Structure and mechanical properties of ZrO$_2$-based systems

Sergey N. Kulkov ▪ Tomsk State University ▪ Institute of Strength Physics and Materials Science SB RAS, Tomsk, 634021, Russia ▪ kulkov@ms.tsc.ru
Svetlana P. Buyakova ▪ Tomsk State University ▪ Institute of Strength Physics and Materials Science SB RAS, Tomsk, 634021, Russia
László A. Gömze ▪ Department of Ceramics and Silicate Engineering, Miskolc University, H-3515 Hungary ▪ femgomze@uni-miskolc.hu

Érkezett: 2014. 02. 14. ▪ Received: 14. 02. 2014. ▪ http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.1

Abstract

The structure and phase composition of zirconia-based nanosystems are studied. It is shown that during mechanical activation this nanosystem is divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of the quasi-amorphous (X-ray amorphous) phase therewith increases. Through varying the heating rate of such a nanosystem in sintering we may purposefully vary its shrinkage at the stage of isothermal sintering. It is shown that through heating rate variation at sintering of such a nanosystem one can purposefully vary its shrinkage at the isothermal sintering stage. The higher the sintering temperature, the slower the compaction process at the isothermal stage. This allows producing materials with various porosity values but high strength of sintered material.

Keywords: ceramics, mechano-chemistry, nanostructure, nanocrystalline ZrO$_2$, phase composition, sintering

Prof. Sergey N. Kulkov

Head of Department of Ceramics in the Institute of Strength Physics and Materials Science of the Russian Academy of Science since 1989. He has got scientific degrees „Candidate of Physics and Mathematical Sciences" at Tomsk State University in 1981; and „Doctor of Physics and Mathematical Sciences" in 1990. Since 1992 he's working as professor both in Tomsk State University and in Tomsk Polytechnic University. He has a wide range experiments in research of structural ceramic composites and in development of new material composition and technology of high-tech products. His research works are represented in 5 books, more than 150 articles, 18 patents and many International Symposiums and Conferences. In 1997 he had a Soros Professor grant. At present he is head of chair „Theory of Strength and Mechanic of Solids", member of „The American Ceramic Society" of „The APMI- International" and the DYMAT Society (France). His scientific activities are the followings: ceramic matrix composites with transformation toughening, transformations and mechanical properties, shockwave treatment of ceramic powders, superplasticity of CMC, ceramic and ceramic reinforced metal fiber with high porosity for medical applications.

Prof. Svetlana P. Buyakova

Doctor of Sciences from 2008, full Professor from 2013. She is specialist in material sciences of ceramic and ceramic matrix composites based on oxides and carbides. She is author and co-author more than 100 papers. Three Ph.D. students and one person makes they dissertations under her guidance in period 2010-2013. Now, she is chief scientist in ISPMS RAS and professor in Tomsk State University and Tomsk Polytechnic University. Her teaching experience: Introduction to Materials Science, Fundamentals of Materials Engineering, Materials and their Applications.

Prof. László A. Gömze

Establisher (in July 1st, 1999) and head of Department of Ceramics and Silicate Engineering in the University of Miskolc, Hungary. Since then 7 students from the department have successfuly completed their PhD theses and 4 of them were managed by Prof. Gömze. Until today he is author of 2 patents, 4 books and more than 250 scientific papers. He was the chair of International Scientific Advisory Board of the international conferences *ic-cmtp2* in 2012 and *ic-rmm1* in 2013. Recently, he is the chair of the International Organization Board of the 3rd International Conference *ic-cmtp3* on Competitive Materials and Technological Processes.

1. Introduction

The use of nanopowders enables the fabrication of fine-grained ceramics which, as a consequence, offer higher strength in comparison with their large-grained analogs [1-4]. At the same time, practical application of fine powders presents a number of difficulties, the most serious of which is their polydispersity, due to their tendency to aggregate. The inhomogeneous packing of agglomerated powder particles in the forming process leads to low density [5] and, hence, low strength of the sintered material and considerably reduces the performance of nanocrystalline powders for the fabrication of high-strength materials.

Nanocrystalline powders produced by plasma-chemical methods show much promise for the production of zirconia-based ceramics [6]. In the course of production they acquire a uniform, as compared to ordinary technologies, component distribution and accumulate a high, in comparison to coarse powders, excess energy. In this case, both the properties of zirconia powders and final properties of products made of them greatly depend on the amount of the stabilizing agent. Of interest in this respect is a zirconia-based system stabilized by various oxides (yttrium, magnesium, etc.). As distinct from other ZrO$_2$-based ceramic materials like [3] and [7, 8], it allows thermal treatment with drastic changes in mechanical properties.

There are several approaches to improve the particle size uniformity of nanopowders. One of them is milling. In this process, disaggregation is accompanied by an activation of the powder: the formation of a highly imperfect structure and new surfaces and the removal of adsorbed gases [9]. It should, however, be kept in mind that mechanical processing of fine powders may cause not only disaggregation but also the reverse process: aggregation. The possibility of using mechanical processing of nanopowders in the fabrication of ceramic articles requires an in-depth study of its effect on the microstructure and properties of ceramics.

The purpose of this work was to study the effect of grinding of ultrafine ZrO$_2$-3wt.%MgO powder after ball-milling processes on the microstructure and properties of the ceramics produced from the powder.

2. Experimental

ZrO$_2$ powder was prepared by decomposing an aqueous solution of zirconium and magnesium nitrates in a high-frequency plasma. Plasma pyrolysis of liquid precursors is among the most effective processes for the preparation of fine zirconia powders. One important advantage of this method is that the reactions involved take place under nonequilibrium conditions, which ensure rapid nucleation and slow growth of new phases. At the same time, this method has a number of drawbacks, the main of which is its low selectivity. The broad size distribution of particles produced by the plasma pyrolysis of liquid precursors is due not only to aggregation but also to the large difference in geometry between individual particles [10, 11]. Ultrafine ZrO$_2$-3wt.%MgO powder was used in the present studies. It was dry-ground in a tumbling mill with high-density alumina ceramic media for up to 50 h. Ceramic samples were produced by hot pressing at 50 MPa and 1400°C for 10 min and were tested in three-point bending. The morphology of the particles and the micro-structure of the ceramics were examined by scanning electron microscopy on a Philips SEM 515. Phase composition and lattice parameters were determined by X-ray diffraction on diffractometer with CuKα, radiation.

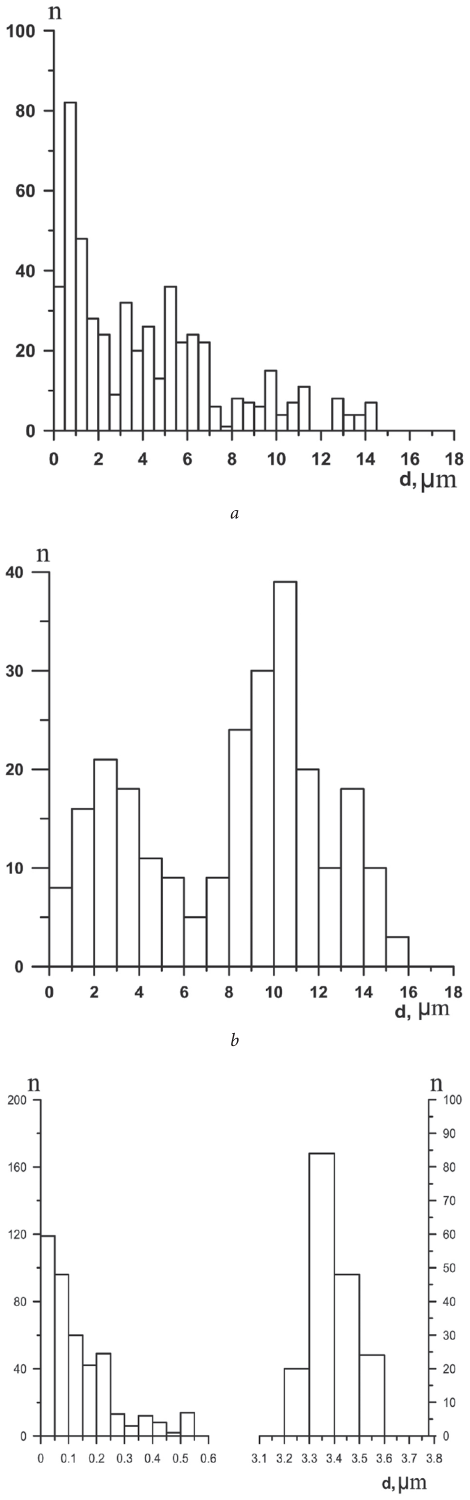
3. Results and discussion

The data of transmission electron microscopy have shown that powders consisted of spherical particles and a large number of irregular shaped particles among which fragments of hollow spheres and films are present [12]. According to the obtained estimates, the amount of the spherical particles was about 20 % of the total amount of particles in the studied powders. Some particles both spherical and irregular shaped were transparent for the electron beam and it may thus be inferred that their thickness did not exceed 50 nm. The irregular shaped particles formed numerous agglomerates in the powder, while the spherical particles were mostly isolated. The size of the majority of the agglomerates was less than 0.25 µm, however, the powder contained interparticle agglomerates and large spherical particles of size up to 6 µm.

The crystallite size distribution in ZrO$_2$ powder obtained by TEM can be characterized as “wide”: dispersion comprises σ = 11.1. The size of largest (more than 30 nm) crystallites amounts to 80 nm, though their contribution is not significant and does not exceed 10 %. The average crystallite size defined by electron microscopy coincides with the average size determined by X-ray diffraction (20 nm) and is close to the average crystallite size (22 nm) observed in similar ZrO$_2$ powders [12]. X-ray diffraction examination showed that the main phase in the powder was high-temperature cubic zirconia. The net fraction of the tetragonal and monoclinic phases was within 8%. The average crystallite size of the cubic zirconia was 25 nm as determined from the width of its X-ray lines.

During milling, a transition from one competing process to another was observed: from aggregation to disaggregation. In the initial stage of milling, aggregation prevailed. After 5 h of milling, the powder contained few or no separate particles: it consisted of aggregates with an average size above that in the as-prepared powder (*Fig. 1a*). At the same time, further milling led to disaggregation of the powder, breaking both the aggregates that had already been present before milling and those that had been formed during milling. After 25 h of mechanical processing, the powder was the least aggregated. The average particle size was 0.13 µm, the powder contained a much smaller percentage of electron-opaque particles, and there were no thin-walled spherical particles.

Milling for more than 25 h led to re-aggregation of the powder (*Fig. 1b*), but the resulting aggregates consisted of particles more uniform in size compared to the un-milled powder. After milling for 50 h, the powder consisted of spherical aggregates (granules) 0.12 µm in average size (*Fig. 1c*).



a

b

c

Fig. 1. Average size distributions of powder particles at increasing time of treatment after ball-milling processes: a –initial state, b – 10h, c – 50h
1. ábra Szemcseméreteloszlás a bolygó golyósmalommal végzett őrlésidő függvényében: a – az őrlés kezdetekor, b – 10 óra őrlés, c – 50 óra őrlés után

In an earlier study [1] and [13], powder disaggregation during milling was accompanied by an increase in the percentage of an X-ray amorphous (quasi-amorphous) phase: the X-ray diffraction pattern of the powder showed an increased background at small diffraction angles, and the particles in electron-microscopic images had a halo.

The disaggregation of the powder during milling was accompanied by an increase in its specific surface area and bulk density. Re-aggregation also led to an increase in the bulk density of the powder. In particular, the powder had the highest bulk density ($0.2\ \rho_{theor}$) after milling for 50 h. After 25 h of milling, its bulk density was $0.1\ \rho_{theor}$.

The ratio of the integral intensity of the strongest reflection of the zirconia cubic phase $I_{(111)}$ to the background radiation intensity I_b was calculated. Similar phase transformations into cubic phase were observed after high energy high speed collisions in Si_3N_4 particles embedded in alumina matrix [14] and in NiO-Al-Al_2O_3 system after high temperature synthesis [15]. The calculation shows that for the time of powder refinement up to 5 h this ratio remains almost unchanged and decreases at further increase of the mechanical treatment time (*Fig. 2*). It is significant that the kink in the time dependence of background intensity coincides with the beginning of powder separation in two independent subsystems and appearance of an ultrafine fraction with the “halo” around particles.

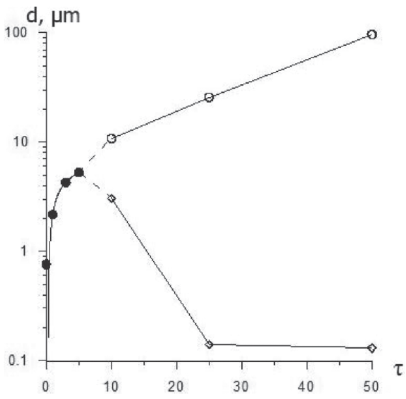


Fig. 2. *The ratio of the (111) reflection intensity of cubic phase to the background radiation intensity in X-ray diffraction patterns of powder after mechanical treatment of different duration*

2. ábra *A köbös fázisú (111) részecskék röntgen diffrakciós reflexió intenzitásának nagysága az őrlésidő függvényében*

The estimation of the crystallite size and lattice microdistortion of the cubic phase in the activated powder shows that the average crystallite size remains almost unchanged under mechanical treatment, but lattice microdistortion grows proportionally to the treatment time and is evidently induced by microstresses. A different character of the dependence of fine structure parameters on the time of refinement is observed for the zirconia monoclinic phase. With increasing mechanical treatment time the crystallite size reduces, while the lattice microdistortion value increases.

Fig. 3 gives the diagram of powder compaction under continuous loading and the compacting pressure dependence of the relative compact volume in double logarithmic scale (measurements were made after the removal of specimens from the mold). In the diagram three linear portions with different slopes are well pronounced. A kink is also observed in the compacting pressure depending on the relative compact volume, though at a higher applied pressure. The portions with different slopes in the given dependences reflect the change of the prevailing mechanisms of powder compaction. The difference of pressure under which the diagram of continuous powder compaction and the compacting pressure dependence of the relative compact volume kink stems from a decrease in the actual compact density due to elastic aftereffect after specimen removal.

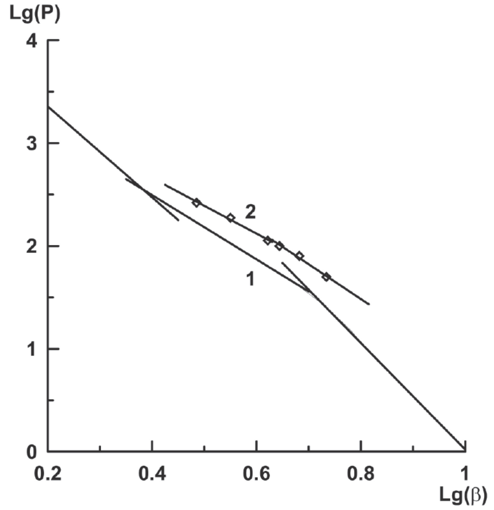


Fig. 3. *Plot of relative density vs. compaction pressure for the compaction curve (1) and densification body (2) of powders*

3. ábra *A sajtoló nyomás hatása a vizsgált porok relatív sűrűségére (1) valamint a sajtolási tömörödésre (2)*

The X-ray phase analysis data show that the monoclinic phase content in compacts constantly increases starting from a minimum pressure. Despite the fact that the phase composition analysis was performed on the compact surface from the active die side and therefore data on the monoclinic phase content were somewhat increased relative to the entire volume (owing to a nonuniform application of pressure to different specimen volumes at the cost of interparticle friction and friction of powder particles on the mold walls), it can be observed that the monoclinic phase during compaction is formed already at low pressure (less than 50 MPa) whose value is much lower than the strength of macroscopic zirconia specimens under compression (above 500 MPa). This is due to the fact that in nanocrystalline powder with a very complex morphological structure stress localization can occur, considerably exceeding the average stress level already at the initial loading stage. Thus, even at the initial stages of powder compaction the transfer of particles to the free pore space is accompanied by their failure.

The increase of the zirconia monoclinic phase content in powder at compaction is not monotonic; the most intensive failure of powder structural elements takes place in the compacting pressure interval from 50 to 100 MPa. The pressure value at which a kink occurs in the dependence reflecting the ZrO_2 monoclinic phase content growth during compaction corresponds to the pressure under which the compacting pressure dependence of the compact density kinks. Since the failure of powder particles was observed in the whole compacting pressure interval, the kinks in the compaction diagrams are probably related to the beginning of failure of stronger structural elements of powder.

The constructed dependences of compact density variation at sintering show that the most intensive compaction of specimens for all temperature conditions takes place at the heating stage, while isothermal aging for 7 h allows ceramics density to increase by no more than 5…7%. Rapid shrinkage of nanocrystalline powders at the nonisothermal sintering stage was already discussed in papers [16, 17] where the mechanism of mutual slipping of powder particles and compaction at the cost of recrystallization-induced grain growth are considered as the mass transfer mechanisms.

Analysis of shrinkage value dependences at the isothermal sintering stage (*Fig. 4*) reveals that the exponent *n* of the shrinkage kinetics equation where $\Delta L/L$ is the relative shrinkage, *K* is the kinetic coefficient of the process rate, and *n* is the constant reflecting the compaction mechanism), first, is almost the same for the sintering regimes at homologous temperatures 0.56 and 0.63 and, second, exceeds a few times the exponent for the sintering regime at homologous temperature 0.63. This might result from the fact that at the stage of compact heating a strong matrix stable to further compaction at isothermal aging is formed. In this case, the higher the sintering temperature, the more stable the material to compaction at isothermal aging. The temperature gradient existing in compacts at heating evidently promotes the failure of barriers and displacement of powder particles, whereas the established thermodynamic equilibrium at isothermal aging hinders active displacement of particles.

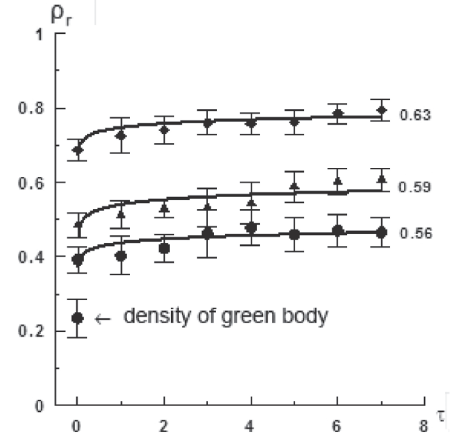


Fig. 4. Plots of relative density for samples sintered at different homologous temperatures
4. ábra A különböző időtartam hosszan homológ hőmérsékleten égetett minták relatív sűrűsége

By the dependence of the exponent *n* from the shrinkage kinetics equation on the shrinkage value $\Delta L/L$ one can determine the value of *n* at which no shrinkage at all would occur at isothermal aging. *Fig. 5* illustrates the obtained dependence. The experimental points with high correlation coefficient are approximated by a linear functional dependence by which one can easily define the heating temperature prior to isothermal aging, at which no compaction of ceramics would take place; this corresponds to temperature 1700° C. Certainly, at a varying density of sintered compacts the temperature of isothermal aging without compaction would be different. It is thus possible to govern the process of structure formation in ceramics both at the heating stage and isothermal aging stage as well as if it is necessary to obtain a developed porous structure in the material. The porous matrix formed during heating would provide porosity in the material, while isothermal aging would increase the strength of interparticle bond.

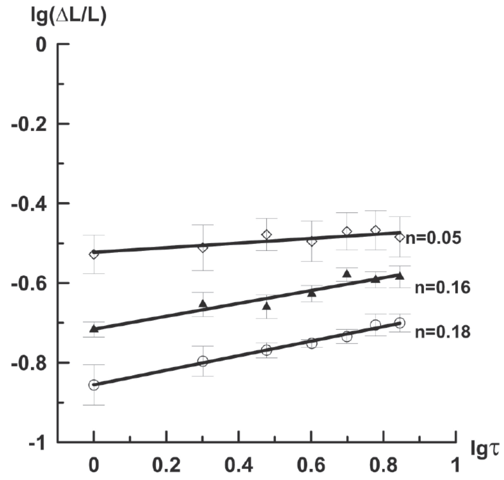


Fig. 5. Plots of exponent n of the shrinkage kinetics equation
5. ábra Az n hatványkitevő értékének hatása a zsugorodás kinetikájára

As would be expected, the disaggregation of the powder led to an increase in the density of the ceramics produced from it (*Fig. 6*). The highest density was realized by the ceramic produced after milling the powder for 25 h, which ensured the lowest degree of aggregation. The density of that ceramic considerably exceeded that of ceramic samples produced from the as-prepared powder. The ceramic prepared from the powder consisting of spherical granules (after milling for 50 h) had considerable residual porosity both within and between the granules, even though the powder had the lowest bulk density. The ceramic produced after milling the powder for 5 h (the highest degree of aggregation) had the lowest density.

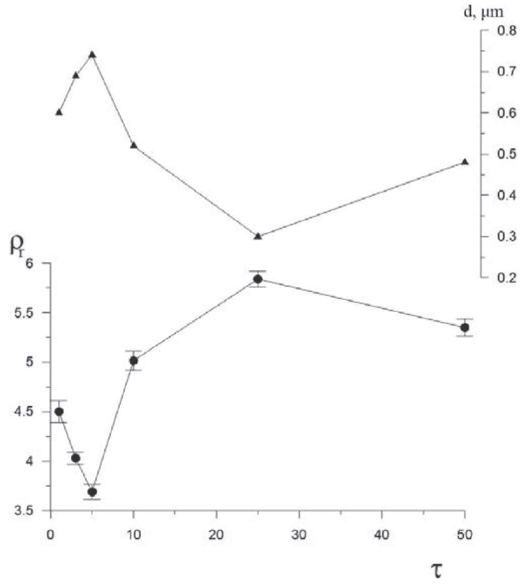


Fig. 6. The effect of milling time on the relative density and average grain size of ceramics produced from zirconia powders
6. ábra Az őrlésidő hatása a cirkon-dioxid termékek relatív sűrűségére és szemcseméretére

Milling also influenced the grain size of the ceramics. The average grain size determined on fracture surfaces increased with an increase in the degree of aggregation during milling and decreased upon disaggregation. Owing to powder disaggregation, we were able to reduce the grain size in the ceramics by almost a factor of 2 (*Fig. 6*): the average grain size in the ceramic produced from the unmilled powder was 0.6 µm, and that in the ceramic produced after milling the powder for 25 h was 0.3 µm.

Milling the ultrafine ZrO_2-3wt.%MgO powder markedly increased the strength of the ceramic produced from it. According to the three-point bending test results, the strength of the ceramic produced after milling the powder for 25 h was 640 MPa, exceeding that of the samples prepared from the unmilled fine powder by more than a factor of 2. Even though the ceramic produced from the powder reaggregated during milling had considerable residual porosity, its strength was comparable to that of the ceramic fabricated from the powder with the lowest degree of aggregation and its density was higher.

4. Conclusions

The structure and phase composition of zirconia-based nanosystems was studied. The present results demonstrate that, during low-energy milling in a tumbling mill, ultrafine ZrO_2-3wt.%MgO powder prepared by decomposing liquid precursors in an HF-plasma undergoes first aggregation and then disaggregation. Powder disaggregation during milling leads to an increase in the density, a reduction in the grain size, and a marked increase in the strength of the ceramics produced from the powder. The morphological structure of ultrafine-grained ZrO_2 powder as well as its variation under mechanical activation, compaction and annealing was investigated. It was shown that in the course of mechanical activation the given nanosystems are divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of a quasi-amorphous (X-ray amorphous) phase therewith increases. This enables purposeful variation of the characteristics of sintered materials.

It was shown that through heating rate variation at sintering of such a nanosystem one can purposefully vary its shrinkage at the isothermal sintering stage. The higher the sintering temperature, the slower the compaction process at the isothermal stage. This allows producing materials with various porosity values but high strength of sintered material.

References

[1] Kulkov, S. N. – Buyakova, S. P.: Phase Composition and Structural Evolution of Nanocrystalline ZrO_2, Ross. *Nanotekhnol.*, 2007, n.1-2, pp. 119-132.

[2] Gusev, A. I. – Rempel, A. A.: Nanokristallicheskie materialy (Nanocrystalline Materials), *Moscow: Fiz-matlit*, 2001.

[3] Orosz, V. – Gömze, A. L.: Effect of ceramic additives on mechanical properties of alumina matrix composites, *Int. J. Microstructure and Materials Properties*, 2012, vol. 7, no. 2/3, pp. 205-219

[4] Gömze, A. L. – Gömze, L. N.: Hetero-modulus alumina matrix nanoceramics and CMCs with extreme dynamic strength, 2011 *IOP Conf. Ser.: Mater. Sci. Eng.* **18** 082001 http://dx.doi.org/10.1088/1757-899X/18/8/082001

[5] Trusova, E. A.: Obtaining of Ultradispersed and Mesoporous Raw Products by Wet and Combined Methods, 2013 *IOP Conf. Ser.: Mater. Sci. Eng.* 47 012043 http://dx.doi.org/10.1088/1757-899X/47/1/012043

[6] Kulkov, S. N. – Grigoriev, M. V.: Sintering of Al_2O_3 ceramics based on different sizes powders. *Építőanyag*, 2010, vol. 62., no.3, pp. 66-69. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2010.13

[7] Chu H. L. – Wang C. L. – Lee H. E. – Sie Y. Y. – Chen R. S. – Hwang W. S. – Wang M. C.: Effect of sintering process parameters on the properties of 3Y-PSZ ceramics, 2013 *IOP Conf. Ser.: Mater. Sci. Eng.* 47 012005 http://dx.doi.org/10.1088/1757-899X/47/1/012005

[8] Kalatur E. S. – Kozlova A. V. – Buyakova S. P. – Kulkov S. N.: Deformation behavior of zirconia-based porous ceramics, 2013 *IOP Conf. Ser.: Mater. Sci. Eng.* 47 012004 http://dx.doi.org/10.1088/1757-899X/47/1/012004

[9] Boldyrev V. V.: Mechanochemistry and Mechanical Activation of Solids, *Usp. Khim.*, 2006, vol. 75, no. 3, pp. 203-216.

[10] Zhang S. C. – Messing G. L., *J. Amer. Ceram. Soc.*, 1990, vol. 73, no. 1, pp. 61-67.

[11] Dubois B. – Ruffier D. – Odier Ph., *J. Amer. Ceram. Soc.*, 1989, vol. 72, no. 4, pp. 713-715.

[12] Buyakova S. P. – S. N. Kulkov, *Inorganic Materials*, 2010, vol.46, No.10, pp.1155-1158.

[13] Gömze A. L.: Mechanochemical Phenomena during Fine Comminution of Clay Minerals for Ceramic Bricks and Roof-Tiles, *2010 Mater. Sci. Forum* 659 19 http://dx.doi.org/10.4028/www.scientific.net/MSF.659.19

[14] Gömze A. L. – Gömze L. N.: Alumina-based hetero-modulus ceramic composites with extreme dynamic strength – phase transformation of Si3N4 during high speed collisions with metallic bodies, 2009 *Építőanyag*, vol. 61, no.2, pp.38-42, http://dx.doi.org/10.14382/epitoanyag-jsbcm.2009.7

[15] Ainabayev A. – Arkhipov M. – Baideldinova A. – Omarova K. – Ksandopulo G.: Out-of-Furnace Synthesis of High-Temperature Ceramic Materials in the Revolving Reactor, 2013 *IOP Conf. Ser.: Mater. Sci. Eng.* 47 012044 http://dx.doi.org/10.1088/1757-899X/47/1/012044

[16] Nikitin D. S. – Buyakova S. P. – S. N. Kulkov, *Inorganic Materials*, 2004, vol.40, No.7, pp.869-872.

[17] Gömze, A. L. – Gömze, L. N. – Egész, Á. - Ojima, F. *2013 IOP Conf. Ser.: Mater. Sci. Eng.* 47 012030 http://dx.doi.org/10.1088/1757-899X/47/1/012030

Ref.:

Kulkov, S. – **Buyakova,** S. – **Gömze,** L.: *Structure and mechanical properties of ZrO_2-based systems*

Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 66, No. 1 (2014), 1–6. p.

http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.1

ZrO_2 anyagrendszerek szerkezete és mechanikai tulajdonságai

Jelen dolgozat a cirkon-bázisú nano-anyagrendszerek szerkezeti struktúrája, fázisösszetétele és mechanikai tulajdonságai közötti összefüggéseket tanulmányozza. A kapott eredmények azt mutatják, hogy ezek a nano-anyagrendszerek a mechanikai aktiválás során jól elkülönülő két alrendszerre oszthatók az átlagos szemcseméret nagysága alapján; amelyek akár két nagyságrenddel is eltérhetnek egymástól a különböző szerkezeti elemek két nagyságrenddel. A finom frakció arányának növekedésével megnő a kvázi-amorf (röntgen amorf) fázis mennyisége, aránya. Az ilyen nano-szerkezetű anyagrendszerek szinterelése során változó felfűtési sebességek esetén is az előzetes igényeknek megfelelően az izotermikus szakaszban jelentős mértékben befolyásolható – szabályozható – a szinterelési zsugorodás mértéke. A vizsgálatok során kapott eredmények jól mutatják, hogy a fűtési sebesség változtatásával az ilyen nano-szerkezetű anyagrendszerekben céltudatosan változtatható a zsugorodás a szinterelés izoterm szakaszában. A vizsgálati eredmények azt mutatják, hogy minél magasabb a szinterezési hőmérséklet, annál lassabban megy végbe a zsugorodás az izoterm szakaszban. Ennek megfelelően kívánt – akár jelentős – porozitású, ugyanakkor nagy mechanikai szilárdságú nano-szerkezetű szinterelt ZrO_2 kerámiák állíthatók elő ezzel a nyersanyag előkészítési és hőkezelési módszerrel.