Journal of Nuclear Materials 385 (2009) 137–141

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

ADAGIO technique: From UO_2 fuels to MOX fuels

Y. Pontillon [a,*], L. Desgranges [a], A. Poulesquen [b]

[a] CEA, DEN, DEC, SA3C, F-13108 Saint-Paul-lez-Durance, France
[b] CEA, DEN, DANS, DPC, SECR, Centre d'Etudes de Saclay, Bat 450 91191 Gif sur Yvette cedex, France

ABSTRACT

The amount of gas at the grain boundaries plays an important role in the fuel transient behaviour during accident conditions, such as a loss-of-coolant accident (LOCA) or a reactivity-initiated accident (RIA). Direct experimental determination of the grain boundary gas inventory has been performed for MOX fuel irradiated in an EDF pressurised water reactor (PWR) using the ADAGIO technique (ADAGIO is a French acronym meaning 'Discriminatory Analysis of Accumulated Inter-granular and Occluded Gas'). The ADAGIO protocol applied to a MOX MIMAS fuel produced inter-granular gas fraction results that were consistent with those reached with other methods of evaluation i.e. electron probe microanalysis (EPMA). Furthermore, a new methodology for the numerical treatment of ^{85}Kr release kinetics which was developed for UO_2 was applied to MOX fuels. The corresponding results evidenced two types of release kinetics. These kinetics were attributed to the inter-granular bubbles of the UO_2 matrix and the bubbles located in the restructured zones, i.e. Pu agglomerates.

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1. Introduction

Fission gas release (FGR) is a key phenomenon that must be accurately assessed for fuel rod design and licensing under both normal and off-normal operating conditions. Under normal conditions, FGR is a potential limiting design factor due to its impact on the fuel rod internal pressure. Moreover, the maximum fuel burn-up has been regularly increased to improve fuel cycle costs, and the accurate prediction of FGR becomes more critical at high burn-ups. Under off-normal conditions, FGR is important input data in terms of both the radioactive source term relative to the consequences of a nuclear accident on the environment, and the driving force regarding fuel damage. Correctly predicting its release under these conditions (e.g. RIA, power transients, LOCA, etc.) remains an important R&D goal.

Generally speaking, the global gas inventory can be schematically divided into two main parts in irradiated PWR fuels: intra-granular gas and inter-granular gas, i.e. inside the grain matrix and at the grain boundaries, respectively. Over the last decades, many experiments focusing on fission gas behaviour under thermal transients have highlighted the active role played by gas at grain boundaries, especially during a sequence representative of an RIA [1] and/or LOCA [2]. In parallel, the improvement of fission gas release modelling in nuclear fuel performance codes needs direct experimental determination of the local gas distribution inside the fuel sample.

Within this context, an experimental program called 'ADAGIO' was launched by the CEA, EDF and AREVA NP in 1998 to develop a new technique designed to accurately measure the local gas distribution in irradiated PWR fuel samples [3]. Such data will provide the information needed to continue developing more realistic and mechanistic models of FGR from fuels.

The ADAGIO technique, which was modified from the Canadian experiment [4] on the basis of CEA expertise in radioactive gas measurement, is used to determine the amount of inter-granular gas through the partial oxidation of the nuclear ceramics in the oxygen baring atmosphere, which causes the grain boundaries to open. After this 'oxidation phase', the temperature is increased, and vacuum sublimation may be performed to make sure that all the gas has been released from the sample. During these experiments, the gas release is measured as a function of time.

In addition to the results normally obtained from these experiments, and using the new ADAGIO mathematical data treatment of the release kinetics [5], comparison of the ^{85}Kr release kinetics with the fuel oxidation kinetics highlights two different types of gas release kinetics in the case of UO_2 fuels. One is proportional to the oxidation kinetics, while the other shows a sigmoid shape which may be correlated to the gas release of the so-called High Burn-up Structure (HBS)[1] [6]. As the first phase of the programme – applied to UO_2 samples – provided very encouraging results, it was deemed worth to try to extend the method to MOX fuels. However, it is clear that MOX structural properties, i.e. $(U, Pu)O_2$ agglomerates, increase the difficulty in doing this. There are many research

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* Corresponding author. Tel.: +33 (0) 4 42 25 72 26; fax: +33 (0) 4 42 25 44 79.
E-mail address: yves.pontillon@cea.fr (Y. Pontillon).

[1] HBS is characterised by the formation of a porous, small-grained microstructure in the rim area of the fuel pellet.

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doi:10.1016/j.jnucmat.2008.10.013

papers discussing the influence of Pu enrichment upon the global fuel oxidation process [7], though they mainly concern un-irradiated fuels. It was therefore decided to perform several scoping tests in order to check if it was possible to: (1) determine the global gas content in MOX fuel by air ingress, i.e. the total amount of fission gas in the fuel sample, (2) evaluate the total inter-granular gas fractions, i.e. jointly in the matrix and Pu agglomerates, and (3) assess the inter- and intra-granular gas fractions both in the matrix and in the Pu agglomerates separately.

This paper sets out to describe how this method can be developed to cover MOX fuels, considering it has already been applied to UO_2 fuels (ADAGIO + numerical treatment of the oxidation kinetics).

After describing the general methodology previously applied to UO_2 fuels, the experimental facility and the samples used in the MOX case will be presented. The corresponding results will be discussed, with special emphasis on the location and behaviour of gas during the oxidation phase. More specifically, it will be shown how the ADAGIO protocol applied to MOX fuel gives inter-granular gas fraction results that are consistent with the results obtained with other types of evaluation methods (e.g. EPMA measurements). It will also be shown that the new analytical data treatment of the FGR kinetics could be used to separate the contribution of gas from the Pu agglomerates and the matrix.

2. Methodology applied to UO_2 fuels [3,8,5]

2.1. ADAGIO process (or inter-granular gas inventory determination)

The ADAGIO global process has been already described in detail elsewhere [3,8], which is why only the key steps are recalled in this paper.

According to the ADAGIO technique, the intra- versus inter-granular fission gas inventory in UO_2 fuels can be evaluated by controlled fuel oxidation. Pre-irradiated[2] fuel samples are annealed under air flow at low temperature (between 380 °C and 450 °C) in order to induce the oxidation of UO_2 into $U_4O_9\gamma$ (called the 'oxidation phase' throughout the paper). As this oxidation step occurs preferentially along the grain boundaries and due to the corresponding volume expansion (caused by UO_2 to $U_4O_9\gamma$ phase change), grain boundary separation occurs. As a consequence, the inter-granular gas is released[3] and the intra-granular gas contribution is determined by the ^{133}Xe release.[4] After this step, the temperature is increased to extract the remaining gas inventory. During these operations, the ^{85}Kr and ^{133}Xe release are continuously monitored by the online gamma spectrometer (see Section 3.1).

2.2. Numerical treatment of oxidation kinetics (or evidence of two types of gas release kinetics)

The ^{85}Kr release observed in this type of experiment is a direct consequence of the ceramic oxidation (the matrix oxidation proceeded from irradiated UO_2 to $U_4O_9\gamma$ as reported by Thomas [9]). The kinetics of this reaction may be reproduced by the modified [5,10] Janders' equation [11,12] (although this equation is not fully justified [13]). This modified equation was used successfully to reproduce the oxidation kinetics for several weight gain data sets, and agreement proved to be rather good [14]. Considering that the ^{85}Kr release kinetics are driven by the oxidation of UO_2 into $U_4O_9\gamma$ in the ADAGIO experiment, the ^{85}Kr release curve was compared with that of the modified Janders' equation. Fig. 1 shows the results taken from [5] and obtained with a 6-cycle UO_2 sample submitted to an 18-h period of annealing under air. The ^{85}Kr release can be reproduced by the sum of two curves: the first reproduces the oxidation kinetics of the irradiated UO_2 ceramic, while the other starts at approximately 150 min and is more or less linear with time.

The first ^{85}Kr release kinetics are described by the modified Janders' equation. Considering that the modified Janders' equation describes the propagation of an oxidation front within the solid, and assuming that this oxidation front occurs inside ceramic fragments, i.e. along grain boundaries, the correlation between Janders' equation and the inter-granular gas release suggests that the released gas corresponds to the inter-granular one. The second ^{85}Kr release kinetics are linked to the gas released from the HBS. The gap between the fuel and the cladding is, in fact, closed due to the high burn-up of the sample. This prevents oxygen from directly accessing the HBS. As a consequence, oxygen must first diffuse through the fuel fragment before reaching the HBS. This is why the additional gas release is observed after an incubation time. The linear shape of the release kinetics may be explained if we assume there is a constant oxygen flux into the HBS resulting from the diffusion of oxygen through the ceramic to reach the HBS.

Generalisation of the method has also been investigated [15] during which various UO_2 fuels with different geometries were used successfully, i.e. the same type of behaviour was obtained.

3. Experimental section

3.1. Annealing test facility

The annealing tests were performed in the MERARG loop, which has already been detailed elsewhere [16]. The MERARG facility is located in the LECA-STAR hot cell laboratories at Cadarache. The key components are the induction furnace located in a shielded hot cell, the gamma spectrometry device, and the gloves box where any gas coming out of the furnace is trapped. During the whole annealing process, the sample is swept by a controlled air flow. Released fission gases are carried away with the sweeping gas; it flows through aerosol filters before passing through the counting chamber located in front of the gamma spectrometer. The gas flow ends up in the gloves box where the fission gases are trapped. The counting chamber is used to record variations in the activity signal over time.

3.2. Sample characteristics

The main characteristics of the samples used during this campaign are given in Table 1. They were taken from rods irradiated in a PWR operated by EDF. The fuel pellets were fabricated by a standard industrial process.

The first series of experiments were performed on MOX samples irradiated to a burn-up of 46 GWd t_M^{-1} (sample S1, 3 irradiation cycles in PWR). The second sample (S2-sample) concerned MOX irradiated to 44 GWd t_M^{-1}.

Furthermore, since the process required much more controlled compared to UO_2, it was decided to perform the study with non re-irradiated fuel and on entire fuel pellets.

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[2] In a material testing reactor (MTR) to create short half-life fission products distributed throughout the fuel matrix.

[3] The irradiation is performed at low temperature to generate fission gas tracers inside the grain and under an inert atmosphere to avoid any fuel oxidation. As a consequence, comparison between the short half-life radioactive gases (e.g.: ^{133}Xe mainly created inside the grain) and the long half-life ones (^{85}Kr) – whose concentration and location are not modified by re-irradiation – allows us to determine the fraction of gas located at the grain boundaries.

[4] Generally speaking, ^{133}Xe release – representing intra-granular gas behaviour – in this type of experiment is very low (below 1% of the initial inventory).

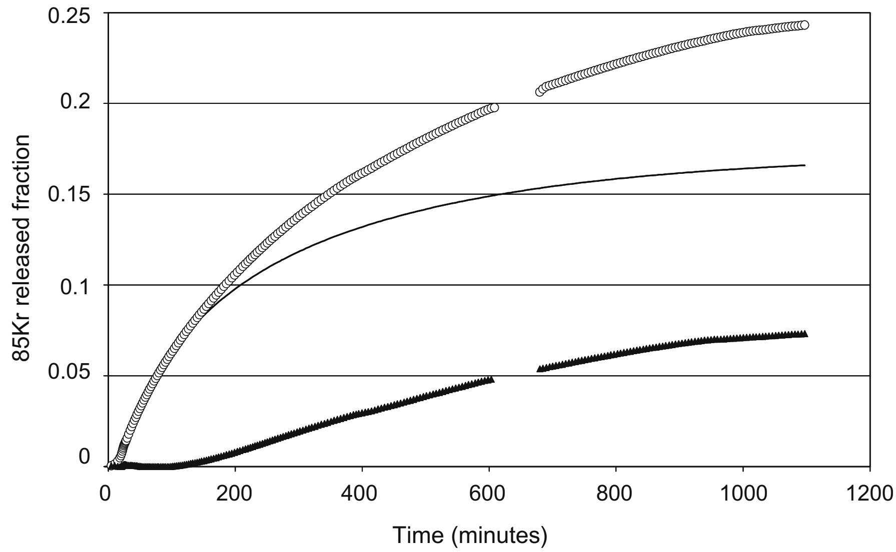

Fig. 1. ^{85}Kr release curve (open circle), fitted curve with the modified Janders' equation (straight line) difference between these two curves (plain triangle), 6-cycle UO_2 samples.

Table 1
Main characteristics of the samples.

Fuel (sample)	MOX (S1)	MOX (S2)
Pu/(U + Pu)	5.92%	7.25%
Cycles/BU	3/46 GWd/t_M	3/44 GWd/t_M
Re-irradiation	No	No

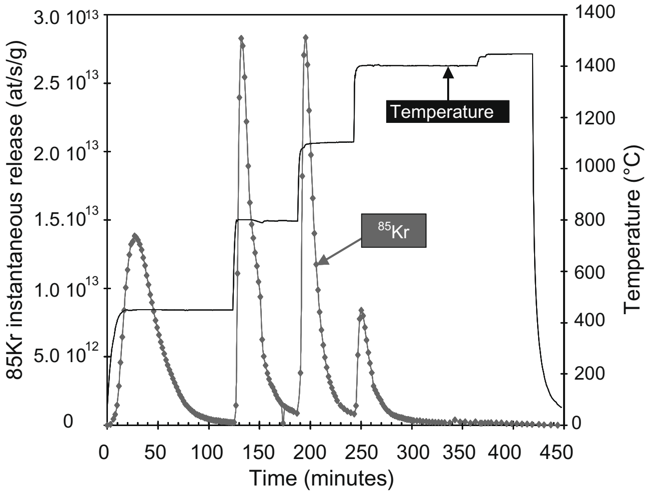

Fig. 2. ^{85}Kr release kinetics during the complete ADAGIO process (S1-sample).

3.3. Annealing test characteristics

Two series of experiments were performed.

The first series corresponds to the classical 'oxidation plateau' of the ADAGIO technique applied to MOX fuels. Two different annealing experiments (S1 and S2 samples) were carried out in the MERARG facility. These experiments were dedicated to studying the low temperature oxidation plateau, i.e. temperature of 450–430 °C.

The second series of experiments was devoted to the complete ADAGIO process, i.e. oxidation step at 450 °C and temperature increased to 1450 °C by steps (800 °C, 1100 °C, 1400 °C and finally 1450 °C) in order to extract the total gas inventory.

The ^{85}Kr instantaneous release kinetics obtained during the last series of experiments is given in Fig. 2 for S1-sample.

4. Results and discussion

4.1. ADAGIO process (inter-granular gas inventory)

^{85}Kr release starts as the fuel temperature increases according to a burst release (Fig. 2). At the end of the 'oxidation plateau', approximately 32% and 34% of the initial gas inventory was released for the S1 and S2 samples, respectively. Concerning the S1-sample, 90% of the total gas was released below 1200 °C and the total amount of Kr was extracted at the end of the isothermal plateau at 1400 °C, since no additional release was recorded during the last high temperature plateau at 1450 °C, and the expected amount of gas was obtained (calculated on the basis of the fission product code CESAR).

Based on the three main objectives detailed in the introduction, it can be said that:

- The global gas retention in MOX fuel (inter- plus intra-granular) can be experimentally determined by this technique. It seems that it is easier for MOX than for UO_2 fuels [3] since the totality of the gases is extracted between 1200 °C and 1400 °C,
- The inter-granular gas fraction, deduced from the ^{85}Kr release at the end of the oxidation plateau (32–34% depending on the fuels), seems to be consistent with previously reported results (Fig. 3 taken from [17]). In this case, the inter-granular gas fraction was estimated by the author based on EPMA measurements performed on numerous MOX fuels according to the following procedure. Since EPMA only measures gas (xenon in this case) in solution or precipitated in very small bubbles ($<\sim$100 nm), the difference between the gas which was created during the irradiation in PWR and the EPMA xenon concentration (minus the fission gases released during the base irradiation) corresponds to the gas accumulated into large size bubbles (inter + intra). The intra-granular contribution may

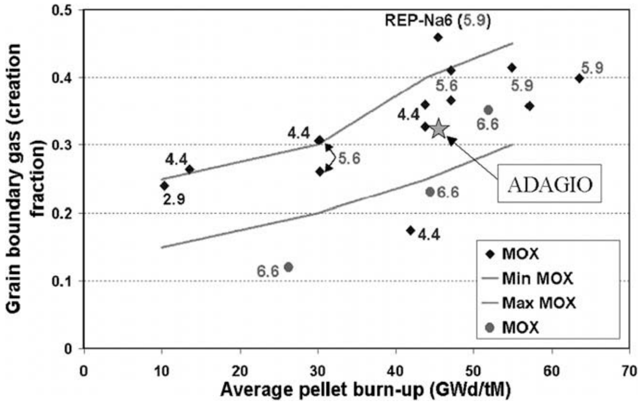

Fig. 3. Inter-granular gas fraction in MOX fuels, comparison between ADAGIO determination and EPMA evaluation (taken from [17]). The numbers represent Pu initial enrichments.

> be neglected for most of the MOX fuels. This value, deduced from EPMA xenon measurements, is therefore a slight underestimation of the inter-granular gas content, assuming that most of the inter-granular gas is in bubble-form in these MOX fuels.

Determining the inter-granular gas fraction in the matrix and in the Pu agglomerates separately based on the release kinetics technique is the subject of the following section.

4.2. Numerical treatment of the oxidation kinetics (or evidence of two types of gas release kinetics)

From a general point of view, the cumulated ^{85}Kr release kinetics are very different when compared to UO_2 samples since they appear to be more or less linear as a function of time up to 100 min of the oxidation plateau (Fig. 4, S2-sample). However, the methodology described above (Section 2.2) was applied. The corresponding results are also given in Fig. 4. As previously obtained with UO_2 fuels, the experimental results can be well reproduced by adding two contributions: (i) the first reproducing the oxidation kinetics of the irradiated UO_2 ceramic and fitted by the modified Janders' equation, and the second starting at approximately at 10 min and being more or less linear with time. The main difference between UO_2 and MOX concerns the ratio between these two contributions.

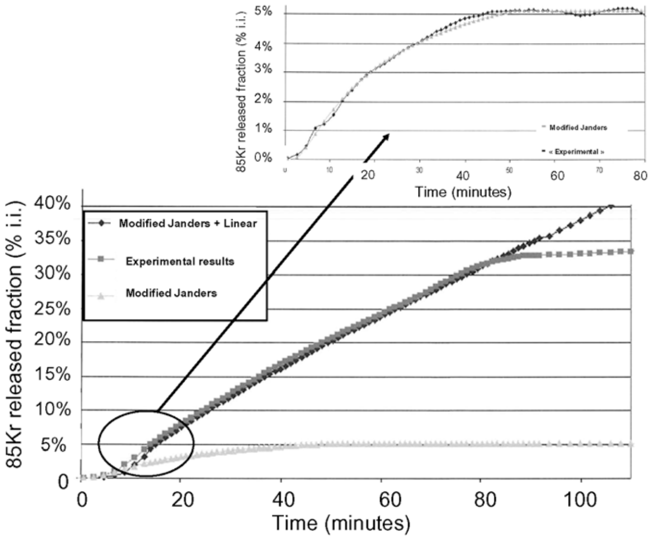

Fig. 4. ^{85}Kr release curve (pink), fitted curve with the modified Janders' equation (yellow), fitted curve with the modified Janders' equation plus a linear contribution (blue). Inset: ^{85}Kr cumulated release kinetics obtained by subtraction of the experimental results of the linear contribution (blue), fitted curve with the modified Janders' equation (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In order to be sure that the experimental curve does indeed 'include' a contribution from the oxidation kinetics of the irradiated UO_2 ceramic (which is reproduced by the modified Janders' equation), the linear contribution was subtracted and the corresponding curve was fitted with the modified Janders' equation (inset in Fig. 4). The resulting curve is very well reproduced up to the maximal contribution of the corresponding phenomena (~5% of the initial gas inventory) adjusting B, κ and G to 0.11 min^{-1}, 6.9×10^{-3} min^{-1} and 5.1%, respectively.

In short, by analogy with UO_2 fuels, it can be stated that the two contributions to the global ^{85}Kr release in the MOX case can be attributed to: (1) UO_2 ceramic oxidation, which means that the corresponding released gas is the inter-granular gas at the UO_2 matrix grain boundaries. The matrix contribution (oxidation) is well confirmed by post-test SEM analysis which shows (Fig. 5) the matrix conversion into powder with the grain size in the range of 5–20 μm. The other granules (size around 100 μm) are the Pu agglomerates. Furthermore, the corresponding release starts at the beginning of the experiment since the UO_2 oxidises faster than the Pu agglomerates; (2) Pu agglomerates contribution (instead of

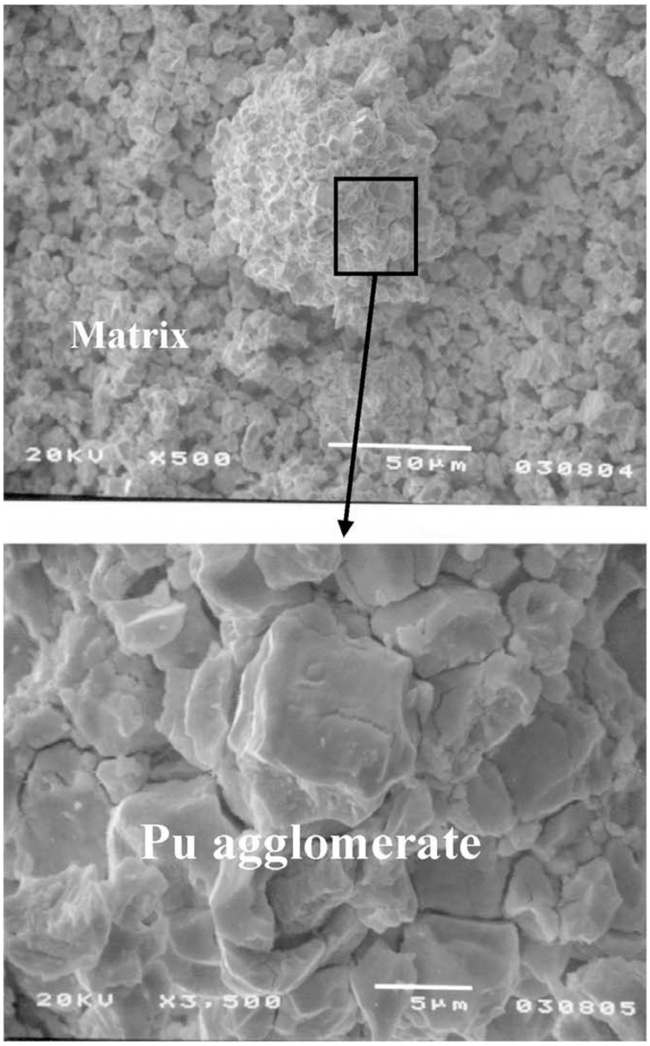

Fig. 5. SEM details of both the UO_2 matrix and the Pu agglomerates (S1-sample).

HBS in the UO_2 case). The latter contribution is also well highlighted by SEM examinations, which show a great number of open grain boundaries (Fig. 5). Compared to UO_2, the much stronger contribution to the global ^{85}Kr release is due to the difference regarding the amount of gas located in the restructured zone between the two types of fuel: ∼40/60% (centre/rim, respectively) for UO_2 against ∼10/90% (matrix/Pu agglomerate, respectively) for a MOX fuel. Since all the gas contained in the Pu agglomerates may be considered as inter-granular, the ratio between the matrix and the restructured zones can be obtained by this methodology.

Finally, even though the intra-granular gas contribution is very low due to the fact that penetration of the oxidation front into the grain is limited during these ADAGIO experiments, this contribution correspond to one of the main uncertainties regarding the absolute inter-granular gas fraction.

5. Conclusion

The amount of gas at the grain boundaries plays an important role in the fuel transient behaviour during accident conditions, such as a LOCA or a RIA. Direct experimental determination of the grain boundary gas inventory has been performed for MOX fuel irradiated in an EDF PWR using the ADAGIO technique. The ADAGIO protocol applied to a MOX MIMAS fuel produces inter-granular gas fraction results that are consistent with those obtained by other types of evaluation methods (e.g. EPMA).

Furthermore, a new methodology for the numerical treatment of the ^{85}Kr release kinetics developed for UO_2 was also applied to MOX fuels. The corresponding results evidenced two types of release kinetics. These kinetics were attributed to the inter-granular bubbles of the UO_2 matrix and the bubbles located in the restructured zones, i.e. Pu agglomerates.

This opens the path to improved characterisation of the inter-granular gas inventory inside irradiated MOX nuclear fuels, but remains to be validated on more numerous and re-irradiated samples.

Acknowledgements

The authors are greatly indebted to Electricité de France (EDF) and AREVA NP for their financial support. They would also like to thank J. Piquemal, M. Pontillon, and G. Volle for their contribution to the MERAG experimental work.

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[10] $\alpha = \exp(\frac{-1}{B*t}) * [1-(1-\sqrt{\kappa t})^3]$, where α is the ratio of the molar number of formed $U_4O_9\gamma$ to that of the initial UO_2, t is time and κ is a constant related to the grain size and the oxygen diffusion. The added term, $\exp(\frac{-1}{B*t})$, modifies the curve only for the lower oxidation rates, and allows to take into account the “induction” period observed in experiments performed on irradiated samples (sigmoid shape of weight grain curve).
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