HYDROTHERMAL SYNTHESIS OF CALCIUM PHOSPHATES SPHERICAL PARTICLES

Koji IOKU, Akira OSHITA, Hirotaka FUJIMORI, Yoshinori NAKAMURA*, Keiko FUJIWARA*, Seishi GOTO and Masahiro YOSHIMURA**

Division of Applied Medical Engineering Science, Graduate School of Medicine, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

* Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

**Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, Kanagawa 226-8503, Japan

Abstract Spherical particles of hydroxyapatite with β -tricalcium phosphate were prepared from spherical calcite particles by hydrothermal method. The spherical calcite particles of about 2.5 mm in size as the starting materials were formed through the process which transformed hard water to soft water. 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 $2.0 \text{ mol} \cdot \text{dm}^{-3}$ diammonium hydrogen phosphate solution, hydroxyapatite was formed with a small amount of β -tricalcium 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.

INTRODUCTION

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: HA) and β -tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$: β -TCP) are promising implant materials as a bone substitute owing to its excellent osteoconductive properties^{1,2)}. In addition, HA can be used as ion exchangers, separators and sensors. The spherical particles of calcium phosphates will be useful in many fields such as packing media of chromatography for separating amino acid, protein etc³⁻⁵⁾. Calcite (CaCO_3) 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^{6,7)}. The present study deals with the hydrothermal

preparation of spherical particles of calcium phosphates from spherical calcite particles using the diammonium hydrogen phosphate ((NH₄)₂HPO₄) solution.

EXPERIMENTAL

Spherical calcite particles of about 0.25 g were soaked in 2.0 mol · dm⁻³ (NH₄)₂HPO₄ aqueous solution of 13.5 cm³, and then they were treated hydrothermally using a mini-autoclave at temperatures from 150 °C 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 (NH₃ aq.). Pure calcite powders (Wako pure chemical, reagent grade, Japan) were treated hydrothermally under 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.

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-monochromatized CuKα 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 curve⁸⁾ in order to estimate the quantities of HA and β-TCP. Fourier transform infrared spectra (FT-IR; Perkin Elmer Spectrum 2000, USA) were obtained from powdered samples mixed with spectroscopic grade KBr. The morphology of the samples was observed by scanning electron microscopy (SEM; JEOL JSM25S, Japan).

RESULTS AND DISCUSSION

Starting Material

No phases other than calcite⁹⁾ were detected by XRD and FT-IR. Chemical compositions of the starting material analyzed by AAS were as follows; CaO 95.5,

MgO 2.7, SrO 0.4, MnO 0.0, Na₂O 1.4, K₂O 0.0 mol%. The major impurities were Mg, Na and Sr. The spherical calcite particles had a porosity of about 20%. Fractured surface of the particle showed the shape of polyhedron which is a part of calcite crystal shape.

Samples after Hydrothermal Treatment

The shape of samples was not changed after hydrothermal treatment (FIGURE 1).

FIGURE 1 Spherical particles of calcium phosphates prepared by hydrothermal treatment at 270 °C for 96 h with a 2.0 mol · dm⁻³ (NH₄)₂HPO₄ aqueous solution. The solution was pH-controlled with an aqueous NH₃ (pH=10).

The formed crystal phases due to hydrothermal reaction were calcium phosphates of HA¹⁰⁾ and β-TCP¹¹⁾. 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 the period of hydrothermal treatment with pH control by addition of aqueous NH₃ is shown in FIGURE 2. Unreacted calcite was not recognized in the sample prepared at 270 °C for 96 h with high pH solution (pH10 at room temperature). According to FT-IR measurement of the samples treated hydrothermally at 270 °C, 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 (FIGURE 3).

FIGURE 2 Patterns of XRD for the samples treated hydrothermally at 270 °C in $2.0 \text{ mol} \cdot \text{dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ aqueous solution with pH control by aqueous NH_3 (pH=10); (a) starting calcite, (b) for 24 h, (c) for 96 h.

FIGURE 3 SEM observation for the sample treated hydrothermally at 270 °C for 96 h in $2.0 \text{ mol} \cdot \text{dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ aqueous solution with pH control by aqueous NH_3 (pH=10).

FIGURE 4 Relationship between (a) magnesium concentration of treatment solution and formed phase, (b) magnesium concentration in the solution before and after treatment.

Effect of Mg²⁺ on Phase Formation

In the past report, HA was formed from aragonite containing a small amount of Mg²⁺, and β-TCP was formed from calcite containing larger amount of Mg²⁺ ¹²⁾. In addition, Mg²⁺ containing whitlockite was formed from the reaction system containing 3 mol% Mg²⁺ in the reaction solution¹³⁾. Therefore, it was considered that formed phases of calcium phosphates depended on the existence of Mg²⁺. In order to investigate the influence of Mg²⁺ on the phase formation, the reagent grade calcite without Mg²⁺ was treated hydrothermally at 270 °C for 48 h with 2.0 mol · dm⁻³ (NH₄)₂HPO₄ solution or the solution containing Mg²⁺. From XRD, only HA was formed from the pure calcite by hydrothermal treatment in the solution without Mg²⁺. In the contrast, β-TCP was formed by hydrothermal treatment with the solution containing Mg²⁺. The amount of β-TCP increased linearly with the increasing concentration of Mg²⁺ (FIGURE 4(a)). When the Mg²⁺ concentration of the solutions exceeded 1.6×10^{-2} mol · dm⁻³, only the formation of β-TCP was observed without HA. FIGURE 4(b) shows the concentration of Mg²⁺ in the solution of 2.0 mol · dm⁻³ (NH₄)₂HPO₄ before and after the hydrothermal treatment. When the concentration of Mg²⁺ before the treatment was below 1.6×10^{-2} mol · dm⁻³, Mg²⁺ was not detected in the solutions after hydrothermal treatment. Therefore, it can be

elucidated that Mg^{2+} existed in HA and β -TCP crystal structures. The result of phase formation for hydrothermally treated spherical calcite at 270 °C for 96 h agreed with the results indicated in FIGURE 4(a). The amount of maximum Mg^{2+} in β -TCP was 10 mol%, which was estimated from the sample of only β -TCP without HA formed hydrothermally in $1.6 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ aqueous solution.

SUMMARY

Spherical particles of calcium phosphates were prepared hydrothermally from spherical calcite particles. Carbonated hydroxyapatite with β -tricalcium phosphate was synthesized by using diammonium hydrogen phosphate solution with addition of aqueous ammonia. The formation of β -tricalcium phosphate was caused by Mg^{2+} in the spherical calcite.

ACKNOWLEDGEMENT

The present work has been supported by cooperative programs in the Material and Structures Laboratory of Tokyo Institute of Technology, and supported partly by RSP project of Yamaguchi Prefecture, Japan. The authors also wish to thank Ube Materials Co. Ltd., Japan for the sample supply.

REFERENCES

1. H. Aoki, *Medical Applications of Hydroxyapatite*, Ishiyaku Euro America Inc., Tokyo, St. Louis (1994).
2. K. Ioku, *J. Soc. Inorg. Mater. Japan*, **8**, 153-159 (2001).
3. T. Okuyama, T. Ogawa, and M. Ebihara, *J. Soc. Inorg. Mater. Japan (Gypsum & Lime)*, [210], 65-73 (1987).
4. T. Kawasaki, *Ceramics Japan*, **20**, [3], 195-202 (1985).
5. K. Nakamura, *Ceramics Japan*, **23**, [11], 1065-1068 (1988).
6. K. Ioku, M. Yoshimura and S. Somiya, *Nippon Kagaku Kaishi (J. Chem. Soc. Japan)*, [9], 1565-1570 (1988).
7. M. Yoshimura and H. Suda, "Hydrothermal Processing of Hydroxyapatite: Past, Present, and Future", in *Hydroxyapatite and Related Materials*, edited by P. Brown, B. Constantz, CRC Press, Boca Raton, Ann Arbor, London, Tokyo (1994).
8. K. Ioku, T. Murakami, Y. Ikuma and M. Yoshimura, *J. Ceram. Soc. Japan*, **100**, [8], 1015-1019 (1992).
9. Powder Diffraction File, Card #5-586
10. Powder Diffraction File, Card#9-432
11. Powder Diffraction File, Card #9-169
12. D. M. Roy and S. K. Linnehan, *Nature*, **247**, 220-222 (1974).
13. K. Hashimoto, Y. Toda, T. Arakawa, T. Saitoh, T. Kanazawa and S. Udagawa, *J. Soc. Inorg. Mater. Japan (Muki-materiaru)*, **2**, 171-180 (1995).