Journal of Nuclear Materials 392 (2009) 434–438

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Specific low temperature release of ^{131}Xe from irradiated MOX fuel

J.-P. Hiernaut [a,*], T. Wiss [a], V.V. Rondinella [a], J.-Y. Colle [a], A. Sasahara [b], T. Sonoda [b], R.J.M. Konings [a]

[a] *European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany*
[b] *CRIEPI, 2-11-1 Iwado-Kita, Komae-Shi, Tokyo 201-8511, Japan*

ARTICLE INFO

Article history:
Received 30 July 2008
Accepted 3 April 2009

ABSTRACT

A particular low temperature behaviour of the ^{131}Xe isotope was observed during release studies of fission gases from MOX fuel samples irradiated at 44.5 GWd/tHM. A reproducible release peak, representing 2.7% of the total release of the only ^{131}Xe, was observed at ~1000 K, the rest of the release curve being essentially identical for all the other xenon isotopes. The integral isotopic composition of the different xenon isotopes is in very good agreement with the inventory calculated using ORIGEN-2. The presence of this particular release is explained by the relation between the thermal diffusion and decay properties of the various iodine radioisotopes decaying all into xenon.

1. Introduction

Fission gas release (FGR) is a key issue affecting in-pile safety and performance of MOX fuel [1]. A joint ITU–CRIEPI research programme has started with the aim of clarifying fission gas release mechanisms from MOX fuel from the experimental and modelling points of view. MOX spent fuels obtained by commercial reactors and/or research reactors were used for these studies.

Measurement and analysis of the release behaviour of fission products during thermal annealing of spent fuels is a practical and relatively straightforward way to study the migration and segregation of fission products in uranium and plutonium containing oxide fuels [2–5]. The first release stage of volatile fission products is associated with migration to the grain boundaries [4,6]; therefore, the overall release behaviour is also strongly dependant on the original position of the fission products in the fuel. This, in turn, depends not only on mechanistic and chemical considerations related to the species considered [3,7,8], but also, in the case of nuclides not directly generated in the fission event, on the properties of the parent isotopes in the fission products decay chain. The last effect has been considered to understand the particular low temperature release (~1000 K) observed for ^{131}Xe.

2. Samples, experimental and results

Post-Irradiation Examination (PIE) was performed on commercial MOX spent fuel PN19–P497, irradiated to a final average burnup of 44.5 GWd/tHM. The PIE was focused on fission gas release fraction as a function of annealing temperature in effusion tests using a shielded Knudsen cell apparatus coupled with a mass spectrometer. This paper focuses on the results for specimens coming from the radial periphery: $0.89 < r/r_o < 0.64$ of the fuel pellet. Fig. 1 illustrates the typical morphology of one of these spent fuel samples used for the annealing tests. All the samples studied exhibit the High Burnup Structure (HBS) in the Pu-rich islands, implying a low temperature irradiation ($500 < T_{irrad} < 800$ K) and a local burnup higher than 80 GWd/tHM.

Samples of irradiated MOX were analysed at ITU. A detailed description of the technique and of the apparatus can be found elsewhere [1,9]. The temperature range of the experiments was ~500–2650 K. All tests were performed under vacuum with a heating rate of 10 K/min. No background peaks like hydrocarbons were presents in the mass region of Xe and no interference occurs at mass 131. The gas release was measured on line as a function of the temperature. In this paper, special attention is paid to the release of the different isotopes of xenon, especially at low temperature. The release pattern of xenon is shown in Fig. 2.

The local burn up of the specimens studied in this work, determined by fitting the measured isotopic composition with the isotopic compositions of Xe calculated using the ORIGEN-2 code as a function of burnup, was found to be 44.5 GWd/tHM, not too far from the nominal average burnup of the fuel pellet.

At ~1000 K, a peak representing about 2.7% of the total value of ^{131}Xe was observed. The release study of xenon was performed on three similar samples and reproducible results were obtained. At higher temperature, the release curves of the different isotopes of xenon show essentially parallel trends. This is confirmed by analysing the curves in Fig. 3, where the ratios

$$^{i}\mathrm{Xe}/\Sigma_i\,^{i}\mathrm{Xe},$$

with $i = 131$, 132, 134 and 136 are plotted as a function of the annealing temperature. In this figure, the scatter observed at low temperature ($T < 1000$ K) is due to the poor signal to back ground ratio; the low T release for ^{131}Xe is clearly evident at 1000 K; at

---

[*] Corresponding author. Tel.: +49 7247 951 385; fax: +49 7247 951 99385.
E-mail address: Jean-Pol.Hiernaut@ec.europa.eu (J.-P. Hiernaut).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.04.002

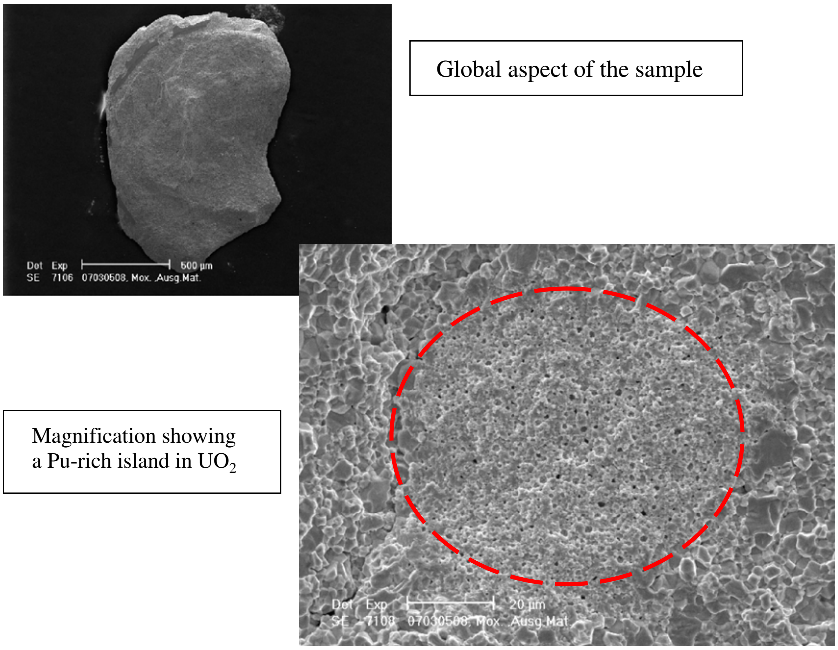

Fig. 1. SEM pictures showing a global view and the microscopic morphology of the irradiated MOX sample.

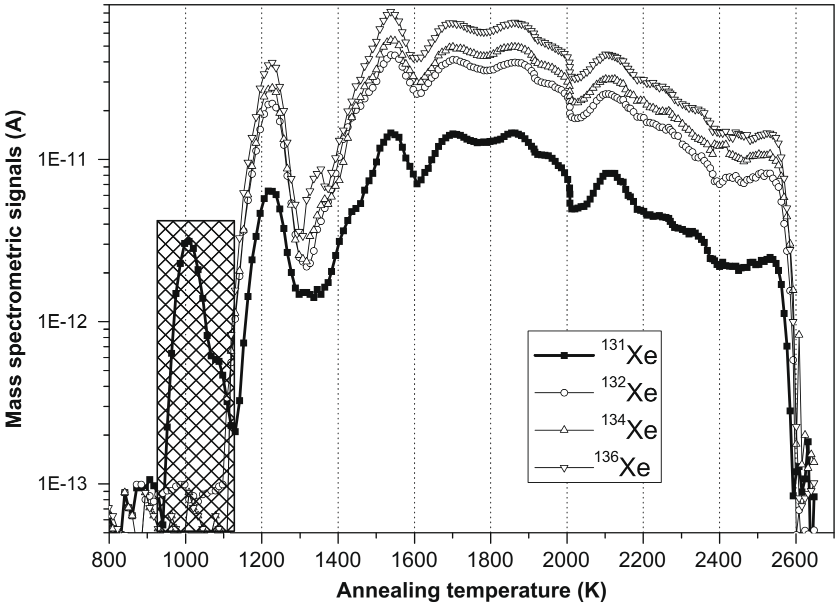

Fig. 2. Release of long lived xenon isotopes (mass spectrometry signal) as a function of annealing temperature performed under vacuum with a heating rate of 10 K/min. The shaded area highlights the specific release peak of ^{131}Xe at low temperature.

higher temperature the essentially constant values of the ratio (within the experimental scatter) indicate congruent effusion corresponding to the isotopic composition of the xenon inventory.

The anomalous behaviour of ^{131}Xe around 1000 K is also emphasised in the normalised fractional release curves shown in Fig. 4.

In order to verify if the low temperature release could be associated to any alterations in the structure of the fuel, a specimen was annealed up to 1100 K and subsequently examined by SEM. Fig. 5 shows SEM micrographs of the irradiated MOX fuel sample before and after thermal annealing at 1100 K. Pictures (A) and (B) illustrate the morphology before annealing. The nicely crystallised UO_2 bulk with well defined grains of dimension varying between 2 and 7 µm, and the completely restructured Pu-rich agglomerates characterised by microcrystal of 0.2–1.0 µm and small pores of 1.0–2.0 µm characteristic of a high burnup structure are shown in pictures (A) and (B), respectively. Pictures (C) and (D) show the corresponding images after annealing at 1100 K. Comparison between corresponding pictures evidences that no major changes occurred in the Pu-rich agglomerates (pictures (B)–(D)), except possibly a certain coarsening of the grains, while for the UO_2 bulk (pictures (A)–(C)), the grains remain with the same size, but a complex sub-structure appears at the grain boundary.

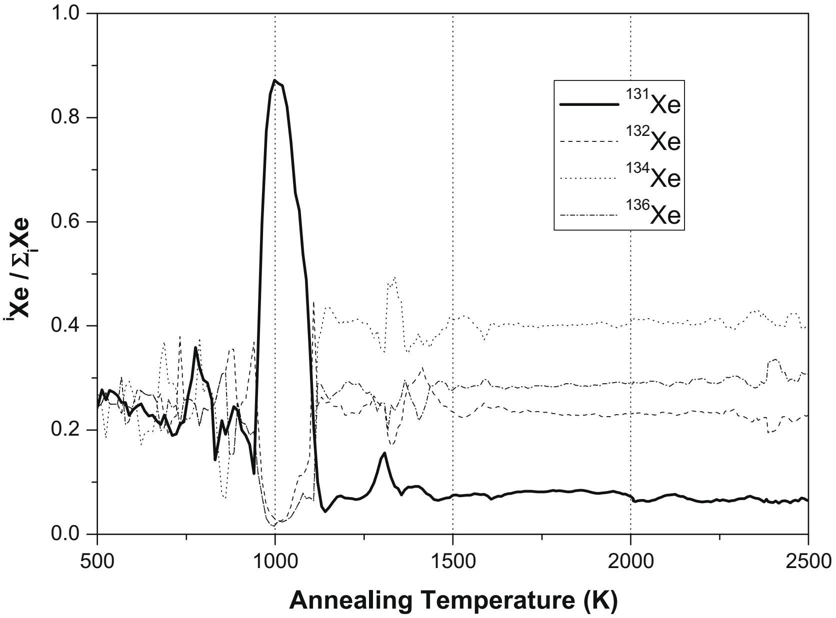

Fig. 3. Ratios ^{i}Xe/Σ_i ^{i}Xe; i = 131, 132, 134 and 136 as a function of the annealing temperature in K.

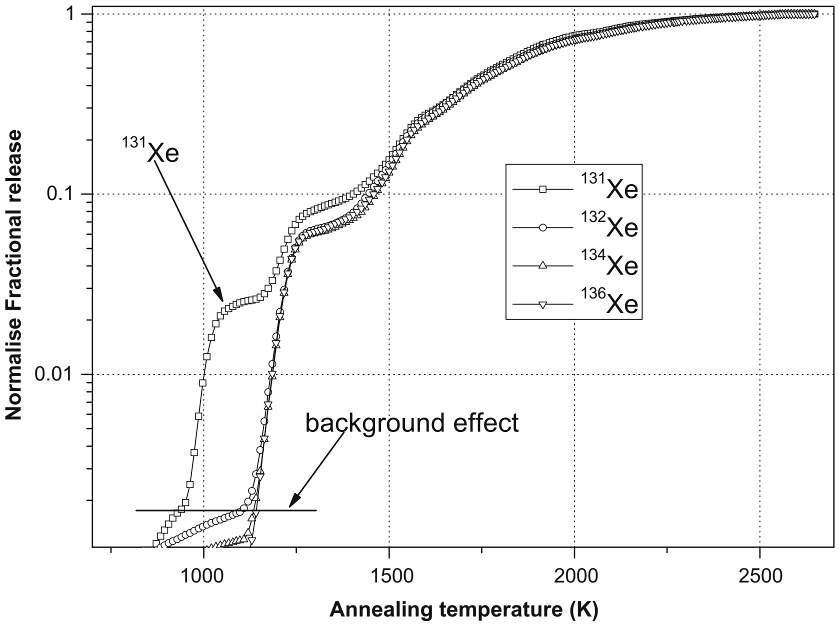

Fig. 4. Normalised fractional release of all measured isotopes of xenon as a function of the annealing temperature.

3. Discussion and conclusion

The isotopes of Xe observed in the spent fuels are all decay products of iodine [10]:

^{136}I(84 s) → ^{136}Xe

^{134}I(52 m) → ^{134}Xe

^{132}I(2.3 h) → ^{132}Xe

^{131}I(8.02 d) → ^{131}Xe.

Among the iodine parents, only ^{131}I has a relatively long life. This is the key to explain the particular release behaviour of ^{131}Xe at 1000 K.

Calculations with the ORIGEN-2 code of the inventory during irradiation and 100 days after the end of life for different MOX show that the ^{131}I concentration increases very rapidly, reaches a steady state (slightly decreasing) during the irradiation period, and decays very rapidly at the end of life, with half-life of ~8 days [10]. ^{131}Xe, on the other end, is a stable isotope, thus its inventory increases continuously during irradiation and remains almost constant after the end of life. The ratio ^{131}I/^{131}Xe depends on the irradiation history (burnup) and on the fuel enrichment in fissile materials. For the sample used in this work, this ratio varies between 1% and 4%.

The temperature of the sample during irradiation was around 800 K. The low temperature ^{131}Xe release occurs at a temperature

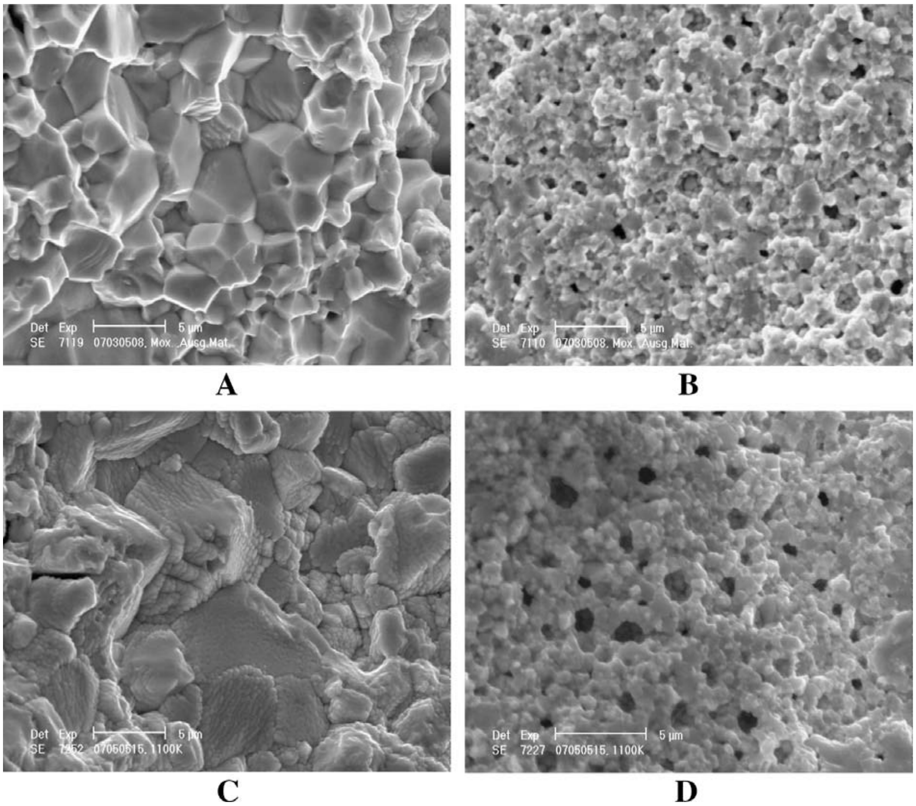

Fig. 5. Microscopic aspect of the MOX sample: micrographs (A) and (B) represent, respectively, the uranium oxide matrix and the plutonium rich agglomerates observed on the sample as received (before annealing). (C) and (D) are representative of the same regions after annealing at 1100 K.

where thermally activated mass transport is not the dominant effect for Xe mobility, whereas athermal diffusion occurs due to radiation [9,11–13]. Both iodine and xenon are normally almost insoluble in UO_2 matrix [14,15] (in hyperstoichiometric UO_{2+x} the solubility of Xe increases substantially together with its thermally activated diffusion coefficient (for $T > 1300$ K) [16–18]). Our results are in agreement with the diffusion coefficient measurements by Turnbull et al. [19], showing a diffusion coefficient for iodine, D_I, hundred times larger than for xenon, D_{Xe}, at the irradiation temperature of the samples (800 K). The insoluble ^{131}I migrates >100 times more rapidly than the Xe-nuclides to the grain boundary, where a fraction of it decays into ^{131}Xe. By considering the thermal diffusion coefficient of iodine in UO_2 recently published [20], the diffusion length of 131-iodine in the fuel during ten radioactive periods ($T_{1/2} = 8.05$ d) has been calculated in the irradiation temperature range of the investigated sample i.e., 500–800 K. The maximum diffusion length has been calculated to be $\sim$4 nm. By considering fuel grains of 200 nm, an external shell of 3 nm thickness represents $\sim$2.6% of the volume (by assuming a spherical geometry). The fraction of iodine that would have time to escape to the grain boundaries and to decay into 131-Xe corresponds to the one that is measured (2.7%). The calculations confirmed that with these conditions, the other isotopes would have had no time to migrate significantly outside from the grain. However, with a small increase in temperature, the thermal diffusion of iodine increases significantly, allowing also to the shorter living I-isotopes to migrate. This is the explanation why in most of the xenon release profiles there is no isotopic segregation. The microstructure and irradiation conditions (high burnup and temperature) where particularly favourable for this specific sample to observe this effect. In general, the irradiation temperature history is a determining parameter to allow for such segregation. The observation of a single 131-xenon peak can thus be indicative that the temperature has not exceeded the one necessary for the short living iodine isotopes to move to the grain boundaries.

In many samples, like very high burnup UO_2 [8] or heterogeneous MOX of larger burnup and different irradiation temperature, this particular behaviour of ^{131}Xe is hidden by the simultaneous release of all other xenon isotopes at this temperature. This low release temperature (800–1000 K) is related to high local burnup which results to local restructuring of the sample, the fission gas then precipitate in big pores or voids and are released at low temperature.

Acknowledgement

The authors want to thank Mr F. Capone and H. Thiele for performing Knudsen cell measurements and SEM observations of the samples.

References

[1] K. Maeda, K. Katsuyama, T. Asaga, J. Nucl. Mater. 346 (2005) 244.
[2] F. Capone, J.P. Hiernaut, M. Martellenghi, C. Ronchi, Nucl. Sci. Eng. 124 (1996) 436.
[3] J.Y. Colle, J.-P. Hiernaut, D. Papaioannou, C. Ronchi, A. Sasahara, J. Nucl. Mater. 348 (2006) 229.
[4] W.H. Hocking, R.A. Verrall, I.J. Muir, J. Nucl. Mater. 294 (2001) 45.
[5] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.
[6] P. Blair, A. Romano, C. Hellwig, R. Chawla, J. Nucl. Mater. 350 (2006) 232.
[7] E.H.P. Cordfunke, R.J.M. Konings, J. Nucl. Mater. 201 (1993) 57.
[8] J.P. Hiernaut, T. Wiss, J.Y. Colle, H. Thiele, C.T. Walker, W. Goll, R.J.M. Konings, J. Nucl. Mater. 377 (2008) 313.
[9] H. Matzke, Radiation Effects in Insulators, Arco, Lago di Garda, 1982. p. 3.
[10] J. Magill, Nuclides.net, Springer-Verlag, Heidelberg, 2003.
[11] H. Matzke, European Applied Research Reports Fission Gas behaviour in Nuclear Fuel, Karlsruhe, Germany, 1978.

[12] H. Matzke, R.P. Agarwala (Eds.), Diffusion Processes in Nuclear Materials, Elsevier, Amsterdam, 1992.

[13] I. Sato, T. Nakagiri, T. Hirosawa, S. Miyahara, T. Namekawa, J. Nucl. Sci. Technol. 40 (2003) 104.

[14] G. Busker, R.W. Grimes, M.R. Bradford, J. Nucl. Mater. 312 (2003) 156.

[15] S.G. Prussin, D.R. Olander, W.K. Lau, L. Hansson, J. Nucl. Mater. 154 (1988) 25.

[16] G. Busker, R.W. Grimes, M.R. Bradford, J. Nucl. Mater. 279 (2000) 46.

[17] W. Miekeley, F.W. Felix, J. Nucl. Mater. 42 (1972) 297.

[18] M. Saidy, W.H. Hocking, J.F. Mouris, P. Garcia, G. Carlot, B. Pasquet, J. Nucl. Mater. 372 (2008) 405.

[19] J.A. Turnbull, C.A. Friskney, J.R. Findlay, F.A. Johnson, A.J. Walter, J. Nucl. Mater. 107 (1982) 168.

[20] T.L. Markin, The plutonium–oxygen and uranium–plutonium–oxygen systems: a thermochemical assessment, Tech. Report Ser. No. 79, IAEA, 1967.