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ELECTROCHEMICAL OXIDATION OF Ti6Al4V TITANIUM ALLOY IN MALIC ACID SOLUTIONS

The results of research the influence of electrolysis parameters on the process of oxidation of Ti6Al4V titanium alloy in malic acid solutions have been given. It has been shown that the character of the forming dependences is defined by the value of the used current density. It has been shown that for the formation of oxide films it is necessary to use an anode current density of at least $0.5 \text{ A} \cdot \text{dm}^{-2}$. At lower current densities, the film is not formed and the dependence of the cell voltage on the electrolysis time has a complex shape due to the parallel processes of film dissolution and the formation of intermediate oxides. At current densities above $0.5 \text{ A} \cdot \text{dm}^{-2}$, the forming dependences obtained on the alloy have the form of straight lines, which indicates the formation of continuous barrier-type oxide films with good passivating properties. The growth rate of the oxide under these conditions is directly proportional to the used value of j_a , which is evidence that the entire used current is spent on the formation of titanium dioxide, which forms the passive layer. The effect of the final cell voltage, current density, and electrolyte concentration on the time to reach the maximum thickness of the oxide film on the alloy has been studied. The influence of the value of the final voltage on the cell manifests itself in an increase in the duration of electrolysis, which corresponds to a larger film thickness. This effect is due to the fact that the oxide is formed under conditions of a constant potential gradient in the film. The limiting thickness of the oxide will increase in direct proportion to the increase in cell voltage, since the increase in V causes the potential gradient in the film to be maintained for a longer time. The result of electrochemical oxidation of alloy Ti6Al4V in malic acid solutions at current densities greater than $0.5 \text{ A} \cdot \text{dm}^{-2}$ is the formation of interference-colored oxide films with good adhesion to the metal surface. The color of the film depends on the final value of V on the cell. The limiting thickness and color of the oxide film are defined by the forming voltage and do not depend on other electrolysis parameters.

Key words: titanium, forming dependences, oxide film, anode oxidation, passivity, electrical resistance, barrier layer.

1. Introduction. Titanium is an active metal, but under ordinary conditions, a natural oxide film forms on its surface [1]. This film is a protective barrier passivating titanium in many oxidizing mediums. In some cases, such a film acts like a functional material with increased corrosion resistance [2] and properties of biological inertness [3] and compatibility [4]. Artificially obtained films are

characterized by a certain structure and thickness, as well as, as a rule, a more developed relief [5]. These properties, along with the homogeneity of the chemical composition, determine sufficiently high protective properties of the films and allow the formation of a highly developed surface, which is important in the case of using titanium for the manufacture of medical implants [6].

Artificial films on titanium are obtained by thermal oxidation [7] or plasma oxidation [8], diffusion introduction of oxygen [9] and anodic oxidation [10]. The latter method of oxidation, sometimes referred to as anodizing, is the most widely spread.

2. The aim of research. Establishment of the influence of electrolysis parameters on the process of electrochemical oxidation of Ti6Al4V titanium alloy in the malic acid solution.

3. Research tasks. *a)* Show the influence of electrolysis parameters (current density, voltage, electrolyte concentration) on the forming dependences of alloy oxidation. *b)* Determine the dependence of the electrolysis duration (time to reach the limiting film thickness) on the electrolysis parameters.

4. Experimental technique. Titanium alloy specimens in the form of rectangular plates were used for research. The specimens were polished, degreased and flushed with tap water. Degreased specimens were etched in the mixture of nitric and hydrofluoric acids (3:1) and then flushed with the tap water and distilled water. The electrolysis was carried out in the galvanostatic mode, setting the cell voltage in the range of 10–100 volt with a step of 10 volt using a power source. A change in the cell voltage value was recorded by the multimeter Keithley-2000. A beaker with a volume of 250 cm³ made of chemically resistant glass was used as a cell for electrolysis. Lead was used as the auxiliary electrode.

5. Results and discussion. The most informative for the research of the anodizing process is the study of forming dependences, which show the change in the cell voltage during electrolysis. Such dependences make it possible to study the dynamics of film growth and establish the influence of the electrolysis mode on the features of oxide formation and its structure. Experimental data show that the general type of the forming dependence is determined by the used current density of electrolysis (j_a) and is the same for the entire range of used voltages V . The forming dependences of the alloy were obtained in a solution containing 100 g·dm⁻³ of acid at $V = 60$ volt (Fig. 1). At $j_a = 0.2\text{--}0.5 \text{ A} \cdot \text{dm}^{-2}$, the dependences are non-linear and are often not reproduced (Fig. 1, 1 and 2). At $j_a = 0.2 \text{ A} \cdot \text{dm}^{-2}$, the preset V value is not reached at all. This is due to the fact that the process of oxide formation consists of two processes: the electrochemical formation of the film and its dissolution as a result of chemical interaction with electrolyte components. The first process increases the film thickness and its electrical resistance. Chemical dissolution reduces film thickness. The horizontal plateau in dependence 1 (Fig. 1) indicates that the oxidation is

carried out in a stationary mode, in which the rate of electrochemical formation of the film is equal to the rate of its chemical dissolution [11]. With an increase j_a to 0.5 A dm⁻² (Fig. 1 and 2), a plateau on the curve is appeared, after which a gradual increase in the cell voltage is observed with a final achievement of the preset V . The process is characterized by the presence of a deceleration period, which indicates a change in the kinetics of film formation and the transition of the film structure to one that is less sensitive to the effect of the electrolyte.

Increasing the density j_a to 1–5 A·dm⁻² results to a linear trend of dependences (Fig. 1, 3–6), which indicates the formation of minimum porous films with protective properties. The color of the obtained film depends on its thickness, the value of which is defined by preset value of the final cell voltage.

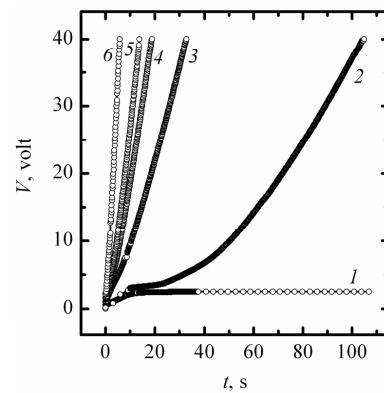


Fig. 1. Dynamics of oxide film formation on Ti6Al4V alloy in malic acid solutions. Electrolysis conditions: $j_a, \text{A} \cdot \text{dm}^{-2}$: 0.2(1); 0.5(2); 1(3); 0.75(4); 2(5); 5(6); $V = 60$ volt; $c_A = 100 \text{ g} \cdot \text{dm}^{-3}$

The dependence of the time to achieve a preset voltage on the current density has a characteristic shape, which is not changed for the entire series of curves obtained on specimens oxidized in the same mode (Fig. 2, 1–3).

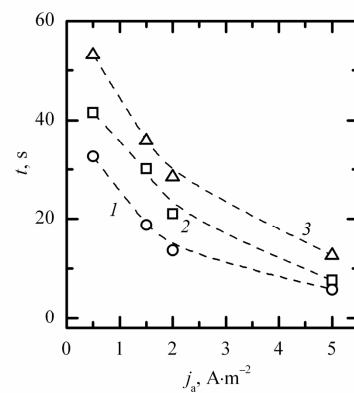


Fig. 2. Dependence of the time to reach the limiting thickness of the oxide film on the anodic current density. V , volts: 40(1); 60(2); 80(3). $c_A = 20 \text{ g} \cdot \text{dm}^{-3}$

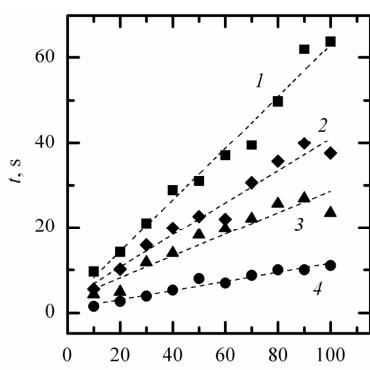
With a sequential increase in voltage, an increase in time t is observed (Fig. 2, dependences from 1 to 3). The value of the time interval required to achieve a preset V corresponds to the time to achieve the limiting film thickness for the given electrolysis conditions and is the maximum possible duration of electrolysis.

The dependence of the time to achieve the limiting film thickness on U for a series of equal current densities is linear (Fig. 3). The slope of these dependences does not remain constant, but decreases with increasing cell voltage.

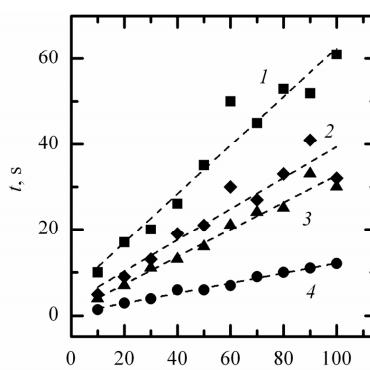
Experimental data (Fig. 4) show that a change in the electrolyte concentration in the solution within 5–100 g·dm⁻³ does not influence the change in the duration of film growth. The limiting film thickness depends only on the preset value V . For a series of electrolyte solutions with the equal acid concentration, the dependence $t=f(V)$ is linear (Fig. 5, a, b). The slope of the dependences in all cases is the same for the entire studied range of electrolyte concentrations. Some deviations that are noticeable in the figure are due to inaccuracies in the measurement of time, as

well as the difference in the surface area of the oxidized specimens.

Thus, the data obtained show that the limiting film thickness depends only on the preset value of the final voltage. The formation of an oxide film occurs as a result of the counter migration of ions Ti^{4+} and O^{2-} . The motive force of the process is a significant intensity of the electric field in the film during the anode oxidation [12]. The increase in the film thickness practically is stopped as soon as the value of the potential gradient is achieved, that fails to provide the motion of ions through the oxide. If the oxide is formed at a constant current density, the film voltage should increase linearly. Therefore, the thickness of the oxide film of a barrier type is defined by the formula $\Delta = a \cdot U$, where a – constant of the film growth (nm·volt⁻¹). The values of this constant for titanium, given in the literature, are changed in the range of 1.9 to 6.0 nm·volt⁻¹. The value of a is influenced by the electrolysis parameters, the method of measuring the oxide thickness, the preparation of the specimen, the physical properties of the film (density, crystal structure, morphological properties – surface uniformity and porosity) [13].

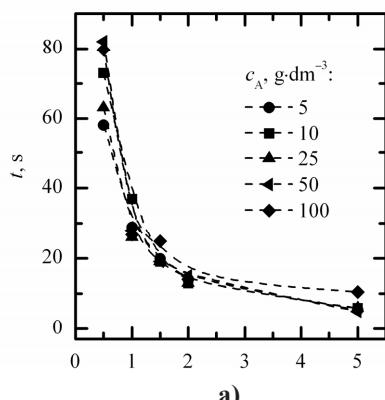


a)

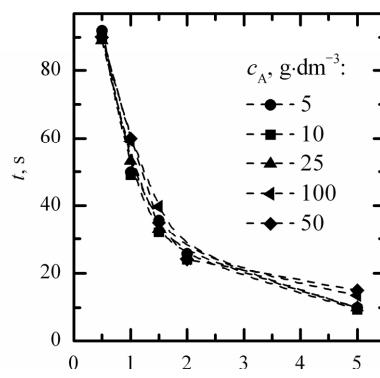


b)

Fig. 3. Dependence of the time to reach the limiting thickness of the oxide film during anodic oxidation: a) – $c_A = 30 \text{ g} \cdot \text{dm}^{-3}$; b) – $c_A = 50 \text{ g} \cdot \text{dm}^{-3}$. $j_a, \text{A} \cdot \text{dm}^{-2}$: 1(1); 1.5(2); 2(3); 5(4)



a)



b)

Fig. 4. Dependence of the time to reach the limiting thickness of the oxide film during anodic oxidation of the alloy Ti6Al4V: a) – $V = 50 \text{ volt}$; b) – $V = 100 \text{ volt}$

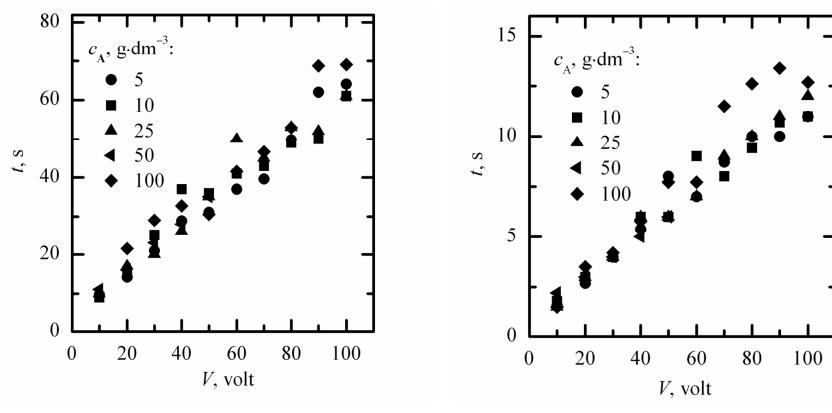


Fig. 5. Dependence of the time to reach the limiting thickness of the oxide film during anodic oxidation of the alloy Ti6Al4V. j_a , $\text{A} \cdot \text{dm}^{-2}$: a) – 1; b) – 5

The above facts explain the independence of the limiting film thickness from the current density of electrolysis and electrolyte concentration. Indeed, the film thickness is defined only by the forming voltage. As it increases, the potential falling gradient in the oxide gradually decreases. The oxide is not formed when the critical value of the gradient potential is achieved. Therefore, the thickness and color of the film is defined only by the voltage value. An increase in the value of V increases the electrolysis duration and promotes the formation of a thicker oxide.

6. Conclusions. The process of electrochemical oxidation of Titanium alloy Ti6Al4V in malic acid solutions has been studied. It has been shown that the anodic current density decisively influences on

the character of the forming dependence of the alloy specimen. At $j_a < 0,5 \text{ A} \cdot \text{dm}^{-2}$, a continuous oxide film is not formed and the preset voltage is not achieved. With an increase in $j_a > 0,5 \text{ A} \cdot \text{dm}^{-2}$, a linear character of the dependences is observed, indicating the formation of minimum porous films. Films obtained at $j_a > 0,5 \text{ A} \cdot \text{dm}^{-2}$ are interference-colored. The limiting thickness of the oxide film is defined by the forming voltage and does not depend on other parameters of electrochemical machining of metal. For a series of equal voltage values, the dependence of the time to achieve the limiting thickness of the film on the current density is linear. A change in the electrolyte concentration in the range of 5–100 $\text{g} \cdot \text{dm}^{-3}$ does not influence the change in the duration of film growth.

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Саввова О.В., Зайцева І.С., Смірнова О.Л., Воронов Г.К., Фесенко О.І., Пилипенко О.І.
ЕЛЕКТРОХІМІЧНЕ ОКСИДУВАННЯ ТИТАНОВОГО СПЛАВУ Ti6Al4V У РОЗЧИНАХ ЯБЛУЧНОЇ КИСЛОТИ

Наведені результати дослідження впливу параметрів електролізу на процес окиснення титанового сплаву Ti_6Al_4V у розчинах яблучної кислоти. Показано, що характер формуючих залежностей визначається значенням використаної густини струму. Показано, що для формування оксидних плівок необхідно використовувати анодну густину струму не меншу, ніж $0,5 \text{ A}\cdot\text{dm}^{-2}$. За менших густин струму плівка не утворюється і залежність напруги на комірці від часу електролізу має складну форму внаслідок протікання паралельних процесів розчинення плівки та утворення проміжних оксидів. При густині струму більше за $0,5 \text{ A}\cdot\text{dm}^{-2}$ отримані на сплаві формувальні залежності мають вигляд прямих ліній, що свідчить про формування суцільних оксидних плівок бар'єрного типу з хорошими пасивуючими властивостями. Швидкість росту оксиду в цих умовах прямо пропорційна використаному значенню j_a , що свідчить про те, що весь використаний струм витрачається на утворення діоксиду титану, який формує пасивний шар. Дослідженій вплив кінцевої напруги на комірці, густини струму та концентрації електроліту на час досягнення максимальної товщини оксидної плівки на сплаві. Вплив величини кінцевої напруги на комірці проявляється у збільшенні тривалості електролізу, що відповідає більшій товщині плівки. Цей ефект обумовлений тим, що оксид утворюється в умовах постійного градієнта потенціалу в плівці. Границя товщина оксиду буде збільшуватися прямо пропорційно збільшенню напруги комірки, оскільки збільшення V призводить до того, що градієнт потенціалу в плівці зберігається постійним протягом більш тривалого часу. Результатом електрохімічного окиснення сплаву Ti_6Al_4V у розчинах яблучної кислоти при густині струму вище $0,5 \text{ A}\cdot\text{dm}^{-2}$ є утворення інтерференційно-забарвлених оксидних плівок з хорошою адгезією до поверхні металу. Колір плівки залежить від кінцевого значення V на комірці. Границі товщина і колір оксидної плівки визначаються напругою формування і не залежать від інших параметрів електролізу.

Ключові слова: титан, формувальна залежність, оксидна плівка, анодне окислення, пасивність, електричний опір, бар'єрний шар.