AN IMPACT OF SYNTHESIS PROCESS PARAMETERS UPON THE STRUCTURE AND SIZE OF TITANIUM DIOXIDE PARTICLES

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By the means of thermo-gravimetry, electronic microscopy, and x-ray phase analysis has been studied the process of obtaining titanium dioxide of different morphology and phase composition. AN impact of pH hydrolysis, initial substances and SAS concentration, and pre-cursor incineration temperature influence upon particles size and obtained titanium dioxide structure has been investigated.

Keywords: titanium dioxide, synthesis, particles, anatase, rutile, surface-active substances

Non-organic chemistry on its current development stage plays as a fundamental basis for the creation of new generations of functional materials. Characteristics of hardphase multi-component materials in metastable condition are defined not only by their chemical composition, but also by their different levels' structure. A preparation of materials with a given characteristics complex present special requirements to the conditions of obtaining **intermediate products (pre-cursors)** with a definite chemical and phase composition and high homogeneity that must be secured on the synthesis stage and saved through all way to the final product [1, 2]. The importance of these requirements is affirmed while synthesizing oxide materials' pre-cursors that are in fact the basis of accurate ceramics. Their functional characteristics are defined by the presence of definite crystal and homogeneous structure in their composition.

For example, an implementation of nanostructures titanium dioxide in photo-catalytic water conversion will allow us, in future, to realize the process of hydrogen obtaining by a more economic method that, in its turn, will allow us to use hydrogen as an ecological material in the production of electric energy. Among the existing polymorphous forms titanium dioxide in its anatase modification shows the greatest activity in photo-stimulated catalytic and photo-electric reactions. The photoactivity strengthening is explained by a higher Fermi level of anatase (3,3–3,4 eV), compared to rutile (3,1–3,2 eV) [3].

To define a possibility to obtain titanium dioxide with a programmed characteristics complex a research, aimed for defining the correlation between main synthesis technology parameters (pH environment, reagents' concentration, SAS presence) and final product characteristics has been carried out.

Experimantal part

Hydrated titanium dioxide has been obtained via its deposition from titanium tetrachloride solutions. Water ammonia solution was used as an alkaline agent. The process realization was carried out on a continuous scheme and it secured the constant correlation of involved components within the process. In experiments solutions of $TiCl_4$ with a concentration of 0,046–0,13 mole per liter and water ammonium with a concentration of 0,186–0,541 mole per liter was used. Hydrolysis was carried out under constant indexes of pH_d that equal 1,0; 2,0; 3,0; 5,0; 7,0, and 9,0. Isopropanol and butanol were used in experiments with SAS. The definition of titanium oxy-hydrate synthesized samples' particles' size (titanium dioxide pre-cursors) was done on a laser particles analyser Microsizer-201 and on the scanning electric microscope S-3400N («Hitachi», Japan). Processes that take place under the warming of titanium oxy-hydrate were studied via method of synchronized thermal analysis on the facility «STA 449 C Jupiter» («Netzsch», Germany). The batch mass equaled 10-15 mg, and argon warming up to 1000^0C speed in atmosphere was 10 degrees per minute. The control of phase substances composition was carried out on an x-ray difracturemeter XRD 7000, (Shimadzu, Japan).

Results and discussions

Summarizing experiments we have discovered that within the process of chemical titanium oxy-hydrate deposition under $pH_d = 1$, its particles' size equals 30-50 nm, while the sample that was deposed under $pH_d = 9$ initial particles' size reaches 100-120 nm. Along with the increase in pH_{os}, particles become more homogeneous according to their granulometric composition. An increase in reagents' concentration provides for the obtaining material with bigger particles. It is why pre-cursor synthesis process should be carried out with $pH_d < 3$ and using the most diluted initial solutions.

On the thermogram of titanium oxy-hydrate sample (Fig. 1) one endothermic and two exothermal effects are present: endoeffect is observed in within temperature interval

65-220 °C, it is accompanied by a decrease in sample mess by 55 % and is related with the removal of water molecules from the deposition. An index of seemed energy of pre-cursors dehydration activation process (E_{ak}), calculated via the methodic [4, 5] is located in the interval of 24,4–32,3 kJoule per mole and generally increases along with a decrease in pH_{oc}. Under warming up to 300-400 °C takes place a condensation of OH-groups, left in TiO_2 (mas loss equals 2,5 %) and the formation of anatase phase within the sample, its presence is defined by x-ray graphics. Warm that deposes under the substance crystallisation dependents the general exothermic character of the undergoing processes.

The undertaken research shows that under the warming of samples take place the processes, that can be characterized by the following scheme:

$$TiO_2\times 4H_2O \xrightarrow{-4H_2O(t=30\text{-}388^oC)} TiO(OH)_x \xrightarrow{-xOH(t=388\text{-}600^oC)} TiO_2\ (\text{anatase}) \xrightarrow{(t=600\text{-}1100^oC)} TiO_2\ (\text{rutile}).$$

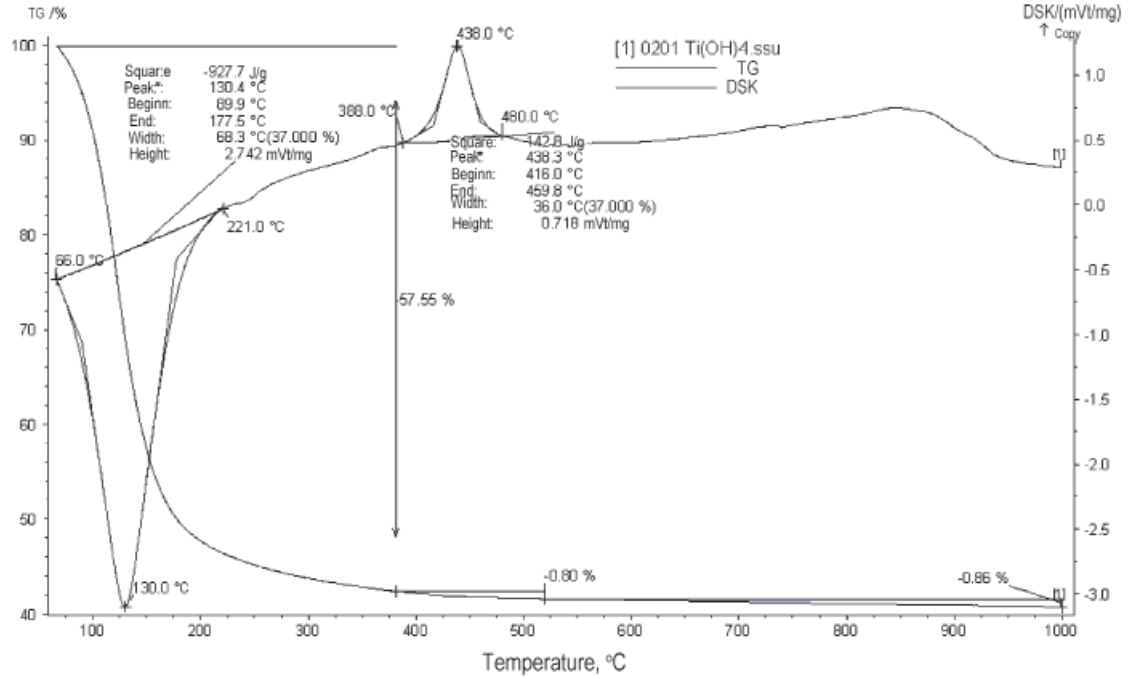

Fig. 1.Thermogram of titanium oxy-hydrate, obtained under pH = 9

From the example of titanium oxy-hydrate, synthesized under pH = 9,0, an impact of thermal processing conditions upon a phase composition of obtained material has been observed. It has been defined that under the process of thermal processing of the sample takes place a reconstruction of its crystal structure: under the worm up to 300–600 °C the anastase phase prevails in the material, and under its ignition up to 1100 °C the rutile titanium dioxide modification does.

Besides pH_{oc}, the hydrolysis process speed and, therefore, the formed deposition particles' construction and morphology can be affected by the alcohol additions that are present in the reaction solution, they show their surface-active characteristics [6-8]. In experiments iso-propile (IPA) and butile (BA) alcohol was used as an organic addition. Such coise was determined by the presence of highly-reactive groups within them.

As shown by experiments (Fig. 3), the usage of SAS allows us to obtain titanium dioxide precursor with more homogenuous in their structure particles, between which a division difference is observed. Obviously, this effect is explained by the particles' surface stabilisation and, therefore, their agglomeration ability decrease.

SAS presence in the deposition of titanium oxy-hydrate influences the process of phase formation under warming. It has been defined that SAS presence significantly slows down the transformation of obtained product from its amorphous structure into crystal, thus impacting the obtained titanium dioxide particles' size (Fig. 4, table).

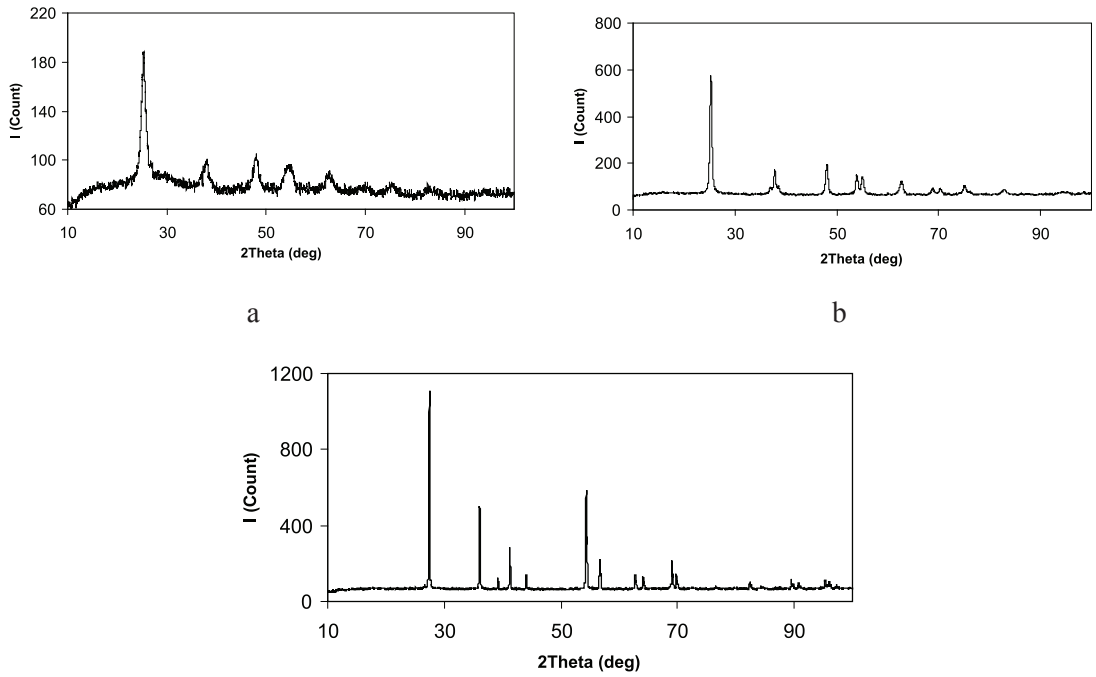

Fig. 2. X-ray picture of titanium dioxide samples, ignited under the temperature (°C): 300 (a), 600 (b), and 1100 (c)

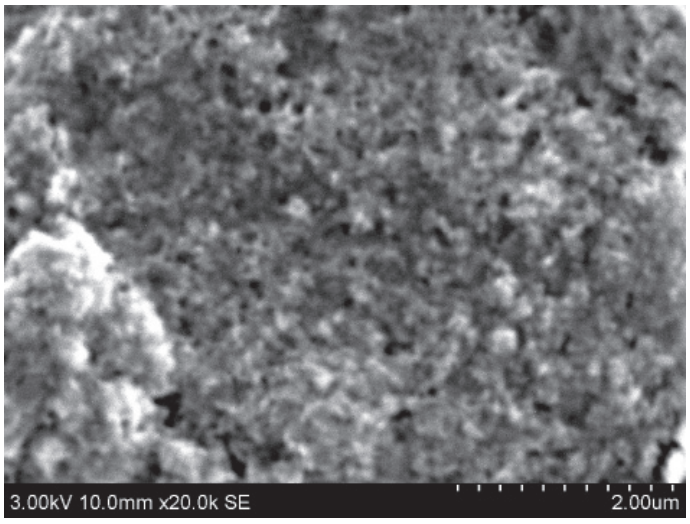

Fig. 3. SEM microphotography of titanium oxy-hydrade particles, obtained with an addition of 5% butile alcohol

The dependence of the average crystal grin size on the sample receipt conditions

Product receipt conditions	t_{ig} = 300 °C with SAS addition	t_{ig} = 300 °C without SAS addition	t_{ig} = 600 °C with SAS addition	t_{ig} = 600 °C without SAS addition	t_{ig} =1100 °C with SAS addition	t_{ig} = 1100 °C without SAS addition
D_{av}, Nm	3,1	21,1	45,2	65,8	158,1	210,7

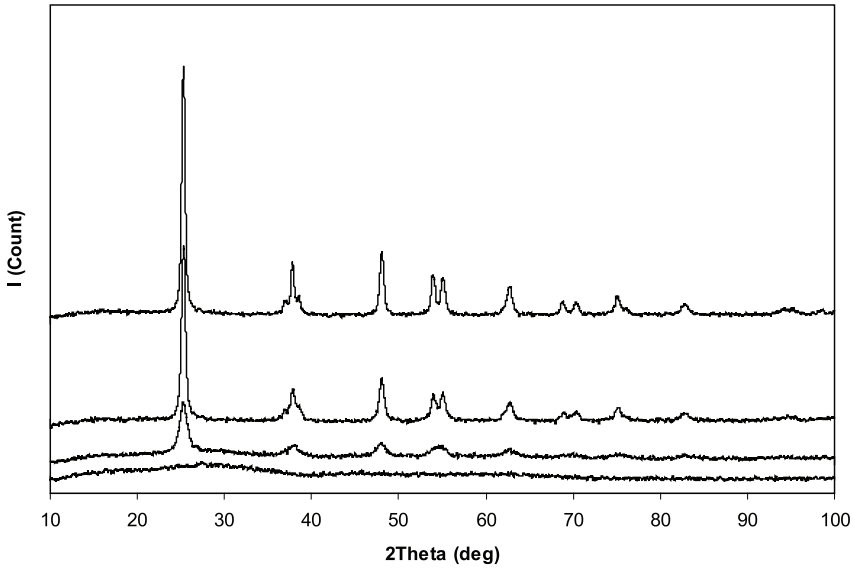

Fig. 4. X-ray -tures of samples, obtained after the titanium oxy-hydrate ignition:
1 – sample, obtained under the temperature 3000C with an addition of SAS, 2 – sample, obtained under the temperature of 300 °C without the addition, 3 – sample obtained under the temperature 600 °C with an addition of SAS, 4 – obtained under the temperature 600 °C without the addition

The correlation between titanium dioxide samples' synthesis conditions and the average size of formed crystal grain (D_{av}) that was calculated with the equation of Sherrer [9], is shown in the table below.

As shown by the table, titanium dioxide crystal enlargement takes place along with the raising of temperature. In the meantime the size of the powder particles that have been received with an addition of surface-active substance is significantly smaller, compared to its analogue that has been received without the addition.

Thus, the received experimental data and revealed dependences allow us to select the most satisfactory process realization conditions depending on what characteristics should the synthesized titanium dioxide posses. It gives us the ability to synthesize new materials with a controlled physics-chemical characteristics' complex.

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