Investigation of plasmachemical synthesis of oxide compositions for plutonium-thorium dispersion nuclear fuel

A G Karengin, A A Karengin, I Yu Novoselov and A E Tikhonov
National Research Tomsk Polytechnic University, Lenina Avenue, 30, Tomsk, 634050, Russia
E-mail: karengin@tpu.ru

Abstract. This paper presents the results of experimental studies on the process of plasmachemical synthesis of fuel oxide compositions for plutonium-thorium dispersion nuclear fuel. Precursors were simulated water-organic nitrate solutions, which have a lower calorific value near 8.4 MJ/kg. The precursors consisted of an organic component (acetone) and mixed water nitrate solutions including a matrix metal (magnesium, yttrium), samarium (instead of plutonium), and cerium (instead of thorium). The authors determined the compositions and modes of processing simulated solutions that provide plasmachemical synthesis of nanosized complex oxide powders imitating plutonium-thorium dispersion nuclear fuel.

1. Introduction
A significant part of nuclear power in the twenty-first century is a nuclear power plant with thermal neutron reactors. Such reactors use ceramic nuclear fuel from uranium dioxide enriched in the isotope uranium-235. This technology, along with advantages, has a number of disadvantages: low thermal conductivity; fragility and tendency to cracking; short cycle of use (3-5 years); high costs for the disposal of spent nuclear fuel; limited natural resources of the isotope uranium-235 [1].

When using isotopes thorium-232 and plutonium-239, there is no need for expensive isotopic enrichment, and the cycle of using such nuclear fuel can be prolonged up to 10-15 years. At the same time, the predicted resources of thorium in the earth crust are 3-5 times greater than that of uranium. Moreover, the use of nuclear fuel in the form of oxide compositions based on plutonium and thorium makes it possible to “burn” the accumulated stocks of weapons-grade and energy-grade plutonium. However, such a nuclear fuel still has a significant drawback - low thermal conductivity.

One of the promising areas for further development of nuclear power in Russia is the use of dispersion nuclear fuel, including oxides of fissile metals (uranium, plutonium, thorium), uniformly distributed in an oxide matrix with high thermal conductivity and a small cross section of neutron absorption [2, 3].

The methods used for producing oxide compositions (separate production and mechanical mixing, sol-gel process, etc.) have the following disadvantages: multistage; duration, the need to use a large number of chemical reagents, uneven distribution of phases, additional hydrogen reduction, high energy and labor costs [3].

It is promising to use air plasma for plasmachemical synthesis of oxide compositions from dispersed water nitrate solutions, which provides: one-stage, high speed, the ability to actively influence the size and morphology of particles, homogeneous phase distribution [4]. However, plasma
processing of only water nitrate solutions requires significant energy consumption (up to 4 MWh/t) and does not allow the production of oxides of the required phase composition in one stage in air plasma without additional hydrogen reduction.

A significant reduction in energy consumption can be achieved by plasma processing in an air-plasma flow of optimal (in composition) dispersed water-organic nitrate solutions (WONS), including water nitrate solutions (WNS) and an organic component (alcohols, ketones) [5, 6].

The work objective is to establish the regularities of the influence of the WONS composition and the modes of their plasma processing on the physical-chemical properties of the obtained oxide powders.

2. Calculation of flammability and composition of water-organic nitrate solutions

The net calorific value of WONS \( Q_l \) was determined by the equation [7]:

\[
Q_l = \frac{(100 - W - A) \cdot Q_{lo} - 2.5 \cdot W}{100},
\]

where \( Q_{lo} \) – net calorific value of an organic component in WONS, MJ/kg; \( W \) and \( A \) – content of water and non-combustible components, %; 2.5 – the value of the latent heat of evaporation of water at 0 °C, MJ/kg.

A more objective indicator of the flammability of WONS is the adiabatic combustion temperature [7]:

\[
T_{ad} = \frac{Q_l + C_{WONS} \cdot t_{WONS} + \alpha \cdot v_0^{\text{ox}} \cdot C_{\text{ox}} \cdot t_{\text{ox}}}{V \cdot C},
\]

where \( C_{WONS} \) – average mass heat capacity of WONS, kJ/(kg·grad); \( t_{WONS} \) – temperature of WONS, C; \( \alpha \) – oxidizer (air) consumption coefficient; \( v_0^{\text{ox}} \) – theoretical oxidizer consumption, m³/m³; \( C_{\text{ox}} \) – average heat capacity of oxidizer, kJ/(m³·grad); \( t_{\text{ox}} \) – temperature of oxidizer, °C; \( V \) – specific volume of products of plasma processing of WONS (m³/kg); \( C \) – volumetric heat capacity of products of plasma processing of WONS, MJ/(m³·grad).

WONS with \( Q_l > 8.4 \) MJ/kg and \( T_{ad} > 1200 \) °C ensure their energy-efficient plasma processing and obtain oxide compositions with high physical-chemical properties [5-10].

3. Experimental technique

Experimental studies on the process of plasmachemical synthesis of oxide compositions “samarium oxide - cerium oxide - magnesium oxide” were carried out with the help of the plasma module based on a high-frequency generator (Fig. 1). Used modelling WONS include an organic component (acetone) and mixed water nitrate solutions of a matrix metal (magnesium) and fissile-modelling metal (samarium instead of plutonium, cerium instead of thorium). Fissile-modelling metals have similar physical-chemical properties with fissile metals (plutonium and thorium).
As a result of the studies, we determined the following optimal modes of joint operation of a high-frequency generator (operating frequency – 13.56 MHz, oscillatory power 60 kW), a high-frequency torch plasmatron and a plasmachemical reactor as part of a plasma module:

- high-frequency generator ($U_{\text{node}}=5.6$ kV, $I_{\text{node}}=3.5$ A, $I_{\text{grid}}=1.2$ A);
- high-frequency torch plasmatron ($P_{\text{flow}}=15$ kW);
- plasmachemical reactor ($S_{\text{impeller}}=1320$ cm$^2$, $Q_{\text{flow}}=0.95$ kg/s).

Preliminarily prepared WONS were supplied at a constant flow rate (300 l/h) to the disperser 1 and then dispersed into the reactor, where, in the course of processing in an air-plasma flow, the plasmachemical synthesis of oxide compositions “samarium oxide - cerium oxide - magnesium oxide” at a temperature in the reactor $T_r = 1100\pm50$ °C. $T_r$ was monitored with a high-precision digital infrared pyrometer 14. After the reactor, the dust-steam-gas mixture was fed to the centrifugal-bubbling apparatus of the unit for wet cleaning (UWC) of exhaust gases 8, where it was rapidly cooled (“quenched”) with circulating water to form water suspensions of the obtained oxide compositions. The cleaned exhaust gases were taken in with the help of a high-pressure exhaust fan 9 and discharged into the atmosphere. The obtained water suspensions of oxide compositions were pumped out in a stainless steel container. Samples were taken to determine the particle size distribution. Water suspensions were settled, the precipitates were separated, filtered and calcined for 20 minutes at a temperature of 150 °C. Obtained powders of oxide compositions were sent for examination their physical-chemical and technological properties.

4. Analysis of oxide compositions

Studies of the morphological, structural, crystalline and other properties of the obtained oxide compositions “samarium oxide - cerium oxide - magnesium oxide” were carried out with the help of
To determine the particle size distribution of oxide compositions in water suspensions, we used the method of laser diffraction (LD) implemented on Shimadzu SALD-7101. For comparison with other properties of powders, a quantitative result was used in the form of a median value of the obtained distribution, equal to the parameter D50. The size of particles in a water suspension was determined regardless of their structure, including agglomerates, this result was used to determine the degree of agglomeration of the obtained powders of oxide compositions.

The specific surface area of the obtained oxide powders (SSA) was estimated by the Brunauer-Emmett-Teller (BET) method with the help of Sorbi-M device. The obtained data were recalculated into the particle size, based on the assumption of their spherical geometry.

X-ray phase analysis (XRD) of the obtained powders of oxide compositions was implemented on Shimadzu XRD-7000 using a standard database of crystal structures of inorganic materials. The phase composition of the obtained powders, the parameters of the crystal structure of the detected phases, as well as the average sizes of the regions of coherent scattering of crystallites \( D_{\text{cryt}} \) in the composition of the obtained powders were determined.

Table 1 shows the composition of WONS and the physical-chemical properties of the obtained oxide compositions “samarium oxide - cerium oxide - magnesium oxide”, simulating plutonium-thorium dispersion nuclear fuel, obtained at \( \alpha = \text{Sm}_2\text{O}_3/(\text{Sm}_2\text{O}_3+\text{Ce}_2\text{O}_3) = 0.1 \) – 0.3, the frequency of rotation of the disperser \( f_d = 50 \) Hz and the flow rate of circulating water \( Q_w = 2.8 \) kg/s for the hardening of oxide compositions.

From the analysis of the presented results (Table 1), it follows that an increase in the mass fraction of the matrix (MgO) in the oxide compositions “samarium oxide - cerium oxide - magnesium oxide” from 10 % to 30 % \( (\alpha = 0.1, f_d = 50 \) Hz \( , Q_w = 2.8 \) kg/s) leads to a decrease in the particle size in the water suspension after UWC from 9.9 \( \mu \)m to 7.4 \( \mu \)m. In this case, the specific surface area of the obtained powders increases from 7.9 m\(^2\)/g to 14.1 m\(^2\)/g, and the crystallite size in their composition decreases from 110 nm to 67 nm.

**Table 1.** WONS compositions and physical-chemical properties of oxide powders “samarium oxide - cerium oxide - magnesium oxide”, imitating plutonium-thorium dispersion nuclear fuel \( (f_d = 35 \) Hz, \( Q_w = 2.8 \) kg/s)

| #  | WNS composition | Oxide composition | Physical-chemical properties |
|----|----------------|------------------|-----------------------------|
|    | WONS | Acetone | Oxide | Sm\(_2\)O\(_3\), % | Ce\(_2\)O\(_3\), % | MgO, % | \( D_{50}, \mu \)m | SSA, m\(^2\)/g | \( D_{\text{cryt}}, \text{nm} \) |
| 1  | 28.7 | 267.9 | 160.2 | 62.2 | 9.0 | 81.0 | 10.0 | 9.9 | 7.9 | 110 |
| 2  | 25.5 | 278.7 | 320.4 | 60.3 | 8.0 | 72.0 | 20.0 | 9.4 | 11.2 | 86 |
| 3  | 22.3 | 264.0 | 480.6 | 58.4 | 7.0 | 63.0 | 30.0 | 7.4 | 14.1 | 67 |
| 4  | 57.4 | 238.1 | 160.2 | 62.2 | 18.0 | 72.0 | 10.0 | 12.3 | - | - |
| 5  | 51.0 | 211.6 | 320.4 | 60.3 | 16.0 | 64.0 | 20.0 | 9.8 | - | - |

\( \alpha = \text{Sm}_2\text{O}_3/(\text{Sm}_2\text{O}_3+\text{Ce}_2\text{O}_3) = 0.1 \)

\( \alpha = \text{Sm}_2\text{O}_3/(\text{Sm}_2\text{O}_3+\text{Ce}_2\text{O}_3) = 0.2 \)
An increase in the mass fraction of the matrix (MgO) in the composition of oxide compositions from 10 % to 30 % (α = 0.2, f_d = 50 Hz, Q_w = 2.8 kg/s) also leads to a decrease in the particle size in water suspensions after UWC from 12.3 μm to 6.6 μm, which suggests that the obtained powders of oxide compositions also consist of nanosized crystallites.

An increase in the mass fraction of the matrix (MgO) in the composition of oxide compositions from 10 % to 30 % (α = 0.3, f_d = 50 Hz, Q_w = 2.8 kg/s) also leads to a decrease in the size of the formed particles in water suspensions after UWC from 5.9 μm to 4.9 μm. In this case, the specific surface area of the obtained powders increases from 15.2 m^2/g to 16.2 m^2/g, which suggests that the obtained powders of oxide compositions also consist of nanosized crystallites.

Thus, the compositions of the WONS and the modes of their plasma processing have been determined. They ensure the plasmachemical synthesis of nanosized oxide compositions “samarium oxide - cerium oxide - magnesium oxide”, imitating plutonium-thorium dispersion nuclear fuel.

5. Conclusion
The results of the study can be used to create an energy-efficient technology for the plasmachemical synthesis of nanosized oxide compositions for plutonium-thorium dispersion nuclear fuel.

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