Electrochemical noise analysis of the corrosion of high-purity Mg-Al alloys

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Abstract
Corrosion of high-purity Mg-Al alloys containing 3, 6 and 9 wt.% Al was investigated using electrochemical noise (EN) analysis. Changes in the EN signals were correlated with macroscopically observable events on the sample surfaces, which were recorded using time-lapse photography. Steady-state corrosion in all alloys was highly localised. For the Mg3%Al alloy, localised corrosion was preceded by a period of general corrosion. The corrosion rate of the as-cast Mg9%Al alloy was less than those of the other materials but increased with solution annealing time. The results are consistent with strong galvanic coupling between Al-depleted and -enriched zones of the α-phase.

Keywords: A. Magnesium; B. Alloy; C. Pitting corrosion; C. Passive films

1 Introduction
Mg alloys have the lowest density of structural engineering metals, which makes them particularly useful in lightweighting applications. Despite a large volume of literature, which has been summarised in a number of exhaustive reviews [1-3], corrosion of Mg alloys still remains a critical issue for material producers and end users. Consequently, the use of Mg alloys for structural components in contact with aqueous environments remains limited.

The primary alloying element used in commercial Mg alloys is Al. The addition of Al is generally perceived to be beneficial to the corrosion resistance of Mg alloys [1-3]. However, there remains much uncertainty regarding the mechanisms underpinning this relationship. A common theme in the literature is that these mechanisms somehow involve the β-phase (Mg11Al12) [4-16]. Various workers have shown that the β-phase has a more positive corrosion potential than the α-phase and that this potential difference may act as a driving force for localised corrosion [17-24]. It has also been proposed that, in the form of a continuous grain boundary network, the β-phase may increase corrosion resistance by acting as an internal corrosion barrier [25,26]. However, it should be emphasised that such microstructures are uncommon; evidence in the literature suggests that they occur only in materials that have undergone very rapid heating and cooling [27-29]. Less well recognised in the literature is the importance of the Al distribution in the α-matrix, which may be highly inhomogeneous [17,30-33]. The corrosion potential of the α-matrix is also dependent on the concentration of Al in solid solution [17,34]. Thus, there may also exist galvanic couples between Al-enriched and -depleted regions of the α-matrix. Indeed, recent studies [35-37] using scanning confocal laser microscopy (SCLM) and scanning electron microscopy (SEM) have shown a correlation between Al concentration and local dissolution in the α-matrix. This correlation has been associated with enrichment of the passive film with Al, which has been detected by several workers using transmission electron microscopy (TEM) [38] and X-ray photoelectron spectroscopy (XPS) [39-41]. The influence of impurities (e.g. Fe, Ni and Cu) on the corrosion behaviour of Mg alloys must also be recognised [42-46]. Of particular importance to commercial Mg alloys is Fe, which may combine with Al to form highly cathodic intermetallic particles [44]. Thus, the influence of Al on the corrosion resistance of low-purity Mg-Al alloys may be related to their Fe concentrations [44].
Electrochemical noise (EN) analysis is a non-invasive technique for evaluating the rate and mechanism of corrosion in real-time. Examples of the application of EN analysis to Mg alloys are few. Lafront et al. [47] tested commercial AZ91 and AJ62 Mg alloys in a solution of 0.1 M NaOH, 0.05 M NaCl and 0.025 M H2O2. The measured noise signals were characterised by alternating passive and active periods, with the active periods corresponding to an increased corrosion rate. The change from passive to active behaviour was attributed to metastable pitting, whereas more stable signals were attributed to conventional pitting processes. Zhang et al. [48] showed that corrosion of a commercial AZ91D Mg alloy in 0.05 M NaCl at pH 12 occurred in three stages in which the EN signals were dominated by: (i) anodic dissolution coupled with H2 evolution; (ii) metastable pitting; and (iii) repassivation. In a subsequent paper [49], the same authors applied stochastic models to EN measurements for Mg-Gd-Y-Zr Mg alloy, AZ91D and pure Mg in 0.05 M NaCl saturated with Mg(OH)2. The results showed that the probability of pit initiation and growth was higher for the Mg-Gd-Y-Zr alloy than for the other two materials. Winzer et al. [50] used EN analysis to evaluate the corrosion resistance of Mg-Al weldments. In a more recent paper, Winzer et al. [51] performed preliminary EN measurements using as-cast Mg-Al alloys, identical to those used in the present study, in 3.5 wt.% NaCl. The results showed that there was a general increase in the corrosion rate with decreasing total Al concentration.

The aim of this paper was to evaluate the relative importance of the factors related to Al concentration and β-phase morphology on the mechanisms for corrosion of Mg-Al alloys. For that purpose, high-purity Mg-Al alloys with various total Al concentrations were heat-treated to obtain various contrasting microstructures. The rates and mechanisms of corrosion were evaluated in real-time using EN analysis and correlated with in-situ time-lapse photography of the sample surfaces.

2 Experimental

The test materials were binary Mg-Al alloys with nominal Al concentrations of 3, 6 and 9 wt.% as used previously by Winzer et al. [51]. The materials were prepared by permanent mould chill casting at Helmholtz-Zentrum Geesthacht, Germany. The reference material was commercially-pure Mg, which was provided in the form of cast ingots by Magnesium Elektron, UK. The compositions of the materials were measured by Germanische Lloyd Prüflabor, Germany, using vacuum emission spectroscopy. The results of this analysis are given in Table 1 [51].

The Mg-Al ingots were machined into bars of dimensions 20 x 20 x 150 mm. Some of the bars were retained in the as-cast condition whilst the remainder were heat treated to obtain various concentrations and morphologies of the β-phase. The heat treatments were performed in an air furnace with the bars covered in graphite powder to prevent excessive oxidation. The bars were quenched in water immediately after each heat treatment phase. A summary of the heat treatment protocols is given in Table 2. All three alloys were solution treated at 420 °C for 24 hours [52] in order to obtain nearly-homogeneous microstructures (the S24 condition). Additional samples of the Mg9%Al alloy were partially solution treated at 420°C for 1, 3, 6 and 9 hours (Mg9%Al S1 – S9) in order to obtain microstructures with different concentrations of the β-phase. Others were fully solution treated at 420 °C for 24 hours and then artificially aged at 200 °C for 16 hours and at 340 °C for 8 hours (Mg9%Al A1 and A2 respectively) in order to obtain microstructures with different β-phase morphologies. The heat-treated bars were subsequently machined into 10 x 10 x 10 mm cubes for microstructural analysis and EN testing.
Microstructural characterisation was performed using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. The procedure for SEM sample preparation has been described in Winzer et al. [51].

EN measurements were performed using a three-electrode setup consisting of two working electrodes and a saturated calomel reference electrode as per Winzer et al. [51]. The working electrodes were macroscopically identical cubes of the test materials. Care was taken to ensure that the distance between all electrodes was consistent in each test. The working electrodes were prepared by attaching insulated wires to the cubes and embedding them in pairs in epoxy resin such that only one face of each cube was exposed. The exposed surfaces were ground with up to 1200 grade emery paper and cleaned with ethanol immediately prior to testing. The test environment was 0.5 M NaCl buffered to pH 12 using 0.5M NaOH. All solutions were prepared from deionised water and analytical grade reagents. The tests were performed at open circuit potential over a period of 12 hours beginning immediately after immersion of the electrodes in the electrolyte. The current between the two working electrodes and the potential between the working electrodes and the reference electrode were simultaneously recorded at a frequency of 5 Hz using a Gamry Reference 600™ potentiostat. The measurements were performed in a faraday cage to prevent external noise interference. All tests were performed in a climate-controlled laboratory with a nominal temperature of 22 °C. All signal analysis was performed using Python.

Time-lapse photography was used to correlate the voltage and current signals with macroscopically-visible events on the surface. The images were taken at one minute intervals over a 12 hour period using a Nikon D200 digital camera and a 105 mm macro lens. The samples were illuminated using a ring light mounted on the lens. These measurements were performed with the door to the faraday cage open to ensure a clear view of the sample. Thus, the results may have been affected by external noise. The images were compiled into videos that can be viewed on the online version of this article.

3 Results

3.1 Microstructural characterisation

The microstructures of the as-cast Mg-Al alloys are shown in Figure 1. The microstructure of the pure Mg was relatively featureless and, consequently, is not shown. The microstructures of the as-cast materials are as previously reported [51] and have been described here for the purpose of comparison with the heat-treated materials. All as-cast alloys contained a significant volume concentration of intermetallic particles. The size and concentration of the intermetallic particles increased with increasing total Al concentration. The composition of the particles, measured using EDX, was consistent with that of the β-phase, i.e. Mg17Al12. In the Mg3%Al alloy, the β-phase particles took the form of small, discrete particles. In contrast, the β-phase particles in the Mg6%Al and Mg9%Al alloys took the form of large, partially-divorced interdentritic particles. In all as-cast alloys, the β-phase occurred both within grains and at grain boundaries. In the Mg6%Al and Mg9%Al alloys, β-phase precipitates at grain boundaries were surrounded by clusters of α- and β-phase lammelae. The two morphologies are shown in higher magnification in Figure 2. Small Mn- and Fe-rich particles were present in all materials, though these tended to be located within the β-phase. This suggests that such particles are precipitated early in the solidification process and act as nucleation sites for the precipitation of the β-phase.

An important outcome of this analysis was that the Al concentration of the α-phase was highly inhomogeneous. This was evidenced by the uneven topography in the α-phase, as
shown in Figure 1 and Figure 2, which was attributable to the selective dissolution of Al-deficient regions due to etching. The non-uniform topography was particularly apparent for the Mg6%Al and Mg9%Al alloys, though it should be noted that these materials were etched using a different solution than that used for the Mg3%Al alloy [51]. The Al concentration of the α-phase in the grain interior (i.e. where the topography was relatively uniform) was measured for each material using EDX analysis at a minimum of 20 points in at least 3 grains. The average concentrations were 1.06 wt.% for Mg3%Al, 1.92 wt.% for Mg6%Al and 3.95 wt.% for Mg9%Al. Figure 3 shows the results of EDX measurements taken in each material at a series of collinear points through grain boundaries that were not decorated with second-phase particles. In each case there was an increase in Al concentration at the grain boundary. This corresponded with a raised topography in the SEM image. The maximum Al concentration at the grain boundary increased with the total Al concentration from 5.3 wt.% for Mg3%Al, to 9.7 wt.% for Mg6%Al and 10.3 wt.% for Mg9%Al. The difference between the peak Al concentration at the grain boundary and the minimum Al concentration in the grain interior, which was indicative of the overall inhomogeneity of the Al distribution in the α-phase, was greater for the Mg6%Al alloy (~8 wt.%) than for the Mg3%Al and Mg9%Al alloys (~5 wt.%). It should be noted, however, that not enough grain boundaries were sampled to obtain a statistically significant relationship between the total Al concentration and the segregation of Al at grain boundaries.

Figure 4 shows the microstructures of the Mg9%Al alloys in the as-cast condition and after heat treating at 420 °C for 1, 3, 6, 9 and 24 hours. There was a general reduction in the concentration of the β-phase over time. The lamellar β-phase was first to dissolve; after 3 hours only the partially-divorced structure remained (Figure 4C). The homogeneity of the Al distribution in the α-phase, which was evidenced by the evenness of the surface topography, also increased over time. After 6 hours the dendritic morphology of the Al-depleted regions was clearly visible (Figure 4D). After 24 hours the Al distribution in the α-phase appears largely uniform (Figure 4F). This indicated that Al atoms in the β-phase and concentrated at grain boundaries diffused rapidly into the bulk at 420 °C. Figure 5 shows the microstructures of all three alloys in the S24 condition, i.e. after heat treating for 24 hours at 420 °C. The microstructures of the Mg3%Al S24 and Mg6%Al S24 were largely devoid of the β-phase (Figure 5A and B), though some small β-phase particles remained in the Mg9%Al S24 material (Figure 5C). Small Al-Mn-Fe particles were present in all of the solution-annealed materials; this was indicative of their high thermal stability relative to the β-phase.

The average grain sizes of the alloys in the as-cast and solution-annealed conditions were approximated using the line intercept method. In all cases these were in the range 100 – 150 μm.

Figure 6 shows the microstructure of the Mg9%Al alloy after solution annealing at 420 °C for 24 hours and then artificially ageing at 200 °C for 16 hours (A1 condition) or 340 °C for 8 hours (A2 condition). Both microstructures contained partially-divorced intermetallic β-phase particles, which were similar in concentration and morphology to those in the Mg9%Al S24 material. This suggests that they were retained from the solution-treated microstructure, i.e. that they do not dissolve further at temperatures ≤340°C. The Mg9%Al A1 material was largely composed of agglomerates of α- and β-phase lamellae and entirely α-phase regions in roughly equal proportions. In contrast, the β-phase in the Mg9%Al A2 material took the form of small, continuous particles, which decreased in concentration with increasing distance from the nearest grain boundary. The microstructures of the Mg9%Al alloy in the A1 and A2
conditions were consistent with the influence of temperature on the aging process proposed by previous workers [53,54].

3.2 Electrochemical noise analysis

Figure 7 shows images of the Mg3%Al working electrodes after immersion in the test environment for 1, 5 and 12 hours as well as the voltage and current signals versus immersion time for the entire test period. The voltage and current measurements for the Mg3%Al samples were characterised by 2 distinct phases. The first phase, which lasted in this case ~5 hours, was characterised by relatively high current and voltage noise. This corresponded with lateral spreading of the corroded area on one of the electrodes. Large changes in the current direction during this period (e.g. during the first hour in Figure 7) correlated with the initiation of corrosion on alternate electrodes. This did not affect the voltage signal, which was the average of the potential difference between the two working electrodes and the reference electrode. The second phase, which began after ~5 hours, was characterised by relatively stable average voltage and current signals and low voltage and current noise. This corresponded with a cessation of lateral spreading and, instead, deepening of pits at discreet points. This lateral spreading of the corroded region also occurred for the pure Mg and solution-annealed Mg3%Al S24 alloy but not for the Mg6%Al and Mg9%Al alloys; corrosion for these materials occurred at a single point for the entire test period.

Figure 8 shows different transient shapes in the voltage and current signals for the pure Mg, Mg6%Al, Mg9%Al and Mg9%Al S1 materials. Lateral spreading of the corroded region on the pure Mg and Mg3%Al alloy samples was characterised by delta-shaped transients with a period of ~1 min (Figure 8A). It is important to note that the voltage and current measurements were made independently between different combinations of electrodes. Thus, it is unimportant whether the voltage and current transients are out of phase. The voltage and current measurements for the Mg6%Al and Mg9%Al samples were characterised by relatively high-amplitude transients with a period of 20 – 30 sec (Figure 8B) and lower-amplitude transients with a period of ~2 sec (Figure 8C). These were superimposed onto very high-amplitude, irregularly-shaped transients with periods of up to 1 hr (Figure 8D). The transients shown in Figure 8B were characterised by a relatively slow increase in voltage and current followed by a sudden reduction to the mean value. In the case of Mg alloys, for which hydrogen is a product of the dissolution reaction [1-3], such transient shapes are consistent with the evolution (and corresponding reduction in the effective sample area) and desorption of H2 gas bubbles from the sample surface. The source of the low-amplitude transients shown in Figure 8C is still unclear.

The power spectral densities (PSDs) of the voltage and current signals, \( \mathcal{P}_V \) and \( \mathcal{P}_I \) respectively, for the pure Mg, Mg6%Al and Mg9%Al materials were evaluated over a period of 5 hours beginning 7 hours after immersion of the sample in the electrolyte, when the signals had stabilised. The voltage and current signals during this period were divided into 40 overlapping segments of length 4096 data points. In the case of the Mg3%Al materials, \( \mathcal{P}_V \) and \( \mathcal{P}_I \) were evaluated for 25 segments (a total duration of 3 hours) beginning 9 hours after immersion. For each segment, the voltage and current signals were conditioned by subtracting a simple linear trend and then applying a Hanning window as per Winzer et al. [51]. \( \mathcal{P}_V \) and \( \mathcal{P}_I \) were calculated by applying a fast Fourier transform to the conditioned signals and averaging over all segments. Figure 9 shows \( \mathcal{P}_I \) for pure Mg as well as the as-cast Mg-Al alloys. In all cases, the PSD curves are highly non-linear. Consequently, the curves were not fitted with trend lines in order to determine parameters such as the slope and Y-intercept of the curves. In the case of pure Mg, \( \mathcal{P}_V \) tends towards white noise below ~10 mHz and also
approaching the Nyquist frequency. This may be indicative of general corrosion, which is usually associated with relatively high-frequency, low-amplitude events [55,56]. It is worth noting that the frequency of the transients shown in Figure 8A was ~20 mHz. The tendency towards white noise above and below this frequency implies that this is the dominant transient for pure Mg. There is a significant disparity between the \( \Psi_1 \) curves for the Mg3\%Al sample in the first and second phases. The cessation of lateral spreading corresponded with a shift of the \( \Psi_1 \) curve towards lower frequencies. This is indicative of the change in corrosion mechanism from general corrosion to pitting [55,56]. The \( \Psi_1 \) curves for the Mg6\%Al and Mg9\%Al alloys show a distinct peak at 0.5 Hz as well as a broader spectrum of peaks in the range 20 – 200 mHz. These are broadly consistent with the frequencies of the transients shown in Figure 8B and C. There is no white noise in the low frequency regions of the \( \Psi_1 \) curves for the Mg6\%Al and Mg9\%Al alloys, although the curves do tend towards white noise close to the Nyquist frequency. This may be indicative of the predominance of pitting corrosion, which is usually associated with very low frequency processes, and is consistent with the low-frequency transients shown in Figure 8D [55,56].

The steady-state corrosion rates of the materials were characterised in terms of the noise resistance, \( R_N \). It has been proposed by various workers that the \( R_N \) is equivalent to the polarisation resistance [57-60] and, thus, according to the Stern–Geary equation inversely proportional to the corrosion rate [61]. \( R_N \) was evaluated from the EN measurements according to [51]:

\[
R_N = \sqrt{\Psi_{V,1mHz}/\Psi_{I,1mHz}}
\]

where \( \Psi_{V,1mHz} \) and \( \Psi_{I,1mHz} \) are the power spectral densities (PSDs) of the voltage and current signals at 1 mHz. This frequency was suggested by Cottis [57]; however, the choice of frequency was largely inconsequential since \( R_N \) was independent of the frequency below 0.5 Hz for all materials. Figure 10 shows the reciprocal of \( R_N \) under steady state conditions for all materials. There was no significant difference between the corrosion rates of the Mg3\%Al and Mg6\%Al alloys in the as-cast and solution-annealed (S24) conditions (Figure 10A). In the case of the as-cast alloys, the increase in Al concentration from 6 to 9 wt.% resulted in a sharp decrease in the corrosion rate. By comparison, the decrease in the corrosion rate of the solution-annealed alloys with increasing Al concentration from 6 to 9 wt.% was less pronounced. The corrosion rate of the Mg9\%Al alloy increased with increasing solution-annealing time (Figure 10B), although the corrosion rate of the Mg9\%Al S24 material was still less than those of the as-cast and solution-annealed Mg3\%Al and Mg6\%Al alloys. Subsequent aging of the solution-annealed Mg9\%Al alloy at 200 or 340°C resulted in a recovery of the corrosion resistance; the corrosion rates of the Mg9\%Al A1 and A2 materials were only slightly higher than that of the as-cast Mg9\%Al alloy. \( 1/R_N \) for pure Mg was approximately twice that of the Mg9\%Al alloy.

The online version of this article features videos that were compiled from the time-lapse photographs of the samples shown alongside: (A) the current and voltage signals; (B) the instantaneous \( \Psi_1 \) spectrum; and (C) the instantaneous \( 1/R_N \) value. \( \Psi_1 \) and \( R_N \) were averaged over 7 overlapping segments, each of length 1024 data points, at 1 min intervals, i.e. corresponding to each photo. For the Mg3\%Al alloy, the \( \Psi_1 \) spectrum was relatively linear during the first phase, i.e. lateral spreading. During the second phase, i.e. localised corrosion, the \( \Psi_1 \) spectrum was shifted towards lower frequencies, as shown in Figure 9B. \( 1/R_N \) increases over the test duration, albeit at a diminishing rate. The sudden change in the current direction at ~1.5 hr is attributable to the initiation of corosion on alternate electrodes. This results in a peak in \( 1/R_N \), though this is probably an aberration rather than an indicator of a sudden increase in the corrosion rate. For the Mg6\%Al and Mg9\%Al alloys, the \( \Psi_1 \) spectrum
remained relatively constant, suggesting that the same corrosion mechanism predominated for the entire test duration. In the case of the Mg6%Al alloy, 1/R_{N} increases from a relatively low point, eventually reaching a steady-state towards the end of the test duration. In contrast, for the Mg9%Al alloy 1/R_{N} remained relatively constant through the test duration.

3.3 Corrosion morphology

The morphology of corrosion in the as-cast materials was evaluated by immersing samples in the test environment for 2 and 14 days. The results were generally consistent with the morphology of corrosion of the materials in 3.5% NaCl [51]. Figure 11 shows the morphology of early-stage corrosion on the surfaces of pure Mg and as-cast Mg-Al alloys after immersion in the test environment for 2 days. Corrosion on the surface of the pure Mg samples had a filiform morphology with the corrosion channels having some preferred crystallographic orientation (Figure 11A). In contrast, early-stage corrosion on the surfaces of the Mg-Al alloys took the form of elliptical pits, which were characteristic of a metastable pitting mechanism (Figure 11B – D). The morphology of the pits was consistent with selective dissolution of the Al-deficient dendritic regions of the α-Mg matrix, i.e. furthest from the Al-enriched grain boundaries and β-phase particles. They also appeared unaffected by Fe-rich particles, which were generally embedded within the β-phase (Figure 11D).

Figure 12 shows cross-sections through the corroded regions of the pure Mg and as-cast Mg-Al alloys after immersion in the test environment for 14 days. The corrosion morphology for the pure Mg sample was characterised by wide, shallow pits and tunnels that penetrated further into the bulk material (Figure 12A). The tunnels in each grain were oriented parallel to one another, suggesting that their growth mechanism was affected by crystallographic orientation. The corrosion morphology of the Mg-Al alloys was consistent with selective dissolution of the Al-deficient dendritic regions of the α-Mg matrix (Figure 12B – D). Corrosion of the Mg3%Al and Mg6%Al alloys was characterised by deep pits that tended to cross grain boundaries (Figure 12B – C). This is characteristic of an autocatalytic pitting mechanism. Corrosion of the Mg9%Al alloy was relatively superficial and limited to dissolution of the Al-deficient interior of a single grain at the surface (Figure 12D). This suggests that the Al-enriched interdendritic regions and β-phase particles act as barriers to pit growth.

4 Discussion

The results of this study underscore the profound influence that the homogeneity of the Al distribution in the α-phase can have on the corrosion resistance of Mg-Al alloys. Various workers have shown that strong galvanic couples may exist between the α- and β-phases [17-24] and that the corrosion potential of the α-phase is greatly dependent on the Al concentration [17,31-37]. In the present study, the volume concentration of the β-phase in all of the test materials was relatively low. In the as-cast materials, the β-phase particles were invariably surrounded by Al-enriched α-phase regions, which dissolved less readily than the Al-deficient regions. The Al-enriched α-phase regions would thus serve as a shield between the β-phase particles and the Al-depleted α-phase, such that the effective surface area of the β-phase in contact with the solution inside a pit, and therefore the ability of β-phase particles to behave as local cathodes, was greatly reduced. This implies that the galvanic coupling between the Al-enriched and -deficient regions was the dominant driving force for localised corrosion in the as-cast materials.

The influence of the homogeneity of the Al distribution in the α-phase is further evidenced by the corrosion morphology. Figure 12B – D show that the Al-enriched α-phase regions act as
internal barriers against pit propagation, which is consistent with previous reports [26,31-37]. This barrier effect may be used to explain most of the trends observed in the present study. Firstly, the differences in the steady-state corrosion rates of the as-cast alloys may be rationalised in terms of the differences in the Al concentrations at grain boundaries and grain interiors. Figure 3 shows that the maximum Al concentration at grain boundaries, and thus their propensity to behave as corrosion barriers, was higher in the Mg9%Al than in the other two alloys. Moreover, the difference between the maximum Al concentration at the grain boundaries and the minimum Al concentration in the grain interior for the Mg9%Al alloy was less than that for the Mg6%Al alloy. Thus, the potential for internal galvanic coupling between regions with different Al concentrations may be greater for the Mg9%Al alloy than for the Mg6%Al alloy. Secondly, the increase in the corrosion rate of the Mg9%Al due to solution treatment may be attributable to the increasing role of the galvanic coupling between the α- and β-phases. Homogenisation of the α-phase results in lowering of the corrosion barriers afforded by the Al-enriched α-phase and an increase in the potential difference between the α- and β-phases, which would result in an increase in the cathodic activity of the β-phase particles.

The recovery in corrosion resistance of the solution-annealed Mg9%Al alloy by artificial aging cannot easily be rationalised in terms of the homogeneity of the Al distribution in the α-phase, though it should be emphasised that no effort has been made in the present study to evaluate the distribution of Al in the α-phase in these materials. It is also unclear why the Mg3%Al alloy undergoes (initially) a period of general corrosion. One possibility is that this is related to the influence of microstructure on the composition of the oxide layer. Several workers have shown that Al enriches the oxide layer formed on Mg alloys in aqueous solutions [38-41]. This has been associated with an increase in corrosion resistance. Thus, the surface film formed on the Mg3%Al alloy in the test environment may be less stable than those formed on the Mg6%Al and Mg9%Al alloys due to its lower Al concentration, thereby increasing its susceptibility to general corrosion.

It is unlikely that the corrosion behaviour of the test materials in the as-cast or solution-annealed conditions were influenced significantly by the presence of the Al-Mn-Fe phase. Liu et al. [44] compiled a comprehensive review of published data on the influence of Fe on the corrosion rate of pure Mg and Mg-Al alloys in Cl-containing solutions. Based on this data, they proposed that corrosion of Mg-Al alloys containing <170 wt. ppm Fe but Fe/Mn ratios >0.032 was affected by the influence of Fe. This tolerance limit is reduced to <30 wt. ppm with the addition of >1 wt.% Al. The Fe concentrations of the materials used in the present study were in the range 30 – 50 wt. ppm, i.e. well below the tolerance limit for pure Mg but in line with that for binary Mg-Al alloys with >1 wt.% Al. The Fe/Mn ratios were close to unity. It is important to note that the Fe-rich particles analysed using EDX invariably contained Mn and were usually embedded within the β-phase. Given that the β-phase is more cathodic than α-Mg, this may mitigate the galvanic coupling between the Fe-rich particles and α-Mg. Thus, such particles could be expected to have a greater influence on the corrosion behaviour of the solution-annealed materials. However, this is not consistent with the results of the present study, which showed that the corrosion rates of the solution-annealed Mg3%Al and Mg6%Al alloys were no higher than those of the as-cast alloys with the same Al concentrations.

5 Conclusions

1. The steady-state corrosion rates for the as-cast Mg3%Al and Mg6%Al alloys in 0.5 M NaCl at pH 12 at open circuit potential were relatively consistent, but much higher than that of as-cast Mg9%Al alloy. The corrosion rate of Mg9%Al alloy increased with gradual
homogenisation of the microstructure by solution annealing at 420 °C for up to 24 hours. Artificial aging of the Mg9%Al alloy after solution annealing resulted in a recovery of its low corrosion rate. Solution annealing of the Mg3%Al and Mg6%Al alloys for 24 hours did not result in a significant change in their corrosion rates.

2. For the Mg-Al alloys, steady-state corrosion was highly localised, usually occurring at a single point on one of the sample surfaces. For the Mg3%Al alloy in the as-cast and solution-treated conditions, pitting was preceded by an initial period of general corrosion. For the pure Mg, only general corrosion occurred. The resistance of the Mg6%Al and Mg9%Al alloys to general corrosion may be due to the effect of Al on the thickness and stability of the surface film.

3. The pit morphology for the Mg3%Al and Mg6%Al materials was characteristic of an autocatalytic mechanism, in which the Al-depleted α-Mg dendrites were preferentially dissolved. In contrast, the pit morphology for the Mg9%Al materials was characteristic of a metastable mechanism, in which corrosion was halted at Al-enriched interdendritic α-Mg and grain boundaries. The results are consistent with a strong galvanic coupling between Al-depleted and -enriched zones of the α-phase.

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7 References

[40] M. Liu, S. Zanna, H. Ardelean, I. Frateur, P. Schmutz, G. Song, A. Atrens, P. Marcus, A first quantitative XPS study of the surface films formed by exposure to water on Mg
and on the Mg-Al intermetallics Al₃Mg₂ and Mg₁₇Al₁₂, Corros. Sci. 51 (2009) 1115-1127.


Figure 1: Microstructure of the as-cast alloys A) Mg3%Al, B) Mg6%Al and C) Mg9%Al.
Figure 2: Detailed view of the microstructure of the as-cast alloy Mg9%Al showing the constituent phases.

Figure 3: EDX line scans though grain boundaries in a) Mg3%Al, b) Mg6%Al and c) Mg9%Al as-cast alloys.
Figure 4: SEM micrographs of the Mg9%Al alloy in the a) as-cast, b) S1 (420 °C for 1 hour), c) S3 (420 °C for 3 hours), d) S6 (420 °C for 6 hours), e) S9 (420 °C for 9 hours) and f) S24 (420 °C for 24 hours) conditions.
Figure 5: SEM micrographs of the a) Mg3%Al, b) Mg6%Al and c) Mg9%Al alloys in the fully solution annealed S24 (420 °C for 24 hours) condition showing constituent phases.
Figure 6: Microstructures of the artificially-aged materials a) Mg9%Al A1 and b) Mg9%Al A2.

Figure 7: In-situ images of EN samples of the as-cast Mg3%Al materials after (A) 1 hours, (B) 5 hours and (C) 12 hours in the test environment as well as the measured voltage and current signals in the time domain.
Figure 8: Different transient shapes in the voltage and current signals for the (A) pure Mg, (B) as-cast Mg6%Al, (C) as-cast Mg9%Al and (D) Mg9%Al S1 materials.
Figure 9: Power spectral densities of the current signal, $\Psi_i$, for (A) pure Mg, (B) Mg3%Al, (C) Mg6%Al and (D) Mg9%Al. In (A), (C) and (D), $\Psi_i$ has been calculated for the period from 5 to 12 hours after immersion. In (B), $\Psi_i$ has been calculated for the periods from (i) 1 to 4 hr and (ii) from 9 to 12 hours after immersion.
Figure 10: Reciprocal of the EN resistance, $1/R_N$, at 1 mHz for: (A) pure Mg and the Mg-Al alloys in the as-cast, solution treated (S24) and artificially aged (A1 and A2) conditions; and (B) Mg9%Al alloy as a function of solution annealing time ($N \geq 3$).

Figure 11: Backscatter electron images of early-stage corrosion initiation on the surfaces of (A) pure Mg, (B) Mg3%Al, (C) Mg6%Al and (D) Mg9%Al after immersion in the test environment for 2 days.
Figure 12: Backscatter electron images of cross-sections through corroded regions in (A) pure Mg, (B) Mg3%Al, (C) Mg6%Al and (D) Mg9%Al after immersion in the test environment for 14 days.
Table 1: Compositions of the test materials [51].

<table>
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<tr>
<th>Material</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Ca</th>
<th>Zr</th>
<th>Sn</th>
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<tbody>
<tr>
<td>Mg</td>
<td>0.002</td>
<td>0.005</td>
<td>&lt;0.003</td>
<td>&lt;0.005</td>
<td>0.003</td>
<td>0.004</td>
<td>&lt;0.001</td>
<td>0.002</td>
<td>&lt;0.0001</td>
<td>&lt;0.0005</td>
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<tr>
<td>Mg3%Al</td>
<td>3.006</td>
<td>0.002</td>
<td>0.015</td>
<td>0.011</td>
<td>0.001</td>
<td>0.005</td>
<td>&lt;0.0005</td>
<td>0.012</td>
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<td>&lt;0.001</td>
<td>0.005</td>
<td>0.01</td>
<td>&lt;0.005</td>
<td>0.003</td>
<td>&lt;0.0005</td>
<td>0.011</td>
<td>&lt;0.001</td>
<td>&lt;0.0005</td>
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<tr>
<td>Mg9%Al</td>
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<td>0.004</td>
<td>&lt;0.001</td>
<td>0.003</td>
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Table 2: Summary of specimen nomenclature and heat treatment protocols.

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<th>Solution treatment</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Aging</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
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<td>24</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>24</td>
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