Electrochemical formation of bioactive surface layer on titanium

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Materials

ABSTRACT

Purpose: Electrochemical oxidation method to form thin gel-like layer and activate titanium surface for calcium phosphate deposition

Design/methodology/approach: Titanium was anodised galvanostatically with low current density from cathodic potential in 2 M H_3PO_4 solution up the steady state potential. This treatment produced two-layer surface film with thin (about 100 nm) gel-like phosphate film over the oxide layer with thickness of about 30 nm on the titanium surface. The composition and chemistry of electrochemically treated titanium surfaces were examined by X-ray photoelectron spectroscopy (XPS). The effectiveness of the new treatment was examined by comparing the behavior of treated and untreated titanium when used for biomimetic coating with the Electrochemical Impedance Spectroscopy (EIS) used for this purpose.

Findings: A thick Ca–P coating was formed on the treated titanium after immersion in SBF solution and surface morphology was then examined using SEM equipped with EDS facilities.

Practical implications: new electrochemical method of coating titanium and its implant alloys with bioactive surface layer is more efficient and faster than the other in practical use.

Originality/value: This study continues to support the further investigation of active phosphates for improved orthopedic applications.

Keywords: Biomaterials; Electrochemical treatment; EIS examination; Bioactivity assessment

1. Introduction

Different surface and coating methods [1-4] have been applied to insure deposition of hydroxyapatite on titanium in order to improve implant bioactivity for biomedical applications [5,6]. The bioactivation of the titanium surface was achieved by a sol–gel [2], the alkaline [7] or chemical methods [8,9]. The cathodic treatment [10,11] has led to the formation of the amorphous film of Ca–P deposits on titanium in a supersaturated calcium and phosphate solution. Among surface treatments the anodizing showed to be effective in modifying surface properties of metals [12], particularly in inducing the bioactivity of titanium

[13-16]. Anodic oxidation of titanium implants, demonstrates changes of various oxide properties, not only oxide thickness, but also surface morphology, pore configuration, crystallinity, chemical composition, and surface roughness [14]. Anodic oxidation of titanium implants in phosphoric/sulphuric acid electrolyte systems found to form thicker anodic oxide [14-16] which demonstrated a significantly enhanced bone response in comparison to control implants [17].The interest in the uptake of phosphate by titania arises from problems encountered in the study of corrosion, and in the development of biomimetic materials. Phosphate reactions with titania have been studied due to its relevance in understanding biomineralization processes involved in promoting bone growth on titanium implants [18].

The importance of negative electric charges in activating titanium surfaces was also indicated [19]. The body environment of these functional groups assumes a negative surface charge that stimulates apatite growth. This work describes the results of work on developing the electrochemical method of titanium bioactivation by a gel-like layer formation on titanium in phosphoric acid solutions.

2. Experimental

2.1. Samples preparation

Titanium samples (TIMET Ltd UK, 0.5 cm^2 surface area) were abraded with 600 silicon carbide paper, polished with alumina, washed with distilled water, degreased with acetone and then left in air at ambient temperature. Electrochemical treatments were performed with 2 M H_3PO_4 in a standard three electrode glass cell with an ATLAS 9831 Electrochemical Interface (Poland). Prior to the galvanostatic anodizing samples were kept in the solution for 300 s at – 0.8 V with respect to a saturated calomel electrode (SCE) and then the anodic galvanostatic polarization with current density 0.5 Am^{-2} was performed for 900s till the samples reached the potential plateau values ranging 2-3 V (SCE). Electrodes were removed from the electrolyte with the potentiostat switched on, washed with distilled water, dried and transferred through air to further analysis. The chemistry of anodically treated titanium surfaces were examined by Scanning Microscopy (JLM 5600), equipped with EDS facilities. The VSW apparatus equipped with a 18-channel detector was used in XPS measurements. The samples were exposed to AlKα (1486.6eV, 200W) radiation under the operating pressure less than 5×10^{-8} mbar. Carbon C1s photoelectron peak was used for calibration and fixed at binding energy (BE) equal to 284.6eV. The XPS spectra were fitted using a nonlinear least squares routine. Electrochemical Impedance Spectroscopy with ATLAS 9831 FRE (Poland) was used to investigate the behaviour of anodized surfaces immersed into SBF solution. The morphology of samples were again examined by SEM after 9 days.

3. Results and discussion

3.1. SEM characterisation of anodic layers

The SEM/EDS examinations revealed that surface layers formed on titanium in two electrolytes consisted of TiO_2 with phosphates deposits (Fig. 1).

In case of anodic layer formed in 2 M H_3PO_4 the phosphate deposits were distributed almost homogeneously over the entire surface of the sample and covered by an additional gel-like layer consisting of 76,3±3,6 wt. % of phosphorus and 23,7±1.5 wt. % of oxygen. The presence of gel-like layers above the anodic films could be discerned by scanning electron microscopy. These layers were formed in both the 0.5 M (Fig. 1a, an arrow) and 2 M (Fig. 1b) electrolytes, but in the latter they were readily revealed as lighter layers extensively distributed over the anodic films.
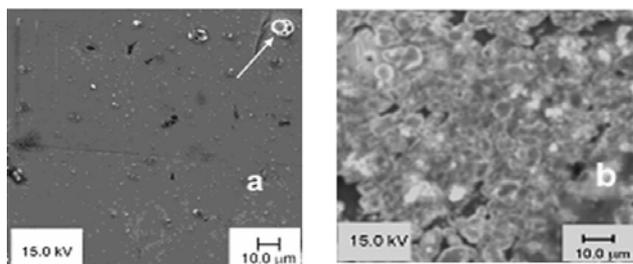
Fig. 1. SEM micrographs of titanium surface layers anodised in 0.5 M and 2M H_3PO_4 mag. × 5000

3.2. XPS results

Fig. 2 shows the Ti2p XPS spectra of the surface of the titanium subjected to 2 M H_3PO_4 treatment, compared with that of the untreated materials. While the untreated titanium revealed the Ti2p doublet peaks of Ti2p1/2 at 453.5 eV and Ti2p3/2 at 459.5 eV ascribed to the Ti-Ti bond, the treated titanium sample showed peaks at higher binding energies of 458.2 and 464.0 eV, which were ascribed to the Ti-O bond [20].
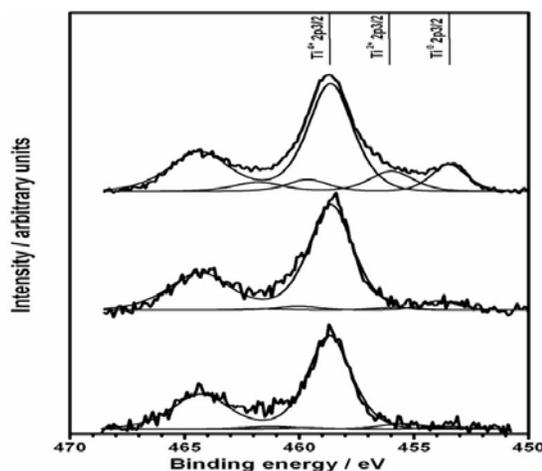
Fig. 2. Ti2p XPS spectra grown on titanium anodized in 0.5 and 2M H_3PO_4 solutions at 0.5 A/m^2 and temp 298 K

The latter peaks disappeared after anodising in 2 M H_3PO_4. The Ti 2p3/2 region for the same samples show a separated pair of approximately equal intensity peaks at 461 and 455 eV, and a single peak at 461eV after air exposure. These results are consistent with those observed after the pretreatment of titanium at -0.5V (SCE) [21] when a Ti(III) metaphosphate with some Ti(II) metaphosphate, whose Ti3p and Ti2p features have a binding energy comparable to that of the metal, were formed. Fig. 3 shows the O1s XPS spectra for the surface of the titanium subjected to the 2 M H_3PO_4 treatment. The O1s region consists of peaks due to oxide (around 529–530 eV), hydroxide (around 531.5 eV), and phosphate (530–532 eV). The treated titanium material exhibits a weak O1s peaks due to the thin passive layer of titanium oxide on its surface and an apparent peak at 532.8 eV ascribed to the P=O bond. Fig. 4 shows the P2p XPS spectra of

the surface of titanium samples, untreated and anodized in 0.5 and 2 M H_3PO_4. A strong P2p single peak of an increasing intensity with a peak at binding energy of 133.7 eV was detected on all samples that clearly can be assigned to phosphate-type species and the presence of phosphated titanium oxides (e.g.$Ti(HPO_4)^{2-x}$, $TiPO_4$,etc.).
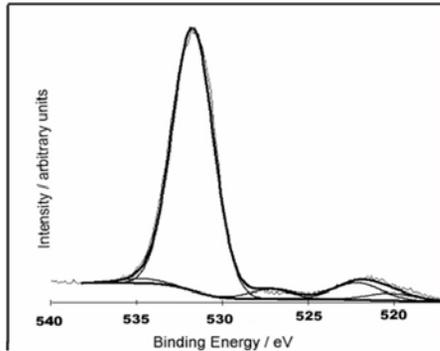
Fig. 3. O1s XPS spectrum grown on titanium anodized in 2 M H_3PO_4 solution at 0.5 A/m^2 and temp 298 K
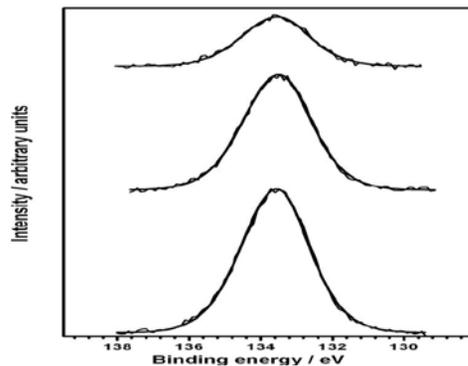
Fig. 4. P2p XPS spectra for titanium anodized in Ti2p XPS spectrum grown on titanium anodized in 0.5 and 2 M H_3PO_4 solutions at 0.5 A/m^2 and temp 298 K

3.3. EIS examination

To assess the coating development titanium specimens were examined after 1, 48, 96, 144, and 192h of immersion in Ringer's solution. Examples of the impedance Bode spectra obtained at different exposure times for the specimens anodized in 0.5 M H_3PO_4 and 2 M H_3PO_4 are shown in Fig. 5 and Fig. 6, respectively. It was observed that variations in the impedance spectra occurred after the first 48 hours of exposure. Changes, which resulted from the evolution of the electrochemical behavior of the system within 48-96 h were less noticeable with time elapsing, and after the following 144 hours exposure, an almost stationary behavior was reached. These observations clearly show that the electrochemical properties of the film change with exposure time, but they are different for two investigated materials. The impedance spectra displayed in Fig. 5 for the specimens anodized in 0.5 M H_3PO_4 solution exhibit one time

constants at all exposure times, whereas the Bode spectra for specimens anodized in 2 M H_3PO_4 solution show transformation into the two time constants during soaking. Such spectra can be divided into two distinct frequency regions. The first is the time constant in the high-frequency part, which arises from the uncompensated ohmic resistance due to the electrolytic solution and the low-frequency part accounting for the processes taking place at the substrate/electrolyte interface resulting from the penetration of the electrolyte through a porous film.
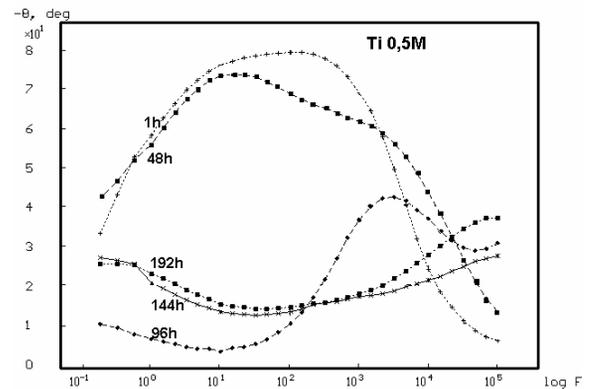
Fig. 5. Impedance spectra for Ti anodized in 0.5 M H_3PO_4 recorded during immersion in Ringer's solution, temp. 298 K
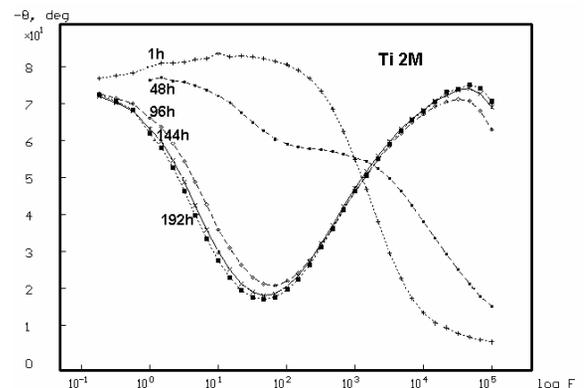
Fig. 6. Impedance spectra for Ti anodized in 2 M H_3PO_4 recorded during immersion in Ringer's solution, temp. 298 K

3.4. SEM results after immersion in Ringer's solution

After 192 h of soaking in Ringer's solution the specimens were dried in a desiccator for 48 h prior to examination. SEM and EDS investigations revealed that after 9 days of soaking in Ringer's solution the thick coating consisted of Ca-O-P globular deposits, which merged in large clusters over the cracked surface layer. The ratio of Ca/P ranging from 1.36 to 1.49 corresponded to non-steochiometric hydroxyapatite. The cracking appeared to develop in the gel-like layer due to shrinkage of the gel by dehydration (Fig. 7).

Fig. 7. SEM micrograph of surface layers on anodised samples of Ti in 2 M H_3PO_4 after immersion for 192h in Ringer's solution at 298 K, mag x 3000

The applied *in vitro* "bioactivity test" consisting in soaking the investigated material in the Ringer's solution clearly confirmed that titanium samples anodized in 2 M H_3PO_4 can be consider bioactive. After only 2 days in the solution an apatite layer started to precipitate on their surface. A more fundamental research is necessary to understand the processes occurring at biological interfaces, thus clarifying the role of materials surface on bone formation process.

4. Conclusions

The XPS spectra of the anodic oxide films galvanostatically grown on titanium in phosphoric acid solutions allowed to characterize them as a mixed oxides, with mainly TiO_2 consisting phosphorus-containing species incorporated into the oxide. The surface bi-layer formed in 2 M H_3PO_4 included an additional gel like-layer of phosphates readily covered by thick layer of Ca-O-P deposits when immersed in Ringer's solution. The formation of a gel-like bioactive phosphate film on titanium has considerable potential applications especially for biomedical situations.

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