

Characterization of TiO_2 films obtained by electrochemical plasma treatment of titanium

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Received May 11, 2010

The structure and the properties of the oxide films formed on Ti by means of electrochemical plasma treatment at application of varied interelectrode potential in the specially selected electrolytes have been studied. The chemical and phase composition as well as the topography, the microstructure and the grain size of the formed layers depend on the applied voltage. The formed films increase the resistance of Ti to corrosion in the alkaline and in the Ringer solution.

Исследована структура и свойства оксидных пленок, полученных на Ti с помощью электрохимического плазменного метода с применением изменяемого межэлектродного потенциала в соответственно подобранных электролитах. Химический и фазовый состав, а также топография, микроструктура и размер зерна сформированных слоев зависят от приложенного напряжения. Рассмотрено влияние сформированных пленок на коррозионную стойкость Ti.

1. Introduction

The most important characterictics of materials for bone implants include the good chemical compatibility with the bones enabling the deposition of cells and the growth of tissue on the implant surface and the mechanical properties as close to those of bones as possible, ensuring the similar behavior of implant and bone under a stress. It is common knowledge, the titanium and its alloys are the most promising biomaterials for producing of the implants [1]. In order to promote the growth of bone tissue, the bioceramic layers are formed on titanium surface. For this purpose, surface treatments to modify the chemical composition, roughness and porosity of the implant surface have been applied [2]. The formation of different oxide layers has been achieved by the anodic oxidation, laser and plasma surface treatment and spark discharge [3, 4]. The anodic oxidation in the sparkling regime (microarc anodic oxidation — MAO) seems to be a very promising technique to form a ceramic coating on the Ti surface since it does not need any sophisticated facilities, allows to form various types of Ti oxides [5, 6] and to incorporate different species into the layer by modification of electrolysis regime [6] and of electrolyte nature [5]. Calcium and phosphate can be precipitated on oxide films in an electrolyte containing Ca and P elements. During the MAO process, sparks appear and move rapidly across the treated surface, and the temperature and pressure inside a discharge channel can reach 10^3–10^4 K and 10^2–10^3 MPa, respectively, which are sufficiently high to induce a thermochemical interaction between the substrate and electrolyte [7]. Therefore, the oxide films are composed of substrate materials, oxide and electrolyte materials.

In this work, some results concerning the chemical and phase composition, topography and corrosion resistance of the titanium oxide layers formed by microarc treatment are presented.

2. Materials and experimental procedure

Titanium sheets of technical purity with the total content of impurities (Fe, Si, Al, Mn) lower than 1 wt. % were subjected to the microarc oxidation. Before the treatment, Ti anode was polished, degreased, etched in $HF + HNO_3$ mixture, washed in distilled water and dried, then placed into the electrochemical cell (200 ml volume) at constant oxidation temperature (293–300 K). In order to avoid of the metal substrate deterioration by the effect of microarc, a special oxidation procedure was applied [8, 9]. The electrode was polarized galvanostatically by increased current up to the sparkling regime and then polarized by constant interelectrode voltage (from 100 to 130 V) for 30 min. The process was carried out in the alkaline polyphosphate solution [8]. The surface of the anodized samples was observed in a Hitachi S 4200 scanning electron microscope at magnification up to 10,000X with attached ESEM-50 Philips EDS analyzer. The energy dispersion analysis was done. The Callotte tests [10] were done by rotating a 30 mm bearing steel ball against the studied surface for up to 24 h. The thickness of the modified surface layer was calculated from the diameters of formed rings at an error of ±5 %. The X-ray diffraction spectra were recorded by a Siemens D5000 diffractometer using CuK_α radiation. The obtained spectra were analyzed using the JCPDS PDF-2/2001 database [11].

The susceptibility to corrosion was checked in non-deaerated 2 M NaOH and Ringer (8.6 g/l NaCl, 0.3 g/l KCl, 0.48 g/l $CaCl_2$) solutions by comparing the values of open circuit potentials (E_{ocp}).

3. Results and discussion

As is seen in Fig. 1, the layer formed by microarc treatment includes large rounded grains with holes (doughnut-like) and the mixture of the fine acicular grains. Sometimes, the holes are filled with small grains. Such a rounded grains provide the good sliding ability of the surface that is important for hip joints. As follows from Fig. 2, the interelectrode voltage affects strongly the surface layer structure. As is seen, the maximum size of doughnut-like grains decreases with the increasing voltage (Fig. 2a), but the layer thickness increases with interelectrode voltage up to about 125 V (Fig. 2b).

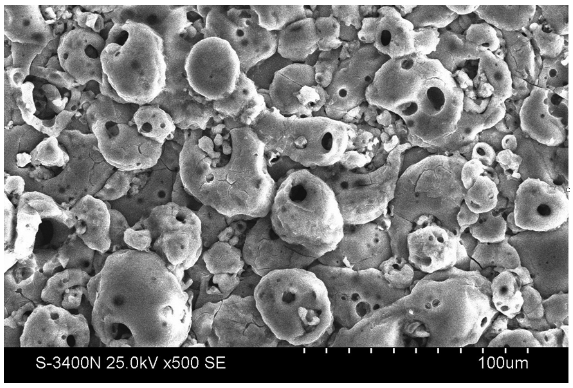

Fig. 1. Scanning electron image of microarc treated surface of Ti (100 V).

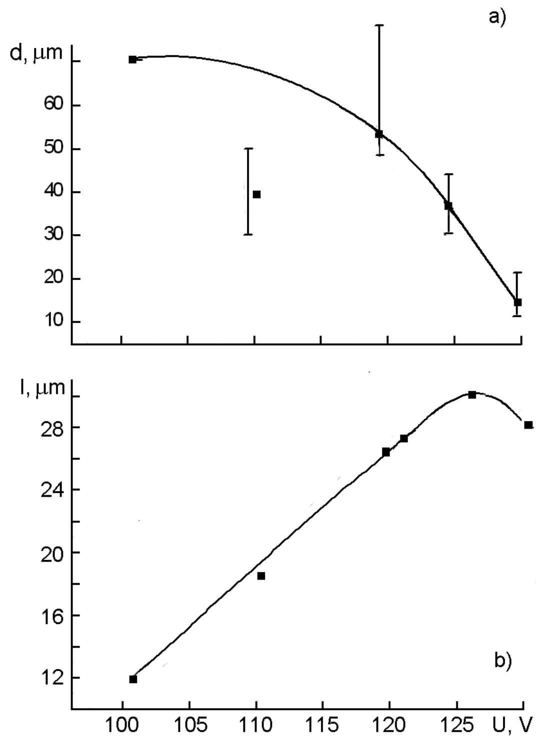

Fig. 2. Effect of voltage on grain size and thickness of formed oxide layers.

As follows from the EDS results (Fig. 3a), the X-ray characteristic spectrum taken from the surface (Fig. 1) reveals the presence of other elements beside Ti and O in the layer. The atomic content of P, K evaluated from the obtained spectra not taking into account the presence of O, H and B are shown in Fig. 3b. It is seen that with increasing voltage the amount of P increase, whereas the amount of K decreases. It should be noted that in the case of anodic oxidation in H_3PO_4, the amount of P reached about 10 at % [12]. It is to note that the analysis of the X-ray spectra

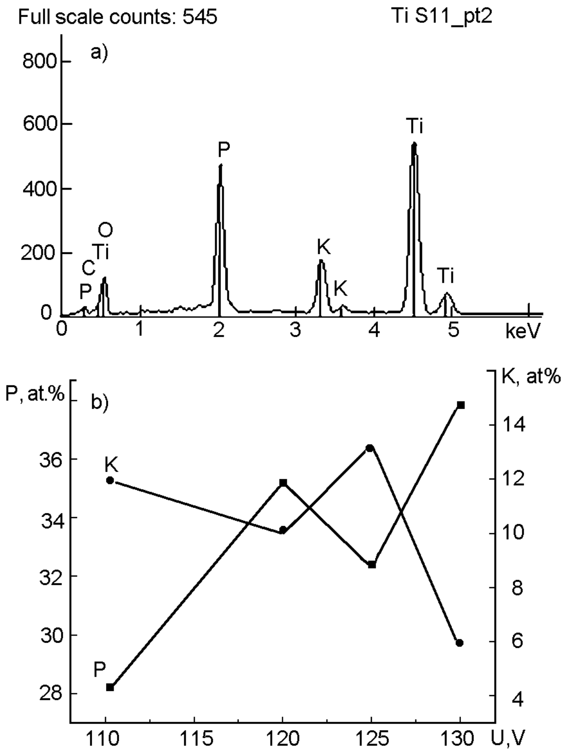

Fig. 3. a) X-ray spectrum taken from the microarc treated surface of Ti (100 V). b) Effect of voltage on P and K content in the surface layer.

obtained by the routine procedure shows the presence of different kinds of titanium oxide and titanium phosphate, depending on the applied interelectrode voltage: Ti_3O and TiO_2 at 110 V, Ti_3O, Ti_6O oxides and $Ti(HPO_4)_2xnH_2$ at 125–130 V. The presence of TiO_6 and TiO_3 is due to oxygen ordering in the hexagonal α-Ti and can be explained by oxygen diffusion in the α-Ti initial lattice. In [13], it has been shown that the higher the accumulated laser fluence is, the higher is the oxidation degree, i.e. at a high oxygen diffusion, samples will trap more oxygen in the melted phase.

At breaking, the obtained oxide layer exhibited the ductile fracture and the good adhesion to the substrate (Fig. 4) regardless of the applied interelectrode voltage. This provides no splinters to be chipped off from implant.

The results of the electrochemical measurements done in the 2 M NaOH and Ringer solutions are presented in Table. It is seen that the microarc oxidation increases substantially the corrosion resistance, as follows from the shift of the open circuit potential (E_{ocp}) into the anodic direction. The lowest corrosion resistivity in both solutions

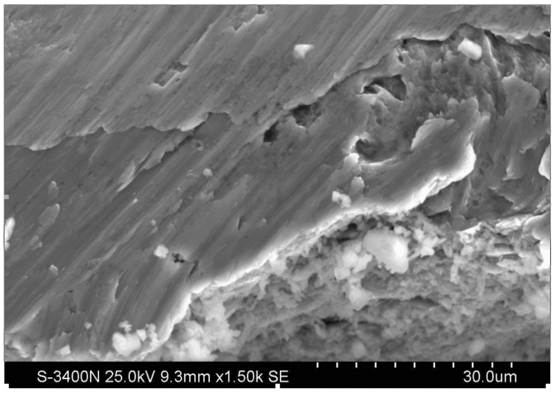

Fig. 4. Fracture surface of oxide layer.

Table. Open circuit potential values (E_{ocp}) of obtained oxide layers

Interelectrode voltage, V	E_{ocp}, mV 2 M NaOH	E_{ocp}, mV Ringer solution
0	−600	−410
110	+380	+58
120	+570	+900
125	+425	+510
130	+405	+120

reveal oxide layers formed at 110 V. Some conclusions may be drawn from the comparison of the obtained electrochemical results with the topography of the formed surface layers. In the case of oxide layers formed at 120 V, the highest anodic value of the open circuit potential may be associated with the close packed doughnut-like grains filled with the small grains. The lowest corrosion resistance of oxide layer formed at 110 V may be associated with the cracking of the formed layer which promotes the penetration of electrolyte to the substrate. In the case of artificial hip joint, the crucial parameters are the good sliding ability and the preventing of falling-off the chips which is provided by the low surface roughness. In all the cases, no splinters of the implant should be chipped off. The doughnut-like, compact structure of oxide layer, especially formed at 120 V, may accommodate the above demands.

4. Conclusions

The oxide layers (up to 30 μm) containing the alloying elements (P, K) can be formed on Ti by means of the anodic polarization in the spark-discharge regime (interelectrode voltage 100 to 130 V). The chemical and phase composition, the topography, the grain size of the formed layers can be adjusted by varying the applied voltage. All the oxide layers formed by microarc technique increase substantially the corrosion resistance of Ti in the alkaline and in the Ringer solutions. The obtained non brittle oxide layers of good adhesion are promising for bio-applications of various demands.

Acknowledgement. This work has been supported by the Polish Committee for Scientific Research under grant KBN 3 T08A 006 26. The authors thank all of participants of the grant.

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Характеризація плівок TiO_2, отриманих електрохімічною плазмовою обробкою титану

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Досліджено структуру та властивості оксидних плівок, сформованих на Ti за допомогою електрохімічного плазмового методу з застосуванням змінного міжелектродного потенціалу у відповідно підібраних електролітах. Хімічний та фазовий склад, а також топографія, мікроструктура та розмір зерна сформованих шарів залежать від напругиб що застосовано. Розглянуто вплив сформованих плівок на корозійний опір Ti.