

Raman and ESR study of gas detonation deposited hydroxyapatite coatings

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Structural modification of hydroxyapatite (HAP) formed by gas detonation HAP deposition on metal substrates has been studied using Raman spectroscopy and electron spin resonance (ESR) techniques. It was revealed, that the detonation deposition of the initial HAP powder has been found to result in a considerable broadening of the main Raman band peaked at 960 cm^{-1} and the appearance of additional ones near 947 cm^{-1} and 970 cm^{-1} . In ESR spectra, the signals originated from intrinsic HAP defects such as O_3^- -radicals and F-centers are observed. The changes in the Raman and ESR spectra indicate local variations of HAP structure, namely amorphization at the coating/substrate interface, partial dehydration and increased concentration of intrinsic defects. Nucleation of a new structural phase, oxyapatite, has been also observed.

Методами комбiнационного рассеяния света (КРС) и электронного парамагнитного резонанса (ЭПР) изучена структурная модификация гидроксилатапата (ГАП), полученного методом детонационного осаждения на металлические подложки. Выявлено, что детонационное осаждение исходного порошка ГАП ведет к существенному уширению основной полосы с максимумом около 960 см^{-1} , а также к появлению дополнительных полос около 947 и 970 см^{-1} . В спектрах ЭПР наблюдается дефект, соответствующий O_3^- -радикалу и F-центрам. Наблюдаемые изменения в спектрах КРС и ЭПР указывают на локальные изменения в структуре ГАП, а именно, на аморфизацию на интерфейсе подложка-покрытие, частичную дегидратацию и увеличение концентрации собственных дефектов. Также наблюдается зарождение новой фазы оксиатапата.

Calcium phosphates, first of all hydroxyapatite (HAP) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, are the subject of intensive studies because they form an inorganic basis of bone tissues and dental enamel [1, 2]. These compounds not only possess biological compatibility with a human organism, but accrete with a bone tissue due to direct biochemical bonds and transform gradually into a bone. Because of such unique properties, these materials are widely used in medicine for regeneration of human bones and tooth and for coatings of metal implants.

To deposit such coatings, the plasma spray method is used most often. However, the method has a number of substantial drawbacks. When a flux of fused HAP particles having temperature above 1500°C strikes a much colder (about 800°C) metal substrate, a sharp cooling (quenching) causes essential disordering in the HAP crystal structure as well as formation of glass-like HAP phase at the coating/substrate interface. On the one hand, this phenomenon improves mechanical properties of the coating, especially its adhesion [3, 4].

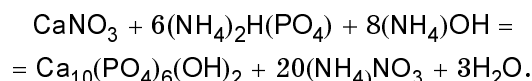
On the other hand, fast resorption of the amorphous phase was observed *in vivo* and *in vitro* [5]. This circumstance is essential for application of those coatings on surgical implants. Besides, at cooling of the deposited HAP coating from 800°C to room temperature, thermal stresses and microcracks appear on the HAP/substrate interface due a considerable difference in thermal expansion coefficients between HAP and the substrate material, thus reducing the coating adhesive strength and increasing resorption rate. To reduce thermal stresses, thickness of coatings should be limited (not more than 50 μm). However, such thin coatings get dissolved much faster than the required lifetime (up to 20 years). The similar phenomena accompany all high-temperature deposition methods such as plasma and magnetron sputtering, pulse laser deposition, etc. Besides, the majority of deposition methods have a number of other disadvantages such as insufficient adhesion, high porosity, crystal structure imperfection, disorder of coating chemical and phase structure as well as the small thickness thereof due to low productivity of the process.

Taking into account the operating conditions of bioactive implants (exposure to blood plasma, enzymes, osteoclasts, cells of immune system, etc), methods of HAP coating deposition should provide low heating of HAP powder and the substrate during the deposition, high adhesion, low porosity of the coating and minimum possible contamination level, preservation of HAP chemical and phase composition, high process productivity and reasonable thickness of the coating. Such conditions are realized when the coating adhesion is provided by high kinetic energy of HAP particles bombarding a substrate, as it occurs in the gas detonation technique. In this method, the coating deposition is done by using the energy of the detonation (explosion) of gaseous mixtures to achieve the acceleration of powder particles.

The gas detonation technique provides the highest coating quality, the lowest substrate temperature, high productivity and very economical manufacturing operation. The method provides coatings of any thickness. Adhesion of bioactive ceramic coatings obtained can be 4–6 times higher than ISO standard requires. Due to interaction of a high energy flux of HAP particles with a cold metal substrate followed by quenching of the deposited layer, the hydration rate, phase composition and crystal structure of

the coating may sufficiently differ from those of the initial HAP powder. For plasma and laser deposited coatings, this problem has been studied. The HAP modification upon gas detonation deposition on metal substrates is studied in this work.

The stoichiometric hydroxyapatite powder was used for the gas detonation deposition. The powder was synthesized using coprecipitation from a solution of calcium nitrate and disubstituted ammonium phosphate according to the reaction



The precipitation was realized at room temperature and pH = 12 under intense stirring of the solution. The precipitate was kept together with the mother liquor during 24 hours. At the same time, the solution was periodically stirred up, boiled during 1 hour, cooled, settled, decanted, added hot distilled water and settled again. After 5 times repeating of that procedure, the precipitate was washed with hot distilled water.

The powder so obtained was dried at 120°C and annealed in air at 1000°C for 1 hour. Sintering and shrinkage (about 10 % of linear dimensions) were observed during the annealing. Then the precipitate was transformed into a homogeneous conglomerate having porosity of 30 % and strength of 5–7 MPa. According to X-ray analysis, the synthesized material was pure crystalline HAP with specific surface of about 1 m²/g which corresponds to 2 μm primary particles of powder. Then the sintered precipitate was ground in a porcelain mortar and sieved to obtain a powder of optimum particle size for gas detonation deposition (60–80 μm). The obtained powder particles had a shape of irregular splinters with the same porosity as the sintered conglomerate.

The HAP coatings were deposited on titanium and copper substrates of various thickness. A home-made original gas detonation setup was used for deposition. The detonation was generated by igniting an explosive mixture of oxygen and a combustible gas (hydrogen, acetylene, or propane-butane) in the explosion chamber. The wave propagated along the gun tube and caught up a portion of HAP powder injected into the gun. Particles of the material were accelerated up to 5M of speed (M is the Mach number) and bombard a substrate, forming

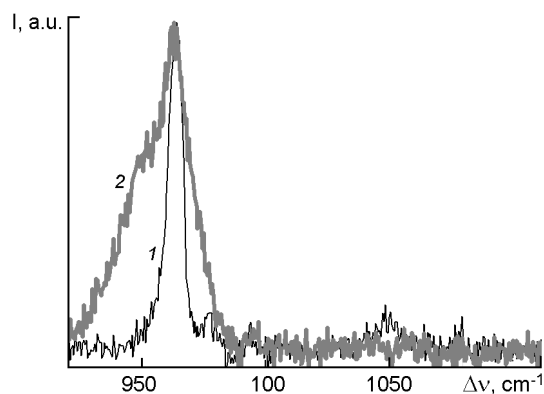


Fig. 1. Representative Raman spectra of the initial HAP powder (1) and the deposited coating (2).

a continuous coating due to physical and chemical interaction with the substrate material. A programmable displacement of the detonation gun or the substrate provided coating of a large area or multi-surfaced substrates. The explosive mixture composition, detonation shots frequency, and deposition duration were varied depending on the substrate type and thickness.

Raman spectra of initial HAP powders and deposited coatings were investigated at room temperature using a DFS-24 double monochromator and photon counting system for recording. The continuous radiation of about 50 mW power and 532 nm wavelength from a diode-pumped solid state laser or 514.5 nm from an argon ion laser were used for excitation. The magnetic resonance measurements were carried out at room temperature using X-band (microwave frequency $\nu \approx 9.4$ GHz) ESR spectrometer Radiopan X-2544 with 100 kHz magnetic field modulation. The estimated accuracy of g -factor determination for observed ESR lines was $\pm 2 \cdot 10^{-4}$.

HAP contains PO_4^{3-} molecular groups [6–8], characterized by to four main vibrations of P–O bonds at $\nu \approx 960$ cm^{-1} and much weaker bands at $\nu \approx 435$ cm^{-1} , $\nu \approx 1050$ cm^{-1} , and $\nu \approx 590$ cm^{-1} [7]. Variations of ν band spectral parameters (intensity, frequency, and linewidth) are used for diagnostics of structural features and composition of calcium phosphate coatings obtained by various methods [6–8]. The disordering effects in HAP occurring at gas detonation deposition were investigated by comparison of Raman spectra for the initial HAP powders and the obtained coatings. Fig. 1 shows those data for one of the samples. The con-

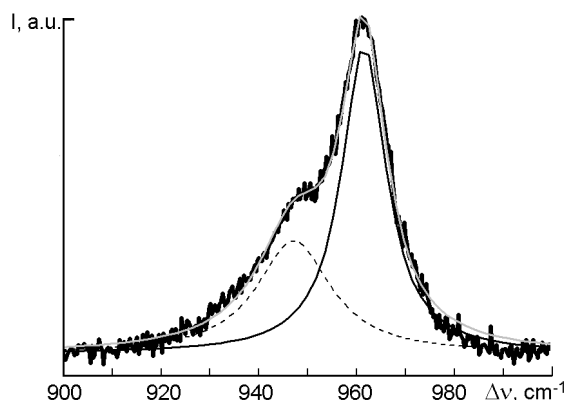


Fig. 2. The example of two-Lorentz peak fitting of the Raman spectrum of a HAP coating.

siderable broadening of the main vibration band $\nu \approx 960$ cm^{-1} and appearance of an additional low-frequency component are seen well.

Fig. 2 shows the experimental Raman spectrum and its computerized simulation. Two Lorentz profiles peaked at $\nu \approx 947$ cm^{-1} and $\nu \approx 961$ cm^{-1} were used as the fitting components. The first profile corresponds to the crystalline component of the HAP coating. It is broadened noticeably (linewidth of about 14 cm^{-1}) as compared to the spectrum of the initial HAP powder (linewidth of 7 cm^{-1}) evidencing the crystal phase disordering or high impurity concentration in the coating. The second profile corresponds probably to the amorphous phase of the HAP coating coinciding well with that was observed in [9, 10] ($\nu \approx 950$ cm^{-1}). As for the relative spatial distribution of amorphized and crystalline components in the HAP coating, it is obvious enough that, due to high thermal conductivity of a metal substrate, the cooling rate of the interface coating layer is considerably higher and stimulates amorphization process. For plasma deposited HAP, this reason has been confirmed in [3, 11].

To study how the substrate temperature and cooling rate influence the crystal structure of deposited HAP coatings, the gas detonation deposition conditions were varied as follows. Four film samples of the same thickness of $d = 150$ μm were obtained at the same operating mode of the detonation gun. Two of them were deposited onto a thin ($d \approx 0.2$ mm) copper foil, two others, onto a thick ($d \approx 1.2$ mm) copper plate. The coatings on each substrate type were deposited at two various distances between the gun and substrate, $L = 10$ cm and $L = 20$ cm. It was supposed that due to sufficient difference

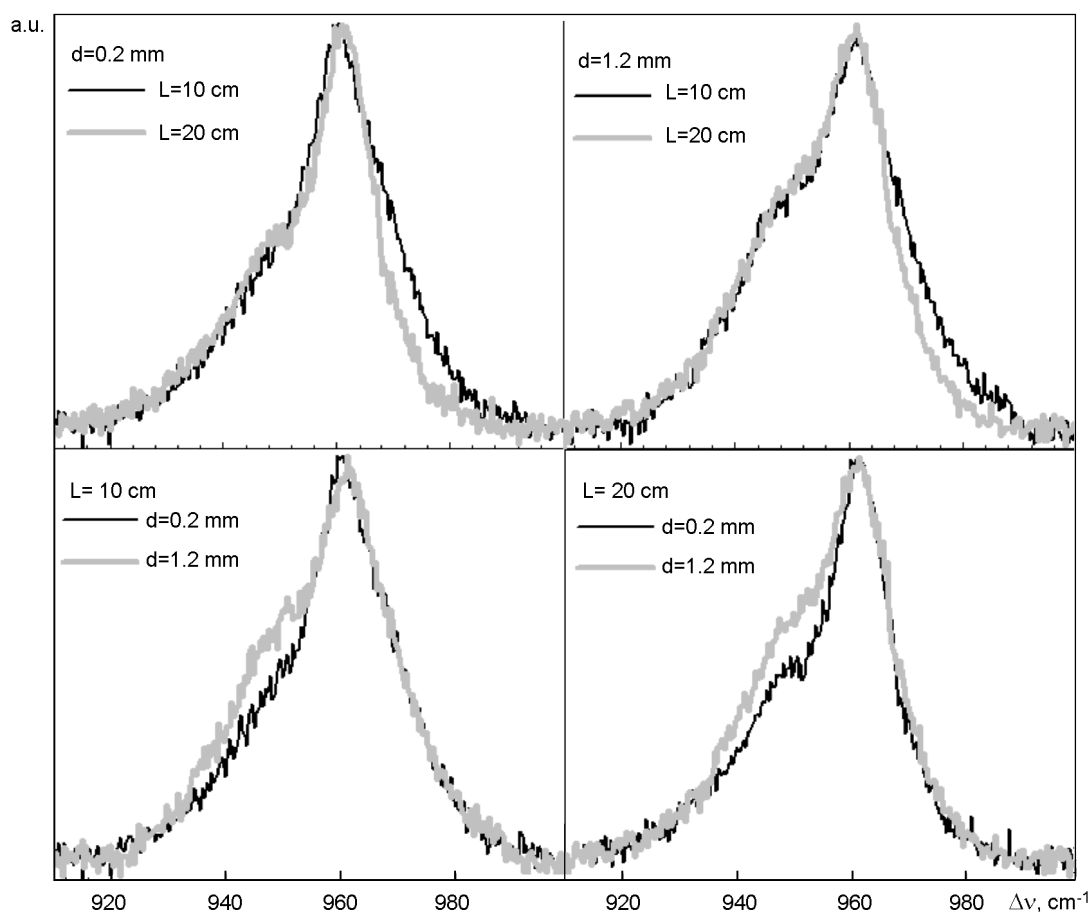


Fig. 3. Raman spectra for the four samples obtained on thin ($d = 0.2$ mm) and thick ($d = 1.2$ mm) substrates at different distances between the detonation gun and the substrate ($L = 10$ and 20 cm). The spectra are normalized to the intensity of the main peak $\nu_2 \approx 961$ cm^{-1} and plotted in the manner to show the effect on the lineshape of the gun-substrate distance, L , and substrate thickness, d .

in substrates thickness, the thick substrate is less heated during the deposition period (15 s) and faster cooled after deposition (as well as the interface HAP layer).

An essentially higher heating of the thin foil and slower cooling of the HAP coating thereon are confirmed by appearance of high temperature oxide tint on the back foil side. Decreasing the distance between the substrate and detonation gun from 20 cm to 10 cm increases temperature of the deposited material. Raman spectra of the mentioned samples are presented in Fig. 3, grouped in the manner to show the effect of the gun-substrate distance, L , and substrate thickness, d , on the line shape. Comparison of the spectra allows two following conclusions to be made.

1. For the intensity of the low-frequency spectrum component, $\nu \approx 947$ cm^{-1} , the critical factor is the cooling rate of the deposited coating but not the temperature of the

depositing material. This is in correlation with the amorphous nature of the interface HAP layer causing this band.

2. At higher coating deposition temperature (i.e. for $L = 10$ cm), an additional signal appears in the high-frequency wing of the main vibration band for both thin and thick substrates. In this case, the experimental spectrum should be described as superposition of three bands with the additional high-frequency profile $\nu_3 \approx 970$ cm^{-1} (Fig. 4) instead of superposition of two profiles (Fig. 2). This result reflects possible modification of the HAP structure in the top (external) layer of the coating caused by high temperature influence in open air. In this case, especially intensive degradation of HAP occurs accompanied by replacement of two OH^- ions onto O^{2-} ion and formation so-called hydroxyl-oxapatite [7, 12].

The structural modifications of the HAP powder upon deposition observed by Raman

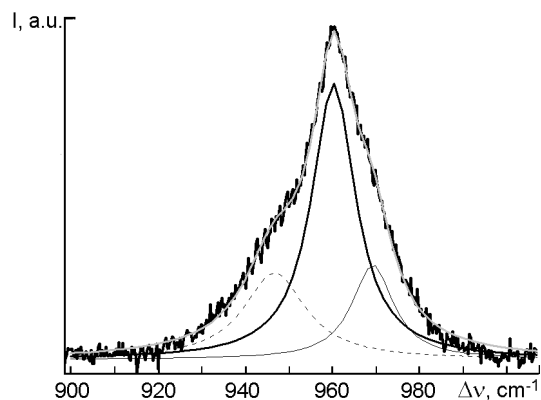


Fig. 4. Fitting of the Raman spectrum of the sample with $L = 10$ cm, $d = 0.2$ mm taking into account the contribution of the third component, $\nu_3 \approx 970$ cm^{-1} .

spectroscopy is accompanied by a change in magnetic properties of the samples. Fig. 5 shows ESR spectra of the initial HAP powders and the coatings deposited onto copper foil at various L . The spectrum of the initial HAP material (Fig. 5, a) demonstrates only a weak ESR signal with $g = 4.3$. In the coatings, three types of ESR signals are generally observed with intensities depending on the deposition conditions. The Type

1 signal (line 1 in Fig. 5, a) represents a single asymmetric line with the same parameters (g -factor $g \approx 4.3$ and line width $\Delta H_{pp} \approx 10$ mT) as for the initial material (but more intense) and allows its definite assignment to isolated Fe^{3+} ions [15]. The presence of this signal in the coatings is caused by uncontrollable incorporation of atomic iron impurity in the HAP structure. Probably this is caused by features of technological process of the detonation deposition where the HAP powder contacts with the metal tube of the detonation gun when moving along it at an ultrasound speed. Short-term rise of the HAP temperature occurring thus results in a structural modification of the material that is testified by Raman data.

Another effect of the HAP powder interaction with the metal gun tube is formation of an additional phase, namely nanoparticles of iron or its oxides, in the deposited coating. Such nanoparticles are responsible for occurrence of very strong magnetic resonance signals of type 2 with $g \approx 2$ (lines 2 in Fig. 5, a). Additional experiments showed that the temperature behavior of those signals differs essentially from that of types 1 and 3 ones (see below). While

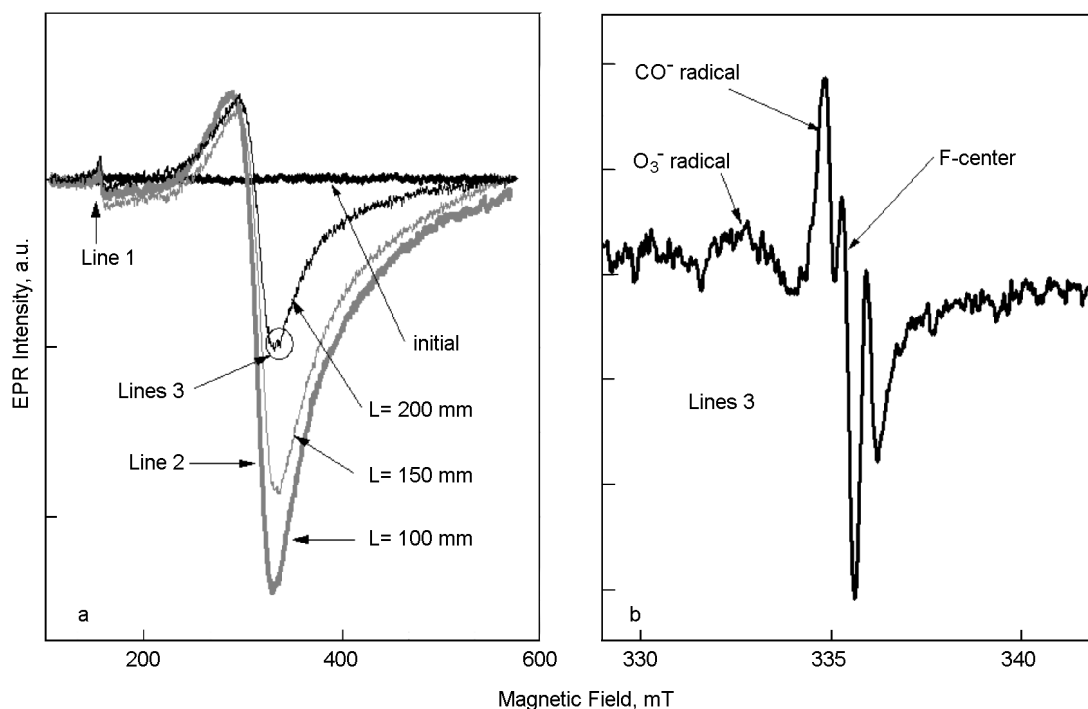


Fig. 5. ESR spectra for the initial HAP powder and the coatings obtained on copper substrates (a). Lines 3 on a large scale for a film deposited at $L = 20$ cm (b).

intensities of signals 1 and 3 increase when temperature decreases (that is normal for paramagnetic materials), intensity of signals 2 depends only slightly on temperature (that is typical for superparamagnetics [16]). The Type 2 signals are observed also in the coatings deposited onto nonmetal (glassceramics) substrates evidencing that their nature is not related to the metal substrate (copper or titanium).

Depending on technological modes (oxygen content in the detonation mixture, distance to the substrate, its thickness, etc.), concentrations of atomic and nanostructure impurities as well as relation therebetween are varied. This results in respective changes of the spectra observed, for example, when distance to a substrate increases, intensities of signals 2 decrease (Fig. 5, a). Signals of Type 3 (Fig. 5, a and 5, b) represent group of ESR lines caused by intrinsic defects of the HAP structure being various in nature and generated during the detonation deposition process. The radiospectroscopic parameters of the separate ESR lines in signals 3 indicate presence of O_3^- radicals ($g_x = 2.0105$, $g_y = 2.0180$, $g_z = 2.0029$) [17], F-centers (electrons localized on vacancies of hydroxyl groups, $g = 2.0019$) [18] and probably CO^- radicals ($g_x = 2.0065$, $g_y = 2.0041$, $g_z = 2.0018$) [17].

The relative intensities of individual Type 3 ESR signals depend on technological parameters of deposition, in particular, on oxygen content in the explosive mixture. Thus, the detonation deposition causes formation of the intrinsic paramagnetic defects localized near to 6-fold axis (O_3^- radicals and F-centers). Such local structure imperfections result in partial amorphization of the HAP and in local transformation of HAP into oxyapatites. That effect is intensified when oxygen content in the explosive mixture increases. Similar results were observed in studies of thermal treatment influence on HAP structure. It was shown that HAP loses under heating a fraction of its hydroxyl groups [9, 13, 14] and O^{2-} ions replace two OH groups in crystal lattice forming oxyapatite [3, 19].

Thus, the comparative study of initial hydroxyapatite powders and coatings deposited by gas detonation reveal a partial disordering of the material crystalline structure during deposition. The disorder results in

broadening of the main Raman band at 960 cm^{-1} and to appearance of additional bands at 947 cm^{-1} and 970 cm^{-1} . The appearance of the new bands is related to nucleation of new phases, amorphous HAP (947 cm^{-1}) and oxyapatite (970 cm^{-1}). In ESR spectra of the HAP coatings, the lines from intrinsic defects noticeably gain in intensity. Radiospectroscopic parameters of these lines allowed identifying of O_3^- radicals and F-centers. The general character of the defects and their localization corroborate the Raman results concerning nucleation of the new phases as well as formation of nanostructured iron.

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Дослідження методами спектроскопії КРС та ЕПР гідроксилапатитних покриттів, отриманих методом газодетонаційного осадження

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Методами комбінаційного розсіяння світла (КРС) і електронного парамагнітного резонансу (ЕПР) досліджено структурну модифікацію гідроксилапатиту (ГАП), отриманого методом детонаційного осадження на металеві підкладки. Виявлено, що детонаційне осадження вихідного порошка ГАП веде до суттєвого уширення основної смуги з максимумом близько 960 см^{-1} , а також до появи додаткових смуг близько 947 і 970 см^{-1} . У спектрах ЕПР спостерігається дефект, що відповідає O_3^- -радикалу і F-центрам. Зміни у спектрах КРС і ЕПР вказують на локальні зміни у структурі ГАП, а саме на аморфізацію на інтерфейсі підкладка-покриття, часткову дегідратацію та збільшення концентрації власних дефектів. Також спостерігається зародження нової фази оксіапатиту.