INVESTIGATION OF PROCESSES THAT TAKE PLACE UNDER THE WARMING OF TITANIUM DIOXIDE, RECEIVED VIA HYDROLYSIS OF VARIOUS TITANIUM ALCO-OXIDES

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Processes that take place under the warming of titanium dioxide pre-cursors, received via hydrolysis of various titanium alco-oxides have been studied. Temperature intervals have been investigated within which processes of dehydration, deposition, and crystallization take place, as well as a phase composition of products that form under pre-cursors thermal processing.

Keywords: titanium dioxide, anatase, rutile, titanium alco-oxides, pre-cursor, thermal processing, synchronized thermal analysis, X-ray phase analysis

One of the main objectives of modern non-organic chemistry is the development of new methods of substances' synthesis that provide the receipt of materials with a regulated exploitation characteristics' complex, first of all, with high frequency and fixed granulometric structure [1]. This problem arises particularly in the creation of new powder materials, production of which nowadays is one of the major goals of the world economy. Besides, especially high development progress can be observed in the production and implementation of non-metal powders, among which an important place is occupied by a highly toxic titanium dioxide [2]. It is used in the production of special ceramics, sensors, photo-catalysts, microwave technics, etc [3-5]. All works, aimed for the development of titanium dioxide receipt methods with stable exploitation characteristics are considered to be urgent nowadays [1].

Alco-oxide method is referred to the most perspective means of fine dust TiO_2 powders receipt. Its important advantage is the ability to achieve homogeneity of powders up to their molecular level. Alco-oxide method implies the undergoing of titanium alco-oxide hydroxylation reaction with a deposition of gel-pre-cursor – oxy-hydroxide of titanium that transforms into the titanium dioxide under its further thermal processing. The selection of pre-cursor thermal processing conditions defined the characteristics of the received TiO_2 powder, its granulometric and phase structure in particular.

The objective of this work is the investigation of processes that take place under the warming of **titanium dioxide pre-cursors (TD)**, received via hydrolysis of various titanium alco-oxides thermal processing and the definition of phase structure of products that form under products' thermal processing. To synthesize TD samples we have used alcohol solutions of titanium tetra-etoxide (TD-1 sample), titanium tetra-isopropoxide (TD-2), titanium tetra-propoxide (TD-3), tetra-butoxide (TD-5). After deposition and washing, sediments were dried to a constant mass consecutively on air and in drying bottle over melting $CaC1_2$.

Thermal analysis was carried out on a facility STA 449C Jupiter (Netzsch, Germany) (joint hinge mass equaled 7-14 mg, argon atmosphere, warming up to 1000 °C with speed 10 degrees per minute). The control of phase, morphological, and chemical composition of substances that formed on different pre-cursors' formation stages was carried out via methods of X-ray phase analysis (diffractometer XRD 7000, Shimadzu, Japan), electric microscopy, and X-ray spectre analysis (electronic microscope S-3400N with an attachment for PCA, Hitachi, Japan).

The analysis of received termogrammes (Fig. 1-5) shows that they contain endothermic effects that are accompanied by a decrease in substances' mass, and exothermic, that undergo without alterations in mass or with its little alterations. Endothermic effect is also linked to processes of water and alcohol remains removal from pre-cursors composition that teke place under the warming of materials up to 280-320 °C. As X-ray phase analysis showed, materials that have been dried on air under indoor temperature, as well as those that have been ignited under the temperature that doesn't exceed 320 °C, stay in X-ray amorphous condition and doesn't reflect on the X-ray picture. Under further TiO_2 pre-cursors warming, in interval of 350-600 °C, takes place the process of anatase phase and X-ray amorphous TiO_2 that is reflected in thermogrammes by the exothermic effect, and in X-ray pictures – by a strengthening of anatase line intensity. The ignition of samples under the temperature higher than 650 °C leads to the formation of rutile phase and the decrease in anatase phase in their structure.

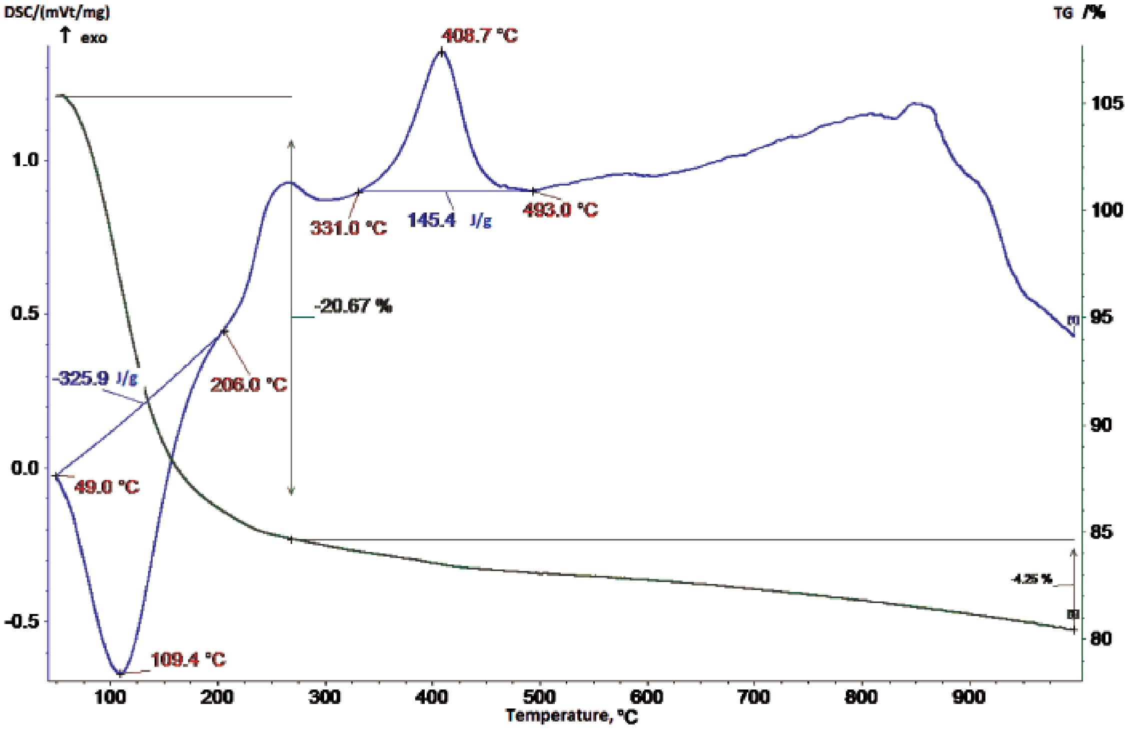


Fig. 1. TD-1 pre-cursor thermogram

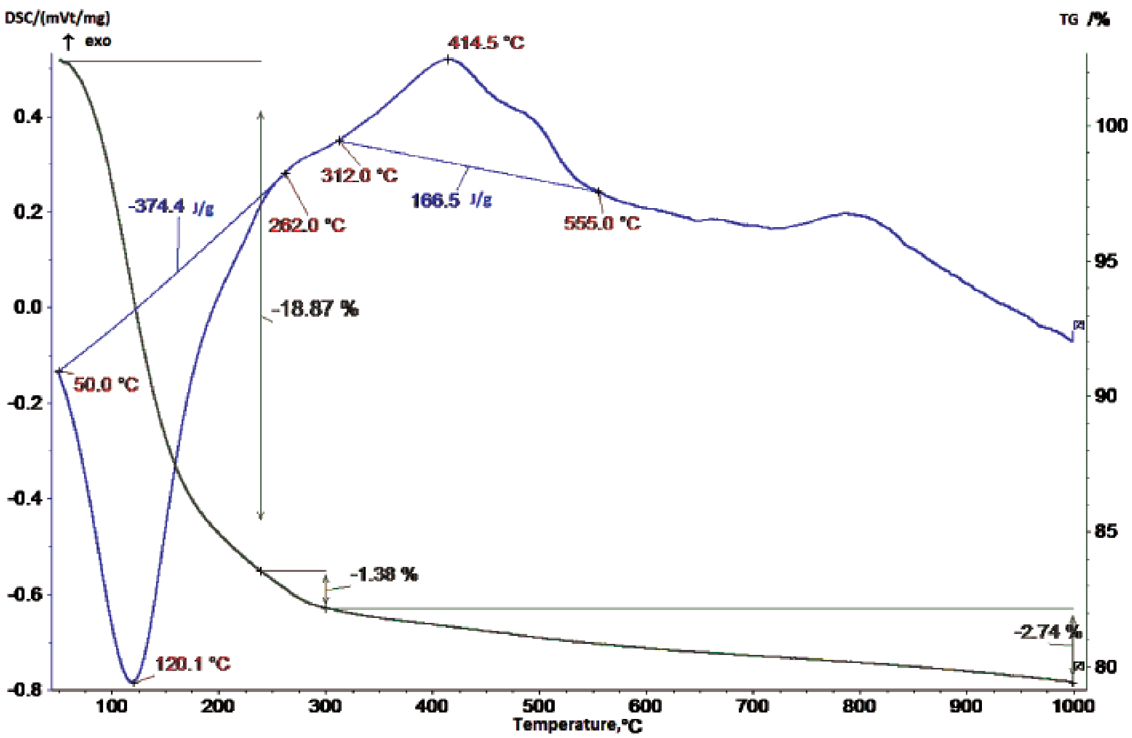


Fig. 2. TD-2 pre-cursor thermogram

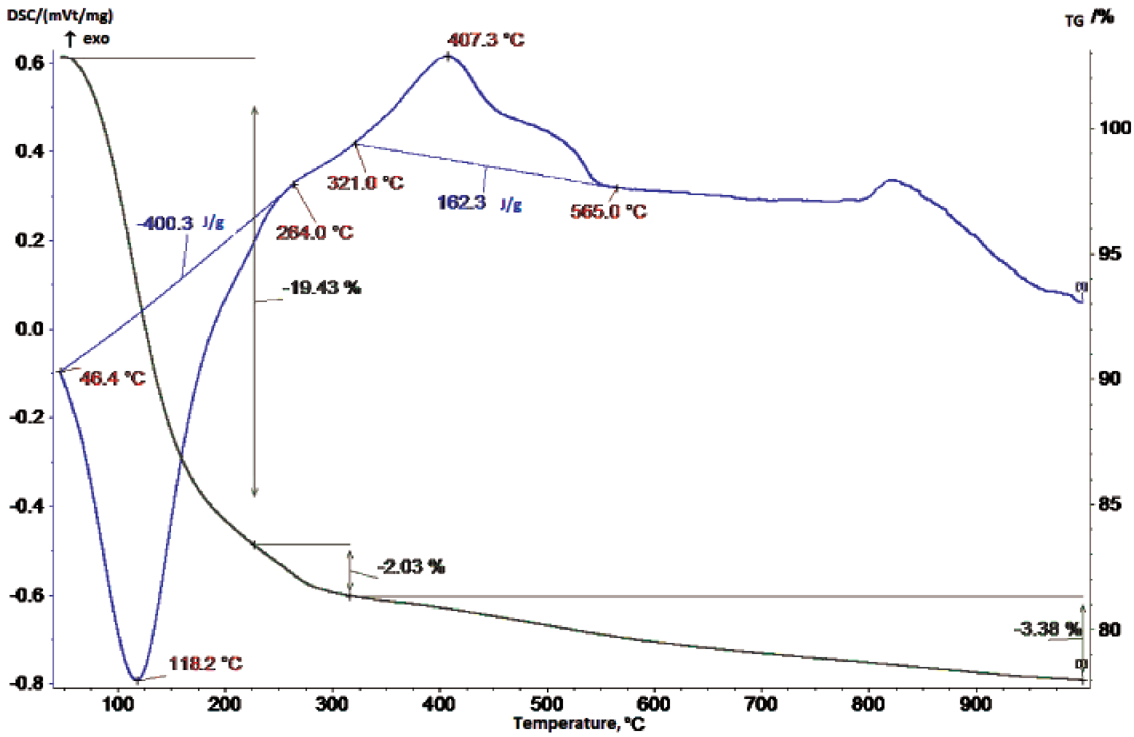


Fig. 3. TD-3 pre-cursor thermogram

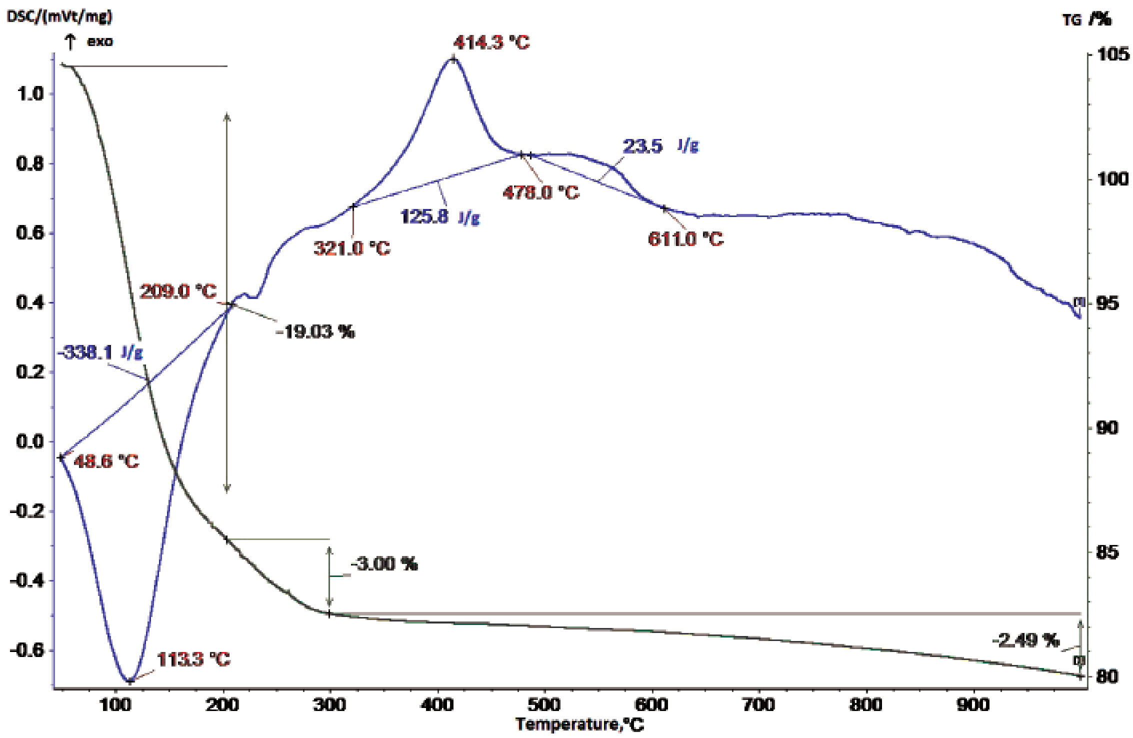


Fig. 4. TD-4 pre-cursor thermogram

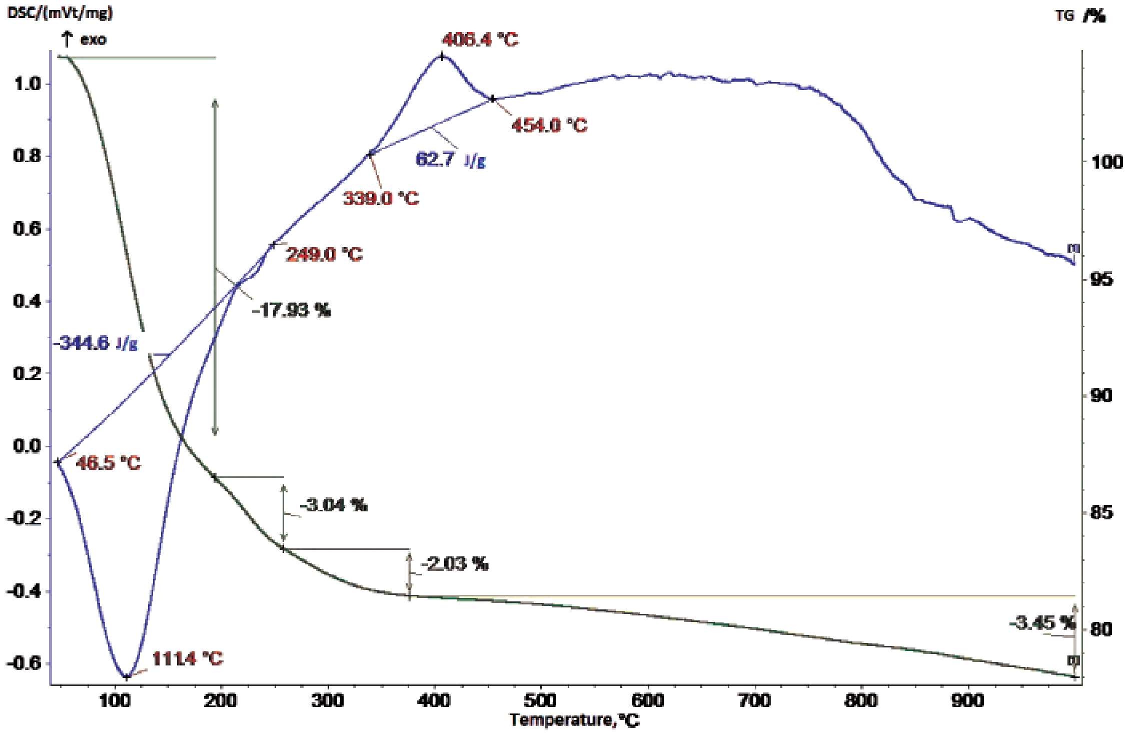


Fig. 5. TD-5 pre-cursor thermogram

In materials, ignited up to 900 °C rutile phase is exposed by X-ray picture (TD-2, TD-4, and TD-5) or a mixture of rutile and anastase phase (TD-1 and TD-3). The highest main rutile peak intensity and, therefore, the highest content of this phase has the sample TD-4. In samples TD-1, TD-2, and TD-5 rulite content is approximately equal.

In all samples that have been ignited up to temperature higher than 900 °C X-ray picture exposes only the rutile phase. The structure formation process undergo under the warming of TiO_2 pre-cursor is illustrated in the table, on the example of TD-4 sample.

An impact of TD-4 sample ignition temperature upon the intensity of line I/I_0 = 100% on the X-ray picture

Warming temperature, °C	Phase composition	Line intensity, imp.
20	X-ray amorphous	103
400	Anatase	278
600	Anatase	648
920	Rutile	1150

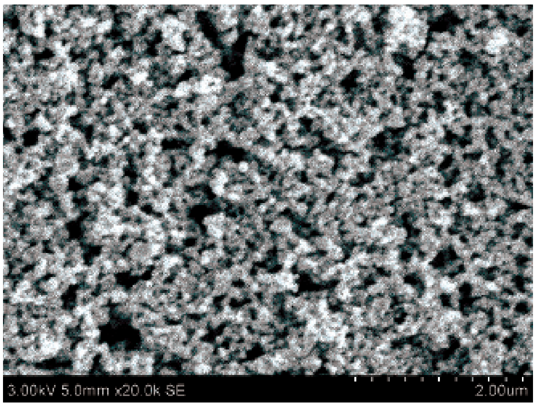
The comparison of the beginning, extremum (peak), and ending temperature of dehydration and anatase crystallization processes on thermogrammes of pre-cursors' samples shows that temperature of titanium alco-oxide that is used for a pre-cursor receipt, weakly influence these parameters: the difference does not exceed 10-15 °C.

Heat effects (**ΔH**) of these processes within TiO_2 pre-cursors also faintly depend on a chemical nature of titanium alco-oxide that has been used for their synthesis. Though some decrease in dehydration process ΔH is observed in the line TD1 > TD2 > TD3 > TD4 > TD5 from 49 to 37 Joule per mole of TiO_2, it might testify a weakening of molecules' connection to substances' structure. ΔH of anatase crystallization in the described line grows from –16 to –7 kJoule per mole of TiO_2.

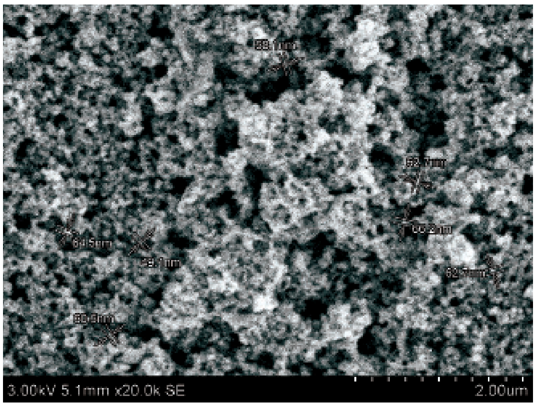
From Fig. 1-5 it is seen that anatase crystallization in X-ray amorphous samples of TD-1, TD-4, and TD-5 undergoes in one stage, while for samples TD-2 and TD-3 it takes two stages. It can be linked to the received pre-cursors' samples' size and agglomeration degree.

As shown by SEM microphotographies, initial particles' size of all pre-cursors' samples that have been dried under indoor temperature equals 60-120 nm (Fig. 6). Samples of TiO_2

pre-cursors TD-4 and TD-5 have the smallest particles' size, in average 88 and 60 nm correspondingly, they are grown to each other into agglomerates and are close to sphere shape. In samples TD-1, TD-2, and TD-3 particles are more agglomerated. Obviously, agglomeration of samples' particles complicates the undergoing of anatase crystallization process from X-ray amorphous dioxide. This statement is also testified by the widening of the corresponding peaks that is observed in the thermogrammes of these samples.



a



b

Fig. 6. SEM microphotographies of titanium dioxide pre-cursors TD-1(a) and TD-5(b)

According to the results of this research, we can conclude:

1. Under the warming of pre-cursors two kinds of processes take place: substances' dehydration (with a removal of alcohol remains) and their crystallization. Because of eolation-oxeolation processes takes place an ordination of pre-cursors' structure that is accompanied by the substance transformation from X-ray amorphous into crystal condition – consequently to anatase and rutile modification of titanium dioxide. Close indexes of dehydration ad crystallization processes' heat effects of TiO_2 pre-cursors that were received from various titanium alco-oxides testify a weak impact of the initial substances' chemical nature upon the formation of materials' crystal structure.

2. Depending on pre-cursors' thermal processing conditions, final product (titanium dioxide powder) can be received either with disordered crystal structure (pre-cursor ignition under a temperature lower than 300 °C), or with an anatase structure pre-cursor ignition under a temperature lower than 350-650 °C), or with a rutile structure pre-cursor ignition under a temperature higher than 900 °C).

3. Chemical nature of titanium dioxide dependent pre-cursors' morphological characteristics: the smallest particles and the lowest agglomeration are present in titanium dioxides, received from titanium tetra-butoxide and tetra-tretbutoxide. Considering the value and availability, titanium tetra-butoxide is recommended for use as an initial material.

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