

Preparation of Hydroxyapatite Powder through Chemical Bath Deposition

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The optimum preparation condition of hydroxyapatite powder through chemical bath deposition was established. By refluxing the 2-ethoxyethanol solution containing calcium nitrate and dichlorophenylphosphine at its boiling point for 6 to 48h, crystalline precipitates were obtained. The single phase of hydroxyapatite was obtained by heating the precipitates at 600°C for 1h, the precipitate obtained by refluxing for 48h. However, hydroxyapatite coexisted with either CaO or CaCO₃ in the case of the reflux time below 24h, irrespective of heating temperature. In these results, the optimum condition for preparing hydroxyapatite was found that the crystalline precipitates were obtained by refluxing the mixed solution for 48h and heated at 600°C for 1h. From FT-IR measurement, CO₃²⁻ was detected in the hydroxyapatite obtained at 1000°C, which was found to be due to the replacement of CO₃²⁻ with PO₄³⁻ in hydroxyapatite obtained.

Key words: Hydroxyapatite, Powder, Preparation, Solution.

1. INTRODUCTION

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂: HAp) and related calcium phosphates are used as attractive materials for human hard tissues [1-3], because they show bio-compatible such as the easily bonding to the living bone. Many preparation processes of their powder have been proposed, such as solid-state reaction, spray-pyrolysis technique, sol-gel method and bio-mimetic process [4-8], etc. However, these methods require either the high temperature or the long time on its formation. For example, the former three processes need to heat the HAp powder above 1000°C, and the later process was required long time more than a week for preparing its powder. In order to prepare the HAp at low temperature and for short time, therefore, we have tried to synthesis its powder by the new processes other than four processes described above. From the processes tried, we prepared successfully the HAp powder at low temperature for short time; the crystalline precipitates were obtained through chemical bath deposition and then heated at 600°C for 1h.

In the present work, hydroxyapatite powder was prepared through chemical bath deposition. The optimum condition for preparing hydroxyapatite is described, and then the crystal structure and the chemical composition of hydroxyapatite powders obtained are examined.

2. EXPERIMENTAL

The preparation procedure of hydroxyapatite

powder is shown as a block diagram in Fig. 1. Calcium nitrate (Ca(NO₃)₂ · 4H₂O: hereafter CN)

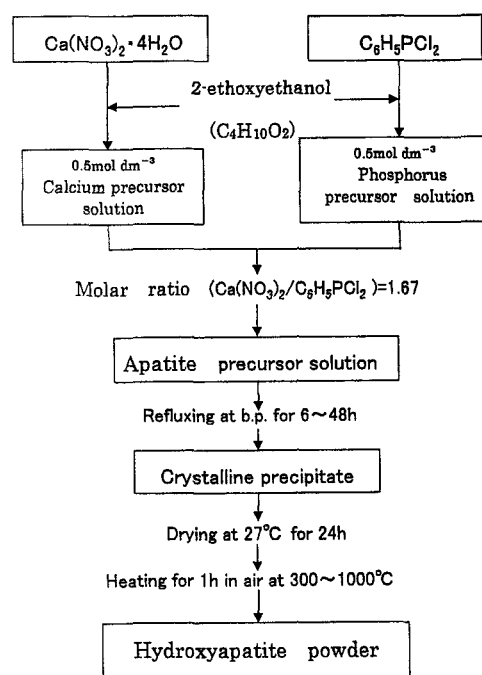


Fig. 1 Preparation procedure of hydroxyapatite powder through chemical bath deposition.

and dichlorophenylphosphine (C₆H₅PCl₂: DCP) were used as the raw materials. The CN and the DCP were dissolved separately into 2-ethoxyethanol (C₄H₁₀O₂), whose concentration was 0.5 mol dm⁻³. These two solutions were mixed

with a molar ratio of CN to DCP (CN/DCPP) of about 1.67, corresponding to the chemical composition of hydroxyapatite. The mixed solution prepared was used as a precursor solution for hydroxyapatite.

By refluxing the precursor solution at its boiling point for various times, crystalline precipitates were obtained from the solution. The precipitates were dried at 27°C for 24h and then heated for 1h in air at the temperature ranging from 300 to 1000°C.

The changes of the structure by heating the precipitates were determined by means of X-ray diffraction measurement (XRD) and infrared spectroscopy (FT-IR). And also, the thermal decomposition of the obtained precipitates was studied by thermogravimetry-differential thermal analysis (TG-DTA).

3. RESULTS AND DISCUSSION

In Fig.2, the amount of crystalline precipitates with the reflux time of precursor solution is shown.

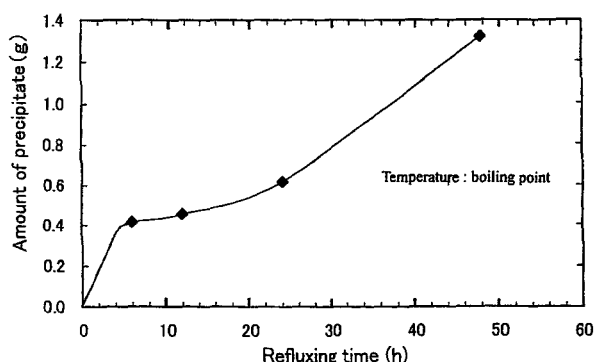


Fig. 2 The amount of crystalline precipitates with the reflux time of precursor solution.

The amount of precipitates increased with the increase of the reflux time and reached to 1.34g for 48h. By the chemical analysis in the residual solution after refluxing for 48h, no existence of calcium and phosphorus were detected on the filtrate. The amount of the precipitates when the solution was refluxed for 48h is supposed to be comparable with the theoretical one precipitated by the reaction between CN and DCP, that is, CN and DCP in the precursor solution are consumed completely by the precipitation of the crystalline powder.

The XRD patterns of the precipitates with the heating temperature are shown in Fig.3, the precipitates prepared by refluxing the precursor solution for 48h being used. As can be seen in the figure, the diffraction peaks, other than HAP phase, were observed in the precipitates heated

below 300°C. In order to determine the crystal structure, we examined the structure by Hanawalt

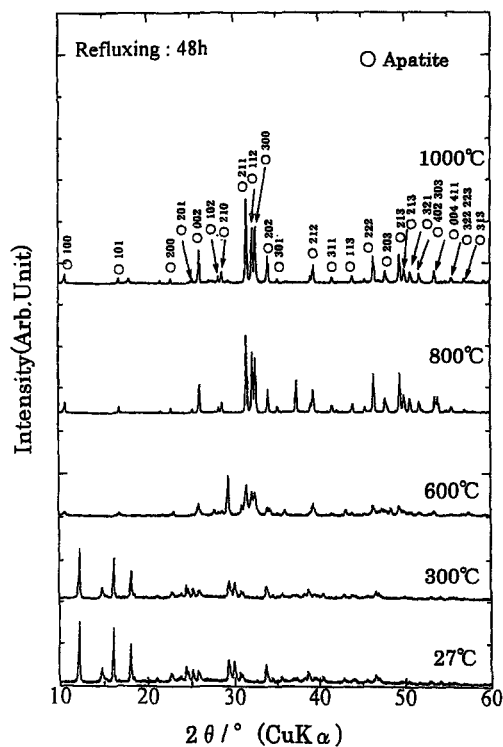


Fig. 3 XRD patterns of the precipitates obtained by heating at several temperatures for 1h; the precipitates being prepared by refluxing the precursor solution for 48h.

Search and JCPDS cards. However, the crystal structure was not able to be clear. The single phase of HAP was obtained by heating above 600°C and the intensity of diffraction lines increased with the increase of the heating temperature.

Table 1 Crystal phase of precipitates obtained by refluxing for various times and by keeping at several temperatures for 1h.

Temperature (°C)	Refluxing time (h)			
	6	12	24	48
27	NI	NI	NI	NI
300	NI	NI	NI	NI
600	Apatite CaO	Apatite CaCO ₃	Apatite CaCO ₃	Apatite
800	Apatite CaO	Apatite CaO	Apatite CaO	Apatite
1000	Apatite CaO	Apatite CaO	Apatite CaO	Apatite

Note: the symbol of NI means that the crystal phase is not identified.

XRD measurements of all the precipitates prepared from the precursor solution with different reflux times, such as 6, 12 and 24h, were carried out. The results are summarized in Table 1, together with the results of the samples refluxed for 48h. At 600°C, either CaO or CaCO₃ phase in addition to the HAp phase were observed in the samples obtained by refluxing below 24h, as can be seen from the table. With increasing the heating temperature of the samples, HAp phase

coexisted with CaO phase. However, the samples obtained by refluxing for 48h gave only the HAp phase by heating above 600°C. From these results, the optimum condition for preparing HAp is supposed as follows; the crystalline precipitates are prepared by refluxing the precursor solution for 48h and then heated above 600°C for 1h.

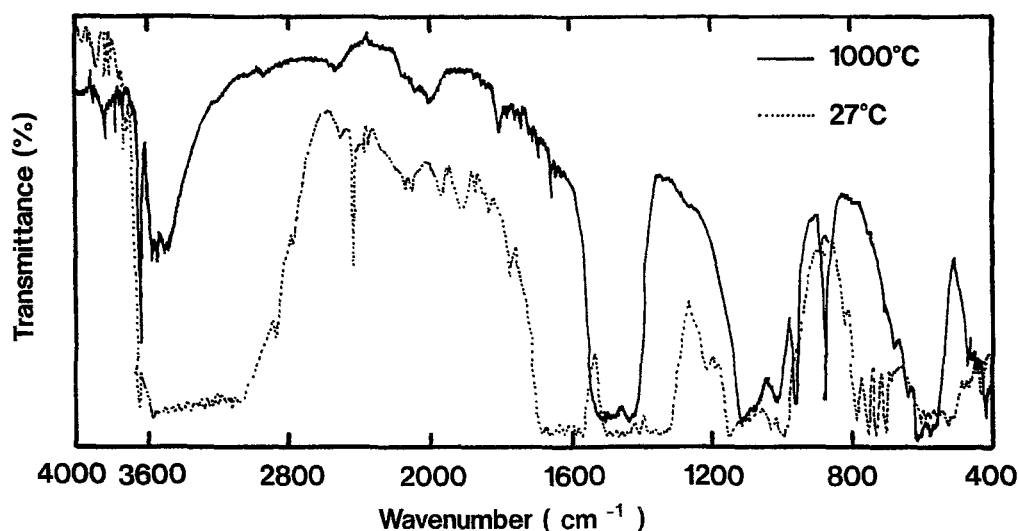


Fig. 4 FT-IR spectra of the precipitates heated at 27 and 1000°C for 1h; the precipitates being prepared by refluxing the precursor solution for 48h.

In Fig. 4, FT-IR spectra of the samples obtained at 27 and 1000°C are shown, the samples prepared by refluxing for 48h being used. At 27°C, the many adsorption peaks assigned to various molecules were observed, such as OH⁻ in the range from 3650 to 3200 cm⁻¹, P-H at 2400 cm⁻¹, benzene around 1680 cm⁻¹, CO₃²⁻ around 1430 cm⁻¹ and PO₄³⁻ around 1200 cm⁻¹, etc. In the case of the sample obtained at 1000°C, the adsorption peaks corresponding to OH⁻, CO₃²⁻ and PO₄³⁻ became a sharp, and the peak of CO₃²⁻ were assigned to that due to the replacement of CO₃²⁻ with PO₄³⁻ in HAp. Therefore, it is found that the HAp containing CO₃²⁻ can be prepared through chemical bath deposition. As the existence of CO₃²⁻ in the HAp was confirmed from FT-IR measurement, the HAp prepared by heating at 1000°C may be anticipated to be the chemical composition of Ca₁₀(PO₄)_{6-x}(OH)_{2-y}(CO₃)_{x+y}.

In order to examine the thermal decomposition of the as-precipitate sample, TG-

DTA measurement was carried out with a heating rate of 10 °C min⁻¹, as shown in Fig. 5. Many exothermic peaks with weight loss were observed up to 600°C, due to the thermal decomposition of organic compounds included in the precipitate. Because the organic compounds such benzene existed in the crystalline precipitates, as shown in Fig. 4. The endothermic peak with weight loss was observed at 750°C. In the result of TG-DTA on the HAp after heating at 1000 °C, the endothermic peak with weight loss was also observed at 750°C, suggesting no elimination of the organic compounds described above. As it is known that the amount of CO₂ gas adsorbs on the surface of HAp, the weight loss at 750°C may be supposed to be due to the elimination of CO₂. The adsorbed amount of CO₂ gas was found to be about 2wt% on the HAp prepared in the present work.

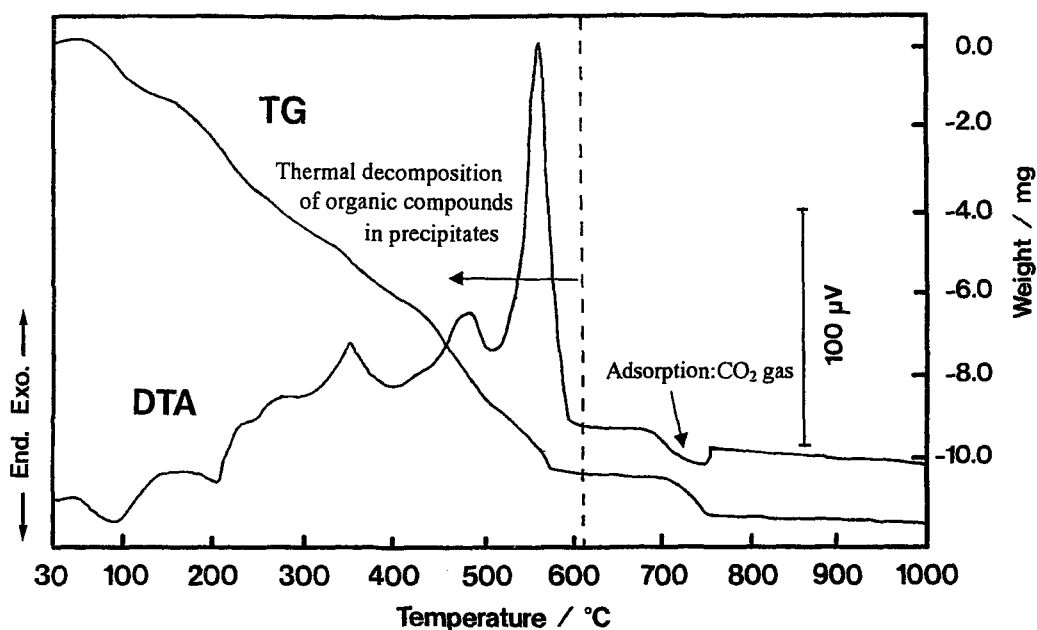


Fig. 5 TG-DTA curve of the precipitates prepared by refluxing the precursor solution for 48h.

4. CONCLUSION

The preparation condition of HAp powder through chemical bath deposition was established, and then the crystal structure and chemical composition of HAp prepared were examined.

Crystalline precipitates were obtained by refluxing the precursor solution at its boiling point for various times. The amount of precipitates increased with the increase of the reflux time.

The optimum condition for preparing HAp powder was as follows; the crystalline precipitates were prepared by refluxing the precursor solution at its boiling point for 48h and then heated at 600°C for 1h. From FT-IR measurement, the existence of CO_3^{2-} in the HAp obtained at 1000°C was observed, due to the replacement of CO_3^{2-} with PO_4^{3-} in HAp obtained.

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