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Deposition of thin hydroxyapatite films by 335 nm Nd:YAG laser ablation

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The characteristics of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) thin films deposited by the pulsed laser deposition technique have been describrd. The laser used was a Nd:YAG, operating at the wavelength of 355 nm. All films were deposited at room temperature, either in ambient water vapour or in vacuum, and were annealed, after deposition in air, at 600 °C. Next, they were examined with the use of an X-ray diffractometer, Fourier transform infrared spectrometer, atomic force microscope, micro scratch tester and scanning electron microscope. The analyses showed that crystalline films exhibiting very strong adhesion to the substrate have been obtained.

Keywords: *pulsed laser deposition; hydroxyapatite; biomaterials*

1. Introduction

Growth of thin films of chemically complex materials by the pulsed laser deposition has several advantages. The method is versatile – the laser energy source is outside the chamber and can be changed; practically any material can be vaporized; targets can be used, either in vacuum or in a atmosphere consisting of various reactive gases; sequential ablation of suitable targets allows deposition of multilayered films of various materials. Very precise control of the film thickness is possible, by adjusting the laser pulse mode. High quality films with good adhesion to the substrate can be fabricated with a high deposition rate.

Other advantage of the method is that the stoichiometry of the target is preserved in the deposited films, even in the case of materials having a complex structure. This

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probably results from the fact that a high energy flux to the surface of a target causes all material constituents to be vaporized practically at the same time, regardless of their evaporation temperature. Stoichiometry is, in fact, preserved only in the vicinity of a target. At further distances it is lost due to differences in the molecular masses of the expanding elements and the resulting differences in their rates of expansion.

In this work, the films produced by laser ablation of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) were studied. Synthetic hydroxyapatite (HA) is a biocompatible ceramics. It is chemically similar to the mineral component of mammalian bone. For this reason, the human body (and bodies of other mammals as well) can adapt HA. HA into it. HA is classified as a bioactive material, forming strong chemical bonds with surrounding bones, unlike other materials such as alumina and zirconia, which are identified as foreign materials and become encapsulated by fibrous tissue. HA is deposited onto orthopaedic implants in order to increase the surface area of bone –implant contact.

Important factors determining the quality of the HA coating are the cohesive strength, the degree of crystallinity and the adherence to the metal surface. In addition, phase stability is essential for successful growth of the osteoblast cells on the film. In the case of hydroxyapatite, it has been found that good coatings are obtained when the ambient gas is water vapour or argon mixed with water vapour at the pressure of 10–150 Pa [1, 2]. In all cases, heating of the substrate over 400 °C is necessary in order for the deposited films to have a crystalline structure. Otherwise amorphous films are obtained which exhibit rapid in vivo degradation, and are unsuitable for medical applications that require biological fixation of the implant to bony tissue [1]. In the case of human joint replacements, titanium alloy Ti_6Al_4V is a typical substrate used for film deposition. On the other hand, films deposited on Ti_6Al_4V substrates at elevated temperatures exhibited very poor substrate adhesion, which was attributed to softening of the substrate, formation of a titanium oxide layer between the hydroxyapatite film and the Ti_6Al_4V substrate, and thermal stresses [1]. Also, the shapes of real implants are complicated and they cannot be heated during deposition as easily as flat substrates. Deposition at room temperature increases adhesion [1, 3] but then post-deposition annealing of hydroxyapatite thin films is necessary to obtain a crystalline film structure. Those experiments, conducted at room temperature, were made with a KrF laser operating at the wavelength of 246 nm and fluency 1–5 $J\cdot cm^{-2}$ [1, 3, 4].

In this work, a Nd:YAG laser was used. A hydroxyapatite (HA) target was ablated under various conditions, i.e. during expansion into vacuum or water vapour. The substrate was kept at room temperature. Next, the deposited HA films were annealed and examined.

2. Experimental

An Nd:YAG Quantel YG981 laser was operated at the wavelength of 355 nm with a pulse energy of 100 mJ and 10 ns pulse duration. The repetition rate was 10 Hz. The hydroxyapatite target was a dense disk, acquired from the Berkeley Advanced Biomaterials, Inc. The laser fluence was ~3.3 $J\cdot cm^{-2}$ (intensity $I = 0.33$ $GW\cdot cm^{-2}$). The incident angle of the laser beam was 45° to the surface normal. The deposition was made in a PLD chamber, either in vacuum or in ambient water vapour, at the pressure of 20 Pa. The number of pulse changes ranged from 12 000 to 18 000. The substrates were Ti_6Al_4V alloy discs positioned at the distance of 4 cm from the target and kept at room temperature. All substrates were polished with abrasive grinding paper and cleaned with acetone, isopropanol and distilled water before use. The roughness of the substrate surface, as measured with a Form Talysurf scanning profilometer, indicated that the Mean square deviation of the substrate surface was about 0.05 μm.

The deposition rate was about 0.18 nm per pulse in water vapour and 0.5 in vacuum. The difference is understandable because in the presence of an ambient gas, the ablated particles are scattered in collisions with the gas molecules and only part of them reach the substrate. After deposition, the substrates were annealed for 1 h in ambient air at 600°C. Next, they were examined with the use of an X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FTIR), Atomic force microscope (AFM), micro scratch tester (MST) and a profilometer. All tests were made at least in duplicate, showing good reproducibility of results.

3. Results

3.1. Film structure

The identification of phases present in the deposited films was made with the use of X-ray diffractometry. The CuK_α line of the wavelength of 1.54 Å was used. The spectra are shown in Fig. 1. Figure 1a shows the diffractogram of the HA target, Fig. 1b shows the diffractogram of HA film deposited after 18 000 pulses in an atmosphere of water vapour under the pressure of 20 Pa, and Fig. 1c shows the diffractogram of HA film deposited after 12 000 pulses under vacuum. One should note that the deposition rate is much higher in vacuum and that the 12 000 pulse coatings are about twofold thicker than the 18 000 pulse coatings obtained in water vapour. All the pertinent peaks of the HA target are present in the deposited films, although some of them are overshadowed by titanium or steel peaks arising from the substrate. All peaks are narrow, which indicates that polycrystalline phase prevails in the deposited films. The only peaks not present in the pattern for the HA target are the titanium peaks, which means that the HA films are not contaminated by any of the dehydrated forms of HA, such as α-tricalcium phosphate (α-TCP) or β-TCP [5].

Absorption spectra of the deposited films, as obtained with the use of the Fourier transform infrared spectrometer (FTIR), are shown in Fig. 2. Characteristic bands [6] of HA are present in all the spectra, i.e., the phosphate band PO_4, the carbonate band CO_3, the hydrocarbon band CH and the hydroxyl band OH.

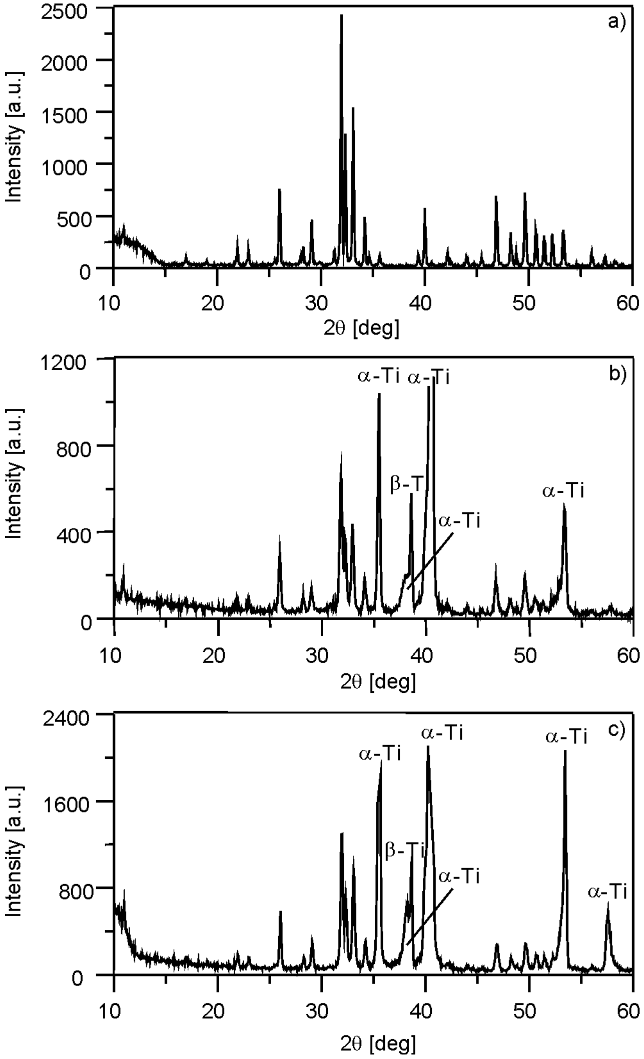

Fig. 1. Diffractograms (CuKα, 1.54 Å) of the HA target and deposited films. All peaks, except for Ti6Al4V, correspond to hydroxyapatite: a) HA target, b) HA film deposited in water vapour, 18 000 pulses, c) HA film deposited in vacuum, 12 000 pulses

Four vibrational modes of phosphate ions, denoted as ν1, ν2, ν3 and ν4, are observed. The ν1 mode has the frequency of 950–1000 cm^{-1}, the ν2 mode 430–460 cm^{-1}, the ν3 mode 1040–1090 cm^{-1}, and the ν4 mode 520–660 cm^{-1}. In both cases, namely for 18 000 pulses in water vapour or 12 000 pulses in vacuum, three well-defined and sharp peaks, occurring at 566, 598 and 630 cm^{-1}, are observed in the ν4 phosphate band. Also, the ν3 phosphate band has well defined peaks at 962, 1000, 1060 and 1087 cm^{-1}. Weak carbonate bands ν3 lie at 1415 and 1465 cm^{-1}. Peaks corresponding to hydrocarbon bond are situated at 2850 and 2930 cm^{-1} and a broad hydroxyl band in the 3000–3600 cm^{-1} range. Narrow peaks indicate the presence of a polycrystalline phase.

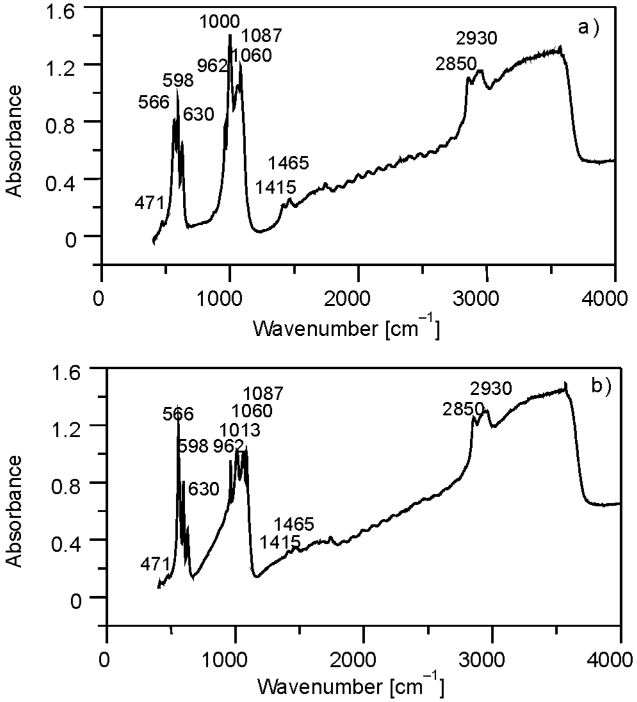

Fig. 2. FTIR spectra of deposited films:
a) 18 000 pulses, water vapour, b) 12 000 pulses, vacuum

3.2. Topography

The topography of the deposited films was studied by the atomic force microscopy, using a Veeco Multi Mode IV SPM. The microscope was used in a tapping mode together with phase mode imaging. In the tapping mode, a stiff cantilever is oscillated close to the sample in an intermittent contact mode. Part of the oscillation extends into the repulsive regime, thus the tip intermittently touches or “taps” the surface. This mode avoids the surface damage associated with contact mode imaging, in the case of soft samples. In phase mode imaging, the phase shift of the oscillating cantilever relative to the driving signal is measured. Contrasts between these phase shifts can be correlated with specific properties of materials such as adhesion forces, surface inhomogeneities, etc. However, in the case of hydroxyapatite such an analysis is still not reliable. Therefore pictures obtained from phase imaging are not presented here.

The topography of the deposited films is shown in Fig. 3. The coating deposited in ambient water vapour after 18 000 laser pulses (Fig. 3a) exhibits a fine-grained structure in comparison with coatings deposited under a lower pulse count. This coating is characterized by a highly homogeneous distribution of grains.

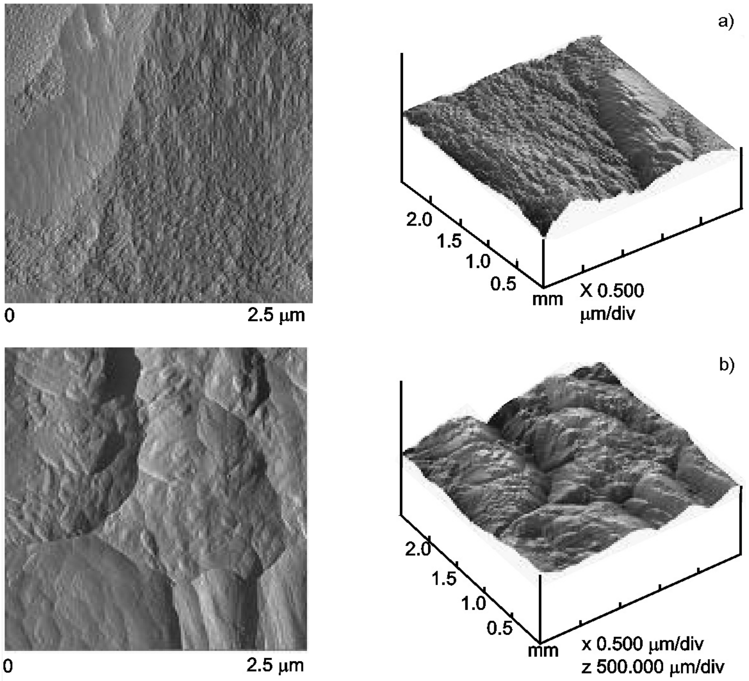

Fig. 3. Topography of deposited layers of hydroxyapatite from AFM:
a) 18 000 pulses, water vapour, b) 12 000 pulses, vacuum

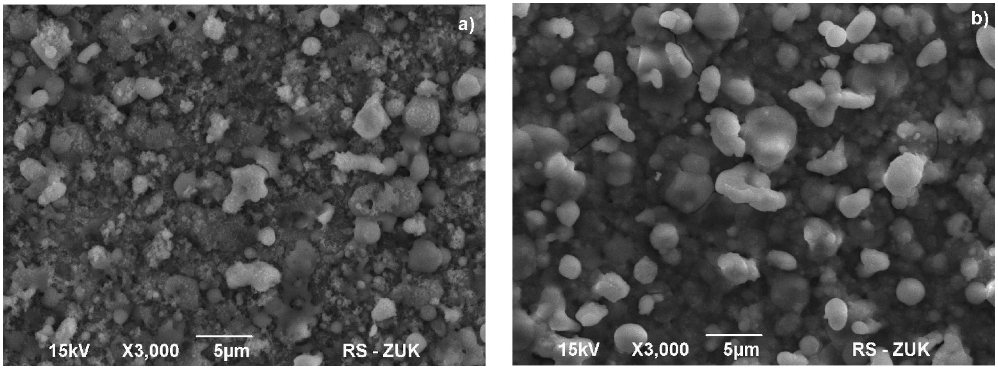

Fig. 4. SEM images of the HA coatings; a) 18 000 pulses, water vapour, b) 12 000 pulses, vacuum

In the case of 12 000 laser pulses in vacuum (Fig. 3b), the topography of the surface coating is considerably different. The grains are of a larger size and on the surface of large grains appear much smaller grains. The images from a scanning electron microscope (Fig. 4) show the same differences. Roughness parameters of films were also measured with a Form Talysurf scanning profilometer. Mean arithmetic deviation was 0.314 μm and 0.557 μm in the case of 18 000 laser pulses in water vapour and 12 000 laser pulses in vacuum, respectively.

3.3. Adhesion

The adhesion of the deposited HA films to the substrate was evaluated by scratch tests. The tests were made with the use of a CSM micro-scratch tester equipped with a Rockwell indenter tip of 200 μm radius. The tip was drawn across the coated surface under progressive loading. The scratch test parameters were as follows: load: 1–70 N, loading rate: 20 N/min, scratch length: 3 mm, scratch speed 0.87 mm/min. Typical results are presented in Fig. 5, which shows the frictional force and the friction coefficient as the normal force increases. The acoustic emission signals were very weak and therefore they are not presented. The characteristic feature of the signals presented in Fig. 5 is that when the load reaches the value at which the HA film becomes cracked or delaminated from the titanium substrate, both the frictional force and the friction coefficient change abruptly. The images obtained during scratch tests were additionally examined under a scanning electron microscope to confirm conclusions drawn from the scratch tester results (Fig. 6).

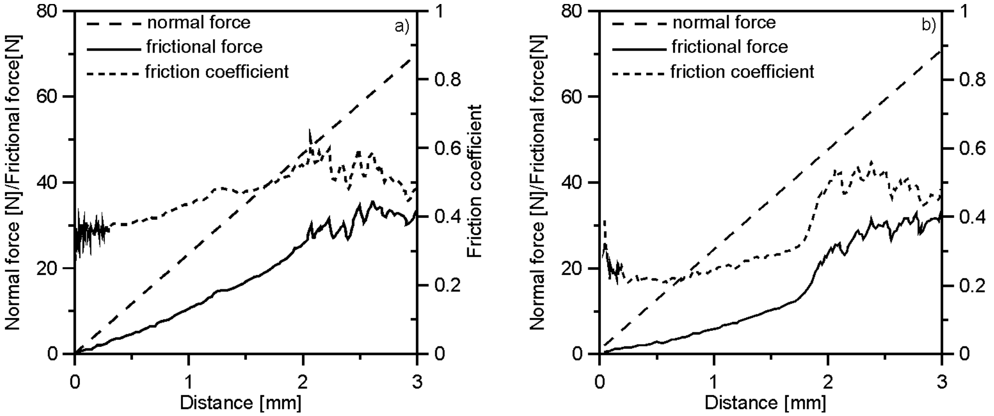

Fig. 5. Scratch tests of HA coatings a) 18 000 pulses, water vapour, b) 12 000 pulses, vacuum

The critical loads at which the first transverse crack lines appear were 43±5 N. Significant differences between the 18 000 pulse coatings deposited in water vapour and the 12 000 pulse coatings deposited in vacuum have not been observed. Before the critical load was reached, the films were only squeezed and dislocated to the sides of the scratching track. No major film delamination was observed in any of the coatings, thereby indicating their high adherence.

The results are encouraging in comparison with those obtained for elevated substrate temperatures. Arias et al. [7] deposited HA coatings in a water vapour atmosphere under the pressure of 45 Pa, using an ArF laser at the fluence of 1 J·cm^{-2}. The substrates were heated to 460 °C. All the coatings were 0.9 μm thick. The scratch tests were made using a CSM micro-scratch tester equipped with a Rockwell tip of 200 μm radius. The displacement of films was observed at the load of ca. 10 N.

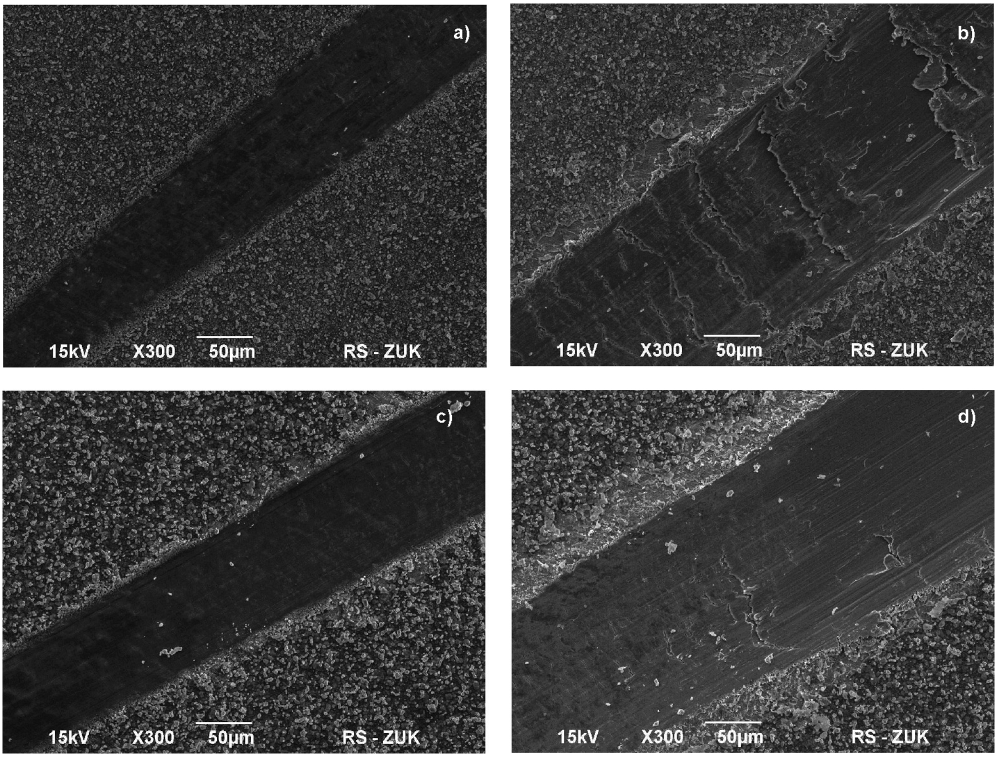

Fig. 6. Scanning electron microscope images from the scratch tests: a) 18 000 pulses, water vapour, *d* = 0.7 mm, b) 18 000 pulses, view of the transverse crackings at *d* = 2 mm, c) 12 000 pulses, vacuum, *d* = 1 mm, d) 12 000 pulses, vacuum, view of the transverse crack lines for *d* = 1.9 mm

In experiments conducted by Fernandez-Pradas et al. HA coatings were deposited in a water vapour atmosphere under a pressure of 45 Pa using a KrF excimer laser operating at 248 nm at the fluence of 2.3 J·cm^{-2}. The substrates were heated to temperature of 575 °C. The scratch tests were made using a 50 μm radius tip. Film displacements were found to be dependent on the pulse count. The displacements occurred at the loads of 5.7, 2.9, 1.7 and 0.3 N, corresponding to pulse counts of 2000, 4000, 9000 and 18 000, respectively. The thicknesses of these films were 0.17, 0.35, 0.75 and 1.5 μm, respectively. In othe experiments of the same authors [9], HA coatings were deposited in a water vapour atmosphere under the pressure of 10 and 45 Pa using a Nd:YAG laser with the operational wavelength of 355 nm. The laser fluence was 3.1 J·cm^{-2}. The scratch tests were made using a 50 μm radius tip. Crystalline coatings 1–4 μm thick were obtained at the substrate temperatures between 500 °C and

600 °C. Under these conditions the critical loads were about 1 N. In addition, the coatings obtained under the pressures of 10 Pa or 45 Pa, contained either CaO and TetraCP phases (at 10 Pa), or α-TCP phase (at 45 Pa).

Comparison of the results of scratch tests is difficult as the tips in individual experiments have different radii. Very rough estimation can be made based on geometrical similarity [10] which requires equal ratios of the layer thickness to the scratching tip radius. Hence results of the scratch tests of 3–6 μm thick coatings should be compared with those for 0.75–1.5 μm thick coatings scratched with 50 μm tip. Additional condition of equal pressures requires scaling the critical loads with the square of tip radius. This means that critical loads obtained with a 50 μm tip should be multiplied by a factor of 16 to be compared with our results. This scaling leads to a critical load 5–27 N for 1.5 and 0.75 μm thick films obtained in [8] and 16 N for films obtained in [9].

The critical load determined with the use of a 20 μm tip, was 2 N [3]. The authors of the paper do not report the film thickness. However, the experimental conditions (vacuum, laser fluence 4–5 $J\cdot cm^{-2}$) suggest that the films were very thick (over 10 μm) and the results cannot be compared with those obtained in the present work.

4. Conclusions

The results show that satisfactory deposition of thin films of hydroxyapatite can be achieved using an Nd;YAG laser operating at 355 nm. The HA films can be obtained at room temperature, provided post-deposition annealing in ambient air is performed. Such processing makes it possible to obtain good HA films either in ambient water vapour or in vacuum. The crystalline structure of the deposited films is not contaminated by any of the dehydrated forms of HA. The scratch tests showed that HA coatings 3–6 μm thick adhere strongly to the Ti_6Al_4V substrates.

Acknowledgments

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