Progress in Organic Coatings 78 (2015) 455–461

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

The effect of exposure condition on the degradation behavior of magnesium rich coatings☆

Rebecca L. DeRosa[a,*], Istvan Szabo[b], Gordon P. Bierwagen[c], Dante Battocchi[c]

[a] Corning Incorporated, Corning, NY, United States
[b] ProUnlimited, NY, United States
[c] North Dakota State University, Fargo, ND, United States

ARTICLE INFO

Article history:
Received 4 October 2013
Received in revised form 5 September 2014
Accepted 9 September 2014
Available online 3 October 2014

Keywords:
Magnesium rich coating
Corrosion protection
Aluminum
Open circuit potential
XPS
SEM

ABSTRACT

We evaluated magnesium rich epoxy polyamide primers under different environmental exposure conditions. The purpose was to highlight differences in deterioration of these types of coatings as a function of exposure condition. We compared data for samples under constant immersion in dilute Harrison's solution (DHS-CI) to identical samples exposed to 90% relative humidity (90% RH). E_{OCP}, XPS and SEM analysis of the coatings supported our findings that the samples under DHS-CI undergo rapid dissolution and deterioration compared to the 90% RH samples. The difference was that the latter were able to form carbonate corrosion products, which are known to provide additional passivating protection.

1. Introduction

Metal rich coatings protect the underlying substrate via cathodic protection; when two dissimilar metals are in contact, the one lower in the electromotive force (EMF) series (more active metal) will preferentially corrode over the more noble metal. Metal rich coatings are formulated near the critical pigment volume concentration (CPVC) using an active metal powder. Particle packing at or above the CPVC ensures continuous electrical contact among the metal particles and with the substrate. The use of active metal particles dispersed in the coating is ideal due to the high surface area afforded by the particles, which act as the sacrificial anode.

Magnesium satisfies criteria for corrosion protection of aluminum alloys due to its position in the EMF series. Bierwagen et al. were the first to study magnesium rich primer coatings (MgRC) for corrosion protection of aluminum alloys [1–10].

Nanna and Bierwagen [1] published results for an array of primers formulated with magnesium pigments at different pigment volume concentrations (PVC). Their goal was to formulate a suitable magnesium rich coating for corrosion protection of aluminum alloys commonly used in the aerospace industry. They used open circuit potential (E_{ocp}) and electrochemical impedance analysis (EIS) to assess the corrosion protection abilities of the coatings under constant immersion in 3 wt% NaCl. In addition the coatings were monitored after exposure to cyclic salt spray following Prohesion conditions. According to their results, a primer system consisting of a Mg-pigment doped epoxy-urea interpenetrating network (IPN) showed the best overall performance. These initial results however showed no clear trend with respect to PVC and coating performance. Battocchi et al. [5] continued the work, assessing a silane-modified multi-layer IPN formulated with 50 wt% PVC magnesium powder. Through electrochemical testing (E_{ocp} and EIS) as well as energy dispersive X-ray analysis, they found the coating system followed two modes of protection. In the first stage, the Mg particles shift the E_{ocp} of the system (−1.0 to −1.2 V vs. saturated calomel electrode (SCE)) to below the pitting corrosion potential of aluminum (−0.5 to −0.6 V vs. SCE). Battocchi et al. believe that Mg inhibits pit nucleation and growth in the Al alloy, during this stage. They also reported that continued electrochemical activity leads to stage-2 and to the formation of a porous magnesium oxide layer, which inhibits corrosion by passivating the aluminum substrate.

☆ This article belongs to special issue 'Studies of Coating and Polymer Films'.

* Corresponding author. Tel.: +1 607 974 6104; fax: +1 607 974 2166.
E-mail address: derosarl@corning.com (R.L. DeRosa).

http://dx.doi.org/10.1016/j.porgcoat.2014.09.006
0300-9440/© 2014 Elsevier B.V. All rights reserved.

Our overall goal is to understand specifically the role of the magnesium particles as sacrificial anodes in MgRCs on Al-2024 in a corrosive environment. With this in mind, we set out to find the corrosion products that develop on the surface of the primer during the early stages of exposure. However, we found that the exposure conditions can have a pronounced effect on the chemical form of magnesium, thereby affecting its role as a sacrificial anode.

Magnesium oxidation is quite complex due to the environment and variables associated with the electrochemical cell. The oxidation products are highly dependent on the chemical environment. Since aluminum alloys contain additional metals, they can react with Mg to form passivating corrosion products. For a magnesium rich coating, the oxidation state of the magnesium particles significantly affects the resulting electrochemical behavior of the system.

1.1. Oxidation mechanisms for magnesium

The oxidation of magnesium has been studied in many different environments: oxygen [11–15], water vapor [12,14,16–20], salts [21,22] -aerated and dearated [23], with and without the presence of CO_2 [22,24]. The following, is an overview of magnesium corrosion by-products that can form based on different environments.

In the presence of oxygen, magnesium oxidizes according to Eq. (1)–(3) [11,25].

$$1/2O_2 + 2e^- \rightarrow O^{2-} \quad (1)$$

$$Mg \rightarrow Mg^{2-} + 2e^- \quad (2)$$

$$1/2O_2 + Mg \rightarrow MgO \quad (3)$$

In the presence of water vapor, but no CO_2, magnesium hydroxide (brucite) begins to form. The reactions leading to the formation of brucite are given in Eqs. (4)–(7). Initially anodic dissolution of Mg occurs (Eq. (2)) coupled with the reduction of water (Eq. (4)) to give the reaction in Eqs. (5) and (6). An alternate path is from MgO to $Mg(OH)_2$ (Eq. (7)).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

$$Mg + 2OH^- \rightarrow Mg(OH)_2 + 2e^- \quad (5)$$

$$Mg + 2H_2O^- \rightarrow Mg(OH)_2 + H_2 \quad (6)$$

$$MgO + H_2O \leftrightarrow Mg(OH)_2 \quad (7)$$

In atmospheric conditions with the presence of CO_2, $Mg(OH)_2$ quickly changes to a magnesium carbonate, magnesite. The reaction can be followed in Eq. (8). With abundant amounts of CO_2 and H_2O, a hydrated carbonate, nesquehonite, will form according to Eq. (9).

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \quad (8)$$

$$MgCO_3 + H_2O \rightarrow MgCO_3{\cdot}H_2O \quad (9)$$

Although we are reporting work on the behavior of MgRC on aluminum alloys, it is helpful to understand the mechanisms associated with Mg alloys. This is done with the thought that if a breach in the coating occurs, metal ion impurities from the substrate may become part of the final corrosion protection mechanism.

Research on magnesium alloys has elucidated the formation of additional Mg carbonates. Jönsson et al. [22] exposed Mg Alloy AZ91D to 95% relative humidity and dilute concentrations of NaCl. After exposures longer than 6 days they found pits containing brucite ($Mg(OH)_2$) covered with an insoluble hydrated magnesium carbonate, hydromagnesite, crust. Hydromagnesite can form through various routes, but Jönsson et al. believed it formed via Eq. (10).

$$4MgCO_3{\cdot}H_2O \rightarrow 3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O + CO_2 + 8H_2O \quad (10)$$

Lindström et al. analyzed the corrosion rate and subsequent corrosion products formed on high purity die-cast MgAl alloys in the presence of dilute NaCl and controlled CO_2 environment. They found that, in the presence of CO_2, the corrosion rate decreased. Examination of the corrosion product revealed the formation of a thick passivating magnesium hydroxyl carbonate layer, giorgiosite. This carbonate was believed to form according to Eq. (11).

$$5Mg(OH)_2 + 4HCO_3^- + H_2O \rightarrow Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O + CO_2 + 4OH^- \quad (11)$$

Lindström noted that although chlorine was present in X-ray diffraction results, it was found to be physically embedded into the $Mg(OH)_2$ corrosion product that formed. Only a few researchers report the formation of magnesium hydroxyl chloride hydrates, $Mg_{10}(OH)_{18}Cl_2{\cdot}5H_2O$; $Mg_2Cl(OH)_3{\cdot}4H_2O$; Mg_2OHCl [26,27].

To this end, we set out to evaluate the difference in electrochemical behavior of MgRC as a function of exposure condition. In practice, 3 different electrolyte solutions are used to monitor corrosion behavior of coated metal substrates along with other customized tests used to emulate specific conditions: 5% NaCl solution is used to compare results with ASTM B-117 salt spray [28], 3.5% NaCl solution is used to represent marine salt water, and dilute Harrison's solution is used in some tests because it is considered to emulate atmospheric conditions due to the incorporation of $(NH_4)_2SO_4$ [8].

We chose one customized exposure, 90% relative humidity (90% RH), and compared it to a standard system, constant immersion in dilute Harrison's solution (DHS-CI). The 90% RH condition was chosen to represent a milder corrosion environment. This choice is supported by Upadhyay et al. [10] who recently reported the electrochemical behavior of MgRC at various relative humidity. They indicated standard accelerated exposure conditions exceed normal ambient conditions but the fundamental corrosion mechanism remains the same. 90% RH was chosen to cause the onset of corrosion of the Mg, but retain the Mg particles in the coating so we could evaluate chemical and physical changes occurring during the early stages of protection. Samples were evaluated using open circuit potential (E_{ocp}) polarization, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) in their as-received state and after varying times of exposure.

2. Materials and methods

2.1. Samples

Samples used for testing were epoxy poly-amide based resin formulated at 45% PVC with magnesium powder on Al-2024-T3. The magnesium-rich primer was made using a stabilized Mg particulate, with an average diameter of 30–40 μm, manufactured by Non Ferrum-Metallpulver GmbH, Salzburg, Austria. As magnesium ingots are ground, a naturally occurring layer of magnesium oxide (MgO) is instantly formed on the micron-sized particles. This naturally occurring MgO layer prevents the Mg powder from becoming pyrophoric when exposed to air. Samples were spray coated with a nominal thickness of 150 ± 40 μm. Coating thickness was determined using an Elcometer 345 under non-ferrous conditions. At least 10 points were measured for each sample area (exposed versus unexposed regions).

2.2. Exposure conditions

Samples were analyzed under four conditions: (i) as-received, (ii) DHS-CI, (iii) 90% RH with electrolyte exposure and (iv) cycled 90% RH + DHS-CI for electrochemical studies that needed to be