

Some Factors Affecting the Diffusion of Actinide Elements in UO_2 *

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Synopsis

In connection with the influences of the densification of sample, the evaporation of diffusant during diffusion annealing and the grain size of starting material on the diffusion of actinide elements in UO_2 , three types of experiment were performed by the sectioning method using ^{237}U and ^{233}Pa as tracers. In all cases, the logarithm of the concentration in a deeper region varied linearly with penetration depth, as is characteristic of grain-boundary diffusion. Near the surface, the lattice diffusion or the evaporation made a considerable contribution to the concentration, thus showing a nonlinear concentration profile. The extent of this deviation increased with the increases of initial density of the pellet and of grain size of starting material. The concentration near the surface decreased with the approach to it in the presence of evaporation.

I. Introduction

The diffusion of actinide elements in UO_2 has been widely studied to see the high temperature behavior of UO_2 . A number of works had been thus far directed towards obtaining diffusion coefficients at various temperatures, but the agreement between the published values is generally poor. For example, the reported values for the activation energy of diffusion of uranium in UO_2 vary from 52 to 108 Kcal/mole.^{(1),(2),(3),(4),(5)} The reasons for these differences are considered to be as follows: (1) the difference in the method of measuring diffusion coefficient, (2) the evaporation of diffusant and sample during diffusion annealing, (3) the formation of bound surface layer during diffusion annealing, (4) the densification and grain growth of sample during diffusion annealing, (5) the presence of grain-boundary diffusion, (6) the density and grain size of starting material, and (7) the stoichiometry of sample. A few studies^{(6),(7),(8)} have been made of the effects

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- (1) R. Lindner and F. Schmitz, *Z. Naturf.*, **16a** (1961), 1373.
- (2) A.B. Auskern and J. Belle, *J. Nucl. Mat.*, **3** (1961), 311.
- (3) C.B. Alock, R.J. Hawkins, A.W.D. Hills and P. Mcnamara "Thermodyanmics" (IAEA, Vienna, 1966), Vol. 2, p. 57
- (4) P. Nagels, W.V. Lierde, R. Dehatist, M. Denayer, L.D. Johghe and R. Gevers, "Thermodyanomics" (IAEA, Vienna, 1966), vol. 2, p. 311
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- (6) R.E. Carter and R.D. Richardson, *J. Metal*, **6** (1954), 1244.
- (7) J.F. Marin, H. Michand and P. Contamin, *Compt. Rend., Series C*, **264** (1967) 1633.
- (8) L.E. Poteat and C.S. Morgan, *Ceramic Bulletin*, **47** (1968), 413.

connected with these phenomena other than the grain-boundary diffusion.

Four methods for measuring diffusion coefficient of actinide element in actinide oxide have been developed: (a) the method of surface activity decrease, (b) the method of peak-height comparison, (c) α -energy degradation method and (d) the sectioning method. It is very difficult to discriminate the above effects, when the diffusion coefficient is measured by the methods of (a) and (b).

In the present paper, the results of three types of experiment in connection with the effects of the densification, the evaporation during diffusion annealing and the grain size of the starting material on the concentration profile, are shown and discussed separately. The concentration profiles were obtained by the sectioning method, and ^{237}U and ^{233}Pa were used as tracers, and UO_2 and $\text{Th}_2\text{-UO}_2$ (1:3) solid solution were selected as diffusion bodies.

II. Experimental procedures

II-1. Experiments with UO_2 pellet

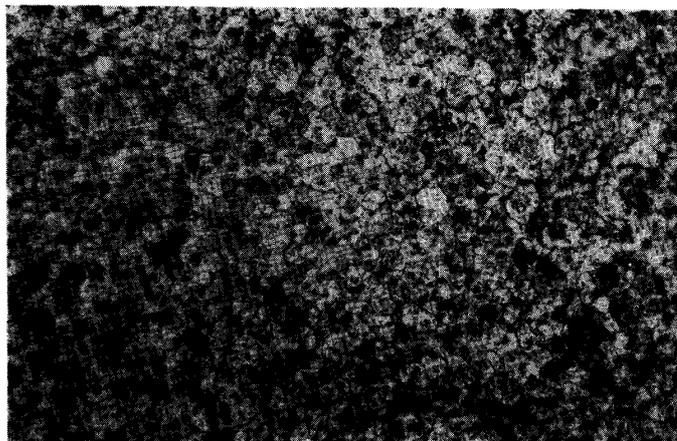
The diffusion pellets used as diffusion bodies for studying the effect of densification were prepared in the following way. The green pellets, approximately 10 mm in dia. and 10 mm thick, were prepared by cold-pressing the fine powder, and subsequently sintered for 2 hours at 1410° , 1480° and 1510° in order to make the densities of the pellets to be 87, 90 and 93% theoretical, respectively. The

Table 1. Details of 93% pellets.

Sample No.	Diameter (mm)	Thickness (mm)	Density	
			g/cm ³	(Th. D%)
1	9.12	8.96	10.15	92.6
2	9.07	9.00	10.25	93.5
3	9.08	9.02	10.26	93.6
4	9.08	8.96	10.18	92.9
5	9.10	9.04	10.17	92.8
6	9.08	8.98	10.20	93.2
7	9.09	9.07	10.20	93.1
8	9.09	9.09	10.18	92.9
9	9.07	9.04	10.23	93.3
10	9.09	9.09	10.22	93.2

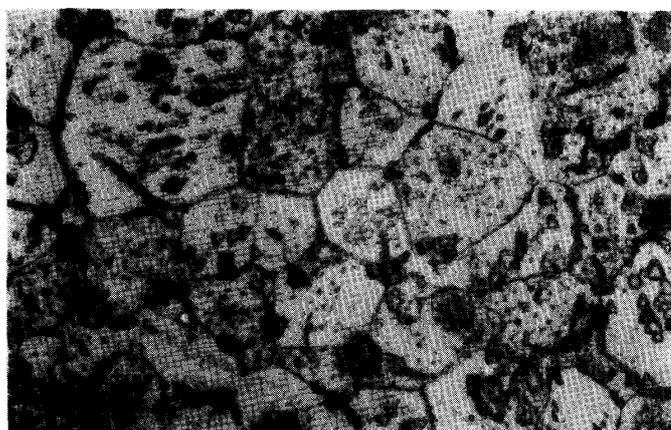
densities of the pellets were determined from geometrical volume and weight, and its variation among the pellets was within $\pm 0.8\%$. Typical results obtained with 10 pellets of the density of 93% theoretical are shown in Table 1. The photomicrograph of the polished and etched section is shown in Photo. 1.

The pellets for studying the effect of evaporation were prepared by sintering the pellets of the density of 93% theoretical at 2000°C for 2 hours in the sealed tantalum capsule filled with argon. The density obtained was above 96% theoretical and the average grain size was from 10 to $20\ \mu\text{m}$. The photomicrograph of the polished and etched section is shown in Photo. 2. After measuring the density, one surface of every pellet was ground with diamond paste to become optically flat.



($\times 100 \times 2/3$)

Photo. 1. Photomicrograph of 93% pellet. (after heat treatment at 1510°C for 2 hours)



($\times 100 \times 2/3$)

Photo. 2. Photomicrograph of the pellet for studying the effect of evaporation. (after heat treatment at 2000°C for 2 hours)

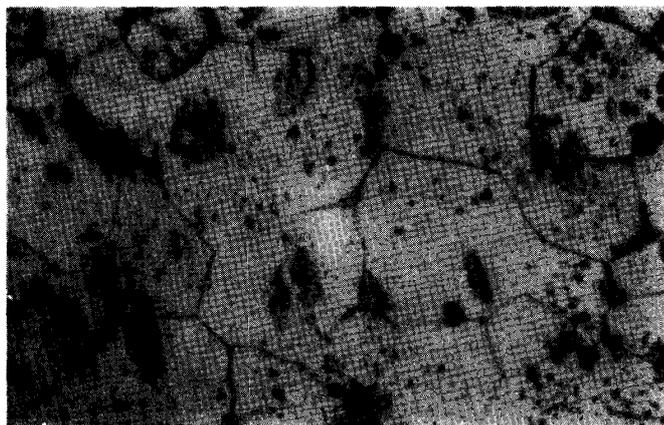
The ^{237}U used as a tracer was prepared by bombarding natural uranium with high-energy bremsstrahlung from linear electron accelerator. Details of the irradiation and the purification of ^{237}U are stated in another paper.⁽⁹⁾ The UO_2 powder labelled with ^{237}U was evaporated on the ground surface of two pellets at the same time. In the case of studying the effect of densification, two activated pellets, which were enveloped in a molybdenum foil, were sealed in tantalum capsule with UO_2 powder in the manner that permitted the activated surface of the pellet to be tightly held with the active surface of one pellet opposite to that of the other.

In the case of studying the effect of evaporation, and activated pellet was sealed in a tantalum capsule with UO_2 powder. All diffusion annealings were performed for 2 hours at 2000°C in both cases. Details of the diffusion annealing, the sectioning and the counting are stated in another paper.⁽⁵⁾

(9) E. Akatsu, T. Kuroyanagi and T. Ishimori, *Radiochemica Acta*, **2** (1963), 1.

II-2. Experiments with ThO₂-UO₂ (1:3) solid solution pellet

Pellets of ThO₂-UO₂ (1:3) solid solution were selected as the diffusion bodies for studying the effect of grain size in order to minimize the evaporation loss during heat treatment at temperatures above 2100°C. They were first prepared by cold-pressing the mixed powder of ThO₂ and UO₂ at 3 t/cm² and subsequently heated from room temperature to 1700°C at the rate of 200°C/h in vacuum and maintained at this temperature for 2 hours. The pellets were further sintered for 2 hours at 2000°, 2100°, 2200° and 2300°C in the sealed tantalum capsule in order to prepare the pellets of various grain sizes. The pellets obtained by this procedure had the density higher than 98% theoretical, and the average grain size varied from 20 to 120 μm. However, the grain size was not always the same even if the sintering was performed under the same condition. Therefore, the average grain size was measured photomicrographically before diffusion annealing. The photomicrograph of the polished and etched section is shown in Photo. 3.



($\times 100 \times 2/3$)

Photo. 3. Photomicrograph of the pellet for studying the effect of grain size. (after heat treatment at 2100°C for 2 hours)

The ²³³Pa used as a tracer was prepared by irradiating ThO₂ disk, approximately 10 mm in dia. and 1 mm thick, with thermal neutron in a nuclear reactor. A tracer disk was placed between two diffusion pellets. These pellets were wrapped in a 0.1 mm thick tantalum foil and fastened with tantalum wire in the manner that permitted the polished surface of the upper diffusion pellet to be placed in the position separated by a limited distance (nearly 0.5 mm) from the upper surface of the tracer pellet. Only protactinium atoms migrate through this interface and diffuse into the diffusion pellet because of a large difference in the vaporization between ThO₂ and PaO₂. All diffusion annealings were performed at 2000°C for 2 hours. Concentration profiles were obtained only from the upper diffusion pellet. Details of the diffusion annealing, the sectioning and the counting are shown in another paper.⁽¹⁰⁾

(10) H. Furuya and S. Yajima, J. Nucl. Mat., 25 (1968), 38.

III. Results and discussion

III-1. Effect of densification

The concentration profiles were obtained with samples of various initial densities. The logarithm of the observed values never varied linearly with the square of penetration depth, as predicted from the simple solution of diffusion equation. Fig. 1 shows the typical concentration profiles. In these curves, the

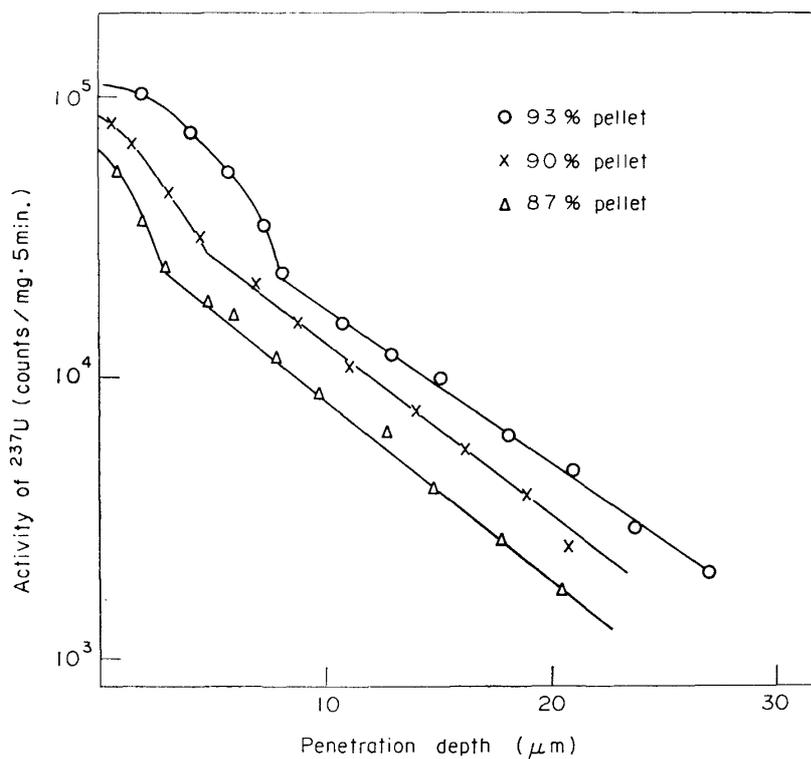


Fig. 1. Concentration profiles of ^{237}U in the pellets having various initial densities.

Table 2. Effect of grain size on concentration profile.

Heat treatment before diffusion annealing (°C)	Specimen (%)	Depth of deviation (μm)
1410	87	3
"	87	not detect
"	87	2
"	87	3
"	87	not detect
"	87	3
1480	90	5
"	90	7
"	90	5
"	90	not detect
"	90	8
"	90	7
1510	93	8
"	93	7
"	93	10
"	93	7
"	93	8
"	93	8

logarithm of the concentration in a deeper penetration depth shows almost linear decrease with increasing depth. Near the surface, small deviations from this slope were observed, although they are not so clear as the one in the diffusion pellet of grain size large enough for analysis as described previously.⁽⁵⁾ It is seen, further, that the extent of these deviations becomes large with increasing density of the pellet. Details of the obtained data are given in Table 2. The average grain size of every pellet after annealing was from 10 to 20 μm , and the density was above 98% theoretical.

Since Fisher's solution,⁽¹¹⁾ a number of solutions for separating the grain-boundary diffusion from the lattice diffusion have been reported to obtain both diffusion constants, but their complex expressions make the practical use less convenient. It should be noted, nevertheless, that the logarithm of concentration contributed by grain-boundary diffusion varies linearly with the penetration depth or 6/5 power of the penetration depth in a deeper penetration depth despite the boundary condition used.

Although the unknown width of grain boundary and the variations of density and grain size with time make the mathematical treatment of the observed values impossible, the comparisons of the concentration profiles in the pellets of various initial densities suggest the following understanding.

In an early stage of diffusion annealing, the extent of densification and the grain growth are so small in comparison with the average penetration depth that the transport of diffusant takes place almost entirely by grain-boundary diffusion. When the diffusion proceeds appreciably and the extent of densification and the grain growth become large, the lattice diffusion becomes comparable with the grain-boundary diffusion. The rapid densification and the grain growth in the pellet of high initial density result in a large contribution of lattice diffusion to the observed value and so show a large deviation in comparison with the case of the pellet of low initial density.

The formation of bound layer at surface is considered as another possible explanation for the deviation near the surface. However, the depth of bound layer observed in the diffusion experiment is generally very small in comparison with the observed penetration depth and does not account for the deviation.

Wuensch et al.^{(12),(13)} have shown the concentration profiles similar to the curve in Fig. 1 in their studies of the grain-boundary diffusion of Ni in MgO. Furthermore, they have reported that the presence of porosity or grain growth did not effect the concentration profile. No detail of starting materials and no explanation have been given. It is considered that the transport of diffusant takes place in the way reminiscent of the behavior observed in the present study, since they used the specimen of a large grain size as the final specimen after diffusion annealing.

(11) J.C. Fisher, *J. Appl. Phys.*, **22** (1951), 74.

(12) B.J. Wuensch and T. Vasilos, *J. Am. Ceram. Soc.* **47** (1964), 63.

(13) B.J. Wuensch and T. Vasilos, *J. Am. Ceram. Soc.*, **49** (1966), 433.

III-2. Effect of evaporation

Fig. 2 shows the typical results plotted as the logarithm of concentration versus the penetration depth. The concentration profile in a deeper penetration depth indicated the grain-boundary diffusion, as described in the previous section. Near the surface, the effect of strong evaporation appeared, and the concentration decreased with the approach to the surface. Maximum value in an intermediate region and its position varied in dependence on the evaporation rate and the total amount of deposit.

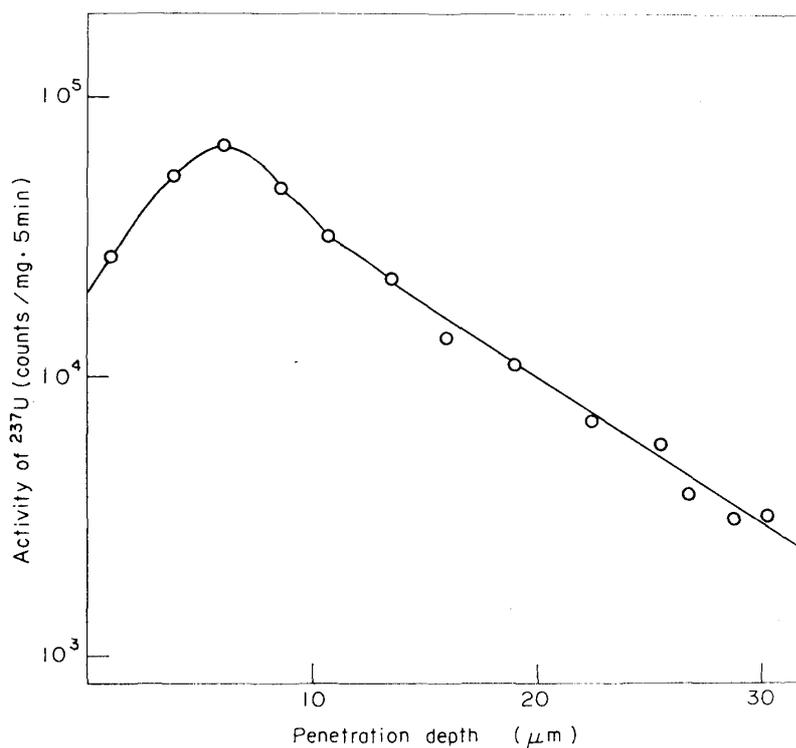


Fig. 2. Concentration profile in the presence of evaporation.

There is no rigorous solution for the grain-boundary equation by taking the evaporation into consideration, and so it is impossible to analyse the results numerically. However, it is apparent that the evaporation has strong effect on the measurement of diffusion coefficient, especially in the methods of surface activity decrease and of peak-height comparison. Therefore, the diffusion coefficient should be measured with a great care of the evaporation.

III-3. Effect of particle size

Fig. 3 shows the typical results obtained with the pellets of various grain sizes. The lattice diffusion makes a considerable contribution to the concentration near the surface and the extent of the contribution increases with increasing grain size, while the grain-boundary diffusion is dominant in a deeper depth. No variation of grain size before and after diffusion annealing was observed. Details of the data are given in Table 3.

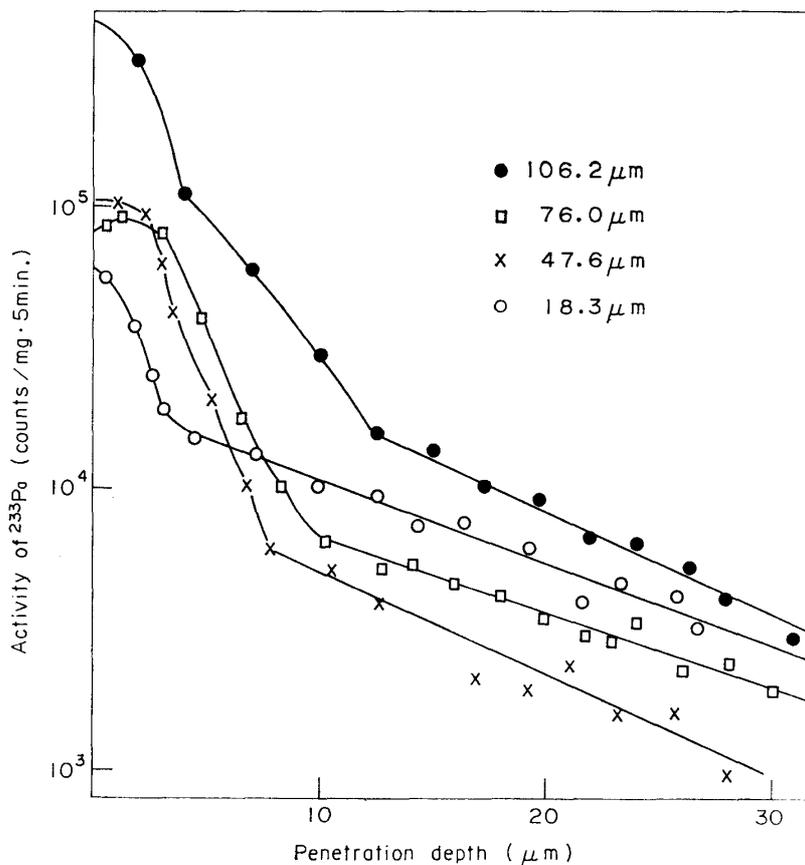


Fig. 3. Concentration profiles of ^{237}U in the pellets having various grain size.

Table 3. Effect of grain size on concentration profile.

Heat treatment before diffusion annealing (°C)	Average grain size (μm)	Depth of deviation (μm)
2000	20.3	3
"	15.7	not detect
"	18.3	3
"	13.6	4
2100	47.6	8
"	40.5	6
"	38.1	7
"	60.2	8
2200	72.0	8
"	59.6	11
"	65.0	9
"	76.0	10
2300	106.2	12
"	121.3	12
"	113.1	10
"	130.9	13

Suzuoka^{(14),(15)} has solved theoretically the equation of grain-boundary diffusion by taking the grain size into consideration, and analysed experimental results obtained in the study of the diffusion of Co in Fe.

(14) T. Suzuoka, *Trans. JIM.*, **2** (1961), 25.

(15) T. Suzuoka, *Trans. JIM.*, **2** (1961), 176.

According to his solution, the grain size should be above twice the length of the observed penetration depth in order to obtain the accurate diffusion coefficient by separating the grain-boundary diffusion from the lattice diffusion. If this condition is not satisfied, the transport of diffusant takes place from the grain boundary between the first and the second grain from the free surface and parallel to it, and so the numerical treatment is impossible.

In the present experiment, the pellet of the average grain size higher than about $70\ \mu\text{m}$ satisfies this condition, and two regions are observed. However, such two regions are observed even in the pellets of average grain size below this value, although the region near the surface is smaller than the former. This fact is considered to show that the diffusion from the parallel grain boundary makes a little contribution to the concentration in the pellet of the grain size comparable with the penetration depth, and the smaller grain size makes it larger, resulting in the shorter depth at which the lattice diffusion is detectable.

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