-layer coating increases with the number of passes. Thus, it can be shown that the sol–gel coatings served as an effective barrier against corrosive electrolyte ingress during EIS measurements. Increasing the thickness by raising the number of passes for a single-layer coating provides a better barrier with higher impedance values.

4. Conclusion

Corrosion protection of Mg was achieved by applying multilayer coatings. The coatings consist of an anodised layer and one or two sol–gel layers. A porous anodised Mg layer served as an intermediate layer, which enhanced the adhesion of subsequently applied sol–gel layers. Electrochemical analyses show that the sol–gel layers provide corrosion protection by physically sealing pores in the anodised layer and acting as a barrier. Since defects and porosity in the coatings are the main causes of degradation, applying multilayers eliminates diffusion paths for corrosive species to reach the metal surface, thereby limiting the incidence of localised attack.

References


