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Thermochemical Embrittlement of the Zirconium Cladding of a Fuel Rod and Oxidative Recrystallization of the Fuel Material in the Course of Spent Nuclear Fuel Reprocessing

M. M. Metalidi*, S. V. Shapovalov, R. V. Ismailov, M. I. Skriplev, V. I. Beznosyuk, and Yu. S. Fedorov

Khlopin Radium Institute, 2-i Murinskii pr. 28, St. Petersburg, 194021 Russia
** e-mail: mmetalidi@khlopin.ru*

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Abstract—The conditions for thermochemical operations of fuel cladding embrittlement and oxidation of spent nuclear fuel with a burn-up of 60 GW day t^{-1} U on a Mini-Khrust installation with UO_2 loading of up to 450 g were checked. The yields of volatile and gaseous activation and fission products (^3H, ^{14}C, ^{129}I, ^{137}Cs) released in the course of these operations were found to be 99.6, 53.8, 36.3, and less than 1%, respectively. The use of head-end thermochemical operations in fuel reprocessing allows selective recovery of tritium to more than 99%, which is the main prerequisite for the reduction of liquid radioactive waste in spent nuclear fuel reprocessing technology.

Keywords: voloxidation of spent nuclear fuel, fuel cladding embrittlement, oxidation

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Studies on thermochemical embrittlement of zirconium alloys in oxygen, nitrogen–oxygen, and nitrogen atmospheres were performed starting from the 1970s. All the researchers found that the Zr oxidation in a wide temperature interval was strongly influenced by the simultaneous presence of oxygen and nitrogen in the gas medium [1–4].

Voloxidation, or oxidative recrystallization, of spent nuclear fuel (SNF) was suggested in the 1960–1970s as an additional head-end operation in reprocessing of uranium oxide fuel [5–8]. The main aim of the oxidative recrystallization of the fuel consists in separation of the fuel from the cladding and removal of gaseous and volatile fission (FP) and activation products from the fuel material.

Interest in thermochemical methods for break-up of zirconium cladding of fuel rods and subsequent oxidative recrystallization of spent nuclear fuel (SNF) increased in the past decade in connection with the development of novel radiochemical technologies. At the existing plants for SNF reprocessing, liquid radioactive wastes (RW) containing iodine and tritium are discharged into the environment. As the environmental safety requirements become more and more stringent, it becomes necessary to develop more efficient process operations involving the recovery of tritium and iodine into separate fractions in the head-end steps of SNF reprocessing [9], which would allow localization of aqueous RW within the framework of a common technology of SNF reprocessing.

The use of thermochemical methods allows simplification of reprocessing of SNF from thermal reactors, with the recovery and localization of tritium prior to the fuel dissolution, which is the main prerequisite for the reduction of liquid process RW. This approach to the head-end step of radiochemical reprocessing is used in the design of the Experimental and Demonstration Center (EDC) to be constructed at the Mining and Chemical Combine. EDC should serve as a prototype of a radiochemical plant of the next generation for reprocessing SNF from thermal reactors [10].

Previous studies on the thermochemical embrittlement of fuel cladding and oxidative recrystallization of the fuel, performed with small amounts of SNF, have shown that these methods are promising for SNF reprocessing [9].

Thermochemical embrittlement of zirconium cladding as an alternative to the presently used cutting is a promising method for fuel stripping. The zirconium cladding embrittlement is based on the dissolution of oxygen in zirconium, occurring at high temperatures. As a result, the mechanical properties of zirconium change, and it becomes brittle. The fuel cladding after the thermochemical embrittlement can be broken with a force that is 10–20 times lower than the force required without embrittlement [9].

This study is aimed at checking the conditions of thermochemical operations for cladding embrittlement and oxidation of SNF with a burn-up of 60 GW day t^{-1} U on an installation with a UO_2 loading of up to 450 g and at determining the amounts of volatile and gaseous activation and fission products released in the course of these operations.

EXPERIMENTAL

The Mini-Khrust installation for studying thermochemical head-end operations of SNF reprocessing was assembled in hot cells of the Research and Experimental Complex of the Radium Institute in Gatchina (Leningrad oblast, Russia) (Fig. 1).

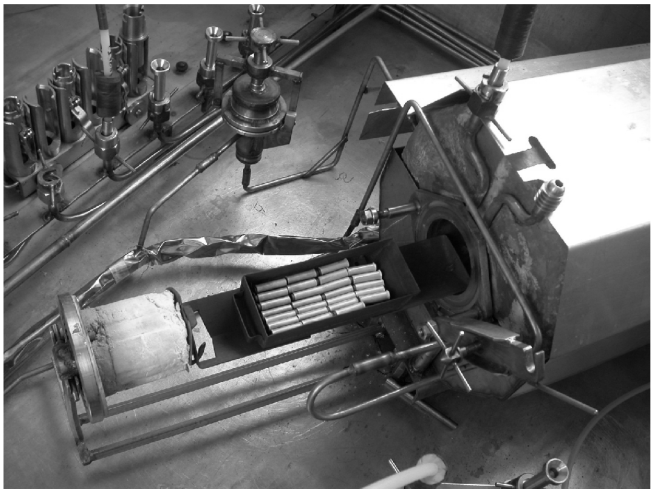

Fig. 1. Mini-Khrust installation for checking head-end thermochemical operations.

Prior to putting into operation, the installation was operated in the test mode with samples of unirradiated fuel, after which a series of experiments were performed with SNF samples from WWER-1000 (1000-MW water-cooled water-moderated energy reactor) with the burn-up of 60 GW day t^{-1} U and storage time of approximately 2 years. In addition, the conditions of the thermochemical operations were checked with SNF samples from WWER-1000 with the burn-up of 50 and 70 GW day t^{-1} U and storage time of 7 and 10 years, respectively.

The installation was loaded with 30-mm-long fuel rod fragments, each containing approximately 13 g of UO_2. The total amount of UO_2 in the loaded portion was about 400 g. The thermochemical cladding breakup was performed in the temperature range 1000–1100°C in a nitrogen medium with recycling of the gas phase. After the required temperature was reached, the calculated amount of oxygen was introduced into the cycle. This amount was determined from our data on the dependence of the ultimate tensile strength of the nitrogenized fuel claddings F on the absorbed gas amount Δm (see below). The volume of the gas absorbed by zirconium was determined from the decrease in the pressure in the system.

Δm, %	0	1.62	3.48	4.03	5.26	7.45	9.83
F, N	403	35.4	30.8	17.4	16.2	15.1	8.3

After that, oxidative recrystallization of the fuel material was performed in the 50 vol % O_2–50 vol % N_2 atmosphere at 450–600°C. The UO_2 oxidation was performed with recycling of the gas phase, with feeding oxygen in accordance with the decrease in the pressure, so as to maintain in the system the absolute pressure of 1 atm.

The gas flowing out from the reactor was passed through an aerosol filter to remove volatile fission products (oxides of Cs, Tc, Mo, etc.) and fed to apparatuses of the gas treatment system. A nonwoven material consisting of Si, Al, and Zr oxides was used as aerosol filter. Tritium, carbon, and iodine were trapped in four absorbers filled with a 2 M NaOH solution. An afterburner in which tritium present in the form of HT was oxidized on copper oxide was arranged before the absorbers. After the gas-thermal operations, SNF was dissolved in 6 M HNO_3, and the solution was analyzed for the content of fission products.

On-line monitoring of gas-thermal transformations of irradiated nuclear fuel was performed by the gas uptake rate and by the ^{85}Kr yield. The tritium amount in the absorbers and in the nitric acid solution of SNF was determined on a β-ray radiometer with ZhS-8 liq-

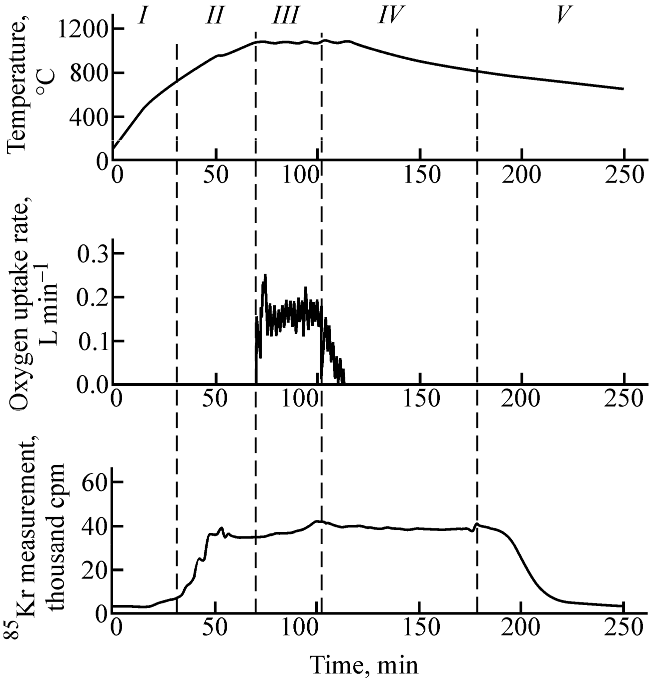

Fig. 2. Diagram of thermochemical embrittlement of fuel rod cladding. SNF from WWER-1000, burn-up 60 GW day t^{-1} U. (*I*) Reactor heating with nitrogen purging, (*II*) reactor heating with recycling the gas phase, (*III*) cladding embrittlement with recycling the gas phase and dosing 9.6 L h^{-1} oxygen, (*IV*) reactor cooling with recycling the gas phase, and (*V*) reactor cooling with nitrogen purging.

uid scintillator after preliminary purification. The tritium-containing solution was purified by double distillation. The total amount of tritium determined in all the gaseous and liquid reprocessing products in the given experiment was taken as 100%. The amounts of ^{129}I and ^{14}C in the absorbers were determined by radiometry using internal references. The aerosol filter after gas-thermal operations with a given SNF portion was etched in 3 M HNO_3 for 3 days. The aerosols were washed out from the filter material and passed into the solution. The resulting solution was analyzed with a γ-ray spectrometer.

RESULTS AND DISCUSSION

In the course of test run of the equipment, thermochemical operations were performed with unirradiated nuclear fuel. The conditions ensuring 99% conversion of UO_2 into U_3O_8 were determined from the uptake rate and amount of oxygen taken up in the course of fuel cladding embrittlement and fuel oxidation. The thermochemical embrittlement of the cladding leads, along with changes in the mechanical properties, also to the formation of a ZrO_2 scale; it is appropriate to separate it in the step of nitric acid solution clarification. The amount of the scale formed was 7% of the total fuel weight. The particle-size distribution of the scale in the oxidized nuclear fuel separated from the cladding is given below.

Particle size, mm	Fraction of scale, %
>2.5	5.1
1.6–2.5	12.0
0.4–1.6	53.8
0.3–0.4	3.7
0.05–0.3	15.9
<0.05	9.5

The oxygen uptake in the course of thermochemical embrittlement of the SNF cladding occurred uniformly and was determined by the rate of oxygen dosing. The major amount of ^{85}Kr was released from the fuel via thermal diffusion in the course of heating. The release of only small amounts of ^{85}Kr in the course of oxygen dosing indicates that the fuel material does not undergo noticeable changes (oxidation). The fuel claddings underwent uniform embrittlement in the course of the experiments. Figure 2 shows the results of one of the experiments on measuring the oxygen uptake rate and the ^{85}Kr release in the course of thermochemical embrittlement of claddings of fuel rod segments.

Oxidation of unirradiated nuclear fuel was performed at 450°C. Passing from unirradiated to spent nuclear fuel required adjustment of the conditions for fuel material oxidation.

Fission products form a continuous series of solid solutions with UO_2, stabilizing the cubic lattice. Therefore, it is necessary to perform oxidation of the irradiated fuel at a higher temperature. Our experiments on SNF oxidation were performed at 500–550°C.

Oxidative recrystallization of spent fuel after thermochemical embrittlement of the fuel cladding is accompanied by the cladding destruction with the formation of an open surface of UO_2, which is intensely oxidized. The fuel oxidation occurs with the peak oxygen uptake in a period lasting for 60–70 min. The process is accompanied by the intense release of ^{85}Kr. As judged from the amount of oxygen taken up in the course of spent fuel oxidation, the degree of conversion of UO_2 into U_3O_8 was 97–99% in different experi-

Distribution of volatile and gaseous activation and fission products in head-end operations of SNF reprocessing

Isotope	Thermochemical operations		SNF dissolution	
	cladding embrittlement	fuel oxidation	gas released in dissolution	solution fed to extraction
^{3}H	3.99×10^9 Bq (53.22 %)	3.48×10^9 Bq (46.41%)	2.25×10^6 Bq (0.03%)	2.55×10^7 Bq (0.34 %)
^{14}C	4.27×10^5 Bq (8.6%)	2.24×10^6 Bq (45.2%)	2.29×10^6 Bq (46.2%)	–
^{129}I	1.95 mg (5.2%)	11.66 mg (31.1%)	23.88 mg (63.7%)	<0.005 mg
^{137}Cs	1.80×10^{10} Bq (0.86%)		–	2.09×10^{12} Bq (99.14%)

ments. The dynamics of the oxygen uptake and ^{85}Kr release in one of the experiments on fuel oxidation is shown in Fig. 3.

The cladding embrittlement and fuel material oxidation are accompanied by the almost quantitative release of tritium. It should be noted that the tritium dissolved in the zirconium cladding is released in the embrittlement step, and the tritium from SNF is released in the oxidation step. The other volatile activation and fission products were removed incompletely. The degree of removal decreased in the following order: ^{3}H > ^{14}C > ^{129}I. The experiments show that the Cs volatility from SNF in the thermochemical operations was low and did not exceed 1% of the total amount of cesium in SNF. Data on the release of volatile and gaseous activation and fission products in one of the experiments performed with a portion of SNF having the burn-up of 60 GW day t^{-1} U and containing 400 g of UO_2 are given in the table.

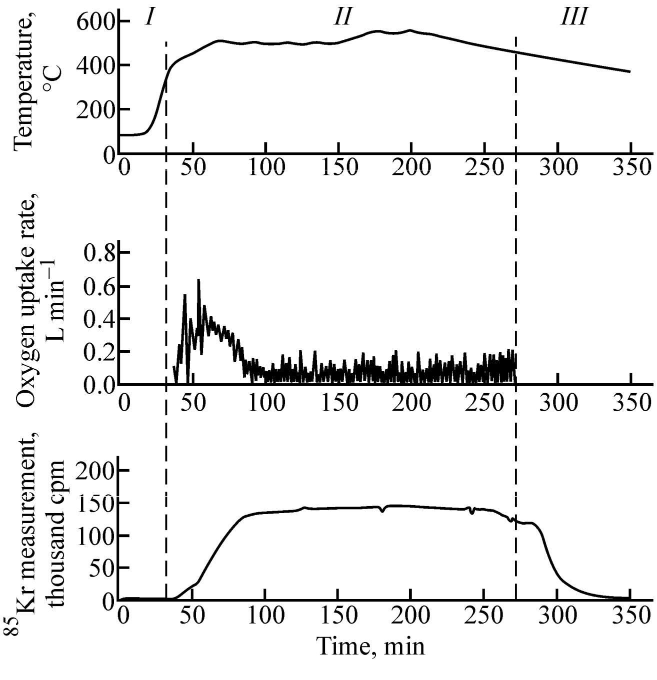

Fig. 3. Diagram of oxidation of fuel rod fragments. SNF from WWER-1000, burn-up 60 GW day g^{-1} U. (*I*) Reactor heating with making the $N_2 : O_2 = 1 : 1$ gas mixture, (*II*) SNF oxidation with recycling the gas phase and dosing oxygen, and (*III*) reactor cooling in nitrogen stream.

The experiments we performed allowed us to choose the conditions for thermochemical embrittlement of zirconium cladding of SNF and for SNF oxidation after the embrittlement. The thermochemical treatment under the chosen conditions in the head-end operations of the SNF reprocessing allows efficient break-up of the zirconium cladding of fuel rod segments, separation of the fuel from the cladding, and efficient removal of tritium into the gas phase without appreciable release of cesium.

The chosen conditions for embrittlement of fuel cladding and for fuel oxidation were checked with SNF of WWER-1000 with the burn-up of 50 and 70 GW day t^{-1} U, stored for 7 and 10 years, respectively. The conditions that we developed require no adjustment in going to fuel with higher or lower burn-up.

The thermochemical treatment of SNF allows not only break-up of the zirconium cladding without using a cutting installation, but also selective removal of tritium from the fuel into the gas phase without appreciable release of cesium in the head-end operations. This method opens prospects for complete cessation of the discharge of liquid wastes in SNF reprocessing.

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