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Correlation between electrochemical impedance measurements and corrosion rates of Mg-1Ca alloy in simulated body fluid

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ABSTRACT

The corrosion behaviour of an Mg-1Ca alloy in simulated body fluid (SBF) for 14 days was investigated by electrochemical impedance spectroscopy (EIS), hydrogen evolution measurement, weight loss and observation of the corroded alloy surfaces, with the aim of establishing a clear correlation between the values of the parameter obtained from EIS fitting and corrosion rates. It was found that corrosion proceeds in three stages, characterized by differences in the values of resistances and by the weight of the relative contribution of the inductive behaviour to the overall EIS response. Among all the parameters obtained from EIS fitting, only the charge transfer resistance presented a good correlation with the corrosion rate over the whole duration of the measurement, and an apparent Stearn-Geary coefficient could be calculated. Based on the EIS results, a better understanding of the corrosion behaviour of the Mg-1Ca alloy in SBF solution was attained.

1. Introduction

Favourable biological compatibility and appropriate mechanical properties make magnesium and its alloys promising materials for biomedical applications [1–3]. In such applications, the corrosion rate of magnesium needs to fall within a well-defined range, since the implant should maintain its mechanical function for the time required for healing, and subsequently it should progressively dissolve, allowing the bloodstream to remove the corrosion products and the hydrogen gas generated. Magnesium and its alloys immersed in physiological media for 12 weeks [4,5] exhibit complex corrosion behaviour associated with the high electrochemical activity of magnesium and its electronegative potential with respect to the hydrogen evolution reaction [6]. Since the equilibrium potential for magnesium oxidation is −2.37 V vs. SHE, there is a large thermodynamic driving force for magnesium oxidation in aqueous environments. During corrosion process in NaCl solutions, a magnesium oxide/hydroxide film is developed due to the increase of pH associated with hydrogen evolution. This film is relatively insoluble in alkaline environment, offering some degree of protection against further corrosion. In addition, the 'negative difference effect' related to accelerated hydrogen evolution rate with increasing anodic polarization is often observed [7–12].

Compared with NaCl solutions, a simulated body fluid solution contains ions like HPO_4^{2-}, HCO_3^{2-} and SO_4^{2-}, in addition to Cl^- ions, and also contains cations like Mg^{2+}, Ca^{2+}. When a magnesium alloy is exposed to SBF solution, phosphate/carbonate compounds can be formed along with $MgO/Mg(OH)_2$·As a consequence, the protective properties of the film on magnesium surface are different compared to those typical of films generated in chloride only containing solutions [13,14]. Thus, the change of phosphate/carbonate compounds, in terms of composition, thickness and morphology with exposure time may also play an important role on protection of magnesium alloys from further corrosion. Therefore, the corrosion behaviour of a magnesium alloy in a simulated body fluid is much more complicated than that in NaCl solutions, and it is particularly true for a long-term exposure.

Potentiodynamic polarization has been commonly applied to provide kinetic information including relative anodic and cathodic reaction kinetics, and calculation of corrosion rates [15]. However, for magnesium alloys, underestimation of corrosion rates using the polarization has been reported by some researchers [15–19]. Electrochemical impedance spectroscopy (EIS) can also be used to evaluate corrosion rates, since it is not destructive and therefore particularly suitable for long-term studies [20,21]. In recent years, some investigations have been conducted to establish correlations between values of resistances extracted from EIS spectra and corrosion rates which were obtained by hydrogen evolution and/or

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weight loss in NaCl solutions for magnesium alloys [16,17,22–25]. These correlations can be expressed in a form of Stern-Geary equation: $j = B/R$, where R is a value of resistance (Ω cm^2) obtained from the fitting of EIS spectra, j is corrosion current density (mA/cm^{-2}) and B is the 'apparent' Stern-Geary coefficient (mV). The correlation coefficient is, for magnesium, an empirical factor which is determined by alloy-solution system and exposure time in solutions.

The aim of this paper is to establish a correlation between the electrochemical impedance responses and the corrosion rate of Mg-1 wt%Ca alloy in simulated body fluid at 37 °C for 14 days. The corrosion rates were measured by hydrogen evolution and weight loss. The changes of corrosion behaviour of the magnesium alloy with exposure time are discussed, based on the analysis of the time-dependent impedance responses and the observation of corroded surface by optical imaging and SEM observation.

2. Experimental

The magnesium electrodes used in this work were obtained from an Mg-1Ca alloy (nominal composition: 0.8–1.1 wt% Ca, <0.01 wt% Al and Fe, <0.2 wt% Mn, Bal. Mg) plate supplied by China National Remanufacturing Laboratory. Alloy specimens were cut into 10 mm × 10 mm × 5 mm, degreased in acetone, connected to an electrical cable and embedded in epoxy resin. Subsequently, they were mechanically polished with 400–2400 grit SiC paper, degreased in acetone, dried in cold air and stored in a desiccator, if not used immediately for testing.

Corrosion potential and electrochemical impedance spectroscopic (EIS) measurements were performed using a VersaSTAT 4 potentiostat/frequency response analyser. A three-electrode electrochemical cell was used, with a saturated calomel electrode (SCE) as the reference electrode, a platinum sheet as the counter electrode and the mounted sample as working electrode. Electrochemical impedance spectroscopy was measured on all samples at selected times by applying a sinusoidal potential perturbation of 10 mV amplitude from 1 MHz to 10 mHz at the open circuit potential. Digital images were acquired and recorded using a USB digital microscope (Maplin plc). pH values were recorded by a HANNA HI-98103 Pocket pH Tester, with the pH probe placed at 5 cm from the magnesium surface. All the electrochemical experiments were performed at 36.5 ± 0.5 °C to simulate human body environment in SBF solution.

3. Results

3.1. Time evolution of the corrosion potential of Mg-1Ca alloy in SBF solution

The time evolution of the corrosion potential of an Mg-1Ca electrode in SBF solution is presented in Fig. 1. During the first hours of immersion, the potential increased rapidly and then slowly approached the value of −1.83 V at 24 h. The corresponding time evolution of the electrolyte pH is shown in Fig. 1b. It is evident that the pH value follows a similar trend to the free corrosion potential. Initially, the pH increased rapidly from the initial 7.3 value, and subsequently approached slowly the value of 7.8 after 24 h. It's worth noting that pH increased by 1.1 units after 240 h immersion and its value at 240 h was 8.4 (see the supplementary information in Fig. A1).

Fig. 2 displays the optical images of Mg-1Ca alloy surface during immersion in SBF solution up to 12 h. During the first hour of immersion, abundant hydrogen bubbles originated from the whole surface, with small bubbles growing to form larger bubbles that

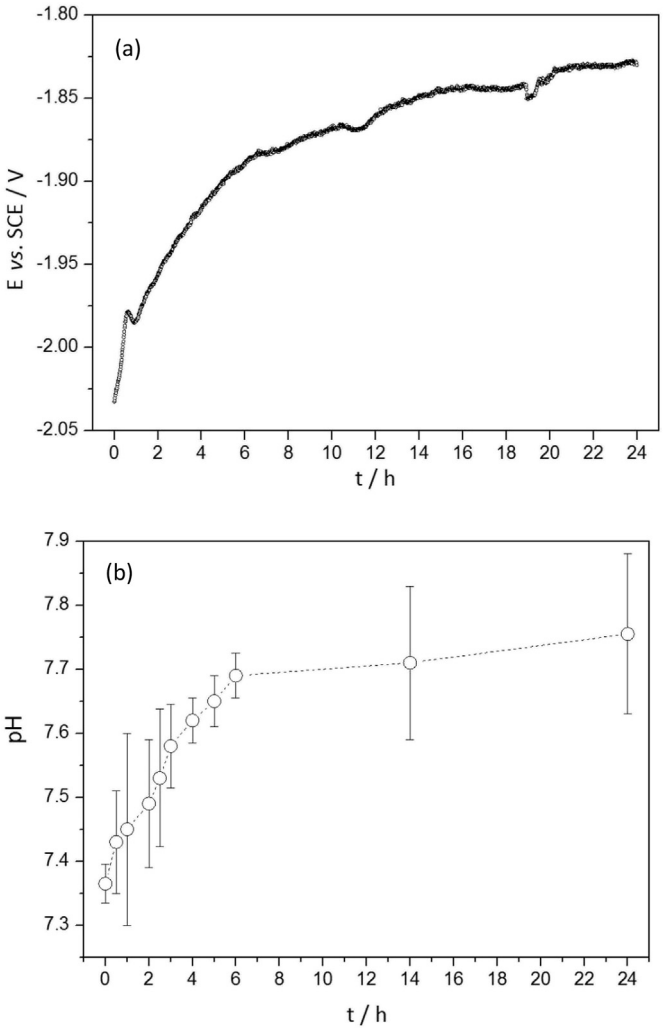

Fig. 1. Time evolution of (a) the corrosion circuit potential of Mg-1Ca alloy in SBF and (b) electrolyte pH.

remained attached to the surface before floating to the electrolyte surface. Within the first hour of immersion, a small fraction of surface area started to change appearance, from silvery to grey. After 2 h of immersion, the vast majority of the surface was covered by grey areas. Corroded dark areas occupied the electrode after 12 h, with some randomly distributed regions that appeared uncorroded. The local colour of the corroding surface appeared to be related to the orientation of grains within the alloy.

Fig. 3 presents the surface and cross-section SEM micrographs of the Mg-1Ca alloy immersed in the SBF solution after 2 min, 4 h, 12 h and 120 h. For the Mg-1 wt% Ca alloy, the secondary phase (Mg_2Ca) is more active than α-Mg, thus it oxidized preferentially during the early stages of corrosion. In the SBF solution, this initial dissolution resulted in the formation of the corrosion products film and precipitation of phosphate and carbonate compounds, rather than in the propagation of corrosion along the grain boundaries. Thus, after 2 min, the corrosion initiated along the grain boundaries due to enrichment of Ca at these locations, and formed thick corrosion products. Subsequently, the corrosion products thickened also on the surrounding regions, i.e. above the grain bulk. After 4 and 12 h, a two-layer structure developed: the bottom layer was formed by magnesium oxide/hydroxide and the top layer was formed by precipitated phosphate/carbonate.