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

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ABSTRACT

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 and scanning electron microscopy. At lower concentrations of H₂O₂, the coating consists of mixed phases of dicalcium phosphate dehydrate, octa-calcium phosphate, and hydroxyapatite, whereas increased H₂O₂ concentrations results in a dual phase of octa-calcium phosphate and hydroxyapatite being deposited. Furthermore, with increasing H₂O₂ concentration, the voltage must be reduced in order to avoid H₂ evolution. The best conditions for Ca-P deposition were achieved at −1.4 V and 1.5 wt% H₂O₂. The morphological changes at different deposition times as well as the crystallographic orientation of deposited crystals were studied using scanning electron microscopy and transmission electron microscopy. It was found that the crystal growth of Ca-P coatings is a time-dependent process. During the first stage of deposition ($t = 1$ min), the electrolyte is supersaturated and randomly oriented polycrystals of Ca-P nucleate and form nanoplates. During the second stage ($t = 3$ min), crystals grow slightly in a more oriented fashion and form micro-sized plates. During the third stage ($t > 10$ min), the deposited crystals grow in a highly directional manner and the morphology of the coating consists of elongated ribbon-like single crystals.

1. Introduction

Biomaterials are an important and integrated part of modern medicine of which orthopedic implants are one of the most frequently used. The development and improvement of orthopedic biomaterials is an important challenge, with these mostly being composed of Titanium (Ti) and its alloys due to their desirable properties, such as high mechanical strength, suitable elastic modulus, biocompatibility with bone tissue, and low toxicity [1]. Despite all its favorable attributes, titanium exhibits rather poor bioactivity and osteoconductivity. As a result, Ti implants often become encapsulated by fibrous tissues and so healing time is prolonged [2,3]. In order to improve the osteoconductivity of metallic implants, some surface modifications are suggested for promoting direct chemical bonding between the implant and the host bone tissue. One approach is depositing calcium phosphate (Ca-P) ceramic coatings on the implant surface. Ca-P compounds have excellent biocompatibility due to their compositional similarity to natural bone mineral and exhibit a surface chemistry that promotes the formation of bone-like hydroxyapatite on its surface. The ability of Ca-P ceramics to

improve osteoconductivity and bone-tissue integration and also being nontoxic in any quantity, make them favorable among other coatings for metallic implants [4–7]. Ca-P compounds have several types of crystalline phases such as, for example, hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂), octa-calcium phosphate (OCP, Ca₈H₂(PO₄)₆·5H₂O), tri-calcium phosphate (TCP, Ca₃(PO₄)₂), and dicalcium phosphate dihydrate (DCPD, CaHPO₄·2H₂O). Each phase has a different crystalline structure with different Ca/P ratio as well as variable degradability in biological environments. Among these phases, HA has been used frequently as a coating for metallic implants, since it is thermodynamically more stable and is the main component of hard tissues [7–11].

Ca-P coatings can be synthesized by different techniques such as the biomimetic method [12], plasma spraying [13,14], sputtering deposition [15], sol-gel process [16], electrophoretic deposition [17] and electrochemical deposition (ECD) [10]. Compared to other methods, the electrochemical deposition technique seems more favorable for Ca-P coatings because of its advantages such as sufficiently low cost, simplicity of performance, low temperature and rapid deposition. Moreover, it is not a line-of-sight technique, enabling highly irregularly

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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 H_2O_2 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 to identify the main mechanisms responsible for the nucleation and growth of electrodeposited Ca-P crystals which leads to different morphologies and crystallographic orientations. To the best of our knowledge, the crystal growth behavior of Ca-P coatings has not been studied comprehensively. The understanding of the nucleation and growth mechanism of Ca-P coatings during ECD will be highly beneficial for the design of biomedical Ca-P coatings.

2. Materials and methods

2.1. Materials and preparation

A commercially pure Ti sheet with dimensions of 15 mm × 10 mm × 1 mm was used as a substrate. Prior to electrodeposition, the surface of the substrate was mechanically ground with SiC papers from P120 to P1000 grit to achieve a uniform surface roughness. Subsequently, it was rinsed with distilled water, ultrasonically cleaned in acetone for 10 min, rinsed with distilled water again, and dried with a drying apparatus. An electrolyte solution containing 0.042 M $Ca(NO_3)_2 \cdot 4H_2O$ and 0.025 M $NH_4H_2PO_4$ with a Ca/P ratio of 1.67 was prepared in distilled water. Different concentrations of

H_2O_2 were added to the electrolyte solution resulting in various concentrations (0.1, 0.5, 1.0, and 1.5 wt%). The pH of the electrolyte was 4.3 and the temperature of the electrolyte was fixed at $65 \pm 1^\circ C$ with the use of an electric heater.

2.2. Pulsed electrodeposition

Pulsed electrodeposition was conducted in a regular two electrode cell in which the prepared Ti substrate was used as the cathode and a platinum sheet as the anode. The surface area of the platinum sheet was larger than that of the Ti sheet. The distance between the cathode and anode was fixed at 2 cm. Pulse deposition was carried out with fixed frequency (1 Hz) in potentiostat mode at different cathodic potentials ranging from -1.8 to -1.4 V. Both the pulse on and off times were $t = 0.5$ s. In order to observe the crystal growth of the coating, different deposition times of 1, 2, 3, 5 and 30 min were used. After deposition, the specimens were removed from the electrolyte solution, rinsed with distilled water, and dried under ambient conditions.

2.3. Coating characterization

The phase and chemical composition of the coatings were analyzed by X-ray diffraction (XRD, Bruker D-8 Advance-Germany Spectrometer), with $Cu-K_\alpha$ radiation of $\lambda = 1.5406 \text{ \AA}$ generated at 40 kV and 40 mA. Data was collected from $2\theta = 5\text{--}52^\circ$ 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 $\pm 30^\circ$. 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. H_2O_2 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 H_2O_2 are shown in Fig. 1. It can be seen that, at different concentrations of H_2O_2 , coatings consist of mixed phases of Ca-P. All XRD patterns show the main peaks of hydroxyapatite at 2 theta 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 H_2O_2 .

depending on the H_2O_2 concentration. The XRD pattern of the coating deposited with 0.1 wt% of H_2O_2 shows mixed phases of DCPD, OCP and HA. The main peaks of DCPD at 11.7, 21.0 and 34.4° have a high intensity, indicating that the predominant phase is DCPD. By increasing the concentration of H_2O_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_2O_2 , the Ca-P coatings mainly consist of HA and OCP and further increasing the H_2O_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]:

The OH^- ions produced during these reactions lead to a local increase in pH near the cathode surface. In electrochemical deposition, the main reason of adding H_2O_2 to the electrolyte is to increase the concentration of OH^- ions. As the concentration of the OH^- ions increases in the electrolyte solution, the concentration of HPO_4^{2-} and PO_4^{3-} ions increases as well, according to the following reactions:

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 [10]:

At a deposition voltage of -1.4 V and 0.1 wt% H_2O_2 , the OH^- concentration is not high enough to convert all the phosphate species to PO_4^{3-} . This means that reaction (8) is only partially completed and the dominant phosphate species is HPO_4^{2-} . As a result, a combination of DCPD, OCP, and HA is obtained. However, by increasing the concentration of H_2O_2 , more PO_4^{3-} ions are produced due to the increasing OH^- concentration and consequently, the main components in the coating are OCP and HA. According to the reaction (11), excessive OH^- at higher concentration of H_2O_2 promotes the formation of HA.

At a constant H_2O_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_2O_2 , two concentrations of H_2O_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_2O_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_2O_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_2O_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_2O_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_2O_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_2O_2 on the adhesion of HA, did not find any relationship between the current density and the amount of H_2O_2 . They demonstrated that higher amounts of H_2O_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_2O_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_2O_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 V (a and d), -1.6 V (b and e) and -1.8 V (c and f) with H_2O_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 V with 1.5 wt% H_2O_2 concentration and (b) higher magnification of (a).

Fig. 4. SEM images of coating deposited in 1 (a), 2 (b), 3 (c), 5 (d), and 30 min (e).

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

Fig. 5. Bright-field images (a) and (b), and corresponding SADP (c) of the coating deposited in 1 min. Bright-field image (d) and corresponding SADP (e) of coating deposited in 3 min. The diffraction pattern was obtained from the area enclosed by a dotted circle.

Fig. 6. Simulated SADPs of (a) HA, (b) OCP, and (c) the superimposing of these patterns with [100] zone axis (the black spots and red circles correspond to the HA and OCP patterns, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 $(022)_{\text{HA}}$ and $(022)_{\text{OCP}}$ are clear and make the angle of 39.8° and 35° with the (002) spot,

respectively. The brightness of the spot corresponding to $(031)_{\text{OCP}}$ is too weak in this pattern, whereas the $(030)_{\text{HA}}$ spot is much brighter. Therefore, the HA structure is dominant in this pattern. Likewise, in Fig. 7d, $(022)_{\text{HA}}$ and $(022)_{\text{OCP}}$ spots make the angle of 39.2° and 35° with the (002) spot, respectively. The spots which were assigned as $(030)_{\text{HA}}$ and $(030)_{\text{OCP}}$ indicate that the plane spacing is 0.271 nm and 0.306 nm, respectively. This result is in good agreement with the reported $d_{030,\text{HA}}$ (0.269 nm) and $d_{030,\text{OCP}}$ (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, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ for hydroxyapatite and $a = 1.9715$ nm, $b = 0.9534$ nm, $c = 0.6839$ nm, $\alpha = 90.14^\circ$, $\beta = 92.52^\circ$ and $\gamma = 108.67^\circ$ for OCP. Furthermore, the bright spot of $(031)_{\text{OCP}}$ 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-

Fig. 7. Bright-field image of ribbons deposited in 30 min (a) and corresponding SADP (b) of crystal with dominant HA structure. Bright-field image (c) and corresponding SADP (d) of crystal with dominant OCP structure. The electron beam direction is [100]. The diffraction pattern was obtained from the area enclosed by a dotted circle.

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 $12.5\mu\text{m}$ and width of $1.8\mu\text{m}$. 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 ($d_{002,HA} = 0.344\text{ nm}$). 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 $10\text{--}15\mu\text{m}$. 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 (ΔG^*) at a given thermodynamic driving force ($\Delta\mu$). According to the classical nucleation theories, the nucleation rate (J) is given as [33–38]

$$J = B \exp \left[-\frac{\Delta G_{\text{homo}}^*}{(kT)^2 \ln(1 + \sigma)} f(\theta) \right] \quad (\text{Eq. 1})$$

with

$$\Delta G_{\text{homo}}^* = \frac{16\pi\Omega^2\gamma_{\text{cf}}^3}{3kT\ln(1 + \sigma)} \quad (\text{Eq. 2})$$

Fig. 8. (a) Bright-field image and (b) corresponding SADP of ribbon-like HA crystal. (c) Bright-field image and (d) corresponding SADP of ribbon-like OCP crystal. The electron beam direction is $[100]$. The diffraction pattern was obtained from the area enclosed by a dotted circle.

where B is a kinetic constant, Ω is the volume of growth unit, γ_{cf} is the specific interfacial free energy, k is the Boltzmann constant, T is the absolute temperature, σ 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 (Ω), interfacial energy (γ_{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 H_2O_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 H_2O_2 is composed of mixed phases of DCPD, OCP and HA. Increasing the concentration of H_2O_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 H_2O_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 H_2 bubble evolution which leads to detachment of the coating from the substrate; this effect is exacerbated at higher H_2O_2 concentrations. Therefore, the applied voltage and H_2O_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% H_2O_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

- [1] D. Lahiri, S. Ghosh, A. Agarwal, Carbon nanotube reinforced hydroxyapatite composite for orthopedic application: a review, *Mater. Sci. Eng. C* 32 (7) (2012) 1727–1758.
- [2] M. Roy, A. Bandyopadhyay, S. Bose, Induction plasma sprayed nano hydroxyapatite coatings on titanium for orthopaedic and dental implants, *Surf. Coat. Technol.* 205 (8–9) (2011) 2785–2792.
- [3] T.R. Rautray, R. Narayanan, T.Y. Kwon, K.H. Kim, Surface modification of titanium and titanium alloys by ion implantation, *J Biomed Mater Res B Appl Biomater* 93 B (2) (2010) 581–591.
- [4] D. Gopi, J. Indira, L. Kavitha, A comparative study on the direct and pulsed current electrodeposition of hydroxyapatite coatings on surgical grade stainless steel, *Surf. Coat. Technol.* 206 (11–12) (2012) 2859–2869.
- [5] K. Kulpetchdara, A. Limpichaipanit, G. Rujijanagul, C. Randorn, K. Chokethawai, Influence of the nano hydroxyapatite powder on thermally sprayed HA coatings onto stainless steel, *Surf. Coat. Technol.* 306 (2016) 181–186.
- [6] Q. Yuan, T.D. Golden, Electrochemical study of hydroxyapatite coatings on stainless steel substrates, *Thin Solid Films* 518 (1) (2009) 55–60.
- [7] M. Sadat-Shojai, M.T. Khorasani, E. Dinpanah-Khoshdargi, A. Jamshidi, Synthesis methods for nanosized hydroxyapatite with diverse structures, *Acta Biomater.* 9 (8) (2013) 7591–7621.
- [8] M. Roy, V.K. Balla, A. Bandyopadhyay, S. Bose, Compositionally graded hydroxyapatite/tricalcium phosphate coating on Ti by laser and induction plasma, *Acta Biomater.* 7 (2) (2011) 866–873.
- [9] I.A. Karampas, C.G. Kontoyannis, Characterization of calcium phosphates mixtures, *Vib. Spectrosc.* 64 (2013) 126–133.
- [10] D.Y. Lin, X.X. Wang, Electrodeposition of hydroxyapatite coating on CoNiCrMo substrate in dilute solution, *Surf. Coat. Technol.* 204 (20) (2010) 3205–3213.
- [11] M.H. Prado Da Silva, J.H.C. Lima, G.A. Soares, C.N. Elias, M.C. de Andrade, S.M. Best, I.R. Gibson, Transformation of monetite to hydroxyapatite in bioactive coatings on titanium, *Surf. Coat. Technol.* 137 (2) (2001) 270–276.
- [12] X. Fan, J. Chen, J.P. Zou, Q. Wan, Z.C. Zhou, J.M. Ruan, Bone-like apatite formation on HA/316L stainless steel composite surface in simulated body fluid, *Trans. Nonferrous Metals Soc. China* 19 (2) (2009) 347–352.
- [13] M.F. Hasan, J. Wang, C. Berndt, Evaluation of the mechanical properties of plasma sprayed hydroxyapatite coatings, *Appl. Surf. Sci.* 303 (2014) 155–162.
- [14] F. Brossa, A. Cigada, R. Chiesa, L. Paracchini, C. Consonni, Post-deposition treatment effects on hydroxyapatite vacuum plasma spray coatings, *J. Mater. Sci. Mater. Med.* 5 (12) (1994) 855–857.
- [15] H.J. Kim, Y.H. Jeong, H.C. Choe, W.A. Brantley, Hydroxyapatite formation on biomedical Ti–Ta–Zr alloys by magnetron sputtering and electrochemical deposition, *Thin Solid Films* 572 (2014) 119–125.
- [16] A. Balamurugan, G. Balossier, S. Kannan, S. Rajeswari, Elaboration of sol–gel derived apatite films on surgical grade stainless steel for biomedical applications, *Mater. Lett.* 60 (17–18) (2006) 2288–2293.
- [17] T.M. Sridhar, U. Kamachi Mudali, M. Subbayan, Preparation and characterisation of electrophoretically deposited hydroxyapatite coatings on type 316L stainless steel, *Corros. Sci.* 45 (2) (2003) 237–252.
- [18] M. Shirkhanzadeh, Direct formation of nanophase hydroxyapatite on cathodically polarized electrodes, *J. Mater. Sci. Mater. Med.* 9 (2) (1998) 67–72.
- [19] H. Wang, N. Eliaz, L.W. Hobbs, The nanostructure of an electrochemically deposited hydroxyapatite coating, *Mater. Lett.* 65 (15–16) (2011) 2455–2457.
- [20] R. Schmidt, V. Hoffmann, A. Helth, P.F. Gostin, M. Calin, J. Eckert, A. Gebert, Electrochemical deposition of hydroxyapatite on beta-Ti-40Nb, *Surf. Coat. Technol.* 294 (2016) 186–193.
- [21] Z.S. Seyedraoufi, S. Mirdamadi, Effects of pulse electrodeposition parameters and alkali treatment on the properties of nano hydroxyapatite coating on porous Mg–Zn scaffold for bone tissue engineering application, *Mater. Chem. Phys.* 148 (3) (2014) 519–527.
- [22] E.C. Meng, S.K. Guan, H.X. Wang, L.G. Wang, S.J. Zhu, J.H. Hu, C.X. Ren, J.H. Gao, Y.S. Feng, Effect of electrodeposition modes on surface characteristics and corrosion properties of fluorine-doped hydroxyapatite coatings on Mg–Zn–Ca alloy, *Appl. Surf. Sci.* 257 (11) (2011) 4811–4816.
- [23] N. Eliaz, T.M. Sridhar, Electrocrystallization of hydroxyapatite and its dependence on solution conditions, *Cryst. Growth Des.* 8 (11) (2008) 3965–3977.
- [24] N. Ribeiro, S.R. Sousa, F.J. Monteiro, Influence of crystallite size of nanophased hydroxyapatite on fibronectin and osteonectin adsorption and on MC3T3-E1 osteoblast adhesion and morphology, *J. Colloid Interface Sci.* 351 (2) (2010) 398–406.
- [25] Z. Zhuang, T.J. Fujimi, M. Nakamura, T. Konishi, H. Yoshimura, M. Aizawa, Development of a,b-plane-oriented hydroxyapatite ceramics as models for living bones and their cell adhesion behavior, *Acta Biomater.* 9 (5) (2013) 6732–6740.
- [26] K. Anselme, P. Davidson, A.M. Pupa, M. Giazson, M. Liley, L. Ploux, The interaction of cells and bacteria with surfaces structured at the nanometre scale, *Acta Biomater.* 6 (10) (2010) 3824–3846.
- [27] S. Okada, H. Ito, A. Nagai, J. Komotori, H. Imai, Adhesion of osteoblast-like cells on nanostructured hydroxyapatite, *Acta Biomater.* 6 (2) (2010) 591–597.
- [28] Z. Zhuang, H. Yoshimura, M. Aizawa, Synthesis and ultrastructure of plate-like apatite single crystals as a model for tooth enamel, *Mater. Sci. Eng. C* 33 (5) (2013) 2534–2540.
- [29] M.S. Džojić, V. Panić, J. Stojanović, M. Mitrić, V.B. Mišković-Stanković, The effect of applied current density on the surface morphology of deposited calcium phosphate coatings on titanium, *Colloids Surf. A Physicochem. Eng. Asp.* 400 (2012) 36–43.
- [30] D.J. Blackwood, K.H.W. Seah, Electrochemical cathodic deposition of hydroxyapatite: improvements in adhesion and crystallinity, *Mater. Sci. Eng. C* 29 (4) (2009) 1233–1238.
- [31] M.I. Kay, R. Young, A. Posner, Crystal structure of hydroxyapatite, *Nature* 204 (1964) 1050.
- [32] M. Mathew, W.E. Brown, L.W. Schroeder, B. Dickens, Crystal structure of octacalcium bis(hydrogenphosphate) tetrakis(phosphate)pentahydrate, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$, *J. Crystallogr. Spectrosc. Res.* 18 (3) (1988) 235–250.
- [33] M. Ma, W. Ye, X.-X. Wang, Effect of supersaturation on the morphology of hydroxyapatite crystals deposited by electrochemical deposition on titanium, *Mater. Lett.* 62 (23) (2008) 3875–3877.
- [34] H. Wang, S. Zhu, L. Wang, Y. Feng, X. Ma, S. Guan, Formation mechanism of Ca-deficient hydroxyapatite coating on Mg–Zn–Ca alloy for orthopaedic implant, *Appl. Surf. Sci.* 307 (2014) 92–100.
- [35] H. Jiang, X.-Y. Liu, Principles of mimicking and engineering the self-organized structure of hard tissues, *J. Biol. Chem.* 279 (40) (2004) 41286–41293.
- [36] X. Lu, Y. Leng, Theoretical analysis of calcium phosphate precipitation in simulated body fluid, *Biomaterials* 26 (10) (2005) 1097–1108.
- [37] Y. Furukawa, K. Nakajima, *Advances in Crystal Growth Research*, Elsevier, 2001.
- [38] X. Liu, Heterogeneous nucleation or homogeneous nucleation? *J. Chem. Phys.* 112 (22) (2000) 9949–9955.