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THERMAL-VACUUM METHOD FOR OBTAINING NANODISPERSED ZIRCONIUM DIOXIDE[†]

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An energy-efficient thermal-vacuum method for continuous production of nanodispersed powder of amorphous zirconium dioxide from zirconium hydroxide has been developed. This approach is based on a principle of creating an aerodynamic flow with an initial powder-like material in the cavity of the heating element of a thermal-vacuum installation. In this way, short-term contacts of particles of zirconium hydroxide with the inner surface of the heating element made in the form of the winding helical are created. As a result, the crushing of the particles is carried out due to the high thermal stresses in the particles contacted. This process is aggravated by the presence of residual moisture in the original powdery material. Transformations of the zirconium hydroxide in the process of thermal-vacuum treatment have been investigated. Amorphous dioxide has been obtained. The study of structural composition of the material in the initial state and processed in a thermal-vacuum installation was carried out using X-ray analysis and scanning microscopy. Experimental data on the structural-phase composition of the original material and data on the closest structural prototypes of crystalline-impurity compounds are presented. They are also given data on the volume of crystal cells and estimates of the molar concentration of the components. A mass spectrometric assessment of the elemental composition of the obtained zirconium dioxide is given. Thermal-vacuum method allows toobtain highly dispersed zirconium dioxide in its amorphous state directly from zirconium hydroxide without using liquid media and, moreover, in a short time – within 15...20 s.

Keywords: zirconium hydroxide, zirconium dioxide, fabrication, dispersion method, nanopowder.
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One of the problems of current interest associated with the needs of modern technology is the scientific and technical principles of creating nanostructured materials for products and structures of industrial production and other technical needs. Objects of interest include zirconium dioxide, which is widely used in the manufacture of fire-resistant materials, as well as in dentistry.

To create nanosized zirconium dioxide, the method of forced hydrolysis [1], as well as the method of pyrolysis of sprayed salt solutions [2], have recently been used. There is also a method for producing zirconium-dioxide nanopowders by the method of electron beam evaporation and vacuum deposition [3]. However, this process is lengthy and energy intensive. Hydrothermal synthesis is one of the most industry-wide methods for obtaining nanodispersed ZrO_2 powders [4]. But this process requires acid treatment. And in this case, it is necessary to change in a wide range the temperature, pressure, concentration and acidity of the solutions used. Nano-dispersed zirconium dioxide is obtained by its heterophase synthesis from zirconium oxychloride with the participation of solutions of different bases (for example, from the compound $ZrOCl_2 \cdot 8H_2O$ in aqueous solutions of KOH, NaOH or ammonia [5]).

So, the methods described above make it possible to obtain nanodispersed zirconium dioxide using aqueous solutions of acids, alkalis and alcohols.

The featured thermal-vacuum method makes it possible to obtain highly dispersed zirconium dioxide directly from the hydroxide without using liquid media and, moreover, in a short time – 15...20 s. This takes place in the air flow through the heating element duct. On the basis of this, in particular, a nanodispersed graphite powder was obtained – a material that can be used in printers and other copying equipment [6].

THERMAL-VACUUM INSTALLATION FOR DISPERSION AND DEHYDRATION

On the basis of the performed theoretical and experimental studies, an energy-efficient thermal-vacuum method for continuous dispersion and dehydration of wet powdery materials had been developed [7]. This method is based on combining a fast evacuation process – creating aerodynamic driving force – and thermal heating to a required temperature. This is accompanied by acts of direct contact of surface layer of particles of original material with the inner surface of the hollow heater, what provides instantaneous heating of the material particles in a vacuum.

For the closest contact with the initial powdery material, the heater is made in the form of a helical spiral. The physical principle of this technique is that the decrease in pressure inside the heating element, produced by a vacuum pump, creates a pressure gradient that stimulates an intense flow of air with powder. When such a flow moves in the spiral, due to its sufficient speed and inertia of the particles, an impact contact of the particles with the inner surface of the heater occurs, which makes it possible to efficiently use the heat of the heating element in this process. An instantaneous heating of the surface layer of zirconium hydroxide particles to a high temperature occurs. This stimulates the fragmentation of particles.

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Under the conditions of the existence of residual moisture in the original powder in combination with a reduced air pressure, the process of crushing particles can be aggravated. So, in this case, the temperature of the contacting layer becomes higher than the temperature of moisture evaporation. This causes intense vapor release from the surface layer of zirconium hydroxide – a steam explosion, which facilitates the crushing process. The physical details of the powder dispersion process are described in [6-7].

The thermal-vacuum installation is shown in Fig. 1[6, 8]. It consists of a feed hopper (1), a hollow heater (2), a vacuum pump (3), tunnels (4, 11), a cyclone (5), a receiver for dried raw materials (6), and a floodgate (7). The installation has a thermocouple (8, 13), a control panel (9), a conveyer (10), a filter (12), a level sensor for dried raw materials (14), and a vacuum gauge (15).

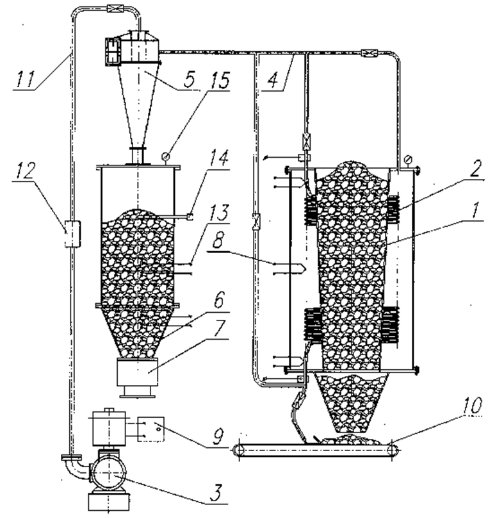

Figure 1. Thermal-vacuum scheme.

This design of the installation provides highly efficient dispersion of material in a space thermally insulated from the external environment, and, simultaneously, its continuous dehydration. In general, effectiveness of dispersion depends on thermal-physical properties of material and its state: on the relationship between thermal conductivity, heat capacity and thermal coefficient of expansion, on dispersion and moisture content of original material, on ambient pressure, and on the heater temperature. In our case, the heater temperature is 350ºC.

EXPERIMENTAL

As is known, zirconium hydroxide – the original material in our studying – is obtained by chemical processing zircon concentrate [4]:

$$ZrSiO_4 + [(Na,K)OH + CaF_4] \rightarrow \ldots \rightarrow (Na,K)_2ZrF_6 + ZrO_2 + CaSiO_3 \tag{1}$$

By treating the resulting mixture in a hydrochloric acid solution, zirconium oxychloride $ZrOCl_2$ is obtained from the first two products, from which zirconium hydroxide is then precipitated in an ammonia solution. In this case, insoluble impurities may remain [4].

The study of structural composition of the material in the initial state and processed in a thermal vacuum installation was carried out using X-ray structural analysis and scanning microscopy. The X-ray measurements were carried out on a DRON4-07 diffractometer with CuK_α radiation recording by a proportional counter using the pair of Soller slits.

A semi-quantitative phase analysis was performed using a full-profile X-ray diagram, and this referred to the original material. Based on the measurement results, the molar portion of the structural components of the material was estimated by integrating the intensity of X-ray reflection recorded as profiles of the $I(\theta)$ diagram in the coordinates of the diffraction angle θ. Integration was carried out over polar coordinates in the volume of the sphere of reflections (Ewald's sphere). The initial variable of integration is reduced to an analog of the diffraction vector: $s = \sin\theta/\lambda$, where λ is the radiation wavelength. The following formula was used to calculate the averaged parameter of the reduced intensity of an individual phase or fraction, which is directly related to the numerical content of the reflecting molecular units of this fraction:

$$i = \frac{u}{U}\int_{s_0}^{s_M} \frac{I(s)}{P(\theta) f^2(s)} s^2 ds = \frac{u}{U}\frac{1}{\lambda^3}\int_{\theta_0}^{\theta_M} \frac{I(\theta)}{P(\theta) f^2(s)} \sin^2\theta \cos\theta d\theta \quad \left[U = \int_{\theta_0}^{\theta_M} s^2 ds,\right], \tag{2}$$

Herein the first integrand is the integration of the full-profile intensity of reflections from some of the phases or fractions, taken individually, over the volume of the reciprocal lattice space bounded by the limiting radii of the Ewald sphere s_0 and s_M; $P(\theta)$ – multiplier of correction for the polarization of the reflected beam: $P(\theta) = (1 + \cos^2 2\theta)/2$; U is the volume of the integration area in the space of reciprocal lattices; f is the atomic factor; u is the volume fraction of the space of reflections attributable to any node of the reciprocal lattice: $u = 1/8v$, where v is the real volume of the molecular unit (~ 10^{-22} cm^3).

The f-factor expresses the diffraction effect due to the size of atoms and the number of its electrons (ordinal number N), and is presented as an algebraic sum over the atoms of a molecular unit with their stoichiometric numbers n_i:

$$f^2(s) = \sum_i n_i f_i^2(s) \tag{3}$$

We limited this to the region of non-large diffraction angles and the values of $f_i(0)$ as parametric coefficients when integrating according to the formula (2). This approach is sufficient for estimating the content of phases and fractions at the level of their scales.

In general, the molar concentration of the j-th phase or fraction was estimated by the ratio $c_j = i_j/\Sigma i_k$ (2), with which the normalization condition $\Sigma c_k = 1$ is met.

RESULTS

X-ray CuK$_\alpha$-diagrams of the original and processed material are shown in Figure 2.

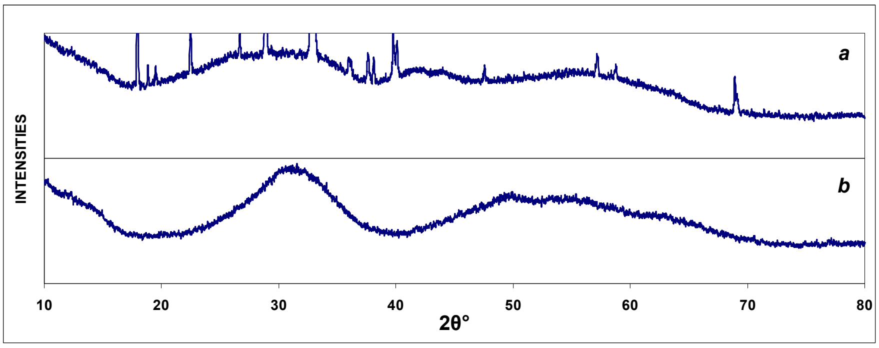

Figure 2. X-ray diagrams of the original zirconium hydroxide (a) and the dioxide obtained after thermal-vacuum treatment (b).

The presence of elements of similarity in the general form of angular distributions (Fig. 2a,b) gave grounds to believe that the original material contains a significant amount of zirconium dioxide.

According to the analysis of the complex of X-ray lines in the diagram (Fig. 2a), it was found that the original material contains two crystalline phases of an unidentifiable nature. Apparently, these are impurities of precipitates remaining after the preliminary treatment of zirconium oxychloride in an ammonia solution to obtain hydroxide. It is assumed that these are structures based on $(Na,K)_2ZrF_6$ and $CaSiO_3$ (1), modified by other elements in the course of chemical separation reactions.

Table 1 shows experimental data on the structural-phase composition of the original material and data on the closest structural prototypes of impurity compounds with a crystalline nature. Data on the volume of crystal cells and estimates of the molar concentration of the components are also given. Molar concentrations were estimated from chart analysis based on the approach described in the previous section.

Table 2 shows the mass spectrometric estimates of the elemental composition of the obtained zirconium dioxide.

Table 1. Structural-phase composition of the original material.

composition	structure	a (nm)	b (nm)	c (nm)	V (nm^3)	mol. %
exp.	cubic	0.667 (0.471)	0.667 (0.471)	0.667 (0.471)	0.296 (0.105)	0.5
K_2ZrF_6	rhombic	0.658	1.144	0.694	0.522	
exp.	rhombic	0.987	0.792	0.553	0.4325	3
$CaSiO_3$	triclinic	1.01 99.5°*	0.731 83.4°	1.106 100.6°	0.789	
Zr hydroxide	amorphous					32-45
ZrO_2	amorphous					53-66

(*) – angles between two other basal planes of the lattice.

Table 2. Elemental composition of the obtained zirconium dioxide.

el.	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	K
at.%	0.0003	4.64	0.56	67.9	2.64	0.067	0.045	0.08	0.36	0.018	0.09	0.018	0.028
el.	Ca	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Sr	Zr	Sn
at.%	0.4	0.008	0.001	0.048	0.004	0.29	0.015	0.003	0.043	0.004	0.003	22.8	0.003

These data indicate the predominance of impurities C, N, Ca, Si, Fe and F in the resulted dioxide. This, in particular, confirms the result of the analysis of the crystalline-impurity composition of the original material (Table 1).

By the method of thermal-vacuum dispersion, amorphous zirconium dioxide was obtained with 20...200 nm size of the powder particles (Fig. 3). There were no conglomerates in the powder.

DISCUSSION

The original material with zirconium hydroxide (Fig. 2a) was a powder with a moisture content of 12.5%. The obtained dioxide in the amorphous state (Figs. 2b, 3) has a moisture content of 1.8%. The presence of hydroxide in its environment, had noted by analyzing the diagrams (Fig. 2a,b), is associated with the time period before X-ray measurements, during which it gained atmospheric humidity up to 6%.

Of course, the dispersion process is determined by the physical capabilities of the thermal-vacuum installation. However, the actual result depends also on the characteristics of the filters. In our case, a system of two filters was used. Amorphous zirconium dioxide was retained by a fine filter (Fig. 3). Crystalline-impurity fractions were retained in the coarse filter. The process time of the entire technological cycle is 15...20 s.

As a result, the amorphous zirconium dioxide was obtained with a yield of 30 wt%, the apparent density of 1.64 g/cm^3, wherein the apparent density of zirconium hydroxide was 1.05 g/cm^3.

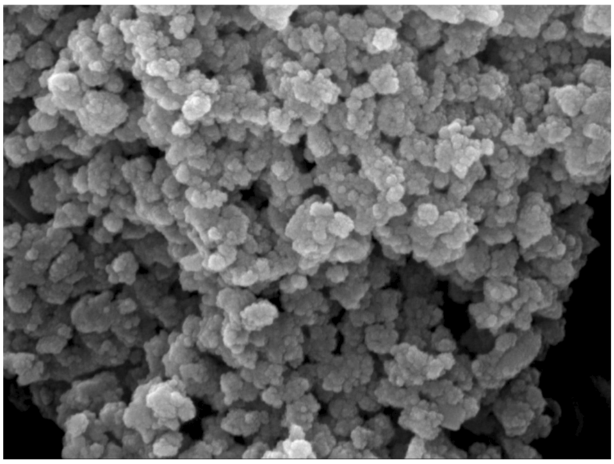

Figure 3. ZrO_2 in the amorphous state

SUMMARY

1. As a result of thermal-vacuum treatment of a powder based on zirconium dioxide containing zirconium hydroxide, pure dioxide was obtained in the amorphous state with a moisture content of 1.8%, a particle size of 20...200 nm and an yield of 30%.

2. It is noted that this method makes it possible to obtain fine and nanodispersed powders in a cycle of 15...20 s. This is due to a combination of sharp thermal effects when particles come into contact with the heater surface, the design feature of the heater, and the aerodynamic conditions of the process – with a positive effect of the residual moisture content of the powder material on the process.

3. It is noted that in the process of thermal-vacuum treatment, the material is able to change the crystalline-structure state under the conditions of the existing variety of its known crystallographic modifications. Under such conditions, an amorphous state of zirconium dioxide was obtained.

The described thermal vacuum-method significantly reduces the technological process and energy consumption – and can be used for the continuous and energy-efficient production of nanodispersed materials, as well as for drying powder materials.

The principle of this method provides wide possibilities for physical-mathematical developments on optimization industrial dispersion processes for various specific types of powder materials.

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ТЕРМОВАКУУМНИЙ СПОСІБ ОДЕРЖАННЯ НАНОДИСПЕРСНОГО ДІОКСИДУ ЦИРКОНІЮ

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У даній роботі наведено енергоефективний термовакуумний спосіб безперервного отримання нанодисперсного діоксиду цирконію з гідроксиду цирконію. У цьому підході закладено принцип створення аеродинамічного потоку з вихідним порошкоподібним матеріалом в порожнині нагрівального елементу. Таким способом створюються короткомоментні контакти частинок з внутрішньою поверхнею нагрівального елементу. В результаті цього дроблення частинок здійснюється завдяки високим термічним напруженням в частинках, що контактують. Цей процес посилюється існуванням залишкової вологи у вихідному порошкоподібному матеріалі. Досліджено фазові перетворення у процесі термовакуумної обробки гідроксиду цирконію. Отримано аморфний діоксид цирконію. Дослідження структурного складу матеріалу в початковому стані і обробленого в термовакуумній установці здійснено за допомогою рентгеноструктурного аналізу і скануючої мікроскопії. Приведено експериментальні дані зі структурно-фазового складу вихідного матеріалу і дані по найближчим структурним прототипам домішкових сполук кристалічного характеру. Наведено також дані з об'єму кристалічних комірок і оцінка молярної концентрації компонентів. Дана мас-спектрометрична оцінка елементного складу отриманого діоксиду цирконію. Термовакуумний метод дозволяє отримувати високодисперсний діоксид цирконію у аморфному стані безпосередньо з гідроксиду цирконію без використання рідких середовищ і до того ж за короткий час – протягом 15...20 с.

Ключові слова: гідроксид цирконію, діоксид цирконію, виробництво, метод диспергування, нанопорошок.