

**MICROSTRUCTURE AND ELECTROCHEMICAL CORROSION BEHAVIOR OF CaP/PEO
DUPLEX COATING ON AZ31 MAGNESIUM ALLOY**

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Abstract

Plasma electrolytic oxidation (PEO) coatings with and without calcium phosphate (CaP) were prepared on AZ31 magnesium alloy including the CaP coating on AZ31 alloy. The microstructure of all coatings was characterized using an electron scanning microscope with energy dispersive spectroscopy (SEM/EDS). The PEO coating revealed the presence of many pores and microcracks on its surface. The deposition of CaP on the PEO layer led to the cover of these microstructural defects. Potentiodynamic polarization in 0.15 M NaCl medium showed that CaP/PEO, CaP and PEO coatings led to the improvement in the corrosion resistance when compared to bare AZ31 alloy. However, the corrosion resistance of CaP/PEO duplex coating was lower than PEO coating even though the CaP crystals covered the pores and microstructural defects.

Keywords: Plasma electrolytic oxidation, AZ31 alloy, calcium phosphate, coating, corrosion

1. INTRODUCTION

In the last few decades, magnesium-based materials have gained much attention as bioabsorbable metal implants due to their good mechanical properties, biocompatibility and biodegradability in physiological environments [1-4]. The use of Mg materials in-vivo is limited mainly by their high reactivity and associated low corrosion resistance. Under physiological conditions corrosion is facilitated especially in the presence of chlorides, which are contained in the body around 100 mmol·l⁻¹, [1,5]. Although the resulting corrosion products of Mg are non-toxic, the side effects of degradation, i.e. the development of large amounts of hydrogen gas and surface alkalization are of concern. The hydrogen accumulated around the implant can cause cracks in the bone tissue and the alkalization of the body fluid can lead to tissue necrosis [1-5].

Plasma electrolytic oxidation (PEO) is a process based on conventional anodic oxidation, from which it differs in deposition conditions and the electrolyte used. This technology is used to deposit coatings mainly on magnesium alloys [6-7]. The principal of the method is the generation of microplasma discharges by the passage of an electric current at the metal/electrolyte interface. Depending on the deposition conditions, the PEO layer reach a thickness of 5-100 μm and their porosity varies from 5 to 50 %. The PEO coating improves the short-term corrosion resistance of magnesium materials. However, due to the porous structure, the corrosive environment can easily penetrate the pores to the magnesium substrate. However, PEO coating appears to be a suitable intermediate layer for the application of other biodegradable coatings such as calcium phosphate (CaP) coatings, or other composite coatings [6-8].

A suitable candidate for improving corrosion properties is the application of a coating based on calcium phosphates and hydroxyapatite by hydrothermal treatment. Hydrothermally prepared CaP coatings on Mg

materials have shown increased corrosion resistance in corrosive environments where their deposition can better control the rate of Mg degradation [9-10].

In this study, the corrosion resistance and surface morphology were evaluated for PEO coating on AZ31 alloy and for CaP and CaP/PEO coatings prepared by hydrothermal treatment on AZ31 alloy. The main goal of this work was to determine whether the CaP coating can effectively seal the pores and microcracks of the PEO coating on AZ31.

2. EXPERIMENTAL

The elemental composition of the AZ31 alloy is identical to that reported in the previous paper [11]. Original sheet plate was cut into smaller samples with dimensions of approx. 20 mm × 20 mm × 5 mm. The surface of these samples was mechanically ground using SiC grinding papers with a final step using 1200 grinding paper. The ground samples were rinsed with water, isopropyl alcohol, and finally air-dried.

PEO coating was prepared in a phosphate-based electrolyte containing 12 g·l⁻¹ Na₃PO₄·12H₂O and 1 g·l⁻¹ KOH dissolved in deionized water according to the previous study [6]. The pH value of the electrolyte bath was adjusted to 12.5 ± 0.3 and the current density of 0.05 A·cm⁻² was applied to the magnesium sample. The deposition time was set to 10 minutes.

CaP coatings were fabricated on the AZ31 alloy with and without PEO coating via hydrothermal treatment. Firstly, solution A was prepared by dissolving Ca(NO₃)₂·4H₂O (0.15 mol·l⁻¹) in 175 ml of distilled water. Then, 125 ml of solution B containing 0.14 mol·l⁻¹ of NH₄H₂PO₄·H₂O was dropwise added into the vigorously stirred the solution A at room temperature to form solution C. The pH value of solution C was set to 5 by NaOH solution. Magnesium alloy samples or PEO-coated magnesium samples were hung on a special holder coated with Teflon tape and together with 150 ml of solution C were transferred into a 250 ml Teflon-lined SS pressure vessel. The pressure vessel was placed in the Memmert UF55 electric oven heated to 120 °C for 150 minutes. Then the pressure vessel was cooled down to room temperature. Treated samples were rinsed with water, isopropyl alcohol, and air-dried.

Zeiss EVO LS-10 scanning electron microscope (SEM) was used to characterize the surface morphology of all studied samples before and after corrosion. Electrochemical measurements were performed using the Bio-Logic VSP-300 potentiostat/galvanostat (BioLogic, Seyssinet-Pariset, France) in 0.15 mol·l⁻¹ NaCl solution at room temperature. A three-electrode system with saturated calomel electrode (reference electrode), platinum mesh (counter electrode), and measured samples with an exposed area of 1 cm² (working electrode) was used. The measured potential ranged from -200 mV to +500 mV vs. open circuit potential (OCP). The scan rate was set to 1 mV·s⁻¹. The OCP (stabilization time) was determined to be 60 minutes. Values of corrosion potential E_{corr} and corrosion current density i_{corr} were determined by the Tafel analysis using Biologic EC-Lab® software.

3. RESULTS AND DISCUSSION

Figure 1 shows the surface morphologies of ground AZ31 alloy, CaP coating on AZ31 alloy, PEO coating on AZ31 alloy, and CaP/PEO duplex coating on AZ31 alloy. In the case of the magnesium alloy (**Figure 1a**), grinding grooves were observed on the surface.

Figure 1b clearly shows that the hydrothermal synthesis resulted in the formation of the CaP coating with coarse crystals on the ground AZ31 alloy. The deposition completely covered the surface of the alloy. From (**Figure 1b** and the detail of **Figure 1b**) it is evident that the hydrothermally prepared coating was not compact and the resulting calcium phosphate crystals formed clusters of needle and plate-like formations with pores present between them.

The PEO coating on the AZ31 alloy exhibited a smooth appearance surface with open pores and micropores with microcracks around these pores along the radial directions (**Figure 1c**) [6]. Cracks observed on the surface were formed due to the rapid solidification of molten MgO during the fabrication [10]. The size of the pores and other structural defects is strongly dependent on the coating preparation parameters, such as the applied current density [6].

The deposition of CaP coatings on PEO coatings again resulted in a complete overlay of the surface and the formation of needle and plate-like clusters (**Figure 1d**). **Figure 1b** and **Figure 1d** showed a different surface morphology. Compared to CaP-coated AZ31 alloy, a different morphology of CaP crystals was observed in the case of CaP/PEO duplex coating (details in **Figures 1b** and **1d**). In the case of the CaP/PEO duplex coating, the growth of CaP crystals occurred on the previously deposited PEO coating consisting mainly of MgO, Mg(OH)₂, and Mg₃(PO₄)₂ phases, whereas the growth of CaP crystals was occurring directly on the Mg alloy in the case of CaP-coated AZ31.

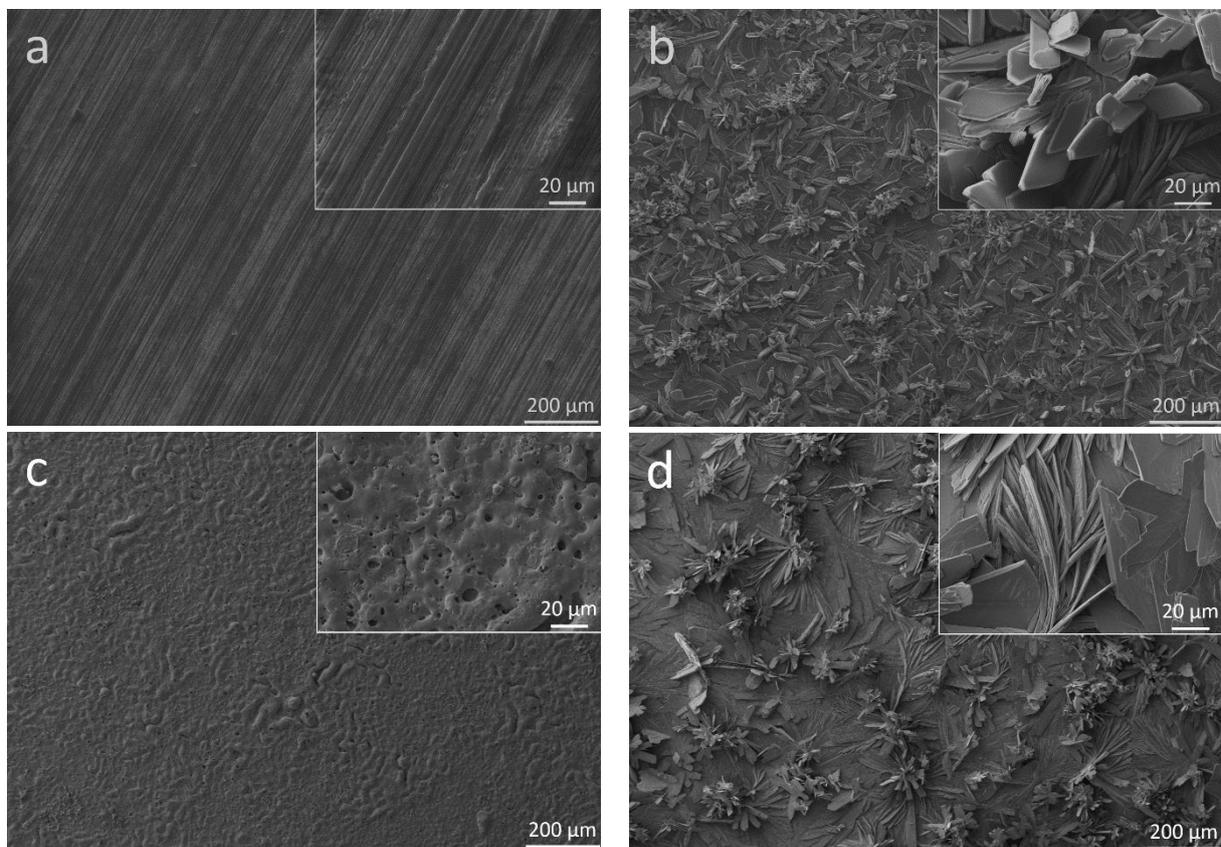


Figure 1 Surface morphology of a) ground AZ31 alloy, b) CaP-coated AZ31 alloy, c) PEO-coated alloy, d) CaP/PEO duplex coating on AZ31 alloy

The potentiodynamic polarization curves of all samples are shown in (**Figure 2**). The corresponding electrochemical parameters including corrosion potential E_{corr} , pitting potential E_{pt} and corrosion current density i_{corr} are shown in **Table 1**.

The deposition of CaP, PEO, or CaP/PEO duplex coating resulted in a decrease in corrosion current density and a shift of E_{corr} to more negative values compared to bare AZ31 Mg alloy. The lowest corrosion current density was achieved for the PEO coating on AZ31 alloy. The measured i_{corr} value was three orders of magnitude lower than that of AZ31 alloy **Table 1**. Unfortunately, the deposition of the CaP coating on the PEO/AZ31 alloy did not improve the corrosion resistance of the PEO coating, although the PEO coating was covered with CaP crystals. The penetration of the corrosive media apparently occurred through the present

pores between the clusters of calcium phosphate crystals (CaP coating) and through the open pores and cracks in the PEO coating to the surface of the AZ31 alloy [9,10,12].

However, CaP/PEO duplex coating on AZ31 alloy had the best value of corrosion potentials unlike other coatings. This indicates a lower tendency to corrode from a thermodynamic point of view. The anodic branches of the polarization curves contain a sharp break inducing pitting corrosion [13]. Unlike other samples, CaP/PEO duplex coating on AZ31 alloy did not show a sharp break and its pitting potential value E_{pt} was the highest. The occurrence of pitting corrosion was observed on the surface of the all samples after measuring the potentiodynamic polarization (**Figures 3a-d**).

Figure 3a shows extensive areas of corrosion attack including pitting corrosion on the surface of AZ31 alloy. The large localized areas of corrosion occurred on the surface of the CaP/AZ31 alloy (**Figure 3b**). In the case of PEO coatings, the corrosion attack was limited to small pits on the surface (**Figure 3c**).

As shown in (**Figure 3d**) the corrosion was similar to the PEO-coated AZ31; the pitting occurred between CaP crystals. Probably, the corrosion medium pass between the CaP crystals onto the PEO coating, and further to the Mg substrate through the pores present in the PEO coating [14]. The decrease in corrosion resistance may probably be due to the fact that the PEO coating, consisting mainly of MgO, Mg(OH)₂ and Mg₃(PO₄)₂ phases, have been partially attacked by ammonium ions during the hydrothermal synthesis of the CaP coating. According to literature [15,16], ammonium NH₄⁺ ions in the hydrothermal solution may penetrate into the MgO and Mg(OH)₂ phases in PEO coating and dissolve them, according to the Equation (1). As a result, the porosity of the PEO coating increases.

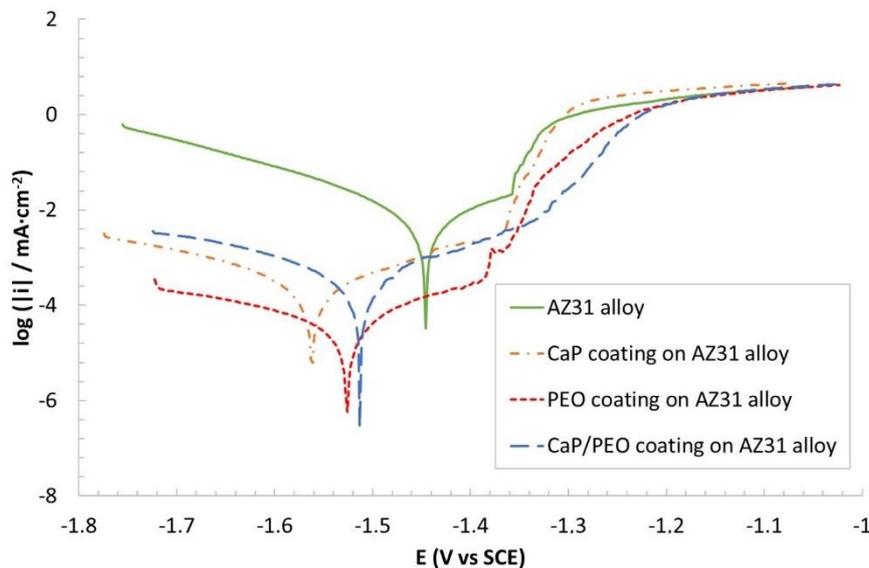


Figure 2 Potentiodynamic polarization curves of measured samples

Table 1 Electrochemical parameters of polarization curves

Sample	E_{corr} (V)	E_{pt} (V)	i_{corr} ($\mu A \cdot cm^{-2}$)
AZ31 alloy	-1.45	-1.36	7.29
CaP coating on AZ31 alloy	-1.56	-1.37	0.23
PEO coating on AZ31 alloy	-1.56	-1.38	0.03
CaP/PEO duplex coating on AZ31 alloy	-1.50	-1.33	0.26

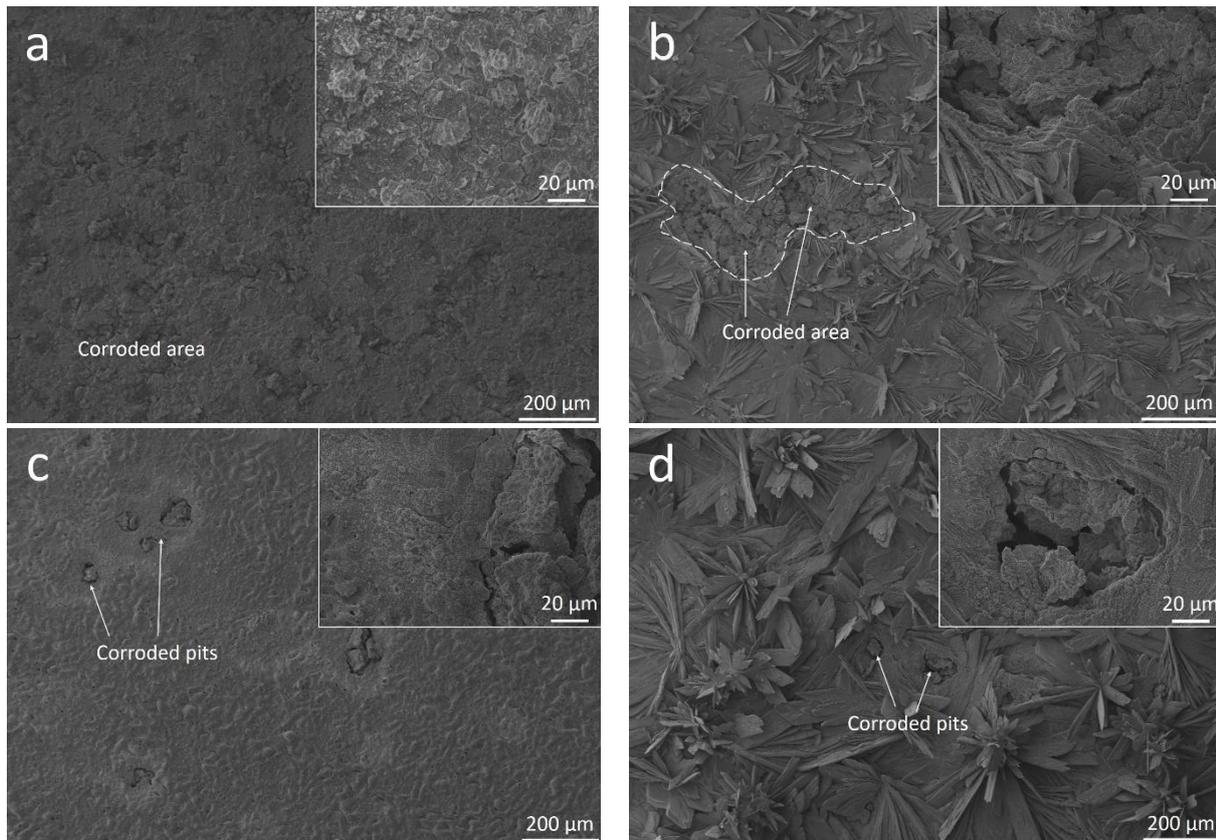


Figure 3 Surface morphology of exposed samples to corrosion media a) ground AZ31 magnesium alloy, b) CaP-coated AZ31 magnesium alloy, c) PEO-coated magnesium alloy, d) CaP/PEO duplex coating on AZ31 alloy

4. CONCLUSION

In this study the deposition of CaP, PEO and CaP/PEO coatings on the surface of AZ31 alloy was carried out to improve the corrosion resistance.

The surface morphology showed that the coarse CaP crystals evenly covered the surface of the AZ31 alloy. Plasma electrolytic oxidation resulted in a smooth surface coating with open pores and micropores and other structural defects. Subsequent application of CaP on the surface of PEO coating by hydrothermal synthesis resulted in the complete overlay of original PEO coating by CaP crystals with needle and plate-like clusters. The results of potentiodynamic measurements showed that the application of CaP, PEO and CaP/PEO coatings resulted in a significant improvement in corrosion resistance compared to AZ31 alloy. The best corrosion resistance was achieved for PEO coating on AZ31 alloy, even though pores and microcracks were present in the microstructure of the PEO coating. Contrary to expectations, the CaP coating did not improve the corrosion resistance of the PEO coating, although the CaP coating evenly sealed pores and microcracks. The reduction in corrosion resistance can be attributed to the fact that the PEO coating was partially attacked by ammonium ions during the hydrothermal synthesis of the CaP coating and, as a result, there was a partial dissolving of the PEO coating.

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