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SELF-DIFFUSION IN GAMMA URANIUM

by

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SELF-DIFFUSION IN GAMMA URANIUM

S. J. Rothman,* L. T. Lloyd,* R. Weil** and A. L. Harkness***

ABSTRACT

The self-diffusion coefficient of uranium has been measured at four temperatures in the gamma phase. The data are fitted by an Arrhenius-type equation:

$D = 2.33 \times 10^{-3} \text{ cm}^2/\text{sec} \exp(-28,500 \text{ cal per mol}/RT)$,
and agree well with previously reported results.^(1,2) The value of D_0 is lower than that predicted by Zener's theory⁽³⁾ and the activation energy is much less than the value expected from various empirical correlations.

I. INTRODUCTION

The present work is an outgrowth of a program designed to measure the anisotropy of self-diffusion in alpha uranium. The measurements are of interest because they may throw some light on both the nature of the structure and the mechanism of deformation of alpha uranium during reactor irradiation.⁽⁴⁾ Since such measurements of the diffusion coefficient as a function of crystal direction can be made only on single crystals, the conditions of diffusion from an infinitesimally thin layer into a semi-infinite solid had to be chosen. Further, since this is a study of self-diffusion, a tracer technique had to be used. U^{235} was selected as the tracer isotope since the only other isotope available in any quantity, U^{233} , presents difficult handling problems. In order to avoid difficulties with the measurement of absorption coefficients and in order to obtain enough data from one diffusion run to be able to calculate a diffusion coefficient from the penetration plot with reasonable confidence, the sectioning method was chosen.

Difficulties were expected in the deposition of an isotope layer onto a uranium sample, and in the penetration of the isotope into the sample, due to the great chemical reactivity of the material. Cleaning the sample by cathodic sputtering in an atmosphere of purified gas and depositing the

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isotope layer without removing the sample from the protective atmosphere appeared to be a workable solution; however, no penetration of the U^{235} was detected in the first experiments on diffusion in alpha uranium. This could have been due to reaction layers at the sample surface or to a very slow diffusion rate. (A slow diffusion rate was expected because the top of the stability range of alpha uranium is only 667°C , or $2/3$ the temperature of melting; this expectation has since been confirmed).⁽⁵⁾ Thus, it became necessary to test the isotope-deposition techniques by experiments in a temperature range where the diffusion coefficient would be appreciably larger than that expected for the alpha phase. This report describes the experiments performed on self-diffusion in the high-temperature phase, body-centered-cubic gamma uranium.

II. EXPERIMENTAL TECHNIQUES

A. Materials

A special material had to be prepared for the study of self-diffusion in alpha uranium because normal uranium contains 0.71% U^{235} , an amount sufficient to mask the quantity of U^{235} that would diffuse in from a thin layer (see Appendix I). Therefore, it was necessary to use uranium metal containing a much smaller concentration of U^{235} and, in addition, sufficiently pure for the ultimate preparation of single crystals of alpha uranium. Such material would also yield more accurate values of the diffusion coefficient D for diffusion in the gamma phase.

The starting material was a two-kilogram ingot of highly depleted uranium ($\sim 0.03\%$ U^{235}), containing 5,000 ppm by weight Fe, 1,000 ppm Cr and other impurities. Chips turned from this ingot were converted to UCl_3 and mixed with LiCl-KCl eutectic to make up a fused salt bath for the preparation of high-purity uranium by electrolysis.⁽⁶⁾ The balance of the ingot was cast into 0.5 in. diameter anode rods for the electrolytic cell.

The electrolysis was carried out by R. A. Noland and E. J. Moretti. The electrolytic crystal product was cleaned and consolidation melted⁽⁶⁾ by B. Blumenthal and W. J. Stupartiz.

The chemical composition of the final ingot, B-700, is given in Table I. The U^{235} concentration varied somewhat along the length of the ingot - a rough value was 0.03% U^{235} .

A portion of the ingot was rolled to about 0.5 in. diameter and swaged to 0.391 in. Samples 0.5- to 1.0-cm thick were cut from this rod and heat-treated by water quenching from 690°C and annealing at 450°C . These constituted the samples used in the present study.

TABLE I

Chemical Composition of Uranium Used in This Study*

(parts per million by weight)

Element	Isotope Source Cover**	Isotope Source Cylinder**	Highly Depleted Uranium **
C	103,135	40, 32	19, 22
N ₂	-	-	L10
O ₂	-	-	9, 10
Ag	L1	L1	L1
Al	7	7	7
As	L10	L10	L10
B	0.3	L.1	L.1
Be	L.5	L.5	L.5
Bi	L1	L1	L1
Ca	L20	L20	L20
Co	L5	L5	L5
Cr	3	1	10
Cu	2	L1	5
Fe	100	30	20
K	L50	L50	L50
Li	L1	L1	L1
Mg	200	30	1
Mn	10	2	3
Mo	100	L20	L20
Na	L10	L10	L10
Ni	15	8	10
P	L50	L50	L50
Pb	L1	L1	L1
Sb	L1	L1	L1
Si	500	30	10
Sn	L5	L5	L5
Ti	L50	L50	L50
Zn	L50	L50	L50

*C, N and O₂ analyses under the direction of Ralph Bane;
others under the direction of Joe Goleb.

**L = less than

The grain size at the diffusion temperature (varying from 0.2 mm to several mm) was checked by thermally etching a sample at 880°C for 13.25 hours in a dynamic vacuum. Figure 1 shows a photomicrograph of the thermally etched surface. The deformation of the sample on cooling

Figure 1: Gamma Grain Boundaries in a Sample Thermally Etched by Heating at 880°C for $13\frac{1}{4}$ Hours in a Dynamic Vacuum. The arrow indicates a gamma grain boundary.

25,239

Bright Field

75X

made the detection and following of the gamma grain boundaries difficult. Attempts to reveal the boundaries by Lacombe's method⁽⁷⁾ were unsuccessful, probably because the material was too pure.

The source of U^{235} for deposition as a thin layer on the diffusion sample was a hollow cylinder, 5 cm in diameter, 3.8 cm high, with a 0.025 in. wall, mounted on legs which were welded to a thin ring. In addition, there was a separate cover which rested on the top of the cylinder (Figure 2). The chemical analyses of these two pieces are given in Table I. Both pieces contained about 93.2% U^{235} .

B. Preparation of Diffusion Couples

One end of the diffusion sample was given a metallographic polish. The sample was then electropolished in a bath consisting of 5 parts H_3PO_4 , 5 parts ethylene glycol and 8 parts 95% ethyl alcohol. The isotope source was electropolished in a bath consisting of 46% H_2SO_4 , 9% glycerine and 45% H_2O . Both sample and isotope source were placed into the sputtering apparatus immediately after electropolishing.

Figure 2: Sputtering Set-up.

A-sample; B-isotope source;
C-glass legs; D-aluminum plate;
E-electrodes; F,G-manipulators;
H-sample cover.

25,020

The uses of cathodic sputtering for the cleaning of surfaces and for the deposition of thin layers has been reviewed thoroughly by Holland.⁽⁸⁾ The surface to be cleaned, or from which material is to be removed, is made the cathode in a glow discharge and is bombarded by gas ions. These ions "knock off" first any adsorbed gas and oxide skin on the metal, and then atoms of the metal itself.

In these experiments the sputtering was carried on in a fifteen-inch-diameter bell jar. Argon, purified by passing through a long gas-treatment train (Drierite, CuO at 700°C, Drierite, Ascarite, U turnings at 250°C, Cu turnings at 700°C, Zr turnings at 800°C, P₂O₅, and a mechanical

screen), was pumped through the system continuously. The rough adjustment of the pressure inside the bell jar was made (when the apparatus was built) by closing with a clamp the stainless steel tube through which the gas entered, and then backing the clamp off so that the stainless steel tube could spring back. The pressure was adjusted at the beginning of each run by throttling the vacuum pumps and, as a rule, did not have to be changed during the run. The optimum gas pressure was about 2×10^{-2} mm Hg, as measured by a thermocouple gauge about six inches from the glow discharge. The rate of gas flow was not measured.

The power for the glow discharge was furnished by an ordinary DC high-voltage source. The base plate of the bell jar was grounded and served as the anode. Four electric leads entered the bell jar through insulators soldered into the base plate. Wires, enclosed in glass capillaries to protect them from ion bombardment, led from the insulators to electrical contacts (Figure 2,E) which protruded slightly from the glass legs.

The arrangement inside the bell jar is shown in Figure 2. The sample, A, and isotope source, B, stood on glass tubes, C (Pyrex 12/30 standard taper joints). These fit into an aluminum plate, D, resting on brass legs which screwed into the base plate. Manipulators, F and G, which entered the bell jar through Wilson seals in the base plate, were used to move the isotope source from one set of glass legs to the other and to remove the specimen cover, H.

The following procedure was used in the sputtering: The bell jar was evacuated to about 4×10^{-6} mm Hg; gas was flushed through the system for about fifteen minutes and the pressure was stabilized at about 2×10^{-2} mm Hg. The isotope source, which was placed over the covered sample, was then cleaned by making it about 3 kv negative with respect to ground and sputtering it at a current density of about 0.2 mamp/cm², including electron emission. Exact adjustments of the pressure, voltage, and current density were not critical. The sample was kept covered during this time to prevent reaction with the gases liberated in the sputtering.

Degassing of the area around the sample by the glow discharge, combined with the gettering effect of the uranium that had been sputtered off and with the "burial" of gases by the metal deposited in various parts of the bell jar, purified the sputtering atmosphere. After about an hour of sputtering, the isotope source, which discolored shortly after the sputtering started, became shiny again, and the bell jar began to be darkened by the uranium that was sputtered off. At this point, the current was turned off, the isotope source was moved to the other sputtering stand, and the specimen was uncovered and cleaned by bombarding it at a current density of about 1 mamp/cm² for about ten minutes. The isotope source was then placed over the sample again, and both it and the sample were sputtered for a few minutes, after which the isotope source was sputtered over the

uncovered sample for four or five hours. The sample was never made positive, since this would have subjected it to severe heating by electron bombardment.

C. Diffusion Treatment

After the isotope layer was deposited and the apparatus had cooled, the sample was transferred as rapidly as possible from the bell jar into a tantalum cup, and covered with another piece of uranium. The tantalum cup was dropped into a quartz capsule which was then put on a vacuum line. The capsule was flushed five times with purified argon, evacuated, degassed at 300°C, and sealed under a vacuum of about 4×10^{-6} mm Hg for the diffusion anneal.

The samples were annealed in one of two vertical tube furnaces with Kanthal windings. Each furnace was controlled by a Pt-Pt/10% Rh or a Chromel-Alumel thermocouple and a West "Gardsman" controller operating a high current-low current circuit. The quartz tube containing the sample fit loosely into a large nickel block, which helped to stabilize the temperature and reduce thermal gradients. The nickel blocks were lined with platinum to prevent bonding between the nickel and the quartz tube. The temperatures in both furnaces were measured by Pt-Pt/10% Rh thermocouples that had been calibrated against an NBS-calibrated couple, and a Leeds and Northrup type K potentiometer. The hot junctions of these thermocouples were in the nickel blocks, at the same level as the samples. In order to lessen distortion of the samples due to phase transformations and anisotropic thermal expansion, they were heated to and cooled from the beta-gamma transformation temperature slowly, either in the annealing furnace (the samples annealed at 803.5, 981 and 891°C) or in a small furnace on top of the annealing furnace.

D. Sectioning and Analysis

After cooling, the sample was broken out of its capsule. Any U^{235} that may have diffused in from the cylindrical surface was removed by machining about 1/16 in. off the radius for a distance of about 3/32 in. from the original interface. The diameter of the reduced section was measured with a micrometer and the sample was then sectioned on a lathe.

In sectioning a diffusion sample it is very important that the original interface be exactly perpendicular to the lathe axis. In these experiments exact alignment was facilitated by a special chuck, shown in Figure 3. The chuck consisted of the jaw assembly, 1, from a small three-jaw chuck* mounted on a chuck adapter plate, 2, which had machined on its back a convex spherical radius that mated with a concave one machined into the head stock bar, 3. The head stock bar was held in a 3/4 in. collet. The

*Louis Levin and Sons, Los Angeles, Cat. No. ABEX

Figure 3: Precision Chuck and Chip Catcher

1-jaw assembly; 2-chuck adapter plate; 3-head stock bar;
4-screws; 5-spherical washers; 6-sample; 7-chip catcher;
8-tailstock support; 9-tool bit; 10-funnel; 11-glass vial;
12-hole for introducing helium.

specimen, 6, was lined up by tilting the chuck adapter plate with respect to the lathe axis, using the four screws, 4, that threaded into the adapter plate. Mating spherical washers, 5, kept the thrust of each screw normal to the head stock bar plate. The radius of curvature on the chuck adapter plate was such that the center of curvature was near the front face of the specimen. This made the adjustment quite sensitive.

The sample alignment was checked with a 0.0001 in. dial gauge mounted on the lathe bed. Proper alignment was made difficult by surface

distortions of the order of 3×10^{-3} cm. The samples were finally aligned so that four points near the periphery, equally spaced, gave as nearly the same readings as possible on the dial indicator.

Quantitative chip recovery is desirable in such experiments, since then it is not necessary to remove the sample from the chuck for weighing after each section is cut. The Lucite chip catcher used for this, 7, was similar to one described by Bohlin and Ross.⁽⁹⁾ The tailstock support, 8, and the boring bar that held the carbide tool bit, 9, passed through O-rings. Although an O-ring groove was also turned into the head stock bar, it was not necessary to use an O-ring in it; helium introduced through the hole in the top, 12, kept the chips from burning.

The chips fell through a stainless steel funnel, 10, into a glass vial, 11. Chips that missed the funnel were swept into the vial with a small brush. Any burr left on the sample was also scraped into the vial. Chip losses were usually no more than 1-3%.

Fourteen sections, 2.5×10^{-3} to 10×10^{-3} cm thick, were cut from each sample. The thickness of each section was computed from the chip weight, which was determined by difference weighing, i.e., the glass vial in which the chips of that section were caught was weighed before and after cutting the section. In addition, the sample was weighed before machining and after the fifth, tenth and fourteenth sections, and the individual section weights were uniformly adjusted so that their sum equaled the weight difference. (This was not done on the samples annealed at 981 and 891°C.) All weighing was done on a Chainomatic balance to an accuracy of 0.1 mg. The length of the sample was measured with a micrometer before and after sectioning.

Since all the isotopes of uranium are radioactive, special techniques of analysis had to be devised. A method using pile irradiation and fission product gamma-radiation counting was developed, but was abandoned in favor of mass spectrography because of the greater speed of the latter method. The samples were analyzed in a 12-inch, 60° mass spectrometer. This instrument was equipped with a surface ionization source consisting of a single tantalum filament mounted in a vacuum lock. Each sample was completely dissolved in nitric acid and a portion, estimated to contain about 50 micrograms, was deposited on the filament as uranyl nitrate.

III. DATA AND RESULTS

A. Data

The data on section weights, concentrations, etc., are given in Tables II-VII. The columns give:

1. section number,
2. the weight of the section,
3. in Tables IV, VI and VII the weight of the section corrected so that the sum of the weights of five (or four) sections equals the difference in the sample weight before and after cutting those five (or four) sections (this column is omitted in Tables II, III and V),
4. the thickness of the section, corrected for thermal expansion so as to represent the section thickness at the temperature of the diffusion anneal; (extrapolations of the density data given by Foote⁽¹⁰⁾ were used for the thermal expansion corrections),
5. the distance of the center of the section from the original interface,
6. the total U^{235} concentration in the section.

Other data on the specimen, including dimensions and the annealing time are also given in these tables. For the samples heated to and cooled from the beta-gamma transformation temperature in the annealing furnace, the annealing time was corrected using formulae analogous to those of Armstrong,⁽¹¹⁾ with the additional assumption that diffusion in the beta and alpha phases could be neglected.

For the calculation of the diffusion coefficient, the concentration of interest is the concentration of in-diffused U^{235} , i.e., the total U^{235} concentration minus the U^{235} that was originally in the basis metal. The latter was taken as 0.0343%, the value obtained on a piece of the material that did not come from a diffusion sample. Values lower than this were obtained on several diffusion samples, indicating isotopic inhomogeneity in the ingot. Since this introduces a big uncertainty into the net concentration near the tail ends of several penetration curves, the last one or two points on these curves were not used in calculating D . The first points on the penetration plots were high because the first section included some oxidized U^{235} that had not taken part in the diffusion; these points were also omitted in calculating D . The data of Tables II-VII are presented in the customary $\log C$ vs. X^2 plots in Figure 4.

TABLE II

Concentration-Penetration Data for Sample Diffused at 803.8°C

Section No.	Weight (grams)	Thick-ness* (cm)	X* (cm)	Total U^{235} (%)	Section No.	Weight (grams)	Thick-ness* (cm)	X* (cm)	Total U^{235} (%)
1	0.0372	0.00509	0.00254	1.38	8	0.0853	0.01168	0.05136	0.0355**
2	0.0401	0.00549	0.00783	0.885	9	0.0628	0.00860	0.06150	- **
3	0.0413	0.00566	0.01341	0.579	10	0.0718	0.00982	0.07071	0.0315**
4	0.0409	0.00560	0.01904	0.327	11	0.0670	0.00917	0.08016	- **
5	0.0480	0.00656	0.02512	0.147	12	0.0799	0.01092	0.09021	- **
6	0.0458	0.00627	0.03154	0.0682	13	0.0732	0.01002	0.10068	- **
7	0.0793	0.01085	0.04009	0.0385	14	0.0707	0.00968	0.11053	0.0345**

*Corrected for thermal expansion and weight differences.

**Not used for calculating D.

Diameter = 0.706 cm

Length Removed = 0.1095 cm (micrometer)

Length Removed = 0.1144 cm (weight difference)

Length Removed = 0.1145 cm (sum of section weights)

Time = 4 hr 12 min

Corrected time = 4 hr 35 min

 $D = 4.43 \times 10^{-9} \text{ cm}^2/\text{sec}$ $D = 4.07 \times 10^{-9} \text{ cm}^2/\text{sec}$ (corrected for micrometer)

TABLE III

Concentration-Penetration Data for Sample Diffused at 891°C

Section No.	Weight (grams)	Thick-ness* (cm)	X* (cm)	Total U^{235} (%)	Section No.	Weight (grams)	Thick-ness* (cm)	X* (cm)	Total U^{235} (%)
1	0.0208	0.00285	0.00143	0.418	8	0.0791	0.01087	0.05988	0.052
2	0.0351	0.00481	0.00526	-	9	0.0742	0.01020	0.07041	0.036
3	0.0547	0.00751	0.01145	0.225	10	0.0705	0.00967	0.08035	0.0362
4	0.0794	0.01090	0.02062	0.171	11	0.0674	0.00925	0.08980	0.0325
5	0.0606	0.00832	0.03023	0.117	12	0.0655	0.00900	0.09893	0.031
6	0.0676	0.00930	0.03904	0.082	13	0.1190	0.01633	0.11159	0.0306
7	0.0783	0.01075	0.04907	0.0601	14	0.0732	0.01005	0.12478	0.0316

*Corrected for thermal expansion

Diameter = 0.705 cm

Length Removed = 0.132 cm (micrometer)

Length Removed = 0.130 cm (weight difference)

Time = 10 hr 9 min

No diffusion coefficient

TABLE IV

Concentration-Penetration Data for Sample Diffused at 947.5°C

Section No.	Weight (grams)	Corrected Weight (grams)	Thickness* (cm)	X* (cm)	Total U ²³⁵ (%)	Section No.	Weight (grams)	Corrected Weight (grams)	Thickness* (cm)	X* (cm)	Total U ²³⁵ (%)
1	0.0553	0.0556	0.00813	0.00406	- **	8	0.0648	0.0652	0.00954	0.06880	0.080
2	0.0604	0.0608	0.00890	0.01258	0.182	9	0.0678	0.0683	0.00999	0.07857	0.0651
3	0.0619	0.0623	0.00911	0.02159	0.170	10	0.0724	0.0729	0.01067	0.08890	0.0556
4	0.0554	0.0557	0.00815	0.03022	0.154	11	0.0714	0.0714	0.01045	0.09945	0.0483
5	0.0616	0.0620	0.00907	0.03883	0.132	12	0.0699	0.0699	0.01023	0.10980	- **
6	0.0715	0.0720	0.01053	0.04862	0.116	13	0.0612	0.0612	0.00895	0.11939	0.0384
7	0.0688	0.0693	0.01014	0.05896	0.0967	14	0.0726	0.0726	0.01062	0.12917	0.0373

*Corrected for thermal expansion.

**Not used for calculating D.

Diameter = 0.6835 cm

Length Removed = 0.137 cm (micrometer)

Length Removed = 0.132 cm (weight difference)

Length Removed = 0.1313 cm (sum of section weights)

Time = 17 hr 16 min

 $D = 1.67 \times 10^{-8} \text{ cm}^2/\text{sec}$ $D = 1.79 \times 10^{-8} \text{ cm}^2/\text{sec}$ (corrected for micrometer)

TABLE V

Concentration-Penetration Data for Sample Diffused at 981°C

Section No.	Weight (grams)	Thickness* (cm)	X* (cm)	Total U ²³⁵ (%)	Section No.	Weight (grams)	Thickness* (cm)	X* (cm)	Total U ²³⁵ (%)
1	0.0355	0.00520	0.00260	0.351	8	0.0554	0.00811	0.05760	0.206
2	0.0384	0.00562	0.00801	0.318	9	0.0593	0.00868	0.06600	0.183
3	0.0700	0.01025	0.01594	0.309	10	0.0546	0.10799	0.07434	0.160
4	0.0547	0.00801	0.02508	0.303	11	0.0571	0.00836	0.08252	0.142
5	0.0554	0.00811	0.03314	0.268	12	0.0779	0.01140	0.09240	0.119
6	0.0537	0.00786	0.04112	0.252	13	0.0710	0.01039	0.10330	0.094
7	0.0581	0.00851	0.04930	0.230	14	0.0670	0.00991	0.11346	0.0831

*Corrected for thermal expansion.

Diameter = 0.683 cm

Length Removed = 0.1225 cm (micrometer)

Length Removed = 0.1184 cm (weight difference)

Time = 25 hr 20 min

Corrected time = 25 hr 37 min

 $D = 1.99 \times 10^{-8} \text{ cm}^2/\text{sec}$ $D = 2.11 \times 10^{-8} \text{ cm}^2/\text{sec}$ (corrected for micrometer)

TABLE VI

Concentration-Penetration Data for Sample Diffused at 1069.5°C

Section No.	Weight (grams)	Corrected Weight (grams)	Thickness* (cm)	X* (cm)	Total U^{235} (%)	Section No.	Weight (grams)	Corrected Weight (grams)	Thickness* (cm)	X* (cm)	Total U^{235} (%)
1	0.0283	0.0289	0.00384	0.00192	0.166**	8	0.0663	0.0672	0.00894	0.03840	0.0575
2	0.0413	0.0422	0.00561	0.00664	0.143	9	0.0464	0.0470	0.00625	0.04599	- **
3	0.0306	0.0313	0.00416	0.01153	0.131	10	0.0427	0.0433	0.00576	0.05200	- **
4	0.0387	0.0396	0.00527	0.01625	0.117	11	0.0383	0.0368	0.00489	0.05732	0.0365
5	0.0312	0.0319	0.00424	0.02100	0.102	12	0.0377	0.0362	0.00481	0.06217	- **
6	0.0433	0.0439	0.00584	0.02604	0.0872	13	0.0403	0.0387	0.00515	0.06716	- **
7	0.0369	0.0374	0.00497	0.03144	0.0701	14	0.0347	0.0333	0.00443	0.07195	0.0336**

*Corrected for thermal expansion.

**Not used in calculating D.

Diameter = 0.7168 cm

Length Removed = 0.0739 cm (micrometer)

Length Removed = 0.0728 cm (weight difference)

Length Removed = 0.0727 cm (sum of section weights)

Time = 1 hr 7 min

 $D = 5.70 \times 10^{-8} \text{ cm}^2/\text{sec}$ $D = 5.87 \times 10^{-8} \text{ cm}^2/\text{sec}$ (corrected for micrometer)

TABLE VII

Concentration-Penetration Data for Sample Diffused at 1069.8°C

Section No.	Weight (grams)	Corrected Weight (grams)	Thickness* (cm)	X* (cm)	Total U^{235} (%)	Section No.	Weight (grams)	Corrected Weight (grams)	Thickness* (cm)	X* (cm)	Total U^{235} (%)
1	0.0889	0.0912	0.0132	0.0066	- **	8	0.0427	0.0436	0.00632	0.04717	0.193
2	0.0646	0.0663	0.00961	0.01800	0.369	9	0.0304	0.0311	0.00451	0.05258	0.165
3	0.0277	0.0284	0.00412	0.02487	0.309	10	0.0600	0.0613	0.00889	0.05928	- **
4	0.0265	0.0272	0.00394	0.02890	0.306	11	0.0409	0.0423	0.00613	0.06679	0.106
5	0.0211	0.0216	0.00313	0.03243	0.281	12	0.0181	0.0187	0.00271	0.07121	- **
6	0.0313	0.0320	0.00464	0.03632	0.255	13	0.0240	0.0248	0.00360	0.07437	- **
7	0.0362	0.0370	0.00537	0.04132	0.226	14	0.0544	0.0562	0.00815	0.08025	0.069

*Corrected for thermal expansion.

**Not used in calculating D.

Diameter = 0.6866 cm

Length Removed = 0.0841 cm (micrometer)

Length Removed = 0.0829 cm (weight difference)

Length Removed = 0.0808 cm (sum of section weights)

Time = 3 hr 30 min

 $D = 5.47 \times 10^{-8} \text{ cm}^2/\text{sec}$ $D = 5.62 \times 10^{-8} \text{ cm}^2/\text{sec}$ (corrected for micrometer)

Figure 4. Penetration Plots for Self-diffusion in Gamma Uranium.

24,905

B. Treatment of Data

The diffusion coefficients were calculated by fitting the concentration-penetration data to the appropriate solution of the diffusion equation. For the case of diffusion from an infinitesimally thin layer into a semi-infinite body this is:(12)

$$C = [q/(\pi Dt)^{1/2}] \exp(-X^2/4Dt)$$

or

$$\log_{10} C = \log_{10} q/(\pi Dt)^{1/2} - X^2/9.212 Dt \quad ,$$

where C is the concentration of in-diffused U^{235} in a section (the total U^{235} concentration of the section minus 0.0343%), X the distance of the center of this section from the original interface, D the diffusion coefficient, t the annealing time and q the amount of isotope initially deposited. The second of the equations may be written as

$$Y = A + bZ \quad ,$$

where

$$Y = \log_{10} C; A = \log_{10} q/(\pi Dt)^{1/2}; b = -1/9.212 Dt; \text{ and } Z = X^2.$$

The regression coefficient b is easily obtained by the method of least squares,⁽¹³⁾ and D can be calculated from b . The diffusion coefficients calculated from the data of Tables II-VII by this method are given in the tables.

The diffusion coefficients were corrected so that the total thickness removed equaled the thickness removed as measured by the micrometer, that is,

$$D_{\text{corr}} = D \frac{(\text{total thickness according to micrometer})^2}{(\text{total thickness according to weights})^2}.$$

This adjustment was justified as follows: The micrometer readings were in error certainly due to warping of the end surfaces, and possibly due to other causes. The micrometer measurement of the total thickness removed would have been larger than the value calculated from the weights if the only errors were due to warping and chip loss. The opposite of this was true for the sample annealed at 803°C, suggesting that other errors were responsible for the discrepancy, probably errors in the measurements of the diameter of the reduced section or changes of the cross-sectional area along the length of the reduced section. In this case, the micrometer measurements would be more accurate and were therefore used.

C. Results

The variations of the diffusion coefficients from the present data and the data of others^(1,2) with temperature are shown in Figure 5. A least-squares fit of the present results to an Arrhenius-type equation:

$$D = D_0 \exp (-Q/RT) \quad ,$$

where Q is the activation energy, R the gas constant, and T the absolute temperature, yielded $D_0 = 2.33 \times 10^{-3} \text{ cm}^2/\text{sec}$; $Q = 28.5 \text{ kcal/mol}$. A least-squares analysis of the three sets, leaving out the Russian results obtained by autoradiographic methods,⁽¹⁾ gave $D_0 = 1.12 \times 10^{-3} \text{ cm}^2/\text{sec}$; $Q = 26.5 \text{ kcal/mol}$. These are probably the best values.

D. Errors

The precision in the mass spectrographic determination of the U^{235}/U^{238} ratio was $\pm 1\%$. The annealing times, as corrected, were accurate to $1/2\%$. The maximum variation in the annealing temperature during a run

Figure 5: Arrhenius Plot for Self-diffusion in Gamma Uranium.

25,393

was 3° , except in the $803^\circ C$ run, where the time was calculated for an "average" temperature that had been obtained by graphical integration. The 3° temperature variation caused at most an error of 5% in D .

The errors in D due to misalignment were calculated from the equations given by Shirn et al.⁽¹⁴⁾ The misorientation was assumed to equal the maximum surface roughening, and although this is large, $2(Dt)^{1/2}$ is much larger. In the worst case (the specimen annealed at $803^\circ C$) the error in D due to misalignment was only 4%. It should be emphasized that the very large diffusion coefficients permitted errors in alignment that would have ruined a diffusion experiment on, say, silver. The excellent agreement between the three sets of data (Figure 5) is further evidence of the absence of substantial experimental errors.

The total error in the diffusion coefficients was thus less than 7%.

IV. DISCUSSION

For the 891°C run, the plot of $\log C$ vs. X^2 was curved, whereas the plot of $\log C$ vs. X was linear, indicating that grain boundary diffusion predominated in this run.⁽¹⁵⁾ This can be explained by the greater impurity content of the specimen. Figures 6 and 7 show the microstructure of this sample and of another sample cooled at nearly the same rate. The sample

Figure 6: Microstructure of Specimen Diffused at 891°C.

24,897 As Polished, Bright Field 50X

Figure 7: Microstructure of Specimen Diffused at 981°C.

24,898 As Polished, Bright Field 50X

annealed at 891°C contained much more second-phase material than the other. Since diffusion along the interphase boundaries could account for the anomalous penetration curve obtained, the following discussion does not apply to it.

The values of D_0 and of the activation energy merit discussion. The D_0 value is lower than the value predicted by Zener's theory.⁽³⁾ The entropy of activation is at the most zero. The activation energy is about one-half of what would be predicted from correlation with melting temperatures or heats of vaporization,⁽¹⁶⁾ or about 0.7 of that predicted from Nachtrieb's correlation⁽¹⁷⁾ between the activation energy for self-diffusion and the latent heat of melting - for uranium, 2.35 kcal/mol.⁽¹⁸⁾

Low D_0 values and low activation energies have usually been explained^(3,19) on the basis of diffusion along short-circuiting paths, such as grain boundaries or dislocations. The former can be excluded here, because: first, the $\log C$ vs. X^2 plots are linear; second, the grain size of the gamma uranium is very large; third, autoradiographic studies⁽¹⁾ showed no evidence of grain boundary diffusion; fourth, the experiments were carried out at temperatures ($> 3/4 T_m$) at which grain boundary diffusion is usually not found; and fifth, the close agreement between the present results and those of other investigators (Figure 5). All these indicate that the results are valid, that is, representative of volume self-diffusion in gamma uranium.

The above analyses,^(3,19) as well as LeClaire's,⁽²⁰⁾ considered that diffusion in body-centered-cubic (BCC) metals took place by a ring mechanism and that in face-centered-cubic (FCC) metals by a vacancy mechanism. The presence of Kirkendall effect in BCC metals^(21,22,23) indicated that the vacancy mechanism was dominant in BCC metals. At the same time, other experimental evidence indicated that self-diffusion in the alkali metals took place by a vacancy mechanism,⁽²⁴⁾ and at the present time the vacancy mechanism is supposed to be responsible for self-diffusion in both FCC and BCC metals.

A Kirkendall effect has been found in chemical diffusion in several gamma-uranium alloy systems,^(25,26,27) indicating that a defect mechanism is predominant under these conditions. The formation of porosity in the diffusion zone of such couples indicates that the defects are vacancies. On the other hand, it is difficult to reconcile the low activation energy and D_0 value for self-diffusion in gamma uranium with a vacancy mechanism. What then are the possible alternatives?

The first alternative is, of course, that the vacancy mechanism is dominant. If this is the case, the present analyses of activation energies

for self-diffusion and of D_0 values in terms of the vacancy mechanism^(3,17,19,20) are wrong. An experimental study that might throw some light on this would be the measurement of the vacancy formation energy by quenching, dilatometry, etc., or the study of the effect of pressure on self-diffusion in gamma uranium. These studies pose formidable experimental problems, and are not at present underway.

The second possibility is that diffusion takes place by the ring mechanism.⁽³⁾ Since this mechanism does not involve mass transport, this possibility may be checked by measuring the activation energy for a volume diffusion process that does involve mass transport and comparing it with the activation energy measured in the tracer diffusion experiments. Sintering, if it takes place by volume diffusion, is a process involving mass transport, and experiments on the measurement of the activation energy for the sintering of gamma uranium are underway.

Another possibility is an activated state that is neither an activated ring nor an atom on the saddle point between two vacant lattice sites. A fluctuation that rearranges the atoms in the gamma-uranium lattice into regions similar to the beta- or alpha-uranium lattice suggests itself. Such an arrangement would have a negative entropy of activation since the beta- and alpha-uranium lattices have lower symmetry than the gamma. Further, since the alpha- and beta-uranium lattices are also stable configurations of uranium metal, the energy of activation may not be as high as in the usual case.

It is also possible that diffusion takes place along short-circuiting paths, to wit, dislocations, and that the density of dislocations is so great that this preferential penetration shows up neither in autoradiographs nor in deviations of the penetration curves from the expected. To account for such heavy material transport, at least 10^{12} dislocation lines/cm² are needed. Although such a concentration of dislocations could conceivably be introduced by the density change on the beta-gamma transformation, most of them should anneal out at such high temperatures. However, if the bonding in gamma uranium is partly covalent,⁽²⁸⁾ this may be hindered.

Some support has been given to the ring mechanism by the recent work of Paxton and Gondolf⁽²⁹⁾ and of Pound, Bitler and Paxton.⁽³⁰⁾ Paxton and Gondolf have measured self-diffusion in the BCC metal chromium and have found $D_0 = 10^{-4}$ cm²/sec; $Q = 52$ kcal/mol. One would expect $Q = 88$ kcal from the Q - T_m relation. Pound et al.⁽³⁰⁾ have put forward the following hypothesis to explain the results: In order for a ring to rotate, the atoms in the ring must "synchronize" their motions. This involves a considerable ordering, and therefore a decrease of entropy, calculated to be on the order of 20 eu. Using the formulae of Pound et al., an entropy of synchronization of -19 eu is obtained for a three-atom ring and of -28.4 eu

for a four-atom ring in uranium. The entropy of activation is calculated to be -6 eu, using Pound's formula, so the entropy of ring motion would have to be 13 or 22.4 eu, which is quite a bit higher than is usually assumed.⁽²¹⁾ However, strict quantitative agreement is probably not to be expected. The formulae given by Pound et al., however, are not adequate to explain the very low activation energy found for self-diffusion in gamma uranium.

This report then offers no explanation of this latest example of the unconventional behavior of uranium metal. It is hoped that the results and discussion presented here will stimulate theoretical work leading to a satisfactory explanation.

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APPENDIX I

Calculation of U^{235} Concentrations Expected in
Self-diffusion Experiments in Alpha Uranium

The purposes of the calculations reported here were twofold: first, to see how thick an isotope layer is permissible with the solution of the diffusion equation given earlier; and second, to calculate the concentrations to be expected in a diffusion experiment on alpha uranium.

Consider diffusion from a finite rod of length "h" into a semi-infinite rod. The initial concentration of isotope in the finite rod is C_0 , in the semi-infinite rod, zero. The solution of the diffusion equation for these initial conditions is⁽³¹⁾

$$C = \frac{C_0}{2} \left[\operatorname{erf} \frac{X+h}{2(Dt)^{1/2}} + \operatorname{erf} \frac{X-h}{2(Dt)^{1/2}} \right]$$

$$\text{Here } \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-n^2) dn.$$

Now let "h" approach zero, keeping the amount of isotope in the layer finite. The initial conditions then become

$$C(X,0) = C_0 h \delta(X),$$

where $\delta(X)$ is the Dirac delta function. The solution for these initial conditions is

$$C/C_0 = [h/(\pi Dt)^{1/2}] \exp(-X^2/4 Dt)$$

This solution is much easier to use than the above, especially because it does not involve measuring "h." The question then is: with how thick an isotope layer (how large "h") can this solution be used

Since the quantity $(Dt)^{1/2}$ is the "characteristic length" of the diffusion, a reasonable condition is $h \ll (Dt)^{1/2}$. Table VIII presents calculated values of C/C_0 for different values of X , h and $(Dt)^{1/2}$. " C/C_0 , true" refers to the two-error functions solution, " C/C_0 , approx" to the exponential solution. Table VIII shows that if $h = 0.1 (Dt)^{1/2}$ the numerical values of the concentrations obtained from the two solutions are the same. This result is independent of "D," and should also apply to gamma uranium.

TABLE VIII

Concentrations Expected in Alpha-uranium Diffusion Sample for
Different Values of D, t and h

X (10 ⁴ cm)	h = 1.25 x 10 ⁻³ cm		h = 0.01 x 10 ⁻³ cm	
	C/C ₀ , true	C/C ₀ , approx.	C/C ₀ , true	C/C ₀ , approx.
D = 10 ⁻¹² cm ² /sec; t = 5 x 10 ⁵ sec; (Dt) ^{1/2} ≈ 7 x 10 ⁻⁴ cm				
0	7.90 x 10 ⁻¹	1.00 x 10 ⁰ *	8.00 x 10 ⁻³	8.00 x 10 ⁻³
1	7.87 x 10 ⁻¹	9.95 x 10 ⁻¹	7.95 x 10 ⁻³	7.97 x 10 ⁻³
2	7.81 x 10 ⁻¹	9.80 x 10 ⁻¹	7.82 x 10 ⁻³	7.84 x 10 ⁻³
5	7.34 x 10 ⁻¹	8.82 x 10 ⁻¹	7.04 x 10 ⁻³	7.05 x 10 ⁻³
10	5.86 x 10 ⁻¹	6.06 x 10 ⁻¹	4.84 x 10 ⁻³	4.85 x 10 ⁻³
20	2.26 x 10 ⁻¹	1.35 x 10 ⁻¹	1.08 x 10 ⁻³	1.08 x 10 ⁻³
30	3.52 x 10 ⁻²	1.11 x 10 ⁻²	8.86 x 10 ⁻⁵	8.89 x 10 ⁻⁵
40	2.80 x 10 ⁻³	3.30 x 10 ⁻⁴	2.68 x 10 ⁻⁶	2.64 x 10 ⁻⁶
D = 10 ⁻¹³ cm ² /sec; t = 10 ⁶ sec; (Dt) ^{1/2} = 3.16 x 10 ⁻⁴ cm				
0	9.95 x 10 ⁻¹	2.23 x 10 ⁰	1.79 x 10 ⁻²	1.79 x 10 ⁻²
1	9.94 x 10 ⁻¹	2.18 x 10 ⁰	1.75 x 10 ⁻²	1.74 x 10 ⁻²
2	9.90 x 10 ⁻¹	2.02 x 10 ⁰	1.62 x 10 ⁻²	1.62 x 10 ⁻²
5	9.54 x 10 ⁻¹	1.20 x 10 ⁰	9.61 x 10 ⁻³	9.62 x 10 ⁻³
10	7.12 x 10 ⁻¹	1.83 x 10 ⁻¹	1.47 x 10 ⁻³	1.47 x 10 ⁻³
15	2.88 x 10 ⁻¹	8.04 x 10 ⁻³	6.50 x 10 ⁻⁵	6.44 x 10 ⁻⁵
20	4.60 x 10 ⁻²	1.02 x 10 ⁻⁴	7.97 x 10 ⁻⁷	8.18 x 10 ⁻⁷
30	4.43 x 10 ⁻⁵	3.81 x 10 ⁻¹⁰	3.03 x 10 ⁻¹³	3.05 x 10 ⁻¹³
D = 10 ⁻¹⁴ cm ² /sec; t = 10 ⁶ sec; (Dt) ^{1/2} = 10 ⁻⁴ cm				
0	1.00 x 10 ⁰	7.04 x 10 ⁰	5.64 x 10 ⁻²	5.63 x 10 ⁻²
1	1.00 x 10 ⁰	5.48 x 10 ⁰	4.38 x 10 ⁻²	4.38 x 10 ⁻²
2	1.00 x 10 ⁰	2.59 x 10 ⁰	2.07 x 10 ⁻²	2.07 x 10 ⁻²
5	1.00 x 10 ⁰	1.36 x 10 ⁻²	1.10 x 10 ⁻⁴	1.09 x 10 ⁻⁴
10	9.61 x 10 ⁻¹	9.82 x 10 ⁻¹¹	7.85 x 10 ⁻¹³	7.85 x 10 ⁻¹³
20	5.80 x 10 ⁻⁸	- -	- -	- -

* These values were calculated by Frank Taraba.

It is also evident from the tables that if several micron-thick slices with concentrations different from that of the basis metal are to be taken from each sample, highly depleted uranium has to be used as the basis material.

APPENDIX II

Metallographic Studies of Layers Deposited by Cathodic Sputtering

At the beginning of this work, extensive metallographic studies were made on layers deposited by cathodic sputtering, which will be called sputtered layers.⁽³²⁾ This work established the similarity between sputtered and electrodeposited layers [Figures 8⁽³²⁾, 9⁽³³⁾, 10⁽³²⁾, 11⁽³²⁾, 12 and 13⁽³³⁾]. Both the sputtered and electrodeposited layers have long, columnar grains parallel to the direction of deposition. The ends of these grains appear to be dome-shaped (Figures 10 and 11). The nature of the intergranular spaces which are very evident in Figure 10 is not clear. (The replica of Figure 10 is shadowed more heavily than that of Figure 11, exaggerating the size of the intergranular spacing somewhat.) It is probable that impurities segregate in these spaces, and it is also very likely that the misorientations and strains involved with these spacings and this structure account for the great reactivities of sputtered uranium layers. Nodules (Figure 12) sometimes form in the sputtered layers; these are similar to the nodules found in electrodeposits (Figure 13). The nodules were considered to have been caused by gas pressure fluctuations larger than 10 microns Hg,⁽³²⁾

It was also found⁽³²⁾ that when uranium was sputtered onto a stainless steel pin and the two were allowed to interdiffuse, diffusion layers (intermetallic compounds, Figure 14) that were entirely like the ones obtained in more conventional diffusion couples⁽³⁴⁾ formed.

Further metallographic work reproduced the layered structures shown in Figure 8 (see Figure 15). This last micrograph shows very well the long, columnar grains, parallel to the direction of deposition, which make up the sputtered layers. The striations parallel to the interface were supposed to be due to a periodic codeposition of impurities,⁽³²⁾ although later some correlation between interruptions in the deposition and the layers was also found. In the work done up until early 1958, the striated structure persisted after electropolishing. After the new sputtering routine (the one described under Section II B.) was adopted and the uranium chips in the gas train were replaced by Zr, a short electropolish removed the striated appearance.

When the difficulties in detecting penetration, which were mentioned in the Introduction, persisted after annealing in the gamma phase, metallographic studies were made in an attempt to detect the presence of a barrier layer. Such a layer is shown in Figure 16; it is made up of 1 - UC, 2 - UO₂, 3 - U(C,N,O). It was the observation of microstructures like this that led to the changes mentioned in the preceding paragraph.

Figure 8: Sputtered Uranium Deposit.⁽³²⁾

Silver
Coating

Sputtered
Uranium

Substrate
Uranium

16,406

Bright Field

2,000X

Figure 9: Electroplated Nickel Deposit.⁽³³⁾

16,440

800X

Figure 10: Sputtered Silver Surface.⁽³²⁾

Electronmicrograph 1681A

10,000X

Figure 11: Electroplated Silver Surface.⁽³²⁾

Electronmicrograph 1859E

4,000X

Figure 12: Nodule in Sputtered Uranium

21,572

Bright Field

2,000X

Figure 13: Nodules in Electroplated Nickel.⁽³³⁾

16,439

800X

Figure 14: Uranium-Stainless Steel Diffusion Zones.⁽³²⁾

16,405

Bright Field

1,000X

Figure 15: Sputtered Uranium Deposit.

21,570

Bright Field

2,000X

Figure 16: Barrier Layer between Sputtered Layer and Substrate.

Identified inclusions: 1 - UC, 2 - UO_2 , 3 - $\text{U}(\text{C},\text{N},\text{O})$.

Two samples sputtered by the new routine were examined metallographically. One was not annealed, the other was annealed at $1061 \pm 5^\circ\text{C}$ for two hours. These samples were taper-sectioned in order to increase the width of the sputtered layer.

Figure 17 shows the as-sputtered sample after mechanical polishing and a very short electropolish. The surface makes an angle of 18° with the original interface. The original interface is marked by a row of inclusions. Between these and the heavily oxidized part of the sputtered layer there is a thin layer of apparently metallic uranium. The thickness of this layer, 3.5 microns, is in fair agreement with the thicknesses calculated from plots of the areas under the concentration vs. distance of sectioned diffusion samples (1-2.4 microns).

Figure 17: Sputtered Uranium Deposit, as Sputtered.

Even the metallic part of the isotope layer was much thicker than usually used in diffusion work. The extra thickness was necessary to raise the concentration of diffused U^{235} above the U^{235} content of the basis metal. Since the layer thicknesses were still much less than $(Dt)^{1/2}$, the above solution of the diffusion equation could still be used.

Weil⁽³²⁾ observed a similar structure after alpha annealing (Figure 18).

Figure 19 shows the annealed sample etched by cathodic sputtering. The darker material is believed to be the sputtered layer. The twins were probably formed during cooling from the diffusion temperature. That these

Figure 18: Sputtered Uranium Deposit, Alpha Annealed.⁽³²⁾

16,404

Bright Field

1,000X

Figure 19: Sputtered Uranium Deposit, Gamma Annealed.

24,893

Polarized Light

250X

twins extend into the sputtered layer implies that the layer was an epitaxial deposit at the time of twin formation. The reason for its darker color is not known, although it is probably due to preferential oxidation of the sputtered layer, the structure of which is less perfect than that of the substrate metal. The part of the sputtered layer beyond the epitaxial portion was quite heavily oxidized and, judging by the penetration plots, parts of it flaked off. Some black powder was found in the quartz capsules after annealing; X-ray analysis showed that it was composed of UO_2 and various U-Si compounds. The latter, and part of the former, were very probably products of a reaction between the quartz tube and evaporating uranium. The occurrence of such a reaction was further indicated by the severe discoloration of the quartz tubes after annealing.

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