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# Synthesis and evaluation of $MgF_2$ coatings by chemical conversion on magnesium alloys for producing biodegradable orthopedic implants of temporary use

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**Abstract**. The aim of the present work was the synthesis of biodegradable $MgF_2$ coatings by chemical conversion on the commercial Elektron 21 and AZ91D magnesium alloys, in aqueous HF solutions for different concentrations and temperatures. The chemical composition and morphology of the coatings were analyzed by scanning electron microscopy (SEM-EDX) and X-ray diffraction (XRD). On the other hand, their corrosion behavior was evaluated by gravimetric and electrochemical measurements in Hank´s solution at 37ºC for different immersion times. The experimental results revealed that chemical conversion in HF produced $MgF_2$ coatings which corrosion resistance was enhanced by increasing the HF concentration. Further, the microstructure and composition of the base alloy played a key role on the growth and degradation mechanisms of the $MgF_2$ coatings.

## 1. Introduction

Nowadays, research into biomedical applications has been focused on a new category of biodegradable implants [1]. These devices can perform a specific function for a certain period of time and then gradually disappear, avoiding long-term complications, and progressively transfer the load to the surrounding tissue. In these sense, Mg alloys potential candidates as biodegradable materials due to several advantages: Mg is non-toxic and it may stimulate the growth of new bone tissue [2]; its in-vivo degradation generates corrosion products that can easily be dissolved, absorbed and/or excreted after tissue healing, avoiding the need of the second additional surgery to remove the implant [3, 4]; and their mechanical properties (density, elastic modulus, and compressive yield strength) are close to those of the human bone that is a great advantage in order to minimize the stress shielding phenomenon [5].

However, the main limitation of magnesium alloys for their use as implant material is its excessively high degradation rate in body fluids, which can lead to the loss of mechanical properties of the implant before the bone has healed. Further, the corrosion process of magnesium alloys also generates hydrogen gas bubbles that, if the local hydrogen saturation of blood and tissues are exceeded, might accumulate in the tissue cavities [6, 7]. In this regard, there are generally two possible ways to improve the corrosion behaviour of Mg and its alloys: i) tailor their composition and microstructure and ii) modified their electrochemical behaviour through surface treatment. Among the

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surface treatments currently used for magnesium alloys, the chemical conversion route is one of the most simple and effective processes to produce a protective layer on the surface. Particularly, chemical conversion in hydrofluoric acid allow obtaining magnesium fluoride ($MgF_2$) coating that has been reported to be an effective alternative for improving the corrosion resistance of potential biodegradable Mg-based implants [8-10]. Based on these statements, the aim of the work was to synthesize and evaluate $MgF_2$ coatings by chemical conversion on magnesium alloys for producing biodegradable orthopaedic implants for temporary use.

## 2. Experimental procedure

Two magnesium alloys were used in the present investigation: the AZ91D (Al: 8.5-9.5%; Zn: 0.45-0.9%; Mn: 0.17-0.3%; others: 0.08%; Mg: balance (%wt.)) and the Elektron 21 (Zn: 0.2-0.5%; Nd: 2.6-3.1%; Gd: 1.0-1.7%; Zr: saturated; Mg: balance (%wt.)) magnesium alloys. These alloys were supplied by Magnesium Elektron Ltd. specimens were wet ground through successive grades of silicon carbide abrasive papers, from 120 to 600, rinsed in alcohol and dried in a warm stream of air. For conversion treatment, the samples were immersed vertically in a plastics bottle containing HF of concentration 1.6, 2.4, 3.2 and 4.0 v/v %. at room temperature for 24 h. The treated samples were then rinsed with deionized water, dried at 120°C (30 min.) and weighed. Coatings were characterized using Scanning Electron Microscopy (SEM). Finally, corrosion resistance of the coatings was evaluated by immersion and anodic potentiodynamic polarization tests in Hank´s solution at 37°C.

## 3. Results and discussion

Figure 1 shows the electron micrographs of the $MgF_2$ coatings performed by chemical conversion in HF 4%v/v solution at room temperature and 24 hours on the AZ91 and elektron 21 magnesium alloys.

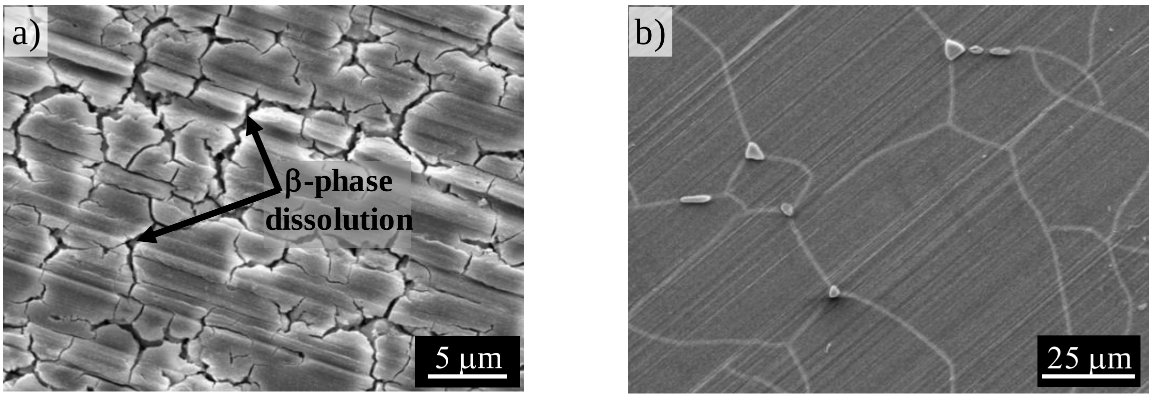


**Figure 1.** Electron micrographs of the $MgF_2$ coatings performed by chemical conversion in HF 4%v/v solution at room temperature: (a) AZ91 and (b) elektron 21 magnesium alloys.

The preferential dissolution of the reactive β-phase ($Mg_{17}Al_{12}$) in the AZ91D alloy promotes the growth of irregular $MgF_2$ coatings with thickness ranged between 3 and 10 µm. Conversely, the more homogeneous microstructure of elektron 21 alloy favoured the formation of continuous, uniform coatings, 5 µm thick, where the intermetallic $Mg_{12}(Nd_xGd_{1-x})$ phase remained stable on the top surface, without any evidence of partial dissolution or degradation.

Figure 2 represents the mass gain versus time for the AZ91D and Elektron 21 alloys treated by chemical conversion in different HF solution after immersion in Hank´s solution.

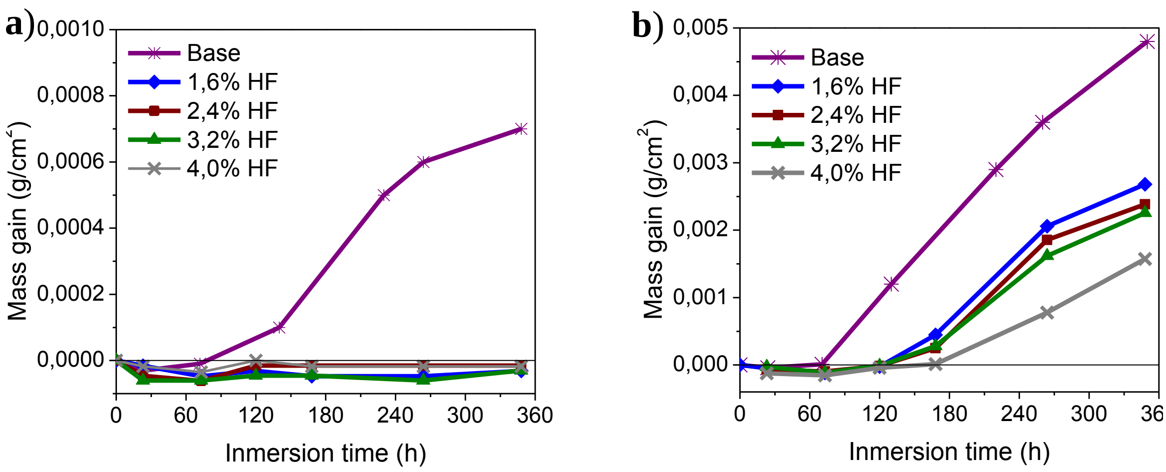


**Figure 2.** Mass gain curves of the magnesium alloys treated in different HF solutions after immersion in Hank´s solution at 37ºC for: (a) AZ91D and (b) elektron 21.

It was noticed that chemical conversion of magnesium alloys significantly reduced the corrosion rate of the specimens, especially for the AZ91D alloy (figure 2 (a)). Interestingly, coatings performed on the Elektron 21 specimens showed a corrosion mechanism divided in two stages or process, in which inflexion point probably indicates the beginning of the dissolution of the magnesium alloy underneath. Moreover, it is also evident that an increase in the HF concentration affected positively the corrosion behavior, retarding the degradation of the metallic substrate. This particular behavior may be suitable in design of biodegradable coatings for short-term applications.

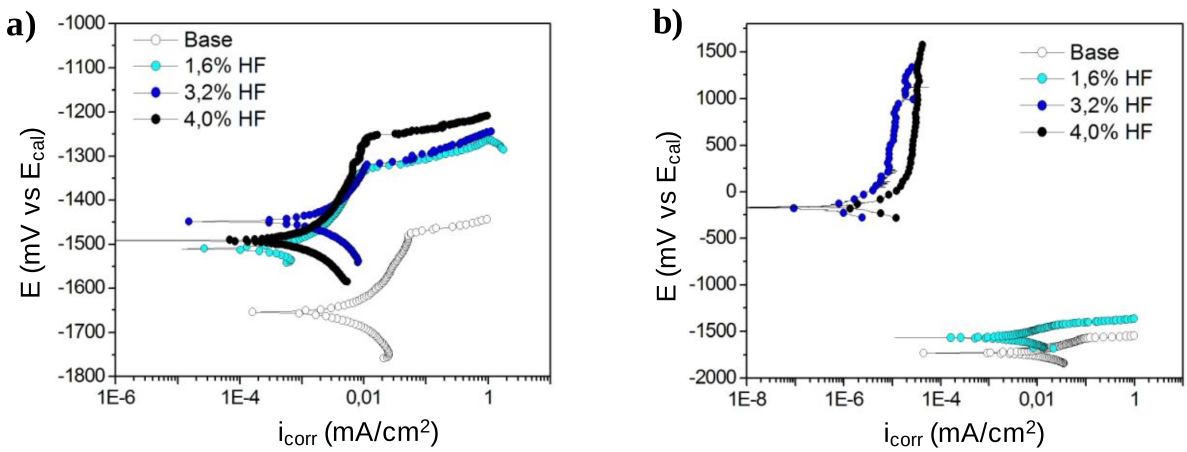


**Figure 3.** Anodic polarization curves of the magnesium alloys treated in different HF solutions after immersion in Hank´s solution at 37ºC for 60 min: (a) AZ91D and (b) elektron 21.

On the other hand, figure 3 shows the anodic polarization curves for the same specimens and conditions. Compared to the parent alloy, the AZ91D coated specimens exhibited better corrosion performance with reduction of corrosion current density by about one order of magnitude, while the corrosion potential was displaced toward more noble values. On the other hand, conversion coating of the Elektron alloy resulted in a much more evident improvement. In this regard, the specimens coated in HF solutions with concentrations higher than 3,0% v/v, showed passive properties for the entire potential range selected; and experienced reduction of the corrosion current density in three and four orders of magnitude with a displacement of the corrosion potential by more than 1000 mV.

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## 4. Conclusions

Conversion coating of the AZ91D and Elektron 21 magnesium alloys in HF solution resulted in $MgF_2$ layer which provide an excellent protection against corrosion, where the microstructure (presence and nature of different intermetallic phases) plays a key role in its growth. Further, an increase in the HF concentration affected positively in the corrosion behavior of both alloys retarding even more the anodic dissolution of the metallic substrate. Coatings performed on the Elektron 21 exhibited an interesting corrosion mechanism divided in two stages, which is suitable in design of biodegradable coatings for short-term applications.

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