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Directionally solidified dilute Zn-Mg alloys: Correlation between microstructure and corrosion properties

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ABSTRACT

Zinc–Magnesium (Zn–Mg) alloys have been addressed as potential biodegradable biomaterials. These alloys enable to overcome the main drawbacks of Mg, its high corrosion rate and hydrogen evolution. Moreover, homogeneous corrosion degradation is also an interesting issue to ensure the success of load-bearing biodegradable implants. In this work, two directionally solidified dilute alloys, Zn-0.3wt-%Mg and Zn-0.5wt-%Mg were studied. Both alloys having different microstructural morphologies (cellular and dendritic arrays) depending of the distance to the cooling bottom were evaluated to correlate their microstructural features with corrosion properties. Kinetics and corrosion mechanism have been evaluated by means of DC and AC electrochemical techniques in low chloride containing solution, 0.06 M NaCl. Coarser microstructures are shown to promote higher corrosion rate. Like Zn the corrosion mechanism occurs throughout a multistep dissolution process involving the formation of intermediate monovalent Zn^{I}, and soluble zinc hydroxychloride compounds resulting of the reaction of zincate ions with chloride ions.

1. Introduction

Historically, Zn-based alloys are known for their ability to cathodically protect steel against corrosion due to their preferential dissolution with respect to steel. Zinc coatings based on Zn-Al, Zn-Fe and Zn-Mg alloys are reported in literature for civil and building construction applications [1,2]. These alloys are quite reactive when exposed to the atmosphere forming surface corrosion products that protect the steel and reduces its corrosion rate.

Although magnesium is potentially a candidate as implant material due to its non-toxicity to the human body, its rapid dissolution and hydrogen release are generally an intrinsic response of magnesium to chloride containing solutions such as the body fluids becoming an important drawback. Recent application of Zn-Mg alloys as implants materials has shown that inside the human body they can be gradually biodegrade in situ at slower rate than Mg [3]. Moreover, Hennig et al. [4], found that zinc as antioxidant and endothelial membrane stabilizer protected constituent cells from lipid- or cytokine-induced perturbation and Yamaguchi et al. [5] observed that the presence of zinc enhanced bone mineralization.

On the other hand, as zinc is a nobler metal than magnesium, Zn-Mg alloys may possess higher corrosion resistance and thus, a smaller dissolution rate than magnesium.

Some studies reported in the literature have described the corrosion performance of Zn-Mg alloys mentioning the role not only of the magnesium content but also of the microstructure [6–10]. However, there is still a lack of more comprehensive correlations between the as-solidified microstructure and the corrosion behavior, since solidification is an inherent phenomenon occurring in both the hot-dip coating process and the casting process along the manufacturing route of metallic implants. There is not a general rule relating microstructural features to the corrosion behavior. As an example, a recent work concerning the corrosion analysis of as-cast Al-Mg-Si alloy samples has shown that finer cellular and dendritic microstructural arrays are associated with lower corrosion current densities and more positive corrosion potential when compared with coarser microstructures [11].

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Conversely, for Pb-Bi alloys, the corrosion resistance has been shown to increase considerably when the alloys are cast under lower cooling rate, i.e., when the matrix is characterized by coarser cells. Furthermore, the effect of eventual Bi segregation was shown to have also an important role, that is, if the coarse microstructure is associated with local increase in Bi content, this changes the anode/cathode area ratio increasing the corrosion resistance [12].

A recent work by the present authors has examined the evolution of microstructure of hypoeutectic Zn-Mg alloys under an extensive range of cooling rates during solidification under transient heat flow conditions [13]. The microstructure has been shown to be formed by a Zn-rich matrix and two kinds of competitive eutectic mixture (Zn-$Zn_{11}Mg_2$ and Zn-Zn_2Mg). In addition, the morphology of the Zn-rich matrix varied from high cooling rate plate-like cells to a granular dendritic morphology associated with low cooling rates. However, investigations focusing on interrelations of structural aspects of as-cast Zn-Mg alloys, that is, the morphology of both macrostructure and microstructure, the length scale of the phases forming the microstructure and the resulting electrochemical behavior are missing in the literature.

The aim of this work is to correlate microstructural features of directionally solidified dilute Zn-0.3wt-%Mg and Zn-0.5wt-%Mg alloys with the corresponding electrochemical behavior. Samples of these alloys having different microstructural morphologies (cellular and dendritic arrays) were studied by mean of polarization curves and electrochemical impedance spectroscopy (EIS). Hence, both the corrosion kinetics and the mechanism were determined in a NaCl solution at room temperature. Simulations with equivalent circuits will be carried out to give support in the elucidation of corrosion mechanisms.

2. Experimental procedure

2.1. Directional solidification and samples for metallography and corrosion tests

The nominal compositions of the dilute Zn-Mg alloys analyzed in the present study are: Zn-0.3wt-%Mg and Zn-0.5wt-%Mg. The compositions of metals used to prepare these alloys are shown in Table 1.

The solidification experiments were carried out in a water-cooled apparatus, which was designed to promote directional solidification under transient heat flow conditions. The details of experimental casting apparatus, melting and solidification procedure have been described in a previous study by the authors [13]. In a single directionally solidified (DS) casting a significant range of solidification microstructures can be obtained from the cooled bottom to the top of the casting, i.e. along a decreasing profile of cooling rates ($\dot{T}$). Higher cooling rates are associated with finer microstructures and vice-versa. This is shown schematically in Fig. 1, where a typical macrostructure of dilute Zn-Mg alloys (left side) is correlated with the evolution of solidification cooling rates along the length of the DS casting and with the microstructure morphology of the Zn-rich phase (right side). As described in a preceding investigation [14], the temperature profiles around the *liquidus* temperature of each alloy, provided by cooling curves recorded by thermocouples located along the length of the DS castings, were used to determine the coefficients of a 5th-order polynomial via the least square method, thus permitting temperature (T) vs. time (t) functions to be generated. The derivative of these functions with respect to time yielded cooling rate functions $\dot{T} = f(t)$. The experimental time corresponding to the *liquidus* front passing by each thermocouple is then inserted into the $\dot{T} = f(t)$ function to permit $\dot{T}$ to be determined.

Table 1
Chemical composition (wt. %) of metals used to prepare the alloys.

Element	Zn	Mg	Mn	Cr	Fe	Al	Pb	Si
Zn	balance	–	–	–	0.015	–	0.012	0.003
Mg	0.01	balance	0.01	0.01	0.01	0.11	–	–

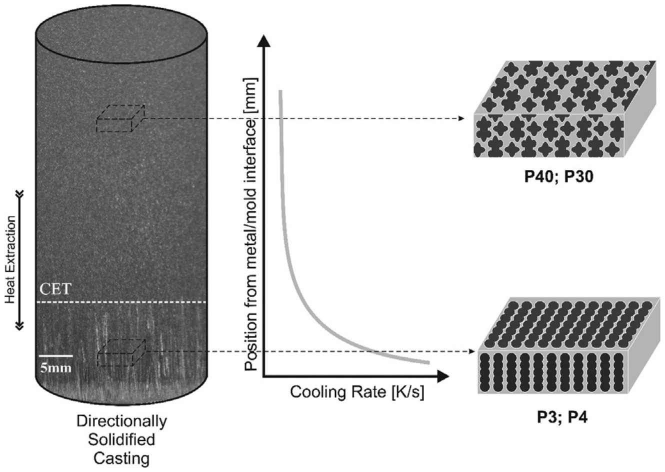

Fig. 1. Typical macrostructure of the DS castings of both Zn0.3wt-%Mg and Zn-0.5wt-%Mg alloys: columnar from bottom to the columnar/dendritic transition –CET and equiaxed from CET to the top of the casting (left side); Solidification cooling rate profile (center) and schematic representations of microstructures in opposite regions of the DS casting.

To analyze the effect of cooling rate on microstructural features, samples were extracted from extreme positions along the length of the DS Zn-Mg cylindrical castings for metallography. For each alloy composition, one sample closer to the cooled bottom (represented by P3 and P4 in Fig. 1, where the numbers represent the distance in mm from the cooled surface of the casting) and one closer to the top of the casting (P30 and P40). An etching solution (Nital 10%) has been applied during 7s to reveal the microstructures on the cross section of each sample. The microstructures were analysed by optical microscopy, using an Olympus Inverted Metallurgical Microscope (model 41GX). Microstructural characterization was carried out by scanning electron microscopy – SEM (ZEISS-EVO-MA15). The interlamellar spacing (λ) of the eutectic mixture was measured from SEM images. To investigate the influence of microstructural features on the corrosion behavior of the dilute Zn-Mg alloys, samples for corrosion tests were also extracted from the same positions P3; P40 (Zn-0.3wt-%Mg alloy) and P4; P30 (Zn-0.5wt-%Mg alloy).

2.2. Corrosion tests

Electrochemical tests were performed in a 0.06 M NaCl solution using a Gamry Reference 600 potentiostat. The electrochemical cell used was a three-electrode cell; where an Ag/AgCl (saturated KCl) electrode was the reference electrode, the counter-electrode was a platinum wire, and the working electrode was the sample under study. The exposed area of the samples was 0.17 cm^2. The volume of electrolyte used for electrochemical tests was 30 mL. All the tests were done in aerated conditions at room temperature.

Before the polarization curves the evolution of the open circuit potential (OCP) was recorded for 15 min. A potential step of −0.1 V with respect to the corrosion potential was applied, starting the sweep in an anodic direction at a polarization scan rate of 0.16 mV/s until reaching a limit current density value of 0.25 mA/cm^2.