Development of a fuel element on the basis of the composition (Zr,U)N for a high-temperature reactor

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Abstract. In order to create (Zr,U)N nitride fuel for the first time by direct nitridation of the Zr – 5; 10 % wt. U alloy at 2400°C, using the approach of the oxidative constructing, reproducing the shape of the original metal billet ceramics was obtained. In the process of high-temperature nitridation of the alloy, a decrease in the uranium content in the near-surface layer occurs with its simultaneous concentration in the unreacted metal phase, in which the formation of three-dimensional defects (cavity) is possible. After the process of complete nitridation of the alloy is completed and it is heated at a synthesis temperature in a nitrogen atmosphere, the collective recrystallization of zirconium nitride occurs, as well as leveling of the concentration of uranium nitride from the volume of the sample to its surface proceeds.

1. Introduction
Currently, great attention is paid to the development of new low-power HTR, which can be used as special-purpose reactors. They are characterized by high specific energy release of the reactor core (RC) (temperature up to 1500°C), availability of materials, and reliability of the design. This type of reactor includes high-temperature gas-cooled reactors (HTGR), however, their existing concepts have certain disadvantages. The increased energy release of the reactor core places special demands on the structural and fuel materials of the reactor.

In the present work, an attempt to develop nitride fuel (Zr,U)N was made. The material based on (Zr,U)N is characterized by ease of preparation using the approach of oxidative constructing [1]. Figure 1 shows a cross section of a prototype fuel rod assembled from plates, which are a composite of (Zr,U)N coated with ZrN.

The (Zr,U)N composition has a high melting point (~ 3 000°C). The applied thermal scheme is single-circuit, heat removal is carried out by helium, and regulation is done by boron carbide rods.

2. Materials and experimental technique
In order to create a nitride fuel for a promising high-temperature reactor, an Zr – 5; 10 wt. % U alloy was obtained by the method of argon-arc melting. Plates of 0.3 mm thickness were rolled from this alloy. Then the plates gave the desired shape. After that, using the approach of the oxidative constructing, they were nitridated at 2400°C, as a result of which the (Zr,U)N composition was
The selected nitridation mode is the most optimal for obtaining nitride ceramics with specified characteristics [2].

Figure 1. The design of a fuel rod of a high-temperature reactor.
1 - fuel assembly casing (FA) (molybdenum, vanadium alloy, titanium nitride or zirconium nitride);
2 - fuel plate; A - the cross-section of the fuel plate

The morphology of the surface and transverse chips of the samples was investigated by scanning electron microscopy (SEM) (LEO 1420 microscope, Carl Zeiss with energy dispersive microanalysis system INCA Energy 300, Oxford Instruments).

The study of the phase composition of the samples was performed by X-ray diffraction (XRD) with an angular-spread beam with Zeeman-Bolin focusing on a vertical X-ray diffractometer SHIMADZU XRD 6000 at room temperature in monochromatic copper radiation [3].

3. Results and its discussion

The surface of the initial samples of the obtained Zr-U alloy was investigated by SEM (Figure 2).

Figure 2. X-ray diffractograms and SEM images of the initial surface of the Zr-U alloy with different uranium contents: a - 5 wt. %, b - 10 wt. %
As a result of energy dispersive microanalysis of the initial surface of the samples, it was established that the percentage of uranium in the alloy corresponds to the declared one of regular distribution.

Within 6 minutes of nitridation on the surface of the sample alloy Zr - 5 wt. % U forms a nitride layer with a nitrogen content corresponding to the ZrN equiatomic composition. The uranium content in the resulting surface layer is less than in the original alloy (Figure 3), which can be explained by the fact that the chemical interaction of zirconium with nitrogen begins at a lower temperature and proceeds faster than with uranium, as well as diffusion of zirconium from the sample volume to its surface.

| Spectrum | N, at. % | Zr, at. % | U, at. % |
|----------|----------|-----------|----------|
| Spectrum 1 | 45.44 | 54.23 | 0.34 |
| Spectrum 2 | 44.00 | 54.86 | 1.14 |
| Spectrum 3 | 38.09 | 61.71 | 0.20 |
| Spectrum 4 | 30.23 | 68.90 | 0.87 |
| Spectrum 5 | 44.49 | 54.98 | 0.53 |

Figure 3. SEM image of the surface of the alloy Zr - 5 wt. % U, after nitridation at 2400°C for 6 minutes.

In the process of nitridation (11 minutes), the concentration of uranium in the unreacted metal phase reaches the ratio Zr/U ~ 1.5 (Figure 4). With an increase in the nitride content and an increase in the uranium content in the unreacted metallic phase, three-dimensional defects (cavities) containing conglomerates with a high uranium content were found in the bulk of the sample (Figure 5). The presence of phases with a structure different from that of zirconium nitride was detected in the volume of the formed nitride.

After complete nitridation of Zr - 5 wt. % U alloy proceeds leveling of the concentration of uranium nitride from the sample volume to its surface. The composition of zirconium nitride in the volume of the sample does not correspond to the equiatomic one and is characterized by a lack of nitrogen ZrN1-x (Figure 6). Heating the sample in a nitrogen atmosphere for 90 minutes initiates the process of collective recrystallization of zirconium nitride [4], accompanied by the redistribution of uranium with localization in structure defects — mainly along grain boundaries (Figure 7). According to X-ray diffractometry, an insignificant content of uranium intermetallic compounds is detected in the sample volume.
| Spectrum | N, at. % | Zr, at. % | U, at. % |
|---------|---------|-----------|----------|
| Spectrum 1 | 0.00 | 56.98 | 43.02 |
| Spectrum 2 | 0.00 | 58.85 | 41.15 |
| Spectrum 3 | 0.00 | 62.39 | 37.61 |
| Spectrum 4 | 0.00 | 62.19 | 37.81 |

**Figure 4.** SEM images of the transverse cleavage of the sample obtained at 2400°C for 11 minutes.

**Figure 5.** SEM image of the cavity in the sample volume.
| Spectrum | N, at. % | Zr, at. % | U, at. % |
|----------|---------|----------|---------|
| Spectrum 1 | 58.53 | 40.74 | 0.73 |
| Spectrum 2 | 0.00 | 72.81 | 27.19 |
| Spectrum 3 | 43.83 | 51.15 | 5.01 |

**Figure 6.** SEM image of the transverse chipping of a sample of Zr alloy - 5 wt. % U, after complete nitridation at 2400°C

**Figure 7.** SEM images of the transverse chipping of the sample obtained at 2400°C for 90 minutes

4. **Conclusion**

For the first time, nitride ceramics reproducing the shape of the initial metal billet was obtained by direct nitridation of the Zr-U alloy using the oxidative constructing approach.

In the process of high-temperature nitridation of the alloy, a decrease in the uranium content in the near-surface layer with its simultaneous concentration in the unreacted metal phase is observed. This phenomenon is associated with a high chemical affinity of zirconium to nitrogen compared to uranium. Zirconium diffuses from the sample volume onto its surface with the formation of ZrN while uranium is localized in the bulk of the unreacted metal phase in which the formation of three-dimensional defects (cavity) is possible.

After complete nitridation of the alloy and heating it at a synthesis temperature in a nitrogen atmosphere, the collective recrystallization of zirconium nitride occurs, as well as leveling of the concentration of uranium nitride from the volume of the sample to its surface proceeds.

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5. **References**

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