



Surface characterisation of Ti–15Mo alloy modified by a PEO process in various suspensions



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ABSTRACT

This paper reports on the surface modification of a Ti–15Mo alloy by plasma electrolytic oxidation (PEO). This process was carried out in solutions of 0.1 M $\text{Ca}(\text{H}_2\text{PO}_2)_2$ with various concentrations of tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), wollastonite (CaSiO_3), or silica (SiO_2) using voltages of up to 350 V. The surface microstructure (SEM, cross-section of coating), roughness and chemical composition (energy-dispersive X-ray spectroscopy, thin layer X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy) of the porous oxide layers were investigated. The concentration of powder added to the solution changed the chemical composition and morphology of PEO coatings on the Ti–15Mo alloy surface. Calcium and phosphorous compounds were detected in the coatings formed on the substrate by the PEO process at 300 V.

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1. Introduction

Titanium and its alloy Ti–6Al–4V are widely used in biomedical applications. Titanium materials exhibit corrosion resistance and favourable biocompatibility with natural bone [1–3]. Moreover, cell growth and differentiation are observed on the Ti surface. As vanadium and aluminium are toxic [4], vanadium and aluminium-free titanium alloys have been investigated as alternative materials, including Ti–15Mo, Ti–13Nb–13Zr, Ti–18Nb–13Zr, Ti–5Al–2.5Sn, Ti–35Nb–5Ta–7Zr, and Ti–8Nb–13Zr [5,6]. Surface modification is necessary to make titanium alloys biologically active. Many studies have been conducted to develop materials for long-term implantation in the human body [7].

Plasma electrolytic oxidation (PEO) is one effective method used to modify the surfaces of self-passivating metals (Ti, Mg, Al, Zr, and Ta) and their alloys. Coatings formed on the substrate during the process can be enriched by compounds from the solution. During the first

stage of PEO treatment, a barrier oxide film is formed on the surface. When the voltage increases and spark discharges occur, the oxide film breaks down locally and a porous structure is formed (second stage). Depending on the surface, the growth of appropriate oxides is observed. The coatings obtained by PEO have multiple layers. Under sparking voltage conditions, films with a non-uniform thickness are formed, and the surfaces of these films are rougher than the metal/film interface. Some regions may form a barrier film, similar to but thicker than that formed at voltages below the breakdown voltage. Increasing the anodising time allows for the further development of nanocrystals and oxygen bubbles. Local high temperatures promote the growth of nanocrystals in regions of the barrier film adjacent to the breakdown site and the nucleation of crystals in previously amorphous materials [8].

The surfaces of titanium and its alloys have been treated by plasma electrolytic oxidation in various solutions. For example, the PEO process has been conducted in an aqueous solution composed of 1 M H_2SO_4 or 1 M H_3PO_4 [9–11], Na_3PO_4 [12], H_3PO_4 solutions containing NaH_2PO_2 with $\text{Ca}(\text{H}_2\text{PO}_2)_2$ [13], and KOH solutions with H_3PO_4 or $\text{K}_4\text{P}_2\text{O}_7$ [14]. The surfaces of titanium or its alloys have also been treated using the PEO process in solutions with organic additives [15], for example, in solutions containing glycerophosphate and calcium acetate [16,17] or in solutions

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composed of $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Na_2SiO_3 , EDTA-2Na, and NaOH [18]. Different oxide layers can be formed during the anodisation of titanium depending on the composition of the bath, additives to the bath and the applied voltage. Surface of pure titanium was modified in five different electrolytes by plasma electrolytic oxidation at 350 V. Spark (and porous structure formation) occurred at 310 V in Na_2CO_3 with KOH solution, at 270 V in NaAlO_2 with KOH solution and above 265 V in solution composed by NaAlO_2 , KOH and NaF, or by NaAlO_2 with NaF [9]. Thickness of coatings was different, the thicker oxide layer was formed on the substrate when the PEO process was carried out in solution containing Na_2CO_3 with KOH. The oxide layers were composed of anatase and rutile, and in the case of the electrolyte containing NaAlO_2 , a TiAl_2O_5 phase was also detected by XRD analysis. The characteristic morphology of coatings formed on titanium surface was also obtained when PEO process was carried out in an electrolyte containing a mixture of $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (8.8 g dm^{-3}), Na_2SiO_3 (14.2 g dm^{-3}), EDTA-2Na (15 g dm^{-3}), and NaOH (20 g dm^{-3}) [18]. Depending on applied voltage (200–450 V), duty cycle of 600 Hz and 8.0% and treatment time (1, 3, 5, 10, and 30 min) a change in the surface morphology was observed. When the oxidation time was increased from 3 to 5 min, the pore sizes of the PEO coatings clearly increased. The microstructure, chemical composition, surface roughness and wettability of the formed coatings differ depending on the conditions during the PEO process. This process and the characterisation of the PEO layers formed on the surfaces of Ti and its alloys have been reviewed in detail [8]. Plasma electrolytic oxidation is most frequently carried out in solutions with soluble compounds. However, to obtain a coating with a higher concentration of bioactive compounds on the substrate, the PEO process can be carried out in suspensions. D. Wei et al. reported the results of a Ti-6Al-4V surface treatment using a PEO process in electrolytes containing nano-hydroxyapatite (HA) powder, calcium acetate, calcium dihydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), disodium ethylenediaminetetraacetate (EDTA-2Na), and sodium hydroxide (NaOH) [19]. The results indicate that the addition of HA to the electrolyte solution influenced the structure and in vitro bioactivity of the coating formed on Ti-6Al-4V. Similar results have been reported in other studies [20]. Samples of Ti-6Al-4V were anodised in solutions of Na_2HPO_4 with hydroxyapatite powder. The authors suggested that the HA-TiO₂ composite formed on the substrate can be used in dental implants. To improve the antibacterial properties of the surface of the Ti-6Al-7Nb alloy, the PEO process can also be conducted in solution with Ag powder [21].

The coatings formed on materials that will be used as artificial bone-like implants should be multifunctional. The implant should have appropriate roughness, chemical composition, corrosion resistance, bactericidal activity and bioactivity [22,23]. Bone is mainly composed of collagen fibres and an inorganic bone mineral (hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) [24]. However, a variety of materials have been developed to improve osseointegration between the implant and bone. Tricalcium phosphate, wollastonite and silica are promising ceramic compounds that can be used to enhance the bioactivity of implant surfaces for medical applications.

Tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, TCP) is also considered a biocompatible and osteoinductive material that is useful for healing bone defects. TCP is biodegradable and affects cell adhesion and proliferation in appropriate environments [25–27]. Wollastonite (calcium silicate, CaSiO_3) has been studied as a ceramic material for artificial bone and dental roots. Apatite can form on wollastonite coatings in SBF solution according to the mechanism explained by X. Liu et al. [28]. In vitro investigations with osteoblast cells obtained from the calvaria [29] demonstrated that wollastonite promotes the proliferation of osteoblasts on plasma-sprayed titanium alloy surfaces. Various substitutions exist in the mineral component of bone (particularly carbonate ions, which are found at up to 8 wt.%) that have an influence on the biological activity of bone mineral. Silicon is among these elements (<1 wt.%) and has been found to be essential for proper bone and cartilage growth [29,30].

Silicon has been reported to be a bioactive component of glass and active surface substitutes and has exhibited biocompatibility with bone. In recent years, in vitro and in vivo investigations have indicated the increase and influence of Si-containing materials on osteoblast cell proliferation and gene expression. Si-incorporated in TiO₂ layer formed on titanium surface by plasma electrolytic oxidations exhibited favourable conditions for MG-63 cell adhesion. Cell proliferation on PEO-coating was higher than Si-free coating formed on titanium surface by the PEO process [31]. Cellular activities, such as proliferation, differentiation, gene and mRNA expression of osteoblast or SAOS-2 cells could be stimulated by silicon compounds present in biomaterials [32–34]. Cytocompatibility of silicon species was also improved on other materials. Bioglass surfaces mainly composed of silica led to favourable differentiation of rat bone marrow cells to osteoblast-like cells and to the production of a large amount of mineralised tissue [35]. Bioglass or scaffolds composed of silica-like compounds have also been reported to enhance biocompatibility and integration with hard or soft tissue [36,37].

In few researches the influence of anodising solution and applied voltage on properties of coatings formed on titanium or its alloys has been studied. However, oxide layers formed in suspensions by PEO process have not been characterised enough in literature. It needs further studies, especially PEO-layers formed on a surface of β -type titanium alloy. This work investigates the surface modification of a Ti-15Mo alloy by plasma electrolytic oxidation in various suspensions composed of osteoinductive additives, such as tricalcium phosphate, wollastonite and silica. The morphology, cross-section, chemical composition and surface roughness of the coatings formed on the substrate by the PEO process were investigated.

2. Materials and methods

2.1. Material and surface pretreatment

The following composition of Ti-15Mo alloy (BIMO Metals, Wrocław, Poland) was used in this investigation: 14.73–14.98 wt.% Mo, 0.016 wt.% N, 0.06 wt.% Fe, 0.08 wt.% C, 0.15 wt.% O, 0.01 wt.% H, and Ti balance. The sample was round with a diameter of 10 mm and a thickness of 5 mm. Before anodisation, the sample surfaces were ground using abrasive paper (SiC) with 600 and 1000 granulation. The samples were etched in a 1 M HF with 4 M H₂SO₄ solution and rinsed ultrasonically in deionised water for 5 min.

2.2. Surface modification

The Ti-15Mo alloy samples were anodised in a basic 0.1 M $\text{Ca}(\text{H}_2\text{PO}_2)_2$ (Alfa Aesar, Germany) solution with the different additive

Table 1
The chemical composition of the anodising bath.

Bath	Component			
	$\text{Ca}(\text{H}_2\text{PO}_2)_2$ mol dm ⁻³	$\text{Ca}_3(\text{PO}_4)_2$ g dm ⁻³	CaSiO_3 g dm ⁻³	SiO_2 g dm ⁻³
Basic	0.1	–	–	–
TCP50	–	50	–	–
TCP100	–	100	–	–
TCP150	–	150	–	–
W50	–	–	50	–
W100	–	–	100	–
W150	–	–	150	–
S50	–	–	–	50
S100	–	–	–	100
S150	–	–	–	150

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