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THERMAL VACUUM PROCESS FOR PRODUCTION OF SPECIAL PURPOSE NANODISPERSED MATERIALS

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The effects of relaxation processes occurring during production of nanodispersed zirconia from zirconium hydroxide in a thermal vacuum installation are presented. The data on structural properties and purity of zirconia are reported. The spectra of oxygen (O1s) in zirconia have been investigated.

In our days, the installation created energy-efficient thermal processing providing production of materials (zirconium dioxide, coal, salt, chalk and other materials) with nanocrystalline structure, developed processes to improve the efficiency of production of nanomaterials with desired properties. Nanomaterials are now widely used in the manufacture of ceramics and ceramic metal, powders, fibers and composites. They are used as polishing compositions, dyes, sorbents, abrasives, cutting materials and functional materials for a particular electrical, piezo-electric, optical, magnetic and other properties. On special place is preparation catalysts comprising an active phase in the form of particles of nanometer dimensions.

Nanomaterials are used in nuclear power, high-frequency absorption systems and X-ray radiation in the manufacture of tablets of fuel rods from ultrafine powders UO_2 [1]. The properties of these materials are largely due to grain size and phase composition, which in turn determines their subsequent characteristics. In the transition from the macro to the nanometer range are changed lattice parameters, electronic structure, the Debye temperature and the Curie point.

Development of energy-saving technology for continuous production of nanosized materials presented by example of preparation of nanosized zirconia from zirconium hydroxide in thermal vacuum installation. Fig. 1.

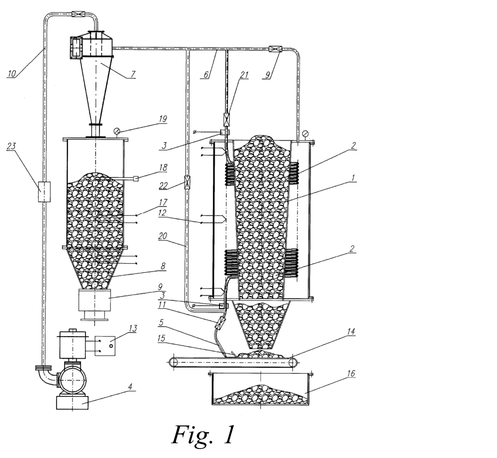


Fig. 1

This design provides a high and continuous process for preparing nanosized material shows stable performance, has a simple structure. [2]. The resistance of the heating element thermal vacuum installation is calculated in such a way that it will be possible to provide required heat energy Q, to produce nanomaterials.

$$I_H^2 \frac{4L\rho}{\pi\left(d_1^2 - d_2^2\right)} = \frac{Q}{\tau} = \frac{Q_1 + Q_2 + Q_3 + Q_4 + Q_5}{\tau} \tag{1}$$

where I_H - current heating element A; L – length of the heating element, m; d_1 – the outer diameter heating element, m; d_2 – the inner diameter of heating element, m; ρ – the resistivity of the heating element material Om·m; $Q_{1,2,3,4}$ – the amount of thermal energy used to heat: dry matter, moisture, parts and components of the installation, the evaporation of moisture, J; Q_5 – the amount of heat that goes into the environment, J; τ – time of work of installation, s.

To receive nanosized zirconia to provide rapid delivery of particles of zirconium hydroxide into the heating element 2 which has the shape of a coil. This can be realized if particles of zirconium hydroxide with air fed into the lower cavity of the heating element. There is a biphasic system of gas - solids. Movement two phase flow occurs in upstream in the sealed space of the heating element. In the thermal-vacuum installation continuous upstream inside the heating element created by vacuum pump 4. For effective supply of zirconium hydroxide into the cavity of heating element mass concentration of wet material in a stream of less than 1.2 g per 1 liter of air. Interaction between the solid particles and gas appears in the form of the aerodynamic force acting on the particle in the direction of movement. Speed of solid particles in upstream depends on its shape, size, weight, and condition of the surface material of the heater When forming a two-phase gas - solid particles must ensure that the speed of movement the two environments simultaneously from the point of entry to the heating element to the place of exit from the installation. From the results of experimental studies found that two-phase flow velocity ω, which ensures the efficiency of the thermal vacuum installation, can be determined from the expression.

$$\omega = \frac{\pi \cdot r^2 \cdot d^2 \cdot P_c \cdot (\rho_1 - \rho_2) \cdot V}{2 \cdot R \cdot l \cdot \mu}, \tag{2}$$

$$P_c = \frac{P_1 - P_2}{2},$$

where ω – speed two-phase flow in the heating element having a coil shape, m/s; r – radius of the heating element, m; d – diameter of the particle, m; P_C – average pressure inside the heating element, Pa; P_1, P_2 – initial and final pressures at the ends of the heating element, Pa; ρ_1 – material density kg/m^3; ρ_2 – medium density, kg/m^3; V – velocity of the conveying flow in m/s; R – coefficient of resistance, kg/s; l – length of the heater, m; μ - the coefficient of dynamic viscosity of air, Pa·s.

The rate of removal of moisture from the zirconium hydroxide is determined from the expression [3].

$$\frac{dm_{\text{mois}}}{d\tau} = \frac{\alpha S(T_{en} - T_{vap}) - (c_1 m_1 + c_2 m_2)\dfrac{dT}{d\tau}}{c_3 + c_4(T_{vap} - T_{\text{evap}})}, \qquad (3)$$

where *a* – coefficient of heat transfer; S – area of particles of zirconia, m^2: T_{en} – temperature of the environment in drying chamber K, T_{vap} – the temperature to which the heated vapor evaporating from the surface of drying material, c_1, c_2, – heat capacity of dry matter, moisture, J/(kg K), c_3 – the heat of vaporization, J/kg; c_4 – average specific heat of the vapor at P = const, J/(kg.K); $d\overline{T}$ – change in the average temperature of the material in an infinitely small time interval, K; T_{evap} – temperature of the evaporation of moisture, K; dm_{mois} – the mass of evaporated moisture in the time interval dτ, kg.

The first term of the numerator of (3) is the heat of the heater, which is transferred from the heater to the wet material with area S in an infinitely small time interval dτ.

$$dQ = \alpha\, S(T_{en} - T_{vap})d\tau. \qquad (4)$$

The second term of (3) - is the internal heat which goes to heating the material and its moisture during the same time period.

$$dQ = (c_1 m_1 + c_2 m_2)d.\overline{T}\ . \qquad (5)$$

Quantity of heat for evaporation of moisture from the surface of zirconium hydroxide is determined from the expression

$$dQ = (c_1 m_1 + c_2 m_2)d\overline{T} + [c_3 + c_4(T_{vap} - T_{evap})]dm_{mois}. \qquad (6)$$

In thermal vacuum installations continuous process of removing moisture is divided into two stages. At the initial time when the zirconium hydroxide with the air enters to the heating element 2, the body temperature decreases for some time and continues to decrease. Warming zirconia due to an external heat source is absent $\alpha S\cdot(T_{en} - T_{vap}) = 0$. At this time, moisture is removed from the surface of zirconium hydroxide by uniflow air flow which enters the heating element and the internal energy of the material, whereby the costs of heat for evaporation of moisture from the surface to cause reduction of the body temperature. From the surface particles of zirconium hydroxide released vapor, its temperature equals the temperature of evaporation $T_{vap} = T_{evap}$, therefore the second term of the denominator of (3) vanishes. Then, for an initial period of moisture removal expression (3) can be rewritten as:

$$\frac{dm_{\text{mois}}}{d\tau} = \frac{-(c_1 m_1 + c_2 m_2)\dfrac{dT}{d\tau}}{c_3}. \qquad (7)$$

During this period the rate of removal of free water from the surface of zirconium hydroxide, depends on the expression $(c_1m_1 + c_2m_2)\dfrac{dT}{d\tau}$, and the temperature of the particle T_1 becomes below the temperature of evaporation T_{evap}, ($T_1 < T_{evap}$). On the surface formed rough, porous, dry film (Fig. 2).

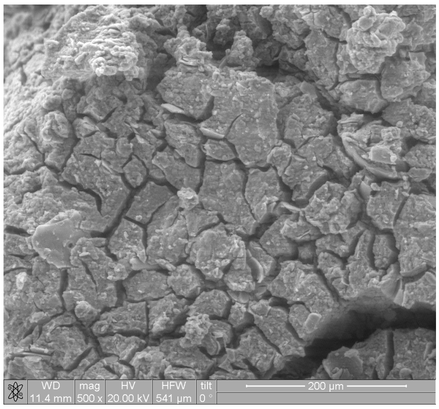


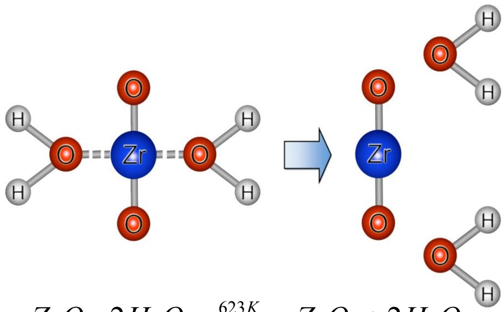
Fig. 2

Moving in the heater cavity, a spiral channel, zirconium hydroxide particle velocity increases. Formed rotational motion of the particle, which has an impact on the centrifugal force.

$$F = \frac{1}{6}\pi\ d^3 \Delta p\ \omega^2\ r\ . \qquad (8)$$

where $\Delta\rho$ – the difference in density between solid and liquid phases, kg/m^3; ω – rotational speed s^{-1}; r – istance from the particle to the axis of rotation m.

Centrifugal force presses the particles of zirconium hydroxide to a wall heating element, thereby providing thermal contact, which allows maximum use of heat from heater. Wet particle receives a strong flow of heat from heater in a short period of time and is heated to moisture vaporization temperature. At the same time evaporation zone is moved into the material. Excess heat transferred from the heating element to the wall part, as the result is internal steam generation, accompanied by an intense boiling of the liquid phase. An instant destructive internal stress occurs. The shell cracks under withstand critical pressure. Zirconium hydroxide breaks down into small particles. Moisture from zirconium hydroxide leaves into the surrounding space. At this time αS (Тс-Тп) ≠ 0. Depending on operating parameters the thermovacuum process and physical characteristics of the material being dried change occurs in its physical, chemical and mechanical properties. Zirconium hydroxide is converted to the fine zirconium dioxide (Fig. 3).



$$ZrO_2 \cdot 2H_2O \xrightarrow{623K} ZrO_2 + 2H_2O$$

Fig. 3

Upon further passage of zirconia particles in the cavity of heating element they crushed further by repeated collision of the heating element and the wall of the impact force of particulate material between them This continues until such time while the system is in the locally equilibrium state Heated and ground powder of zirconia with evaporated moisture enters the cyclone 7, Fig. 1, wherein the moisture is separated from the zirconia powder. Moisture has evaporated flows into the vacuum pump, zirconia - to storage hopper 8. Duration of receiving of zirconia from zirconium hydroxide occurs in less than 10 seconds. At the same time, the amount of energy consumed to produce a fine zirconia with 0.5% humidity from zirconium hydroxide with 85% humidity at a temperature of the heating element 623K and ambient pressure $1{,}33 \cdot 10^4$ Pa - 0.34 kWh / kg. The particle size of the zirconia is from 0.07 to 10 microns. Conglomerates in the resulting powder are absent Fig. 4.

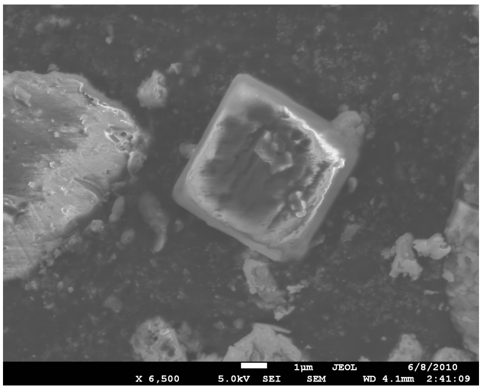


Fig. 4

Thermovacuum process for producing zirconia from of zirconium hydroxide is reduced by more than three times compared to the existing process [5]. At the same time three stages (drying, roasting, grinding with sieving into fractions) are combined into one. Occur continuously, energy-saving, high-performance process of getting nanosized zirconia powder with a monoclinic structure of high purity (Table 1).

Table 1

Chemical analysis zirconia

Elements	ZrO_2	Fe	Al	Ca	Cu	Sn	Si	Cr	Mn	Ti	Mg	Pb
%	<99.4	>0.1	>0.1	>0.1	0.012	0.0073	>0.1	0.038	0.016	>0.1	0.0015	0.026

Structural studies of powdered zirconia ZrO2 produced by X-ray diffractometer DRON-1 in Cu-kα radiation (U = 42 kV, I = 6 mA).

The recording conditions:

1) slots 0.5 × 0.5 × 0.5 mm;
2) velocity of counter 0.25° / min;
3) chart speed belt 300 mm/hour;
4) interval of diffraction pattern 2θ = 15…80°.

Table 2

Structural data zirconia powder ZrO_2

2θ°	d, Å	hkl
23.4	3.8	100
25.82	3.45	110
38.46	2.34	111
44.36	2.04	210

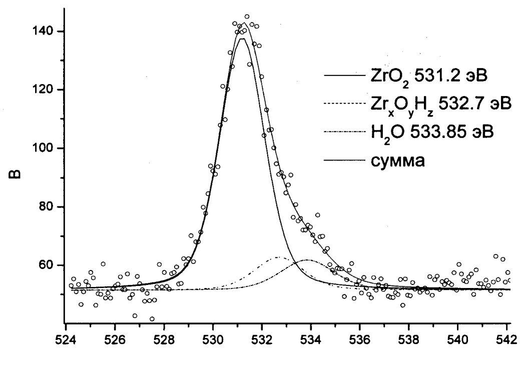


Fig. 5

Using X-ray photoelectron spectroscopy study the spectra oxygen (O1s) in the resulting sample of zirconia (Fig. 5).

The most intense line corresponds to zirconia (line 531.2 eV). On the surface of the zirconia contains up to 10% adsorbed moisture (line 533.85 eV). Water absorbed onto the surface from the atmosphere during the experiment. Also has a place (10%) chemisorption (line 532.7 eV). During contact with air zirconium hydroxide absorbs moisture from the environment with the formation of chemical compound. Moisture penetrates into the zirconia granules on the skin depth.

CONCLUSIONS

Found that the zirconia received by thermal vacuum, has a monoclinic crystal structure with a size of particles 0.07...10 micrometers.

An X-ray photoelectron spectroscopy confirms that zirconia has a low moisture content.

These data show the high efficiency of thermal vacuum method for nanopowder materials. Technological opportunities created thermal vacuum systems can be used to produce nanopowders of various materials of high purity.

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ТЕРМОВАКУУМНЫЙ МЕТОД ПОЛУЧЕНИЯ НАНОДИСПЕРСНЫХ МАТЕРИАЛОВ

В.А. Кутовой, Ю.Г. Казаринов, А.С. Луценко, А.А. Николаенко, В.И. Ткаченко

Изложены результаты релаксационных процессов при получении нанодисперсного порошка диоксида циркония из гидроксида циркония в термовакуумной установке. Приведены структурность порошка диоксида циркония и его чистота. Исследованы спектры кислорода (O1s) в диоксиде циркония.

ТЕРМОВАКУУМНИЙ ПРОЦЕС ОТРИМАННЯ НАНОДИСПЕРСНИХ МАТЕРІАЛІВ

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Викладено результати релаксаційних процесів під час одержання нанодисперсного порошку діоксиду цирконію з гідроксиду цирконію в термовакуумній установці. Наведено структурність порошку діоксиду цирконію та його чистота. Досліджено спектри кисню (O1s) у діоксиді цирконію.