Journal of Nuclear Materials 71 (1977) 117–123

THE MIGRATION OF INTRAGRANULAR FISSION GAS BUBBLES IN IRRADIATED URANIUM DIOXIDE

C. BAKER
Central Electricity Generating Board, Berkeley Nuclear Laboratories, Berkeley, Gloucestershire, UK

Received 31 May 1977

The mobility of intragranular fission gas bubbles in uranium dioxide, irradiated at 1600–1800°C, has been studied following isothermal annealing at temperatures below 1600°C. The intragranular fission gas bubbles, average diameter approximately 2 nm, are virtually immobile at temperatures below 1500°C. The bubbles have clean surfaces with no solid fission product contamination and are faceted to the highest observed irradiation temperature of 1800°C. This bubble faceting is believed to be a major cause of bubble immobility. In fuel operating below 1500°C the predominant mechanism allowing the growth of intergranular bubbles and the subsequent gas release must be the diffusion of dissolved gas atoms rather than the movement of entire intragranular bubbles.

La mobilité de bulles intergranulaires de gaz de fission dans du dioxyde d'uranium irradié à 1600-1800°C a été étudiée au cours d'un recuit isotherme à des températures inférieures à 1600°C. Les bulles de gaz de fission aux joints des grains, d'un diamètre moyen approximatif de 2 nm sont pratiquement immobiles aux températures inférieures à 1500°C.

Les bulles ont des surfaces propres sans contamination par des produits de fission solides et présentent des facettes pour la température maximale d'irradiation observée de 1800°C. Cet aspect facetté des bulles est considéré comme la cause majeure de l'immobilité des bulles.

Dans un combustible fonctionnant en dessous de 1500°C, le mécanisme prédominant permettant la croissance des bulles intergranulaires et le dégagement ultérieur de gaz doit être la diffusion des atomes de gaz dissous plutôt que le mouvement de bulles intergranulaires entières.

Die Beweglichkeit intrakristalliner Spaltgasblasen in Urandioxid, das zwischen 1600 und 1800°C bestrahlt worden war, wurde nach einer isothermen Wärmebehandlung unterhalb 1600°C untersucht. Die intrakristallinen Spaltgasblasen mit einem mittleren Durchmesser von etwa 2 nm sind unterhalb 1500°C praktisch unbeweglich. Die Blasen haben eine saubere Oberfläche ohne eine Kontamination fester Spaltprodukte und sind facettiert bei der höchsten beobachteten Bestrahlungstemperatur von 1800°C. Diese Blasenfacettierung ist vermutlich ein Hauptgrund für die Blasenunbeweglichkeit. In einem Brennstoff, der unterhalb 1500°C in Betrieb ist, müsste der vorherrschende Mechanismus, der das Wachstum interkristalliner Blasen und die nachfolgende Gasfreisetzung zulässt, eher die Diffusion gelöster Gasatome als die Bewegung ganzer intrakristalliner Blasen sein.

1. Introduction

At irradiation temperatures at which the grains in uranium dioxide remain equi-axed the migration of fission gas to the grain boundaries is the first stage of gas release. The intragranular fission gas forms small bubbles (~2 nm dia.) but these are unstable and can be re-dissolved by close-passing fission fragments [1]. It is thought that the diffusion of singly dissolved gas atoms is the predominant mechanism allowing transfer of gas to grain boundaries [2]. However, there is some controversy over the contribution that the movement of intragranular gas bubbles can make to the accumulation of gas at grain boundaries.

Dollins and Ocken [3] and Dollins [4] propose that gas bubbles can move and coalesce. The experimental evidence in favour of gas bubble mobility has been obtained from electron microscope examination of isothermally annealed foils. However, the bubbles were produced in uranium dioxide by annealing material irradiated at low temperature [5] or by gas-ion injection [6]. On the other hand, Turnbull [7] from

observations on intragranular gas bubbles formed in uranium dioxide during irradiation finds no evidence of gas bubble mobility.

The present study is an attempt to quantify the mobility of the intragranular fission gas bubbles which are created in uranium dioxide during irradiation. The uranium dioxide had been irradiated in the temperature range 1600–1800°C and the bubble movements were followed on subsequent out-of-pile annealing at lower temperatures.

2. Experimental

The uranium dioxide was taken from pellets from an experimental SGHWR fuel pin which had been irradiated in the UKAEA's Winfrith SGHWR. The sample had been irradiated to a dose of 7860 MWD/te at a rating of 28 W. g and with centre and surface temperatures of 1830 and 830°C, respectively [8].

Transverse sections were cut from the pin sample using a diamond slitting wheel and these were ground on both sides to a thickness of ~0.25 mm. The sections were fractured along the cracks which arise during irradiation. Large pieces were selected which had irradiation temperatures in the range 1600–1800°C and these were electrolytically polished to produce thin foils using a "UNITHIN" twin jet polishing machine mounted in a shielded glove box [9].

The foils were examined at 100 kV in a transmission electron microscope and thin areas were mapped out for annealing. The foils were isothermally annealed in hydrogen containing 1% water vapour. After annealing, the foils were replaced in the holder in the same position and the mapped areas were re-examined. The foil tilt was kept the same by always using the same diffracting conditions although a limitation was imposed on this by the single tilt stage.

Uranium dioxide was lost by vaporization during the anneals and often the mapped areas were lost. At the higher annealing temperatures the foils were only mapped out after the first anneal because the very thin areas were lost during this anneal.

Positive prints of the electron micrographs were made on transparent film at a magnification of 3.3×10^5. The images of the same area following isothermal anneals could then be superimposed. The displacement of the bubbles was measured with a measuring eyepiece on images taken in the overfocused condition so that the bubbles appeared dark. Bubble diameters were measured on under focused images [8]. Great care was taken to ensure that no tilt had occurred between successive micrographs and only pairs which yielded exact superimposition of bubbles over the whole field of view were used. An example of the discrepancies introduced by even small tilts can be seen in that a 1° tilt between micrographs produced images which seemingly superimpose very well (a 10 cm length becomes 9.9985 cm). However, the parallax movement of bubbles near the top and bottom surfaces of a foil 100 nm thick when it is tilted 1° is ~2nm.

3. Results

The gas bubbles observed in the foils had diameters in the range 1–4.0 nm and nucleated in lines [8] (N.B., in this reference fig. 5 has the wrong units on the y axis, nm should be Å). The bubbles were visible as dark spots when imaged over-focus and dark rings with a light centre when imaged under-focus. The bubbles often had a square image.

Foils which had been irradiated at temperatures of 1650 and 1800°C were annealed at 1300 and 1400°C, respectively. There was no observed growth or movement of bubbles in these foils up to cumulative times of 4 h (fig. 1). The foil which had been irradiated at 1800°C exhibited a heterogeneous distribution of gas bubbles [8]. The bubble density was higher near grain boundary bubbles and there were areas within the grains denuded of bubbles. On annealing, no new bubbles nucleated in the bubble-free areas indicating that these areas were free of fission gas.

A foil which had been irradiated at 1700°C was annealed at 1500°C for times up to a cumulative 4 h. There was no evidence of bubble growth but following the anneal for 2 h there was evidence that 1 in 10 of the bubbles had moved $\leq$1 nm. It was not possible to obtain any relationship between size and movement.

The foil annealed 4 h at 1500°C was subsequently annealed at 1570°C to a cumulative time of 2 h. There was still no evidence for bubble growth but

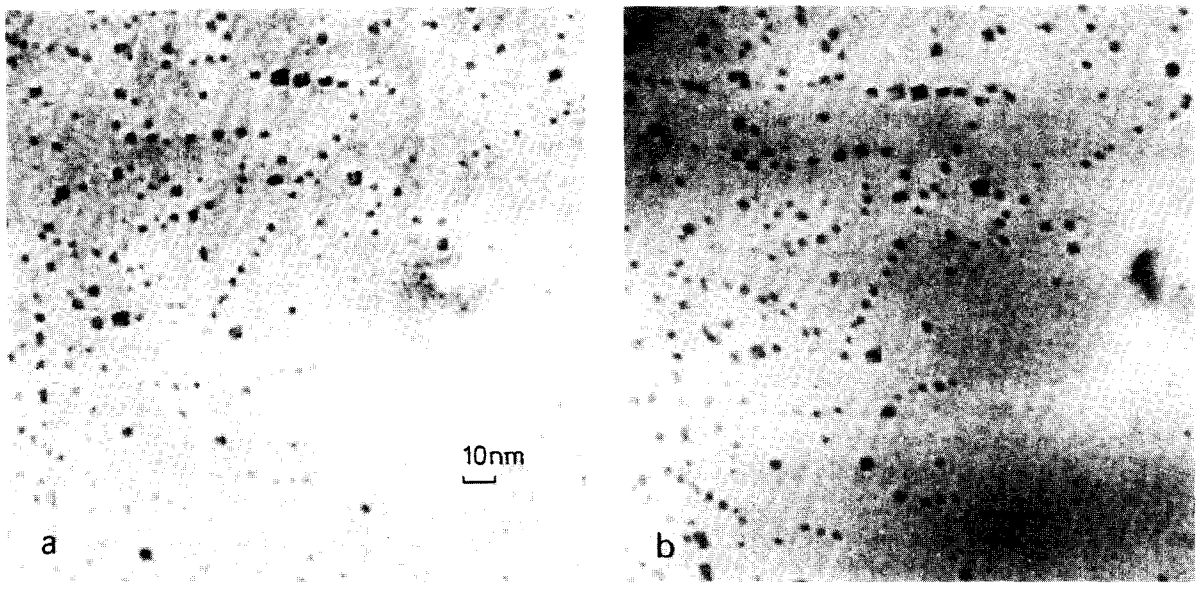

Fig. 1. Transmission electron micrographs of uranium dioxide irradiated at 1800°C and subsequently annealed at (a) 2 h at 1400°C and (b) 4 h at 1400°C. The micrographs are of the same area and are taken over-focus so that the bubbles appear dark.

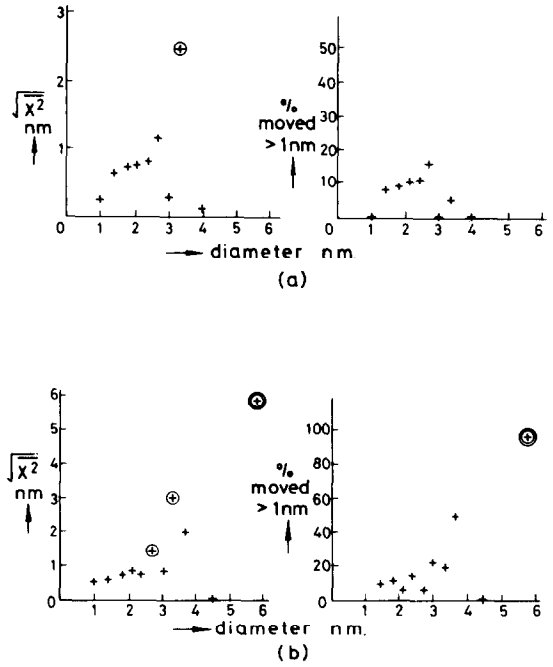

Fig. 2. The dependence of the root mean square bubble movement $\sqrt{x^2}$ on bubble diameter after (a) $\frac{1}{2}$ h and (b) 1 h at 1570°C. The points ringed include one large movement and those with two rings are only for single bubbles.

there was some bubble movement. The bubble movement was again small and the results for $\frac{1}{2}$ h and 1 h anneals are shown in fig. 2, with mean values for all the bubbles in table 1. Considering all the bubbles, about 1 in 3 had moved. However, of these only about 1 in 10 had moved more than 1 nm. The percentage of bubbles which had been lost owing to surface evaporation was ~4% and 9% at $\frac{1}{2}$ and 1 h, respectively. There was no obvious relationship between movement and bubble radius over the radius range 0.5–2.0 nm. In some cases a single bubble in one of the measured size ranges moved a large distance resulting in a larger mean movement and this is indicated in fig. 2. Perhaps the one feature which was observed was that large movements were more

Table 1

Annealing time at 1570°C (min)	30	60
Mean bubble diameter (nm)	2.1	2.2
% of bubbles moved (overall)	30	26
% of bubbles moved more than 1 nm	10	11
Movement (overall) (nm)	0.3	0.4
Movement^2 (overall) (nm)	0.8	1.1

frequent at the largest bubble sizes, where the number of bubbles in each size range was very small.

To quantify the relationship between movement and bubble radius it is necessary to anneal at higher temperatures. However, above 1600°C the vaporization rate became so great that any thin areas were lost during the anneal.

The bubbles were often faceted and in the as-irradiated and irradiated and annealed condition the bubbles often showed a square or rectangular image [8]. The straight sides of the images seemed to be parallel with {110}. However, annealing uranium dioxide, which had been irradiated at 1500°C, for 1 h at 1700°C produced bubble growth (to ~5 nm mean diameter) and also clarification of the bubble morphology. After this treatment all the bubbles formed into what must be their equilibrium shape (fig. 3). The bubble morphology was confirmed as an octahedron with the faces parallel to {111} with truncation on the {100} planes at the corners.

The most impressive examples of bubble movement were observed in-situ in the electron microscope. The foil which had been annealed at 1570°C for 2 h had undergone vaporization at the grain boundaries and consequently many of the grains were only attached by narrow bridges. Also, the annealing atmosphere of wet hydrogen could have reduced the excess oxygen in the uranium dioxide, at least compared with the as-irradiated value, resulting in a lower thermal conductivity. The consequence of these two effects was that extensive beam-heating occurred and some grains were slowly vaporized. In some grains the temperature rise only produced slight vaporization and limited bubble growth. The bubbles in these grains developed facets and formed into the equilibrium octahedron shape with a size and appearance comparable with that after the anneal of 1 h at 1700°C.

In grains exhibiting rapid vaporization the bubbles were spherical, had grown to 5–20 nm diameter, and moved (fig. 4). The movements were recorded on video-tape from a television camera mounted in place of the plate camera. The temperatures in these grains can be estimated with some certainty as >1700°C. The bubbles tended to vibrate with a superimposed overall movement. This overall movement was, in some instances, directed with the movement towards the thin vaporizing edge. Not all the bubbles in any area moved and while some bubbles moved ~50 nm other similar sized bubbles remained stationary. In some areas the smaller bubbles seemed to begin vibrating first but in areas where appreciable bubble mo-

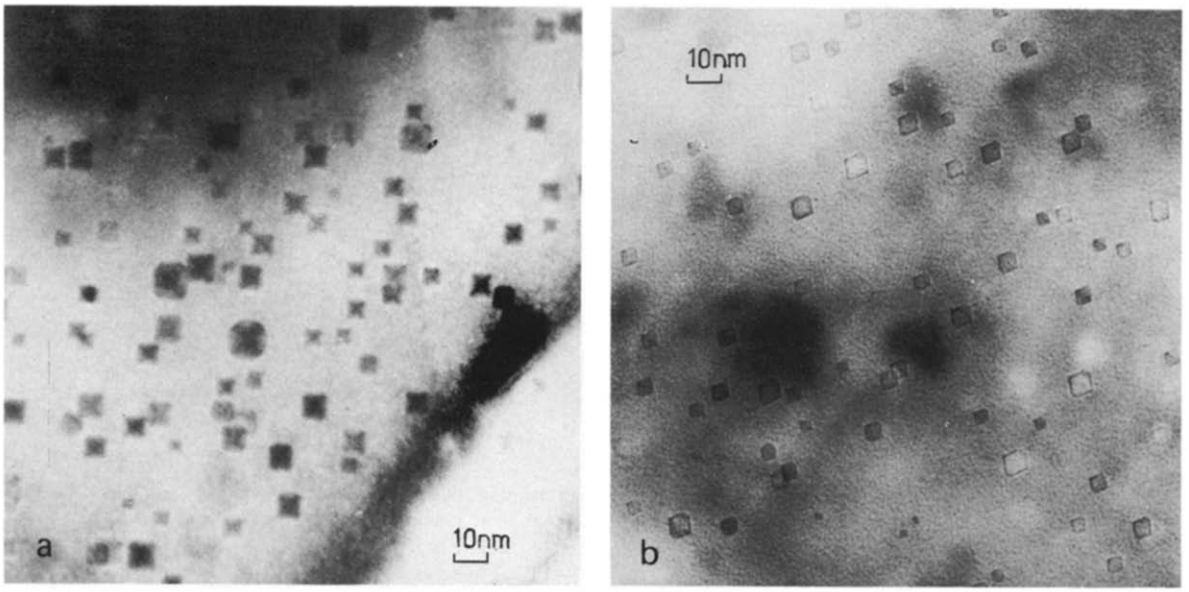

Fig. 3. Tramission electron micrographs taken over-focus of uranium dioxide irradiated at 1500°C and annealed for 1 h at 1700°C. (a) (100) orientation and (b) (110) orientation.

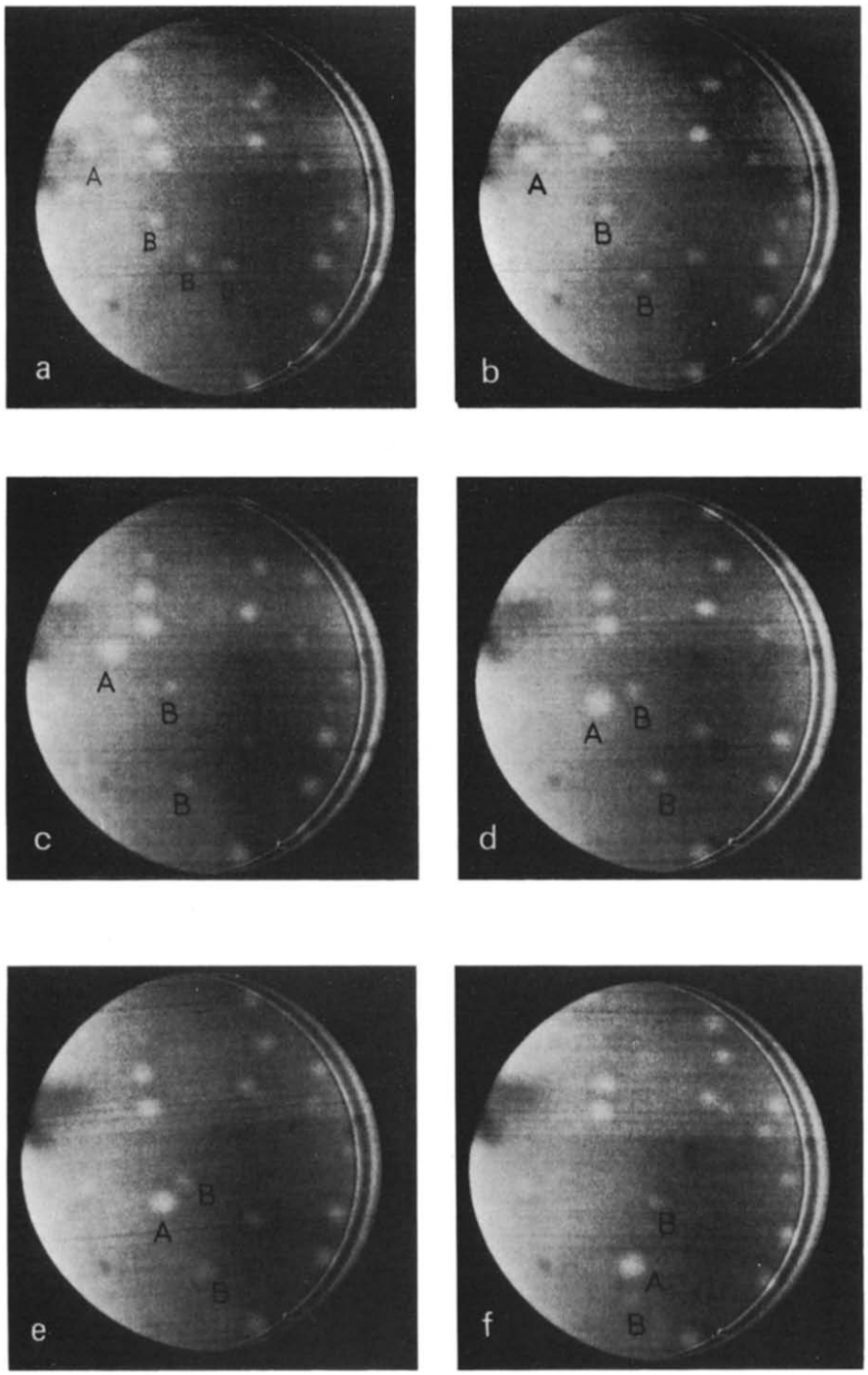

Fig. 4. Frames from a video-tape showing in-situ movement of bubbles in the electron microscope. Estimated foil temperatures is >1700°C. Bubble marked A undergoes a continuous movement in the same direction whereas bubbles marked B move around randomly. The micrographs are taken at 4-s intervals.

tion occurred there was no clear dependence of bubble movement on radius. The largest bubble, 20 nm dia., moved 20 nm in ~5 s and then reached the surface. The surface healed within a fraction of a second of the bubble striking it, indicating that the surface diffusion rate was very high at these temperatures.

4. Discussion

The results confirm the preliminary results of Turnbull [7] that fission gas bubbles are not mobile at temperatures pertaining to the majority of fuel in thermal reactors. In the present study uranium dioxide has been annealed at temperatures below its irradiation temperature.The fission gas bubbles are essentially immobile at temperature up to 1500°C. Above 1500°C the bubbles move small distances. It is possible from the mean square distance moved ($\overline{x^2}$) after time t to calculate the bubble diffusion coefficient, D_b, using the relationship $D_b = \overline{x^2}/4t$. From the values in Table 1 the values of D_b, for a mean bubble radius of ~1 nm, are 9 and 8×10^{-19} cm^2/s^{-1} for $\frac{1}{2}$ and 1-h anneals, respectively, at 1570°C. These values are considerably less than those determined by Gulden [5] from mobility measurements on gas bubbles precipitated by out-of-pile annealing of uranium dioxide irradiated at low temperature. At 1500°C Gulden [5] measured D_b for bubbles of mean radius 1.65 nm as 6×10^{-17} cm^2/s. Gulden [5] measured the bubble mobility over the radius range 1.65–6.25 nm. The bubbles over this range were spherical and the majority of bubbles contained an inner solid fission product precipitate. Dollins [4], in his estimates of bubble mobility during irradiation, used values for D_b which are 10^2 times higher [10] than those of Gulden [5].

In the present study the bubbles in the as-irradiated uranium dioxide and in material irradiated and annealed at temperatures up to 1700°C are well faceted and the bubble surfaces are clean with no evidence of adhering solid fission product precipitates. The equilibrium shape of the bubbles is an octahedron with the faces parallel to {111} with truncation on {100} planes on the corners. This is identical with the morphology of the irradiation-induced voids in many fcc metals [11].

Willertz and Shewmon [12] and Beeré [13] have shown that for faceted bubbles, bubble migration may be limited by the rate at which new steps are nucleated on the facets. The rate of bubble motion is then decided by the rate of nucleation of steps and not by the time it takes atoms to diffuse across the bubble surface. Willertz and Shewman [12] found that faceted helium bubbles in gold diffuse a factor 10^{-4} to 10^{-5} slower than theoretically possible from the unrestrained diffusion of surface atoms. Beeré [13] has re-analyzed Gulden's data [5] and confirmed that the data are best described by a nucleation-controlled mechanism. For the bubbles in the present study faceting must also be having a pronounced effect in restricting bubble motion.

The foil which became hot in the electron microscope has yielded further information on bubble behaviour. As in the foils isothermally annealed outside the electron microscope, the bubbles undergoing in-situ heating formed into the equilibrium octahedron shape at the temperature at which rapid vaporization was beginning. Above this temperature, estimated at 1700°C, the foil vaporized, the bubbles became spherical, vibrated and moved either randomly or in a directed manner. The reason for this directed motion is most likely bubble movement up the small temperature gradients which arise owing to the variation of thickness at the foil edge.

The temperature range for bubble mobility corresponds with that for columnar re-structuring during irradiation. In this regime extensive bubble movement up the temperature gradient has been observed.

5. Conclusions

(1) Small intragranular fission gas bubbles (average diameter ~2 nm), formed during the irradiation of uranium dioxide at temperatures >1600°C, are virtually immobile on subsequent annealing at temperatures <1500°C. This is in contrast to previous studies which have found significant and measurable mobility of slightly larger bubbles precipitated by the out-of-pile annealing of uranium dioxide irradiated at low temperature.

(2) The intragranular bubbles in uranium dioxide irradiated at temperatures <1800°C are faceted and this could be a major cause of their immobility.

(3) The bubble surfaces are clean with no visible contamination by solid fission products.

(4) In fuel operating below 1500°C the predominant mechanism allowing the growth of intergranular bubbles and the subsequent gas release must be the diffusion of dissolved gas atoms rather than the movement of entire intragranular bubbles.

(5) Bubble movement has been observed at annealing temperatures >1700°C for bubbles of diameter 5–20 nm. At these temperatures the bubbles are spherical.

Acknowledgement

This paper is published by permission of the Central Electricity Generating Board.

References

[1] J.A. Turnbull and R.M. Cornell, J. Nucl. Mater. 36 (1970) 161.
[2] M.V. Speight, Nucl. Sci. Eng. 37 (1969) 180.
[3] C.C. Dollins and H. Ocken, J. Nucl. Mater. 45 (1972/3) 150.
[4] C.C. Dollins, J. Nucl. Mater. 60 (1976) 107.
[5] M.E. Gulden, J. Nucl. Mater. 23 (1967) 30.
[6] R.M. Cornell and G.H. Bannister, Proc. Brit. Ceram. Soc. 7 (1967) 355.
[7] J.A. Turnbull, J. Nucl. Mater. 62 (1976) 325.
[8] C. Baker, J. Nucl. Mater. 66 (1977) 283.
[9] C. Baker, G.L. Reynolds and G.H. Bannister, Post Irradiation Examination Techniques (BNES Conference, Reading, 1972) p. 191.
[10] B.J. Buescher and R.O. Meyer, J. Nucl. Mater. 48 (1973) 143.
[11] G.L. Kulcinski, J.L. Brimhall and H.E. Kissinger, Radiation Induced Voids in Metals (Proc. Conf. Albany, New Yorl, 1971) p. 449.
[12] L.E. Willertz and P.G. Shewmon, Metall. Trans. 1 (1970) 2217.
[13] W. Beeré, J. Nucl. Mater. 45 (1972/3) 91.