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Immersion characteristics of electrolytic calcium phosphate coated Ti in simulated physiological fluid

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The electrolytic calcium phosphate coatings have been deposited on titanium at room temperature and presented several differences with respect to other documented reports. The present study aimed to investigate the immersion behaviors of the uncoated titanium, the hydroxyapatite (HA) coated and the dicalcium phosphate dihydrate (DCPD) coated in the simulated physiological fluid (Hank's solution) at 37°C for 1, 7, 14, and 30 days. For the evaluation in dissolution or precipitation, morphology, composition, and crystal structure, the specimens were characterized by weight variation, X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy before and after immersion. The plate-like DCPD structure was not stable in Hank's solution. However, its dissolution revealed the enhancing effect on the precipitation of newly formed hydroxyapatite. The calcium deficient hydroxyapatite (CDHA) can be conducted directly by the HA as-coated or the HA500 (annealed at 500°C, Ca/P = 1.63), or indirectly by the DCPD coated (Ca/P = 1.58), but not by the HA700 (annealed at 700°C, Ca/P = 1.80). The newly formed granular hydroxyapatite showed the more crystallization than the as-coated. Besides, the annealing enhanced the crystallization of the as-coated hydroxyapatite. Generally, the electrolytic CaP coating including the DCPD coated, HA as-coated, HA500, and HA700 specimens played an important role on the precipitation of newly formed hydroxyapatite in Hank's solution, but the uncoated Ti did not. *© 2004 Kluwer Academic Publishers*

1. Introduction

Recently, bone substitutes in orthopedic and dental surgeries have been an increasing demand. Bone grafts would appear to provide the ideal material for bone reconstruction. However, autografts are necessarily limited in volume and xenografts or allografts should be considered with caution due to the potential risk for transmission of virus (C hepatitis) on nonconventional agents (prions) [1]. Consequently, the hard tissue replacement is still recognized as the effectual and convenient healing process.

Metals have been used in various forms as implants due to their superior mechanical properties and undemanding fabrication. Biocompatibility, corrosion resistance, and fixation with native bone tissue, however, would be the concerned drawbacks. Calcium phosphate (CaP) ceramics, in particular hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), assemble mineral phase in human bone and have excellent biocompatibility. The inferior mechanical strength makes CaP inadequate to apply in load-bearing areas. Consequently, metallic prostheses with bioactive calcium phosphate ceramic coatings on their surface are recognized as the very promising candidates for bone replacement.

The dissolution rate of the monophase CaP ceramics increased in the order of stoichiometric hydroxyapatite (SHA), calcium deficient hydroxyapatite (CDHA), oxyhydroxyapatite (OHA), β-tricalcium phosphate (β-TCP), α-tricalcium phosphate (α-TCP), and tetracalcium phosphate (TTCP) [2]. CDHA receives greater biological interest than SHA because of the Ca/P ratio in bone is lower than 1.67. CDHA elicits an immediate precipitation of bioequivalent apatite on its surface and SHA requires some induction time when they immersed in a simulated physiological fluid [3].

The transformation of the surface due to dissolution, reprecipitation or recrystallization is believed to be an important early step in the process that ultimately leads to the adhesion of bone to the implant surface [2, 4, 5]. HA and DCPD (dicalcium phosphate dihydrate) coatings were electrolytic deposited on titanium at room temperature through controlled current densities in our previous work [6]. HA coating was characterized as CDHA coating due to the non-stoichiometric

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Ca/P ratio. Adherent, purer, and more crystalline HA coating could fulfill the requisition of implant materials. However, the dissolution/precipitation behavior of the coatings obtained by electrochemical deposition has not been investigated. In the present work, dissolution/precipitation behavior of the uncoated titanium, the DCPD coated, the HA as-coated, and the HA heated were investigated before and after immersion in the simulated physiological fluid, Hank's solution.

2. Experimental

2.1. Electrochemical deposition and heating

As-received commercial pure titanium (ASTM F67, grade 2) sheets were cut into disks of diameter 16 mm and thickness 1 mm. After cutting, the specimen was then wet ground to #2000 grit level with SiC abrasive papers, rinsed with acetone in an ultrasonic bath, and washed with distilled water. The electrolyte used in this study contained 0.042 M $Ca(NO_3)_2$ and 0.025 M $NH_4H_2PO_4$ and its pH value was 4.11. Electrochemical deposition of DCPD and HA coated specimens were carried out with EG&G Model 273A potentiostat/galvanostat at the controlled current densities of 1 and 10 mA/cm^2, respectively, for 30 min, at room temperature (25°C). The Ti disk was the cathode and the Pt plate was the anode. After deposition, the specimens were rinsed in distilled water to remove residual electrolyte and dried in air for 24 h. Some HA coated specimens were heated at 100°C for 10 min and then at 500°C for 1 h (HA500) or at 700°C for 1 h (HA700) to obtain more crystallized coatings.

2.2. Immersion and characterization

The uncoated Ti and DCPD coated, HA as-coated, and HA heated (HA500 and HA700) specimens were immersed in 30 ml Hank's solution at 37 ± 1°C for 1, 7, 14, and 30 days. The chemical composition of Hank's solution is given as NaCl 8.00 g/L, $CaCl_2$ 0.14 g/L, KCl 0.40 g/L, $NaHCO_3$ 0.35 g/L, glucose 1.00 g/L, $MgCl_2 \cdot 6H_2O$ 0.10 g/L, KH_2PO_4 0.06 g/L, $MgSO_4 \cdot 7H_2O$ 0.06 g/L, and Na_2HPO_4 0.06 g/L [7]. The pH value was 7.40 at 25°C measured by a pH-meter (Sartorius AG Model: BP211D, Germany). After immersion, the specimens were removed and rinsed in deionized water and dried in air. A digital balance (accuracy ≤ 0.02 mg) was used to weigh the specimens before and after immersion. The crystallography of specimens were analyzed by X-ray Diffractometry (XRD) in a MAC MO3XHF diffractometer with Cu K_α radiation and operated at a tube voltage of 40 kV and a current of 30 mA. The range of 2θ was from 10 to 50° with a scanning rate of 1°/min. The surface morphology and the elemental analysis of the coatings were observed by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS, JEOL JSM-5400 Japan).

3. Results and discussion

3.1. Weight variations of specimens after immersion

The weight variation in percentage of coatings after immersion in Hank's solution is shown inFig. 1. The weight variation of Ti was not shown here because it was smaller than 0.05 mg and could be neglected after immersion. For the other specimens with coatings, the weight variation presented a close correlation with the weight of the coating before test. The weight of DCPD coated specimens revealed a massive reduction for the first day and the weight were regained gradually after 7 days. It is known that DCPD is unstable at pH > 4.2 [8], i.e., it dissolves rapidly and enhances the degree of supersaturation of ions around the samples. Subsequently, the precipitation of other calcium phosphates, such as HA, could be facilitated through the dissolution of DCPD in Hank's solution, since HA is the only stable phase at pH > 4.2. For the same reason, HA as-coated and HA500 specimens revealed a increment in place of reduction in weight for the first day, and the increment gradually became saturated after 7 days. In other words, the ions contained in Hank's solution could further precipitate onto the surface of the coatings and approach an equilibrium state. In comparison, the amount and rate of HA precipitate on HA500 is greater than on the as-coated. The precipitation rate on the HA700 specimens was slower than on the HA as-coated or HA500 specimens. The HA700 specimens represented a maximum weight gain for 14 days. However, a drop off of weight could be observed after 30 days immersion.

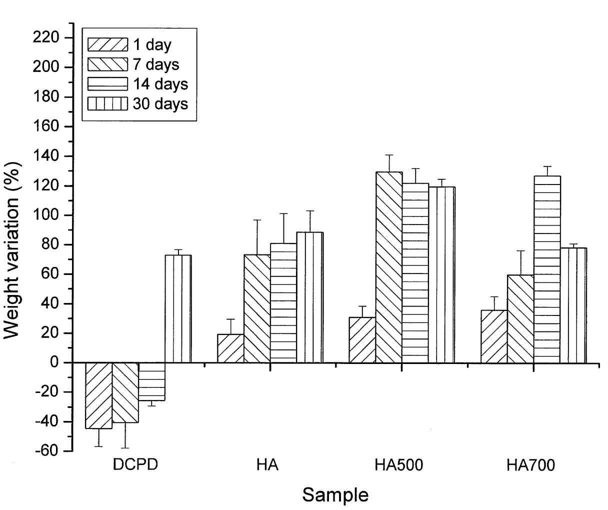


Figure 1 Weight change in percentage of various samples immersed in Hank's solution at 37°C.

3.2. XRD analysis of immersed specimens

No change of XRD patterns for the uncoated Ti was found before and after immersion. The diffraction peak intensities of DCPD were dramatically decreased and some weaker diffraction peaks were disappeared for 1 day immersion. On the other hand, HA (0 0 2) and (2 1 1) diffraction peaks start to show up. After immersion for 7 days, only HA diffraction peaks was found, as shown inFig. 2. The intensity of HA (2 1 1) and (0 0 2) peaks increased with immersion time. This result is consistent that DCPD was dissolved immediately in Hank's solution and the massive weight loss was found, as shown in Fig. 1. HA, the stable phase at pH > 4.2, precipitated gradually onto the surface of specimens. Initially, the dissolution rate of DCPD was much greater than the precipitation rate of HA. Finally,

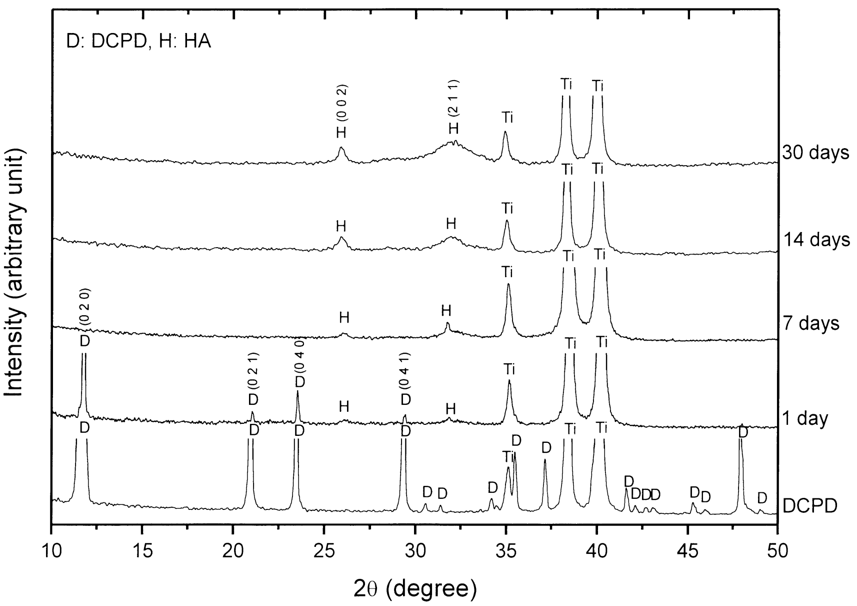


Figure 2 XRD patterns of DCPD coated specimens detected before and after immersion.

the precipitation of HA elevated the weight of the specimen when the dissolution rate of DCPD decreased. This result also agreed that HA is the stable phase at pH values between 5 and 9 in aqueous solutions [9].

Fig. 3 illustratesthe diffraction patterns of HA coated specimens before and after immersion. The $CaCO_3$ (1 0 4) peak was found. The formation of $CaCO_3$ was possibly caused by the following reaction

$$Ca^{2+} + 2OH^- + CO_2 \rightarrow CaCO_3 + H_2O \quad (1)$$

The high concentration of OH^- was supplied by the cathodic reaction

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (2)$$

at the high current density of 10 mA/cm^2. The $CaCO_3$ (1 0 4) peak had almost vanished for 7 days immersion. This means that $CaCO_3$ was unstable in Hank's solution. On the other hand, the HA (0 0 2) peak became sharper and the intensities of the broaden peak including HA (2 1 1), (1 1 2), and (3 0 0) peaks were increased. The increasing intensity was linked to the precipitation (or weight gain) of HA for the 7 days immersion, as shown in Fig. 1. Also, the sharper peak means the more crystalline structure. Consistent with the weight variation, the XRD patterns varied scarcely after 7 days.

Compared to the HA as-coated, the XRD patterns of HA500 specimens before immersion revealed more crystalline, as shown inFig. 4, the bottom diagram. The annealing at 500°C has enhanced the crystallization of HA, but no effect on the stability of $CaCO_3$ in Hank's solution. The further immersion for HA500 specimens has less effect on the crystallization of hydroxyapatite than for HA specimens.

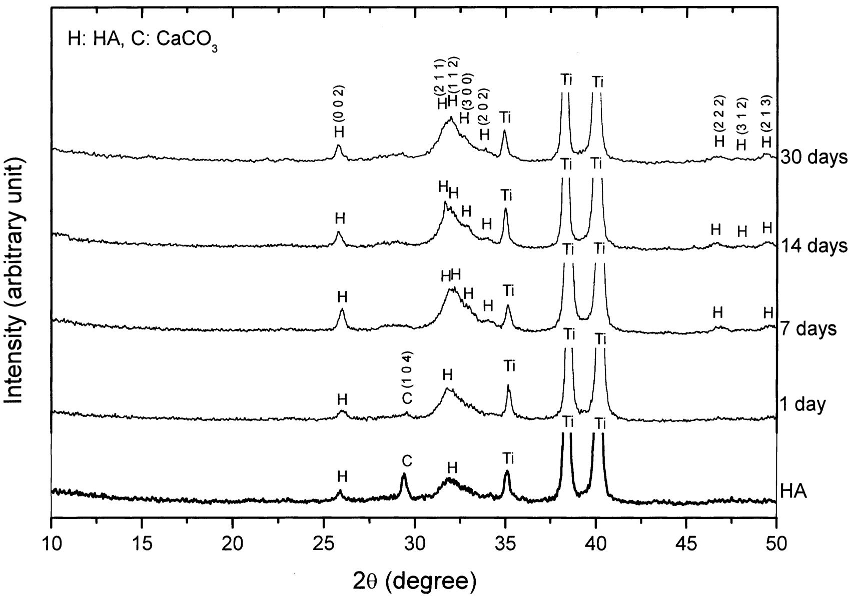


Figure 3 XRD patterns of HA coated specimens detected before and after immersion.

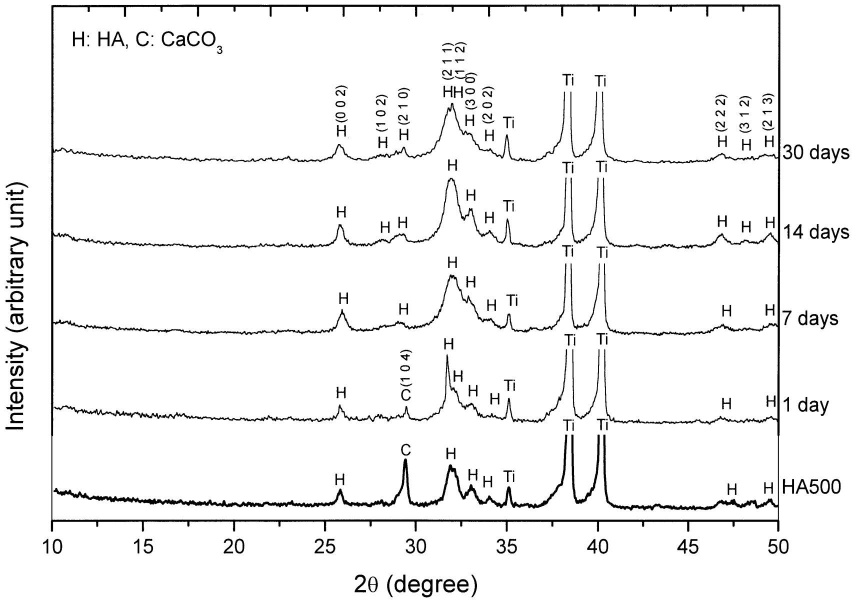


Figure 4 XRD patterns of HA500 specimens detected before and after immersion.

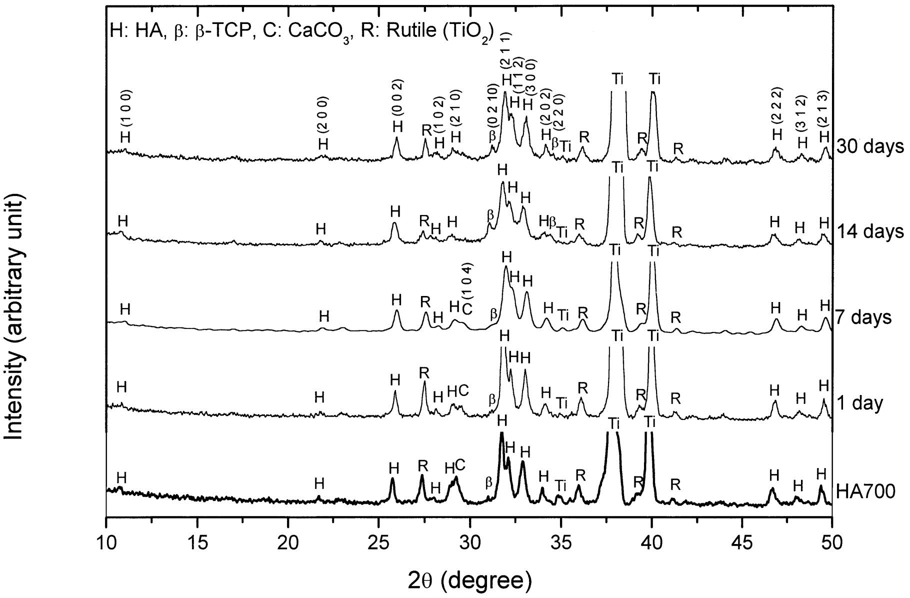


Figure 5 XRD patterns of HA700 specimens detected before and after immersion.

More enhancing effects on the crystallization of hydroxyapatite was found for HA700 specimens, as shown inFig. 5, the bottom diagram. However, the β-TCP phase was found. This means that the transformation from hydroxyapatite into β-TCP initiated at 700°C. Also, rutile (TiO_2) was formed due to oxidation in the air. The higher temperature annealing did not reveal any effect on the stability of $CaCO_3$ in Hank's solution. Although the dissolution of β-TCP was not obvious for 30 days immersion from the XRD diagrams, the weight gain was decreased, as shown in Fig. 1.

3.3. Ca/P ratios of specimens after immersion

With the commercial hydroxyapatite powders as the standard, Ca/P ratios of the specimens after immersion in Hank's solution were detected by energy

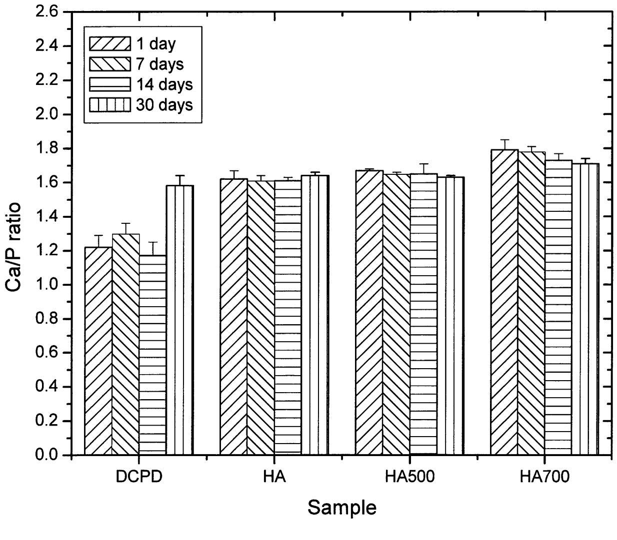
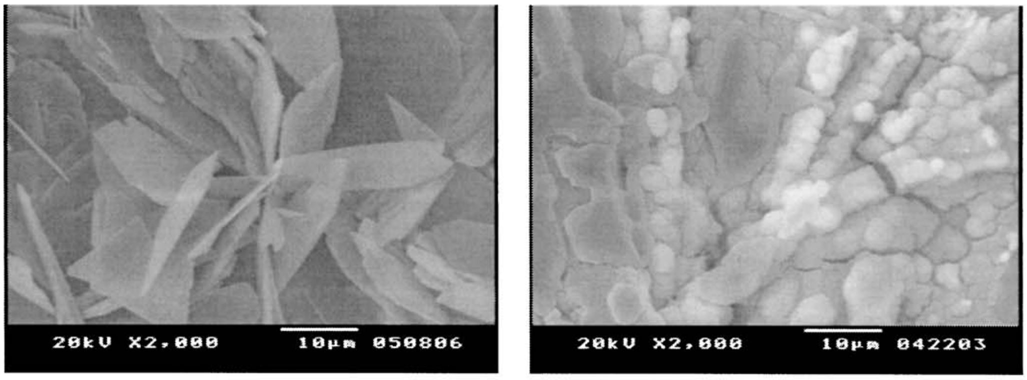


Figure 6 Ca/P ratios of various samples detected after immersion.

dispersive spectroscopy (EDS), as shown inFig. 6. The theoretical Ca/P ratio of DCPD ($CaHPO_4 \cdot 2H_2O$) is 1.00. For 1–14 days immersion, the ratio increased to 1.2 ± 0.1 due to the precipitation of HA, as shown in Fig. 2. For 30 days immersion, it even increased to 1.58 since the more weight of hydroxyapatite deposition was gained, as shown in Figs 1 and 3. In contrast, the Ca/P ratios of HA and HA500 specimens always kept around 1.63 which is calcium deficient. However, the Ca/P ratio of HA700 was 1.8. The higher ratio may be caused by the matrix effect of β-TCP, as shown in Fig. 5. When the β-TCP was gradually dissolved in Hank's solution (weight gain decreased, as shown in Fig. 1), the Ca/P ratio approached to 1.7.

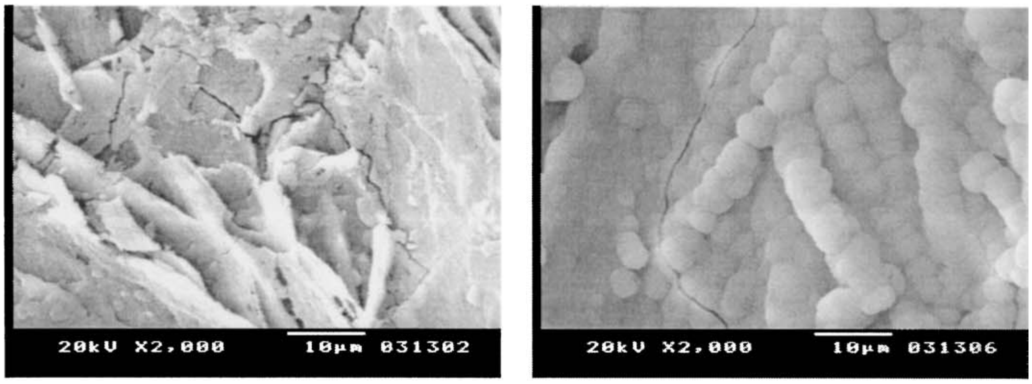
3.4. SEM observation of immersed specimens

SEM photographs of various specimens after immersion for 30 days are shown inFig. 7 (a) DCPD coated and (b) HA as-coated. No apparent variation was observed on the surface of Ti after immersion test. For DCPD coated specimen, the dissolution of DCPD phase resulted in the disappearance of the plate-like structure. More and more granular particles precipitated on the surface after 14 and 30 days. The surface of HA coating after first day immersion was slightly rougher than that before test due to the new deposition of HA from Hank's solution, as shown in Fig. 7b. The precipitated HA phase presented as many small granular particles on the HA coating. The size of these granular particles



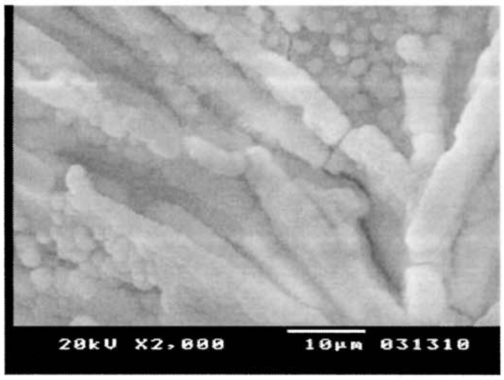
Before immersion

1 day



7 days

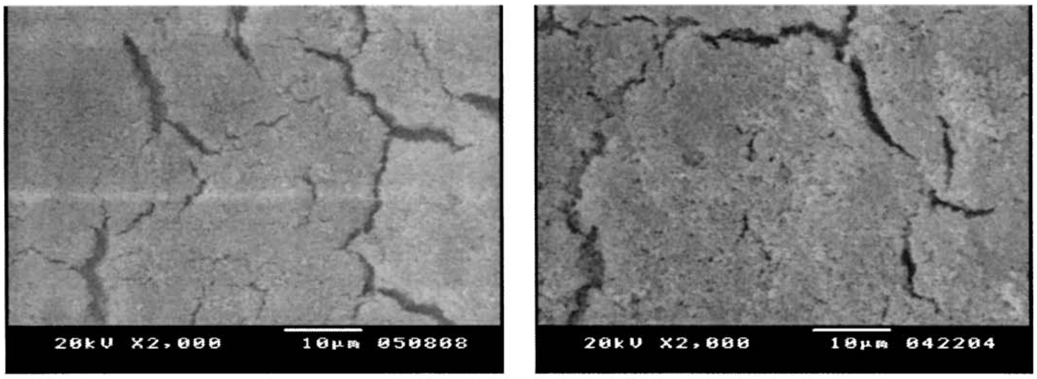
14 days



30 days

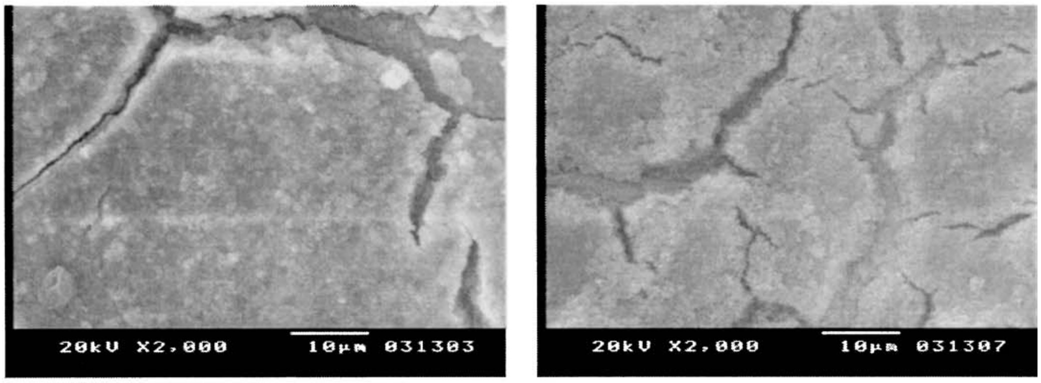
(a) DCPD

Figure 7 SEM photographs of (a) DCPD coated and (b) HA as-coated specimens before and after immersion. (*Continued*)



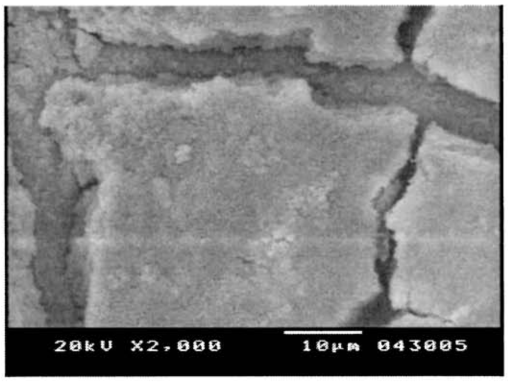
Before immersion

1 day



7 days

14 days



30 days

(b) HA

Figure 7 (*Continued*).

was smaller than that precipitated on the DCPD coating. Similar surface morphology was found for HA500 and HA700 specimens. Generally, the electrolytic CaP coating including DCPD coated, HA as-coated, HA500, and HA700 played as a significant precursor in the precipitation process of newly formed HA phase in Hank's solution, but the uncoated Ti did not.

4. Summary and conclusions

A room-temperature process of electrolytic deposition for the formation of calcium deficient hydroxyapatite (CDHA) coatings has been successfully conducted on the ASTM F-67 grade 2 pure Ti to investigate its immersion characteristics in Hank's solution. Through the electrolytic coating, annealing, immersion, weight variation, XRD analysis, and surface observation, several conclusions are drawn

1. The plate-like DCPD structure was not stable in Hank's solution. However, its dissolution revealed the enhancing effect on the precipitation of newly formed hydroxyapatite.

2. The by-product $CaCO_3$, which was found at the high current density of 10 mA/cm^2, cannot be decomposed by annealing but may be dissolved in Hank's solution.

3. The calcium deficient hydroxyapatite (CDHA) can be conducted directly by the HA as-coated or the HA500 process ($Ca/P = 1.63$), or indirectly by the DCPD process ($Ca/P = 1.58$), but not by the HA700 process ($Ca/P = 1.80$).

4. The newly formed granular hydroxyapatite showed the more crystallization than the as-coated. Besides, the annealing enhanced the crystallization of the as-coated hydroxyapatite.

5. Generally, the electrolytic CaP coating including DCPD coated, HA as-coated, HA500, and HA700 played an important role on the precipitation of newly formed hydroxyapatite in Hank's solution, but the uncoated Ti did not.

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