Research paper

Improved mechanical performance and delayed corrosion phenomena in biodegradable Mg–Zn–Ca alloys through Pd-alloying

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The influence of partial substitution of Mg by Pd on the microstructure, mechanical properties and corrosion behaviour of Mg72−xZn23Ca5Pdx (x = 0, 2 and 6 at.%) alloys, synthesized by copper mould casting, is investigated. While the Mg72Zn23Ca5 alloy is mainly amorphous, the addition of Pd decreases the glass-forming ability, thus favouring the formation of crystalline phases. From a mechanical viewpoint, the hardness increases with the addition of Pd, from 2.71 GPa for x = 0 to 3.9 GPa for x = 6, mainly due to the formation of high-strength phases. In turn, the wear resistance is maximized for an intermediate Pd content (i.e., Mg70Zn23Ca5Pd2). Corrosion tests in a simulated body fluid (Hank’s solution) indicate that Pd causes a shift in the corrosion potential towards more positive values, thus delaying the biodegradability of this alloy. Moreover, since the cytotoxic studies with mouse preosteoblasts do not show dead cells after culturing for 27 h, these alloys are potential candidates to be used as biomaterials.

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1. Introduction

Most of conventional orthopaedic implants used for repairing joint and bone fractures consist of metallic biomaterials with polycrystalline microstructure that exhibit good corrosion resistance, high hardness and excellent fatigue and wear resistance. Amongst metallic biomaterials, austenitic steels, Co–Cr–Mo, titanium and Ti–6Al–4V alloys have been the most frequently employed (Geetha et al., 2009). In spite of their extended use, the Young's modulus of these materials typically ranges between 120 and 250 GPa and is thus much higher than the Young's modulus of human bone (20–30 GPa) (Black and Hasting, 1998). As a consequence, the load transfer from the implant to the adjacent bone is considerably prevented, leading to the so-called “stress shielding effect”, which can cause bone resorption, cell death and implant loosening (Nagels et al., 2003). For certain specific applications (e.g., dental prostheses, heart valves, hip prostheses, etc.)
ceramic implants such as alumina, bioglass or hydroxyapatite (calcium phosphate) are also used (Whitters et al., 2005). These ceramics exhibit low Young’s modulus (up to 30 GPa) but are usually rather brittle compared to that of metallic implants.

In most cases, once the patient has recovered from the traumatic injury, a revision surgery is required in order to remove the implant from the body and avoid problems associated with joint wear, osteopenia or inflammation of adjacent tissues that could ultimately cause sarcoma. To circumvent post-extraction of the implant, intensive efforts have been made in recent years to develop the so-called “biodegradable implants”, i.e., non-toxic materials that become reabsorbed by the human body after a certain period of time. These implants are usually based on organic molecules that polymerize to form fibres and solid composites. Some examples are: polyglycolic acid, poly(dl-lactic acid), poly(p-dioxanone) or poly-beta-hydroxybutyric acid (Ambrose and Clanton, 2004). The main drawbacks of these materials are their relatively high cost and their rather low mechanical strength. Sometimes these organic polymers can also react with human tissues, leading to osteolysis and eventually synovitis. For these reasons, it is highly desirable to develop cost-effective metallic alloys, with better mechanical performance than polymers, to be used as biodegradable implants.

Owing to their good biocompatibility and rather low mechanical stiffness (i.e., low Young’s modulus), Mg-alloys are potential candidates for biodegradable implants (Staiger et al., 2006; Witte et al., 2005). However, the problem with some magnesium alloys is their exceedingly high corrosion rates in physiological conditions, which makes their biodegradability to be faster than the time required to heal the bone (Li et al., 2008). For this reason it is important to decrease the degradation rate of magnesium alloys using different techniques such as purification, alloying, surface coating (Song, 2007) or amorphization (Zberg et al., 2009). Amorphous Mg-alloys, also termed Mg-based metallic glasses, are usually produced by rapid solidification techniques. Because of the lack of grain boundaries, which can favour the occurrence of galvanic pairs, the corrosion rate in metallic glasses is typically slower than in crystalline alloys. However, most of Mg-based metallic glasses obtained over the years contain harmful elements like Ni and La (González et al., 2009). The substitution of these elements by non-toxic elements such as Zn and Ca has permitted the fabrication of biocompatible glassy Mg-based alloys (Zberg et al., 2009; Gu et al., 2005) with potential use as biomaterials. It has been recently reported that the corrosion resistance of Mg–Zn–Ca metallic glasses can be tuned by adjusting the alloy composition (Zberg et al., 2009). However, its kinetic biodegradation is still too fast for biomedical applications.

In this work we show that the addition of Pd constitutes a proper and effective way to improve the mechanical behaviour and, simultaneously, delay the beginning of corrosion phenomena in Mg–Zn–Ca alloys. Palladium has been used for many years as major component in dental casting alloys due to its high corrosion resistance and low toxic activity (Wataha, 2000). There is a dearth of literature about the elimination of Pd from the body and it mostly refers to Pd(II) compounds (Kielhorn et al., 2002). The excretion of Pd via faeces and urine has been demonstrated in in-vivo studies with rats and rabbits. Remarkably, small addition of Pd, in the 2–6 at.% range, already results in a significant increase of hardness and wear resistance. The obtained results are correlated with the microstructural differences existing among the investigated compositions.

2. Material and methods

Ingots were obtained by melting a mixture of pure elements (>99.9 at.%) of Mg, Zn, Ca and Pd in an induction furnace. Rod samples with diameter of 2 mm and up to 20 mm length were obtained by remelting the master alloy in a quartz tube and subsequent injection into copper mould in an inert gas atmosphere. The structure of the as-cast samples was studied by X-ray diffraction (XRD) (Phillips X’Pert) with monochromated Cu Kα radiation (30°–90° 2θ range, counting time: 10 s, step size: 0.030°) and the thermal stability was investigated by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7) at a constant heating rate of 40 K/min up to 575 K. The microstructure was observed with a scanning electron microscope (SEM) (Zeiss Merlin) equipped with energy dispersive X-ray (EDX) analysis.

The elastic properties were evaluated at room temperature by means of ultrasonic measurements (pulse-echo overlap technique), using an ultrasonic pulser-receiver model 5072PR and an oscilloscope model TDS 2022B Tepronix, along with density assessment (Archimedes’ method). Nanoindentation experiments were also carried out in load control mode, at room temperature, on the discs’ cross section, at approximately half the radius distance from the disc centre, using a diamond Berkovich-type tip. Prior to nanoindentation, the specimens were polished until the surface exhibited a mirror-like appearance. The indentation function consisted of a loading segment of 150 s, to a maximum load of 500 mN, followed by a load holding segment of 50 s and an unloading segment of 150 s. This high load was selected so that the indentation impression size was sufficiently large to embrace the different existing phases. The thermal drift was kept below 0.05 nm s⁻¹. The results shown in this work correspond to the average of a total of 50 indentations for each sample. The hardness (H) and reduced elastic modulus (E_r) values were derived from these load–displacement curves using the method of Oliver and Pharr (1992). The elastic (U_{el}) and total energies (U_{tot}) during nanoindentation were calculated as the areas between the unloading curve and the x-axis and between the loading curve and x-axis, respectively. The indentation plastic energy (U_{pl}), is the difference U_{tot} – U_{el}.

The corrosion behaviour of the samples was studied qualitatively by potentiodynamic polarization tests in a Hank’s solution (simulated body fluid, SBF, purchased from Aldrich) at 37 °C. The electrochemical experiments were performed in a thermostatized, one-compartment three-electrode cell. A double junction Ag | AgCl reference electrode was used with 3 M KCl inner solution and 1 M NaCl outer solution. A Pt sheet acted as a counter electrode. Initially, the specimens were immersed in the Hank’s solution to determine the open circuit potential (OCP). The potential became usually stable after 3 h immersion. Immediately afterwards, the potential was swept at a rate of 0.1 mV s⁻¹ from 300 mV below the OCP towards 300 mV above the OCP.
The corrosion current density \( (i_{\text{corr}}) \) values were determined by extrapolation of the anodic and cathodic Tafel slopes to the corrosion potential \( (E_{\text{corr}}) \).

Mouse preosteoblasts (MC3T3-E1, ATCC) were used in the cytotoxicity study. They were cultured in alpha minimum essential medium (Invitrogen) supplemented with 10% foetal bovine serum at 37 °C in a humidified atmosphere of 5% CO\(_2\). The discs of the three compositions, \( \text{Mg}_{72-x}\text{Zn}_{23}\text{Ca}_x\text{Pd}_x \) \( (x = 0, 2 \) and 6) were placed individually on glass coverslips introduced into a 4-multwell culture plate and sterilized by UV for at least 2 h. Then, 50,000 preosteoblasts were seeded into each well and cultured for 27 h. Control cells were seeded directly on the glass coverslip in the absence of the alloy. Cytotoxicity was assessed using the LIVE/DEAD Viability/Cytotoxicity Kit for mammalian cells (Invitrogen) according to the manufacturer’s protocol. This kit detects the activity of intracellular esterases, allowing to distinguish live cells (able to hydrolyze calcein AM) from dead ones. Samples were analysed under an Olympus IX71 inverted microscope equipped with epifluorescence.

3. Results and discussion

3.1. Morphology and microstructure

In order to reveal any possible microstructural and/or phase change caused by the addition of Pd to \( \text{Mg}_{72}\text{Zn}_{23}\text{Ca}_x \) alloy, an XRD study was carried out. Fig. 1 shows the XRD patterns of the \( \text{Mg}_{72-x}\text{Zn}_{23}\text{Ca}_x\text{Pd}_x \) \( (x = 0, 2 \) and 6) rods. The Pd-free \( \text{Mg}_{72}\text{Zn}_{23}\text{Ca}_0 \) alloy exhibits a broad halo centred at around 2\( \theta \) = 39°. Superimposed to this halo there is a broad peak located at 2\( \theta \) ~ 37°, suggesting that this alloy consists of an amorphous matrix with some nanocrystals embedded. When Pd is added, a fully crystalline structure develops, as noted from the appearance of narrow reflections. These main reflections of the XRD patterns can be assigned to hexagonal \( \text{CaZn}_5 \) \( (a = b = 0.5406 \text{ nm}, c = 0.4280 \text{ nm}) \), hexagonal \( \text{MgZn} \) \( (a = b = 2.557 \text{ nm}, c = 1.814 \text{ nm}) \), cubic \( \text{Mg}_6\text{Pd} \) \( (a = b = c = 2.01 \text{ nm}) \) and trigonal \( \text{Mg}_6\text{Ca}_2\text{Zn}_3 \) \( (a = 0.970 \text{ nm}, c = 1.000 \text{ nm}) \) phases (Jardim et al., 2002). Moreover, additional \( \text{Mg}-\text{Zn} \) compounds might be also present since their diffraction lines would match the angular positions of some of the small peaks observed in the XRD patterns. The relative intensity of the XRD peaks changes as the Pd content is increased from \( x = 2 \) to \( x = 6 \). This indicates that the corresponding volume fractions of the different phases composing the samples vary with the alloy composition. In particular, the intensity of the peaks associated to \( \text{Mg}_6\text{Pd} \) and \( \text{MgZn} \) phases increases with Pd addition. In contrast, a decrease in the relative intensity of the reflections attributed to \( \text{Mg}_6\text{Ca}_2\text{Zn}_3 \) phase is noted, which mainly stems from the formation of the \( \text{MgZn} \) and \( \text{Mg}_6\text{Pd} \) phases. Actually, as Pd enters the alloy in substitution of Mg, the quantity of \( \text{Mg}_6\text{Pd} \) phase that is formed increases. This invariably brings about a decrease in the amount of Mg available to constitute the \( \text{Mg}_6\text{Ca}_2\text{Zn}_3 \) phase.

In order to study the thermal behaviour of the \( \text{Mg}_{72}\text{Zn}_{23}\text{Ca}_5 \) alloy, the DSC scan of this sample was compared with that of \( \text{Mg}_{70}\text{Zn}_{23}\text{Ca}_5\text{Pd}_2 \) (Fig. 2). The \( \text{Mg}_{72}\text{Zn}_{23}\text{Ca}_5 \) alloy displays rather low glass transition \( (T_g \sim 372 \text{ K}) \), which is actually similar to that of other amorphous alloys with similar composition (e.g. \( \text{Mg}_{70}\text{Zn}_{25}\text{Ca}_5 \) and \( \text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4 \)) (Gu et al., 2010). Several exothermic peaks are observed at higher temperatures, suggesting the occurrence of various crystallization events. In contrast, the scan of the \( \text{Mg}_{70}\text{Zn}_{23}\text{Ca}_5\text{Pd}_2 \) sample is almost featureless (i.e. no \( T_g \) is detected). This suggests that these rods are fully-crystalline. Neither glass transition nor crystallization events were observed in the \( \text{Mg}_{66}\text{Zn}_{23}\text{Ca}_5\text{Pd}_6 \) alloy (not shown). This behaviour could be expected considering that the same phases were detected in the as-cast \( \text{Mg}_{70}\text{Zn}_{23}\text{Ca}_5\text{Pd}_2 \) alloy (Fig. 1) and that the glass forming ability decreases with the addition of Pd. These results indicate a high thermodynamic stability of the crystalline phases found in the as-cast Pd-containing alloys.

In order to determine the phase distribution and morphology along the cross-section of the rods, the samples were characterized by SEM. The global microstructures of the \( \text{Mg}_{72}\text{Zn}_{23}\text{Ca}_5, \text{Mg}_{70}\text{Zn}_{23}\text{Ca}_5\text{Pd}_2 \) and \( \text{Mg}_{66}\text{Zn}_{23}\text{Ca}_5\text{Pd}_6 \) rods at approximately half their radius are displayed in Fig. 3(a)–(c) respectively. Magnified details of the microstructure are shown in the corresponding insets.

The backscattered SEM image of \( \text{Mg}_{72}\text{Zn}_{23}\text{Ca}_5 \) alloy is shown in Fig. 3(a). A rather featureless contrast is observed. From EDX measurements, the alloy composition is practically
Fig. 3 – SEM images (backscattered electrons) of (a) Mg$_{72}$Zn$_{23}$Ca$_5$, (b) Mg$_{70}$Zn$_{23}$Ca$_5$Pd$_2$ and (c) Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ rod. The insets show the magnified details of the microstructure of the Mg$_{70}$Zn$_{23}$Ca$_5$Pd$_2$ and Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ samples (in panels (b) and (c)). The same throughout the sample and is similar to the nominal composition.

Completely different microstructures, consisting of several regions with different contrast are observed in the SEM image (using backscattered electrons) of the Mg$_{70}$Zn$_{23}$Ca$_5$Pd$_2$ and Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ alloys (Fig. 3(b) and (c)). These results indicate a decrease of glass forming ability of the Mg–Zn–Ca system with the addition of Pd. The Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ alloy consists of small dark areas surrounded by a grey phase, along with white dendrites (inset of Fig. 3(c)). Although the microstructure and phase distribution present in the two Pd-containing alloys appear to be similar, the volume fraction of dark regions and white dendrites as well as the size of dendrites is larger in the alloy with $x = 6$.

In order to identify which crystalline phase composes each of the regions observed in the SEM images, elemental EDX mappings were obtained from the disc-centre of the Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ rod (Fig. 4). The results show that the grey regions are rich in Ca and Zn, the white dendrites in Pd and Mg and the dark regions mainly correspond to Mg and Zn. This suggests that the dendrites could correspond to Mg$_6$Pd, the grey regions to CaZn$_5$ and the black regions to MgZn. Considering that the weight fraction of Mg$_6$Zn$_3$Ca$_2$ is lower than that of MgZn it could be expected that the scarce Mg$_6$Zn$_3$Ca$_2$ phase present in the Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ alloy could correspond to the areas of darkest tonality that lie within the dark regions associated to MgZn.

### 3.2. Acoustic measurements and nanoindentation studies

The elastic properties of the alloys have been evaluated at room temperature by means of acoustic measurements. Table 1 lists the values of density ($\rho$), shear modulus ($G$), bulk modulus ($B$), Young’s modulus ($E$), $G/B$ ratio and Poisson’s ratio ($\nu$) of the investigated alloys. The density values of these alloys are rather low although $\rho$ increases progressively with the increase of Pd content, as could be expected considering
that the density of Pd (12.023 g cm\(^{-3}\)) is much higher than that of Mg (1.738 g cm\(^{-3}\)). Remarkably, the Young’s modulus of these alloys raises significantly with an addition of 2 at.% Pd, while only a moderate further increase is observed for x = 6. This cannot be simply explained in terms of compositional variations among the samples but is probably mainly related to the aforementioned microstructural changes that occur when small amounts of Pd are added to the system. Indeed, the presence of only 2 at.% Pd causes a drastic change in the microstructure, from a mainly amorphous one (for \(x = 0\)) to a fully crystalline one (for \(x = 2\)), thus inducing large variations in E. The relatively low Young’s modulus of the Mg\(_{72}\)Zn\(_{23}\)Ca\(_5\) alloy can be attributed, at least in part, to the presence of free volume within the glassy matrix, which causes the average interatomic spacing to be larger than in fully crystalline alloys. The so-called elastic-softening of metallic glasses also depends on the type of atomic displacements that occur during elastic deformation of these materials. Namely, contrary to crystalline alloys, elastic deformation in metallic glasses not only involves the nearest-neighbour atomic shell but also more distant shells, resulting in overall larger elastic strains (i.e., lower Young’s modulus) than in crystalline alloys (Hufnagel et al., 2006). Similar to the evolution of E, the values of G and B also increase with the addition of Pd because all these parameters depend on the atomic bonding; E is indicative of the elastic resistance in the direction of the applied load, B represents the elastic resistance to volume compression and G denotes the elastic resistance to shear stress.

Considering that Mg-based bulk metallic glasses and crystalline Mg alloys generally exhibit low ductility and poor macroscopic deformability at room temperature, nanoindentation tests have been performed. Since nanoindentation is a very local technique the influence of porosity or other flaws is avoided and permits to get reliable results when studying the influence of Pd addition on the mechanical properties. The load–displacement (P–h) nanoindentation curves, with a maximum load of 500 mN, are shown in Fig. 5(a). Pop-in events are detected in the loading segment of all three specimens. However, some differences can be observed depending on the alloy composition. In the mainly amorphous alloy (\(x = 0\)) a large amount of uniformly distributed pop-ins are detected and their displacement tends to increase with the applied load. Conversely, in the fully crystalline alloys, the load at which pop-ins are detected and their displacement appear to be more random, which is consistent with the microstructure. Actually, pop-in events in amorphous alloys are considered to be related to the motion of individual shear bands; since the distance shear bands can propagate increases with the applied load, this causes the indentation serrations to become more pronounced. However, for crystalline alloys, the length of the pop-ins is related to the distance dislocations propagate, which depends mainly on the grain size and the distance between the indenter tip and grain boundaries with which dislocation pile-ups can interact. During nanoindentation of a crystalline alloy, the initial stress-field generated during loading can create a dislocation source, hence initiating a pop-in event. The process continues until the dislocation source stops operating due to the inverse pileup stress that reduces the net stress to zero. A new pop-in will be generated only when the indentation load is sufficiently increased to create a new dislocation source.

### Table 1 – Elastic properties evaluated from acoustic measurements at room temperature. Note that \(\rho\), G, B, E and \(\nu\) denote, respectively, the density, shear modulus, bulk modulus, Young’s modulus and Poisson’s ratio of the investigated alloys.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Mg(<em>{72})Zn(</em>{23})Ca(_5)</th>
<th>Mg(<em>{70})Zn(</em>{23})Ca(_5)Pd(_2)</th>
<th>Mg(<em>{66})Zn(</em>{23})Ca(_5)Pd(_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho) (g cm(^{-3}))</td>
<td>2.84</td>
<td>3.01</td>
<td>3.40</td>
</tr>
<tr>
<td>G (GPa)</td>
<td>19.47</td>
<td>25.60</td>
<td>28.97</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>40.66</td>
<td>43.5</td>
<td>50.54</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>50.38</td>
<td>64.20</td>
<td>72.98</td>
</tr>
<tr>
<td>G/B</td>
<td>0.48</td>
<td>0.58</td>
<td>0.57</td>
</tr>
<tr>
<td>(\nu)</td>
<td>0.29</td>
<td>0.25</td>
<td>0.26</td>
</tr>
</tbody>
</table>

**Fig. 5**  – (a) Load–displacement (P–h) nanoindentation curves of Mg\(_{72-x}\)Zn\(_{23}\)Ca\(_5\) alloys (x = 0, 2 and 6) and (b) backscattered SEM image showing some indents made close to the centre of the Mg\(_{70}\)Zn\(_{23}\)Ca\(_5\)Pd\(_2\) rod.
The stochastic nature of this process makes the indentation serratations to be distributed in a less regular manner than for the glassy Mg72Zn23Ca5 alloy.

Some of the indentation impressions obtained at half the radius of the Mg70Zn23Ca5Pd2 rod are shown in Fig. 5(b). The image reveals that the indentation marks for a maximum load of 500 mN are sufficiently large to embrace all the existing crystalline phases, suggesting that the obtained mechanical properties will be representative of the average behaviour of the composite material. The values of H, Er, Upl, Upl/Utot ratio and maximum indentation depth (hmax) for the three investigated alloys are listed in Table 2. Interestingly, addition of 2 at.% Pd has a large influence on the hardness, which increases from 2.71 GPa (for x = 0) to 3.56 GPa (for x = 2). The hardness increase can be mainly attributed to the lack of free volume in the crystalline alloy (x = 2) as compared to the mainly amorphous one (x = 0). Also the large volume fraction of Mg6Ca2Zn3 phase may have a hardening effect but not as much as that reported for Mg–Zn–Ca (Bamberger et al., 2002; Park et al., 2001) and Mg–Zn–Ca–Zr alloys (Shepelev et al., 2009) since the distance between intermetallic particles is relatively large and thus the dislocation arrest due to the Corman mechanism would not be so effective. The hardness further increases for x = 6, up to 3.90 GPa. This is consistent with the decrease of maximum indentation depth from 2.905 μm (for x = 2) to 2.673 μm (for x = 6). However, from the relative intensity of XRD peaks it can be inferred that the volume fraction of Mg6Ca2Zn3 phase decreases when the concentration of Pd varies from 2 to 6 at.% Hence, the large hardness in the alloy with x = 6 suggests that the MgZn and Mg6Pd phases also contribute to induce mechanical hardening, in an analogous way as the Mg6Ca2Zn3 phase. Note that the reduced Young's modulus increases with the Pd content, in agreement with the results from acoustic measurements.

Since most biomaterials are subjected to wear, it is necessary to have materials with high wear resistance to minimize wear debris. Hardness is usually regarded to be an important property for evaluating wear resistance. However, some authors have shown that the wear resistance can be better estimated from the H/Er ratio (Oberle, 1951), rather than the hardness itself. This ratio is related to the elastic strain to failure. Another parameter, also related to the wear performance, is the resistance to plastic deformation, which is proportional to H3/Er2 (Tsui et al., 1995). Table 2 shows that the maximum H/Er and H3/Er2 values are attained by the Mg70Zn23Ca5Pd2 alloy, indicating that this alloy exhibits the highest wear resistance. Furthermore, nanoindentation also allows extracting some information about the intrinsic plasticity of the alloy, from the ratio between the indentation plastic energy (Upl) and the total indentation energy (Utot). From the obtained results (see Table 2), no pronounced differences in plasticity are observed for the three investigated alloys. It is also worth mentioning that the values of Upl/Utot for the investigated Mg-based alloys are similar to those reported for Zr52Cu44Al7.5Er1 metallic glasses (Upl/Utot ∼ 0.6 (Tekaya et al., 2009) and Upl/Utot ∼ 0.7 (Yang et al., 2009), respectively) and clearly larger than for brittle Fe-based glasses (Upl/Utot ∼ 0.37 Fornell et al., 2010). In fact, the ratio Upl/Utot has been sometimes used to characterize the mechanical behaviour of brittle materials which are often difficult to test using macroscopic tensile tests (Milman, 2008). Remarkably, most brittle materials (like ceramics) show relatively low Upl/Utot values (around 0.3–0.4 for SiC or Al2O3), whereas ductile metals (like Cu or Al) can show Upl/Utot values larger than 0.9 (Milman, 2008).

3.3. Corrosion behaviour in simulated body fluid and cytotoxicity

Fig. 6(a) shows the equilibrium potential reached in samples containing different amounts of Pd in the Hank’s solution at 37 °C. The OCP shifts towards more positive values as the Pd content increases, owing to the noble character of Pd, in the following sequence: Mg72Zn23Ca5 base (−1.15 V) > Mg70Zn23Ca5Pd2 (−1.04 V) > Mg66Zn23Ca5Pd6 (−0.93 V). One would expect the Pd-containing alloys to be more prone to corrosion than the Pd-free partly glassy alloy due to both the crystallinity and the existence of noble phases, such as MgPd, that would promote the well-known galvanic corrosion phenomena. However, it rather seems that both factors do not play a major role. Instead, the ability to form thicker, more stable passive layers onto the specimens’ surface would contribute to the enhanced corrosion resistance, at least at the working time scales used. This shift towards more positive potential can thus be ascribed to the formation of a thicker oxide/hydroxide film onto the specimen’s surface, as commonly observed in this type of alloys (Fekry and Amer, 2011). However, the effectiveness of this passive Mg(OH)2 layer in preventing corrosion is rather limited because the layer is destroyed and dissolved in solutions containing chloride ions, as it is the case of the Hank’s solution (Ng et al., 2010). The observed trends in the OCP values are consistent with the potentiodynamic polarization curves shown in Fig. 6(b). As expected, the corrosion potential (Ecorr) shifts towards more anodic values with an increase in the Pd content, pointing to a clear delay of the corroding phenomena. The

<table>
<thead>
<tr>
<th></th>
<th>Mg72Zn23Ca5</th>
<th>Mg70Zn23Ca5Pd2</th>
<th>Mg66Zn23Ca5Pd6</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (V)</td>
<td>2.71</td>
<td>3.56</td>
<td>3.90</td>
</tr>
<tr>
<td>H (GPa)</td>
<td>51.01</td>
<td>59.10</td>
<td>77.70</td>
</tr>
<tr>
<td>H3/Er2</td>
<td>0.053</td>
<td>0.060</td>
<td>0.050</td>
</tr>
<tr>
<td>Upl (GPa)</td>
<td>398.3</td>
<td>326.7</td>
<td>337.2</td>
</tr>
<tr>
<td>Upl/Utot</td>
<td>0.696</td>
<td>0.628</td>
<td>0.695</td>
</tr>
<tr>
<td>hmax (μm)</td>
<td>3.204</td>
<td>2.905</td>
<td>2.673</td>
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</table>
corrosion current density values obtained by the Tafel extrapolation method become slightly larger as Pd is progressively added to the alloy: Mg$_{72}$Zn$_{23}$Ca$_5$ (1.7 mA cm$^{-2}$) < Mg$_{70}$Zn$_{23}$Ca$_5$Pd$_2$ (2.1 mA cm$^{-2}$) < Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ (2.7 mA cm$^{-2}$). It is noteworthy that although the reasonability and reliability of the corrosion current density values obtained from electrochemical techniques in Mg-based alloys is a source of debate due to the so-called “abnormal polarization behaviour”, the potentiodynamic polarization tests still remain one of the most employed methods (Ng et al., 2010; Song, 2005). Compared to the weight-loss method, the electrochemical techniques provide real time information of the corrosion rate rather than an average rate. Hence, they still can be considered valid from the qualitative viewpoint. Our results are in agreement with the beneficial effect attributed to Pd when alloyed with other biomedical-oriented glassy alloys, such as the Ti-based ones (Oak and Inoue, 2008).

The SEM surface morphologies of Mg$_{72}$Zn$_{23}$Ca$_5$ and Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ as-cast alloys after the corrosion tests are shown in Fig. 7(a) and (b), respectively. At first sight, the surface of Mg$_{72}$Zn$_{23}$Ca$_5$ appears to be slightly rougher, showing a higher density of microcracks. In fact, when the internal or external tensile stresses are combined with the effect of the corrosion agents, a pressure corrosion cracking commonly appears. These results suggest a higher vulnerability of the protective oxide/hydroxide film formed onto the Mg$_{72}$Zn$_{23}$Ca$_5$ surface, in agreement with the trends observed in both the OCP and $E_{\text{corr}}$ values. Moreover, some holes can also be observed, while the Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ surface is virtually free from these holes and just exhibits macrocracking. This macrocracking can be ascribed to the contracting forces occurring upon drying (Qin et al., 2009). From the OCP and $E_{\text{corr}}$ trends it can be deduced that the passivation behaviour of Mg$_{70}$Zn$_{23}$Ca$_5$Pd$_2$ is intermediate between that of Mg$_{72}$Zn$_{23}$Ca$_5$ and Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ alloys (Fig. 6) and thus also the surface. A homogeneous distribution of bright particles throughout the cross-section of the samples is observed for both alloys. Oxygen, calcium and phosphorus elements coming out from the Hank’s solution have been identified in the EDX spectra (Fig. 7). Bearing in mind that these elements are present in hydroxyapatite (i.e. Ca$_{10}$(PO$_4$)$_6$(OH)$_2$), one might conclude that the alloys have a large apatite-forming ability and, thus, good bioaffinity. Remarkably, a significant decrease of the relative percentage of Mg is encountered, likely due to the anodic dissolution of Mg. In aqueous solutions Mg dissolves according to the following reactions:

**Anodic reaction**: 

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (1)$$

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (2)$$

**Cathodic reaction**: 

$$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2. \quad (3)$$

---

**Fig. 6** – (a) Time dependence of the OCP and (b) potentiodynamic polarization curves of Mg$_{72-x}$Zn$_{23}$Ca$_5$Pd$_x$ ($x = 0, 2$ and $6$) alloys.

**Fig. 7** – SEM images (secondary electrons) showing the surface of corroded (a) Mg$_{72}$Zn$_{23}$Ca$_5$ and (b) Mg$_{66}$Zn$_{23}$Ca$_5$Pd$_6$ alloys after potentiodynamic polarization tests. Insets: magnified images of the surface morphologies.
In the presence of Cl\(^-\) ions, Mg(OH)\(_2\) transforms into soluble MgCl\(_2\), resulting in an excess of hydroxide ions. In addition to the expected formation of a Mg(OH)\(_2\) layer, other insoluble products are likely to precipitate onto the specimen's surface provided that other ions (such as Ca\(^+\) and H\(_2\)PO\(_4^-\)) are present in the solution. In particular, Mg\(_x\)Ca\(_y\)(PO\(_4\))\(_z\) compounds have been identified as key corrosion products in Mg-based alloys immersed in simulated body fluids (Zhang et al., 2010). The percentages of O, Mg, P, Ca elements encountered on the surface of Mg\(_{72}\)Zn\(_{23}\)Ca\(_5\) and Mg\(_{66}\)Zn\(_{23}\)Ca\(_5\)Pd\(_6\) alloys after the potentiodynamic polarization tests are relatively high, above 5 at.%, which is consistent with the formation of Mg\(_x\)Ca\(_y\)(PO\(_4\))\(_z\) products (Table 3). These phosphates containing Mg and Ca ions have been identified in magnesium implants tested in vivo (Zhang et al., 2009). In our case, the (Mg + Ca)/P ratio is 2.63 and 1.61 for the Mg\(_{72}\)Zn\(_{23}\)Ca\(_5\) and Mg\(_{66}\)Zn\(_{23}\)Ca\(_5\)Pd\(_6\) alloys, respectively. Meanwhile, the Ca/P ratio is close to 1 in both cases, which is not far from the Ca/P ratio of hydroxyapatite (i.e., 1.66) (Fig. 8).

To better understand the potential use of these biodegradable implants as biomaterials, their cytotoxicity has been studied. The viability of preosteoblasts cultured for 27 h on a sterile coverslip without sample (Fig. 9(a)) and with Mg\(_{66}\)Zn\(_{23}\)Ca\(_5\)Pd\(_6\) sample (Fig. 9(b)) was compared. No differences were observed, thus confirming that the alloying elements are not cytotoxic and thus the alloys can be used as biomaterials.

### 4. Conclusions

The influence of Pd addition on the microstructure, mechanical properties and corrosion behaviour of Mg–Zn–Ca alloys has been investigated. The main results can be summarized as follows:

#### Table 3 - Semi-quantitative atomic percentages determined by EDX analyses on the corroded surface of Mg\(_{72}\)Zn\(_{23}\)Ca\(_5\) and Mg\(_{66}\)Zn\(_{23}\)Ca\(_5\)Pd\(_6\) alloys.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg(<em>{72})Zn(</em>{23})Ca(_5)</th>
<th>Mg(<em>{66})Zn(</em>{23})Ca(_5)Pd(_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>68.98</td>
<td>70.1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>11.79</td>
<td>5.68</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>7.01</td>
<td>9.18</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.32</td>
<td>0.45</td>
</tr>
<tr>
<td>Calcium</td>
<td>6.67</td>
<td>9.18</td>
</tr>
<tr>
<td>Zinc</td>
<td>5.23</td>
<td>5.05</td>
</tr>
<tr>
<td>Palladium</td>
<td>–</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Fig. 8 – EDX spectra of the (a) Mg\(_{72}\)Zn\(_{23}\)Ca\(_5\) and (b) Mg\(_{66}\)Zn\(_{23}\)Ca\(_5\)Pd\(_6\) alloys after the potentiodynamic polarization tests in Hank’s solution.

Fig. 9 – Preosteoblasts cultured (a) on a sterile glass coverslip without alloy or (b) with Mg\(_{66}\)Zn\(_{23}\)Ca\(_5\)Pd\(_6\) alloy. Live cells are stained with Calcein-AM (green) and dead cells are stained with EthD-1 (red). No dead cells are observed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
- The microstructure of the Mg$_{72}$Zn$_{23}$Ca$_5$ alloy, which consists of an amorphous matrix with finely dispersed crystallites, drastically changes with small Pd contents, i.e., 2 at.% Pd is sufficient to obtain a fully crystalline microstructure.
- The addition of Pd increases the hardness of the alloy, mainly due to the formation of mechanically hard crystalline phases, which are virtually not present in the glassy Mg$_{72}$Zn$_{23}$Ca$_5$ alloy.
- The values of the elastic constants (E, B, and G) raise with the increase of Pd content, which is consistent with the increase of reduced Young’s modulus measured by nanoindentation.
- The hardness and Young’s modulus increase at a different rate with the Pd content. For this reason the maximum wear resistance, estimated from the $H/E_r$, $H^2/E_r^2$ ratios, is attained in the Mg$_{70}$Zn$_{23}$Ca$_5$Pd$_2$ alloy (i.e., for an intermediate Pd content).
- The corroding phenomena are greatly delayed with Pd addition, as evidenced from the shift in the corrosion potential towards more positive values. The surface of the corroded samples is smoother and contains lower amounts of holes in the Pd-containing alloys.
- Cytotoxicity tests do not show the presence of death cells after culturing for $27$ h, which confirms that these alloys are not toxic and thus can be used as potential implants.

In summary, this work shows that by optimizing the Pd content it is possible to modify and improve the properties of biocompatible Mg-Zn-Ca-Pd alloys, thus making these materials potential candidates to be used as biodegradable implants.

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