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INFLUENCE OF SURFACE MODIFICATION ON PROPERTIES OF STAINLESS STEEL USED FOR IMPLANTS

WPLYW MODYFIKACJI POWIERZCHNI NA WŁAŚCIWOŚCI STALI NIERDZEWNEJ STOSOWANEJ NA IMPLANTY

The aim of the study was assessment of the influence of stainless steel 316 LVM surface modification on its functional properties. The analyzed steel undergone a surface treatment consisting of the following processes: mechanical polishing, chemical passivation and deposition of Al_2O_3 layers by Atomic Layer Deposition method. The proposed variant of surface treatment will undoubtedly contribute to improving the functional properties of stainless steel intended for implants. In order to assess functional properties of the steel, electrochemical studies, adhesion (scratch test), wetting angle tests and topography of surface (AFM method) were performed. The obtained results of the study showed clearly that the proposed by the authors way of surface treatment including: mechanical polishing, chemical passivation and deposition of Al_2O_3 layer by means of the ALD method effectively improves the corrosion resistance of stainless steel.

Keywords: ALD method, pitting corrosion, scratch test, wettability, AFM

Celem pracy była ocena wpływu modyfikacji powierzchni stali nierdzewnej 316 LVM na jej właściwości funkcjonalne. Obróbka powierzchni składała się z następujących procesów: polerowanie mechaniczne, chemiczna pasywacja i naniesienie warstw Al_2O_3 metodą ALD (Atomic Layer Deposition). Zaproponowany wariant obróbki powierzchni niewątpliwie przyczyni się do poprawy właściwości funkcjonalnych stali przeznaczonej na implanty. W celu oceny właściwości funkcjonalnych stali przeprowadzono badania elektrochemiczne, badania adhezji warstw (scratch test), oraz badania zwilżalności (kąt zwilżania i badania topografii powierzchni metodą AFM). Uzyskane wyniki badań wykazały wyraźnie, że zaproponowany przez autorów sposób obróbki powierzchni, w tym: polerowanie mechaniczne, pasywacja chemiczna i naniesienie warstw Al_2O_3 metodą ALD skutecznie poprawia odporność na korozję stali nierdzewnej.

1. Introduction

Material implanted into tissues and body fluids should be characterized by bioelectronic compatibility, and as a consequence have the appropriate electrical properties (semiconducting and piezoelectric) and magnetic properties similar to those of surrounding living matter (mostly dielectric). Furthermore, the mechanical properties should provide a good cooperation in the system: implant - tissue - body fluids, which are indispensable to the realization of biophysical cooperation and flexible load carrying. The selected set of physicochemical properties of the implanted material will protect against damage process, and in consequence, general and reactive responses as well as metalosis will be minimized [1].

In order to prevent these negative phenomena, surface treatment of implants, (e.g. coating) is applied. So far, however, fully satisfactory results in this field has not been achieved. Therefore, the search for the best solutions of the chemical composition and physicochemical properties of the produced layers is constantly ongoing. Thus, ceramic coatings seems to

be very attractive for their good resistance to heat, corrosion, and wear (higher than metals) [2-5]. In recent years TiO_2 has been the focus of extensive research its due to versatile applications in self-cleaning surfaces, sterilization, air- and water-purifications, solar cells, and bio-compatible devices etc [6-8]. TiO_2 and its mixture with other oxides such as SiO_2 , Al_2O_3 have also been used as protective coatings to stainless steel [9-11].

Among many techniques of applying layers (sol-gel method [12-14], anodic oxidation [15,16]), special attention should be put on ALD (Atomic Layer Deposition) technique, because it allows to control the process of deposition of thin layers and modify their properties by changing the reactants and parameters of the deposition process. The ALD method is distinguished by two features: sequencing of the process and the self-limitation of layers growth. The sequencing is based on the fact that the reactants (precursors) are alternately introduced to the growth chamber, while each dose of the precursor is separated from the next by washing the chamber with an inert gas (e.g. nitrogen). The ALD process therefore

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consists of cycles comprising the sequential introduction of the precursors to the growth chamber. In one cycle, the following stages can be distinguished: introduction of the precursor (I), purge, introduction of the precursor (II), purge. A unique advantage of the ALD method is the ability to obtain layers that very well coincide geometrically complex surfaces such as for example stents. In this respect, this method is unrivaled (Fig. 1). Moreover, this method is characterized by excellent reproducibility and the possibility of vapor deposition even at room temperature.

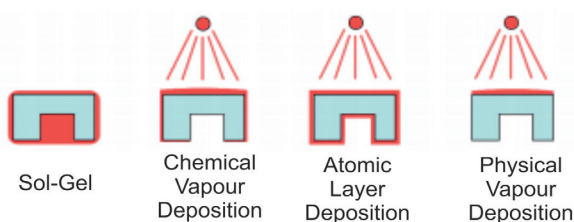


Fig. 1. Comparison of methods for layers deposition in terms of their homogeneity [17]

Preliminary results concerning the improvement of physical and chemical properties of stainless steel covered by TiO_2 and Al_2O_3 using ALD layers were already obtained by Matero et al. (1999) [18], which supposed that the conformal ALD coatings could increase the corrosion resistance of different metal alloys. In 2007, Shan et al. [19] used TiO_2 ALD layers to protect an undefined stainless steel, obtaining only a limited effect. In 2011, Marin et al. [20], Diaz et al. [21] and Potts et al. [22] clearly showed that the residual porosity of ALD layers decreases increasing the thickness of the layer, thus improving the protection of the substrate. In most cases [20-22] the nanometric ALD layers clearly showed a corrosion protection similar, if not superior to conventional protective techniques and thicker coatings, even if common industrial tests (salt spray) performed on Plasma Enhanced ALD by Potts et al. [22] clearly showed a time-limited corrosion protection.

In this paper the preparation of amorphous Al_2O_3 films onto stainless steel substrates using ALD is shown. The electrochemical and mechanical properties, wettability and topography of surface were also discussed.

2. Material and method

Under the study was a rod of the stainless steel with a diameter of 8 mm. The chemical composition of the steel was shown in Table 1. The samples were subjected to the following

surface treatment: mechanical polishing (the samples were polished using emery paper with a grain size of 800 and 1200), chemical passivation (in 45% HNO_3 solution at 60°C for 1h) and deposition of Al_2O_3 layers (at 200°C in 630 cycles).

The first stage involved the study of mechanical properties of the analyzed samples in the framework of which substrate hardness and adhesion tests, using scratch test method, were studied. The hardness measurement was carried out using the Vickers method (the loading was equal to 1 kg). In turn, the adhesion test and the determination of other symptoms of mechanical damage was done by scratch test method using the open platform equipped with CSM microtester. The idea of the test was to scratch the surface of the material with the use of the penetrator - Rockwell diamond cone - with a gradual increase of the normal force loading the penetrator. Critical force, which is a measure of adhesion, is the smallest normal force resulting in the loss of adhesion of the coating to the substrate. To assess the value of the critical force, the changes of acoustic emission signals, the friction force and the coefficient of friction were recorded and analyzed. Moreover, microscopic observations on the optical microscope, which is an integral part of the platform, were also carried out. The study was conducted on the samples with the Al_2O_3 layer deposited on the polished surface and with the layer deposited on the polished and the passivated samples. The test was performed by increasing the loading force of 0.03 to 15 N at the following operational parameters: load rate - 10 N/s, speed of the table - 10 mm/min and the length of the scratch - 2 mm. For each variant 3 measurements were carried out [23].

Subsequently, the surface topography test (AFM) was conducted for the samples with a surface formed by the successive steps of the surface treatment by means of N TEGRA Spectra (NT MDT). The scanned area was 100 x 100 μm .

Then, in order to evaluate the electrochemical properties of the prepared samples potentiodynamic and impedance tests were performed. Pitting corrosion test was performed for the samples of the particular variants of surface treatment by potentiodynamic method (recording of anodic polarization curves). On this basis characteristic parameters were set: corrosion potential E_{kor} [mV], breakdown potential E_{np} [mV], repassivation potential E_{cp} [mV], corrosion current density i_{cor} [$\mu\text{A}/\text{cm}^2$], polarization resistance R_p [$\text{k}\Omega\text{cm}^2$]. The beginning of the test consisted of setting the value of open circuit potential E_{OCP} . Then, anodic polarization curves were recorded. The measurements started with a value for the potential $E_{\text{INIT}} = E_{\text{OCP}} - 100$ mV. The potential change was in the direction of the anode at a rate of 1 mV/s. When the anode current density reached $i = 1$ mA/cm²

TABLE 1

The chemical composition of the stainless steel selected for the research

Material	Standard	Mass concentration, %							
		C	Si	Mn	P	S	Cr	Mo	Ni
Stainless steel	ISO	0.030 max.	1.0 max.	2.0 max.	0.025 max.	0.01 max.	17.0	2.25	13.0
	÷						÷	÷	
	2007	19.0	3.0	15.0					
	control analysis	0.022	0.59	1.67	0.015	0.001	17.5	2.75	14.25

direction of polarization was changed (the return curve was recorded) [12-16].

As part of the electrochemical impedance spectroscopy research, impedance spectra were determined and the obtained data were fitted to the equivalent circuit. On this basis, values of resistance R and capacitance C of the analyzed systems were determined. Impedance spectra of the analyzed system were presented in the form of Nyquist diagrams for different values of frequency and in the form of Bode diagrams. The obtained spectra were interpreted, after fitting by least squares method, to the replacement of the electrical system. The choice of this method allowed to characterize the impedance of steel - surface layer - solution interface by approximation of the impedance data with the use of the equivalent circuit model. Testing of the electrochemical properties was carried out in the Ringer's solution at the temperature of $37 \pm 1^\circ\text{C}$ using the AUTOLAB PGSTAT 302N measuring system equipped with the FRA2 module [14].

One of the physicochemical properties determining quality of material is its wettability. This is a feature that affects the degree of absorption and aggregation of the material. This is connected with the physical phenomena occurring on its surface, mainly the surface energy, the size of which determines rate and extent of aggregation factors such as bacterial plaque, hydrophobicity or hydrophilicity of the material. The degree and time, in which the material absorbs moisture, has a large influence on the strength of implants and protection of patients against the risk of the formation of inflammation. Therefore, the final stage of the study included the wettability of the prepared samples. The aim of such study was to determine the size of the contact angle. In the case where the angle is $< 90^\circ$, it is assumed that the material is hydrophilic, and when the angle is $> 90^\circ$, the material is hydrophobic [24, 25]. The studies were conducted on the Surfens Universal goniometer using Surfens 4.3 in the automatic mode for samples with various methods of surface modification - Fig. 2. Prior to the testing, the samples were subjected to washing in the Bandelin Sonorex Digitec ultrasonic washer and then dried. The prepared samples were placed on a table under the dispenser. The dispenser was filled with distilled water. The volume of droplet dispensed for each sample was 2 nm^3 . Prior to testing, calibration was performed using markers. 20 seconds after dispensing the drop on the sample, the measurement was carried out, which lasted 60 seconds. The measurement was recorded every 1 s - Fig. 2b

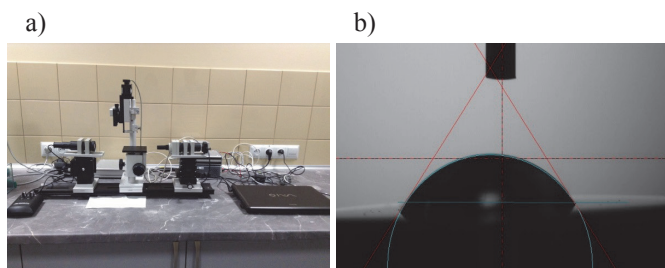


Fig. 2. Contact angle measurement: a) the Surfens Universal goniometer, b) example picture of contact angle measurements

3. Results and discussion

In the first place, measurements of the Vickers hardness on the longitudinal and transverse samples at the load of $F = 9.81 \text{ N}$ were performed. It was found that the hardness on the longitudinal and transverse samples was similar, which means that the material was uniformly hardened. The hardness of a metallic substrate made of stainless steel (316LVM) was in the range of 333 - 375 HV1. In the study of mechanical properties the adhesion test by means of scratch test was also conducted. To assess the value of the critical force, the record the changes of acoustic emission signals, the friction force and the coefficient of friction was applied as well as microscopic observations made on an optical microscope, which is an integral part of the Platform. The obtained results indicate a low adhesion of the Al_2O_3 layer to the stainless steel substrate. On the basis of the obtained results, it was found that regardless of the applied surface treatment the values of critical force causing delamination of the layers was similar and was equal to $L_{c3} = 3.80 \text{ N}$ (for the polished sample with the Al_2O_3 layer) and $L_{c3} = 3.81 \text{ N}$ (for the polished and passivated sample with the Al_2O_3 layer) respectively - Fig. 3 [12-14]. Regardless of the substrate material during the test the acoustic emission signal was not recorded which indicates that the energy of the bond between the coating and the substrate was too low.

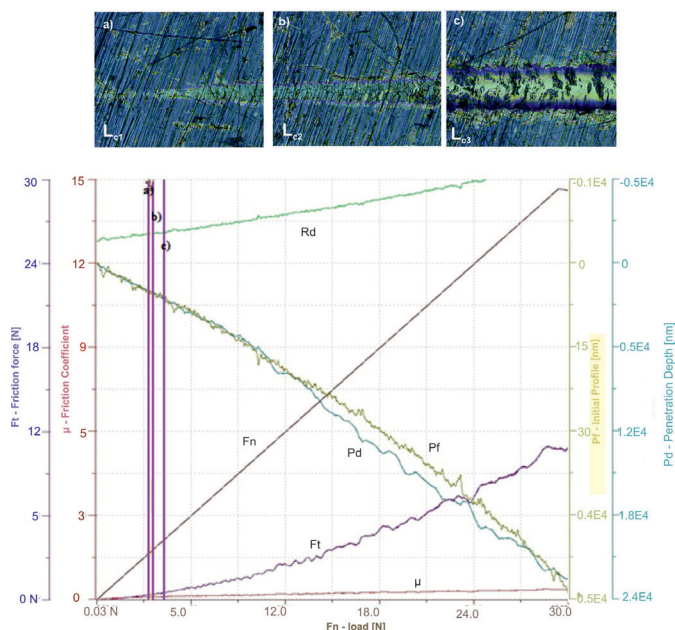


Fig. 3. Example results of adhesion of the polished, passivated and Al_2O_3 coated sample: L_{c1} - crack, b) L_{c2} - delamination, c) L_{c3} - complete break

The next step was to study the surface roughness of the surface formed by the successive stages of surface treatment. It was found that the mean of the R_a parameter after polishing was $0.08 \mu\text{m}$. Chemical passivation process did not affect the change in surface roughness. On the other hand, for the samples after the combined process of polishing, chemical passivation, and deposition of Al_2O_3 layer, the surface roughness increased and equaled $0.13 \mu\text{m}$ - Fig. 4.

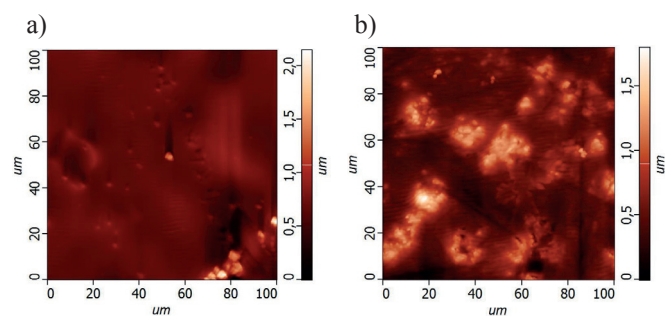


Fig. 4. AFM images of stainless steel a) without layers b) with Al_2O_3 layers

Further studies were aimed to evaluate the electrochemical properties of the prepared samples in which potentiodynamic and impedance research was conducted. First, the test was conducted by recording potentiodynamic anodic polarization curves. The tests were performed on samples with various methods of surface preparation. On the basis of the obtained results (Table 2), it was found that the processes of polishing and chemical passivation as well as the above mentioned combined with deposition of Al_2O_3 layer were beneficial to corrosion resistance of the stainless steel – Fig. 5

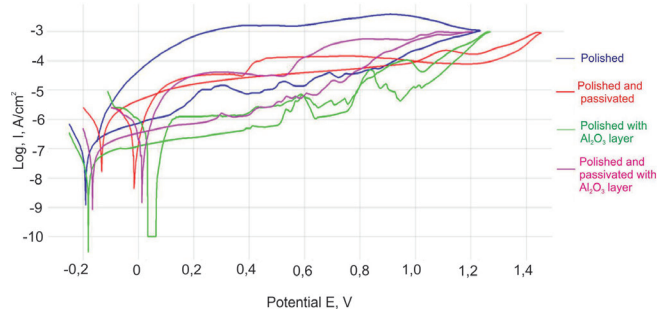


Fig. 5. Curves of anodic polarization of samples after different surface modification

The impedance study for the samples with various methods of surface preparation showed the presence of a double layer with different values of charge transfer resistance R_{ct} . These values equaled: $R_{ct} = 1452 \text{ k}\Omega\text{cm}^2$ for the polished samples, $R_{ct} = 1785 \text{ k}\Omega\text{cm}^2$ for polished and passivated samples, $R_{ct} = 2644 \text{ k}\Omega\text{cm}^2$ for the polished samples with the Al_2O_3 layer - Table 3. The appearance of this layer is the result of a chemical reaction which was caused by the impact of the Ringer's solution at the modified surface of the steel. The best fit of the model spectra to the

TABLE 2

Results of corrosion resistance

Corrosion parameters	Polished sample	Polished and passivated sample	Polished sample with ALD layer	Polished and passivated sample with ALD layer
E_{cor} [mV]	-187.6	-128	-177	-163
R_p [$\text{k}\Omega\text{cm}^2$]	177.7	236	222.3	605
E_B [mV]	1040	1360	1170	930
i_{cor} [$\mu\text{A}/\text{cm}^2$]	0.15	0.11	0.12	0.04

TABLE 3

EIS analysis results

Sample	R_s , Ωcm^2	R_{ct} , $\text{k}\Omega\text{cm}^2$	CPE _{dl}		C_d , μF	R_p , $\text{k}\Omega\text{cm}^2$	CPE _p		C_p , μF
			Y_{dl} , $\Omega^{-1}\text{cm}^{-2}\text{s}^{-n}$	n_{dl}			Y_p , $\Omega^{-1}\text{cm}^{-2}\text{s}^{-n}$	n_p	
Polished	58	1452	0.5463e-5	0.77	-	15.41	0.1632e-4	0.71	--
Polished and passivated	5	1785	0.4182e-4	0.78	-	145.01	0.2091e-4	0.76	--
Polished with Al_2O_3 layer	57	2644	0.4923e-5	0.68	-	6.14	0.7869e-5	0.70	--
Polished and passivated with Al_2O_3 layer	56	2663	0.5113e-5	0.62	-	248.80	-	-	66.8

TABLE 4

Results of Θ contact angle measurements

Measurement	Polished sample	Polished and passivated sample	Polished sample with Al_2O_3 layer	Polished and passivated sample with Al_2O_3 layer
	Θ [°]			
Mean	65.70	62.15	68.32	59.77
Maximum value	67.00	63.38	69.83	61.15
Minimum value	64.38	60.87	66.76	58.35
Standard deviation	0.7733	0.7302	0.9161	0.8311

impedance spectra was observed for the sample subjected to the polishing, passivation and deposition on Al_2O_3 layer – Fig. 6. Based on the obtained results the highest charge transfer resistance of the analyzed samples was equal to $R_{ct} = 2663 \text{ k}\Omega\text{cm}^2$.

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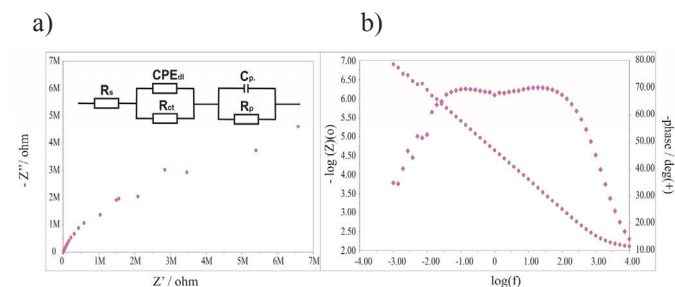


Fig. 6. Examples of impedance spectra obtained for the polished and passivated samples with Al_2O_3 layer: a) Nyquist diagram, b) Bode diagram

The last conducted study was the measurement of the contact angle. The study was conducted for samples with various options of surface preparation. On the basis of the obtained results it was found that chemical passivation slightly affected the reduction of the Θ contact angle. In addition, the beneficial reduction of the Θ contact angle for the samples subjected to the process of polishing, passivation and the deposition of the Al_2O_3 layer was also observed. The proposed surface treatment has a positive effect on the osteoconductive properties of the biomaterial – Table 4.

4. Conclusions

The obtained results of the study showed clearly that the proposed way of surface treatment including: mechanical polishing, chemical passivation and deposition of Al_2O_3 layer by means of the ALD method effectively improves the corrosion resistance of stainless steel. This is confirmed by both potentiodynamic and impedance research – Tables 2 and 3, Figures 5 and 6. For the mentioned surface treatment the lowest contact angle in relation to the initial state was also observed – Table 4. The decrease of the contact angle has a positive effect on the osteoconductive properties of the analyzed biomaterial. Appropriate surface treatment option using the ALD method has a promising significance and will contribute to the development of the technological deposition conditions of oxide coatings on implants used in bone surgery.

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