CHARACTERIZATION OF Ti6Al4V ALLOY FOR CORROSION BEHAVIOR IN MAYER-FUSAYAMA ARTIFICIAL SALIVA

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Metallic materials are unavoidable materials in maxillofacial reconstructive surgery. One of the most important and critical factors affecting the maxillofacial prostheses is the electrochemical corrosion of the metallic implants in the human body. The aim of this study is to determine the corrosion behavior of the Ti6Al4V used in the manufacture of maxillofacial prosthesis in artificial saliva environment. The corrosion behavior was studied by monitoring the evolution in time of electrochemical potential in Mayer-Fusayama artificial saliva, the measurement of electrochemical impedance spectroscopy and by determination of the corrosion rate of Ti alloy.

Keywords: Ti6Al4V, corrosion, corrosion resistance, pH, artificial saliva, maxillofacial prosthesis

1. Introduction

Biomedical prostheses are artificial replacements that are used in the human body, in an effort to provide the function of the replaced part. Prosthetic devices are made of metallic, polymeric or ceramic materials, depending on the intended use. The main requirement for any material to be placed / inserted in the human body is that it should be biocompatible and not cause any adverse reaction in the body. Corrosion of the manufacturing material is included in the biocompatibility concept of the prostheses being an important factor in the release of metal ions in the body environment and in the degradation of the prostheses metal [1].

The metallic materials used in maxillofacial reconstruction, permanently maintained in saliva electrolyte, undergo a progressive and slow degradation as result of an electrochemical corrosion. The human body is a very aggressive environment in terms of the corrosion behavior of materials used in the prostheses' manufacture since the tissue fluid in the body contains different salts (NaCl, KCl, $CaCl_2$), proteins (albumin, fibrin, collagen etc.), cells (osteoblasts, fibrinoblasts, etc), water, dissolved oxygen and different ions [2].

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In recent years, titanium and its alloys are widely used for medical and dental applications, being the most promising materials for use as implants [3] due to their remarkable characteristics such as: excellent corrosion resistance, mechanical resistance, chemical inertia, low density and especially, biocompatibility [4-7]. Titanium and its alloys are considered to be immune from corrosive attack in saline environment where conventional materials often fail. They exhibit increased resistance to a wide range of acids, alkalis and natural waters [8-10]. The excellent corrosion resistance of titanium and its alloys in different test solution saliva is due to the formation of very protective layer of oxide TiO_2 on their surfaces [1]. In medical field, titanium and its alloys are well known for being "metals that do not corrode" [11].

Ti6Al4V alloy structure was the first titanium alloy registered as implant material in ASTM standards (F-136-84) [12]. However, this alloy has certain limitations. Despite its favorable properties, this material can release metal ions into the tissues surrounding the implant, which react with human fluids. They form hydroxides or oxides with the water and produce the local change of the pH [13].

This paper aims an experimental study of corrosion behavior in artificial saliva of the Ti6Al4V alloy used in the manufacture of maxillofacial prosthesis. This experimental research is part of a complex study regarding the design and manufacturing of personalized maxillofacial prostheses [14]. The experimental prosthesis was designed using Computer Aided Design software, based on the virtual model generated from Computer Tomography scans, which allowed preserving the facial aesthetics. Having digital models, a Finite Element Analysis of the prosthesis was easily introduced into the design route to optimize the shape for mechanical requirements [15]. Then the prosthesis was manufactured as-cast only and received together with material specimens, in order to test them.

The aim of this study is to investigate and compare the influence of pH on the corrosion behavior of Ti6Al4V alloy in artificial saliva using electrochemical techniques. The corrosion behavior of Ti6Al4V was studied in Fusayama-Mayer artificial saliva at different pH, namely 6.9 (neutral), 4.2 (acid) and 8.2 (alkaline), using the following techniques: open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2.Experimental procedures

2.1 Materials preparation

The working electrodes were cast from Ti6Al4V alloy with composition in weight % of: 6.15 Al, 4.4 V, 0.09 Fe, 0.05 C, 0.08 O, 0.015 N, rest Ti. The electrodes were supplied in the form of as-cast massive cylindrical rods from Titanium Casting International Company (England), together with the experimental maxillofacial prosthesis. The experimental electrodes were obtained using a water-jet machine to cut the rods. Each metallic samples was screwed to an electrical cooper wire and coated with acrylic polymer, keeping as "cast-only" fixed exposed surface areas for Ti alloy throughout the whole measurements. The surface of samples exposed to artificial saliva solution was an average of 1.6 cm^2. The 6 samples used for testing were as follow: samples 1.0 and 1.1 for neutral environment, samples 2.0 and 2.1 for acid environment and samples 3.0 and 3.1 for alkaline environment.

All potentials during experiments were measured and reported with reference to a saturated $Ag/AgCl_{sat}$ electrode, using an auxiliary platinum electrode. The used electrolyte (Fusayama-Mayer artificial saliva) was freshly prepared from p.a. chemical reactives with a composition as follow: NaCl 0.40 gL^{-1}, KCl 0.40 gL^{-1}, $CaCl_2 \cdot 2H_2O$ 0.795 gL^{-1}, $NaH_2PO_4 \cdot H_2O$ 0.69 gL^{-1}, $Na_2S \cdot 9H_2O$ 50 mgL^{-1}, Urea 100 gL^{-1} [16]. The neutral pH (6.9) obtained was modified using NaOH solution to get alkaline pH (8.2) and respectively HCl 2M solution to get acid pH (4.2).

2.2 Methods and research equipments

Open-circuit potential (OCP), anodic polarization and electrochemical impedance spectroscopy (EIS) measurements were performed using the electrochemical workstation GAMRY impedance analyzer provided with Echem Anaysis 5.58 software.

There were performed the following techniques:

- *Potential – time dependency (OCP)* was registered during 1630 h of exposure, according to static immersion method, in standard Fusayama-Mayer solution [17].
- *Electrochemical Impedance Spectroscopy* measurements were carried out in the frequency range from 100 kHz to 0.01 Hz, at different exposure periods of time in corroding media. EIS spectra were obtained at open circuit potential with a perturbing signal of 10 mV. The impedance diagrams were recorded at the steady OCP;
- *Potentiodynamic polarization* curves were performed in the potential range from –100 mV to +100 mV (OCP reported), with a scan rate of 2.5mVs^{-1} at pH = 8.2; 4.2 and 6.9, at 25°C for electrochemical and corrosion parameters measurements, according [18].
- *Corrosion rates* were calculated from Tafel slopes at different pH values of artificial saliva.

A three-electrode cell assembly consisting of Ti6Al4V alloy as working electrode, platinum sheet as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode was used for the corrosion measurements.

The metallic electrodes were immersed in Fusayama-Mayer artificial saliva solution at three different pH: 6.9 neutral, 4.2 acid and 8.2 alkaline, at 25^0C under naturally aerated conditions. The experiments were repeated 2 times for each pH to ensure reproductibility of electrochemical curves. Fresh solution of artificial electrolyte was used for each experiment.

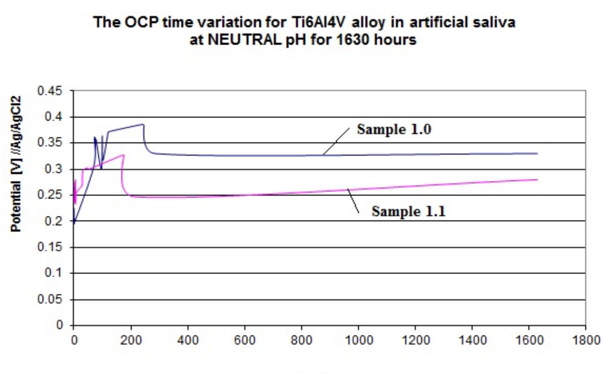
3. Results and discussions

3.1 Open-circuit electrode potential (OCP) measurements

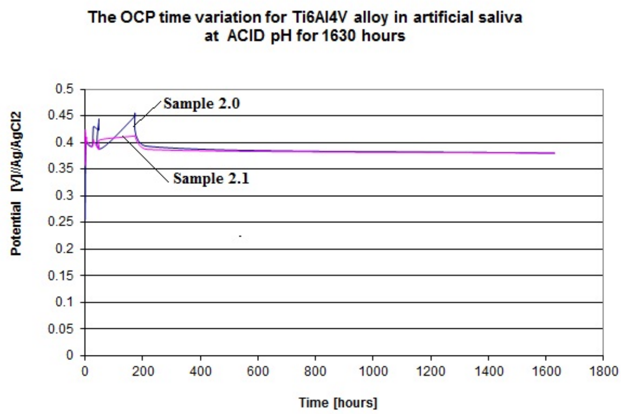
The chemical properties of the TiO_2 layer play an important role in the biocompatibility of titanium implants and the surrounding tissues and it must not break down if the implant needs to be successful [19]. From the medical point of view, the biocompatibility of a prosthetic implant is determined by the stability of the oxide film and the ability to incorporate ions from solution [20].

The simple way to study the corrosion behavior (eg. film formation and passivation of prosthesis/alloys in a solution) is to monitor the open-circuit potential (OCP) of material as a function of time. Increasing the potential in the positive direction indicates the formation of a passive film, and a steady state potential indicates that the film remains intact and protective. A drop of potential in the negative direction indicates breaks in the film, dissolution of the film, or no film formation [21].

The potential-time variation rate, reflecting oxide formation rate, was high after a time of immersion and decreased with time to reach a steady state. The OCP time variation at different pH values can be noticed in Fig. 1 a, b, c.



a)



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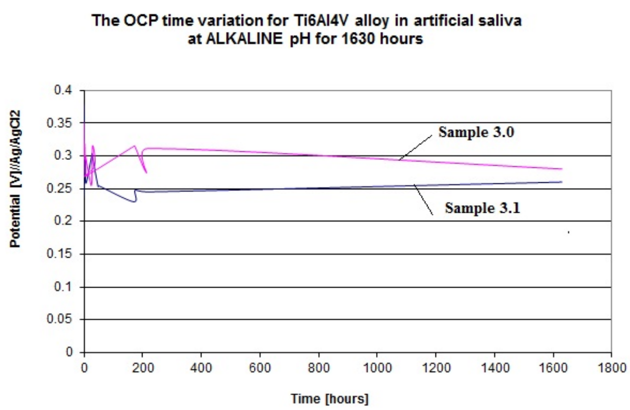

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Fig. 1. The OCP time variation for Ti6Al4V alloy in artificial saliva at different pH: a) 6.9, b) 4.2, c) 8.2 for 1630 hours

A special titanium alloy stability was observed with a tendency to stabilize the stationary potential value (with small fluctuations of 10-15 mV). Fluctuation frequency was higher in the first minutes of immersion, between the passive film spontaneously formed on the surface of the alloy and corrosive environment, followed by a continuous rise in potential towards noble direction to attain finally the steady state potentials. These results revealed a presence of competition between film dissolution and film formation, which end by a potential indicating thickness and self-healing of surface film.

The potential variation rate, which reflects oxide formation rate, was high after few minutes of immersion, and decreased with time to reach a steady state.

Also, the pH of environment controls the corrosion process as follows, in acidic media the OCP's values are controlled by the reduction of H^+ ions, whereas at near neutral pH (6-7), the reduction of oxygen is the most significant cathodic reduction reaction [22]. The corrosion processes of titanium and titanium alloys in aqueous environments are anodically controlled because of the reinforcement of the natural passive film attested by moving toward positive values of OCP.

The maximum corrosion potential was observed for sample 2.0 at acid pH, namely 0,455V after 173 hours of immersion.

Since after 1630 hours of immersion stationary potential remains practically constant (0; 0,39V), it highlights the good corrosion resistance of studied material in artificial biochemical environments.

3.2 Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy (EIS) is a common technique for studying the passivation of metals in electrolytes. The EIS data of Ti6Al4V surfaces were examined in order to establish the corrosion behavior of these samples in artificial saliva at 3 different pH values. Before each experiment the sample was left immersed in the respective pH electrolyte for about 90 minutes, until a quasi-stabilized potential was reached. The experimental impedance results for Ti6Al4V samples were expressed in Nyquist plots of Z"(ω) as a function of Z'(ω), where ω=2πf [16].

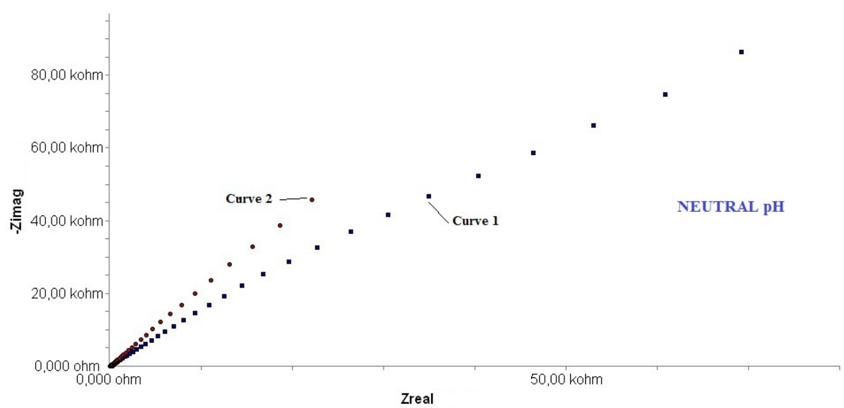


Fig. 2. Niquist curves of Ti6Al4V in artificial saliva at NEUTRAL pH immediate (Curve 1) and after 250 hours of immersion (Curve 2)

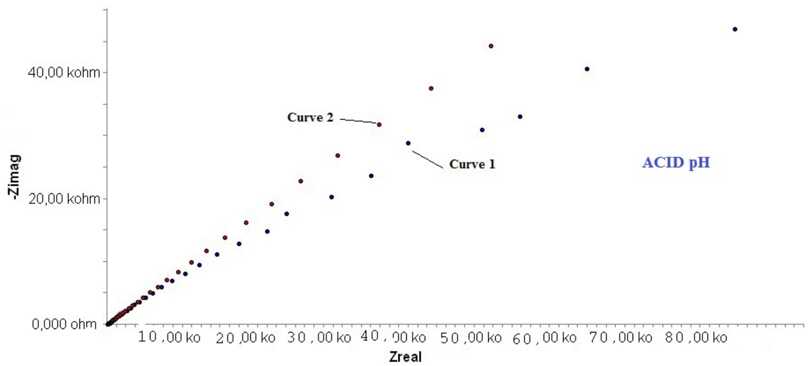


Fig. 3. Niquist curves of Ti6Al4V in artificial saliva at ACID pH immediate (Curve 1) and after 250 hours of immersion (Curve 2)

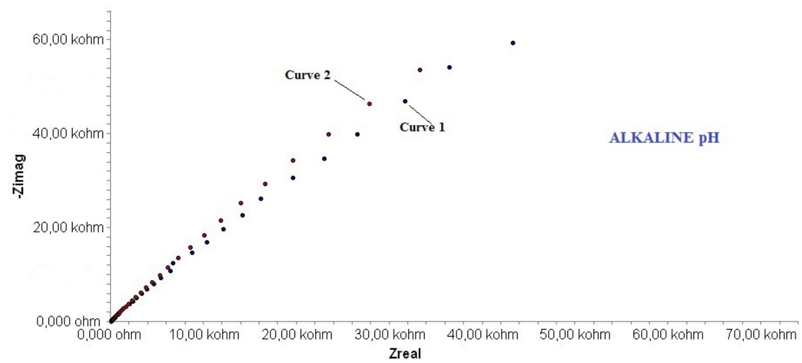


Fig. 4. Niquist curves of Ti6Al4V in artificial saliva at ALKALINE pH immediate (Curve 1) and after 250 hours of immersion (Curve 2)

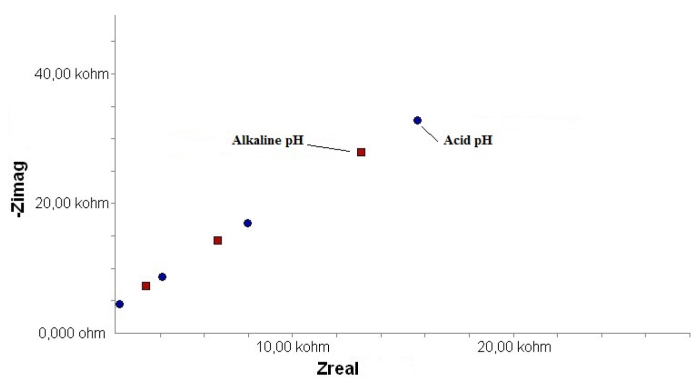


Fig. 5. Niquist plots after 250 h of immersion, in artificial saliva for acid (bullet markers) and alkaline pH (square markers)

The Niquist diagrams show after 250 h in artificial saliva, a mixt diffusion and corrosion control of the process (Fig. 2, 3, 4). Under open circuit conditions, it was suggested that the leading force for surface oxide film formation on the metal was the free electrons exchange of the reaction between the metal alloy and the test solution [23].

From this technique more information about corrosion resistance can be determinate:

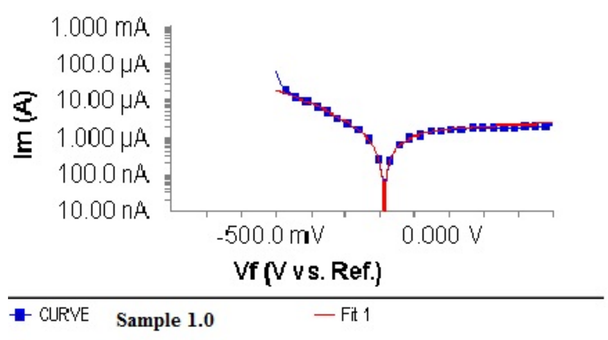
- when the material is immersed in artificial saliva, on the surface is forming a passive film (titanium oxide), which consolidates in the presence of chlorine ions from saliva;
- after 250 hours of immersion, the film reinforces passivity.

It appears that the different pH values do not influence corrosion behavior of the material. Note, however, that at the material interface with electrolyte do not occur electrode processes, but occurs only diffusive transport through the passive film (liniar dependency at 45^0 angle between the two impedance components). That explains the stationarity of OCP, at the interface material-solution where is taking place only electrons exchange (Fig. 5).

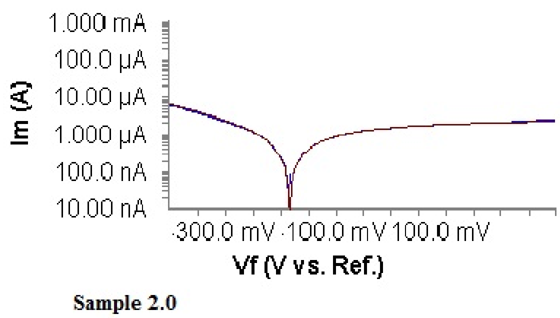
3.3 Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were used to determine the active-passive characteristics of Ti6Al4V alloy in 3 different pH values of artificial saliva solution.

The polarization curves of the Ti6Al4V alloy in artificial saliva solution for pH 6.9, 8.2 and 4.2 are represented in Fig. 6. a, b, c. The corrosion rates in artificial saliva were determined using Tafel analysis.



a)



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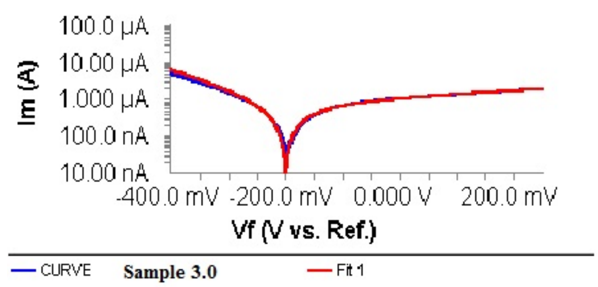

c)

Fig. 6. Tafel plots and curve fit of Ti6Al4V in artificial saliva at different pH values: a) 6.9, b) 4.2, c) 8.2

The values of corrosion parameters such as: E_{corr}. (corrosion potential), i_{corr}. (corrosion current density) and calculated corrosion rates for the Ti6Al4V alloy in different pH values of saliva with the help of potentiodynamic polarization technique are presented in Tab.1.

The values of corrosion parameters and polarization curves shape demonstrate that the corrosion rate of Ti6Al4V alloy electrodes decreases with an increase in pH value of test solution (see neutral vs. alkaline pH) , with a concomitant shift in the corrosion potential to more positive values and an increase in the corrosion density current.

The primary objective of Tafel analisys based on experimental measurements was the determination of the corrosion current density (i_{corr}) and the corrosion rate (v_{corr}) [24].

Table 1

Electrochemical parameters calculated by EchemAnalysis software using experimental data

pH	$\mathbf{E_{cor}}$ [a)] [mV]	$\mathbf{i_{cor}}$ [b)] [μA/cm²]	$\mathbf{v_{cor}}$ [c)] [μm/an]
Neutral (6.9)	-188	1,90	4,8
Acid (4.2)	-183	1,92	4,8
Alcaline (8.2)	-198	0,73	1,77

The corrosion rate has been calculated through Faraday's law (Eq. 1) knowing the sample exposed area and the corrosion parameters values from Table 1, and the obtained results were comparable with the ones from the literature, where E_{corr} was found to be -207 mV [25] and corrosion rate was determined at 4,83 mm/year [25].

$$v_{cor} = \frac{3.27 \cdot 10^{-3} \cdot i_{cor} \cdot E_{cor}}{\rho} \text{ [mm/year]} \quad (1)$$

where ρ = 4,51 g/cm³ (Ti6Al4V alloy density)

v_{corr} = corrosion rate;

i_{corr} = corrosion current density;

E_{corr} = corrosion potential.

4. Conclusions

The electrochemical techniques used in this investigation led to the following conclusions:

- The experimental results illustrate that the studied material has high corrosion resistance, and the stationary potential is virtually constant regardless of pH test medium used;
- The experiments demonstrated that Ti6Al4V alloy used in the manufacture of studied maxillofacial prosthesis is stable at corrosion in the Fusayama-Mayer artificial saliva;
- The studied titanium alloy does not show any aggressive phenomena corrosion, on the samples surfaces forming protective oxides film which gives the material stability in artificial saliva.

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