

Mechanochemical synthesis of hydroxyapatite from $\text{Ca(OH)}_2\text{-P}_2\text{O}_5$ and $\text{CaO-Ca(OH)}_2\text{-P}_2\text{O}_5$ mixtures

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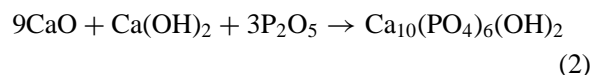
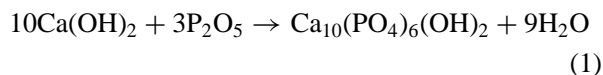
Dry grinding of $\text{Ca(OH)}_2\text{-P}_2\text{O}_5$ and $\text{CaO-Ca(OH)}_2\text{-P}_2\text{O}_5$ mixtures was conducted by a planetary ball mill to investigate the mechanochemical solid-phase reaction for the synthesis of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp). HAp was synthesized by grinding of the two sets of mixtures. The formation of HAp from the $\text{Ca(OH)}_2\text{-P}_2\text{O}_5$ mixture was more advantageous than that from the $\text{CaO-Ca(OH)}_2\text{-P}_2\text{O}_5$ one. This synthesis reaction from the former mixture was almost completed within 30 min of grinding. The presence and amount of H_2O contained in the starting mixtures played a key role to promote the formation of HAp. Especially, in the former mixture, the prolonged grinding assisted the solid-phase reaction of the intermediate DCPD and Ca(OH)_2 to produce HAp more effectively. © 2000 Kluwer Academic Publishers

1. Introduction

Because of compositional and biological similarity to native tissue, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) is one of the most attractive materials for vertebrate and dental implants [1, 2]. Associated with the biological importance, HAp has been widely studied and a number of reviews have described its chemistry [3–5]. Conventionally, HAp is prepared in bulk by normal ceramic processing methods [6, 7]. There have also been investigations on dissolution and precipitation of HAp and its precursor phases [8, 9], sol-gel [10] and acid-base reaction [11, 12] from Ca^{2+} and PO_4^{3-} bearing solutions. Most of the processing methods need the precise controls for the preparation of HAp. Thus, the compositions and properties of final products are strongly influenced by the various parameters such as nature of the starting materials used, pH of the solutions, reaction times and temperatures, etc.

In the present work, the mechanochemical synthesis of HAp from its constituent powder mixtures is attempted. For the synthesis of HAp, two sets of powder mixtures containing two or three solid reactants, namely, $\text{Ca(OH)}_2\text{-P}_2\text{O}_5$ and $\text{CaO-Ca(OH)}_2\text{-P}_2\text{O}_5$ mixtures are prepared. The synthesis reactions for HAp from the both mixtures would be mainly achieved by solid-state acid-base reaction between the solids activated either at the surface or in the bulk by intensive dry grinding. Although this process of mechanical activation has been convinced in some cases as a simple and promising tool to prepare ceramic powders [13], there have been virtually no investigations reported concerning the mechanochemical solid-phase reaction for HAp at room temperature. The explanation for the formation

mechanism of HAp is also attempted. The reactions for the formation of HAp from the both mixtures may be represented as follows.



The appreciable difference in these reactions is the presence of free H_2O released when the mixtures are transformed into HAp completely. If the reaction superiority between the two mixtures exists during grinding, it implies, in other words, that the amount of H_2O content of the starting mixtures might be one of the main factors to control these synthesis reactions. The present work, therefore, describes the synthesis and reaction mechanism for HAp according to the amount of H_2O content of the mixtures during dry grinding.

2. Experimental

The solid reactants selected for use in this experiment were calcium hydroxide (Ca(OH)_2 , Wako Chemicals, Japan), calcium oxide (CaO) and phosphorus oxide (P_2O_5 , Wako Chemicals, Japan). The CaO was prepared by heating Ca(OH)_2 in air at 850°C for 2 hr. The mean particle sizes of the Ca(OH)_2 and CaO used were 4.8 and 3.9 μm , respectively. Each of the starting materials was kept in a sealed box to avoid moisture contamination before experiment. With keeping away from absorbing excess moisture in air, the starting

materials were weighed to coincide the stoichiometric HAp (Ca/P ratio: 1.67). These mixtures were mixed separately using an agate mortar with a pestle prior to grinding. The mixture prepared prior to grinding was called unground mixture in this experiment. A planetary ball mill (Fritsch Pulverisette-7, Germany) with a pair of zirconia pots of 50 cm³ inner volume containing seven zirconia balls of 15 mm diameter was used for the grinding the mixtures. The mixture (3.5 g) was put in the mill pot and ground at 790 rpm in rotational speed of the mill. The duration of grinding was varied from 5 to 120 min. The grinding was suspended for 10 min after every 10 min grinding to avoid excess temperature increase inside the mill pots.

X-ray diffraction (XRD) analysis was employed using Cu-K α radiation with a pyrolytic graphite monochromator (RAD-B System, Rigaku) to investigate the phases and crystallinity of the ground mixtures. Infrared absorption spectra of the ground mixtures were measured by Fourier-transform infrared spectroscopy (FT-IR) using a conventional KBr wafer technique (FTS-40A, BIO-RAD). The ground mixtures were also subjected to thermogravimetric (TG) and differential thermal analysis (DTA) simultaneously in air at a heating rate of 10°C/min (TAS-200, Rigaku).

3. Results and discussion

3.1. Synthesis

Fig. 1 shows the XRD patterns of Ca(OH)₂-P₂O₅ mixture ground for different times. After 15 min of grind-

ing, the peaks of Ca(OH)₂ degrade significantly and most of the starting materials convert to amorphous phases. Simultaneously, the very weak peaks of HAp are formed in the ground mixture, suggesting that mechanochemical solid-phase reaction proceeds when the interface of the solids surface is closely contacted and sheared by grinding. When the grinding progresses to 30 min, the synthesis reaction is markedly enhanced. Though a marginal increment of the peaks intensity of HAp is observed in the XRD profiles, the synthesis reaction almost seems to complete within 30 min of grinding.

Fig. 2 shows the XRD patterns of CaO-Ca(OH)₂-P₂O₅ mixture ground for different times. With comparison to the result in Fig. 1, the time required for the formation of HAp is noticeably retarded. The peaks intensity of HAp formed is gradually increased as grinding progresses, however, the synthesis reaction for HAp from the mixture seems to be less advantageous than that from the former one. There have been related investigations by the authors who have postulated that the rate of mechanochemical solid-phase reactions among powder reactants went through a maximum in their dependence on H₂O content [14, 15]. As the same reason that the active role of presence of free H₂O of the starting mixtures, the synthesis reaction from the former mixture with much hydrated reactants is considered to be more favorable for the preparation of HAp. Especially, most of P₂O₅ readily reacts to neighboring H₂O and converts to phosphoric acid (H₃PO₄). Simultaneously, dicalcium phosphate (CaHPO₄, DCPD) is formed as an intermediate phase by the typical

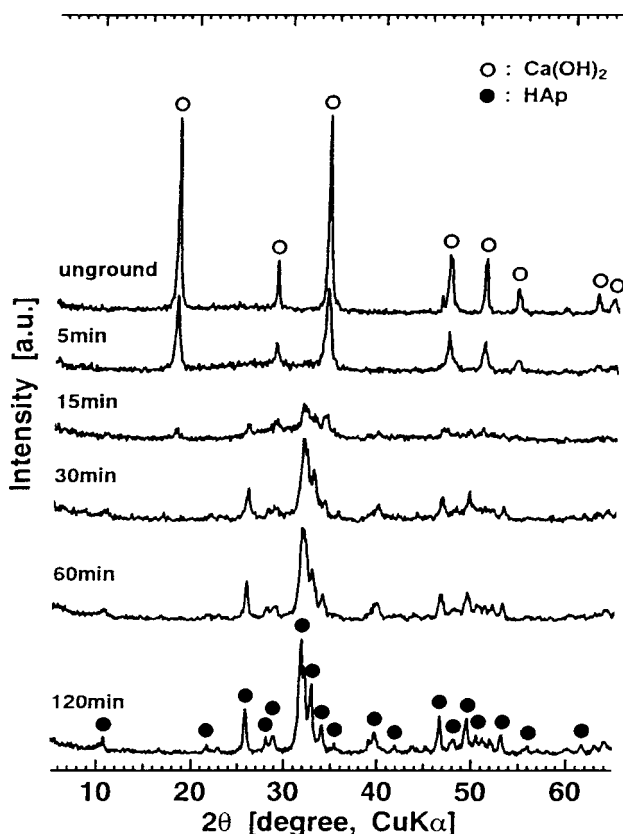


Figure 1 XRD patterns of Ca(OH)₂-P₂O₅ mixture ground for different times.

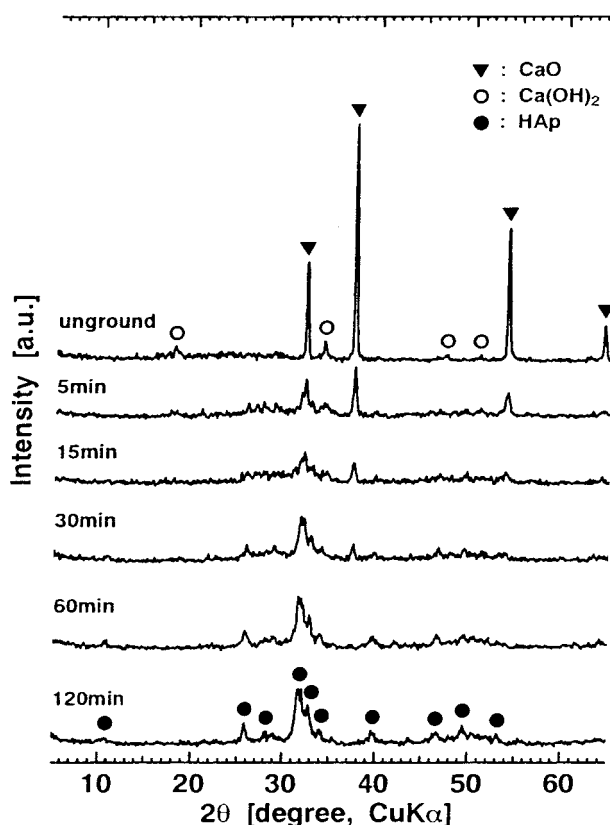


Figure 2 XRD patterns of CaO-Ca(OH)₂-P₂O₅ mixture ground for different times.

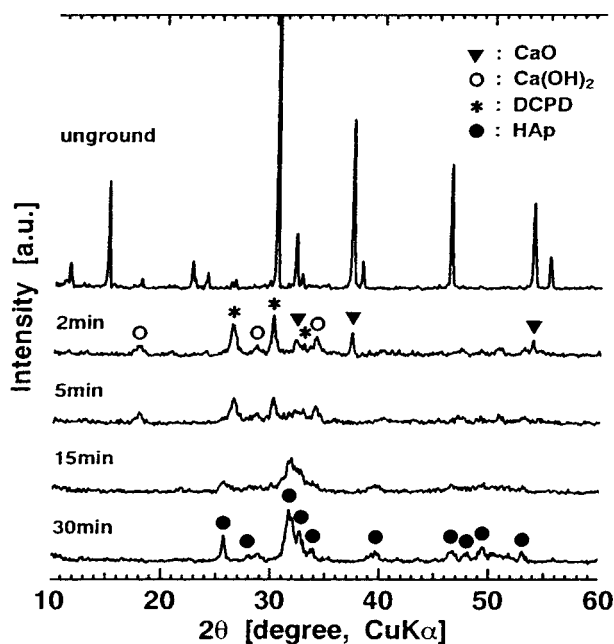
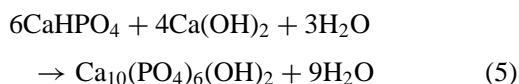
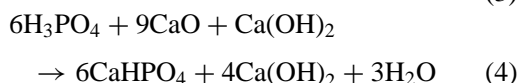
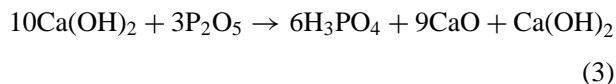


Figure 3 XRD patterns of $\text{Ca}(\text{H}_2\text{PO}_4)_2\text{H}_2\text{O}$ -CaO mixture ground for different times.

acid-base reaction as given by Equations 3 and 4. Thus the overall reactions occurred during grinding within 30 min can be expressed as follows.



However, unfortunately, no further distinct information about the progress of these reactions for HAp can be obtained from the present results. Actually, the complete reaction between DCPD and $\text{Ca}(\text{OH})_2$ to produce HAp could be accomplished by prolonged grinding. The mechanochemical solid-phase reaction of DCPD and $\text{Ca}(\text{OH})_2$ might be potentially explained by the result as shown in Fig. 3. The result obtained from the grinding of calcium dihydrogenphosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2\text{H}_2\text{O}$) and CaO mixture shows the formation of two intermediate phases, DCPD and $\text{Ca}(\text{OH})_2$, within 2 min. In this early stage of grinding, the interfacial reaction for neutralization between the starting reactants takes place to produce more stable compounds. It is noted that these intermediate phases tend to diminish as the grinding progresses, suggesting that the reaction between DCPD and $\text{Ca}(\text{OH})_2$ is progressed by the strong grinding energy.

3.2. pH measurement

Fig. 4 illustrates the pH change of the powder suspensions of $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (A) and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (B) mixture as a function of time after grinding. The 0.5 g of ground mixture was removed from the mill pot

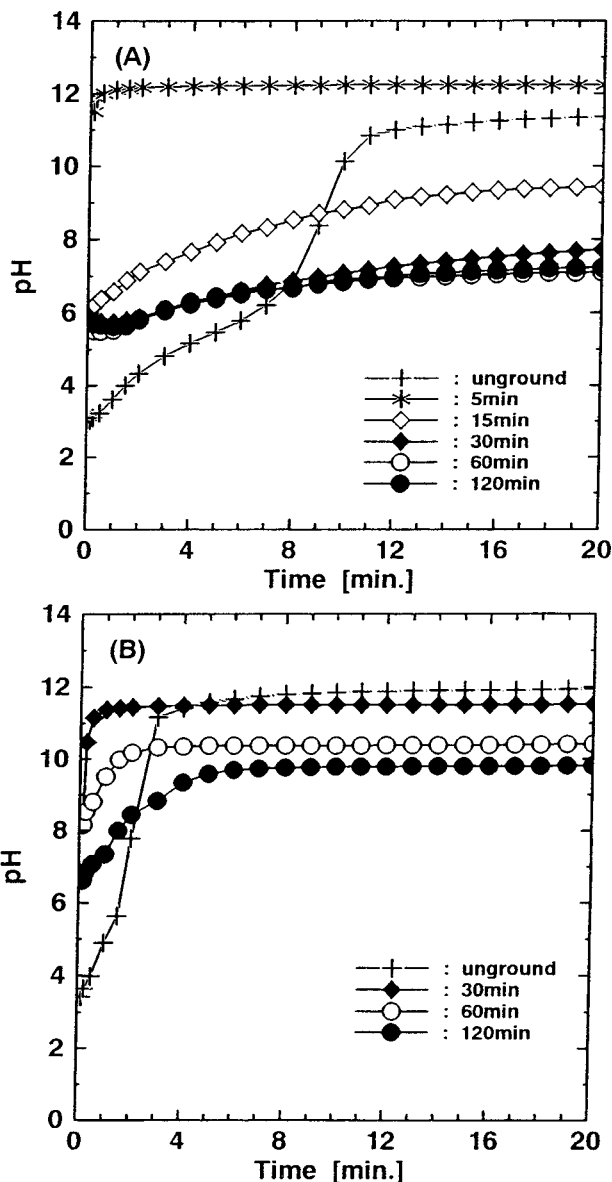


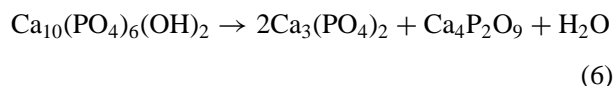
Figure 4 pH of the powder suspensions of $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (A) and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (B) mixture as a function of time after grinding.

and placed in 150 ml of distilled water with magnetic stirrer. The variation of pH of suspensions was then determined continuously. In Fig. 4A, the pH of unground mixture varies at wide range over the measuring time. The acidity of initial pH seems to the dissolution of H_3PO_4 formed in air before grinding. With an increment of the measuring time, the pH shifts rapidly to alkaline region and keeps constant at around 11 due to the dissolution of $\text{Ca}(\text{OH})_2$. In the ground mixtures, however, the pH change becomes small and the equilibrium pH tends to decrease as the grinding progresses. Consequently, the pH of 30 min-ground mixture is measured as neutral value and no noticeable change is observed in the mixtures for further grinding. This confirms the reaction between the two reactants is almost completed within 30min of grinding. Although similar trends can be seen in the $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ mixtures (Fig. 4B), the values of equilibrium pH of the ground mixtures are still high. This means that the amorphous phases of the starting materials are still remained in the ground mixtures, though not detected in the XRD profiles.

3.3. FT-IR and TG-DTA

Fig. 5 shows the FT-IR spectra of the $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (A) and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (B) mixture after grinding. The resolution bands at 1127, 1087, 999 and 656 cm^{-1} detected in the spectrum of the mixtures are attributed to the PO_4 assignments of HAp formed. The bands at 1127 and 1087 cm^{-1} are assigned to the asymmetric P-O vibrating and the band at 999 cm^{-1} is to the symmetric P-O vibrating mode [16]. The band detected at 656 cm^{-1} seems to be the O-P-O and -OH vibrating of HAp. With an increment of grinding time, these typical resolution bands of HAp are observed more clearly and the development is enhanced in the former mixture as expected previously at the same grinding time.

Fig. 6 shows TG-DTA curves of the 60min-ground mixtures. In the $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ mixture (A), a distinct endothermic peaks with corresponding weight loss at the vicinity of the dehydration temperature of H_2O (a) released from the synthesis reaction for HAp is noticeable. It is worth mentioning that no peaks of appreciable thermal reactions of the starting reactants are detected at the temperatures examined. The small exothermic peak detected at around 890°C (b) may be the beginning of the decomposition of HAp into $\beta\text{-TCP}$ by the following reaction [17].



Separately, in the $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ mixture (B), an exothermic peak is observed at around 270°C (c) in the DTA curve. This may be attributed to the crystallization

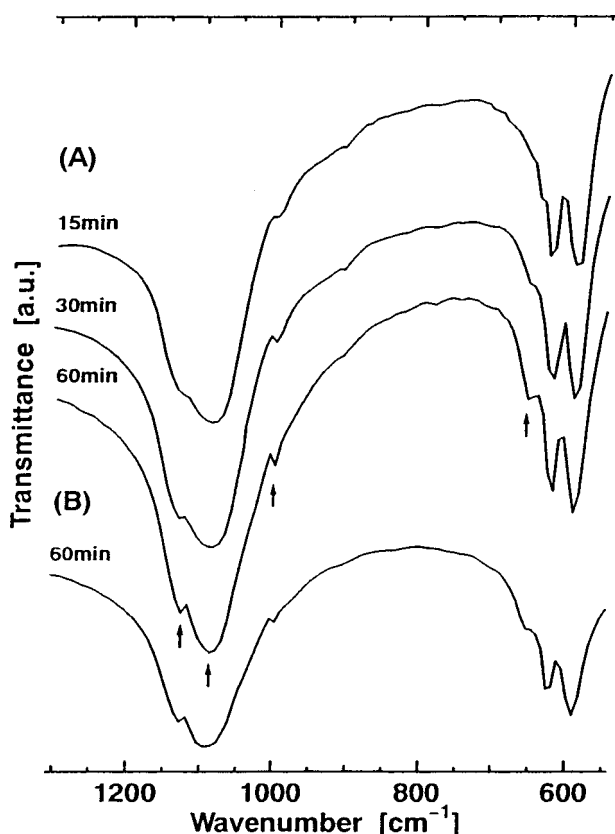


Figure 5 FT-IR spectra of $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (A) and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (B) mixture after grinding.

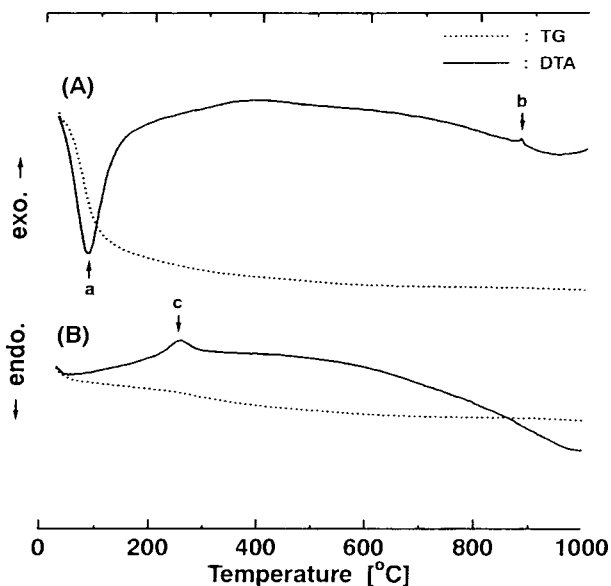


Figure 6 TG-DTA curves of $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (A) and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ (B) mixture after grinding for 60 min.

of HAp from the amorphous compounds or unreacted species of the starting materials. This indication implies that the mechanochemical solid-phase reaction is less ineffective in the case of the $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ mixture, too.

4. Concluding remarks

Mechanochemical synthesis of HAp from $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ powder mixture with a Ca/P molar ratio of 1.67 was conducted by dry grinding using a planetary ball mill at room temperature. The experimental results obtained from the present work are summarized as follows.

(1) HAp could be synthesized by grinding of the two sets of mixtures. The formation of HAp from the $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ mixture was more advantageous than that from the $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ one. The synthesis reaction of the former mixture was almost completed within 30 min of grinding.

(2) The presence and amount of H_2O contained in the starting mixtures played a key role to promote the synthesis reaction. Especially, in $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ mixture, the grinding assisted the solid-phase reaction of intermediate DCPD and $\text{Ca}(\text{OH})_2$ to produce HAp more effectively.

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