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Formation of Nanostructures in UO_2 Fuel at High Burn-ups

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In the present paper it is assumed that above a limiting value of fission fluency (burn-up) a more intensive process of irradiation induced chemical interaction occurs. A significant part of fission gas product is thus expected to be chemically bounded in the matrix of UO_2 fuel. The fission gas atoms substituting, for example, uranium atoms in the crystallographic lattice can form weak facets. At a certain saturation condition, division of the grains can occur at the weak facets and the increase in fission-gas-products release may be expected. The fact that the process of grain division for high burn-ups (70–80 MWd/kgU) forms an extremely fine structure up to a temperature as high as 1100°C and simultaneously the observed decrease in fission gas concentration in the fuel supports this concept. The analysis of fission gas concentration change due to the formation of nanostructures in UO_2 fuel at high burn-ups in terms of total surface area change in a function of burn-up and knock-out process is presented.

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1. Introduction

A microstructure of UO_2 fuel resulting from steady state irradiation to high burn-up consists of several typical zones [1]. In the centre of the fuel rod, a zone is formed, which is characterised by some grain growth. Proceeding towards the fuel surface, there follows a zone with a morphology very similar to the original structure. Further towards the fuel surface is a zone with a typical thickness of 100–200 μm, where very small grains of less than 400 nm diameter exist. The experimental data show that the distribution of the sub-grain sizes appear to begin from 60 nm. So, the subdivision process is formed in the cold part of a fuel rod.

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Since the mechanism leading to the fabrication of the nanostructures in the UO_2 fuel is not yet fully understood, this paper focuses on a better description of the conditions of the fabrication of the nanostructures in the UO_2 fuel.

2. Experimental data presented in the literature

The onset of the grain subdivision process is observed at a burn-up approximately from 60 MWd/kgU to 75 MWd/kgU [2].

For fuel cross section average burn-ups below $\approx$ 60 MWd/kgU, this structure is confined to an area about 150 to 200 μm wide, though it can extend much deeper into the UO_2 pellets at a high burn-up (e.g. 1.6 mm depth at 74 MWd/kgU cross-sectional average burn-up) [3].

It has been confirmed by numerous measurements performed by electron probe microanalysis (EPMA) that xenon depletion of the matrix occurs, due to athermal release of xenon from the UO_2 grains [1, 2, 4]. The experimental results indicate that nearly all xenon that has been swept out of the original grains is contained in the newly formed fission gas pores [2, 5, 6].

The grain subdivision is observed by transmission electron microscopy (TEM) using small fuel fragments extracted from the fuel rim, and by taking scanning electron microscopy (SEM) images of fractured fuel surfaces. The sub-grain formation is often particularly clearly visible on the inner surfaces of pores or large fission gas bubbles [3, 7] (see Fig. 6. of Ref. [3]).

In a histogram of the measured sub-grain sizes as revealed by TEM shown in Fig. 3. of Ref. [3] a distribution of sub-grain sizes is presented which appears to be bimodal with peaks at $\approx$ 160 nm and 300 nm.

The local xenon concentrations in the UO_2 matrix measured by EPMA as a function of the local burn-up is presented in Fig. 4 of Ref. [2]. Included are data from different reactors (BWR, PWR, Belgim BR-3 reactor) for fuel from different vendors, fuel of different design, and xenon measurements from different labs. These differences explain most of the scatter of the reported Xe concentrations [2].

It is interesting to remark that even though EPMA indicates only a few retention of fission gas in the restructured grains, TEM examinations of fully transformed material still reveal a large amount of gas within the restructured grains. Indeed, as shown in Fig. 10 of Ref. [8], still plenty of gas bubbles are still observed within the small grains (150–300 nm). These features can remain at burn-ups far beyond the rim-transformation threshold (e.g. $>$ 80 MWd/kgU) [8].

3. Analysis of the experimental data

According to the experimental data presented above, the nanostructure begins to form at the local burn-up threshold of 60 MWd/kgU, when the local temperature is sufficiently low.

At present it is not known what this temperature limit is [2].

The experimental data showing that the re-crystallised grain region is adjacent to the sub-divided grain region [9] enables us to infer that the re-crystallization temperature for the grains at a high burn-up above 60 MWd/kgU assigns the temperature below which the polygonization can occur.

In order to obtain more precise information about the temperature limit below which the polygonization process occurs we have concentrated on the threshold temperature of the UO_2 grain growth.

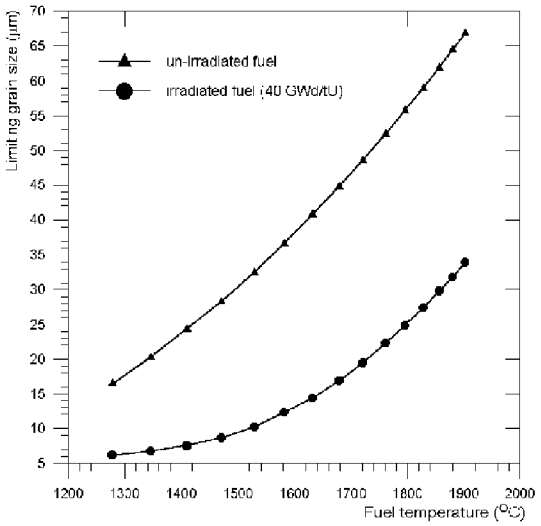

Fig. 1. Limiting grain size in a function of fuel temperature for the un-irradiated and the irradiated fuel (experimental data taken from [10]).

According to the experimental data presented by Bagger et al. [10] much smaller values for the limiting grain size must be assumed at higher burn-up than in the Ainscough grain growth model [11]. Figure 1 presents the comparison of limiting grain size in a function of temperature for the unirradiated fuel and the irradiated fuel (40 MWd/kgU). The experimental results show that while decreasing the temperature the limiting grain size for burn-up of 40 MWd/kgU decreases asymptotically to 5 μm and practically reaches the value at the temperature of about 1000°C.

Based on these assumptions we have been able to modify the constant of limiting grain size D_m

$$D_m = 2.23 \times 10^3 \exp\left(-\frac{7620}{T - 520\left[1 - \exp\left(-\frac{B}{8400}\right)\right]}\right) + 5\left[1 - \exp\left(-\frac{B}{8400}\right)\right] [\mu\text{m}], \tag{1}$$

where B is the burn-up in MWd/tU, T is the fuel temperature [K] in the Ainscough differential equation of grain growth which describes the grain growth kinetics.

Assuming that the Vitanza curve [12] describes the change of uranium dioxide re-crystallization temperature it was inferred that the grain growth rate depends on the burn-up in the way given by the best fit of the grain size change with the curve [13].

From Eq. (1) it follows that the higher the initial grain size is, the higher is the threshold temperature of re-crystallization of the grain.

The process of strong binding of the fission gas fragments with the irradiation defects is described in the literature as a process of chemical interaction with UO_2 [14]. It is further assumed that the vicinity of the fission fragment trajectory is the region of intensive irradiation-induced chemical interaction of the fission gas products with UO_2 [14].

It seems to be natural that the chemically bounded fission gas atoms substituting, for example, an uranium atom in the crystallographic lattice can form weak facets. At certain saturation conditions subdivision of the grains can occur and the increase in fission gas products release may be expected. So it can be stated that either re-crystallization or subdivision have to occur in the saturation circumstances.

Considering the formation of the weak facets in crystallographic lattice of the grain due to substitution of the uranium atom by the fission gas atom, we have to keep in mind that the grain consists of a large number of atoms. Some of the gas atoms can become noble gas atoms again and thus to be no longer chemically bounded with the UO_2 fuel, electrical neutrality is restored and in consequence their chemical inertness is restored. By becoming noble gas atom again, fission gas products create weak sites in the uranium dioxide matrix.

The higher is the concentration of gas atoms immobilised in the uranium dioxide matrix, the more "weak" crystallographic sites are created. When the threshold gas atom concentration is exceeded, the weak sites can form new grain boundaries. We assume that the weak sites are formed preferentially in their neighbourhood and in consequence the weak facets in the crystallographic lattice lead to the formation of new boundaries and the process of grain subdivision begins.

As can be seen from Fig. 4 in Ref. [2] the threshold Xe concentration, when the subdivission process begins, lies in the range from 0.65 wt% to 1 wt% which corresponds to a burn-up of 50–80 MWd/kgU. The threshold Xe concentration is defined as the concentration begins to deviate from the generated Xe concentration. Continuing the irradiation, a decrease in Xe concentration is observed until it approaches equilibrium at a burn-up of about 120 MWd/kgU. This is an indirect evidence that the process of polygonization continuous until the equilibrium between the generated and released Xe is reached. In consequence, if we treat for simplicity each grain separately then for a certain grain the polygo-

nization process begins at 50 MWd/kgU and for another grain the process may begin at 120 MWd/kgU.

If we consider all the grains in the entire pellet, it can be expected that a certain amount of grains begin to become subdivided at different burn-ups in the range of 50 to 80 MWd/kgU. And this we assume as the threshold burn-up for the pellet.

This arguing is supported by the experimental observation that the transformation of the original grain structure is a heterogeneous process [2]. At the depth of 1.6 to 1.65 mm from the fuel surface, grain subdivision occurred only apparently at very few preferential sites [3].

Simultaneously with the process of polygonization, the increase in local porosity [8] and the decrease in local density [15] in a function of burn-up occurs, which leads to the increase in total surface area.

Keeping in mind that the fission gas release from the UO_2 grains during the polygonization is athermal [1, 2, 4] we infer that the knock-out release process is a significant one. So the same processes take place in the transformed fuel as in the original fuel, with the difference that the total surface area is so big that the whole fuel element can be treated as a one affected by the knock-out process. The gas atoms will not be accumulated in the bulk of the fuel but their concentration will reach a certain saturation level since the fission gas release rate will be equal to the production rate according to the defect trap model [16–19].

For the steady state and for a step function of the fission rate, the solution of the adequate equations of the defect trap model [16–19], gives the following expressions for the concentration (M_r) of gas atoms immobilised in the lattice and the concentration of bubbles (N_{tr}):

$$M_r = \frac{\beta}{\alpha_1 \left[\left(\frac{1}{\alpha_2} - \frac{g_3 g g_1}{\alpha_2 (g_2+g_3)^2} \right) - 1 \right]}, \tag{2}$$

where $\alpha_1,\ g,\ g_1,\ g_2,\ g_3$ — constants, $\alpha_2 = 1 - g g_1/(g_2 + g_3)$.

To calculate the concentration of retained Xe for the stable state when the equilibrium between the generated and released Xe is approached, the following appropriate values for the constants were used: $\alpha_1 = 10^{-19}$ cm^3, $g = 10^{-18}$ s^{-1}, $g_1 = 10$, $g_2 = 10^{-15}$ cm^3, $g_3 = 10^{-17}$ cm^3. Some comments on the constant parameters estimation were presented previously [16, 17]. The xenon fission yield is approximated by 0.268.

With this values of constants, using Eq. (2), we calculated that the xenon concentration is 2.67×10^{20} atoms/cm^3 which corresponds to about 0.5 wt% of Xe concentration. This theoretical result is very close to the experimental result of 0.25 wt% given by Lassmann et al. [2].

4. Conclusions

We are convinced that the grain growth and the grain subdivision cannot be considered separately.

Since the re-crystallization temperature of the fuel determines at the same time the temperature of polygonization, it is deduced that either re-crystallization or grain subdivision have to occur in the burn-up saturation circumstances. The grain growth excludes the polygonization and vice versa.

The temperature below which the nanostructure can be formed depends on the initial grain size. The higher is the initial grain size, the higher is the threshold temperature of re-crystallization and polygonization.

Above the limiting value of fission fluency a significant part of fission gas products are chemically bounded in the UO_2 matrix. At certain saturation conditions the chemically bounded fission gas atoms substituting, for example, the uranium atoms can restore their closed "shell electronic" structure due to "the electrical spike" created by fission fragments and in consequence can form weak facets where the subdivision can take place.

The process of grain growth and the process of grain subdivision are the processes of purging the contaminated lattice to some extent.

The calculated and the experimental results of fission gas concentration in the fuel after polygonization are very close, which certainly offers support for the concept and the interpretation presented in this paper.

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