

Investigation of rutilizing additive influence in hydrated titanium dioxide at thermal processing

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Abstract. The influence of a rutilizing additive in hydrated titanium dioxide is studied at its dehydration within the range of temperatures from 100 to 230° C. The quantity of major impurities is determined using an atom-emission spectrometer. Also, the X-ray diffraction analysis of obtained samples is performed.

1. Introduction

Heterogeneous reactions occupy a dominant position in the technologies of rare, scattered, and radioactive elements. The majority of processes belong to this type of reactions. The processes of dehydration and calcination are accompanied by boiling and vaporization. The multistage sequential flow of a process and the product formation are the main features of heterogeneous reactions. The main objective of heterogeneous kinetics is to determine a rate-limiting stage of a technological process and the rate of the whole process. All the processes have a multistage character, and it is impossible to separate individually each stage, therefore, the total energy of activation is determined, which consists of elementary steps [1]. The activation energy is a criterion of the rate-limiting stage. The higher activation energy is, the more difficult for molecules to interact, and the slower the whole process runs. The activation energy is associated with a rate constant. It is possible to determine the rate constant experimentally [2]. Determination of kinetic parameters is confined to measuring the rate of reaction at various temperatures; it is defined as a mass-change of one of reacting substances in time [2].

Hydrated titanium dioxide (HTD) has a complex molecular structure, and it could contain a variable amount of hydroxyl groups tied with titanium. At thermal processing of HTD the processes of dehydration and polymorphic transformation of anatase into rutile occur. In this case, the temperature range, in which these processes are implemented, depends, to a large extent, on conditions of HTD obtainment, the size of its crystals, the presence of impurities, and other parameters.

2. Experimental

At carrying out the work kinetic research of HTD thermal processing has been conducted with a rutilizing additive and without it at various temperatures. The installation for kinetic research is shown in Figure 1.

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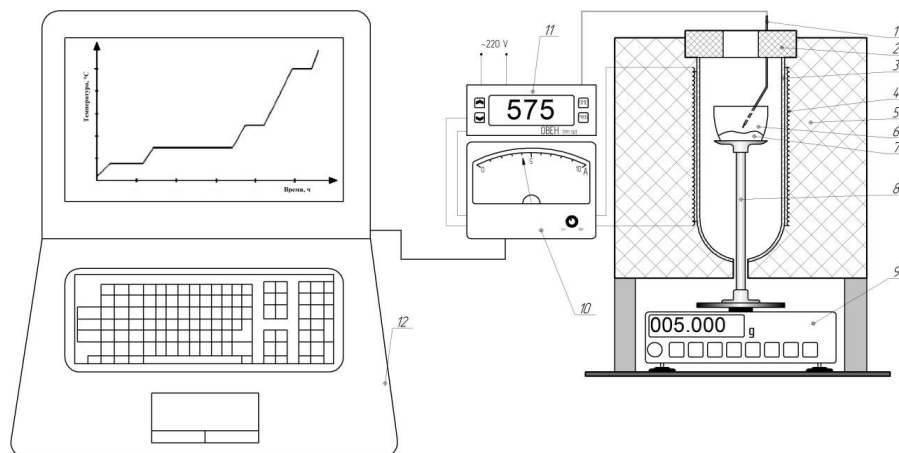


Figure 1. Scheme of a kinetic installation: 1 – a thermocouple; 2 – a cover; 3 – a quartz tube; 4 – an electric heating tube; 5 – heat insulation; 6 – a platinum crucible; 7 – a weighed amount of the studied substance; 8 – a crucible stand; 9 – an electronic weighing machine; 10 – an ammeter; 11 – a programmable thermostat controller "OVEN" TPM 501; 12 – a personal computer.

The weighed amounts of hydrated titanium dioxide (11 g) were dissolved in chlorohydric acid at pH = 2 with the addition of zinc metal (Zn), or aluminum (Al) as a rutilizing additive. After 3 hours of reaction the unreacted metal was removed from the solution, and then the 25% aqua-ammonia solution was added to pH = 8. The resulting precipitate was separated from the solution, and it was washed with distilled water. The resulting precipitate was studied using the kinetic installation, the process of dehydration was examined according to weight loss, which was, mainly, caused by H₂O evaporation and NH₃ excess. The drying temperature varied from 100° C to 230° C, dehydration time - from 1 to 3 hours[3].

The structure of a crystal lattice in the samples obtained after thermal processing was determined using the X-ray diffraction analysis (XRD) at the X-ray diffractometer XRD-7000S of Shimadzu Company. The content of major impurity elements was defined at the atomic emission spectrometer iCAP 6300 Duo of Thermo Electron Corporation Company [4].

3. Results and discussion

The experimental data for constructing dependence diagrams of mass-change on time were obtained at various temperatures, using the installation at HTD thermal processing with a rutilizing additive and without it. The results are shown in Figure 2.

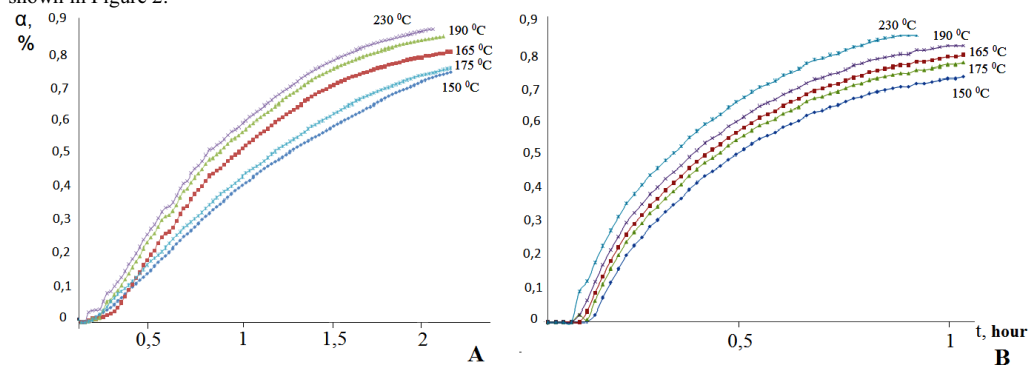


Figure 2. Dependence of water removal rate from hydrated titanium dioxide on time at various temperatures: A – without adding a rutilizing additive; B - with adding a rutilizing additive.

Initially, a dehydration process runs intensively with kinking at $\alpha \sim 0.8$, the temperature of 190 - 230° C (after, approximately, 40 minutes). The processes proceed evenly at the temperature below 190° C, similar to the processes with addition of the rutilizing additive - zinc metal.

The process of HTD dehydration proceeds with even dependence of mass-change on time (Figure 2). Several sections with different rates of evaporation are traced in all dependencies: the first section – HTD heating for 10

minutes, the second section - intensive water evaporation (generation and volatilization of gases), and then the processes achieve a plateau, where dehydration occurs. The rate of water evaporation increases with the increase of a temperature. Application of a rutilizing additive influences thermal decomposition, and the process runs faster than without rutilization.

The activation energy of the process is of 2356.3 J/mol within the range of temperatures from 150° C to 230° C (Figure 2 A).

For this process the dependence of water removal rate from the precipitate on the time and temperature is as follows:

$$\alpha = 1 - \left(1 - 2,4 \cdot \exp\left(-\frac{2356,3}{R \cdot T}\right) \cdot t \right)^3$$

The process runs in an intra-diffusion reaction area. It is determined by a dense structure of hydrated titanium dioxide and also by the complexity of water evaporation through a HTD isolation layer. The process can be intensified using mechanical mixing.

The activation energy of the process is of 1107.8 J/mol within the range of temperatures from 150° C to 230° C at HTD drying with the use of rutilizing additives (Figure 2 B).

Water removal rate in the given range is calculated as follows:

$$\alpha = 1 - \left(1 - 2,4 \cdot \exp\left(-\frac{1107,8}{R \cdot T}\right) \cdot t \right)^3$$

Consequently, the process of dehydration runs in the intra-diffusion reaction area, and it is limited by the diffusion of resultants in pores. The method used to stimulate the process is mechanical mixing.

According to the results of the samples studied using the X-ray diffraction analysis, it is observed that recrystallization of an anatase form into a rutile one occurs as a result of thermal processing.

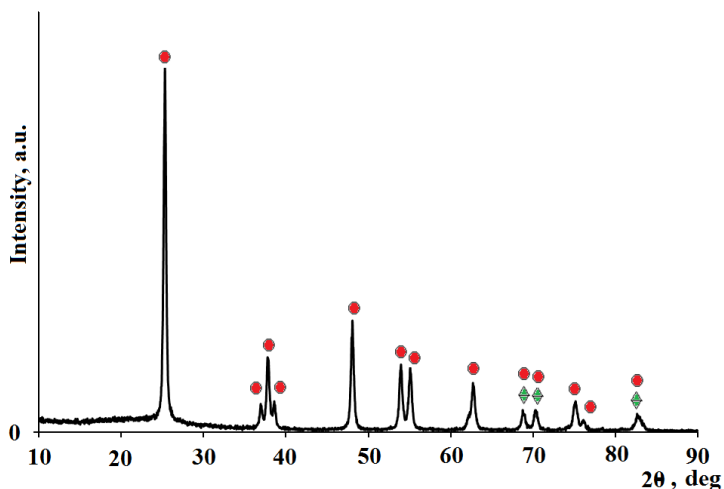




Figure 3. Diffraction patterns of samples without a rutilizing additive:  - TiO₂ (rutile),  - TiO₂ (anatase)

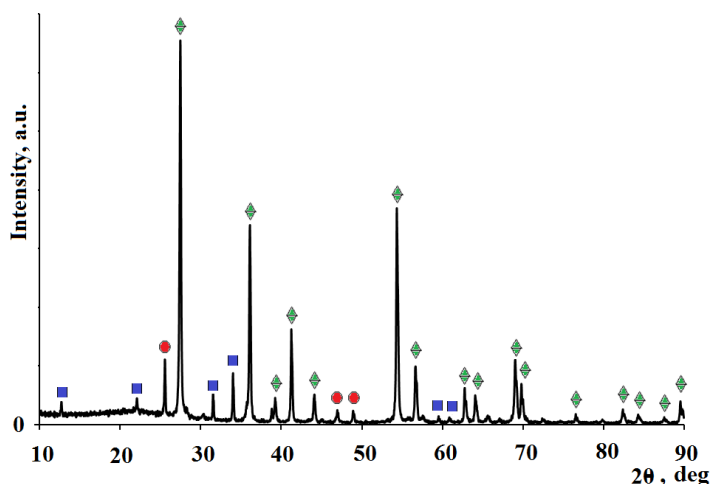


Figure 4. Diffraction patterns of samples with a rutilizing additive: - TiO₂ (rutile), - TiO₂ (anatase), - Zn₂SiO₄ (villemite).

The results of the analysis for Sample №1 (fig.3) - without addition of a rutilizing additive, and Sample №2 (fig.4) - with addition of it analyzed at the atomic emission spectrometer iCAP 6300 Duo are shown in Table 1.

Table 1. Results of element analysis at the atomic emission spectrometer iCAP 6300 Duo

Denotation	Content of main components, %	Content of main impurities, %	
	Ti	Fe	Zn
Sample 1	58,21	0,29	0,094
Sample 2	59,75	0,078	0,23

The results of the element analysis show that Zn metal addition decreases the content of Fe by substitution. TiO₂ has a sorption activity, and, apparently, Zn²⁺ displaces Fe³⁺.

4. Conclusion

Based on experimental data dehydration of hydrated titanium dioxide with addition of a rutilizing additive and without it is calculated using mathematical processing within the range of temperatures from 100 ° C to 230° C in time. The results of a structural analysis show as follows: addition of the rutilizing additive in the form of Zn metal decreases the temperature of thermal processing and facilitates formation of crystallization rutile centers. For speeding up the processes, which run in the intra-diffusion area, it is necessary to remove the layer inhibiting a chemical reaction from reacting particles. It could be arranged in rotating machines.

References

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