

Increasing of the corrosion resistance of the Ti6Al4V alloy by high thickness anodic oxidation

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Oxide films with different thicknesses and electrochemical properties can be anodically formed on titanium and titanium alloys. In this work the resistance, and particularly, the passivity currents of a Ti6Al4V alloy anodized under different conditions were evaluated. The tests were performed in a physiological solution simulating the environment of the human body. A significant reduction in the passivity current and an increase of the range of passive potentials have been observed on anodized specimens. Consequently the anodic oxidation of the Ti6Al4V alloy to obtain an high thickness oxide film can be considered an important improvement in the finishing of prosthetic devices.

1. Introduction

Titanium alloys, in particular Ti6Al4V, are largely used as biomaterials for orthopaedic applications because of the following characteristics [1, 2]: high resistance to generalized and localized corrosion; good mechanical properties, in particular fatigue resistance; good compatibility with human tissue.

Nevertheless these alloys have certain limitations. In particular, the release of some metallic ions of the alloy (aluminium and vanadium), although in small amounts, even if they may form stable oxides [3], may cause local irritation of the tissues surrounding the implant or, in long-term implantations (up to 20 years) the patient may become sensitized to the metallic ions released by the implant [4]. Moreover, in articular prostheses (hip and knee joints) tribologic phenomena may take place, causing increase in fretting corrosion of the titanium alloy, and weight loss of the polymeric components (ultra high molecular weight polyethylene); this weight loss is more prone to occur with the titanium alloy than with other materials currently used in orthopaedic applications (cobalt alloys, stainless steels, alumina) [5–7].

Considerable attention has been paid on the surface treatment and finishing (ion implantation, PVD nitriding, special lappings) of the alloy [8–11] to reduce these adverse phenomena. These techniques have been developed specially to increase the tribological behaviour of the prosthetic couplings and are utilized for the finishing of femoral heads.

High thickness electrochemical oxidations of titanium and titanium alloys have been also proposed, but a complete characterization of the corrosion resistance of these films in physiological environments has not been yet performed. This is partly due to the difficulty of evaluating accurately the very low corrosion rates that titanium and titanium alloys assume in

the human body in stationary conditions (lower than 1 nA cm^2). In the present work, the potentiodynamic curves and measurements of the passivity currents of a Ti6Al4V alloy, electrochemically oxidized in different conditions, has been examined. Special attention has been paid to the setting up of an experimental apparatus able to evaluate the corrosion rates under passivity conditions.

2. Anodic oxidation in H_3PO_4

It is well known that the thickness of the oxide film produced on titanium and titanium alloys, when anodized in H_3PO_4 baths, can be varied from a few ångströms to a few thousand ångströms depending on anodizing conditions and, in particular, on the final anodic potential and anodic current [12, 13]. Initially the film is a matrix of amorphous oxides and is very porous. This matrix can transform, for thicknesses greater than 80 nm, to microcrystals with the characteristics of anatase (density 3.84 g cm^{-3}). Still increasing the thickness, the brookite (density 4.17 g cm^{-3}) and finally the rutile (density 3.84 g cm^{-3}) can be formed [14]. Also the insulating properties of the oxide increase with the thickness of the film [15].

The electrochemically obtained titanium oxide films are characterized by peculiar optical properties. They are perfectly transparent but acquire particular colours due to interference effects resulting from the multiple reflection of light between the external and internal surfaces of the film. This phenomenon is well known [16].

The colour obtained depends on the film thickness. Since the film thickness depends on the potential applied at the end of the anodization process, it has been possible, by ellipsometric measurements, to obtain chromatic scales which relate the potential applied to the oxide thickness and to the colour [14, 17].

In this work two different series of specimens with oxides of varying characteristics and thicknesses were prepared with various types of oxidation. More precisely the first of these was realized by anodization in a H_3PO_4 solution (30 g l^{-1}) at low current density, and the second one in the same solution but with high current density.

For reference purposes, the oxide films for some specimens were also obtained by standard oxidation in air.

The specimens were anodized with the following procedures: (1) degreasing of the specimens in acetone; (2) pickling in HNO_3 , 400 g l^{-1} + HF , 40 g l^{-1} ; (3) anodizing in H_3PO_4 at 25°C with a current density respectively of 0.3 A dm^{-2} or 3 A dm^{-2} until the chosen final potential was reached;

Four final potentials were chosen (12, 20, 60, 100 V) to which correspond different colours and thicknesses of the oxide: yellow (20 nm), blue (80 nm), pink (140 nm), green (210 nm).

Some analyses carried out by Auger spectroscopy have shown that the oxide film developed into H_3PO_4 baths contains a small percentage of phosphorus in addition to alloy elements and oxygen [18].

3. Anodic oxidation in NaOH

High thickness anodic films can also be obtained on titanium and titanium alloys following NaOH treatment. In these baths the original oxide film was replaced by a compact, uniform, mouse-coloured, velvet-like layer, about 400 nm thick. This layer was completely different, even in its electrochemical and electrical properties (especially conductivity), from films formed by using the traditional method of anodization of Ti6Al4V in H_3PO_4 baths [19]. The glow discharge which occurred simultaneously with the oxidation process significantly increased the temperature of the sample surface from the initial temperature of 30°C . It was verified that during film formation this temperature reaches some hundreds of degrees centigrade. X-ray powder patterns showed the films to be made of titanium dioxide and to have the structure of rutile [20]. The films obtained in NaOH baths were particularly characterized by anti-galling properties.

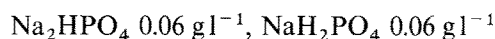
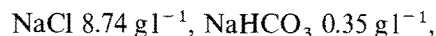
For this work, Ti6Al4V specimens were anodized in a concentrated alkaline bath ($\text{NaOH } 800 \text{ g l}^{-1}$) at a voltage (35 V) sufficiently high that a glow discharge was produced on the electrode surface [21]. The anodic current densities ranged from 2.5 to 4 A cm^{-2} and the treatment time ranged from 10 to 20 s (a longer treatment time did not change the characteristics of the film).

4. Corrosion tests

To characterize the corrosion properties of the specimens, traditional potentiodynamic tests and long time passivity current measurements were performed.

All the tests were at a temperature of 38°C in a buffered physiological solution [16] with the follow-

ing composition:



The test solution (already used in previous work [22]) has a pH of 7.8.

4.1. Potentiodynamic tests

Potentiodynamic tests were performed to evaluate the general corrosion behaviour of the various oxide films formed by using the described methods.

Round specimens (15 mm diameter) were used; the total surface area exposed to the testing solution was 0.78 cm^2 . All the specimens were ground with Emery paper up to 4000 mesh; the reference specimens were also polished with diamond pastes up to $1 \mu\text{m}$ and oxidized in air for 24 h; the electrochemically oxidized specimens were anodized without any further mechanical polishing.

The tests were performed in a electrochemical cell according to the ASTM G5-82 Standard Practice. The following testing instrumentation was used: potentiostat AMEL Mod.551/SU, interface Mod.560, electrometer Mod.631, X-Y recorder HP 7040A. The sensitivity of the testing apparatus was evaluated on 10 nA cm^{-2} . The testing solution was degassed with N_2 for 24 h, and the cell was filled under N_2 head. After 1 h of free corrosion, anodic polarization starting from the free corrosion potential was imposed with a constant rate of 10 mV min^{-1} for an extension of about 4 V, and the circulating current was measured. All the potentials were referred to the standard calomel electrode (SCE).

4.2. Potentiostatic tests

For a better evaluation of the corrosion characteristics of the different oxide films under conditions similar to those in the human body, some potentiostatic tests were specifically set up to measure the passivity currents at a potential that titanium alloys usually show in this environment.

For this purpose $5 \times 15 \text{ cm}^2$ strips, 1 mm thick (exposed surface of about 150 cm^2) were used. The specimens were ground with Emery paper up to 4000 mesh and either oxidized in air or anodized by using one of the previous mentioned electrochemical methods. The specimens were inserted in a 5 l cell, filled with deaerated physiological solution. During the tests the solution was continuously deaerated by bubbling of N_2 . The strips were positioned on a PTFE support; a titanium wire, covered with a PTFE insulating coating, was spot welded to every specimen to obtain an electrical connection with the testing instrumentation.

The potentiostatic tests were simultaneously performed on 11 specimens, connected in parallel to the working channel of the potentiostat (AMEL Mod.552). To obtain an uniform distribution of the current, the counter electrode was placed in the centre of the cell so that the specimens were symmetrically positioned.

The specimen were anodically polarized at a potential of + 500 mV (against the SCE), which corresponds to a potential slightly higher than the one assumed in the human body by the titanium alloys [17]. To measure each circulating current, a 100 k Ω resistance was connected in series to every specimen, and the potential drop between the ends of each resistance was measured by a Data Logger ORION 3530. The sensitivity of the testing apparatus was evaluated on 0.1 nA cm⁻². The current density values were acquired every 0.2 h from 0 to 4 h, every 2 h from 4 to 100 h, every 10 h from 100 to 200 h, and every 20 h for the remaining test period.

Two tests were repeated for a testing time of 400 h, by using a single specimen directly connected to the potentiostat. The results showed good correspondence between the two testing methodologies, especially after the end of the initial transient period.

5. Results and discussion

The results of the potentiodynamic tests in physiological solution are reported in Figs 1–3. On Ti6Al4V specimens oxidized in air, the current density remained low up to a potential lower than 1 V (SCE); over this value the current density increased reaching a value of 100 $\mu\text{A cm}^{-2}$ at a potential of about 3 V (SCE).

As far as the specimen anodized in NaOH is concerned (Fig. 1), the behaviour was similar to that of the specimen oxidized in air.

The corrosion behaviour of the specimens anodized in H₃PO₄ exhibited a much improved performance. The current density remained very low up to potentials higher than 2 V (SCE) for the low thickness films and 3 V (SCE) for the high thickness films. A very small increase in the current density was observed at higher voltages, although no generalized or localized corrosion was observed on the specimens at the end of the tests.

In the comparison of the specimens anodized with low current density (Fig. 2) and high current density (Fig. 3), it was possible to observe slightly better behaviour of the specimens anodized with the high current density. For the specimens with higher thicknesses of

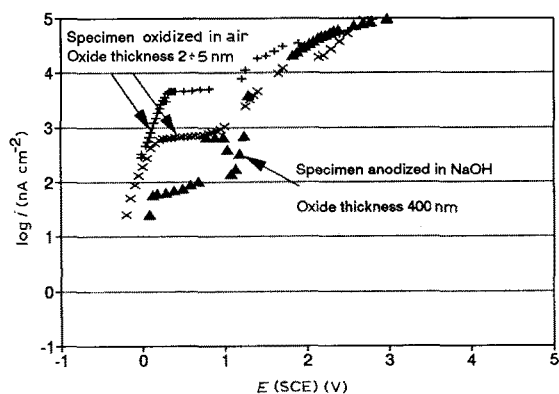


Figure 1 Potentiodynamic tests in physiological solution on Ti6Al4V specimens, oxidized in air and anodized in NaOH 800 g l⁻¹.

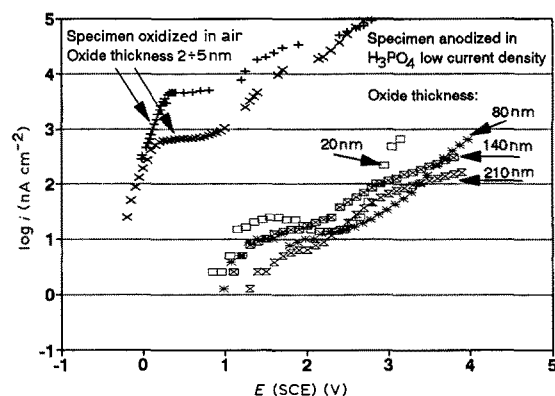


Figure 2 Potentiodynamic tests in physiological solution on Ti6Al4V specimens, oxidized in air and anodized in H₃PO₄ 100 g l⁻¹ low current density.

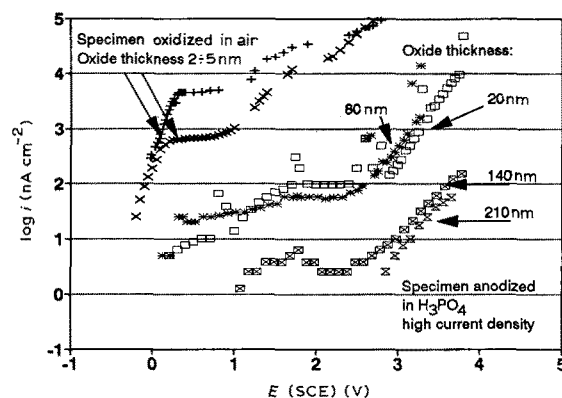


Figure 3 Potentiodynamic tests in physiological solution on Ti6Al4V specimens, oxidized in air and anodized in H₃PO₄ 100 g l⁻¹ high current density.

the oxide films, the range of potential with current density comparable to the minimum sensitivity of the experimental instrumentation was about 1 V higher for the specimens anodized at high current density than for those anodized at low current density.

From the potentiostatic tests in physiological solution at + 500 mV (SCE), it was possible to observe that the passivity current decreased progressively with time. A stationary value was asymptotically reached after a very long time, but after about 600 h the current density was approximately equal to the equilibrium value.

In Figs 4–6 the results of the potentiostatic tests are reported. They have been calculated by using the smoothing technique on five measurements for the specimens oxidated in air, on 10 measurements for the specimens with 20 nm and 80 nm oxide film thickness, and on 20 measurements for the specimens with higher film thickness.

The mean value and the standard deviation of the passivity current density measured in the range between 600 and 825 h was evaluated for each specimen; the results are reported in Fig. 7.

The passivity current density values of the specimens anodized in H₃PO₄ are remarkably lower than those oxidized in air and anodized in NaOH. The

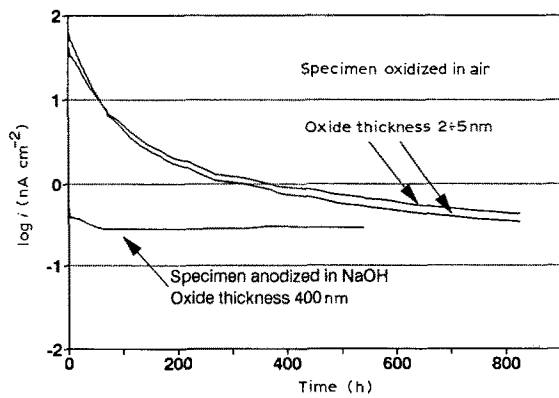


Figure 4 Potentiostatic tests in physiological solution on Ti6Al4V specimens, oxidized in air and anodized in NaOH 800 g l^{-1} .

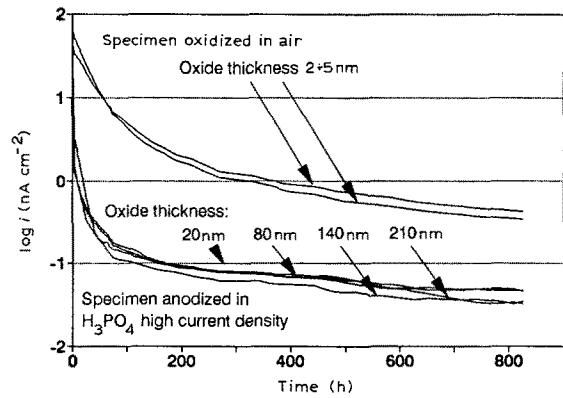


Figure 6 Potentiostatic tests in physiological solution on Ti6Al4V specimens, oxidized in air and anodized in H_3PO_4 100 g l^{-1} high current density.

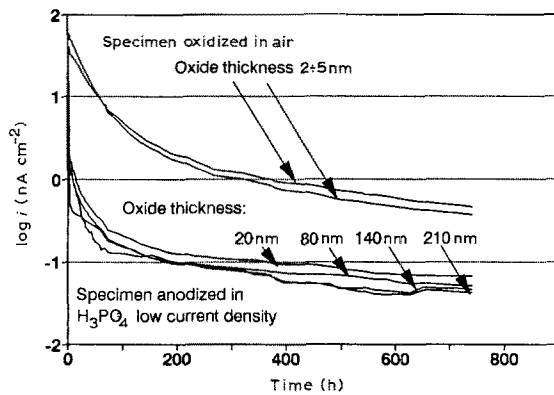


Figure 5 Potentiostatic tests in physiological solution on Ti6Al4V specimens, oxidized in air and anodized in H_3PO_4 100 g l^{-1} low current density.

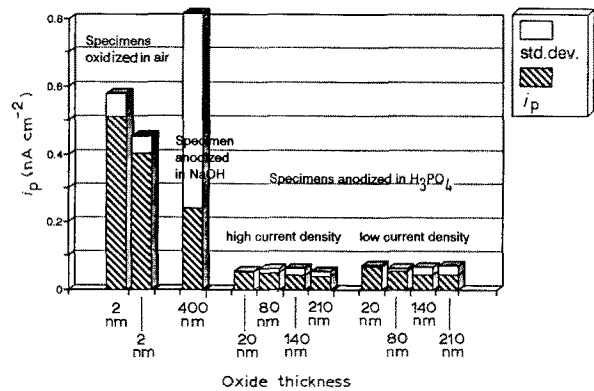


Figure 7 Average passivity currents (between 600 and 800 h) and standard deviations in physiological solution of Ti6Al4V specimens, oxidized and anodized in different conditions.

ratio is about respectively 1:10 and 1:5 in semi-stationary conditions, the ratio is much higher if the transitory period is taken into account.

The standard deviation for the case of NaOH anodization was much higher than the one for H_3PO_4 anodization; this was attributed to the higher porosity of such a film.

Smaller differences exist among the specimens with different thicknesses of the oxide films anodized in H_3PO_4 . In any case the passivity current density decreases with increasing thickness. On the contrary, the standard deviation, an index of a greater scattering of the results, increases.

No significant differences between the specimens anodized with low current density and with high current density have been observed.

It is important to assess whether the decrease in the passivity current determined by high thickness anodizations, is able to improve the biocompatibility of titanium alloys used for orthopaedic applications. In this regard it is possible to observe that increasing the oxide film thickness the electrical resistance increases. Consequently, we might suppose, according to Zitter and Plenk [3], a better behaviour of anodized titanium than the one spontaneously oxidized in air or by traditional passivity methods. In fact a practically insulating oxide can prevent the formation of galvanic

elements which may cause redox reactions of the metallic surface, even in the absence of corrosion.

6. Conclusions

The high thickness electrochemical anodization of titanium alloys in H_3PO_4 is noticeably interesting for the surface finishing of devices for application in the human body (in particular, hip and knee joints). With this technique it is possible to obtain a significant decrease in the release of metallic ions (titanium and above all aluminium and vanadium), decreasing the risks of local irritation or long-term sensitization due to diffusion of metallic ions in the surrounding tissues.

To evaluate qualitatively the improvement of tribological behaviour of titanium alloys in the presence of high thickness titanium oxides (both regarding the fretting corrosion of the metal, and regarding the wear of UHMWPE polymeric inserts for orthopaedic prostheses), tests on a hip joint simulator have been set up. *In vivo* tests have been scheduled to evaluate the reactions *in vivo* of the tissues in the presence of these oxides.

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