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Phytic acid coating on Mg-based materials for biodegradable temporary endoprosthetic applications

L.A. Hernández-Alvarado [a], L.S. Hernández [b], M.A. Lomelí [b], J.M. Miranda [b], L. Narváez [c], I. Diaz [d], M.L. Escudero [d, *]

[a] Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico
[b] Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, Av. Sierra Leona No,550, Lomas 2ª Sección, 78210 San Luis Potosí, Mexico
[c] Facultad del Hábitat, Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico
[d] Centro Nacional de Investigaciones Metalúrgicas, CENIM-CSIC, Avda. Gregorio del Amo 8, 28040 Madrid, Spain

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ABSTRACT

Mg-based materials are especially attractive as biodegradable implants, but they degrade so fast in physiological media that some corrosion protection is needed. This paper evaluates the long-term biodegradation kinetics of powder metallurgy Mg and AZ31 alloy coated with a phytic acid chemical conversion layer and tested in a saline phosphate buffer solution (PBS) at 37 °C. The morphology and chemical nature of the conversion coating and the corrosion products were analysed by SEM/EDX, XRD and FTIR. Corrosion resistance of the as-received and coated specimens was determined by hydrogen release, mass loss and potentiodynamic polarisation curves. The results indicate that the inherent heterogeneity and porosity of the powder metallurgy magnesium specimens, both as-received and coated with phytic acid, promoted rapid hydrogen release and led to their premature fragmentation and complete dissolution before 250 h of immersion. In contrast, the phytic acid coating on AZ31 improves corrosion resistance in long-term tests up to 336 h without affecting biocompatibility, biodegradability and resorbability for use as a temporary endoprosthetic implant.

1. Introduction

The low corrosion resistance and excellent biodegradability and biocompatibility of magnesium and its alloys makes them suitable candidates for use as resorbable implants [1–3]. With mechanical properties like density (1.7–2.0 g/cm^3) and elastic modulus (41–45 GPa) close to those of bone (1.8–2.1 g/cm^3, 10–40 GPa) [2], the effect of osteopenia associated with the use of prosthetic implants (stress shielding) is minimised. Magnesium also offers a higher damping capacity (ability to absorb energy) than any other metal and great workability [4]. Magnesium and its alloys have hitherto been studied in the biomedical field as coronary stents, porous scaffolds for bone repair and support materials for load-bearing bones [4,5], and magnesium is a necessary element for calcium incorporation in bones [6] and the stimulation of new tissue growth [7]. Once it has fulfilled its mission as an ostesynthesis material it degrades in the body fluids, overcoming some of the limitations of permanent implants such as second surgery for implant removal, restenosis, thrombosis, permanent irritation and inability to adapt to growth in young patients [8]. Moreover, magnesium corrosion products can be potentially beneficial to patients [9]. But although magnesium is a biodegradable material it presents a very high corrosion rate in physiological media due to the high chloride ion concentration (~104 mmol), a fact that may jeopardise its mechanical integrity during the healing of a fractured bone, and additional measures must therefore be taken in order to control its degradation kinetics [3,9].

Chemical conversion coatings have received considerable attention in relation with the protection of magnesium and its alloys due to their uniformity, good adhesion and low cost [10,11]. One of the great challenges in this field is to control degradation and improve corrosion resistance without affecting biocompatibility, biodegradability and resorbability. One potential coating that is harmless to the human body and the environment is phytic acid (PA) ($C_6H_{18}O_{24}P_6$), an organic macromolecule with 12 hydroxyl groups and 6 carboxyl phosphate groups that is present in cereals and pulses [12]. Phosphate ions have a negative charge and a low

* Corresponding author.
E-mail address: escudero@cenim.csic.es (M.L. Escudero).

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density which allows them to interact chemically with numerous metallic cations, and for this reason they are applied in the remediation of metal-contaminated soils [13], as corrosion inhibitors in paints and pigments [14], and in the formation of conversion coatings and self-assembled monolayers (SAM) on a range of metallic materials [15–23].

In the case of magnesium and its alloys, PA has been used to generate conversion coatings [24–44] that do not jeopardise the biocompatibility and biodegradability of magnesium [40] in temporary endoprosthetic applications. In addition to this, being an organic compound it can avoid the formation of galvanic cells that are sometimes generated with inorganic coatings. Liu et al. [24,30–32] and Cui et al. [25,26,33,34] have systematically studied the protection afforded by PA coatings on high purity magnesium and AZ91 alloy, varying the PA concentration, pH, immersion time and temperature. The results show that the anticorrosive properties of PA conversion coatings are comparable to those of conversion coatings with chromates. However, the presence of microcracks in PA coatings accelerates their degradation and reduces their protective effect against corrosion in chloride environments [41]. Eliminating the presence of microcracks has been addressed by means of the following actions: a) combining PA coatings with cerium salts [32,37,42], stearic acid [39], alumina [43] or hydrotalcite [44] b) alkaline pretreatment prior to PA coating [40], and c) heat treatment of the specimens after coating [38,41,43]. Most of the studies cited above do not consider the possibility of using this coating for bone implants, an application that is only now starting to be developed in view of its biocompatibility [35,38–41].

Although the excellent behaviour of phytic acid as a coating on magnesium-base substrates has been described in the medical field [45–47], it has normally been tested for only short immersion times (hours or a few days) in corrosive media. The present work reports the characterisation of phytic acid coatings on powder metallurgy magnesium and AZ31 alloy immersed for a long time of up to 14 days in a saline phosphate buffer physiological solution at 37 °C for biodegradable temporary endoprosthetic applications.

2. Experimental procedure

2.1. Preparation of specimens

The materials used as substrates were: powder metallurgy (PM) pure Mg and AZ31 alloy. Mg powder (325 mesh) was supplied by Alfa Aesar, USA. The certified powder composition given by the supplier was specified as 99.8% pure Mg. The chemical composition of the powders, determined by wavelength dispersive X-ray fluorescence (WDXRF) was as follows: 0.032 wt.%Al, 0.131 wt.%Si, 0.194 wt.% Ca, 0.019 wt.% Mn, 0.017 wt.%Fe (balance Mg). The powders were cold-pressed by slowly increasing pressure up to 310 MPa in a die specially designed for this purpose. The resulting compacts of 40 mm in diameter were extruded at 420 °C employing an extrusion of 16:1 to obtain cylindrical bars of 10 mm in diameter. The AZ31 alloy was received from Magnesium Elektron Limited, UK, in the form of a rolled 3 mm thick sheet in O-temper condition (annealed at 345 °C). The chemical composition of the AZ31 alloy was determined by WDXRF to be: 3.37 wt.% Al, 0.78 wt.% Zn, 0.22 wt.% Mn (balance Mg).

The Mg PM and AZ31 specimens were set in a quick-curing acrylic resin leaving a surface area of 0.78 cm^2 and 0.81 cm^2, respectively, exposed to the electrolyte. Prior to coating deposition all the specimens were polished with SiC paper to grade 1200. The phytic acid coating was deposited by immersion for 1 h at a temperature of 60 °C in a 0.5% phytic acid solution prepared with deionised water [24]. The pH of the solution was adjusted to 5.0 with triethylamine.

2.2. Surface and coating characterisation

The surface and cross-section morphology of the coating and corrosion products was observed by scanning electron microscopy (SEM) using a JEOL JXA-840 electron microscope equipped with a Link System electron microprobe. The composition of the coating applied on the different substrates was characterised by SEM/EDX, by infrared spectroscopy and by X-ray diffraction.

Infrared spectroscopy analysis was performed with the coating adhered to the substrates using an IRAffinity-1 FTIR spectrophotometer by Shimadzu incorporating a PIKE attenuated total reflectance cell with ZnSe crystal. The applied resolution was 4 cm^{-1}, the number of scans 10 and the spectral interval from 4000 to 650 cm^{-1}. Infrared spectra were obtained at two different points on the surface of each specimen. The coating adhered to the substrates was also characterised by X-ray diffraction (XRD) with a D8 Brukers AXS diffractometer using the parallel beam technique in film mode (Göbel mirror) with an angle of incidence of 2°. This analysis involved the use of copper Kα radiation (λ = 1.54060 Å), a voltage of 40 kV, a current of 40 mA, a scanning angle from 4 to 65°, a step width of 0.02° and an acquisition time of 2 s per step by using the power diffraction file of the International Centre for Diffraction Data (data, 2010).

2.3. Evaluation of corrosion

The corrosion behaviour of the as-received and coated specimens was evaluated in a saline phosphate buffer solution (PBS) with the following composition: 8.0 g L^{-1} NaCl, 0.2 g L^{-1} KCl, 0.2 g L^{-1} KH_2PO_4, 1.15 g L^{-1} Na_2HPO_4.

Immersion tests in the PBS solution at pH = 7.4–7.6 and 37 °C for hydrogen evolution were carried out at least in triplicate, and in some cases in larger numbers until reproducible results were obtained.

For the hydrogen evolution test specimens with dimensions of 1.5 cm × 0.7 cm x 0.3 cm were placed vertically exposing the entire surface at the bottom of a glass beaker, placing an inverted funnel over the specimen and a burette over the funnel which was then filled with 400 mL PBS solution.

A separate specimen of each material was used to measure changes in pH during the course of the immersion tests.

The reaction kinetics of the Mg materials was evaluated by measuring the hydrogen evolution kinetics, according to the following reaction:

$$Mg + 2H_2O = Mg(OH)_2\downarrow + H_2\uparrow \quad (1)$$

Prior to immersion in the PBS solution all the specimen sides are polished with SiC paper to grade 1200. After the immersion time of 336 h the specimens are washed with a solution of 200 g/l CrO_3 and 10 g/l $AgNO_3$ in order to remove the corrosion products. They are then placed in a dessiccator for 24 h and subsequently weighed in order to determine the corrosion rate by mass loss.

The hydrogen evolution rate, V_H (mL/cm^2h), is calculated by means of Equation (2):

$$V_H = \text{Volume } H_2 \text{ release}/A\ t_{\text{immersion}} \quad (2)$$

Since the oxidation of one mol of Mg generates one mol of hydrogen gas, it is possible to determine the corrosion rate of Mg (expressed in mg/cm^2h), by the amount of hydrogen collected at the end of each experiment [48]. Assuming that H_2 behaves as an ideal gas and occupies a volume of 22.4 L under standard conditions