Zirconia – based nanopowders synthesized by the chemical precipitation method

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Abstract. The influence of annealing on the structure and properties of ZO$_2$ – Y$_2$O$_3$ and ZrW$_2$O$_8$ powders obtained by the chemical precipitation method is studied. It is shown that the increase in annealing temperature leads to the decrease in the average size of particles, which initially represent porous agglomerates with high specific surface, to the size of monolithic polydomain particles, the sizes of which are comparable with the sizes of crystallites. The grain growth in the ZO$_2$ – Y$_2$O$_3$ system during annealing is defined by surface diffusion. ZrW$_2$O$_8$ has a negative thermal expansion and it was equal to $-12 \times 10^{-6}$ C$^{-1}$.

1. Introduction

It is known that various methods of oxide powder production do not allow one, as a rule, to obtain powders of the same composition identical in structure, morphology, and properties [1, 2]. The most promising among them is a method of coprecipitation of salts from solutions, with the use of which it is possible to produce homogenous disperse powders of complex composition highly active to sintering [3, 4]. This method is technologically quite simple; for its realization, inexpensive reagents and simple equipment are used. Information about the behavior of such powder systems during annealing is required, since it determines the modes during sintering of dense ceramic materials.

The purpose of the present work is the investigation of ZrO$_2$ – Y$_2$O$_3$ and ZrW$_2$O$_8$ powder systems synthesized by the chemical precipitation method after annealing [5].
2. Materials and methods

To synthesize powders of the ZrO$_2$–Y$_2$O$_3$ system, the method of reverse coprecipitation of zirconium and yttrium nitrates in an ammonia solution was used [4]. After synthesis, the gel-like deposit washed and filtered was dried in a microwave oven for 6 h. Next, the ZrO$_2$–Y$_2$O$_3$ mixture was mechanically treated in tumbler with the use of grinding bodies from a high-density alumina ceramic in the mode of dry grinding. The ratio of the grinding body weight to the powder weight was held at 2:1. The duration of the mechanical treatment was 25 h. Then the powder was annealed at 573–1373 K for 1 h in air.

The precursor ZrW$_2$O$_7$(OH)$_2$*2H$_2$O used for obtaining of ZrW$_2$O$_8$. The powder was calcined at 773 K for 1 h in air to remove organics. Then powders were annealed at 1327 K for 1 hour in air and at 1423, 1427, 1523 K for 10 minutes in a nitrogen atmosphere. After sintering powders were quenched to avoid decomposition of the resulting zirconium tungstate on oxides ZrO$_2$ and WO$_3$.

X-ray phase analysis (XPA) of samples was performed with filtered copper radiation. The samples were photographed in the range of 20° - 80° (2θ) with a 0.05° step of the goniometer and exposure duration at every point sufficient to obtain a relative error of the calculation rate against the background of no more than 3%. The coherently diffracting domain was estimated by the widening of the most intense X-ray reflexes at small diffraction angles [6]. The specific surface of the powders synthesized was measured by the low-temperature nitrogen adsorption method (BET) [7]. The particle morphology of powders formed (size of microparticles and aggregates, structure, and shape) was studied with the use of a Philips SEM 515 scanning electron microscope. Dilatometric studies were carried out on a quartz mechanical dilatometer.

3. Results and discussion

Figure 1 shows SEM images and size distribution of particles of ZrO$_2$–Y$_2$O$_3$ powder samples in the initial state, after mechanical treatment, and annealed at 573 and 1273 K. It is seen that the powder particles in the initial state are big blocks of chips and agglomerates of irregular shape consisting of them (Fig. 1a). The average size of the initial powder particles is 32 μm. The particle structure of powders subjected to mechanical treatment and annealed at various temperatures changes insignificantly relative to the initial powder (Figs. 1b, 1c); however, the value of the average particle size decreases substantially, and for temperatures of 573 and 1273 K, the values are 3.7 and 2.5 μm, respectively.

![Figure 1](image-url)

**Figure 1.** SEM images and size distribution of particles of ZrO$_2$–Y$_2$O$_3$ powders: (a) initial powder, (b) annealed at T = 573 K, (c) annealed at T = 1273 K.

Similar associations were observed in the ZrW$_2$O$_8$ powder. Starting powder
ZrW$_2$O$_7$(OH)$_2$•2H$_2$O consists of dense agglomerates with an average size is 27 μm (Fig.2 (a)). Annealing the precursor to the 1373 leads to decreasing of the agglomerate size. At temperature above 1423 K the high agglomerated needle-shaped particles in a powder were formed (Fig. 2 (c)). With increasing temperature the average lengths of needle-shaped particles increases from 8.2 μm at 1423 K to 16.3 μm at 1523 K and its average diameter has 0.2 μm (Fig.3).

![Figure 2. SEM images powders: (a) ZrW$_2$O$_7$(OH)$_2$•2H$_2$O, (b) annealed at T =1373K, (c) annealed at T = 1423 K.](image1)

![Figure 3. Dependence the average size of (a) agglomerates, (b) needle-shaped particles vs. temperature.](image2)

According to XPS data, the phase composition of ZrO$_2$–Y$_2$O$_3$ powder in the entire temperature range of annealing is represented by the high-temperature tetragonal modification of zirconium dioxide, and the width of bands especially at low annealing temperatures is large. X-ray study of the powder showed that after annealing at 500 °C material is amorphous. With increasing annealing temperature up to 1100 °C forming the cubic phase of zirconium tungstate in the material. The lattice parameter is a = 9.1482 Å, which agrees quite well with the published data, 9.1540 Å.

Samples ZrW$_2$O$_8$, sintered at 1373 K has the ranges of temperature in which the material has a negative coefficient of thermal expansion and it was equal to -12 * 10$^{-6}$ C$^{-1}$.

Figure 4a shows the dependence of the value of the specific surface on the annealing temperature. The initial powder has Sss = 5 m$^2$/g; the mechanical treatment of such powder...
leads to increases in the specific surface value to $S_{sp} = 8 \text{ m}^2/\text{g}$. The following annealing at 573 K leads to a sharp rise of the specific surface, which upon a further rise of the temperature decreases.

Such a sharp rise of the specific surface at 573 K is probably connected with the fact that, already at low temperatures, the removal of the adsorption water from the particle surface occurs [8]. The further increase in temperature leads to recrystallization and crystallite growth.

**Figure 4.** (a) Dependence of specific surface of ZrO$_2$ – Y$_2$O$_3$ powder on annealing temperature; (b) Dependence of particle size of ZrO$_2$ – Y$_2$O$_3$ powder and coherently diffracting domain on annealing temperature.

Figure 4b gives the dependences of the sizes of ZrO$_2$–Y$_2$O$_3$ powder particles on annealing temperature calculated by three different techniques: first, by SEM images at various magnifications by the random linear intercept method [9]; second, by the value of the specific surface under the assumption that particles are spherical; third is the dependence of the sizes of the coherently diffracting domain [6]. The analysis of these dependences showed that the average size of agglomerates (curve 1) decreases from 4.5 to 2.5 $\mu$m, but the coherently diffracting domain and particle size calculated by the specific surface increase. Such a ratio indicates that agglomerates measured by SEM are polycrystalline. With the rise of annealing temperature, the agglomerates are separated into individual particles. The extrapolation of dependences 1 and 2 to the region of high temperatures (Fig. 4b) allowed one to determine their intersection, the temperature at which was ~1400 K. At this temperature, the average size of ZrO$_2$ – Y$_2$O$_3$ powder particles is 2 $\mu$m. In this case (loose powder), the agglomerates in the powder system degrade to individual monolithic polycrystalline particles, the average size of which upon a further increase in temperature will increase by means of their sintering.

With the use of the obtained dependence of the change in the sizes of the coherently diffracting domain with rise of temperature, the activation energy of the grain growth can be estimated [10] (Fig. 5) (the value of the coherently diffracting domain at 573 K was taken as the initial one). The activation energy of the crystallite growth process obtained by the linear approximation is 45 kJ/mol. This energy is an order of magnitude less than the activation energy for the ZrO$_2$–CaO system, for which the activation energy of Zr and Ca self-diffusion is 390 and 420 kJ/mol, respectively [10, 11]. This indicates that the grain growth process in the system under investigation is determined by the surface diffusion.

From Fig. 5, it can be noted that the initial and end pieces have different slopes. This
allows one to conclude that the activation energy or pre-exponential factor apparently depends on temperature. The estimation of the activation energy at the initial and final stages of annealing showed that, at low temperatures, it is 35 kJ/mol, and at high temperatures, it is 70 kJ/mol. This is probably connected with the fact that, at low and high temperatures, various mechanisms of diffusion are realized—at low temperatures the surface diffusion, and with a rise of temperature, the grain growth is determined by the volume diffusion.

**Figure 5.** Dependence of change in size of coherently diffracting domain in «$D^2 - 1 / T$» coordinates.

### 4. Conclusions

The influence of the thermal treatments on the structure and morphology of powder of ZrO$_2$–Y$_2$O$_3$ composition synthesized via the method of reverse chemical precipitation showed that the rise of the annealing temperature leads to the decrease in the average size of particles, which were initially porous agglomerates with a high specific surface, to monolithic polydomain particles, the sizes of which are comparable with the sizes of crystallites. The grain growth during annealing is determined by the surface diffusion.

In the system ZrW$_2$O$_8$ the average size of the agglomerates decreases with increasing temperature. Formation of needle-shared particles occurs in powders synthesized at a temperature above 1423 K. The values of length of needle-shaped particles increases and its diameters was equal to 200 nm. The beginning of the formation ZrW$_2$O$_8$ was at temperatures more than 1373 K. The synthesized material has a negative thermal expansion and it was equal to $-12 \times 10^{-6}$ C$^{-1}$.

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