SVET and SECM imaging of cathodic protection of aluminium by a Mg-rich coating

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Abstract

The mechanism of cathodic protection of an aluminium substrate by a Mg-rich coating was investigated using localized techniques. Both scanning vibrating electrode techniques (SVET) and scanning electrochemical microscopy (SECM) were used to investigate the processes occurring at the surface of exposed metal when electrically connected or disconnected in a galvanic couple with the Mg-rich coating. The SVET has shown the evolution of the pit activity with time under conditions of sacrificial protection, whereas the SECM allowed indirect sensing of the cathodic activity above the electrodes. It was shown that the cathodic protection provided by magnesium to aluminium substrates acts by both preventing pit nucleation and inhibiting the growth of the pre-existing pits.

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1. Introduction

Protection of metal substrates by the use of metal-rich sacrificial coatings has been applied for many years to steel substrates, using zinc powder dispersed in an organic
matrix, its action being based upon the formation of a galvanic couple between the substrate and the pigment. The procedure requires the pigment to be in a lower position in the galvanic series, in order to cathodically polarize the substrate, but also electric contact between pigment and substrate are necessary for the galvanic effect to be effective. Although the basics are well understood, feasibility is often affected by a number of problems. This is the case of aluminium and its alloys, because of the low position of this metal in the galvanic series. Further, the concept of sacrificial protection is usually applied to uniform corrosion of steel, whereas aluminium typically suffers pitting corrosion in most aggressive media. The insidious nature of pitting attack leads to different requirements in terms of electrochemical protection. While in uniform corrosion there is a semi-direct correlation between the drop of the corrosion rate and the extension of the service lifetime, in pitting corrosion very different chemistries can occur on the surface, with highly aggressive solutions inside the pits and milder solutions outside the pit, making the distribution of current more complex. Further, the existence of only one isolated pit can be disastrous, which makes the protection effectiveness most important.

In previous publications the development of a sacrificial primer for protection of aluminium alloys was presented [1] and it was concluded that the Mg-rich coating can act by three mechanisms [2], corresponding to different stages of degradation: in new systems, a barrier effect is provided by the polymer matrix to the coated substrate; later, at defective areas such as scratches, the magnesium particles provided cathodic protection; finally, at a late stage in the process, there was also a barrier effect at the scratches, provided by a layer of magnesium oxides precipitated at the cathodic areas. The techniques used so far gave only surface-averaged information on the system, but the novel localized techniques open new possibilities in terms of the research. One of the most promising techniques is the scanning vibrating electrode technique (SVET), which assesses corrosion phenomena by measuring the local ionic currents in solution by means of a vibrating microelectrode [3,4]. The technique has been used for several corrosion problems, such as the corrosion of bare aluminium [5], the galvanic activity at scribes or cut edges [6,7], the influence of inhibitors [8,9] or the galvanic corrosion of soldered copper [10] and of zinc–steel corrosion cells [11].

Another non-intrusive localized electrochemical technique is the scanning electrochemical microscope (SECM), a technique that uses a non-vibrating scanning microprobe to perform electrochemical measurements [12–14]. The SECM has been applied to several corrosion problems, such as pitting corrosion [15–17], mapping of the surface conductivity of aluminium alloys [18] and also to galvanic corrosion of zinc–iron [11]. Assessment of surface electrochemical activity can be made by reducing or oxidizing any dissolved reactants or products in solution in the vicinity of an electrode [19,20], provided only one species is being oxidized/reduced and the solvent is stable. With the microprobe, the same kind of approach has been used to sense variations in the concentration of dissolved oxygen on cathodic areas [21,22].

In the present work both the SVET and the SECM are applied for a better insight of the capability of cathodic protection of an aluminium substrate by the Mg-rich coating.

2. Experimental

Specimens were cut from Aluminium panels of AA 2024-T3, supplied by Q Panel Lab products (Cleveland OH). The magnesium-rich primer was prepared as described
elsewhere [2] and applied through an air spray gun to a thickness of approximately 70 μm. A coated specimen was mounted on a sample holder near a piece of the bare alloy of the same dimensions. The specimens were electrically connected by means of a switch at the back of the sample holder. Adhesive tape was used to obtain the reservoir for the electrolyte and the surface was levelled using a small air-bubble level. Pure 99.9% magnesium foil (Johnson Matthey Comp.) was used in the SECM experiments. All experiments were performed in dilute Harrison solution (DHS), consisting of 0.35 wt% (NH₄)₂SO₄ and 0.05 wt% NaCl in distilled water (pH = 5). This solution was chosen because AA2024 is known to be highly prone to pitting corrosion in this solution, even at ambient temperature.

The SVET measurements were made using a system from Applicable Electronics (Forestdale, MA). The vibrating probe consisted of a 20 μm platinum-black-coated tip that was placed above the surface of the substrate at a height of about 200 μm – Fig. 1. The vibrating amplitudes of the scanning probe were adjusted to 20 μm, both parallel and normal to the surface. When all adjustments had been made, 5 mL of electrolyte solution was added to the cell and the platinum-black-coated reference and the bath ground electrodes were subsequently placed in the solution. Galvanic coupling experiments of the type employed here have been a useful approach to study active metal coating interactions [5,23]. The electrodes of bare aluminium and of primed electrode were left unbiased. The electrodes consisted of rectangles with 1 mm × 2 mm each, mounted on a resin cylinder, parallel to each other and 2 mm apart. This separation is important because of the high electrochemical activity of magnesium, which underwent corrosion with significant hydrogen evolution. The bubbling was much more intense when the electrodes were not connected, but remained with low intensity even when the circuit was closed. With this setup the measurements were made only above the bare electrode and therefore the gas bubbles from the Mg were kept away from the probe, thus avoiding instability of the measurements. The samples were partially coated with adhesive tape, leaving only an exposed area of typically 1 × 1.5 mm², over which a scan consisting of 400 data points obtained on a 20 × 20 grid was made. The integration time was 1 s per point, corresponding to an acquisition time of ~10 min per scan. Scans were initiated 2–4 min after immersion and were repeated every 30 min, although only a few selected scans are presented. The results are displayed as three-dimensional plots, with the current density (Z-direction) plotted as a

Fig. 1. Schematic of the set up used in the SVET measurements.
function of the \((X, Y)\) position in the probe scan plane. Video–microscope images are also presented for observation of the most significant features on the substrate surface.

The SECM equipment model CHI900 (CH Instruments, Austin, TX) was equipped with a 10 \(\mu\)m platinum tip microprobe, an Ag/AgCl/KCl saturated reference electrode and a platinum counter electrode. Because of the possibility of approaching the probe to the surface, an arrangement with bare metals was chosen, in order to decrease the roughness. Thus, the specimens consisted of a rectangular strip of AA2024 (5 mm \(\times\) 0.75 mm) and a foil of pure Mg (5 mm \(\times\) 0.25 mm), both embedded in epoxy resin. Wires for electrical connection between the two electrodes were left at the back of the resin mount. 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 corrosion took place at the spontaneous potential of the system. The front of the resin + specimen setup was polished before each experiment and the reservoir for the electrolyte was obtained applying plastic tape around the epoxy cylinder. The setup was used for cyclic voltammetry and for amperometric measurements along line scans across the specimens’ cross sections. With this purpose, the electrode was scanned by a stepper motor, with increments of 1 \(\mu\)m, at time intervals of 0.017 s.

3. Results

3.1. SVET measurements

With the single electrode, the ionic currents above the surface of the aluminium showed no significant activity in the first hour of immersion – Fig. 2. A pit typically nucleated in this solution after a few hours, and local anodic activity was observed over the pit – Fig. 3a, while the cathodic activity was spread uniformly over the remaining surface. Connection of the bare substrate to the coated sample lead to a sudden drop of the anodic currents above the surface – Fig. 3b – due to cathodic polarization of the aluminium alloy by the magnesium particles. Although the overall current at the aluminium was cathodic, some anodic activity remained at the pit. This anodic activity decreased with time – Fig. 4a. Upon disconnection the anodic current boosted to the values observed

![Fig. 2. Current density map of the single AA2024 electrode after 30 min immersion.](image-url)
before – Fig. 4b – and the pit grew significantly, as confirmed by video–microscope – Fig. 4(c).

Visualization of pit evolution by plotting one line scan extracted from the SVET maps that crosses the pit and following their changes with time (Fig. 5) shows that for the single electrode the current was practically constant and very close to zero at the beginning of the experiment. In practice the values are slightly offset to negative currents in the case of this particular line, which can be due to heterogeneities over the surface. After pit nucleation (curve (b)) there was intense anodic activity located at the pit and some counter cathodic activity outside the pit. Upon coupling to the primed sample there was still anodic activity at the pit (curve (c)), although globally the cathodic currents had become more intense. With time the cathodic current distribution was nearly constant, whereas the anodic activity at the pit decreased. The current at the pit only became cathodic after sufficient time, which in this case was \( \sim 3 \) h (curve (e)).

In a different experiment the aluminium electrode was permanently connected to the Mg-primed sample, the two electrodes having identical exposed areas. In the first minutes

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**Fig. 3.** Current density maps at the bare AA2024 electrode after 19–20 h; (a) isolated electrode, just before connecting; (b) 10 min after connection to the Mg-primed electrode.
of immersion there was again an apparent small cathodic current over the whole surface – Fig. 6a. After a number of hours in constant immersion the cathodic current increased – Fig. 6b. The delay in the development of the cathodic activity is probably related to the time required for water to penetrate the polymer matrix at the primed sample and to activate magnesium [2]. For long exposure times an anodic local site nucleated, in spite of the cathodic protection – Fig. 6c. The anodic currents observed above this pit reached approximately 2.5 $\mu$A/cm$^2$, which is well below the currents measured in the isolated sample. At this stage the electrodes were removed from the setup and additional area of the Mg-primed electrode was exposed, increasing its area to $\sim$3 mm$^2$ and therefore doubling the anode/cathode area ratio. When the samples were re-exposed there were still some signs of anodic activity, but after a few hours all the aluminium electrode had become cathodic again – Fig. 6d. Towards the end of the experiment the cathodic currents had increased to $\sim$10 $\mu$A/cm$^2$.

3.2. SECM measurements

At neutral pH, the reactions expected to occur at the surface are the corrosion of Al and of magnesium and the reduction of oxygen and of water:

$$\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (1)$$
Sensing the corrosion activity in solution with the SECM could in principle be made by reducing or oxidizing at the microprobe any of the soluble species, either reactants or products. Of the species present in solution and involved in the reactions, Al$^{3+}$ and Mg$^{2+}$ would be hard to detect due to their extremely negative reduction potentials. Oxygen is the easiest species to sense, since it can easily be reduced to another soluble species. Fig. 7 depicts the cyclic voltammogram obtained in the bulk solution, away from the surface of the electrodes. Reduction of oxygen occurs at potentials below $-0.4$ V and its limiting current is achieved at approximately $-0.7$ V. In order to test the effectiveness of the procedure, the voltammogram was repeated in the same solution after the addition of two drops of H$_2$O$_2$ (3 wt%). There was significant increase of the reduction current, attributed essentially to reaction (3) consuming the oxygen resulting from peroxide decomposition:

$$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (5)$$

The cathodic current decreased slowly with time and after $\sim 2$ h it reached the values measured in the solution before the H$_2$O$_2$ addition.

Amperometric scan curves were made at $-0.75$ V. With this purpose, 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 $-0.75$ V to the SECM tip and by scanning it over the surface, according to a procedure used before [7]. 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 neighboring resin – Fig. 8. After connection to magnesium, there was a drop of the cathodic current measured.
Fig. 6. Current density maps at bare AA2024 with the electrode permanently connected to Mg-primed anode, after an immersion time of (a) 10 min; (b) 12 h; (c) 39 h; (d) 70 h. Primed electrode to bare electrode area: (a)–(c) 1.0; (d) 2.0.

Fig. 7. Cyclic voltammograms obtained with the SECM microprobe in the bulk solution (DHS). Scan rate: 0.1 V/s; scan direction indicated in the plot; (a) quiescent solution; (b) after addition of H₂O₂; potentials vs. Ag/AgCl.
above the aluminium. This reaction occurred in parallel with the cathodic reduction of 
$H_2O$, confirmed by some gas evolution observed on the surface.

Magnesium is electrochemically very active and undergoes severe corrosion in 
water, with intense hydrogen evolution. This gas evolution was easily observed over the

![Amperometric scan curves obtained at $-0.75$ V vs. Ag/AgCl, over the AA2024 electrode at a constant 
distance of 500 μm from the surface. Scan direction as indicated; (a) isolated electrode; (b) electrode cathodically 
protected by the Mg anode.](image1)

![Amperometric scan curves obtained at $-0.75$ V vs. Ag/AgCl, over the magnesium electrode at a constant 
distance of 200 μm from the surface; (a) single electrode; (b) electrode connected to the Al electrode.](image2)
electrically isolated sample but it nearly stopped 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. 9.

4. Discussion

The SVET applied to study the evolution of pitting corrosion has given information that was not possible using non-localized techniques and brings a relevant development in the understanding of pitting corrosion. The technique has shown the time evolution of the anodic current at the pit, on a globally cathodic surface. Inhibition of corrosion in pre-existing pit is a slow process, which results from the different pH and chemistry inside and outside the pit. It took nearly 3 h for the pit to become cathodic, although even at that stage the local currents were less negative than on the outer surface. Further, uncoupling aluminium from magnesium resulted in recovery of the pit activity, at least for the relatively short exposure times tested. In a previous study it was concluded that the protection provided by the polymeric Mg-rich coating can be described by three stages [2]: 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 are sufficiently packed to ensure 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 scribes or defects of the coating. It can be expected that for long exposure times, when the pH rise at the cathodic areas exceeds the critical pH for MgO precipitation, this barrier effect may inhibit pitting propagation.

The use of the SECM to assess the oxygen concentration over the electrodes also gave valuable information for corrosion studies. Whereas the SVET has shown the spatial distribution of the cathodic and anodic areas, the amperometric curves have shown 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; this means 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. When magnesium is coupled to nobler alloy, its potential is shifted to less negative values and the global reduction rate is decreased. 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 H₂O that is slowed down. The largest 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 (Fig. 9, curve (b)). This possibly derives from the fact that the total solution volume is small and therefore whenever the reaction rate is high, steady state cannot be achieved. The gradient of oxygen concentration reaches the entire electrolyte depth, in spite of some further dissolution of oxygen from the air, and consequently the average concentration decreases 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, cathodic protection can act by shifting the potential of Al to more negative potentials, below the pitting potential and therefore inhibiting pitting nucleation. In this respect, magnesium is effective. The open circuit potential in DHS [24] is \( \sim -1.9 \) V for magnesium and \( \sim -0.5 \) V for AA2024 (vs. SCE), corresponding to a large electromotive force of 1.4 V that is capable of cathodically polarizing Al. Once a pit is nucleated, however, it is the cathodic current that is crucial for pit repassivation. Naturally, this current depends on the cathodic-to-anodic area ratio. For a 1:1 area ratio, the cathodic current on Al was typically 10 \( \mu \)A/cm\(^2\). In the long term, this can lead to high pH values on aluminium. The pH rise can have two different actions: it can lead to precipitation of Mg oxides, which will in principle provide some protection, but 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 a new way of monitoring the effect of cathodic protection on pitting corrosion of AA2024. The cathodic protection provided by the magnesium-rich coating is capable of inhibiting pit nucleation and of decreasing the anodic activity at pre-existing pits. The rate of decrease of the anodic activity at the pit on a globally cathodic surface was monitored and it was observed that the time for anodic activity to be totally suppressed was of a few hours. The anode/cathode area ratio was shown to have a significant role in the pit activity, although at the cost of increased cathodic activity over the surface. 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 at a probe.

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