Environmental degradation of Ti alloys in artificial saliva and a role of fluorides

INTRODUCTION

Titanium and its alloys possess specific properties, among them high corrosion resistance and biocompatibility. Bioinertness of Ti assed in short time tests seems almost perfect: the corrosion rate in simulated body fluids varied between 0.01 and 0.1 µg/cm²d, and after 48 weeks from an implantation of the Ti6Al4V alloy into animal body, only traces of metallic elements were found in tissues [1]. The corrosion resistance significantly depends on acidity of solution: in lactic and formic acids the general corrosion of the Ti6Al4V alloy was observed after 4 weeks [2]. Even if titanium is bioinert in neutral solutions, corrosion may appear in physiological saliva [3].

The saliva can be assumed as relatively aggressive environment [4]. The weight corrosion rate in artificial saliva was assessed as 0.28 g/cm². At pH = 3 or lower, the passive current density for commercially pure Ti increased markedly with decreasing pH. The corrosion was observed [5] in saliva as dependent on a surface state, with a few times higher corrosion after sandblasting than after polishing.

Fluoride ions are aggressive ions for the oxide layers of Ti and its alloys. Their presence may initiate localized degradation by pitting and crevice corrosion. Such conditions may happen as the toothpasthes and prophylactic gels contain fluoride ions. So far results are confusing. As shown in [6], the effect of fluoride ions was weak at pH from 6.15 to 3.0 but below the last value Ti and its alloys suffered from localized corrosion. On the other side, even if titanium revealed ion releases 0.01÷0.1 µg/cm²d, similar as gold alloys, the ion release increased to 500 µg/cm²d in presence of fluoride [7]. Low pH values accelerate this effect even more. Therefore it is recommended to avoid the presence of fluoride or to reduce contact time. In another paper [8] the strong effect of presence of fluorides on corrosion density was observed for pure Ti and Ti6Al4V as corrosion current density 1.5 µA/cm² in Fusayama artificial saliva, 3.5 in acidified to pH 2.5 artificial saliva but it increased to 9 in presence of 0.1 g/dm³ fluoride in saliva and as highly as 480 µA/cm² in acidified fluoridated saliva. The fluoride-related corrosion was observed in presence of albumin, but this compound significantly decreased the general corrosion rate [9].

The Ti and its alloys may fail under hydrogen embrittlement mechanism. For a beta titanium orthodontic wire examined by means of delayed-fracture test in acid and neutral fluoride aqueous solutions, the time to fracture increased with decreasing applied stress in 2.0% and 0.2% acidulated phosphate fluoride (APF) solutions [10]. The fracture mode changed from ductile to brittle when the applied stress was lower than 500 MPa in 2.0% APF. The delayed fracture did not occur within 1000 h in neutral NaF solutions, although general corrosion was similar to that in APF solutions. The amount of absorbed hydrogen was 5000÷6500 mass ppm under an applied stress in 2.0% APF solution for 24 h. It was concluded that immersion of Ti in fluoride solutions may result in degradation of mechanical properties and fracture of beta titanium alloy due to hydrogen absorption. In other work [11] hydrogen absorption behaviour of beta titanium alloy in acidic fluoride solutions was analysed. The amount of absorbed hydrogen increased with immersion time in 2.0% APF solution. In the case of immersion time 60 h, the amount of absorbed hydrogen exceeded 10 000 mass ppm. The amount of hydrogen absorbed in 0.2% APF solution was several times smaller than that in 2.0% APF solution at the same immersion time. During the later stage of immersion, the amount of absorbed hydrogen markedly increased under higher applied stress, although the applied stress did not enhance hydrogen absorption during the early stage of immersion. These results on hydrogen absorption behaviour are consistent with the delayed fracture characteristics of beta titanium alloy.

Similar behaviour was observed for Ni-Ti alloys. Superelastic Ni-Ti wire is widely used in orthodontic clinics, but delayed fracture in the oral cavity can appear. Fracture of the Ni-Ti alloys may be attributed to the degradation of mechanical properties due to hydrogen absorption [12]. The hydrogen embrittlement of work-hardened Ni-Ti alloy in APF solutions was noted as particularly significant [13]. Upon immersion in 2.0% APF solution at pH 5.0, tensile strength decreased significantly with immersion time. Moreover, the fracture mode changed from ductile to brittle, due to brittle layer formation at the peripheral parts of the specimen.

The presence of fluorides in acid solution may cause an interesting effect: formation of nanotubular oxide layer [14÷17]. The process is generally observed in acid solutions but it may also occur at higher pH. Thus, it shows the potential danger of fluorides for corrosion resistance and then biocompatibility, and their importance for localized corrosion.

This paper is based partly on some previous results described in [18, 19]. The novelty is demonstration of physical-chemical model, which shows the contribution of fluoride ions into degradation of Ti alloys, by enhancing localized corrosion, facilitating hydrogen entry and thus promoting hydride-related embrittlement. Careful investigations of this problem are especially important as presence of fluorides, low pH and mechanical stresses certainly appear in human mouth.

MATERIALS AND METHODS

The commercial TIMET Ti6Al4V alloy was used for electrochemical tests. The specimens of 17.5×12.2×4 mm dimensions were prepared. They underwent grinding with abrasive papers of different grain size from 150 to 1500. Some of them were also polished with alumina powder. The tests were made in artificial saliva according to the ISO 10271 (in wt %): 0.4 NaCl, 0.4 KCl, 0.795 CaCl₂, 0.78 NaH₂PO₄, 0.005 NaS and 1% of urea. The solutions were adjusted to pH 7, 5 and 3 with hydrochloric acid. The potentiokinetic tests were made with ATLAS potentiostat, beginning from cathodic and then into anodic direction, at 10 mV/min. voltage change rate; polarization curves made it possible...
to estimate the corrosion potential and current, and passivation potential and current. The Saturated Calomel Electrode (SCE) was taken as a reference electrode.

The two-phase (α + β) Ti13Zr13Nb alloy was investigated by slow strain rate tests. The standard specimens for tensile tests were prepared from the alloy sheet of 80×220×2 mm in dimensions. The slow strain rate tests were made at 10⁻⁵ s⁻¹ strain rate after surface preparation. The cathodic polarisation was applied by means of direct voltage supply and polarising Pt electrode.

The slow strain rate tests were made either in laboratory air or in artificial saliva solution, with or without 0.1 mass pct. of HF, at open circuit potential or at cathodic polarisation at current density 100 A/m². The artificial saliva was composed of (in g/dm³): NaCl 1.2, KCl 1.2, Na₂S 6.015, Na₂HPO₄ 4.14, CaCl₂ 2.04, urea CO(NH₂)₂ 3.0, lactic acid 29.1.

Figures 1-6 demonstrate the examination results of fracture faces after slow strain rate tests. Generally, no decrease in plasticity in artificial saliva, mild effects at H charging and deep decrease of plasticity in presence of fluorides are observed.

The ductile fracture (Fig. 1) is observed for specimen tensed in air. No brittle cracks appear. Similar ductile appearance is shown for specimen fractured in artificial saliva (Fig. 2). The results show that in neutral artificial saliva no hydrogen-enhanced degradation may appear.

For specimens tensed in artificial saliva at cathodic polarisation the initiation and propagation of transcry stalline cracks are similar to that in air, fracture occurs by brittle crack propagates and is accompanied by ductile decohesion in adjacent area (Fig. 3, 4).

In Figures 5 and 6 the transcry stalline fracture for specimen tensed in artificial saliva with an addition of fluorides is shown as again accompanied by mainly ductile decohesion inside the grains. The amount of brittle cracking is higher than in the previous cases.

The presence of fluorides can result in formation of nanotubular oxide layer (Fig. 7, 8). Such behaviour is generally known to occur via some chemical reactions, including localised corrosion caused by fluoride ions.

Summarising the results, typical fracture mechanism occurs in the presence of fluorides or cathodic polarisation, by an appearance of some single brittle cracks surrounded by area of ductile cracking. The brittle cracking is very localised and occur by initiation and propagation of the main crack accompanied by a few other secondary cracks.

RESEARCH RESULTS

The results of electrochemical potentiokinetic tests are shown in Table 1 as corrosion potential and current values. The distinct effect of surface state and minor effect of pH are observed.

Table 1 illustrates the results of slow strain rate tests performed in different conditions. Taking into account the possible error made at calculation of proof stress, the results may be summarised as follows: (i) no effect of an exposure in artificial saliva, (ii) moderate effect of cathodic polarisation and (iii) significant effect of fluorides are observed.

Table 2. Results of slow strain rate tests in different environments

<table>
<thead>
<tr>
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<td>0</td>
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<td>743</td>
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<tr>
<td>Artificial saliva</td>
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<td>764</td>
<td>653</td>
<td>3.3</td>
<td>17.20</td>
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Table 1. Effects of surface roughness on measured electrochemical parameters

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<td>5</td>
<td>-0.802</td>
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<td>3</td>
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<td>0.003</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.005</td>
<td>0.004</td>
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</table>
Fig. 3. Fracture surface of a specimen tensed in an artificial saliva, at cathodic polarisation, 100 A/m² of current density; SEM

Rys. 3. Przełom próbki rozciąganej w sztucznej ślinie przy polaryzacji katodowej, 100 A/m²; SEM

Fig. 4. Fracture surface of a specimen tensed in an artificial saliva, at cathodic polarisation, 100 A/m² of current density; SEM

Rys. 4. Przełom próbki rozciąganej w sztucznej ślinie przy polaryzacji katodowej, 100 A/m²; SEM

Fig. 5. Fracture surface of a specimen tensed in an artificial saliva in presence of fluorides; SEM

Rys. 5. Przełom próbki rozciąganej w sztucznej ślinie zawierającej jony fluorokwowe; SEM

Fig. 6. Fracture surface of a specimen tensed in an artificial saliva in presence of fluorides; SEM

Rys. 6. Przełom próbki rozciąganej w sztucznej ślinie zawierającej jony fluorokwowe; SEM

Fig. 7. Nanotubular oxide layer obtained in 1 M H₃PO₄ + 0.5% HF, at different magnification; SEM

Rys. 7. Nanotubularna warstwa tlenkowa otrzymana w 1 M H₃PO₄ + 0.5% HF, przy różnych powiększeniach; SEM

Fig. 8. Nanotubular oxide layer obtained in 1 M H₃PO₄ + 0.3% mass. HF on the Ti13Zr13Nb alloy oxidized for 30 min. and subsequently heat treated; SEM

Rys. 8. Nanotubularna warstwa tlenkowa otrzymana w 1 M H₃PO₄ + 0.5% HF na stopie Ti13Zr13Nb utlenianym przez 30 min. i następnie obrabianym cieplnie; SEM

**MODEL OF DEGRADATION IN REAL CONDITIONS**

Developing the degradation model, one may assume that all metallic biomaterials used in mouth, i.e. dental implants and
orthodontic implants, can be sensitive to corrosion and hydrogen-enhanced degradation. All carried out so far research has given an evidence that Ti-based alloy, including Ni-Ti alloys, may suffer from electrochemical corrosion and hydrogen-enhanced cracking.

The real dissolution of any alloy, which is protective thanks to its oxide layer, may occur by three different paths. The first is obvious formation of electrochemical cells and dissolution of material at anodes provided that an oxide layer is permeable, or, in other words, is imperfect. Even if this process is usually considered as an exclusive one, it depends in great extent to real imperfections and particularly on presence of corrosion tunnels (cracks, grain boundaries etc.). However, there is almost neither data on the real nanostructure of oxide layer nor knowledge on how the oxide nanostructure depends on oxidation method and conditions. This problem likely decides about unexpected shortening on a lifetime of Ti implants: from some 25 yrs. to 15 or even less as recently observed, 30% of implants should be removed and substituted by other ones after this time. The reason can be brittle cracking of oxide layer, which is brittle nano- or microceramics; thicker the oxide, greater tendency to form new short cracks through the layer.

Dissolution of an oxide layer is the second mechanism. Again, there is no valuable data on whether and how quickly may the rutile layer dissolve in biological environment. Taking some data from research made on minerals one may find that the rutile dissolves very quickly in 4 M HCl, 80% in 120 min [20]. The corrosion in acidic environment is likely to occur by preferred dissolution, i.e. by pitting corrosion which quickly creates corrosion tunnels. The crucial question is at which pH value and in which environment such corrosion may result in localized dissolution of rutile, on what area and how does it influence the total dissolution rate.

Third mechanism of dissolution is that occurring via diffusion of Ti or other alloy elements through an oxide layer. At normal temperature conditions, the flow of titanium ions through the oxide diffusion barrier can be neglected because of high diffusion energy. The factor, which may seriously increase diffusion and then make this mechanism important, is electrochemical potential. However, this third mechanism may play an important role for totally protective, perfectly fabricated impermeable layers rather than for imperfect layers in acidic environments in which localized corrosion cannot be avoided, especially in presence of fluorides.

The present electrochemical results show only minor effect of surface roughness and pH on corrosion process parameters. The effect of roughness is obvious. The higher corrosion resistance is observed for specimens with polished surfaces rather than for those with grinded surfaces. The corrosion potentials of the polished specimens became about 0.03 V more cathodic with those with grinded surfaces. The corrosion potentials of the observed for specimens with polished surfaces rather than for effect of roughness is obvious. The higher corrosion resistance is surface roughness and pH on corrosion process parameters. The corrosion current of grinded specimens increased with decreasing pH and in the mostly acidic environment the highest decrease in corrosion resistance was observed. With the polished samples it was otherwise: corrosion current initially fell down, while at pH 3 the increase of current was noticed. The density of anodic current at negative potential –0.65 V for polished specimens increased, while the solution became more acid. The more aggressive the environment, the higher density of anodic current, resulting from faster formation of the passive layer. For the polished specimens after the experiments the continuous surface layer was observed; for grinded specimens the process of pitting corrosion occurred. The pits' appearance was dependent on pH value: in acid environment the pits were more numerous and deeper, and at pH 7 they were scarce, smaller and more shallow. Such behaviour is an evidence that pitting may occur on rough surfaces, even if it substantially influenced corrosion rate.

The Ti alloy in absence of fluorides is not highly prone to local corrosion at moderate pH values in artificial saliva. In such conditions the dissolution rate even at low pH 3 is similar to that in neutral conditions. Even if corrosion takes place, the alloy quickly repassivates. Thus, in electrochemical tests, at moderate pH, corrosion seems to occur mainly through already existing imperfections in an oxide layer, repassivated during anodic run; at low pH the rutile layer itself is destroyed, likely by intensive localized dissolution, and the exposed bare metal surface dissolves quickly. The presence of fluorides accelerates the process. The fluorides rather activate previous imperfections than create new ones. Such a model suggests necessity to investigate the oxide layers before and after the tests by high resolution SEM or TEM. Mainly, the nanostructure of oxide layers and its imperfections, and corrosion ways in presence of acids and fluorides as well as modelling the effect of electrochemical potential on diffusion of Ti ions through perfect oxide layer even if an existence of corrosion paths seems unavoidable and therefore the last mechanism may be unimportant. Another interesting question is a dissolution of oxide layer in environment no enhancing the localized corrosion. The new long term exposure weight tests combined with highly sensitive chemical spectroscopy techniques will be used by the authors to recognize the mechanisms of corrosion at different pH and exposure time.

The obtained results of slow strain rate tests of the Ti alloy, their appearance and intensity, can be explained in terms of environment-related brittle cracking taking into consideration the corrosion behaviour. The model of hydrogen degradation should involve the following mechanisms: (i) hydrogen evolution at interface liquid – metal, (ii) hydrogen entry into the metal, (iii) hydrogen diffusion into some regions of the highest tensile stresses, (iv) hydrogen-enhanced crack initiation and propagation.

The hydrogen evolution is moderate at neutral solutions and increases with cathodic polarisation almost linearly with square root of cathodic current density. Then one might expect the highest embrittlement in highly acidic solutions or at cathodic polarisation. In this case no such behaviour is observed; hence, another determinants are important.

The second stage is hydrogen entry into the metal. This stage comprises of two concurrent reactions: hydrogen recombination and hydrogen passage into the metal through an interface. In normal conditions some 95% of hydrogen combines into gaseous hydrogen molecules and evaporates. So-called hydrogen ingress promoters may change the equilibrium constant of the
recombination reaction and then may enhance hydrogen absorption. They are much more effective than an increase in cathodic current from steady-state value. Among such promoters the substances like As derivatives are known; there is no data whether fluorides may act in similar way and the authors do not take a risk of such assumption without further studies.

However, the second stage may be enhanced by specific corrosion effect caused by fluorides, what is able to explain the observed abnormal embrittlement in the presence of these species. Generally, halides are known to cause a localised corrosion, i.e. pitting. However, fluorides for Ti alloys are known to degrade metal in a specific way, leading to formation of nanotubular oxide layer. The process is very complex, based on successive oxidation and deep pitting within small spaces between nanotubes. The fluorides may substantially, more than other halids, destroy the oxide layer drilling the corrosion tunnels inside it. There is no local corrosion, no hydrogen absorption as long as the oxide layer remains stable and impermeable; an evidence is a weak effect of pH on corrosion shown in this paper. Likely, very high electrochemical cathodic potential or highly concentrated acids may eventually dissolve the layer; such conditions are hardly expected in a mouth.

The next stages involve hydrogen diffusion into regions of the highest triaxial stresses. Such regions are frequent during slow strain rate test of polycrystalline alloy. The test is similar the conventional tensile test; at usually applied strain rates between $10^{-5}$ and $10^{-8}$ s$^{-1}$ the cracking rate and hydrogen absorption rate are highest triaxial stresses. Such regions are frequent during slow absorption. They are much more effective than an increase in recombination reaction and then may enhance hydrogen absorption. It may mean that localised corrosion is very important for an initiation of cracking.

**CONCLUSIONS**

The mechanism of environmental degradation is relatively complex. The main determinants are: real microstructure of an oxide layer, form and rate of electrochemical dissolution process related to electrochemical potential and pH, and stress state.

The Ti alloys are generally resistant to hydrogen-enhanced failure in an artificial saliva. The presence of fluorides can be a factor intensifying the process. The low pH and application of cathodic polarisation may promote the process but the localised corrosion seems to be the main determinant; cathodic polarisation delivers hydrogen, fluorides open the ways to its entry.

The decohesion of the Ti alloy proceeds under two different mechanisms. Generally, the alloy cracks in transgranular ductile manner. In area of sufficiently high hydrogen content, the single brittle transgranular cracks may appear.

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**REFERENCES**


