

Rheology and porosity effect on mechanical properties of zirconia ceramics

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Abstract

Porous ceramics obtained from ultra-fine powders have been studied. The porosity of ceramic samples was found between 15 to 80 %. The structure of the ceramic materials was a cellular structure. A distinctive feature of all the deformation diagrams obtained in the experiment was their nonlinearity at low deformations which was described by parabolic law. It was shown that the observed nonlinear elasticity for low deformations on deformation diagrams is due to mechanical instability of the cellular elements in the ceramic carcass.

Keywords: zirconia, porosity, sintering, activation energy, mechanical properties

Kulcsszavak: cirkónium-oxid, porozitás, szinterelés, aktiválási energia, mechanikai jellemzők

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1. Introduction

Porous ceramic materials have been successfully used in various fields, including thermal insulating building materials, because they are durable, corrosion resistant and they possess stable thermal features [1-3]. Porous ceramics are also promising materials for medical use as osteoplastic material or as 3D scaffold for tissue engineered bone equivalent modeling [4].

Ceramics based on partially stabilized zirconium are the most interesting among the variety of ceramic materials due to their inherent high fracture toughness because of their inherent transformational conversion. It is known that the characteristics are determined by the quality of source ceramic powder (particle shape, particle size distribution), the conditions of compacting and sintering modes and any features that are presented in each phase, and how these phases, including pores, are arranged in relation to each other. The most important factor in the successful application of materials is to understand the features of a structure emerging in them on their behavior under mechanical impact.

Plasma spray synthesis and chemical co-precipitation methods are the main efficient routes for ultra-fine powder production as it activates a sintering process [5]. The sintering process for these powders with identical chemical composition may be very different and final structure of a sintered body depends on particle size, surface energy strain conserved in the whole system etc. [6]. For example, one can obtain hollow-ball particles, which forms will stipulate a special morphology structure of materials [7].

The aim of the work is the investigation of densification, structure and mechanical properties of materials based on zirconia-based powders produced by plasma spray synthesis and sintered at different temperatures.

2. Materials and methods

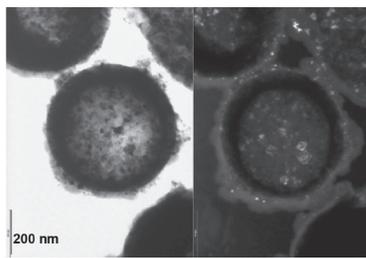
The materials for the study were ceramics obtained from powders of $ZrO_2(MgO)$, $ZrO_2(Y_2O_3)$, liquid-phase

decomposition of precursors synthesized in high-frequency discharge plasma (the plasma chemistry method). Porous ceramic $ZrO_2(MgO)$, $ZrO_2(Y_2O_3)$ powder was prepared by pressing and subsequent sintering of compacts homologous temperatures ranging from 0.63 to 0.56 during the isothermal holding duration of 1 to 5 hours. The porosity of ceramics $ZrO_2(MgO)$, $ZrO_2(Y_2O_3)$ ranged from 15 to $\approx 45\%$ and ≈ 30 to 80%, respectively. X-ray studies were carried out on a diffractometer with filtered $CuK\alpha$ radiation. The studies on the ceramic structure were carried out on the scanning electron microscope (SEM) Philips SEM 515.

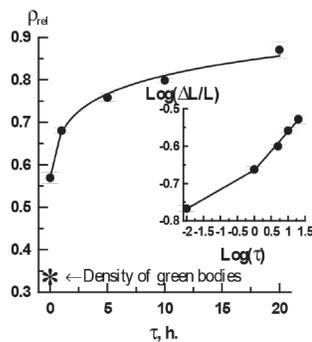
3. Results and discussion

Zirconia powder was characterized by spherical particles and their agglomerates, Fig. 1.a. An average particle size was 0.5 μm . It was measured that specific surface of chemically precipitated powder was equal to 7 m^2/g . According to the X-ray data the tetragonal phases of ZrO_2 was predominant in the amount of 95 % with an average CDD size 20 nm. An average CDD size of monoclinic phase was equal to 20 nm.

Density dependences during sintering process are represented in Fig. 1.b and one can conclude that most intensive densification occurred at heating stage. The analyzing of this dependence using equation of the form $DL/L = K \cdot t^n$, DL/L – relative shrinkage, K – kinetic coefficient; n – constant of densification rate, in log-log coordinates, were revealed that n for the samples made from plasma-sprayed powder is twice as much as for samples based on chemically precipitated powder; 0.1 and 0.04 accordingly [7].



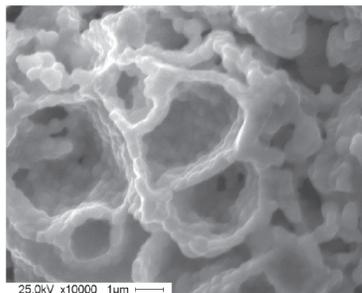
(a)



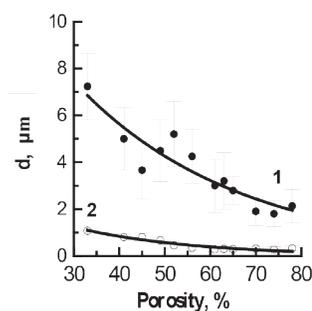
(b)

Fig. 1. ZrO_2 powder, synthesized by plasma-sprayed method: a) TEM image, bright and dark filed; b) dependences of relative density on the duration of isothermal holding for ZrO_2 powder and kinetic dependences of samples shrinkage during isothermal holding

1. ábra Plazma eljárással szintetizált ZrO_2 por jellemzői: a) TEM felvétel, világos és sötét kiemelés; b) izotermális kezelés hatása a sűrűsége és a zsugorodásra



(a)



(b)

Fig. 2. a) Fracture surface of sintered ceramic samples. Cellular structure of porous ceramics (Porosity 30 %);
 2. b) The dependence of average size of the interior of the cells (1) and of average size of grain (2) from porosity.
 2. a) ábra Szinterelt kerámia minták törési felülete. Porozus kerámiák (30% porozitás) cellás szerkezete;
 2. b) ábra Porozitás hatása a belső cellák méretére (1) és az átlagos szemcseméretre (2)

X-ray analysis had shown, that the tetragonal phase content in sintered ceramics was decreasing with increasing of the holding time up to 5 hours for materials based on plasma-sprayed powder from 95 up to 60 %, further increasing of holding time did not influence the phase composition.

The structure of the ceramic materials produced from plasma-sprayed ZrO_2 powder was represented as a system of cell and rod structure elements, Fig. 2.a. Cellular structure formed by stacking hollow powder particles can be easily seen at the images of fracture surfaces of obtained ceramics. There were three types of pores in ceramics: large cellular hollow spaces, small interparticle pores which are not filled with powder particles and the smallest pores in the shells of cells. The cells generally did not have regular shapes. The size of the interior of the cells many times exceeded the thickness of the walls which was a single-layer packing of ZrO_2 grains.

The increase of the pore space in the ceramics was accompanied by the decrease of the average size of voids inside the cells and the average grain size. Quantity and the size of pores and the grain size in the materials produced by powder technology are highly depended on thermokinetic sintering conditions, Fig. 2.b.

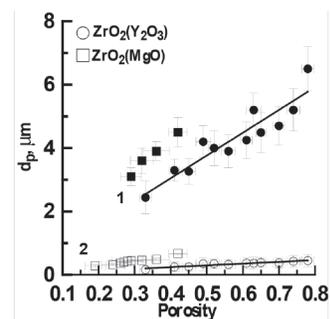


Fig. 3. The dependence of the average pore size vs. porosity of ZrO_2 ceramics: 1) - the average size of large pores spherical-like shape; 2) - the average size of interparticle pores.

3. ábra Az átlagos pórusméret függése a porozitástól: 1) nagyméretű, gömb alakú pórusok átlagos mérete; 2) szemecskéző pórusok átlagos mérete

The average pore size vs. porosity of ZrO_2 ceramics are shown in Fig. 3. As one can see the average size of interparticle pores does not depend on porosity, but sizes of cellular-like pores increases significantly - it is seen that the increase in the volume of pores in the material from ≈ 30 to 80 % which was achieved by reducing the sintering temperature of the samples and it was accompanied by an increase in the average size of large pores from 2 to 6 microns.

So, changing the porosity of the material had practically no influence on the average size of interparticles pores, the average size of which was 0.5 microns. It can be assumed that the presence of large pores close to a spherical shape in the ceramics is due to the presence of hollow spherical particles in source powders, since their average size is commensurate with an average size of presented large pores in the sintered material.

By using these data we have determined the activation energy of the crystallites growth for $ZrO_2(Y_2O_3)$ and $ZrO_2(MgO)$ ceramics, see Fig. 3. It was obtained according to re-plotting of crystallite sizes with increasing sintering temperature (Fig. 6). Activation energy for growth of crystallites of $ZrO_2(Y_2O_3)$ was 160 kJ/mol, for system $ZrO_2(MgO)$ – 75 kJ/mol (Fig. 6), these values are well agree with literature data [8], suggest that the predominant mechanism in the sintering $ZrO_2(MgO)$ is the surface diffusion and for the system $ZrO_2(Y_2O_3)$ is a bulk diffusion.

Stress-strain diagram of porous ceramics which were gained from plasma-sprayed method are presented in Fig. 5.a. The

obtained stress-strain diagrams had descending branch with a monotonic decrease of stress. It is an evidence of damage accumulation in the samples in contrast to the stress-strain diagrams of brittle materials with a homogeneous structure. Micro-damages appearing in the material had local nature and the sample under load retained the ability to resist increasing load. A distinctive feature of all the $s - \epsilon$ diagrams obtained in the experiment was their nonlinearity at low deformations which was described by parabolic law. Cyclic loading of samples on parabolic section of diagrams did not reveal residual strain. Therefore, the nonlinearity in the stress-strain diagrams was due to the elastic deformation of ceramics with cellular structure.

Replotting deformation diagrams in log-log (natural logarithm) coordinates allowed us to determine the exponent of the equation *Hollomon* [9]: $s = Ke^n$, where s - true stress; ϵ - true strain; n - parabolic index; K - constant for a given material, defined as a value of true stress at true strain at zero value from the experimental data. In this case, the index takes the value of the power function of the slope of the strain diagram in logarithmic scale, *Fig. 3.b*.

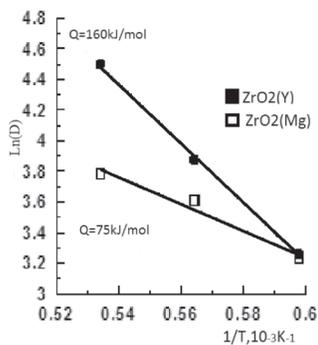


Fig. 4. The activation energy calculated from dependence of the crystallites size vs sintering temperature of porous ceramics ZrO₂

4. ábra Porózus ZrO₂ kerámiák számított aktiválási energiája a kristályméret és a szinterelési hőmérséklet alapján

The dependences of maximum stress σ_{max} and the stress corresponding to emergence of micro-damages in material σ_d from porosity were presented in *Fig. 4.a*. It can be seen that during decreasing the porosity in the ceramics from 80 to 30 % - the maximum stress and the stress corresponding to emergence of micro-damages in material increased from 50 to 400 MPa and from 50 to 250 MPa accordingly. With the increase in the quantity of pores in the ceramics difference between the maximum stress and the stress corresponding to emergence of micro-damages decreased. When the volume fraction of pores in the samples was more than 60 % σ_{max} and σ_d were identical. Rising and descending branches of stress-strain diagrams became gentler.

The dependence of strain corresponding to the end of the parabolic section on the rising branches of the stress-strain diagrams ϵ_1 (1) and the strain corresponding to the maximum value of stress in ceramic samples ϵ_{max} (2) from porosity were presented on *Fig. 4.b*. When porosity was about 30 % ϵ_{max} and ϵ_1 were identical. The increase of porosity from 30 to 80 % caused the increase of ϵ_{max} from 1.5 to 4 %. The obtained values of relative strain (up to ≈ 4 %) were significantly higher than values for nonporous ceramics.

With the increase of porosity from 30 to 50 % there was an intensive decrease of the strain corresponding to the end of the parabolic section on the rising branches of the stress-strain diagrams from 1.5 to 0.5 %. Further increase of porosity up to 80 % did not change the strain value which was 0.5 %. The character of the received dependence was probably a result of change of porosity type. When the value of porosity was from 30 to 50 % both isolated pores and interconnecting pore clusters were presented in the material.

The stress-strain diagrams for ceramics with porosity higher than 50 % has a remarkable features on initial stage of deformation, *Fig. 5.a*, which is denoted ϵ_1 value. This is absolutely atypical for the loading curves of sintered materials. Such dependences can be described by a power function of the type $Y=bX^n$ and n -values can be obtain by re-plotting "stress-strain" curves in "log-log" coordinates, this is shown in *Fig. 5.b*. As one can see the experimental values of n fit well into the two lines, i.e. there is a critical porosity value at which the deformation pattern of the porous body changes drastically - an exponent of the power function arises which is much higher than in the initial state. This is most likely associated with a change in the pore distribution pattern - from isolated pores to continuous porous structure. Experimental data are shown that no displacement of material volumes to the pore space has been found and we may thus assume that no compaction but only elastic deformation, i.e. elastic interaction of elementary volumes in the porous structure, takes place. However, the presence of so high values of $n \sim 2-4$ under deformation without residual strain is absolutely unexpected, which points to the fact that highly nonlinear mechanisms of deformation response to the applied load are implemented in specimen structures. Particularly, we may attribute to them a mechanism based on the known solution of the *Hertz* problem about the contact of two homogeneous bodies [10]. By extending the problem solution [10] for the case of contact between arbitrarily shaped bodies, we will have, passing on to engineering stresses: $s \sim A_c E e^{3/2}$

where A_c is the constant depending on the packing density of contacting grains and their size ratio, E is the modulus of elasticity. Thus, for grain systems having lamellar or cell structure reverse bending that disappears after unloading is possible. The deformation response of such structures after stability loss (in the subcritical state the response is described by *Hooke's* law) can be estimated with the application of the known *Euler's* elastic problem [2]. In this case, for post-critical strain one can find corresponding sizes of rods or cells and grain sizes of porous structure, in which the material is deformed without fracture but with stability loss [2]. According to these estimates, even at stability loss in rod-shaped structures with a small number of elements they may undergo noticeable macroscopic deformation in the elastic region as structural elements, which are observed experimentally.

4. Conclusions

It was shown that the structure of ZrO₂(Me_xO_y) ceramics, obtained from powders consisting of hollow spherical particles with a porosity more 30 % is represented as a cellular carcass with a bimodal porosity, formed of a large pore close to a

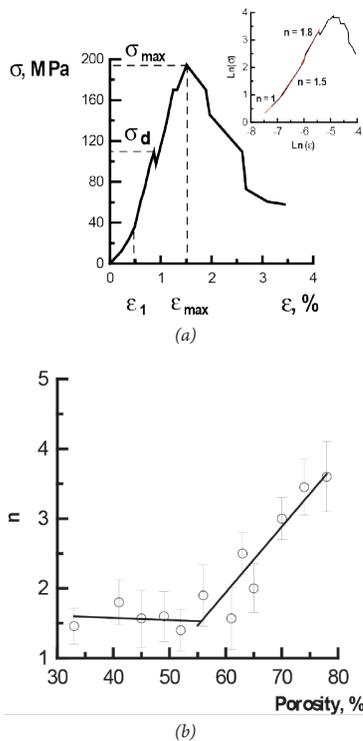


Fig. 5. a) Stress-strain diagrams of ceramics compression with porosity 50 %;
 5. b) The dependence of parabolic index from porosity.
 5. a) ábra Kerámiák nyomófeszültség-összenyomódás ábrája 50% porozitás esetén
 5. b) ábra A hatványkitevő függése a porozitástól

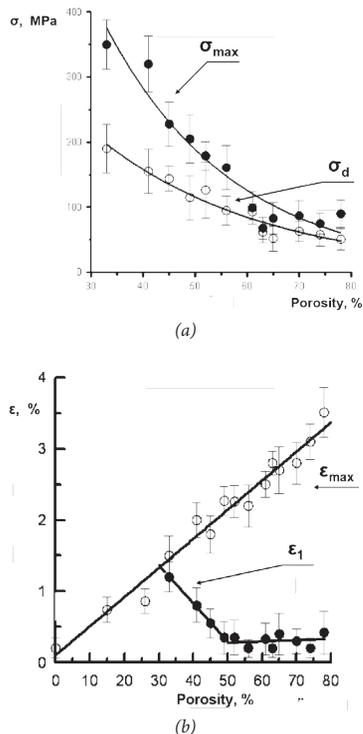


Fig. 6. a) The dependence of maximum stress σ_{max} and the stress corresponding to emergence of microdamages in material σ_d from porosity;
 6. b) The dependence of strain corresponding to the end of the parabolic section on the rising branches of the stress-strain diagrams ϵ_1 , and the strain corresponding to the maximum value of stress in ceramic samples ϵ_{max} from porosity.
 6. a) ábra A legnagyobb nyomófeszültség és a mikro-tönkremenetel megjelenéséhez tartozó feszültség függése a porozitástól
 6. b) ábra A feszültség-alakváltozás ábra felszálló, parabolikus ágának végéhez tartozó fajlagos alakváltozás és a legnagyobb feszültséghez tartozó fajlagos alakváltozás függése a porozitástól

spherical shape and the pores that were not filled with the powder particles during the compaction.

It has been shown that the most intensive densification of studied materials took place during heating stage. In the stress-strain diagrams the nonlinearity occurred due to the elastic deformation of ceramics with cellular structure. The character of the received strain-porosity dependences was probably a result of porosity type change.

It was shown that the stress-strain diagrams on the initial stage of deformation has a nonlinear behavior with high parabolic factor of strain-stress curves. It has been shown that fracture of the materials was observed from the elastic area and has rod-like and cellular-like parts in its structure.

It was found that in the range of sintering temperatures 0.56-0.63 ceramic ZrO₂(MgO) activation energy of crystallite growth of 75 kJ/mol, which corresponds to the surface diffusion, and for ceramic ZrO₂(Y₂O₃), 160 kJ/mole, which corresponds to the bulk diffusion.

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