

CORROSION BEHAVIOUR OF PRESERVED PEO COATING ON AZ31 MAGNESIUM ALLOY

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Resume

A surface treatment process, composed of plasma electrolytic oxidation (PEO) and sealing by temporary oil preservation system containing corrosion inhibitors, was performed on AZ31 magnesium alloy in order to improve its corrosion resistance in environments containing chlorides. Both atmospheric and immersion conditions were evaluated by electrochemical tests in 0.1M NaCl solution together with salt spray test according to STN EN ISO 9227 standard. The obtained results confirmed significant improvement of corrosion resistance reached by the PEO sealing in aggressive environments compared to the pure PEO coating on AZ31 surface. Hence, such a duplex coating is a very perspective alternative for magnesium alloy applications in severe conditions or for temporary protection of magnesium products coated by the PEO during marine transport.

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1 Introduction

Magnesium alloys are the lightest commercially used metal structural material. Their weight saving potential exceeds 50 % for some components, which leads to an increased usage of Mg alloys in the industrial fields in the last few years. Specifically, substituting other materials for Mg alloys in automotive and aircraft industry, leads to reduction in fuel and CO₂ emission, being a very actual topic [1-2]. Apart from extensive use in automotive industry, Mg-based alloys are utilized in production of parts for computers and other portable devices, aircraft, military, recreational and orthopaedic equipment, diving gear and sports goods [3-4]. However, magnesium has many undesirable properties, as well, including low abrasion resistance, low creep resistance, high-chemical reactivity, including flammability and especially very low corrosion resistance [5]. The addition of several alloying elements such as Al, Zn and rare earths can improve the corrosion resistance of Mg alloys. However, the technological requirements for several applications remain still unsatisfied [6-7]. Therefore, magnesium alloys must be treated before they are used in practice by appropriate surface treatment techniques including electrochemical plating, chemical conversion, physical vapour deposition, laser cladding, anodic oxidation, plasma electrolytic oxidation, etc. [8-10].

Among these techniques, the plasma electrolytic oxidation (PEO), provides a thick and adherent ceramic-like coating on metal substrates improving the corrosion

resistance in chloride-containing solution and also providing high wear resistance. Unfortunately, the performance of PEO coatings on magnesium alloys deteriorates drastically under the long-term exposure in aggressive environments [11-12]. This is caused by the presence of defects as pores and cracks in the PEO layer, created naturally during the PEO process, which form the pathways for corrosive species impairing the total protective effect of PEO [3]. Additionally, the PEO process increases surface roughness, which can be harmful if the alloy has to be used in sliding parts [13]. Considerable strategies, regarding optimization of factors influencing the PEO process (electrolyte composition and additives, electrical parameters setting, etc.) have been proposed for improving the corrosion performance of the PEO coatings. However, complete elimination of the micro pores and defects during the PEO treatment is still impracticable due to its discharge assisted growth mechanism [14]. A desirable strategy to overcome this drawback is to seal these defects or to create the second layer that would fill the pores and even improve the overall surface qualities.

Different surface post-treatment approaches for the PEO coatings were investigated, including organic, sol-gel and polymer coatings, in order to avoid the early failure of the PEO coatings on Mg alloys due to their permeability to the environment [6]. It is possible to meet with chemical conversion, electrophoretic deposition, hydrothermal treatment, chemical vapour deposition (CVD) and other standard techniques optimized for this purpose [14]. Very

Table 1 Chemical composition of AZ31 magnesium alloy (wt. %)

component	Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
wt. %	2.96	0.828	0.433	0.004	0.004	<0.001	0.002	rest

hot topic represents application of various impregnators containing corrosion inhibitors [14-15].

However, the above mentioned techniques of post-treatment create a permanent duplex coatings that are not suitable for applications where just temporary corrosion protection of the PEO is required (for example a marine transport of final Mg products treated by PEO) or these techniques are not cost effective. For these reasons, the effective preservation method of applying mineral oil containing corrosion inhibitors meeting the above criteria and its effect on level of corrosion protection of AZ31 magnesium alloy covered by PEO was studied in this paper.

2 Experimental material and methods

The tested material was continually casted AZ31 magnesium alloy homogenized at 420 °C for 16 hours used also in previous studies [16-20]. Its chemical composition is listed in Table 1.

The process of PEO preparation was based on authors' experience from previous studies [21-23]. The plates of AZ31 (5 mm thick) were ground by an emery paper p1000 to provide the same roughness across the treated surface. Subsequently, samples were rinsed by demineralized water, ethanol and air-dried. The PEO process was performed on a laboratory DC power source Keysight N8762A. The sample was connected as an anode in the two-electrode system. The cathode was provided by stainless steel plate. The PEO electrolyte was composed of 12 g/l $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 1 g/l KOH and its pH was adjusted to 12.3 at 22 ± 1 °C. The electrolyte was cooled with water and constantly stirred during the PEO procedure in order to ensure the better distribution of active species and to keep the temperature below 50 °C. The current density was set to 0.05 A/cm² for 14 minutes. Applied current was maintained at a constant value. The morphology of the prepared PEO coating was observed using the Carl Zeiss Merlin scanning electron microscope (SEM).

The created PEO coating was subsequently sealed by commercially available preservation mineral oil VpCI®-369 containing corrosion inhibitors, applied by brushing while dipping, in order to reach complete uniform coverage within a single applied layer (average thickness ~ 100 µm). After the application, the samples were left for 24 hours in desiccator in order to give the inhibitors enough time to naturally impregnate through the PEO coating and seal the pores.

Two different electrochemical measurement techniques were used to compare and determine the corrosion resistance of AZ31 magnesium alloy after the PEO process and sealing: the potentiodynamic polarization

measurements (PDP) and the electrochemical impedance spectroscopy (EIS) measurements in a solution of 0.1M NaCl (simulating an environment containing aggressive chloride ions). All the electrochemical measurements were performed at 22 ± 2 °C on at least three samples of each type, so that reproducibility of the test results was ensured. The most representative curves are presented in graphs.

A technique with a constant potential change per time unit was used for the PDP measurements. The PDP tests were performed over the potential range from -200 mV to +500 mV vs. an open circuit potential (E_{oc}) value after 1 hour of stabilization in the 0.1M NaCl test environment. The constant change of applied potential during the measurements was 1 mV.s⁻¹. The measured area of samples was 1 cm². The Tafel analysis of the measured curves was performed using the EC-Lab V11.10 software.

The EIS measurements were realized after various exposure times from 1 to 168 hours in order to observe behaviour of the electrochemical system on AZ31 samples with sealed PEO coating. The measurements were performed in the frequency range from 100 kHz to 10 mHz with the frequency 10 times per decade. Amplitude of the applied AC voltage was 15 mV around the open circuit potential value (E_{oc}). The outputs of the EIS measurements were represented by the Nyquist diagrams, which were analysed by the equivalent circuits (Figure 1) with the EC-Lab V11.10 software. The main evaluated element was a polarization resistance (R_p) representing the element, which is inversely proportional to the corrosion rate and is estimated from the Nyquist diagram as

$$R_p = |Z(j\omega)|_{\omega \rightarrow 0} - |Z(j\omega)|_{\omega \rightarrow \infty} \quad (1)$$

$z(j\omega)$ that denotes the impedance as a function of radial frequency ω in an imaginary unit j according to an expression analogous to the Ohm's law. The solution resistance (R_s) was estimated from the impedance at high frequency ($|Z(j\omega)|_{\omega \rightarrow \infty}$), while the sum of R_p and R_s was estimated from the impedance at low frequency ($|Z(j\omega)|_{\omega \rightarrow 0}$). The difference between these two impedance values results in the polarization resistance [24]. In a system with one capacitive loop, R_p is equivalent to pore resistance (R_{po}). In the case of 2 capacitive loops, the R_p value was the sum of the pore resistance (R_{po}) and charge transfer resistance (R_{ct}). The R_{po} is generally interpreted as the pore resistance of the coating resulting from the penetration of the electrolyte and is detected in the high-frequency region. The R_{ct} is resistance to charges transfer, determining the corrosion rate of reaction and is a measure of electric charges transfer

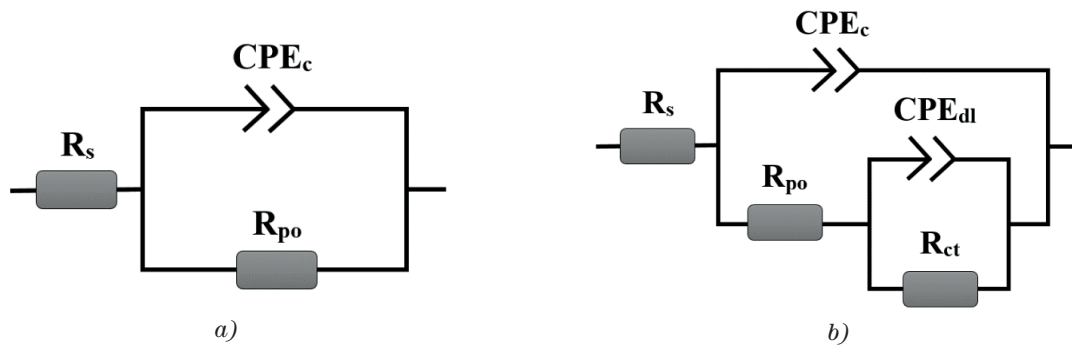


Figure 1 Equivalent circuits for diagrams with one capacitance loop (a) and two capacitance loops (b)

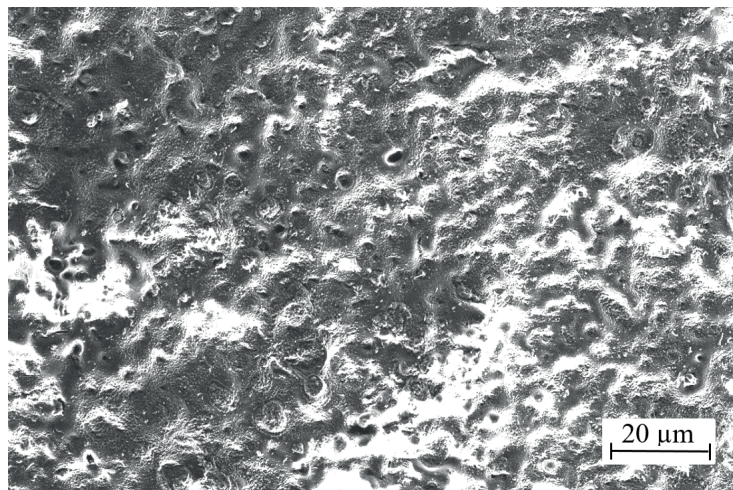


Figure 2 Surface morphology of prepared PEO coating

through the electrode surface [25-27]. In practical, the measured impedance spectra may differ from ideal or theoretical behaviour. The loops (or time constants) do not show a perfect semi-circle shape in the Nyquist representation. This non-ideal behaviour may arise from coating heterogeneities as roughness, inhomogeneous composition, etc. In such a case, the coating cannot be described by a simple capacitor [28]. This one is generally replaced by a constant phase element (CPE) that is defined as [29]:

$$CPE \approx C = [C(j\omega)^n]^{-1}, \quad (2)$$

where n accounts for non-ideal behaviours: when it equals to 1, the CPE is a pure capacitance and when it equals zero, the CPE is a pure resistance. The CPE_c is a suitable parameter to show the amount of penetration of water into the coating, while the CPE_{dl} indicates the capability of the adhesive bond failure and penetration of electrolyte to the interface of coating/metal [30].

The corrosion tests were performed in a simulated neutral salt spray atmosphere according to STN EN ISO 9227 standard in Votsch VSC KWT 1000 corrosion chamber. The test was carried out at a continuous temperature of 35 °C. The sodium chloride solution for the salt spray production was prepared by dissolution of pure sodium chloride of concentration 50 g/l \pm 5 g/l in demineralised water with a conductivity not higher than

20 μ S/cm at 25 °C. The pH of the solution was within the required range from 6.5 to 7.2 (measured at 35 \pm 1 °C) during the whole salt spray test. In order to prevent evaporation of water from the sprayed droplets, the air was humidified before entering the atomizer, by passage through a saturation tower containing water with a temperature 45 °C. The absolute pressure of the used compressed air was set to 120 kPa. The tested samples were inserted to the chamber on an inert plastic holder.

3 Results and discussion

The SEM image of the PEO coating prepared on tested AZ31 magnesium alloy in accordance to authors' experience from previous studies [21-23] is presented in Figure 2. The PEO layer exhibits a porous structure typical for the PEO process. Formation of micropores is associated with presence of the molten oxides and gas bubbles produced during the discharges occurred on the surface of samples [22, 31].

Evaluation of the PEO surface treatment effect on the corrosion resistance of magnesium alloy AZ31 in 0.1M NaCl solution, using PDP and EIS tests, was already performed in authors' previous studies [21-23]. Some of these results are used in the following discussion.

The results from the potentiodynamic polarization measurements of the AZ31 samples, covered by the

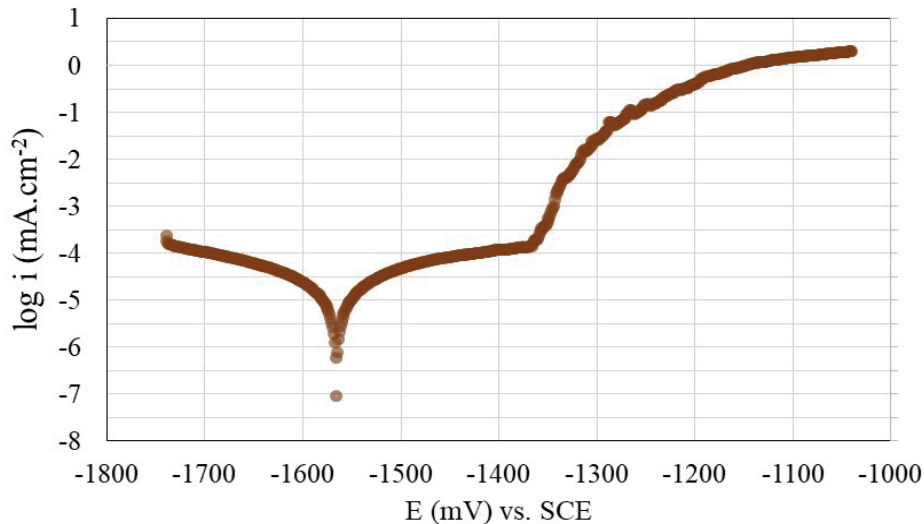


Figure 3 Potentiodynamic curve of the PEO coating sealed by oil based preservation layer containing corrosion inhibitors on AZ31 in 0.1M NaCl solution

Table 2 Electrochemical corrosion characteristics obtained from potentiodynamic curve of the PEO coating sealed by oil based preservation layer containing corrosion inhibitors on AZ31 in 0.1M NaCl solution

E_{corr} (mV)	E_{pit} (mV)	i_{corr} ($\mu\text{A.cm}^{-2}$)	β_a (mV/dec.)	β_c (mV/dec.)	r_{corr} ($\mu\text{m.year}^{-1}$)
-1568±22	-1367±30	0.014±0.007	159±12	159±3	0.53±0.16

sealed PEO coating, are presented in a form of the average potentiodynamic polarization curve shown in Figure 3. The average values of individual electrochemical corrosion characteristics were obtained by Tafel analysis and are presented in Table 2. When comparing to results from the PDP measurements reported in the previous work [21], it can be seen that sealing of the PEO layer with the tested preservative containing corrosion inhibitors caused a slight deterioration of the PEO, what is documented by shifting the average corrosion potential to more negative values by 67 mV compared to the simple PEO layer prepared at the longest processing time. Hence, as a consequence of sealing the PEO coating with the tested preservation system ultimately reached a corrosion potential almost identical to the corrosion potential of the base material (the difference of 11 mV is negligible in terms of measurement deviations). Thus, it can be stated that the tendency of the sealed PEO surface system to corrosion in the tested environment is almost identical compared to the base material from the thermodynamic point of view. On the contrary, there is a theoretical deterioration caused by impregnation compared to the simple PEO coating. However, this degradation of the thermodynamic corrosion properties is negligible from a practical point of view due to still extremely low nobility of the overall surface system. More important is a kinetic aspect. There, impregnation of the PEO coating with a preservative containing corrosion inhibitors effectively reduced the sensibility of the system to polarization in the anodic region, to the level

comparable to cathodic polarization (almost identical values of β_a and β_c). The surface system also exhibited similar behaviour to that observed for some metals able to create passive layers. This is underlined by the presence of a step potential change in the anodic region responding to the pitting potential (E_{pit}) [32-34]. At this point, there is a severe local corrosion damage present on the surface of the sample. The potential region in which the E_{pit} was located was almost identical to the region recorded on the simple PEO coating. Much more radical was the change in kinetic electrochemical corrosion characteristics, which provide information on the rate of corrosion reactions in a corrosion environment. A simple PEO coating can reduce the instantaneous corrosion rate of the AZ31 alloy surface by more than three orders of magnitude to a level of about $2 \mu\text{m.year}^{-1}$. Sealing this layer with the tested preservative reduced this corrosion rate to just $0.53 \mu\text{m.year}^{-1}$. Thus, the instantaneous corrosion rate of this duplex coating system on AZ31 alloy, in an aqueous environment containing chlorides, can be considered to be almost zero even after one hour of exposure. Unfortunately, these excellent values are not sustainable in the long run, as the environment constantly interacts with this system during the longer exposure, which is reflected in its degradation and decline in its protective function. However, it is more appropriate to use a non-destructive method such as EIS to monitor this process, which can be used to continuously assess development of individual relevant electrochemical characteristics on the same sample over a longer time horizon.

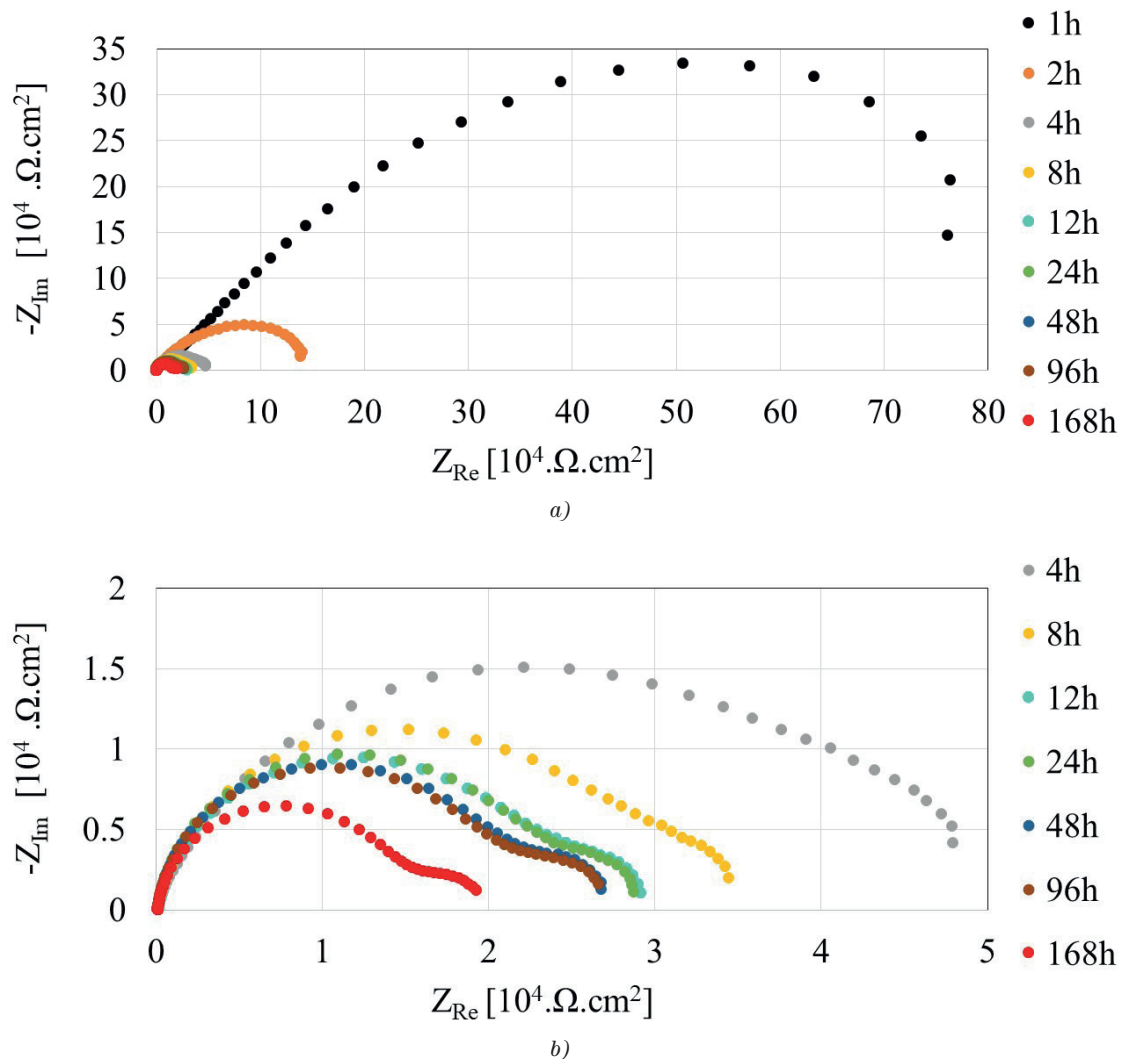


Figure 4 Nyquist diagrams of PEO coating sealed by oil based preservation layer containing corrosion inhibitors on AZ31 in 0.1M NaCl solution after various exposure times: a) overall view; b) detail of higher exposure times

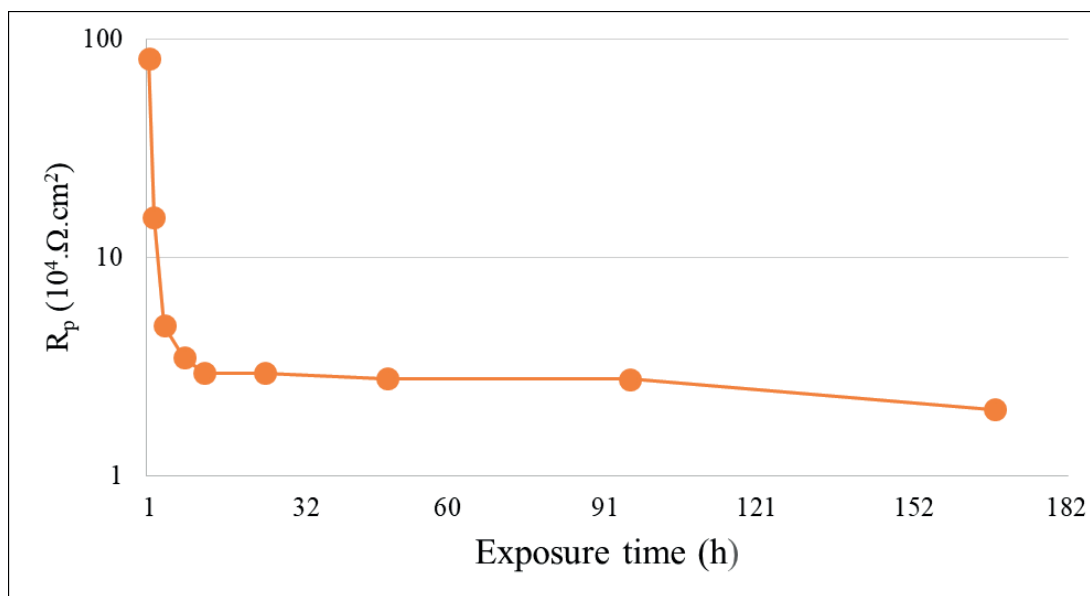
The measured Nyquist diagrams of AZ31 alloy with sealed PEO coating after various exposure times are shown in Figure 4. The electrochemical characteristics obtained by their analysis are shown in Table 3 and the graph of evolution of the R_p values obtained on the sealed PEO coating after individual exposure times in 0.1M NaCl solution is shown in Figure 5. After 1 hour of exposure to the electrolyte, the sealed PEO surface reached more than four times higher R_p value compared to the simple PEO layer [23], which fully corresponds to the results of kinetic corrosion parameters evaluation within the PDP measurements. This improvement is primarily caused by the physical barrier effect of the added preservative in the initial stages of exposure. However, since it is not a permanent, but only a temporary liquid preservative system, the barrier effect gradually lost its effectivity with prolonged exposure and the electrolyte penetrated further through the PEO to the base material. When the penetrating electrolyte reached the base material under the PEO coating, a second capacitive loop was recorded on the Nyquist diagram revealing the detection of a new interface. This was observed after 4 hours of exposure in the considered case. Up to that point,

the entire resistance of the surface to the corrosion process was held by R_{po} . From 4 hours of exposure, R_{ct} contributed to the total polarization resistance of the system, as well. As can be seen from Figure 5, the decrease in the total polarization resistance was very sharp in the first stages of exposure up to 12 hours, which was mainly related to weakening of the barrier effect of the preservative and PEO coating, saturation of the surface system with electrolyte and degradation of the soluble MgO (its dissolution process in NaCl solution is described elsewhere [35-36]) representing the substantial part of created PEO coating [37]. Subsequently, the decrease was significantly inhibited to near saturation trend, which was caused by action of the corrosion inhibitors retarding the corrosion processes at the base material / electrolyte interface and also by sealing the critical areas by corrosion products forming a certain barrier to the corrosion processes (an effect similar to that observed on unprotected material during long-term exposure [23].) This theory is supported by values and trends of individual partial electrochemical corrosion characteristics.

The R_{po} provided the largest portion in the total

Table 3 Electrochemical corrosion characteristics obtained from the Nyquist diagrams of the PEO coating sealed by oil based preservation layer containing corrosion inhibitors on AZ31 in 0.1M NaCl solution after various exposure times

Time	R_s ($\Omega \cdot \text{cm}^2$)	R_{po} ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	R_p ($\Omega \cdot \text{cm}^2$)	CPE_c ($\text{F} \cdot \text{sn}^{-1} \cdot 10^{-6}$)	CPE_{dl} ($\text{F} \cdot \text{sn}^{-1} \cdot 10^{-6}$)	n_1	n_2
1h	120	814065		814065	1.7		0.8	
2h	125	151776		151776	2.5		0.7	
4h	134	23125	25562	48687	2.7	12.8	0.8	0.8
8h	137	23962	10702	34664	3.2	74.2	0.9	0.8
12h	138	20162	9384	29546	3.7	124.8	0.9	0.8
24h	138	19777	9652	29429	4.2	137.1	0.9	0.7
48h	138	18096	9699	27795	4.5	151.2	0.9	0.7
96h	136	17877	9683	27560	4.9	175.6	0.9	0.7
168h	138	13145	6933	20078	5.6	247.4	0.9	0.7

**Figure 5** Evolution of the R_p on AZ31 magnesium alloy coated by the PEO and sealed by oil based preservation layer containing corrosion inhibitors in 0.1M NaCl solution after various exposure times

polarization resistance of the system AZ31+PEO+sealing in all the stages of exposure. Due to the sealing of the pores and the barrier effect of the preservative, a high level of corrosion protection was achieved at the beginning of the exposure comparable to the passive layer on titanium [38]. This type of resistance depends on several factors playing a key role in terms of a longer exposure in electrolytes. It can be determined according to Equation [28]:

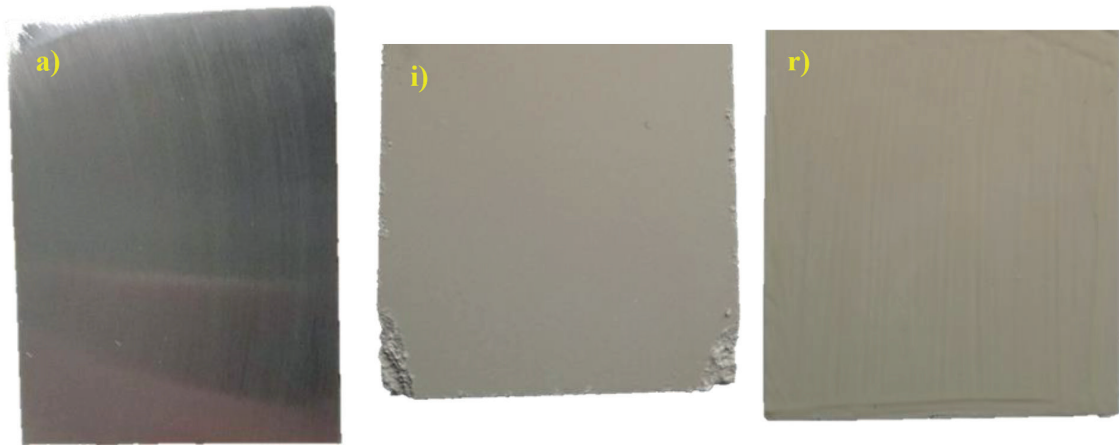
$$R_{po} = \frac{\rho \cdot d}{A_p}, \quad (3)$$

where ρ is the electrolyte resistivity in the pores, d the pore length (~coating thickness) and A_p the total pore surface area.

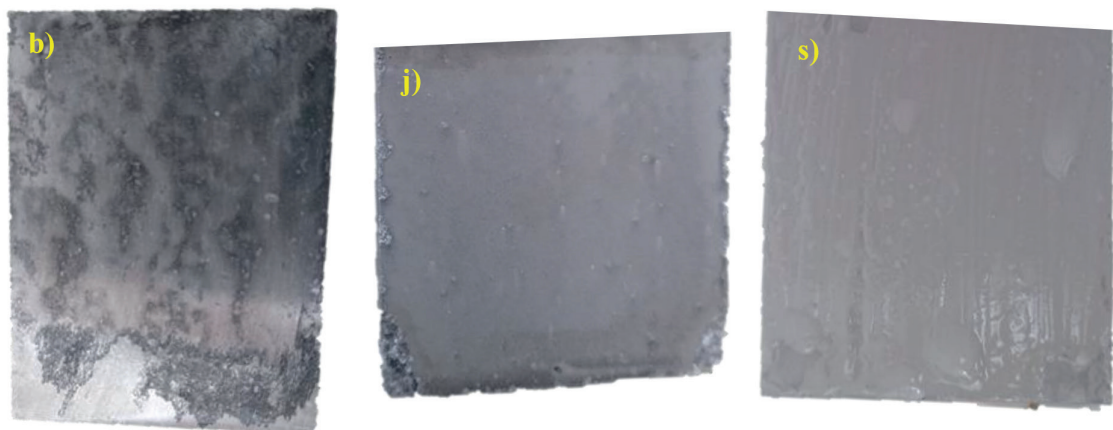
Generally R_{po} decreases as the electrolyte penetrates the coating and fills the pores [28]. In this case, the highly conductive electrolyte containing chloride ions entered the surface pores where diffused through the sealing system and further penetrated through the PEO coating while filling the empty pores and lowering intensively the overall

resistivity. This was one of the main reasons for the massive R_{po} decrease in the first hours of immersion. The decrease of R_{po} with time was also related to increase of A_p , which could be explained by an increase of number of the filled pores or an increase of their area if delamination occurs [28]. When the process of electrolyte penetration through the coating system was finished, the rapid decline in the R_{po} values was significantly decelerated, with the gradual dissolution of the PEO coating and its associated reduction (reduction of parameter d) becoming the main factor responsible for the further R_{po} decrease. However, the dissolution rate of the PEO coating was considerably inhibited by the oil-based preservative, which has a non-polar character and thus did not directly interact with the polar 0.1M NaCl aqueous solution. This deceleration was also supported by the above-mentioned formation of the corrosion products at the base material / PEO coating interface, which filled the formed and emerging pores from the inside.

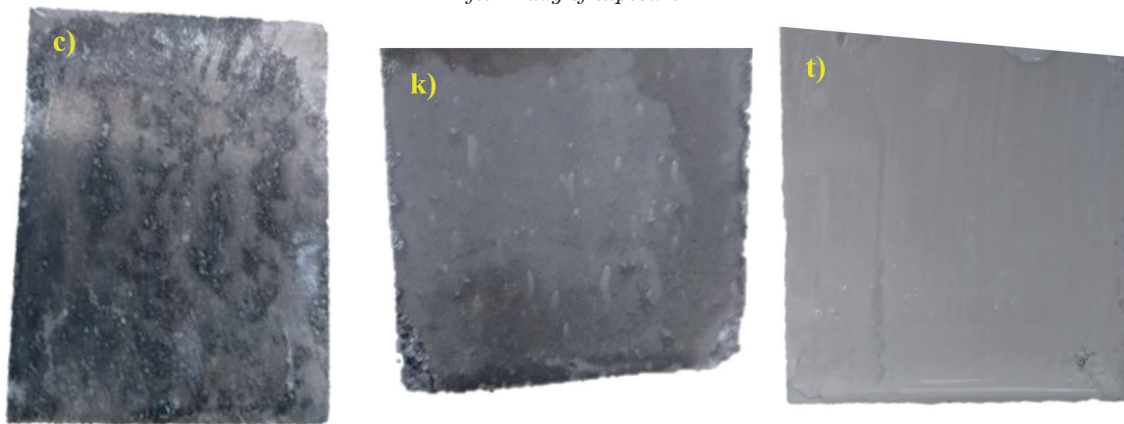
The R_{ct} is the resistance to charges transfer, determining the corrosion rate of reaction and is a measure of electric



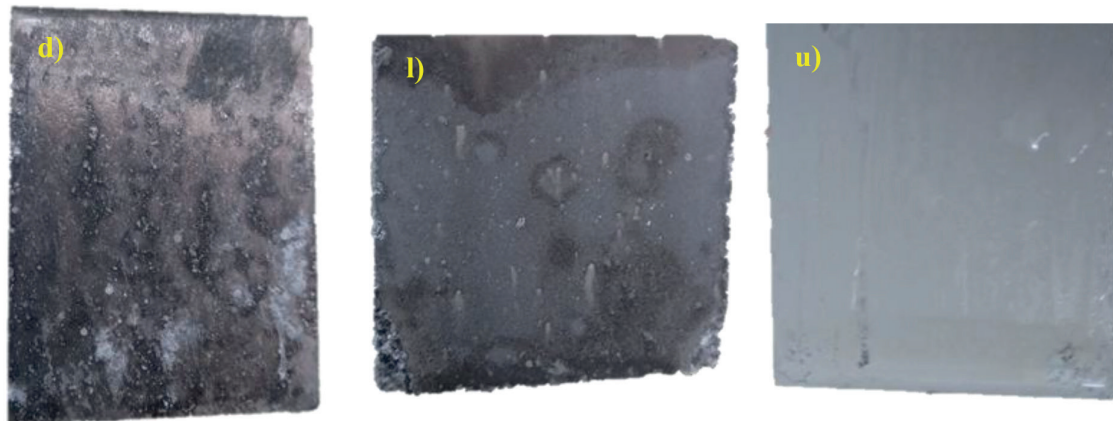
Prior to exposure



After 1 day of exposure



After 2 days of exposure



After 3 days of exposure

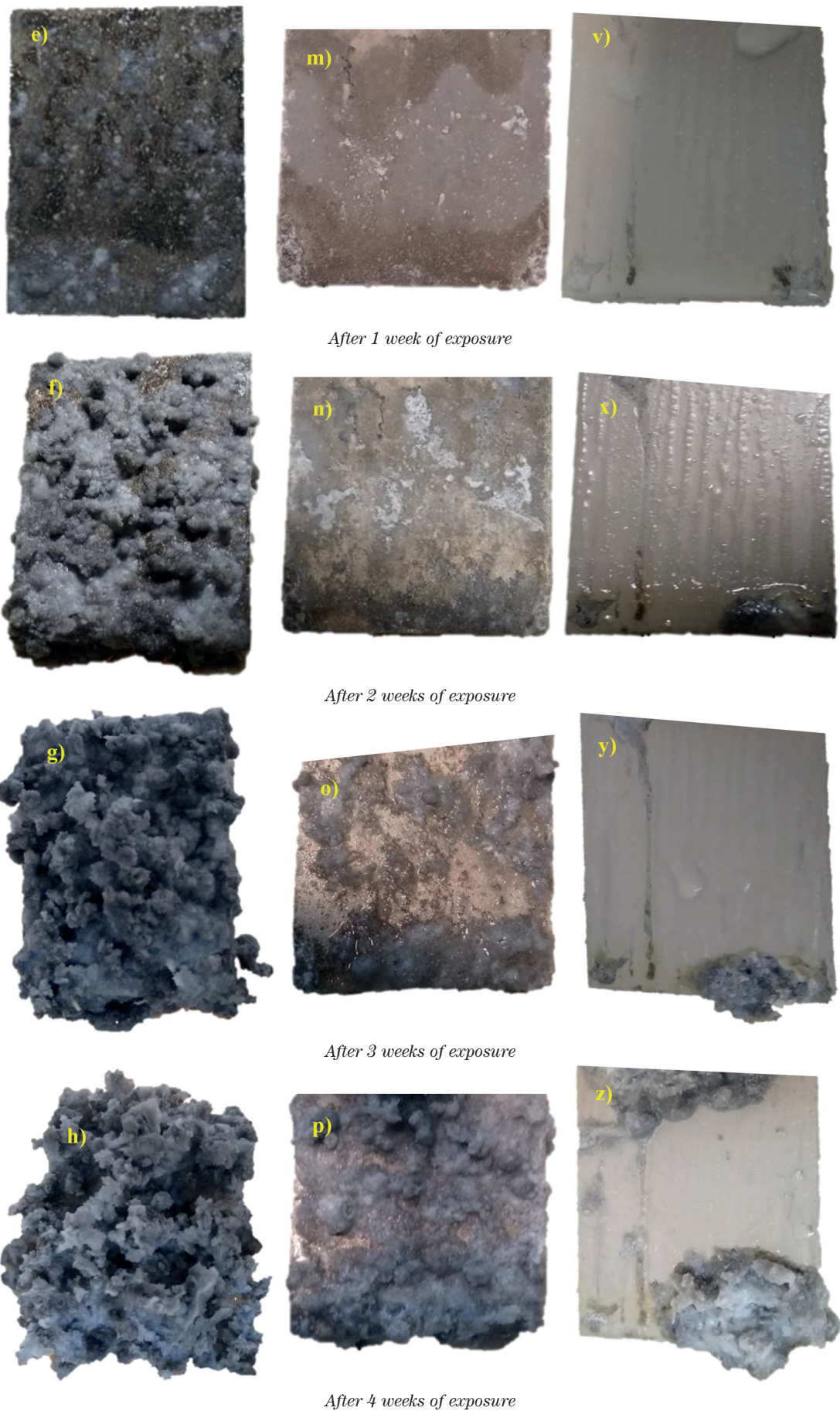


Figure 6 AZ31 samples after various surface treatment and exposure to the salt spray test according to STN EN ISO 9227: a)-h) ground surface (P1000); i)-p) PEO treatment; r)-z) PEO + sealing

charges transfer through the electrode surface (or metal / electrolyte interface in our case) [26]. It is an appropriate parameter to evaluate the corrosion in the beneath coating and separation of coating from the metal substrate [30]. Generally, high values of the charge transfer resistance and low values of double layer capacitance signify a coating of better performance [39]. In the considered case, the R_{ct} appeared after 4 hours of exposure and decreased for more than one-half in next 4 hours. Subsequently, the decrease significantly decelerated. However, it is unlikely that the process of delamination caused by the gradual penetration of the electrolyte through the PEO and its degradation was finished at that moment. The explanation is indicated by evolution of the CPE_{dl} values. Since the value of the parameter n_2 is almost constant and approaching the value 1 during the whole exposure, one can describe development of the CPE_{dl} by parameters influencing the C_{dl} . The C_{dl} is the double electric layer capacitance resulting from ions and water molecules adsorbed, due to the potential difference between the electrode suffering corrosion and the electrolyte [26]. Hence, the double-layer capacitance is proportional to the active metallic area (area in contact with the electrolyte) [28]. Since the CPE_{dl} values continually increased even after 4 hours of exposure in this case, the process of delamination and enlargement of the active area was still not finished. An explanation of the non-corresponding trend of the R_{ct} development lies in the effect of added corrosion inhibitors, which did not prevent the increase of the active area of the base material and delamination of the PEO layer, but slowed down the electrode processes, namely charge transfer through the interfacial interface leading to moderate decrease of the R_{ct} values.

The synergistic effect of an oil-based preservative and corrosion inhibitors resulted in significantly better corrosion protection of AZ31 alloy coated by the PEO in aqueous media containing aggressive chlorides, when even after 168 hours of exposure the total polarization resistance of the surface system was almost 2-times higher than R_p of the simple unsealed PEO surface after the same exposure time (based on results from [23]).

In addition to electrochemical tests in an aqueous medium containing chlorides, the salt spray tests were performed on the tested samples according to STN EN ISO 9227, as well. Magnesium and its alloys are generally well corrosion resistant to atmospheric conditions as long as relatively low humidity and low content of impurities and contaminants are maintained. However, the salt spray test according to STN EN ISO 9227 represents a very aggressive environment for magnesium alloys combining the high air humidity, increased temperature and increased oxygen content compared to exposure tests in aqueous solution and especially high content of aggressive chloride ions. Moreover, the aggressive atmosphere is continually changed to fresh (opened circuit), thus preventing the depletion of aggressive components or local increase in pH, which could change the nature of corrosion products and thus affect the corrosion protection of the surface treatment system. The corrosion attack on individual test

samples with various level of surface treatment during the exposure in the salt spray is shown in Figure 6. During the PEO process performed for longer times (in order to form a thicker oxide layer), sharp edges on the samples/products can be dissolved. However, even these damaged edges are well covered with a protective layer. This rare phenomenon was also chosen for evaluation in the salt spray test (Figure 6i), in order to see its effect on the corrosion attack of the whole sample. The PEO-coated sample, sealed with the tested preservative, was visually flawless prior to exposure.

The course of the corrosion attack on the ground unprotected AZ31 sample, which served as a reference, was very intense (Figure 6a-h). The local form of the corrosion attack in the first days of exposure can be attributed to the typical microstructure of AZ31 alloy, which contains the intermetallic β -phase $Mg_{17}Al_{12}$ acting as a microcathode, which causes microgalvanic corrosion of the matrix in its vicinity [40]. Generally, the film formed on an Mg surface, after exposure to humid air at higher relative humidity and temperature, is formed by a bilayer structure with an apparently dense outer layer (mainly $Mg(OH)_2$) and a cellular inner layer (mainly MgO). However, the structure and formation mechanism of this surface film are affected by the chemical composition of the Mg alloy, the constituents of the atmosphere, the temperature and humidity [40]. This mechanism was observed on the unprotected sample of AZ31 in the considered case too, where it was possible to observe formation of the black MgO in the initial stages and the growth of the coarse white $Mg(OH)_2$ corrosion products in the later stages. However, the presence of chlorides in the atmosphere significantly increased their solubility and reduced their protective barrier effect. Chlorides also caused the formation of their own reaction products with the magnesium base material in a form of unstable $MgCl_2$, thus further disrupting the integrity of the oxide layers. As a result, the tested sample of unprotected magnesium alloy was almost completely corroded after 4 weeks of exposure (Figure 6h), which completely eliminates its unprotected use in industrial applications in aggressive environments containing chloride ions.

Local corrosion initiation centres can be observed after only 1 day of exposure on a sample with an unsealed PEO layer (Figure 6j). The presence of pores significantly accelerated the progress of chlorides and moisture to the base material and also the intensity of dissolution of the PEO layer, which was visually observed after only 2 days of exposure (formation of areas with different colour shades on the surface). However, the resulting corrosion centres were relatively stabilized up to 1 week of exposure and the sample did not significantly change its volume, so the main degradation mechanism was the dissolution of the PEO layer. However, intense corrosion of the base material through the already weak layer of the PEO was observed after 2 weeks of exposure, which also led to development of the corrosion products of a large volume. This caused a significant change in geometry of the original sample. After 4 weeks of exposure, more than 90 % of the sample was already covered with corrosion products, which means that

the PEO layer has already lost its protective function and the sample would behave as unprotected with continued exposure. An interesting trend of the corrosion attack was observed on the mentioned corroded corners of the sample, which did not represent a significant initiation centre of the corrosion attack during the exposure, as the rate of corrosion attack at these places was almost similar to the rest of the sample. This was an important fact from a practical point of view.

The best results were obtained on AZ31 sample with the sealed PEO coating (Figure 6r-z). Although the first local corrosion initiation centres were observed after only two days of exposure in the salt spray, the overall geometry of the sample remained almost unchanged until 2 weeks of exposure. The barrier effect of the preservative and its non-polar character, significantly inhibiting corrosion processes on the sample, were well manifested in this type of corrosion test. However, the course of the corrosion attack was not widespread as in previous cases, but was very localized. Even after 4 weeks of exposure, a large part of the surface was almost unchanged from a visual point of view. The corrosion attack of the base material spread from the local initiation corrosion centres on the sealed PEO surface by the delamination mechanism, by which the active components of the environment overcame the protective surface barrier even in places with almost perfect coverage. The fact that the whole process of the corrosion attack focused only on the local areas becoming local anodes, caused the corrosion attack at this areas to reach larger dimensions than on a simple unprotected sample with the PEO coating. However, the cause of such a weak critical point could have a different possible origins out of standard considered presence of pores and microcracks in the PEO layer. These problems could appear also due to the base material including presence of impurities, cracks, or other phases protruding to the surface where the PEO layer did not form properly. Another danger was represented by the surface areas with the most intense adsorption of the condensate (bottom of the sample where droplets form from the flowing condensate). In order to achieve the maximum corrosion protection of the AZ31 alloy surface, it is therefore necessary to ensure the cleanest possible microstructure without defects, creation of very homogeneous PEO coating, very precise application of preservative and elimination of increased environmental humidity, which could lead to subsequent crevice or local microgalvanic corrosion.

4 Conclusions

Based on the measured data and analyses we concluded:

1. Application of an oil-based preservative containing

corrosion inhibitors to the PEO coating caused a negligible deterioration of the nobility of the surface system in a 0.1M NaCl solution from a thermodynamic point of view. However, an almost 4-fold reduction in the instantaneous corrosion rate in a given environment was caused by this sealing of PEO coating compared to the unsealed PEO coating.

2. Sealing the PEO coating with a preservative caused a significant increase in the overall polarization resistance of the surface system. Moreover, this beneficial effect was maintained even after 168 hours of exposure in 0.1M NaCl solution.
3. Decrease in the R_p values during the exposure in 0.1M NaCl could be divided into two stages: 1. intense decrease caused by electrolyte penetration through the surface system during the first 12 hours of exposure; 2. a very slight stabilized decrease caused by an action of the corrosion inhibitors at the base material / electrolyte interface in combination with the additive barrier effect of the non-polar preservative.
4. Sealing of the PEO layer using a preservation system ensured a significant extension of the protection period of the AZ31 alloy sample even in an aggressive simulated atmosphere containing chlorides. However, any corrosive attack on a given surface system had a significant local character causing intensive delamination of the surface protective layer.
5. Temporary additional surface treatment of the PEO coated magnesium alloy with an oil-based preservative containing corrosion inhibitors, which can be safely and ecologically removed with a degreaser, represents a simple and ecological solution to increase corrosion protection of AZ31 magnesium alloy for overseas transport or applications, where it may come into contact with aggressive environments containing chloride ions both in aqueous or atmospheric environments.

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