Transformation mechanism of different chemically precipitated apatitic precursors into $\beta$-tricalcium phosphate upon calcination

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Abstract

The Ca-deficient apatite (CDHA) was prepared from the precursors of (CH$_3$COO)$_2$Ca·xH$_2$O, Ca(NO$_3$)$_2$·4H$_2$O and H$_3$PO$_4$, (NH$_4$)H$_2$PO$_4$ to investigate the transformation mechanism of $\beta$-tricalcium phosphate ($\beta$-TCP). X-ray diffraction analysis shows that the development of $\beta$-TCP is not via direct reaction between Ca and P for all the different combinations between Ca and P precursors. The activation energy of $\beta$-TCP formation with (NH$_4$)H$_2$PO$_4$ as precursor was higher than that with H$_3$PO$_4$. Following the Johnson–Mehl–Avrami equation, the reaction kinetics of $\beta$-TCP phase formation is found one-dimension growth with interface-controlled and diffusion controlled growth depending on the annealing temperature. There exists a transition between 750°C and 825°C, and the transition rate from interface-controlled to diffusion-controlled growth is precursor-dependent. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ca-deficient apatite; $\beta$-tricalcium phosphate; JMA equation; Transformation kinetics

1. Introduction

Bioactive ceramic materials, such as hydroxyapatite (HA) or tricalcium phosphate (TCP), were introduced as bone substitutes. Due to the chemical similarity between HA and mineralized bone of human tissue, synthetic HA exhibits strong affinity to host hard tissues [1]. TCP has been shown to be resorbable in vivo with new bone growth replacing the implanted TCP [2]. This property is a significant advantage of TCP compared to other biomedical materials that are not resorbable. Two techniques were usually adopted for the preparation of $\beta$-TCP. One is solid-state reaction [3–5] and the other is “wet-chemical method” [6–19]. The latter method was most commonly used but usually results in the formation of a non-stoichiometric apatite whose molar ratio of Ca/P is from 1.33 to 1.65 [6,7,10–14]. Non-stoichiometric apatite with formula Ca$_{10-x}$(HPO$_4$)$_x$(PO$_4$)$_{6-x}$(OH)$_2-x$ (0 $\leq x \leq$ 1) exhibits the same crystal structure as stoichiometric HA. When Ca/P molar ratio is equal to 1.5, corresponding to $x$ = 1 in the above-mentioned formula, the Ca$_9$(HPO$_4$)(PO$_4$)$_3$(OH) is called Ca-deficient apatite (CDHA), which has an apatite crystal structure and the molar ratio of Ca/P is equal to TCP (Ca/P = 1.5). When the CDHA was calcined above 700–800°C, it will be transformed into $\beta$-TCP, as described by Eq. (1).

\[
\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_3(\text{OH}) \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O}. \tag{1}
\]

The phase transformation from CDHA to $\beta$-TCP has been investigated by using X-ray diffraction (XRD) and FT-IR spectra [7,10–13,15,20–22]. However, very few papers have been focused on the transformation kinetics from CDHA to $\beta$-TCP although several studies have paid attention to the formation mechanism of HA [23–27]. Recently, Lopatin et al. studied the crystallization kinetics of sol–gel derived HA and TCP and reported that the activation energies for amorphous to HA and HA to TCP are 189 and 492 kJ/mol, and $n$ values are 0.66 and 1.5 for both transformations, respectively [27]. However, no systematical discussion was made especially for the wet-chemical derived powder since the transformation kinetics as well as activation energy are sensitive to phase structure/composition of initially prepared materials. Therefore, different precursors will be used to study the phase evolution from CDHA to $\beta$-TCP in this work. The effect of precursors on the
formation mechanism of $\beta$-TCP with annealing temperature is also proposed to clarify the role of precursor.

2. Experimental procedure

2.1. Sample preparation

The starting materials used in this investigation were analytical grade reagents ($\text{CH}_3\text{COO})_2\text{Ca} \cdot x\text{H}_2\text{O}$ (99%, Aldrich Chemical company, Inc., USA) and $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%, Alfa Aesar, USA) as the Ca sources, and $\text{H}_3\text{PO}_4$ (99%, Riedel-deHaen, Seelze, Germany) and $(\text{NH}_4)\text{H}_2\text{PO}_4$ (98%, Aldrich Chemical Company, Inc., USA) as the P sources. Four systems were prepared to yield the stoichiometric ratio of Ca/P = 1.5 and summarized in Table 1. Both $\text{H}_3\text{PO}_4$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ solutions were dissolved in deionized water and slowly dropped into the vigorously stirred $(\text{CH}_3\text{COO})_2\text{Ca} \cdot x\text{H}_2\text{O}$ and $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ aqueous solution for 2 h at room temperature. The pH value for all of the solutions was adjusted above 9 with ammonia solution (Merck). After filtering and washing, the mixture was dried overnight at 120°C. The dried powder was placed in an $\text{Al}_2\text{O}_3$ crucible, heated at a desired temperature for various holding time, using a heating rate of 10°C/min, and then rapidly quenched in air. The quenched powder was ground for X-ray diffractometer analysis to determine the formed amount of $\beta$-TCP.

2.2. Phase analysis

X-ray diffractometer (M18XHF, Mac Science, Tokyo, Japan) was used for determining the phase structure and the degree of reaction. The scanning rate of 4° 2θ per min over a range of 2θ = 20–60° was used for phase identification. For kinetic study, the scanning rate was 0.5° 2θ per min over a range of 2θ = 28–33°. Reaction kinetic data were accumulated by integrating the $\beta$-TCP (0 2 10) peak area for each sample. The fraction of $\beta$-TCP at any time $t$, was calculated by comparing the (0 2 10) peak area (2θ = 31.02°) of the sample containing 100% $\beta$-TCP to that of the partially reached sample, i.e., fraction of fraction $f = A_t / A_{100\% \beta$-TCP}. Each datum appearing on the calcinations temperature/time curves was the average of three test results. The deviation of the data was around 5%.

For TEM analysis, the powder sample was ultrasonically dispersed in ethanol to form very dilute suspensions and then a few droplets were dropped on copper grids with carbon coated. Transmission electron microscopy (TEM, JEOL-2000FX), operating at an accelerating voltage of 200 kV, was used to observe the powder morphology. Fourier transform Infrared ray (FT-IR) spectra were performed using KBr pellets (2 mg per 300 mg KBr) on a spectrometer (Model 580, Perkin–Elmer) with a resolution of 4.00 cm\(^{-1}\). Infrared spectra were recorded in the range of 4000–400 cm\(^{-1}\) to evaluate the function group of the specimens.

3. Results and discussion

3.1. Crystalline phases

The XRD patterns for the four aqueous systems dried overnight at 120°C are shown in Fig. 1. Similar XRD patterns are obtained for these systems and can be indexed as CDHA phase according to ICDD No. 9-432. The needle-like particles can be observed by transmission electron microscopy as shown in Fig. 2, and are rather similar to that of stoichiometric HA or non-stoichiometric apatite synthesized by wet-chemical processing [28–40]. An axial zone in some needle-like particles can be clearly observed as marked with the arrows in Fig. 2. Suvorova et al. reported that the needle-like HA easily forms aggregated crystal when higher concentration and fast mixing were applied to the solutions [35]. Mao et al. suggested that the HA crystals tend to grow along [0 0 0 1] direction, the fastest growth direction, resulting in needle-like morphology [36].

![Fig. 1. XRD patterns of as-prepared samples for four aqueous systems.](image-url)
Fig. 3 illustrates the FT-IR absorption spectra of the as-prepared samples. The bands at 1092 and 1040 cm\(^{-1}\) are assigned to the components of the triply degenerate \(\nu_3\) antisymmetric P–O stretching mode. The 962 cm\(^{-1}\) band is assigned to \(\nu_1\), the non-degenerate P–O symmetric stretching mode. The bands at 601 and 571 cm\(^{-1}\) are assigned to components of the triply degenerate \(\nu_4\) O–P–O bending mode and the bands in the range of 462–474 cm\(^{-1}\) are assigned to the components of the doubly degenerate \(\nu_2\) O–P–O bending mode. Molecular and adsorbed water bands are also discerned at 1640 and 3400 cm\(^{-1}\). A significant concentration of hydroxyl groups remains in the structure as observed from the intensity of the stretching and librational bands at 3572 and 632 cm\(^{-1}\) [41–45]. In addition, the band at 1380–1403 cm\(^{-1}\) assigned to NH\(^+\) was only observed in systems B and D [46]. This phenomenon is possibly related to the fact that different P precursors, H\(_3\)PO\(_4\) and (NH\(_4\))H\(_2\)PO\(_4\), were used in our study. A very weak band near 875 cm\(^{-1}\) is possible the P–O(H) stretching in HPO\(_4^{2-}\) groups or \(\nu_2\) vibration mode of CO\(_2^{3-}\) groups. However, no \(\nu_3\) vibration mode (near 1490 and 1426 cm\(^{-1}\)) of CO\(_2^{3-}\) groups was observed in the FT-IR spectra. Therefore, it was believed that the weak peak at 875 cm\(^{-1}\) was primarily characteristic of the HPO\(_4^{2-}\) although CO\(_2\) has a very affinity to apatite crystal during the synthesis process.

The phase transformation from CDHA to \(\beta\)-TCP was performed by heating the samples at the temperature range of 500–1000°C with a heating rate of 10°C/min. After the required temperature was reached, it was immediately cooled to room temperature without maintaining any time in this indicated temperature. Fig. 4 shows that the phase transformation in system A occurs within the temperature region of 800–900°C. In order to close inspect the transformation, similar experiments were performed for system A at 10°C intervals between 800°C and 900°C (without any holding). Fig. 5 reveals that within this temperature range, a two-phase mixture of CDHA and \(\beta\)-TCP, according to ICDD No. 9-169, was obtained. A small mount \(\beta\)-TCP occurred at 810°C and CDHA.
disappeared above 900°C. Similar phase transformation of CDHA to $\beta$-TCP was observed in the other three aqueous systems. It seems to imply that the final product was not affected by the starting Ca and P precursors upon acid-base reaction. Similar phenomenon is also reported in other wet chemical methods [7,10–13]. However, it was noted that the pH value of the solution during the synthesis has a decisive effect on the dissociation of the $\text{H}_3\text{PO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ reagent, the characteristic of precipitates and further phase reaction [11]. That is because in both $\text{H}_3\text{PO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ solutions, the $\text{PO}_4^{3-}$ ions start to dominate only above a critical pH value. At a lower pH value, a large number of protonated phosphate ions, i.e., $\text{H}_2\text{PO}_4^{+}$ and $\text{HPO}_4^{2-}$, are present in the solution. On the other hand, the increase in solution pH promotes the dissociation of $\text{H}_3\text{PO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ and enhances the formation of $\text{PO}_4^{3-}$.

3.2. Reaction kinetic

XRD traces from the four aqueous systems heated at 700–825°C for different periods were taken to investigate the reaction kinetics. Fig. 6 shows the phase evolution of system A isothermally annealed at 700°C. It was observed that the minute $\beta$-TCP starts to appear in 1 h and completely forms at 30 h. The formation fraction of $\beta$-TCP in the system A fired at 700–825°C as a function of time was shown in Fig. 7. All of the transformation curves are sigmoidal in shape, indicating that the formation of $\beta$-TCP proceeds with nucleation and growth processes. The crystallization rate, as characterized by the slopes in the rapidly rising portion, increases with the increase of annealing temperature. A solid-state reaction model derived by Johnson–Mehl–Avrami (JMA) equation was used to investigate the reaction kinetics of $\beta$-TCP formation [47–49].

$$f = 1 - \exp(-kt^n),$$

(3) where $f$ is the formed fraction of $\beta$-TCP at time $t$, $k$ rate constant, and $n$ the Avrami exponent. The possible $n$
values, depending on the mechanism of phase transformation, are listed in Table 2 [50]. Both values of \( n \) and \( k \) can be calculated by rearranging Eq. (3) as follows:

\[
\ln[n/(1-f)] = \ln k + n \ln t.
\]

(4)

The data shown in Fig. 7 can be replotted as \( \ln[n/(1-f)] \) vs. \( \ln t \) and given in Fig. 8. Using the linear least-squares fit method, both values of \( n \) and \( \ln k \) can be calculated from the slopes and the intercepts of these lines. Following the Arrhenius relationship (\( \ln k \) vs. \( 1/T \)), the activation energy of \( \beta \)-TCP formation from 700°C to 750°C can be calculated as \( \sim 261.4, 336.2, 264.9 \) and 352.7 kJ/mol for systems A, B, C and D, respectively. When \( \text{NH}_4^+ \) ions were adsorbed on the surface of the powders, it leads to the reduction of the phase transformation reaction. Therefore, a higher energy was required for the transformation of CDHA into \( \beta \)-TCP in both systems B and D than both systems A and C due to the absorption of \( \text{NH}_4^+ \) on the powder surface. If they adsorbed only to powder surface, two situations might happen: physical and chemical adsorption. However, from the previous study, it should be a sort of chemical adsorption. If it does, then they are strongly bonded to the lattice defect and make a further transformation of lattice structure more difficult, so does the energy term [51]. As shown in Fig. 9, the \( n \) values of the four systems vary with annealing temperatures. It seems to indicate that there exist different transformation mechanisms from CDHA to \( \beta \)-TCP between low temperature (700°C) and high temperature (825°C). Since the particle of \( \beta \)-TCP phase presents lath-shaped morphology, shown in Fig. 10, it might suggest that the reaction belongs to one-dimension growth. When all of the systems were annealed between 700°C and 750°C, a nearly constant \( n \) value of 0.95 was obtained, which reflects that the reaction is probably an interface-controlled growth.

When the samples were heated above 750°C, it was found that the \( n \) values decrease with increasing temperature. Furthermore, systems A and C exhibit similar behavior but show different trend as comparing with that of systems B and D. In other words, during the

![Fig. 8. Avrami's analysis according to Eq. (4) to determine \( n \) and \( k \) of system A at different temperatures.](image)

![Fig. 9. The \( n \) values dependence of isothermal annealing temperatures for the four systems.](image)

![Fig. 10. TEM bright field (BF) image of system A annealed at 700°C for 2 h.](image)
transition stage between 750°C and 825°C, the decrease of n value with increasing temperature is faster in the latter (systems B and D) than the former (systems A and C). Lopatin et al. studied both transformations of amorphous to HA and HA to TCP and reported that the n values are 0.66 and 1.5 for the former and the latter, respectively [27]. It was reported that the difference in n values are dependent on the composition change between the two phases from [Ca/P]_{HA} = 1.667 to [Ca/P]_{TCP} = 1.5. However, in our case, the Ca/P ratio in all the studied systems is constant (1.5).

Therefore, it is believed that the different behavior between these two types is found strongly dependent on the starting phosphate precursors. In systems A and C, H3PO4 was used as the P precursor. On the other hand, systems B and D employed the (NH4)H2PO4 as the P precursor. As the annealing temperature exceeds 825°C, the n values become close to 0.5, indicating that the reaction (n = 0.5) is dominated by diffusion-controlled growth.

4. Conclusions

(1) The phase evolution from CDHA to β-TCP occurs independent of Ca and P precursors.

(2) The activation energy of β-TCP phase formation with (NH4)H2PO4 as the precursor was higher than that with H3PO4.

(3) The reaction kinetics of β-TCP phase formation is found one-dimension growth with interface-controlled at temperature below 750°C but becomes diffusion-controlled at the annealing temperature more than 825°C.

(4) There exists a transition from interface-controlled to diffusion-controlled growth and transition rate is precursor-dependent.

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References


