

## 1. Introduction

Under normal conditions, the surface of titanium is covered with an oxide film, which causes its passivity [1]. The disadvantage of films is small thickness, which limits their use. Artificial films are used for surface modification of medical implants [2–4]. Films are produced by thermal [5], plasma oxidation [6], electrochemical and hydrothermal treatment [7], diffusion [8], electrochemical oxidation [9]. Thermal oxidation is a simple and cheap method based on the formation of  $\text{TiO}_2$  on the surface of titanium during heating [10]. The films obtained by this method have good protective properties, but the process is carried out in a chamber that should not contain  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ . Oxidation by the plasma method [6] consists of applying  $\text{TiO}_2$  powder on the metal surface and melting it with plasma to form a film. Obtaining a film requires pure  $\text{TiO}_2$ , careful preparation of the metal and suspension, and a chamber with a controlled atmosphere. The same drawbacks are inherent in the diffusion saturation method [8].  $\text{TiO}_2$  films are obtained by the sol-gel method [11] by sequential treatment with solutions of the titanium salt and the precipitant. The precipitate is heated for its strong adhesion to the base. The method requires the use of highly pure substances and thorough washing of the precipitate, since the pollution of  $\text{TiO}_2$  is undesirable. Ion implantation involves treating titanium with a high-energy particle beam [12]. The process is expensive, which limits the possibility of its mass implementation. Electrochemical oxidation allows controlling the film thickness [13]. The process is carried out to obtain thin films [10]. Studies on the effect of the oxidation regime on the growth dynamics of films are absent, therefore, work in this direction is an urgent task.

The aim of research is studying the anodic behavior of titanium alloy BT6 in acid solutions.

The objectives of research are as follows:

- to establish the influence of the electrolysis mode on the formation dynamics of oxide films on the BT6 alloy in acid solutions;
- to establish the influence of the electrolysis mode on the duration of the formation of oxide films of maximum thickness.

## 2. Methods of research

Rectangular plates with dimensions of  $70 \times 20 \times 2$  mm were used as working electrodes. Samples were degreased with a suspension of  $\text{Na}_2\text{CO}_3$ , washed with water and etched in a

## ELECTROCHEMICAL FORMATION OF OXIDE FILMS ON $\text{Ti}_6\text{Al}_4\text{V}$ ALLOY

Alexei Pilipenko

PhD

Department of Technical Electrochemistry

National Technical University «Kharkiv Polytechnic Institute»

2 Kyrpychova str., Kharkiv, Ukraine, 61002

opilipenko1984@gmail.com

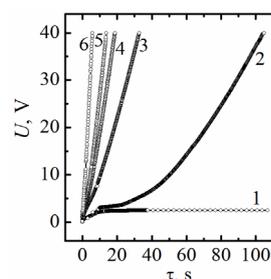
**Abstract:** The results of the study of the process of electrochemical oxidation of  $\text{Ti}_6\text{Al}_4\text{V}$  titanium alloy in solutions of tartaric, citric and oxalic acids are presented. It is shown that the nature of the forming dependencies of the alloy depends on the magnitude of the current density. When  $j_a < 0,5 \text{ A}\cdot\text{dm}^{-2}$ , a continuous oxide film does not form on the alloy surface and the specified voltage value is not reached. At  $j_a > 0,5 \text{ A}\cdot\text{dm}^{-2}$ , a continuous oxide film forms on the surface of the alloy and linear dependences are observed. Films produced under these conditions are interference colored. The maximum thickness of the film is determined by the specified value of the forming voltage  $U$  and does not depend on other parameters of electrolysis. For a number of identical values of  $U$ , the dependence of the limiting film thickness has a linear form. The color of the oxide film is determined by the voltage value and does not depend on the current density and electrolyte concentration. It is established that the color of the film corresponds to the magnitude of the forming voltage in the range of 10–100 V. The effect is due to the fact that film formation during anodic polarization occurs under the presence of a potential gradient, the magnitude of which is constant for titanium. An increase in a given value of  $U$  leads to a proportional increase in the limiting thickness of the oxide, which determines the color of its color. The research results to determine the effect of electrolysis parameters on the characteristics of oxide films make it possible to substantiate the regime for producing  $\text{TiO}_2$  films on the surface of the  $\text{Ti}_6\text{Al}_4\text{V}$  alloy. The obtained data are the basis for the development of technology for the electrochemical oxidation of titanium alloys to give their surface functional properties.

**Keywords:** anodic polarization, electrochemical oxidation, oxide film, forming dependence, potential gradient.

mixture of  $\text{HNO}_3$  and  $\text{HF}$  (3:1). The electrolysis was carried out by setting the voltage on the cell in the range of 10–100 V with a step of 10 V using the B5-49 power source. The signal of the end of the process was the operation of the power supply relay. The voltage was monitored with a Keithley-2000 multimeter (USA). The cell was a  $250 \text{ cm}^3$  beaker placed in a  $5 \text{ dm}^3$  crystallizer with water. Lead served as an auxiliary electrode. The acids used for the study (citric, tartaric, oxalic) corresponded to the “f” reagents.

## 3. Results

The most informative for studying the anodizing process are the forming dependences  $U-\tau$ , which allow to investigate the dynamics of film growth. It is established that the type of dependence is determined by the anode current density  $j_a$  and is the same for the entire range of  $U$  (Fig. 1). At  $j_a < 0,2-0,5 \text{ A}\cdot\text{dm}^{-2}$ , the dependences are nonlinear and can't be reproduced (Fig. 1, dependences 1 and 2); the specified value  $U$  is not reached. The appearance of a plateau on the dependence of 1 Fig. 1 indicates a steady-state oxidation mode in which the rate of electrochemical growth is equal to the rate of chemical dissolution of  $\text{TiO}_2$ . At  $j_a = 0,5 \text{ A}\cdot\text{dm}^{-2}$  (Fig. 1, dependence 2), a plateau appears, after which there is a gradual increase in voltage with a final output to a given  $U$ . At  $j_a = 1-5 \text{ A}\cdot\text{dm}^{-2}$ , the dependences are linear (Fig. 1, 3–6), which indicates the formation of dense films. The nature and concentration of the electrolyte does not affect the type of dependence.



**Fig. 1.** Forming dependences of the  $\text{Ti}_6\text{Al}_4\text{V}$  alloy at  $j_a, \text{ A}\cdot\text{dm}^{-2}$ : 0,2(1); 0,5(2); 1(3); 0,75(4); 2(5); 5(6).  $U = 40 \text{ V}$ ;  $c_A = 100 \text{ g}\cdot\text{dm}^{-3}$

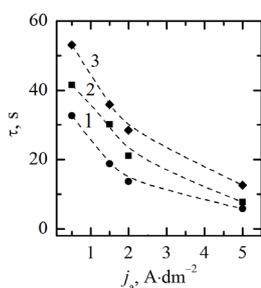
The color of the film is determined by the thickness of  $\text{TiO}_2$ , which depends on the value of  $U$ . The correspondence between the color of the film and the voltage is given in Table 1.

**Table 1**

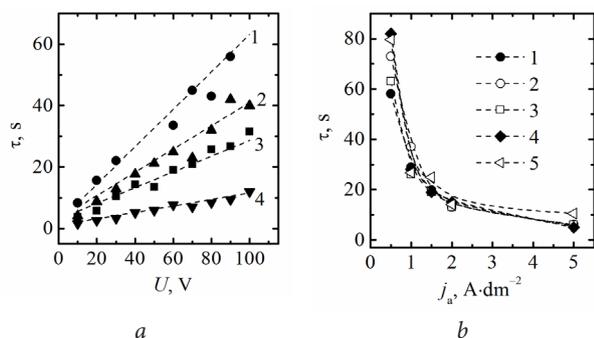
 The correspondence between the color of the oxide film and the  $U$  value

$U, V$	Film color
10	brown
20	dark blue
30	blue
40	light green
50	yellow
60	golden
70	crimson
80	dark turquoise
90	light turquoise
100	green

The dependence of the time to reach a given  $U$  on the current density of the electrolysis has a characteristic shape that is maintained for the entire series of dependences obtained on samples processed in the same mode (Fig. 2). A consistent increase in  $U$  causes an increase in the time  $\tau$  (Fig. 2, dependences 1–3). The time required to reach the given  $U$  corresponds to the duration of the film growth with the maximum thickness.



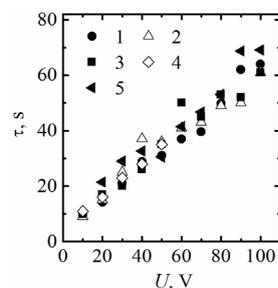
**Fig. 2.** Dependence of  $\tau$  on the current density during the oxidation of the Ti6Al4V alloy.  $U, V$ : 40(1); 60(2); 80(3).  $c_A=100 \text{ g}\cdot\text{dm}^{-3}$



**Fig. 3.** Dependences of  $\tau$  on voltage and current density during oxidation of the Ti6Al4V alloy: *a* – dependence of  $\tau=f(U)$  at  $c_A=10 \text{ g}\cdot\text{dm}^{-3}$  and  $j_a, \text{ A}\cdot\text{dm}^{-2}$ : 1(1); 1,5(2); 2(3); 5(4); *b* – dependence  $\tau=f(j_a)$  at  $U=40 \text{ V}$  and  $c_A, \text{ g}\cdot\text{dm}^{-3}$ : 5(1); 10(2); 25(3); 50(4); 100(5)

The dependence of  $\tau-U$  for the same current density is linear (Fig. 3, *a*). The slope of the dependences does not remain

constant, but decreases with increasing  $U$ . The change in  $c_A$  within  $5\text{--}100 \text{ g}\cdot\text{dm}^{-3}$  does not affect the duration of film growth (Fig. 3, *b*). The maximum film thickness depends only on the given value of  $U$ . For a number of electrolytes with the same concentration, the dependence  $\tau=f(U)$  is linear (Fig. 4). The slope of the dependencies is the same for the entire investigated interval  $c_A$ .



**Fig. 4.** Dependence  $\tau=f(U)$  in the oxidation of the Ti6Al4V alloy.  $j_a=1 \text{ A}\cdot\text{dm}^{-2}$ ;  $c_A, \text{ g}\cdot\text{dm}^{-3}$ : 5(1); 10(2); 25(3); 50(4); 100(5)

Some deviations noticeable in Fig. 4 are caused by the measurement error of the sample area.

#### 4. Discussion of obtained results

The forming dependencies (Fig. 1) show that an increase in  $j_a$  contributes to an increase in the growth rate of the film. This observation corresponds to the Faraday law, for which the current density is the rate of electrochemical oxidation. The linear character of the dependences  $U=f(\tau)$  at  $j_a>0.5 \text{ A}\cdot\text{dm}^{-2}$  indicates the formation of barrier-type oxide films whose electrical resistance is proportional to their thickness. Such a conclusion can be made on the basis of the data shown in Fig. 2, 3. The thickness of the oxide film formed at  $j_a=\text{const}$  depends on the applied  $U$ . The growth of the film is possible provided there is a certain value of the voltage drop across the thickness of the oxide, which ensures the movement of ions in the  $\text{TiO}_2$  lattice. A decrease in the gradient under conditions of a given  $U$  leads to the cessation of oxide growth. At  $j_a=\text{const}$ , an increase in  $U$  will increase the maximum thickness of the oxide or the duration of electrolysis proportional to it. The effect does not depend on other process parameters, which is confirmed by the results of the experiment. Somewhat contradictory are the data shown in Fig. 4. Based on the theoretical assumptions, one should expect a linear course of the dependences  $\tau=f(j_a)$ . However, some linearity appears only when  $j_a>0.5 \text{ A}\cdot\text{dm}^{-2}$ . It is likely that the formation of an oxide film at low values of  $j_a$  occurs under the conditions of chemical dissolution of  $\text{TiO}_2$  at a rate close to the oxidation rate of titanium.

Thus, the anodic polarization of the Ti6Al4V alloy leads to the formation of thin oxide films. The thickness of the films obtained at  $c_A=5\text{--}100 \text{ g}\cdot\text{dm}^{-3}$  and  $j_a>0.5 \text{ A}\cdot\text{dm}^{-2}$  in the range  $U=10\text{--}100 \text{ B}$  is determined only by the voltage value. The resulting  $\text{TiO}_2$  layer has good protective properties. The research results can be used to develop the technology of electrochemical oxidation of Ti6Al4V titanium alloy. Further work is necessary to study the structure and morphology of the films and to establish the relationship between the electrolysis mode and the properties of  $\text{TiO}_2$ .

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