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Corrosion kinetics of magnesium alloys for bioresorbable biomedical implants coated by plasma electrolytic oxidation

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Magnesium alloys are currently employed in the development of bioresorbable medical devices, such as osteosynthesis implants and cardiovascular stents. For the successful application of these devices, it is essential to precisely control the degradation rate by tailoring the corrosion kinetics through alloying strategies and/or the application of biocompatible coatings, for instance via plasma electrolytic oxidation (PEO). The aim of this study is to evaluate the effect of PEO coatings produced in phosphate-based electrolytes on the corrosion kinetics of Mg-RE and Mg-Y-RE alloys (EV31A and WE43B, respectively), and commercially pure magnesium (Mg-CP), which was used as a reference. For all materials, oxygen- and phosphorus-rich coatings with thickness in the 20-30 μm range were obtained. Hydrogen evolution corrosion tests, carried out in isotonic solution (0.9% NaCl) at 37 °C, revealed a reduction in corrosion rates for the coated specimens compared to their uncoated counterparts, but mainly in alloys with intrinsically lower corrosion resistance.

KEYWORDS: MAGNESIUM, MAGNESIUM ALLOYS, PLASMA ELECTROLYTIC OXIDATION, CORROSION;

INTRODUCTION

Bioresorbable biomedical implants have gained increasing attention over the past decade as a promising alternative to permanent implants in various clinical applications [1]. Their ability to gradually degrade in the human body and be replaced by natural tissue eliminates the need for removal surgeries and reduces long-term complications associated with traditional permanent implants [2]. Typical applications of bioresorbable devices include orthopedic fixation systems—like screws, plates, and pins for osteosynthesis procedures—as well as cardiovascular stents designed to support blood vessels during the healing process [3-6]. Among the various materials investigated for such applications, magnesium and its alloys have emerged as highly attractive candidates due to their combination of good mechanical properties, excellent biocompatibility and natural degradability in physiological environments. Furthermore, its corrosion products are generally well tolerated by the human body. Compared to bioresorbable polymeric materials such as polylactic acid or polycaprolactone, magnesium-based alloys offer superior load-bearing capacity, making

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them suitable for temporary structural applications under mechanical stress [1, 7, 8]. However, a critical challenge in the deployment of magnesium alloys in biomedical devices lies in the control of their corrosion rate. Excessively rapid degradation can lead to premature loss of mechanical integrity and excessive hydrogen release, while overly slow degradation may hinder natural healing and tissue regeneration [9]. Therefore, tailoring the corrosion kinetics of magnesium alloys is essential to align the degradation with the healing process. Two main approaches are usually applied to modulate corrosion rates: the addition of alloying elements—among others, rare earth (RE) elements and yttrium [10]—and the application of surface coatings. Among coating strategies, plasma electrolytic oxidation (PEO) has emerged as a particularly promising method, capable of producing adherent and biocompatible oxide layers that significantly enhance corrosion resistance of Mg implants without compromising biofunctionality [11, 12]. Therefore, the aim of this study is to characterize the structure of novel PEO coatings produced in phosphate-based electrolytes on pure magnesium and two different Mg-RE/Mg-Y-RE alloys (EV31A and WE43B), and to evaluate the impact of these coatings on the corrosion behavior in simulated physiological environments.

MATERIALS AND METHODS

The tests were conducted on two different magnesium alloys: EV31A (Mg 96.5%, Nd 3%, Zn 0.5%) and WE43B (Mg 93%, Y 4%, Nd 3%), in comparison with commercially pure magnesium (Mg-CP, Mg > 99.9%). Cylindrical specimens (5 mm in height) were machined from 11 mm diameter bars for the two alloys and from a 12.7 mm diameter bar for Mg-CP. The specimens were ground using SiC abrasive papers up to 4000 grit and subsequently some of them were coated by plasma electrolytic oxidation (PEO). PEO treatment was performed under pulsed direct current (DC) conditions, using a programmable AC voltage-controlled power source (AST1501, Ametek, USA). The specimens were immersed in an aqueous alkaline electrolyte consisting of 100 mM KOH and 25 mM $Na_6[(PO_3)_6]$, using a cylindrical AISI 304 stainless steel mesh as a cathode. A pulsed unipolar square waveform with a 50% duty cycle was applied at a frequency of 800 Hz, reaching a maximum voltage of 420 V over a total treatment duration of 10 minutes. Following the PEO process, the samples were thoroughly rinsed with deionized water and subsequently dried using compressed air. The morphology and chemical composition of the anodized layer were characterized using a field emission scanning electron microscope (FE-SEM, Zeiss Sigma 300) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford X-act). Metallographic cross-sections from one specimen of each type were analyzed. The corrosion resistance of the samples was assessed in aerated isotonic solution (0.9% NaCl), kept at 37±1 °C throughout the whole test duration. The volume of test solution to exposed surface ratio was set at 15 mL/cm^2. Corrosion kinetics were evaluated using a hydrogen evolution setup, with measurements carried out over the first 48 hours of immersion. Duplicate tests were performed on both uncoated and PEO-coated specimens.

RESULTS AND DISCUSSION

All specimens analyzed in this study exhibited the formation of a relatively uniform oxidation layer, with a thickness ranging between 20-30 μm, as shown in Fig. 1a, b, c. However, numerous defects typically associated with this type of coating were observed. These defects, which varied significantly in shape and size, locally reduced the coating thickness. Nonetheless, even in the case of large defects that appeared to extend down to the substrate surface, a thin oxide film—on the order of a micron—was still detectable at the coating-substrate interface. The characteristic microstructures of the EV31A and WE43B alloys, containing coarse secondary phases, did not seem to hinder the growth of the oxide layer; however, they contributed to an increased occurrence of the previously mentioned defects within the PEO coating. Such behavior has been previously reported for PEO-coated AZxx alloys, where the presence of secondary phases with distinct chemical compositions and morphologies promotes an heterogeneous oxide growth and the formation of porosity [13].

Regardless of the substrate material, the PEO film composition was predominantly composed of magnesium, oxygen and phosphorus (Fig. 1d, e, f).

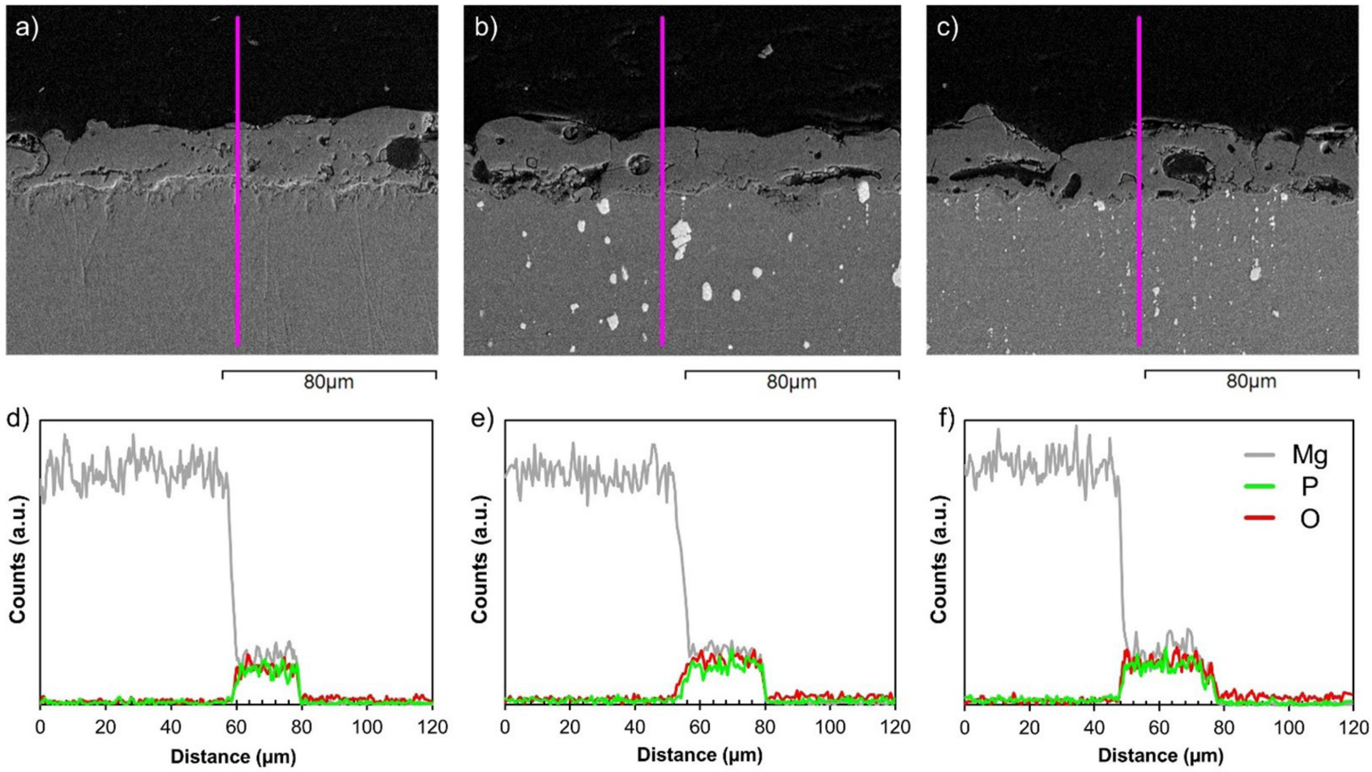

Fig.1 - (a, b, c) Micrografie FE-SEM e (d, e, f) linescan EDS degli strati di ossidazione dei provini Mg-CP, EV31A e WE43B, rispettivamente / *(a, b, c) Oxidation layers FE-SEM micrographs and (d, e, f) EDS linescan of Mg-CP, EV31A and WE43B specimens, respectively.*

During the 48 hours of immersion, significant differences in terms of corrosion behavior were observed among the investigated uncoated alloys (Fig. 2a). As reported in the scientific literature [14], Mg-CP exhibits extremely high reactivity, leading to considerable hydrogen evolution during the initial hours of exposure, followed by a subsequent plateau. The decrease in corrosion kinetics over time has been ascribed to the alkalization of the environment, which occurs very rapidly in the case of Mg-CP and promotes the deposition of corrosion products that shield the metallic substrate. In contrast, the addition of rare earth (RE) elements in EV31A and of both yttrium and RE in WE43B significantly reduced the corrosion kinetics from the very beginning of the test. Furthermore, the total amount of hydrogen evolved by Mg-CP at the end of the test was approximately one order of magnitude higher than that observed for the two alloys. Among the materials studied, WE43B showed the best corrosion performance. The superior corrosion resistance of the two alloys confirmed the beneficial effect of RE and, especially, Y on the stability of the oxide film, due to the formation of mixed oxide films.

Following the application of the PEO coating, generally a lower reactivity was observed for all materials during the initial stages of the test (Fig. 2b). Notably, PEO-coated Mg-CP exhibited hydrogen evolution values comparable to those of coated EV31A and WE43B. Additionally, both EV31A and WE43B alloys displayed a delay of approximately one hour before any measurable hydrogen evolution was detected. These results can be attributed to the barrier effect provided by the oxide layer, which effectively shields the metallic substrate. At longer exposure times, Mg-CP still exhibited higher cumulative hydrogen evolution compared to the two alloys; however, unlike the uncoated specimens, the overall hydrogen evolution values remained within the same order of magnitude for all materials.

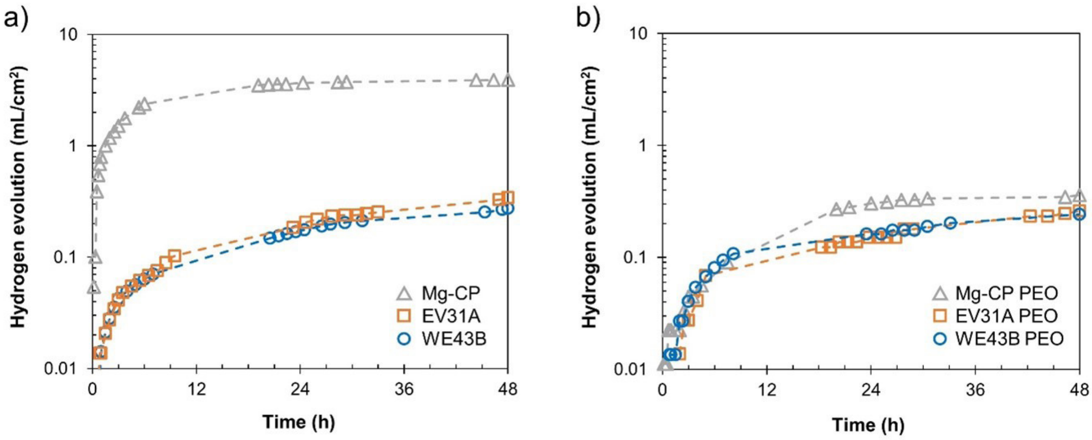

Fig.2 - Curve cumulative di evoluzione di idrogeno nel tempo in soluzione isotonica a 37 °C per i campioni (a) non rivestiti e (b) rivestiti tramite PEO / *Cumulative curves of hydrogen evolution over time in isotonic solution at 37 °C for (a) uncoated and (b) PEO-coated specimens.*

The hydrogen evolution data was subsequently used to calculate the corrosion rates of the analyzed materials. Indeed, the corrosion process of magnesium can be described by the following reaction:

$$Mg + 2H_2O \rightarrow Mg^{2+} + H_2 + 2OH^-$$

Therefore, starting from the measured volume of evolved hydrogen for exposed surface area, it is possible to calculate the mass of corroded magnesium for exposed surface area using the ideal gas law (P=101300 Pa, T=310 K). This value can then be used to determine the average corrosion rate over the 48-hour exposure period. As shown in Fig. 3, Mg-CP benefits the most from the application of the PEO coating, which can reduce the average corrosion rate by approximately 88% with respect to uncoated material. In contrast, the coating has a significantly lower impact on the two Mg alloys. Specifically, the EV31A alloy exhibited an almost negligible reduction in the average corrosion rate (about 30%) while the WE43B alloy showed essentially no differences between uncoated and PEO-coated specimens. These results may be partly attributed to the higher porosity of the coatings on EV31A and WE43B alloys. However, it has been demonstrated that such defects mainly lead to a local thinning of the oxide layer rather than to its complete absence. Moreover, the average corrosion rates of the coated EV31A and WE43B alloys are still slightly lower than those of the coated Mg-CP. Therefore, these results indicate that the application of PEO coatings is particularly advantageous for materials with inherently low corrosion resistance. For alloys with superior corrosion resistance, which naturally form more protective oxide films, the benefits of applying PEO coatings become progressively less significant as the intrinsic corrosion resistance increases.

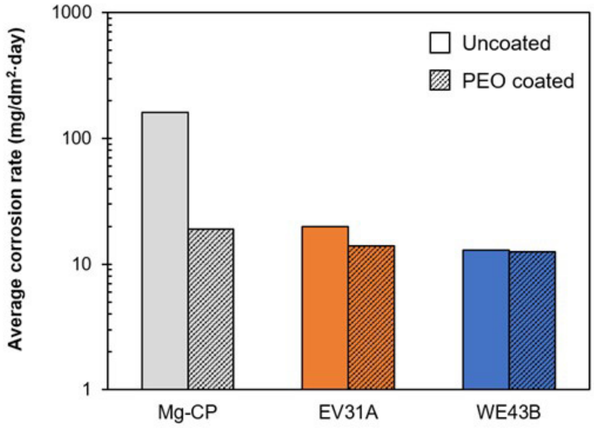

Fig.3 - Velocità di corrosione medie al termine delle 48 ore di esposizione dei provini non rivestiti e rivestiti con PEO / *Average corrosion rates after 48 hours exposure for uncoated and PEO-coated specimens.*

CONCLUSIONS

This study evaluated the characteristics of PEO coatings obtained in a phosphate-based electrolyte on Mg-RE/Mg-Y-RE alloys (EV31A and WE43B) and commercially pure magnesium, as well as the effect of these coatings on corrosion kinetics, assessed in isotonic solution at 37 °C. The main findings can be summarized as follows:

- The PEO process resulted in the formation of an oxidation layer rich in Mg, O, and P, with a thickness ranging between 20-30 μm and showing several endogenous defects, especially in EV31A and WE43B alloys.
- The application of such coating demonstrated a beneficial effect on the corrosion kinetics of all the materials studied, reducing both the initial degradation rates and the overall average corrosion rates.
- The improvement in corrosion performance was most pronounced in the case of commercially pure magnesium, while it became progressively less significant with increasing intrinsic corrosion resistance of the base material.

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Cinetiche di corrosione di leghe di magnesio per impianti biomedici riassorbibili rivestite tramite ossidazione elettrolitica al plasma

Le leghe di magnesio sono attualmente utilizzate per lo sviluppo di dispositivi biomedici a progressivo riassorbimento come mezzi di osteosintesi e stent cardiovascolari. Per il successo di tali dispositivi, è necessario definire accuratamente i tempi di degradazione, regolando le velocità di corrosione intervenendo sulla composizione chimica e/o applicando rivestimenti biocompatibili, per esempio tramite ossidazione elettrolitica al plasma (PEO). Lo scopo di questo lavoro è valutare le caratteristiche di rivestimenti PEO realizzati in soluzioni elettrolitiche contenenti fosfati sulle cinetiche di corrosione di leghe Mg-RE e Mg-Y-RE (EV31A e WE43B, rispettivamente) e di magnesio commercialmente puro (Mg-CP), utilizzato come riferimento. In tutti i materiali, sono stati ottenuti strati ricchi di ossigeno e fosforo con uno spessore variabile tra 20-30 µm. Le prove di corrosione di evoluzione di idrogeno, effettuate in soluzione isotonica (0.9% NaCl) a 37 °C, hanno mostrato una riduzione delle cinetiche di corrosione dei provini rivestiti rispetto agli omologhi non rivestiti, ma principalmente nelle leghe con una resistenza a corrosione intrinseca più bassa.

PAROLE CHIAVE: MAGNESIO, LEGHE DI MAGNESIO, OSSIDAZIONE ELETTROLITICA AL PLASMA, CORROSIONE;

TORNA ALL'INDICE >