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INVESTIGATION OF pH EFFECT ON HYDROXYAPATITE FORMATION IN PLASMA ELECTROLITIC OXIDATION PROCESS IN TITANIUM ALLOYS

Plasma Electrolytic Oxidation (PEO) was performed on Ti in electrolyte containing calcium acetate monohydrate $(Ca(CH_3COO)_2(Ca\ (CH_3COO)_2 \cdot H_2O)H_2O)$ *and sodium phosphate monobasic dehydrate* $(Na_2HPO_4 \cdot (Ca\ (CH_3COO)_2 \cdot H_2O)2H_2O)$ *using a pulse power supply. Scanning electron microscopy (SEM) with EDS and X-ray diffraction (XRD) were employed to characterize the microstructure, elemental composition and phase components of the coatings. All oxidized coatings contained Ca and P as well as Ti and O, and the porous coatings were composed of anatase, rutile and hydroxyapatite. After hydrothermal treatment, the hydroxyapatite was precipitated on the surface of the sample plate obtained by PEO and the hydroxyapatite thickness was about 15* μm.

Key words: *plasma electrolytic oxidation, hydroxyapatite, titanium, biomaterials.*

Introduction

In the last years, titanium and its alloys have been successfully used as dental and orthopedic biomaterials because of their good mechanical properties, corrosion resistance and biocompatibility with living tissue after implantation into the bone (1–3). The most interesting reason for titanium used in medical applications is the ability of apatite formation spontaneously on titanium surface in the simulated body fluid (SBF) or in environment of a living organism (4, 5). Thus, recently, fixation of titanium implants to the bone usually depends on the biological fixation of its porous surfaces. If titanium metals have an ability to bond to the bone strongly without formation of intervening fibrous tissue, implants may be able to achieve long-term stability even without porous coatings. Various ways of physical and chemical treatments of Ti surface have been proposed to overcome this drawback and to produce a better biocompatible implant surface. The most common technique is that of the production of hydroxyapatite (HA). HA is a naturally occurring mineral form of calcium apatites and a major mineral component of bones and teeth. The biocompatibility of HA has been thoroughly investigated, and it has been established and proved that when HA is applied on titania, it is spontaneously bond with living bone (6–8). Various methods were used for depositing an HA layer on titania, such as plasma spray (9–11), sol-gel methods (12, 13), electrochemical deposition (14, 15) and electrophoresis (16, 17). Any of these methods have some disadvantages, like delamination of the HA layer from the titania due to the poor bonding between the coating and the substrate, or the difficulty in applying uniform coatings on implants with complex geometry (6, 18). Plasma electrolytic oxidation (PEO) is a recently developing technique which can produce a porous, relatively rough, and firmly adherent titanium oxide film on titanium surface (1, 2). The process combines electrochemical oxidation with a high voltage spark treatment in an aqueous electrolytic bath which also contains modifying elements in the form of dissolved salts (e.g. calcium and phosphorous) to be incorporated into the resulting coating. PEO produces good results in the formation of an HA layer on titania. It deserves to be noted that, unlike for any deposition technique, the HA layer produced by PEO is formed simultaneously with the formation of titania, so that the surface layer forms much stronger bonds with the substrate (19). In this study, hydroxyapatite-containing titania coatings were prepared by controlling the applied voltage and electrolytes used in the PEO, and the thickness, phase, composition and morphology of the oxide coating were monitored. The dependence of bioactivity to the surface containing hydroxyapatite was discussed.

Experimental

Commercial Ti plates and implants (sample size 0.025, 0.11and 0.17 dm^2) were used in the study. Samples were abraded by SiC sandpaper #1000 then degreased by alcohol and finally washed with acetone in an ultrasonic cleaner. The oxidation was performed in AC mode by the industrial 50 Hz sine voltage (± 400 V, nominally) at the end current density 0.7- 3.3 ± 0.2 A / dmI for 10-90 min on a home-made 40 kVA PEO station with a water-cooled bath made of stainless steel, which served as the counter electrode. Electrolytes were prepared by dissolution of the calcium clycerosphate (Spectrum, practical grade) and calcium acetate (Spectrum, practical grade) in water. Electrolyte contained 0.25 M $(Ca(CH_3COO)_2)$ and 0.06 M $C_3H_7CaO_6P$ in tap water.

The thickness of oxide layers was measured by a micrometer, coating thickness gauge CM-8825 and by SEM. The surface morphology, structure and composition were inspected on SEM JEOL JSM6510LV equipped with an

NSS7 EDS analyzer (Correction Method Proza – Phi-Pho-Z was used for the quantitative analysis). Cross-section samples prepared according to standard metallographic protocols were used for SEM and EDS. Conductivities and pH of the electrolytes were measured by YK-2005WA pH/CD meter, the thickness of oxide layers was measured by a micrometer, coating thickness gauge CM-8825.

The surface areas were measured by the Brunauer–Emmett–Teller (BET) (19) method using a Micromeritics ASAP 2020 (Micromeritics, Norcross, GA) instrument. Fifteen-point adsorption isotherms of nitrogen were collected in the P/P0 relative pressure range (P0 = saturation pressure) of 0.05–0.30 at -196 °C. Prior to analysis, each sample was degassed under vacuum at 200 °C for 4 h.

Results and discussion

In this experiment, it was shown that the preparation of titanium surface containing hydroxyapatite could be formed by PEO. After 20 minutes of PEO treatment of titanium specimens, an amorphous layer is formed (Fig. 1). The layer has a typical for the PEO treatment «moon surface» morphology with numerous crater-like pores resulted from plasma micro-discharges in the course of the process. The thickness of the layer is 9–15 µm. The surface morphology is essentially independent on the PEO processing time (Fig. 1).

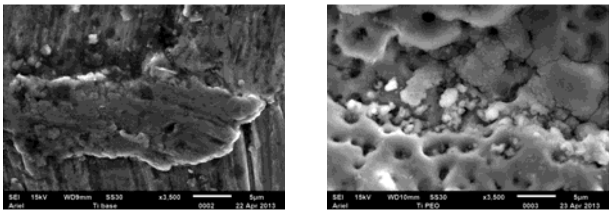


Fig.1. SEM images of samples surface morphology before PEO (left) and after PEO (right) 20 minutes of PEO

The pores formed in the layer can, by themselves, improve the osseointegration of the titanium implant (20). The Ca/P ratio on the surface was 1.7 which is close enough to that of HA (1.67). Examinations of the ability of titanium surface to nucleate hydroxyapatite have shown that the nucleation depends on the amount of the hydroxyl groups present on the titanium surface (21). As it can be seen from Fig. 1, the treatment by PEO affects the porosity of a sample. Crystals, consisting mainly of hydroxyapatite and calcium titanate eventually grow inside the pores formed on the surface of the sample after the 20 minutes the experiment (Fig. 1). The degree of crystallinity influences the dissolution and biological behaviour of HA layers.

The element composition obtained by measuring EDS spectra on the surface of a typical PEO treated titanium sample, is given in Fig. 2 and Table 1.

Table1 – Element composition (EDS) of oxide layers on titanium surface after PEO treatment

Sample 1	Element	Atom %	Ca:P
Ti 1	P	5.11	1.32
	Ca	6.67	
	Ti	17.39	
	O	70.74	
Ti 2	P	11.25	1.88
	Ca	21.12	
	Ti	12.61	
	O	55.02	
Ti 3	P	10.33	1.93
	Ca	19.94	
	Ti	19.19	
	O	50.54	

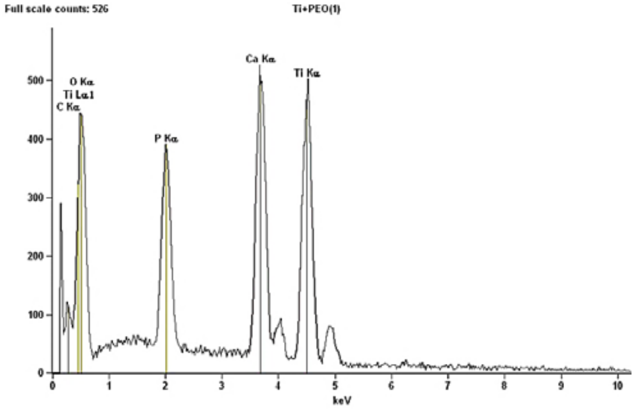


Fig. 2. EDS spectra of sample surface after PEO

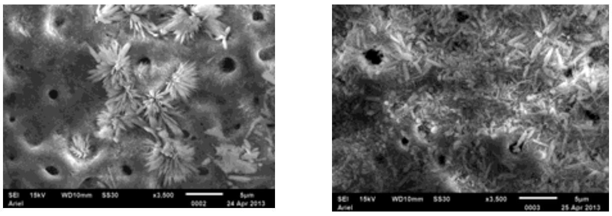
After the PEO processing samples were hydrothermally treated (HTT) in water (pH=7), water alkali (pH=11) for 2 hours, 4 hours at 200 єC in a pressurized reactor (the pressure during the treatment was 16 bar). After the hydrothermal treatment the element composition of the surface layer has changed (Table 2).

Table 2 – Element composition (EDS) of oxide layers on titanium surface after PEO with the following hydrothermal treatment

pH	Element	Atom %	Ca:P
7 (2 hours)	P	5.64	1.18
	Ca	6.65	
	Ti	21.48	
	O	63.50	
11 (2 hours)	P	5.88	1.56
	Ca	9.17	
	Ti	19.94	
	O	63.71	
7 (4 hours)	P		
	Ca		
	Ti		
	O		
11 (4 hours)	P	7.03	1.79
	Ca	12.61	
	Ti	15.62	
	O	64.62	

As can be seen from the comparison in Table 2 with Table 1, the surface layer is enriched with calcium for all the samples after hydrothermal treatment has not undergone any significant change in the concentration. The study of surface morphology shows that the surface becomes more developed after hydrothermal treatment (Fig. 3). Figure 3 shows the formation of acicular crystals inside the pores and on the surface of the sample (Fig. 3*a*, *b*). The size of these crystals in the 0.1–5 microns and their form is characteristic of HA. The presence of crystals of this form indicates that received very developed surface.

To evaluate the resulting developed surface hydroxyapatite was checked BET (Surface Area Analyzers). In this analysis a comparison was made of the surface area of the sample of pure titanium surface area relative to PEO and samples after hydrothermal treatment (at different treatment time and pH). Results of this analysis are presented in Table 3.


a pH 7 (2 hour) *b* pH 11 (2 hour)

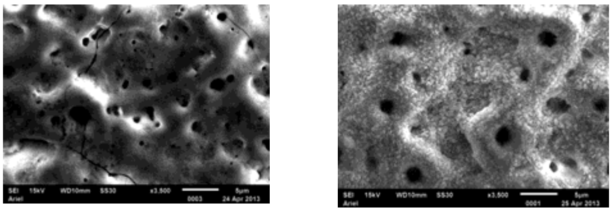

c pH 7 (4 hour) *d* pH 11 (4 hour)

Fig. 3. A SEM image of the oxide layer after the hydrothermal treatment (at different treatment time and pH)

Table 3

Sample	BET S.A, m^2	BET S.A, m^2/gr
Ti-1 pure	-	
Ti-2 after PEO	0.0539±0.0055	1.65±0.17
Ti-3 pH 7	0.2941±0.0064	11.22±0.62
Ti-4 pH 11	56.92±0.73	2013.54±25.56

As shown from the results of the BET, the most advanced surface was obtained after the hydrothermal treatment at pH = 11. At the same time, Ca / P ratio does not change throughout the entire process of hydrothermal treatment, only changes the shape and size of HA crystals.

Conclusions

Titanium surfaces can be modified by PEO treatment for better osseointegration. In this study, the hydroxyapatite-containing coating was produced by PEO treatment in Ca- and P-containing electrolytic solution. The coating was mainly composed of amorphous phase, and displayed a more developed surface and porous structure. After the hydrothermal treatment at a different time, and the pH is a more developed surface of HA, which contributes to more lasting and friendly bonding HA on the surface of the implant, with the tissues of the dental and orthopedic biomaterials. It can be seen that the hydroxyapatite crystals are formed mainly inside the pores of the sample from the previous processing PEO. For the treatment PEO affects the thickness, porosity, and the Ca: P ratio of the oxide layer. For longer PEO values of Ca: P are higher. Hydrothermal treatment has virtually no effect on the Ca: P ratio in the oxide layer, but also leads to more expressed phase of hydroxyapatite.

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Коссенко А.[1], Луговськой С.[1], Асташина Н.[2], Казанський Б.[1] **Дослідження впливу pH на утворення гидроксиапатита в процесі ПЕО титанових сплавів**

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Плазмове електролітичне оксидування (ПЕО) проводили на Ti в електроліті моногідрата ацетату кальцію $(Ca(CH_3COO)_2(Ca\ (CH_3\ COO)_2\ \cdot\ H_2O)H_2O)$ *і дигідрату одноосновного фосфату натрію*$(Na_2HPO_4\cdot\ (Ca\ (CH_3\ COO)_2\ \cdot\ H_2O)2H_2O)$*, використовуючи імпульсне джерело живлення. Дослідження характеристик мікроструктури, елементний склад і фазовий склад компонентів покриттів проводили за допомогою скануючої електронної мікроскопії (СЕМ) і рентгенівської дифракції. Усі окислені покриття містили Ca і P, Ti і O, а також пористі покриття складалися з анатазу, рутилу і гидроксиапатита. Після гідротермальної обробки, гидроксиапатит осаджували на поверхні зразка (пластини), отриманою ПЭО, при цьому товщина шару гидроксиапатита складала приблизно 15 мкм.*

Ключові слова: *плазмове електролітичне оксидування, гидроксиапатит, титан, біоматеріали.*

Коссенко А.[1], Луговской С.[1], Асташина Н.[2], Казанский Б.[1] Исследование влияния pH на образование гидроксиапатита в процессе ПЭО титановых сплавов

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Плазменное электролитическое оксидирование (ПЭО) проводили на Ti в электролите моногидрата ацетата кальция $(Ca(CH_3COO)_2(Ca\ (CH_3\ COO)_2 \cdot H_2O)H_2O)$ *и дигидрата одноосновного фосфата натрия* $(Na_2HPO_4 \cdot (Ca\ (CH_3COO)_2 \cdot H_2O)2H_2O)$*, используя импульсный источник питания. Исследования характеристик микроструктуры, элементный состав и фазовый состав компонентов покрытий проводили с помощью сканирующей электронной микроскопии (СЭМ) и рентгеновской дифракции. Все окисленные покрытия содержали Ca и P, Ti и O, а также пористые покрытия состояли из анатаза, рутила и гидроксиапатита. После гидротермальной обработки, гидроксиапатит осаждали на поверхности образца (пластины), полученной ПЭО, при этом толщина слоя гидроксиапатита составляла примерно 15 мкм.*

Ключевые слова: *плазменное электролитическое оксидирование, гидроксиапатит, титан, биоматериалы.*
