# Analysis of the degradation process and electrochemical behaviour of AZ31 magnesium alloy in artificial saliva

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**ABSTRACT:** This work applies a combination of immersion tests, surface analysis techniques, and electrochemical methods to characterise the degradation process of AZ31 magnesium alloy when it is exposed to artificial saliva for 28 days. The surface of the alloy was evaluated in two conditions: bare and with an MgF<sub>2</sub> layer. This conversion layer was formed by soaking AZ31 in hydrofluoric acid (HF). SEM images revealed differences in the corrosion attack of the two surface conditions, specifically in the vicinity of Al-Mn intermetallic particles. Both EDS and XPS analysis indicated that the composition of the corrosion layers formed during immersion tests corresponds mainly to Mg(OH)<sub>2</sub> and Ca<sub>10</sub>(PO<sub>4</sub>)6(OH)<sub>2</sub> for the bare sample, whereas for the treated surface the principal corrosion product was MgCO<sub>3</sub>. The polarisation resistance ( $R_p$ ) value estimated from EIS experiments was two orders of magnitude higher for the HF-treated samples than that of the bare samples. In addition, the corrosion rate (*CR*) calculated from the potentiodynamic polarisation (PDP) curves was lower for the HF-treated surface than for that of the bare AZ31 surface. All results indicate that the HF-treatment on AZ31 magnesium alloy surface improves significantly its corrosion resistance in artificial saliva.

**KEYWORDS:** Artificial saliva; AZ31; Degradation rate; EIS; HF treatment; Polarisation curves; Polarisation resistance

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**RESUMEN:** Análisis del proceso de degradación y comportamiento electroquímico de la aleación de magnesio AZ31 en saliva artificial. En el presente trabajo se ha aplicado una combinación de pruebas de inmersión, técnicas de análisis de superficie y métodos electroquímicos para caracterizar el proceso de degradación de la aleación de magnesio AZ31 cuando ha sido expuesta a saliva artificial durante 28 días. La superficie de la aleación fue evaluada en dos condiciones: simple y con una capa de MgF<sub>2</sub>. Esta capa de conversión se formó sumergiendo el AZ31 en ácido fluorhídrico (HF). Las imágenes SEM revelaron diferencias en el ataque de corrosión de las dos condiciones de la superficie, específicamente en la vecindad de las partículas inter-metálicas de Al-Mn. Tanto el análisis EDS como XPS indicaron que la composición de las capas de corrosión formadas durante las pruebas de inmersión corresponde principalmente a Mg(OH)<sub>2</sub> y Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> para la muestra simple, mientras que para la superficie tratada el producto de corrosión principal fue MgCO<sub>3</sub>. El valor de resistencia a la polarización ( $R_p$ ) estimado a partir de los experimentos EIS fue dos órdenes de magnitud mayor para las muestras tratadas con HF que para las muestras simples. Además, la velocidad de corrosión (CR) calculada a partir de las curvas de polarización potenciodinámica (PDP) fue menor para la superficie tratada con HF que para la superficie simple de AZ31. Todos los resultados han indicado que el tratamiento con HF en la superficie de aleación de magnesio AZ31 mejora significativamente su resistencia a la corrosión en saliva artificial.

**PALABRAS CLAVE:** AZ31; Curvas de polarización; EIS; Resistencia a la polarización; Saliva artificial; Tratamiento en HF; Velocidad de degradación

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## **1. INTRODUCTION**

Metallic dental implants usually display electrochemical activity when in contact with the fluids in the oral cavity. The anodic and cathodic reactions occur at the metal/electrolyte interface, leading to the emission of free electrons when the oxidation of the metal occurs, which produces a corrosive attack on the metal surface. The common metals employed for dental implants are titanium, gold, silver, platinum, stainless steels, and other alloys, as Ni-Ti based alloys (Echavarria and Arroyave, 2003). Nevertheless, those materials may release toxic ions into the human body, and present a mismatch in mechanical properties, which leads to stress shielding effects on the surrounding bone (Poinern et al., 2012). The products released during corrosion may cause allergic reactions and discolouration of soft tissues around the implant. Among the allergies are oral edema, perioral stomatitis, gingivitis, and some produce eczematous eruptions in patients prone to this type of reaction (Chaturvedi, 2009).

Magnesium alloys as new materials for biodegradable implants have been object of study due to their unique features, including adequate mechanical properties, high biocompatibility, and non-toxicity (Riaz et al., 2018). However, Mg-based materials are very reactive in aqueous solutions containing chlorides, such as physiological fluids. As a consequence, a rapid degradation of Mg and its alloys is observed and thus, the reduction in the mechanical stability, due to a stress corrosion cracking effect (Asgari et al., 2018). Therefore, it is necessary to develop strategies to diminish the degradation rate of Mg alloys when they are exposed to body fluids. For instance, Wen et al. (2009) developed a hydroxyapatite coating on AZ31 magnesium alloy surface by soaking the alloy samples in HF for 10 minutes, in order to activate their surface, and then applying a cathodic electrodeposition method. The resulting surface modification improved the corrosion resistance of AZ31 when immersed in simulated body fluid (SBF). Moreover, Carboneras et al. (2011) reported the application of a HF treatment on AZ31 surface for 24 h. They concluded that such treatment enhanced the growth of osteoblastic cells in vitro and permitted the formation of new bone tissue in vivo.

The use of artificial saliva for the assessment of dental alloys enables oral cavity conditions to be simulated, where the pH and chloride concentration play an important role in determining the corrosivity of this medium (Renita *et al.*, 2016). The aim of the present investigation was to assess the degradation process and electrochemical behaviour of AZ31 when it has been exposed to artificial saliva for 28 days and compare the performance between bare and HF-treated surfaces.

#### 2. MATERIALS AND METHODS

#### 2.1. Samples and solution preparation

The AZ31 magnesium alloy (Alfa Aesar, Ward Hill, MA, USA) employed in this work was composed (in weight percentage) of 3% Al, 1% Zn, 0.2 % Mn, and Mg the remaining. The alloy was cut into sheets of 1 cm x 1 cm x 0.1 cm, and all surfaces were sanded with SiC papers from 400 to 1200 grit, polished with a 0.3 µm alumina ethanolic suspension, sonicated in ethanol for two minutes, and dried in air at room temperature (21 °C). Some of the samples were immersed in a hydrofluoric acid (HF) solution at 40% for 48 hours, then triple rinsed with distilled water and dried in air at room temperature. The artificial saliva solution (pH = 7) was prepared according to literature (Eisenburger et al., 2001) employing the following reagents with analytical grade: 0.1029 g CaCl<sub>2</sub>·2H<sub>2</sub>O, 0.04066 g MgCl<sub>2</sub>, 0.544 g KH<sub>2</sub>PO<sub>4</sub>, 4.766 g HEPES, 2.2365 g KCl, and 1000 mL of ultrapure deionized water (18.2 M $\Omega$ · cm).

#### **2.2. Immersion tests and surface characterisation**

The AZ31 samples were divided into two sets: bare and treated with HF. They were immersed in triplicate in 30 mL of artificial saliva solution for periods of 7, 14, and 28 days at room temperature, according to ISO 16428 (2005). The solution was replaced every day in order to maintain a constant pH value and mimic excretion conditions.

The surface of AZ31 in its two different conditions was analyzed through scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS, Jeol JSM-7600F, Japan). The corrosion products layers formed after each period of exposure to artificial saliva were characterised by SEM-EDS, as well as by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, Waltham, MA, USA). The exposed AZ31 surfaces were evaluated by SEM after a cleaning procedure done as specified by ASTM G1-03 (2017).

#### **2.3. Electrochemical experiments**

A three-electrode cell configuration was employed for electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP) measurements, with the AZ31 samples (bare and treated) as working electrodes, a platinum mesh (Alfa Aesar, Ward Hill, MA, USA) as auxiliary, and a saturated Ag/AgCl/KCl reference electrode (CH Instruments Inc., Austin, TX, USA). The experiments were conducted with an Interface-1000E potentiostat (Gamry Instruments, Inc., Philadelphia, PA, USA), with the electrochemical cell inside a Faraday cage. The working electrode area was 0.8 cm<sup>2</sup>. The EIS data was acquired after 30 min of immersion of the

working electrode in artificial saliva, once the open circuit potential (OCP) was stable. The AC perturbation signal applied during EIS measurements was  $\pm 10 \text{ mV}$  (vs OCP), with a frequency interval from 100 kHz to 10 mHz. The EIS spectra were analysed with the Gamry Echem Analyst software (Gamry Instruments, Inc.), which was employed to fit an electrical equivalent circuit to the impedance data. The PDP scans were carried out after 30 min of immersion in artificial saliva, by applying polarisation from the OCP to  $\pm 0.5$  V, with a scan rate of 1 mV s<sup>-1</sup>. The obtained PDP curves were examined with the Gamry Echem Analyst software in order to calculate the corrosion rates through Tafel extrapolation method, as stated by the ASTM G102-89 (2015).

## 3. RESULTS AND DISCUSSION

# 3.1. Surface analysis by SEM-EDS

Figure 1 shows SEM images of the AZ31 surface before and after the treatment in HF. Table 1 present the EDS quantification of the marked sites in Fig. 1. The bare surface of the alloy displays the typical microstructure of AZ31 (Mena-Morcillo *et al.*, 2018), where the composition of the  $\alpha$ -matrix (site 1) and that of the Al-Mn intermetallics (site 2) was confirmed with the EDS analysis. In the case of the treated surface, the formed layer after its immersion in HF for 48 h presented evident roughness caused by the treatment itself, and the composition of such layer (site 3) was correlated with the MgF<sub>2</sub> phase, as reported by Da Conceicao *et al.* (2010).

The SEM images of the surfaces (bare and HF-treated) after immersion tests for 7, 14, and 28 days are displayed in Fig. 2. In general, the layer on the bare surface of AZ31 (Figs. 2A, 2C,

and 2E) was very cracked and presented several products/deposits on it, whereas on the HF-treated surface (Figs. 2B, 2D, and 2F) such layer was less cracked and with less deposits on it. After exposure to artificial saliva for 28 days, the corrosion layers formed on the AZ31 surfaces (Figs. 2E and 2F) were analyzed with EDS, and the acquired results are presented in Table 2. On the AZ31 bare surface (Fig. 2E), the corrosion product (site 1) has a high weight percentage of oxygen, reaching the 70% of the total quantification, suggesting that the oxygen may be related to oxides/hydroxides, with the presence of P and Ca. Meanwhile, on the cracked layer (site 2), O, P, and Ca are the elements with a higher percentage, which fact may be attributed to the deposited layer of the calcium phosphate phase. The products/deposits on the HF-treated surface (Fig. 2F, site 3) had oxygen and carbon as the elements with higher weight percentage, whereas the surface layer (site 4) is composed by the F element, having about 50 % quantification value, as a part of the MgF<sub>2</sub> layer. As additional elements, C, Ca y P were also present. Figure 3 shows the surface of the bare AZ31 after corrosion products removal. It can be observed that the corrosion damage caused deep cavities with different size, in the vicinity of the

 TABLE 1.
 Chemical composition (in wt.%) of the marked sites in Fig. 1 obtained by EDS

Element	Site 1	Site 2	Site 3
Mg	96.45	38.04	39.19
Al	2.57	45.30	1.11
Zn	0.98	-	0.27
Mn	-	16.66	-
F	-	-	59.43



FIGURE 1. SEM images of the surface of AZ31: (A) prior to the HF-treatment, (B) after the HF-treatment. The marked regions indicate the sites were EDS analysis was performed.



FIGURE 2. SEM images of the surface of AZ31 immersed in artificial saliva for: (A) 7 days, bare; (B) 7 days, HF-treated; (C) 14 days, bare (D) 14 days, HF-treated; (E) 28 days, bare; (F) 28 days, HF-treated.

TABLE 2. EDS quantification (in wt.%) of the layers formed on AZ31 bare surface and HF-treated, after their immersion in artificial saliva for 28 days

Element	Site 1 (bare)	Site 2 (bare)	Site 3 (HF-treated)	Site 4 (HF-treated)
Mg	4.57	13.18	5.26	15.60
Al	3.52	4.89	2.95	0.95
Zn	0.34	4.13	0.51	0.23
F	-	-	1.73	51.16
С	7.31	3.78	12.61	5.74
0	70.03	35.19	60.54	19.95
Р	9.12	19.99	9.47	4.06
Ca	3.66	18.84	4.73	2.14
K	1.45	-	2.20	0.17

Al-Mn intermetallic particles, which served as cathodes and maintained on the surface. The attack on the bare sample was more pronounced than on the treated one.

## 3.2. Surface characterisation through XPS

In order to confirm the phases formed on the AZ31 surfaces (bare and HF-treated), XPS analysis was performed on the samples exposed to artificial saliva for 28 days. The full XPS spectrum (Fig. 4) of the bare surface revealed peaks of Mg, Zn, O, Ca, C and P, whereas the HF-treated surface (Fig. 5) displayed peaks of Mg, F, O, C and P. The value of the binding energies of Mg showed one peak centered approximately: at 50.5 eV for the bare surface, and at

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FIGURE 3. SEM images of the AZ31 surface after corrosion products removal: (A) bare, and (B) with HF-treatment.



FIGURE 4. XPS full spectrum and high-resolution spectra of the elements of interest observed on the bare surface of AZ31 after immersion for 28 days in artificial saliva.



FIGURE 5. XPS full spectrum and high-resolution spectra of the elements of interest observed on the HF-treated surface of AZ31 exposed for 28 days in artificial saliva.

51.5 eV for the HF-treated surface, which are associated to Mg(OH)<sub>2</sub> and MgCO<sub>3</sub> respectively (Moulder, *et al.*, 1992). In the case of the bare sample, it can be seen that the spectrum for Ca shows two peaks centered at 347.9 eV and 351.5 eV approximately, whereas the spectrum for P has one peak at 134 eV. These values are linked to the bonding between  $(PO_4)_3^-$  and Ca in the form of  $Ca_{10}(PO_4)_6(OH)_2$  (Mena-Morcillo *et al.*, 2018). On the other hand, for the HF-treated sample, the spectrum for F showed a peak positioned at about 685.4 eV, which is related to the MgF<sub>2</sub> phase (Moulder *et al.*, 1992). The XPS results showed to be well correlated with the EDS quantification values obtained in the previous section (Table 2).

#### **3.3. Electrochemical tests**

Figure 6 illustrates the EIS Nyquist diagrams performed for both bare and HF-treated AZ31 surfaces, after their exposure to artificial saliva for 30 min. The data were fitted to an equivalent electrical circuit (Fig. 6), the parameters of which are presented in Table 3. According to Murray *et al.* (1988),  $R_s$  is associated with the resistance of the solutions,  $R_1$  with the initial corrosion stage,  $R_2$  with the discharge of intermediate adsorbed species. These resistive parameters could also be related to local changes occurring close to anodic and cathodic regions, such as the presence of H<sub>2</sub> bubbles (Curioni *et al.*, 2015). The capacitive elements



FIGURE 6. Nyquist diagrams of the EIS data obtained for the bare and treated surfaces of AZ31 alloy, after 30 min of immersion in artificial saliva. The dashed lines correspond to the equivalent electrical circuit fitting.

TABLE 3. Fitting parameters of the equivalent electrical circuit obtained from the EIS spectra (Fig. 6) of AZ31 bare surface and HF-treated, exposed to artificial saliva

Parameter	Bare surface	HF-treated
$R_S(\Omega \text{ cm}^2)$	387.0	384.3
$CPE_I$ (µF cm <sup>-2</sup> )	10.9E	22.3
$n_1$	0.86	0.93
$R_I(\mathrm{k}\Omega~\mathrm{cm}^2)$	3.0	795.7
$CPE_2$ (mF cm <sup>-2</sup> )	0.87	3.28
$n_2$	0.90	0.42
$R_2$ (k $\Omega$ cm <sup>2</sup> )	1.34	19.95
$R_P (\mathrm{k}\Omega \mathrm{cm}^2)$	4.34	815.65

 $CPE_1$ , and  $CPE_2$  represent the capacitance of the corrosion product film and the capacitance formed by the double layer at the metal/electrolyte interface, respectively (Delgado *et al.*, 2017).

From the fitting parameters, it was possible to calculate the polarisation resistance  $(R_p)$  value for each surface condition. The  $R_p$  is inversely proportional to the corrosion current density, as shown in the Stern-Geary Eq. (1):

$$j_{corr} = B / R_p \tag{1}$$

where  $j_{corr}$  is the corrosion current density, *B* is the Stern-Geary constant, and  $R_p$  is the polarisation resistance value. Thus, if the  $R_p$  value increases, the  $j_{corr}$  decreases, which leads to a lower corrosion rate, as stated by ASTM G102-89 (2015). The  $R_p$ value for the bare surface was 4.34 k $\Omega$  cm<sup>2</sup>, while the  $R_p$  for the treated surface was 815.65 k $\Omega$  cm<sup>2</sup>. The above indicates that the  $j_{corr}$  value (related to the corrosion rate) of the treated surface should be



FIGURE 7. Potentiodynamic polarisation curves (PDP) performed on AZ31 alloy, on bare surface and HF-treated, after 30 min of immersion in artificial saliva.

about two orders of magnitude lower than that of the bare surface.

Figure 7 displays the curves acquired from the potentiodynamic polarisation (PDP) applied on the surface of AZ31 in its different conditions (bare and treated), after 30 min of exposure to artificial saliva. The cathodic curve of the bare surface indicates that the reduction of oxygen is more intense than that corresponding to the HF-treated surface: both facts indicate that this process occurs with a greater difficulty on the HF-treated surface, because of the formed MgF<sub>2</sub> layer. In the anodic curves of AZ31 oxidation it can be observed that the current density values of the bare surface are about two orders higher than those of the HF-treated surface, which is also an indication of a greater corrosion resistance, provided by the protective layer of MgF<sub>2</sub> formed on the HF-treated AZ31 surface. The Tafel extrapolation method was used to estimate the corrosion potential  $(E_{corr})$  and the corrosion current density  $(j_{corr})$ . Additionally, the  $j_{corr}$  value was employed to calculate the instantaneous corrosion rate (CR) of both the bare and treated surface, according to the following Eq. (2) provided by the ASTM G102-89 (2015):

$$CR = K \cdot j_{corr} \cdot E_W / \rho \tag{2}$$

where K is a constant  $(3.27 \times 10^{-3} \text{ mm g/}\mu\text{A cm year})$ ,  $j_{corr}$  is the corrosion current density ( $\mu\text{A}\cdot\text{cm}^{-2}$ ),  $E_W$  is the equivalent weight of AZ31 (12.2, dimensionless),  $\rho$  is the density of AZ31 (1.74 g·cm<sup>-3</sup>). Table 4 shows the estimated values of  $E_{corr}$  and  $j_{corr}$ , as well as the calculated *CR* values. It can be noted that the corrosion rate of the AZ31 HF-treated surface was in fact two orders of magnitude lower than the *CR* of the bare surface, as predicted with the results of EIS.

TABLE 4. Tafel fitting parameters obtained from the PDP curves (Fig. 7) for AZ31 alloy, on bare surface and HF-treated, after 30 min of immersion in artificial saliva

Surface condition	$E_{corr}$ (V)	j <sub>corr</sub> (A·cm <sup>-2</sup> )	CR (mm·year <sup>-1</sup> )
Bare surface	-1.57	0.98E-6	2.26E-8
HF-Treated	-1.59	1.12E-8	2.56E-10

# 4. CONCLUSIONS

- The degradation process and electrochemical behaviour of AZ31 in artificial saliva was evaluated in two different surface conditions: bare and HF-treated. The morphology of the exposed surfaces, evaluated in different periods of immersion, showed cracked layers and formation of products (deposits), with greater damage in the case of the untreated samples. The corrosion attack on the bare AZ31 presented deep cavities with different size, in the vicinity of the Al-Mn intermetallic particles, which served as cathodes. On the HF-treated surface, the corrosion layer was thin and less aggressive attack was observed. The corrosion products detected by EDS and confirmed with XPS on the surface of the bare sample correspond to Mg(OH)<sub>2</sub> and deposits of  $Ca_{10}(PO_4)_6(OH)_2$ , whereas for the HF-treated sample it was possible to detect MgCO<sub>3</sub> phase.
- The EIS results indicated that the polarisation resistance  $(R_p)$ , which is related to the corrosion rate, was 2 orders of magnitude higher for the HF-treated AZ31 surface than for the bare surface.
- The corrosion rates (CR) calculated from the potentiodynamic polarisation (PDP) curves agree with the EIS results, since the CR of HF-treated AZ31 was two orders of magnitude lower than the CR of bare surface. Results indicate that the HF-treatment significantly improves the corrosion resistance of AZ31 magnesium alloy when exposed to artificial saliva up to 28 days.

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