Electrochemical Studies on the Stability and Corrosion Resistance of Ti-6Al-4V Alloy for Biomedical Applications

Jelliti Sami¹, Richard Caroline¹, Retraint Delphine², Demangel Clémence³, Landoulsi Jassem⁴

¹) Roberual laboratory, UMR 6253 CNRS, University of Technology of Compiègne, 60200 Compiègne, France
²) Charles Delaunay Institute, LASMIS, UMR STMR CNRS 6279, University of Technology of Troyes, 10100 Troyes, France
³) CRITT-MDTS, 08900 Charleville-Mézières, France
⁴) Surface Reactivity Laboratory, CNRS UMR 7197, University Pierre & Marie Curie, Site of Ivry-Le Raphael, 94200 Ivry-sur-Seine, France
⁵) Laboratory of Mechanics & Rheology EA2640, University of Tours François Rabelais, 37000 Tours, France

Titanium and titanium-based alloys are widely used in various biomedical applications. This is due to the stability and corrosion resistance exhibited by titanium, which in turn is related to the spontaneous formation of a passive oxide film, typically with a thickness of a few nanometers, which protects the metal from further oxidation. By means of Surface Mechanical Attrition Treatment (SMAT), a nanostructured surface layer was formed on a Ti-6Al-4V alloy. Microstructural features of various sections in the surface layer, from the strain-free matrix to the treated top surface, were systematically investigated by using Optical microscope (OM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) observations. Corrosion resistance of Ti-6Al-4V in a Ringer’s solution was studied by potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) measurements. Overall results of all studies identified beneficial impacts of SMAT on corrosion behaviour of Ti6Al4V.

The surface oxide film formed on Ti-6Al-4V and its stability in biological environments play a decisive role for the biocompatibility of implants. In this study, passive oxide films formed on Ti6Al4V surfaces and their natural growth in a Ringer’s solution have been investigated by Scanning Electron Microscopy (SEM), microhardness and X-ray Photoelectron Spectroscopy (XPS).

Keywords: Corrosion, Ti-6Al-4V, microstructure, oxide films, Ringer’s solution

1. Introduction

Today, titanium alloys are one of the most important metallic materials used in orthopaedics and dental surgery. Despite their high corrosion resistance in the physiological environments and their high specific strength, the finding at revision surgery of damage at the metal surface and consequent periprosthetic metallosis indicates that failures of the implant occur in vivo.

Indeed, the degradation of metallic biomaterials in vivo mainly due to combined wear and corrosion processes results in the formation of particulate and ionic metallic debris, which are recognized as major factors limiting the lifespan of joint replacements.

Generally, the passive films formed on titanium and its alloys consists mainly of amorphous titanium dioxide. The physico-chemical and electrochemical properties of the oxide film as well as its long-term stability in biological environments play a major role in the biocompatibility of titanium implants.

Most material failures occur on the surfaces including a stress fracture, wear and corrosion. Accordingly, controlling the surface properties can effectively improve the overall behavior of the material. To this purpose, one promising way consists of generating a nanostructured layer on the titanium surface, in view of improving the performance of the material. This type of surface modification, called surface nanocrystallization (SNC), will be able to improve the surface properties without changing the chemical composition.

Since 1999, the LASMIS, University of Technology of Troyes in conjunction with the Institute of Metal Research, Shenyang (China-AMT), under the influence of the work of J. Lu and K. Lu made the nanocrystallization Superficial (NCS) a major priority. From there, three French-Chinese patents have been filed to the method of manufacture of nanocrystalline structures by Surface Mechanical Attrition Treatment (SMAT) a process similar to ultrasonic peening.

In this study, the Ti6Al4V alloy is treated by SMAT to form a nanostructured layer on the surface. Electrochemical tests were carried out in Ringer’s solution to investigate the corrosion behavior of the material. In addition to surface observations, X-ray Photoelectron Spectroscopy (XPS) analyses were performed on titanium prior to and after SMAT treatment.

2. Effect of SMAT on the Microstructure of Ti6Al4V Alloy

2.1 SMAT

This technique is based on the vibration and movement into granules by means of an ultrasonic power generator. The pellets are placed in a chamber which is vibrated by the use of an ultrasonic generator. Because of the high frequency system (20 kHz), the entire surface of the sample to be treated is peened with a large number of impacts on a very short period of time.

Figure 1 shows a schematic illustration of the surface mechanical attrition treatment. The main control parameters of the process are the processing time, the
ball diameter, the number of balls, the amplitude of vibration and temperature.

Figure 1. Schematic illustration of SMAT

Figure 2 is a photograph of the equipment having two types of ultrasonic concentrators, also called sonotrode, which produce different amplitudes of vibration of the surface.

Figure 2. Photograph of the ultrasonic system

The diameter of the beads commonly used for this type of process is 0.4-8 mm, which is much higher than those used for the treatment of conventional shot peening.

The method that has been used to generate a nanostructure surface is similar to a system for ultrasonic peening. It involves projecting perfectly spherical balls towards the workpiece by means of exciting a system by ultrasonic waves.

This is a vibrating piezoelectric generator with a sonotrode 20kHz via a transmitter and a booster. The workpiece and the balls are placed in a chamber bounded by the horn and a fairing. In contact with the sonotrode, the balls are thrown randomly in the chamber during processing. And they come and impact the workpieces.

2.2 Microscopic Observations

The material tested in this study is:
- A titanium alloy Ti6Al4V, the chemical composition of the Ti6Al4V alloy is given in the following Table 1:

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>5.5</td>
<td>5.5</td>
<td>0.3</td>
<td>0.08</td>
<td>0.2</td>
<td>0.05</td>
<td>0.015</td>
</tr>
</tbody>
</table>

The initial microstructure of Ti6Al4V can be seen in Figure 3:

Figure 3. SEM micrograph of Ti6Al4V

We can clearly distinguish:
- the primary α phase occurs as nodular, the average diameter of the nodules is of the order of 10µm.
- Secondary α phase has a lamellar structure.
- The phase β grains which are difficult to identify. Only electron microscopy backscattered electrons could lead to a correct view of this phase.

Figure 4. SEM micrograph of Ti6Al4V (SMAT 15 min)

To confirm the presence of a nanostructure, TEM observations of the outermost surface were performed. Since the deformations are diminishing with depth and go through a maximum in extreme surface, the evolution of the microstructure obtained for different depths can give us the key mechanisms by which the grains are refined.

From the microstructural features observed at different depths and therefore different levels of deformation, we can conclude about the formation of twins in
the form of microstrips and distortion during the progress in processing time.

Figure 5. Microstructure observed by SEM in the sub layer of Ti6Al4V (SMAT 30min)

Figure 6. Twins observed in bright field at about 30µm deep by relative to the surface Ti6Al4V treated by SMAT

3. Electrochemical Tests

Electrochemical experiments were performed in a cylindrical cell, equipped with a conventional three-electrode electrochemical cell, the sample as working electrode, platinum as auxiliary electrode and a calomel saturated reference electrode (SCE). They are equipped with a double jacket for regulating the temperature via a thermostatic bath. The tests were normally repeated twice, checking that they presented reproducibility.

3.1 Open Circuit Potential

The optimized procedure used for SMAT treatments of the Ti6Al4V alloy are the following:

- **SMAT1**: Amplitude= ±100% Time= 15 min.
  - Diameter of beads= 2 mm.
- **SMAT2**: Amplitude= ±100% Time= 30 min.
  - Diameter of beads= 3 mm.

The evolution of the open circuit potential (OCP) of titanium obtained in Ringer’s solution (pH 7.2, at 37°C) as a function of time is presented in Figure 7. The chemical composition of the Ringer’s solution is: NaCl 8.6 g/L, CaCl2 0.322 g/L and KCl 0.3 g/L. The potential is approximately -0.55 V for the untreated Ti6Al4V. During the first hours of immersion, we notice a sudden displacement of OCP towards positive potentials. This initial rise seems to be related to the formation of an oxide film on the metal surface. This layer may improve the stability of the material during the immersion. Moreover, the variation of corrosion potential with immersion time in Ringer’s solution was almost similar for three samples.

Figure 7. Evolution of the open circuit potential (OCP) of Ti6Al4V immersed in Ringer’s solution

We can first see that both treated samples exhibit a passivation layer, which is much more effective than the untreated sample. Indeed, their potential is more important, it stabilizes at values close to -0.19 V/SCE. This value is almost the same for both samples (SMAT1 and SMAT2), so we have a significant influence of the SMAT process on evolution of the free potential of titanium alloy Ti6Al4V.

3.2 Polarizations Curves

Polarization curves were performed using a potentiostat type GAMRY after immersion in Ringer’s solution (pH 7.2, at 37°C).

For the Ti6Al4V alloy, the curves (SMAT1 and SMAT2) are offset relative to the crude and there is a variation of corrosion potential.

Values of corrosion current density corroison (Icorr), corrosion potential (Ecorr) for the three samples Ti6Al4V are shown in Table 2.
According to the results in Table 2 we can conclude that:

- The corrosion current densities ($I_{corr}$) decrease after SMAT.
- The values of $E_{corr}$ increase after SMAT.
- Studies by polarization curves also confirm previous results using the potential free tests. These results are explained by the formation of a passive layer, stable and insoluble in the corrosive medium on the surface of the titanium alloy that protects the substrate against corrosion.

In conclusion, the SMAT has an effect on the titanium alloy Ti6Al4V, and it remains to confirm these results with observations on the sample surface to see the evolution of the passive film.

### 3.3 Electrode Impedance Spectroscopy Tests

The tests have been conducted at free corrosion potential by applying a sinusoidal potential signal of ±5mV superimposed to the open circuit potential value. The electrode response was analyzed in the range 0.001-10000 Hz by means of a frequency response analyzer.

Both the experiments and the data acquisition were computer controlled using appropriate software. This technique was utilized substantially to provide an alternative way of determining $R_p$.

The impedance diagrams obtained for all the samples of Ti6Al4V are shown in figure below.

These diagrams are represented by portions of loops more or less resolved. This type of diagrams is usually interpreted as a mechanism of charge transfer on an inhomogeneous surface. The same behavior is observed for other samples treated by SMAT.

When SMAT treatment is applied, we note that increasing the size of the capacitive loop, which can be attributed to charge transfer process, is well marked and that the value of the impedance obtained in the case of witness is lower than those obtained for samples treated by SMAT.

This result reflects the influence of SMAT treatment on the process at the interface metal/layer/solution.

### 4. Surface Hardness

Microhardness tests have been performed prior to and after SMAT treatment to gain information regarding the effect of SMAT on the mechanical properties of the surface.

Figure 10 shows the surface hardness as a function of loading for treatment SMAT (condition 1 and 2). By comparing the obtained results, we can see that samples treated by SMAT with condition 1 and 2 have a maximum hardness in comparison with the untreated sample (without SMAT).
Indeed, for the treated samples (SMAT1 and 2) it has a maximum hardness of 370 Hv, while for the untreated sample, the hardness measured is about 260 Hv. These results can be explained by the fact that after the SMAT, a nanostructured layer is formed on the surface of the treated samples.

These results are in good agreement with results obtained in the literature.

5. Chemical Analysis of Surfaces by XPS

The XPS characterization was performed on three samples of titanium alloy (Untreated, SMAT1 and SMAT2). Analyses were performed on samples after immersion in Ringer’s solution at 37°C for one week. These samples are removed from the corrosive medium, rinsed with distilled water and ethanol then dried under nitrogen gas flow.

The composition of titanium surfaces with and without SMAT treatments may be determined on the basis of survey spectra (Figures 12-14).

Typical XPS survey spectra evidenced the presence of Ti, C, O, N, Al, V and Na elements, independently of the sample treatments. High resolution XPS pics are not available in the present study. It is reasonable to consider that oxygen is mainly involved to titanium oxide. However, it must be kept in mind that a small amount of oxygen is due to organic species, originating from adventitious contamination. This is systematically observed on oxidized surfaces, owing to their high surface energy.

By considering that oxygen is mainly involved in titanium oxide, and based on the molar concentrations of O and Ti elements, it is possible to give an average stoichiometry values regarding the passive oxide layer.

Data given in Table 3 show a noticeable enrichment of oxygen on treated samples, indicating that SMAT treatments enhance the formation of the passive oxide layer, as expected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Untreated</th>
<th>SMAT1</th>
<th>SMAT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (%)</td>
<td>8.21</td>
<td>41.4</td>
<td>22.15</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>16.56</td>
<td>12.23</td>
<td>34.09</td>
</tr>
</tbody>
</table>

In conclusion, XPS analysis has highlighted the
presence of various oxides after immersion in Ringer's solution of the titanium alloy Ti6Al4V for one week.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>TiO₂ and pure Ti</td>
</tr>
<tr>
<td>SMAT1</td>
<td>TiO₂</td>
</tr>
<tr>
<td>SMAT2</td>
<td>TiO₂, Ti₃O₅ and pure Ti</td>
</tr>
</tbody>
</table>

6. Conclusions

The objective of this work is to improve the chemical properties (corrosion resistance) and surface properties of the alloy Ti6Al4V by the SMAT process. Initially, microscopic observations have shown the existence of a nanocrystalline layer on the surface of the treated samples.

Then, an electrochemical study has highlighted the effect SMAT on the corrosion behavior of titanium alloy, where it was observed the stability in the passive film with a net increase of free potential of samples treated with SMAT.

Surface treatments, such as SMAT, bring about an increase of passive and corrosion values as a consequence of the increase of the surface exposed to the aggressive environment.

Further study will be performed using a duplex treatment SMAT-Nitriding to determine the impact of this treatment on the corrosion resistance and wear resistance of Ti6Al4V alloy.

REFERENCES