DEVELOPMENT OF BIOACTIVE COATING ONTO COBALT BASE ALLOY BY ND:YAG LASER TREATMENT

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In this investigation, a coating of Hydroxyapatite (HAp) powders was made to the ASTM F75 cobalt base alloy to generate a dense coat of Hap using technique the Nd: YAG of laser deposition and generating a union on the surface by fusion using pulses, varying the parameters: power, energy by pulses, scanning speed and repetition frequency by pulses. Subsequently the coatings were immersed in SBF to evaluate their bioactivity *in vitro* after 21 days, the coatings were characterized by X-ray diffraction (XRD), to identify the phases present on the surface and by scanning electron microscopy (SEM) to evaluate the structure and surface morphology, the atomic composition of the material deposited on the samples was determined by X-ray energy dispersion spectroscopy (EDS). The results showed the presence of the phases of the alloy and hydroxyapatite, without encountering undesirable phases, on the other hand, the formation and nucleation of apatite on the surface after *in vitro* tests was confirmed, confirming that this deposition technique It is feasible to be applied for cobalt base alloys.

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1. Introduction

In the actuality, one of the metalic biomaterials used to replace parts of the human body are cobalt base alloys, specifically the Co-Cr-Mo alloy (ASTM F75) [1], which is widely used as a bone replacement material, to its excellent mechanical properties, good corrosion resistance and appropriate biocompatibility [2], but presents a slight disadvantage, which is not bioactive [3]. Hydroxyapatite (HAp) is ideal for promoting bioactivity between the implant and the tissue, since it is a bioactive ceramic material that promotes osseointegration when it is in contact with blood plasma [3]. Hydroxyapatite also shows a remarkable osteoconductivity, which is a property of a material that stimulates new bone formation and remains close to or adheres to the surface [4]. However, its mechanical properties are deficient, compared to those of a metallic biomaterial.

Because Co-Cr-Mo alloys (ASTM F75) are bio-inerts, other techniques to generate a superficial coating have appear such as: sol-gel [5], electrophoretic deposition [6], biomimetic coatings [7], simultaneous vapor deposition [8], plasma sprayed [9], thermal treatment [10], which characteristics of analysis in general are: adhesion, thickness, porosity and bioactivity generated, as well as the disadvantages: poor adherence, modification of mechanical properties of substrates, cracks and scalable techniques.

With the laser deposition technique, can be obtained: the fusion of powders on the surface, the coating of materials, even more complex processes such as the manufacture of additives such as laser network (LENS), selective laser sintering (SLS) and injection by laser fusion [11].

The equipment to perform the coating is a pulsed Nd: YAG, which uses a laser beam that has yttrium oxide and crystalline aluminum whose network acts as the host since it is doped with

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neodymium, which improves the coherence and directionality of the beam generating a melt in very small spaces and very short times affecting only the substrate surface [12].

The purpose of this research is to generate a highly bioactive surface in ASTM F75 cobalt base alloy by of laser surface treatment, using HAp powders as a coating, to generate a fusion bond on the surface between the ceramic material and the metal, to evaluate its bioactivity in simulated physiological fluids.

2. Experimental

2.1. Materials

To generate the coating, powders of HAp (< 0.2 μm, ≥ 97 wt%, Sigma-Aldrich) were used as precursors. The Test samples (7 mm x 7 mm x 7 mm) were prepared ussing the process based on the ASTM F75 standard (Co-Cr-Mo) for alloys with biomedical applications [1], which were used as substrates. Samples were polish and roughened on one side with abrasive SiC sandpaper (320, 500, 800), ensuring that the surface that will be in contact with the laser is smooth, fine and without imperfections. The surface was left dull seeking more absorption of the beam on the surface. Afterward the samples were washed in an ultrasonic bath with acetone for 15 minutes, to remove organic material before the deposition.

The HAp powders were uniformly distributed on the polished surface of the substrate and subjected to an axial pressure of 20 MPa for 2 minutes, with the intention of generating a thin compacted layer of HAp powders of approximately 1 mm in thickness, completely covering the surface.

2.2. Laser surface treatment

For the deposition of the HAp powders as a coating, a pulsed laser equipament Nd: YAG was used, which uses the power of the laser to melt the powders on the surface of the metallic substrate matrix [12]. The paramters alternated in the laser deposition process for the specimens were: power 90-100 W, energy per pulse 6-7 ms, sweep speed 0.3-0.5 m / s, repetition frequency per pulse of 4.5 Hz. was performed in the air where the laser beam was focused on the objective at a 90 ° angle with a suprasil lens (f = 30 cm), maintaining a distance between the substrate and the lens of 4 cm. At the end of the fusion process, the test pieces were individually isolated and stored in a desiccator.

2.3. In vitro bioactivity tests

For the in vitro evaluation of the samples, immersion tests were performed in simulated body fluids (SBF), the specimens were cleaned with deionized water. Each one of them was placed at the bottom of the polyethylene cans with 150 ml of SBF [13], later they were stored in an incubator at 37 °C of temperature, the incubation times were 7,14 and 21 days with the intention of evaluating the bioactivity in vitro of the surface treated during each of these periods. After the immersion period established for each sample, they were removed from the solution, washed with deionized water and stored in a desiccator.

2.3. Coating characterization

The samples coated with HAp by Nd: YAG laser deposition were characterized by X-ray diffraction (XR quantity, model PW3040), to identify the phases present on the surface of the specimens after being immersed in SBF, scanning electron microscopy (MEB, Philips, model XL 30 ESEM, in order to analyze and evaluate the capacity of apatite formation on the surface coated. The atomic composition of the surface of the specimens was determined by X-ray energy dispersion spectroscopy (EDS, software Genesis of EDAX.) The calculation of the Ca/P ratio was performed by semi-quantifying the EDS spectra.

3. Results and discussion

3.1. Coating characterizations

Fig. 1 shows the X-ray diffraction patterns (XRD) for the specimens that showed the best bioactivity results on the surface after being immersed in SBF at 21 days. Table 1 shows the relationship of the samples and the parameters of the laser surface treatment process to which they were submitted.

Table 1. Parameters of laser surface treatment by pulses, applied to the samples of the Co-Cr-Mo alloy with the HAp coating.

Sample	Average power (W)	Pulse duration (ms)	Travel speed (mm/s)	Pulse frequency (Hz)
a	80	7	0.5	4.5
b	90	7	0.5	4.5
c	90	6	0.3	4.5

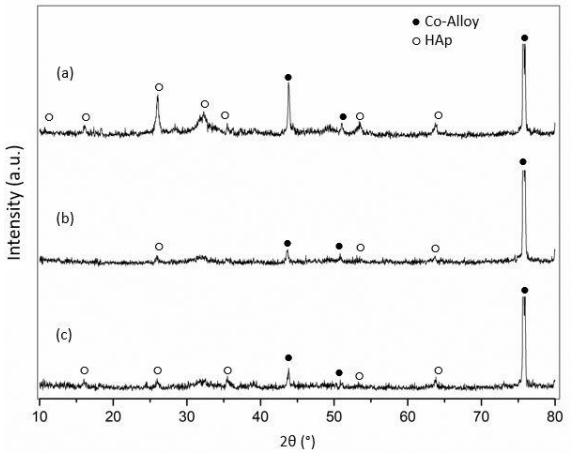

Fig. 1. Diffraction patterns of the metal specimens of the Co-C-Mo alloy with the HAp coating, using different parameters of the laser process after being immersed in SBF for 21 days.

The laser beam was used as a heat source to produce the fusion and densification of the HAp powders on the surface of the metal substrate (Co-Cr-Mo), as a result the coating material partially melts, resulting in the solidification and compacting of the coating and a smooth surface [14], in addition presents a strong metallurgical union with the substrate [15]. Under these treatment parameters the presence of other phases on the surface of the coating was not detected. The relation of the size of the reflection is a function of the change of the parameters of the laser treatment process: power, energy per pulse and the speed of scanning, while the power was lower the intensity of the reflections of HAp, the patterns present an amorphous phase to previous studies [16].

The results of the analysis by scanning electron microscopy (SEM) and X-ray energy dispersion spectroscopy (EDX) for the sample (1), after 21 days of immersion in SBF are shown in Fig. 2, the formation of spheres Fig. 2 (a), which indicate the formation of a surface layer of apatite, the EDX reveals the presence of Ca, P and O which are elements of the composition of the HAp, in addition to the presence of Mg which can be attributed to the SBF and C to the chemical composition of the Co-Cr-Mo alloy, the EDX reveals that there is no change in the composition of the coating. The atomic ratio of Ca/P on the surface for this test sample was 1.50.

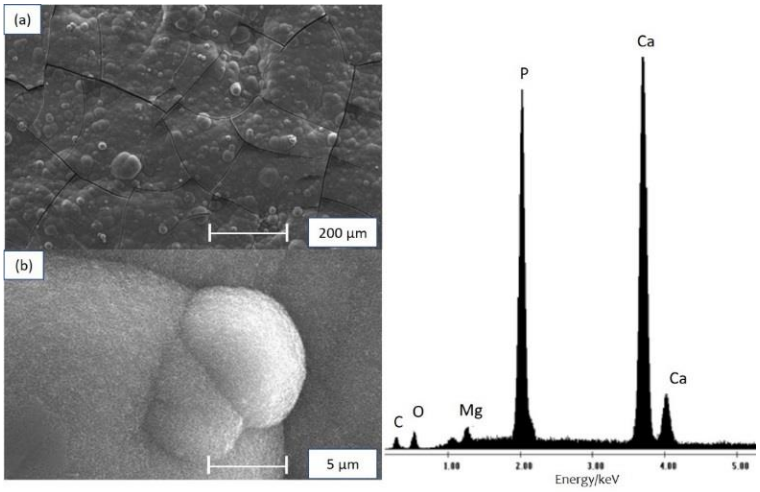

Fig. 2. Micrograph of the surface of the alloy CO-Cr-Mo coated with HAp of the specimen (1), after 21 days of immersion in SBF.

In Fig. 3 (a), of the micrograph of the specimen (2), a formation of micro fractures is observed in the coating at 200 µm, which may be due to the coefficient of thermal expansion induced during the laser treatment, in Fig. 3 (b) the spherical morphology of apatite is observed in detail. The EDX reveals the presence of Ca, P and O which are elements of the composition of the HAp, in addition to the presence of Si and Cr which are attributed to the chemical composition of the Co-Cr-Mo alloy, an atomic ratio of Ca/P of 1.44 was obtained for this specimen.

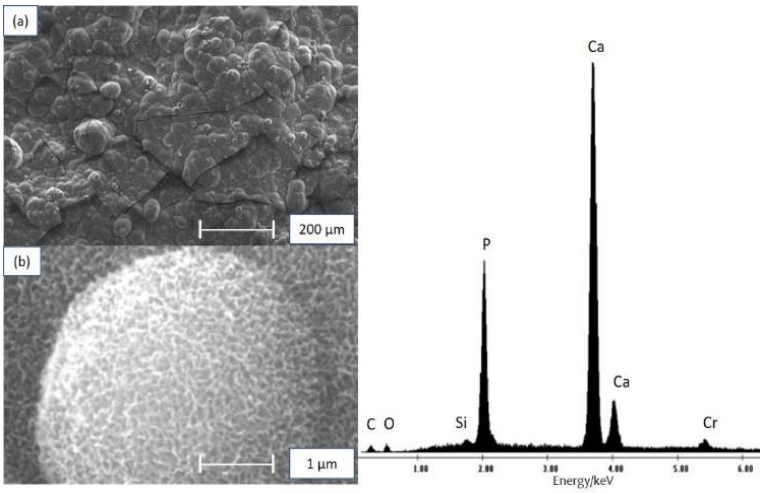

Fig. 3. SEM and EDS of specimen (2) of the surface of the alloy CO-Cr-Mo coated with HAp, after 21 days of immersion in SBF.

Fig. 4 (a) shows a dense formation of agglomerates on the surface of the micrograph at 50 µm after being immersed for 21 days in SBF, the EDX shows the presence of Ca, P and O which are elements of the composition of the HAp, in addition to the presence of Mg which is attributed to the SBF, the atomic ratio was 1.52 of Ca/P for the test sample (3).

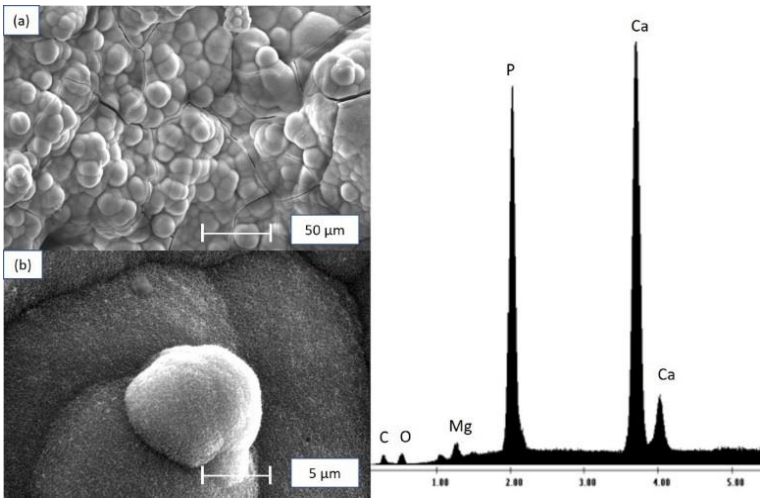

Fig. 4. Micrograph of the specimen (3) of the CO-Cr-Mo alloy coated with HAp, after 21 days of immersion in SBF.

The atomic ratio Ca/P of the three samples were slightly low (1 = 1.50, 2 = 1.44, 3 = 1.52), compared with the ideal Ca/P ratio for hydroxyapatite (1.68) [17], despite this the test samples showed a high bioactivity on the surface and are within the range of apatite osseum formation (1.2-1.7) [18].

4. Conclusions

Because the use of the pulsed Nd: YAG laser deposition technique, dense bioactive coatings of HAp were obtained on the surface of the metal substrates (Co-Cr-Mo). Most of the laser power was transmitted and dispersed with the HAp powders and finally absorbed by the metal substrates through a succession of pulses of short duration. Through the mentioned technique and parameters, the presence of some undesirable phase was avoided, such as chromium oxides, which can reduce the amount of available sites to generate the nucleation of apatite on the surface [3]. This was verified through the analysis of the samples by X-ray diffraction (XRD) and it can be attributed to the fact that the heat input is minimal, the heating is localized and it reduces the thermal distortion, which does not generate phase transformation. During the coating, the HAp powders are maintained at a low temperature before being trapped in the metal surface.

After the samples were immersed for a period of 21 days in SBF, the formation of apatite on the surface was observed in each one of them, through the MEB analysis, which denotes a bioactive behavior and with the EDS analysis the presence was revealed of characteristic elements in the nucleation of apatite (Ca, P). The Ca/P ratio was not ideal, but they are within the range of bone apatites (1.2-1.7).

With the use of the Nd: YAG laser surface treatment process, a highly bioactive surface was obtained in the ASTM F75 cobalt base alloy using HAp as a ceramic material, which considerably promoted the nucleation of apatite on the surface of metallic substrates.

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