

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY CHARACTERIZATION OF ZW3 MAGNESIUM ALLOY COATED BY DCPD USING LASV DEPOSITION TECHNIQUE

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Abstract

The contribution deals with the preparation of the dicalcium phosphate-dihydrate (DCPD) coating on ZW3 magnesium alloy surface. The coating was prepared using large amplitude sinusoidal voltammetry (LASV) electrodeposition technique in water solution of 0.1M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ + 0.06M NH_4HPO_4 + 10 ml.dm⁻³ of 50 vol.% H_2O_2 . The influence of the DCPD coating on electrochemical characteristics was examined using potentiodynamic polarization (PD) tests and electrochemical impedance spectroscopy (EIS) at the temperature 22 ± 2 °C in 0.1M NaCl. The obtained PD curves were analysed using Tafel extrapolation method and the data obtained by EIS measurements in a form of Nyquist plots were analysed quantitatively by equivalent circuit method. The results showed the increase of corrosion resistance after application of DCPD coating on ZW3 Mg alloy in sodium chloride solution.

Keywords: magnesium alloy, corrosion, cathodic deposition, calcium phosphate

1 Introduction

Magnesium and its alloys are the lightest structural materials and in combination with their excellent specific strength and recyclability they are a very popular choice of engineers in automotive and aerospace industry [1-4]. Among standard biomedical materials for implants and stents such as Ti alloys and stainless steels, Mg alloys become widely used in biomedical applications due to their biocompatibility and nontoxicity [5-11]. Despite of this, the main limitation of their usage is their low corrosion resistance which can lead to the earlier degradation of the constructions. This problem could be caused by impurities and intermetallic phases in Mg alloys that create galvanic couples and such that accelerate the corrosion [12]. The corrosion of Mg is accompanied with anodic hydrogen evolution in form of bubbles and this fact limits application in biomedicine [13,14]. According to this, surface treatment has to be applied on the Mg surface to slow down the corrosion degradation [15,16]. The calcium phosphate-based coatings (hydroxyapatite, calcium phosphate-dihydrate, octacalcium phosphate, tricalcium phosphate, etc.) represent the non-expensive and environmentally friendly solution of this issue and show also good biocompatibility [17-21]. The calcium phosphate-dihydrate (DCPD) can be easily prepared on the Mg surface using cathodic electrodeposition method in proper electrolyte [22, 23]. The common electrodeposition methods use the application of constant potential/current on the Mg alloy but the coating does not have a very good adhesion to the substrate due to the hydrogen bubbles as a result of relatively strong cathodic polarization [14,

24, 25]. The application of AC potential could overcome this problem as the applied potential is changing during the deposition process and cathodic hydrogen evolution is not so intensive.

2 Experimental material and methods

The non-heat treated extruded ZW3 Mg alloy has been used as an experimental material. Chemical composition has been determined using EDXRF analysis on ARL QUANT'X EDXRF spectrometer and the obtained values are mentioned in **Tab. 1**. The samples for metallographic evaluation have been prepared according to the standard metallographic procedures and etched using 1 % Nital, then washed by demineralised water, ethanol and dried by stream of air. The ZEISS AXIO Imager.Z1M light microscope has been used for evaluation of ZW3 microstructure.

Table 1 Chemical composition of ZW3 magnesium alloy

Component	Zn	Zr	Mn	Co	Fe	Mg
wt. %	2.88	0.96	0.01	0.006	0.002	balance

The coating examined in this contribution is the DCPD coating created by large amplitude sinusoidal voltammetry (LASV) technique using VSP Biologic potentiostat at the temperature of 22 ± 2 °C. The three electrode system have been used for preparation of the coating with electrode configuration set as follows: sample set as a cathode, Pt electrode set as an anode, saturated calomel electrode set as a reference electrode. The electrolyte for coating preparation consists of $0.1\text{M Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + 0.06\text{M NH}_4\text{HPO}_4 + 10 \text{ ml.dm}^{-3}$ of 50 vol.% H_2O_2 and 500 ml of demineralised water and its pH was 4.2 [26]. The potential ranged from -1.9 to -1.5 V vs. SCE with frequency of 0.017 Hz has been applied on the sample within 60 min [27]. The stereomicroscope Nikon AZ100 with software NIS-Elements D3.1 has been used to investigate the surface of the non-coated and DCPD coated samples. The picture of the cross section view of DCPD coating and coating thickness has been evaluated by ZEISS AXIO Imager.Z1M using camera AxioCam MRc5 and software AxionVisionRel 4.5.

The electrochemical corrosion characteristics of non-coated and DCPD coated samples have been measured by potentiodynamic polarization (PD) tests and electrochemical impedance spectroscopy (EIS) measurements in 0.1M NaCl [28,29] solution at the temperature of 22 ± 2 °C in three-electrode cell configuration. All the measurements have been performed on the VSP Biologic potentiostat (equipment supported by ERDF – project ITMS 26220220048) and have started after 5-minute stabilization of sample-electrolyte potential.

Potential from -200 mV to +500 mV vs. OCP with the rate of 1mV.s^{-1} has been put on the sample during PD measurements. The obtained curves for non-coated and coated samples have been analysed by EC Lab V10.34 software using Tafel extrapolation method.

The EIS measurements have been performed after various exposition times (5 min, 1 h, 2 h, 4 h, 8 h, 12 h, 24 h, 48 h, 96 h, 168 h). The measured frequency ranged from 100 kHz to 10 mHz and amplitude of applied sinusoidal voltage was set to 15 mV. The obtained curves in the form of Nyquist plots have been quantitatively analysed by EC Lab 10.34 software using equivalent circuit model. Equivalent circuit for Nyquist plot with one capacitance loop (homogenous surface) is listed in **Fig. 1** and the equivalent circuit for plot with two capacitance loops (places with different electrochemical behaviour) is showed in **Fig. 2**. The element R_Ω represents solution's resistance, CPE is constant phase element and it represents the heterogeneity of the electrode's surface and the element R_p represents the polarization resistance of the Mg substrate-electrolyte interface or the DCPD coating-electrolyte interface. In the case of Nyquist plot

created by two capacitance loop, the final value of R_p is the sum of polarization resistances R_{p1} and R_{p2} [30].

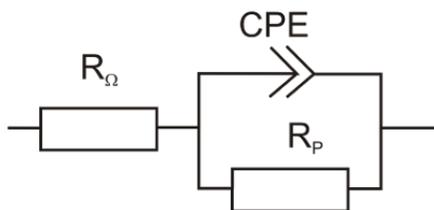


Fig. 1 Equivalent circuit for Nyquist plot with one capacitance loop

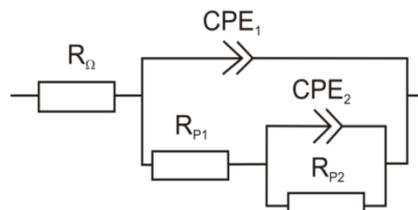


Fig. 2 Equivalent circuit for Nyquist plot with two capacitance loops

3 Results and Discussion

Microstructure of ZW3 Mg alloy (**Fig. 3**) is represented by polyedric grains of supersaturated solid solution of Zn, Zr and other alloying elements in magnesium with locations of intermetallic phase $ZrZr_2$ and large areas consist of solid solution of alloying elements with high amount of Mg.



Fig. 3 Microstructure of ZW3 Mg alloy

The surface of the non-coated ZW3 sample is listed in **Fig. 4**. The state of surface after deposition of DCPD is shown in **Fig. 5** and **Fig. 6**. As can be seen from **Fig. 5** and **Fig. 6** the DCPD coating exhibits quite porous crystalline morphology with crystals growing from their centre towards periphery. The average thickness of the coating is $14.2 \mu\text{m}$.

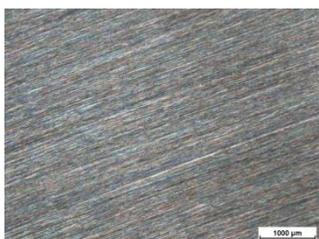


Fig. 4 Surface of the non-coated ZW3 sample



Fig. 5 Surface of the DCPD coated ZW3 sample

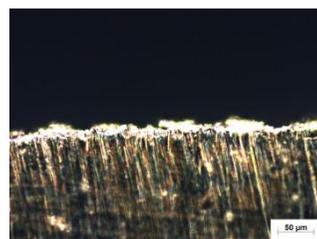


Fig. 6 Cross section view of DCPD coating

The **Fig. 7** illustrates potentiodynamic curves for non-coated and DCPD coated samples obtained by PD tests measured in 0.1M NaCl and the **Tab. 2** shows the values of corrosion potential E_{corr} , corrosion current density i_{corr} and corrosion rate r_{corr} obtained by Tafel extrapolation analysis. It can be seen that the DCPD coated samples exhibit more positive potential (-1336mV) in comparison to the samples without coating (-1451 mV) such that the DCPD coated samples are thermodynamically more stable. In the corrosion kinetics point of view, coated samples have reached more than 5-times lower value of i_{corr} ($7.7 \mu\text{m}.\text{cm}^{-2}$) compared to the value reached by non-coated samples ($41.1 \mu\text{m}.\text{cm}^{-2}$). The corrosion rate r_{corr} is continually proportional to the i_{corr} values such that the corrosion rate is lower in case of the DCPD coated samples.

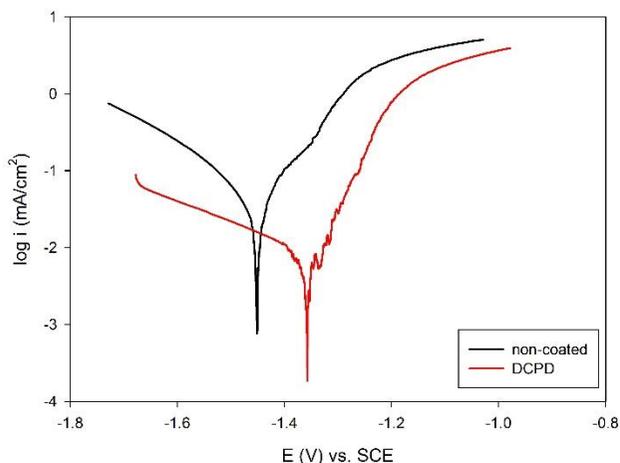


Fig. 7 Potentiodynamic polarization curves of ZW3 magnesium alloy in 0.1M NaCl

Table 2 Electrochemical characteristics of ZW3 magnesium alloy in 0.1M NaCl

State of the surface	E_{corr} [mV]	i_{corr} [$\mu\text{A}.\text{cm}^{-2}$]	β_a [mV/dec.]	β_c [mV/dec.]	r_{corr} [mm/year]
Non-coated	-1451±18	41.1±2.2	133±12	188±8	1.88±0.04
DCPD	-1336±12	7.7±0.6	65±5	359±16	0.35±0.002

The Nyquist plots measured in 0.1M NaCl after various exposure times for non-coated and coated samples are displayed in the **Fig. 8** and **Fig. 9** respectively. The values of electrochemical characteristics obtained by equivalent circuit method for non-coated samples and DCPD coated samples are showed in **Tab. 3** and **Tab. 4**.

It can be seen that the non-coated samples (**Fig. 8, Tab. 3**) immersed in 0.1M NaCl exhibit the increase of R_p values with increasing immersion time up to 8 h of exposure time when the samples have reached the value of $1310 \Omega.\text{cm}^2$. This fact can be explained by formation of corrosion product layer (CPL) on the sample's surface which acts as a temporary barrier. As the exposure time increases, the thickness of the layer increases which leads to the increase of R_p . The decrease of R_p values has been observed after 12 h of exposition caused by degradation of CPL at certain places of the surface such that the corrosion reaction could be realized here. After that, the increase of the R_p values has been observed until the 168 h of exposure time. At the places where the CPL has been damaged, the corrosion reaction leads to sealing up the CPL by

repeated creation of corrosion products which made the CPL more compact and resistant to the corrosive environment. This explanation is proved by the shape of the Nyquist diagram created by one capacitance loop.

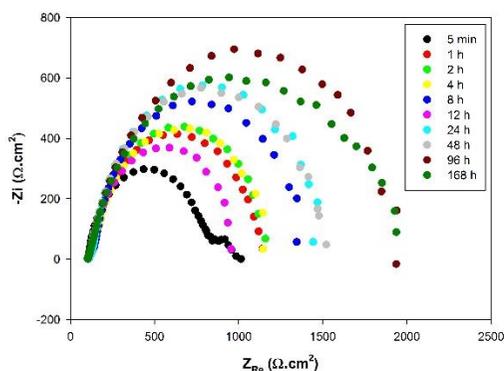


Fig. 8 Nyquist plots of non-coated ZW3 samples in 0.1M NaCl

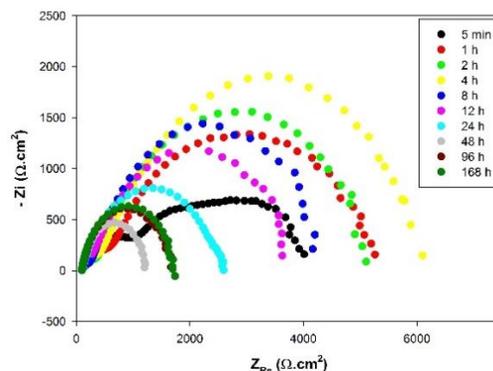


Fig. 9 Nyquist plots of DCPD coated ZW3 samples in 0.1M NaCl

Table 3 Electrochemical characteristics of non-coated samples obtained by EIS in 0.1M NaCl

Time	R_{Ω} [$\Omega \cdot \text{cm}^2$]	R_{p1} [$\Omega \cdot \text{cm}^2$]	R_{p2} [$\Omega \cdot \text{cm}^2$]	R_p [$\Omega \cdot \text{cm}^2$]	CPE_1 [$10^{-6} \cdot \text{F} \cdot \text{s}^{n-1}$]	CPE_2 [$10^{-6} \cdot \text{F} \cdot \text{s}^{n-1}$]	n_1	n_2
5 min	107 ± 16	705 ± 25	151 ± 12	856 ± 37	15 ± 2	22 ± 2	0.91 ± 0.02	0.91 ± 0.01
1 h	111 ± 14	1054 ± 60	-	1054 ± 60	27 ± 5	-	0.84 ± 0.01	-
2 h	112 ± 7	1104 ± 57	-	1104 ± 57	38 ± 9	-	0.78 ± 0.04	-
4 h	113 ± 9	1116 ± 36	-	1116 ± 36	59 ± 8	-	0.78 ± 0.02	-
8 h	114 ± 16	1310 ± 41	-	1310 ± 41	82 ± 12	-	0.81 ± 0.01	-
12h	114 ± 12	875 ± 22	-	875 ± 22	108 ± 17	-	0.91 ± 0.03	-
24 h	113 ± 10	1421 ± 32	-	1421 ± 32	103 ± 14	-	0.91 ± 0.02	-
48 h	107 ± 7	1440 ± 46	-	1440 ± 46	103 ± 20	-	0.82 ± 0.04	-
96 h	105.8 ± 14	1893 ± 84	-	1893 ± 84	90 ± 11	-	0.71 ± 0.03	-
168 h	104.1 ± 9	1828 ± 71	-	1828 ± 71	83 ± 11	-	0.72 ± 0.04	-

The DCPD coated samples (**Fig. 9, Tab. 4**) have reached R_p value of 4277 $\Omega \cdot \text{cm}^2$ after 5-minute exposition. This value is almost 5-times higher compared to the value reached by non-coated sample (856 $\Omega \cdot \text{cm}^2$) after the same exposure time. In the following time, the increase of the R_p has been observed to its maximum value (6089 $\Omega \cdot \text{cm}^2$) reached after 4 h of exposure time. At the coating imperfections the reaction between calcium phosphate and sodium chloride solution took place which led to the sealing up the imperfections by corrosion products. This has been

demonstrated by the increase of the polarization resistance. In the next stages, the decrease of the R_p has been observed due to the starting degradation of DCPD layer. After 24 h of exposure time the DCPD samples have reached the R_p value of $2440 \Omega \cdot \text{cm}^2$. This value is still almost 2-times higher compared to the value of non-coated sample after the same exposure time ($1421 \Omega \cdot \text{cm}^2$). The marked decrease of R_p has been observed after 48 h ($1140 \Omega \cdot \text{cm}^2$) because of the delamination of the DCPD layer. After 168 h the increase of the R_p ($1625 \Omega \cdot \text{cm}^2$) has been observed due to the formation of corrosion products at the delaminated areas of the samples.

Table 4 Electrochemical characteristics of coated samples obtained by EIS in 0.1M NaCl

Time	R_Ω [$\Omega \cdot \text{cm}^2$]	R_{p1} [$\Omega \cdot \text{cm}^2$]	R_{p2} [$\Omega \cdot \text{cm}^2$]	R_p [$\Omega \cdot \text{cm}^2$]	CPE_1 [$10^{-6} \cdot \text{F} \cdot \text{s}^{n-1}$]	CPE_2 [$10^{-6} \cdot \text{F} \cdot \text{s}^{n-1}$]	n_1	n_2
5 min	71.1 ± 6	716 ± 46	3561 ± 113	4277 ± 159	1 ± 0.2	33 ± 5	0.74 ± 0.02	0.51 ± 0.05
1 h	93.2 ± 10	459 ± 21	4765 ± 147	5224 ± 168	1 ± 0.2	16 ± 2	0.71 ± 0.02	0.69 ± 0.03
2 h	98.1 ± 14	261 ± 18	4825 ± 162	5086 ± 180	2 ± 0.4	18 ± 3	0.66 ± 0.04	0.75 ± 0.06
4 h	92 ± 14	354 ± 17	5735 ± 156	6089 ± 173	6 ± 0.5	21 ± 2	0.62 ± 0.01	0.72 ± 0.02
8 h	83.6 ± 10	263 ± 24	3955 ± 114	4218 ± 138	70 ± 9	27 ± 3	0.55 ± 0.03	0.87 ± 0.02
12h	93.9 ± 11	654 ± 41	3015 ± 124	3669 ± 165	29 ± 6	31 ± 6	0.49 ± 0.05	0.86 ± 0.04
24 h	109.1 ± 8	2440 ± 220	-	2440 ± 220	28 ± 2	-	0.77 ± 0.02	-
48 h	101.8 ± 9	1140 ± 98	-	1140 ± 98	51 ± 8	-	0.94 ± 0.08	-
96 h	101.9 ± 12	1620 ± 143	-	1620 ± 143	51 ± 5	-	0.83 ± 0.05	-
168 h	98.6 ± 7	1625 ± 114	-	1625 ± 114	37 ± 4	-	0.83 ± 0.06	-

4 Conclusions

The DCPD coating realized by large amplitude sinusoidal voltammetry on ZW3 Mg alloy surface has been investigated in this study. The deposition process has led to the creation of the DCPD layer which has been further tested by PD tests and EIS in 0.1M NaCl. The potentiodynamic polarization tests proved that the DCPD coated alloy is thermodynamically nobler and kinetically more stable compared to the non-coated ZW3 alloy. In terms of medium-term EIS measurements, coated samples have shown higher polarisation resistance up to 48 h of exposure time in the testing environment thus providing enhanced corrosion resistance.

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