COMPARISON OF Y_2O_3 AND ZrO_2 SYNTHESIZED FROM WATER NITRATE SOLUTIONS AND WATER-ORGANIC NITRATE SOLUTIONS

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СРАВНИТЕЛЬНЫЙ АНАЛИЗ Y_2O_3 И ZrO_2, СИНТЕЗИРОВАННЫХ ИЗ ВОДНЫХ НИТРАТНЫХ РАСТВОРОВ И ВОДНО-ОРГАНИЧЕСКИХ НИТРАТНЫХ РАСТВОРОВ

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Аннотация. *В статье представлены результаты по плазмохимическому синтезу порошков Y_2O_3 и ZrO_2 из водно-органических нитратных растворов. Произведено сравнение полученных данных с аналогичными данными, полученными в случае использования водных нитратных растворов. Показано, что порошки, синтезированные из водных нитратных растворов и водно-органических нитратных растворов, имеют близкие характеристики. Главное отличие состоит в фазовом составе порошков. Доказано, что добавление органического компонента резко повышает выход по порошку и снижает удельные энергозатраты на процесс синтеза, что делает его энергоэффективным.*

Introduction. One of the priorities in the development of modern material science is the technology based on nanosized powders, which is due to the desire for miniaturization of products, unique properties of materials in the nanostructured state, etc.

Yttrium oxide (Y_2O_3) and zirconium oxide (ZrO_2) are widely used in various industries. For example, high temperature yttrium oxide ceramic is used in aggressive environments (engine pistons, turbine parts) due to its chemical resistance. Transparent ceramic based on Y_2O_3 has high light transmission, high melting point, high heat resistance, mechanical and electrophysical properties. ZrO_2 is used for the production of highly refractory products, heat-resistant enamels, refractory glasses, various types of ceramics, pigments, etc.

The most common technologies for producing such nanosized oxides are laser sublimation, chemical precipitation from solutions, hydrothermal method and sol-gel technology. Each method has its advantages and disadvantages, while the choice of technology is determined by the purpose of the powder, the state of its microstructure, method performance, complexity and cost of the equipment used. The disadvantages of the methods used to obtain nanosized powders include: multi-staging, long process duration, low productivity, the need to use a large number of chemicals, non-uniform distribution of phases in the powders, and high cost.

Taking into account the above, the use of low-temperature plasma is promising for obtaining nanosized metal oxide powders. The advantages of plasma-chemical synthesis from water nitrate solutions (WNS) include the following: one-staging, high process speed, homogeneous phase distribution with a given stoichiometric

composition, the ability to actively influence the size and morphology of particles, and the compactness of technological equipment. However, plasma treatment of only WNS due to high energy costs (up to 4.0 kW·h/ g) [1] is not widely used, and it is possible to significantly reduce energy consumption and increase productivity by introducing an organic component in the composition of the initial WNS.

Theory. Firstly, the optimal compositions of water-organic nitrate solutions (WONS) based on acetone and WNS $Y(NO_3)_3$, as well as acetone and WNS $ZrO(NO_3)_2$ were calculated. For this, the values of lower calorific value were determined for various mass fractions of acetone in WONS. Liquid combustible compositions are considered to be compositions with a lower calorific value of more than 8.4 MJ/kg [2], so the following compositions of WONS-1 (based on $Y(NO_3)_3$) and WONS-2 (based on $ZrO(NO_3)_2$) were considered as optimal:

- WONS-1: [31 wt. % C_3H_6O : 35 wt. % H_2O : 34 wt. % $Y(NO_3)_3$];
- WONS-2: [32 wt. % C_3H_6O : 43 wt. % H_2O : 25 wt. % $ZrO(NO_3)_2$].

Secondly, in order to determine the optimal modes of the process under study, it was determined the influence of the mass fraction of the air plasma coolant on the adiabatic combustion temperature of WONS. It is believed that the complete combustion of such solutions in chambers with low heat loss to the environment is observed in compositions with an adiabatic combustion temperature of at least 1200 °C [1], it is important that this temperature excludes the formation of carbon (soot) in the condensed phase, ensuring purity powders. The following air plasma coolant – WONS ratios were considered as optimal:

- 69 wt. % air : 31 wt. % WONS-1;
- 72 wt. % air : 28 wt. % WONS-2.

Compositions of gaseous and condensed products of plasma-chemical synthesis of powders of yttrium and zirconium oxides from WONS-1 and WONS-2, respectively, were calculated with the use of TERRA program. The calculations were performed for atmospheric pressure (0.1 MPa), a wide range of operating temperatures (300–4000 K) and various mass fractions of an air plasma coolant (10–90 %). The main gaseous products of the synthesis process are N_2, H_2O and CO_2; only Y_2O_3 (or ZrO_2) is formed in the condensed phase.

Experiments. The studies were carried out using plasma module based on the high-frequency generator. For plasma treatment, WONS-1 and WONS-2 were prepared according to the optimal compositions determined for them, while the concentration of $Y(NO_3)_3$ and $ZrO(NO_3)_2$ salts was 97 g/100 ml of water and 57 g/100 ml of water, respectively. The prepared solutions were processed in a high-frequency torch plasma. During the plasma treatment, after liquid evaporation and crystallization of the salt, yttrium and zirconium oxides were formed as a result of thermolysis, which were quenched in centrifugal bubblers. The obtained oxide powders were sent for analysis.

Analysis of Y_2O_3 and ZrO_2 powders. To study the main parameters of the obtained powders, scanning electron microscopy, BET analysis, and X-ray phase analysis were performed. The obtained results were compared with data [3] on the parameters of yttrium and zirconium oxide powders obtained by plasma-chemical synthesis from WNS (without the addition of an organic component). A comparative analysis is presented in table 1.

Table 1

The results of a comparative analysis of the processes of plasma-chemical synthesis of nanoscale powders of yttrium and zirconium oxides from WONS and WNS

Parameter	Synthesis from WONS		Synthesis from WNS	
	Y_2O_3	ZrO_2	Y_2O_3	ZrO_2
Coherent scattering region, nm	41	66	40	68

Phase composition	cub.	tetr., cub.	cub.	monocl.
Specific surface area, m^2/g	30	13	27	17
Yield, kg/h	85	50	20	20
Specific energy consumption, kW·h/kg	0,5	0,8	4	4
Quenching	with	with	without	without

As seen from the analysis of the data presented', it follows that the powders obtained by plasma-chemical synthesis from WONS-1 and WONS-2 are comparable in a number of parameters (CSR size, specific surface area) with powders obtained by plasma-chemical synthesis from WNS solutions. However, zirconia powders obtained by plasma-chemical synthesis from a WONS-2 solution are in the tetragonal and cubic phases, and obtained from WNS in the monoclinic phase, which is explained by the use of quenching in the first case. In this case, the inclusion of the organic component in the composition of the WNS leads to an increase in powder productivity by 2.5–4 times and to a decrease in energy consumption for producing 1 kg of nanosized powders by 5–8 times.

Conclusion. Considering the obtained results, it can be argued that the plasma-chemical synthesis of yttrium and zirconium oxides is an energy-efficient method for producing nanosized powders, which can be used to obtain oxide nanosized powders of other metals.

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