STRUCTURE AND CORROSION PROPERTIES OF ELECTROCHEMICALLY TREATED SURFACE OF 1.4301 (AISI 304) STEEL FOR MEDICAL APPLICATIONS

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Abstract

1.4301 steel as a basic stainless material used for undemanding applications is studied in this paper. Some of surgical instruments as well as other medical devices are manufactured from this material so its biocompatibility and corrosion resistance must be guaranteed. Electrochemical properties of this steel are closely connected to oxidic layers created on surface of material, so these properties can be improved by modification of the layer. This paper is basically focused on anodization process of substrate to gain enhanced corrosion properties. The structure of substrate was studied before and after anodization by light and electron microscopy, for basic chemical analysis of structural components of substrate before anodization and structure of created layers on surface EDX analysis was used. Relation between wettability of surface and parameters of anodization was studied. Electrochemical behaviour of anodized materials was tested in Tyrode's solution. Open circuit potentials were found, corrosion potentials, polarization resistances or corrosion rates were determined by Tafel and Stern methods. Potentials of depassition and repassivation were measured by potentiodynamic polarization method. Electrochemical impedance spectroscopy was used for even closer description of physical characteristics of layer deposited during the anodization. For this equivalent electric circuit was found and parameters like resistance and capacitance of the layer were specified. Process of anodization is partially similar to electrochemical etching, so the relation between parameters of anodization and surface profile are also studied in this paper.

Keywords: Stainless steel, electrochemical corrosion, polarization methods, biocompatibility, EIS method

1. INTRODUCTION

Metallic materials are still the most common materials used in fields like surgery, implantology and other specific medical disciplines. Commercial pure titanium of different grades or its alloys (Ti6Al4V, Ti6Al7Nb) have become very popular for long term applications during last three decades [1]. Although stainless steels are still the most often used material in medicine. Main aspect of material selection in medicinal fields is its biocompatibility and corrosion resistance. Different medical applications require different level of corrosion resistance in different environments. Applications for body implantation purposes have to be resistant to body environment with different pH, which contains chloride ions, organic and inorganic salts, etc. For other applications like medical tools and instruments high level of disinfection solution resistance is expected among others [2].

Austenitic stainless steel EN 1.4301 (AISI 304, X5CrNi18-10) has favourable ratio of material properties, corrosion resistance and price for unit. It is used for less stressed parts of medical devices or other medical equipment like hospital beds constructions or infusion stands. These parts are usually manufactured by CNC machining so their surfaces bears machining traces from cutting tool. The grooves and other defects have to be mechanically removed during product finishing [3].

Anodization is a way how to create a layer of specific oxides on surface of metallic materials. During this process a sample is placed into an anodization solution and connected to positive pole of electric circle. During anodization, local surface defects like shallow scratches and grooves are dissolved as a reason of higher current density. Uniform surface without defects make disinfection process more effective and help to prevent

bacterial colonies growth. Adhesion of bacteria on surface of material affects the risk of formation of bacterial colonies as well. Batteries are mostly transferred by fluids (in droplets) or by direct contact, so the wettability of surface is important factor too. Contact angle can be affected by parameters of anodization [4].

This paper is aimed to finding relation between parameters of anodization and corrosion properties, wettability and change of surface roughness.

2. MATERIALS AND METHODS

2.1. Material and its characteristics

Stainless steel X5CrNi18-10 was chosen for this particular research. Rods 10mm in diameter from Fegip Materialy a. s. were used for sample preparation. Chemical composition and mechanical properties for this grade of steel are standardized in ISO 15510 [5] and EN ISO 377 [6]. Chemical composition and basic mechanical properties are illustrated in **Table 1** resp. **Table 2**. By material list steel rods were annealed, pickled, cold drawn and polished. Microstructure of the material is shown at **Figure 1**.

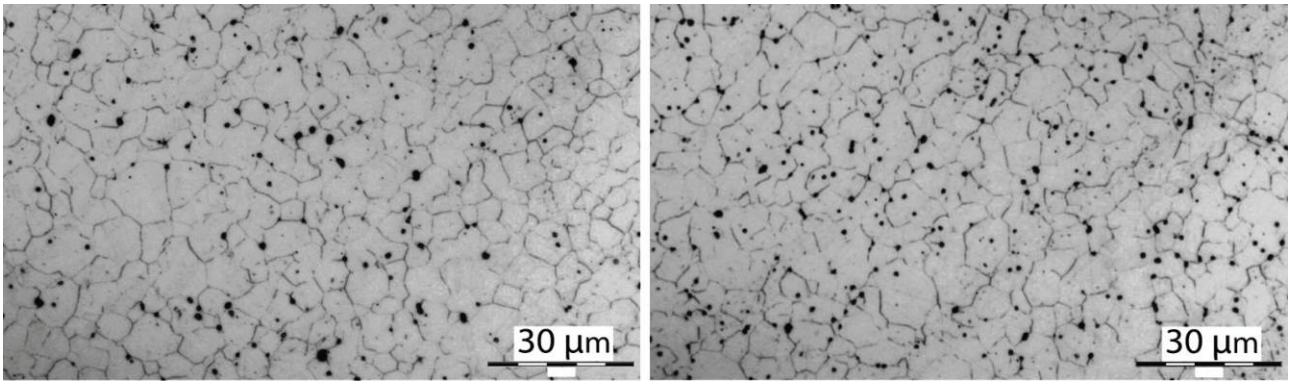

Figure 1 Microstructure of rods cross-section

Table 1 Chemical composition of tested steel from material list

Chemical composition (%)										
C	P	S	Si	Mn	Cr	Ni	Mo	Ti	N	Cu
0.022	0.033	0.030	0.308	1.467	18.240	8.050	0.344	0.004	0.090	0.367

Table 2 Mechanical properties of tested steel from material list

Material properties					
R_p 0.2% (MPa)	R_p 1% (MPa)	Rm (MPa)	Z (%)	A (%)	Hardness (HB)
583	668	731	70	41	216

2.2. Surface structure, roughness analysis and wettability tests

Special samples for surface roughness analysis were prepared by lathe turning. All samples were prepared by same tool, cutting depth, cutting speed and feed rate to obtain as similar surface roughness for all samples as possible. Surface profile measurement was performed by Taylor Hobson Talysurf 50 device equipped by standard stylus arm with 2 µm radius diamond tip. Speed rate of the tip was 1 $mm \cdot s^{-1}$ for this particulars measurement. Scanning electron microscope JEOL JSM-6490 with accelerating voltage 15 and 20 keV was used for surface structure and morphology observation. Basic chemical analyses were performed by EDX analyzer. Wettability of samples was inspected by optical contact angle measuring system, snapshots of drops

on surface were taken and pictures were evaluated by ImageJ software using DropSnake and LB-ADSA methods. For this procedure 10±1 µl droplets of artificial Tyrode's physiological solution prepared according ISO/TR 10993-15 were used [7]. Special flat samples from cross-sections of rod were used for this experiment. These samples were further processed identical way as rod-like samples. Chemical composition of Tyrode's physiological solution is: NaCl (8.00 g/l), $CaCl_2$ (0.20 g/l), KCl (0.22 g/l), $NaHCO_3$ (1.00 g/l), Na_2HPO_4 (0.05 g/l), $MgCl_2$ (0.20 g/l), Glucose (1.00 g/l). All chemicals were supplied by VWR International.

2.3. Process of anodization

Main aim of anodization process was to create special layer on substrate surface. This layer consists from oxidic layer of characteristic morphology. Anodization is an electrochemical process used to create oxidic layers on surface of metals. During the anodization, passive layer on surface is continuously disturbed by chemicals from anodizing solution. There was 2 electrode cell used for anodization, where platinated titanium plate was used as negative electrode and sample was fixed to positive electrode. Anodization solution of distilled water, ammonium fluoride (0.1M, purity >99.5%) and nitric acid (0.05M) was prepared and later mixed with ethylenglycol in weight ration 10:90 (90% for E-Glycol). DC laboratory power source Matrix MPS-3005D generated stable voltage of 20 V during the procedure. Ratio of solution volume vs. anodized surface was approx. 3 ml / mm^2. The procedure was carried out at room temperature 20 ± 2 °C. Each sample was anodized for different time according **Table 3**.

Table 3 Designation of samples and times of anodization

Sample designation	1	2	3	4	5	6
Time of anodization (min)	5	10	20	40	80	0 (REF.)

2.4. Corrosion tests and electrochemical impedance spectroscopy

Potentiodynamic polarization tests were performed according ASTM 2129 standard [8] in corrosion cell of 1000 ml volume tempered to temperature 37 ±1 °C. Tyrode's solution was used as corrosion environment for these measurements. Potentiostat Voltalab PGZ 100 with software Voltamaster 10 was used for this particular experiment and polarization rate 10 mV / s was set. Sample was fixed as working electrode, saturated calomel electrode was used as reference one and platinated titanium plate was fixed as AUX electrode to create homogenous electric field. Exposed surface was 3 cm^2. Samples were immersed in electrolyte for 1 hour to stabilize corrosion potential. After that interval OCP was measured. During next step pitting or crevice corrosion was initiated and tested by potentiodynamic polarizing of sample to potential more noble values than corrosion potential. During this polarization pitting or crevice corrosion is marked by general increase of current density. When current density increased to value 2 mA / cm^2, reverse polarization of sample has started.

Electrochemical impedance spectroscopy was used for closer observation of electrochemical properties of anodized layers. Value of 20 mV was set as wave amplitude and measurements were carried out for OCP. Subsequently frequencies of AC were changed from 10^6 Hz to 1 mHz. Experimental data were exported to EIS Analyser software where equivalent current circuits and parameters (capacitance, resistance and phase shift) of the circle were found out.

3. RESULTS

3.1. Influence of anodization to surface structure, roughness and wettability

Surface structures were observed by electron microscope using secondary electron mode and these are shown in **Figure 2**. By EDX analysis was found out that chemical composition of surface was changed only insignificantly- surfaces contained traces of fluorine ions after anodization. The layer consisted of 48 at. % iron,

21 at. % chromium, 27 at. % oxygen and 2 at. % of fluorine. Resting 2 at. % consisted of manganese, silicon and sulfur.

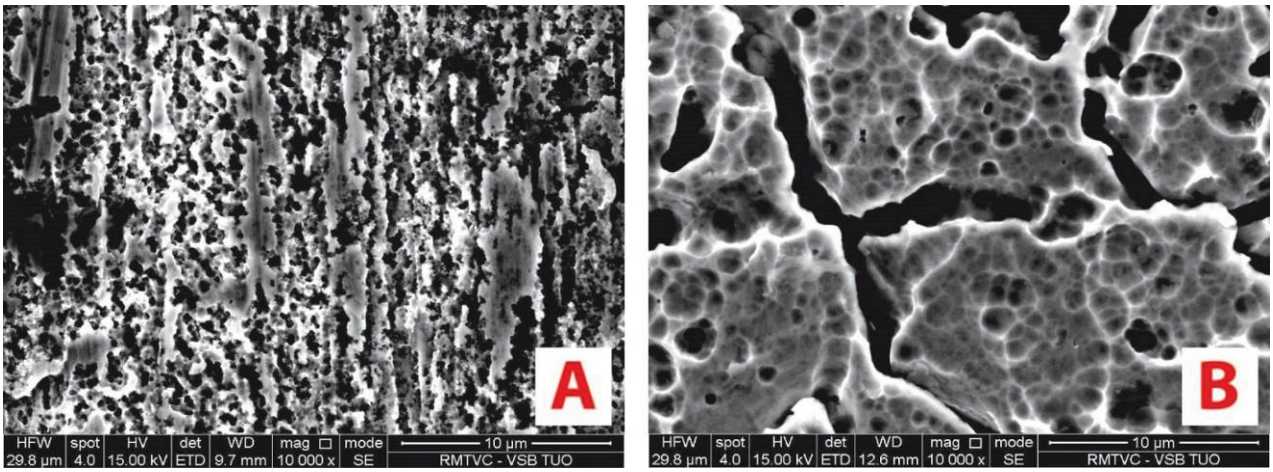

Figure 2 Structure of surface after 5 min. of anodization (A) and after 80 min. of anodization (B)

Wettability of surface affects effectivity of chemical surface disinfection, bacterial or mold and fungus adhesion. There was a relation between wettability and osseointegration confirmed-for long term implants lower contact angle is required, on the other hand for temporary implants higher contact angle is recommended [9]. Contact angle between surface and artificial Tyrode's physiological solution was measured ten times for each sample. Average values are shown in **Table 4**.

Table 4 Relation between contact angles of Tyrode's solution droplets and time of anodization

	Contact angle by "Drop snake" method			Contact angle by LB-ADSA method		
SAMPLE	Average value (°)	Deviation (°)	Median (°)	Average value (°)	Deviation (°)	Median (°)
T	75	2	74	78	2	76
U	81	1	82	83	3	81
V	89	1	90	91	2	90
X	98	1	97	98	1	99
Y	106	1	106	108	1	108
Z (REF.)	55	2	58	53	1	54

The surface roughness was measured 3 times for each sample; rod was rotated 120° before each measurement. Change of surface profile was studied before and after anodization and change of roughness indexes could be calculated. **Table 5** illustrates average values of roughness indexes for each sample before and after anodization.

Table 5 Surface roughness indexes for measurements before and after anodization

	Average R_a Index (µm)			Average R_z Index (µm)		
SAMPLE	Before anod.	After anod.	Difference	Before anod.	After anod.	Difference
1	0.9568	0.9006	0.0562	4.0752	4.0144	0.0608
2	0.9693	0.8994	0.0699	4.0481	3.9490	0.0991
3	0.9590	0.8784	0.0806	4.0808	3.9780	0.1028
4	0.9771	0.8949	0.0822	4.1138	3.9811	0.1328
5	0.9487	0.8729	0.0759	3.9978	3.8460	0.1518
6 (REF.)	0.9579	---	0.0000	3.9169	---	0.0000

3.2. Corrosion properties

OCP was measured for each sample after 1 hour immersion in testing solution. Potentiodynamic polarization method was used for determination of basic corrosion parameters like corrosion potential, polarization resistance or corrosion rate. Taffel and Stern method was used for finding these parameters. Potential of breakdown (depassivation) was found out by intersection method (extrapolation of polarization curve and its intersection with X axis). Also conventional method was used: the values of breakdown potential were found by polarization curve where the current density reaches the value of 10^{-4} A / cm^2 [8]. Results from these measurements are compared in at **Table 6**, where all values of potentials are vs. SCE.

Table 6 Corrosion parameters of tested samples

Sample	OCP (mV)	Corrosion potentials (mV)		Corrosion rate (µm/year)	Polar. resistances R_p (kΩ·cm^2)		Breakdown potentials (mV)	
		Taffel	Stern	Taffel	Taffel	Stern	Intersection	Conventional
1	-121	-171	-166	1.63	154	160	251	260
2	-117	-167	-160	1.59	152	146	236	224
3	-114	-158	-159	1.52	139	128	225	219
4	-110	-140	-151	1.47	123	95	218	230
5	-103	-124	-136	1.48	112	101	209	213
6 (REF.)	-165	-202	-209	2.64	212	205	198	186

By EIS measurements the equivalent electric circle was modeled and its parameters were found out. From these parameters equivalent capacitance of anodized surface was calculated using derivate equation of ZARC element (1), where *C* is capacitance, *R* is resistance of layer and *Q* and *n* are parameters of constant phase element [10]. Values of capacitance are illustrated specified in **Table 7.**

$$C = \frac{(Q*R)^{\frac{1}{n}}}{R} \quad (1)$$

Table 7 Values of capacitance

Samples	41	42	43	44	45	46
Capacitance (µF/cm^2)	281	405	553	699	739	99

4. CONCLUSION

Anodization process of 1.4301 steel in solution of ammonium fluoride, distilled water, ethylenglokol and nitric acid was described. Porous layer formed on surface was observed by electron microscope. It was found out that time of anodization significantly increases contact angle from approx. 55° for untreated surface to approx. 105° for sample after 80 minutes of anodization. Effect of anodization process on surface roughness of lathe turned samples was studied and changes of characteristic parameters were defined. It was found out that longer times anodization decrease surface roughness. Corrosion properties were studied by potentiodynamic polarization method. It was found out that longer time of anodization decreases polarization resistance and increases OCP and corrosion potential from approx. -200 mV for untreated sample to approx. -110 mV for sample after 80 min. anodization (potentials are vs. SCE). Break-down potentials of anodized samples are also higher than unanodized. Electrochemical behavior of porous surface was studied by EIS method. Equivalent circle was found out and its parameters were defined. The capacitance of porous surface was calculated by these parameters. Due to obtained results, anodization can be recommended as common

surface treatment for 1.4301 steel used in medicine. Longer time of anodization in solution of used composition improves most of studied parameters, but times over 40 minutes leads to corrosion of grain boundaries. This effect can be suppressed by change of solution composition or voltage used for anodization.

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REFERENCES

[1] ELIAS C. N., LIMA J. H. C., VALIEV R., MEYERS M. A. Biomedical Applications of Titanium and its Alloys. *Biological Materials Science*, 2008, vol. 60, no. 3, pp. 46-49

[2] GAVIRIA L., SALCIDO J. P. I., GUDA T. Current trends in dental implants. *Journall of Korean Association for Oral Maxillofacial Surgery*, 2014, vol. 40, no. 2, pp. 50.

[3] SHRIVASTAVA S. Medical devices manufacturing. In *Proceedings from the Materials & Processes for Medical Devices Conference.* Anaheim: ASM INTERNATIONAL, 2003, pp. 533

[4] SUBBIAHDOSS G., GRIJPMA D. W., BUSSCHER H. J., KUIJER R. Microbial biofilm growth versus tissue integration on biomaterials with different wettabilities and a polymer-brush coating. *Journal of biomedical materials research*, 2010, Vol. 2, pp. 94.

[5] ISO 15510:2014 Stainless steels -- Chemical composition : *International Organization for Standardization*, 2014

[6] ISO 377:2013 Steel and steel products - Location and preparation of samples and test pieces for mechanical testing. *International Organization for Standardization*, 2013

[7] ISO/TR 10993-9:1999 Biological evaluation of medical devices Part 9: Framework for identification and quantification of potential degradation products. *International Organization for Standardization*, 1999

[8] ASTM F2129 - 15 Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements to Determine the Corrosion Susceptibility of Small Implant Devices. *American Society for Testing and Materials*, 2015

[9] MEKAYARAJJANANONTH T., WINKLER S. Contact Angle Measurement on Dental Implant Biomaterials. *Journal of Oral Implantology,* 1999, Vol. 4, pp. 25.

[10] HIRSCHORNA B., ORAZEMA M. E., TRIBOLEBT B., VIVIERB V., FRATEURC I., MUSIANID M. Determination of effective capacitance and film thickness from constant-phase-element parameters. *Acta Electrochimica*, 2010, Vol. 21, pp. 6218-6227.