Synthesis of hydroxyapatite via mechanochemical treatment

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Abstract

Hydroxyapatite powder was synthesized with calcium pyrophosphate (Ca₂P₂O₇) and calcium carbonate (CaCO₃) through solid-state reaction. The two powders were mixed in acetone and water, respectively, and the single phase of hydroxyapatite was observed to occur only in the powder milled in water, without the additional supply of water vapor during heat-treatment at 1100°C for 1 h.

The results were explained in terms of the mechanochemical reaction that could supply enough amount of hydroxyl group to the starting powders to form a single phase of hydroxyapatite. Practical implication of the results is that the powder of high crystalline hydroxyapatite can be obtained by the simple milling in water and subsequent heat-treatment. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxyapatite; Calcium pyrophosphate; Calcium carbonate; Mechanochemical reaction; Solid-state reaction

1. Introduction

Synthetic hydroxyapatite is a representative material for a bone substitute because of its chemical similarities with the inorganic phase of bone [1–3]. As a consequence, many investigations have been already carried out to prepare hydroxyapatites [4–20] and most of them can be classified into two groups according to the processing method; one is wet [4–13] and the other is dry process [17–20]. The advantages of the wet process are that the by-product is almost water [9,10] and the probability of contamination during processing is very low. However, the disadvantages are the composition of the resulting product is greatly affected by even a slight difference in the reaction conditions and the time needed for obtaining the hydroxyapatite of a stoichiometric composition takes around 20 days, which is inconceivable in an industrial scale production. Thus, the handling of the materials and the operation of the apparatus become complicated so they cause poor reproducibility and high processing cost. Therefore, when producing high crystalline hydroxyapatite in mass, the dry process is more suitable than the wet process because it shows high reproducibility and low processing cost in spite of the risk of contamination during milling.

The calcium and phosphorous compounds used as the starting materials in the dry process are dicalcium phosphate anhydrous (CaHPO₄) [19], dicalcium phosphate dihydrate (CaHPO₄·2H₂O) [19], monocalcium phosphate monohydrate (Ca(H₂PO₄)₂·H₂O) [20], calcium pyrophosphate (Ca₃P₂O₇) [17], calcium carbonate (CaCO₃) [19,20], calcium oxide (CaO) [19,20], and calcium hydroxide (Ca(OH)₂) [19], etc. From the above materials, Fowler [17] has reported the process that adopted the combination of calcium pyrophosphate and calcium carbonate as the starting materials; the two powders were mixed in acetone, calcined in vacuum, and then finally heat-treated with the supply of water vapor as the source of hydroxyl group for the formation of hydroxyapatite. However, the procedure and the apparatus for this process are complicated, so it is not suitable for the mass production of hydroxyapatite powders.

In the present investigation, a simple process to prepare pure hydroxyapatite powder via mechanochemical treatment and subsequent heat-treatment is suggested. The two powders, calcium pyrophosphate and calcium carbonate, were re-used as starting materials [17] and they were mixed in acetone and water, respectively. As a result, only in the powder milled in water, the single phase of hydroxyapatite could be obtained after heat-treatment at 1100°C for 1 h. The results were explained in terms of the mechanochemical
reaction that could supply enough amount of hydroxyl group to the starting powders to form a single phase of hydroxyapatite.

2. Materials and methods

Calcium pyrophosphate was prepared by the heat-treatment of dicalcium phosphate dihydrate (Showa Chem. Co., Ltd., Japan) at 1000°C for 3 h and then sieved with a 60-mesh (250 μm) sieve before use. Calcium carbonate (Wako Pure Chem. Ind., Ltd., Japan) was used as received. The ratio of calcium pyrophosphate to calcium carbonate was 3:4 (mole ratio), i.e. the stoichiometric Ca/P content in the composition of hydroxyapatite (Ca/P = 1.67). The amounts of the powder and water or acetone used in each preparation were 23.2530 and 155 g, respectively. The acetone (for chromatography, Merck, Darmstadt, Germany) used in the experiment contained 0.1% water. Hereafter, the powders mixed in acetone and water will be referred to as A- and W-specimens, respectively.

Millings were carried out for 2, 4, 6, and 8 h with the rotating speed of ~170 rpm in a high-density polyethylene bottle (500 ml) using the balls of zirconia (60 vol% of bottle). After milling, the slurry was dried completely in a convection oven at 150°C for 24 h and then heat-treated at 1100°C for 1 h.

The crystalline phases of the samples before and after the heat-treatment were examined by X-ray diffractometer (DMAX IIIB, Rigaku Co., Tokyo, Japan). The surface areas of the initial and milled powders for each time periods were determined from nitrogen adsorption isotherms (ASAP2400, Micro-Metrics Co., Atlanta, USA). Before carrying out the measurements, each sample was degassed under a reduced pressure of 10⁻¹ Torr at 200°C for 2 h. The content of adsorbed water after milling were measured using Fourier transformed infrared (FT-IR) transmission spectroscopy (Spectrum 2000, Perkin Elmer Co., Norwalk, USA) with the resolution of 2 cm⁻¹. For IR spectroscopy measurements, the pulverized specimens were diluted 100 fold with KBr powder and the background noise was corrected with pure KBr data. The microstructures of the A- and W-specimens milled for 2 and 8 h were examined by field emission scanning electron microscopy (XL30S, Philips Electron Optics b.v., Eindhoven, Netherlands).

3. Results and discussions

Fig. 1 shows the results of XRD measurements on the A- and W-specimens after milling at each time periods. No noticeable changes, except the peak broadening of the initial two powders, were observed with increasing milling time. It implies that the powders became smaller during the milling without the formation of a new phase. In fact, the surface area of the W-specimen milled for 8 h increased about 980% (11.2542 m²/g) compared to the initial calcium carbonate powder (1.0391 m²/g), while that of the A-specimen milled for the same time increased only about 260% (3.7674 m²/g) as shown in Fig. 2.
The microstructures of the A- and W-specimens milled for 2 and 8 h showed remarkable differences in their sizes and shapes (Figs. 3 and 4). The reduction of the particle size occurred for both the specimens but the degree of occurrence was greater in the W-specimen as noted earlier in Fig. 2. The particle shapes of the A- and W-specimens after milling for 2 h were very similar (Figs. 3 and 4 (a)), but that of the W-specimen became non-uniform (Fig. 4 (b)), while that of the A-specimen became uniform and spherical (Fig. 3 (b)) after milling for 8 h.

Fig. 5 shows the reduced content of the adsorbed water of the initial two powders, A-, and W-specimens after milling at each time periods. The height of the band of the adsorbed water that appeared at around 3425 cm$^{-1}$ was measured using FT-IR and each height was reduced by the height of initial calcium pyrophosphate, which was the smallest. The amount of the adsorbed water of the W-specimen milled for 8 h increased about 70 times, while that of the A-specimen milled for the same time increased only about 20 times. It means that the amount of the adsorbed water is critically dependent on the media of milling. In the A-specimens, the slight increase of the adsorption with milling time is conjectured to originate from the reaction with little amount of water that existed in the acetone (0.1%).

Fig. 6 shows the results of XRD measurements on the A- and W-specimens after heat-treatment at 1100°C for 1 h without the supply of water vapor. In addition to the phase of hydroxyapatite (denoted by ‘H’ in the figure), the phase of $\beta$-tricalcium phosphate (denoted by ‘T’) also occurred in both of the specimens. However, it was observed only at the early stage of milling in the W-specimens, while it still remained even after milling for 8 h in the A-specimens. Calcium oxide (denoted by ‘C’) also occurred in both of the specimens but it was observed only at the early stage of milling (2 h).

Fig. 7 shows the results of FT-IR measurements on the A- and W-specimens after heat-treatment at 1100°C for 1 h. The profiles of both the specimens were exactly the same. The asymmetrical stretching ($\nu_3$) and bending
\( u_4 \) modes of PO\(_4\) ion were detected at around 1089 and 1043, and 601 and 572 cm\(^{-1} \), respectively. The symmetric stretching modes \((u_1\) and \(u_2\)) of the PO\(_4\) ion were also found at around 962 and 474 cm\(^{-1} \), respectively [17,21]. The stretching and liberation modes of OH ion were detected at around 3572 and 630 cm\(^{-1} \), respectively [17].

The above results suggest that the formation of the single phase of hydroxyapatite is critically dependent on the amount of the adsorbed water formed during milling and it again relates with the surface area of the powders. For the explanation of the different experimental results between the A- and W-specimens, the following reaction equations are believed to be appropriate.

When there is no water during the heat-treatment with calcium pyrophosphate and calcium carbonate, the products of the reaction will be tricalcium phosphate and calcium oxide as in Eq. (1).

\[
3\text{Ca}_2\text{P}_2\text{O}_7 + 4\text{CaCO}_3 \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + 4\text{CO}_2(\text{g})\uparrow
\]

Eq. (2) fits well with the results of the whole stage of milling in the A-specimen (Fig. 6 (a)) and the initial stage of milling in the W-specimen (Fig. 6 (b); 2 and 4 h). It is noted that the phases of hydroxyapatite and tricalcium phosphate actually occurred. The calcium oxide that is observed in the early stage of milling in both of the specimens might result from the inhomogeneous mixing of calcium carbonate due to the lack of milling time.

\[
3\text{Ca}_2\text{P}_2\text{O}_7 + 4\text{CaCO}_3 + x\text{H}_2\text{O} \rightarrow x\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 3(1 - x)\text{Ca}_3(\text{PO}_4)_2 + 4\text{CO}_2(\text{g})\uparrow
\]

(1)

Eq. (3) fits well with the results of the later stage of milling in the W-specimens (Fig. 6 (b); 6 and 8 h); only the single phase of hydroxyapatite actually occurred.

From the above results, it can be presumed that the formation of the single phase of hydroxyapatite with the
starting powders, which have not enough amounts of initial hydroxyl groups to convert all the powders to hydroxyapatite, can be possible by the supply of additional hydroxyl groups through the mechanochemical reaction during milling in water. Actually, as milling time increased, the surface area of the powders (Fig. 2) increased, and consequently it produces more sites for adsorbing water (Fig. 5). The single phase of hydroxyapatite can be obtained when the amount of newly formed hydroxyl groups exceeds a certain limit (Eq. (3)), which can convert all the starting powders to hydroxyapatite (Fig. 6(b)).

4. Conclusions

Hydroxyapatite powder was synthesized with calcium pyrophosphate (Ca$_3$P$_2$O$_7$) and calcium carbonate (CaCO$_3$) through solid-state reaction. The two powders were mixed in acetone and water, respectively, and then heat-treated without the additional supply of water vapor. The single phase of hydroxyapatite could be obtained only in the powder milled in water. The hydroxyl group needed for the formation of hydroxyapatite during the heat-treatment might be supplied from the mechanochemical reaction between the starting powders and water during milling. This process is very simple and economical so it is recommendable to the mass production of high crystalline hydroxyapatite.

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Fig. 7. FT-IR transmission spectra of the (a) A- and (b) W-specimens milled for each time periods and then heat-treated at 1100°C for 1 h.
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