Investigation of the corrosion mechanism of WE43 Mg-alloy in a simulated body fluid: The effect of electrolyte renewal

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In the last decade, the investigation of Mg-alloys as potential biodegradable materials for orthopedic and cardiovascular implant applications has increased considerably. Mg is an attractive material for such applications mainly due to its biocompatibility and good mechanical properties. Mg biodegradation occurs by corrosion. However, it corrodes too fast in the body, leading to a premature decrease in the mechanical properties and implant failure and to the formation of hydrogen gas at quantities that cannot be bioabsorbed by the body. Current research efforts aim to the development of new Mg-alloys with improved corrosion resistance and biocompatibility. However, this is hampered by the lack of a complete understanding of the Mg-alloy corrosion mechanism in the real physiological environment (body) and by difficulties at emulating such environment *in vitro*. In the body, the concentration of the Mg-alloy corrosion products, i.e., divalent Mg and hydroxide ions, is regulated by homeostasis. However, in *in vitro* experiments, a fast increase in the concentration of these ions in solution often occur, leading to an increase in the electrolyte pH and thus, possibly affecting the Mg-alloy corrosion mechanism and degradation rate. Although in some *in vitro* investigations reported in the literature, daily electrolyte renewal in order to simulate physiological homeostasis was performed, the effect of such procedure on the degradation (corrosion) process of Mg-alloys has not yet been reported. Therefore, the objective of this work was to investigate the effect of daily electrolyte renewal on the short-term corrosion behaviour of a commercial WE43 Mg-alloy in a modified simulated body fluid.

Test samples were prepared from cast WE43 Mg-alloy and were embedded in epoxy resin to have a final area of 2 cm^2 exposed to the electrolyte. Modified simulated body fluid (m-SBF) with an initial pH of 7.4 was used as electrolyte. Immersion experiments were performed for a period of time up to 5 days, but the complete electrolyte renewal was performed daily. Each experiment was carried out in triplicate. Open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), volume of hydrogen evolved and inductively coupled plasma optical emission spectroscopy (ICP-OES) were used to investigate the kinetics and mechanisms of the alloy corrosion. The alloy surface morphology was characterized by scanning electron microscopy (SEM). The chemical characterization of the surface corrosion layer was carried out by energy-dispersive spectroscopy (EDS), attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

SEM, EDS and XRD analyses revealed the presence of an amorphous surface corrosion layer containing Mg, Ca, O, P, Cl and C elements, implying the formation of a Ca/Mg carbonate/phosphate-containing Mg-hydroxide. This was further confirmed by ATR-FTIR, which evidenced the presence of carbonate and phosphate functional groups, and by XPS surface analysis, which evidenced the presence of Mg-hydroxide. Cross-sectional analysis of the samples after 5 days of immersion showed a non-uniform corrosion layer with a thickness in the range of 20-130 µm. A gradual increase in the electrolyte pH was observed, mostly as a result of the removal of hydrogen ions (as hydrogen gas) during the corrosion process. The highest pH increase, of about 0.4 pH units, was observed after the first day of immersion, suggesting a decrease in the corrosion rate over time. This was in agreement with ICP-OES results, which showed a decrease in the concentration of Mg^{2+} in the electrolyte at longer immersion times. OCP results showed a fast increase in the corrosion potential during the first 24 hours of immersion, followed by a slower increase until a quasi-constant potential value was reached after 72h. Although an overall increase in OCP was observed, a decrease in the OCP was observed after each renewal of the electrolyte. This behaviour suggested an alternating increase and decrease in the protective ability of the corrosion film as a result of both electrolyte composition and pH fluctuations after electrolyte renewal. The changes in the protective ability of the corrosion layer as a consequence of electrolyte renewal were further evidenced by EIS results. An overall increasing impedance was related to the formation and thickening of a partially protective corrosion layer. The impedance response was fitted using a three time constant-equivalent circuit and the fitting parameters were related to the processes occurring at the sample-electrolyte interface, i.e., charge transfer, Mg^{2+} diffusion through the corrosion layer and adsorption of Mg intermediates. A temporary decrease in the impedance response, observed after each electrolyte renewal, was related to an increase in the porosity of the corrosion layer and thus, a decrease in its protective ability. Normalized corrosion rate values calculated from EIS, ICP-OES and hydrogen evolution experiments showed a good agreement (Figure 1). An overall decrease in the corrosion rate with time can be observed. However, intermittent small increases in corrosion rate can also be observed after electrolyte renewal, with a diminishing effect with time.
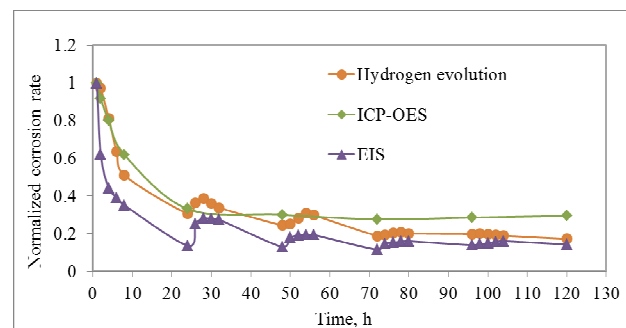

Figure 1. Normalized corrosion rate of WE43 Mg-alloy in mSBF after different immersion times, obtained by hydrogen evolution, ICP-OES and EIS.

It can be concluded that electrolyte renewal affects the Mg-alloy corrosion process by perturbing the corrosion layer-electrolyte solubility equilibrium. The following corrosion mechanism stages are proposed: a) Initial formation of a partially protective Mg/Ca phosphate/carbonate-containing Mg-hydroxide layer, b) Increase in the protective ability of the corrosion film promoted by the accumulation of corrosion products in solution, i.e. increase in pH and concentration of Mg^{2+} ions, and c) Onset of pitting corrosion of a formed passive layer.