

Corrosion behaviour of polished and sandblasted titanium alloys in PBS solution

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In this work, we performed comparative studies of the effect of surface preparation of Ti6Al4V and Ti6Al7Nb biomedical alloys and the influence of endothelial cells on their corrosion behaviour in PBS (Phosphate Buffered Saline). Two different methods of surface modification were applied – polishing and sandblasting. The polished Ti6Al7Nb alloy was found to have the best resistance against general corrosion in PBS. It was characterized by the lowest corrosion rate, the widest passive range and the lowest reactivity. Both alloys prepared by sandblasting exhibited worse corrosion properties in comparison to the polished ones. This can be associated with a greater development of their surface and the presence of Al₂O₃ grains which caused an increase of corrosion potential but might also influence the weakening of the passive layer. Results of potentiodynamic anodic polarization indicated that more resistant to pitting corrosion was Ti6Al7Nb alloy regardless of the method of surface preparation. In those cases, anodic polarization caused only an increase of passive layer, while in the case of sandblasted Ti6Al4V alloy it caused a pitting corrosion. The results obtained allowed us to conclude that the niobium-titanium alloys had higher corrosion resistance than titanium alloys with vanadium. Moreover, it was stated that endothelial cells improved the corrosion resistance of all the titanium alloys examined.

Key words: corrosion, PBS solution, polishing, sandblasting, titanium alloys

1. Introduction

In 1965, Branemark described the ability of commercially pure titanium to integrate with bone tissue, i.e., osseointegration [1]. Therefore, titanium and its alloys are among the most used metallic biomaterials, particularly in orthopedics and dentistry. In dentistry, titanium was initially used mainly in the form of finished manufactured goods. Nowadays, a lot of dental structures, such as veneered bridges and crowns, fixed and removable partial dentures, may be made of titanium in the laboratory conditions [2], [3]. Over the past few decades, due to more favorable mechanical properties of titanium-based alloys compared to pure

titanium, Ti6Al4V, two-phase $\alpha + \beta$ alloy, containing 6% aluminum (Al) and 4% vanadium (V), has gained considerable popularity. This alloy is characterized by high corrosion resistance, strength and flexibility [4]. Implants made of Ti6Al4V can be subjected to higher loads compared to implants made of pure titanium. However, due to the high toxicity of vanadium, many vanadium-free titanium alloys, e.g., Ti6Al7Nb alloy, have been developed since the 1980s, [5]–[7]. Niobium like vanadium stabilizes the β phase, but in contrast to vanadium, is a vital element which does not cause inflammation and allergic reactions [8]. It has been shown that Ti6Al7Nb alloy, without toxic vanadium, is characterized by a higher biocompatibility and enhanced corrosion resistance

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in physiological solutions compared to Ti6Al4V alloy [7], [9], [10].

Various surface development of titanium-based alloys is required depending on the application of designed implants. Smooth surfaces required for dental implants adjacent to the gingiva are achieved by polishing the surface of a material [11]. On the other hand, a significant increase in the development of biomaterial surface, and thus potentially better tissue integration [12], is obtained by the use of sandblasting, a treatment involving bombardment of the surface by the solid particles such as Al_2O_3 [13].

It is commonly known that every surface treatment determines mechanical properties [14] and corrosion resistance of biomaterials in a highly corrosive biological environment.

The aim of this study was to determine the effect of sandblasting and polishing of Ti6Al4V and Ti6Al7Nb alloys' surfaces on their corrosion behaviour in PBS (Phosphate Buffered Saline). In addition, the influence of endothelial cells on these properties was examined as every biomaterial during implantation has inevitable contact with blood, blood elements, blood vessels and endothelium lying the inner surface of blood vessels.

To achieve our goal various electrochemical techniques were used. In order to evaluate the resistance against general corrosion of titanium alloys under examination, the measurements of corrosion potential in an open circuit, the linear polarization method (Stern–Geary's characteristics) and electrochemical impedance spectroscopy (EIS), were performed. In order to assess resistance of the biomaterials examined against pitting corrosion, a method of anodic polarization in a wide range of potentials was used.

2. Materials and methods

The samples of titanium alloys were disc-shaped with a diameter of 20 mm and a height of 3 mm for Ti6Al4V and 6 mm for Ti6Al7Nb alloy. After the initial grinding on abrasive papers one group of the samples was polished with an aqueous suspension of silica-based oxide (Struers), whereas the other samples were sandblasted by Al_2O_3 with grains of 110 microns in size, at an angle of 45° and at a pressure of 4.5 bar. Then the samples were cleaned in an ultrasonic bath in acetone and in deionized water for 10 min sequentially. Evaluation of surface morphology and analysis of the elemental composition of the

surface layer were made with the use of scanning electron microscope HITACHI S-3000N with an X-ray analyzer, EDS THERMO NORAN. Percentage of individual elements in the surface layer of polished titanium alloys (the average value of the elemental composition in % wt. with a standard deviation) is shown in Table 1. The content of main alloying elements in both polished titanium alloys is compatible with ISO standards [15]. The results of SEM-EDS measurements of sandblasted samples revealed the presence of Al_2O_3 grains embedded in the surface of the alloys.

Table 1. Elemental composition [% wt.] of the surface layer of polished titanium alloys

Element	Polished Ti6Al4V	Polished Ti6Al7Nb
Ti	89.47 ± 0.46	87.09 ± 0.43
Al	6.01 ± 0.07	5.63 ± 0.06
Nb	–	7.28 ± 0.17
V	4.52 ± 0.24	–
Total	100	100

All corrosion measurements were performed at 37 °C in deoxygenated PBS (Phosphate Buffered Saline) solution, at pH 7.4, composed of: 8 g NaCl, 0.2 g KH_2PO_4 , 2.9 g $Na_2HPO_4 \cdot 12H_2O$ and 0.2 g KCl in 1000 ml of solution [16], [17]. Electrochemical corrosion measurements were performed in a three-electrode potentiostatic system in which the working electrode was the sample with an area of contact with the solution equal to 0.64 cm², the auxiliary electrode was Pt foil and the reference electrode – calomel electrode in saturated NaCl solution. All potentials in this paper are given versus this calomel electrode ($E^0 = 0.236$ V vs. SHE). Immediately before the measurements the samples were cleaned in an ultrasonic bath in acetone and three-times distilled water, dried with argon and heated in a thermostatic cabinet at 37 °C for 10 min. The potentiostats/galvanostats PGstat30 and PGstat128N (AutoLab) were used in corrosion measurements. A typical cycle contained the measurements of the corrosion potential, Stern–Geary's characteristic, impedance and potentiodynamic characteristic in a wide range of anodic polarization [18].

Human endothelial cells line EA.hy 926 (CRL-2922) used in this study were obtained from American Type Culture Collection. Corrosion tests evaluating the influence of endothelial cells on corrosion resistance of titanium alloys were performed after 48 hours of incubation of samples with a suspension of cells in the Dulbecco's Modified Eagle's Medium (Gibco) supplemented with 10% fetal bovine serum (Sigma

Aldrich), penicillin, streptomycin and HAT. The cells were cultured under 100% humidity and 5% CO₂ at 37 °C on the surfaces of the samples that were autoclaved in advance and placed into the wells of standard culture plates [19]. For these samples, electrochemical measurements were performed immediately after removing samples from the culture medium, rinsing them with PBS solution and dried with argon.

Electrochemical measurements were performed for three samples of each type. Data presented in this work are averages with standard deviations or the most representative results for the particular type of samples.

The study of surface morphology and elemental composition of the surface layer of representative samples after the corrosion tests was performed with the use of SEM-EDS microscopy.

3. Results

In order to determine the corrosion potential, the potential of the samples according to the reference electrode in an open circuit during 2000 s was recorded. Final potential was taken as the corrosion potential E_{cor} . Figure 1 shows the E_{cor} values for each type of samples. Corrosion potentials of sandblasted Ti6Al7Nb and Ti6Al4V alloys are close to each other and are approximately -0.35 V, while of polished ones are lower and equal to -0.48 V and -0.52 V, respectively. The presence of endothelial cells on the surfaces examined shifts E_{cor} of both alloys to ca.

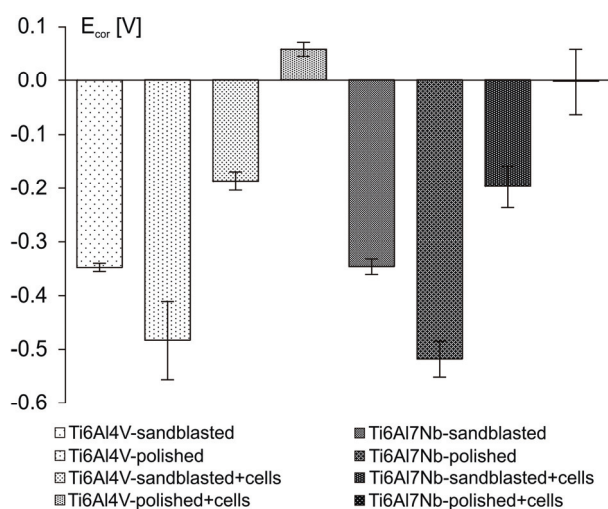


Fig. 1. Corrosion potential of titanium alloys in PBS

-0.19 V and ca. -0.20 V for sandblasted samples, and to ca. 0.06 V and ca. 0.00 V for polished samples.

Polarization resistances R_p were determined by polarization of the samples in a typical potentiostatic connection in the potential range from $E_{cor} - 0.02$ V to $E_{cor} + 0.02$ V with the scan rate of $0.3 \text{ mV} \cdot \text{s}^{-1}$. The results of R_p measurements are shown in Fig. 2. The values of polarization resistance R_p of both sandblasted titanium alloys are similar to each other and are ca. $2.3 \cdot 10^5 \Omega \cdot \text{cm}^2$. Polarization resistances of polished alloys are higher and differ from each other – R_p of polished Ti6Al4V alloy is ca. $6.7 \cdot 10^5 \Omega \cdot \text{cm}^2$, while R_p of polished Ti6Al7Nb alloy is ca. $2.3 \cdot 10^6 \Omega \cdot \text{cm}^2$. Contact of the surfaces examined with endothelial cells increases about 7 to 9 times R_p of sandblasted titanium alloys and about 7 times of polished titanium alloys.

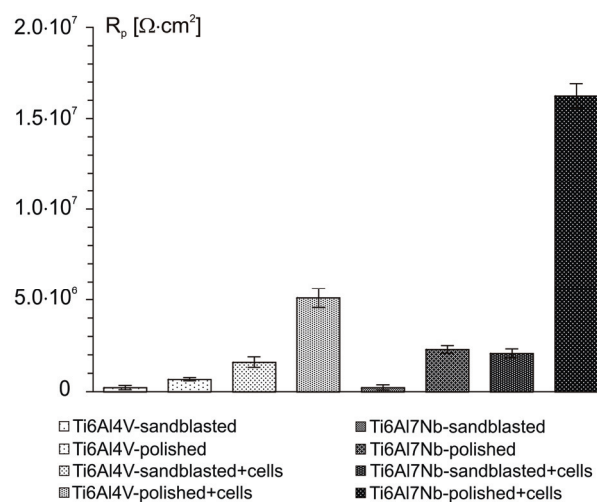


Fig. 2. Polarization resistance of titanium alloys in PBS

On the basis of the polarization resistance R_p the corrosion rate CR was calculated. The calculation of CR was based on the ASTM Standard G 102-89 [20], according to the formula

$$CR = K \frac{i_{cor}}{\rho} EW,$$

where CR – corrosion rate in $\text{mm} \cdot \text{yr}^{-1}$, $K = 3.27 \cdot 10^{-3} \text{ mm} \cdot \text{g} \cdot \mu\text{A}^{-1} \cdot \text{cm}^{-1} \cdot \text{yr}^{-1}$, i_{cor} – corrosion current density in $\mu\text{A} \cdot \text{cm}^{-2}$, ρ – density in $\text{g} \cdot \text{cm}^{-3}$, EW – equivalent weight.

Corrosion current density was calculated from the approximate relation

$$i_{cor} = \frac{0.026}{R_p}.$$

The EW values were calculated from the formula

$$EW = \frac{1}{\sum \frac{n_i f_i}{M_i}},$$

where n_i – valence of the i -th element in the alloy, f_i – mass fraction of the i -th element in the alloy, M_i – the atomic weight of the i -th element in the alloy.

Calculations of the corrosion rate CR include only those components whose content in the alloy is not less than 1% wt. For calculations of EW values both for polished and sandblasted titanium alloys, the elemental compositions of polished titanium alloys were adopted. It was assumed that the Al_2O_3 grains embedded in sandblasted surfaces of titanium alloys are not subjected to corrosion under conditions in which measurements were performed [21]. EW values, calculated in accordance with the above assumptions, are presented in Table 2.

Table 2. Calculation of Equivalent Weight (EW)

Ti6Al4V					Ti6Al7Nb				
Element	f_i	n_i	M_i [g·mol ⁻¹]	EW	Element	f_i	n_i	M_i [g·mol ⁻¹]	EW
Ti	0.895	4	47.90	11.90	Ti	0.871	4	47.90	12.06
Al	0.060	3	26.98		Al	0.056	3	26.98	
V	0.045	3	50.94		Nb	0.073	5	92.91	

The graph of corrosion rate CR for different types of samples is shown in Fig. 3. Because both alloys have similar EW and similar density ($\rho_{Ti6Al4V} = 4.43 \text{ g}\cdot\text{cm}^{-3}$, $\rho_{Ti6Al7Nb} = 4.52 \text{ g}\cdot\text{cm}^{-3}$), changes in CR values are practically proportional to the changes of inverse of R_p . Both sandblasted titanium alloys have the largest, close to each other corrosion rates, equal ca. $1.3\cdot 10^{-3} \text{ mm}\cdot\text{yr}^{-1}$. For polished titanium alloys a considerable difference was observed – CR of Ti6Al4V alloy is ca. $3.5\cdot 10^{-4} \text{ mm}\cdot\text{yr}^{-1}$, while CR of Ti6Al7Nb alloy is ca. $9.8\cdot 10^{-5} \text{ mm}\cdot\text{yr}^{-1}$. Corrosion rate of sandblasted titanium alloys with endothelial cells has a value equal to approximately $1.5\cdot 10^{-4} \text{ mm}\cdot\text{yr}^{-1}$ for Ti6Al4V alloy and about $1.1\cdot 10^{-4} \text{ mm}\cdot\text{yr}^{-1}$ for Ti6Al7Nb alloy. It means that contact with endothelial cells results in about 9 and 12 times reduction in the corrosion rate of these alloys. CR of polished titanium alloys with endothelial cells also varies depending on the type of titanium alloy – CR of polished Ti6Al4V with endothelial cells alloy is ca. $4.6\cdot 10^{-5} \text{ mm}\cdot\text{yr}^{-1}$, while CR of polished Ti6Al7Nb alloy with cells is ca. $1.4\cdot 10^{-5} \text{ mm}\cdot\text{yr}^{-1}$.

Reduction of corrosion rate is about 7 times compared to the corrosion rate of both polished titanium alloys without cells.

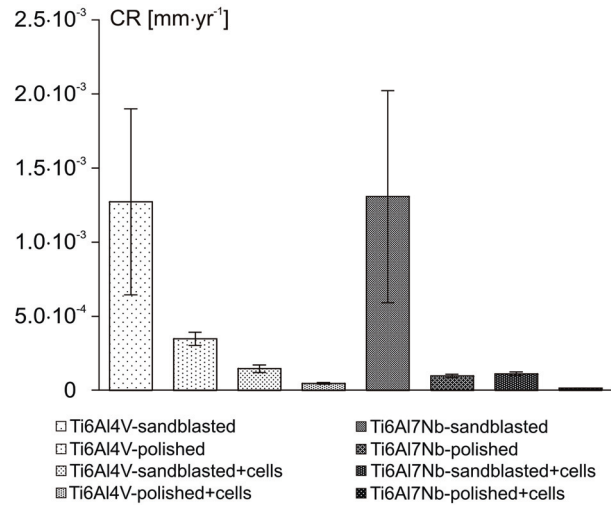


Fig. 3. Corrosion rate of titanium alloys in PBS

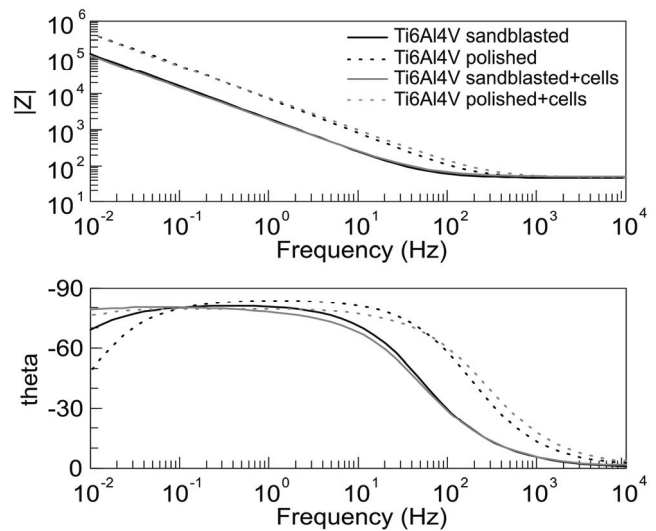


Fig. 4. Impedance characteristics in the Bode representation for Ti6Al4V alloy

Electrochemical impedance characteristics were measured at the corrosion potential E_{cor} in the potentiostatic mode with harmonic signal $E_{AC} = 10 \text{ mV}$ for

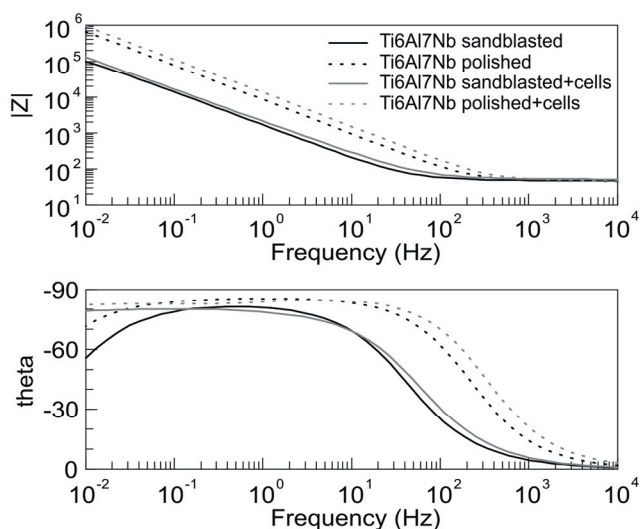


Fig. 5. Impedance characteristics in the Bode representation for Ti6Al7Nb alloy

50 points in frequency range from 0.01 Hz to 10 kHz. Typical characteristics in the Bode representations for Ti6Al4V and Ti6Al7Nb alloys are shown in Figs. 4 and 5, respectively. Impedance characteristics for both samples, polished and sandblasted, have the typical shape for the presence of an oxide layer. It can be observed from the course of these characteristics that polished samples of titanium alloys are characterized by the higher impedance. Endothelial cells have only little effect on the impedance of the samples of titanium alloys at high and medium frequencies, while they increase the impedance at low frequencies.

The potentiodynamic characteristics in a wide range of anodic polarization were performed with the scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$ from the starting potential $E_{cor} - 0.2 \text{ V}$ to the final potential of 9 V or to the potential at which the current density achieved a value of $5 \text{ mA}\cdot\text{cm}^{-2}$. After reaching the above-mentioned maximum values, the direction of polarization was reversed to the starting potential. Generally, in the study of bio-materials polarization to 4 V is enough because it is assumed that the real differences of potentials in the human body do not exceed 2.5 V [21]. Setting the anodic polarization up to 9 V was designed to detect specific differences that may occur between individual samples, and in particular to determine the conditions under which pitting corrosion may occur. The obtained potentiodynamic characteristics of Ti6Al4V and Ti6Al7Nb alloy are shown in Figs. 6 and 7, respectively. For better readability sections of return branches in both figures have been cut off. The characteristics of the sandblasted samples of both titanium alloys have a narrow passive range up to about 1 V. The

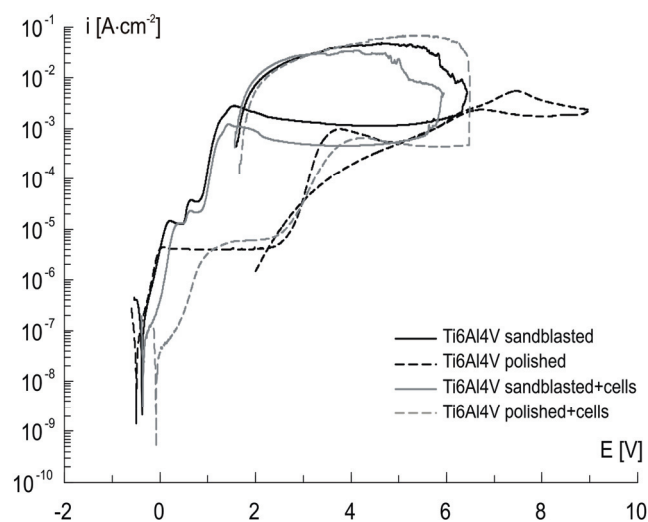


Fig. 6. Potentiodynamic characteristics of Ti6Al4V alloy

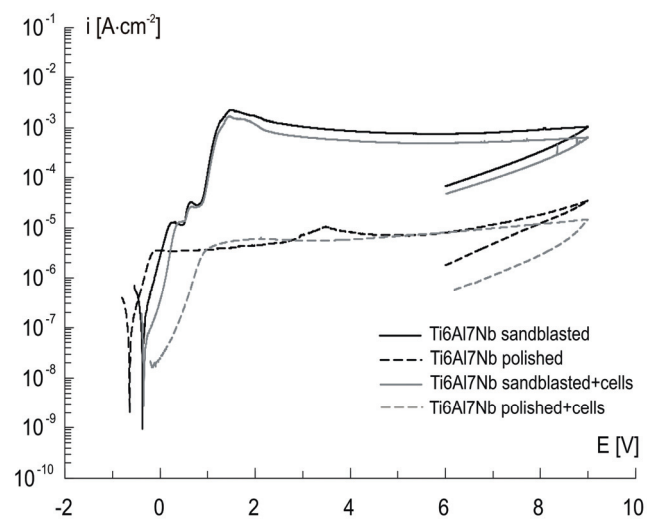


Fig. 7. Potentiodynamic characteristics of Ti6Al7Nb alloy

maximum transpassivation current is reached at potential of about 1.5 V. During further polarization in both cases current plateau is observed with the current density in the order of $10^{-3} \text{ A}\cdot\text{cm}^{-2}$. In the high anodic potentials differences in the behavior of sandblasted titanium alloys are revealed. In the case of sandblasted Ti6Al4V alloy pitting corrosion occurs in the range from 5.5 V to 6.3 V, while sandblasted Ti6Al7Nb alloy can be polarized up to 9 V without any pitting. The potentiodynamic characteristics of polished titanium alloys differ significantly from each other. For polished Ti6Al4V alloy passive range ends at ca. 2.5 V, and above this potential transpassivation occurs. Polished Ti6Al7Nb alloy behaves ambiguously – for some of the samples the passivation range reaches 9 V, while for the other samples a breakdown at the potential of about 8 V is observed. In the pas-

sive range the currents for both titanium alloys are in the order of $10^{-5} \text{ A}\cdot\text{cm}^{-2}$. Endothelial cells have no significant effect on the shape of characteristics for the potentials above ca. 1 V. The characteristics of polished Ti6Al7Nb alloy are the same as for samples of this alloy without cells, whereas in the case of polished Ti6Al4V alloy pitting corrosion occurs at a potential of ca. 6.5 V.

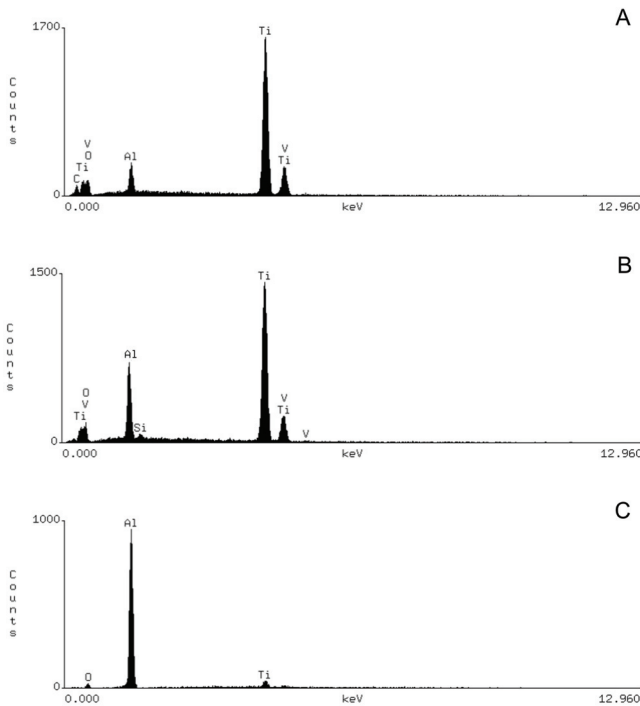
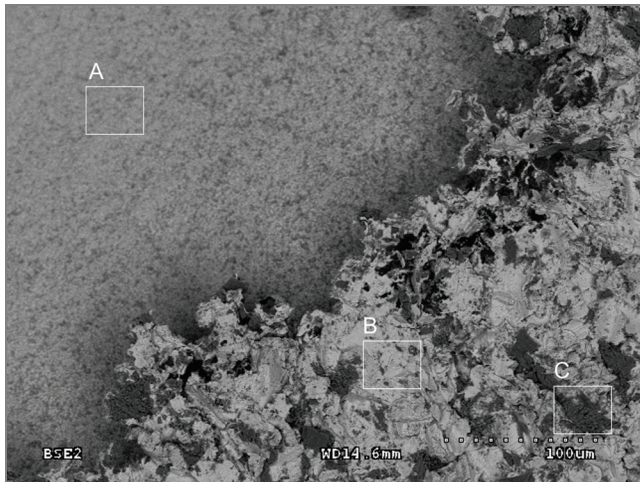


Fig. 8. SEM-EDS analysis of sandblasted Ti6Al4V alloy after corrosion: A – composition of the surface inside a pit, B – composition of the surface outside a pit, C – composition of the inclusions on the surface

The occurrence of pitting corrosion was confirmed by the microscopic analysis of the surface of titanium alloys. With the use of SEM-EDS microscopy the

surface morphology and elemental composition of the surface layer of all samples after corrosion were analyzed. The results of SEM-EDS analysis for a chosen sandblasted Ti6Al4V sample is presented in Fig. 8. Spectrum A shows the composition of the surface inside a pit, spectrum B shows the composition of the surface area which had a contact with a corrosive solution, spectrum C – the composition of the inclusions on the surface. Spectrum A indicates that the elemental composition within the pit is the same as the elemental composition of polished titanium alloy. Inside the pit no presence of embedded Al_2O_3 grains was found. In contrast, these grains are present in the area outside the pit, which is confirmed by spectra B and C.

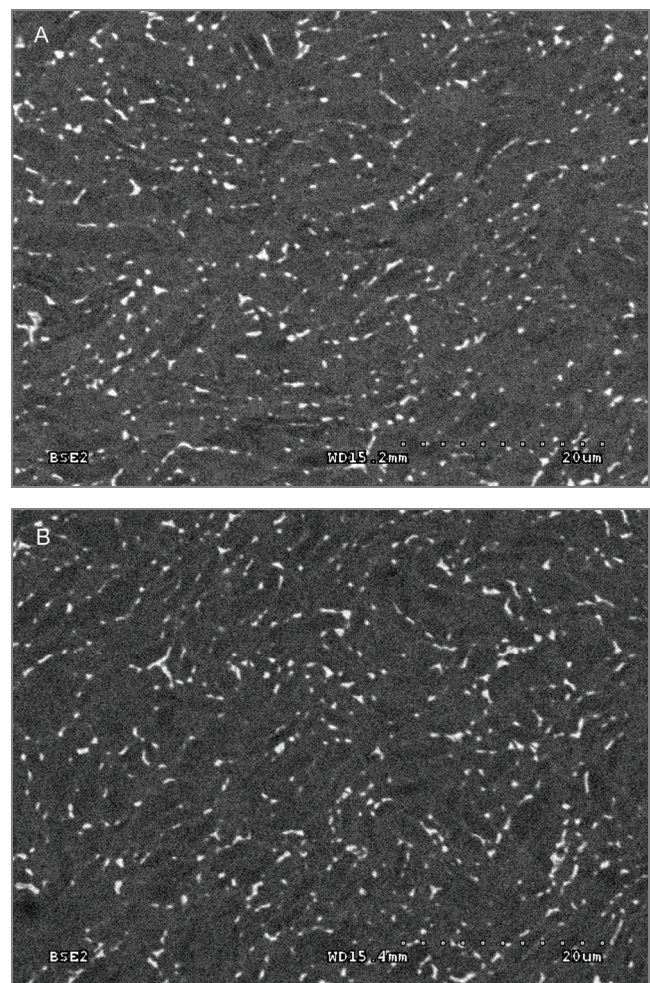


Fig. 9. SEM images of polished Ti6Al7Nb alloy: A – before and B – after anodic polarization

Figure 9 presents SEM images of polished Ti6Al7Nb alloy before and after anodic polarization in a wide range of potentials. Comparison of these two images suggests that the anodic polarization does not change the surface morphology of this alloy.

4. Discussion

Changes in corrosion potential E_{cor} are systematic: polished samples have the lowest E_{cor} values, sandblasted samples have higher values, whereas samples after contact with endothelial cells have the highest E_{cor} values. Because corrosion potential is associated with corrosion resistance [23], on the basis of E_{cor} values the corrosion resistance of titanium alloys examined can be set in order as follows: Ti6Al4V (polished) \cong Ti6Al7Nb (polished) < Ti6Al4V (sandblasted) \cong Ti6Al7Nb (sandblasted) < Ti6Al7Nb (sandblasted + cells) \cong Ti6Al4V (sandblasted + cells) < Ti6Al7Nb (polished + cells) \leq Ti6Al4V (polished + cells).

The order of corrosion resistance of the first two pairs in the above series is rather surprising as is well known that polishing improves the corrosion resistance of the material [24]. The higher corrosion potential of the sandblasted alloys in comparison with polished alloys may be explained by the presence of Al_2O_3 grains on the surface of sandblasted alloys.

Both R_p and CR are clearly associated with the corrosion resistance and can be analyzed together. Thus, corrosion resistance of alloys investigated can be now set in order as follows: Ti6Al4V (sandblasted) \cong Ti6Al7Nb (sandblasted) < Ti6Al4V (polished) < Ti6Al7Nb (sandblasted + cells) \cong Ti6Al4V (sandblasted + cells) < Ti6Al7Nb (polished) < Ti6Al4V (polished + cells) < Ti6Al7Nb (polished + cells).

In this case, the changes in corrosion resistance are consistent with those expected: polished alloys have higher corrosion resistance than sandblasted alloys. This fact can be explained by a large surface development of sandblasted alloys in comparison with polished alloys. Influence of endothelial cells can be associated with the formation of biofilm on the surface of the alloy during contact of the samples with the culture medium, as well as possible blocking of some part of the surface by the cells located on it. Probably, this biological barrier is composed mainly of proteins from culture medium supplemented with fetal bovine serum as well as the proteins from extracellular matrix that are possibly produced by the cells adhered to the surface of the samples. The protein biofilm, formed in this way, together with endothelial cells, reduces the surface of titanium alloys available for chemical processes. Experimental verification of this hypothesis is difficult – it would require the measurements of surface composition *in situ*, because after removing the samples from the culture medium, cell adhesion to the alloy surface strongly decreases and the degree of surface coverage changes. Comparison of the cor-

rosion resistance of both titanium alloys indicates the greater resistance of polished Ti6Al7Nb alloy in comparison to polished Ti6Al4V alloy, both with and without cells. On the other hand, both sandblasted titanium alloys have similar corrosion resistance.

Impedance characteristics allow us to determine the physicochemical properties of the sample–corrosion medium interface by means of fitting them with equivalent electrical circuits. For fitting these characteristics, ZView 2.9 program (Scribner Associates Inc.) was used. Good fitting in the full range of frequencies was obtained using the circuit shown in Fig. 10. Identical circuit is frequently used in the analysis of impedance studies of Ti alloys [17], [25], [26]. The values of the electrical elements of the circuit presented in Fig. 10 are shown in Table 3. The goodness of fit is testified by the value of Chi squared (χ^2), which only in the case of Ti6Al7Nb polished alloy with endothelial cells was $2.0 \cdot 10^{-3}$, and for all other did not exceed $1.2 \cdot 10^{-3}$ (Table 3). Interpretation of the individual elements can be as follows: R_s – uncompensated electrolyte resistance, CPE1 – phase-constant element associated with the differential capacity of the interface, R1 – resistance of charge transfer across the interface examined. Analysis of the CPE1-T values indicates that these values are from 4 to 7 times higher for sandblasted titanium alloys compared to the corresponding polished ones. The reason of this effect is many times greater surface development of sandblasted samples. On the other hand, CPE1-P values of 0.88–0.96 suggest “not ideal” capacity of the interface. Analysis of R1 values gives information that endothelial cells cause a large increase in the value of this element, ca. 55 and 88 times for sandblasted Ti6Al4V and Ti6Al7Nb alloys, respectively, and about 12 and 5 times for the polished ones. This effect may be associated with the formation of a barrier layer for the electrode reactions. The layer, as already signaled above, is the result of contact of the cell culture medium and the cells with the surface of titanium alloys. The presence of such a barrier layer and the cells on the surface of Ti6Al7Nb alloy is confirmed by the microscope image shown in Fig. 11. A similar effect was also observed for Ti6Al4V alloy.

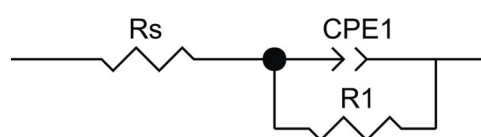


Fig. 10. Equivalent electrical circuit

Table 3. Values of equivalent electrical circuit elements and goodness of fit (χ^2)

	Sample	Rs [$\Omega\cdot\text{cm}^2$]	CPE1-T	CPE1-P	R1 [$\Omega\cdot\text{cm}^2$]	χ^2
Ti6Al4V	sandblasted	49.07 ± 0.20	$(1.22 \pm 0.16)\cdot 10^{-4}$	0.913 ± 0.003	$(1.88 \pm 0.41)\cdot 10^5$	0.0012
	polished	47.90 ± 0.30	$(2.30 \pm 0.24)\cdot 10^{-5}$	0.935 ± 0.009	$(6.78 \pm 0.62)\cdot 10^5$	0.0008
	sandblasted + cells	50.6 ± 2.0	$(1.03 \pm 0.01)\cdot 10^{-4}$	0.882 ± 0.003	$(1.03 \pm 0.84)\cdot 10^7$	0.0012
	polished + cells	48.24 ± 0.35	$(2.56 \pm 0.02)\cdot 10^{-5}$	0.889 ± 0.002	$(7.86 \pm 0.51)\cdot 10^6$	0.0002
Ti6Al7Nb	sandblasted	48.46 ± 0.66	$(1.16 \pm 0.08)\cdot 10^{-4}$	0.916 ± 0.005	$(1.75 \pm 0.52)\cdot 10^5$	0.0009
	polished	46.97 ± 0.54	$(2.29 \pm 0.35)\cdot 10^{-5}$	0.955 ± 0.001	$(2.52 \pm 0.01)\cdot 10^6$	0.0003
	sandblasted + cells	51.5 ± 2.0	$(8.77 \pm 0.52)\cdot 10^{-5}$	0.893 ± 0.007	$(1.54 \pm 0.74)\cdot 10^7$	0.0008
	polished + cells	47.21 ± 0.39	$(1.26 \pm 0.15)\cdot 10^{-5}$	0.951 ± 0.014	$(1.18 \pm 0.29)\cdot 10^7$	0.0020

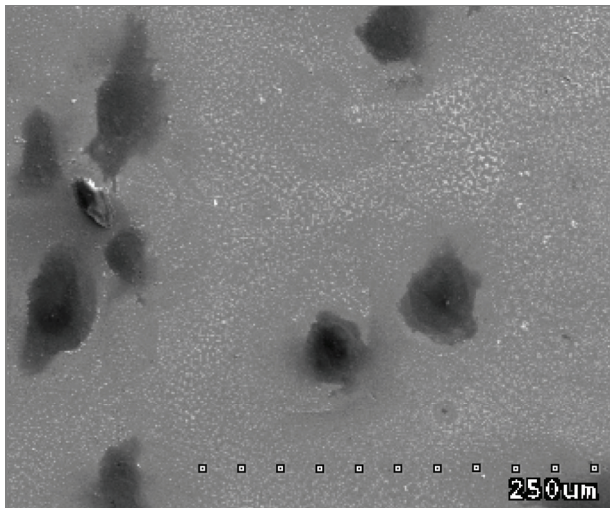


Fig. 11. SEM image of polished Ti6Al7Nb alloy after contact with the cell culture medium and the cells

The potentiodynamic characteristics in a wide range of anodic polarization allow us to define resistance of specified materials to pitting corrosion in a corrosive environment. Titanium biomaterials are characterized by good resistance to pitting corrosion due to the presence on their surface of a thin (4–6 nm) titanium oxide layer formed in a natural way as a result of its contact with air or water [11]. Additionally, in the case of titanium-based alloys alloying elements (Al, Nb, V) in oxidized form (Al_2O_3 , Nb_2O_5 or V-oxides) are also present in a forming oxide film [11]. Based on the recorded anodic characteristics shown in Figs. 6 and 7, it can be stated that polished surfaces of both titanium alloys exhibit significantly improved corrosion resistance compared to sandblasted surfaces. The reduced (about 100 times) passive current densities observed on polished specimens are in agreement with literature data [27], and are attributed to the reduced surface development compared to sandblasted surfaces.

Sandblasting in comparison to polishing increases the electrochemical activity of both alloys under study in the range from 0 to about 1.5 V. In this range,

a rapid increase in current density by two orders of magnitude identical for both sandblasted titanium alloys is observed. It is associated with the transpassivation process. On the basis of the shape of the potentiodynamic characteristics it was stated that alloys prepared by sandblasting have different resistance to pitting corrosion. Hysteresis loop in the reverse scan, typical of pitting corrosion, was observed only for Ti6Al4V alloy. Thus, it can be concluded that an oxide layer forming on the surface of sandblasted Ti6Al7Nb alloy, as a result of anodic polarization, has better anticorrosion properties than the oxide layer on Ti6Al4V alloy.

It was found that the corrosion properties of both polished titanium alloys are different in the wide anodic polarization. Potentiodynamic characteristics for polished Ti6Al4V alloy have a relatively wide passive range (up to ca. 2.5 V) above which the transpassivation process is observed. Despite the increase in the measured current at high values of polarization potential, there was no pitting corrosion observed. The course of the backward curve proves that anodic polarization caused an increase of the oxide layer thickness. On the other hand, for Ti6Al7Nb alloy measured current remains at a constant level of $10^{-5} \text{ A}\cdot\text{cm}^{-2}$ practically in the whole range of polarization. It indicates a highly passive character of the oxide layer formed on the Ti6Al7Nb surface. The lower value of current density of Ti6Al7Nb compared to Ti6Al4V can be attributed to the presence of Nb in the oxide layer, which is the stabilizer of β phase [28], [29]. Similarly, better corrosion properties of Ti6Al7Nb alloy were also found in a Hank's solution by Al-Mobarak and co-workers [29].

5. Summary

Summarizing the results described above, it can be stated that:

1. The best corrosion resistance in PBS is shown by polished Ti6Al7Nb alloy – it is characterized by the lowest corrosion rate, the widest passive range and the lowest reactivity.

2. For both types of titanium alloys the samples after sandblasting have worse corrosion properties in comparison to the polished samples, which can be associated with a greater development of the surface and the presence of Al₂O₃ grains. These grains increase the corrosion potential but may also influence the weakening of the passive layer.

3. Ti6Al4V alloy undergoes pitting corrosion only in the case of sandblasted surface.

4. Anodic polarization increases the passive layer for both polished and sandblasted samples of Ti6Al7Nb alloy.

5. Endothelial cells improve the corrosion resistance of both titanium alloys under examination subjected to polishing and sandblasting.

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