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HEAT TREATMENT OF TiO_2 NANOTUBES, A WAY TO SIGNIFICANTLY CHANGE THEIR BEHAVIOUR

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Lucrarea de față prezintă un studiu al comportamentului nanotuburilor de TiO_2 *tratate termic. Tratamentul termic a fost aplicat nanotuburilor obținute prin anodizarea titanului. S-a pornit de la ideea că monitorizarea condițiilor de calcinare a nanotuburilor cu dimensiuni diferite poate conduce la nanoarhitecturi cu comportament diferit şi deci la posibile aplicații legate de modificarea balanței hidrofil–hidrofob, biocompatibilitate, nanoporozitate, stabilitate, etc. Comportamentul electrochimic al nanotuburilor a fost monitorizat prin voltametrie ciclică şi determinări de potențial în circuit deschis; rezultatele sunt discutate în legătură cu caracteristicile de suprafață evaluate din microscopie electronică de baleiaj (SEM), microscopie de forță atomică (AFM) şi măsurători de unghi de contact.*

The paper presents a study of the behaviour of thermally treated TiO_2 *nanotubes, fabricated via anodizing of titanium. The heat treatment was applied, starting from the idea that monitoring the annealing conditions of nanotubes with various dimensions leads to nanoarchitectures with different behaviour and various potential applications related to the change of hydrophilic–hydrophobic balance, biocompatibility, nano-porosity, stability, etc. The electrochemical behaviour of the nanotubes was monitored by cyclic voltammetry and open circuit potential determinations; the results are discussed in connection with surface features evaluated from scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle measurements.*

Keywords: TiO_2 nanotubes; Thermal treatment; Electrochemical stability; Surface analysis

1. Introduction

The development of surfaces with controlled properties was intensively investigated in the last decades and various procedures devoted to enhancing stability, mechanical properties and biocompatibility of metallic materials were performed and discussed [1-4]. Recent developments in nanoscience created the

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opportunities to modify the surface properties at nanometric level and processes such as sol–gel [5], chemical vapour deposition (CVD) [6], physical vapour deposition PVD [7] and anodizing [8] were considered successfully. In this approach, Ti and Ti alloys, well known for their excellent stability [9] mechanical properties and biocompatibility [10] were modified and various kinds of nanoarchitectures based on titanium were elaborated [11]; thus, a better cellular response is obtained, due to a nanostructure in the entire bulk [12,13] or at surface level [14,15]. TiO_2 nanotubes are among these nanoarchitectures. The present work reports investigations on improving nanotubes properties *via* thermal treatment of TiO_2 nanotubes with various diameters. The process of obtaining annealed TiO_2 nanotubes consisted of two steps as follows: firstly, anodizing of Ti in order to obtain TiO_2 nanotubes with controlled diameters and secondly, annealing. The corrosion behaviour of the as-formed and heat treated nanotubes was studied in Hank solution and discussed in comparison with literature data for nanotubes with other dimensions and behaviour.

2. Experimental part

2.1 Materials

Titanium substrates were of 99.90% purity, donated by the Institute for Non-Ferrous and Rare Metals, Bucharest. Before anodizing, the samples were mechanically polished, degreased in ethyl alcohol, chemically etched for a few minutes in a solution of 4% HF and 5 mol/L HNO_3 1:1 volumetric ratio, washed with de-ionized water and dried at 50^0C. The testing solution for stability experiments, for both as-formed and annealed nanotubes was Hank bioliquid with the following composition:

$$NaCl\text{ - }8\,\mathrm{g/L}, CaCl_2\text{ - }0.14\,\mathrm{g/L}, KCl\text{ - }0.4\,\mathrm{g/L}, MgCl_2\cdot 6\mathrm{H_2O}\text{ - }0.1\,\mathrm{g/L},$$

$$Na_2HPO_4\cdot 12\mathrm{H_2O}\text{ - }0.06\,\mathrm{g/L}, MgSO_4\cdot 7H_2O\text{ - }0.06\,\mathrm{g/L}, \mathrm{glucose}\text{ - }1\,\mathrm{g/L}.$$

2.2 Methods

2.2.1 Anodizing and heat treatment

The samples were the anodes in a two-electrode configuration custom-made electrochemical cell, with a Pt electrode as cathode. A constant voltage between anode and cathode was applied using a DC power supply. The nanotubes were prepared in a solution of acetic acid to 0.5% w/v hydrofluoric acid 1:7 volumetric ratio in water at 5, 10, 15, 20 V for 30 or 50 min. The annealing treatment was done at 500^0C using a Naberthem furnace with a maximum temperature of 1100^oC for 2 h.

2.2.2 Surface analysis of the TiO_2 nanotubes before and after heat treatment

Surface analysis was done by scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle measurements. All measurements were performed before and after thermal treatment. The hydrophilic/hydrophobic balance was evaluated from contact angle measurements, using a Contact Angle Meter – KSV Instruments CAM 100. Each contact angle value is the average of minimum 10 measurements. The investigation was carried out with an accuracy of $\pm 1^0$ at 25^0C temperature.

Pores diameters and walls thickness of the obtained nanotubes were calculated with **Image J program**.

2.2.3 Electrochemical methods

In order to characterize the electrochemical behaviour of TiO_2 nanotubes before and after heat treatment, open circuit potential determinations and cyclic voltammetry were used. The Ag/AgCl electrode was used as reference electrode in all measurements. Cyclic voltammetry measurements were done within the potential domain from -0.8V to +4.0V with a scan rate of 2mV/s., using a VoltaLab 40 (PGZ301 Universal Potentiostat & VoltaMaster 4). Linear polarization measurements were carried out with the purpose of evaluating the corrosion potential (E_{cor}), current density (i_{cor}), passivation current (i_{pas}) and corrosion rate (v_{cor}).

2.2.4 Statistical analysis

Statistical treatment of open circuit potential data allowed establishing the regression equations.

3. Results and discussion

The anodizing conditions used for obtaining TiO_2 nanotubes at room temperature are presented in Table 1. The electrolyte was CH_3COOH + 0.5 % HF, 1:7 volumetric ratio in water.

Table 1

Anodizing conditions used for obtaining TiO_2 nanotubes

Sample	Anodizing potential, V	Time, min
S1	5	30
S2	10	30
S3	15	30
S4	20	30
S5	5	50
S6	10	50

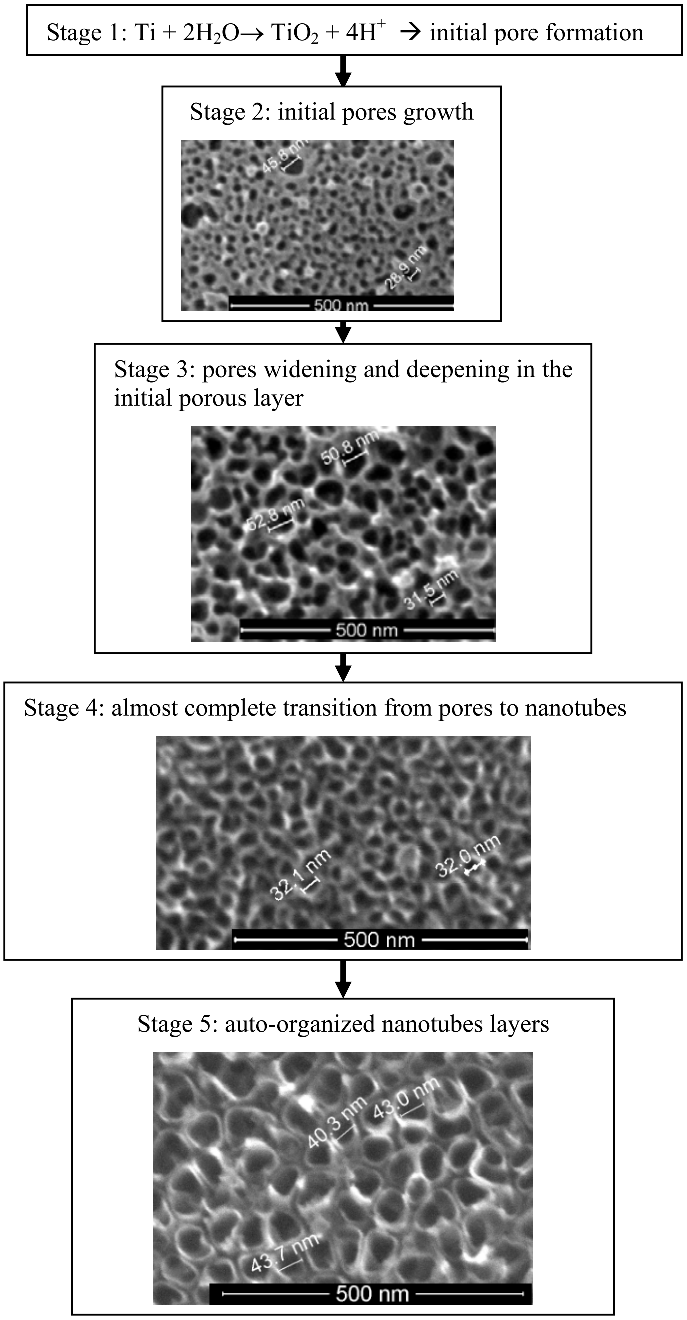

Fig. 1. SEM images of the various stages in obtaining self-organized TiO_2 nanotubes

For samples S1, S2, S3 and S4 the anodizing time was the same, but the values for the anodizing potential were increased in order to obtain larger interior diameters. Samples S5 and S6 were obtained using the same anodizing potential as for samples S1 and S2, but the anodizing time was increased to 50 min.

The SEM images of the obtained self-organized TiO_2 nanotubes according to their formation stages are presented In Fig. 1. A compact TiO_2 structure is obtained in the majority of anodizing electrolytes for Ti. In fluoride-containing electrolytes, an oxide layer forms on the surface of titanium, but after a time, due to the presence of fluoride ions (F^-) the oxide layer partially dissolves and forms pits. These concurrent processes of anodic oxidation and dissolution lead to the formation of nanotubes arrays in the five steps illustrated in Fig. 1.

The SEM images from Fig. 1 are consistent with literature data [8] regarding the nanotubes formation *via* anodizing in fluoride electrolytes. Surface features of elaborated nanotubes are given in Table 2 including average roughness from AFM (Ra) and contact angle (CA) values. The measurement of the obtained nanotubes dimensions – interior diameter (d) and wall thickness (t_{wall}) – showed the variation domain presented in Table 2.

Table 2

Surface analysis data of the as-formed samples

Sample	**Nanotube dimensions**		**AFM:**	**CA**
	d, nm	**t_{wall}, nm**	**Ra, nm**	**Value, deg.**
Ti	—	—	—	76.03
S1	20-30	6-11	17.7	73.7
S2	25-40	7-12	—	73.15
S3	30-50	8-14	—	—
S4	15-45	—	—	—
S5	18-23	6-9	16.4	50.60
S6	40-50	4-6	—	45.96

From the data presented in the above table it can be seen that sample S6 has the most uniform structure, taking into account the variation of diameters and walls thickness. When the anodizing time is increased the contact angle values decrease; the samples with higher anodizing times have a more hydrophilic character, e.g.: CA S5< CA S1 and CA S6 < CA S2. The more organized and uniform the nanotubes are, the more the contact angle values decrease to a more hydrophilic character.

As it can be seen in Table 2 the smallest nanotubes dimensions are for samples S1, S4 and S5. The nanotubes properties are size dependent [15, 16]. AFM and SEM images are presented for the selected sample S1 in Fig. 2. The figure contains the 2D and 3D topographies as well. It can be seen that the diameter of the nanotubes is quite small, in the range of 20-30 nm.

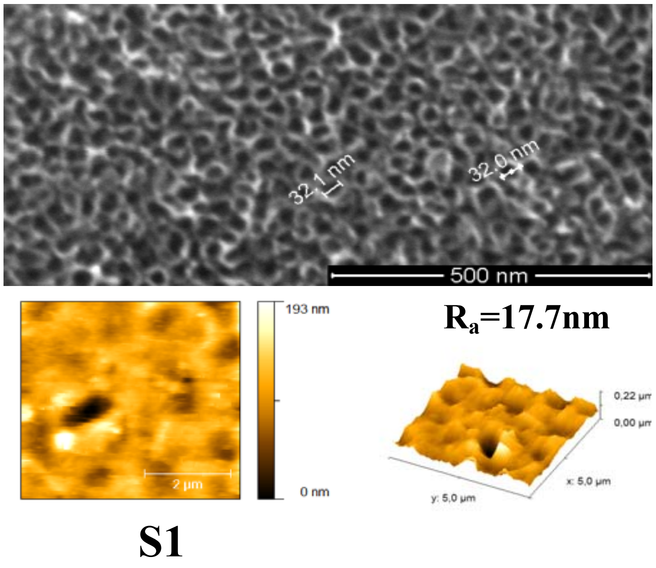

Fig. 2 SEM image and 2D, 3D topography (AFM) for sample S1

The roughness of the other samples was too high to be measured in good conditions. Taking into account the nanotubes dimensions, samples S1 and S2 were chosen to be further annealed. Fig. 3 and Fig. 4 represent the SEM images for these samples before and after annealing at 500°C for 2h. It can be clearly seen that after annealing the surface is changed (the diameters are decreased and walls thickness is increased).

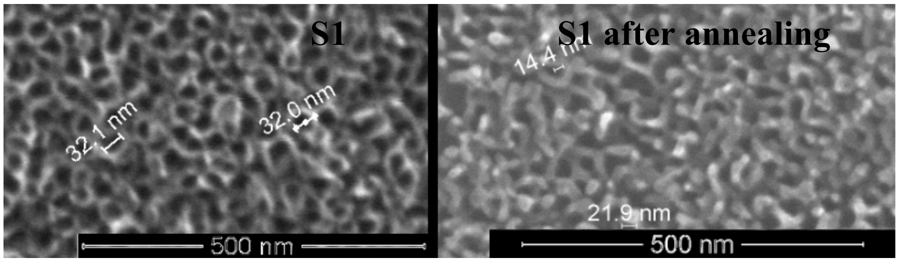

Fig. 3 SEM images of sample S1, before and after annealing at 500°

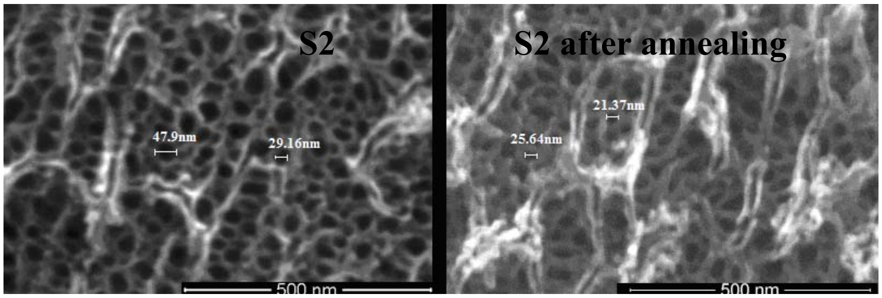

Fig. 4 SEM images of sample S2, before (left) and after (right) annealing

The surface analysis data before and after annealing is presented in Table 3. The CA values after annealing indicate that the samples are more hydrophilic: CA S1 annealed < CA S1 (27.61<73.7) and CA S2 annealed < CA S2 (17.61<73.15). The nanotubes dimensions after the annealing confirmed the previous observation, e.g. for the sample S1 the diameter decreased from 20-30nm to 10-20nm and the wall thickness increased from 6-11 nm to 12-18 nm.

In order to compute the percentage of diameter increase and wall thickness decrease after annealing, the average values before and after annealing have been obtained. These average values for diameter ($\bar{d}$) and wall thickness ($\bar{t}_{wall}$) and the percentages of diameter decrease and wall thickness increase are presented in Table 4. For example, annealing induced a modification of the nanotubes for sample S1 as follows: diameters decreased by 18.64% and walls thickness increased by 74.32%.

Table 3

Surface analysis before and after annealing

Sample	Before annealing			After annealing		
	Nanotubes dimensions		CA, deg.	Nanotubes dimensions		CA, deg.
	d, nm	t_{wall}, nm		d, nm	t_{wall}, nm	
Ti	—	—	76.03	—	—	—
S1	20-30	6-11	73.7	10-20	12-18	27.61
S2	25-40	7-12	73.15	18-30	9-17	17.61

Table 4

Modification of the average diameter and wall thickness of nanotubes after annealing

Sample	Before annealing		After annealing		Difference	
	$\bar{d}$, nm	$\bar{t}_{wall}$, nm	$\bar{d}$, nm	$\bar{t}_{wall}$, nm	$\bar{d}$, %	$\bar{t}_{wall}$, %
S1	21.73	8.06	17.68	14.05	**- 18.64**	**+ 74.32**
S2	34.10	9.51	22.36	12.9	**- 34.43**	**+ 35.65**

The electrochemical behaviour of the annealed samples was characterized by open circuit potential and cyclic voltammetry. The electrochemical experiments were done in Hank solution. Fig. 5 presents the variation in time of the open circuit potential for S1 annealed and for the TiO_2 nanotubes obtained in the same electrolyte as S1; Fig. 6 presents the variation in time of the open circuit potentials for the annealed annealed S1 and S2.

It can be seen that the values of the open circuit potentials for the annealed samples relative to the reference electrode Ag/AgCl, are all positive and have a tendency towards more electropositive values than the initial ones. Also, the open circuit potential for S1 annealed is more electropositive than that of S2 annealed (see Fig. 6), which indicates the presence of a more stable structure with regard to corrosion on its surface. The same can be noticed about the difference between S1 annealed and as-formed TiO_2 nanotubes, S1 annealed being more stable with regard to corrosion. With respect to the regression equations, the correlation coefficients are close to 1 in all cases and the annealed samples have a logarithmical trendline, while the as-formed sample has a polynomial one.

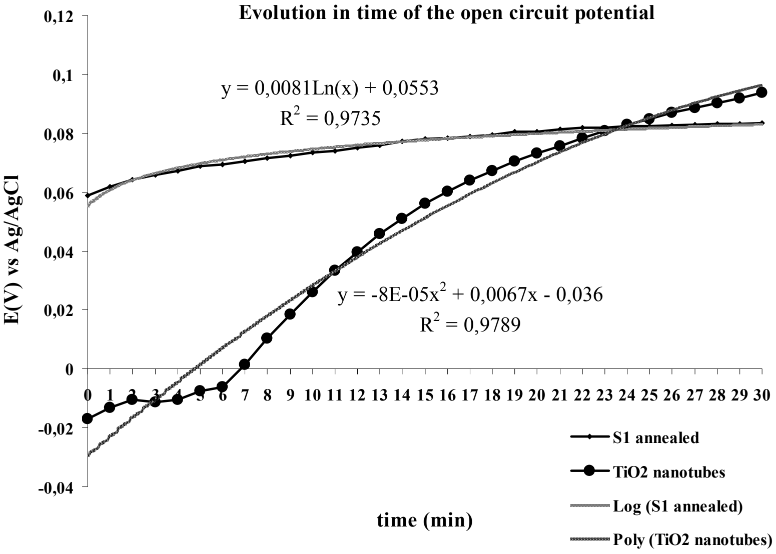

Fig. 5. Evolution in time of the open circuit potential for samples S1 annealed and as-formed TiO_2 nanotubes, in Hank solution

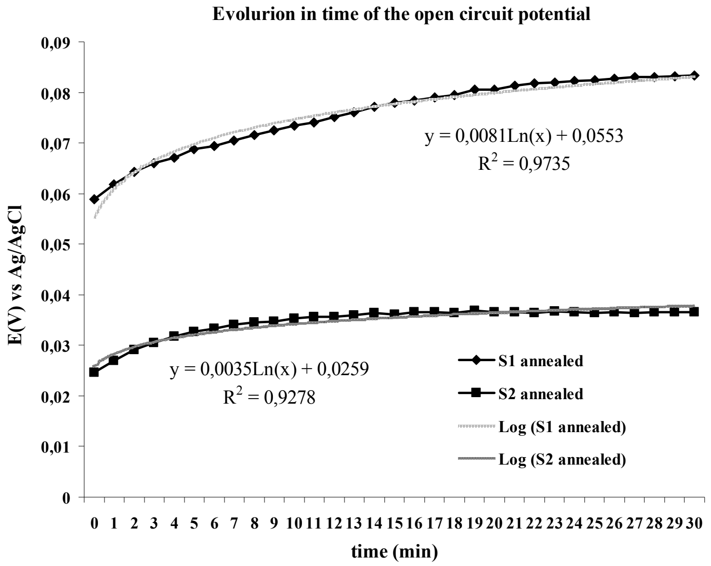

Fig. 6. Evolution in time of the open circuit potential for samples S1 annealed and S2 annealed, in Hank solution

Fig. 7 presents the cyclic voltammetry curves for S1 annealed and S2 annealed. The nature of the polarization curves indicates stable passive behaviour. The current density achieved a constant value (i_{pas}) on anodic polarization without exhibiting any active-passive transition.

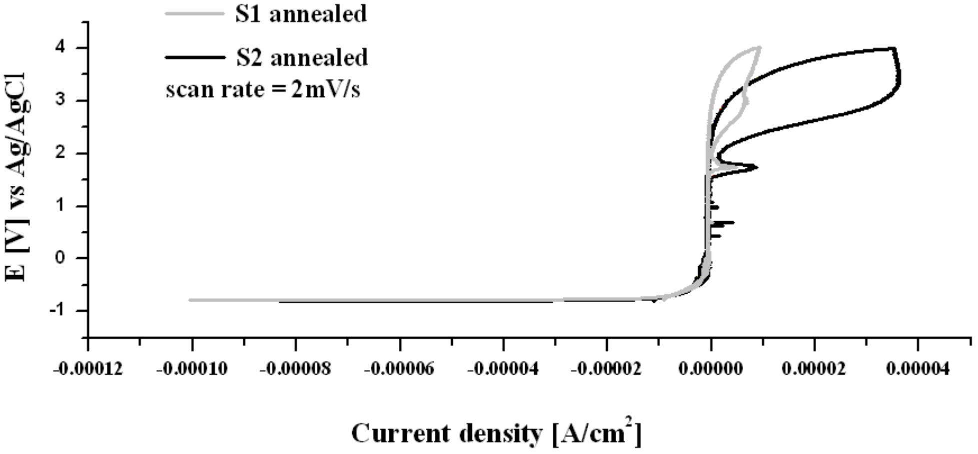

Fig. 7. Cyclic voltammetry curves for samples S1 annealed and S2 annealed, in Hank solution

Corrosion parameters have been obtained from the cyclic voltammetry curves for samples S1 annealed, S2 annealed and the as-formed TiO_2 nanotubes. Reference values for commercially pure titanium (cpTi) were taken from literature [17]. The corrosion parameters are presented in Table 5: corrosion potential (E_{cor}), corrosion current (i_{cor}) and rate of corrosion (v_{cor}), passivation current (i_{pas}) and polarization resistance (R_p).

Table 5

Comparison of corrosion parameters for: S1 annealed, S2 annealed, as-formed TiO_2 nanotubes and cpTi

Sample	**E_{cor}, mV**	**i_{cor}, µA/cm^2**	**i_{pas}, µA/cm^2**	**v_{cor}, mm/Y**	**R_p, kOhmcm^2**
cpTi	-606	2.32	8.5	$5.7 \cdot 10^{-2}$	—
TiO_2 nanotubes	-497.3	1.0160	0.0401	$1.963 \cdot 10^{-2}$	0.574
S1 annealed	666.2	0.6714	0.682	$1.297 \cdot 10^{-2}$	8.05
S2 annealed	429.5	1.8403	0.579	$3.555 \cdot 10^{-2}$	18.11

S1 annealed has the most electropositive value for E_{cor}, thus indicating the presence on its surface of a more stable structure in what corrosion concerns. The presence of nanotubes on the surface leads to a significant decrease of the corrosion rate.

A comparison between the annealed samples leads to the conclusion that S1 annealed is more stable, due to a smaller corrosion rate (the corrosion rate for S1 annealed is three times smaller than that for S2 annealed).

The data from Table 5 allowed the evaluation of the annealing treatment's efficiency from the point of view of electrochemical stability, computed using the following expression:

$$\eta = \frac{\left(v_{corTiO_2nanotubes} - v_{corS1}\right)}{v_{corTiO_2nanotubes}} \times 100 \qquad (1)$$

$$\rightarrow \eta = 33.93\%$$

When comparing S1 annealed with as-formed nanotubes, the corrosion rate for S1 annealed is smaller than that for TiO_2 nanotubes, which indicates that the annealing process helped to increase the stability of the nanotubes surface, the annealing efficiency being of 33.93%.

4. Conclusions

As a result of the annealing treatment, a decrease of the contact angle was observed, the samples becoming more hydrophilic. Regarding the nanotubes dimension, an increase of the wall thickness (with approx. 74.3%, respectively 35.6%) with a decrease of their diameters (with approx. 18.6%, respectively

34.4%) was observed for samples anodized at 5 and 10 V for 30 minutes and annealed at 500°C for 2 hours.

It is to be noted that the presence of nanotubes on the surface leads to a significant decrease of the corrosion rate.

The electrochemial behaviour of annealed samples was characterized by the open circuit potentials and cyclic voltammetry in Hank solution. After annealing, the sample obtained at a lower anodizing potential (5V) is more stable, which was sustained by the fact that it had a more electropositive corrosion potential and a smaller corrosion rate.

The annealing treatment improved the stability of samples (the annealing efficiency regarding the corrosion rate is 33.93%). This aspect is also corroborated with the fact that the corrosion rate for the annealed sample obtained at a lower anodizing potential is smaller than that for the as-formed TiO_2 nanotubes.

The electrochemical behaviour of the studied annealed samples recommends their use in implantology, but further *in vivo* studies are necessary.

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