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PHYSIOCHEMICAL PROPERTIES OF TiO_2 NANOPARTICLE THIN FILMS DEPOSITED ON STAINLESS STEEL

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Preliminary Note – Prethodno priopćenje

The purpose of this study was to evaluate the usefulness of TiO_2 layer to improve hemocompatibility of 316LVM stainless steel. The TiO_2 layers studied in this work were deposited from $TiCl_4$ and H_2O in a low-pressure Atomic Layer Deposition (ALD) reactor taking into account number of cycles and process temperature. As a part of the research electrochemical studies of the layer after 28 days exposure to artificial plasma were carried out. In particular, potentiostatic, potentiodynamic and impedance studies were conducted. The obtained results were the basis for selection of surface treatment method dedicated to blood-contacting stainless steel implants.

Key words: TiO_2, 316LVM, ALD method, polarization, electrochemical impedance spectroscopy (EIS)

INTRODUCTION

The main problem of the use of steel 316LVM in blood-contact implants applications is the hemocompatibility. Currently, a lot of research is focused on improving its quality by modifying the surface. The most popular methods of surface modification used for medical products are chemical methods (eg. chemical passivation, sol-gel method) and electrochemical (eg. anodic oxidation, glow-processing) [1-3]. These methods do not provide the constancy of the geometrical characteristics of the entire length of the implants and especially in their miniaturized forms (coronary stents). In this context, forward-looking method enables uniform application of the surface layer depostion is the ALD (Atomic Layer Deposition) [3-9]. This method allows for the practical use as precursors the chemical elements witch high hemocompatibility (eg. Ti, Si, Zr, C) [4, 6]. ALD is characterized by sequentiality, which involves alternately introducing the reagent into the process-chamber in which the film deposition takes place. Each introduction of precursor is followed by introduction of an inert gas (eg. nitrogen) to remove by-products of reactions occurring in the process. In addition to the geometrical characteristics of the surface remaining unchanged deposited layers, ALD method has other advantages such as follows: reproducibility, ability to deposit very thin layers at low temperatures range. Research executed by the authors [3, 5, 9] have shown that titanium oxide formed on the surface of implants influenced favorably the improvement of implants hemocompatibility. This phenomenon, in turn, had a positive impact for improving the functional properties of the implant.

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Earlier investigations of the studied authors [9] also demonstrated a favorable effect of the TiO_2 layer which improves the electrochemical properties. The authors also showed the impact of application performance to the final layer quality. They clearly prove that the slayer of TiO_2 deposited with ALD method in 500 cycles mode in the temperature range between 200 – 300 °C has a suitable barrier properties for Ni and Fe ions. Due to the fact that the implant stays in the body for a long period of the time, and for the first few days after implantation it is in direct contact with blood, and therefore it is appropriate to determine possible changes resulting surface layer. Hence, the authors attempted to assess the electrochemical properties TiO_2 layer treated to the 28 days of exposure in conditions simulating the human blood environment. The comparison was aimed to test the stability of the layer and thus its barrier properties in human body fluids environment.

MATERIAL AND METHODS

For undertaken investigations it was chosen steel 316LVM in the form of discs with an diameter d=14mm and a thickness g=2mm. Surfaces of the specimens were subjected to electrochemical polishing treatment carried out in an acid-bath containing phosphate sulfate. Polishing lasted until a surface roughness was R_a < 0,12 μm recommended for implants used in the circulatory system. In next step the samples were subjected to chemical passivation in 40 % HNO_3. These two steps are the basic treatment for forming on the surface of the stainless-steel used for miniaturized geometrical implants. Then, for the as-prepared surface was deposited a layer of TiO_2 with ALD method. TiO_2 films studied in this work were grown from $TiCl_4$ precursor and H_2O in a low type low-pressure ALD reactor [4]. 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 deposited at 500 cycles at 200 °C and 300 °C.

In the last step the samples were sterilized with ethylene oxide. Then specimens were immersed in a solution of artificial plasma at a temperature of T = 37 °C for 28 days. In order to identify the phenomena occurring at the interface and thus assess the suitability of the proposed surface modification potentiostatic, potentiodynamic, impedance investigations were executed. In addition, samples were examined in the Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) to determine the surface topography and morphology. Tests of resistance for pitting corrosion was performed by potentiodynamic polarization curves. The test rig consisted a potentiostat (VoltaLab PGP201), reference electrode (saturated calomel electrode SCE type KP-113), the auxiliary electrode (platinum electrode type PtP-201), the anode (the test sample) and a PC with software (VoltaMaster). The change of the potential was occurred in the direction of the anode at a rate of 0,16 mV/s. to the anodic current density of 1 mA/cm^2. In turn, the test of resistance to crevice corrosion resistance was performed by potentiostatic method with the change in current density at a potential of + 800 mV at t = 15 min. The test rig in this step was the same as previous. Impedance measurements (EIS) were carried out using the measurement system AutoLab PGSTAT 302N provided with the module 2 FRA (Frequency Response Analysis). The test rig used the same electrode arrangement as in corrosion tests. Impedance spectra of the test are shown in the form of a Nyquist diagrams for different frequencies (10^4 - 10^{-3} Hz) and in the form of a Bode diagrams. The voltage amplitude of the sinusoidal excitation signal was 10 mV. Obtained EIS-spectra diagrams were interpreted by the least-squares fitting to the electrical equivalent circuit. Potentiodynamic, potentiostatic and impedance studies was performed in an simulation environment: artificial plasma (chemical composition complies with the recommendations of the ISO-standard [10]), at temperature T = 37±1 °C and pH = 7,0 ± 0,2. Due to the significant influence on the early and late cardiac system-reactions an atomic force microscope using a non-contact mode for as-prepared surface samples was performed. The scanned area is 10 x 10mm with a resolution of 256 x 256. Additional observations was performed with scanning electron microscope ZEISS SUPRA 35 detector type SE (Secondary Electrons) for secondary electrons in the magnification range 1 000 – 70 000x.

RESULTS

Potentiodynamic studies have shown that exposure to artificial plasma has reduced resistance for the pitting corrosion regardless of the applied temperature of deposition process – Figure 1. R_p and E_b values were de-

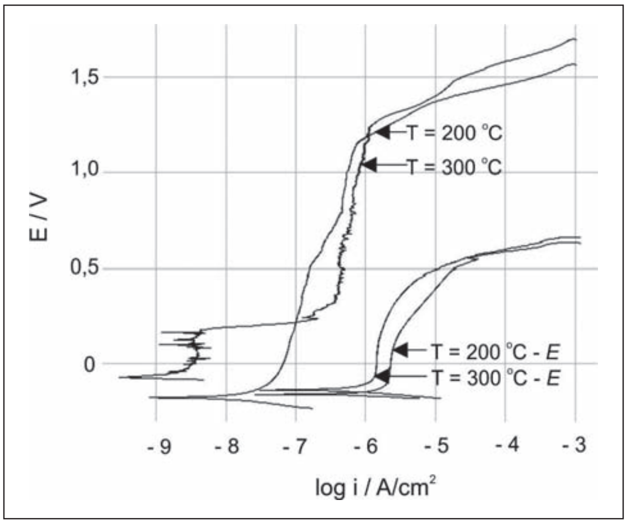

Figure 1 Polarization curves of samples with a layer of TiO_2 before and after 28 day exposure in artificial plasma solution

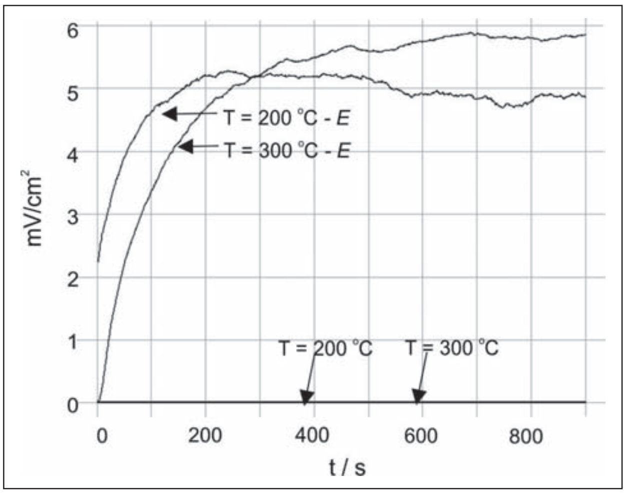

Figure 2 Potentiostatic curves determined on a modified surface of steel 316LVM

creased for the samples after exposure (T = 200 °C (*E*) - E_{corr} = - 180 mV, R_p = 10 kWcm^2 and E_b = + 595 mV; T = 300 °**C** (*E*) - E_{corr} = - 157 mV, R_p = 17 kWcm^2 and E_b = + 624 mV) relative to the baseline (T = 200 °C - E_{corr} = - 214 mV, R_p = 415 kWcm^2 and E_b = + 1 584 mV; T = 300 ° C - E_{corr} = - 138 mV, R_p = 276 kWcm^2 and E_b = + 1 608 mV). The TiO_2 barrier layer after exposure in the plasma was not well resistant also to crevice corrosion - Figure 2.

The presence of the double layer (porous) with low electrochemical properties (R_{pore}) have been also confirmed in impedance studies (EIS) - Table 1, Figure 3

Prepared layer was characterized by a large surface development which could cause penetration of metal ions and also a small chemical stability. In turn, the sublayers formed during the application of TiO_2 by ALD method is characterized by a high resistance for corrosion which contributed to the high value of the charge transfer resistance R_{ct}. This value has also increased as a result of the impact of artificial plasma which can be

Table 1 **EIS analysis results**

Temperature of process	E_{OCP}/ mV	R_s/ Ωcm²	R_{pore}/ kΩcm²	CPE_{pore}		R_{ct}/ MΩcm²	CPE_{dl}	
				Y_0/ Ω⁻¹cm⁻²sⁿ	n		Y_{dl}/ Ω⁻¹cm⁻²sⁿ	n_{dl}
Before 28 days exposure								
200 °C	- 268	27	15	0,8268 E-5	0,96	43	0,2002 E-4	0,81
300 °C	- 227	26	65	0,2328 E-4	0,98	7	0,4322 E-5	0,85
After 28 days exposure								
200 °C - *E*	- 340	27	30	0,1737 E-4	0,86	140	0,8621 E-5	0,86
300 °C - *E*	- 475	26	42	0,8225 E-4	0,72	86	0,4873 E-5	0,93

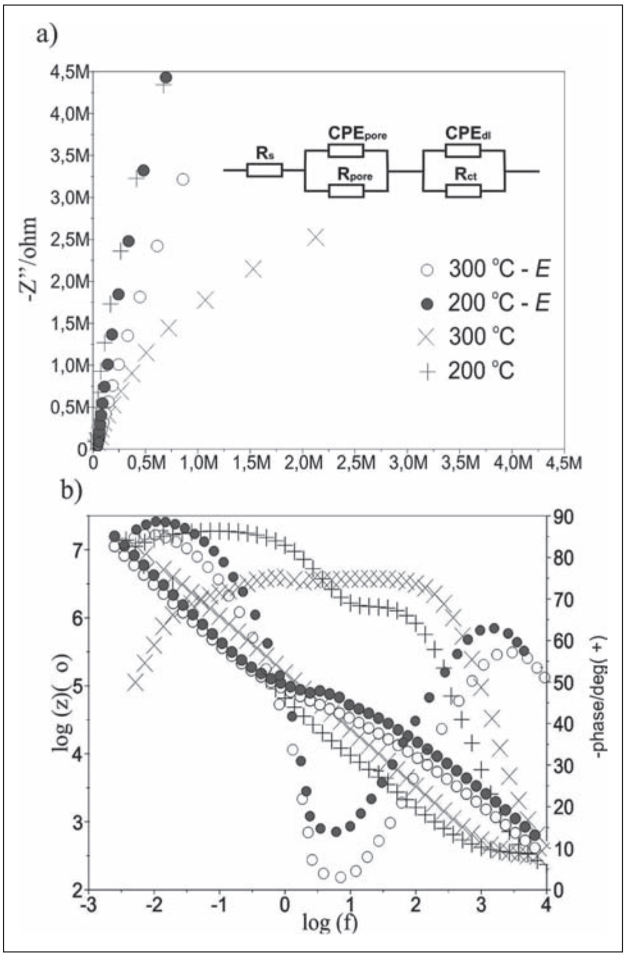

Figure 3 Impedance spectra for the modified surface of steel 316LVM: a) Nyquist diagram, b) Bode diagram

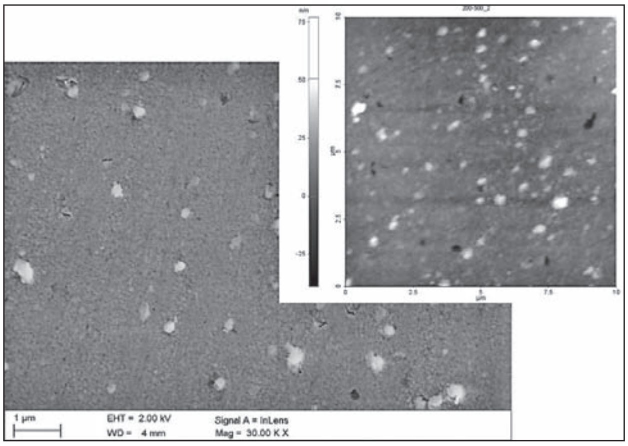

Figure 4 The morphology and topography of the surface after 28 days exposure, for the layer deposited at T = 200 °C

associated with the reconstruction of the TiO_2. In addition, it was also found that the 28 day exposure tests did not affect the morphology and topography of the surface compared to the initial state - Figure 4.

CONCLUSIONS

Performed electrochemical studies showed no significant differences between the used depostion process temperature (T = 200 °C – 300 °C). Obtained in the voltamperometric studies results shows the negative impact of artificial plasma to corrosion resistance of deposited layers. Regardless from the process temperature TiO_2 layer during exposure underwent rebuild, thereby causing the appearance on the surface of the additional porous layer with low chemical stability. This layer is characterized by low resistance to corrosion in contact with the artificial plasma. On the other hand sublayers of TiO_2 as a result of ongoing reaction surface does not deteriorate its barrier properties – Table 1.

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