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Preparation of Solid Solutions of Uranium and Cerium Oxides from Their Nitric Acid Solutions Using Microwave Radiation

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Abstract—A procedure was developed for preparing powders of solid solutions of uranium dioxide with 3 or 10 wt % Ce (as Am surrogate) from nitric acid solutions using microwave radiation. The powders obtained consist of particle aggregates of size no larger than 400 μm; the fraction of particles of size smaller than 25 μm does not exceed 1 wt %. The tap density of the powders is 2.3–2.5 g cm^{-3}, and their specific surface area is 2.2–2.5 m^2 g^{-1}. The powder characteristics meet the requirements to powders of ceramic quality for nuclear fuel fabrication. The method developed can be used for producing mixed U–Am oxides on a unit for spent nuclear fuel reprocessing at the Pilot Demonstration Power Engineering Complex with the aim of Am transmutation in the BREST-OD-300 reactor.

Keywords: uranium, cerium, uranium dioxide, nuclear fuel, denitration, microwave radiation

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The uranium product of ore reprocessing is uranyl nitrate, which is used in nuclear fuel production. Spent nuclear fuel (SNF) reprocessing also leads to the formation of actinide (U, Np, Pu) nitrates, which are separated from fission products and transplutonium elements. The isotopes ^{241,243}Am ($T_{1/2}$ = 432.6 and 7369 years, respectively) and ^{244}Cm (18.1 years), on the one hand, make the major contribution to the α-radioactivity of high-level waste (HLW) and, on the other hand, require long-term environmentally safe storage and/or disposal. Therefore, it is necessary to isolate and separate Am and Cm from HLW, which, first, will enhance the radiation safety of the waste management and, second, will make the deep disposal of solidified HLW unnecessary. As a result, the activity of the isolated Cm will considerably decrease in the course of approximately 70-year storage of the solidified partitioned HLW, and the decay product, Pu, can be returned to the fuel cycle. On the other hand, Am separated from Cm and rare earth elements (REE) in the form of a solid solution of its dioxide in a UO_2 matrix will be subjected to transmutation in the BREST-OD-300 fast reactor at the Pilot Demonstration Power Engineering Complex [1].

Therefore, the development of a process for producing powders of solid solutions of U and Am dioxides directly from their nitric acid solutions becomes a topical problem. Studies on production of uranium oxides from its compounds and on reprocessing of substandard ceramic UO_2 pellets by microwave treatment were performed previously at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences [2–4]. We also studied the microwave denitration of actinide-containing nitric acid solutions from SNF reprocessing in the Purex process with the aim of preparing powdered actinide oxides [5–8]. In other countries, microwave radiation was also used in separate radiochemical studies [9–12]. On the whole, our [2–8] and published data allow a conclusion that microwave treatment shows promise for direct preparation of powdered UO_2 or mixed actinide dioxides from their nitric acid solutions with the preliminary decomposition and removal of nitrate ions and subsequent conversion of the powders to ceramic pellets of oxide or nitride nuclear fuel.

In this study, we examined the specific features of the preparation of U and Ce (Am surrogate) oxide solid solutions by direct reductive thermal denitration of their nitric acid solutions using microwave radiation, and also the composition and properties of the products obtained.

EXPERIMENTAL

Powders of U + Ce oxides were prepared from nitric acid (0.5 M) solutions containing 400 g L^{-1} U and 12.4 or 44.4 g L^{-1} Ce (hereinafter, solutions R-1 and R-2, respectively) in two steps on an installation whose main element was a microwave oven with a frequency of 2.45 GHz and radiation power of up to 800 W. The power could be controlled by decreasing the time of the magnetron operation in the pulse mode. The first step involved denitration of solution R-1 or R-2. To this end, a 500-mL quartz flask was charged with 250 mL of the solution, placed into the chamber of the microwave oven, and purged for 15 min with the reducing gas mixture (hereinafter, RGM) Ar–5 vol % H_2 without bubbling through the solution. Then, the microwave oven was switched on at the radiation power of 800 W, the nitric acid solution was distilled, and the nitrates obtained were decomposed for 35–40 min. The use of hydrogen favored not only the reduction of U(VI) to U(IV), but also the decomposition of the NO_3^- anion to NO and N_2 [13]. The gas from the flask together with water and acid vapors and nitrogen oxides flew through the condenser to the condensate collector connected to a buffer vessel and a liquid seal. After the completion of the evolution of nitrogen oxides, the microwave oven was switched off, and the flask with the product (black powder with orange inclusions) was taken off. Hereinafter, the products obtained by denitration of solutions R-1 and R-2 are denoted as $(U,Ce)O_x$-1 and $(U,Ce)O_x$-2, respectively. The powders obtained were transferred into an agate mortar for mixing and grinding.

The finely divided $(U,Ce)O_x$-1 and $(U,Ce)O_x$-2 powders were returned to the flask, the flask was again placed into the microwave oven, and the second step of the process was performed in the RGM atmosphere to reduce U in the powders and obtain solid solutions of UO_2 with Ce. Hereinafter, the resulting solid solutions are denoted as $(U,Ce)O_2$-1 and $(U,Ce)O_2$-2, respectively. We studied how the microwave radiation power (from 180 to 800 W) and treatment time influence the physicochemical properties of the powders obtained.

X-ray diffraction analysis of U–Ce oxide powders was performed with an ULTIMA-IV X-ray diffractometer (Rigaku, Japan). The phases were identified using PDF-2 database in the Jade 6.5 program package (MDI). The uranium oxidation state in the powders was also monitored by spectrophotometry (Unicam UV-300, the United States) after dissolving the weighed portions of the powders in a mixture of 4 M HCl + 0.1 M HF, and the U amount in the solutions was determined by radiometry (Alpha Analyst spectrometer, Canberra, the United States).

The powder particle morphology was studied with a LEOSupra 50 VP electron microscope (Carl Zeiss, Germany). The particle-size distribution of the powders was studied with a Hsiangtai LS-300 vibration sieve analyzer (Taiwan) with the set of sieves 20 cm in diameter. The powders were sieved at the motor rotation rate of 3000 rpm for 15 min. The tap density of the powders was determined with an Autotap powder tapping device (according to OI 001.350-2004 document), and the specific surface area, with a Quadrasorb SI/Kr installation (BET method). Gravimetric measurements were performed with an HR-250AZG nonautomatic analytical balance (A&D, Japan).

RESULTS AND DISCUSSION

Studies of the particle-size distribution and U oxidation state in various fractions of $(U,Ce)O_x$-1 and $(U,Ce)O_x$-2 powders obtained by denitration of solutions R-1 and R-2, respectively, have shown that these particles contain mainly coarse particles of size larger than 400 μm, consisting of U(IV), U(VI), and cerium oxides. As shown in Table 1 by the example of the $(U,Ce)O_x$-2 powder, particles of size larger than 40 μm make up ~86% of the powder. On the other hand, the powder contains no dust-forming fraction (particle size <25 μm). The U(IV) content of the powder was from 13 to 33% and was maximal in the coarsest fraction with the particle size larger than 4000 μm (about 40% of the powder weight).

The subsequent heating of the powders obtained, $(U,Ce)O_x$-1 and $(U,Ce)O_x$-2, under the action of microwave radiation in an RGM stream led to quantitative reduction of U. The rate of the U reduction in the powders decreased with an increase in the Ce content. For example, no less than 99% reduction of uranium at a microwave radiation power of 800 W was reached in 2

Table 1. Particle-size distribution and U(IV) and U(VI) content of the powder of mixed oxides (U,Ce)O_x-2 prepared by denitration of solution R-2 under the action of microwave radiation

Particle size *x*, μm	Relative amount, wt %	Content in fraction, wt %	
		U(IV)	U(VI)
x > 4000	39.9	33.0	67.0
1000 < *x* < 4000	31.6	17.8	72.2
400 < *x* < 1000	14.7	12.6	87.4
125 < *x* < 400	9.3	15.9	84.1
50 < *x* < 125	3.3	17.0	83.0
25 < *x* < 50	1.2	21.9	78.1
x < 25	–	–	–

Table 2. Particle-size distribution of (U,Ce)O_2-1 and (U,Ce)O_2-2 dioxide powders obtained under the action of microwave radiation of 800 W power

Particle size *x*, μm	Relative content in indicated sample, wt %	
	(U,Ce)O_2-1	(U,Ce)O_2-2
x > 4000	29.5	11.8
1000 < *x* < 4000	19.7	35.1
400 < *x* < 1000	13.6	15.9
125 < *x* < 400	28.6	17.3
50 < *x* < 125	8.1	12.5
25 < *x* < 50	0.6	7.4
x < 25	–	–

Table 3. Particle-size distribution of ground (U,Ce)O_2-2 powders obtained under the action of microwave radiation of 180 and 800 W power

Particle size *x*, μm	Relative content in powder, wt %	
	180 W	800 W
x > 400	–	0.2
125 < *x* < 400	32.8	53.4
50 < *x* < 125	20.0	39.4
25 < *x* < 50	46.7	7.1
x < 25	0.5	–

and 3 h for (U,Ce)O_2-1 and (U,Ce)O_2-2 powders, respectively. On the other hand, the U reduction rate also significantly decreased with a decrease in the microwave radiation power. For example, the time of the quantitative reduction of U in the (U,Ce)O_2-2 powder at a power of 450 and 180 W increased to 4.5 and 6 h, respectively.

The grain-size distribution of the powders obtained appeared to be virtually equal irrespective of the microwave radiation power in the range 180–800 W. However, the major fraction (60–70%) of the powder particles had the size larger than 400 μm, which exceeds the particle size required for the production of fuel pellets. For example, in the powders prepared under the action of 800-W microwave radiation, the fraction of particles of size larger than 400 μm was about 63% (Table 2). To obtain powders with the particle size in the optimum range 25–400 μm, the coarse particles were ground on a vibration sieve analyzer using a duralumin grinding disk 19.8 cm in diameter and 2 mm thick. The disk was placed in a sieve with the mesh size of 400 μm over the powder bed. Almost half (46.7%) of the ground (U,Ce)O_2-2 powder obtained at 180 W consisted of 25–50-μm particles. Their content was considerably higher than that in the powder obtained at 800 W (Table 3).

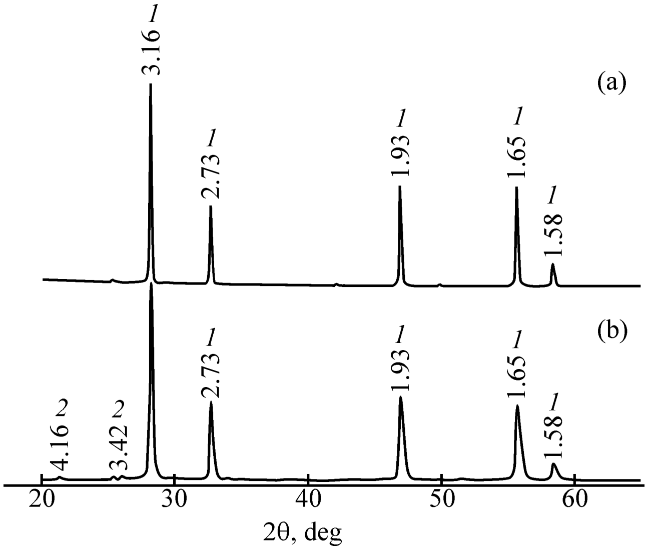

Fig. 1. Diffraction patterns of (U,Ce)O_2-2 solid solution powders prepared from nitric acid solutions using microwave radiation with a power of (a) 800 and (b) 180 W. (*1*) UO_2 (41-1422) and (*2*) U_3O_8 (47-1493).

X-ray diffraction analysis shows that the powders obtained are solid solutions of UO_2 with Ce irrespective of the microwave radiation power. The Ce content is 3 and 10 wt % in (U,Ce)O_2-1 and (U,Ce)O_2-2 powders, respectively. The diffraction patterns of powders, e.g., (U,Ce)O_2-2 (Fig. 1), contain peaks characteristic of UO_2 (uraninite), and the content of the possible U_3O_8 impurity, detected, e.g., in the (U,Ce)O_2-2 powder obtained at 180 W (Fig. 1b), did not exceed 1 wt %, which meets the standard requirements to UO_2 of ceramic quality [14]. No impurities of other U or Ce oxides were detected. The mean crystallite size in the powders decreases with a decrease in the microwave radiation power. For example, the mean crystallite size in the (U,Ce)O_2-2 powder samples obtained at 800 and 180 W was 218 and 37 nm, respectively (Figs. 1a, 1b, respectively).

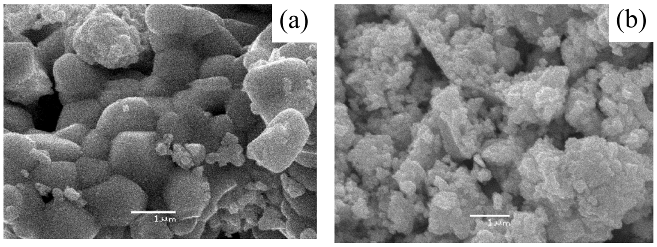

Fig. 2. SEM images of $(U,Ce)O_2$-2 powders prepared from nitric acid solutions under the action of microwave radiation with a power of (a) 800 and (b) 180 W.

The specific surface area of powders significantly increased with a decrease in the microwave radiation power. For example, the specific surface area of $(U,Ce)O_2$-2 increased from ~0.3 $m^2\ g^{-1}$ at 800 W to ~1.0 $m^2\ g^{-1}$ at 450 W and 2.2–2.5 $m^2\ g^{-1}$ at 180 W, reaching the required level (no lower than 1.8 $m^2\ g^{-1}$ [14]). Apparently, an increase in the specific surface area of the powders with a decrease in the microwave radiation power is due to a decrease in the mean size of their crystalline particles (Table 3) and to changes in their morphology. According to the SEM data, low specific surface area of $(U,Ce)O_2$-2 powders obtained at a high microwave radiation power (800 W) is associated with the presence of coarse aggregates of crystals of approximately 1 μm size (Fig. 2a). On the other hand, particles of the $(U,Ce)O_2$-2 powder obtained at the microwave radiation power of 180 W consist of crystals of no more than 0.2 μm size (Fig. 2b). Apparently, the presence of coarse micron-sized crystals is associated with the fact that the action of the microwave radiation of 800 W power can lead to local heating of the powders to temperatures higher than 1000°C, exceeding the recommended temperature (about 700°C) of the preparation of ceramic UO_2 [15]. These results demonstrate the need for controlling the powder temperature in the course of microwave treatment to avoid overheating.

The tap density of the powders obtained, $(U,Ce)O_2$-1 and $(U,Ce)O_2$-2, irrespective of the microwave radiation power, was 2.4 ± 0.1 g cm^{-3}, meeting the requirements of [14] (2.2–3.5 g cm^{-3}).

Thus, powders of solid solutions of U and Ce dioxides with the physicochemical properties meeting the requirements to powder of ceramic quality for nuclear fuel fabrication can be prepared from nitric acid solutions of U and Ce using microwave radiation. To this end, it is necessary to perform the solution denitration in an RGM atmosphere under the action of microwave radiation with a power of up to 800 W, followed by quantitative reduction of U in the resulting oxide in an RGM atmosphere at a power no higher than 180 W for approximately 6 h.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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