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PRELIMINARY STUDY FOR DEGRADATION CHARACTERISTICS OF HYDROXYAPATITE COATINGS ON TITANIUM IN RINGER SOLUTION

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ABSTRACT. The aim of this work was to study the effect of electrochemical and electrophoretic deposition of hydroxyapatite (HA) on commercial pure titanium substrates, regarding the corrosion behaviour of the coated biomaterials during their preservation in physiological media. The coated surfaces were analyzed by X-Ray Diffraction and Scanning Electron Microscopy. The degradation characteristics of HA coated on the Titanium implants was investigated as a function of immersion time in Ringer solution, using the Electrochemical Impedance Spectroscopy (EIS) technique. A double-layer model of the coated film was found; a compact protective inner layer and a porous external layer with open or sealed pores, as a function of immersion period.

Keywords: Coating, Titanium implants, Hydroxyapatite, Electrochemical Impedance Spectroscopy

INTRODUCTION

Metallic materials have found wide application in restorative surgery as basic biomaterials for manufacturing implant prostheses for skeletal replacements and fixtures. In this case, metallic materials, which combine good mechanical characteristics, high corrosion resistance and good compatibility with biological materials, are chosen. Titanium and its alloys have been used extensively in the last several decades as materials for orthopedic implants, dental implants, and medical devices due to their low density, excellent biocompatibility, corrosion resistance and mechanical properties [1-9]. When the prosthesis are placed in the human body, the passive film undergo further transformations, namely thickening of the passivating film and stoichiometric changes, as well as metal dissolution [10, 11]. Both passivation and metal dissolution are electrochemical processes.

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There are few reports describing the electrochemical process on the alloy during the growth of hydroxyapatite (HA). Bioactivity of titanium surfaces is not high enough to induce the direct growth of the bone tissue and good bone fixation takes several months. Modifications of metal surfaces often are employed as a mean of controlling tissue-titanium interactions and shortening the time of bone fixation [12]. The hydroxyapatite coatings on metallic implant devices offer the possibility of combining the strength of the metals with the bioactivity of the ceramics [13-16]. Many different techniques have been used for preparation of HA coatings among them ion sputtering, plasma spraying, sol-gel coating, electrodeposition and a biomimetic deposition [17].

This investigation was aimed to study the effect of electrochemical and electrophoretic deposition of hydroxyapatite on commercial pure titanium substrates, regarding the corrosion behaviour of the coated biomaterials during their preservation in physiological media. In the present work electrochemical impedance spectroscopy (EIS) measurement were carried out in order to understand the structure of the electrochemical deposed layer/substrate interface. EIS spectra were recorded and the data were analysed to evaluate the equivalent circuit (EC) parameters as a function of time storage of the coated metal in Ringer's solution.

RESULTS AND DISCUSSIONS

Samples depositions and characterization

The short deposition time in electrochemical deposition entail just an initiation of the coating process, creating only the centre for ulterior deposition of HA after implantation. The nucleus of deposed phase can be observed on SEM micrographs (Figure 1a).

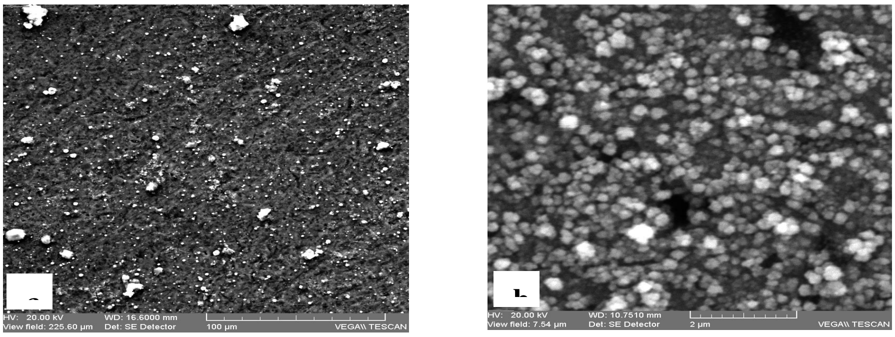


Figure 1. SEM micrographs of the electrochemically coated titanium

The microstructure of these hydroxyapatite islands is presented in Figure1b at a higher magnification. The EDX spectrum for surface presented in Figure 1a indicating the presence both the calcium phosphate compounds and titanium oxides (Figure 2).

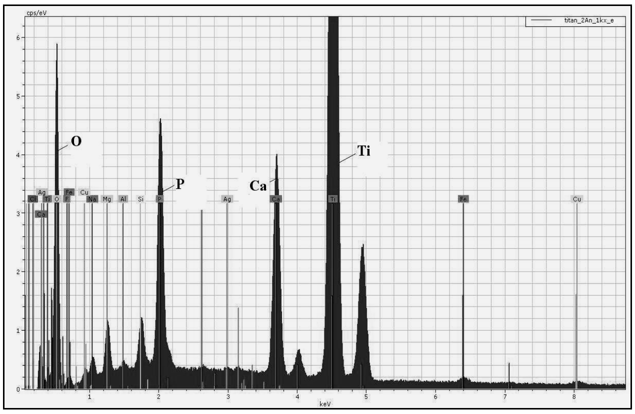


Figure 2. EDX spectrum for electrochemically coated titanium surface

The XRD spectrum after electrochemical deposition of calcium phosphate, presented in Figure 3a, attest the presence of Monetite on titanium surface. Taking into account the reduced intensities of the characteristic peaks one can confirm that the deposed material is in a very small quantity.

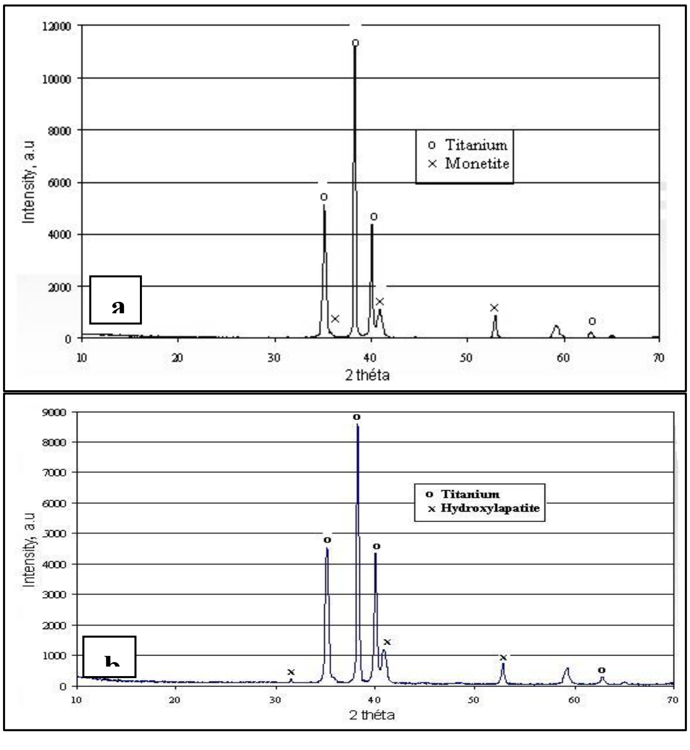


Figure 3. XRD patterns of the coated titanium surface after electrochemical deposition (a) and after monetite→hydroxyapatite conversion (b)

The XRD spectrum registered after monetite→hydroxyapatite conversion (Figure 3b), confirm this transformation by hydroxyapatite peaks occurrence, in the same small quantity.

The surface structure after electrophoretic deposition of hydroxyapatite is presented in Figure 4, before and after annealing process.

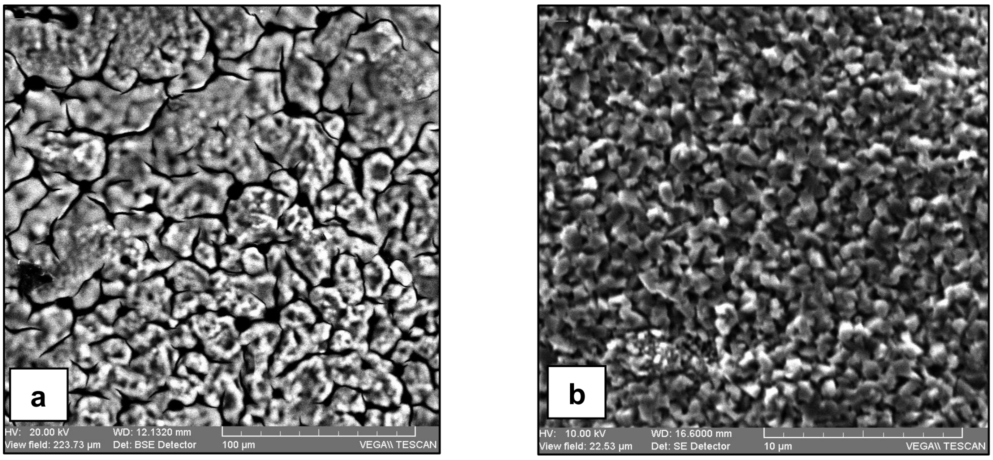


Figure 4. SEM micrograph of the electrophoretically coated hydroxyapatite (a) after deposition; (b) after calcinations for 2.5 hours at 800°C

One can remark the uniform coating of titanium surface with a compact layer of very well packed HA particles (Figure 4a), and the fine microstructure of the hydroxyapatite crystals (1-1.5 µm) after calcination (Figure 4b).

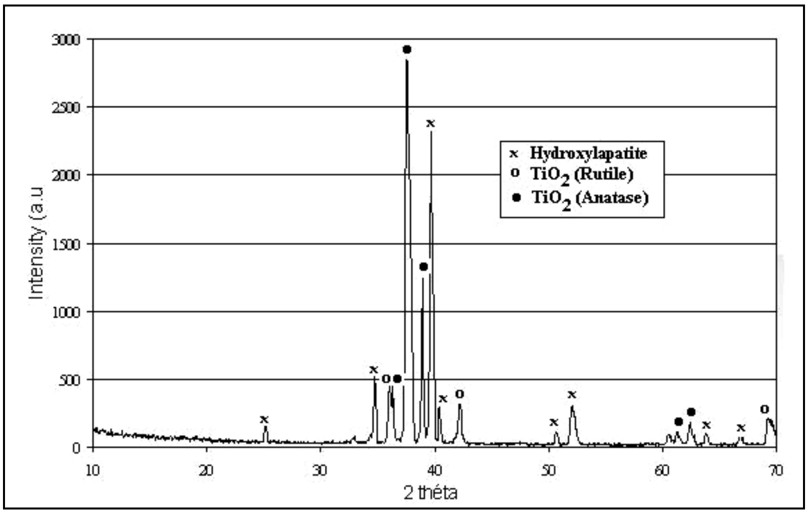


Figure 5. XRD pattern for electrophoretically coated and sintered sample

The XRD pattern obtained for sample coated by electrophoretic method and calcinated (Figure 5) indicate the fact that heating titanium coated with hydroxyapatite at 800°C a crystalline hydroxyapatite is obtained. On the other hand, by this heating the free surface of titanium plate was oxidized to TiO_2; a mixture of rutile and anatase being identified.

Electrochemical measurements

Electrochemical impedance spectroscopy measurements offer useful information regarding the superficial layer of the coated sample and their time evolution in Ringer solution. EIS measurements were performed at the open circuit potential. Typical impedance spectra obtained for different immersion period in Ringer solution of the electrochemical HA-coated sample are shown in Figure 6. They are presented as Bode diagrams.

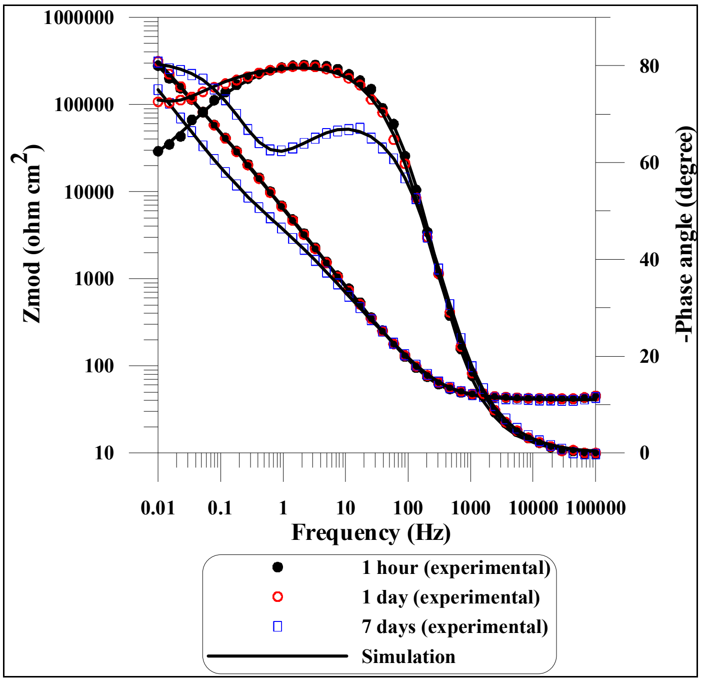


Figure 6. EIS data, for electrochemical HA-coated titanium sample, immersed in Ringer solution for different times, measured at open circuit potential.

Generally, three frequency regions referring to the high, intermediate and low frequency values are distinguished from impedance spectra. The high frequency plateau of the impedance values at frequency higher than 10^4 Hz, with the phase angle approaching to zero, yields the value of the solution resistance (R_{sol}). The intermediate frequency region (10^3 to 10 Hz) has the maximum phase angle and the logarithm of impedance versus logarithm of the frequency slope approaching to -1. These impedance responses correspond to the capacitive behaviour of the electrode and describe the dielectric properties of the electronically conducting surface film. The low frequency region (under 10 Hz) detects the mass transfer (diffusion or migration) processes, or other relaxation processes taking place at the film-electrolyte interface or within the pores of the surface film.

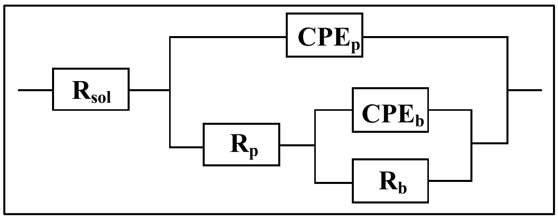
From Figure 6, the phase angle observed at low frequency for the sample after 1 hour immersion was -60^o. However, at intermediate frequency, the phase angle shifted to -80^o and remind constant over a wide range of frequency, indicating a capacitive response for the sample. One can observe that the changes of the surface properties are less noticeable after 1 day of immersion. The Bode plots for sample immersed for one day and for one hour are similar. Once with increase of the immersion time to 7 days, two distinct capacitive behaviours can be evidenced and, at low frequencies, the phase angle values are shifted to -80^o. The high-frequency region evidences the penetration process of the electrolyte through the porous film and the low-frequency domain evidences the processes taking place at the substrate/ electrolyte interface [18]. Such behaviour is typical for a metallic material covered with a porous film, which is exposed to an electrolytic environment.

It was found that the whole set of experimental data could be satisfactorily fitted with two EC presented in Figure 7. The impedance data of electrochemical HA-coated titanium specimen maintained for one hour and one day in Ringer solution were fitted with the EC presented in Figure 7a, while for the same sample maintained for seven days in solution was better fitted with the EC presented in Figure 7b.

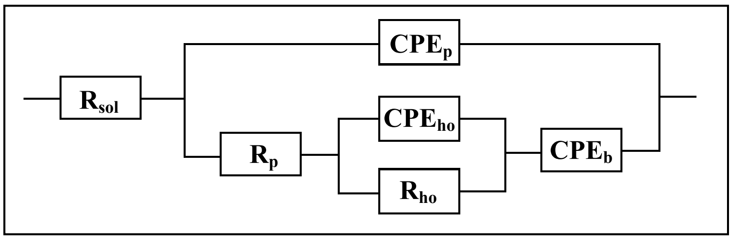
In these equivalent circuits CPE is the constant phase element and “n” the exponent of the constant phase element, described by an empirical impedance function of the type [19]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \qquad (1)$$

where: “Q” is the combination of properties related to both the surfaces and electro-active species independent of frequency; “n” (exponent of the frequency term) is related to the slope of the lg Z_{mod} vs lg Frequency in Bode plots and varies between –1 an +1, “ω” - the angular frequency and j is imaginary number ($j^2 = -1$).



(a)



(b)

Figure 7. Equivalent circuit for Two-layer model: a compact inner layer and a porous external layer: (a) with unsealed pores and, (b) with sealed pores.

The EC presented in Figure 7a contains the following elements: solution resistance (R_{sol}), constant phase element (CPE_p) of the intact (non-defective) coating layer, charge transfer resistance associated with the penetration of the electrolyte through the pores or pinholes existing in the coating (R_p), the polarization resistance of the substrate (R_b) as well as the electrical double layer constant phase element at the substrate/electrolyte interface (CPE_b).

The circuit presented in Figure 7b was developed to represent a sealed anodic oxide film [20]. The EC is similar to that proposed by R.M. Souto et al for plasma-sprayed HA-coatings on Ti6Al4V in physiological media [18]. That is, the model represented by circuit presented in Figure 7a modified to take in account the precipitation of some hydrates/precipitates inside the external porous film. In this case, the CPE_{ho} and R_{ho} introduced in circuit represent the constant phase element and resistance of hydrates/precipitates inside the pore of the superficial film.

The quality of fitting was judged by the error distribution vs. frequency, comparing experimental with simulated data for different models. These error distributions indicate the fact that in the case of electrochemically coated sample the "two-layer model of unsealed porous film" can be successfully used to fit the EIS data for short times of immersion (1 day), while the "two-layer model of a sealed porous film", can be used to best fit the EIS data for long time immersions (7 days); in both situations, the errors being of less than 5%.

The values of the circuit elements from equivalent circuits that fit best the experimental data in the case of electrochemical-coated sample are presented in Table 1.

Table 1. Impedance parameters for electrochemical HA-coated titanium sample after different immersion times in Ringer's solution

	CPE_p ($S\ cm^{-2}\ s^n$)	n_p	R_p ($\Omega\ cm^2$)	CPE_b ($S\ cm^{-2}\ s^n$)	n_b	R_b ($\Omega\ cm^2$)	R_{ho} ($\Omega\ cm^2$)	CPE_{ho} ($S\ cm^{-2}\ s^n$)	n_{ho}
1 hour	2.4×10^{-5}	0.90	2×10^5	8.9×10^{-6}	0.81	6×10^5	-	-	-
1 day	3.1×10^{-5}	0.88	1×10^5	9.8×10^{-6}	0.80	5×10^5	-	-	-
7 days	3.5×10^{-5}	0.85	5×10^3	4.7×10^{-5}	0.79	-	1×10^5	2.4×10^{-5}	0.65

The sample maintained 7 days in solution appear to be un-protected at action of solution, from point of view of the charge transfer resistance (R_p) (for highly corrosion resistance materials the values may even reach 1 MΩ cm^2 [21]). However, this effect seems to be compensated by polarization resistance of substrate (R_b) that is sufficiently high. The same value for solution resistance, R_{sol} of the test electrolyte, equals 45 ± 5 Ω, was observed for the specimens, indifferent of the immersion time, and was not inserted in Table 1.

The EIS spectra for the electrophoretically deposition of hydroxyapatite on pure commercially titanium immersed in Ringer solution are shown as Bode plots in Figure 8.

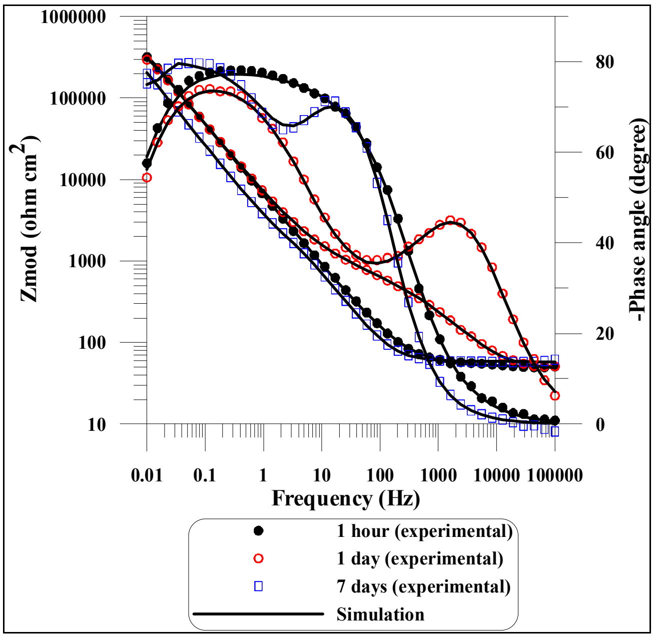


Figure 8. Bode plots for electrophoretical HA-coated titanium sample, recorded at open circuit potential, after different time of immersion in Ringer solution

In Figure 8, the experimental data are shown by individual points, while the theoretical spectra resulting from the fits to a relevant equivalent circuit model are shown by continuous lines. For the electrophoretical HA-coated commercial pure titanium specimen EIS recorded at open circuit potential after 1 hour of immersion in Ringer solution a capacitive behaviour, is indicated from medium to low frequency by phase angle approaching –80^o. In this case, noticeable changes after 1 day of immersion were observed. With increase in time to 1 day of immersion the sample exhibited two distinct capacitive behaviours. At 7 days of immersion, the nature of Bode plots was similar to that of 1 day of immersion.

The impedance data for electrophoretical coated sample maintained for 1 hour in Ringer's solution (initial moment) are best fitted with EC presented in Figure 7a, while for sample maintained both one day and 7 days in Ringer solution are best fitted with the EC presented in Figure 7b. The circuit elements values are draw in Table 2.

Table 2. Impedance parameters at different immersion times in Ringer solution for electrophoretical HA-coated titanium sample

	CPE_p ($S\ cm^{-2}\ s^n$)	n_p	R_p ($\Omega\ cm^2$)	CPE_b ($S\ cm^{-2}\ s^n$)	n_b	R_b ($\Omega\ cm^2$)	R_{ho} ($\Omega\ cm^2$)	CPE_{ho} ($S\ cm^{-2}\ s^n$)	n_{ho}
1 hour	3.1×10^{-5}	0.86	2×10^5	9.4×10^{-6}	0.85	6×10^5	-	-	-
1 day	3.5×10^{-5}	0.88	5×10^3	3.7×10^{-5}	0.70	-	5×10^5	3×10^{-5}	0.75
7 days	3.9×10^{-5}	0.90	5×10^3	1.8×10^{-5}	0.70	-	2×10^5	3.5×10^{-5}	0.81

In this case, after only one day of immersion the EIS spectrum reflects that the pores in the coated layer are filled with precipitates. The metal dissolution continues through the coating, because the impedance spectra are below $10^6\ \Omega\ cm^2$ at all exposure times.

CONCLUSIONS

1. By short time electrochemical coating one can obtain an initiation of the hydroxyapatite deposition on pure titanium surface, whereas by electrophoretic method in the same time period (10 min) a consistent hydroxyapatite layer can be deposed. A previous etching and/or alkaline activation of the metal surface favour these depositions.

2. Through heating at 800^{o}C the partial amorphous deposition is transformed in a crystalline hydroxyapatite.

3. Electrochemical impedance spectroscopy is a useful technique for studying the corrosion behaviour of surgical metallic implants, even when they are coated with a ceramic material such as hydroxyapatite. In the case of electrochemical HA-coated commercial pure titanium specimen after a sufficient time of immersion in Ringer's solution (more than a 1 day)

the electrolyte penetrate in the metal substrate trough the pores of the substrate film (most probable Hydroxyapatite and TiO_2). The nature of the materials which fill the superficial pores was not investigated in this study, but may probably be the result of metal phosphate formation or incorporation of metal ions in the HA structure, correlated with the presence of oxygen from air. In the case of the electrophoretic HA-coated titanium only after one day of immersion in Ringer's solution the Bode plots exhibited two distinct capacitive behaviours. The pores are penetrated much more rapid by electrolyte and after 1 day of immersion the pores of the superficial layer are blocked. Also, one can be remark that after a significant time of exposure (7 days) both coated samples have similar electrochemical behaviour.

4. The EIS spectra are fitted using an equivalent circuit. For coated samples maintained short time in Ringer solution, a two-layer model of an unsealed porous surface film is suitable, while for coated samples maintained long time in Ringer solution, a two-layer model with sealed pores is adequate.

EXPERIMENTAL SECTION

Materials

The pure titanium plates (60x12x5 mm) used as substrate for HA coating were first roughened by acid etching for 60 min at 60°C, in a mixed acidic solution (18% HCl and 48% H_2SO_4). Then, acid-treated surfaces are ultrasonically cleaned successively with acetone, ethanol and distilled water for 10 min each and dried in air at 120°C.

The electrolytic deposition of hydroxyapatite was realized via monetite. For this purpose o potential difference of 2V between titanium (cathode) and platinum (anode) was applied for 25 min. The electrolyte medium was a solution rich in Ca^{2+} and PO_4^{3-} ions, whose composition is: 0.5M $Ca(OH)_2$, 0.5M H_3PO_4 and 1M Lactic acid (CH_3CHCO_2HOH). The electrochemical reaction was conducted in an electrochemical cell with three electrodes, the reference being a saturated calomel electrode. The cathodic deposition vas carried out with a VOLTALAB 40 potentiostat (PGZ 301 type – Radiometer Copenhagen). The temperature was controlled in the domain 70 – 75°C. During the deposition process the current density has been varied between 0.6 and 0.2 $\mu A/cm^2$. After deposition the sample was washed with deionised water and dried at 120°C. By this process on the titanium surface was formed the monetite, $CaHPO_4$, The conversion of monetite to hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was realized immersing the covered sample in 0.1M NaOH for 67 hours at ordinary temperature.

For electrophoretic deposition, the roughened sample was firstly activated by an alkaline treatment in 10M NaOH for 4 hours at 75°C. The electrophoretic coating was realized from a suspension of Hydroxyapatite powder in an aqueous-organic media (4.2 g HA, 100 mL isopropyl alcohol and 5 mL 0.5N HCl) in a two-electrode cell, with titanium as cathode and platinum as anode. A potential of 63 V was applied for 10 min. After washing, the sample was dried at 120°C and then burn off for 2.5 hours at 800°C.

Samples characterization

The coated surfaces were investigated using a VEGA-TESCAN Scanning Electron Microscope equipped with QUANTAX Bruker AXS Microanalysis system. The XRD patterns were obtained with a Philips Analytical PW3710 XPERT system equipped with a Ni filter and Cu Kα (λ =1.5418 Å) radiation (40 kV, 30 mA) at 0.05° steps at the rate of 10 s per step over the range $10° < 2\theta < 70°$.

Electrochemical measurements

The corrosion behaviour and time evolution of the coated surfaces were analyzed by Electrochemical Impedance Spectroscopy (EIS). The measurements were carried out at 25°C in a naturally aerated Ringer's solution (NaCl – 6 g/L, KCl – 0.4 g/L, $CaCl_2 2H_2O$ – 0.2 g/L, sodium lactate – 3,05 g/L) at pH=6.5, in a three electrodes cell: the studied sample, a platinum counter-electrode and saturated calomel - as reference electrode (SCE). The measurements were made with a PAR 263 A potentiostat/ galvanostat connected with a PAR 5210 lock-in amplifier, controlled by a computer (Princeton Applied Research). The impedance spectra were acquired in the frequency range of 10^5 Hz to 10^{-2} Hz with a 10 mV amplitude sine wave. Nyquist and Bode plots were registered, at the open circuit potential. The analysis of the EIS data was performed using commercial software package Electrochemistry Power Suite (ZSimpWin).

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