STRUCTURAL STUDIES OF TITANIA NANOTUBES

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Abstract

The crystal structure of TiO_2 nanotubes was studied by X-ray diffraction and transmission electron microscopy. The structure was identified as -phase of TiO_2. A model based on this structure was created - a 2D sheet rolled into a tube - and used for calculations of powder X-ray diffraction patterns with varied model parameters: the lattice cell parameters: *a*, *b*, *c*, and angle _.

Introduction

After discovery of carbon nanotubes (having large surface area) other nanotubular systems were studied. At the end of 90th of the last century, TiO_2 nanotubes (Ti-NT) were prepared by very simple and cheap method – hydrothermal treatment of TiO_2 powder. Unfortunately, the structure of these nanotubes is not clearly understood and several different structures have been reported.

TiO_2 based materials show remarkable, in particular photocatalytic, properties and they are of high application interest. In addition, Ti-NT have large surface area which is also useful for catalytic applications. Other potential applications of Ti-NT can be found for example in lithium batteries where they can improve the rate of diffusion intercalated lithium ions – small size of lithium ions and structure of Ti-NT – ionic transport in interlayer [1]. The first reported structure of Ti-NT was anatase structure of TiO_2. The study was published by Kasuga et al. [2], who used the single alkali treatment of TiO_2 powder. Since that, high interest in this material began and the amount of possible structures increased. In several papers, the presence of sodium ions in the Ti-NT structure was mentioned. For example in [3], possible structures of $Na_2Ti_2O_4(OH)_2$ or $H_2Ti_2O_4(OH)_2$ type were suggested as mixed $Na_xH_{2-x}Ti_2(OH)_2$. Other reported structures were trititanate [4] ($H_2Ti_3O_7$) or sodium trititanate ($Na_3Ti_2O_7$), $H_2Ti_2O_5$ H_2O [5] or for example $H_2Ti_4O_9$ H_2O [6]. The authors of [5] studied dependence Ti-NT structure on time of hydrothermal method and it was shown how the nanotube is created by rolling the 2D sheet.

Sample Preparation

Samples of Ti-NT were prepared at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic (IMC). The preparation method was a simple hydrothermal treatment of initial powder. In this work, microcrystalline rutile was used as a starting TiO_2 powder. The hydrothermal method consists of heating the initial TiO_2 powder with 10M NaOH.

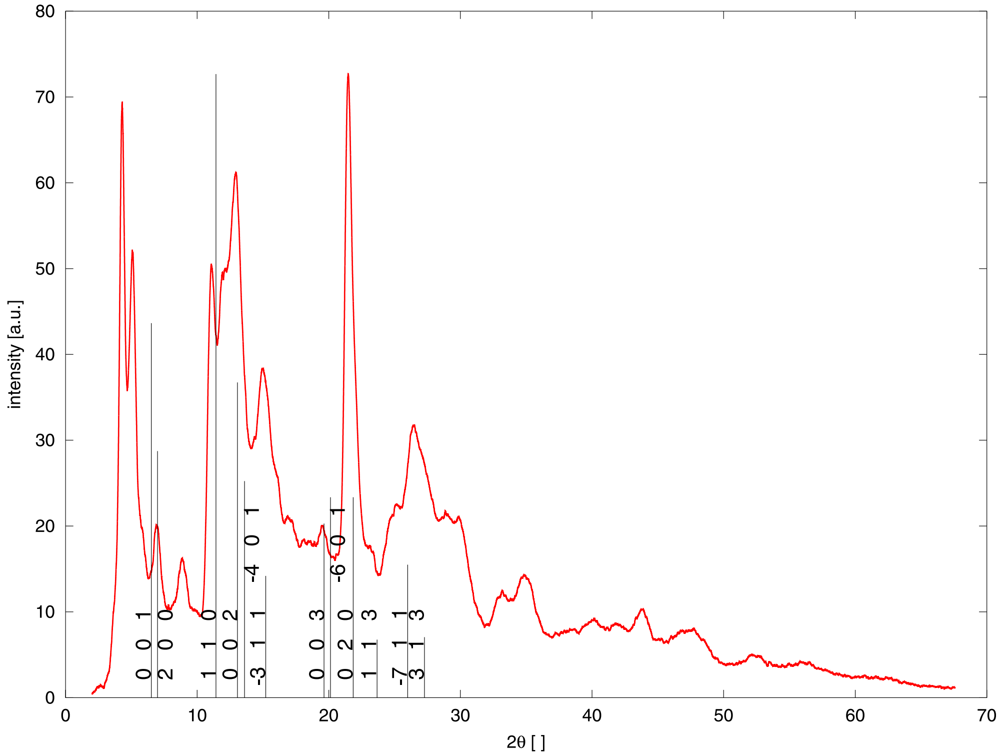

Figure 1. Measured PXRD pattern and theoretical positions of peaks (bars) of -TiO_2.

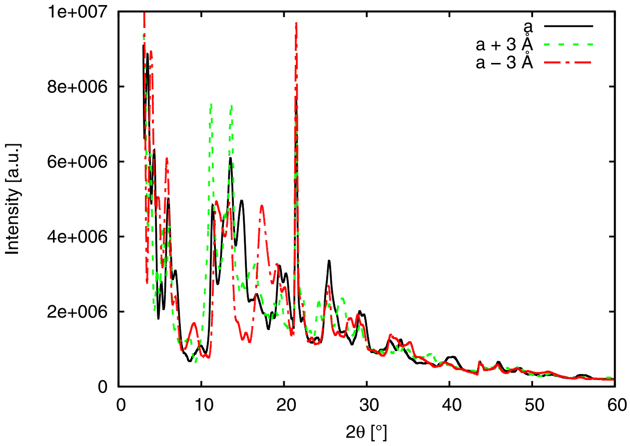

Figure 2. Simulated changes of PXRD pattern due to variations of the lattice parameter *a*.

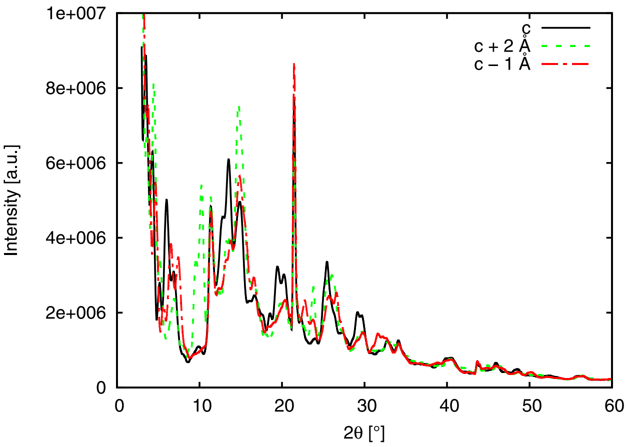

Figure 3. Simulated changes on PXRD patter due to variations of the lattice parameter *c*.

The obtained powder was neutralized by HCl and dried. More details on the preparation can be found in [7].

Measurement

Samples of Ti-NT were measured in the transmission geometry in diffractometer Rigaku Rapid II with Mo-K radiation and 0.3 mm collimator. This diffractometer is equipped with 2D cylindrical image plate detector (Debye-Scherrer geometry). The specimens to the diffractometer were prepared in the following way: the small amount of Ti-NT were mixed with solvent and it was placed into a copper wire holder that was formed into a loop. Measured X-ray 2D pattern was converted to conventional powder X-ray diffraction (PXRD) pattern by the software 2DP.

Transmission electron microscopy (TEM) was performed on 120 kV Tecnai G^2 Spirit 120 with LaB_6 emission gun. The sample preparation technique for TEM can be found in [7]. TEM investigation was performed at IMC.

Results and discussion

In this paper, we will focus on possible structure of Ti-NT that was identified as a -phase of TiO_2. This possible structure was reported in [8]. Here, we have investigated the influence of changes of individual lattice parameters on the calculated X-ray diffraction powder pattern. Measured pattern and calculated position of diffraction peaks of -TiO_2 phase are shown in Figure 1. Some disagreement in peak positions of -TiO_2 taken from the database and those of measured PXRD pattern can be noticed. This disagreement could be due to two different structure - bulk material and nanotubes. -TiO_2 has monoclinic crystal structure, space group *C*2/*m* with the lattice cell parameters: *a* = 12.1787 Å, *b* = 3.7412 Å, *c* = 6.5249 Å, = 107.054° [9]. A structural model of nanotube was made by rolling 2D sheet made from -TiO_2. The variable parameters in this model are the lattice cell parameters of -TiO_2 and multiples of all lattice cell parameters. The multiple of the parameter *c* is given by numbers of walls in nanotube. This can be resolved from high- resolution transmission electron microscopy. The multiples of the other lattice cell parameters *a*, *b* have effect just on the broadening of the diffraction peaks and are not discussed here. The sharp peak at 2 ~ 22° corresponds to the length of the tube – the axis of the tube is given by the lattice cell parameter *b* (from Figure 1). Hence is it possible to find the correct value of this parameter directly. The lattice parameter *c* is going around the circumference of the nanotube and *a* is in the direction to the center of tube cross-section plane. These two lattice cell parameters and the angle cannot be clearly identified directly from the PXRD pattern. In order to understand their role, computer simulations by means of the Debye formula were performed for their different values. The final simulated PXRD was convoluted with the Gauss function that simulated instrumental function of the diffractometer. The corresponding shapes of PXRD patterns obtained for several values of the parameter *a* are depicted in Fig. 2.

It is not easy to distinguish which peaks depend only on this parameter but it is possible to see peaks that do not depend on it, particularly in the low-angle region. For high diffraction angles this cannot be done due to high number of peaks in this monoclinic cell structure. The changes of PXRD patterns due to variations of the parameters *c* and are quite similar (see Fig 3. and Fig. 4).

These simulations can help to see possibilities for obtaining better agreement by variations of free parameters. In general it is difficult for the monoclinic structure to derive clear effects of all the parameters on the pattern. The non-linear least square method was used finally for obtaining the best agreement between the measured and calculated PXRD patterns. The result is shown in Fig. 5. The morphology of the nanotubes can be seen on TEM images (Fig. 6). It can be seen that basic features of the PXRD pattern are modeled well but further improvement cannot be done by variations of the used parameters. Hopefully, including texture effects into calculations can lead to better agreement.

Summary

Titania nanotubes prepared by hydrothermal method were studied by X-ray diffraction in the transmission geometry. A structural model of the nanotube was created by the rolling of the sheet from the monoclinic structure of -TiO_2. It

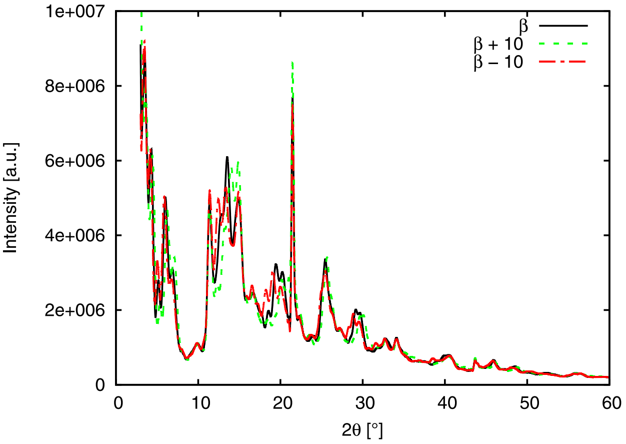

Figure 4. Simulated changes on PXRD patter due to variations of the lattice parameter .

was used for calculation of the PXRD pattern by the Debye formula and main features of the experimental pattern could be explained by this approach. For better agreement of calculated and measured PXRD patterns models of preferred orientation suitable for calculations should be considered and applied together with the Debye formula.

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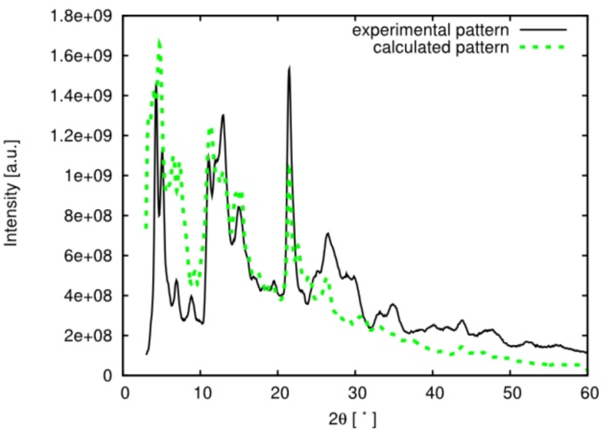

Figure 5. Comparison between measured and calculated PXRD patterns.

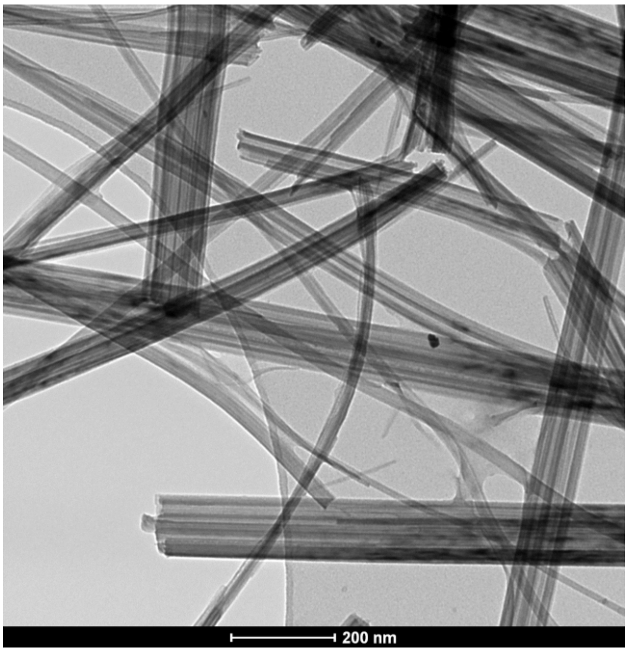

Figure 6. Morphology of Ti-NT (TEM image).

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PREPARATION AND ANALYSIS OF Fe-Zr, Fe-Ti, AND Fe-V COMPOSITES FOR HYDROGEN STORAGE

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Abstract

Fe, Ti, V, and Zr composites were prepared by mixing and dry milling of ferrihydrite with V, TiH_2, and ZrH_2 powders. The samples were annealed in vacuum and hydrogen atmosphere during measurements of the temperature dependence of their magnetic moments in temperature range 20 – 800 °C. Pure metal -Fe, -Zr; Fe_2Zr, TiFe, and Ti_2Fe intermetallic phases and various Fe, Zr, V and Ti oxides were formed by these heat treatments.

Introduction

Transition metals based composites still belong to candidates for hydrogen batteries. Their practical application, however, are connected with some difficulties due to high temperature and relatively slow kinetics of hydrogen desorption of absorption. Their nanocrystalline states exhibit much faster kinetics and lower temperature of hydriding/dehydriding in comparison with coarse grained materials with the same composition [1-3].

It was shown that Zr-rich phases disproportionate and reproportionate by absorbing of hydrogen and $FeZr_2$ and $FeZr_3$ were observed. Zr_2FeH_5 was formed by hydride absorption at room temperature. The disproportionation of Zr_2Fe was unstable and it was very quickly followed by a reproportionation to Fe_2Zr [4-5]. Mechanical alloying of a $Ti_{45}Zr_{38}Ni_{17}$ powder mixture formed an amorphous phase, but subsequent annealing caused the formation of an icosahedral quasicrystalline phase with a small amount of the Ti_2Ni-type crystal phase [6]. After high-pressure hydrogenation at 573 K at a hydrogen pressure of 3.8 MPa, the amorphous phase transformed to a TiH_2-type hydride, while the icosahedral phase was structurally stable even after the hydrogenation.

Experimental details

TThe samples were prepared by from pure ferrihydrite (Sigma Aldrich) and V, TiH_2, and ZrH_2 (Alfa Aesar) powders by dry ball milling or mixing in an agate mortar. The original composition of the composites was 39 wt% of ferrihydrite and 61 wt% of the V, TiH_2, and ZrH_2. The as-mixed powders were compressed into pellets and annealed during the measurement of the temperature dependence of magnetic moment in temperature range 20°C - 800°C in vacuum (10^{-4} Pa) and in the hydrogen (5N). Magnetic measurements were carried out using vibrating sample magnetometer in 50 Oe external field.

The X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were applied for structure and phase analysis. XRD was carried out using X'Pert diffractometer and CoK radiation with qualitative analysis by HighScore® software and the JCPDS PDF-4 database. For a quantitative analysis HighScore plus® with Rietveld structural models based on the ICSD database was applied. ^{57}Fe Mössbauer spectra were measured using ^{57}Co/Rh source in standard transmission geometry with detection of 14.4 keV -rays. The computer processing of the spectra for phase analysis was done using CONFIT package [7].

Results

The XRD phase analysis of the as-mixed samples exhibited mainly presence of the precursors. The composites prepared in an agate mortar contained 61 wt% V and 61 wt% TiH_2 which almost identical with the nominal composition. The dry milled V and TiH_2 based samples showed also the original precursor phases of nominal composition but in ZrH_2 based composite formation of magnetite (33 wt%) and ZrH_2 (68 wt%) was observed. The Mössbauer spectra correspond to the ferrihydrite in V and TiH_2 composites and ferrihydrite and magnetite, -Fe and $ZrFe_2$ in ZrH_2 composite. Changes in the phase compositions during the 20°C - 800°C annealing were detected by the measurement of the temperature dependence of the magnetic moments. The Curie temperatures of -Fe, magnetite, hematite and Fe_2Zr phases were observed there. The presence of these magnetic phases was confirmed by XRD and Mössbauer phase analysis. The phase compositions of the annealed samples are given in Tables 1 and 2. There are significant differences after annealing in vacuum and in hydrogen. The hydrogen atmosphere helped to reduce ferrihydrite to pure iron and to form of intermetallic phases. The powders contain small or negligible amount of oxides even after the handling in ambient atmosphere by preparation of the samples for XRD and Mössbauer measurements. The vacuum annealing caused formation of Zr, Ti, and V oxides but their formation after the annealing during the sample preparation for the phase analysis cannot be excluded. Iron ions embedded in the matrix of oxides stabilize of tetragonal (t-ZrO2) form, which is present in the sample together with the stable monoclinic (m-ZrO2) form. This is confirmed by the presence of 0.06 atom fraction of Fe(III) detected by means MS.

Table 1. Results of the phase analysis of the annealed composites prepared by mixing in an agate mortar.

XRD [wt. %]				
TiH_2 + ferrihydrite (vacuum)	2 $FeTiH_{0.06}$	10 Ti_2Fe	42 -Fe	46 Ti_xO
TiH_2 + ferrihydrite (hydrogen)	7 $FeTiH_{0.02}$	10 Ti_2Fe	11 FeTi	71 $TiO_{0.325}$
V + ferrihydrite (vacuum)	11 V_2H	25 $VO_{0.03}$	64 Fe_3O_4	
V + ferrihydrite (hydrogen)	21 V_2H	70 -Fe	9 Fe_3O_4	
Mössbauer spectroscopy [Fe atom fractions]				
TiH_2 + ferrihydrite (vacuum)	0.39 -Fe	0.32 Fe-Ti	0.29 Fe(III)	
V + ferrihydrite (vacuum)	0.93 Fe_3O_4	0.07 Fe(III)		
V + ferrihydrite (hydrogen)	0.97 -Fe	0.03 Fe(III)		

Table 2. Results of the phase analysis of the annealed composites prepared by dry ball milling.

XRD [wt. %]				
TiH_2 + ferrihydrite (vacuum)	34.5 TiH_2	32.4 Fe_3O_4	9 Fe	24.1 $TiO_{0.48}$
ZrH_2 + ferrihydrite (vacuum)	53.9 m-ZrO_2	14.7 t-ZrO_2	7.6 -Fe	23.9 -Zr
V + ferrihydrite (vacuum)	10.7 V_2H	24.6 $VO_{0.03}$	64.7 Fe_3O_4	
V + ferrihydrite (hydrogen)	20.8 V_2H	69.9 -Fe	9.3 Fe_3O_4	
Mössbauer spectroscopy [Fe atom fractions]				
TiH_2 + ferrihydrite (vacuum)	0.35 -Fe	0.6 Fe_3O_4	0.05 Fe(III)	
ZrH_2 + ferrihydrite (vacuum)	0.06 Fe(III)	0.14 -Fe	0.8 Fe_2Zr	
ZrH_2 + ferrihydrite (hydrogen)	0.07 Fe(III)	0.59 -Fe	0.34 Fe-Zr-H	

Conclusions

From the above results we can conclude that formation of intermetallic phases which can be interesting for hydrogen absorption can be yielded by annealing in hydrogen atmosphere. The presence of FeTi, Ti_2Fe and Fe_2Zr intermetallic was confirmed but Zr_2Fe and Zr_3Fe phases well known for their ability to store hydrogen were not detected in the Zr based samples.

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