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INFLUENCE OF PURGE, TIME OF WAITING AND $TiCl_4$ DOSING TIME IN A LOW-PRESSURE ATOMIC LAYER DEPOSITION (ALD) REACTOR ON PROPERTIES OF TiO_2 LAYER

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Preliminary Note – Prethodno priopćenje

The aim of the study was to evaluate the influence of the ALD process parameters on mechanical properties and corrosion resistance of TiO_2 layer. The TiO_2 layer was deposited on stainless steel surfaces at constant temperature T = 200 °C and number of cycles n_c = 500 (g ≈ 25 nm). The applied methodology consisted of potentiodynamic and impedance studies, as well as adhesion test. The obtained results were the basis for selection of surface treatment method for stainless steel implants for contact with blood. Appropriate parameters of surface treatment realized by means of the ALD method is of significant importance. It will contribute to the development of technological conditions of specified deposition parameters of TiO_2 layers on steel implants.

Key words: 316LVM, TiO_2, ALD method, electrochemical properties, mechanical properties

INTRODUCTION

Improvement of hemocompatibility of 316LVM stainless steel by deposition of a TiO_2 layer in the ALD process depends on the correct selection of process parameters [1-3]. Previous works of the authors allowed for the optimization of process temperature and the thickness of the layer by specifying the number of cycles [4,5]. Besides the number of cycles affecting the thickness or temperature enabling correct chemisorption of the layer, one of the important ALD process parameters is the injection time of precursor. It directly affects the accuracy of filling the chamber and the process efficiency. On the other hand, there are no reports in the literature on its influence on the quality of the surface layer [6]. Hence the authors attempted to determine the influence of the injection time of the $TiCl_4$ precursor on mechanical and electrochemical properties of the TiO_2 layer deposited on a stainless steel substrate by means of the ALD method.

MATERIAL AND METHODS

The material used in the study was the 316LVM stainless steel in the form of discs with a diameter d = 14 mm and a thickness s = 2 mm. The surfaces of the samples were subjected to electrochemical polishing carried out in a bath based on a phosphate-sulfate acid until. The obtained surface roughness was Ra < 0,12 μm which is recommended for products used in the circulatory system. Then the samples were subjected to chemical passivation in 40 % HNO_3. The next step of surface treatment was deposition of a TiO_2 layer by means of the ALD method. TiO_2 layers studied in this work were grown from $TiCl_4$ and H_2O in a low-pressure ALD reactor [7]. The deposition process consisted of repeated ALD cycles. Each cycle included a $TiCl_4$ pulse, purge time, H_2O pulse and another purge time. TiO_2 layer was applied at 500 cycles at 200 °C. The variable process parameter was the injection time of each precursor in the range of t = 0,1 – 0,3 s - Figure 1. In order to evaluate the influence of the injection time of the precursors on the physicochemical properties of the deposited layers, studies of pitting and crevice corrosion resistance as well as impedance studies were carried out. Additionally, the adhesion of the deposited layers to the metal substrate was evaluated.

Tests of pitting corrosion resistance were performed using potentiodynamic method by recording polarization curves. The measuring set-up consisted of the VoltaLab PGP201 potentiostat, the reference electrode (saturated calomel electrode KP-113 type), the auxiliary electrode (platinum electrode PtP-201 type), the anode (the test sample) and a PC with VoltaMaster software. The change in potential was toward the anodic direction until the anodic current density reached 1 mA/cm^2. The applied scan rate was equal to 0,16 mV/s. Impedance measurements (EIS) were carried out using the AutoLab PGSTAT 302N measuring system provided with the module FRA2 (Frequency Response Analyse). The EIS studies used the same electrode arrangement as in the corrosion tests. Impedance spectra of the test have been shown in the form of a Nyquist diagrams for different frequencies (10^4 - 10^{-3} Hz) and in the form of Bode diagrams. The sinusoidal voltage amplitude of the excitation signal was 10 mV. The obtained EIS spectra

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were interpreted by the least-squares fit to the equivalent electric circuit.

The potentiodynamic and impedance studies were performed in the artificial plasma which chemical composition complies with the recommendations of the standard [8] at the temperature T = 37 ± 1 °C and pH 7.0 ± 0,2. Studies of the TiO_2 layers adhesion deposited on the 316LVM stainless steel substrate were performed by means of the scratch test, according to the standard [9], using the open platform equipped with the CSM Micro-Combi-Tester. The test involved generating a controlled scratch with a penetrator - Rockwell diamond cone – drawn across the coated surface with gradual, incremental load. To assess the value of the critical force Lc, the changes of acoustic emission signals, friction force and friction coefficient have been recorded. Additionally, microscopic observations with the use of the optical microscope, which is an integral part of the platform have been carried out. The tests were performed with increasing loading of 0,03 – 30 N and at the following parameters: loading rate 10 N / min, table feed rate of 10 mm / min, the length of the scratch ~ 3 mm.

RESULTS

The results demonstrated the influence of the injection time of TiO_2 and H_2O on corrosion resistance. This is evidenced by the characteristic parameters determined on the basis of the potentiodynamic studies - Figure 1. It was found that the greatest resistance to pitting corrosion was observed for the sample with a TiO_2 layer (t_1 = 0,1 s). For this case, the lowest value of the breakdown potential Ecorr and the highest value of polarization resistance R_p were recorded - Table 1.

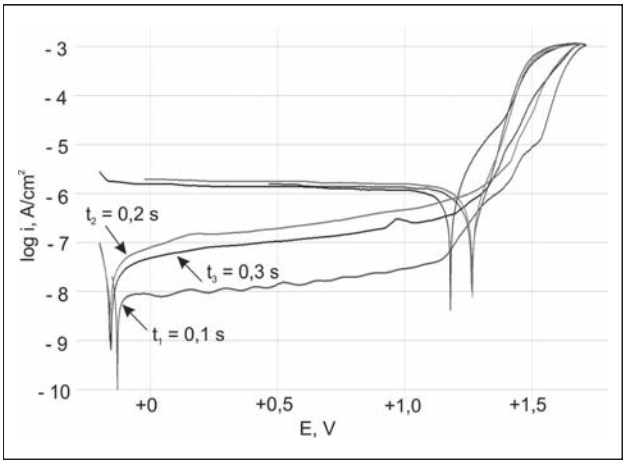
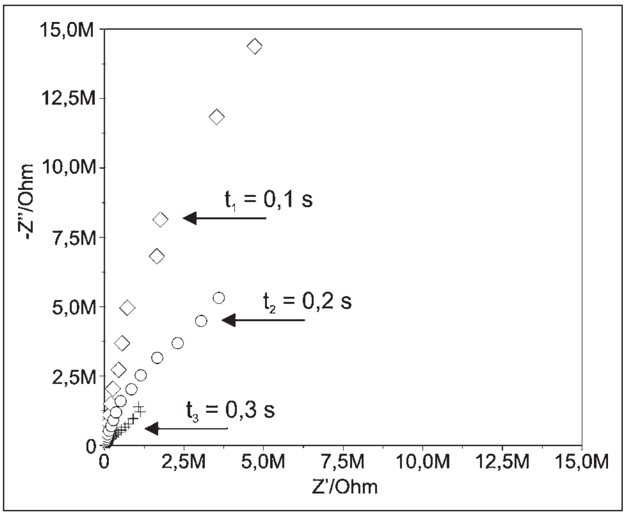


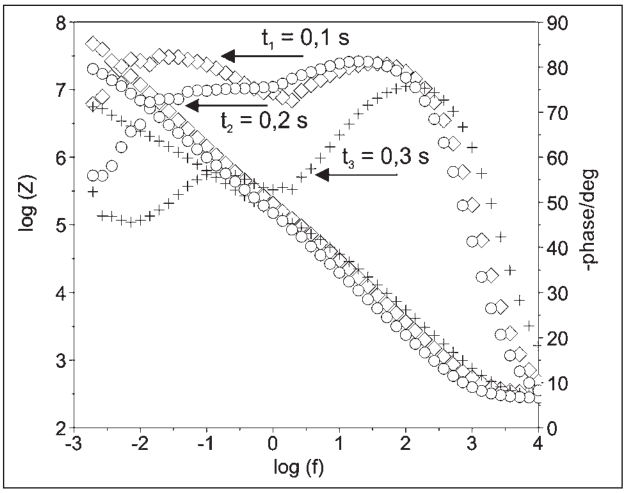
Figure 1 Polarization curves of the samples with the TiO_2 layer for different times of injection

Table 1 **Potentiodynamic analysis results**

Time of each precursor t/ s	E_{corr}/ mV	E_b/ mV	E_{cp}/ mV	R_p/ kΩ·cm²
0,1	- 135	+ 1 593	+ 1 389	2 140
0,2	- 152	+ 1 535	+ 1 236	1 310
0,3	- 148	+ 1 518	+ 1 314	763



a)



b)

Figure 2 The impedance spectra for the samples with the TiO_2 layer of: a) Nyquist diagram b) Bode diagram

Impedance spectra obtained for the TiO_2 layer (t_1 = 0,1 s and t_2 = 0,2 s) - Figure 2 were interpreted by comparing to an electric equivalent circuit, which indicates the existence of the double layer (as shown in the diagram, two time constants), wherein R_s is the resistance of the artificial plasma R_{pore} - the resistance of the electrolyte in the pores, CPE_{pore} - the capacity of a double layer (porous, surface), whereas R_{ct} and CPE_{dl} - resistance and capacitance of the oxide layer.

The use of two constant phase elements in the equivalent electric circuit positively influenced the quality of the curves fitting determined experimentally - Figure 3a. On the other hand the sample with the TiO_2 layer (t_3 = 0,3 s) showed the presence of additional adsorption layer of a near-capacitive nature. This layer was described by the additional electric circuit R_{ad}, CPE_{ad} – Figure 3b. The presence of this layer is related to the adhesion process of ions to the surface during contact with the artificial plasma.

Studies of layers adhesion also showed diverse results, depending on the injection time of the individual precursor - Figure 3. It has been found that the best adhe-

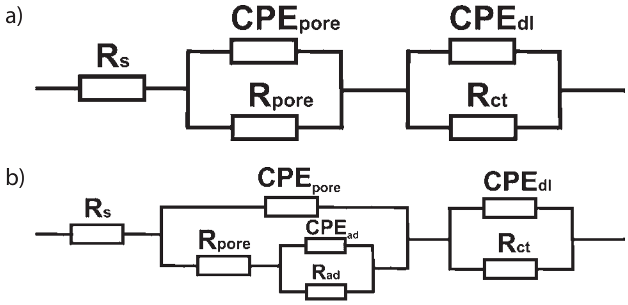


Figure 3 Equivalent electric circuits of the TiO_2 layer – artificial plasma system: a) 0,1 s and 0,2 s, b) 0,3 s

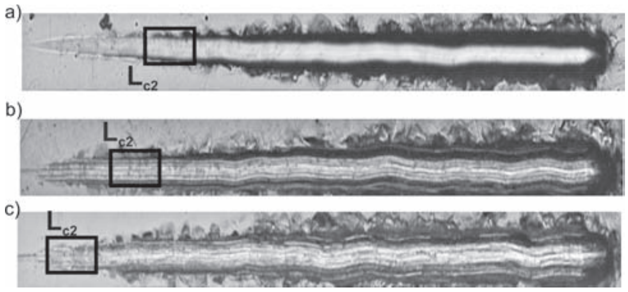


Figure 4 Scratch of the TiO_2 layer: a) 0,1 s, b) 0,2 s, c) 0,3 s

Table 2 **EIS analysis results**

Time of each precursor t/ s	E_{OCP}/ mV	R_s/ Ωcm²	R_{pore}/ kΩcm²	CPE_{pore}		R_{ct}/ MΩcm²	CPE_{dl}	
				Y_0/ $Ω^{-1}cm^{-2}s^{-n}$	n		Y_0/ $Ω^{-1}cm^{-2}s^{-n}$	n
0,1	-170	26	15,1	0,6345E-5	0,96	87,9	0,3385E-5	0,92
0,2	-182	25	24,4	0,1164E-4	0,98	12,1	0,5265E-5	0,89
0,3*	-193	26	22,9	0,2026E-4	0,91	3,4	0,1012E-4	0,85

*R_{ad} = 349 kΩcm²; *CPE_{ad} (Y_{dl} = 0,2458E-4 $Ω^{-1}cm^{-2}s^{-n}$; n = 0,83)

sion was observed for the TiO_2 layer deposited by the ALD at t_1 = 0,1 seconds. For this case, the critical force was the largest and was equal to F = 7,22 N. On the other hand, for another injection times was equal to F = 3,57 N (t_2 = 0,2 s), F = 2,76 N (t_3 = 0,3 s) respectively. In each case the discontinuous plastic perforation of the layer was observed - Figure 4. Furthermore, no acoustic signal was recorded which may indicate that the binding energy between the layer and the substrate was too low.

CONCLUSIONS

On the basis of the electrochemical and mechanical studies the influence of injection time of the individual precursors on the final form of the deposited TiO_2 layer was found. The electrochemical studies have shown that with increasing injection time of the precursors the decreasing of corrosion resistance is observed - Table 1 and 2. This is evidenced by the reduction of corrosion potential E_{corr} and polarization resistance R_p recorded in the potentiodynamic studies. In the EIS studies unfavorable decrease of the charge transfer resistance R_{ct} and the existence of the additional adsorption layer in the porous layer providing to increase the porosity of the TiO_2 layer have also been found. The increase in porosity is a negative phenomenon [10]. Extending of the injection time from 0,1 s to 0,3 s resulted in the reduction of adhesion to the substrate - Figure 3. The confirmation of this phenomenon is lowering of the critical force LC_2 for the time 0,3 s as compared to 0,1 s. Summarizing, the performed studies have clearly demonstrated that the increase of the injection time causes adverse effects on chemisorption of the layer to the substrate forming on the surface so called agglomerates which influences its porosity and reduction in adhesion.

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Note: The responsible translator for English language is Iwona Bąbel (Learning Center – Future), Poland