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Thermal stability of titanate nanorods and titania nanowires formed from titanate nanotubes by heating

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ABSTRACT

The structure of titanate nanowires was studied by a combination of powder X-ray diffraction (XRD) and 3D precession electron diffraction. Titania nanowires and titanate nanorods were prepared by heating of titanate nanotubes. The structure of final product depended on heating conditions. Titanium nanotubes heated in air at a temperature of 850 °C decomposed into three phases — $Na_2Ti_6O_{13}$ (nanorods) and two phases of TiO_2 — anatase and rutile. At higher temperatures the anatase form of TiO_2 transforms into rutile and the nanorods change into rutile nanoparticles. By contrast, in the vacuum only anatase phases of TiO_2 were obtained by heating at 900 °C. The anatase transformation into rutile began only after a longer time of heating at 1000 °C. For the description of anisotropic XRD line broadening in the total powder pattern fitting by the program MSTRUCT a model of nanorods with elliptical base was included in the software. The model parameters — rod length, axis size of the elliptical base, the ellipse flattening parameter and twist of the base could be refined. Variation of particle shapes with temperature was found.

1. Introduction

Since many potential applications of titanium nanotubes (Ti-NT) need some thermal treatment it is important to study the changes of the structure of Ti-NT due to the temperature variations and also the preparation process. Titanium nanowires can be obtained from Ti-NT just by heating. Similarly to Ti-NT, several phases of nanowires have been reported. Two kinds of thermal behaviour of Ti-NT were reported depending on the presence of sodium ions in the initial structure. The case with the Na ions has been studied by Morgado et al. [1]. The authors studied three samples with different amounts of Na ions. The sample with the highest amount of sodium ions contained sodium hexatitanate ($Na_2Ti_6O_{13}$) and sodium trititanate ($Na_2Ti_3O_7$). The middle sample was a mixture of sodium hexatitanate ($Na_2Ti_6O_{13}$), rutile phase of TiO_2 and anatase phase of TiO_2. These two samples were heated to 800 °C. The last sample with the least amount of sodium ions was heated only to 550 °C and the final phases found there were anatase and metastable β-TiO_2. Nikolic et al. [2] found that the structure of Ti-NT was stable up to 500 °C and then it transformed to sodium hexatitanate nanorods at 700 °C. Yu et al. [3] prepared nanotubes without sodium ions. During the heating at about 400 °C the anatase structure appeared which afterwards transformed to rutile at 700 °C; the transformation was completed at 900 °C. After calcination, aggregates of particles with the diameter between 100 nm and 300 nm were found. Weng et al. [4] reported that the heating (800 °C) leads to decomposition of the tubular structure to nanoparticles. Suzuki and Yoshikawa [5] obtained a combination of rutile TiO_2 and TiO_2 (B) after heating at 800 °C.

This contribution is focused on a study of structural changes of Ti-NT after heating at three temperatures: 850 °C, 900 °C and 1000 °C, respectively. Studies at these higher temperatures are not very frequent in the literature and moreover they were usually performed only in air. More detailed study can help understand better the structural transformations of the nanotubes. For this reason, sets of samples were prepared — they were heated in air and in vacuum, respectively, in order to study the effect of oxygen deficiency. In air, the samples were heated for three different times (105 and 1000 min, respectively) and at two different temperatures (850 °C and 900 °C). In the vacuum, different heating times (105 min and 3000 min) and heating temperatures were chosen (850 °C, 900 °C and 1000 °C). For longer heating times, a set of PXRD patterns was collected in-situ. In both cases (heating in air and in vacuum) one sample was used for continuous heating. The studies were followed by investigations of final shape of particles obtained after heating. The final composition of the sample was verified by total powder diffraction pattern fitting including a new feature in the software, scattering on oval nanorods.

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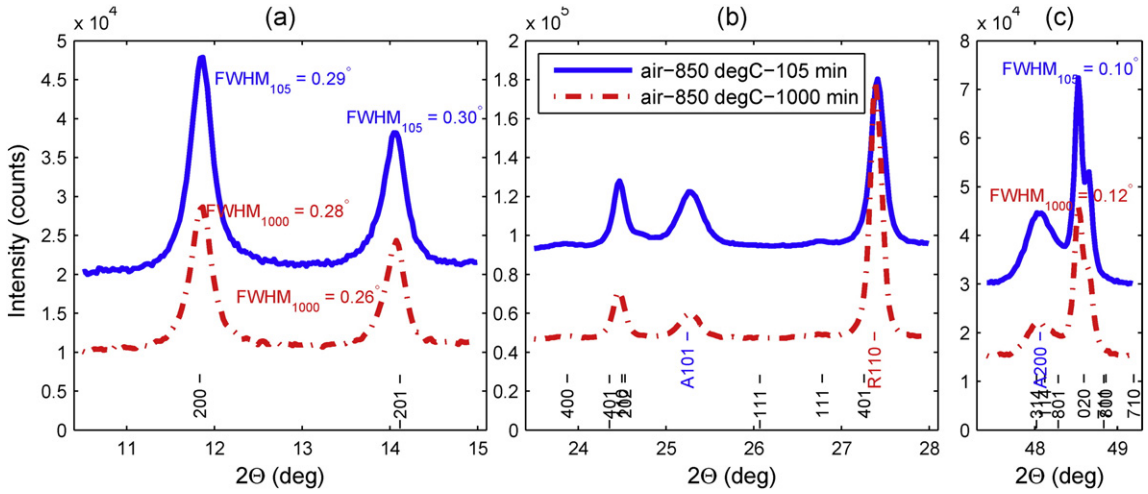

Fig. 1. Parts of PXRD patterns of the sample heated in air at 850 °C: (a) close to low angle $Na_2Ti_6O_{13}$ reflections (bottom black *hkl* marks), (b) close to strong anatase (A) and rutile (R) reflections, (c) close to the (020) $Na_2Ti_6O_{13}$ reflection. Sample heated for 105 min — blue line, 1000 min — dot-dashed red line. Widths of selected lines are marked. [010] direction is expected to be the $Na_2Ti_6O_{13}$ rod axis.

2. Experimental Setup

For phase identification of titanium nanowires and nanorods two complementary methods were applied: powder X-ray diffraction (PXRD) and 3D rotation electron diffraction (PED). The phase transformation was observed in-situ in a PXRD diffractometer. For morphological studies scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied and energy dispersive X-ray spectroscopy (EDX) was used for the determination of chemical composition.

The X-ray measurements were performed on a PANalytical MPD diffractometer equipped with MRI high temperature chamber. As heating elements, both direct heating platinum strip and Pt radiant heater were used. The specimens were mixed with a solvent and spread directly on platinum strip heater. The samples were measured in the Bragg–Brentano geometry with CuKα radiation, and the PIXcel detector. Powder diffraction patterns were measured in the 2θ range from 5° to 80° with the step size of 0.0263° 2θ; total integrating time for one step was 180 s. Incident beam was conditioned by the Soller slits (divergence 0.04 rad) and a beam mask of 5 mm width. Automatic divergence slits were used both in primary and diffracted beams in order to keep an irradiated area constant during the measurement (5×8 mm^2). In front of the PiXcel detector (in scanning mode), other Soller slits (0.04 rad divergence) and Ni β-filter were placed.

ED patterns were collected on a single nanorod as well. As the interaction of electrons with matter is ~10^4 times stronger than that for X-rays, dynamical effects should be taken into account and the interpretation of ED patterns is more complicated than that of XRD patterns. In order to overcome this problem, digital precession electron diffraction (PED) [6] was used to collect ED data. In this method, the electron microscope is controlled by dedicated software only. The electron beam is rotated along a circle at a certain angle (so-called precession angle; 2° in this work) around the optical axis of the microscope. The beam rotation along the circle is sampled with a fixed azimuthal step (3° in this work) which results in 120 individually beam-tilted ED patterns. These patterns are combined into the final PED pattern by (1) aligning all patterns against each other using cross-correlation and (2) summing up the aligned patterns. The set of structure factors extracted from the final PED pattern is closer to kinematical intensities. PED patterns were recorded on JEOL JEM 2100 LaB6 operated at a 200 kV accelerating voltage.

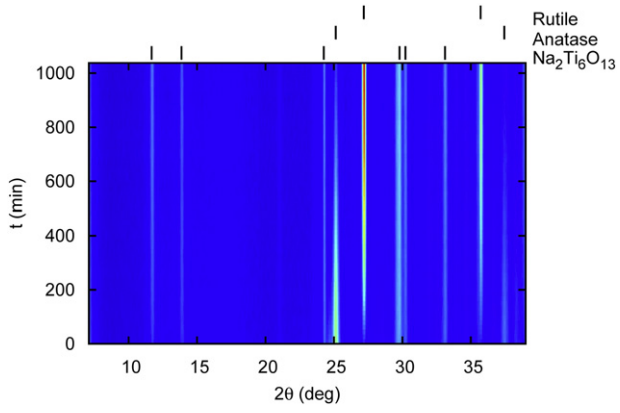

Fig. 2. Time evolution of the diffraction pattern of the sample heated in air at 850 °C for 1000 min.

The TEM observations were performed using the JEOL JEM 2000FX transmission electron microscope. This microscope used tungsten filament as a source of electrons and operated at 200 kV. Nanorods were ultrasonically dispersed in ethanol and a drop of the sample was spread on a holey carbon-coated microscope copper grid.

SEM experiments were performed on a Tescan Mira3 microscope. This microscope had auto emission electron gun operated at 15 keV. Samples were ultrasonically dispersed in ethanol and then a drop of the sample was spread on a special microscope holder.

EDX analyses were also performed on a Tescan Mira3 microscope. Samples were placed on carbon adhesive tape to eliminate the signal from the aluminium microscope sample holder.

3. Measurements

Ti-NT were prepared by the hydrothermal method. The details of the preparation could be found for example in [7]. The nanowires and nanorods were obtained from Ti-NT by heating. The structure of titanate nanotubes was identified as the one of $H_{2-x}Na_xTi_2O_5$ H_2O phase with x ~ 0.4. The structure of Ti-NT was determined with the aid of a combination of X-ray diffraction and electron microscopy (more details could be found in our previous paper [8]). Here, seven samples of titanate nanowires/nanorods under different heating conditions were studied. Three samples were heated in air and five samples were heated in vacuum.

The heating in air was performed in the following way: at first, the sample was heated at 850 °C for 105 min. Then the sample was cooled down and PXRD pattern, SEM images and EDX analysis were taken. In the next step, the sample was heated at 850 °C for 1000 min and after