

Hydrothermal Preparation of Apatite Spherical Particles

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Spherical apatite particles were prepared from spherical calcite particles by hydrothermal treatment. The spherical calcite particles of about 2.5 mm in size as the starting materials were formed in the apparatus which transformed hard water to soft one. The major impurities in calcite particles were Mg, Na and Sr. The spherical calcite particles were treated hydrothermally in the solution of diammonium hydrogen phosphate under the saturated vapor pressure. In the case of hydrothermal condition at 270 °C for 96 h using 2.0 mol·dm⁻³ diammonium hydrogen phosphate solution, apatite was identified by XRD, with a small amount of Mg-containing tri-calcium phosphate. From the SEM observation for the sample treated hydrothermally at 270 °C for 96 h with a solution of pH10, needle-like particles of about 2 μm in length was observed on the fractured surface.

Key words: calcite, hydroxyapatite, Mg-containing tri-calcium phosphate, hydrothermal reaction

1. INTRODUCTION

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; HA) is one of the promising implant materials as a bone substitute owing to its excellent osteoconductive properties [1]. In addition, HA can be used as an ion exchanger, separator, sensor and so on. The spherical HA particles will be useful in many fields such as packing media of chromatography for separating amino acid, protein etc [2-4]. Calcite (CaCO₃) spherical particles are formed in the apparatus during the processing of hard water to soft one. They are disposed as waste without any applications. Hydrothermal processing has been shown to be suitable for preparation of HA with the controlled composition and shape [5, 6]. The present study deals with the hydrothermal preparation of spherical HA particles from spherical calcite particles using the diammonium hydrogen phosphate ((NH₄)₂HPO₄) solution. The spherical apatite particles must be useful for many applications.

2. EXPERIMENT

2.1 Sample preparation

Spherical calcite particles of about 0.25 g were soaked in the solution of diammonium hydrogen phosphate of 13.5 cm³ with concentrations in the range of 0.1 to 2.0 mol·dm⁻³, and then they were treated hydrothermally using a mini-autoclave at the

temperatures from 150 ° to 270 °C for periods up to 96 h under saturated vapor pressure. The pH value of the solutions was controlled from 8 to 10 at room temperature by addition of aqueous ammonia (NH₃aq.), because HA is formed under alkaline conditions. Pure calcite powders (Wako pure chemical, reagent grade, Japan) were treated hydrothermally at the same conditions as that of the spherical calcite in order to investigate the influence of impurities in spherical calcite particles on the phase formation during the hydrothermal reaction.

2.2 Characterization

Chemical compositions of samples and the treatment solutions after hydrothermal treatment were analyzed by atomic absorption spectrometry (AAS; HITACHI Z-5310, Japan). The produced phases were identified by powder X-ray diffractometry with graphite-monochromated CuK α radiation (XRD; MAC Science MXP³, Japan). The integrated intensity of XRD lines of HA (2θ = 31.8°) and β-TCP (2θ = 31.0°) was compared with the calibration curve [7] in order to estimate the quantities of HA and β-TCP. Fourier transform infrared spectra (FT-IR; Parkin Elmer Spectram 2000, USA) were obtained from powdered samples mixed with spectroscopic grade KBr. The morphology of samples was observed by scanning

Table I Chemical composition of calcite particles

	CaO	MgO	SrO	MnO	Na ₂ O	K ₂ O
	mol%					
Spherical calcite	95.5	2.7	0.4	0.0	1.4	0.0
Reagent calcium carbonate*	99.5	0.0	0.2	0.0	0.3	0.0

* Calcite, Wako pure chemical, Japan

electron microscopy (SEM; JEOL JSM25S, Japan).

3. RESULTS AND DISCUSSION

3.1 Starting material

No phases other than calcite were detected by XRD [8] and FT-IR. Chemical compositions of the starting material analyzed by AAS are shown in Table I. The major impurities were Mg, Na and Sr. The photograph of spherical calcite particles and the fractured surface of the calcite are shown in Figs. 1 and 2. These particles had a porosity of about 20%. Fig. 2 shows the shape of polyhedron which is a part of calcite crystal shape.

3.2 Samples after hydrothermal treatment

The shape of samples was not changed after hydrothermal treatment. The formed crystal phases after hydrothermal reaction were calcium phosphates of HA [9] and β -TCP [10]. Patterns of XRD for the powdered products prepared hydrothermally at 270 °C for 24 h without pH control showed that unreacted calcite remained in the hydrothermally treated samples. The effect of period of hydrothermal treatment with pH control by addition of aqueous ammonia were shown in Fig. 3. Unreacted calcite was not recognized in the sample prepared at 270 °C for 96 h with high pH solution (pH10 at room temperature). Typical FT-IR spectra of the sample treated hydrothermally at 270 °C for 48 h is shown in Fig. 4. The peaks around 650 cm^{-1} and 3570 cm^{-1} due to OH⁻ group are seen with a small peak around 1420 cm^{-1} due to CO₃²⁻ group. Therefore a part of OH⁻ in HA must have been exchanged by CO₃²⁻, and thus the formed HA was carbonated-hydroxyapatite. From SEM observation of samples treated hydrothermally at 270 °C for 96 h with pH10 solution, needle-like particles of about 2 μm in length were observed on the fractured surface (Fig. 5).

3.3 Effect of Mg ion on phase formation

D. M. Roy et al. had reported that HA was formed from aragonite containing a small amount of Mg, and β -TCP was formed from calcite containing larger

amount of Mg [11]. K. Hashimoto et al. also had reported that Mg containing whitlockite was formed from the reaction system containing 3 mol% Mg ion in the reaction solution [12]. Therefore, it was considered that formed phases of calcium phosphates depended on the existence of Mg ion. In order to investigate the influence of Mg ion on the phase formation, the reagent grade calcite was treated hydrothermally at 270 °C for 48 h with 2.0 $\text{mol}\cdot\text{dm}^{-3}$ (NH₄)₂HPO₄ solution or 2.0 $\text{mol}\cdot\text{dm}^{-3}$ (NH₄)₂HPO₄ solution containing Mg ion. From XRD, only HA was formed from the pure calcite by hydrothermal treatment in the solution without Mg ion. In the contrast, β -TCP was formed by hydrothermal treatment with the solution containing Mg ion. Fig. 7 shows the Mg ion concentration of solutions before and after hydrothermal treatment. The amount of β -TCP increased linearly with the increasing concentration of Mg ion. When the Mg ion concentration of solutions over 1.6×10^{-2} $\text{mol}\cdot\text{dm}^{-3}$, only β -TCP was recognized without HA. Fig. 7 shows the concentration of Mg ion in the solution of 2.0 $\text{mol}\cdot\text{dm}^{-3}$ (NH₄)₂HPO₄ aq. before and after hydrothermal treatment. When the concentration of Mg ion before treatment was below 1.6×10^{-2} $\text{mol}\cdot\text{dm}^{-3}$, Mg ion was not detected in the solutions after hydrothermal treatment. Therefore, Mg ion existed in HA and β -TCP crystal structure. The result of phase formation for hydrothermally treated spherical calcite at 270 °C for 96 h agreed with the results indicated in Fig. 6. The amount of maximum Mg ion in β -TCP was 10 mol%, which was estimated from the sample of only β -TCP without HA formed hydrothermally in 1.6×10^{-2} $\text{mol}\cdot\text{dm}^{-3}$ (NH₄)₂HPO₄ aqueous solution.

4. SUMMARY

Spherical apatite particles containing β -tricalcium phosphate were prepared hydrothermally from spherical calcite particles. Apatite was synthesized by using diammonium hydrogen phosphate solution with high pH value controlled by addition of aqueous ammonia. The

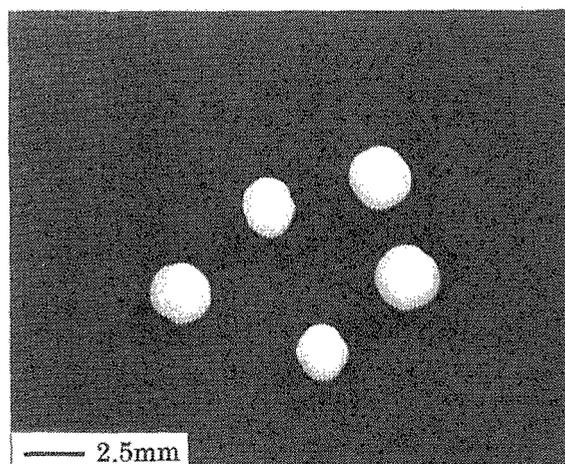


Fig. 1 Calcite particles. The particle diameter is in the range of 2-3 mm.

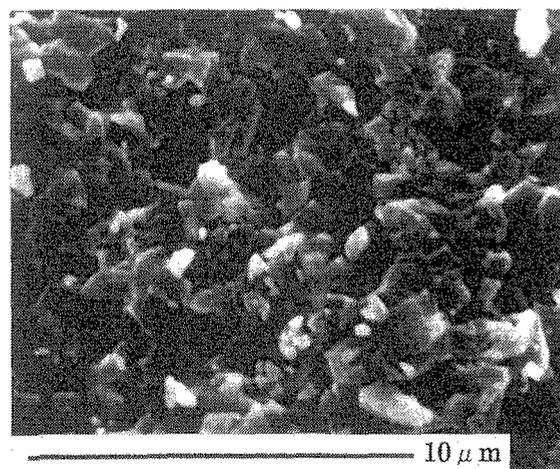


Fig. 2 SEM observation for fractured surface of the calcite particle.

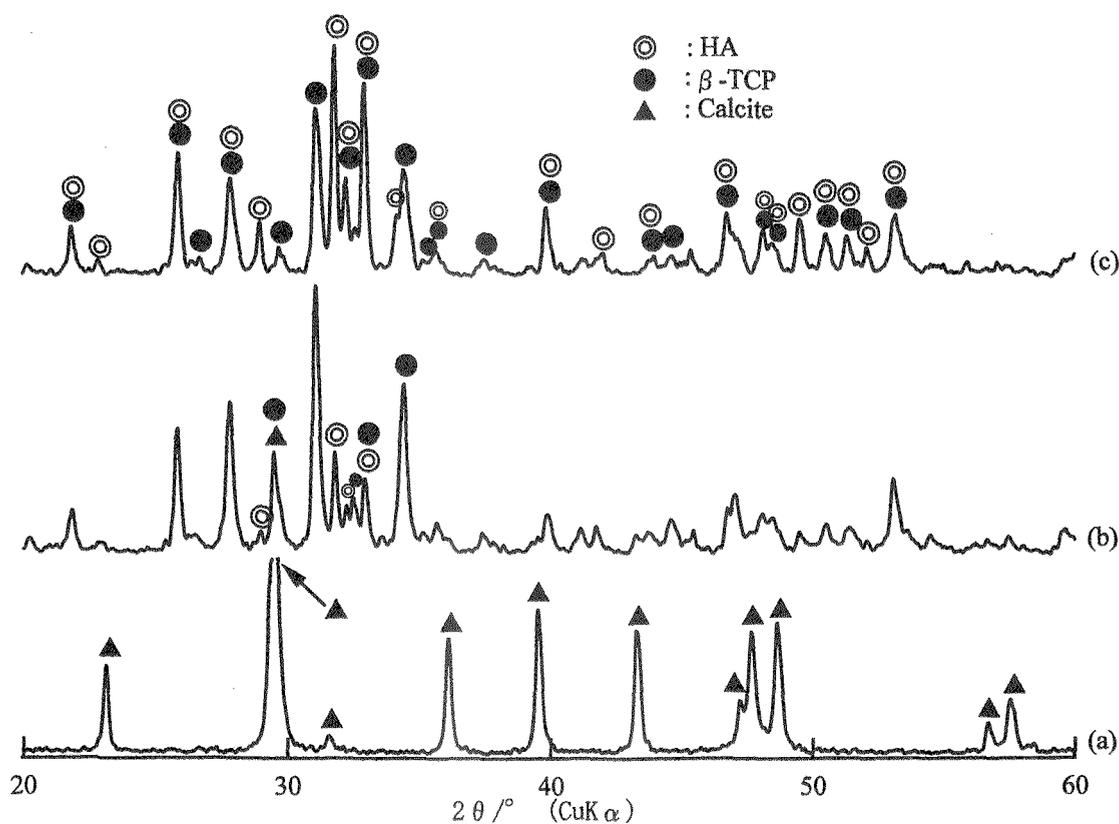


Fig. 3 Patterns of XRD for the samples treated hydrothermally at 270 °C in 2.0 mol·dm⁻³ (NH₄)₂HPO₄ sol. with pH control (pH 10 at room temp.) by NH₃ addition. (a) starting calcite, (b) for 24 h, (c) for 96 h.

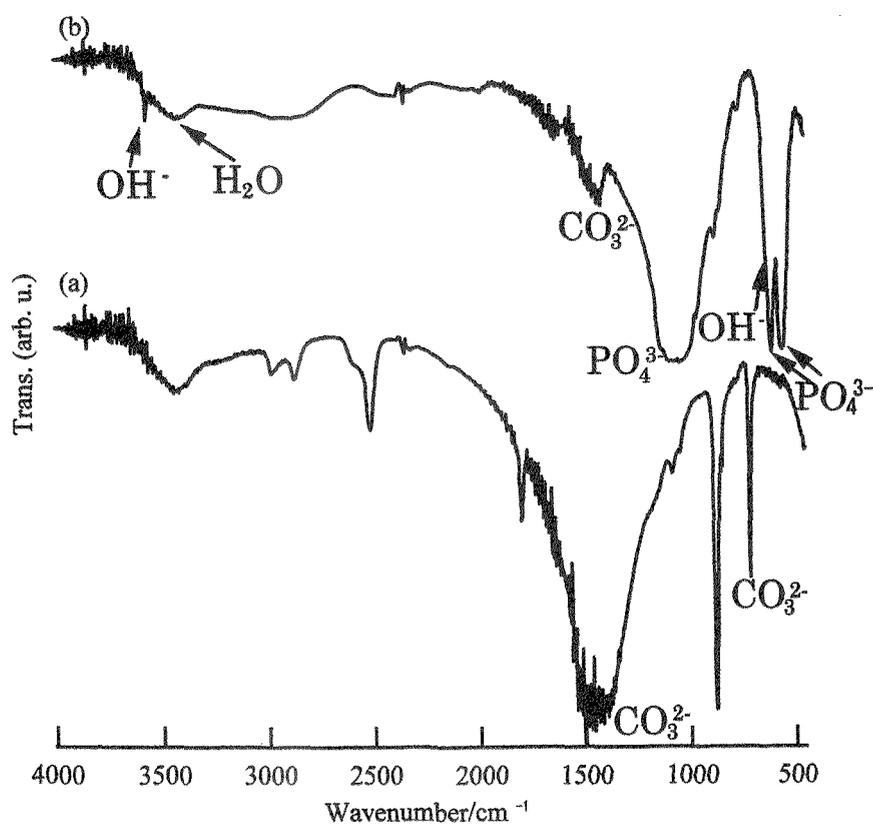


Fig. 4 FT-IR spectra of (a) starting calcite and (b) sample treated hydrothermally at 270 °C for 48 h in 2.0 mol·dm⁻³ (NH₄)₂HPO₄ sol. (pH=10 at room temp.).

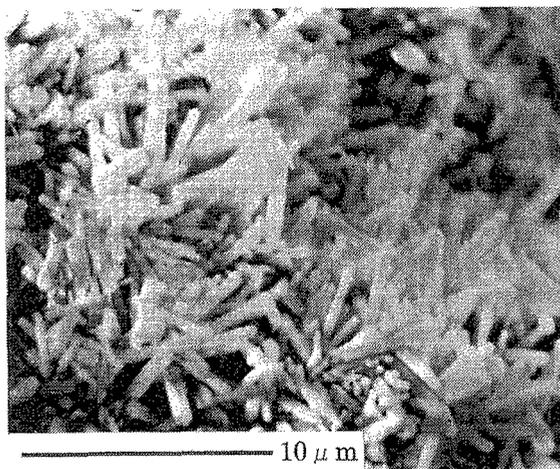


Fig. 5 SEM observation for the sample treated hydrothermally at 270°C for 96 h in 2.0 mol·dm⁻³ (NH₄)₂HPO₄ sol. (pH=10 at room temp.).

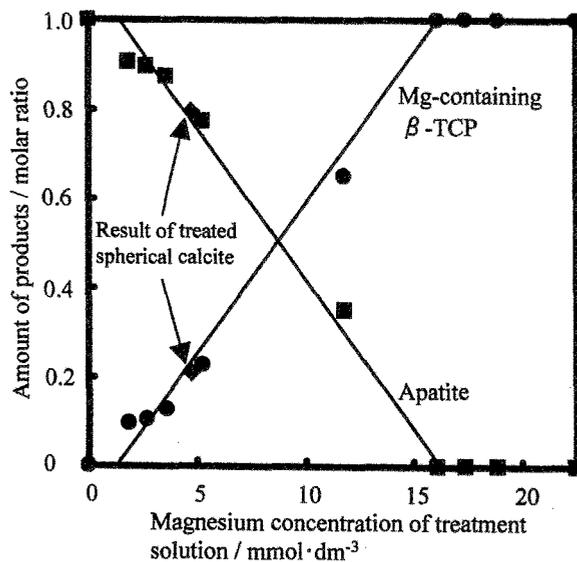


Fig. 6 Relationship between magnesium concentration of treatment solution and formed phase.

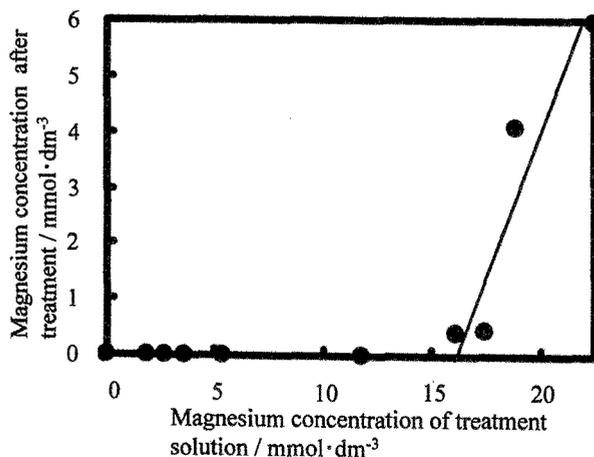


Fig. 7 Relationship between magnesium concentration in the solution before and after treatment.

formation of β -tricalcium phosphate was caused by Mg ion in the spherical calcite.

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