INFLUENCE OF SILICATES AND PHOSPHATES ANIONS ON THE FORMATION OF CERAMIC COATINGS ON MAGNESIUM

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Abstract

Magnesium and its alloys are promising materials for temporary biomedical implants due to their properties that resemble bone tissue; however, low corrosion resistance hinders their clinical application. Surface engineering, particularly through oxide ceramic layers, offers a viable solution to enhance wear and corrosion resistance, thereby improving biocompatibility. Plasma electrolytic oxidation (PEO) was applied to modify pure magnesium samples using sodium silicate electrolytes with different types and concentrations of phosphates. Multiple characterization techniques were used for surface analyses, including SEM, EDS, contact angle measurements, and profilometry. The results delineate the influence of electrolyte composition and applied voltage on coating thickness, pore size, and elemental incorporation. The PEO coatings exhibited porous structures with diverse pore sizes, influenced by the electrolyte composition and voltage. Morphological analysis revealed a scaffold-like surface structure with spherical and irregularly shaped pores. Elemental analysis confirmed the uniform incorporation of Si and P into the coatings. Anionic interaction played a significant role in forming the oxide layer, which is crucial for potential biomedical application. The study highlights the varied thickness levels and quality of PEO coatings, influenced by electrolyte composition and applied voltage. Coatings from a C4 electrolyte showed higher P and Si contents and the C4 electrolyte at 250 V demonstrated favourable characteristics, positioning them as promising candidates for biomedical applications on biodegradable magnesium alloys.

Keywords: *biodegradable magnesium implants, PEO coating, phosphate, silicate, biocompatibility*

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Introduction

Magnesium is typically preferred for applications as temporary biomaterials. This material has the advantages of degradability, elastic modulus, and density similar to that of bones [1,2]. The main obstacles to magnesium and magnesium alloy in clinical application are low corrosion resistance, high hydrogen release rate, and high solution alkalinity [3].

Non-metallic coatings, in the form of oxide ceramic layers, are a modern engineering solution to improve the temporary metal biomaterials' wear resistance or corrosion resistance [4,5]. Non-metallic coatings also show significant prospects in the functionality of the surface. There are several methods to form oxide ceramic coatings. For example, coatings may be formed by deposition from precursor oxides, by brushing, spraying, or condensation from a vapour or liquid phase, or by thermal or electrochemical conversion of a portion of the surface of the metal substrate into an oxide. The presented deposition coating techniques allow the use of a wide range of oxide materials but do not always provide good coating adhesion, uniformity, and surface finish [6-8].

In recent years, plasma electrolytic oxidation has received growing attention due to the unique possibilities of forming a porous outer surface layer on metallic materials [3]. The properties of such ceramic layers are thicker, denser, and more complicated than other surface engineering techniques [1,9]. Moreover, the PEO coating has untapped potential to improve the material's surface properties, especially in biofunctionalization. Using the electrolyte's type and concentration profoundly affects the coating's properties. Therefore, proper treatment can enhance corrosion resistance, wear resistance, and surface bioactivity. There are many variants of the electrolyte composition for Mg-based materials. Some of the most reported compounds used for Mg coatings are based on inorganic additives, such as silicate, aluminate, phosphate, and fluoride ions [3,10]. Phosphate-based electrolyte composition seems to be the best choice for orthopaedic implants because phosphates are essential for bone regeneration [11]. Silicate sodium electrolyte is beneficial for developing uniform and compact anodic coatings. On the other side, phosphates accelerate dielectric discharges and promote the rapid growth of PEO coating. The alkaline environment serves to promote electrolytic conductivity and to adjust pH [12]. Although much research has been conducted to investigate the effect of silicates and phosphates on PEO coatings, few publications have investigated the mechanism of anion interaction [1,12].

The novelty of this research can be found in using specific optimized process parameters (chemical composition of the electrolyte and applied energy input) from our previous studies [13]. Therefore, our research aims to understand the comprehensive interactions between silicate and phosphate anions and the surface properties of magnesium implants following plasma electrolytic oxidation (PEO) in the context of biomedical applications.

Materials and Methods

The pure Mg (99.99%) was obtained from Polmag (Kędzierzyn-Koźle, Poland). Sodium silicate - Na_2SiO_3, Na_2HPO_4, NaH_2PO_4 and sodium hydroxide - NaOH were purchased from Sigma–Aldrich (St. Louis, MO, USA). Pure magnesium cubes with 1x1x1 cm size were used as the substrate for plasma electrolytic oxidation (PEO). The sample surfaces were prepared by grinding with SiC paper up to a #1000 grade, followed by rinsing with deionized water and propanol, and then drying in air. Before the PEO treatment, the samples were immersed for 10 s in 20% HNO_3 to remove oxide layers and washed with distilled water.

TABLE 1. Chemical composition of the PEO bath electrolytes.

Electrolyte	Na_2HPO_4 [g·dm^{-3}]	NaH_2PO_4 [g·dm^{-3}]	$Na_2SiO_3·5H_2O$ [g·dm^{-3}]	NaOH [g·dm^{-3}]	H_2O [dm^3]
C1	10	-	10	5	1
C2	5	-	10		
C3	-	5	10		
C4	-	10	15		

TABLE 2. Description of samples and process parameters; j = 100 mA cm^{-2}, t = 180 s.

Sample no	Electrolyte	Voltage [V]
C1 200	C1	200
C1 225		225
C2 200	C2	200
C3 200	C3	200
C3 250		250
C4 250	C4	250

The PEO process was conducted in a plastic, externally cooled electrolyzer (500 cm^3) fitted with a titanium cathode ring and a magnetic stirrer. The process was realized in electrolytic baths (TABLE 1) maintained at 10°C by an automated cooling system during the coating process. Anodic oxidation was performed under an impulse current until a fixed voltage was reached, facilitated by a high-voltage power supply (PWR 800H, Kikusui, Japan). The PEO process was accomplished under a limiting anodic current density of 100 mA·cm^{-2} and voltage (TABLE 2). The treatment time (t) was set to 180 s. The process parameters and samples labelling are presented in TABLE 2.

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDS) were applied to characterize the morphology and elemental composition of the modified magnesium samples (Hitachi TM-3000, accelerating voltage = 15 kV, BSE mode; Phenom-World BV, Eindhoven, The Netherlands at an accelerating voltage of 15 kV, BSE mode; EDX spectroscopy was performed using Phenom-ProX equipment). The size of the pores was calculated using Image J software [14]. Cross-sectional analysis was used to evaluate the structure and thickness of the PEO coating layer, following the methodology outlined in our previous publication [13]. The wettability of the surfaces was investigated through static contact angle (CA) measurements. These experiments were conducted using a video-based optical contact angle measuring instrument (OCA 15 EC, Data Physics, USA). The CA value was recorded for ultrapure water for at least three parallel measurements. Contact profilometry (Surftest SJ-301, Mitutoyo, Japan) was used to describe the macroscopic roughness of the modified surfaces of the Mg samples. The 2-D roughness is described in the Ra values. 4 mm-long sections of the surface were measured at least 3 times for 3 samples.

Results and Discussions

Phosphate-containing electrolyte formulations were used for fabricating PEO coating, aiming to design a ceramic layer and control the coating properties. The surface morphology of PEO coatings has typical porous structures with a variable diameter of pores (FIG. 1).

SEM images show the net-like (scaffold-like) surface morphology of the PEO coatings formed on the magnesium substrate. This morphology, characterized by a microstructured network of pores, is commonly observed in PEO coatings deposited on magnesium in a silicate electrolyte [15,16]. Most of the pores were spherical; however, some irregularly shaped and lenticular pores were also observed [17].

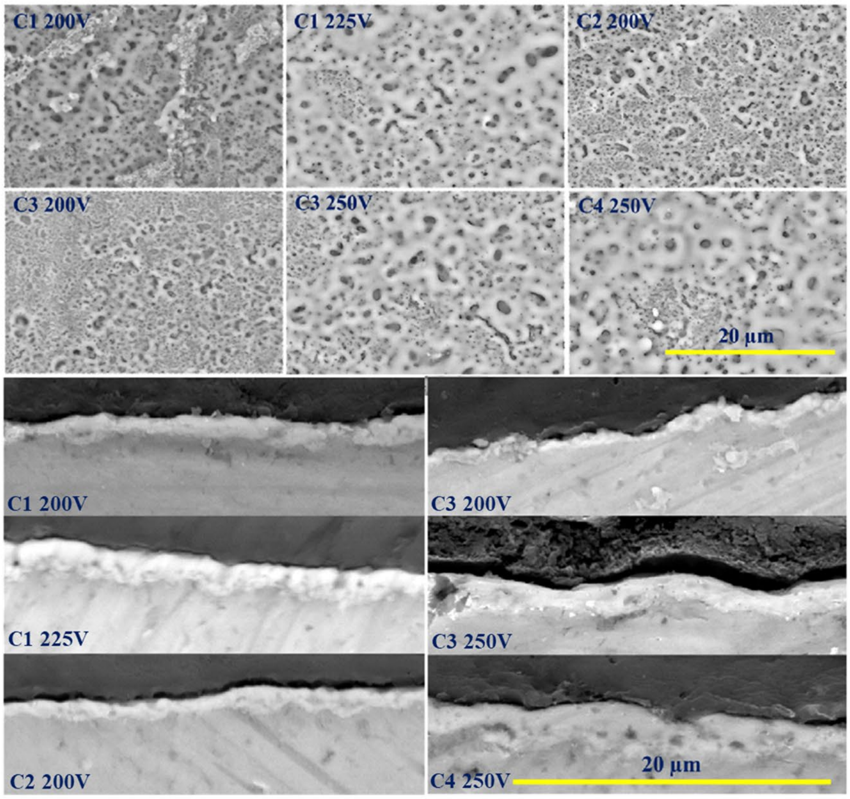

FIG. 1. Surface (upper) and cross-section (lower) morphology of the PEO coatings.

TABLE 3. Average pore area of PEO coatings [μm^2].

C1 200V	C1 225V	C2 200V	C3 200V	C3 250V	C4 250V
0.07 ± 0.012	0.13 ± 0.33	0.05 ± 0.11	0.04 ± 0.11	0.08 ± 0.24	0.1 ± 0.21

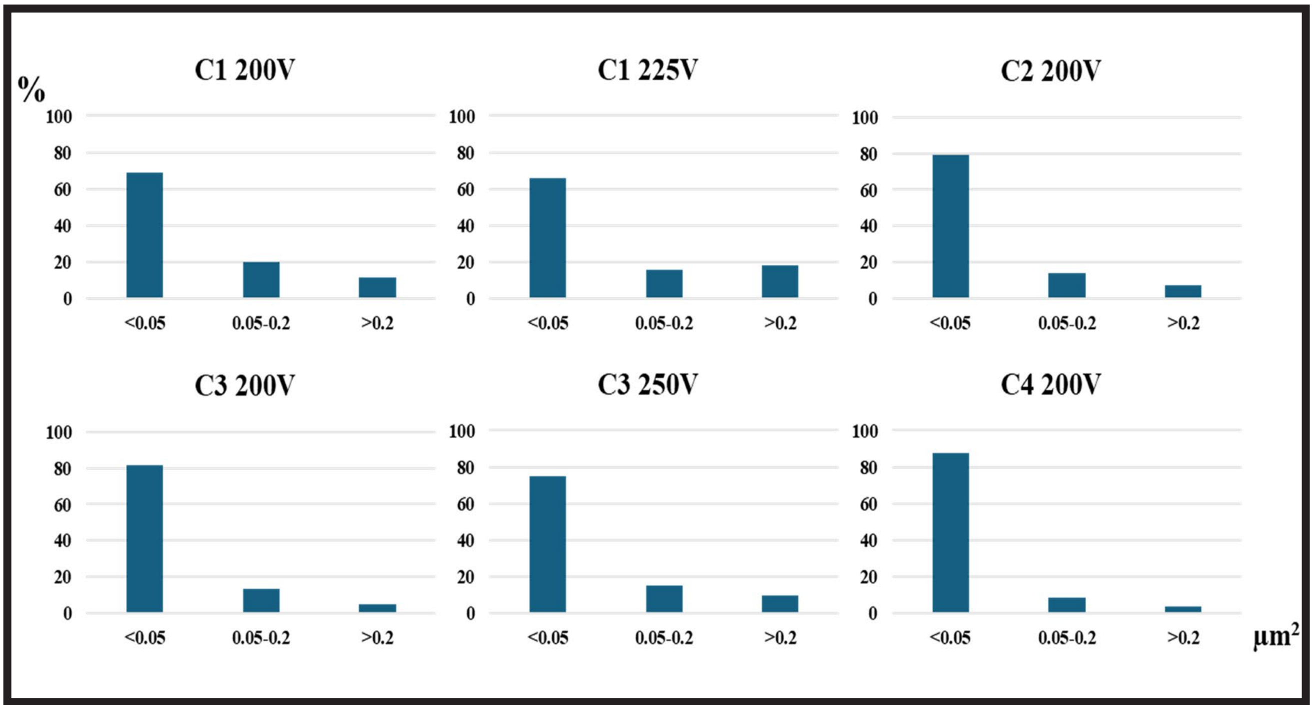

FIG. 2. Pore area distribution as a function of the applied voltage and the type of electrolyte [μm^2].

To better understand the surface characteristics of PEO coatings obtained from different electrolytes, the average pore size was estimated for each type, and the obtained results are summarized in TABLE 3. The anodized surfaces exhibit a characteristic of dispersed pores, ranging in areas from nanometers to 0.13 μm^2 (TABLE 3, FIG. 2). The formation of micropores, with areas ranging from 0.05–0.5 μm^2, occurs as a result of continuous discharges and the breakdown of the coating layers during the oxidation process, along with the escape of entrapped gases from the discharge channels [18,19]. Coatings produced under higher voltage conditions display a more uniformly distributed pore pattern. There was no observable variance in the pore size as a function of the applied voltage. As illustrated in FIG. 1, micropores are not evenly distributed throughout the ceramic coating, ending in micro-pore walls. This is detrimental to corrosion protection but could be beneficial in orthopaedic applications by promoting cell adhesion and osseointegration [18].

The chemical nature of PEO coating depends on the substrate and the electrolyte type, and the species in the electrolyte. The coating formation process consists of magnesium cations diffusing out from the substrate and reacting with ions forming a ceramic coating (TABLE 4). The PEO coatings revealed the presence of Mg, P, Si, O, and Na. A significant amount of O confirmed the oxide character of the surface layers. The low concentration of Na indicated the lack of influence of impurities in the chemical composition of the coatings. Silicate and phosphorus were integrated into the layers from the electrolyte bath. The coating formed in the C4 electrolyte exhibits a higher concentration of P and Si compared to the other coatings, which can be related to the higher concentration of silicate. As previously discussed, plasma electrolyte oxidation is a process in which the substrate's elements and the electrolyte bath play a significant role in the formation of an oxide coating. Inorganic phosphates have been widely used as the main electrolyte in biological applications to provide sufficiently bioactive phosphorus [20]. So, it is clear that phosphates and silicon elements from the electrolyte have been involved in the formation of this oxide layer [21].

EDS maps were also performed to identify the element distribution of the obtained coatings. Si and P were detected in all coatings, indicating that these elements are uniformly incorporated into the coating (FIG. 3). A pronounced layer of phosphate and silicate elements can be detected at all coatings' substrate/coating interfaces. Based on the EDS results (TABLE 4), it can be observed that the content of P and Si increased after applying high voltage.

TABLE 4. Semi-quantitative EDS analysis of the surface of PEO coatings fabricated on magnesium in different electrolytes [at.%].

Type of coating	Mg	O*	Si	P	Na
C1 200V	39.34	52.61	4.39	2.79	0.87
C1 225V	35.50	57.38	5.27	3.56	1.30
C2 200V	42.89	51.12	4.42	1.41	0.16
C3 200V	42.42	51.53	1.74	0.28	0.28
C3 250V	29.28	60.11	6.56	2.97	1.08
C4 250V	24.85	61.30	8.15	3.94	1.76

* the values are to be regarded as only informative

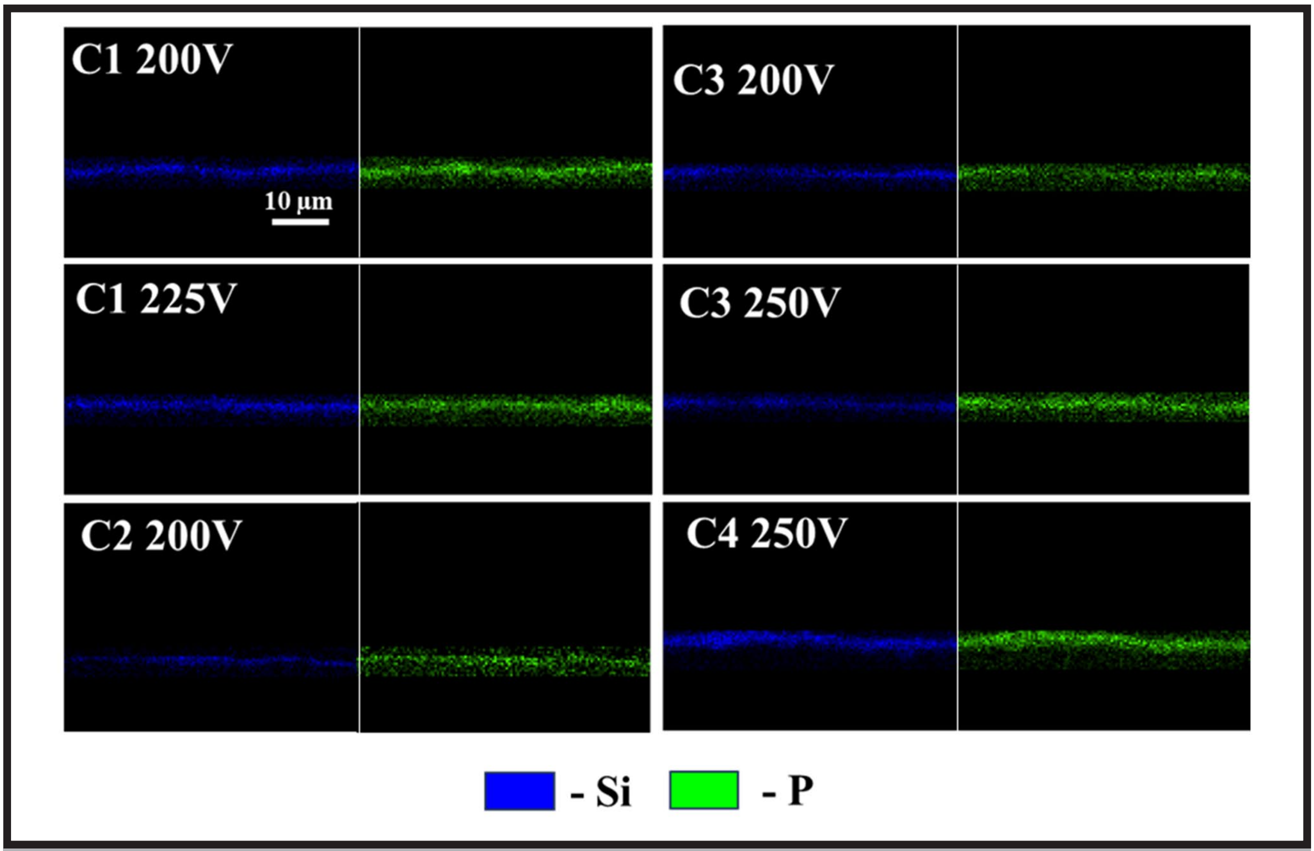

FIG. 3. Cross-section elemental distribution map of PEO coatings.

In forming the PEO coating, the substrate of Mg is chemically transformed into its oxide. The coating grows simultaneously inwards and outwards from the bulk metal surface (FIG. 1). Since no discontinuities are observed between the coatings and the substrate, the coating adheres well to the substrate [21]. The thickness of the prepared PEO coatings was measured using cross-sectional observations (TABLE 5). A key feature is that the coatings demonstrate a significant difference in thickness [22]. As seen from the cross-section, the coatings became thicker in the presence of high voltage. Moreover, high voltage influences the formation of a relatively compact and porous inner region for C1 225V, C3 250V, and C4 250V. Commonly, surface roughness increases with thickness due to the large channels remaining from single sparking. However, this tendency is characterized only for C4 coating. The C1, C2, and C3 coatings reveal the same Ra values despite their different thicknesses. Wettability is one of the important physicochemical properties of hard surfaces. Modification of magnesium samples in the proposed electrolytes resulted in enhanced hydrophilicity of the surfaces, facilitating the penetration of water droplets into the coating. The static contact angle for PEO coatings showed wettability in the range between 21° and 33°. The obtained results indicate that the surfaces of PEO coating in the sodium silicate-, phosphate-based electrolyte demonstrate characteristics indicative of biocompatibility (TABLE 5). The presence of silicates and phosphates in the electrolyte improved the wettability of the coatings.

TABLE 5. Wettability, roughness measurements, and thickness of the obtained PEO coatings.

Type of coating	CA [°]	Ra [µm]	Thickness [µm]
C1 200V	33 ± 5	0.28 ± 0.03	1.3 ± 0.3
C1 225V	25 ± 7	0.28 ± 0.02	1.7 ± 0.4
C2 200V	31 ± 4	0.26 ± 0.02	1.1 ± 0.3
C3 200V	30 ± 5	0.25 ± 0.01	1.1 ± 0.3
C3 250V	21 ± 3	0.34 ± 0.02	1.8 ± 0.4
C4 250V	31 ± 4	0.4 ± 0.04	2.2 ± 0.53

PEO offers distinctive opportunities for the production of protective ceramic oxide coatings. The essential characteristics of such coatings for degradable materials involve a porous morphology. The chemical composition is also the most important factor affecting the biodegradability process. Silicate-based electrolytes are commonly employed in PEO processing due to the stability and hardness of the resulting coatings. Additionally, the coexistence of silicates and phosphorous improves the cytocompatibility of the coatings, as reported in previous research [23]. From this investigation, it was understood that it is possible to obtain a compact, thick, Si- and P-containing PEO coating on magnesium. Even though the pore morphology was similar, samples C1 225V, C3 250V, and C4 250V looked finished. In the cross-section, these coatings are characterised by a compact and porous layer. The combination of solution composition and treatment parameters yielded promising properties for the PEO coatings. In summary, silicate significantly influences the PEO process. According to the literature data, silicate increases the electrolyte conductivity which enhances micro-discharge intensity by injecting electrons to the conductive band of the growing oxide [24]. Strong micro-discharges can promote electrolyte diffusion and Si and P incorporation in the inner part of the coating. Obtained results allow to extend the PEO treatment and the subsequent investigations on potential biodegradable alloys for possible applications as bioimplants.

Conclusions

The plasma electrolytic oxidation (PEO) of magnesium alloy in a silicate-based electrolyte containing varying types of phosphate can yield coatings of different thickness levels under similar processing conditions. Changes in voltage influenced the quality of the ceramic-like coatings. Coatings produced in a C4 electrolyte contained higher amounts of P and Si. The electrolyte composition and applied voltage have a combined effect on the thickness and quality of the final PEO layer. The C4 samples processed at 250V represent a promising candidate for integration in biodegradable magnesium alloys for biomedical applications.

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