Assessment of the corrosion protection of aluminium substrates by a Mg-rich primer: EIS, SVET and SECM study

Alda Simões a,*, Dante Battocchi b, Dennis Tallman b, Gordon Bierwagen b

a IST, Technical University of Lisbon, ICEMS and Department of Chemical and Biological Engineering, 1049-001 Lisboa, Portugal
b NDSU, Department of Coatings and Polymeric Materials, Fargo, ND, USA

Article info
Article history:
Received 13 July 2007
Received in revised form 13 February 2008
Accepted 19 February 2008

Keywords:
Steel
Magnesium
Cathodic protection
Electrochemistry

Abstract
Magnesium-rich coatings have the capability of providing sacrificial corrosion protection to aluminium substrates and therefore present a new and challenging field of development. In this work the mechanism of protection of an aluminium substrate by a Mg-rich coating was investigated using the scanning vibrating electrode technique (SVET) and scanning electrochemical microscopy (SECM). The SVET has shown the evolution of the pit activity with time under sacrificial protection, whereas the SECM allowed indirect sensing of the cathodic activity above the electrodes. The study was complemented by classical electrochemical techniques, namely electrochemical impedance spectroscopy and open circuit potential measurement.

The results show that magnesium acts in a first stage by both preventing nucleation of pits and inhibiting the growth of the already existing ones, whereas at a later stage the precipitation of a porous layer of magnesium oxide at defective areas leads to some degree of barrier protection.

1. Introduction

Several techniques with enhanced spatial resolution have been introduced recently to the field of corrosion science, with the advantage of giving microscopic information on the processes occurring locally at electrochemically active surfaces. The scanning Kelvin probe [1,2], and localized electrochemical impedance spectroscopy (EIS) [3,4] have been quite successful. Mapping of ionic currents in solution is also a promising approach. This is based upon scanning a microelectrode over the immersed specimen, either in a static mode (scanning reference electrode technique, SRET) or in a vibrating mode (scanning vibrating electrode technique, SVET), allowing for mapping of either current or potential in the solution [5]. These techniques have been effective in monitoring the progress of many corrosion situations [6,7]. Since the first applications of the SVET to science, the technique has been used for several problems, such as the corrosion of bare aluminium [8], the galvanic activity at scribes [9], the influence of inhibitors [10] and the galvanic corrosion of soldered copper [11] and of zinc–steel corrosion cells [12]. The SVET is based upon the existence of an electric field associated with ionic concentration gradients over electrochemically active surfaces. A microprobe is made to vibrate in this electric field, and its potential is measured versus a stationary electrode. From the potential maximum and minimum, and taking into consideration the solution resistivity, the ionic current flow in solution can be determined. The sign of the current can also be determined and therefore, by scanning the surface, it is possible to map the anodic and cathodic areas, and also to compare the relative current densities.

Another novel localized electrochemical technique is the scanning electrochemical microscope (SECM), in which a non-vibrating ultra-microelectrode is used as a scanning electrochemical micro-probe [13]. The SECM has been applied to aluminium alloys to map the conductivity of the surface and also to the corrosion of bare metals [12]. Assessment of surface electrochemical activity can be made in several ways, such as cyclic voltammetry or local potentials in solution. It can also be used in the amperometric mode, in which a constant potential is applied to the probe. Under this applied potential, electrochemical reactions will take place at the probe; namely, it is possible to assess the concentrations of dissolved reactants or products in the vicinity of an electrode [14], provided only one species is being oxidized/reduced and the solvent is stable. With the microprobe, this approach has been used to sense variations in the concentration of dissolved oxygen near cathodic areas [15,16]. Thus, if a potential is applied to the probe in a potential range at which dissolved oxygen becomes reduced, scanning the probe over the surface allows assessing depletion of oxygen over the cathodic areas, whereas at the anodic areas the oxygen is not affected.
In previous publications the development of a sacrificial primer for protection of aluminium alloys was presented [17,18] and it was concluded that the Mg-rich coating can act by three mechanisms, corresponding to different stages of degradation: in fresh systems, there is a barrier effect provided by the polymer matrix to the coated substrate; at the defective areas such as scratches, the magnesium particles provide cathodic protection; finally, at a later stage in the process, there is also a barrier effect at the scratches, provided by a layer of magnesium oxides precipitated at the cathodic areas. The techniques used so far only gave surface-averaged information on the system, but the use of localized techniques opens new research possibilities and has been applied in this work.

2. Experimental

Aluminium panels of AA 2024-T3 (Q Panel Lab products, Cleveland, OH) were used with the exception of a test using a scribed sample, in which the results presented refer to AA7075-T6. The samples to be used as bare alloys were polished to grit 600 and rinsed with distilled water and ethanol, whereas those to be coated with the Mg-rich primer were wire-brushed and rinsed with distilled water and hexane. The magnesium-rich primer was made using a 30–40 μm stabilized Mg particulate (Non-Ferrum-Metallpulver GmbH, Austria), consisting of Mg covered with a thin layer of MgO, intended to control the reactivity of magnesium. The dispersion was made using a silane-modified multi-layer/interpenetrating polymer network matrix. In order to ensure electronic conduction, the Mg-rich primer was formulated with a pigment volume concentration (PVC) of 50% (which is approximately the critical PVC of the system), with a total thickness of ∼70 μm. Macroscopically, the dry coating was matte and rough, as a result of the large magnesium particles. SEM inspection of the cross-section shows that the coating consists essentially of magnesium particles covered by a thin layer of binder, with a distance between neighbour particles of ∼1 μm [18].

The electrochemical cell consisted of a glass cylinder reservoir clamped on the surface through an o-ring and filled with the electrolytic solution, leaving an exposed area of 7.1 cm². A saturated calomel electrode (SCE) and a Pt mesh with approximately 1 cm² area were used as reference and counter electrode, respectively. The electrochemical tests were conducted in 0.1 wt.% NaCl or dilute Harrison’s solution (DHS), which emulates acid rain and consists of 0.35 wt.% (NH₄)₂SO₄ and 0.05 wt.% NaCl in distilled water. A Gamry PC4/300 potentiostat/galvanostat with EIS 300 software was used to collect the electrochemical data. Impedance spectra were collected at the open circuit potential (OCP), using 5 mV of signal amplitude for the magnesium electrode and 10 mV for the other systems. Currents values are normalized to 1 cm². Potentiodynamic plots were obtained at a scanning rate of 5 mV/s, starting from the OCP.

For the SVET investigations a coated specimen was mounted on a resin holder, near a piece of the bare alloy of the same dimensions, Fig. 1. The electrodes, which consisted of rectangles with 1 mm × 2 mm each, were mounted on a resin cylinder, parallel to each other and 2 mm apart, and could be electrically connected through a switch at the back of the sample holder. The gap between the two electrodes is important because of the high electrochemical activity of magnesium, which undergoes corrosion with significant hydrogen bubbling. Adhesive tape was used to obtain the reservoir for the electrolyte and the surface was leveled using a small air-bubble level. Experiments were performed in 5 mL of DHS. The vibrating probe consisted of a 20-μm platinum-black-coated tip, placed 200 μm above the substrate. The vibrating amplitudes of the scanning probe were adjusted to 20 μm, both parallel and perpendicular to the surface. The electrodes were left unbiased. Each scan consisted of 400 data points obtained on a 20 × 20 grid, with an integration time of 1 s per point. A complete scan required ∼10 min.

The SECM equipment model CHI900² was equipped with a 10-μm platinum tip microprobe, an Ag/AgCl/KCl saturated reference electrode and a platinum counter electrode. The specimens consisted of AA2024 (5 mm × 0.75 mm, corresponding to 4.0 mm² exposed area) and pure Mg (5 mm × 0.25 mm, corresponding to 1.25 mm² exposed area), both embedded in epoxy resin. Wires

---

¹ Gamry Instruments Inc., 734 Louis Drive, Warminster, PA 18974.
² CH Instruments, Austin, TX.
for electrical connection between the two electrodes were left at the back of the resin mount, Fig. 2. Apart from the connection between the aluminium and the magnesium, there was no other electrical connection of the specimens, i.e., the corrosion process was followed exclusively from the solution-side and took place at the spontaneous potential of the system. The front of the resin + specimens setup was polished before each experiment and the reservoir for the electrolyte was obtained applying plastic tape around the epoxy cylinder. The technique was used to obtain amperometric line scans across the specimens’ cross-sections.

3. Results

3.1. DC polarization and impedance measurements

The dc potentiodynamic plot for Mg is approximately symmetrical around the corrosion potential, revealing an active state – Fig. 3 – with a corrosion rate of approximately 0.4 mA cm$^{-2}$. For the bare alloy, the cathodic curve has a plateau corresponding to the diffusion-limited reduction of dissolved oxygen, followed by a current increase, due to hydrogen evolution. Aluminium is susceptible to localized corrosion at its OCP, as shown in the anodic branch of the polarization curve, for which a small anodic polarization leads to a current burst of several orders of magnitude, with fast growth of pits.

For the primed sample, the cathodic branch corresponds to the simultaneous reduction of oxygen and H$^+$, whereas the anodic branch has two regions: below the pitting potential of the Al alloys the Tafel plot has a high slope and reaches a limiting current. Near the corrosion potential of the bare alloy, the slope decreases abruptly, revealing pitting of the substrate together with Mg oxidation. Clearly, the effect of the Mg-rich primer in protecting the Al alloy results not so much in decreasing its dissolution rate, but rather in polarizing the alloy below its pitting potential.

Pure magnesium exhibited very low impedance with visible bubbling on the surface, corresponding to a high corrosion rate. The impedance spectrum reveals only one time constant with an impedance of 100$^\Omega$ – Fig. 4 – corresponding to intense corrosion. Due to the rapid dissolution, the experiment had to be restricted to short times. The impedance of magnesium was smaller than that of the bare aluminium substrate by nearly two orders of magnitude, in good agreement with the results from potentiodynamic polarization. When the Mg-rich coating was applied, the total impedance of the system increased significantly, again in good agreement with the potentiodynamic observations.

For the primed alloy, EIS fitting is presented in Fig. 5. In this approach, capacitive responses were described by constant phase elements (CPE), defined as

$$Z_0 = \frac{1}{Q^1(j2\pi f)^n}$$

On the high frequency part of the spectrum, there is an ill-defined capacitance ($Q_1$) that goes out of the working frequency window and that is followed by a resistance ($R_c$) at $\sim 10^4$ Hz. These can only be due to the polymer phase in the coating [18], which in practice corresponds to an extremely thin layer of polymer. The capacitive region following in the spectrum, at intermediate frequencies, probably corresponds to the double layer at the surface of the magnesium particles ($Q_1$). This capacitance is initially very small, because magnesium particles are not only coated with the polymer, but also covered by a layer of magnesium oxide. As water penetrates across the coating and the oxide becomes dissolved, the number of particles exposed to water increases, increasing the total active area and consequently increasing the capacitance. This is also revealed in a charge transfer resistance ($R_c$) drop, also observed in Fig. 6 in the decrease of the plateau at $\sim 1$ Hz.

The physical meaning of the low frequency process (represented by $R_c$ and $Q_1$) is not totally clear. It may be due to the cathodic reaction on the exposed areas of aluminium. If this is the case, then it can be related to a mass diffusion process of charged species, possibly of H$^+$ or of OH$^-$. Abreu et al. [19] obtained similar spectra with a zinc-rich primer applied on steel substrates and proposed that the zinc oxide layer could lead to a capacitive loop in the spectrum.

The evolution of the coating parameters can be better observed in Fig. 7. The time decay of the coating resistance is consistent with a process of water penetration, whereas the decrease of the charge transfer resistance and the growth of the double layer capacitance reveal increasing exposed area or increasing corrosion rate of the magnesium particles.

3.2. Mechanism of action at defective areas

In order to assess the efficiency and protection mechanism at defective areas of the primer, a large defect (area 1 cm$^2$) was made
Fig. 5. (a) Fitting of impedance spectrum of Mg-rich primer on AA2024 after 1 h of immersion; symbols: experimental data; line: fitted spectrum; (b) equivalent circuit. Fitting data:

- $R_s = 583 \ \Omega \ \text{cm}^2$;
- $Q_1 = 3.14 \times 10^{-8} \ \text{F cm}^2 \ \text{s}^{-1}$; $n_1 = 0.79$;
- $R_c = 7173 \ \Omega \ \text{cm}^2$;
- $Q_2 = 6.22 \times 10^{-8} \ \text{F cm}^2 \ \text{s}^{-1}$; $n_2 = 0.85$;
- $R_{ct} = 4.05 \times 10^5 \ \Omega \ \text{cm}^2$;
- $Q_3 = 1.91 \times 10^{-6} \ \text{F cm}^2 \ \text{s}^{-1}$; $n_3 = 0.93$;
- $R_f = 3.49 \times 10^6 \ \Omega \ \text{cm}^2$.

Fig. 6. Impedance spectra of Mg-rich primer on the Al alloy in NaCl solution at various exposure times (1 hour – 2 days).

Fig. 7. Evolution of parameters estimated from fitting of impedance data: (a) coating resistance, (b) charge transfer resistance, and (c) double layer capacitance.
rent distribution was nearly constant, whereas the anodic activity at the pit decreased. The current at the pit only became cathodic after sufficient time (curve d).

One alternative way to monitor the electrochemical activity at an electrode is to sense ionic concentrations in solution using the SECM. In neutral aerated solution the cathodic reactions are the reduction of water and of oxygen:

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$  \hspace{1cm} (1)
and
\[ \text{Mg anode}. \]

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

whereas at the anode the oxidation of metal takes place, either
\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \] (3)

or
\[ \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \] (4)

Reaction (1) was easily detected by the gas evolution at the electrode surface. Reaction (2), in contrast, cannot be visually detected, and typically proceeds under diffusion control. As a result of these reactions, depletion of oxygen will occur near the cathode and accumulation of metal cations will occur near the anode. Amperometric scan curves can in principle be used to sense the concentration of species in solution. If a microelectrode is used to scan the surface with a constant potential applied, then it is possible to detect the concentration gradients by the changes in the potentiostatic currents at the microelectrode. With the aim of assessing the oxygen dissolved in solution, amperometric reduction currents were measured. The aluminium electrode was connected to a pure Mg electrode and the local concentration of dissolved molecular oxygen was sensed by applying a constant potential of \(-0.75\text{ V}\) to the SECM tip and by scanning it over the surface, according to a procedure used before [15]. The profile of oxygen reduction current across the isolated aluminium electrode was nearly constant, with only a slight depression above the aluminium compared to the mounting resin, Fig. 12. Upon connection to magnesium, there was a drop of the cathodic current measured at the tip above the aluminium, meaning that the aluminium had become more cathodic, and therefore more protected.

Magnesium is electrochemically very active and undergoes severe corrosion in water, with intense hydrogen evolution. This gas evolution was easily observed in the electrically isolated sample but was nearly suppressed whenever the electric connection was established with the nobler Al electrode. The amperometric scans made across the Mg electrode revealed a reduction current minimum above the metal. This minimum was practically unaffected by the coupling to the Al electrode, Fig. 13.

**4. Discussion**

The SVET applied to the evolution of pitting corrosion has given information that was not possible using non-localized techniques. The technique has shown the time evolution of the anodic current at the pit, on a globally cathodic surface, which cannot be observed with the classical electrochemical techniques. Inhibition of corrosion in pre-existing pit is a slow process, which results from the differences in pH and chemistry inside and outside the pit. Even under cathodic protection, it still took a few hours for a pit to become cathodic, although even at that stage the local cathodic currents measured over the pit were less negative than those measured on the outer surface. This shows how slow the repassivation process of a pit can be even under cathodic protection. In a previous study it was concluded that the protection provided by the polymeric Mg-rich coating could be described by three stages [18]: in the first, the barrier effect of the polymer predominated; in this stage water penetrated gradually into the coating, reaching the magnesium particles and eventually the substrate. This led to the second stage, in which sacrificial protection was active, provided the magnesium particles provided electrical conduction. The time length of this second stage depends on the total amount of magnesium available and on its consumption rate. Finally, in a third stage, precipitation of magnesium oxide at the exposed aluminium areas leads to another barrier effect, this time at the defective areas. For long exposure times, when the pH rise at the cathodic areas exceeds the critical pH for MgO precipitation, this barrier effect can be expected to inhibit pitting propagation.

The use of the SECM to assess the oxygen concentration over the electrodes gave valuable information for corrosion studies. Whereas the SVET has shown the spatial distribution of the cathodic and anodic areas, the amperometric curves show that oxygen depletion in the vicinity of the electrodes became intense on aluminium when it became galvanically protected by magnesium. Further, it revealed that the local minimum in the cathodic amperometric curves over the magnesium was independent of the coupling to Al, meaning that the reduction of oxygen still proceeds on Mg even when it acts as anode in the galvanic couple.

Magnesium is a very active metal. The reduction reactions occurring on Mg in a corrosion process are both water reduction with hydrogen evolution, and oxygen reduction (reactions (1) and (2)),

![Fig. 12. Amperometric scan curves obtained at \(-0.75\text{ V}\) vs. Ag/AgCl over the Al alloy, scan direction as indicated: (a) isolated electrode and (b) electrode coupled to the Mg anode.](image)

![Fig. 13. Amperometric scan curves obtained at \(-0.75\text{ V}\) vs. Ag/AgCl over the pure magnesium electrode: (a) isolated and (b) coupled to the aluminium electrode.](image)
influence on its rate and it is essentially the reduction of H\textsubscript{2}O that conditions, the potential shift due to galvanic coupling has little Fig. 14. Since oxygen reduction proceeds under diffusion limiting whereas the anodic reaction is metal oxidation, reaction (3). When magnesium is coupled to the Al alloy, its potential is shifted to less negative values and the global reduction rate is decreased, Fig. 14. Since oxygen reduction proceeds under diffusion limiting conditions, the potential shift due to galvanic coupling has little influence on its rate and it is essentially the reduction of H\textsubscript{2}O that is slowed down. The most important difference is observed in the “bulk” concentration, i.e., the concentration measured away from the electrode, which was reduced to nearly half the initial value in Fig. 13, curve (b). This possibly derives from the small solution volume, which results in a gradient of oxygen concentration across the entire electrolyte depth and to a decrease of the average concentration with time. For aluminium, in contrast, the activity is quite low when it is passivated by alumina. When it becomes cathodically polarized by the magnesium anode, reduction of both oxygen and of hydrogen takes place, preferentially at defective sites on the film. This leads to significant depletion of oxygen over the surface, as observed in the SECM measurements. Cathodic protection of aluminium can be a complicated process due to the susceptibility of this metal to localized corrosion. Because aluminium is passive in many situations and its pitting potential is very close to its spontaneous potential in neutral chloride solutions, coupling to magnesium shifts the potential of Al to more negative potentials, below the pitting potential and therefore inhibits pit nucleation. The OCP of magnesium in DHS [20] is approximately −1.9 V for magnesium and −0.5 V for AA2024 (vs. SCE), corresponding to a large electromotive force of 1.4 V that is capable of cathodically polarizing Al. Once pits already exist, however, it is the cathodic current that is crucial for pit repassivation. Naturally, this current depends on the cathode-to-anode area ratio. For a 1:1 ratio, the cathodic current on Al was typically 10 \mu A/cm\textsuperscript{2}. In the long term, this can lead to high pH values on aluminium. The pH rise can have two different actions: it can lead either to precipitation of Mg oxides, which will in principle provide some protection, or it can also cause destruction of the passive film and activation of aluminium. This question requires further study.

5. Conclusions

The use of non-intrusive localized electrochemical techniques provided an innovative means of monitoring the effect of cathodic protection on pitting corrosion of AA2024. Cathodic protection provided by the magnesium-rich coating was capable of inhibiting pit nucleation, by shifting the potential of the system in the cathodic direction and by decreasing the anodic activity at pre-existing pits. The rate of decay of the anodic activity at the pit on a globally cathodic surface was monitored and decreased gradually over a period of several hours. The high corrosion activity of magnesium leads to some maintenance of the cathodic reaction on Mg surface even when it behaved as sacrificial anode for aluminium. This could be assessed by changes in oxygen reduction current measured by a microprobe.

References