Corrosion and fracture of Ti bioalloys

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Abstract. Titanium alloys are nowadays the candidate biomaterials for long term implants in joint arthroplasty and for dental implants. Both implants are subjected to complex effects of corrosion environment and mechanical loads. Such conditions may result in pure corrosion, corrosion-enhanced fracture and hydrogen-enhanced fracture, and stress-enhanced and wear-enhanced corrosion. The application of thick oxide layers and hydroxyapatite coatings may additionally promote the undesired phenomena. The latest approaches stimulating the bioactivity of implants, like creation of scaffold/porous structures, may be disadvantageous when susceptibility to fracture is considered. Another problem to be solved is the effect of presence of nanotubular TiO_2 coating on initiation of fatigue cracks. The new testing and optimization procedures are also desirable and here proposed. The variety of interrelated factors makes the optimisation by artificial intelligence techniques necessary.

Introduction

Corrosion of Ti and its alloys is relatively low and thus difficult to measure. However, there is a lot of factors which can deteriorate the degradation resistance and increase the sudden failure risk. At first, during long term exposure of the Ti bioalloy in human body the pH value may drop down because of some inflammatory processes at the metal-tissue interface, and Ti is not essentially resistant to organic acids at low pH. Secondly, the presence of various mechanical stresses may initiated a number of mechanisms like wear-enhanced/fretting corrosion and environment-enhanced failure. Such mechanisms may appear as the Ti bioalloys are relatively susceptible to wear that destroys the oxide layer.

This paper is aimed to review the state-of-art on the corrosion and environment-assisted fracture of Ti bioalloys and propose the new approaches to Ti degradation mechanisms, test procedures and optimisation techniques.

Corrosion of Ti bioalloys

Electrochemical corrosion. The general corrosion rate is very low for Ti biomaterials in Simulated Body Fluids (SBF), some nA/m^2 (ranged between 0.01 and 0.1 $\mu g/cm^2 d$) [1]. It strongly depends on pH: tests made in lactic and formic acids showed the general corrosion after only 3 week exposure at 37°C [2], and below $pH < 4$ the dissolution became higher [3]. The bovine albumin acts as a corrosion inhibitor, decreasing the corrosion rate of the Ti-6Al-4V, Ti-6Al-7Nb and Ti-13Nb-13Zr alloys in phosphate buffered saline (PBS) [4]. 0.9% NaCl, artificial salive and calf serum are less corrosive environments than solutions of L-cisteine, lactic acid and HCl during 7 days [3].

For Ti alloys the selective dissolution is possible. In case of the Ti-6Al-4V alloys and Ti-15Zr-4Nb-4Ta alloys, the quantity of dissolved Ti and (Zr+Nb+Ta) was much lower than (Al+Nb) [3].

Titanium and its alloys are resistant to pitting in physiological solutions. The corrosion rate increases in presence of fluorides and peroxides. In Ringer`s solution the destruction of the surface oxide layer increased at temperature only 37°C [5]. The mechanism of pitting includes migration of chloride ions and their accumulation within the interface base-oxide layer. In buffered saline solution the tight internal layer and porous external layer are formed, the last one improving its properties in presence of phosphate ions.

The alloy fabrication and resultant microstructure determine also the corrosion form and rate. The powder metallurgy P/M Ti alloys of highly porous structure demonstrated much higher corrosion rate than that of cast alloys, presumably because of strong crevice corrosion [6].

The surface treatment of Ti bioalloys is performed to increase the roughness and then the bone in-growth rate and strength of bone-implant interface. The rough surface is, on the other hand, more prone to corrosion, as comparing to polished one, likely because of more inhomogeneous surface and creation of electrochemical microcells. The treatment of the Ti-6Al-4V alloy with 700 µm grain corundum or vacuum plasma spraying of rough titanium, results in increase of passivation and corrosion current values, as compared to those for the alloy polished with abrasive paper No. 600 [7].

The crevice corrosion may occur especially at interface between metallic implant and bone cement (inert polymer PMMA) [9].

The dissolution of alloy elements in surrounding tissues in tests made *in vivo* is negligible in short time: after 48 weeks after implantation of the Ti-6Al-4V alloy in tibia tissues only traces of Ti, Al and V were found, for the Ti-15Zr-4Nb-4Ta the quantity of dissolved Ti was even lower, and quantities of Zr, Nb and Ta – extremely low [1]. As now the best implants made of Ti alloys (for total hip replacements THR) are predicted to be used for some 15-20 years; for example, for the Zweymuller stems made of Ti-6Al-4V and Ti-6Al-7Nb alloys, rough grit-blasted, total 111 hips and mean age of a patient 56 y, after 10 years the survival rate has reached almost 98% [10]. Ti biomaterials are then generally resistant to corrosion if properly designed and manufactured. The aim of a present research is to further increase the corrosion resistance in order to secure 20-25 yrs as implants.

Stress-enhanced and wear-enhanced corrosion

Wear may enhance corrosion due to mechanical damage of the oxide layer and formation of cracks. At conditions of pure corrosion the conventional Ti-6Al-4V alloy was more susceptible, but tribocorrosion was greater for new alloys [4,11]). Wear caused a substantial increase in corrosion of the Ti-6Al-4V and Ti-15Mo-5Zr-3Al alloys, but the Ti-15Zr-4Nb-4Ta remained resistant [12].

The mechanism of tribocorrosion is not fully understood yet. Such damage may even result from wear made by bones, bone cements, tissues acting on the oxide layer. The degradation was postulated as fretting damage (small amplitude wear) caused by friction between implant surface and bone or PMMA cement [6].

Corrosion-enhanced and hydrogen-enhanced fracture

Hydrogen embrittlement has not been reported for hip and knee joint endoprostheses. The serious hydrogen cracking has been observed in artificial salive in presence of fluorides which likely accelerate hydrogen absorption by Ti alloy [13,14].

There is neither stress corrosion cracking nor corrosion fatigue suggested as a source of early damage of implants. However, for 80% of endoprostheses which failed, the mechanical fatigue mechanism was proposed [12]. It seems that as the present standard cannot distinguish between purely mechanical and corrosion fatigue, a lot of such cases reported as mechanical failures may be in reality corrosion- or hydrogen-enhanced fatigue damage [15].

Effect of hydroxyapatite coating on corrosion and environment-assisted fracture

The deposition of phosphate layer, like hydroxyapatite (HA) by vacuum or air spraying, or apatite layers by precipitation in SBF, is now a common practice to increase the bone ingrowth. However, an application of such layers may create a number of problems. The HA coating decreased a general dissolution rate of the Ti-6Al-4V alloy previously passivated in HNO_3, but increased when the alloy was aged in hot water after mechanical treatment [8]. The phosphate containing solutions enhanced creation of porous layers and accelerate pitting [16].

Mechanisms of corrosion of Ti biomaterials

As to assess the possibility of mechanical damage or chemical dissolution of the oxide layer one must take into account that it is ionic ceramics as a material. Such materials can be considered as relatively resistant to chemical degradation, and prone only to some specific chemical or electrochemical reactions, depending on thermodynamic stability of oxides in a specific environment. There is no precise data on dissolution kinetics of aluminia or other oxides in body fluids. However, the dissolution of passive film could be quite significant [17]. Such data can be helpful in understanding whether and to what extent the film dissolution can be responsible for presence of Ti, Al and V in body tissues after long term exposure. Neither thermodynamic equilibrium constants nor kinetic dissolution parameters are known for oxide layer and alloy body in these very specific model solutions have been given. The general physical and chemical mechanisms of reactions with ions considered as aggressive, like chlorides, are familiar, but the details and especially the kinetics of such reactions have been also scarcely investigated. The problem becomes even more complex as there is a number of various ions present in body fluids which can enhance synergic effects.

The electrochemical corrosion is an expected phenomenon. Generally, the top surface oxide layer should possess inhomogeneous electrochemical potential e.g. for the Ti-Al-V alloy because of presence of various Ti, Al, V and complex oxides and a number of structural imperfections (grain boundaries, slip lines and bands, etc.). Despite that, no satisfactory work has been done to characterize such behaviour in terms of a presence of electrochemical cells and creation of mixed potentials. Even the research on structure of oxide layers has not brought a clear image, e.g. in [18] such structure was described as composed of Ti oxides on the top and Al oxides on the bottom part of the surface layer. According to [19], the passive film on the Ti-6Al-4V layer is a TiO_2 containing a small amount of Al_2O_3, hydroxyl groups and bound water. The continuous process of partial dissolution and reprecipitation [19] makes an exact description of the such unstable oxide layer very difficult task. In Hank`s (SBF) solution the film consisted of titanium oxide and titanium oxy-hydroxide containing titanium phosphate [19]. Even if it has been claimed that no V oxides are present in surface layer, a lot of oxides appeared following laser melting in liquid nitrogen: two TiO_2 oxides, rutile and anatase, Ti_3O_5, Ti_2O, Ti_3O, VO_x, $V_2Ti_3O_9$ [20], and Al_2O_3. TEM and AFM techniques showed the presence of Ti oxides in various forms: columnar or dome shapes [21,22].

The growth rate of the oxide scale, as well as its composition, structure and morphology showed no important relation on microstructure of the base material. The oxidation of the Ti-48Al-2Cr in air, initially resulted in the formation of α-Al_2O_3, TiO_2 (rutile), Ti_2AlN, and TiN. After longer exposure times, the mixed-oxide scale with an alumina-rich layer at the outside was overgrown by the fast-growing TiO_2, responsible for the rapid kinetics [23].

The composition of oxide layer is believed to influence the corrosion properties. When studying the Ti-13Nb-13Zr alloy, its high corrosion resistance was directly attributed to the high percentage of vanadium in a passive layer [22]. In other work the chemical stability of multilayer alumina and titania, prepared by a sol–gel procedure was investigated. The top layers contained γ-AlOOH fired at 400 °C, anatase–TiO_2 fired at 300 °C and anatase–TiO_2 fired at 450 °C. In organic solvents the corrosion rate was highest for the of γ-AlOOH at pH 2, then two times lower for the anatase–TiO_2 membrane fired at 300 °C (low crystallinity), and no corrosion was observed for highly crystalline anatase–TiO_2 membrane fired at 450 °C [24].

Second degradation mechanism can be diffusion of Ti, Al, V elements (ions) through a perfect crystal oxide lattice. The diffusion coefficients for mass transport of Ti ions cannot be found and it is unclear whether this phenomenon may be responsible for an appearance of metallic elements in surrounding tissues and human organs many years after implantation. The apparent diffusion coefficients are dependent on crystal imperfections, like grain boundaries or other interfaces, which constitute the easy diffusion paths.

Third and last mechanism which can be proposed is due to reaction of body fluid compounds with bare metal. Such process needs a direct contact of the liquid with a bare metal. There are a lot of factors which make such contact possible. Generally, they all include creation of easy liquid transport ways by mechanical or chemical actions.

The ceramics are known as brittle species, with their resistance to cracking extremely dependent on their thickness. At too thick coatings and excessive strains the oxide layer may crack allowing the penetration of liquid into the metallic matrix. The exfoliation of the layer may result with decohesion at the interface layer-bulk, occurring at too thick layer and too weak layer-bulk bond strength [25]. The excessive strains may be reason for cracking of the layer even if its thickness remains reasonable. The mechanical damage of the layer may result from wrong surgery procedure, e.g. a use of mechanical load to fix the implant.

Wear may cause breakdown of the passive layer [17] and even if disruption or damage of oxide film is repaired very quickly, bare metal is able to release some ions before the oxide layer is rebuilt.

Therefore, dissolution of any Ti alloy is either a result of dissolution of oxide layer or of ionic transport, or of dissolution of the bare metal provided that corrosion tunnels, exfoliation or mechanical cracks locally destroy the oxide layer. There is a number of factors which decide on dissolution rate on this area: dissolution kinetics of the bare metal, electrochemical characteristics of the surface, local environment, depolarization rates related to precipitation rate of corrosion products, oxygen or hydrogen ions` diffusion etc., characteristics of corrosion tunnels, mechanisms and kinetics of anions` diffusion through crystal lattice, perfect and imperfect, crystalline or amorphous. In order to design a proper material and to estimate its lifetime, these mechanisms should be quantitatively developed in a general model.

Test procedures

The current test solutions do not exactly fit those met in human body. A lot of different corrosion test solutions is used, e.g. Ringer`s solution, calcium-free Hank`s solution, human blood plasma, Gomoris, Sorensen and Michaelis buffers, pseudoextracellular Homsys liquid, α modified Eagl solution, etc. All of them contain generally chlorides, phosphates, carbonates and sulphates as anions, and sodium, magnesium, potassium as the cations. The chloride, dissolved oxygen and pH levels are the most important, and body fluids appear slightly less aggressive than seawater [6]. It seems that except chlorides all other ions separately are mild, but the whole environment is concluded to be very aggressive [26]. Thus, the synergetic effects of phosphates, chlorides and other ions on stability of oxide layer may be considered.

The SBF do not correspond to the human blood composition. The oxygen levels in blood are lower than those in SBF saline solutions exposed to atmosphere, and bicarbonate levels are even twenty times higher in blood. Moreover, an inflammatory response of the body tissues after implantation is an appearance of hydrogen peroxide [6]. There is no so far what test environments would be the best to predict *in vivo* corrosion based on *in vitro* tests, and progress in area is desirable.

The weight loss assessment is no useful tool for corrosion process in human body that occurs at a very low rate. Therefore such tests are in formic and lactic acids. At low weight reduction the made errors are great and procedure details should be very carefully obeyed. The authors think that better way would be to make exposure tests in mild SBF for a very long time and measure the amount of dissolved ions by chemical spectral analyses.

The comparison of different materials by performing full polarization curves is a common practice. However, in normal conditions the pitting potential should not be reached, and those procedures may be used only to check whether a new material is not extraordinarily susceptible to localized corrosion. Another critical point is pre-exposure: even the largest time is much smaller than that expected in human body for initiation of the oxide layer damage. The corrosion tests may be then directed towards an assessment of possible corrosion in some critical conditions (potentiokinetic tests) or an assessment of a quality of the layer (impedance tests) but they are no able to predict the long term dissolution.

The present standard for an assessment of a fatigue limit implies the testing at frequency 10 Hz. The up-to-date results show that hydrogen-enhanced and corrosion-enhanced fatigue may be observed when two conditions are fulfilled. At first, the rates of corrosion dissolution (extremely low in body fluids for Ti bioalloys) and crack propagation are similar. Secondly, the load or deformation change rate should be about or higher than 10^{-2} s^{-1} [27]. That means that tests are to be performed at frequency 0.1 – 0.001 Hz at the load change rate about 10^{-2} s^{-1}.

There is no uniform standard for tribocorrosion which seems a very important case, e.g. for implant of knee joint.

Optimization of corrosion resistance

There is a lot of factors influencing the corrosion form and rate, including chemical and mechanical properties, chemical and phase composition, structure and microstructure of the biomaterial. Therefore, the simple evaluation procedures cannot be utilized: they do not take into account those complex relations and need performing the great number of tests. The proper approach seems to be an application of artificial intelligence techniques, especially the neural network approach. Neural networks methods have been successfully used to model various relations and phenomena in steels [28], aluminium alloys [29,30], Ni-base superalloys [31], mechanically alloyed materials [32] and in titanium alloys [28,33,34]. Neural networks have been very useful for the analysis in application cases, e.g. creating fatigue stress life diagrams for Ti6Al4V alloy and corrosion resistance of titanium alloys [28].

The necessary steps to be made can include establishing: application of the material, working conditions and risk factors, and finally mechanical, chemical and physical properties of the accessible materials. If the properties are selected, their weights indicating of relative importance are to be of set up; if some properties have not been selected, it simply means zero weight. If possible, the functional relationships between considered properties and their limit values can be looked for.

Let us consider one simple case: the stem of the metallic joint implant, often made of Ti6Al4V ELI alloy. In this case one may want to achieve the best chemical properties limited to resistance to corrosion in a different form in human body fluids. However, one must take into account at least such forms of corrosion: general corrosion, localised corrosion, wear-enhanced corrosion (for knee joint), fatigue corrosion. All of them can be treated as output values; even if the best values (lowest corrosion rate or no environment-enhanced failure at any conditions) are desired, a variety of qualitative output values causes that one must reach a compromise. For that reason, some limiting values can be proposed: for electrochemical and wear-enhanced the corrosion rate no higher than the limit value, and for environment-assisted fracture the lack of damage at test conditions.

As input values can be, among chemical properties, considered chemical contents of all compounds, pH, temperature, mixing the solution, oxygen concentration in test solution, form and value of wear stress - in electrochemical corrosion test only. In fatigue corrosion tests the mechanical parameters are to be included, like frequency, extreme loads, load change rate. As physical parameters, the structure, microstructure, local chemical and phase composition of the alloy are important.

These assumptions are true for a material well polished, and no-coated with hydroxyapatite (HA). Another factor that should be considered is the oxide layer thickness and composition, which can be influenced by special oxidation techniques. Thus, there are then tens of different factors which are to be investigated or modelised by e.g. NN tool. The example of such NN for above case is shown in Fig. 1.

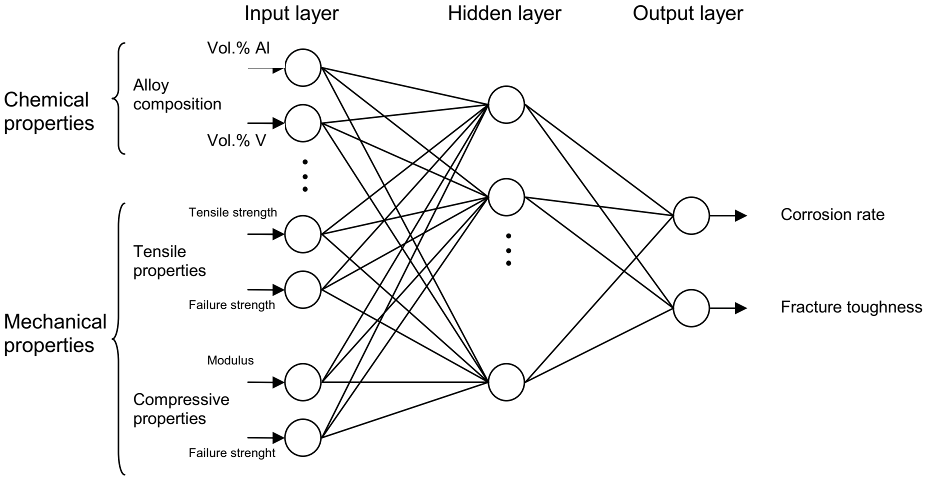

Fig. 1. General neural network structure for corrosion prediction.

Conclusions

Dissolution of titanium and its alloys may proceed by three different forms: chemical or electrochemical dissolution of layers composed of various simple and complex oxides, diffusion of

Ti and other elements through the oxide crystal lattice and its imperfections, electrochemical reaction of corrosive environment with a bare metal in tunnels and cracks within the oxide layer.

The structure, thickness and properties of the oxide layer, the interface layer-material strength, the stresses imposing on the Ti bioalloys are to consider when predicting and improving the corrosion resistance of the whole system.

The present test techniques cannot properly predict behaviour of implants in a very long time, especially as regards the temporary corrosion rate and corrosion fatigue limit.

In order to modelise the complex relationships between chemical (environmental), mechanical and structural factors the artificial intelligence techniques, like neural network method, should be applied.

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