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Use of Microwave Radiation for Denitration of Uranyl Nitrate Solution and Subsequent Sintering of Uranium Dioxide Fuel Pellets

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Abstract—Fabrication of ceramic UO_2 fuel pellets using microwave radiation was studied. The UO_2 powder was prepared by microwave denitration of a nitric acid solution containing 400 g L^{-1} uranium. The tapped density (2.39 g cm^{-3}) and total specific surface area (2.70 m^2 g^{-1}) of the powder obtained met the requirements to the powder for nuclear fuel fabrication (TU (Technical Specification) 95 414–2005: Uranium Dioxide Powder of Ceramic Grade with the Uranium-235 Isotope Content Lower than 5.0%). Pellets were pressed from the UO_2 powder under varied conditions including pressure, its application mode, pressing time, and presence of binder. The pressed pellets were sintered at 1650°C for 2 h in an Ar + 10 vol % H_2 atmosphere under the action of microwave radiation. The density of the samples obtained, 10.40 ± 0.02 g cm^{-3}, meets the requirements to ceramic fuel pellets used in thermal reactors.

Keywords: microwave radiation, denitration, uranyl nitrate solutions, actinides, uranium dioxide, pellet sintering, nuclear fuel

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UO_2 fuel pellets are used as a nuclear fuel for thermal reactors. High density, porosity, and large granule size are important parameters for evaluation of the pellets as a nuclear fuel. Nuclear fuel pellets are sintered in electric resistance furnaces; the process involves the use of a large amount of expensive heating elements and refractory materials for reaching high temperature and maintaining it for a long time. In addition, such furnace consumes much energy. The use of microwave radiation in thermal processes used in the technology of oxide nuclear fuel production is promising, because UO_2 and U_3O_8 are dielectrics that intensely absorb the microwave radiation energy. In the process, they are heated to high temperatures with considerably lower consumption of electric power compared to convective heating [1].

The use of microwave radiation for sintering UO_2 pellets beyond Russia has been reported [2–6]; however, the pellets obtained in these studies never met the requirements to UO_2 fuel pellets (TU 95 414–2005: Uranium Dioxide Powder of Ceramic Grade with the Uranium-235 Isotope Content Lower than 5.0%).

This study was aimed at determining the possibility of preparing ceramic UO_2 pellets using microwave radiation, including preparation of UO_2 powder from a nitric acid $UO_2(NO_3)_2$ solution and subsequent sintering of the pressed fuel pellets.

EXPERIMENTAL

The following chemicals were used in the study: $UO_2(NO_3)_2\cdot 6H_2O$ (analytically pure grade, ^{235}U content 0.21 wt %, VTU-RU (Temporary Technical Specification) 966-53, USSR Ministry of Chemical Industry), HNO_3 (chemically pure grade, KhimMed, Russia), HCl (chemically pure grade, KhimMed, HF (ultrapure grade, KhimMed), Zn (pure grade, Reakhim,

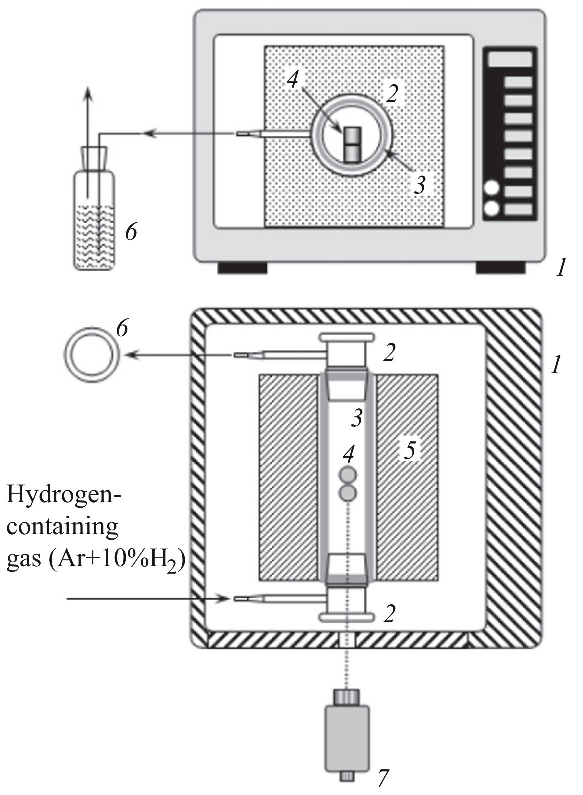

Fig. 1. Scheme of the installation for sintering UO_2 pellets under the action of microwave radiation: (*1*) microwave oven, (*2*) ground-in quartz stopper with a tube for feeding or removing the gas mixture, (*3*) Alundum tube with female joints, (*4*) UO_2 pellets, (*5*) heat-protecting casing made of light fibrous composite, (*6*) liquid seal trap with water, and (*7*) visual pyrometer.

Russia), double-distilled H_2O (GOST (State Standard) 4517–87), Ar + 10 vol % H_2 gas mixture (TU 2114-0, 16-459057115–2015, NII KM, Russia), glycerol (analytically pure grade, Reakhim), and polyvinyl alcohol (analytically pure grade, Reakhim).

UO_2 powder was prepared by microwave irradiation of a $UO_2(NO_3)_2$ solution containing 400 g L^{-1} U. A 500-mL quartz flask containing 250 mL of the $UO_2(NO_3)_2$ solution was placed in the chamber of a Samsung MW73VR microwave oven (radiation frequency 2.45 GHz, magnetron power up to 800 W) onto a heat-protecting support made of a light fibrous ceramic composite. The flask was stoppered with a ground-in Teflon stopper with two holes 3 and 6 mm in diameter, into which Teflon and quartz tubes of the corresponding diameter were inserted. Though a hole 15 mm in diameter in the upper part of the chamber, the Teflon tube was connected to a gas cylinder for feeding the Ar + 10 vol % H_2 gas mixture, and the quartz tube was connected to a preliminarily assembled system for collecting the condensate and trapping nitrogen oxides, consisting of a reflux condenser, a vessel for condensate collection, a buffer vessel, and two liquid seal traps with water.

The $UO_2(NO_3)_2$ solution was evaporated at a microwave radiation power of 800 W in a stream of an Ar + 10 vol % H_2 gas mixture to obtain a black spongy cake. The microwave oven was switched off, and the flask with the cake was taken off and shaken to detach the particles from the walls. The powder was manually ground in the flask with a spatula. After that, the flask with the powder was again placed in the microwave oven and connected to the systems for feeding the gas mixture and collecting the condensate. The magnetron was switched on at a microwave radiation power of 180 W, and the powder was heated for 4 h in a stream of the gas mixture used (flow rate 1 L min^{-1}). The resulting powder was placed in a Hsiangtai LS-300 vibrosieve analyzer (Hsiangtai Machinery Industry) onto a sieve 20 cm in diameter with the mesh size no larger than 0.4 mm. A duralumin rubbing disk 19.8 cm in diameter and 2 mm thick was placed into the sieve over the powder. The powder particles were ground and fractionated using additional sieves with the mesh size of 0.125, 0.05, and 0.025 mm at the motor rotation rate of 3000 rpm for 15 min. After determining the particle-size distribution, fractions were combined and mixed, and the powder was examined for compliance with the requirements of TU 95 414–2005, Uranium Dioxide Powder of Ceramic Grade with the Uranium-235 Isotope Content Lower than 5.0%.

The uranium weight fraction and, correspondingly, the degree of its reduction in the powder obtained were determined by the previously developed procedure [7] using spectrophotometry (Unicam UV-300), thermal gravimetric analysis, and differential scanning calorimetry (STA 409 PC Luxx synchronous thermal analyzer, Netzsch), and also powder X-ray diffraction (ULTIMA-IV, Rigaku). The specific surface area of the UO_2 powder was determined with a Quadrasorb SI/Kr installation, and the tapped density, in accordance with the OI 001.350–2004 document, Uranium Dioxide Powders. Testing Procedure for Determining the Tapped Density, with an Autotap installation (Quantachrome) at a tapping rate of 4.4 s^{-1} and a total analysis time of 30 min.

Table 1. Characteristics of the powder obtained by microwave denitration of nitric acid $UO_2(NO_3)_2$ solutions

Characteristic	Values determined in this study	Requirements of TU (Technical Specification) 95 414–2005: Uranium Dioxide Powder of Ceramic Grade with the Uranium-235 Isotope Content Lower than 5.0%
Particle size, μm (relative content in sample, %)	$x > 400$ (0.3) $125 < x < 400$ (46.5) $50 < x < 125$ (28.1) $25 < x < 50$ (25.0) $x < 25$ (0.1)	No requirements formulated
Weight fraction of uranium (uranium reduction completeness, %)	88.1 (99.6)	No less than 87.4
Specific surface area, $m^2 g^{-1}$	2.70	2.0–3.5
Tapped density, $g cm^{-3}$	2.39	1.8–2.5
Weight fraction of moisture, %	~0.1	No more than 0.4

The moisture content of the powder was estimated by thermal gravimetric analysis and differential scanning calorimetry.

The UO_2 powder obtained was pelletized on a PGR laboratory hydraulic press (LAB TOOLS) with the mold and punch diameter of 10 mm. The mold surface was lubricated with glycerol. We varied the applied pressure (from 2 to 6 tf cm^{-2}), pressing mode (one- or two-side), and powder weight per pellet; in addition, we performed pressing with a plasticizer (8.5% aqueous suspension of polyvinyl alcohol and 0.5 wt % glycerol) and without it. The weight was measured with an HR-250AZG analytical balance (A&D Company), and the pellet size (diameter and height), with a TOPEX 0–25 mm 31C629 micrometer (TOPEX) with an accuracy of 10 μm. Prior to the subsequent sintering, the pressed pellets were dried at 90°C to reduce the residual moisture content below 1 wt %.

Sintering was performed in a KOCATEQ MWO2100/34 E microwave oven (Korean Refrigeration Company) with a power of up to 2.1 kW and a microwave radiation frequency of 2.45 GHz (Fig. 1). The oven is equipped with two dissectors for uniform distribution of microwaves in the oven chamber. The pellets were placed in a gastight reactor arranged in the oven chamber. The reactor consisted of an Alundum tube 400 mm long and 32 mm in diameter with the wall thickness of 2 mm. Ground-in quartz stoppers were inserted into the tube from both ends. The stoppers had tubes for feeding the gas mixture into the reactor and discharging it through the trap into the atmosphere, which excluded the air access into the reactor. The reactor was arranged in a heat-protecting casing made of a light fibrous ceramic composite (State Research Institute of Chemical Technology of Organoelement Compounds, Russia).

The magnetron power in the course of pellet sintering was controlled with a voltage stabilizer and a laboratory autotransformer. The pellets were heated to $1650 \pm 20°C$ at a rate of approximately 9 deg min^{-1}, kept at this temperature for 4 h, and cooled to ~800°C at a rate of approximately 8 deg min^{-1} in a stream of an Ar + 10 vol % H_2 gas mixture without applying microwave radiation. The temperature of the pellets being sintered was monitored through transparent quartz tubes with a Promin' visual pyrometer (Teplopribor Group of Companies, Russia).

The density of the sintered pellets was determined by hydrostatic weighing on an HR-250AZG analytical balance equipped with a Sartorius YDK-01 hydrostatic weighing unit (Sartorius Corporate).

RESULTS AND DISCUSSION

By microwave denitration of a nitric acid solution of $UO_2(NO_3)_2$, we obtained UO_2 powder (Table 1) with the particle size mainly in the range 25–400 μm (Figs. 2, 3). The tapped density and specific surface area of the powder (Table 1) meet the requirements;[1]

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[1] TU (Technical Specification) 95 414–2005: Uranium Dioxide Powder of Ceramic Grade with the Uranium-235 Isotope Content Lower than 5.0%.

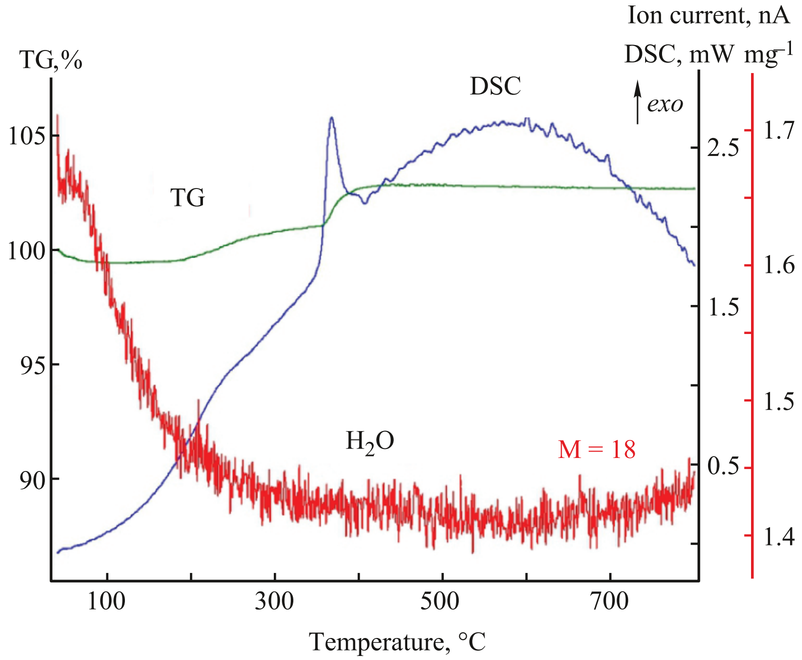

Fig. 2. Data of thermal gravimetric analysis and differential scanning calorimetry for the powder obtained by microwave denitration (heating in air).

the mass spectrum of the gas phase contained no water peak ($m/z = 18$).

To choose the optimum sintering mode, we studied the dependence of the UO_2 density in the sintered pellets on the pressing and sintering conditions (Fig. 4); each pressing run was performed in duplicate.

The required density of the sintered pellets, no less than 10.40 g cm^{-3} (95% of the theoretical UO_2 density equal to 10.97 g cm^{-3}), is reached when the sample is kept at 1650 ± 20°C for no less than 4 h. A decrease in the heating time from 4 to 2 h leads to a decrease in the density of the pellets obtained to ~10.35 g cm^{-3}. The density of the pellets obtained is virtually independent of the pellet weight in the interval 2–6 g (Table 2), of the pelletizing pressure in the interval 2–6 tf cm^{-2}, and on the pressing mode (one- or two-side) (Table 3).

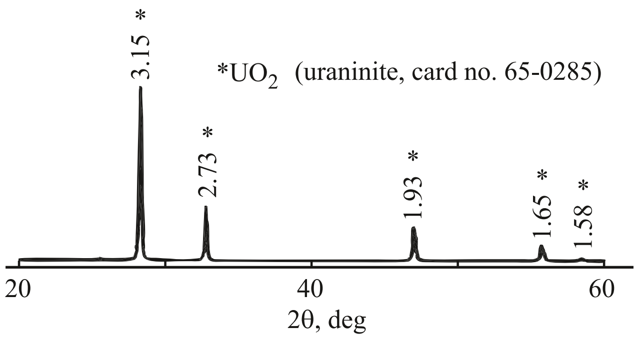

Fig. 3. Diffraction pattern of the powder obtained by microwave denitration.

In addition, we pressed and sintered in the chosen mode UO_2 pellets from the specially prepared UO_2 powder containing 80% 1–0.5 mm fraction, 5% 0.2–0.1 mm fraction, and 15% 0.01–0.003 mm fraction. Such particle-size distribution of the UO_2 powder should ensure reaching the density equal to 96% of the theoretical UO_2 density. However, sintering of UO_2 pellets pressed by this procedure revealed no appreciable increase in the density of the sintered UO_2 pellets.

CONCLUSIONS

UO_2 fuel pellets can be fabricated using microwave radiation. The UO_2 powders obtained by thermal denitration of nitric acid $UO_2(NO_3)_2$ solutions meet the requirements of TU 95 414–2005 to nuclear fuel, and the process itself involves formation of no liquid radioactive waste. Sintering of UO_2 fuel pellets using microwave radiation occurs in a shorter time than sintering by the traditional procedure, and the UO_2 pellets obtained meet the requirements: The density of the sintered pellets is no lower than 10.40 g cm^{-3}.

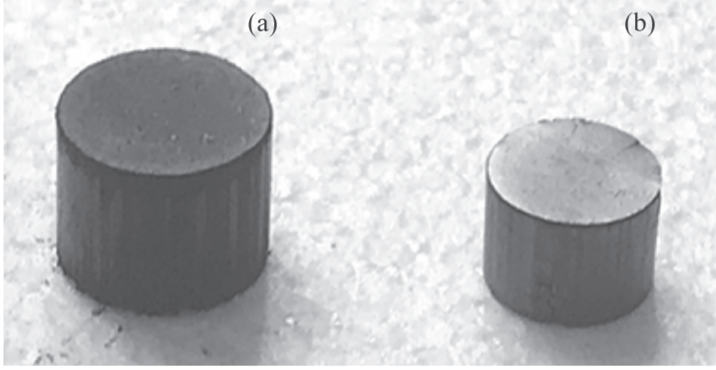

Fig. 4. Photographs of a UO_2 pellet: (a) pressed and (b) sintered under the action of microwave radiation.

Table 2. Density of UO_2 pellets pressed and sintered under the action of microwave radiation. Pressing conditions: pressure 3 tf cm^{-2}, pressing time 15 min (one-side), sintering at 1650°C for 4 h

Powder weight, g	Pellet weight, g		Pellet density, g cm^{-3}	
	pressed	sintered	pressed	sintered
2.0021	1.9932	1.9828	6.44	10.43
3.0889	3.0849	3.0502	6.51	10.41
5.0194	5.0008	4.9702	6.57	10.40

Table 3. Density of UO_2 pellets pressed and sintered under the action of microwave radiation as a function of pressure and mode of pressing UO_2 powder. Pressing conditions: powder weight about 5 g, pressing time 15 min (one-side) and 15 + 15 min (two-side), sintering at 1650°C for 4 h

Pressure, tf cm^{-2}	Density of pressed pellet, g cm^{-3}		Density of sintered pellet, g cm^{-3}	
	one-side pressing	two-side pressing	one-side pressing	two-side pressing
2	6.50	6.59	10.39	10.38
3	6.56	6.64	10.42	10.39
4	6.65	6.68	10.40	10.43
6	6.79	6.81	10.38	10.41
Average	–	–	10.40 ± 0.02	10.40 ± 0.02

The results are of indubitable interest for implementing the process for manufacturing ceramic nuclear fuel under the action of microwave radiation. This process is considerably less power-consuming compared to sintering of the pellets by convective heating in the existing technologies of nuclear fuel manufacturing in three-section electric furnaces.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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