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SURFACE MODIFICATION OF IMPLANTS FOR BONE SURGERY

MODYFIKACJA POWIERZCHNI IMPLANTÓW ORTOPEDYCZNYCH

The study discusses the methods of surface modification methods for AISAI 316 L steel and Ti6Al4V ELI titanium alloy, dedicated to complex design implants used in bone surgery. Results of structural tests have been presented along with those evaluating the physicochemical properties of the formed surface layers. Clinical feasibility of the surface layers has also been evaluated.

The developed surface modification methods improved the resistance to pitting, crevice and stress corrosion and ensured better biocompatibility. Moreover, the layers formed are marked by plasticity. Results of the tests performed show applicability of the evaluated methods of surface modification in complex shape implants for the clinical use.

Keywords: AISI 316L stainless steel, Titanium alloy Ti6Al4V, Surface layer, Corrosion and wear resistance, Biocompatibility.

W pracy omówiono metody modyfikacji powierzchni stali AISAI 316 L oraz stopu tytanu Ti6Al4V ELI przeznaczonych na implanty o złożonej konstrukcji stosowanych w chirurgii kostnej. Przedstawiono wyniki badań struktury oraz własności fizykochemicznych wytworzonych warstw wierzchnich. Określono również przydatność wytworzonych warstw do zastosowań klinicznych.

Opracowane metody modyfikacji powierzchni zwiększyły odporność na korozję wżerową, szczelinową i naprężeniową oraz poprawiły biokompatybilności. Ponadto wytworzone warstwy cechują się podatnością do odkształceń. Wyniki badań wykazały przydatność zastosowanych metod modyfikowania powierzchni implantów o złożonych kształtach do zastosowań klinicznych.

1. Introduction

Metal based biomaterials continue to dominate among the surgical implants used in orthopaedics and traumatology, bony face surgery dentistry and endovascular surgery [1-5].

In order to select relevant properties of a metal biomaterial dedicated to perform a given function, the following decisive factors are taken into account: design of an implant, surgical procedures used for particular tissue lesions, duration of use as well as the biomechanical properties of the reconstructed tissue and their physicochemical characteristics. The most complex issues are those regarding selection of mechanical and physicochemical properties of implants used for reconstruction of the osteoarticular system.

There are still certain obstacles preventing a comprehensive consideration of relations between the mechanical factors of bone remodeling and the type and value of stress needed for

remodeling, ensuring long-term therapeutic effect. An major issue is also the quality of the implant surface layer. Studies carried out by the leading research centres are focusing now on modification of the implant surface with layers or coats adhering well to the metallic base, deformable during preoperative modeling and ensuring plastic, cyclic deformation upon use. The surface of the biomaterial should show high resistance to different types of corrosion (pitting, crevice, stress, wear) as well as biocompatibility. Such properties are ensured by carbon coatings formed on steel AISI 316L implants. The coatings are obtained with the use of a variety of technologies so that consequently their structure and properties may be shaped. We differentiate between hydrogen carbon coatings (a-C:H) and hydrogen free ones (a-C). The latter are obtained through magnetron sputtering, arch sputtering or laser ablation. The carbon coatings, on the other hand, are produced by decomposition of hydrocarbons through PACVD procedures. Depending on the production

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parameters of DLC layers, the following may be distinguished within a-C:H structures: diamond, graphite or $\text{CH}_n = 1,2,3$ polymer groups. Their shares determine the ultimate properties of the coatings [6-12].

On the other hand, modifications on the surface of titanium alloy implants are accomplished through anodization which makes it possible to produce oxide films of different thickness and morphology as well as beneficial physicochemical properties, in particular when with the dominating share of TiO_2 [13-17]. New implant surface modification technologies have recently been implemented to ensure highly favourable physicochemical properties and biocompatibility with the cardiovascular system. Worth mentioning are, plasma oxynitriding or nitriding and nitriding or carbonitriding accomplished through pulsed laser deposition [18,19]. Glow discharge technologies, based on both, plasma and cathode potential, ensure surface layers of diffusive character with the outer zone of nanocrystalline TiN , or TiO_2 .

An original technology to modify the surface of biomaterials, including those on the titanium base, highly applicable for the cardiovascular implants, is the low-temperature hybrid laser technology [20-24]. Coatings produced in this way may contain DLC, TiN , $\text{Ti}(\text{C},\text{N})$, SiDLC and TiDLC phases. Such coatings were shown to have favourable properties in terms of their antithrombogenic properties, effect upon blood morphogenetic factors and the immunological system.

The surgical procedures recommended for bone fractures demand, if needed, the selection of identical structural shape of the fixators, made however of alternative biomaterials, tailored to individual reactivity of a patient. A biomaterial applied should show comparable biochemical properties to ensure comparable biomechanical quality of fixation within the bone-implant scheme. Taking into account varied chemical composition of the biomaterial, the surface topography and modification should be accomplished in a way to minimize the peri implant reaction associated with initiation and development of corrosion. The course of the corrosive process, different for individual areas of fixation, needs to be preceded by evaluation of stress, deformation and displacement of the fixator elements [25-29]. The complex shape of the surface of implants, components of bone fixators demands such surface processing methods which would ensure homogenous and comparable physical and chemical conditions.

The study presents results of evaluation of the effect of modification of surface of implants used in bone surgery, made of AISI 316L steel and Ti6Al4V ELI titanium alloy, upon their physicochemical properties.

2. Material and methods

The study used AISI 316L steel in strengthened state ($R_m = 1036 \text{ MPa}$, $R_{p0.2} = 827 \text{ MPa}$, $A_5 = 19\%$). The structural quality complied with the requirements of ISO 5832-1 standard. Ti6Al4V ELI alloy was also in strengthened state ($R_m = 960 \text{ MPa}$, $R_{p0.2} = 870 \text{ MPa}$, $A_5 = 16\%$). The dual phase structure of $\alpha + \beta$ alloy met the requirements of ASTM F 136-08e1 standard.

The implants made of AISI 316L steel were electrolytically polished in the solution of sulphuric acid, phosphoric acid, acetanilide, glycerine, oxalic acid and corrosion inhibitors to achieve roughness $Ra \leq 0,16 \mu\text{m}$ and the surface was next passivated in the nitric acid solution. During the following stage the passive layer was coated with a carbon film, making use of radio frequency plasma assisted chemical vapour deposition (RF PACVD) process in CH_4 atmosphere [30].

In order to evaluate the structure and properties of the surface layers, the first stage of the study comprised tests of the mechanical properties of the base materials, making use of Criterion 45 testing machine by MTS. Moreover, film adhesion was evaluated through a 'scratch test' with the use of CSEM Revetest device. Nanohardness and the surface Young modulus were measured on a platform furnished with Nanoindentation Tester by CSM. Microstructures were evaluated with the use of Zeiss Axio light microscope, Observer Z1m and the transmission high-resolution electron microscope JEM 3010 by EOL. High-resolution images were edited with Digital Micrograph software. Auger and Raman surface spectroscopy used a spectrometer by Varian. For XPS spectroscopy a multifunctional electron spectrometer PHI 5700/660m by Physical Electronics was used, ensuring Al K α monochromatic radiation of 1486,6 eV energy. Topographic examination of the modified surfaces were carried out with the use of atomic force microscopy (AFM) during a contact operation mode of NTegra Spectra unit by NT-MDT as well as Supra 35 scanning electron microscope by ZEISS. Structural evaluation of the layers was performed before and after the corrosion tests. Resistance to pitting and crevice corrosion was defined by the potential dynamic array method as per PN-ISO 10993-15 and ASTM F 746. The potentiostat used was PGP201 by Radiometer with calomel reference electrode while the supporting one was a platinum electrode. The tests were performed in Ringer physiological solution at the temperature $37 \pm 1^\circ\text{C}$ with $\text{pH} = 6.8-7.4$. Steel resistance to crevice corrosion of the implants was tested taking into consideration different condition of the prepared surface. The carbon film thickness was measured by ellipsometric spectroscopy.

Steel resistance to stress corrosion was tested in the inert environment – glycerine, and in the corrosive one – Ringer solution. The test was performed through extension of the samples at the constant rate of $4.95 \times 10^{-3} \text{ mm/min}$. The assumed steel resistance criteria were K_σ and K_τ indices, corresponding respectively to the ratio of maximum tensile stress $\sigma_{k\text{max}}$ in the corrosive environment to the maximum tensile stress $\sigma_{0\text{max}}$ in the inert environment and the time ratio before breaking of the sample in the corrosive environment τ_k and in the inert one τ_0 . Fractography of the implants' surface after the tests was carried out with the use of a scanning electron microscope.

Corrosive resistance was also tested for the implants bent at the angle ranging between 10° and 90° , on cylinders of 20, 30, 40, 60 and 80 mm in diameter. Implants made of AISI 316L steel were also biologically evaluated "in vivo" in pre-clinical and clinical conditions, while evaluation of Ti6Al4V ELI alloys was performed "in vitro".

3. Results

The developed method of electrolytic polishing and chemical passivation of implants of AISI 316L steel ensures roughness $Ra \leq 0,16 \mu\text{m}$, with the original value of $Ra = 60\text{-}40 \mu\text{m}$. Such method of polishing and passivation [31] ensured also intensified digestion of iron and nickel from the surface layer. Consequently, the structures of the passive layer, within the thickness range 12-15 nm, showed elevated concentration of chromium, by approx. 4.8%, and molybdenum, by approx. 2.3%, as compared to the base concentration of the elements. Chromium was present mainly as Cr_2O_3 and CrO_2 , while molybdenum in the form of MoO_2 and MoO_3 . Observation of the layer structure with the use of high-resolution transmission electron microscope, showed some 4-8 nm nanocrystals in the amorphous structure. Analysis of the nanocrystalline phase was performed through Fourier transform images. On this basis individual crystallites of the oxide phase were identified – Fig. 1. Good corrosive resistance of steel was achieved. At the mechanically polished state the corrosive potentials E_{cor} ranged between $-140 \div -110 \text{ mV}$, while the breakthrough potential E_b ranged between $+390 \div +457 \text{ mV}$. Following polishing and passivation in the given conditions, the potentials increased as follows: $E_{cor} = -16 \div +37 \text{ mV}$ and $E_b +943 \div +1020 \text{ mV}$. Polishing in the traditional electrolyte on the basis of $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{CrO}_3$ allows only for $E_{cor} = -40 \div -60 \text{ mV}$ and $E_b = +560 \div +650 \text{ mV}$ – Fig. 2. A passive layer, enriched with chromium and molybdenum, on the steel surface, appears also as a favourable base for carbon coating through RF PACVD.

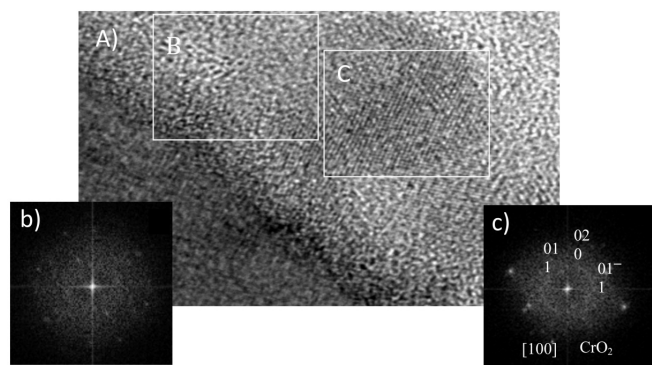


Fig. 1. Structure of the passive layer – cross-section: A – microscopic image of the structure, b – Fourier transform for the amorphous phase area B, c – Fourier transform for the crystalline area C

The DLC-passive coating adhered well to the steel base. The “scratch test” pointed to the average value of force effecting in destruction of the layer, reaching $F_c = 114.6 \text{ N}$. The coat thickness ranged between 40 and 60 nm, nanohardness was 474 HV and Young modulus 705 GPa.

The DLC coat structure shows different crystallinity degrees. The upper part of the coating was composed of areas of coherent scattering. Those were areas of nanocrystalline and amorphous phase. Down towards the base material the share of the crystalline phase was.

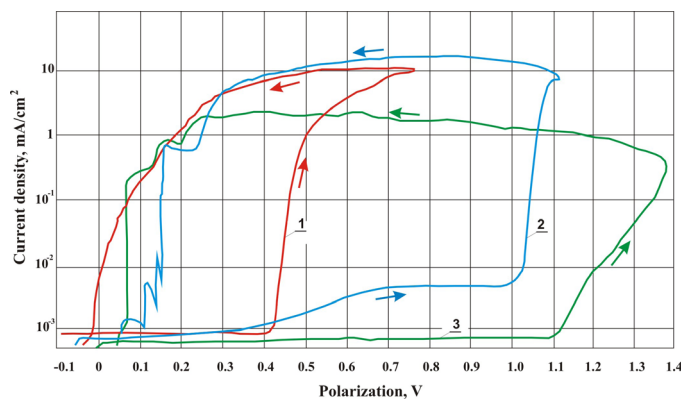


Fig. 2. Anodic polarization curves for AISI 316L steel implants in Ringer solution: 1 – ground surface, 2 – electrolytically polished and passivated surface, 3 – electrolytically polished, passivated surface with DLC coating

In the coating structure, Raman spectroscopy pointed to phase type sp^3 (diamond with wavenumber $\nu = 1356 \text{ cm}^{-1}$) and type sp^2 (graphite with wavenumber $\nu = 1591.7 \text{ cm}^{-1}$). The peak intensity quotient for both phases J_D/J_G was 0.98.

XPS examination of the coating determined its chemical composition. Evaluation of the deep seated profile showed that preliminary etching caused no significant changes in the composition of the passive layer, prepared throughout electrolytic polishing and chemical passivation. The obtained thin passive-DLC coating, showing favourable amorphous and nanocrystalline structure and good adhesion to the steel base, also offers very good properties. The coating has even greater potentials, with the corrosive one $E_{cor} = +60 \text{ mV}$ and breakthrough potential $E_b = +1160 \text{ mV}$.

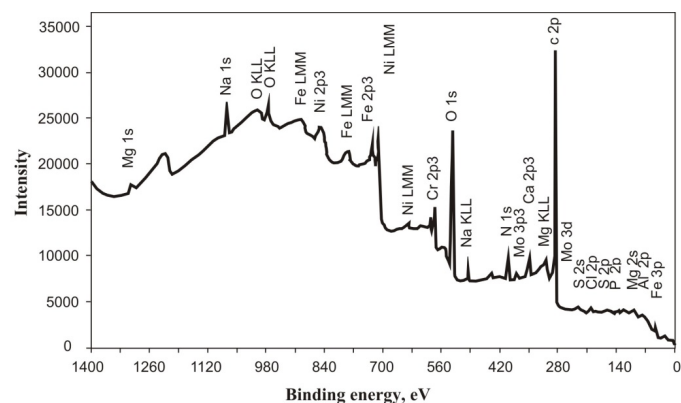


Fig. 3. XPS spectrum of passive-DLC coating on AISI 316L steel surface

Such passive-DLC coating is highly deformable, preventing decohesion and preserving resistance to pitting, crevice and stress corrosion in Ringer solution. Moreover, implants with replaceable coating maintain plasticity up to considerable deformations. This has been proved by stable values of corrosive potentials before and after deformation and lack of any corrosive damages on the implant surface.

Susceptibility of passive-DLC coatings to sterilization was tested as in clinical conditions, i.e. in an autoclave and with

saturated water steam at 121°C, during 20 minutes. Evaluation comprised the presence of both, aerobic and anaerobic bacteria. Bacteriological tests pointed to no changes in corrosive potential of the implants or in the surface quality. Sterilization of the implant surface protects successfully against the development of bacterial flora. Final verification of quality and evaluation of usefulness of the implant coating was performed “in vitro” and “in vivo” upon pre-clinical and clinical tests [32,33]. No reactive complications or general body reactions were observed.

The elements of Ti6Al4V ELI alloy implants were modified with different preparation options: preliminary (grinding, tumbling, mechanical polishing, sandblasting), electrochemical (electrolytic polishing) and final (anodic oxidation, steam sterilization) [34].

The produced surface layers differ in colour, depending on the applied voltage of anodic oxidation and on the geometrical structure of the surface – Fig. 4.

Susceptibility to degradation of the outer layers of Ti6Al4V ELI implants was evaluated through the measurement of resistance to pitting and crevice corrosion and the measurement of the number of metal ions penetrating the solution after 28 days of storage in Ringer solution [35-40].

Polarization curves are different after different surface modification procedures – Fig. 5. Anodic oxidation and sterilization following directly the mechanical processing are marked by the absence of hysteresis loop, regardless of the anodic oxidation voltage – Fig. 5, curve I. This points to the effective passivation of the implant surface. On the other hand, implants subjected to anodic oxidation after electrolytic polishing are marked by the hysteresis loop and the repassivation potential E_{rep} , regardless of the voltage – Fig. 5, curve II. The alloy is prone to pitting corrosion, as proved by microscopic observation – Fig. 6. Such course of the polarization curves was observed for both, the sterilized samples as well as those sterilized and stored for 28 days in Ringer solution.

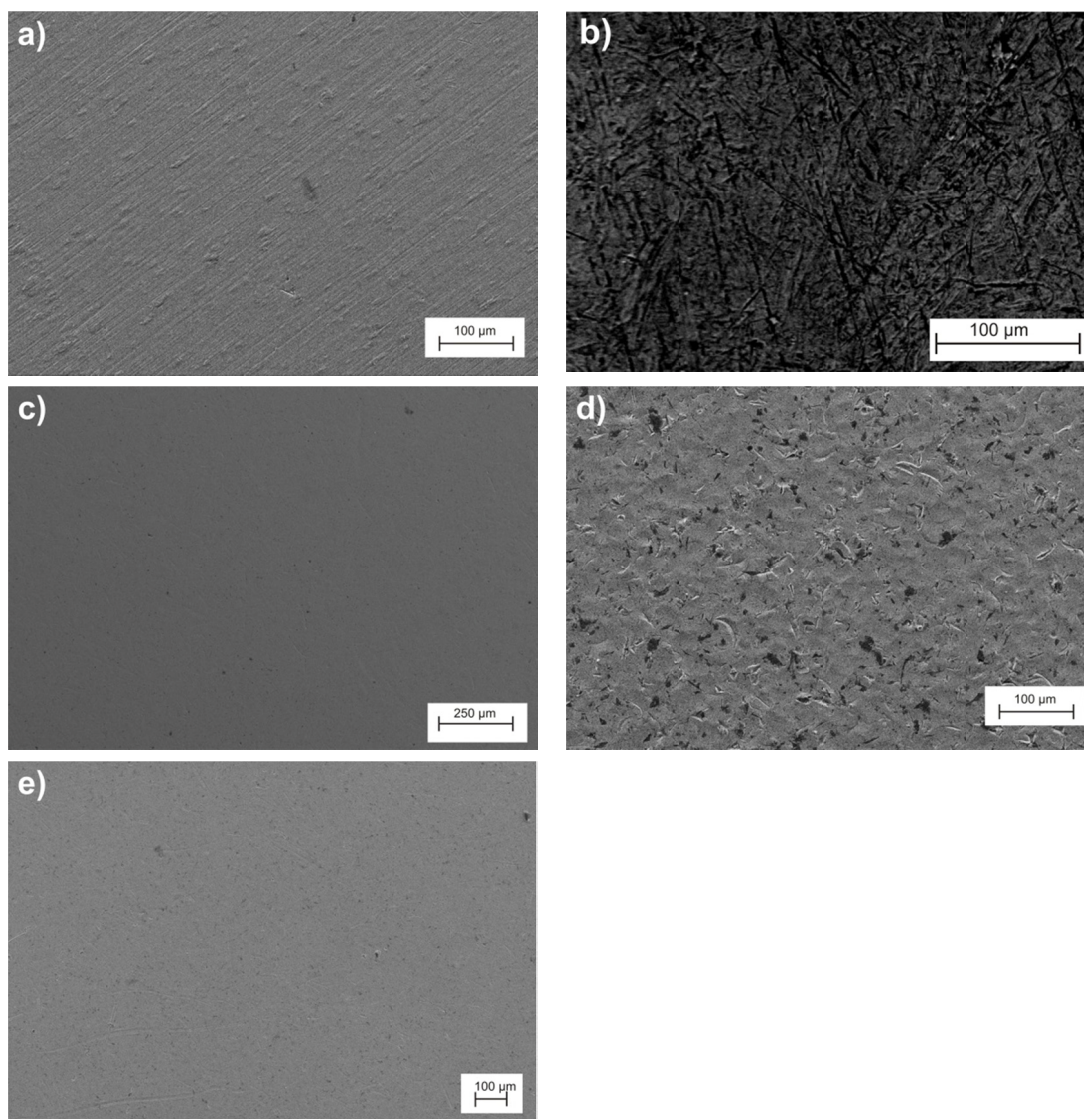


Fig. 4. Surfaces of implants of Ti6Al4V ELI alloy after: a) grinding, b) grinding, tumbling, c) grinding, tumbling, mechanical polishing, d) grinding, tumbling, mechanical polishing, sandblasting, e) grinding, tumbling, mechanical polishing, sandblasting, electrolytic polishing, SEM

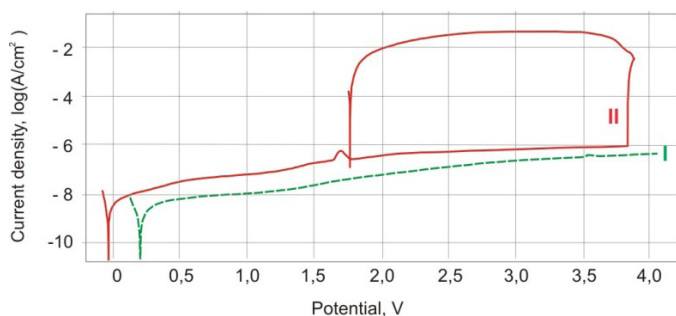


Fig. 5. Characteristic polarization curves for Ti6Al4V ELI alloy samples, I – samples anodized and sterilized after machining, II – samples anodized and sterilized after electropolishing

cessing [39–42]. Moreover, passive layers formed on the base of Ti6Al4V ELI alloy show good hydrophilous properties (wetting angle of about 63°). Studies carried out by other authors [43–45] showed that such surface layers ensure good osteoconductive properties of the implants.

Distinguished in the structures of the formed layers was mainly TiO_2 as well as oxides of the alloy elements and the phosphorous oxide. Aluminium was usually present in the form of Al_2O_3 , the share of which was reduced along with the growing distance from the surface, while concentration of the metallic aluminium increased. Phosphorous, introduced to the passive layer during anodic oxidation, was present on the layer

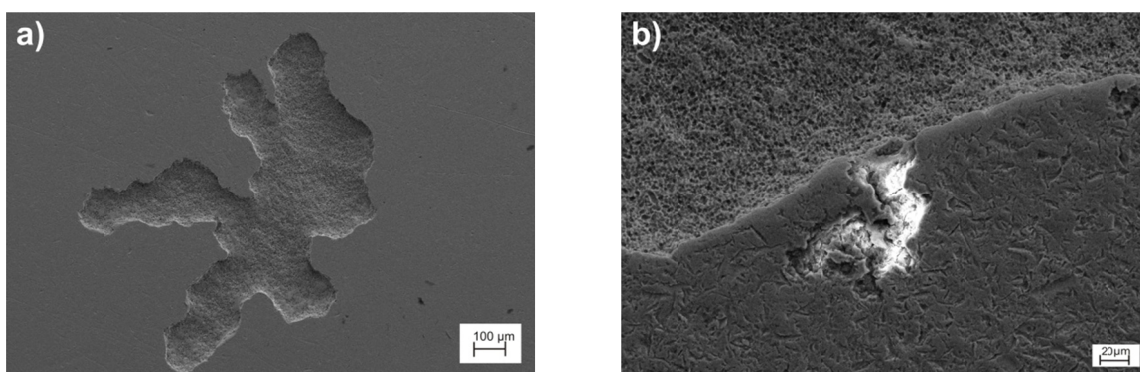


Fig. 6. Surface corrosive damage of Ti6Al4V ELI alloy samples after anodic oxidation and sterilized after electrolytic polishing preceded by mechanical polishing, SEM

Evaluation results showed resistance to crevice corrosion, regardless of the methods of modification of the outer layers, on the base of Ti6Al4V ELI alloy.

Measurements of metal ions concentration penetrating from the alloy modified surface showed that their type and concentration depend on the initial method of modification of the surface layer, preceding anodic oxidation and sterilization. Strengthening of the layer through sandblasting has a favourable effect, reducing the number of ions diffusing into the solution. Moreover, it was shown that concentration of ions diffusing into the solution decreases along with the growing anodic oxidation voltage and current [39].

Topographic examination of the surface layers showed its relations to the initial surface modification methods. The greatest roughness was observed in surfaces which were subjected to anodic oxidation and sterilization following sandblasting and electrolytic polishing ($R_a = 310$ nm), while the lowest score was observed in the surface layers after mechanical polishing, electrolytic polishing, anodic oxidation and sterilization ($R_a = 111$ nm). It was also noted that regardless of the preliminary processing method employed prior to anodic oxidation and sterilization, the increase in anodic oxidation voltage (from 57 V to 97 V), effects in the increased thickness of the passive layer, by about 80 nm. Electrolytic polishing performed before anodic oxidation and sterilization allows for thicker passive layers, as compared to anodic oxidation and sterilization preceded by mechanical pro-

cessing in the form of phosphates, while in the oxidized layer it appeared as phosphides.

Evaluation of the deep seated profiles showed differentiation of their chemical composition, depending on the initial modification procedures [39]. Sandblasting of Ti6Al4V ELI alloy, before anodic oxidation and sterilization, produces surface layers showing no presence of vanadium – Fig. 7.

It appeared however in the passive layer in the form of V_2O_3 oxides, while deeper into the layer it showed a metallic form. The use of electrolytic polishing prior to anodic oxidation and sterilization effects in introduction of phosphorous to the greater depth, as compared to the layers after sandblasting. Moreover, it was observed that long time storage of titanium alloy with modified surface layer in Ringer solution effects in the increased thickness of the passive layer – Fig. 7.

The most favourable properties are shown by a surface layer obtained through grinding, mechanical polishing, sandblasting, anodic oxidation at 97 V and steam sterilization. No vanadium is observed on the surface, neither on the implants following sterilization, nor after storage in Ringer solution. Al_2O_3 oxides are present on the surface only after storage in the solution.

The fixators have also been subjected to cyclic loading ($n = 1000$) within the range of physiological as well as long term exposure to a corrosive environment. Macroscopic examination of the fixator element surfaces, following exposure to a corrosive environment, showed some minor mechanical damage.

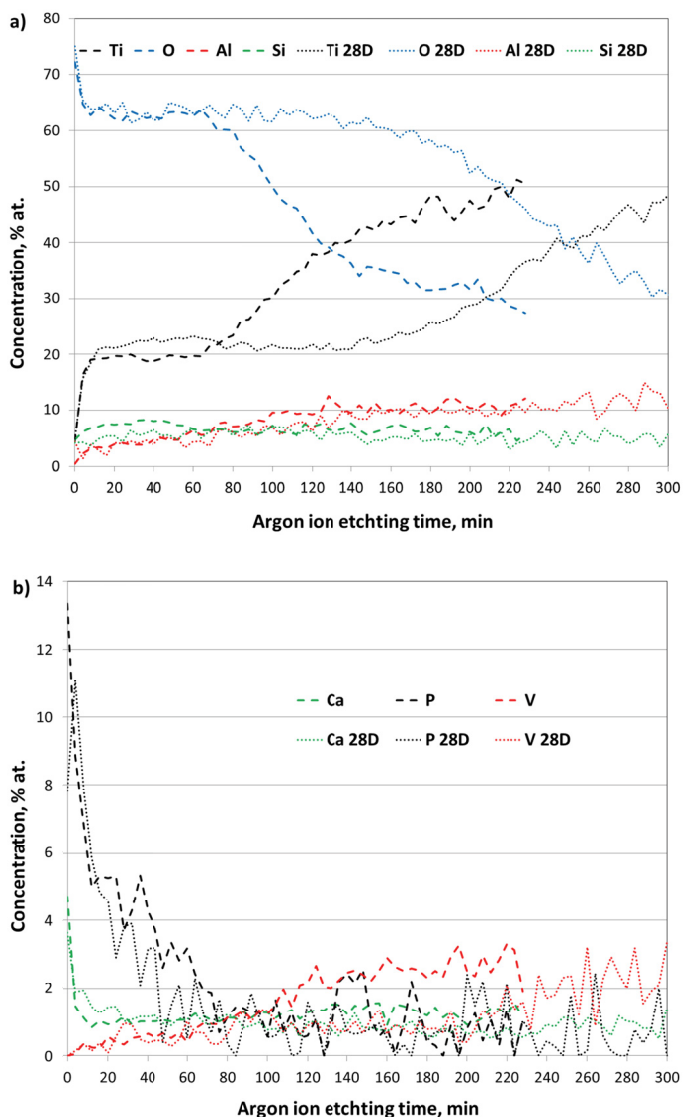


Fig. 7. Chemical composition profile of the outer layer on the base of Ti6Al4V ELI obtained through grinding, mechanical polishing, sandblasting, anodic oxidation and steam sterilization. Starting point and after 28-day exposure to Ringer solution (28D), a) Ti, O, Al, Si, b) Ca, P, V

Their location and character indicate that they occurred upon implantation procedure or during cyclic loading. The damaged surfaces were repassivated which was proved by the absence of corrosive damage. This means that the developed method for surface processing of implants of different size and shape is useful in clinical applications. The outer layers formed on the implants ensure high stability of fixation and susceptibility to elastic deformation throughout rehabilitation. This ensures proper conditions for the bone tissue repair and activation through the electromechanic effect. The coating performs as the protective barrier, preventing corrosion of the implants and minimizing the risk of reactive complications caused by degradation products.

The outer layer formed on the base of titanium alloys shows no cytotoxic effect [39]. No changes have also been observed in morphology or organization of cells incubated with extracts of titanium alloy with the modified outer layer. The most favourable properties of the outer layer are obtained as the result of

grinding, mechanical polishing, sandblasting, anodic oxidation at 97 V and steam sterilization.

4. Conclusions

The developed method of producing passive-DLC coatings through dual stage electrolytic polishing, chemical passivation and RF PACVD offers coating of different shapes of implants made of AISI 316L steel. Such layers, with amorphic-nanocrystalline structure, adhere well to the metallic base, are deformable, show high resistance to pitting, crevice and stress corrosion and are biocompatible. Usefulness of the applied technologies for implant surface modification has been proved throughout the test procedures, designed to meet recommendations of the valid standards for “in vitro” and “in vivo” procedures.

Quality of the final physicochemical properties and biocompatibility of Ti6Al4V ELI implants are determined by mechanical processing preceding anodic oxidation and sterilization. Among the evaluated options for modification of the outer layer on the base of implants of different geometrical patterns, most favourable properties are shown by an outer layer obtained through grinding, mechanical polishing, sandblasting, anodic oxidation at 97 V and steam sterilization.

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