

STUDY OF VVER FUEL WITH DOPANT ADDITIVES

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This is a report of a study of the effect of alloy additives on the properties of fuel under conditions typical of water cooled reactors. The behavior of uranium oxide fuel with added mixtures of the oxides of aluminum, silicon, niobium, and iron during reactor irradiation of experimental fuel elements is investigated in the MIR research reactor. The feasibility of using aluminum-silicate additives for improving the operating characteristics of fuel pellets under reactor irradiation conditions is demonstrated.

One of the approaches for improving the characteristics of fuel elements is to optimize the microstructure of the fuel (grain size, porosity) by means of alloy additives [1].

The work reported here was done for the purpose of studying the effect of alloy additives on the properties of fuel under the operating conditions for fuel elements in water cooled reactors. The behavior of uranium oxide fuel with added mixtures of the oxides of aluminum, silicon, niobium, and iron during reactor irradiation of experimental fuel elements was investigated in the MIR research reactor.

An experiment with an abrupt change in the power of VVER-1000 fuel elements was conducted in 1991 in the PVK-2 loop of the MIR reactor using a technique developed at the NIIAR [2]. An irradiation device (Fig. 1) with 72 experimental fuel elements (Fig. 2) was loaded into channel 2-6 in the assemblies for units Nos. 1, 5, 6, and 4 with 18 fuel elements apiece. The characteristics of the fuel elements are listed in Table 1.

During the experiments, the device with the test fuel elements is mounted in the channel of a loop assembly in which the parameters of the coolant are maintained at levels corresponding to the VVER. The reactor is brought to a power sufficient to ensure attainment of the required initial conditions of the experiment in the loop channel. The control rods closest to the loop channel lie below it. After all the parameters are stabilized and equilibrium states are reached at this power level, the power is abruptly increased by the required amount. This is done by extracting the nearest control rods with compensation of the resulting positive reactivity by inserting control rods in other sites within the core.

Test Procedure. The variation in the parameters during the experiment is illustrated in Fig. 3. The abrupt power increase took place over 13 min. Then the fuel elements were tested at the higher power for another 10.5 h, after which the reactor was stopped to unseal the fuel elements in another loop channel. According to the readings of the shell seal control system, all the fuel elements in this experimental device remained intact. A maximum amplitude of the power increase for the fuel

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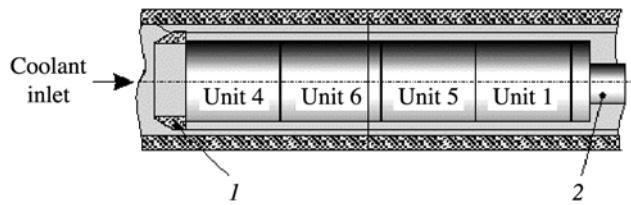


Fig. 1. STS (heat discharge) irradiation device (channel 2-6): 1) flow separator; 2) clamp.

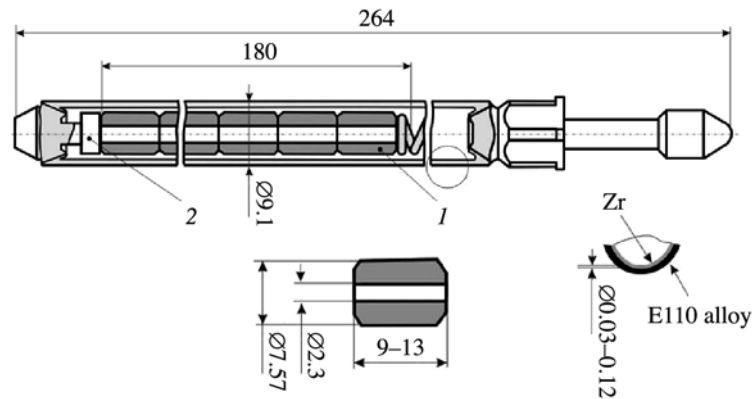


Fig. 2. An experimental fuel element: 1) pellet; 2) bottom cap.

elements was detected for the units lying in the central portion of the experimental devices (Nos. 5 and 6). Table 2 lists the maximum power per unit length for units 5 and 6 at points 1–5 calculated from the measured coolant parameters.

Experimental 265-mm-long VVER fuel elements have been irradiated in channel 2-6 of the PVK-2 loop of the MIR reactor in the STS (heat discharge) device since August 1990. The range of fuel elements in the units has varied: fuel elements with the standard VVER shell and core and modernized variants of these, in different combinations (bimetallic shell, core of uranium dioxide with added Nb_2O_5 and mixtures of Al_2O_3 , Fe_2O_3 , and SiO_2). Fuel elements of standard design were irradiated in the neighboring channel 3-7 in order to study the effect of an abrupt change in power. During the excursions in power in channel 3-7, the power at the fuel elements installed in channel 2-6 also increased. At this time, no signs of seal failure were observed in channel 2-6. The test of the fuel elements was continued in a steady state.

When the MIR reactor was brought to power after a long (~1.5 months) shutdown, a sharp increase in the activity of the coolant was observed in the loop. On a test stand for testing the seals in the holding tank, visual inspection revealed a unit in which fuel element No. 92 had a lengthwise through crack. The core of this fuel element was made of uranium dioxide with added 0.25% Nb_2O_5 with a bimetallic shell: E100 alloy with an outer zirconium coating. At the time it was removed from the irradiation device, the fuel burnup was 12.6 MW·day/kg; it had endured two jumps in power corresponding to experiments with abrupt power increases in channel 3-7 in October and November 1991.

Reactor tests of the remaining fuel elements were continued. The shell integrity monitoring system indicated a new burst of activity in the loop coolant in September 1992; after 6 hours the tests were halted and the units were unloaded and placed in the holding tank.

On the test stand for checking the shell seals, a spectrometric analysis of water samples from the fuel elements revealed two fuel elements with presumed seal failures. Then, after a 4 month shut-down cooling the seals of all the fuel elements were checked in the same way.

Subsequent liquid vacuum-leak tests revealed clear signs of seal failure in fuel element No. 104 – an intense release of gas bubbles from a localized segment of the shell – and a less intense localized release of bubbles was discovered from

TABLE 1. Position of Fuel Elements in the STS (heat discharge) Irradiation Device

Unit No.	Shell material	Fuel	Number of fuel elements
1	E110	UO ₂	18
5	E110K	»	3
	E110	»	3
	»	UO ₂ + 0.25% (Fe ₂ O ₃ + Al ₂ O ₃ + SiO ₂)	4
	E110 (bimetal)	UO ₂	1
	E110	UO ₂ + 0.25% Nb ₂ O ₅	2
	E635	UO ₂	5
6	E110	UO ₂ + 0.25% Nb ₂ O ₅	5
	»	UO ₂ + 0.25% (Fe ₂ O ₃ + Al ₂ O ₃ + SiO ₂)	3
	»	UO ₂ + 0.1% (Fe ₂ O ₃ + Al ₂ O ₃ + SiO ₂) + 0.2% Nb ₂ O ₅	6
	»	UO ₂ + 0.1% mullite	2
	E110 (bimetal)	UO ₂	1
	E110K	»	1
4	E110	»	4
	»	UO ₂ + 0.25% (Fe ₂ O ₃ + Al ₂ O ₃ + SiO ₂)	2
	E110 (bimetal)	UO ₂ + 0.25% mullite	7
	»	UO ₂	3
	E110	»	1
	»	UO ₂ + 0.1% (Fe ₂ O ₃ + Al ₂ O ₃ + SiO ₂) + 0.2% Nb ₂ O ₅	1

TABLE 2. Maximum Power per Unit Length for Fuel Elements in Units Nos. 5 and 6

Point No.	T _{in} , °C	T _{out} , °C	q ₁₅ , W/cm	q ₁₆ , W/cm
1	255	278	314	242
2	273	303	583	448
3	281	316	611	470
4	289	320	472	360
5	294	324	450	341

fuel element No. 83. Both fuel elements had been in the same unit, No. 6, as fuel element No. 92 during the reactor tests. The other fuel elements showed no sign of the bubble release characteristic of seal failure in fuel elements.

The shells of fuel elements Nos. 104, 83, and 92 were made of bimetallic pipes. The composition of the fuel differed from the standard as additives were combined with the uranium oxide. The additives for No. 104 were 0.1% Fe₂O₃ + Al₂O₃ + SiO₂ and 0.2% Nb₂O₅, and for No. 83, 0.25% Fe₂O₃ + Al₂O₃ + SiO₂. A plot of the variation in the power per unit length for fuel elements No. 104 and 83 was the same as for No. 92; then, after an almost two-month shutdown of the reactor the power per unit length was maintained at a level of at least 300 W/cm for 9 days.

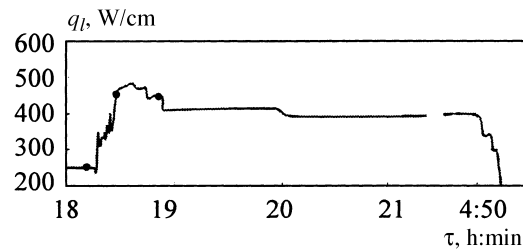


Fig. 3. Variation in the maximum power per unit length in the experiment.

Materials Studies. Examination of fuel element No. 92 revealed an extended crack along the generatrix of the shell (Fig. 4). In sections of the shell above and below the upper and lower ends, respectively, of the core a slight deviation in the direction of crack propagation from the main route was observed, while in the edge regions its expansion decreased until it ended in the region of the welding seams. One characteristic feature of the shape of the crack in the cross section sample is a shift in its direction away from radial, beginning at the outer surface to an angle of 45° to this direction near the inner surface. The thickness of the portion of the shell with a radially directed crack is $3/4$ of the overall thickness. A 1.6-mm-wide annular layer of the core at a distance of 65 mm from the upper end is fragmented by finer radial cracks than near the end. There is no central hole in the core. A region with a diameter of 3.6 mm in the core is filled with fuel with radial cracks and is separated from the annular layer by a circular crack. The gap between the core and the shell is insignificant.

The state of the shell of the fuel element at this stage is characterized by strong hydrogen absorption, especially near the outer surface. The thickness of the oxide films on the outer surface of the shell varies along the perimeter of a cross-section slice. The thickest oxide films are found in the segment located 90° from the crack along the embrittled shell. There the thickness of the uniform oxide film reaches $30\ \mu\text{m}$, and sites of external corrosion with a thickness of up to $70\ \mu\text{m}$ are encountered. The inner surface of the shell is also coated in places with an oxide film. The thickest oxide films have a layered structure and their thicknesses are as high as $70\ \mu\text{m}$ on the inner surface. One feature of the corrosion state of the shell is a concentration of the hydride phase in the metal along the outer surface to a high level in segments whose inner surface is more highly oxidized; in the segments with the thickest oxide films on the outer surface of the shell, the amount of hydrides is low and they were uniformly distributed over the cross section of the shell. Strong hydration of the shell with predominant concentration of the hydrides near the outer surface is, in fact, observed over the entire perimeter of a cross-section slice. The inner surface of the shell is coated with thick (up to $80\ \mu\text{m}$) layered oxide films.

In a sample cut from the shell a distance of 30 mm from the upper end of the core for microscopic analysis, another crack extending radially from the outer surface for $2/3$ of the shell thickness was discovered near the through crack. In the region of this crack, the structure of the shell was strongly hydrated. The concentration of hydrides falls off from the outer to the inner surface.

The surface of fuel element No. 104 had a dark gray color. No distinct defects, such as the crack in No. 92, could be seen on its surface. Only a dark spot, with a shape resembling a depression in the form of a crater and located 67 mm from the upper edge of the shell, was noteworthy. Liquid vacuum-leak testing of the seal for this fuel element revealed rapid production of gas bubbles in the upper part, separated by 67 mm. This pattern was not observed in other sections of the fuel element.

A fine zigzag shaped crack directed radially from the inner surface of the shell half way into the wall thickness was observed during microscopic study of a cross-section slice. However, further slicing and polishing of the sample with inspections in between showed that it had not developed further. Evidently, in this case a crack with a small surface of development was observed of the type characteristic of defects under iodine fatigue conditions.

The microstructure of the fuel in the section near the defect varied in the radial direction: around the central hole there was a layer of thickness $50\ \mu\text{m}$ with a small number of pores; this is followed by a zone of columnar grains faced by chains of fine pores; after this there are zones with equiaxial grains and fine grain (the original) structures. The maximum size of the columnar grains in the longitudinal direction is $300\ \mu\text{m}$ and, in the transverse direction, $100\ \mu\text{m}$. The bulk of the

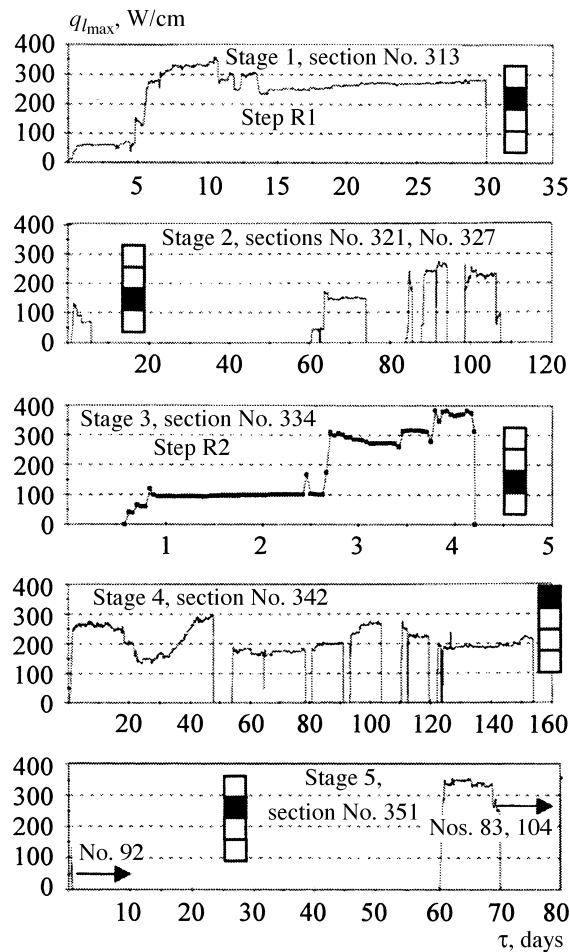


Fig. 4. Irradiation history of fuel elements No. 83, 92, and 104: ■) unit with fuel elements; →) unsealed fuel elements removed.

columnar grains are smaller in size. The elongation of these grains is not great – the maximum length to width ratio is less than 4. The boundary between the zones of columnar and uniaxial grains is smeared out; the columnar grain zone extends for 1.1–1.5 mm. The equiaxial grains are smaller in size than the columnar grains and their size gradually decreases to that of the original grains with distance from center of the core.

In a segment located 5 mm above the assumed defect, the microstructure of the fuel indicates no distinct zone of columnar grains. Instead, grains of smaller size with variable shape are observed, without a preferred orientation and a large amount of fine pores. No other significant differences relative to the microstructure of the fuel were observed.

Post-Reactor Studies of the Fuel Elements. A through crack was observed along the generatrix of the shell with its origin on the inward outer surface of the shell in fuel element No. 92 with 12.6 MW·day/kg burnup. The structure of the shell is characterized by substantial hydrogen absorption, especially near the outer surface. The thickness of the oxide films on the outer surface varies along the perimeter of a cross-section slice. The thickest oxide films were noticed in a section along an arc roughly 90° from the crack. The thickness of the film reaches 30–70 μm at this place. On a sample of the shell cut 30 mm below the upper end of the core, a non-through crack originating from the outer surface was observed near the through crack.

The shell of fuel element No. 104 was unsealed at a distance of roughly 70 mm from the upper end of the fuel element. A crack propagated from the inner surface of the bimetallic shell. A study of the microstructure near the defect showed that the hydride phase is distributed nonuniformly over the cross section of a slice. In the section with maximum oxidation

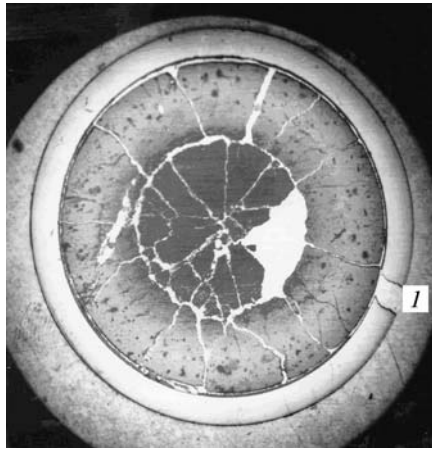


Fig. 5. Macrostructure of a transverse cross section of the core of fuel element No. 92 at a distance of 65 mm from the upper end of the core: *I*) is the site at which the element was unsealed.

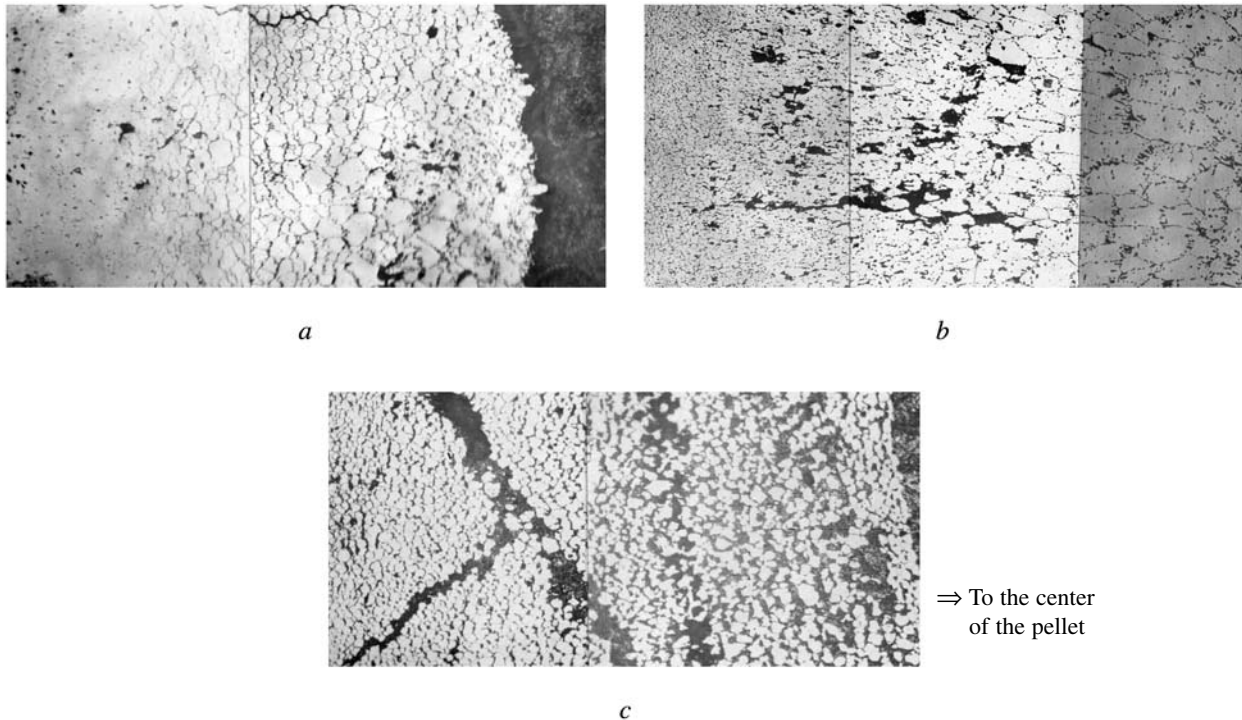


Fig. 6. Microstructure of transverse cross sections of fuel elements Nos. 92 (*a*), 104 (*b*), and 83 (*c*) at distances of 25, 67, and 122 mm, respectively, from the upper end of the core.

of the outer surface, the amount of hydrides is low and they are oriented tangentially. The extent of the segment with maximum oxidation (30 μm) follows an arc of roughly 90° . The inner surface at this segment of the shell is coated with an oxide film up to 40 μm thick. In other segments, where no significant oxidation of the outer surface was observed, the hydrides are concentrated to a greater extent near the outer surface and form a continuous pattern. In these segments, the inner surface of

the shell is highly oxidized; the oxide layers have thicknesses up to 100 μm and the films, themselves, are layered. In the lower part of the fuel element, there is less oxidation of the inner and, especially, the outer surface. Near the gas collector, the outer surface of the shell is not oxidized.

The proposed site for unsealing the shell of fuel element No. 83 lies a distance of 78 mm from the upper end of the element. In this segment of the outer surface, a continuous oxide film was found in a 90° sector; the thickness of this film (maximum 30 μm) gradually decreases and the film vanishes outside this sector.

It should also be noted that fuel elements No. 92, 104, and 83, having reached average burnups of 13 MW·day/kg, underwent jumps of 280–540 and 310–500 W/cm in the power per unit length without taking the burst in energy release at the ends. All the unsealed fuel elements were found to have high oxidation of the outer surface of the shell in the upper part. This oxidation is nonuniform in the azimuthal direction and occurs mainly in a localized section. This oxidation behavior is a sign of localized overheating of the shell.

Discussion. Post-reactor material studies showed that the fuel pellets with additives swelled and came into contact with the shell at burnups of no more than 13 MW·day/kg. For fuel element No. 92, the swelling of the fuel led to plastic deformation of the shell in the diametral direction to 9.4–9.7 mm. The central hole in the pellet was filled with fuel (Fig. 5); the dark region of the structure of the fuel indicates substantial development of porosity associated with grain boundaries (Fig. 6a).

In fuel element No. 104, the diameter of the central hole was reduced from 2.3 to 0.8–1.5 mm. This fuel element is characterized by the presence of a zone with columnar grains in a cross section near the site where unsealing occurred. The columnar grain zone occupies a region of 1.1–1.5 mm after which there is a region with equiaxial grains. A substantial part of the pellet is filled with a porous structure (Fig. 6b).

In fuel element No. 83, the diameter of the central hole also fell to 0.8–1.5 mm and there is no gap between the shell and the core. The microstructure of the fuel is characterized by the presence of a highly porous spongy structure in the central region (Fig. 6c).

Thus, in all the fuel elements discussed here the fuel pellets experienced substantial swelling. Swelling is known to be related to the growth of gas bubbles of fission products at the boundaries and in the volume of the grains. Grain-boundary swelling is the most typical for uranium oxide fuel. It may be assumed that adding niobium and iron lead to significant acceleration of the diffusion of gaseous fission products, in particular, of xenon to the grain boundaries with subsequent formation of a grain-boundary lattice and “tunnels” of gas bubbles. The results obtained here are consistent with data on the effect of additives on diffusion processes in fuel. Thus, it has been shown that adding niobium oxide speeds up the diffusion of xenon by a factor of 50 [3]. A similar effect is created by adding titanium – TiO_2 , Ti-Si-O . This is explained by the fact that the diffusion coefficient of xenon, which determines the rate of transport of atoms of this noble gas, is proportional to the concentration of vacancies in the crystalline structure of uranium dioxide, while the number of vacancies increases substantially when the concentration of dissolved additive cations, in this case niobium and iron, is increased.

In the experiments discussed here, the fuel with added aluminosilicate did not cause unsealing of the fuel elements. These results, as well as data on the effect of SiO_2 in reducing the diffusion coefficient of xenon indicate that they could be used for reducing the yield of gaseous fission products and lessening the swelling of the fuel. Increasing the size of the grains should also facilitate these effects.

Increasing the grain size should suppress the mechanical interaction of the fuel and shell because there is less swelling of the fuel pellets. In the present study, the grain size was not changed but remained the same as for the standard pellets. Thus, the swelling process, as is the yield of gaseous fission products under the shell of a fuel element, is most likely related only to the dopant additives. The experiment showed that adding the oxides of niobium and iron makes the fuel pellets swell faster.

Irradiation at high powers per unit length and burnups as high as 13 MW·day/kg has demonstrated, at least, the possibility of using aluminosilicate additives for improving the characteristics of fuel pellets under reactor irradiation conditions. Evidently, appropriate dopant additives and regulated coarse-grain structure for the fuel pellets will make it possible to optimize the operational characteristics of the fuel, including under high burnup conditions.

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