High temperature dilatometry of simulated oxide nuclear fuel

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Abstract. High temperature dilatometry of model systems based on uranium dioxide with additives of burnable neutron absorbers both as Gd$_2$O$_3$ and as AlGdO$_3$, and fission products simulators (FPS) was performed. It shown that in some cases instead of high temperature samples shrinkage there is a sharp transition to the expansion, which is associated with an increase of the samples volume due to the formation of liquid phases. The beginning of a complex composition eutectic melting starts at temperatures from 1950 to 2250 °C in the uranium dioxide samples containing significant amounts of Al, Gd, and FPS. Thus, in the analysis of oxide nuclear fuel behavior at high temperatures should be considered that the formation of liquid phases is possible at a temperature of 1000 °C lower than a melting point of pure stoichiometric uranium dioxide if its initial composition became more complex.

1. Introduction
Currently, the VVER core forms from fuel assemblies containing oxide nuclear fuel based on enriched by U$^{235}$ up to 4 - 5% uranium dioxide with burnable neutron absorber (BNA) (for example Gd$_2$O$_3$) that allow compensate the initial reactivity, align the energy release in a core volume and maintain the temperature reactivity coefficient for a given level, thereby, increasing the degree of nuclear fuel burn-up. The nuclear uranium dioxide (UO$_2$) or UO$_2$ with gadolinium oxide (Gd$_2$O$_3$) fuel pellets also contain small amounts of dopants (D) in the form of Al and Si oxides. Presence of the alumina-silicate phase, gadolinium oxide and fission products accumulated in a pellets during the reactor operation which may form the substitutional solid solutions with UO$_2$ or distinct phases reduces the thermal conductivity, increases complexity of phase composition, and hence, increases the fuel temperature and makes possible a phase transitions. The presence of phase transitions is one of the limitations of nuclear fuel performance as they leads to changes in volume and properties that can have a significant impact on the reactor fuel assemblies (FA) performance. In this paper analysis of a phase transitions presence in the model nuclear fuel samples was decided to hold with a help of high-temperature dilatometry.

2. Samples
Studies were performed on the model nuclear fuel (MNF) samples produced on the basis of uranium dioxide (table 1). All samples contained D in the following estimated amounts 0.005% Al + 0.0025% Si + 0.006% Cr. As the BNA additive Gd$_2$O$_3$ which forms a solid solution with UO$_2$ or AlGdO$_3$ compound in the form of self-phase was used. To simulate the phase composition of the fuel with burn up additives of fission products simulators (FPS) was used which total amount is equivalent to the 11 at. % burn up. The type and content of the specific FPS are presented in table 2.
Samples containing D and BNA were prepared by mixing powders of the components with an intermediate briquetting and rubbing through a sieve. FPS addition was performed on the stage of preparation of uranium dioxide powder by means of joint co-precipitation to ensure uniform elements distribution. Subsequently the powders were pressed with a force of 250 MPa and sintered at 1750 °C in a dry hydrogen atmosphere for 3 hours.

Microstructure and composition studies of the model fuel samples individual phases was performed using a scanning electron microscope JEOL 6610LV, equipped with energy dispersion spectrometer (EDS) element analysis system.

The microstructure of the batch 1 samples represents a uniform grains distribution with an average size of 10 - 12 micrometers. Porosity in turn evenly distributed. Increased porosity observed in local areas with length from 30 to 100 micrometers. Outside of these areas there are individual pores or their absence. Gadolinium is unevenly distributed, but all located in solid solution in the UO\textsubscript{2} matrix.

The microstructure of the batch 2 samples shows unevenly size distribution of the uranium dioxide grain with Al\textsubscript{2}O\textsubscript{3} and AlGdO\textsubscript{3} inclusions. Part of Gd is dissolved in the UO\textsubscript{2}, thus released Al reacts with excess oxygen and form Al\textsubscript{2}O\textsubscript{3}. Alumina is unevenly distributed on the microsection surface. The matrix grain structure has a bimodal distribution with small (0.2 - 1.5 micrometers) and large (5 - 10 micrometers) grain. Fine grains are mainly formed around the second phase precipitates.

For the batch 3 samples mean grain size was 2 - 3 micrometers. Element analysis indicated that the uranium content in the matrix almost not varies from one grain to another, but the FPS addition distributed less evenly. Ba and Mo which must be allocated in separate phases, sometimes occur in solid solution. Electron microprobe analyzes allow us to conclude that the sample contains from three phases: fluorite phase having the average composition U\textsubscript{0.904}La\textsubscript{0.078}Y\textsubscript{0.004}Zr\textsubscript{0.014}O\textsubscript{2}, metallic phase based on Mo (Ru), and perovskite-type phase BaZrO\textsubscript{3}.

The microstructure of batch 4 samples is generally similar to batch 3, wherein AlGdO\textsubscript{3} is also in the form of self-phase precipitates.

Samples phase composition is also confirmed by X-ray data.

### 3. Equipment and methods

A high-temperature dilatometer DIL 402 E/8 «Pyro» (Netzsch, Germany) was used for the sample length measurements. The initial sample dimensions were measured with an electronic TESA micrometer calibrated with a set of standards.

To protect the graphite elements of dilatometer the test samples of MNF was placed in tungsten containers consisting of a tube with a diameter of 8 mm and two 1.5 mm thick spacers tight-fitting the container form the both sides. Use of the protective container imposes a limitation on the maximum temperature. The dilatometer is not suitable for measurements where graphite sample holder is in contact with the tungsten at temperatures above 2400 °C, so that the maximum temperature of the measurement was 2390 °C.
To avoid oxidation of samples, measurement of thermal expansion was carried out in an atmosphere of helium class is not worse than 5.0 (99.999%) with an additional heated MonoTorr gas filter.

The following temperature program was used: preheating to 1200 °C at a rate of 50 °C / min and then heating at a heating rate of 20 °C / min to a maximum temperature of 2390 °C, and then cooling without exposure in reverse order. Writing data of a linear displacement sensor while cooling was carried out to 800 °C.

4. Results and discussion

Figure 1 shows the dilatometric data for sample batch 1. It is seen that changes in the size of the sample at the initial stage of heating is due to thermal expansion. When approaching the sintering temperature of samples (1750 °C), the rate of expansion is slowing, due to densification. However, up to the maximum test temperature the expansion prevails over the shrinkage. At temperatures above 1956 °C small deflection starts, and at 2097 °C noise appears on the dilatometric curve which may be due to a liquid phase formation as will be shown below. It should be noted that the effects at these temperatures are repeated at the cooling of sample too, that indicates the constant composition of the phases formed. In the process of cooling the sample has a smooth decrease in its size, while in the high temperature part of the curve of expansion there spikes.

The microstructure of the batch 1 samples after the test remained virtually unchanged. It is still a solid solution with a grain size increased to 20 µm with reduced porosity and uniform distribution of Gd. The presence of other phases has not been observed.

According to the UO₂-Gd₂O₃ phase diagram [1] in equilibrium for a given gadolinium content it must be a solid solution without forming any other phases. A possible reason for the appearance of features on the extension curve at high temperatures can be a phase transitions associated with the formation of eutectic with low melting temperature in the solid-solution and dopants system. For example, according to [2] in the UO₂-Al₂O₃ system at temperatures above 1930 °C two immiscible phases can exist and the eutectic formed at this temperature (figure 2).

The reason that these phases are not detected in the analysis of the microstructure may be a very small amount of dopants used in the manufacture of nuclear oxide fuel.
Dilatometric curves obtained for the batch 2 samples, are shown in figure 3. On the curve 1, corresponding to the first heating shrinkage about of 4% associated with densification is visible. Unlike of the batch 1 samples in this case shrinkage dominates expansion since the 1695 °C but at 2220 °C dependence drastically reversed and the noise appears on the curve. Curve 2 in figure 3 corresponds to reheat of the same sample after re-polishing of its end surfaces. There is practically no traces of shrinkage, but some features are also appears close to above mentioned temperatures. Apparently a sharp transition from the expansion to shrinkage and noise appearance on the curves at 2220 °C is associated with an increase in the sample volume due to the formation of significant amounts of liquid phase. This confirms by the analysis of the microstructure on the end surfaces of the sample (figure 4), which showed the presence of the phase that was in the liquid state during tests. Element analysis shows that the melted phase is a eutectic type Al₂O₃ - UO₂ with small additions of gadolinium and there is almost no aluminum in the body of the matrix grains.

Thus, in the UO₂ + D + 8.9% AlGdO₃ system very small amounts of low temperature melting eutectics is formed at a temperature of about 1700 °C due to the high content of aluminum oxide [3] that results in a significant densification acceleration due to the liquid phase formation on the grains boundary. Further, the composition of this phase is complicating, and at a temperature of about 2220 °C the formation of considerable amounts of liquid phase leads to a noticeable increase in sample volume. The analysis of the cooling and reheating curves should take into account that the composition of the melting phase may be changed in the case of long-term measurements as well as
the part of the molten phase may evaporate at high temperatures, so the phase transition temperatures may vary.

Results of dilatometry of the batch 3 sample are shown in figure 5. The amount of shrinkage associated with densification of sample was 4.3%. Melting of significant amounts of the substance has not been detected.

The microstructure of batch 3 sample after the test is shown in figure 6. According to the quantitative element analysis the uranium and fission products simulators content is somewhat different in different areas: on the grain boundaries uranium content is slightly smaller, and additives - a few more. Some places with the metallic phase on the basis of molybdenum, ruthenium and tungsten were found on the sample surface that was in contact with tungsten spacer. The presented microstructure shows that, firstly, the process of thermal etching occurred, and part of the material was evaporated, and secondly, there are submelting traces on the surface, but liquid phase separation was not observed as in samples with a high aluminum and gadolinium content.

Figure 5. Temperature dependence of the batch 3 sample length (UO$_2$-11% FPS).

Figure 6. The microstructure of the batch 3 sample end face heated up to 2390 °C in a high temperature dilatometer.

Figure 7 shows the temperature dependence of the length change of the batch 2 and 4 samples, which composition differs only by the FPS presence. Curve for batch 2 is displaced downward for drawing readability, the ordinate axis corresponds to the curve for the batch 4. It can be seen that the introduction of FPS slightly increases the temperature of shrinkage over expansion predominance, but the temperature of a significant quantity of liquid appearance is reduced.

Figure 7. Temperature dependence of the batch 2 (UO$_2$ + D + 8.9% AlGdO$_3$) and 4 (UO$_2$ + D + 8.9% AlGdO$_3$ + FPS) samples length change

Microstructure analysis of the batch 4 samples end faces showed the presence of more complex eutectic composition containing Al$_2$O$_3$, UO$_2$, Gd and some FPS similarly to batch 2 samples.
5. Conclusion
1. It is shown that high temperature dilatometry can be used to detect phase transitions and to determine the liquid phase formation temperature in the oxide nuclear fuel samples with FPS and a BNA additions.
2. Shrinkage of samples mainly associated with they sintering occurs in the 1800-2000 °C temperature range.
3. In samples of uranium dioxide containing dopants and BNA in the form of Gd₂O₃ or AlGdO₃ at temperatures from 1950 to 2250 °C complex composition eutectics melting is observed both on the sample surface and in the bulk. Most low temperature melting phases composed mainly of Al, Gd and Si oxides and contained a small amount of uranium and FPS. Samples microstructure and composition element analysis of the individual phases after the tests confirmed the melting of some components of the structure.
4. The liquidus line has not been reached for all batches of samples in the presently investigated temperature range (T_max = 2400 °C), i.e. there always remains an unmelted frame of uranium dioxide or a solid solution based on it.
5. For the final interpretation of the results, it is beneficial to measure the melting points of the individual components of the structure.

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