NANOSIZED ELECTRODEPOSITED PHOSPHATE MASSES ON STAINLESS STEEL

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Materials as stainless steel, CoCrMo or titanium alloys are presently used for dental or orthopaedic applications in human body. To increase their stability and the biocompatibility, these materials are coated with phosphate masses such as hydroxyapatite or fluorohydroxyapatite. The present paper is focused on elaborating fluoridated hydroxyapatite masses on OL 304 substrate, using an electrochemical technique. Working parameters for thermal treatment after deposition were selected in order to obtain phosphate coatings with good molar ratios and low dissolution of the coating in saline solution. Coating characterization was performed using infrared spectroscopy, scanning electronic microscopy, contact angle measurements, and inductively coupled mass spectrometry. For longer calcination time the nanosized uniform fluoridated coatings formed on stainless steel have the molar ratio Ca/P closer to the one existing in bone, a better hydrophilic character and higher dissolution resistance.

Keywords: OL 304, phosphate masses, electrodeposition, coating process, stainless steel, inductively coupled mass spectrometry

1. Introduction

The human body is an aggressive environment towards the metallic implant materials as stainless steel, cobalt chromium alloys and titanium alloys, which are used nowadays after surface modifications which increase their stability properties [1,2]. In such way, the extension in use of stainless steel alloys as implant materials, is due to the various possibilities to enhance surface properties of such cheaper implant bio alloys comparing with other metallic materials [2,3]. Being not expensive and having good corrosion resistance in bio liquids, biocompatibility and mechanical properties close to the human bone, medical

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stainless steel are intensively used in dental and orthopaedic applications [4,5]. The stability is due to the mixture of native passive oxides layer [6] formed at their surface which was modified via various depositions for the enhancement of their performance [3,7].

Phosphate masses deposition have the advantage of bio activation when the final product is hydroxyapatite [8,9] or its precursor. The procedure was performed especially on Ti and Ti alloys [10]. Deposition of doped hydroxyapatite with elements such as fluoride [11], able to substitute OH^-, was proposed as well [12], leading to higher bonding strength and lower dissolution rate. According to the investigation of fluoridated hydroxyapatite on titanium [11] it was suggested that with a controlled moderate content of F^-, an enhancement of the coating properties could be reached, leading to a compromise among cell response and dissolution resistance of phosphate coating.

In this approach the novelty of the present paper is focused on finding the fabrication conditions of phosphate masses on cheaper substrate as OL 304. The procedure is electrochemical, as in the titanium case [11]. In order to obtain phosphates deposits with good molar ratios, the selection of the conditions regarding thermal treatment was performed.

As other novel aspects in electrodeposition investigation, regression equations were established for samples alloys using Origin software program and a prognosis for starting dissolution time have been proposed.

2. Materials and methods

The electrodeposition samples were OL 304. Samples were polished on SiC abrasive papers (600, 800 and 1200), then etched in HF 4% (2 minutes) and ultrasonicated in acetone: ethanol (1:1), for 15 minutes to remove particles from the SiC paper. Finally the samples were rinsed in distilled water and dried at room temperature.

According to literature data [11,13] the composition of the electrolyte solution for electrodeposition process is as following: 0.025M $(NH_4)_2HPO_4$ (3.2964g/L); 0.042M $CaCl_2 \cdot 2H_2O$ (6.1746g/L) and 0.012M NH_4F (0.4444g/L).

The chemical composition of working electrodes is presented in table 1.

Table 1

Chemical composition of working electrodes (according to ASTM A240)

OL 304 Alloy								
Element	Fe	Cr	Ni	Mn	C	P	S	Si
Weight %	Balance	17.5-19.5	8-10.5	0-2.0	0-0.07	0-0.05	0-0.02	0-1

Coating elaboration process

The coating process was performed at room temperature using an electrochemical cell with OL 304 as working electrode (cathode), platinum plate as counter electrode (anode), and Ag/AgCl as reference electrode. All the experiments were performed using a PGZ 301 potentiostat/ galvanostat controlled by a computer equipped with Volta Master 4 Software. Working parameters for coating process were: $-1mA/cm^2$ current density and 60 minutes for electrodeposition proces.

The initial pH of the electrolyte solution was 4.8. In order to enhance the deposition process of dense coating by the release of H_2 gas and production of HO^-, 3% H_2O_2 was added, with the volume ratio H_2O_2: electrolyte solution (1:10).

$$H_2O_2 + 2e^- \rightarrow 2HO^-$$

After electrodeposition all samples were calcinated to increase the crystallinity and purity of the coating. The calcination is beneficial for strengthening the bonds of apatite coatings. It was performed in 2 different ways, keeping in both situations the temperature at 450^0C, but increasing the heating time from 60 to 90 minutes. OL 304 samples were named with A for sample with thermal treatment at 450^0 for 60 minutes, and B for sample with thermal treatment at 450^0C for 90 minutes.

Coating characterization

The morphology and stoichiometry composition of OL 304 coated samples were carried out using a scanning electron microscope HITACHI, S-2600N Model. The elemental analysis was performed using an energy dispersive module (EDX).

The FT-IR spectroscopic analysis on coated OL 304 samples for fluoride detection was carried out with Perkin Elmer FTIR spectrophotometer (Spectrum 100 Model) with an attenuated total reflection accessory ATR.

Coating dissolution was studied using Inductively Coupled Mass Spectrometer ICP-MS, ELAN DRC-e, Perkin Elmer model. Working conditions were selected for coating dissolution in time [14]. The stainless steel samples were hold in saline solution (0.9% NaCl) for different periods of time.

The contact angle measurements of a drop of distilled water with the coating surface were done with a CAM 100 Equipment. The values represent the average from 5 determinations.

3. Results and discussion

Fig. 1 shows the chronopotentiograms obtained during the electrochemical deposition of fluoridated apatite coatings on two similar OL304 samples.

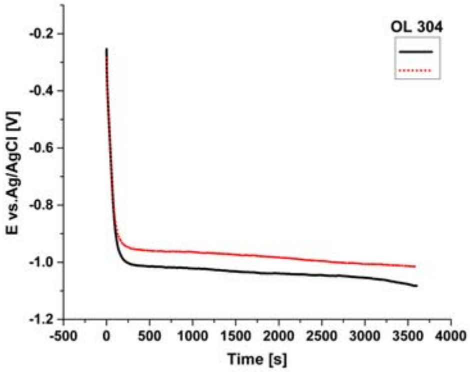

Fig.1. Chronopotentiograms during the electrochemical deposition of fluoridated apatite coatings on two similar OL304 samples

It can be observed that at the beginning of electrodeposition the potential decreased sharply and after 400 seconds it reaches a plateau in the domain of more negative potential values. The coatings on OL 304 samples start to dissolve, around 2500-2600 seconds.

Using an Origin soft program, regression equations and correlation coefficients for electrodeposition process are:

$$y_1 = -1.0391 + 0.77165\times e^{-0.01446x} \quad \text{with } R^2 = 0.94 \qquad (1)$$

$$y_2 = - 0.9839 + 0.69284\times e^{-0.01446x} \quad \text{with } R^2 = 0.93 \qquad (2)$$

The fluoride existence in the coating was confirmed from FT-IR spectra which presents characteristic bands at 671 and 674 cm^{-1}[11,15]. The spectra have all phosphate bands as well, according to previous papers related to hydroxyapatite deposition [16,17]. In this way the reaction proposed for deposition of fluoridated hydroxyapatite on titanium in literature [11] is suitable for such deposition on stainless steel according to the equation:

$$Ca_5(PO_4)_3OH + xF^- + xH^+ \rightarrow Ca_5(PO_4)_3F_x(OH)_{1-x} + xH_2O$$

3.1. SEM and EDX analysis

In Fig. 2 are presented the SEM images of coated OL 304 samples. Various morphologies with different compositions were obtained.

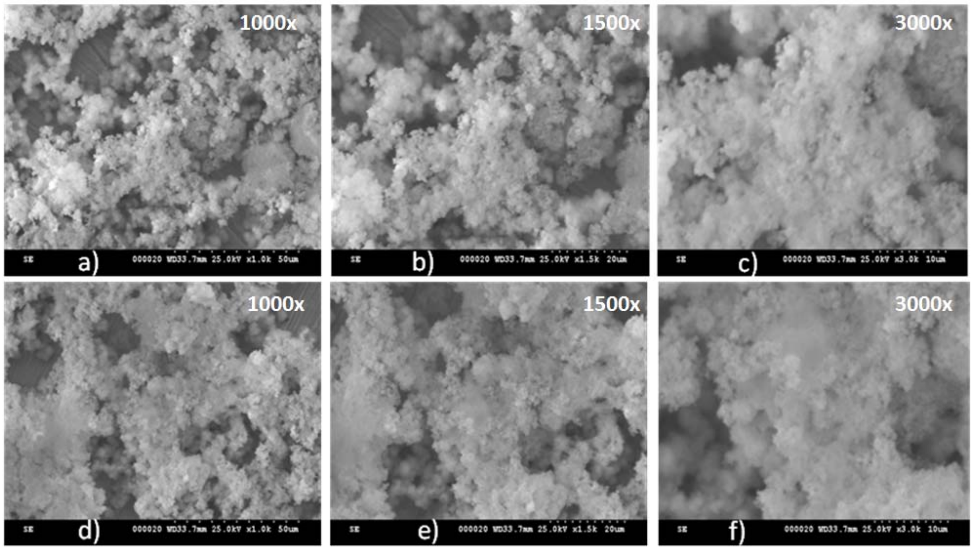

Fig.2. SEM images of apatite coatings for sample A (coated OL 304 calcinated at 450^{0}C for 60 minutes at increased magnitudes - a, b, c and for sample B (coated OL 304 calcinated at 450^{0}C for 90 minutes at increased magnitudes - d, e, f.

When comparing sample A and B it can be noticed that fluoridated apatite deposition on OL 304 is uniform which indicates a good adherence. Phosphate masses deposited on OL 304 have a spherical agglomeration morphology consisting in very small particles with nano size.

The EDX spectra analysis, Fig. 3, revealed the presence of calcium and phosphorus, but also the presence of ions substrate as iron, cobalt, chromium, molybdenum.

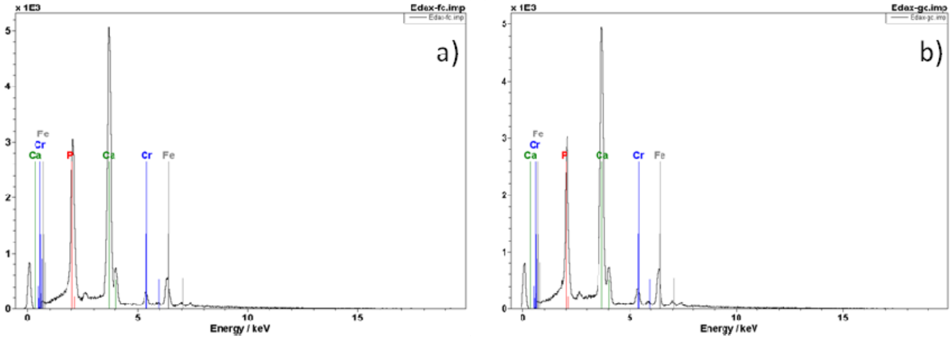

Fig. 3. EDX spectra of phosphate masses coatings: a) sample A; b) sample B

The EDX data allow the evaluation of molar ratio Ca/P as a function of calcination time. The obtained value for molar ratio of the sample A, was 1.85 and the value for sample B, coated OL 304 90 minutes at 450^0C was 1.74. These values show that the coated OL 304 samples are easily higher in calcium. However, for longer calcination time, the ratio Ca/P becomes closer to 1.67, which is the ratio in human bone that indicates a better biocompatibility of the coated OL 304 with the bone.

3.2 Coating dissolution

Ca^{2+} ion release in physiological serum (NaCl 0.9%) as it can be seen in table 2, it has smaller values for the sample calcinated longer time (sample B).

Table 2

Ca^{2+} ion release in NaCl 0.9%

Time (h)	Sample A Ca^{2+} (μg/mL)	Sample B Ca^{2+} (μg/mL)
3	0.97	0.95
9	0.97	0.92
72	14.87	14.97
84	15.58	14.58
96	15.50	14.61

The evolution in time of Ca^{2+}dissolution is presented in Fig. 4 together with corresponding regression equations. It is to point out that the curves aspect for both samples is similar with a linear initial part followed a plateau. Starting time for plateau initiation is shorter for sample B and corresponds to smaller amounts of Ca^{2+} ion release. Such experimental data confirm the improving of dissolution resistance for a longer calcination time.

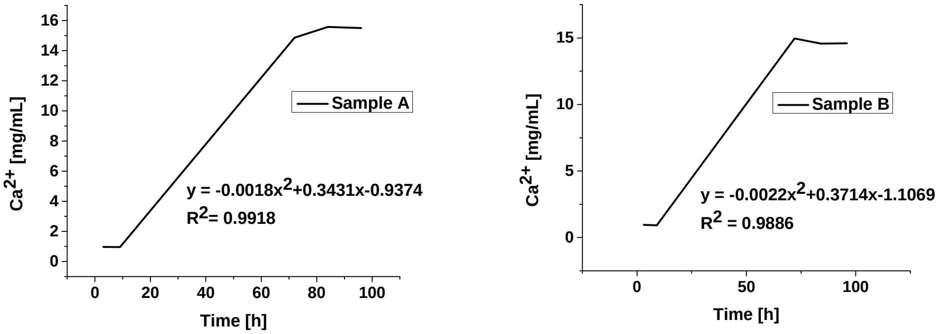

Fig. 4. Ca^{2+} ions release in 0.9% saline solution for sample A (left) and sample B (right)

Contact angle measurements lead to average values of 15 and 11 for sample A and B respectively. These values indicate that the hydrophilic/hydrophobic balance is in the hydrophilic domain. It is to point out that the sample B, calcinated for a longer time is more hydrophilic.

4. Conclusions

Electrodeposition of fluoridated phosphate masses was investigated using FT-IR, SEM and EDX analysis, and contact angle measurements. Based on experimental data we can confirm that the electrochemical method for apatite deposition on OL 304 is efficient one a longer calcination time enhances the coating properties.

Coatings are uniform, formed of spherical nanosize agglomerations. Molar ratios Ca/P in phosphate masses are close to the human bone being proper for longer calcination times. An increase of hydrophilic character of the sample calcinated for longer time was observed as well. In this case the calcium ion release in time is smaller, denoting higher dissolution resistance as well.

Aknowledgement

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