Structural Evaluation of Titanate Nanotube and Nanosheet

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Nanomaterials with one-dimensional nanostructures have attracted much attention due to their potential applications in a variety of novel devices. Especially, TiO2-derived nanotubes which are prepared by a hydrothermal treatment of TiO2 particles in a concentrated NaOH aqueous solution are expected to be useful for several application studies on such as proton conduction, photoinduced hydrophilicity, photocatalysts,and dye-sensitizing solar batteries. However, the crystalline structure and formation mechanism of TiO2-derived nanotubes are still topics under discussion. The elucidation of the crystalline structure and formation mechanism for TiO2-derived nanotubes will be expected to lead to the further development of novel functional materials with one-dimensional nanostructures. The structural change on the molecular scale of anatase-type TiO2 during a hydrothermal treatment was investigated in detail by various analytic techniques such as neutron diffraction in order to clarify the formation mechanisms of titanate based nanotubes.

Two grams of anatase-type TiO2 powder as a starting material were used. They were added in 10 M NaOH aqueous solution. Then the specimens were treated under the hydrothermal reaction at 383 K for 1 to 96 h. Obtained products after hydrothermal treatments were sufficiently washed with deuterated water and dilute HCl aqueous solution and were subsequently separated from the washing solution by filtration. After the washing treatment, they were filtered and subsequently dried at temperatures above 323 K for more than 12 h in an electric oven. Structural evaluation of titanate nanotube samples were evaluated by neutron diffraction at HEMES station. The neutron powder diffraction experiments were conducted for room temperature using the HERMES powder neutron diffractometer installed on Tl-3 port of JRR-3M reactor in the Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. An incident neutron wavelength λ = 1.8196 Å was obtained from a Ge (311) monochromator. The ND data were collected on thoroughly ground powders by a multiscanning mode in the 2 θ range from 5 °to 155 °with a step width of 0.10 °. The 3 g powder sample was wrapped by tungsten foil to form a cylindric shape (10 $\phi \times$ 30 mm).

Fig.1(A) shows the typical structure image of nanotube products prepared by the hydrothermal process. The neutron diffraction pattern shows that the spectrum was unsufficient for the analysis because of the unsifficient substitution of deuterated water in the nanotube structure, as shown in Fig.1(B). It was hard to analysis because there were high backgrounds in the observed data. This is thought to be why the presence of a slight amount of H (H2O) in the measuring sample. For this result, it was found that it was very difficult to prepare a specimen of TiO2-derived nanotubes for ND measurements by using soft chemical process. However, it revealed that the nanosheet-like products composed of highly distorted TiO6 octahedra were generated by a hydrothermal treatment of anatase-type TiO2 and then the anatase-like structures are partially built up with the formative nanotubes by scrolling up these nanosheet-like products.

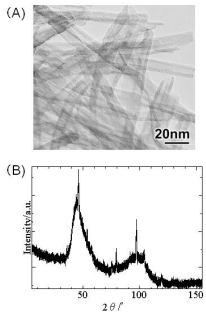

Fig. 1. Fig.1 (A)Typical strucutral image of nanotube and (B) Neutron diffraction of nanotube