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THE KINETICS OF Ti-1Al-1Mn ALLOY THERMAL OXIDATION AND CHARCTERISTIC OF OXIDE LAYER

CHARAKTERYSTYKA WARSTW TLENKOWYCH OTRZYMANYCH W PROCESIE TERMICZNEGO UTLENIANIA STOPU Ti-1Al-1Mn

The main goal of the study was to carry out the treatment of cyclic oxidation of Ti alloy (Ti-1Al-1Mn) in air atmosphere. Based on measurements of mass gain of titanium alloy samples (Ti-1Al-1Mn) the kinetic oxidation curves during cyclic annealing were determined. The oxidized surface of the titanium alloy was carefully observed with optical microscopy equipment and the geometrical development, shape and surface morphology were defined. The phase composition of the obtained oxide layers on the Ti-alloy with qualitative analysis of the X-ray were defined. Since titanium alloys are among the most widely used metallic materials in dental prosthetics the corrosion measurements in a solution simulating the environment of the oral cavity were carried out. The results confirmed that the used titanium alloy easily covered with oxides layers, which to some extent inhibit the processes of electrochemical corrosion in artificial saliva solution.

Keywords: Ti-alloy, artificial saliva, kinetic of oxidation, dental alloy

W pracy zaprezentowano wyniki badań nad kinetyką narastania warstw tlenkowych w efekcie cyklicznego termicznego utleniania stopu Ti-1Al-1Mn. Zabiegi utleniania przeprowadzono podczas sześciu 1-godzinnych cykli wygrzewania w atmosferze powietrza. Na podstawie pomiarów przyrostu masy próbek ze stopu tytanu (Ti-1Al-1Mn) wyznaczono krzywe kinetyki utleniania. W pracy przedstawiono również obserwacje mikroskopowe utlenionej powierzchni oraz na podstawie jakościowej analizy rentgenowskiej zidentyfikowano składniki strukturalne, będące produktem utleniania powierzchni. Z uwagi na fakt, że tytan i jego stopy są jednymi z najczęściej stosowanych w protetyce dentystycznej materiałami metalicznymi, przeprowadzono również testy korozyjne w środowisku imitującym warunki panujące w jamie ustnej człowieka. Wyniki potwierdziły, że tytan w podwyższonych temperaturach z łatwością pokrywa się warstwami tlenkowymi, które w pewnym zakresie hamują procesy korozyjne w roztworze sztucznej śliny.

1. Introduction

Among the many prospective biomaterials groups it should be mentioned titanium and its alloys, and due to the fact that the exposure time of titanium in the organism (in the immediate vicinity of tissue) may be longer than 25 years, these materials are classified as long-term biomaterial. Titanium alloy are applied mainly in bone surgery, as a prosthetic implants, rods and joint replacement, components for anastomosis of bone fragments such as screws and bolts. In the other hand the titanium and its alloy are used in cardiac surgery e.g. as mechanical heart valve or any artificial heart components [1-6]. Titanium and its alloy are most commonly used in dentistry, in the dental titanium implants manufacturing. In dentistry both as well as pure titanium and as well as its alloys are applied. Usually, the dentistry implants are prepared with technical titanium, which contains a small amount of additives such as oxygen, nitrogen, carbon and hydrogen but also prepared with titanium alloy, which include additive elements, such as: Al, Sn, Mo, V, Mn, Fe, Cr, which significantly lead to the strength increasing, and the greatest increase in tensile strength has been observed for the alloys containing Mn, Cr, Fe, Mo, and V [6, 9-11].

Considerable popularity of titanium and its alloys (as well as others metallic materials) used in in prosthetics and surgery results from a very high biocompatibility with body fluids and tissues in human body, and as well as corrosion resistance to physiological media (particularly in the case of galvanic corrosion) [7,8]. The electrochemical standard potentials (E) of titanium, are [9]:

$$E = 1.63V(Ti \rightarrow Ti^{2+} + 2e) \quad (1)$$

$$E = 1.23V(Ti \rightarrow Ti^{3+} + 3e) \quad (2)$$

As its results from Eq. 1 and 2 titanium is an active metal, but in practice, by comparing the electrochemical properties and corrosion characteristics with others metals, such as Fe, Cr, Ni, Mo, Ta, Nb and Zr, titanium proved to be the metal is not only resistant to corrosion in many natural environments, but also non-reactive with most of acids [7,9]. High affinity of titanium for oxygen makes that at room temperature on the surface creates a tight titanium oxide layer, a phenomenon

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occurs spontaneously and very rapidly, marked decrease in oxidation rate of the process takes place only with the saturation of the surface in oxygen. And the high corrosion resistance of titanium is explained by spontaneously forming of the oxide film on its surface. The presence of oxide layer significantly reduces the metal contact with corrosive media and in the same way reduces damaging effects environment.

As it is apparent in the equilibrium system [10] at room temperature the oxides do not enriched surface layer of titanium in oxygen. The oxygen solubility in titanium increases at higher temperatures and oxygen progressively diffuses into the material interior and the TiO, TiO_2, Ti_3O_2 oxides are created.

Due to the fact that titanium oxides layers are bioinert, do not show the cytotoxicity, and furthermore, as shown in a number of publications the presence of oxide layers on the titanium implants is conducive to tissue growth, the oxidation treatment is used for most of the components of the implant system (endoprostheses, stabilizers, screws, plates, etc.). There are many techniques of titanium oxidation, but the most important are: anodic oxidation and thermal oxidation [11-14]. However, one of the least complicated processes of high-temperature oxidation treatment is carried out in a ventilated furnaces.

The materials with more and better biocompatibility searching increasingly conducting research to improve the metallic material for biomedical applications. However, the thorough knowledge of both the structure and processes occurring on the titanium surface are very important. The aim of this study was to evaluate the titanium alloy (Al and Mn) oxidation kinetics.

2. Experimental procedure

Increase rate of oxide layer has been studied on the basis of weight gain with respect to the surface of the oxidized samples. Samples were periodically oxidized at 800°C for 6 hours (six of 1-hour cycle). The experiments were made with the use of cyclic thermal oxidation process performed on samples made of Ti-1Al-1Mn alloy (chemical composition of the alloy is shown in Table 1).

TABLE 1

The chemical composition of Ti-1Al-1Mn alloy

Alloy	Chemical composition, % mass.					
	Al	Fe	Cr	Si	Mn	Ti
Ti-1Al-1Mn	0.4÷1.4	0.3	0.3	0.12	0.5÷1.3	rest

The commercial alloy was melted in an induction furnace and casted into molds, giving the cylindrical shape of samples (l = 5 mm, ø = 20 mm (±0.5 mm)). Samples were carefully grinded and polished using abrasive papers of different grit, finishing at 1000. Before the oxidation process samples were degreased with alcohol. The oxidation was carried out in a chamber furnace at 800°C (Fig. 1). The process of annealing was carried out periodically and independently for six Ti-1Al-1Mn samples. All specimens were removed after a predetermined time from the furnace, cooled in the air, weighed, and placed in a furnace chamber, the oxidation time was measured from the time when the thermocouple indicated the temperature of 800°C.

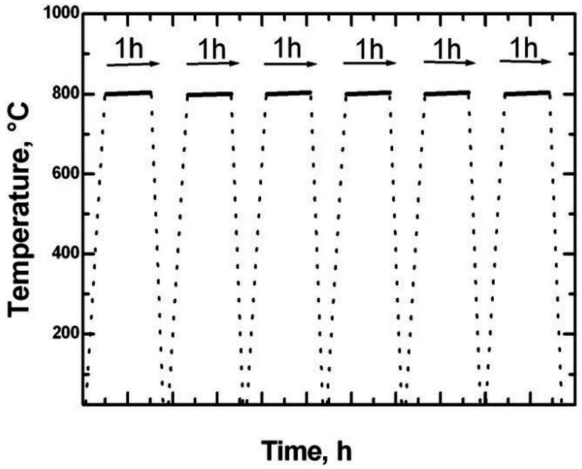

Fig. 1. Scheme of cyclic thermal oxidation of Ti-1Al-1Mn alloy

The oxidation process and the oxide layers characteristic has been evaluated according to:

i. The oxide phases on the Ti-1Al-1Mn alloy surface identification with X-ray diffraction (XRD 3003 T of the Seifert). The analysis was carried out based on the database of crystallographic phases DHN - PDS (X Powder Diffraction System). The parameters of the process:
   - wavelength KαCo = 0.179 nm,
   - voltage – 40kV
   - current intensity – 30mA
   - the range of diffraction angles 2θ = 20 to 90°
   - the angle step of 0.2°
   - time t = 3s

ii. The potentiokinetic polarization curves measured in solution simulating oral cavity (artificial saliva) with the composition:
   - NaCl - 0.7 g/cm^3
   - KCl - 1.2 g/cm^3
   - Na_2HPO_4 - 0.28 g/cm^3
   - $NaHCO_3$ - 1.5 g/cm^3
   - KSCN - 0.33 g/cm^3
   - urea - 1.3 g/cm^3

The examinations were carried out in a typical tri-electrode electrochemical measuring system connected to the electrochemical measurement station AutoLab. An essential element of the measuring system was electrochemical container in which the test samples were placed and the tested area was 0.2 cm^2. Potentiokinetic tests have been carried out in temperature of 37°C and the disk, with potential change from cathodic to anodic direction, ranging from -1.5V to +3.0V with a scan rate of 10 mV·s^{-1}. All potentials are expressed vs. Ag/AgCl auxiliary electrode.

3. Results and discussion

Based on measurements of weight change of the Ti-1Al-1Mn samples subjected to cyclic thermal oxidation (oxidation temperature of 800°C) kinetic curves for six independent measurements were determined. In Fig. 2 the aver-

age result of Ti-1Al-1Mn alloy oxidation kinetic curve with a standard deviation is presented.

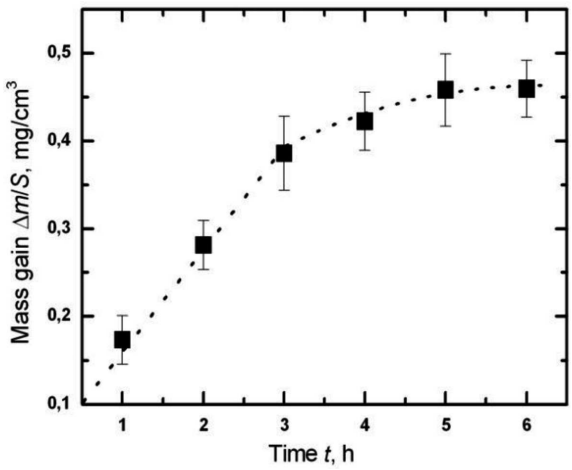

Fig. 2. The Ti-1Al-1Mn alloy oxidation kinetic curve (oxidation temperature 800°C)

As it is shown in Fig. 2 the greatest weight gain occurred during the first three cycles of oxidation, the curve in this rage is a close to linear. The slopes of straight lines are the measure of oxidation rate, after the fourth of 1-hour cycle clearly slowing down of the mass gain and oxidation process respectively can be seen. Probably this is due to limited access reactant (oxygen) to the metal surface.

With the assumption of titanium oxidation thermodynamics in the first hours of annealing can be expected oxidation process according to the scheme [10]:

$$Ti + O \rightarrow Ti(O) \rightarrow Ti_6O \rightarrow Ti_3O \rightarrow Ti_2O \rightarrow Ti_3O_2 \rightarrow TiO \rightarrow Ti_2O_3 \rightarrow TiO_2 \quad (3)$$

According to the literature for short-term oxidation (pure Ti) at 800°C the oxide coating consists the structure of rutile TiO_2 (anatase less) and metal is enriched with oxygen. With longer times of oxidation and at higher temperatures than 800°C also appear oxide phase TiO and Ti_2O_3. Based on peak intensities matching to the patterns crystallographic phases on the base DHN – PDS (X Powder Diffraction System) was obtained. The diffraction analysis of the sample surface Ti-1Al-1Mn alloy after 6-hour oxidation in the furnace chamber on Fig. 3 is presented.

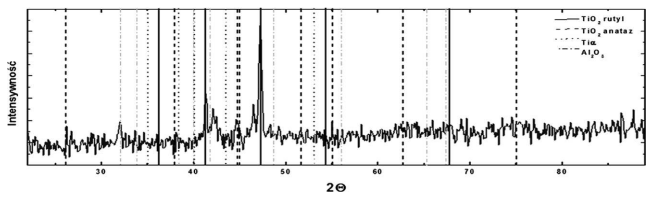

Fig. 3. X-ray pattern obtained for the oxidized surface of Ti-1Al-1Mn alloy

According to the assumption of X-ray phase analysis showed that the oxide layer covering the surface of the alloy is mainly composed of TiO_2 in the rutile variant. On the basis of the intensity of the peaks was also found that the TiO_2 oxide layer is also in a variation of anatase as well as a small amount of aluminum oxide Al_2O_3, which results from the alloy composition. It can be assumed that the metal surface was tightly covered with a layer of oxides, because on the diffraction pattern is not observed the presence of a phase Tiα, or other identifiable phases in the alloy Ti-1Al-1Mn.

The microscopic observation has shown that the shorter oxidation time alloy initially covered with light yellow blue or purple color coating. After 4-hour oxidation oxide layer is colored in dark gray and progressively covers the entire surface. For longer times, on the gray oxidation layer the white areas are visible (probably TiO_2 – rutile) and the layer begins to lose continuity.

Longer annealing process give the ability to create a porous oxide film with color from light yellow to yellow-brown with poor adhesion to the substrate. It can therefore be concluded that the shorter oxidation of titanium alloy promotes the formation of uniform, evenly spaced oxide layers. After 6 hours of oxidation, on the surface layer appeared characteristic white color oxide *islands*. Based on the observed locations expand the topography can be seen that in areas covered by a white area oxide, the layer loses its adhesion to the substrate, and begins to ”peel” (Fig. 4 and 5).

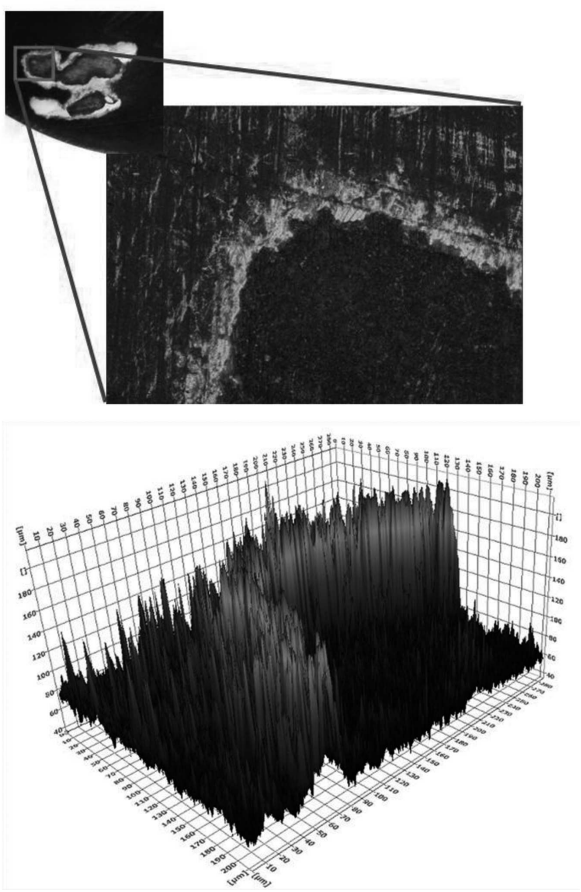

Fig. 4. The image of the Ti-1Al-1Mn alloy surface after 6 hours of oxidation (a), the surface topography of the selected area (b)

To verify the effectiveness of the heat treatment and surface oxidation the electrochemical tests in solution simulating the mouth environment were carried out. In Fig. 6 the potentiokinetic curves determined for the polished and covered with a oxides layer in artificial saliva solution are presented.

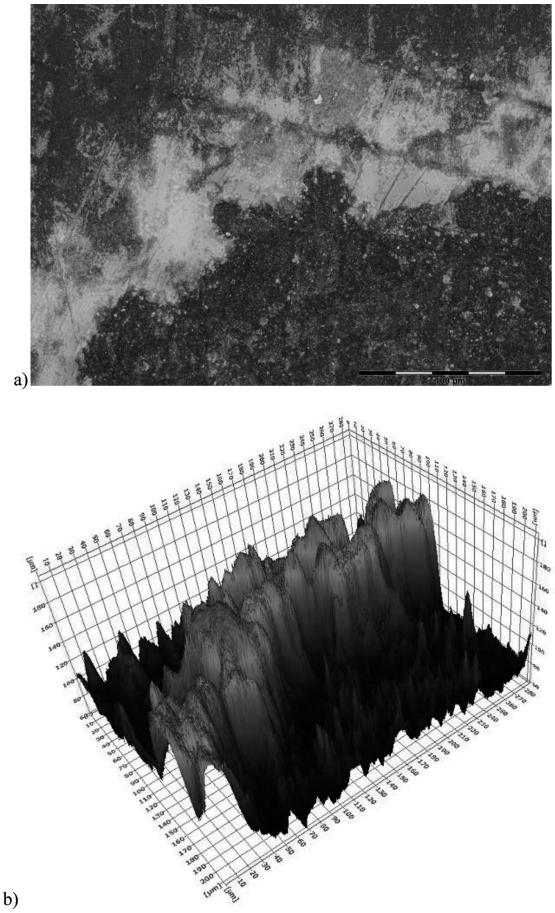

Fig. 5. The image of the Ti-1Al-1Mn alloy surface after 6 hours of oxidation (a), the surface topography (b)

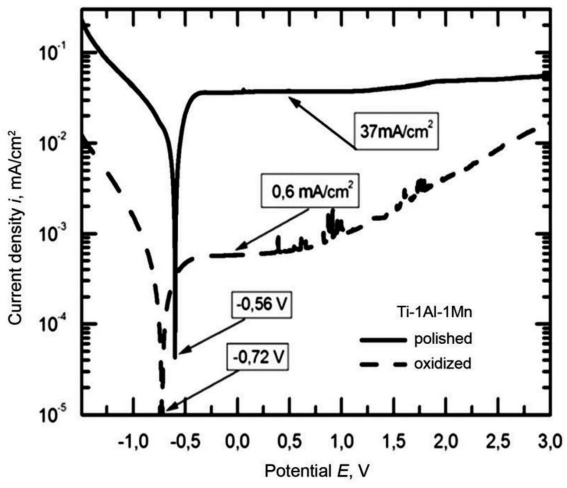

Fig. 6. Potentiokinetic polarization curves of Ti-1Al-Mn alloy. Experimental conditions: artificial saliva solution, potential scan rate 10 mV s^{-1}, temperature 37°C

Applied oxidizing heat treatment had a positive impact on the polarization characteristics of the tested titanium alloy. As can be seen (Fig. 6) surface oxidation caused corrosion potential displacement toward negative values (which may be the result of lack of integrity of the oxide layer) and for polished Ti-1Mn-1Al alloy E_{corr} value is -0.56 V, while for the alloy with oxidized surface E_{corr} value is -0.72V. The most important is the fact that the current density in the passive range have been reduced by an order of magnitude of 37μA/cm^2 to 0.6 μA/cm^2.

4. Conclusions

The Ti-1Al-1Mn alloy during oxidation process at 800°C in air atmosphere easily cover with oxide layers. Layer of oxides, which is the dominant TiO_2 – rutile, also the presence of TiO_2 – anatase, and Al_2O_3 found. Based on the oxidation kinetics curves, it can be concluded that the process occurs quickly during the first three hours of oxidation. However, 6-cyclic oxidation at 800°C in air atmosphere improves the corrosion resistance of the Ti-1Al-1Mn alloy reduce the corrosion current density in the passive range.

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