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NANOMATERIALS AND NANOTECHNOLOGIES

Production of Chemically Pure Zirconia-Based Nanoceramics in the $ZrO_2(Y_2O_3)$–Al_2O_3 System for Restorative Dentistry

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Abstract—The synthesis technology of a chemically pure nanodisperse precursor powder (10–12 nm) based on a tetragonal solid zirconia (t-ZrO_2) solution in the ZrO_2 system (Y_2O_3)–Al_2O_3 for restorative dentistry is developed. A ceramic material with a crystallite size of 60–65 nm is obtained; its phase composition, dispersion, microstructure, and physical and mechanical properties are investigated; and its low-temperature moisture aging structural stability is established.

Keywords: zirconia, chemical precipitation, nanocrystalline powders, nanoceramics, restorative dentistry
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INTRODUCTION

The development of current nano- and biotechnologies is closely related to the development of high-tech multifunctional materials based on nanostructured metal oxides. The use of ceramic materials in medicine has received a noticeable development in the last decade, so the creation of new medical materials is an important task, being a significant segment of the modern high-tech market. An analysis of the scientific literature [1–4] makes it possible to conclude that a new scientific branch has formed: biomaterial science, the main task of which is to solve the problem of obtaining medical biomaterials based on oxide nanocompounds. The scientific approach to this problem is the development of innovative technologies for the production of powder precursors, on the basis of which biomaterials with desired physicochemical and mechanical properties will be created in the future.

In the last decade, the demand for oxide nanocompounds has been observed in restorative dentistry. Ceramic materials from zirconia stabilized in tetragonal modification (t-ZrO_2) are the most popular [4–6], because they have a complex of unique physical and mechanical properties: chemical and structural stability; high crack resistance, hardness, and strength; and light transmission, similar in performance to natural dental tissues. In addition, ZrO_2 is biologically compatible with the mucosa and tissues of the oral cavity and does not cause allergic reactions. However, it should be taken into account that t-ZrO_2-based ceramics are characterized by the effect of low-temperature moisture aging at 100–400°C due to the uncontrolled phase transition t-$ZrO_2 \rightarrow m$-ZrO_2 (zirconia monoclinic modification), leading to a ~4% increase in volume and cracking of ceramics. A possible way to overcome low-temperature degradation can be the use of a tetragonal ZrO_2 stabilizer, for example, aluminum oxide [6].

For the time being, the main manufacturers of zirconia disperse powder used for dental purposes are foreign companies such as Tosoh (Japan), Sax IBS Ceramic Applications (Germany), and Zirkonzahn (South Tyrol, Italy). These companies obtain t-ZrO_2 using a complex technological scheme: zirconium oxychloride synthesis by $ZrSiO_4$ chlorination in the presence of coke at 900–1000°C → zirconium and yttrium chlorides hydrolysis → drying → calcination → grinding → the introduction of organic binders → spray drying → stabilized zirconia granulate. Foreign technology gives a fairly good result, but the complexity and duration of this process, consisting of eight stages and requiring high energy costs, should be noted. Also, this technology does not solve the problem of obtaining precursor powders with a uniform component distribution, and the particle size of the powders exceeds 350 nm.

The development of synthesis technologies of highly dispersed oxide powders is a priority in modern materials science and engineering [7]. Therefore, the creation of innovative technological bases for the production of dispersed and relatively cheap zirconia solid solution precursor powders will provide at least the partial import substitution of the foreign product in domestic dentistry.

The purpose of this work was to develop a simple and economical technology for the synthesis of chemically pure nanopowder based on the t-ZrO_2 solid solution in the $ZrO_2(Y_2O_3)$ system—5 wt % Al_2O_3 with particle dimentional homogeneity, which can be used as a ceramic material for restorative dentistry.

EXPERIMENTAL

Research Methods

The following research methods were used in the work.

(A) X-ray phase analysis (XFA, Bruker D8-Advance diffractometer) to determine the powders structure and phase composition. Using the Selyakov–Scherer formula, $d_{\text{hkl}} = k\lambda/(\beta\cos\theta)$, the average crystallite size was calculated from the profile of the most intense diffraction line [8].

(B) The low-temperature nitrogen adsorption method to determine the specific surface area of xerogels and powders (S_{BET}) (Quantachrom NOVA 4200e gas sorption analyzer).

(C) Differential thermal analysis (DTA, MOM Q–1000 derivatograph) in air in a temperature range of 20–1000°C to study the processes of powder thermolysis.

(D) Thermal treatment of the powders to study the processes of phase formation and sintering in a temperature range of 100–1400°C (Naberterm electric furnace, silicon furnace with SiC heaters).

(E) Electron microscopy to study the texture of the powders and sintered ceramics (electron microscope EM-125 with $U_{\text{acc}} = 75$ kV).

(F) Hydrostatic weighing for determining the open porosity of the ceramic samples (GOST 2409–2014).

(G) The indentation method for determining the Vickers hardness and crack resistance of the ceramics (PMT-3M hardness tester, GOST R 8.777–2011).

(H) Three-point bending for determining the mechanical strength of the ceramics (GOST R 50526–93).

(I) The ceramics were tested for aging resistance according to ISO 13356–2008, exposing the samples to water vapor at a temperature of 140°C and a pressure of 0.2 MPa for 5 h in an autoclave.

Synthesis of a $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 Powder Precursor

The most popular method for producing nanodispersed oxide systems is hydroxides coprecipitation, which provides for compositional homogeneity and does not require special equipment or expensive chemical agents. The use of additional physicochemical effects on the resulting precipitate, such as cryochemical processing [9], makes it possible to expand the capabilities of coprecipitation and reduce the extent of agglomeration of the particles.

The composition in the $ZrO_2(Y_2O_3)$–Al_2O_3 system was synthesized by the method of coprecipitation. The amount of yttrium oxide was determined from the need to obtain the ZrO_2–3 mol % Y_2O_3 tetragonal solid solution phase. The amount of Al_2O_3 was 5 wt % to the synthesized *t*-ZrO_2 to preserve the structural homogeneity and physical and mechanical properties of the zirconia-based ceramics. A higher content of aluminum oxide in the ceramic composition will adversely affect the value of crack resistance and thermal conductivity of the material.

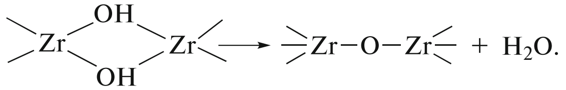
Nitrate salts $ZrO(NO_3)_2 \cdot 2H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (all of C.P. quality), from which diluted aqueous solutions were prepared (~0.1 M), and ammonia solution (~1 M) were used as the initial reagents. The powders were synthesized by reverse chemical precipitation with additional cryochemical treatment of the obtained precipitate. A mixture of zirconium, yttrium and aluminum salts solutions was added dropwise into NH_4OH, vigorously mixed and the pH value was controlled in the reaction vessel. When carrying out the process of coprecipitation in the $ZrO_2(Y_2O_3)$–Al_2O_3 system, the following conditions should be met [10, 11]:

(A) Hydroxide precipitation should be carried out from dilute salt solutions with an excess of ammonia solution and at a minimum rate ($V_p = 0.02$ cm^3/s) in order to ensure the spatial distance of the hydroxide nucleation centers from each other and to slow down their growth;

(B) The pH in the reaction vessel should be maintained in the range of 9.2–9.4, since a small increase in this value initiates the process of aluminum hydroxide dissolvement, which can lead to a violation of a given oxides ratio in the $ZrO_2(Y_2O_3)$–Al_2O_3 system;

(C) The formed precipitate should be thoroughly mixed to achieve its composition homogeneity;

(D) The residence time of the precipitate in the mother liquor should be minimal to prevent aging of the precipitate and the formation of hard agglomerates, which occurs as a result of the irreversible transformation of hydroxogroups (OH) into oxo groups (oxolation process), causing the formation of hard agglomerates and the violation of precipitate homogeneity [11]:



The obtained gel-like precipitate was separated from the mother liquor by vacuum filtration and frozen at –25°C for 24 h. According to the XFA data, the xerogel formed after the cryochemical treatment was a mixture of an X-ray amorphous substance and a crystalline phase (Fig. 1). The xerogel textural characteristics are given in Table 1.

An electron microscopic study showed that the size of the agglomerates in this xerogel does not exceed 500 nm (Fig. 2). The knowledge of the SBET value made it possible to estimate the size of the primary ZrO_2-based xerogel particles in terms of sphericity of their shape according to the following relationship:

$$d_{\text{BET}} = 6\times10^{-4}/\rho S_{\text{BET}},$$

where ρ is the theoretical phase density; d_{BET} is the diameter of a spherical primary particle.

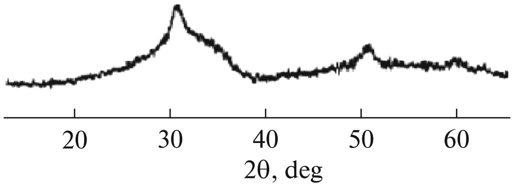


Fig. 1. Diffractogram of the xerogel in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system after cryochemical treatment of the precipitate at –25°C (24 h).

The study of the xerogel thermolysis suggests that the cryochemical treatment of the coprecipitation product affects the process of its thermal decomposition. The DTA curve demonstrates an insignificant endothermic effect in a temperature range of 250–350°C, corresponding to residual xerogel dehydration; the mass loss of the studied sample is ~10–12% (Fig. 3a). In this regard, it can be stated that treatment at –25°C results in the removal of most of the water component from the precipitate. An exothermic effect with a maximum of 450°C on the DTA curve characterizes xerogel crystallization with the formation of a cubic metastable $ZrO_2(Y_2O_3, Al_2O_3)$ solid solution in the C-type structure (Fig. 3b), the textural parameters of which are given in Table 1.

An increase in the burning temperature to 700°C leads to the formation of a nanodispersed precursor powder with a crystallite size of 10–12 nm (Fig. 4a) based on the t-ZrO_2 phase. The formation of the zirconia tetragonal phase is indicated by splitting of the diffraction maxima in the range of $2\Theta = 35°–36°$, 50.5°–51.5°, and 60°–61.5° (Fig. 4b).

According to spectral analysis, it was established that the amount of impurities in the synthesized precursor powder is insignificant (Table 2) and, in qualitative terms, they cannot pose a danger to the human body.

Figure 5 reflects the main stages of the nanodispersed t-ZrO_2 powder synthesis in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system. The proposed technology has a number of undeniable advantages over foreign technology:

(A) It does not require expensive reagents and can be carried out on standard equipment.

(B) It provides the homogeneous distribution of the initial reagents in the synthesized product, which makes it possible to synthesize nanopowder with a given structure and chemical composition at a temperature of 800°C.

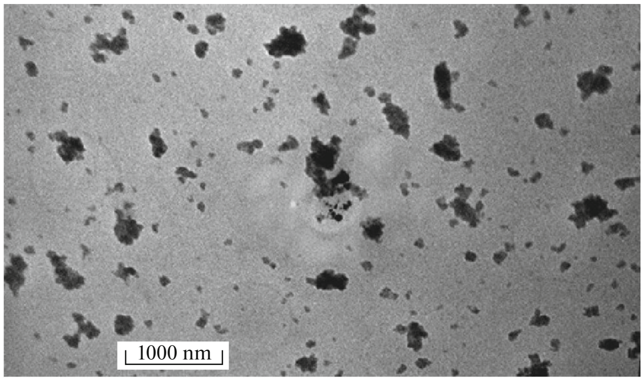


Fig. 2. Microphotograph of the xerogel in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system after cryochemical treatment of the precipitate at –25°C (24 h).

(C) The number of technological stages is reduced to four (the number of stages in foreign production is eight).

(D) It has the ability to synthesize powders in sufficiently large quantities.

(E) By-products of the t-ZrO_2-based powder synthesis do not exceed the maximum permissible concentrations in terms of the amount of harmful impurities and they meet sanitary standards; therefore, they do not require additional cleaning or special disposal measures, so we can assume that this technology is environmentally friendly and safe.

The technology for producing the nanodispersed precursor powder based on the t-ZrO_2 solid solution has been patented [12].

Sintering the Powder Precursor in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 System

It was found that heat treatment of the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 precursor powder in the temperature range of 800–1400°C improves the crystal structure of the zirconia-based solid solution without disturbing its phase composition. On the powder diffractograms (Fig. 6), after burning at 1000 and 1400°C, only the t-ZrO_2 phase is displayed; the α-Al_2O_3 phase is not traced, probably because of its

Table 1. Textural parameters of the xerogel and powders in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system

Xerogel		Powder (500°C)		Powder (700°C)	
S_{BET}, m^2/g	d_{BET}, nm	S_{BET}, m^2/g	d_{hkl}, nm	S_{BET}, m^2/g	d_{hkl}, nm
315	4–5	143	6–8	93	10–12

S_{BET} is the specific surface area, d_{BET} is the size of the xerogel primary particles, and d_{hkl} is the average powder crystallite size.

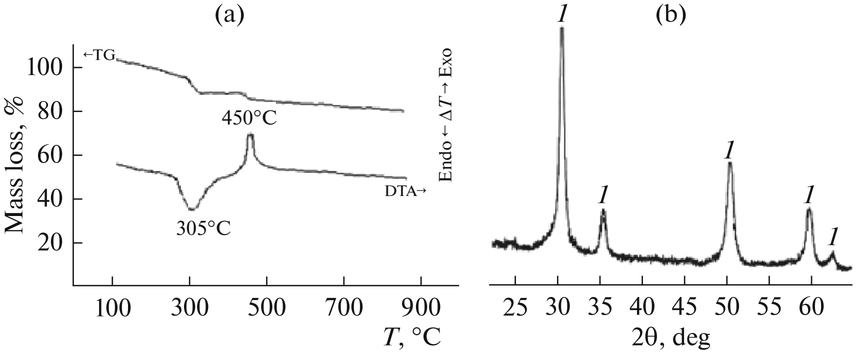


Fig. 3. Thermogram of the xerogel in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system (a) and diffractogram of the ZrO_2-based solid solution after the heat treatment of xerogel at 500°C (b). (*1*) C-type solid solution cubic structure.

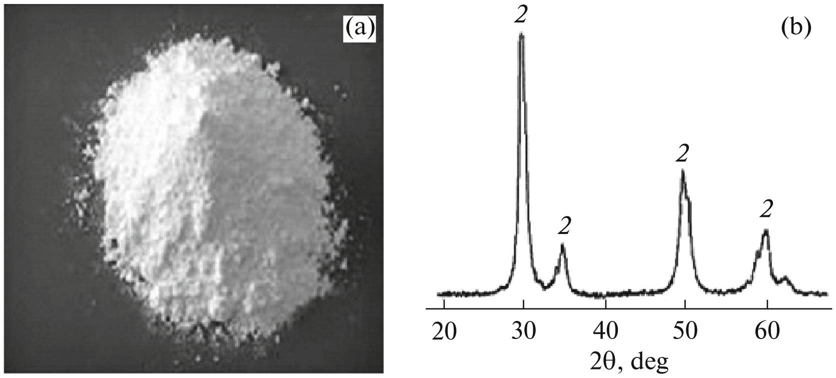


Fig. 4. Appearance (a) and diffractogram (700°C) of the *t*-ZrO_2-based powder precursor in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system; (b) (*2*) *t*-ZrO_2 phase.

high dispersion due to the synthesis technology and low content in the *t*-ZrO_2 solid solution.

The dynamics of changes in the average crystallite size of the zirconia-based solid solution in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system was studied in a temperature range of 500–1400°C (Fig. 7). For comparison, this figure also shows the crystallite size of the stock ZrO_2(3 mol % Y_2O_3) solid solution. Obviously, the presence of aluminum oxide in the ZrO_2 solid solution matrix slows down the main phase crystallite growth and blocks the recrystallization process.

Compacts were molded from the precursor powder (700°C) with a formed crystal structure (see Fig. 4) by uniaxial pressing under 200 MPa, which were burnt at 1400°C with an isothermal holding time of 2 h; the heating rate was ~350–400°/h. A sufficiently high heating rate was chosen in order to reduce the crystallite growth rate. After burning, the sintered compacts were immediately removed from the furnace, since hardening of ceramic zirconia-based samples leads to a higher density than furnace cooling, which is due to the squeezing effect of the outer material layers that occurs during rapid cooling [13]. It should also be noted that, when the ceramic samples are furnace cooled, a recrystallization process takes place (a growth of the *t*-ZrO_2 grain to 120 nm), which initiates a *t*-ZrO_2 → *m*-ZrO_2 phase transition with the expansion of the crystal lattice, causing microcracking of the ceramics and a decrease in its density.

Table 2. Impurity content in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 powder after heat treatment at 700°C

Impurity	HfO_2	CaO	Fe_2O_3	Na_2O	BaO	SiO_2
Content, wt %	1.3	<0.01	<0.01	<0.01	<0.001	0.01

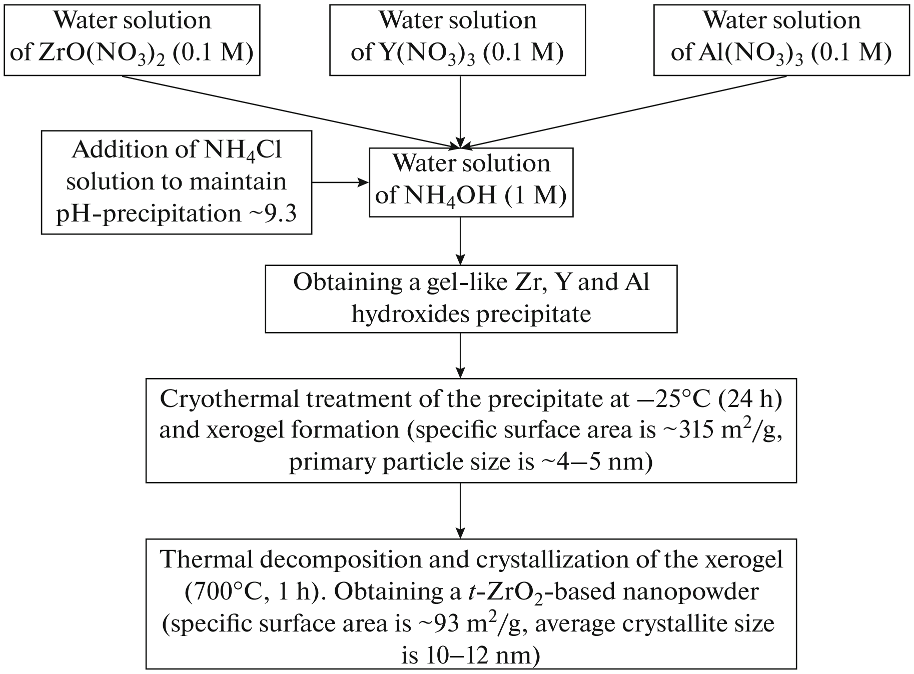


Fig. 5. Main stages of the t-ZrO_2-based powder precursor synthesis in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system.

It was established that the process of ceramic compacting proceeds mainly when the powder is heated up to 1400°C, reaching a density of ~0.97 from the theoretical value. Increasing exposure to 3 h does not lead to a further increase in the density of the ceramic material. The average shrinkage of the studied samples is ~24%. Figure 8 shows the appearance and microphotography of the sintered $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 ceramics. The microstructure of the ceramic material is a dense package of well-formed crystallites with a size of less than 100 nm.

Properties of the Sintered Ceramics in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 System

The physical and mechanical properties of the sintered ceramics in the ZrO_2 (Y_2O_3)—5 wt % Al_2O_3 system (Table 3) were determined. For comparison, this table also shows the properties of the ZrO_2-based ceramics, produced by the Sax IBS design office, which is offered on the international dental materials market. A comparative analysis of the characteristics of the produced ceramics and the foreign counterpart shows that the t-ZrO_2-based ceramic material, synthesized according to the technology developed by us, is not inferior in parameters to the material produced by Sax IBS, and even surpasses it in some indicators.

RESULTS AND DISCUSSION

According to the XFA results, the unit-cell tetragonality (c/a) of the t-ZrO_2 solid solution in the sintered ceramics was calculated, which is 1.43016. It can be assumed that such a high degree of tetragonality is associated both with the technological features of the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 powder synthesis and with the presence of aluminum oxide in the ceramic composition. Removing most of the water component in the form of OH^-—groups during the cryochemical processing promotes the formation of additional oxygen vacancies ($O_o \leftrightarrow 1/2O_2 + V_o^{2+} + 2\bar{e}$) and specific rearrangement of the zirconia oxygen sublattice, in

Table 3. Physical and mechanical properties of t-ZrO_2-based ceramics

Ceramic chemical composition	d, nm	P, %	H_v, GPa	K_{1C}, MPa $m^{1/2}$	σ_{bend}, MPa
$ZrO_2(Y_2O_3)$—5 wt % Al_2O_3	60–65	1	13.5	10	900
$ZrO_2(Y_2O_3)$ (Sax IBS, Germany)	≥350	No.	12.5	7	<900

P is open porosity, H_v is Vickers hardness, K_{1C} is crack resistance, and σ_{bend} is bending strength.

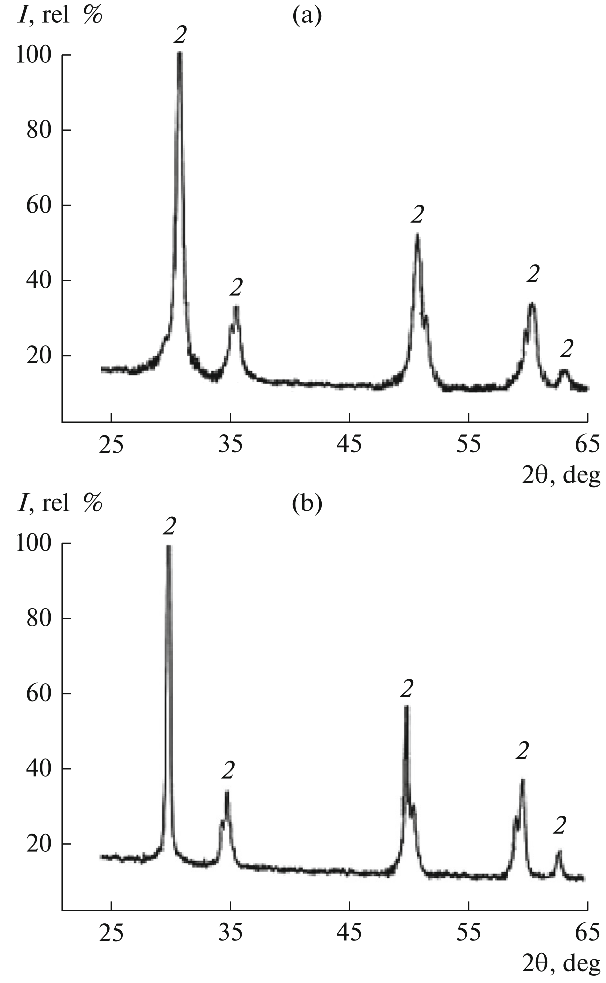


Fig. 6. Diffractograms of the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 powder after burning at 1000°C (a) and 1400°C. (b) (*2*) *t*–ZrO_2 phase

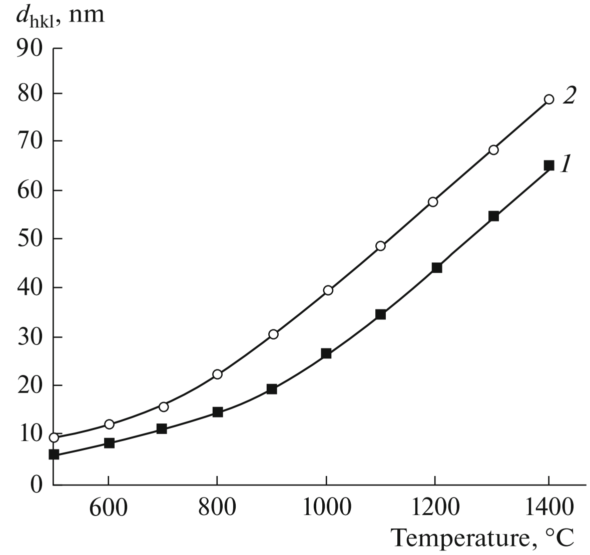


Fig. 7. Change in the average crystallite size of the ZrO_2-based solid solutions (d_{hkl}) depending on temperature: (*1*) Al_2O_3—5 wt % solid solution in the $ZrO_2(Y_2O_3)$ system; (*2*) ZrO_2 solid solution (3 mol % Y_2O_3).

which one half of the oxygen atoms significantly shifts relatively the other half, which leads to a significant elongation of the unit cell parameter *c* in the direction of the displacement of oxygen atoms (the phenomenon of distortion [14]). Al_2O_3 slows down the crystallite growth of the *t*-ZrO_2-based solid solution during ceramics heat treatment, preventing the achievement of a critical crystallite size when a spontaneous phase transition *t*-$ZrO_2 \rightarrow$ *m*-ZrO_2 is possible, maintaining a high c/a value.

The effect of low-temperature aging in water vapor on the structure of ceramic samples in the $ZrO_2(Y_2O_3)$ system—5 wt % Al_2O_3 was studied. According to the ISO 13356 requirements, the stability of the tetragonal zirconia phase after aging is determined by the content of the *m*-ZrO_2 phase before and after treatment in a humid environment. It was established that the initial samples after water-vapor treatment at a temperature of 140°C do not have cracks and destructions and according to the XFA results and retain a single-phase crystalline structure corresponding to the *t*-ZrO_2-based solid solution; there is only a slight increase in the average crystallite size of the *t*-ZrO_2 phase up to 75 nm. The phase stability of the ceramic samples in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system during their

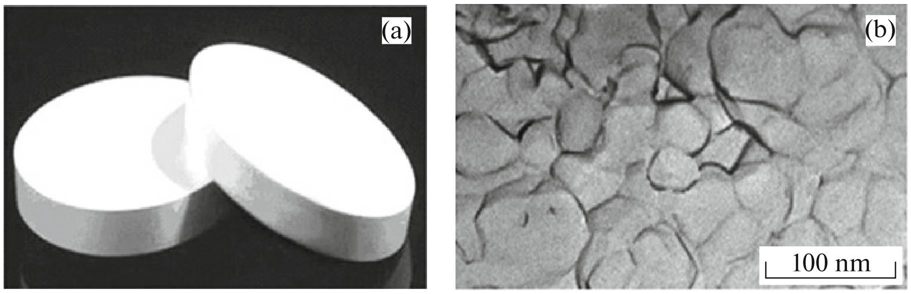


Fig. 8. Appearance (a) and microstructure (b) of nanoceramics in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system.

hydrothermal treatment can be explained by the high degree of tetragonality of the synthesized zirconia solid solution, which inhibits the *t*-ZrO_2 –> *m*-ZrO_2 phase transition during the ceramics low-temperature moisture aging [15] while maintaining its structural stability.

CONCLUSIONS

The use of the hydroxides coprecipitation in the $ZrO_2(Y_2O_3)$—5 wt % Al_2O_3 system with additional cryochemical precipitate treatment made it possible to significantly reduce the extent of agglomeration of the synthesized product and to obtain, upon further heat treatment, a nanodispersed single-phase chemically pure solid-solution precursor powder (10–12 nm) based on the *t*-ZrO_2 zirconia tetragonal modification.

The optimal sintering conditions for the *t*-ZrO_2 precursor powder were selected to obtain dense nanocrystalline ceramics with a stable phase composition.

It was shown that the sintered ceramics in the $ZrO_2(Y_2O_3)$–Al_2O_3 system have high physical and mechanical characteristics and retain structural stability during low-temperature moisture aging.

The preliminary calculation, made with allowance for the features of the technology developed by the authors and foreign technology, showed that the estimated cost of the synthesized *t*-ZrO_2-based precursor powder is 15–20% lower than that of the imported analogue, while it retains the high quality of the finished product. In this regard, it can be assumed that the use of the developed synthesis technology will reduce the dependence of domestic dentistry on imported materials, as well as elevate the quality of dental treatment to the European standards.

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