Diffusion of Xenon-133 in UO_2 Single Crystals

P. Spindler * and R. Lindner

Chemistry Department, CCR Euratom, Ispra

(Z. Naturforschg. **21 a,** 1723—1725 [1966]; received 19 September 1966)

There is hardly a fission gas diffusion system more intensively investigated, but with a larger spread of results than UO_2. Two parameters were shown to be very important: the composition of UO_2 and the irradiation dose, the latter leading not to diffusion enhancement by radiation damage, but to slower diffusion by formation of trapping centers for gas atoms.

We considered it useful to conclude a number of previous studies [1, 2] on this problem by the present investigation, which we consider our final contribution to this specific problem, our main interest turning over to UC [3]. A very important point was the availability of UO_2 single crystals, produced by the school of Amelinckx [4] in Belgium, of size and purity not obtained before.

Experimental Details

Single crystals of UO_2 ($O/U = 2.0001 \pm 0.0001$) were crushed and sieved to a dimension of 30 microns. All operations were performed in a glove box filled with pure nitrogen. The grains were annealed in purified H_2 for 12 hrs at 1000 °C and irradiated in the Ispra I reactor in a position corresponding to a flux of $2.2 \cdot 10^{13}$ thermal neutrons/cm²sec (dose ca. 10^{18} nvt). After irradiation the material was taken from the evacuated quartz ampoule and introduced into the diffusion apparatus. The whole diffusion apparatus was flushed with purified hydrogen for 12 hrs before starting the experiment.

Because of the relatively large size of the crystals, compared to the small irradiation dose only small values for the fractional release of fission gas were expected. This necessitated a measuring geometry of highest possible efficiency. Instead of continuous measurement in a gas stream the released fission gas was trapped therefore in a cold trap, which was periodically changed and inserted into a well-type scintillation counter for registration of the 81 keV γ-line of xenon 133. This procedure ensured the highest possible counting efficiency. An eventual contamination of the Xe-133 with other volatile isotopes can be easily detected and accounted for by γ-spectrometry.

The experimental setup (Fig. 1) included an active charcoal trap (10) for iodine (activated with Ag, Cu and Cr) which was effective to adsorb iodine vapour to at least 99.6% [5]. Two cold traps (11) for adsorption of xenon were used in parallel and measured alternatively after suitable time intervals. The hydrogen passing the diffusion cell was purified by means of a BTS copper catalyst (2) and dried in a $CaCl_2$ tower (3). For the final purification turnings of Zr and Ti heated to 600 °C (4) and a cold trap (5) cooled with liquid nitrogen were used.

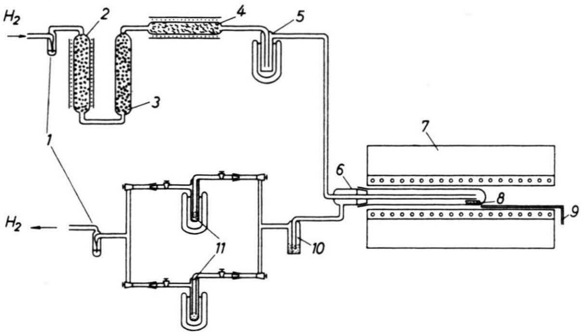

Fig. 1. Schematic view of gas purification and sampling equipment.

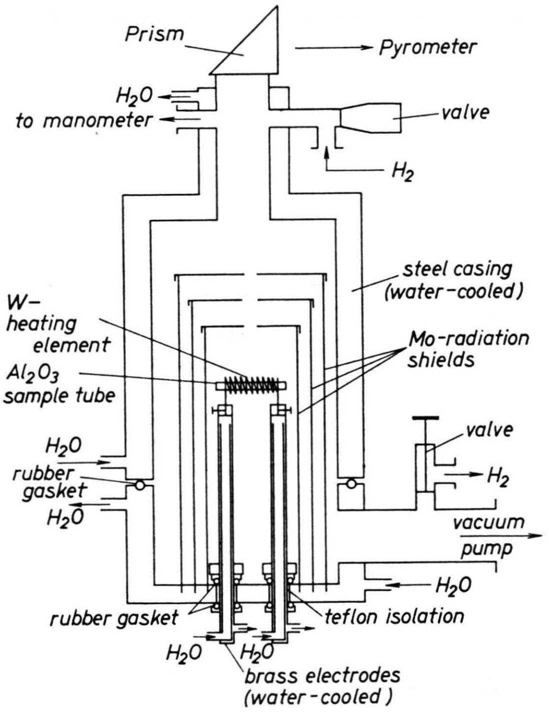

Fig. 2. Schematic view of high temperature furnace.

For temperatures up to 1300 °C conventional furnaces with heating elements of "Kantal" or SiC were

---

* Diplomarbeit, Braunschweig 1964.

[1] R. Lindner and Hj. Matzke, Z. Naturforschg. **14 a,** 582 [1959]; **14 a,** 1074 [1959]; **15 a,** 1082 [1960].

[2] Hj. Matzke and R. Lindner, Z. Naturforschg. **16 a,** 845 [1961].

[3] K. Papathanassopoulos, Ph. D. Thesis, Techn. Hochschule Braunschweig 1964.

[4] W. van Lierde, R. Strumane, E. Smets, and S. Amelinckx, J. Nucl. Mater. **5,** 250 [1962].

[5] R. E. Adams and W. E. Browning, US Report ORNL 2872 [1960].

used, the temperatures being regulated within ±5 °C and measured with Pt/Pt-Rh thermocouples. For higher temperatures a special furnace with a heating element of W was constructed and the temperature determined by means of a calibrated pyrometer (Fig. 2).

Evaluation of the Diffusion Runs

All evaluation is based on the value of *fractional* release, i. e. the amount diffused from the sample divided by the total amount of fission gas present in the sample. For this purpose the total fission-gas activity must be known, which involves the destruction of a part of the irradiated material in order to set free all gas by dissolving it in a melt of $KHSO_4$ at 700 °C (6 – 7 hrs).

It was checked carefully that all iodine was adsorbed by the respective trap and that no losses of xenon occured during the transport of the measuring trap from the diffusion apparatus to the counter. In preliminary experiments it could be demonstrated that after removal of the trap from the liquid nitrogen bath it took about 3 minutes before desorption of Xe-133, together with the carrier gas (H_2), set in. Thus the activity measurement had to be completed within this time period in order to avoid any gas losses.

Measurements and Results

Characteristic release curves are reproduced in Fig. 3 from which the following can be deduced:

The total release was of the order of 1%. An initial "burst" has not been observed; the first point was taken after 1 hour diffusion time. After about 5 hours the slope of these curves changed to smaller values. Consequently two temperature functions were obtained. The activation energies thus deduced do not differ very much from each other.

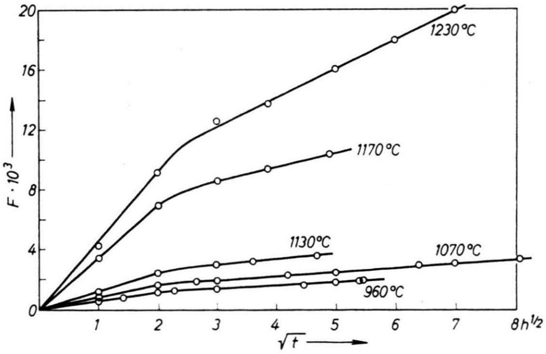

Fig. 3. Fission gas release from UO_2 single crystals at different temperatures.

The change of the slopes can be explained by trapping centers for fission gas atoms which are already present in the sample (such as enclosed pores) or which may be produced by irradiation [6, 7]. The centers very strongly affect the release mechanism. In order to account for this effect an additional term has to be introduced into the diffusion equation:

$$dc/dt = D \cdot \Delta c - dm/dt , \qquad (1)$$

where:

$$dm/dt = D\, c/L^2 - b\, m , \qquad (2)$$

L being the average distance between trapping centers ("diffusion length for trapping").

In order to solve Eq. (2) dimensionless terms β and γ are introduced defined as:

$$\beta = a/\pi L , \qquad \gamma = a^2 b/(\pi^2 D)$$

where: a is the crystal radius and b a probability factor for the reentry probability of a gas atom from a trapping center into the lattice. The release rate function can then be reproduced graphically as function of these parameters (Fig. 4) [8].

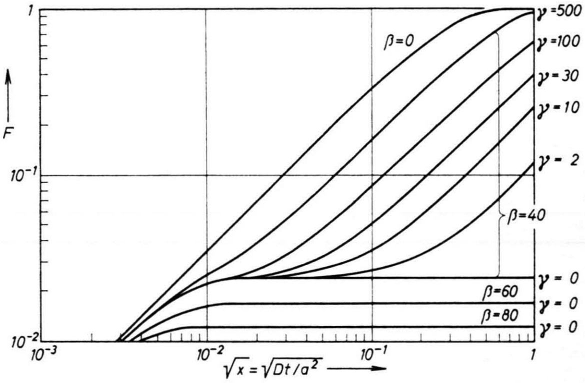

Fig. 4. Theoretical solutions of Eq. (1) with different β and γ-parameters (taken from ref. [7]).

In order to obtain information on the average trapping length L the experimental curves were superimposed to curves with arbitrary values of β, γ being neglected, under the assumption that its influence shows up only for very long diffusion period, as can be seen from Fig. 4. The values for L thus obtained are reproduced in Fig. 5 as a function of the annealing temperature.

Concerning the diffusion parameters, D_0 and Q, the following results can be deduced:

Both parts of the release curves can be attributed to normal, or almost normal diffusion processes of the fission gas within the uranium dioxide lattice. The change in slope of the release curves (Fig. 3), due to the trapping phenomenon, has practically no influence on the Q values.

The diffusion coefficients evaluated from the second part of the curve are reproduced in Fig. 6. They fit an exponential relation (with the exception of low tempe-

---

[6] J. R. McEwan and W. H. Stevens, J. Nucl. Mater. **11**, 77 [1964].

[7] R. M. Carroll and O. Sisman, J. Nucl. Mater. **17**, 306 [1965].

[8] D. G. Hurst, Report AECL 1550 [1962].

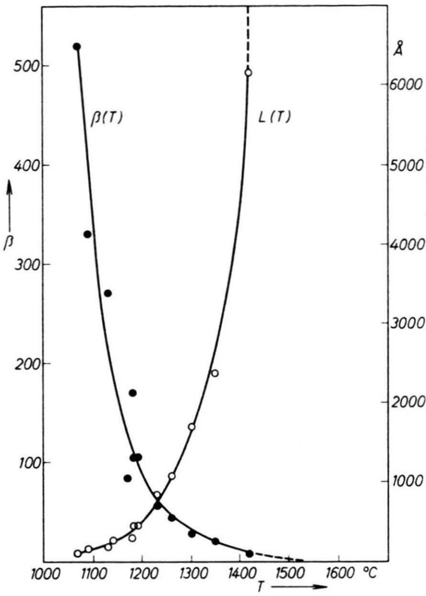

Fig. 5. Temperature dependence of β and the "diffusion length for trapping" L for UO_2 single crystals, derived under the assumption that re-emission does not occur during the annealing period.

ratures and two deviating results in the temperature range of 1000 to 1100 °C, which can be explained by experimental complications). The numerical relationship is:

$$D = 1.6 \cdot 10^{-3} \exp(-96.8 \pm 3.0)/R\,T\,.$$

If the temperature function is deduced from the first part of the release curves, the respective relation is:

$$D = 5.5 \cdot 10^{-3} \exp(-87.3 \pm 4.5)/R\,T\,.$$

Finally from Fig. 5 it can be deduced, that the average path length L a xenon atom moves before being trapped varies in the temperature range 1070 to 1420 °C between 900 and 6000 Å (equivalent to ca. 150 – 1000 atom layers) in uranium dioxide single crystals. This temperature dependence agrees with theoretical considerations, the extent of annealing of defects increasing with temperature.

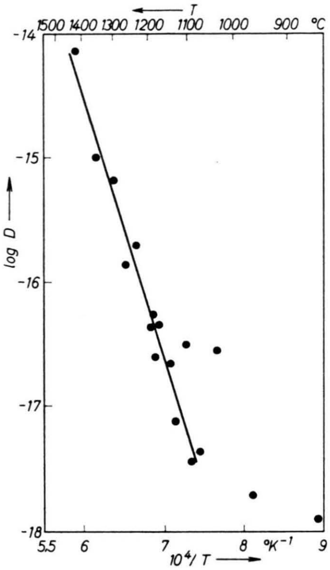

Fig. 6. Arrhenius plot of the Xe diffusion in UO_2 single crystals.

Conclusions

Contrary to earlier measurements on less well defined material the temperature function for xenon diffusion is nearly comparable to that for uranium self-diffusion in UO_2 of stoichiometric composition (104 kcal/mole [9]). In addition, it agrees closely with values obtained by the recently established ion-bombardment technique: 96 – 103 kcal/mole [10], 89 kcal/mole [11]. At the time of the conclusion of the experimental work this coincidence seemed to support the assumption that fission-gas atoms migrate via uranium vacancies, as diffusion measurements of xenon, oxygen and uranium in doped UO_2 [10] did not contradict this assumption. Recent experiments by Matzke [11] have shown, however, that doping strongly affects uranium self-diffusion but not xenon diffusion. Thus at present the conclusion is at hand that in spite of the striking coincidence of activation energies, the transport mechanism can not be related to vacancy diffusion.

We thank Drs. Hj. Matzke, R. Kelly, and H. L. Scherff for discussions.

---

[9] F. Schmitz and R. Lindner, J. Nucl. Mater. **17**, 259 [1965].

[10] R. Kelly and Hj. Matzke, J. Nucl. Mater. **17**, 179 [1965].

[11] Hj. Matzke, Nucl. Appl. **2**, 131 [1966].

[12] G. Long, W. P. Stanaway, and D. Davies, UK Report AERE-M 1251 [1964].