



# Multilayer coatings formed on titanium alloy surfaces by plasma electrolytic oxidation-electrophoretic deposition methods



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## ABSTRACT

Tricalcium phosphate was deposited on the surface of anodized titanium alloys (Ti-6Al-7Nb, Ti-13Nb-13Zr and Ti-15Mo) using the electrophoretic technique (EPD). The multilayer coatings were formed by a three-step experiment. The influences of voltage (step I), time (step II) and concentration of TCP in the suspensions (step III) on the ceramic particle deposition was investigated. The appropriate conditions were determined for each titanium alloy surface modification. The total thickness of the anodized titanium alloys increased, the surface roughness decreased and the wettability increased after TCP particle deposition. A TL-XRD investigation showed that the multilayer coatings were mainly amorphous. All the coatings adhered well to the substrate. The surface modifications increased the corrosion resistance in Ringer's solution, particularly for the Ti-15Mo alloy. In addition, the multilayer coatings formed on this titanium alloy exhibited the best cytocompatibility with MG-63 osteoblast-like cells.

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## 1. Introduction

Multilayer (hybrid) coatings are formed on metals, ceramics, or polymers. The coatings are usually composed of organic-inorganic, inorganic-inorganic, polymer-organic or inorganic compounds [1–5]. The coatings may be formed using one technique (e.g., sol-gel [6], multi-arc ion plating [7], magnetron sputtering [8]); two techniques (e.g., anodization and sol-gel [9], anodization and electrophoretic deposition [10], pack cementation and sol-gel [11]); or a combination of several techniques (e.g., physical vapor deposition, anodization, electrodeposition and hydrothermal treatment [12]). The coatings are formed to add specific functions to the substrate or to change its physicochemical, electrochemical or biological properties. Anodization is an effective and easy surface modification method for valve metals using an electrochemical technique. The ceramic particles may be also deposited on the anodic oxide layer by electrophoretic deposition (EPD). The oxide layer is characterized by good adhesion to the substrate, whereas adhesion of the ceramic layer deposited on the substrate

only by EPD is often insufficient. Therefore, the advantages of both techniques may be combined and used to modify metal surfaces, such as titanium alloys.

Vanadium-free titanium alloys are considered for manufacturing of novel long-term bone implants. However, the bioactivity of the titanium alloys should be improved. A porous oxide layer formed by plasma electrolytic oxidation (PEO) is known to enhance the osseointegration [13,14]. The PEO process has been carried out in solution with various osteoconductive compounds, primarily calcium phosphates e.g. hydroxyapatite and tricalcium phosphate, that are often used for bone repair. The bioactivity of the metal surface is influenced by surface morphology, roughness, wettability, chemical composition, and material corrosion/degradation products. It has been reported that the morphology of a porous oxide layer (particularly with a pore size of approximately 2 μm) is a favorable surface for adhesion of osteoblast precursor cells [15].

On the other hand, the electrochemical parameters for the deposition of ceramic particles on a previously anodized surface depend on many factors. The successful deposition of particles on an anodized surface depends on the thickness of the oxide layer and its chemical composition [16]. In addition, the size of the ceramic particles, solution type, deposition time and applied voltage and current density strongly influence the deposition and adhesion of ceramic to the layer. The oxide layer partially increases

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the resistivity of the substrate. The electric field is higher in pores in the oxide layer, and the formation of a uniform ceramic layer on the top of the oxide is difficult.

The aim of this work was to obtain a multilayer ceramic-oxide coating on three of the most promising titanium alloys surfaces for bone implants: Ti-6Al-7Nb, Ti-13Nb-13Zr, and Ti-15Mo. These titanium alloys are composed of non-toxic elements, and have lower Young's modulus than titanium and Ti-6Al-4V alloy. The particles of tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ , or TCP) were deposited on the previously anodized titanium alloys. The morphology, oxide layer, chemical composition, surface roughness, wettability and adhesion of the multilayer coatings were investigated. The cytocompatibility of the coatings was evaluated using osteoblast-like cells MG-63. The corrosion resistance of the modified titanium alloy surfaces was examined in Ringer's solution.

## 2. Experimental

### 2.1. Material and surface pretreatment

The chemical compositions of the Ti-6Al-7Nb, Ti-13Nb-13Zr, and Ti-15Mo alloys (BIMO Metals, Poland) used in this study are shown in Table 1.

The samples were cylindrical with a height of 5 mm, and the diameters were 8.0, 9.5 and 10.0 mm for Ti-6Al-7Nb, Ti-13Nb-13Zr, and Ti-15Mo, respectively. Before anodization, the sample surface was ground using abrasive paper (SiC) with 600 and 1000 granulation, etched in a 1 M HF and 4 M  $\text{H}_2\text{SO}_4$  solution, and rinsed ultrasonically in deionized water for 5 min.

### 2.2. Surface modification

#### 2.2.1. PEO process

The conditions (current density, voltage, solution) needed for plasma electrolytic oxidation of the titanium alloy surfaces were determined in the previous investigations [17,18]. The titanium alloy samples were anodized in 0.1 M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Alfa Aesar, Germany) solution with the addition of tricalcium phosphate (TCP)  $\text{Ca}_3(\text{PO}_4)_2$  (Avantor, Poland) powder. The PEO process was conducted in a cooled electrolyzer at a current density of 100 mA/cm<sup>2</sup> for the Ti-15Mo alloy and of 150 mA/cm<sup>2</sup> for the other titanium alloys. The PEO process was carried out using a DC power supply (PWR800H Kikusui, Japan) for 5 min. The volume of the anodizing bath was 0.3 dm<sup>3</sup>, and the distance between the substrate and the cathode during the PEO process was 50 mm. The voltage limits were 300 V for the Ti-15Mo alloy and 350 V for the Ti-13Nb-13Zr and Ti-6Al-7Nb alloys. Titanium mesh was used as the cathode, and anodized samples were used as the anodes. After the anodized, the samples were rinsed ultrasonically in deionized water for 5 min.

#### 2.2.2. Electrophoretic deposition of tricalcium phosphate

Several suspensions were prepared to determine the best conditions for the electrophoretic deposition of tricalcium phosphate (TCP) on the anodized titanium alloy samples. For the preparation of the TCP suspensions, 5, 10, 15, and 20 g/dm<sup>3</sup> of

the powder ( $\text{Ca}_3(\text{PO}_4)_2$ ; particles gradation below 10  $\mu\text{m}$ ; Avantor, Poland) were added to 0.05 dm<sup>3</sup> of 25%vol. of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and  $\text{NH}_3$  in  $\text{H}_2\text{O}$  to adjust the pH value of the suspensions, which ranged from pH = 10 to pH = 11. Following this,  $6.78 \cdot 10^3$  g/dm<sup>3</sup> of polyethylene glycol (average  $M_n$  400 mol wt.; Sigma-Aldrich, Poland) was added, which acts as a dispersant to stabilize the suspension. The suspension was stirred for 24 h and then sonicated using an ultrasonic cleaner for 30 min.

The anodized titanium alloy was used as the cathode, and platinum mesh was used as the anode. The distance between electrodes was 15 mm. The EPD process was carried out at ambient temperature using a DC power supply (PWR800H Kikusui, Japan) equipped with Wavy software. The electrolyzer was equipped with a reflux condenser to maintain the concentration of ethanol in the bath. The sample labels, wettability, surface roughness of the investigated samples determined by an optical profilometer are presented in Table 2. The surface modification was carried out according to the scheme presented in Fig. 1.

### 2.3. Microstructure and chemical composition of the coatings formed on titanium alloy surfaces

#### 2.3.1. Scanning electron microscopy investigations

The morphology of the multilayer coatings formed on the titanium alloy surfaces was examined using a scanning electron microscope (SEM, Hitachi TM-3000, accelerating voltage = 15 kV). For the cross-section analysis, the samples were embedded in epoxy resin and were then ground using abrasive paper (SiC) with 600, 1000, 1200 and 1500 granulation. The cross-section of the modified titanium alloy samples was examined using the same scanning electron microscope. The samples before SEM observation were covered by a thin gold layer (Cressington Sputter Coater 108 Auto).

#### 2.3.2. Surface roughness

The sample roughness was measured using a non-contact optical profilometer (Wyko N9300, Veeco, 5 $\times$  magnification). The arithmetical average roughness (Ra), root mean square roughness (Rq), maximum relative height on the profile curve, in a sampling length (Rt), and the sum of the maximum value of profile peak height on the profile curve, and the maximum value of profile valley depth in a sampling length (Rz) were determined [19]. The result is an average of the measurements from surface sample area (1.3 mm  $\times$  0.9 mm) of each sample (Table 2).

**Table 2**

The sample labels, wettability, surface roughness of the investigated samples determined by an optical profilometer.

Sample	wettability, deg.	surface roughness, $\mu\text{m}$		
		Ra	Rq	Rz
TAN	51.2 $\pm$ 4.7	0.30	0.48	1.48
TAN-15	95.1 $\pm$ 6.6	0.58	0.78	19.94
TNZ	120 $\pm$ 5.0	0.51	0.63	9.77
TNZ-10	131.4 $\pm$ 5.4	2.29	2.76	25.85
TM	47.6 $\pm$ 5.7	0.28	0.36	0.30
TM-10	71.0 $\pm$ 4.2	1.14	1.49	24.19

**Table 1**

The chemical composition of the titanium alloys (wt%).

Titanium alloy	Al	Nb	Zr	Ta	Mo	Fe	C	N	H	O	Ti
Ti-6Al-7Nb (TAN)	6.05	6.80	–	0.35	–	0.08	0.04	0.01	0.003	0.11	balance
Ti-13Nb-13Zr (TNZ)	–	13.30	13.00	–	–	0.08	0.05	0.009	0.005	0.10	
Ti-15Mo (TM)	–	–	–	–	14.73–14.98	0.06	0.08	0.016	0.01	0.15	

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