Multi-Scale Monitoring the First Stages of Electrochemical Behavior of AZ31B Magnesium Alloy in Simulated Body Fluid

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This work applies electrochemical noise technique (EN) and scanning electrochemical microscopy (SECM) to investigate the initial stages of degradation of AZ31B magnesium alloy in simulated body fluid (SBF). The fluctuations in potential and current, caused by the alloy’s spontaneous degradation, were analyzed in both time and frequency domains to determine the type of attack and the fractal nature of the degradation. Substrate-generation/tip-collection mode SECM mapped the hydrogen evolution activity at the Mg surface during the initial corrosion process. This electrochemical information was correlated with pH changes of the solution, Mg ion concentration, mass loss, SEM-EDS and XPS analysis. The Mg matrix dissolution was promoted by Al-Mn intermetallic particles, which acted as cathodic sites. The corrosion products film was mainly composed by Mg(OH)2 and Ca10(PO4)6(OH)2, and its fast formation allowed a slower degradation and H2 evolution rates. Combining EN and SECM methods allowed the description of the early degradation processes of AZ31B in SBF as a persistent stationary process, related to fractional Gaussian noise, which was characterized by the quasi-uniform corrosion of the alloy.

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Biomaterial science has found very interesting applications of magnesium alloys as non-toxic degradable implants. The main attraction of these materials are mechanical properties similar to natural bone, biocompatibility, and high corrosion rates in physiological media. Among available commercial magnesium alloys, AZ31 (Mg-3%Al-1%Zn) presents particular advantages for biomedical applications, including: lower cost, reduced aluminum content, and comparable corrosion resistance with other Mg alloys. In vivo tests have also demonstrated that AZ31 is not harmful to tissue and promotes new bone cell formation.

The reported microstructure of AZ31B mainly consists of intermetallic Al-Mn particles, such as Al11Mn4, Al8Mn5, ε-AlMn, and β-Mn(Al), which are cathodically active with respect to the Mg matrix. Nevertheless, the corrosion mechanism will directly depend on not only these particles and their distribution, but also the composition of the solution. Simulated body fluid (SBF) was selected in this work as test media due to its stability and ions concentration close to that of blood plasma. Furthermore, it has been found that calcium and phosphate ions present in SBF may lead to formation of partially protective corrosion product layers on Mg alloys.

Previous electrochemical studies have been conducted on the biodegradation of AZ31 alloy, usually employing techniques such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). However, due to the fact that magnesium is a very active metal in aqueous solutions, it is necessary to study these Mg-based materials with alternative techniques in order to overcome some limitations which arise from their rapid and continuing dissolution. For instance, corrosion caused by PDP may alter the surface which occurs during the anodic scan; and EIS technique is susceptible to corrosion that occurs over time (changing measured surface area and consequently the results). Thus, assessing AZ31 corrosion through in situ methodologies could lead to obtain valuable additional information about its degradation process under relevant physiological conditions. Therefore, one goal of the present investigation is to monitor AZ31B bio-corrosion at different scales with non-polarized electrochemical techniques.

Electrochemical Noise

The spontaneous fluctuations of potential or current associated with corrosion phenomena are known as electrochemical noise (EN). Measuring, processing and analyzing EN may help to evaluate corrosion mechanisms without applying any external perturbation. Thereby, electrochemical noise technique has been employed to identify corrosion type by simple examination of the time record signal, or by calculations of some statistical parameters from current or potential data. Furthermore, electrochemical signals can be digitally filtered and then transformed to the frequency domain by fast Fourier transform (FFT), in order to analyze their power spectral density (PSD). The slope of the PSD versus frequency provides the spectral power exponent, −β, which is used to distinguish between series with contributions of fractional Gaussian noise (fGn, −1 < β < +1) and/or fractional Brownian motion (fBm, +3 < β < +1). The fGn is related with stationary processes, whereas the fBm is associated with non-stationary ones. Additionally, β exponents are a measure of the strength of persistence in a process. This methodology has been successfully applied by our group to characterize the first stages of corrosion of pure copper, aluminum, and the stainless steels 304 and 316L in Caribbean sea water.

Scanning electrochemical microscopy.—The scanning electrochemical microscopy (SECM) technique has been shown to be a powerful tool which allows in situ monitoring of corrosion processes with high spatial and electrochemical resolution. SECM technique is usually based in the electrochemical response of a mobile microelectrode situated close to a substrate of interest immersed in an electrolytic solution. For instance, hydrogen produced by magnesium corrosion in neutral or basic aqueous media (Equation 1), can be selectively detected with SECM operated in the substrate-generation/tip-collection mode, employing a platinum microelectrode (Equation 2).

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2 [1]
\]

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- [2]
\]

The aim of the present study is to combine the capabilities of EN and SECM techniques with conventional immersion tests and SEM-EDS surface analysis, in order to achieve a multi-scale assessment of the first stages of degradation of AZ31B magnesium alloy in

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SBF. The findings of this study are expected to enlarge the knowledge about the AZ31B alloy degradation process in physiological environments for future development of new surface treatments or coatings that allow control of its degradation rate.

Experimental

Samples and solution preparation.—Commercial AZ31B magnesium alloy sheet supplied by Alfa Aesar (Ward Hill, MA, USA) was employed as test material in this study. The provided certified composition of the alloy is: 2.5–3.5% Al; 0.6–1.4% Zn; 0.2% Mn; and the balance Mg. The sheet was cut in square samples of 1 cm² and separated into different sets, some of which were employed for immersion tests and others were embedded in epoxy resin as electrodes for electrochemical experiments. Additionally, one micrometric sample (120 μm x 100 μm approximately) was prepared for SECM measurements by cutting a fine strip of the alloy and then fixing it in epoxy resin. Before tests_measurements, all samples were abraded with 400, 800 and 1200 grit SiC papers using ethanol as lubricant, then they were polished with 0.3 μm alumina-ethanol slurry, sonicated in ethanol, and dried in air at room temperature.

The physiological solution used in this work was simulated body fluid (SBF) prepared with analytical grade reagents: (NaCl, NaHCO₃, Na₂CO₃, KCl, K₂HPO₄·3H₂O, MgCl₂·6H₂O, HEPES, CaCl₂, Na₂SO₄, NaOH), and ultrapure deionized water (18.2 MΩ cm) as described elsewhere.¹⁰

Immersion tests and surface characterization.—AZ31B specimens were soaked in 30 mL of SBF at room temperature for 2 d, following ISO 16428 standard.¹⁰ The immersion test and the electrochemical experiments were not performed at body temperature of 37 °C, because the use of a thermostatic bath would introduce additional noise to the measured signals of EN and SECM measurements, both sensitive to external perturbations. In this way, all results could be properly correlated.

After 24 h and 48 h of exposure, the pH of the test solutions was measured in order to detect changes, while the concentration of the released Mg²⁺ ions was established by photometry (H183200, Hanna Instruments, Woonsocket, RI, USA). The samples were withdrawn, rinsed with deionized water, and dried in air at room temperature for subsequent mass loss measurements according to ASTM G31-12a standard.¹⁰ All tests and measurements were triplicated to ensure repeatability.

In addition, corrosion products formed on the alloy surface after 48 h were characterized through X-ray photoelectron spectroscopy (XPS, K-Alpha,Thermo Scientific, Waltham, MA, USA).

Microstructure and morphologic changes of AZ31B surface were investigated under scanning electron microscopy (SEM-EDS, Philips XL-30, Amsterdam, the Netherlands). SEM images were acquired from the same sample in order to track its corrosion process as follows: first on the freshly polished surface of AZ31B; then, after 24 h and 48 h of exposure to SBF; and finally, after a cleaning procedure done as specified by ASTM G1-03 standard.¹⁰

Measurement and analysis of electrochemical noise.—Electrochemical noise measurements were carried out according to ASTM G199-09 standard.¹⁰ The experimental setup consisted of a three-electrode cell inside a Faraday cage as follows: two identical AZ31B working electrodes and a saturated Ag/AgCl/KCl reference electrode (CH Instruments Inc., Austin, TX, USA) were connected to the potentiostat (Interface-1000E, Gamry Instruments, Philadelphia, PA, USA) in zero resistance ammeter (ZRA) mode. EN data was acquired for 48 h in open circuit potential (OCP) conditions, with a sampling frequency of 1 Hz. The acquired current and potential signals were plotted versus time, and visually inspected to detect the occurrence rate of the time transients. A specific section of the time record of the current was selected for further analysis. This section of the series was preprocessed employing Matlab software by detrending the spectrum with a least squares fit, and then applying a Hanning parabolic window. Afterwards, preprocessed data was transformed in the frequency domain by FFT, to plot the power spectral density (PSD) of the current. The PSD was analyzed in the bi-logarithmic scale of power per unit frequency (A² Hz⁻¹) versus frequency (Hz), where the slope, β, was established by fitting a straight line to the data plotted at low frequencies (f ≤ 0.01). The β value allowed determining the fractal characteristics of the degradation process of AZ31B in SBF. Data acquisition and processing were done with Electrochemical Signal Analyzer V.7.0.1 software (Gamry Instruments, Philadelphia, PA, USA).

SECM measurements procedure.—A home-made scanning electrochemical microscope⁴⁵ was employed to monitor hydrogen evolution from AZ31B surface at the first 1, 1.5, and 2 hours of immersion in SBF. SECM was operated in the substrate-generation/tip-generation mode with a 10 μm platinum microelectrode (Pt-ME) as sensing probe, fabricated as described elsewhere.¹⁰ During SECM experiments, the Pt-ME was used as working electrode and the AZ31B substrate was always left at its OCP. The electrochemical cell was completed with a 0.7 mm thick Pt wire (Alfa Aesar, Ward Hill, MA, USA) as counter electrode, and a saturated Ag/AgCl/KCl reference electrode. Positioning of the Pt-ME was achieved by recording an approach curve above the insulating resin, with the tip set at –0.65 V in order to reduce dissolved oxygen in the SBF. The parameters for hydrogen collection were: tip-substrate distance of 7 μm, bias of –0.05 V, scanning area of 200 μm x 200 μm, and scan rate of 20 μm s⁻¹. Obtained data was plotted as 3D maps, where Z coordinate represents the current response produced by H₂ oxidation at the polarized tip.

Results and Discussion

SEM-EDS and XPS surface characterization.—Figure 1 shows SEM images acquired over the same area of an AZ31B sample at different stages of experiment: A) prior to immersion, B) after 24 h of exposure, C) after 48 h of exposure, and D) after removal of corrosion products. Moreover, EDS analysis (Table I) was performed in different areas and specific points, as presented in Figure 1. It can be observed that the initial freshly polished surface presents many white particles in the SEM image (Figure 1A), distributed all over the scanned area. EDS analysis revealed that they are composed of Al and Mn elements, which are correlated to Al-Mn phases with fine granular morphology reported for this alloy.¹¹ The content of Mg, Al, and Zn, obtained...
Table I. EDS analysis results obtained in sites marked on Figure 1.

| Element (wt%) | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 | Site 8 |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Mg           | 38.04 | 96.45 | 15.87 | 9.08  | 12.70 | 6.83  | 47.15 | 95.85 |
| Al           | 45.30 | 2.57  | 25.96 | 7.21  | 10.13 | 6.32  | 40.27 | 3.19  |
| Zn           | 0.98  | 0.69  | 2.02  | 0.77  | 2.41  | -     | 0.96  | -     |
| Mn           | 16.66 | -     | 11.91 | -     | 11.91 | -     | 12.58 | -     |
| C            | -     | 12.46 | 9.33  | 15.27 | 10.67 | -     | -     | -     |
| O            | -     | 22.18 | 43.04 | 33.63 | 37.14 | -     | -     | -     |
| P            | -     | 6.17  | 17.06 | 11.88 | 18.83 | -     | -     | -     |
| K            | -     | -     | 12.46 | 9.33  | 15.27 | 10.67 | -     | -     |
| Ca           | -     | 4.76  | 12.26 | 11.29 | 17.80 | -     | -     | -     |

by EDS (Table I) on the alloy matrix, coincides with the certified composition provided by the supplier.

Figures 1B and 1C display the morphology of AZ31B after 24 h and 48 h of immersion in SBF, respectively. It can be seen that a corrosion products layer was formed on the alloy surface, which was mainly composed by Mg, Al, Zn, C, O, P, and Ca, elements. According to previous studies, the presence of Mg, Al and Zn corresponds to the alloy matrix, whereas the other elements could be related to Mg(OH)$_2$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ phases. The cracks on the surface layer could be a consequence of its irradiation with the electron beam in SEM, which caused dehydration of Mg(OH)$_2$·$n$H$_2$O to Mg(OH)$_2$, according to suggestions of authors. The above would confirm the existence of Mg(OH)$_2$ phase on the alloy surface. It has also been reported that the calcium phosphate formation is promoted by Mg corrosion through P and Ca precipitation from SBF solution.

In order to establish the composition of the corrosion products film, XPS analysis was performed on the sample immersed in SBF for 48 h (Figure 2). The obtained full spectrum revealed peaks corresponding to Mg, Al, Zn, C, O, P, and Ca, which agrees with EDS results. The high-resolution spectrum for Mg displayed one peak centered at 50.4 eV, which has been associated to Mg(OH)$_2$ phase, as reported elsewhere. On the other hand, the spectrum for Ca split into two peaks centered at 347.4 eV and 351.1 eV as a result of spin orbit splitting, whereas the spectrum for P exhibit one peak at 133.3 eV originated from bonding between (PO$_4$)$_3$$^-$ and Ca in the form of calcium phosphate. Thus, it may be considered that the layer of corrosion products on AZ31B consists mainly of Mg(OH)$_2$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$.

Figure 1D shows the alloy surface after removal of the corrosion products. The cleaning procedure revealed a non-localized attack on the surface of AZ31B after 48 h of exposure in SBF. SEM-EDS analysis coincide with those observed before immersion (Figure 1A), corresponding to the alloy matrix and Al-Mn intermetallics. Figure 3 presents SEM images of AZ31B surface after removal of the corrosion layer (Figure 3A) and a cross-sectional image (Figure 3B), which shows that the corrosion attack was quasi-uniform.

Test solution monitoring and mass loss measurements.—Figure 4 presents the SBF pH values and concentration of Mg$^{2+}$ released ions from AZ31B surface into the solution after 24 h and 48 h of immersion. A minimal increase of pH was recorded, as expected for the SBF buffered solution. However, the pH increment ($\Delta$PH) diminished over time. The same trend was observed for Mg ion concentration, which suggests the formation of a partially protective corrosion products layer, as observed by SEM-EDS.

In addition, average corrosion rates (CR) were determined through mass loss, according to the following equation:

$$CR = \frac{(K \cdot \Delta m) \cdot (A \cdot t \cdot \rho)^{-1}} {3} \quad [3]$$

Figure 2. XPS spectra acquired from AZ31B surface after 48 h of immersion in SBF.
solution in form of Mg ions. Further, it has been reported that when Mg alloys are immersed in physiological solution, the existing chloride ions (concentration of about 0.1 M) transform the insoluble Mg(OH)₂ produced on the underlying magnesium matrix into highly soluble MgCl₂ (Equation 4), which is easily dissolved in body fluid (Equation 5):

\[
\text{Mg(OH)}_2 + 2\text{Cl}^- \rightarrow \text{MgCl}_2 + 2\text{OH}^- \quad [4]
\]

\[
\text{MgCl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^- \quad [5]
\]

Electrochemical noise analysis.—Fluctuations of potential and current recorded for 48 h are shown in Figure 5. It can be seen that during the first 16–18 hours both time records were unstable. The corrosion potential shifted gradually (350 mV approximately) to less negative values the first 14 h, until it reached a steady state. In the meantime, the current density decreased (in around 190 μA cm⁻²) till a minimum peak was attained, and then it increased (in about 60 μA) and stabilized. This initial behavior was related with a fast corrosion and film-forming process occurring at alloy surface. It should be noted that the recorded current variation (Figure 5B) represents both processes, anodic dissolution and hydrogen evolution cathodic one, which occurred on the magnesium alloy surface of AZ31B (Equations 1 and 2). For this reason, starting from positive anodic current values, a shift to negative ones could be considered as a contribution of the intensive cathodic hydrogen evolution (Equation 2). This non-stationary stage will be further evaluated and discussed in SECM section.

The steady state of both signals after 18 h indicates equilibrium at alloy/SBF interface. A stationary EN signal is mandatory for second-order statistics, such as PSD, to be valid.66 Thereby, a window from 18 to 48 hours (Figure 5A) exhibited a decreasing behavior of approximately 25 mV, which suggests slow and smooth degradation of the metal surface.

From current data (Figure 5B, highlighted section), the pitting index (PI) was calculated (Equation 6) in order to disclose AZ31B susceptibility to localized corrosion:

\[
\text{PI} = \sigma_i/i_{\text{rms}} = (198.03 \text{nA})/(415.28 \text{nA})^{-1} = 0.47 
\]

where \(\sigma_i\) and \(i_{\text{rms}}\) are the standard deviation and the root mean square of current noise, respectively. According to ASTM standard related to EN,35 PI values above 0.6 may indicate localized corrosion. Thus, the calculated PI value suggests that AZ31B may not present pitting corrosion in SBF solution for up to 48 h of exposure.

Figure 6 displays the PSD plot of the preprocessed current signal from the marked section in Figure 5B, and its corresponding slope (β), also known as spectral power exponent. According to fractal analysis, this β value is related to fractional Gaussian noise process (fGn, \(-1 < \beta < 1\)).72–75 The fGn is a representative property of self-similarity and persistent stationary processes, as suggested by Eke et al.36 Thus, the EN results lead to the conclusion that the quasi-uniform corrosion of AZ31B in SBF from 18 h to 48 h of immersion was a stationary persistent process. The persistence measures the correlations between adjacent values within a time series, whereas the stationary persistence seems to be high and the uniform corrosion seems to be low.

| Period (h) | \(\Delta m\) (mg) | \([\text{Mg}^{2+}]\) (mg cm⁻²) | CR (mm yr⁻¹) |
|-----------|-----------------|-------------------------------|--------------|
| 24        | 5.0 ± 0.05      | 2.18 ± 0.015                 | 5.55 ± 0.08  |
| 48        | 5.3 ± 0.10      | 3.09 ± 0.020                 | 3.31 ± 0.10  |

**Table II. Corrosion rates of AZ31B in SBF, mass loss, and Mg²⁺ concentration.**

On the other hand, when comparing \(\Delta m\) and \([\text{Mg}^{2+}]\) values (Table II), it can be suggested that a fraction of the mass is transformed into corrosion products, whereas the other portion is released to the corrosion products layer, which slows down the anodic dissolution of AZ31B.

where \(K = 8.76 \times 10^4\) (dimensionless constant); \(\Delta m = \text{mass loss (g)}\); \(A = \text{area (cm}^2\); \(t = \text{time (h)}\); \(\rho = 1.738 \text{ g cm}^{-3}\). The CR units were expressed in mm year⁻¹ and their calculated values for each period are presented in Table II. The decrease of CR after 48 h, compared to that of 24 h, is another indication of the formation of the partially protective corrosion products layer, which slows down the anodic dissolution of AZ31B.

**Figure 3.** SEM images of (A) AZ31B surface at 100X, and (B) its cross-section, after corrosion products removal.

**Figure 4.** Monitored changes in pH and [Mg²⁺] during AZ31B exposure to SBF.
aspect reflects that all moments are independent of the length of the time series. The latter could be related to partial passivity state of AZ31B, due to the formed corrosion layer, which promotes a slower degradation in SBF.

H$_2$ detection with SECM.—Figure 7 shows hydrogen evolution maps and optical images acquired over the AZ31B surface at early times of exposure to SBF. High levels of H$_2$ evolution (Equation 2) are indicated in the maps by the reddish colors.

It can be observed (Figure 7A) that hydrogen evolution is highly localized at 1 hour of immersion. Such activity was attributed to the presence of an Al-Mn intermetallic particle on alloy surface (as seen in Figure 7D), which acted as a cathode for Mg matrix corrosion. This result agrees with the SEM-EDS surface characterization results (Figures 1). After 1.5 and 2 hours of immersion (Figures 7B and 7C), H$_2$ flux gradually decreased over time. Farther times of exposure will lead to similar current response observed in Figure 7C.

Hence, the unstable stage observed during the first hours of EN experiments is probably due to the intense heterogeneous activity between the alloy matrix and the Al-Mn cathodic particles. This fact was also observed in the current noise signal, when an evident decay occurs from 0 h up to around 2 h. After that time, the alloy/SBF interface seems to be more equilibrated. All results obtained in this study with different tests and techniques point to that the rapid formation of the corrosion products film decreased both degradation and H$_2$ evolution rates.

Conclusions
A successful multi-scale electrochemical characterization of AZ31B magnesium alloy in simulated body fluid (SBF) was carried out with EN and SECM techniques, combined with SEM-EDS analysis and immersion tests. The in situ obtained results indicated that the sharp initial fluctuations of the electrochemical signals monitored by EN technique were related with a rapid corrosion and film-forming process since the first hours of alloy immersion. Moreover, SECM and SEM-EDS results revealed that the cathodic sites correspond to Al-Mn phases, where H$_2$ evolved intensely from the alloy surface during its very early stages of exposure to SBF. The H$_2$ evolution rate, the corrosion rate, and the $\Delta$PH decreased over time due to the formation of a corrosion products layer, as evidenced by SECM, SEM, and immersion tests results. EDS and XPS analysis showed that such a layer mainly contained Mg, Al, Zn, C, O, P, and Ca, which correspond to Mg(OH)$_2$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ phases. During EN measurements, the potential and current density values reached steady state, which allowed the analysis of the electrochemical signals in both time and frequency domains. A quasi-uniform corrosion process of AZ31B in SBF was proposed, after visual inspection of both current and potential signals, as well of a pitting index calculation. In addition, SEM images, acquired after corrosion product removal, revealed a non-localized attack on the alloy surface. Spectral power exponent $\beta$, calculated from PSD plots, indicated that the degradation of AZ31B in SBF was a persistent stationary process, related to fractional Gaussian noise.

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Figure 7. SECM plots of hydrogen evolution from AZ31B surface in SBF at: (A) 1, (B) 1.5, and (C) 2 hours of immersion. Scan dimensions: 200 μm x 200 μm. Color scale indicates tip current (nA). Dotted outline on plots indicates alloy border. Optical images acquired (D) before, and (E) after the experiment.
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