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Corrosion protection of AZ91D magnesium alloy by a duplex coating

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Abstract: A duplex coating was formed under potentiostatic conditions on magnesium alloy AZ91D in order to improve its corrosion resistance in simulated physiological environment. The first layer was formed by anodization at low potentials in molybdate solution. The outer layer was a PPy film electro-synthesized in sodium salicylate solution. The conditions of the formation were determined to obtain a layer with globular morphology. The bilayer was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The corrosion protection properties of the coatings were examined in Ringer solution by monitoring the open circuit potential (OCP), polarization techniques, and electrochemical impedance spectroscopy (EIS). The obtained results showed that the bilayer improves the corrosion resistance of the substrate. Moreover, the duplex coating presented better anticorrosive properties than the single PPy film. Afterwards, the bilayer was modified by cementation of silver ions from a solution containing AgNO₃. The modified electrode exhibited good antibacterial properties.

Keywords: Mg substrate; anticorrosion; electrodeposited polypyrrole; molybdate; salicylate.

INTRODUCTION

Nowadays, steel and titanium are the common biocompatible materials used for biomedical implants. However, these metals release corrosion products that are human health harmful¹. This issue leads to the necessity of a second surgery to remove the implant in order to avoid infections. The removal surgery not only implies additional costs but also exposed the patient to a stressful and sometimes painful situation². Thus, biodegradable materials have been studied for their use in the biomedical field. Magnesium alloys have attracted attention as orthopedic implants due to its similar mechanical properties to the bone (as young's modulus,

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light weight, tensile strength) and biodegradability³⁻⁵. These properties make Mg and its alloys attractive for the fabrication of temporary orthopedic implants such as bone plates, rods, screws, wires, joint replacements, and also for cardiovascular implants like stents^{1,6}. Under physiological conditions, magnesium corrodes and degrades completely. Mg is naturally presented in the human body, so it could be easily metabolized and excreted without causing any health damage^{1,7}. Thus, Mg and its alloys are good alternatives as temporary implant materials such as plates, rods materials, since, after the tissue heals, they will be corroded and eliminated from the body avoiding the necessity of a second surgery for implant removal. However, their fast degradation rate in the physiological environment leads to early loss of mechanical integrity and a high local pH value surrounding the tissues, which are undesired for the use as implant materials^{4,5}. Therefore, it is very important to improve the corrosion resistance of Mg alloys in order to ensure their suitability.

Conducting polymers are suitable materials for corrosion protection of metallic substrates, especially polypyrrole (PPy) due to its high stability⁸, good biocompatibility⁹, adhesion and interesting redox properties¹⁰. Several reports showed an improvement in the corrosion performance of Mg alloys by the electrosynthesis of PPy coatings. Dissolution rate of Mg alloys is reduced in presence of salicylate solution^{11,12}. That is why this anion is widely used as electrolyte for the electropolymerization of PPy onto these materials¹¹⁻¹⁴.

It has been reported in previous works that the electrosynthesis of PPy in salicylate solution leads to the formation of diverse structures. Hollow rectangular microtubes of polypyrrole were formed potentiostatically onto 316L stainless steel, onto Nitinol and onto AZ91D Mg alloys in neutral and alkaline solutions of salicylate (Sa)¹⁵⁻¹⁷. We also reported the electrodeposition of PPy films with microtubular structure on a first layer obtained by anodization of AZ91D alloy in molybdate solution¹⁷. The duplex coating shows an improved anticorrosive performance with respect to the PPy film. This improvement is associated with the combination of characteristics such as the protective properties of the inner film, the ability of the polymer to maintain the metal in the passive state and the inhibitor characteristics of salicylate. The incorporation of silver particles into the duplex coating allowed increasing the anticorrosive performance of the films. The Ag-modified bilayer exhibited also good antibacterial activity against *E. coli*.

The main goals of the present work are to evaluate and improve the anticorrosive performance of PPy films with granular morphology electrosynthesized on AZ91D Mg alloy from a salicylate solution. In this regard, the polymer was deposited onto a film electroformed in molybdate solution. Electrochemical impedance spectroscopy (EIS) and other electrochemical techniques were used to study the inhibition ability of films in simulated physiological solution. The coating remained protecting, stable and adherent during long exposure times. Silver-modified bilayer presented antibacterial activity.

EXPERIMENTAL

Materials and methods

Die-cast AZ91D magnesium alloy (composition wt%: 8.978 Al, 0.6172 Zn, 0.2373Mn, 0.2987 Si, 0.1189 Cu, 0.00256 Ni, 0.017 Fe, 0.00164 Ca, 0.01154 Zr, balance Mg) were used as working electrodes. The samples were prepared from rods and embedded in a Teflon holder with an exposed area of 0.070 cm². The surface of the electrode was wet mechanically polished successively with 600 and 1000 grit finish using SiC before each experiment. After this process, the exposed surfaces were degreased with acetone and washed with triply distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. All the potentials were measured against a saturated Ag/AgCl and a platinum sheet was used as a counter electrode. The cell was a 20 cm³ Metrohm measuring cell.

Solutions were purified with a saturated atmosphere of nitrogen gas at 25 °C. Pyrrole (Py, Sigma-Aldrich) was freshly distilled under reduced pressure before use. All chemicals were reagent grade and solutions were made in twice distilled water.

Electrochemical measurements were done using a potentiostat-galvanostat Autolab/PGSTAT 128N and VoltaLab40 Potentiostat PGZ301. EVO 40 XVP (LEO) microscope, with an accelerating voltage of 20 keV was used to examine surface morphology of coatings. X-ray diffraction analysis (XRD) was carried out using a Rigaku X-ray diffractometer (model Dmax III-C) with Cu K α radiation and a graphite monochromator. Film adhesion was tested measuring the force necessary to peel-off the film using a Scotch® Magic™ double coated Tape 810 (3M) and a Mecmesin basic force gauge (BFG 50N).

The variation of the open circuit potential (OCP) as a function of time, potentiodynamic method and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion behavior in Ringer solutions at 37 °C. The composition of Ringer solution is (per liter) 8.60 g NaCl, 0.30 g KCl and 0.32 g CaCl₂·2H₂O. The electrodes were allowed to equilibrate at the fixed voltage before the ac measurements.

The Tafel tests were carried out by polarizing from cathodic to anodic potentials with respect to the open circuit potential at 0.001 V s⁻¹ in Ringer solution. Estimation of corrosion parameters was realized by the Tafel extrapolation method. The extrapolation of anodic and/or cathodic lines for charge transfer controlled reactions gives the corrosion current density (j_{corr}) at the corrosion potential (E_{corr}). Electrochemical impedance spectra were obtained at the open circuit potential (OCP) in the frequency range from 100 kHz to 100 mHz, and the signal amplitude was 10 mV. Furthermore, the EIS data were analyzed and modeled into equivalent electrical circuits (EEC) with Z-View software. All experiments were conducted after the steady-state E_{corr} was attained. Measurements were repeated four times for each coating investigated to ensure reproducible and significant data.

The antibacterial activity against the Gram-negative bacteria *Escherichia coli* was evaluated by a modified Kirby-Bauer technique¹⁸. The method was previously standardized by adjusting the microbial inoculation rate and the volume of the agar medium layer. A stock culture of *E. coli* ATCC 25922 (stored at -70 °C in Trypticase Soy Broth (TSB) (BK 046HA, Biokar Diagnostics) supplemented with 20 % v/v glycerol (Biopack, Argentina) was used. A loop of frozen cells was cultured in TSB during 24 h at 37 °C, harvested by centrifugation at 5.000 x g for 10 min (Labofuge 200, Kendro, Germany), washed twice with phosphate-buffered saline (PBS: 0.15 mol l⁻¹ NaCl, 0.05 mol l⁻¹ KH₂PO₄, 0.05 mol l⁻¹ K₂HPO₄, pH 7.2) and then, cell pellets were suspended in PBS to achieve a population of ca. 7.0 log CFU (colony forming units) ml⁻¹ using a spectrophotometer (Thermo Spectronic Genesys 20, Thermo Electron Corporation, MA, USA). One milliliter of this suspension was mixed with

twenty five milliliters of Muller-Hinton Agar (BK, Biokar Diagnostics) melted and cooled at 43 °C, and then, placed on a Petridish. The coated electrodes were pressed onto bacteria-overlaid agar and were incubated at 37 °C for 48 h. The data were expressed as growth inhibitory zone diameter (mm) for three replicates.

RESULTS AND DISCUSSION

Polypyrrole coatings

The PPy film was easily formed by electrochemical anodic oxidation from a sodium salicylate (NaSa) solution containing the monomer. It was reported that hollow rectangular microtubes of PPy were electrodeposited on AZ91D Mg alloy in a solution containing 0.50 M NaSa and Py¹⁷. The typical PPy globular structure was generated for lower NaSa concentrations. Fig. 1 shows the $i-t$ curves obtained for AZ91D Mg alloy at 1.15 V during 600 s in a solution containing 0.50 M NaSa and 0.50 M Py (Fig. 1A) and at 0.80 V during 1800 s in a solution containing 0.10 M NaSa and 0.25 M Py (Fig. 1B).

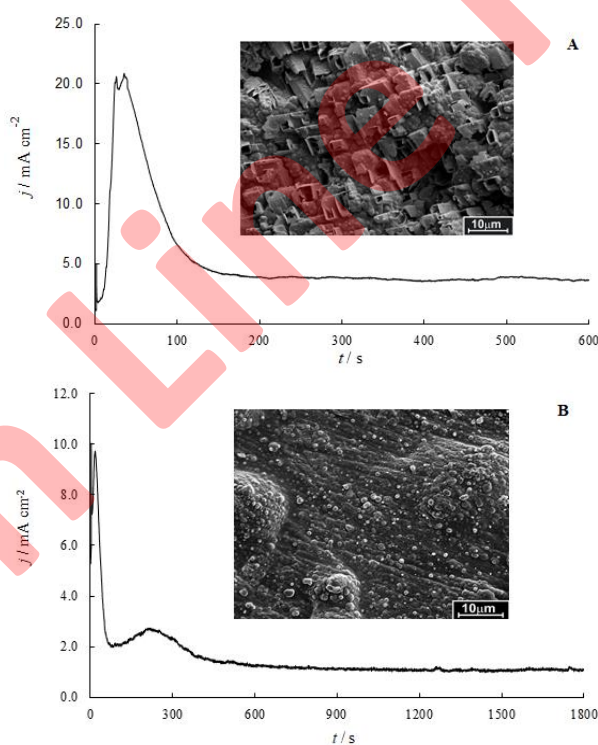


Fig. 1. Chronoamperometric curves obtained during the electrosynthesis of: **A** - PPy_{0.50} and **B** - PPy_{0.25} films. SEM images of the films are also presented.

SEM images of the obtained films are also shown in the figure. Rectangular microtubes of PPy were formed in the solution with the higher Sa content, while

the granular PPy morphology was obtained for the lower Sa concentration. The coatings will be called PPy_{0.5} and PPy_{0.25}, respectively. Higher current densities were registered during the formation of the microtubular structures, but the samples were prepared by using the same electropolymerization charge.

Fig. S-1 in Supplementary material compares the potentiodynamic polarization plots recorded for the bare sample and the alloy covered by the PPy_{0.25} and PPy_{0.5} coatings. The increase in the anodic current density registered for the uncoated electrode is related to active dissolution of the alloy. As it can be observed, the presence of both coatings produces a displacement of the onset potential, reaching a more positive value in the case of PPy_{0.25}. This result can be explained by considering that the porosity of the microtubular PPy_{0.5} coating allows an easier diffusion of corrosive ions to the electrode surface. The more compact globular coating leads to an increased corrosion resistance. Then, we decided to improve the corrosion protection imparted by the PPy_{0.25} film.

Bilayer coating

A protective film was generated onto the AZ91D Mg alloy using a low-voltage anodizing method in a molybdate solution¹⁷. In order to improve the corrosion resistance of the AZ91D alloy, a bilayer was prepared by first applying anodization to modify the substrate, and then depositing a PPy_{0.25} film. For simplification the coating will be named RMo-PPy_{0.25}. The bilayered system with the best performance was obtained when the substrate was anodically polarized at 1.0 V in 0.25 M Na₂MoO₄ solution during 20 s. After this treatment, the PPy film was electrosynthesized at 0.80 V during 1800 s in an electrolyte solution containing 0.10 M NaSa and 0.25 M Py. A SEM image shows that the globular polymeric film covers the electrode surface (Supplementary material Fig. S-2).

If the potentiodynamic polarization curves of the alloy covered by PPy_{0.25} and RMo-PPy_{0.25} in Ringer solution are compared, it could be notice that the bilayer provides the better corrosion protection (Fig. S-3, curve c).

The OCP of the alloy covered by RMo-PPy_{0.25} was measured in Ringer solution over a period of 30 h (Fig. S-4). Immersion time was shorter for the bare and PPy_{0.25}-covered electrode because of the high corrosion rate of these samples. The alloy covered by the PPy_{0.25} reveals a continuous potential decrease until the corrosion potential of the bare alloy is attained after 6 h of immersion (Fig. S-4, curve b). In contrast, the OCP for the RMo-PPy_{0.25} is more positive than that of the untreated alloy even after a long period of immersion (Fig. S-4, curve c). Moreover, there was no sign of corrosion damage visible at naked eye for this bilayer coated sample after the OCP experiment.

After 5 h of alloy samples immersion the Ringer solution was analyzed to determine the Mg concentration. The released amount of Mg by the untreated alloy was 3.90 mg/L, whereas it was 2.10 mg/L for the PPy_{0.25}-covered sample. The concentration diminished to 1.81 mg/L in the case of the RMo- PPy_{0.25}.

Representative Tafel plots obtained for the different samples in Ringer solution are presented in Fig. 2. The curves show qualitatively similar behaviour but with different values of their electrochemical data. Table I presents the corresponding corrosion parameters. PPy_{0.25} and RMo-PPy_{0.25} caused a positive displacement in the corrosion potential relative to the value of the bare alloy. The highest potential shift of about 0.350 V was observed for the RMo-PPy_{0.25}-covered sample. It can be also seen that the corrosion current density of the RMo-PPy_{0.25} coated specimen becomes one order of magnitude lower than that for the uncoated alloy.

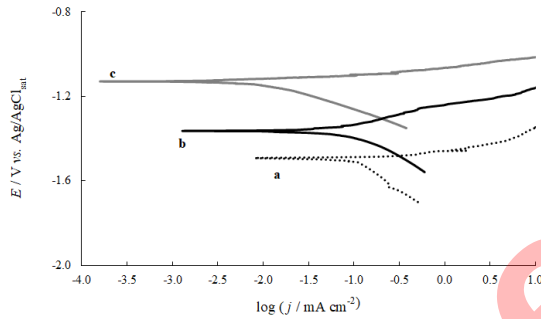


Fig. 2. Tafel curves obtained in Ringer solution after 60 min of immersion for: (a) uncoated alloy and the alloy covered with: (b) PPy_{0.25}; (c) RMo-PPy_{0.25}

TABLE I. Corrosion parameters calculated from Tafel polarization plots for the uncoated alloy and the alloy covered with PPy_{0.25} and RMo-PPy_{0.25}. The mean values and their standard deviation are presented.

| SAMPLES | $E_{\text{corr}} / \text{V}$ | $j_{\text{corr}} / \text{mA cm}^{-2}$ | $b_a / \text{V dec}^{-1}$ | $b_c / \text{V dec}^{-1}$ |
|-------------------------|------------------------------|---------------------------------------|---------------------------|---------------------------|
| AZ91D | -1.501 ± 0.050 | 0.1050 ± 0.0050 | 0.045 | - 0.293 |
| PPy _{0.25} | -1.363 ± 0.030 | 0.0589 ± 0.0050 | 0.107 | - 0.142 |
| RMo-PPy _{0.25} | -1.150 ± 0.020 | 0.0174 ± 0.0050 | 0.055 | - 0.128 |

EIS was used to evaluate the corrosion behavior of uncoated (Fig. 3A) and RMo-PPy_{0.25} coated Mg alloy (Fig. 3B) in Ringer solution under open circuit conditions. The impedance spectra of the coated substrate obtained during different immersion times is presented. The Nyquist plot of the bare sample after 2 h of immersion is characterized by two overlapping capacitive semicircles followed by an inductive loop. The impedance of the coated sample is higher than that of the bare alloy indicating a good corrosion protection imparted by the coating.

In order to analyze the results in more detail, EIS data were fitted with the equivalent circuits proposed in the literature for magnesium alloys immersed in chloride-containing solutions (Fig. S-5A)^{20,21} as well as for metallic materials coated by PPy films (Fig. S-5B)²². The equivalent circuits make use of a constant phase elements (CPE) as a substitute for a capacitor. The fitting data are listed in Table II. The model simulates the experimental data well, considering that the errors of fitting are lower than 5 % for all the parameters.

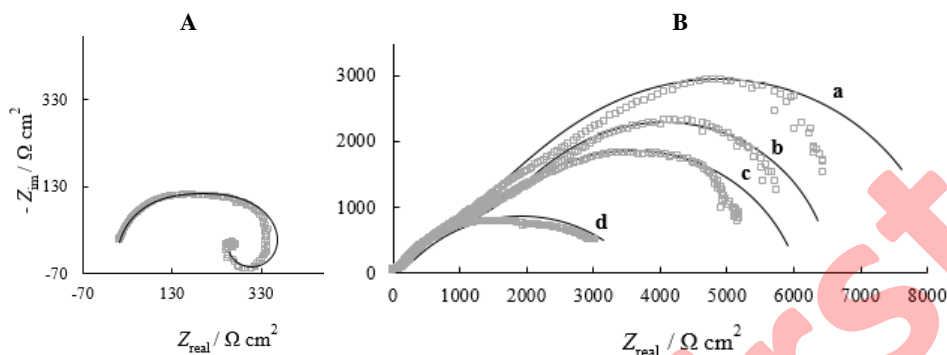


Fig. 3. Nyquist plot for **A** - uncoated alloy registered at OCP in Ringer solution after 2 h of immersion and **B** - RMo-PPy_{0.25}-coated alloy registered at OCP in Ringer solution after immersion during: a - 2, b - 5, c - 8 and d - 24 h. (□) experimental data; (-) fitted data.

TABLE II. Values for the parameters of the equivalent circuit obtained from the best fit to the impedance data.

| | AZ91D | | RMo-PPy _{0.25} | | |
|---------------------------------------------|-----------------------|-----------------------|-------------------------|-----------------------|-----------------------|
| <i>t</i> / h | 2 | 2 | 5 | 8 | 24 |
| <i>R_s</i> / Ω cm ² | 11.33 | -- | - | - | - |
| <i>R₀</i> / Ω cm ² | - | 26.6 | 24.5 | 26.0 | 12.0 |
| <i>C</i> / F cm ² | - | 6.43 10 ⁻⁸ | 7.14 10 ⁻⁸ | 6.35 10 ⁻⁸ | 8.28 10 ⁻⁸ |
| <i>R₁</i> / Ω cm ² | 243.60 | 116.97 | 91.53 | 93.63 | 81.08 |
| <i>R₂</i> / Ω cm ² | 162.2 | 2145 | 2040 | 1550 | 3498 |
| <i>CPE₁</i> , F cm ⁻² | 2.14 10 ⁻⁴ | - | - | - | - |
| <i>n</i> | 0.79 | - | - | - | - |
| <i>CPE₂</i> , F cm ⁻² | 4.08 10 ⁻⁵ | 2.12 10 ⁻⁵ | 1.98 10 ⁻⁵ | 1.98 10 ⁻⁵ | 8.74 10 ⁻⁵ |
| <i>n</i> | 0.86 | 0.64 | 0.63 | 0.63 | 0.58 |
| <i>R₃</i> / Ω cm ² | - | 5645 | 4434 | 4413 | 77 |
| <i>CPE₃</i> , F cm ⁻² | - | 2.07 10 ⁻⁵ | 3.30 10 ⁻⁵ | 3.14 10 ⁻⁵ | 1.44 10 ⁻⁵ |
| <i>n</i> | - | 0.93 | 0.95 | 0.83 | 0.70 |
| <i>L</i> / H | 700 | - | - | - | - |

In the case of the equivalent circuit proposed for the bare sample, *R_s* is the solution resistance, *CPE₁* and *R₁* represent the capacitance and resistance of the surface film, respectively. *CPE₂* and *R₂* are related to the double layer capacitance and the charge transfer resistance at the surface of the alloy. The inductance (*L*) is attributed to the presence of adsorbed/desorbed intermediates or other species on the bare surface of the sample^{23,24}.

In the equivalent circuit proposed for the coated sample, *R₀* is the sum of the electrolyte solution and polymer film resistances. *R₁* and *C₁* represent, respectively, the pore resistance and the capacitance of the coating. *CPE₂* and *R₂* are related to the charge transfer of the reaction between the PPy film and the substrate. Finally, *CPE₃* and *R₃* represent the interface between RMo and the substrate.

It can be observed that the fitted values of the capacitive components in the circuit remained nearly constant with immersion time. It was postulated that galvanic coupling of the polymer to the substrate contribute to oxidize the substrate forming a passive film. The slow decrease in R_2 values with time may indicate that the reaction between the PPy film and the substrate is not inhibited. In spite of part of the polymer matrix was reduced its resistance (R_0) remained unaltered. The decrease in R_3 values can be interpreted as the result of a progressive dissolution of the RMo film²⁰.

The obtained results suggest that anodization in molybdate solution helps in maintaining the alloy in a more passive state. On the other hand, the RMo-PPy_{0.25} coating has a better adhesion than the PPy_{0.25} film (Table III).

TABLE III. Adherence force obtained for the different coatings after peel-off testing.

| Sample | Adherence force, N |
|-----------------------------|--------------------|
| PPy _{0.25} | 16.25 |
| RMo-PPy _{0.25} | 21.70 |
| RMo-PPy _{0.25} -Ag | 12.95 |

Silver deposition

Another objective of this work was to study silver deposition on the bilayer coating. It is well known that metallic Ag can be spontaneously deposited on PPy. The RMo-PPy_{0.25}-covered electrodes were immersed in 0.05 M AgNO₃ solution during 4 h under open circuit conditions. As seen in Fig. S-6, the RMo-PPy_{0.25}-covered sample shows a deposit of silver platelets.

Fig. 4 shows XRD spectra for coated and uncoated AZ91D Mg alloy. XRD analysis of the coating confirms the presence of silver. Two intense diffraction peaks detected at 2θ values of 38.14° and 44.34° correspond to the Bragg reflections to the planes of Ag (111) and (200)²⁵.

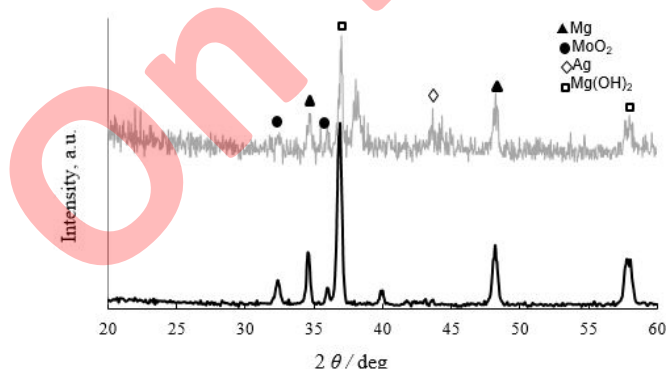


Fig. 4. XRD spectrum for: a - uncoated alloy and b - the alloy covered with RMo-PPy_{0.25}-Ag.

The amount of Ag is higher for RMo-PPy_{0.5}¹⁷ than for RMo-PPy_{0.25}. This can be related to a higher surface area of the microtubular polymer in contact with the AgNO₃ solution and also by considering a higher amount of Sa anions available.

By comparing the XRD patterns of both samples it can be also concluded that the coated sample presents diffraction peaks corresponding to the substrate. Peaks of MoO_2 are also observed. There are no peaks corresponding to MoO_3 although the presence of amorphous MoO_3 should not be ruled out^{26,27}. The polarization curve indicates that active dissolution of the substrate shifts to appreciably nobler values after Ag deposition (Fig. S-3, curve c). Thus, according to this result silver deposition significantly improved the corrosion resistance property of the bilayered coating.

The OCP variation with time for the Ag-modified sample exposed to Ringer solution is presented in Fig. S-4, curve d. Except for the first hours of immersion, the corrosion potential is near to the value of the bare alloy. On the other hand, the quantity of Mg released is practically the same than that obtained with the bilayered coating (1.81 mg/L).

Tafel plots for the sample covered by the Ag-modified coating were not reproducible. In spite of this, the i_{corr} values were always around that corresponding to the RMo-PPy_{0.5}-covered sample.

The Ag-modified coatings were compact but their adhesion to the substrate surface was poor (Table III). The bad protection against alloy corrosion for long immersion times as well as the irreproducibility in some measurements can be explained considering this poor adherence of the coating. Research is going on in order to improve the adhesion degree.

We investigated the antibacterial activity of immobilized silver against the Gram-negative bacteria *E. coli* ATCC 25922 by determining the width of the inhibition zone around the coated surfaces. The RMo-PPy_{0.25} film does not inhibit the growth of the bacteria but an inhibition zone with a mean value of 14 mm was observed in the case of the RMo-PPy_{0.25}-Ag coating. The presence of inhibition zones indicates the release of silver to the surrounding environment and subsequent antimicrobial effect. The antibacterial activity of RMo-PPy_{0.25}-Ag films could be explained by the penetration of the released Ag^+ ions and colloid silver particles through the bacteria cell wall. Their complexation with enzymes in the cell membrane results in the inhibition of the enzymatic activity and the bacteria death²⁸.

Conclusions

A PPy film with granular morphology electrodeposited onto AZ91D Mg alloy in Sa solution presents better anticorrosive properties than the same polymer with microtubular morphology. In order to improve the corrosion behavior of the substrate, the globular polymer was deposited on top of a film electroformed in molybdate solution. The bilayer system had a valuable effect on lowering the corrosion current density of the alloy in Ringer solution. The coating remained protecting, stable and adherent during long exposure times. Silver deposition was carried out on the duplex coating at OCP conditions. Preliminary results indicate that this film has antibacterial activity.

SUPPLEMENTARY MATERIAL

Additional data are available electronically from the journal web site: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД
ЗАШТИТА ОД КОРОЗИЈЕ ЛЕГУРЕ МАГНЕЗИЈУМА AZ91D ПРИМЕНОМ ДУПЛЕКС
ПРЕВЛАКЕ

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Дуплекс превлака је формирана под потенциостатским условима на легури магнезијума AZ91D у циљу побољшања њене корозионе отпорности у симулираној физиолошкој средини. Први слој је формиран анодизацијом на ниским потенцијалима у раствору молибдата. Спољашњи слој је био филм полипирила (PPy) који је синтетисан из раствора натријум-салицилата. Услови за формирање су подешени тако да се добије слој глобуларне морфологије. Двоструки слој је карактерисан скенирајућом електронском микроскопијом (SEM) и дифракцијом X-зрака (XRD). Ефикасност корозионе заштите превлака је испитивана у Рингеровом раствору праћењем потенцијала отвореног кола, поларизационим мерењима и спектроскопијом електрохемијске импеданције. Добијени резултати су показали да двоструки слој побољшава корозиону отпорност подлоге. Штавише, дуплекс превлака је показала боља антикорозиона својства од једнослојне превлаке PPy. На крају, двоструки слој је модификован цементацијом јона сребра из раствора који је садржао AgNO₃. Модификована електрода је показала добра антибактеријска својства.

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On Line First

SUPPLEMENTARY MATERIAL TO
Corrosion protection of AZ91D magnesium alloy by a duplex coating

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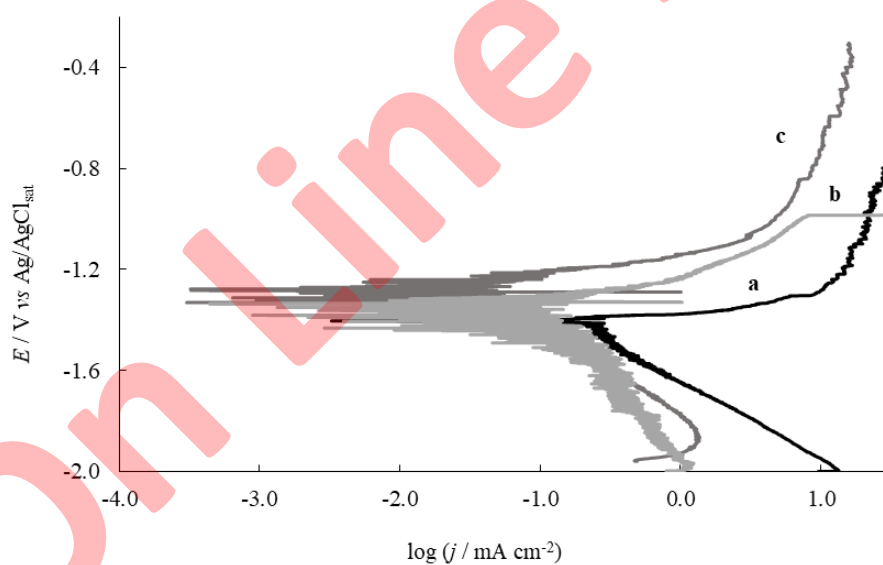


Fig. S-1. Potentiodynamic polarization curves in Ringer solution for: **a** - uncoated AZ91D alloy and **b** - alloy covered with: PPy_{0.25}; (c) PPy_{0.50}. The scan rate was 0.001 V s⁻¹.

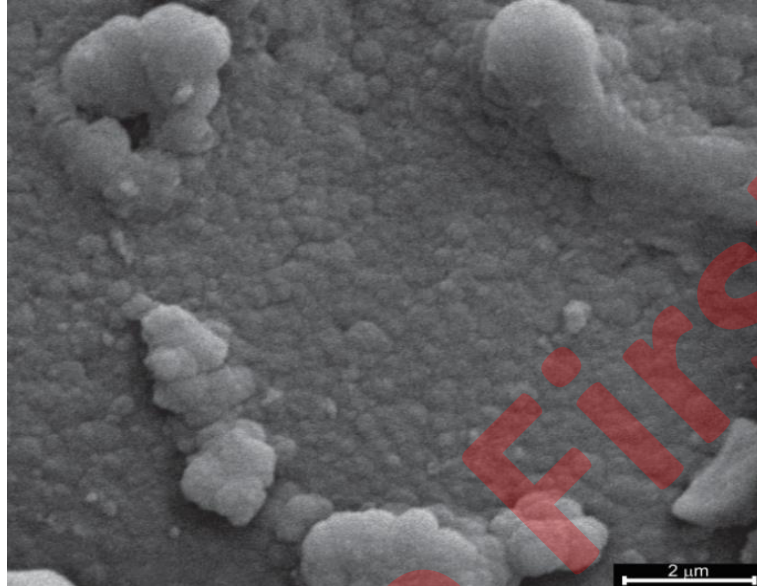


Fig. S-2. SEM image of the RMo-PPy_{0.25} film synthesized onto AZ91D alloy.

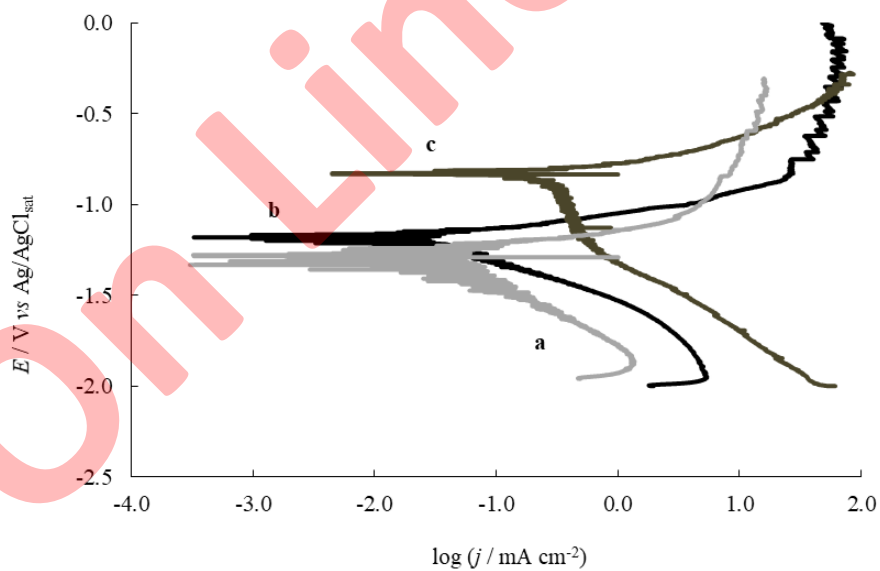


Fig. S-3. Potentiodynamic polarization curves in Ringer solution for the AZ91D alloy covered with: **a** - PPy_{0.25}; **b** - RMo-PPy_{0.25} and **c** - RMo-PPy_{0.25}-Ag. The scan rate was 0.001 V s⁻¹.

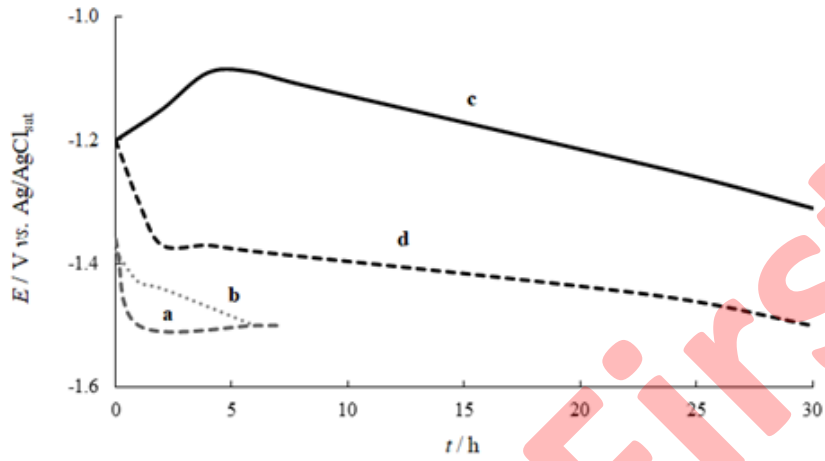


Fig. S-4. Time dependence of the OCP in Ringer solution for: **a** - uncoated alloy and **b** - the alloy covered with: $PPy_{0.25}$; **c** - $RMo-PPy_{0.25}$; **d** - $RMo-PPy_{0.25}-Ag$.

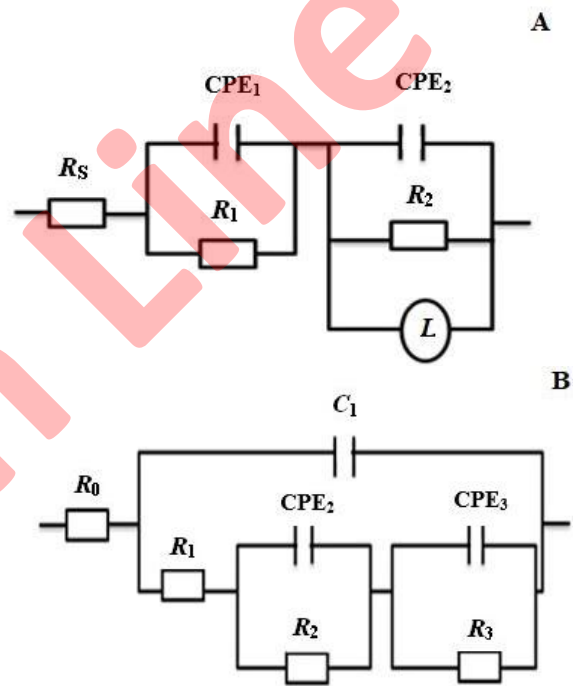


Fig. S-5. Equivalent circuit used for fitting experimental EIS data for: **A** - uncoated alloy and **B** - $RMo-PPy_{0.25}$ -covered AZ91D alloy.

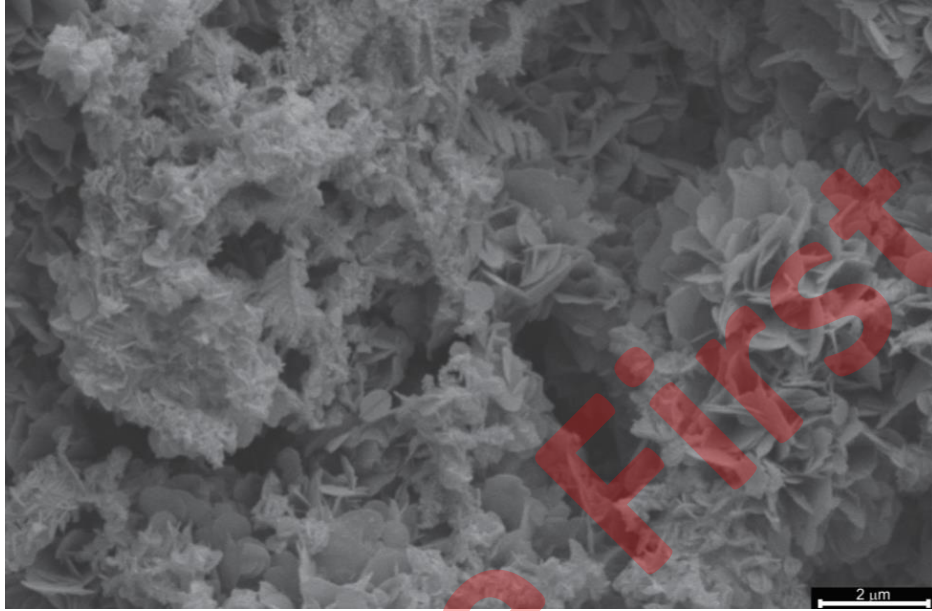


Fig. S-6. SEM images of the RMo-PPy_{0.25}-covered AZ91D Mg alloy immersed in 0.05 M AgNO₃ solution during 4 h under open circuit conditions.