Mg and Mg alloys have been shown to be susceptible to the formation of laterally-spreading products, which tend to manifest as thread-like “filaments” or radially-expanding “discs” during corrosion in aqueous NaCl solutions.1-12 Williams et al. have offered critical insights into the electrochemical mechanism of this unique localized corrosion mode on pure Mg1,5,7 and the Mg-Al-Zn-Mn alloy AZ31B8 by employing the scanning vibrating electrode technique (SVET), where their SVET measurements showed that the corrosion filaments/discs became cathodically-activated following their formation. It was proposed that the net cathode on the locally corroded regions galvanically coupled with the adjacent intensely anodic regions to drive the lateral propagation of the corrosion products across the exposed surface. The formation of discs versus filaments was suggested to depend on whether the catalytic efficiency of the locally corroded region allowed for galvanic coupling with its perimeter, or merely along the most anodic pathways of the microstructure.7 This “differential electrocatalytic” mechanism was also shown to drive filiform corrosion on coated Mg as determined by scanning Kelvin probe (SKP) measurements.1

The mechanism, however, by which the cathodic reaction (H2 gas evolution) is enhanced on corroded Mg or Mg alloys continues to be unclear. Proposed mechanisms include (i) the enrichment of noble secondary phase constituents such as iron (Fe) impurity particles (for pure Mg) or Al-Mn intermetallic particles (for AZ31B) within the corroded regions2,9,13,14 (ii) an increased catalytic tendency of the corroded filaments/discs to catalyze the cathodic H2 gas evolution reaction. The formation of an Al-rich layer on the film/alloy interface at time, due to the incongruent dissolution of the alloy, was not able to stop the initiation and propagation of the filaments.

Interestingly, a Zn-enriched layer was also identified at corroded regions5,9,13,14 (ii) an increased catalytic tendency of the corrosion product.16 The SVET measurements reported by Williams et al. suggested that a significantly reduced cathodic activation was exhibited by the as-cast AZ31B corrosion filaments1 relative to the corrosion discs on pure Mg.5 This finding agrees well with the noble secondary phase theory, since Fe particles are known to be more efficient cathodes than Al-Mn particles.17

A cross-sectional transmission electron microscopy (TEM) investigation of the corrosion filaments formed on AZ31B-H24 sheet was recently carried out by Cano et al.12 to establish possible links between the cathodic activation and the composition and/or structure of the corroded filaments. It was argued that the cathodic activation was likely a combined result of the formation of a thick MgO film containing significant populations of pores and cracks and the Al-Mn intermetallic particles catalyzing the cathodic reaction (i.e. H2 gas evolution). Interestingly, a Zn-enriched layer was also identified at the filament/alloy interface and was observed to become significantly thicker after ageing in the NaCl solution. This noble (relative to Mg) solute element enrichment at the corrosion filament/alloy interface was, thus, proposed as an additional active cathode contributing to the observed sustained cathodic activity of the corrosion filaments. The present study was conducted to further develop a fundamental understanding of the cathodic activity that drives the filiform-like corrosion observed on Mg-Al alloys. For this purpose, the filament-like corrosion of the Mg-Al-Mn alloy AM30 was investigated using electrochemical and TEM techniques with reference to the previously reported AZ31B results of Cano et al.12 AM30 nominally contains 3 wt% Al and 0.4 wt% Mn, with the absence of Zn being the compositional factor differentiating it from AZ31B.18 Microstructurally, AM30 is similar to AZ31B in that it is a solid solution alloy containing a relatively small volume fraction of intermetallic Al-Mn particles.19,20 Studies documenting the corrosion behavior of AM30 in aqueous NaCl solutions have revealed that filaments form during exposure.10,20 Thus, AM30 was well suited for the intended purpose.

### Experimental

The AM30 alloy used in this work was in the form of a thin-walled (3.0 mm) extruded prismatic tube. The chemical composition the alloy, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), was (wt%): 2.9% Al and 0.4% Mn as major alloying elements with less than 0.004% Fe being present, per the ASTM compositional limits for AZ31B.15,21 The cross-sectional microstructure comprised a fine-grained interior with coarse-grained “skin” surface layers, as revealed by light optical microscopy (Nikon Eclipse LV100). To eliminate any grain size effects on the corrosion filament behavior, the coarse-grained skin layer (~500 μm thick) was removed from the extrusion direction-transverse direction (ED-TD) plane (i.e. the working electrode) by grinding.

An aqueous solution of 0.05 M NaCl at a near-neutral pH was employed throughout this investigation. This electrolyte was selected because corrosion filaments initiated spontaneously (i.e. at the open circuit potential (OCP)) within a convenient time period (typically between 1 to 5 h after immersion), with corrosion filament propagation occurring slowly enough to allow for spatially-resolved SVET measurements to be acquired. This solution was also used in the previously mentioned TEM investigation of the corrosion filaments formed on AZ31B.15 The electrolyte was prepared from NaCl powder (Fisher Scientific, 99.0% min. assay) and deionized water naturally aerated with room temperature laboratory air. For each electrochemical test, the corrosion cell (with all electrodes in position) was filled with approximately 800 mL of the electrolyte immediately prior to the start of electrochemical measurements.

For OCP and potentiodynamic polarization measurements, steel wires were fixed to the ED-TD plane of the 5 mm × 5 mm samples, which were subsequently mounted in epoxy such that the ground

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ED-TD plane with the fine-grained interior revealed was immersed in the electrolyte. The working surface was then ground to a 1200-grit finish using SiC paper with ethanol as a lubricant. Fast-curing epoxy was applied around the edges of the working surface to avoid localized corrosion at the working surface/epoxy mount interface. All electrochemical measurements were conducted using a standard three-electrode configuration within a Uniscan Instruments Environmental TriCell with a mount holder fixed to its base. A saturated calomel electrode (SCE) was used as the reference electrode, whereas two graphite rods positioned on opposite sides of the working electrode were used as counter electrodes. A computer-controlled Solartron 1287 potentiostat was used to make the measurements.

The OCP was recorded over a 24 h period and a high-resolution video camera positioned directly above the corrosion cell was used to simultaneously monitor the appearance of the working surface. Potentiodynamic polarization measurements were made after immersion times of 1 h and 24 h at the OCP for the purpose of investigating the anodic and cathodic kinetics at two different stages of corrosion. For the 1 h OCP polarization measurement, anodic and cathodic scans were completed separately using freshly-prepared electrolytes and working surfaces. For the 24 h at OCP polarization measurement, the anodic scan was completed following the cathodic scan with 1 h rest at OCP between the two scans. The potential was swept at a scan rate of 0.1667 mV/s from the OCP to $-1.75 \, V_{\text{SCE}}$ for the cathodic scan and from the OCP to $-1.35 \, V_{\text{SCE}}$ for the anodic scan. Each polarization measurement was repeated three times using freshly-prepared electrolyte and working surfaces to ensure reproducibility.

For the SVET measurements, 10 mm $\times$ 10 mm samples were mounted in epoxy to expose only the ED-TD plane with the finer-grained interior revealed. The working surfaces were ground to a 1200-grit finish using SiC paper with ethanol as a lubricant. Fast-curing epoxy was applied around the edges of the exposed surfaces to avoid localized corrosion at the working surface/epoxy mount interface. Working electrodes were immersed in the electrolyte for 24 h. During immersion, the evolution of spatially resolved ionic currents as a function of time were determined across the working surface using SVET measurements taken as vectors normal to the exposed surface.

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For the TEM investigation, two 10 mm $\times$ 10 mm samples were prepared with the finer-grained interior of the ED-TD plane revealed by grinding to a 1200-grit finish using SiC paper with ethanol as a lubricant. The samples were immersed in separate Petri dishes containing the 0.05 M NaCl electrolyte. One sample was immersed for 3.5 h, which allowed for the initiation of corrosion filaments and subsequent propagation for approximately 2 h. The other sample was immersed for 21 h, which provided sufficient time for the initial corrosion filaments to age in the electrolyte.

A Zeiss NVision 40 FIB microscope was used to prepare thin-foil cross-sections from three sites of the sample surfaces. Note that a tungsten (W) coating was applied to the outer surface of each sample location before FIB milling to preserve the original morphology of the corroded structures. Each thin-foil cross-section was deposited onto a Cu grid before being placed in the TEM sample chamber. The thin-foil cross-sections were examined using a JEOL 2010F TEM/STEM operating at 200 kV. The TEM/STEM was equipped with an Oxford Inca silicon (lithium drifted) (Si(Li)) energy dispersive X-ray spectrometer (EDS) detector. TEM examinations were conducted using a cryogenically-cooled stage (95 K) to minimize electron beam-induced damage to the samples. The surface films were examined using bright field (BF) imaging along with selected area diffraction (SAD). The surface films were also characterized in STEM mode, with a high-angle annular dark-field (HAADF) detector utilized for imaging and EDS used to determine the composition of various microstructural features. EDS area maps and line profiles were acquired to identify any compositional enrichment across the film/ alloy interface. Elemental compositions were also measured semi-quantitatively using the built-in k-factors of the EDS software.

**Results**

**Microstructural examination.**—The mean grain size of the working electrode surface (Figure 1a), as determined using the ASTM E112-10 linear intercept method, was found to be 133 ± 19 μm (95%). Intricate particles present in the microstructure were readily visible by their bright contrast observed using scanning electron microscopy (SEM) with back-scattered electron imaging (Figure 1b) (JEOL JSM-7000F). As described in more detail below, these intermetallic particles were characterized by TEM to be Al5Mn3.

**Electrochemical measurements.**—A typical OCP transient is shown in Figure 2 and summative OCP data in Table I. The OCP increased from approximately $-1.7 \, V_{\text{SCE}}$ to $-1.6 \, V_{\text{SCE}}$ within the first 100 s after immersion and increased thereafter at a more gradual rate. After an immersion time within the range of 1 to 5 h, a sudden drop in the OCP was observed (Figure 2, black arrow). This event coincided with the initiation of a dark corrosion filament on the working electrode surface and the evolution of H2 bubbles from this location. After this initiation (i.e. breakdown) event, relatively large OCP fluctuations were observed (Figure 2) as the surface became increasingly covered.
Table I. Comparison of electrochemical kinetic parameters.

| Parameter                        | After 1 h at OCP        | After 24 h at OCP       |
|----------------------------------|-------------------------|-------------------------|
| Final OCP (V SCE)                | $-1.509 \pm 0.004$      | $-1.513 \pm 0.001$      |
| Breakdown Time (h)               | Not Observed            | $2.97 \pm 4.30$         |
| $E_b$ (V SCE)                    | $-1.423 \pm 0.043$      | Not Observed            |
| $i_{corr}$ ($A/cm^2 \times 10^{-6}$) | $17.6 \pm 6.3$          | $23.3 \pm 10.4$         |
| $i_c$ at $-1.6$ V SCE ($A/cm^2 \times 10^{-6}$) | $81.7 \pm 28.5$          | $110 \pm 35.0$          |

by corrosion filaments. It should also be pointed out that, in all cases, a stable OCP was not established prior to the breakdown event.

Representative potentiodynamic polarization curves following 1 h and 24 h of immersion at the OCP are presented in Figure 3 and a summary of the determined electrochemical kinetic parameters derived from them provided in Table I. It should be noted that the 1 h polarization curve exemplifies the anodic and cathodic kinetics prior to localized film breakdown, as no corrosion filaments initiated within 1 h of immersion at the OCP. The 1 h anodic polarization curve displayed an average breakdown potential ($E_b$) of $-1.423 \pm 0.043$ V SCE (see Table I and Figure 3), above which the anodic current density rapidly increased as a function of applied potential. As expected, a breakdown potential was not observed for the 24 h anodic polarization curve as spontaneous breakdown had occurred prior to the polarization measurement (Figure 3). The average corrosion current density ($i_{corr}$) for both polarization curves was calculated by extrapolating the linear portion of the cathodic curves to the corrosion potential ($E_{corr}$) of each sample. As shown in Table I, the average 1 h and 24 h $i_{corr}$ values were determined to be $(17.6 \pm 6.3) \times 10^{-6} A/cm^2$ and $(23.3 \pm 10.4) \times 10^{-6} A/cm^2$, respectively, and, thus, were not significantly different.

![Figure 3](image-url)

The average cathodic current density ($i_c$) at a potential chosen within the linear portion of the cathodic curves ($-1.6$ V SCE) was also not significantly different between the 1 h and 24 h values (i.e. $(81.7 \pm 28.5) \times 10^{-6} A/cm^2$ vs. $(110 \pm 35.0) \times 10^{-6} A/cm^2$, respectively (see Table I)).

Selected SVET maps recorded during immersion at the OCP are presented in Figure 4. Images of the scan area at the corresponding immersion times are provided alongside the SVET maps. It should be noted that the SVET maps are not completely time-resolved as

![Figure 4](image-url)
the anodic and cathodic areas may have moved appreciably during the time required to complete a scan (approximately 25 min). For this reason, either the SVET scan immediately after or prior to each immersion time was selected for presentation based on whether the bottom half of the scan area (i.e. the first half scanned) or the top half (i.e. the second half scanned) was of specific interest. In addition, the initiation of corrosion filaments generally occurred earlier than during standard OCP measurements, which could be attributed to (i) increased solution convection caused by the scanning of the SVET probe and/or (ii) the Pt tip on the probe tending to remove insulating H2 bubbles adhering to the alloy surface, thereby increasing the direct exposure time of the surface to the electrolyte. The morphology and linear propagation rate of the corrosion filaments following breakdown were not significantly affected by the SVET probe movement.

Localized corrosion sites, as evidenced by local anodic current density peaks and H2 evolution (observable at the corresponding locations of the scan area image) were initiated within 30 min. of immersion (Figure 4a). Multiple corrosion filaments propagated laterally from these locations toward the bottom-left of the scan area, with anodic peaks and H2 evolution being observed at the moving fronts of the corrosion filaments and cathodic currents observed in the dark areas left behind (Figures 4b,4c). Cathodic currents were also detected in the lower area of the scan area not affected by the corrosion filaments, albeit with lower magnitudes than the upper areas that were previously consumed by the corrosion filaments (Figure 4b). The cathodic currents detected above the corrosion filaments diminished in magnitude with increasing immersion time (Figure 4d). Additional corrosion filaments propagated across the surface upon further exposure, but the cathodic current density on the consumed surfaces was generally lower (Figures 4d–4f) than those observed on the previously consumed surfaces.

The average magnitudes of the anodic and cathodic current densities within a 0.6 mm × 0.6 mm area outlined by the small frame in the scan area images of Figure 4 are shown in Figure 5. This plot illustrates cathodic current variations of a defined region of the corrosion filaments as a function of immersion time. A diminished cathodic current following the passing of a set of corrosion filaments was observed between the 1-h and 5-h immersion times. Repeated passes of corrosion filaments near or within this area (as highlighted by the anodic current density peaks at approximately 10 and 17 h after immersion) did not result in a significant change in the cathodic current density (Figure 5).

**Figure 5.** Average current density values within the area outlined by the small frame outlined in the scan area images in Figure 4, recorded after immersion at the OCP in 0.05 M NaCl.

TEM examination of surface films.—The first thin-foil cross-section for TEM examination was taken from a site on the sample immersed for 3.5 h that had not been affected by a corrosion filament (Figure 6a). The surface film characterized from this cross-section will be referred to in the subsequent text as the “intact film”. The second cross-section, also from the sample immersed for 3.5 h, was taken near the head of a corrosion filament that was propagating at the time of removal from the electrolyte (Figure 6a). The surface film of this cross-section will be referred to as the “fresh corrosion filament”. The third cross-section was taken from the sample immersed for 21 h and was taken from the tail of a corrosion filament that had been aged in the electrolyte for approximately 11 h after formation (as determined from a high-resolution video recording, see Figure 6b). The surface film from this cross-section will be referred to as the “aged corrosion filament” in the subsequent discussion.

A BF-TEM image of the intact film cross-section is shown in Figure 7a. The film was reasonably uniform and compact with no obvious defects (i.e. interconnected porosity and cracking). The thickness of the film varied from ~70 nm to ~160 nm, with an average thickness of 106 ± 5 nm with 95% confidence. The SAD pattern collected from the framed region shown in Figure 7a. (Figure 7b) was indexed as cubic MgO. A HAADF-STEM image of the film/alloy interface shown in Figure 7c revealed that fine-scale particles were embedded within both the intact film and underlying alloy. Figures 8b–8g shows a set of EDS elemental maps for the imaged region of the film/alloy interface shown in Figure 8a. The film was composed of Mg and O as major elements and Al and Cl as minor elements. Al appeared to be enriched at the film/alloy interface. This finding was confirmed through EDS line profiling, taken at the location specified in Figure 8h. The results

**Figure 6.** SEM image showing the site-specific FIB cross-section locations selected from working surface after immersion in 0.05 M NaCl for (a) 3.5 h and (b) 21 h.

**Figure 7.** (a) BF-TEM image of the intact film in cross-section, (b) SAD pattern collected from the area indicated in (a) and (c) HAADF-STEM image film showing the presence of fine Al-Mn particles.
Figure 8. (a) HAADF-STEM image of intact film and (b)-(g) corresponding EDS maps for O, Mg, Al, Zn, Mn and Cl across the intact film/alloy interface. A normalized Al concentration line profile was summed across ten adjacent lines located between the marked bars in the “Line Profile” image in (h) (result shown in Figure 9).

Figure 9. Normalized Al EDS concentration (on an atomic % basis) line profiles across the film/alloy interface for the three films.

Figure 10. (a) HAADF-STEM images of particles found in the bulk microstructure, (b) SAD pattern obtained from a relatively large Al-Mn intermetallic particle.

of this analysis, along with those from additional films, are shown in Figure 9.

The alloy microstructure captured in the FIB-prepared thin-foil cross-section shown in Figure 10a contained fine particles ranging from approximately 20 to 200 nm in size. The particles had an average spherical diameter of 23.7 ± 2.2 nm at 95% confidence. EDS spot analysis of the matrix and particles revealed that the particles were largely composed of Al and Mn. The SAD pattern collected from one of the larger particles (Figure 10b) was indexed to Al5Mn3. An EDS quantification was performed on six particles and the Al:Mn atomic ratios calculated from these measurements. The original Al-Mn quantification results overestimated the proportion of Al in the particles, since the EDS interaction volume contained a certain proportion of the surrounding matrix (≈2.5 at.% Al in solid solution). For this reason, a portion of the Al was subtracted proportionate to the quantified Mg analysis as the Mg signal was assumed to originate solely from the matrix. The mean Al:Mn ratio at 95% confidence calculated after this correction procedure was 1.33 ± 0.30, which is within the compositional range of Al5Mn3. No evidence was found for dissolved Fe within the Al-Mn particles, nor was there any evidence of the β-Mg17Al12 phase.

BF-TEM images of a fresh corrosion filament cross-section are shown in Figures 11a, 11b. The maximum thickness of the filament was ≈2 μm. The filament contained several through-thickness cracks and was found to lie underneath what was assumed to be the intact film. Horizontal bands of pores were present within the filament (Figure 11c). The SAD patterns collected from the fresh filament and overlying intact film (Figures 11c, 11d) were both indexed to cubic MgO. The HAADF-STEM image shown in Figure 11e revealed the presence of Al-Mn particles in the fresh filament. Figures 12b-12g shows a set of EDS elemental maps for the filament/alloy interface shown in Figure 12a. The filament was composed of Mg and O as major elements and Al and Cl as minor elements. Unlike the intact film, Al was not enriched at the filament/alloy interface. This finding was confirmed through EDS line profiling, taken at the location specified in Figure 12h and presented in Figure 9.

BF-TEM images of the aged corrosion filament in cross-section are shown in Figures 13a, 13b. The maximum thickness of the fresh filament was found to lie underneath what was assumed to be the intact film. Two through-thickness cracks are visible in Figure 13a. The SAD diffraction rings (collected from what was assumed to be the intact film (Figure 13c) and filament (Figure 13d) were indexed to cubic MgO. However, diffraction spots characteristic of Mg(OH)2 were also observed in the SAD pattern collected from the intact film (Figure 13c). The HAADF-STEM image shown in Figure 13e revealed the presence of Al-Mn particles within the aged corrosion filament. Furthermore, a bright layer was present at the filament/alloy interface, suggesting that Al enrichment occurred at the interface similar to that observed at the intact film/alloy interface shown in Figure 7c). However, EDS elemental line profiling across the filament/alloy interface (Figure 14h, results shown in Figure 9) revealed no significant Al enrichment at this interface. This observation and the EDS line profiles of the intact and fresh filaments will be discussed in detail below.
Discussion

The SVET measurements revealed that the regions consumed by the corrosion filaments on the AM30 surface acted as net cathodes while strong net anodic activity was present at the filament heads. However, rapid H₂ gas evolution was visually observed at the filament heads (for example, rising streams of gas bubbles can be seen in Figures 5a, 5b), as was also noted in previous investigations.¹,⁹,¹² This is indicative of strong cathodic activity at the filament head which was not revealed by the SVET measurements. Excess H₂ production (described by the negative difference effect (NDE)) has been shown to be proportional with Mg oxide/hydroxide film formation²⁵,²⁶ and is expected to account for the rapid H₂ gas evolution at the filament heads according to the overall filament formation reaction (Equation 1):¹²

\[ \text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2 \]  

Anodic (i.e. positive) currents associated with the anodic portion of Equation 1 would not have been detected by the SVET measurements.

References

²⁵,²⁶
because the vibrating electrode was positioned above the filament formation region. The fact that a net positive anodic current was present at the filament head in spite of this indicates that a second source of cathodic activity (i.e. separate from the cathodic portion of the filament formation reaction, Equation 1) was driving the anodic activity detected with SVET measurements. This second source of cathodic activity, attributed to cathodic activation of the corrosion filaments, is the sole focus of the discussion below.

A comparative summary of the key characteristics of the three site-specific films examined by TEM for AM30 and AZ31B-H2412 is provided in Table II. Two key similarities include: (i) formation of a thin, relatively compact MgO-based film that contained embedded Al-Mn intermetallic particles and (ii) formation of a significantly thicker, non-compact MgO-based corrosion filament that contained Al-Mn intermetallic particles. These two key similarities indicate that the same cathodic activation mechanism was likely operative, which has been argued to be a combined result of the formation of a thick, non-compact MgO-based film (i.e. with significant populations of pores and cracks) and the ability of Al-Mn intermetallic particles to catalyze the cathodic reaction (H2 gas evolution) resulting from the increased number of particles (and surface area) in contact with the electrolyte.12

Recently Salleh et al.16 demonstrated that the kinetics of the H2 gas evolution reaction on a Mg(OH)2 covered surface were significantly higher than those on a pristine Mg surface, indicating that the Mg(OH)2 corrosion product could be a significant source of cathodic activation. No evidence was found of crystalline Mg(OH)2 within the fresh corrosion filament, which was found to exhibit significant cathodic activity. It was possible that Mg(OH)2 was present, but was dehydrated to MgO by electron beam irradiation.27–29 However, such damage is considered unlikely as the cross-section foils were cryogenically-cooled during the TEM examination and there was no evidence of electron beam damage, as documented for corrosion films formed on Mg and Mg alloys reported in the literature.30–32 Given the strong thermodynamic tendency for MgO to hydrate when in contact with water, it is possible that the MgO-based corrosion filaments hydrated to a small extent, as was indeed detected at the top surface of the aged filament in the present TEM examination (Figures 13b, 13c). The hydration extent was expected to be limited to the MgO surface as the hydration reaction is known to be self-limiting.33 Thus, although bulk Mg(OH)2 can be ruled out as being necessary for enhanced cathodic activity, its role as a surface layer on MgO cannot be ruled out at this time.34

It is recognized that the composition of the Al-Mn intermetallic particles embedded in the films was different in the present AM30 alloy versus the previously studied AZ31B12 – i.e. Al8Mn in the AM30 films verse Al11Mn2 in the AZ31B-H24 films. Although Al-Mn particles with lower Al:Mn ratios are generally reported to be more noble and, thus, more conducive to microgalvanic corrosion in Mg alloys,35,36 they are not considered to have played a significant role other than catalyzing the cathodic reaction (H2 gas evolution) when in contact with the electrolyte.

A key difference between the AM30 and AZ31B cases in Table II includes solute enrichment at the film/alloy interface. Zn was found to have been enriched at each interface of the AZ31B-H24 films, whereas Al was found to have enriched only at the intact film/alloy interface of AM30. This is highlighted in Figure 9, which plots the normalized Al content acquired as EDS at.% concentration profiles across the three AM30 film/alloy interfaces. These line profiles were averaged across ten adjacent lines located between the marked bars in the “Line Profile” images shown in Figure 8h, Figures 12h and 14h. As shown in Figure 9, the relative Al enrichment across the film/alloy interface was different for each film. As seen in Table II, Al enrichment at the film/alloy interface was only detected in the case of the intact film. Moreover, Figure 9 shows that Al was enriched within the MgO-based intact and aged corrosion filaments, whereas there was no significant difference in Al enrichment between the alloy and MgO-based fresh corrosion filament.

The observed Al enrichment at the intact film/alloy interface was somewhat surprising since a similar Al-enriched layer had only been previously observed at the film/alloy interface for higher Al-content Mg alloys containing the β-Mg17Al12 phase.37–40 Danie et al.41 examined this layer formed on Al-rich eutectic Mg grains of AM50

![Figure 14.](image)
(Mg-4.4%Al-0.3%Mn) in some detail using low-loss and core-loss electron loss energy spectroscopy (EELS). They observed a sharp plasmon peak characteristic of the metallic state from the Al-enriched layer. The authors concluded that the layer was most likely a highly-defective Al$_2$O$_3$ formed by the preferential (incongruent) dissolution of Mg from the alloy at this location (a eutectic Mg grain), which had a high Al content (11–12 wt%). A similar EELS analysis of the Al-rich layer underneath the intact film was attempted in this study, but insufficient resolution prevented a determination of the chemical state. Close inspection of the EDS maps across the intact film/alloy interface (Figures 8b and 8d) reveals that O was depleted within the Al-enriched layer relative to the MgO-based film, suggesting that the layer was more likely metallic Al rather than a highly-defective Al$_2$O$_3$. The lack of Al enrichment at the fresh corrosion film/Alloy interface, despite the large volume of metal that corroded during filament formation, suggests that the intense local anodic activity at the head of a filament was strong enough to dissolve (i.e., was above the dissolution potential of) the alloying elements; thus precluding the incongruent dissolution of the alloy. The lack of significant interfacial re-enrichment of Al observed after ageing suggests that any residual anodic dissolution that occurred underneath the non-compact filament at sites where the alloy was in direct contact with the electrolyte again precluded the incongruent dissolution of the alloy. If no incongruent dissolution occurred during ageing, then a secondary contribution to the cathodic activity, such as from a solute enriched layer in contact with the electrolyte, was unlikely. The tendency for the cathodic current density measured over a fixed region above a filament to decrease with immersion time (Figure 5) is consistent with the observations of Williams et al. for as-cast AZ31B.9 They argued that the cathodic throwing power of a defined region of a corrosion filament was not sufficiently to continue coupling with the anodic head as the distance between them increased. It is interesting to note that, in the absence of secondary phase formation, Zn alloying significantly affects the cathodic kinetics.41 Thus, it would be interesting to utilize SVET measurements to probe the cathodic activity of aged corrosion filaments on AZ31B-H24 to determine if Zn-enrichment12 leads to a secondary effect.

Al-enrichment within the films formed on Mg-Al alloys has been frequently observed.30–32,42–46 It has been argued that this Al-enrichment improves corrosion resistance by reducing film growth rates relative to pure Mg.30–32 The mechanism by which Al enriches in the films formed has not yet been elucidated. The higher affinity of O$_2$ for Al than for Mg, since Al$_2$O$_3$ (~788 kJ/mol Al) has a lower Gibbs free energy of formation than MgO (~559 kJ/mol Mg), has been argued to be a critical factor.42 For corrosion filaments, Al that was dissolved during filament formation may have migrated toward the filament/metal interface when the anodic propagation front moved away, and the local potential returned below the Al dissolution potential. Although it was likely incorporated into the film, Al was not likely present as a discrete MgAlO$_3$ or Al$_2$O$_3$ phase in the film.32 For this reason, it was not surprising to see Al enrichment within the intact film and aged corrosion filament (Figure 9). However, it was surprising to see no such enrichment in the fresh corrosion filaments. These findings suggest that Al enrichment was a relatively slow process versus the rapid MgO formation process and, thus, developed with time. This time dependence could be indicative of a mass transport controlled process within the MgO film. It would be interesting to track the composition of the intact film and freshly formed corrosion filament immediately upon immersion and formation, respectively, as they age.

The findings presented and discussed above serve to indicate that a generalized cathodic activation mechanism is likely driving the filament-like corrosion exhibited by Mg-Al alloys (i.e., the AZ and AM series): namely a combined result of the formation of a thick, significantly defective film (this case, having significant populations of pores and cracks) with Al-Mn intermetallic particles in direct contact with the electrolyte, thereby catalyzing the cathodic reaction (H$_2$ gas evolution). The new insight includes elucidating the complex role played by the alloyed Al: (i) forming an enriched metallic layer at the intact film-substrate interface and (ii) incorporating into the intact film and aged corrosion filaments. Both aspects have been argued to be beneficial from a corrosion resistance perspective: the enriched metallic layer providing a more tortuous path for Mg dissolution,30,31,37–49 and its incorporation into the film reducing the film growth rate.30–32 Interestingly, neither was effective in preventing the corrosion filaments from initiating on and propagating across the AM30 surface during immersion.

Conclusions

The filament-like corrosion behavior of wrought (extruded) AM30 was investigated in a dilute NaCl solution using OCP, potentiodynamic polarization and SVET measurements. TEM was also employed to characterize the localized corrosion structures to further develop a fundamental understanding of the cathodic activity that drives the filament-like corrosion observed on Mg-Al alloys. The main findings of the investigation are as follows:

1. The electrochemical measurements confirmed that the localized corrosion filaments that form on AM30 during immersion in the dilute near-neutral NaCl electrolyte were cathodically activated relative to the original intact film. This enhanced cathodic activity was necessary to drive the intense net anodic activity detectable by SVET measurements at the heads of the filaments.

2. The TEM examination of the fresh corrosion filaments revealed the formation of a much thicker, significantly more-defective MgO-based film relative to the adjacent intact film formed on the non-corroded region. This highly defective structure served to increase the effective surface area of the Al-Mn intermetallic particles (active cathodes) embedded in the film and in contact with the electrolyte. The formation of bulk Mg(OH)$_2$ can be ruled out as a cause of the enhanced cathodic activity; however, its role as a catalytic surface layer formed on MgO cannot be ruled out at this time.

3. Alloyed Al was found to have a complex role in film formation: (i) forming an enriched metallic layer at the intact film-substrate interface and (ii) by incorporating itself into the intact film and aged corrosion filaments. Interestingly, neither was effective in preventing the corrosion filaments from initiating on and propagating across the AM30 surface during immersion.

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