Evaluation of the corrosion resistance of electroless Ni-P coatings on magnesium

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ABSTRACT

Magnesium and its alloys offer a wide range of applications due to their excellent properties, however, their high chemical reactivity depends on their possible application in environments that have high chloride contents, because the development of an efficient method of surface protection and Easy implementation on an industrial scale is necessary. In the present work, nickel-phosphorus (Ni-P) electrolytic coatings on magnesium substrates were obtained from a chromate-free method. Subsequently, these coatings were evaluated electrochemically by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in NaCl 3.5% wt solution. The results indicate that the coatings obtained manage to produce greater thermodynamic stability to the magnesium surfaces and reduce approximately the corrosion rate by a factor of 1000. Therefore, the methodology for obtaining the Nickel-phosphorus coatings that we propose in this work is susceptible to industrial scale.

Keywords: magnesium, electrolytic coating, Nickel-phosphorus, corrosion rate, electrochemical techniques.

1. INTRODUCTION

During the past decades, the need to obtain lighter materials has led to increasing research efforts on low-density metals performance seeking to attain lighter alloys. Among this sort of metals, magnesium (Mg) and its alloys have gained big interest because besides a low density these alloys have good characteristics regarding mechanical processing, thermal conductivity and dissipation of mechanical vibrations; all of these, make magnesium alloys promising, for use in fabrication of electronic components, automotive and aeronautic parts and home appliances [1-5].

However, magnesium alloys have restricted use, especially in those applications involving chlorides, due to the high chemical reactivity of Mg, which results in low corrosion and wear resistance [6-9]. Nowadays, several surface treatments have been applied to magnesium alloys to improve their corrosion resistance; some of those treatments are conversion coatings, anodizing, organic, metallic and ceramic coatings [10-18]. Nonetheless, most of these treatments require the use of hexavalent chromium compounds, which is considered highly toxic, carcinogenic and dangerous to the environment [19-21]. Within the different treatment possibilities for Mg, nickel-phosphorus (Ni-P) coatings appear to be very interesting, in particular for the electronic industry due to its good conductivity. These coatings are known for increasing both corrosion and wear resistance in various substrates [22-25]. However, the Ni-Mg system is a classic example of a cathodic coating on top of an anodic substrate [25], which, in addition to the high chemical reactivity of Mg, makes a big challenge obtaining these coatings on Mg alloys without the use of complex and toxic treatments [24-26].

In the present work, it was studied the corrosion resistance of magnesium substrates modified by applying an electroless nickel-phosphorus coating, employing a simple procedure, free of chromates and using

and ammonium hydrogen difluoride as alternative source of F$^-$ ions, easier to handle and less toxic than HF and NaF.

2. MATERIALS AND METHODS

Samples of commercially pure Mg (99.9%) were employed, with a working area of about 1 cm^2; these were mounted in unsaturated polyester resin and the electrical connection was attained by using a steel screw. The samples were polished with SiC grid paper up to # 400 and then sandblasted with alumina particles of about 150 μm at a pressure of about 40 psi. The samples then were degreased in ethanol during 10 minutes in an ultrasonic bath and finally etched in a solution made of 37 g/L NaOH and 10 g/L Na$_3$PO$_4$ at a temperature of 65 ℃ ± 2 ℃ for 10 minutes.

The electroless Ni-P coatings were obtained by treating the samples consecutively in the three solutions presented in Table 1. The pH was adjusted by means of ammonium hydroxide and the electroless bath temperature was keep at about 80 ℃ by employing a thermostatic bath.

Table 1: Parameters and chemical composition of the three electroless baths employed to obtain the Ni-P coating.

BATH	PH	IMMERSION TIME	CHEMICAL COMPOSITION
1	10.5	30 min	Nickel sulphate Sodium hypophosphite Succinic acid Lactic acid Propionic acid Ammonium hydrogen difluoride
2	6.5	30 min	Nickel sulphate Sodium hypophosphite Succinic acid Lactic acid Propionic acid Ammonium hydrogen difluoride
3	6.5	4 h	Nickel sulphate Sodium hypophosphite Lactic acid Ammonium hydrogen difluoride

For obtaining the coatings various concentrations of F$^-$ ions in the bath 1 were studied, namely: 4 g/L, 12 g/L and 20 g/L. In order to analyze the effect of this variable on the corrosion resistance of the sample, a random experimental design was employed with triplicates samples for each concentration and an uncoated sample with a total of 12 experiments (see Table 2).

Table 2: Experimental design employed to study the effect of F$^-$ ions concentration in bath 1.

F$^-$ IONS CONCENTRATION			
Uncoated	**4 (g/L)**	**12 (g/L)**	**20 (g/L)**
$Y_{0,1}$	$Y_{4,1}$	$Y_{12,1}$	$Y_{20,1}$
$Y_{0,2}$	$Y_{4,2}$	$Y_{12,2}$	$Y_{20,2}$
$Y_{0,3}$	$Y_{4,3}$	$Y_{12,3}$	$Y_{20,3}$

The electrochemical tests were carried out using a flat cell of three electrodes, with calomel saturated electrode as reference and a platinum mesh as counter-electrode. Potentiodynamic polarization curves were obtained varying the potential from -0.5 V to 1.5 V at a constant rate of 1 mV/s. From these curves, the Tafel graphs were plotted in order to calculate the corrosion rate according to the ASTM G102 standard [27]. The electrochemical impedance spectroscopy (EIS) tests were performed by applying a 5mV amplitude signal,

sweeping a frequency spectrum from 5 mHz to 10 kHz. All electrochemical tests were carried out at room temperature using NaCl 3.5% wt as electrolyte solution.

3. RESULTS AND DISCUSSION

Potentiodynamic polarization curves were used to evaluate the effect of the various coatings developed here on the corrosion performance of Mg samples. Figure 1 shows that the coatings obtained in this investigation have a highly reproducible performance. It can be seen that the three samples analyzed respond in a manner very similar to the potential sweep that was applied during potentiodynamic polarization tests.
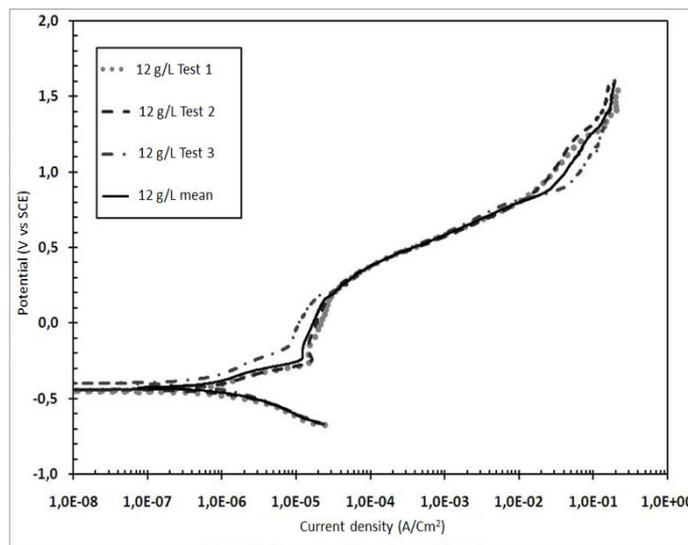

Figure 1: Potentiodynamic polarization curves for the triplicate samples obtained when adding a concentration of F⁻ ions source of 12 g/L and the resulting average curve.

Figure 2 shows the average curves obtained for the three concentrations of F ions tested. It is seen how the curves for the three coatings are shifted in comparison with the uncoated surface to both a more noble potential and a lower corrosion current. This result indicates that the coatings obtained reduce significantly the corrosion rate of the Mg substrates.
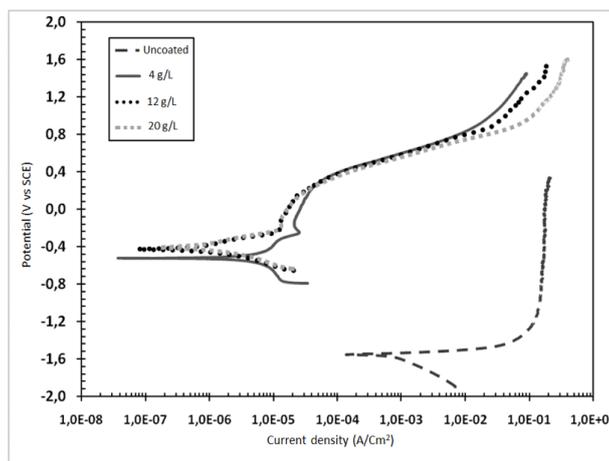

Figure 2: Average potentiodynamic polarization curves for the coated samples obtained when adding different concentration of F ions source and using as electrolyte a NaCl 3.5% wt solution at room temperature.

Analysis of the coating obtained with 4 g/L of F⁻ ions source, reveals that despite showing more clearly an anodic passivation zone, it offers the lower corrosion protection as it is located to lower potentials and

higher current densities. On the other hand, the coatings obtained by adding 12 g/L and 20 g/L of F⁻ ions source, shown very similar corrosion protective behavior. Table 3 shows the corrosion potentials, current densities and the corresponding corrosion rates that was calculated for each coating following ASTM G-102 standard [27]. A small difference of 20 mV can be observed in the corrosion potential between the 12 g/L coating and the 20 g/L coating, this suggests that this last coating. It offers greater resistance to corrosion, however, the parameter that interests us most when analyzing the protective efficiency of a coating is the current of corrosion. In table 3 we can see that the 12 g/L coating is the one with the lowest value in this parameter, so this coating is the one that offers the greatest protection to the magnesium substrate.

Under the experimental conditions of this study, we found a difference in the corrosion potential of approximately 1125 mV between the substrate and the surface covered with 12g/L and a reduction in the corrosion current from 848 µA to 0.527 µA. Similar works inform that the corrosion potential can get to present differences approximately of 790 mV, nevertheless, it is not informed that the reduction of the corrosion current is significant as it is in our case [23-26].

Table 3: Potentials, currents and corrosion rates calculated for the coatings and the uncoated sample.

Sample	E_{corr} (mV vs SCE)	I_{corr} (A)	V_{corr} (mm/yr)
Uncoated	-1555	$8.483*10^{-4}$	16.804521
4 g/L	-528	$7.073*10^{-7}$	0.0158688
12 g/L	-430	$5.272*10^{-7}$	0.0120384
20 g/L	-410	$5.928*10^{-7}$	0.0135356

Figure 3 shows the EIS Nyquist graphs obtained for the uncoated and coated samples analyzed. The Nyquist graph for the uncoated (Figure 3a), shows two capacitive loops, the first one at high frequencies is due to charge transfer processes and the second generally related to mass transfer processes in solid-state, including the formation of MgO and Mg(OH)$_2$ layers. In addition, an inductive loop at low frequencies is observed, which can be due to the presence of Mg(OH)$_{ads}$ y MgH$_2$ on the surface [8].

For the coated samples (Figure 3b), the curves obtained were similar in shape, which indicates that basically, the same processes take place in all cases. It was observed that all Nyquist graphs obtained for the three different coatings, showed a capacitive loop at high frequencies which are related to charge transfer processes and the no well-resolved part at low frequencies could be associated to ion transfer across the coating [8]. Besides, in the samples with electroless Ni-P coating, only a capacitance loop was observed and the EIS spectra were similar except for the difference in the diameter of the loops. This meant that the corrosion mechanisms of the samples were similar, but their corrosion rates were different [28-29].
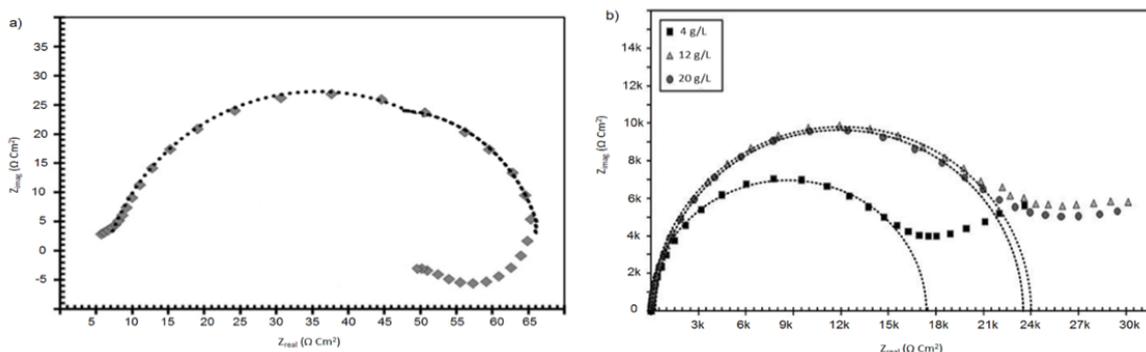

Figure 3: Nyquist graphs for a) uncoated and b) the three coated samples.

Extrapolation of the first capacitive loop of the Nyquist graphs presented in Figure 3, allows calculation of the polarization resistance (R_p) for the various samples. On the other hand, based in ASTM G-102 standard [27], R_p was also calculated from the Tafel graphs obtained from the potentiodynamic polarization curves. Comparison of these R_p values (see Table 4), indicates that the error percentage is relatively low for

the three coated samples whereas the uncoated sample shows a high error. This high error value could be due to mass transfer processes which control the corrosion process taking place on the bare Mg surface, precluding the application of the Tafel method for calculation of R_p [30].

Table 4: Polarization resistances calculated from the Tafel and Nyquist curves.

Sample	R_p (Ω) Taffel	R_p (Ω) Nyquist	%Error
Uncoated	10.139	60.515	496.85
4 g/L	18296	17533	4.17
12 g/L	24740	24033	2.86
20 g/L	22333	23533	5.37

Variance analysis of the polarization resistance calculated values for the three coated samples (Table 5), indicated that the differences in these data were due to the variation in the concentration of the F⁻ ions source (see Table 2) and they were not related to experimental variations during the coating of the samples.

Table 5: Variance analysis of the Rp calculated values for the three different concentrations of F ions source under study.

Variation source	Sum of squared values	Freedom degrees	Mean square	F ratio	P value
Intergroup	7.85E7	2	3.93E7	66.53	0.0001
Intragroup o Error	3.54E6	6	5.90E5		
Total (Corr.)	8.20E7	8			

The results obtained in the Fischer multiple comparison test make it possible stated that the coatings obtained in the solutions containing 12 and 20 g/L of F⁻ ions source were not statistically different (see Table 6). This was because the effect of the F⁻ ions in bath 1 was to create an initial MgF_2 layer on the Mg surface which was later replaced for the electroless Ni-P coating. The MgF_2 layer inhibits the corrosion of the substrate in the bath, improving the adhesion of the Ni-P coating. A F⁻ ions source concentration of 4 g/L appears to be insufficient for a rapid and homogeneous formation of the MgF_2 layer on the Mg surface and consequently the Ni-P coating presented a lower R_p value. As for a concentration of 12 g/L the same statistically results were obtained as for 20 g/L, it indicates that at a concentration of 12 g/L there was enough F⁻ ions to form an appropriate MgF_2 layer and additional F⁻ ions have not further effect on the coating process.

Table 6: Results of the analysis with the multiple comparisons Fischer test for a 95% confidence level.

Concentration	Number of samples	Average R_p	Homogeneous groups	Contrast	Significance	Difference
1 (4 g/L)	3	17533	X	1 - 2	Si	-6500.0
3 (20 g/L)	3	23533	X	1 - 3	Si	-6000.0
2 (12 g/L)	3	24033	X	2 - 3	No	500.0

Using scanning electron microscopy, the surface and cross section of the coatings were analyzed. Figure 4a, shows the surface morphology of the 12 g/L coating. The micrograph reveals the cauliflower typical features of electroless Ni-P coatings [24]. It was also observed that the coating is compact, and it covers homogeneously the substrate, that is, the presence of microcavities was not evident between nodular cusps of the deposited coating (Figure 4a), which is in agreement with observations in [29,31]. The cross section of the same sample (Figure 4b), shows a coating free of pores or cracks with an approximate thickness of 27 μm, and there is no evidence of double-layer structure, which indicate that the excellent adhesion between inner magnesium and outer Ni-P layer. Also, there are metal bond and sintered interlocking between the Ni-P and

Mg alloy substrate, and No blistering, crinkle, broken off were observed. These results show that the adhesion of the composite coating is excellent.
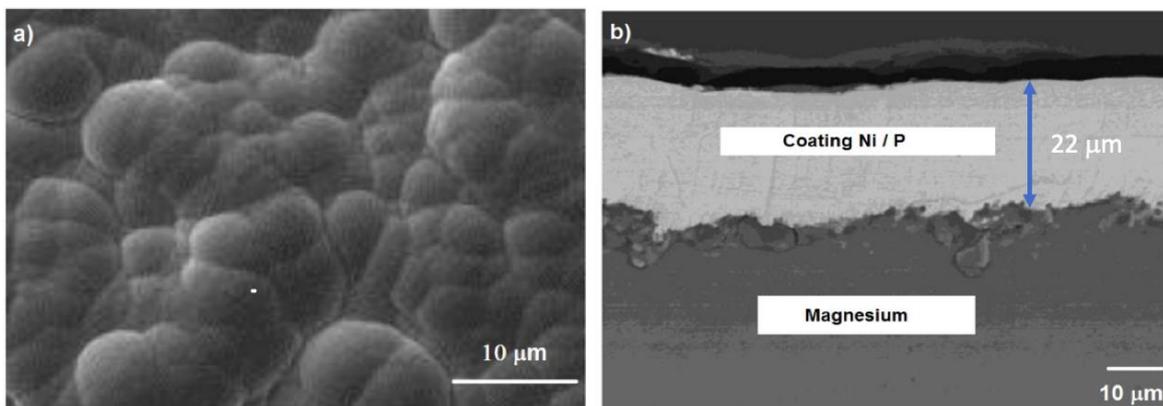

Figure 4: SEM micrographs of the 12 g/L coating: a) surface b) cross section.

4. CONCLUSIONS

With the methodology proposed in our investigation, it was possible to obtain electroless nickel-phosphorus coatings without using chromates to activate the magnesium surface. The three types of coatings obtained showed a protective effect of the magnesium surface in the presence of an environment with chlorides.

The Nickel-phosphorus coating that generated the highest corrosion resistance was obtained using an electrolytic bath with 12 g/L of ammonium hydrogen difluoride. Additionally, it was observed that mass transfer processes control the corrosion kinetics of discovered magnesium surfaces, so in this case, Tafel's method of analysis should not be applied with quantitative purposes.

This allows us to propose the method of obtaining the coatings that we have developed as an alternative for obtaining nickel-phosphorus coatings on magnesium on an industrial scale.

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