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Effect of PEO Surface Treatment on Biodegradable Magnesium Alloy ZK60

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Abstract. Magnesium alloy ZK60 is a biocompatible and biodegradable material that has gained attention for its potential use in biomedical applications due to its high mechanical strength, lightweight properties, and biocompatibility. However, the high chemical reactivity and poor resistance to corrosion of magnesium alloys limit their use. This study evaluates the results from a potentiodynamic polarization test (PD) on ZK60 with surface treatments of plasma electrolytic oxidation (PEO) and PEO+PVA (Polyvinyl Alcohol with Glycerin). The aim is to understand the impact of these treatments on the corrosion behavior of ZK60 and to improve its properties for medical applications. The results showed that the PEO surface treatment significantly improved the corrosion resistance of ZK60, and the combination of PEO and PVA resulted in further improved corrosion behavior. This study highlights the potential of PEO and PEO+PVA treatments for improving the corrosion resistance of ZK60 and its suitability for use in biomedical applications.

Introduction

Magnesium alloys have gained recognition for their biodegradability and biocompatibility, making them a potential material for use in the biomedical field. Among the different magnesium alloys available, ZK60 stands out due to its relatively high mechanical strength and lightweight properties. The high strength-to-weight ratio of ZK60 allows it to be used in applications where weight reduction is critical without compromising on strength. This makes it an ideal material for applications such as sutures, screws, intramedullary nails, and plates, which are used as temporary support for damaged biological tissue or bone fractures [1].

ZK60 is an attractive option for biomedical applications due to its excellent biocompatibility, which means that it is well tolerated by the human body and does not cause adverse reactions. The biodegradability of ZK60 ensures that it does not pose long-term health risks and it can be gradually absorbed by the body, reducing the need for additional surgeries to remove it [2].

Despite the many desirable properties of ZK60, its high chemical reactivity and poor resistance to corrosion have limited its use in many applications. The high chemical reactivity of ZK60 means that it reacts readily with other substances, and it has poor resistance to corrosion in aqueous solutions, making it susceptible to galvanic corrosion. To overcome these limitations, researchers

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have been exploring various surface modification techniques to improve the corrosion resistance of ZK60 [3].

One promising approach is the use of Plasma Electrolytic Oxidation (PEO) process for electrochemical surface treatment. PEO is a process that creates a rough, hard, and dense ceramic coating on lightweight metal construction materials, such as magnesium. In addition, the PEO process provides increased resistance to wear and corrosion, thermal stability, dielectric properties, improved bioactivity, and biocompatibility suitable for medical applications [4]. The PEO process involves anodic electrochemical dissolution, the combination of metal ions with anions to form ceramic compounds, and spark-induced condensation on the substrate [5]. The PEO technology is used to apply ceramic coatings to ZK60 to improve its tribological properties and protect it from corrosion [6].

The performance of the coatings produced by the PEO process strongly depends on process parameters such as the chemical composition of the material, the current density and voltage of the PEO process, the conductivity of the cathode metal, the electrolyte used, and the pH of the electrolyte.

In conclusion, ZK60 is a promising material for use in the biomedical field due to its high mechanical strength, lightweight properties, and excellent biocompatibility. While its high chemical reactivity and poor resistance to corrosion limit its use in many applications, the use of PEO surface treatment and the combination of PVA polymer layer with PEO layering provide improved corrosion properties, making ZK60 a more suitable material for use in biomedical applications [4].

Material and Methods

The extruded magnesium alloy ZK60 was selected as the experimental material. The ZK60 experimental material was treated with plasma electrolytic oxidation (PEO) in an environmentally friendly electrolyte on the surface of the extruded magnesium alloy. Furthermore, the PEO-processed surface was treated with a water-soluble polymer coating PVA (polyvinyl alcohol + glycerin) to be applied on the resulting porous PEO layer, in order to achieve higher corrosion resistance of the biodegradable experimental material ZK60.

The elemental composition of the alloy is listed in Table 1, with the composition data based on the analysis using a hand-held X-ray analyzer type VANTA VCR with an SDD detector with GRAPHENE window.

Table 1. Chemical composition of extruded alloy ZK60

Elements	**Zn**	**Al**	**Fe**	**Ni**	**Cu**	**Zr**	**Mg**
[wt. %]	5.54	<0.01	<0.01	<0.01	<0.01	0.55	Bal.

The microstructure of the extruded alloy ZK60 was studied using a ZEISS AXIO Imager.A1m optical microscope. The preparation of metallographic samples for optical analysis was carried out on grinding papers with grits of P800 and P1200. In the next step, the samples were polished on a polishing plate with the simultaneous application of a diamond paste with a particle size of 1 and 3 microns. Then, the samples were rinsed with demineralized water, ethanol, and dried with airflow and etched with a solution of 2.1 g of picric acid, 2.5 ml of acetic acid, 35 ml of ethanol, and 5 ml of distilled water. The exposure time was 15 seconds (1).

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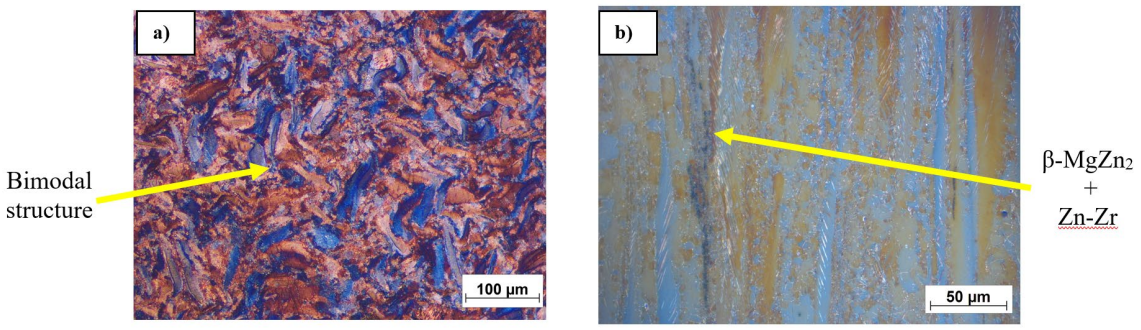

Fig.1. *Microstructure of Mg alloy ZK60: a) transverse section b) longitudinal section, etchant: picral, polarized light.*

The microstructure of extruded ZK60 alloy is shown in Fig.1, with a transverse section in (a) and a longitudinal section in (b). The polarized light method was used to observe the grain morphology. The structure is characterized by a bimodal grain morphology of deformed and fine grains, which is a typical result of the extrusion process [8]. The extrusion process usually takes place at a temperature of 400°C, near 0.56 times the melting temperature of the alloy (923 K). The grain size is not uniform and small grains can be seen between the larger grains. This is due to dynamic recrystallization that occurs during extrusion and results in the formation of fine-grained structures [8], [9]. The recrystallized grain size is estimated to be between 2-8 µm.

In the longitudinal section of the extruded ZK60 alloy, the grain orientation is along the extrusion direction (Fig.1b). The intermetallic compound β-$MgZn_2$ is visible as chains, as well as a small amount of Zn-Zr compound. These intermetallic particles may act as nucleation sites for dynamic recrystallization and prevent grain growth, leading to fine recrystallized grains near the intermetallic compounds [10].

The samples of extruded ZK60 alloy for potentiodynamic (PD) tests were ground on gridding papers with P1200 grain size. Similarly, samples of ZK60 alloy for the surface treatment PEO process were prepared. Keysight N8762A was used as the power supply source. The ZK60 sample was connected as the anode in a two-electrode system, with the cathode secured by a stainless steel plate. Both electrodes were placed in the PEO electrolyte, which was a solution of 12 g/l Na3PO4.12H2O and 1g/l KOH at room temperature (22 ± 1°C) and pH = 12.4. The electrolyte was continuously cooled with water and stirred up during the PEO procedure, both to improve the distribution of active ions and to maintain the temperature below 50°C. The current density was set to 0.05 A/cm^2 for 14 minutes [11]. After the PEO process, the samples were immersed into a polymer bath of PVA with glycerine solution. The corrosion resistance of ground samples of extruded ZK60 alloy and samples with PEO and PEO+(PVA+glycerin) layers were evaluated using potentiodynamic (PD) tests, which were performed on the SP-300 potentiostat with the samples placed in a corrosion cell at a temperature of 37 ± 2°C (Fig.30). The stable temperature was maintained using the Heating Bath Circulator.

The corrosive environment selected was a 0.9% NaCl solution, simulating the presence of chloride ions in a body environment with pH 6.8. Potentiodynamic polarization corrosion tests started after 1 hour of potential stabilization between the experimental sample and the 0.9% NaCl electrolyte being tested. The range of applied potential was from -200 mV to +500 mV, and the potential range was set with consideration for the open-circuit potential (OCP), and the scanning speed was 1.0 mV/s. The data obtained in the form of potentiodynamic curves were analyzed using the Tafel extrapolation method with the EC Lab V10.40 software. For statistical processing, three grounded samples ZK60, samples with PEO conversion layer, and samples after the PEO process with a created PVA+glycerin polymer coating were measured.

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Results and Discussion

The PEO process involves the application of high voltage and current between the electrode and the magnesium alloy, leading to the creation of a ceramic-like oxide layer on the surface of the metal. The SEM image of the PEO coating on the ZK60 biodegradable magnesium alloy (as demonstrated in Fig.2) reveals its visibly porous structure, with pore sizes ranging from 2-10 micrometers. This is a typical characteristic of the PEO process, as the formation of micropores is associated with the presence of molten oxides and gas bubbles produced during the discharges that occur on the surface of the samples.

This porosity is a result of the formation of oxide pores during the PEO process. The PEO process involves the application of high voltage and current, which releases oxygen from the electrolyte solution. This oxygen reacts with the magnesium surface to form oxide pores, resulting in a porous structure on the surface of the metal. The size of the pores depends on the process parameters, such as voltage and current, as well as the composition of the electrolyte solution [13].

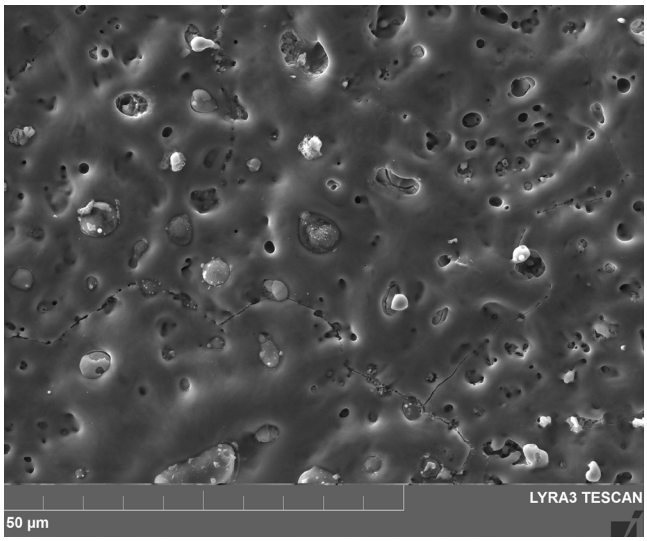

Fig.2. *Surface morphology of PEO coatings formed in phosphate-based electrolyte.*

It is important to note that the porous structure of the PEO-treated layer has both advantages and disadvantages. On one hand, the pores provide a large surface area for the adsorption of corrosion inhibitors, which can improve the corrosion resistance of the magnesium alloy. On the other hand, the pores can also act as corrosion initiation sites if not properly filled or sealed. In general, this porous structure can provide benefits such as improved corrosion resistance, enhanced surface hardness and wear resistance, and improved biocompatibility.

The potentiodynamic curves obtained for the grounded sample, the PEO treated sample, and the PEO+(PVA+glycerin) treated sample are shown in Fig.3. The electrochemical characteristics obtained from the Tafel analysis are listed in Table 2. We can observe from the potentiodynamic curves and the electrochemical characteristics that the corrosion potential of the ground sample, E_{corr}, was -1458 mV. The PEO and PEO+(PVA+glycerin) treated samples had slightly higher E_{corr} values compared to the ground sample, which indicating lower thermodynamic stability. However, the key factor for corrosion resistance is the kinetic aspect of the process, specifically the corrosion current density i_{corr}, which is directly proportional to the corrosion rate r_{corr}.The PEO coating achieved over 5 times lower corrosion rate (0.447 mm/year) compared to the ground surface (2.547 mm/year). An even more significant improvement in the corrosion rate was achieved with the PEO

coating in combination with the PVA+glycerin polymer coating, with the corrosion rate being 7 times lower (0.356 mm/year) compared to the grounded sample surface.

The results of electrochemical tests in 0.9% NaCl at a temperature of 37 ± 2°C showed that the sample treated with PEO showed significant improvement in corrosion resistance compared to the ground sample. However, when compared to a study [15] with the same electrical parameters (constant current density of 0.05 A/cm^2 and DC mode) and temperature conditions for PD tests (37 ± 2°C), the PEO layer or the PEO+PVA+glycerol composite layer on the ZK60 magnesium alloy showed slightly lower corrosion resistance. One possible explanation for this could be the extruded state of the sample, which had finer grains resulting in a higher density of grain boundaries, which can cause localized corrosion in Mg alloys. Despite this, the results of the PEO+PVA sample are promising as the goal is to slow down the degradation of the alloy, not to completely prevent it, so that the implants can be safely absorbed within an acceptable timeframe once they have served their purpose.

On the other hand, PD analysis showed that the porous structure of the PEO surface combined with the PVA+glycerol polymer coating had higher corrosion resistance compared to the pure PEO layer. Adding PVA to the PEO coating can fill its porous structure, potentially leading to improved corrosion resistance compared to the grounded P1200 sample and the PEO-only sample. This is based on the idea that filling the pores could prevent active surface exposure during corrosion and maintain the integrity of the PEO layer

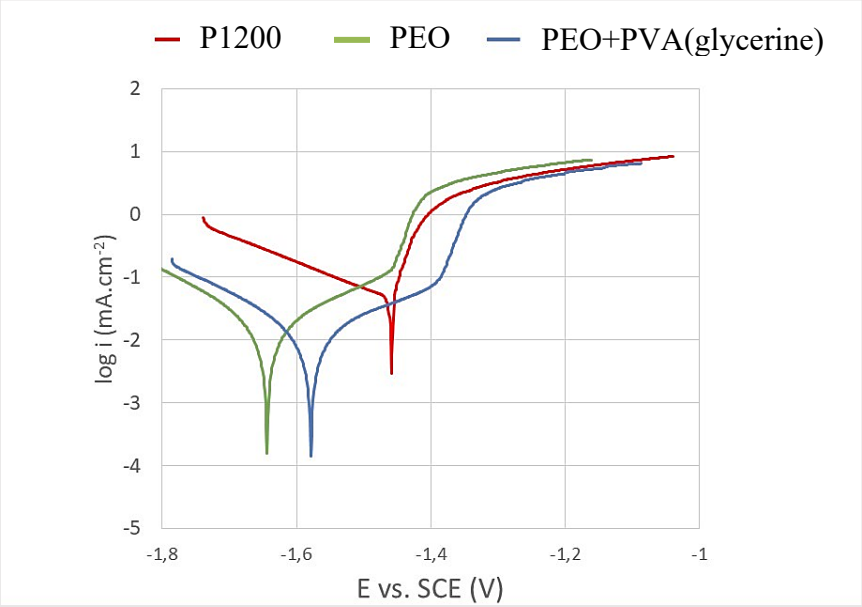

Fig.3. *Polarization curves for different surface treated samples measured in a 0.9% NaCl solution at a temperature of 37 ± 2 °C.*

Table 2. Determined electrochemical characteristics of the untreated and coated extruded ZK60 magnesium alloy.

	Ground P1200	**PEO**	**PEO+(PVA+glycerine)**
E_{corr} **[mV]**	-1458 ± 29	-1644 ± 35	-1578 ± 25
i_{corr} **[µA/cm^{-2}]**	111.7 ± 5.2	20.6 ± 1.8	15.9 ± 1.6
r_{corr} **[mm.yr^{-1}]**	2.547 ± 0.118	0.447 ± 0.039	0.356 ± 0.008

Conclusion

The results of potentiodynamic polarization confirmed the improved corrosion resistance of the PEO layer with the PVA+glycerine polymer coating compared to the grounded sample, with a significant reduction in corrosion current density (i_{corr} = 111.7 μA.cm^{-2} > 15.99 μA.cm^{-2}) in the case of the PEO-coated sample compared to the grounded sample (i_{corr} = 20.6 μA.cm^{-2}), leading to a similar reduction in corrosion rate for the sample treated with only the PEO process.

The created PEO layer achieved more than 5 times lower corrosion rate (0.447 mm/year) compared to the not treated grounded surface (2.547 mm/year), The PEO layer combined with the PVA+glycerine polymer coating achieved a significantly better corrosion rate, 7 times lower (0.356 mm/year) compared to the grounded surface of the sample.

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References

[1] Z. Sheikh et al. Biodegradable Materials for Bone Repair and Tissue Engineering Applications, Materials 8 (2015) 5744-5794. https://doi.org/10.3390/ma8095273

[2] N.T. Kirkland et al. Assessing the corrosion of biodegradable magnesium implants: A critical review of current methodologies and their limitations, Acta Biomater. 8 (2012) 925-936. https://doi.org/10.1016/j.actbio.2011.11.014

[3] J.Telegdi et al. Biocorrosion—Steel, In: Encyclopedia of Interfacial Chemistry, Surface Science and Electrochemistry, 2018, 28-42. https://doi.org/10.1016/B978-0-12-409547-2.13591-7

[4] T. Schilling et al. Cardiovascular Applications of Magnesium Alloys, In: M. Aliofkhazraei (Ed.) Magnesium Alloys, IntechOpen, 2017. http://doi.org/10.5772/66182

[5] S. Sikdar et al. Plasma electrolytic oxidation (PEO) process – processing, properties, and applications, Nanomaterials 11 (2021) art.1375. https://doi.org/10.3390/nano11061375

[6] H. Hu et al. Corrosion and Surface Treatment of magnesium alloys, In: M. Aliofkhazraei (Ed.) Magnesium Alloys, IntechOpen, 2017. https://doi.org/10.5772/58929

[7] N.T. Kirkland et al. In-vitro dissolution of magnesium-calcium binary alloys: Clarifying the unique role of calcium additions in bioresorbable magnesium implant alloys, J. Biomed. Mater. Res. Part B Appl. Biomater. 95 (2010) 91-100. https://doi.org/10.1002/jbm.b.31687

[8] B. Chen, J. Zhang. Microstructure and mechanical properties of ZK60-Er magnesium alloys, Mater. Sci. Eng. A 633 (2015) 154-160. https://doi.org/10.1016/j.msea.2015.03.009

[9] J. Chen et al. Effect of heat treatment on mechanical and biodegradable properties of an extruded ZK60 alloy, Bioact. Mater. 2 (2017) 19-26. https://doi.org/10.1016/j.bioactmat.2016.12.002

[10] Y. Xue et al. Corrosion Protection of ZK60 Wrought Magnesium Alloys by Micro-Arc Oxidation, Metals 12 (2022) art.449. https://doi.org/10.3390/met12030449

[11] D. Kajanek et al. Effect of applied current density of plasma electrolytic oxidation process on corrosion resistance of AZ31 magnesium alloy, Commun. – Sci. Lett. Univ. Zilina 21 (2019) 32-36. https://doi.org/10.26552/COM.C.2019.2.32-36

[12] F. Pastorek et al. Corrosion behaviour of preserved PEO coating on AZ31 magnesium alloy, Commun. – Sci. Lett. Univ. Zilina 23 (2021) B76-B88. https://doi.org/10.26552/COM.C.2021.2.B76-B88

[13] B. Hadzima. Korózia zliatin Mg-Al-Zn., Ph.D. thesis, Žilinská univerzita v Žiline, Žilina, 2003. [Online]. Available from: http://katalog.utc.sk/ukzu/epubl/ddz-Hadzima-KoroziaZliatinMg-Al-Zn-low.pdf

[14] Z. Shi et al. Measurement of the corrosion rate of magnesium alloys using Tafel extrapolation, Corros. Sci. 52 (2010) 579-588. https://doi.org/10.1016/j.corsci.2009.10.016