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The phase transition of calcium phosphate coatings deposited on a Ti–6Al–4V substrate by an electrolytic method

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Abstract

The phase transition of calcium phosphate bioceramics electrodeposited on a Ti–6Al–4V at 10 V, 60 °C for various times has been investigated. At the beginning of electrodeposition, the $\{040\}$ textured dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$, DCPD) obtained is with a coral-like morphology. The major DCPD platelets occur within the first 30 min in deposition and the minor hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) needles form increasingly with time. After 30 min, HAP steadily dominates and is identified as partially transformed from DCPD.

Keywords: X-ray diffraction; Electrochemical reactions

1. Introduction

Synthetic hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) offers excellent osteoconductivity, and has been used to produce a biologically active coating on a biologically inert medical implant [1]. The electrochemical deposition of calcium phosphate bioceramic coatings has attracted considerable attention because of a variety of advantages [2–5].

When an electrolyte contains Ca^{2+} and $H_2PO_4{}^{1-}$, it produces calcium phosphate powders, such as dicalcium phosphate dihydrate (DCPD, $CaHPO_4{\cdot}2H_2O$), and HAP, etc. [6,7]. Wang et al. [5] have pointed out that when calcium phosphate coating is deposited on the Ti–6Al–4V substrate by an electrolytic method under 80 Torr, smooth integrated deposits of HAP and DCPD are obtained.

The mechanism of the electrodeposition of HAP on the Ti–6Al–4V substrate has not been clarified, however, it is generally thought to be caused by a pH change on the cathode [8]. The main objective of this study is to investigate the phase transition of the calcium phosphate deposited on the Ti–6Al–4V substrate. A 0.04 M monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2{\cdot}H_2O$, MCPM) solution has been used to synthesize the HAP on the Ti–6Al–4V substrate by an electrolytic process.

2. Experimental

This work used a Ti–6Al–4V alloy plate (ASTM standard F-136) and a platinum plate as the cathode and anode, respectively. A Ti–6Al–4V alloy plate with a size of 15 mm × 15 mm × 3 mm was mechanically ground and polished to mirror finish.

A saturated 0.04 M electrolyte was prepared by dissolving 1 g analytical grade monocalcium phosphate monohydrate [$Ca(H_2PO_4)_2{\cdot}H_2O$, MCPM; Showa Chemical Co. Ltd., Tokyo, Japan] in 100 ml water. Electrolysis was carried out at 60 °C, 10 V and 80 Torr for 1–120 min. The distance between the electrodes and the cathode area was maintained at 3 cm and 1.057 cm^2, respectively.

The crystalline phases of the samples were examined by X-ray diffraction (XRD, Rigaku D-Max/IIIV, Tokyo, Japan) with a scanning speed of $4^\circ\ min^{-1}$. The operation tube voltage and current were 30 kV and 20 mA, respectively.

The coating microstructure and morphology were investigated with a scanning electron microscope (SEM, Hitachi S2700 SEM, Tokyo, Japan).

3. Results and discussion

Fig. 1 illustrates the XRD patterns of the electrodeposits in the 0.04 M MCPM solution for various times at 60 °C, 10 V and 80 Torr. At the beginning of the deposition process, the

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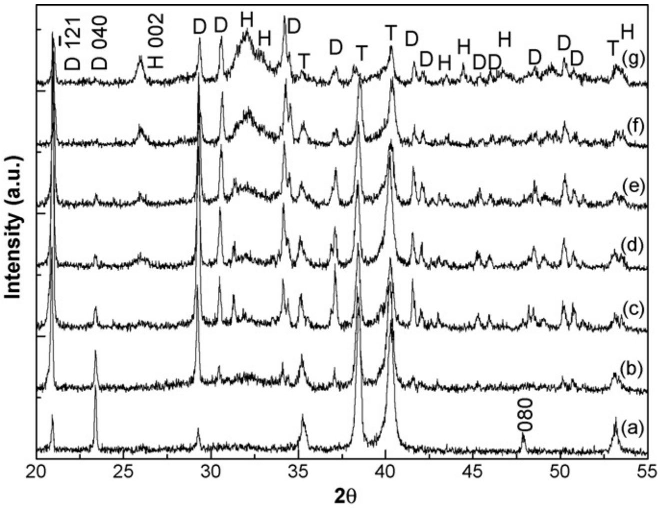

Fig. 1. XRD patterns of the samples electrodeposited at 10 V and 60 °C for different times: (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (f) 30 min, (g) 60 min, and (h) 120 min (D: DCPD, H: HAP, T: Ti).

initial phases were identified as the {0 4 0} textured dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$, DCPD) phase with the reflection of the Ti–6Al–4V alloy substrate in Fig. 1(a). Curry and Jones [9] have pointed out that the initially grown DCPD is {0 4 0} textured. The normal DCPD (*n*-DCPD) phase steadily becomes more dominant after 5 min, and the (0 4 0) reflection intensity decreases with time. This result is due to the fact that the content of DCPD phase is reduced with increasing deposition time. The HAP phase also appears after 5 min deposition, and then increases slowly until 30 min. The reflection intensity of the DCPD reaches a maximum at 30 min and then decreases with a sudden increase in the reflection intensity of the HAP. Fig. 1 also reveals that the reflection intensity of Ti decreases with increasing deposition time, while the film thickness increases with deposition time.

In order to characterize the exact relation between DCPD and HAP, an XRD decline curve analysis has been performed as follows. The commercial DCPD (Riedel-de Haën, Germany) and synthesized nano-sized HAP powders have been mixed with various compositions in order to prepare the standard calibration powders. According to the prior study [5], the HAP formed during electrodeposition is a nano-sized needle-like crystal. Hence the HAP made by hydrolysis in $NaOH_{(aq)}$ is used as a standard sample [10]. The mixed powders of 1DCPD–0HAP, 0.9DCPD–0.1HAP, . . ., 0DCPD–1HAP have been tested with XRD using a scan speed of 1° min^{-1}. The (1 2 1) reflection of the DCPD and the (0 0 2) reflection of the HAP have been chosen to obtain the calibration curve in Fig. 2, where the integrals of the reflections are calculated to get a straight line. The data fitting of the reflection results in an exponential decay line of the composition ratio, as shown in Fig. 2.

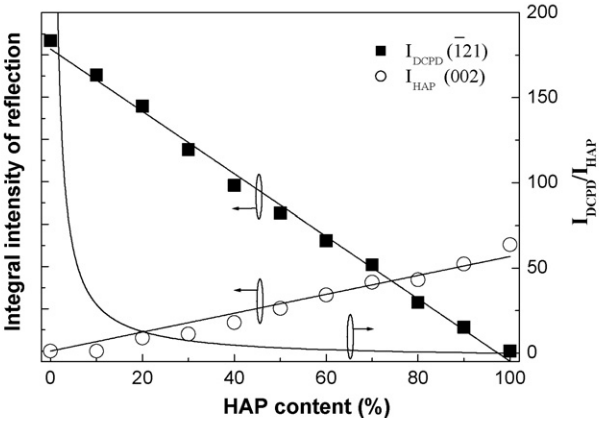

Fig. 2. Decline curve analysis using XRD.

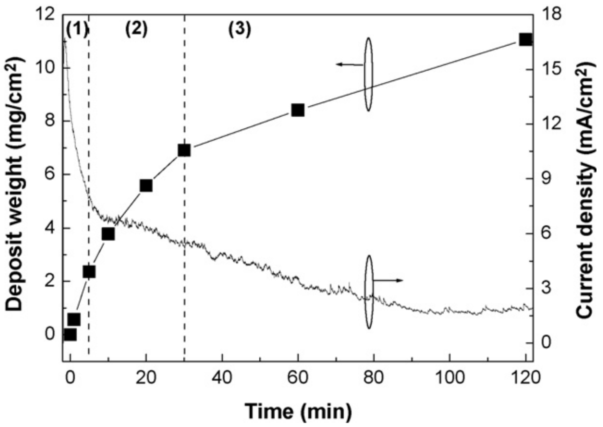

Fig. 3. Deposit weight and current density in the electrodeposition at 60 °C, 10 V for various times.

Fig. 3 indicates that during the electrodeposition at 10 V and 60 °C, the current decreases with the electrodeposition time. In the first 5 min, a sharp decrease in current is observed because the electrical resistance rapidly increases. After 5 min, the rate of current decrease is reduced because the main deposition reaction occurs in the first stage. When the deposition time is above 30 min, the current change approaches a stable value. This phenomenon is caused by the fact that the deposition film of calcium phosphate completely covers the substrate and the thickness increases with time, leading to increased surface elec-

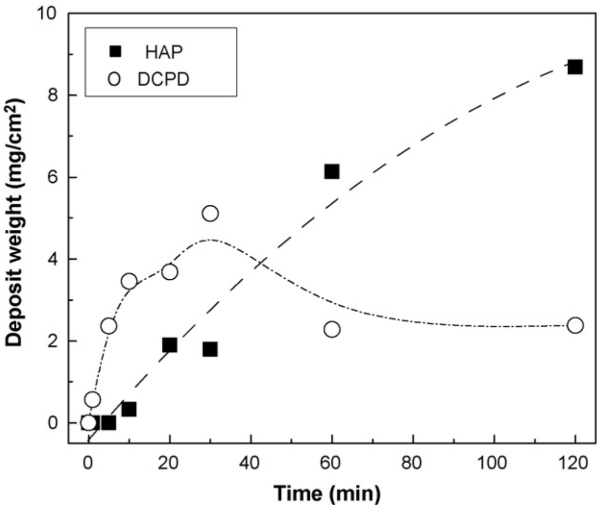

Fig. 4. Deposit weight of DCPD and HAP in the electrolysis of calcium phosphate at 60 °C, 10 V for various times.

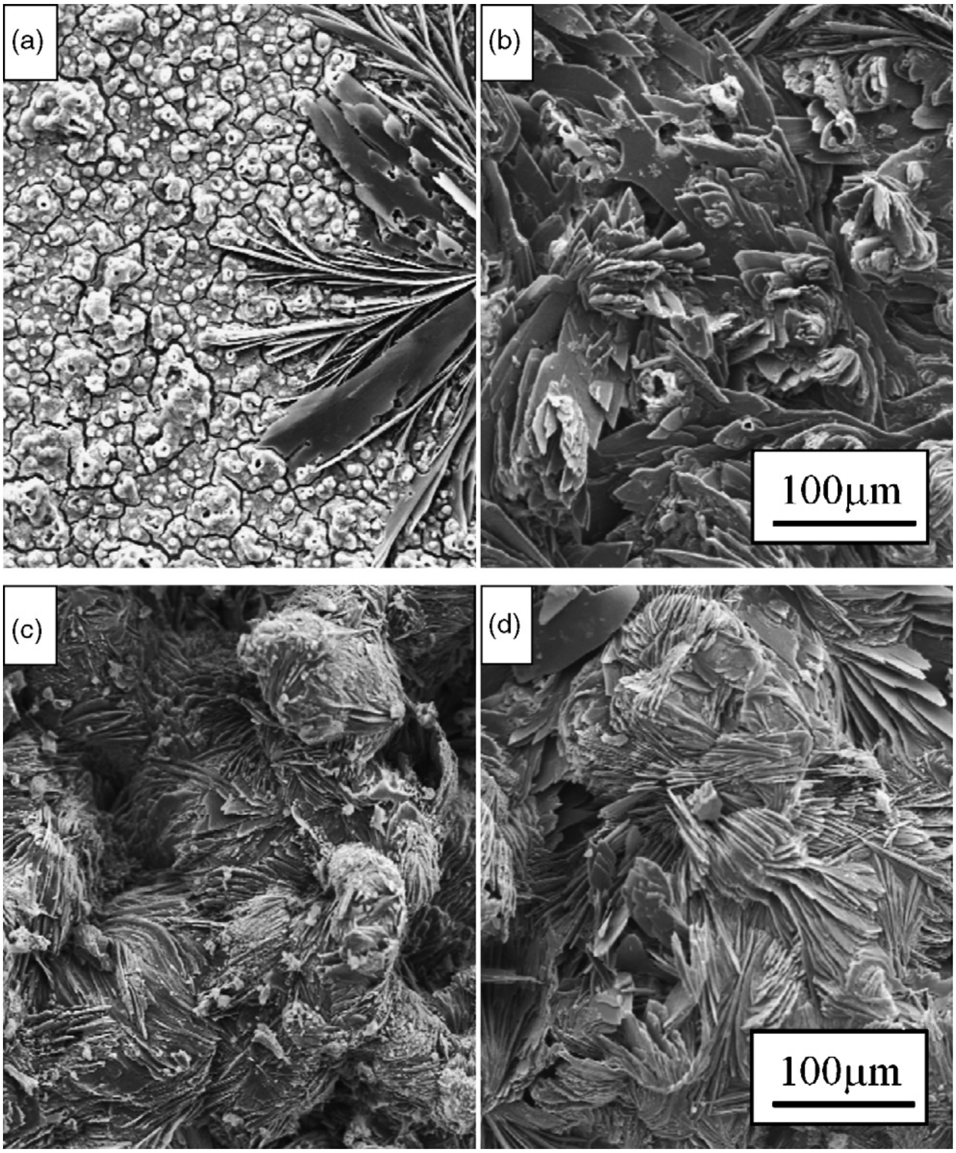

Fig. 5. SEM micrographs of the calcium phosphate deposited at 10 V and 60 °C for various times: (a) 1 min, (b) 10 min, (c) 30 min, and (d) 120 min.

trical resistance. Fig. 3 also reveals that the current ripples with the deposition time. This phenomenon is due to the electrolytic dissociation of water which creates hydrogen gas on the cathode surface [5]. Although the applied pressure of 80 Torr removes the hydrogen quickly, the above reaction cannot be avoided.

As shown in Fig. 3, the weight of the deposit has also been measured for various times and reveals the major weight gain along with the current density reduction. The weight gain curve can be separated into three regions: (1) quick deposit gain along with rapid current density decrease in the first 5 min, (2) slower deposit gain implying slack current density decreasing from 5 to 30 min, and (3) stable deposition rate after 30 min.

Compared with Fig. 1, the quick deposition of the initial DCPD (*i*-DCPD) in 5 min is the major reason for resistance increase. The *n*-DCPD phase deposition on the *i*-DCPD slackens the deposition rate and increases resistance and is followed by formation of the minor HAP phase. After 30 min, the increasing amount of the HAP and the steady deposition rate are caused by the pH variation on the cathode surface due to the reduction of H^+ ions [8].

Following Figs. 1 and 2, the composition ratio of calcium phosphate deposits for various time are identified and multiplied by the total deposit weight from Fig. 3, to obtain the deposit weight of the DCPD and HAP, as shown in Fig. 4. From 0 to 10 min, the DCPD curve matches the total weight curve from Fig. 3 with little HAP formed. From 10 to 30 min, the HAP amount increased to almost the same as DCPD, so the deposition rate of the DCPD slowed down. After 30 min, the HAP content suddenly increases accompanied with the decrease of the DCPD, revealing that a part of the HAP may transform from DCPD. Thereafter, the deposit weight of the DCPD remains stable and that of the HAP steadily increases with time.

The SEM microstructures of the calcium phosphate samples deposited at 10 V and 60 °C for various times are shown in Fig. 5. Fig. 5(a) illustrates that in the sample deposited for 1 min, the major coral-like *i*-DCPD is observed with microcracks, and the *n*-DCPD platelet crystals also appear. Fig. 5(b) shows the morphology of the sample deposited for 10 min, and it is found that the DCPD platelet crystals cover the surface and the same *i*-DCPD-like morphology can still be observed. However, the thinner *n*-DCPD platelet crystals deposited for 30 min are found in Fig. 5(c) without *i*-DCPD like materials. Furthermore, there are round precipitates on the edges of *n*-DCPD crystals when deposition lasts for 120 min as shown in Fig. 5(d) and are identified as nano-sized HAP [5]. However, the amount of the HAP precipitates is not consistent with the results in Fig. 1(e), and the transformation of *n*-DCPD to HAP found in Fig. 4.

4. Conclusions

The phase transition of the electrodeposit on the Ti–6Al–4V substrate in the 0.04 M monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2{\cdot}H_2O$, MCPM) solution for various times at 80 Torr, 60 °C, 10 V has been studied. The results of the current behavior show that the electrodeposition of the calcium phosphate occurs within the first 30 min. The $\{0\,4\,0\}$ textured dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$, DCPD) and Ti are the initial phases of the deposition. The major normal DCPD and minor hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) phases are observed when deposition lasts for 5 min and increases with time. After electrodeposition for 30 min the HAP content increases with time and DCPD decreases, revealing the phase transformation caused by the pH variation which occurs at the cathode surface.

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References

[1] G. Daculsi, Biomaterials 19 (1998) 1473–1478.
[2] T.V. Vijayaraghavan, A. Bensalem, J. Mater. Sci. Lett. 10 (1994) 1782–1785.
[3] M.H.P. Da Silva, J.H.C. Lima, G.A. Soares, C.N. Elias, M.C. de Andrade, S.M. Best, I.R. Gibson, Surf. Coat. Technol. 137 (2001) 270–276.
[4] S. Ban, J. Hasegawa, Biomaterials 23 (2002) 2965–2972.
[5] S.H. Wang, W.J. Shih, W.L. Li, M.H. Hon, M.C. Wang, J. Eur. Ceram. Soc. 25 (2005) 3287–3292.
[6] M. Schirkhanzaden, J. Mater. Sci. Lett. 10 (1991) 1415–1417.
[7] M. Schirkhanzaden, J. Mater. Sci.: Mater. Med. 9 (1998) 67–72.
[8] J.M. Zhang, C.J. Lin, Z.D. Feng, Z.W. Tian, J. Electroanal. Chem. 452 (1988) 235–240.
[9] N.A. Curry, D.W. Jones, J. Chem. Soc. A (1971) 3725–3729.
[10] W.J. Shih, Y.F. Chen, M.C. Wang, M.H. Hon, J. Crystal Growth 270 (2004) 211–218.