Lattice and Grain-boundary Diffusion of Uranium in UO_2

Lattice and Grain-boundary Diffusion of Uranium in UO$_2$*

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Synopsis

The lattice and the grain-boundary diffusion of uranium ion in sintered UO$_2$ were measured within the temperature range 1900°~2150°C with uranium-237 as a tracer by the sectioning method. The data obtained were analysed in the light of the theory of the grain-boundary diffusion based on an instantaneous source model. The lattice diffusion coefficient D can be obtained by the following equation:

$$D = 5.82 \times 10^{-5} \exp\left(-\frac{72,700}{RT}\right) \text{ cm}^2/\text{sec}.$$

On the other hand, the product $D' \cdot 2a$ peculiar to the grain-boundary diffusion follows the equation:

$$D' \cdot 2a = 5.19 \times 10^{-9} \exp\left(-\frac{47,200}{RT}\right) \text{ cm}^3/\text{sec},$$

where D' and $2a$ are the grain-boundary diffusion coefficient and the grain-boundary width, respectively.

I. Introduction

The self-diffusion of uranium ion in UO$_2$ at high temperatures is of great importance in reactor technology other than the diffusion of fission products in UO$_2$. In the present study, the uranium-237, being the most active uranium isotope, was used as a tracer in place of U-233 or U-235 which had been used in other works.[1]-[4] The sectioning method, in which the diffusant activity is measured in thin slices cut parallel to the free surface, gives rise to concentration profiles (penetration curve) after diffusion annealing. In the penetration curve, the lattice diffusion term giving its diffusion coefficient can be distinguished from the grain-boundary diffusion term from which its diffusion constant is derived.

II. Preparation of uranium-237

Dominant reactions in bombarding natural uranium with high energy Bremsstrahlung are as follows:[5]

* The 1260th report of the Research Institute for Iron, Steel and Other Metals.
(1) A.B. Auskern and J. Belle, J. Nucl. Mat., **3** (1961), 311.
(2) J. Belle and B. Lustman, Westinghouse Atomic Power Laboratory (USA) Report WAPD–184 (1957).
(3) R. Lindner and F. Schmitz, Z. Naturfor., **16a** (1961), 1373.
(4) P. McNamara, IAEA Technical Reports Series, No. 39 (1965), p. 76.
(5) E. Akatsu, T. Kuroyanagi and T. Ishimori, Sonderdruck aus Radiochimica Acta, **2** (1963), 1.

$$^{238}U \; (\gamma, n) \; ^{237}U$$
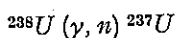
$$^{238}U \; (\gamma, f) \; \text{fission products.}$$

A UO$_2$ pellet, approximately 10 mm in diameter and 3 mm in thickness, was irradiated for 4 hr with 20 MeV Bremsstrahlung of the linear electron accelerator. The irradiated UO$_2$ was dissolved in conc. HNO$_3$, and the fission products were then removed by TBP. After being purified, the U–237 was identified by the γ-ray spectrometer. Finally, uranium ions in aqueous solution were converted again into UO$_2$ powder by a conventional method.

III. Preparation of UO$_2$ pellets and diffusion annealing

Diffusion UO$_2$ pellets, approximately 10 mm in diameter and 10 mm in thickness, were first preheated up to 1600°C at the rate of 150°C/hr to make its density greater than 96% theoretical, and were then sintered for 2 hr at 2300°C in an inert atmosphere in order to make the grain size large enough for analysis and to stop grain growth during diffusion annealing. The average grain size was above 100μ, and one surface of the pellets was ground with diamond paste to be flat.

The UO$_2$ powder labelled with U–237 was evaporated on the ground surfaces of the two pellets at the same time by using evaporator at 10^{-5}mmHg. The radioactivity of the evaporated layer was about 20$\sim$30 times as large as that of the UO$_2$ pellets before evaporation.

As shown in Fig. 1, two activated pellets were sealed in a tantalum capsule with UO$_2$ powder in such a way that the activated surface of the pellets was tightly held with the active surface of one pellet opposite to that of the other. The sealing was done in an inert atmosphere.

Diffusion runs were carried out for 1$\sim$8.5 hr within the temperatrature range 1900$\sim$2150°C in the annealing furance consisting of tantalum heater. The furnace temperatures were maintained within the difference of 10°C.
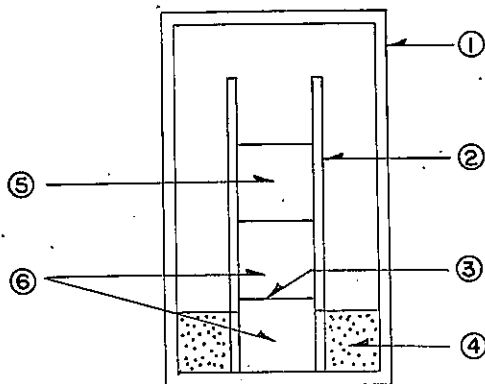

Fig. 1. Tantalum capsule

| 1. Tantalum capsule | 2. Molybdenum capsule | 3. U-237 evaporated surface |
| 4. UO$_2$ powder | 5. UO$_2$ pellet as a weight | 6. UO$_2$ diffusion pellets. |

After diffusion annealing, the successive thin layers were removed from the active surfaces of the pellets with abrasive paper by using the sectioning device. The layer thickness was calculated by weighing the pellets with a micro-balance before and after the grinding.   Each cut had an average thickness of $2 \sim 3$ microns.

The radio-activity of the ground-off powder was counted with the well-type scintillation counter for 5 min, and calibrated in terms of the half-life.

IV.   Experimental results

The penetration curves at each temperature are shown in Fig. 2.   In these curves, the logarithm of concentration in a deeper region varies lineally with depth, as is characteristic of grain-boundary diffusion (the second region).   Near the surface, the lattice diffusion makes a contribution comparable to the concentration, thus showing a nonlinear curve (the first region).
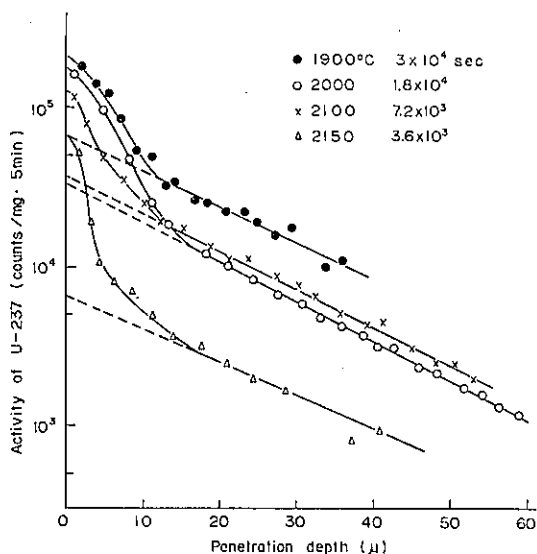

Fig. 2.   Penetration curve.

V.   Diffusion model

Let the grain-boundary be an isotropic slab of a uniform width $2a$ having a diffusion coefficient D' which is greater than the lattice diffusion coefficient D.   Take y axis normal to the free surface and x axis parallel to the free surface.   Assuming that the plane of the slab is normal to the free surface, the concentration c at an arbitrary point (x, y) and at a time t varies according to the following equations:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right), \qquad \qquad |x| > a. \qquad (1)$$

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial y^2} + \frac{D}{a} \frac{\partial c}{\partial x}, \qquad\qquad |x| = a. \qquad (2)$$

These equations have been studied by many workers[6]-[10] in the constant source case after first Fisher's solution.[11] In the instant source case, it has been worked by Suzuoka.[12]-[14] The boundary condition in the instantaneous source case can be expressed by

$$\left(\frac{\partial c}{\partial y} \right)_{y=0} = 0, \qquad\qquad c(x, 0, t) = c(x, t). \qquad (3)$$

$$c(x, y, 0) = k\,\delta(y), \qquad\qquad c(\infty, \infty, t) = 0. \qquad (4)$$

Considering the grain size parameter n and integrating with respect to x axis, the concentration $c(y, t)$ at an arbitrary depth, which satisfies Eqs. (1), (2), (3) and (4) can be expressed as follows:

$$c(y, t) = \frac{k}{\sqrt{D\pi t}} \left(c_1 + \frac{1}{n} c_2 \right), \qquad (5)$$

where

$$c_1(y, t) = \exp\left(-\frac{1}{4} \eta^2 \right), \qquad (6)$$

and

$$c_2(y, t) = \int_1^\Delta \left(\frac{\eta^2}{\sigma} - 2 \right) \exp\left(-\frac{\eta^2}{4\sigma} \right) \sqrt{\frac{\Delta - \sigma}{\Delta - 1}} \left(\frac{e^{-x^2}}{\sqrt{\pi}} - X\,erfc\,X \right) \frac{d\sigma}{\sigma}. \qquad (7)$$

In Eq. (7) the following dimensionless parameters are introduced;

$$\left. \begin{array}{ccc} \eta = \dfrac{y}{\sqrt{Dt}}, & n = \dfrac{b}{\sqrt{Dt}}, & \Delta = \dfrac{D'}{D}, \\[3mm] \beta = \dfrac{2a(\Delta - 1)}{\sqrt{Dt}}, & X = \sqrt{\dfrac{\Delta - 1}{\Delta - \sigma}} \dfrac{\sigma - 1}{\beta}, & \end{array} \right\} \qquad (8)$$

where $2a$ and $2b$ are the grain-boundary width and the average grain size, respectively. The value c_1 is an expression for lattice diffusion, and c_2 represents the contribution of grain-boundary diffusion.

(6) R.E. Hoffman and D. Turnbull, J. Appl. Phys., 22 (1951), 634.
(7) R.T.P. Whipple, Phil. Mag., 45 (1954), 1225.
(8) S.R.L. Couling and R. Smoluchowski, J. Appl. Phys., 25 (1954), 1538.
(9) V.T. Borisov, V.M. Golikov, B.Y. Ljubov, and G.V. Shtsherbedinsky, *Radioisotopes in Scientific Research* edited by R.C. Extermann, 1 (1957), 212.
(10) H.S. Levine and C.T. MacCallum, J. Appl. Phys., 31 (1960), 595.
(11) J.C. Fisher, J. Appl. Phys., 22 (1951), 74.
(12) T. Suzuoka, Trans. Jap. Inst. Metals, 2 (1961), 25.
(13) T. Suzuoka, Trans. Jap. Inst. Metals, 2 (1961), 176.
(14) T. Suzuoka, J. Phys. Soc. Japan, 19 (1962), 1285.

VI. Lattice diffusion

When the grain size was greater than $\sqrt{Dt}$, two methods were adopted to separate the lattice diffusion and the grain-boundary diffusion in the curves obtained.   One has been developed by Suzuoka,[12],[13] in which the lattice diffusion coefficients are determined by the self-consistent method. According to this method, the lattice diffusion coefficient, $(D=2.88\times10^{-12}$cm²/sec), was given of the sample No. 1 annealed at 1900°C for 3×10^4 sec.

The other is a simple graphical method developed by several workers.[15],[16] Following this method, the contribution of grain-boundary diffusion in the first region would be given by a straight line obtained by extrapolation of the linear slope of the "log c versus y" curve in the second region. By this method, the lattice diffusion coefficient, $(D=3.11\times10^{-12}$ cm²/sec), was obtained of the sample No. 1. This value was in good agreement with that calculated by the previous method. In general, the difference between the values obtained by the two methods was within 10% when β was amply large $(\beta>10)$. Since β was sufficiently large in the present work, as shown in Table 1, the latter method was applied to the analysis of the remaining experimental data. Thus, the lattice diffusion coefficients obtained are given in Table 1, and the temperature dependence of the lattice diffusion coefficient is shown in Fig. 3. They can be expressed by

$$D = 5.82 \times 10^{-5} \exp\left(-\frac{72,700}{RT}\right),$$

where the activation energy is expressed in calories.

Table 1.   Diffusion parameter.

Sample No.	1	2	3	4
annealing temp. (°C)	1900	2000	2100	2150
annealing time (sec)	3×10^4	1.8×10^4	7.2×10^3	3.6×10^3
$D\times10^{11}$(cm²sec⁻¹)	0.311	0.569	1.31	1.49
$\sqrt{Dt}$ (μ)	3.05	3.10	3.07	2.32
$D'\cdot2a\times10^{13}$(cm³sec⁻¹)	1.10	1.48	2.68	3.09
Grain size (μ)	120.6	122.7	183.3	200.6
β	45.1	35.1	28.8	38.7

VII. Grain-boundary diffusion

If the lattice diffusion coefficient is obtained, the product $(D'\cdot2a)$ of the grain-boundary diffusion coefficient D' and the grain-boundary width $2a$, peculiar to grain-boundary diffusion, is given by Eq.(8)[17]:

(15)   T.S. Lundy and J.I. Federer, Trans. AIME, **224** (1962), 1285.

(16)   Simon M. Sze and Ling Y. Wei, Phys. Rev., **124** (1961), 84.

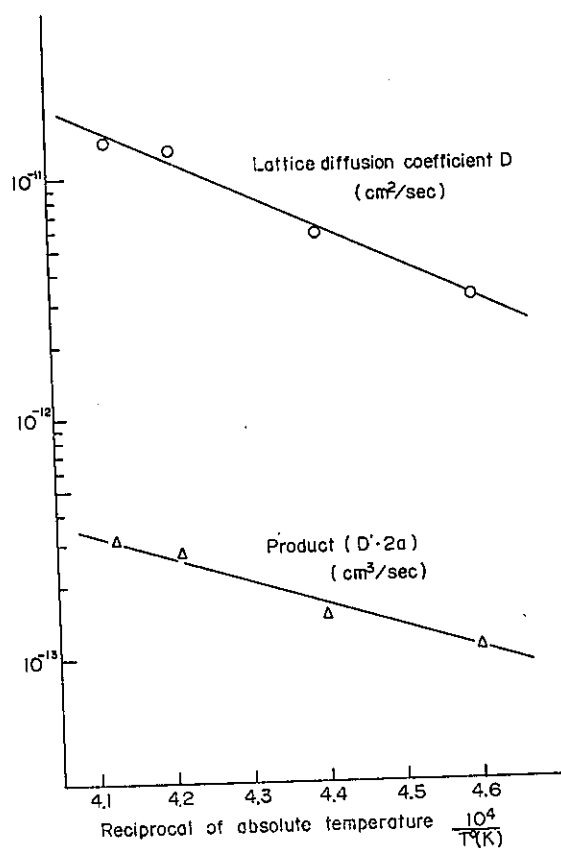(17)   A.D. Leclair, Brit. J. Appl. Phys., **14** (1963), 351.

Fig. 3. Temperature dependence of lattice diffusion coefficient D and product $D' \cdot 2a$.

$$D' \cdot 2a = \left(\frac{\partial \ln c_2}{\partial y^{6/5}}\right)^{-5/3} \left(\frac{4D}{t}\right)^{1/2} \left\{\frac{\partial \ln c_2}{\partial \left(y \beta^{1/2}\right)^{6/5}}\right\}^{5/3}. \tag{10}$$

Using Eq. (10) with the observed penetration curves, the products $D' \cdot 2a$ are given in Table 1, and their temperature dependence is shown in Fig. 3. They can satisfy the equation,

$$D' \cdot 2a = 5.19 \times 10^{-9} \exp\left(-\frac{47,200}{RT}\right),$$

where the activation energy is expressed in calories.

VIII. Discussion

The self-diffusion in UO_2 has been studied by many workers at relatively low temperatures by using U–233 and U–235. These results have been analyzed by the surface activity decrease method, without taking the grain-boundary diffusion effect into consideration. The frequency factor D_0 and the activation energy Q of

Table 2.   Comparison with other data.

	Frequency factor D_0	Activation energy Q (Kcal)
Present work	5.82×10^{-5}	72.7
Belle et al.	4.3×10^{-4}	88.0
Lindner et al.	0.23	104.6
McNamara et al.	1.18	108.0

lattice diffusion are shown in Table 2.   This discrepancy is due to the following factors: (1) negligence of grain-boundary diffusion; (2) estimation error in the effective α particle range in UO_2 and in air; (3) evaporation of UO_2 from the surface and the formation of bound-surface layers during diffusion annealing; (4) the difference in atmosphere during diffusion annealing.

The substoichiometry and the inclusions of metallic uranium in the sintered pellets must be taken into consideration as other factors which have influences on the diffusion measurements.   In order to reduce the deviation from stoichiometry of UO_2 specimen as much as possible, UO_2 powder was put into the capsule.   Although heat treatment and diffusion annealing (at temperatures above 1600°C) were done in 7 to 8 atmospheric pressures of argon saturated with UO_2 vapor from the inserted UO_2 powder, very little inclusions of metallic uranium were only observed by a microscope in the UO_2 pellets sintered at 2300°C.   Most portion of these inclusions was concentrated near the surface of the pellets, so that they were removed by grinding before the diffusion annealing.   X-ray diffraction examinations of the diffusion pellets before and after heat-treatment and annealing showed that the lattice constants were in good agreement within the experimental error. Therefore, the effects of metallic inclusions on the diffusion measurements are negligible.   However, the effects of substoichiometry on the diffusion measurements are complicated and are not avoided to some extent in the materials of this kind, especially, at high temperatures.   No specific experiment was performed to investigate the relation between substoichiometry and diffusion coefficient. These problems should be investigated in future.