Corrosion products on the WE43 Mg alloy – On the corrosion resistance in sodium chloride solution

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ABSTRACT

Mg-based alloys are promising light materials for structural applications, but most of them are prone to corrode. This work aims to evaluate the corrosion behavior of the WE43 alloy (Mg-Y-Nd-Zr) in 3.5 wt% NaCl solution. Commercial pure Mg was included as comparison. Immersion tests and electrochemical measurements showed the superior corrosion resistance of the WE43 over the pure Mg, which was ascribed to the development and integrity of a protective product layer. The nature of the corrosion products and their spalling caused by the hydrogen evolution at the cathodic sites were discussed in terms of the alloys’ microstructure and composition.

KEYWORDS: Magnesium; Rare earth elements; Weight loss; EIS; AFM.
1. INTRODUCTION

Aerospace industry has been traditionally driven the development of Mg alloys, given the strict demand of this industry for lightweight materials to operate under increasingly demanding operational conditions. Magnesium, characterized by its low density of 1.7 g/cm$^3$, is one of the most abundant element on the Earth’s crust [1]. However, pure Mg cannot be used as a structural material due to its insufficient mechanical properties for most applications (low mechanical tensile strength, hardness, and elastic modulus in compression and tension), and because of its elevated chemical reactivity and poor corrosion resistance [2]. Some alloying elements on Mg enable on one hand the hardening mechanisms to increase its mechanical properties and on the other hand the formation of protective products to enhance its resistance against corrosion [3–5]. Mg-based alloys are therefore regarded as important structural materials for the context of weight reduction for sustainable transportation vehicles.

Most conventional Mg alloys do not form a natural corrosion product layer that protects the underlying active bare surface against severe corrosion degradation [6–9]. The non-resistant corrosion products are composed mostly of Mg hydroxide or Mg carbonate, which are porous, non-adherent, and friable, therefore, inefficient to prevent the progress of severe corrosion attack [7–10]. The high corrosion activity of pure Mg in 0.6 M NaCl solution is closely related to the inherent activity of Mg and the strain-induced grain refinement with more crystalline defects [11]; the products eventually formed on its surface is mainly composed of Mg(OH)$_2$, allowing the ease ingress of corrosive species such as chlorides and the fast Mg$^{2+}$ egress [8,11]. Products from further reaction of Mg$^{2+}$ has little resistance in a solution containing chloride, and they are sensitive to the presence of impurities such as Fe, Ni, and Si commonly found in cast Mg alloys [12–14].

Studies have shown that the corrosion resistance of pure Mg and more conventional Mg alloys can be minimized by the addition of rare earth elements, “mishmetals”, which are a mixture of internal transition elements – TR, alkali and alkaline-earth metals [4,10,14,15]. Among the Mg-based alloys, the non-flammable Mg WE43 (Mg-Y-Nd-Zr) is of increasing interest [15–23]. WE43 is a high strength Mg alloy that finds use in aerospace engineering components given its low density, tolerable operating temperatures up to 300 °C, with the benefit of the good corrosion resistance, much superior to most conventional Mg alloys such as the RZ5.

The intermetallic phases formed by the addition of some rare earth elements ensure the formation of a thicker protective corrosion layer on the alloy surface, recognized to be more
compact, adherent, and stable, constituting an efficient physical barrier between the bare alloy surface and the corrosive medium. Xei et al. [24] reported that the addition of certain rare earth elements improves corrosion resistance of Mg and its alloys due to: (1) the rare earth help in reducing impurities harmful (Fe, Ni, Cu) by the formation of intermetallic compounds with the impurities and decreasing cathode activity, (2) the electrode potentials these rare earth elements are similar to Mg, and their intermetallic phases formed have low electrode potentials, so as to help lowering the micro-galvanic corrosion, (3) the grain refinement by adding rare earth elements – grain refinement can reduce the pitting initiation by lowering the mismatch stress between Mg matrix and surface layer –, (4) the addition of rare earth elements can promote the formation of denser corrosion product films on the Mg surface, so as to further improve the corrosion resistance of Mg.

Corrosion product layer formed on rare-earth containing Mg alloys is known to improve the corrosion resistance compared to pure Mg and Mg alloys such as AZ91, AM60, AM50, and AZ31 [7,8,23–29]. Zucchi et al. [31] observed that the corrosion behavior of the WE43 alloy is worse in chloride solutions than in sulfate solutions because chlorides, unlike sulfates, interfered on the formation and maintenance of a protective layer of corrosion products. Leleu et al. [29] observed that the film was more protective for the WE43 Mg alloy than for the pure Mg in 0.2 M NaCl solution, due to the incorporation of alloying elements. Przondziono et al. [32] reported that the corrosion rate of WE43 alloy increases with the chloride content (0.01 – 2 M NaCl) and, irrespective of the concentration of the solution, the WE43 alloy is prone to undergo pitting corrosion. Ninlachart et al. [15] evaluated the “passive-like“ behavior of the WE43 alloy in dilute alkaline solutions containing different chloride concentrations. The corrosion resistance of the WE43 alloy was better in the heat-treated (T5) condition compared to other conditions, and the protective layer was composed of MgO, Mg(OH)$_2$, and rare earth oxide phases. Heat treatment provides homogeneously and finely dispersed second phase particles, which are beneficial to form a continuous film of corrosion products. Also, these second phases can act as physical barriers to hinder the spread of corrosion [33]. Rzychoń et al. [34] investigated the corrosion rates of WE54 and Elektron 21 alloys after 7 days of immersion in 0.6 NaCl. They found that the corrosion rate of the WE43 alloy was almost unchanged within the immersion time and finally reached a maximum value of 0.26 mg/cm$^2$day, which was smaller compared to those displayed by the Elektron 21 and WE54 alloys.

Most studies report that intermetallics containing RE elements (e.g. Y, Nd or Zr) were
always cathodic compared to the Mg matrix [26,35–39]. However, some studies revealed the anodic role of these intermetallics [40]. Coy et al. [39] reported that all phases of the WE43 alloy showed positive Volta potential differences relative to the matrix, indicating cathodic behavior, and no evidence of galvanic corrosion attack was observed. Liu et al. [40], in contrast, discussed the anodic role of second phases and a value very close to the Volta potential between the Mg matrix and the second phase in EW75 alloy; the second phases in EW75 are more active than the Mg matrix, being preferably dissolved in the initial corrosion stage.

Despite the existence of studies on the corrosion aspects of the WE43 alloy in saline environments, little is reported about its time-dependent evolution and integrity of the protective layer ascribed to grant the interesting corrosion resistance to the WE43 alloy, essential for structural applications. This work aims to evaluate the corrosion behavior of the WE43-T5 alloy. Special care was taken to analyze the corrosion products formed, their protectiveness against corrosion, and their integrity upon the hydrogen evolution from the cathodic reaction. The results showed that the protective layer on the WE43 alloy was more compacted and adherent than that on pure Mg, constituting a more efficient physical barrier between the bare alloy and the corrosive medium, decreasing the reaction rate and improving the corrosion resistance. The kinetics of the cathodic reaction played an important role during the formation and spalling of the corrosion products on the WE43 and pure Mg.

2. EXPERIMENTAL PROCEDURE

2.1 Material

WE43C-T5 Mg alloy (referred to as WE43 hereafter), acquired from Magnesium Elektron N.A. Inc, and commercially pure Mg acquired from the RIMA industrial (referred to as pure Mg hereafter), were considered in this study. Their chemical compositions are detailed in Table 1. The laminated WE43 is a precipitation hardening alloy that was treated at the T5 condition, based on artificial aging. Test specimens were machined from a 370 mm x 190 mm x 30 mm plate in the TL direction, where L stands for lamination direction and T the transverse direction. Preliminary results showed that the equiaxed grain morphology in the TL and LT planes are similar, as well as the results of the mechanical tests shown in Table 2.
Table 1: Chemical composition of the WE43 alloy and commercial pure Mg from energy-dispersive x-ray spectroscopy (EDX) measurements.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mg</th>
<th>Y</th>
<th>Nd</th>
<th>Zr</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE43</td>
<td>Bal.</td>
<td>2.7</td>
<td>1.6</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg pure</td>
<td>Bal.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.202</td>
<td>0.039</td>
<td>0.018</td>
<td>0.031</td>
<td>0.007</td>
<td>0.005</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 2: Mechanical properties of the WE43 from tensile tests conducted in air and at room temperature.

<table>
<thead>
<tr>
<th>Property</th>
<th>Specimen TL</th>
<th>Specimen LT</th>
</tr>
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<tbody>
<tr>
<td>$\sigma_y$, MPa</td>
<td>268</td>
<td>246</td>
</tr>
<tr>
<td>$\sigma_{UTS}$, Mpa</td>
<td>366</td>
<td>373</td>
</tr>
<tr>
<td>E, GPa</td>
<td>43</td>
<td>43</td>
</tr>
</tbody>
</table>

2.2 Microstructural characterization

The samples were ground using #80 to #4000 sandpapers and ethanol as a lubricant to avoid excessive oxidation. 1- and 0.25-μm diamond pastes and colloidal silica with average size particles of 0.04 μm were used for polishing. Picral etching reagent (10 ml acetic acid, 4.2 g picric acid, 10 ml H$_2$O, and 70 ml ethanol) was used to reveal the microstructure. Analysis of the microstructure was undertaken by optical microscopy (OM), using a Carl Zeiss™ model AxioLab, and by scanning electron microscopy (SEM), using an FEI® model FE-50 in secondary (SE) and backscattered electron (BSE) mode.

2.3 Immersion test

Ø 20 × 5 mm discs were considered for immersion tests. The surfaces were ground using #600 to #2000 sandpapers and cleaned with acetone. After drying, the mass and surface of the specimens were measured. The samples were submerged in a large volume of 0.6 M NaCl solution at 25 °C, 19.4 cm$^2$/l, by hanging the specimens in an Erlenmeyer for different elapsed times: 24 h, 72 h, 120 h and 168 h. The Erlenmeyer was sealed with cork to prevent excessive evaporation. After a given immersion period, the samples were cleaned with 200 g CrO$_3$, 10 g AgNO$_3$, 20 g BaNO$_3$ and 1000 ml of demineralized water and then the weight loss measured according to the ASTM G31-72 [41]. Repeatability was ensured by analyses in triplicate. The corrosion rate was determined according to Equation 1 [41]:

$$\text{Corrosion Rate} = \frac{\Delta m}{A \times t}$$
\[
CR = \frac{\Delta m \times K}{\rho \times A \times t}
\]
Eq. (1)

where:
- \( CR \) = Corrosion rate (mm/yr)
- \( \Delta m \) = Weight loss (g)
- \( K \) = Constant (87600)
- \( \rho \) = Density of Mg (g/cm\(^3\))
- \( A \) = Exposed area (cm\(^2\))
- \( t \) = Immersion time (h)

The phases present on the samples’ surface, before and after the immersion, were identified using x-ray diffraction (XRD) in a Bruker D8 ADVANCE diffractometer with Cu-K\(\alpha\) radiation.

### 2.4 Electrochemical tests

Electrochemical measurements were conducted in a conventional three-cell set-up, using a Gamry 600+ potentiostat. The working electrodes were the WE43 alloy and the commercially pure Mg (polishing up to #1200 SiC; exposed area of 0.5 cm\(^2\)). A Pt grid and a saturated calomel electrode were used as counter and reference electrodes, respectively. The electrolyte was a 0.6 M NaCl solution prepared using demineralized water and high purity NaCl (> 99%). Electrochemical impedance spectroscopy (EIS) was performed after 24 h of immersion, considering an amplitude of 10 mV\(_{\text{rms}}\) around the open circuit potential, with a frequency range between \(10^5\) to \(10^2\) Hz. The data treatment was based on the use of an equivalent circuit (EC) using the EC-Lab software from Biologic\(^\circ\). Potentiodynamic polarization measurements were carried out as complement after 24 h of immersion, from –300 mV against the open circuit potential up to \(10^2\) A/cm\(^2\), using 1 mV/s as scan rate.

### 2.5 Kelvin Probe Force Microscopy (KPFM)

KPFM is an atomic force microscopy (AFM) module that measures the potential difference between contacting surfaces, alloying to create maps of the surface topography in a nanometric scale. The analyzes were used to determine the relative Volta potential differences between micro-constituent phases and the Mg matrix. After grounding and polishing the samples, as described for the metallographic analysis, the specimens were then cleaned in an
ultrasonic bath using ethanol. The analyzes were performed using a Park model NX10 atomic force microscope in KPFM mode, with the results analyzed in a Gwyddion software.

3 Results

3.1 Microstructural analyses

Figure 1 shows the microstructure and the XRD patterns of pure Mg and WE43 alloy. The microstructure of pure Mg in Figure 1a is composed of coarse grains, approximately 1000 μm, with some twinning as indicated by the arrows. The microstructure of the WE43 alloy shown in Figure 1b and c contains more refined grains than the pure Mg, with an average size of 20 μm. Less twinning than in pure Mg was observed. The WE43 alloy shows recrystallized matrix where fine precipitates are uniformly dispersed. Precipitates are also present at grain boundaries, as shown in Figure 1c; the arrows indicate the precipitates with different morphologies and in different regions, similar to what has been reported for Mg alloys containing rare-earth elements [19,39]. Some studies suggest that these precipitates are promoted from the heat treatment, resulting in different morphologies: needle-like and irregulars (spherical or cubic). According to these studies, the precipitates with needles-like morphology and those formed at the grain boundaries were Nd- and Y-enriched phases. Those with irregular morphology were rich in Y or Zr [15,19,29,33,39,42,43].

The XRD patterns in Figure 1d and e display the α-Mg peaks. However, the WE43 alloy present also peaks ascribed to precipitates such as Mg₄₁Nd₅ and Mg₂₄Y₅. The microstructure of the WE43 alloy is the result of the alloying elements, manufacturing process, and the thermal treatment of precipitation hardening, composed of three steps: a solution heat treatment, tempering, and artificial aging. The aging aims to provide a dispersion of fine precipitates within the α-Mg matrix [44,45], as observed in Figure 1c. The irregular particles containing Y or Zr observed are probably not dissolved by the solution-treatment due to their high melting temperatures [15,33].
**Figure 1.** Microstructure of pure Mg and WE43 alloy. a) OM image of pure Mg, b) OM image of WE43 alloy, and c) SEM image, in BSE mode, of the WE43 alloy; XRD pattern of pure Mg (d) and WE43 alloy (e). Besides the identification of the Mg phase in both materials, there are some precipitates of Mg$_{24}$Y$_5$ and Mg$_{41}$Nd$_5$ in the WE43 alloy.

### 3.2 Immersion testing

Immersion tests were performed to investigate the corrosion behavior and to evaluate the corrosion resistance of pure Mg and the WE43 alloy, as shown in **Figure 2**. The corrosion rates are presented in **Figure 2a**, where a comparison between both alloys reveals a large discrepancy of values. **Figure 2b** shows a zoomed view of the dashed rectangle in **Figure 2a**, allowing a better visualization of the corrosion rate of the WE43 alloy. Pure Mg showed an average corrosion rate of 28.15 mm/year after 24 h of immersion, and this rate increased within the immersion time, reaching a value of 51.64 mm/year after 168 h of testing. The WE43 alloy, on the other hand, showed a corrosion rate of 1.41 mm/year after 24 h of immersion; this rate decreased with the time of immersion, reaching a value of 0.33 mm/year after 168 hours. The pronounced difference between pure Mg and WE43 in terms of corrosion rates as well as the opposite effect of the immersion time will be addressed in detail in the **Discussion Section**.
Figure 2: Corrosion rates of pure Mg and WE43 alloy from immersion tests. a) Comparison between pure Mg and WE43 alloy on a large scale (0 to 65 mm/year), and b) zoomed view (0 to 1.6 mm/year) to better observe the low corrosion rate of the WE43 alloy. The immersion was conducted in a 0.6 NaCl solution at 25 °C for different periods.

The impact of the significant difference in the corrosion rate is observable by comparing the macroscopic morphologies of pure Mg and WE43 alloy before and after the immersion tests. Figure 3. Pure Mg, Figure 3a, displayed a surface that suffered severe and extensive corrosion, with degradation increasing with the elapsed time of immersion, as highlighted from the fresh metal on the left to the rough and degraded surface on the right. The surface appearance of the WE43 alloy after testing was considerably different, Figure 3b. The surfaces were flat and smooth regardless of the immersion time, with the formation of adhered corrosion products.

Figure 3. Images of the samples after different immersion periods in 0.6 M NaCl. a) Severe corroded Mg surfaces, and b) the initiation and development of the corrosion products formed on the WE43 alloy.
A detailed view of the corroded surfaces of pure Mg and the WE43 alloy is given in Figure 4, from SEM observations. Figure 4a-d show the severely corroded surfaces of pure Mg since the first 24 h of immersion. Broad and deep corroded areas increased over time of immersion. Figure 4e-h exhibit the surface of the WE43 alloy after the immersion tests. The cracks in the corrosion product layer are mainly attributed to the dehydration during the drying process, as reported in [46]. Over time, the corrosion surface of the WE43 alloy shows deeper cracks due to the thicker layer of the corrosion product (Figure 4h), indicating the formation of a corrosion layer but compacted on the surface of the alloy with increasing test time, acting as a protective-like layer to prevent further severe corrosion.

![Figure 4. SEM images in SE mode of the surface after immersion test in 0.6 M NaCl solution at 25 °C for 24 h, 72 h, 120 h, and 168 h. a-d) Surface morphology of pure Mg after immersion, and e-h) surface morphology of WE43 alloy after immersion. Different magnifications required given the discrepancies in the corroded surfaces between pure Mg and WE43.](image)

Figure 5 shows the XRD patterns from the pure Mg and WE43 alloy after immersion at different times. XRD patterns of the pure Mg after testing, Figure 5a, indicate the presence of Mg ascribed to the substrate and the Mg(OH)$_2$ from the corrosion process. The corrosion products expelled from the samples’ surface and deposited at the bottom of the Erlenmeyer were also analyzed (Figure 5b). The corrosion products were Mg(OH)$_2$ regardless of the immersion period. XRD results from the WE43 surface indicate that, besides Mg(OH)$_2$, the corrosion products were also composed of Y$_2$O$_3$ and Nd$_2$O$_3$, Figure 5c. No appreciable corrosion products were observed at the bottom of the Erlenmeyer after testing the WE43 alloy, even after 168 h of immersion.
Figure 5: XRD patterns of the surface of pure Mg and WE43 alloy after immersion tests. a) The surface of the pure Mg and b) collected products deposited at the bottom of the Erlenmeyer from the corrosion of pure Mg. c) The surface of the WE43 alloy. Immersion tests were conducted at different times in the 0.6 M NaCl solution at 25 °C.
3. DISCUSSION

From the microstructural perspective, the pure Mg had coarser grains, about 1000 μm, while the WE43 alloy displayed a homogeneous microstructure with a grain size of about 20 μm, which is favorable to improve the corrosion resistance of Mg-alloys. Refined grains favor uniform and dense protective layers on the surface [47,48], enhancing the corrosion resistance as observed for the WE43 alloy. In addition, the smaller the grain, the greater the number of grain boundaries. The grain boundaries reduce the intensity of the galvanic couple between the core and the boundary of grains, the first being more prone to corrode, leading to a more uniform degradation compared to the microstructure of larger grains [48,49]. Another factor that influences the corrosion resistance of pure Mg and WE43 alloy are crystalline defects such as twinning observed in almost the entire microstructure of pure Mg [46]. The crystal twinning increases the anodic activity, therefore, leading to a faster dissolution [47,50].

Corrosion rate values from immersion tests in 0.6 M NaCl solution highlighted large differences between the pure Mg and WE43 alloy, as shown in Figure 2. Pure Mg exhibited increased values of corrosion rate with elapsed time. Since pronounced roughening occurs upon corrosion of pure Mg, Figure 3a, a larger active area is exposed to the corrosive medium, which may be related to the superior corrosion rates observed within the immersion time. At the beginning of the immersion test of pure Mg, it was possible to observe small white particles, identified as Mg(OH)₂, first stacked on the surface (Figure 5a) but continuously spalled (Figure 5b) due to the intense hydrogen evolution to sustain the severe dissolution of Mg. The intensity of the peaks ascribed to Mg(OH)₂ on the corroded surface does not follow a clear trend, Figure 5a, probably because of the constant and heterogeneous spalling of the corrosion products from the surface, thus forming a heterogeneous roughened surface, as can be seen in Figures 3a and 4a-d. After 24 h of immersion, the surface of the pure Mg has been considerably modified, and a rough morphology was visible as well as a considerable amount of corrosion products deposited at the bottom of the Erlenmeyer.

The corrosion phenomenon at the pure Mg in 0.6 M NaCl is detailed in Figure 6. Mg dissolution, Figure 6a, is followed by the formation of Mg(OH)₂ on the surface. The cathodic reaction occurs at the underlying bare metal, where hydrogen gas evolves, Figure 6b. Because the corrosion of Mg is fast, i.e., the charge-transfer resistance is low, the coupled cathodic reaction represented by the hydrogen gas production must be elevated, Figure 6c. Since the Mg(OH)₂ is porous and friable, the intense hydrogen gas production at the metal underneath the corrosion products shown in Figure 6d causes their permanent spalling as reported in [52].
The proposed equivalent circuit (EC) illustrated in Figure 6e was thus held to represent the corrosion occurring at the pure Mg, where: $R_e$ is the electrolyte resistance, CPE is the constant phase element (characterized by $Q$ and $\alpha$) to represent the capacitive-like response, and the $R_{ct}$ is the charge transfer resistance. An inductor element characterized by the resistance $R_L$ and the inductance $L$ was included, accounting the breakdown of the corrosion layer and the localized corrosion [53,54]. Even if some Mg(OH)$_2$ products remain at the surface of pure Mg, they are non-adherent and porous in such a way that their contribution as a significant physical barrier is negligible; hence, their contribution to the EIS data was deemed to be negligible. The same EC has been used to model the electrochemical process of Mg alloys [12].

Figure 6 a-c) Representation of the corrosion at the pure Mg interface, highlighting the severe spalling of the corrosion products, Mg(OH)$_2$, due to the elevated rate of H$_2$ gas evolution from the cathodic reaction. d) Picture taken after the first minutes after immersion reveals the pronounced gas evolution from the pure Mg samples. e) Proposed equivalent circuit to represent the corrosion process occurring at the pure Mg/electrolyte interface.
Mg is a highly active metal, since the oxide film can be formed immediately when exposed to air (reaction 1). In aqueous solutions, magnesium corrodes through an electrochemical reaction with water (reaction 2), producing a porous layer of Mg (OH)₂ that covers the MgO layer. The lower solubility of Mg(OH)₂ compared to MgO in aqueous solutions implies the precipitation of Mg (OH)₂.

\[
\begin{align*}
\text{Mg} + \frac{1}{2} \text{O}_2 & \rightarrow \text{MgO} \quad \text{(R. 1)} \\
\text{MgO} + \text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2 \quad \text{(R. 2)}
\end{align*}
\]

Once the corrosion started in Mg, the active dissolution of the metal occurs due to the aggressiveness of the corrosive medium with Cl⁻ ions, moreover, the integrity of the corrosion product formed on the surface of pure Mg are sensitive by the presence of impurities like Fe, Ni, Cu (Table 1) and defects as twins (Figure 1a). The impurities act as cathodic centers that are less active than anodic Mg, thus promoting micro-galvanic corrosion. The anodic reaction (reaction 3) will be the oxidation of the Mg matrix and impurities, the cathodic reaction (reaction 4) will be the reduction of water (evolution of hydrogen) that occurs on the surface of the Mg. The dissolution of Mg can be summarized by the general corrosion reaction (reaction 5) [23].

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2\text{e}^- \quad \text{(R. 3)} \\
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow 2\text{OH}^- + \text{H}_2 \quad \text{(R. 4)} \\
\text{Mg} + 2\text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \quad \text{(R. 5)}
\end{align*}
\]

The WE43 alloy exhibited a decreasing corrosion rate with immersion time, associated with the low roughening and especially with the formation of a protective and compact oxide layer that remains on the alloy’s surface, Figures 3b and 4e-h. One observes in Figure 3b that the surface was little attacked, having a uniform appearance after testing, where the corrosion products remain virtually intact throughout the tests. It is known that the intermetallic phases formed by the controlled addition of Y and Nd favor the formation of a thicker protective layer on the alloy’s surface, Figure 4e-h. This layer is more compact and adherent in the We43 alloy than in the pure Mg, acting as a more efficient physical barrier between the alloy and the corrosive medium, decreasing the reaction speed and improving the corrosion resistance. The Mg alloys with the addition of Y and Nd induce the precipitation from the saturated solid
solution, derived from the grouping of atoms ordered in the hexagonal network of Mg, which
ensure the formation of a protective layer to resist the corrosion attack [48], as shown in Figure
5c.

The WE43 corrosion interface is illustrated in Figure 7. The corrosion process at the
surface in Figure 7a results in the formation of a product layer more adherent and compact,
Figure 7b. This behavior is due to the addition of Y and Nb, enabling the formation of
protective-like oxides, Figure 7c, which remain at the surface because of the rate of the
hydrogen gas evolution is low. Besides the formation of a more protective layer, the corrosion
rate of the WE43 is lower, i.e., higher charge transfer resistance, so the rate of hydrogen gas
evolution to sustain the anodic reaction is low. Indeed, Figure 7d illustrates that the corrosion
products and the hydrogen gas evolution on the WE43 alloy in 0.6 M NaCl are much bland
than that observed for pure Mg in Figure 6d. The EC detailed in Figure 7e was thus selected
to represent the electrochemical process at the WE43 alloy interface, where: $R_e$ is the electrolyte
resistance, $CPE_f$ is the constant phase element (characterized by $Q_f$ and $\alpha_f$) to represent the
capacitive-like response of the protective film, and the $R_f$ is the resistance of the protective
film. The $R_{ct}/CPE_{dl}$ is the charge transfer resistance and the double-layer-like capacitance. An
inductor element characterized by the resistance $R_L$ and the inductance $L$ was included to
account the breakdown of the corrosion layer and the localized corrosion [53,54]. The same
EC has been used to model the electrochemical process of Mg alloys [12], and those alloyed
with Y and Nb [15].
Figure 7 a-c) Illustration of the corrosion at the WE43 interface, highlighting the mild damage of the corrosion product film, Mg(OH)_2 and Y- and Nb-oxides, due to the slow rate of H$_2$ gas evolution from the cathodic reaction. d) Picture taken after the first minutes after immersion reveals the low rate of gas evolution from the WE43 samples. e) Proposed equivalent circuit to represent the corrosion process occurring at the pure WE43/electrolyte interface.

Figure 8 presents the Nyquist and Bode plots of pure Mg and WE43 alloy after 24 h of immersion in 0.6 M NaCl solution. The Nyquist plot, Figure 8a, of the pure Mg displays one apparent time constant with a clear inductive-like response at low frequencies. The WE43 plot in Figure 8a is different, with a two-time constant and an inductive-like response at low frequencies. Note the much superior impedance for any frequency of WE43 in Figure 8a compared to the pure Mg, this latter only observable in the zoomed inset. Bode plots in Figure 8b show that the shape of the high-frequency curves of both pure Mg and WE43 are similar, especially in terms of the relaxation event around frequencies between $10^2$ and $10^4$ Hz. However, the |Z| values increase at a higher pace for the WE43 alloy. The main differences are in the lower frequency range, where the WE43 alloy exhibit another time constant related to the protective film composed of the corrosion products while only the inductive-response is
seen for pure Mg—comparing the information of the experimental EIS data and the proposed ECs in Figures 6e and 7e, the physical process occurring at the corroding interface is considered.

**Figure 8** a) Nyquist and b) Bode plots of the WE43 and pure Mg alloys in 0.6 NaCl solution after 24 h of immersion. Symbols represent the experimental data, and the solid red lines the results from the fitting considering the equivalent circuits depicted in Figure 6e, and Figure 7e. The inserted graph in (a) is the zoomed region of the Nyquist plot to enable a better visualization of the pure Mg result.
Table 3 summarizes the ensemble of the parameter from fitting the ECs of Figures 6e and 7e to the experimental EIS data, Figure 8, using the EC-Lab software from BioLogic. For all data fitting, the normalized chi-square ($\chi^2/|Z|$) values were inferior to $10^{-3}$, meaning a high convergence level between the fitted results and the experimental data. The $R_c$ values of the WE43 alloy is higher compared to those of pure Mg (703 against 210 $\Omega$.cm$^2$), indicating that the kinetics of Mg dissolution and hydrogen gas evolution of the WE43 is slower. Both presented $\alpha_{dl}$ and $Q_{dl}$ values reasonable to a capacitive-like behavior related to the double-layer. The WE43 alloy also showed a clear response related to the protective film composed of the corrosion products on its surface. The related $R_f$ was high, 7030 $\Omega$.cm$^2$, and the $CPE_f$ presented a capacitive behavior with $\alpha_f$ $0.87$ and $Q_f$ of $33 \mu\Omega$/cm$^{-2}$s$^{-\alpha_f}$, both typical to the values ascribed to protective corrosion products on Mg-based alloys [29]. The additional time constant effectively contributes to providing further corrosion resistance to the WE43 alloy. Concerning the inductive component, the WE43 alloy exhibited superior $R_L$ values than the pure Mg, also indicating higher resistance against the ingress of the corrosive electrolyte along the deposit of the product on the metals’ surface.

<table>
<thead>
<tr>
<th></th>
<th>WE43 Alloy</th>
<th>Pure Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_e$ ($\Omega$.cm$^2$)</td>
<td>64</td>
<td>65</td>
</tr>
<tr>
<td>$R_{ct}$ ($\Omega$.cm$^2$)</td>
<td>703</td>
<td>210</td>
</tr>
<tr>
<td>$CPE_{dl}$</td>
<td>$\alpha_{dl}$</td>
<td>0.84</td>
</tr>
<tr>
<td>$Q_{dl}$ ($\mu\Omega$/cm$^{-2}$s$^{-\alpha_{dl}}$)</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>$R_f$ ($\Omega$.cm$^2$)</td>
<td>7030</td>
<td></td>
</tr>
<tr>
<td>$CPE_f$</td>
<td>$\alpha_f$</td>
<td>0.87</td>
</tr>
<tr>
<td>$Q_f$ ($\mu\Omega$/cm$^{-2}$s$^{-\alpha_f}$)</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>$R_L$ ($\Omega$.cm$^2$)</td>
<td>1735</td>
<td></td>
</tr>
<tr>
<td>L (H/cm$^2$)</td>
<td>1023</td>
<td></td>
</tr>
</tbody>
</table>

Potentiodynamic polarization measurements after 24 h of immersion in 0.6 M NaCl were performed as a complement, Figure 9. It is seen that the associated $i_{corr}$ value of the WE43 alloy is lower than for pure Mg. Also, and more importantly, a current density plateau upon anodic polarization of the WE43 was observed and attributed to the protective corrosion products on its surface. Pure Mg, in contrast, exhibited a monotonically increase in current.
density upon anodic polarization, in agreement with the non-protective nature of the remaining corrosion products on its surface.

Figure 9 Potentiodynamic polarization curves of WE43 and pure Mg alloys in 0.6 NaCl solution after 24 h of immersion. \(i_{\text{corr}}\) determined from the cathodic branch since the region displayed Tafel’s like behavior.

During the interaction of the WE43 with the aqueous medium, Mg (reaction 3), Y (reaction 6) and Nd (reaction 7) react within an electrochemical corrosion process in anodic regions, being the coupled cathodic reaction the reduction of water (reaction 4). Further reactions of the metallic ions with hydroxyls forms solid products on the surface, following the reactions 8, 9 and 10. Charges in the oxidation degree may occur, and the Mg-, Y-, and Nd-hydroxides partially transformed into oxyhydroxides and oxides of the metallic elements.

\[
\begin{align*}
Y & \rightarrow Y^{3+} + 3e^- \quad (R. \ 6) \\
Nd & \rightarrow Nd^{3+} + 3e^- \quad (R. \ 7) \\
Mg^{2+} + 2OH^- & \rightarrow Mg(OH)_2 \quad (R. \ 8)
\end{align*}
\]
Some of the hydroxides may be dehydrated when exposed to air (reactions 11, 12 and 13), resulting in the cracks observed in Figures 4 e-h. The reduction of internal micro-galvanic corrosion may be due to similar electrode potentials between the Mg matrix (Mg, -2.37 V) and the alloying elements (Y: -2.37 V, Nd: -2.44 V), more continuous distribution of the second phases and more homogeneous microstructure (smaller grain size and less twinning) [24]. Trend of passivation on the anodic side of the polarization curve, the second capacitance loop on the Nyquist graph and the DRX analysis prove the existence of an oxide film on the surface of the Mg alloy, as reported by Song et al. [56].

\[
\begin{align*}
Y^{3+} + 3\text{OH}^- & \rightarrow Y(\text{OH})_3 \quad (\text{R. 9}) \\
\text{Nd}^{3+} + 3\text{OH}^- & \rightarrow \text{Nd(OH)}_3 \quad (\text{R. 10}) \\
\text{Mg (OH)}_2 & \rightarrow \text{MgO} + \text{H}_2\text{O} \quad (\text{R. 11}) \\
2\text{Y(OH)}_3 & \rightarrow \text{Y}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (\text{R. 12}) \\
2\text{Nd(OH)}_3 & \rightarrow \text{Nd}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (\text{R. 13})
\end{align*}
\]

Kelvin Probe Force Microscopy (KPFM) analysis was performed for a better understanding of the influence of second phases on uniform corrosion of the WE43 alloy. KPFM was used to measure the relative potential differences between intermetallic particles and the Mg matrix. Since no evidence of precipitation was found in the pure Mg in the XRD analysis, the KPFM analysis was only conducted in a selected area of the WE43 alloy. Error! No s'ha trobat l'origen de la referència. shows the surface topography and the contact potential difference map over a 8 x 8 µm² area. Some line scans along some precipitates and grain boundaries are shown in Error! No s'ha trobat l'origen de la referència.c and d. The second phase with high hardness remained in the matrix after grinding and polishing, therefore the 3D maps show these protrusions out of the smooth surface in Error! No s'ha trobat l'origen de la referència.a. The brighter regions correspond to the cathodic areas (higher potential values), whereas darker regions correspond to the anodic areas (lower potential values) in Error! No s'ha trobat l'origen de la referència.b [39].
Figure 10 Kelvin Probe Force Microscopy (KPFM) analysis showing a surface area of 8 x 8 µm² of the WE43 alloy: a) 3D surface topography, b) contact potential difference map, c) and d) Volta potential distribution along with the line scans drawn in (b). Observe how the Volta potential is altered close of precipitates in c) and grain boundaries in d).

Since the second phases in the needle-like and irregular forms are small and dispersed within the α-Mg matrix, it was not possible to distinguish the elements of the second phase. It was possible to observe a small precipitate (line 1) with a more significant potential (approximately +300 mV) than the matrix; this precipitate can act as a more effective cathode in a micro-galvanic corrosion process with the matrix. Coy et al. [39] identified this precipitate as being rich in Zr. Larger fraction of precipitates inside the matrix (line 2) and along the grain boundaries (line 3) with the smaller potential, approximately -400 mV than the matrix, were seen, demonstrating that the Mg matrix is nobler than the second phases, as also reported by Liu et al. [40]. These areas can act as adequate anodes in a corrosion process. This difference
in potential of micro-constituents is cited by several authors as one of the leading causes of micro-galvanic corrosion, indicating that the particles may be preferred locations for pitting corrosion of Mg alloys in a corrosive environment [30,39,40,57,58].

Even with an expressive potential difference, based on the surface corrosion morphology (Figure 4), the second phase did not have a significant influence on the galvanic corrosion behavior of the alloy. This behavior can be explained by the uniform microstructure (few defects and impurities) with well distributed and fine anodic precipitates; that is, the second phases is likely to corroded preferably as micro-anodes, and the Mg matrix is protected as micro-cathodes.

4. CONCLUSIONS

The corrosion behavior of the WE43 alloy in 0.6 M NaCl was appraised and compared to that of a commercially pure Mg. Immersion tests and electrochemical measurements were performed to highlight the corrosion resistance of the WE43, which was ascribed to the characteristics of formation and nature of the corrosion products. The following conclusions can be drawn:

- The WE43 alloy exhibited equiaxed grains of α-Mg containing precipitates of Mg₄₁Nd₅ and Mg₂₄Y₅ homogeneously dispersed within the matrix and along the grain boundary.
- WE43 alloy displayed a decreasing corrosion rate upon the immersion time, ranging from 1.41 mm/year after 24 h to 0.33 mm/year after 168 h of elapsed time. Commercially pure Mg, in contrast, presented increasing corrosion rate of 28.14 mm/year after 24 h to 51.64 mm/year after 168 h.
- The decreasing corrosion rate seen for the WE43 is ascribed to the formation, thickening and densification of the corrosion product layer that remains on the surface. The increasing corrosion rate of pure Mg is caused by the permanent spalling of the corrosion products due to the intense hydrogen gas evolution from the cathodic reaction and the increasing exposed area because of the roughening.
- WE43 enabled the production of protective corrosion product layer composed of, besides Mg(OH)₂, Y₂O₃ and Nd₂O₃. This layer remains at the surface and is not severely cracked since the rate of cathodic reaction (hydrogen gas evolution) at the underneath bare alloy is mild. Severe spalling of the low protective Mg(OH)₂ layer on commercially pure Mg occurred mainly because of the severe hydrogen gas evolution.
• The corrosion processes occurring at the surface of WE43 alloy and commercially pure Mg was represented by EC analogs to interpret the experimental EIS data. It was found the important contribution of the alloying elements to reduce the charge transfer reaction and to provide a protective layer, both contributing for the superior corrosion resistance of WE43 over commercially pure Mg.

• KPFM results demonstrated that, despite the significant differences of Volta potential values between the precipitates and matrix in the WE43 alloy, uniform corrosion occurred because the dissolution of some precipitates formed protective oxides and their presence increase the charge transfer resistance.

5. ACKNOWLEDGMENTS

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6. REFERENCES


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