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Thermal treatment of uranium oxide irradiated in pressurized water reactor: Swelling and release of fission gases

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Abstract

Unstressed samples of uranium oxide taken from pressurized water reactor (PWR) fuel after two normal operating cycles, i.e., with a burn-up of 25 GWd/tU, were subjected to thermal treatment in a laboratory furnace at temperatures between 1130°C and 1715°C for durations between 5 min and 10 h. The variation of the quantity of fission gas released over time was determined at each temperature. The experimental results were found to compare with those of an existing numerical model, and it would thus appear that the release of gas after formation in tunnels at the grain boundaries is controlled by the diffusion of these gases from the material towards the grain boundaries. These samples were also subjected to a series of isothermal swelling measurements. Their comparison provides information on intergranular, intragranular, open and closed porosity. The study carried out finally makes it possible to interpret the behaviour of fission gases in the event of a temperature rise. Initially, swelling and release are controlled by a single mechanism: bubble coalescence. Subsequently, these phenomena are controlled by separate mechanisms: swelling continues through coalescence and release is due to the diffusion of the fission gases from the matrix to the tunnels at the grain boundaries. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

A power transient corresponds to an increase in the temperature at the centre of the fuel and a substantial increase in the temperature difference between the centre of the pellet (hot) and the outside edge (cold). Under the effect of the temperature and the thermal gradient, fission gases can diffuse and precipitate, creating gas bubbles in the fuel. These bubbles cause substantial swelling of the pellet. The fission gases can diffuse both in atomic form or in the form of bubbles towards a free surface where they escape from the fuel.

The release of fission products is an important factor in the increase in pressure inside the cladding. As for the swelling, it contributes to the pressure of the pellet against the cladding. These two phenomena must therefore be taken into consideration in assuring cladding integrity in power transients. This article is intended to help understand them. For the purpose, uranium oxide fuel previously irradiated in a pressurized water reactor (PWR) up to 25 GWd/tU was therefore treated at high temperature in a hot laboratory furnace.

2. Experimental study

2.1. The material

The samples consisted of unstressed pieces of uranium oxide a few millimetres in size, recovered when taking a section some 8 mm long.

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Table 1
Main characteristics of samples

Fuel rod	
Type of rod	UO_2
Number of cycles	2
Filling gas	He
Internal pressure (bar)	26
Fuel before irradiation	
Enrichment with U_{235} (%)	4.5
Average grain size (μm)	9.3
Density by immersion (g/cm^3)	10.39[a]
Density by immersion (percent of theoretical density)	94.75
Fuel after irradiation	
Burn-up (GWd/tU)	25
Density by immersion (g/cm^3)	10.39[a]
Average grain size (μm)	9.3

[a] Densification and swelling explain that fuel density before and after irradiation are the same.

The samples, whose main characteristics are indicated in Table 1, were derived from a UO_2 fuel rod having operated in a PWR under normal conditions for two cycles, i.e., with a burn-up of 25 GWd/tU (Fig. 1). The fuel has been submitted to a thermal radial gradient whose core temperature does not exceed 1100°C. This fuel has the advantage of having a simple microstructure, i.e., a relatively uniform distribution of fission gases dissolved in the matrix system [1].

2.2. The thermal treatment

The treatment temperatures range from 1130°C to 1715°C and the durations vary between 5 min and 10 h, being representative of the conditions attained in the power transients created in an experimental reactor. The samples were placed in a tungsten crucible in vacuum ($< 10^{-3}$ mbar) then heated by induction in a high-frequency laboratory furnace, previously calibrated with a bichromatic optical pyrometer. The temperatures were accurate within ±20°C. The samples were loaded and unloaded at room temperature. The temperature rise time was 2.5 min and the cooling time was 2 min.

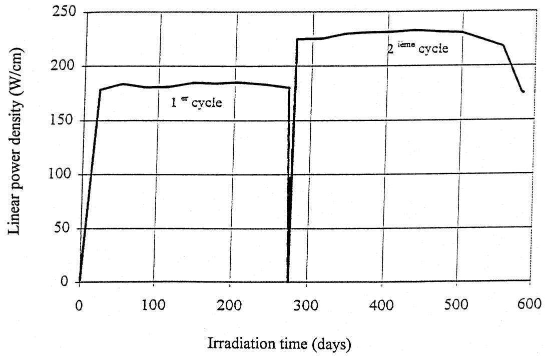

Fig. 1. Power history of irradiated UO_2 fuel (25 GWd/tU).

2.3. Measurement of release

The dynamics of the release of fission gas during each thermal treatment was determined by sampling the fission gases released by means of a pump circuit. The fission gases extracted, whose volumes were measured at room temperature, were recovered in ampoules and subsequently analysed by mass spectrometry.

The release of xenon was characterised by the fraction of xenon released (f_{Xe}). This represents the ratio between the volume of xenon released by the sample during thermal treatment and the volume of fission gas formed by irradiation. The volume of xenon formed by irradiation in this type of fuel and with this burn-up of 25 GWd/tU (enriched with 4.5% U_{235}), is taken to be equal to [2]

$$V_{\mathrm{Xe\,formed}} = 0.625 \times M_{\mathrm{UO_2}}$$

where $V_{\mathrm{Xe\ formed}}$ is the volume of xenon formed (cm^3 STP); and M_{UO_2} is the mass of UO_2 (g).

The release of fission gas during irradiation, estimated at 0.18%, was disregarded. The relative uncertainty concerning the fraction of xenon released was ±2.5%.

2.4. Measurement of swelling

As a general rule, the swelling (S) of the various samples is defined as the ratio between the variation of volume between an initial state (i) (irradiated and untreated) and a final state (f) (irradiated and treated) over the initial volume of the sample:

$$S = \frac{V_{(\mathrm{f})} - V_{(\mathrm{i})}}{V_{(\mathrm{i})}}.$$

The material studied is porous. Measurement of the volume can vary as a function of the technique adopted. This leads to different swelling calculations, which supply complementary information. Three techniques were used: hydrostatic weighing, hydrostatic weighing after varnishing and image analysis. The first makes no allowance for open porosity, the second does, and measurement by image analysis only makes allowance for porosity of sufficient size.

2.4.1. Measurement by hydrostatic weighing

With the hydrostatic weighing technique, swelling is calculated on the basis of measurement of densities ρ_{i} and ρ_{f} of the samples before and after their heat treatment.

This method consists in weighing the samples in air then impregnating it with bromobenzene (2 h) in vacuum (10^{-2} mbar). The measures were realised in accordance with the laboratory specification. The swelling is then given by the formula

$$S_1 = \frac{\rho_i - \rho_f}{\rho_f \left(1 + \frac{\Delta m}{m_f}\right)},$$

where Δm is the loss of the mass during treatment and m_f the final mass of the sample.

In this study, the maximum mass loss by release of fission gases corresponding to the maximum temperature and the maximum time is equal to 0.07%. $\Delta m / m_f$ is therefore negligible relative to 1. Hence,

$$S_1 = \frac{\rho_i - \rho_f}{\rho_f}. \qquad (1)$$

The maximum uncertainty concerning measurement is ±0.3%.

2.4.2. *Measurement by hydrostatic weighing after varnishing [1]*

This technique has been improved to make allowance both for closed porosity and open porosity by prior varnishing of the UO_2 samples:

$$S_2 = \frac{\rho_i - \rho_f}{\rho_f}. \qquad (2)$$

This technique has been also used with water instead of bromobenzene. The results were identical [1].

Its qualification has revealed high reproducibility of the results, although with a systematic overestimation of the volume of 5% which was taken into account. It was therefore only adopted for estimating overall swelling, having to be used with particular care.

2.4.3. *Measurement by image analysis*

The third technique is one of microscopic scale, used to determine swelling by observation of the microstructure of the material before and after treatment. Swelling was given by the formula

$$S_3 = \frac{V_v(P)_{(f)} - V_v(P)_{(i)}}{1 - V_v(P)_{(f)}}, \qquad (3)$$

where $V_v(P)_{(i)}$ and $V_v(P)_{(f)}$ are respectively the volume fractions before and after treatment.

To determine the fractions per unit volume of the samples, polished sections were used. The analysis was conducted using grey scale images obtained with a scanning electron microscope in the backscatter mode (Fig. 2), at enlargements of 2000 and 3500. The section is restricted to a single window (same location at enlargements of 2000 and 3500), representative of the entire surface. An automatic processing procedure was specifically developed for this application [1]. This enabled measurement of the pore area factor per image. As our equipment gave a stationary random set, the average pore area factor of the window gave the fraction per unit volume. This was used to deduce the swelling using Eq. (3). Absolute accuracy of measurement of swelling was estimated at ±1%.

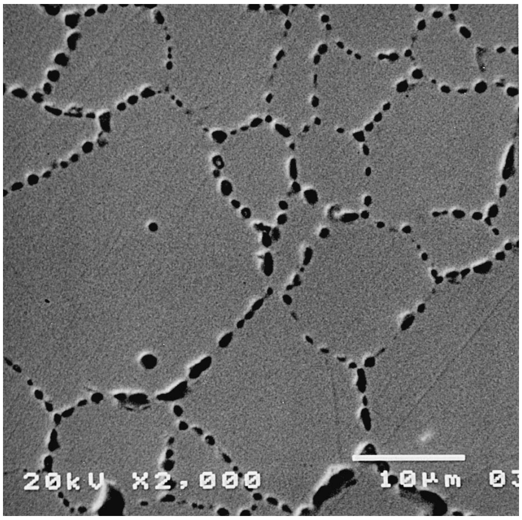

Fig. 2. Backscatter mode images of a sample of two-cycle UO_2 treated at 1545°C for 1 h.

The swelling as determined by the analysis of images obtained by scanning electron microscope makes allowance for intergranular bubbles of diameters of around 1 μm. Conversely, bubbles of diameters below 0.1 μm in all the thermal treatments are too small to be observed at these enlargements. The swelling determined was essentially intergranular.

3. Experimental results: measurement of swelling and of release of fission gases

3.1. *Swelling*

The above three techniques made it possible to monitor variation of swelling with treatment time and temperature. Similar rates were observed at all temperatures (Fig. 3), consisting of two phases: a rapid swelling phase for up to 60 min and a second phase in which the process slows. Swelling is activated by temperature.

The intergranular swelling, determined by image analysis as a function of treatment time, at different temperatures is shown in Fig. 3. At 60 min, the swelling reaches 4.1% at 1545°C and 7.4% at 1715°C. Then, in the following 9 h, it increases by approximately a further 3% at 1545°C and 2% at 1715°C.

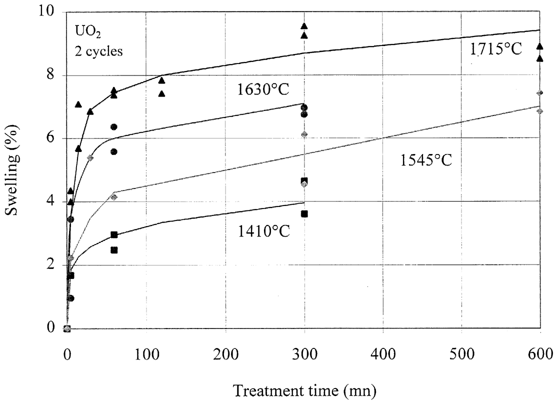

Fig. 3. Intergranular swelling determined by image analysis as a function of treatment time at different temperatures.

3.2. Xenon release

The release of fission gases varies in the same manner as swelling. The xenon release curves shown in Fig. 4 show a fast increase in the first 60 min of treatment followed by a slow increase accelerated by temperature. Substantial swelling is thus accompanied by a large release of fission gases and vice versa. The thermal release of fission gases becomes significant only above 1130°C.

The curves also show considerable scatter of points at 1715°C. This is attributed to the temperature measurement uncertainty, which strongly affects a release in this range.

3.3. Comparison

The swelling values obtained using the conventional hydrostatic weighing method are more reliable than those obtained with the other two methods (image analysis and the improved hydrostatic weighing method) (Fig. 5). As the conventional method does not account for the open porosity, it can be deduced that its contribution is significant. Indeed, micrographic examination indicates the presence of channels at the grain boundary edges beyond 1410°C, which, it is assumed, participate in open porosity, as they are open to the exterior (Fig. 6).

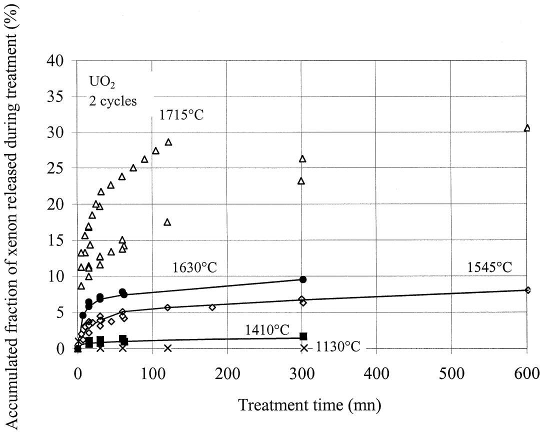

Fig. 4. Release of xenon as a function of treatment time at different temperatures.

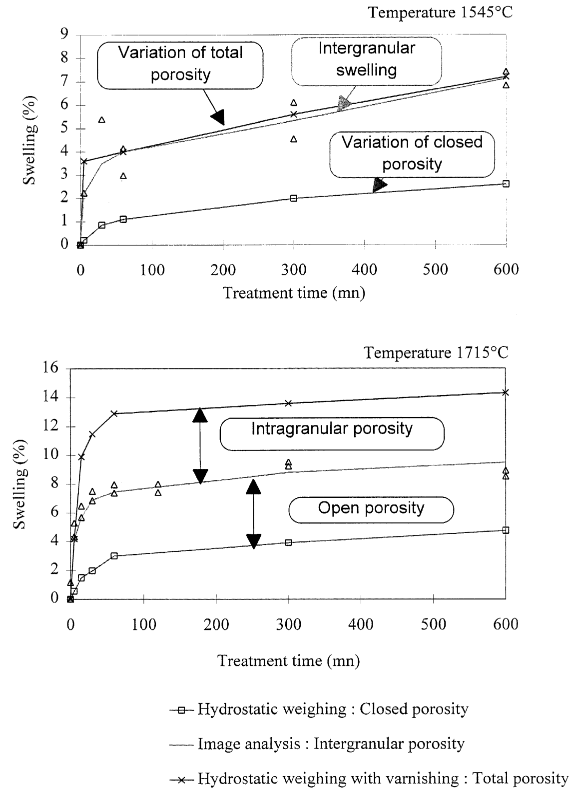

Fig. 5. Comparison of the results of swelling obtained by the three methods as a function of treatment time at 1545°C and 1715°C.

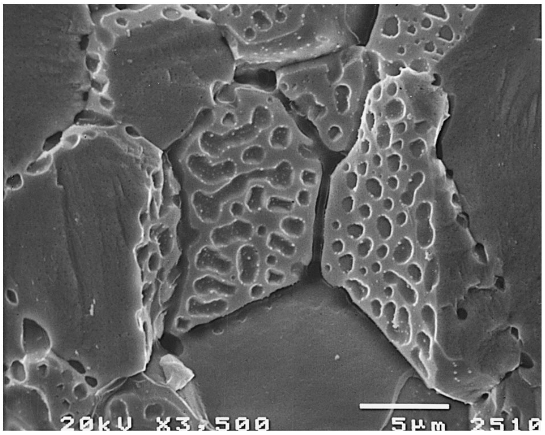

Fig. 6. Scanning electron microscope examination of fractures of samples (25 GWd/tU) untreated and after heat treatment: formation of tunnels on the grain boundary edges.

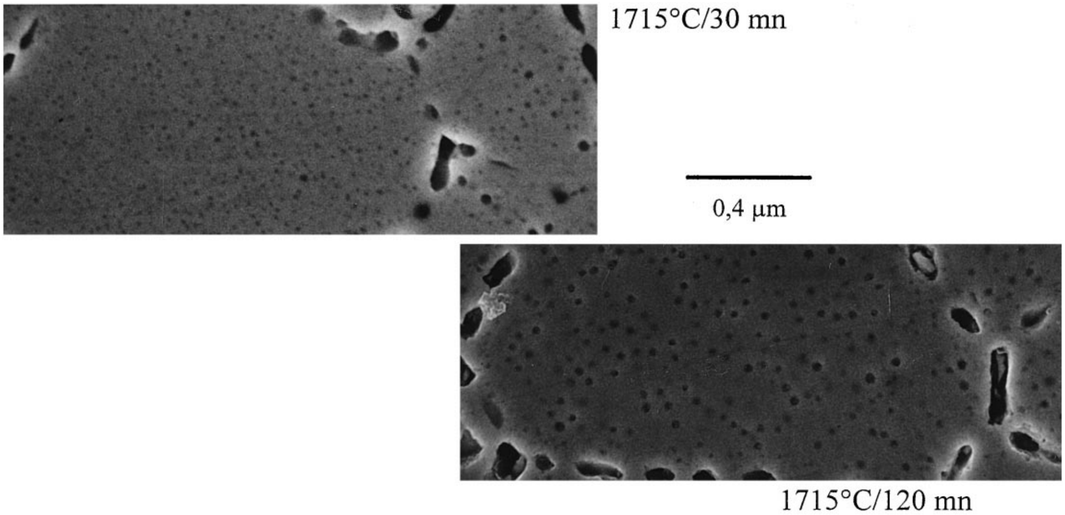

Fig. 7. Formation of intragranular bubbles in a fractured sample (25 GWd/tU) treated at 1715°C for 5 h.

A comparison was made between the values obtained with the improved hydrostatic weighing method (with varnishing) and those obtained by image analysis. These are close for temperatures below 1630°C (Fig. 5). This observation made it possible to validate the two methods. On the other hand, at 1715°C, the values obtained by image analysis are lower than those obtained by hydrostatic weighing with varnishing. This difference can be interpreted by the fact that image analysis does not allow for bubbles with a thickness greater than one pixel. In view of the microstructure of the material, the bubbles are essentially intragranular in nature. This agrees with the scanning electron microscope observations which show the presence, at 1715°C, of numerous small intragranular bubbles smaller in diameter than 0.1 µm (Fig. 7). Using the difference between these two types of measurements, it is possible to determine the evolution of intragranular swelling as a function of time at different temperatures (Fig. 8). This was found to be very limited at 1410°C and then to gradually increase with temperature to around 5% at 1715°C. However, up to 1715°C, it remains lower than the intergranular swelling.

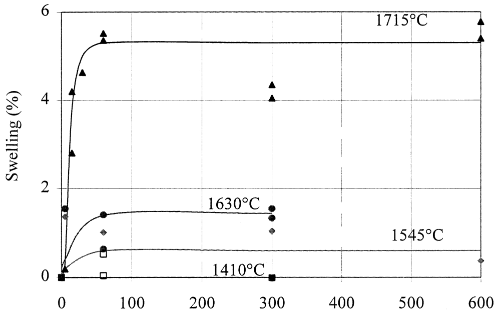

Fig. 8. Intragranular swelling as a function of treatment time at different temperatures.

4. Interpretation of the isothermal release of fission gases

The mechanisms controlling the release of fission gases during thermal treatment have been identified by different authors [3–5], who have identified two phenomena which successively predominate.

(a) Initially, the release of fission gases is rapid due to the interconnection of the intergranular bubbles and the formation of tunnels leading to the free surfaces. This interconnection allows massive release of fission gases to the exterior; this is the main mechanism in the first phase of fission gas release.

(b) Subsequently, the release is controlled by the diffusion of the fission gases into the grain boundaries where the atoms, which encounter tunnels formed by interconnected bubbles, are immediately released to the exterior. This mechanism, which is initially masked by the massive release due to the formation of tunnels, subsequently becomes predominant. This marks the beginning of the second phase of release.

Our results are interpreted on the basis of these mechanisms, beginning with release controlled by diffusion of the fission gases.

4.1. Study of release of fission gases by diffusion

The migration of fission gas atoms towards the grain boundaries can be due to atomic diffusion and the migration of intergranular bubbles. This second mechanism, according to the literature, only starts at temperatures above 1545°C [3,6,7]. Now we wish to determine whether the atomic diffusion mechanism was predominant over the

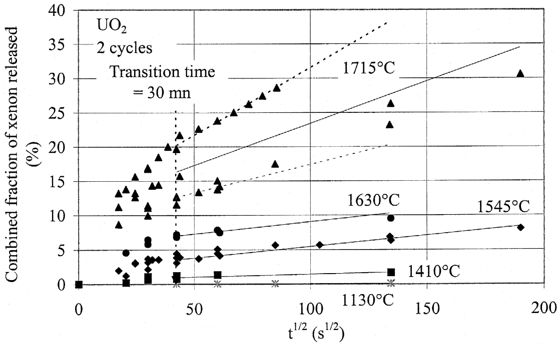

Fig. 9. Release of xenon as a function of the square root of the treatment time at different temperatures.

entire temperature range studied (1130°C–1715°C) or if it became negligible with respect to the random migration of bubbles at very high temperatures.

The experimental data was compared to a theoretical model of fission gases released by atomic diffusion, using the following equation (in view of the short time approximation) [8,9]:

$$f_{\mathrm{Xe}} = \frac{6}{\sqrt{\pi}}(D't)^{1/2}, \tag{4}$$

where D' is an empirical coefficient in relation with the apparent coefficient D and the grain size a ($D' = D/a^2$) [1].

It expresses a mechanism characterised by linear variation with the square root of the treatment time, as can be seen in Fig. 9, after 30 min of treatment. The D' points determined as a function of temperature and plotted in Fig. 10 follow an Arrhenius law of the following shape:

$$D'_{(\mathrm{Xe})} = D'_{0(\mathrm{Xe})}\exp\left(\frac{-E_{\mathrm{a(Xe)}}}{RT}\right) \tag{5}$$

with a constant activation energy (E_{a}) of 445 kJ/mol, i.e., 4.6 eV/atom. The diffusion of the xenon atoms is thus the mechanism which controls the release between 1130°C and 1715°C. Indeed, the determined activation energy of 4.6 eV/atom thus agrees perfectly with the activation energy of 4.7 eV/atom proposed by Matzke [10].

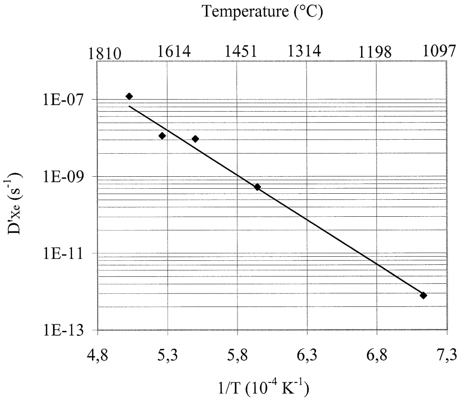

Fig. 10. Empirical coefficient D'_{Xe} of xenon as an inverse function of the temperature.

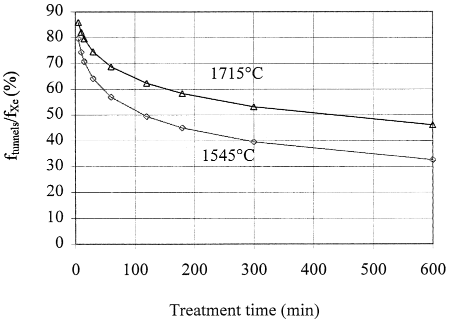

Fig. 11. Contribution of the accumulated release of xenon by the formation of the tunnels to the total release as a function of treatment time at two different temperatures.

4.2. *Study of the release of fission gases by the formation of tunnels*

A study was made of the first phase of fission gas release. It should be borne in mind that, here, release is due to the interconnection of intergranular bubbles and the formation of tunnels which, when they reach a free surface, release their fission gas to the exterior. This was estimated by subtracting release by atomic diffusion (Eq. (4)) from total release.

Fig. 11 shows the contribution of release by the formation of tunnels to the total release, as a function of treatment time. After a few minutes, this amounts to around 85%, varying to around 40% at 600 min.

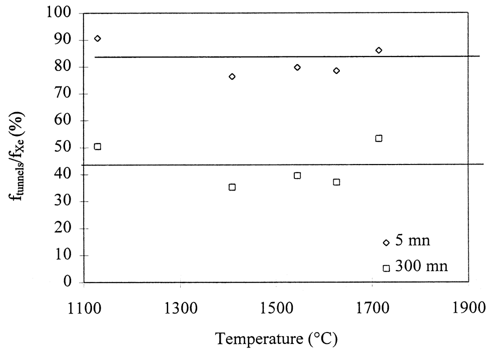

Fig. 12. Contribution of the accumulated release of xenon by the formation of the tunnels to the total release, as a function of temperature for two different treatment times.

Fig. 12 shows that this contribution at the two different treatment times remains virtually constant with temperature.

5. Behaviour of fission gases at high temperature

The combined analysis of release and swelling makes it possible to suggest an interpretation of the behaviour of fission gases at high temperatures. At the initial instant, the fission gases, produced during base irradiation in the reactor, are present as a solid solution state or in the form of microbubbles in the matrix.

5.1. Treatment time less than 5 min

When the temperature is raised, the fission gases precipitate and form microbubbles. After 5 min, and at temperatures between 1130°C and 1715°C, the bubbles which have formed at the grain boundaries reach a size observable with a scanning electron microscope. However, within the grains, no change in the bubbles is visible. No treatment shorter than 5 min was performed.

5.2. Treatment time between 5 min and 30 min

The growth of the intergranular bubbles is controlled by the phenomenon of coalescence. This results in an increase in the size of bubbles and a decrease in the number of bubbles over time. The swelling is due to the coalescence of the bubbles.

The coalescence of the bubbles also results in a rapid interconnection of the bubbles and the edges common to a number of grains and, sometimes, at the faces of certain grains. This results in a formation of tunnels leading to the exterior. These tunnels constitute open pores. Open pores become larger as the temperature rises. The bubbles which have created tunnels are then massively released to the exterior, causing a sudden burst of gas. In this phase, swelling and release are thus closely linked.

5.3. Treatment time between 30 min and 10 h

Tunnels are already formed, but the fission gases arriving from the matrix by diffusion reach the tunnels and are released. This mechanism become predominant. Furthermore, coalescence of bubbles at the surfaces of the grains without access to the exterior continues. In the second phase, swelling and release are two independent phenomena.

6. Conclusion

Different samples of UO_2 from PWR fuel with a burn-up of 25 GWd/tU were treated in a laboratory furnace at temperatures between 1100°C and 1715°C for durations between 5 min and 10 h. Free swelling and release were measured. The following conclusions were reached.

Swelling and release developed in parallel: a rapid increase in the first 60 min of treatment, followed by a slow change accelerated by temperature.

The intragranular bubbles are only observed at a temperature of 1715°C. At lower temperatures, their contribution to overall swelling is negligible.

In the first few minutes, release is controlled by the formation of tunnels at the grain boundaries which open. Thereafter, when the tunnels are formed, the diffusion of fission gas atoms in the matrix into the grain boundaries controls the process. During the second phase, the activation energy of the mechanism is 4.6 eV/atom.

An interpretation of the behaviour of the fission gases during thermal treatment is proposed. Initially, swelling and release are controlled by the coalescence of bubbles. Subsequently, these phenomena are controlled by two distinct mechanisms: swelling continues by coalescence and release is due to diffusion of fission gas from the matrix into the tunnels at the grain boundaries.

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