Structural-phase state and creep of mixed nitride fuel

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Abstract. By the analysis of thermal creep data in conjunction with structural-phase state the most likely mechanisms of UN creep are considered. An equation relating the thermal and radiation creep of nitride fuel with such important parameters as plutonium content, porosity, grain size, the content of impurities of transition metals and oxygen, the carbon content has been suggested. At stationary operating parameters in reactor the creep of nitride fuel with technical purity is defined by the thermal component at mechanism of intergranular slip and by the radiation component, which plays a significant role at temperatures below 1100 °C. Both types of creep in a first approximation have a linear dependence on the stress.

1. Introduction
Mixed uranium-plutonium nitride is a promising fuel for nuclear fast reactors. Thermal creep of nitride defines its technological properties (e.g., sintering, hot pressing of pellets) and radiation creep determines characteristics of mechanical interaction of the fuel with cladding.

The complexity of the problem, in addition to the lack of systemic research on uranium nitride creep, is that the required range of parameters is outside the scope of the parameters that are usually studied experimentally. For example, for designers of fuel elements it's important to know the parameters of fuel creep at strain rates $\dot{\varepsilon}$ from 10^{-7} to 10^{-6} h^{-1} (rate of core deformation caused by swelling) on the basis of several years at temperatures typically below 1400 °C.

Creep deformation is quite a complex process that depends on many factors. To describe such multivariable processes the phenomenological approach was used. To reduce the uncertainty of the parameters in the equation for UN creep, the correlation between self-diffusion and creep has been used.

In this paper, based on general theoretical approaches the equation was suggested relating thermal and radiation creep of nitride fuel with such important parameters as plutonium content, porosity, grain size, the content of transition metal impurities and oxygen, the carbon content.

2. The correlation between thermal creep and self-diffusion
The equation of creep from common positions should contain in addition to traditional factors such as stress, temperature, grain size also other factors associated with structural-phase state of the material.

Data analysis at approximation of the thermal creep rate dependence on the stress σ and the temperature T by the Arrhenius equation $\dot{\varepsilon} \sim \sigma^n \exp(-E/kT)$ indicates that the uranium nitride corresponds to the general laws for the isomorphic compounds: monocarbide uranium [1-3] mononitrides Zr, Ti, and other metals [4].

In order to describe the apparent change of n (from 1 to 6), and E (from 0.4 to $1.2E_{SD}$) two mechanisms of thermal creep were selected for the range of assumed operating parameters of nitride fuel T<1400 °C (0.55Tm) and $\dot{\varepsilon} = (10^{-7}$-$10^{-6})$h^{-1}.

First mechanism is the traditional mechanism with power law on stress with $n \sim 4.5$ and creep activation energy E equal to that of the volume self-diffusion E_{vSD}. Second mechanism is the "linear" creep by grain boundary sliding, such as creep by Gifkins [8], with the activation energy equal to that for boundary self-diffusion $E_{bSD} \approx 0.5E_{SD}$.

Based on data analysis for the second mechanism were selected the following values: $n = 1$ and the dependence from characteristic grain size L_G^{-1}. However, this mechanism is also considered for the boundaries between the matrix and the precipitations of second phases.

On this basis, the interrelation between self-diffusion and thermal stationary creep is described by the equations:

$$\dot{\varepsilon}_0 = a_1\sigma^n \exp\left(-\frac{E_{vSD}}{kT}\right) + a_2\sigma\frac{\psi^0}{kT}\exp\left(-\frac{E_{bSD}}{kT}\right) \tag{1}$$

$$D_{SD} = D_{vSD} + \psi^0 D_{bSD} = b_1\exp\left(-\frac{E_{vSD}}{kT}\right) + b_2\psi^0\exp\left(-\frac{E_{bSD}}{kT}\right), \tag{2}$$

where: a_1, a_2, b_1, b_2 – constants, σ – stress, n – exponent (for pure compounds is usually in the range of from 4 to 5), ψ_0 – the total volume fraction of the boundaries, E_{vSD} and E_{bSD} – respectively the activation energies of volume and boundary self-diffusion of less mobile atoms, in our case U and Pu, k – Boltzmann constant, T – temperature in K.

Compilation of experimental data on the temperature dependence of self-diffusion shows that the data can vary by three orders of magnitude for nitride with different purity. Trend is the acceleration of self-diffusion in "dirty" mononitrides while reducing the apparent activation energy E and the exponent n.

In [8] self-diffusion coefficient of U (cm^2/s) in the single crystal of high purity UN is defined by the Arrhenius equation:

$$D_{vSD}^{Th} = 5.4 \cdot 10^{-3}\exp\left(-\frac{5.0}{kT}\right). \tag{3}$$

For uranium nitride the activation energy of boundary diffusion D_B is unknown, so the data for the isomorphic compound UC were used.

For UC measured ratio of the activation energies of the boundary and volume self-diffusion is 0.53 [12], which is within the interval of typical values for metal compounds $E_{bSD} = (0.5$-$0.6) E_{vSD}$.

Using the defined ratio for pre-exponential factors for volume and boundary diffusion of UC we obtain the probability boundary diffusion coefficient for UN in cm^2/s:

$$D_{bSD}^{Th} \square\ 1.4 \cdot 10^{-4}\exp\left(-\frac{0.53E_{vSD}}{kT}\right). \tag{4}$$

At temperatures below the temperature of (U,Pu)N dissociation (<1700 °C) Pu redistribution over the cross section of the fuel pellets was not observed. So, it was decided that the self-diffusion of U and Pu in the temperature range of interest differ insignificantly, and to describe the creep one may consider the average value for self-diffusion. To determine the average value depending on plutonium content C_{Pu}=Pu/(U + Pu) the linear correlation E_{vSD} in eV with the melting temperatures of PuN (2760 K) and the UN (3030 K) was used:

$$E_{vSD} = 5.0f_{Pu}, \quad f_{Pu} = 1 - 0.09C_{Pu}. \tag{5}$$

The total volume fraction of boundaries ψ^0 formed by grains and impurity precipitates of second phases and included in (2) can be represented as:

$$\psi^0 = \psi_{gb} + \psi_O + \psi_C + \psi_{tm}, \tag{6}$$

where ψ_{gb} – effective volume fraction of grain boundaries; ψ_O, ψ_C and ψ_{tm} – respectively effective volume fractions of boundaries formed by the precipitates of uranium and plutonium oxides, uranium carbides at (N + C) content above stoichiometry and transition metal compounds (TM) with nitrogen or uranium.

With an average width of the high angle boundaries $\sim$ 0.5 nm, the volume fraction of grain boundaries will be:

$$\psi_{Gb} = \frac{1.5 \cdot 10^{-3}}{L_G},\tag{7}$$

where L_G – characteristic grain size in μm.

To evaluate other components in ψ^0 it was assumed that the density of spherical precipitates of the second phase is about of 10^{10} cm^{-3} (the observed density of the oxide phase in UN at the oxygen content $\sim$ 1300 ppm [13]) and accepted effective width of the diffusion boundary between the phases with different lattice parameters $\sim$ 1 nm.

If we assume the solubility limit of oxygen in the UN $\sim$ 650 ppm [13] then the volume fraction of the boundaries formed by dioxide precipitates will be:

$$\psi_O \approx 1.1 \cdot 10^{-7}(C_O - 650) \text{, at } C_O < 650 \text{ ppm } \psi_O = 0.\tag{8}$$

Since carbon is soluble in the UN, we must take into account the concentration of carbon above stoichiometry (N + C) / U = 1 which leads to the formation of higher carbide. With the same parameters for UC$_2$ as for the oxide phase, the volume fraction of the boundaries at the carbon content above the stoichiometry C_C^* in ppm will be:

$$\psi_C \approx 0.8 \cdot 10^{-7} C_C^*.\tag{9}$$

Contamination of transition metals TM mainly occurs by elements belonging to the industrial metal equipment (Fe, Cr, Ni, refractory metals) and ceramic materials (Al, Si, etc.). The volume fraction of diffusion boundaries formed by precipitates of TM (C_{tm} is concentration in ppm) is estimated by relation:

$$\psi_{tm} \approx 0.5 \cdot 10^{-7} C_{tm}.\tag{10}$$

3. The equation for thermal creep of uranium mononitride

In general terms the equation of thermal creep for uranium nitride when correlated with the activation energy of self-diffusion has the power and linear components:

$$\dot{\varepsilon}_0^{Th} = a_1 \sigma^{(4.5+\Delta n)} \exp\left(-\frac{(5.0+\Delta E)f_{Pu}}{kT}\right) + a_2 \psi^0 \frac{\sigma}{kT} \exp\left(-\frac{2.65 f_{Pu}}{kT}\right)\tag{11}$$

$$\dot{\varepsilon}^{Th} = \dot{\varepsilon}_0^{Th} \exp(0.2P),\tag{12}$$

where Δn and ΔE – respectively change in the exponent and activation energy with the dispersion hardening by impurity phases.

The porosity factor P, % in (12) is typical for sintered ceramic materials within the porosity of up to 20% [14].

Coefficients in (11) are determined by correlation with refractory ceramic: $a_1/(a_2\psi_0) \sim 10^2$ (for $\psi_0 \sim 10^{-3}$, $a_1/a_2 \sim 0.1$). For $\dot{\varepsilon}^{Th}$ in h^{-1} and σ in MPa the coefficients a_1 and a_2 has the order of 10^6 and 10^5 respectively.

In the dispersion-strengthened carbides and nitrides the activation energy may increase on (1-2) eV, while the exponent n reaches the value of 6-7.

Figure 1 shows a comparison of calculated (P = 10%, L_G = 10 μm) and experimental data. As can be seen from figure 1b dispersed phases formed by impurities may have both reinforcing and softening effect (indicated by arrows in figure 1b).
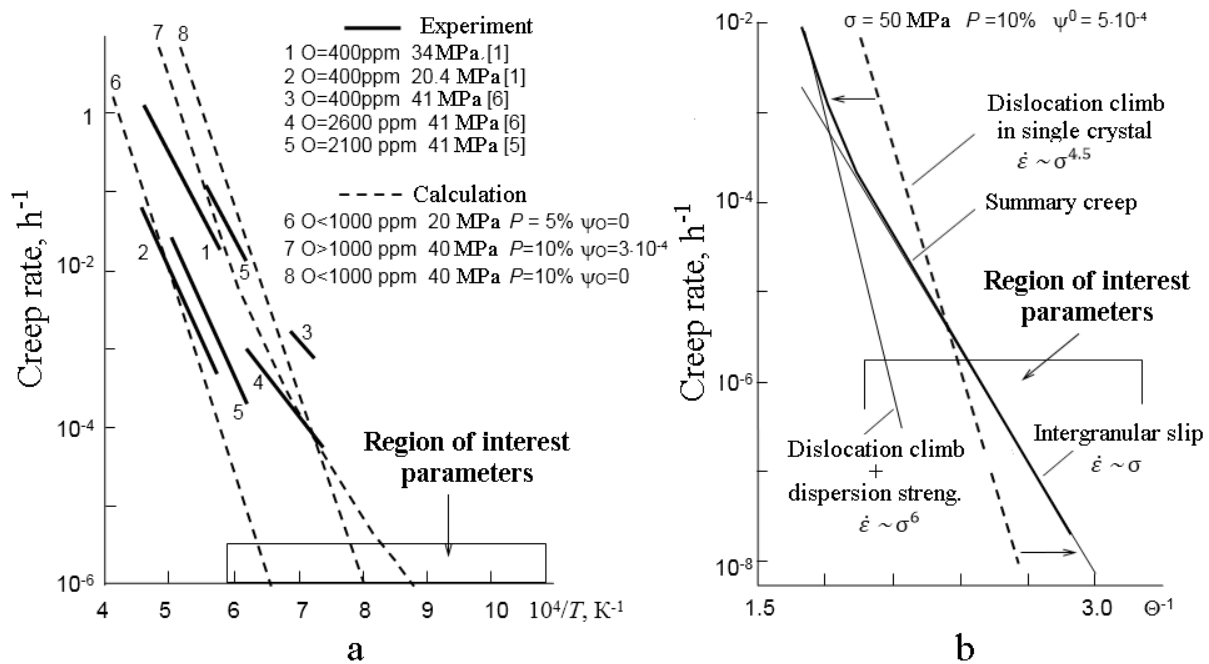
Figure 1. Comparison of the calculated and experimental data on thermal creep of UN (a) and deformation mechanisms (b) depending on the homologous temperature $\Theta = T/T_m$.

4. Comparison of thermal and radiation creep

For determining the contribution of thermal creep under stationary operating conditions of nitride fuel, it's sufficient to compare the linear component of thermal creep $\dot\varepsilon^{Th}$, defined by parameter ψ_0, with radiation creep $\dot\varepsilon^{R}$, determined by the fission rate G.

According to data the dependence of radiation creep $\dot\varepsilon^{R}$ in h^{-1} from fission rate G in cm^{-3}s^{-1} and σ in MPa for «dirty» UN ($P = 7\%$, $UO_2 \sim 10$ vol.%, $L_G = 15$ µm, the estimated value $\psi^0 \sim 7{\cdot}10^{-4}$) taking into account (12) can be written as:

$$\dot\varepsilon^{R} = (2.5 - 3.3)\cdot 10^{-22} G\sigma \exp(0.2P). \tag{13}$$

Linear thermal creep component, according to (11) and (12) is defined by:

$$\dot\varepsilon^{Th} = 10^5 \psi^0 \frac{\sigma}{kT} \exp\left(-\frac{2.65}{kT}\right)\exp(0.2P). \tag{14}$$

Figure 2 shows the estimated radiation and thermal creep of UN of nitride samples with mentioned above characteristics (a) and shows the probable temperature dependence for nitride fuel under parameters of operation in reactor (b).

In the range of interests parameters ($T < 1400$ °C, $\sigma < 50$ MPa, $\psi_0 \sim 3{\cdot}10^{-4}$) creep of nitride fuel will be determined by the thermal and radiation components both having the linear stress dependence.
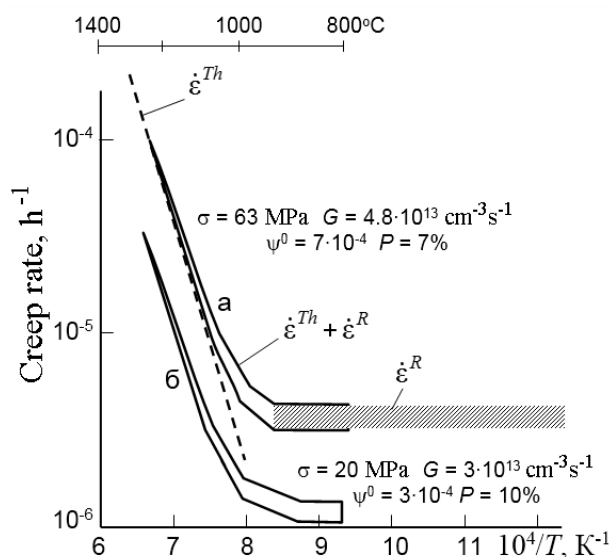
Figure 2. Comparison of the calculated thermal (dotted line) and radiation (shaded area [15]) creep of UN.

5. Conclusions

Data on thermal creep of mononitride fuel can be described by two components: the creep caused by climb of dislocations - the power law creep, and creep due to intergranular slip - linear creep. The temperature of transition from one creep to another depends on the nitride structure and the level of stress (strain rate).

For a correct forecast of thermal creep under the proposed approach the following minimum set of data is required: plutonium content, porosity, grain size, the content of impurities of transition metals and oxygen, the carbon content above stoichiometric ratio (N+C)/(U+Pu) = 1.

At stationary operating parameters of nitride fuel ($T < 1400$ °C) creep is defined by a thermal component with the mechanism of intergranular slip and radiation component, which is beginning to play a significant role at temperatures below 1100 °C. Both types of creep in the first approximation should have a linear dependence on stress (strain rate from 10^{-7} to 10^{-6} h^{-1}).

Acknowledgements

References

[1]   Routbort J L and Singh R N 1975 *Journal of Nuclear Material* **58** 78
[2]   Tokar M 1971 *High Temperature Compressive Creep and Hot Hardness of Uranium-Plutonium Carbides* Report LANL LA-4704
[3]   1981Gemlin Handbook of Inorganic Chemistry. *U Uranium: The Behavior of Uranium Fuels in Nuclear Reactors*. Springer Verlag Berlin
[4]   Zubarev P V 1985 *Zaroprochnost faz vnedreniya* (*Hot strength of interstitial phases*). Moscow. Metallurgia (in Russian)
[5]   Masaaki, Uchida, and Michio 1973 *Journal of Nuclear Materials* **49** 91
[6]   Fassler MH et al. *Compressive Creep of UC and UN*. 1965 US Report PWAC-482. Part 1
[7]   Kutty T R G, Kaity S and Basak C B, 2012 *Nuclear Engineering and Design* **250** 125.

[8]   Gifkins R C 1968 *Journal of the American Ceramic Society* **51** 2

[9]   Bradbury M H, Michael H and Matzke Hj 1978 *Journal of Nuclear Materials* **75** 68

[10]   Bradbury M H and Matzke Hj 1980 *Journal of Nuclear Materials* **91** 13

[11]   Singh R N 1976 *Mechanical-property and diffusion data for advanced carbide and nitride fuels.* Argonne National Lab. USA. Report ANL-AFP-15

[12]   Delvoye F 1988 *Etude des nitrudes d'uranium et de plutonium a faibles teneures en oxigene et en carbone*. Rapport CEA (France), CEA-R-5434

[13]   Bakynov V S 1994 Refractories **35** V 10 317

[14]   Hayes S L et al. 1989 *Development of creep rate porosity correction factor*. Report Texas A&M University ANFL-10-O