Tribological and Electrochemical Characterization of a Titanium Alloy in a Physiological Solution.

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Abstract - Titanium alloys are used primarily for biomedical and/or dental applications. They are characterized by a better mechanical compatibility with the tissues and a good biocompatibility in the body fluids. The alloy TA6V4 used in orthodontics is subject to degradation by wear and corrosion. In this context, we are primarily interested in the study of the dry friction wear of the TA6V4 / Al2O3 torque by means of a rotating Ball / Disc tribometer. In order to evaluate the biocompatibility of this alloy, an electrochemical study in a physiological solution was carried out using conventional electrochemical measurement methods (time-dependent monitoring of the corrosion potential, potentiodynamic curve) as well as Electrochemical impedance spectroscopy. The results of tribology, the friction of the torque TA6V4 / Al2O3 against each other, revealed a friction coefficient of 0.2 and a wear volume of the order of 22.579.10⁻¹² mm³/N.mm. The wear mechanism studied by scanning electron microscopy revealed abrasive and adhesive degradation. From the electrochemical point of view, the TA6V4 alloy in Hank’s solution exhibited good corrosion resistance with a polarization resistance of 44 540 Ω. Analysis by electrochemical impedance spectroscopy indicated that this alloy is passive in nature, following the formation of a surface-stable two-phase oxide layer composed of an internal compact layer which has good corrosion resistance and an external porous layer which is favorable to osteointegration.

Key words - Alloy TA6V4, corrosion behavior, Friction.

1. Introduction

Titanium and its alloys are considered among the most promising engineering materials in a range of application sectors and are the best candidates for use in biomedical applications such as dental implants and orthopedic surgery because of a unique combination of their attractive properties such as: good mechanical strength, modulus of elasticity close to that of bone, adequate biocompatibility, and high resistance to corrosion in body fluids compared to other metal biomaterials [1]. The good corrosion resistance and the biocompatibility of the titanium alloys is associated with the formation of an extremely thin and adherent titanium oxide film on the protective surface. The presence of this oxide film which forms
spontaneously in the passivation or repassivation process is a major criterion for the excellent biocompatibility and corrosion resistance of titanium and its alloys [2]. However, titanium and these alloys have a relatively low wear resistance [3]. Nevertheless, biomaterials present in the human body are frequently exposed to simultaneously mechanical and chemical / electrochemical stresses which can cause alteration of the biocompatibility of alloys used as biomaterials in the biological environment because the body fluid is very aggressive due to the presence of chloride ions and proteins [4,3]. The aim of this work is to study the dry friction wear of the TA6V4 / Al2O3 couple and to evaluate the electrochemical behavior of the TA6V4 alloy in Hank’s solution.

2. EXPERIMENTAL TECHNIQUES

The chemical composition obtained by the EDS analysis of the titanium alloy TA6V4 used in this study is given in Table I. For a study of the friction and wear behavior, we used a CSM Instrument type ball / Pion-disc against an alumina ball with a load of 4 N and a speed of 1 cm/s over a distance of 20 m. The wear equation proposed by Archard [5] was used as a basis for calculating the wear rate using the following equation:

\[ \text{Wear Rate} = \frac{V}{W L} \]

Where V is the wear volume, W is the applied load, and L is the displacement distance. For the electrochemical study, open-circuit equilibrium potential measurement, potentiodynamic polarization curve, and impedance spectroscopy analysis are performed to study the corrosion susceptibility and stability of this alloy in Hank’s solution. All electrochemical measurements were carried out using a Potentiostat / Galvanostat Biologic SP300. A three-electrode cell was used: a saturated calomel reference electrode, a platinum wire counter electrode and the sample to be studied as working electrode. The potentiodynamic polarization tests were carried out from -500 to +1000 mV Vs / SCE with a scanning speed of 1 mV / s. The EIS measurements were produced with a sinusoidal disturbance of 10 mV in a frequency range of 100 kHz to 10 mhz.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Weight</th>
</tr>
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<tbody>
<tr>
<td>Ti</td>
<td>88.4</td>
</tr>
<tr>
<td>Al</td>
<td>8.19</td>
</tr>
<tr>
<td>V</td>
<td>3.41</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 Tribological Behavior

The evolution of the coefficient of friction (COF) as a function of the distance for the torque TA6V4 / Al2O3 is presented in figure 1. The COF curve for this alloy shows a general shape characterized by two friction steps: a start-up step with a rapid increase in the coefficient induced by the lapping of the surface asperities and the introduction of the particles into the contact region until it reaches a maximum value and then a stabilization step. The friction of this alloy against the alumina ball revealed a coefficient of friction of 0.2 and a wear rate of \( 0.28 \times 10^{-3} \text{mm}^3 / \text{N.mm} \).
3.2 ELECTROCHEMISTRY

3.2.1 Open circuit potential:

Figure 3 shows the evolution of the open-circuit potential (OCP) as a function of the immersion time of the alloy TA6V4 in Hank’s solution. An increase in OCP over time is observed, indicating spontaneous passive behavior due to the growth of a surface passive layer and high corrosion resistance [1]. The value of the potential at the end of 2H is given in Table 2.

3.2.2 Potentiometric polarization (Tafel)

Figure 4 shows the potentiodynamic polarization curve of the alloy TA6V4 in Hank’s solution. According to the curve, it is observed that the alloy TA6V4 has a narrow passivation zone characteristic of passive behavior, and then the corrosion current density (Icorr) increases suggesting a rupture of this film with potential (Erp = -0.295 V), this film then regenerates at a reproducibility potential (Erep = -0.120 V). This value indicates that the TA6V4 alloy has a high resistance to pitting corrosion in Hank’s solution [6].

The various corrosion parameters (Corrosion Potential (Eoc), Corrosion Current Density...
Icorr (µA/cm²), corrosion rate Vcorr (mmpy), resistance of polarization (Rp), obtained are summarized in Table 2.

Table 2: Corrosion parameters of the alloy TA6V4.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Parameters</th>
<th>E_OCP (V)</th>
<th>E_corr (V)</th>
<th>I_corr (µA/cm²)</th>
<th>V_corr (mmpy)</th>
<th>R_p (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA6V4</td>
<td></td>
<td>-0.443</td>
<td>-0.494</td>
<td>0.309</td>
<td>2.62 x 10^-2</td>
<td>44540</td>
</tr>
</tbody>
</table>

3.2.3 Impedance

The electrochemical impedance (SIE) technique was used to study the corrosion resistance of the TA6V4 alloy in Hank's solution after 24 hours of immersion. Figure 5 shows the impedance spectrum of the alloy TA6V4 presented in the Nyquist plane (FIG. 5a) and Bode (FIG. 5b).

The appearance of the impedance spectrum obtained shows two capacitive loops and two time constants which are separated in the frequency domain shown in the Bode presentation of the phase angle (Fig. 5b) suggesting that the corrosion interface of this alloy can also be characterized by a capacitive behavior at the metal / electrolyte interface. The oxide layer formed on the surface of these alloys consists of two layers: an inner barrier layer and a porous outer layer [2].

The electrochemical behavior of this alloy is illustrated by the equivalent circuit (Fig. 6), widely used for titanium and its alloys, and which is interpreted in terms of two time constants. The equivalent circuit used in this study is based on a model used by Pan et al. [7]. Accordingly, in the equivalent circuit shown in Fig. 6, R1 is the solution resistance, R3-CPE3 and R2-CPE2 are the resistance and the elementary phase constant of the inner and outer films respectively. The fit results are summarized in Table 3.
Fig. 6: Equivalent circuit used for the simulation of the impedance data of the alloy TA6V4.

Table 3: Smoothing parameters of the alloy TA6V4-24H.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$R_1$ ($\Omega \text{ cm}^2$)</th>
<th>$Q_1$ ($\mu F \text{ cm}^2$)</th>
<th>$R_2$ ($\Omega \text{ cm}^2$)</th>
<th>$Q_2$ ($\mu F \text{ cm}^2$)</th>
<th>$R_3$ ($\Omega \text{ cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA6V4</td>
<td>53.02</td>
<td>6.556$\times10^{-6}$</td>
<td>979 773</td>
<td>7.291$\times10^{-6}$</td>
<td>2.112$\times10^{-6}$</td>
</tr>
</tbody>
</table>

According to the values of the resistors shown in Table 3, a very high charge transfer resistance value (R3) is observed with respect to (R2), which implies that the passive inner film is compact and therefore has a resistance to corrosion.

4. CONCLUSION

In this work we studied the dry friction wear of the TA6V4 / Al2O3 couple and the biocompatibility of this alloy by evaluating its tribological and electrochemical behavior in physiological solution. The conclusions are as follows:

1. The mechanisms of abrasive and adhesive wear are clearly observed for the alloy TA6V4.

2. The alloy TA6V4 has a high resistance to corrosion.

3. The impedance diagram plotted in the plane of Nyquist and Bode shows that the oxide film formed on the surface of the titanium alloys studied is composed of an internal compact layer which has good resistance to corrosion and an external porous layer which is favorable to osteointegration.

REFERENCES


alloy by the addition of element Ag, Acta Biomater 7 (2011) 2758-2767