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Comments on 'Thermal treatment of uranium oxide irradiated in pressurized water reactor: swelling and release of fission gases'[1] by I. Zacharie, S. Lansiart, P. Combette, M. Trotabas, M. Coster and M. Groos

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Abstract

In analysing their detailed post-irradiation results on UO_2, Zacharie et al. interpret the diffusion of fission gases to grain boundaries in terms of atomic gas atom diffusion. In this comment, the basis for this conclusion is questioned and when other evidence is considered, it is suggested that there is little support for the mechanism. On the other hand, calculations using the model based on the directed bubble diffusion up induced vacancy gradients towards grain boundaries show that gas release and intragranular swelling, and their response to annealing temperature, are of the right magnitude to fit the experimental data. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In two papers, Zacharie et al. [1,2] have presented results of detailed post-irradiation experiments on unstressed samples of UO_2 taken from pressurised water reactor fuel after a burn-up of 25 GWd/tU. While the second paper concentrated on the analysis and modelling of intergranular swelling, the paper of interest here is the first where results on intragranular swelling and gas release were included for anneals over the range from 1130 to 1715°C. The coincidence during annealing of this swelling and the release of gas from within grains to grain boundaries was clearly demonstrated while at 1715°C the scanning electron micrographs showed gas bubble precipitation and growth within the grains over the same time period.

In the present comment, firstly we discuss the results of Zacharie et al. [1] and question their conclusion that the arrival of intragranular fission gas at grain boundaries is due to the atomic diffusion of gas atoms to the boundaries. Secondly, this note examines the release data in terms of a more recent bubble diffusion model. Reasonable agreement with the data is claimed.

2. Results of Zacharie et al. [1]

In discussing their interpretation of their gas release curves, Zacharie et al. consider only two mechanisms: the atomic diffusion of gas atoms and the random migration of bubbles. The latter was excluded in agreement with previous workers (e.g. [3,4]) as being too slow, thus leaving only the former mechanism as an option. The supporting evidence provided by Zacharie et al. for such gas release was suggested from isothermal release curves (made over the range 1130 to 1715°C), an analysis of which, using the Booth approach [5] with a transition time invariant with anneal temperature, indicated an activation energy of 4.6 eV/atom. This value was said to agree with the activation energy of 4.7 eV/atom proposed by Matzke [6].

It is important to note that the particular value of 4.7 eV was not singled out in Ref. [6]. Instead, Matzke gave the range 3.6–3.9 eV for single gas atom diffusion, with a

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range of 0 to 0.87 eV added (to give a maximum of 4.7 eV) to allow for temporary trapping effects. Although trapping is nowhere mentioned in [1], it must be assumed that the claimed agreement was intended to include the trapping element in the activation energy.

The problem with the approach of Zacharie et al. [1] is that the additional activation energy of up to 0.87 eV suggested by Matzke (Table 4) appears to be applicable to relatively low gas levels and only allows for 'temporary trapping, weak gas damage, gas-defect or gas-gas interactions'. Trapping to bubbles was not mentioned in the context of the activation energy spread and clearly a difficulty must arise over what value might be appropriate to such trapping and the subsequent gas atom release from bubbles. Calculations of solution energies of the heavier rare gases in UO_2 show that effectively they are insoluble [7,8] with energies above 9 eV. Such values appear too high to allow the possibility of any gas release mechanism involving such diffusion.

This argument is supported by experimental evidence. Early work recognised 'the extreme insolubility of the fission product gases' [9,10] while one can cite the very many examples of bubble formation and growth in UO_2 during both the early and later stages of annealing (e.g. [1,10,11]), all of which point to the strong tendency for fission gas atoms to precipitate. In addition, an experiment using thermal desorption and transmission electron microscopy on Kr ion implanted UO_2 [12] specifically designed to detect any thermal resolution of inert gas from bubbles showed that the release of krypton at nearby surfaces during annealing coincided with bubble movement. There was no earlier release that might have been associated with any single gas atom diffusion.

Comparison with the data reviewed by Matzke therefore cannot be used to support the conclusion of Zacharie et al. [1] that their gas release results can be interpreted in terms of single gas atom diffusion.

3. Modelling of data in terms of bubble diffusion

3.1. Fission gas release

As stated at the start of the previous section, Zacharie et al. only considered two mechanisms of gas release. However, they ignored a third possibility that has been presented recently [13–16]. A mechanism has been considered in which 'directed' bubble diffusion takes place in the vacancy gradient set up between the grain boundary vacancy source that operates during annealing, and the intragranular bubble population. The non-randomness of the bubble diffusion direction can hugely increase diffusion distances relative to the simple random diffusion previously excluded as a release mechanism. Both the physics of cavity movement in vacancy gradients and the efficiency of grain boundaries as vacancy sources in solids have long been known. The major signature of the latter effect, the initial coarsening of bubbles near vacancy sources [17–19], is seen clearly for UO_2 in the results of Kashibe et al. [20] and has been reported in the work of Small [21]. It is worth recognising that in a 10 μm diameter spherical grain, almost 50% of the uniform fission gas concentration lies within 1 μm of the grain boundary. Thus the induced motion of bubbles need not be large, even for appreciable gas release.

The directed bubble diffusion model has been applied to literature data with some success in previous papers. Many features of gas release such as the variation of amount released with burn-up and the kinetics of release have been modelled [15,16] while the interesting and large effects of annealing in an oxidising atmosphere has also been simulated [22]. In the present case, the gas release data in Fig. 4 of the paper by Zacharie et al. [1] is modelled using data from their paper (bubble sizes, grain size, starting gas concentration), and parameters used previously including the surface energy and the important UO_2 self-diffusion parameter. These parameters are summarised in Table 1.

In Fig. 1, release curves using the model (a full description is available in Refs. [13–15]) are plotted for the

Table 1
Parameters used in the model calculations

UO_2 self-diffusion, D [13]	0.3 exp(−4.5eV/kT) cm^2/s
Bubble size [2]	50 nm
Grain size [2]	9.3 μm
Gas concentration [1]	0.57%
Surface energy	1 J/m^2

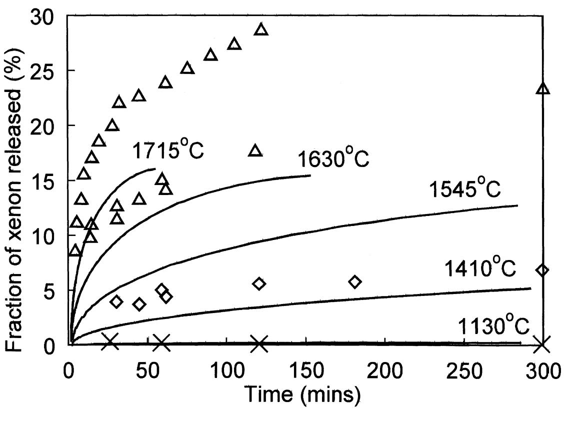

Fig. 1. A comparison of calculated gas release (full lines) with experimental data points of Zacharie et al. [1] for 1130°C (×), 1545°C (◇), and 1715°C (△).

five annealing temperatures used by Zacharie et al., together with their Fig. 4 data for the representative temperatures 1130, 1545 and 1715°C. In the model there is no specific initial transient release; a relatively fast early release is a characteristic of the release mechanism. It would be an exaggeration to claim that the agreement between experiment and the model results is particularly good; on the other hand, the agreement is not unreasonable considering the experimental difficulties (as shown for example by the two bands of experimental data at 1715°C), the absence in the model of any burst release effects, and the dependence of the model calculations on input parameters. An example of the latter case is the dependence on surface energy. Halving its value would increase all the gas release data points by a factor of two. Against this background, there is no doubt that some general features of the experimental curves can be simulated reasonably, particularly the time scale and order of magnitude of gas release and the overall effect of changing the anneal temperature between 1130 and 1730°C.

3.2. Intragranular swelling

In their careful experiments, Zacharie et al. [1] have been able to extract information on the various components of the overall swelling. Although most of the emphasis was on the swelling at the grain boundary that forms the basis for their detailed second paper [2], they have estimated the intragranular component by subtracting the intergranular swelling from the total swelling. The results are given in their Fig. 8 [1], and when compared with the time scale of the gas release curves show very clearly that the gas release and swelling appear to be intimately connected. Although this has been demonstrated during annealing in the analogous structure of krypton bubbles in nickel [23], the experimental data of Zacharie et al. are an excellent example of the same effect in UO_2.

This result is important to the directed bubble diffusion model since the increase of intragranular swelling is an essential element in maintaining the vacancy flux from the grain boundary into the growing bubbles. The vacancies allow the initial bubble population to come to equilibrium while at the same time bubble coarsening via coalescence requires further vacancies for equilibrium to be maintained. Thus the intragranular swelling and the release of fission gas to boundaries must occur simultaneously; that this occurs in practice is clearly consistent with the model. There is no difficulty in calculating the net intragranular swelling. In Fig. 2, model data are presented for the same temperatures as Fig. 1, along with the experimental data taken from Fig. 8 in the paper by Zacharie et al. As for the gas release curves, and for the same reasons, no exact match of data is possible. Nevertheless, the swelling figures are not unreasonable.

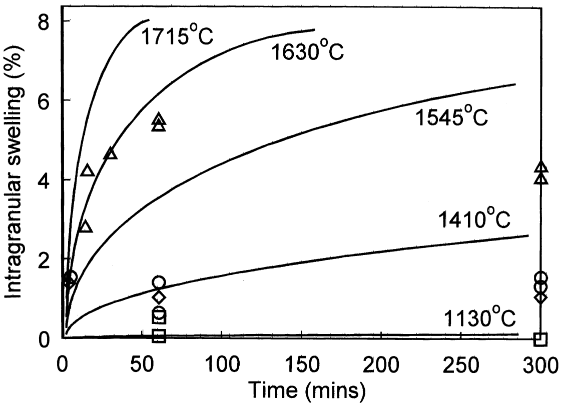

Fig. 2. A comparison of calculated intragranular swelling (full lines) with the experimental data points of Zacharie et al. [1] for 1410°C (□), 1545°C (◇), 1630°C (○) and 1715°C (△).

4. Discussion

The arguments in the previous sections suggest that the Zacharie et al. [1] interpretation of their post-irradiation gas release data via the atomic diffusion of gas atoms cannot be substantiated. It would be rather easy to suggest that the reasonable agreement of their activation energy measurement of 4.6 eV with the value of 4.5 eV used in the directed bubble diffusion mechanism would be support for this latter mechanism. However, the accuracy of applying the Booth approach (a method originally devised for low amounts of fission gas) after a transition period during which, in some cases, a substantial fraction of the gas is released, and when the total release is eventually a large factor less than the theoretical 100%, might be open to question.

An additional important point in this context is that a comparison of mechanisms or models based on a single activation energy measurement can hardly be satisfactory. It must be essential to compare model results with the actual gas release curves and predict other general trends such as the increase of gas release with burn up and the fast release under oxidising atmospheres. As stated earlier, the present model can simulate both these trends correctly [15,16,22], while as shown in this letter it can also explain the important result that the swelling and gas release occur simultaneously.

Against this background, the evidence presented in this letter that the results of Zacharie et al. [1], both on gas release and on intragranular swelling, can be simulated within reasonable quantitative bounds by the mechanism of directed bubble diffusion, adds to the support for this model.

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