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Corrosion behaviour of titanium after short-term exposure to an acidic environment containing fluoride ions

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Abstract The negative effect of fluoride ions on titanium has been known in dentistry for a long time. The presented work was aimed at the interaction between titanium and model saliva following a short-term exposure of a specimen to a model medical preparation rich in fluoride ions. The experimental work was carried out using titanium grade 2 in a physiological solution (pH non-adjusted, 5.8, 4.2; 5000 ppm F^-) and in model saliva. Electrochemical measurement techniques were supplemented with XPS analysis. The presence of fluoride ions resulted in partial degradation of the passive layer even in a slightly acidic environment. The decrease of pH to the value of 4.2 and the presence of 5000 ppm F^- caused titanium activation followed by a slow repassivation in model saliva. Formation of low soluble compound rich in fluorine explains experimental data. Short medical treatment can result in relatively long period of increased titanium corrosion.

1 Introduction

Information about the negative effect of fluoride ions on titanium is contained in corrosion-related textbooks (e.g. [1]). The danger of this phenomenon in the field of stomatology has been discussed in literature since the 1990s [2–8]. Fluorine has been found in tissues taken from the vicinity of failed implants [9], and the presence of titanium was recorded in pigmentations of soft tissues in the oral cavity [10].

Nakagawa et al. [11] used electrochemical and exposure tests to study the corrosion behaviour of titanium grade 2 in a saliva model with fluorides added and the pH value adjusted in the range of 3.0–7.0. The authors determined the relation between the pH, free fluoride ions, the concentration of non-dissociated hydrofluoric acid, and the stability of the passive layer on titanium. Their results provided a linear relation between pH and pF (i.e. $-\log c_F$). The authors stated that in terms of titanium activation, the presence of hydrofluoric acid was of major importance, and its boundary concentration leading to activation was 21 ppm. A thermodynamic analysis of the behaviour of a Ti–F-saline environment system (NaCl, Ringer's, Fusayama's and SAGF solutions) was published by Fovet et al. [12]. Based on a thermodynamic model, the authors calculated equilibrium dependencies between the pH (for pH = 0–6.5) and the fluoride ions content (pF = 0-4). In the region corresponding to titanium use in dentistry, i.e. pH > 3, the calculated pH-pF dependencies were of a linear shape. This theoretical study and the above mentioned experimental study showed only minimal differences in the determination of the border concentration of H^+ ions leading to the degradation of the passive layer at a given concentration of fluoride ions. In the concentration range 200–3000 ppm F, i.e. again the region which is of interest from the stomatological point of view, these differences were at a level of <0.1 pH.

The major problem of dental practice rests in the use of medical preparations with a high content of fluoride ions mostly in an environment with pH in the acidic region where their effect is the strongest [3, 13]. The effect of prophylactic preparations during simulated teeth cleaning was studied in the work [14]. Authors concluded that the negative effect of fluorides was proved beyond doubt. Stajer et al. [15] pointed out the negative effect of mainly

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prophylactic gels in patients with implants and dental appliances made of titanium based on a cell study.

Mentioned above was only a part of the relatively rich literature dealing with fluorides and titanium in relation to dentistry. The negative effect of fluoride ions on titanium used in dental applications may be considered proved. Possible negative reactions of the organism to corrosion products or changes in the functionality of dental appliances largely depend on the dose, i.e. on the extent to which a periodical application of fluoride preparations may really cause problems. We have not as yet found any study in available literature that would deal with long-term changes in the corrosion behaviour of titanium after exposure to an acidic environment rich in fluoride ions.

The objective of this work was to study the interaction between titanium grade 2 and artificial saliva after the specimen's short-term exposure to the model of a medical preparation with a high concentration of fluoride ions.

2 Materials and methods

Electrochemical measurements were carried out using titanium grade 2 specimens in the shape of cylinders with a diameter of 8 mm and height of 20 mm. For the surface analysis, specimens of the same diameter were used, but their height was limited to 3 mm by the testing equipment. Prior to each measurement, the specimen surface was ground using paper P1200 (P2500 for the surface analysis), rinsed with distilled water, ethanol and acetone, and then sterilized/passivated with saturated water vapour at 120°C for 20 min (BMT Ecosteri).

The measurements were conducted in a model saliva solution, henceforth referred to as MS (Table 1), which was bubbled by a mixture of air and carbon dioxide (10 vol.% CO_2) 1 h prior to the measurement [16]. A medical preparation with a high content of fluoride ions was modelled using a buffered physiological solution (PS). A buffer solution of potassium hydrogenphtalate with sodium hydroxide was used to adjust the pH [17]. Fluoride ions were added in the form of sodium fluoride. All measurements were conducted at a temperature of 37.0°C ± 0.1°C (Haake DC10). For the sake of clarity, the combinations of the used exposure environments and conditions are in the following text denoted with codes explained in Table 1.

Electrochemical measurements were conducted using a FAS1 (Gamry) potentiostat, XBM datalogger with an XB 2K measuring head (Gryf HB) was used for the potentials-time dependencies measurement. An all-plastic cell (PTFE) was used for the measurements. The reference silver/silver chloride electrode (3 mol/l KCl) Theta RE 402 (Theta '90) was placed in a plastic saline bridge filled with a KCl solution and closed with Agar. The auxiliary electrodes were made of graphite. The measured potentials were recalculated and they are presented in relation to a standard hydrogen electrode (SHE).

Potentiodynamic dependencies were scanned in the respective environments, after a 5-min delay on E_{ocp}, in the range -0.05 V/E_{ocp} to 0.5 V/SHE, at a rate of 1 mV/s.

In modelling the effect of fluoride containing preparations, the specimen was for 15 min exposed to a physiological solution of a respective pH value, containing 5000 ppm F^- ions (PS-pH/5000). In this stage only the potential was scanned. The specimen was then quickly and without rinsing transferred to a model saliva solution. Over the first about 5 min, when the open circuit potential mostly changed very quickly, only this value was being recorded. In the further course of the exposure, both the open circuit potential and polarization resistance were measured. Polarization resistance was measured in the range ±15 mV from E_{ocp} at a potential change rate of 0.5 mV/s. This procedure was tested using a model and it was found out that an increase in the potential change rate did not have any negative effect on the correctness of the measurement. The total time of exposure to a model saliva solution was 60 min in general. In the case of exposures extended to 58 h, the periodical scanning concerned the open circuit potential, polarization resistance (±15 mV from E_{ocp}, 0.1 mV/s) and the impedance spectrum (50 kHz–1 mHz, ac amplitude 10 mV) was carried out.

Table 1 Exposure environment and conditions

Abbreviation	pH	Composition	Exposure time (min)
PS-n.a.	Not-adjusted	NaCl (9 g/l)	15
PS-n.a./5000	Not-adjusted	NaCl (9 g/l) + 5000 ppm F^-	15
PS-5.8	5.8	NaCl (9 g/l), buffer solution	15
PS-5.8/5000	5.8	NaCl (9 g/l), buffer solution + 5000 ppm F^-	15
PS-4.2	4.2	NaCl (9 g/l), buffer solution	15
PS-4.2/5000	4.2	NaCl (9 g/l), buffer solution + 5000 ppm F^-	15
MS	6.8	1.5 g/l KCl, 0.5 g/l $NaH_2PO_4 \cdot H_2O$, 1.5 g/l $NaHCO_3$, 0.5 g/l KSCN, 0.9 g/l lactic acid	60

For the surface analysis, the exposed specimen was quickly and intensively rinsed with distilled water, ethanol and acetone prior to its placement in the spectrometer entry chamber. The measurements were conducted using an ESCAProbeP spectrometer (Omicron Nanotechnology). The monochromatic excitation source was the line Al K_α, the binding energies were corrected to the C 1s peak ($E_b = 285.0$ eV). The pressure in the analyzing chamber was 2×10^{-8} Pa. The measured specimen area was 1.3 mm^2. The survey spectra were scanned with an energy change step of 0.1 and 0.05 eV in the case of detailed spectra.

The analyses of the layer formed during exposure to a fluoride environment of pH = 4.2 were conducted using a Raman dispersion spectrometer Labram HR (Jobin–Yvon) with a confocal microscope (Olympus). The excitation source was a laser of a wave length of 532 nm. RTG diffraction spectra were scanned using a diffractometer X′Pert PRO (PANalytical). An RTG radiation source with a Cu anode was used (40 kV, 30 mA).

3 Results

The course of potentiodynamic curves as shown in Fig. 1 reflects the negative effect of fluoride ions under all the applied conditions. It is demonstrated by a shift of the curves both towards higher current densities and towards more negative potentials.

Time dependencies of the course of the open circuit potential and polarization resistance when modelling the effect of a medical preparation with a high content of fluoride ions on subsequent repassivation in model saliva are shown in Fig. 2. In an environment with fluorides and a non-adjusted pH, the open circuit potential of titanium was increasing while in a solution with pH = 5.8 it was decreasing all the time (x symbol, Fig. 2a, b). Subsequent exposure to model saliva proceeded in a similar way in both cases—the open circuit potential was increasing slowly and was in a range nearing 0 V (Δ and ● symbols, Fig. 2a, b). Polarization resistance was increasing constantly during exposure to model saliva in both cases, only its values after exposure to PS-5.8/5000 were roughly half of those recorded in the case of PS-n.a./5000 (☐ symbol, Fig. 2a, b). A similar course could be expected because after the removal of the aggressive agent, gradual restoration of the surface could be expected linked with a growth of polarization resistance and a shift of the potential in the positive direction.

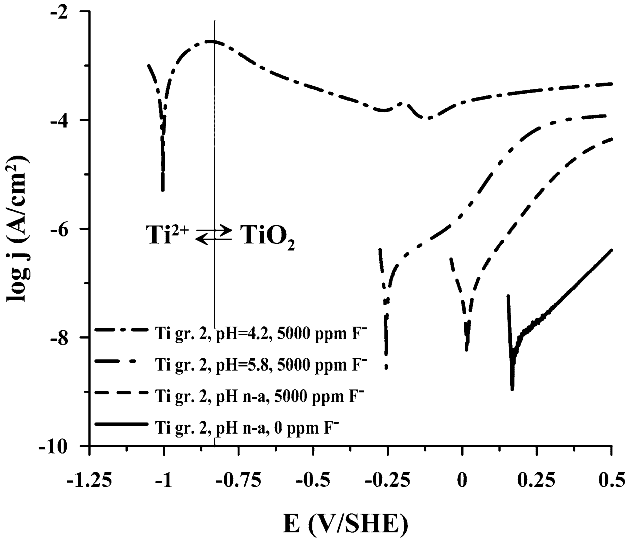

Fig. 1 Potentiodynamic dependencies

The behaviour of specimens exposed to the PS-4.2/5000 environment was entirely different (Fig. 2c). At the start of the exposure, an almost jump-like change of the potential to ∼−1.0 V occurred (x symbol, Fig. 2c). After a delay in this region, the potential grew to a level of −0.8 V in the final minutes of the exposure. During subsequent exposure in MS, the potential stabilized at a value of −0.64 V (Δ and ● symbols, Fig. 2c), and it also stabilized at a comparable level in the case of extended exposure to PS-4.2/5000 (Fig. 3). The time dependence of polarization resistance during subsequent exposure to model saliva was also different as compared with environments with a higher pH (☐ symbol, Fig. 2c). The dependence went through the maximum and the level of the measured values was distinctly lower than in the two preceding cases.

Figure 4 shows time dependencies of the open circuit potential and polarization resistance in a situation when the PS-4.2/5000:MS measurement was not finished after 1 h. The open circuit potential started to grow after about 10 h. Polarization resistance followed this trend only after about 15 h. In order to allow for comparison, the figure shows E_{ocp} and R_p time dependencies of titanium grade 2 which was exposed only to a physiological solution of pH = 4.2, without any fluoride ions added (PS-4.2:MS).

Given the atypical course of both the open circuit potential and polarization resistance during the PS-4.2/5000:MS exposure, information about corrosion behaviour was supplemented with measurements of impedance spectra, and a surface analysis conducted using the XPS method. In agreement with the preceding measurements, the impedance spectra summarized in Fig. 5 show significant changes going on for at least 30 h. For the spectra analysis, a broader set of phase boundary models was tested. Figure 6 shows equivalent circuits whose application allowed for the most accurate description of the course of the measured data. Each parallel combination of resistance and capacitance in the scheme represents a phase boundary over which the charge is carried. Given that the

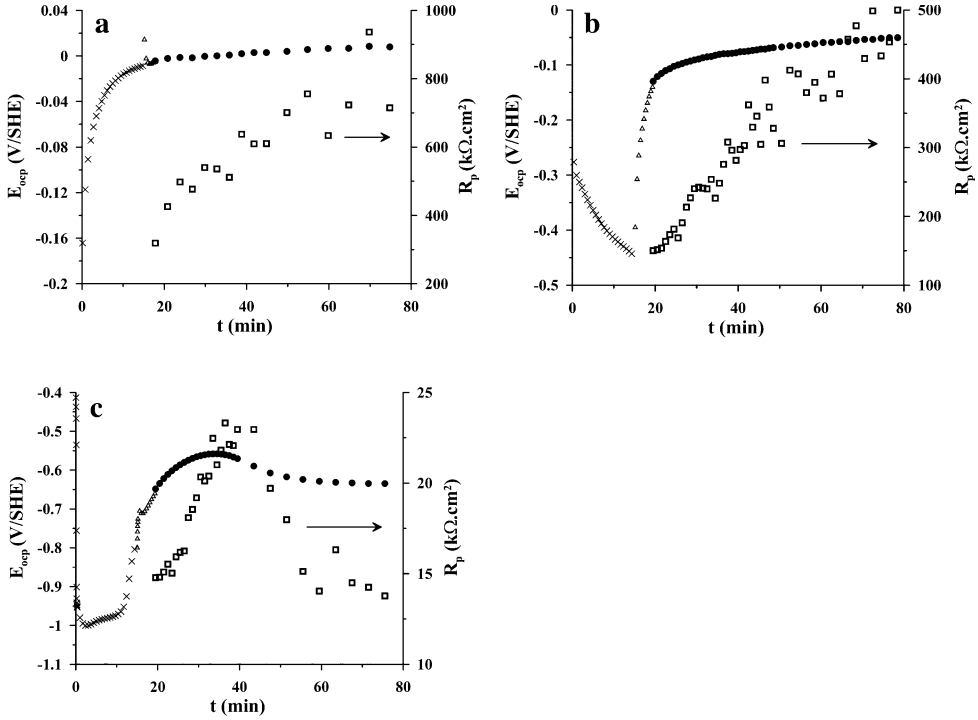

Fig. 2 E_{ocp} and R_p time dependencies (**a** PS-n.a./5000:MS, **b** PS-5.8/5000:MS, **c** PS-4.2/5000:MS)

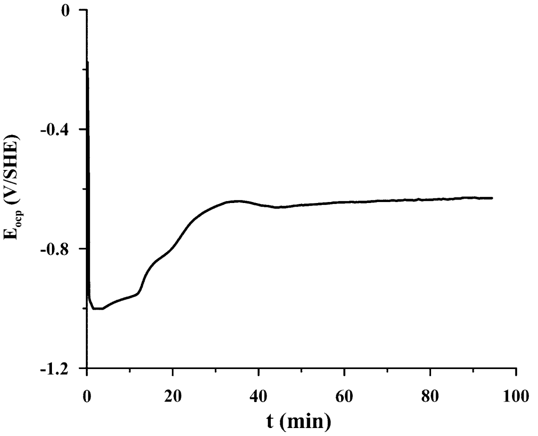

Fig. 3 E_{ocp} time dependence in PS-4.2/5000

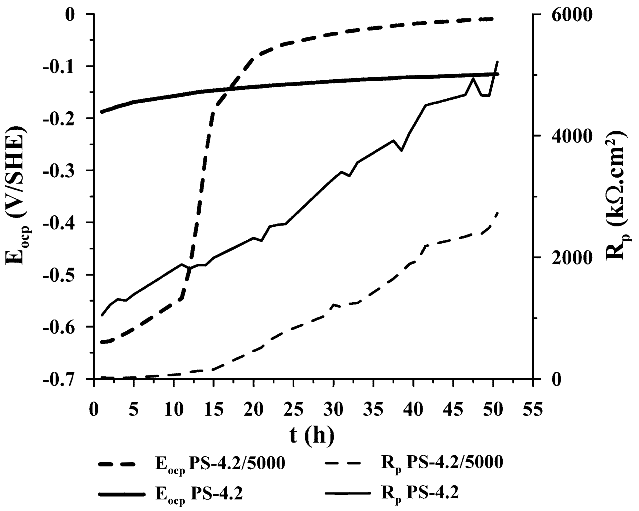

Fig. 4 E_{ocp} and R_p long-term time dependencies in MS

system did not behave ideally, elements with a constant phase respecting this non-ideality were used instead of pure capacitors [18–20]. Coefficient α ranged between 1—the element corresponded to a capacitor and 0—corresponding to a resistor. The time dependencies of the values of the equivalent circuit elements modelling non-porous layer are shown in Fig 7. The results make it clear that no stabilization of the passive layer properties occurred throughout the measurement.

Table 2 gives the composition of the titanium grade 2 surface as determined using the XPS method after exposures modelling the effect of fluoride ions on the oxidic layer and the effect of the length of repassivation in model saliva on changes in the surface state. The exposure conditions included PS-4.2, PS-4.2/5000, and PS-4.2/5000:MS. In the latter case the time of exposure in model saliva was 30 min (the region of maximum R_p time dependence), 60 min (standard exposure), and 48 h. Quantification was made on the basis of the detailed spectra of individual elements, i.e. on the basis of Ti 2p, O 1s, F 1s, K 1s, Na 1s and P 2p peaks. Figure 8 shows the dependencies of the shape of Ti 2p peaks measured under the above conditions. The binding state of titanium was changing gradually. In the first phase, broad peaks were detected that gradually passed to characteristics corresponding to the published characteristics of TiO_2 [21].

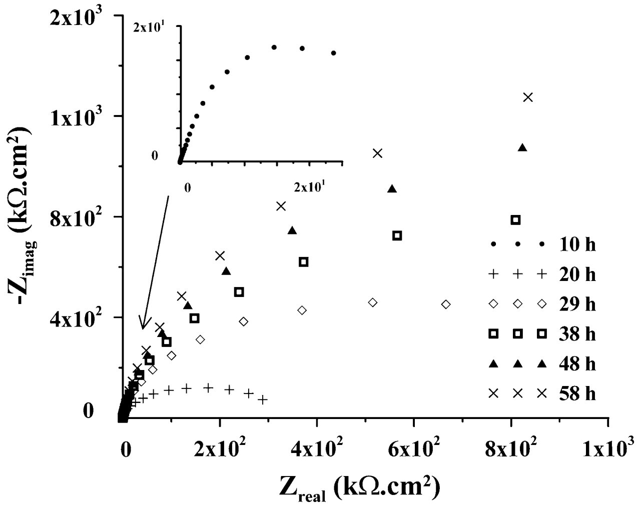

Fig. 5 EIS spectra—repassivation in model saliva after the PS-4.2/5000 exposure

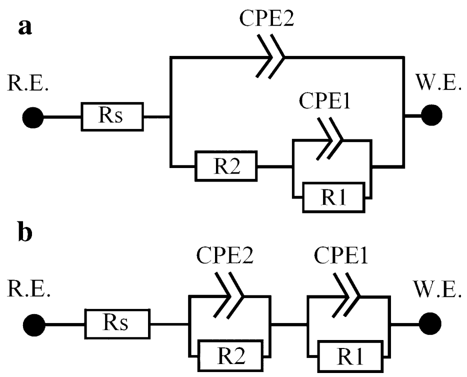

Fig. 6 Equivalent circuits (**a** porous surface layer, **b** non-porous surface layer)

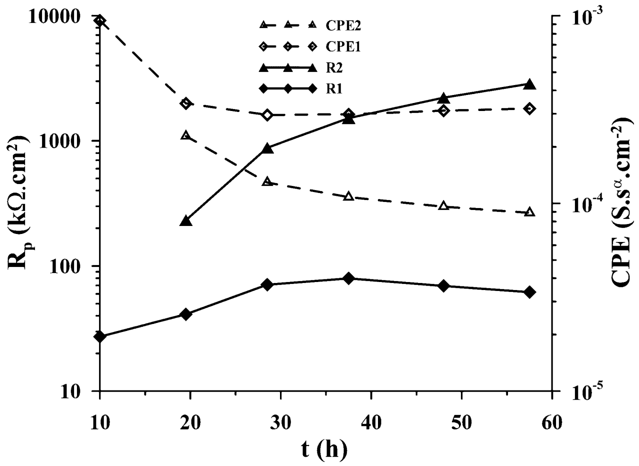

Fig. 7 EIS spectra analysis—time dependence of equivalent circuits elements

Table 2 XPS analysis of the exposed specimens (at.%)

Conditions/element	Ti	O	F	K	Na	P
Passivated surface	27.5	72.5	–	–	–	–
End of PS-4.2/5000 exposure	8.3	7.4	48.1	32.3	3.9	–
30 min. in MS	10.3	59.1	4.3	9.4	0.6	16.3
60 min. in MS	9.8	61.8	1.5	11.3	0.9	14.7
48 h. in MS	10.3	63.5	0.4	9.3	0.8	15.7

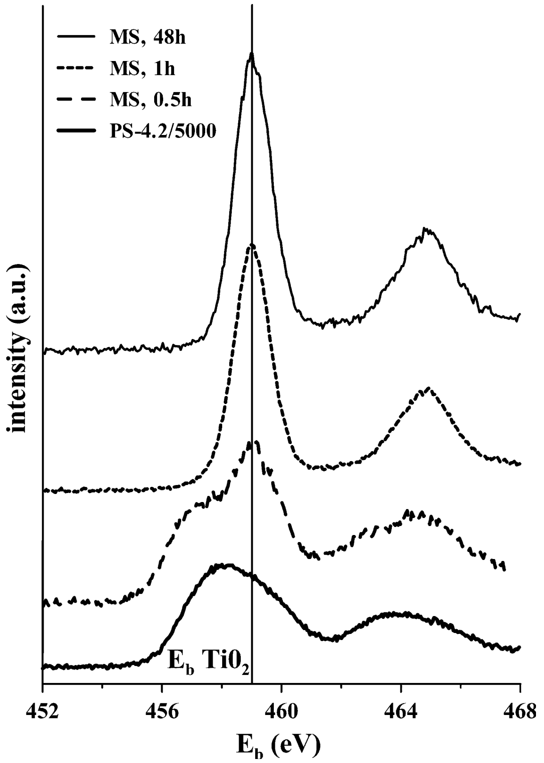

Fig. 8 Development of the Ti 2p doublet shape

Raman microspectroscopy and an RTG diffraction analyses were used to identify the composition of the layer originating after the PS-4.2/5000 exposure. Raman spectroscopy excluded the presence of titanium in the form of titanium dioxide, but the measured bands could not be attributed using the available databases. The result of the XRD measurement was similarly unsatisfactory. Clearly identified were titanium and the phase isostructural with $BaZrO_3$. Corresponding data failed to be found for seven weaker reflections.

4 Discussion

The potentiodynamic curve of titanium grade 2 in a physiological solution is a passive material curve with a positive corrosion potential and a corrosion current density at a level of 10^{-8} A/cm^2. The presence of fluoride ions combined with a decrease in pH, caused deterioration of the properties of the passive layer formed during the specimens sterilization under all the studied conditions. This was reflected in the increase of current densities and a shift of the corrosion potential in the negative direction. This trend was most evident in the curve measured in the PS-4.2/5000 environment. The corrosion current density was four orders higher ($\sim 4.6 \times 10^{-4}$ A/cm^2) as compared with a neutral solution without any fluoride ions, with a distinct passivation peak on the curve. The original passive layer formed during sterilization was chemically attacked in such a way that the potential dropped below −0.78 V, i.e. below the equilibrium value for the reaction $Ti^{2+} \rightarrow TiO_2$ at a Ti^{2+} ions concentration of 1.0×10^{-6} mol/l [22]. The course of the potentiodynamic dependence makes it clear that activation occurred under the given conditions.

The results of modelling the effect of medical preparations on the corrosion behaviour of titanium grade 2, as summarized in Fig. 2, yet more clearly illustrate the largely different effect of a change in pH on the passive layer stability in an environment containing the same amount of fluoride ions. During the PS-n.a./5000 exposure, a slight increase in the open circuit potential above the initial value of −0.17 V occurred. Transition to model saliva was not recorded on the open circuit potential time dependence. A decrease in polarization resistance during the PS-n.a./5000 exposure to the level of 300 kΩcm^2 testified to the changing properties of the passive layer. Its value rose to 1000 kΩcm^2 during subsequent exposure to model saliva.

A change in the pH of the physiological solution to 5.8 (PS-5.8/5000:MS) had a more substantial effect on titanium surface. The decrease of the potential in the medical preparation model was permanent. During subsequent exposure to model saliva, the initial polarization resistance value was 150 kΩcm^2. However, polarization resistance reached high values again at the end of exposure to model saliva, even though they were roughly half of those recorded in the preceding case.

A similar results could be expected because after the removal of the aggressive agent, gradual restoration of the surface could be expected linked with a growth of polarization resistance and a shift of the potential in the positive direction.

Exposure to an environment with pH = 4.2 followed by an exposure in model saliva (PS-4.2/5000:MS) resulted in a substantial change in the course of the monitored dependencies. The open circuit potential practically jumped to the value of −1 V, which is in the region of titanium activity [23], and it did not change in any substantial way over most of the exposure time. At the end of a 15 min delay, however, the potential rose by 0.2 V. The course of the measured data indicated that after the initial activation and a delay in the active state, the surface passivated again. Subsequent exposure to model saliva stabilized the potential at −0.636 V, which is deep in the region of TiO_2 stability [23]. In accordance with the potential level, polarization resistance was 15 kΩcm^2 at the beginning of exposure to model saliva, i.e. lower by order of magnitude in comparison with the preceding cases. Based on the course on the time dependence of the open circuit potential, which rose by 250 mV and stabilized, a similar course of polarization resistance could be expected—i.e. a gradual growth corresponding to the assumed development of the passive layer. However, the measured dependencies did not correspond to this assumption, with polarization resistance passing through the maximum and subsequently decreasing. This course was reproducible, the mean time to reaching maximum was 1950 s (SD = 180 s), and the value of polarization resistance was 30.9 kΩcm^2 (SD = 7.7 kΩcm^2) at the maximum.

Titanium interaction with fluoride environment with non-adjusted pH and pH = 5.8 proceeded in a way that could be assumed based on the published data [12, 24]. The layer affected by fluorides recovered after the removal of aggressive ions. In contrast, the results recorded in the case of the PS-4.2/5000:MS exposure indicated a different corrosion mechanism.

A prolongation of the PS-4.2/5000 exposure led to the stabilization of the open circuit potential at −0.643 V (SD = 0.010 V) in about the 42nd min (Fig. 3). It was a level comparable with the potential delay in the repassivation phase of measurements under the conditions of PS-4.2/5000:MS (Fig. 2c).

At the beginning of a prolonged PS-4.2/5000:MS measurement, when the exposure to model saliva was extended to 50 h (Fig. 4), the open circuit potential was increasing slowly. Its value changed by +0.11 V over the first 11 h, but during the next 4 h it rose by +0.37 V. Polarization resistance was changing accordingly. Its value rose from 24 to 174 kΩcm^2 within roughly 16 h of exposure, then the growth rate increased. The values of both the open circuit potential and polarization resistance indicate that the influence of the fluoride environment continued over the first roughly 15 h of exposure to model saliva and the corrosion process was controlled by a mechanism different from that applied in the second phase, when the behaviour of specimens exposed to environments with and without fluoride ions was similar.

Impedance spectra determined for the PS-4.2/5000:MS exposure (Fig. 5), again with an extended time of exposure to model saliva, confirmed the development of the specimen's corrosion behaviour for at least 20–30 h. The PS-4.2/5000 exposure led to the formation of a surface layer whose properties were changing very slowly during subsequent interaction with model saliva. The character of the first spectrum corresponded to a porous layer (model a in Fig. 6) on the specimen surface. The second spectrum could be analyzed with identical success by models of both porous and nonporous layers (models a and b in Fig. 6). As of the third measurement, the behaviour changes were not so distinct. The data course is best expressed by the nonporous layer model. The time dependencies of the values of the equivalent circuit elements are given in Fig. 7. As far as the behaviour of the whole system is concerned, the properties of the outer phase boundary layer-electrolyte were dominant in all cases. Its resistance was increasing and its capacitance decreasing throughout the exposure, which testified to an increasing thickness of the layer.

It followed from the corrosion study that after the PS-4.2/5000 exposure, the specimen surface was covered with a layer of corrosion products, or a precipitated layer that originated by the reaction of the corrosion products with the environment. In order to verify this finding, the surface of the exposed specimens was analyzed using the XPS method. The differences in the composition of the titanium grade 2 surface after the PS, PS-4.2/5000, and PS-4.2/5000:MS exposures are obvious from Table 2. Carbon was not included in the results, the C1 s peak corresponded mainly to contamination carbon at $E_b = 285.0$ eV. In the case of titanium exposed in a fluorides-free environment, the peaks of oxygen, titanium and carbon were dominant. The surface state after the PS-4.2/5000 exposure was markedly different. The peaks of titanium, oxygen and carbon were represented in the spectrum but their concentrations were markedly lower. This expectable set of elements was supplemented with distinct peaks of fluorine, potassium and sodium. During their transfer from the corrosion environment to the spectrometer, the specimens were intensively washed by a stream of demineralized water and subsequently by acetone. It may thus be assumed that the layer was soluble to a limited extent, and that it was relatively firmly adherent. A similar finding has been reported by Huang. Using a SEM EDS analysis, he found a saline layer with an atomic ratio of Na:Ti:F—24:11:65 on titanium after exposure (8 h, NaCl 1%, NaF 1%) [25]. This layer and a layer formed on TiAlV [26] were also studied by the same author using the XPS method. The composition was attributed to Na_2TiF_6 in both cases. However, the author does not state any data on elements binding energies corresponding to the given compound. The existence of a saline layer is also noted in the work by Mobilleaua et al. [27]. The authors based their findings on the results of SEM EDS measurements (Ti, artificial saliva, 2.5% NaF, exposure for 9 days). The presence of a layer containing fluorine on titanium specimens after exposure to an environment containing 1% NaF (pH = 4.5) was confirmed by Stajer et al. [15] by way of XPS spectrometry. In the XPS spectra, the authors found a detectable F 1s peak even after the surface etching by an Ar beam for 30 min. Takemoto et al. [28] detected titanium, mainly in the form TiO_2, together with a fluorine peak in XPS spectra after exposure to a fluoride environment of pH = 5.

In order to allow for a more accurate determination of the originating compound/compounds, an atypically broad Ti 2p doublet (FWHM of both peaks 3.4 eV) was analyzed. The determined binding energies of the synthetic components, supplemented with a detailed analysis of other elements spectra, could not be attributed to any described compounds based on literature data or available databases.

Based on the photoelectron spectroscopy, Raman and XRD analyses we may say that exposure under the conditions of PS-4.2/5000 led to the origin of a relatively firmly adherent layer composed of titanium, potassium, fluorine and oxygen.

In this layer, transformation occurred after the specimen transfer into model saliva. In the first stage of the exposure, the content of fluorine and potassium decreased substantially, and phosphorus occurred. Subsequent changes in the chemical composition were less substantial. The impedance measurements showed that polarisation resistance grew with the disappearance of the initial porosity. Its growth subsequently slowed down gradually.

Changes in the titanium surface state after the PS-4.2/5000:MS exposure are evident from the development of the shape of the Ti 2p XPS peak (Fig. 8). After 30 min of exposure (region of R_p maximum, Fig. 2c), the component at $E_b = 458.8$ eV, which corresponds to the binding state of Ti 2p3/2 in TiO_2, was emphasized. After the exposures of 1 h and 52 h, both peaks of the Ti 2p doublet corresponded to titanium dioxide at a binding energy of Ti 2p3/2 458.8 eV and doublet separation 5.7 eV [21].

The interaction of the surface with oxygen dissolved in the model saliva solution caused titanium transition into titanium dioxide. However, the layer was not formed solely by this oxide, with the presence of phosphorus and other elements indicating its more complicated composition.

5 Conclusions

The presence of fluoride ions led to the degradation of the passive layer on titanium even in a slightly acidic environment. Under these conditions the passive state stability depended on the ratio between the rates of the layer electrochemical repassivation and chemical dissolution.

A decrease in the pH value to 4.2 and the presence of 5000 ppm fluoride ions led to titanium activation, with a layer rich in fluorine subsequently formed on its surface under these conditions. Its presence largely decelerated repassivation during exposure to model saliva. The obtained results show that the destabilization of titanium passive state caused by a short medical treatment may take a long time to abate, with many possible negative consequences.

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