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# Hydroxyapatite crystal growth on calcium hydroxyapatite ceramics

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Calcium hydroxyapatite (Ca-HAP) ceramics containing tricalcium phosphate (TCP) were soaked in three solutions: phosphate buffer, tris buffer, and simulated body fluid (SBF). Petal-like crystals of Ca-HAP were deposited on the Ca-HAP ceramics when (i) Ca-HAP ceramics contained $\alpha$-TCP, (ii) the soaking solution contained phosphate ion and (iii) the pH of soaking solution was higher than 7.3. These conditions facilitate the presence of $HPO_4^{2-}$ and $Ca^{2+}$ ions, the latter from dissolution of $\alpha$-TCP. A well-defined X-ray diffraction pattern for the deposited Ca-HAP crystals indicates preferred growth of $\{002\}$ planes. Slower crystal growth of Ca-HAP was found for SBF (pH = 7.5) than in the phosphate buffer, due possibly to the lower phosphate ion content in SBF.

## 1. Introduction

Calcium phosphate ceramics, especially calcium hydroxyapatite (Ca-HAP) and tricalcium phosphate (TCP), form bonds with living bone due to their biocompatibility and, therefore, many experimental investigations have been carried out [1] in order to use those ceramics as hard tissue implant materials. It is well known that some by-products have been found in these ceramics after sintering in the range of 1100 to 1300° C [2, 3], such as calcium oxide, TCP, and other kinds of calcium phosphate. Decomposition of the ceramics or fluctuation of the Ca/P ratio results in this formation of by-products. It is necessary to clarify their effect on biocompatibility in order to use these ceramics as biomaterials. In the present experiments, surface changes have been studied for Ca-HAP ceramics with various Ca/P ratios sintered at several temperatures after soaking in a few lymph-like aqueous solutions.

## 2. Experimental procedure

Ca-HAP powders with atomic ratio Ca/P = 1.48 and 1.67 were prepared as follows. An aqueous solution of $(NH_4)_2HPO_4$ was added drop-wise to a $Ca(NO_3)_2 \cdot 4H_2O$ solution at 25° C, where the pH of both solutions was adjusted at about 11 by addition of an $NH_4OH$ solution. After being mixed, the reaction solution was heated up to its boiling point and refluxed for 20 min. It was then left standing for 20 h at room temperature without stirring. The Ca-HAP precipitates were removed from the mother liquor by centrifugal filtration and dried at 110° C for 24 h. Crystallites of these Ca-HAP powders were spherical in shape according to scanning electron microscopic (SEM) observation, and their BET specific surface area was approximately $70\,m^2\,g^{-1}$. The dried powders were pulverized, isostatically pressed into cylindrical shapes at a pressure of $2000\,kg\,cm^{-2}$, and sintered at several temperatures in the range 800 to 1400° C. The sintered ceramics were cut into cylinders about 5 mm in height and 5 mm in diameter, and used for the soaking experiments. All the dried powders in this study were identified as Ca-HAP (JCPDS 9-432) by the X-ray diffraction (XRD) method. Pulverized powders of ceramics sintered above 800° C showed the XRD patterns of $\alpha$-TCP (JCPDS 9-348) and $\beta$-TCP (JCDPS 9-169) as well as Ca-HAP, while no other calcium phosphates nor calcium oxide were detected in this study.

The Ca-HAP ceramics containing TCP were soaked at 25° C up to 480 h in three solutions: (i) phosphate buffer (M/15 $Na_2HPO_4$ + M/15 $KH_2PO_4$); (ii) tris buffer (M/10 HCl + M/5 $(CH_2OH)_3CNH_2$); (iii) simulated body fluid (SBF) [4]. The content of inorganic components in SBF is nearly the same as in human plasma. Solution pH values were adjusted in the range of 6 to 10 by controlling the mixing amount of each component solution (for Solutions (i) and (ii)) and by the addition of M/10 HCl and M/5 $(CH_2OH)_3CNH_2$ (for Solution (iii)).

After being soaked, the ceramics were taken out from the solution, washed in distilled water and subsequently in acetone, and dried at room temperature. The morphology of the crystals deposited on the surface of the ceramics was observed under SEM. The deposited crystals were identified by means of a thin-film diffraction (TFD) apparatus (Rigaku RAD-RB).

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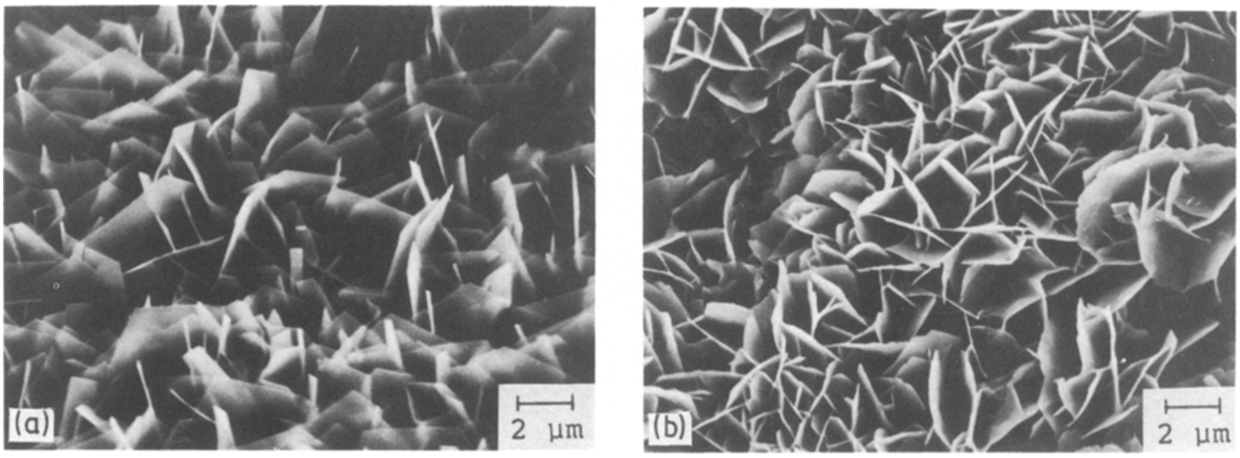


*Figure 1* (a, b) HAP crystals deposited on Ca-HAP ceramic with Ca/P = 1.48 sintered at 1400° C for 1 h, after being soaked in phosphate buffer (pH 7.5).

# 3. Results and discussion

## 3.1. Deposition of Ca-HAP crystals

### 3.1.1. Criteria for deposition of Ca-HAP crystals

Petal-like Ca-HAP crystals, shown in Fig. 1, were grown on the surface of the Ca-HAP ceramics when the following three conditions were simultaneously satisfied: (i) the ceramics contained $\alpha$-TCP, (ii) they were soaked in solutions containing phosphate ions ($PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^-$), and (iii) the pH of the solution was higher than 7.3. In the TFD pattern of the deposited Ca-HAP crystals shown in Fig. 2, the intensity for $\{0\,0\,2\}$ planes is the strongest, in contrast to the JCPDS data (9-432) where $I_{002}/I_{211} = 0.4$. This enhanced $\{0\,0\,2\}$ peak intensity indicates preferred growth of $\{0\,0\,2\}$ planes in the deposited Ca-HAP crystals.

### 3.1.2. Effect of phosphate ions

In the tris buffer, petal-like crystals were not deposited irrespective of the presence of $\alpha$-TCP, while cavities were formed on the surface of the ceramics containing $\alpha$-TCP, as shown in Fig. 3. This cavity formation suggests the dissolution of $\alpha$-TCP from the ceramics. Therefore, it is considered that the deposition of Ca-HAP petal-like crystals occurs by the reaction between $Ca^{2+}$ and $PO_4^{3-}$ ions both from dissolved $\alpha$-TCP or by the reaction between $Ca^{2+}$ from $\alpha$-TCP and phosphate ions ($PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^-$) from the buffer solutions. Re-deposition of $\alpha$-TCP probably does not take place since the solubility of $\alpha$-TCP is higher than that of Ca-HAP [5]. Monma and co-workers [6–10] have reported the transformation of $\alpha$-TCP to HAP in aqueous solutions of NaCl, KOH, $NH_4Cl$ and $CH_3COONa$. The $\alpha$-TCP changed its shape from spherical to petal-like after transformation when it was treated at temperatures above 60° C. The transformation did not take place below 60° C, while in the present study the petal-like crystal deposition was observed on ceramics which were soaked even at room temperature. This difference between the two studies with respect to the deposition of petal-like crystals may be attributable to the presence or absence of phosphate ions in the soaking solution. However, it

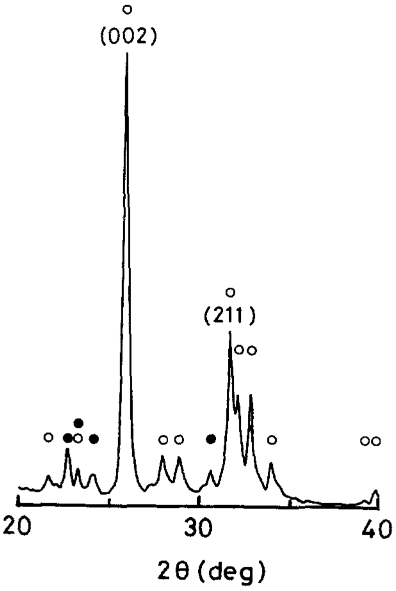


*Figure 2* TFD pattern (Cu*Kα*) of HAP crystals deposited on Ca-HAP ceramic with Ca/P = 1.48 sintered at 1400° C for 1 h, after being soaked in phosphate buffer (pH 7.5) for 24 h. (○) Ca-HAP, (●) $\alpha$-TCP.

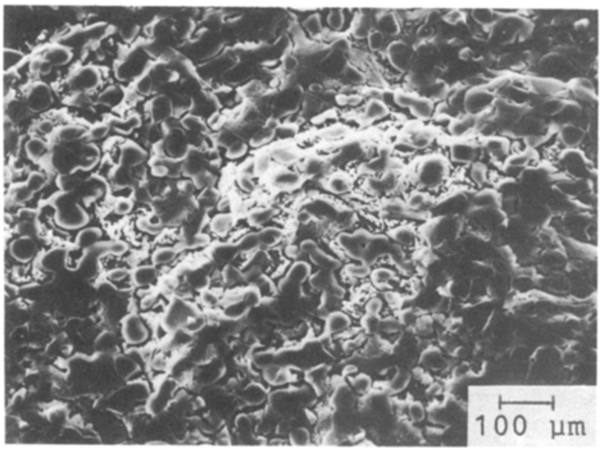


*Figure 3* Surface of ceramic containing $\alpha$-TCP after being soaked in tris buffer (pH 7.5) for 24 h.

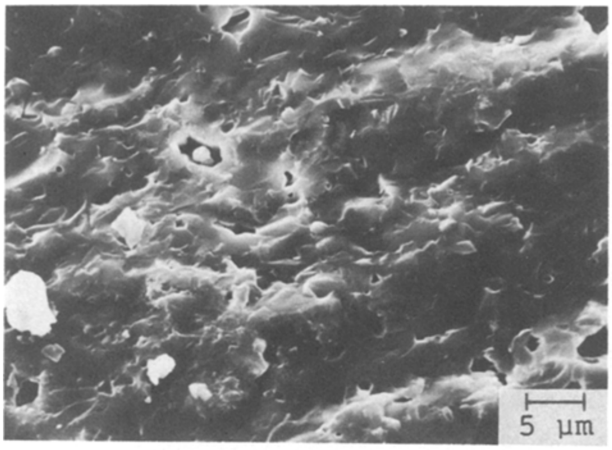


*Figure 4* Surface of ceramic containing $\beta$-TCP after being soaked in phosphate buffer (pH 7.5) for 24 h.

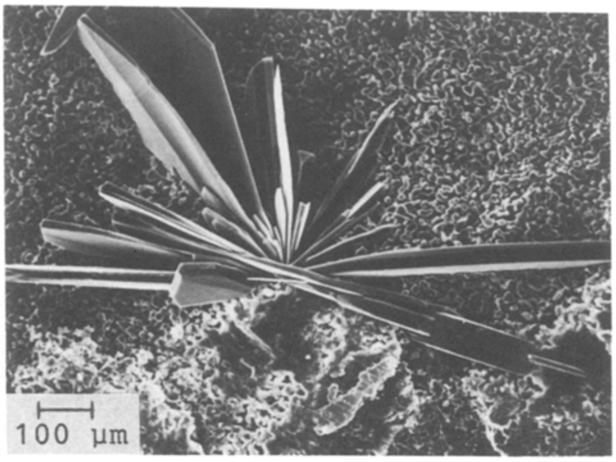


*Figure 5* Surface of ceramic containing $\alpha$-TCP after being soaked in phosphate buffer (pH 7.1) for 24 h.

is also possible that the formation of petal-like crystal proceeds through different reaction mechanisms in the two experiments.

### 3.1.3. Effect of TCP

When the ceramics consisted only of Ca-HAP or of Ca-HAP and $\beta$-TCP, petal-like crystals were not deposited even if the soaking solutions satisfied Conditions (ii) and (iii) in Section 3.1.1. Fig. 4 shows a typical SEM photograph of a surface without petal-like crystals for $\beta$-TCP-containing ceramic after being soaked in phosphate buffer at pH 7.5 for 24 h. The surface of the ceramics did not change compared to the surface before soaking, which is the same as in Fig. 6a below. Hence the difference between $\alpha$-TCP and $\beta$-TCP with respect to Ca-HAP crystal deposition is mainly caused by the different solubilities of the two compounds [11], i.e. the greater solubility of $\alpha$-TCP.

### 3.1.4. Effect of pH

Fig. 5 shows large unidentified plate-like crystals about 300 $\mu$m in length grown on the surface of ceramics containing $\alpha$-TCP which have been soaked in phosphate buffer in the lower pH region (6 to 7.3), though in the high pH region (7.3 to 10) small petal-like Ca-HAP crystals (2 to 5 $\mu$m) are deposited on the ceramics (Fig. 1) as indicated above.

A possible way of understanding the effect of pH on Ca-HAP deposition is as follows. The fact that Ca-HAP is deposited in the higher pH region ($> 7.3$) probably indicates the importance of the equilibrium among the phosphate ions. That is, whether Ca-HAP is deposited or not depends on the existence of $HPO_4^{2-}$ ions which are present mainly in the pH region above 7.2. The Ca-HAP crystals deposited in this study are

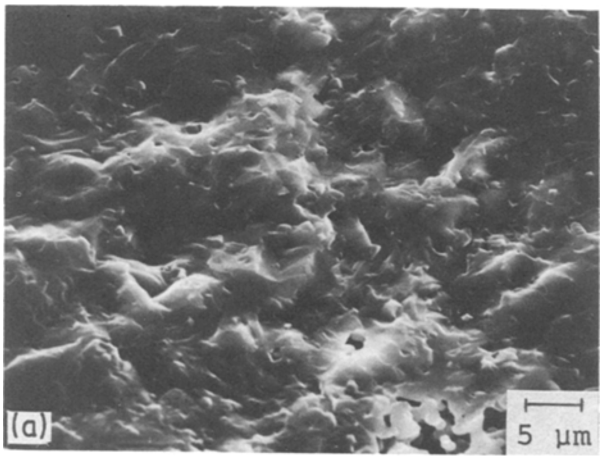
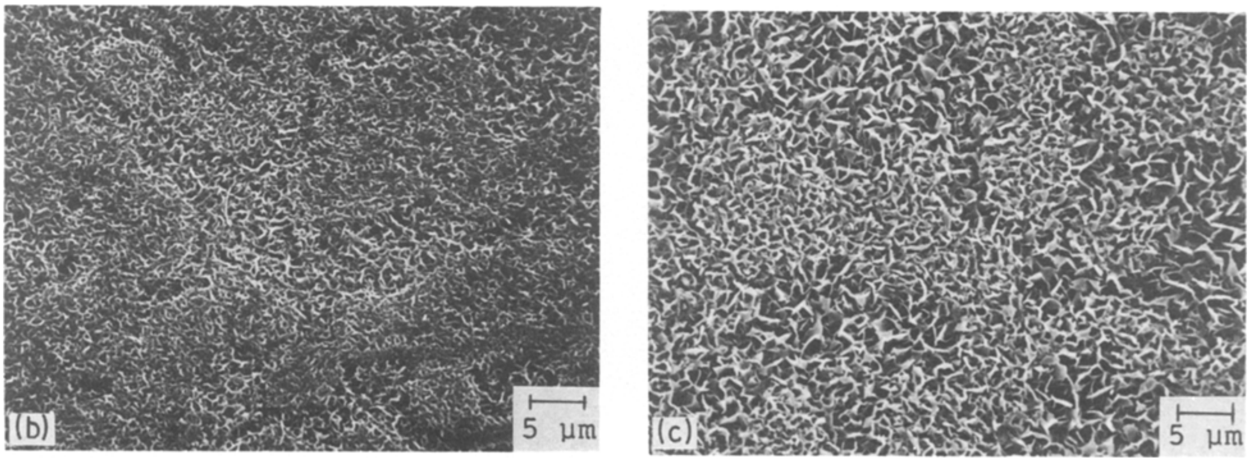


*Figure 6* Change of the surface of ceramic containing $\alpha$-TCP with soaking time in phosphate buffer (pH 7.5): (a) 0 h, (b) 0.5 h, (c) 10 h.



probably calcium-deficient Ca-HAP ($Ca/P < 1.67$) because Ca-HAP preferably crystallizes in a calcium-deficient crystal structure in solutions with a non-stoichiometric ratio Ca/P ($< 1.67$) [2]. In fact, an excess of phosphate ions over the stoichiometric amount is present in the soaking solution (the phosphate buffer), which may favour the deposition of calcium-deficient Ca-HAP. Calcium-deficient Ca-HAP contains $HPO_4^{2-}$ ions in its crystal structure to maintain the charge balance [2]. Therefore, it can be concluded that Ca-HAP petal-like crystal deposition has been observed in the pH region above 7.3 because the existence of $HPO_4^{2-}$ ions in the soaking solution is necessary for Ca-HAP deposition.

## 3.2. Development of surface microstructure

Fig. 6 shows SEM photographs of the surfaces of Ca-HAP ceramics with $Ca/P = 1.48$ sintered at 1400° C for 1 h which have been soaked in phosphate buffer (pH 7.5) for 0, 0.5 and 10 h. After 0.5 h, a protuberance was formed on the ceramic and grew with soaking time. The shape of the protuberance turned out to be petal-like (Fig. 1) after being soaked for 15 to 20 h. When ceramics containing α-TCP were soaked in SBF (ph 7.5), Ca-HAP crystallites could be detected on the surface in about a week, and the surface was entirely covered with the petal-like crystals after four weeks' soaking. One of the possible reasons for this slower crystal growth compared with phosphate buffer is the lower content of the phosphate ion, $HPO_4^{2-}$, in SBF. Further study will be necessary on the crystal growth rate.

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