Interaction of Uranium-Zirconium Carbonitride Fuel Composition with Refractory Structural Materials

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Abstract. This paper uses the results of material science studies whose purpose was to investigate contact compatibility of uranium-zirconium carbonitride-based fuel pellets with the chosen refractory structural materials under the conditions of high-temperature pre-irradiation tests. Monocrystalline W-3Ta spacers with [110], [123], [112] orientations and polycrystalline W and Mo spacers served as contact pairs for the fuel pellets. The fuel and structural materials underwent annealing at various temperatures significantly exceeding 1200 °C. Duration of experiments for contact pairs with monocrystalline spacers was 80 and 300 hours, for polycrystalline materials the exposure was 50, 100 and 150 hours. High stability of microstructure and chemistry of the U,Zr(C,N)-based composition was observed throughout the entire temperature-time diapason of the tests. No formation of intermediate phases capable of impairing air-tightness and operability of the cladding materials have been found in the interface zone. As a result of the studies performed, it has been found that orientation of W-3Ta monocrystals has no impact on the diffusion rate. Depth of uranium atoms penetration into monocrystalline samples didn’t exceed 15μm in the entire temperature-time diapason. For polycrystalline materials this value was 40 and 350 for W and Mo respectively.

1. Introduction
Uranium-zirconium carbonitride U,Zr(C,N), is a high-density high-temperature fuel with high thermal conductivity and high content of the fissile material per volume unit making it a promising material for using in various reactor types, high-temperature ones included [1]. Before wide application of this fuel composition becomes possible, a lot of research and development problem remain to be solved, and of these the principal ones are irradiation experiments. Activities on certification of the properties of the uranium-zirconium carbonitride-based high-temperature fuel and production of fuel elements using this fuel composition are currently underway. The problem of nuclear fuel compatibility with structural materials is central to development of fuel elements for high-temperature nuclear power units. Therefore the goal of this work is investigation of contact compatibility of refractory metals (W, Mo) with the proposed fuel composition and assessment of feasibility of using these materials as candidates for the container-type fuel element cladding. The main criteria of compatibility between the fuel and structural materials are the absence of interaction at the interface capable to result in formation of new phases and the depth of diffusion of the fissile material not exceeding the fuel element cladding thickness throughout the duration of the entire reactor campaign.
2. Object of studies

The object of studies in this work is pellets made of uranium-zirconium carbonitride-based fuel composition. Oxygen impurity content in the fuel didn’t exceed 0.1 % wt. Monocrystalline W-3Ta spacers with orientations [110], [123], [112] and polycrystalline W and Mo spacers served as the contact pairs for the fuel pellets.

In its original state the material of the fuel pellets is a uniform solid solution with lattice parameter \(a = 4.895 \text{Å}\). The fuel microstructure appears to be uniform with equiaxial polyhedral grains with a size of 20 to 30 \(\mu\)m. Spherical pores the size of 1-5 \(\mu\)m are evenly distributed across the section of the pellet and predominantly located within the grain body (figure 1). Microscopy revealed neither micro nor macro defects.

Contact surfaces of the spacers in their original state are ideally planar and contain no visible defects. The average grain sizes of polycrystalline spacers are 40 \(\mu\)m and 30 \(\mu\)m for W and Mo respectively. Lattice parameters of the used spacer materials are as follows: W – \(a = 3.1648 \text{Å}\); Mo – \(a = 3.1468 \text{Å}\); taking errors into account, those correlate with the tabular values.

![Figure 1.](image)

**Figure 1.** Original state of UZr(C,N)-based fuel composition: a – fracture; b – polished cut.

3. Experimental

The tests were carried out by the method of high-temperature annealing in a vertical vacuum furnace in the following way: packets of five fuel pellets and four spacers were assembled into stacks with a load applied from above by a tungsten weight with a mass of 67.72 g. The resulting assembly was inserted into an air-tight tungsten ampoule (figure 2), which in turn was vertically mounted into the heating device.

High-temperature annealing was carried out in a VEGA-31 vacuum furnace in compliance with the preset parameters (Table 1). Prior to transition for the operational mode, preliminary degassing annealings were carried out at a temperature of 1800 K for 1 hour in vacuum \(~1 \times 10^{-3} \text{ mm Hg}\).

| Ampoule No. | Spacer materials       | Temperature, °C | Duration, hour | Medium              |
|-------------|------------------------|-----------------|----------------|---------------------|
| 1           | monocristalline        | 1800            | 300            | Vacuum             |
| 2           | monocristalline        | 2000            | 80             | ~ 10^{-3} mm Hg    |
| 3           | polycristalline        | 1800            | 50             | ~ 10^{-3} mm Hg    |
| 4           | polycristalline        | 1800            | 150            | ~ 10^{-3} mm Hg    |
Attestation of the original state and post-test examination of the contact pair samples included the following: metallographic analysis, X-ray phase analysis, electronic microscopy and radiometry, as well as microhardness measurement.

Studies of the structural components of contact pairs were carried out using OLYMPUS GX-51 and OLYMPUS SZ61 optical microscopes. Electronic microscopy of the samples was carried out using a TESKAN VEGA 3XMU scanning electron microscope equipped with an energy-dispersing auxiliary unit made by OXFORD INSTRUMENTS X-MAX80, in high vacuum mode under accelerating voltage of 30 kV.

Microhardness of the fuel and structural materials was measured using a DuraScan microhardness tester made by EMCOTEST, by Vickers hardness test method with loads applied to the indenter varying from 25 to 100 g, depending on the structural element hardness. For each measurement at least five indentations were made.

X-ray phase analysis was carried out using a D8 ADVANCE X-ray diffractometer made by Bruker, using CuKα rays. Shooting was carried out within the interval of values of 2θ angle from 15° to 145° with a resolution of 0.02° and exposure 0.2 s. PDF-2 database was used for performance of qualitative phase analysis.

Assessment of the depth of uranium penetration into the spacer materials was made using layer-by-layer radiometric analysis using a dosimeter-radiometer consisting of a DKS-96 control unit and a BDZA 96t alpha-particle counter.

4. Theoretical assessment of the depth of diffusion

As a criterion for performance of expedited testing for diffusion compatibility, to a first approximation the value of the diffusion mean-square displacement of the atom can be chosen as the product of the diffusion coefficient multiplied by time:

\[ x^2 = D \cdot t \]  

Temperature dependences of the coefficients of U diffusion into W and Mo from the constant source can be written as follows [2]:

\[ D_W = 0.45 \cdot \exp(-\frac{399200}{RT}) \text{ cm}^2/\text{s} \]  

\[ D_{Mo} = 0.32 \cdot \exp(-\frac{341100}{RT}) \text{ cm}^2/\text{s} \]

With the total duration of the reactor test being assumed as 30000 hours and the temperature at the interface ~1600 K, the value (D-t), e.g. for Mo, is \(2.57 \cdot 10^{-4}\text{cm}^2\). The same value of the mean-square displacement (D-t) can be obtained in a shorter time at elevated temperatures due to the diffusion coefficient increasing exponentially. The scale of acceleration will be numerically equal to the ratio between the diffusion coefficients at nominal and elevated temperatures. Thus, the ratio between the co-
efficient of U diffusion in Mo at an elevated temperature of 2073 K and the coefficient of diffusion at 1600 K is 346. In case of using tungsten, the respective ratio will be 936. Results of assessment of the anticipated depths of penetration of U into W and Mo basing on the criterion of diffusion are presented in Table 2.

Table 2. Anticipated depth of U atoms diffusion from the constant source into W and Mo.

| Spacer material | T, K  | D_U diffusion coefficient, cm²/s | Time, hour | (D_U:t), cm² | x, depth of diffusion, μm. |
|-----------------|------|---------------------------------|------------|--------------|--------------------------|
| W               | 2073 | 4.0·10⁻¹²                      | 150        | 2.2·10⁻³     | 46                       |
| Mo              | 2073 | 8.3·10⁻¹⁰                      | 150        | 6.0·10⁻⁴     | 244                      |

The presented temperature dependencies of the volumetric coefficients of U diffusion in W and Mo are provisional and applicable only in the temperature range (0.5 – 0.8)·T_m, where diffusion occurs predominantly through mono-vacancies. The anticipated regular operational temperature of the experimental capsule at the level of 1600 K is relatively low for tungsten and corresponds to 0.4T_m. Therefore in case of employment of tungsten as the cladding material, the actual depth of uranium atoms penetration can prove greater due to additional diffusion through structural defects.

5. Discussion

5.1. Contact compatibility of fuel with monocrystalline W-3Ta materials

In the process of cutting ampoule No.1, after testing at T=1800 °C for 300 hours, the pellets and spacers freely separated from each other. Ostwald ripened carbonitride fuel was found at all contact surfaces of the spacers. Crystals of the Ostwald ripened fuel are non-uniformly and are most numerous at the central zone. Thickness of the Ostwald ripened layer in this area is ~ 3 – 4 μm. Maximum quantities of the fuel were found on the [110] W-3Ta spacer (figure 3a). According to the results of X-ray phase analysis, reduction of lattice constant of the Ostwald ripened UZr(C,N) (a=4.885 Å) is visible, as compared with the bulk part of the pellet (a=4.895 Å). This is indicative of alteration of the fuel solid solution composition and supported by the results of the electron microprobe analysis. No new phases resulting from interaction between the fuel and structural materials have been found.

After the tests, contact surfaces of the fuel pellets retained their outward appearance. In the bulk of the pellet densification can be observed resulting from additional sintering in the process of tests, grain size growth to 30÷40 μm and reduction of porosity to ~4%, which is mostly localized in the body of grain (figure 3b). According to the results of local electron microprobe analysis the fuel at the contact surfaces of the pellets, by its composition, is quite similar to the Ostwald ripened. As compared with the original state, the phase composition of the contact surfaces of the pellets didn’t change. Reduction of the lattice parameter is related to diffusion of the elements of the solid solution into the spacer. Electron microprobe analysis carried out at the contact surfaces and in the bulk of the fuel pellets, has shown absence of the elements other than those forming the solid solution. Reduction of microhardness of the fuel, in comparison with the original state, from 870 to 810 kg/mm² can be connected with an insignificant change of its composition.

In the process of cutting ampoule No. 2 after testing at T=2000 °C within 80 hours, the pellets and spacers have also freely separated from each other.

The analysis of the state of the contact surfaces of the spacers after testing demonstrates that the process of Ostwald ripening of the fuel in ampoule 2 occurs more intensively than in ampoule 1. Oswald ripened fuel covers almost the entire spacer surface with virtually continuous layer. The thickest Oswald ripened fuel слой (~5–6 μm) was recorded at the central zone of the [110] spacer. A new phase formed in the peripheral zone of the [112] and [123] spacers. Elementary composition analysis of the new phase shows that it consists of uranium, tungsten and carbon. Quantitative assessment indicates UWC₂ is that phase. Additionally, at the contact surfaces of the [112] and [123] spacers in the spots of new phase formation, sintering-induced adherence and loss of the fuel from the fuel pellet surface. Composition of the Oswald ripened fuel somewhat differs from that of the pellet. The results of X-ray
phase analysis also confirm this. Structural changes of the fuel after testing are related to its densification due to additional sintering, reduction of porosity down to 3-4% and grain growth up to 30-40 μm. The pores are mainly contained within the grain bulk and uniformly distributed across the section of the pellet. Like in the case of Ampoule 1 after testing, the fracture of the pellet is strictly transcrystalline. Fuel microhardness equals 830 kg/mm² and within the margins of measurement errors corresponds to the one measured after testing at 1800 °C for 300 hours.

Qualitative estimation of the results of the electron microprobe analysis of the fuel testing is indicative of a slight compositional changing of the solid solution. These results correlate with the results of X-ray phase analysis. The results of the analysis are indicative of an insignificant fuel lattice parameter reduction from the original a=4.895Å to a=4.893Å after testing, likely caused by diffusion of the elements of the U,Zr(C,N) solid solution into the spacer.

Studies of the depth of uranium diffusion into structural materials performed by means of local electron microprobe analysis from the transversal section and layer-by-layer radiometric analysis demonstrate that this value doesn’t exceed 15 μm.

5.2. Contact compatibility of the fuel with polycrystalline W and Mo.

After testing as part of Ampoule No. 3, at a temperature of 1800 °C for 50 hours, zones of typical morphology formed by grains of the molybdenum spacer adhered by sintering can be seen on the pellet surface at CNF-Mo interface. At CNF-W interface the pellet surface is smooth with no visibly adherent grains. Results of the structure-phase state analysis of the fuel pellets after testing demonstrate their densification due to additional sintering, grain growth up to 18-20 μm, pore coalescence to 2-2.5 μm. Like in the original state, the pores are mainly located in the grain bulk. Microhardness of the fuel material within the margins of measurement errors remained the same as that of the original state. Change of the lattice parameter of U,Zr(C,N) solid solution, as compared with the original state, was observed at the CNF-Mo interface, which is indicative of occurrence of diffusion processes in the zone of interface. At the CNF-W interface as well as in the bulk of the pellet, the solid solution lattice parameter remains unchanged.

Analysis of the contact surfaces of the spacers is indicative of occurrence of thermal etching in the course of testing. This is especially apparent for the molybdenum spacer. For the tungsten spacers this is less apparent and can be visually noticed mainly as scratches left by the abrasive material after polishing (figure 4a). Change of the microstructure of the molybdenum spacer as compared with the original state manifests itself as grain growth up to ~60 μm. After testing, tungsten grains acquired a polyhedral shape close to equiaxial, with straight and smooth boundaries. Their size can become as large as 70-80 μm. The fractures in both spacers are of mixed nature, predominantly intercrystalline.
As compared with the original state, microhardness of molybdenum didn’t change, while that of tungsten has reduced due to changes of its structural state after annealing. Results of the electron microprobe analysis has shown that the depth of uranium diffusion into molybdenum after testing at T=1800 °C for 50 hours equals 250 μm along the grain boundary and 140 μm in the grain bulk. Local electron microprobe analysis revealed no uranium diffusion into the tungsten spacer.

If the experiment duration is prolonged up to 150 hours it becomes apparent that at the surface of the pellet in contact with molybdenum separate grains and their boundaries are visible caused by thermal etching of the solid solution. The surface of the pellet in contact with tungsten is more uniform showing no signs of thermal etching. Microstructural analysis of the solid solution shows that with the increase of exposure further densification of the pellet occurs due to the additional sintering it undergoes, reduction of porosity and grain growth up to 40 μm. The fracture of the pellet is predominantly transcrystalline.

Results of X-ray phase analysis of the contact surfaces of the pellet demonstrate further reduction of the solid solution lattice period at the CNF-Mo interface down to a=4.878Å. The lattice period of the solid solution at the CNF-W interface didn’t change as compared with the original state. Local electron microprobe analysis of the longitudinal polished cut of the fuel pellet revealed no elements other than those forming the solid solution.

During testing, the surface of the molybdenum spacer underwent a severe thermal etching to the extent that the grain boundaries became deeply etched leading to a weakened grain-to-matrix connection and grain breaking off during sintering-induced adhesion to the pellet (figure 4b). Therefore, formation of microcaverns occurs at the contact surface of molybdenum. Nothing like that has been observed for the tungsten spacer.

![Figure 4. Contact surfaces after testing UZr(C,N) with polycrystalline materials: a) - general view of W spacer; b) – general view of Mo spacer.](image)

The microstructure along the longitudinal section of the molybdenum spacer appears to be non-uniform. There are polyhedral grains close to equiaxial shape with a size of ~80 μm in the middle part of the section. Fracture in this part of section is of a mixed nature, predominantly intercrystalline. The microstructure of the surficial zone is significantly different. It is notable for its coarse grain structure with the grain size being equal to 100-200 μm and intergranular boundaries of a serrated shape. Fracture in this part of section is of strictly transcrystalline nature. Also notable is densification of the spacer due to additional sintering during testing, indicated by lack of porosity in the section. Probably densification results in a minor (9 %) microhardness gain. Phase composition of the contact surface and molybdenum lattice period didn’t change as compared with the results of the previous testing. Results of local electron microprobe analysis of the molybdenum spacer have shown that after testing at T=1800 °C for 150 hours, uranium diffusion along the grain boundaries equals 350 μm, being equal to 300 μm in the grain bulk.
Microstructure of the longitudinal section of the tungsten spacer can be characterized as uniform, with a polyhedral grain shape close to equiaxial, with a grain size of ~80 μm. Contrary to molybdenum, there is uniformly distributed porosity in the bulk of tungsten spacer. Fracture type is strictly intercrystalline. Reduction of tungsten microhardness, as observed, is related to its structural state, similar to the previous test. Tungsten lattice parameter didn’t change as compared with the original state. Local electron microprobe analysis revealed no uranium diffusion throughout the body or along the grain boundaries.

6. Conclusions
On the strength of all the results of material science studies made by X-ray phase analysis, electron microprobe analysis, electronic microscopy and microhardness measurements the following conclusions can be made:

1. The fuel composition based on U,Zr(C,N) has shown highly stable structure and chemistry throughout the entire temperature-time diapason of testing.
2. Electron microprobe analysis and X-ray phase analysis revealed an insignificant fuel transfer at the contact surfaces of all the monocristalline W-3Ta spacers and polycristalline Mo spacer which underwent testing. The more intensive fuel transfer was observed for Ampoule No. 2. Maximum layer thickness of the Oswald-ripened fuel on the spacers from Ampoule No. 2 didn’t exceed 6 μm. Also formation of a new phase (presumably UWC₂) was detected in the contact zones of the pairs which underwent testing being part of Ampoule No. 2.
3. As a result of the testing it has been found that orientation of W-Ta monocrystals has no impact on diffusion intensity. Depth of uranium atom penetration into monocrystalline samples didn’t exceed 15 μm throughout the entire temperature-time diapason. For polycristalline tungsten and molybdenum this value amounted to 40 and 350 μm respectively.
4. According to the aforesaid results of diffusion interaction studies monocrystalline materials are the most preferable for application as structural elements for production of the experimental capsules for irradiation experiments, although in terms of contact interaction and relative simplicity of fabrication, employment of polycristalline tungsten seems to be more practical.

References:
[1] Alekseev S V and Zaitsev V A 2013 Nitride Fuel for Nuclear Energy (Moscow: Tekhnosfera) p 240.
[2] Bakhin A N, Vishnevsky V Yu, Tukhvatulin Sh T, Galev I E and Kotov A Yu 2019 Theoretical Assessment of Contact Compatibility of Uranium-Zirconium Carbonitride-Based Fuel with Refractory Materials (Natural and Technical Sciences vol 3) (Moscow: Sputnik Plus) pp 228-230.
[3] Smithells C J 1992 Metals Reference Book (Oxford: Butterworth-Heinemann Ltd.) 7th Edition p 447.