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STRUCTURE AND MORPHOLOGY OF ZIRCONIUM OXIDE (IV) POWDERS SYNTHESIZED BY THE THERMAL METHOD FROM DIFFERENT PRECURSORS

ZrO_2 powders were synthesized from different precursors by the thermal method: zirconium hydroxide ($ZrO(OH)_2$) and zirconium oxalate ($ZrOC_2O_4$). In synthesized samples by XRD analysis it was researched phase composition; sample, synthesized from $ZrO(OH)_2$, consists of, mainly, the monoclinic modification, and sample, synthesized from $ZrOC_2O_4$ – of the tetragonal modification. It was calculated crystal grates parameters of obtained ZrO_2 powders by the method of XRS analysis. It was fined crystallite's sizes: for standart, synthesized from $ZrO(OH)_2$, and sample, synthesized from $ZrOC_2O_4$, respectively, 74,5 nm and 29,4 nm. By the methods of scanning (MIRA3 TESCAN) and translucent (ПЕМ 125К) electron microscopy it was determined morphology and minimal size of ZrO_2 particles. Sample, synthesized from $ZrO(OH)_2$, has granule structure with minimal particle size 100 nm, and sample, synthesized from $ZrOC_2O_4$ has porous structure with minimal grain size 30 nm. It was determined the specific surface and particle size of ZrO_2 samples by the desiccator method of benzene steam adsorption, which are for sample, synthesized from $ZrO(OH)_2$, and sample, synthesized from $ZrOC_2O_4$, respectively, 10,4 m^2/g, 104,9 nm i 39,1 m2/g, 27,9 nm. It was made comparison of ZrO_2 particles size calculated on the base of data according to different methods.

Introduction

Development and research of rational methods of zirconium oxide (IV) (ZrO_2) represent great scientific and practice interest. ZrO_2-based materials characterized by special chemical, physical, optical, dielectric, mechanical properties, such as high thermal and mechanical stability and chemical inertness. All of the above properties allowed to use it in a variety of practical applications: fuel cells, catalytic systems, oxygen sensors, ceramic biomaterials, as well as in various fields of microelectronics [1].

Zirconium oxide (IV) exists in three modifications: monoclinic (stable up to 1170 °C), tetragonal (stable up to 2370 °C) and cubic (stable from 2370 °C to melting the substance at 2700 °C) [2]. Monoclinic ZrO_2 is a typical mineral of baddeleyite rocks and magnetite ores. It is used in the ceramics industry and in the production of refractories. Zirconium oxide (IV) of the tetragonal modification is used for production ceramic dental appointment. Cubic ZrO_2 is used in jewelry as an imitator of diamonds and also as an electrolyte in fuel cells. At the same time different doping additives (usually yttrium (III), cerium (III) and calcium) must be added for obtaining the tetragonal or cubic modification of ZrO_2 [2].

At present, ultra- and nanodispersed ZrO_2 are obtained by thermal methods [2], by the deposition method (co-precipitation) from solutions [3, 4], by the hydrothermal method [5], by sol-gel technology [6] etc. The thermal method is the simplest among the methods listed above. It allows obtainning, depending on the conditions of synthesis, ultra-fine particles of ZrO_2 with sizes ranging from 20 to 300×400 nm. Thermally unstable compounds are used with the decomposition temperature up to 900 °C.

The great advantage of the thermal method is the possibility of obtaining of usually pure ZrO_2 [7, 8]. However, despite the apparent simplicity of the thermal method of research synthesis conditions zirconium oxide (IV) by this method is relatively small. In addition, depending on the parameters of the process, such as temperature and duration of the decomposition, the nature of the precursor, ZrO_2 particles can have different morphology and structure (modification) [8], which, in turn, has a significant impact on their final properties. The dependence of the properties of ZrO_2 on the nature of the precursors or their premodification are not strange enough. Regarding this, the study of the influence of temperature and thermal decomposition, the nature of precursors, as well as preliminary chemical modification of the latter on the structure and morphology of ZrO_2 powders is an actual problem.

Formulation of the problem

The objective of this investigation is the study influence of preliminary chemical modification of zirconium hydroxide on the structure and mor-

phology of ZrO_2 powders obtained by the thermal decomposition.

Materials and methods

The following reagents were used for synthesis of ZrO_2 powders: zirconium oxychloride ($ZrOCl_2$) (chemically pure qualification), 25 % aqueous ammonia solution (NH_4OH) (chemically pure qualification), oxalic acid ($H_2C_2O_4$) (chemically pure qualification). For synthesis of ZrO_2 it was prepared the solution of $ZrOCl_2$ with a concentration 320 g/L of ZrO_2. It was added the solution of ammonia (25 %) to pH 10 for complete precipitation of zirconium hydroxide ($ZrO(OH)_2$) according to reaction (1):

$$ZrOCl_2 + 2NH_4OH = ZrO(OH)_2 + 2NH_4Cl. \quad (1)$$

The resulting suspension was filtered and the precipitate was washed with distilled water on a Buchner funnel until the negative reaction of chloride ions. After that, the wet $ZrO(OH)_2$ was separated into two approximately equal parts.

The first part of the precipitate was dried and calcined in a muffle furnace at 900 °C for 1 hour. In this way ZrO_2 (sample 1) was formed by the reaction (2):

$$ZrO(OH)_2 \rightarrow ZrO_2 + H_2O \uparrow. \quad (2)$$

The second part was transferred into a heat-resistant glass, in which poured 10 % solution of oxalic acid was added. The mixture was boiled until complete dissolution of zirconium hydroxide following the evaporation of the solution to dryness. The resulting powder of zirconyl oxalate ($ZrOC_2O_4$) was calcined at 900 °C for 1 hour. It was obtained ZrO_2 powder (sample 2) by the reaction (3):

$$ZrOC_2O_4 \rightarrow ZrO_2 + 2CO_2\uparrow. \quad (3)$$

XRD and XRS analysis's of samples were carried out using an apparatus DRON-3M with Cu-radiation and a step scan 0,005 deg.

The electron microscopy of ZrO_2 powders were carried out with scanning (MIRA3 TESCAN) and transmission (TEM 125K) electron microscopes.

The specific surface area was determined by the desiccator method of the adsorption of benzene vapor.

Results and discussion

Figure 1 shows the diffraction patterns of the samples: sample 1 (*a*) and sample 2 (*b*). As could be seen from the diffraction patterns, two different modifications were obtained. According to the standard cards JCPDS № 41-0017 and 42-1164, monoclinic modification of ZrO_2 was obtained from $ZrO(OH)_2$ (*a*), and tetragonal modification of ZrO_2 – from $ZrOC_2O_4$ (*b*).

For these samples parameters of crystal grates and the crystalline sizes were calculated.

The lattice constant of ZrO_2 was calculated using the relation (4):

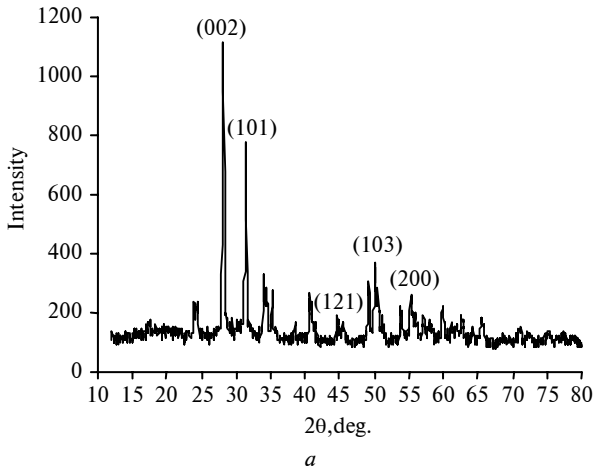
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}, \quad (4)$$

where *h, k, l* are the Miller indices; *a*, *b*, *c* are the constants, nm; *d* is the glancing angle, nm [9].

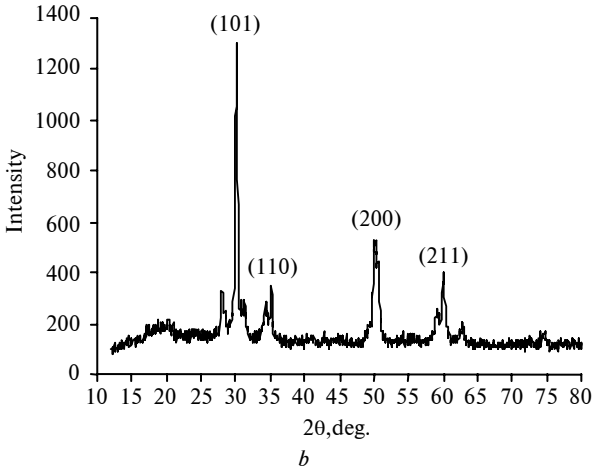
The crystalline sizes of samples of ZrO_2 were calculated by the Debye-Scherrer's formula (5):

$$t = \frac{0,9 \cdot \lambda}{B \cdot \cos\theta}, \quad (5)$$

where λ is the wavelength of X-ray, nm; *B* is the full width half of the peaks; θ is the Bragg angle [10].



a

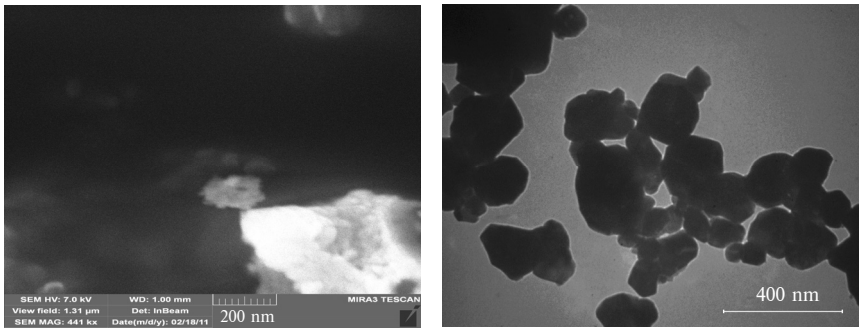


b

Fig. 1. Diffraction patterns of ZrO_2 samples: *a* – sample 1, *b* – sample 2

***Table* 1**. The structural parameters of ZrO_2 samples

Samples	*hkl*	2θ, deg.	Glancing angle *d*, nm	*B*, rad.	Crystalline size, nm	Lattice constant, nm		
						a	*b*	*c*
Sample 1	002	28,1	0,31755	0,00198	74,5	0,333	0,557	0,649
Sample 2	101	30,1	0,29689	0,00488	29,4	0,364	0,364	0,527



a *b*

Fig. 2. SEM (*a*) and TEM (*b*) micrographs of sample 1

Some of the diffraction Bragg angles can be founded in [11]. The structural parameters (lattice constant and crystalline sizes) were calculated using the equations ((4) and (5)) and tabulated in Table 1.

The calculation of lattice constants will help to determine the distortion in the crystal grates of the synthesized of ZrO_2 samples, that can take place during synthesis. Standard values of *a*, *b*, *c* (nm) for the monoclinic and tetragonal modifications are 0,333, 0,557, 0,649 and 0,364, 0,364, 0,527 respectively. Comparing obtained data with the calculated values of *a*, *b*, *c* for samples of ZrO_2 it should be noted that the distortion of crystal grates of the samples does not occur (Table 1).

Figures 2 and 3 show electron micrographs of samples 1 and 2, respectively.

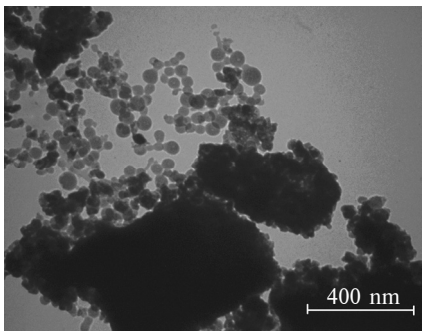


Fig. 3. TEM micrograph of sample 2

Figure 2 shows the SEM and TEM images of the sample ZrO_2 synthesized from $ZrO(OH)_2$ (sample 1). From the micrographs it can be concluded that obtained ZrO_2 particles have a structure of densely packed granules with a minimum size of 100 nm.

Figure 3 shows a TEM micrograph of the sample ZrO_2, obtained from $ZrOC_2O_4$.

It can be see that the synthesized particles of ZrO_2 are porous with a minimum particle size of 30 nm.

The specific surface area of the samples was determined by desiccator method of benzene vapor adsorption. The specific surface area of ZrO_2 samples was calculated by the formula (6):

$$S_s = a_m \cdot N_A \cdot S_0, \qquad (6)$$

where a_m is molar adsorption, mole/g; N_A is Avogadro constant, $mole^{-1}$; S_0 is surface area of adsorbent occupied by one molecule of adsorbate, m^2 [11].

The specific surface areas (S_s) for sample 1 and sample 2 were calculated: 10,4 m^2/g and 39,1 m^2/g respectively.

Assuming that the ZrO_2 particles have a spherical shape, their sizes were determined by the equation (7):

$$d = \frac{6}{\rho \cdot S_s} \cdot 10^9, \qquad (7)$$

where d is size of ZrO_2 particles, nm, ρ is density of ZrO_2 particles, kg/m^3; S_s is a specific surface area, m^2/kg [12].

The particle sizes for samples 1 and 2 were determined by the different methods and are presented in Table 2.

***Table* 2**. The particles sizes of ZrO_2 (*d*) determined by the different methods

Sample of ZrO_2 powders	*d*, nm			S_s, m^2/g
	XRD	TEM	The desiccator's method	
Sample 1	74,5	100	104,9	10,4
Sample 2	27,4	35	29,7	39,1

Conclusions

Based on experimental results the following conclusions can be done:

- The preliminary chemical modification of zirconium hydroxide with subsequent heat treatment allows obtaining of the particles of tetragonal ZrO_2, under its absence the monoclinic phase can be obtain.
- Sample from $ZrO(OH)_2$ has a structure of densely packed grains with an average size of 100 nm, and sample from $ZrOC_2O_4$ has a porous structure with average grain size of 30 nm.
- Sample from $ZrOC_2O_4$ has more developed surface (39,1 m^2/g) than sample from $ZrO(OH)_2$ (10,4 m^2/g).
- Scientific novelty is the use of chemical modification of precursor of zirconium hydroxide, resulting in ZrO_2 powder was obtained of the tetragonal modification without the addition of doping additives with more developed surface.

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