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TiO₂ NANOSTRUCTURE FORMATION BY PLASMA ELECTROLYTIC OXIDATION

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Abstract. *With the advancement of medicine, the use of prostheses has become increasingly common, especially in dentistry. One of the most used materials for these procedures is Titanium (Ti) for its natural biocompatibility with the human body. Some studies aim to the improvement of these characteristics by Ti surface modification, such as, electrochemical anodizing which is the most widespread and common procedure for oxidation of the surface of materials used as implants. Therefore, this work aims to study a new method of treatment of titanium surface by using the Plasma Electrolyte Process, this method has the advantages of reducing time and expenses in the process of coating Ti surfaces. Plasma electrolytic oxidation (PEO) requires high values of the electrical voltage applied to the material for the generation of plasma on the surface that one wishes to work, however, the exposure time is up to 80% shorter.*

Keywords: *Electrolytic Oxidation to Plasma, Titanium; Plasma technology; Nanotubes; Surface Engineering.*

1. INTRODUCTION

The purpose of the surface treatment of the materials is to give the material new characteristics without altering its internal and functional properties, and therefore, to increase the field of its applications. Many technologies have been developed to improve the chemical, mechanical and biological properties of materials. Nowadays, with the advent of nanotechnology, we can improve the properties of a material by changing the size of the grains which compose its structure. The properties of a material on the nanoscale tend to be different or are potentiated to the properties of this same material when compared to the macroscale. One of the properties that undergo major modifications is related to the surface area of the nanomaterials, which on the "Nano" scale is much larger when compared to the same material mass on the macroscopic scale. This change in fundamental properties related to particle size variation is known as the "Size Effect", meaning that the high surface area of the nanoparticle affects for example its reactivity and solubility. In the case of biomaterials used as dental and orthopedic implants we can improve biocompatibility and osseointegration, when the surface interaction increases, favoring the formation of bone tissue on the implant surface.

The modification of surfaces is usually performed in the materials to achieve characteristics that are not found in their natural form and, thus, expanding their application possibilities. From screws to complex spaceships, surface treatment

deserves greater prominence every day, not only for the performance it offers to products and materials, increasing its service life and protecting against environmental aggressions but also for the possibility of expanding the options for use by the unique features it provides. (DOROZHKIN, 2012; MINATI, 2014).

Particularly for some materials, the use of pretreatments is an essential technology in some industrial sectors. For example, corrosion in aluminum alloys occurs mainly due to their composition and a study on alternative coatings that eliminate or minimize the formation of these galvanic pairs is of paramount importance (DOROZHKIN, 2012; MINATI, 2014). This process can be an attractive alternative for processing materials for obtaining thin protective films in metal alloys (RANDHAWA, 1987). All existing materials have natural characteristics, and some may undergo important surface changes making these characteristics of high, medium or low intensity such as: aggressive, corrosive, biologically incompatible, sensitive to light, heating or oxidation, hydrophilic, transparent and / or viscous. Depending on situations and applications, such properties are desirable or undesirable. In the latter case, to eliminate unwanted properties, the surfaces of these materials must be modified. To produce surfaces with characteristics suitable for your application. In general terms this has applications for chemistry, mechanical engineering, electrical engineering and many other areas (DOROZHKIN, 2012; MINATI, 2014).

Titanium has an inert characteristic and chemical stability compared to other metals that have biocompatibility (DOROZHKIN, 2012). However, its bioinert characteristics require changes in its surface to become bioactive and improve its osseointegration (MINATI, 2014). It is the metal most used as dental and orthopedic implants due to its inert characteristic; have chemical stability compared to other metals; biocompatibility and does not cause adverse biological reactions (DOROZHKIN, 2012). However, there is the possibility of modifying and improving its surface properties and increasing the degree of biocompatibility of the implant in relation to bone tissue through the development of nanostructures on its surface. Titanium is biocompatible (non-toxic and is not rejected by the body), it can be used in many applications for medical use and mainly in the replacement of human bone, ie used as implants and surgical elements, such as together and hip fittings (joint replacement), dental implants that can remain in place for up to 20 years. This biomaterial is allowing use in dental implants that can last more than 30 years. This property is also useful for orthopedic implant applications (KARLSSON et al, 2000; VULCAN, 2019). They benefit from the lower modulus of elasticity of titanium (Young's modulus) to get closer to the bone that these devices should repair. As a result, skeletal loads are more evenly shared between the bone and the implant, leading to a lower incidence of bone degradation due to protection against stress and periprosthetic fracture, which occur within the limits of orthopedic implants. However, the stiffness of titanium alloys is even more than twice that of bone, so the adjacent bone supports a very small load and can deteriorate (ROSA, 2013; VULCAN, 2019).

The Electrolytic Plasma Oxidation (PEO) process that has been used to deposit ceramic coatings in Al, Ti, Nb, Stainless Steel among others. Electrolytic oxidation of plasma (PEO) allows coatings to form containing several desirable properties on the surface of the Titanium sample. Its porous structure, a result of the PEO process, can provide a good biological fixation to the surrounding tissue due to bone growth into the porous surface after implantation (ROSA, 2013). PEO is a term used to describe a variety of electrochemical processes that occur at the electrode interface and electrolyte solution when the applied voltage exceeds a certain critical value, typically hundreds of volts (LARLSSON et al, 2000; CHEN et al, 2006).

Compared to the conventional electrochemical process, PEO can be performed in a single step and reduce processing time, this is possible due to the high voltages in the energy source used in the process, which establish the plasma in the electrolytic medium of the growth layer, therefore also called plasma anodizing or plasma galvanizing. The simultaneous action of electrical discharges can be performed in a direct current (DC) source, but the research revealed that alternating current (AC) sources allow the production of films with less surface porosity, that is, more uniform (ZHU et al, 2016). Currently, pulsed, bipolar or hybrid sources have been used in research to obtain superior coatings (LUGOVSKOY et al, 2013). In the development of this work, we used the characteristics of Surface Engineering as a fundamental element to change the properties and surface functionalities of biomaterials and use plasma engineering as a technological means for this development, an area with great applications in the electronics, aerospace, metallurgical, biomedical, waste and debris treatment industries. To enable this project, a DC power supply ranging from (0 - 20 A) and (0 - 1000 V) was used. Glycerol solutions (50 % vol) + H₂O_(Distillate) (50% vol) + NH₄F (Ammonium Fluoride) is the electrolytic solution proposed for the generation of TiO₂ (Titanium Oxide) nanostructures on the surface of pure titanium (Ti) samples. In this process, the Ti samples are in electrolytic solution configured of negatively polarized electrode and a Ti counter electrode to close the electrolytic circuit. The samples used Ti with rectangular geometry (10x20 mm) and 2 mm thickness inserted inside the electrolytic solution and subjected to the high temperature plasma arc that removes the atoms from the surface, exposing the Ti samples to the "Top-Down" process of manufacturing nanomaterials, mechanism and miniaturized structures for the nanometric scale. Technology that uses erosion or wear methods to produce building blocks and/or devices from a larger part, i.e., a Top-Down construction that is instantly oxidized (ROSA, 2013; VULCAN, 2019), in this way by "sculpting" the nanostructures in the Ti samples. A disadvantage of this process is the loss of material mass during the process. In this work, the variation of the distance between the electrode and counter electrode, exposure time of the electrode to PEO and electric current provided by the source was explored as an investigative element. These parameters were explored to define the best physical parameter that will provide better formation of the nanostructures of the studied coating, thus avoiding changing the chemical parameters such as concentration, quantity of components

inserted in the electrolytic solution. To characterize the coatings, microstructural analyses were made, chemical composition of the coatings through metallographic analysis and fractography SEM, EDS, DRX and FEG and the difference of the masses of the samples before and after the process.

2. MATERIALS AND METHODS

2.1. Sample preparation and growth of TiO₂ coatings

Titanium plates, purity 99%, with dimensions (10×20×1) mm were used in this work. And because the entire surface is uniformly anodized by electrolytic plasma, a sanding process has been done. This procedure is extremely important, eliminating scratches, marks, dirt etc. Two different equipment was used to carry out the process: the automatic circular sander was used for sandpaper 180 to 400 and track sander for sandpaper 600, 1200 and 2000. Figure 1 shows diagram and dimensions of the Ti sample used.

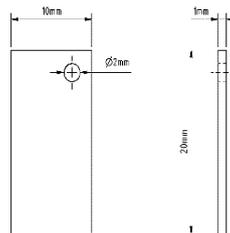


Figure 1: Representation of the dimensions of the Ti sample

2.2. Electrolytic Solution and Chemical Reactions

In a solution of 1000 ml, 50% vol of C₃H₈O₃ mixed with 50% vol of H₂O (distilled) and 1 g of NH₄F in a Becker inside a reservoir with circulating water system to keep the solution at a temperature of approximately 70 °C. A FISATOM mechanical mixer is used to maintain homogeneous solution with pH = 5, Figure 2.

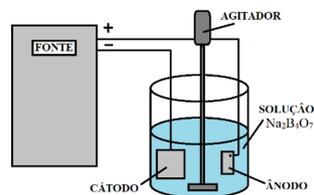


Figure 2 - Experimental setup diagram

The chemical reaction is induced inside the discharge due to the increase in temperature by modifying the structure, composition and morphology of the oxide coatings. The composition and concentration of the electrolyte play a crucial role in obtaining the coatings of nanostructured oxide structures desired by PEO.

This nanostructured coating, formed by oxidation microarcs, is composed of a porous outer layer and a compact inner layer in which the composition and thickness depend on the nature of the electrolyte [16]. The process can be study as follows:



With anodizing happening first is created a layer of TiO₂ on the Ti under conditions investigated in this work for generation of nanotubes by the manufacturing process Top-Down with the objective of creating the structured nanotubes through selective corrosion through TiF₆²⁻. If you allow too much of the time to pass the chemical dissolution, it begins by corroding the nanotubes and deform them until they cease to be nanotubes and become only a layer of Titanium Dioxide (TiO₂) and with more time all the titanium dioxide to undo in Titanium Hexafluoride (TiF₆), shown in Figure 3.

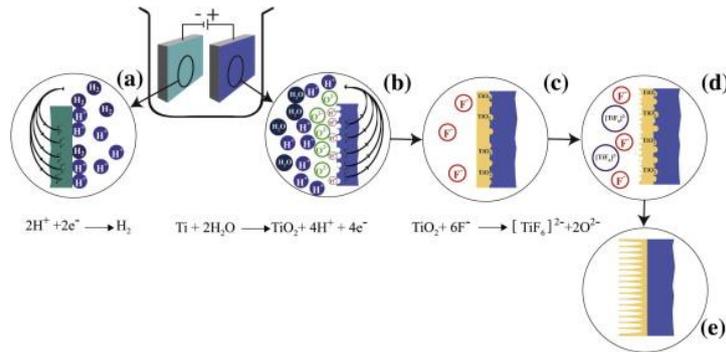


Figure 3 - Anodizing Process for the Formation of TiO₂ - (Rosa, 2013)

Also, small amounts of electrolyte components are incorporated into the oxide layer during anodizing, as chemical conversion of the substrate metal occurs in its oxide and grows both inside and outside the original surface of the metal. By growing inside the substrate, it has excellent adhering to the metallic substrate. As this process uses much higher stresses (hundreds of volts) than those applied in conventional anodizing, which allows the appearance of micro plasmas on the surface of the part to be treated (CHEN et al, 2006).

Plasma anodizing is a single-step treatment, and it does not need to use aggressive solutions to man or the environment (CHEN et al, 2006; DARBAND et al, 2017). The presence of micro plasmas in the working electrode (anode) causes increased electrochemical reactions within the electrolytic solution, which results in a faster process, and with higher rates of deposition of oxide films (DARBAND et al, 2017).

However, as well as conventional on the other hand and other electrolyte treatments, the surface changes resulting from the process depend on the parameters applied, such as the working voltage, current, temperature, chemical composition of the parts to be treated and the types of electrolytes among other parameters (CHEN et al, 2006; DARBAND et al, 2017).

2.3. Mass Variation Rate and Percentage of Mass Loss

The rates of mass variation and the percentage of mass loss corroborate the a fore mentioned microstructural evolution after oxidation tests. According to Jun Li et al., the rates of mass and thickness variation were obtained using Equations (3) and (4), respectively,

$$R_M = \frac{m_i - m_f}{\Delta t} \quad (\text{Average mass loss rate}) \quad (3)$$

$$\%M = \frac{m_i - m_f}{m_i} \times 100 \quad (\text{Percentage of Mass Loss}) \quad (4)$$

The equation (3) presents the average rate at which selective corrosion attacks the Ti sample as a function of the time for the formation of the nanostructures. And the equation (4) shows the percentage of mass loss in the top-down manufacturing process, that is, the amount of mass lost in the manufacturing process of the Nanotubes of TiO₂.

2.4. Electrolytic Plasma

The process (PEO) consists of two electrodes immersed in an electrolytic solution with a high voltage applied that involves anodizing where numerous thin sparks (microarcs) are produced continuously along the surface of the coating, accompanied by gas release. For the development of this project, the facilities of the Electrolytic Plasma Laboratory (LaPE), installed at FATEC - Pindamonhangaba, were used.

The electrolytic system that will be used in plasma anodizing processes is shown in Figure 4, consisting of the following equipment:

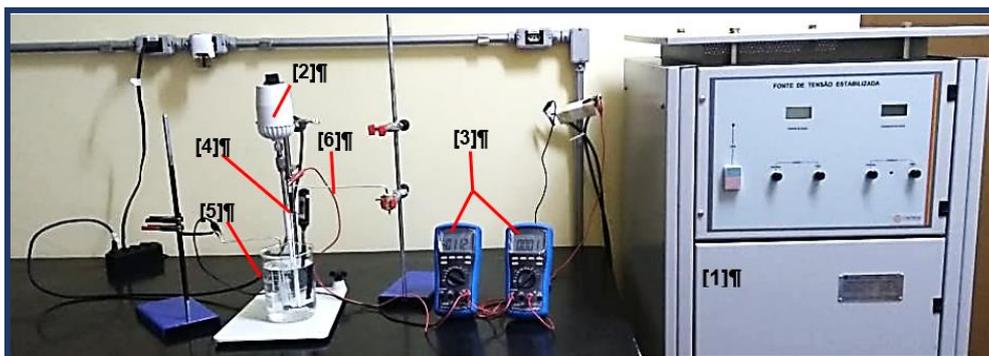


Figure 4 - Experimental Device Photo - LaPE

[1] CTRLTECH stabilized voltage source, with variable voltage from 0 to 1000 V CC, and variable current 0 to 20 A CC.

[2] FISATOM mechanical agitator for solutions up to 1.5 litres and 25 W power.

[3] Multimeters MINIPA model ET2030A, for voltage and current measurements.

[4] Mercury thermometer (0°C - 200°C), for measurements of the temperature of the solution.

[5] Stainless steel electrolytic tub or glass beaker.

[6] Thin Titanium rod, 1.25 mm in diameter, used to hold substrates within the electrolytic cell. This rod is isolated by a Teflon tape not to participate in the process.

2.5. DATA ANALYSIS:

For metallographic analysis of the nanostructured material formed on the surface of the Ti we used FEG (Field Emission Gun) - Tescan/Mira 3 installed in the Associated Laboratory of Sensors and Materials of the National Institute of Space Research (LAS/INPE).

MEV and EDS were used in the Materials and Processes Department of the Technological Institute of Aeronautics (ITA) being the Tescan Veja 3 XMU model. X-ray diffractometer - PANalytical Empyrean. To monitor the variation of the mass of the samples, an Electronic Balance FA2104N scale was used.

3. RESULTS AND DISCUSSION

The experimental conditions for the electrolytic solution were maintained in the following parameters:

In a solution of 1000 ml, 50% vol of $C_3H_8O_3$ mixed with 50% vol of H_2O (distilled) and 1 g of NH_4F in a Becker inside a reservoir with external circulating water system to keep the solution at a temperature of approximately 70 °C. A FISATOM mechanical mixer is used to maintain the homogeneous solution with pH = 5.

The samples are completely submerged in the electrolytic solution and their surfaces have been completely oxidized making all porous and macroscopic roughness visible in 3 dimensions (3D). The operating conditions considered the parameters presented in Table 1. In this table we have the number of samples tested, although only condition 4 presented the formation of nanostructures. In this same table is presented the distance (D) between electrode and counter electrode, the time (t) of exposure to PEO, the current (I) provided by the DC source, the mass measurements (m_i) before PEO and mass (m_f) after PEO.

Table 1 - Parameters obtained in the collection of experimental data

sample	D (mm)	t (min)	I (A)	m_i (g)	m_f (g)	R_m (mg/min)	%M
1	20	10	2	0.6900	0.6790	1,1	1,59
2	20	15	2	0.6201	0.6196	0,03	0,02
3	20	15	1	0.5968	0.5938	0,2	0,50
4	20	20	1,4	0.5820	0.5610	1,05	3,61
5	30	10	1	0.6521	0.6327	1,94	2,98

Source; the Author

Figure 5 presents and compares the images of a sample before and after oxidation and shows the visual difference between a Titanium sample before and after plasma anodization.

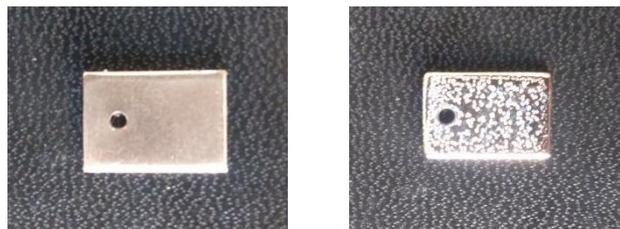
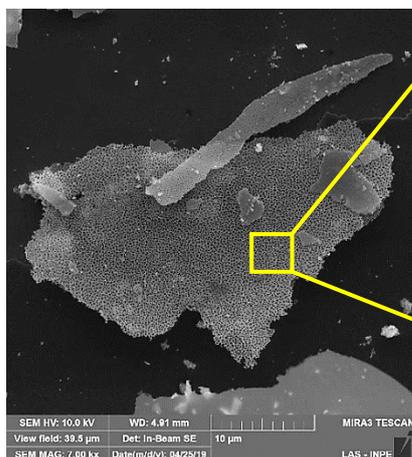


Figure 5 - Sample before anodizing (left) / Sample after anodizing (right)

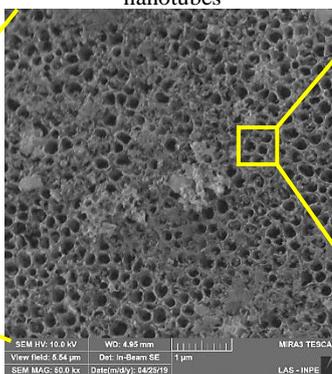
For the sample (4) the analysis with SEM-FEG presents the formation of nanostructured nanomaterials fixed to the Ti surface in a smaller amount, in relation to the free nanomaterials (loose) in the form of plaques throughout the surface of the Ti after its formation, many nanostructures plates were observed. In Figure 6, we observed nanostructures in the form of "alveoli" of TiO₂ forming a set of "loose" plates with independent structures. This formation indicates possible formation of TiO₂ nanotubes that will be confirmed with the analysis of EDS and DRX to verify the chemical composition of the components in these "loose" plates on the surface of the Ti. Figure 7 shows in greater detail the formation of nanostructured nanotubes due to greater enlargement in the formation of uniform "alveoli" with diameter around 200 nm, considering the actual scale in Figure 7.

Figure 6 - Formation of nanostructure plates



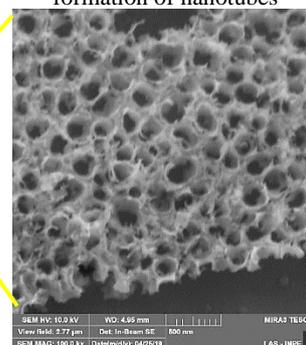
7.00 kx

Figure 7 - Formation of structured nanotubes



50 kx

Figure 8 - Shows uniform formation of nanotubes

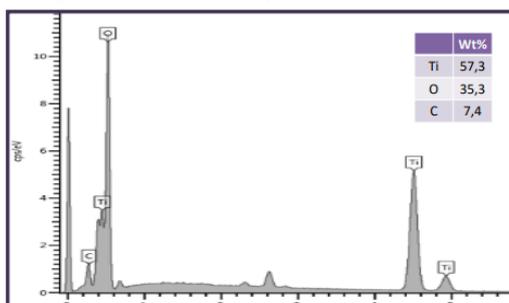


100 kx

Figure 8 presents the independent nanostructures formed with uniform configuration of approximately 200 nm in diameter confirming the analysis previously performed.

The following is presented the analysis by EDS, in this chemical analysis we can observe in Graph 1, the strong indication of the presence of Ti and O on the surface of sample 4. This strong clue shows the possibility of the existence of TiO₂ on the surface of the Ti sample.

Graph 1 - EDS to identify the chemical composition of the PEO coating on Ti samples.



Source: Author

Studying the chemical composition of the surface by dispersive energy spectroscopy (EDS) - Graph 1 - we can observe the predominance of titanium oxide, due to the combination of 57.3% m/m Ti and 35.3 %m/m of O, in order to improve the biocompatibility of sample 4. We can analyze through the EDS map the chemical composition and distribution of the

components on the surface of sample 4. We can observe the homogeneity of the coating and the dominant presence of Ti and O, Figure 9.

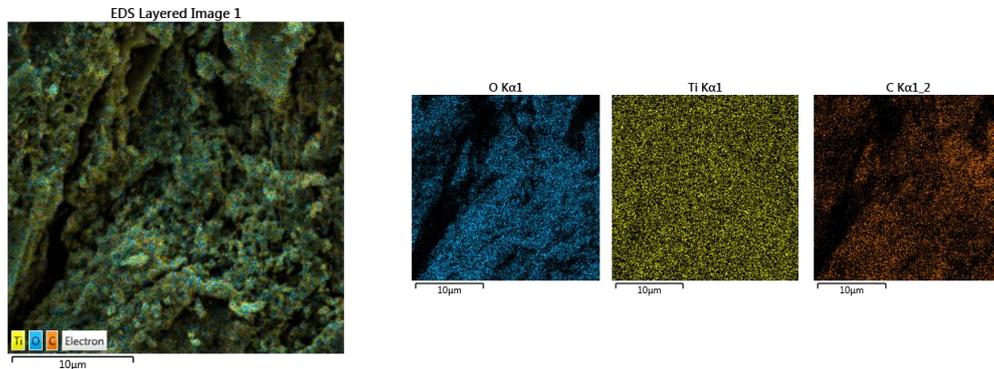
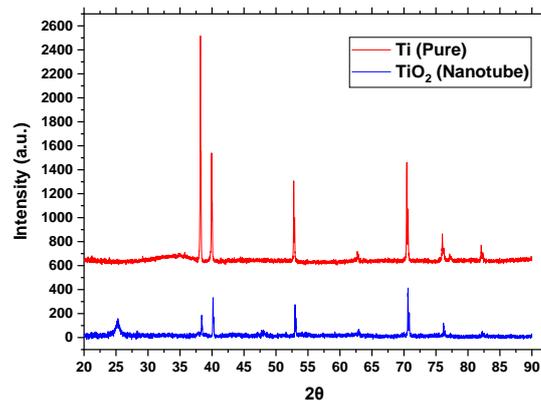


Figure 9 - EDS to identify the chemical composition on the surfaces of the Ti sample.

The DRX analyses of the surfaces of pure Ti and Ti submitted to PEO were performed and taken as a reference in relation to the uncoated surface in relation to the modified surface with nanotube growth with PEO.

Figure 10 - DRX chemical analysis between pure Ti surface and PEO coated Ti.



Source: Author

In the Figure 10 are presented the crystalline structure of the Pure Ti (red) and the sample with Nanotube coating processed by PEO (blue). In this analysis we can observe the predominance of Titanium oxide on the surface, because there are allotropic elements of Ti, in this assay we have the formation of Brokita ($2\theta = 25^\circ$ and $2\theta = 38^\circ$) forming orthorhombic crystalline network, together with the formation of Anatase ($2\theta = 48^\circ$ and $2\theta = 75^\circ$) forming tetragonal crystalline network, these fundamental elements for the formation of TiO_2 structure that can favor the formation of osseointegrated and biocompatible layers on the surfaces of implants coated with these characteristics.

Note the values highlighted in table 1, these parameters favored in this assay the formation of structured nanotubes on the surface of sample 4 of Pure Ti. In this condition associated with the distance between the electrodes, the time of exposure to electrical discharge inside the electrolytic tank, shows the necessary condition for the formation of structured nanotubes.

By analyzing the data in table 1 we can calculate two important parameters to understand the formation of structured nanotubes of TiO_2 . The sample mass loss rate (R_m) is associated with the production rate of TiO_2 nanotubes through the Top-Down process of manufacturing nanotubes, as in this process corrosion or controlled wear occurs from above the sample surface down. In this case, it presented a mass loss rate of 1.05 (mg/min), comparing with the other values of the same table we observed this value equivalent to the values of samples 1 and 5. More that drew attention was the percentage of mass loss for sample 4, presenting the highest value of the table compared to the other samples. This parameter associated with the mass loss rate shows that we can associate the percentage of mass loss with the formation of structured nanotubes. These two parameters are complete. For sample 4, the two parameters are high and may indicate an important parameter association for the next assays.

To better present the parameters that the samples were submitted in this study, table 1, shows the main information and characteristics of the samples. In this same table is also presented the rates of mass loss (R_m) and percentage of mass loss (%M).

4. CONCLUSIONS

In this work we can observe that the objective of formation of nanotubes nanostructures using PEO in solution of 50 % vol of glycerol added to 1g of ammonium fluoride was reached. The PEO process proved to be extremely versatile and easy to handle, but some adjustments should be made to improve the process, such as pH control of the solution, exposure time, distance between electrodes, efficient heat exchange system among others to favor the control of the technique.

The process showed that it can be done coating Ti with nanostructured nanotubes.

The rate of mass loss and the percentage of mass loss are associated with the formation of nanotubes.

The 20-minute assay of exposure to electrolytic plasma associated with a distance of 20 mm proved to be the most appropriate parameters for the formation of nanostructures.

The formation of Ti allotropics with Brookite and Anatase indicated by DRX is in accordance with the reference literature, and that the experiments are conducted on the right track to improve the efficiency in the crystallization of the structures involved.

With the advance and deepening of the analyses it will be possible to distinguish better conditions for a process optimization and better result on the surfaces of the worked material.

5. ACKNOWLEDGMENT

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