PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Hydrothermal Synthesis of Potassium Titanate Nanotubes Doped with Magnesium, Nickel, and Aluminum

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Abstract—Study of the phase formation in the systems TiO_2–$MO(M_2O_3)$–KOH–H_2O (M = Mg, Ni, Al) from crystalline and coprecipitated X-ray-amorphous mixtures demonstrated that doped potassium titanate nanotubes can be obtained in a hydrothermal treatment of coprecipitated hydroxides in the temperature range 170–220°C. The average outer diameter of the thus synthesized nanotubes strongly depends on the element being introduced and is 5 to 10 nm. The nanotubes have a large specific surface area (200–300 m^2 g^{-1}) and are stable up to a temperature of 500°C, above which they decompose to give potassium hexatitanate. The nanotubes can be used as sorbents, photocatalysts, and components of composite materials for frictional and construction purposes.

Alkali metal polytitanates of general formula $M_2Ti_nO_{2n+1}$ (M = Na, K) have, depending on n, a layered (n = 3, 4, 5) or tunnel structure (n = 6, 7, 8) formed by zigzag layers of titanium-oxygen octahedra. Figure 1 shows schematically the arrangement of layers at various values of n [1]. Depending on their composition and structure, these compounds can be used as solid electrolytes, insulators, sorbents, and photocatalysts and also can serve as a basis for composite frictional and construction materials [2–8]. These complex oxides can be effectively used in many of these application fields only when obtained in the highly dispersed phase. Recently, a large number of publications have been concerned with various methods for synthesis of these compounds in the nanosize state. Nano- and microscopic rods, as well as nanowires and whiskers, are obtained by high-temperature calcination of a mixture of mechanically dispersed components and by the method of crystallization in a melt [1, 2, 9–11]. Rolling-up of zigzag layers into tubular structures is observed under hydrothermal conditions, which makes substantially larger the specific surface area of the resulting material [4].

Russian and Indian researchers have extensively studied the influence exerted by various substitutions in the octahedral framework of ceramic $K_2Ti_4O_9$ [6, 7, 11–14]. The effect of doping of titanate nanotubes with cobalt on the photocatalytic activity in the reaction of decomposition of organic compounds was studied in [15]. According to the results of these studies, the substitution of titanium with cations of another valence leads to a change in the energy gap width, shift of optical parameters, and increase by approximately an order of magnitude in the specific surface area. Therefore, a study of isomorphic substitutions in potassium titanate nanotubes seems to be a topical task whose solution will extend even more the opportunity for application of materials based on alkali metal polytitanates.

The goal of our study was to examine the influence exerted by the crystalline state of the starting mixtures and by parameters of the hydrothermal treatment on the formation of potassium titanate nanotubes in substitution of a part of titanium ions with ions of another valence (Al, Mg, and Ni).
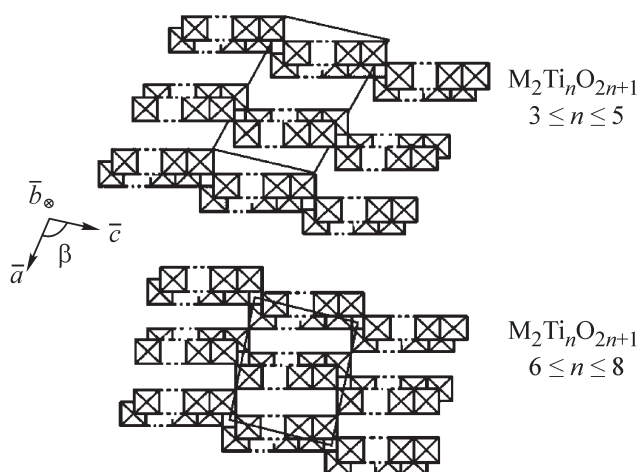
Fig. 1. Schematic structure of polytitanates $M_2Ti_nO_{2n+1}$ (M = Na, K) at varied content of titanium [1].

EXPERIMENTAL

We synthesized samples by the hydrothermal treatment of two different starting mixtures. The first of these was produced by mixing of stoichiometric amounts of oxides of the required metals, and the second, by coprecipitation of hydroxides of the metals.

For the first synthesis method, we took weighed portions of the oxide TiO_2 (special-purity grade) in the anatase modification and oxides of doping metals MgO (chemically pure), NiO (pure), and Al_2O_3 (chemically pure). The fraction of the oxides being introduced was 2.5 mol %. The oxides were mixed in an agate mortar with a minor amount of water, and after drying the mixture was placed in a 10 M aqueous solution of KOH (chemically pure) and agitated with a magnetic rabble for 1 h. Further, the suspension was placed in autoclaves for a hydrothermal treatment. The ratio between the oxides and the alkaline solution was 1 g per 10 mL of the solution; the inner volume of the autoclaves was 80% filled with the suspension. The samples produced by the given method were subjected to a hydrothermal treatment for 24 h at temperatures of 170–180°C, the pressure in the autoclaves was 1–10 MPa. Steel autoclaves with a Teflon liner were used to synthesize samples at 170–180°C, and those with a platinum liner, for synthesis at 220°C.

To obtain the starting precursors by the second method, we precipitated the hydroxides with NH_4OH (23-5 brand, special-purity grade) from mixtures of aqueous solutions of titanium tetrachloride ($TiCl_4$, special-purity

grade) and salts of the doping elements: $MgSO_4·7H_2O$ (chemically pure), $NiCl_2·6H_2O$ (chemically pure), and $Al(NO_3)_3·9H_2O$ (special-purity). The amounts of the salts were taken so that the content of a doping element was 2.5 and 5.0 mol % in terms of the corresponding oxides. The precipitation was performed at pH 9, and after that the resulting precipitates were thoroughly washed with distilled water to remove soluble impurities and filtered until a negative reaction to chlorine ions was reached. Prior to a hydrothermal treatment, the obtained compositions were dried at $T = 100$°C for 3 h and mechanically ground. The hydrothermal treatment of this set of samples was performed in the temperature range 170–180°C. The ratio between the alkaline solution and the air-dry powder, treatment duration, and degree of autoclave filling was the same as those in the first case.

The phase composition of the samples was found from powder diffraction patterns measured with a DRON-3 X-ray diffractometer (CuK_α radiation). An integrated thermal analysis was made on a Netzsch STA 429 thermal analyzer in the temperature range 25–1200°C at a heating and cooling rate of 20 deg min^{-1}, with the sample mass being about 100 mg. The onset of a thermal effect was determined from the intersection of tangents to the base line of DSC curve and to the initial branch of the thermal-effect curve. The shape and size of nanoparticles was determined by high-resolution transmission electron microscopy (HRTEM) on a JEOL-2100F electron microscope at an accelerating voltage of 200 kV (wavelength 0.25 Å) (Physical-Technical Institute, Russian Academy of Sciences). The specific surface area of the starting samples was determined by the method of low-temperature nitrogen adsorption and processing of the resulting data by the Brunauer–Emmett–Teller (BET) equation. The measurements were made with a Quantachrome Nova-1200e gas analyzer. The samples were preliminarily dried at 200°C for 1 h. The error in determining the specific surface area did not exceed 5%.

According to the results of an X-ray phase analysis (XPA), the treatment for 24 h at a temperature of 180°C was insufficient, when anatase was used as a starting component, for a full occurrence of the reaction in which nanotubes were formed, with a considerable amount of unreacted titanium oxide remaining in the product (Fig. 2, curve *1*). In this case, potassium titanate nanotubes were obtained under the hydrothermal conditions at a synthesis temperature of 220°C. Introduction of oxides
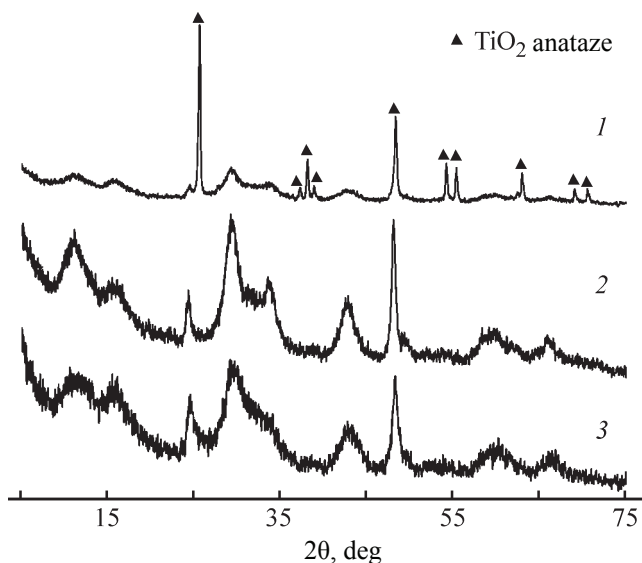
Fig. 2. Diffraction patterns of samples produced by hydrothermal treatment in a 10 M KOH solution for 24 h: TiO_2 with anatase structure at (*1*) 180 and (*2*) 220°C and (*3*) hydrated titanium dioxide at 170°C. (2θ) Bragg angle; the same for Figs. 3 and 6. TiO_2 (anatase)
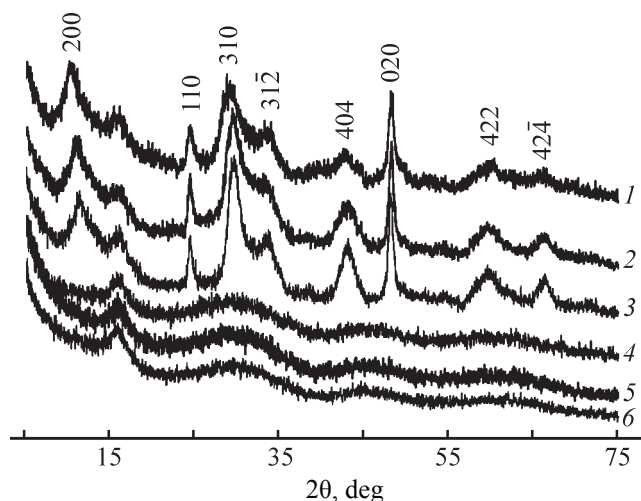

Fig. 3. Diffraction patterns of (*4–6*) starting mixtures produced by the coprecipitation method and (*1–3*) products of their hydrothermal treatment in a 10 M KOH solution for 24 h. The composition of the precipitate corresponded to the ratio $0.95TiO_2 : 0.05MO$ (M_2O_3), where M is (*1, 4*) Ni, (*2, 5*) Al, and (*3, 6*) Mg. The *hkl* indices are specified according to [16].

Fig. 4. Micrographs of potassium titanate nanotubes produced by hydrothermal treatment of precipitates of composition $0.95TiO_2 : 0.05MO$ (M_2O_3), where M = (a) Ni, (b) Al, (c) Mg.

of doping metals into the starting stock does not yield a homogeneous product, with reflections related to the oxides being introduced present in the diffraction patterns. If the coprecipitation method is used to prepare the starting mixtures, the temperature of the reaction in which nanotubes are formed decreases (Fig. 2).

According the XPA with the diffraction patterns presented in Fig. 3, the starting mixtures are strongly amorphized powders with the strongly broadened peaks at 2θ angles in the ranges 20–40 and 40–50°, in which the strongest reflections lie upon a hydrothermal treatment. This confirms that an intimate bonding between metal-oxygen octahedra is already formed in this stage.

Under the hydrothermal conditions, nanotubes crystallize from the precipitated hydroxides, which is confirmed both by the results of XPA (Fig. 3, curves *1–3*) and by TEM data (Fig. 4). The results of a microprobe analysis (EDX) confirmed that nanotubes contain doping components in the amount corresponding to that introduced in precipitation, which confirms the isomorphic incorporation of magnesium, nickel, and aluminum into titanium-oxygen layers. In this case, a change in the average size of the octahedra affects the outer diameter of nanoparticles being crystallized. Nickel-doped nanotubes have an average outer diameter of 10–11 nm and specific surface area of 301 m² g⁻¹,
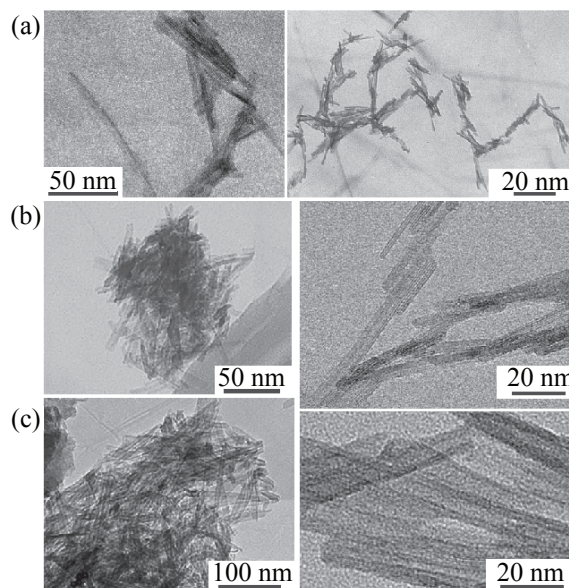
and those containing magnesium and aluminum, 7–8 nm (294 m² g⁻¹) and 5–6 nm (220 m² g⁻¹), respectively.

Despite their largest outer diameter, the larger specific surface area of the nickel containing titanate nanotubes,
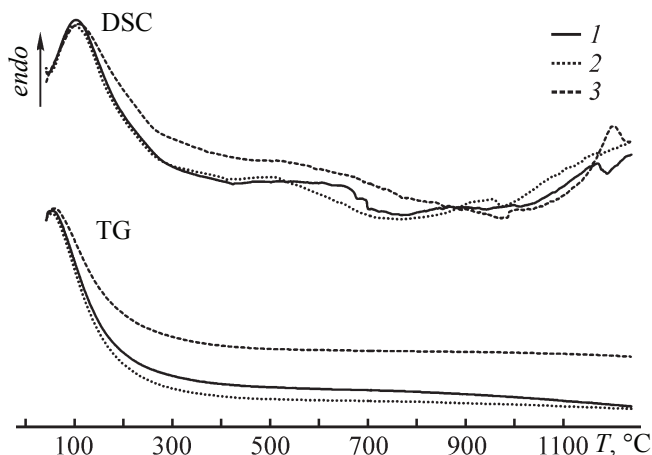
Fig. 5. DSC and TG curves for heating of potassium titanate nanotubes nanotubes produced by hydrothermal treatment of precipitates of composition $0.95TiO_2 : 0.05MO$ (M_2O_3), where M = (*1*) Ni, (*2*) Al, (*3*) Mg. (*T*) Temperature.

seen in the micrographs in Fig. 4, is in all probability due to their weaker agglomeration.

The thermal stability of the resulting nanomaterials was examined by means of an integrated thermal analysis. It was found (Fig. 5) that, up to a temperature of 300°C, there occurs dehydration of the synthesized nanoparticles, accompanied by a strong endothermic effect and by a loss of mass in the range from 8 to 12%. Upon further heating in the temperature range 500–1050°C, the tubular structure gradually disintegrates, which is accompanied by a strongly broadened exothermic effect in the DSC curves.
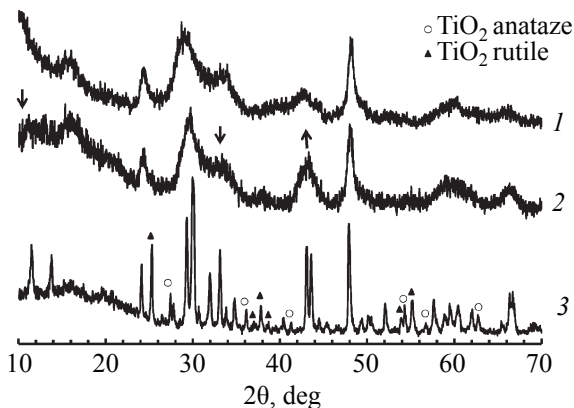

Fig. 6. Diffraction patterns of nickel-doped potassium titanate nanotubes (*1*) before and (*2*, *3*) after calcination for 1 h at temperature of (*2*) 600 and (*3*) 900°C (the peaks not indicated at the curves belong to the $K_2Ti_6O_{13}$ phase).

The X-ray diffraction patterns of samples calcined at 600°C show a decrease in the intensity of the [200] and [312] reflections, which is probably due to the gradual formation of particles having a different morphology. The recrystallization and sintering, with particle size growing from nano- to micrometers, occurs in the temperature range 900–1200°C (Fig. 6), with the main crystallizing phase being in this case $K_2Ti_6O_{13}$ and residual TiO_2. In the temperature range 850–1000°C, there also occurs a phase transition of anatase formed in the decomposition of nanotubes to rutile.

CONCLUSIONS

(1) It was found that, with the method of joint precipitation of hydroxides used to obtain the starting mixtures, it is possible to lower the hydrothermal treatment temperature necessary for crystallization of potassium titanate nanotubes from 220 to 180°C and to effectively introduce doping components in this stage.

(2) It was demonstrated that the isomorphic substitution of titanium ions in the octahedral framework with other cations leads to a change in the geometric size and, accordingly, in the specific surface area of the resulting nanotubes: nickel-doped samples have an average outer diameter of 10–11 nm, and those containing magnesium and aluminum, about 8 and 5–6 nm, respectively.

(3) The thermal properties of the nanotubes were examined. It was shown that the samples are stable up to 500°C and decompose above this temperature.

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