

# Physical and Chemical Characterization of the Magnesium Surface Modified by Plasma Electrolytic Oxidation – Influence of Immersion in Simulated Body Fluid

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**Abstract**—Pure magnesium (Mg) degrades very quickly and uncontrollably upon contact with water. It also oxidizes in the air. Plasma electrolytic oxidation (PEO) is a promising method for surface modification of metal alloys, which can contribute to controlling corrosion of Mg. Additionally, modifications with the PEO lead to the formation of mesoporous topography and changes in physical and chemical properties of Mg surfaces, e.g., their wettability, and to increase in their surface area. Our project aimed at modification of surfaces of Mg implant by the PEO method using silicate-based bath electrolyte in order to enhance resistance to corrosion, biocompatibility, and antibacterial properties of the implants. The use of silicate in the PEO bath electrolyte leads to changes in the surface morphology. The obtained surface layers acquire rich morphology with pores and craters of various sizes. This substantially increases the total surface area and change wettability. In addition, the formation of silicate oxide layers provides protection from corrosion and can lead to an improvement in the long-term stability of implants.

**Keywords**—Mg, Plasma Electrolytic Oxidation, bath electrolyte, silicates, corrosion resistance, bioactive surface.

## I. INTRODUCTION

Bioresorbable materials have to possess certain criteria for biomedical application, such as porosity, the ability for biodegradation, biocompatibility, resistance to the formation of bacterial biofilms, and mechanical properties. Mg-based materials are widely used in medicine for various orthopedic and maxillofacial surgeries due to their appropriate mechanical characteristics, biodegradation and solubility in physicochemical fluids [1,2].

The magnesium-based implants corrode *in vivo* as a result of the biological response on the implant-tissue interaction [3]. Unfortunately, this electrochemical reaction leads to producing of magnesium hydroxide and the release of hydrogen gas [4]. The released metallic ions are generally considered to be physiologically harmless as they can be utilized by the surrounding tissues [5]. However, a rapid degradation of magnesium-based implants can seriously influence their mechanical characteristics and negatively

affect the healing process in both hard and soft tissues [6]. Therefore, the development of *in vivo* applications of magnesium and its alloys requires more research on corrosion resistance of magnesium in aqueous solutions.

Alloying with various elements (Mg–Ca, Mg–Zn, Mg–Sr, and Mg–Ag) can be used to raise the corrosion resistance and to control the degradation rate of magnesium-based implants in aqueous solutions, as well as to preserve their mechanical strength and diminish their side effects [7].

Progressive improvements of magnesium corrosion resistance via the formation of surface coatings by plasma electrolytic oxidation have been suggested. The ceramic-like oxide coating formed during the PEO is firmly attached to the substrate and protects magnesium-based implants from a corrosive attack *in vivo* [6]. The properties of the layers attained with the PEO process can be modified by electrical parameters, the composition of the bath electrolyte, the material of the substrate, and duration of the coating process [8, 9].

Bath electrolytes based on potassium and/or sodium hydroxide with additions of phosphates and/or silicates, potassium fluoride, sodium fluoride, and sodium aluminate have been used for the PEO coating process on Mg alloys [10]. The influence of the electrolyte additives on the microstructure and morphology of the coatings has been intensively investigated. However, conditions during the PEO coating process commonly diverge in various sources [11] and still require further clarifications.

Therefore, we set up a study to examine the chemical composition, surface morphology, and corrosion resistance of the PEO treated magnesium alloys depending on the inclusion of various types of alkaline additives into the silicate-based bath electrolyte.

## II. MATERIALS AND METHODS

### A. Materials and Plasma Electrolytic Oxidation

$\text{Na}_2\text{SiO}_3$ ,  $\text{NH}_4\text{F}$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{HPO}_4$  were purchased from Sigma-Aldrich (St. Louis, MO, USA). Magnesium samples ( $1 \times 1 \times 1 \text{ cm}$ ) were polished with graded SiC papers, ultrasonically cleaned in acetone, and quickly rinsed in distilled water. The electrolyte composition and the corresponding identification codes of the samples are represented in Tab. 1.

TABLE I. SAMPLES CODES AND THEIR RESPECTIVE BATH ELECTROLYTE COMPOSITIONS DURING THE PEO PROCESSING

Sample code	Composition of the bath electrolyte
Bath electrolyte 1 (sample S1)	10g/L $\text{Na}_2\text{SiO}_3$ + 5g/L $\text{NH}_4\text{F}$ + 10g/L $\text{NaOH}$
Bath electrolyte 2 (sample S2)	10g/L $\text{Na}_2\text{SiO}_3$ + 5g/L $\text{NH}_4\text{F}$ + 10g/L $\text{Ca}(\text{OH})_2$

The PEO was done under an impulse current density of  $0.1 \text{ A cm}^2$  with the final voltage of up to 250 V for 10 min. The surface area of the treated samples was equal to  $1 \text{ cm}^2$ . The specimens were washed with deionized water three times.

### B. SBF Immersion Test

The corrosion resistance of obtained coatings was evaluated in a simulated body fluid (SBF) immersion test. The composition of the SBF is described elsewhere [2]. Samples were immersed in 50 mL of SBF solution (pH 7.4) for 3, 3, 7, and 63 days at  $37^\circ\text{C}$ . The solution was refreshed every two days. After each period, the samples were removed from the solution, washed in distilled water, and dried in air to reach constant weight. The corrosion rate was evaluated by measurements of weight loss. The samples were weighed before the test and after each period of immersion. The weight loss value was calculated as follows:

$$(m_0 - m_1/m_0) \times 100 = \omega(\%) \quad (1)$$

$m_0$  – initial weight,  $m_1$  – weight after immersion test.

### C. Scanning Electron Microscopy

Scanning electron microscope SEO-SEM Inspect S50-B (FEI, Brno, Czech Republic) was used to characterize the surface morphology of the PEO anodized samples. The pore size distribution was evaluated by ImageJ 1.50c software (<https://imagej.nih.gov/ij/>). The chemical composition of the surface layers was evaluated by an energy-dispersive X-ray spectrometer AZtecOne with X-MaxN20 detector (Oxford Instruments plc) attached to the SEM. The data of surface chemical composition were collected before and during the immersion test.

### D. Measurement of Roughness of the PEO Surfaces

Surface roughness and wear profile are crucial components of the overall characteristics of the surface morphology of metals. In our study, we measured the following roughness parameters: the arithmetic mean of the sum of the roughness profile values ( $R_a$ ) and ten-point height ( $R_z$ ) values. The digital data was obtained using a surface roughness tester (Surftest SJ-301, Mitutoyo, Kawasaki, Kanagawa, Japan). The multiplicity of the reconciliation step was 10 mm.

### E. Measurement of Contact Angle

Hydrophilicity and wetting properties of the surfaces were determined based on the measurements of the contact angle (CA) with water droplets. The experiments were performed using a video-based optical contact angle measuring instrument OCA 15 EC, Series GM-10-473 V-5.0 (Data Physics, Filderstadt, Germany). An average value for the contact angle was determined by measuring five different spots for each sample.

## III. RESULTS AND DISCUSSION

The PEO coatings of treated samples acquired rich morphology with different porous structures (Fig. 1). The surface morphology of the sample S2 was more rough and porous. The oxide layer displayed a crater-like microstructure with a pore size of up to  $7 \mu\text{m}^2$ . During the PEO process, pores tend to fuse, leading to gap formation. The distinguishing feature of the S1 coating was a more uniform crater-like layer and pore size of up to  $1 \mu\text{m}^2$ . Micro-cracks are not detected on either surface.

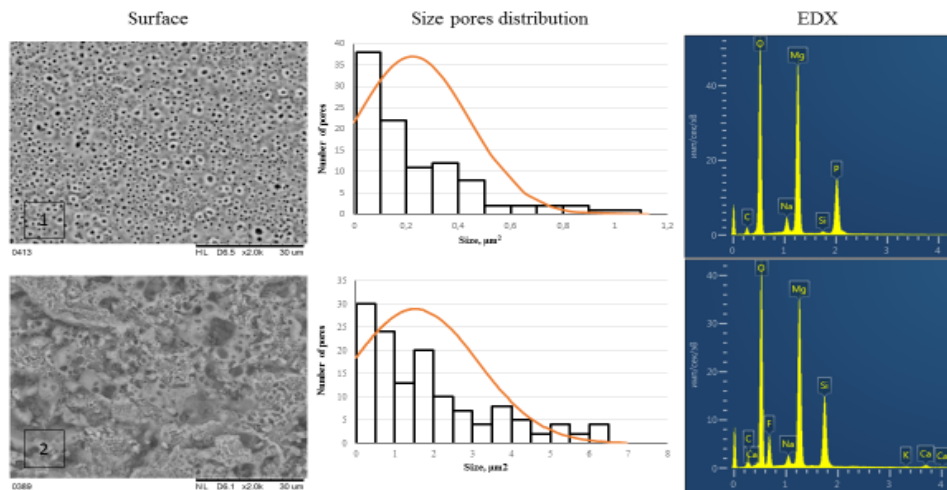


Fig. 1. Analysis of morphology and chemical composition of the surfaces by SEM. Left panels, SEM images of samples anodized at 250 V in silicate based bath electrolytes 1 and 2; middle panels, distribution of pore sizes; right panels, mapping of EDX spectra with analysis of the elemental composition of the sample surfaces.

The elemental composition of the surface coatings was evaluated using EDX mapping (Fig. 1). It revealed that Mg and O represent the bulk volume of the coatings. A massive presence of O confirmed the oxide character of the surface layers. The low concentration of Ca and Na indicated the lack of influence of impurities in the chemical composition of the coatings.

The roughness profile ( $R_a$ ) and ten-point height ( $R_z$ ) of the PEO coatings are presented in Tab. 2. The  $R_a$  and  $R_z$  values increase when Ca is added to the electrolyte as compared to Na. Such a high roughness index is due to arcing on the surface, which leads to the appearance of discharge channels and larger craters. Due to this, it is possible to draw a conclusion that the thickness of the oxide layer in the samples for bath electrolyte 2 is higher. The pronounced mesoporous surface structure leads to an increase in the total surface area. This, in turn, can promote better adhesion of biological structures to the modified surfaces.

TABLE II. AVERAGE ROUGHNESS AND CA OF THE PEO COATINGS FORMED ON MG IN SILICATE BASED BATH ELECTROLYTES

Sample	$R_a, \mu m$	$R_z, \mu m$	CA
S1	0.39±0.01	2.83±0.13	22.7 °
S2	1.67±0.08	11.6±1.24	16.62 °

Hydrophilicity or hydrophobicity is one of the important physicochemical properties of hard surfaces. The conditional line of demarcation of the level of wetting is the numerical value of the contact angle, namely, higher (hydrophobic) or lower (hydrophilic) than 90 degrees. Modification of magnesium samples in silicate electrolytes led to an improvement in the wettability of the surfaces, which allowed the water droplet to easily wet the surface and to quickly penetrate into the coating. The static contact angles (22.7 and 16.62 degrees) indicated that the surfaces of both silicate containing oxide coatings exhibited hydrophilic

properties. Notably, the PEO in bath electrolyte 2 provided better hydrophilicity. This suggests that the PEO modified surfaces show signs of biocompatibility, as they can promptly interact with water-based biological fluids.

The corrosion resistance of the experimental magnesium samples was examined after immersion in the simulated body fluid for various incubation times. Corrosion resistance was evaluated based on the measurement of the weight loss of the samples and the EDX analysis of the surfaces. The sample obtained in the PEO with the bath electrolyte 1 loosed 6.2% of its weight after 63 days of immersion in SBF, while the sample with the bath electrolyte 2 loosed only 4.88% of its weight. The dynamics of weight change per day is presented in Tab. 3.

TABLE III. WEIGHT LOSS OF THE SAMPLES WITH THE PEO COATINGS FORMED ON MG IN SILICATE-BASED BATH ELECTROLYTES AFTER IMMERSION TEST IN THE SBF

Sample	1d, %	3d, %	7d, %	63d, %
S1	0.33	-0.32	-0.24	-6.20
S2	0.44	-0.36	-0.24	-4.88

Elemental analysis by the EDX on the PEO surfaces after 1, 3, 7, and 63 days of immersion test is presented in Tab. 4. After the first day of the SBF immersion test, the bulk volume of the coatings was represented by both Mg, and O. Massive presence of O confirmed the oxide character of the surface. Both Si and F were incorporated from the components of the bath electrolytes (see Tab. 1). It is of note that the presence of these elements was more intense for the sample S2. Low concentrations of Ca and Na indicated the relative purity of the chemical compounds used. This pointed to the effect of  $Ca(OH)_2$  in the bath electrolyte 2 and further emphasized the diverse nature of the coatings obtained in different bath electrolytes. The content of both Si and F decreased after 7 days into the SBF immersion test.

TABLE IV. SEMI-QUANTITATIVE EDX ANALYSIS OF THE MAGNESIUM SAMPLES AFTER THE CORROSION TEST IN THE SBF SOLUTION

Bath electrolyte 1								
Days/%	O	Mg	Si	F	C	Na	Ca	P
0	46.89	27.54	8.74	5.02	9.99	1.48	0.20	-
1	54.99	16.50	2.69	2.83	7.06	0.30	6.98	8.56
3	55.17	12.86	1.02	5.4	7.69	0.45	7.88	9.52
7	57.24	10.29	0.27	-	4.89	1.38	11.67	13.82
63	60.25	7.29	-	-	6.48	1.94	12.17	11.87
Bath electrolyte 2								
Day/%	O	Mg	Si	F	C	Na	Ca	P
0	45.49	21.11	10.24	9.08	12.07	1.24	0.67	-
1	41.25	20.36	15.61	17.40	8.48	0.4	2.75	-
3	40.82	18.99	4.34	18.29	8.43	0.22	4.06	4.85

Bath electrolyte 1								
7	56.80	8.41	-	-	4.30	1.38	13.61	15.14
63	54.49	8.50	-	-	10.20	1.21	13.21	12.39

A reduction in the content of Mg and an increase in the content of O had a similar tendency in both cases. The rise in the content of Ca could indicate possible depositions on the PEO surfaces in simulated body environments.

### CONCLUSIONS

The PEO coatings in both versions of the experimental surfaces are presented as relatively homogeneous oxide layers. The mesoporosity of the surface appears in a variety of forms, with minimal pore size for the bath electrolyte 1 and much larger pores for the bath electrolyte 2. Both PEO surfaces are highly hydrophilic. The PEO in the bath electrolyte 2 gives better corrosion resistance. The obtained results call for further investigation of the PEO coatings on Mg specimens in *in vitro* and *in vivo* studies, in particular, to determine the level of their cytotoxicity and possible antibacterial effects.

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