Study of particles of plasma dynamic synthesis product in the Ti-O system by high-resolution transmission electron microscopy

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Abstract. The paper demonstrates the possibility of obtaining a dispersed product in the Ti-O system by the method of plasma dynamic synthesis. It was revealed that the product consists of two modifications of TiO₂: anatase and rutile. The degree of crystallinity is at a level of ~ 98.0%, which indicates the practical absence of an amorphous component. The predominant phase is anatase, which is confirmed by the results of quantitative X-ray phase analysis and high-resolution transmission electron microscopy.

1. Introduction

Hydrogen is used in many areas of the chemical industry and fuel cells; therefore, the search for efficient methods for the production of H₂ has attracted widespread attention [1, 2]. Most often, the specified chemical compound is obtained by reforming oil or natural gas, however, recently many researchers have been focusing on the synthesis of H₂ through the photocatalytic water cleavage [3-5]. This process makes it possible to split water into oxygen and hydrogen under the influence of sunlight, which makes this method quite simple and environmentally friendly. Titanium (IV) oxide (titanium dioxide) is most widely used as a sorbent and photocatalyst [6-8] due to its low cost, non-toxicity, high catalytic activity and chemical stability. This material has a number of properties, such as high photoactivity, relatively low cost, non-toxicity, and chemical stability [9-11]. Unfortunately, TiO₂ is sensitive only to ultraviolet region due to its large band gap (the band gap is 3.0–3.2 eV). Moreover, due to the fast recombination rate of photogenerated electron-hole pairs, TiO₂ has a low quantum efficiency [12-14]. Thus, the production of titanium dioxide with increased photocatalytic activity, which can be used in visible light, is a relevant task.

The papers [15, 16] show the fundamental possibility of synthesizing ultrafine titanium dioxide by the plasma dynamic method. Plasma dynamic synthesis, like other currently existing methods, also makes it possible to obtain dispersed materials. Nonetheless, its advantages can be noted: ease of obtaining material, fast operation speed, one-stage, no need for preliminary preparation of the raw material. Due to the nonequilibrium flow of crystallization processes, it is possible to obtain defective structures by means of plasma dynamic synthesis, which can have a positive effect in the
2. Experimental part
The system for the implementation of plasma dynamic synthesis (PDS) process for obtaining of titanium dioxide is based on the operation of a pulsed high-current high-voltage coaxial magnetoplasma accelerator (CMPA) of the erosion type. The electrodes are made of BT-1-0 titanium. The pulsed power supply of the CMPA is carried out from a capacitive energy storage with a capacity of \( C = 14.4 \text{ mF} \) at a charging voltage of \( U_{ch} = 2.5 \text{ kV} \). Plasma chemical reaction was implemented in a sealed and durable stainless steel reactor chamber (CR). The volume \( V_{CR} = 0.017 \text{ m}^3 \) was filled with a gaseous mixture of oxygen \( \text{O}_2 \) and argon \( \text{Ar} \) at normal pressure \( p_0 = 1.0 \text{ atm} \) and room temperature \( T_0 \approx 20^\circ\text{C} \). Partial pressure ratio \( \text{O}_2/\text{Ar} \) was 50%/50%.

During the operation of the CMPA titanium, which is the main precursor of synthesis, is produced by electroerosion wear from the surface of the accelerating channel and displacement of the plasma structure in it. The accelerator device and its operating principle are described in more detail in [16].

The product of plasma dynamic synthesis was investigated by X-ray diffractometry using an X-ray diffractometer (Shimadzu XRD7000S, CuK\(_\alpha\)-radiation). The analysis of the obtained diffraction patterns was carried out using the PDF4+ structural database. The quantitative analysis of the phase composition of the synthesized product was studied using the "PowderCell2.4" software package. High resolution transmission electron microscopy (HRTEM) was carried out using a Jeol JEM 2100F microscope equipped with a Gatan camera. The crystal structure of typical product particles was studied in the software “Gatan Digital Micrograph”.

3. Results and discussion
Figure 1 shows a typical diffractogram of the product synthesized under the conditions specified in the previous paragraph. The presence of only two crystalline modifications of titanium dioxide was revealed: anatase \((a = b = 3.7852 \text{ Å}; c = 9.5139 \text{ Å})\) and rutile with a tetragonal system \((a = b = 4.5933 \text{ Å}; c = 2.9592 \text{ Å})\). Dominant phase in the powder material is anatase, its percentage is 61.7%. The calculation results in the “Dxta Application” software showed the degree of crystallinity at the level of \( \sim 98.0\% \), which indicates the practical absence of an amorphous component.

![Diffractogram of the synthesized product.](image)

Figure 1. Diffractogram of the synthesized product.

Figure 2 shows the results of HRTEM analysis. In the direct resolution mode, a uniform and clear streaky contrast is observed in their bodies in one of the crystallographic directions, a fragment of which is shown in figure. This shows the presence of long-range order in the crystal structure of the entire particle and indicates its monocrystalline structure. The two-dimensional picture of the fast Fourier transform (FFT) in the selected region has the form, characteristic of a nanocrystal, of pairs of equivalent points-reflections 1-1’, 2-2’ lined up along one line. The determined average value of the interplanar distance was \( d = 0.351 \text{ nm} \). By the points-reflections 2-2’, the value \( d = 0.178 \text{ nm} \) was
determined in a similar way. These values are quite close to the basic values $d_{(101)} = 0.351706$ nm and $d_{(202)} = 0.175853$ nm of the structural model of anatase. Apparently, figure 2 shows faceted particles with a size of ~ 120.0 nm.

![Figure 2](image)

**Figure 2.** Results of high-resolution transmission electron microscopy.

### 4. Conclusion

The possibility of obtaining dispersed titanium dioxide by the method of plasma dynamic synthesis is shown. X-ray diffractometry studies have demonstrated the abundance of only two polymorphs, anatase and rutile with tetragonal syngony. According to the results of quantitative X-ray phase analysis, the modification of anatase is predominant, and its percentage is 61.7%. Calculations of the degree of crystallinity (~ 98.0%) showed the practical absence of an amorphous component. According to HRTEM studies, the dominant phase in the powder material is anatase, which is consistent with the results of quantitative X-ray phase analysis. The synthesized product contains faceted monocrystalline particles ~ 20 nm in size.

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