ELECTRODEPOSITION OF HYDROXYAPATITE COATINGS ON STAINLESS STEEL 316 L

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Abstract *The problem of increasing the quality of older people life witch suffers of bones and dental disease has led to important research for the development of biocompatible materials with high resistance to the action of biological factors and to the mechanical stress.*
The present study has like object to obtaining hydroxyapatite coatings on stainless steel using electrochemical method. By varying the deposition conditions were obtained layers with different coverage and morphologies. The hydroxyapatite deposits were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). The method used does not require large investments and by optimizing the parameters may be obtained deposition that present interest for the biocompatibility study.

Keywords: hydroxyapatite, characterization, deposition, coating.

INTRODUCTION

Biomaterials have received intense research in recent decades due to their use as replacement materials for different body parts and organs. They participate in: the establishment of a diagnostic device, or a substitute for a tissue or an organ, or a functional replacement device (assistance device) [1].
Another class of material used as a bone tissue for implants includes calcium phosphate, especially HAP. Due to its excellent biocompatibility and corrosion resistance, hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$) is one of the most promising ceramic materials. For the improvement of the ceramic materials properties based on HAP, are used reinforcing elements made from metallic or polymer materials. In addition, there are used bone implants made of metal or alloys covered with HAP [2-3].
One of the most important clinical applications of HAP is represented by layers deposited on metal substrates. These deposits have a series of essential functions. First of all, they permit stable fixation of the implant in human bone and reduce the adverse reactions. This is because of the fact that it feeds the bone tissue with a biocompatible substance [4]. Also, the films of HAP reduce the diffusion of metallic ions from the implant, towards the biological tissue and protect the metallic surface from the aggressive attack of the environment.
The principal properties asked for a coat of HAP are: phase stability, high crystalline, maintained stoicheometry (Ca/P=1, 67), high chemical purity, important adhesion voltage, high corrosion voltage, density, porosity control, the control of formation of nuclei and there morphology, homogeneity, low reabosporbtion in tissues, impermeability between ions or/and titan atoms and high resistance to mechanic stretch [5]. HAP has tensile strength and bending low, good resistance to compression and a low resistance to shock.
The support metallic on which is settled the ceramic layer must provide high corrosion resistance and does not interact with living tissue and organic liquids forming toxic products.
For the first deposition was used as the support stainless steel 316 L, used for biomedical applications, especially for bone anchoring systems, such as dental and orthopedic implants. The interest for stainless steel in the medical field is due to its mechanical properties, its mechanic resistance, corrosion resistance and its excellent biocompatibility.

MATERIALS AND METHODS OF CHARACTERIZATION

As support material were used stainless steel 316 L plates. That is a strong steel alloy containing in particular chromium 17%, nickel 12% and molybdenum 2%. His microstructure, fully austenitic, is presented in fig 2.

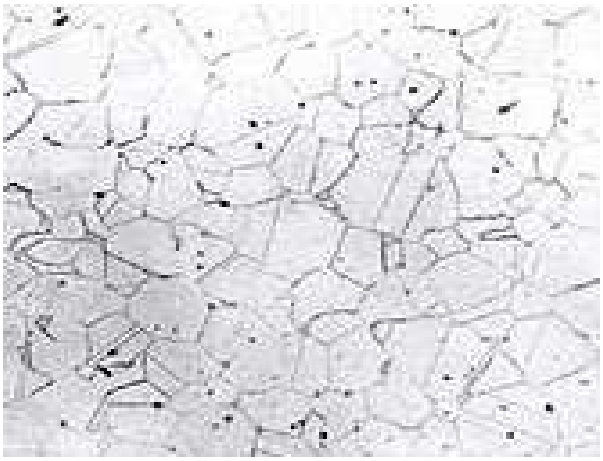

Fig. 1 Microstructure of stainless steel 316L, 3% nital etching, 100X

The samples are filled in the same conditions (agitator, the temperature of deposition: 90 degrees C, pH: 4.5, potential: -1.4 V), the only difference being the time used to deposit.
The samples were cut on the dimensions 10 mmx10 mmx2.5 mm. Before deposition, the plates were polished with abrasive paper of successive grades: 180, 320, 600, 1000, 2400, 4000 and alumina 8000°A.
The samples were cleaned with water, ethanol (10 min), and distilled water (5 min). Stripping electrolytic of samples was done in a solution of NaOH 0.2 mol/L for five minutes. After alkaline pre-treatment, samples were washed in distilled water for 5 min.
The electrolytic working solution in which the samples were immersed during the experiment is a solution which imitates a biological medium. This is a mixed solution of 0.61m moles Ca $(NO_3)_2$ and 0.36m moles $NH_4H_2PO_4$ dissolved in distilled water. [7, 8]
For the electrochemical method it was used an electrochemical cell with three electrodes dipped in solution: one reference electrode of calomel (Ag/AgCl) saturated with KCl, one auxiliary electrode (platinum electrode) and one work electrode. The device used for the experiment is a Voltalab GPS 201.

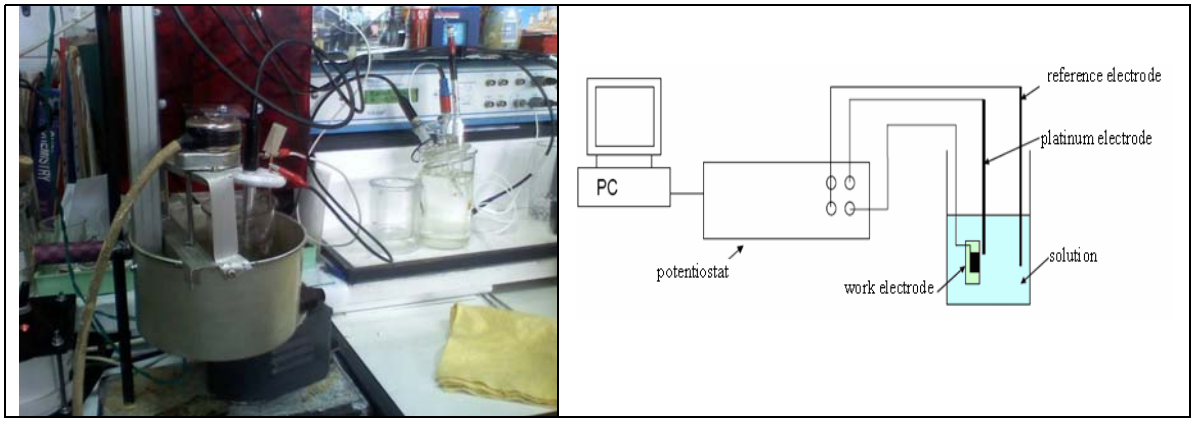

Fig. 2 Electrochemical cell used for deposition

Films formed on the metal support will be characterized using EDX, SEM and XRD. Scanning electron microscopy is more adapted for the observation of samples submitted because of the depth of the reaction field and increases the possibility of observing the most important morphologies. In addition, a system of X spectrometry with energetic dispersion permits a qualitative description of the chemical composition from the coatings of HAP electrodeposited.
The deposition of HAP is influenced by crystallographic structure and orientation of the metal used as substrate. This filing is distinguished from the typical process because of two distinct stages. In the first 12 minutes, formation of nuclei is instantaneous and is accompanied by growth. The sequential biodimensional nucleuses becomes progressive and is accompanied by a three dimensional growth. The crystal growth and electrodeposition properties can be significantly influenced by substrate surface preparation, chemical bath, oxygen content, pH, potential applied, and temperature and cells geometry [6]
The treatment in solution used in this study consisted in next steps: [9]
Reactions of oxido-reduction:

$$O_2 + H_2O + 4\,e^- \rightarrow 4(OH)^-_{ads}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2(OH)^-_{ads}$$

During the electrochemical deposition ECD, a lot of OH^- ions are formed in the reduction of water. The concentration of OH^- is sufficient to convert all HPO_4^{2-} into PO_4^{3-} using the following reaction:

$$HPO_4^{2-} + OH^- \rightarrow PO_4^{3-} + H_2O$$

HAP can then be deposited on the cathode surface by the following reaction:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2$$

In the coating limit, accordingly there is a sensible increase in the concentration of OH-(which increases pH) and phosphate ions. Presence is ensured by calcium nitrate, calcium, the presence of products is based on calcium phosphates formation more or less hydrolysis. [10].

EXPERIMENTAL RESULTS

The SEM microstructures of the calcium phosphate samples illustrates that in the sample deposited for 5 min (fig 5 a), is formed HAP nuclei, and is also observing that the HAP crystals begin to appear, but their growth does not occur. In case of the sample deposited for 40 min (fig 5 b), it is found that the crystals cover the surface of the sample but not totally. The analysis of sample deposed for 120 min, showed in Figure 3 (c), it is noted that the deposit is uniform, and covers the entire surface of the substrate.
The deposed realized between 40 and 120 min show an acicular crystalline structure of HAP coatings, but can also be observed that the growth is concentrated in one direction.

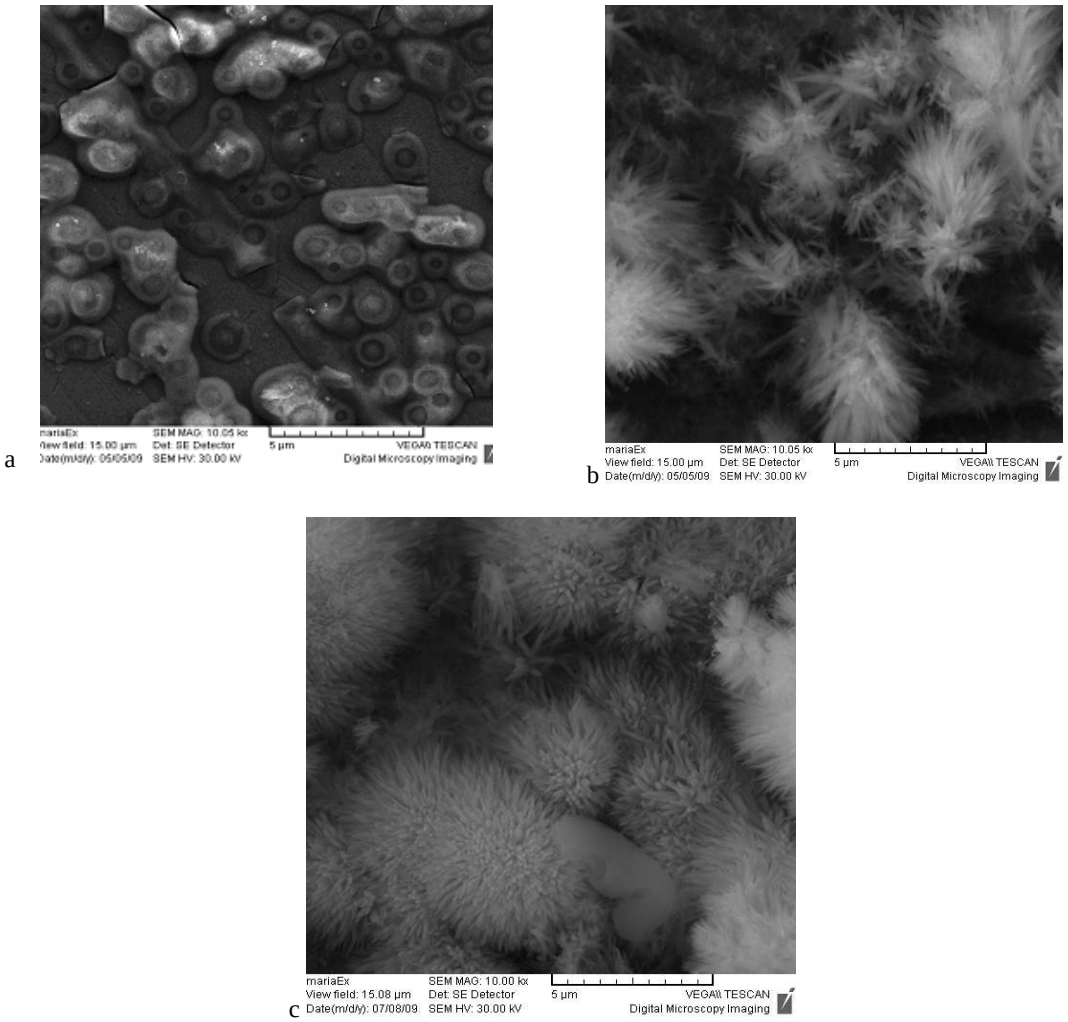

Fig 3 SEM micrographs of the calcium phosphate deposited at -1,4V and 90 ◦C for various times: (a) 5 min, (b) 40 min, (c) 120 min.

The SEM-EDX analysis showed that the peaks (in Fig. 4) are composed mainly of hydroxyapatite, but also the stainless steel 316 L due to the smolls tichness of the depositions. Molar ratio Ca / P is 1.67.

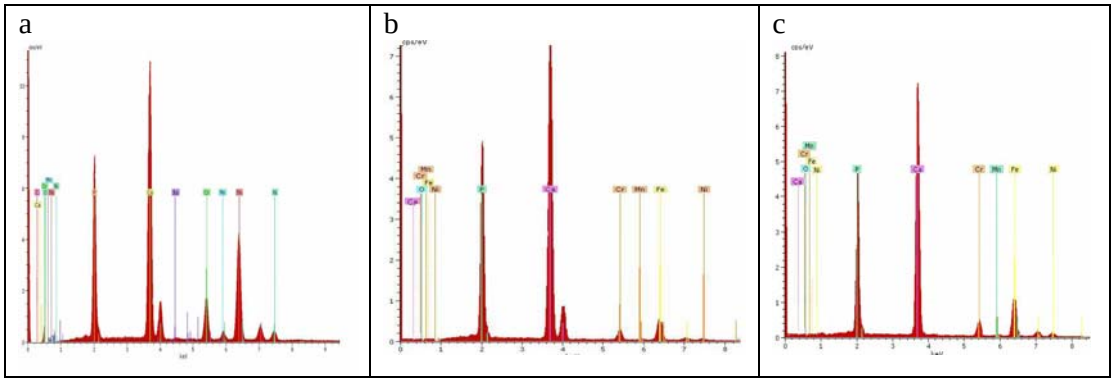

Fig. 4 The EDX results for: (a) 5 min, (b) 40 min, (c) 120 min.

EDX analysis of the coating shows the presence of Ca and P as major peaks due indicated that the coating composed of apatite phase. Also can see and substrate peaks, indicating that the cover was not thick enough to prevent penetration of X-ray beam up to the substrate surface.
In “Figure 5” are presented diagrams of X-ray diffraction obtained for the deposits made with HAP of stainless steel 316L substrate. In the XRD sample (fig 5), the hydroxyapatite peaks can be observed at different degrees. All peaks are very sharp, indicating that hydroxyapatite is well crystallized; also we can identify lines of diffraction of apatite and the substrate.

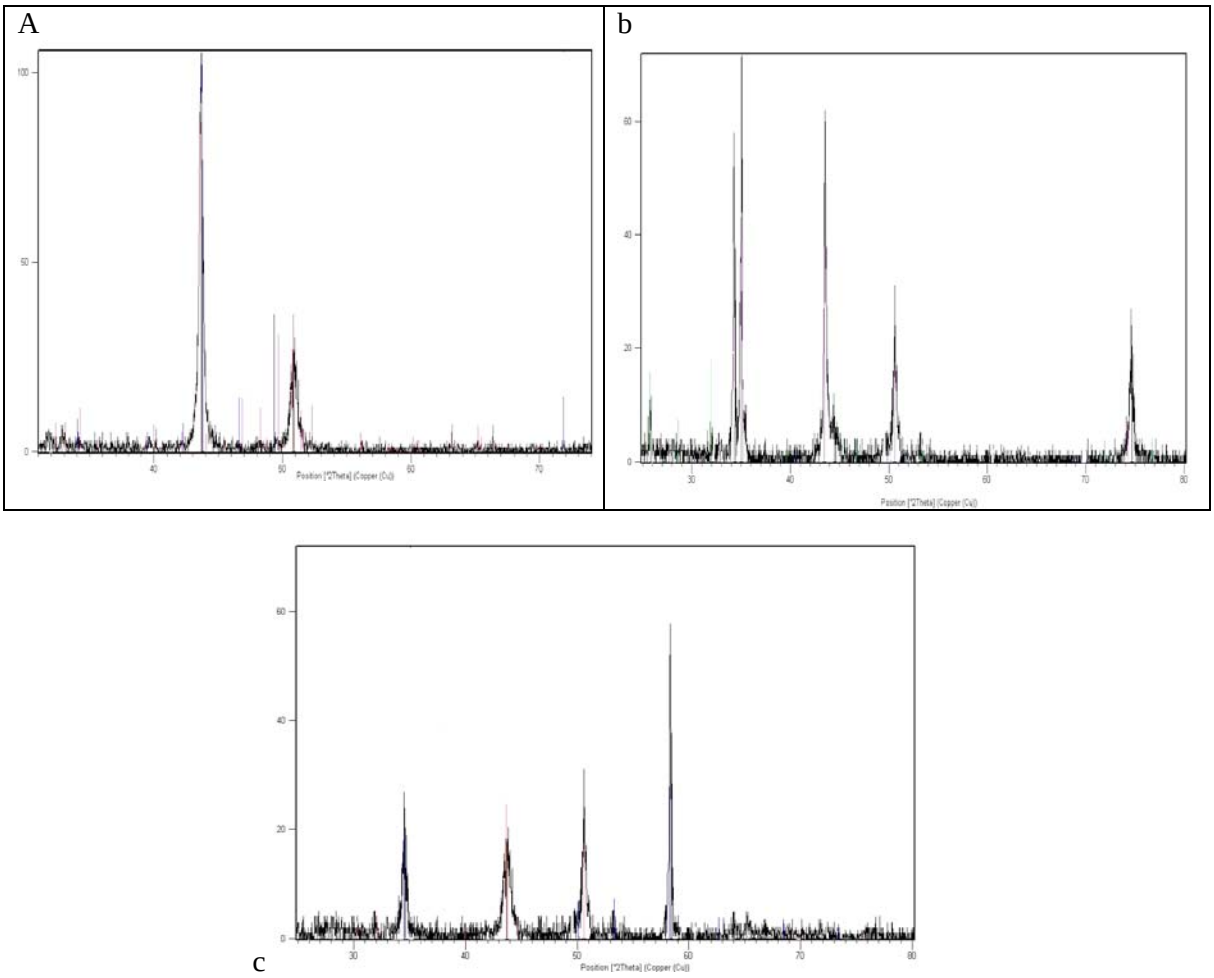

Fig.5 Diagram X-ray diffraction of HAP coatings made on stainless steel 316L support: (a) 5 min, (b) 40 min, (c) 120 min

To identify the components, I choose to represent the HAP with a rose color and stainless steel 316 L with green or blue color.

CONCLUSIONS

Coating of HAP was deposited on metal support by electrochemical method.

Electrochemical deposition is a potentially attractive process for synthesising bio ceramic coatings from aqueous solutions on metallic implant surfaces.

The same solution, for same conditions of temperature and voltage, increasing the duration of deposition determine substrate’s coverage growth and determine the increase of layer thickness.

In case of coatings deposed on short durations are observed only a nucleation process without crystal growth and an incomplete coverage of the substrate. In case of deposit with duration over 40 min is observed a significant increase of coverage and crystal growth. From the studied deposits, it’s

very important the layer realized at 120 min, this layer covers completely the entire surface of the substrate and has the growth crystals oriented.

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