Deformation behavior of zirconia-based porous ceramics

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Abstract. It has been studied a porous ceramics obtained from nanocrystalline ZrO₂ powders. Samples were obtained by pressing and sintering of compacts, the porosity of ceramic samples was from 20 to 80 %. The average grain size in the studied ceramics increased from 0.4 to 4 microns with increasing sintering temperature and duration of isothermal holding from 1400 to 1600 °C and 1 to 5 hours, respectively. 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 a rod-like and cellular-like parts in its structure.

1. Introduction
Plasma spray synthesis and chemical co-precipitation methods are the main efficient routs for ultra-fine powder production as it’s activate a sintering process [1]. The sintering process for these powders with identical chemical composition may be very different and final structure of a sintered body depends on a particle size, surface energy strain conserved in the whole system etc. [2]. For example, one can obtained hollow-ball particles, which forms will stipulate a special morphology structure of materials [3].

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
Ceramic samples made from plasma-sprayed and chemically precipitated (97 mol. % ZrO₂ + 3 mol. % Y₂O₃) powders were studied. To study densification kinetics samples were produced by pressing as-received powders till relative density 0.33 and sintering at 1500 °C during [0-20] hours.

Structure investigation were carried out on the samples sintered in the temperature range 1400 – 1650 °C during isothermal holding from 1 up to 5 hours after uniaxial compression with the loading speed 4*10⁻⁴ s⁻¹.
Phases identification and evaluation of coherently diffracted domains (CDD) were determined from X-ray diffractometry data [4,5]. Scanning electron microscope observations operated at 20-30 kV were used to determine the structure and average grain and pore size.

3. Results and discussion
Zirconia powder was characterized by spherical particles and their agglomerates, figure 1 (a). An average particle size was 1.5 µm. It was measured that specific surface of chemically
precipitated powder was equal to 7 m²/g. According to the X-ray data the tetragonal phases of ZrO₂ 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.

Figure 1. ZrO₂ 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 ZrO₂ powder and kinetic dependences of samples shrinkage during isothermal holding

Density dependences during sintering process are represented on figure 1 (b) and one can concludes that most intensive densification occurred at heating stage. The analyzing of this dependence using equation of the form \( \Delta L/L = K \cdot \tau^n \), \( \Delta L/L \) – 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 [6].

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 didn’t influence the phase composition.

The structure of the ceramic materials produced from plasma-sprayed ZrO₂ powder was represented as a system of cell and rod structure elements, figure 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 ZrO₂ 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, figure 2 b.
Figure 2. a) Fracture surface of sintered ceramic samples. Cellular structure of porous ceramics (Porosity 30%); b) The dependence of average size of the interior of the cells (1) and of average size of grain (2) from porosity.

Stress-strain diagram of porous ceramics which were gained from plasma-sprayed method are presented on figure 3 a. The obtained stress-strain diagrams had descending branch with a monotonic decrease of stress. It is an evidence of damages accumulation in the samples in contrast to the stress-strain diagrams of brittle materials with a homogeneous structure. Microdamages 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 $\sigma$ - $\varepsilon$ diagrams obtained in the experiment was their nonlinearity at low deformations which was described by the 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 ln-ln coordinates allowed us to determine the exponent of the equation Hollomon [7] ($\sigma = K \varepsilon^n$, when $\sigma$ - true stress; $\varepsilon$ - 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, figure 3 b.

Figure 3. a) Stress-strain diagrams of ceramics compression with porosity 50%; b) The dependence of parabolic index from porosity.
The dependences of maximum stress $\sigma_{\text{max}}$ and the stress corresponding to emergence of microdamages in material $\sigma_{d}$ from porosity were presented on figure 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 microdamages 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 microdamages decreased. When the volume fraction of pores in the samples was more than 60 % $\sigma_{\text{max}}$ and $\sigma_{d}$ 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 $\varepsilon_1$ (1) and the strain corresponding to the maximum value of stress in ceramic samples $\varepsilon_{\text{max}}$ (2) from porosity were presented on picture 4 (b). When porosity was about $\approx$ 30 % $\varepsilon_{\text{max}}$ and $\varepsilon_1$ were identical. The increase of porosity from 30 to 80 % caused the increase of $\varepsilon_{\text{max}}$ from 1.5 to 4 %. The obtained values of relative strain (up to $\approx$ 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.

**Figure 4.** a) The dependence of maximum stress $\sigma_{\text{max}}$ and the stress corresponding to emergence of microdamages in material $\sigma_{d}$ from porosity; b) The dependence of strain corresponding to the end of the parabolic section on the rising branches of the stress-strain diagrams $\varepsilon_1$ and the strain corresponding to the maximum value of stress in ceramic samples $\varepsilon_{\text{max}}$ from porosity.

**4. Conclusions**

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 probably was 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 a rod-like and cellular-like parts in its structure.

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