# Improving the HA deposition process on Ti-based advanced alloy through sandblasting

G. ZEGAN[a], R. CIMPOEȘU[b,*], M. AGOP[b], I. ȘTIRBU[b], D. L. CHICET[b], B. ISTRATE[c], A. ALEXANDRU[b], B. ANTON PRISACARIU[d]

[a] *Department of Surgery, Faculty of Dental Medicine, "Gr. T. Popa" University of Medicine and Pharmacy, University str. no. 16, 700115, Iaşi, Romania*

[b] *Faculty of Materials Science and Engineering, "Gheorghe Asachi" Technical University of Iasi, Prof. dr. docent Dimitrie Mangeron Rd., No. 59A, 700050, Iasi, Romania*

[c] *Faculty of Mechanics, "Gheorghe Asachi" Technical University of Iasi, Prof. dr. docent Dimitrie Mangeron Rd., No. 59A, 700050, Iasi, Romania*

[d] *"Gr. T. Popa" University of Medicine and Pharmacy, University str. no. 16, 700115, Iaşi, Romania*

To realize satisfactory fixation of hydroxyapatite (HA) and bio-functionality of metallic mini-implants, a few mechanical surface modifications, such as threaded surface through sandblasting, have been produced to accelerate the tissue formation and partial bone growth. Usually the mechanical operation purpose is to clean the material surface by the contaminants and to process the surface in order to increase the effective surface area. In addition, we propose a deposition of HA layer on the metallic surface. The chemical and physical properties of the layers were determined using a micro-indenter equipment (type CETR-UMT, Bruker), S.E.M (Scanning Electron Microscope, type VegaTescan LMHII), E.D.A.X (Energy Dispersive X-ray analysis, type Bruker) and XRD (X-ray diffraction, type X'Pert) analyze instruments. The results present variation of surface modifications based on the sand blasted process parameters and in some cases the original surface area can be roughly doubled under mild sandblasting operation, the partial contamination of the surface with the sand particles and variation of homogeneity of thin HA layer.

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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 wettability) 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 sandblasting is comparable with shot-peening or laser-peening 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 sustainability of the metallic element implants. Nowadays a Ti-based alloy used in dentistry as mini-implants has a few months necessity to integrate at least partially with its adjoining bone. In order to decrease this healing time we propose to improve the quality of the implant using thin layers of hydroxyapatite (HA) which can be deposited on the metallic material as a thin layer after the sandblasting operation. When the retrieved Ti implants were analyzed the results showed that the contact report between bone and implant is not perfect with a mean percentage of 60 and 80% even for good successful implants that had used for up to 17 years [1, 2] fact that shows the incomplete character of the osteo-integration process during a long time. By these means we can appreciate that are still many things to be solved for the improvement of the surface quality metallic material implants (dental or orthopedic case), in terms of the rate and strength of its osteo-integration [1].

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 obtain through material removal by chemical or electro-chemical action either by mechanical influences (by sandblasting, shot or laser-peening). In a straight dependence on the blasting experimental conditions (like sand nature or size and the surface coverage percentage) at the surface zone a new compressive residual stress appear. Secondly the convex surface texture can be achieved by depositing different materials through one of several physical or chemical depositing methods or as alternative by solid-state diffusion bonding [3].

The sandblasting operation include three specific purposes first the cleaning surface contaminants (usually used in pre-deposition process), secondly roughening surfaces to increase effective surface area and the producing of beneficial surface compressive residual stress, all three depending on the blasting conditions. As a result the modified surfaces exhibit bigger activation

energy of the surface (conducting to higher surface chemical and physical activities and improving fatigue strength and life). A good enabled bond strength as in any possible couples like HA bonding scheme (HA/Ti bonding or bone/Ti implant) can be usually explained by a favorable result of blasting (a high number of small indentations on the metallic surface) to increase the effective surface area [4].

The study in this article propose the increase of effective surface area through sandblasting 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

Ti-based alloys (Ti6Al4V) acquisitioned from Zirom Giurgiu brand [5] under bar form with 10 mm diameter and 20 mm length were analyzed.

Samples were sandblasted using a Shot Blasting Cabinet model SB974 equipment and classical foundry sand at 100 psi (7 bar) air pressure for distance between the equipment gun and sample of 100 mm with 5, 10 and 15 seconds interaction time. The chemical composition of classical foundry sand is 95% CO2 and 5% $Al_2O_3Fe_2O_3$.

Deposition system of HA on metallic was an electrophoresis installation. Preparatory operations applied previous deposition process, were for chemical activation, by immersion in NaOH (10M) solution for 3 hours at 60 °C temperature. After activation the sample was wash 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 (tension 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 Fig. 1. During the process a 75V tension was applied between anode (Ti6Al4V alloy) and cathode (Pt) for 15 minutes for 20 mm distance between electrodes. 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. After deposition the sample was washed with water and dry in a laboratory oven at 110 °C for 2 hours and calcinated at 800 °C for 2 hours.

The Ti6Al4V alloy surface after sandblasting and after deposition of HA was investigated using a scanning electrons microscope model VagaTescan LMH II with SE detector.

The 3D image was obtained using the SEM software Vegatescan. It was used a 500x 2D microscopy at a 10% Z-scale, elevation 60 and rotation 32 for all analyzed cases.

The chemical composition of the surface, before and after deposition, was determined with EDAX Bruker detector (PBZAF automatic mode) and by XRD using X'PERT PRO MRD in Scan- Continous mode, Start Angle: 20 and End Angle 80, step size: 0.0131303, time per step: 61.20, scan speed: 0.05471, number of steps: 7616 with X-ray Tube: Cu anode. Mechanical properties of the thin HA layer were determined using a micro-indenter equipment type CETR-UMT, Bruker.

## 3. Experimental results

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

Even if titan 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 that are presented in Fig. 1 by 2 and 3D scanning microscopy.

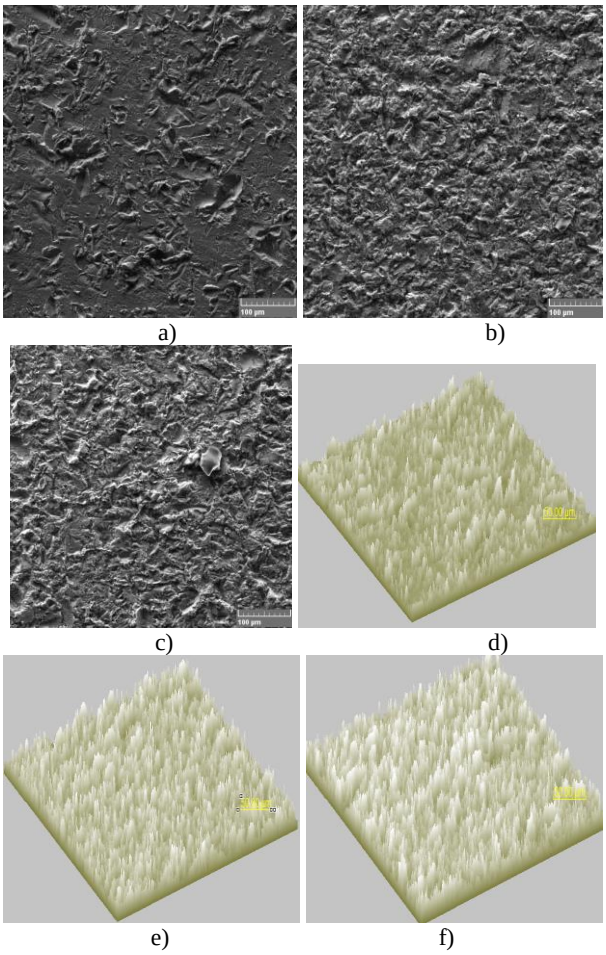


*Fig. 1. Surface state of Ti6Al4V alloy after sandblasting for 5, 10 and 15 seconds by 2D in a), b) and c) and 3D in d), e) and f) scanning microscopy*

All samples, cylinders of 20 mm in diameter and 20 mm height were sand blasted from 100 mm distance for 5, 10 and respectively 15 seconds (sample 1, 2 respectively 3). In Fig. 1 a), b) and c) the surface aspect of Ti6Al4V alloy after sandblast is presented and the modifications appeared observed like differences of coverage modifications between first and the next two samples. Even the procedure can be adjusted modifying the sandblast parameters the surface suffer high modification by structural point of view with big, sometimes irregular, depths on the surface and chemical contaminants on the surface, Fig. 1c).

*Table 1. Micro-structural determination of metallic blasted surfaces*

| Sample | Diameter (μm) | | | Standard deviation (μm) | Depth (μm) | Coverage degree (%) | Final active surface (%) |
|---|---|---|---|---|---|---|---|
| | minimum | average | maximum | | | | |
| 1 | 12.83 | 22.82 | 46.44 | 6.63 | 7.5 | 90 | 85.5 |
| 2 | 18.65 | 24.9 | 32.91 | 3.35 | 5.5 | 100 | 95 |
| 3 | 13.15 | 23.02 | 38.96 | 6.03 | 6.8 | 100 | 95 |

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, Fig. 1 d), e) and f), of the surface we determine the depth average values of the sandblast effect on surface, presented in Table 1, and we can consider that the effects of sand blasting coverage on surface was of 90, 100 and 100 % respectively for sample 1, 2 and 3.

For effective area estimation of a surface that increase by sandblasting with particle with 300 μm average than a tenth part (around 30 μm) will be indented in the surface [2]. In our case we confirm through media values of the indents, presented in Table 1, an average of 22.82 μm in first case for a 5 seconds of sandblasting and 24.9 and 23.02 μm for 10 and 15 seconds. An active surface (AS) after the mechanical grinding can be define in function of the known original surface A0 and using the effective area increment of the surface equal with (AS-A0)/A0x100 (%) where $AS=(\alpha/360)x4\pi r^2$. Paying respect for the medium value of the sand (300 μm), the average diameter of the indents (table 1) and each original known surface the results of final active surface are approximate of plus 85.5 % in the first case and 95 % in the others case, results presented in table 1. It can be considered that for 10 or 15 seconds of sand blast the active surface is almost doubled.

The blasting process present also disadvantages like adverse effects of the surface most important being surface contamination (based on the blasting media nature). At nano-scale the distortions of blasted sample depending on the blasting process parameters like distance, time and intensity [9]. Even if we use reduce blasting rates and cooling environments the worked surfaces were found to be affected physically by the abrasive constituent elements (sand particles). Through investigation by EDAX equipment the presence a $SiO_2$ particles sticked in the metallic surface is observed in Fig. 2. The chemical nature of the particle was evidenced using a mapping analyze mode in detail from Fig. 2. It seems that the contamination of Ti alloys is connected to its reactivity and off course its hardness in spite of other precaution measurements like water cooling and slow speed abrading and the Ti surfaces were obviously contaminated. Contaminants observed on the surface have dimensions ranging from about10 to 30 μm. Related to the alloy hardness the contamination resulted from a primarily reaction with abrasive materials for mechanical preparation could also negatively influence titanium's resistance to corrosion and its biocompatibility [4]. In our case we use the sandblasting operation to improve the adhesion of a HA layer and depending on how thick is the layer analyze of influence of contaminants can be done.

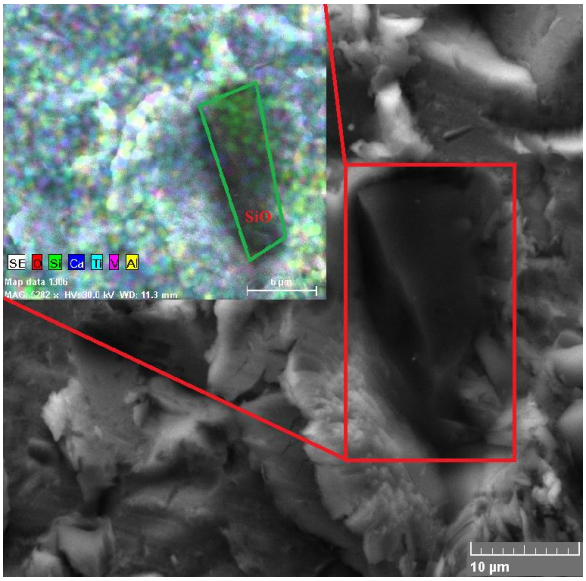


*Fig. 2. Contaminated surface of Ti6Al4V with $SiO_2$ particles*

Using electrophoresis method thin HA layers were obtained and the surface investigated using scanning electrons microscopy. The surface state for those three cases of the samples different mechanically worked by sandblasting after deposition of the HA layer is presented in Fig. 4. Hydroxyapatite layers are homogeneous macro-structural, in all cases, but present some micro-structural defects like pores, Fig. 3 a) – sample 1, or micro-cracks observed on Fig. 3 c) on the surface of sample 3.

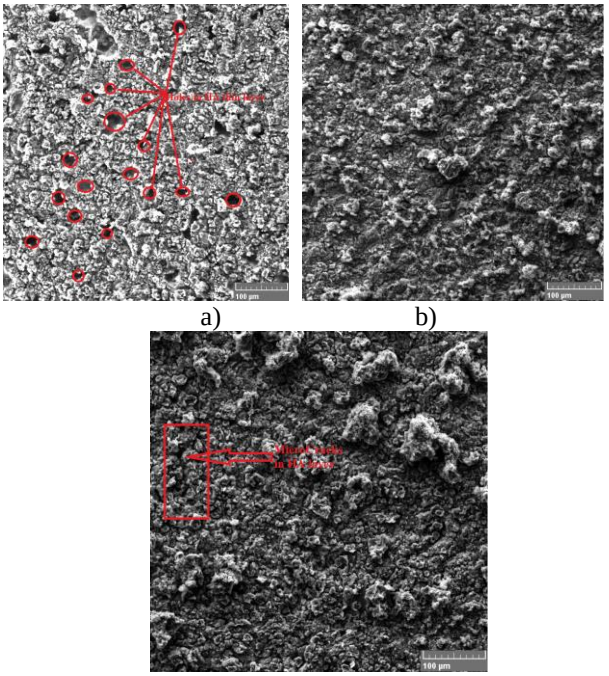

*Fig. 3. Microscopy of HA layer deposited on sandblasted Ti6Al4V alloy processed for a) 5, b) 10 and c) 15 seconds*

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, sample 1 present the biggest depths from all three of all of 7.5 µm and big diameters of maximum 46.44 µm. These sandblast created 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.

In order to analyze the influence of the sandblast process and of the deposition on the final product Ti6Al4V-HA XRD technique was used to determine the contaminants presents or the HA deposition on the metallic substrate. In this paper only the presence of the contaminants after the sandblast process and the deposition results were analyzed by XRD the influence of the surface state on final properties by XRD analysis will be the subject of another paper. First of all, in Fig. 4 a), we determine the characteristic peaks of the substrate, which present α and β phases, at 2θ: 35.40, 38.50, 39.45, 40.45, 53.30, 57.00, 63.55, 71.00, 74.90, 76.80 and 78.10 with d (nm) respectively: 0.2536, 0.2338, 0.2284, 0.2230, 0.1719, 0.1614, 0.1464, 0.1328, 0.1268, 0.1241 and 0.1224. The β phase is clearly characterized by the (110) and (200) reflections whit characteristic lattice distance mentioned above of 0.2284 and respectively 0.1614 nm [7].

Fig. 4 b) shows the XRD patterns of the HA target based on a standard XRD pattern of HA (JCPDS 9-0432). Hydroxyapatite has a hexagonal crystal structure with the main diffraction peaks at 2θ= 25.9, 29.0, 31.8, 32.2, 32.9, 34.0, 39.8, 46.7, 49.5, 50.5 and 53.1, which correspond to the crystal orientation planes of (002), (210), (211), (112), (300), (202), (310), (222), (213), (321) and (004), as shown in figure 4 b). Figure shows that the XRD pattern of the HA target is in agreement with the JCPDS 9-0432 [8]. The sintered HA target showed a crystalline HA structure with some tri-calcium phosphate (TCP), $Ca_3(PO_4)_2$ being formed during the sintering process [11].

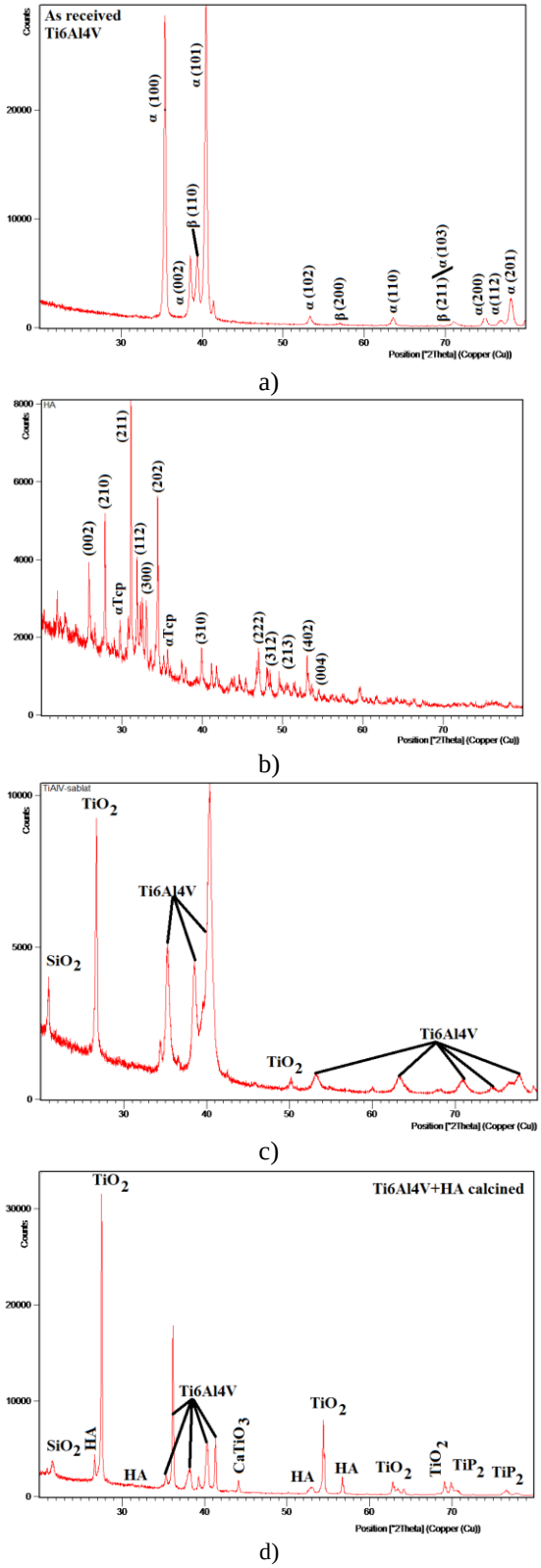


*Fig. 4. XRD results on a) Ti6Al4V substrate; b) HA bulk material, c) sandblasted Ti6Al4V and d)*

Chemical elements investigation and the real state of chemical bonds analyze of the metallic contaminants from the surface were realized using X-ray dispersive energy detector. X-ray diffraction (XRD) of the expose to sandblast surface was done in order to identify the contaminants and the results presented in Fig. 4 c). The presence of $SiO_2$ (2θ: 20.65 and other) on the surface is identified and the formation of $TiO_2$ is observed (2θ: 26.7 and 50.21). Our measurements present no significant line shift of α phase for any of three samples. On the contrary, the β phase present clear evidence of line shift suggesting lattice distortion after the sandblasting process especially. This is clearly a case of lattice distortion related to the internal stress provoked by the mechanical preparation of the sample.

For deposited sample, Fig. 4 d) when the post-heat temperature is higher than 400°C, the coatings were transformed into high-quality crystalline HA. The coatings were highly-crystalline HA, including some TTCP. As shown in figure the XRD patterns showed the main HA peaks, which correspond to the crystal orientation planes of (002), (210), (211), (112), (300), (202), (222), (213) and (004). The positions and the relative intensities of the main HA peaks were in agreement with that of the target and the JCPDS 9-0432. The characteristic peak of $SiO_2$ is also present, with a smaller intensity based on the thickness of the HA layer, and new peaks of $TiO_2$ appear during the process of deposition and remain after the calcinations of the material but with a further good influence for medical applications [9-11]. So far there are no references about a proper roughness of the metallic bio-materials. On the macroscopic level (>10 μm) the rugosity will influence the mechanical properties of the interface between metal and HA, the way the stress is shared and transmitted, the mechanical blocking of the interface and the bio-compatibility of biomaterials. On a smaller scale, surface roughness in the range from 10 nm to 10 μm may influence biologically the interface based on the same order size as cells and large bio-molecules [12]. Micro-indentation tests were carried out on all deposited samples (1-3) 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. Three tests were performed to compare the homogeneity of the thin film in all three cases and the indents obtained were analyzed by SEM in order to observe the material behavior under stress.

Discrete displacement bursts (pop-ins presented in Fig. 6), each with a magnitude of 160 nm, were 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.

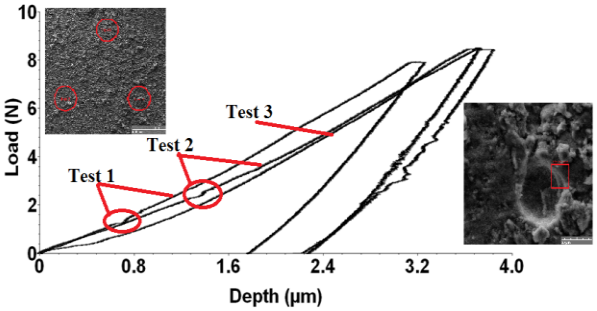


*Fig. 5. Depth vs Load representation of three tests, the schematic view of the test position is present in detail on the up-left side, realized on HA deposited sample 2 with a SEM image of detail Rockwell indent in the down - right part of the image*

Initially, these were thought is a result of corner cracking on the indentation hole. However, the SEM images (typical image shown in Fig. 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. Other researchers [13], 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 2.

*Table 2. Mechanical behavior of sandblasted and HA deposited Ti6Al4V alloys*

| Sample | | Hardness (GPa) | Young's Module (GPa) | Contact area (μm$^2$) | Contact stiffness (N/μm) |
|---|---|---|---|---|---|
| Sample 1 | Test 1 | 2.24 | 127.6 | 4026 | 8.53 |
| | Test 2 | 1.52 | 103.12 | 5947 | 8.55 |
| | Test 3 | 1.55 | 94.44 | 5806 | 7.79 |
| Sample 2 | Test 1 | 2.78 | 116.13 | 3023 | 6.79 |
| | Test 2 | 2.24 | 114.78 | 3754 | 7.49 |
| | Test 3 | 2.37 | 113.17 | 3565.4 | 7.2 |
| Sample 3 | Test 1 | 2.04 | 112.54 | 4409 | 7.97 |
| | Test 2 | 2.31 | 119.43 | 3910 | 7.92 |
| | Test 3 | 2.57 | 110 | 3507 | 6.96 |

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 [14-16].

Therefore, the faceted pile-up region in the SEM image suggests that the observed pop-ins are indeed due to dislocation plasticity [17]. Hardness and Young's module present near values, Table 2, for sample 2 and 3 that represent a good mechanical homogenization of the HA layer and only reduce variation for sample 1 that can be assigned to the microstructural variation observed in figure 3 a). One of the roles of contact stiffness is to calculate the real contact area of the indenter on the surface and represent an important interfacial parameter for the contact dynamics and interface understanding. It is known that the real hardness of a thin layer deposited on a metallic substrate can be modeled by describing how the contact stiffness or the modulus changes with increasing of depth during indentation. Real information on the interface between Ti6Al4V and HA can be obtained following, in a further work, analyze of more contact stiffness results. The contact area dimensions, confirmed by the SEM microscopy, bring more information about the material rigidity, so for similar values of hardness – sample 1 test 1 and sample 2 test no 2, we obtain different contact areas and a less rigid alloy-ceramic complex for sample 1 in this case.

## 4. Conclusions

Similar Ti-base alloys surface was sandblasted in order to deposit a thin layer of hydroxyapatite through electrophoresis. Experimental results present differences between Ti6Al4V surfaces based on different process preparation parameters. 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 and we have big depths from all three of all of 7.5 μm and big diameters of maximum 46.44 μm. These sandblast created indents influence the thin layer homogeneity, especially for smaller thicknesses than 30 μm, and can cause pores or micro-cracks in the deposited layer. The positions and the relative intensities of the main HA peaks were in agreement with that of the target and the JCPDS 9-0432. The faceted pile-up region in the SEM image suggests that the observed pop-ins is indeed due to dislocation plasticity.

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*Correspondent author: ramonahanu@yahoo.com