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Synthesis and Electrochemical Characterization a Coating of β -Tricalcium Phosphate Deposited on Steel 316LVM

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Beta tricalcium phosphate thin films they were deposited on austenitic steel by means of a magnetron sputtering with r.f. (13.56 MHz) from tricalcium phosphate (TCP) which it was used as a sputtering target. In order to study the effect of the content of the coating; in the corrosion rate and electrochemical response function of time (0, 24, 196 and 720 hours) of the coated steels, corrosion rate is studied by polarization curves Tafel and the electrochemical response by electrochemical impedance spectroscopy, microstructural characterization was performed using scanning electron microscopy (SEM). Finding himself a decrease of 32% in the corrosion rate for the system evaluated to 720 hours. The ion exchange capacity indicates an increase in corrosion resistance.

Keywords: tricalcium phosphate; Physical vapor deposition; Corrosion; Biomaterials

1. INTRODUCTION

The main motivation behind the use of bioceramics based on calcium orthophosphate as bone substitute material is its chemical similarity to the mineral component of bones and teeth of mammals [1-3]. However, studies over the years this motivation step into the background and the discovery that these materials are nontoxic, are biocompatible, they are not known as foreign elements in the body and most importantly, exhibiting a bioactive behavior and integrated into living tissue, ie leading to a physical-chemical bond between the bone and implant which is known as osseointegration [4-5].

Bioceramics based on calcium phosphates have been used consistently in recent decades as prime candidates for replacing bone material under low load conditions, such as bone void fillers engineering or surface coatings femoral shaft hip endoprosthesis and dental roots [6-8]. Among the more important for these applications are phosphates micro and nanocrystalline calcium such as hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HA) and ß-tricalcium phosphate(ß-$Ca_3(PO_4)_2$), hydroxyapatite which he has gained more interest as to the regeneration of bone in the defect sites crystallographically as is the structure of the dominant network hard tissue [9].

Chemically, the vast majority of calcium orthophosphate bioceramics are based on the has, β-TCP, α-TCP and / or biphasic calcium phosphate (BCP), which is an intimate mixture of any of β-TCP + HA or α-TCP + HA [10]. When compared both α-TCP and β-TCP with HA, the latter is a more stable phase under physiological conditions because it has a lower solubility (0.0003 g / l) and therefore a speed slower absorption kinetics [11]. Because of this, as to BCP, optimum balance to be used is determined by its composition, i.e., a more stable phase of HA and TCP more soluble [12]. Furthermore, because the component α-TCP or β-TCP in the presence of HA, generate a PCB, the reactivity of this compound increases with rising ratio of TCP / HA, therefore, a process in-vivo bioresorbability BCP it can be controlled through the phase composition, like his behavior biodegradable [13].

The ß-tricalcium phosphate (beta TCP) is used for replacing bone material under low load conditions, for example as bone void fillers; particularly as coatings on surfaces engineering femoral hip endoprosthesis shaft and tooth roots [14]. These calcium phosphate coatings show pronounced osteoconductivity and functionalized with recombinant human bone morphogenetic proteins (rhBMPs) [15]. They provide osteoinductive properties that generate faster integration of the graft, these calcium phosphates becoming indispensable components of modern endoprosthesis [16].

The stable phases of calcium phosphate ceramics depend largely on the temperature and the presence of water, either both or the processing of these present in the environment [17]. That is why the body temperature only two kinds of calcium phosphates are stable in contact with aqueous media such as body fluids. At pH values less than 4.2, the phase that is stable is $CaH(PO_4)\,2H_2O$, while for values above this stable phase is the HA [18]. Regarding temperature phases as tricalcium phosphate or ß-TCP and tetracalcium phosphate ($Ca_4P_2O_9$) are present at high temperatures. In turn these phases not hydrated calcium phosphate they can interact with water or body fluids to form physiological hydroxyapatite at 37 ° C [19].

On the other hand, the mechanical behavior of these ceramics is influential for use in implants, because the bending strength, compression and fatigue depend on the purity of the stage, as well as the grain size, sintering temperature and total porosity either in the form of micropores smaller than 1 micron due to incomplete sintering or as macropores with diameters greater than 100 microns artificially created to allow bone growth [20].

Within the fields of engineering focused in bone tissue, coatings based on calcium phosphates are used to improve the osseointegration of the implant by improving cell adhesion, proliferation and differentiation, as it mentioned above, leading to a close and stable connection between the implant and the host bone. Being more calcium phosphates HA employees and β-TCP [21].

In this article the coating is carried out as a layer of calcium phosphate coating on the metal implant substrate steel 316LVM, was doing a study of the degradation of the layer and the development of assays were performed as a function of time at 0, 24, 196 and 720 hours.

2. MATERIALS AND METHODS

In order to design thin films in multilayer form, to improve both mechanical, tribological and biocompatible properties deposited on a metal substrate of stainless steel AISI 316LVM. The thin films were deposited by rf magnetron-sputtering. Such coatings were obtained using a tricalcium phosphate target of 10 cm diameter.

To generate the plasma pressure mbar 5.21×10^{-3} work was used, with the substrate at room temperature, with a discharge current of 250 mA and a discharge power of 400W. Argon flow of 9 sccm was used. All coatings were deposited with a target-substrate distance of 4cm. In addition, a titanium film between the substrate and the coating to improve adhesion was deposited, this interlayer had a thickness of 100 nm.

For evaluation of the corrosion resistance in static condition was used a galvanostat – potentiostat. Techniques electrochemical impedance spectroscopy (EIS) and polarization curves are used. Electrochemical corrosion tests were performed at a temperature of 37 ± 0.2 ° C, using as electrolyte solution hanks (Hanks Balanced Salt Solution, Sigma), Immersion tests performed for 1 months performance evaluation in the months according to the time at 0, 24, 196 and 720 hours. EIS data was generated at the open circuit potential (OCP) after one hour stabilization. For assembling was used a cell comprising a platinum counter electrode (CE), a reference electrode of silver / silver chloride (WE) as the working electrode and 316LVM coatings were used with an exposed area of 0.79 cm^2. Nyquist plots were obtained by performing frequency sweeps in the range of 0.001 Hz to 100 kHz using an amplitude of the sinusoidal signal of 10 mV. Polarization measurements were performed after 60 min of immersion in an aerated Hanks Balanced Salt Solution. Breakdown potential (Eb) in this solution condition approaches closely to corrosion potential (Ecorr) and it was very difficult to determinate correctly. Therefore, the solution was de-aerated with nitrogen 35 min prior to introduce the WE into the electrochemical cell, to remove the oxygen, then polarization measurements were performed after 30 min of immersion in a de-aerated 3.5% NaCl aqueous solution at room temperature. In both cases, the WE was polarized cathodically starting at the Ecorr, followed by an anodic scan after the open circuit potential had stabilized. Was used applying a scan rate of 1mV/s. The materials were polarized anodically to - 0.25 V SCE.

The technique of scanning electron microscopy (SEM) with 1-nm resolution at 30 kV, it allowed the microstructural study at 0 hours of exposure and after performing the anodic polarization curves, 720 hours.

3. RESULTS AND DISCUSSION

In Figure 1, the Bode diagram is observed where the phase angle as a function of frequency is represented wherein the performance of tricalcium phosphate layer is evaluated, a decrease in capacitance as time progresses is observed, this may be associated with corrosion of films deposited by PVD, low permeability of corrosive electrolyte is also seen as not penetrate into the substrate but that a passivating layer is created, the ceramic coating can be regarded as a capacitor; this indicates that the coating creates a more stable phase under physiological conditions since it has low solubility and therefore, a rate more slowly of degradation kinetics. Due to this, the reactivity of this compound increases evolve over time indicating stability time 720 hours stability time of biodegradable behavior.

The other aspect is to evaluate the ratio of coating temperature and the presence of electrolyte either both or the processing of these present in the environment of electrochemical evaluation. Since the evaluation was performed at body temperature, the response calcium phosphates is stability in contact with aqueous media as simulated body fluids. As it can be concluded that these calcium phosphate phases unhydrated they can interact with water or body fluids physiological to form calcium phosphate at 37 ° C [22].

The capacitive behavior of the compound has no cation-cation columns which it is related to different distributions of calcium atoms which have an effect on the stability and electronic properties. In particular, calcium vacancies uniformly distributed throughout the structure and stabilize the compound give low solubility, as regards degradation, it shows a good ability to biodegrade and properly bioreabsorberse, it can be quantified by anodic polarization curves [23].

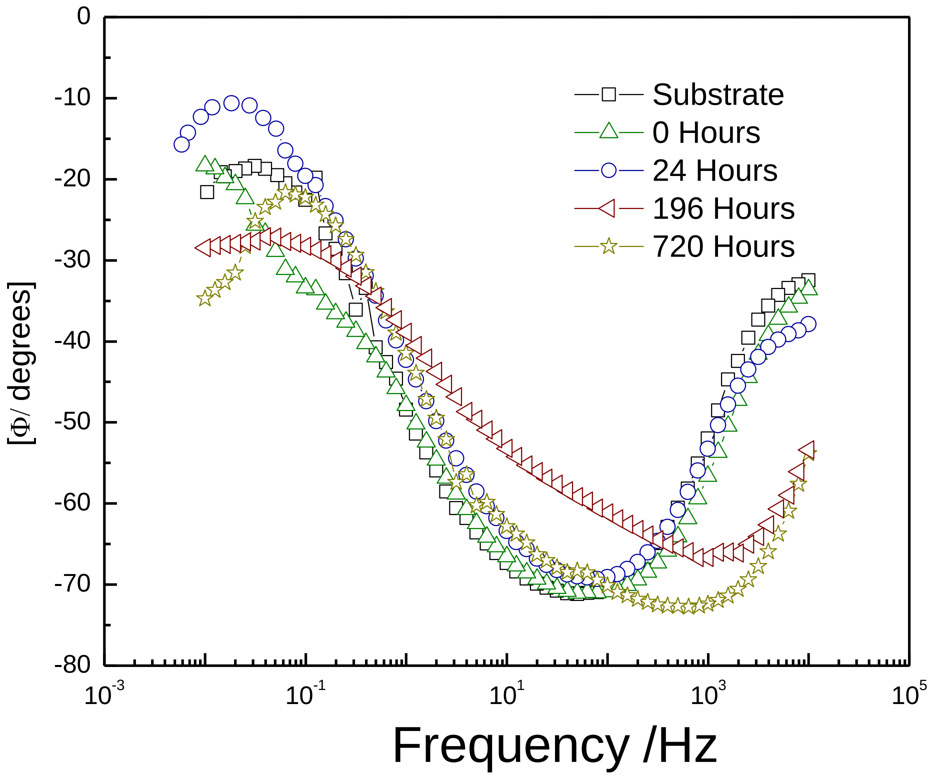


Figure 1. Bode plot of frequency versus phase angle for the evaluated time-dependent coating.

In Figure 2, the Bode plot of the polarization resistance according to the frequency is observed, the protective layer is observed in terms of corrosion resistance and reaction to a biocompatible solution, in order to improve performance in service and the biological response of implanted devices like life of orthopedic systems, ie, to be present and provide durability. Coating the response is adequate and substantially improved compared to the substrate, as the coating increase its corrosion resistance by 52%, subsequently increases its resistance to three times higher than the 720 hours, where the electrochemical response time stabilized, This behavior is due to their surface chemistry, physical and structural properties. Therefore, a coating may optimizes the design of the interface between the tissue and the material is achieved, and it reduces the adverse reactions that can cause and increase the surface properties [24].

The success of tricalcium phosphate it is generated because it is stable at pH values above 7, solution slightly basic characteristics showing essentially bioinert. The properties considered most important are the porosity and roughness of the coating (obtained in the synthesis process of coating), because they are necessary to promote growth of bone cells.

The polarization resistance increases with time and is due to coating thickness (2um), therefore the mechanical performance required by the coating is expected, since the mechanical properties are dependent on the metal block the coating generates increased lifetime in the substrate metal.

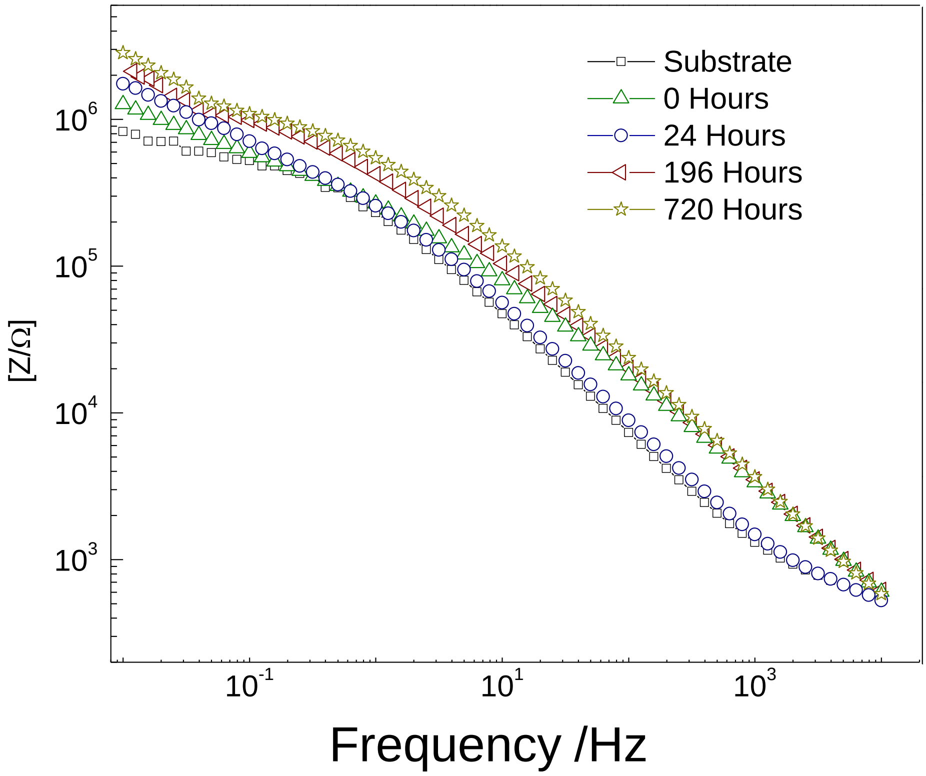


Figure 2. Bode diagram representing the impedance of the substrate and coating tricalcium phosphate, which was evaluated in function of time.

Fig. 3 shows in the four cases, the time of evaluation shifted the Ecorr in the active direction to give values of -0.022 V for the 0 hours, -0.011 for 24 hours, -0.002 for 196 hours and -0.002 for the 720 hours vs Ag/AgCl. The Ecorr showed similar values in the time of the evaluations increase. In contrast to the behaviour in short evaluation times, the anodic branch in 720 hours solution is controlling the corrosion process. This branch showed a passive region characterized by a passivity plateau where the current density is approximately constant. Ecorr was defined by a sharply increase in the current density. The polarization curve for the tricalcium phosphate did not exhibit any fluctuations in the passivity plateau. The potential curves are shown, wherein the coatings can determine an increase in the lifetime of the material obtained as a substrate, this is because the structure as a surface coating layer is obtained by a deposition process that acts as a crack inhibitor and increasing the corrosion resistance. It can be seen that all curves representing the coating evaluated at different times are above corresponding to AISI 316LVM, indicating that the corrosion potential of these is more positive and therefore there is less prone to corrosion in simulated environment, also it shows that the curves are displaced to the left which infer that the corrosion current density is lower in the coating tricalcium phosphate with respect to the substrate, this effect may be the result of the reaction of the surface with Hanks solution, as it is observed that the coating has different reduction potentials, it is nobler to 720 hours of very similar to 196 hours of evaluation evaluation, due to this analogy, it determined that this is the time of stabilization of the surface with simulated solution, with respect to the different times it was determined that the more active corrosion potential corresponding to 0 hours and evaluation is that it has not generated the passivating layer, as evidenced within 24 hours of evaluation wherein the mechanism generates a corrosion potential to a noble region and a diminution of density corrosion [25].

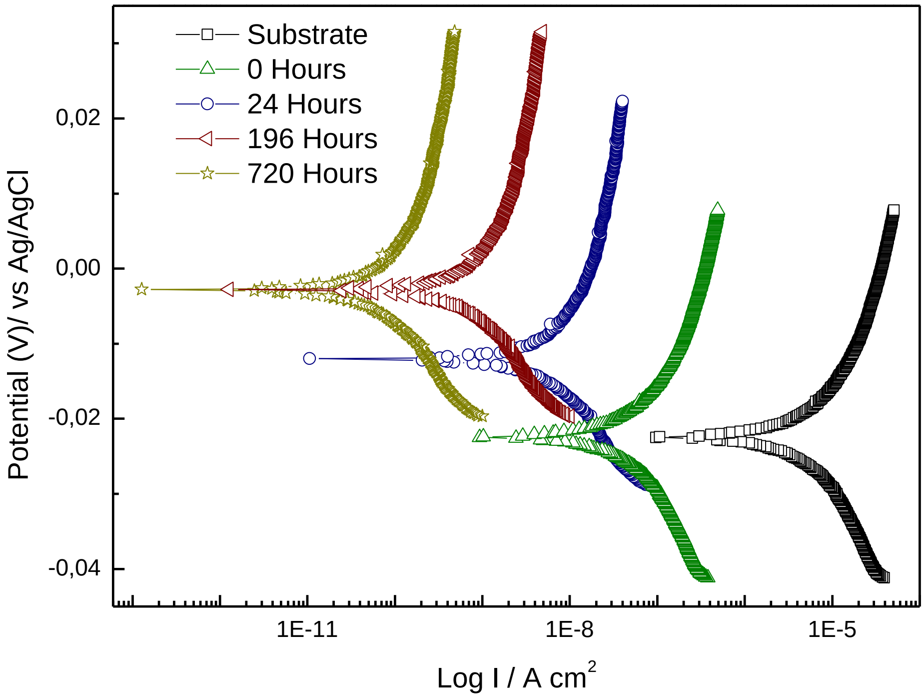
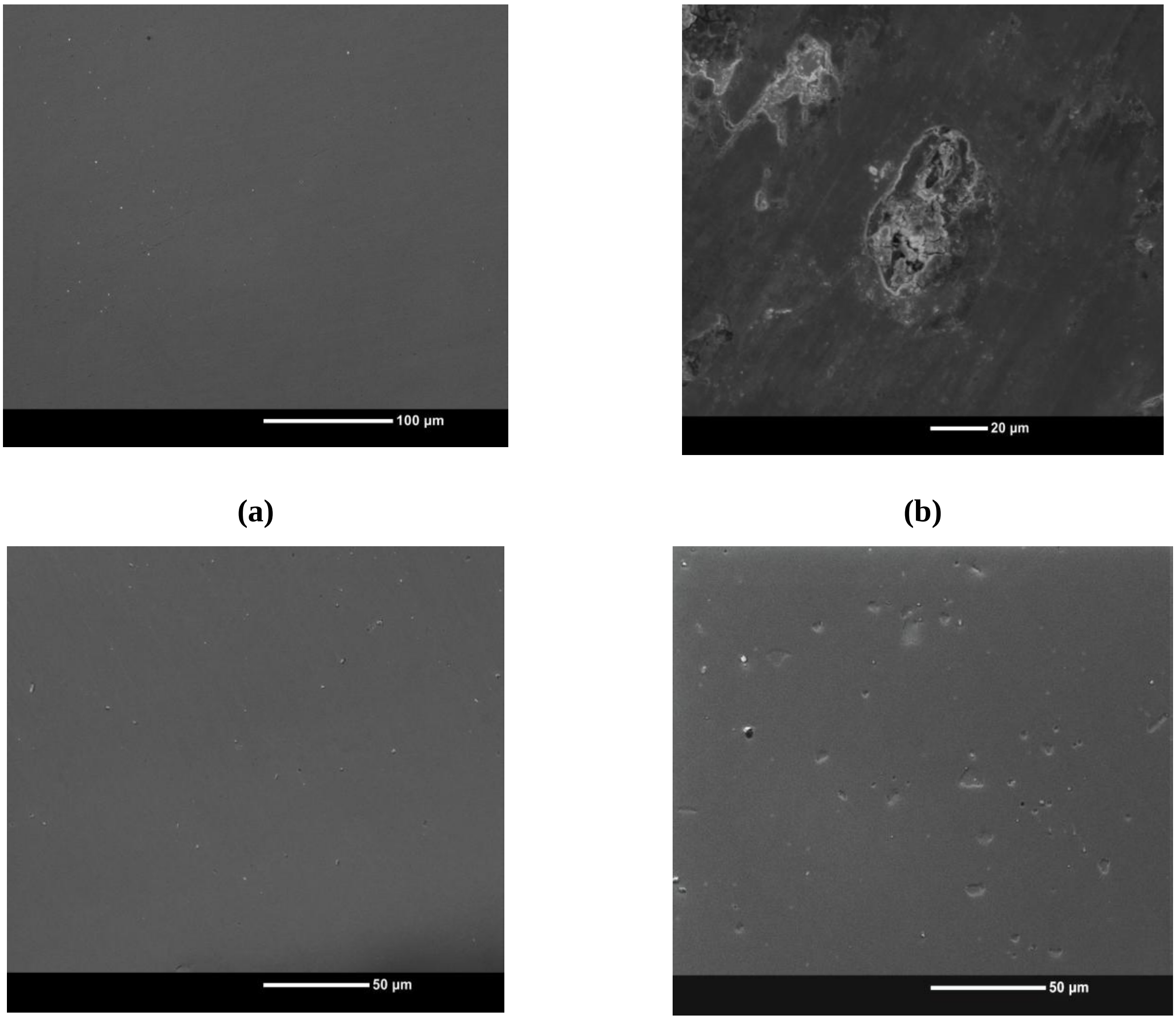


Figure 3. Polarization curves of the substrate and the coating after the evaluation in contact with Hanks solution.

In Figures 4, micrographs of the substrate and the coating is observed, in Figure 4a corresponds to the substrate after removing the steel surface of the oxide, the surface is finished, where a metallic sheen is acquired. In Figure 4b, it is then obtained from test Tafel polarization curve, wherein a surface degradation is generated due to increased pore size and interconnectivity affecting fluid, this may be due to increased protein adsorption, fixing cell migration and proliferation that may affect the smooth running of the coating [26]. In Figure 4c, the micrograph of the coating is exposed before degradation, the presence of imperfections is due to the growth process of the coating which can generate macropores their osteoconductive properties and can promote cell colonization. After the evaluation 720 hours, the coating generates a low surface involvement, this surface area can serve to exchange fluids penetrate tissue, turn promoting the adhesion of macromolecules and proteins for selective adsorption later. The coated surface presents no delamination during contact with body fluids.



(a) **(b)**

(c) **(d)**

Figure 4. Micrograph by SEM, images a and b corresponding to the substrate before and after evaluation against fluids simulating bodily conditions, the images c and d they are relevant to the coating evaluated similarly to the substrate.

4. CONCLUSION

This type of coating can be applied as metal implants, because their properties can ensure a long lifespan of orthopedic type systems, because it meets the characteristics of electrochemical nature, biological aspects evaluated to assess their biocompatibility; such as good response to Hanks solution.

The improved surface properties by the deposition of separate layers having different types of effects on their surfaces, as corrosion protection and wear it generates a diffusion barrier and adhesion to the substrate.

Bode plots have a similar shape for Tricalcium Phosphate, two capacitive behaviour are observed. The Ecorr parameter, associated with corrosion resistance, exhibits better values for the longer time in the system. This can be related with the presence of calcium reactions which offer high corrosion resistance.

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