Journal of Nuclear Materials 256 (1998) 189–196

High burn-up rim structure: evidences that xenon-depletion, pore formation and grain subdivision start at different local burn-ups

J. Spino [a,*], D. Baron [b], M. Coquerelle [a], A.D. Stalios [b]

[a] *European Commission, CEC Joint Research Centre, Institute for Transuranium Elements, P.O. Box. 2340, D-76125 Karlsruhe, Germany*

[b] *Electricité de France, Direction des Etudes et Recherches, Centre Les Renardières, BP1, 77250 Moret Sur Loing, France*

Received 7 January 1998; accepted 3 April 1998

Abstract

An experimental LWR fuel with high ^{235}U enrichment (8.6%) and large UO_2 grain size (15–20 μm) was analysed by optical microscopy, SEM and EPMA. Although the high burn-up reached (69.8 GWd/tM), the porosity growth in the rim zone was found equivalent to a standard LWR fuel with barely 40 GWd/tM burn-up. Also, the grain subdivision associated with the rim structure was absent or scarcely visible around the pores of the outermost periphery, being evidenced that the three typical features of this structure, i.e. Xe depletion, pore formation and grain subdivision, did not appear simultaneously, but sequentially in this order as the local burn-up increased. According to the results, the use of higher ^{235}U enrichments in LWR fuels may help to shift all these steps to higher local burn-ups, whereas the grain size of the UO_2 matrix may play only a secondary role in the initiation of these processes.

1. Introduction

Since a number of years a program is being conducted at the Hot Cells of the Institute of Transuranium Elements in co-operation with the industry, in order to characterise the structural changes and the thermal–mechanical behaviour of PWR fuels irradiated to high burn-ups. The data acquired up to the present show that the structural changes occurring principally at the pellet periphery (rim zone) [1] do not worsen but improve the mechanical properties of the fuel, with an expected better behaviour under pellet–cladding interaction conditions [2,3].

However, a limitation at the end of life of the fuel in reactor appears with regard to the fission gas release, as indicated by the steep increase of the fractional release rates at average burn-ups above ≈60 GWd/tM [4]. This gas release enhancement is partially attributed to the elevation of the fuel temperatures due to the lower thermal conductivity of the rim zone [5] (larger porosity and fission product content [6]) and partially to the extension of the restructured zones into fuel regions where thermally activated processes begin to operate [4]. Thus, it is of technological importance to determine via which process the gas in the 'cold' fuel regions is incorporated to pores and under which conditions this gas can escape to the plenum.

SEM and TEM observations of the high burn-up structure indicate a predominant feature of ≈0.5–1 μm pores surrounded by submicron grains [1,7,8], with part of these grains being free of dislocations and gas bubbles [8,9], part showing intragranular and intergranular bubbles [7,10], and part of the surrounding material presenting still numerous tangled dislocations and intragranular bubbles [7,9]. Also, TEM observations showed that the coarsened bubbles are overpressurised, according to the dislocation punching observed around them [7], and SEM observations confirmed that towards the pellet interior the restructured zones localise on the boundaries of original matrix grains [2,11].

* Corresponding author.

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PII: S0022-3115(98)00060-9

With part of the above information the authors of Refs. [7,9] developed a model for the 'rim structure' where first undistorted and bubble free sub-grains (nuclei) are formed, whereupon coarsened bubbles (pores) are built up via sweeping of the neighbouring gas (atoms and bubbles) during nuclei growth [12]. This model [12], or any other assuming a grain subdivision-aided Xe migration [13,14], would have the implication that matrix Xe depletion would be restricted to restructured areas of the fuel. However, early EPMA examinations of high burn-up fuels indicated that the characteristic Xe depletion in the rim zone was associated to only a local porosity increase with no reference to grain restructuring [15], or, when grain subdivision was detected, that Xe depletion extended deeper into the fuel than the microstructure changes did [16].

An alternative description to Ref. [12] was given in Ref. [1] and also in Refs. [17,18] interpreting the grain subdivision as a possible consequence of the formation of pressurised gas bubbles (pores) via a loop-punching mechanism. However, at the time of writing the paper [1] no evidence was available about the formation of rim pores without grain subdivision, or vice versa [1]. In the present work, dealing with an experimental LWR-fuel with high initial ^{235}U enrichment and a fabrication grain size of UO_2 larger than usual, the evidence is supplied that the grain subdivision step is definitely preceded by pore formation, with the confirmation that this last event starts after matrix Xe depletion has been detected by EPMA.

2. Experimental

2.1. Fuel description

The fuel cross section analysed corresponds to the maximum power position of a test fuel rod irradiated in the BR3 reactor, Belgium, under simulated LWR conditions. The fuel material was UO_2 with an initial ^{235}U enrichment of 8.6%, a fabrication density of 10.32 g/cm^3 and a fabrication grain size of 15–20 μm. The cladding tube was a recrystallised Zry-4 type alloy supplied by the company Vallourec, France. Conditions of the cladding treatment were 2h/575°C. Nominal pellet diameter, cladding outer diameter and cladding wall thickness were, 8.03 mm, 9.47 mm and 0.65 mm, respectively. The He filling pressure was 1 bar. According to reactor data, the estimated average pellet burn-up of the cross section studied was 69.8 GWd/tM. The measured average cross section burn-up via integration of the Nd concentration profile (EPMA) (see Fig. 4) was 68.5 GWd/tM. The maximum linear powers experimented by the fuel rod were 300–312 W/cm during the irradiation period corresponding to the burn-up range 18.2–27.4 GWd/tM. The maximum centreline temperatures have been 1320°C during the first cycle (34 GWd/tU), 1000°C during the second cycle (55 GWd/tU) and 1100°C during the last cycle. Then, apart the first cycle, the fuel operated with temperature gradients representative of LWR operating conditions.

2.2. Results

Fig. 1 shows a characteristic optical micrograph obtained for this fuel cross section after 15 min ion etching. Remarkable features of the micrograph are the retention of the original fuel-grain structure even up to the edge fuel grains attached to the interaction layer with the cladding, and a predominant intragranular porosity, starting at approximately $r/r_0 = 0.96$ (i.e. ≈160 μm from the pellet edge) and growing in density towards the pellet edge (Fig. 1). As important for the discussion of formation mechanisms, the reader is requested to note in Fig. 1 the lack of any particular accumulation of pores on smaller grains, in other words the lack of a manifest

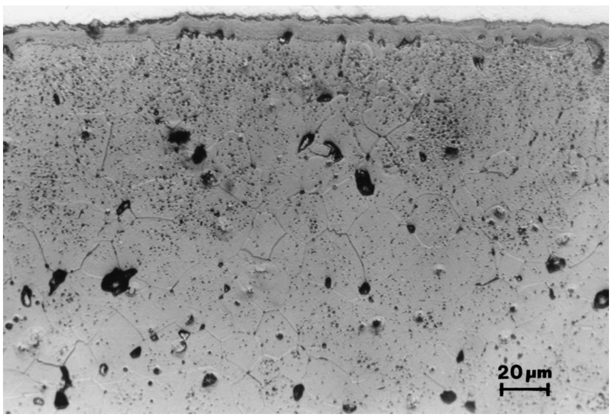

Fig. 1. BR-3 fuel microstructure at the pellet periphery. Ion-etched cross-section, fuel radius: $r_0 \cong 4110$ μm.

'resistance' of the larger grains to pore development, and the absence of noticeable accumulation of pores on grain boundaries. Inspection of the whole pellet circumference under the microscope led to similar results as in Fig. 1.

In Fig. 2 the same features of Fig. 1 can be appreciated from the perspective of a SEM-fractography that covers the first 100–110 μm of the fuel at the pellet edge. It is important to point out again the lack of any particular accumulation of pores around the grain boundaries, as indicated in grains broken in transgranular mode, for instance just in the first grain attached to the fuel–cladding interaction layer (left side in Fig. 2(a) and magnification in Fig. 2(b)). In the opposite sense, at a distance of few fuel-grains from the pellet edge, a depletion of pores at the grains periphery was noticed (Fig. 2(a) right side and Fig. 2(c)). This last fact can be seen also in some grains of Fig. 1.

It should be noted that in the magnified image of Fig. 2(b), albeit retention of the original grain structure, it is possible to appreciate an incipient grain subdivision (submicron size range) around the pores, in the same form as described for commercial LWR fuels in regions just beside the fully restructured rim (decreasing pore density) [1,2]. However, it is to remark that the incipient grain-subdivision observed around pores rapidly vanishes within a distance of few grains from the pellet edge (Fig. 2, note vanishing restructuring around pores from $r/r_0 \leqslant 0.99$ (Fig. 2(b)) to $r/r_0 \approx 0.98$ (Fig. 2(c))). In such a small radial interval, the absence of incipient grain restructuring cannot be attributed to thermal recovery effects.

Fig. 3 shows the porosity profile corresponding to Fig. 1 and equivalent micrographs (optical microscopy and SEM), obtained by quantitative metallography. The figure compares the values of the present fuel with those of a standard LWR fuel with an average burnup of ≈40 GWd/tM according to previous data [1,2] and further determinations in this work on enlarged optical micrographs. Characteristics of this LWR fuel material were an initial ^{235}U enrichment of 3.5% and a fabrication grain size of UO_2 of 7–10 μm [1,2]. It is shown that a more or less similar porosity gradient was established for both fuels, with the onset of the porosity growths at $r/r_0 \approx 0.96$, although for the present

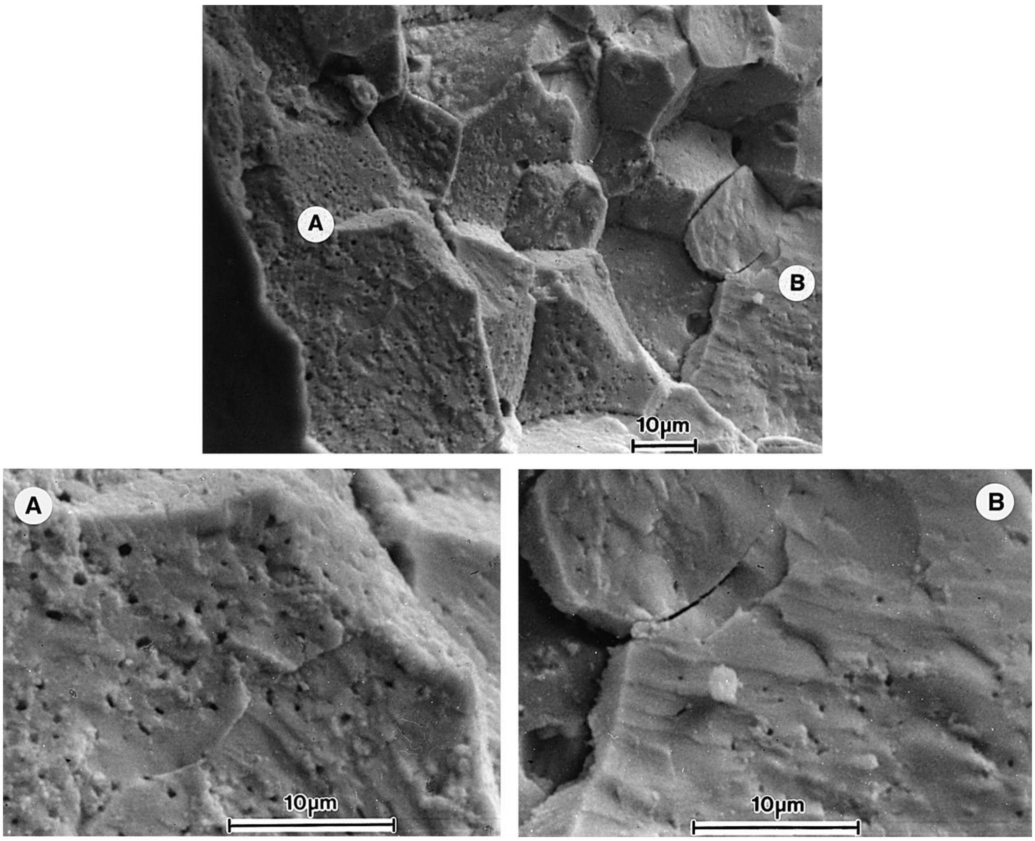

Fig. 2. SEM-fractography of BR3-fuel at the pellet periphery. Fig. 2(a): general view; Fig. 2(b),(c): regions A and B of Fig. 2(a) at higher magnification. (The dark zone at the left side of Fig. 2(a) corresponds to the fuel–clad interaction layer.)

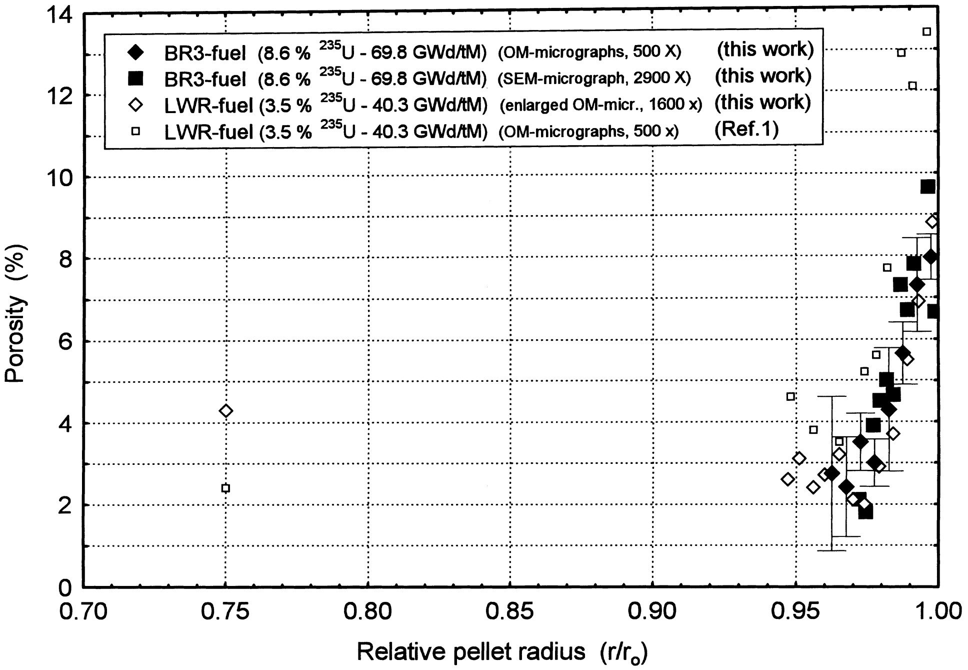

Fig. 3. Porosity profiles obtained by quantitative metallography. Comparison of BR3 fuel (69.8 GWd/tM) with a LWR fuel (40.3 GWd/tM).

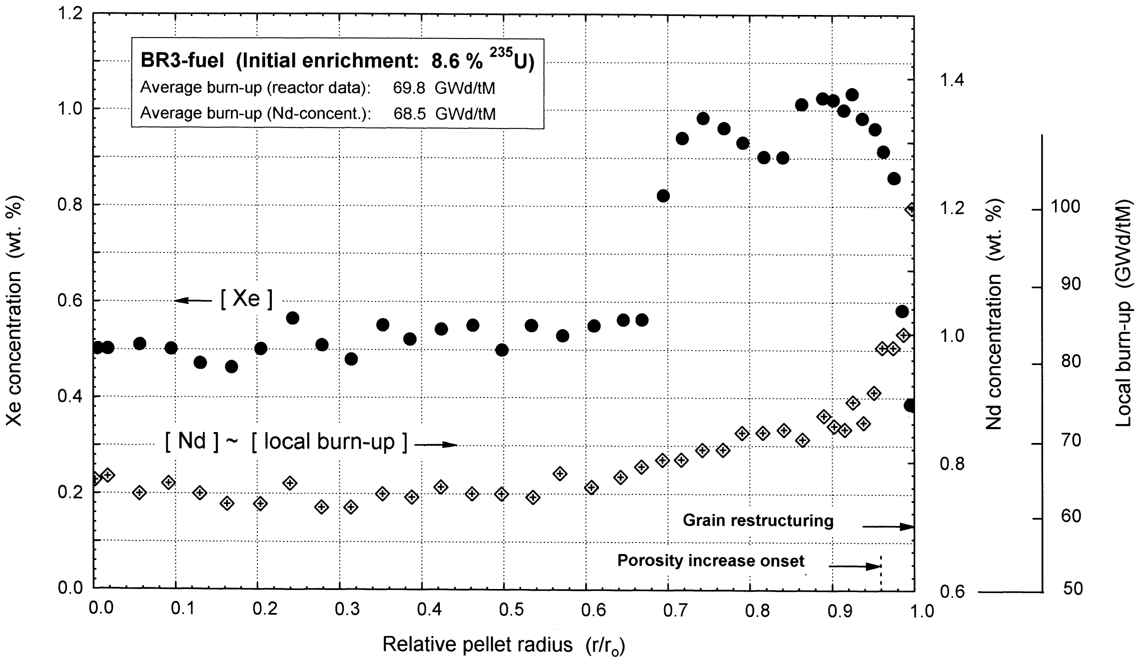

Fig. 4. Radial Xe and Nd concentration profiles of the BR3 fuel obtained by EPMA. Cross section average burn-up according to Nd profile: 68.5 GWd/tM.

BR3 fuel a much higher pellet average burn-up of ≈70 GWd/tM was achieved.

Fig. 4 shows the radial Xe and Nd concentration profiles obtained for the BR3 fuel by EPMA [19]. To convert the Nd concentrations into local burn-ups the approximation 0.12 w/o Nd ≈10 GWd/tM was used [20]. From Fig. 4 it is evident that the matrix Xe depletion at the pellet periphery started when local burn-ups in the range 73–75 GWd/tM were reached ($r/r_0 \approx 0.94$). Other local threshold burn-ups cited in the literature for the same phenomenon in standard LWR fuels lie in the range 65–75 GWd/tM [10,16,20].

The corresponding radial Pu-concentration profile measured also by EMPA [19] is given in Fig. 5. This plot shows the typical increase of the Pu content at the pellet periphery due to the conversion of ^{238}U into fissile ^{239}Pu by resonance absorption of epithermal neutrons (rim-effect), which causes the increase of the local burn-ups at the pellet edge visible in Fig. 4. It is to be noted, however, that due to the high enrichment used in the present BR3 fuel (8.6% ^{235}U), leading to a lower Pu conversion rate, the edge burn-up increase here is less pronounced than in a standard LWR fuel (3.2–4.2% ^{235}U) with a similar average burn-up. The influence of these variations in the results obtained is discussed in the next section.

Fig. 4 indicates also that the onset of the porosity increase at the pellet periphery appeared for the present BR-3 fuel at slightly higher burn-ups than the onset of matrix Xe-depletion, i.e. at 75–77 GWd/tM ($r/r_0 \sim 0.96$, Figs. 3 and 4). However, the main shift to higher burn-ups was found in the onset of grain restructuring, which in the present case did not occur even at $r/r_0 = 1$, where local burn-ups of about 100 GWd/tM were achieved (Figs. 1, 2 and 4). Just for comparison, standard LWR fuels of equivalent average burn-ups show full matrix restructuring already at $r/r_0 \approx 0.95$ [1,2] (associated local burn-ups around 75 GWd/tM [21]), with even larger (non-uniform) penetration to more internal fuel regions (transition zone $r/r_0 < 0.9$), with associated local burn-ups as low as 60 GWd/tM [1,2,4,21].

3. Discussion

It can be said that the present results basically agree with those earlier reported in the literature [15,16], showing that during the rim structure formation the matrix-Xe depletion, as detected by EPMA, penetrates deeper into the fuel than the observed structural changes.

The important evidence added with the present work is that, in terms of growing local burn-ups, the second step following the apparently first detectable step of matrix-gas depletion, would be that of pore formation, followed by a third step of grain subdivision, predominantly

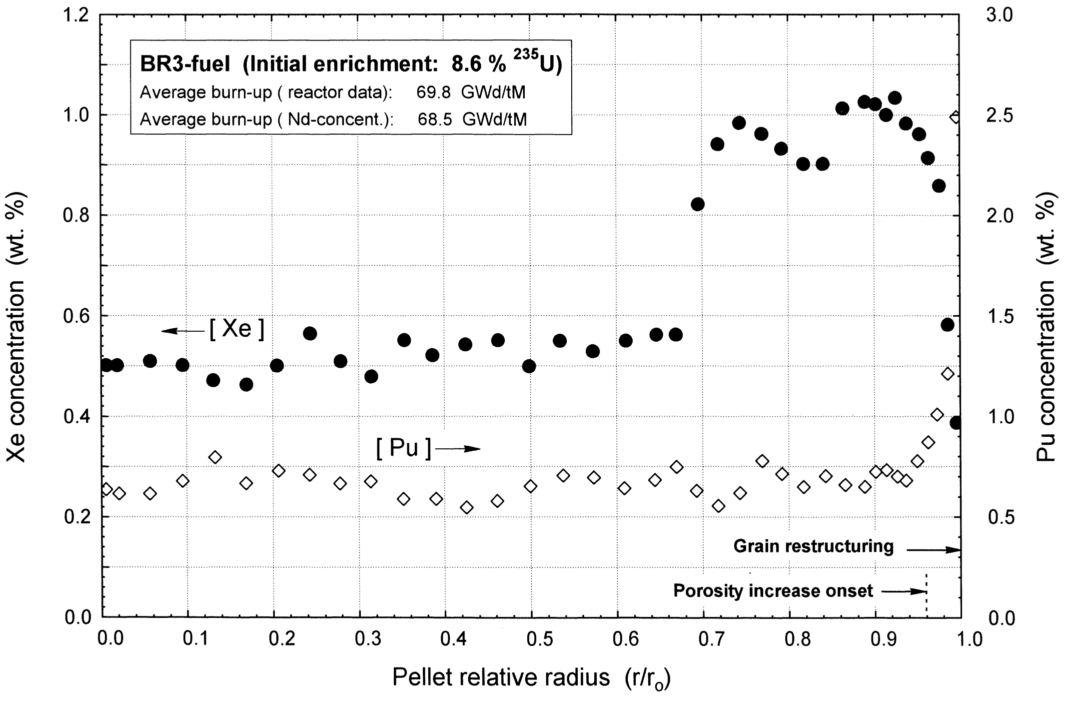

Fig. 5. Radial Xe and Pu-concentration profiles of the BR3-fuel obtained by EPMA. Cross section average burn-up according to Nd profile: 68.5 GWd/tM.

concentrated around pores. This last step may eventually depend on other fuel parameters than only the local burn-up, i.e. irradiation temperature, fission rate, fuel grain size, level of pore pressurisation, etc., so that under certain conditions still not well elucidated, the grain subdivision may be not so pronounced or widespread that the original grain boundaries still remain intact and could act as barriers for the escape of fission gases to the plenum.

The preferential concentration of subdivided grains around pores is nowadays a recognised characteristic of the rim-structure formation, which had been already described in several works, namely by the present authors in Refs. [1,2] concerning standard PWR fuels, by authors of Refs. [8,9] concerning an experimental HWR fuel and standard BWR fuels, respectively, and recently by authors of Ref. [24] with regard to French commercial LWR-UO_2 fuels. The remaining question is, however, whether the grain subdivision process must be considered a cause or a consequence of pore formation. As outlined in the introduction, various models of the rim structure have been constructed on the base of the first option [12–14]. However, with the present results, we believe that evidences are supplied that the second option is most likely valid, i.e. that the rim pores act as precursors of the grain subdivision process.

An alternative description of the rim structure formation was given by the present authors in Refs. [1,2] considering that the grain subdivision around pores could be caused by the stress field created around them due to pressurisation with fission gases. The mechanism proposed was a kind of strain-induced or creep-induced mechanism (dislocation-loop punching), known in strained metals as dynamic recrystallization [22]. Even if the applicability of this mechanism valid for metals would be questionable when referred to the poorly deformable ceramic fuel, the influence of the local stresses in the creation of new subgrains might be considered still as a plausible hypothesis. In this sense, it is remarked that also authors of Refs. [17,18] have proposed the overpressurization of dispersed gas bubbles as possible reason for local initiation of the high burn-up structure, as discussed recently in Ref. [25].

Considering the cold fuel periphery, where the rim structure certainly begins to form, the present results show that neither the larger grains were less prone to the initiation of this process nor the grain boundaries were preferentially affected. On the contrary, Figs. 1 and 2 show that the first layers of grains at the pellet periphery were more or less homogeneously affected by the process, independent of their size, and that at a short distance from the pellet edge, even a depletion of intragranular pores, with their associated grain-subdivided microregions, was observed near the grain boundaries.

The above remarks seem to contradict previous observations by us and other authors that the burn-up induced transformation appears preferentially concentrated on grain boundaries [2,11,12], and that the larger grains seem to be less affected by the transformation than the smaller ones [11]. However, these statements refer more to the propagation of the process towards the pellet interior than to its initiation at the pellet periphery. In fact, as shown in Fig. 6 for a LWR fuel with an average burn-up of ≈67 GWd/tM at 450 μm from the pellet edge, the high burn-up transformation propagates non-uniformly towards the pellet centre along grain-boundary paths, with progressively less intensity as the hotter parts of the fuel are reached [1,2]. In the restructured areas of this so-called ‘transition zone’, also Xe depletion is detected by EPMA as in the pellet periphery [4,21].

According to that, it seems that a fourth step in the development of the rim structure is to be considered regarding its propagation to the hotter parts of the fuel, and during which the process tends to concentrate on grain boundaries. The reason for this behaviour is not clear, although it may be possible that, if the formation of the high burn-up structure is related to the pressurisation of pores, the thermally activated migration of gases to the grain periphery, contributing to the depressurisation of the intragranular bubbles and pores, may help to the disappearance of the process at the grain interiors and to its concentration on grain boundaries. As apparently suggested by the experimental observation [11,12], the utilisation of larger grains may help to delay this propagation step, due to the availability of less grain boundary area.

A subject that still needs to be discussed concerns the influence of the Pu concentration and the associated local burn-up profile in the here obtained results. As mentioned in the previous section, due to the high enrichment of the present BR3-fuel (8.6% ^{235}U) and its consequently lower Pu conversion rate, a flatter Pu distribution and hence a flatter local burn-up profile occurred in the rim

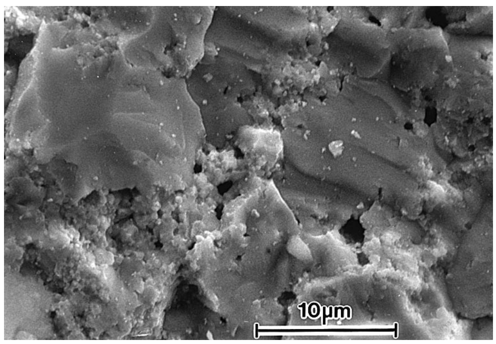

Fig. 6. SEM fractography of a standard LWR fuel showing localised fuel restructuring on grain boundaries at radial positions distant from the pellet edge. Average burn-up: 67 GWd/tM, fuel radius: $r_0 \cong 4630$ μm, $r/r_0 = 0.908$.

zone as compared to a LWR fuel with standard enrichment (3.2–4.2% ^{235}U). To quantify this effect, the local burn-up profile for the present BR3-fuel was calculated with the neutronic code APOLLO-2 [26], assuming alternatively the enrichments 8.6% and 3.2% ^{235}U, keeping the average burn-up constant (68.5 GWd/tM). These results and the measured burn-up profile according to Fig. 4 are shown in Fig. 7.

It is seen that the above calculations agreed well with the experimental data in the range $r/r_0 = 0$–0.94, though an overestimation of 6–10% occurred in the range $r/r_0 > 0.94$ (Fig. 7). More complex calculations with this code [26], using basically smaller radial intervals, can reduce this scatter to about 5% [27]. Beyond that, Fig. 7 shows that an enrichment change like considered would affect the results mainly in the outermost periphery ($r/r_0 > 0.94$). Then, for the observed onset of Xe depletion ($r/r_0 \approx 0.94$, Fig. 4), less influence on the associated local burn-ups must be expected under such conditions (Fig. 7). Contrarily, for processes occurring at higher local burn-ups, as apparently the grain subdivision, this influence may be stronger, being these processes moved towards the fuel edge if the enrichment is increased (Fig. 7). This would explain partially why in this BR3-fuel the grain subdivision was absent or shifted to $r/r_0 = 1$ (Fig. 4), compatible with a threshold burn-up of ≈100 GWd/tM according to Fig. 7. However, as formerly indicated, the grain subdivision in standard LWR fuels can penetrate, localised on grain boundaries, up to radial positions associated with local burn-ups as low as ≈60 GWd/tM [4,21] (see also Fig. 6), suggesting that other parameters besides only the local burn-up may play there a role.

Finally, the Pu concentration, from the chemical point of view, seems to have less influence on the above processes, especially on that of the grain subdivision. In the present case, where the Pu concentration at the pellet edge was lower than in a standard LWR-fuel with similar burn-up, this process was inhibited. In the opposite case of higher Pu concentration, i.e. in the Pu rich particles of MOX fuels, where very high burn-ups (≈200 GWd/tM) are reached via nearly exclusively ^{239}Pu-fissions, the grain subdivision in the cold zone is also found less pronounced than in the rim-zone of standard LWR-fuels, though equivalent or even higher porosity is developed [3]. This seems therefore to exclude any direct correlation between the Pu-content and the degree of grain restructuring.

4. Conclusions

As a conclusion, we suggest that in the peripheral regions of the fuel where thermally activated processes are

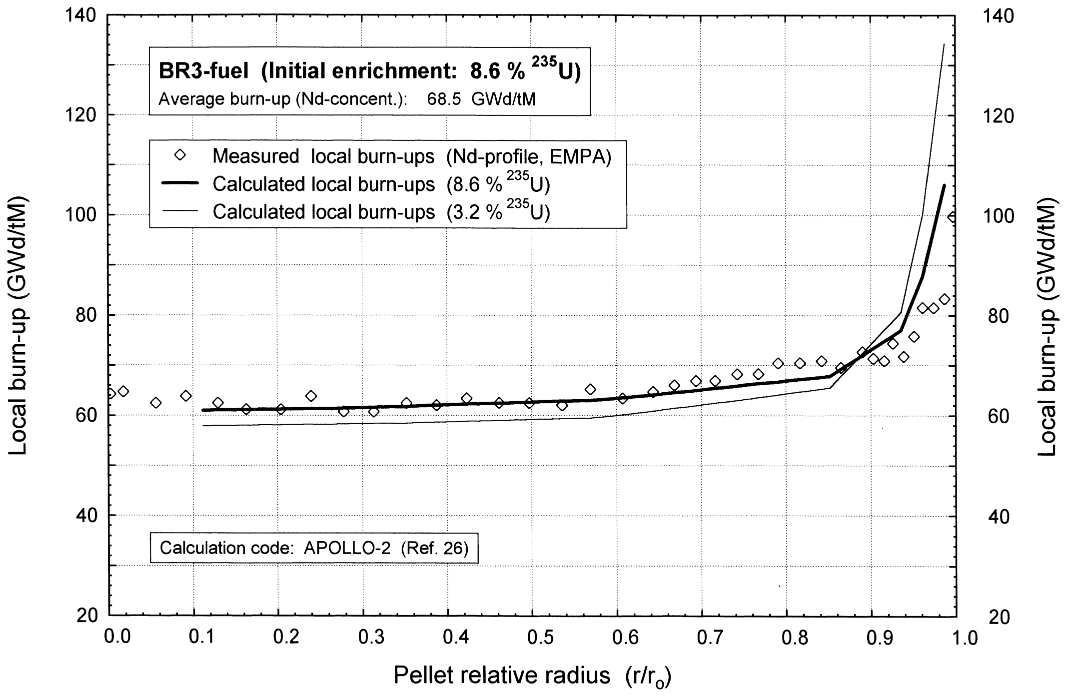

Fig. 7. Influence of the ^{235}U enrichment on the local burn-up profile. Calculations code: APOLLO-2 (Ref. [26]). Experimental data: idem Fig. 4.

excluded, the rim structure formation may follow the sequence: matrix Xe depletion, pore formation and local grain subdivision around pores, as the local burn-up increases. Furthermore, instead of assuming a kind of nucleation-growth mechanism of dislocation-free subgrains as in Refs. [12,23], where the temperature may even play an activating role [23], it is suggested that the grain subdivision may be originated by a stress-induced mechanism, emerging from pressurised matrix sites (gas bubbles or pores) as suggested in Refs. [1,2,17,18]. In this locally initiated process at the pellet periphery, the grain size of the matrix may play only a secondary role.

On the contrary, due to reasons not yet clarified, the ^{235}U enrichment, with effects on the fission rate, the irradiation temperature and the local burn-ups, may have an important influence on the processes described, delaying the porosity growth and more especially the grain subdivision, if higher initial contents of fissile ^{235}U are utilised.

Acknowledgements

The authors would like to thank Dr C.T. Walker for the performance of the EPMA examinations, Dr Hj. Matzke for the critical reading of the manuscript and Mr. F. Rousseau for his careful porosity determinations by quantitative metallography.

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