Preparation of Powdered Uranium Oxides by Microwave Heating of Substandard Ceramic Pellets of Oxide Nuclear Fuel

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Abstract—Microwave (MW) heating of substandard ceramic UO_2 pellets in air allows their rapid conversion into powdered U_3O_8, from which UO_2 can be obtained again in a reducing atmosphere. Comparative analysis of the physicochemical and technological properties of the U_3O_8 and UO_2 powders obtained under the action of MW radiation with the industrial (standard) powders demonstrated their suitability for fabricating fuel pellets. The power consumption for MW heating appears to be lower by an order of magnitude than the power consumption for performing similar operations with electric resistance furnaces.

Keywords: uranium oxides, microwave heating, oxide nuclear fuel

The base material of fuel elements for the majority of nuclear reactors is oxide nuclear fuel, which is prepared from ^{238}U dioxide enriched in ^{235}U. The $^{238+235}UO_2$ powder exhibiting ceramic properties is pressed and sintered in reducing atmosphere at 1750°C [1] to obtain ceramic pellets of the oxide fuel. Their shape should meet with an accuracy of tens of micrometers the requirements of the standard used in production of fuel elements for nuclear reactors. Substandard ceramic pellets, whose amount reaches 10–15% of the total amount of the oxide nuclear fuel produced, require refabrication. They are converted into a powder by heating to 500°C in air for no less than 5 h in electric resistance furnaces to obtain U_3O_8, which is then dissolved in nitric acid. This is followed by precipitation of ammonium diuranate (ADU), which is separated by filtration, dried, and calcined to obtain U_3O_8 or UO_2. These procedures are multistep and time- and power-consuming. Therefore, the development of new procedures for reducing the time and power consumption for the utilization of substandard oxide nuclear fuel is an urgent problem.

Microwave heating, compared to convective heat supply, has a number of advantages: The heating occurs uniformly throughout the bulk of the material without its contact with heating elements. Microwave heating considerably reduces the power consumption for performing such physicochemical processes as dehydration, decomposition of hydroxide and salt-forming compounds, synthesis of multicomponent substances, and sintering of ceramics; it accelerates chemical reactions [2–5]. Therefore, the use of the MW radiation energy, which is absorbed by semiconductors such as uranium oxides, is an alternative and promising way of their efficient thermal decomposition, compared to convective heating in electric resistance furnaces.

EXPERIMENTAL

Experiments were performed in a Samsung MW83UR microwave oven with the radiation frequency of 2.45 GHz and power from 100 to 800 W. Ceramic pellets were placed in a fused quartz flask whose neck was plugged with a quartz wool tampon permeable to gases but retaining dust particles that could be ejected into the gas phase in the course of breakdown of the samples. The experiments and subsequent analysis of the product were performed according to the procedures described in detail previously [6]. The physicochemical and technological properties of the U_3O_8 and/or UO_2 powders prepared in the microwave oven from substandard fuel pellets were determined by the test procedures used at the Machine-Building Plant (Elektrostal, Moscow oblast, Russia).

Table 1. Physicochemical and technological properties of U_3O_8 and UO_2 powders prepared using MW radiation and by standard plant technology

Parameter	U_3O_8 (MW)	U_3O_8 (standard)	UO_2 (MW)	UO_2 (standard)
	%			
Fraction, mm:				
+1.0	0.39	0.00	0.00	0.00
+0.63	0.11	0.00	0.00	0.00
+0.4	0.08	0.00	1.19	0.40
+0.315	0.05	0.00	3.72	18.20
+0.2	2.31	0.00	18.93	31.90
+0.14	0.00	0.00	7.53	9.60
+0.1	4.07	0.50	14.33	14.30
+0.063	16.26	1.30	9.91	11.40
+0.05	5.68	1.00	4.03	7.60
−0.05	71.06	97.20	40.36	6.60
U_{tot}, wt %	84.70	84.78	87.76	87.69
H_2O, wt %	0.041	0.035	0.03	0.080
MCPS, μm	3.20	2.24	0.408	0.432
MPSS, μm	51	27	119	198
BD, g cm^{-3}	1.92	1.91	3.00	1.93
BDS, g cm^{-3}	3.39	3.22	4.75	2.99
TSSA, m^2 g^{-1}	0.4	0.72	<0.4	3.12
Flowability, g s^{-1}	3.4	3.2	15.3	26.0
OC	2.67	2.78	2.014	2.059

RESULTS AND DISCUSSION

As we showed previously, heating of a ceramic UO_2 pellet in air under the action of MW radiation leads to its intense breakdown with the formation of powdered U_3O_8, which transforms into UO_2 under the conditions of MW heating in reducing atmosphere [6]. In accordance with Contract no. 71/54 of February 2, 2011 on the scientific and technical cooperation between the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences and the Machine-Building Plant, the UO_2 and U_3O_8 powders obtained in the microwave oven from substandard pellets were subjected to quality tests by the procedures adopted at the Machine-Building Plant. Their physicochemical characteristics [mean conventional particle size (MCPS), mean particle size by sieving (MPSS), bulk density (BD), bulk density after shakedown (BDS), total specific surface area (TSSA), oxygen coefficient (OC)] were determined. The results are given in Table 1 and are compared with the related properties of standard U_3O_8 and UO_2 powders industrially produced in accordance with the requirements of TUs (Technical Specifications) 95 414–2005 and 52 000–13 and of GOSTs (State Standard) 18 318–94, 19 440–94, and 20 899–75.

As seen from Table 1, the parameters of the U_3O_8 and UO_2 powders prepared by different procedures are similar to each other. However, the powders obtained by the MW procedure differ from the standard powders in the total specific surface area. The relative content of particles of size smaller than 100 μm is 93% in U_3O_8 (MW) and more than 99% in U_3O_8 (standard), and the TSSA of U_3O_8 (MW) and U_3O_8 (standard) could be expected to be similar, but actually TSSA of the U_3O_8 (MW) powder is two times lower. The relative content of such particles in UO_2 is 54% for the MW sample and only 26% for the standard sample, so that the MW sample could be expected to have larger TSSA, but actually it is considerably lower.

The possible cause of these differences is high temperature (~1000°C) at which the U_3O_8 (MW) and UO_2 (MW) powders are obtained. As a result, the activity of their surface is low, and the capability of the powder for the subsequent sintering is decreased. As seen from Table 1, the oxygen coefficient of UO_2 prepared using MW radiation, which heats the oxide powder to ≥1000°C, is the closest to the stoichiometric value (U : O = 1 : 2) [7]. It should be noted that the reduction temperature in the standard technology is usually maintained within 600–700°C to obtain the powder with ceramic properties, capable of being pressed and

Table 2. Results of testing a mixture of 90 wt % standard UO_2 (ADU) powder with additions of 10% U_3O_8 (MW) and UO_2 (MW) for "compressibility" and "sinterability" of pellets prepared from them

Sample	"Raw" density, g cm^{-3}	Sintered density, g cm^{-3}	Grain size in test sample, μm
UO_2 (standard)	5.23	10.77	–
UO_2 (standard) + 10% U_3O_8 (MW)	5.46	10.55	12
UO_2 (standard) + 10% U_3O_8 (standard)	5.36	10.61	10
UO_2 (standard) + 10% UO_2 (MW)	5.54	10.50	9.5

sintered into a pellet with a density of no less than 10.5 g cm^{-3} [8].

The technological properties such as "compressibility" into a pellet and its "sinterability" were determined for the powders obtained by adding 10 wt % U_3O_8 (MW) and UO_2 (MW) to the standard UO_2 powder prepared from ammonium diuranate (ADU process). The results are given in Table 2.

As can be seen, the "raw" density for the mixed samples of standard UO_2 (ADU) powder with additions of 10% U_3O_8 (MW) and UO_2 (MW) (5.46 and 5.54 g cm^{-3}) did not differ significantly from the values typical of process powders (5.23 and 5.36 g cm^{-3}). The "sintered" density of the pellets prepared from mixed samples of standard UO_2 (ADU) powder with additions of 10% U_3O_8 (MW) and UO_2 (MW) is 10.55 and 10.5 g cm^{-3}, respectively, and is slightly lower than the density of the test sample (10.61 g cm^{-3}) prepared with the addition of standard U_3O_8. Nevertheless, the values obtained meet the GOST requirements to the density ($\geq$10.5 g cm^{-3}). Hence, U_3O_8 (MW) and UO_2 (MW) can be used as 10% additives to powders of standard UO_2 used for fuel element fabrication.

The microstructure of the sintered pellets prepared from the mixed powders was studied on the polished cross section with a POLYVAR optical microscope using the Avtomet image analysis system at the magnification from ×20 to ×400. The microstructure is shown in Figs. 1 and 2. As can be seen, the samples with the additions of U_3O_8 (MW) (Figs. 1a, 1c) and UO_2 (MW) (Figs. 2a, 2c) are characterized by the granular structure and have the porosity close to that for the standard samples (Figs. 1b, 1d, 2b, 2d). The mean grain size is from 12 to 8.8 μm.

Thus, the U_3O_8 (MW) and UO_2 (MW) powders prepared using MW radiation are similar in ceramic properties to the standard samples and can be used as additives to uranium dioxide when preparing ceramic oxide fuel pellets by the standard technology.
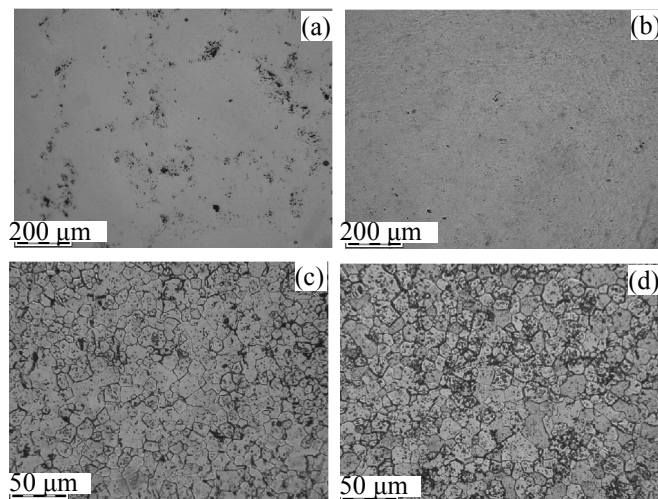

Fig. 1. Photomicrographs of the specimens: (a, c) UO_2 (standard) + 10% U_3O_8 (MW), 91.0% pores with $d <$ 10 μm, mean grain size 12.0 μm; (b, d) UO_2 (standard) + 10% U_3O_8 (standard), 98.1% pores with $d <$ 10 μm, mean grain size 9.2 μm. (a, b) Polished section and (c, d) granular structure.

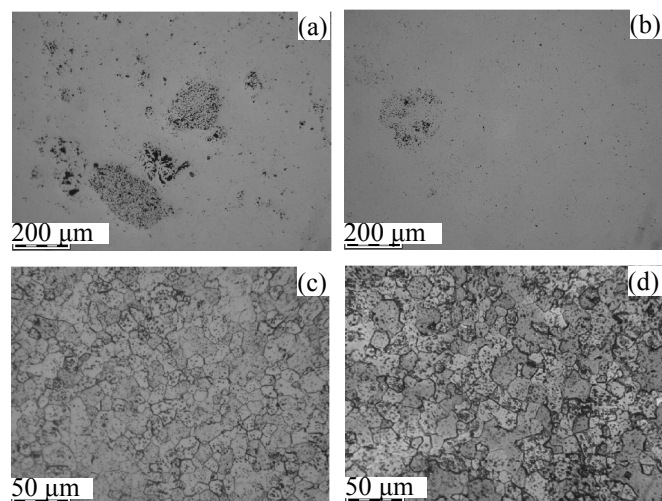**Fig. 2.** Photomicrographs of the specimens: (a, c) UO_2 (standard) + 10% UO_2 (MW), 91.5% pores with $d <$ 10 μm, mean grain size 9.5 μm; (b, d) UO_2 (standard), 98.5% pores with $d <$ 10 μm, mean grain size 8.6 μm. (a, b) Polished section and (c, d) granular structure.

We performed a comparative experiment on the breakdown of 10 g of substandard ceramic UO_2 pellets in air by two procedures: thermal heating in a resistance furnace and heating with MW radiation. The conversion of the same amount of pellets from UO_2 into U_3O_8 powder required in the first case 3 h of heating at a voltage of 220 V and a current of 2 A (power consumption 1.32 kW h). The same procedure performed using MW radiation took 10 min at a voltage of 220 V and a current of 4.6 A, i.e., the power consumption was 0.18 kW h. As can be seen, in the latter case the power consumption is considerably lower.

Short (10-min) MW irradiation (600 W) in air of UO_2 (with ~3.8% weight gain) and U_3O_8 (without weight changes) in combination with MW irradiation of UO_2 and U_3O_8 samples in an Ar + 10 vol % H_2 atmosphere, when the UO_2 weight does not change and the U_3O_8 weight decreases by 3.8%, can be used as a diagnostic method allowing quick determination of the composition of the available uranium oxide sample.

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