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Tantalum effect on the corrosion behavior of titanium-tantalum alloys in an environment containing fluoride ions

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Abstract

Titanium exhibits high corrosion resistance in biological environments. The main objective of its alloying with beta-stabilizing elements is to decrease modulus of elasticity. It is important to preserve corrosion resistance. The presented study was aimed at corrosion properties of Ti15Ta and Ti30Ta alloys in comparison with titanium. Measurements were performed on titanium, both alloys and tantalum in the physiological solution without or with fluoride ions. Electrochemical study was based on electrochemical impedance spectroscopy. Corrosion behavior of the studied alloys was significantly influenced by titanium. In the physiological solution, both alloys displayed stable passivity. Titanium is highly sensitive to the presence of fluoride ions. Its alloying with tantalum had a positive effect under the given conditions, which applied particularly to the Ti30Ta alloy. Titanium-tantalum binary alloys are not considered for direct use, yet the knowledge of their behavior may contribute to a more rational design of alloy systems applicable in dental practice.

Key words: Ti-Ta alloys, corrosion, fluoride ions, surface analysis, impedance spectroscopy

1. Introduction

Titanium exhibits high corrosion resistance in most biological environments. In addition, the metal is easily accepted by the surrounding tissue, and it has a good capacity for biointegration. These properties predetermine titanium as a first-choice metallic material in medical applications, yet it is not an ideal material. The main reason is that its Young's modulus is higher approximately by order of magnitude than that of cortical bone (10–20 GPa [1]). This is why current research in the field of metallic biomaterials focuses on the development of materials with a lower elasticity modulus. Ti-based alloys with a beta-structure represent a possible solution. These alloys have Young's moduli around 60 GPa [2, 3] and they are easier to work, which is particularly important in dentistry where small components of complicated shapes are often needed. The beta structure is stabilized by way of titanium alloying with niobium, zirconium, molybdenum and other elements [4]. New alloys development is most often focused primarily on meeting metallurgical requirements, which in this case means achieving a beta structure with the required mechanical properties. The alloys are subsequently evaluated in terms of their utility properties, with the determination of their corrosion behavior being part of evaluation process.

Corrosion tests are performed on several levels. The basis consists in evaluating materials behavior in electrolytes simulating body environment (SBF, physiological solution, Ringer solution, model saliva, etc.) [5, 6]. These tests may be followed by a more strict evaluation modeling the boundary conditions of real exposure (increased environment aggressiveness in consequence of an inflammation, etc.). This may also include tests carried out in environments containing fluoride ions at pH values in the acidic region, which are used in the testing of dental alloys [6–8].

Zhou et al. [9] studied the influence of tantalum on the corrosion resistance of Ti-based alloys in great detail. The studied materials included pure titanium, Ti6Al4V and $Ti_{1-x}Ta_x$ (x = 10, 30 and 70 at.%). Corrosion behavior was discussed based on the course of potentiodynamic curves measured in the environ-

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ment of hydrochloric acid of a concentration of 5 wt.%. Tantalum-containing alloys exhibited more positive corrosion potentials and lower current density values in the passive state. Based on their results, the authors declared a positive effect of tantalum alloying which in the given environment increased corrosion resistance. These results are in agreement with de Souza et al. [10] who evaluated corrosion resistance of Ti20Ta, Ti40Ta, pure Ti and Ta in sulfuric acid with concentrations of 20, 40, 60 and 80 wt.%. Corrosion properties were based on comparison of the open circuit potential time dependences, potentiodynamic curves and impedance spectroscopy results. The positive effect of tantalum on decreasing corrosion rates in the studied materials was proved under all the studied conditions. Alloys with tantalum content above 40 % were resistant even in environments where active dissolution of titanium had already occurred.

The interaction of fluoride ions and pure titanium is relatively broadly described in literature. Their negative effect on the stability of the passive layer of titanium, and in an acidic environment in particular, has been clearly proved [11–18]. However, only a small attention has as yet been devoted to Ti-based alloys with tantalum. Robin et al. [6] compared corrosion resistance of Ti23Ta and Ti6Al4V alloys in a model saliva environment with a fluoride ions content ranging from 0 to 10000 ppm, and with pH ranging from 2 to 7. Based on the measured impedance spectra and potentiodynamic dependences, the authors noted a slightly higher corrosion resistance of Ti-23Ta as compared with Ti6Al4V. Trillo et al. [19] have reported a comparable corrosion resistance of alloys Ti-40Ta, Ti50Ta and Ti6Al4V in a model body environment, based on potentiodynamic measurements. Corrosion behavior of alloys $\mathrm{Ti}_{1-x}\mathrm{Ta}_x$ ($x = 30$, 40, 50 and 60 wt.%) in an environment of model saliva with fluoride ions added has been evaluated by Mareci et al. [20]. Both in non-modified and acid saliva, alloys with tantalum exhibited corrosion resistance which was comparable with that of the reference Ti6Al7Nb alloy. In an acidic environment containing fluoride ions, however, the corrosion resistance of tantalum alloys was higher than that of Ti6Al7Nb. The impedance spectra showed a compact surface layer under all conditions. Corrosion data survey literature state insufficient tantalum resistance in hydrofluoric acid but the data refers to industrial environment [21].

The above survey clearly shows that information on corrosion resistance of titanium-tantalum alloys in specific environments relating to their possible application in dentistry is hardly sufficient. The presented study thus aimed to compare corrosion properties of pure titanium and Ti15Ta and Ti30Ta alloys in a relatively non-aggressive physiological solution and in an identical environment with a lowered pH and a fluoride ions content.

2. Experimental

Measurements were performed on specimens including titanium grade 2 (Bibus, Brno), Ti15Ta and Ti30Ta alloys (UJP Prague), and tantalum (purity 99.85 wt.%; Inkosas, Prague). In order to achieve a homogeneous structure, the specimens of alloys were remelted five-times (vacuum electric-arc furnace L200, Leybold-Heraeus). The ingots were subsequently annealed at a temperature of 650 ℃ for 15 min so as to remove strain, and then left to cool freely in air. For electrochemical measurements, we used cylinder-shaped specimens ($\varnothing\ 8 \times 20\,\mathrm{mm}^2$), with an internal thread to fix them in a holder made of PTFE (in accordance with the ASTM G5-94 standard). Specimens of 8 mm in diameter and 3 mm in height were prepared for surface analysis. Prior to measurements, the specimens were wet ground (up to FEPA P1200 paper – electrochemistry, P2500 – XPS analysis), rinsed with distilled water, ethanol and acetone. Subsequently they were sterilized-passivated in saturated water vapor (120 ℃/20 min; BMT Ecosteri), and after cooling in air they were exposed to a corrosion environment.

The measurements were carried out in a physiological solution ($9\,\mathrm{g\,l}^{-1}$ NaCl, abbreviated PS in the text), at a temperature of 37.0 ± 0.2 ℃. The pH of the physiological solution was either non-adjusted (abbreviated pH n.a.) or adjusted to 5.8 or 4.2 using a phthalate buffer solution [22]. The effect of fluoride ions, which are commonly used in dental preparations up to a concentration of 12500 ppm [17, 18], was simulated by adding sodium fluoride. The fluoride ions concentration of 1000 ppm ($0.053\,\mathrm{mol\,l}^{-1}$) was used for the environment with pH of 5.8. Under these conditions the specimens were exposed in the titanium dioxide stability region. The addition of 200 ppm ($0.011\,\mathrm{mol\,l}^{-1}$) of fluoride ions was used in the case of pH 4.2, which corresponded to the boundary of titanium dioxide stability – titanium activation [13]. The exposure conditions are given in tables and figures using the abbreviation pH/fluoride ions concentration in ppm (e.g. pH n.a./0F, pH 4.2/200F).

Electrochemical measurements were carried out in a standard three-electrode arrangement. A chloride-silver electrode with a chloride ions concentration of $3\,\mathrm{mol\,l}^{-1}$ (SSCE) was used as a reference electrode. This electrode was placed in a plastic saline bridge closed with Agar, in order to prevent fluoride ions contact with the electrode glass body. The measurements were performed in a cell made of PTFE.

The course of measurements in model solutions was as follows: stabilization of the open circuit potential for a period of 11 h, measurement of the impedance spectrum, and determination of the potentiodynamic dependence in the range of –0.05 V from the open circuit potential to a potential of 1 V/SSCE at a rate of $1\,\mathrm{mV\,s}^{-1}$. Electrochemical impedance spec-

Table 1. Open circuit potentials

Environment	E_{ocp} (V/SSCE)			
	Ti	Ti15Ta	Ti30Ta	Ta
pH n.a./0F	–0.019	0.038	0.108	–0.215
pH 5.8/1000F	–0.314	–0.280	–0.271	–0.212
pH 4.2/200F	–1.004	–0.511	–0.489	–0.187

tra were scanned at the open circuit potential (frequency range of 50 kHz – 1 mHz, amplitude 10 mV). All electrochemical measurements were performed using a Gamry FAS 1 potentiostat (Gamry). Impedance data were evaluated using the Echem Analyst v.5.58 software (Gamry).

An ESCAprobe P (Omicron Nanotechnology) spectrometer with a monochromatic Al Kα (E = 1486.7 eV) radiation source was used for surface analysis. The pressure in the analyzing chamber was 2×10^{-8} Pa. The spectra were scanned with an energy step of 0.05 eV, and normalized to a peak binding energy of C1s (285.0 eV) [23]. Prior to inserting into the spectrometer the specimens were intensively rinsed with distilled water, ethanol and acetone. The period between the specimens' withdrawal from the electrolyte and their insertion into the input chamber of the spectrometer was about 2 min.

The rate of titanium and tantalum release from the studied materials was measured by way of direct determination of metal ions released into the solution. The specimens with a surface treated in a standard way were exposed in a physiological solution containing 200 ppm of fluoride ions and pH decreased to 4.2 for a period of 16 h. Exposure was done in 20 ml plastic weighing bottles. The solution was subsequently stabilized by 5 ml HNO_3 (1 : 1 vol.) (Merck Suprapur). Titanium and tantalum concentrations were determined using the mass spectrometry method with induction-coupled plasma excitation source (ICP mass spectrometer ELAN 6000, Perkin Elmer).

3. Results and discussion

The open circuit potential values of the studied materials at the end of 16 h exposure are summarized in Table 1. The course of potentiodynamic curves is shown in Fig. 1. In view of the similarity of their course, we present only the dependences for the environment of a physiological solution with non-adjusted pH and that with pH 4.2/200F, which corresponds to environments with the lowest and highest aggressiveness.

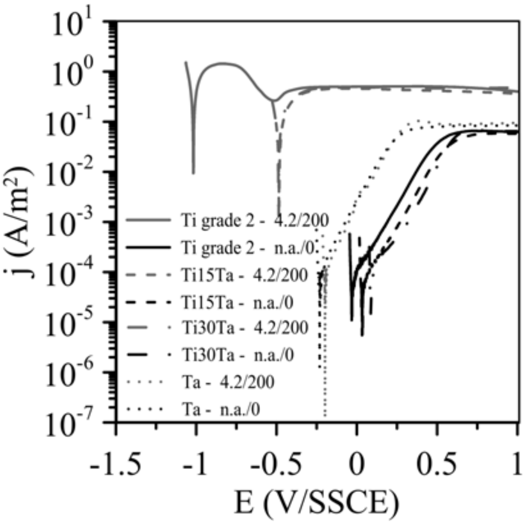

Fig. 1. Potentiodynamic curves.

The open circuit potentials of titanium and its alloys in the physiological solution ranged at the same level, and their potentiodynamic curves had a basically identical shape, too. The open circuit potential of tantalum in this environment was shifted by 200 mV in the negative direction, and the curve shape again did not differ in any substantial way. It is obvious that the alloys behavior was strongly determined by the corrosion behavior of titanium under these conditions. In the pure physiological solution, all materials were in the passive state. With an increasing aggressiveness of the environment, i.e. increasing concentration of fluoride ions and decreasing pH, a decrease of the open circuit potential occurred in both titanium and its alloys. The passive layer was chemically degraded by hydrofluoric acid, whose formation under the given conditions was described in [11]. In the physiological solution pH 5.8/1000F, open circuit potentials continued to stay in the stable passivity region of both titanium and tantalum. A significant change occurred during exposure in the physiological solution pH 4.2/200F. In this case the open circuit potential of titanium grade 2 settled at –1.004 V/SSCE, i.e. at a value corresponding to the equilibrium of the reaction

$$TiO_2 + 4H^+ + 2e^- \leftrightarrow Ti^{2+} + 2H_2O$$

(the equilibrium potential at pH 4.2 ranges from –0.927 to –1.104 V/SSCE for Ti^{2+} ions concentrations from 10^{-8} to 10^{-2} mol l^{-1} [24]). The open circuit potential of alloys was in the passive region under these conditions. Its value for tantalum was not affected by the corrosion aggressiveness of the environment.

The potentiodynamic curve of titanium in a physiological solution of pH 4.2/200 ppm fluoride ions clearly shows the passivation peak at a potential of –0.830 V/SSCE with a current density at a level of

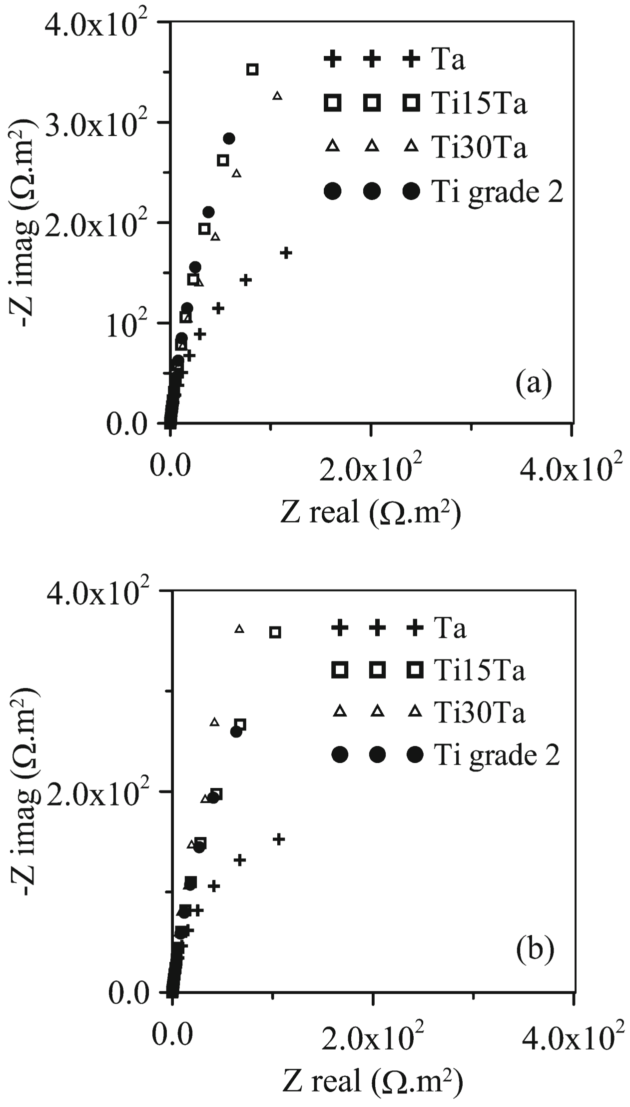

Fig. 2. Impedance spectra of the studied materials in a physiological solution pH n.a./0F (a) and pH 4.2/0F (b).

5 A m^{-2}. For both titanium grade 2 and the alloys, the current density in the passive state ranged at a level of 0.5 A m^{-2} under the given conditions (the course of curves in Fig. 1 is practically undistinguishable). In the case of tantalum, changes in the environment aggressiveness did not cause any significant change in its corrosion behavior, and the passive current density was lower by order of magnitude. Strong influence of titanium on the corrosion behavior of its alloys was again evident.

More detailed information about processes on the metal-electrolyte phase boundary was obtained based on an impedance spectra analysis. Electrochemical impedance spectroscopy (EIS) spectra of all materials measured in the physiological solution pH n.a./0F and pH 4.2/0F are given in Fig. 2. In all cases they could be fitted with a function based on an equivalent circuit as shown in Fig. 5a [25–28]. In this circuit, R_s stands for the electrolyte resistance, CPE$_\mathrm{dl}$ is the constant phase element which is used instead of a capacitor and takes into account the non-ideal behavior of the system, and R_p is the resistance of the metal-electrolyte phase boundary. In the low frequency region, R_p corresponds to polarization resistance measured by DC technique (Table 2). The constant phase element impedance is defined as $Z = [C\cdot(\mathrm{j}\omega)^\alpha]^{-1}$, where $\alpha \in \langle 0;1\rangle$, with $\alpha = 1$ corresponding to pure capacitance and $\alpha = 0$ to resistance [25]. Behavior of all the studied materials was capacitive. The calculated values of the equivalent circuit elements are summarized in the pH n.a./0F and pH 4.2/0F parts of Table 3a. EIS measurements confirmed high corrosion resistance of titanium and its alloys as well as tantalum. Corrosion rates determined from the R_p values were in the range of 10^{-2} µm year^{-1}. The measurements again revealed the dominant effect of titanium on the corrosion behavior of alloys.

Table 2. Polarization resistances

	R_p (Ω m^2)			
Environment	Ti	Ti15Ta	Ti30Ta	Ta
pH n.a./0F	1715	1420	1200	810
pH 5.8/1000F	1.99	2.33	4.48	640
pH 4.2/200F	0.045	0.213	0.393	570

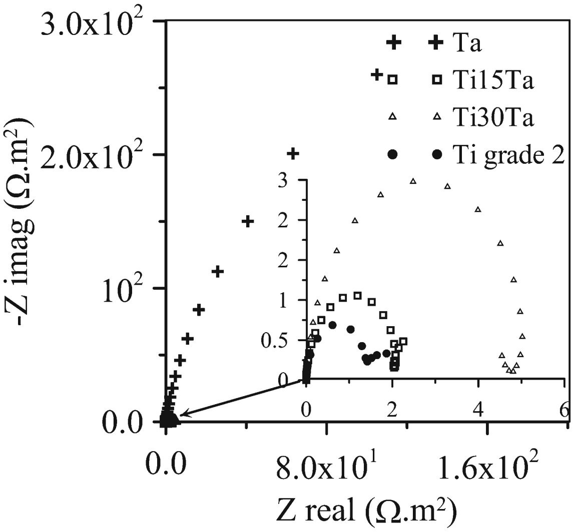

Fig. 3. Impedance spectra of the studied materials in a physiological solution pH 5.8/1000F.

The impedance spectra of the studied materials as measured in a physiological solution pH 5.8/1000F are given in Fig. 3. In all cases except that of tantalum, capacitance increased and polarization res-

Table 3a. EIS – values of the equivalent circuit elements – equivalent circuit 5a

Environment		Q_{dl} ($\mathrm{S\,s^{\alpha}\ m^{-2}}$)	α_{dl}	R_{p} ($\Omega\,\mathrm{m}^2$)	R_{s} ($\Omega\,\mathrm{m}^2$)
pH n.a./0F	Ti	4.1×10^{-3}	0.937	2.7×10^{3}	41.6×10^{-4}
	Ti15Ta	3.2×10^{-3}	0.936	2.7×10^{3}	40.5×10^{-4}
	Ti30Ta	3.3×10^{-3}	0.939	2.2×10^{3}	30.5×10^{-4}
	Ta	4.9×10^{-3}	0.940	4.2×10^{2}	27.6×10^{-4}
pH 4.2/0F	Ti	4.3×10^{-3}	0.929	2.1×10^{3}	27.6×10^{-4}
	Ti15Ta	3.0×10^{-3}	0.927	2.2×10^{3}	29.5×10^{-4}
	Ti30Ta	2.4×10^{-3}	0.938	2.1×10^{3}	35.7×10^{-4}
	Ta	5.3×10^{-3}	0.930	4.2×10^{2}	20.2×10^{-4}
pH 5.8/1000F	Ti	1.4×10^{-2}	0.947	1.5	20.0×10^{-4}
	Ti15Ta	9.4×10^{-3}	0.957	2.2	12.6×10^{-4}
	Ti30Ta	6.1×10^{-3}	0.948	5.3	15.7×10^{-4}
	Ta	4.0×10^{-3}	0.939	9.6×10^{2}	17.5×10^{-4}
pH 4.2/200F	Ta	5.4×10^{-3}	0.934	7.0×10^{2}	17.8×10^{-4}

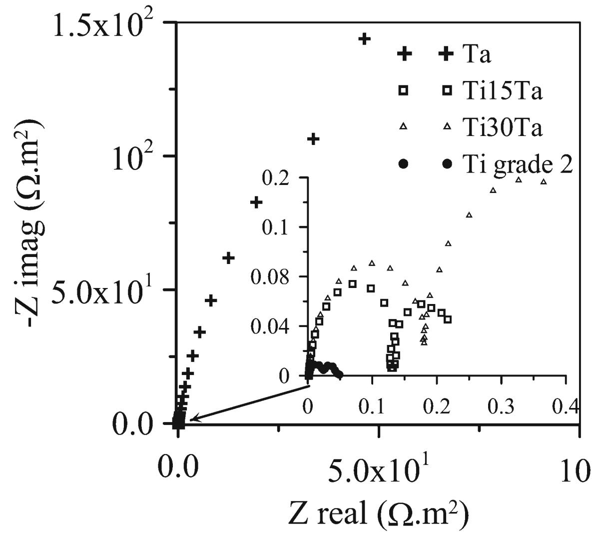

Fig. 4. Impedance spectra of the studied materials in a physiological solution pH 4.2/200F.

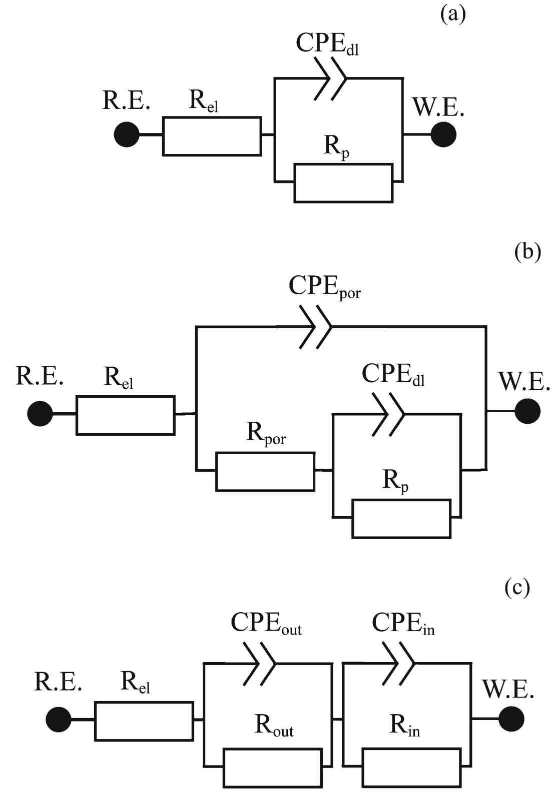

Fig. 5a,b,c. Equivalent circuits used in analysis of measured electrochemical impedance spectra.

istance decreased, which was reflected in the transition of the spectra shape into a typical flattened arc. In the low frequency region, inclination to the so-called pseudo-inductive loop occurred. This phenomenon was ascribed to reverse precipitation of corrosion products [29, 30]. The data were fitted using the equivalent circuit in Fig. 5a, the low-frequency part was not considered in calculations. In the case of tantalum, no significant changes occurred in the course of the spectrum due to a higher aggressiveness of the environment, and the spectrum retained a capacitive character. Given the general capacitance growth in the studied systems – with the exception of tantalum – we may assume that the surface layer thickness decreased in the course of exposure. The most significant capacitance growth and polarization resistance decrease was noted for titanium grade 2. Tantalum influence was expressed to a certain extent in this environment. Polarization resistance was approximately 1.5-times higher for Ti15Ta and 3.5-times higher in the case of Ti30Ta as compared with titanium grade 2.

The impedance spectra of titanium grade 2 and the

Table 3b. EIS – calculated values of equivalent circuit elements

Equivalent circuit 5b								
Environment		Q_{out} ($\mathrm{S\,s^{\alpha}\,m^{-2}}$)	α_{out}	R_{out} ($\Omega\,\mathrm{m^2}$)	R_{s} ($\Omega\,\mathrm{m^2}$)	R_{por} ($\Omega\,\mathrm{m^2}$)	Q_{por} ($\mathrm{S\,s^{\alpha}\,m^{-2}}$)	α_{por}
pH 4.2/200F	Ti	1.8	0.808	0.022	17.4×10^{-4}	0.023	2.3×10^{-2}	0.875
	Ti15Ta	8.9	1	0.141	17.5×10^{-4}	0.142	3.4×10^{-2}	0.969
	Ti30Ta	4.1	1	0.314	15.4×10^{-4}	0.188	3.3×10^{-2}	0.941
	Ta (eq. circuit 5a)	5.4×10^{-3}	0.934	7.0×10^{2}	17.8×10^{-4}			
Equivalent circuit 5c								
Environment		Q_{out} ($\mathrm{S\,s^{\alpha}\,m^{-2}}$)	α_{out}	R_{out} ($\Omega\,\mathrm{m^2}$)	R_{s} ($\Omega\,\mathrm{m^2}$)	R_{in} ($\Omega\,\mathrm{m^2}$)	Q_{in} ($\mathrm{S\,s^{\alpha}\,m^{-2}}$)	α_{in}
pH 4.2/200F	Ti	1.8	0.808	0.022	17.4×10^{-4}	0.022	2.4×10^{-2}	0.874
	Ti15Ta	3.4	0.967	0.140	17.5×10^{-4}	0.112	2.5×10^{-2}	0.944
	Ti30Ta	4.1	1	0.318	15.4×10^{-4}	0.185	3.3×10^{-2}	0.941

Table 4. Rate of titanium and tantalum release from the studied materials (pH 4.2/200F)

	Release rate µg cm^{-2} h^{-1}	Standard deviation µg cm^{-2} h^{-1}	Release rate µg cm^{-2} h^{-1}	Standard deviation µg cm^{-2} h^{-1}
	Ti		Ta	
Ti	21.5	1.7		
Ti15Ta	18.9	1.4	2.49	0.32
Ti30Ta	3.064	0.086	0.923	0.013

Ti-Ta alloys as measured in the physiological solution pH 4.2/200F clearly show two time constants (Fig. 4). The spectra could be successfully fitted with functions based on equivalent circuits as shown in Figs. 5b,c. The fit quality was practically identical (5.3×10^{-4} vs. 5.4×10^{-4}, i.e. the difference between the measured and calculated data was at the level of percents in both cases). The presented circuits describe the electrochemical response of the layer-covered surface [25, 31–33]. In the case of equivalent circuit 5b it is a porous layer and R_{s} represents the electrolyte resistance, R_{por} is the porous solution resistance, $\mathrm{CPE}_{\mathrm{por}}$ is the capacitance of the outer porous layer, R_{p} stands for the resistance of the metal-electrolyte inner phase boundary, and $\mathrm{CPE}_{\mathrm{dl}}$ is its capacitance. The elements in circuit 5c are of a standard sense (electrolyte-layer and layer-alloy phase boundaries). The values of individual elements of equivalent circuits are summarized in Table 3b. These results do not allow for any decision about the corrosion behavior mechanism. We may state that the surface was covered with a layer/porous layer that affected the charge transfer. The tantalum impedance spectrum again stayed practically unchanged. It was fitted with a function based on the equivalent circuit shown in Fig. 5a, and corresponded to passive behavior. Titanium alloying with tantalum led to an increase in the system's overall resistance as compared with titanium grade 2. The level of tantalum content did not have any significant effect and the polarization resistance values were practically identical for both alloys.

Electrochemical measurements revealed a positive effect of tantalum on the corrosion behavior of alloys in an environment containing fluoride ions. The same result was recorded in the measurement of the rate of corrosion products release. The measured values are summarized in Table 4. However, these measurements showed a clear difference in the behavior of alloys with a 15 and 30 wt.% tantalum content. The lower tantalum content led to only a slight decrease in the titanium release rate, but a significant drop in its release rate was noted in the case of Ti30Ta – roughly 8×. Consequently, the XPS analysis, whose results are shown in Tables 5 and 6 and in Figs. 6 and 7, was focused on differences in the surface state of titanium, tantalum, and particularly their alloys.

After exposure in an unmodified physiological solution, titanium was found on the specimens surface in oxidation states Ti^{0} to Ti^{4+}, and tantalum appeared in oxidation states Ta^{0} and Ta^{5+}. A detailed analysis of titanium and tantalum spectra of Ti30Ta sample exposed in a physiological solution is given in Fig. 6. The spectra were fitted with doublet separation 5.7 eV for TiO_2 and 6.1 eV for lower oxidation states of titanium [23]. Tantalum spectra were fitted with doublet separation 1.9 eV [23]. The passive layer was

Table 5. XPS – ratio of titanium and tantalum surface concentrations (at.%)

	Ti15Ta		Ti30Ta	
	Ti	Ta	Ti	Ta
Not exposed	95.5	4.5	89.8	10.2
pH n.a./0F	88.4	11.6	74	26
pH 5.8/1000F	84.5	15.5	41.2	58.8
pH 4.2/200F	7.1	92.9	42.2	57.8

Table 6. Surface composition after the exposure in physiological solution pH 4.2/200F (at.%)

	Ti	Ta	F	Na	K	O
Ti15Ta	1.8	23.7	18.4	1.1	15.7	39.2
Ti30Ta	14.2	11.6	8.1	1.1	5.3	59.7

formed mostly by titanium and tantalum dioxides. In the case of tantalum, there was a relatively significant signal corresponding to its oxidation state 0. The titanium and tantalum concentration ratio, regardless of other elements forming the surface layer (mainly oxygen), is summarized in Table 6. The basic analysis of non-exposed specimens with a surface merely cleaned using an argon ions beam corresponded to the declared alloys composition. In the course of exposure in the physiological solution, the passive layer was enriched with tantalum (Table 5), possibly due to a higher stability of tantalum dioxide. The Gibbs energy of formation of Ta_2O_5 at 298 K is –1911 kJ mol^{-1} as compared with –889 kJ mol^{-1} in the case of TiO_2 [22].

The specimens' exposure in environments pH 5.8/1000F and 4.2/200F led to another growth of tantalum surface concentration in the case of both alloys. The surface representation of tantalum in the case of Ti15Ta increased substantially after exposure under conditions pH 4.2/200F (Table 5). After exposure in environments containing fluoride ions, however, the signals of fluorine, potassium and sodium were easily detectable in the spectra, too. In view of the specimens intensive rinsing prior to their placement in the spectrometer, we may assume that a relatively firmly adherent and low soluble layer of corrosion products was formed on their surface. This fact was in agreement with impedance measurements – the EIS dependences were layered system spectra, and the occurrence of a pseudo-inductive loop was noted in the low-frequency region of dependences measured in environments containing fluoride ions.

The ratio of titanium and tantalum surface areas was about 95 : 5 in Ti15Ta, i.e. the titanium surface area was about 19-times larger as compared with tantalum. In the case of Ti30Ta, the ratio was 90 : 10, i.e. the titanium surface area was 9-times larger. The specimens' state was identical at the start of exposure – the surface of both types of alloys was covered with an oxide passive layer formed by sterilization, which was documented by the XPS spectra. Titanium and tantalum release in environments containing fluoride ions is a chemical process resulting in the degradation of the passive layer. The system's polarization resistance (resistance part of EIS spectra) corresponds to its reconstruction at the given potential. We may assume that the initial rate of corrosion products release depends on titanium and tantalum surface areas. Consequently, the initial rate of corrosion products release from Ti30Ta is likely to be roughly 2.1-times lower than that from Ti15Ta. Titanium compounds are always the dominant products. Tantalum corrodes too,

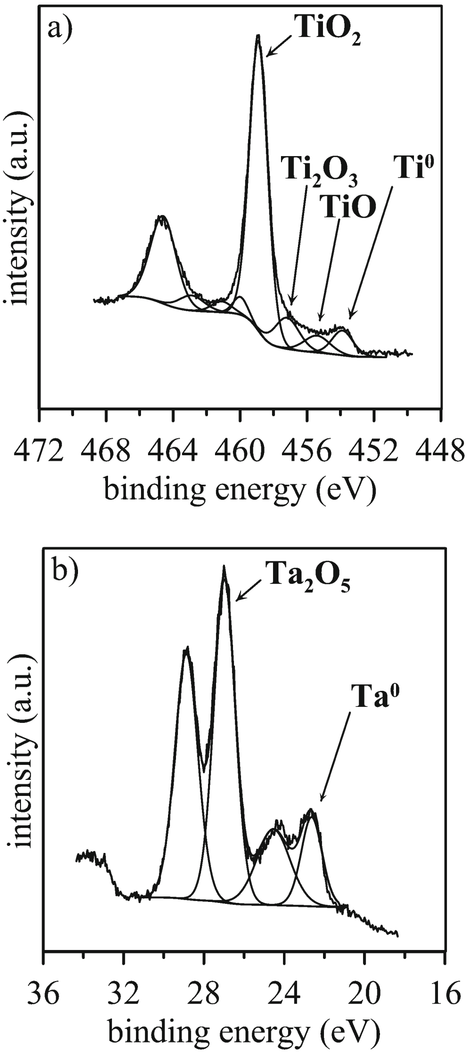

Fig. 6. Ti 2p (a) and Ta 4f (b) spectra of the Ti30Ta alloy after exposure in a physiological solution pH n.a./0F (binding energies [23]).

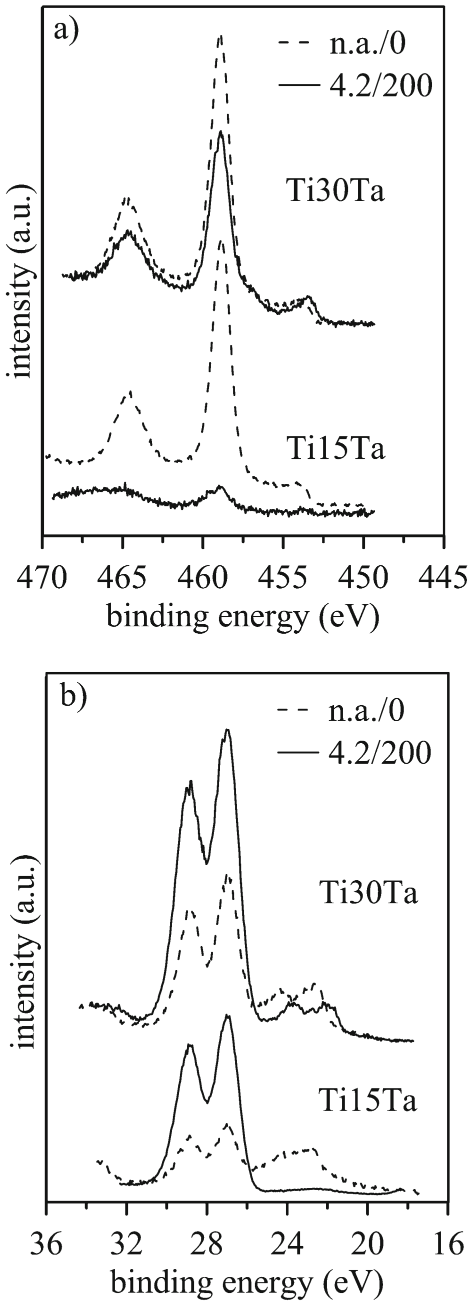

Fig. 7. Effect of exposure on the shape of Ti 2p (a) and Ta 4f (b) spectra of Ti15Ta and Ti30Ta samples.

but its corrosion rate is lower by orders of magnitude. After exposure, titanium and tantalum oxides in the highest oxidation states were detected on the specimens of both alloys. The signal on lower binding energies of Ti 2p and Ta 4f, which after exposure in a fluorides-free environment corresponded to oxides in lower oxidation states, changed both in terms of energy and intensity. We assume that the given changes were caused by the presence of a layer of corrosion products, but their identification using the available databases and literature sources was not successful [23]. The above facts allow for the assumption that the surface was gradually changing in the course of exposure, and its changes led to a lower rate of titanium release. The changes affected both the possibility of the corrosion environment contact with the oxide surface and the corrosion products transport. Both the electrochemical and XPS measurements showed differences in the protective ability and the character of layers on the Ti15Ta and Ti30Ta alloys. For Ti15Ta, the real impedance component (resistance) was 1.9-times lower and the rate of electrochemical reactions was thus higher in a corresponding way as compared with Ti30Ta. The course of the EIS spectrum also indicated a more significant enforcement of the secondary layer of corrosion products in the case of the Ti15Ta alloy.

Corrosion behavior of both alloys was basically comparable. The initial passive layer, composed of both titanium and tantalum oxides, was degraded by fluorides/hydrofluoric acid and consequently both titanium and tantalum were released into the environment. The rate of these processes was higher for Ti15Ta, which was probably the reason why the solubility product of both titanium and tantalum compound/compounds was exceeded earlier. They also caused growth of tantalum surface concentration, which was substantial in the case of Ti15Ta, and limited the rate of corrosion products release, which was notable in the case of Ti30Ta.

4. Conclusion

The main objective of titanium alloying with beta-stabilizing elements is to achieve the required structure and properties of the resulting alloys. It is also important, however, to prevent the loss of excellent corrosion properties of titanium. The corrosion behavior of the studied alloys – Ti15Ta and Ti30Ta – was basically determined by titanium. In a physiological solution, both alloys displayed stable passivity and very high polarization resistance values, i.e. corrosion behavior comparable to that of titanium.

Titanium or titanium oxides forming the passive layer are highly sensitive to the presence of fluoride ions/hydrofluoric acid. The specific conditions relating to dental applications concern both medical treatment (preparations with a low pH and a high fluoride ions concentration) and common prophylaxis. In these cases titanium activation may occur together with a significant decrease of its corrosion resistance. Its alloying with tantalum has a positive effect under the given conditions, which applies particularly to the Ti30Ta alloy. Titanium-tantalum binary alloys are not considered for direct use in dentistry, yet the knowledge of their behavior and of the behavior of other binary systems may contribute to a more rational design of more complex alloy systems applicable in practice.

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