HYDROTHERMAL SYNTHESIS OF TiO_2 NANOTUBES FROM CONCENTRATE OF TITANIUM ORE OF PIZHEMSKOE DEPOSIT (RUSSIA)

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A high cost of TiO_2 nanoparticles and their demand in industry determine the timeliness of the hydrothermal method of synthesis of titanium dioxide nanotubes from the low-cost natural mineral raw materials. The starting material (non-magnetic fraction of gravity concentrate of titanium ore of Pizhenskoe deposit) and synthesized samples were characterized by scanning electron microscopy, X-ray diffraction and X-ray fluorescence methods.

Keywords: TiO_2 nanotubes, hydrothermal method, titanium ore, Pizhenskoe deposit.

ГИДРОТЕРМИЧЕСКИЙ СИНТЕЗ НАНОТРУБОК ДИОКСИДА ТИТАНА ИЗ КОНЦЕНТРАТА ТИТАНОВОЙ РУДЫ ПИЖЕМСКОГО МЕСТОРОЖДЕНИЯ (РОССИЯ)

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Высокая стоимость наночастиц TiO_2 и их востребованность в промышленности определяют актуальность синтеза нанотрубок диоксида титана гидротермическим методом из недорогого минерального сырья. Исходный материал (немагнитная фракция гравитационного концентрата титановой руды Пижемского месторождения) и синтезированные образцы были исследованы с помощью сканирующей электронной микроскопии, рентгенодифракции, состав определен рентгенофлуоресцентным методом.

Ключевые слова: нанотрубки TiO_2 , гидротермический синтез, титановая руда, Пижемское месторождение.

Introduction

Titanium is one of the strategic metals of modern industry. The demand for titanium has been steadily increasing, and this trend will obviously continue. In Russia there are mainly undeveloped deposits, titanium concentrate is not produced. On the territory of Komi Republic the prospects of mining industry are associated with the largest deposits of titanium (Yaregckoe and Pizhenskoe). New applications of titanium ore based on its mineralogical and processing characteristics have a real commercial interest: the list of commodity products is expanding (and consequently the prospects for production), energy costs are reducing, environmental risks are decreasing, efficiency of sustainable development of region is increasing. One of the promising directions of solution of this problem can be the synthesis of titanium dioxide nanotubes from mineral raw materials (for example from titanium ore of Pizhenskoe deposit).

In recent decades one-dimensional nanostructure materials, derived from titanium dioxide, have been widely used in photocatalysis, as a base for catalysts, implants, reagents enhancing blood coagulability, batteries etc. [1–5].

Due to a high cost of commercially available TiO_2 nanoparticles their synthesis from cheap natural raw materials by hydrothermal method becomes very important.

The aim of this article: the development of scientific basics of synthesis of titanium dioxide nanotubes based on the mineral raw materials using a simple hydrothermal method.

Experimental Procedure

Titanium nanotubes can be obtained by several methods, such as sol-gel, electrospinning, template synthesis, chemical vapor deposition (CVD), etc. Each method has its advantages and disadvantages depending on the implementation. After the pioneer works by T. Kasuga et al. [6] the hydrothermal method became one of the most applied methods for the production of one-dimensional (1D) nanostructured TiO_2 products. The authors previously published a number of works on the synthesis of TiO_2 nanotubes from synthetic analogs of titanium minerals and their application [7–9].

TiO_2 nanotubes were produced by a simple hydrothermal method. The procedure for the preparation of nanostructures from synthetic TiO_2 is described elsewhere [7, 9]. In this work this procedure is adapted for the non-magnetic fraction of gravity concentrate of titanium ore of Pizhenskoe deposit.

In a typical preparation 0.8 g of starting ore (reduced size) was placed in 100 ml autoclave, where 80 ml of 10 M NaOH solution were added. The autoclave was kept at 110 °C

Fig. 1. Diffraction pattern of the starting material (Q – quartz, R – rutile)

Рис. 1. Дифрактограмма исходного сырья (Q – кварц, R – рутил)

Fig. 2. Diffraction pattern of synthesized sample (Q – quartz, T – sodium titanate)

Рис. 2. Дифрактограмма синтезированного образца (Q – кварц, T – титанат натрия)

during 24 h (temperature sensor was mounted on the stove, not inside the autoclave). After the hydrothermal reaction the autoclave was cooled to room temperature, and the resulting flaky precipitate was washed successively by distilled water and solution of hydrochloric acid (0.1 M) until neutral pH (6.5-7). The washed samples were dried in the oven at 90 °C for 12 hours.

The shape and size of the starting ore and synthesized samples were obtained by scanning electron microscopy (TESCAN Vega 3). The crystalline structures of the initial ore and synthesized samples were analyzed by diffractometer (Shimadzu XRD-6000), the material composition was studied by X-ray fluorescence (XRF Shimadzu-1800).

Results and Discussion

Until recently the starting material for TiO_2 nanotubes synthesis was only high-purity synthetic analogs [1–5, 7]. In 2011 a group of scientists published a paper [10], which provided data on the production of titanium dioxide nanotubes by the hydrothermal method from Thai leucoxene. According to those data, Thai leucoxene was

enriched. The starting material for nanotubes was a rutile concentrate with a TiO_2 content more than 93 %.

Mineral and chemical composition of bulk concentrates of titanium ore of Pizhenskoe deposit is given in [11]. Beside leucoxene pseudorutile, Fe-ilmenite, ilmenite and siderite were found. Chemical composition (wt. %): TiO_2 – 50.07, SiO_2 – 30.52, Fe_2O_3 – 13.37, MnO – 0.26, CaO – 0.04, MgO – 0.17, Al_2O_3 – 2.16, K_2O – 0.77, Na_2O – 0.02, P_2O_5 – 0.16, ZrO_2 – 0.10, S – 0.09, CO_2 – 1.90, H_2O^+ – 0.39.

In comparison with bulk concentrates of titanium ore of Pizhenskoe deposit characterized in [11] the used starting material – non-magnetic fraction of gravity concentrate of titanium ore of Pizhenskoe deposit – the content of Fe_2O_3 and TiO_2 is lower, while content of SiO_2 and Al_2O_3 – higher. Chemical composition (wt. %): TiO_2 – 42.12, SiO_2 – 46.57, Fe_2O_3 – 1.04, Al_2O_3 – 7.57, K_2O – 1.61, MnO – 0.06, CaO – 0.13, MgO – 0.37, SO_3 – 0.06, P_2O_5 – 0.17, ZrO_2 – 0.05, NbO – 0.11. The average particle size after grinding – 20–40 μm .

The X-ray diffraction pattern (Fig. 1) indicates that the starting ore is mainly a mixture of two phases: rutile and quartz. The peaks are clear, that testifies to a high crystallinity of these phases. The weak reflections of clay minerals, ilmenite and anatase are present.

The synthesized sample (Fig. 2) is a mixture of two phases: quartz and hydrogen titanate ($\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$), which is consistent with the results of [1–3]. Chemical composition (wt. %): TiO_2 – 74.68, SiO_2 – 12.64, Fe_2O_3 – 5.44, Al_2O_3 – 4.71, Na_2O – 0.14, K_2O – 0.93, MnO – 0.64, CaO – 0.12, MgO – 0.25, P_2O_5 – 0.09, ZrO_2 – 0.08, NbO – 0.14.

The formation of titanium dioxide nanotubes takes place in several stages: the slow dissolution of raw is accompanied by the epitaxial growth of layered sodium titanate nanosheets → exfoliation of nanosheets → folding of nanosheets into tubes → growth of nanotubes along X axis → exchange of sodium ions by protons during washing and separating of nanotubes from each other. The crystalline lattice of initial rutile is converted into amorphous product

Fig. 3. Titanium dioxide nanotubes
Рис. 3. Нанотрубки диоксида титана

at alkali processing, after treatment with distilled water and solution of hydrochloric acid the titanium dioxide nanotubes are formed. According to [7], the nanotubes consist of layers of titanate, which composition depends on such synthesis conditions as temperature and duration of treatment, ratio of solid and liquid phases.

Fig. 3 shows SEM image of synthesized TiO_2 nanotubes. The channels inside the produced nanotubes are clearly visible. The resolution of scanning electron microscope allows evaluating their outside diameter (70–100 nm) and length (up to 4500 nm). The synthesized TiO_2 nanotubes have a large surface area, which is, according to [7], by orders higher than the specific surface of the starting raw, which provides high sorption properties.

Conclusion

The TiO_2 nanotubes were obtained using simple hydrothermal method in Laboratory of mineral raw technology in Institute of Geology Komi SC UB RAS. An inexpensive natural raw material – non-magnetic fraction of gravity concentrate of titanium ore of Pizhemsкое deposit – was used as a starting material. The synthesized titanium dioxide nanotubes have outer diameter 70–100 nm and length up to 4500 nm. The synthesized TiO_2 nanotubes have a large surface area that results in a good sorbent material.

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