

Preliminary results on hydroxyapatite growth on advanced Ti-base alloy using electrophoretic deposition process

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In order to improve the biocompatibility of implantable Ti-based alloy deposition of hydroxyapatite (HA) thin layers represent a natural and proper solution for osseointegration process. In this paper we present the preliminary results of electrophoretic deposition of HA on Ti6Al4V substrate using an own experimental cell and HA suspension. The resulted layers were evaluated using scanning electron microscope (SEM) for HA layer morphological aspects and thickness and X-ray dispersive energy analyze (EDAX) for chemical considerations. The final products will be analyzed by "in vitro" and "in vivo" experiments.

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1. Introduction

The surface characteristics of dental implants are recognized as one of the most critical factors stimulating the osseo-integration process). For this reason, several attempts have been made to modify the implant surface composition and morphology in order to optimize bone-to-implant contact and improve osseo-integration. Currently, hydroxyapatite (HA) is widely used for implants as a coating material on implants for fixation and faster bone healing.

Deposition through electro-phoretic technique represents a method that uses the loaded particles movement in a suspension in the presence of an electric field. This electric field permit the formation of well established particles in thin layers modified on a layer indifferently of the layer shape or even in self standing thicker layers [1].

To obtain a successful technically deposition through electro-phoretic process few parameters must be respected and controlled like colloidal solution stability, deposition kinetic but also drying problems and layer synthesis if this operations are necessary. First applications of electrophoretic deposition process were applied in processing of ceramic materials and in production of covering layers.

New applications of electro-phoretic depositions suppose the decreasing of price in laminated composite materials case, obtaining of functional materials and bio-materials and moreover deposition through electro-phoretic process of ceramic materials has a high potential

for improving some applications like piezo-ceramic materials, ultra sounded biomedical elements, chemical sensors and multi-functional thin layers with or without bio-activity. Also this deposition method evolve like an important instrument in nano-technologies domain like a technique that permit the production of components at industrial scale and with nanometric scale dimensions like: nano-particles, nano-tubes or nano-rods [2].

This technique present a high interest in manipulating process of bio-materials and of biological components like natural polymers, proteins, bacteria's and cells. The process is useful for growth of thin films (polymers, pigments, ceramic or metallic materials) on any kind of surface of an electric conductive material. Since the local composition of the deposit during the electro-phoretic deposition process is straight connected to the concentration and composition of the suspension at the moment of deposition, this technique permit the processing of functionally graded materials with a continuous gradient in composition by adjusting the suspension composition in time.

Hydroxyapatite (HA) is a major component and an essential ingredient of normal bone and teeth. Hydroxyapatite makes up bone mineral and the matrix of teeth. It is hydroxyapatite that gives bones and teeth their rigidity. The response of hard tissue to implant metallic materials, calcium phosphate is probably the most compatible of materials known. In the last few years, much attention has been paid to hydroxyapatite as potential biomaterials for a bone substitute but those mechanical properties are far low from the metallic

materials. A good implantation of metallic biomaterials in the skeleton is evidenced by an ability to reach full integration of the non-living implant with the living environment of the bone. Biological apatites are made of nanometer-sized crystals and a poor crystallinity doubled by nonstoichiometry and a variety of ionic (cationic and anionic) substitutions, such as Mg for Ca, CO_3 for PO_4 or OH, F for OH, etc. The type and amount of the ionic substitutions in the apatite phase varies from the wt.% level (e.g. 3–8 wt.% CO_3) to the ppm–ppb level (e.g. Mg or Sr). The substitution and incorporation of ions affects the properties of apatite, such as lattice parameters, crystal size and crystallinity, which in turn influence the stability and solubility characteristics of HA.

Hydroxyapatite molecules can group together (crystallize) to form microscopic clumps. If these tiny crystals of hydroxyapatite are deposited by mistake in or around joints, they may cause inflammation of the joints and nearby tissues, such as tendons and ligaments, particularly causing rotator cuff problems in the shoulder.

Coatings of hydroxyapatite are often applied to metallic implants (most commonly titanium/titanium alloys and stainless steels) to alter the surface properties. In this manner the body sees hydroxyapatite-type material which it is happy to accept. Without the coating the body would see a foreign body and work in such a way as to isolate it from surrounding tissues. To date, the only commercially accepted method of applying hydroxyapatite coatings to metallic implants is plasma spraying [3-7].

Ti-based metals and alloys have achieved great success as medical implants. Chemically, titanium is a group IV transition element, its valence of 4 being the same as silicon. However, titanium and its alloys are not osteoconductive, and hence research has been directed towards modifying the surface of metallic materials using methods such as alkali and acid treatments, and further heat treatment. The chemical treatment results in the formation of an amorphous titania gel layer. The functional groups thereby formed are able to induce apatite nucleation and the formation of bone-like apatite, which in turn provides the most favorable surface for bone cell differentiation *in vitro* and bone bonding *in vivo*. In addition to sol-gel coating of titania, titania/HA composites on the surface of Ti have also been attempted to achieve improved bioactivity.

In this paper we present the results obtained by SEM and EDAX techniques on the thin HA layer deposited on Ti6Al4V through electro-phoretic process. We made in our own laboratory deposition cell for HA suspension solution.

2. Experimental details

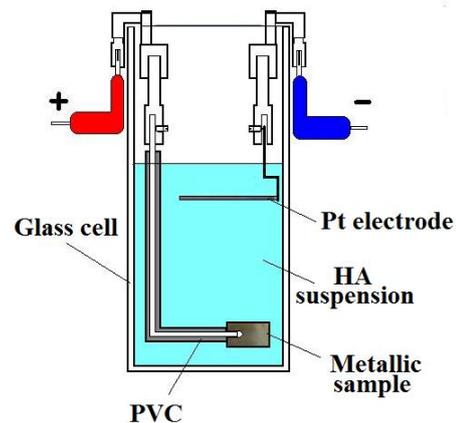
To obtain HA deposited layers we use an electrophoretic equipment with a Consort EV 261 power supply (tension 0-600V, current from 0 to 1000 mA and power 0-300W with PC connection), and an own deposition cell presented schematically in Fig. 1 a) and in

real image in b). There was hydroxyapatite superficial layers deposited using similar deposition parameters.

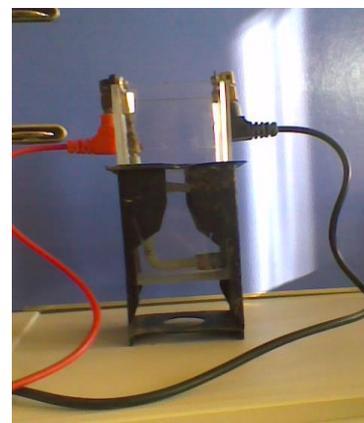
Colloidal processing offers the potential to reliably produce ceramic films and components through control of the initial suspension and its evolution during shaping.

The presence of the electric field also offers the possibility to orient anisotropic powders allowing texturing of materials. The equipment is very application specific, but can be home made at low cost.

Also modeling of the electrophoretic deposition process, especially for functionally graded materials has been successful applied.



a)



b)

Fig. 1. Laboratory equipment for electro-phoretic deposition
a) schematic view and b) effective cell.

The power voltage apply between anode (Ti6Al4V alloy) and cathode (Pt plate with 4 cm^2 area) was of 75V which is sufficient for HA micro-particles activation (diameter of $0.61 \mu\text{m}$) from solution. The maintaining time of tension through solution was of 900 seconds and the distance between anode and cathode was of 20 mm.

As suspension for HA particles deposited during electrophoretic process we use a solution with HA powders in isopropyl alcohol stabilized with a superficial agent type Tween 80.

The electrolyte solution is formed from 4g HA in 100 ml alcohol isopropyl + 1 ml Tween 80. After deposition the sample was washed with water and dried in a laboratory oven at 110 °C for 2 hours and calcined at 800 °C for 2 hours [8].

The thin layers obtained were analyzed using Scanning electron microscopy using a SE detector of VegaTescan LMHII equipment (the electron gun was powered at 30 KeV). The Vega software was also used to obtain 3D images of the thin film surface in order to obtain insights about the surface profilometry. For chemical composition analyze we use X-ray energy dispersive analyze (7 Kcps signal and 15.5 mm working distance), EDAX in order to obtain the Ca:P report characteristic for HA materials [8-11]. For micro to nano areas chemical determinations we use the Point analyze mode from Esprit software.

3. Experimental results

After deposition the layers were morphologically analyzed using scanning electron microscopy and chemically characterized using X-ray energy dispersive analyze.

In Fig. 2 few aspects of the thin layer of HA deposited on Ti6Al4V are presented. We observe a good homogeneity of the HA layer, Fig. 2 a), with two sizes of HA particle at the macroscopic level. No pores or micro cracks were observed on the surface of the thin layer in the central part of the deposition.

Along the edge of the substrate (Ti6Al4V) with HA thin layer macro cracks appear, Fig. 2 b), with depths of 8-10 μm in the HA layer measured from the morphology of the HA layer presented through 3D image – Fig. 2 b).

Analyzing the material on the edge we measure the thickness of the HA layer with a media value of 28 μm , Fig. 2 c), and we observe a compact HA layer with variation of compactness between the interface with the metallic material and the rest of the layer. Both compactness and porosity of the HA layer require further investigations in order of experimental applications (some medical applications need the porous state of the HA in order to increase the osseo-integration process) of this material.

The HA microstructure is presented in Fig. 2 d-f) for different dimension scale and for different areas: Fig. 2 d) is from the edge area of the layer and the other two from the layer surface.

Electro-phoretic deposition is a colloidal processing technique that allows not only to shape free standing objects but also allows to deposit thin films and coatings on substrates keeping the shape of the substrate, Fig. 2 c). One of the most attractive ideas in electro-phoretic deposition process is represented by the possibility to process continuously graded functionally materials and components [11, 12].

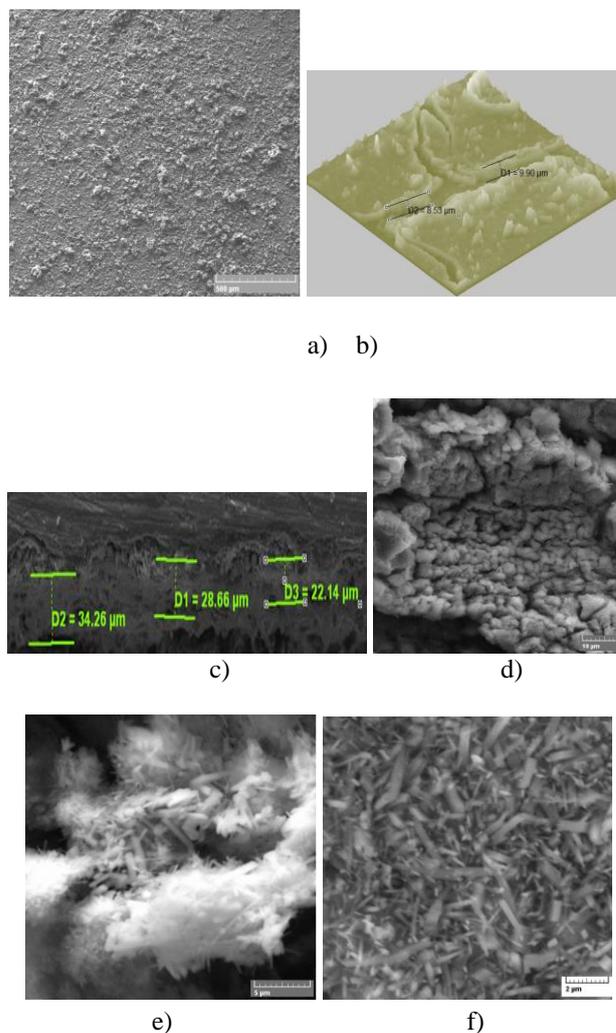


Fig. 2. SEM of HA layer a) general view of the layer (100x), b) 3D image of deposited layer (500x), c) image on the edge of the sample, d), e) and f) microstructure aspects of HA layer (2000x, 10000x respectively 15000x)

There were larger aggregates of tiny particles and the aggregates did not possess any definite shape [10]. The larger aggregates (1–1.5 mm) with similar morphological features are formed at 800 °C, Fig. 2 d-f). In general, it can be observed that particle size of derived HAp is highly dependent on the heating temperature. Moreover, the SEM micrographs also demonstrate that formed $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ tends to form highly porous agglomerates [12-14].

In Fig. 3 are selected three areas for chemical composition determinations. The report Ca/P obtain has an average value of 1.76 with very small differences between areas showing a homogeneous layer chemically speaking.

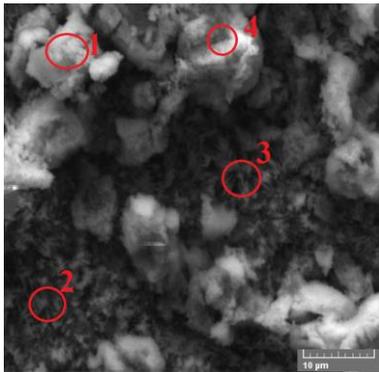


Fig. 3. Chemical analyze of thin HA layer deposited through electro-phoretic process in different areas

Even the classical report Ca:P of hydroxyapatite is 1.67 we obtain an appropriate value, the difference fitting to the EDAX equipment error for calcium and phosphorus elements. Therefore, the EDX analysis data confirmed that the samples are composed of phosphate and the main crystalline phase is HA.

4. Conclusions

For the deposition of HA as thin layers on Ti6Al4V metallic substrate we use electro-phoretic process technique. The process was applied on our own laboratory deposition cell with a Pt 4cm² square cathode. Using electro-phoretic deposition system and depending on the powder composition and dimension size different thin films of a few μm up to 300 μm can be directly deposited on a conductive substrate of any shape from a stable colloidal suspension.

The microstructure of HA is one of the most frequently used bio-ceramics for bone and dental tissues reconstructions. Moreover, the Ca/P molar ratios of the samples determined by EDX analysis let us to conclude that the ratio of Ca/P of HA in the product can be controlled by changing the heating temperature from 600 to 800 °C. The thin layer obtained through electro-phoretic deposition process is chemically homogeneous and have 1.76 report of Ca:P.

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