THE PROBLEM OF EFFECTIVE PRESSURE ON CONSOLIDATION OF ZIRCONIA NANOPOWDERS AND ITS SOLUTION WITH SPARK-PLASMA SINTERING

Prof. PhD. Eng. Edvin GEVORKYAN[1], **Sen. Staff Scientist Yury GUTSALENKO**[2,1], **Sen. Lecturer PhD. Vladimir CHISHKALA**[3,1], **Sen. Lecturer PhD. Olga MELNIK**[4,1], **Postgraduate, Magister Maxim KISLITSA**[1,3]

[1]Ukrainian State Univ. of Railway Transport, edsgev@gmail.com

[2]**Nat. Tech. Univ. "Kharkov Polytechnic Inst.", gutsalenko@kpi.kharkov.ua,**

[3]**V. N. Karazin Kharkov Nat. Univ., vchishkala@ukr.net**

[4]Ivan Kozhedub Kharkov Univ. of Air Force, melhik@ro.ru

Kharkov, Ukraine

Abstract: *The problem of physical and mathematical prediction of rational pressure during spark-plasma sintering of zirconia nanopowder is being considered. The physical aspects of this problem are defined, and it is presented an approach to the calculation of the pressure in the compression cycle at the stage of pre-production and experimental development. The calculation is based on the use of the Paschen law in relation to the considered model of spark plasma consolidate of nanopowders under pressure. The calculation result is compared with the practical experience of energy-saving high-speed spark-plasma sintering of the fine high-density ceramics from* $(Zr_{0.94}Y_{0.06})O_{1.88}$ *nanopowder.*

Keywords: zirconia, nanopowder, spark-plasma sintering, electrical discharge, Paschen law, compaction pressure, fine high-density ceramics.

1. INTRODUCTION

It is known [1]=[1] that most of the properties of solids substantially size-dependent with a decrease in particle size to several interatomic distances in one, two or three dimensions. The production of refractory ceramics with high performance we associate with our own development of modern technological approaches [2] and equipment [3] for nanopowder metallurgy that goes back to the origins of the Japanese method of spark-plasma sintering (SPS) [4]. For the development of ceramic materials in the direction of ensuring a new level of technological heredity of production preparation of various articles thereof requires nanocrystalline ceramic powders with desired morphology, phase composition, the properties of the bulk phase and surface.

The unique combination of high performance stabilized zirconia by mechanical strength, fracture toughness, fire resistance, chemical resistance, bioinertness makes it an indispensable material in a number of modern technological processes and production of metallurgy, mechanical engineering and instrument making to medical equipment and dentistry [5-8].

A variety of solid phase, gas phase and liquid phase methods [9-17] are used in order to receive nanocrystalline metal oxides now. Nanopowders are prepared by either physical methods – evaporation-condensation, high energy destruction, or chemical methods – plasma-chemical and mechanochemical synthesis, thermal decomposition. The choice of a method for producing a powder is determined by the requirements for its particle size distribution and the

chemical purity, the scale of production and technical and technological capabilities. If the physical methods of obtaining nanopowders can provide greater flexibility particle size and shape control, the chemical, as a rule, are more versatile and productive. Fine powders of zirconia and solid solutions based on it are obtained primarily by chemical methods. One of them – thermal decomposition of aqueous solutions of salts in the low-temperature plasma – makes it possible to obtain high-temperature phases of zirconia with improved physical and mechanical properties [18].

In the modern age retrospective practice the use of different methods of synthesis leads to the formation of zirconia nanocrystals with different crystal structure, morphology, with different and usually quite broad particle size distribution[19-22, 11, 12, 15, 23].

Technological parameters of the formation of nanocrystalline zirconia, as the achievable space-geometrical and physical-mechanical results, greatly vary not only from method to method but also in the use of one method as it follows, for example, from practice of hydrothermal synthesis method [19-22, 11, 12, 15, 23]. This method is widely used in connection with the possibility of getting practically isolated zirconia nanocrystals with a narrow particle size distribution. However, in the variety of works of various researchers there is no single or predominant opinions on temperature and other conditions, as well as about the mechanism of formation of nanocrystals of zirconium dioxide under hydrothermal conditions. Preparation of nanocrystalline powders of metal oxides by hydrothermal method from aqueous salt solutions associated with the technological difficulties and requires special devices to provide significant temperature and very high pressure. In current practice preference is given to the combined method [30] which consists of a preliminary preparation of the mixture of precipitated hydroxides and their subsequent high-temperature hydrothermal decomposition. Method of co-precipitation allows to achieve a high degree of homogeneity of the starting compounds at the molecular level, and high-temperature hydrolysis contributes to the formation of primary slaboaglomerirovannyh nanocrystalline zirconia particles.

According to the results of a special study [31], histograms of the grain size distributions for nanopowders of stabilized zirconia are formally similar and have similar boundaries and range of basic sizes (minimum 95%) in real search range of choice of rational technological regime parameters of the hydrothermal synthesis.

Our research of zirconia SPS is performed with using of powder from the same manufacturer as in research [32] that operates with its own resource base, that is ours and [32] conditions are fully comparable in terms of the initial powder.

Realized [32] technological route involves two basic operations of ceramic production from initial nanoscale powder: compacting and sintering. The first (preliminary) is performed on the isostatic press. This is followed by an intermediate auxiliary operation of recess a pre-compacted samples from elastic forms of isostatic load. The second (final) is performed in an air oven. In the technological alternatives on the SPS method under pressure with direct current supply to the work area [2] compacting and sintering process is positionally overlapped, and the process is implemented by steps on cyclogram of electrical and press loads in a single operation, as shown in [33].

2. THE PROBLEM AND PHYSICAL APPROACH TO DECISION

Minimization of porosity determines success of the consolidation of nanopowders in tasks of high-density material obtaining. Therefore, the problem of effective pressure for consolidation of nanopowders in the implementation to technological approaches [32] and [2] in both cases is related to the suppression of porosity. The physical nature of the effective permissions of this problem in the SPS technology under pressure with direct current supply into the work area is more complex than for the conventional powder compaction and sintering of nanoceramics [34, 35], and with it more perfect. This is indicated by analysis of the conditions in experimental obtaining the best results on the structure and properties of the sintered samples.

In [32] the best result was obtained at the highest pressure which is provided by the technical capabilities of a particular press (400 MPa). In this case the revealed threshold of effective cold mechanical fracture grain agglomerates (~ 300 MPa) is exceeded and the entire process of compaction is regarded as purely mechanical.

Our choice of compacting and sintering of stabilized zirconia by the technological method with direct current supply in the working area comes not only from the known conductivity of this ceramics [36, 37]. We take into account also that the electrical effects in the formed nano-sized zirconia ceramics occur much more active since the conductivity of stabilized zirconium dioxide in the nanoscale powder materials with a high degree of dispersion is greatly increased [38].

Our technical possibilities of pressure in the SPS cycle are limited to the strength of the material of the working cameras for electric consolidation [3] which is made of a dense fine grained graphite (80 MPa [33]).

However, competitive to [32] the sintering result, we have already received at a pressure of 30 MPa and a holding time of 5 minutes at a maximum temperature of 1,200 °C (see Table 1). We consider the explanation of this phenomenon with a position to participate the electrical processes in the suppression of porosity in the consolidation as shown by Raychenko [39], and from the standpoint of optimizing for maintenance of these processes by electrical discharges on the Paschen-Penning [40, 41]. For the first time this hypothesis has been formulated and was confirmed in [42]. Its essence is as follows. The gradient of electric field strength increases in a neighborhood of the pores in electrically conductive medium, and more for large pores (Fig. 1). Locally increased heat generation caused by the action of an electric current causes a more active growth of crystallites and reduction of pore size, particularly the largest [39]. Minimization of voltage for initiation of electrical discharge in the pore by optimum pressure [40, 41] on the largest pores increases increases the probability of their suppression. Firstly, due to the additional heat buildup in electrical discharge channel, in thermophysical analogy crystallite growth stimulation [39]. Secondly, due to chemical reactions with the contents of the gas medium of pores, particularly because of ozone which is a typical for electrical discharge in the presence of the air oxygen, and is known as an active oxidizing agent, with simultaneous displacement of some gaseous reaction products, thereby decreasing the volume of the pores. In the carbon-containing graphite cameras - including with the formation of carbon monoxide according to the mechanism of atomic carbon capture, similar to that shown in [43], and its crowding out into the open porosity of these cameras [33].

Table 1. Characteristics of the SPS [23] and the conventional [32] ceramics from nanopowder of stabilized zirconia

Ceramics	Bulk density, %	Average crystallite size, nm	Microhardness, GPa	Compressive strength, MPa
[23]	98.0	50-200	14.1	2,580
[32]	88.5	about 1,200	11.8	440

According to the hypothesis [42] about optimization of pressure in a cycle of consolidation and sintering of nanopowders by SPS method, in the general case its value is defined by the formula [44]:

$$P_{opt} = k \cdot (P \cdot h)_{opt} / h, \quad (1)$$

where $(P \cdot h)_{opt}$ – characteristics of minimum of potential discharge ignition in gas, Pa·м; h – dimensional characteristics of nanopowder, equivalent to the highest expectation of the discharge gap (the grain diameter in the spherical model), m; k – correction factor that takes into account the geometry of the gap in the pores, the composition and thermal backdrop of gas medium in them; in the general case $k > 0$, and, in particular, with high expectation $0 < k < 1$ in initially normal humid environments of real compacting.

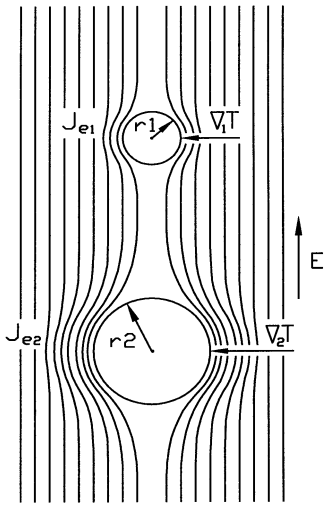


Fig. 1. Change of current density ($J_{e2} > J_{e1}$) and temperature gradient ($\nabla_2 T > \nabla_1 T$) in the electric field with intensity E [39].

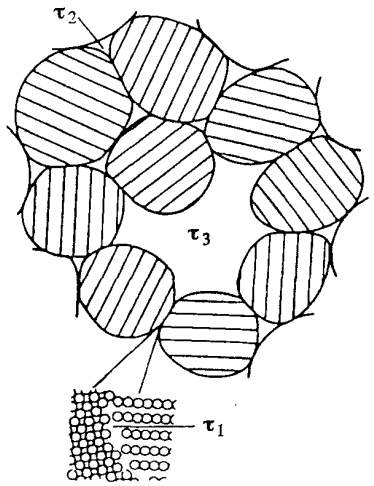


Fig. 2. Dimensional model of nanocrystalline material [46]: vacancy in the dividing boundary (positron lifetime τ_1); vacancy agglomerate in the triple junction of the crystallites (τ_2) and large pore (τ_3) in place of the absent crystallite.

The value of P_{opt} in the SPS tasks to continuity defects with any gaseous medium, simple or complex (multi-component), in the first approximation with allowable assumption

of clean air and, moreover, dry, when $(P \cdot h)_{opt} = 0.8$ Pa·м [45] and $k = 1$ [40], is inversely proportional to h ($k \cdot (P \cdot h)_{opt}$ – proportionality coefficient) as it follows from (1). We proceed in assessing h as grain diameter from the conventional model [46] for the maximum single pore in nanomaterials with crystalline grain structure (Fig. 2).

3. EXISTENCE, ANALYSIS AND DISCUSSION OF THE RESULTS

The accuracy of grain size determination resulting from methodological, hardware and other influences, including the quality of the grain, in particular purity boundaries and their possible partial amorphization [47] shoud be taken into consuderation in operating with grain size. The methods of X-ray diffraction are usual approach to the calculation of the size of nanocrystals in modern analysis of solids. This is due to the known difficulties of directly determining such small particle size, especially with volumetric analysis [48].

However, a priori generally accepted dimensional identity of average crystallite size and indirectly controlled by the hardware of the coherent scattering by Debye-Scherrer can actually be quite approximate, because of boundary defects of crystallite quality a real size of the coherent scattering smaller than the crystallite.

According to the modern research [49] in certain methodical situation the calculated results of X-ray diffractometry, particularly with uncertainty crystallite form, at all should not take as a powder particle size . The generally accepted definition of the average error of the

Given this expectation of noticeable average error at estimating the grain size in its volume study, we jointly and severally together with the Russian researchers [32, 16, 23] used also current means of control planimetry control and optical imaging. Study of size of the powder was carried out using transmission electron field emission microscope JEOL JEM-2100 (TEM). The phase composition of the synthesized zirconia powder stabilized with yttrium after heat treated was determined by X-ray diffraction Rigaku Ultima (XRD) (CuKα radiation, Ni filter). Examinations of the elemental composition were carried out by using electron ion microscope Quanta 200 3D (SEM).

By transmission microscopy revealed that the used powder $ZrO_2(Y)$ consists of spherical shape particles with an average size of ~ 3-15 nm, forming a weakly bound agglomerates with an average size of ~ 100-500 nm [16, 23]. Before milling in a ball mill that is the previous to compacting and sintering, the original powder $ZrO_2(Y)$ [32] had similar dimensional characteristics, respectively 5-10 nm and 100-200 nm. Similarly [32], the main fraction of our powder after hour milling in a ball mill was reduced to the dimension from 1.5 nm up to about 50 nm.

From (1) it follows that the main target in the suppression of porosity in our experience (P_{opt} = 30 MPa) were nanocavities with an average size of 25-30 nm, which corresponds exactly to the modal area of normally distributed grain sizes of the initial powder.

Together with Russian researchers [16, 23] and with using of the raster ion-electron scanning microscope Quanta 200 3D in terms of their research base, we performed X-ray analysis to determine the exact elemental composition of the initial powder. It was found that the composition of the powder material described by the formula of non-stoichiometric species $(Zr_{0.94}Y_{0.06})\ O_{1.88}$. According to the catalogs ICDD [51] obtained material is a single-phase solid solution and has a tetragonal crystal lattice with space group P42/nmc.

Character of $(Zr_{0.94}Y_{0.06})O_{1.88}$ nanopowder SPS is shown in Fig. 3. The heating was carried out at temperatures ranging from 20 °C to 1550 °C at a rate of 20 °C/min. The temperature and compact linear deformation was monitored using high-temperature dilatometer Netzsch L75HX.

Dilatometric data show that shrinkage was approximately 2% in the range from 1400°C to 1500°C, and it practically stops with achievement of 1500°C. It was decided that we can neglect the relatively little increment of density at increased sintering temperatures to maintain a high dispersion of the crystal structure of the ceramic product. In this connection it was decided to limit the heat load of the compact up to maximum temperature of 1200 °C and ripening at this temperature during 5 min. Characteristics of the obtained SPS ceramics (Table. 1) convincingly confirm the value of harmonious solutions in the context of the well-known hot sintering thermalphysic contradiction between density maximizing and dispersibility minimizing of the powder compact.

Estimation of the volume density of the obtained SPS nanopowder ceramics which is shown in Table 1 were made using a helium pycnometer AccuPyc II 1340. Microhardness of the ceramic samples was determined by an automatic micro-hardness tester Affri DM-8B by Vicker's test at a test load of 1 kg during 15 seconds. The uni-axial compressive tests were carried out in air at ambient temperature by means of testing machine Instron 300LX.

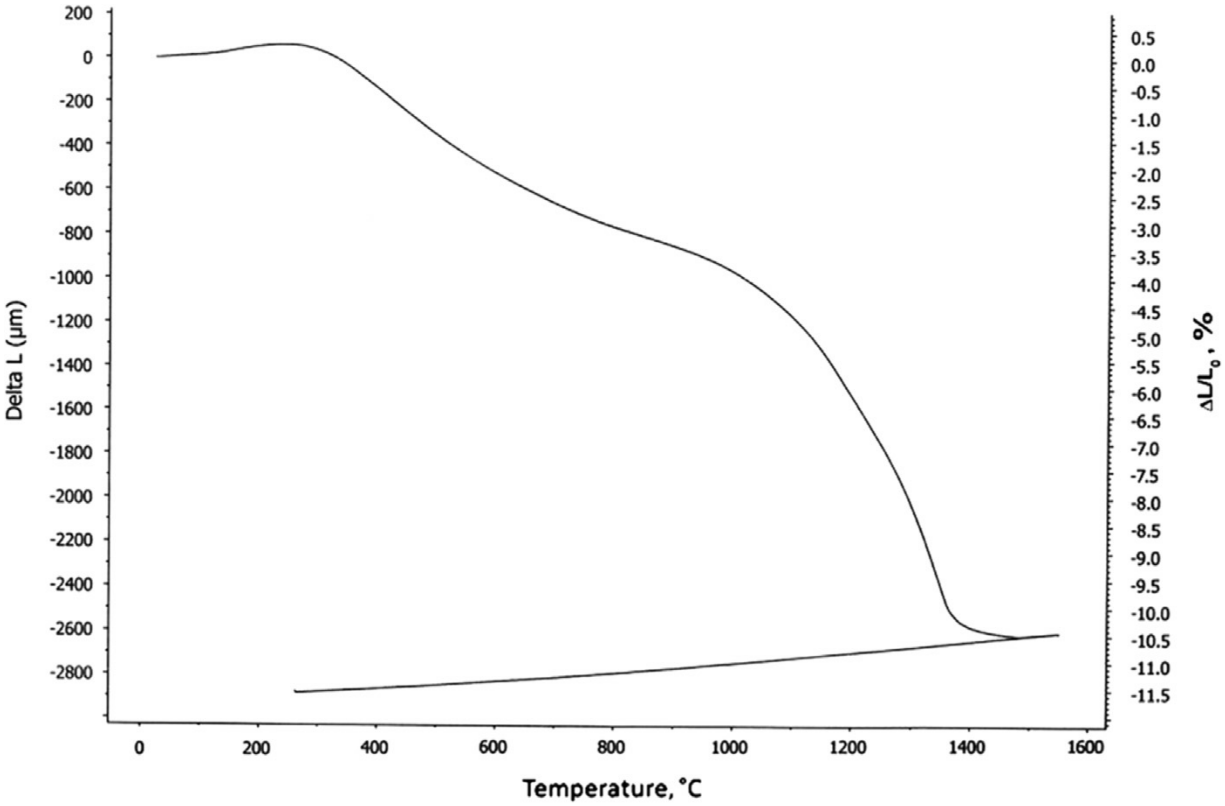
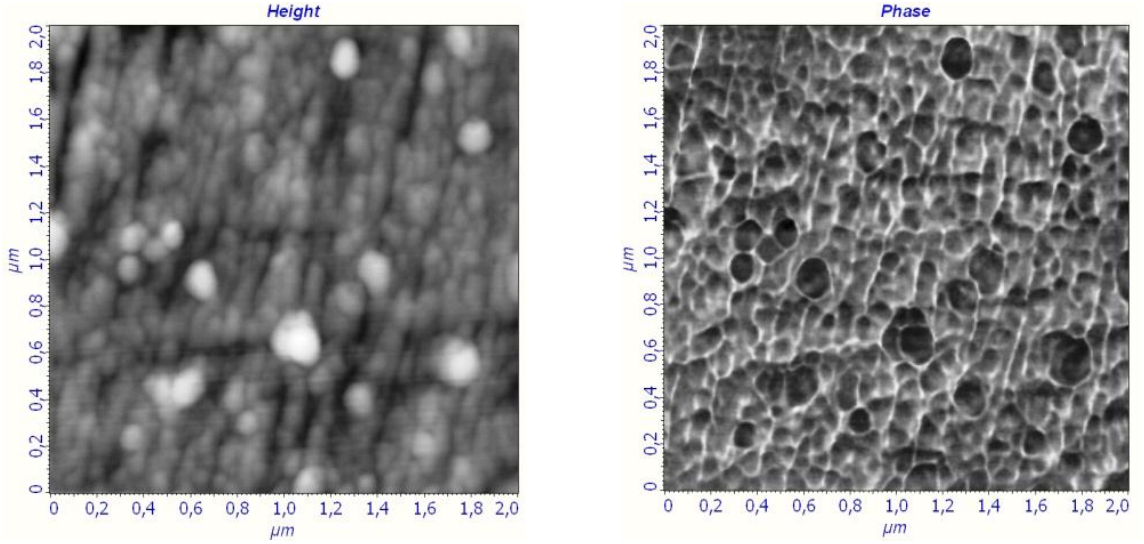


Fig. 3. The temperature dependence of shrinkage for $(Zr_{0.94}Y_{0.06})O_{1.88}$ nanopowder compact



a b

Fig. 4. $(Zr_{0.94}Y_{0.06})O_{1.88}$ ceramics after hot pressing by SPS under the Ntegra Aura scanning probe atomic-force microscope: 2D visualization (a) and phase contrast (b)

Figures 4 and 5 represent images of $(Zr_{0.94}Y_{0.06})O_{1.88}$ ceramic structures which are hot-pressed by SPS method at 1200 °C with a soaking time of 5 min. These images were obtained on the equipment of the AFM (Fig. 4) and SEM (Fig. 5) microscopic studies. From the point of view of identification of the formed dense nanoscale structures, images are in good agreement with each other and with the medium size range of the main array of the crystallites (50-200 nm) declared in the Table 1.

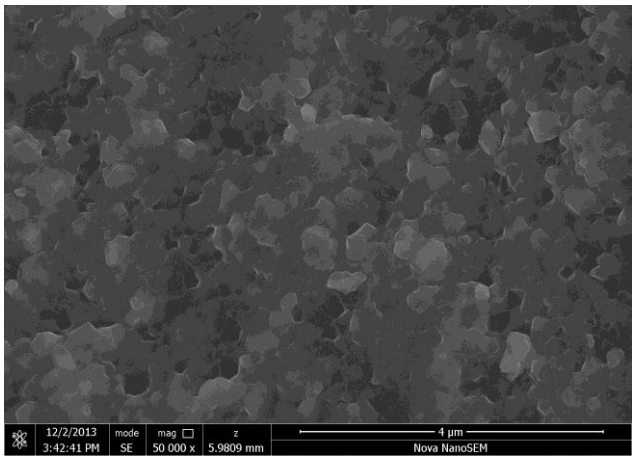


Fig. 5. $(Zr_{0.94}Y_{0.06})O_{1.88}$ ceramics after hot pressing by SPS under the Nova NanoSEM 450 scanning electron microscopy

4. INSTEAD OF CONCLUSIONS

It should be noted that with compatibility the technological results of such alternative technologies as a SPS under pressure with direct current supply to the area and in a daisy chain of cold isostatic pressing and hot sintering in favor of SPS, SPS is also much preferable to the level of expenses for the preparation of related production, productivity and energy efficiency. The temporal order of SPS operational cycle with rising of temperature and pressure – a few minutes [52], typically less than 10 [2], with soaking at the maximum temperature and pressure for a few minutes, for example 2 [53], whereas only the conventional sintering operation [32] lasted more than 6 hours. Power inputs to [32] above, respectively. Funding for preparation of production only at the position "press for cold isostatic pressing" (CIP of model series Belgian-American company EPSI on example [32]), taking into account the carrying amount of 2,650.19 thousands rubles on the 8th year of the operation (2016) with a linear depreciation according to [54] and without mitigation its residual value as a secondary feedstock to the end of estimated useful lives, amounts to 42,167.3 thousands rubles or 637.2 thousands US dollars at the official exchange rate in Russia [55]. Information on the valuation of the main equipment for the implementation of similar tasks of consolidation and sintering on the author's method [3] is commercial and is not announced openly. But it is quite another, much lower cost, lower by 1-2 orders.

REFERENCES

[1] **Sherman, D., and D. Brandon.** Mechanical Properties of hard materials and their relation to microstructure. Advanced Eng. Mater. Vol. 1 (1999), Iss. 3-4, pp. 161-181.

[2] **Gevorkyan, E. S.** Dense and porous constructional materials from nano and submicron powders of WC, Al2O3 and SiC for multifunctional purpose. Doctoral Thesis of Techn. Sc. [in Russian]. Kharkov, Ukrainian State Academy of Railway Transport, 2008, 289 p.

[3] **Gevorkyan, E. S., et al.** Device for hot-pressing of powders by direct transmission of electric current. Utility Patent No.72841 Ukraine [in Ukrainian]. IPC, 2012.01 B22F 3/00, No. u 2012 03031, Appl. 15.03.2012, Publish. 27.08.2012, Bull. No. 16.

[4] **Tokita, M.** Recent Advanced Spark Plasma sintering is (SPS): Technology , Systems and Applications in Japan. 2nd International Scientific Workshop "Advanced Technologies of Electromagnetic Field Assisted Consolidation of Materials". Laboratory of Electromagnetic Field-Assisted Methods for Processing of Novel Materials, National Research Nuclear University "MEPhI", Moscow, 20-23 May 2013, 65 p. Available online 24 May 2013 <http://lemc-lab.mephi.ru/content/file/news/tokita.pdf>.

[5] **Azhazha, V. M.**, et al. Zirconium and alloys: production processes , fields of application: Review [in Russian]. Kharkov, NSC KIPT, 1998, 89 p.

[6] **Lomonova, E. E.** Technology, Properties and Applications of crystals based on zirconium dioxide. Doctoral Thesis of Techn. Sc. [in Russian]. Moscow, General Physics Institute of RAS, 2001, 220 p.

[7] **Yamashita, I., M. Kudo, and K. Tsukuma.** Development of highly transparent zirconia ceramics. Tosoh Research & Technology Review [Tosoh, Corp., Japan, Tokyo]. Vol. 56 (2012), pp. 11-16.

[8] **Ali, S. A., et al.** Zirconia: properties and application – a Review. Pakistan Oral & Dental Journal. Vol. 34 (2014), No. 1, pp. 178-183.
[9] **Niederberger, M., and N. Pinna.** Metal Oxide Nanoparticles in Organic Solvents. Synthesis, Formation, Assembly and Application. Springer-Verlag London Limited, 2009, 217 p.
[10] **Sokovnin, S. Yu., and V. G. Il'ves.** Application of pulsed electron beam to produce nanopowders of some metal oxides [in Russian]. Ekaterinburg, UB RAS, 2011, 318 p.
[11] **Chen, Z., et al.** Internal stress and grain size effect jn the phase stabilization of ZrO2 deposited by MOCVD. Material Science Forum, Vol. 675-677 (2011), pp. 1201-1204.
[12] **Arsent'ev, M. Yu.** Synthesis and physico-chemical properties of nanoscale nanoceramics and nanoscale films based on oxides of zirconium and transition metals. PhD Thesis of Chem. Sc. [in Russian]. Saint-Petersburg, Inst. of Silicate Chemistry of RAS, 2011, 178 p.
[13] **Mikhailov, M. D.** Chemical methods for the preparation of nanoparticles and nanomaterials [in Russian]. Saint-Petersburg, Publishing House of the Polytechnic. University Press, 2012, 259 p.
[14] Kilimnik, A. B., and E. Yu. Ostrozhkova. **Electrochemical synthesis of nano-dispersed metal oxide powders [in Russian]. Tambov, Publisher of Tambov State Technical University, 2012, 144 p.**
[15] **Rudkovskaya, L. M.** Nanostructured zirconia synthesized by the hydrothermal method from decomposition products of zirconium concentrate. Nanosystems, nanomaterials and nanotechnologies [in Russian]. Vol. 10 (2012), Iss. 2, pp. 351-360.
[16] **Sirota, V., V. Ivanisenko, and I. Pavlenko.** Synthesis of Nanosized Stabilized Zirconium Dioxide under Hydrothermal Conditions. NANOCON 2013, Oct. 16th-18th 2013, Brno, Czech Republic, EU. 5th International Conference, Conference Proceedings. Issued by: Tanger, Ltd., Ostrava, Czech Republic, EU. 1st Edition, 2014, pp. 252-255.
[17] **Ananth, A., and Y. S. Mok.** Dielectric barrier discharge plasmamediated synthesis of several oxide nanomaterials and its characterization. Powder Technology, Vol. 269 (2015), pp. 259-266.
[18] **Buyakova, S. P.** Properties, structure, phase composition and regularities in the formation of porous nanosystem based on ZrO_2. Doctoral Thesis of Techn. Sc. [in Russian]. Tomsk, Institute of Strength Physics and Materials Science SB RAS, Tomsk State Univ., Tomsk Polytechnic Inst., 2008, 280 p.
[19] **Yuan, Z. X., J. Vleugels, and O. Van Der Biest.** Preparation of Y_2O_3-coated ZrO_2 powder by suspension drying. J. Mater. Scien. Let., Vol. 19 (2000), Iss. 5, pp. 359-361.
[20] **Schmid, C., and O. Sbaizero.** Ultrasonic homogenization of equivolumetric Al_2O_3/ZrO_2 suspension. Journal of Materials Science. 2000. Vol. 35 (2000), Iss. 5, pp. 1213-1217.
[21] **Pozhidaeva, O. V., et al.** Formation of zirconium dioxide nanocrystals in hydrothermal media with different chemical composition [in Russian]. Journal of General Chemistry. Vol. 72 (2002), Iss. 6, pp. 910-914.
[22] **Shveikin, G. P., et al.** Hierarchy of particle size of zirconium hydroxide deposited on the surface of inert carrier [in Russian]. Inorganic Materials. Vol. 41 (2005), Iss. 5, pp. 557-563.

[23] **Sirota, V., et al.** Synthesis and consolidation of (Zr0.94Y0.06)O1.88 nanopowders // Ceramics International, Vol. 41 (2015), Iss. 4, pp. 5263-5269.
[24] **Dodd, A. C., and P. G. McCormick.** Factors Affecting the Particle Size of Powders Synthesised by Mechanochemical Processing. Journal of Metastable and Nanocrystalline Materials. Vols. 15-16 (2003), pp. 545-552.
[25] **Al'myasheva, O. V., et al.** Synthesis of aluminum oxide nanocrystals under hydrothermal conditions [in Russian], Inorganic materials, Vol. 41 (2005), Iss. 5, pp. 540-547.
[26] **Meskin, P. E., at al.** Ultrasonically assisted hydrothermal synthesis of nanocrystalline ZrO2, TiO2, NiFe2O4 and Ni0.5Zn0.5Fe204 powders. Ultrasonics Sonochemistry. Vol. 13 (2006), Iss. 1, pp. 47-53.
[27] **Al'myasheva, O. V., and V. V. Gusarov,** Hydrothermal synthesis of nanoparticles and nanocomposites in the system ZrO2–Al2O3–H2O. Alternative Energy and Ecology, Vol. 45 (2007), Iss. 1, pp. 113-114.
[28] **Krivtsov, I. V., et al.** Synthesis of zirconia nanoparticles via thermal decomposition of zirconium complex with citric acid [in Russian]. Bulletin of South Ural State University, Chemistry Series. Vol. 5 (2013), Iss. 4, pp. 38-41.
[29] **Sirota, V. V., et al.** Particulars of Hydrothermal Synthesis of Nanosize Powder (Zr1–xYx)Oy. Glass and Ceramics. Vol. 71 (2014), Iss. 1, pp. 54-56.
[30] **Tsukrenko, V. V., et al.** Synthesis and properties of powders in the system ZrO2–CeO2–Y2O3 [in Russian]. Current Problems of the Physical Science of Materials, Coll. of Sc. Works. Kiev, IPM, NAS of Ukraine, Iss. 17 (2008), pp. 46-51.
[31] **Sirota, V. V., et al.** Properties of nanostructured ceramics on example of the analysis of a zirconia powder's microstructure and silicon nitride mechanical characteristics [in Russian]. Bulletin of the Novgorod State University. Vol. 2 (2013), Iss. 73, pp. 113-116.
[32] **Sirota, V. V., E. V. Gruzdeva, and V. V. Ivanisenko.** Influence of the compacting pressure on the structure and mechanical properties of ceramics ZrO_2-8%Y_2O_3 [in Russian]. Scientific Bulletin of the BSU. Ser.: Mathematics. Physics. Vol. 27, 2012, Iss. 11 (130), pp. 127-133.
[33] **Virgil'ev, Yu. S.** Graphite for reactor engineering. Moscow, FGUP «NIIgrafit», 2011. 89 p.
[34] **Khasanov, O. L.** Scientific bases of dry compaction of ultrafine powders in manufacturing technology of nanoceramics. Doctoral Thesis of Techn. Sc. [in Russian]. Tomsk, Tomsk Polytechnic. Univ., 2003, 371 p.
[35] **Karban', O. V.** Structure and properties of oxide nano-dispersed ceramics obtained by compacting. Doctor of Physical and Mathematical Sciences [in Russian]. Moscow, Institute of Radio Engineering and Electronics of the RAS, 2010, 272 p.
[36] **Eichler, A.** Tetragonal Y-doped zirconia: Structure and ion conductivity. Phys. Rev. B [American Physical Society], Vol. 64 (2001), Iss. 17 (174103), pp. 1-8.
[37] **Zavodinsky, V. G.** The mechanism of ionic conductivity in stabilized cubic zirconia. Physics of the Solid State, Vol. 46 (2004), No. 3, pp. 453-457.175.
[38] **Barbashov, V., et al.** Influence of the size effect on the conductivity of the partially stabilized zirconia [in Russian]. Solid State Physics, Vol. 50 (2008), Iss. 12, pp. 2165-2166.

[39] **Raychenko, A. I.** Fundamentals of the process of sintering of powders by passing an electric current [in Russian]. Moscow, Metallurgiya, 1987, 128 p.
[40] **Paschen, F.** Ueber die zum Funkenübergang in Luft, Wasserstoff und Kohlensäure beiverschiedenen Drucken erforderliche Potentialdifferenz. Annalen der Physik und Chemie. 1889, Nr. 5 (273), ss. 69-96.
[41] **Penning, F. M.** Electrical Discharges in Gases. New York, Macmillan, 1957, 118 p.
[42] **Gevorkyan, E. S., and Yu. G. Gutsalenko.** Features and a place of electric consolidate by the AC direct action in the system of the methods of the submicron and nanopowder sintering under pressure [in Russian]. Visnyk NTU "KhPI". 2010, No. 49, pp. 144-161.
[43] **Gevorkyan, E. S., and Yu. G. Gutsalenko.** Genesis expansion of tungsten semicarbide in tungsten ceramic tool composites of hot pressing with electrical consolidation of nanopowders based on monocarbide [in Russian]. Visnyk NTU "KhPI". 2010, No. 53, pp. 19-30.
[44] **Gutsalenko, Yu. G.** The Paschen's law application to determine the pressure for hot compaction at electric consolidation of nanostructured infusible ceramics [in Russian]. Surface engineering and renovation products. Proceedings of the 13th International Scientific-Technical Conference 03-07 June 2013, Yalta. Kyiv, Association of Mechanical Engineering Technologists of the Ukraine, 2013, pp. 67-70.
[45] Physical Encyclopedic Dictionary [in Russian]. **Ed. A. M. Prokhorov.** Moscow, Sovetskaya enciklopediya, 1983, 928 p.
[46] **Schaefer, H.-E.** Interfaces and Psysical Properties of Nanostructured Solids. Mechanical Properties and Deformation Behavior of Materials Having Ultrafine Microstructure, Proceedings of the NATO Advanced Study Institute on Mechanical Properties and Deformation Behavior of Materials Having Ultrafine Microstructure, Porto Novo, Portugal, June 28 – July 10, 1992. Ed. by M. Nastasi, Don M. Parkin, and H. Gleiter. NATO ASI Series, Ser. E: Applied Sciences. Vol. 233, pp. 81-106.
[47] **Klopotov, Yu. A. et al.** Fundamentals of X-ray diffraction in materials science. Tomsk, Publishing house of the Tomsk State University of Architecture and Building, 2012, 276 p.
[48] **Volkov, D. S.** Integrated approaches to the characterization of nanodiamonds of detonation synthesis and their colloid solutions. PhD Thesis of Techn. Sc. [in Russian]. Moscow, Lomonosov Moscow State University, 2015, 238 p.
[49] **Mamonova, D. V.** Synthesis and study of the properties of nanoparticles of complex oxides on the example of yttrium aluminum garnet and bismuth ferrite. PhD Thesis of Techn. Sc. [in Russian]. Saint-Petersburg, St. Petersburg State University, 2015, 136 p.
[50] **Tsybulya, S. V.** X-ray diffraction analysis of nanocrystals: the development of methods and structure of metastable states in nonstoichiometric metal oxides. Doctor of Physical and Mathematical Sciences [in Russian]. Novosibirsk, Boreskov Institute of Catalysis SB RAS, 2004, 337 p.
[51] Website of the **International Centre for Diffraction Data**: < http://www.icdd.com>.
[52] **Gevorkyan, E. S., and Yu. G. Gutsalenko.** Selection of the optimal modes of hot pressing the Al2O3-WC nano powder mixtures for instrumentation applications [in Russian]. Eastern-European Journal of Eenterprise Technologies. No. 5/1(47) (2010), pp. 13-18

.
[53] **Gevorkyan, E., at al.** The obtaining of high-density specimens and analysis of mechanical strength characteristics of a composite based on ZrO2-WC nanopowders. Nanoscale Research Letters, Vol. 9 (2014), Iss. 1, pp. 355-359.
[54] Website of the **Belgorod State National Research University**. The network database of information system for application monitoring of the equipment: <http://equip.bsu.edu.ru/index.php?r=Equipment/view&id=102669>.
[55] Website of the **Central Bank of the Russian Federation**. The network database on exchange rates: <http://www.cbr.ru/currency_base/daily.aspx?date_req=05.05.2016>.