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SYNTHESIS OF URANIUM-THORIUM OXIDE POWDERS IN LOW-TEMPERATURE PLASMA OF HIGH FREQUENCY TORCH DISCHARGE

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The article discusses the process of plasma chemical synthesis of uranium-thorium oxide powders for a new generation dispersion nuclear fuel. In the course of research, the combustion parameters of the precursors were calculated. Precursors were water-organic nitrate solutions based on uranyl nitrate and thorium nitrate (fissile components), as well as magnesium nitrate (matrix material). The organic component of the solutions was acetone due to the sufficiently high calorific value and good mutual solubility. In the course of thermodynamic calculations, the optimal modes of processing of the water-organic nitrate solutions in low-temperature plasma were determined. These modes ensured the synthesis of oxide powders of the necessary stoichiometry without impurities of unoxidized carbon (soot). Experiments to obtain the samples of powders were carried out with the model solutions in which uranyl and thorium nitrates were replaced by neodymium and cerium ones, which are in the same group of the periodic table. The synthesis was carried out with the use of a plasma chemical unit based on a high frequency torch plasmatron. The synthesized powders were subjected to a number of analyzes including electron microscopy, particle size analysis, X-ray phase analysis and BET analysis. The results showed that the powders can be classified as nanosized.

Keywords: high frequency torch discharge, plasma, powder, nuclear fuel, uranium, thorium, analysis.

Introduction

Most of the operating nuclear power plants use ceramic nuclear fuel from uranium dioxide enriched in the isotope uranium-235.Such fuel along with its undoubted advantages also has significant disadvantages which are low thermal conductivity limiting the specific power of the reactor in terms of melting temperature, fragility, tendency to cracking, short cycle of use (3–5 years), high costs for the disposal of spent fuel and finally limited resource of the uranium-235 isotope. In case of uranium-238 and thorium-232 isotopes, there is no need for expensive isotopic enrichment, and the cycle of use of such nuclear fuel can be brought up to 10–15 years. Moreover, the predicted reserves of thorium in the earth's crust are 3–5 times greater than that of uranium [1–6]. One of the promising directions for the further development of nuclear power is the use of dispersion nuclear fuel, in which inclusions of fissile materials (e.g. uranium, thorium) in the form of granular oxide compounds (OC) are placed in a matrix with a high thermal conductivity coefficient. The use of a matrix made of metal powders (aluminum, molybdenum, tungsten, stainless steel, etc.) increases the thermal conductivity, but leads to a deterioration in the neutron balance due to the high resonance absorption of neutrons. In addition, the use sol-gel process to obtain microspheres from mixed water nitrate solutions is associated with the following disadvantages: multistage, long duration, low productivity, the need to use a large number of chemical reagents, the need for additional hydrogen reduction. In addition, separate production and further mechanical mixing of fissile and matrix materials do not provide a homogeneous phase distribution in such dispersion nuclear fuel. Table 1 shows some advantages and disadvantages of some prospective methods to obtain oxide powders.

The undoubted advantages of using plasma for the OC plasma chemical synthesis from water nitrate solutions in comparison with another methods include one-stage, high process rate, the ability to actively influence the particle size and morphology and compactness of technological equipment. It should be noted that the addition of an organic component (alcohol, acetone, etc.) to the nitrate solution will reduce the specific energy consumption, thus, the use of water-organic nitrate solutions (WONS) is preferable [7].

The work objective is to study the process of synthesis of oxide compositions for uranium-thorium nuclear fuel under conditions of non-equilibrium air plasma of a high frequency torch discharge.

Table 1. Pros and cons of some prospective methods to obtain oxide powders.

	Method	Advantages	Disadvantages
1	Ultrasound dispersion	Powders are distinguished by the uniformity of particle sizes of the dispersed phase	Long process duration
2	Mechanical synthesis	Low process temperature	Long process duration, high energy intensity
3	Chemical sedimentation	Accessibility	Wide distribution of particle size values
4	Hydrothermal method	Accessibility	High cost and complexity of equipment
5	Electric explosion of metal wires	Small particle size	High energy intensity, low productivity

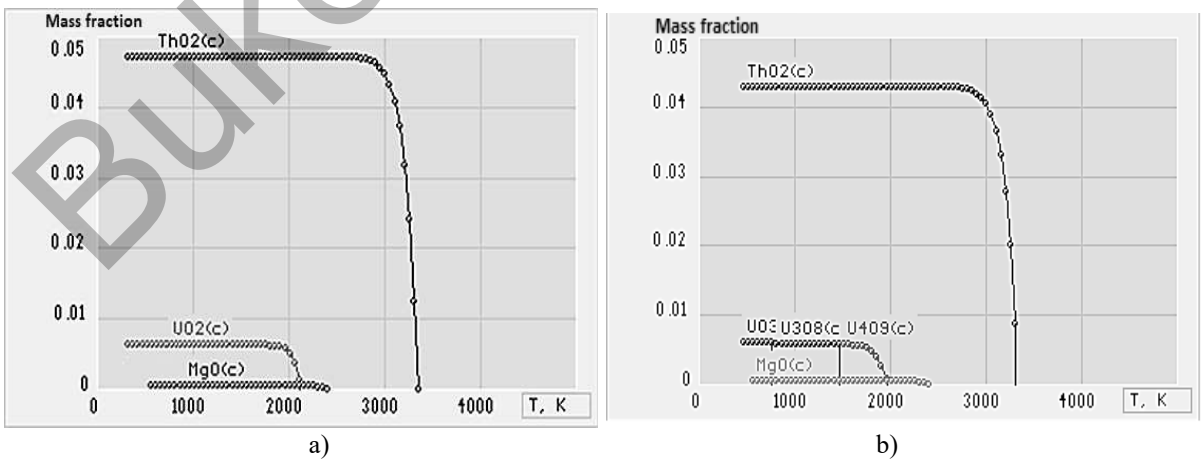
1. Theoretical part

In this work, uranium and thorium oxides were considered as a fissile component of dispersion nuclear fuel, and magnesium oxide was considered as a matrix material. The initial precursors were nitrates of uranyl, thorium and magnesium nitrates, and acetone was an organic component, which has a sufficiently high calorific value and good mutual solubility. Thus WONS was considered as a mixture of water solutions of $UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and C_2H_6O. Firstly, to determine the optimal WONS composition, the net calorific value Q_l of the solutions was calculated according to the equation [8]:

$$Q_l = \frac{(100 - W - A)Q_{lc}}{100} - \frac{2.5W}{100},$$

where Q_{lc} is lower heat value of combustible component of WONS, MJ/kg; W and A are content of water and noncombustible components, wt.%; 2.5 is the value of latent heat of vaporization for water at 0 °C, MJ/kg. It was shown that WON Shaving $Q_l \geq 8.4$ MJ/kg can provide a significant reduction in energy consumption for the plasma chemical synthesis of oxide compounds [8, 9]. Thus, for the synthesis of OC of various compositions, the optimal compositions of WONS having $Q_l \geq 8.4$ MJ/kg were determined and are given in Table 2. In the course of calculations, the ratio of fissile components was taken $UO_2/(ThO_2+UO_2) = 0.1$, and the proportion of the matrix varied from 1 to 10% [3].

Further, a thermodynamic calculation of the process of plasma chemical synthesis of oxide compositions from WONS was carried out in the program “TERRA”. This program provides an opportunity to make thermodynamic calculations of the phase compositions of heterogeneous systems. The calculations were carried out at atmospheric pressure, in a wide temperature range (300–5000 K) and mass fractions of air plasma coolant (0.1–0.9). Figure 1 shows the temperature dependence of the mass fraction of formed oxide products obtained after plasma treatment of WONS-1 at a mass fraction of air of 67% (a) and 70% (b).



a) b)

Fig.1. Temperature dependence of the mass fraction of formed oxide products obtained after plasma treatment of WONS-1 at a mass fraction of air of 67% (a) and 70% (b).

Table 2. Calculations of WONS compositions.

OC composition	WONS composition, wt.%.				
	H_2O	C_2H_6O	$UO_2(NO_3)_2{\cdot}6H_2O$	$Th(NO_3)_4{\cdot}6H_2O$	$Mg(NO_3)_2{\cdot}6H_2O$
WONS-1					
89.1%ThO_2– 9.9%UO_2– 1.0%MgO	28.4	29.0	3.5	37.9	1.2
WONS-2					
87.8%ThO_2– 9.7%UO_2– 2.5%MgO	28.4	29.0	3.4	36.3	2.9
WONS-3					
85.5%ThO_2– 9.5%UO_2– 5.0%MgO	28.4	29.0	3.1	33.8	5.7
WONS-4					
83.3%ThO_2– 9.2%UO_2– 7.5%MgO	28.4	29.0	2.9	31.5	8.2
WONS-5					
81.0% ThO_2 – 9.0% UO_2– 10.0%MgO	28.4	29.0	2.7	29.4	10.5

An analysis of the equilibrium compositions shows that plasma treatment of WONS-1 at a mass fraction of air of 67% and temperatures up to 2000 K (Figure 1a) leads to the plasma chemical synthesis of the required OC "89.1% ThO_2– 9.9% UO_2– 1.0% MgO". An increase in the air fraction above 69% in the temperature range 1000–1600 K leads to the formation of oxide U_3O_8 instead of the required UO_2 (Figure 1b). A decrease in the proportion of air below 67% leads to the formation of carbon in the condensed phase (soot) in the composition of the products, which contaminates the synthesis products. Similar results were obtained for the rest WONS.

2. Experimental technique

Experimental studies with the purpose of producing samples of oxide powders were carried out using a plasma chemical unit based on a high-frequency torch plasmatron (Figure 2).

The unit is designed to carry out the processes of plasma treatment of dispersed water-salt solutions of various compositions. The torch plasmatron generates a low-temperature (mass-average temperature up to 3000 °C) nonequilibrium air plasma. The auto electronic type of emission, which is realized in this case, excludes the erosion of the electrode and thus prevents the contamination of the synthesized products. Due to the absence of an opportunity to deal with uranium and thorium at the university laboratory all experiments were carried out with model WONS. Fissile materials $UO_2(NO_3)_2{\cdot}6H_2O$, $Th(NO_3)_4{\cdot}6H_2O$ in the course of the experiments were replaced by metal salts respectively $Nd(NO_3)_3{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ that are in the same group of chemical elements with uranium and thorium. The prepared WONS (Table 1) was dispersed using a mechanical atomizer into a plasma-chemical reactor, where it was treated with a plasma jet and oxide powder was synthesized during thermolysis.

3. Results and discussion

The synthesized powders were subjected to a number of analyzes. Scanning (SEM) and transmission (TEM) electron microscopy were performed to analyze particle size and morphology, X-ray phase analysis, particle size analysis to study the particle size distribution, and BET analysis to determine the specific surface area [10]. The morphological characteristics were qualitatively assessed using electron microscopy.

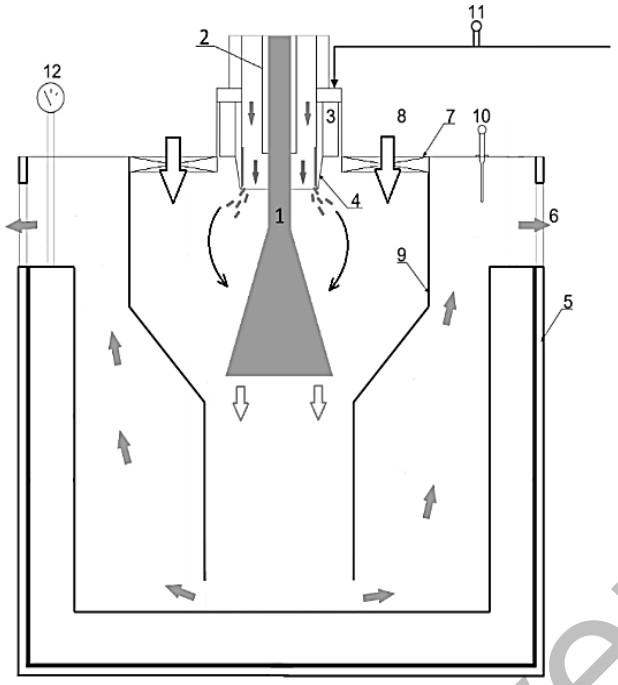
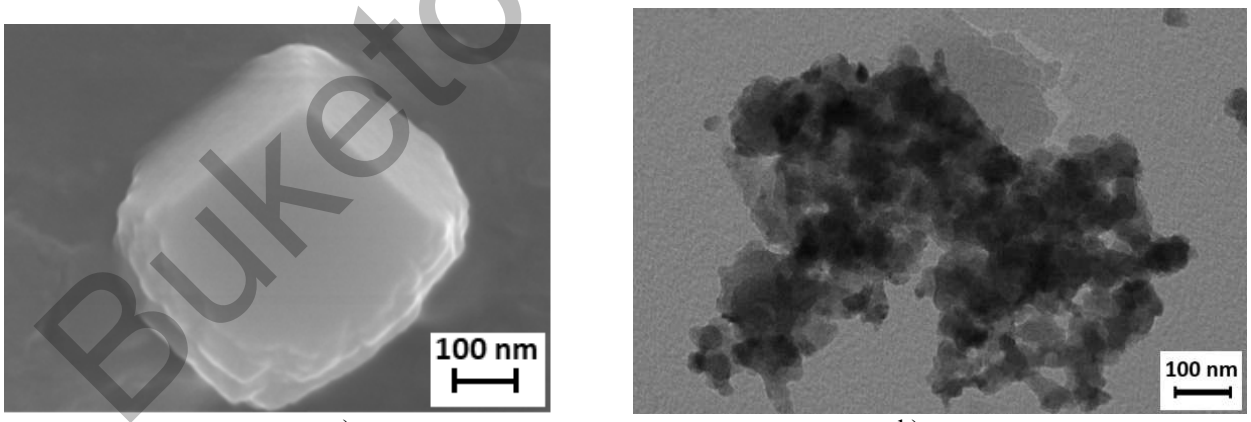


Fig.2. Plasmachemical unit based on a high-frequency torch plasmatron: 1 – plasma generated by high-frequency torch plasmatron;2 – quartz discharge chamber; 3 – sleeve; 4 – mechanical atomizer; 5 – reactor case; 6 – exhausted gases; 7 – sliding shutter; 8 – air entraining; 9 – reactor; 10, 11 – thermal couples; 12 – manometer.

SEM was performed using JSM-7500FA microscope (Figure 3a), TEM was performed using a Philips CM30 microscope (Figure 3b). An analysis of the SEM image results suggests that the powder has agglomerated into dense bulk structures 400–500 nm in size. The TEM image, on the other hand, allows to examine individual polydisperse powder particles in agglomerates. The particle size varies in the range of 30–120 nm, the shape of the particles is round. The X-ray phase analysis (Figure 4) showed the presence of the target oxides Nd_2O_3, CeO_2, and MgO in the powder sample. The size of the coherent scattering region, identified with the particle size, according to the analysis results is 87 nm.



a) b)

Fig.3. Micrographs of the powder obtained from WONS-1: SEM (a) and TEM (b).

Results demonstrates that all major peaks correspond to target oxides, indicating pureness of powder. The specific surface area of the powder was determined by the Brunauer-Emmett-Teller (BET) method and is 11 m^2/g. The resulting area value was recalculated into the size of the particles, based on the assumption of their spherical geometry. Thus, the BET particle size is 82 nm.

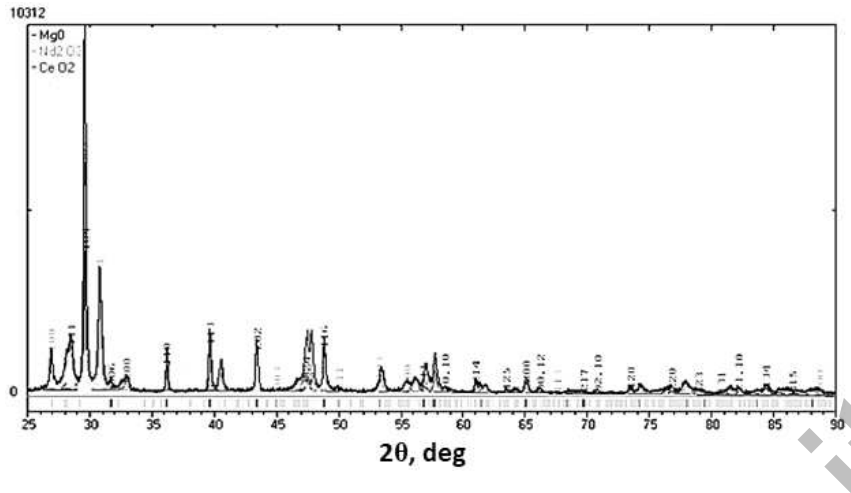


Fig.4. X-ray phase analysis of powder synthesized from WONS-1.

The results of the analyzes are in satisfactory agreement with each other without any conflicting, and make it possible to classify the powder synthesized in plasma as a nanosized

Conclusions

As a result of the studies, it was established the possibility of carrying out the process of plasmachemical synthesis of oxide compounds for dispersion nuclear fuel of the uranium-thorium cycle. It is shown that the optimal proportion of air plasma coolant for the synthesis of a composition of the required stoichiometry is 67%. Analysis of the obtained powders in the course of experimental studies shows that the average size of particle agglomerates is 500 nm, while the powder particles themselves have a size of 30–120 nm and a round shape. The size of coherent scattering region of the powder is 87 nm, the particle diameter determined by the BET method is 82 nm, and the specific surface area is 11 m^2/g. The results of the analyzes are in satisfactory agreement with each other, and make it possible to classify such a powders as a nanoscale.

It is important to note that the nanoscale dimensionality of the powder can provide an increase in the density of the pellets produced on their basis; in addition, it can provide a decrease in the compacting pressure and sintering temperature of fuel pellets. The described plasmachemical synthesis technology can be used to obtain other simple and complex oxide powders for fabricating promising types of nuclear fuel.

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