Effect of KOH Content in the Electrolyte on Corrosion Properties of PEO-Coated EV31 Magnesium Alloy

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Abstract. This study analyzed the influence of electrolyte composition on the corrosion resistance of plasma electrolytic oxidation (PEO) coatings on EV31 magnesium alloy. An electrolyte solution was prepared by mixing 12 g/l Na_3PO_4 and various levels of KOH (1, 2, and 4 g/l). The PEO coating was produced with a direct current (DC) regime of 0.05 mA.cm^{-2} current density and a maximum voltage of 630 V. Electrochemical impedance spectroscopy was performed to assess the corrosion resistance after one hour exposure in 0.1 M NaCl. The results indicated that KOH content has a substantial effect on the morphology and corrosion resistance of the PEO coating and align with previous similar studies. The lowest porosity and highest polarization resistance were observed in the PEO coating prepared with 2 g/l of KOH in the electrolyte, resulting in the best corrosion resistance among the evaluated samples. The presence of only one capacitive loop in the Nyquist diagram and low polarization resistance R_p values of the samples with 4 g/l of KOH in the electrolyte indicated insufficient compactness due to high porosity of the coating.

Introduction

Magnesium and its alloys have gained increasing attention in recent years as lightweight materials with excellent mechanical properties and high strength-to-weight ratios. This has led to a growing interest in their use for a wide range of applications, including aerospace, biomedical, and automotive industries [1, 2]. Despite their attractive properties, the widespread use of magnesium alloys is hindered by their high reactivity and low corrosion resistance, particularly in harsh environments. The low corrosion resistance of magnesium alloys can result in a reduction in the lifetime and performance of magnesium-based components, making it a major concern for their practical applications [3, 4].

To overcome this challenge, surface modification techniques have been developed to improve the corrosion resistance of magnesium alloys. One of the most promising techniques is plasma electrolytic oxidation (PEO), which has gained significant attention due to its environmentally friendly nature and ability to form dense, corrosion-resistant coatings on magnesium alloys. The PEO process involves the formation of a protective oxide layer on the surface of the magnesium alloy through the application of a high voltage electric field in an electrolyte solution. The resulting oxide layer provides excellent protection against corrosion and has been shown to be effective in improving the corrosion resistance of magnesium alloys [5-9].

The PEO process is a complex one, and a wide range of factors can influence the properties of the resulting oxide layer. These factors include the composition of the electrolyte solution, the applied voltage, the duration of the treatment, and the type of magnesium alloy being treated. Understanding the relationships between these factors and the properties of the oxide layer is

crucial for the optimization of the PEO process and the development of high-quality coatings for practical applications [10, 11].

One of the major advantages of the PEO process is its environmentally friendly nature. Unlike traditional surface modification techniques, such as thermal spray, the PEO process does not generate harmful pollutants or require the use of hazardous materials. This makes it an attractive option for industries that are focused on reducing their environmental impact, and it also has the potential to reduce the cost and complexity of the surface modification process [12-14].

Another advantage of the PEO process is its ability to form dense, corrosion-resistant coatings with excellent mechanical properties. The high-quality oxide layer formed by the PEO process provides excellent protection against corrosion and has been shown to significantly improve the overall performance of magnesium alloys in harsh environments. Additionally, the PEO process can be used to create coatings with unique surface textures, such as micro- and nano-structures, which can further improve the corrosion resistance of magnesium alloys [15, 16].

Despite its advantages, the PEO process still faces a number of challenges that need to be addressed in future research and development. For example, the resulting oxide layer can be porous and prone to cracking, which can limit its effectiveness as a corrosion barrier. Additionally, the optimization of the PEO process is an ongoing area of research, as it is important to ensure that the desired properties of the oxide layer are achieved while minimizing the formation of unwanted features, such as porosity and cracks [17].

Therefore, further research and optimization of the PEO process is needed to address the challenges associated with the formation of porous and cracked oxide layers and to develop high-quality coatings for practical applications.

Experimental Methods

Experiments were conducted on samples made from the extruded EV31 alloy. The samples were prepared for PEO treatment through grinding with emery paper p1200. The solution used for the PEO coating was made up of 12g/l of $Na_3PO_4.12H_2O$ and different amounts of KOH (1, 2, and 4 g/l) dissolved in deionized water. The experiments utilized a two-electrode circuit with the EV31 alloy sample as the anode and a stainless-steel plate as the cathode. The electrolyte was kept agitated using a laboratory stirrer operating at 500 rpm to ensure a consistent supply of reactants. The 1.5 L container with the electrolyte was immersed in a 15 L container with a cooling medium to regulate the temperature of the PEO electrolyte, which was maintained at below 50 °C during the entire coating preparation process. The PEO coating preparation utilized DC mode with a constant current density of 50 mA.cm^{-2}.
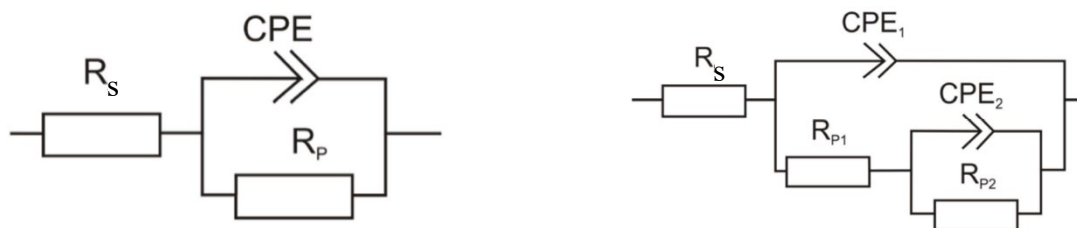

Fig.1. The equivalent circuits used for analyzing Nyquist diagrams a) circuit with a single capacitive loop and b) circuit with two capacitive loops.

The electrochemical impedance spectroscopy (EIS) method was used to examine the corrosion properties of PEO coated samples in a corrosive environment after 1 hour of exposure. The EIS measurements were conducted in a frequency range between 100 kHz and 10 mHz, with the frequency changing every decade. The amplitude of the alternating current voltage signal applied was set at 15 mV and the mean value of the voltage component was the same as the open potential.

The results were presented as Nyquist diagrams and analyzed using equivalent circuit method with the EC Lab 10.42 software from Biologic SAS. The equivalent circuits used in the analysis are shown in Fig. 1, with a simple Randles circuit used to describe Nyquist diagrams with one capacitive loop and more complex circuits used to describe diagrams with two capacitive loops. These circuits suggest the presence of different electrochemical behaviors in the regions, which may indicate the presence of a surface layer, a layer of corrosion products, and a subsurface or double layer on the surface. The R_s element in the circuits represents the electrolyte resistance, while the CPE element, which replaces a capacitor, represents the inhomogeneity of the electrode surface. The polarization resistance (R_p) is the most crucial element in determining corrosion resistance, as it directly relates to the corrosion resistance of the measured surface. When two capacitive loops are present, the total polarization resistance is calculated by adding the R_{p1} and R_{p2} partial resistances.

Results and Discussion

The surface micrographs of PEO coated samples with prepared different KOH content in electrolyte are shown in Fig. 2. When comparing the micrographs of individual coatings, common characteristics such as porosity and the presence of microcracks across the layers can be observed. These phenomena are typical for this type of coatings and arise from the very nature of the PEO process [18]. Fig. 2a presents a coating prepared with 1 g/l of KOH, which is commonly [19] used KOH content for PEO coating preparation. When comparing the images of individual coatings, differences between the coatings become apparent. With the increase of KOH content from 1 g/l to 2 g/l, there was a noticeable reduction in both pore size and count. However, further increasing the concentration to 4 g/l did not produce the same result, as the coating with 4 g/l of KOH (Fig. 2c) had the highest porosity and pore size, around 20 µm, of all three samples.

The Nyquist plots of the EV31 samples, surface-treated with PEO coating in electrolyte with different KOH contents, exposed in 0.1M NaCl environment for 1 hour are shown in Fig 2. The values of the electrochemical characteristics obtained from the analysis of the measured data are listed in Table 1.
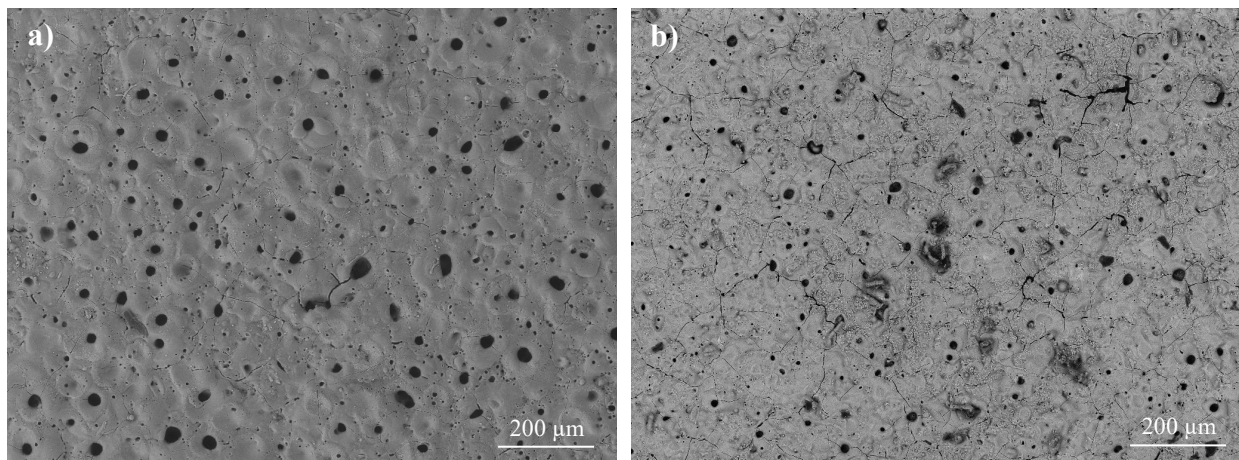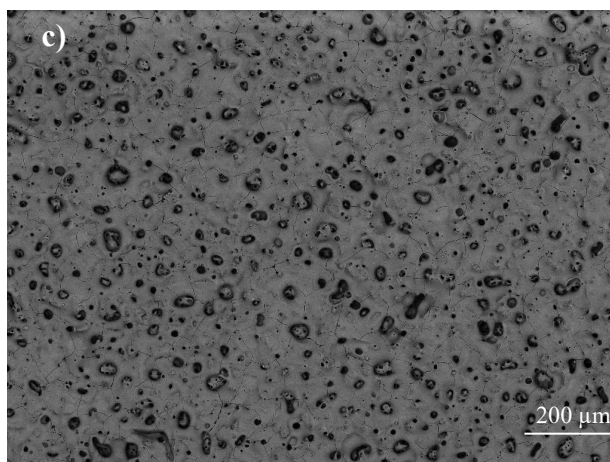
Fig.2. *Surface micrographs for samples with different KOH additions to electrolyte a) 1 g/l of KOH b) 2 g/l of KOH c) 4 g/l of KOH.*
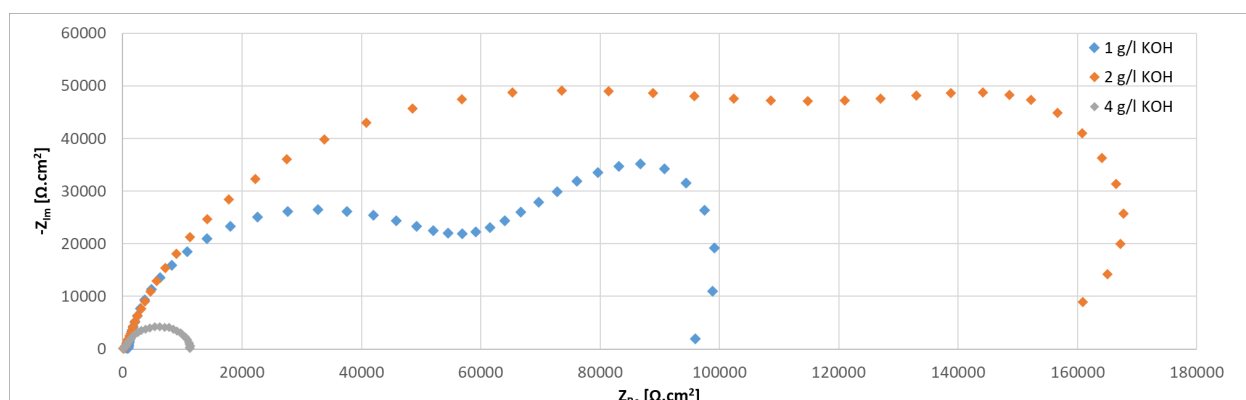

Fig.3. *Nyquist diagrams resulting from EIS measurement after 1h of exposure in 0.1M NaCl for 1, 2, and 4 g/l of KOH.*

Table 1. *Electrochemical characteristics resulting from EIS measurement after 1h of exposure in 0.1M NaCl for 1, 2, and 4 g/l of KOH*

KOH content	1 g/l KOH	2 g/l KOH	4 g/l KOH
R_s ($\Omega.cm^2$)	107 ± 9	91 ± 14	115 ± 7
R_{p1} ($\Omega.cm^2$)	43908 ± 1353	$114\,371 \pm 5723$	$12\,233 \pm 827$
R_{p2} ($\Omega.cm^2$)	57582 ± 2489	$42\,612 \pm 1472$	-
R_p ($\Omega.cm^2$)	101490 ± 3862	$156\,983 \pm 7195$	$12\,233 \pm 827$
CPE_1 ($F.sn^{-1}.10^{-6}$)	1.7 ± 0.1	0.3 ± 0.02	0.9 ± 0.05
CPE_2 ($F.sn^{-1}.10^{-6}$)	14 ± 0.3	18 ± 0.9	-
n_1	0.70	0.65	0.7
n_2	0.85	0.85	-

The comparison of calculated values of polarization resistance R_p for the samples with different KOH addition to electrolyte (Table 1) shows that samples with addition of 2 g/l of KOH exhibited over a 50 % increase in polarization resistance R_p compared to the values obtained for 1 g/l of KOH samples and over a 10-fold increase compared to the samples with 4 g/l of KOH. Higher

values of polarization resistance represent higher corrosion resistance; hence it can be concluded that from the evaluated samples the PEO coating prepared with the 2 g/l of KOH provides the most effective barrier that slows down the degradation of the EV31 magnesium alloy.

As can be seen from the shapes of the respective plots, both 1 g/l and 2 g/l KOH in electrolyte samples' diagrams consist of two capacitance loops. This means that two values of polarization resistance R_p were obtained. The first loop of the Nyquist diagram represents the resistance of the porous layer (resistance R_{p1}), and the second capacitance loop represents the resistance to charge transfer at the sample/electrolyte interface (resistance R_{p2}). In the case of the coating created with 4 g/l of KOH in the electrolyte, due to its insufficient compactness resulting from very high porosity, it shows significant decrease in R_p compared to the other two samples. The presence of only one capacitive loop in the Nyquist diagram of this sample is likely caused by penetration of the electrolyte to the surface of the bare substrate through the defects and pores. Therefore, the PEO coating was not detected significantly during the EIS measurement [20].

These results confirm that KOH content has a significant influence on the morphology and corrosion resistance of PEO coating. In a similar study [21] they observed the influence of KOH content on the PEO coating formed on AZ91 Mg alloy in a silicate electrolyte. They compared the use of 0.09 M and 0.27 M of KOH and the results showed that the use of 0.27 M KOH electrolyte improved the corrosion protection of the alloy due to a significant reduction of the pore size. Although the KOH concentrations in this study were different, their findings are in agreement with the results of the current study and further strengthen the conclusion that the KOH concentration in the electrolyte affects the corrosion resistance and morphology of PEO coatings.

Conclusions

The following conclusions are drawn from the performed experiments, results, and analysis:

- The results showed that KOH content has a significant influence on the morphology and corrosion resistance of PEO coating and the findings are in agreement with similar studies.
- The low values of polarization resistance R_p and the presence of only one capacitive loop in the Nyquist diagram indicate that the PEO coating created with 4 g/l of KOH in the electrolyte shows insufficient compactness due to high porosity of the coating.
- The PEO coating prepared with 2 g/l of KOH in the electrolyte provides the lowest porosity and highest polarization resistance, leading to the highest corrosion resistance from the evaluated samples.

Acknowledgement

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