Gas emission from the UO₂ samples, containing fission products and burnable absorber

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Abstract. The process gas released from the fuel pellets of uranium fuel during fuel burn-up reduces the thermal conductivity of the rod-shell gap, enhances hydrogen embrittlement of the cladding material, causes its carbonization, as well as transport processes in the fuel. In this study a technique of investigating the thermal desorption of gases from the UO₂ fuel material were perfected in the temperature range 300-2000 K for uniform sample heating rate of 15 K/min in vacuum. The characteristic kinetic dependences are acquired for the gas emission from UO₂ samples, containing simulators of fission products (SFP) and the burnable neutron absorber (BNA). Depending on the amount of SFP and BNA contained in the sample thermal desorption gas spectra (TDGS) vary. The composition of emitted gas varies, as well as the number of peaks in the TDGS and the peaks shift to higher temperatures. This indicates that introduction of SFPs and BNA alters the sample material structure and cause the creation of so-called traps which have different bonding energies to the gases. The traps can be a grid of dislocations, voids, and contained in the UO₂ matrix SFP and BNA. Similar processes will occur in the fuel pellets in the real conditions of the Nuclear Power Plant as well.

1. Introduction
In connection with the development of fuels for safe and profitable ensuring operationing of the nuclear energy sector and the creation of advanced nuclear power plants, we have created a modified oxide nuclear fuel, which will allow:
- to compensate reactivity by placing Gd in the surface layer;
- to increase the thermal conductivity at the pellet peripheral region by using an AlGdO₃ stable phase;
- to slow down the rim-zone formation by using depleted uranium in the surface layer of the pellet.

Using the combined (two-band) pellets based on modified oxide nuclear fuel in WWER allows to solve the problem aiming to improve the fuel efficiency at high burnup [1,2]. The developing of the experimental method for studying uranium dioxide samples thermal desorption and UO₂ samples gas release investigating, containing different amount of simulators of fission products (SFP) and the burnable neutron absorbers (BNA) at a constant heating rate in a vacuum was the task of this researching [3,4]. The problem is actual because the process gas evolving from uranium fuel pellets during burn up reduces the thermal conductivity of the core-shell gap, enhances hydrogen embrittlement of the cladding material, induces its carbonization, and transport processes in the fuel. The composition of the process gases may comprise: CO₂, CO, N₂, H₂, hydrocarbons, water vapor, and others. Using the method of thermal desorption is caused by its large abilities which allow to receive

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in a wide range of temperatures the information on number, composition and mobility of gases, in dependence to structural parameters of the material.

2. Experiment
The investigation of the gas release from the UO$_2$ samples, containing SFP and BNA kinetics was performed with a high-vacuum mass spectrometer installation. Washed in ethanol and dried UO$_2$ samples were placed in a loading system having a form of a disc with vertical holes and rotating around its axis. The heating was provided by a programmable MINITE-RM400 (made in Russia). The electrical resistance heater is made of a molybdenum tube and allows to heat the sample at a constant rate from room temperature to 2000 K. In this study heating is carried at 15 K / min in the temperature interval 300 - 2000 K. The evacuation of the vacuum system is carried out by the pump station Hi Cube 80 and allows to obtain a vacuum of about $10^{-5}$ Pa.

Gases released from the test sample as a result of its thermal heating mass spectrum is obtained by means of a mass spectrometer MX-7304, with its sensor connected to the analysis chamber through the valve DU-25 (made in Russia). The sensitivity to hydrogen at a linear heating is about $3 \times 10^{-14}$ molecules or concentration of $6 \times 10^{-5}$ at. % (0.01 ppm). The thermal desorption mass spectrum is recorded on a PC using the software package Labview 2012.

3. Results

Figure 1a shows typical kinetic dependences of the UO$_2$ gas samples emission, non- SFP and BNA. Herein a single peak M2 (hydrogen) at 600 K and a peak at 1100 K is presented.

Figure 1b shows typical kinetic dependences of the UO$_2$ gas samples, containing 8% SFP emission. In this figure, there is one M2 peak (hydrogen) at 670 K and two M28 peaks - at 880 K and 1320 K, respectively.

Figure 1c shows the experimental values for the UO$_2$ sample, containing 11% SFP. There are three M2 peaks (at 670 K, 1020 K and 1320 K). For this sample the M28 peak is observed with wide plateau in the temperature range 950 - 1200 K. There are two M44 peaks - at temperatures of 1050 K and 1300 K. Also there are two M12 peaks at 1050 K and 1300 K and one M16 peak at 1300 K.

The dependencies for UO$_2$ sample with 6.9% Gd$_2$O$_3$ are shown in Figure 1d, which contains five M2 peaks (580 K, 680 K, 820 K, 970 K and 1130 K), three M28 peaks (830 K, 1130 K, 1430 K) and single M44 peak at 1130 K.

Figure 1e shows the data for UO$_2$ with 8.9% AlGdO$_3$ (6% Gd). In this figure, there is one M2 peak (at 660 K), three M28 peaks (850 K, 1150 K, 1450 K) and single M44 peak at 850 K.

Figure 1f shows the typical kinetic dependences of the gas emission from a UO$_2$ sample with 8.9% AlGdO$_3$ (6% Gd) and 11% SFP. Figure 1f shows four M2 peaks (560 K, 670 K, 800 K, 1300 K), one M28 peak at 1450 K, five M44 peaks (670 K, 770 K, 910 K, 1050 K and 1370 K), one M12 peak at 1370 K and single M16 peak at 1370 K.

4. Discussion

Based on the analysis of the UO$_2$ samples gas evolving kinetic dependences it can be concluded that M2 and M28 gassing from the UO$_2$ samples occurs from the fuel pellet volume. The typical shape of the kinetic dependences indicates that H$_2$ and CO gassing occurs by diffusion, and the binding energy of the M2 and M28 is different in the sample. The UO$_2$ samples with 8% of SFP (Figure 1b) also exhibit diffusion gassing of M2 and M28.

However, it is seen that the M2 peak shifts to a temperature of 670 K that indicates the increase in the M2 binding energy within the sample volume and on the kinetic dependence of M 28 gassing a peak shifts to a temperature of 1320 K and formation of an additional peak is observed at 880 K. This indirectly indicates that at the introduction of the UO$_2$ sample additional 8% SFP defects are formed, which segregate and gases have larger binding energy with them.
Figure 1. Thermodesorption spectra of evolved gases for the samples:

a – UO$_2$; b – UO$_2$+8% SFP; c – UO$_2$+11% SFP; d – UO$_2$+6,9%Gd$_2$O$_3$; e – UO$_2$+8,9%AlGdO$_3$; f – UO$_2$+8,9% AlGdO$_3$+11% SFP

The kinetic release of gases dependences of UO$_2$ samples containing 11% SFP (Figure 1c) have a saturated range of gas emission peak emission both in the number of peaks and the amount of generated mass emissions (M2, M28, M44, M12 and M16). It can be suggested that the more complex system defects (dislocations, dislocation networks, dislocation loops, gas bubbles) which can trap gases is formed into the UO$_2$ fuel pellet with 11% of SFP. However, by to the characteristic emission of gas kinetic dependences type can be said that the gassing takes place by diffusion. The kinetic gas emission dependences at UO$_2$ samples with content 6,9% Gd$_2$O$_3$ also are having several peaks of the sample gas outlet: at the gas M2 there are five peaks, at the M28 - three peaks, and M44 - one peak. In this case M2, M28 and M44 peak is observed at one temperature - 1130 K. The presence of multiple peaks gassing also implies the presence of several places trapping gases in the UO$_2$ sample, and the existence of peaks gassing with varying mass (M2, M28, M44) at the same temperature 1130 K suggests that the yield of gases takes place in one way, possibly at gas bubbles chain at the grain boundaries. For samples with UO$_2$ AlGdO$_3$ 8,9% (6% Gd) also exhibits several peak gassing M28 are observed at the kinetic gas emission dependences what suggests the presence of several types defects by trapping gases. And the coincidence of peaks gassing M28 and M44 at a temperature of 850 K, suggests gas exit of the same mechanism, namely, at chain of gas bubbles. In this case the peak of gas output from sample has a steep look. For UO$_2$ with UO$_2$ AlGdO$_3$ with 8,9% (6% Gd) and 11% of SFP samples with kinetic dependence gassing (Figure 1f) are even richer spectrum peaks gassing as in the
number of peaks, and as the amount of generated gas mass (M2, M28, M44, M12 and M16). This implies that the sample has formed a complex system defects that can trap gases. The presence of the kinetic dependences of the gas emission with masses of the M12, M16 in Figure 1c and Figure 1f allows to suggest that precipitated mass M28 corresponds to CO, and the mass of M44 corresponds to CO$_2$. The kinetic dependence of the release of gas from the M2 corresponds to H$_2$.

The presence of sharp peaks of the emission of gas M28 and M44 (Figure 1e) in a narrow temperature range about 850 K, and M2, M28 and M44 (Figure 1d) in the temperature range of about 1130 K said suggests that the yield of gases occurs through the chain of gas bubbles at the grain boundaries. In another case, flatter curves indicate that the yield of gas occurs through the diffusion of atoms of the gas molecules. These atoms move to the surface of the material by grain boundary diffusion and then combined into the molecular compounds.

5. Conclusion

In this study the technique was perfected for carrying out experiments on the vacuum thermal desorption of gases from UO$_2$ fuel pellets, containing SFP and BNA. It was found that the thermal desorption spectrum of gases released depends on the concentration of SFP and BNA in UO$_2$ fuel pellet. This is due to the fact that the defects are created in the UO$_2$ samples which are effective gas traps to a sufficiently high temperature (1500 K). The gas composition released from the fuel pellet is the following: H$_2$, CO, CO$_2$.

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