Novel hybrid sol–gel coatings for corrosion protection of AZ31B magnesium alloy

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Abstract

This work aims to develop and study new anticorrosion films for AZ31B magnesium alloy based on the sol–gel coating approach. Hybrid organic–inorganic sols were synthesized by copolymerization of epoxy-siloxane and titanium or zirconium alkoxides. Tris(trimethylsilyl) phosphate was also used as additive to confer additional corrosion protection to magnesium-based alloy. A sol–gel coating, about 5-\textmu m thick, shows good adhesion to the metal substrate and prevents corrosion attack in 0.005 M NaCl solution for 2 weeks. The sol–gel coating system doped with tris(trimethylsilyl)-phosphate revealed improved corrosion protection of the magnesium alloy due to formation of hydrolytically stable Mg–O–P chemical bonds.

The structure and the thickness of the sol–gel film were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The corrosion behaviour of AZ31B substrates pre-treated with the sol–gel derived hybrid coatings was tested by electrochemical impedance spectroscopy (EIS). The chemical composition of the silylphosphate-containing sol–gel film at different depths was investigated by X-ray photoelectron spectroscopy (XPS) with depth profiling.

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1. Introduction

Magnesium-based alloys have a number of advantageous physical and mechanical properties that make them an attractive material for many industrial applications. They are considered to be an excellent material for reducing vehicle weight, lowering fuel consumption and, thereby, reducing CO\textsubscript{2} emissions [1]. Magnesium has a density that is only 65\% that of aluminum and 25\% that of iron. Thus, magnesium-based alloys are used in the fields where weight reducing of the product is of significant concern. Apart from extensive use in the automotive industry, Mg-based alloys are applicable in the production of parts for portable devices, aircraft, military equipment, orthopedic equipment, diving gear and sport goods.

One of the main reasons limiting or even preventing larger scale use of light magnesium alloys for various applications is their high corrosion susceptibility. Therefore, improving the corrosion protection of Mg alloys without the loss of high strength/weight ratio is a real challenge that can lead to a breakthrough in many industrial areas.

Thin (0.2–10 \textmu m) hybrid organic–inorganic sol–gel coatings exhibit a number of properties which make them an attractive approach to partially overcome the problem of corrosion [2]. Sol–gel coatings provide an additional dense barrier for corrosive species and assure good adhesion of the organic paint system to the metal substrate. From the point of view of synthesis, the sol–gel route offers versatile ways to synthesize effective coatings with specific properties. Functionality is optimized by variation of experimental parameters such as chemical

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structure, composition and ratio of precursors and complexing agents, rate and conditions of hydrolysis, synthesis media, embedding of additional active species (e.g., encapsulated or directly introduced corrosion inhibitors), aging and curing conditions, deposition procedure, etc. [2–6]. Recent achievements in sol–gel technology allowed successful fabrication of durable hybrid organic–inorganic sol–gel coatings, which are used as anticorrosion pre-treatments for aluminum alloys [7–14], combining active and passive protection.

In spite of clear industrial demand, creating a stable coating for Mg-based alloys is still a challenge. Only a few attempts to apply sol–gel films on Mg-based alloys have been reported very recently [15–21].

US patents by Ostrovsky [15,16] disclose treatments for improved magnesium and magnesium alloys surface corrosion resistance. The patents describe the acid pickling solutions and the compositions of water/organic solutions of hydrolyzed silanes.

Surface preparation plays a critical role for passivation of the substrate and coating adhesion. Corrosion protection performance of AZ31B alloy after acid pickling with different components is compared in Refs. [17,18]. In contrast to majority of standard procedures [22], the reported acid solutions are chromium free. It is demonstrated [17] that the sol–gel film composed of methyltrimethoxysilane and tetraethoxysilane increase the corrosion resistance of AZ31B. Addition of corrosion inhibitors into the sol–gel coating further decreases the corrosion rate. However, the authors chose the volumetric monitoring of hydrogen gas evolution for the evaluation of effectiveness of the coatings. This technique does not give adequate estimation of corrosion protection efficiency of the coating at the early stages. Moreover, the corrosion processes can be sufficiently localized and corrosion-induced damage due to propagation of local defects can be higher than the values obtained by volumetric methods. Electrochemical methods, especially electrochemical impedance spectroscopy (EIS), give possibility to estimate corrosion protection efficiency of coatings in more adequate way. EIS is one of the most intensively used and powerful techniques for investigation and prediction of corrosion protection. Impedance provides indication of changes in coating and metal interface performance long before visual changes can be observed using traditional exposure tests [23,24]. The frequency dependence of the complex impedance of the coated substrate allows an effective evaluation of the different components of the system such as capacitance and resistance of the protective layers, polarization resistance and double layer capacitance. Representation of these parameters as a function of time allows assessment of the corrosion protection performance of the coating system.

The influence of a silane functionality on the corrosion resistance of a WE43 magnesium alloy, containing rare earths was studied in Ref. [18]. Samples coated with a hydrophobic silane compound with a long aliphatic chain (n-octadecyltrimethoxysilane) and a silane with a mercapto group (3-mercapto-propyl-trimethoxysilane) were immersed 4 days in 0.1N Na2SO4 solution (that is equal to 0.05 M Na2SO4 solution). Although no equivalent circuit for fitting EIS spectra of sol–gel films with specific, magnesium-oriented properties. Tris(trimethylsilyl) phosphate (tTMSPh) was chosen as an additive to reinforce the formulation of the sol–gel coating since this bi-functional compound forms chemical bonds with magnesium substrate imparting superior adhesion. Moreover, tTMSPh can be polymerized with other components of intermediate solutions in the course of synthesis without destroying their barrier properties.

In the present paper we demonstrate the new formulations of the sol–gel films with specific, magnesium-oriented properties. The plates of cast AZ31B magnesium alloy used in this study as the metallic substrate were obtained from Alubin (Israel). Apart from Mg, the alloy contains about 3 wt% Al and 1 wt% Zn.

2. Experimental

2.1. Materials

The plates of cast AZ31B magnesium alloy used in this study were treated with 3-mercapto-propyl-trimethoxysilane and a silane with a mercapto group (3-mercapto-propyl-trimethoxysilane) were immersed 4 days in 0.1N Na2SO4 solution (that is equal to 0.05 M Na2SO4 solution). Although no equivalent circuit for fitting EIS spectra of sol–gel coated Mg-based alloy and fitted parameters are presented.
All AZ31B coupons were chemically etched by 0.5 M solution of nitric acid for 30–60 s and rinsed with distilled water before application of sol–gel films.

2.2. Synthesis of sol–gel coatings

The organic–inorganic films were synthesized by using a controllable sol–gel route, mixing two different sols. An organosiloxane alkosol was combined with another alkosol containing titania or zirconia precursors in order to obtain the hybrid sol.

Two different types of sol–gel films were produced. The first type of coating is composed by in situ synthesized zirconia nanoparticles and (3-glycidoxypropyl)-trimethoxysilane (GPTMS) (Fig. 1a). Silane-based alkosol was prepared by hydrolysis of GPTMS in 2-propanol solution by adding diluted aqueous solution of HNO₃ (pH 0.5) under stirring at room temperature for 1 h. The second alklosol, containing zirconia nanoparticles, was obtained by controlled acidic hydrolysis (pH 0.5) of zirconium (IV) tetra-propoxide (TPOZ) in 2-propanol in the presence of ethylacetocetate as complexing agent under ultrasonic agitation. Finally, the two alkosols were mixed in 2:1 volume ratio, respectively. The hybrid organic–inorganic system was stirred and ultra-sonically agitated for one more hour. Then it was aged for 1 h at room temperature and deposited on the AZ31B substrates. The described sol–gel coatings are in use for pre-treatments for aluminum-based alloys. The detailed procedure of synthesis is reported in our previous papers [8,25,26].

For the second type of sol–gel coatings, the composition of precursors was modified in order to enhance the adhesion and corrosion resistance specifically for Mg-based alloys. The whole procedure of sol–gel preparation remained the same but the silane-based alklosol was supplemented with a bi-functional organic compound—tris(trimethylsilyl) phosphate (tTMSPh) (Fig. 1b). It was chosen to be added to GPTMS since it interacts chemically with the magnesium substrate and can be polymerized without destroying the structure of GPTMS. In the second sol, TPOZ was substituted for titanium diisopropoxide bis(acetylacetonate) (TAP) (Fig. 1c). The hydrolysis of TAP was controlled by acetylacetone as a complexing agent. The sol–gel films on metallic substrates were applied by a dip-coating procedure. Then the samples were cured at 160 °C for 1 h.

2.3. Experimental techniques

EIS technique was employed here to evaluate the corrosion protection performance of the developed hybrid sol–gel films on AZ31B during 2 weeks immersion in 0.005 M NaCl solution. EIS measurements were carried out using a Gamry FAS2 Femtostat coupled with a PCI4 Controller at open circuit potential applying 10 mV sinusoidal perturbations in the 100 kHz to 10 mHz frequency range. Per frequency decade, seven experimental points were collected during the measurements. A conventional three-electrode cell was used, consisting of a saturated calomel reference electrode, a platinum foil as a counter electrode and sol–gel coated AZ31B substrate as working electrode with a surface area of 3.3 cm². All measurements were performed in a Faraday cage in order to avoid any electromagnetic interference. At least two samples were measured for each coating to check the reproducibility of results. A simplex method was employed to fit the impedance plots using Gamry Echem Analyst software, Version 1.35.

Low concentration of chloride-containing electrolyte, 0.005 M NaCl, was chosen in order to decrease the corrosion rate of the electrochemically active Mg-based alloy. It is necessary to note, that the sol–gel films under study are only the pre-treatments, rather than the final coatings. The main role of the pre-treatment is to deactivate the surface of the metal and assure good adhesion to the top coating. The slow rate of the corrosion processes allows estimating correctly corrosion at the early stages and differentiates the protective properties of different sol–gel films. Meanwhile, as it is shown below, such concentration of NaCl is enough to cause the large corrosion impact in the uncoated AZ31B. It also has been reported earlier [27–29] on the practicality of use of diluted NaCl solution for study the corrosion of pre-treated metallic substrates (aluminium- and magnesium-based alloys) at early stages.

The microstructure and general chemical composition of the sol–gel films before and after immersion tests was studied by SEM/EDS Hitachi S-4100 system with electron beam energy of 25 keV. The nanostructure of the sol–gel coating was observed by TEM/EDS JEOL JEM 2010 microscope.

X-ray photoelectron spectroscopy measurements were performed using a Microlab 310 F (from Thermo Electron - former Vg Scientific). Thin, about 1 μm, coatings were prepared on polished AZ31B substrates for XPS/Auger etching and analysis. The spectra were taken in CAE mode (20 eV), using an Al (non-monochromate) anode. The accelerating voltage was 15 kV. The quantitative XPS analysis was performed using the Avantage software. The relative atomic concentration (Aᵢ) was calculated using the relation:

\[ A_i = \frac{\text{normalised peak area} \times 100}{\sum \text{normalised peak areas}} \]

where the subscript (i) refers to the quantified specie and the subscript (x) refers to the other species detected in the XPS spectra. The normalised peak area was obtained by dividing...
the intensity of the XPS peak of the species (after background subtraction) by the sensitivity factor of the corresponding species. The background subtraction was performed using the Shirley algorithm, which gives a curve S-shaped and assumes that the intensity of the background is proportional to the peak area on the higher kinetic energy side of the spectrum. The quantification was performed after peak fit. The peak fit function used was a Gaussian–Lorentzian product function and the algorithm was based on the Simplex optimisation as used in the Avantage software.

3. Results and discussion

3.1. Sol–gel coatings

The TPOZ/GPTMS-based sol–gel coatings have been under study as environmentally friendly pre-treatments for 2024 aluminum-based alloy for more than 3 years already [7,19–21]. This system was chosen to be a standard formulation for Mg-based alloys. The properties of these coatings are reported in our previous papers [8,25,26,30]. Before application on metallic substrates, the sol–gel solution is homogenous, transparent and has light-yellow color. The viscosity of hybrid mixed sols remains in the range 12–35 cP within 1 month [30]. The TEM image of a cured TPOZ/GPTMS coating is presented in Fig. 2. It shows that the coating contains uniform amorphous nanoparticles enriched with zirconium, which are homogeneously distributed into the organosiloxane-based matrix. The nanoparticles were formed in situ, during the hydrolysis of TPOZ and have diameter about 4 nm.

Introduction of tTMSPh in TPOZ/GPTMS-based sols, forming sol–gel coatings equal by their inorganic precursor, is impossible because an insoluble product forms at the stage of mixing the two alkosols—TPOZ-based with GPTMS-tTMSPh-based. Formation of highly insoluble zirconium phosphate is the most likely event since the solubility product for complexes of Zr with PO$_4^{3−}$ is one of the lowest known (10$^{-132}$ [31]) and, therefore, hydrolysis of tTMSPh can be shifted in the direction of PO$_4^{3−}$ formation.

Thus, the TPOZ of “inorganic” sol of the standard TPOZ/GPTMS-based formulation was substituted for the titania precursor TAP. The hydrolysis and condensation reactions of the titanium alkoxides leading to formation of titanium oxo/hydroxo precipitates are very fast usually, but these processes can be controlled using various complexing agents such as, for example, acetylacetone. Formation of complexes with the coordination number of Ti higher than its valence occurs due to the fact that titanium alkoxides are Lewis acids and they can interact with compounds which have a lone pair of electrons with formation of Lewis acid-based complexes. Due to bidentality of complexing ligand the new precursor, titanium diisopropoxide bis(acetylacetonate), has different molecular structure with coordination number of six for Ti, a lower reactivity and hydrolyzes less readily than titanium iso-propoxide. This fosters formation of gels instead of crystalline structures [32].

Fig. 2. TEM image of the cured TPOZ/GPTMS-based sol–gel film.

Fig. 3. (a) SEM image of AZ31B specimen coated with TAP/tTMSPh-based sol–gel film; (b) cross-sectional image of the same sol–gel film deposited on AZ31B.
Therefore, the final sol–gel coatings applied on AZ31B plates have double-net structure: inorganic-based (titania or zirconia) net into organosiloxane-based hybrid.

3.2. SEM characterization

SEM images (Fig. 3) show the plane and cross-section views of the deposited TAP/tTMSPh-based sol–gel film. No cracks were visible on the surface at 1500 times magnification. The thickness of the sol–gel layer is around 5 μm. The thickness of TPOZ/GPTMS-based coating is about 4 μm (not shown).

3.3. Visual observation

Comparative optical photos of blank AZ31B specimen and samples coated with two different sol–gel films after 2 weeks of immersion are presented in Fig. 4. Neither signs of corrosion attack nor indication of delamination of the sol–gel film are visible on the surface of the sample coated with TAP/tTMSPh-based film (Fig. 4a). Formation of filiform corrosion is obvious on the surface of sample coated with TPOZ/GPTMS-based sol–gel film (Fig. 4b). The AZ31B blank specimen is very corroded (Fig. 4c). The presented results already give promising indication concerning the efficiency of the developed sol–gel films. However, the detailed electrochemical study using EIS was done in order to understand the processes occurring during corrosion.

3.4. EIS measurements

Electrochemical impedance spectroscopy measurements, which provide a quantitative estimation of coating degradation and corrosion processes, were carried out in the course of immersion of sol–gel coated samples in 0.005 M NaCl aqueous solution. The blank specimen of AZ31B magnesium alloy was tested as well. Taking into account the direct relation between stability of the native oxide and the heat-treatment “history” and to equalize the properties of the native magnesium oxide formed on blank AZ31B and on the specimens coated with sol–gel, the plates of blank AZ31B were preliminary heat-treated at 160 °C for 1 h. As the results of two parallel measurements, the values of low frequency impedance of two tests converged within 30%.

Fig. 5 presents the evolution of the impedance spectra of uncoated AZ31B after different times of immersion in NaCl solution. One well-defined time constant can be observed in the EIS spectra of blank AZ31B at around 10 Hz at the beginning of immersion tests. This relaxation process is associated with electrochemical activity of the bare alloy surface immersed in the electrolyte and can be ascribed to the capacitance of electrochemical double layer, \(C_{DL}\), on the interface metallic surface/electrolyte. The resistive response at low frequencies corresponds to the polarization resistance, \(R_{polar}\), increases with immersion time at the beginning, from 1st to 2nd day, due to the formation of a passive film of corrosion products (mainly hydroxides) on the metal surface. However, longer immersion leads to partial breakdown of the protective layer due to the starting of localized corrosion attack causing slight decrease of the polarization resistance again.

Fig. 4. Optical photos of AZ31B coated with (a) TAP/tTMSPh-, (b) TPOZ/GPTMS-based sol–gel films, and (c) blank AZ31B alloy after 2 weeks of immersion in 0.005 M NaCl solution.
Fig. 5. Evolution with immersion time of the Bode plots for blank magnesium-based alloy AZ31B.

(Fig. 5, for 8th and 14th days). The formation of the hydroxide layer is confirmed by a new time constant which appears in the high frequency range, around 20 kHz, $C_{\text{hyd}}$ and $R_{\text{hyd}}$. It is ascribed to the signal from the growing Mg(OH)$_2$ layer: 

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2.$$ 

This reaction occurs as a consequence of cathodic: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \uparrow$ and anodic 

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$$ 

processes. Formation of passive hydroxide film is possible at pH values above 9 according to the Pourbaix diagram [33]. The alkalinization of the electrolyte is provided by the cathodic reaction mentioned above. The time constant related to the formed hydroxide film becomes well pronounced on the 5th day of immersion as it is shown in Nyquist plots (Fig. 6).

Fig. 6. Variation of Nyquist plots for blank AZ31B alloy with immersion time.

Detailed interpretation of EIS spectra was performed by numerical fitting of Bode plots by using the equivalent circuit presented in Fig. 7. Quantification of parameters was made using a simplex method. The circuit for blank AZ31B is composed of two time constants: the hydroxide resistance $R_{\text{hyd}}$ and constant phase element CPE$_{\text{hyd}}$ (corresponding to capacitance $C_{\text{hyd}}$) and the polarization resistance $R_{\text{polar}}$ and double layer capacitance $C_{\text{DL}}$ represented by CPE$_{\text{DL}}$. The resistance of the NaCl solution $R_{\text{sol}}$ is placed in series with all other elements of the equivalent circuit. Constant phase elements instead of capacitances were used for fitting of all the bare and coated samples. Such modification is obligatory in the case the phase shift of a capacitor is different from $-90^\circ$ [34]. The values of capacity $C_{\text{hyd}}$ and $C_{\text{DL}}$ were calculated using the following equation:

$$C = Q(\omega_{\text{max}})^{N-1}$$

where $\omega_{\text{max}}$ is the frequency at which the imaginary impedance reaches a maximum for the respective time constant, $Q$ and $N$ are the components of CPE [34]. The evolution of the parameters obtained by fitting is presented in Fig. 8. The resistance of growing Mg(OH)$_2$ layer on the bare alloy surface, $R_{\text{hyd}}$, increases with time whereas the capacitance $C_{\text{hyd}}$, decreases. This tendency demonstrates growth of the hydroxide film on the alloy. Although this fact is in line with the literature [21,35] it needs

Fig. 7. Equivalent circuit used for fitting experimental EIS spectra of blank AZ31B.

Fig. 8. Evolution of parameters depicted in Figs. 5 and 7 for blank AZ31B alloy in the course of immersion in 0.005 M NaCl solution.
Fig. 9. Evolution of Bode plots for AZ31B pre-treated with (a) TAP/TMSPh-based sol–gel film; (b) TPOZ/GPTMS-based sol–gel film.

Further study. However, the aim of this article is to study the protection conferred by sol–gel films deposited on AZ31B, thus, the details of corrosion degradation of the blank alloy are out of the scope of this article.

The impedance spectra of the coated alloy have two time constants as in the case of bare metal after 5 days of immersion. The difference is that the high frequency time constant, around $10^4$ Hz, is related to the hybrid sol–gel film applied on the alloy rather than to the formed passive hydroxide layer. The resistance $R_{SG}$ and capacitance $C_{SG}$ of sol–gel coating can be clearly distinguished from the response of the alloy/sol–gel film interface (Fig. 9a and b), in contrast to recently published data [21], where the absence of the time constant characteristics of the undoped silane coating was reported. In spite of fast decrease of the initial values of the impedance and increase of respective capacitance, which occurs due to the electrolyte uptake, the coating capacitance and resistance could be clearly distinguished from the corrosion response even after 2 weeks of immersion. This fact points out the good barrier properties of the coatings and their stability in time.

As in the case of the blank alloy, the time constant at around 1 Hz on the EIS spectra of the TPOZ/GPTMS- and TAP/TMSPh-coated specimens (Fig. 9) can be attributed to the capacitance of double layer existing at the surface of metal/electrolyte interface, $C_{DL}$. This time constant is well-pronounced after a week of immersion, while at the beginning of immersion tests this time constant is uncompleted (Fig. 9a, 1st day) and is shifted to lower frequency (Fig. 9a and b, 1st day) because of good barrier properties of sol–gel film which does not allow the penetration of the electrolyte to the metal surface.

For quantitative estimation of the corrosion protection, experimental EIS impedance spectra were fitted using an equivalent circuit which simulates the response of the sol–gel coated alloy (Fig. 10). This equivalent circuit is constituted by two relaxation components related with the capacitance of sol–gel film $C_{SG}$ and the double layer capacitance $C_{DL}$ originated from the electrochemical corrosion activity at the alloy surface. In the equivalent circuit $R_{sol}$ is the resistance of the NaCl solution, $R_{SG}$ is the resistance of the sol–gel film, CPE$_{SG}$ (composed by $Q_{SG}$ and $N_{SG}$ for fitting experimental spectra) represents the capacitance of the film. Although the presence of initial layer of MgO/Mg(OH)$_2$ on the alloy surface is undisputed [33,36] it is impossible to single out the response from the oxide/hydroxide layer in the impedance spectra (which was described above for the spectra of blank alloy and is very well-pronounced in the case of sol–gel coated aluminium alloys [27]), due to insufficient barrier properties of this layer.

Comparison of the impedance spectra of different samples (uncoated and coated ones) after 2 weeks of immersion test is presented in Fig. 11. The results of numerical simulation of the EIS spectra using the above equivalent circuits along with respective fitting parameters (Table 1) are also presented. The measured points at the low frequency range in the Bode plots of the blank alloy show some scattering. This fact together with the signs of the diffusion Limited process in the case of blank alloy leads to the deviation observed in the fitting of the low frequency range. Comparing the low frequency impedance in Fig. 11, which is one of the parameters that can be easily used to assess the corrosion protection performance of different systems,
the hybrid film prepared with titanium precursors and tTMSPh demonstrates the highest protection of AZ31B. The low frequency impedance for this sample is about 0.6 $\Omega$ cm$^2$ after 2 weeks of immersion in sodium chloride solution that is 1.5 order of magnitude higher than for uncoated AZ31B alloy.

The resistance and capacitance of the dielectric sol–gel film depend on the porosity of the coating, its crack ability, amount of absorbed water and thickness [37–43]. The evolution of resistance and capacitance of the sol–gel films as well as the parameters related to the corrosion process on the alloy/film interface during the immersion is presented in Fig. 12. $C_{SG}$ and $C_{DL}$ were calculated using Eq. (1). Fitted parameters $Q_{SG}$, $N_{SG}$, $Q_{DL}$, and $N_{DL}$ are presented in Table 1. Fast dropping of $R_{SG}$ and increase of $C_{SG}$ at the first hours of immersion is usually observed for sol–gel coatings of such type [25,27] and can be assigned to the water absorption. Slow change of the parameters of sol–gel coatings after the 1st day of immersion is the evidence of good barrier properties and stability. Both films confer corrosion protection to the AZ31B, especially the one doped with tTMSPh. Significant difference of absolute values of resistance and capacitance after 300 h ($1.6 \times 10^4$ $\Omega$ cm$^2$ and $1.3 \times 10^{-8}$ F/cm$^2$ for TAP/tTMSPh-based coating; $1.8 \times 10^3$ $\Omega$ cm$^2$ and $4.3 \times 10^{-8}$ F/cm$^2$ for TPOZ/GPTMS-based coating) of the two sol–gel films results from lower porosity and higher hydrolytic stability of the tTMSPh-doped sol–gel film. Absence of filiform corrosion and improved protective properties of the TAP/tTMSPh-based coating can also be the result of the formation of hydrolytically stable Mg–O–P bonds at the alloy/sol–gel film interface. One order of magnitude difference of initial values of $R_{SG}$ indicates significantly lower amount of conductive pathways (pores and micro-cracks) for the TAP/tTMSPh-based coating. The rate of the corrosion process can be compared using the polarization resistance. $R_{polar}$ of TAP/tTMSPh-based coated specimen after 1 day of immersion drops and remains at the level of $1 \times 10^6$ $\Omega$ cm$^2$ that is 1.5 order of magnitude higher than for the bare alloy ($R_{polar}$ is about $3 \times 10^4$ $\Omega$ cm$^2$). The polarization resistance of TPOZ/GPTMS-based coated sample is lower due to worse barrier properties of the film. The above results demonstrate improvement of the corrosion protection due to introduction of the sylilphosphate into sol–gel coating.

3.5. XPS study

The main idea of introduction of sylilphosphate in the composition of the sol–gel coating is the reinforcement of corrosion protection and adhesion of coating, which can be achieved due to
chemical interaction and formation of chemical bonds between magnesium oxide/hydroxide of the alloy surface and partly hydrolyzed tris(trimethylsilyl) phosphate of sol–gel coating. The electrochemical and visual observations of the coatings during accelerated immersion tests confirmed good protection efficiency when silylphosphate is added to the sol–gel formulation. XPS analysis combined with depth profiling of TAP/tTMSPh-based sol–gel coating was performed with different times of etching in order to study the sol–gel/metal interface and to understand the mechanism of corrosion protection improvement.

Fig. 13 shows the P 2p ionization obtained after different etching times. The spectra obtained prior etching, revealed the presence of carbon, silicon, oxygen, titanium and phosphorus. The P 2p core level spectra consists of a single peak at approximately 134.1 eV, which can be assigned to P–O bonds of the phosphorous pentavalent oxidation state of the PO$_4^{3-}$ groups [44,45].

The silylphosphate-containing sol–gel film was etched using an Ar ion beam and the new exposed surface was again investigated by XPS. After 1000 s, the analysis detected a weak signal from Mg, suggesting that the etching was approaching the metallic substrate. At this stage, the P 2p ionization reveals a new peak in the low binding energy side, at approximately 131.2 eV. This result denotes an increase of the electronic state density of the phosphorous atoms as the etching approaches the interface sol–gel/magnesium and can be assigned to the presence of P–O–Mg bonds at the sol–gel/metal interface. The electronegativity of silicon is higher than that of magnesium. Therefore, when the P–O–Si bonds are replaced with P–O–Mg bonds, the electronic density is shifted towards the P–O side, due to the positive character of Mg atoms, leading to a decrease of the P 2p binding energy. Shifts of the binding energies for the P 2p atoms due to a secondary neighbor and changes of electronic density around the oxygen atoms have been reported for phosphate-glassy materials [46,47].

XPS measurements carried out on the AZ31B substrate treated with a few nm thin film of pure tTMSPh also revealed a shift of the P 2p ionization towards lower binding energies (spectra not shown). In this case, the P 2p shift was observed for etching times as short as 100 s.

The inset in Fig. 13 shows the ratio of the 134.1 and 131.2 eV peak’s areas obtained from the P 2p ionization after peak fitting. The intensity of lowest energy peak (131.2 eV) increases as the sol–gel layer is being removed and the metallic substrate exposed. This ratio is 1:0 at the outer surface and changes to 1:1.1 after 3500 s of etching. This trend reveals that the P–O–Mg bonds contribution becomes more important at the film/metallic substrate interface.

Presence of P–O–Si(CH$_3$)$_3$ groups in the structure of tTMSPh makes the chemical interaction of tTMSPh with GPTMS a likely event, forming a hybrid organic–inorganic sol–gel network. This

![Fig. 13. P 2p ionization obtained on AZ31B specimens coated with TAP/tTMSPh film after different etching times: from outer surface (0 s) to the metallic substrate (3500 s). The inset shows the ratio of the area of the peaks assigned to different chemical interaction P–O–Si/P–O–Mg.](image-url)
system does not display defined organic and inorganic layers, as it could be in the case of chemical pretreatment of Mg alloy with phosphoric acid. Therefore, introduction of tTMSPh into the sol–gel system leads to formation of a gradual by depth film with enhanced adhesion and improving the anticorrosion performance of the coating. The general scheme of the siloxane-based net obtained with a specific tailored interface is presented in Fig. 14.

4. Conclusions

- Well-adhered thin nanostructured anticorrosion coatings for highly corrosive AZ31B magnesium-based alloy were synthesized by using the sol–gel route.
- The effectiveness of corrosion protection is confirmed by EIS measurements. The anticorrosion performance of titania-based tris(trimethylsilyl)phosphate-containing sol–gel pretreatment allows immersion of AZ31B magnesium alloy in 5 mM neutral aqueous NaCl solution for at least 2 weeks without destructive outcomes.
- The tris(trimethylsilyl)phosphate-containing sol–gel coating confers good corrosion protection due to its chemical interaction with the magnesium substrate which, most probably, leads to the formation of a graded and stable in-depth film.

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