The impact of thermal treatment conditions on the formation of crystalline structure of Ce-Zr-oxide composite obtained by a modified sol-gel technique

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Abstract. We present the results of the modified sol-gel synthesis of ultrafine ceria-doped zirconia powder for medical ceramics (implants) and catalytic purposes (environmental catalysis and petrochemistry). Special attention has been paid to study the influence of thermal treatment on crystallite size and crystal lattice parameters of zirconia doped by ceria. Zirconyl chloride and cerium nitrate were used as metal sources, and tetraethylammonium hydroxide (TEAH) was used as a sol stabilizer at molar ratio TEAH/Σ (Ce + Zr) equal to 0.5. It was proved that zirconium and cerium practically completely were included in the obtained solid solutions, since their phase compositions fully correspond to initial quantities of cerium and zirconium in reaction mixture. It was shown that average crystallite size of the obtained powders did not exceed 75Å, and the powders were resistant to thermal treatment. It was established that stabilization of the crystal lattice of ZrO$_2$ occurs through formation of a cubic ceria sublattice.

1. Introduction

Ultrafine powders of zirconia doped by ceria, are promising materials with a wide application range in a different innovative technologies of solid oxide fuel cells, gas sensors, oxygen-conducting materials, a fine-grained composite ceramics with grain size less than 2 microns for medical purposes and catalysis [1]. During last 10-15 years, solid solutions CeO$_2$-ZrO$_2$ attracted attention of researchers in the fields of physical chemistry, technology of ceramics and nanotechnology. It is known that solid solutions CeO$_2$-ZrO$_2$ have high oxygen capacity, high mobility of lattice oxygen and high thermal stability [1]. Increasing demand of modern Hi-tech industry in the new materials with high oxygen capacity need in development of novel commercially scaled techniques for synthesis of ultra-dispersed powders [2].

Modified sol-gel technique is one of the technologically acceptable methods, which allows constructing of the structure of materials with new properties at the atomic and molecular level. Thermal treatment is important step of a structure formation, because this stage conditions determine not only a form of definite structure, but also ensure high dispersion of the material formed.

Previously, we reported about modified sol-gel synthesis of ultrafine Ce$_x$Zr$_{1-x}$O$_2$ powders with average crystallite size of 8 - 11 nm [3]. The aim of this work is to develop modified sol-gel synthesis of ultrafine zirconia doped by ceria for medical ceramics (implants) and catalytic purposes.
Environmental catalysis and petrochemistry. Special attention is paid to study the influence of thermal treatment on crystallite size and crystal lattice parameters of ZrO$_2$, stabilized by CeO$_2$.

2. Experiment

2.1. Preparation
Zirconyl chloride and cerium nitrate were used as metal sources, and tetraethylammonium hydroxide (TEAH) was used as sol stabilizer at a molar ratio TEAH/$\sum$ (Ce + Zr) equal to 0.5. Sol-gel synthesis was carried out by stirring with a magnetic stirrer at a temperature of 80-90°C in the course of 40 min. Then the sol was evaporated and the product was calcined at a temperature of 500-550°C for 1-21 hours.

2.2. Characterization
The phase composition was study by X-ray diffraction on a DRON-3 and Shimadzu XRD-6000 diffractometeres with monochromatic radiation CuK$_\alpha$, and identification of crystalline phases was carried out by using a database JCPDS 2003. The crystallite size was calculated by Scherrer formula: $D = \frac{0.94 \lambda}{\cos \theta (b - b_i)}$, where $\lambda$ - wavelength; $b$ - broadening (full width at half maximum) of X-ray lines; $b_i$ - instrumental broadening; $\theta$ - angle reflection.

3. Results and discussion
According to X-ray diffraction (Figure 1) obtained powders were single-phase systems with general formula Ce$_{0.06}$Zr$_{0.94}$O$_2$. All of them were nanopowders, as the crystallite size did not exceed 75 Å. It was proved that zirconium and cerium practically completely included in the obtained solid solutions, since their phase compositions fully correspond to initial quantities of cerium and zirconium in reaction mixture. This phenomenon was confirmed by yield of powders from theoretical around 96-99%. The absence of characteristic for amorphous phase halo on the diffractograms of the samples also proves the full inclusion of initial amounts of cerium and zirconium in the composite. The appearance of a small halo visible in all diffraction patterns may be due to lithol (industrial petroleum vaseline) which was used for attachment the powders in the cell of diffractometer. Comparison of diffraction patterns of composites Ce$_{0.06}$Zr$_{0.94}$O$_2$ (Figure 1) and pure ZrO$_2$ shows that they are almost identical.

Figure 1. XRD patterns of samples: $a$- Ce$_{0.06}$Zr$_{0.94}$O$_2$ calcined at a 500°C for 1 hour, $b$ - Ce$_{0.06}$Zr$_{0.94}$O$_2$ calcined at 550°C for 21 hours, $c$ – ZrO$_2$
Table 1. Average crystallite size (D), microdeformation (e), and lattice parameters (a and c) of composites Ce\textsubscript{0.06}Zr\textsubscript{0.94}O\textsubscript{2}, obtained in different modes of thermal treatment.

| Thermal treatment conditions | D, Å | e, % | a, Å | c, Å |
|-----------------------------|------|------|------|------|
| Temperature, ºC | Duration, h | | | |
| 500 | 1 | 63 | 0.98 | 3.618 | 5.146 |
| 500 | 21 | 73 | 0.79 | 3.608 | 5.169 |
| 550 | 1 | 75 | 0.77 | 3.607 | 5.179 |

Apparently, the characteristic for ceria cubic crystal was formed as a sublattice in the structure of ZrO\textsubscript{2}. Table 1 shows the results of X-ray diffraction of composites Ce\textsubscript{0.06}Zr\textsubscript{0.94}O\textsubscript{2}, obtained under different conditions of thermal treatment. It is shown, that duration and treatment temperature weakly affect the dispersion of composite systems, stabilized by ceria. Thus, prolongation of calcination at 500 ºC from 1 to 21 hs leads to the crystallite growth from 63 to 73 Å. At the same time the amount of microdeformations reduced significantly, and the parameters correspond to the tetragonal crystal lattice of ceria doped zirconia \[4\]. If the calcination temperature increases from 500 to 550 ºC for the duration of 1 h, the crystallite size increases from 63 to 75 Å. The microdeformation amount reduced significantly, and the parameters correspond to the tetragonal crystal lattice of ceria doped zirconia too \[4\].

Figure 2 shows the plot of average crystallite size of the duration of the composite Ce\textsubscript{0.06}Zr\textsubscript{0.94}O\textsubscript{2} calcination at 500 ºC. When the thermal treatment duration is 16 or more hours crystallite growth became slower and did not exceed 75 Å.

4. Conclusions

- Method of obtaining the single-phase composites Ce\textsubscript{0.06}Zr\textsubscript{0.94}O\textsubscript{2} by modified sol-gel synthesis with using of TEAH was developed.
- It was shown that obtained powders have average crystallite size don’t exceed 75 Å, and are resistant to thermal treatment.
- It is established that the stabilization of the crystal lattice of ZrO\textsubscript{2} occurs through the formation of a cubic CeO\textsubscript{2} sublattice.

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