Optimized anodization setup for the growth of TiO_2 nanotubes on flat surfaces of titanium based materials

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Abstract. An extensive research work on development of nanostructured TiO_2 layers on the surface of titanium based materials for biomedical implants led the authors to the optimization of process parameters of electrochemical anodization in phosphate/fluoride based electrolytes. Based on those parameters, a dedicated optimized electrochemical anodization setup was originally designed and realized. The anodization bath was designed in order to provide a proper circulation of electrolyte and the possibility of distance anode-cathode modification, the DC power supply was designed accordingly to the electrical parameters requested by the nanotubes development, and a dedicated software (Nanosource) was developed for process control and ease and flexibility of process parameters acquisition, storage and processing.

1 Introduction

Metallic biomedical implants made of pure titanium or titanium alloys, especially Ti6Al4V, are nowadays widely used in dental implantology, cranio-facial surgery and orthopedic surgery. They present good mechanical properties, but more important, due to the spontaneous formation of a thin oxide layer onto the surface, they are highly resistant to corrosion and biocompatible. Their osseointegration is the clinical goal of any surgical intervention, and today is well acknowledged that the surface modification of implants enhances the osseointegration.

In the recent years, the surface modification at nanoscale level is a research direction that is followed by many teams. Nanostructured TiO_2 layers with nanoporous or nanotubular morphologies are under intense research focus, due to the fact that studies show their enhanced osseointegration [1-8]. Cells sense and interact with titania nanotubes (TNT) through changes in morphology, proliferation, differentiation, and absorption. TNT

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are capable of promoting bone cell function mainly due to: increase surface roughness/energy, the incorporating of fluoride ions (in the case of TNT developed in fluoride based solutions), and the ability to mechanically stimulate cells (this means the geometrical fitting between nanotubes opening of 15…100 nm and the diameter of surface proteins, ~ 10 nm, which are absorbed onto the nano modified surface; these proteins are sensed by integrins, the surface receptors of bone cell membrane, and to them bone cells are attaching to).

Electrochemical anodization is a method which allows the modification of titanium based surfaces at nano scale level if process parameters are optimized [9-13]. Depending on electrolyte properties (composition, temperature, pH, conductivity), current parameters (anodization potential, sweep rate, anodization duration), initial surface shape and preparation, other specific features in anodization cell (distance anode-cathode), titania layers that are developing can be either compact, either nanostructured.

The electrochemical anodization process was optimized by the authors allowing the development, in a reproducible manner, of uniform, self-organized TiO_2 layers on the flat, polished or micro rough surfaces of pure titanium and dual phase ($\alpha+\beta$) Ti6Al4V alloy, in phosphate/fluoride based electrolyte. The optimization of the process was made by using a custom-build anodization setup (that will be denoted as *initial electrochemical anodization setup - IEAS*), by several sets of experiments whose results are presented elsewhere [14-18], and which allowed the tuning of the process parameters. Based on these results, an *optimized electrochemical anodization setup (OEAS)* was originally conceived and realized by the authors, being presented in current paper. The DC power supply was designed accordingly to the electrical parameters requested by the nanotubes development. The anodization bath was designed in order to provide a proper circulation of electrolyte. The holding system for the samples allows the modification of their position and distance anode-cathode. The setup is completed by all necessary arrangements for process monitoring instrumentation (thermometer, ph-meter, conductivity meter) installation.

2 Methodology

The anodization experiments presented in present study were performed in new optimized electrochemical anodization setup (OEAS), using the same type of samples (shape, dimensions, surface preparation) and anodization process parameters, as in the old initial electrochemical anodization setup (IEAS), in order to be possible to realize a comparison of resulting titania nanotubular layers.

Samples, made from pure titanium or Ti6Al4V alloy, are in form of disc shape of 16 mm in diameter and 3 mm in height. Before the anodization process the samples were subjected to a thorough cleaning process. The samples were connected at the anode of the cell; cathode: ∅16 x 3 mm disc, made of high purity copper (99.99%); distance anode-cathode: 15 mm; electrolyte: 1M H_3PO_4 + 0.5 wt% HF; room temperature; anodization potential: 20 V, applied with a sweep rate of 0.1 V/s; anodization time: 30 min. The surface morphology was evaluated by using scanning electron microscopy (SEM), performed in a JSM 5200 (JEOL) scanning electron microscope, operated at 25 kV. The dimensions of nanostructures developed on the modified surfaces were measured on SEM micrographs by using an open source graphical image processing software (Gimp).

3 Results and discussion

Figure 1 presents the *block scheme of the optimized electrochemical anodization setup* that has been conceived. The main components of the OEAS are: anodization bath (tank), DC power supply, peristaltic pump (with its power supply), instrumentation for electrolyte parameters monitoring (thermometer, pH – meter, conductivity meter). The electrical anodization process parameters are computer controlled and monitored by dedicated software originally developed – Nanosource.

Each component of the OAS was carefully designed: the anodization bath was designed in order to provide a proper circulation of electrolyte, and to have a holding system for the samples that allows the modification of their position and distance anode-cathode; the DC power supply was designed accordingly to the electrical parameters requested by the nanotubes development.

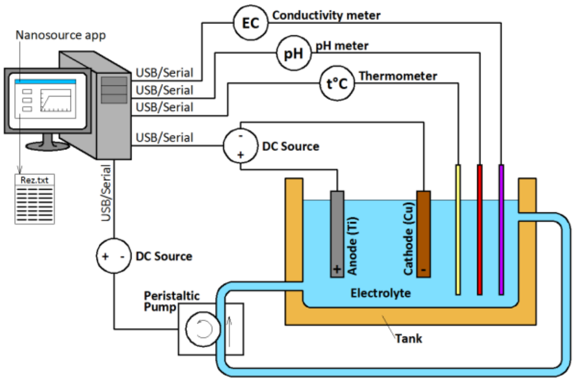

Fig. 1. Block scheme of optimized electrochemical anodization setup (OEAS).

Fig. 2 presents the design of the *anodization bath* complex. Its main feature is the tank (1), perforated with two holes (2) for the recirculation of the electrolyte by means of a peristaltic pump (not represented here). At the top, the tank is capped by a cover piece (3). The mobile support (4) is used to fix the copper cathode (5) with the help of a clamping bolt (6) and two gaskets (7 and 8) to prevent the infiltration of the electrolyte inside the channel of the electric wire (9) coming from the DC source. The titanium-based anode (10) is fixed on the opposite side using a second clamping bolt (11) and its corresponding gasket (12). The anode is pressed into position with a rod and a spring (13) which also have the role of passing the current from the DC source.

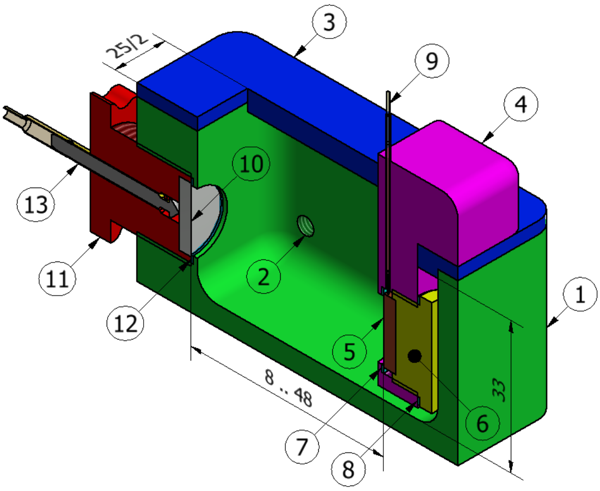

Fig. 2. Design of anodization bath.

The mobility of the cathode support makes possible the precise adjustment of the distance between the anode and the cathode (using a scale on the cover of the tank) in the range of 8 mm to 48 mm. This allows the testing of the influence of this distance on the formation and quality of the nanotubes.

A *dedicated DC power supply* was designed in order to obtain the required supply voltage, applied with a specific sweep rate, using discrete non-programmable electronic components, such as counter, digital to analog converter, linear amplifiers using rail to rail operational amplifier (Fig. 3 and Fig. 4). The ramp supply voltage generator has two major parts, the ramp generator and the analog output circuit. The first part assures the required ramp (in V/s), while the second part interfaces the generators output with the load.

The ramp generator provides a ramp with n bit resolution, where the value is increased by each clock cycle and the start and stop value can be defined by the user. The slope is defined by the clock input.

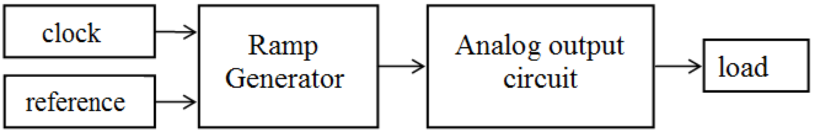

Fig. 3. Block scheme of DC power supply.

The ramp is generated by a n digital-analog converter (DAC) which has at the input a modulo N (with $N \le 2^n$) counter. After reaching the value N, the counters outputs remain in this state until the process ends. The reference voltage of the DAC controls the ramps step.

The counters clock can be set at different values to be adapted for the required values as the output of the ramp generator will have a step of value $(N/2^n) \cdot U_{REF}$ in every period of the clock signal. The ramp duration is $T_{RAMP} = N \cdot T_{clock}$, the duration until the final time can be set manually, depending on the controlled process. The maximum value of the output voltage is $U_{OUTmax} = A \cdot N \cdot q$, where A is the gain of the non-inverting amplifier and $q = U_{REF}/N$ is the quantum corresponding to one step.

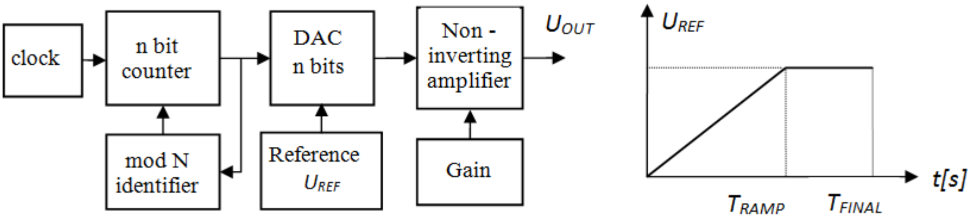

Fig. 4. The ramp supply voltage generator.

For a supply voltage domain $U_{OUT} = 1 \div 20\ V$ with a ramp of $0.1\ V/s$ results that T_{RAMP} is $200\ s$. By using a reference $U_{REF} = 5\ V$, the quantum is $q = 5/256 = 0.01953125\ V$, after 200 steps the output of DAC is $3.90625\ V$. By setting the clock to $1\ Hz$ and the gain of the analog output circuit at $A = 20/3.90625 = 5.12$ the proposed values are obtained. The used DAC is a CMOS 8-bit successive approximation converter (DAC0804) having a resolution $\pm(1/4)LSB$ with a conversion time of 100 µs. The non-inverting amplifier is realized with an extended supply voltage operating range and rail-to-rail output operational amplifier. The current consumption is usually under $50 \div 100\ mA$, there is no need for current amplification.

In order to conduct repeatable experiments, the parameters of the anodization system need to be monitored and controlled. Solving of this problem was realized by creating a *dedicated control and monitoring software - Nanosource*, developed in Labwindows CVI. This software is able to control the anodization source voltage and current limit and also to log the temperature of the anodization bath together with the measured voltage and current from the source. The equipment items are connected with the process control computer through electrically isolated USB ports which at device level are accessible as virtual serial ports. The communication with the devices is controlled by a predefined timer with a period of 0.1s. The developed software has two modes of operation: a *manual* one, in which the prescribed value is entered in the *Uset* or *Ilim* box on the graphical user interface; the second operation mode is an *automated* mode, with a starting ramp with specified slew rate for starting the anodization process, then a potential hold mode for the continuous growth mode. In this mode, the user can set the starting voltage *U_start*, the slew rate *V/S*, the hold voltage *U_hold* and the time for the continuous growth *Hold time (s)*. The total time of the process *Total (h:m:s)* is displayed on the user interface by following the setting of the process parameters. The output of the anodization source is switched automatically on at the start, and off at the end of the process. Data is logged at every measuring interval and files for every process conducted are recorded separately.

By using this OEAS there were developed TiO_2 layers on flat surfaces of pure titanium and Ti6Al4V alloy in phosphate/fluoride based electrolytes, at an anodization potential of 20 V. The obtained nanotubes were uniform, self-arranged and presented diameters in 50-110 nm range and are fully comparable with those obtained in IEAS.

Figure 5.a presents the SEM image (top view, collected at 35000X magnification), of the TiO_2 layer developed using OEAS, showing well developed nanotubular morphology, with nanotubes diameter in 50-110 nm range. The nanotubes walls are well separated and the nanotubes are uniformly distributed and self-arranged. This proves that the OEAS provides reliable results on proper nanostructures development.

Fig. 5.b presents the registration of the anodization potential U [V] and the anodization current I [A] taken by the Nanosource software during the anodization process, and the graph of potential and current evolution, processed in Excel by importing data from Nanosource. This shows the advantages of OAES over IAES, which are the ease of process control and monitoring, and the ease and flexibility of data collecting, storage and processing.

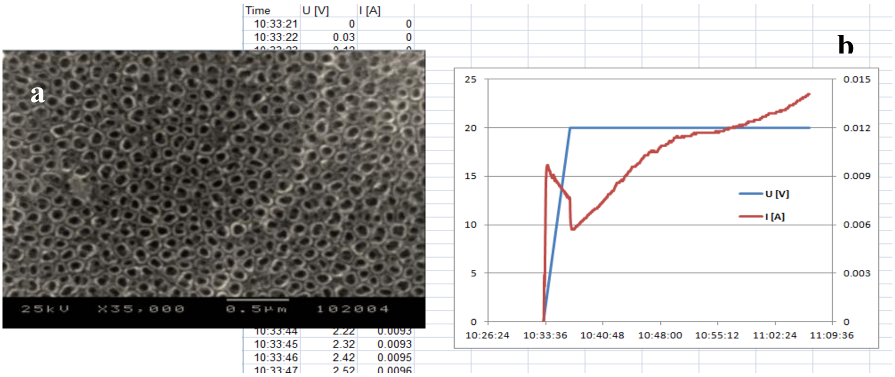
Time	U [V]	I [A]
10:33:21	0	0
10:33:22	0.03	0
10:33:44	2.22	0.0093
10:33:45	2.32	0.0093
10:33:46	2.42	0.0095
10:33:47	2.52	0.0096

Fig. 5. SEM micrograph of TiO_2 nanotubes developed in OEAS (a). The evolution of anodization potential and current during the electrochemical anodization; data were collected and stored using dedicated Nanosource software (b).

All the further work that will be carried on nanostructured TiO_2 layers development on flat surfaces of pure titanium and titanium based alloys by electrochemical anodization will be performed from now by using the OEAS.

4 Conclusions

The obtained results have proven that it was possible to develop nanotubular oxide layers on the surfaces of titanium based materials for biomedical implants by using an optimized electrochemical anodization setup (OEAS) originally designed and developed by the authors.

The carried-out work on setup optimization led to the realization of: a dedicated electrochemical bath (tank), specially designed in order to allow a proper circulation of chemical electrolyte and the modification of anode-cathode distance; a dedicated DC power supply, which was designed and realized in concordance with the electrical parameters requested by the nanotubes development; and a dedicated software Nanosource which was designed and realized for process control and monitoring.

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