Investigation of Growth and Decomposition of Ca-Deficient Hydroxyapatite
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1. Introduction
Calcium-deficient hydroxyapatite (Ca\(_{10-Z}(HPO_4)_Z(PO_4)_{6-Z}(OH)_{2-Z} \cdot nH_2O\), \(Z = 0-1\): Ca-def HAp), having crystal structure similar to biological bone apatite, is one of important biomaterials. It has been reported that hydrolysis of \(\alpha\)-tricalcium phosphate (\(\alpha\)-Ca\(_3(PO_4)_2\): \(\alpha\)-TCP) in a mixture of water and alcohol gives the Ca-def HAp whiskers [1] and it is decomposed into stoichiometric hydroxyapatite (Ca\(_{10}(PO_4)_6(OH)_{2}\), hexagonal, \(a = 0.943\) nm, \(c = 0.688\) nm: s-HAp) and \(\beta\)-tricalcium phosphate (\(\beta\)-Ca\(_3(PO_4)_2\): \(\beta\)-TCP) by annealing above 800 °C [2], which show good biocompatibility and high bioactivity. This paper deals with crystal growth of the Ca-def HAp whiskers produced by hydrolysis and a microstructural change of the whiskers annealed at various temperatures, by high-resolution transmission electron microscopy (HRTEM) [3–5].

2. Experimental
High purity \(\alpha\)-TCP powder (Taihei Chemical Industries Co., Ltd.) was stirred at 70 °C in a water solvent suspending 1-octanol [1]. An initial pH value of the solvent was adjusted to 11.0 with NH\(_4\)OH. The suspensions hydrolyzed for 0-48 hours were sampled and dropped onto Cu grids with holey film for TEM. In order to observe the initial stage of hydrolysis on \(\alpha\)-TCP crystals, thin \(\alpha\)-TCP disks with a hole prepared by compressing, sintering, and dimpling, were also hydrolyzed in the water with adjusted pH value of 11.0 without stirring to protect the thinned region of the disk. Ca-def HAp whiskers grown by the hydrolysis were annealed (heating rate: 5 °C/min) at 200-1100 °C for 2-6 hours in air. Hydrolyzed specimens and annealed ones were observed with a JEOL, JEM-2010/SP microscope equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer, and a JEOL, JEM-2000EX microscope, operated with an accelerating voltage at 200 kV. X-ray diffraction (XRD) analysis and infrared absorption spectroscopy (IR) analysis were also carried out.

3. Results and discussion
TEM images of the surface of the thinned \(\alpha\)-TCP crystals before and after hydrolysis are shown in Fig. 1. The surface of the crystal was clean before hydrolysis, while that of the crystal hydrolyzed for a few hours was covered with an amorphous layer. Nuclei appeared not on the \(\alpha\)-TCP crystal but on the surface of the amorphous layer, and they grew into the dendritic structure composed of twigs with a few nm in width and trunks with several tens nm in width. The dendrites are regarded as an embryo of a Ca-def HAp crystal.

Figure 2 shows growth process of the whiskers by hydrolysis of the \(\alpha\)-TCP powder. Needle-like crystals with a few tens nm in width and a few hundreds nm in length grew around the \(\alpha\)-TCP particle after hydrolysis for 1 hour. After 3 hours hydrolysis, most of grown crystals had whisker-like shape 2-5 \(\mu\)m in length and 0.1 \(\mu\)m in diameter that was elongated along \(c\) axis. Growth of the needle-like crystal occurs at first, and then deposition on the needle-like crystals and aggregation of them form whiskers. Ca/P molar ratio of the whiskers, measured by inductive coupled plasma analysis, was 1.58.

The shape of the Ca-def HAp whiskers remained in the specimens annealed below 600 °C. The tips of the crystals were rounded off with increasing annealing temperature between 600 °C and 800 °C, and some of the crystals annealed at 900 °C grew into large grains. The analysis of the peak intensities originated in \(\beta\)-TCP crystals appeared in the XRD patterns for the specimens annealed at various temperatures revealed that thermal decomposition of the Ca-def HAp crystals begins at about 800 °C and finishes at about 900 °C.
Planar defects traversing in the whisker in parallel with the (100) plane of the HAp crystal were often observed in HRTEM images of the specimens annealed at 600-800 °C as shown in Fig. 3. The defect expanded into unidentified layered phase with increasing annealing temperature. A thickness of the layer reaches about 10 nm and boundaries between the phase and the Ca-def HAp matrix are coincident. A periodicity of the layer parallel to the (100) plane of the HAp crystal is 1.43 nm, which is not found out in the spacings for the crystal structures of various calcium phosphates and calcium oxides. Since the layered phase was observed only in the specimens annealed at a narrow temperature range of 700-800 °C, it is regarded as a metastable phase appearing in the thermal decomposition process of the Ca-def HAp crystals. The results of EDS microanalysis and IR analysis suggest the metastable phase is a Ca-rich phase. Taking care of the relation between the Ca-def HAp crystal and the Ca-rich metastable phase, lattice constants of the phase are analyzed into $a = 2.86$ nm, $b = 0.943$ nm, and $c = 0.688$ nm with orthorhombic crystal system.

References


Fig. 1 TEM images of the surface of the thinned $\alpha$-TCP crystals (a) before and after hydrolysis for (b) 2 and (c) 4 hours.

Fig. 2 (a-c) TEM images of the $\alpha$-TCP powder samples hydrolyzed for 1, 2, and 3 hours, respectively.

Fig. 3 (a-c) HRTEM images of the Ca-def HAp whisker annealed at 600, 700, and 800 °C, respectively.