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ANODIZATION TREATMENT OF Ti6Al4V IN ELECTROLYTES CONTAINING HF

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ABSTRACT

The Ti6Al4V alloy is already well-known likely material for implant applications. As well as pure titanium, Ti6Al4V alloy possess the ability to form spontaneously a thin passive oxide layer on the surface. This oxide layer provides an enhanced biocompatibility and may be optimum for the osseointegration if it is applied a tailoring of the surface topology and chemistry. The present paper addresses a study of Ti6Al4V surface modification by anodization as function of HF concentration in electrolyte and time, with the purpose to achieve an ordered porous titanium oxide layer. Prior to the anodization treatment the as-prepared surfaces were microstructurally characterized by SEM, EDX and XRD. The oxidized surfaces were subjected to SEM measurement in order to observe the achieved morphology.

KEYWORDS: anodization, nanotube, nanopore, oxide, HF concentration

1. Introduction

Titanium and its alloys are the most used metallic materials for biomedical applications, due to their mechanical, biological and chemical properties. The α+β titanium alloys, such as Ti6Al4V and Ti6Al7Nb, are well-known metallic materials used for implant applications. Ti6Al4V possesses a good corrosion resistance and good physical properties even if there are some limitations regarding the mechanical properties (high Young's modulus value) [1].

Its biocompatibility is related to spontaneous formation of TiO_2 thin adherent layer. This layer is specific to titanium and its alloys and beside TiO_2 contains also the alloying element oxides (Al and V are valve metals [2]) such as Al_2O_3 and V_2O_5.

In recent years the surface modification techniques on "classical metallic biomaterials" showed a great interest for many researchers [3-4]. The anodization treatment is a new electrochemical method for surface modification [5]. Most of the anodization studies on Ti6Al4V were performed in electrolytes containing different amounts of NH_4F [6-8], NaF [7] or HF [8].

The present study is focused firstly on obtaining nanotubular oxide layers on Ti6Al4V substrate using the anodization technique in HF mixtures with H_3PO_4 and secondly, tno characterizing the achieved layers as function of electrolyte composition and anodization time.

2. Experimental results

2.1. Alloys characterization

The cast alloy Ti6Al4V disks (2 mm thickness and 11mm diameter) were microstructurally investigated before the anodization process. The samples were metallographically prepared and the polished surfaces were etched in a solution of 2% HF for a couple of seconds and subsequently analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Furthermore the samples were subjected to the x-ray diffraction analysis (XRD).

The chemical composition of cast alloy samples was determined using inductively coupled plasma optical emission spectrometry analysis (ICP-OES). A very good agreement with the nominal composition was revealed.

2.2. Anodization treatment

Prior to the anodization treatment, the Ti6Al4V disks were ground with emery papers up to 2500, polished with 6μm diamond paste and cleaned by sonication in ethanol and distilled water. The electrochemical cell consisted of a two-electrode configuration with platinum foil as a counter electrode and Ti6Al4V sample as working electrode with a 0.28cm^2 surface area exposed to the electrolyte. The anodization experiments were carried out using a high-voltage potentiostat 2400 Source Meter Keithley connected to a digital multimeter (Keithley 2700 Multimeter /Data Acquisition System) interfaced to a computer. The electrolyte used for anodization treatment was a solution of 1 M H_3PO_4 with addition of 0.1 wt. % HF (E1) and 0.2 wt.%HF (E2) at room temperature. The anodization treatment comprised a potential ramp from open circuit potential (OCP) to 20V with a sweep rate of 20mV/s [6]. The potential of 20V was held constant for 2400s, 3600s and 7200s in each electrolyte. After the anodization treatment all samples were rinsed in distilled water and dried.

The structural and morphological characterization of the oxide layers was carried out with the Leo 1530 Scanning Electron Microscope (SEM). Moreover, the SEM analysis performed on nanotubular/nanoporous oxide layers allows us to measure the D_{inner} (inner diameter), D_{tube} (intertube distance), t_{wall} (wall thickness). The measurement error limit was around ± 5nm for D_{inner}, D_{tube} and around ±2 nm for t_{wall}.

3. Results and discussions

3.1. Alloys characterization prior anodization

The microstructure characteristics are important aspects for further electrochemical response of an alloy.

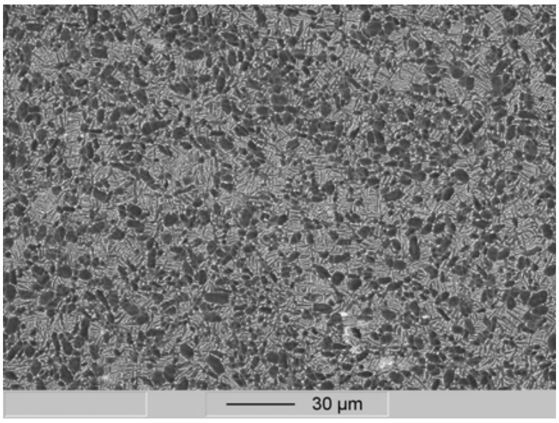

Fig. 1. *SEM images (BSE mode) of a Ti6Al4V sample cross section*

Hence, a detailed analysis of the Ti6Al4V substrates was conducted by means of SEM and XRD.

Fig. 1 shows a SEM image in the composition of an HF etched cross-sectional area of a Ti6Al4V disk sample. The Ti6Al4V microstructure is clearly revealed with both phases α and β.

The EDX measurement (Fig. 2) shows that α-phase corresponds to the dark contrast areas and the β-phase to the bright areas. The α-phase contains the Al element while the β-phase comprises the V element. The phase distribution is important for subsequent studies since, in electrolytes containing HF, the electrochemical behaviors of the α and β-phases may be different [6], [9].

The chemical composition of the investigated Ti6Al4V samples (as determined by ICP-OES) was 89.19% Ti, 6.27% Al and 4.07% V. Thus, it is in very good agreement with the nominal composition.

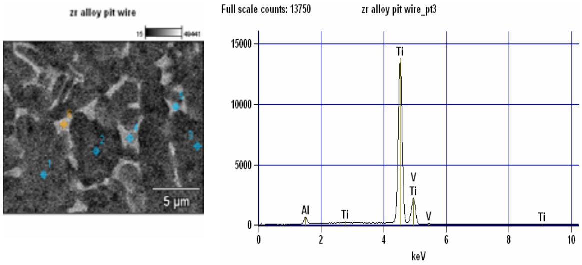

Fig. 2. *EDX images of a Ti6Al4V sample*

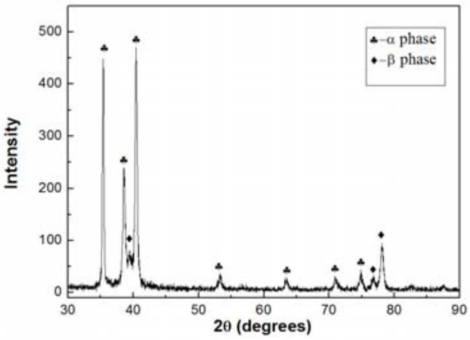

Fig. 3. *XRD pattern of Ti6Al4V sample*

The alloys XRD patterns (Fig.3) have shown that the main intensity diffraction peaks correspond to the α-phase, since this phase is the major one. The main β-phase reflections were recorded around 2θ=76.8°and 2θ=77.8°.

3.2. Characterization of the anodized alloys surface

Scanning electron microscopy was employed for the structural and morphological characterization of the Ti6Al4V sample surfaces after the anodization process.

The anodization treatment in both electrolytes for 2400s and 7200s has shown only etched surfaces.

Thus, it can be assumed that the HF concentration of electrolytes is less important since for more and less than 3600 s the result was the same. This phenomenon is attributed to the last stages in the mechanism of TiO_2 growth [12-14]. The HR-SEM image of the alloy surface anodized in E1, for 3600s (Fig.4) shows that the alloy phases are differently affected by the treatment in fluoride-containing solution. Under these conditions on α-phase region a nanotubular oxide structure (Fig. 5) had formed, while on the β-phase region only a porous oxide structure was observed. In literature, it was found similar behavior of the α and β regions on Ti6Al4V anodized surface even the electrolytes were NH_4F [6], or HF [8] solutions.

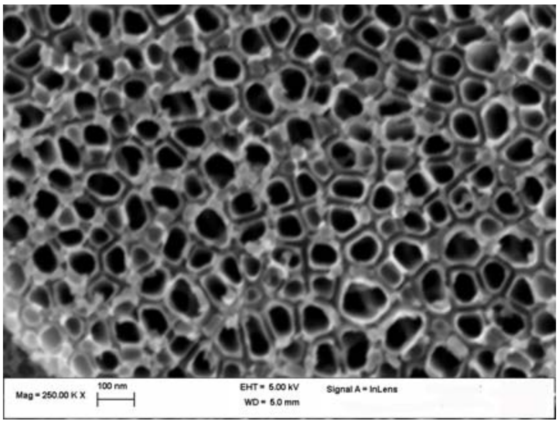

***Fig. 4**. Ti6Al4V HR-SEM image of α surface anodized in E1, for 3600s*

The D_{inner} of the tubes growth on α-region was around 70nm while the D_{tube} and t_{wall} were around 90nm and 20nm, respectively. Moreover, the nanopores D_{inner} growth on β-region could be measured and the value was around 60nm.

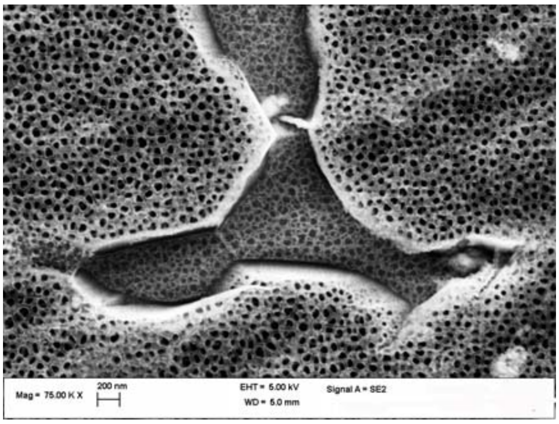

***Fig. 5**. Ti6Al4V HR-SEM image of α+β surface anodized in E1, for 3600s*

The nanopores D_{inner} is smaller than the nanotubes one, this aspect may be typical for Ti6Al4V anodized surface [6]. It should be mentioned that this method has certain limitations regarding measurement accuracy, and, for this reason an error limit of 5nm was taken.

For the second electrolyte E2, with higher HF concentration, for 3600s polarization a porous structure was achieved for both α and β regions (Fig. 6).

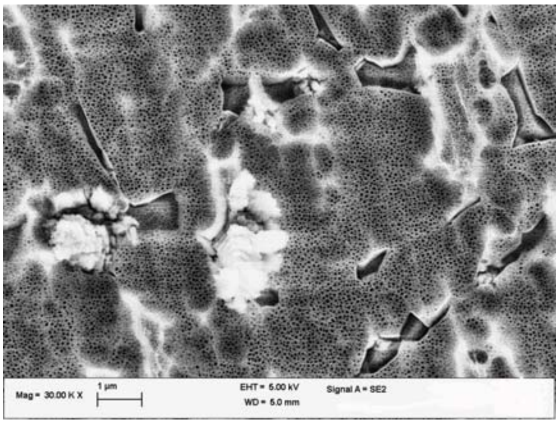

***Fig. 6.** Ti6Al4V SEM image of α+β surface anodized in E2, for 3600s*

The α-regions have shown a much ordered nanoporous structure (Fig.7). This aspect was also found in literature [6] for α-phase region. The nanopores D_{inner} was found around 60nm (±5nm).

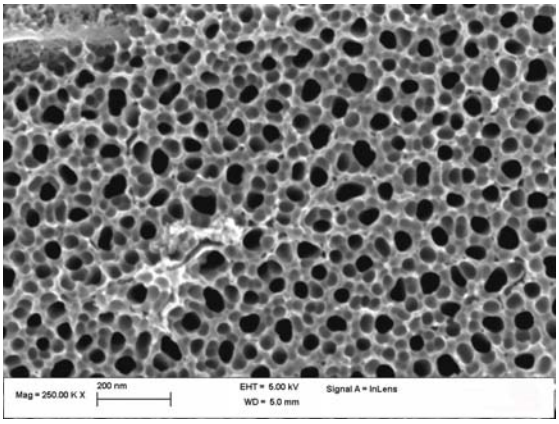

***Fig. 7.** Ti6Al4V HR-SEM image of α+β surface anodized in E2, for 3600s*

The behavior of the phases of the α+β titanium alloys is different depending of the β stabilizer element.

Thus, even if Ti6Al7Nb is also an α+β titanium alloys, in literature it was found that anodization in HF electrolyte contain led to upper ordered nanoporous layer growth on β-region [9].

4. Conclusions

The investigations regarding the anodization behavior of the α+β Ti6Al4V alloy were conducted in H_3PO_4/ 0.1 wt% HF (E1) and 0.2 wt% HF (E2) electrolytes applying a potential of 20V for up to 7200s potential and then sweeping the potential with 20mV/s. Nanotubular oxide structures were obtained and it was demonstrated that the optimum polarization time is 3600s for an 0.1wt% HF concentration (E1). The D_{inner} of the oxide nanotubes were about 70nm. while the β-phase regions showed only a random disordered nanoporous structure. Furthermore, at 2400s and 7200s anodization time no nanotubular or nanoporous layers were observed.

It can be concluded that employing the presented anodization parameters a nanotubular oxide structure was observed already after 3600s in electrolyte with less HF concentration.

Acknowledgment

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