POTENTIODYNAMIC POLARIZATION OF AZ31 MAGNESIUM ALLOY WITH DCPD

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Abstract:
Potentiodynamic polarization is the main laboratory technique used for the most relevant electrochemical corrosion characteristics determination. The Mg-3Al-1Zn biodegradable alloy electrodeposited by dicalcium phosphate dihydrate (DCPD) coating was investigated in this study. The 0.9 % NaCl solution simulating human body chloride concentration environment was used as a corrosion electrolyte. Testing temperature corresponded to human body fluids temperature (37 °C). Electrodeposition of DCPD was realized in water solution of $Ca(NO_3)_2.4H_2O$, NH_4HPO_4 and H_2O_2. The influence of this surface treatment on corrosion potential and corrosion current density was evaluated. Basic potentiodynamic curves, obtained from the voltamperometric tests, were analyzed by the Tafel analyses. The improvement of the short-time electrochemical behavior after the DCPD electrodeposition on tested alloy surface was reported.

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1. INTRODUCTION

Magnesium alloys have shown desirable properties for potential application in biomaterial area, for example, high strength and Young modulus close to a natural bone. However, the high dissolution rate of magnesium alloy is a problem due to its high chemical activity. The surface modification is an effective approach to solve this problem and improve the application of magnesium alloy as potential biomaterial [1].

One of the most perspective coatings for implants are calcium phosphates [2]. Calcium phosphates have extensively been studied due to their biocompatibility, chemical stability and similarity in composition with the mineral phase of teeth and bone and use as bone substitutes in biomedical industry. Among the most studied calcium phosphates are hydroxyapatite (HAP), octacalcium phosphate (OCP), brushite or dicalcium phosphate dihydrate (DCPD), monetite, monocalcium phosphate monohydrate (MCPM), tricalcium phosphate (TCP), tetratricalcium phosphate (TTCP) and amorphous calcium phosphate (ACP) [3].

For these reasons, the aim of this study was to electrodeposit the DCPD coating on an AZ31 magnesium alloy surface and to improve its electrochemical corrosion properties in that way.

2. EXPERIMENTAL MATERIAL AND METHODS

The tested AZ31 magnesium alloy was continually casted at Brandenburgische Universität in Cottbus, Germany and chemical composition was analysed at the Magnesium innovation center MagIC GKSS Geesthacht, Germany. The chemical composition is listed in Tab. 1. The specimens for metallographic observation were prepared by the conventional metallographic procedures. For visualization of the magnesium alloy microstructure, etchant consisting of 2.5 ml acetic acid + 2.1 g picric acid + 5 ml H_2O + 35 ml of ethanol was used [4]. The microstructure of AZ31 alloy (Fig. 1) was observed by the CARL ZEISS AXIO Imager A1m light metallographic microscope in the laboratories of Department of Materials Engineering, University of Žilina. The microstructure consisted of polyhedral grains of solid solution of aluminum, zinc and other

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alloying elements in magnesium. The average grain size is 220 µm.

Table 1. Chemical composition of AZ31 ally (in wt. %)

Al	Zn	Mn	Si
2.96	0.828	0.433	0.004
Cu	Ni	Fe	Mg
0.004	<0.001	0.002	balance

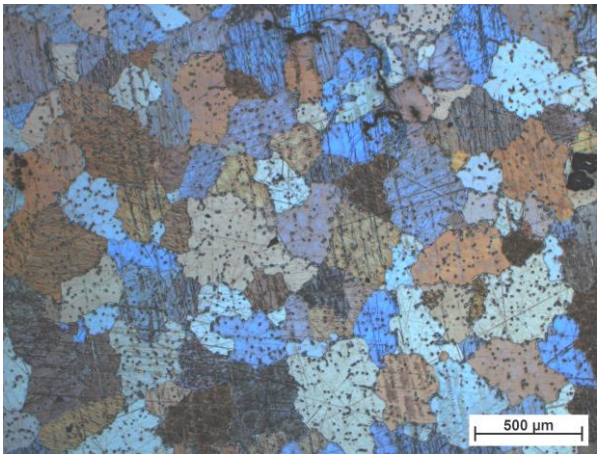

Fig. 1. Microstructure of AZ31 magnesium alloy, light microscopy, etch. picric acid + ac. acid + ethanol + water

2.1 Experimental material surface preparation

For evaluation of the DCPD surface treatment influence on electrochemical characteristics, the specimen surfaces were ground with 1000 grit SiC paper to ensure the same surface roughness, then rinsed with demineralized water and ethanol, and dried using a stream of air. After the described pre-treating, the DCPD was deposited on the specimens' surfaces. The treatment electrolyte solution was prepared with 0.1 M $Ca(NO_3)_2.4H_2O$, 0.06 M NH_4HPO_4, 10 ml.dm^{-3} of 50 vol. % H_2O_2. The solution pH was 4 and the electrodeposition was carried out at room temperature 22 ± 2 °C. The ground AZ31 specimen was used as the cathode, while a platinum electrode served as the anode. Electrodeposition was performed with constant potential -100 mV vs saturated calomel electrode (SCE) for 1 hour on a laboratory apparatus VSP (producer BioLogic SAS France). After electrodeposition specimens were immediately rinsed with demineralized water and dried using a stream of air.

2.2 Experimental methods

The surface morphology of the treated samples was assessed by a stereomicroscope Nikon AZ100 with a digital camera using NIS Elements software. The corrosion characteristics of the untreated and DCPD-coated AZ31 in 0.9% NaCl were evaluated by the potentiodynamic polarization using a potentiostat/galvanostat/frequency response analyzer VSP from BioLogic SAS France. All the corrosion experiments were performed at 37±1 °C. A saturated calomel electrode and a platinum electrode served as the reference and auxiliary electrodes, respectively. The treated and untreated AZ31 samples formed the working electrode in such a way that only 1 cm² area of the working electrode surface was exposed to the electrolyte solution in a corrosion cell.

The potentiodynamic polarization tests were carried out from -200 to + 500 mV vs SCE with respect to the OCP (open circuit potential) at a scan rate of 1 mV.s^{-1}. Measured potentiodynamic curves were analysed using Tafel fit by EC-Lab software.

The Tafel graph is displayed in logI vs E_{we} where the two linear regressions are automatically made using the least square method and the software deduces the open circuit potential (E_{corr}) to linear regressions intersection and the corrosion current density value (i_{corr}) [5]. The potentiodynamic polarization measurements were repeated at least three times, so that reproducibility of the test results was ensured.

3. RESULTS AND DISCUSSION

Electrodeposition under the specified conditions led to the creation of a thin layer of calcium phosphate DCPD (Fig. 2).

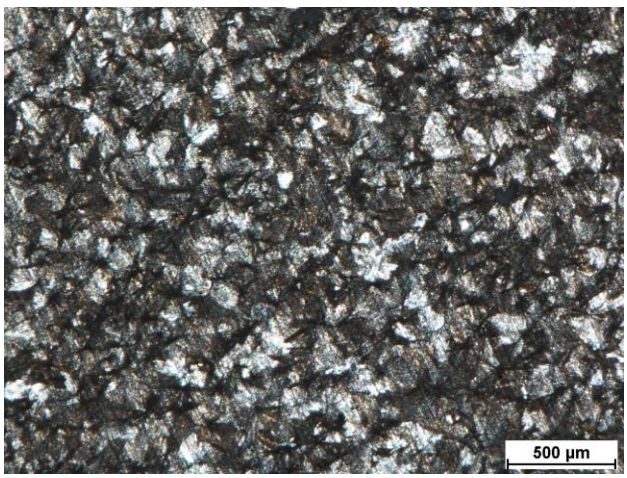

Fig. 2. Surface morphology of AZ31 after DCPD electrodeposition

As can be seen from the figure, the continuous layer covering the entire surface is composed of

irregularly branched units that overlap each other. According to [6] the chemical composition of the observed layer is $CaHPO_4.2H_2O$

Measured potentiodynamic curves of AZ31 magnesium alloy samples, before and after electrodeposition of calcium phosphate (DCPD), are shown in Fig. 3. The curves are plotted in semi-logarithmic coordinates for a better interpretation of the measured data and electrochemical characteristics. Based on the Tafel analysis performed by the EC-Lab program V10.12, the values of the corrosion potential E_{corr} and the corrosion current density i_{corr} together with added values of the corrosion rate r_{corr} were obtained. Particular obtained electrochemical characteristics are shown in Tab. 2.

Tab. 2. Electrochemical characteristics of AZ31 Mg alloy surface after various treatments

Surface treatment	E_{corr} [mV_{SCE}]	i_{corr} [$\mu A.cm^{-2}$]	r_{corr} [$mm.y^{-1}$]
grinded surface	-1 631.6	74.3	3.40
surface with DCPD coating	-1 486.2	1.3	0.06

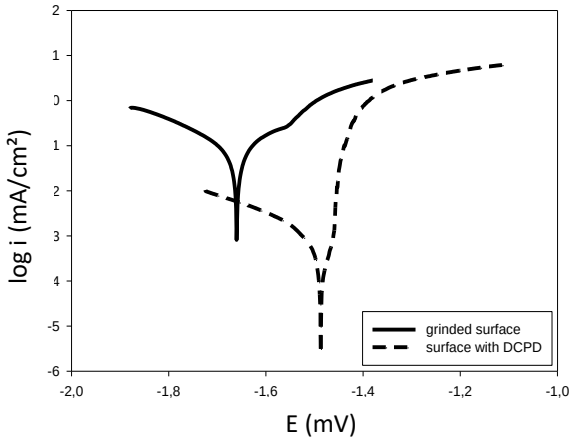

Fig. 3. Potentiodynamic curves of untreated and treated surfaces of AZ31 alloy in 0.9% NaCl at 37±1 °C

The more positive corrosion potential value (-1486.2 mV) is observed on samples with the surface covered by DCPD. The just ground AZ31 magnesium alloy samples show the corrosion potential value E_{corr}=-1631.6 mV. Those results demonstrate that the surface of AZ31 magnesium alloy coated by DCPD is electrochemically nobler and hence thermodynamically more stable. Moreover the samples coated by the DCPD show significantly lower values of i_{corr}. The untreated samples achieve the i_{corr} value of 74.3 $\mu A.cm^{-2}$, while samples with DCPD achieve only 1.3 $\mu A.cm^{-2}$, which represents a 57-fold reduction. This finding is very important for assessing the kinetics of corrosion, since corrosion current density is directly related to the corrosion rate and therefore tells us about the intensity of the ongoing corrosion process in the specific electrolyte. From this perspective, the application of DCPD coating presents significant progress in terms of increasing the corrosion resistance of AZ31 surface layer.

4. CONCLUSIONS

Based on the measured data and analyses the following conclusions were drawn:

1. The DCPD layer created by electrodeposition continuously covers the entire surface of the substrate and is formed by irregular branched units that overlap each other.
2. The corrosion potential E_{corr} value (-1486.2 mV) of the surface covered by DCPD is more positive compared to untreated samples (E_{corr} = -1631.6 mV).
3. Samples with DCPD coating reach 57-fold reduction of corrosion current density i_{corr} compared to untreated samples.
4. Taking into account both electrochemical corrosion resistance criteria (thermodynamic and kinetic), the application of DCPD coating presents a significant progress in terms of increasing the corrosion resistance of AZ31 surface layer.

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