GROWTH OF HYDROXYAPATITE WHISKER BY HYDROLYSIS OF α-TRICALCIUM PHOSPHATE STUDIED BY TRANSMISSION ELECTRON MICROSCOPY

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A hydroxyapatite (Ca$_{10}$P$_4$O$_{31}$(OH)$_2$: HAp) whisker has been much interested in as a source material to produce porous body which has crystal structure similar to a bone. Nakahira and his collaborators reported that hydrolysis of α-tricalcium phosphate (α-Ca$_3$(PO$_4$)$_2$: α-TCP) in a mixture of water and alcohol gives whisker shaped Ca-deficient HAp (Ca$_{10-z}$(HPO$_4$)$_z$(PO$_4$)$_{7-z}$(OH)$_{2-z}$·nH$_2$O: $z=0$~$1$). In the report, it is revealed that α-TCP transforms completely to Ca-deficient HAp within several hours and shape of the grown crystal depends on a kind of the alcohol. However, there are few crystallographic investigations on a transformation mechanism and a growth process of an HAp whisker. In this paper, we discuss the crystal growth of an HAp whisker produced by hydrolysis by transmission electron microscopy (TEM).

A high purity α-TCP powder (Taihei Chemical Industries Co., Ltd.) was stirred at 70°C in a water solvent suspending 1-octanol (60ml of 1-octanol in 100ml of water). The initial pH value of the solvent was adjusted to 11.0 with NH$_4$OH. The suspensions containing reaction products were sampled at 1, 3 and 48 hours after hydrolysis and then dripped on Cu grids with holey film for TEM. Observations were performed with JEOL JEM-2010SP and JEM-2000EX operated with an accelerating voltage at 200kV.

Figure 1 shows a TEM image of an α-TCP particle hydrolyzed for 1 hour. Needle-like HAp crystals with a few ten nm in width and a few hundred nm in length grew around the α-TCP particle. After 3 hours of hydrolysis, most of growing HAp crystals had whisker shape (Fig. 2) and there were few needle-like crystals seen in Fig. 1. These images show that at first growth of the needle-like HAp crystal occurs on the surface of the α-TCP, and then deposition of HAp on the needle-like crystals and aggregation of them form HAp whiskers. Fig. 3 shows an image of HAp obtained by the hydrolysis for 48 hours. The whiskers grew along [0001] axis with atomically flat (10-10) surfaces. Some whiskers united on the surfaces with parallel c-axes each other.

As the α-TCP powder used for the specimen preparation mentioned above is too thick for TEM observation, we prepare a thinner specimen by another method to observe the surface of the α-TCP where nucleation of HAp occurs. A sintered α-TCP was shaped into a small thin disk with 3mm in diameter and 0.1mm in thickness. Then the center of the disk was thinned with a dimple grinder until a small hole appears. The holey disk was dipped in water with adjusted pH value of 11.0 for several hours without stirring to protect the thinned region of the disk. Fig. 4 shows a TEM image of an edge of the hole after hydrolysis for 4 hour. The surface of α-TCP was covered with amorphous layer and dendritic structures composed of twigs with 1~2 nm in width and trunks with ~20nm in width are observed on the layer. The dendrite is regarded as an embryo of the needle-like HAp crystal. The image shows nucleation of HAp occurs not on the surface of α-TCP particle but on the amorphous layer.
From these observation results, we can summarize growth process of HAp whiskers by the hydrolysis of α-TCP in the followings. At first, the surface of the α-TCP is dissolved by the solvent and is covered with an amorphous layer. In the next, nucleation of HAp crystals occurs not on the α-TCP but on the amorphous layer, and then deposition of HAp from the solution makes dendrite structures on the nuclei. As the hydrolysis proceeds, the dendrites grow into needle-like HAp crystals with a few ten nm in width and a few hundred nm in length. Finally, the successive deposition of HAp on the crystals and aggregation of the crystals form HAp whiskers.

References