Production of Nanosize Interference-colored Oxide Films on the Ti6Al4V Alloy Surface Using the Method of Electrochemical Oxydation in Succinate Eletrolytes

Galina Shevchenko
Department of technical electrochemistry
National Technical University «Kharkiv Polytechnic Institute»
Kharkiv, Ukraine
e-mail: galinashevchenko@gmail.com

Alexei Pilipenko
Department of technical electrochemistry
National Technical University «Kharkiv Polytechnic Institute»
Kharkiv, Ukraine
e-mail: opilipenko1984@gmail.com

Tetiana Shkolnikova
Department of general and inorganic chemistry
National Technical University «Kharkiv Polytechnic Institute»
Kharkiv, Ukraine
e-mail: shkollnikovatv@gmail.com

Svetlana Gura
Department of chemistry and Chemistry technology
National University of Civil Defence of Ukraine
Kharkiv, Ukraine
e-mail: gyra@nuczu.egu.ua

Olga Smirnova
Department of technical electrochemistry
National Technical University «Kharkiv Polytechnic Institute»
Kharkiv, Ukraine
e-mail: oleleo1970@gmail.com

Abstract—The research data obtained for the specific features of the formation of thin interference-colored films on the Ti6Al4V alloy surface in succinic acid solutions have been given. A maximum film thickness for given conditions is defined by the voltage value independent of the electrolysis mode. The oxide film color is defined by the preset forming voltage value independent of the current density and the electrolyte concentration. The obtained data are explained by that the formation of oxide in galvanostatic mode occurs under the conditions of the availability of the constant potential gradient in the oxide film. An increase in the value of voltage applied to the cell will condition a proportional growth of a maximum thickness of the oxide film because it result in an increase of the amount of electricity passed through the cell and in an appropriate increase in the oxidized metal mass

Keywords—anode polarization, electrochemical oxidation, oxide film, barrier layer

I. INTRODUCTION

The main consumers of titanium and titanium alloys are the aircraft industry, the rocket production, shipbuilding and chemical industries that use these material for the production of crucial items that combine an excellent specific strength, a low weight and a high corrosion resistance. Medicine is one more field that is of importance for the use of titanium materials for the production of different instrumentation, dentures, joint elements, sutures, meshes and the items for maxillofacial surgery [1]. Due to the availability of natural oxide film, titanium materials possess the properties of bioinertness and biocompatibility and cause no allergic reactions and are quickly overgrown with musculoskeletal tissue whose structure remains unchanged throughout the entire life of a patient in the future [2]. The field of application for titanium dioxide films or mixed oxide coatings based on it is not limited by the formation of bioinert and bioactive coatings for surgical implants. Due to the combination of its unique properties, titanium dioxide can be used for the production of insulating films and surface passivating coatings for microelectronic components [3], sensitive elements used by the sensors [4] and also for the units intended for the photocatalytic oxidation of harmful admixtures in water and gaseous media [5].

II. ANALYSIS OF REFERENCES AND THE PROBLEM STATEMENT

Pure titanium is elastic and it has insufficient strength therefore the titanium alloy Ti6Al4V is widely used for the production of mechanically loaded implants. A drawback of titanium alloys is a decrease in the corrosion resistance with an increase in the amount of alloying elements. The undesirable consequence of the implant corrosion is a possibility of the surface destruction that is accompanied by the metal particle coloring and the formation of soluble vanadium and aluminum compounds that exert a toxic effect on the organism and can cause inflammatory processes in the tissues [6]. Natural oxide films have a shallow thickness (5 to 6 nm), therefore in order to impart functional properties to the surface of titanium materials ceramic, phosphate and oxide coatings [7] are formed. Oxide films are formed on titanium using several methods, in particular the method of thermal oxidation and plasma oxidation, combined method of electrochemical and hydrothermal treatment, diffusion and also the method of electrochemical oxidation (anodizing) [8]. The latter method of oxidation is the most widely spread, because it enables the formation of uniform films of a specified thickness and structure on the items of any configuration.

III. OBJECTIVE AND RESEARCH TASKS

The purpose of this research was to study the peculiarities of the behavior of Ti6Al4V alloy under the conditions of anodic polarization in the succinic acid solution. To achieve the set goal we need to solve the following problems:

— establishing the possibility of the formation of oxide films on the Ti6Al4V alloy during the electrochemical oxidation in $C_4H_6O_4$ solutions;

– establishing the influence of the electrolysis mode (acid concentration, current density, final voltage value) on the specific features of the formation of oxide films.

IV. Methods of Experimental Investigations

Oxide films are formed on the surface of titanium alloy Ti6Al4V using the method of electrochemical oxidation in galvanostatic mode and the power supply source B5-49. The final cell voltage was varied in the range of 10 to 100 V. A change in the cell voltage value was recorded during the electrolysis by the multimeter Keithley-2000.

Rectangular alloy specimens of 70x20x5 mm were used for the oxidation. The specimens were polished with the abrasive flap wheel to remove coarse grooves and scratches [9]. Polished specimens were degreased by the aqueous sodium carbonate suspension and flushed with water. Degreased specimens were etched in the HNO_3 and HF (3:1) mixture, and then flushed with the tap water and distilled water.

The glass cup with the volume of 250 ml made of chemically stable glass was used as the cell. To prevent the cell heating during the electrolysis, it was placed in the crystallizer with the volume of 5 l filled with water. The electrolysis was carried out at the electrolyte temperature of 20 °C using the auxiliary lead electrode. The relay operation of the power supply source switching from the direct current operation mode to the direct voltage operation mode signaled the process end. A value of the time interval between the beginning of electrolysis and the relay operation was equal to the oxide film formation length. The oxide film thickness was calculated using the obtained coulometric data. The solutions required for the preliminary specimen treatment and the electrolytes were prepared using distilled water and analytical reagents.

To obtain the points shown in the graphs, 5 parallel experiments were performed. From the obtained values, the average value was deduced, which was given in the figures.

V. Experimental Data

Electrochemical oxidation of the surface of titanium materials can occur either with the formation of the soluble products of anodic reaction or it can result in the formation of oxide layer [10]. 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 oxide structure obtained in the second case is mainly defined by the interaction of electrolyte components with the obtained film. If the oxidation is carried out in the electrolyte of a weak etching action with regard to oxide it will result in the formation of the dense homogeneous TiO_2 layer of a barrier type. In this case, the oxidized surface will acquire the coloring resulting from the light interference at the "metal-air" interface and the film of a certain thickness

will correspond to each color of it. In the case of interaction of the oxide layer with the electrolyte the films with regular or irregular porosity will be formed.

The thickness of the film of a barrier type that was obtained using the method of electrochemical oxidation is defined by the voltage value; the porosity is defined by the type of electrolyte, the electrolysis mode and the alloy composition.

In the case of thin interference-colored oxide films the corrosion is mainly caused by the defects that disintegrate the oxide film. Actually, the corrosion of titanium materials with the oxide coating of an ideal structure should be minimal due to a high ohmic resistance of TiO_2.

From this standpoint, the investigation of the processes of electrochemical oxidation of the titanium alloy Ti6Al4V in the solution of such a weak electrolyte as succinic acid whose first stage dissociation constant is equal to $K_{a1} = 7{,}4 \cdot 10^{-5}$ is of great interest. It should condition a weak etching action of the solution with regard to the oxide film and result in the formation of the oxide layers of a barrier type.

Fig. 1 gives the dependences for the duration of the electrochemical oxidation of the surface of the Ti6Al4V alloy that were obtained for the electrolysis in galvanostatic mode. The values of time intervals τ that correspond to the
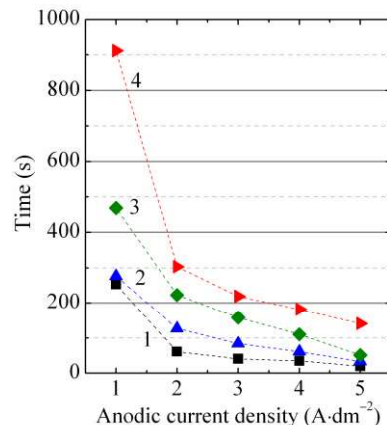

a
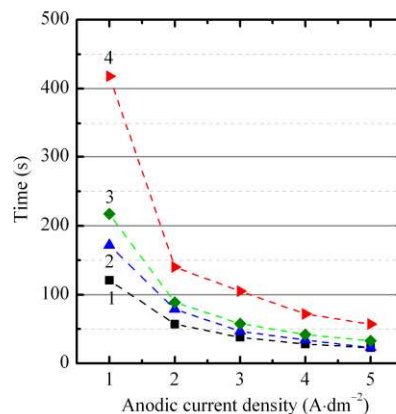
b

Fig. 1. The dependence of the duration of galvanostatic electrolysis for the Ti6Al4V alloy oxydation in succinate electrolytes. c_A, g·l^{-1}: $a - 5$; $b - 50$

time of oxide formation in the stationary mode show a strong dependence of the rate of film formation on the used current density. The obtained relationships can conventionally be subdivided into the two sections.

In the range of j_a = 2–5 A·dm^{-2} the oxide formation rate is directly proportional to the current density value. At lower values of j_a (the first point in Fig. 1) the linear trend of curves is not observed due to the insufficient titanium oxidation current density. A decrease in the electrolysis duration with an increase in j_a is explained by that the electrochemical oxidation reaction rate is increased with an increase in the quantity of current passed through the electrode per unit of time. Since an increase in the current density is conditioned by an increase in the value of electric current, the alloy oxidation rate is increased with an increase in j_a.

Further investigations were carried out to detect the influence of the electrolyte concentration and the cell voltage on the film growth length for the anode oxidation of the alloy surface. The obtained data allowed us to establish that a change in the concentration of $C_4H_6O_4$ in the solution within 5 to 50 g·l^{-1} has no effect on the film growth length (Fig. 2, a). It shows that a change in the concentration of succinic acid has no effect on the electrolyte etching ability.
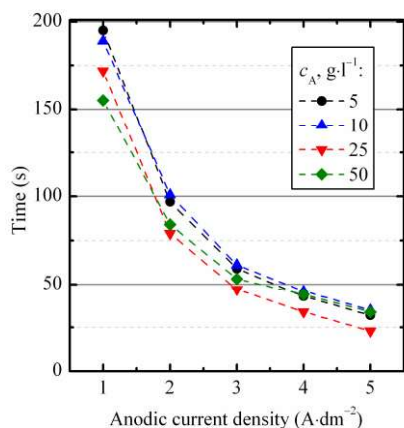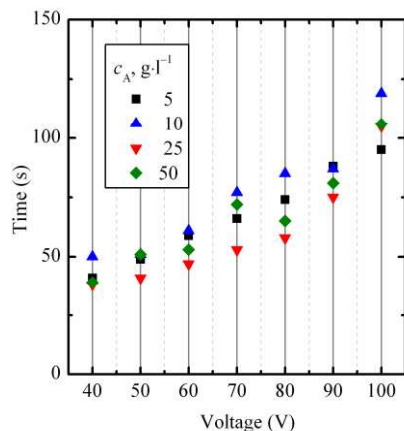
Fig. 3. The surface of specimens made of the Ti6Al4V alloy after their oxidation in galvanostatic mode

A value of the final cell voltage has an essential influence on the oxide layer formation time for the oxidation in the succinate electrolyte.

The data given in Fig. 2, b show that the film formation time is directly proportional to the voltage value and it is explained by the peculiarities of the formation of oxide of a barrier type. In fact, the motive force of the anodizing process is the availability of a high intensity of the electric field in the film during the anode oxidation. An increase in its thickness is stopped as soon as the potential gradient is achieved that fails to provide the motion of ions through oxide. The metal oxidation in galvanostatic mode requires constant field intensity through-thickness of the formed film.

When oxide is formed at j_a = const the film voltage should increase linearly, i.e. we will observe the linear equation of an $x = ay$ type, where x is the film thickness, y is the forming voltage, a is the proportionality factor (the film growth constant). The value of a is changed for titanium in the range of 1.9 to 6.0 nm·V^{-1}. Therefore, the film thickness is only defined by the preset voltage. As the film thickness is increased the potential gradient Δ is gradually decreased and the film formation is stopped as soon as a certain critical value of Δ is achieved that fails to provide the motion of ions in the oxide lattice.

The assumptions of the formation of the films of a barrier type are confirmed by the pictures of the specimens taken after their oxidation (Fig. 3). The anode oxidation results in the formation of interference-colored films on the alloy surface. The film color is defined by the final cell voltage and it is independent of the used current density and the electrolyte concentration and it complies with the Dewald's theory of the electrochemical formation of oxide films of a barrier type.

Coulometric data obtained during the electrolysis enabled the computation of the film thickness (Table 1). The obtained data are indicative of that the thickness of formed films is within 30 to 120 nm and it exceeds 5 to 20 times the thickness of natural oxide layer.

a

b

Fig. 2. The dependence for the galvanic electrolysis time when the Ti6Al4V alloy is oxidized in succinate electrolytes. a − U = 60 V; b − j_a = 3 A·dm^{-2}.

TABLE I.   THE CORRESPONDENCE BETWEEN VALUES OF VOLTAGE, THE FILM THICKNES AND ITS COLOR OBTAINED FOR THE TI6AL4V ALLOY

U, V	δ, μm	Color
40	0.072	light green
50	0.090	yellow
60	0.104	golden
70	0.119	crimson
80	0.151	dark-turquoise
90	0.178	light turquoise
100	0.215	green

The calculation done allowed us to set up a correspondence between the cell voltage value and the oxide thickness and its color that allows us to form easily the wanted film not only to get the appropriate coating but also to use the anodizing for the marking of different items.

Titanium anodic oxidation is typically described by equation $Ti - 4e + 2H_2O \rightarrow TiO_2 + 4H^+$, 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. 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 or nickel in alkaline electrolytes. Another case is the formation of oxide layers during anodic polarization of steels in and copper in alkaline solutions. 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}. 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.

From the standpoint of the electrochemical activity of titanium implants, the data obtained for the formation of oxide films in succinate electrolytes are of interest for the prediction of their corrosion resistance in physiological internal environment. The films of a barrier type are supposed to have an optimal structure. These are characterized by the composition uniformity and minimum porosity [11]. These films are supposed to have good protective properties due to the insulating properties of titanium dioxide that would provide a deep passivation of the implant surface.

VI. CONCLUSIONS

It was shown that the anode polarization of Ti6Al4V alloy in succinate electrolytes results in the formation of thin proportional to the current density in the range of $j_a = 2$–5 A·dm^{-2}. At $j_a < 0.5$ A·dm^{-2}, a continuous oxide film is not formed and the assigned U is not reached. At $j_a > 2.0$ A·dm^{-2}, dependences $U=f(\tau)$ are linear, which indicates the formation of low porosity films. The anodic polarization of the alloy Ti6Al4V in solutions of succinic acid 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 concentration of the electrolyte 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.

REFERENCES

[1] A. M. Khorasani, M. Goldberg, E. H. Doeven, and G. Littlefair, "Titanium in biomedical applications – properties and fabrication: a review", Journal of biomaterials and tissue engineering, vol. 5, pp. 593–619, 2015.

[2] Y. Li, C. Yang, H. Zhao, S. Qu, X. Li, and Y. Li, "New developments of Ti-based alloys for biomedical applications", Materials, vol. 7, pp. 1709–1800, 2014.

[3] D. Rathee, S. K. Arya, and M. Kumar, "Analysis of TiO_2 for microelectronic applications: effect of deposition methods on their electrical properties", Frontiers of Optoelectronics in China, vol. 4, pp. 349–358, 2011.

[4] N. Dwivedi, R. Yeo, H. R. Tan, R. Stangl, A. G. Alberle, C. S. Bhatia, A. Danner, and B. Liao, "Evidence for chemicals intermingling at silicon/titanium oxide (TiO_x) interface and existence of multiple bonding states in monolithic TiO_x, Advanced Functional Materials, vol. 28, p. 1707018, 2017.

[5] M. E. Achhab, and K. Schierbaum, "Gas sensors based on plasma-electrochemically oxidized titanium foils", Journal of sensors and sensor systems, vol. 5, pp. 273–281, 2016.

[6] C. Him, A. Tsang, K. Li, Y. Zeng, W. Zhao, T. Zhang, Y. Zhan, R. Xie, D. Y.C. Leung, and H. Huang, "Titanium oxide based photocatalytic materials development and their role of in the air pollutants degradation: overview and forecast", Environment International, vol. 125, pp. 200–228, 2019.

[7] M. V. Diamanti, S. Codeluppi, A. Cordioli, and M. P. Pedeferri, "Effect of thermal oxidation on titanium oxides' characteristics", Journal of Experimental Nanoscience, vol. 4, pp. 365–372, 2009.

[8] E. T. Sul, E. Byon, and A. Wennerberg, "Surface characteristics of electrochemically oxidized implants and acid-etched implants: surface chemistry, morphology, pore configurations, oxide thickness, crystal structure, and roughness", International journal of oral & maxillofacial implants, vol. 23, pp. 631–640, 2008.

[9] M. Ivashchenko, O. Smirnova, S. Kyselova, S. Avina, A. Sincheskul, and A. Pilipenko, "Establishing the patterns in the formation of films on the alloy Ti6Al4V in carbonic acid solutions", Eastern-European Journal of Enterprise Technologies, vol. 5, pp. 21–26, 2018.

[10] A. Pilipenko, H. Pancheva, V. Deineka, R. Vorozhbiyan, and M. Chyrkina, "Formation of oxide fuels on VT6 alloy in the conditions of anodial polarization in solutions H_2SO_4", Eastern-European Journal of Enterprise Technologies, vol. 3, pp. 33–38, 2018.

[11] H. Pancheva, G. Reznichenko, N. Miroshnichenko, A. Sincheskul, A. Pilipenko, and V. Loboichenko, "Study into the influence of concentration of ions of chlorine and temperature of circulated water on the corrosion carbon steel and cast iron", Eastern-European Journal of Enterprise Technologies, vol. 4, pp. 59–64, 2017.