Представлені результати дослідження особливостей утворення тонких інтерференційно-забарвлених оксидних плівок на сплаві Ti6Al4V у розчинах карбонових кислот. Встановлено, що зміна напруги на комірці, яка відповідає формувальній залежності сплаву, залежить від анодної густини струму. При густинах струму <0,5 А·дм$^{-2}$ суцільна оксидна плівка на поверхні сплаву не утворюється і задане значення напруги не досягається. Підвищення густини струму до значень більших за 0,5 А·дм$^{-2}$, обумовлює лінійну зміну напруги у часі з кінцевим виходом на задану величину U. Максимальна для даних умов товщина плівки визначається встановленою величиною напруги і не залежить від режиму електролізу. Колір оксидної плівки визначається заданим значенням напруги формування і не залежить від густини струму, природи і концентрації карбонової кислоти.

Збіг формувальних залежностей оксидування, одержаних у різних електролітах, дозволяє припустити, що утворення оксиду проходить за однаковим механізмом. Одержані дані пояснюються тим, що формування оксиду у гальваностатичному режимі проходить в умовах наявності постійного градієнта потенціалу у оксидній плівці. Збільшення величини прикладеної до комірки напруги обумовлює пропорційний ріст максимальної товщини оксиду, оскільки приводить до зростання пропущеної через комірку кількості електрики і відповідного зростання маси окисленого металу. Результати дослідження з визначення впливу природи карбонової кислоти на процес формування оксидної плівки на сплаві Ti6Al4V методом електрохімічного окислення показали, що природа електроліту не впливає на особливості її утворення. Одержані дані дозволяють стверджувати, що вибір електроліту для розробки технології електрохімічного оксидування титанових імплантатів повинен ґрунтуватися на результатах дослідження функціональних властивостей одержаних покриттів

Ключові слова: анодна поляризація, електрохімічне окислення, оксидна плівка, формувальна залежність, градієнт потенціалу

ESTABLISHING THE PATTERNS IN THE FORMATION OF OXIDE FILMS ON THE ALLOY TI6AL4V IN CARBONIC ACID SOLUTIONS

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1. Introduction

Titanium and titanium alloys are among the most popular materials of modern technology. High corrosion resistance, relative cheapness (in comparison with Zr, Hf, Nb and Ta), manufacturability of titanium made it an indispensable metal for use in industry and medicine. The special feature of titanium is the insufficient strength properties when it is used under conditions of varying mechanical loads. The titanium-based alloys are more widely used since as a result of its alloying with other elements, a material with the required properties can be obtained. In particular, the titanium alloy Ti6Al4V is widely known, which contains vanadium and aluminum. The alloy has a high corrosion resistance, specific strength, can be easily machined by cutting and drilling. Ti6Al4V is used for the manufacture of critical parts in industry and medical implants. In the latter case, an important property of the alloy is its corrosion resistance. Corrosion resistance of titanium alloys typically decreases with an increasing number of alloying elements [1, 2]. The latter circumstance is especially important in the manufacture of implants, since their corrosion can lead to surface destruction, chipping, and penetration of metal particles into the surrounding tissues of the body. To increase their

corrosion resistance, oxide films are formed at the surface of implants [3]. The method of electrochemical oxidation is most widely used for this purpose, which does not require complex instrumentation and allows obtaining films of a certain thickness and structure [4, 5]. Oxidation reduces the probability of destruction and improves the biocompatibility of implants, which is especially important at the initial period of their contact with body tissues [6].

2. Literature review and problem statement

Many studies tackle the processes of electrochemical oxidation of titanium and its alloys. Attention to the method is predetermined by that the application of electrochemical techniques makes it possible to obtain films of various structures and with a wide range of properties. For example, papers [7] and [8] investigated the oxidation of titanium in solutions of inorganic acids in order to identify the relationship between the process mode and the coloration of oxide films. In [9], chromatics of the oxide films obtained in solutions of citric acid was examined. The results obtained show that the molding voltage exerts a decisive effect on the color of the film. These studies contain no data on the effect of process parameters on the dynamics of film growth. In [10], authors investigated the effect of electrolysis conditions on the structure of an oxide film formed on titanium under a potentiostatic mode in a 0.5 M solution of H_2SO_4. It was established that the structure and composition of the film depend on the temperature and molding voltage U, however data on the dynamics of film growth are missing. In paper [11], it was shown that the color properties of films are defined by the thickness and structure of the oxide. The growth dynamics of the films in the article is not studied. Anodic oxidation of titanium in a mixture of tartaric, oxalic, and sulfuric acids for surface modification of titanium alloys is proposed to be used in [12]. The structure, morphology, and corrosion resistance of the films were investigated, but there are no data on the course of the oxidation process under the galvanic static mode. Authors of [13] reported an analysis of the effect of voltage on a color change of titanium anodized in an electrolyte containing citric acid and sodium bicarbonate. It was established that the color of the film depends on U. The effect of electrolysis parameters on the film growth rate is not shown. The surface modification of titanium implants by oxidation in a sulfate electrolyte is studied in [14]. A change in the morphology and roughness of the samples was explored. The molding dependences of the samples were not investigated. The structure of TiO_2 films obtained in a mixture of citric and sulphaminic acids is studied in [15]. Valuable data on the effect of electrolysis conditions on the film structure are given, but there are no data about the formation dynamics. The effect of halide ions on the anodic behavior of titanium alloys in solutions of citric acid was studied in [16]. The alloys are prone to a transition to the passive state, but the features of oxide formation were not investigated. The effect of the nature of the electrolyte on the growth of an oxide film on titanium in alkaline and acidic solutions is shown in [17]; however, the effect of the electrolysis regime is not studied. The electrochemical fabrication and behavior of TiO_2 nanotubes is considered in [18]. The properties of nanotubes depend on the anodizing conditions; however, continuous films must be used to coat the implants. The oxidation of the titanium alloy Ti-6.5Al-1Mo-1V-2Zr in H_2SO_4 and a mixture of tartaric and sulfuric acids is conducted in [19]. The work focuses on determining the optimal concentrations of $C_4H_6O_6$, which reduces the dissolution of the film and the degree of its crystallinity. The polarization curves obtained on titanium oxidized in H_2SO_4 and H_3PO_4 solutions are investigated in [20]. The effect of the electrolysis mode in the production of films on polarization dependences was not studied. Paper [21] established the effect of tartaric acid on the growth of TiO_2 in a sulfate electrolyte on the structure of the film, its chemical dissolution, and the intensity of oxygen evolution. The effect of $C_4H_6O_6$ concentration, current density, and molding voltage on these processes is not shown.

Thus, an analysis of publications that address the electrochemical oxidation of titanium and its alloys allows us to conclude that there is an insufficient volume of data on the influence of the electrolysis mode on the formation of TiO_2 films. Carrying out a research in this direction would be a prerequisite for the development of the controlled technique for obtaining films with the predefined properties.

3. The aim and objectives of the study

The aim of this work is to study the formation of oxide films on the alloy Ti6Al4V in carboxylic acid solutions and to determine an effect of the electrolysis mode on the oxidation process. To achieve this goal, it is necessary to solve the following tasks:

– to investigate the dynamics of the formation of oxide films on the alloy Ti6Al4V in carboxylic acid solutions;

– to determine effect of the electrolysis mode on the time of formation of oxide films with maximum thickness.

4. Procedure of research into oxide films formation

Plates the size of 70×20×5 mm, made from alloy Ti6Al4V (3.5–5.3 % V, 5.3–6.8 % Al), were used as working electrodes. The plates were polished with a sandpaper, degreased with an aqueous suspension of Na_2CO_3, and etched in a mixture of HNO_3 and HF (3:1). Between operations, the samples were washed with tap and distilled water. The oxidation was conducted in solutions of oxalic, tartaric, and citric acids under the galvanic static mode, setting the voltage across the cell (10–100 V with a step of 10 V) using the source B5-50 (USSR). A signal of the end of the process was the triggering of switching relay of the power source when the specified voltage was reached. Voltage on the cell during electrolysis was measured with the multimeter Keithley-2000 (USA). A 250-ml beaker, made from chemically resistant glass, was used as the electrolyzer for the process. To exclude the heating of the glass by current, it was placed in a 5-liter crystallizer filled with water. Lead served as an auxiliary electrode. The acids used in the study matched the reagents of "pure" grade.

The experimental points shown in Fig. 2–4 were obtained as a result of a series of measurements on five samples for each selected electrolysis parameter. The arithmetic mean value was derived from the obtained data, which served as a function of dependences. The impact of a systematic error on the experimental results was not considered. Random errors, the cause of which was the difference in the surface area of the samples, are not shown in Figures due

to the inconvenience of visual perception of dependences, caused by the proximity of the latter's positioning.

5. Results of research into electrochemical oxidation of the alloy VT6

5. 1. Studying the dynamics of the oxide film formation

Oxidation in solutions of carboxylic acids is used to produce thin colored films that are related to the interference colored ones. The large value of the resistivity of titanium dioxide predetermines a significant electrical resistance of the films. Mechanical resistance of films is low. The oxide layer is easily abraded under load. In the case of using the films to cover the implants, the latter is not so important. The presence of a solid oxide is important only at the initial moment after putting the implant into the tissues of the body.

The study of the dynamics of oxidation was conducted by deriving the molding dependences $U=f(\tau)$ of the alloy samples. It was established that the nature of carboxylic acid does not affect the molding dependences of the alloy. Current density has a decisive effect on the dependences' character. At its values <0.5 A·dm^{-2}, the graphs are non-linear in nature (Fig 1, dependence 1). The specified value of U is often not achieved, which is predetermined by the progress of two opposite processes. The first is the electrochemical formation of the film, the second is its chemical dissolution in the electrolyte. As a result of the first process, voltage on the cell increases. Chemical dissolution causes a decrease in voltage. Oxidation at $j_a=0.5$ A·dm^{-2} leads to the emergence of a plateau, after which a gradual increase in U is observed. The process is characterized by the inhibition, which corresponds to the gradual filling of the metal's surface by an oxide film.
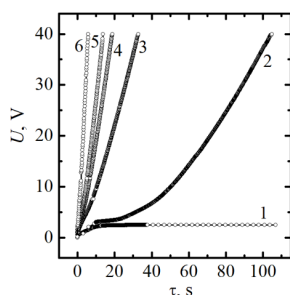

Fig. 1. Molding dependences of the alloy Ti6Al4V in carboxylic acids. j_a, A·dm^{-2}: 0.2(1); 0.5(2); 1(3); 0.75(4); 2(5); 5(6). U=40 V; c_A=50 g·dm^{-3}

When oxidizing at $j_a=1-5$ A·dm^{-2}, the low-porous films are formed. This is indicated by the linear dependence $U=f(\tau)$. The films have a high electrical resistance, which provides for their good protective properties. Color of the film depends on its thickness, that is, the assigned magnitude U.

5. 2. Effect of oxidation mode on growth of the oxide film

The characteristic dependence of the time to reach the maximum film thickness for these conditions, τ_{pr}, on molding voltage is maintained for the entire series of samples, oxidized under the same conditions (Fig. 2, $a-c$).
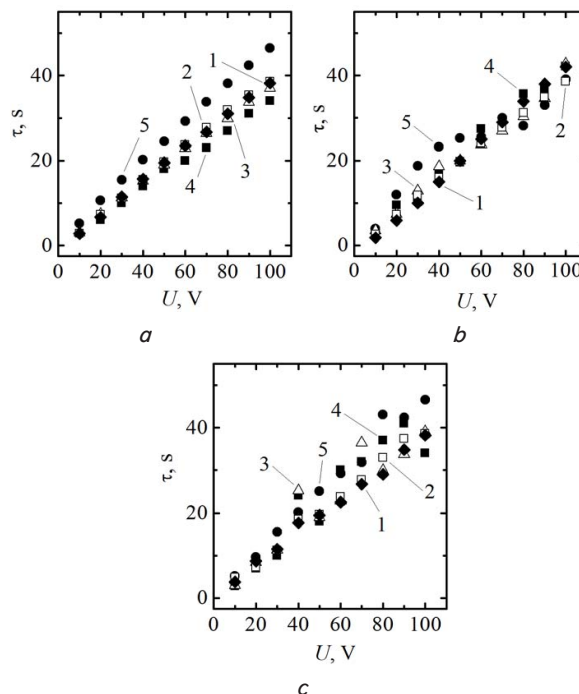

Fig. 2. Dependences of τ on voltage during oxidation of the alloy Ti6Al4V: a — dependences of τ on voltage, obtained in tartaric acid; b — dependences of τ on voltage, obtained in citric acid; c — dependences of τ on voltage, obtained in oxalic acid. j_a=2 A·dm^{-2}; c_A, g·dm^{-3}: 5(1), 10(2), 25(3), 50(4), 100(5)

The time required to reach the maximum film thickness during oxidation under the galvanic static mode depends on the molding voltage and increases linearly at its increase. At $j_a=2$ A·dm^{-2}, a linear dependence is observed for all examined acid solutions. The magnitude of τ does not depend on the nature of the used acid. With an increase in the value for U, an increase in the duration of electrolysis is observed (Fig. 2).

Experimental data reveal that for a series of identical current densities, the linear character of the time τ_{pr} required to reach the assigned voltage U is also observed (Fig. 3). The value of τ for each specific current density increases linearly with an increase in the molding voltage and does not depend on the electrolyte concentration for all carboxylic acid solutions.
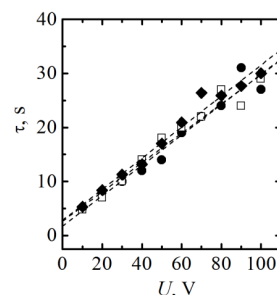

Fig. 3. Dependences of τ on molding voltage U, obtained in oxalic acid. c_A=50 g·dm^{-3}; j_a, A·dm^{-2}: 1(1), 2(2), 3(3)

A change in the concentration of carboxylic acid in the range of $5-100$ g·dm^{-3} does not affect the time of film growth, that is, the limiting film thickness depends primarily on the molding voltage (Fig. 4, a, b).
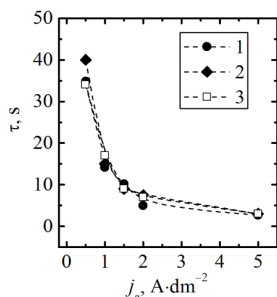
Fig. 4. Dependences of τ on the oxidation current density, obtained in tartaric (1), citric (2) and oxalic (3) acids. U=20 V; c_A=50 g·dm^{-3}

Thus, the obtained experimental data show that the magnitude of the specified molding voltage has a decisive effect on the thickness of the oxide film. The nature of carboxylic acid, its concentration, as well as current density, do not affect the thickness of the film. The current density affects the rate of attaining the maximum film thickness, since for an electrochemical reaction, j_a is its rate. An interesting observation is that the dependences, shown in Fig. 4, are nonlinear, which violates a condition for the proportionality of oxidation rate on the assigned j_a.

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

Titanium anodic oxidation is typically described by equation Ti$-$4e$+$2H$_2$O$\rightarrow$TiO$_2$$+$4H$^+$, which is the result of a complex process. One of its stages is the ionization of titanium with the formation of a Ti^{4+} ion, which, under the action of an electric field gradient in an oxide film, migrates through the oxide's lattice. A zone in which the meeting of Ti^{4+} and O^{2-} ions occurs is not precisely established. It is widely believed that it occurs at the outer surface of the electrode. This statement is confirmed by the fact that at anodic oxidation the obtained oxide does not match the stoichiometric composition. The oxide layer is enriched with oxygen from the side of the electrolyte, which is a very common case at anodic polarization. This situation is observed when active anodes are dissolved, for example, copper in acid [22] or nickel in alkaline [23] electrolytes. Another case is the formation of oxide layers during anodic polarization of steels in [24, 25] and copper [26] in alkaline solutions. Sometimes, the formation of oxides with a non-stoichiometric composition occurs during the oxidation of metals susceptible to a transition to the passive state [27] or the formation of oxide-salt films when polishing copper [28]. The driving force of the anodizing process is the presence of significant electric field strength in the film during anodic oxidation. An increase in the film thickness ceases when a potential gradient is reached, which cannot ensure the movement of ions through the oxide. During the oxidation of a metal under the galvanic static mode, in order to maintain the specified current density, a constant field strength is required over the thickness of the formed film. If the oxide is formed at j_a=const, voltage on the film should increase linearly, that is, a linear equation of the from $x=ay$ would be observed, where x is the film thickness, y is the molding voltage, a is the proportionality coefficient (a film growth constant), which varies for titanium within 1.9–6.0 nm·V^{-1} [29].

The above-stated explains the experimental results. The molding dependences of the alloy (Fig. 1) show that an increase in j_a contributes to an increase in the growth rate of the oxide film. This observation is in full accordance with the fundamental laws of electrolysis, according to which current density is the rate of electrochemical metal oxidation. The linear character of dependences $U=f(\tau)$ at $j_a>0.5$ A·dm^{-2} indicates the formation of a barrier-type oxide films whose electrical resistance is proportional to their thickness. Such a conclusion can be drawn based on the data shown in Fig. 2, 3. The thickness of the oxide film formed at j_a=const depends only on the applied U. Film growth is possible under the condition that there is a certain value of voltage drop across the oxide thickness, which ensures the movement of ions in the TiO$_2$ lattice. A decrease in the gradient under conditions of the assigned U leads to the cessation of oxide growth. At j_a=const, an increase in U will increase the maximum thickness of the oxide or the duration of electrolysis proportional to it. A given effect should not depend on other process parameters (nature and concentration of electrolyte, current density), which is confirmed by the results of the experiment. Somewhat contradictory are the data shown in Fig. 4. Based on the theoretical assumptions, we should expect a linear course of dependences $\tau=f(j_a)$. However, some linearity appears only when $j_a>0.5$ A·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 TiO$_2$ at a rate close to the oxidation titanium rate. The further linearity of curve 2 in Fig. 1 is explained by the combination of individual sections of the film, which have arisen in places of active growth, with the formation of a continuous oxide.

Results of the study conducted show that the formation of oxide films on the alloy VT6 in solutions of carboxylic acids leads to the formation of thin colored films. The maximum film thickness obtained in solutions of carboxylic acids at c_A= 5–100 g·dm^{-3} and $j_a>0.5$ A·dm^{-2} in the range U=10–100 V is defined only by the magnitude of voltage. Experimental data indicate that the anodic polarization of the alloy VT6 is accompanied by the formation of a barrier-type films, which have good protective properties due to the large ohmic TiO$_2$ resistance. The results are sufficient for the development of technological processes of electrochemical formation of films; however, it is necessary to conduct a set of studies into the properties of the obtained materials. In particular, the effect of the electrolyte and the mode of production of films on their properties was not studied. Therefore, further work should be directed to studying the structure and morphology of films, the establishment of relationships between the parameters of electrolysis and the chemical resistance of the alloy in model media.

7. Conclusions

1. The dynamics of the formation of oxide films on the titanium alloy Ti6Al4V in solutions of carboxylic acids was investigated. It was established that the crucial effect on the character of dependences $U=f(\tau)$ is exerted by the value of the used current density. At $j_a<0.5$ A·dm^{-2}, a continuous oxide film is not formed and the assigned U is not reached. At $j_a>0.5$ A·dm^{-2}, dependences $U=f(\tau)$ are linear, which indicates the formation of low porosity films. For the examined solutions of carboxylic acids, a coincidence of the molding

dependences of the alloy is observed, which suggests the same mechanism of formation of the oxide film.

2. The anodic polarization of the alloy Ti6Al4V in solutions of carboxylic acids leads to the formation of thin interference-colored films at the surface of the samples. It is shown that the limiting film thickness is determined by the magnitude of U and does not depend on the nature of the electrolyte, its concentration, and current density. During electrolysis under the galvanic static mode, linear dependences $U=f(\tau)$ and $\tau=f\ (U)$ are observed, which indicates the formation of a barrier-type TiO_2 films. An increase in j_a leads to a more rapid formation of the oxide, although no linear dependence $\tau=f(j_a)$ is observed. The results obtained are explained by that film growth occurs in the presence of a certain potential gradient, decreasing which leads to the cessation of oxide formation.

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