Porosity and Mechanical Properties of Zirconium Ceramics

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Abstract
Porous ceramics have been studied obtained from ultra-fine ZrO2 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

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 ZrO2(Me O2) 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 ZrO2(MgO), ZrO2(Y2O3), liquid-phase decomposition of precursors synthesized in high-frequency discharge plasma (plasma chemistry method). Porous ceramic ZrO2(MeO), ZrO2(Y2O3) 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 ZrO2(MgO), ZrO2(Y2O3) ranged from 15 to ≈ 45% and ≈ 30 to 80%, respectively. X-ray studies were carried out on a diffractometer with filtered CuKa 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•10^-4 s^-1 in uniaxial compression.

3. Results and discussion

3.1 Powders

Fig. 1 represents the SEM-picture of ZrO2 powder (3 mol.% Y2O3), synthesized by the method of plasma chemistry and
particle size distribution of the powder size. ZrO₂ powders (3 mol.% MgO) and ZrO₂(3 mol.% Y₂O₃) 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 ZrO₂(MgO), ZrO₂(Y₂O₃) was 1.8 and 1.5 microns, respectively.

The phase composition of ZrO₂ powder (Y₂O₃) is presented by tetragonal and monoclinic ZrO₂. In the powder ZrO₂(MgO) the cubic, tetragonal and monoclinic phases of ZrO₂ were present. The ratio of tetragonal ZrO₂ powder ZrO₂(Y₂O₃) was about 95%, and ZrO₂ in the cubic phase ZrO₂ powder (MgO) – 75%. The average size of the coherent scattering regions (SCR) tetragonal ZrO₂ in ZrO₂ powder (Y₂O₃) was 20 nm, and the monoclinic modification – 50 nm. The average size of cubic modification SCR of ZrO₂ in ZrO₂ powder (MgO) was 20 nm, monoclinic ZrO₂ – 30 nm, in the tetragonal phase – 15 nm.

3.2 Sintered ceramics

Fig. 2 represents the SEM-picture of ZrO₂ ceramics structure (Y₂O₃) and pore size distribution. ZrO₂ ceramics structure (MgO), ZrO₂(Y₂O₃) 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 ZrO₂ 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 ZrO₂(MgO), ZrO₂(Y₂O₃), 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.
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 $\sigma_{\text{max}}$, which corresponds to the limiting strain $\varepsilon_{\text{max}}$.

Such a $\sigma$-$\varepsilon$ 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.

Fig. 3. Deformation diagrams in compression for ZrO$_2$ porous ceramics (MeO$_y$) and dependence of the exponent $n$ on ZrO$_2$ ceramics porosity (Me$_x$O$_y$). Inset: Deformation diagrams of high porous foams with cellular structure for different types of loading.

Restructuring of $\sigma$-$\varepsilon$ diagrams of ZrO$_2$ porous ceramics (Y$_2$O$_3$), ZrO$_2$(MgO) in double logarithmic coordinates allows us to determine the value of the exponent in the law of deformation ($= K^n$) 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$_x$O$_y$), 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 $\sigma_1$ (1), and the ultimate strength $\sigma_{\text{max}}$ (2) from porosity of ZrO$_2$ ceramics (Y$_2$O$_3$).

Increasing the porosity in ZrO$_2$ ceramics (Y$_2$O$_3$) with a bimodal distribution of pore size $\approx$ from 30 to 80% led to the decrease in magnitude from $\sigma_d \approx 200$ to 50 MPa and a tensile strength $\sigma_{\text{max}}$ of $\approx 400$ to 100 MPa. With increasing porosity, the difference between the amount of stress that causes the first micro-damages $\sigma_{d}$ and ultimate strength $\sigma_{\text{max}}$ was reducing, which indicates that the emergence of micro-damages leads to the destruction of the material on the whole.
(2), on the surface area of pores in ZrO₂ ceramics of (MeₓOᵧ) 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 ε₁, which averaged 0.5%.

![Fig. 5. The dependences of deformation ε₁ (1) and ultimate strain εmax (2) from surface area of pores.](image)

**Fig. 5.** The dependences of deformation ε₁ (1) and ultimate strain εmax (2) from surface area of pores in ZrO₂ ceramics of (MeₓOᵧ) at a porosity of more than 30% with a bimodal pore size distribution. The surface area of pores was calculated by the assumption of sphericity. Increasing the surface area of pores had virtually no impact on the amount of strain ε₁, which averaged 0.5%.

### 4. Conclusions

It was shown that the structure of ZrO₂ ceramics (MeₓOᵧ), 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 ZrO₂ ceramics (MeₓOᵧ) 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 cirkón-oxid kerámiai és mechanikai tulajdonságok

A tanulmány nagynöfödségű ZrO₂ porból készített porózus kerámiai vizsgálatával foglalkozik. A minták sejtszerkezetes struktúrával, és 15–80% közötti porozitással rendelkeznek. A mechanikai vizsgálatok során kapott valamennyi deformációt a károsodott kerámia lineáris jelleg figyelhető meg. A kis deformációhoz tartozó formációváltozó elaszticitás oka, a károsodott kerámia szerkezet elemi celláinak mechanikai instabilitása. Kulcszzavak: cirkón-oxid kerámiai; plazma kémiai módszer; porozitás; szemcseméret-eloszlás; mechanikai jellemzők.