Corrosion resistance hydroxyapatite assessment and tricalcium beta phosphate coating, deposited on stainless steel low carbon vacuum melted

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Abstract. 316 stainless steel low carbon vacuum melted, used for surgical implants, has good corrosion resistance, but it is degraded in the body fluids presence, generating problems for the receiver, therefore it is necessary to apply coatings that improve their biocompatibility. In the current work hydroxyapatite and tricalcium beta phosphate coatings were applied on 316 stainless steel substrates, by the radio frequency magnetron sputtering technique, with a 2 m thickness for possible biomedical applications. The coatings characterization was performed, using scanning electron microscopy, found the Ca/P ratio of 1.639 for hydroxyapatite and 1.515 for phosphate, the friction coefficient was additionally evaluated by pin on disk tribometer, with a lower coefficient of beta tricalcium phosphate in relation to hydroxyapatite. The corrosion evaluation was carried out using the electrochemical polarization technique Tafel, in Ringer lactate, as simulated biological fluid. It was observed that the coatings improve the steel electrochemical behavior and between the two coatings the one that best behaves is the tricalcium beta phosphate, with a corrosion low rate.

1. Introduction

Biomaterials have evolved according to expectations in quality of life, health care and as a consequence the increase in global longevity [1], increasing the adult population, potential prosthetic patients, both dental and knee and hip joints, and fixation elements, screws, among others [2].

In biomedical bone replacement applications, one of the materials used for their biocompatibility properties, bending, fatigue, corrosion resistance and low price is stainless steel 316LVM [3]; however, it is susceptible to localized corrosion from bites, cracks and subsequent fracture, in contact with physiological fluids, which accelerate aging, in addition to the detachment of chromium and nickel ions around the implant, extremely toxic and aggressive to the body [4-8].

In the sciences of biomaterials, different coatings have been made and by various techniques, such as polymeric, ceramic and composite; particularly ceramic coatings such as hydroxyapatite (HA) and beta tricalcium phosphate (β-TCP), which play a critical and excellent role in biomedical applications [9-11]. This is due to its similarity with the bone composition, especially the HA which constitutes about seventy percent [12,13], so it allows it to dissolve in the bodily fluids and precipitate in the form of apatite, helping cell proliferation [14,15]; therefore the use of these phosphates as protective materials of 316LVM stainless steel is considered relevant and appropriate.

Compared to the techniques used in the coating process, the sputtering magnetron (SM), presents important advantages in the films application on substrates such as; the thickness control, surface
homogeneity, low temperature deposition, the possibility of evaporating different materials, the deposition of mixtures and alloys, maintaining the composition of the target, the good adhesion of the deposited film and the control of the spraying speed of the target [6-8].

On the other hand, before taking a decision on the material utility and/or coating in biomedical applications, studies on corrosive behavior are required [11], so in this work it is proposed to evaluate the behavior against the coatings corrosion of HA and β-TCP, deposited on 316LVM stainless steel, by the technique MS of RF radio frequency. In order to make appropriation of knowledge and technological development in the country.

2. Experimental procedure

2.1. Materials
316LVM stainless steel rod with a diameter of 8.99 mm, white HA and β-TCP with a purity of 99.9%, Argon gas and sputtering magnetron.

2.2. Sample preparation method
Stainless steel samples of 316LVM, with a height of 5 mm, were cut and machined, exposing a circular area of 2.54 cm², this surface was prepared for the coatings application, making a polishing with sands and cloths, up to mirror brightness, an ultrasound cleaning with isopropyl alcohol for 15 minutes, with acetone for another 15 minutes, and then carried inside the deposition chamber for cleaning, by ionic bombardment for 20 minutes to ensure coatings good adhesion.

2.3. Conditions for coatings application
It becomes empty, with the combination of a mechanical rotary pallet pump and a molecular turbo of magnetic bearings, until reaching a pressure of 6x10⁻⁶ mbar, then a constant argon flow of 60 sccm (standard cubic centimeters per minute), to bring to a constant working pressure of 3.8x10⁻² mbar, to obtain coatings. The substrate temperature was constant 300 °C and whites were deposited at a power of 400 W for HA and 500 W for β-TCP, with a RF frequency radio source of 13.56 MHz and a time bias polarization voltage of -20 V.

3. Results and discussions

3.1. Scanning electron microscope
Analysis was performed with the scanning electron microscope (SEM) by the technical energy dispersive X-rays spectroscopy (EDS), evidencing the coating presence of HA and β-TCP, on stainless steel 316LVM, by the constituent elements presence of this calcium phosphates type, such as phosphorus, calcium and oxygen and traces chromium, iron and nickel, this because the electrons reach the steel substrate.

Table 1 shows the basic chemical composition as a percentage by weight, where the ratio of Ca/P of 1.515 for beta-tricalcium phosphate and 1.639 for hydroxyapatite was found, being in accordance with the information found in the literature of 1.5 and 1.67 respectively [12], evidencing each of the coatings presence.

3.2. Tribological test
The tribological properties were assessed using a pin on disk tribometer, using a pin, ball type with a diameter of 3.82 mm, made of bovine bone. In Figure 1, the friction coefficient is observed as a function of the path for uncoated steel and monolayer coating of β-TCP and HA. The graph shows important areas during the wear process; the first region shows a sudden increase in the friction coefficient due to the initial contact of the pin and the test piece from 0 m to 20 m of travel, then shows a slight coefficient stability between 20 m and 100 m of travel, as a settlement consequence of resulting from the decrease in the initial surface roughness [13].
Table 1. HA elemental composition and β-TCP coatings, on 316LVM stainless steel obtained by EDS.

| Element | HA average %At | β-TCP average %At |
|---------|----------------|-------------------|
| O k     | 53.70          | 52.84             |
| P k     | 17.07          | 14.70             |
| Ca k    | 25.90          | 23.95             |
| Cr k    | 0.79           | 1.19              |
| Fe k    | 2.28           | 2.91              |
| Ni k    | 0.26           | 0.31              |
| Total   | 100.00         | 100.00            |

Figure 1. Friction coefficient for distance, for uncoated 316LVM and with HA and β-TCP coatings.

Table 2 shows the tests results, such as: mass loss and friction coefficient of 316LVM steel, not coated and with the HA and β-TCP coatings. The parameters for all tests were: 100 rpm (revolutions per minute), 100 travel meters, load of 3 newtons, radius of circle 7 mm, pin of bone and diameter of 3.82 mm. Noting that the coating best performance is the tricalcium beta phosphate, with a coefficient of 0.14, which implies less wear and thus better performance by conserving and reducing energy, increasing the part in service.

Table 2. Test parameters and coefficient of friction for monolayer coatings of β-TCP and HA, on 316LMV steel and uncoated steel.

| Parameters                  | 316LVM | Value β-TCP | HA  |
|-----------------------------|--------|-------------|-----|
| Pin mass before (mg)        | 75.70  | 76.34       | 77.92|
| Pin mass after (mg)         | 75.72  | 76.35       | 77.93|
| Samples mass before (mg)    | 5920.30| 5957.00     | 5942.40|
| Samples mass after (mg)     | 5920.00| 5956.60     | 5941.90|
| mass pin loss (mg)          | 0.40   | 0.10        | 0.10 |
| sample mass loss (mg)       | 0.30   | 0.40        | 0.50 |
| Coefficient of friction     | 0.21   | 0.14        | 0.16 |

3.3. Evaluation of the corrosion

The coatings corrosive behavior was evaluated under static conditions, using a Gamry galvanostatic potentiostat, model PCI-4. The samples were analyzed through the anodic polarization curves Tafel. The test pieces were placed in contact with Ringer’s lactate saline at room temperature using a cell composed of an against electrode of platinum (CE), a reference electrode (ER) of Ag/AgCl and as a working electrode (ET) in the different test pieces, of 316LMV, not coated and with the coatings of HA and β-TCP, with a sweep rate of 0.5 mV/s in a voltage range of -0.25 V to 0.5 V, using an exposure area of 1.5 4cm² in contact with Ringer’s lactate, as biological fluid, as shown in Figure 2.
In Figure 3, it can be seen that the corrosion potential $E_{corr}$ shifts to the less negative direction and the larger current corrosion density $I_{corr}$, which causes further the material, degradation for stainless steel 316LVM without coating [14]. In the coatings it is observed that the potential becomes more negative, being less for $\beta$-TCP followed by HA and lower current density for $\beta$-TCP, then the beta tricalcium phosphate coating is the one with the best corrosion performance.

Table 3 shows the Tafel analysis information, such as the corrosion potential $E_{corr}$, corrosion current density $I_{corr}$ and corrosion rate of stainless steel 316L uncoated, and coated with HA and $\beta$-TCP, consistent for this material type deposited from behind techniques [15].

| Surface or coating | $-E_{corr}$ (mv) | $I_{corr}$ (na.cm²) | Rate of corrosion (mpy) |
|--------------------|------------------|---------------------|------------------------|
| AISI 316L          | 366              | 338.000             | 0.152                  |
| HA                 | 446              | 22.090              | 0.081                  |
| $\beta$-TCP        | 528              | 7.674               | 0.022                  |

4. Conclusions

Single layer coatings of $\beta$-TCP and HA were applied with stainless steel 316LVM by magnetron sputtering with a thickness of 2 m respectively. The EDS results obtained in a SEM confirm the coatings elementary composition and the Ca/P relationship, consistent with the one found in the bibliography.

The tribological test performed with pin on disk shows an improvement in the friction coefficient, in systems with coatings in relation to uncoated steel, and between the two coatings the $\beta$-TCP has the lower value than HA.

The electrochemical behavior study was carried out by Tafel, showed that the coatings protect 316LMV steel from corrosive processes and that $\beta$-TCP has the lowest corrosion value velocity compared to HA.
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