Studies of behavior of the fuel compound based on the U-Zr micro-heterogeneous quasialloy during cyclic thermal tests

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Abstract. This paper provides the description of temperature cycle testing of U-Zr heterogeneous fuel composition. The composition is essentially a niobium-doped zirconium matrix with metallic uranium filaments evenly distributed over the cross section. The test samples 150 mm long had been fabricated using a fiber-filament technology. The samples were essentially two-bladed spiral mandrel fuel elements parts. In the course of experiments the following temperatures were applied: 350, 675, 780 and 1140 °C with total exposure periods equal to 200, 30, 30 and 6 hours respectively. The fuel element samples underwent post-exposure material science examination including: geometry measurements, metallographic analysis, X-ray phase analysis and electron-microscopic analysis as well as micro-hardness measurement. It has been found that no significant thermal swelling of the samples occurs throughout the whole temperature range from 350 °C up to 1140 °C. The paper presents the structural changes and redistribution of the fuel component over the fuel element cross section with rising temperature.

1. Introduction
Specific nature of operation of research and propulsion reactor fuel elements imposes additional requirements on them, as compared with the fuels used by conventional power-generating reactors:

- Safety and reliability, while the weight characteristics of the reactor tend to be minimal;
- Fission products retention within the fuel composition;
- Reliable heat take-off under significant thermal loads;
- Lack of heat barriers between the fuel compound and cladding;
- Extended surface of heat transfer;
- Operability in transient conditions.

These requirements can be satisfied by using dispersion fuel elements. The kernels of such fuel elements are made of a homogeneous compound consisting of nuclear fuel (fissile materials) and matrix based on metals, their alloys, ceramics, graphite, etc. Uranium-zirconium (U-Zr) alloys are among the types of such compounds. In order to get the maximum neutron flux inside the test channel of the reactor, kernels of the technological area fuel elements were hitherto fabricated using an alloy of zirconium and uranium enriched by $^{235}$U to 90%, with uranium weight fraction ranging between 2 and 4%. The alloys with such relatively small uranium content are malleable enough to enable fabrication of the set of core fuel elements by metal forming processes, in which the fuel kernel and cladding together undergo simultaneous plastic deformation (pressure molding, drawing, rolling, etc.).
Implementation of the International “Reduced Enrichment for Research and Test Reactors” (RERTR) Programme stipulating replacement of 90%-enrichment uranium with uranium of 19.75% enrichment by $^{235}$U led to fuel content growth up to 15-20% vol. in U-Zr alloys [1]. Since such a high uranium concentration results in degraded plastic properties of these alloys [2], application of homogeneous kernels in simultaneous deformation methods for fuel element fabrication is no longer possible. At the premises of the FSUE “SRI SIA “LUCH” a process was developed for fabrication of the fuel kernel constituting a heterogeneous compound of Zr matrix doped with Nb, with threads (fibers) of metallic uranium almost uniformly dispersed throughout the cross section.

The design features of a fuel element with such composition may result in emergence of the processes potentially affecting its performance, namely:

- Thermal swelling: heterogeneity of U-Zr compound creates prerequisites for different swelling dynamics of the two metallic phases. This leads to changes of the fuel compound volume, fuel geometry and fuel assembly hydraulic properties;
- Diffusion-induced mass exchange between the quasialloy component phases U and Zr may result in formation of undesirable phases as well as redistribution of uranium across the section and its escape beyond the fuel element boundaries;
- Mechanical properties of the fuel element may become anisotropic as a result of non-uniformity of stresses and strains in the course of fabrication and operation, potentially causing deformation of the fuel element during the operational lifetime.

Additionally, it is known that multiple cyclic temperature variations, or so-called thermal cycling treatment (TCT) cause dimensional instability in samples of polycrystalline uranium and its alloys, manifesting itself as unidirectional change of dimensions, distortion and roughening of the surface, fracturing of the samples and changing of their microstructure [3]. These manifestations are similar to those observed during irradiation of uranium and its alloys, though their corresponding natures conditioned by TCT and irradiation are different. Therefore TCT is commonly used as a method of preliminary evaluation of the material’s radiation stability. It is also worth keeping in mind that periodic variations of the fuel temperature occur because of burnup, power density changes, shutdown and restart of the reactor, necessitating additional studies of uranium and its alloys behavior during TCT [4].

2. Experimental method

Test specimens 150 mm long containing 20-25 % wt. of uranium were fabricated using fiber-thread method and had a form of two-bladed spiral-rod fuel elements. The initial structure of the fuel element specimens as-etched is shown on figure 1a. Fuel (uranium) components have non-equiaxial prolate shape and are spaced chaotically relative to each other, although their distribution within the zirconium matrix remains mainly uniform. During fabrication, less than 1 micron thick UZr2 intermetallic layer formed on the fuel element boundaries (figure 1b). Local electron micro probe analysis of the zirconium matrix revealed no uranium in the center and at the periphery of the fuel element cross section.

The fuel element specimen was placed inside a quartz vessel, which was in turn placed inside an airtight stainless steel container. Three THA-01 cable thermocouples were mounted at the outer surface of the container. To remove residual moisture the operational volume was evacuated to $\sim 9 \times 10^{-6}$ torr and filled with high-purity argon as per TU6-21-12-94 (O$_2$ not exceeding 0.0002% vol., H$_2$O not exceeding 0.0003% vol.) up to little positive pressure (~ 0.1 bar). Afterwards the container was placed inside a muffle furnace (figure 2).
Figure 1. Initial structure of the fuel element: a) – general view of the fuel element cross section; b) – a single fuel thread.

Figure 2. Experimental apparatus layout.

Cyclic thermal testing of the fuel element specimens was performed in four stages with parameters presented in Table 1. Temperature boundary for each stage was chosen as follows:
1. Operational temperature of the research reactor at the maximum power (60 MW);
2. Temperature of α→β transition of U and exposure in β-region;
3. Temperature of β→γ transition of U and exposure in γ-region;
4. Melting point of U.
Table 1. Test parameters

| Stage number | First stage | Second stage | Third stage | Fourth stage |
|--------------|-------------|--------------|-------------|--------------|
| Fixed point  | Design operational conditions | $\alpha\rightarrow\beta$ transition of U (667 °C) | $\beta\rightarrow\gamma$ transition of U (775 °C) | Melting point of U (1130 °C) |
| Experimental temperature | 350±5 °C | 675±5 °C | 780±5 °C | 1140±5 °C |
| Number of cycles | 30 | 5 | 5 | 1 |
| Total operational time, hours | 200 | 30 | 30 | 6 |

Post-test examination of the fuel element specimens included: geometric measurement of the specimens, metallographic, XRD and SEM analyses as well as microhardness measurement.

Longitudinal and lateral samples with diameter of 0.25 mm were cut from the fuel elements for microstructure analysis.

Examination of the fuel element structural components was performed with OLYMPUS GX-51 and OLYMPUS SZ61 optical microscopes. Scanning electron microscopy (SEM) of the samples was performed using a TESKAN VEGA 3XMU scanning electron microscope additionally equipped with an OXFORD INSTRUMENTS X-MAX80 energy-dispersion unit in high vacuum under 30 kV accelerating voltage.

Microhardness of the fuel element materials was determined with an EMCOTEST DuraScan microhardness testing machine according to Vickers test procedure with the load at the indenter varying from 25 to 100 g, depending on the structural element hardness. At least five impressions were made during each measurement.

X-ray phase analysis was performed with a Bruker D8 ADVANCE X-ray diffractometer using CuK$_\alpha$ radiation. The images were made in the range of 20 angles 25° – 70° with an increment of 0.02° and exposure of 0.2s. Qualitative phase analysis was performed using PDF-2 database.

3. Discussion
The results of the post-test materials science studies of the U-Zr micro-heterogeneous alloy fuel compound are presented on figures 3-6.

The analysis of changes of the geometric parameters as well as visual inspection of the specimens before and after testing found no signs of swelling and/or distortion resulting in macro changes of the geometric shape. Thus, the fuel element specimens demonstrate dimensional stability throughout the entire range of temperatures used (figure 3).

Figure 3. External appearance of the fuel element specimens after tests
Under test temperature of 350 °C the samples keep not only their outer parameters, but the parameters of their structural elements as well. The dimensions and shape of the fuel elements as well as the intermetallic layer thickness remain the same as in the pre-test state (figure 4a). No uranium diffusion into the zirconium matrix was detected in the center and at the periphery of the cross section.

A significant reduction of intermetallic layer thickness (down to 18 μm) in the fuel elements is observed when the temperature exceeds the $\alpha \rightarrow \beta$ phase transition temperature. Intercrystalline diffusion of uranium metal to the depth of ~ 15 μm was detected (figure 4b). The electron micro probe

**Figure 4.** State of the fuel elements after testing: a) $T=350$ °C; $n=30$ cycles; $\tau_\Sigma = 200$ hours; b) $T=675$ °C; $n=5$ cycles; $\tau_\Sigma = 30$ hours; c) $T=780$ °C; $n=5$ cycles; $\tau_\Sigma = 30$ hours; d) $T=1140$ °C; $n=1$ cycles; $\tau_\Sigma = 6$ hours.
analysis has shown that at the distances from the fuel threads beyond the aforementioned value, no traces of uranium were found both in the center and at the periphery of the fuel element cross section. As uranium diffuses into body of the matrix, it reveals the grain boundaries. Comparing the distances between the adjacent boundaries in the longitudinal and lateral cross sections, it can be said that (α-Zr) matrix grains are of polyhedral and nearly equiaxial shape with their size being ~ 7 μm.

| Point | Zr   | U    | Sum  |
|-------|------|------|------|
| 1     | 91.17| 8.83 | 100.00|
| 2     | 99.46| 0.54 | 100.00|
| 3     | 99.16| 0.84 | 100.00|
| 4     | 99.81| 0.19 | 100.00|
| 5     | 99.98| 0.02 | 100.00|
| 6     | 100.00| 0.00| 100.00|
| 7     | 99.85| 0.15 | 100.00|
| 8     | 100.00| 0.00| 100.00|
| 9     | 100.00| 0.00| 100.00|

Figure 5. Microstructure of the fuel element specimens after testing:
a) T=780 °C; n=5 cycles; τΣ = 30; b) T=1140 °C; n=1 cycle; τΣ = 6

Figure 6. Results of local electron micro probe analysis of the peripheral area after testing
(T=780 °C; n=5 cycles; τΣ = 30 hours)
As the temperature grows further ($\beta \rightarrow \gamma$ transition of U) it can be seen, that due to UZr$_2$ intermetallic formation, the fuel thread volume has grown to such levels, that the particles came into contact with each other (figure 4c). The fuel element still retains its heterogeneous structure. Because of non-compensated diffusion flow of uranium into zirconium matrix, formation of channels with $\sim$20 $\mu$m diameter occurred in the center of the fuel elements. The matrix microstructure is uniform with 10-15 $\mu$m equiaxial polyhedral grains. The microstructure of fuel threads also appears to be uniform, equiaxial, polyhedral with grain size of $\sim$ 60 $\mu$m (figure 5a). Local electron micro probe analysis of the fuel thread cross section revealed no signs of uranium metal, i.e. the fuel thread after testing at T=780 °C consists of the intermetallic and U-Zr solid solution. Uranium content in the inter-fiber space is $\sim$ 1.5 % wt. Taking into account the intensity of uranium diffusion, no uranium was found at a distance of $\sim$ 20 $\mu$m from the fuel element surface (figure 6).

Table 2. Results of X-ray phase analysis of the fuel element specimens before and after testing

| Studied sample | Phase composition       |
|---------------|-------------------------|
| Initial state | $\alpha$-Zr + $\alpha$-U |
| Stage 1       | $\alpha$-Zr + $\alpha$-U |
| Stage 2       | $\alpha$-Zr + $\alpha$-U + UZr$_2$ |
| Stage 3       | $\alpha$-Zr + UZr$_2$   |
| Stage 4       | $\alpha$-Zr + UZr$_2$   |

As the temperature exceeds the melting point of uranium, fuel threads dissolve in the matrix (figure 4d) and the fuel element acquires a uniform homogeneous structure with increased uranium content in the central part of the cross section as compared with the periphery. The fuel element microstructure contains mostly large polyhedral grains with sizes of up to 350 $\mu$m, as well as 30-35 $\mu$m grains at the triple boundary junctions as a result of incomplete secondary (collective) recrystallization (figure 5b). The fuel element grain is of non-uniform composition. Under high magnification non-aligned dark precipitates in the form of branched flakes and needles can be seen against the background of gray grain bulk. The concentration of the lighter areas decreases radially. Local electronic micro probe analysis has shown that the lighter areas correspond to the higher uranium concentration (up to $\sim$ 23% wt.), while the darker ones – higher zirconium concentration (up to 98% wt.). It was noticed that due to diffusion the lighter areas reach the fuel element surface and go beyond it. Uranium content in the 50×50 $\mu$m near-surface area is $\sim$ 5 % wt. The results of X-ray phase analysis have shown that after testing at T=1140 °C the fuel element contains two phases: $\alpha$-Zr and UZr$_2$ intermetallic (Table 2).

Microhardness studies revealed that as the test temperature grows, the hardness of the fuel element kernel and cladding generally lowers a little, from 179 kg/mm$^3$ in the initial state to 166 kg/mm$^3$ after testing at 780 °C. Since the fuel threads dissolved in the matrix at a test temperature of 1140 °C, the hardness was measured using a lateral section in radial direction with measurement interval $\sim$ 250 $\mu$m. The highest microhardness is recorded in the central area of the sample where mostly intermetallic is concentrated, and the lowest, comparable with that of the cladding and kernel in the initial state – at the edges.

4. Conclusions

1. Thermal cycle testing was performed on the fuel element specimens made of a fuel compound based on U-Zr micro-heterogeneous quasialloy in temperature interval from 350 °C to 1140 °C.
2. The testing revealed no thermal swelling of the suggested fuel compound throughout the entire temperature range and time span.
3. Under the design operational temperature of the reactor no increase of quantity of UZr$_2$ intermetallide phase forming at the fuel thread-matrix interface was detected as compared with the initial state. Testing at 675 °C and above revealed intensive growth of the intermetallide.

4. In the temperature interval from 350 °C to 780 °C the fuel component does not escape beyond the cladding surface.

5. Basing on the results of zirconium matrix and fuel element cladding microhardness measurements, a prediction can be made that the mechanical properties of the suggested uranium-zirconium compound will not degrade.

6. Structural and geometric stability demonstrated by the fuel elements opens a prospect for their potential use as research reactor fuel.

References
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