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Present and Future Trends in TiO_2 Nanotubes Elaboration, Characterization and Potential Applications

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The paper is focused on TiO_2 nanotubes elaboration, characterization and potential applications, starting from the idea that monitoring anodizing conditions is a way to obtain nanotubes with various dimensions and various potential applications related to the change of hydrophilic – hydrophobic balance, biocompatibility, nano-porosity, stability, etc. Such properties are important for the use of Ti as biomaterial, as self–cleaning, solar energy conversion, controllable wettability, photocatalysis, etc. The electrochemical behaviour of the nanotubes was monitoring by Tafel plots and open circuit potential determinations, and was discussed in connection with surface features evaluated from scanning electron microscopy, atomic force microscopy and contact angle measurements.

Keywords Electrochemical stability; surface analysis; titania nanotubes

1. Introduction

It is well known that titanium and its alloys with a thin passive stratum, predominant TiO_2 represent materials providing excellent physical mechanical and biocompatible properties [1]. In the past, many attempts have been made to improve the surface properties of Ti-based materials by modifying topography, chemistry, and surface energy to better stability, or integrate into bone as implant materials. Such surface modification techniques included chemical methods as acid etching, and the use of various coatings) [2–5]. Through these approaches, a better performance in electrochemical stability and biocompatibility of Ti and Ti alloy has been achieved due to the creation of optimal micro-scale surface features.

In the last decade various groups of research begun exploring the formation of nanostructured materials, particularly the nanotopography of surfaces using self-organization. Different methods of self organization have been investigated as physical vapor deposition (PVD), MOCVD meniscus ordering of micro and nanobeads, and thin polymer films [6].

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Using all of these methods coatings with well-defined nanoscale surface properties were obtained and new applications were proposed [7,8]. In this approach, various techniques were performed in order to get TiO_2 nanostructure and anodizing was a choice for a chip and convenient one. Changing anodizing parameters as voltage, pH electrolyte compositions and time of electrolysis a large variety of structure with various potential applications could be identify [9,10]. Such potential applications are related to the change of hydrophilic – hydrophobic balance, biocompatibility, nano-porosity, stability, properties important first for the use of Ti and Ti alloys as biomaterials, and in other fields, as self –cleaning, solar energy conversion, controllable wettability, electrochromic devices, photocatalysis, as well [8,9]. Anatase TiO_2 nanocrystallites are considered to be the most active crystalline structure of TiO_2 photocatalyst. Ultrafine anatase nanocrystallites, particles, less than 10 nm possess unique photochemical properties due to quantum size effects. It has been reported that Q-sized TiO_2 nanocrystallites can expedite the diffusion of electrons and holes to the surfaces and inhibit electron-hole recombination through charge carrier trapping and, as a result, the photocatalytic activity can be remarkably enhanced [11] and used in applications such as: water purification, solar cells, removal of different pollutants and of different gases [12].

Further on, when adding TiO_2 in polymer electrolytes, strengthened ionic conductivity and better mechanical properties are obtained [13]. Also an important feature of TiO_2 particles is represented by the light scattering property. This property vary with the shape, size, concentration, surface roughness and spatial arrangement of the particles, and is important for industrial applications such as paint industry and solar cells [14].

Regarding elaboration of controllable properties of oxide layers on Ti surface, anodizing seems to be promising nano-modification technique [15,16] and, in this light, has been found set of Ti anodizing conditions which create nanotubes with mimetic features of natural bone [16]. Taking into account that collagen, the main organic component of bone, is a triple helix 300 nm in length, 0.5 nm in width, and hydroxyapatite (HA), the inorganic component has particle sizes around 20–40 nm long it is possible to assume that bone cells are accustomed to a nanoscale tubular environment rather than the micron-scale environment [17]. Moreover, biocompatibility studies indicated bone forming functionality on diameter controlled TiO_2 nanotube surfaces [18] and how TiO_2 diameter directs cell fate as an expression of relation between nanosize and vitality [19].

Experimental

Materials and Methods

Ti samples were 99.76% purity, donated by Institute for Non-Ferrous and Rare Metals, Bucharest. The other components were, Fe, Al, O_2, N_2, C. The samples are foils with 2 mm thickness and were prepared being mechanically polished, degreased in acetone, washed for five minutes in de-ionized water and then immersed in a HF and HNO_3 solution for 30 seconds. Then washed again with de-ionized water for five minutes and dried at 40°C. Samples were mounted like an anodic electrode in a electrochemical cell with a two–electrode configuration, serving as cathode a Pt grid. A constant voltage between anode and cathode was applied by a power supply and current transients were recorded. The anodizing procedure was performed at room temperature for 120 minutes at 20 V constant value in a mixture of fluoride as following:

$$\text{HF } 0.5\%,\ \text{HF } 0.5\% + 5\text{g/l } NH_4F,\ \text{HF } 0.5\% + H_3PO_4\ 1\text{M}, 1\text{M } (NH_4)_2SO_4 + 0.5\ \text{wt.}\%\ \text{NaF}$$

Surface analysis have been investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), and contact angle measurements for various anodizing conditions. The surfaces changes in the topography and nanotubes diameter as a function of anodizing electrolyte were observed using Environmental Scanning Electron Microscope FEI/Phillps XL30 ESEM, with pressure 0.7 Torr. Pores diameter was calculated with Image J program. The morphological modifications analysis was completed with roughness evaluation carried out with an atomic force microscope from APE Research, Italia. The balance hydrophilic/hydrophobic was evaluated from contact angle measurements, using a Contact Angle Meter – KSV Instruments CAM 100. The surface hydrophilicity of anodizing Ti was studied by measuring static contact angle with sessile drop of distilled water deposited on the sample surface as a function of electrolyte composition. Each contact angle value is the average of minimum 10 measurements. The investigation was carried out with an acurrancy of ±1° at a temperature of 25°C. Electrochemical methodology for stability involved open circuit potential determinations in Na Cl and the cyclic potentiodynamic polarization measurements applied beginning from -0.8 V to $+4.0$ V (vs. SCE). Cyclic polarization was performed with a scan rate of 2 mV/sec, using a Voltalab 40 equipment with its Volta Master 4 program. Also, the linear polarization measurements were carried out with the purpose to obtain the polarisation resistance (R_p), the corrosion current densities (i_{corr}) and the corrosion rates (V_{corr}). A Voltalab 80 equipment with its VoltaMaster 4 program were used and as testing solution was chosen Hank bioliquid with the following composition; NaCl 8 g/l; $CaCl_2$ 0.14 g/L; KCl 0.4 g/L; $MgCl_2 \cdot 6H_2O$ 0.1 g/L $Na_2HPO_4 \cdot 12H_2O$ 0.06 g/L; $MgSO_4 \cdot 7H_2O$ 0.06 g/lL glucose 1 g/L.

Results and Discussion

In the majority of anodizing electrolytes for Ti, a compact TiO_2 structure is obtained, according to following reaction:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+$$

The oxide is amorphous if the anodizing took place at 20 V, or crystalline at higher voltage. Generally depending on conditions, a mixture of crystalline anatase and rutile is formed. In fluoride-containing electrolytes, an oxide layer forms on the surface of titanium as well at the beginning. Depending on the conditions, after a time, in the presence of F^- the oxide layer partially dissolves and forms pits according to the reaction $TiO_2 + 6HF \rightarrow [TiF_6]^{2-} + 2H_2O + 2H^+$.

These concurrent processes anodic oxidation and dissolution leads to the formation of nanotube arrays, corresponding to a schematic proposed model (Fig. 1) according to literature data [7–10], including our previous work with elemental surface analysis [10].

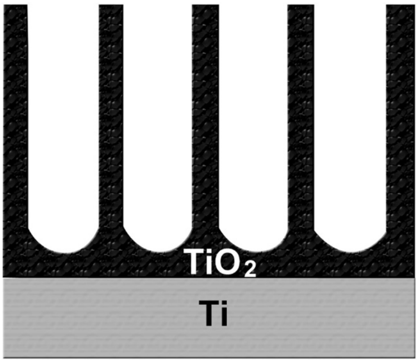


Figure 1. Schematic model of nanotubes formation.

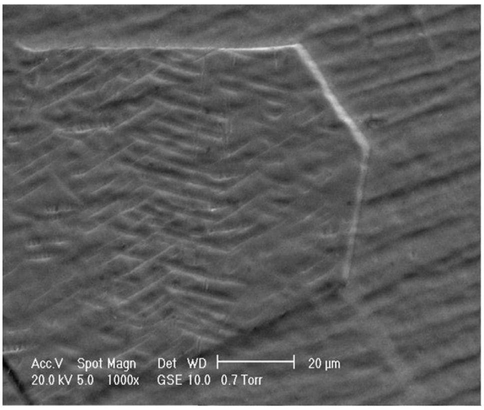
In the case of electrolytes with fluoride on TiO_2 compact structure, self – organized TiO_2 nanotubes are grown as a result of monitoring conditions as potential, time and temperature.

Surface analysis. The surface SEM images are presented in Figure 2, where a top view of TiO_2 nanotubes fabricated in HF 0.5% is together with a microscopic image of a native TiO_2 microstructure.

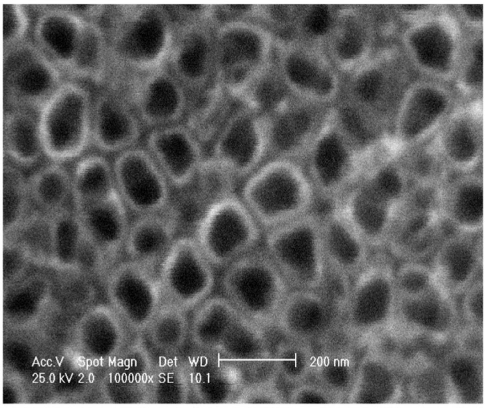
The 2D AFM images of TiO_2 self-organized layers elaborated in various fluoride solutions are presented in Figure 3, which permitted the evaluation of roughness as Root Mean Square (RMS) parameter R_q, and the Roughness Average (R_a).

The roughness values obtained for nanotubes are listed in Table 1 and compared with 11 and 15 nm respectively values for reference specimen, the natural passivated titanium surface [10]. In Table 1, together with roughness values, the diameters and contact angle are presented as function of anodizing conditions.

In a previous work [20] the nanostructure fabrication was pursued using glycerol containing 4% water and 0.36 M NH_4F. Starting at 20 V anodizing procedure gives self organized nanotubes with 40–55 nm diameter and clear an ordered aspect, but with the increase in voltage, the ordered structures shift from nanotubular aspect towards a porous distribution. At 40 V, the nanotubes are incorporated by porous structures of the same diameter. The incorporation process accentuates for the higher voltage and at 80 V applied voltage gives a final porous-only surface. Such data sustain the idea of a strong dependence between TiO_2 nano pattern and fabrication conditions. The contact angle values for native TiO_2 is 49 and this is a reference value. The contact angle values for anodizing Ti as function of electrolyte composition and nanotube geometry varied from a very weak hydrophilic value (83) to the best hydrophilic value as 16. Such results indicate that obtaining nanotubes architecture is not always a way to increase hydrophilicity of surfaces. Taking into account that wettability is a crucial factor in cell adhesion, self cleaning, etc., such variation for hydrophilic/hydrophobic balance supports the idea that for each potential application nanostrucure could be an improvement only for a specific geometry. Refering to biomedical application, to cell adhesion in particular as an aspect of biocompatibility literature data afirme that osteoblast adhesion is enhanced on Ti anodized to possess nanotubes compared to those not anodized [17] and this fact should be correlated both to surface roughness and to contact angle, parameters that for native TiO_2 are usually direct correlated, for smoother surfaces the contact angle being larger



(a)



(b)

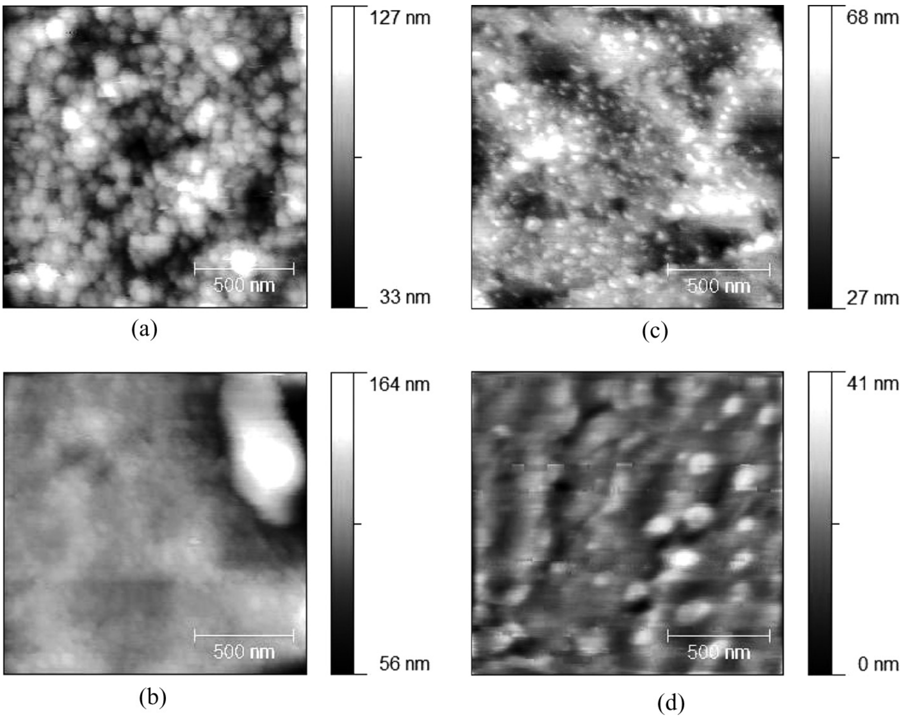
Figure 2. SEM structure of the (a) TiO_2 native passive stratum, (b) TiO_2 nanotubes self-organized layer.

[21]. That means that smooth surface can improve cell adhesion, but this fact is more complex in nanotubes cases where TiO_2 diameter seems to direct cell fate [19,22].

Electrochemical Stability. The initial event during the immersion of titania nanotubes in bioliquids, is the hydrolysis and the establishing of the equilibrium surface-solution. This dissolution process may conduct to species as $Ti(OH)_2$ or hydroxocomplex like $TiO(OH)_2$. Immediately after immersion in bioliquids as NaCl 0.9% as can be seen in Figure 3, the corrosion potential presents electronegative values. A tendency to more noble values are taking place after a short period of behavior in NaCl, the difference consisting in the range of potential values, which is in the more electropositive domains for the self organized nanotubes structures.

According to Figure 4, dissolution and repassivation of Ti are expressions of the film stability in both cases, but both aspects are more pronounced in the case of native TiO_2. The tendency to steady state is evident for TiO_2 nanotubes after shorter period of time.

Regarding cyclic voltammetry recorded in Hank biofluids, the curves for various nanotubes architectures presented in Figure 5 indicate as a more stable TiO_2 geometry, the one elaborated in HF 0,5% + 5 g/l NH_4F.



(a) (c)

(b) (d)

Figure 3. Image of Ti surface anodized in: (a) HF 0.5%, (b) HF 0.5% + 5 g/l NH_4F, (c) HF 0.5% + H_3PO_4 1 M, (d) 1 M $(NH_4)_2SO_4$ + 0.5 wt.% NaF.

Electrochemical parameters from Tafel plots are subject of Table 2. Comparing the obtaining values can be observed that the corrosion potential for Ti/TiO_2 nanotube electrode are anodical shifted from −162,4 mV to −62,2 mV by changing the anodizing condition and as a consequence the nanotubes geometry. Also, it is clear from the calculated values that TiO_2 nanotube coatings increase the surface stability by reducing the corrosion current densities and increase the polarization resistance in a specific manner as a function of their dimensions.

According to Table 2 all corrosion rates for various TiO_2 nanotubes fabricated in different electrolytes correspond to the class "very stable." The smallest corrosion rate from table 2 which sustained the best stability for nanotubes fabricated in the mixture HF 0.5% + 5 g/l NH_4F is associated with the largest passive domain from Figure 4 and with the smallest diameter. Taking into account corrosion rate for

Table 1. Surface characteristics as a function of anodizing electrolyte composition

No.	Electrolyte composition	R_a (nm)	D Diameter (nm)	R_q (RMS) (nm)	Contact angle, °
1	H HF 0.5%	19	100	23	83,39
2	H HF 0.5% + 5 g/l NH_4F	16	60	21	55,45
3	H HF 0.5% + H_3PO_4 1 M	14	400	19	77,45
4	1 $(NH_4)_2SO_4$ + 0.5 wt.% NaF	23	120	29	16

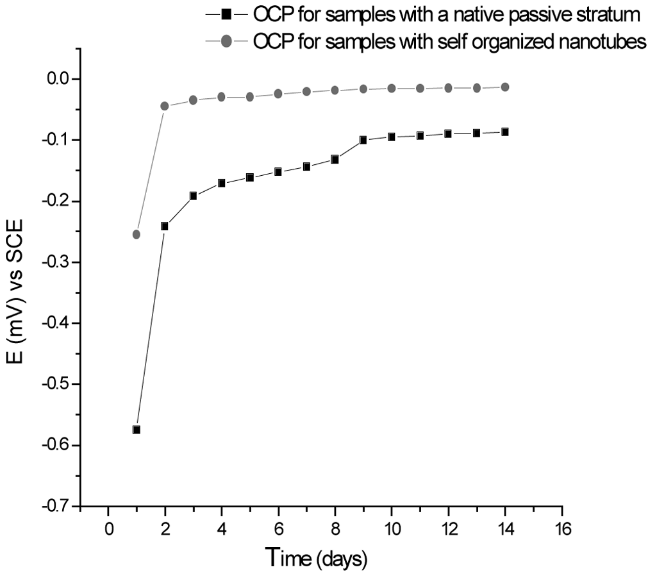


Figure 4. The evolution of potential in time for TiO_2 nanotubes (fabricated in $(NH_4)_2SO_4$ + 0.5 wt.% NaF) and for native TiO_2.

natural passive stratum which is 68,28 (μm/year), such data reveal nanotubes as more stable structure.

The stability test of nanotubes TiO_2 structure in Hank solution indicated that the corrosion current densities obtained by Tafel lines extrapolation decrease in the following direction: i_{corr} HF 0.5% + H_3PO_4 1 M > i_{corr} HF 0.5% > i_{corr} HF 0.5% + 5 g/l NH_4F. The same range is for the decrease of nanotubes diameter. The increase of electrochemical stability in other biofluids as saliva was related in a previous study [23] to an increase of biocompatibility. The behavior of fibroblast

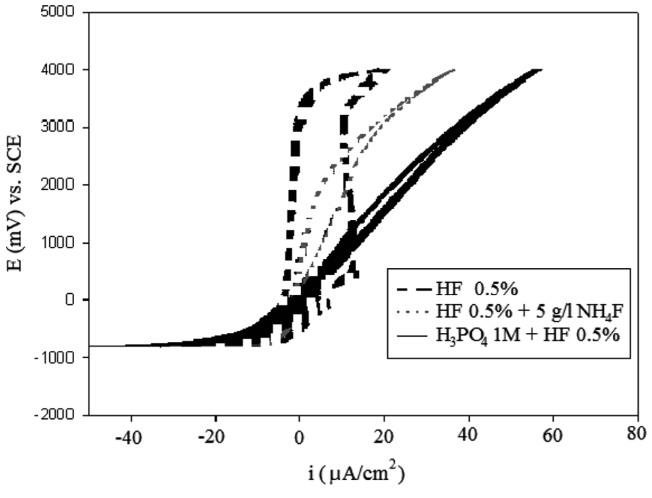


Figure 5. Cyclic voltametry curves for nanotubes fabricated in various electrolytes.

Table 2. Electrochemical parameters from Tafel plots

Anodizing on conditions	Diameter, (nm)	E_{cor} (mV) vs. SCE	I_{cor} ($\mu A/cm^2$)	V_{cor} ($\mu m/y$)	R_p (Ωcm^2)
HF 0.5%	100	−89,6	2.31	6.49	1359.3
HF5% + 5 g/l NH_4F	60	−62,4	1.97	2.98	709.14
H 0.5%HF + H_3PO_4 1 M	400	−162,4	9.98	8.85	2495.6

cells was evaluated in the imunofluorescent signals which revealed a better fibronectine expression and fine reticular organization on TiO_2 nanotubes compared to the native TiO_2 This suggests a more tight cell adhesion on such support, the cell density being higher in this case. It is an indication that nanotubes are preferred by the cells. Recent papers have found that osteoblast adhesion is enhanced on Ti anodized to possess nanotubes [17] compared to those anodized to posses nanoparticles and those not anodized at all, and mesenchymal stem cells has size selective behavior.

Conclusions

1. Using anodic deposition with an applied voltage of 20 V for 2 hours at room temperature in a mixture of various fluoride electrolytes, different architecture of highly ordered self organized TiO_2 nanotubes layers were obtained.
2. The surface was analysed with scanning electron microscopy and atomic force microscopy and revealed a porous nanotube structure of the oxide surfaces with an average diameter between 60 and 400 nm, and a somewhat rough surface, depending on the electrolyte content.
3. The contact angle data indicated a hydrophilic domain for all studied nanostructure, but depending of their fabrication condition the hydrophylic character varied from very week (83.39) to strong (16).
4. The stability test of nanotubes TiO_2 structure in Hank solution indicated that the corrosion current densities obtained by Tafel lines extrapolation decrease in the following direction: i_{corr} HF 0.5% + H_3PO_4 1 M > i_{corr} HF 0.5% > i_{corr} HF 0.5% + 5 g/l NH_4F. The same range was put in evidence for the decrease of nanotubes diameter.
5. The various geometry and hydrophilic character of self–organized TiO_2 nanotubes layers induced different characteristics which can be exploit in different potential applications, from biomedical to environment and energy.

Acknowledgments

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