CORROSION PROPERTIES OF ANODIZED TITANIUM

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Abstract
In this paper corrosion properties and microstructure features of amorphous self-organised TiO_2 nanotubes electrochemically deposited on titanium are discussed. There was titanium of second grade used as a substrate for these experiments. There was a specific solution of ammonium fluoride, ethylenglycol and deionized water used to create an oxide layer with advantageous properties. Relation between changes of roughness indexes before and after anodization was found out. The wettability (contact angle) of artificial plasma on surface was measured using sessile drop method. It was found out that titanium dioxide nanotubes formed on the surface significantly decreases contact angle and time of anodization reduces it even more. Corrosion potentials, corrosion rate or polarization resistance were determined by linear polarization methods performed by ASTM standards. Corrosion potential of anodized samples is substantially more positive (≈ -50mV) compared with non-treated sample (≈ - 280mV). On the other hand polarization resistance was significantly higher for non-treated sample. Also potentials of passive layer breakdowns were found. Structure of nanotubes and influence of anodization on surface profile was studied by SEM.

Keywords: Anodization, corrosion, coating, titanium dioxide

1 Introduction

First experiments with titanium as a material for implants are dated to 1952, when Swedish surgeon placed titian screw into the rabbit's bone and the healing process of surrounded tissue had been studied. After several months, when the healing process was finished, the implant should be removed. This task seemed nearly impossible as the screw was fully integrated into surrounding bone tissue. This phenomenon was named osseointegration and has been studying for more than 60 years. Titanium alloys have become one of most preferred materials for long term implants manufacturing since then. Osseointegration process of Ti implants is connected to titanium dioxide layer created spontaneously on surface of material. Titanium is known for its corrosion resistance which is basically caused by passive oxide layer created on the surface [1-4]. TiO_2 layer created artificially on surface also protects underlying substrate from corrosion even more by intensification of barrier effect [5]. Thick layer of non-conductive oxide behaves like capacitor and conductor if connected into circuit of alternating current. This research is

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aimed to finding relation between parameters of anodization and resulting properties of formed layers on surfaces of Ti substrate. Corrosion and wettability test together with EIS (electrochemical impedance spectroscopy) method allow to evaluate the biocompatibility of studied surfaces. Commercially pure titanium grade 2 with electrochemically treated surface was chosen for this research. This material is abundantly used for tooth implants manufacturing and simulates real implants parameters effectively [3-6].

2 Experimental materials and methods

2.1 Substrate and its preparation

For this experiment titanium rods 12.7 mm in diameter from Bibus Metals Company were used. There were 6 samples prepared for this experiment. Five of them was used for anodization, the sixth was used as reference one. Microstructure of tested material is illustrated in **Fig. 1**.

2.2 Fabrication of TiO_2 nanotubes, corrosion and technological properties tests

Anodization is an electrochemical process used to create specific oxide or oxide-based layers on the substrate. Two electrode cell with 250 ml volume was used for anodization in this experiment, where sample was connected to anode and perforated platinum coated Tisheet was used as cathode. Solution of distilled water, ammonium fluoride (0.2mol/l, purity >99.5%) and nitric acid (0.1mol/l) was prepared and later mixed with ethylenglycol in weight ration 10:90 (90% for E-Glycol), all chemicals were supplied by VWR International. Stable voltage of 30V was generated by DC laboratory power source Matrix MPS-3005D during anodization. Ration of solution volume and exposed surface of each sample was approx. 10ml/mm^2. Each sample was anodized for different time (30, 60, 90, 120, 150 minutes).Structure, topography and morphology of samples surfaces were studied by scanning electron microscope JEOL JSM-6490. Roughness measurement was performed using Taylor Hobson Talysurf 50. Contact angle between surface and artificial blood plasma was found out using DropSnake and LB-ADSA methods of ImageJ software [7, 8]. For corrosion testing solution of artificial blood plasma was used. All corrosion measurements were performed according to ASTM F 2129 with scan rate 1.0 mV/s. Main equipment used for this experiment was potentiostatVoltalab PGZ 100 and software Voltamaster 10. Saturated calomel electrode (SCE) served as a reference electrode. Firstly, open circuit potential was measured. During next step pitting or crevice corrosion was initiated and tested by potentiodynamic polarizing.

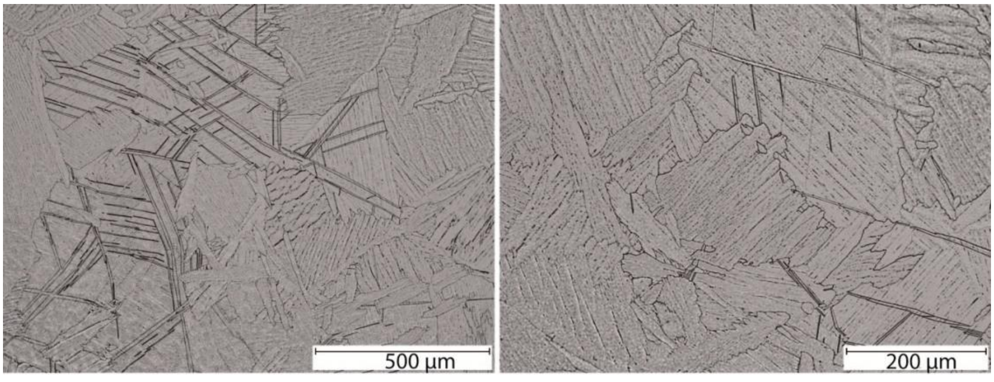

Fig. 1 Microstructure of tested material

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3 Results

Nanotubes formation process is illustrated in **Fig. 2** step by step where (A) shows Ti substrate after polishing. **Fig. 2(B)** illustrates substrate spontaneously covered by thin layer of TiO_2, **Fig. 2(C)** shows chemical dissolution of titanium dioxide layer in solution containing fluoride ions. **Fig. 2 (D)** shows self-organised nanotubes on surface of titanium substrate after anodization [9-13].

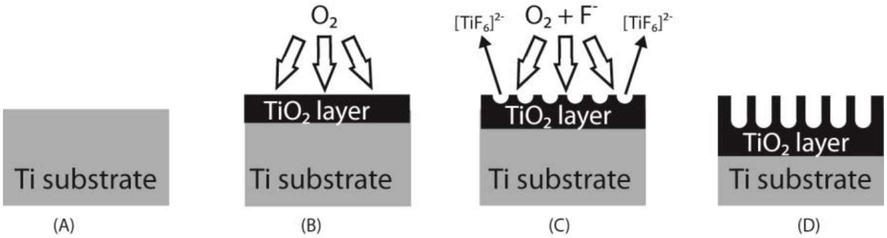

Fig. 2 Nanotubes formation process, (A) pure substrate, (B) passivated surface, (C) anodization process, (D) surface covered by oxide nanotubes

Surface structure after 150 minutes of anodization is shown in **Fig. 3**. There are TiO_2 nanotube ends clearly visible on the surface of substrate. Diameter of nanotubes and wall thickness is primary determinated by applied voltage and composition of solution. Surface without protrusions is needed for most of implants to make their implantation as easy as possible and without any additional tissue damage [12, 13].

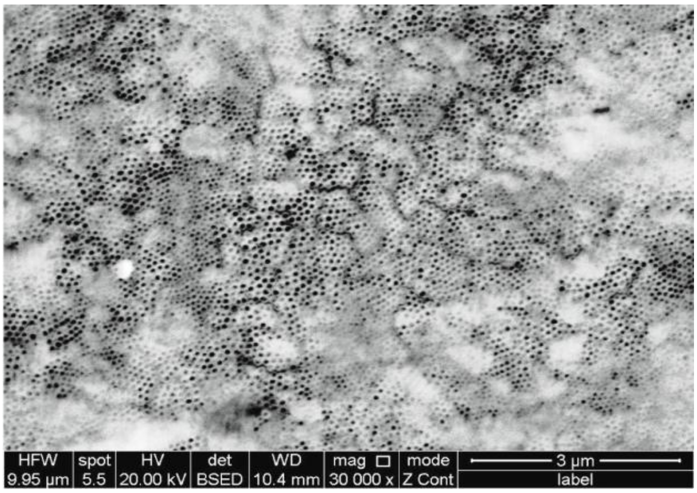

Fig. 3 Surface structure after anodization

Three measurements of roughness were done for each sample and values were averaged. Relation between time of anodization and difference of R_z roughness index values is shown in **Fig. 4**. It was found that surface roughness decrease with longer time of anodization. It is probably caused by the fact, that current density is much higher around local protrusions so these are dissolved preferably during the process.

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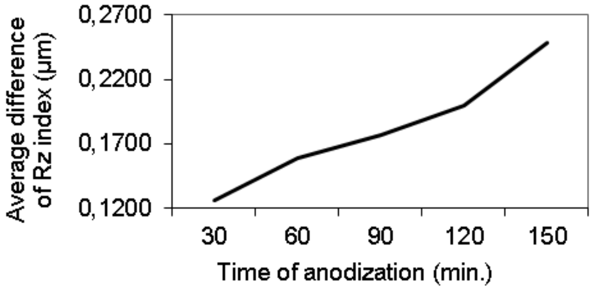

Fig. 4 Roughness R_z index for different anodization time

Wettability of surface is closely connected to process of osseointegration-the contact angle (θ) of body fluids determinates mechanism of healing process [14].Measured values are compared in **Table 1**.

Table 1 Contact angle of artificial blood plasma and anodized surface

SAMPLE anodizing time [min]	**"Drop snake" method**		**LB-ADSA method**	
	Average value **θ**[°]	Deviation **θ** [°]	Average value**θ**[°]	Deviation **θ** [°]
30	35	2	35	2
60	33	1	32	2
90	31	2	31	1
120	30	2	29	2
150	28	1	28	1
REF (0)	67	1	66	2

The differences of contact angles for anodized and unanodized samples are very significant and testify for suitability of the particular treatment. It was confirmed that lower contact angle between implant and body fluid makes healing process faster. The wettability effect of surface is illustrated on **Fig. 5**, where (A) shows droplet on unanodized surface and (B) after 150 min. of anodization.

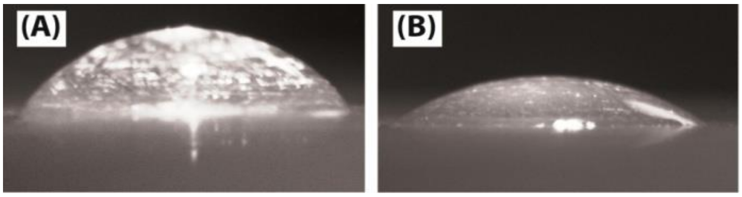

Fig. 5 Effect of artificial blood plasma wettability of surface before (A) and after (B) anodization

Results from OCP (open circuit potential) measurement and basic corrosion properties found out by potentiodynamic polarization method are listed in **Table 2** (corrosion rate was calculated using Faraday's law of electrolysis). Corrosion rate of tested samples decreases with longer time of anodization. OCP method was used after 1hour samples immersion in solution.

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Potentiodynamic polarization was performed for each sample to find corrosion rate and polarization resistance values [15-20].

Table 2 Corrosion parameters found out by OCPand potentiodynamic polarization method

Sample anodizing time [min]	**OCP vs. SCE [mV]**	**E_{corr} vs. SCE [mV]**	**Corrosion rate [µm/year]**	**Polarization resistance R_p[kΩ.cm^2]**
		Taffel method	Taffel method	Taffel method
30	-59	-50	8,88	44,1
60	-75	-79	7,92	47,5
90	-113	-133	5,18	55,9
120	-198	-209	2,59	171
150	-213	-231	2,55	167
REF	-280	-285	1,40	129

4 Conclusions

Anodization process of samples from commercially pure titanium grade 2 was performed in solution of ammonium fluoride, distilled water, ethylene-glycol and nitric acid. There was influence of anodization time on surface roughness found out. It was observed that surface with lower roughness is produces by this process. The roughness decreases with longer times of anodization. Wettability of surface by artificial blood plasma before and after anodization was inspected and significant difference between contact angle θ (67° before vs. 28° after 150 minute of anodization) was determined. It was proved, that lower contact angle between implant and body environment makes the osseointegration and healing process faster. Relation between time of anodization and corrosion potential was studied and it was proved that increasing the time of anodization causes lower nobility of layer (-50 mV for 30min vs. -231mV for 150 min. of anodization). It was also proved by potentiodynamic polarization method that longer times of anodization cause decrease of corrosion rate approx. three times (from 8.88 µm/year for 30 minutes to 2.55 µm/year for 150 minutes of anodization).

References

[1] P. I. Branemark, U. Breine, B. Johansson: Acta Anatomica, Vol. 1, 1964, p. 5
[2] R. B Osman, M. V. Swain: Materials, Vol. 8, 2015, p. 932-958
[3] B. Johansson, C. H. Han, A. Wennerberg, T. Albrektsson: Oral Maxillofacial, Vol. 13, 1998, p. 315-321
[4] C. N. E. Email, J. H. C. Lima, R. Valiev: Biological Materials, Vol. 60, 2008, p. 46-49
[5] W. H. Lee, C.W. Lai, S.B.A Hamid: Materials, Vol. 8, 2015, p. 2139-2153
[6] R. K. Alla, K. Ginjupali, N. Upadhy: Reviews on Advanced Materials Science, Vol. 25, 2011, p. 112-118
[7] M. F. Rashid, M. R. Lani: Surface Roughness Prediction for CNC Milling process using Artificial Neural Network, In.: World Congress on Engineering, London, UK, 2010
[8] ISO10993-9:2009Biological evaluation of medical devices, Part 9:Framework for identification and quantification of potential degradation products, ed. 2, ISO/TC 194, Berlin, 2009, p. 9
[9] E. Cominim, C. Barato: Sensors and Actuators, Vol. 19, 2013, p. 559-567

DOI 10.12776/ams.v23i3.982 p-ISSN 1335-1532
e-ISSN 1338-1156

[10] K. Gayo, J. Kohout, M. Senator, T. Sramko: General and inorganic chemistry, first ed., ALFA, Bratislava, 1974, (in Slovak)
[11] P. Roy, S. Serger, P. Schmuki: Angewandte Chemie, Vol. 13, 2011, p. 2904 – 2939
[12] L. Gaviria, J. Salcido, T. Guda: Journal of Korean Assoc. for Oral Maxillofacial Surgery, Vol. 50, 2014, p. 50-60
[13] T. Kuboto, S. Yamaguchi: Materials, Vol. 3, 2009, p. 48-63
[14] T. Mekayarajjananonth, S. Wikler: Journal of Oral Implantology, Vol. 25, 1999, p. 230-236
[15] J. Szewczenko, W. Walke1, K. Nowińska, J. Marciniak: Materialwissenschaft und Werkstofftechnik, Vol. 41, 2010,p. 360-371
[16] M. Kaczmarek, K. Jurczyk: Materials Science, Vol. 51, 2016, p.5257-5279
[17] T. Hanawa: Science and Technology of Advanced Materials, 2002, Vol. 3, p. 289-295
[18] T. Kokubo, H. Takadama: Biomaterials, Vol. 27, 2006, p. 2907–2915
[19] Q. Chen, G. A. Thouas: Materials Science, Vol. 87, 2015, p. 1–57.
[20] J. B. Park, R. S. Lakes: Biomaterials: An Introduction, third ed., Springer-Verlag, New York, 2007, DOI:10.1007/978-0-387-37880-0

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