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POTENTIOSTATIC, POTENTIODYNAMIC AND IMPEDANCE STUDY OF TiO_2 LAYERS DEPOSITED OF 316 LVM STEEL USED FOR CORONARY STENTS

The objective of the study is assessment of suitability of the ALD method for application of a TiO_2 layer on surface of 316LVM steel used for production of vessel stents. Selection of the appropriate process parameters for application of the layer affects its electrochemical properties, which largely determine resistance of the biomaterial to corrosion in the blood environment, thus affecting its hemocompatibility. To assess resistance of the AISI 316LVM steel with modified surface to corrosion, voltammetric and impedance measurements were conducted. The proposed variant of surface processing allows safe deformation of the TiO_2 layer without its delamination.

Keywords: AISI 316LVM, TiO_2 layer, ALD method, coronary stents, corrosion resistance,

1. Introduction

The literature data show that the process of electrochemical polishing is the basic stage in developing functional properties of metal biomaterials used for vessel stents due to their miniaturisation. The process of chemical passivation is the basic stage in developing functional properties of Cr-Ni-Mo steel (316LVM type) intended for production of implants. However, for improvement of electrochemical properties of surfaces in finished products for contact with blood, surface layers on the basis of such elements as Si, Ta or Ti are used more and more often. These elements have definitely higher values of corrosion potential in the environment of human physiological liquids than Fe or Cr. There are many methods of surface modification of metal biomaterials. Those used most often include anodic passivation, the sol-gel method or PVD [1-4]. These modifications of surface of metal biomaterials by way of application of surface layers, resulting improvement of their physical and chemical properties in various degrees. One of more important aspects in reference to vessel stents is ensuring stability of their geometric features along the entire length, which cannot be achieved with the said modifications. For this reason, the most suitable modification of surface in this context is achieved with application of layers with the ALD method (Atomic Layer Deposition) [5-9].

The literature spares little space for the issues related to susceptibility of surface layers to deformation, in particular those applied on vessel stents. During the implantation, these products are subject to major form formation, which may result in the making of the top layer. Breaking its continuity results in formation of a local galvanic cell, later leading to initiation and development of corrosion phenomena. In such a miniature form of the implant, corrosion causes breaking of the continuity of geometry, thus destabilising the expanded place of the vessel and its contraction. It also affects the processes of blood coagulation resulting from the electrical phenomenon of corrosion current. Apart from unfavourable phenomena related to deformation of geometry, thus opening the possibility of stress corrosion, crevice corrosion may also occur in coronary stents. It is directly related to its structure as well as micro-crevices originating between the arms of the stent and the blood vessel. Therefore, the authors have proposed a comprehensive assessment of resistance corrosion in artificial plasma of the TiO2 layer applied on the surface of AISI 316LVM steel, taking into consideration the process of implantation of the stent in the blood vessel. The study assessing suitability of the proposed technology for application of the layer with the ALD method under the assumed conditions included tests of resistance to pitting corrosion, crevice corrosion and stress corrosion with voltammetric and impedance methods, taking into consideration the process of medical sterilisation.

2. Material and method

The material for the study came from the samples collected from a rod steel (AISI 316LVM) in stabilised condition, diameter d = 14 mm, d = 8 mm and d = 1.0 mm. The surface of the samples was subjected to electrochemical polishing in the phosphate-sulphide bath. This treatment allowed to obtain the roughness of the surface recommended for this type of products: Ra < 0.16 μm. Then, the samples were subject to chemical passivation in 40% HNO_3 at the temperature T = 60 °C during the time t = 1 h. Application of the TiO_2 layer was executed with the ALD method in two temperatures of the process T = (200 °C and 300 °C), selected on the basis of the earlier studies conducted by the authors of [10,11] A fixed number of cycles Lc = 500 was proposed, which allowed

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obtaining a similar thickness of the TiO_2 layer. The TiO_2 films investigated in this study were grown from $TiCl_4$ and H_2O in a low-pressure ALD reactor [9]. The deposition process consisted of repeated ALD cycles. Each cycle included a $TiCl_4$ pulse, the purge time, H_2O pulse and another purge time. In the last stage, the samples were subjected to the process of steam sterilisation under pressure in the Basic autoclave (T = 135 °C, p = 2.1 bar, t = 12 min.). Taking into account the technique of coronary stent implantation, some samples collected from their rod with diameter d = 1.0 mm were deformed by the angle 20°, 40° and 60° with bending radius R = 5 mm, simulating bending of the arms of the stent. These deformed samples were subject to tests of resistance to stress corrosion.

The potentiodynamic tests included the test of resistance to pit and stress corrosion. The test stand comprised VoltaLab PGP201 potentiostat, the reference electrode (type KP-113 saturated calomel electrode SCE), the supporting electrode (type PtP-201 platinum electrode), the anode (test sample) and a PC with VoltaMaster 4 software. The potential changed along the anode direction at the rate of 0.16 mV/s. Once the anodic current density reached the value of 1 mA/cm^2, the polarization direction was changed.

Evaluation of resistance to crevice corrosion made use of the potentiostatic method [12], recording changes in current density at +800mV potential during 15 minutes. The measurement system was identical to one used for potentiodynamic tests.

In order to achieve additional information on electrochemical properties of the surface of the evaluated samples, electrochemical impedance spectroscopy (EIS) was used. Such method allowed for analysis and interpretation of processes and phenomena occurring at the phase boundary: implant – tissue environment. The measurements were made with AutoLab PGSTAT 302N system with FRA 2 (Frequency Response Analyse) module. The system of electrodes applied was identical to that used in potentodynamic tests. The impedance spectra of the assessed system were presented as Nyquist diagrams for different frequency values ($10^4 \div 10^{-3}$ Hz) and also as Bode diagrams. The amplitude of the sinusoid voltage inducing signal was 10 mV. The obtained EIS spectra were interpreter following adjustment to the equivalent circuit with the use of the smallest square method [1].

All electrochemical test were carried out in the environment of artificial plasma with the chemical composition recommended by the standard [3,13,14] at the temperature T = 37±1°C, and pH = 7.0±0.2

3. Results and discussion

The results of the test of resistance to corrosion of non-deformed and deformed samples for all the analysed variants of surface treatment are given in Table 1. Changes in corrosion current density icorr in the function of potential E are presented in Fig. 1. For all the variants of samples in both initial state and with the applied TiO_2 layer, breakthrough potential was not detected, with the determination of transpassivation potential (Fig. 1), corrosion potential and polarisation resistance. No significant changes were found in the value of transpassivation potential and in the value of polarisation resistance depending on the degree of bending of the samples - Table 1. The obtained results constituted reference values for the samples with TiO_2 layers applied under various conditions of the ALD process and subjected to bending tests. Application of the layer resulted in lowering of the values of corrosion potentials, irrespective of the parameters of the process, as compared with the initial state, this tendency being maintained irrespective of the angle of bending of the samples (Table 1, Fig. 1).

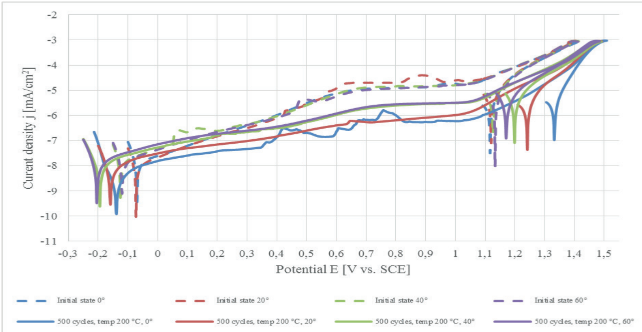

Fig. 1. Curves of polarization of samples after different surface modification

The analysis of the value of polarisation resistance Rp for the samples with the oxide layer showed their clear increase

TABLE 1

Results of potentiodynamic tests for bending specimens in initial state and after ALD surface modification

Surface	No	Bending angle, °	E_{corr}, mV	E_{tr}, mV	R_p, kΩcm^2
Initial state	1	0	-60(16)	+1365(10)	1573(110)
	2	20	-86(18)	+1290(4)	1641(169)
	3	40	-121(8)	+1290(3)	1663(180)
	4	60	-119(1)	+1282(1)	1707(117)
TiO_2 500 cycles 200 °C	5	0	-140(6)	+1397(8)	4408(117)
	6	20	-149(11)	+1390(6)	3371(84)
	7	40	-182(13)	+1382(11)	1871(84)
	8	60	-198(5)	+1376(4)	1550(127)
TiO_2 500 cycles 300 °C	9	0	-161(14)	+1409(21)	5129(199)
	10	20	-143(12)	+1425(4)	2894(132)
	11	40	-161(1)	+1437(11)	1885(35)
	12	60	-188(8)	+1416(4)	1580(114)

as compared with the initial state, which proves advantageous lowering of activity of the surface of the tested biomaterial in corrosive environment. Moreover, the stable tendency was noticed to lower its value along with the increase of bending angle: Fig. 1, Table 1. The finding was that for 500-cycle ALD technological processes conducted at the temperature of 200°C and 300°C, only for bending angle 60° achieving the values close to the initial state of about Rp = 1600 kΩcm^2.

The results of the tests of resistance to crevice corrosion of the samples in the initial state and with the applied TiO_2 layer are given in Fig. 2 and in Table 2.

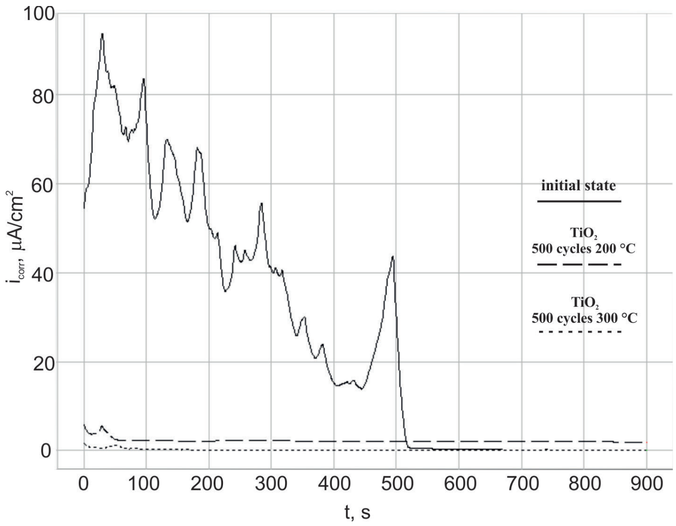

Fig. 2. Exemplary curves of current density in function of time for the initial state, with the TiO_2 layer 200°C and 300°C samples

The tests conducted with electrochemical impedance spectroscopy for 316LVM steel in the initial state and after modification of the surface are presented in Fig. 3 and in Table 3.

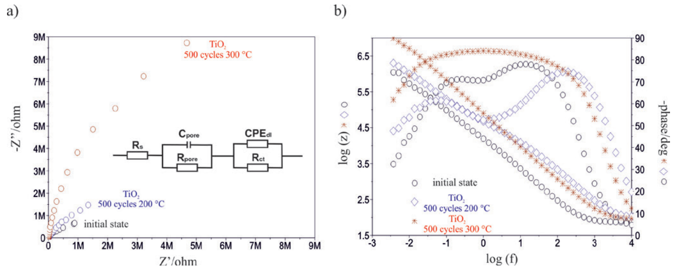

Fig. 3. Impedance spectra for AISI 316LVM steel (initial state, TiO_2 layer): a) Nyquist diagram, b) Bode diagram

The impedance spectra for the tested samples were compared with the substitute electric system, which indicates occurrence of a double layer on the surface. R_s – means resistance of the artificial plasma, R_{pore} – is resistance of the electrolyte in the sublayer pores, and C_{pore} – is capacity of the sublayer (porous, top), whereas R_{ct} and CPE_{dl} are resistance of charge transfer and capacity of the double layer. Application of two constant phase elements in the electric substitute circuit was beneficial for the quality of adjusting the curves determined experimentally [3].

4. Conclusions

The conducted tests of resistance to pit corrosion, crevice corrosion and stress corrosion proved that they depend on electrochemical properties of the surface layer. These properties are developed in the processes of surface modification. The authors propose application of the ALD method for application of a TiO_2 layer on surfaces of 316LVM steel used for products intended for contact with blood. The TiO_2 layer has better hemocompatibility than passive layers (Cr_2O_3). In the ALD method, the number of cycles and the temperature of the process are major parameters that affect the final quality of the layers.

TABLE 2

Results of tests of resistance to crevice corrosion

Surface treatment	Resistance to crevice corrosion	Current density after 20 s μA/cm^2	Current density after 900 s μA/cm^2	Charge density mC/cm^2
Initial state	Yes	93.3	0.2	23.6
TiO_2 500 cycles 200 °C	Yes	5.5	1.9	2.1
TiO_2 500 cycles 300 °C	Yes	0.7	0.1	0.1

TABLE 3

EIS analysis results

Sample	R_s, Ωcm^2	R_{pore}, kΩcm^2	C_{pore} μF	R_{ct}, kΩcm^2	CPE_{dl}		E_{OCP}, mV
					Y_0, $\Omega^{-1}cm^{-2}s^{-n}$	n	
Initial state	17	5	29	1148	0.1572E-4	0.88	-109
500 cycles 200°C	25	12	2	4510	0.6986E-5	0.76	-184
500 cycles 300°C	26	3	21	26480	0.2369E-5	0.92	-197

Earlier works of the authors allowed finding the number of cycles and the range of temperatures for layers with the most advantageous set of physical and chemical properties [10,11]. On this basis, a TiO_2 layer was proposed to be applied on surfaces of the steel at the temperature T = 200°C and 300°C in the 500-cycle process. Taking into consideration application of these layers as protective layers on the surface of vessel stents, they were additionally subjected to effect of sterilising agent: steam under pressure at the temperature T = 135 °C, and then deformed with the preset angle in the bending process. The value of the angle was determined on the basis of own research. Due to the miniaturised form of the implant and the place of implantation, this layers are also exposed to crevice corrosion. The conducted tests of resistance to pit corrosion clearly proved that the TiO_2 layer applied on 316LVM steel improves resistance to this type of corrosion: Tab. 1, Fig. 1. The obtained results confirm the findings of E. Marin and C. X. Shan [12,15,16]. They have also found advantageous effect of TiO_2 layers on improvement of corrosion resistance of austenic steel as compared with the material in the initial state. In particular, they proved reduction in current density and increase of the area of perfect passivation as compared with samples without the applied oxide layer. The tests also proved importance of the process of medical sterilisation in developing electrochemical properties of surface layers. The finding was that steam sterilisation reduces corrosion resistance of steel after the process of chemical passivation and with the TiO_2 layer applied at the temperature of 200 °C. This process was advantageous for improvement of corrosion resistance of steel with a TiO_2 layer applied at 300 °C. This phenomenon may result from varied temperature of formation of oxide on the surface of steel. The temperature of the process of chemical passivation (T = 60 °C) and application of a TiO_2 layer (T = 200 °C) may cause formation of oxide with low thermodynamic stability in higher temperatures (sterilisation T = 135 °C). Thus, these layer enriched with O and H may become modified under the impact of steam under pressure, which was proved in the EIS research (a sublayer with large surface development). TiO_2 layer applied at the temperature of 300 °C is more stable under the impact of these elements, thus resulting in better properties protecting steel against impact of corrosive environment. Irrespective of the type of the surface layer (Cr_2O_3, TiO_2), steam sterilisation had no negative effect on resistance to crevice corrosion: Tab. 2 and Fig. 2. The tests of resistance to stress corrosion justify the conclusion that safe deformation of the produced TiO_2 layers is possible at the temperature of both 200°C and 300°C up to the bending angle of 40°, sufficient for permanent deformation of geometry of the stent in the coronary vessel. A higher value of the angle (60°) may result in weakening of the TiO_2 layer, leading to opening the metal biomaterial base, thus initiating the corrosion process. All in all, the conducted tests allow the unequivocal statement that the TiO_2 layer applied at the temperature of 300 °C is stable and offers the most advantageous set of electrochemical properties in the environment of artificial plasma.

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