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Surface modification of magnesium alloy AZ31 by hydrofluoric acid treatment and its effect on the corrosion behaviour

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Abstract

In the present study, the effect of hydrofluoric acid (HF) treatment on the surface composition and corrosion behaviour of the magnesium alloy AZ 31 was investigated. The HF treatment of the samples was performed with various concentrations and at different treatment times. The samples surfaces were analysed by Fourier transform infrared spectroscopy, optical emission spectroscopy, x-ray photoelectron spectroscopy and scanning electron microscopy. The results showed the formation of hydroxides, oxides and compounds of the general formula $Mg(OH)_x F_{2-x}$ on the samples surfaces, as well as variations on impurities concentrations. The process led to distinct surfaces, each having its specific corrosion resistance, which was evaluated by electrochemical impedance spectroscopy and potentiodynamic polarization. The most improved corrosion protection was achieved using the concentrations of 14 and 20 mol L⁻¹ and 24h of treatment time, resulting in corrosion rates 20 times lower than those of untreated samples. These two solutions also resulted in an improved corrosion protection for further polymeric coatings, showing that this treatment is an excellent pre-treatment for corrosion protective layers on magnesium alloys.

Keywords: HF acid treatment; Magnesium; AZ31; Corrosion

1 – Introduction

The relatively poor corrosion resistance of magnesium and its alloys in aqueous media is a major drawback for their widespread use in automotive and aerospace industries. Nevertheless, there is a great interest in these materials due to their good physical properties, such as low density and high strength/weight ratio, which allow the construction of lighter

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vehicles, a very important issue concerning the fuel consumption and greenhouse effect. Further, Mg alloys have mechanical properties close to those of human bones and their corrosion products are harmless to the human body, what makes magnesium alloys potential candidates for orthopaedic implants [1, 2]. Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) is formed when the metal is in contact with water but it is not stable in the presence of anions like Cl^- , SO_4^{2-} or under acidic conditions, resulting in dissolution of the metal [3,4].

The presence of impurities on magnesium alloys surfaces has a crucial effect on their corrosion behaviour. Chemical species with a nobler potential can form a galvanic couple in which magnesium acts as an anode, and therefore its corrosion rate increases. This is one of the reasons why corrosion protection methods like plasma electrolytic oxidation [5-7], conversion coatings [8-10], polymeric coatings [11-12] and others are preceded by a cleaning procedure that may consist of a simple grinding and polishing process, blasting, or of chemical processes such as acid pickling.

Among the acids used for cleaning, hydrofluoric acid (HF) has received attention due to the formation of a protective layer on the metal surface which improves its corrosion resistance [10, 13, 14]. In fact, some studies in the literature discuss HF treatment of magnesium as a final process instead of a pre-treatment, e.g. Chiu *et al.* [13] who studied the corrosion behaviour of HF-treated magnesium in simulated body fluid solution. In this study, Chiu reported an increase of about 30 times on the impedance of the samples after the HF treatment, showing the protective effectiveness of the process. This impedance increase was attributed to the formation of the hydrophobic MgF_2 layer on the surface, which acted as a barrier between the metal and the environment, preventing the metal corrosion.

Despite the environmental and health concerns on the use of HF, various research groups have studied this treatment on magnesium and its alloys at different concentrations. Chiu *et al.* [13] treated pure magnesium ingots with 48% HF, Supplit *et al.* cleaned Mg alloy AZ31 with 12% HF [14] and Elsentriecy *et al.* reported the cleaning of Mg alloy AZ91 with 0.5% and 0.25% HF [10]. Gray *et al.* [15] reported the use of HF as part of pre-treatments of magnesium alloys for plating and anodizing processes, as in the plating of nickel over magnesium substrates, where HF is used in the concentration range of 15-25 wt.%. An improvement in adhesion of zinc coatings on magnesium compounds after fluorine treatment is reported as well [15]. All together, it shows that besides the removal of impurities, the building of a protective layer by the HF treatment of magnesium compounds can improve the adhesion of coatings, what is a very important subject for polymer coatings.

The literature reports the use of different polymers for the corrosion protection of metals, and shows the high degree of protection provided by these coatings [4, 16-18]. However, when water reaches the metal/polymer interface, polymer coatings undergo delamination [16] and defect formation due to gas evolution [17], what considerably decrease their protective properties. A pre-treatment that removes impurities, increases the hydrophobicity of the metal surface and enhances adhesion is of great interest. The HF treatment can provide all these characteristics and is a very interesting candidate as a pre treatment for polymer coatings.

The above mentioned references use HF under different conditions, but neither report the influence of different concentrations and treatment times on the resulting impedance and surface composition, nor the effect of this treatment on the corrosion behaviour of polymeric coatings. The aim of the present study is to determine at which concentration and treatment time the HF treatment of Mg alloy AZ31 results in the best corrosion protection, correlating this with the properties of the formed protective layer and impurities concentration. The influence of this treatment on the performance of further polymeric coatings was also evaluated. With this purpose, the surfaces of HF-treated specimens were analysed by Fourier transform infrared spectroscopy (FT-IR), optical emission spectroscopy (OES), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), and their electrochemical behaviour was evaluated by impedance spectroscopy (EIS) and potentiodynamic polarization measurements. Additionally, the influence of this treatment on the behaviour of polymer coatings was evaluated by immersion tests and impedance spectroscopy.

2 – Experimental details

2.1 – HF treatment

AZ31 samples, with chemical composition shown in Table 1 and dimensions of 20 mm x 50 mm, were immersed as-received in 80 mL HF in the concentrations of 7, 14, 20 and 28 mol L⁻¹ for 1; 5; 15 and 24h, at room temperature. These concentrations and treatment times were selected for practical reasons. The solutions were prepared by dilution of the concentrated 28 mol L⁻¹ acid. After the treatment time, the samples were washed with excess of deionised water, dried with non-fuzzing tissue paper to remove water from the surface ,and then placed in a vacuum oven at 40 °C for 1h. The solution that resulted in the best corrosion

protection was also used for samples grinded with papers of 800 to 2000 grade to verify the influence of grinded surfaces on the corrosion protection. For all samples, the weight was measured before and after the immersion, using a Mettler Ac 100 analytic balance (± 0.1 mg), to evaluate the weight change. The thickness of the layer formed on the samples surfaces was measured using a profilometer Hommel Tester T100, performing a scan from a treated to an untreated area of the sample. For this analysis, the samples were not completely immersed in the HF solution and the not immersed part served as reference for the layer thickness determination. Five measurements were performed for each condition.

2.2 – Polymeric coatings

The samples with higher corrosion protection after the HF treatment were dip coated with poly(ether imide) [PEI], poly(vinylidene difluoride) [PVDF] or poly acrylonitrile [PAN] in N,N'-Dimethylacetamide (DMAc) solutions, in the concentration of 15 wt.% (PEI and PVDF) and 6 wt.% (PAN). These polymers were selected due to their good film forming properties, solvent solubility and hydrophobicity. The concentrations were selected as a result of previous tests showing promising results. The specimens were dipped for 20 seconds in the respective solution, removed from it and dried in a vacuum oven for 2h at 80-100 °C. For sake of comparison, the same coating process was applied to samples cleaned with acetic acid (300 g L⁻¹) during 2 minutes, as well as grinded and as-received samples. After cooling down to room temperature, the dried samples were stored under clean conditions until required. The thickness of the polymeric coatings was measured using an eddy-current gauge MiniTest 2100 from ElektroPhysik. Five measurements were performed for each condition.

2.3 – Surface analyses

2.3.1 OES analyses

The influence of the HF treatment on the impurities and alloying elements concentration was evaluated using optical emission spectroscopy (OES). The analyses were performed in a spectrometer Spectrolab M9, model 2003. The results shown in Table 1 represent an average of three measurements each, performed at different points of the sample surfaces.

2.3.2 FT-IR investigations

The compounds formed at the samples surfaces were analysed by FT-IR spectroscopy, using a Bruker Tensor 27 IR-spectrometer. The samples were measured without any further treatment. The surface was analysed by reflectance at an angle of 30 degrees with 2048 scans and a resolution of 4 cm^{-1} between 300 cm^{-1} and 5000 cm^{-1} . The spectra were automatically converted to the absorbance mode using the OPUS 6.5 (Bruker) software.

2.3.3 SEM investigations

The morphology of the surfaces was studied using a scanning electron microscope (SEM) Cambridge Stereoscan 200 with an acceleration voltage of 10 kV. The samples were analysed without sputtering due to their good surface conductivity.

2.3.4 XPS analysis.

X-ray photoelectron spectroscopy (XPS) was performed in a Kratos DLD Ultra Spectrometer using an Al- K_{α} X-ray source (monochromator) as anode. For the survey spectra as well as for the region scans a pass-energy of 160 eV was used. The area of interest was limited to 55 μm by an aperture in all cases. The concentration and the chemical state of the elements were investigated. The total integral of the XPS intensities (peak area) was used for determining the chemical composition while a linear background subtraction was performed. Depth profiling was carried out by using argon sputtering with an energy of 3.8 keV and a current density of 195 $\mu\text{A}/\text{cm}^2$. The etching rate was calibrated to 36 nm/min using Ta_2O_5 .

2.4 – Electrochemical analysis.

The corrosion behaviour of the samples was evaluated in a three-electrode cell with the sample as working electrode, a platinum mesh as counter electrode and a Ag/AgCl as reference electrode, connected to a potentiostat Gill AC(ACM instruments). A sample area of 1.54 cm^2 was exposed to a 3.5% NaCl solution under continuous stirring. The open circuit potential (OCP) was measured for 30 minutes and then the impedance test was carried out at OCP by applying a sinusoidal potential with frequencies ranging from 10^4 to 10^{-2} Hz and amplitude of 10 mV. For the measurement of the polymeric coatings, the cell was connected

to a Fempto amp detector and placed inside of a Faraday cage to minimize noise. The amplitude was, in this case, set to 15 mV to increase the signal intensity.

For the HF-treated samples, 30 minutes after the impedance test was completed the polarization analyse was performed. A potential sweep was applied at a constant scan rate of 12 mV/min, starting 150 mV bellow OCP and finishing at the current limit of 0.1 mA cm⁻². Three to four measurements were carried out for each treatment condition as well as for the untreated sample. The corrosion current was taken by extrapolating the cathodic curve to the corrosion potential. Then, the corrosion rate (CR) was calculated using equation 1.

$$CR = i_{cor}M/nFd \quad (1)$$

where M is the molar mass of the metal, n is the number of electrons transferred, F is the Faraday constant and d is the density of the metal.

3 – Results and Discussion

3.1 – Weight change and SEM analyses

The immersion of Mg alloy AZ31 in HF solutions resulted in a gas evolution at the starting period of the treatment. The gas emission is related to hydrogen formed by the reaction of HF with Mg, according to equation 2 [3,4].



Figure 1a shows the samples weight change in function of treatment time, for the different HF concentrations. At 1h of immersion, all solutions produced a weight loss, indicating a higher rate of material dissolution than of protective layer formation. After 5h of immersion, a gradual weight gain (compared to the weight at 1h of treatment) was produced by the concentrations of 7 and 14 mol L⁻¹. This indicates that the rate of protective layer formation became higher than the rate of material dissolution. After 24h of treatment, the samples treated with 7 and 14 mol L⁻¹ had a weight gain of 0.14 mg cm⁻² and 0.10 mg cm⁻², respectively, corresponding to a layer thickness of *ca* 2 μm, as shown in Figure 1b

The samples treated with the concentrations of 20 and 28 mol L⁻¹ showed weight increase only after 15h of immersion. After 24h, these solutions resulted in a weight gain of

around 0.05 mg cm^{-2} . This smaller weight gain indicates that the rate of protective layer formation was smaller for these concentrations, when compared to 7 and 14 mol L^{-1} . Figure 1b corroborates this result, showing that these concentrations produced thinner layers after 24h of treatment. These results suggest that, for the used concentration range, the higher the HF concentration the lower the protective layer formation rate. This trend is probably associated to a higher material dissolution rate at higher concentrations.

Figure 2 shows SEM images of a sample treated with 7 mol L^{-1} HF at different treatment times. After 5h of treatment, Figure 2b, it is possible to observe the deposition of compounds on the sample surface, especially when comparing to the surface after 1h of treatment, shown in Figure 2a. After 15h, Figure 2c, the entire surface was covered by a smooth layer, which took an irregular morphology after 24h of treatment, as shown in Figure 2d. This result is in agreement with the weight change measurements, which showed a gradual weight gain produced by the concentration of 7 mol L^{-1} after 5h of treatment. Similar analyses of samples treated with other HF concentrations also confirmed the weight change results.

Figure 1a also shows that the reaction of magnesium AZ31 alloy with HF has a slow kinetics at the applied conditions. Only small quantities of protective layer (less than 0.2 mg cm^{-2}) were formed on the samples surfaces, even after 24h of treatment. Comparing to the work of Chiu *et al.* [13], who reported a weight gain of 35 mg cm^{-2} for pure magnesium ingots, after 24h of immersion in 28 mol L^{-1} HF, it can be conclude that the reaction of AZ31 with HF is much slower than that of pure magnesium ingots. This leads to the suggestion that the alloying elements Al, Zn and Mn improve the chemical stability of magnesium compounds in acidic fluoride environments, in a similar manner as they improve it in chloride environments, as reported by Pardo [19].

The appearance of the samples changed markedly with treatment time and concentration, as shown in Figure 3. For the concentrations of 7 and 14 mol L^{-1} the surface colour was golden/yellowish, with dark spots and some green and brown areas, especially for those specimens treated with 14 mol L^{-1} HF. For the concentration of 20 and 28 mol L^{-1} HF the samples had a grey colour which became darker with increasing treatment time, finally resulting in a black colour. A more detailed view at these black samples reveals some dark green and brown areas, like the ones in the samples treated with 7 and 14 mol L^{-1} HF. This different aspect of the samples suggests the presence of different compounds on the metal surface.

3.2 – OES analyses

The OES results of samples treated with 14 and 28 mol L⁻¹ HF and of as-received and grinded samples are given in Table 1. A slight decrease of the magnesium concentration could be observed after the HF treatment, due to metal dissolution. This magnesium dissolution resulted in an enrichment of some elements, like Al and Mn, for the sample treated with the concentration of 14 mol L⁻¹.

Iron, copper and nickel are the most deleterious impurities for magnesium alloys [4, 20, 21]. These impurities have a low solid-solubility in magnesium, what provides active cathodic sites that enhance magnesium oxidation [20]. Only the iron concentration was reduced by the HF treatment, reaching values close to those of the bulk composition, in particular, for the concentration of 28 mol L⁻¹. Nickel and copper were not dissolved during the treatment, probably due to their presence in more stable phases, as described by Liu *et al.* for copper [22].

An important parameter for the corrosion of magnesium is the Fe/Mn ratio [4, 20, 21]. Studies in the literature show that a considerable decrease in the corrosion rate of magnesium alloys was obtained when 1% wt. of Mn was added [23]. The Fe/Mn ratio is considered as a critical factor in corrosion of magnesium [24]. According to Reichel *et al.* [25] the critical Fe/Mn ratio for magnesium alloys is 0.032, the same value is reported by other authors for AZ91 [26]. In the present study, the treatment of magnesium AZ31 alloy samples with 14 and 28 mol L⁻¹ HF reduced the Fe/Mn ratio from 0.035, of the as-received samples, to 0.024 and 0.023, respectively, below the critical value, showing that this treatment is a cleaning process with respect to iron. In fact, no removal of copper and nickel took place, but as reported by Liu *et al.* [22] at these concentrations of nickel and copper the corrosion of magnesium alloys is governed by its iron content.

3.3 – FT-IR and XPS investigations

According to the previous literature [10, 13], the treatment of Mg alloys with HF results in the formation of a MgF₂ layer at the metal surface. Although this assumption is well accepted, a detailed IR study of HF-treated magnesium alloys is not provided to confirm this. Instead, the characterisation is usually performed using other techniques such as x-ray diffraction spectroscopy and XPS [13]. Magnesium fluoride has intense IR bands only below 600 cm⁻¹, but in the IR spectra of treated Mg AZ31 samples (Figure 4) there is a broad signal

up to 3000 cm^{-1} , a duplet at 2364 cm^{-1} , another signal at 1640 cm^{-1} and some broad signals below 900 cm^{-1} . This clearly indicates that not only MgF_2 was formed at the surface of the specimens

The broad signal up to 3000 cm^{-1} is related to the O-H stretching of hydroxides and to water molecules linked to the surface by hydrogen bonds. The deconvolution of this signal, Figure 5a, results in four different O-H stretching modes. The signal at 3280 cm^{-1} can be attributed to adsorbed water, and the other three signals can be related to $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ [27]. Another O-H stretching appears between 2500 and 3000 cm^{-1} in some samples and is related to water molecules that have hydrogen bonds with fluorides. Scholz *et al.* [28] report a similar signal. The intensity of these different O-H signals decreased with an increase of the HF concentration which is caused by the high hydrophobic character of the fluoride [29]. In general, an increasing in the treatment time resulted in an increase in the signals intensity. An exception is the concentrated HF (28 mol L^{-1}) where no hydroxides were observed (Figure 4b).

The signal at 1640 cm^{-1} is related to the bend mode of the H-OH bond, which confirms the presence of adsorbed water. The presence of a shoulder at 1570 cm^{-1} indicates different interactions between water and hydroxides at the metal surface, which agrees with the high quantity of different O-H signals. The duplet at 2364 cm^{-1} is related to CO_2 adsorbed from the environment [30].

In general, below 900 cm^{-1} the spectra shows series of signals (Figure 5b), usually with an intense one at 650 cm^{-1} and three signals of lower intensity around 745 , 800 and 840 cm^{-1} . By increasing the treatment time, these signals shifted to higher wave numbers. On the other hand, the signals shifted to lower wave numbers with increasing HF concentration. The number of signals in this range also increased with treatment time and decreased with acid concentration. This suggests that the signals that were present only at low HF concentrations and higher treatment times are related to hydroxides and/or to oxides.

According to the previous literature, the signals below 900 cm^{-1} can be related to stretching and bending modes of hydroxide, oxide, carbonate and fluoride species [27,30-33]. At this range, signals related to compounds of the general formula $\text{Mg}(\text{OH})_x\text{F}_{2-x}$ (e.g. $\text{Mg}(\text{OH})_{1.6}\text{F}_{0.4}$, $\text{Mg}(\text{OH})_{1.2}\text{F}_{0.8}$) as described by Prescott *et al.* [34] are also reported. The presence of such compounds was investigated using XPS, and the results are shown in Table 2. Table 2 indicates that the F/Mg ratio varies from values of 1.7 to 2.0, depending on acid concentration and etching time. As the F/Mg ratio of MgF_2 should be equal to 2, lower values indicate the presence of other magnesium compounds, e.g., $\text{Mg}(\text{OH})_2$. As the O/Mg

ratio varies from 0.2 to 0.3, in almost all samples, and the summation of O/Mg and F/Mg equals 2, considering a variation of 0.15 in the ratios, the presence of the compounds $\text{Mg(OH)}_{0.3}\text{F}_{1.7}$, $\text{Mg(OH)}_{0.2}\text{F}_{1.8}$ and $\text{Mg(OH)}_{0.1}\text{F}_{1.9}$ is suggested. Nevertheless, as the oxygen content can be attributed to oxides and to complex bonded water molecules, further investigations will have to be performed in order to confirm the presence of these species.

The formation of $\text{Mg(OH)}_x\text{F}_{2-x}$ in acid environments is well documented in the literature, despite the fact that its mechanism is not well understood [13, 35]. Verdier suggests that this compound is formed either by simultaneous reaction between the Mg^{2+} ion and the anions OH^- and F^- or by a substitution reaction, where the hydroxide anions of the magnesium hydroxide film are gradually replaced by fluoride [35]. Since the quantity of hydroxides on the metal surface increases with treatment time, instead of decreasing, a substitution of the fluorides by hydroxides is suggested, instead the one proposed by Verdier. This is consistent with the fact that the signal related to MgF_2 appeared in the initial phase of the treatment, and the signals related to the hydroxides appeared only at the end. Booster *et al.* [36] reported the conversion of magnesium fluoride to magnesium hydroxide showing that this reaction is thermodynamically possible. Nevertheless, as the reaction conditions reported by Booster *et al.* were different from those prevailing in the present study, the exact mechanism remains unknown, and further investigation will have to be performed to clarify this.

3.4 – Electrochemical investigations

Figure 6 shows the results of the impedance measurements of samples treated with 20 and 28 mol L⁻¹ HF, after 15min of exposure to a 3.5% NaCl solution. The Nyquist plot of the samples treated with 20 mol L⁻¹ HF during 24h comprise only one capacitive loop, as shown in Figure 6a, instead of a high frequency capacitive loop and a low frequency inductive loop, present in the spectra of the others samples shown in Figure 6a and 6c. According to the literature, the high frequency capacity loop is related to the protective layer resistance and the inductive loop corresponds to pitting corrosion [7, 13, 37]. The samples treated with 14 mol L⁻¹ HF during 24h had a behaviour similar to those treated with 20 mol L⁻¹ HF during the same time, and the higher impedance was obtained for these two conditions, as shown in Table 3, three orders of magnitude higher than the untreated sample.

The inductive loop is also visible in the Bode plots. At low frequencies it is obvious that there is a decrease in the impedance, followed by an increase. This impedance decrease

stands for the corrosion of the metal, and the subsequent increase indicates the deposition of corrosion products on the metal surface [8-10]. For all treated samples the Bode plots also show impedance at least one order of magnitude higher than that of an untreated sample.

In general, the impedance increases with increasing treatment time, due to the higher amount of protective layer deposited on the samples surfaces, as previously discussed. Due to different factors the treatment with 7 and 28 mol L⁻¹ HF resulted in a lower corrosion protection. In the case of 7 mol L⁻¹ HF, the higher hydroxide concentration was detected by FT-IR spectroscopy. This high hydroxide concentration have a weakening effect on the protective properties of the layer, since that Mg(OH)₂ is unstable in the presence of Cl⁻ solutions. In the case of 28 mol L⁻¹ HF, the samples were heavily etched and showed a weight loss even after 5 h of treatment, indicating a very slow deposition of protective layer. This suggests that even after 24 h the surface was not completely covered by a layer, resulting in a lower corrosion protection. With a lower quantity of hydroxide and a faster protective layer formation process, the solutions 14 and 20 mol L⁻¹ HF resulted in a better corrosion protection.

Figure 7 shows the impedance of samples treated with 14 and 20 mol L⁻¹ HF during 24h, at different exposure times to 3.5% NaCl solution. After 20h of exposure the impedance of the treated samples was similar to the untreated one, showing that the layer has already failed. This result shows that, in the present study, the HF treatment is not suitable as a final corrosion protection process, because it does not produce long-term stable conversion coatings. However, it considerably increases the impedance of AZ31 samples for short exposure times, showing higher impedance than other conversion coatings described in the literature [9, 37], indicating that this treatment has a good potential to be used as a pre-treatment for further coating processes.

Additionally, the corrosion behaviour was evaluated by polarization measurements, as presented in Figure 8. To prevent excessive dissolution of the samples, an anodic current limit was set at 0.1 mA cm⁻². In general, the polarization curves did not have a defined anodic slope and showed direct dissolution of the metal above the corrosion potential. This suggests the presence of defects in the protective layer. Table 3 shows the results of the cathodic slope analysis, where it can be seen that the samples treated with 20 mol L⁻¹ HF and 14 mol L⁻¹ HF for 24h had the lower corrosion rate, around 0.2 mm/year, 20 times lower than the untreated sample, corroborating the results of the impedance spectra. For all samples, no correlation between the corrosion potential, E_{corr} , and the corrosion rate was observed.

The electrochemical results indicate that the improved corrosion behaviour obtained by HF treatment of AZ31 alloys is mainly related to the protective layer formed on the surface and not to the removal of impurities. The OES results showed that the solutions 14 and 28 mol L⁻¹ HF resulted in similar reductions of the Fe/Mn ratio, below the tolerance limit. Nevertheless, the EIS spectra and the potentiodynamic results showed a much better corrosion protection produced by the concentration of 14 mol L⁻¹ than of 28 mol L⁻¹.

Comparing the results of the electrochemical analyses, considering the lower corrosion rate and standard deviation, the best conditions for the HF treatment of the magnesium alloy AZ31 are: a concentration of 20 mol L⁻¹ and a treatment time of 24h. For comparison, the 20 mol L⁻¹ HF solution was also used for the treatment of grinded samples, and the results of the electrochemical tests are shown in Table 3. By comparing these results with those of the non-grinded samples it can be observed that the grinding process had no beneficial effect on the corrosion resistance. Instead, a higher corrosion rate was obtained. This is related to the removal of the partially protective MgO film during the grinding process. In the HF treatment, besides impurities removal (in the first hours of immersion), part of the MgO film present on the as-received sample is maintained. The grinding removes impurities (as does the HF treatment) but completely removes the partially protective MgO film. For this reason, the grinded samples showed slightly worse behaviour. Therefore, the HF treatment can be applied directly on the as-received material.

3.5 – Polymer coatings

As previously mentioned, the treatment of magnesium AZ31 alloy with 14 and 20 mol L⁻¹ HF resulted in interesting properties for a pre-treatment. The effect of this treatment on the behaviour of further coatings was evaluated by preparing polymeric coatings of PEI, PVDF and PAN on HF-treated substrates. The same coatings were prepared over grinded, as-received and acetic acid cleaned substrates for comparison. Figure 9 shows the appearance of samples coated with PEI after immersion tests in 3.5 % NaCl, where can be seen the best performance of the samples previously treated with HF when compared to the others pre-treatments.

After 2 days of immersion, the grinded and as-received coated samples showed several corrosion areas and delamination close to the lower edge (Figure 9a). Samples previously treated with acetic acid showed corrosion products close to cut edges and delamination after 16h, Figure 9b, whereas samples previously treated with 14 mol L⁻¹ HF had no visible

corrosion evidence after 2 days of immersion in the same solution (Figure 9c). After 6 days of immersion, the coated 14 mol L^{-1} HF treated sample still showed good appearance, with some small corrosion spots on the surface. Even after 6 days of immersion, no delamination was observed. For all samples, the polymeric coating thickness was about $10 \mu\text{m}$.

A similar behaviour was observed for samples coated with PAN over substrates treated with 20 mol L^{-1} , as shown in Figure 10. The samples previously grinded and cleaned with acetic acid showed delamination and corrosion products on the surface after 16h of immersion, whereas the sample previously treated with 20 mol L^{-1} showed only a few corrosion spots after 4 days of immersion, and no delamination was observed. After 7 days of immersion the coated sample treated with HF did not show delamination, what indicates that this treatment considerably improved the performance of polymeric coatings.

Figure 11 shows the impedance spectra of samples coated with PVDF and PEI, over grinded and HF-treated substrates, at different exposure times to the corrosive solution. It can be observed that the samples previously treated with HF had higher impedance than the grinded ones at the exposure time of 30 minutes. For both polymers a considerable decrease in impedance was observed during the first 20h of exposure, from $10^8 \Omega \text{ cm}^2$ ($10^9 \Omega \text{ cm}^2$ for PVDF) to $10^7 \Omega \text{ cm}^2$, indicating that water was penetrating the coating. Nevertheless, after 13 days of exposure the impedance of the HF-treated samples still was in the range of $10^7 \Omega \text{ cm}^2$, showing a much better behaviour than the grinded ones, which had impedance values of $10^6 \Omega \text{ cm}^2$ after much shorter exposure times. For PEI coatings on grinded samples, the impedance at 30 minutes was close to $10^8 \Omega \text{ cm}^2$ but it decreased to around $10^5 \Omega \text{ cm}^2$ after only 3 days. For the PVDF coatings on grinded samples, after 20h of exposure to the corrosive solution, the impedance was close to $10^5 \Omega \text{ cm}^2$ whereas the HF-treated samples showed impedance in the range of $10^7 \Omega \text{ cm}^2$ at the same exposure time. The samples maintained this impedance after 3 and 13 days, respectively. These results show that the HF treatment resulted in higher impedance values at shorter and longer exposure times for polymeric coated samples, being a very interesting pre-treatment for the corrosion protection of magnesium alloys. The different behaviour of PVDF and PEI coatings, shown in Figure 11, will be part of further discussions and investigations.

4 – Conclusions

The HF treatment of Mg alloy AZ31 reduced the Fe/Mn ratio below its critical value and led to different compounds such as hydroxides, oxides and fluorides at the metal surface,

depending on the acid concentration and treatment time. In general, lower concentrations and longer treatment times resulted in higher quantities of hydroxides at the surface in the form of a compound with the general formula $Mg(OH)_x F_{2-x}$. The protective layer formation rate was slow, and the maximal weight gain was 0.15 mg cm^2 , produced by the HF concentration of 7 mol L^{-1} after 24h of immersion. The higher protective layer thickness was $2 \text{ }\mu\text{m}$. The best corrosion protection was achieved by the concentrations of 14 and 20 mol L^{-1} HF at a treatment time of 24h, resulting in a corrosion rate 20 times lower than that of the untreated sample.

Nevertheless, these conditions did not produce long-term stable conversion coatings, and after 20h of exposure to the corrosive solution, the impedance of the treated samples was in the same range of the untreated ones. However, this treatment considerably improved the corrosion behaviour of further polymer coatings, showing higher impedance values at short and longer exposure times as well as better adhesion. All the three tested polymers showed better corrosion protection over the HF-treated substrate than over the grinded, as-received and acetic acid cleaned ones, which shows the positive effect of this treatment as a pre-treatment for corrosion protection of magnesium alloys.

5 – References

- [1] M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, *Biomaterials* 27 (2008) 1728.
- [2] H. Wang, Y. Estrin, Z. Zuberova, *Mater. Lett.* 62 (2008) 2476.
- [3] L.L. Shreir, R.A. Jarman, G.T. Burstein, *Corrosion, Metal/ Environment Reactions*, Butterworth-Heinemann, vol 1, 3th Edition, 1994.
- [4] R.W. Revie, *Uhlig's Corrosion Handbook*, John Wiley & Sons, 2 Edition, 2000.
- [5] A. Ghasemi, V.S. Raja, C. Blawert, W. Dietzel, K.U. Kainer, *Surf. Coat. Technol.* 202 (15) (2008) 3513.
- [6] P.B. Srinivasan, C. Blawert, W. Dietzel. *Mater. Sci. Eng. A.* 517 (1-2) (2009) 197.
- [7] P.B. Srinivasan, C. Blawert, W. Dietzel, K.U. Kainer, *Scr. Mater.* 59 (1) (2008) 43.
- [8] W. Zhou, D. Shan, E. Han, W. Ke, *Corros. Sci.* 50 (2008) 329.
- [9] F. Zucchi, A. Frignani, V. Grassi, G. Trabanelli, C. Monticelli, *Corros. Sci.* 49 (2007) 4542.
- [10] H.H. Elsentriecy, K. Azumi, H. Konno, *Surf. Coat. Technol.* 202 (2007) 2007.
- [11] Y. González-García, S. González, R.M. Souto, *Corros. Sci.* 49(9) (2007) 3514.

- [12] G.A. Moraga, G.G Silva, T. Matencio, R.M. Paniago, *Synth. Met.* 156 (16-17) (2006) 1036.
- [13] K.Y. Chiu, M.H. Wong, F.T. Cheng, H.C. Man, *Surf. Coat. Technol.* 202 (2007) 590.
- [14] R. Suplit, T. Koch, U. Schubert, *Corros. Sci.* 49 (2007) 3015.
- [15] J.E. Gray, B. Luan, *J. Alloys Compd.* 336 (2002) 88.
- [16] G. Grundmeier, W. Schimidt, W. Stratmann, *Electrochim. Acta.* 45 (2000) 2515
- [17] N. Scharnagl, C. Blawert, W. Dietzel, *Surf. Coat. Technol.* 203 (10-11) (2009) 1423.
- [18] F. Deflorian, L. Fedrizzi, P.L. Bonora, *Prog. Org. Coat.* 23 (1993) 73.
- [19] A. Pardo, M.C. Merino, A.E. Coy, R. Arrabal, F. Viejo, E. Matykina, *Corros. Sci.* 50 (2008) 823.
- [20] L. Song, A. Atrens, *Adv. Eng. Mater.* 1 (1999) 11.
- [21] J.D. Hanawalt, C.E. Nelson, J.A Peloubet, *Trans. AIME.* 147 (1942) 273.
- [22] M. Liu, P.J. Uggowitzer, A.V Nagasekhar, P. Schumtz, M. Easton, G. Son, A. Atrens, *Corros. Sci.* 51 (3) (2009) 602.
- [23] W.S. Loose, *Corrosion and Protection of Magnesium.* ASM Int, Materials Park, OH 1946, p 173.
- [24] M. Zamin, *Corrosion* 37 (1981) 627.
- [25] K.N. Reichek, K.J. Clark, J.E. Hillis, *Controlling the salt Water Corrosion Performance of Magnesium AZ91 alloy*, SAE Technical Paper series 850 417 (1985).
- [26] G.L. Makar, J. Kruger, *Int. Mater. Rev.* 38 (1993) 138.
- [27] J.T. Klopogge, L. Hickey, R.L. Frost, *J. Raman Spectrosc.* 35 (2004) 967.
- [28] G. Sholz, M. Krossner, A. Dummer, R. Stösser, *J. Mol. Struct.* 505 (2000) 117.
- [29] R.D. Lide, *CRC Handbook of Chemistry and Physics – 84th*, 2003.
- [30] M. Jönsen, D. Persson, D. Thierry, *Corros. Sci.* 49 (2007) 1540.
- [31] B. Karmakar, P. Kundu, R.N. Dwivedi, *J. Non-Cryst. Solids* 289 (2001) 155.
- [32] W.L. Wolf, *The Infrared Handbook*, Washington, Office of naval research, 1978.
- [33] C. Morterra, G. Cerrato, P. Cuzzato, A. Masiero, M. Padovan, *J. Chem. Soc. Faraday Trans.* 88 (15) (1992) 2239.
- [34] H.A. Prescott, Z. Li, E. Kemnitz, J. Deutsch, H. Lieske, *J. Mater. Chem.* 15(2005) 4616.
- [35] S. Verdier, N. Laak, S. Delalande, J. Metson, F. Dalard, *Appl. Surf. Sci.* 235 (2004) 513.
- [36] J.L. Booster, A.V. Sandwijk, M.A. Reuter, *Miner. Eng.* 16 (2003) 273.

[37] L. Kousini, M. Azzi, F. Dalard, S. Maximovich, Surf. Coat. Technol. 192 (2005) 239.