# Electrochemical assessment of the Mg-Zn-Ca alloy degradation in Hanks' physiological solution

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**ABSTRACT:** The effect of Zn (0.95% wt.) and Ca (0.15% wt.) alloying elements on the general degradation mechanism of Mg was investigated in this work. Pure Mg and Mg-Zn-Ca alloy surfaces were characterized during their exposure to Hanks' physiological solution (at 37 °C) for up to 7 days by SEM-EDS and XPS techniques. The layers formed on the alloy surface contained Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, which may improve the bone compatibility. The intermetallic particles composed of Mg<sub>2</sub>Ca-phase, as well as the presence of Zn, promoted the formation of a more uniform protective layer. The EIS and electrochemical noise (EN) tests indicated that the polarization resistance ( $R_p$ ) of pure Mg is one order of magnitude lower and the current noise resistance ( $R_n$ )  $\approx$  5 times, than those of Mg-Zn-Ca alloy. The pitting index (PI) values of each material were below 0.6, suggesting that the corrosion attack is not highly localized. At the end of the immersion tests, the concentration of Mg-Zn-Ca ( $0.35 \pm 0.03 \text{ mg}\cdot\text{cm}^{-2}$ ). Consequently, the calculated corrosion current density ( $j_{corr}$ ) for pure Mg was two times higher (1.33  $\mu$ A·cm<sup>-2</sup>) than that of ZX10 Mg-alloy (0.59  $\mu$ A·cm<sup>-2</sup>).

KEYWORDS: EIS; Magnesium; Mg-ion release; MgZnCa alloy; PDP; SEM-EDS; XPS

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**RESUMEN:** Evaluación electroquímica de la degradación de la aleación de Mg-Zn-Ca en la solución fisiológica de Hanks. En el presente trabajo se ha investigado el efecto de los elementos aleantes Zn (0,95% en masa) y Ca (0,15% en masa) en el mecanismo de degradación del Mg. Las superficies del Mg puro y de la aleación Mg-Zn-Ca han sido caracterizadas durante su exposición a la solución fisiológica de Hanks (a 37 °C) hasta siete días, utilizando las técnicas SEM-EDS y XPS. La capa formada en la superficie de la aleación contiene Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, que puede mejorar la compatibilidad ósea. Las partículas intermetálicas compuestas de la fase Mg<sub>2</sub>Ca, así como la presencia de Zn, han promovido la formación de una capa protectora más uniforme. Las pruebas de EIS y ruido electroquímico (EN) han indicado que la resistencia a la polarización ( $R_p$ ) del Mg puro es un orden de magnitud menor y la resistencia al ruido de la corriente ( $R_n$ ) ≈ 5 veces menor, que los de la aleación de Mg-Zn-Ca. Los valores del índice de picadura (PI) de cada material fueron inferiores a 0,6; lo que sugiere que el ataque de corrosión no está altamente localizado. Al final de las pruebas de inmersión, la concentración de iones de Mg liberados durante la degradación ha sido ≈ 4,5 veces mayor para Mg puro (1,63 ± 0,02 mg·cm<sup>-2</sup>) que para Mg-Zn-Ca (0,35 ± 0,03 mg·cm<sup>-2</sup>). En consecuencia, la densidad de corriente de corrosión ( $j_{corr}$ ) calculada para el Mg puro fue dos veces mayor (1,33  $\mu$ A·cm<sup>-2</sup>) que la de la aleación de Mg ZX10 (0,59  $\mu$ A·cm<sup>-2</sup>).

PALABRAS CLAVE: Aleación MgZnCa; EIS; Liberación de iones de Mg; Magnesio; PDP; SEM-EDS; XPS

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## **1. INTRODUCTION**

Mg-based biomaterials have attracted an increasing interest for their application as resorbable temporary implants, owing to the combination of high strength and ductility that they exhibit, the value of Young's modulus of Mg (40 GPa, close to cancellous bones) and their degradability in physiological medium (Zhang et al., 2011; Hänzi et al., 2012; Bohlen et al., 2015). During these materials degradation process Mg-ions are released, which are involved in various chemical reactions in the human body, as well as in the bone healing (Yamasaki *et al.*, 2002; Zreiqat et al., 2002; Yamasaki et al., 2003; Revell et al., 2004), that may be enhanced when Mg is alloyed with Zn and Ca elements (Tapiero and Tew, 2003; Stefanidou et al., 2006). The ZX series of Mg-Zn-Ca alloys have been thermo-mechanical processed in order to refine their grain sizes (Zhang et al., 2010; Zhang et al., 2012) and develop a weak basal fiber texture by hot extrusion (Li et al., 2015). Both modifications improve significantly the corrosion properties of these alloys (Hofstetter et al., 2014; Jafari et al., 2017).

The aim of this work is to characterize the initial stages of electrochemical degradation of one representative of Mg-Zn-Ca alloys (ZX10) and compare its activity with pure Mg, during their immersion for 168 h (7 days) in Hanks' physiological medium (at 37 °C). By means of electrochemical impedance spectroscopy (EIS), electrochemical noise (EN), and potentiodynamic polarization (PDP) techniques, the calculation of important parameters is provided. The obtained results were correlated with SEM-EDS and XPS surface characterization of the formed surface layers and concentration of Mg-ions release. To our knowledge, the electrochemical degradation behaviour of ZX10 in Hanks' solution has not been reported yet.

## 2. MATERIALS AND METHODS

#### 2.1. Materials and electrolyte preparation

The ZX10 alloy and pure Mg (99.99%) were fabricated by Magnesium Innovation Center MagIC in extruded bar form. The chemical composition (wt.%) of ZX10 is: Al (0.01), Cu (0.0014), Mn (0.0034), Fe (0.0023), Zn (0.95), Ca (0.15), Si (0.0032), Ce (0.00272) and Mg (balance).

Both materials were cut into disc-shaped samples of about  $0.8 \text{ cm}^2$ , some of which were used for immersion tests and others were embedded in epoxy resin for electrochemical experiments. Prior to measurements, all samples were abraded with subsequent 400 to 4000 grit SiC papers, sonicated with ethanol, and dried in air at room temperature.

The electrolyte employed in this study was the Hanks' physiological solution, which was prepared

with the following reagents (analytical grade): NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, CaCl<sub>2</sub>, and ultrapure deionized water (18.2 M $\Omega$ ·cm) as described elsewhere (Kuwahara *et al.*, 2001).

#### 2.2. Electrochemical experiments

A three-electrode cell configuration was employed for electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP) measurement, carried out applying an Interface-1000E potentiostat (Gamry Instruments Inc., Philadelphia, PA, USA), with the cell inside a Faraday cage. The pure Mg and ZX10 alloy samples were used as working electrodes, whereas a Pt mesh (Alfa Aesar, Ward Hill, MA, USA) and a SCE reference electrode (CH Instruments Inc., Austin, TX, USA), to were employed to complete the electrochemical cell. The impedance spectra were obtained at 48, 120 and 168 h of samples immersion in Hanks' solution, using a perturbation amplitude of  $\pm 10 \text{ mV}$  (vs open circuit potential, OCP), and a frequency interval from 100 kHz to 10 mHz. EIS data were analyzed and fitted to electric equivalent circuits with Gamry Elchem Analyst software (Gamry Instruments Inc., Philadelphia, PA, USA).

On the other hand, for the electrochemical noise (EN) monitoring of potential and current fluctuations, two identical working electrodes of each material (pure Mg and ZX10) and the SCE reference electrode were connected to the potentiostat in zero resistance ammeter (ZRA) mode. The EN measurements were carried out according to ASTM G199-09 (2014). The potential and current noise signals were acquired at OCP conditions after 168 h. EN results were plotted versus time, and visually inspected to detect the occurrence rate of the time transients. In addition, noise resistance value  $(R_n)$  and the pitting index (PI) were calculated from both potential and current time series. Data acquisition and calculations were performed with Electrochemical Signal Analyzer V.7.0.1 software (Gamry Instruments Inc., Philadelphia, PA, USA).

The potentiodynamic cathodic and anodic scans (PDP) were carried out after an hour of samples immersed in Hanks' solution to establish a steady state OCP, and then starting from -0.5 V to +0.5 V vs OCP, at a scan rate of 1 mV·s<sup>-1</sup>. The values of  $E_{corr}$  and  $j_{corr}$  were obtained from PDP curves, according to ASTM G102-89e1 (2015), in order compare the corrosion rate (CR) of pure Mg and ZX10 alloy.

# 2.3. Immersion tests and characterization of the surface

Samples of pure Mg and ZX10 were exposed in triplicate to Hanks' solution (20 mL) maintained at 37 °C for 168 h, following ISO 16428 (2005).

The electrolyte was replaced every 8 h in order to maintain a constant pH value and avoid alkalization (Zainal et al., 2011). The wastes were stored in independent containers for their further analysis by photometry (HI83200, Hanna Instruments, Woonsocket, RI, USA), in order to measure the concentration of the released Mg-ions. At the end of the tests, the samples were withdrawn, rinsed with deionized water, and dried in air at room temperature. Field scanning electron microscopy coupled with energy dispersive X-ray spectrometry (FESEM-EDS, Jeol JSM-7600F, Japan) and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, Waltham, MA, USA) were employed to characterize the surfaces of pure Mg and ZX10, before and after their exposure to Hanks' solution. Mass loss measurements were carried out according to ASTM G31-12a (2012) at the end of the immersion tests.

#### **3. RESULTS AND DISCUSSION**

#### **3.1. Electrochemical tests results**

The EIS Nyquist diagrams of pure Mg and ZX10 alloy exposed to Hank's solution for 168 h (7 days) are shown in Fig. 1, as well as the electrical

equivalent circuit used to fit and model the EIS spectra (Song *et al.*, 2012; Song *et al.*, 2014; Roche *et al.*, 2019). In addition to the solution resistance  $(R_s)$ , the suggested circuit includes a constant phase element  $(CPE_l)$ , and a resistance  $(R_l)$ , both associated with the double layer and charge transfer resistance. The capacitor  $CPE_2$  ( $Q_2$ ) and resistance  $R_2$  are characteristic of the corrosion process, which occurs at the metal surface through the corrosion layer. The constant phase elements (*CPEs*) have been used, because of the microscopic roughness of the sample surfaces, which produces a heterogeneous distribution (Cordoba-Torres *et al.*, 2015).

At high frequencies the EIS Nyquist plots show the total impedance associated with the solution resistance ( $R_s$ ) at the metal-electrolyte interface (Fig. 1). Table 1 and Table 2 displays the fitting parameters corresponding to each exposure time and material.

The Nyquist diagrams (Fig. 1) present two capacitive loops, which are reported to be associated with charge transfer, formed layer effects, and mass transport. Research of authors (Xin *et al.*, 2009) suggest that the general corrosion mechanism of Mg and its alloys involves the oxidation of Mg to  $Mg^{2+}$  with



FIGURE 1. EIS Nyquist diagrams of: (a) pure Mg and (b) ZX10 alloy, for up to 7 days of exposure to Hanks' solution; (c) equivalent circuit employed for EIS fitting.

Pure Mg				
48 h	120 h	168 h		
$90.02 \pm 0.66$	89.80 ± 0.61	$91.32 \pm 0.62$		
$18.11\pm0.17$	$30.92\pm0.81$	$36.23 \pm 0.94$		
$0.89\pm0.007$	$0.89\pm0.005$	$0.88\pm0.004$		
$2.45E3 \pm 86.24$	5.81E3 ± 165.9	5.17 E3 ± 134.2		
$689.1 \pm 107.9$	$922.6 \pm 245.4$	$1320 \pm 412$		
$0.67\pm0.04$	$0.92 \pm 0.11$	$0.80\pm0.05$		
$1.50E3 \pm 92.22$	$1.66E3 \pm 263$	1.35 E3 ± 119.6		
3.91 E3	7.502 E3	6.60 E3		
	48 h $90.02 \pm 0.66$ $18.11 \pm 0.17$ $0.89 \pm 0.007$ $2.45E3 \pm 86.24$ $689.1 \pm 107.9$ $0.67 \pm 0.04$ $1.50E3 \pm 92.22$ $3.91 E3$	Pure Mg48 h120 h $90.02 \pm 0.66$ $89.80 \pm 0.61$ $18.11 \pm 0.17$ $30.92 \pm 0.81$ $0.89 \pm 0.007$ $0.89 \pm 0.005$ $2.45E3 \pm 86.24$ $5.81E3 \pm 165.9$ $689.1 \pm 107.9$ $922.6 \pm 245.4$ $0.67 \pm 0.04$ $0.92 \pm 0.11$ $1.50E3 \pm 92.22$ $1.66E3 \pm 263$ <b>3.91 E37.502 E3</b>		

TABLE 1.Parameters obtained from the EIS spectra fitting of Mg, after their<br/>exposure to Hanks' solution for up to 168 h

 TABLE 2.
 Parameters obtained from the EIS spectra fitting of ZX10 alloy, after their exposure to Hanks' solution for up to 168 h

	ZX10 alloy				
Parameter	48 h	120 h	168 h		
$R_s (\Omega \text{ cm}^2)$	$80.42 \pm 1.87$	$81.18 \pm 1.8$	$66.40 \pm 1.66$		
$CPE_{I}$ (µS s <sup>n</sup> cm <sup>-2</sup> )	$17.31 \pm 0.43$	$2.86 \pm 0.44$	$1.77 \pm 0.19$		
$n_1$	$0.78 \pm 0.003$	$0.73 \pm 0.01$	$0.75 \pm 0.01$		
$R_I(\Omega \text{ cm}^2)$	10.33 E3 ± 322.5	$915.8 \pm 50.4$	1.14 E3 ± 38.9		
$CPE_2$ (µS s <sup>n</sup> cm <sup>-2</sup> )	695.1 ± 247	$8.45 \pm 0.5$	$9.14\pm0.01$		
$n_2$	$0.76 \pm 0.14$	$0.80\pm0.009$	$0.80\pm0.007$		
$R_2 (\Omega \text{ cm}^2)$	$3.04 \text{ E3} \pm 675$	42.81 E3 ± 573	36.91 E3 ± 385.3		
$R_p (\Omega \text{ cm}^2)$	1.35 E4	4.62 E4	3.78 E4		

simultaneous reduction of water. Local alkalization occurs by the cathodic reaction of  $H_2$  evolution that leads to the precipitation of  $Mg(OH)_2$  (Xin *et al.*, 2009; Zhang *et al.*, 2011).

Table 1 (pure Mg) and Table 2 (ZX10 alloy) display the fitted parameters estimated from the EIS diagrams, corresponding to each exposure time and material. It may be seen that the resistance from the oxide layer ( $R_2$ ), as well as the polarization resistance ( $R_p$ ) of pure Mg are in one order of magnitude lower than those of ZX10 alloy.

Figure 2 presents the current noise signals, acquired for Mg and ZX10 alloy samples after 168 h immersion in Hanks' solution. In order to analyzer EN data, a stationary signal is required (Huet, 2006).

Thus, after 168 h of immersion in Hanks' solution both signals presented a steady state, indicating an equilibrium at metal / electrolyte interface (Fig. 2). Both signals revealed fluctuations with low amplitude, which are characteristics of uniform corrosion (Legat and Dolecek, 1995). Small variation in potential fluctuations suggested slow degradation of the both material surfaces.

It can be noted that the fluctuations in current noise are centered closer to zero for the ZX10 alloy than for pure Mg. The current noise resistance  $(R_n)$  was estimated and the values (Table 3) indicate that it is  $\approx 5$  times higher for ZX10 Mg alloy, compared with that of pure Mg.

In order to reveal the susceptibility to localized corrosion of each metals, the pitting index (PI) (Dawson, 1996) was calculated according to the follow equation:

$$PI = \frac{\sigma_i}{I_{rms}} \tag{1}$$

where  $\sigma_j$  is the standard deviation and  $j_{rms}$  is the main square root of current noise.

According to ASTM G199-09 (2014), PI values higher than 0.6 suggest highly localized corrosion. At the end of the test, PI of both materials was less



FIGURE 2. Fluctuations of current noise recorded at 168 h (7 days) for pure Mg (red) and ZX10 alloy (blue) exposure to Hanks' solution.

TABLE 3. Average values of noise resistance  $(R_n)$ , absolute value of the mean current noise  $(j_{mean})$  and pitting index (PI) obtained from the EN

Parameter	Pure Mg	ZX10 alloy	
$R_p (\Omega \text{ cm}^2)$	2.15	11.31	
$j_{mean}(\mu A)$	1.86	0.62	
PI	0.36	0.13	

than 0.6 (Table 3), therefore they seem to present a quasi-uniform corrosion (Mena-Morcillo *et al*, 2018), being the PI of ZX10 alloy about 2.5 times lower than that of pure Mg.

Potentiodynamic polarization (PDP) curves, acquired for pure Mg and ZX10 Mg-alloy after exposure to Hanks' solution for 2 h, are shown in Fig. 3. It can be seen that the PDP curves of ZX10 alloy are shifted to a lower current density region than those of pure Mg. The oxidation (degradation) process of the pure Mg and ZX10 alloy is represented by their anodic polarization branches and they show distinctive inflection points where the curves change their slope. This occurs owing to the kinetic barrier effect, probably through the accumulation of corrosion product layer on the surface, followed by its breakdown at more positive polarization (Zhao et al., 2008; Wang et al., 2010). It seems that on the ZX10 surface, the formed layer has a greater resistant effect and, consequently, the anodic current in the first branch of the curve tends to reach limit value. The cathodic polarization branches of both materials reveal a similar dynamic of the process, attributed to hydrogen evolution by means of reduction of water (Chang et al., 2007). However, the cathodic process occurs in one order lower current densities for ZX10 surface, and this fact coincides with the lower anodic current density



FIGURE 3. Potentiodynamic polarization (PDP) curves of pure Mg and ZX10 alloy after their immersion in Hanks' solution for 2 h.

of the alloy. It may be noted that neither branch, cathodic or anodic, of either material presents Tafel regions.

Because of the absence of Tafel regions, the  $R_p$  value was estimated at small potential polarization (±10 mV) of the anodic polarization branch (Fig. 3) and its respective corrosion current density value  $j_{corr}$  ( $\Delta E/\Delta I$ ) was calculated. Based on Stern-Geary equation, the 'apparent' Tafel constant (B') was estimated, as stated by the ASTM G102-89e1 (2015):

$$i_{corr} = \frac{B'}{R_p} \tag{2}$$

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The values of the corrosion current density  $(j_{corr})$  were used to calculate the rate of mass loss (MR) as follows:

$$MR = K \times i_{corr} \times E_W \tag{3}$$

where K is a constant ( $K = 8.954 \times 10^{-3} \text{ g cm}^2 \mu \text{A}^{-1} \text{ m}^{-2} \text{ d}^{-1}$ ), and  $E_W$  is the equivalent weight of Mg.

TABLE 4. Values of 'aparent' Stern-Gary constant B', corrosion current density  $(j_{corr})$  and mass loss (MR) of pure Mg and ZX10 alloy after their immersion in Hanks' solution for 2 h (at 37 °C), calculated from PDP curves

Parameter	Pure Mg	ZX10 alloy
B'(mV)	52.80	36.5
$j_{corr}$ ( $\mu A \text{ cm}^{-2}$ )	1.64	0.65
MR $(g m^{-2} d^{-1})$	0.18	0.072

The values of corrosion potential ( $E_{corr}$  vs SCE), corrosion current density ( $j_{corr}$ ) and mass loss rate (MR) are shown in Table 4.

The results suggest that the corrosion current density  $(j_{corr})$  and mass loss (MR) of pure Mg are approximately two times higher than those of ZX10 alloy (Table 4). These results are attributed to the faster degradation of Mg surface, accompanied by more intensive evolution of H<sub>2</sub> gas. On the other hand, the Mg-alloy ZX10 involves two alloying elements, Zn and Ca, which are incorporated in the Mg-matrix. Researches have reported that the presence of small addition of intermetallic phases improves the corrosion resistance of Mg (Song et al., 1997; Li et al., 2010). This fact is associated, for example, with the refining of  $\beta$ -phase intermetallic, as a phase less harmful to the Mg matrix and formation of more continuous network; this contribute to the stability of the formed protective layer, because of the incorporation of alloying elements (Wu et al., 2005; Ben-Hamu et al., 2008).



FIGURE 4. SEM images of (a) pure Mg and (b) ZX10 alloy surfaces before exposure, and after their immersion in Hanks' solution for 168 h (7 days) at 37 °C: (c) pure Mg and (d) ZX10 alloy.

					• /			
Element (wt.%)	С	0	Na	Mg	Р	Cl	Ca	Zn
Particle A	-	4.5	-	61.0	-	-	34.5	-
Zone 1	-	2.5	-	96.4	-	-	-	1.11
Zone 2	10.5	29.7	0.3	47.8	5.3	0.2	6.2	-
Zone 3	6.2	55.7	0.3	30.4	3.5	1.2	2.7	-
Zone 4	9.8	48.8	2.0	5.9	13.6	2.5	17.4	-
Zone 5	10.4	27.8	3.2	45.0	4.5	3.5	5.6	-

TABLE 5. EDS analysis of pure Mg and ZX10 alloy surfaces (Fig. 4) before and after their exposure to<br/>Hanks' solution for 168 h (7 days) at 37 °C

# **3.2.** Surface analysis by SEM-EDS and XPS after immersion tests

Figure 4 shows SEM micrographs of the bare surfaces of pure Mg (Fig. 4a) and ZX10 (MgZnCa) alloy (Fig. 4b) before their exposure and after 168 h (7 days) of immersion in Hanks' solution (Figs. 4c and 4d). On the alloy surface, the intermetallic particles of Mg<sub>2</sub>Ca-phase are observable (particles A, Fig. 4b), which composition was acquired by EDS analysis (Table 5) and coincides with previous studies (Kirkland *et al.*, 2010; Kirkland *et al.*, 2011; Zhang *et al.*, 2011). The presence of Zn, as alloying element, is also detected (zone 1, Fig. 4b).

After 168 h (7 days) of exposure to Hanks' solution, the layers formed on the surface of both materials during their degradation present the elements of Mg, O, Ca, P, C and Cl. The EDS analysis (Table 5) suggested magnesium hydroxide  $[Mg(OH)_2]$  as corrosion product and hydroxyapatite  $[Ca_{10}(PO_4)_6(OH)_2]$ , originated from the Hanks' solution, as well as CaCO<sub>3</sub> (Zhang *et al.*, 2011). It is reported that Ca acts as a capture of CO<sub>2</sub>, present in the environment, forming CaCO<sub>3</sub> (Wu *et al.*, 2020). It was observed that on the alloy surface of ZX10 there was a layer, maintained up to the end of the experiment.

XPS analysis (Fig. 5) was performed to support the SEM-EDS results (Table 5) of both materials after 7 days of exposure to Hanks' solution. The high-resolution spectrum for Mg peaks are assigned to 1s hybridization (~1303.8 eV), which has been related to Mg(OH)<sub>2</sub> (Haycock *et al.*, 1978; Moulder *et al.*, 1992). Ca exhibited two peaks at 347.3 and 350.9 eV, corresponding to 2p hybridization, and C and O are attributed to 1s hybridization at 284.7 and 531.3 eV, respectively. The spectrum for P displayed a peak centered at 133.28 eV coming from calcium phosphate (Xin *et al.*, 2009; Xin *et al.*, 2011). As consequence, it can be considered that the layers formed on the pure Mg and ZX10 alloy contain mostly Mg(OH)<sub>2</sub>, and  $Ca_{10}(PO_4)_6(OH)_2$ , as well as  $CaCO_3$ . These compounds may delay the corrosion process, while  $Ca_{10}(PO_4)_6(OH)_2$  may improve the bone compatibility (Li *et al.*, 2008).

It is reported that the presence of aggressive agents, such as chloride ions, and cathodic intermetallic particles (Mg<sub>2</sub>Ca) contribute to the faster degradation of the anodic Mg-matrix (Makar and Kruger, 1993; Song *et al.*, 1997; Witte *et al.*, 2008; Song *et al.*, 2012; Matsubara *et al.*, 2013). However, the low content of alloying elements may adjust the microstructure of the intermetallic phases and improve the corrosion resistance of Mg alloy (Ben-Hamu *et al.*, 2008).

Hanks' solution contains Cl<sup>-</sup> ions that rapidly convert a fraction of  $Mg(OH)_2$  into soluble  $MgCl_2$ , which is easily dissolved in the physiological medium (Witte *et al.*, 2008; Li *et al.*, 2008), according to the following reactions:

$$Mg(OH)_2 + 2Cl^- \rightarrow MgCl_2 + 2OH^-$$
 (4)

$$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$$
 (5)

To estimate the released Mg-ions and the mass faction that was converted into corrosion products,  $Mg^{2+}$ -ion concentration was measured and the mass loss ( $\Delta m$ ) was calculated (Table 6). Additionally, the average corrosion rate (CR) was obtained according to the equation below:

$$CR = (K \times \Delta m)/(A \times T \times D) \tag{6}$$

where  $K = 8.76 \times 10^4$  (dimensionless constant);  $\Delta m = mass loss in g; A = area in cm^2; t = time in h; D = Mg density in g cm^{-3} (1.738). The CR is expressed in mm year<sup>-1</sup>.$ 

It may be noted that at the end of the tests, the increase in  $[Mg^{2^+}]$  was approximately 4.5 times higher for pure Mg than for ZX10 alloy.



FIGURE 5. XPS spectra of pure Mg and ZX10 alloy surfaces after 168 h of immersion in Hanks' solution at 37 °C.

Mg and ZX10 Mg-anoy for up to 106 if (/days) in Hanks solution (at 57 C)						
Material Time	Mg 48 h	ZX10 48 h	Mg 120 h	ZX10 120 h	Mg 168 h	ZX10 168 h
Δm (mg)	$3.7 \pm 0.45$	$1.4 \pm 0.20$	$1.5 \pm 0.25$	$1.6 \pm 0.31$	$1.9 \pm 0.15$	$1.7 \pm 0.30$
CR (mm·year <sup>-1</sup> )	$2.11\pm0.10$	$0.80\pm0.07$	$0.43\pm0.05$	$0.45\pm0.06$	$0.31\pm0.01$	$0.22\pm0.02$
$[Mg^{2+}] (mg \cdot cm^{-2})$	$0.35\pm0.03$	$0.14\pm0.02$	$0.60\pm0.02$	$0.27\pm0.06$	$1.63\pm0.02$	$0.35\pm0.03$

TABLE 6. Mass loss ( $\Delta m$ ) and Mg-ion release increment ( $\Delta [Mg^{2+}]$ ) after immersion of Mg and ZX10 Mg-alloy for up to 168 h (7days) in Hanks' solution (at 37 °C)

Note: initial concentration of Mg-ions =  $10 \text{ mg} \cdot \text{L}^{-1}$  in Hanks' solution.

#### 4. CONCLUSIONS

- The initial electrochemical activity of pure Mg and ZX10 Mg-alloy surfaces, immersed in Hanks' physiological medium (at 37 °C), was studied for 168 h (7 days), in order to reveal the effect of Zn (0.95%) and Ca (0.15%) alloying elements on the mechanism of Mg degradation. The changes in the morphology and elemental composition (SEM-EDS) of the formed layers have shown that the intermetallic particles of Mg<sub>2</sub>Ca-phase, as well as the presence of Zn, provided the formation of more continuous protective layer. Consequently, the calculated corrosion current density ( $j_{corr} = 1.33 \,\mu \text{A} \cdot \text{cm}^{-2}$ ) for pure Mg was approximately two times higher than that of ZX10 Mg-alloy ( $j_{corr} = 0.59 \ \mu \text{A} \cdot \text{cm}^{-2}$ ), also the concentration of the released Mg-ions was  $\approx 4.5$  times higher (1.63  $\pm 0.03$  mg·cm<sup>-2</sup>). There results correlate well with the one order lower current densities of cathodic and anodic processes, which occur on ZX10 Mg-alloy surface, according to the PDP polarization curves.
- The equivalent electric circuit obtained for EIS, which models the behavior of pure Mg and ZX10 alloy, fitted satisfactorily with the Nyquist plots. The EIS diagrams showed that the polarization resistance ( $R_p$ ) of pure Mg is in one order lower than that of ZX10 alloy, which alloying elements are Zn (0.95%) and Ca (0.15 wt.%).
- The current density fluctuations of pure Mg and ZX10 alloy were considered as electrochemical noise (EN) and the estimated current noise resistance ( $R_n$ ) and pitting index (PI) were calculated. The PI values were below than 0.6, indicating that the corrosion attack is not highly localized. The  $R_n$  was  $\approx 5$  times higher for ZX10 Mg alloy, which contains Zn and Ca, less with that of pure Mg.
- Using a small anodic polarization (+10 mV), the polarization resistance  $(R_p)$  and corrosion current density  $(j_{corr})$  values were estimated from the anodic PDP curve, as well as with the application of the Stern-Geary equation. The obtained values matched well with those estimated from EIS equivalent circuits (1.33  $\mu$ A·cm<sup>-2</sup> and 0.59  $\mu$ A·cm<sup>-2</sup> for Mg and Mg-Zn-Ca, respectively). The results indicated that the Zn (0.95 wt.%)

and Ca (0.15 wt.%) as alloying elements in the Ma matrix has led to diminishing of the corrosion process.

- SEM-EDS and XPS analysis suggested that the layers formed on the pure Mg and ZX10 alloy contain mostly Mg(OH)<sub>2</sub> and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, and CaCO<sub>3</sub>. These compounds may delay the corrosion process, just as Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> may improve the bone compatibility.
- The observed positive effect of Zn and Ca incorporation as alloying elements to Mg-matrix on the corrosion process in Hanks' medium, should be considered as a consequence of the more difficult cathodic process of hydrogen evolution and Mg-ions release trough the formed layer on ZX10 Mg-alloy.

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