Porosity and Mechanical Properties of Zirconium Ceramics

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Abstract
Porous ceramics have been studied obtained from ultra-fine ZrO_2 powders. The porosity of ceramic samples was from 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 the 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: zirconium oxide ceramics; plasma chemistry method; porosity; particle size distribution; mechanical properties

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1. Introduction

Porous ceramic materials have been successfully used in various fields, including heat-insulating building materials, because they are durable, corrosion resistant and they possess stable thermal features [1-3]. The combination of these characteristics is especially important for construction in seismic regions.

Ceramics based on partially stabilized zirconium are the most interesting among the variety of ceramic materials [4-6] due to their inherent high fracture toughness that is attributed to their inherent transformational conversion. It is known that the characteristics are determined by the quality of source ceramic powder (particle shape, particle size distribution) [7, 8], the conditions of compacting and sintering modes [9, 10] and any features that are presented in each phase, and how these phases, including pores, are arranged in relation to each other [11]. The most important factor in the successful application of materials is the understanding of the features of a structure emerging in them on their behavior under mechanical impact [12].

The aim of the paper is to examine the effect of $ZrO_2(Me_xO_y)$ pore structure of ceramics on features their deformation behaviour and mechanical properties.

2. Materials and experimental procedure

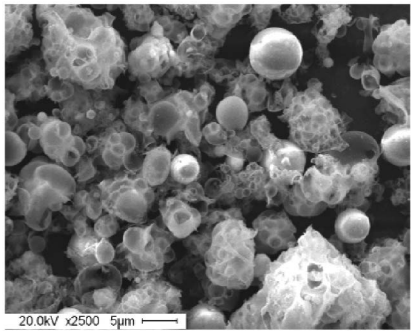
The materials for the study were ceramics obtained from powders of $ZrO_2(MgO)$, $ZrO_2(Y_2O_3)$, liquid-phase decomposition of precursors synthesized in high-frequency discharge plasma (plasma chemistry method). Porous ceramic $ZrO_2(MgO)$, $ZrO_2(Y_2O_3)$ powder was prepared by pressing and subsequent sintering of compacts at 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 ≈ 45% and ≈ 30 to 80%, respectively. X-ray studies were carried out on a diffractometer with filtered CuKα radiation. Studies on the ceramic structure were carried out by scanning electron microscope (SEM) Philips SEM 515. Mechanical tests on samples of porous ceramics were carried out by INSTRON-1185 universal testing device at a constant rate of loading $4 \cdot 10^{-4}$ s^{-1} in uniaxial compression.

3. Results and discussion

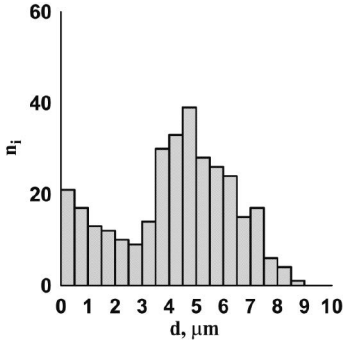
3.1 Powders

Fig. 1 represents the SEM-picture of ZrO_2 powder (3 mol.% Y_2O_3), synthesized by the method of plasma chemistry and

particle size distribution of the powder size. ZrO_2 powders (3 mol.% MgO) and ZrO_2(3 mol.% Y_2O_3) practically have no difference in morphological structure and they consist of hollow particles of a spherical shape and a large number of units having no regular form. The average particle size of the spherical powders ZrO_2(MgO), ZrO_2(Y_2O_3) was 1.8 and 1.5 microns, respectively.



a)



b)

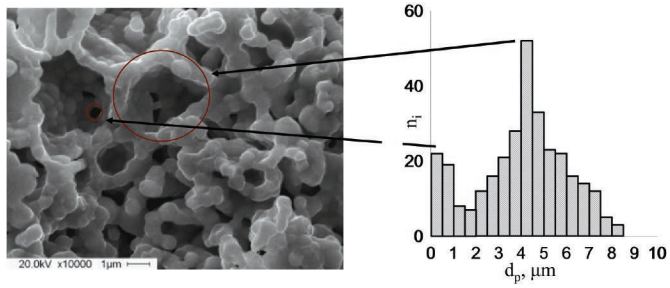
Fig. 1. SEM - picture of ZrO_2 powder (Y_2O_3), synthesized by the method of plasma chemistry (a) and particle size distribution of ZrO_2 powder (Y_2O_3) size (b).
1. ábra Plazma-kémiai módszerrel előállított (Y_2O_3) stabilizált ZrO_2 por SEM-képe (a) és szemcseméret-eloszlása (b)

The phase composition of ZrO_2 powder (Y_2O_3) is presented by tetragonal and monoclinic ZrO_2. In the powder ZrO_2(MgO) the cubic, tetragonal and monoclinic phases of ZrO_2 were present. The ratio of tetragonal ZrO_2 powder ZrO_2(Y_2O_3) was about 95%, and ZrO_2 in the cubic phase ZrO_2 powder (MgO) – 75%. The average size of the coherent scattering regions (SCR) tetragonal ZrO_2 in ZrO_2 powder (Y_2O_3) was 20 nm, and the monoclinic modification – 50 nm. The average size of cubic modification SCR of ZrO_2 in ZrO_2 powder (MgO) was 20 nm, monoclinic ZrO_2 – 30 nm, in the tetragonal phase – 15 nm.

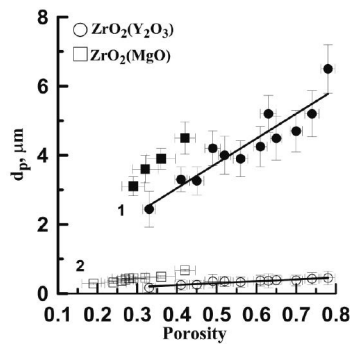
3.2 Sintered ceramics

Fig. 2 represents the SEM-picture of ZrO_2 ceramics structure (Y_2O_3) and pore size distribution. ZrO_2 ceramics structure (MgO), ZrO_2(Y_2O_3) were represented as a cellular frame. Cells had a nearly spherical shape. The cell size exceeded by many times the thickness of the walls, which was represented as a single ZrO_2 layer stacking grain.

Pore size distribution was bimodal. The first maximum pore was formed by interparticle pores that were not filled with powder particles during compaction and the second - with the larger pores close to a spherical shape. From the data presented in *Fig. 2.b* dependences of interparticles pores and larger spherical pores from porosity in ceramics ZrO_2(MgO), ZrO_2(Y_2O_3), it is seen that the increase in the volume of pores in the material from ≈ 30 to 80% 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. Changing the porosity of the material had practically no influence on the average size of interparticle 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.



a) *b)*



c)

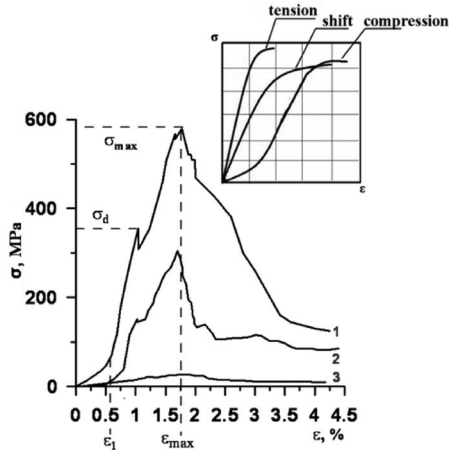
Notations for part c) / Jelmagyarázat a c) ábra részhez:
1) the average size of large pores close to a spherical shape;
a gömbszerű nagy pórusok átlagmérete;
2) the average size of interparticle pores;
a szemcseközi pórusok átlagmérete.

Fig. 2. SEM-Picture of ZrO_2 ceramics structure (Y_2O_3), the characteristic pore size distribution of ZrO_2 ceramics (MgO) with a porosity of ≈ 40% (a) and the dependence of the average pore size on the porosity of ZrO_2 (MgO) and ZrO_2(Y_2O_3) ceramics (b) – as well as average pore sizes as function of porosity (c).
2. ábra A közel 40% pórustérfogatú ZrO_2(Y_2O_3) és ZrO_2(MgO) kerámiák SEM-felvétele (a) és pórus-szerkezete (b) – valamint ezek átlagos pórusátmérője mint a porozitás függvénye (c).

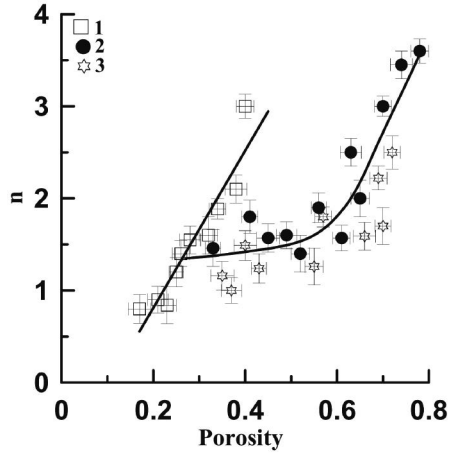
Fig. 3.a shows the deformation diagram during the compression loading of ZrO_2 ceramic samples (Y_2O_3), ZrO_2(MgO) having a porosity more than 30%. For these ZrO_2 ceramics samples (Y_2O_3), ZrO_2(MgO) it is characteristic a bimodal pore distribution. Ascending branches of the deformation diagrams of porous ceramics (stage active deformation) can be characterized by two distinctive features: I – Nonlinear behaviour to the strain ε_1, II – the presence of vertical sections of the reset stress associated with the advent of micro-material. The appearance of the first micro-damages in the material was recorded as the first vertical portion stress reset σ_d. Despite the appearing of separate

material damage which had a local character, the macro-value of loaded sample generally retained the ability to resist the increasing load until the stress value σ_{max}, which corresponds to the limiting strain ε_{max}.

Such a σ-ε type of the diagrams is also characteristic for materials that have a core or cellular structure. The authors of the study [13] have shown that during the compression loading of ZrO_2 porous ceramics, the structure of which is represented as a ceramic frame consisting of randomly oriented rod elements, there is a reversible loss of mechanical stability of the core elements (micromechanical instability [14]), which leads to the emergence of the nonlinear coupling between stress and strain in the elastic deformation of the material.



a)



b)

Notations for part b) / Jelmagyarázat a b) ábra részhez:
1) ceramics $ZrO_2(MgO)$ with bimodal pore size distribution - $ZrO_2(MgO)$ / kerámiák bimodális pórusméret eloszlással;
2) ceramics $ZrO_2(Y_2O_3)$ with bimodal pore size distribution - $ZrO_2(Y_2O_3)$ / kerámiák bimodális pórusméret eloszlással;
3) ceramics $ZrO_2(Y_2O_3)$ with unimodal pore size distribution - $ZrO_2(Y_2O_3)$ / kerámiák uni-modális pórusméret eloszlással;

Fig. 3. Deformation diagrams in compression for ZrO_2 porous ceramics (Me_xO_y) and dependence of the exponent n on ZrO_2 ceramics porosity (Me_xO_y). Inset: Deformation diagrams of high porous foams with cellular structure under different types of loading.

3. ábra Porózus ZrO_2 kerámiák deformációs görbéje (a). (Me_xO_y) valamint az anyagtörvényben szereplő n kitevő függése a ZrO_2 kerámia porozitásától (b) (Me_xO_y).Kiskép az (a) ábrán: A sejtes szerkezetű nagy porozitású habok deformációs görbéi különböző terhelési állapotokban.

Fig. 3.a – and (inset) [15] presents a chart deformation of highly porous foams with cellular structure for different types of loading. It is seen, that the form of the deformation diagrams during compression of foams σ-ε is similar to the diagrams of ZrO_2 porous ceramics (Y_2O_3), ZrO_2(MgO), obtained in the present study.

Loading in the load - unload mode of studied ZrO_2 porous ceramics (Y_2O_3), ZrO_2(MgO) in the initial section to strain values, ε_1 revealed no residual strain, which indicates that the elastic nature of the deformation of ceramics caused a reversible loss of stability of cellular elements.

Restructuring of σ-ε diagrams of ZrO_2 porous ceramics (Y_2O_3), ZrO_2(MgO) in double logarithmic coordinates allows us to determine the value of the exponent in the law of deformation (= K^n) *n* from the experimental data.

Fig. 3.b shows the dependences of the exponent *n* in the law of deformation on porosity in ZrO_2 ceramics (Me_xO_y), from which it is evident that exponent *n* is increasing together with the increase of porosity of both systems, however, with porosity of 30 to 50%, the value of the exponent *n* is changed slightly and averages 1.3.

Fig. 4 represents the dependences of the stress that causes the first micro-damages σ_1 (1), and the ultimate strength σ_{max} (2) from porosity of ZrO_2 ceramics (Y_2O_3).

Increasing the porosity in ZrO_2 ceramics (Y_2O_3) with a bimodal distribution of pore size ≈ from 30 to 80% led to the decrease in magnitude from σ_d ≈ 200 to 50 MPa and a tensile strength σ_{max} of ≈ 400 to 100 MPa. With increasing porosity, the difference between the amount of stress that causes the first micro-damages σ_d, and ultimate strength σ_{max} was reducing, which indicates that the emergence of micro-damages leads to the destruction of the material on the whole.

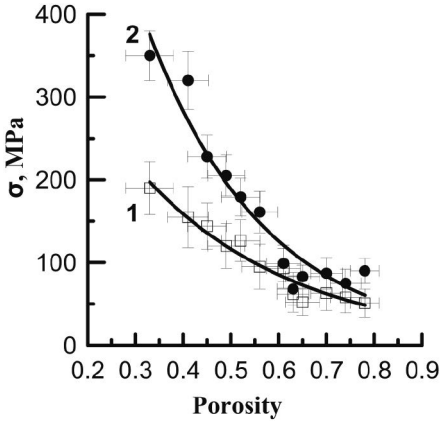


Fig. 4. Stress that causes the first microdamages σ_1 (1), and the ultimate strength σ_{max} (2) from porosity of ZrO_2 ceramics (Y_2O_3)

4. ábra A ZrO_2 kerámiák porozitásában az első mikro károsodást okozó (1) valamint a maximális (2) feszültségek

Dependences of ultimate strength σ_{max} and stress that causes the first micro-damages σ_d in ZrO_2 porous ceramics (MgO), on the porosity had a similar form: the increase of the porosity from ≈ 15 to 45% resulted in a decrease of the σ_d value from ≈ 800 to 100 MPa and σ_{max} from 1200 to ≈ 200 MPa.

Fig. 5 shows the dependences of the strain at which the mechanical instability of the cellular elements appears ε_1 (1) and ultimate strain ε_{max} corresponding to ultimate strength

(2), on the surface area of pores in ZrO_2 ceramics of (Me_xO_y) with a bimodal pore size distribution. The surface area of pores was calculated by the assumption of sphericity. Increasing the pore surface area led to an increase of the ultimate strain to ≈ 3.5%. Dependence of the deformation corresponding to the mechanical instability of the cellular elements on the pores surface area had a different form. Increase of the surface area of pores in ceramics had virtually no impact on the amount of strain ε_1, which averaged 0.5%.

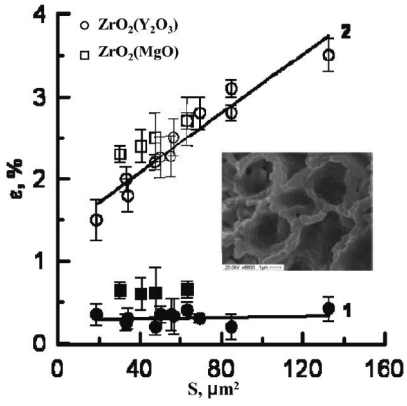


Fig. 5. The dependences of deformation ε_1 (1) and ultimate strain ε_{max} (2) from surface area of pores

5. ábra Az ε_1 deformáció (1) és az ε_{max} törőszilárdság (2) függése a pórusfelület nagyságától

4. Conclusions

It was shown that the structure of ZrO_2 ceramics (Me_xO_y), obtained from powders, consisting of hollow spherical particles with a porosity of 30 % is represented as a cellular carcass with a bimodal porosity, formed of a large pore close to a spherical shape and the pores that were not filled with the powder particles during the compaction. It was found that ZrO_2 ceramics (Me_xO_y) at a porosity of more than 30% with a bimodal pore size distribution demonstrate micromechanical instability during loading that is caused by deformation of the reversible cellular elements. For such ceramics the increase of pore volume is accompanied by an increase of strain in the elastic area.

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Porózus cirkon-oxid kerámiák és mechanikai tulajdonságuk

A tanulmány nagyfinomságú ZrO_2 porból készített porózus kerámiák vizsgálatával foglalkozik. A minták sejtszerkezetes struktúrával, és 15–80% közötti porozitással rendelkeztek. A mechanikai vizsgálatok során kapott valamennyi deformációs görbe, kis deformációs zónájában egyedi, nemlineáris jelleg figyelhető meg. A kis deformációhoz tartozó négyzetesen változó elaszticitás oka, a károsodott kerámia szerkezet elemi celláinak mechanikai instabilitása.

Kulcsszavak: cirkón-oxid kerámiák; plazma kémiai módszer; porozitás; szemcseméret-eloszlás; mehanikai jellemzők