ISSN 1063-7850, Technical Physics Letters, 2017, Vol. 43, No. 1, pp. 16–19. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © A.A. Sivkov, D.Yu. Gerasimov, D.S. Nikitin, 2016, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2016, Vol. 42, No. 23, pp. 21–27.

Direct Dynamic Synthesis of Nanodispersed Phases of Titanium Oxides upon Sputtering of Electrodischarge Titanium Plasma into an Air Atmosphere

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Received June 14, 2016

Abstract—Experimental investigations of the possibility of directly synthesizing nanodispersed crystalline phases of titanium dioxides with rutile and anatase structures in a hypervelocity jet of electroerosion plasma generated by a coaxial magnetoplasma accelerator with titanium electrodes are presented. A powder product containing nanosized polymorphic phases of titanium dioxide with a spherical shape of particles has been manufactured.

DOI: 10.1134/S1063785016120105

The problem of obtaining titanium oxides is important because of their wide applications in manufacturing thermally resistant plastics, in producing hard films as a reinforcing agent, in photocatalysis and helioenergetics, and as a catalyst in chemical and pharmaceutical production [1–3]. Titanium oxides are widely used due to their high stability, self-cleaning ability, self-sanitizing, and photocatalytic activity, as well as the antibacterial and anticorrosion properties of these compounds [4–6].

Developing methods for direct synthesis of nanodispersed titanium oxide is an important scientific problem because the activity of titanium oxide particles considerably increases in the nanosize state [7]. Nanodispersed crystalline materials can be synthesized in a high-velocity pulse jet of dense electroerosion plasma. The jet is generated by a pulsed high-current (on the order of 100 kA) erosion-type coaxial magnetoplasma accelerator (CMPA). Its construction is based on a classical Z-pinch accelerator, the main elements of which are a central electrode and barrel electrode with a cylindrical accelerating channel (AC). The accelerator is called "erosion-type" because the main material necessary for the synthesis of the required product is produced by the electroerosion way from the cylindrical AC surface on which reference spots of the accelerated high-current Z-pinch type discharge are displaced [8]. Thus, the task of this work is to implement the synthesis of nanodispersed titanium oxides in a high-velocity pulsed jet of dense electroerosion plasma.

The used method is direct because the process is completely implemented in a single short-time (on the order of 1 ms) cycle of CMPA operation. The main consumable material (titanium) is produced in an electroerosion fashion from the AC surface and captured by the accelerated discharge in the melted state. At a temperature of several thousand degrees, it is transferred to the plasma state, accelerated to hypersonic velocities, and carried out of the AC to the space of the cylindrical reactor chamber filled with air. The electric power is supplied to the CMPA from a pulsed source—a capacitive energy storage.

It has been shown in [8] that, at a given AC geometry and material of the accelerator electrodes, the magnitude of energy W delivered and dissipated in the acceleration channel is the main factor determining the magnitude of the eroded mass m and plasma flow rate θ at the AC cross section. The magnitude of specific electroerosive wear m/W is directly proportional to specific delivered energy W/V (V is AC volume). The energy delivered in the course of the experiment was determined by integration of the discharge power curve obtained by waveforms of current $I(t)$ and voltage $U(t)$ at the CMPA electrodes. Mass m carried out of the AC was determined by weighting the barrel before and after the plasma shot. The obtained dynamic synthesis product was selected several hours after the deposition of the weighted fraction on walls of the reactor chamber at room temperature. Analytical investigations were carried out using X-ray diffractometry (Shimadzu XRD7000, CuK_α) and transmission electron microscopy (Philips CM 30).

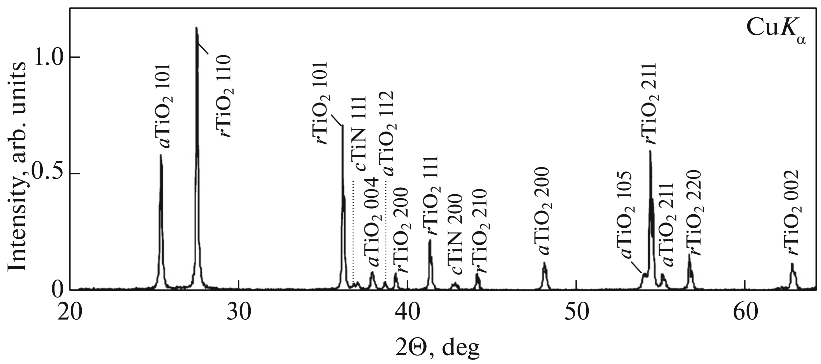

Fig. 1. X-ray diffractogram of a powder product obtained by a CMPA with titanium electrodes in an air atmosphere.

Experiments on dynamic synthesis of nanodispersed crystalline phases of titanium oxide were carried out on a CMPA with titanium electrodes. The central electrode of the accelerator was made of a titanium pin with a diameter of 18 mm; the barrel electrode was made of a titanium tube with AC diameter $d = 21$ mm and length $l = 280$ mm. The experiments were carried out under conditions of plasma jet efflux into the reactor chamber with an air atmosphere at normal pressure. Capacitive energy storage $C = 24$ mF was charged to $U_{ch} = 3.5$ kV. At current pulse amplitude $I_m = 230$ kA and delivered energy $W = 94$ kJ, a white powder product with mass $m_p = 9.3$ g was produced. The deposited powder product was a 5- to 6-mm-thick loose coating. In the process of collection, the powder tends to agglomeration, which is typical for nanopowders [9].

Figure 1 presents a typical X-ray diffractogram taken on one of samples of the powder material. Its character testifies to the absence of the amorphous phase. Full-profile structural phase analysis, the main results of which are presented in the table, demonstrates that the dynamic synthesis product is approximately 98% made up of polymorphic crystalline phases of titanium dioxide: 59% with the structure of rutile rTiO$_2$ and 39% with the structure of anatase aTiO$_2$. In this product, one can also identify the phase of cubic titanium nitride cTiN (no more than 2%).

Judging by the average size of the coherent scattering region (CSR), the obtained product can be classified as a nanodispersed powder. The insignificant deviations of lattice parameters of crystalline phases from theoretical values (according to the international PDF4+ database) seem to be caused by the high level of internal microstresses and high deficiency of the structure.

The data of X-ray diffractometry are completely corroborated by the results of investigations by transmission electron microscopy (TEM). They are presented in Fig. 2. The TEM photograph (Fig. 2a) shows the aggregate of particles of the product under consideration. The pattern of electron diffraction on this aggregate (Fig. 2b) contains a large number of reflexes corresponding to crystalline phases of TiO$_2$ and individual reflexes of diffraction on planes of cubic titanium nitride cTiN. The dark-field photograph (Fig. 2c) with two spherical particles depicted in it was obtained in the reflex of rTiO$_2$ 101. This gives additional grounds for identifying the spherical nanoparticles as particles of titanium dioxide. Analysis of the collection of dark-field TEM photographs obtained in the region of the reflex of cTiN 111 made it possible to refer not numerous polyhedral (often close to round-shaped) particles to this phase. The reliability of the identification is also verified by a visual assessment of the relationship between the (much larger) number of ideally spherical particles (TiO$_2$)

Main data of full-profile structural phase analysis of the dynamic synthesis product obtained using the CMPA with titanium electrodes

Crystalline phase	Concentration, wt %	CSRs, nm	$\Delta d/d \times 10^{-3}$	Lattice parameters, experiment/PDF4+, Å	
				a	c
rTiO$_2$	59	89	2.43	4.5959/4.5940	2.9616/2.9590
aTiO$_2$	39	48	3.28	3.7790/3.7970	9.5697/9.5790
cTiN	2	57	2.39	4.2388/4.2410	–

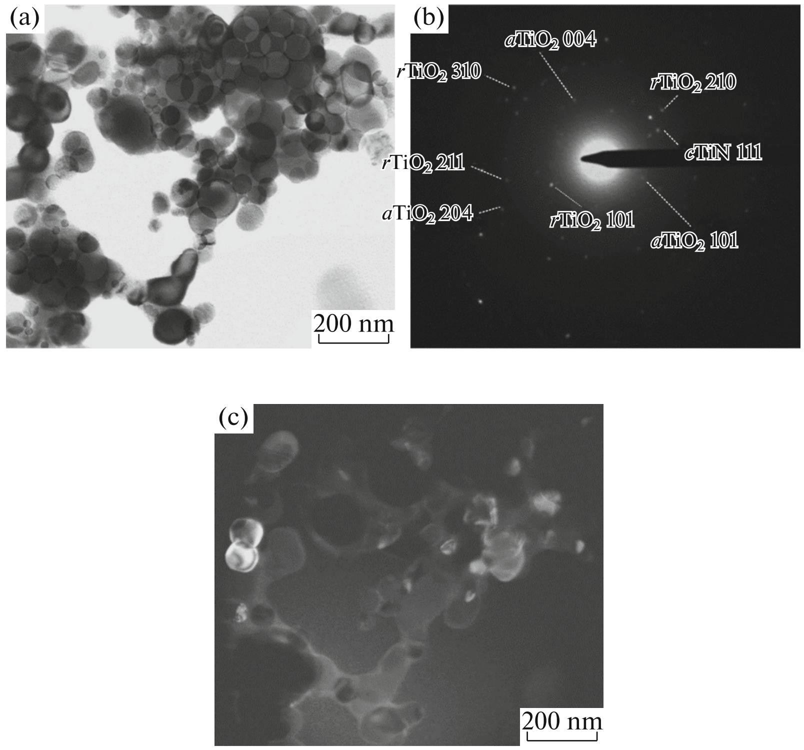

Fig. 2. Data of TEM investigations of a powder product obtained in an air atmosphere: (a) light-field TEM photograph of an aggregate of particles, (b) electron diffraction pattern of the corresponding aggregate, and (c) dark-field TEM photograph obtained in the rTiO$_2$ 101 reflex.

and the number of polyhedral (nonspherical) particles (cTiN).

The particle size was estimated using light-field TEM photographs. The size distribution range is approximately 10–100 nm, and the distribution law is close to the normal logarithmic law with a maximum in the region of approximately 50 nm (Fig. 3). Results of this estimation well coincide with data of the full-profile structural phase analysis by average CSR size (see table) of identified phases of the product obtained using the CMPA with titanium electrodes in an air atmosphere at normal pressure.

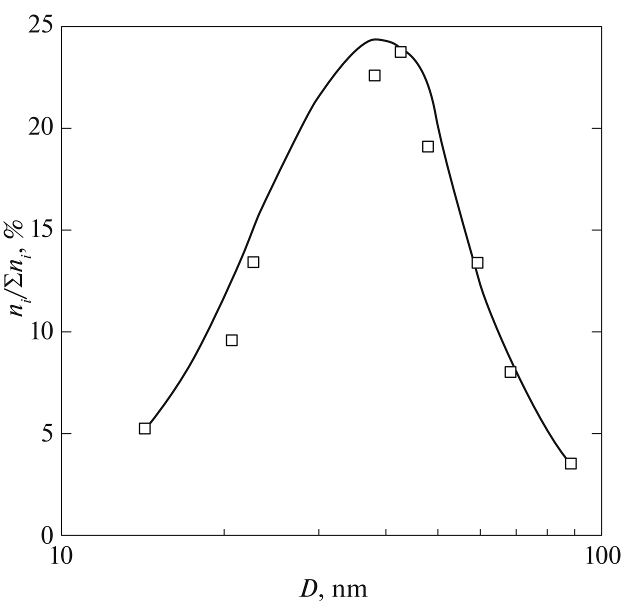

Fig. 3. Size distribution curve of titanium dioxide particles in a powder product of dynamic synthesis.

The performed experimental investigations demonstrated the possibilities of direct dynamic synthesis of nanodispersed crystalline phases of titanium dioxides with rutile and anatase structures in a hypervelocity jet of electroerosion plasma using a system based on a CMPA with titanium electrodes. The efflux of a titanium-containing plasma jet into the air atmosphere is accompanied by the synthesis of nanosize polymorphic phases of titanium dioxide with the spherical shape of particles.

Acknowledgments. This work was supported by the Russian Science Foundation, project no. 15-19-00049.

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Translated by A. Nikol'skii