

THE KINETIC PARAMETERS IN ELECTROCHEMICAL BEHAVIOUR OF TITANIUM IN ARTIFICIAL SALIVA

Daniela Ionescu*, Belarisa Popescu and Ioana Demetrescu

In this paper various electrochemical techniques were performed on titanium in dental media: open circuit electrode potential, linear polarisation test, cyclic polarisation measurement. In order to evaluate the susceptibility to local pitting corrosion of titanium and its alloys in dentistry, the breakdown potential φ_{Br} , the protection potential φ_p , the difference between them were evaluated from anodic potentiodynamic curves. The influence of various ions, like F^- , Cl^- , etc, on the electrochemical parameters, which characterise the corrosion, was discussed, taking into account the role of pH , and ion release from analytical data. A model based upon double layer concept and the surface analysis was proposed.

Introduction

Titanium system is well known as materials in orthopedic and odontology having chemical inertia, mechanical resistance, resistance to corrosion and biocompatibility [1]. In the present paper the complex electrochemical process involved in titanium system behaviour in specific dental media was investigated, in order to put in evidence the corrosion resistance, which is closely linked to the experimental conditions. The metallic biomaterials follow the general patterns for metal degradation in environmental situations[2].

Materials and Methods

The specimens were made from Ti. Titanium samples are pretty close to commercially pure, grade 1 Ti, casting material. Composition of electrodes are: Ti: 0,056% N_2 ; 0,015%Fe; 0,205% O_2 ; 0,015% H_2 ; Ti rest.

All metallic biomaterials were used as cylindrical electrodes. Before each measurement, the electrodes were abraded with emery paper, degreased in boiling benzene, chemically polished in 3-wt % $HF+20\%HNO_3$ for 3 minutes, and then thoroughly rinsed with tap and distilled water.

Composition of electrolytes:

- modified artificial saliva: KCl 15g/l; $NaHCO_3$ 1,5 g/l; NaH_2PO_4 0,5g/l $KSCN$ 0,5g/l; lactic acid 0,9g/l.

Other used electrolytes were:

- Saliva + $NaCl$ 0,1m;
- Saliva + NaF 0,01m.

* "I.G. Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Splaiul Independentei 202, 77208-Bucharest, Romania

The solution temperature was kept at 37°C, taking into account that this is the normal temperature of the human body.

The experiments were performed in saliva in the presence of various ions implicated in complex chemistry of the oral cavity using following methods:

Open circuit electrode potential measurement

The electrical potential at the metal electrolyte surface is strongly dependent on the nature and the concentration of the electrolyte, pH and surface conditions. As a result, the electrochemical reactions at this interface vary with time. In open circuit experiments curves potential versus time were obtained; final experiments time was 20 days, and simultaneously the variation pH-time was followed with a MX870 MESSGERA digital pH-meter.

Linear polarization test (Stern-Geary method)

This test is a simple method for evaluating the corrosion rate, sufficiently sensitive to measure even a low corrosion rate; Voltalab 21 equipment with Volamaster program determines and displays the corrosion current as the ordinate of the intercept between the two Tafel lines extrapolated at the $\phi = \phi_{(i=0)}$. The test was conducted at a scanning rate of 5 mV/min, and the potential amplitude was ± 20 mV. The current densities were calculated with reference to the samples geometrical area.

$$v_{\text{cor}} = \frac{3.27 \cdot 10^{-3} \cdot i_{\text{cor}} \cdot E}{S \cdot d} \text{ [mm/year]}$$

v_{cor} is corrosion rate in millimetres per year, i_{cor} is the corrosion current density in $\mu\text{A}/\text{cm}^2$, E is the equivalent weight in grams and d is the metal density in g/cm^3 .

Cyclic polarization experiments

Cyclic polarisation data were recording by VoltaLab21 electrochemical laboratory system with VoltaMaster[®]1 electrochemistry software. The polarisation scan was initiated after immersing the specimen for 30 minutes and scanning the potential in the more noble direction at the scan rate of 100 mV/min. When 4000 mV were reached, the scanning direction was reversed.

Potentiodynamic measurements were carried out in order to determine the initiation and propagation of local corrosion, which is associated with the breakdown of passive protective film.

The breakdown potential (ϕ_{Br}) is the one at which the anodic current increases considerably with applied potential. The potential at which the hysteresis loop is completed upon reverse polarisation scan, is known as the protective potential or repassivation potential.

Spectral analysis

An atomic absorption spectrophotometer with flame type Zeiss AAS L30 was used in order to put in evidence the ion release.

Results and discussions

In spite of the complexity of biological phenomena, the metallic biomaterials follow the general patterns for metal degradation in environmental situations [3]. The problem of metal ion release, is only one facet of a very important issue, the biological, chemical, and clinical behaviour of implant materials.

Electrode potential and Pourbaix Diagrams

A basic concept for metallic implants is that metals used are in a passive state, and this means that they have a low corrosion rate due to the presence of the protective layer, which usually is an oxide. If the film is damaged some corrosion will occur, the amount depending of film reformation.

In order to study the electrochemical behaviour of titanium systems in condition close to those of clinical reality, it is absolutely necessary to have oxidised layers characteristics of stationary state.

In the case of Ti, the good corrosion resistance results from the formation of very stable, continuous, highly adherent, and protective oxide film on metal surface. The nature, composition and thickness of the protective surface oxides that form on titanium alloys depend on environmental conditions. As is widely known, the Pourbaix (potential-pH) diagram for titanium-water system at 25°C [4] depicts the wide regime over which the monoxide, trioxide and dioxide of titanium is predicted to be stable, based on thermodynamic (free energy) consideration.

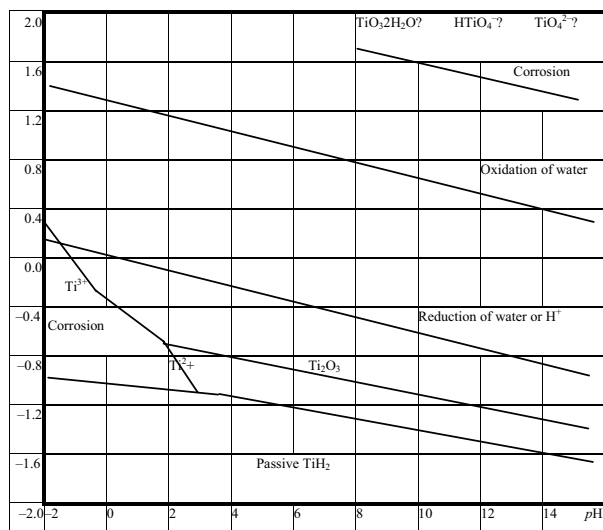


Fig. 1: Pourbaix (potential-pH) diagram for Ti-H₂O system of 25°C.

During 20 days artificial saliva achieved $pH = 8.5$ when the curve potential vs. time (Fig. 2) and Pourbaix diagram corresponds to the TiO_2 film.

Artificial saliva with NaCl 0.01 M has $pH = 3$, and in saliva with NaF $pH = 4$ at the same exposure time. At smaller pH , the potential trends to negative values (curve with NaF).

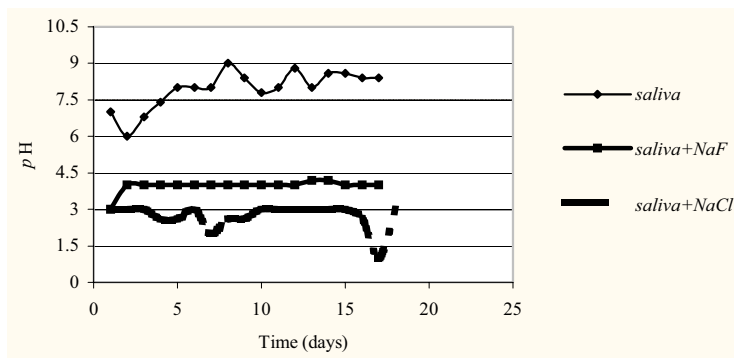


Fig. 2: pH vs. time for artificial saliva.

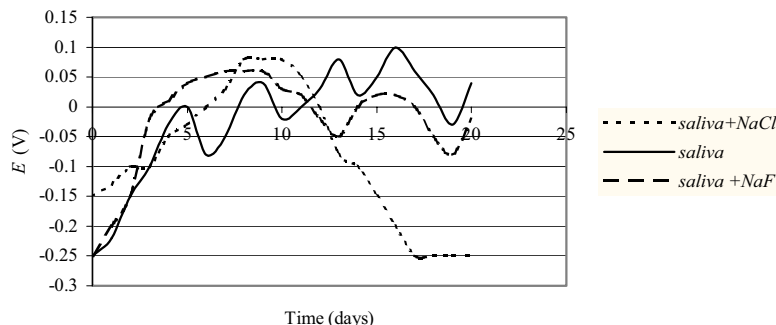


Fig. 3: The variation of open circuit potential with time.

The open circuit electrode potential varied from $-0.25V$ to $0.05V$ SCE. Generally for $pH > 5$ case of artificial saliva, the open circuit potential increased with time. For the $pH < 5$ saliva with halogen ions Cl^- and F^- potential decreased with time as result of diminish of thickness of passive film and remodeling of protective film because of change in oxidation number of titanium oxides (Ti_2O_3 , TiO_2).

Dissolution kinetics of the passive film [5]

During anodic or cathodic polarisation, or at open circuit, ion transfer reaction of metal ions and oxygen ions will take place. A clear process is the anodic corrosion of a passive metal in the steady state. In such a case, metal ions travel through the oxide film with a constant rate and are transferred in an ion transfer reaction at the interface oxide/electrolyte. The rate of that passive film dissolution depends on the local potential drop at the interface, the pH and the activity of the metal ions at the oxide surface [6]. In a non-saturated solution, the

oxide may dissolve even at open circuit conditions. The overall current will be zero and the oxide film thickness decreases with time until a steady state is reached.

The corrosion of passive film is supported by experimental data (Table 1) from Stern method (Corrosion current and corrosion rate from polarization resistance).

Table 1. Electrochemical parameters for Ti from the Stern method

Physiological Media	φ_{cor} (mV)	i_{cor} (mA/cm ²)	v_{cor} (mm/year)
Artificial saliva	14	$8 \cdot 10^{-6}$	0.0002
Saliva +NaCl 0.01m	-30	$5.6 \cdot 10^{-5}$	0.00014
Saliva +NaCl 0.01m	-30	$5.6 \cdot 10^{-5}$	0.00014
Saliva + NaF 0.01m	-70	$1.816 \cdot 10^{-3}$	0.0045
Lactic acid 10%	-380	0.0020	0,048
Lactic acid 50%	-380	0.0025	0,062

As it is possible to see from Table 1 under static conditions, the rate of attack of titanium passive film is pretty small. In the presence of chloride and fluoride ions the corrosion rate is increasing being higher in fluoride media. This observation is consistent with literature data; in lactic acid (it is to point out that this acid is one of the most important products of the metabolism of pathogenic bacteria) the corrosion rate is greater and the pH dropped from neutral value to acid value.

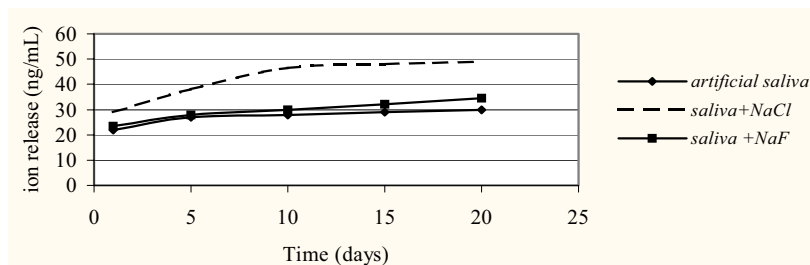


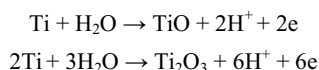
Fig. 4: The dependence of titanium ions release versus in artificial saliva (from A.A.S.data).

The concentrations of titanium release during the exposed time periods (20 days) are presented in Fig. 4.

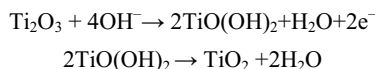
The amount of titanium ion released in every solution increased with increasing immersion time. The relation between the released amount and the immersion time was not proportional, but parabolic (Fig. 4). The amount of titanium released in modified saliva was less than from in saliva with Cl⁻ and F⁻ ions.

Passive dissolution and ion release

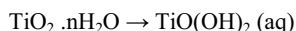
Immediately as TiO forms, an oxidation process to trivalent state of titanium and dehydrate occurs as:



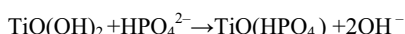
Healy [7] model and T. Hanawa [8] studies based on the dates obtained by electrochemical technique and analysis for titanium surface (A.E.S.), (X.P.S) (SEM) confirmed the following reaction in neutral and alkaline solution:



Dissolution of oxide films is due to hydrolysis of hydrated TiO_2 :



Phosphate ions exist in artificial saliva solution employed in this study. The exchange reaction between Ti-OH surface sites and the adsorbed P-containing species is



In order to evaluate the susceptibility to local pitting corrosion of titanium and its alloys in various physiological media, the breakdown potential ϕ_{Br} , the protection potential ϕ_{Pr} and the difference between them were evaluated from anodic cyclic polarization experiments [5].

Breakdown potential is a sign of local corrosion but the measure of pitting susceptibility is the difference potential between the breakdown potential and the repassivation one. The protection potential represents the potential at the intersection of hysteresis curve with passive domain. Below this potential the propagation of existing localized corrosion will not occur. If the difference between breakdown and the repassivation potential is increasing, the chance in the appearance of pitting is greater and its propagation in depth is more intense. In other words, the hysteresis loop increases as the susceptibility of material to corrosion increases. All these values for titanium in oral cavity physiological media are presented in Table 2.

Table 2. Effect of Cl^- and F^- on cyclic anodic parameters for Ti

Solution	ϕ_{Br} (mV)	ϕ_{Pr} (mV)	$\phi_{\text{Br}} - \phi_{\text{Pr}}$ (mV)
Saliva	700	500	200
Saliva +NaCl 0,01m	300	50	250
Saliva +NaF 0,01m	275	10	265

Usually passive films form a barrier, but under special conditions an immediate increase of local conductivity, a passivity breakdown is observed [9]. The reasons for this local destruction of the passive may be different:

- Corrosion of passive film locally;
- Aggressive ions like chloride may penetrate into the film. The penetration/dissolution mechanism: Cl^- migrates or diffused into the oxide, destabilises it and finally causes active dissolution;

- The breakdown /adsorption mechanism: At first, the oxide film breaks down due to the mechanical stress. Then, Cl^- ions are adsorbed at the bare metal and enhances active dissolution;
- At low potentials hydrogen can be incorporated into the film or the metal, hydrogen gas is evolved, and the film is reduced, dissolves or flakes off.

Conclusion

1. Titanium present less corrosion susceptibility in artificial saliva without Cl^- and F^- anions confirmed by the breakdown potential and protection potential in presence of anions
2. The amount of titanium ion released in every solution increased with increasing immersion time. The relation between the released amount and the immersion time was not proportional, but parabolic (Fig. 4).
3. The amount of titanium released in modified saliva was the least, less than from in saliva with Cl^- and F^- ions.

REFERENCE

1. Barbosa, M. A. (1992) *Biomaterials*, 257-283.
2. Popescu, B., Ionescu, D., Martinof, A. and Demetrescu, I. (2001) *The influence of various ions on titanium dental corrosion*, Proceedings The fifth International Symposium on Titanium In Dentistry Japan, June 2001, 15.
3. Ionescu D, Popescu, B, and Demetrescu, I. (2000) *About the corrosion of various metallic biomaterials in simulated physiological media*, Proceedings of the E.M.R.C., May 2000 Budapest (CD).
4. Pourbaix, M. (1963) *Atlas d'Equilibres Electrochimiques a 25°C*, Gauthier Villars. Paris.
5. Murgulescu, I.G. (1986) *Introducere in Chimia Fizica*, vol 1-4, Ed. Acad., Bucuresti.
6. Schultze, E. (2000) *Electrochimica Acta*, 48-58.
7. Healy, K. and Ducheyne, P. (1992) *J. of Biomedical Materials Research* **26**, 319.
8. Hanawa, T., Asami, K. and Asaoka, K. (1998) *Journal of Biomedical Materials Research* **40**, 530.
9. Marcus, P., Baroux, B. and Keddad, M. (Eds.) (1994) **Modification of passive film European Federation of Corrosion Publication. 12**, The Institute of Materials, London, England.