

EFFECT OF GLYCEROL-2-PHOSPHATE AND EDTA ON THE PREPARATION OF CaP COATING ON AZ31 MAGNESIUM ALLOY UNDER NEUTRAL pH CONDITION

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Abstract

Magnesium and its alloys are very promising candidates for the development of degradable implants, but their application is limited by high corrosion rates. The corrosion resistance of magnesium materials can be increased by suitable surface treatment. In this work, calcium phosphate (CaP) coatings were hydrothermally prepared with and without organic additives (ethylenedinitrilotetraacetic acid, 2-glycerol-phosphate) on AZ31 alloy with Mg(OH)₂ interlayer. The morphology was dependent on the additive used and the composition of the coatings corresponded to hydroxyapatite. The corrosion resistance of the coatings in 0.15 M NaCl was much higher than that of AZ31 alloys, but the protective function was mainly attributed to the Mg(OH)₂ interlayer. The CaP coating could mainly provide biocompatibility.

Keywords: AZ31 alloy, CaP coating, glycerol-2-phosphate, EDTA, corrosion

1. INTRODUCTION

Magnesium and its alloy are a light metal with an excellent strength-to-weight ratio having great potential for use in the automotive, aerospace and other engineering industries. [1]. Magnesium alloys have been also widely studied for biocompatibility and biodegradability, as they can be used for biomedical applications [2]. Poor corrosion resistance is the biggest limiting factor for their wider use in practice. Magnesium materials oxidize easily in normal environments due to the highly negative electrode potential. Hydroxides and oxides produced by corrosion on the surface of magnesium materials are uneven and loose, therefore they cannot protect the magnesium substrate from further deterioration, especially in the presence of chloride ions [3,4]. The rate of corrosion can be moderated by suitable alloying elements with optimum concentration in the alloy or surface treatment through the formation of a protective coating [4-7].

A suitable candidate for improving corrosion properties is the fabrication of a calcium phosphates (CaP) coating using hydrothermal treatment. Hydrothermally prepared CaP coatings on magnesium materials have shown increased corrosion resistance in corrosive environments [9-10]. Their advantage is also that they increase biocompatibility with bone tissue [8]. The preparation and properties of CaP coatings can be influenced by reaction conditions such as temperature, time, pH of the solution. The organic additives used can also have a significant impact. The chelating agent ethylenedinitrilotetraacetic acid (EDTA) is very often used and causes the formation of finer crystals of the CaP coating [9-10]. Other organic additives that have already been investigated are, for example, nitrilotriacetic acid (NTA), citric acid, various surfactants, amino acids [9,11-13]. In this work, attention was paid to the effect of EDTA and 2-glycerol-phosphate (BGP).

The aim of the work was to prepare CaP coatings on magnesium alloy AZ31 in the presence of EDTA or BGP and in the absence of these substances. The prepared coatings were characterized and subjected to potentiodynamic polarization in 0.15 M NaCl.

2. MATERIALS AND METHOD

2.1 Material

AZ31 magnesium samples were used in this experiment. The alloy elemental composition was determined by Glow-Discharge Optical Emission Spectroscopy (GDOES; Spectrumat GDS 750, Spectruma Analytik GmbH, Hof, Germany) and summarized in **Table 1**. Dimensions of these samples were 30 mm × 20 mm × 5 mm. The samples were surface treated by grinding with 800 and 1200 SiC paper, rinsed with deionized water and isopropanol and dried with hot air.

Table 1 Elemental composition of magnesium alloy AZ31

Content (wt.%)	Al	Zn	Mn	Si	Fe	Sn	Zn	Mg
AZ31	3.60	1.34	0.28	0.03	0.002	0.01	-	Bal.

2.2 Coating preparation

The ground samples were hydrothermally pre-treated in 1 M NaOH solution at 120 °C for 20 h to form Mg(OH)₂ layer. Then, the samples were rinsed in distilled water and ethanol and air dried.

The preparation of the reaction mixture for CaP coatings was carried out as follows: 125 ml of 0.14 M KH₂PO₄ was added dropwise with constant stirring to a mixture of 175 ml of 0.15 M Ca(NO₃)₂ with or without 0.035 M Na₂-EDTA (ethylenedinitrilotetraacetic acid disodium salt) or 0.035 M BGP (glycerol-2-phosphate). The pH value was adjusted to 7 using 1 M NaOH solution.

The pre-treated sample of AZ31 alloy was placed on a Teflon-coated holder and transferred to a 250 ml Teflon insert in a stainless steel pressure vessel containing 150 ml of the reaction mixture. The pressure vessel was placed in an oven at 120 °C for 2 h. The coated magnesium samples were rinsed with deionized water, ethanol and air dried.

2.3 Characterization

SEM and EDS analysis

A scanning electron microscope (SEM, ZEISS, EVO LS-10) with an energy dispersive X-ray spectroscope (EDS, Oxford Instruments plc, Abingdon, UK) was used to characterize the surface morphology and elemental composition of the CaP coatings

PDP measurements

Potentiodynamic polarization (PDP) measurements were performed using a Bio-Logic VSP-300 potentiostat (BioLogic, Seyssinet-Pariset, France). The measured samples were used as working electrode. The exposed area of the measured samples was 1 cm². The saturated calomel electrode (SCE) was used as the reference electrode and Pt mesh as the counter-electrode. A 0.15 M NaCl solution without pH adjustment was used as a corrosive medium in the corrosion cell with a volume of 200 ml. Open circuit potential (OCP) were stabilized during 60 min of exposure. Afterwards, PDP measurements were performed in the potential range from -150 mV to 500 mV vs. OCP at a scan rate of 1 mV/s.

FTIR spectrometry

Fourier transform infrared (FTIR) spectrometry (Nicolet iS10 spectrometer) was used to characterize CaP coatings. Measurements were performed by attenuated total reflection (ATR) in the spectral range 4000-400 cm⁻¹ and a resolution of 4 cm⁻¹ with an average of 128 scans. A clean and dry diamond crystal was used for the ATR measurements.

3. RESULTS AND DISCUSSION

The CaP coating prepared without the organic additive is displayed in **Figure 1A**. The sample was for the most part covered with a layer of very fine crystals, which in some places were arranged in larger clusters. These clusters ranged in size up to approximately 2 μm . The area of a weaker layer of CaP coating with an interlayer of $\text{Mg}(\text{OH})_2$ can be seen in the lower part of the image. The coating prepared in the presence of EDTA consisted of very fine crystals (**Figure 1B**), which in some places formed clusters with dimensions up to 3 μm . Both mentioned coatings contained cracks that could have been created during the formation of the coating or during SEM analysis. The CaP coating prepared in the presence of BGP uniformly covered the surface of $\text{Mg}(\text{OH})_2/\text{AZ31}$ (**Figure 1C**). It was made up of very fine crystals and did not contain cracks unlike other coatings. A comparison of SEM analysis showed that the presence of organic substances had an impact on the surface morphology (**Figure 1**).

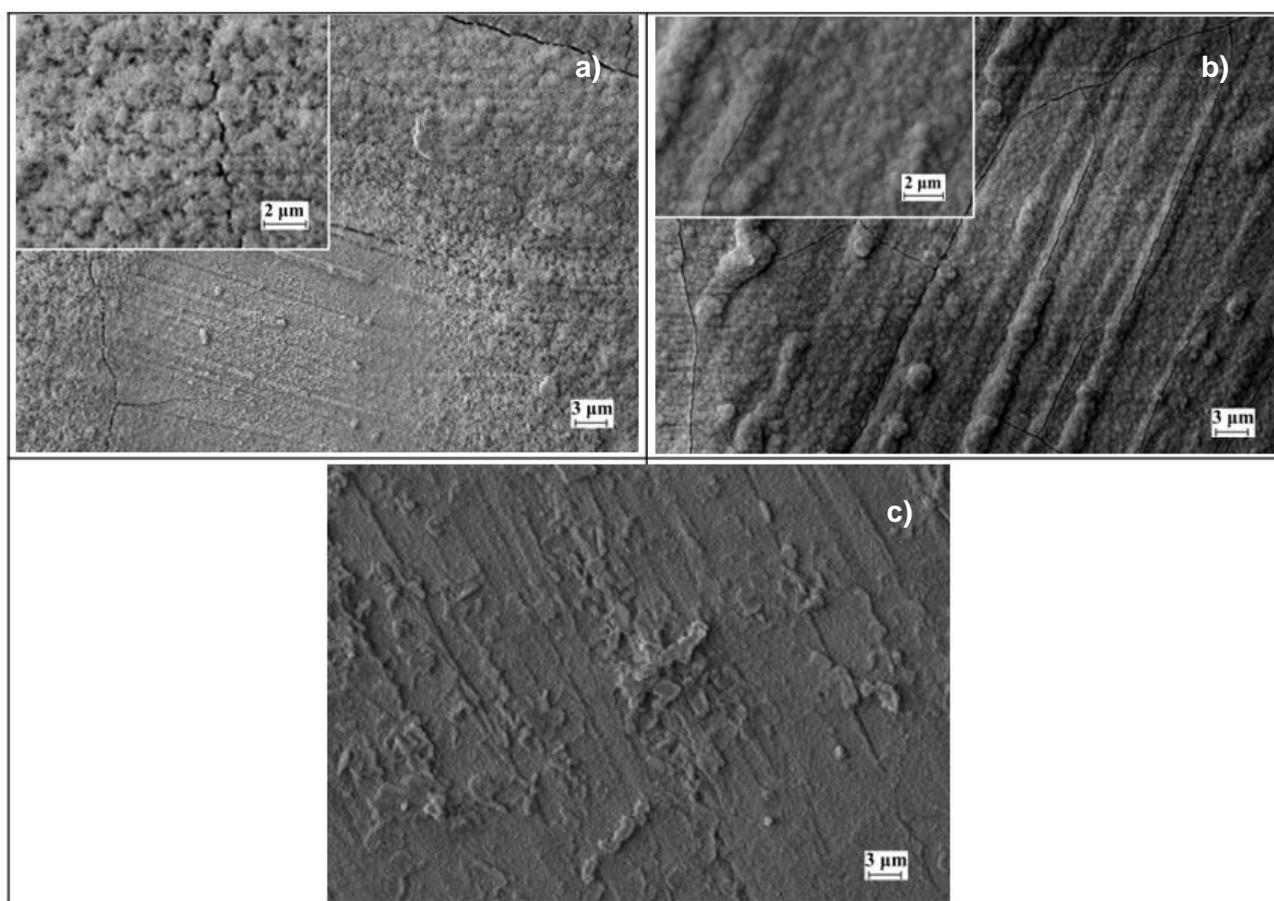


Figure 1 SEM analysis of CaP coatings prepared on $\text{Mg}(\text{OH})_2/\text{AZ31}$ without organic additive (a), with EDTA (b) or with BGP (c)

Table 2 Elemental composition of CaP coatings determined by EDS analysis and calculated values of atomic ratios

Sample	Elemental composition (at.%)							Atomic ratio		
	C	O	Na	Mg	P	Ca	Al	Ca/P	O/Ca	O/P
CaP	6.87	53.65	-	7.91	8.99	22.30	0.28	2.48	2.41	5.97
CaP with EDTA	9.86	43.21	1.18	5.05	12.29	28.41	-	2.31	1.52	3.52
CaP with BGP	15.59	50.22	0.54	3.50	11.10	19.05	-	1.72	2.64	4.52

The calculated atomic ratios (**Table 2**) from EDS analysis suggest that the CaP coatings were composed of hydroxyapatite which have the theoretical atomic ratios of 1.67, 2.60 and 4.33 for Ca/P, O/Ca and O/P, respectively. The presence of hydroxyapatite in the coatings was also indicated by FTIR analysis. The formation of hydroxyapatite at pH 7 is consistent with the literature [9].

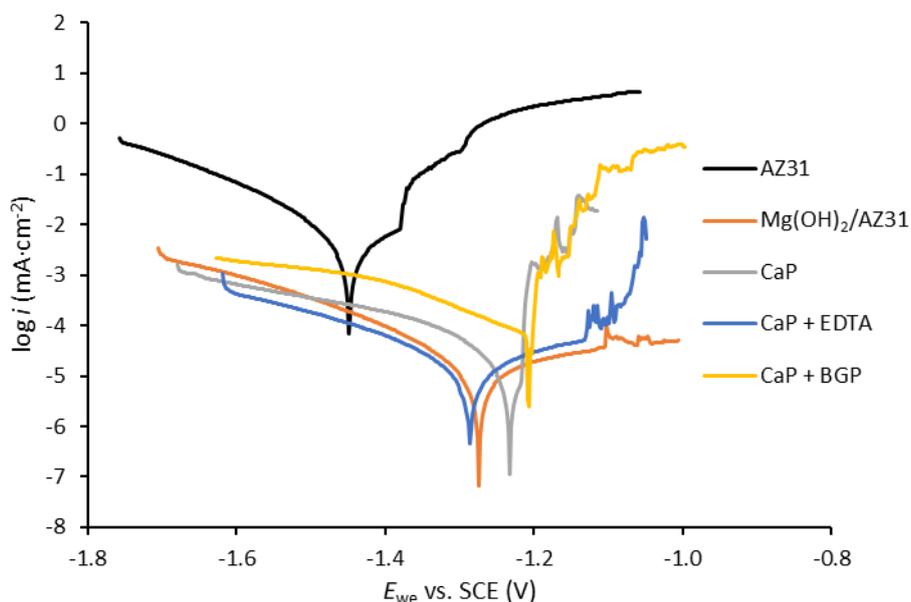


Figure 2 Potentiodynamic polarization curves of AZ31 alloy, Mg(OH)₂/AZ31 and CaP coatings prepared without the organic additive and with EDTA or BGP

Table 3 The obtained values of the corrosion current density (i_{cor}) and corrosion potential (E_{cor}) of AZ31 alloy, Mg(OH)₂/AZ31 and CaP coatings prepared without the organic additive and with EDTA or BGP

Sample	i_{cor} ($\mu\text{A}/\text{cm}^2$)	E_{cor} (V)
AZ31	6.75	-1.45
Mg(OH) ₂ /AZ31	0.01	-1.27
CaP	0.04	-1.23
CaP with EDTA	0.02	-1.29
CaP with BGP	0.07	-1.21

Pre-treatment of AZ31 alloy resulted in the formation of a Mg(OH)₂ layer that provided a significant improvement in the corrosion properties, **Figure 2** and **Table 3**. The prepared CaP coating on Mg(OH)₂/AZ31 negligibly increased the current density corrosion, which may be related to the slight disruption of Mg(OH)₂ during CaP coating preparation. The CaP coating prepared in the presence of EDTA had corrosion resistance comparable to Mg(OH)₂/AZ31 and to the CaP coating prepared in the absence of EDTA. Slightly lower corrosion resistance was observed in the case of CaP coating prepared in the presence of BGP compared to CaP coatings and to Mg(OH)₂/AZ31. On the other hand, this coating showed the most positive corrosion potential value, which may indicate a lower susceptibility to corrosion from a thermodynamic point of view. The results from the PDP measurements indicate that the corrosion resistance in 0.15 M NaCl was ensured mainly by Mg(OH)₂, which was prepared by pre-treatment on the AZ31 alloy. From the perspective of our experiments, the importance of the CaP coating should be mainly attributed to its biocompatibility with bone tissue [8]. Considering the chemical properties of the CaP coating, it is possible to assume that these coatings could

participate in corrosion protection in environments containing a more diverse composition including inorganic and/or organic components.

The FTIR spectra of the CaP coatings (**Figure 3**) contained two prominent bands at 1019 and 559 cm^{-1} and also weak bands at 874, 600 and 473 cm^{-1} . All these bands were attributed to the phosphate groups of hydroxyapatite [14,15]. This is consistent with EDS analysis, which revealed atomic ratios that best corresponded to hydroxyapatite. The spectrum of the CaP coating prepared with BGP and without organic additives also has a band at 3695 cm^{-1} , corresponding to the vibration of the OH groups that originated from the $\text{Mg}(\text{OH})_2$ interlayer [16].

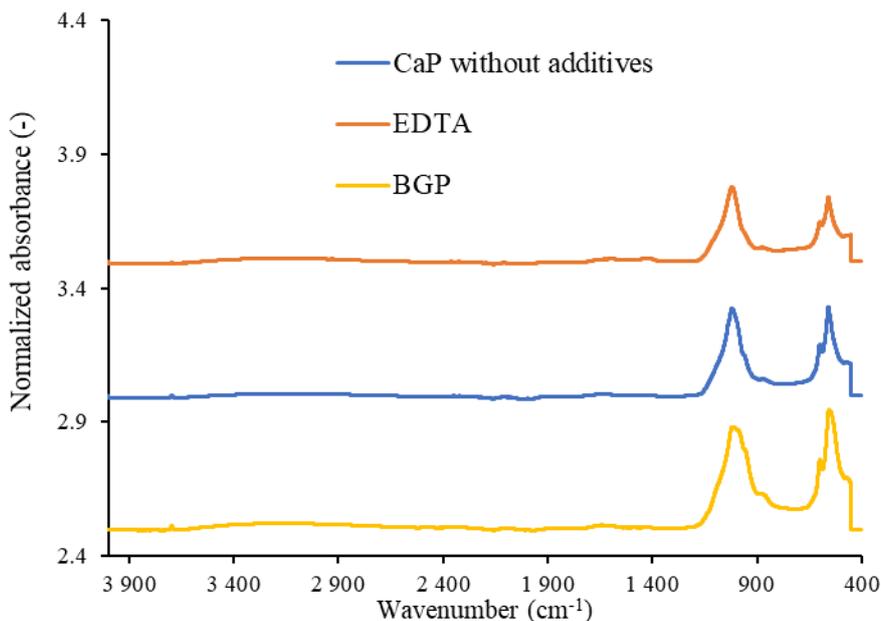


Figure 3 FTIR spectra of CaP coatings prepared without the organic additive and with EDTA or BGP

4. CONCLUSION

CaP coatings were prepared on the AZ31 alloy with a $\text{Mg}(\text{OH})_2$ interlayer in the presence of EDTA, BGP and in absence of the organic additives. The surface morphology was influenced by the organic additives. The chemical composition of the prepared CaP coatings corresponded to hydroxyapatite. The corrosion resistance of the coatings was comparable to each other and to $\text{Mg}(\text{OH})_2/\text{AZ31}$, but significantly higher than the bare AZ31 alloy. The results suggest that the corrosion resistance in 0.15 M NaCl was dominated by the $\text{Mg}(\text{OH})_2$ layer rather than the CaP coating. The prepared CaP coating could mainly provide the biocompatibility of the material to bone tissue.

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