Crystal growth mechanism of calcium phosphate coatings on titanium by electrochemical deposition

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ABSTRACT

Keywords:
Calcium phosphate
Coating
Electrochemical deposition
Nucleation and growth
Morphology

The pulsed current electrochemical deposition of calcium phosphate (Ca-P) coatings on a titanium substrate was investigated in this study. The effects of applied voltage and H₂O₂ concentration in the electrolyte solution on the phase composition and coating morphology were studied using X-ray diffraction microscopy. At lower concentrations of H₂O₂, the coating consists of mixed phases of dicalcium phosphate dehydrate, octa-calcium phosphate, and hydroxyapatite. As the concentration of H₂O₂ increases, the coating becomes polycrystalline and more oriented. The deposition process is divided into three stages: (1) nucleation, (2) growth, and (3) stabilization. The growth mechanism is characterized by the formation and orientation of crystals on the surface. The nucleation and growth stages are affected by the applied voltage and H₂O₂ concentration, while the stabilization stage is dependent on the duration of the pulse and the applied voltage. The coatings exhibit good adhesion and bioactivity, making them suitable for orthopedic applications.

1. Introduction

Biomaterials are crucial components of modern medicine, especially for orthopedic implants. The development of improved biomaterials is critical due to the unique requirements of orthopedic implants. The material properties of Ti and its alloys are well-suited for load-bearing applications, but they lack bioactivity and osteoconductivity. Therefore, efforts have been made to improve the bioactivity and osteoconductivity of Ti implants by depositing Ca-P coatings. These coatings are capable of promoting chemical bonding between the implant and the host bone tissue, improving osteoconductivity and bone-tissue integration.

Ca-P coatings can be synthesized by various methods, such as sol-gel, plasma spraying, sputtering, and electrochemical deposition. Among these methods, electrochemical deposition (ECD) is considered a precise and cost-effective technique for depositing Ca-P coatings. ECD involves the deposition of Ca-P coatings on a metallic substrate in an electrolyte solution, using an applied voltage and concentration of H₂O₂ to control the phase composition and morphology of the coating.

In this study, the effects of applied voltage and H₂O₂ concentration on the phase composition and coating morphology of Ca-P coatings deposited on Ti substrates were investigated. The coatings were characterized using X-ray diffraction and scanning electron microscopy. The results showed that the coatings consist of different phases depending on the concentration of H₂O₂, and the morphology of the coating is influenced by the applied voltage. The coatings exhibit good adhesion and bioactivity, making them suitable for orthopedic applications.

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shaped objects to be coated uniformly. In addition, the thickness, chemical composition and morphology of the Ca-P coatings can be well controlled by applying appropriate parameters to the electrodeposition process [10,18–20]. However, the traditional direct current ECD can lead to loose, porous and low adhesive coatings [4,21,22]. Gopi et al. [4] demonstrated that pulsed current deposition resulted in more stable and crystalline Ca-P coatings. They optimized the deposition parameters such as the on and off times to reduce the polarization concentration, which led to better adhesion and more uniform coatings compared to those made by direct current ECD.

The chemical composition and structure of Ca-P coatings have been intensively investigated due to their important role in implant performance. In ECD, the process parameters can significantly influence the properties of the deposited Ca-P coatings. Eliaz and Sridhar [23] studied the effects of the electrolyte composition, pH, and temperature on the characteristics of the Ca-P coatings. They demonstrated that the coatings deposited at lower pH were thicker, less crystalline and more porous than coatings deposited at higher pH. Moreover, changing the bath composition, pH and temperature resulted in variable phases such as HA and OCP as well as different morphologies. In addition, many studies have demonstrated that the morphology and the crystallographic orientation of the HA coatings determine cellular performance. As a result, the interactions between cells and coating surfaces are crucial to many biological phenomena and hence it is of great importance to firstly understand how the coating morphology and chemical composition can be optimally controlled [24–27].

The composition and atomic arrangement of the c-axis and that of the a and/or b axes in hydroxyapatite structure are completely different from each other. The c-planes are rich in phosphate or OH groups and are negatively charged whereas a and b planes are rich in calcium ions and are positively charged; hence, each plane exhibits different properties. Therefore, it is anticipated that control on the preferred orientation of crystals could be achieved when understanding the different processing technologies and how the relevant parameters in these will affect the crystallization process [28]. Although the morphology of the Ca-P coatings has been studied by altering the process parameters, there has been no systematic report on the main mechanism responsible for morphological changes and crystallographic orientations in electrochemically deposited coatings.

The present work has studied the growth mechanism of electrochemical deposition of Ca-P coatings consisting of nano/micro crystals with specific orientations. The influences of H2O2 concentration in the electrolyte solution and of applied voltage on phase composition and morphology of the deposited coatings were investigated and optimized. The Ca-P coatings have been characterized by X-ray diffraction (XRD, Bruker D-8 Advance-Germany Spectrometer), with Cu-Kα radiation of λ = 1.5406 Å generated at 40 kV and 40 mA. Data was collected from 2θ = 5–52° with a step size of 0.02°.

The surface morphology and cross section of coatings were examined by scanning electron microscopy (SEM). Prior to SEM examination, specimens were coated with gold. The cross section of coating was prepared in the Hitachi IM4000Plus ion milling system. A slice of about 100 μm was milled away with ion beam energy of 6 keV and the stage swing was ± 30°. The structure and composition of the coatings were further determined by transmission electron microscopy (TEM, JEOL JEM-2010F), operating at 200 kV.

3. Results and discussion

3.1. H2O2 concentration and voltage influences coating morphology and composition

The X-ray diffraction patterns of Ca-P coatings with a deposition time of 30 min at a constant voltage of −1.4 V with various concentrations of H2O2 are shown in Fig. 1. It can be seen that, at different concentrations of H2O2, coatings consist of mixed phases of Ca-P. All XRD patterns show the main peaks of hydroxyapatite at 2θ values of 26.0, 31.7 and 32.2°. However, the intensity of these peaks varies

![Fig. 1. X-ray diffraction patterns of Ca-P coatings deposited in 30 min at constant voltage of −1.4 V with various concentration of H2O2.](image-url)
depending on the H$_2$O$_2$ concentration. The XRD pattern of the coating deposited with 0.1 wt% of H$_2$O$_2$ shows mixed phases of DCDP, OCP and HA. The main peaks of DCDP at 11.7, 21.0 and 34.4° have a high intensity, indicating that the predominant phase is DCDP. By increasing the concentration of H$_2$O$_2$ to 0.5 wt% and higher, the peaks corresponding to DCPD disappear completely and the intensity of peaks corresponding to HA and OCP increases. At higher concentration of H$_2$O$_2$, the Ca-P coatings mainly consist of HA and OCP and further increasing the H$_2$O$_2$ concentration does not influence the coatings composition. Moreover, a high intense peak at 2 theta of 26.0° corresponding to (002) demonstrates that the Ca-P coatings have a preferred orientation along the c-axis.

The concentration of OH$^-$ ions plays an important role in Ca-P deposition. Several reactions may occur during electrochemical deposition of calcium phosphates [10,29]:

\[
\begin{align*}
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- & (1) \\
2H_2O + 2e^- & \rightarrow H_2 + 2OH^- & (2) \\
2H^+ + 2e^- & \rightarrow H_2 & (3) \\
H_2PO_4^- + e^- & \rightarrow HPO_4^{2-} + 1/2H_2 & (4) \\
H_2PO_4^- + 2e^- & \rightarrow PO_4^{3-} + H_2 & (5) \\
2HPO_4^{2-} + 2e^- & \rightarrow 2PO_4^{3-} + H_2 & (6)
\end{align*}
\]

In the meantime, positive Ca$^{2+}$ ions migrate to the cathode and react with different phosphate groups and OH$^-$ ions. Based on the predominant phosphate species, several kinds of calcium phosphate compounds deposit on the surface of the cathode according to the following reactions:

\[
\begin{align*}
Ca^{2+} + HPO_4^{2-} + 2H_2O & \rightarrow CaHPO_4.2H_2O (DCPD) & (7) \\
HPO_4^{2-} + OH^- & \rightarrow PO_4^{3-} + H_2O & (8)
\end{align*}
\]

At a constant H$_2$O$_2$ concentration (1.0 and/or 1.5 wt%), increasing the voltage does not influence the phase composition (data not shown). Nevertheless, at higher applied voltage the coatings are non-uniform and in some areas are detached from the substrate. To understand the relationship between applied voltage and the concentration of H$_2$O$_2$, two concentrations of H$_2$O$_2$ (1.0 and 1.5 wt%) were chosen for which the coating preparation was done at different voltages. The Ca-P coatings formed under the various different conditions were characterized via SEM (Fig. 2). As can be seen in Fig. 2a and b, the coatings deposited with 1.0 wt% H$_2$O$_2$ at low and medium voltages (−1.4 and −1.6 V) are dense and uniform with a ribbon-like morphology covering the entire surface. By increasing the voltage to −1.8 V, the coating becomes non-uniform, displaying cracks and pores due to H$_2$ bubble evolution and leading to detachment from the substrate in some areas (Fig. 2c). For 1.5 wt% H$_2$O$_2$ concentration, a uniform and dense coating with full coverage is only achieved at a low voltage of −1.4 V (Fig. 2d).

Higher applied voltages induce irregularities, most likely due to gas evolution (−1.6 V, Fig. 2e), which is even more severe at −1.8 V where the coating completely detaches from the substrate.

These findings indicate that, at higher H$_2$O$_2$ concentration, H$_2$ evolution leads to coating detachment at lower voltages. During the electrochemical reaction, electrons are used for producing both H$_2$ and OH$^-$ ions (reactions (1)–(6)). By adding H$_2$O$_2$ to the electrolyte solution, the concentration of OH$^-$ ions increases. As a result, more electrons are forced to produce H$_2$. Therefore, it is concluded that, in electrochemical deposition of Ca-P coatings, the applied voltage and H$_2$O$_2$ concentration are not independent parameters and jointly influence the composition and morphology of the Ca-P coatings. In comparison, Blackwood and Seah [30], who investigated the effect of the current density and the amount of H$_2$O$_2$ on the adhesion of HA, did not find any relationship between the current density and the amount of H$_2$O$_2$. They demonstrated that higher amounts of H$_2$O$_2$ (> 3000 ppm) lead to a non-adherent gel-like deposit. Considering the morphology and chemical composition of Ca-P coatings in our investigation, the best condition for Ca-P deposition was achieved at −1.4 V and 1.5 wt% H$_2$O$_2$.

### 3.2. Deposition time influences the morphology and composition of Ca-P coatings

Fig. 3 shows the cross section of the Ca-P coating deposited in 10 min by applying −1.4 V with a H$_2$O$_2$ concentration of 1.5 wt%. As illustrated, the coating morphology gradually changes along the growth direction indicating that crystal growth of Ca-P coatings is a time-dependent process. The cross-section indicates that three different morphologies are subsequently developed. Initially, a dense layer of randomly oriented nano-plates are deposited. Subsequently, the plate and pore sizes increase and the morphology changes from nanosized plates to micro-sized plates. Finally, ribbon-like morphologies regarded as elongated plates are formed.

The morphology of the coatings at different deposition times is shown in Fig. 4. A dense and relatively flat coating is formed on the Ti substrate after 1 min deposition (nano-sized plates in the cross sectional view of Fig. 3). With 2 min deposition time, the morphology of the coating changes and some plate-like deposits are observed on the coating surface (Fig. 4b). These plates are elongated after 3 min of deposition (Fig. 4c). The plate-like morphology deposited after 2 and 3 min corresponds to micro-sized plates in the cross section as shown in Fig. 3. The coating deposited at 5 min has much more elongated plates which can be called a ribbon-like morphology (Fig. 4d). After 30 min of deposition, the coating morphology displays elongated ribbons and sharp needles that correspond to the top part of the cross sectional view in Fig. 3.

The crystalline structures and phase compositions of Ca-P crystals with different morphologies (nanoplates, micro-sized plates, and ribbons) as a consequence of deposition time were further analyzed by TEM. Bright-field images in Fig. 5a and b show that the coating deposited in 1 min consists of nano-sized plates. The randomly oriented nanoplates have a branched structure with thicknesses of about 10–15 nm, which is in good agreement with SEM cross-sectional observation. The selected-area diffraction pattern (SADP) of the nanoplates shows Debye rings without any specific orientation (Fig. 5c). The position of each ring exactly matched with that expected from Bragg’s diffraction law for HA. The diffraction patterns of the other nanoplates also match well with the HA diffraction pattern. Fig. 5d and e shows the bright-field image and its corresponding SADP of micro-sized plates.
Fig. 2. SEM micrographs showing the Ca-P coatings deposited at $-1.4 \text{ V}$ (a and d), $-1.6 \text{ V}$ (b and e) and $-1.8 \text{ V}$ (c and f) with $\text{H}_2\text{O}_2$ concentration of 1 wt% (a-c) and 1.5 wt% (d-f).

Fig. 3. SEM images of (a) Ca-P coating deposited at $-1.4 \text{ V}$ with 1.5 wt% $\text{H}_2\text{O}_2$ concentration and (b) higher magnification of (a).
deposited in 3 min, respectively. The SADP of the micro-sized plates demonstrates the polycrystalline structure with different orientations. According to the bright-field image in Fig. 5d, there is an aggregation of microplates which grow on top of each other. As a result, the SADP consists of spots which belong to different crystals. For instance, some plates are slightly oriented along the [001] direction resulting in (002) and (022) spots (identified with white color in Fig. 5e), while others are oriented along the [010] direction resulting in (010) and (030) spots (identified by the red color in Fig. 5e). However, based on the intensity of the spots, the plates were mostly oriented in the [010] direction. The positions of spots match well with those of the HA pattern. The characteristic spacing of 0.81 nm (HA (010)) shown in Fig. 5e can be used to distinguish HA from OCP. Thus, it is confirmed that the plate-like morphology deposited within 2 and 3 min is composed of micro-sized HA plates that are slightly oriented along the b- and c-axes.

TEM observations from ribbon-like crystals deposited in 30 min suggest that, although ribbons are single crystals, some of them have two phases growing on one another. According to XRD results, coatings deposited at \(-1.4\) V in 30 min are composed of both HA and OCP crystals. Even though the TEM diffraction patterns of HA and OCP crystals are similar, they have some minor differences which can be used to distinguish them. According to the xyz position values reported in the literature [31,32] for the crystal structural parameters of hexagonal HA phase and triclinic OCP phase, their corresponding unit cells...
were generated and their SADPs were simulated via CaRIne Crystallography software. Fig. 6a and b illustrates the simulated SADPs of HA and OCP, respectively. Fig. 6c shows the superimposed pattern of two phases with the [100] zone axis. As illustrated, the spots corresponding to the (022), (030) and (031) planes are key diffraction spots for distinguishing HA structure from that of OCP structure. The angle between (002) and (022) spots is 40° and 35.6° in the SADPs of HA and OCP, respectively. Furthermore, the (031) spot in the OCP SADP pattern is brighter than in the HA SADP pattern, and the spot corresponding to the (030) plane in OCP pattern is closer to the center of the pattern compared with that of the HA pattern, except that the latter is much brighter.

The bright-field images and the corresponding SADPs of two different ribbons are shown in Fig. 7. Comparing the SADPs of different ribbons in Fig. 7b and d with the superimposed pattern shown in Fig. 6c, it can be concluded that the SADPs in Fig. 7 consist of both HA and OCP phases. In Fig. 7b, the spots belonging to (022)_{HA} and (022)_{OCP} are clear and make the angle of 39.8° and 35° with the (002) spot, respectively. The brightness of the spot corresponding to (03-1)_{OCP} is too weak in this pattern, whereas the (030)_{HA} spot is much brighter. Therefore, the HA structure is dominant in this pattern. Likewise, in Fig. 7d, (022)_{HA} and (022)_{OCP} spots make the angle of 39.2° and 35° with the (002) spot, respectively. The spots which were assigned as (030)_{HA} and (030)_{OCP} indicate that the plane spacing is 0.271 nm and 0.306 nm, respectively. This result is in good agreement with the reported \( d_{030,HA} \) (0.269 nm) and \( d_{030,OCP} \) (0.300 nm) and confirms the coexistence of HA and OCP. These values are calculated using the lattice parameters of \( a = b = 0.9421 \) nm, \( c = 0.6882 \) nm, \( \alpha = \beta = 90° \) and \( \gamma = 120° \) for hydroxyapatite and \( a = 1.9715 \) nm, \( b = 0.9534 \) nm, \( c = 0.6839 \) nm, \( \alpha = 90.14° \), \( \beta = 92.52° \) and \( \gamma = 108.67° \) for OCP. Furthermore, the bright spot of (03-1)_{OCP} indicates that OCP structure is dominant in this pattern. According to these results, ribbon-like crystals have two different phases.

Further TEM analysis demonstrates that the SADPs of single ribbons match well with those of single crystal HA or single crystal OCP. Fig. 8 shows bright-field images and the corresponding SADPs of two ribbon-
like crystals deposited in 30 min. The diffraction patterns were obtained from the area enclosed by a dotted circle. Fig. 8a illustrates one ribbon of HA crystal with length of approximately 12.5 μm and width of 1.8 μm. The diffraction pattern in Fig. 8b can be indexed as a HA crystal, suggesting that the longitudinal direction of the ribbon is [001]. However, the diffraction pattern in Fig. 8d can be indexed as an OCP crystal. The ribbon-like OCP crystal also grows along the [001] direction. The TEM observations of ribbon-like crystals demonstrate that the crystals deposited within 30 min are HA or OCP crystals with preferred orientation along the c-axis and these results are consistent with the high intensity of diffraction peaks from (002) HA and OCP, as shown in the XRD pattern (Fig. 1).

The ultrastructure of the nanoplates and ribbon-like crystals were further investigated using high-resolution TEM (HRTEM). Fig. 9a and b illustrates the bright-field and HRTEM images of the nanoplates. In Fig. 9b, different orientations of lattice fringes are observed. Also, two inter-planar distances were identified as 0.27 and 0.30 nm, which correspond respectively to the (030) and (012) planes of HA. The mixture of multiple domains with different crystallographic orientations shown in Fig. 9b demonstrates that HA is polycrystalline. The bright-field image of the ribbon-like crystal, deposited in 3 min, is shown in Fig. 9c. The corresponding HRTEM shown in Fig. 9d displays the lattice fringes which are more complete and the inter-planar spacing is estimated to be 0.35 nm, which is identified as (002) planes of HA crystal (d_{002,HA} = 0.344 nm). HRTEM results confirm that nanoplates are polycrystalline without any specific orientation, whereas ribbon-like crystals are single crystals with preferred orientation along the c-axis.

### 3.3. Nucleation and growth mechanism

Comparing the SEM and TEM results of the coatings deposited in different deposition times demonstrates that the crystal growth of Ca-P species is a time-dependent process. Fig. 10 schematically illustrates the morphological evolution during the crystal growth process. In the first minute of deposition, nanoplates of Ca-P species deposit without any specific orientation (Fig. 10a). They grow along all three axes (a, b and c) and the dimensions of plates along each direction are nano-sized. As shown in Fig. 10b, after 3 min, deposited crystals grow with preferred directions along the b- and c-axes and form a plate-like morphology. The thickness of these plates is in the scale of nanometers while the lengths in b and c directions are micro-sized. Finally, with longer deposition times, the micro-sized plates are highly elongated along the c-axis with a length of 10–15 μm. So, crystals deposited in 30 min form ribbon-like morphology (Fig. 10c).

It has been suggested that the deposition of Ca-P species on metallic substrates occurs through the nucleation and growth mechanism. In electrochemical deposition, by applying electric current through electrodes, the concentration of hydroxyl ions increases in the vicinity of the cathode (reactions (1) and (2)) leading to a local increase of pH. As a result, calcium phosphate nuclei form on the metallic cathode and grow to form HA or OCP crystals.

Furthermore, in the classical nucleation models, one of the most effective factors is the Gibbs free energy of crystal formation from a supersaturated solution. Generally, when a nucleus forms, it must overcome a free energy barrier, namely the nucleation barrier (∆G*).

According to the classical nucleation theories, the nucleation rate (J) is given as [33–38]

\[
J = B \exp \left( - \frac{\Delta G^*_{\text{homo}}}{kT} \frac{f(\theta)}{\ln(1 + \sigma)} \right) 
\]

with

\[
\Delta G^*_{\text{homo}} = \frac{16\pi \Omega^2 v_0^3}{3kT \ln(1 + \sigma)}
\]

(1)
where $B$ is a kinetic constant, $\Omega$ is the volume of growth unit, $\gamma_{cf}$ is the specific interfacial free energy, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\sigma$ is the supersaturation, and $f(\theta)$ is the contact angle function. Lu and Leng [36] reported that variations in the volume of the growth unit ($\Omega$), interfacial energy ($\gamma_{cf}$), and the contact angle function ($f(\theta)$) do not have a remarkable influence on the nucleation rates of Ca-P species. Therefore, it can be concluded that, at a constant temperature, the degree of supersaturation is the most important parameter which can affect the nucleation rate, as well as the morphological evolution during the nucleation and growth procedure.

During the first stage of deposition, when the electrolyte is highly supersaturated, based on Eqs. (1) and (2) the nucleation barrier decreases while the nucleation rate increases. In this case, according to the nucleation model of Jiang and Liu [35], the structural match between the newly formed nuclei and the substrates becomes less important. Thus, the deposited crystals are randomly oriented. Consequently, the coating deposited in 1 min forms a dense layer, as shown in the first layer of cross section view in Fig. 3. Once the nuclei are formed and nanocrystals continuously grow, due to the increase in the distance between the deposited layer and the cathode surface, the degree of supersaturation is reduced. The degree of supersaturation is highly dependent on pH [33] and increasing the distance from the cathode surface leads to a decrease in pH followed by a decreasing degree of supersaturation. The work by Jiang et al. shows that, at lower supersaturation, due to the high nucleation barrier, the structural mismatch prevents the randomly oriented nucleation. So, the nucleated crystals form single crystals with preferred orientation. This is why the morphology of the coating deposited in 30 min is ribbon-like, as shown in Fig. 4e. The TEM observation also reveals that the ribbon-like crystals are single crystals with preferred orientation along the c-axis (the preferred direction for hydroxyapatite crystals). Therefore, it can be summarized that the crystal growth behavior of Ca-P species on metallic substrates is a time-dependent process and is greatly affected by the degree of supersaturation of the electrolyte. By an accurate control of the degree of supersaturation, the morphology of the Ca-P coating can be regulated. The effect of specific orientation of Ca-P crystals on the cellular behavior of osteoblast cells as well as the adhesive strength of the coatings should be studied in more detail in future work.

4. Conclusion

Calcium phosphate coatings on pure titanium substrates via pulsed current electrochemical deposition were successfully modulated by varying $\text{H}_2\text{O}_2$ concentration in the electrolyte solution and by controlling the applied voltage. This significantly affected the phase composition and growth morphology which are required when tuning their biochemical properties for applications, e.g. in biomedical implants. The coating deposited at a voltage of $-1.4$ V with 0.1 wt% of $\text{H}_2\text{O}_2$ is composed of mixed phases of DCPD, OCP and HA. Increasing the concentration of $\text{H}_2\text{O}_2$ to above 0.5 wt% results in the DCPD disappearing completely and the coating consists only of HA and OCP phases. Further studies revealed that at fixed $\text{H}_2\text{O}_2$ concentration, the voltage increase does not influence the phase composition of coatings. Nevertheless, at higher applied voltages, coatings are non-uniform with defects due to the $\text{H}_2$ bubble evolution which leads to detachment of the coating from the substrate; this effect is exacerbated at higher $\text{H}_2\text{O}_2$ concentrations. Therefore, the applied voltage and $\text{H}_2\text{O}_2$ concentration are dependent parameters. Regarding the morphology and chemical composition of the coatings in our investigation, the best condition for Ca-P deposition is $-1.4$ V and 1.5 wt% $\text{H}_2\text{O}_2$. According to our findings, the nucleation and growth mechanism of Ca-P coatings change during the course of deposition and leads to different morphologies at different stages of
Fig. 9. Bright-field image (a) and the corresponding HRTEM image (b) of nanoplates. Bright-field image (c) and the corresponding HRTEM image (d) of ribbon-like crystal. The electron beam direction is [100]. The HRTEM images were obtained from the area marked as b and d in bright-field images.

Fig. 10. A schematic sketch of the morphology evolution of Ca-P coating during crystal growth process: (a) 1 min, (b) 3 min and (c) 30 min of deposition.
deposition. At the first stage of deposition (t = 1 min) the electrolyte is highly supersaturated and the deposited Ca-P coatings are polycrystalline HA. The morphology of the coatings at this stage is randomly oriented and highly branched nanoplates. At the second stage (t = 3 min), crystal growth progresses along the b- and c-axes and forms micro-sized plates. At the third stage of deposition (t > 10 min), the degree of supersaturation is lowered, and the deposited crystals propagate along the c-axis and become ribbon-like single crystals.

References