Conversion of Calcium Fluorapatite into Calcium Hydroxyapatite under Alkaline Hydrothermal Conditions

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The exchange of F^- ions in synthetic calcium fluorapatite single crystals with OH^- was investigated under alkaline hydrothermal conditions. Experiments were performed at various temperatures from 600 to 800°C at 100 MPa, for intervals between 6 and 192 h, in 5 and 10 M KOH solutions. The fluorapatite single crystals were sluggishly dissolved at temperatures over 700°C, which resulted in the ion exchange of F^- with OH^-. The rate of conversion was accelerated by increasing the reaction temperature or concentration of the alkaline solution. The ion-exchange reaction started from the prismatic ends of the fluorapatite single crystals to form acicular small crystals and holes in the original crystal along the *c*-axis. The acicular crystals had a lower content of F^- resulting from the ion exchange, and they broke away from the original crystal as the ion exchange proceeded. This phenomenon may be due to the accumulation of residual stress, which was generated by the lattice expansion along the *a*-axis caused by the ion exchange. The ion-exchange reaction proceeds by a dissolution and precipitation process. The influence of the apatite structure on the conversion mechanism developed under alkaline hydrothermal conditions is proposed. © 2000 Academic Press

Key Words: calcium fluorapatite; hydrothermal treatment; ion-exchange; dissolution precipitation.

INTRODUCTION

Mineral and biological calcium apatites incorporating OH^-, F^-, and Cl^- in their structure have been well studied, both crystallograhyically (1, 2) and experimentally (3–10). The formation of continuous solid solutions was observed in the binary system of calcium hydroxyapatite (hereafter referred to as OHAp) – calcium fluorapatite (hereafter referred to as FAp) over the entire compositional range (7). However, almost all of these synthetic solid solutions were produced by chemical reactions that did not implicate an ion-exchange mechanism.

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The first experimental evidence of an ion-exchange reaction was presented by Elliott and Young (8), who studied the conversion of calcium chlorapatite (hereafter referred as ClAp) and FAp single crystals to OHAp single crystals, at 1000–1380°C and under ambient pressure in water vapor for 2 weeks. The results showed that ClAp was more easily converted than FAp due to the instability of ClAp at elevated temperatures. X-ray precession photographs of the reaction products demonstrated that the reaction products were essentially single crystals of OHAp.

One the factor that may control the rate of the exchange of F^- ions in FAp with OH^- ions is the concentration of OH^- ions in the ion exchange medium. Hydrothermal treatments seem to provide a considerable concentration of OH^- ions, even when pure water is used as an ion-exchange medium, because the ion product of water increases at high temperatures and pressures. This fact was confirmed by Brenan (3), who determined the influence of the pressure on the diffusion coefficients of anions in the apatite structure during hydrothermal treatments. The ion exchange in solid state proceeded fast under hydorthermal conditions at high pressures, and the interface of the reaction in apatite single crystals remains smooth, bearing anion concentration gradients.

Recently, Yanagisawa *et al.* (11) have studied the ion-exchange process under alkaline hydrothermal conditions, and observed that the ion exchange in ClAp single crystals was accelerated by using alkaline solutions. The ClAp single crystals were converted into OHAp single crystals under alkaline hydrothermal conditions at temperatures as low as 300°C in 6.25 M KOH solution for 12 h. The ion-exchange reaction under these conditions is conducted by a topotaxial dissolution and precipitation process, which enhances the conversion of the ClAp to OHAp without changing the original dimension and shape of the ClAp crystals. The development of a peculiar texturization, tiny tunnels normal to the *a*-axis on the exchanged OHAp single crystals, was mainly attributed to a compensation

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of the lattice contraction as a result of the Cl–OH ion exchange.

In the present study, experiments were directed to observe the possibility of ion exchange of F^- ions in synthetic FAp single crystals with OH^- ions under alkaline hydrothermal conditions. Initial attempts were made to determine the experimental conditions (temperature, time, and concentration of the alkaline fluid) for the hydrothermal conversion reaction. The difference in the mechanism between the conversion from ClAp to OHAp and that from FAp to OHAp is discussed.

EXPERIMENTAL PROCEDURE

(1) Preparation of Fluorapatite Single Crystals

Gem-quality, single crystals of FAp were prepared by means of the flux method using KF as a flux (12). Reagent grade $CaHPO_4 \cdot 2H_2O$, $CaCO_3$, and CaF_2 with the stoichiometric composition of FAp were used as solute. The solute (15 mol%) was heated with the flux (KF) in a platinum crucible at 1200°C for 10 h, followed by cooling to 600°C at a constant rate of 5°C/h. Prismatic hexagonal single crystals, 4–12 mm long and 0.5–2 mm wide, were synthesized under these conditions. The FAp single crystals had the hexagonal space group $P6_3/m$, with unit cell dimensions of $a = 9.369 \pm 0.003$ Å and $c = 6.884 \pm 0.003$ Å. The chemical composition of FAp single crystals determined by electron microprobe analyses is shown in Table 1.

(2) Hydrothermal Treatments

Two different concentrations (5 and 10 M) of KOH solutions were employed as reaction media. For each run, approximately 20 mg of the large hexagonal prism single crystals of FAp (4–12 mm long) were placed at the bottom of a platinum capsule (30 mm length, 2.7 mm inner dia-meter). A volume of approximately 40 μl of the alkaline solution was subsequently added. The capsule was then welded shut with an electric arc.

The hydrothermal treatments were carried out using a test tube type vessel made of Stellite 25. The platinum capsule was placed at the bottom of the vessel prior to the treatments. During all experiments, an internal pressure of 100 MPa was imposed inside the vessel using distilled water as a pressure medium. The vessel was then heated to a predetermined temperature (600–800°C). After being held at each temperature for an interval between 3–192 h, the vessel was cooled to room temperature by removing the furnace from the vessel. During the treatments, temperature measurement was carried out on the outside wall of the vessel with a thermocouple at the position corresponding to the bottom of the capsule. Leakage of the capsules was checked for by weighing the capsules before and after the treatments. After the hydrothermal treatments, the capsule was cut open, and the content was washed with deionized distilled water by successive decanting. For a few experiments, the weight of the solid was measured after the treatments to estimate the weight loss caused by dissolution. The pH value of the remaining solution was checked using pH paper, and in a few cases the solutions were analyzed by inductively coupled plasma (ICP).

(3) Characterization

Powder X-ray diffraction analyses were employed to determine the crystalline phases and the lattice constants of the treated crystals. Measurements we made on a Rigaku X-ray diffractometer with graphite-monochromatized $CuK\alpha$ radiation. Moreover, morphological aspects on the crystals were examined by scanning electron microscopy (Hitachi S-530). In addition, infrared absorption spectra

TABLE 1
Summary of the Electron Micropobe Analyses

Sample ID	Temp. (°C)	Solution and concentration	Time (h)	Chemical composition (wt%)				Chemical formula[a]
				Ca	P	K	F	
FAp				39.70 ± 0.25	18.42 ± 0.15	0.05 ± 0.02	3.75 ± 0.15	$Ca_{9.99}K_{0.01}(PO_4)_6F_{1.99}$
800SC1	800	KOH, 5 M	24	39.83 ± 0.20	18.47 ± 0.15		1.51 ± 0.20	$Ca_{10}(PO_4)_6F_{0.80}(OH)_{1.20}$
800SC2	800	KOH, 10 M	24	39.85 ± 0.10	18.48 ± 0.10		0.94 ± 0.15	$Ca_{10}(PO_4)_6F_{0.50}(OH)_{1.50}$
800SC4[b]	800	KOH, 10 M	24	39.86 ± 0.15	18.48 ± 0.10		0.64 ± 0.20	$Ca_{10}(PO_4)_6F_{0.34}(OH)_{1.66}$
750SC1	750	KOH, 10 M	48	39.85 ± 0.22	18.48 ± 0.20		1.12 ± 0.18	$Ca_{10}(PO_4)_6F_{0.59}(OH)_{1.41}$
800LC3	800	KOH, 10 M	48	39.86 ± 0.20	18.48 ± 0.10		0.80 ± 0.10	$Ca_{10}(PO_4)_6F_{0.42}(OH)_{1.58}$
800SC3	800	KOH, 10 M	48	39.86 ± 0.15	18.48 ± 0.10		0.72 ± 0.15	$Ca_{10}(PO_4)_6F_{0.38}(OH)_{1.62}$

Note. LC = large crystals, SC = small crystals.
[a] Formula proportions are based on 10 cations and the amount of OH^- was determined by charge balance.
[b] The amount of FAp single crystals used for reaction was 5 mg.

were recorded with a Perkin Elmer 1600 spectrometer, over the range from 3500 to 3600 cm^{-1}, using 2 mg of a powdered sample mixed with 200 mg of KBr. Prior to the analyses, the mixture was dried overnight at 120°C, and then pelletized in a 13-mm-diameter die under vacuum.

The compositions of the treated crystals and the single crystals obtained by the treatments were determined by electron microprobe analysis (Jeol, JXA-8600NX). The standards (ASTIMEX) employed and the elements determined were as follows: synthetic fluorapatite [$Ca_5(PO_4)_3F$] for Ca, P, and F; and sanidine ($KAlSi_3O_8$) for K, respectively. The analyses were conducted at a constant filament current of 15 nA. The amount of each element (wt%) was computed by using the ZAF correction procedure. The amount of each element (wt%) was computed by using the ZAF correction procedure. The composition was determined from an average of 40 points on the polished surface of each sample. In addition, fluorine concentration profiles were obtained on the polished cross-section surface of the treated FAp crystals, mounted in resin along the c-axis, the direction in which the conversion reaction front proceeds.

RESULTS

Morphological Observations

The experiments for the conversion of FAp to OHAp under hydrothermal conditions were directed toward evaluation of the effects of the following factors: temperature, reaction interval, and the concentration of the reaction medium (KOH).

At 600°C, no morphological differences were observed in FAp single crystals, even those treated in a concentrated KOH solution (10 M), when compared with the original FAp single crystals (Fig. 1a). In contrast, as the treatment temperature was increased beyond 700°C, the morphology of the resulting crystals differed markedly from that of the raw crystals. Images of the FAp single crystals treated at 800°C in 10 M KOH solution for 96 h are shown in Figs. 1b and 1c. Under these conditions, the FAp single crystals exhibited significant damage, as represented by a preferential fracture at the prismatic ends (Fig. 1b). The deep holes were formed along the c-axis in these large crystals. A large number of small crystals (Fig. 1c) were also produced at the bottom of the capsule during the hydrothermal treatment. The small crystals were colorless and transparent, exhibiting acicular forms with prism surfaces.

X-Ray Diffraction Analyses

Effect of the temperature. Figure 2 shows typical X-ray diffraction patterns obtained from the large crystals remaining after treatments at different temperatures. It can be seen that the crystals treated at 600°C even for a long interval

(192 h) in 10 M KOH solution retained their original hexagonal FAp structure. However, the presence of a second crystalline phase is seen in the samples treated at temperatures beyond 700°C. The new peaks corresponding to this phase were satisfactorily matched to the OHAp structure. The conversion of the FAp single crystals to the OHAp structure under alkaline hydrothermal conditions was gradually accelerated with the increase in temperature. Thus, at 800°C, the residual crystals exhibit only the presence of the OHAp phase. The patterns of the small crystals obtained at 800°C (Fig. 2e) correspond to the OHAp single phase. Although the X-ray diffraction pattern of the acicular OHAp crystals was similar to that of hexagonal OHAp structure (JCPDS card 9–432), the converted acicular OHAp crystals were indexed to the monoclinic structure (space group $P2_1/b$), because Weissenberg precession photographs revealed superlattice spots which corresponded to this space group. It should be noted that the chemical compositions determined by the electron micropobe analyses showed that a small amount of F$^-$ remained in the treated crystals (Table 1), even though they were assigned to the OHAp structure.

Effect of the concentration of KOH solutions. When the FAp crystals were treated in pure water at 800°C for 96 h, the crystals retained their original FAp structure without any changes in shape. On the other hand, small acicular crystals were formed in alkaline solutions and the original crystals were damaged. Typical X-ray diffraction patterns of the converted products (small crystals) obtained at 800°C for 24 h, using 5 and 10 M KOH solutions, are shown in Fig. 3. These crystals were assigned to the OHAp structure. When the FAp crystals were treated in 10 M KOH solution, the X-ray diffraction pattern of the small crystals was slightly shifted to a lower angle, in comparison with that of the crystals obtained in 5 M KOH solution. This small difference is attributed to the amount of F$^-$ remaining in the small crystals, which is greater in the crystals produced in 5 M KOH solution (Table 1, sample 800SC1).

A semiquantitative evaluation of the fluorine content was estimated from the infrared spectra of the small crystals produced in 5 and 10 M KOH solutions (Fig. 4). In general, the small crystals exhibit a single sharp OH stretching band at approximately 3567 cm^{-1}, which is near the value (3572 cm^{-1}) reported for stoichiometric OHAp (9,13). Furthermore, an extra band was observed at approximately 3540 cm^{-1}. The presence of this band occurring at lower wavenumbers than the OH stretching band is commonly attributed to the perturbation of the OH stretching band by F$^-$ ions neighboring the OH$^-$ ions in the X-channels (9, 14). From our results (Fig. 4), a difference in the OH content is clearly depicted by the gradual increase of the intensity of the OH stretching band, as a result of the increase of the concentration of the reaction medium and temperature.
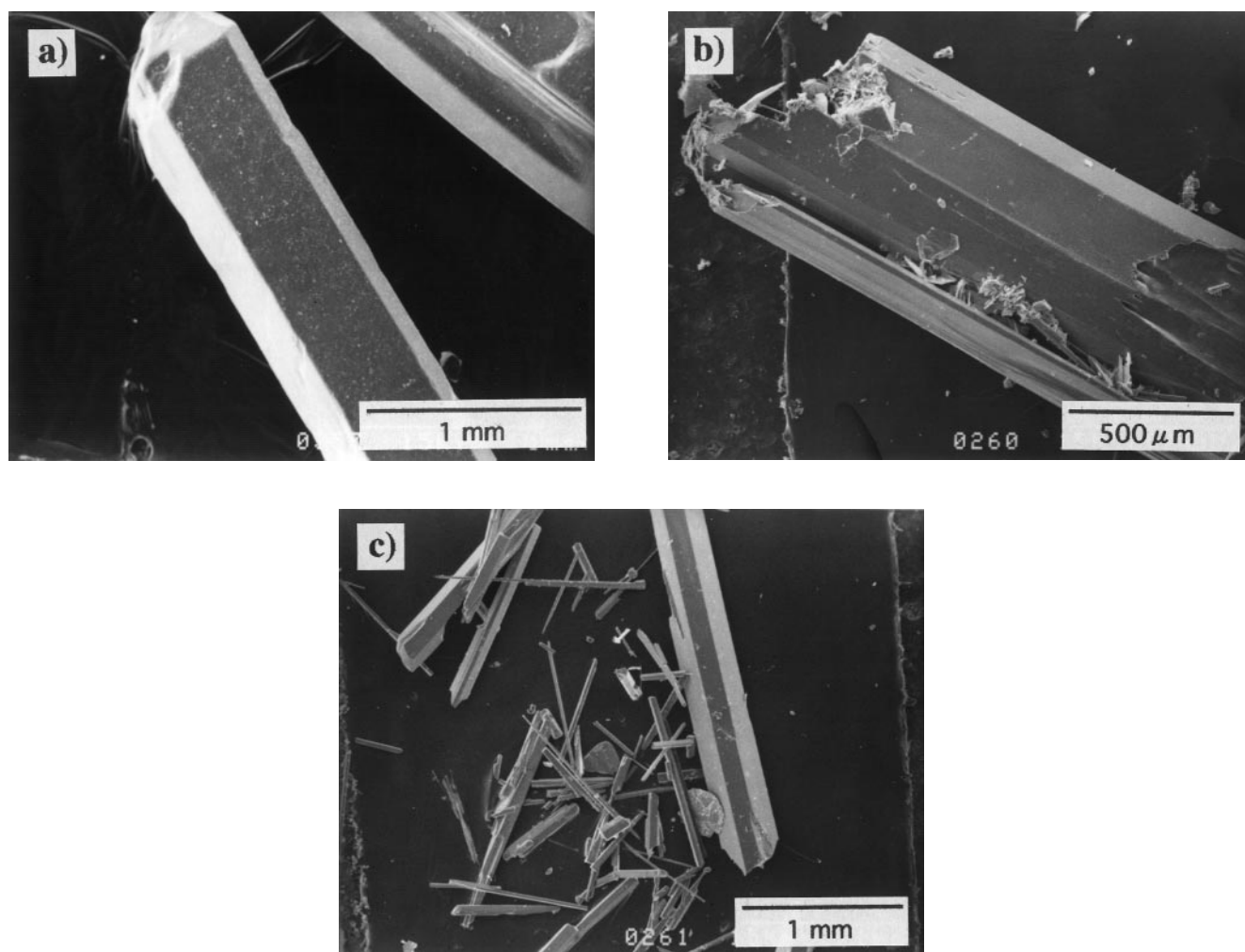
FIG. 1. SEM micrographs of (a, top) raw FAp single crystals, and (b, beside) large and (c, bottom) small crystals obtained after hydrothermal treatment in a solution of 10 M KOH at 800°C for 96 h.

The compositions of the small acicular and large crystals, determined by electron microprobe analyses, are summarized in Table 1. The small and large crystals obtained at 800°C for 48 h in 10 M KOH solution did not exhibit a significant difference in the content of the residual F^- (samples 800SC3 and 800LC3), while the small crystals produced at 750°C (sample 750SC1) exhibit a higher concentration of F^-, in comparison with that determined in the crystals obtained at 800°C. The above-mentioned results are in good agreement with the results of IR spectra (Fig. 4). On the other hand, when the weight of the starting FAp crystals was reduced to 5 mg, the content of F^- in the synthesized small crystals (sample 800SC4) was less than that obtained when 20 mg of FAp crystals was used. It is clear from the above results that if the ratio of OH^- against the amount of the FAp crystals is large, the exchange of F^- with OH^-

proceeds faster and the synthesized OHAp solid solutions incorporate less F^-. Hence, the OHAp solid solutions in this study are not stable intermediates. In addition, a release of potassium present in the original crystals is observed during the hydrothermal treatment (Table 1).

The pH value of the solution after the treatments did not exhibit significant changes and was always over 14 for all experiments. The chemical analysis of the solution after the treatment at 800°C for 48 h in 10 M KOH solution showed that the concentration of Ca was 3925 ppm in the solution, which corresponded to 3.92×10^{-7} moles of FAP. On the other hand, the weight loss determined on 20 mg of the FAp single crystals after the treatment was 0.4 mg, which corresponded to 3.97×10^{-7} moles of FAp. These results suggested that FAp crystals were almost stoichiometrically dissolved in the KOH solution.
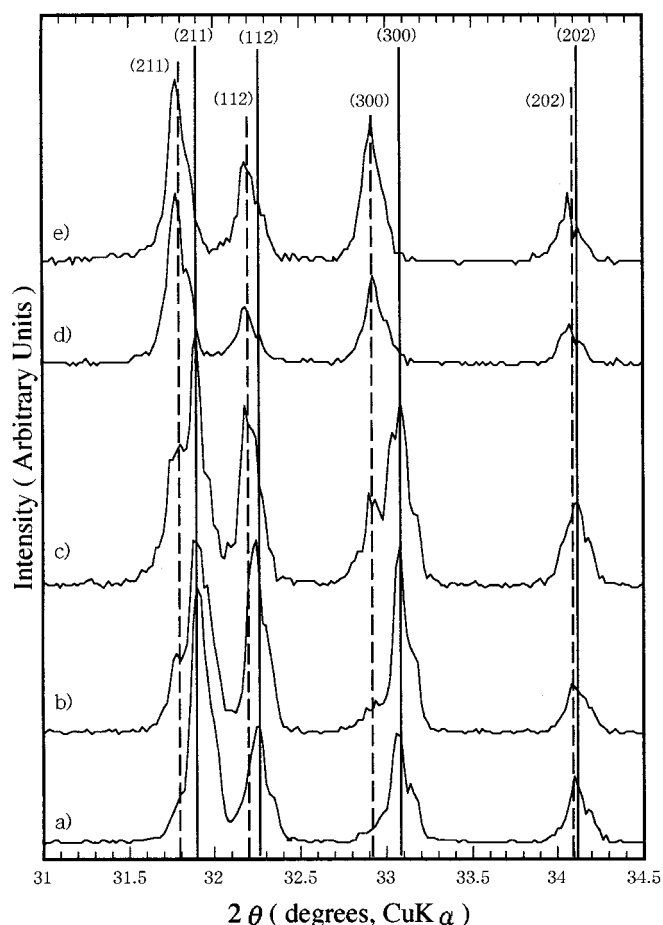
FIG. 2. X-ray diffraction patterns of residual large crystals after hydrothermal treatments in a 10 M solution of KOH at (a) 600°C for 192 h, (b) 700°C for 96 h, (c) 750°C for 48 h, and (d) 800°C for 96 h. The X-ray pattern (e) corresponds to the small crystals produced at 800°C for 96 h in 10 M KOH solution. Solid line, fluorapatite; dotted line, hydroxyapatite.

DISCUSSION

Characteristics of the Hydrothermal Conversion of FAp to OHAp

We found that the conversion of FAp to OHAp had a characteristic texture, in contrast to the results previously reported (3), in which the ion exchange of F^- with OH^- proceeded by diffusion in the solid state. This texture is more noticeable on the crystals ends as shown in Fig. 1b. Figure 5 shows the texture observed on the cross section (parallel to the c-axis) of an FAp crystal treated at 800°C for 6 h in 10 M KOH solution. At earlier stages of the reaction, holes parallel to the c-axis were markedly formed in the FAp single crystal. The depth of the holes was further increased as the conversion reaction gradually proceeded. As a result, acicular small crystals were produced at the end of the FAp single crystals. The formation of the holes during

the conversion to OHAp is due to a localized dissolution of the FAp crystals (15).

Fluorine concentration profiles were obtained by electron microprobe analyses on the cross section of the partially reacted crystal, shown in Fig. 5. The concentration profiles were determined in the direction in which the conversion reaction proceeded, parallel to the c-axis within a distance of approximately 600 μm from the acicular crystal end toward the center of the FAp single crystal (distance between the arrow in Fig. 5). The profile (Fig. 6) reveals a marked difference of the fluorine concentration between the acicular crytal and the raw crystal, suggesting that the acicular crystals were OHAp converted from the FAp single crystal. The F^- concentration profile shows a sharp boundary between two plateaus, which suggests that the conversion from FAp to OHAp proceeds by a dissolution–precipitation mechanism (16) rather than by diffusion in a solid state. Furthermore, this result is also in good agreement with the XRD patterns that indicate that the conversion to OHAp is conducted without formation of continuous solid solutions between FAp and OHAp (Fig. 2).

The replacement of small F^- ions with ionic radius of 1.32 Å (17) by larger OH^- ions with ionic radius of 1.68 Å (17) in the apatite structure must cause an expansion of the cell volume. According to JCPDS cards (FAp 15–876 and OHAp 9–432), the conversion of FAp to OHAp must yield the following changes of the lattice parameters: a_0 from
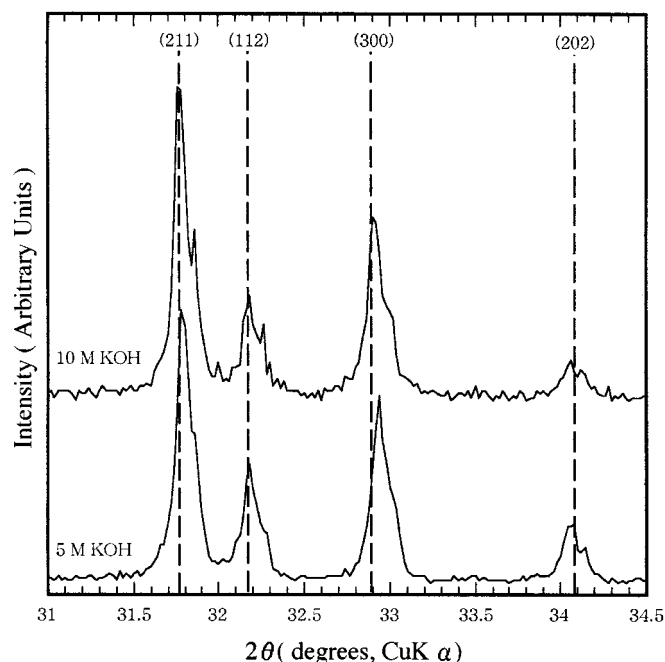

FIG. 3. X-ray diffraction patterns of the small OHAp single crystals obtained after hydrothermal treatment at 800°C for 24 h in alkaline solutions of KOH with concentrations of 5 and 10 M. Solid line, fluorapatite; dotted line, hydroxyapatite.
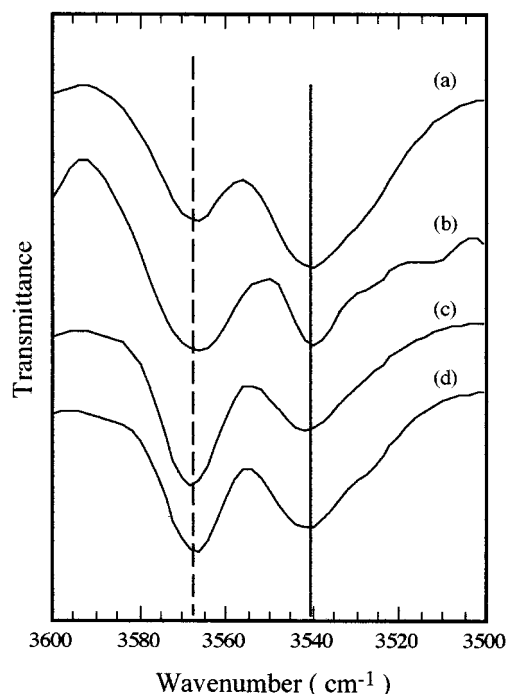
FIG. 4. Infrared spectra of the OH stretching band determined on the small OHAp single crystals, obtained by hydrothermal treatment in 5 M KOH at 800°C for 24 h (a), and in 10 M KOH at 750°C for 24 h (b), at 800°C for 12 h (c), and at 800°C for 96 h (d). Dotted line, OH stretching band; solid line, F extra band.

9.3684 to 9.418 Å and c_0 from 6.8841 to 6.884 Å. A large expansion and a slight contraction along the a-axis and c-axis, respectively, are expected to occur during the conver-
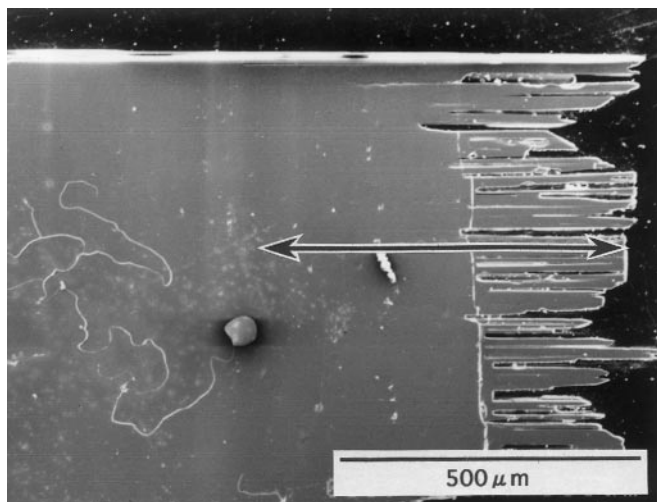

FIG. 5. Microstructural aspects of the FAp single crystals at earlier stages of reaction, which were revealed along the cross sections parallel to the c-axis. The FAp crystals were hydrothermally treated at 800°C for 6 h in a solution of 10 M KOH. Electron microprobe analyses were conducted in the distance between the arrows.
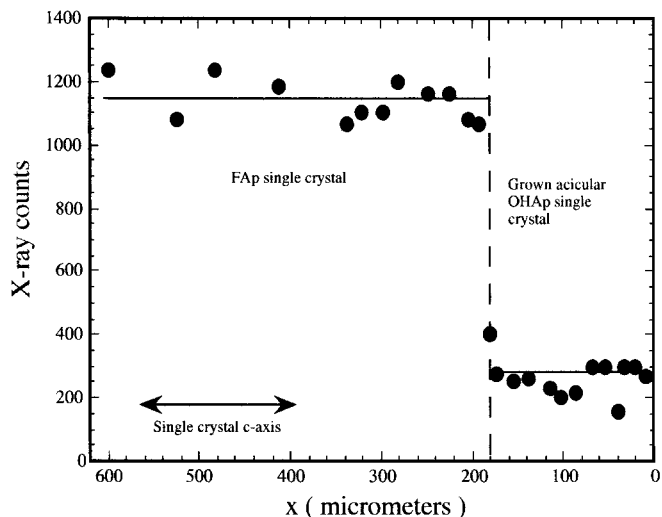

FIG. 6. Fluorine concentration vs distance profile (parallel to c), which was obtained on partial run FAp crystal product. The profile was measured from the tip of the acicular crystals up to the original FAp part. These result was obtained on crystals treated at 800°C for 6 h in a solution of 10 M KOH.

sion, which may result in the fracture of the acicular crystals. Brenan (3) has observed the formation of microcracks, as a result of the compensation of the lattice volume change caused by the F–Cl ion exchange between ClAp–FAp crystals in the solid state. We considered that the completely converted small OHAp crystals obtained after the hydrothermal treatments were produced by fracture of acicular crystals from the original FAp crystals, but not by a recrystallization process, which is observed in ordinary hydrothermal treatments, especially with a temperature gradient. In general, during hydrothermal treatments, the original crystals are dissolved into the reaction fluid, and then transported to the low-temperature zone with low solubility by convection of the hydrothermal fluid. Thus, recrystallization of new crystals normally occurs under these conditions. In our experiments, the converted OHAp crystals were formed at the bottom of the capsule, and so it is not likely that the species dissolved in the fluid were transported for long distances. The acicular crystals obtained in this study were faceted but they often had huge grooves along the c-axis (Fig. 7). These grooves are seldom produced by the ordinary dissolution precipitation mechanism. This evidence supports the hypothesis that the OHAp small crystals are formed at the end of the FAp single crystals during hydrothermal treatments.

Differences between the FAp–OHAp and ClAp–OHAp Conversions

Elliott and Young (8) previously evaluated the conversion of FAp to OHAp. The transformation to OHAp structure
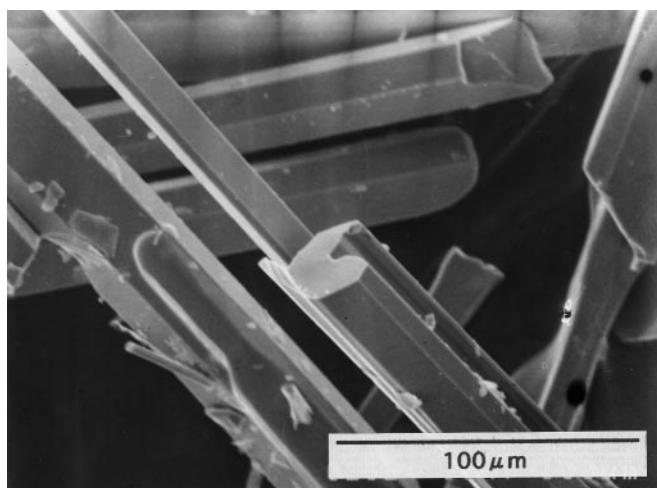
FIG. 7. Microstructural aspects of the completely converted small OHAp. The crystals were obtained under hydrothermal conditions at 800°C for 6 h in a solution of 10 M KOH.

was carried out by heating FAp single crystals at 1360°C for 2 weeks in water vapor at atmospheric pressure. Under these conditions, they found that the ion-exchange reaction did not take place in the original FAp single crystals. These results depict the high stability of the FAp structure even at elevated temperatures in water vapor. In contrast, Brenan (3) reported that the exchange of ionic species in FAp and ClAp crystals occurs by solid-state diffusion under hydrothermal conditions, providing the solution is saturated with apatite. Thus, it was found that the diffusion coefficient of anions measured along the c-axis was much larger than that along the a-axis. In the solid-state ion exchange, the motion of ions in the apatite structure is more easily within the X-channels rather than through the six-fold screw (6_3) axis. The mechanism that promotes the ionic motion in these sites is an interchange of ions with vacancies (2). In the present study, however, all the results cannot be associated with the solid-state ion-exchange mechanism.

In contrast, Yanagisawa *et al.* (11) have reported that the conversion of ClAp to OHAp proceeds under alkaline hydrothermal conditions. This reaction on ClAp crystals begins at low temperatures (300°C), and occurs along both of the a- and c-axes by a topotaxial dissolution–precipitation mechanism. This mechanism allows the converted OHAp crystals to retain their original dimensions and shapes. The ClAp crystals are dissolved as clusters, larger than ionic species, and the precipitation of the clusters takes place almost at the same site. Thus, the ion exchange of Cl^- with OH^-, and the incorporation of alkaline metal ions (K or Na from the reaction medium), are simultaneously conducted at the surface of the clusters. On the other hand, the conversion of FAp to OHAp heterogeneously proceeds along the c-axis only at temperatures over 700°C under alkaline hy-

drothermal conditions. The reaction advances only from the prismatic ends of the FAp crystals and produces deep holes in the original FAp single crystals along the c-axis, as well as the small acicular OHAp crystals. Furthermore, alkaline ions were removed from the original FAp crystals, but never incorporated into the converted OHAp crystals. These results gave clear evidence indicating that the conversion of FAp to OHAp under hydrothermal conditions proceeded by dissolution and precipitation processes of ionic species.

The differences between the conversion mechanism from ClAp to OHAp and that from FAp to OHAp are principally associated with the crystal structures of the individual apatite. This property seems to play an important role in the control of the conversion mechanism. The results obtained in this study suggest that the reactivity of FAp crystals is very low in comparison with that of ClAp. This difference in reactivity between FAp and ClAp is attributed to the size of the anions located within the Ca triangles (six-fold screw (6_3) columns), which are oriented along the X-channels of the apatite structure. In other words, a high bonding strength along the a-axis is produced by the incorporation of small ions, i.e. F^-, in the apatite structure, which must result in the decrease of the dissolution capability of FAp.

CONCLUSIONS

FAp single crystals (4–12 mm long and 0.5–2 mm wide) prepared by the flux method were converted to OHAp under alkaline hydrothermal conditions. The reaction was accelerated by increasing the treatment temperature and concentration of the alkaline solution. During the hydrothermal conversion to OHAp, the anisotropic dissolution of FAp single crystals along the c-axis begins at temperatures over 700°C, and holes as well as acicular small OHAp crystals incorporating a small amount of F^- are formed on the end of the crystals. The rupture of the acicular crystals is attributed to a compensation of residual stress produced by the structural change. The conversion of FAp to OHAp proceeds only at high temperatures by dissolution and precipitation of ionic species, though the ClAp single crystals are topotaxially transformed to OHAp single crystals even at 300°C. Small ions such as F^- achieve high bonding strength along the basal plane of the apatite structure, which results in the structure stabilization.

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