ELSEVIER

Journal of Nuclear Materials 275 (1999) 56–62

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Assessment of the radial extent and completion of recrystallisation in high burn-up UO_2 nuclear fuel by EPMA

C.T. Walker *

European Commission, Institute for Transuranium Elements, Joint Research Centre, Postfach 2340, D-76125 Karlsruhe, Germany

Received 25 January 1999; accepted 27 March 1999

Abstract

Questions concerning the correctness of the Xe concentration measured in the recrystallised UO_2 grains and the reliability of the values obtained for the width of the zone of recrystallisation in the fuel are answered. It is argued that since the Cs concentration is correct and since both Xe and Cs are determined simultaneously and under the same conditions the measured Xe concentration is also correct. In addition, experimental evidence is presented to show that EPMA provides a true indication of the zone width of recrystallisation because it detects islands of recrystallised fuel that are not taken into account in the optical microscopy results so far reported. EPMA results contained in the paper show that the transition zone between the normal UO_2 structure and the fully developed high burn-up structure extends from about 60 to roughly 120 GWd/tU and that the width of the zone containing recrystallised fuel increases considerably with the pellet burn-up.

1. Introduction

It is well established that when the average burn-up of UO_2 fuel exceeds 40–45 GWd/tM (where M = U + Pu) the UO_2 grains at the fuel surface begin to recrystallise. The transformed microstructure, which is termed the high burn-up structure, shows a pronounced decrease in fuel grain size, a high density of small faceted pores [1] and is characterised by loss of the fission gas Xe from the fuel matrix [2]. From X-ray fluorescence analysis it is known that at least a large part of the gas missing from the fuel matrix is contained in the pores [3,4].

Today, the high burn-up structure is probably the most studied phenomenon in UO_2 fuel. This is because there are concerns that its formation in the outer region of the fuel may cause a deterioration in the in-pile performance of the fuel. In particular, it is predicted that the local degradation in thermal conductivity that accompanies the formation of high levels of gas porosity will increase the temperature in the central region of the fuel causing enhanced thermal fission gas release and enhanced fuel swelling. Much of the work carried out on the high burn-up structure is aimed at understanding the irradiation effects that lead to its formation [5] and at clarifying the effects of temperature and burn-up on its evolution [6].

Electron probe microanalysis (EPMA) is probably the analytical tool that has provided the most data on the evolution of the microstructure transformation with burn-up. At the Institute for Transuranium Elements, EPMA is used routinely to estimate the radial extent of recrystallisation by measuring the distance over which Xe depletion occurs in the outer region of the fuel. Such measurements have shown that the local burn-up threshold for recrystallisation is close to 60 GWd/tM and that the transformation of the microstructure is complete at around 120 GWd/tM [2,4]. They also reveal that when the local burn-up throughout the fuel is higher than the threshold value, the restructuring that accompanies thermally activated fission gas release at about 1200°C limits the distance over which the change in microstructure occurs [1]. Another notable finding is that at high burn-up above 120 GWd/tM, the concentration of Xe in the recrystallised UO_2 grains is consistently of the order of 0.20–0.25 wt% [2,4].

* Tel.: 49-7247 951 477; fax: 49-7247 951 590

0022-3115/99/$ - see front matter
PII: S0022-3115(99)00108-7

Lately, the reliability of the data supplied by EPMA has been called into question. In a recent publication it was reported that Xe depletion in the fuel matrix occurs in advance of recrystallisation [7]. If this is so, then clearly EPMA provides values for both the width of the recrystallised zone and the local threshold burn-up that are unsafe. Further, several workers have inquired about the correctness of the Xe concentrations measured in the recrystallised fuel. Their reservations about the data appear to result from a perception that the emitted X-ray intensity is lowered by the gas pores which have been shown under other circumstances to affect the depth of electron penetration and the level of X-ray absorption [8]. The present paper reports experimental evidence proving that the EPMA data for the width of the recrystallised zone and for the local concentration of retained Xe are fundamentally sound.

2. Analysis of Xe by EPMA

EPMA is carried out at an electron acceleration potential of 25 kV and a beam current of 250 nA using Sb as a standard for Xe [9]. At 25 kV, the depth of analysis in UO_2 as calculated using the expression of Castaing [10] is about 1.8 μm and based on the arguments of Reed [11] 99% of the X-rays are generated in a volume of diameter 3.5 μm. The conventional microprobe matrix correction is made either with the QUAD2 program of Farthing et al. [12] or the PAP [13] option in the XMAS® program marketed by SAMx, France. The concentrations obtained with these programs differ by less than 0.1 wt%.

Around 40 data points are used to construct the radial distribution profile of Xe in the UO_2 matrix. In the outer region of the fuel, where the high burn-up structure is found, the points are spaced at intervals of 50 μm, with the first one located nominally 10 μm from the pellet rim. In the central region of the fuel the points are spaced further apart at intervals of 150 and sometimes 250 μm. At each location six peak intensity measurements are made up to 10 μm apart. In the high burn-up structure direct interaction of the electron beam with the gas pores was kept to a minimum by using the specimen current image (electron absorption image) to position the electron beam.

Generally, the radial distributions of Xe, Cs, Nd, Pu and U are measured in all samples of irradiated UO_2 fuel received for EPMA. It is important to note that the concentrations of Xe and Cs are determined simultaneously and at exactly the same location in the fuel matrix, as are the concentrations of U and Pu, which are determined in a second run. Neodymium, which is used as an indicator of the local burn-up, is analysed independently. Xenon is analysed using the $L\alpha_1$ X-ray line and a 1011 quartz diffracting crystal whereas Cs is analysed using the $L\beta_1$ X-ray line and a LiF diffracting crystal.

It is also pointed out that the reported xenon concentrations are not corrected for the effect of gas bubble size and distribution. The correction procedure, which was developed by Ronchi and Walker [8] may not be applicable. It assumes that gas bubbles are at equilibrium pressure, i.e., $p = 2\gamma/r$, where γ is the surface energy and r the bubble radius, which is a requirement for swelling. There is convincing evidence, however, that the gas pores in the high burn-up structure are overpressurised [14,15].

3. Radial distribution of Xe in high burn-up UO_2 fuel

Fig. 1 shows the radial distribution of Xe in a pressurised water reactor (PWR) fuel with an average cross-section burn-up of 67 GWd/tM. It can be seen that in addition to thermal gas release in the central region of the fuel, gas has been released from the fuel matrix in the region between $r/r_0 = 0.74$ and the pellet surface which is a distance of about 1 mm. Initially, the concentration of retained Xe decreases gradually as the fuel surface is approached, but at $r/r_0 = 0.93$ it falls sharply to about 0.2 wt% at the pellet rim. The gas release is a direct result of the formation of the high burn-up structure.

Shown in the figure is the burn-up at $r/r_0 = 0.74$ and at $r/r_0 = 0.99$ where the Xe concentration reached 0.2 wt%, its lowest level. At $r/r_0 = 0.74$ the burn-up was 62 GWd/tM and $r/r_0 = 0.99$ it was 120 GWd/tM. Both burn-up values are derived from the local concentration of Nd measured by EPMA.

In Fig. 2 the local Xe concentrations measured in the outer region of 38 UO_2 fuel sections with average burn-ups in the range 40–70 GWd/tU are plotted as a function the local burn-up. The broken line represents the build-up of Xe in the fuel grains without release. It can be seen that with accumulation of burn-up to 60–75 GWd/tM the Xe concentration increases linearly to about 1 wt%. Once this saturation level is reached, the Xe concentration falls sharply to around 0.2 wt% at about 120 GWd/tM. The maximum in the concentration curve at 60–75 GWd/tM marks the threshold burn-up for the formation of the high burn-up structure, and the onset of a region of constant low concentration at 120 GWd/tM indicates the burn-up at which the microstructure is completely transformed. Accordingly, 60 and 120 GWd/tM demarcate a transition zone in which the fuel microstructure still contains some original, untransformed UO_2 grains. In an earlier paper [2] the high burn-up structure was mistakenly said to be developed fully at 75 GWd/tM instead of 120 GWd/tM.

It is pointed out that Fig. 2 includes data from fuel irradiated in PWRs, in BWRs, and in the Belgium BR-3 reactor, data from fuel of various designs and ^{235}U

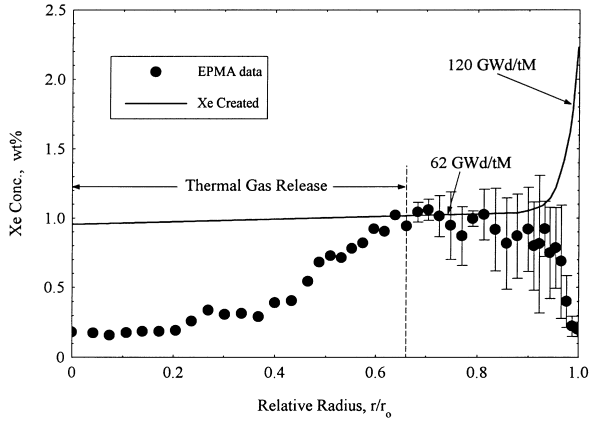

Fig. 1. Radial distribution of Xe in a PWR fuel with a burn-up of 67 GWd/tM. The concentration of Xe falls sharply in the vicinity of the pellet rim due to the formation of the high burn-up structure. The profile for the created amount of Xe is derived from the burn-up profile given by the radial distribution of fission product Nd. The error bars on the data points in the outer region of the fuel mark the confidence limits at the 95% level (2σ).

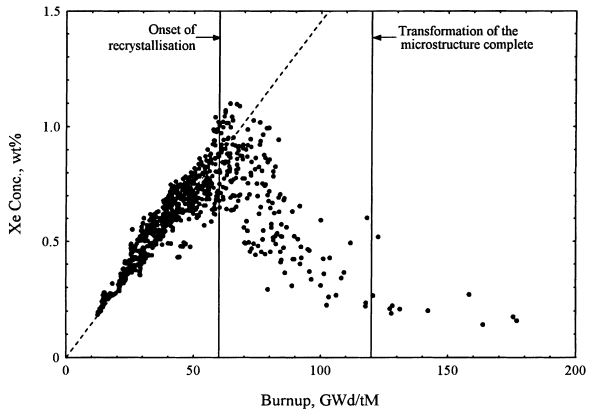

Fig. 2. Local Xe concentration in the outer region of UO_2 fuel between $r/r_0 = 0.7$ and the pellet rim related to the local burn-up. The Xe concentration falls sharply at 60–75 GWd/tM as a result of recystallisation. The broken line represents the calculated relationship without release.

enrichments, as well as Xe measurements carried out by AEA Technology, Windscale, UK. Consequently, the burn-up values quoted above are judged to have universal validity.

4. Correctness of the Xe concentrations measured in recrystallised UO_2 fuel

As stated in Section 2, Xe is analysed together with Cs. Thus, both fission products are analysed at exactly the same location in the fuel and under identical conditions. These elements are adjacent in the Periodic Table with atomic numbers of 54 and 55, respectively. Xenon is analysed using the $L\alpha_1$ characteristic X-ray line and Cs the $L\beta_1$ characteristic line. It can be seen from Table 1 that the excitation potentials and wavelengths of these lines are similar, as is their absorption in U, Xe and Cs. Consequently, if the gas porosity in the high burn-up structure causes a decrease in the emitted intensity of the Xe X-rays, it should also cause a similar decrease in the emitted intensity of the Cs X-rays.

Table 1
Some properties of the Xe $L\alpha_1$ and Cs $L\beta_1$ X-ray lines

Property	Xe $L\alpha_1$	Cs $L\beta_1$
Critical excitation energy (keV)	4.781	5.358
Wavelength (pm)	301.7	268.4
MAC [a], $(\mu/\rho)^{U}$, cm^2 g^{-1}	1310.4	1225.1
MAC [a], $(\mu/\rho)^{Xe}$, cm^2 g^{-1}	357.1	262.5
MAC [a], $(\mu/\rho)^{Cs}$, cm^2 g^{-1}	384.6	282.7

[a] Mass absorption coefficient (after Heinrich [16]).

In Fig. 3 the local concentration of Cs in the outer region of three PWR fuels is plotted against the Nd concentration representing the local burn-up. It can be seen that the measured Cs concentration increases linearly with the concentration of Nd and that the data points cluster along the line representing the predicted buildup of Cs with burn-up. These findings show not only that Cs is completely retained in the high burn-up structure, but also that EPMA accurately measures the concentration of Cs present. This proves unequivocally that the gas porosity in the high burn-up structure has a negligible effect on the emitted intensity of the Cs $L\beta_1$ X-ray line. The data in Fig. 3 are from fuel sections with average burn-ups of 63, 67 and 78 GWd/tM and the EPMA determinations were made in the radial interval between $r/r_0 = 0.8$ and the pellet rim. In this region the high burn-up structure was clearly visible in the electron absorption image and the radial Xe concentration profile measured by EPMA indicated that a substantial amount of gas was missing from the UO_2 matrix (see e.g., Fig. 1). The line representing the predicted buildup of Cs was drawn assuming that a burn-up of 10 GWd/tU produces 0.105 wt% Nd and 0.071 wt% Cs. The latter concentration is much lower than that obtained by summing the fission yields of the stable and long-lived isotopes ^{133}Cs, ^{135}Cs and ^{137}Cs ($\simeq$0.105 wt% for thermal fission of ^{235}U [17]). This reflects the fact that a large fraction of ^{135}Xe and part of ^{133}Xe were removed by neutron capture before they could decay to ^{135}Cs and ^{133}Cs.

Since the emitted intensity of the Cs $L\beta_1$ X-ray line is not significantly affected by the gas porosity in the high burn-up structure it follows that the emitted intensity of Xe $L\alpha_1$ X-ray line is also little affected. This being the case, the Xe concentrations measured in the high burn-up structure by EPMA can be accepted as accurately reflecting the content of gas in the recrystallised fuel grains.

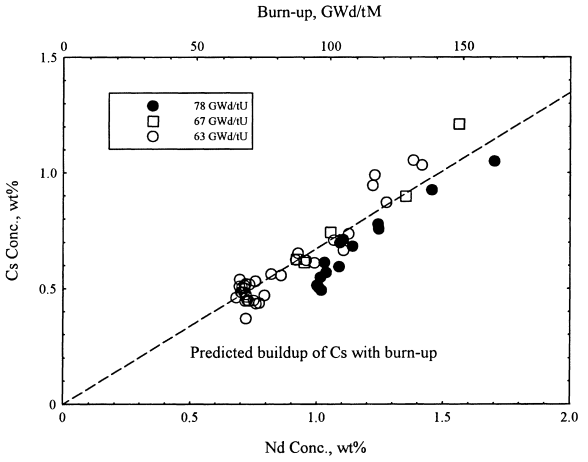

Fig. 3. Local Cs concentration in the outer region of four PWR fuels between $r/r_0 = 0.8$ and the pellet rim related to the local Nd concentration representing the burn-up. The Cs concentration increases linearly indicating full retention and showing that the measured Cs concentrations are unaffected by the gas porosity in the high burn-up structure.

Although the Xe concentrations measured by EPMA in individual untransformed and recrystallised grains is evidently correct, in the transition zone where unrestructured and recrystallised fuel regions exist side by side, the measured Xe concentrations exhibit a large scatter (see Fig. 2). This is because the concentrations plotted are the average of six determinations distributed between untransformed and recystallised fuel grains which contain high and low concentrations of Xe, respectively.

5. Reliability of the values given for the width of the recrystallised zone

Cunningham et al. in their paper on the development and characteristics of the rim region in high burn-up UO_2 fuel [3] present figures and tables in which the zone width for the high burn-up structure measured by EPMA is seen always to be larger than that found by optical microscopy. Recently, Spino et al. [7] reported that matrix xenon depletion detected by EPMA occurred in advance of the precipitation of the gas porosity associated with the high burn-up structure. If correct, this finding provides strong support for the proposal that pressurised gas pores act as nucleation sites for recrystallisation [18,19].

Table 2 shows the penetration depth of the high burn-up structure in fuel sections from Battelle's High Burn-up Effects Program [3,20,21] as found by optical microscopy and EPMA. The optical microscopy data are taken from Table 2 in the paper of Cunningham et al. [3]. These data derive from measurements on etched specimens and represent the width of a narrow zone at the pellet rim that is characterised by a high density of gas pores and no discernible grain structure. The EPMA data are revised figures obtained during a recent review and re-evaluation of the microprobe analysis results obtained in the High Burn-up Effects Program [4]. It is seen from the table that for the fuel sections with burn-ups of 67 GWd/tM and above, EPMA gave zone widths for the high burn-up structure that were considerably larger than those obtained by optical microscopy. For example, in the case of fuel section BK365-46 (average burn-up 83.1 GWd/tM) the optical microscopy result indicates that the high burn-up structure was confined to the vicinity of the pellet rim, whereas the EPMA result indicates that it was present throughout the fuel cross-section.

Table 2
Penetration depth of the high burn-up structure in fuel sections from the Battelle High Burn-up Effects Programme as found by optical microscopy and EPMA

Fuel section	Burn-up	Radial distance, μm	
	(GWd/tU)	EPMA, (Ref. [4])	Optical microscopy, (Refs. [3,21])
BK365-46	83.1	2900 [a]	140
BSH-06-49	72.4	660	120
3-138-50	70.4	960	70
BK365-86	67.1	1410 [a]	120
BLH-64-43	62.5	100	85
H8/36-4-220	54.9	150	80
H8/36-4-48.2	44.8	150	120

[a] The high burn-up structure extended from the pellet rim to the surface of the central hole.

Fig. 4 shows the microstructure in the outer region of a UO_2 fuel with a burn-up of roughly 70 GWd/tM as revealed by the absorbed electron image during EPMA. The EPMA concentration profiles for Xe, Nd and Pu reported by Spino et al. [7] were measured along the fuel radius shown in the micrograph. Marked in the figure are the radial positions at which quantitative optical microscopy first revealed an increase in porosity in the surface region of the fuel ($r/r_0 = 0.965$) and the onset position for Xe depletion from EPMA ($r/r_0 = 0.94$) as reported by Spino et al. [7]. The white spots in the micrograph are the gas pores of the high burn-up structure.

It is clearly seen from the absorbed electron micrograph in Fig. 4 that islands of high burn-up structure are present from approximately $r/r_0 = 0.99$ up to and even beyond $r/r_0 = 0.94$. Hence, the finding of Spino et al. that matrix xenon depletion occurred in advance of the formation of gas pores almost certainly results from the fact that in the region between $r/r_0 = 0.94$ and 0.965 some of these islands of high burn-up structure were included in the EPMA determinations. The burn-up at $r/r_0 = 0.94$ as calculated from the local Nd concentration is 73 GWd/tM. (A conversion factor of 0.12 wt% Nd = 10 GWd/tU was used since the initial ^{235}U enrichment of the fuel was 8.6%.) As seen in section 3, the transition zone starts at 60–75 GWd/tM and ends at around 120 GWd/tM. Since the burn-up at the pellet rim was 100 GWd/tM, it follows that the transition zone in which partial transformation of the fuel microstucture had occurred extended from $r/r_0 = 0.94$ to the pellet rim. This is confirmed by the existence of unrestructured areas of fuel at $r/r_0 = 0.99$ in Fig. 4 and by the observation of untransformed grains at the fuel rim by Spino et al. [7].

In Fig. 5 the radial position at which the high burn-up structure is first detected by optical microscopy and EPMA is plotted as a function of the average burn-up of the fuel. It can be seen that the results from optical microscopy indicate that the high burn-up structure is confined to the pellet rim region independent of the burn-up level. In contrast, the EPMA results reveal that the

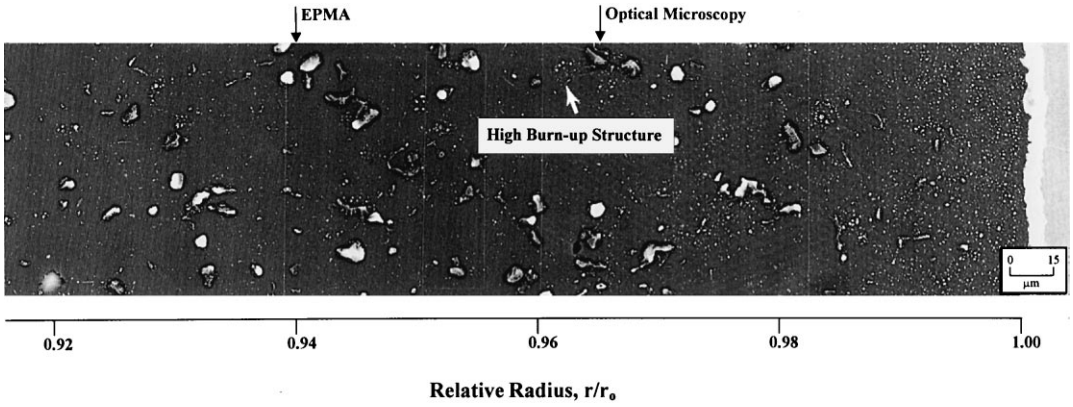

Fig. 4. Absorbed electron image showing the microstructure in outer region of a UO_2 fuel with an average burn-up of 70 GWd/tU. Islands of high burn-up structure are clearly visible up to and even beyond $r/r_0 = 0.965$ the radial limit for the formation of gas porosity in the outer region of the fuel according to Spino et al. [7].

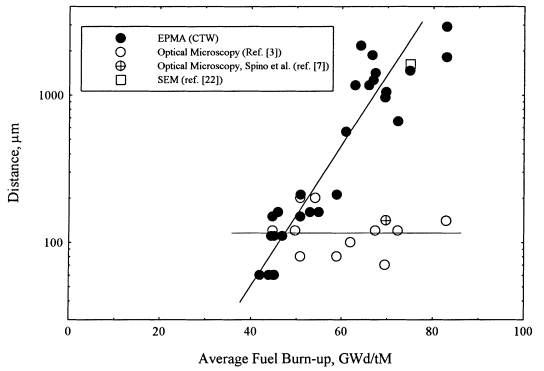

Fig. 5. Width of the zone in which the high burn-up structure occurs as a function of the average fuel burn-up. Optical microscopy indicates that independent of the burn-up the high burn-up structure is confined to the pellet rim region whereas EPMA shows that the width of the region affected increases considerably with burn-up. The lines drawn through the two data sets serve to guide the eye. □: [22].

penetration depth of the high burn-up structure increases markedly with the average burn-up of the fuel.

6. Conclusions

Doubts about the correctness of the xenon concentrations measured by EPMA in the recrystallised grains of high burn-up fuel are unfounded. The porosity in the high burn-up structure has a negligible effect on the emitted intensity of the Xe $L\alpha_1$ X-rays. This being so, the Xe concentrations measured in the high burn-up structure by EPMA are recognised as accurately reflecting the gas content of the recrystallised fuel grains. The large scatter in the Xe concentrations measured by EPMA in the transition zone where areas of unrestructured and recrystallised fuel exist side by side is a consequence of the measurement procedure adopted. This requires that at each radial position the intensity of the Xe X-ray peak is measured six times at different localised points in the fuel. The scatter in the data arises because at each radial position the contributions made to the six intensity measurements by areas of high burn-up structure and areas of unrestructured grains are different. Clearly, an alternative way to analysis the transition zone is to treat it as a duplex structure and measure the concentration of Xe in the unrestructured and recrystallised regions separately. The Xe distribution in the transition zone derived from the repeated measurement of the average local concentration of the gas, however, fulfils an important technological need; it provides a measure of the radial extent of recrystallisation. The EPMA procedure outlined in this paper gives a true indication of the zone width of recrystallisation because it detects islands of recrystallised fuel in the transition zone. In the few cases where the radial penetration of the high burn-up structure has been determined by optical microscopy, these islands of recrystallisation have not been taken into account. Consequently, at average fuel burn-ups above 60 GWd/tM the transformation of the fuel microstructure is reported to be confined to a much narrower zone than found by EPMA.

References

[1] C.T. Walker, T. Kameyama, S. Kitajima, M. Kinoshita, J. Nucl. Mater. 188 (1992) 73.
[2] K. Lassmann, C.T. Walker, J. van de Laar, F. Lindström, J. Nucl. Mater. 226 (1995) 1.
[3] M.E. Cunningham, M.D. Freshley, D.D. Lanning, J. Nucl. Mater. 188 (1992) 19.
[4] M. Mogensen, J.H. Pearce, C.T. Walker, J. Nucl. Mater. 264 (1999) 99.
[5] K. Une, K. Nogita, S. Kashibe, T. Toyonaga, M. Amaya, in: Procedings of the Internationl Topical Meeting on Light Water Reactor Fuel Performance, Portland, Oregon, USA, March 2–6, 1997, ANS, La Grange Park, IL, 1997, p. 478.
[6] M. Kinoshita, S. Kitajima, E. Kolstad, Hj. Matzke, in: Proceedings of the International Topical Meeting on Light Water Reactor Fuel Performance, Portland, Oregon, USA, March 2–6, 1997, ANS, La Grange Park, IL, 1997, p. 530.
[7] J. Spino, D. Baron, M. Coquerelle, A.D. Stalios, J. Nucl. Mater. 256 (1998) 189.
[8] C. Ronchi, C.T. Walker, J. Phys. D 13 (1980) 2175.
[9] C.T. Walker, J. Nucl. Mater. 80 (1979) 190.
[10] R. Castaing, in: L. Marton (Ed.), Advances in Electronics and Electron Physics, vol. 13, Academic Press, New York, 1960, p. 317.
[11] S.J.B. Reed, in: R. Castaing, P. Deschamp, J. Philbert (Eds.), Proceedings of Fourth International Congress on X-ray Optics and Microanalysis, Herman, Paris, 1966, p. 339.
[12] I. Farthing, G. Love, V.D. Scott, C.T. Walker, Mikrochim. Acta Suppl. 12 (1992) 117.
[13] J.L. Pouchou, F. Pichoir, in: K.F.J. Heinrich, D.E. Newbury (Eds.), Electron Probe Quantitation, Plenum, New York, 1991, p. 31.
[14] K. Nogita, K. Une, J. Nucl. Mater. 226 (1995) 302.
[15] K. Une, K. Nogita, S Kashibe, T. Toyonaga, M. Amaya, in: Proceedings of the International Topical Meeting on Light Water Reactor Fuel Performance, Portland, Oregon, USA, March 2–6, 1997, ANS, La Grange Park, IL, 1997, p. 478.
[16] K.F.J. Heinrich, in: J.D. Brown, A.H. Packwood (Eds.), Proceedings of Eleventh International Congress on X-ray Optics and Microanalysis, Univ. of Western Ontario, 1986, p. 67.
[17] M.E. Meek, B.F. Rider, Report NEDO-12154, 1974.
[18] H. Matzke, A. Turos, G. Linker, Nucl. Instrum. Meth. B 91 (1994) 294.

[19] J. Spino, K. Vennix, M. Coquerelle, J. Nucl. Mater. 231 (1996) 179.
[20] J.O. Barner, M.E. Cunningham, M.D. Freshley, D.D. Lanning, Nucl. Technol. 102 (1993) 210.
[21] M.E. Cunningham, M.D. Freshley, D.D. Lanning, J. Nucl. Mater. 200 (1993) 24.
[22] I.L.F. Ray, Hj. Matzke, H.A. Thiele, M. Kinoshita, J. Nucl. Mater. 245 (1997) 115.