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DIMENSIONAL INSTABILITY OF URANIUM—III

Third Annual Progress Report for June 30, 1957
to June 30, 1958

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TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	5
I. INTRODUCTION	6
II. ANISOTROPY OF SELF-DIFFUSION OF ALPHA-URANIUM. . .	6
III. EFFECT OF GRAIN SIZE ON THE GROWTH OF ALPHA-URANIUM DURING IRRADIATION	10
IV. PROJECTED IRRADIATION EXPERIMENTS	11
V. FUTURE WORK	12
REFERENCES	13
APPENDIX	17

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ABSTRACT

The mechanism of dimensional instability of uranium is under investigation. In order to confirm an assumption of the diffusion theory, the magnitude of diffusion anisotropy in alpha-uranium single crystals is being determined by measurement of the self-diffusion coefficients along principal crystallographic directions. Initial measurements have yielded values of 5×10^{-15} cm²/sec along the [010] and 4×10^{-15} cm²/sec along the [001]. These values are being rechecked. In addition, in-pile experiments designed to further clarify the effect of grain size on growth under irradiation have been initiated.

I. INTRODUCTION

The importance of the dimensional instability phenomenon as it affects the use of uranium in nuclear reactors is by now well known. It is generally agreed that the irreversible growth of alpha-uranium under neutron bombardment is somehow connected with its anisotropic properties, and several theories have been advanced to explain the mechanism. The anisotropy in thermal expansion and mechanical properties has served as the basis for theories advanced by Pugh, Bettman and others⁽¹⁾. Seigle and Opinsky⁽²⁾ have proposed that the anisotropic diffusion of displaced atoms and vacancies, produced in the lattice by fission and by fast neutron collisions, could be responsible for the observed effects. Their theory advanced the idea that the net diffusional flux of displaced atoms occurs preferentially in the [010] crystallographic direction, thereby causing growth in that direction, and emphasized the role that grain boundaries play as vacancy and interstitial sinks. In view of the accumulating evidence that processes within the grain interiors are important, this theory has been modified to allow for the action of dislocations and sub-grain boundaries⁽³⁾. The principal ideas of the original model are, however, retained.

The experimental program is designed to confirm the main assumptions of the diffusional theory, and has as its objectives:

- (a) To determine the anisotropy in the self-diffusion coefficient of uranium; and
- (b) To determine the effects of grain and sub-grain size upon the growth characteristics of irradiated uranium.

II. ANISOTROPY OF SELF-DIFFUSION OF ALPHA-URANIUM

To measure the anisotropy of diffusion quantitatively, it is necessary to trace the diffusion of a uranium isotope along each of the crystallographic directions in uranium single crystals. This has turned out to be an extremely difficult task. Most of the experimental problems and their eventual solution were dealt with in detail in the previous reports^(4,5). They consisted of (a) the preparation of large single crystals; (b) development of a method for depositing adherent layers of the isotope, U²³³, onto the surface of the single crystals; and (c) evolving a suitable method for measuring the very shallow penetration of isotope which must be expected from the limiting diffusion temperature of 640°C.

One single crystal of uranium was obtained from the Argonne National Laboratory through the courtesy of Mr. E. S. Fisher. During the past year, this has been supplemented by several smaller crystals which have been prepared at this Laboratory from an ingot of high-purity uranium, also obtained from ANL, employing the procedures developed by Fisher⁽⁶⁾. A method has been developed for grinding faces on each crystal perpendicular to one of the

major crystallographic directions with the aid of a special goniometer which aligns the crystal along the desired direction and holds the orientation during grinding. Considerable care must be exercised to remove all cold working caused by the grinding processes in order to prevent re-crystallization during the subsequent diffusion anneal.

The method for depositing the layer of isotope also has been covered in detail in the previous reports^(4,5). Basically, it consists of cleaning the surface of the crystals by cathodic sputtering, and following with thermal evaporation of U^{233} . Both operations are conducted in the same apparatus so that the specimen need not be exposed to air. The only new changes made in the procedure have been designed to improve the safety aspects. Since the alpha activity of U^{233} is of the same order as that of Pu^{239} , it seemed advisable to inspect the methods employed at ANL in handling Pu^{239} . As a result of this inspection and discussions with ANL personnel, it was felt that the precautions originally set up were insufficient. Therefore, the glass sputtering-evaporation apparatus was modified so that it could be operated in an air-tight drybox. A fitting was welded to the bottom of the box, which permits the vacuum pumps to remain outside; however, the pump exhaust is carried to a general contaminated exhaust system. The drybox itself is maintained under a negative pressure by the same exhaust system. This prevents the leakage of contamination from the box when material is being admitted or removed. With this setup, even if the glass apparatus should break during a run, all contamination will be contained by the drybox. Fig. 1 is a photograph of the experimental arrangement.

The only method now being used to analyze the diffusion couples is the surface decrease procedure discussed in SEP-246⁽⁵⁾. The other procedure still under consideration involves grinding thin layers perpendicular to the diffusion direction and measuring the activity in the individual layers in order to obtain a concentration curve. Although the method is feasible, the working limitations imposed by the dryboxes make it extremely cumbersome.

A detailed account of the procedure now being used is as follows:

1. A single crystal is ground in such a manner that a flat surface is made perpendicular to either the $[100]$, $[010]$, or $[001]$ direction. The ground surface is then slightly electropolished to remove all traces of cold work, but the flatness of the surface is still maintained.
2. The specimen is placed in the sputtering-evaporation apparatus along with a small piece of uranium alloy containing 5% U^{233} .
3. The surface of the diffusion couple is first cleaned by sputtering and immediately thereafter, U^{233} is evaporated onto the cleaned surface.
4. The specimen is removed from the apparatus and sealed in an evacuated quartz tube. The tube is sealed by means of a carbon

arc, which eliminates the need for bringing an oxygen gas torch into the drybox.

5. The encapsulated specimen is removed from the drybox and placed in a resistance furnace at 640°C. As a further precaution, the furnace is situated in an efficient chemical hood.
6. After a suitable annealing time of six to eight weeks, the specimen is removed and exposed to a type NTA nuclear track emulsion. Two exposures are made, one with the ground face of the specimen in direct contact with the emulsion, and one with a 0.00035" nickel foil interposed. The density of alpha particle tracks in both exposures is then measured with a counting grid at a magnification of 700 diameters. By using a set of exposures made with a sample of 5% U²³³ as a standard, the density of tracks measured in the bare exposure can be related to the total quantity of isotope present in the specimen, and therefore to the mass of the initial deposit; the track density in the exposure made with the nickel foil interposed is related to the quantity of isotope present in a narrow layer at the surface. From these data, the self-diffusion coefficient is calculated using the expression

$$C = \frac{Q}{\sqrt{\pi Dt}} \quad (1)$$

where C is the concentration of isotope in the surface layer; Q is the product of the initial concentration of isotope and the thickness of the deposit; t is the diffusion time; and D is the self-diffusion coefficient for the direction considered.

Up to the present time, one diffusion couple has been prepared for each of the three directions. Diffusion anneals of six and ten weeks duration at 640°C have been completed for the [001] and [010] crystals respectively. The four nuclear track exposures made for each specimen are illustrated in Fig. 2. The results of the counting procedure are given in Table I.

TABLE I.
COUNTS/GRID SQUARE/MIN.

<u>Specimen</u>	<u>Exposure A</u>	<u>Exposure B</u>	<u>Exposure C</u>	<u>Exposure D</u>
010	0.302	3.813	0.033	0.162
001	0.302	3.813	0.026	0.080

From the ratio of counts in exposures B and D, the concentration of U²³³ in the volume counted is obtained, and from this, the thickness of the initial deposit of 5% U²³³ may be calculated.

The ratio of counts in exposures A and C gives the surface concentration of the diffused specimen since the foil permits only alpha particles emitted from the surface region to enter the emulsion.

These data when inserted in equation (1) yield values for the self-diffusion coefficient of $5 \times 10^{-15} \text{ cm}^2/\text{sec}$ and $4 \times 10^{-15} \text{ cm}^2/\text{sec}$ for the [010] and the [001] directions respectively.

Fig. 3 is a plot of the concentration-penetration curves calculated from the measured diffusion coefficients for the two specimens. The indicated counting depth was calculated from the Bragg-Kleeman relation⁽⁷⁾.

$$R_s = 0.0003194 \frac{R_a \psi_s}{d_s} \quad (2)$$

where R_s = range of alpha particles in the material considered; R_a = range in air; ψ_s = square root of the atomic weight of the material; and d_s = density of the material.

The foil thickness is taken as 0.00035"

The above data must be considered as initial and tentative, since the apparent lack of a significant difference in diffusion rate in the [010] and [001] directions is surprising. An analysis of the counting procedure had previously been performed in order to determine the effect of small variations in foil thickness on the density of alpha particle tracks registered in the film. The details of the calculation are in the Appendix. The result of this analysis had shown that a variation of approximately one and one-half percent in foil thickness (.000005") will cause an error of twenty percent in the ratio of the number of counts obtained with a foil interposed between the specimen and emulsion to the number obtained without the foil. Such an error can change the computed diffusion coefficient by an order of magnitude. To avoid this difficulty, an attempt was made to position the specimen over the same area of the foil during each exposure. It is not certain whether this was accomplished. Furthermore, a considerable amount of personal judgment enters into counting the tracks. Errors caused by this factor have not yet been completely determined. However, as a rough check, two exposures were made with the standard alloy in which the time was varied by a factor of two. The resultant number of counts registered also doubled, as would be expected if the counting were accurate.

A most serious error could be introduced if the interface between the deposited isotope and the base crystal were not perfectly clean, even though considerable precautions have been taken to assure this. In such a case, diffusion would be inhibited at the surface and a low diffusion coefficient would be measured. On the basis of the data given in Table I, it appears certain that some diffusion has taken place, but whether or not it was inhibited at the original interface has not yet been determined.

In view of these uncertainties, additional runs will be made in the same manner as above in order to check the initial results. Further, an attempt will be made to apply the sectioning technique discussed in the previous report(5). If successful, this method of analysis would provide the most satisfactory confirmation of the values.

I. EFFECT OF GRAIN SIZE ON THE GROWTH OF ALPHA-URANIUM DURING IRRADIATION

Some time ago, an experiment was carried out to measure the effect of grain size on the growth of alpha-uranium in which specimens of various grain sizes but with a presumably constant crystal texture were irradiated in the MTR(8). As noted in the last report(5), the observed effect of grain size upon growth rate was unexpectedly small, and since the uniformity of preferred orientation among the samples had been only qualitatively established, the significance of the results was uncertain. Consequently, arrangements were made during the past year to repeat the experiment using specimens with a wider range of grain sizes, and whose uniformity of preferred orientation had been more precisely established. The latter has been accomplished by accurately measuring the thermal expansion coefficient of each specimen using a highly sensitive interferometric dilatometer. Due to the extremely great anisotropy in this property, a small difference in orientation should manifest itself as a measurable difference in thermal expansion.

The specimens, approximately 1/8" in diameter by 3/4" in length, were machined from a rod of high-purity uranium and annealed for various times at 640°C. Since this temperature is well within the alpha region, the grain size differential was obtained by ordinary grain growth. A small piece was cut from the specimens annealed for the shortest and longest times (which had average grain sizes of 20 microns and 100 microns respectively) and machined into a conical shape, as required by the Geartner Model I-1118t1 dilation interferometer. The specimen lengths were then measured as a function of temperature over the temperature range 20° to 60°C in a chamber controlled to $\pm 0.1^\circ\text{C}$.

As can be seen from the results in Table II, the specimens are quite uniform, indicating that the specimen texture has not been substantially altered by grain growth.

TABLE II

Time of Anneal at 640°C	Thermal Expansion Coefficient Parallel to the rod axis x 10 ⁶			Thermal Expansion Coefficient Perpendicular to the rod axis		
	<u>Trial I</u>	<u>Trial II</u>	<u>Average</u>	<u>Trial I</u>	<u>Trial II</u>	<u>Average</u>
15 min.	3.61					
15 "	3.30	3.55	3.43	19.8	20.5	20.2
15 "	3.64					
2 weeks	3.32					
2 "	3.05	3.38	3.35	--	--	--
2 "	3.00					

As soon as the constancy of preferred orientation had been established, arrangements were made with the Irradiation Experiments Group of Knolls Atomic Power Laboratory to encapsulate the samples for irradiation. This has now been done and the specimens were shipped to the MTR for insertion during the first week of May 1958. It is planned to obtain a total irradiation flux of 10^{20} nvt with the specimen temperature at approximately 150°C , i.e., to duplicate the previous irradiation conditions.

IV. PROJECTED IRRADIATION EXPERIMENTS

An experiment was suggested in the previous report⁽⁵⁾ to test the relative effectiveness of inter- and intra-granular processes on irradiation growth by irradiating single crystals of different size. Since large single crystals of uranium are very difficult to obtain, it was thought that crystals of bismuth which also exhibit a high degree of anisotropy might be substituted. The question still remained as to whether or not sufficient atomic displacements would result from neutron bombardment to cause measurable growth in non-fissionable bismuth. In response to a query, it was pointed out by J. A. Brinkman⁽⁹⁾ that it would take a relatively long exposure in the MTR to insure the displacement of each bismuth atom at least once by fast neutron bombardment. Brinkman's calculations indicated, however, that the addition of 0.0016 percent U^{235} to the bismuth would produce a unit concentration of displacements during an exposure of 10^{21} thermal neutrons/ cm^2 . Since it was estimated that a unit concentration might be just sufficient to produce detectable growth, an alloy of this composition was prepared by melting a small quantity of enriched uranium in an ingot of bismuth. To test for homogeneity of the mixture, a small piece of the resultant ingot was polished to a flat face, and exposed for two weeks to a type NTA nuclear track emulsion. Microscopic inspection of the emulsion revealed localized areas of high alpha track density which is evidence that even such small amounts of uranium tend to segregate in bismuth. Since it is apparently impossible to prepare a homogeneous mixture of this alloy, it is unsuitable for the proposed experiments.

As an alternative to the uranium-bismuth crystals, a number of uranium single crystals are now being prepared in the manner already described. These will be used for this and other experiments.

During the past year, the plastic deformational theories and the diffusional theory of dimensional instability have been critically reviewed⁽³⁾ and the latter theory has been modified to allow for the action of vacancy and interstitial sinks within the grains. The influence of sub-grain boundaries, as shown by the rapid growth of "pseudo" single crystals, is emphasized. The presence of such boundaries may mask the effect of the nominal grain size. Shrinkage of single alpha-uranium crystals in the $[100]$ direction may be rationalized by assuming that edge dislocations corresponding to the predominant slip system are active vacancy sinks, as suggested by others. A recomputation of the theoretical growth rates, allowing for the existence

of dislocation sinks, again indicates that a diffusional mechanism is possible if the assumed anisotropy of diffusion exists, and the diffusion coefficients are sufficiently high.

Experiments are currently being considered to test sub-grain boundary effects on dimensional instability. Also, other irradiation experiments are being planned to determine if irradiation produces any evidences of plastic deformation, such as twinning, in perfect single crystals.

V. FUTURE WORK

1. The remaining self-diffusion specimen will be analyzed in the manner described using the nuclear track emulsion. Duplicate sets of specimens will also be prepared.
2. An attempt will be made to apply a sectioning technique to the three self-diffusion specimens.
3. Self-diffusion measurements will be made in the gamma temperature range.
4. The irradiation experiment testing the grain size effect will be completed and the results analyzed.
5. Further irradiation experiments on "perfect" and "imperfect" single crystals will be performed in order to clarify the mechanism of dimensional instability.

REFERENCES

1. S. F. Pugh, "Radiation Damage in Fissile Materials", Progress in Nuclear Energy, 5, Edited by Finniston and Howe, McGraw-Hill (1956)
2. L. L. Seigle and A. J. Opinsky, "Mechanism of Dimensional Instability of Uranium", Nuclear Science and Engineering, 2, No. 1, Feb. 1957 p. 38
3. L. L. Seigle and L. S. Castleman, "Mechanism of Irradiation-Induced Dimensional Instability of Uranium", submitted for publication to 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, Sept. 1-13, 1958.
4. R. Resnick and L. L. Seigle, "Dimensional Instability of Uranium - I", June 1956 (SEP-228)
5. R. Resnick, L. S. Castleman and L. Seigle, "Dimensional Instability of Uranium - II", Feb. 1958 (SEP-246)
6. E. S. Fisher, "Preparation of Alpha-Uranium Single Crystals by a Grain-Coarsening Method", J. of Metals, July 1957, p. 882
7. H. Yagoda, Radioactive Measurements with Nuclear Emulsions, John Wiley and Sons, Inc. (1949)
8. R. Resnick and L. Seigle, 2nd Nuclear Engineering and Science Conference 1957, Paper No. 57-NESC-63
9. J. A. Brinkman, Atomics International, Canoga Park, California, private communication.

Fig. 1.

Fig. 2.

- (a) A standard alloy of 5% U²³³ is exposed to the emulsion with the foil interposed.
- (b) The same standard is exposed to the emulsion without the foil.
- (c) The diffusion couple is exposed with the foil interposed.
- (d) The diffusion couple is exposed without the foil.

Fig. 3.

APPENDIX

Calculation of counting error introduced by variations in thickness of the nickel foil.

R_U = range of alpha particles emitted by U^{233} in uranium as calculated from the Bragg-Kleeman relation (7).

f = foil thickness $\times \frac{R_U}{R_{Ni}}$; where R_{Ni} is the range of the alpha particles in nickel calculated in the same way as R_U .

At a given distance l , within the uranium, all alpha particles emitted whose total path to the emulsion is less than R_U , will penetrate the foil and are assumed to register a track in the nuclear emulsion.

APPENDIX

The number of particles entering the emulsion of those emitted at 1 is

$$dN = N_0 \times A \times dl \times \frac{\text{Area of the segment of a sphere of radius } R_u \text{ subtended by the angle } \theta}{\text{Total surface area of the sphere}}$$

N_0 is the number of alpha particles emitted per unit volume of uranium.

$A \times dl =$ a unit volume.

$$\text{Area of the segment} = 2\pi r h$$

$$r = \frac{f+l}{\cos \theta} = R_u$$

$$h = \frac{f+l}{\cos \theta} (1 - \cos \theta)$$

$$\therefore dN = (N_0 A dl) \frac{2\pi (f+l)}{\cos \theta} \cdot \frac{f+l}{\cos \theta} \cdot (1 - \cos \theta)}{4\pi \left(\frac{f+l}{\cos \theta}\right)^2}$$

$$dN = \frac{N_0 A}{2} (1 - \cos \theta) dl$$

$$= \frac{N_0 A}{2} \left(1 - \frac{f+l}{R_u}\right) dl$$

APPENDIX

The total number of particles which enter the emulsion of those emitted in the region between the surface of a specimen and the depth $R_u - f$ is

$$N = \frac{N_0 A}{2} \int_0^{R_u - f} \left(1 - \frac{f+l}{R_u}\right) dl$$

$$N = \frac{N_0 A}{4} \cdot \frac{(R_u - f)^2}{R_u} = \frac{N_0 A}{4} R_u \left(1 - \frac{T}{R_{Ni}}\right)^2$$

where T is the actual thickness of the foil.

Thus, when no foil is present:

$$N = \frac{N_0 A}{4} R_u$$

The ratio of alpha tracks registered when the foil is used to the number registered without the foil is:

$$\left(1 - \frac{T}{R_{Ni}}\right)^2$$

The percentage change in this ratio with change in foil thickness is:

$$\frac{-2T}{R_{Ni} - T} \cdot \frac{dT}{T}$$