Corrosion of Mg alloy in the presence of ammonium ion. Evidence of hydride sub-products

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A B S T R A C T
Corrosion of AZ31 Mg alloy was systematically investigated by different experimental approaches in the presence and in the absence of NH4+. Remarkable reactivity of Mg/NH4+ system was manifested by copious evolution of hydrogen over a dark corrosion film, associated to active deprotonation of complex Mg hydrides, more likely bridged \{Mg{(\text{NH}_4)\text{H}}}_{2}\text{Mg}^{(\text{H})}_{\text{n}}\} complexes covered by a skin of MgO. Metastability of hydride phases is favored in the presence of species that alter the equilibrium dissociation of water, such as NH4+ and SO4^{2-}. Chemical recombination of hydrogen atoms of oxidic Mg hydrides is proposed as the kinetically determinant process.

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1. Introduction
The corrosion mechanism of magnesium and alloys is still subject of much debate [1,2], regarding in particular the negative difference effect (NDE), which is manifested by the increase of the rate of hydrogen evolution reaction (HER) with increasing applied potential. In turn, Mg dissolution rate calculated from the Faraday law is smaller than that experimentally determined from mass loss (or hydrogen evolved). Several models have been proposed for explaining NDE. The most popular monovalent magnesium ion model [3,4], as well as other theories such as particle undermining model [5,6], magnesium hydride model [7], and chemical equilibrium model [8], have been critically reviewed recently [1]. Although participation of unstable Mg⁺ during anodic dissolution cannot be ruled out [2], its existence in solution has never been confirmed, while dissolution stoichiometry \(n\approx2\) has been experimentally found [9,10]. Particle undermining model does not explain NDE for pure magnesium. Thermodynamic calculations have indicated that formation of MgH2 is possible in the whole pH range [4,7]. Evidence of MgH2 sub-products has been provided for cathodically polarized Mg [11,12]. The chemical equilibrium model considers the alteration of equilibrium between water and its ions as Mg\(^{2+}\) reacts with OH\(^-\) [8]. However, thermodynamic calculations of Mg\(^{2+}\) speciation have suggested that pH changes associated with cation hydrolysis have little effect on HER in the anodic region of Mg dissolution [1]. Experiments with unalloyed Mg in alkaline HCO\(_3^-\)/CO\(_3^{2-}\) buffer solutions have shown no effect of pH on the corrosion rate [11]. Cathodic activation of Mg surface with the anodic dissolution for explaining NDE has been proposed also [1,13]. It has been suggested that such catalytic activation may result from noble metal impurities embedded in the outer layer of the two stratum MgO/Mg(OH)\(_2\) film [14]. However, this consideration has been recently disputed by Song and Uncoc [15], based on the corrosion film composition and microstructure formed on pure Mg at different applied anodic potentials in saturated Mg(OH)\(_2\) solutions (pH 10.5) [15]. The corrosion film was composed of a mixture of MgO and Mg(OH)\(_2\) in each stratum with hydrogen distributed throughout the film. The contribution of MgO to the inner stratum increased with anodic dissolution.

Most studies of NDE have been carried out using SO\(_4^{2-}\) and Cl⁻ based solutions [1.6–10,12–14,16–19]. Studies of Mg corrosion in the presence of HCO\(_3^-\) have highlighted that species promoted in solution play a role by accelerating or slowing down the corrosion rate [11,20–22]. Battochi et al. [23] have found for a Mg electrode smaller corrosion rates in NaCl than in dilute Harrison solution (DHS), which is constituted by a mixture of (NH\(_4\))\(_2\)SO\(_4\) and NaCl. DHS spray at ambient temperature corresponds closely to natural weathering [24]. Similar results have been obtained recently in our group [25], where limited self-inhibition by precipitation of Mg(OH)\(_2\) was related to dissociation of NH\(_4^+\) into NH\(_3\) and H\(^+\) as local pH increases with Mg dissolution. It is to be noticed that NH\(_4^+\) is an important component of the particulate matter in the atmosphere, mainly present as (NH\(_4\))\(_2\)SO\(_4\) and NH\(_4\)HSO\(_4\) [26].

\(^{+}\)To the memory of our colleague, Dr. Anna da Forno, who recently passed away.

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considering the growing interest in Mg alloys as structural materials, understanding Mg corrosion in the presence of NH₄⁺ is relevant for practical applications. A very recent study on different Mg alloys under prolonged exposure to urban and saline atmospheric conditions has shown that chemical composition and microstructure importantly influence the corrosion rate, the latter being much higher for specimens mounted facing the sky [27].

This paper reports a systematic investigation of AZ31 Mg alloy corrosion in the presence of NH₄⁺. The solutions used were (NH₄)₂SO₄ and NH₄Cl, in addition to Na₂SO₄, NaCl, and NaClO₃ for reference purposes. A few experiments were conducted using mixed solutions of the above mentioned salts, including DHS, and AM1 Mg alloy as a substrate. Qualitative observations of corrosion during exposure in pure salt solutions were collected as a start. Corrosion products formed in NH₄⁺ based solutions were analyzed by XRD and TGA. The corrosion mechanism was quantified by measurements as a function of time of free corrosion potential, solution pH, Mg²⁺ concentration, and evolved hydrogen. The electrochemical behavior under AC perturbation and DC polarization was investigated also. The study is complemented by corrosion morphology analysis.

2. Experimental part

AZ31 Mg alloy with nominal composition (wt.%) 2.33Al–0.88Zn–0.24Mn–bal.Mg, was used as a substrate. Metallic specimens (30 × 50 mm) were wet ground up to 1200 grit using SiC paper, then cleaned with ethanol in an ultrasonic bath, and finally covered with an adhesive tape to leave a given active surface area.

Reagents were of high purity grade. Solutions were prepared using water of quality Milli-Q. Test solutions were 0.5 mol/L (NH₄)₂SO₄, 1 mol/L NH₄Cl, 0.5 mol/L Na₂SO₄, 1 mol/L NaCl, and 1 mol/L NaClO₃, and the relative ten-times diluted solutions (0.05 mol/L and 0.1 mol/L), in the following referred to as concentrated and diluted pure salt solutions, respectively. A few experiments were carried out using mixed solutions of (NH₄)₂SO₄ (or NH₄Cl) and Na₂SO₄, NaCl, or NaClO₃, in different proportions (1:1, 1:2, 1:9), but at the total concentrations above indicated for pure salt solutions. The composition of dilute Harrison solution (DHS) was 0.025 mol/L (NH₄)₂SO₄ + 0.01 mol/L NaCl. The pH of the as-prepared solutions was close to 6 ± 0.50, as measured with a combined glass electrode connected to an AMEL pH-meter. All experiments were carried out at room temperature.

Qualitative observations of AZ31 Mg alloy corrosion in the solutions of the pure salts were collected using specimens with active surface area of 6 cm² that were immersed in 50 mL of a given test solution during 20 h. Corroded surfaces were examined at the optical microscope Nicon Eclipse MA200 coupled with a digital photocamera (JVC-C1380). Experiments were repeated for 0.5 mol/L (NH₄)₂SO₄ and 1 mol/L NH₄Cl, using freshly prepared surfaces and 2 h of exposure time. Thereafter, the specimens were rinsed with water, dried with hot air, and left in a desiccator overnight. The corrosion products were removed with the help of a plastic scraper and machine using an agate mortar. The composition and thermal behavior was investigated by X-ray diffraction (XRD) and thermogravimetric (TGA) analyses. Powder XRD diffractograms were collected using a Philips PW 1830 diffractometer with CuKα radiation. The thermograms were collected with Pyris TGA instrument at a heating rate of 20 °C/min under constant flow of N₂ (20 mL/min).

Quantitative experiments consisted in measurements as a function of time of free corrosion potential Ecorr, solution pH, Mg²⁺ concentration [Mg²⁺], and volume of evolved hydrogen (VH₂). For Ecorr monitoring, a steel wire was arc-welded to the upper part of the metallic specimen for external connection. The resulting electrode was properly isolated to leave 4 cm² of active surface area and, thereafter, immersed vertically in a glass beaker containing 200 mL of the pertinent test solution and a Haber-Luggin capillary reference probe with Ag/AgCl/KCl(sat.) reference electrode (+0.200V vs SHE). Working and reference electrodes were connected to Solartron 1286 potentiostat. For pH monitoring, a combined glass electrode was placed in the test solution and connected to the AMEL pH-meter. Measurements were carried out under magnetic stirring during 130 min. Selected specimens were examined at LEO 1430 scanning electron microscope (SEM) equipped with an EDX spectrometer at a chamber pressure of 8 × 10⁻⁶ Torr and 20 keV accelerating voltage.

The same experimental setup was used for the analysis of [Mg²⁺], using freshly prepared surfaces and solutions, but only the glass electrode was left inside the test solution for pH check. During the experiment time (80 min), a volume of 10 mL was collected in 100 mL volumetric flasks every 10 min. The total test volume (200 mL) was replenished by adding 10 mL of fresh solution each time. [Mg²⁺] was determined spectrophotometrically, according to a reported procedure [28]. Briefly, to each volumetric flask containing 10 mL of sample solution the following reagents were added in the order: 1 mL of 0.5 mol/L H₂SO₄, 10 mL of 1% starch, 20 mL of saturated CaSO₄ solution, 10 mL of Titan Yellow (0.05%), 10 mL of 2 mol/L NaOH, and finally water up to 100 mL. After mixing, 25 mL were placed in a conical flask (50 mL) that was tightly closed with a plastic cap and vigorously shaken for 5 min. Transmittance measurements were carried out at 525 nm with a Beckman Coulter DU800 spectrophotometer using glass cuvettes. Solutions with known [Mg²⁺] (between 0.0005 and 0.1 g/L) were similarly prepared using MgSO₄ stock solution (5 g/L) for construction of the calibration curve (Supporting information, Fig. S1).

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The volume of evolved hydrogen VH₂ was determined following a reported approach [29]. The end of a burette with capacity of 50 mL was fixed to the mouth of a funnel containing a glass hook, using a cold working resin. Mg specimen with a drilled hole at the top and of known weight was hooked vertically inside the funnel. The system was positioned inside a beaker containing 800 mL of test solution such as to fill the funnel of capacity of 200 mL and to cover the magnet for stirring. With the help of depression applied through a rubber tube fixed at the top of the burette, this was filled to the 0 mL mark by lifting the liquid up. VH₂ was measured by reading the test solution level in the burette every 10 min during 130 min. At the end of the test, metallic specimens were rinsed with water and immersed in 200 g/L of chromic acid solution saturated with AgNO₃ until no bubbles were produced, in order to remove the corrosion products. Then, specimens were rinsed with abundant amounts of water, dried in a stream of hot air, and placed in a desiccator until constant weight (±0.0001 g).

Corrosion behavior under AC perturbation and DC polarization was investigated using stagnant conditions and an O-ring cell with working electrode surface of 1 cm² (positioned upward). Pt spiral as counter electrode and Haber-Luggin capillary reference probe with a saturated calomel electrode (SCE, +0.244 V vs SHE). The electrodes were connected to the Solartron 1286 potentiostat, which was coupled to the Solartron 1250 frequency generator for impedance measurements. Impedance spectra were recorded at the open circuit potential (Eoc) after 10 min of conditioning in the test solution. The frequency scan was performed from 0.001 Hz to 65000 Hz with an AC perturbation amplitude of ±15 mV. Potentiodynamic polarization curves were recorded at a scan rate of 0.2 mV/s in anodic direction from −1.87 V. Similarly, anodic and cathodic polarization
curves were recorded from $E_{oc}$ (after 10 min of conditioning in the test solution) using separate specimens.

All potentials in the text are referred to SCE. Graphical and quantitative analyses of the experimental data were carried out using OriginPro 9.2 (OriginLab, Northampton, MA).

3. Results and discussion

3.1. Qualitative observations of AZ31 Mg alloy corrosion

The behavior of AZ31 Mg alloy surfaces during exposure in (NH$_4$)$_2$SO$_4$, NH$_4$Cl, Na$_2$SO$_4$, NaCl, and NaClO$_3$ solutions showed similar trends for a given electrolyte, regardless the salt concentration. Fig. 1 shows the images after 20 min exposure of Mg surfaces in different concentrated solutions. Dark regions, where H$_2$ copiously evolved, were developed with time on surfaces exposed in NaCl (Supporting video SV1 and Fig. 1), as observed by others [13,14]. Corrosion in NaClO$_3$ was almost negligible at naked eyes. Nonetheless, as for NaCl, filiform localized attack was revealed by surfaces examination at the optical microscope. This suggest Cl$^-$ generation as a result of the oxidizing action of ClO$_3^-$, while Mg$^{2+}$ combines with OH$^-$ to form a partially protective Mg(OH)$_2$ layer ([1]–[3]):

\[ 3\text{Mg} \rightarrow 3\text{Mg}^{2+} + 6e^- \] (1)
\[ \text{ClO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Cl}^- + 6\text{OH}^- \] (2)
\[ 3\text{Mg} + \text{ClO}_3^- + 3\text{H}_2\text{O} \rightarrow 3\text{Mg}^{2+} + \text{Cl}^- + 6\text{OH}^- \] (3)

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In Na$_2$SO$_4$ and NH$_4^+$ based solutions, uniform dissolution was manifested by evolution of H$_2$ over all the exposed surface, which turned dark with time. However, these processes were distinctly more marked in the presence of NH$_4^+$, i.e., H$_2$ evolved copiously and the surface turned dark-gray almost instantaneously (SV1, Fig. 1). Although the dimensions of gas bubbles were much smaller in NH$_4$Cl than in (NH$_4$)$_2$SO$_4$ (SV2), the characteristic odor of NH$_3$ was perceived after about 2 h, indicating NH$_4^+$ dissociation and NH$_3$ transfer across the liquid/air interface promoted by pH increase and H$_2$ evolution with Mg dissolution ([4]–[6]):

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \] (4)
\[ \text{NH}_3 \leftrightarrow \text{NH}_3^+ \] (5)
\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{H}_2\uparrow + 2\text{OH}^- \] (6)

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The overall reaction can be written as follows:

\[ \text{Mg} + \text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{OH}^- + \text{NH}_3^+ + \text{H}_2\uparrow \] (7)

In addition, by the end of experiments (20 h), H$_2$ production over the dark corrosion film was still remarkable and the fall out of corrosion products was negligible. Corrosion morphology examination at the optical microscope revealed a thick layer and some white deposits, these being more evident for the surfaces exposed in NH$_4$Cl. The surface layer was thinner and presented scarce micro-pits filled with white precipitates in the case of specimens exposed in Na$_2$SO$_4$.

The corrosion films formed in the presence of NH$_4^+$ were easily removed by specimens’ sonication in water, which turned turbid due to the thrown off of dark particles from the surface. Cross-section SEM analysis indicates remarkable decrease of substrate thickness (≥200 μm) (Fig. 2), in addition to exfoliation corrosion in the case of NH$_4$Cl (Fig. 2b) promoted by Cl$^-$ localized attack. According to these qualitative results, AZ31 Mg alloy disintegrates in NH$_4^+$ based solutions through the formation of a very reactive corrosion film. This is likely constituted by agglomerates of small particles that are held together by weak interactions.

Confirmation of the remarkable Mg reactivity in the presence of NH$_4^+$ was obtained from experiments with M1A Mg alloy (nominal composition: Mn 1.2 wt.%, bal. Mg) ([SV 3]). Nevertheless, surface darkening and copious evolution of H$_2$ were produced after about two hours of exposure rather than instantaneously as for AZ31 Mg alloy. Similarly, NH$_3$ transfer was produced at later stages. This indicates that the onset of the related processes depends on the alloy susceptibility to localized corrosion and, thus on the extent of NH$_4^+$ dissociation promoted with Mg dissolution ([4]–[7]). Acid corrosion limiting precipitation of partially protective Mg(OH)$_2$ seems to dominate in NH$_4^+$ based solutions due to the dynamic alteration—balance of the dissociation equilibrium of H$_2$O as OH$^-$ are in part consumed by NH$_4^+$.

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3.2. Characterization of corrosion products formed in NH$_4^+$ based solutions

Dried powders of the corrosion products formed on AZ31 Mg alloy after two hours of exposure in 0.5 mol/l. (NH$_4$)$_2$SO$_4$ and 1 mol/l. NH$_4$Cl presented dark-gray color, being more evident for (NH$_4$)$_2$SO$_4$. Fig. 3a and b shows the corresponding powder X-ray diffractograms and the phases identified. Corrosion products are mainly composed by Mg hydroxysalts, MgO, stable (MgH$_2$) and metastable (Mg(AlH$_4$)$_2$, AlH$_3$) hydride phases, and equilibrium β(Mg$_2$Al) phase. No detection of Zn-containing compounds [30] suggests fast dissolution of this metal by reaction with NH$_3$ with possible formation of Zn$^{2+}$ complexes. Among the hydride compounds, magnesium tetrahydroaluminolate Mg(AlH$_4$)$_2$ is a complex metastable hydride known as magnesium alalanate [31,32]. Concerning the nature of the test solution, diffraction peaks of Mg(OH)$_2$, Mg(OH)Cl dominate the XRD pattern of the corrosion products formed in NH$_4$Cl (Fig. 3b), in correlation with the less marked dark-gray appearance. The more favored precipitation of hydroxy compounds in the presence of Cl$^-$ highlights the importance of neutralization reactions ([4]). In the case of (NH$_4$)$_2$SO$_4$ (Fig. 3a), the broad feature between 15 and 25$^\circ$ could be assigned to amorphous magnesium aluminum sulfate hydrate [33]. Nevertheless, contribution of complex Mg hydrides to this feature is likely also. According to the literature, the intensity and position of Mg(AlH$_4$)$_2$ diffractions lines are sensitive to the preparation method and to the nature of the solvent adduct [34].

Thermogravimetric analysis (TGA) of the powders is reported in Fig. 4. The shape of TG curves, as well as the broad and overlapping features of the corresponding derivative curves (DTG), indicate multi-stage decomposition with no formation of stable intermediates in the two main temperature ranges of weight change. Quantitative analysis of multiphase/multicomponent samples is difficult due to different structural environments, as well as possible reactions between solid phases and gaseous decomposition products. Based on XRD results (Fig. 4a and b), the main species that can be lost as powder sample undergoes decomposition include water, hydrogen and hydroxyl. Weight loss up to 100$^\circ$ corresponds to the removal of weakly absorbed water. Dehydrogening of Mg(AlH$_4$)$_2$ and MgH$_2$ typically occurs between 100 and 120$^\circ$ C and 200–300$^\circ$ C, respectively [32,35–37]. The temperature range 120–200$^\circ$ C is typical of elimination of ligand water molecules, whereas decomposition processes at temperatures above 300$^\circ$ C correspond to dehydroxylation and loss of water of magnesium hydroxysalts to form mixed oxides [38–40].

By comparing DTG curves (Fig. 4a and b), dehydrogening of Mg(AlH$_4$)$_2$ is better discerned for (NH$_4$)$_2$SO$_4$ (peak at ≈100$^\circ$ C). Between 50–250$^\circ$ C (Fig. 4a), the experimental weight loss of ≈22%...
is much higher than the theoretical loss of water molecules of MgAl2(SO4)3·22H2O (≥46%) and is smaller than that corresponding to 5Mg(OH)2·MgSO4·3H2O (≥59%). This supports considering the broad XRD feature between 15 and 25° of 2θ (Fig. 3a) related to amorphous complex hydride structures “embedded” in a solid solution of magnesium hydroxy sulfate. The broad features at higher temperatures (T > 400 °C) are associated to dehydroxylation leading to formation of mixed metal oxides (see below). Structural decomposition of sulfate is not detected as this occurs at much higher temperatures (T ≥ 750 °C). In the case of NH4Cl (Fig. 4b), the loss of OH and Cl as water vapor and gaseous HCl are distinguished by the overlapped peaks between 250 and 500 °C. XRD analysis of the powders after the thermal treatment revealed mixed magnesium aluminum oxides, as shown for (NH4)2SO4 in Fig. 3c. The no decomposition of sulfate salts of Mg and Al is confirmed by the broad feature between 15 and 30°. The broadening of the peak at 43° after the thermal treatment correlates with a decrease of the particle size.

Based on the results presented so far, nucleation and growth of MgH2 and of metastable hydrides, such as AlH3 and complex Mg(AlH4)2, indicate hydrogen diffusion into Mg matrix and into fine eutectics dominated by non-equilibrium γ(Mg17Al12) [41,42]. Since MgH2 layer alone should prevent hydrogen from inward penetration due to the negligible solid solubility of hydrogen in magnesium [43], fast dissolution of alloy matrix exposing γ(Mg17Al12) with high cathodic activity is more likely. Hydrogen adsorption on γ phase leading to the formation of hydrides could proceed by a two-step decomposition followed by a combination of MgH2 with AlH3 to form Mg(AlH4)2 [41].

\[
\begin{align*}
\gamma(Mg_{17}Al_{12}) + 9H_2 &\rightarrow 9MgH_2 + 4\beta(Mg_2Al_3) \quad (8) \\
2\beta(Mg_2Al_3) + 13H_2 &\rightarrow 4MgH_2 + 6AlH_3 \quad (9) \\
MgH_2 + 2AlH_3 &\rightarrow Mg(AlH_4)2 \quad (10)
\end{align*}
\]

\[
\begin{align*}
\gamma(Mg_{17}Al_{12}) + 22H_2 &\rightarrow Mg(AlH_4)2 + 12MgH_2 \\
&+ 4AlH_3 + 2\beta(Mg_2Al_3) \quad (11)
\end{align*}
\]

The processes above are more favored in (NH4)2SO4 than in NH4Cl. In this respect, SO4\(^2\)\(^-\) exists in aqueous solutions mainly as HSO4\(^-\), differently from Cl\(^-\) which is solvated by the solvent without influencing water dissociation [44]. Smaller hydriding resistance in (NH4)2SO4 is supported also by the larger dimensions of gas bubbles produced in this case (SV2). Although hydrogen mobility in MgH2 is limited by its denser structure as compared to complex hydrides with more open structure for hydrogen transportation, hydrogen leaves less readily complex networks such as
The powder XRD patterns of corrosion products formed on AZ31 Mg surface after 2 h of exposure in 0.5 mol/L (NH₄)₂ SO₄ and 1 mol/L NH₄ Cl, respectively, and of the corrosion product in (a) after thermal treatment (Fig. 4a). Symbols indicate the corresponding phases reported in the bottom label.

\(\{\text{Mg(AlH₄)}_2\}_{n}\) with more ordered hydrogen ligands [42,45]. High hydrogen binding energy due to chemisorption has been theoretically predicted for magnesium alanate [46]. In addition, the stability of alanates at ambient conditions is improved by low energy polymeric structures constituted by networks of negatively charged AlH₆ octahedra due to charge transfer from the surrounding Mg²⁺ [45,47]. Concerning MgO, it is well known that oxide crystals with a series of differently coordinated Mg²⁺ and O²⁻ present surface defects that are chemically reactive [48,49]. In particular, dissociative adsorption of hydrogen molecules on the pairs of adjacent low coordinated O²⁻ and Mg²⁺ takes place via an heterolytic mechanism, resulting in the formation of interconnected Mg²⁺H−O²⁻−H⁺ surface groups that stabilize bridged surface hydrides [50,51]. From the present experimental findings and the above considerations, formation of composite amorphous hydrides complexes \(\{\text{Mg}^{2+}(\text{AlH}_4^-)_2\text{Mg}^{2+}H^-\}_2\) covered by a skin of MgO during exposure of AZ31 Mg alloy in NH₄⁺ based solutions is proposed. Electrostatic interactions that held together the oxidic complex hydride network reasonably explain the disaggregation of
the corrosion film upon sonication in water. Complex Mg hydrides are typically dark colored [45].

It is to be noticed that hydride phases can hydrolyze to form hydroxides and hydrogen by the following possible reactions:

\[ \text{MgH}_2 + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow \]  
(12)

\[ \text{Mg(AlH}_4\text{)}_2 + 8\text{OH}^- \rightarrow \text{MgAl}_2\text{(OH)}_8 + 4\text{H}_2 \uparrow \]  
(13)

\[ \text{Mg(AlH}_4\text{)}_2 + 5\text{MgH}_2 + 18\text{OH}^- \rightarrow \text{Mg}_8\text{Al}_2\text{(OH)}_{18} + 9\text{H}_2 \uparrow \]  
(14)

However, the hydriding resistance should increase with the exposure time. This was not observed in this study. Conversely, formation of catalytically active oxide-covered complex hydrides and hydrogen desorption by a recombination mechanism [50] reasonably justify the continuous production of H\(_2\) during Mg corrosion in NH\(_4^+\) based solutions. The above considerations could be extrapolated to AM1 Mg alloy due to the possible formation of metastable complex Mg\(_3\)MnH\(_2\) [45]. Similarly, in the presence of iron impurities, complex Mg\(_2\)FeH\(_6\) might be involved [52].

3.3. Quantification of the corrosion mechanism

Measurements as a function of time of corrosion potential (\(E_{corr}\)), solution pH, concentration of Mg\(^{2+}\) ([Mg\(^{2+}\)]) and volume of evolved hydrogen (\(V_{H_2}\)), were carried out using a smaller ratio between the surface area and volume of test solution, as well as continuous stirring. Nonetheless, the qualitative behavior described above for a given test solution was reproduced. \(E_{corr}\) and pH were simultaneously determined also for mixed solutions containing (NH\(_4\))\(_2\)SO\(_4\) (or NH\(_4\)Cl) and NaCl, Na\(_2\)SO\(_4\) or NaClO\(_3\). Separate experiments were carried out for the quantification of [Mg\(^{2+}\)] and \(V_{H_2}\), using concentrated solutions of pure salts.

3.3.1. Corrosion potential and solution pH

Figs. 5 and 6 show the variation of (a) solution pH and (b) \(E_{corr}\) as a function of time for AZ31 Mg alloy in concentrated and diluted solutions, respectively, of (NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)Cl, Na\(_2\)SO\(_4\), NaCl, and NaClO\(_3\). Representative images of the corresponding corroded surfaces after the exposure tests are also included (Figs. 5c and 6c). The pH-t plots (Figs. 5a and 6a) change little with salt concentration. In the presence of NH\(_4^+\), the pH increases rapidly but stabilizes at values below 8.4, which correspond to the equilibrium pH of Mg(OH)\(_2\) precipitation. Conversely, for Na\(_2\)SO\(_4\), NaCl and NaClO\(_3\), the pH increases less markedly but stabilizes at higher values (between 9.2–9.8). The corrosion morphology at the optical microscope (Figs. 5c and 6c) reproduces the qualitative observations indicated before, and was confirmed by SEM analysis (Fig. 7) of the corroded surfaces exposed in diluted solutions (Fig. 6c). That is, filiform corrosion is promoted in NaCl and NaClO\(_3\) (Fig. 7a and b), uniform dissolution with formation of a thin surface layer and small rounded pits prevails in Na\(_2\)SO\(_4\) (Fig. 7c), and uniform dissolution leading to formation of a thicker corrosion film is produced in NH\(_4^+\) based solutions (Fig. 7d and e). Needle-shaped white deposits growing from the undermining corrosion film formed in NH\(_4\)Cl (Fig. 7e and f) support the more favored precipitation of Mg hydroxy compounds.
(Fig. 3), associated to Cl⁻ localized attack that limits neutralization reactions and thus favors the hydrolysis of oxidic Mg hydrides.

The effect of salt concentration is more evident for $E_{corr}$–$t$ responses (Figs. 5b and 6b). For concentrated pure salt solutions (Fig. 5b), Mg electrode polarizes at potential values between −0.6 and −0.2 V during all the experiment time in the presence of NH₄⁺. Similar $E_{corr}$ values are recorded after about 10 min of exposure in Na₂SO₄ and NaCl but the potential decreases at later stages, more importantly for NaCl. In the case of NaClO₃, $E_{corr}$ oscillates at about −1.7 V during all the experiment time. Although with dilution of the test solution (Fig. 6b) the increase of $E_{corr}$ as a function of the salt nature is similar by the end of the experiment time, i.e., higher in the presence of NH₄⁺ and more negative for NaClO₃, an opposite trend is obtained within the first 30 min of exposure. $E_{corr}$ shifts to less negative values more importantly for Na₂SO₄ and NaCl, as well as for NaClO₃, whereas its increase is notably delayed in NH₄⁺ based solutions, more importantly for NH₄Cl. These differences confirm that Mg corrosion is influenced by reactions that alter the dissociation equilibrium of H₂O, such as NH₄⁺ and HSO₄⁻. With dilution, NH₄⁺ dissociation is less favored, whereas association of SO₄²⁻ with the H⁺ left off as OH⁻ combines with Mg²⁺ is enhanced. The effect of HSO₄⁻ is highlighted further by the closely similar $E_{corr}$–$t$ responses obtained in concentrated and diluted Na₂SO₄ solutions (Figs. 5b and 6b). Furthermore, from experiments carried out using mixed solutions, the shift of $E_{corr}$ to higher values was more important as NH₄⁺ and SO₄²⁻ concentrations were raised, while the pH stabilized between 8 and 9 in all cases (Fig. S2).

Summarizing the above results by plotting $E_{corr}$ as a function of pH (Fig. 8), in the presence of NH₄⁺, the potential tends to stabilize at values ≤ −0.4 V, and the pH at values below 8.4 (dotted line in Fig. 8). Considering the potential-pH diagram of Mg–H₂O system [4,5,7], results correlate with Mg oxidation through MgH₂ intermediate:

$$\text{Mg} \rightarrow \text{MgH}_2 \rightarrow \text{Mg}^{2+} \quad (15)$$

where both MgH₂ and Mg(OH)₂ are not stable. Thus, $E_{corr}$ more likely corresponds to a mixed potential between hydrogen evolution and electron dissolution with hydride intermediate. It is to be noticed that $E_{corr}$ changes little with pH in concentrated solutions. With dilution, the potential abruptly increases by ≥1 V at pH values between 7 and 8 (Fig. 8a and b), associated to the alteration of NH₄⁺ dissociation equilibrium (4) ($pK_a = 9.25$ at zero ionic
strength at 25 °C [53]. Mg oxidation through MgH₂ intermediate is also likely in absence of NH₄⁺ at pH < 8. However, metastability conditions are compromised if saturation with Mg(OH)₂ is favored, as manifested by the marked decrease of $E_{corr}$ in the case of NaCl and NaClO₃. The distinct behavior of Mg in Na₂SO₄ with high $E_{corr}$ values at pH > 8 indicates participation of MgO (isoelectric point at about pH 12) rather than of Mg(OH)₂ in the dissolution processes, being the hydration of the former oxide limited by the action of HSO₄⁻. Present results converge to indicate that H₂ evolution during Mg dissolution is due to the formation of oxide-covered Mg hydride intermediates, whose metastability depends on the extent of neutralization reactions at the metal/solution interface.

3.3.2. Production of Mg²⁺ and H₂

Fig. 9 shows the variation of [Mg²⁺] (mg/cm²) and of $V_{H₂}$ (mL/cm²) as a function of exposure time in the concentrated solutions of (NH₄)₂SO₄, NH₄Cl, Na₂SO₄, NaClO₃, and NaCl. The remarkable reactivity of Mg/NH₄⁺ system is confirmed by the much higher amounts of Mg²⁺ and H₂ produced during exposure in (NH₄)₂SO₄ and NH₄Cl. Good agreement was obtained between the corrosion rate determined from $V_{H₂}$ (pH) and that calculated from weight loss ($P_w$) after removing the corrosion products [29] (Fig. 3). In particular, the weight loss of magnesium was equivalent to the total hydrogen given off, and corrosion rates were higher in the presence of NH₄⁺. The same result is obtained for diluted Harrison solution (DHS) (Figs. 9b and 3) with higher concentration of NH₄⁺ in relation to that of Cl⁻.

Fig. 9 shows that [Mg²⁺] tends to plateau except NaCl, where the marked fluctuations of [Mg²⁺] in this case result from precipitation of Mg(OH)₂ in locally corroded sites. Regardless the salt nature, $V_{H₂}$ increases linearly for equivalent exposure times (80 min). Accordingly, hydrogen evolution follows a zero order reaction kinetics, whereas Mg²⁺ production a steady state kinetics. This indicates that Mg dissolution is governed by surface decomposition processes through the formation/de-hydriding of oxidic Mg hydrides intermediate species. That is, a small fraction of reactive intermediates is continually replenished with corrosion. The contribution of these processes depends on the extent of neutralization reactions at the metal/solution interface.

The effect of the salt nature is better understood from the plots of the instantaneous dissolution rate [$v_{inst} = d[Mg²⁺]/dt$], calculated from [Mg²⁺]–t data, as a function of solution pH (Fig. 10) [54], which was measured just before each sampling for spectrophotometric analysis. Linear regions where log $v_{inst}$ decreases with
pH are clearly discerned for NH$_4^+$ based solutions (pH<8) and for Na$_2$SO$_4$ (pH>8) (Fig. 10a–c). The different pH ranges indicate prevailing H$^+$ attack at oxygen atoms and OH$^-$ attack at Mg atoms on the surface, respectively, leading to formation of MgO$\cdot$H$^+$ and MgOH$^+$·OH$^-$ species. This correlates with OH$^-$ and H$^+$ consumption by NH$_4^+$ and SO$_4^{2-}$ in solution. In the case of NaCl and NaClO$_3$, log $\nu_{\text{lincl}}$ markedly fluctuates and is less pH-dependent (Fig. 10d), suggesting competition between MgO·H$^+$ and MgOH$^+$·OH$^-$ in locally corroded sites, being the dissolution kinetics controlled by both Mg$^{2+}$ and OH$^-$ diffusion. Thus, the salt nature determines the extent of hydration of MgO under free corrosion conditions.

3.4. Electrochemical behavior under AC perturbation and DC polarization

Impedance spectra of AZ31 Mg alloy recorded at the open circuit potential in concentrated solutions of (NH$_4$)$_2$SO$_4$ and NH$_4$Cl were highly disturbed. With dilution, an incomplete semicircle in the high frequency range, referred as HF arc, and noise in the mid-low frequency regions are obtained (Fig. 11a). This behavior does not depend on the low frequency limit (0.01 and 0.1 Hz), the frequency scan direction, as well as on the AC perturbation amplitude [25]. The HF arc contribution to the impedance spectra decreased as NH$_4^+$ concentration is lowered, as shown in Fig. 11b for 0.05 mol/L mixed solutions of (NH$_4$)$_2$SO$_4$ and NaCl, Na$_2$SO$_4$, or NaClO$_3$. In turn, typically reported capacitive semicircles and inductive loops are obtained, being associated to diffusion of Mg$^{2+}$ through the surface film and participation of adsorbed Mg(OH)$_2$ intermediate in the production of Mg$^{2+}$, respectively [55]. Similar result was obtained previously in DHS [25]. Note that Z' and Z" decrease as NH$_4^+$ concentration is raised (Fig. 11a and b), indicating small resistance to charge transfer of Mg/NH$_4^+$ system. The variation of $\overline{E}$ with time before recording the impedance spectra (Fig. 11c) indicates that stationary conditions in pure salt solutions are fulfilled. Accordingly, the HF arc is not an experimental artifact but is more likely related to the instability of Mg/NH$_4^+$ system, considering also previous results with anodized AZ31 Mg alloy in DHS [25].

Fig. 12 shows the potentiodynamic polarization curves recorded in the anodic direction from $-1.87$ V. For (NH$_4$)$_2$SO$_4$ and NH$_4$Cl (Fig. 12a and b), regardless the salt concentration, ohmic behavior is manifested by the linear increase of the current density with potential, even though the current density markedly fluctuates in the case of concentrated solutions (Fig. 12a). In the studied potential range, the current density decreases ten times with dilution.
of the test solution, which indicates that the resistive behavior of Mg/NH₄⁺ system is proportional to NH₄⁺ concentration, regardless the nature of the anion (Cl⁻ and SO₄²⁻). Thus, the polarization resistance $R_p$ (calculated from the $i-E$ slope) increases on average from 15 $\Omega$ cm² to 115 $\Omega$ cm² with dilution. Similarly, the exchange current density ($i_0 = RT/Fp$, where $R = 8.31$ V C/K mol, $T = 298.15$ K, and $F = 96485$ C/mol) decreases on average from 1.5 mA/cm² to 0.20 mA/cm². The no loss of ohmic resistance during polarization of Mg in NH₄⁺ based solutions can be reasonably explained by considering the active deprotonation of highly reactive hydrides, more likely $\text{Mg}^{2+}(\text{AlH}_4^-)_2\text{Mg}^{2+}(\text{H}^-)_2$. It is to be noticed that the onset of anodic processes ($i > 0$) occurs at more negative potentials in (NH₄)₂SO₄ than in NH₄Cl, being more evident with dilution, due to the catalytic effect of HSO₄⁻.

In absence of NH₄⁺ (Fig. 12a and b), the polarization behavior is characterized by a passive region followed by a sudden increase of the current density at a certain breakdown potential ($E_{br} \geq -1.5$ V), increasing in the order: NaCl < Na₂SO₄ < NaClO₃. Only for Na₂SO₄, $E_{br}$ is likely independent on salt concentration ($E_{br} \equiv -1.40$ V) and, with dilution, the current density increases linearly at $E > E_{br}$ with a slope similar to that obtained in the corresponding NH₄⁺ based solutions (Fig. 12b). The linear variation of the current density with potential is less important as the concentration of NH₄⁺ is lowered (1:9 mixed solutions) (Fig. 12c). Similarly, film breakdown is more evident and is detected at less negative potentials as Cl⁻ concentration is raised (Fig. 12c and d), whereas the curves recorded in DHS lie between those for 1:1 and 1:9 mixed solutions of (NH₄)₂SO₄ and NaCl (Fig. 12c and d).

Additional DC experiments consisted in recording anodic and cathodic polarization curves in diluted solutions using separate AZ31 Mg specimens (Fig. 13), as well as AM1 Mg substrates (in (NH₄)₂SO₄ and NH₄Cl) (Fig. 13b). It is to be noticed that, only for NaCl, NaClO₃ and Na₂SO₄ (Fig. 13a) the potential at the beginning of polarizations, i.e., after 10 min of conditioning at $E_{oc}$, differ from that recorded during the first minutes of exposure under continuous stirring of the pertinent test solution (Fig. 6b). That is, under stagnant conditions with the working electrode positioned upward, Mg electrode is polarized at more negative $E_{oc}$. This difference is supported by the effect of the salt nature on the dissolution kinetics, being determined by diffusion of Mg²⁺ and OH⁻. With anodic polarization, passive regions are identified for Na₂SO₄ and NaClO₃, whereas pitting corrosion rapidly onsets in the case of NaCl. Nonetheless, the current density tends towards limiting values as anodic potential is raised further. For NH₄⁺ based solutions (Fig. 13a), anodic and cathodic branches are quite symmetric with remarkable limiting current density regions. The alloy microstruc-
Fig. 9. Variation of (a) [Mg²⁺] and (b) \( V_{\text{H}_2} \) with time of AZ31 Mg alloy during exposure in concentrated solutions of pure salts. \( V_{\text{H}_2} - t \) plot for DHS is included in (b) (see the text).

Fig. 10. Semilogarithmic relationships between the instantaneous dissolution rate of AZ31 Mg alloy and solution pH for concentrated solutions of (a) \((\text{NH}_4)_2\text{SO}_4\), (b) \(\text{NH}_4\text{Cl}\), (c) \(\text{Na}_2\text{SO}_4\), (d) \(\text{NaCl}\) and \(\text{NaClO}_3\).
tillage appears to be unimportant as the anodic (or cathodic) potential is raised, according to the responses obtained for AM1 Mg alloy (Fig. 13b). Similarly, the nature of the second salt, regardless its proportion, as the results with mixed solutions indicate (Fig. 13c and d).

Thus, with increasing the applied potential, the anodic branches converge to similar limiting current densities. Convective diffusion induced by the copious evolution of H₂ should counteract possible concentration gradients between bulk and local (metal/solution interface) solutions. Accordingly, it is proposed that the hydrogen evolution during Mg anodic oxidation is governed by mass transfer limited processes associated to a kinetically determinant chemical process rather than to diffusion-limited transport only. That is, chemical recombination of hydrogen atoms composing the oxidic hydrides intermediates, where the electrical charge is chemically stored in the electrode:

\[
\text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{H}^- + \text{O}_2 + \text{H}_2 \uparrow
\]  

The onset of this process depends more importantly on the alteration of the dissociation equilibrium of H₂O, and in turn on
the extent of hydration of MgO, rather than on the composition of hydride phases determined by Mg alloy nature. The increase of HER with the applied anodic current [1,15] may be reasonably justified by the oxide-mediated (electro) chemical reaction sequence proposed by Atrens et al. [2], but through a catalytically active surface developed with anodic oxidation, as suggested by Frankel et al. [1], due to the formation of oxidative metastable Mg hydrides.

4. Conclusions

The investigation of AZ31 Mg alloy corrosion in different salt solutions by means of different experimental approaches converge to indicate a high reactivity of Mg in the presence of NH$_4^+$, which is manifested by formation of dark corrosion film over which hydrogen copiously evolves. Such reactivity is due to formation of Mg hydrides sub-products, more likely bridged \( \text{Mg}^{2+}(\text{AlH}_4^-)_2\text{Mg}^{2+}(\text{H}^-)_2 \) complexes covered by a skin of MgO, that are promoted by NH$_4^+$ dissociation into NH$_3$ and H$^+$ as local pH increases with Mg dissolution. The remarkable increase of $E_{corr}$ in opposite to that of the pH correlates with Mg dissolution through hydride intermediates under stationary conditions. Similar intermediate sub-products are likely in absence of NH$_4^+$. However, metastability conditions depend on the extent of neutralization reactions in relation to the kinetics of hydration of MgO and thus precipitation of partially protective Mg hydroxy compounds. This is confirmed by the different pH dependence of the instantaneous dissolution rate of Mg for a given salt nature. The no correlation between the concentration of Mg$^{2+}$ released from the surface and the volume of evolved hydrogen can be reasonably explained by surface decomposition processes through the formation of oxidative Mg hydrides that can actively deprotonate. Although the extent of these processes depends on the solution composition, as well as on the alloy nature, the chemical recombination of hydrogen atoms of oxidative metastable hydrides becomes the kinetically determinant process during the anodic oxidation of Mg. A sequence of oxidative (electro) chemical reactions through catalytically active hydride intermediates reasonably justifies the increase of hydrogen evolution along the anodic polarization.

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