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DIMENSIONAL INSTABILITY OF URANIUM—II

Second Annual Progress Report, January 1, 1956
to June 30, 1957

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February 15, 1958

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ABSTRACT

The mechanism of dimensional instability of irradiated 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 diffusion coefficients along the principal directions. Progress made in working out procedures for the preparation of uranium single crystals, preparation of the diffusion couples, measurement of valid concentration-penetration data in very thin diffusion zones by sectioning, and measurement of surface concentrations by means of nuclear tracking emulsions is discussed. Also, in-pile experiments are being designed to further clarify the nature of growth under irradiation.

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 uranium under neutron bombardment is somehow connected with the anisotropy of the properties of alpha-uranium, and several theories have been advanced to explain the mechanism or mechanisms. The anisotropy in mechanical properties (in particular, thermal expansion⁽¹⁾) has served as the basis for theories advanced by Pugh, Bettman, et al⁽¹⁾. Seigle and Opinsky⁽²⁾, on the other hand, 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 advances the idea that the net diffusional flux of displaced atoms occurs preferentially in the (010) lattice direction, thus causing growth in that direction. It emphasizes the role that grain boundaries play as vacancy and interstitial sinks, and predicts that fine-grained uranium should grow more rapidly under irradiation than coarse-grained uranium. The present program was originally undertaken to provide an experimental check of the predictions of the diffusional theory, and had the following two objectives: (a) To determine the anisotropy in the self-diffusion coefficient of uranium; and (b) to determine the effects of grain size upon the growth characteristics of irradiated uranium. The progress made in the program up to the present reporting period is reviewed briefly below.

In the previous progress report⁽³⁾, the seriousness of the problems involved in the measurement of the self-diffusion coefficients in uranium were analyzed in detail. Briefly, they may be summarized as follows: (a) The preparation of single crystals of uranium of sufficiently large size; (b) the preparation of the diffusion couples consisting of a layer of the highly toxic U^{233} isotope on natural uranium; and (c) the measurement of a valid concentration-penetration curve in a very thin diffusion zone (the maximum diffusion temperature must be less than the alpha-beta transformation temperature of 660°C). Much of the work during the previous reporting period had been directed toward the solution of diffusion couple preparation problems. A method was finally adopted in which uranium was deposited as an evaporated thin film on the surface of a uranium disc cleaned prior to deposition by a sputtering process. Also as described in the previous progress report⁽³⁾, one irradiation experiment had been completed on a series of uranium rods cut from the same stock in which grain size gradations had been introduced by annealing treatments of varying duration at 640°C . The dimensions of the rods were checked both before and after an irradiation at the MTR. The results indicated the existence of a grain size effect, but the magnitude of the effect was far less than had been anticipated on the basis of the theoretical calculations, assuming that only grain boundaries acted as sinks.

Work during the past year was continued on both aspects of the program. Considerable effort has been expended upon attempts to grow single crystals of uranium and to set up procedures for analyzing uranium

diffusion couples. Also, a more closely controlled irradiation test has been devised in which the grain size effect is to be rechecked. In the original test, it had been determined that the preferred orientations of the specimens were qualitatively similar (the only processing differences between samples had been the annealing times used), but no accurate texture measurements were undertaken. Since the observed grain size effect was small, and it is well known that the degree of preferred orientation has a marked effect on dimensional stability, it has seemed necessary to repeat this experiment with specimens of carefully controlled preferred orientation. Accordingly, work has been under way to determine quantitative methods of evaluating preferred orientations that are not too time-consuming. Finally, the theory itself has been re-appraised in the light of accumulating experimental evidence. It now seems necessary to consider the action of vacancy and interstitial sinks within the grains, which had been neglected in the original calculations. Finally, new experiments are being designed to obtain further information about radiation-induced growth. The details of the work are discussed in the succeeding sections.

II. ANISOTROPY OF SELF-DIFFUSION OF ALPHA-URANIUM

The diffusion mechanism for the dimensional instability of alpha-uranium is based, in part, on a theoretically computed anisotropic diffusion of lattice vacancies, which should result in the self-diffusion coefficient being a function of crystallographic direction. A strenuous attempt is therefore being made to measure this anisotropy in alpha-uranium single crystals. Most of the preliminary experiments and the difficulties encountered were described in detail in the previous annual report⁽³⁾. As noted then, a procedure has been established to prepare diffusion couples by the evaporation of a thin film of U^{233} on various crystallographic faces of uranium crystals after first cleaning the faces by cathodic sputtering. The major problem still to be solved at that time was the establishment of a suitable technique for measuring the extent of diffusion. Several surface-decrease schemes and one standard sectioning technique were under consideration.

All but one of the surface-decrease techniques have now been discarded as being inapplicable for this particular measurement. The problems involved in the use of a windowed alpha scintillation counter to measure the surface activity of the specimen was discussed in some detail in the previous report. For example, a complex counting geometry presents itself which could be simplified only by collimating the alpha particle beam and making the initial deposit pure U^{233} (to make up for the activity lost in collimation) instead of 5% U^{233} in natural uranium, as planned. The 5% alloy had already been received from Los Alamos before the technique could be evaluated, therefore it was decided to abandon the scintillation-counting technique rather than incur the delay involved in obtaining pure U^{233} . The

surface-decrease method still under consideration is based on the use of Eastman Kodak's type NTA nuclear tracking emulsions, which are sensitive chiefly to alpha radiation. When the method was originally conceived, it was the intention to use the type NTC emulsions, which are sensitive to fission fragments and other highly ionizing particles - in particular, recoil atoms from alpha decay processes. It was believed that since recoil atoms have a very short range, those that could register in the film must come from the very surface of the specimen and could be used to measure surface concentrations. A rod containing 5% U^{233} in natural uranium was placed in contact with the emulsion. After a five-minute exposure, the specimen was removed and the emulsion developed. Upon microscopic examination it was found that numerous alpha particle tracks had registered in the film, and no wide tracks that could be attributed to recoil atoms were visible. The NTC emulsion was not supposed to be sensitive to alpha particles, which it was believed might obscure tracks from recoil atoms, but information obtained from Dr. H. Yagoda of the National Institutes of Health indicated that the range of recoil atoms is so short that they should not be expected to activate the film. As a substitute, a type NTA emulsion was adopted. This type is sensitive chiefly to alpha particles. If the surface of a diffusion couple were placed in contact with the film, alpha particles emitted from as far back as roughly 10^{-3} cm would register. Since it was desired to count only the particles emitted from the surface, various foils were placed between the specimen and the emulsion, their purpose being to stop all particles but those emitted from the surface region.

Foils of aluminum, saran and nickel were used. The thicknesses were measured to within 0.01 mm, using a micrometer, and the number of tracks per unit area of emulsion counted after given times of exposure. The thicker the foil, the fewer the counts registered. An attempt was made to estimate the distance beneath the surface from which the alpha particles were penetrating to the emulsion by making use of the relation between alpha particle energy and stopping distance in various media. Unfortunately, the relation is too approximate to give reliable data, and one cannot be certain that each alpha particle reaching the emulsion registers. Further, the limited resolution of the tracks under the microscope constitutes another uncertainty. It was established, however, that a one-for-one relation exists between foil thickness, exposure time, and the counts per unit area registered in the emulsion. Since the mathematical analysis requires a knowledge only of the relative initial and final surface activities, it appears that the above method is feasible if exposure conditions are exactly reproduced.

The use of foils approximately 0.00025" thick was complicated by their tendency to crinkle. This prevented their lying flat on the emulsion, and alterations in the shape of the foil between the initial and final counts introduced serious error into the measurement. The nickel foils turned out to be most suitable, since they could be made to lie flat by placing a magnet beneath them. In this way it was found that the

counting conditions could always be made reproducible.

Information recently published by the Bureau of Standards⁽¹³⁾ indicates that U^{233} is extremely toxic. If one uses the table of maximum permissible concentrations of isotope in the body as a guide, U^{233} should be classed with Pu^{239} in degree of toxicity. Therefore many precautions have to be taken in order that the U^{233} shall at no time enter the laboratory atmosphere. The procedure employing the nuclear tracking emulsions involves a minimum of handling of U^{233} and this, therefore, is another distinct advantage of this method. Nevertheless, it must be recognized that the nuclear tracking emulsions have never before been used in diffusion measurements, and that all surface-decrease procedures are open to some question. It is therefore felt that at least one diffusion couple must be analyzed by a more acceptable sectioning technique for comparison purposes. If it is found that both methods yield equivalent values for the diffusion coefficient, the surface-decrease method alone will be used for subsequent specimens.

A considerable amount of preparation has been required for the sectioning technique. The large amount of handling of the U^{233} required has resulted in a complex and cumbersome procedure which, tentatively, is as follows:

1. The isotope is loaded into the glass evaporating apparatus inside a large dry box.
2. The evaporation unit is stoppered and carried to a large exhaust hood where it is connected to an exhaust system.
3. The diffusion couple is prepared by first cleaning the surface of a single crystal by cathodic sputtering, and then evaporating U^{233} onto the cleaned surface.
4. The evaporation unit is filled with argon, plugged, and returned to the dry box where the specimen is removed and enclosed in a Vycor capsule.
5. The capsule is exhausted, sealed, and placed in a furnace at 640°C where it remains for about two months.
6. The specimen is removed from the capsule in a dust box and layers are ground perpendicular to the diffusion direction in a sludge of alumina and water.
7. When a layer approximately 0.0001 cm has been removed, the crystal is enclosed in a glass weighing bottle and weighed on a microbalance, which has a sensitivity of about 5×10^{-6} grams. The thickness of the layer removed is calculated from the weight loss during grinding.

8. The uranium grindings, which are now mixed in with the alumina and water, are transferred from the glass grinding surface to a volumetric beaker where the uranium is dissolved in nitric acid. The solution containing the uranium is separated from the residue by filtration.
9. The filtrate is transferred to a volumetric flask from which carefully measured aliquots are removed.
10. These are deposited on metal counting discs where they are dried under a lamp.
11. The residue is counted in a windowless alpha scintillation counter.
12. The quantity of U^{233} in each sample can be determined by the use of a standard sample prepared from the as-received material which contains 5% U^{233} .
13. The total amount of isotope initially deposited on the surface can be estimated from the activity of the ground sections. The data obtained from the above procedure are sufficient to compute the diffusion coefficient from the relation

$$C = \frac{Q}{\sqrt{\pi Dt}} e^{-x^2/4Dt}$$

where C is the surface concentration, t the time in seconds, Q the product of the initial concentration times the thickness of the deposited layer, x the penetration in centimeters, and D the self-diffusion coefficient in the direction considered.

The procedure employed for the surface-decrease technique is as follows:

1. The diffusion couple is prepared in the manner described in steps 1 through 5 above.
2. The specimen is removed from the capsule in the dust box and placed face down on the emulsion for a suitable exposure.
3. The emulsion is developed and the tracks counted under a microscope.
4. The initial count must be determined from a second specimen which is not annealed, since the time required for the film exposure would probably permit oxidation of the deposited film, and this might cause error in the measured diffusion coefficient.

5. The self-diffusion coefficient may then be calculated from the relation

$$C = \frac{Q}{\sqrt{\pi} Dt}$$

where the symbols are the same as before.

The comparative simplicity in handling procedures for the surface-decrease method is obvious.

III. THE EFFECT OF GRAIN SIZE AND OTHER FACTORS ON THE GROWTH OF ALPHA URANIUM DURING IRRADIATION

Since growth under irradiation is known to be a function of preferred orientation, the specimens used in the initial experiment were given a cursory X-ray examination. Visual inspection of forward reflection Laue patterns indicated that the textures were similar, as expected. In view of the small differences in growth encountered, however, it is now felt that a more exact determination of preferred orientation is necessary for significant results. A complete pole figure study is time-consuming, and consideration has therefore been given to the use of thermal expansion measurements to compare textures. The thermal expansion coefficients of uranium are highly anisotropic, and therefore small changes in texture may be revealed as measurable changes in the coefficients⁽⁵⁾.

A new series of specimens was prepared similar to the first set, but this time high-purity uranium was used as stock. This permitted greater grain growth during the alpha annealing than had occurred with the relatively impure uranium used in the initial experiment. The thermal expansion coefficients of the largest- and smallest-grained specimens were measured on a very sensitive interferometric dilatometer at the Massachusetts Institute of Technology through the cooperation of the Metallurgy Department. Unfortunately the results of the measurements were apparently anomalous, since one specimen expanded on heating while the other contracted. This behavior would indicate a crystallographic rotation of 90° during grain growth, which is highly improbable.

A second set of specimens was prepared and sent to the Massachusetts Institute of Technology and the experiment repeated. This time both specimens expanded, but a large difference in thermal expansion coefficients was again found. Table I lists the results of the measurements.

TABLE I

<u>Specimen</u>	<u>Annealed At 640°C</u>	<u>Thermal Expansion Coefficient</u>
A	15 min.	$11.9 \times 10^{-6}/^{\circ}\text{C}$
B	2 weeks	$4.0 \times 10^{-6}/^{\circ}\text{C}$

In an attempt to make these measurements ourselves, an apparatus was constructed that was patterned after one described by H. Muir⁽⁴⁾. The technique permits a very sensitive measurement of thermal expansion coefficients through the use of SR-4 strain gauges. The gauge is cemented to the specimen and waterproofed. Then the assembly is immersed in a water bath and gauge resistance changes measured as a function of temperature. Unfortunately, it was impossible to obtain reproducible results.

Recently, an interferometric dilatometer was obtained that will permit us to make precise thermal expansion measurements by the standard method. Specimens are now being prepared for use in this dilatometer. When a set of specimens of varying grain size but identical texture is obtained, it is planned to repeat the irradiation experiment.

Although some doubt exists about the accuracy of the irradiation experiment performed, it seems from this and other experiments^(5,6) that irradiation growth is affected by grain size in normal polycrystalline samples to a smaller degree than expected. This suggests that processes occurring within the grains are important in the growth phenomena, and it becomes of interest to determine the relative effectiveness of inter- and intragranular processes. Initially, it is felt this could best be done by the irradiation of highly perfect single crystals of alpha-uranium of different lengths. If only surfaces of the specimens are effective sinks for vacancies and interstitials, the increment of growth should be independent of initial length. On the other hand, if bulk effects are dominant, the growth increment should be proportional to the initial length.

In order to perform this experiment, single crystals of usable size must be obtained, and considerable effort has been expended in the preparation of single crystals of alpha-uranium. Although one crystal had been obtained from the Argonne National Laboratory in the past, it was felt that our demands could best be met by setting up our own equipment. Therefore, a small furnace was constructed based on a design described by E. S. Fisher⁽⁷⁾. An ingot of high-purity uranium similar to that used by Fisher in his experiments was also obtained from Argonne. Thus far, only one usable crystal has been prepared, this being about 1/8" in diameter by 3/16" in length. Efforts are being continued in this work using high-purity uranium made at this Laboratory by a carbon reduction technique.

As an alternative to the use of alpha-uranium single crystals, which are difficult to prepare, much thought has been given to the possibility of irradiating single crystals of bismuth which, like uranium, have a highly anisotropic crystal structure and reportedly high anisotropy of self-diffusion ($1.1 \times 10^{-6} \text{ cm}^2/\text{sec}$ parallel to the C axis at 250°C , and 4.9×10^{-12} perpendicular to the C axis at the same temperature⁽⁸⁾).

To test the feasibility of such an experiment, an attempt was made

to compute the number of vacancies that would be created by neutron bombardment of bismuth as compared with natural uranium. Several workers have published theoretical treatments dealing with this type of calculation^(9, 10, 11), but there is considerable question as to their accuracy. According to Seitz⁽⁹⁾, each uranium atom is displaced about 18 times during 10% U²³⁵ burnup due to collision with fission fragments. However, recent considerations suggest that many of the imperfections are almost immediately eliminated by recombination^(11,14). Brooks⁽¹²⁾ has calculated for zirconium that each atom would be displaced about two times by fast neutron bombardment during 60 days in the Materials Testing Reactor. If the calculations of Seitz and Brooks are correct, and if the number of bismuth displacements are comparable to those in zirconium, it is conceivable that enough atomic displacements may occur in bismuth during irradiation in the MTR to cause an observable rate of growth after a maximum period of the order of 540 days and perhaps much less. In addition, it should be possible to prepare single crystals and specimens of varying grain size with relative ease. Further, if a small amount of U²³⁵ can be dissolved in solid bismuth, growth should be enhanced. A small ingot was prepared containing 0.5 w/o natural uranium. Metallographic examination did not reveal any evidence of a precipitate, suggesting that uranium was retained in solution, or in a highly dispersed form in the solid. If it can be ascertained that the uranium is uniformly distributed throughout the bismuth, several specimens will be prepared for irradiation.

IV. FUTURE WORK

1. Work will be continued on measurement of the self-diffusion coefficients of uranium. The first diffusion couple will be analyzed with the aid of nuclear tracking emulsions only. Although the absolute magnitude of the diffusion coefficients determined in this way may be questionable, any anisotropy in diffusion should be revealed. When all the details involved in the application of a standard sectioning technique to these couples have been resolved, the couples will be analyzed again to check the results obtained with the emulsions.
2. Efforts will be continued to grow single crystals of alpha-uranium by the grain-coarsening technique. Experimentation will continue to be guided by the work of E. G. Fisher⁽⁷⁾.
3. Irradiation tests will be made to clarify the mechanism of dimensional instability of alpha-uranium. The first will be a repetition of the early experiment to determine the effect of grain size on growth rate, but using polycrystals of more precisely controlled texture. Secondly, alpha-uranium single crystals of varying size will be irradiated to ascertain the relative importance of surface vs. volume effects upon growth. Finally, it is planned to irradiate single crystals of bismuth, or bismuth with a small quantity of U²³⁵ in solution, to observe radiation growth in another anisotropic metal.

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