Наведені результати дослідження процесу електрохімічного оксидування титанового сплаву ВТ6 у розчинах H2SO4. Показано, що характер залежностей формовки зразків сплаву залежить від величини густини струму. При $j<0,5$ А·дм$^{-2}$ суцільна оксидна плівка на поверхні сплаву не утворюється і задане значення напруги не досягається. При $j>0,5$ А·дм$^{-2}$ на поверхні сплаву утворюється суцільна оксидна плівка та спостерігається лінійна характер залежностей. Плівки, одержані в цих умовах, відносяться до інтерференційно-забарвлених. Гранична товщина плівки визначається заданою величиною U і не залежить від інших параметрів електролізу. Для ряду однакових значень U залежність $\tau–j$ має лінійну форму. Колір оксидної плівки визначається значенням напруги і не залежить від густини струму та концентрації електроліту. Встановлена відповідність кольору плівки і величини U в діапазоні значень $10–100$ В. Ефект пояснюється тим, що утворення плівки при анодній поляризації відбувається в умовах наявності градієнта потенціалу, величина якого для титану постійна. Збільшення заданої величини U приводить до пропорційного збільшення максимальної товщини оксиду, яка визначає колір її забарвлення. Результати дослідження з визначення впливу параметрів електролізу на характеристики оксидних плівок дозволили обґрунтувати режим отримання плівок TiO$_2$ на поверхні сплаву ВТ6. Отримані дані є передумовою для розробки технології електрохімічного оксидування титанових імплантатів для надання їх поверхні функціональних властивостей

Ключові слова: оксидні плівки, діоксид титану, імплантат, електрохімічне оксидування, формувальна залежність

FORMATION OF OXIDE FUELS ON VT6 ALLOY IN THE CONDITIONS OF ANODIAL POLARIZATION IN SOLUTIONS H₂SO₄

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1. Introduction

Titanium is an active metal; however, under normal conditions, its surface is covered with a thick oxide film. The film is a protective barrier that predetermines the passivity of titanium in many environments [1, 2]. Artificial oxide films on titanium possess specific properties and are used to improve biological compatibility and marking of products for medical purposes [3, 4]. Artificial films have a certain thickness and homogeneity of chemical composition. During oxidization, there forms a highly developed surface that makes it possible to improve its contact with the bone tissue [5]. Natural films are unsuitable for this purpose due to small thickness ($5−6·10^{-3}$ μm). The oxide films on titanium are obtained by several methods: thermal and plasma oxidation [6, 7], combined method of electrochemical and hydrothermal treatment [8], diffusion [9], or electrochemical [10–13] oxidation.

The most common method is that of electrochemical oxidation, which is also known as the anodizing. The method makes it possible to obtain films with a predefined thickness on the products of any configuration while using simple equipment. Electrochemical techniques allow accurate control over the amount of reacted material, which is used to obtain miniature objects [14, 15]. For the case of oxide films, using electrochemistry makes it possible to easily adjust thickness of the film and allows changing the properties of a coating in a wide range. Therefore, it is an important task to undertake a research aimed at establishing the influence of an electrolysis mode on the properties of oxide films.

2. Literature review and problem statement

Pure titanium has a small strength, therefore, in order to manufacture implants, its alloys are used. Commonly

applied for this purpose is the alloy VT6 (3.5–5.3 % V, 5.3–6.8 % Al), which has a favorable combination of strength and technological properties [12]. Chemical resistance of titanium alloys reduces with an increase in the number of alloying elements [16, 17]. To improve durability and provide biocompatibility, various coatings are formed at the surface of titanium implants. The most common is the oxidation of titanium, which is carried out by chemical, diffusion, plasma, thermal, or electrochemical techniques.

Thermal oxidation is a relatively simple and cheap method based on the formation of an oxide at the surface of titanium at heating [18]. Film thickness depends on the temperature and duration of heating. The coatings obtained using a given technique are characterized by good protective properties. The shortcoming is conducting the process in a specialized chamber with an oxidizing atmosphere, which should not contain N_2, H_2 and CO_2.

Plasma oxidation method [7] implies the application to the surface of an implant a TiO_2 powder and its subsequent melting by plasma. The result is a ceramic coating of good quality. To obtain a coating using this method it is necessary to have pure TiO_2, thorough preparation of the surface and a TiO_2 suspension for applying the starting layer, the presence of a chamber with controlled atmosphere for plasma treatment.

Similar flaws are demonstrated by a method of obtaining oxide films by diffusion saturation of titanium's surface with oxygen at high temperature [9].

To obtain oxide coatings from TiO_2, paper [2] proposed to employ a sol-gel method [19]. The method implies sequential treatment of an implant's surface with solutions of titanium salt and a precipitant. The resulting precipitate is heated, which ensures its strong adhesion to the base. The method requires the use of particularly pure substances and a thorough washing of the precipitate because the presence of the solutions' components in it may cause, when heated, an undesirable interaction with titanium.

At ionic implantation, the surface of titanium is treated with a high energy particle beam. The result is that the excited oxygen molecules interact with a metal surface, forming the oxide layer [20]. The hardware of the method employs sophisticated equipment, which limits the possibility of mass coatings for implants.

Electrochemical oxidation makes it possible to easily control the thickness and structure of the film [4]. Oxidation reduces the likelihood of surface destruction, spalling, and penetration of metal particles into surrounding tissue, which limits the lifetime of implants [4, 5, 17]. Titanium anodizing is performed in solutions of acids and salts, treating the articles in which makes it possible to obtain interferential-colored oxide films [10, 11]. We could not find any systematic data about the effect of an oxidation mode on the limiting thickness and color of oxide film. A film thickness determines the properties of the oxide coating and affects the duration of an article treatment, which is the main parameter of the process. The scientific literature provides data on a separate impact of current density or forming voltage on these indicators. This is predetermined by that the process of titanium anodizing is well enough understood and researchers are more interested in the results of tests of the oxidized samples. However, detailed research into determining the impact of separate indicators of electrolysis on the dynamics of forming and the properties of oxide films is still relevant. Results to be obtained in this area could be used not only to predict the outcome of the treatment, but to control the structure as well, and, consequently, the properties of the obtained coatings.

3. The aim and objectives of the study

The aim of present research was to study the anodic behavior of the titanium alloy VT6 in solutions of H_2SO_4. The work conducted would make it possible to acquire data on the influence of basic parameters of electrolysis on the dynamics of formation and the properties of oxide films.

To accomplish the aim, the following tasks have been set:

– to establish the effect of current density and electrolyte concentration on the forming dependences of the alloy VT6 at its anodic polarization in solutions of H_2SO_4;

– to determine the dependence of limiting duration of electrolysis on the concentration of electrolyte, current density, and forming voltage.

4. Procedure for electrochemical oxidation of the alloy VT6

We used in the study samples of the alloy VT6 in the form of rectangular plates the size 70×20×5 mm. The samples were polished with a circle petal grinding disc to remove coarse scratches and scrapes. The polished samples were degreased with a Na_2CO_3 aqueous suspension and washed with water. The degreased samples were etched in a mixture of HNO_3 and HF (3:1), washed with tap water and distilled water.

Electrolysis was carried out using the power source B5-49, with a cell voltage in the range of 10–100 V with a 10 V pitch. A signal to the end of the process was the triggering of a relay for switching the mode of power supply from direct current to permanent voltage. Current was monitored using the M2038 type voltammeter, voltage – using the multimeter Keithley-2000.

We used a glass cup with a volume of 250 cm³ as a cell. The research was performed at t=20–22 °C. To prevent the electrolyte from heating, the glass was placed into a glass crystallizer with a volume of 5 dm³, filled with water. Lead acted as an auxiliary electrode. Oxidation was conducted in solutions of H_2SO_4, prepared from acid of pure chemical grade on the distilled water. The concentration of H_2SO_4 in solutions was 10–100 g·dm⁻³. Etching solution was prepared from HNO_3 and HF of pure grade.

5. Results of studying the processes in the titanium alloy VT6 at anodic polarization in solutions of H_2SO_4

The result of the process of titanium anodizing in solutions of H_2SO_4 is the formation of colored oxide films with a thickness of 0.1–0.3 μm that relate to the interferential-colored films. The color of the film depends on its thickness [10]. A decisive influence on the thickness, in addition to an alloy composition, is exerted by the forming voltage magnitude U.

The most informative dependences to study the process of anodizing are the forming dependences of U-τ that make it possible to examine the dynamics of a film growth. Experimental data reveal that the type of a forming dependence is

defined by the anodic current density j and is the same for the entire range of U (Fig. 1). In the range of j=0.2−0.5 A·dm^{-2} the dependences are non-linear and are often non-reproducible (Fig. 1, dependences 1 and 2). At j=0.2 A·dm^{-2}, the assigned magnitude of U is not achieved. This observation is explained by that the process of an oxide formation consists of two processes – electrochemical formation of the film, and its dissolution due to a chemical interaction between components of the electrolyte. The first process contributes to an increase in the film thickness and an increase in the voltage drop on the cell. Chemical dissolution reduces thickness of the film and resistance of the cell. The emergence of a horizontal plateau on dependence 1, Fig. 1, points to the stationarity of oxidation at which the rate of electrochemical formation equals the rate of chemical dissolution of the film. At j=0.5 A·dm^{-2} (Fig. 1, dependence 2), we observe the emergence of the plateau, which is followed by a gradual increase in voltage ultimately reaching the predefined U.
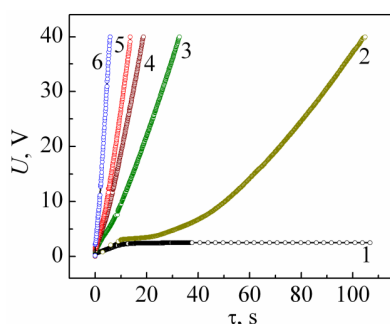

Fig. 1. Forming dependences of the alloy VT6 in solutions of H$_2$SO$_4$ at j, A·dm^{-2}: 0.2(1); 0.5(2); 1(3); 0.75(4); 2(5); 5(6). U=40 V; c=100 g·dm^{-3}

Increasing j to 1–5 A·dm^{-2} predetermines the linear course of dependences (Fig. 1, 3–6), indicating the formation of films with good protective properties. The concentration of H$_2$SO$_4$ in the solution does not affect the shape of the forming dependences.

Color of the film is defined by the thickness of the oxide whose magnitude depends on the value of U. The correspondence between a film color and U is given in Table 1.

Table 1

Correspondence between an oxide film color and the magnitude of U

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

A dependence of the period for reaching the assigned U on current density of the electrolysis has a characteristic shape, which persists for the entire series of curves acquired on samples oxidized under the same mode (Fig. 2).

At a sequential increase in voltage, there is an increase in time τ (Fig. 2, dependences 1–3). The time required to reach the preset U matches the time required to reach the film thickness, which is limiting for these electrolysis conditions, and represents the maximally possible duration of the electrolysis.
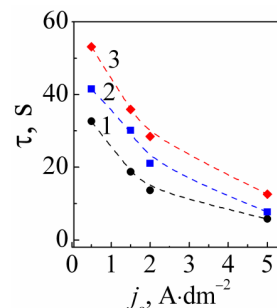

Fig. 2. Dependence of τ on current density during oxidization of the alloy VT6 in solutions of H$_2$SO$_4$. U, V: 40(1); 60(2); 80(3). c=100 g·dm^{-3}

Dependence of τ–U for the same current density is linear (Fig. 3, a). A slope of dependences remains constant but decreases with increasing U. A change in c(H$_2$SO$_4$) within 5−100 g·dm^{-3} does not affect the duration of the film growth (Fig. 3, b). Maximum film thickness depends only on the assigned value of U. If c(H$_2$SO$_4$)<50 g·dm^{-3}, the application of forming voltage that exceeds 70–80 V is impractical as it sometimes leads to the emergence of punctures. Punctures in an oxide film occur due to the presence of inclusions in titanium, as well as the presence of ions-activators in solution that leads to the development of a local film destruction similar to the behavior of steel in alkaline chloride solutions [21, 22].
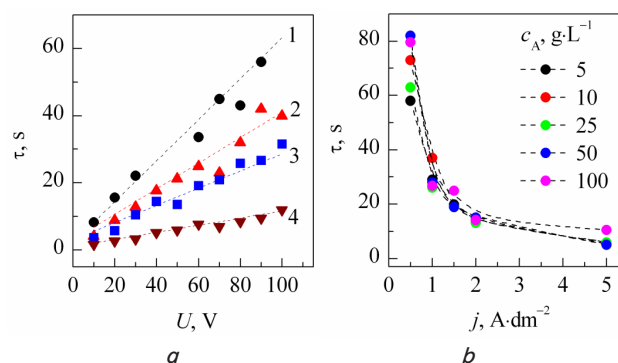

Fig. 3. Dependence of τ on forming voltage and current density during oxidization of the alloy VT6 in solutions of H$_2$SO$_4$: a — dependence of τ on the voltage of forming at c=10 g·dm^{-3} and j, A·dm^{-2}: 1(1); 1.5(2); 2(3); 5(4); b — dependence of τ on current density at U=40 V

For the series of electrolyte solutions with the same concentration of H$_2$SO$_4$ the dependence of τ–U is linear (Fig. 4). The slope of dependences in all cases is the same over the entire examined interval of c(H$_2$SO$_4$).

Some deviations, visible in the Figure, are due to the error in measuring the time and a difference between an actual area of the alloy samples.

Thus, the data obtained show that the limiting thickness of the oxide film depends only on the assigned value of the forming voltage.
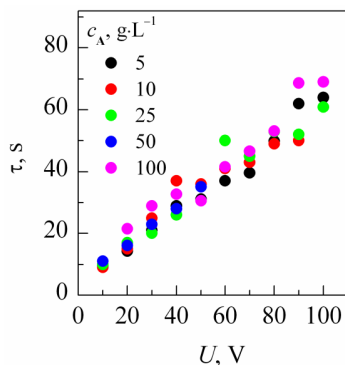
Fig. 4. Dependence of τ on forming voltage during electrochemical oxidization of the alloy VT6 in solutions of H_2SO_4. j_a=1 A·dm^{-2}

6. Discussion of results obtained for the oxidation of the alloy VT6

In a general form, reaction of the anodic oxidation of titanium takes the form:

$$Ti-4e+2H_2O \rightarrow TiO_2+4H^+. \qquad (1)$$

Reaction (1) is the result of a complicated process, one stage of which is the ionization of titanium with the formation of the Ti^{4+} ion. The electrons that are formed during ionization of titanium come into an external circuit to form the current of anodizing. Ti^{4+} ions under the influence of the electric field gradient migrate through the ionic lattice of oxide to its outer surface. During anodic oxidation, the formed oxide does not always match to stoichiometric composition. Typically, a layer of oxide facing the electrolyte contains more oxygen than the deeper layers [21]. In the case of titanium, the oxide acquires stoichiometric composition as a result of the process of sequential oxidation.

The oxygen that is required for the formation of an oxide film at anodic polarization arrives from the electrolyte. There is no any pronounced evolution of the gaseous oxygen on the anode during oxidization. Transition of oxygen from the electrolyte to the oxide film is not a consequence of the anodic reaction of oxygen evolution for reaction:

$$2H_2O-2e \rightarrow O_2+4H^+, \qquad (2)$$

but rather a direct process of the O^{2-} anion formation due to the dissociation of a water molecule:

$$H_2O \rightarrow 2H^+ + O^{2-}. \qquad (3)$$

The O^{2-} ion that is formed at the surface of an oxide according to reaction (3) migrates through the barrier layer towards the ion of Ti^{4+}. In theory, ions SO_4^{2-} or molecules of H_2O can act as the donor of oxygen. If a given suggestion is valid, oxidation in a solution of different electrolyte should have the same characteristics. We chose a solution of oxalic acid to act as such an electrolyte. Results of the conducted research are shown in the Fig. 5, *a*. For comparison, Fig. 5, *a* show data acquired in solutions of H_2SO_4. In general, forming dependences in solutions of $C_2H_2O_4$ and H_2SO_4 coincide. Their character depends on the applied current density and is the same over the entire range of *U*.
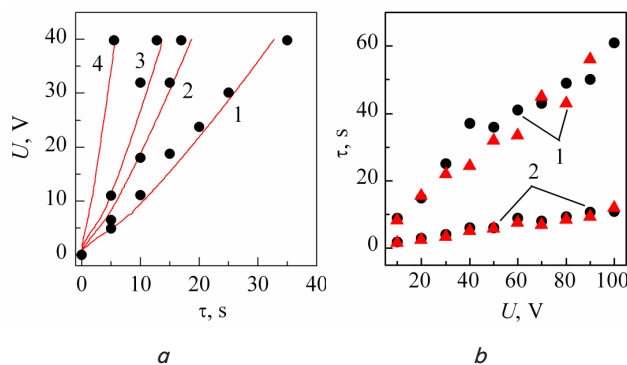

Fig. 5. Dependences of technological parameters of oxidization process of the alloy VT6. *a* — forming dependences in acidic solution at *j*, A·dm^{-2}: 0.2(1); 0.5(2); 1(3); 0.75(4); 2(5); 5(6). *U*=40 V; *c*=100 g·dm^{-3}. Points denote data for H_2SO_4, line — for $C_2H_2O_4$; *b* — dependence τ–*U*. *c*=10 g·dm^{-3}. *j*, A·dm^{-2}: 1(1); 5(2). Points denote data for H_2SO_4, triangles — for $C_2H_2O_4$

Fig. 5, *b* shows dependences of τ–*U*, acquired in acidic solutions. We observe a satisfactory agreement with experimental data. This testifies to that the nature of electrolyte does not affect the process of forming a film. Dependences shown in Fig. 5 indicate that the oxidation in solutions of H_2SO_4 and $C_2H_2O_4$ proceeds through the same mechanism as the coincidence between dependences in different electrolytes is unlikely. Therefore, an oxygen donor in both electrolytes is the molecules of water.

An oxide film forms as a result of counter migration of the ions of Ti^{4+} and O^{2-}. The driving force of the process is the existence of significant electric field strength in the film at anodic oxidation. The thickness of the film stops growing when the gradient of the potential is reached, which could not provide for the movement of ions through the oxide. The magnitude of ionic current of film growth is derived from the Günterschulz-Betz equation [24]:

$$I = Ae^{BE}, \qquad (4)$$

where *I* is the ionic current; *A* and *B* are constants that depend on the nature of a metal and electrolyte; *E* is the electrical field strength, which can be replaced with $\frac{U_f}{\delta}$, where δ is the thickness of the oxide. During anodizing, in order to maintain the assigned current density, a constant field strength is required throughout the thickness of the formed film. If the oxide forma at a constant current density, voltage on the film must grow linearly. Therefore, the thickness of an oxide film of the barrier-type is derived from:

$$\delta = \alpha U_f, \qquad (5)$$

where α is a constant of film growth (nm·V^{-1}). The magnitude of α for titanium, given in the scientific literature, is in the range of 1.9–6.0 nm·V^{-1} [25]. The value of α is affected by the parameters of electrolysis, a method for measuring the thickness of an oxide, sample preparation, film properties (density, crystal structure, morphological properties – homogeneity of the surface, and porosity).

Equation (5) explains the independence of a limiting film thickness magnitude on the current density of electrolysis and electrolyte concentration. Indeed, according to equations

(4) and (5), a film thickness is defined only by U. Increasing δ leads to a gradual reduction of the potential drop gradient with the oxide film terminating its growth when it reaches its critical value. Therefore, the thickness and color depend only on the value of forming voltage, increasing with its growing.

The results of our study demonstrate that the main parameters for electrolysis, which define the dynamics of growth and the limiting duration of electrolysis, are current density and forming voltage. Electrolyte concentration has no effect on the process of oxidation. The data obtained should be considered preliminary because the value of an electrolyte concentration, a method for the alloy pretreatment, electric mode of anodizing, should influence the process. In order to obtain more complete results, it is necessary to work towards studying the influence of treatment on the protective properties of the film. To this end, it is possible to employ a residual current method, voltammetry, potentiometry. Calculations of thicknesses of the obtained films must be carried out in parallel, which will make it possible to derive dependences for the treatment mode and the properties of coatings.

7. Conclusions

1. The process of electrochemical oxidation of the titanium alloy VT6 in solutions of H_2SO_4 was investigated. It is shown that a decisive influence on the character of U–τ dependences is exerted by the value of anodic current density. At $j<0.5$ A·dm^{-2}, a continuous oxide film does not form; the assigned forming voltage is not reached. At $j>0.5$ A·dm^{-2}, we observed linear character of dependences, indicating the formation of small-porous films. The films obtained at current densities of $j>0.5$ A·dm^{-2} relate to the interferential-colored films. A film thickness limit is defined by magnitude U and does not depend on other parameters of the process. For the series of identical values for U dependence of τ–j has a linear shape. A change in $c(H_2SO_4)$ within 5−100 g·dm^{-3} does not affect the duration of film growth.

2. It was established that the anodic polarization of the alloy VT6 in H_2SO_4 solutions leads to the formation of colored films at the surface of samples. A color of the film is determined by the assigned value of U and does not depend on the concentration of acid in a solution and current density. The result of our research is the established correspondence between a color of the film and the magnituds of U in the range of 10−100 V. A given effect is due to the fact that the growth of film at anodic polarization proceeds under conditions of the existence of potential's gradient whose magnitude for titanium is a constant quantity. Increasing the set value of U leads to a proportional increase in the maximum thickness of the oxide, which determines its color.

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