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INVESTIGATION ON SYNTHESIS AND MICROSTRUCTURE OF POTASSIUM TETRATITANATE

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Potassium tetratitanate $K_2Ti_4O_9$ was synthesized from the anatase–K_2CO_3 starting materials by the heating calcination. DTA, TG, DTG and XRD methods were used to study the formation of intermediate compounds and the final product. The characterization of the $K_2Ti_4O_9$ crystals was carried out by means of scanning electron microscope (SEM).

Keywords: *calcination, DTA potassium tetratitanate, SEM, synthesis, TG, XRD*

Introduction

K_2O–TiO_2 system is of some technological interest because crystalline potassium titanates grow readily in fibrous form. In this system the compounds K_4TiO_4, K_2TiO_3, $K_2Ti_2O_5$, $K_2Ti_4O_9$, $K_2Ti_6O_{13}$ and $K_2Ti_8O_{17}$ should form [1–8]. In addition, two new compounds, $K_6Ti_4O_{11}$ [9] and $K_4Ti_3O_8$ [10] have been reported. In other old reports of higher titanates of potassium, Ryan and Knoff [11] obtained X-ray diffraction evidence for $K_2Ti_3O_7$ and $K_2Ti_5O_{11}$. Schmitz-DuMont and Reckhard [12] have determined that these compounds are present in the system $K_2Ti_2O_5$–TiO_2 (a part of system K_2O–TiO_2 which is rich in TiO_2). According to Bamberger *et al.* [10], $K_2Ti_3O_7$ consists of a mixture of $K_2Ti_2O_5$ and $K_2Ti_4O_9$, and $K_2Ti_5O_{11}$ consists of a mixture of $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$.

The crystal structures and physicochemical properties of potassium titanates, $K_2O.\ nTiO_2$, are dependent on the value of n, which gives rise to a wide variety of properties from compound to compound. The nature of the anionic assemblies is strongly affected by the value of n, varying from chains or bidimensional sheets for n=1 to layers for $2 \leq n < 6$ and finally to tridimensional frameworks for $n \geq 6$ [10].

Fibrous and acicular titanates are advanced reinforcing materials for the preparation of composites, frictional materials for brakes, sorbents and photocatalysts [13–15]. In spite of various applications of potassium titanates, the synthesizing methods are limited to calcination [14, 16–18], hydrothermal reaction [19–21] and flux growth [22]. The morphologic control is a difficult and challenging topic in the material synthesis and products with different morphologies, such as grain and whisker may be prepared under different synthesis conditions.

Although high-quality potassium titanate whiskers with a large length/diameter value, a narrow size distribution, good whisker morphology, and high yield can be prepared by flux growth, the flux must be separated and reused, so that this method cannot produce continuously and is costly. The advantages of the calcination method are that it uses no flux and is a continuous-product method with low product cost [14].

In this paper $K_2Ti_4O_9$ compound synthesis was carried out by the calcination and slow-cooling method. Differential thermal analysis (DTA), thermogravimetry (TG), derivative thermogravimetry (DTG) and X-ray diffraction (XRD) were applied to investigate the synthesis of $K_2Ti_4O_9$. The crystal shapes and the size of grown crystals were investigated.

Experimental

Starting materials were dry reagent grade: K_2CO_3 (POCH–Gliwice, purity 99.8%) and TiO_2 in the form of anatase ('Police' Chemical Works, purity 99.5%). A reactant mixture with a TiO_2/K_2O molar value of 4.0 was prepared by mixing the powders, and homogenizing and grinding them. Mechanical treatment is one of methods to increase the reactivity of solids [23–25].

DTA, TG and DTG, were performed using a MOM type derivatograph (Hungary). Conditions: air atmosphere, heating rate 10°C min^{-1}, Pt crucible, Al_2O_3 as reference material, temperature interval 20–900°C. To study the nature of possible intermediate phases, the thermal analysis was interrupted at 500, 650, 700, 770 and 850°C i.e. at temperatures determined on the basis of derivatograms courses. The products obtained during DTA interrupted at various temperatures were cooled to room temperature by re-

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moving the sample in platinum crucible from the furnace and identified by means of X-ray phase analysis.

X-ray powder diffraction analysis of the samples was carried out using a model DRON-2.0 diffractometer (Russia), equipped with a copper anode generating Ni-filtered CuK_α radiation. Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction files [26] were consulted for all phase analyses.

$K_2Ti_4O_9$ compound synthesis was carried out by heating the samples of raw materials mixture up to temperature of 950°C (soaking time at this temperature was 24 h) as well as up to 1150°C (soaking time at this temperature was 3 h) at which melting of $K_2Ti_4O_9$ took place. After calcining at 1150°C slow cooling with the controlled rate of 25°C h^{-1} to the temperature of 950°C was carried out.

The morphologies of the starting materials and samples after calcination were observed via scanning electron microscopy (SEM; Model Tesla BS 340, Czech Republic). Microscope observations were made after coating the samples surface with a thin layer of gold.

Results and discussion

Thermal analysis provided the first information about the temperature region of the potassium titanates formation and determined the thermal stability of titanates [27]. Figure 1 shows DTA, TG and DTG curves of K_2CO_3+4TiO_2 mixture. The intermediate compounds rich in TiO_2 formed by the gradually loss of CO_2 from the starting material within 500–900°C. The mass losses observed on TG and DTG curves are accompanied by three endothermic effects on DTA curve. Their minima are located at about 600, 700 and 850°C.

The derivative of the mass loss curve shows three distinct mass loss steps. Each loss is thought to be accompanied by the possible formation of intermediate phases. The X-ray patterns after heating a sample at various temperatures (Table 1) confirm this hypothesis.

XRD investigation of a sample of the mixture K_2CO_3+4TiO_2 heated to the temperature of 500°C showed on insignificant decrease of intensity of diffraction lines of TiO_2 in comparison with the initial mixture which was not subjected to the heat treatment; formation of new phases was connected with it but their lines were not distinctly marked on the diffraction pattern. The further insignificant decrease in intensity of lines of TiO_2 was determined after heating the sample to the temperature of 650°C; the intensity of lines of new phases, such as $K_2Ti_8O_{17}$ and $K_2Ti_6O_{13}$ was also insignificant.

The decrease of intensity of lines due to the precursors (K_2CO_3, TiO_2) continued together with the increase of the temperature of heat treatment to 700°C. The presence of the intermediate titanates was marked distinctly on the

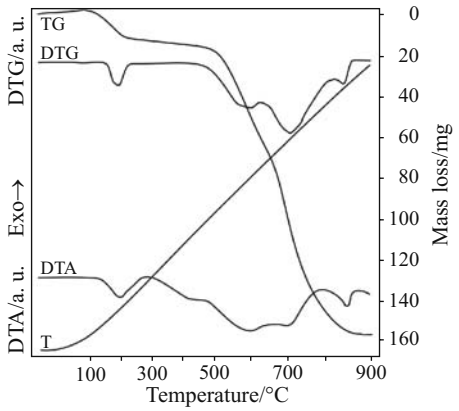

Fig. 1 TG, DTG and DTA curves of mixed solids with molar formula K_2CO_3+4TiO_2

diffraction pattern of the sample. The lines of precursors on the diffraction pattern of the sample heated to the temperature of 770°C were very weak; the diffraction lines of $K_2Ti_6O_{13}$ were the most intensive. According to [28, 29], above 600°C, $K_2Ti_8O_{17}$ tends to decompose to $K_2Ti_6O_{13}$ and TiO_2. According to [30] TiO_2–anatase is formed above 500°C and TiO_2–rutile close to 800°C. The final product $K_2Ti_4O_9$ occurred beside $K_2Ti_6O_{13}$ after heating the sample to the temperature of 850°C. The diffraction pattern of the sample heated to the temperature of 950°C showed only the lines of the final compound $K_2Ti_4O_9$.

Scanning electron micrographs of the starting materials are presented in Figs 2 and 3 show scanning electron micrographs of mixed solids with molar formula K_2CO_3+4TiO_2 heated up to 950°C (24 h holding). Fibrous crystals $K_2Ti_4O_9$ were short.

That is why the consecutive $K_2Ti_4O_9$ syntheses were carried out by heating up the raw materials mixture up to the temperature of 1150°C and then $K_2Ti_4O_9$ was melted. Incongruent melting temperature of $K_2Ti_4O_9$ is 1114±15°C [31]. According to [18], $K_2Ti_4O_9$ melts with decomposition to $K_2Ti_6O_{13}$ stable solid phase and to K_2O-rich liquid phase.

While cooling the sample the products formed as a result of $K_2Ti_4O_9$ decomposition react with each other. Applying the cooling rate of 25°C h^{-1}, $K_2Ti_4O_9$ whiskers of high length to diameter ratio significantly exceeding the minimum value required for whiskers, i.e. 20–25 can be obtained (Fig. 4).

Table 1 Non-isothermal heating of mixed solids

Temperature/°C	Phase composition
20	precursors
500	precursors
650	precursors, intermediate
700	precursors, intermediate
770	precursors, intermediate
850	$K_2Ti_6O_{13}$, $K_2Ti_4O_9$
950	$K_2Ti_4O_9$

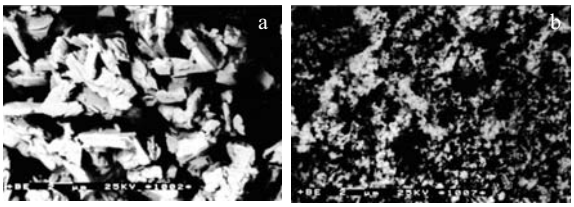

Fig. 2 SEM micrographs of the starting materials: a – K_2CO_3, b – TiO_2–anatase

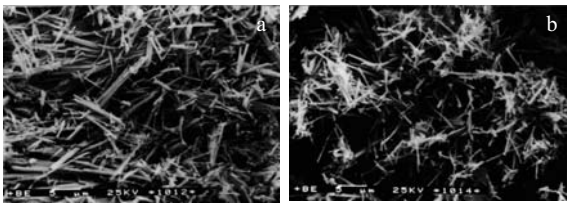

Fig. 3 SEM micrographs of sample calcined at 950°C for 24 h

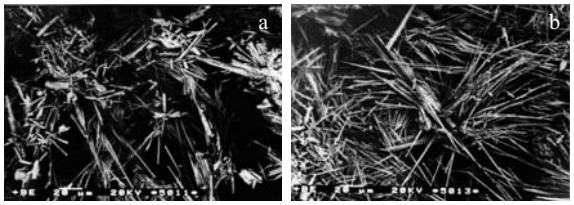

Fig. 4 SEM micrographs of sample calcined at 1150°C for 3 h and cooled to 950°C at a rate of 25°C h^{-1}

As a result potassium tetratitanate whiskers synthesized by calcination–slow cooling method can be used as sorbents and friction materials, which have no strict requirements for morphology and size.

Conclusions

Investigations of synthesis of potassium tetratitanate produced by heating the mixture with molar formula K_2CO_3+4TiO_2, was carried out using thermal and X-ray phase analyses. It was found that compound $K_2Ti_4O_9$ was formed through the intermediate compounds, i.e. potassium titanates rich in TiO_2. $K_2Ti_4O_9$ compound obtained as a result of heating up the raw materials mixture to 950°C (soaking time was 24 h) formed short fibrous crystals. Relatively thin and long $K_2Ti_4O_9$ crystals were obtained by melting $K_2Ti_4O_9$ at the temperature of 1150°C for 3 h, and then slow cooling to the temperature 950°C. Applying the cooling rate of 25°C h^{-1}, $K_2Ti_4O_9$ whiskers of high length to diameter ratio significantly exceeding the minimum value required for whiskers, i.e. 20–25 can be obtained.

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