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As Published: http://dx.doi.org/10.5006/3655

Publisher: NACE International

Persistent URL: https://hdl.handle.net/1721.1/131079

Version: Author’s final manuscript: final author’s manuscript post peer review, without publisher’s formatting or copy editing

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Localized Atmospheric Corrosion of Magnesium-Aluminum Alloys Produced by Semisolid Casting: A 2D and 3D Investigation

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Abstract

The localized corrosion of the two magnesium-aluminum alloys AM50 and AZ91 produced by a semisolid casting method was investigated under atmospheric corrosion conditions, in the presence of NaCl. Gravimetry confirmed the beneficial effect from ambient levels of carbon dioxide (CO2) in suppressing corrosion through the formation of magnesium hydroxy carbonates. Both 2D and 3D characterization revealed that ambient CO2 has a strong influence on the morphology and rate of localized corrosion. In CO2-free atmosphere, the alloys suffered localized corrosion resulting in clustered and interconnected cavities that extended deep into the material. In contrast, corrosion in the presence of ambient levels of CO2 (400 ppm) resulted in evenly distributed shallow corrosion sites. The results indicate that CO2 neutralizes the cathodic areas resulting in diminished cathodic activity and inhibiting NaCl(aq) droplet coalescence.

Keywords: Magnesium-aluminium alloys, Casting, Atmospheric corrosion, Localised corrosion, Corrosion morphology, 3D imaging.
1. Introduction

Among the various magnesium alloy systems, magnesium-aluminium (Mg-Al) alloys are a key lightweight metallic material for the transportation industry – owing to their high specific stiffness, excellent damping properties, castability, and strength to weight ratio [1, 2]. The broader use of such energy-efficient alloy systems in the automotive sector is still however limited, owing in part to limited corrosion resistance [1, 2].

The inadequate corrosion resistance of Mg is because of its high electronegative potential or its low relatively thermodynamic stability ($E^\circ = -2.4$ V vs. Standard hydrogen electrode (SHE)), and the unprotective (non-passivating) nature of the surface film that it forms upon the exposure to most practical aqueous environments. The oxide/hydroxide (MgO/Mg(OH)$_2$) film, is indeed soluble in water (neutral and acidic aqueous solutions) and any partial failure in the surface film triggers localised corrosion on the metal surface [1-3].

In service conditions, degradation of Mg alloys mainly occurs under natural and anthropogenic environments (i.e. in the presence of relative humidity (RH), deicing salts, atmospheric pollutants). The NaCl–induced atmospheric corrosion of Mg and its alloys has been suggested to be principally electrochemical, resembling the process described to occur under aqueous environments [1, 3]. This involves the anodic dissolution of Mg (Equation 1), water reduction (Equation 2), which leads to hydrogen evolution and the formation of hydroxy ions, as one of the dominant cathodic reactions, and the two reactions (Equations 1 and 2) that leads the formation of magnesium hydroxide (Equation 3) [1]:

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \quad (1)$$

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

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s) \quad (3)$$

The corrosion process establishes pH gradients between cathodes (that have a locally elevated pH owing to being sites of hydroxy ion formation (Equation 2)) and the anodic areas, where pH is approximately neutral. Owing to the solubility of the imperfect MgO/Mg(OH)$_2$ films at low pH, the anodic reaction can continue unhindered (thus, in the range pH 2-8, the rate of Mg dissolution increases exponentially with pH). This is significant because Mg corrosion is known to be under cathodic control (see e.g. [4]). There is no rate limitation for the cathodic reaction in the presence of water (Equation 2), i.e. the species being reduced is abundant and this is what the key difference is between systems where oxygen reduction is one of the partial reactions.

Hence, the electrochemical corrosion of Mg can be rapid, especially when the surface water film contains dissolved salts [1, 3, 5]. In addition to such electrochemical processes, the pH of the electrolyte on the alloy surface is largely affected by the gaseous species present in air. For instance, in highly polluted areas and under humid conditions, the Mg surface becomes an efficient getter for SO$_2$ owing to the high pH of the thin electrolyte layer [6]. The outcome is the formation of two highly acidic species, namely hydrogen sulfite (HSO$_3^-$) and sulfite (SO$_3^{2-}$) that results in a rapid dissolution of the MgO/Mg(OH)$_2$ surface film [6]. Another significant example is ambient concentrations of CO$_2$ gas, which is always present in air at a concentration...
of around 400 ppm [5]. This gas inhibits the corrosion of Mg alloys, both under atmospheric [1, 7, 8] and aqueous [9] environments, which has also been attributed to the CO$_2$-induced alterations in the electrolyte pH. The process involves neutralising the alkali generated in the cathodic process (Equation 4) leading to the formation of magnesium hydroxide carbonates (Mg$_5$(CO$_3$)$_4$(OH)$_2$$\times$$x$H$_2$O, where $x = 4–8$), see e.g. Equation 5 [1, 8]:

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$

(4)

$$5Mg^{2+}(aq) + 4CO_3^{2-}(aq) + 2OH^-(aq) + 4H_2O (l) \rightarrow Mg_5(CO_3)_4(OH)_2$$\times$$4H_2O (s)$$

(5)

Magnesium hydroxide carbonates (e.g. Equation 5) formed on the alloy surface in the presence of CO$_2$ have been reposted to be protective [1, 8] (the equilibrium pH of water in contact with Mg(OH)$_2$ is 10.3, whereas the corresponding value for magnesium hydroxide carbonate, hydromagnesite (Mg$_5$(CO$_3$)$_4$(OH)$_2$$\times$$4$H$_2$O) is 8.7 [1]). The interactions between all the above-mentioned electrochemical processes and the inhomogeneous microstructure of cast alloys can generate an intricate corrosion microstructure. When Mg is alloyed, the second phase particles and noble inclusions further enhance the corrosion process through activating micro-galvanic corrosion cells (i.e. localised corrosion). While the effects of the structural features (including different phases and defects) on localised corrosion of Mg-based alloys in various environments have been extensively studied in the literature [9-18], the role played by the main atmospheric gasses in the localised corrosion is, by comparison, less widely studied.

One approach to investigate the localised atmospheric corrosion of alloys is to complement the “traditional” 2D methods by 3-dimensional (3D) methods using e.g. focus ion beam (FIB) milling microscopy (i.e. the Dual-beam systems). There are a very few studies on 3D investigation of corrosion carried out for: aluminium alloys [19], steels [20, 21], and Mg alloys [22]. In the latter case, using 3D imaging and correlative imaging, Krebs et al. [22] suggested that the development of the corrosion front in AZ31 Mg alloy (exposed to a saline environment) could be linked to Al-Mn second phase particles.

Herein, the localised corrosion of AM50 and AZ91 exposed for up to 672 hours at 22°C and 95% RH in the presence and absence of CO$_2$ was studied. In order to resolve the effect of CO$_2$ on the extent of localised corrosion, the results obtained by 2D techniques were supplemented by 3D characterisation using FIB and interference microscopy. In addition, the influence of CO$_2$ on the corrosion rate, the formation and growth of locally corroded areas was discussed. The alloys studied here were produced by semi-solid casting, rheocasting (RC) [23, 24]. Rheocasting produces alloys with a lower fraction of casting defects and microstructures that are slightly different from those of their high pressure die cast counterparts [24-26].
2. Experimental

Test material RC technique, as described in the previous publications [23, 24], was utilised in order to prepare the semi-solid cast specimens. The RC AM50 and RC AZ91 components were manufactured using a vertical casting machine (made by Suzhou Sanji Foundry Co Ltd) with a locking force of 50 tons (and the die having an area of 250 cm²) [24, 27]. The alloys investigated are high purity Mg-Al alloys AM50 and AZ91, see Table I for the chemical composition of the test materials.

Table I

The as-received cast components were cut and machined to produce 15×15×2 mm³ test specimens with an area of ~5.7 cm². Each specimen was first ground on successive silicon carbide (SiC) abrasive papers (from P1000 to P4000 mesh) in the presence of de-ionised water as lubricant. The preparation procedure of the test coupons was then followed by polishing steps using 3 and 1 μm diamond suspension. In the final preparation step, the coupons were polished for up to 10 minutes using a suspension of oxidised porous silicon (OPS), cloth discs, and on a Buehler Microcloth to achieve a mirror-like surface finish. The polished specimens were ultrasonically cleaned dried using a blower (cool air). Next, the test coupons were then stored in a desiccator over a desiccant for 24 hours prior to the atmospheric corrosion exposures and microstructural examinations. The atmospheric corrosion experiments were performed in the presence of sodium chloride (NaCl) contaminations on the surface of the test coupons. To achieve a uniform distribution of salt particles, one gram of NaCl was thoroughly dissolved in a mixed de-ionised H₂O (20 ml)/ethanol (80 ml) and sprayed on the surface of the coupons. Two different amounts of salt, 14 and 70 μg/cm² were applied. The spraying was conducted to make sure an even distribution of NaCl particles on the coupons’ surfaces. Finally, it should also be stated that triplicate coupons were exposed for each condition.

Exposure set-ups and gravimetry The corrosion exposures were carried out at a constant ambient temperature (22 ± 0.05°C) at a constant RH of 95 ± 0.5%, lasted for 672 hours, and the CO₂ concentration of the exposure gas was carefully controlled to be either 0 and 400 ± 20 pm. In the latter case, the experiment were conducted in flowing air by means of a home-built experimental set-up described elsewhere [1, 26, 28]. The CO₂-free corrosion experiments were conducted in a sealed desiccator, wherein a container of a KOH (aq) solution was placed. The function of the KOH (aq) solution was to capture the entire CO₂ gas inside the desiccator and to maintain the RH of the closed (sealed) environment to be 95.0 %, see the details of this experiment in one of authors’ previous publications [16]. The weight of the coupons was measured using a six decimal (0.0001 mg) Sartorius Microbalance in order to register the change in the coupons’ mass as result of corrosion. When the exposures were finished, the coupons were stored in a desiccator for 24-48 hours to allow a complete elimination of the loosely bound water species on the surface of the corroded specimens. The mass gain determined after this process is called ‘dry mass gain’. Finally, the coupons were placed in a container of 20% CrO₃ (aq) solution (ultrasonic agitation) to remove all the corrosion products comprising oxides and hydroxides, allowing determination of the metal loss values [26].
Post-exposure analysis The structure of crystalline corrosion products formed on the surface of the coupons under different atmospheric conditions were first characterised by means of a Siemens D5000 X-ray diffraction (XRD) system. This system was equipped with a Göbel mirror, CuKα radiation ($\lambda = 1.5418$ Å). The XRD data were collected under 2θ: 5–80° and an incidence angle of 0.05° through the Grazing angle incidence arrangement (GI-XRD).

Microstructural studies were carried out before and after the corrosion experiments by means of two scanning electron microscopes (SEMs), namely an FEI Quanta 200 and Ultra 55 FEG SEM. An image analysis software (Carl Zeiss AxioVision) was utilised to determine the area fraction of second phase particles using the SEM micrographs. To better visualise the alloys’ microstructural constituents, a 1% nital etchant (i.e. Nitric acid (HNO$_3$) and (ethyl) Alcohol C$_2$H$_5$OH) was prepared and utilised to treat the as-received cast coupons. The SEM instruments employed in the present research were both equipped with an Oxford Inca energy dispersive X-ray spectroscopy (EDXS) system. The EDXS analysis was carried out to study the local chemical variations and elemental mapping on the alloys’ surface. This was conducted using an accelerating voltage of 15-20 kV. The coupons were placed at the working distance (WD) of 10-15 mm inside the SEM chamber. During the EDXS analysis, aperture size was optimised in order to achieve an ideal signal count., required for a reliable chemical analysis.

After the corrosion product removal procedure (using CrO$_3$(aq) solution) from the surface of the corroded specimens, a quantitative interference microscopy analysis was carried out to study the 3D topography of the coupons’ surfaces by means of a Veeco instrument. The interference microscopy examinations were performed in the instrument’s vertical scanning interferometry (VSI) mode. This involved the vertical range was 0.5 mm with a resolution >10 nm. A 10× objective was utilised, generating a ~460x600 μm² field of view.

The post-exposure analysis of the corroded coupons was continued through operating a successive slicing and imaging procedure by means of a Versa 3D DualBeam FIB microscope. An initial optimisation experiment indicated that an optimal thickness of each slice could be ~500 nm. The slicing step involved milling of the coupons using an ion beam current of 28 nA at 30 kV. In-situ imaging was carried out using the SEM’s secondary electron (SE) mode at 5 kV and WD of 10.0 mm. A schematic showing the 3D analysis comprising: (1) slice and image, (2) 3D reconstruction, and (3) post-preparation analysis is illustrated in Fig 1. It may be noted that the coupons were tilted 7° during the milling step. This allowed preparation of 45° slices in each SE imaging step (Fig. 1). The SE micrographs from the FIB-prepared slices were stack, compiled, aligned, and processed using FIJI software [29], the whole process generating a 3D illustration of the coupons with sites of localised dissolution.

Figure 1
3. Results

3.1. Gravimetry and corrosion products

Tables II lists the dry mass gain values of the two alloys contaminated with different levels of NaCl after 672 hours atmospheric exposure at ambient temperature (22°C) and 95.0% RH. The metal loss values, obtained after the corrosion removal procedure, as a function of the amount of salt contaminations in the presence and absence of CO₂ is presented in Fig. 2 (a). The results (Table II and Fig. 2 (a)) indicate that AM50 experienced 2.0-4.1 times higher corrosion rate as compared to AZ91. Moreover, it is noted that both alloys corroded faster when CO₂ was absent.

Figure 2 (b) shows XRD patterns collected from the surface of the two magnesium- aluminium alloys exposed for 672 hours with 70 µg/cm² added salt, in the presence and absence of CO₂. The structural analysis clearly indicated that CO₂-free exposures led to the formation of brucite (the crystalline form of magnesium hydroxide Mg(OH)₂) was the principal corrosion product accompanied with minor amounts of a MgAl-bearing corrosion product; meixnerite Mg₆Al₂(OH)₁₅·4.5H₂O. However, when CO₂ was present in air, two different types of magnesium hydroxy carbonates, namely Giorgiosite Mg₅(CO₃)₄(OH)₂·5H₂O and Mg₅(CO₃)₄(OH)₂·8H₂O, were detected. It may be noted that hydromagnesite, Mg₅(CO₃)₄(OH)₂·4H₂O, which has been reported to form under similar conditions [1, 23, 8] was not identified. Finally, as anticipated, the intensity of the β-phase (Mg₁₇Al₁₂) peaks relative to the α-Mg peaks was ore highlighted for AZ91 compared to AM50.

Table II and Figure 2

3.2. Microstructure of the cast alloys

Figure 3 shows the cast microstructure of the two alloys, AM50 and AZ91, before the corrosion exposure (polished and etched surface). The alloy microstructure had four constituents, including α-Mg in the matrix, Mg₁₇Al₁₂ (β-phase), Alₓ(Mn,Fe)ᵧ particles wherein the 'X' to "Y" ratio depends on the Fe and Mn concentrations in the alloy, such as Alₓ(Mn,Fe)ᵧ and an Al-rich segregation band, see also [24]. The β-phase particles were situated within the segregation band. As seen in the SEM micrographs, alloy AZ91 contained a higher fraction of β-phase and a slightly higher Al content in the α-Mg grains than alloy AM50 (see Table III). Furthermore, the β second phase particles were finer in AM50 than in AZ91. In addition, the β-phase appeared discontinuous in AM50, whereas it formed a ‘semi-continuous’ network in AZ91 (see Fig. 3).

Table III & Figure 3

3.3. Effect of CO₂ on corrosion microstructure

Regardless of the CO₂ content in air, SEM micrographs from the exposed coupons indicated that the surface of AM50 was more affected by corrosion than AZ91, agreeing well with the
mass gain and mass loss data presented in Table II and Fig. 2. The SE and backscatter electron (BSE) micrographs in Fig. 4 display the morphology of the corrosion products formed on the surface of alloys contaminated with the highest amount of added NaCl (70 µg/cm²) after 672 hours exposure at 22°C and 95% RH. The micrographs inserted in Fig. 4 show the corroded surfaces at higher magnification. The SEM analysis showed the CO₂-free environments led to a more severe corrosion attack as compared with those of the CO₂-containing exposures. This is also in agreement with the respective mass gain and mass loss values (presented in Table II and Fig. 2 (a)). In addition, the alloys exhibited a greater tendency for localised atmospheric corrosion in the CO₂-free environment. Therefore, in the presence of 400 ppm CO₂, corrosion products covered the entire surface, whilst, in the CO₂-free environment, the surface of the coupons was either little or severely (i.e. large amounts of corrosion products) affected by corrosion (compare Figs. 4 (a), (b) related to 400 ppm CO₂, and Figs. 4 (c), (d) from the CO₂-free exposure). The severely corroded areas of the coupon’s surface formed in the CO₂-free environment had a strong tendency to be interconnected, as can be seen in Figs. 4 (c), (d). Examples of such connected corrosion products are indicated by dashed lines in Figs. 4 (c) and (d), e.g. Regions 5 and 6 in the two images exemplify unconnected localised corroded regions. After exposure to CO₂-containing environments, the two alloys formed globular accumulations of corrosion products, which are designated by arrows in the inserted SEM images in Fig. 4. There were also signs of ‘unreacted’ salt particles, occasionally detected, on AZ91 after exposure to the CO₂-containing environment (Fig. 4 (b)).

**Figure 4**

3.4. EDXS analysis of exposed test coupons

This section describes EDXS analysis of AM50 exposed under the atmospheric conditions. The AM50 coupons were selected for imaging because the corrosion attack was more severe for that material. However, the corresponding images for alloy AZ91 were similar with respect to the distribution of elements on the surface. Figure 5 shows EDXS elemental maps of the corroded surface of AM50 (CO₂, 70 µg/cm² NaCl, 672 hours, 22°C, 95% RH). The overlap of the Na and Cl maps indicate the presence of NaCl on the sample surface. The elemental maps were acquired from the neighboring areas of the NaCl particle. It can be seen in Fig. 5 that while chlorine was present on the studied area, no sodium was noticed. Besides, EDXS point analysis at this region (indicated by a yellow cross in Fig. 5) showed that the presence of elements O, Mg, C, and Cl. This indicates that the Cl content was associated with Mg.

**Figure 5**

Figure 6 presents EDXS elemental mapping of AM50 exposed to the CO₂-free environment. In this specific region, there was no sign of salt (Na and Cl), noting the Cl and Na maps displaying little overlapping signals. It was noted however that Na was accumulated in the comparatively uncorroded/unaffect ed regions of the alloy surface and amongst the corrosion product buildups, where little sign of Cl was identified. It was also noted that Na strongly tended to be concentrated in areas with high Al signal, corresponding to segregation bands rich in β-phase particles. Chlorine was dominantly observed on the edges of the corrosion products. In addition,
Cl was mainly detected around the comparatively small corrosion products. An EDXS point analysis (designated in Fig. 5) of the region rich in Cl disclosed that the elements O, Mg, Cl and C, being similar to the point analysis in Fig. 5, pointing towards the formation of magnesium chloride. The carbon content (Fig. 6) detected in this case is believed to be contamination coming from: (a) handling of the exposed coupons in the laboratory air, and (b) carbon contaminations present inside the SEM chamber, see [16].

Figure 6

EDXS elemental maps from typical another region (corresponding to a coupon exposed to the CO\textsubscript{2}-free environment) is presented in Fig. 7. The starkest difference between this region and that shown in Fig. 6 is the pronounced presence of second phase particles (i.e. β- and especially Al\textsubscript{5}(Mn, Fe))\textsubscript{3}, see the Al and Mn EDXS maps in Fig. 7. In this region, Na was accompanied by the Mn-containing second phase particles, i.e. Al\textsubscript{8}(Mn,Fe)\textsubscript{5}, which is frequently referred to as η in the literature [23]. In contrast, there is little overlap between the Al-rich areas with no Mn (i.e. β-phase) and Na maps. An area analysis was carried out at the large Al\textsubscript{8}(Mn, Fe)\textsubscript{5}-phase particle in the boxed area in Fig. 7. This analysis clearly indicated that Na was concentrated at the Al\textsubscript{8}(Mn, Fe)\textsubscript{5}-phase particle.

Figure 7

3.5. Interference microscopy, FIB and 3D imaging

As discussed above (and shown in the plan-view SEM micrographs in Fig. 4), the atmospheric corrosion of the two alloys tended to be localised both in the presence and absence of 400 ppm CO\textsubscript{2}. However, corrosion was obviously more strongly localised in the CO\textsubscript{2}-free environment. In order to investigate the morphology of the affected areas in the two alloys exposed to the two environments, 3D topographical profiles were generated from the coupons after the corrosion product removal (the CrO\textsubscript{3} (aq) treatment). Figures 8 and 9 shows the alloys exposed to the 400 ppm of CO\textsubscript{2}- and CO\textsubscript{2}-free atmospheres, respectively. Furthermore, 2D profiles (see the X- and Y-direction lines) are shown in the respective figures. A region of interest (ROI) was designated in each coupon (indicated in the figures) which could be considered as a representative of typical areas affected by localised atmospheric corrosion.

The situation in the presence of CO\textsubscript{2} is illustrated in Fig. 8, showing sites of localised corrosion with different sizes on both alloys. The distance between these individual sites of dissolution was comparable or similar to the distance between the corrosion product buildups observed in the plan-view SEM images (Fig. 4). Moreover, the measurements indicated that the maximum depth of locally affected area for AM50 (~58 µm) was approximately twice as deep than for AZ91 (~31 µm). Consequently, the ROI measurements in Fig. 8 show that the dissolution sites formed on alloy AM50 were on average deeper than on alloy AZ91.

The situation after exposure in the absence of CO\textsubscript{2} is illustrated in Fig. 9. The 2D and 3D imaging revealed that in this environment both alloys formed were deep and shallow locally affected regions. Figures 9 (a) and (c) show examples of the deep regions while Figs. 9 (b) and
(d) revealed relatively shallow sites of dissolution on AM50 and AZ91. The deep areas were interconnected, forming a network below the alloy surface. The 3D profiles show the absence of individual localised corrosion sites in the vicinity of the network of deep areas of dissolution (see Figs. 9 (a) and (c)). The observed shallow sites of dissolution formed in the CO$_2$-free environment had a distribution which was similar to that seen in the CO$_2$-containing environment. Both classes of localised corrosion regions were deeper for AM50 than for AZ91.

**Figures 8 and 9**

To supplement the optical profilometry results (Figs. 8 and 9), representative regions localised corrosion were selected and carefully analysed by the consecutive steps of FIB cross-sectional milling–SE imaging described in the experimental section and Fig. 1. This experiment was specifically suited to explore the connectivity of locally affected areas by atmospheric corrosion with 500 nm increments (i.e. the thickness of each FIB-milled slice) in each ROIs.

Figure 10 displays some selected cross-sections that were gathered together from the assembled volumes. Figure 10 also shows the plan-view image of the same volume. The sites of localised dissolution formed in the CO$_2$-free environment were connected deep in the bulk (see Fig. 10 (a) and (b)) for both alloys. In contrast, the localised corrosion sites formed in the CO$_2$-containing environment persisted to be unconnected (see Fig. 10 (c) and (d)).

**Figure 10**

### 3.6. Cross-sectional analysis

Figure 11 presents SEM-BSE cross-sectional images for AZ91 after removal of the corrosion product buildups (seen in Fig. 4) formed upon exposure to humid air (70 µg/cm$^2$ NaCl) in the CO$_2$-containing and CO$_2$-free environments. Both images (i.e. Fig. 11 (a) and (b)) show the presence of β- and Al$_x$(Mn, Fe)$_y$-second phase particles in the vicinity of the locally dissolved sites under the alloy surface. In the alloys under investigation herein, the growth of the localised corrosion sites could not effectively be ceased as they reached the β particles and as described in the literature [12]. This can be explained by the 3D nature of the alloy being corroded (or the notion that β phase can never form a 3D network of particles in the alloy). The correlation of localised corrosion and β-phase was even less clear in the case of the AM50 alloy due to the small size of the β-phase particles relative to the size of the localised corrosion sites.

**Figure 11**
4. Discussion

The corrosion process Hydrogen evolution (Equation 2 in the introduction section) and the migration of Na\(^+\) (aq) causes the cathodic regions to become alkaline. In contrast, chloride accumulates at the anodic sites, the resulting MgCl\(_2\) (aq) solution being slightly acidic. Thus, a pH gradient develops between anodic and cathodic areas. In the absence of Faradaic processes, the pH of water in equilibrium with brucite is about 10.0 [30]. Because of the relatively low pH of the anolyte and the presence of chloride, the semi-protective film does not easily heal. Thus, corrosion in NaCl (aq) solution is cathodically controlled and very high corrosion rates are observed for materials containing large amounts of second phase particles and noble inclusions that can act as cathodes [31, 32].

The semi-protective corrosion films formed on Mg-Al alloys are reported to contain Al\(^{3+}\) which is expected to modify corrosion behavior [1, 33-35]. Thus, at neutral pH, MgO and Mg(OH)\(_2\) are soluble while alumina (Al(OH)\(_3\) or Al\(_2\)O\(_3\)) is insoluble. Therefore, the stability of the oxide/hydroxide film at neutral pH (in the anodic areas) is improved somewhat by alloying with aluminium. However, the extensive localised corrosion observed on the two Mg-Al alloys studied in this work shows that the alumina-containing films formed on the α-Mg matrix of Mg-Al alloys are quite susceptible to localised corrosion in NaCl (aq) solution. This is in agreement with the notion that aluminium also suffers localised corrosion (pitting) in NaCl (aq) [36]. In alkaline solutions (at high pH), e.g., on the Mg(OH)\(_2\) surface and especially in the cathodic areas, alumina is soluble forming aluminate ions (Al(OH)\(_4\))\(^-\) (aq)). Consequently, meixnerite (Mg\(_6\)Al\(_2\)(OH)\(_{18}\)-4H\(_2\)O) (also reported as Mg\(_6\)Al\(_2\)(OH)\(_{18}\)-4H\(_2\)O [37]) formed in the CO\(_2\)-free environment. Meixnerite is a layered double hydroxide (LDH) compound and can be precipitated from alkaline solutions containing both magnesium and aluminium. The lack of evidence for meixnerite after exposure to 400 ppm CO\(_2\) may be due to its reaction with CO\(_2\) to form poorly crystalline aluminium magnesium hydroxy carbonate LDHs. Moreover, the pH decrease caused by CO\(_2\) will diminish alumina solubility in the surface electrolyte. It is suggested that the decreased tendency for alumina to dissolve in the surface electrolyte because of neutralisation by CO\(_2\) adds to the corrosion inhibitive effect of CO\(_2\) towards Mg-Al alloys.

The presence of strong pH gradients on the surface is illustrated by the EDXS map of Na in Fig. 6 (AM50 exposed in the CO\(_2\)-free environment) showing that Na is present between two heavily corroded regions. The two regions correspond to anodic areas while Na is concentrated at the cathodic sites. This suggests the presence of large corrosion cells (several tenths of micrometer) on the surface. Moreover, the Na map in Fig. 7 (i.e. alloy AM50 in the CO\(_2\)-free environment) shows that Na is concentrated at the Mn–containing second phase particles (i.e. at the Al\(_x\)(Mn, Fe),\(_y\) particles). According to Jönsson et al. [38] Al\(_x\)(Mn, Fe),\(_y\) (designated as η, in that paper)-phase particles have higher open-circuit corrosion potential than β and α-Mg phase. In addition, in-situ scanning Kelvin probe force microscopy (SKPFM) has indicated the following sequence for the relative Volta potentials in AZ91: Al\(_x\)(Mn, Fe),\(_y\) > β ~ segregation band > α-Mg [38]. Thus, Al\(_x\)(Mn, Fe),\(_y\)-phase, β-phase and the segregation band were all cathodic towards the α-Mg grains. Nevertheless, Jönsson et al. claimed [38] that the Al\(_x\)(Mn, Fe),\(_y\)-phase was not active in the initiation of localised corrosion since it was embedded in the β second phase particles,
far from the anodic matrix (α-phase). However, the cathodic activity of Al₃(Mn, Fe)ₓ second phase particles indicated in the present research agrees with the results of Danaie et al. [39], and Esmaily et al. [35]. Moreover, Arrabal et al. [40] have shown that corrosion of Mg-Al alloys occurred at the interface between β- and Alₓ(Mn, Fe)ᵧ particles and the α-Mg matrix. Hence, the results presented in this paper confirms the notion that both β and Alₓ(Mn, Fe)ᵧ can act as cathodes in Mg-Al alloys, developing micro-galvanic cells (and localised corrosion).

The excellent correlation between Mn and Na in Fig. 7 implies that in that case, Alₓ(Mn, Fe)ᵧ - phase particles are more active cathodes than the β-particles. This can be associated with the high pH in the cathodic areas in CO₂-free environment. As mentioned above, alumina dissolves at high pH. Thus, while the β-phase is expected to be covered by an insulating MgO/Mg(OH)₂ layer at high pH, the Alₓ(Mn, Fe)ᵧ-phase particles are expected to be covered by oxides and hydroxides of manganese. Among these, only Mn(OH)₂ is an electronic insulator while MnO, Mn₃O₄ and MnOOH are semiconductors. Accordingly, Danaie et al. reported that after 96 hours exposure in 1.6 wt.% NaCl solution, Mn₃O₄ formed on the Alₓ(Mn, Fe)ᵧ-phase as a result of high local alkalinity and preferential dissolution of Al [39]. Therefore, the relatively high cathodic activity of Alₓ(Mn, Fe)ᵧ second phase particles in the CO₂-free environment is owing to the formation of an electronically conducting surface film on the particles, alumina dissolving as aluminate ions due to the high pH. This also implies that, because the alumina component in the oxide film becomes less soluble with decreasing pH, the cathodic activity of the Alₓ(Mn, Fe)ᵧ-phase particles is lower in CO₂ containing air.

Surface pH also has important implications for the distribution of electrolyte. Thus, investigating the NaCl-induced atmospheric corrosion of Cu, Chen et al. reported [41] that NaCl (aq) droplets formed on the sample at 80% RH in air tended to spread over the sample surface when the concentration of CO₂ was < 5 ppm. In contrast, there was little spreading of the droplets at ambient levels of CO₂. The effect was suggested to be linked to the cathodic reaction causing a high pH in the periphery of the droplets in CO₂-free exposure. The high pH in such areas is suggested to be an outcome of a negative surface charge, decreasing the surface tension of the oxide-electrolyte interface and favoring wetting of the surface. In the present study Figs. 4 (a) and (b) present closely spaced spherical corrosion products on the surface of alloys after CO₂-containing exposure. The distribution of corrosion product mimics the distribution of the NaCl (aq) droplets formed when the coupons were placed in the exposure chamber at the beginning of the corrosion experiments. In contrast, after the CO₂-free exposures of alloys, there was extensive coalescence of NaCl (aq) droplets and correspondingly extended corrosion cells were observed, resulting in severe localised corrosion.

**Localised corrosion: formation and connectivity** It was noted above that while the areas affected by localised corrosion were evenly distributed in the CO₂-containing environment, severe localised corrosion developed on only a small part of the surface in the CO₂-free environment, large areas remaining relatively uncorroded (see Fig. 4). These observations were corroborated by 3D characterisation after corrosion product removal. Thus, a relatively shallow and isolated sites of localised corrosion formed in the presence of CO₂ is seen in Fig. 8. In contrast, two distinctive groups of dissolution regions were observed after corrosion in the
absence of CO\(_2\) (see Fig. 9), namely (a) very deep connected sites of localised dissolution, and (b) quite shallow isolated dissolution areas. The deep ones, shown in Figs. 10 (a) and (c) and the 3D cross-sectional views are shown in Figs. 11 (a) and (b), correspond to the severely affected areas in Figs. 5 (c) and (d). The images show that individual localised sites of metal loss are connected, forming a network below the surface.

The results regarding the morphology of localised corrosion indicate that, in the CO\(_2\)-containing environment, the corrosion cells on the surface are relatively small (in the range 2-20 \(\mu\)m, considering the distribution of the microstructural constituents) and have a single anodic site situated in the \(\alpha\)-Mg matrix. In contrast, the corrosion cells formed in the absence of CO\(_2\) are much larger and exhibit multiple, closely spaced anodic sites that tend to interconnect. The occurrence of larger corrosion cells in the CO\(_2\)-free environment is attributed partly to the enhanced wetting of the surface and the resulting drop coalescence mentioned above, and partly to the NaOH (aq) catholyte formed in the absence of CO\(_2\) providing greater surface conductivity compared to the Na\(_2\)CO\(_3\) (aq) /NaHCO\(_3\) (aq) solution formed in the CO\(_2\)-containing environment. The large corrosion cells include many cathodic sites (\(\text{Al}_x(\text{Mn, Fe})_y\)- and \(\beta\)-phase particles). Therefore and because of the absence of CO\(_2\), most of the alloy surface within the cell experiences high pH, stabilising the MgO/Mg(OH)\(_2\) semi-protective film. In this scenario, the sites of localised dissolution in the \(\alpha\)-Mg matrix are anticipated to become strongly polarised anodically, in agreement with the rapid growth of locally affected areas observed.

In order to explain the formation of multiple and interconnected locally affected areas, it is suggested that each corrosion cell initially contains only one localised damage. With time, the corrosion cell increases in size as described above, encompassing a growing number of cathodic sites. This will cause the first region of dissolution to become increasingly polarised in the anodic direction, causing it to grow faster. However, with time the area growth will saturate or slow down because of solid precipitates (brucite + meixnerite) blocking the mouth of dissolution sites. This will cause the anodic polarisation of the \(\alpha\)-Mg matrix surface in the vicinity of the initial localised damage to increase, resulting in the formation of a new locally corroded area. The relatively low pH and the chloride ions associated with the initial dissolution site are expected to make the semi-protective film in the vicinity of the original locally affected area more sensitive to attack, contributing to clustering of dissolution sites.

In the CO\(_2\)-containing environment, several of the mechanism proposed herein to cause clustering of the localised corrosion sites are absent. Thus, the NaCl (aq) droplets on the surface do not coalesce so that the corrosion cells do not grow in size and neutralisation by CO\(_2\) is expected to decrease surface conductivity, further restricting the size of the corrosion cells and corrosion current. Furthermore, the decreased pH on the surface is anticipated to destabilise the MgO/Mg(OH)\(_2\) surface film, resulting in an easier initiation of localised corrosion contributing to the occurrence of many small corrosion cells.
5. Conclusions

Using a combined 2D and 3D investigation, the localised corrosion susceptibility of semi-solid cast alloys AM50 and AZ91 was studied in the presence of humid air (95% RH), CO$_2$ (carefully controlled to be either 0 or 400 ppm) and 14-70 µg/cm$^2$ salt (NaCl). As follows, the conclusions that can be drawn from the present investigation is provided:

- The simple 3D characterisation conducted using the focus ion beam milling (FIB) technique was proved to be useful in evaluating the corrosion microstructure of the alloys studied. The 3D investigation (which was performed the three steps: using slice/image, 3D reconstruction, and post-preparation analysis) showed the formation of deep and meandering sites of localised dissolution within the bulk.

- CO$_2$ clearly slowed down the atmospheric corrosion process and markedly influenced the corrosion morphology of the alloys tested. Corrosion in the CO$_2$-containing environment led to a surface that was covered by corrosion products with the structure and composition of magnesium hydroxy carbonates. In the CO$_2$-free environment, a fraction of the alloys’ surface was severely corroded while large regions were seemingly unaffected by corrosion (which was explained by the formation of extended corrosion cells). The corrosion products were mainly brucite (the crystalline form of Mg(OH)$_2$) and the LDH compound meixnerite (Mg$_6$Al$_2$(OH)$_{18}$·4.5H$_2$O).

- In CO$_2$-containing environment, the areas of localised corrosion were evenly distributed over the alloys surface and comparatively shallow. These affected the areas covered by NaCl (aq) droplets formed when the exposure started. In the CO$_2$-free environment, sites of localised corrosion were deeper and clearly tended to cluster. The clustered areas interconnected, forming networks below the surface of the two alloys AM50 and AZ91.

- In the CO$_2$-free environment, the Al$_x$(Mn, Fe)$_y$ second phase particles were cathodically more active than the Mg/Al β second phase particles. The corresponding SEM-EDXS observation is described by the high pH electrolyte causing dissolution of alumina and leaving a manganese oxide/hydroxide (Mn$_3$O$_7$/Mn(OH)$_2$) film on the Al$_x$(Mn, Fe)$_y$ second phase particles. The mentioned Mn-containing film is electronically more conducting than the alumina-dominated film that is present at lower pH.

- In the CO$_2$-free environment, the NaCl droplets, sprayed on the coupons’ surfaces prior to exposures, coalesce, due to enhanced wetting of the surface. This leads to the formation of comparatively large corrosion cells. The clustering of dissolution sites in the CO$_2$-free environment is attributed to the growth of the corrosion cells, encompassing an increasing number of cathodic sites. It was suggested that as a result of the increased anodic polarisation in the neighboring areas of the original dissolution site, new sites of localised corrosion tend to initiate.

- The formation of a protective layer of magnesium hydroxy carbonate and the greater stability of the alumina component in the surface film formed on α-Mg (caused by the lowering of pH) contributes to the corrosion inhibitive effect of atmospheric CO$_2$ in air.
- **Acknowledgement**

The authors of this research express their sincere thanks to the Swedish Foundation for Strategic Research (SSF) for financially supporting the project. Dr. Rikard Ylmén is thanked for his help in the Fourier Transform Infrared Spectroscopy experiments. ME thanks the Swedish Research Council and the Royal Swedish Academy of Engineering Sciences for the financial support.
References


Figure captions

**Fig. 1.** Illustration of FIB milling showing the “slice and image”, “3D reconstruction” and “post-preparation analysis” set-ups.

**Fig. 2.** (a) Metal loss of AZ91 and AM50 in the presence of different amounts of NaCl after 672 h of exposure (RH = 95%, T = 22°C). In the cases where mass gain was < 0.05 mg/cm², the metal loss was calculated from mass gain, based on the corrosion product composition determined by XRD (Fig. 2b), and (b) XRD patterns for AZ91 and RC AM50 samples exposed for 672 h in the presence of 70 µg/cm² NaCl, in the absence and presence of 400 ppm CO₂.

**Fig. 3.** Microstructure of semi-solid cast (a) AM50, and (b) AZ91 after polishing and etching.

**Fig. 4.** Corrosion morphology after 672 h (70 µg/cm² NaCl, 95% RH, 22°C): (a) AM50-400 ppm CO₂, (b) AZ91-400 ppm CO₂, (c) AM50-no CO₂, and (d) AZ91-no CO₂.

**Fig. 5.** EDX map and point analysis of an area close to a salt particle (alloy AM50 exposed in the presence of 400 ppm CO₂ and 70 µg/cm² NaCl for 672 h at 22°C and 95% RH).

**Fig. 6.** EDX map and point analysis for the RC AM50 alloy exposed in the absence of CO₂ and in the presence of 70 µg/cm² NaCl for 672 h at 22°C and 95% RH. Note the difference in redistribution of Na and Cl on the alloy surface.

**Fig. 7.** EDX map and point analysis of alloy RC AM50 exposed in the absence of CO₂ (70 µg/cm² NaCl, 672 h, 22°C, 95% RH). Note the accumulation of Na around the Mn-containing intermetallic particle on the alloy surface.

**Fig. 8.** 3D and 2D depth profiling (using interference microscopy) of alloys AM50 (a) and AZ91 (b), exposed in the presence of 400 ppm CO₂ after corrosion product removal.

**Fig. 9.** 3D and 2D depth profiling (using interference microscopy) of alloy AM50 (a) and (b) and alloy AZ91 (c) and (d) exposed in the absence of CO₂, after corrosion product removal.

**Fig. 10.** 3D imaging (using FIB and SEM; see Fig. 1) of localised corrosion formed on semi-solid cast alloy AM50 and AZ91 exposed at 95% RH and 22°C in the presence of 70 µg/cm² NaCl for 672 h, (a) AM50–absence of CO₂ (b) AZ91–absence of CO₂, (c) AM50–presence of CO₂, and (d) AZ91–presence of CO₂.

**Fig. 11.** BSE cross-sectional micrographs of alloy AZ91, exposed in the presence of 70 µg/cm² NaCl (a) in the presence, and (b) in the absence of CO₂, after removal of the corrosion products.
Figures

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Fig. 11. BSE cross-sectional micrographs of alloy AZ91, exposed in the presence of 70 µg/cm² NaCl (a) in the presence, and (b) in the absence of CO₂, after removal of the corrosion products.
### Tables

**Table I. Alloy composition (wt%). Balanced with Mg.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Ca</th>
<th>Pb</th>
<th>Sn</th>
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<tbody>
<tr>
<td>AM50</td>
<td>5.0</td>
<td>0.01</td>
<td>0.25</td>
<td>0.01</td>
<td>0.0016</td>
<td>0.0010</td>
<td>0.0007</td>
<td>n.a.</td>
<td>n.a</td>
<td>n.a</td>
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<tr>
<td>AZ91</td>
<td>9.4</td>
<td>0.75</td>
<td>0.18</td>
<td>0.07</td>
<td>0.0074</td>
<td>0.0042</td>
<td>0.0007</td>
<td>0.0005</td>
<td>0.0011</td>
<td>0.0008</td>
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</table>

**Table II. Mass gain of semi-solid cast alloys AZ91 and exposed for 672 h at 22.00°C and 95.0% RH.**

<table>
<thead>
<tr>
<th>CO₂</th>
<th>NaCl(µg/cm²)</th>
<th>Average dry mass gain (mg/cm²)</th>
<th>AZ91</th>
<th>AM50*</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 ppm</td>
<td>0</td>
<td>0.020</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>400 ppm</td>
<td>14</td>
<td>0.294</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>400 ppm</td>
<td>70</td>
<td>0.826</td>
<td>1.59</td>
<td></td>
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<tr>
<td>0</td>
<td>0</td>
<td>0.007</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>14</td>
<td>0.310</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>70</td>
<td>1.262</td>
<td>2.53</td>
<td></td>
</tr>
</tbody>
</table>

*The gravimetric results for alloy RC AM50 have been published previously [16].*

**Table III. Area fraction of β-phase and Al content of α-Mg (center of grain).**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al content (wt.%)</th>
<th>Avg. β area fraction %</th>
<th>Standard error %</th>
<th>Avg. Al in α-Mg (wt.%)</th>
<th>Standard error (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC-AZ91</td>
<td>9.40</td>
<td>7.2*</td>
<td>0.5</td>
<td>3.09</td>
<td>0.14</td>
</tr>
<tr>
<td>RC-AM50</td>
<td>5.00</td>
<td>2.1*</td>
<td>0.3</td>
<td>1.92</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*The measurements were performed on 10 random regions on each material, each region having a surface area of 0.026 mm². The segregation band was not included in the measurements.*