

# Morphology and spectral behavior of hydroxyapatite nanocrystalline coatings obtained by gas detonation deposition

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*Received January 17, 2012*

Electronic structure and morphology of hydroxyapatite (HAP), deposited on titanium substrate by gas detonation deposition (GDD), was investigated by scanning probe microscopy of high resolution and spectroscopic methods. Nanoscale structure formation of the coatings in the form of nano-dispersed ceramics was determined. Effects of more advanced surface in the transition of HAP from the crystalline (powder) to nanodispersed (coating) state was studied. It is revealed that the elemental composition of GDD cover surface and subsurface layers remains stable up to the depth of 50 nm. The change of elemental composition of GDD cover subsurface layers in the direction of increasing the calcium and phosphorus content was observed in the range 50–150 nm.

Методами сканирующей зондовой микроскопии высокого разрешения и спектральными методами исследована электронная структура и морфология ГАП при его газо-детонационном осаждении (ГДО) на титановые подложки. Установлено наноразмерное формирование структуры покрытий в виде нанодисперсной керамики. Исследованы размерные эффекты, обуславливающие общую тенденцию увеличения энергии связи остовных электронов атомов при переходе ГАП от кристаллического (порошок) к нанодисперсному (покрытие) состоянию. Выявлено, что элементный состав поверхности и приповерхностных слоев ГДО покрытия остается стабильным до глубины 50 нм. В диапазоне 50–150 нм наблюдается изменение элементного состава приповерхностных слоев ГДО покрытия в сторону увеличения содержания кальция и фосфора.

## 1. Introduction

Products made of hydroxyapatite (HAP,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) belong to the class of bio-ceramic calcium-phosphate materials and have the chemical composition almost identical to the mineral component of bone [1]. Because of high biocompatibility and osteoinductivity HAP can form direct chemical bonds with bone tissue and can be

gradually replaced by live bone tissue [2]. For this reason HAP products are successfully used in dentistry and orthopedics for many years. More than half of all HAP based bioactive ceramics applications is its use as coating material on metallic implants, mainly from titanium. However, titanium is one of bioinert materials, which although doesn't emit any toxic components, but also does not cause the positive

reaction of the organism. This problem can be decided by the deposition of HAP bioactive coatings, which cause the positive response from live tissue that consists in the differentiation of the bone immature cells. Unlike bioinert materials, bioactive materials implantation leads to the formation of chemical bonds with bones across the interface. These bonds are due to the adsorption of non-collagenic proteins that cause the growth of bone on the surface of biomaterials, such as osteocalcin, osteonectin, sialoglikoproteins and proteoglycans.

Most of the coatings are obtained by plasma deposition [3,4], which uses the deposition process of the powder particles on a heated metal surface that results in the change of phase and chemical composition: the appearance of glass phase and coverage material amorphization, as well as the emergence of the stresses and microcracks at the boundary between the coating and metal due to their difference in thermal expansion. Coverage amorphisation can be reduced by the following implant annealing, but the imperfection of the boundary layer and the number of microcracks increase, and the adhesive ability decreases. To decide this problem it was proposed to use gas detonation decomposition method, in which the coating is carried out by the gas mixture detonation (explosion) energy that accelerates the powder particles [5–8]. Coating adhesion is provided here by high kinetic energy of HAP particles, bombarding the substrate.

However, despite receiving the highest quality coatings, that confirmed by research of their characteristics and mechanical properties [9–11], the questions of changes in the coatings phase composition and crystalline structure remain unstudied. These questions for coatings obtained by plasma and laser deposition have been studied in [12–14]. The current work deals with the electronic and crystal structure investigation of HAP deposited on titanium substrate by gas detonation deposition (GDD).

## 2. Materials and methods

Hydroxyapatite was synthesized by precipitation from calcium nitrate and ammonium hydrogen phosphate solutions according to the reaction:

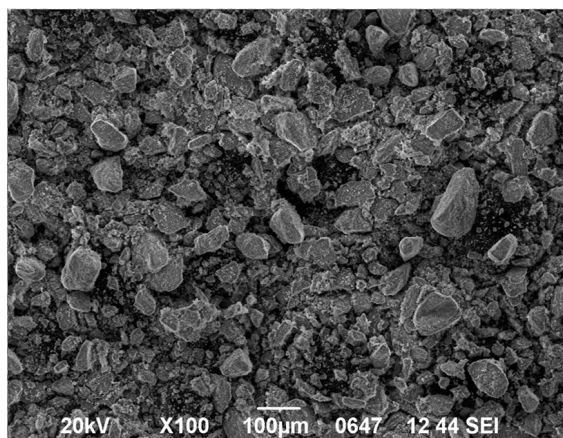
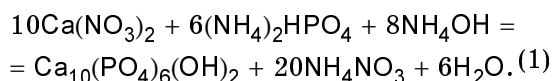


Fig. 1. SEM image of HAP powder obtained.

The resulting powder was dried at 120°C and annealed in air at 1000°C for 1 hour, after that precipitate was transformed into a monotonous conglomerate, with 30 % porosity and 7.5 MPa strength. Then sintered precipitate was ground in the porcelain mortar and sieved to obtain powder with optimal size for gas detonation deposition (60–80 µm) (Fig. 1).

HAP coatings were deposited on titanium substrate (VT-6) with 1 mm thickness. The original gas detonation unit was used for deposition. The detonation wave originated from the ignition of oxygen and combustible gas (hydrogen, acetylene and propane-butane) explosive mixture in the blasting chamber. Wave propagated along the gun pipe and seized the portion of HAP powder, injected into the gun. Particles of the material accelerated to velocities of 5 M ( $M$  — Mach number), received the kinetic energy and bombarded the substrate, forming a continuous coating due to the physical and chemical interaction with the substrate material. The programmable displacement of detonation gun or substrate allowed to obtain coverage over the large area or multisurface substrate. The explosive mixture composition, frequency of detonation shots and duration of deposition varied depending on the type and thickness of the substrate.

Morphology and structure of the coatings was investigated by electron microscopy (SEM) on scanning electron microscope JSM-6490 LV (JEOL) with Oxford Instruments EDS INCAx-act attachment for chemical analysis, and by scanning atomic force microscopy (AFM) on high-vacuum scanning probe microscope JSPM 4610 (JEOL). The cantilever with a diamond tip NSG-10-DLC was used as a scanning probe.

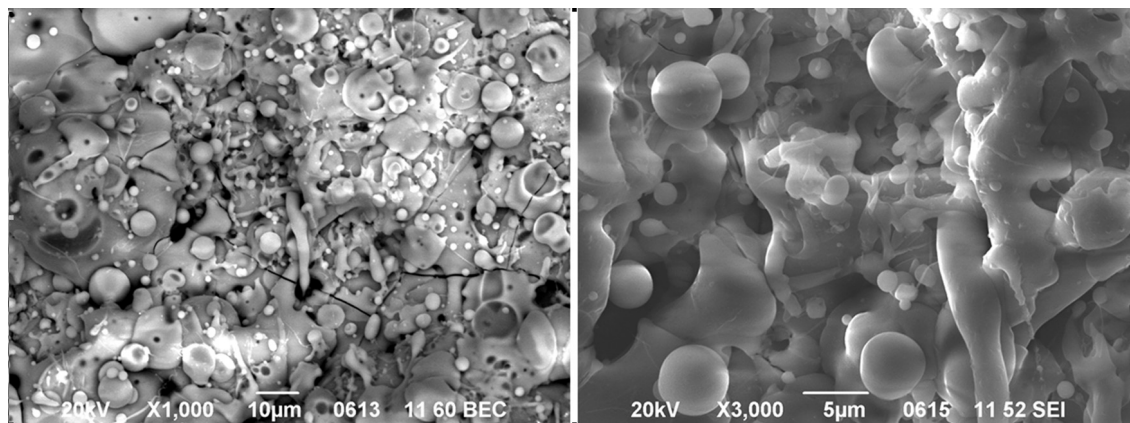


Fig. 2. Electron microscopy micrographs of the coatings obtained by gas detonation deposition.

The value of operating vacuum was not worse than  $10^{-7}$  Pa.

X-ray photoelectron spectra were obtained at "JEOL" photoelectron spectrometer "JSPM-4610", using non-monochromatic Mg  $K\alpha$  (1253.6 eV) X-ray source. The vacuum in the analytical chamber during the experiment was  $10^{-7}$  Pa, the determination accuracy of electron binding energy was 0.1 eV. The thin layer of gold was coated on the sample surface to calibrate the X-ray photoelectron spectra taking into account the charge, accumulating on insulating sample during the experiment. Calibration of X-ray photoelectron spectra was carried by Au 4f lines binding energy of gold, which allowed to obtain a sufficiently high accuracy of electron binding energies for samples element.

The sample surface elemental analysis was performed on Auger electron spectrometer ESA-3. The samples were placed on the console with an angle of 60 degrees to the primary electrons incident beam, what made it possible to obtain depth profiles of etching. Etching was carried out in argon at pressure  $10^{-3}$  Pa. The ion energy was 4000 eV and emission current of 15 mA. Etching was carried out at 5 minutes intervals, after which the spectrum of Auger electrons was taken off. Estimated etching rate at the above parameters was 10 nm per minute.

### 3. Results and discussion

In Fig. 2 it is showed the electron microscopic images of HAP based gas detonation coating. There is a homogeneous coating structure consisting of molten powder deposited single particles. Chemical composition study results obtained by electron mi-

Table 1. Elemental analysis of GDD coating

Element	Wt. %	Atom. %
P	21.01	16.06
Ca	37.06	21.90
O	41.93	62.04

croprobe analysis (Table 1) have shown that the ratio of calcium and phosphorus in the deposited coating is  $Ca/P = 1.36$ , which is significantly less than for the original powder —  $Ca/P = 1.67$ . This fact can indicate the presence of impurity phases in the coating and the shortage of Ca. It should be noted that this method cannot determine the content of hydrogen in the material. Therefore, for correct determination of coatings chemical composition it is necessary to use additionally secondary ion mass spectroscopy method.

For more detailed study of coatings surface morphology we used atomic force microscopy method (Fig. 3). The results of these studies have established the nano-scale formation of the obtained coatings structure, which consist of sintered HAP powder nanoparticles conglomerates. It should be noted that the particles size is 30–40 nm, which corresponds to the size of apatite particles in the native bone. There is some heterogeneity in the nano-conglomerates distribution on the surface. Such heterogeneity and presence of voids between the conglomerates provide reliable fusion of the implant with the bone due to free coming of collagen molecules from interstitial fluid and spontaneous formation of HAP nanoparticles between implant and bone, which eventually leads to the formation of new bone tissue [15].

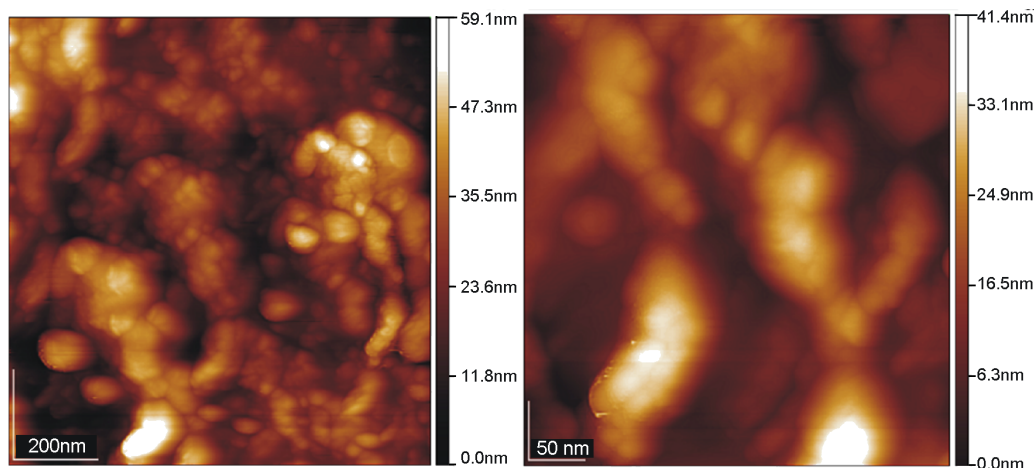


Fig. 3. AFM images of GDD coating.

Under the formation of HAP coating it occurs the transition from crystalline state, with a particle size of 60–80  $\mu\text{m}$ , to nanodispersed state, with a particle size of 30–40 nm, that should be reflected in the electron-energy structure formation and in the nature of the interatomic chemical bonds. To explore these changes, XPS studies of original HAP powder and obtained GDD coating were carried out. The method of X-ray photoelectron spectroscopy was used because of its effectiveness for the characterization of coatings, adsorbed phase and the chemical bonds nature.

XPS data of the samples atoms are shown in Table 2. There is a general trend of increasing binding energy of atoms core electrons in the transition from HAP crystalline (powder) to nanodispersed (cover) state, which indicates a decrease of electron density on the atoms of calcium, phosphorus and oxygen. Such behavior of electron density probably is due to the effect of more advanced GDD HAP surface, which is characterized by greater number of uncompensated bonds in comparison with the original powder. Apatite nanocrystals are so small that in the transverse direction they consist from nothing more than 2–3 unit cells, and from one-half to two-thirds of the

unit cells locate on the surface of the crystals [16–17]. Consequently, the composition of the investigated coatings is largely determined by the composition of the crystals cutting planes. The following supposition is fully justified: every free surface of the unit cell can have 1, 2 or 3 excess  $\text{Ca}^{2+}$  ions and/or one or two excess phosphate groups. Thus, the presence of dangling chemical bonds leads to the output of electron density from oxygen, calcium and phosphorus atoms.

In addition, change in the composition at the crystal surface can significantly affect to the general composition, determined by chemical means. Because of this, the change in the stoichiometric ratio of Ca/P from 1.67 (for powder HAP) to 1.36 (for HAP GDD coating) can be explained by changes in the surface layer of crystals, rather than the presence of impurity phases and/or shortage of calcium.

In order to study depth changes in the coatings chemical composition, there were carried out investigations of atoms XPS spectra changes during etching of the sample surface. Etching was conducted in three stages with the parameters 3 kV and 30 mA during 5 min (Fig. 4).

Table 2. Atoms core levels electron binding energy (eV) and line width (eV) (measured at half height) of the samples

Sample	O 1s	Ca 2s	Ca 2p <sub>1/2</sub>	Ca 2p <sub>3/2</sub>	P 2s	P 2p <sub>3/2</sub>
HAP powder	531.2	438.9	350.7	347.2	190.5	133.1
HAP coating	531.6	439.4	351.1	347.6	190.9	133.5

Note: The electrons binding energy are given relative to the electron binding energy of Au 4f = 87.5 eV. The measurement error is 0.1 eV.

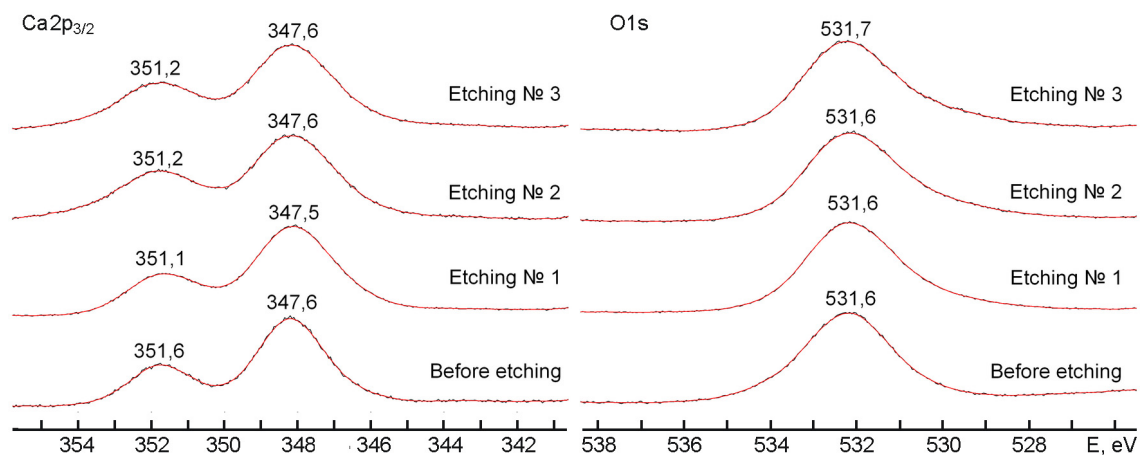


Fig. 4. Ca 2p<sub>3/2</sub> and O 1s XPS spectra of HAP GDD coating.

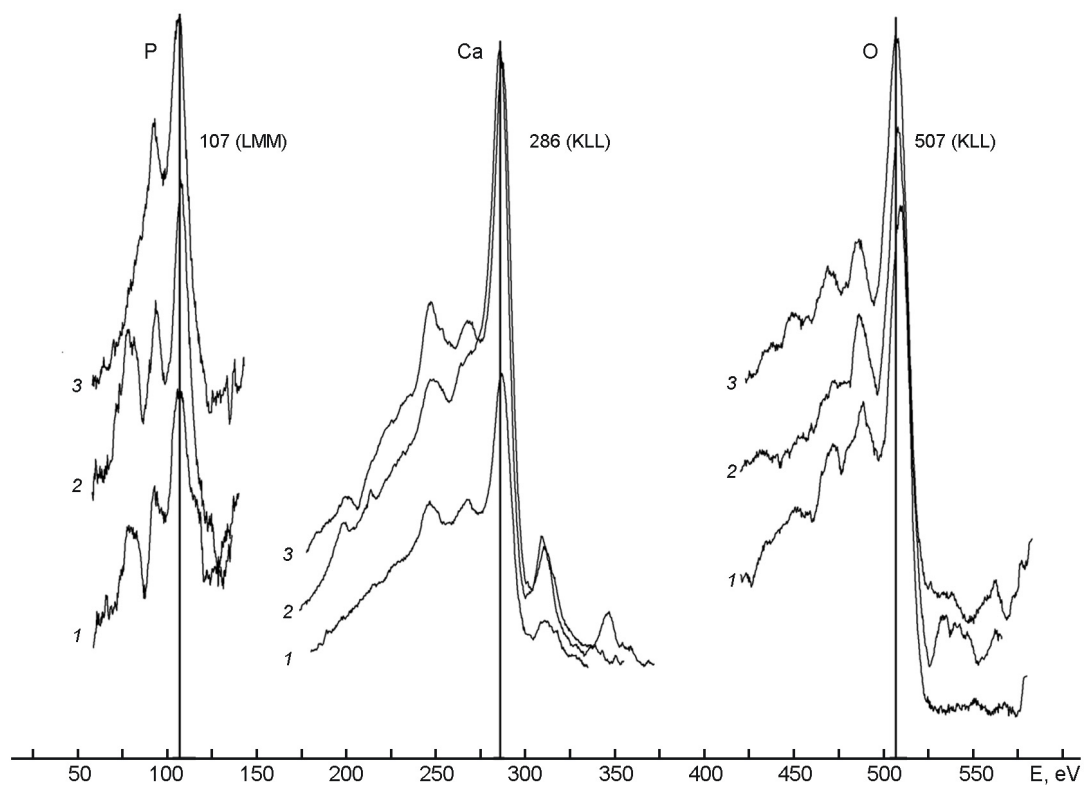


Fig. 5. Auger electrons spectra of phosphorus, calcium and oxygen 1–3 — after etching for 5, 10, 15 min, respectively. The rate of etching was 10 nm per minute.

The results indicate that the change in the core electrons binding energy of the sample atoms during etching occurs within the experimental error (0.1 eV) in all stages of etching (general depth of etching is ~ 50 nm). This fact and the results of AFM and SEM studies suggest that the coating deposits on titanium substrate in the form of nano-dispersed ceramics.

To estimate the surface and subsurface layers elemental composition stability of the coating to a depth of 150 nm, Auger electrons spectra analysis was carried out for calcium, phosphorus and oxygen atoms in three-stage etching (Fig. 5).

The analysis showed constant elemental composition of the coating surface and subsurface layers to a depth of 50 nm (spectrum

1, Fig. 5), which correlates with the XPS data. At the deeper etching to 100 nm and 150 nm (Fig. 5, spectra 2 and 3, respectively), the intensity growth of calcium and phosphorus Auger spectra is observed, that indicates the changes of GDD coating elemental composition at surface layers in the direction of increasing content of these elements.

#### 4. Conclusions

Nanoscale structure formation of the coatings obtained by gas detonation deposition was established.

There is a general trend of increasing the binding energy of atoms core electrons in the transition from HAP crystalline (powder) to nanodispersed (cover) state, which indicates a decrease of electron density on the atoms of calcium, phosphorus and oxygen. Such behavior of electron density probably is due to the effect of more advanced GDD HAP coating surface.

GDD forms on titanium substrate in the state of nano-dispersed ceramics. The elemental composition of GDD coating surface and subsurface layers remains stable down to 50 nm. At the range of 50–150 nm, it is observed the change in the elemental composition of the GDD coating surface layers in the direction of increasing the calcium and phosphorus content.

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**Морфологія і спектральні характеристики  
нанокристалічних покриттів ГАП, отриманих  
методом газодетонаційного осадження**

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Методами скануючої зондової мікроскопії високої роздільної здатності та спектральними методами досліджена електронна структура та морфологія ГАП при його газодетонаційному осадженні (ГДО) на титанові підкладки (ВТ-6). Встановлено нанорозмірне формування структури покриттів у вигляді нанодисперсної кераміки. Досліджено розмірні ефекти при переході ГАП від кристалічного (порошок) до нанодисперсного (покриття) стану. Виявлено, що елементний склад поверхні та приповерхневих шарів ГДО покриття залишається стабільним до глибини 50 нм. У діапазоні 50–150 нм спостерігається зміна елементного складу приповерхневих шарів ГДО покриття в бік збільшення вмісту кальцію і фосфору.