

Biodegradable hydroxyapatite layer obtained on Ti-6Al-4V alloy dental implant material

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Titanium based dental material, Ti6Al4V, was covered with a thin hydroxyapatite layer using a sol gel deposition method. The research follows some coating properties and analyzes the thermal conductive behavior of the substrate and the substrate-layer materials. The substrate was prepared through different chemical procedures to increase the substrate – layer adhesion. Having a continuous and smooth character the coating presents some cracked areas and few micrometer exfoliations that are analyzed as well. Scanning electrons microscopy and X-ray analyses was used to characterize some layer properties and thermal conductivity was determined with TCi equipment.

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1. Introduction

Materials used for tissue engineering applications must be designed to stimulate specific cell response at molecular level. They should elicit specific interactions with cell and thereby direct cell attachment, proliferation, differentiation, and extracellular matrix production and organization. The selection of biomaterials constitutes a key point for the success of tissue engineering practice [1, 2].

The fundamental requirements of the biomaterials used in the tissue regeneration are biocompatible surfaces and favorable mechanical properties. Conventional single-component polymer materials cannot satisfy these requirements. In fact, although various polymeric materials are available and have been investigated for tissue engineering, no single biodegradable polymer can meet all the requirements for biomedical scaffolds.

To date, calcium phosphate biomaterials have been widely used clinically in the form of powders, granules, dense, porous blocks and various composites. Calcium phosphate materials form the main mineral part of calcified tissues. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ named shortly (HA)) is the major mineral component (69% wt.) of human hard tissues, it could be natural or synthetic, and it possesses excellent biocompatibility with bones, teeth, skin and muscles, both in-vitro and in-vivo. HA promotes bone ingrowth, biocompatible and harden in situ and it has Ca/P ratio within the range known to promote bone regeneration (1.50 - 1.67). HA has already been widely used in clinic due to its similarity to bone mineral in structure and composition. Hydroxyapatite (HA) has been widely used as a biocompatible ceramic material in many areas of

medicine, but mainly for contact with bone tissue, due to its resemblance to mineral bone [3].

Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of few materials that are classed as bioactive, meaning that it will support bone in growth and osseointegration when used in orthopedic, dental and maxillofacial applications. The chemical nature of hydroxyapatite lends itself to substitution, meaning that it is not uncommon for non-stoichiometric hydroxyapatite to exist. The most common substitutions involve carbonate, fluoride and chloride substitutions for hydroxyl groups, while defects can also exist resulting in deficient hydroxyapatite. Hydroxyapatite may be employed in forms such as powders, porous blocks or beads to fill bone defects or voids. These may arise when large sections of bone have had to be removed (e.g. bone cancers) or when bone augmentations are required (e.g. maxillofacial reconstructions or dental applications).

In this work a thin HA layer was obtained by sol-gel deposition method, after the substrate surface preparation through chemical methods, and characterize through SEM and EDAX techniques especially on the cover problems like micro cracks and exfoliations. Thermal conductivity of the substrate and separately the substrate covered was analyzed to establish the thin layer influence on the thermal properties.

2. Experimental details and results

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. For a better adhesion between substrate and thin layer deposited the material Ti6Al4V surface were improved by chemical attack conditions the resulted surface states being presented in figure 1.

As can be see immersing the material in a (2 ml HF+4 ml HNO₃) solution at a 70 °C bath temperature and during a 65 minutes period. Engraving surface was 4.40 cm² and doesn't affect more than a classic chemical attack the material surface, see figure 1 a).

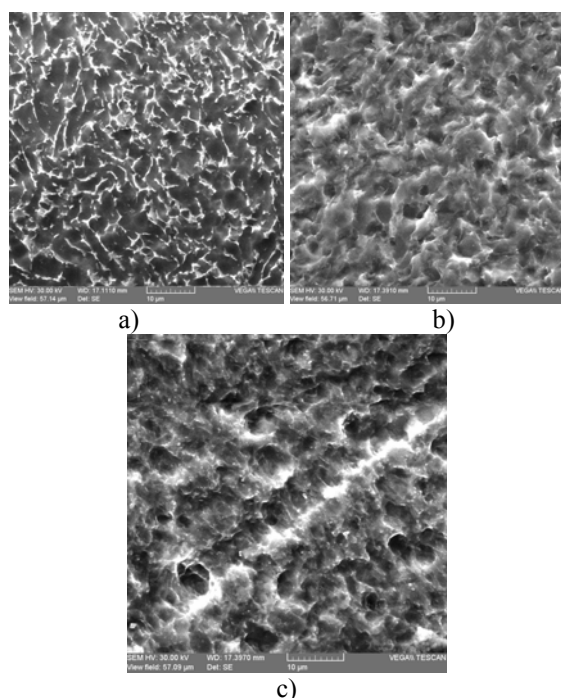


Fig. 1. SEM images of attacked surface of Ti6Al4V alloy on different conditions a) immersion in (2 ml HF+4 ml HNO₃) solution b) immersion in (H₂SO₄ 48% + HCl 18%) solution for a 30 minutes period at a 65 °C temperature c) immersion in (H₂SO₄ 48% + HCl 18%) solution for a 60 minutes period at a 75 °C temperature.

Using a concentrate solution of (H₂SO₄ 48% + HCl 18%) for a 30 minutes period at a 65 °C temperature, in figure 1 b), and for 60 minutes at 75 °C in figure 1 c) can be observe an affected surface with many pores and suitable surface for polymeric or biodegradable materials. Using a material with surface prepared as in figure b) case a thin HA layer was obtained through sol-gel deposition method. HA material is biocompatible and it is widely employed for hard tissue repair in orthopedic surgery and dentistry [4,5]. Inorganic/organic composites aiming to mimic the composite nature of real bone combine the toughness of the polymer phase with the compressive strength of an inorganic one to generate bioactive materials

with improved mechanical properties and degradation profiles.

The sol-gel process, also known as chemical solution deposition, is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (or *sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions.

In this study was used a gel based on phosphorus acid/calcium acetate that have a molar rate of Ca:P of 1.69. The colloidal solution for covering was obtained by mixing 50 mL solution of Ca(CH₃COO)₂, containing 1.7 10⁻² molar acetate in ethylene glycol, with 10 mL H₃PO₄, containing 10⁻² molar H₃PO₄. The concentrations in the mixture were: c(acetate) = 0,283 molar/L, respectively c(H₃PO₄) = 0,167 molar/L. The mixture was kept at ultrasound during 30 minutes and let on rest for 70 hours before experimental using [6-9].

For covering operation the samples were vertically introduced in the phosphorous – calcium gel and pull out very slowly with a reduce rate to avoid gel accumulations in the bottom part of the sample, in this case the rate was of 2,5 mm/minute. After the pulling out operation the samples were dry in an oven to 130 °C temperature and maintaining time of 15 minutes. In this case were growth 5 layers in similar conditions and the final drying was by calcinations at 800 °C for 2.5 hours [10-12].

In figure 2 SEM microscopy is presented of the HA superficial layer deposited on a titanium based alloy. In figure 2 a) a general aspect is presented evidencing an affected area in point 1 detailed in figure 2 b) and on this image another area, marked with 2 and characterized by micro cracks is enlarge and presented in figure 2 c).

The film obtained is relatively smooth and homogeneous but is also presenting some defects as cracks and exfoliations.

On the layer surface can be observe a defects line and an area marked with 1 selected on it that seems to appear based on a substrate surface modification like the line appeared in figure 1 c). From figure 2 b) and c) can be observe that an exfoliation point create some collateral cracks with 1-2 μm thicknesses and 200-300 μm long that affect the layer stability.

Chemical analyze of the covering is presented in table 1 checking the Ca:P rate which is 1.58, a value close to usual HA rate modification, caused by the deposition transfer method, HA transformation behavior during depositing and surface – covering interactions. The titanium, vanadium and aluminum elements signals are poor based on the deposited layer thickness.

Choosing an affected by exfoliation area the chemical variations of most important chemical elements is analyzed to present the elements variation.

In figure 3 a result of elements variation is presented, on a 300 μm length, with respect for the substrate elements

like titanium, aluminum and vanadium and the superficial layer components like calcium, phosphorus and oxygen.

Analyzing the target area, which has an exfoliation zone, presented in detail from figure 3 can be identify the obtained layer homogenization with nice Ca:P rates and the increasing of the substrate chemical elements signals on the exfoliation area. The entire substrate morphology was kept

by the superficial layer form through sol-gel technique and with a 500-1000 nm thickness.

The substrate signals (titanium, aluminum and vanadium) vary on the covered areas as the deposited layer is smoother, cracked or non-homogeneous especially near to the exfoliated area [13-15].

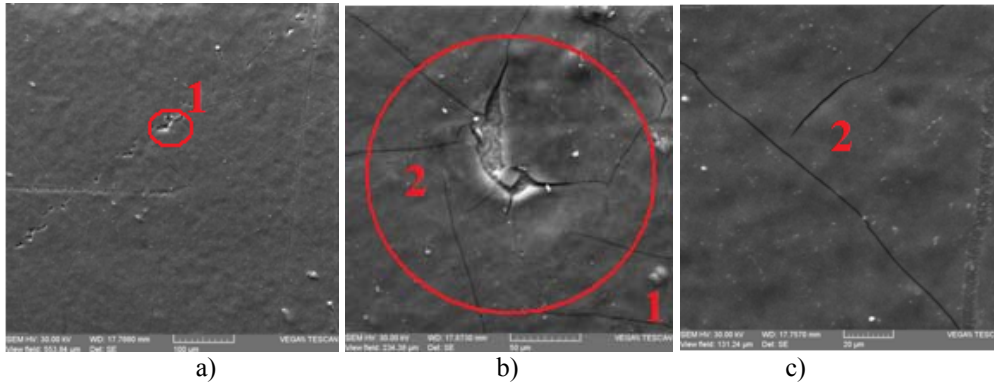


Fig. 2. Scanning electrons microscopy of the superficial HA coating on dental Ti6Al4V alloy a) surface state at 250x, b) detail of area 1 from a) at 1000x and c) detail of 2 area at 2000x

Table 1 Chemical composition of thin superficial HA film on a Ti6Al4V substrate

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Oxygen	8	K-series	6903	78,90181	62,09898	78,35819	127,3719
Calcium	20	K-series	74216	18,84735	14,83364	7,567504	0,583386
Titanium	22	K-series	47476	18,58123	14,62419	6,244947	0,852254
Phosphorus	15	K-series	29078	7,267406	5,719748	4,775669	0,322802
Carbon	6	K-series	3331	1,75212	1,378991	2,347433	0,335828
Vanadium	23	K-series	2640	1,114167	0,876896	0,351955	0,760787
Aluminum	13	K-series	1573	0,59407	0,467558	0,354307	0,061957
			Sum:	127,0581	100	100	

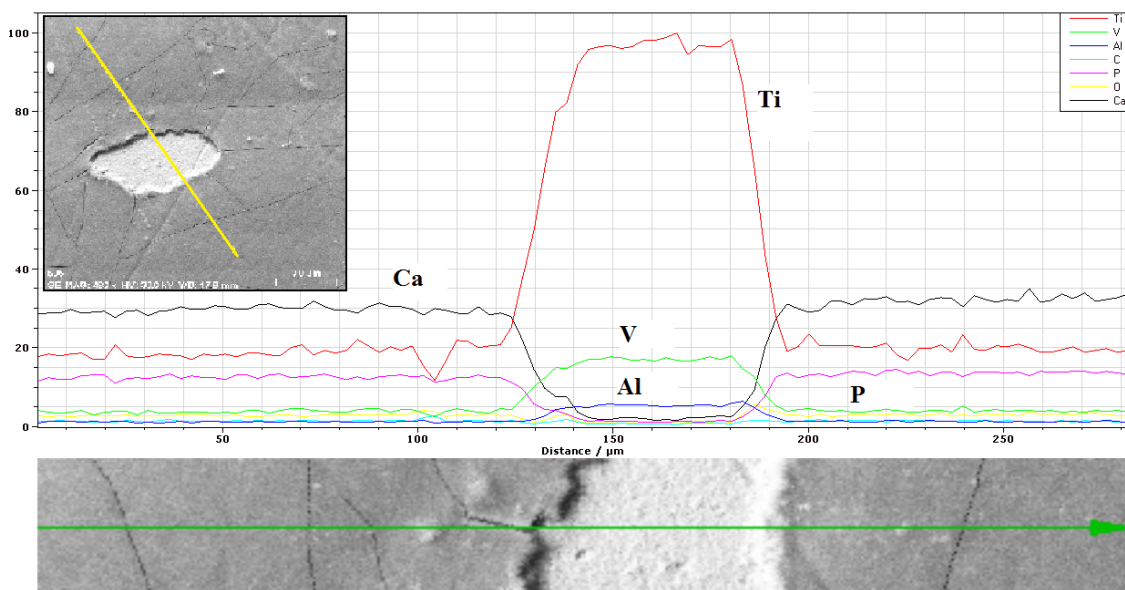


Fig. 3. Chemical elements distribution on a 250 µm line marking a HA superficial layer defect

Having samples with 1,5 and 10 HA layers deposited on a Ti6Al4V substrate by sol-gel method their thermal conductivity was analyzed with results that confirm the role of the superficial layer as a thermal barrier decreasing with a small percentage the thermal conductivity of the new

material. Thermal properties of the samples deposited with superficial HA material and the substrate are presented in table 2. The thermal barrier created by HA superficial layer decrease thermal conductivity of the material from 6.51 to 6.41 W/mK.

Table 2 Thermal conductivity of dental material Ti6Al4V as cast and improved with a thin superficial layer of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)

Ti6Al4V alloy	Effusivity (Ws ^{1/2} /m ² K) x10 ⁻³	Thermal conductivity k (W/mK)	Diffusivity (m ² /s)x10 ⁻¹²	Heat Capacity (J/kgK) x10 ⁶	Depth Penetration (m) x 10 ⁻⁶	R-Value ((m ² K)/W)
Un covered	4650,518	6,516347	509512,6	0,002043	6716,426	2,15043
Covered 1 layer	4650,510	6,516340	509515,3	0,001935	6716,410	2,15920
Covered 5 layers	4617,279	6,415733	518033,4	0,001994	6397,854	2,17012
Covered 10 layers	4617,179	6,405733	518283,4	0,001908	6357,854	2,17327

Recent research suggested that better properties would be achieved if synthetic HA could resemble bone minerals in composition, size and morphology. Thermal properties suffer reduce modifications for more than 2 layers deposited on Ti6Al4V, like five or ten layers, but with big modifications comparing to a single or none deposited substrate. Depth penetration of thermal effect decrease with number of layers deposited and off course with the thickness of the layer but also with the adhesion properties at the substrate.

3. Conclusions

Hydroxyapatite promotes faster bone regeneration, and direct bonding to regenerated bone without intermediate connective tissue. Using a sol-gel chemical deposition method a superficial HA layer with nanometric thickness was obtained on a dental material type Ti6Al4V. The cover is smooth and continuous except some areas characterized by exfoliations and micro-cracks influence by the metallic alloy surface preparation. The hydroxyapatite layer respects a 1.59 rate between Ca and P with generally good adhesion to substrate and a reduced thermal influence on material properties.

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