Effect of impurities and electrolyte thickness on degradation of pure Mg. Study by FEM

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ABSTRACT

The degradation of magnesium due to the presence of impurities and the thickness of electrolyte was studied by solving the Laplace equation with proper boundary conditions using the Finite Element Method (FEM). Magnesium covered by a thick layer of electrolyte suffers severe corrosion attack, but this is significantly reduced when a thin enough layer is on Mg.

INTRODUCTION

Magnesium is the eighth most abundant element on earth. It has excellent specific strength and low density, only two-thirds that of Al, so Mg and its alloys could be used in many applications including temporary bone implants. Magnesium and its alloys are candidates for bone implants and stent applications due to their suitable mechanical properties, including fracture toughness higher than that of ceramics and polymeric materials [1]. Additionally, the elastic modulus of Mg alloys (40-45 GPa) is closer to that of human bones (10-40 GPa) than other commonly used implant metallic materials. Magnesium and its alloys have also shown osteoconductive and osteoinductive properties, thus offering a less invasive repair and temporary support during tissue recovery. The magnesium has the capability of being dissolved or absorbed by the body and then later being eliminated. As biodegradable materials, they will not remain as permanent implants in the body and will not require a second surgical operation after the tissue is repaired. The major drawback of magnesium and its alloys is that they tend to corrode very quickly in the physiological pH (7.4-7.6) environment, thereby losing their mechanical integrity before the end of the period necessary for bone tissue healing.

Mathematical models are promising tools to understand the corrosion process of magnesium and its alloys. Nowadays the advantages of incorporating mathematical modeling as part of a complete experimental design should be obvious. Models extract information from the data, while, at the same time, estimating those parameters within which the researchers are interested. By using the language of mathematics the system under study can be characterized more fully and it is possible to develop hypotheses about how the system works in more detail. So, the efficiency of numerical methods, such as Finite Element Method (FEM) and Boundary Element Method (BEM) for predicting potentials and currents in galvanic corrosion systems has been previously verified in numerous works [2,3,7].

The combination of the experimental data with mathematical models will help us to perform a

detailed study of the phenomena involved in the corrosion process of magnesium materials. The rapid corrosion rate, the low reproducibility of experimental tests and the low correlation between *in vitro* and *in vivo* degradation results has prompted this work. The aim is to study the microgalvanic corrosion formed on the magnesium due to the presence of impurities, with a diameter D , in a physiological environment (PBS) with a variable electrolyte thickness, h , by FEM. In this work, the electrochemical experimental data obtained from polarization curves are used to model mathematically the corrosion process by solving the Laplace equation and the proper boundary conditions through FEM. It also seeks to correlate a parameter that has barely been studied by researchers such as the thickness of electrolyte that bathes the magnesium surface. This last very important variable could explain the different *in vivo* and *in vitro* biodegradation of magnesium.

MATERIAL AND METHODS

Commercial grade 99.8% cast pure magnesium was studied. The chemical composition of the ingot, determined by wavelength dispersive X-ray fluorescence WDXRF is (wt.%): 0.025 Al, 0.014 Si, 0.071 Mn, 0.01 Cu, 0.051 Zn and 0.006 Fe, balance Mg [4]. The phosphate buffer solution (PBS) was used as electrolyte: 0.20 g/l KCl, 0.20 g/l KH₂PO₄, 8.00 g/l NaCl and 1.15 g/l Na₂HPO₄ (anhydrous). The conductivity of the PBS was 1.64 S/m.

A three electrode electrochemical cell with a platinum wire as a counter electrode and Ag/AgCl as a reference electrode were used. The working electrodes were Mg disks. The surface was ground with SiC abrasive paper of increasing grain size from 600 to 1200 in water and finally polished with 1 μ m diamond suspension. Before testing, magnesium surfaces were rinsed ultrasonically in ethanol.

Single sweep potentiodynamic polarization curves were performed at 60 mV/min, from corrosion potential to -0.250 V vs E_{corr} . After cathodic polarization curve, Mg surface was left until stabilization of the E_{corr} . Once stabilization was achieved, anodic polarization curves were drawn from E_{corr} to 1.0 V vs E_{corr} . At least five polarization curves were generated on Mg samples.

Galvanostatic experiments were performed on magnesium surfaces by applying different current values: 10 μ A, 50 μ A, 100 μ A, 150 μ A, 500 μ A and 1000 μ A for 150 s, and potential variation until stabilization was registered.

Basic theory of finite element method

To study the steady state potential distribution in the case shown in figure 1 it is necessary to solve boundary value problem 1, which mathematically describes the problem shown in this figure.

$$\begin{aligned} -k\Delta\phi(x,y) &= 0 \quad (x,y) \in \Omega \\ -k\frac{\partial\phi}{\partial n} &= 0 \quad \text{in } \Gamma_1 \cup \Gamma_2 \cup \Gamma_3 \\ \phi &= \phi_0 \quad \text{in } \Gamma_4, -k\frac{\partial\phi}{\partial n} = PC_{Mg} \quad \text{in } \Gamma_5 \end{aligned} \quad (1)_{\#}$$

Where ϕ is the electrochemical potential in domain Ω , k represents the electrolyte conductivity, and ϕ_0 is the fixed potential of impurities Γ_4 . Γ_1 , Γ_2 , and Γ_3 are the boundaries of the electrolyte considered electrically insulated. Finally, PC_{Mg} is a piecewise linear function that represents the polarization curve of magnesium in PBS and is the condition applied to the boundary Γ_5 .

Problem 1 presents both Neumann and Dirichlet type boundary conditions, which together with the operator used (Laplacian) give rise to a problem with a unique solution, since its corresponding weak

formulation $a(\cdot, \cdot) = l(\cdot)$ has a left side that is bilinear, symmetrical, continuous and H-elliptic, while the function $l(\cdot)$ is linear and continuous [5, 6].

In order to solve problem 1, it is necessary to homogenize the Dirichlet type boundary condition in Γ_4 through a change of variable and then the corresponding variational formulation is generated. This is posed in a space of finite dimension and the FEM is ultimately applied in order to solve the numerical system. In short, considering that the solution ϕ is approximated by the functions Φ_i in the sense

$$\phi \approx \sum_{i=1}^N a_i \Phi_i$$

where N is the number of elements in the selected mesh, the final matricial form of this problem is as follows:

$$\begin{bmatrix} \int_{\Omega} \frac{\partial \Phi_1}{\partial x} \frac{\partial \Phi_1}{\partial x} + \frac{\partial \Phi_1}{\partial y} \frac{\partial \Phi_1}{\partial y} dX & \dots & \int_{\Omega} \frac{\partial \Phi_N}{\partial x} \frac{\partial \Phi_1}{\partial x} + \frac{\partial \Phi_N}{\partial y} \frac{\partial \Phi_1}{\partial y} dX \\ \vdots & \ddots & \vdots \\ \int_{\Omega} \frac{\partial \Phi_1}{\partial x} \frac{\partial \Phi_N}{\partial x} + \frac{\partial \Phi_1}{\partial y} \frac{\partial \Phi_N}{\partial y} dX & \dots & \int_{\Omega} \frac{\partial \Phi_N}{\partial x} \frac{\partial \Phi_N}{\partial x} + \frac{\partial \Phi_N}{\partial y} \frac{\partial \Phi_N}{\partial y} dX \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_N \end{bmatrix} = \begin{bmatrix} \int_{\Gamma_2} PC_{Mg} \Phi_1 \\ \vdots \\ \int_{\Gamma_2} PC_{Mg} \Phi_N \end{bmatrix} \quad (2)$$

The unknown vector $\{a_1, \dots, a_N\}$ is found using a numerical method, and it only remains to change the variable used above, in the reverse direction, in order to recover the original solution of the physical problem.

RESULTS AND DISCUSSION

Potentiodynamic and galvanostatic curves used as Neumann boundary conditions

Figure 2 shows the polarization curves and the galvanostatic measurements performed on the cast pure Mg surfaces immersed in PBS. In this figure, it can be seen that both cathodic and anodic branches coincide adequately when the current tends to zero, i.e. they start at the same corrosion potential even after the cathodic polarization curve has been previously drawn. The galvanostatic measurements made at different anodic potential values are in good agreement with the potentials obtained from the anodic branch of the potentiodynamic curve. Therefore it can be considered that the curves have been obtained in a state close to the steady state.

Experimental polarization curves of magnesium were used as boundary conditions in the magnesium matrix, whereas a constant potential value of -1.3 V was considered where impurities were simulated. This constant potential value was estimated experimentally by scanning Kelvin probe. The anodic polarization curves showed a good reproducibility, but it was decided to study the effect of slight variations in E-i on the electrochemical potential distribution. The slopes of the linear piecewise function PC_{Mg} were changed from 90% to 110% of its average value. Figures 3a and 3b show the potential variations of the Mg matrix (Γ_5) affected by 4 impurities (Γ_4) fixed at -1.3 V considering $h/D > 2.5$ and $h/D = 0.5$, respectively. As can be seen, the potential distribution is barely affected by the changes in the slopes of PC_{Mg} . So, this function can be used to adequately predict the effect of other variables like the thickness of electrolyte, h, on the potential distribution of the Mg matrix.

Profile of potential distribution around impurities. Effect of length ratio of h/D

Figure 4 illustrates the potential distribution for the Mg/impurities galvanic couple in PBS, for

various length ratios h/D , using the configuration shown in Figure 1. It can be seen that, when this relation is small enough, the potential decreases as one moves away from the impurity to reach the corrosion potential value of pure magnesium. The potential values of the magnesium matrix in the areas closer to the impurities are the same, regardless of the value of the thickness of the electrolyte, h . These areas have higher potentials than the corrosion potential values and the result is Mg is corroded. When h/D decreases below 0.5 the magnesium matrix far from the impurities reaches corrosion potential values, so Mg matrix is not affected by the presence of impurities. This means that when Mg is covered by a thin film of electrolyte, galvanic corrosion is focused on the vicinities of impurities, however, far from the impurities, Mg matrix remains near to its corrosion potential with a natural corrosion process. However, if Mg matrix is completely covered by a thick layer of electrolyte, h/D higher than 2.5, the potentials obtained in the Mg surface far from the impurity are higher than its corrosion potential, so the Mg is anodically polarized and it suffers more severe corrosion.

CONCLUSIONS

The potential variation due to the Mg/impurities galvanic couple in PBS provokes a high corrosion rate on the Mg matrix.

When Mg is covered by a thin film of electrolyte, galvanic corrosion is focused on the vicinities of impurities and far from impurities Mg suffers a natural corrosion process.

When Mg is completely covered by a thick layer of electrolyte, h/D higher than 2.5, the Mg is always anodically polarized and it suffers more severe corrosion. There is a threshold electrolyte thickness above which the effect of impurities is extended over the entire Mg surface.

The thickness of the electrolyte must be considered as an important variable that affects drastically the *in vivo* degradation process.

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Figure 1. Schematic representation of the modelled system, where four impurities, Γ_4 with a constant potential, Φ_0 , embedded in a magnesium matrix, Γ_5 which in turn is in contact with an electrolyte Ω . The electrolyte is limited by electrically insulated boundaries Γ_1 , Γ_2 and Γ_3 .

Figure 2. Potentiodynamic curves and galvanostatic measurements for pure Mg immersed in PBS.

a)

b)

Figure 3. Potential variations of the Mg matrix ($\Gamma 5$) affected by 4 impurities ($\Gamma 4$) fixed at -1.3 V as configuration shown in Figure 1. The slopes of the piecewise function of the polarization curve, $PCMg$, were 0.9, 1 and 1.1 times the average slope found experimentally. a) h/D was higher than 2.5, where D is the radius of the impurities. b) $h/D=0.5$

a)

Figure 4. Potential profiles obtained for different values of h/D in the boundary Mg matrix ($\Gamma 5$) affected by the impurities ($\Gamma 4$) following the configuration shown in Figure 1.