Corrosion resistance of Ti6Al4V alloy by Radio Frequency Technique used for Coating Deposition of multilayer (HA/TiN/Ti6Al4V-substrate) for Optimization power

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Abstract: The objective of this study is to perform physical / chemical characterization and to determine the corrosion resistance of calcium-phosphate (HA), TiN-based bio-ceramics and thin metal plating processed by a Ti-6Al-4V process. TiN and HA coating maximum power 150 watts. The presence of TiN200 Watt TiN coating resulted in electrochemical corrosion. High current cathodic and passive anodic polarization shows an active surface. EIS shows the active behavior assumed by the active cathodic currents imposed. And HA on the sample surface, some noise was observed during both polarization and EIS tests.

Key word: sputtering, HA, Corrosion, polarization, TiN, Electrochemical and power.

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1. Introduction

The choice of biocompatible materials depends on their biological compatibility and vital functions. The first characteristic refers to the effect of implantation on surrounding tissues and the second to its ability to tolerate the function of the biological system being replaced. In practice, both properties are closely interrelated and correlated with corrosion resistance. If implant rejection due to mechanical defects is relatively rare, most failures are due to lack of biological compatibility which is directly related to the corrosion resistance of the implant [1], [2]. From biocompatibility and from the perspective of biomechanics, thin coatings may represent advantages over thick PSHA coatings [3]. However, morphology, reduced dimensions and process-dependent configuration may lead to significantly different electro-chemical behavior during bone interaction in the physiological environment. The objective of this study was the physical / chemical characterization and determination of the corrosion resistance of a thin layer of biochemical ceramics based on calcium and P-varying on titanium alloys (Ti-6Al-4V) using electrochemical methods [4]. Excellent tissue compatibility, better corrosion resistance, and use of pure commercial titanium (CPTi) in transplantation processes, but materials were inhibited due to lack of strength and extremely weak corrosion resistance. Interest in the use of Ti-6Al-4V for prostheses [5]. It is evident from the literature that the α cpTi phase, vanadium is added to 4% by weight, which is enough to stabilize at
10% β phase volume at room temperature and also adds 6wt% of aluminum in cpTi. Although starting α+ β alloy Ti-6Al-4V [6].

2. Experimental work

Ti-6Al-4V alloy samples were used in plasma sputtering (3 x 10 x 10) mm using a diamond cutter (Struers, Denmark). Ti-6Al-4V alloys were manufactured by grinding and polishing mirror respectively, using the Struers-RotoPol-21 system, Denmark. The samples were grinded by SiC sheet in the flowing steps: (120, 180, 240, 320, 500, 600, 800, 1000 and 1200μm of grain size). Samples are polished with a DP- suspension for (15, 9, 6, 3, 1μm), and the use of the DP-cloth. The fine polishing of samples was made by the same machine with (0.51μm) alumina powder and DP-Lubricant red. The polished samples are cleaned with a triachloroethyl acetate solution. The diluted samples were washed with deionized water, dried and stored in a dissociator above the silica gel pad and were used in plasma treatments, microscopic development and electrochemical investigation. The system was pumped down to the base pressure (about 10-4 mbar), Argon gas was presented into the chamber. DC discharge of argon fluorescence (argon plasma) was neglected and applied to each sample for one hour. The sample has been cleaned with a break until all the small arcs have disappeared and a uniform glow can be seen throughout the sample. Plasma treatment of argon was used only as a standard measure to clean the surface of Ti alloy samples, reducing and removing the original oxide and the contaminated layer. Argon gas was introduced into the evacuated chamber and the flow rate was adjusted until the pressure was stabilized at the desired pressure, and the droplets were cooled in the same gas. Cooling is performed in the same environment mostly to prevent oxidation of samples. The plasma samples of Ti-6Al-4V were treated under pressure N2 (1-3mbar). Figures were obtained from the circular Ti alloy of diameter 1.5 cm and thickness of 2 mm for polarization and EIS tests in the simulated body fluids (SBF). The samples were prepared for polarization investigations by leaving an area of 1 cm2 exposed and the other sides covered with a special varnish. The test solution was to (SBF) after its composition is shown in Table 1.

| Table 1. Composition of Simulated Body Fluid |
|-----------------|-----------------|
| Reagents        | g/l             |
| NaCl            | 8.035           |
| NaHCO₃          | 0.355           |
| KCl             | 0.225           |
| K₄HPO₄·3H₂O     | 0.231           |
| MgCl₂·6H₂O      | 0.311           |
| CaCl₂           | 0.392           |
| Na₂SO₄          | 0.072           |
| (HOCH₂)₂CNH₂    | 6.118           |
| 1.0 M HCl       | Appropriate amount for adjusting the pH 7.4 |

Using the EG & G electroelectric system, the polarization and ELS tests were achieved: Model 273 Potentiostat (EG & G) + Model 1260 Solartron FRA, in three schematic electrodes where the samples were connected to a working electrode, the Pt wire was used as a resistor for Ag / AgCl as a reference electrode. Tafel polarization tests were performed at a 0.5 mv / sec scan rate and ELS tests were performed by scanning a sine wave (m 5mV) from 100 KHz to 10 MHz. All Nyquist and Bode schemes are recorded in one chart to easily compare. All tests were conducted at room temperature. It should be noted that because of the surface coatings presence, some samples demonstrated severe noise in current and potentials that interfere with the measurements. Below, the electrochemical test results are reported. Figures include "Tafel" polarization followed by EIS schemes from Nyquist and Bode where the results of simulated circuits are collected.

3. Results and discussion

3.1 Corrosion test
The results of electrochemical tests are reported below. The figures include Tafel polarization followed by EIS plots of Nyquist and Bode on which the results of simulated equivalent circuits is superimposed Figure 1(a) result of sample M1 pure Ti6Al4V alloy $E_{OCP} = -105$ mv in Solution: Saturated Body Fluid (SBF).

Figure.1 Electrochemical tests results on sample No.1 in SBF: a. Tafel polarization graph of sample No.1 in SBF.

Figure.1 b. EIS Nyquist plot of sample No.1 and superimposed simulated graph obtained from the proposed equivalent circuit.

Figure.1 c. Bode plot and superimposed simulated graph of sample No.1
Figur1 (b and c) shows Tafel polarization test and EIS diagrams of sample No.1. The polarization shows high cathodic and anodic currents which is typical for Ti alloys. The EIS shows two semi circles one at very high frequency that is due to the adsorbed ions on the surface and the other at medium frequency shows the charge transfer resistance, $R_{ct}$.

Figure 2(a) result of sample M2 pure Ti6Al4V alloy $E_{OCP} = -397$ mv in Solution: Saturated Body Fluid (SBF).
Figure 2 Electrochemical test results on sample No.2 in SBF: a. Tafel polarization graph of sample No.2 in SBF.

Figure 2 b. EIS Nyquist plot of sample No.2 in SBF and superimposed simulated graph obtained from the proposed equivalent circuit.

Figure 2 c. Bode plot and superimposed simulated graph

Figure 2(a and b) indicates corrosion tests of specimen No.2 with 200 Watt TiN coating. High cathodic current and passive anodic polarization shows active surface. The EIS shows active behavior presumably due to the active cathodic currents. Two semicircles one for $R_c$ for cathodic current and the next is for TiN coating reactivity or transfer of ions through it with Warburge diffusion.

Figure 3(a) result of sample M3 pure Ti6Al4V alloy $E_{OCP} = +83$ mv in Solution: Saturated Body Fluid (SBF).
Figure 3 Electrochemical test results on sample No.3 in SBF: a. Tafel polarization graph of sample No.3 in SBF

Figure 3 b. EIS Nyquist plot of sample No.3 and superimposed simulated graph obtained from the proposed equivalent circuit.

Figure 3 c. Bode plot of sample No.3 in SBF and superimposed simulated graph Figures 3 (b and c reflects the behavior of sample No.3 and shows unreactive surface because the $E_{OCP}=+88\text{mv}$ and polarization indicates similar results as before. The $C_{dl}=48\ \mu\text{F}$ but $C_{coating}=300\ \mu\text{F}$.

Figure 4(a) result of sample M4 5 hours nitriding coating $E_{OCP} = +170\ \text{mv}$ in Solution: Saturated Body Fluid (SBF).
Figure 4 Electrochemical tests results on sample No.4 in SBF: a. Tafel polarization graph of sample No.4 in SBF

Figure 4 b. EIS Nyquist plot of sample No.4 in SBF and superimposed simulated graph obtained from the proposed equivalent circuit.

Figure 4 c. Bode plot of sample No.4 in SBF and superimposed simulated graph

Figures 4 (b and c) shows Tafel polarization and EIS for specimen No.4 with 5 hours nitriding process. The $E_{OCP}=+170\text{mv}$ showing more noble surface compared to others. But the $Rct$ in EIS spectra is low presumably due to some weak points on the surface which is not converted to nitride.

Figure 5(a) result of sample M5 100watt 2h HA on Ti$_6$Al$_4$V $E_{OCP} = +58 \text{ mv}$ in Solution: Saturated Body Fluid (SBF).
Figure 5 Electrochemical tests results on sample No.5 in SBF: a. Tafel polarization graph of sample No.5 in SBF.

The polarization curve shows high anodic + cathodic polarization with $E_{OCP} = +58$mv. The presence of HA has protected the surface but $H_2$ formation is a weakness for such coatings. EIS spectra show two semicircles one for $R_{ct}$ with high resistance and the next for HA coating.

Figure 6(a) result of sample M6 150 Watt 3h/Thickness/HA on TiN $T=100 \degree C$ E O.C.P = +93 mv in Solution: Saturated Body Fluid (SBF).

Figure 6 Electrochemical tests results on sample No.6 in SBF: a. Tafel polarization graph of sample No.6 in SBF.
Figure 6 b. EIS Nyquist plot of sample No. 6 in SBF and superimposed simulated graph obtained from the proposed equivalent circuit.

Figure 6 c. Bode plot of sample No. 6 and superimposed simulated graph

Figures 6 (b and c) show the Tafel and EIS of 3 hours at 150-watt TiN processed coating + HA at T=100°C shows again reactive surface in polarization but two semicircles; one at high frequencies for the coatings and one at medium frequencies for the $R_{ct}$. The resistance of the $R_{ct}$ indicates the presence of a resistive coating.

The overlapped EIS and polarization graphs of Ti alloy with different coating and treatments are reported in below. Figure 7 shows the EIS data from Ti$_6$Al$_4$V coated with TiN at different powers. It can be seen that at 50 and 100 Watts better coatings are obtained.

Figure 7 Nyquist Plot in SBF for Ti$_6$Al$_4$V with TiN coatings at different conditions. Figure 8 Polarization curves in SBF for Ti$_6$Al$_4$V and TiN coated Ti$_6$Al$_4$V
The polarization graphs in Fig. 8 confirms the better quality of the coating at lower powers.

In Figure 9, HA-coated samples are compared in which HA with medium power provided better quality coating because it has lost its hydrated water.

The polarization graphs in Figure 10 compares the anodic behavior of the coating in which sample No.5 gives better behavior.

Figure 9 Nyquist Plots in SBF for Ti alloy samples coated with HA at different conditions. Figure 10 Polarization curves in SBF for HA-coated samples.

Figure 11 shows the effect of nitriding process on the corrosion behavior of Ti alloy. Here again nitriding at lower time (5Hours) showed better corrosion resistance in SBF both in EIS and Polarization tests.

Figure 11 Nyquist Plots in SBF of Ti alloy with nitride coating at different duration times. Figure 12 Polarization curves in SBF for Ti alloy with nitride coating at different duration.

Figure 13 and 14 shows the effect of HA-TiN-coatings on Ti alloy at different conditions. High power gives better HA coating and better corrosion resistance.
Figure 13 Nyquist plots of HA-TiN-coated Ti samples with different power and different time.

Figure 14 Polarization curves in SBF of HA-TiN-coated samples with different power and different time.

4. Conclusion

Due to the presence of Ti/ TiN and HA on the surface of the samples, some noises appeared during both polarization and EIS tests. The corrosion rate could not be measured because the anodic and cathodic lines of Tafel polarization were not homogenous. The corrosion rate can be measured by immersion tests. Morphological investigation needed to report the way corrosion occurred on the surface. The sample size was not large enough for wire connection and we could not weld or solder any wire for such connections because it may damage the surface. The coatings looked homogenous but need SEM analysis for detecting weak points. Hydrogen formation is a main problem with implants which the cathodic Tafel lines were showing. It is important also to measure the coatings thickness which may reflect its durability. What we report is only our observations and do not judge about the performance of the samples.

5. References

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