Advanced metallic materials response at laser excitation for medical applications

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To realize satisfactory fixation of hydroxyapatite (HA) and bio-functionality of bio-tolerated and bio-inert materials such as Ti6Al4V few physical surface modifications such as threaded surface through laser interactions have been produced to promote lung tissue and bone growth on a metallic material. Laser interaction with surface purposes are based on cleaning surface contaminants, roughening surfaces to increase effective surface area and producing beneficial surface compressive residual stress, depending on the laser exposure conditions and as a result, such treated surfaces exhibit a higher surface energy. The layers chemical and physical properties were determined using micro-indenter equipment (type CETR-UMT, Bruker), SEM (type VegaTescan LMHII) with 2 and 3 D insights and EDAX (type Bruker with PB ZAF quantification method).

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1. Introduction

Surface modifications are used on metallic biomaterials for two cases one to improve mechanical, physical, and chemical properties (wear and corrosion resistance, biocompatibility and surface wet ability) and secondly to improve the adhesion of new thin films to be deposited on the metallic material. For enhancing the mechanical retention between two areas usually one of the surfaces are modified to increase the effective surface area. Mechanically the procedure of laser-peening is comparable with shot-peening or even sandblasting method. To obtain a high osteo-integration quality represents an accelerated healing process of traumatized bone in the same time with a high stability and durability of the implants. Using current materials and techniques, a titanium-based alloy dental implant requires several months to osteo-integrate with its adjacent bone. In order to decrease this period, or to improve the quality, hydroxyapatite (HA) compound can be deposited on the metallic material as a thin layer. The analysis of retrieved Ti implant showed that the bone to implant contact report is near perfect averaging between 70 and 80%, with a minimum of 60%, even for successful implants that had lasted for up to 17 years [1], suggesting that the osteo-integration process has been incomplete during a long period. Therefore are still many things to be clarified for the improvement of the surface quality of a Ti-based implant (dental or orthopedic case), in terms of the rate and strength of its osteo-integration [2]. Today, there are some minimally-invasive techniques, for example, available to treat the symptoms of emphysema. One technique is based on coils and a proper material can be Ti6Al4V with HA. They are designed to help restore the lung's natural elasticity while holding small airways open, helping you breathe easier, feel better and live a more active life.

Surface modifications in order to deposit thin films are generally divided into two categories: a concave and a surface convex texturing. The concave textures of the surface can be achieved by either material removal by chemical or electro-chemical action or mechanical indentations (caused by sandblasting, shot-peening, or laser-peening). Depending on blasting experimental conditions (including sand media size and surface coverage), beneficial compressive residual stress can be considered at the surface zone. Surface convex textures can be achieved by depositing different types of particles by one of several physical or chemical depositing methods or by solid-state diffusion bonding [3, 4].

Hydroxyapatite (HA) is a material chemically similar to mineral part of bones and hard tissues. The HA material is one of the few materials that are specified as bio-active meaning that it will support bone in-growth and osteo-integration when is used in implants (orthopedic, dental and maxillofacial) applications. When we analyze the chemical nature of HA we observe that lends itself to substitution fact that means it is not uncommon for non-stoichiometric hydroxyapatites to exist.

Replacement materials commonly used involve different compounds like carbonate, fluoride and chloride substitutions for hydroxyl groups, while defects can also exists resulting in deficient hydroxyapatites. HA has the property to integrate in bone structures and support bone in-growth, without breaking down or dissolving (is bioactive). Hydroxyapatite is a thermally unstable compound at high temperatures decomposing at temperature from about 1073-1473K basically depending on its stoichiometry. Generally speaking dense hydroxyapatite does not have the mechanical strength to enable it to succeed in long term load bearing applications. 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 good 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. 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). The bone filler will provide a scaffold and encourage the rapid filling of the void by naturally forming bone and provides an alternative to bone grafts. It will also become part of the bone structure and will reduce healing times compared to the situation, if no bone filler was used.

The study in this article propose the increase of effective surface area through a laser-surface interaction operation (with different process parameters), calculus of the new effective area, deposition of a HA thin layer by electrophoresis method and analyze of the structural, chemical and mechanical properties of the Ti6Al4V-HA material.

2. Experimental details

2.1 Materials

Ti-based alloys (Ti6Al4V) acquisitioned from Zirom Giurgiu brand [5] under bar form with 10 mm diameter and 5 mm length were analyzed.

As HA suspension we use a solution of HA powder in isopropyl alcohol stabilize with a superficial agent type Tween 80. The electrolyte is made of 4g HA in 100 ml alcohol isopropyl + 1 ml Tween 80.

2.2 Methods

Samples were prepared using a Nd:Yag laser and a vacuum chamber where the metallic sample was fixed. We use a laser beam of 533nm wavelength with two different energies 40 MJ respectively 100 MJ to observe the effects on the implant material [6].

Deposition system of HA on metallic was an electrophoresis installation with the schematic cell from figure 1. Preparatory operations applied previous deposition process, were for chemical activation, by immersion in NaOH (10M) solution for 3 hours at 333 K temperature. After activation the sample was washed in ultrasound bath with acetone, ethyl alcohol and water for 1 hour. For deposition of HA thin film a Consort EV 261 Electrophoretic Power supply (voltage 0-600V, current 0-1000 mA, power de 0-300 W and PC connection) was used to activate HA particles (0.61 μm diameter) with the cell presented in figure 1. During the process a 75V voltage was applied between anod (Ti6Al4V alloy) and cathode (Pt) for 15 minutes for 20 mm distance between electrodes. After deposition the sample was washed with water and dry in a laboratory oven at 383 K for 2 hours and calcinated at 1073 K for 2 hours.

The Ti6Al4V alloy surface after laser modification and deposition of HA was investigated using a scanning electrons microscope model VagaTescan LMH II with SE detector. The 3D image was obtained using the 500x 2D microscopy at a 5% Z-scale, elevation 60 and rotation 32 for all analyzed cases.

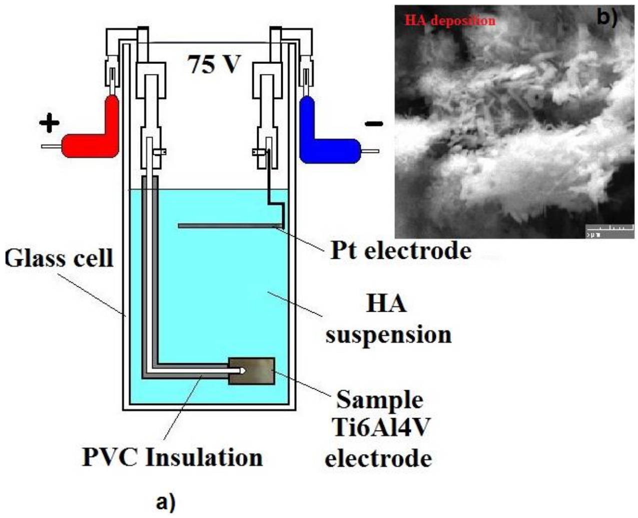


Fig. 1 a) Electrophoretic cell deposition experimental set-up and b) HA deposited aspect

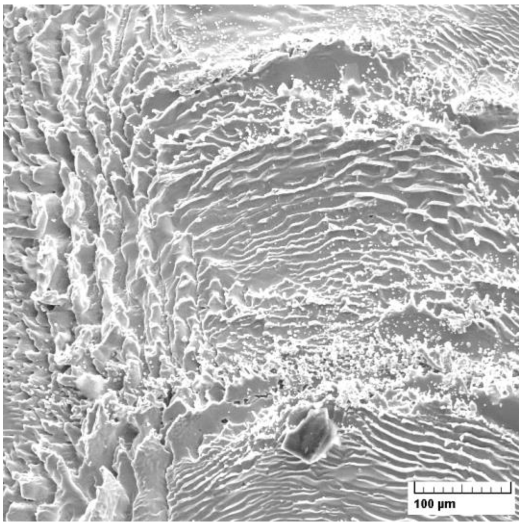
The chemical composition of the surface, before and after deposition, was determined with EDAX Bruker detector (PBZAF automatic mode). Mechanical properties of the thin HA layers were determined using a micro-indenter equipment type CETR-UMT, Bruker.

3. Results and disscutions

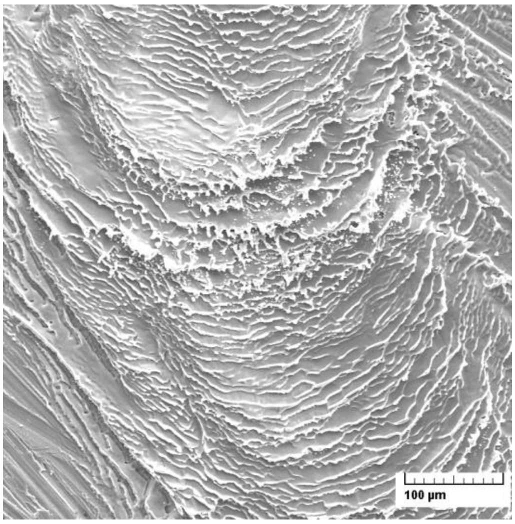
In order to enhance biocompatibility of metallic materials implant Ti-6Al-4V, is a common implant used in dental, orthopedic and lung procedures, a hydroxyapatite (HA) coating on represent a nice solution with good medical results [7]. HA coatings were deposited by electrophoresis method after the metallic material surface was prepared using a laser beam. We analyze the influence of the surface state on the structural and mechanical properties of the thin layer.

Even if titanium or his alloys is known as hard to be blast because of them plasticity, reduce thermal conductivity or chemical reactivity the material surface present numerously modifications after the laser beam action that are presented in figure 2 by 2 and 3D scanning microscopy [8]. All samples, cylinders of 20 mm in diameter and 5 mm height were worked on surface with a laser fasciacle using two different energies respective 40 MJ and 100 MJ (sample 1 respectively sample 2).

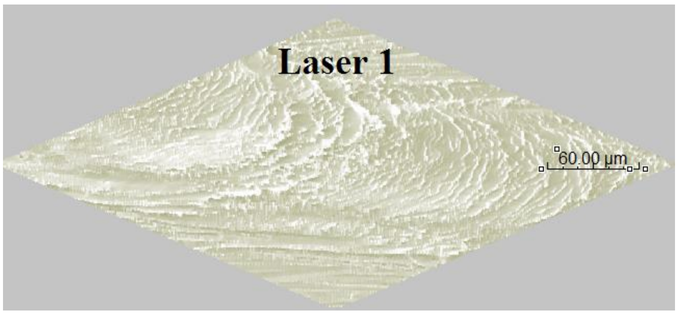
Even the procedure can be adjusted modifying the laser beam parameters the surface suffer high modification by structural point of view with big, sometimes irregular, depths on the surface but no chemical contaminants on the surface are presented, this being one of the laser technology advantage comparing to sandblast for example [9, 10].



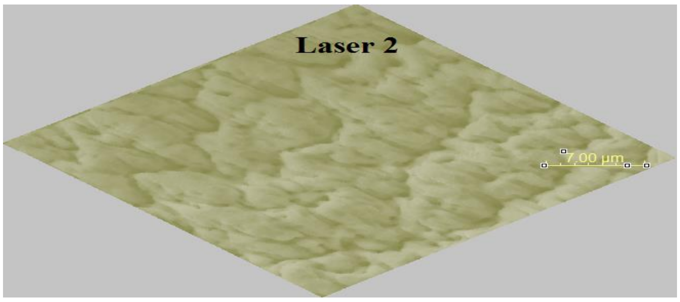
a)



b)



c)



d)

Fig. 2 Surface state of Ti6Al4V alloy after laser influence in two experimental conditions 2D in a) and b) and 3D in c) and d) scanning microscopy

From microscopy made on metallic material surface, especially the 2D representation, two areas are observed: first an area mechanically affected by the laser beam and secondly an area thermally influenced.

Few structural parameters were taken from SEM 2 and 3D images and the results obtained as average of fifty values are presented in Table 1. Using the 3D representation, figure 2 c) and d), of the surface we determine the depth average values of the laser fascicle effect on surface, presented in table 1, and we can consider that the effects of laser blasting coverage on surface was of 90 and 100 % respectively for sample 1 and sample 2.

Table 1 Structural parameters of metallic blasted surfaces

Sample	Radius [μm]				Area [μm²]			
	min	med	max	StDev	min	med	max	StDev
Laser 1	7.3	11.41	18.61	2.81	167.41	433.56	1088.15	218.3
Laser 2	0.77	1.27	1.93	0.28	1.88	5.29	11.74	2.43

	Hmin [μm]	Hmed [μm]	Hmax [μm]	StDev [μm]
Laser 1	2.75	5.68	10.27	2.3
Laser 2	1.3	2.4	3.9	0.8

Using a bigger energy we decrease the effects on surface or maybe the effects are overlaid so we can analyze only the final effect on the surface. Further investigations in this field are necessary using different energies or wavelengths to conclude the interaction between the laser beam and the metallic material.

Using the SEM software to evaluate the effects of the laser beam a standard deviation for each value was determined and can be used for resulted values approximation [11]. In the 3D analyze also for second case, laser 2, we obtain smaller value, less than a half, for the depths that appear on the surface (Hmin, Hmed or Hmax) [12].

Using electrophoresis method thin HA layers were obtained and the surface investigated using scanning electrons microscopy [13, 14]. The surface state for those two cases of the samples different physically worked by laser beam after deposition of the HA layer is presented in figure 3.

Hydroxyapatite layers are homogeneous macro-structural, in both cases don't present micro-structural defects like pores or micro-cracks on the surface, figure 3 a) and b). In this case of preparation of surface no contamination elements were registered based on the technique apply and the vacuum used for deposition. Also the electrophoretic deposition process didn't create other chemical compounds except HA.

The chemical analyses were carried out at macroscopic scale (4 mm^2) and present the compactness of the layer (through variation of the substrate chemical elements: Ti, Al, V), the chemical homogeneity of the layer and the stabilization of the HA layer on the metallic surface [18-20]. In figure 4 four areas were selected for chemical analyze to characterize the thin layer through Ca/P ratio. The chemical analyze is necessary in thin films analyze to determine the chemical homogeneity at micro-scale being a layer with a thickness between 10 to 30 μm [21-23].

Hydroxyapatite is characterized by a Ca/P ratio of 1.67 for laboratory products and commercial HA being very close to the human skeletal system. The results present average of 1.755 Ca / P ratio for the electrophoretic process being a close value to the standard one. In the same time we have to consider the technical error of the equipment EDX used especially for calcium element. The appearance of pores in HA deposited layer can be connected to the material surface state if we consider the depth of the indents in the surface. These laser effects created like indents can influence the thin layer homogeneity, especially for smaller thicknesses than 30 μm, and can cause pores or micro-cracks in the deposited layer [15-17].

Samples was chemically analyzed using a Quantax Bruker system (X ray dispersive energy analyze) in element list mode focusing on elements characteristic to thin layer (Ca, P, O) deposited and to substrate (Ti, Al, V). The results are presented in table 2 by mass and atomic percentage means. Also the error characteristic of the equipment focused on each sample was registered.

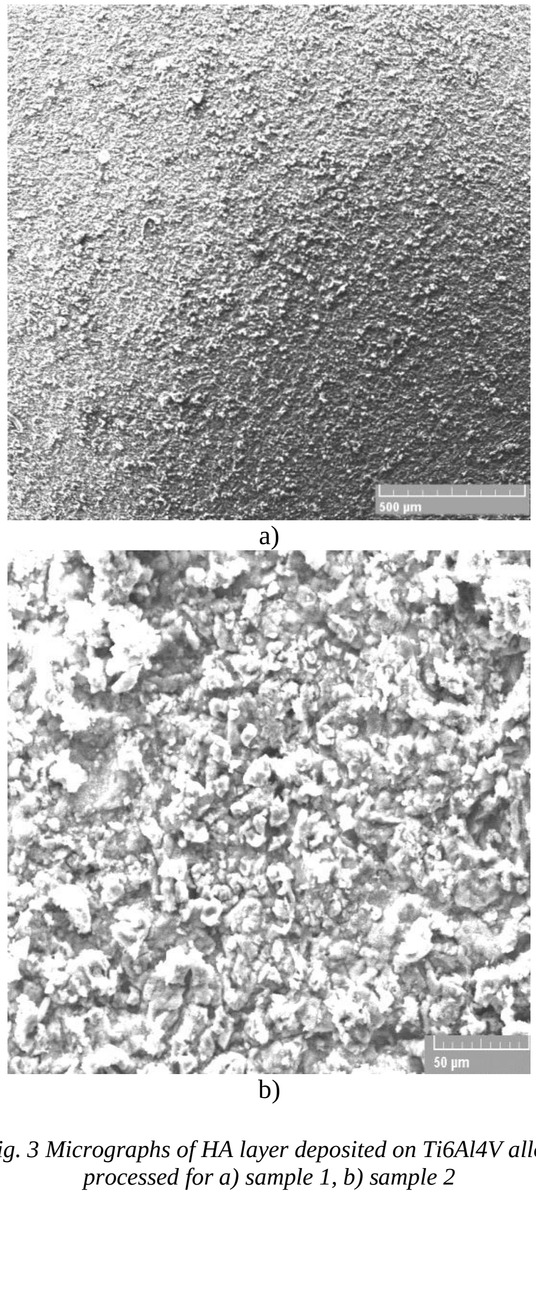


Fig. 3 Micrographs of HA layer deposited on Ti6Al4V alloy processed for a) sample 1, b) sample 2

The HA layer is very homogenous by chemical point of view with smaller variations (less than 2%) of Ca/P ratio even structurally present different morphologies.

Micro-indentation tests were carried out on both deposited samples making three different located experiments, the position being presented in figure 5 in the left-up detail, to determine the mechanical characteristics of the "new" material formed by Ti6Al4V and HA.

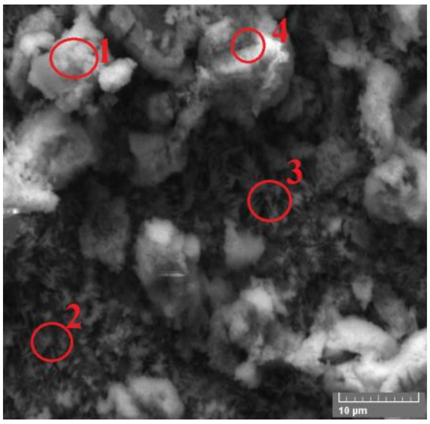
Table 2 Chemical composition of HA layers deposited on sample prepared with a laser beam

Chemical element		Mass percentage %	Atomic percentage %	Error %
Ca	Sample 1	0.07	0.04	0.03
	Sample 2	0.19	0.15	0.03
P	Sample 1	0.25	0.19	0.04
	Sample 2	0.73	0.76	0.06
O	Sample 1	48.46	72.23	4.73
	Sample 2	22.87	45.70	3.36
Ti	Sample 1	44.72	22.27	1.48
	Sample 2	68.54	45.76	2.25
Al	Sample 1	5.34	4.72	0.30
	Sample 2	6.01	0.29	1.01
V	Sample 1	1.12	0.52	0.76
	Sample 2	2.57	1.61	1.72

Three tests were performed to compare the homogeneity of the thin film in all cases and the indents obtained were analyzed by SEM in order to observe the surface material behavior under stress.

Discrete displacement bursts (pop-ins presented in figure 5 each with a magnitude of 160 nm was observed in the first two tests. In first orientation, the main pop-ins was observed to occur at a force P of 1.6 ± 0.1N and for second indentation (test 2) at 2N. Reduced pop-ins was observed further more upon continued increase of the force.

Initially, these were thought be a result of corner cracking on the indentation hole. However, the SEM images (typical image shown in figure 5 right detail) did not show any cracks. Instead, flow of the material along the edges of indentation impressions, referred to as pile-up in indentation literature, was observed.



The Ca/P ratio obtained in four points selected in the SEM image:
Point 1: 1.74
Point 2: 1.76
Point 3: 1.78
Point 4: 1.74

Fig. 4. Chemical analyze of superficial HA thin layer obtained through electrophoretic deposition process in four different areas.

Other researchers [24], who examined the indentation response of the basal planes of Ti_3SiC_2, observed similar pop-ins in the force-depth curves. With the aid of detailed transmission electron microscopy, they showed that this pop-ins are due to delamination of the basal plane due to the relatively weaker bonding between these planes in this particular ceramic and subsequent out-of-plane kinking of the planes. The results obtain after the surface mechanical solicitation are presented in table 3.

Table 3 Mechanical behavior of Ti6Al4V alloys (sample 1 and sample 2)

Sample		Hardness Rockwell (GPa)	Young's Module (GPa)	Contact area (μm^2)	Contact stiffness (N/µm)
Sample 1	Test 1	2,44	137,6	4026	8,53
	Test 2	1,72	109,12	5947	8,55
	Test 3	1,75	98,44	5806	7,79
Sample 2	Test 1	2,98	118,13	3023	6,79
	Test 2	2,44	116,58	3754	7,49
	Test 3	2,57	117,15	3565,4	7,2

Even if a high resistance to dislocation motion is known in ceramics, similar pop-ins in the force-depth curve has been observed in sapphire, aragonite, GaAs and ZnO at room temperatures [25-27].

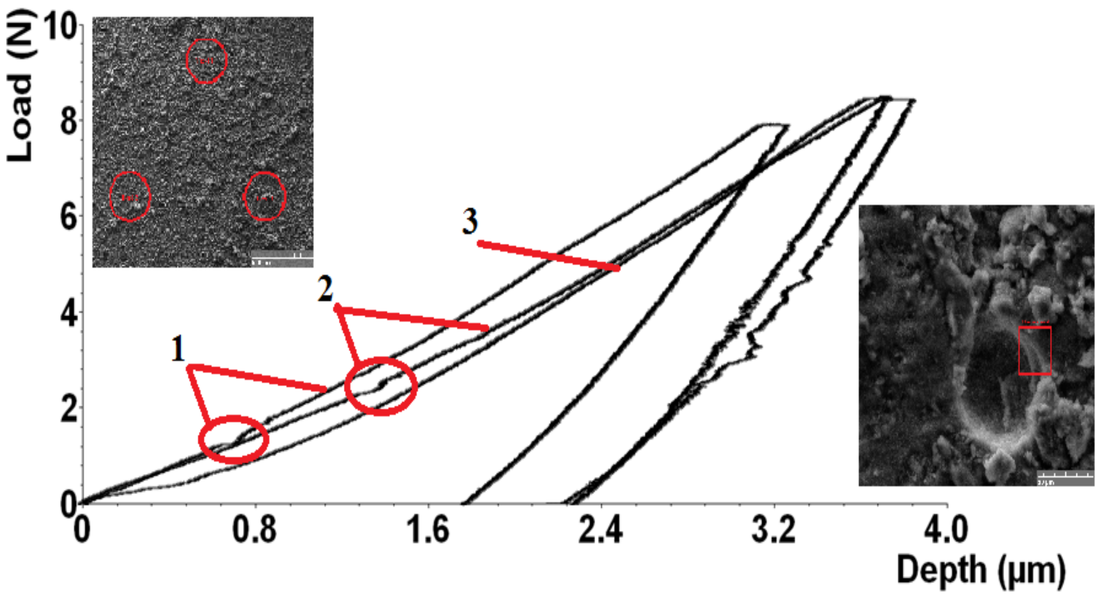


Fig. 5 Depth vs Load plots of three tests, the schematic view of the test position is present in detail on the up-left side, realized on HA deposited sample 1 with a SEM image of detail Rockwell indent in the down-right part of the image

Therefore, the faceted pile-up region in the SEM image suggests that the observed pop-ins is indeed due to dislocation plasticity. Hardness and Young's module present near values, table 2, for sample 1 and 2 that represent a good mechanical homogenization of the HA layer and only reduce variation for sample 2 that can be assigned to the microstructural variation observed in Fig. 4 b).

4. Conclusion

Titanium base alloys were worked on surface with a laser beam in order to deposit a thin layer of hydroxyapatite through electrophoresis. The laser beam effect is quantified as a metal response based on the experimental set-up. Experimental values present good results on the adhesion of non-metallic thin layer on the Ti6Al4V metallic substrate which is a common implant used in dental, orthopedic and lung procedures. The depths obtain after the laser interaction with surface are suitable to HA depositions.

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