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Adherent functional graded hydroxylapatite coatings produced by sputtering deposition techniques

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The aim of this paper was to study the influence of crystallization heat treatments up to 750°C, upon the integrity and structure of hydroxylapatite thin films. Two different types of hydroxylapatite coatings were investigated: abrupt structures prepared by magnetron sputtering and respectively functionally graded structures deposited by a co-sputtering technique. A clear dependence was noticed between adherence values and annealing temperature and was correlated with the SEM, XRD and FTIR results. X-ray diffraction and FTIR measurements showed that the hydroxylapatite coatings annealed at 400°C were less crystalline, similar to biological apatites. Over 550°C, the apatite coatings obtained were well crystallized and preferentially oriented on (002) HA crystal plane. The adherence of HA coating increased with annealing the temperature up to 550°C due to diffusion phenomena. At 550°C the adhesion test results indicated better adhesion values in case of functionally graded structures (> 85 MPa) in comparison with abrupt ones (~ 70 MPa). At 750°C an adherence decreasing occurred for both types of structures. This is mainly due to the effect of a significant thermal stress owed to the mismatch of the thermal expansion coefficients between the crystallized HA and Ti substrate. The presence of rutile lines in XRD spectrum suggests an increasing of the diffusion phenomena and a strong substrate oxidation at the HA/Ti interface with annealing temperature.

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Keywords: Biomaterial; coatings; hydroxylapatite; sputtering techniques; functionally graded materials (FGM); pull-out adherence.

1. Introduction

The increase of life expectancy as well as a tendency for an overactive lifestyle in the developed countries has led to numerous bone-related ailments. Therefore, implantology has become in the last three decades an important branch of medicine. Titanium and some of its alloys are important materials in the medical field due to their excellent biocompatibility and mechanical properties. These materials are considered bioinert and they are harmless for the surrounding tissues, but lack in bone direct integration [1-3]. A successful solution in order to improve the osseous integration of such metallic implants is to coat them with a bioactive material [4-6]. The bioactive materials (e.g. calcium phosphates, apatites, bio-glasses) are able to bond chemically to the bone tissue in order to promote the osteointegration phenomenon and prevent the micro-movements of the medical device [7]. Such a material is hydroxylapatite (HA, $Ca_5(PO_4)_3OH$). The chemical similarity of hydroxylapatite to the bone mineral (a non-stoichiometric carbonated apatite) suggested its intrinsic biocompatibility more then 30 years ago [8, 9].

Presently, the plasma spray technique is the commercial method used for coating various metallic implants required in the field of orthopedic and oral surgery. The success of this technique cannot be denied, but it possesses a certain number of disadvantages including high process temperature, heterogeneity, non-uniformity in thickness and crystallinity of the deposited films, and low values of adhesion [10-14]. In order to determine the performance and the reliability of a HA-coated implant the adhesion coating to substrate and the integrity of the substrate/coating interface are always concerned.

In this study we investigate the magnetron (co)-sputtering technique as a possible alternative method for producing high quality coatings. Magnetron sputtering (MS) techniques yields a greater process control, excellent adhesion and uniform coverage of the metallic substrates [15]. Therefore, sputtering could also be an attractive, simple and low cost method for designing dense and well-adhered HA coatings. This work comparatively evaluates the feasibility of two types of HA sputtering coatings (simple abrupt structures and compositionally graded structures) in terms of post deposition treatments for crystallization and adhesive strength. There are presented results on morphology, microstructure, crystallinity and adherence properties.

2. Materials and methods

2.1 Materials and sputtering deposition process

Commercially pure titanium substrates (Mateck GmbH, cp-Ti gr. 4) were ultrasonically cleaned with acetone and iso-propanol alcohol. The magnetron sputtering target was prepared from a hydroxylapatite (Dentaurum Group) powder with micrometric granular size. An additional solid target of pure titanium was used

for co-sputtering depositions. The substrates were fixed in the centre of an aluminum sample holder.

The working chamber was evacuated to a base pressure of 10^{-3} Pa, and then back-filled with high purity (99.9995%) argon at a 40 sccm flow rate. Prior to deposition, the substrates were etched for 10 min at a 0.4 kV DC bias voltage in argon plasma produced by a wolfram plasmatron. The depositions were carried out for 1 h, using a 1.78 MHz generator at a constant RF power (DC_{bias} target value of 44V). During deposition the substrates reached a maximum temperature of ~150°C due to plasma bombardment. A constant argon pressure of 0.4 Pa was used for all the depositions. The HA sputtering rate was prior estimated from interferential microscopy measurements at 10 nm/min.

The HA/Ti abrupt coatings were prepared by RF magnetron sputtering from the HA target. The substrate holder was rotated during deposition in order to improve the coatings uniformity. The graded $HA/HA_{1-x}Ti_x/Ti$ (x=0-1) structures were prepared by co-sputtering, slowly moving the rotating substrate holder from the Ti target towards the HA one. By this procedure a functionally graded transition zone with variable chemical composition can be formed between the top biofunctional coating and the titanium substrate. This process took 5 minutes, the graded layer thickness being estimated at around ~ 70 nm. Finally the described FGM structures were kept for 1 hour in front of the HA target in order to prepare a biofunctional top HA layer with a thickness of ~ 600 nm.

A schematic of the experimental RF-MS set-up used for the synthesis of HA-FGM structures is shown in Fig.1.

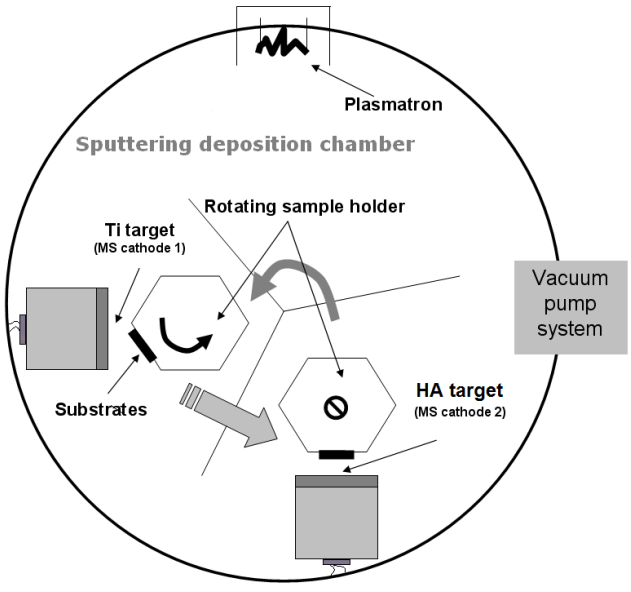


Fig. 1. Schematic diagram of magnetron co-sputtering deposition process.

There were coated titanium substrates of 1 cm^2 area for structural characterizations and for pull-test measurements. Post deposition crystallization annealings were performed in environmental air at 400°C, 550°C and 750°C for 1 hour using a Nabertherm furnace – model L3/12/P320.

2.3 Morpho-structural characterizations and adherence testing

Grazing incidence X-ray diffraction (GIXRD) investigations were performed on a Bruker D8 Advance diffractometer, in parallel beam setting, using Cu $K_{\alpha 1}$ radiation (Ge(220) double monochromator in the incident beam). The films diffractograms were recorded in grazing incidence geometry at glancing angle of 3°. The films morphology was investigated by scanning electron microscopy (SEM, model Zeiss DSM942), all the samples being sputter coated with gold for better visualization. An acceleration voltage of 20 kV was applied. FTIR spectroscopy in reflection mode (ATR) was used for analyzing the functional groups present in the hydroxylapatite (Perkin Elmer BX Spectrum-Pike spectrometer) structure. The analyses were performed in the range 4000 - 400 cm^{-1}, with a resolution of 4 cm^{-1}. In order to test the uniformity of the films surface, a point-to-point measurement was performed using a Pike-MIRacle diamond head (1.8 mm diameter). The bonding strength at the metallic/ceramic interface was estimated by a pull-off method. A PAT_{handy} (DFD Instruments) adhesion equipment was used. Stainless steel test elements of 6 mm^2 area were glued onto the film surface using cyanoacrylate adhesive (maximum bonding force: 85 MPa). Each test element was pulled-off vertically with a calibrated hydraulic pump until detachment. The failure values were registered and then converted in MPa adhesion values.

3. Results

3.1 SEM investigation:

Scanning electron micrographs were made on abrupt and graded HA films prepared by sputtering. Both types of as-deposited samples revealed a compact structure with a uniform and smooth morphology. In case of abrupt structures, local rare delamination phenomena were evidenced at larger magnifications (5000X), these areas being estimated at an average value of ~10% from the total film surface for 550°C annealed samples and respectively 20% for 750°C the annealed ones. The annealed HA graded structures appeared more homogeneous (Fig. 2).

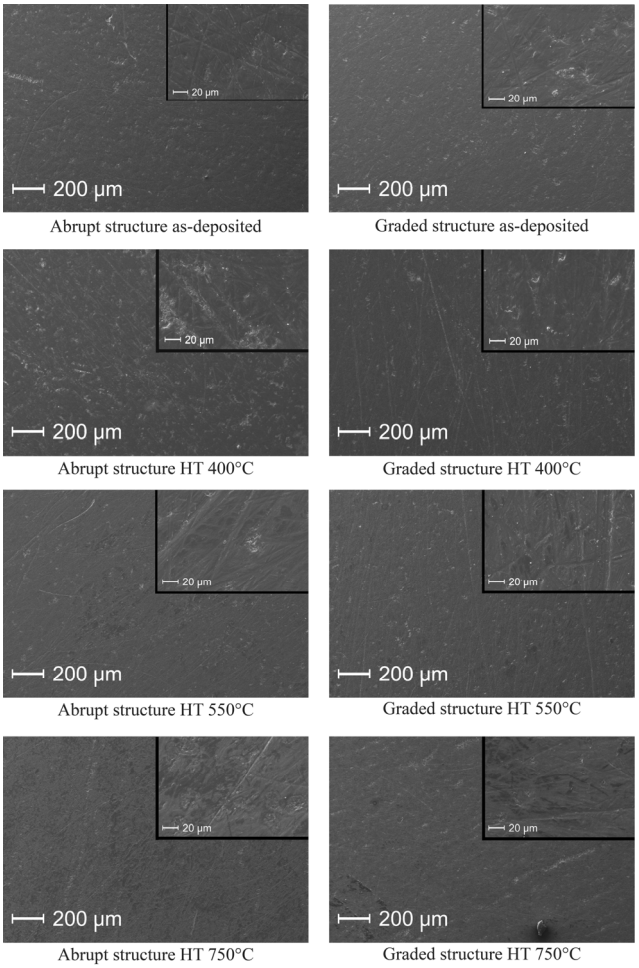
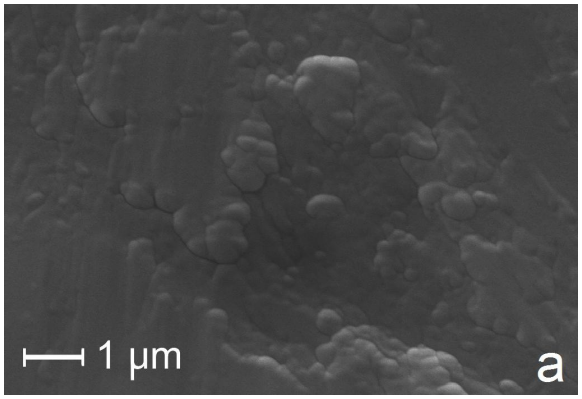


Fig. 2. SEM micrographs of HA samples before and after heat treatment at different temperatures: a) 0.5 k X magnification; b) 5k X magnification.

One can notice a good hydroxylapatite film crystallization for the 550°C treated samples. The well-bred polyhedron shaped grains with an average size of ~ 250 nm, uniformly distributed onto film surface are suggesting the initiating of a densification process of the coatings microstructure. This is stronger for the 750°C annealed structures, HA films displaying clear separated nano-grains (Fig. 3).



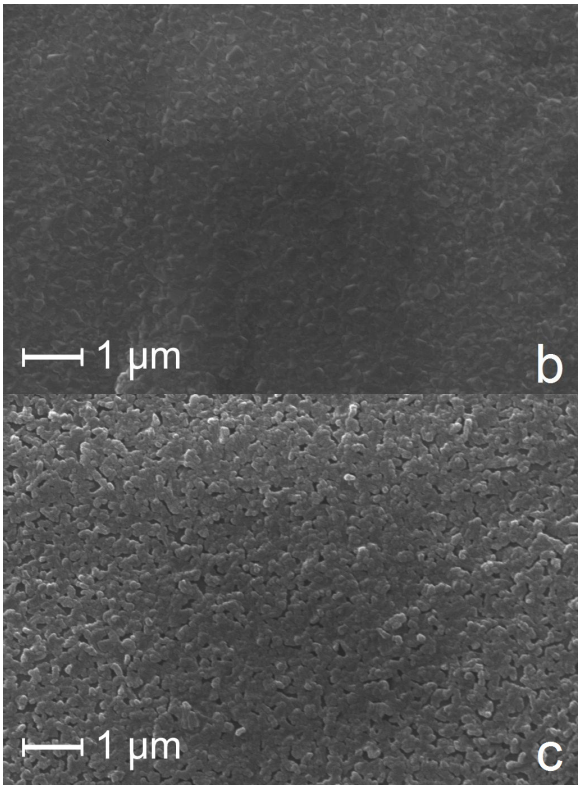


Fig. 3. SEM micrographs of HA FGM samples (100K X magnification): a) as-deposited, b) annealed at 550°C and c) annealed at 750°C for 1 hour.

3.2 XRD characterization

The GIXRD patterns of powder and sputtered samples are presented comparatively in Fig. 4. The analysis revealed that the main crystalline phase is HA (ICDD: 00-09-432) for all the films. There were also noticed strong signals coming from titanium substrate (ICDD: 00-044-1294). The GIXRD analysis showed an increase of films crystallinity vs. annealing temperature. The as-deposited coatings were amorphous and after the 400°C annealing treatment the HA structures displayed a slight increase in the intensity of the amorphous halo (range 2θ=26-34º) (Fig. 4b). The heat treatments at 550°C and 750°C produced well-crystallized HA structures (Fig. 4b). The crystallites display a strong preferential orientation with (002) planes parallel to the substrate, which can be deduced from the higher relative intensity of (002) line compared to the HA powder diffraction file. The higher intensities of the (002) HA line for the FGM structures compared to the abrupt ones suggests a stronger preferential orientation of these films. The average crystallite size was estimated from the FWHM of X-ray diffraction (002) line applying the Scherrer equation [16]. The line width was corrected for instrumental line broadening using a corundum NIST standard reference material 1976. Values of ~36 nm and ~ 46 nm were obtained for the HA nanocrystallites in case of abrupt and respectively graded structures annealed at 550°C and respectively 750°C (Table 1). The better crystallization of graded HA structures during heat treatments compared to

the abrupt structures might be attributed to the diminution of the mechanical stresses. This is in agreement with the better values of adhesion obtained for this type of structure.

Table 1. Average (002) crystallites size vs. annealing temperature.

Structure	Abrupt 550°C	Graded 550°C	Abrupt 750°C	Graded 750°C
Average (002) crystallites (nm)	35.1	45.5	38.2	47.3

All the annealed structures also displayed some weak and broad additional maxima that could be assigned to non-stoichiometric titanium suboxides, $TiO_{2-\delta}$. Clear signals of TiO_2-rutile phase (ICDD: 00-021-1276) were recorded for all HA films annealed at 750°C. Besides, a 0.17° shifting of (002) and (102) Ti lines to smaller angles relative to 550°C annealed structures has been detected. This might indicate an increasing of substrate oxidation due to the diffusion of oxygen atoms in titanium structure with annealing temperature. Previous sintering studies suggested that a diffusion process occurs between titanium and HA, producing various titanium oxides [17-19]. The presence of film defects as micro-cracks and delamination is also promoting the titanium substrate oxidation during heat treatment in environmental air.

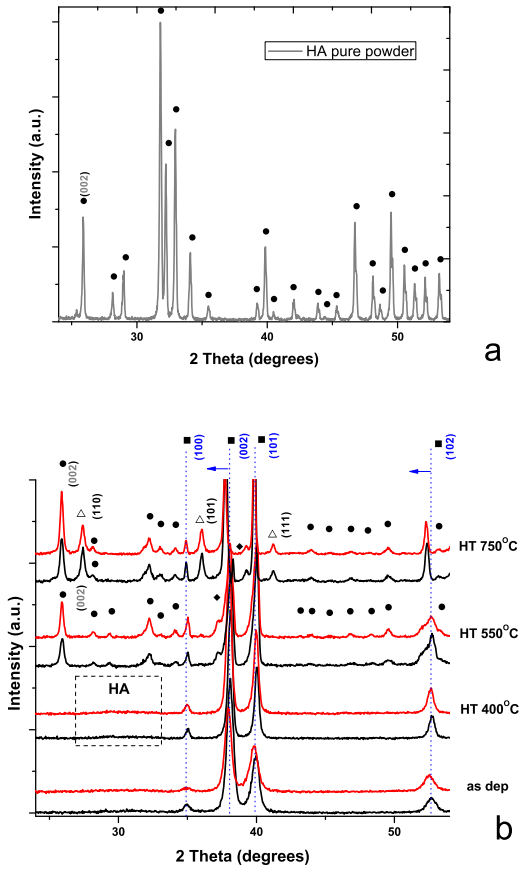


Fig. 4. XRD patterns HA films and powder: a. XRD pattern from Sigma-Aldrich HA material; b. HA abrupt structures (black) and HA graded structures (red).■=Titanium substrate; ●=Hydroxylapatite; △ -TiO_2-rutile; ◆=Possible Titanium sub-oxides.

3.3 FTIR measurements

FTIR spectra of the HA films (Fig. 5 a-b) revealed strong vibrations modes at the following wave numbers: 580, 601, 936-963, 1010-1024, 1070 and 1092 cm^{-1}. These absorption bands could be assigned to bending mode of PØP Q^3, Q^2, Q^1 and Q^0 units (550-600 cm^{-1}) and respectively to symmetric stretching bands of PØP Q^3, Q^2 and Q^1 units (650-800 cm^{-1}). The sharp bands at 1010-1024 cm^{-1}, 1070-1093 cm^{-1} and 963 cm^{-1}, correspond to ν_3 asymmetric, respectively symmetric stretching modes of $(PO_4)^{3-}$ groups [20-24]. One can notice for all the annealed samples a splitting of the stretching IR absorption band at 1082 cm^{-1} in two narrow lines at 1070 and 1093 cm^{-1}. Therefore we consider that the crystallization of MS-HA film has it onset around 400°C.

The shifting of the absorption bands after annealings could be explained by a modification in the crystalline/amorphous phase ratio.

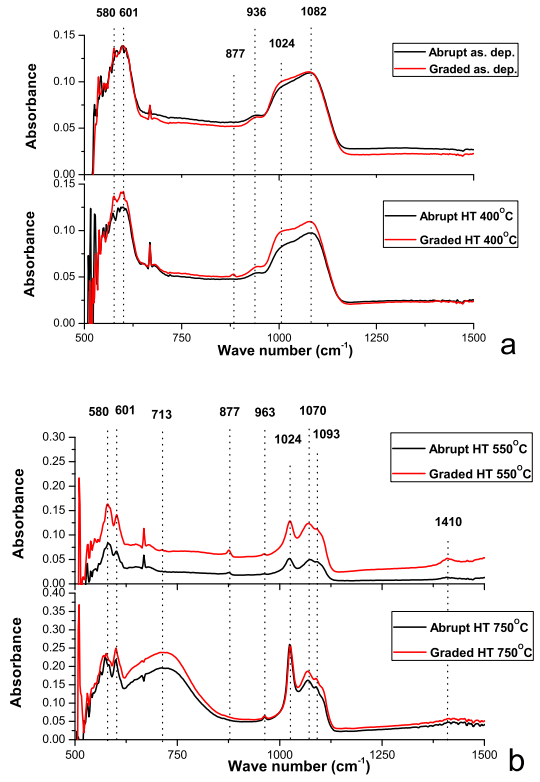


Fig. 5. Comparative IR spectra for studied films: HA abrupt structures (black) and HA graded structures (red): a. As deposited and 400°C HT hydroxylapatite coatings; b. 550°C HT and 750°C HT hydroxylapatite coatings.

The presence of absorption bands at 877 cm^{-1} and 1410cm^{-1} is attributed to carbonate $(CO_3)^{2-}$ structures appeared during the deposition process. Their intensity increased with annealing temperature, being emphasized by easiness of substituting the $(PO_4)^{3-}$ groups [18, 23, 25].

For the samples annealed at 750°C a broad adsorption band in 700-770 cm^{-1} region was the evidenced. As described above, the XRD data are in agreement with this assumption, certifying an increase in TiO_2 crystalline phase content for all the HA samples annealed at 750°C [18]. This phenomenon suggested that Ti substrate suffered a strong oxidation at the interface. This is the result of incorporating oxygen ions not only from hydroxylapatite structure but also from the air due the presence of local delaminations.

In order to test the homogeneity of HA surface morphology a set of point-to-point IR measurements were performed within an area of 10 x 10 mm^2 within the central region of the depositions [26]. We have estimated the relative area of ν_3 asymmetric stretching of phosphate groups for each IR spectrum as an indication of HA coated surface within the area of FTIR Diamond Head (Table 2).

Table 2. $(PO_4)^{3-}$ v3 stretching band area vs. annealing temperature.

Nr./crt.	As sputtered 150°C	Annealing 400°C	Annealing 550°C	Annealing 750°C
Abrupt Structure	14.2±1	14.7±1.4	14.6±1	11±1.7
Graded Structure	14.7±2.2	14.8±1.1	14.8±1.4	10.5±1.4

As noticed in Fig. 6 similar values of FTIR integral intensity were obtained for the abrupt and graded structures annealed up to 550°C which suggest a similar coverage with HA of the titanium substrates. At 750°C for both types of structures one can notice a significant decrease of the mean integral area which can be correlated to the delamination phenomena.

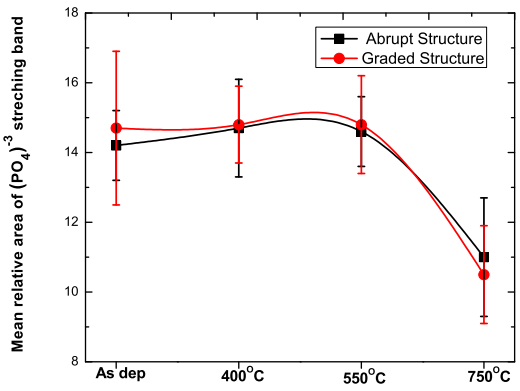


Fig. 6. Dependence on annealing temperature of $(PO_4)^{3-}$ v3 stretching band area.

3.4 Pull- test adherence results

Test batches of abrupt and graded HA structures were evaluated comparatively (Fig. 7). Both types of as-deposited structures displayed similar adherence values ~ 55 MPa. Similar values were obtained for the structures annealed at 400°C. A higher value of ~ 70 MPa was obtained for the 550°C annealed HA/Ti abrupt structures. In case of 550°C annealed graded ones the failure occurred in glue's volume at ~ 85 MPa without damaging the film integrity. As this value represents the bonding limit of the resin as confirmed by the manufacturer, the true coating-substrate adhesion strength could be even higher. For both structures types, 750°C annealed, the pull-off adherence was estimated at ~ 40 MPa, the film being ruined each time.

The adhesion values (Table 3) obtained for the graded samples annealed at 550°C are much better than those generally reported in literature, which do not exceed 60 MPa [27-30]. The mechanical stability is of great importance parameter for high-load bearing implants. Therefore, such coated implants could have an outstanding potential in orthopedic and especially in dental applications. The adherent HA structures with HA_xTi_{1-x} intermediate composite buffer layers might eliminate some of the disadvantages associated with the commercial HA coatings, offering a new perspective over these types of implant structures.

Table 3. Adherence vs. annealing temperature.

Nr./crt.	As sputtered 150°C	Annealing 400°C	Annealing 550°C	Annealing 750°C
Abrupt Structure	57.8±5.3	56.4±4.4	69.5±4.2	43.2±6.3
Graded Structure	52.2±4.2	55.2±4.2	> 85	40.2±4

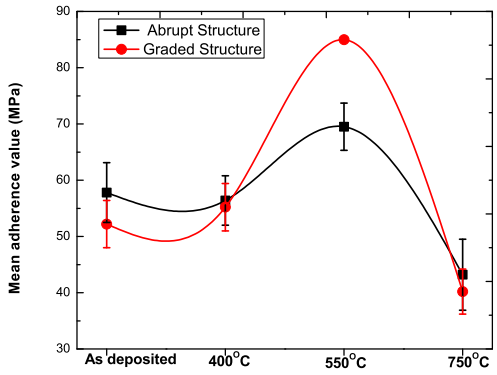


Fig. 7. Dependence on annealing temperature of HA film adherence.

Considering the maximum adhesion value at 550°C, the changing of films integrity can be explained by two distinct phenomena having opposite effects vs. temperature variation:

- The thermal stress which weakens the film's integrity,

- The inter-diffusion HA↔Ti which strengthens the film adherence by smoothing the interface between the two materials.

The mechanical stress at the interface Ti/HA layer is mainly due to the difference of thermal expansion coefficients (CTE) and is probably strongly increasing with annealing temperature. While for titanium the CTE (9.2-9.6 × 10^{-6}/°C) is relatively constant during annealing, in case of the HA layer the value is supposed to be higher than of the titanium (15 × 10^{-6}/°C) [31, 32]. Even if it is difficult to predict its temperature variation, one can expect a contraction of the coatings as a result of phase transition from amorphous (or poor crystalline) to reasonably good crystalline apatite [33].

This contraction is supported also by our SEM images (Fig. 3) which evidenced the growth of clear separated HA nano-grains at high annealing temperatures. The CTE dependence of HA and Ti are probably the main reasons for the mechanical stresses at the HA/Ti interface. Their influence upon the structures surface morphology is more clear in case of abrupt structures which display a stronger phenomenon of film degradation at 750°C in comparison with 400°C and 550°C (Fig. 2). This degradation is in agreement with XRD spectra which asserted an increase of rutile phase (Fig. 4-b) area and respectively FTIR measurements which displayed a broad band at 700-770 cm^{-1} assigned to TiO_2 stretching vibration (Fig. 5). These results suggest that the film is locally exfoliated allowing the substrate to undergo a strong surface oxidation at this high temperature. The $(PO_4)^{3-}$ asymmetric stretching band mean integral area measured in multiple points on film surface is in suit-agreement with this assumption, as for 750°C annealed samples the value had a significant decrease (Fig. 6).

In order to explain the more homogenous surface morphology of the graded structures one has to consider the inter-diffusion HA↔Ti which is the second phenomenon to be considered. This is due to the fact that titanium and hydroxylapatite atoms easily inter-diffuse and mix during heat treatments in the HA-Ti interfacial region, leading to the formation of HA_xTi_{1-x} (x=0÷1) interface layer with chemical gradient composition. Such a phenomenon occurred for the annealed abrupt HA coatings and explained the increasing of adhesion value with the annealing temperature up to 550°C. Based on this design model, HA/HA_xTi_{1-x}/Ti (x=0÷1) graded structures with FGM interface buffer layer (~100 nm) were prepared by co-sputtering techniques from two targets. For these types of structures the adherence value experienced a dramatic improvement at 550°C, the value obtained being higher than 85 MPa. This suggests a cumulating of Ti↔HA inter-diffusion phenomenon during annealing with the continuous gradual transition from the metallic substrate to the ceramic coating. However, at 750°C the adherence value decreases even for the graded structures as an effect of a significant crystallization-induced contraction owed to the mismatch of the thermal expansion coefficient between the crystallized HA and Ti substrate. This leads to high mechanical stress, which overcompensates the diffusion effect above this temperature.

The optimum annealing temperature seems to be 550°C as it produces not only high values of adhesion but also a high crystallinity and proper densification of HA structure. For such structures preliminary in vitro tests in mesenchymal stem cells (MSCs) proved that HA films supported cell viability, attachment, proliferation, ALP producing; the specific osteoblasts differentiation was succeeded in the presence of dexametasone [34].

4. Conclusions

Abrupt and graded hydroxylapatite structures were successfully prepared onto titanium substrates using magnetron sputtering and co-sputtering techniques. Post-deposition annealing effects, at 400°C, 550°C and 750°C, upon the interfaces of these HA/Ti structures were monitored. XRD and FTIR results showed that the heat treatments at 550°C and 750°C produced (002) well-crystallized and carbonated HA films. The surface integrity was found strongly dependant upon the annealing temperature in case of abrupt structures with a percent of peeled off regions up to 20%, while in case of graded ones the integrity was much better. The pull-test adhesion showed similar dependences for both types of structures with similar values for as-deposited and 400°C (~ 55 MPa), 750°C (~ 40 MPa) and with a maximum for 550°C annealed structures. The adherence values at 550°C clearly differs, ~70 MPa for abrupt structures and more than 85 MPa in case of graded ones. Their design attenuates the material interface discontinuity by means of a HA_xTi_{1-x} (x=0÷1) functionally graded buffer layer, increasing the adherence strength. The high adhesion values at obtained after heat-treatment at 550°C may be explained by a prevalence of diffusion phenomena while, at higher

temperatures of 750°C the thermal stress might strongly weakened the HA/Ti interface. These results have shown certain promises that may eliminate some of the disadvantages associated with the commercial HA coatings. A further optimization of the graded structures could become more effective in preventing the bonding strength degradation during annealing at higher temperatures.

Due to the wide variety of medical applications for these adherent hydroxylapatite coatings, as orthopedic and dental prostheses, more in vitro test are also intended in the near feature.

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