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ANODIC OXIDE LAYER FORMATION MECHANISM ON Ti-6Al-7Nb IN SULFURIC ACID

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The formation of anodic layer on titanium alloy Ti-6Al-7Nb in sulfuric acid solution is described in this paper. The real current trend during the process is measured, the oxide's structure and chemical composition are examined. A 3D computer model is used to simulate the growth of the oxide layer during the process of anodizing. The mechanism of anodic film formation in sulfuric acid solution is discussed.

Keywords: oxide growth, layer formation, electrochemical oxidation, anodizing, Ti-6Al-7Nb

1. Introduction

Anodizing is an electrolytic passivation process for formation of protective oxide film, on a metal surface used as a positive electrode (anode) in an electrolytic cell. By introducing various alterations to individual parameters of the electrochemical anodizing cell, such as electrolyte content, voltage, etc., a variety of morphology and structure is obtained. Regarding the structures, it is known, there are two types of oxide layers – porous and nanotubular. Nanotubular layers normally form on titanium and titanium alloys, in the presence of fluoride ions in the electrolyte solution. [1-3]

The anodizing process is commonly used as finishing treatment for titanium and its alloys. Typical benefits of anodizing titanium are improved corrosion resistance, hardening of the surface and decorative look. Another effect of the anodic film is the possibility of changing the color of the surface without using dye. Depending on the process setup, it is possible to customize the properties of the oxide layer. [4-9] Therefore, this treatment can expand the possible range of application of titanium and titanium alloy details and components. However, the acquisition of specific surface properties requires proper setup. In order to choose the right setup, it's necessary to have enough data

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and detailed understanding of the oxide layer formation process. Since conventional gathering data is a long process and optimization is even longer, an available computer simulation model can save valuable time and resources. [10-12]

The mechanical properties of the titanium alloys are defined by their morphology, and the fractions volume of the present phases from the parameters obtained from the manufacturing process. In 1977 the titanium alloy Ti-6Al-7Nb was first synthesized to replace the well-known Ti-6Al-4V for biomedical purposes, because of the negative impact on the human body due to vanadium beta stabilizing element. Niobium exhibits a vanadium-like effect as a stabilization phase in the Ti-Nb binary system, which is required to provide a two-phase structure. Therefore, niobium was used as a beta stabilizing element to obtain the desired microstructure of Ti-6Al-7Nb. The alloy demonstrates improved mechanical properties, corrosion resistance and biocompatibility. It has been in clinical use since 1986. In recent years, it has been observed an increase of the application of the titanium alloy – Ti-6Al-7Nb for several industries. This alpha-beta titanium alloy demonstrates similar properties to Ti-6Al-4V. However, for biomedical application in particular, Ti-6Al-7Nb is preferred, because of the inert nature of niobium as beta stabilizing element.

Anodization of titanium in sulfuric acid has been widely investigated, usually at voltages up to 100V. Depending on the anodizing conditions, the crystal structure has been reported to be anatase (α-TiO_2), a mixture of anatase and rutile ($\alpha + \beta$ TiO_2) or rutile (β-TiO_2). However, notably limited information on the formation and properties of anodic layer on Ti-6Al-7Nb alloy is available [13-20]. All experiments show that the presence of formed nanoporous oxide layer on the anodized Ti-6Al-7Nb surface results in increased electrical resistance.

The formation of porous anodic layer on titanium alloy Ti-6Al-7Nb in sulfuric acid solution is described in this paper. Based on observations of experimental results and analysis of the electrical current trend during the process, the oxide morphology and chemical composition, a computer simulation of the oxide formation is presented.

2. Experimental details

Cylindrical specimens, 4 mm long, were cut off, on low-speed cutting machine, from a hot rolled bar with a 12 mm gauge diameter. The bar made by TIMET (TIMETAL 6-7) had been previously annealed at 750°C for one hour and air cooled. The chemical composition is shown in Table 1 and the mechanical properties are shown in Table 2. [21]

Table 1.

Chemical composition of titanium alloy Ti-6Al-7Nb (TIMETAL 6-7)

Element	Al	C	H	Fe	Nb	N	O	Ta	Ti
% w/w	5.5 - 6.5	≤ 0.080	≤ 0.0090	≤ 0.25	6.5 - 7.5	≤ 0.050	≤ 0.20	≤ 0.50	84 - 88

Table 2.

Mechanical properties of titanium alloy Ti-6Al-7Nb (TIMETAL 6-7)

Property	Tensile Strength	Tensile Strength, Yield	Elongation at Break	Reduction of Area	Modulus of Elacticity	Fatigue Strength
Units	900 - 1000 MPa	800 - 900 MPa	10% - 12%	35%	105 -120 GPa	500 MPa

Before anodizing, the specimens undergo preparation by mechanical grinding, followed by chemical degreasing and deoxidation. After the described pretreatment, electrochemical anodization is performed in 1M H_2SO_4 electrolyte. The solution pH is equal to 0.96 and its temperature was 20.5 °C. The used cathode was made of commercially pure titanium of grade 1. The power supply used for anodizing operates under DC and has high precision regulation range 0-120V (with resolution of 0.1V) and 0-3A (with resolution of 0.01A).

The electrical working current in the electrolytic cell is monitored via custom data acquisition system (DAQ) similar to those described in [22, 23]. The electrical parameters data acquired is visualized with LabVIEW. Morphological and chemical composition analysis are performed on Hitachi S-4700 SEM and EDS, Joel, JSM 6060-LU. All samples were examined at room temperature.

The results from electrochemical anodizing of the titanium alloy Ti-6Al-7Nb, in the range from 10V to 100V are used for the modelling work. The simulation model, developed in this work is largely based on own experimental results, obtained after electrochemical anodizing of Ti-6Al-7Nb in sulfuric acid electrolyte. More of our experimental data concerning the mechanical properties of the oxide layer acquired from the electrochemical anodizing of a titanium alloy Ti-6Al-7Nb in sulfuric acid were presented in [24, 25]. In this paper only some of our experimental results, in regard to the development of microstructure will be presented, which is relative to the model simulations.

3. Results and discussion

3.1. Current fluctuations during the anodizing process

The oxide layer formation is induced by the current applied to the electrolytic cell. Therefore, by monitoring the fluctuations of the current values over time in this process, we can observe the oxide buildup during anodizing. A typical phenomenon, observed during the layer formation, is the characteristic dropping of the current. This fact is due to the dielectric nature of the oxide layer.

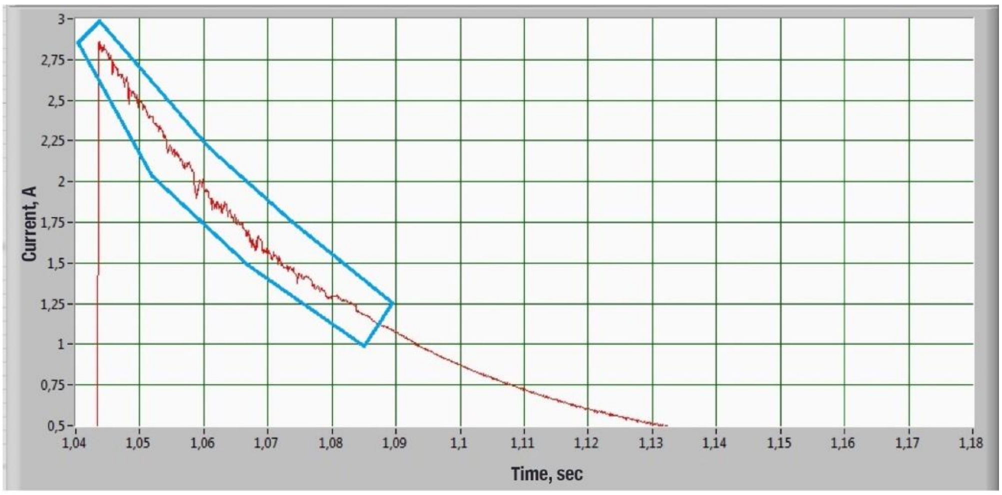


Fig. 1. Fluctuations and alterations indicating the influence of the current during the process of anodizing (the graph presents the amplitude of the current over time)

The measurement of the real trend of the anodizing current and its rapid alterations reveals important details about the formation and development of the anodic oxide layer. In Fig.1, we can observe two processes occurring simultaneously – oxide buildup and its breakdown. When the oxide is building up, the current value decreases as expected, because of the increasing resistance of the oxide film. During the formation process, the oxide structure accumulates internal stress, leading to dislodge and consequently to lower resistance. Accordingly, the current graph displays the observed fluctuations and alterations.

3.2. Microstructure and elemental analysis

After anodization, the microstructure of the anodized layers is examined using scanning electron microscopy (SEM) as can be seen in Fig.2. The microstructure of the oxide layers, produced by anodizing Ti-6Al-7Nb in sulfuric acid solution, appears to be non-uniform. Moreover, it has a variety of thickness, density, microroughness and microhardness, dependent on the setup of the process parameters. The influence of different electrochemical anodizing parameters on the microstructure, microroughness and microhardness of anodized Ti-6Al-7Nb is discussed in [17].

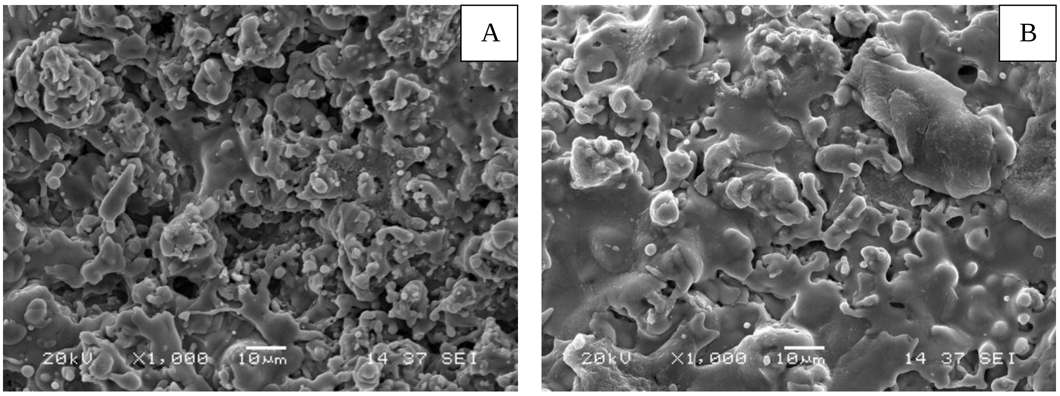
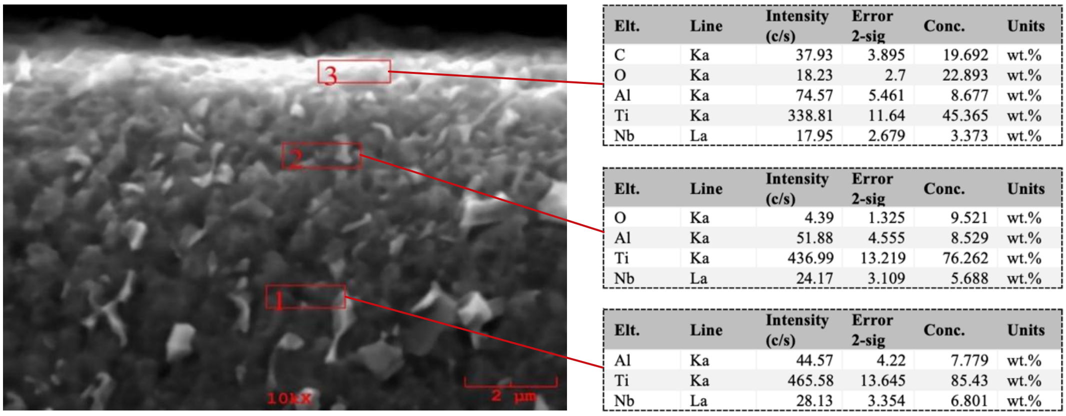


Fig. 2. SEM images of anodic oxide layers, formed on anodized Ti-6Al-7Nb in H_2SO_4
A – at 10V, B – at 100V



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc.	Units
C	Ka	37.93	3.895	19.692	wt.%
O	Ka	18.23	2.7	22.893	wt.%
Al	Ka	74.57	5.461	8.677	wt.%
Ti	Ka	338.81	11.64	45.365	wt.%
Nb	La	17.95	2.679	3.373	wt.%

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc.	Units
O	Ka	4.39	1.325	9.521	wt.%
Al	Ka	51.88	4.555	8.529	wt.%
Ti	Ka	436.99	13.219	76.262	wt.%
Nb	La	24.17	3.109	5.688	wt.%

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc.	Units
Al	Ka	44.57	4.22	7.779	wt.%
Ti	Ka	465.58	13.645	85.43	wt.%
Nb	La	28.13	3.354	6.801	wt.%

Fig. 3. Chemical composition of zones in-depth of anodized Ti-6Al-7Nb detail in H_2SO_4 [25]

Chemical elements distribution analysis is performed in-depth and on the surface of the anodized specimens. The analyzed results indicate that titanium and oxygen are present on the surface (zone 3 from Fig.3) to form an oxide layer with dimensions up to 200 nm, at maximum applied voltage of 100V. Near the surface (zone 2 from Fig.3), the concentration of alpha and beta alloying elements decreases. In-depth (zone 1 from Fig.3) the oxygen content decreases and the presence of aluminum and niobium increases. (Fig.3.) This effect can be explained by the higher activity of titanium to oxygen.

After electrochemical anodizing, we can observe that the alloying elements Al and Nb are not present on the surface of the specimen. The chemical element analysis shows that the only elements present on the surface of the anodized detail to form an oxide layer are titanium and oxygen. Examination points on the surface of anodized specimen in sulphuric acid are displayed in Fig. 4., and the elemental composition of each point is shown in Figs. 4.1 to 4.3.

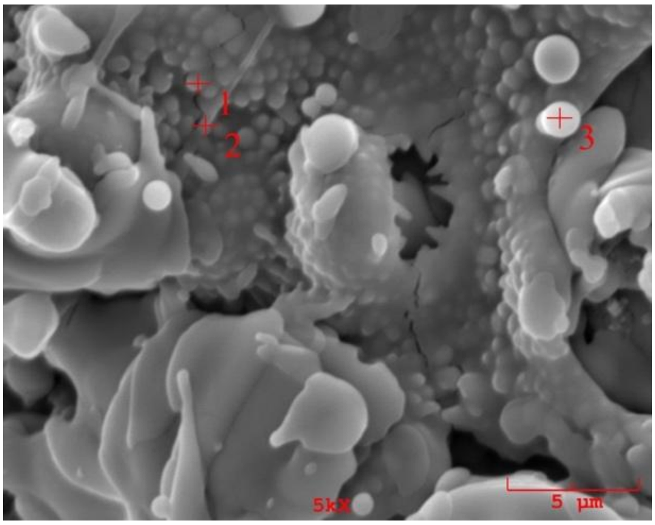
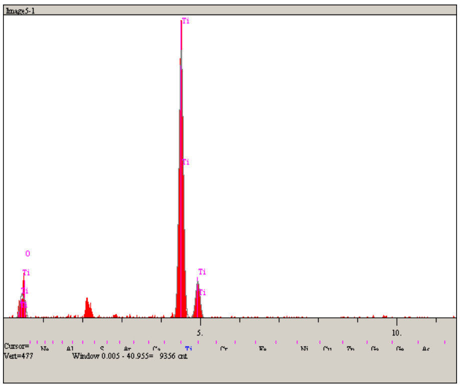
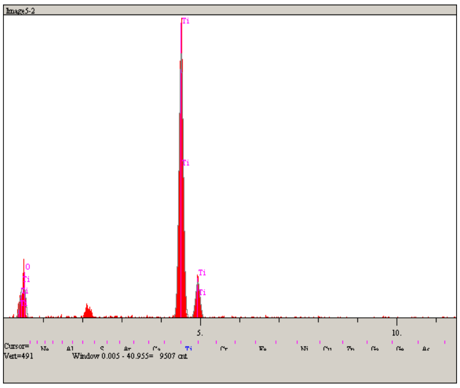


Fig. 4. Chemical composition in points on the surface of anodized Ti-6Al-7Nb detail in H_2SO_4



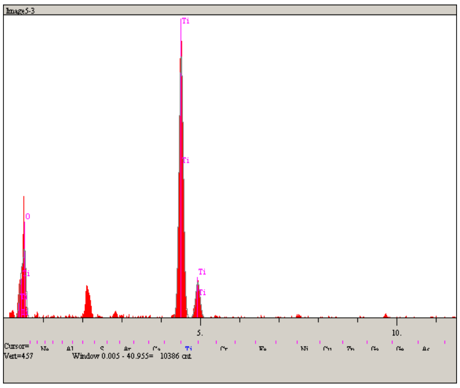
Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	21.28	2.917	55.195	29.166	wt.%	
Ti	Ka	578.73	15.210	44.805	70.834	wt.%	
				100.000	100.000	wt.%	Total

Fig. 4.1. Chemical composition in point 1 on the surface of anodized Ti-6Al-7Nb detail in H_2SO_4



Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	36.28	3.808	64.333	37.612	wt.%	
Ti	Ka	588.12	15.331	35.667	62.388	wt.%	
				100.000	100.000	wt.%	Total

Fig. 4.2. Chemical composition in point 2 on the surface of anodized Ti-6Al-7Nb detail in H_2SO_4



Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	83.90	5.791	77.138	53.003	wt.%	
Ti	Ka	540.05	14.692	22.862	46.997	wt.%	
				100.000	100.000	wt.%	Total

Fig. 4.3. Chemical composition in point 3 on the surface of anodized Ti-6Al-7Nb detail in H_2SO_4

3.3. Chemical reactions during anodizing Ti-6Al-7Nb in H_2SO_4

While the constant electrical current or voltage is applied to the electrolysis cell, there are following reactions occurring during the anodizing process of titanium alloy Ti-6Al-7Nb in sulfuric acid electrolyte:

First process is the oxidation of Ti by anodization:

$$Ti \rightarrow Ti^{4+} + 4e^- \quad (1)$$

The second step is formation of oxide layer:

$$Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+ \quad (2)$$

The overall reaction can be written as a simple hydrolysis:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (3)$$

The Eq. (1) indicates a direct oxidation of Ti into Ti^{4+} tetravalent ion. According to Eq. (2), H^+ ions accumulated during hydrolysis of Ti^{4+} ions. The presence of metal cation vacancies near the metal/oxide interface would facilitate reaction (1) and the Ti^{4+} ions could easily jump to the available vacancy sites. This was marked generally by rise in current when a constant potential is applied. During this state, nanopores were nucleated on the oxide surface.

If we look at the chemical reaction that occurs, the oxide growth is normally illustrated as in Fig. 5, while in reality such model cannot explain the formation of the anodic oxide structures or their real formation mechanism.

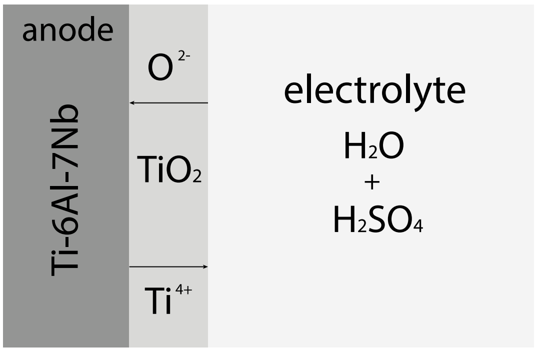


Fig. 5. Illustration of oxide formation on anodized Ti-6Al-7Nb detail

3.4. Computer simulation model of growing oxide layer of anodized Ti-6Al-7Nb in H_2SO_4

While current is applied to the electrolytic cell, the anions from the electrolyte solution are attracted to the positive electrode surface, where the oxide layer forms. Since the oxide layer is dielectric and the current is decreasing during the oxide formation, we can suggest that the oxide doesn't grow simultaneously over the whole anode surface, but it rather does from multiple points. Depending on the surface roughness, oxide clusters are most likely to form on the peaks. When oxygen anion contacts a positively charged point it attaches to it and a cluster forms. While more anions make contact, the cluster grows. As a result, fractal structures are formed. The observations of the reaction's current fluctuations, the formed microstructures and the elemental distribution analysis along with the chemical reaction that occurs in the electrolyte suggest the oxide growth mechanism described.

An implementation of a digital simulation model would give us more accurate and better visualization of the process. There are various mathematical algorithms about growth and transformation. In the case of anodic oxide growth on Ti-6Al-7Nb in sulfuric acid solution, diffusion limited aggregation (DLA) is found to be the most appropriate simulation model. Moreover, it allows the evolution process to be explained at a basic level.

Essentially, DLA is a simulation method for growing certain object of randomly moving particles, sticking together by diffusion to aggregate the object. Once we break down the process of anodizing to ion exchange induced by current, and after we analyze the microstructures we can determine the model. The numerical simulation structure can reproduce the formation of the real structure, but it is normally different, because of the limitations of computing power needed to solve the real molecular dynamics. Stages of a digital 3D simulation model are displayed on Fig. 6.

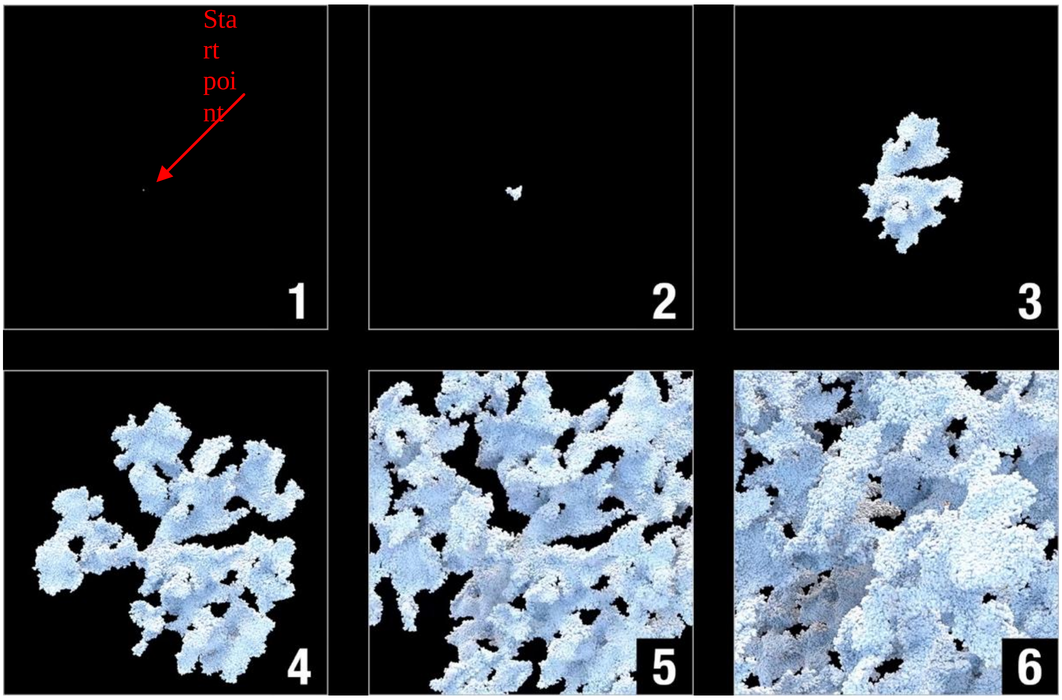


Fig. 6. Simulation stages of anodized oxide layer development.

In our simulation model we have used the classical DLA algorithm. The simulation begins the growth of a fractal pattern with a single "seed" – point in the center of the 3D space. The radius of the points in every simulation case is maintained at a constant value equal to 1. The stickiness probability of the particles is changing for each different simulation by a factor between 0.03 and 0.9, which reflects on the final density of the fractal shape. The simulation time is in relation to the stickiness factor as more calculation time is required when a larger fractal shape with more particles is present in the scene.

A 3D model of DLA is simulated and compared to SEM images of anodic oxide on Ti-6Al-7Nb specimens. As we analyze the structures produced by the digital simulation and those of SEM images, we can acknowledge that the model proposed for anodic oxide formation on Ti-6Al-7Nb in electrolyte of sulfuric acid is reliable. However, we should mention that the computer simulation presented in this article grows from one point only (stage 1 of Fig. 6), when in reality there are multiple points of origin.

4. Conclusions

The anodizing current fluctuates accordingly to the oxide film growth. The thickness of the oxide layer, after anodizing Ti-6Al-7Nb in H_2SO_4 electrolyte, applying voltage in the range 10-100V, is up to 200nm. The alpha and beta alloying elements are not present on the anodized surface.

The chemical reactions of the process are explained and a simulation model for visualization of the evolution of anodic oxide structure is proposed. The model is based on analytical and numerical solutions of the chemical reaction that occurs, as the oxide grows. This model can be a useful tool for optimization of the processing parameters in the electrochemical anodizing of titanium alloy Ti-6Al-7Nb in sulfuric acid electrolyte. A program package including the numerical simulation of the electrochemical anodizing process of titanium alloy Ti-6Al-7Nb was prepared. It consists of a 3D simulation model illustrating the relative density and shape of the microstructure in relation to the mechanical properties of the oxide layer, such as microroughness, microhardness, etc. By input of a desired mechanical property values, the package outputs the optimal operating conditions and 3D simulated approximation of the microstructure. Using this data, numerical simulations and predictions about the incubation time, formation mechanism and thickness of the titanium oxide layer during electrochemical anodizing can be made for new electrochemical conditions.

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