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From nanometric zirconia powder to transparent polycrystal

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Abstract

Coprecipitated zirconia-yttria (8 mol%) gel subjected to hydrothermal treatment at 240 °C resulted in the solid solution powder of 8 nm particle sizes and specific surface area 132.7 m^2/g. Uniaxial compaction followed by cold isostatic pressing under 300 MPa resulted in samples of the extremely small and narrow pore size distribution. Such samples start to shrink at about 200 °C which is related to the desorption of water layers surrounding particles. The state of closed porosity is achieved at 1150 °C. Pore closing was performed in air or oxygen atmosphere. Hot isostatic pressing at 1150 °C for 2 h under 250 MPa argon pressure led to transparent materials. Some pores remained in the material whose preliminary pore closure was performed in air. The samples initially sintered in oxygen atmosphere show no porosity and higher light transmittance than the former ones.

Keywords: Zirconia; Transparent materials; Nanopowders

1. Introduction

Cubic zirconia-yttria of 8 mol% Y_2O_3 solid solutions were extensively studied due to their unique properties e.g., as solid electrolytes applied in solid oxide fuel cells. The interest in this material in its polycrystalline form increased when the refined ceramic process allowed us to eliminate all or nearly all porosity. It has been known that reasonable results can be achieved in the case of materials of the porosity lower than 0.05%. An important property of such a material consists in its very high refractive index of 2.2, which has never been attained in optical glasses. It is even higher than that of other oxides.

Relatively few investigations have been published on the fabrication method of polycrystalline transparent zirconia. In majority of cases the sub-micrometer, commercial powders of 8 mol% yttria content were applied. The effect of titania additive to such powders were described in two papers.[1,2] Commercially available sub-micrometer powders was densified by the post-sintering HIP technique.[1–4] Pore closing in vacuum[3–5] or in an oxygen atmosphere[1] was performed and then hot isostatic pressing led to the pore-free, transparent polycrystals. Spark plasma sintering in vacuum in the case of commercial powder[6] or powder prepared by the glycine-nitrate process[7] was also applied. In the latter case the powder extensive milling was necessary to remove strong agglomerates. They result from calcination of the powder precursor. During this operation strong contacts between newly crystallized particles develop.

Agglomerate strength determines the powder behaviour during cold compaction and sintering. Strong (hard) agglomerates lead to the bi-modal pore size distribution in a powder compact. The fact that such compact characteristics do not densify effectively during sintering was demonstrated in numerous studies.

According to Rumpf[13] tensile strength of an agglomerate is given by the relation:

$$P_c = \frac{9}{8} \cdot \frac{1 - V_p}{\pi d^2} \cdot L_K F_K$$

where V_p is pore fraction in an agglomerate, $L_K$mean number of contacts per particle, F_K force necessary to separate two particles in contact and d particle sizes.

The aim of the present study was based on the application of really nanometric ZrO_2–8 mol% Y_2O_3 powders manufactured

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by crystallization under hydrothermal conditions. Our previous studies indicated that the process performed in distilled water results in isometric solid solution crystallites of nanometric sizes with no first order bonds between particles.[8–12] Although crystallites in the hydrothermally processed powders are of nanometric sizes (low d values), weak contacts between crystallites (low F_K value) should lead to soft agglomerates if pore fraction (V_p) is high and by itself L_K is low.

2. Experimental

An aqueous solution of $ZrOCl_2$ +$Y(NO)_3$ of 1.5 M concentration (both salts together) was introduced to the vigorously stirred aqueous ammonia solution of 4 M concentration. Final pH 9 leads to the quantitative precipitation of the system. The Zr/Y ratio in the starting solution corresponded to 8 mol% Y_2O_3 in ZrO_2. The co-precipitated gel was washed carefully with distilled water until no reaction for Cl^- ions (with $AgNO_3$) was observed. Then the material was subjected to hydrothermal treatment at 240 °C for 4 h under autogenous water vapour pressure. Water suspension of the powder of 8 vol% concentration was then subjected to freeze drying. A low solid state concentration of the suspension was expected to result in high agglomerate porosity (V_p) and hence in soft agglomerate formation.

The samples of 20 mm diameter and 2 mm thickness were compacted uniaxially under 50 MPa and repressed isostatically under 300 MPa. Then they were sintered to the state of closed porosity (1150 °C, 2 h) and hot isostatically pressed (HIP) at 1150 °C for 2 h under 250 MPa Ar pressure. HIP equipment (EPSI) with the molybdenum heating element was used.

Powder purity was analyzed using X-ray fluorescence technique (PANalytical, Axios mAX). Dilatometric measurements (NETSCH DIL 402C) allowed us to follow the shrinkage of powder compacts and DTA/TG (NETSCH STA 449) gave information on the heat effects occurring at elevated temperatures. Gases emitted by the sample at elevated temperatures were analyzed using mass spectrometric measurements (Mass Spectrometer QMD 300 Thermostar). X-ray diffraction (PANalytical, X'Pert PRO) allowed us to determine the powder and sintered samples phase composition, powder crystallite sizes on the basis of the X-ray line (1 1 1) broadening and the cubic phase lattice parameters. CuKα radiation was applied. Powder specific surface area was determined using nitrogen adsorption (Quantochrome Instruments, NOVA 1200e). Pore size distribution in green samples was measured by mercury porosimetry (PoreMastern 60 Quantochrome Instruments). Density of the HIP-ed samples was measured using the helium pycnometer (Micromeritics, AccuPyc II 1340).

FTIR spectrum was recorded with the Bruker Vertex 70v spectrometer. Spectrum was collected in the mid infrared (MIR) regions (4000–1000 cm^{-1}) after 256 scans at 4 cm^{-1} resolution. The sample was prepared by the standard KBr pellets methods.

Transmission electron microscopy (Tecna FEG, 200 kV) allowed us to observe microstructure of the materials. The optical characteristics was performed using the Jasco V-630 spectrophotometer, operating at the range 190–1100 nm. The V-630 JASCO is a double-beam spectrophotometer with a single monochromator, and a halogen/deuterium lamp as a light source. The measurements were provided in the transmittance mode in the range 350–1100 nm, using an integrating sphere (60 mm diameter) with a scanning speed 400 nm/min. For each sample the measurements were made 3 times and the resulting spectra were the averages of these examinations.

3. Results and discussion

Table 1 shows the chemical composition of the hydrothermally crystallized powder Hafnium oxide is the main "impurity". The concentration of Y_2O_3 with relation to $ZrO_2 + HfO_2$ corresponds to 8.04 mol%, close to the assumed value. According to the phase diagram,[14] the applied yttria concentration should lead to the solid solution phase of cubic symmetry. The X-ray diffraction pattern corroborates this assumption.

Fig. 1 shows a transmission electron micrograph of the powder and Table 2 indicates its characteristics and properties of the compact calcined at 500 °C for 1 h with the 1 °C/min rate of temperature increase. D_{BET} and $D_{1\,1\,1}$ values of the starting powder close to each other, indicate that no inter-crystalline boundaries develop during the hydrothermal process and that crystallites of an isometric shape occur. The latter is confirmed by the TEM micrograph in Fig. 1. Micrographs like this one allowed us to assess D_{TEM} expressed in Table 2 as its median

Table 1
Chemical composition of the powder.

Oxide	Concentration, mass%
Na_2O	0.065
Al_2O_3	0.023
SiO_2	0.034
NiO	0.08
ZrO_2	84.227
Y_2O_3	13.681
HfO_2	1.889

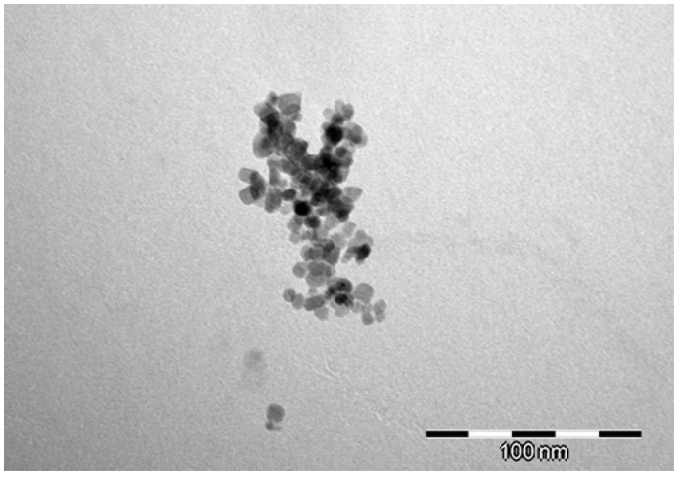

Fig. 1. Transmission electron micrograph of the 8 mol% Y_2O_3-ZrO_2 powder hydrothermally crystallized at 240 °C for 4 h.