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Hydroxyapatite formation through dissolution–precipitation reaction: Effects of solubility of starting materials

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Abstract

Hydrothermal processing has been the subject of much attention for hydroxyapatite (HAp) formation because the formed HAp has various morphology. We investigated the effects of solubility of starting materials on the HAp formation and its morphology under a hydrothermal condition. Single crystals of calcite, fluorite and calcium tartrate tetrahydrate with different solubilities were used as starting materials. After hydrothermal processing for 24 h, HAp formed on the surfaces of all the starting materials. Needle-like HAp formed on the surface of calcite and plate-like HAp formed on the fluorite. In the case of the calcium tartrate tetrahydrate, aggregation of nano-sized HAp was observed on its surface. The difference in the solubility of the starting materials might affect the morphology of HAp formed on their surfaces under hydrothermal conditions.

Keywords: D. Apatite; B. Microstructure-final; Hydrothermal processing

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) has been the subject of much attention in biomedical applications. Because HAp has bone bonding ability and it shows unique protein adsorption [1,2], the performance of HAp in biological application is affected by its morphology. The morphological control of HAp is very important on its applications.

According to previous studies [3–7], hydrothermal processing is one of the typical methods to obtain well-crystallized HAp. Using the hydrothermal processing, HAp with controlled morphology can be obtained [5–7]. In hydrothermal processing, HAp formation and its morphology significantly depends on starting materials and hydrothermal conditions such as temperature for processing, processing period and additives in a solvent.

Ishikawa et al. [8] reported that in the case of calcium carbonate used as a starting material in a phosphate solution, the processing allows HAp transformation from calcium carbonate by the dissolution–precipitation reaction. This reaction might occur at the surface of calcium carbonate. Because calcium ions for HAp formation is supplied by dissolution of calcium carbonate. This means that calcium compounds can be used as starting materials for this processing. Our group reported that calcite single crystals also formed HAp on their surfaces [9]. Crystal face of calcite also affected growth rate and direction of HAp crystals. This effect of crystal face on HAp crystal growth might be derived from the difference in reactivity of each crystal face. Besides, the effects of solubility of starting materials on morphology of resultant products were also reported. Our group already reported [10] that using tricalcium phosphates (TCP, $Ca_3(PO_4)_2$) with different solubilities, α-TCP with higher dissolution rate led to fine and plate-shaped crystals while β-TCP with lower dissolution rate allowed large and well-crystallized HAp crystals through the

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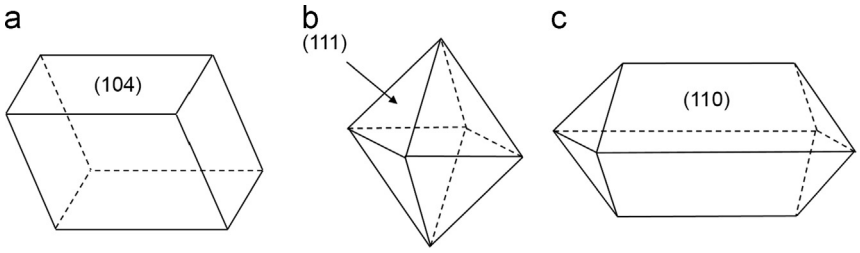

Fig. 1. The illustrations of the single crystals used in this study. (a) calcite, (b) fluorite and (c) calcium tartrate tetrahydrate.

hydrothermal treatment conditions. This means that the dissolution rates of starting materials affect the morphology of resultant production under hydrothermal conditions.

Particle size distribution and specific surface area also affect dissolution behavior of starting materials. The effects on morphology of resultant HAp crystals have to be considered. Because calcium compounds particles are usually used as a starting materials for HAp synthesis by a hydrothermal processing [11–13]. A crystal face of a starting material might show uniform dissolution rate under hydrothermal conditions. Using single crystals of calcium compounds, it is expected that effects of their solubility on morphology of resultant products can be evaluated, without considering the other factors which affect dissolution behavior of calcium compounds. Therefore, the effects of starting materials with different solubilities have to be evaluated basically for the morphology control of HAp. In the present study, we investigated the effects of solubility of starting materials in a phosphate solution under a hydrothermal condition. Single crystals were used as starting materials for the reaction, since each crystal face shows the unique dissolution rate. After the hydrothermal treatment of each single crystal, we evaluated the formed HAp on the surfaces of starting crystals by a dissolution–precipitation reaction.

2. Materials and methods

Single crystals of calcite ($CaCO_3$), fluorite (CaF_2) and calcium tartrate tetrahydrate ($Ca(C_4H_4O_6)\cdot 4H_2O$) were used as starting materials for supplying calcium. The structure of each single crystal used in this study was illustrated as shown in Fig. 1. Optically clear single crystals were used as starting materials.

The single crystals with $10 \times 10 \times 1$ mm in size were placed in Tefron®-lined autoclaves, with 30 cm^3 of 1 mol dm^{-3} diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, Nacalai tesque, Japan) solution. The pH of the solution was adjusted to 9.8 by 25% ammonia solution (NH_4OH, Nacalai tesque, Japan). The autoclaves were then sealed tightly and heated at 160 °C for 24 h. After the withdrawal from the autoclaves, they were cooled immediately with a fan. The samples were removed from the solution, washed with ultra-pure water and acetone to terminate any further reaction and kept at 40 °C to dry.

The reaction products were characterized by a scanning electron microscope (SEM, JSM5600, JEOL Ltd., Japan) to observe the morphologies of their surfaces and cross-sections.

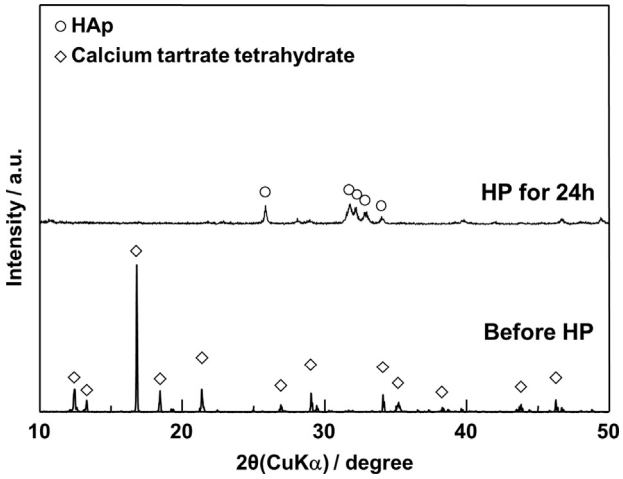

Fig. 2. XRD patterns of the calcium tartrate tetrahydrate before and after hydrothermal processing (HP) for 24 h.

X-ray diffraction (XRD, RINT PC 2100, Rigaku Co., Japan) was used to identify the change in crystal phases through the dissolution–precipitation reaction.

3. Results

After the hydrothermal treatment, the external shape of calcium tartrate tetrahydrate was not maintained, and the product was collected by filtration. The others maintained their external shapes after the hydrothermal treatment.

Fig. 2 shows XRD patterns of the surface of calcium tartrate tetrahydrate before and after hydrothermal treatment for 24 h. After hydrothermal treatment, the peaks for HAp were detected and the XRD pattern of formed HAp seemed to be originated from low-crystalline HAp, while the peaks of calcium tartrate tetrahydrate disappeared. Fig. 3 shows SEM photographs of the calcium tartrate tetrahydrate before and after hydrothermal treatment for 24 h. Although the original calcium tartrate tetrahydrate had smooth surface, spherical HAp particles with 3 μm in size were prepared by the hydrothermal treatment. Through SEM photographs at high magnification, composing spherical particles were observed.

Fig. 4 shows XRD patterns of the surface of calcite single crystal before and after hydrothermal treatment for 24 h. From the XRD pattern after hydrothermal treatment, it was confirmed that the HAp formed on the calcite surface. The 300 reflection was strongly developed. The XRD patterns of HAp