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DETERMINATION OF THE RELATIONSHIP BETWEEN BETA-TRICALCIUM PHOSPHATE/HYDROXYAPATITE MULTILAYERS AND THEIR DETERIORATION IN A SIMULATED BODY FLUID

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ABSTRACT

Considering that the 316LVM regarded as a medical-grade, is one of the most used biomaterials in the manufacturing of joint prosthesis, due to its low cost, and also its mechanical properties and resistance to corrosion, however, in the presence of body fluids, it degrades, liberating ions to the medium and causing rejection of the implant. An alternative to this phenomenon is to employ coatings of one or more materials that isolate the steel from environmental degradation. In this paper, multilayer coatings of hydroxyapatite/beta-tricalcium phosphate were deposited, with a variation in the number of layers (n=1, 10, 30 and 50 layers) at the constant thickness, to analyze the electrochemical behaviour as the number of layers increases. The scanning electron microscopy technique was used to determine the elemental composition of the multilayers and the Ca/P ratio. Atomic force microscopy analyses were also performed to determine the topography. It is obtained that the corrosion current density, decreases to a greater number of multilayers, offering an improved behaviour in the corrosion processes.

Keywords: Hydroxyapatite, Beta-tricalcium Phosphate, Corrosion, Multilayer.

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INTRODUCTION

A common material used in temporary or permanent prosthesis implants is stainless steel, especially 316LVM.[1,2] In the presence of body fluids, the problem with this material is that it suffers from pitting corrosion, releasing chrome and nickel ions into the environment, causing adverse reactions in the tissues around the implant and consequently rejection.[3-5] An important method of reducing the toxicity of the implant is to modify the surface of the stainless steel with the use of coatings, which, by preventing the direct contact of the alloy with the fluids and body tissues, significantly reduce the corrosion, limiting the release of metallic ions produced by the alloy.[6,7] Most used materials as coatings are ceramic biomaterials such as hydroxyapatite HA and beta tricalcium phosphate β-TCP, both of them have a critical and excellent role in biomedical applications.[8] This is due to their similarity with the composition of bone, especially HA which constitutes about seventy percent.[9,10] There are many techniques available for the application of coatings on 316LVM steel, but the implementation of layers by magnetron sputtering MS, presents important advantages in the deposition of thin films, such as: thickness control, homogeneous surface, deposition at different temperature.[11,12] Additionally, the use of the magnetron sputtering technique for the application of alternating bi-layers, called multilayers, presents improved behaviour's by combining their properties and optimizing their biocompatibility.[3-14]

New studies on the combination of HA phosphates and β-TCP, analyzed the formation of BCP two-phase calcium phosphate, presenting a variety of advantages in biological applications, such as bone defect filling[13] application of thin films of BCP, by electron evaporation technique, on a silicon substrate, showing that the technique is viable in the application of this type of coatings.[12-14]

In the present paper a multilayer coating of hydroxyapatite on beta-tricalcium phosphate HA/β-TCP was performed, by the magnetron sputtering technique via radio frequency RF, on stainless steel 316LVM, to study its properties, with the possibility of biomedical applications, for which it was performed;

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morphological characterization by atomic force microscopy AFM, structural by X-ray diffraction, and electrochemistry by Tafel polarization curves.

EXPERIMENTAL

For the preparation of multilayer samples of hydroxyapatite on beta tricalcium phosphate that have been deposited on AISI 316 LVM, which have been ultrasonically cleaned in a 15-minute arrangement of ethanol and acetone. The coatings were obtained by the r.f. magnetron sputtering technique (The magnetron sputtering techniques, is the most suitable for depositing ceramic materials, such as hydroxyapatite). Using targets of hydroxyapatite and beta-tricalcium phosphate with a purity of 99.99%, in a circular shape of 4 inches in diameter, with a total coating thickness of 3 µm. The substrates were subjected for 15 minutes to a bias voltage of - 400 V (r.f.) with a power of 60 W (r.f.) in an argon plasma (Ar) to remove any oxide layer. The coating thicknesses are uniform for each system, the continuity of the layers along the cross-section is observed without cracks or severe deformations, at the same time it is verified that the coatings have a total thickness of 1.3± 0.06 µm.
Through the combination of a mechanical rotary vane pump and a turbo molecular magnetic bearing pump, a vacuum is created until a pressure of $6x10^{-6}$ mbar is obtained, then it is brought to a continuous working pressure of 3. $8x10^{-2}$ mbar, at a constant Argon flux of 60 sccm (standard cubic centimetres per minute) and constant substrate temperature at 300 °C, to begin depositing the coatings at a power of 400 W for HA and 500 W for β-TCP, with a 56 MHz RF radio frequency source and a substrate polarization voltage of -20 V. The application of the HA/β-TCP multilayers proceeded, alternating the deposit of this, originating the application with a layer of β-TCP, in every case, and following the HA and alternating until attaining the number of layers required, where n represents the number of alternating bi-layers of HA and β-TCP. In each case the time was modified depending on the number of layers to be deposited and for a total time of 10500 seconds. Varying the number of bilayers, between n= 1, 10, 30 and 50, aiming for a constant total thickness in the coatings of 2 µm. Table-1 presents the times in seconds for each coating. The variations are originally performed as follows. n=1, n=5, n=10, n=15, n=20, n=25, n=30, n=35, n=40, n=45, n=50, and the experiments presented in the manuscript were performed for each of these variations. However, there are no differences between n=1 and n=5, so it was chosen to leave n=1, this same behaviour was generated for n=15, n=20 and n=25, it was decided to leave n=30; so, the difference in the results was determined for n=10 and n=30, the same for n=50

Table-1: Times for each of the Coatings

Multilayer Coatings	Duration per layer of HA / s	Duration per layer of β-TCP/s	Total, time /s
HA/β-TCP n= 1	5100	5400	10500
HA/β-TCP n=10	510	540	10500
HA/β-TCP n=30	170	180	10500
HA/β-TCP n=50	102	108	10500

The development of a multilayer coating of hydroxyapatite (HA) and beta-tricalcium phosphate (β-TCP) was to use their individual properties since these are bio ceramics with a bioactive, osteoconductive and biocompatible behaviour that allow them to be used in bone replacement mechanisms, thus generating bioactive surfaces. Also, because the requirements for implantable parts (prostheses) demand that the surfaces developed are multifunctional, that is, simultaneously resistant to corrosive, mechanical and tribological effects.
Multi-layer structure coatings are based on the periodic layering of alternating layers of different materials, so these structures improve the adhesion of the coating to the substrate by reducing internal tensions and material brittleness. Also, by reducing the thickness of the bilayers, there is an increasing reduction in internal stresses, an increase in hardness and critical load. The monolayer systems that have been identified for the monolayer of the hydroxyapatite coating, and the tricalcium phosphate, generate bonds that remain the same since both coatings are similar minerals (Apatites), hence the bonds and bonding energies present are similar and exhibit no differences in the form of monolayers.

RESULTS AND DISCUSSION

The Scanning Electron Microscopy (SEM) Analysis

Figure-1 illustrates the micrographs, carried out on the multi-layer coating of HA/β-TCP, where n corresponds to the number of bi-layers of the compounds (a) corresponds to n= 1 bilayer, b) n=10 bilayer, c) n=30 bilayer and d) n= 50 bilayers), on 316LVM stainless steel, where: maintaining the same thickness in all four cases of (2 μm). The similarity between the different coatings is observed (Table-2), this is because they are made up of the same compounds, however with a different number of layers, therefore they present the characteristic elements of the coating, calcium, phosphorus, and oxygen.[15,16] Other minor elements typical of steel 316LVM are also found, since the interaction of radiation with the sample reaches a volume greater than the thickness of the coating.[17,18]

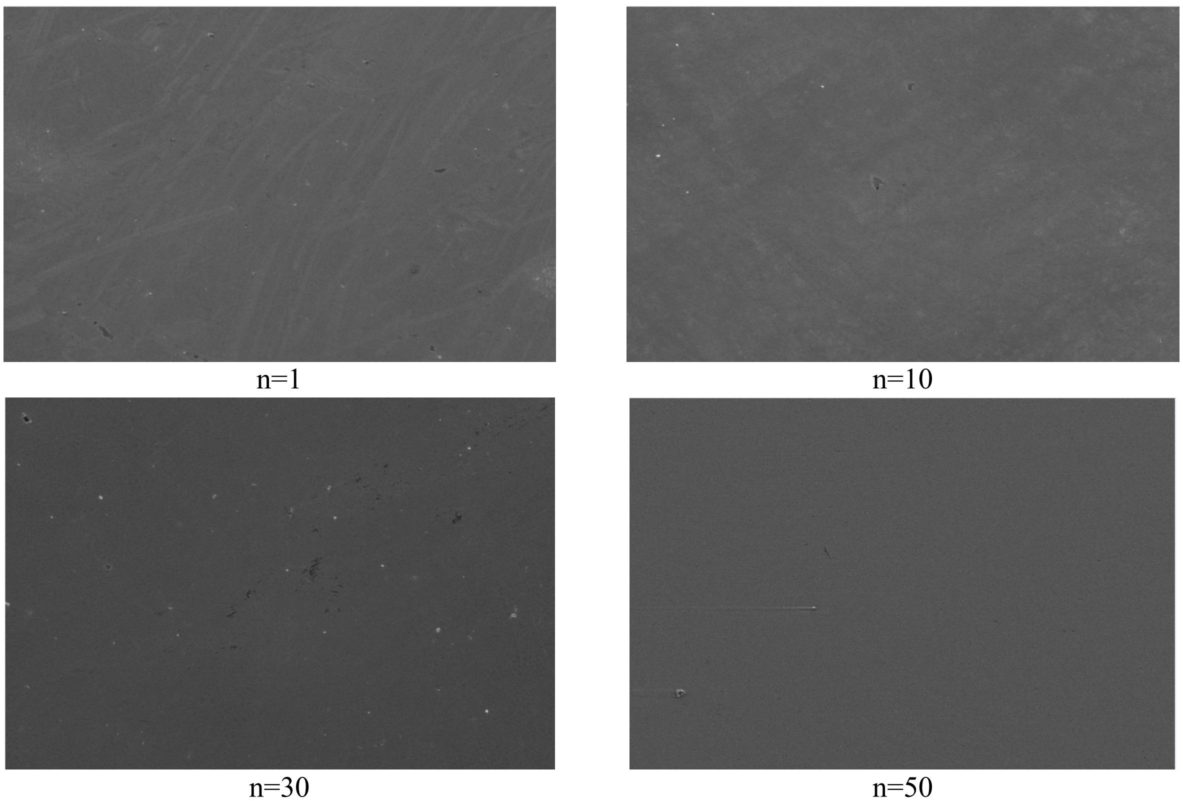

Fig.-1: Scanning Electron Microscopy (SEM) Micrographs of HA/β-TCP, the demarcated area is the region where the elements of the composition of multilayer EDS coatings are found with the respective variation.

The elemental composition of HA/β-TCP multilayer coatings with n=1, 10, 30 and 50 is indicated in Table-2, the characteristic elements of these coatings, such as phosphorus and calcium, are to be found with an average Ca/P ratio found respectively of 1.52, 1.55, 1.61 and 1.61, within the theoretical range of biphasic calcium phosphate, that is the combination of β-TCP and HA (β -$Ca_3(PO_4)_2$ + $Ca_{10}(PO_4)_6(OH)_2$, which is between 1.55 and 1.65, exhibiting well homogenized and integrated multilayers.[19,20]

Table-2: Composition of the Multilayer Coating with n = 1 of HA/β-TCP on AISI 316LVM identified by EDS

Element/ Average	n=1 %At	n=10 %At	n=30 %At	n=50 %At
O k	56,04	55,13	35,47	54,52
P k	16,02	15,87	21,88	15,78
Ca k	24,31	24,56	35,22	25,35
Cr k	0,91	0,89	4,27	0,88
Fe k	2,42	3,22	3,00	3,13
Ni k	0,31	0,33	0,17	0,33

Total	100,00	100,00	100,00	100,00
Ca/P	1,52	1,55	1,61	1,61

Analysis by Atomic Force Microscopy

The topography of the HA/β-TCP coatings reveal a very regular surface of ridges and valleys, typical of crystal growth, as the coatings are applied, exhibiting a homogeneous texture (Fig.-2). It is observed, crystal growth profiles in an angular shape oriented to a specific direction, which demonstrates by itself a homogeneity and optimal crystallization phenomena for the material.[21]

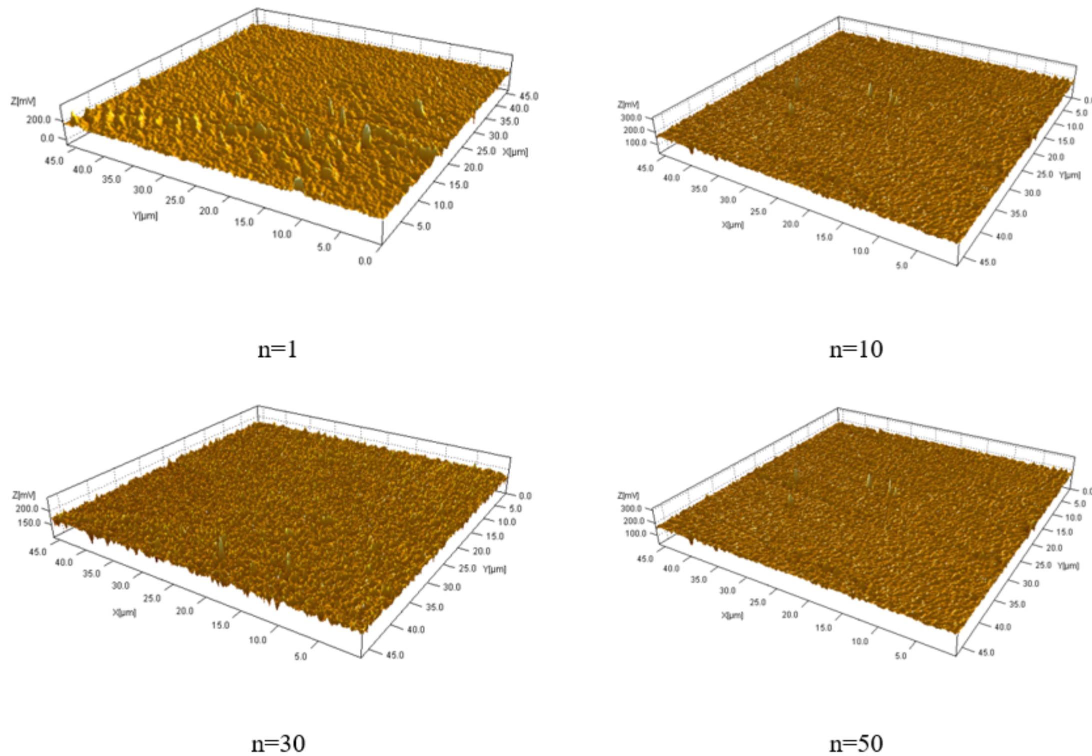

Fig.-2: Roughness Profile in Specific Sections of the Different Coatings, the Topographies for each of the Multilayers are observed

In Table-3, the values calculated for the arithmetical mean height (Sa) and the other reading ranges, such as maximum height (Sz), mean square height (Sq), maximum peak height (Sp) and maximum cavity height (Sv), are presented for each of the HA/β-TCP multilayer coatings. Such values exhibit a reduction that is influenced by the number of bilayers, where it can be seen the roughness behaviour of n=1, is the highest, but as the number of multilayers increases the roughness value decreases progressively, being the specimen with n=50 bilayers that presents improvement inhomogeneity, evidencing a better integration between the two compounds.[22]

Table-3: Surface Roughness Measurements Obtained by AFM

Multilayer	Sa (nm)	Sq (nm)	Sz (nm)	Sv (nm)	Sp (nm)
n= 1	32.287	41.361	379.60	164.27	315.33
n=10	27.757	36.532	362.29	145.60	216.69
n=30	20.575	26.915	268.77	187.55	81.219
n=50	16.002	20.327	163.21	85.516	77.692

Electrochemical Evaluation

Corrosion study of the $(HA/\beta\text{-}TCP)_n$ multilayer coatings was carried out in a potentiostat, under static conditions, using Tafel extrapolation of polarization curves. The samples have been exposed to the lactated Ringer's salt solution at a temperature in the laboratory was between 21 and 22 degrees., employ two other

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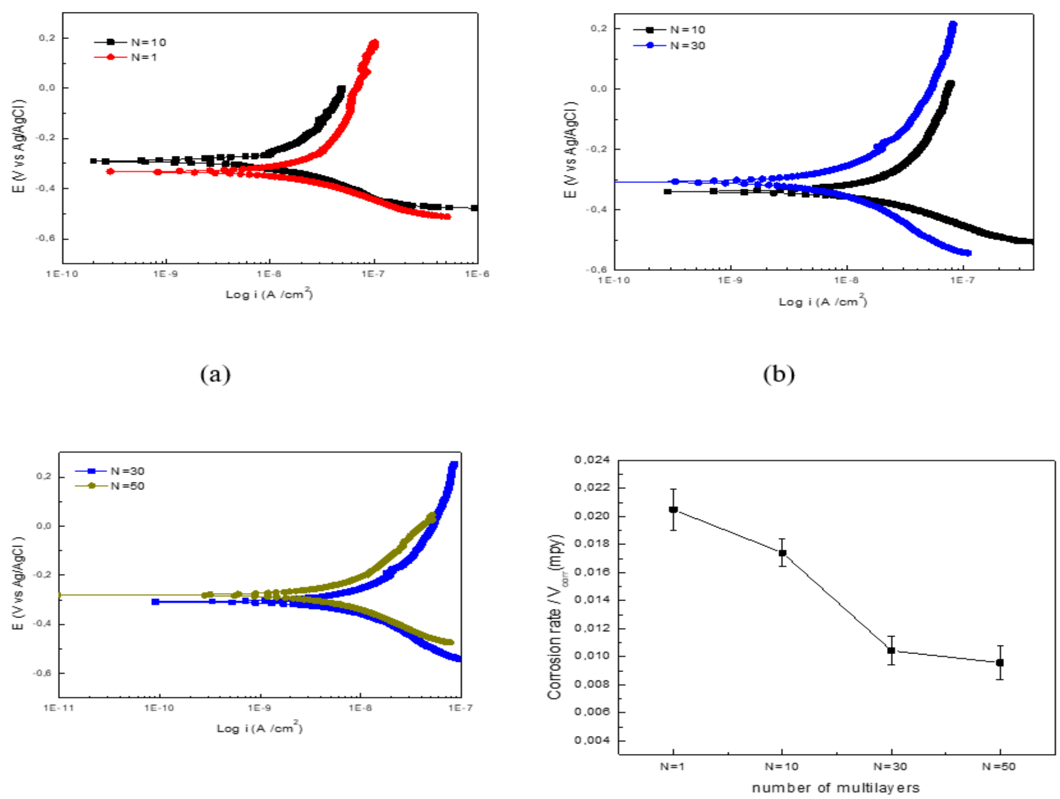
common reference half-cells of a silver chloride reference electrode, a platinum counter electrode, and as an electrode in the different samples with the multilayer coatings, at a scanning rate of 0.5 Millivolts per second in a voltage range of -0.25V to 0.5V, using an exposure area of 1. 54cm^2 in contact with lactated, as a biological fluid. In figure 3, section (a), (b) and (c), the electrochemical polarisation behaviour of Tafel, for multi-layer coatings of (HA/β-TCP)$_n$ on 316LMV stainless steel, is illustrated, the corrosion potential Ecorr, becomes more electropositive, reducing the coating activity, and the corrosion current density Icorr, decreases, as a result of the lower number of charges that are released from the material, resulting in a lower corrosion rate[12]. A very important aspect is that these are the same materials in each case and that the number of layers depends only on the number of layers, which demonstrates the functionality of the system. This is reasonable since the combination of the two materials, by this technique, causes the formation of a microstructure of smaller nanometric grains that give the formation of a superlattice[23]. But also, that the number of layers between 30 and 50 is adequate since stabilization is observed, since the difference of measurement of the corrosion rate is no more significant, revealing that a higher number would be irrelevant, as shown in part (d) of Fig.-3.



(a) (b)

(c) (d)

Fig.-3: Tafel Polarization Curves for HA/β-TCP Multilayer Coatings on 316LVM Stainless Steel, where they are compared: (a) N=1 with N=10, (b) N=10 with N=30, (c) N=30 with N=50 and (d) the Corrosion Rate as a Function of the Number of Multilayers

CONCLUSION

The analysis by SEM indicated the presence of the characteristic elements of the coatings, through a Calcium/phosphorus ratio of between 1.52 and 1.61, typical of biphasic calcium phosphate. As the number of bilayers increases, they become more uniform and integrated, as is evidenced in the micrographs of AFM, since the more bilayers the roughness values decrease.

Tafel polarization analyses indicated that the number of layers, the current density and the corrosion rate decreased, as expected from the integration between the two materials, while between n=30 and 50 multilayers the process stabilized, with the result that a high number would not be relevant.

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