Metabolic Albumin and Its Effect on Electrochemical Behavior of Titanium Implant Alloy

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Abstract. Human albumin is a protein made by the liver. It is the most abundant circulating protein, accounts for 50-60% of total protein in the blood and plays many roles. The most important are the oncotic and non-nociceptive properties. The albumine is part of the family of globular proteins, the most common of which are the serum albumins. All the proteins of the albumin family are water-soluble, moderately soluble in concentrated salt solutions, and experience heat denaturation. Albumin is commonly found in blood plasma and differs from other blood proteins because it is not glycosylated. Thanks to their unique properties and benefits such as superior biocompatibility and good corrosion resistance, Titanium and Titanium alloys have many uses. Their applications include dental implants and parts for orthodontic surgery; replacement parts for hips, knees, shoulders, spine, elbows and wrist joints; bone fixation devices such as nails, screws and nuts; housing parts for pacemakers and artificial heart valves; surgical instruments and components in high-speed blood centrifuges. In SITU electrochemical measurements are: open circuit potential (OCP), polarization resistance (Rp), potentiodynamic polarization (PD) and cyclic voltammetry polarization (CV) were performed to monitor the corrosion process. The optical images of the tested samples have been observed before and after corrosion experiments using an optical microscope (Optika) in order to understand the nature of corrosion and the damages produced by this process.

1. Introduction

Biomaterials have been defined as any substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replaces any tissue, organ, or function of the body.

The research on biomaterials initially started by testing of these materials on animals and their acceptability on the human body system were indirectly established. Nowadays, the mainly familiar kinds of materials used in biomedical applications are Metals, Ceramics, Polymers, and Composites. It is well known that prosthetic devices and components need to fulfill several imperative requirements so that they are successful in service over a longterm usage in the body without rejection and minimal failure.

The field of biomaterials has gathered significant interest as these materials are very used to fix and replace decayed or damaged parts of the human systems such as heart valves, bones, joints and teeth, etc [1]. Biomaterials for medical devices and instruments that come into contact with the human body have to demonstrate a high resistance to wear, hardness, ductility, biocompatibility, biotolerance, and above
all resistance to corrosion reactions [2].

Implants are in contact with body fluids containing dissolved oxygen, chloride, phosphate, and various other organic and inorganic molecules. One of the main components of organic molecules in body fluid is protein. Protein is the first component to interact with implants through a small gap at the implant-tissue interface [3]. The interactions of metal ions with proteins could form colloidal organometallic complexes, change albumin solutions pH level and increase the rate of ion release and corrosion rate [3]. Protein adsorption depends on protein concentration, chemical composition and wettability of the metal oxide film.

Under normal conditions, human joints operate by low-friction articular cartilage bearing surfaces, which are conforming and self-renewing. When natural joints are severely damaged, e.g. due to osteoarthritis, they are often replaced by artificial implants. In total joint replacement, femoral components are generally made of metal–metal, ceramic–polymer or metal–polymer couples. The use of metallic alloys and polymers has increased considerably in total joint replacement in recent years [4].

Titanium has been commercially offered during last more than 60 years and since then several titanium based materials have been developed as a surgical material.

Titanium and its alloys are a class of ideal biomedical materials due to their specific high strength, low elastic modulus, excellent corrosion resistance and biocompatibility and have already been widely used in the medical fields including orthopedics and dentistry. Titanium alloys are better tolerated than pure titanium because it seems that the oxide layer that forms is much larger (about 10-20 μm) and some alloys improve properties such as corrosion resistance and hardness [5].

The aim of study is to investigate and verify if the presence of albumin has an influence on corrosion resistance of Ti-6Al-4V alloy in biological Hank solution, the most aggressive simulated body fluid (SBF). The electrochemical methods as time evolution of free potential (open circuit potential), were used for comparative studies.

2. Materials and methods

A VoltaLab PGZ 301 potentiostat / galvanostat controlled by VoltaMaster4 software was used for electrochemical measurements. Electrochemical measurements were conducted in a three electrode cell with an Ag/AgCl as the reference electrode and a Pt-Rh grid as the counter electrode. The test specimen was served as a working electrode.

Chemical composition and mechanical properties of titanium alloy used are shown in Table 1. Before each corrosion experiment the working electrode was cleaned with NaOH and than HCl, washed with distilled water and finally dried. The surface area exposed to the electrolyte was 3 cm², other surfaces being isolated with resin.

Table 1. Chemical composition and mechanical properties of Ti-6Al-4V alloy.

| Specification     | 8-12-05832-1 | N     | Al    | C     | V     | H     | Fe    | O     | Ti     |
|-------------------|---------------|-------|-------|-------|-------|-------|-------|-------|--------|
| Ti-6Al-4V Grade 5 | Max. [%]      | 0.003 | 6.01  | 0.008 | 3.83  | 0.002 | 0.083 | 0.088 | 89.976 |
|                   | Min. [%]      | 0.003 | 5.86  | 0.008 | 3.73  | 0.002 | 0.068 | 0.084 | 90.245 |
| Mechanical properties |       | Resistance to flow [MPa] | 865  | Tensile strength [MPa] | 937  | Elongation [%] | 11  |

In order to simulate the physiological conditions of the human body, SBF (simulated body fluid) solution was used for in vitro corrosion studies. The chemical composition is given in Table 2. The corrosion resistance of the Ti-6Al-4V alloy was determined in Hank solution; Hank solution doped with 4g/L Albumin and Hank solution doped with 8g/L Albumin, to simulate the severe functional conditions of an implant in surgical situations. The volume of solution used for each experiment was 270 mL. All the experiments were conducted at room temperature 25°C.
Table 2. Composition of artificial Hank solution.

| Compounds [g/L] | Hank solution |
|-----------------|---------------|
| NaCl            | 8             |
| KCl             | 0.4           |
| CaCl$_2$*2H$_2$O| 0.35          |
| Na$_2$HPO$_4$*H$_2$O | 0.25 |
| MgCl$_2$        | 0.19          |
| MgSO$_4$*7H$_2$O| 0.06          |
| Glucose         | 1             |

The electrochemical measurements such as open circuit potential (OCP), linear polarization resistance were carried out to access the anticorrosive characteristics of the Ti-6Al-4V alloy. In order to see the effect of corrosion environment with different concentration of albumin on surface morphology of the Ti-6Al-4V alloy, optical images were taken before and after corrosion experiments using the optical microscope OPTIKA XDS3 MET connected to a computer and controlled with Vision Pro Plus 5.0 software.

3. Results and discussions

3.1. Open Circuit Potential (OCP)

Figure 1 depicts the OCP curves as a function of the immersion time in artificial Hank solution solution doped with two different concentrations of albumin: 4% and 8%.

In all three curves, it can be seen that the initial OCP level changing slowly to quasi-steady-state. This behavior is typically observed in passivation process and in our sample this could be related to the formation of TiO$_2$ film which passivates the Ti-6Al-4V alloy surface. This protective oxide film acts as a barrier for metal dissolution and consequently reduces the corrosion rate, being electrochemically stable at quasi-stationary values of the OCP. The ennobling in time of open circuit potentials denotes the formation of a passive film and a stable state, due to the formation of a compact
adherent titanium oxide film on the Ti-6Al-4V alloy surface. For a lower concentration of albumin the OCP level is shift-down to more negative potentials showing a surface instability.

3.2 Linear polarization resistance
Linear polarization resistance (Rp) is the only corrosion monitoring method that allows corrosion rates to be measured directly, in real time.

For comparative tests 30 polarization resistance points were measured by plotting the linear polarization diagrams with a small potential domain disturbance of ± 40 mV around the free potential, resulting 30 points of polarization resistance, which show the evolution of polarization resistance during immersion time in specific solution, Figure 2 (a, b).

![Figure 2a. The evolution of polarization resistance (Rp) values of: (1) Ti-6Al-4V alloy immersed in Hank solution, (2) Hank solution doped with 8 g/L albumin, (3) Hank solution doped with 4 g/L albumin.](image)

At each polarization diagram the Tafel slopes, the polarization resistance and corrosion current density (corrosion rate) were calculated using the Stern Geary equation in the linear potential domain:

For simple corrosion systems, corrosion reactions are strictly controlled by the mass transfer and the corrosion current density, $i_{cor}$, can be correlated with the polarization resistance, $R_p$, through the relationships:

$$i_{cor} = \frac{B}{R_p}$$  \hspace{1cm} (1)

The corrosion rate is expressed in this case in A / cm$^2$.

B is a constant of the system material/environment given by the relation:

$$B = \frac{b_a|b_c|}{2,303(b_a + b_c)}$$  \hspace{1cm} (2)

Where: $b_a$ and $b_c$ are the Tafel slopes for anodic and cathodic corrosion reactions, respectively.
Figure 2b. The evolution of corrosion rate as penetration rate values of: (1) Ti-6Al-4V alloy immersed in Hank solution, (2) Hank solution doped with 8 g/L albumin, (3) Hank solution doped with 4 g/L albumin.

Increasing the polarization resistance means decreasing the corrosion current density and thus the decreasing the corrosion rate.

The polarization resistance values and corrosion rate values of the Ti-6Al-4V alloy surfaces studied in Hank solution and Hank solution with two different concentration of albumin are presented in Figure 2 (a, b).

From Figure 2a it can be seen that the polarization resistance value is higher in Hank solution, comparatively with polarization resistance resulted in Hank solution doped with 8 g/L albumin and Hank solution doped with 4 g/L albumin.

The increased polarization resistance value means that the formed passive film after immersion in Hank solution is more resistant compared with that formed in Hank solution doped with 8 g/L albumin and Hank solution doped with 4 g/L albumin.

Further from polarization resistance, the calculated corrosion rate expressed as penetration rate is presented in Figure 2b. According with the data plotted in Figure 2b it can be seen that the higher corrosion rate as penetration rate (0.10 µm/year) correspond to Ti-6Al-4V alloy immersed in Hank solution doped with 8 g/L albumin comparatively with the corrosion rate of Ti-6Al-4V alloy immersed in Hank solution doped with 4 g/L albumin (corrosion rate is 0.08 µm/year), or titanium alloy immersed in Hank solution without albumin (0.04 µm/year).

3.3. Potentiodynamic polarization
Potentiodynamic polarization measurements, give the possibility to compare the titanium alloy surface by point of view of passivation domains specific of the alloy immersed in the tested solutions. The potentiodynamic polarization diagrams (PD), Figure 3, were performed between -1000 mV to 3500 mV vs. Ag/AgCl at a potential sweep rate of 5 mV/s.

As it could be seen further in the cyclic polarization diagrams, the picks observed on Potentiodynamic diagrams from Figure 3 have to be correlated with localized corrosion (pitting) installed on 304L stainless steel surface due to chloride ions content of the tested biological solutions.

3.4. Cyclic voltammetry
A good way to analyze corrosion susceptibility for titanium and its alloys is the cyclic voltammetry. The cyclic voltammograms of analyzed samples were recorded from -1.0 V to 3.5 V vs. Ag/AgCl, with a scan rate of 1 mV/s. The corresponding diagrams are shown in Figure 4, having logarithmic
scale for current density, $i_{\text{cor}}$.

As it can be seen from Figure 4 the cyclic polarization diagrams of 304L stainless steel immersed in the two Hank solution doped with albumin are similar but different comparing with the cyclic polarization diagrams of 304L stainless steel immersed in un-doped Hank solution.

![Figure 3](image1.png)

**Figure 3.** The Potentiodynamic polarization diagrams for: (1) Ti-6Al-4V alloy immersed in Hank solution, (2) Hank solution doped with 8 g/L albumin, (3) Hank solution doped with 4 g/L albumin.

![Figure 4](image2.png)

**Figure 4.** The Cyclic voltammetry diagrams for: (1) Ti-6Al-4V alloy immersed in Hank solution, (2) Hank solution doped with 8 g/L albumin, (3) Hank solution doped with 4 g/L albumin.

The breakdown potentials of passive films showed on cyclic polarization diagrams are close for the two Hank solutions doped with albumin and different for un-doped Hank solution, as it can be seen on Figure 4 on returned way of cyclic polarizations diagrams. For Hank solution doped with 8 g / L albumin, the breakdown potential is around the value of 2.11 V vs. Ag/AgCl, whereas for Hank solution doped with 4 g / L, the breakdown potential is around 2.20 V vs. Ag/AgCl. For un-doped Hank solution, the breakdown potential is around the value of 1.69 V vs. Ag/AgCl.
The passivation of metals and alloys and the breakdown of passivity resulting in localized corrosion such as pitting have been the focus of much of the research in the area of corrosion over the past decades [6]. There has been general agreement that the pitting process progresses from pit initiation by passive film breakdown to early stages of pit growth identical to metastable pitting to stable pit growth [6]. The critical factors controlling localized corrosion susceptibility have been debated in the published works but there is still little agreement among the leaders in the field [6]. Some researchers consider that the structure of the passive film is associated with the initial breakdown of the film, whereas others consider that the susceptibility to pitting is controlled by the pit growth kinetics and the stabilization of pit growth [6].

The cyclic polarization diagrams from Figure 4 show the different susceptibility to localized corrosion of 304L stainless steel immersed in Hank solution and Hank solution doped with albumin and must be much deeply further investigated.

![Cyclic polarization diagrams](image)

**Figure 5.** Optical micrographs of Ti-6Al-4V after immersion in tested biological solutions: (a) Ti-6Al-4V alloy immersed in Hank solution; (b) Ti-6Al-4V alloy immersed Hank solution doped with 4 g/L Albumin; (c) Ti-6Al-4V alloy samples immersed in Hank solution doped with 8 g/L Albumin.

3.5. Optical microscopy

The optical micrographs were taken on each surface of 304L stainless steel after corrosion tests. The optical micrographs are showed in Figure 5.

From Figure 5 (a) it can be observed that the Ti-6Al-4V alloy after immersion in Hank solution has a uniform surface with no corrosion defects. After corrosion test in Hank solution doped with 4 g/L Albumin, Figure 5(b), it can be seen some localized corrosion or pitting with small diameters.

The Ti-6Al-4V alloy samples immersed in Hank solution doped with 8 g/L Albumin presents more
localized corrosion having severe pitting damage, Figure 5(c), in comparison with the samples immersed in Hank solution dopes with 4 g/L Albumin, as it can be seen in Figure 5(b).

The pitting damage covers a high surface of the Ti-6Al-4V alloy samples and the pits are deeper into the substrate after immersion in Hank solution doped with 8 g/L Albumin.

The optical micrographs confirm the results observed on cyclic polarization diagrams with breakdown potentials of passive films due to localized corrosion ongoing on 304L stainless steel surface immersed in biological solution with high chloride ions content.

4. Conclusions
This paper presents the corrosion behavior of Ti-6Al-4V alloy medical grade, to be used in biomedical applications, in Hank solution doped with 4 g/L albumin and Hank solution doped with 8 g/L albumin.

The interpretation of open circuit potential results reveals that Hank solution doped with 4 g/L albumin allow to achieve a more ennobled steady state potential of titanium alloy comparatively with Hank solution doped with 8 g/L albumin.

The potentiodynamic polarization measurements reveal that a nobler electrochemical characteristic is achieved for Ti-6Al-4V alloy immersed in Hank solution doped with 4 g/L albumin as compared with Hank solution doped with 8 g/L.

The optical micrographs performed after corrosion tests confirm the results obtained from electrochemical measurements by showing more localized corrosion on Ti-6Al-4V alloy surface immersed in Hank solution doped with 8 g/L albumin.

The research work concludes that all the results from electrochemical methods and optical microscopy are in good agreements.

5. References
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