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Various procedures in electrochemical evaluation of hydroxyapatite films on titanium

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This paper is focused in obtaining and characterization of a uniform HA coating by electrochemical method [2]. FTIR spectroscopy was performed in order to determine the chemical structure of electrochemical deposition and to identify the functional groups. The observations of the samples morphology were carried out with an Environmental Scanning Electron Microscope (ESEM) enabled us to observe the calcium phosphate deposition process. Electrochemical impedance spectroscopy (EIS) was used to characterize the electrochemical behaviour of the titanium covered with HA in 0.9% NaCl solution. The behaviour of samples was typical of metallic material covered by a porous film which is exposed to an electrolytic environment, and can be described in terms of an equivalent circuit.

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1. Introduction

Calcium phosphate ceramics, especially hydroxyapatite (HA), have received much attention as biomimetic coatings and have been clinically applied in orthopaedics and dentistry due to their excellent biocompatibility [1]. The application of hydroxyapatite coatings on metallic implant offers the possibility of combining the strength of metals with the bioactivity of the ceramics.

Application of porous ceramics for the attachment of load-bearing orthopaedic applications is well known [3] as a method of inducing grater biocompatibility and to endow titanium with bioactivity, bonds via bonds formed between its surface and living bone [4]. Among the artificial materials known to be bioactive, HA, chemically and structurally similar to the minerals of bones and teeth, is known to enhance bone formation and is employed for hard tissue repair augmentation of living bone.

Synthetic HA exhibits strong affinity to host hard tissue and promote a better osseointegration especially when Ca/P ratio is close to 1.67, such ratio existing in natural bone. In order to obtain bioactive and strong materials, the formation of hydroxyapatite on an implant with good mechanical properties is considered a good approach. Coatings of hydroxyapatite on metallic implants have been prepared by a variety of techniques, including plasma spraying, sol-gel, electrophoretic deposition, laser ablation, hydrothermal and electrochemical methods [5-8] and despite of various ratio of Ca/P in the coating composition, each method has specific advantages and disadvantages.

Sintered titanium-hydroxyapatite implant materials have been prepared [9].

In vitro hydroxyopatite growth on patterned surfaces (stainless steel, silicon) has been achieved [10].

Calcium phosphate coatings deposited on metal substrates by electrochemical method, seems to be an attractive process because a highly irregular object can be coated relatively quickly at low temperature, and the thickness and chemical composition of coating can be well controlled through adequate conditions of the process.

Regarding the stability, the corrosion resistance of the biomaterial is affected by the presence of the ceramic coating, both depending on the passivation ability of the metallic substrate and the porosity of the coating.

2. Experimental

2.1 Substrates and coating

Commercially pure titanium was used as substrates. The composition in wt % of Ti > 95%. Surface preparation before treatment involved titanium plates, 10×10 mm size, metallographic gritted until 1000 # using SIC emery paper and cleaned with acetone followed by washing with deionised water. Each specimen was dried at room temperature. Calcium phosphate coating have been deposit on metal substrates by electrochemical method using a potentiostat equipment.

The electrolytic method consists of application of a potential difference between a platinum anode and a titanium cathode. The electrodes are immersed in a solution rich in ions Ca^{2+} and PO_4^{3-} which composition is: 0.5M $Ca(OH)_2$, 0.3M H_3PO_4 and 1M lactic acid. The working parameters (temperatures, current and electrolysis time) were manipulated in order to get a uniform coating and the final conditions were as followings:

The temperature 80 ^oC; current density 0.20mA/cm^2; time 60 min. After deposition, the sample was washed in distilled water and air dried. According to the procedure described in literature by Szu-Hao Wan et all [10], the samples was immersed in 0.1 M NaOH at 60 ^oC during 10h for assess bioactivity.

2.2 Evaluation techniques

The coating properties were evaluated using spectral, morphological features and electrochemical, according following procedures and equipments:

- FTIR spectra of HA powder and of the phosphate coating between 400-4000 cm^{-1} was performed using a Shimazu spectro-photometer. Surface analysis was performed with Environmental Scanning Electron Microscope FEI/Phillips XL30 ESEM at a pressure = 0.7 Torr. Working mode was GSE (water vapours). The analysis includes the determination of the surface composition;
- electrochemical by EIS method at the open circuit potential with a Voltalab 40 equipment. A data density of six frequency points per decade was used. The spectra were acquired in a 50 kHz – 5 Hz frequency range. Impedance spectra were represented in both complex impedance diagram, (Niquist plot) and Bode amplitude and phase angle plots. The analysis of EIS was performed using a non-linear least squares fit method to obtain the equivalent electrical model for the substrate-electrolyte interface after different exposure times (1 h, 10 h, 30 days) in the 0.9% NaCl solution. Data analysis was performed using a nonlinear least squares fit method to obtain the equivalent electrical model for the substrate – electrolyte interfaces studied

3. Results and discussion

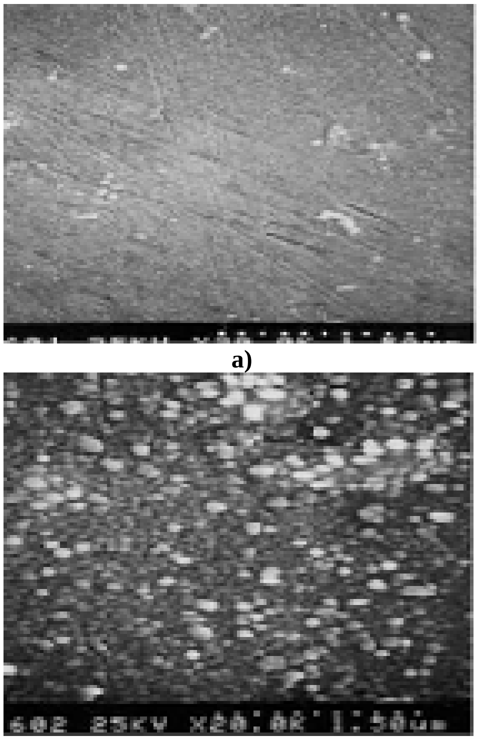
The cathodic reactions occurring in this electrolysis, described in the literature involve reduction phenomenon of O_2, $2H^+$, $2HPO_4^{2-}$ and water according to the reactions [12]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$2H^+ + 2e^- \rightarrow H_2$$
$$2HPO_4^{2-} + 2e \rightarrow 2PO_4^{3-} + H_2$$
$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$

The phosphate ions formed react with calcium cations to form HA and deposit on the cathode, at the acidic pH of 4.1.

The formation of hydroxyapatite layer on the metal surface is controlled by a nucleation mechanism as the in initial step of the further grows process. Fig 1 show images of titanium surface untreated and electrochemically bioactivated; the growth of apatite layer found to be in multiple direction.

The composition of non treated titanium surface is presented in Fig. 2 and Table 1 and the composition of treated sample in Fig. 3 and Table 2.


a)

b)

Fig. 1. ESEM images of the Ti surface a) non- treated; b) electrochemical deposition of HA.

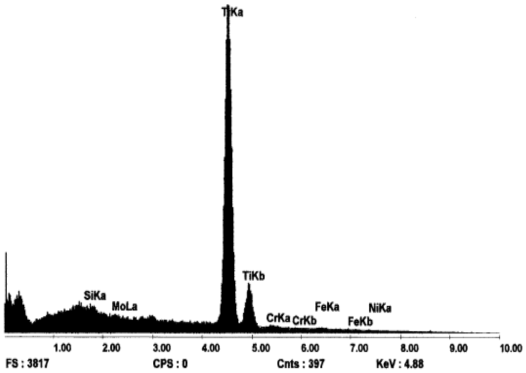


Fig.2. X-ray emission spectrum of untreated Ti

Table 1. Surface composition of non-treated Ti sample

Element	Weight %	Atomic %
Si	0.85	1.464
Mo	1.489	0.747
Ti	95.23	95.647
Cr	0.883	0.817
Fe	1.53	1.325
Total	100.00	100.00

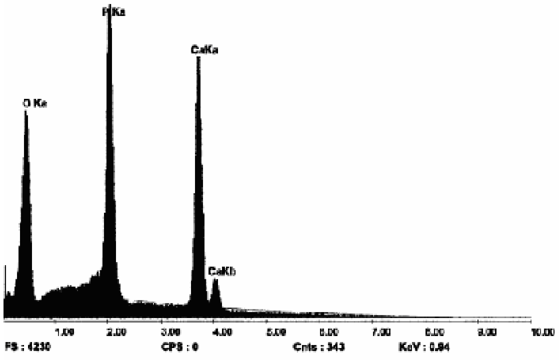


Fig. 3. Spectrum for emission in X-ray from Ti/HA coating.

Table 2.Composition of HA/Ti coating.

Element	Weight %	Atomic %
O	39.72	59.98
P	20.81	16.24
Ca	39.47	23.78

The surface analysis results are sustained by FTIR spectra. The FTIR result of HA power, and the hydroxyapatite coating on titanium is shown in Fig. 1. The multi pleats peaks located around 1000cm^{-1}originated in phosphate modes. The split bands, mainly at 1028 and 1098 cm^{-1}, seem to agree with the formation of well-crystallized apatite. Carbonated bands have been detected at 875, 1420 and 1453 cm^{-1}. Molecular and adsorbed water bands are also discerned at 1583 and 3400 cm^{-1}.

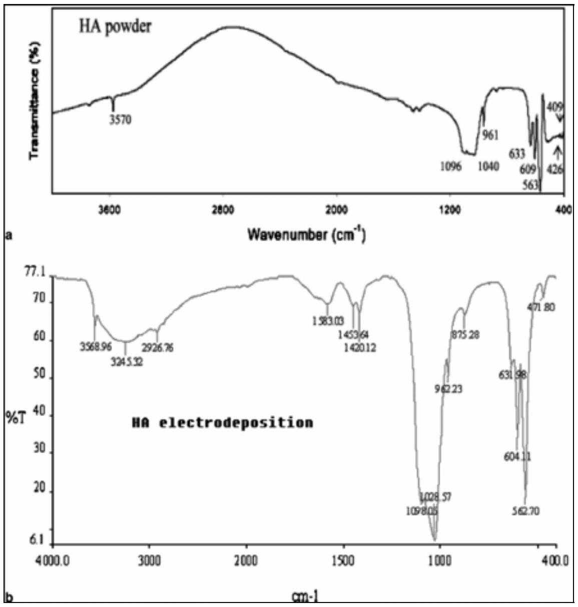


Fig 4. a) FTIR spectrum of the HA (b) FTIR electrochemical HA coating.

Electrochemical impedance determinations were performed at the open circuit potential. Typical examples of impedance spectra (Nyquist diagram, and Bode amplitude and phase angle plot) obtained at different exposure time during the immersion in NaCl 0.9% simulated physiological solution of HA-coated specimen are presented in figure 5. The Bode plots are indicated for the investigation of changes in the electrochemical characteristics at different exposure times. Changes are less noticeable with time elapsing and after 10 day exposure, an almost stationary behaviour was reached. The spectra indicated clearly that the electrochemical properties of the change with exposure time.

The impedance spectra shown in figure 5 exhibit two time constant at all exposure times. That is, they can be divided into two distinct frequency regions: the time constant in the high-frequency part, which arises from the uncompensated ohmic resistance due to the electrolytic solution and the electrolyte through a porous film, and the low-frequency part accounting from the processes taking place at the substrate/electrolyte interface This behavior can be described in terms of an equivalent circuit which accounts for the different electrochemical processes occurring in the system.

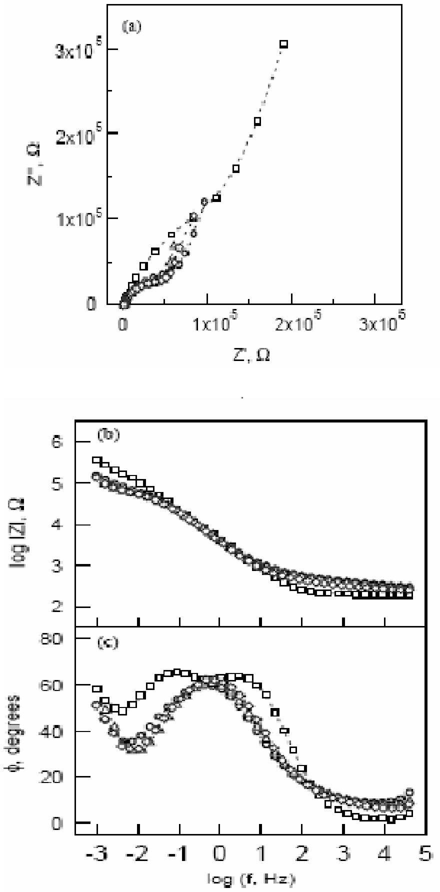


Fig 5. Impedance spectra recorder for Ti/HA coated expose in NaCl 0.9% at diverse exposure time: □ 1h; O 10 h; ◊ 30 day.

The electrochemical response to impedance tests for the HA-coated materials was satisfactorily simulated with the equivalent circuit detailed in figure 6. This circuit represents the electrochemical behavior of a metal covered with an unsealed porous film. [13].

The equivalent circuit consists of the following elements: a solution resistance R_e of the electrolyte, electrical leads, the capacitance C_p of the intact coating layer, the charge transfer resistance associated with the penetration of the electrolyte through the pores existing in the coating R_p, and the polarization resistance of the substrate R_b as well as the electrical double- layer capacitance at the substrate/electrolyte interface C_b. Equivalent circuit used for the interpretation of the measured impedance spectra is presented in Fig. 6.

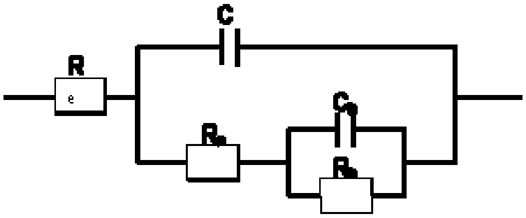


Fig.6. Equivalent circuit used for the interpretation of measured impedance spectra; two-layer model of an unsealed porous surface film

This model of the circuit are based on the consideration of a two-layer model for the surface film, and represent the electrochemical behavior of a metal covered with a unsealed porous film.

The fit of the impedance spectra, for 10 h of immersion, in terms of the equivalent circuit enabled the parameter values for the individual elements to be determined with a least squares analysis, which are: C_p (Fcm^{-2}) = 5.5×10^{-5}, n_p= 0.85; R_p (Ωcm^2) = 7.3×10^3; C_b (Fcm^{-2}) = 4.01×10^{-4}; n_p = 0.8; R_p (Ωcm^2) = 8.02×10^4.

4. Conclusions

FTIR spectroscopy and ESEM surface analysis performed in order to determine the chemical structure of electrochemical phosphate deposition and to identify the functional groups indicated a hydroxyapatite formation.

The electrochemical behavior of the system is characterized by the dissolution and passivation characteristics of the underlying metallic substrate. The corrosion resistance of biomaterials is not greatly affected by the presence of the ceramic coating.

Two-layer models satisfactorily describe the electrochemical behavior of the system by considering a porous film on the metallic substrate.

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