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Electrochemical investigations of Ti6Al4V and Ti6Al7Nb alloys used on implants in bone surgery

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Materials

ABSTRACT

Purpose: The subject of the research work is an analysis of surface roughness impact and the influence of the steam sterilisation process on physicochemical properties of samples made of Ti-6Al-4V and Ti-6Al-7Nb alloys after their exposure in a solution simulating the osseous environment.

Design/methodology/approach: A surface roughness diversification of the samples made of Ti alloys was obtained with the aid of mechanical working – grinding and with the use of mechanical polishing. A corrosion resistance test was performed based on an anodic polarization curves recording. An Electrochemical Impedance Spectroscopy (EIS) method was used as well for assessment of the effects which occur on the surface of the examined alloys.

Findings: The potentiodynamic studies showed favourable influence of steam sterilisation process (in an autoclave) on corrosion resistance of Ti alloys, regardless of the applied mechanical treatment. Exposition of the samples in Ringer' solution caused further increase of corrosion resistance only for Ti-6Al-7Nb alloy. Analysis of impedance spectra showed presence of the capacitive passive layer for all tested variants.

Research limitations/implications: Obtained results of potentiodynamic studies showed how a physicochemical condition of the samples surface, exposed to the solution simulating osseous system environment, was changing. In order to determine properties fully and surface structures of the Ti-6Al-4V and Ti-6Al-7Nb alloys after the sterilisation and the 60-day exposure to Ringer' solution, impedance characteristics, obtained by means of EIS were determined. Differences of parameters describing electrical properties of the layers formed after the exposure to Ringer' solution, are probably caused by a change of their chemical composition.

Originality/value: The potentiodynamic and EIS studies of corrosion resistance in Ringer' physiological solution allow to predict behaviour of Ti-6Al-4V and Ti-6Al-7Nb implants in osseous system environment.

Keywords: Biomaterials; Ti alloys; Corrosion resistance; Electrochemical Impedance Spectroscopy (EIS)

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1. Introduction

Attempts, when titanium and its alloys in bone surgery were used go back to the nineteen-forties. In the initial period of using Ti alloys there were niggles with their mechanical properties, which were too weak comparing with other metallic materials (mainly in comparison with Cr-Ni-Mo steel and Co alloys) which were used to make surgical implants. Extensive research on these alloys allowed to control the process of forming their structure and as a result, to obtain a more beneficial set of utilization properties. Undoubtedly, technological progress has had an influence, resulting in the good quality of these alloys [1-5].

Lengthy clinical observations of Ti alloy implants used in reconstruction surgery, mainly in reference to their bio-tolerance, placed them in a group of prospective materials for medicine. It should also be emphasized that their specific gravity is less than that of iron- and cobalt-based alloys. This is an additional important advantage of this metallic biomaterial that can be used for implants in an articular alloplasty. Beyond any doubt, the small weight of these medical products increases their comfort of use [1-5].

Titanium alloys are mainly used for the production of endoprostheses, dental implants, as well as for the production of implants used in cardio surgery and cardiology treatment. As a consequence of a continuously increasing population of patients who reveal a susceptibility (allergic response) to Cr and Ni (which are present in the austenitic steel used in the production of implants for osteosynthesis), many manufacturers are alternatively using them in the production of elements used for joining bone fractures, such as intramedullary nails, bone plates, and bone screws [6].

The Ti-6Al-4V alloy is primarily used in bone surgery, however, its chemical constitution is not perfect due to the presence of Al and V. Clinical observations on the biotolerance of endoprostheses made of Ti-6Al-4V alloy have revealed that vanadium generates cytotoxic reactions and finally neurogenic disorders. Moreover, aluminium results in the bones softening and neuron damage, and detrimentally affects the activity and functions of enzymes and neurotransmitters. As a consequence, it affects the brain and blood vessels. Because of this, research has been carried out on new types of alloys, which have vanadium or vanadium and aluminium eliminated, and replaced mainly by niobium, tantalum, or zirconium, for instance: Ti-6Al-7Nb, Ti-6Al-(4-9)Nb, Ti-6Al-(3-6)Nb-(1-6)Ta, Ti-5Al-2.5Fe, Ti-13Nb-13Zr, Ti-35Nb-5Ta-7Zr [1, 2, 7-10].

The structure and thickness of a surface layer play the main role in achieving the final quality of implants made of titanium alloy. There are many ways to form it. The structure and the chemical make-up of the implants' layer, which is made of titanium and its alloys, can be modified using different methods, with the dominant methods being mechanical, chemical, electrochemical, and thermal. In addition to this, the physicochemical properties of the implants' surface can depend on the sterilization method applied in the final production process of the implants [1, 11-18].

Mechanical workings are used for modification of a surface topography. The oxide layer properties are difficult to be controlled after using these methods. The main chemical methods are pickling and passivation, which lead to form a thin (< 10 nm) oxide layer consisting mainly of TiO_2 and oxides of alloy metals, and containing impurities of chemical reagents [19]. The repeatable layers, which can be fully controlled according to thickness, microstructure, and chemical constitution, are obtained using high-temperature treatments, embedding in H_2O_2, alkaline pickling, electropolishing, anodic oxidation, and vacuum processing. In addition, surface engineering offers methods, owing to which layers are obtained that consist of elements not occurring in the base. The make-up and the physicochemical properties of these layers depend on their application and functions [12, 13].

It is possible to create layers with very good adhesion to the base, which are of abrasion resistance and they protect metal against expansion of the corrosion process, as well as layers, which are biologically active. Dominant methods are PVD and CVD. There have been recent developments in implantation methods, including a dual-beam method called Ion Beam Assisted Deposition (IBAD). This method allows obtaining low roughness of surface layers. It is possible to obtain layers consisting of several chemical elements. For good adhesion to the base and the presence of a wide interlayer, the layers produced by this method are deformable [18].

Suitability of a particular modification method of an implant's surface requires a series of tests to be made, both in laboratory and clinical conditions. At the beginning of the research, corrosion tests are carried out in *in vitro* conditions, which simulate the specific tissue environment of the system where the implant is to be inserted [17, 20, 21]. For this reason, an analysis has been carried out in the subject research work on an implant's surface roughness impact and a steam sterilization process impact on the physicochemical properties of Ti-6Al-4V and Ti-6Al-7Nb alloys test pieces after their exposure in the Ringer's solution simulating the osseous environment.

2. Materials and methods

Test pieces of Ti-6Al4V (ISO 5832/3:2007) and Ti-6Al-7Nb (ISO 5832/11:2007) alloys were used in the research. The samples were extracted from bars of diameter d = 8 mm. Both the chemical constitution and the alloys structure met the requirements of ISO 5832-3 and ISO 5832-11 norms – Table 1.

Table 1.
Chemical compositions of investigated metallic biomaterials

Element	Ti-6Al-4V alloy		Ti-6Al-7Nb alloy	
	Acc. to ISO	Ladle analysis	Acc. to ISO	Ladle analysis
	Mass concentration, %			
Al	5.5-6.75	5.95	5.50-6.50	6.24
Nb	-	-	6.50-7.50	6.84
Ta	-	-	max 0.50	0.37
C	max 0.08	0.003	max 0.08	0.08
Fe	0.30	0.150	max 0.25	0.22
H_2	max 0.015	0.003	max 0.009	0.003
V	3.5-4.5	3.96	-	-
N_2	max 0.05	0.004	max 0.05	0.03
O_2	max 0.2	0.114	max 0.2	0.18
Ti	balance	balance	balance	balance

The samples with diversified methods of surface preparation were the subject of the research. The surface roughness diversification was obtained using mechanical working – grinding (Ra_{av} = 0.40 µm) and using mechanical polishing (Ra_{av} = 0.12 µm).

The next step was to put prepared two groups of samples through a steam sterilization process in a Mocom Basic Plus autoclave at a temperature of T = 121°C, pressure of p = 1.1 bar, for the period of t = 30 min. Then, in order to simulate conditions which occur in the tissue environment of the osseous system, the test pieces were exposed in the Ringer's physiological solution at a temperature of T = 37±°C for the period of 60 days – Table 2 [2].

Table 2.
Chemical composition of Ringer's physiological solution [2]

Constituents	Constituents concentration, g/dm^3 distilled water
NaCl	8.6
KCl	0.3
$CaCl_2$	0.243
$NaHCO_3$	0.0125

Afterwards, the samples reflecting successive steps of surface preparation, underwent a pitting corrosion resistance test. The test was performed according to the recommendations of PN-ISO 17475:2008(U). The anodic polarization curves were recorded with a Radiometer PGP-201 potentiostat. A KP-113 type Saturated Calomel Electrode (SCE) acted as a reference electrode, while a PtP-201 type platinum electrode acted as an auxiliary electrode. A potential change of speed was 1 mV/s in an anodic direction. The test was made in a Ringer's solution at the temperature of T = 37±1°C. The Stern method was used to determine the corrosion resistance parameters of the examined alloys.

In order to obtain information about the physicochemical properties of the implants' surface made of Ti-6Al-4V and Ti-6Al-7Nb alloys, a test was carried out using the EIS method. Measurements were made using an Auto Lab PGSTAT 302N measurement system equipped with a Frequency Response Analyser 2 (FRA2). The measurement system made it possible to carry out the test at a frequency range of 10^6 - 10^{-3} Hz. Impedance spectrums of the system were determined during the test and the obtained measurement data were adjusted to an auxiliary system. Numerical values of the analyzed systems' resistance "R" and capacitance "C" were determined based on it. The impedance spectrums of the examined system were presented in a shape of Nyquist diagrams for different frequency values and in a shape of Bode diagrams. The obtained EIS spectrums were interpreted after their adjustment to the auxiliary electric system using a minimum chi-square method.

3. Results

3.1. Results of corrosion tests

The anodic polarization curves determined for the Ti-6Al-4V alloy test pieces analyzed during the working process, with a polished surface (Ra_{av} = 0.40 µm), are shown in Fig. 1.

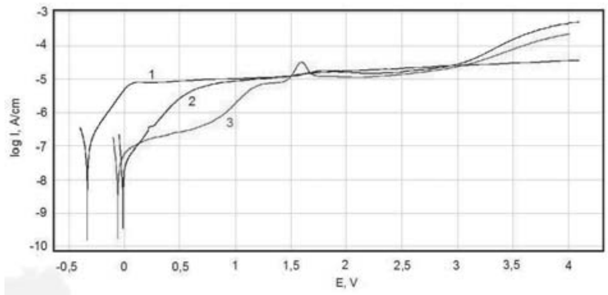


Fig. 1. Anodic polarization curves for Ti-6Al-4V alloy samples of surface: 1 – grinded, 2 – grinded and steam sterilized, 3 – grinded and steam sterilized and exposed in Ringer's solution

Based on the received measurements it was found that an average value of corrosion potential for grinded samples amounted to E_{corr} = -333 mV. The use of the steam sterilization process caused an increase of the corrosion potential average value up to E_{corr} = -11 mV. For the samples which underwent a steam sterilization process and which were exposed in the physiological solution for a period of 60 days, the corrosion potential average value amounted to E_{corr} = -57 mV.

Additionally it was determined, using the Stern method, polarization resistance values Rp and corrosion current density values i_{corr} for particular versions of the samples resulted, correspondingly – Table 3:

- grinded: Rp = 251.7 $k\Omega cm^2$, i_{corr} = 0.103 $\mu A/cm^2$,
- grinded and steam sterilized: Rp = 761.4 $k\Omega cm^2$, i_{corr} = 0.034 $\mu A/cm^2$,
- grinded and steam sterilized and exposed in physiological solution: Rp = 683.4 $k\Omega cm^2$, i_{corr} = 0.038 $\mu A/cm^2$.

The next step of the research work was to determine the anodic polarization curves for particular versions of the samples with mechanically polished surface (Ra_{av} = 0.12 µm) – Fig. 2.

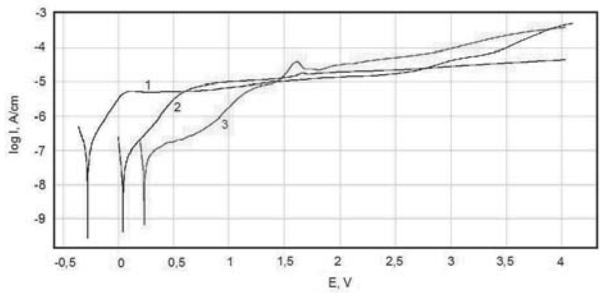


Fig. 2. Anodic polarization curves for Ti-6Al-4V alloy samples of surface: 1 – mechanically polished, 2 – mechanically polished and steam sterilized, 3 – mechanically polished, steam sterilized and exposed in Ringer's solution

The value of the corrosion potential for the samples only through mechanical working averaged E_{corr} = -275 mV. The steam sterilization process caused an increase of the corrosion potential value up to E_{corr} = +48 mV. For the test pieces which were additionally exposed in the physiological solution, the corrosion potential value was E_{corr} = +239 mV.

Determined polarization resistance values Rp and corrosion current density values i_{corr} resulted correspondingly – Table 3:

- polished: Rp = 237.2 kΩcm^2, i_{corr} = 0.110 µA/cm^2,
- polished and steam sterilized: Rp = 552.9 kΩcm^2, i_{corr} = 0.047 µA/cm^2,
- polished and steam sterilized and exposed in physiological solution: Rp = 459.6 kΩcm^2, i_{corr} = 0.057 µA/cm^2.

The next step of the corrosion resistance research work was to determine the anodic polarization curves for the Ti-6Al-7Nb alloy samples with a grinded surface (Ra_{av} = 0.40 µm) – Fig. 3. The value of corrosion potential for the samples only for grinding averaged E_{corr} = -339 mV. The steam sterilization usage also caused an increase of the average corrosion potential value up to E_{corr} = +48 mV. For the samples which underwent steam sterilized process and were exposed in the physiological solution, the corrosion potential value increased up to E_{corr} = +114 mV. In addition, determined polarization resistance values Rp and corrosion current density values i_{corr} resulted correspondingly – Table 3:

- grinded: Rp = 216.3 kΩcm^2, i_{corr} = 0.120 µA/cm^2,
- grinded and steam sterilized: Rp = 552.9 kΩcm^2, i_{corr} = 0.047 µA/cm^2,
- grinded and steam sterilized and exposed in physiological solution: Rp = 3740 kΩcm^2, i_{corr} = 0.007 µA/cm^2.

The last step of the corrosion resistance research work was to determine the anodic polarization curves for particular versions of the Ti-6Al-7Nb alloy samples with the mechanically polished surface (Ra_{av} = 0.12 µm) – Fig. 4.

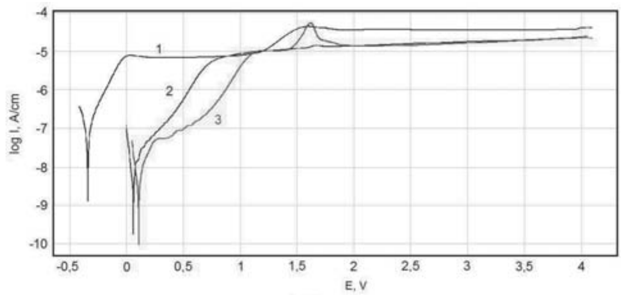


Fig. 3. Anodic polarization curves for Ti-6Al-7Nb alloy samples of surface: 1 – grinded, 2 – grinded and steam sterilized, 3 – grinded, steam sterilized and exposed in Ringer's solution

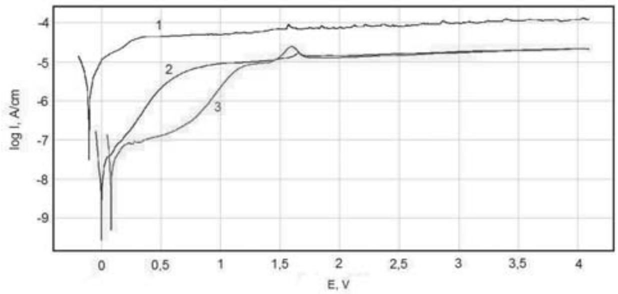


Fig. 4. Anodic polarization curves for Ti-6Al-7Nb alloy samples of surface: 1 – polished mechanically 2 –polished mechanically and steam sterilized, 3 –polished mechanically, steam sterilized and exposed in Ringer's solution

Table 3.
Results of corrosion resistance

Time	Method of surface preparation	Corrosion potential E_{corr}, mV	Corrosion current density i_{corr}, µA/cm^2	Polarisation resistance R_p, kΩcm	Passivation current density (E=+0.4V) i_p, µA/cm^2
		Ti-6Al-4V alloy			
-	Grinded	-333	0.103	251.7	10.00
-	Grinded + steam sterilization	-11	0.034	761.4	1.00
60 days	Grinded + steam sterilization	-57	0.038	683.4	0.25
-	Polished mechanically	-275	0.110	237.2	5.01
-	Polished mechanically + steam sterilization	+48	0.047	552.9	1.26
60 days	Polished mechanically + steam sterilization	+239	0.057	459.6	0.13
		Ti-6Al-7Nb alloy			
-	Grinded	-339	0.120	216.3	6.31
-	Grinded + steam sterilization	+48	0.047	552.9	0.20
60 days	Grinded + steam sterilization	+114	0.007	3 740.0	0.06
-	Polished mechanically	-105	3.133	8.3	39.81
-	Polished mechanically + steam sterilization	+4	0.015	1 710.0	1.00
60 days	Polished mechanically + steam sterilization	+84	0.044	590.3	0.10

The value of corrosion potential for the samples only through the mechanical working averaged E_{corr} = -105 mV and increased up to E_{corr} = +4 mV after additional use of the sterilization process. Exposure of the samples in the Ringer's solution caused a further increase of the corrosion potential value up to E_{corr} = +84 mV.

The rest of characteristic quantities describing the pitting corrosion resistance resulted correspondingly – Table 3:

- polished mechanically: Rp = 8.3 kΩcm^2, i_{corr} = 3.133 μA/cm^2,
- polished mechanically and steam sterilized process: Rp = 1710 kΩcm^2, i_{corr} = 0.015 μA/cm^2,
- polished mechanically and steam sterilized and exposed in physiological solution: Rp = 590.3 kΩcm^2, i_{corr} = 0.044 μA/cm^2.

3.2. Results of electrochemical impedance spectroscopy tests

The first step of measurements was to determine the impedance spectrums for Ti-6Al-4V alloy samples of grinded surface and mechanically polished surface, which underwent steam sterilized process – Fig. 5. The Nyquist diagrams determined for such prepared samples show fragments of large incomplete semicircles, which are of typical impedance response for thin oxide layers – Fig. 5a.

The maximum values of phase shift angles in a wide range of frequency shown in Bode diagrams, apart from the surface roughness, are similar and average θ ≈ 75°. Inclinations of a log|Z| in a full frequency change range are close to 1 which indicates a capacitive character of the passive layer – Fig. 5b. High values of impedance |Z| > 10^6 Ωcm^2 in the range of the smallest frequencies indicate good dielectric and protective properties of passive layers formatted on the surface of the Ti-6Al-4V alloy samples after sterilization using pressurized water vapour.

An impedance characteristic of the phase boundary was taken for the system of: electrode – passive layer – solution, in the Ti-6Al-4V alloy sterilized process made with the aid of pressurized water vapour. This characteristic was taken using an approximation by means of a physical model of the auxiliary electric circuit – Fig. 6.

It was found that the best adjustment of an experimental impendence spectrum is obtained using a substitute electric circuit. The subject adjustment concerns the spectrum with a programmable generated model curve for a real and imaginary component with circuit impedance depending on measurement signal changes. The substitutive electric circuit consists of an arrangement in parallel of a Constant Phase Element (CPE) combined with a resistance of ion transition through the phase boundary for the system of: electrode – R_{ct} solution, and consists of a resistance at high frequencies which can be assigned to R_s electrolyte's resistance [22-24].

A mathematical model of impedance for the system of: Ti-6Al-4V alloy – passive layer – solution is represented by equation (1):

$$Z = R_s + \frac{1}{1/R_{ct} + Y_0 (j\omega)^n} \qquad (1)$$

a)

b)

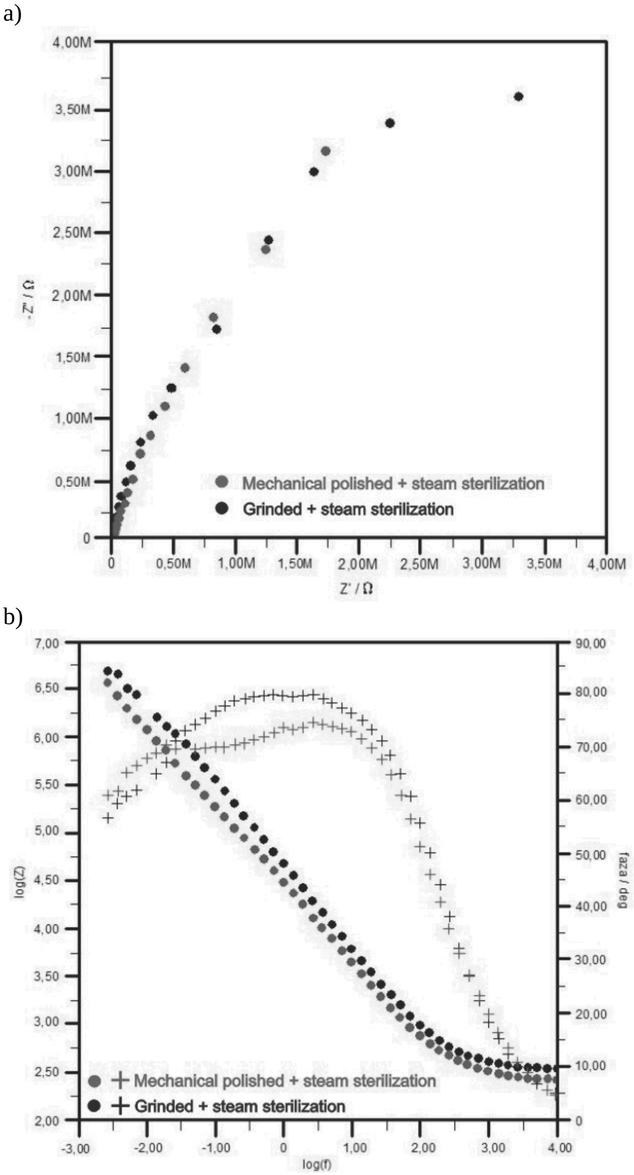


Fig. 5. Impedance spectrums for Ti-6Al-4V alloy: a) Nyquist diagram, b) Bode diagram

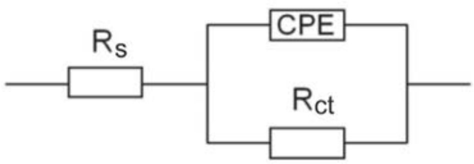
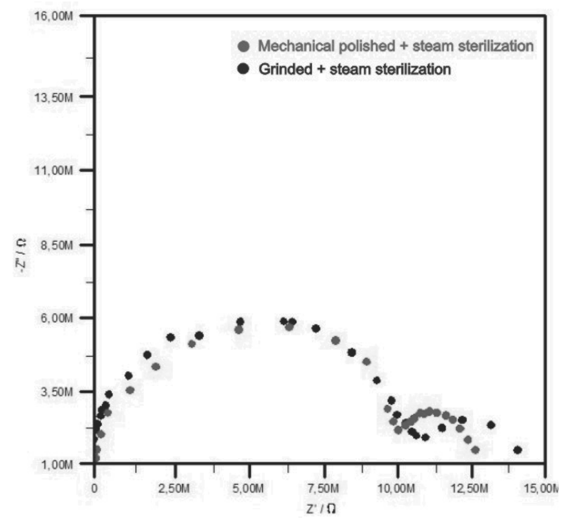


Fig. 6. Physical model for metal – passive film – solution system

The next step was to carry out a test of the Ti-6Al-4V alloy samples, which were exposed in the Ringer's solution, for a period of 60 days – Fig. 7.

a)



b)

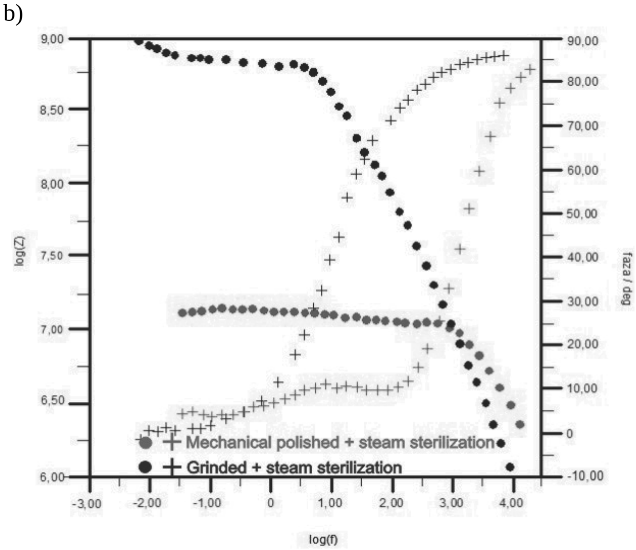


Fig. 7. Impedance spectrums for Ti-6Al-4V alloy after exposure in the Ringer's solution: a) Nyquist diagram, b) Bode diagram

Exposure in the physiological solution had an effect on the character change of the layer. First of all, it manifests as a change at the inclination angle of the log|Z|, which is observed in a frequency range below f = 1000 Hz (for mechanically polished surface) and f = 10 Hz (for ground surface).

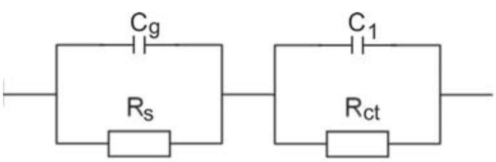


Fig. 8. Physical models for metal – passive film – solution system

An impedance characteristic of the phase boundary was taken for the system of: electrode – passive layer – solution, in the Ti-6Al-4V alloy sterilization process made with pressurized water vapour (after exposure in the physiological solution). This characteristic was taken using an approximation with the aid of a physical model of the auxiliary electric circuit – Fig. 8.

A mathematical model of impedance for the system of: Ti-6Al-4V alloy – passive layer – solution (after exposure in the physiological solution) is represented by equation (2):

$$Z = \frac{1}{1/R_s + j\omega C_g} + \frac{1}{1/R_{ct} + j\omega C_1} \tag{2}$$

Table 4.
Results of EIS for Ti-6Al-4V and Ti-6Al-7Nb alloy

Method of surface preparation	Time	C_g	C_1	R_s	R_{ct}	CPE	
						Y_0	n
	days	nF		Ω	MΩ	μF	-
1	2	3	4	5	6	7	8
Ti-6Al-4V alloy							
Polished mechanically+ steam sterilized	60	15e-3	8	2e6	10	-	-
Grinded + steam sterilized	60	11e-3	13	3e7	11	-	-
Polished mechanically+ steam sterilized	-	-	-	26	16	82	0.82
Grinded + steam sterilized	-	-	-	34	10	53	0.86
Ti-6Al-7Nb alloy							
Polished mechanically+ steam sterilized	60	-	-	16	8	51	0.89
Grinded + steam sterilized	60	-	-	10	13	54	0.91
Polished mechanically+ steam sterilized	-	-	-	21	46	72	0.81
Grinded + steam sterilized	-	-	-	22	29	57	0.88

Recorded impedance spectrums for Ti-6Al-7Nb alloy samples of grinded and mechanically polished surfaces, which additionally underwent steam sterilization process, are shown in Fig. 9. The character of recorded spectrums was similar to the obtained spectrums of the Ti-6Al-4V alloy test pieces – Fig. 5. Slight differences were found only in the values of particular parameters (among other things: electrolyte resistance – R_s, passive layer resistance – R_p) which describe electrical properties of the analyzed system – Table 4. Confirmation for the obtained results is the fact that the best matching of the experimental impendence spectrum, likewise in case of the Ti-6Al-4V alloy, is the substitutive electric circuit. This circuit consists of the arrangement in parallel of the CPE combined with the resistance of ion transition through the phase boundary for the system of: electrode – R_{ct} solution, and consists of resistance at high frequencies, which can be assigned to R_s electrolyte's resistance [25-27] – Fig. 6.

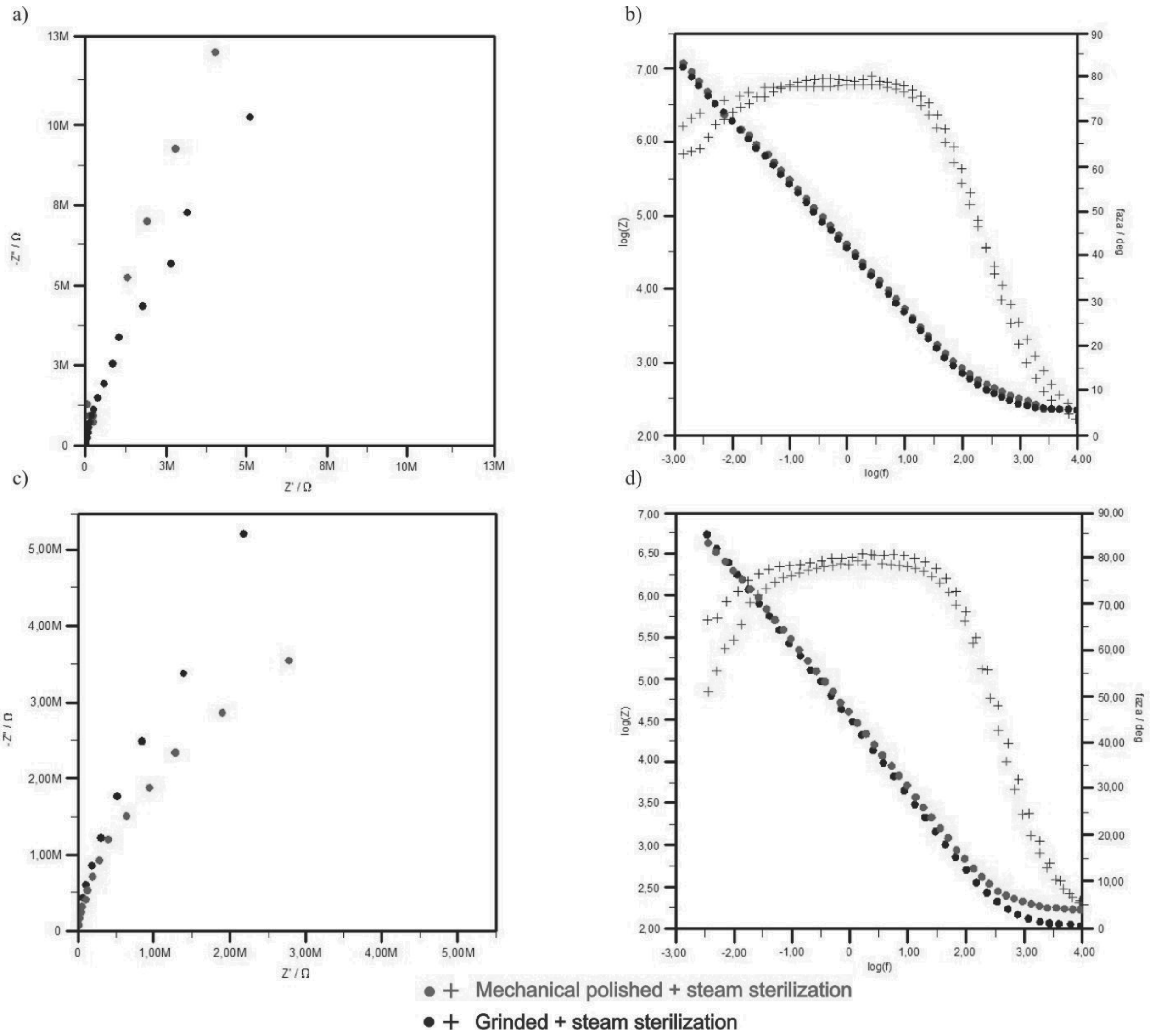


Fig. 9. Impedance spectrums for Ti-6Al-7Nb alloy test pieces: a) Nyquist diagram, b) Bode diagram, c) Nyquist diagram (after exposure in the Ringer's solution), d) Bode diagram (after exposure in the Ringer's solution)

Exposure in the Ringer's solution of the Ti-6Al-7Nb alloy samples with a grinded surface additionally steam sterilized process, did not have an essential effect on the character of the recorded spectrums – Fig. 9. In addition, values of characteristic parameters describing electrical properties of the analyzed system were similar to the values determined for the samples, which were not put through a long-lasting solution impact – Table 4. Taking into consideration the samples with a mechanically polished surface and steam sterilization process and completing a long-term Ringer's solution impact, a decreased value of phase angle θ in the range of small frequencies was found. It can indicate a decrease in the protective properties of the passive layer created during the sterilization process – Figs. 9a and 9b.

4. Conclusions

A significant problem of the utilization properties forming a process of implants used in bone surgery is selection of the metallic biomaterial's mechanical properties and its physicochemical properties. The physicochemical properties of an implant's surface should be adapted to the characteristics of the human tissue environment. The corrosion resistance assessment of metallic biomaterials pertains to the basic criteria of the implant biotolerance assessment. Therefore, the first step of the research work was to carry out corrosion resistance testing of the Ti-6Al-4V and Ti-6Al-7Nb alloys which are currently used for implants in bone surgery.

Potentiodynamic tests, which were carried out in an environment simulating the osseous system of humans (Ringer's solution), revealed a diversified corrosion resistance of selected biomaterials. It was found that the solution interaction lasting 60 days has a positive effect on the analyzed alloys' corrosion resistance. The determined anodic polarization curves, regardless of the type of biomaterial, had no appearance of a hysteresis loop up to the potential value E = +4000 mV, indicating perfect passivation in the full anodic range. In addition to this, a passivation current value was evaluated from the anodic polarization curves for a potential of E = +400 mV. The evaluated values indicate that a thin oxide layer was created on the surface of alloys, which were exposed in the Ringer's solution for the period of 60 days.

This thin oxide layer was of a higher stability in relation to the layer formed as the result of the pressurized water vapour sterilization process. The decreased passivation current value indicates Ti-6Al-4V and Ti-6Al-7Nb alloys' high auto-passivation susceptibility in the Ringer's solution. This fact should be taken as very advantageous for increasing titanium biomaterials' biocompatibility.

The subsequent step was to carry out research using electrochemical impedance spectroscopy for the purpose of fully assessing the surface layer's properties and structure of the selected biomaterials after exposure in the Ringer's solution. Selection of this method allowed to characterize the impendence of the phase boundary of the system of: biomaterial – passive layer (formed during sterilization or after exposure) – solution, by means of impedance data approximation with the aid of an electric model of the substitute electric circuit. The EIS analysis of the Ti-6Al-4V and Ti-6Al-7Nb alloys' passive layers created as the result of the steam sterilization process made it possible to determine the impedance spectrums of the examined system and to adjust data to the substitute system. This substitute system consisted of the arrangement in parallel of the CPE combined with the transition resistance R_{ct} and a residual resistance R_s for high frequencies, which is assigned to resistance in ohm of the Ringer's solution. The obtained results with an admittance value and "n" factor formed the basis for assessing a passive layer's fretting degree during exposure in the Ringer's solution.

The results of admittance (Z^{-1}) and n coefficient for the samples exposed to Ringer' solution showed that passive layer formed during sterilization was not damaged. Only changes of electrical properties of the passive layers were observed (decrease of charge transfer resistance R_{ct}).

To sum it up, on the basis of the electrochemical studies a favourable influence of steam sterilization on corrosion resistance of Ti-6Al-4V and Ti-6Al-7Nb alloys, regardless of the applied mechanical treatment, was observed. Exposition to the solution simulating human osseous system environment (Ringer' solution) did not influence over physicochemical properties of the passive layer.

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