

Investigation of hydroxyapatite on Ti–6Al–4V alloy prepared by plasma electrolytic oxidation

A. KOSSENKO¹, S. LUGOVSKOY¹, B. KAZANSKI¹, N. ASTASHINA²,
A. LUGOVSKOY¹.

¹Ariel University Center of Samaria; Scientific Park; Ariel 40700, Israel

²Perm State Medical Academy, Ministry of Health and Social Development, Perm, Russia

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Abstract

Hydroxyapatite was formed on titanium oxide on the titanium substrate by plasma-electrolytic oxidation (PEO) in electrolyte containing calcium acetate monohydrate ($\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) and sodium phosphate monobasic dihydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) 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 the oxidized coatings contained Ca and P as well as Ti and O, and the porous coatings were made up of anatase, rutile and hydroxyapatite. Such MAO films are expected to have significant applications as artificial bone joints and dental implants.

Introduction

Titanium and its alloys have been widely used for dental implants because of their good chemical stability, appropriate corrosion resistance and acceptable biocompatibility [1-4]. It is difficult to achieve a chemical bonding with the bone tissue and form a new bone on its surface at an early stage after the implantation. Even though titanium as well as its oxides are known to be bio-inert and despite some reports of their direct bonding to bone [5], most authors state that there is no strong bonding between the bone tissue and titanium or its oxide [6]. 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 bonded with living bone [7-9].

Various methods were used for depositing an HA layer on titania, such as plasma spray [10-12], sol-gel methods [13, 14], electrochemical deposition [15, 16] and electrophoresis [17, 18]. 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, 19].

Plasma Electrolytic Oxidation (PEO) method can produce rough, thick, and porous oxide ceramic coatings on valve metals such as Al, Ti, Mg and Zr [20, 21] due to spark discharges at relatively high voltages and has no difficulty with a complex geometry of a specimen. Chemical compounds obtained by PEO method are formed by both the substrate materials and components of electrolytes. 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 [22].

Experimental

Commercial Ti–6Al–4V alloy plates (sample size 30x15x4 mm³) 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 12.5 ± 0.2 A / dm² for 15 min and 1 hour 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 sodium biphosphate (dihydrate, Spectrum, practical grade) and calcium acetate (monohydrate, Spectrum, practical grade) in water. Electrolyte contained 0.26M (Ca(CH₃COO)₂·H₂O) and 0.12 M Na₂HPO₄·2H₂O in tap water.

Conductivities and pH of the electrolytes were measured by a YK-2005WA pH/CD meter, 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, EDS and XRD. X-ray Diffractometer (XRD) Panalytical X'Pert Pro with Cu K α radiation ($\lambda=0.154$ nm) was used with the full pattern identification made by X'Pert HighScore Plus software package, version 2.2e (2.2.5) by PANalytical B.V. Materials identification and analysis made by the PDF-2 Release 2009 (Powder Diffraction File). Phase analysis identification made by XRD, 40kV, 40mA. The XRD patterns were recorded in the GIXD geometry at 1° and 5° in the range of 20-80° (step size 0.05° and time per step 2s).

Results and discussion

In this experiment, it was shown that the preparation of titanium surface containing hydroxyapatite could be formed by PEO. Ca and P ions were incorporated into the oxide coating of titanium, and an amorphous layer with 5 μ m thickness was formed on the surface. The Ca/P ratio on the surface was 2.06 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 [24].

XRD and SEM analyses

Fig. 1 shows typical microstructures of oxide films obtained from the same electrolyte after 15 and 60 min., respectively. As the treatment time increased, it was evident that the number of micropores decreased and surface morphology changed.

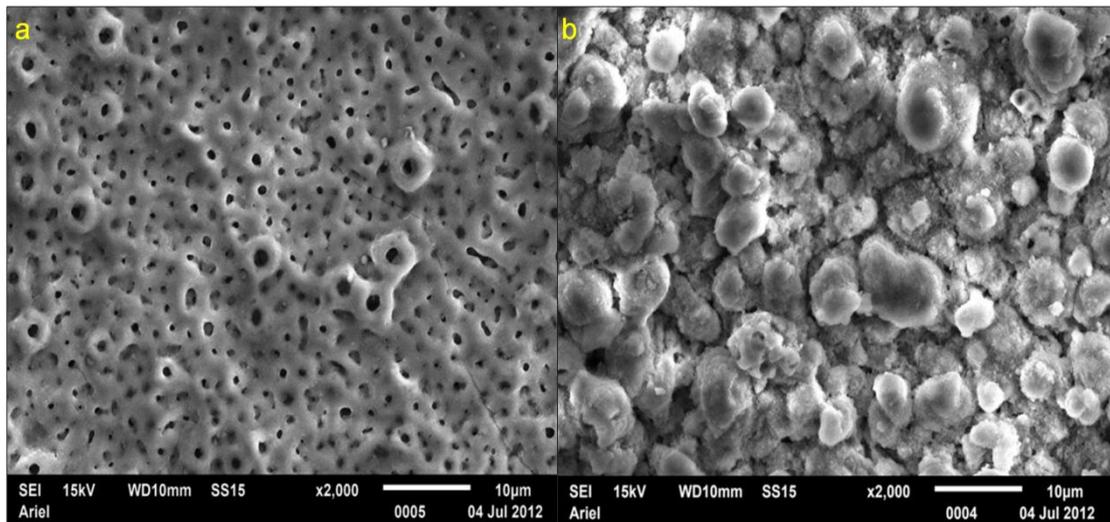


Fig.1. SEM (BEC) of sample's surface after 15 (a) and 60 (b) min PEO.

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 first 15 minutes the experiment (Fig. 1a). The degree of crystallinity influences the dissolution and biological behaviour of HA layers. Crystals of HA formed on the surface of the sample range in size from 2 to 10 microns.

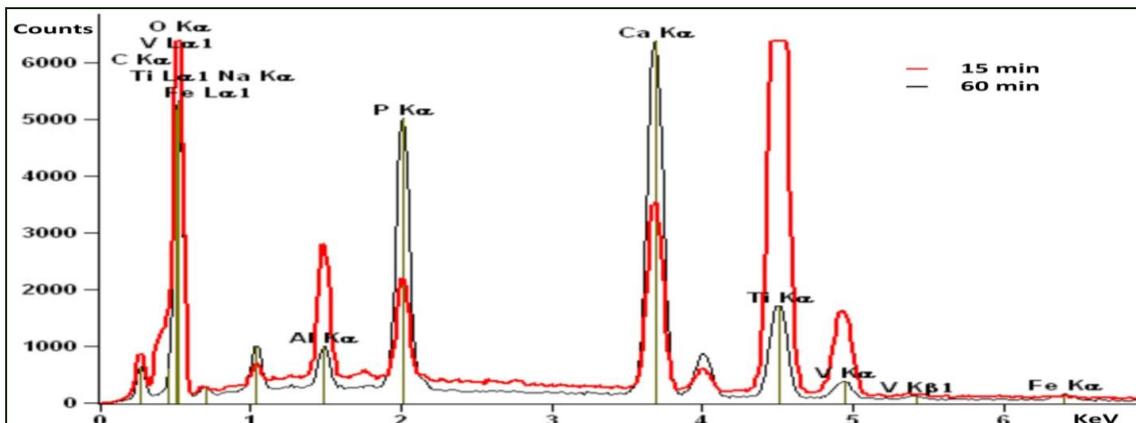


Fig.2. An EDS spectrum of sample surface.

EDS of sample surface presented in Fig. 2 and Table 1 show that after 1 hour titanium concentration decreases, and calcium and phosphor concentration increase significantly.

Table 1. Element composition (EDS, at.%) of a sample surface.

Time	O	Al	P	Ca	Ti	V
15min	62.70	2.90	2.10	5.64	25.52	1.14
60min	65.87	1.10	8.38	17.33	6.87	0.45

Table 1 shows that the surface films obtained are composed of Ti, O, Ca, P, Al and V, which are the elements from the Ti-6Al-4V substrate and from the electrolyte. The concentrations of Ca and P increase with time and do not significantly change with final voltage and current density. The ratio of Ca / P in the sample is 2.68 at 15 min and 2.06 at 60 min.

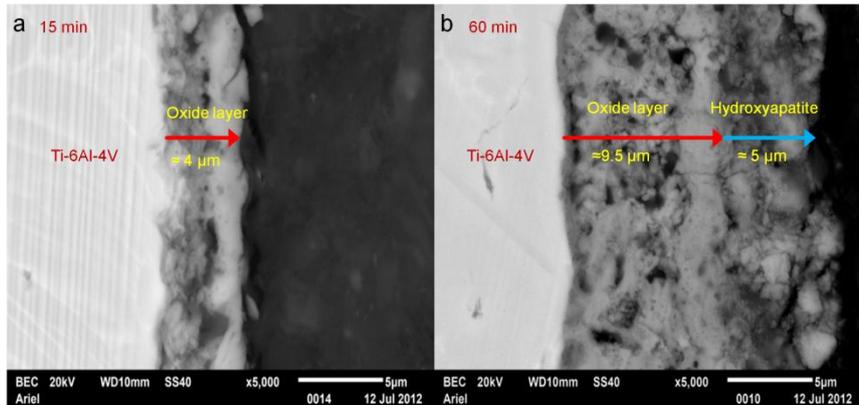


Fig.3. SEM (BEC) of sample's cross section after 15 (a) and 60 (b) min PEO.

The cross-sections of the oxide layers formed with different oxidation time are shown in Fig. 3. The film after 15 minutes is mainly composed of TiO_2 with a loose inner layer and a fused outer layer. As the oxidation time increases, the thickness of the films grows (Fig. 4), and the formation of hydroxyapatite layer begins.

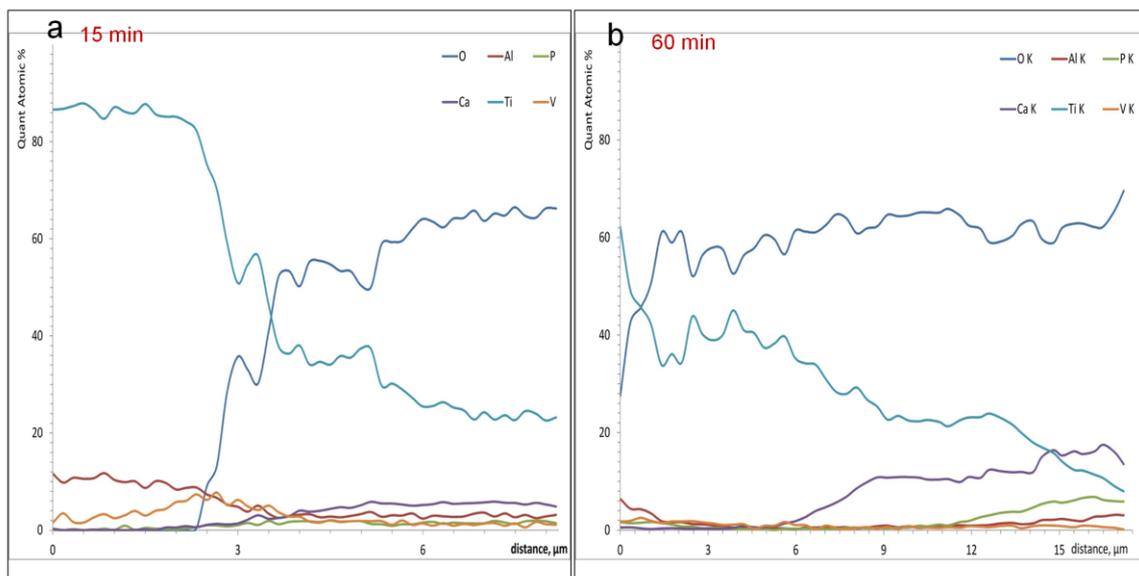


Fig.4. EDS line scan of samples cross section after 15 min (a) and 60 min(b).

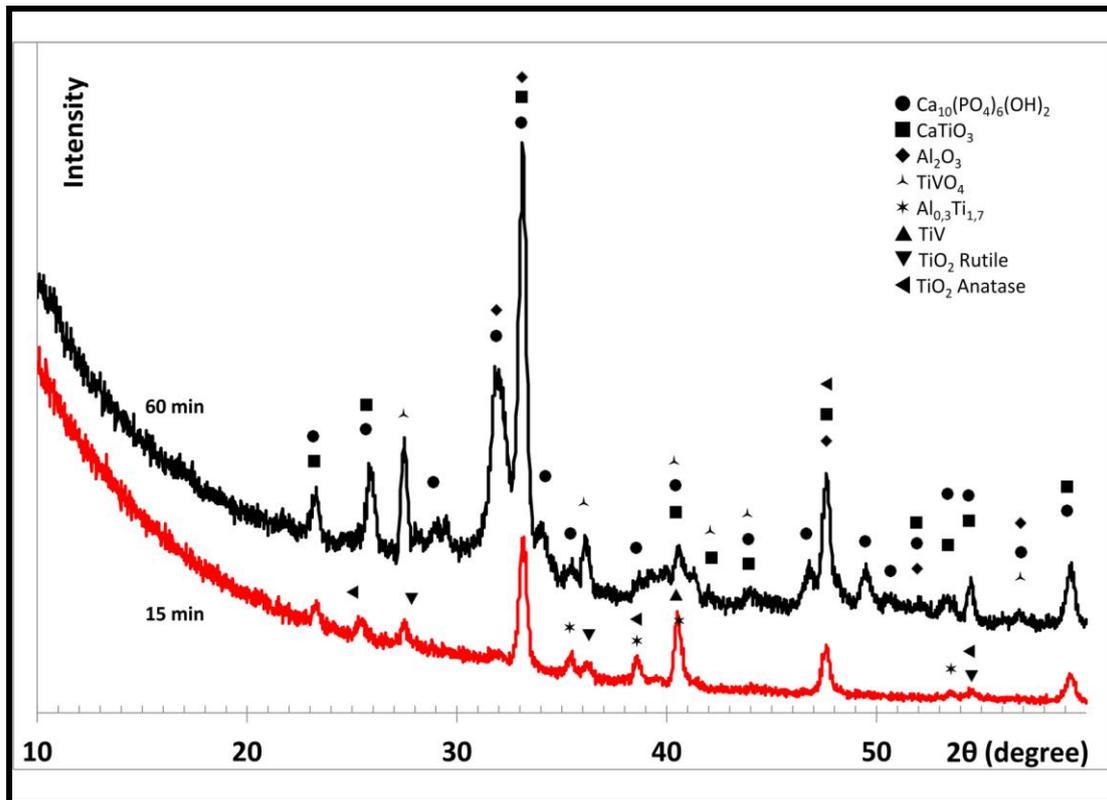


Fig.5. XRD quantitative analyses of samples after 15 and 60 min PEO.

Fig. 5 shows XRD patterns of the surface film for different treatment times. It can be seen that films obtained by PEO consist of a large amount of an amorphous phase, crystalline anatase TiO_2 and rutile TiO_2 and HA. As the treatment time increased from 15 to 60 min, less anatase and rutile were observed, while the diffraction peaks of hydroxyapatite in the coatings became more pronounced. The width of the apatite peaks can be ascribed to the defective, poorly crystalline apatite structure.

Conclusions

This work introduced a simple method to make hydroxyapatite-containing surface layers by PEO method in electrolytes phosphate containing calcium. The hydroxyapatite on the surface of titanium oxide is formed in the pores of an oxide layer in the course of treatment. However, further research is necessary for the establishing of mechanism of the incorporation of Ca or P ions into the surface layer during the PEO treatment.

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