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Daniel Kajanek - Branislav Hadzima - Matej Brezina - Martina Jackova*

EFFECT OF APPLIED CURRENT DENSITY OF PLASMA ELECTROLYTIC OXIDATION PROCESS ON CORROSION RESISTANCE OF AZ31 MAGNESIUM ALLOY

Impact of applied current density during the plasma electrolytic oxidation (PEO) process on corrosion resistance of AZ31 magnesium alloy was studied. The PEO coatings were prepared using four different current densities with values of 0.025 A/cm², 0.05 A/cm2, 0.1 A/cm² and 0.15 A/cm² in electrolyte consisting of 10 g/l Na_3PO_4.12H2O and 1 g/l KOH. Morphology and chemical composition of the coatings was examined using the scanning electron microscopy and EDS analysis respectively. Electrochemical characteristics of ground and coated samples were measured by means of electrochemical impedance spectroscopy (EIS) in 0.1 M NaCl solution. Obtained data in form of Nyquist diagrams were analysed by equivalent circuit method. Results of experiments showed that value of applied current density had significant effect on protective performance of the PEO coatings prepared on AZ31 magnesium alloy surface.

Keywords: *magnesium alloy, plasma electrolytic oxidation, corrosion resistance*

1. Introduction

The main reason, which impedes the wider usage of magnesium alloys in technical applications is their high reactivity and the resulting low corrosion resistance in most of the practical environments. The high rate of corrosion degradation is attributed to presence of inclusions in the structure of the Mg alloys which form microgalvanic cells and thus promote corrosion of the Mg matrix or grain boundaries. Particularly harmful elements are nickel, cobalt and iron. Another cause of insufficient corrosion resistance is the presence of a naturally created surface film based on $MgO/Mg(OH)_2$. The chemical composition of this film depends on the environment to which the alloy is exposed. According to the E-pH diagram, this film is stable only in strongly alkaline environments. In acidic and neutral conditions it does not provide adequate protection [1-3]. Nowadays, there are several well-known methods of protecting Mg alloys such as cathodic protection, platting and preparation of various coatings. The last category is one of the most evolving methods. The surface of the magnesium alloys can be modified in various ways depending on the desired final properties, with surface pre-treatment being very important as well. Frequently used surface treatment methods are cathodic electrodeposition techniques or anodic oxidation. A perspective technique called plasma electrolytic oxidation is getting a lot of scientific attention as it is a method for preparation of protective coatings on Mg alloy in a non-expensive way. In this process, unlike conventional anodic oxidation, much higher voltages are reached/applied and the obtained coatings have a ceramic-like character. The disadvantage is the porosity of these layers resulting from nature of the PEO process. The advantage of the PEO is that there is a variety of environmentally acceptable electrolytes and secondly it is also possible to use both DC and AC power sources. The preparation of such layers is relatively complicated in terms of the obtained coating properties as there is a number of variables in the PEO process such as the value of applied current/voltage, time of preparation, optimal composition of the electrolyte and the applied frequency in the case of alternating power sources. Those parameters have significant impact on the overall properties of the PEO layers [4-6]. This paper is focused on the effect of applied current density on the morphology and chemical composition of prepared layers and on corrosion protective function in an aggressive chloride containing environment.

2. Experimental material and methods

The experimental material AZ31 magnesium alloy produced by continuous casting has been homogenizing at 420 ° C for 16 hours. Its chemical composition, detected by the EDXRF analysis on the ARL QUANT'X EDXRF Spectrometer is shown in Table 1.

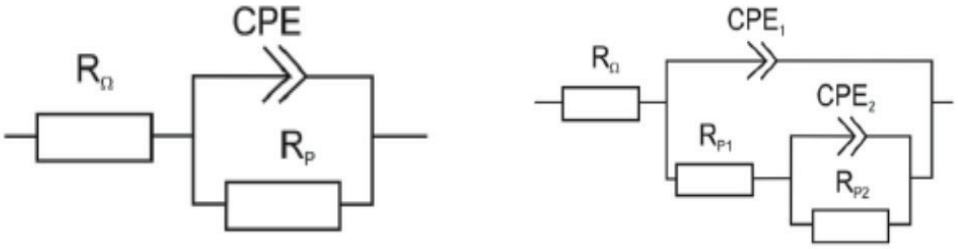
Metallographic samples have been prepared according to the standard metallographic procedures recommended for magnesium alloys. The AZ31 Mg alloy microstructure has been observed by optical microscope ZEISS Axio Observer Z1.m. The images have been created using AxioVision Rel 4.5 software. An etchant consisting of 2.5 ml of acetic acid, 2.1 g of picric acid, 5 ml of demineralized water and 35 ml of ethanol has been used to visualize the microstructure. The etching time has been set to 10 seconds. In the end samples have been rinsed by demineralized water, ethanol and dried by stream of air.

Prior to the PEO coating process, each sample has been ground by an emery paper p1000 to provide the same roughness across the treated surface. Subsequently, samples have been rinsed by demineralized water, ethanol and air-dried. The plasma

* [1,2]Daniel Kajanek, [2]Branislav Hadzima, [3]Matej Brezina, [2]Martina Jackova
[1]Department of Materials Engineering, Faculty of Mechanical Engineering, University of Zilina, Slovakia
[2]Research Centre, University of Zilina, Slovakia
[3]Faculty of Chemistry, Brno University of Technology, Czech Republic
E-mail: daniel.kajanek@fstroj.uniza.sk

Table 1 *Chemical composition of AZ31 magnesium alloy*

Component	Al	Zn	Mn	Si	Cu	Fe	Mg
wt. %	3.31	0.65	0.23	0.114	0.004	0.001	balance



a) *b)*

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

electrolytic oxidation has been carried out using a laboratory DC power source Keysight N8762A with parameters 600 V/ 8.5 A and output of 5100 W. The two-electrode system has been used with the sample AZ31 involved as an anode. The cathode has been provided by stainless steel plate. The PEO has been carried out in an electrolyte composed of 10 g/l $Na_3PO_4.12H_2O$ and 1 g/l KOH and its pH has been stabilized at 12.3. During the PEO procedure, the electrolyte has been cooled with water and constantly stirred with a laboratory stirrer for better distribution of species. The electrolyte temperature was kept below 50° C. Four current densities with values of 0.025 A/cm^2, 0.05 A/cm^2, 0.1 A/cm^2 and 0.15 A/cm^2 have been applied on the surface with the preparation time of 10 minutes. Applied current has been maintained at a constant value. The morphology of the prepared PEO coatings has been observed using the Carl Zeiss Merlin scanning electron microscope and chemical composition has been examined by EDS analysis.

Electrochemical impedance spectroscopy has been used as a tool for evaluation of the corrosion resistance of the ground and PEO coated samples. Measurements have been performed in 0.1 M NaCl at the temperature of 22 ± 1° C on a laboratory potentiostat VSP Biologic. The measured frequencies have been ranged from 100 kHz to 10 mHz. The amplitude of the applied voltage has been set to 15 mV. The mean value of the sine voltage has been equal to the open circuit potential reached after 24 hours of exposure. The outputs of these measurements are the Nyquist diagrams, which can be quantitatively described using the equivalent circuit method (Figure 1). Simple Randels circuit (Figure 1a) has been used for analysis of diagrams with one capacitance loop. Diagrams with two capacitance loops has been analysed by circuit shown in Figure 1b. The most important circuit element for evaluation of corrosion resistance is R_p called the polarization resistance. The higher the R_p value is obtained the higher corrosion resistance is provided. If the Nyquist diagram is formed by the two capacitance loops, the resulting resistance of the surface is given by the sum of the partial resistors R_{p1} and R_{p2}. The element R_Ω expresses the resistance of the electrolyte and the element CPE (constant phase element), which replaces the capacitance C in the circuit, simulates the inhomogeneity of the measured surface [7].

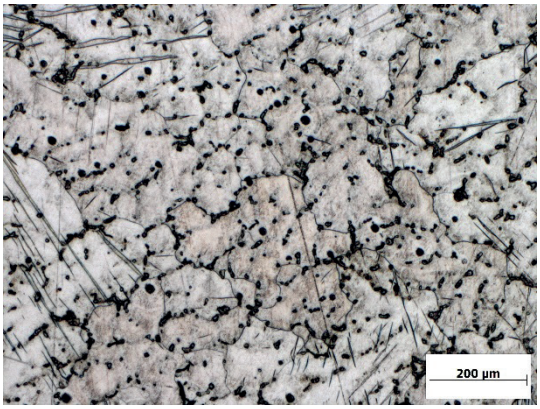


Figure 2 *Microstructure of AZ31 Mg alloy*

3. Results and discussion

The AZ31 magnesium alloy microstructure (Figure 2) is formed by polyhedral grains of solid solution of aluminum, zinc and other alloying elements in magnesium. The intermetallic phase of $Mg_{17}Al_{12}$ is also present in the microstructure. The average grain size is 220 µm. It is also possible to observe twins that were probably formed by deformation during the cutting and samples preparation [8].

The SEM images in Figure 3 show the PEO coatings prepared at a current density of 0.025 A/cm^2 (a) 0.05 A/cm^2 (b), 0.1 A/cm^2 (c) and 0.015 A/cm^2 (d). From the photo documentation, it can be seen that all the layers exhibit a porous structure typical for the PEO process. The formation of micropores is associated with the presence of molten oxides and gas bubbles produced during the discharges occurred on the surface of samples [6]. It is also possible to observe several microcracks resulting from stresses in the PEO layer during rapid solidification of molten substances in a contact with cold electrolyte [9, 10]. Chemical composition of the coatings obtained by EDS analysis is shown in Table 2. It can be seen that from this point of view there is not a significant difference within individual coatings. Therefore it can be assumed that applied current density does not have marginal impact on the chemical composition of PEO coatings. Moreover, it is clear that PEO coatings are consisting of elements present in the electrolyte (P, Na, O) and elements, which came from Mg substrate (Mg, Al). This claim is in good agreement with work [11].

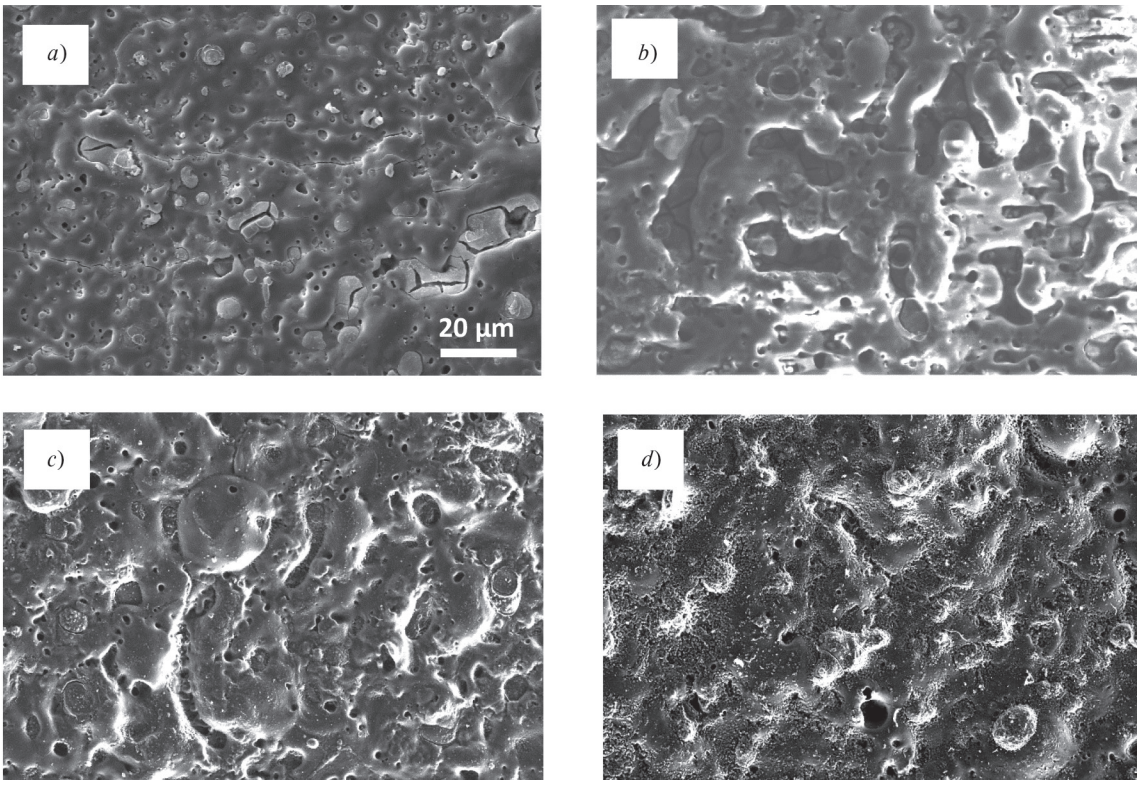


Figure 3 *Morphologies of PEO coatings prepared at 0.025 A/cm² (a), 0.05 A/cm² (b), 0.1 A/cm² (c) and 0.15 A/cm² (d), mag. 2000x*

Table 2 *Chemical composition of AZ31 magnesium alloy*

at. %	0.025 A/cm²	0.05 A/cm²	0.1 A/cm²	0.15 A/cm²
Mg	14.7	12.2	11.5	10.8
O	28.3	26.1	24.5	29.2
P	13.3	14.6	12.4	14.2
Al	0.34	0.14	0.15	0.16
Si	-	0.04	0.04	0.03
Na	1.16	1.74	1.89	2.68

Table 3 *Roughness parameters of the PEO coating prepared with different applied current density*

	0.025 A/cm²	0.05 A/cm²	0.1 A/cm²	0.15 A/cm²
Ra [µm]	0.884	1.016	1.698	2.041
Rz [µm]	8.412	8.763	14.300	17.317

It can be seen that with the increasing current density the layers are more rugged. This is also confirmed by roughness measurements (Table 3) which show increasing trend of Ra and Rz parameters with increasing energy input. Prepared coatings are formed on the surface of the magnesium alloy by intensive discharges which are responsible for formation of the layers. The higher the applied current density the more intensive/larger the discharges are occurring on the surface. However, they are less in numbers [9]. More intensive discharges consequently melt a greater amount of material and form a more rugged layer. Layers prepared at 0.1 A/cm² and 0.15 A/cm² exhibit imperfections in the form of small particles located around the pores and their occurrence is more extensive at the highest applied current density. For a more detailed description of their effect on the quality of the layer, its chemical composition will be performed and deeply studied in the future experiments.

The Nyquist diagrams for different PEO layers and ground samples measured in 0.1 M NaCl after 24 h of exposure are shown in Figure 4. In all the cases, except for 0.1 A/cm², the diagrams are created by two capacitive loops. Occurrence of one capacitance loop in diagram assumes homogeneous conditions on the measured surface during dissolution and two capacitance loops point to the presence of areas with different electrochemical behaviour [7]. Corresponding electrochemical characteristics are shown in Table 4. When comparing polarization resistances, it can be seen that all of the PEO layers exhibit a significantly higher R_p compared to the ground sample with the value of 6765 Ω.cm² and thus have a positive influence on the corrosion resistance. It is resulting from the formation of an effective barrier, which slows down penetration of solution and thus provides sufficient protection for the Mg substrate against harmful activity of the chloride ions present in testing environment. When comparing

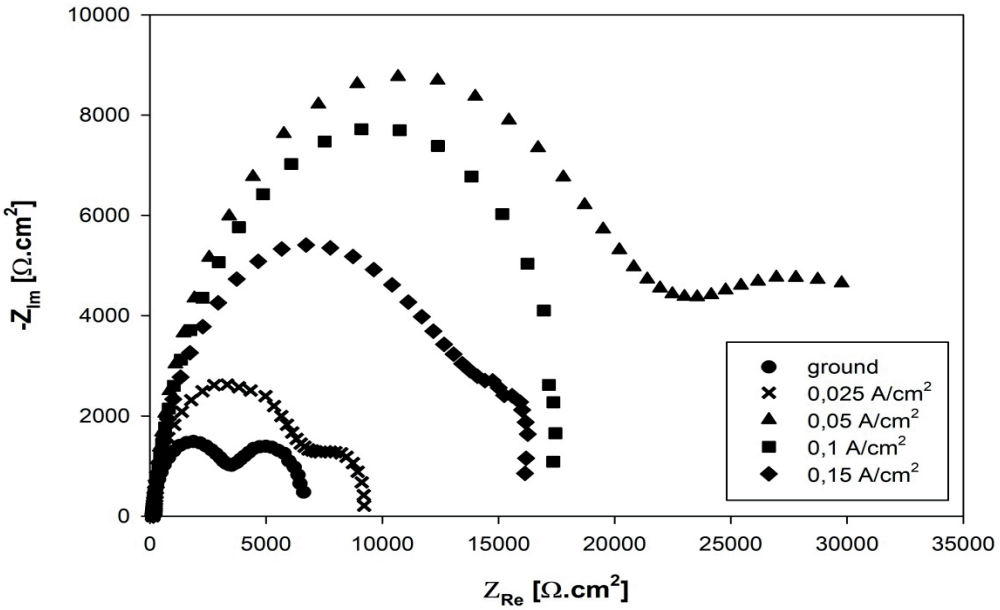


Figure 4 *Nyquist plots of ground PEO treated samples of AZ31 Mg alloy measured in 0.1M NaCl*

Table 4 *Electrochemical characteristics of ground and PEO coated samples of AZ31 Mg alloy in 0.1 M NaCl*

	R_Ω ($\Omega.cm^2$)	R_{p1} ($\Omega.cm^2$)	R_{p2} ($\Omega.cm^2$)	R_p ($\Omega.cm^2$)	CPE_1 [$F.s^{n-1}$]	CPE_1 [$F.s^{n-1}$]	n_1	n_2
ground	115	3699	3066	6765	1.10^{-5}	2.10^{-3}	0.9	0.9
0.025 A/cm²	120	5875	3340	9215	7.10^{-6}	4.10^{-4}	0.9	0.9
0.05 A/cm²	119	18 909	15 592	34 501	6.10^{-6}	2.10^{-4}	0.9	0.7
0.1 A/cm²	128	18 399	-	18 399	6.10^{-6}		0.9	
0.15 A/cm²	133	11 313	5874	17 187	7.10^{-6}	2.10^{-4}	0.9	0.8

the individual layers, differences in the polarization resistance values have been observed. It is obvious that polarization resistance has increased with the increasing applied current density from the 9215 $\Omega.cm^2$ reached by 0.025 A/cm up to the applied current density of 0.05 A/cm², where the maximum of R_p with the value of 34 501 $\Omega.cm^2$ has been reached. With a layer prepared at 0.1 A/cm² decrease of the resistance has been observed from 18 399 $\Omega.cm^2$ to the 17 187 $\Omega.cm^2$ reached by the 0.15 A/cm². This trend can be explained by the synergic effects of several factors. As it was mentioned before, the roughness of the layers has increased with increasing applied current density and the occurrence of heterogeneities and larger pores associated with intensive discharges has been observed. Heterogenities and porosity has increased surface roughness and therefore larger electrochemically active area has been in contact with electrolyte [3, 4, 12]. That is why the PEO layers formed at higher current densities (0.1 A/cm² and 0.15 A/cm²) have been attacked more intensively by aggressive chloride ions compared to a more uniform layer obtained at a current density of 0.05 A/cm². In the case of the layer prepared at 0.025 A/cm² its thickness and compactness are probably not high enough due to the insufficient energy input which has resulted in less intensive sparking effect and thus less promoted formation of the coating. Therefore, the lowest polarization resistance across the prepared layers has been reached. These observations are in good agreement with the results presented in works of [11, 13].

4. Conclusions

According to the performed experiments and analysis several conclusions can be stated:

- Prepared PEO coatings revealed porous structure typical for plasma electrolytic oxidation process.
- Roughness of the PEO coatings increased with the increasing applied current density. In the cases of 0.1 A/cm² and 0.15 A/cm² heterogeneities were observed.
- All of the created PEO layers reached higher values of the polarization resistance compared to the ground samples in 0.1 M NaCl and thus positively influenced the corrosion resistance of AZ31 Mg alloy.
- The highest corrosion resistance was provided by the PEO coating created with current density of 0.05 A/cm², which reached more than 5-times higher polarisation resistance value of 34 501 $\Omega.cm^2$ compared to the ground samples, which reached R_p value of 9215 $\Omega.cm^2$.

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