Influence of the plutonium content on thermochemical stability of a mixed nitride fuel

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Abstract. The results of the thermogravimetric studies of mixed nitride uranium-plutonium (MNIT) fuel formulations at high temperatures (up to 2173 K) are presented. The rates of mass loss of mixed nitride are calculated as a function of the plutonium content. With the increase of the plutonium content in MNIT fuel the rate of mass loss increases. However, there is a deviation from this dependence for some compositions of MNIT fuel.

1. Introduction

To date, the main types of reactors are thermal-neutron reactors that use uranium dioxide as fuel. In the light of the rapidly increasing consumption of electricity, the increasing amount of spent nuclear fuel and the public demand to reduce the radioactive waste deposits, interest in commercial fast-neutron reactor technology has been renewed.

In most cases the use of oxide fuel in developing fast-neutron reactors does not allow to reach a breeding ratio in the active zone greater or equal to one, which eliminates the possibility of fall in the reactivity of the fuel campaign and minimizes the risks of accidents. The use of dense fuel in the reactor, such as nitride (UPu)N, not only solves the abovementioned problems, but also allows to use spent fuel repeatedly as many times as desired, without addition of enriched uranium [1-4].

However, despite a number of advantages, nitride fuel has its drawbacks, one of which is the low chemical stability of the compound at high temperatures. That is, there is a possibility of decomposition of uranium and plutonium nitrides into components, which is unacceptable in the operating nuclear reactor. Therefore, to justify the reliable and safe operation of the reactor, it is necessary to have reliable data on the thermochemical stability of the MNIT fuel.

2. Experimental

2.1. Sample production

Samples with a 5.9, 9.8, 12, 20 and 50 % mass fraction of plutonium amounting to uranium and plutonium were produced from a mixture of uranium and plutonium mononitrides obtained from the initial dioxides by carbothermic synthesis. Sample manufacturing operations were performed in an atmosphere of dry nitrogen (H₂O, O₂ – no more than 100 ppm of each).

The vortex layer device ABC-150, laboratory mill POLYMIX PX-MFC 90 D (Kinematica AG), automatic press "10 TonAutomaticHydraulicPowderPress H-10-2.5" (Western Sintering), pit-type furnaces for synthesis and sintering were used for their production.
The synthesis of nitride and the manufacture of disks were performed according to the procedure used in [5-6]. Below are the main stages of producing final samples.

The raw materials (uranium and plutonium dioxide, carbon black K-354 grade were mixed in the specified proportions in the ABC-150 apparatus. Before the carbothermic synthesis of nitrides, the mixture of the initial reagents was pre-compressed into pellets in order to provide maximally possible reaction passage and to reduce dust losses. Further, they were subjected to heat treatment with isothermal exposure at 1773 K sequentially in the nitrogen flow and a mixture of nitrogen with a volume fraction of hydrogen equal to 8%. In a nitrogen medium, a mixture of uranium and plutonium dioxides was reduced carbothermically to form a mixed mononitride, and in a medium of a nitrogen and hydrogen mixture, residual carbon was removed from it.

The heat-treated nitride pellets were then crashed in a hammer mill PX-MFC 90 D and grinding for 10 minutes using ABC-150. Dry lubrication (up to 0.5 wt. % zinc stearate) was added to the nitride powder, the mixture was blended in a turbulent mixer. At pressures from 250 to 350 MPa green pellets were compressed from the obtained powder.

The compressed pellets were heat treated in a flow of a mixture of nitrogen with a volume fraction of hydrogen equal to 8% with isothermal exposure at 2123 K for 2 to 20 hours.

The internal diameter of the crucible in the NETZSCH STA 449 F1 thermal analyzer is 6 mm, so the sintered 8 mm diameter nitride pellets were crashed into smaller fragments of 50-500 mg, which were used in thermogravimetric analysis.

2.2. Thermogravimetric study
The following methods were applied in the study of thermochemical stability of nitride fuel:
- thermogravimetric analysis;
- scanning electron microscopy;
- electron micro probe analysis.

Thermogravimetric studies were carried out in a flow of high-purity helium using the NETZSCH STA 449 F1 thermal analyzer combined with a quadrupole mass spectrometer to analyze the gas atmosphere in the furnace. The STA was placed in a glove box with an inert atmosphere and a gas cleaning system. For additional purification of helium, a heated purifying MonoTorr getter filter was used, which reduces the amount of impurity in helium to a level of < 1 ppb.

Samples of the MNIT fuel were heated at a constant rate in an open tungsten crucible up to 2173 K and kept at this temperature for 30 minutes.

During the experiment, the change in the mass of the sample (TG), the rate of change in the mass of the sample (DTG) and the dependence of the sample temperature on time (by means of the W-Re thermocouple) were recorded.

Tests were carried out on samples of mixed uranium-plutonium nitride with a plutonium content in the range 5.9, 9.8, 12, 20 and 50 wt.%.

As an example, the results of the thermogravimetric analysis of the MNIT fuel (U_{0.5}Pu_{0.5})N are shown in figure 1.

The mass loss process is one-stage in nature. The rate of mass loss on the isotherm remains almost constant. The sample lost 1.22 mg during the experiment, that is 1.14 wt.%. The average rate of mass loss on the isotherm was 0.034 % per minute. Such behavior of the TG curve is typical for other compositions of MNIT fuel. The temperature at which the decomposition starts lies in the temperature range 1973-2073 K and corresponds to the cross of the zero value by DTG curve and its following dive in the negative region.
Figure 1. Results of the thermogravimetric analysis of the MNIT fuel (U0.5Pu0.5)N at the temperature 2173 K

The results of thermogravimetric experiments are summarized in table 1. The data on the mass loss of samples were evaluated independently, both using the internal scales of the thermal analyzer and the external analytical scales, and coincided within the error.

Table 1. Initial sample masses and the results of thermogravimetric experiments

| Sample composition | Mass, mg   | Mass loss, wt.% | Mass loss, mg | Average rate of mass loss at 2173, %/min |
|--------------------|-----------|-----------------|---------------|----------------------------------------|
| (U0.941Pu0.059)N   | 131.4±0.1 | 0.16            | 0.21±0.01     | 0.0038                                 |
| (U0.902Pu0.098)N   | 109.0±0.1 | 0.33            | 0.36±0.01     | 0.0089                                 |
| (U0.88Pu0.12)N     | 120.1±0.1 | 0.44            | 0.53±0.01     | 0.0122                                 |
| (U0.8Pu0.2)N       | 120.0±0.1 | 0.29            | 0.34±0.01     | 0.0076                                 |
| (U0.5Pu0.5)N       | 106.8±0.1 | 1.14            | 1.22±0.01     | 0.0340                                 |

2.3. Scanning electronic microscopy and X-ray microanalysis
The structure and composition of the experimental samples were studied using a scanning electron microscope-microanalyzer "Zeiss LS 15". For the purposes of comparative analysis, fragments of a mixed nitride pellet were examined, which had not been subjected to thermal tests. Samples surface was photographed in secondary electrons in several sections of the sample at various magnifications.

Figure 2 shows the structures of the initial sample of mixed uranium-plutonium nitride (U0.88Pu0.12)N (a) and samples after isothermal exposure at 2173 K.
Figure 2. Photographs taken in secondary electrons of mixed uranium-plutonium nitride (U<sub>0.88</sub>Pu<sub>0.12</sub>)N: a) initial sample; b) with isothermal exposure of 2173 K

As can be seen from the photographs, the change in the shape of the grains, the formation and growth of grain boundaries, smoothing of angular shapes are observed - "thermal etching" of the sample occurs. Such images are typical for MNIT samples of other composition.

Tables 2 and 3 contain the results of electron micro probe analysis of samples in several places after testing and initial samples of MNIT fuel with plutonium content 12 and 20 wt.%. Electron micro probe analysis of the samples before and after the test shows depletion in plutonium content on the surface. The average difference between the plutonium content in the initial U<sub>0.88</sub>Pu<sub>0.12</sub>N sample and the sample after tests is ~6.4 wt.%. For the other sample of U0.88Pu0.12N composition the difference is around ~3.4 wt. %.

| Table 2. Results of the electron micro probe analysis of the initial sample MNIT fuel (U<sub>0.88</sub>Pu<sub>0.12</sub>)N and samples after isometric exposition |
|---------------------------------------------------------------|
| Plutonium content on the sample surface, wt.% | Initial sample | 11.26 | 11.68 | 14.51 |
|                                             | After test    | 9.10  | 9.77  | 8.54  |

| Table 3. Results of the electron micro probe analysis of the initial sample MNIT fuel (U<sub>0.8</sub>Pu<sub>0.2</sub>)N and samples after isometric exposition |
|---------------------------------------------------------------|
| Plutonium content on the sample surface, wt.% | Initial sample | 18.92 | 19.32 | 18.38 |
|                                             | After test    | 12.49 | 12.00 | 12.07 |

3. Discussion
As a result of experiments, the dependence of the evaporation rate of nitride on the mass content of plutonium at an isothermal holding temperature of 2173 K was constructed (figure 3).
Figure 3. Dependence of the evaporation rate of MNIT fuel on the content of plutonium

In the figure 3 it is shown that in MNIT fuel samples the evaporation rate increases with the increase of the plutonium content. The exception is MNIT fuel sample with the 20 wt.% Pu content. The evaporation rate for this composition is lower than for samples with plutonium contents of 12 and 9.8 wt.%. Moreover, different samples of fuel with 20 wt.% of plutonium were used in the experiments, which eliminates the possibility of defective samples or random error.

According to electron micro probe analysis, the surface of the MNIT fuel samples is depleted by plutonium after high-temperature tests, that may indicate a lower thermochemical stability of plutonium nitride compared to uranium nitride. Moreover, for samples with plutonium content of 20 wt.%, an anomaly was observed: the electron micro probe analysis of the samples before and after the test showed a significant depletion of the surface for plutonium (see table 3). The average value of the plutonium content difference between the initial sample and the sample after the test is ~6.4 wt.% for two distinct fuel batches. At the same time, the rate of mass loss of mixed nitrides with 12 and 9.8 wt.% PuN is also higher, despite the fact that the "more volatile/less stable" component – plutonium nitride – comprises a smaller part of a sample. On the contrary, the difference in the plutonium content on the surface of \((U_{0.88}Pu_{0.12})N\) sample before and after the experiment is only ~3.4 % (see table 2). The obtained TGA data and electron micro probe analysis of the \((U_{0.8}Pu_{0.2})N\) mixed nitride solid solution may indicate the deviation of some properties in a continuous series of solid solutions UN-PuN for this composition, namely a marked reduction in the rate of diffusion of more volatile/less stable component – the PuN.

The confirmation of the non-ideal behavior of the solid solution was found in other studies. Namely, the period of the crystal lattice of solid solution varies by only 0.00157 nm depending on the plutonium content. Though the lattice period does not obey the Vegards law with the change of composition (figure 4) [7], and deviates in both directions. The \((U_{0.8}Pu_{0.2})N\) solid solution has the maximum negative deviation from Vegard's law and its lattice period is 0.489060-0.4892 nm [8], which is consistent with the results of thermogravimetric tests.
However, it is impossible to predict abnormally low evaporation rate of MNIT fuel samples with Pu content of 20 wt.% using the observed deviations. Moreover, the rate of mass loss of this composition will be lower than that of samples with less plutonium content.

4. Conclusion

Thermogravimetric data on MNIT (UPu)N fuel with a plutonium content 5.9, 9.8, 12, 20 and 50 wt.% were obtained. The rates of mass loss of each solid solution composition were determined at the temperature 2173 K in the flow of high-purity helium.

The change of structure after high-temperature tests in helium atmosphere was established. The change in the shape of grains, smoothing of the corners (compared to the initial structure), was observed for the structure.

It was found, according to the results of the electron micro probe analysis of the studied samples, that in mixed uranium-plutonium nitride the mass loss occurs mainly due to plutonium nitride. It was shown that deviations from the ideal behaviour are observed in a continuous series of UN-PuN solid solutions. The rate of mass loss of nitrides \((U_{0.88}Pu_{0.12})N\) and \((U_{0.902}Pu_{0.098})N\) is higher than that of \((U_{0.8}Pu_{0.2})N\) despite the fact that the less stable component – plutonium nitride is contained in them in a smaller amount. The obtained TGA and electron micro probe analysis data for the solid solution of the composition \((U_{0.8}Pu_{0.2})N\) indicate a significant decrease in the diffusion rate of the nitride fuel components at this composition.

The study of the thermochemical stability of nitride fuel is one of the priorities to substantiate the safe exploitation of promising nuclear power plants operating on nitride fuel. The data obtained are not only fundamental, but also can be useful for the analysis of emergency operation of the reactor, when the integrity of the fuel rods is violated and the fuel temperature rises above 2073 K.

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