Effect of the initial composition and irradiation on phase composition, transfer coefficients and solid state swelling of uranium-plutonium nitride

I A Deryabin, D Yu Lyubimov
FSUE «SRI SIA «LUCH», Podolsk, Russia
ivanderiabin@yandex.ru

Abstract. Nitride nuclear fuel is a perspective type of fuel for fast reactors. This type of fuel has a number of advantages, including high thermal conductivity, high density of uranium and low fission gas (FG) release together with moderate swelling. Modeling the change of fuel properties with burnup is of interest from the point of justifying the safe operation of fuel rods. Changes in the phase composition of the fuel during irradiation lead to a complex changes in its properties. This paper examine the thermal conductivity, diffusion coefficient of FG and solid-state swelling change in (U, Pu)N fuel with 20% plutonium content at various stoichiometry and oxygen and carbon impurities. The thermodynamic calculation of the phase composition was carried out with the help of the multi-purpose program complex ASTRA-4 in the burnup range 0-15% fima and temperature range 900-1800 K. The dependences of concentrations of phase inclusions from content of nitrogen and oxygen in the initial fuel are received. Their fraction can attain ~ 50% by volume at significant burnups and deviations from the stoichiometric composition. It is shown, that the main phase inclusion is U$_2$N$_3$, the concentration of which increases with the burnup and stoichiometric coefficient growth of the initial fuel. The increase in stoichiometry leads to a significant decrease in thermal conductivity, an increase in the diffusion coefficient of FG in fuel, and with increasing burnup this effect is enhanced. The calculated solid-state swelling of the fuel is in range 0,25-0,5% per burnup %, which is in satisfactory agreement with the literature data.

1. Introduction
Uranium-plutonium mononitride U$_{0.8}$Pu$_{0.2}$N is a perspective fuel for various reactors due to its properties, such as high thermal conductivity, high density, as well as low gas fission gas release and moderate swelling [1]. One of the main problems with the use of this fuel is its poor studied as compared to standard oxide fuel. Thereby, modeling of the properties of uranium-plutonium mononitride under irradiation is of particular interest.

The initial fuel contains impurities, main of which are oxygen and carbon. Depending on the amount in fuel oxygen can dissolve in fuel matrix, or be precipitated as a separate oxide phase [2]. Carbon is unlimitedly soluble in initial fuel matrix [3]. The stoichiometry of the fuel may not always be maintained in the homogeneity region, which for UN is in range 0.99-0.997 at 1400-3100 K (P$_{N_2}$ <700 mmHg) [4, 5, 6]. In the region of hyperstoichiometry, formation of sesquinitride (U$_2$N$_3$) can occur in fuel, which degrades the properties of fuel composition. Thus, depending on the initial
composition, fuel pellets may contain secondary phase inclusions, which affects the properties of fuel during operation.

Irradiation of uranium-plutonium mononitride by fast neutrons leads to formation and accumulation of fission products which, for example, lanthanides, zirconium and yttrium dissolve in the fuel matrix, changing its chemical composition and stoichiometry, or precipitates as separate condensed phases Ba$_3$N$_2$, Sr$_3$N$_2$, BaTe, LaSe, CsI, pure metals Mo, Ru, Te, intermetallides Rh$_2$Te$_2$, CeRu$_2$, PuRu$_2$, U (Ru, Rh, Pd), changing phase composition of the fuel [7]. The presence of oxygen in irradiated fuel tend to the appearance of such phases, as oxides of barium, strontium and complex oxides, carbon leads to the formation of carbides of barium, strontium, molybdenum and complex carbides [8]. It should be noted that these inclusions of separate phases are formed both inside fuel grains and at their boundary, changing heat and mass transfer coefficients in the fuel.

The present article is devoted to the study of the influence of the initial composition and irradiation on change in transport coefficients and solid-state swelling of U$_{0.8}$Pu$_{0.2}$N in temperature range 900-1500 K and burnup range 0-15% fima.

2. Thermodynamic modeling

Table 1 represents the initial characteristics of simulated samples of uranium-plutonium mononitride. Samples differ in both amount of impurities and coefficient of stoichiometry. Thermodynamic modeling was carried out with the help of multifunctional program complex ASTRA-4 [9] based on a universal thermodynamic method for determining equilibrium characteristics of arbitrary heterogeneous systems, based on the fundamental principle of maximum entropy. The properties of a number of oxides and carbides of uranium, plutonium, barium, strontium, rare earth elements and metals were added to program database. The calculation was carried out at a constant temperature and volume in temperature range 900-1500 K and burnup range 0-15% fima. The fuel rod free volume is 50% of fuel volume, while the fuel density is assumed to be 14.3 g/cm$^3$ [4].

Table 1. Composition of the simulated samples U$_{0.8}$Pu$_{0.2}$N$_2$, containing impurities of oxygen and carbon.

| Sample | Impurity of oxygen (wt. %) | Impurity of carbon (wt. %) | Concentration of nitrogen (wt. %) | Stoichiometry coefficient |
|--------|---------------------------|---------------------------|-------------------------------|--------------------------|
| 1      | 0,13                      | 0,13                      | 5,25                          | 0,995                    |
| 2      | 0,5                       | 0,13                      | 4,91                          | 0,995                    |
| 3      | 0,13                      | 0,13                      | 5,52                          | 1,05                     |
| 4      | 0,5                       | 0,13                      | 5,23                          | 1,05                     |
| 5      | 0,13                      | 0,13                      | 5,78                          | 1,1                      |
| 6      | 0,13                      | 0,5                       | 5,17                          | 1,05                     |
| 7      | 0                         | 0,5                       | 4,97                          | 0,995                    |
| 8      | 0                         | 0,13                      | 5,36                          | 0,995                    |
| 9      | 0,13                      | 0                         | 5,41                          | 0,995                    |
| 10     | 0,5                       | 0                         | 5,08                          | 0,995                    |
| 11     | 1                         | 0                         | 4,63                          | 0,995                    |
| 12     | 0,13                      | 0                         | 5,95                          | 1,1                      |
| 13     | 0                         | 0                         | 5,52                          | 0,995                    |
| 14     | 0,5                       | 0,25                      | 4,8                           | 0,995                    |
| 15     | 0                         | 0                         | 5,81                          | 1,05                     |

The results of thermodynamic modeling of phase composition under the condition of absence of irradiation show that the oxygen impurity leads to the formation of inclusions of UO$_2$, and concentration of such inclusions can reach ~ 7% by mass at a temperature of 900 K (sample 11, figure 1). As the temperature of the fuel increases, concentration of UO$_2$ decreases due to solubility of oxygen in fuel increases. Comparison of samples 1 and 9 shows that presence of a carbon impurity
results in absence of UO$_2$ in initial fuel due to expansion of region of homogeneity and increase in solubility of oxygen [3, 10]. The carbon dissolves in fuel matrix and does not form secondary inclusions. The use of initial fuel hyperstoichiometric composition leads to formation of U$_2$N$_3$, whose concentration can reach ~ 20% by mass at temperatures of 900-1200 K, as in sample 12 (figure 2).

In the process of burnup (table 2 data at burnup 9% fima) large amount of separate phase inclusions are formed, some of which are formed only in a certain range of burn-ups and temperatures. Some compounds, such as CsI, can be present in fuel in the liquid state. More details on the phase composition of UPuN fuel in the presence of burnup were described earlier [11]. It was found, that when burnup is greater than 1% fima, main phase inclusion, having the highest concentration, is U$_2$N$_3$.

| Condensed phase | Sample 1 | Sample 7 | Sample 9 | Sample 12 |
|----------------|----------|----------|----------|-----------|
|                | 900 K    | 1500 K   | 900 K    | 1500 K    | 900 K    | 1500 K   | 900 K    | 1500 K   |
| Solid solution | 88.9     | 90.5     | 92.2     | 92.2      | 85.8     | 85.8     | 64.3     | 64.4     |
| CeRu$_2$       | 0        | 0        | 0        | 0         | 1.2      | 1.16     | 1.17     | 1.16     |
| U$_2$N$_3$     | 3.43     | 2.64     | 0        | 0         | 7.8      | 7.75     | 29.2     | 29.1     |
| BaUO$_3$       | 1.13     | 1.1      | 0        | 0         | 0.95     | 0.95     | 0.95     | 0.95     |
| UPd$_3$        | 0.87     | 0.87     | 0.87     | 0.87      | 0.87     | 0.87     | 0.86     | 0.86     |
| Mo             | 0        | 0        | 0        | 0         | 0.68     | 0.68     | 0.68     | 0.68     |
| SrPuO$_3$      | 0        | 0        | 0        | 0         | 0        | 0        | 0.11     | 0.14     |
| Cs (liq.)      | 0.48     | 0.067    | 0.48     | 0.067     | 0.47     | 0.07     | 0.47     | 0.064    |
| Cs$_2$Te       | 0.45     | 0.45     | 0.45     | 0.45      | 0.45     | 0.45     | 0.45     | 0.45     |
| URh$_3$        | 0.36     | 0.36     | 0.36     | 0.36      | 0.36     | 0.36     | 0.35     | 0.35     |
| Tc             | 0.18     | 0.18     | 0.18     | 0.18      | 0.18     | 0.18     | 0.18     | 0.18     |
| CsI (liq.)     | 0.15     | 0.13     | 0.15     | 0.13      | 0.15     | 0.13     | 0.15     | 0.13     |
| Y$_2$O$_3$     | 0        | 0        | 0        | 0         | 0.006    | 0        | 0        | 0        |
| URu$_3$        | 0        | 0        | 0        | 0         | 0.015    | 0.03     | 0.011    | 0.021    |
| SrO            | 0        | 0        | 0        | 0         | 0.12     | 0.12     | 0.086    | 0.078    |
| Mo$_2$C        | 1.41     | 0        | 0        | 0         | 0        | 0        | 0        | 0        |
| Mo$_2$C$_2$    | 0        | 0.69     | 0        | 0         | 0        | 0        | 0        | 0        |
| BaC$_2$        | 0.052    | 0.063    | 0.48     | 0.48      | 0        | 0        | 0        | 0        |
| UMoC$_2$       | 0.32     | 0.18     | 2.55     | 2.55      | 0        | 0        | 0        | 0        |

Figure 2 shows burnup dependence of U$_2$N$_3$ concentration at 1200 K for samples 1, 2, 5, and 13. One can see that U$_2$N$_3$ concentration increases linearly with burnup, in contrast to UO$_2$, whose concentration drops noticeably with burnup (figure 1, samples 1-15). The presence of impurities reduces amount of formed U$_2$N$_3$ due to a decrease in the fraction of nitrogen.
Figure 1. Concentration of UO$_2$ as a function of burnup and impurity of oxygen.

Figure 2. Concentration of U$_2$N$_3$ as a function of burnup for samples 1, 2, 5, and 13.

The total volumetric concentration of the secondary phases can be conveniently considered as a function of the nitrogen concentration in the initial fuel (Figures 3). Arrows on this figure shows the increasing direction of labeled parameter. It can be concluded that with increasing nitrogen concentration, the total volume fraction of the secondary phases increases due to the formation of U$_2$N$_3$. At temperatures 900-1200 K this fraction can reach 50%. In the region of low nitrogen content (high impurity content) U$_2$N$_3$ is not formed and most of the phase inclusions are consist of oxides and carbides.

An increase in the carbon impurity leads to a decrease in fraction of secondary inclusions at any burnup, while a change in the concentration of oxygen impurity contributes differently to this value. Thus, in the absence of burnup, an increase in oxygen fraction leads to an increase in fraction of secondary phases due to the formation of UO$_2$. With burnup increasing, UO$_2$ decomposes and presence of oxygen impurity reduces amount of formed U$_2$N$_3$, which leads to a decrease in the total fraction of secondary inclusions in fuel.
3. **Determine the change in transfer coefficients.**

The change in the thermal conductivity coefficient due to the formation of phase inclusions was determined by the method given in [11]. Compounds CsI, Cs₂Te, Rh₃Te₂, BaTe, Mo₃C₂, La₂O₃, Nd₂O₃, Pu₂O₃, Ba₃N₂, BaC₂ and SrC₂ were excluded from calculation due to the lack of thermal conductivity literature data. Thermal conductivity of U₂N₃ was theoretically estimated from electrical resistance data at low temperatures [12] and was obtained by extrapolation. The change in thermal conductivity of samples from Table 1 due to the formation of phase inclusions, depending on nitrogen concentration in initial fuel at temperatures 900 and 1500 K and burnups 0 and 15.8% fima is shown in Figure 4. The thermal conductivity of pure UPuN [1] is obtained by equation (1):

\[
\lambda_{UPuN} = \left(1.37 - 1.6C + 1.142C^2\right)T^{0.31} \frac{1-P}{1+P}
\]

where C is fraction of Pu in fuel in relative units, P-porosity in relative units, T-temperature in K. It should be noted that thermal conductivity of the solid fuel solution (U, Pu, Zr, Nd, La, Y) NCO with burnup was also obtained in the same way. Thus, change in thermal conductivity due to soluble fission products is not taken into account; however, this effect can be noticeable [13].

The thermal conductivity of fuel decreases with burnup and an increase in the nitrogen concentration. This is due to increase in the concentration of the U₂N₃ phase in the fuel. Deviation of thermal conductivity of initial fuel from thermal conductivity of pure fuel is observed due to the presence of UO₂ (excess oxygen) or U₂N₃ (excess nitrogen). The maximum reduction in thermal conductivity reaches 25%. With increase in the oxygen and carbon impurities, fuel thermal conductivity reduces not significantly with burnup, which is due both to the lack of data on mentioned carbides and oxides, and to a decrease in fraction of U₂N₃.

Estimation the change in diffusion coefficient of inert gaseous fission products (Xe, Kr) in fuel matrix was carried out in a similar manner, proceeding from the similarity of processes of heat and mass transfer. The diffusion coefficient inside the fuel grain was considered, since it generally limits diffusion of gases in the fuel. As in the case of thermal conductivity coefficient, effect of soluble fission products was not taken into account.
Diffusion coefficient data for most of compounds under consideration are not available in literature. Diffusion coefficients of Xe in pure elements (Mo, U, Ag) and some compounds (CsI, UO$_2$) are much larger than in nitride fuel [11]. It was conservatively accepted that diffusion coefficient in all secondary inclusions for a given temperature range is much greater than in surrounding fuel matrix. Thus, diffusion coefficient will depend only on volume fraction of phase inclusions (Figure 5). This conservative estimate gives an increase in diffusion coefficient by 75% with a total volume fraction of secondary inclusions of 50% (sample 12).

Fig. 5. Increase of fission gas diffusion coefficient as a function of total fraction of secondary inclusions in fuel.

4. Evaluation of solid swelling

Solid swelling is one of components of general swelling of fuel along with gas swelling and, therefore, this value is important from the point of behavior predicting this fuel type during irradiation. Solid swelling is primarily associated with formation of individual phase inclusions. Below (see Figure 6) calculation of solid swelling for samples 2,3,4 and 6 at temperature range 900-1500 K is given.

An increase in stoichiometry coefficient leads to an increase in solid swelling by 0.15-0.2% in temperature range 900-1200 K, and an increase in carbon impurity leads to a notable decrease of this
parameter at 1500 K. The change in oxygen impurity has insignificant effect on solid swelling. In general, magnitude of swelling per 1 percent of burnup lies in range of 0.15-0.55%. Average value is 0.35%, which is in satisfactory agreement with literature data [14].

5. Conclusion
In this paper, effect of the initial fuel composition on transport coefficients and solid swelling of $U_{0.8}Pu_{0.2}N$ fuel in temperature range 900-1500 K and burnup range 0-15.8% was estimated. Thermodynamic modeling has shown that presence of oxygen and carbon impurities, as well as different initial stoichiometric composition, leads to formation of different phase inclusions with burnup increasing. Sesquinitride and uranium dioxide can be formed in initial unirradiated fuel. Estimates show that the change in thermal conductivity coefficient of the fuel and the diffusion coefficient of fission gas atoms upon irradiation due to phase inclusions formation is sensitive to the initial composition of the fuel. With a stoichiometry 1.1, these changes can reach 25% and 75% for thermal conductivity coefficient and diffusion coefficient of fission gas, respectively. The largest contribution in it was made by $U_2N_3$ and $UO_2$.

The evaluation of solid swelling showed that this value weakly depends on considered parameters. The average calculated swelling value is 0.35% per 1% burnup, which agrees well with experimental data.

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