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DIFFUSION IN URANIUM, ITS ALLOYS,
AND COMPOUNDS

by

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FOREWORD

This monograph on "Diffusion in Uranium, Its Alloys, and Compounds" is the third in the monograph series on The Physical Metallurgy of Uranium; the first two dealt with the thermal and electrical conductivity of uranium, respectively. The bibliography of the present monograph includes references up to 1 September 1960; later references will be included in future revisions of the monograph.

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I. Introduction

Several processes of technical importance in the nuclear field, such as the bonding of fuel materials to cladding, or the release of fission gases from fuel elements, involve solid-state diffusion. A large number of laboratory measurements of diffusion rates relating to such processes have been carried out, and, as usual, phenomena of basic scientific interest have been uncovered in their course.

This paper reviews these laboratory diffusion studies. It attempts to evaluate them in the light of present-day diffusion theory, to decide which set of data is to be preferred in the case of conflict, and to indicate what fields of study need further work.

The fundamentals of diffusion in solids have been covered in several recent reviews.⁽¹⁻⁵⁾ Only a brief review of some aspects is given here. Fundamental to the understanding of diffusion problems is a knowledge of the mathematical solutions of the diffusion equation.^(6,7) The diffusion equation, Fick's second law, is

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) \quad , \quad (1)$$

where C is the concentration of the diffusing element, t the time of diffusion, and D the diffusion coefficient. For certain initial and boundary conditions, this equation can be solved, giving

$$C = C(D, x, y, z, t) \quad , \quad (2)$$

where x , y , and z are space coordinates.

To calculate D , one sets up a diffusion experiment, the physical conditions of which correspond to a set of initial and boundary conditions and to the implicit and explicit assumptions upon which the diffusion equation is based. One then measures $C(D, x, y, z, t)$ experimentally, plugs these experimental values into the mathematical solution of the diffusion equation for the initial and boundary conditions in question, and obtains D .

The diffusion work considered in this review can be divided into three major classes according to the type of sample used. These are:

- i. Diffusion in a single-phase solid. The quantity of interest here is the diffusion coefficient, which is usually obtained from the variation of the concentration of the diffusant with distance in the sample (Section II).

- ii. Diffusion in a multiphase solid. The quantities of interest here are the rate constants for the growth of the intermetallic layers (Section III).
- iii. Diffusion of a gas in a solid. The quantity of interest is again the diffusion coefficient; in this case it is obtained from measuring the amount of gas that diffuses out of the solid as a function of time (Sections IV and V).

The following caveats should be heeded for all three cases.

- i. The assumptions implicit in Fick's law must be fulfilled. Diffusion must take place in a homogenous medium, i.e., there should be no paths of easy diffusion, such as grain boundaries, phase boundaries, cracks, or microcracks. Changes in cross section due to porosity or oxide layers at interfaces must be avoided. The presence of some of these can be detected if the variation of concentration with distance or with time, does not follow the laws of diffusion, although this is not always the case. Such deviations are certainly not detected by a method in which only two measurements of concentration, either as a function of distance or of time, are made, such as the absorption method (Section II, B, 3). The process being measured must be controlled by diffusion, not by reactions at phase boundaries; this also can be shown by a plot of C as a function of distance or time that agrees with the proper solution of the diffusion equation.
- ii. The boundary and initial conditions also have to be fulfilled. For instance, in the tracer-thin layer geometry, the thin layer has to be thin ($\leq 0.1 \sqrt{Dt}$); or, when gas is diffused from a solid into a vacuum, the assumption that the concentration of gas at the solid surface drops to zero as soon as the experiment starts should be checked experimentally [cf. discussion of the same problem for liquids⁽⁸⁾].

II. Diffusion in Single-phase Uranium Alloys

A. Mathematical Treatment

Unidimensional diffusion in a one-phase system obeys Fick's

Law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (3)$$

The diffusion coefficient in a homogenous alloy is independent of concentration:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) \quad . \quad (4)$$

The solution of this equation for the semi-infinite couple with a thin layer of tracer (Fig. 1) is (see Ref. 6, p. 11)

$$C = \frac{q}{\sqrt{\pi Dt}} \exp \left(-\frac{x^2}{4Dt} \right) \quad , \quad (5)$$

where q is the amount of tracer deposited initially, and x is the distance from the initial interface. The value of D is determined from a plot of

$\log C$ vs. x^2 , which should be a straight line. If it is not, some other process besides volume diffusion is present. Diffusion predominantly along grain boundaries is indicated by a straight line plot of $\log C$ vs. x .⁽⁹⁾ The use of this geometry is a sensitive method for detecting grain boundary diffusion.

Fig. 1. Schematic sketch of "semi-infinite" diffusion couple.

The solution for the infinite couple (see Fig. 2), with original interface at $x = 0$ (see Ref. 6, p. 12) is

$$C = \frac{C_0}{2} \left[1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right] \quad , \quad (6)$$

where erf means the error function of Gauss:

$$\operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt \quad .$$

If a chemical concentration gradient exists in the sample, D is concentration dependent, and the Matano solution⁽¹⁰⁾

$$D = \frac{1}{2t} \frac{dx}{dC} \int_C^{C_0} x dC \quad (7)$$

has to be used. The applicability of this solution is discussed in several articles.⁽¹¹⁻¹³⁾

B. Experimental Techniques

Experimental techniques for diffusion measurements are described in the standard texts on diffusion^(1,2) and in a recent review by Tomizuka.⁽¹⁴⁾ This section treats problems peculiar to diffusion studies in uranium, which are not covered in the above reviews.

1. Specimen preparation

The preparation of diffusion couples containing uranium is made difficult by the reactivity of uranium, particularly with oxygen and nitrogen. Uranium that has been exposed to air forms a film of oxide on the surface, which must be removed or broken up if diffusion is to take place. Inadequate removal of this film results in either a decreased cross-sectional area or in a rate-limiting reaction at the interface. These conditions must especially be avoided in cladding studies, where one is interested in maximum penetration.

Fig. 2

Schematic sketch of "infinite" diffusion couple.

In the case of the infinite couple (see Fig. 2) (infinite here means $\gg \sqrt{Dt}$), which is used in chemical diffusion and layer-growth studies, the oxide film can be broken up by pressure welding,^(15, 16) hot rolling, squeezing,⁽¹⁷⁾ or swaging⁽¹⁸⁾ the two components together. In the Saclay technique of pressure welding,⁽¹⁵⁾ the uranium and other metal are polished mechanically and electrolytically, placed in a stainless steel clamp, and squeezed together under a pressure of 6,000 kg/cm² in a hydraulic press. The clamp is locked in the closed position, removed from the press, placed

in a vacuum better than 10^{-5} mm Hg, and heated to 450-600°C, depending on the diffusion temperature, for two hours. The sample is removed from the clamp for the diffusion anneal. Couples of U-Cu, U-Al, and U-Ni can be prepared by heating to 400°C for $\frac{1}{2}$ hour under 250 kg/cm².⁽¹⁹⁾

In the picture frame technique,⁽¹⁷⁾ the polished metals are placed into a hollow mild steel square (see Fig. 3) and compressed under 7500 kg/cm², deforming the steel holder. The whole assembly is sealed off in vacuum for the anneal.

Fig. 3. "Picture frame" for making diffusion couples.⁽¹⁷⁾

Coating uranium and aluminum samples with water- and oxygen-free paraffin just before pressure welding is found to inhibit oxide formation at the interface.⁽²⁰⁾ The use of paraffin is not recommended for U-Zr couples because of the possibility of forming an impervious ZrC layer such as is formed in the interdiffusion of zirconium and uranium containing 300 ppm carbon.⁽²¹⁾

A good diffusion bond can supposedly be made by sputtering both halves of the diffusion couple and subsequent pressure welding without exposing the samples to air between the two steps.⁽²²⁾ Diffusion couples can also be made by hot rolling the components together, in the manner described for cladding fuel plates.⁽²³⁾

The bonding of U to U appears to be more difficult than the bonding of U to other metals. For instance, although U-Nb diffusion couples can be made successfully by the picture frame technique,⁽²⁴⁾ U-U couples cannot.⁽²⁵⁾ Pressure welding can be used⁽²⁶⁾ keeping in mind that high pressures and excellent vacuums are required. A U-U bond can also be obtained by hydriding the two pieces of U at 250-300°C, heating to 600°C in vacuum to decompose the hydride, and then pressure welding.⁽²⁷⁾ It should be emphasized that, generally speaking, vacuums between 10^{-6} and 10^{-5} mm Hg, at least, are desirable in work with uranium.

Cylindrical samples in which stainless steel tubing is swaged around a core can also be used in layer-growth studies (see Fig. 4).⁽¹⁸⁾ Since the

Fig. 4

Cylindrical diffusion sample for in-pile diffusion studies.⁽¹⁸⁾

U is completely covered in such a sample, the sample does not have to be encapsulated, and can be heated by passing an electric current through it. If a heating coil is placed at one end, and thermocouples are spot welded at several places along the length of the sample (see Fig. 5), isochronal layer growth can be measured at different temperatures. Such samples are suitable for in-pile studies; the sample shown in Fig. 5 fits into a standard CP-5 research reactor irradiation can (3.1 cm ID, 13.5 cm long). It is important that the sample be swaged properly; otherwise, diffusion across the interface is uneven.

The diffusion of volatile and slightly soluble elements (e.g., Sr or La) in gamma uranium can be measured using a diffusion couple made up of pure uranium and a two-phase alloy of U and the element in question.^(28, 29) The couple is diffused in vacuum, and the diffusion coefficient is calculated from the widths of the zones depleted in precipitate at the vacuum-two-phase alloy and the uranium-two-phase alloy boundaries (ξ_E and ξ_D , respectively, as shown in Fig. 6). A similar method is used to measure the diffusion of nonvolatile, slightly soluble elements such as Ni, Cr, Fe or Si⁽³⁰⁾ in gamma U. A couple is made up by pressure welding pure U and a two-phase alloy, and is annealed at a temperature where the two-phase alloy is in the gamma + liquid zone. The diffusion coefficient is calculated from the known solubility limits and the width of solidified alloy depleted in precipitate (ξ in Fig. 7).

Fig. 5. Diffusion sample for m-pile studies, with thermocouples and leads. (18)

Fig. 6. Diffusion couple for studying the diffusion of volatile elements in gamma uranium. (28, 29)

Fig. 7. Diffusion couple for studying the diffusion of slightly soluble elements in gamma uranium. (30)

The last two methods, although much more rapid than the tracer-sectioning method, are not as clearcut. The assumption that the concentration of volatile element at the vacuum-diffusion couple interface is zero for all $t > 0$ should be justified experimentally. In the method involving the liquid phase, it should be ascertained that the impurity diffuses into the gamma U, and not into the liquid. It is also not clear what is in contact with the pure U, the solid or the liquid.

Methods involving mechanical deformation cannot be used in studies on single crystals. The sample geometry commonly used on them, and in many studies on polycrystals as well, is that of the infinitesimally thin ($\ll \sqrt{Dt}$) layer on the semi-infinite sample (see Fig. 1). The radioactive tracer technique is almost always used with this geometry, since it is the only method sensitive enough to pick up the small concentrations of indiffused material that result from this method [e.g., in studies of self-diffusion in gamma U, use of the doubly infinite couple (26) and U enriched to 20% U^{235} gives a concentration range 20 - 0.7% U^{235} . In the thin layer geometry with 93% U^{235} as the tracer, the maximum U^{235} concentration

found is ca. 1%.⁽³¹⁾] If the layer is thin enough, the entire alloy can be considered homogenous, and nonequilibrium effects due to concentration gradients can be neglected.⁽¹⁴⁾ The layer should therefore be made as thin as is compatible with good counting statistics, remembering that, *ceteris paribus*, the number of counts from each section is proportional to the layer thickness as long as this is $\ll Dt$.

Thin layers can be deposited in three ways: evaporation,^(32,33) cathodic sputtering,^(32,34) and roll bonding or pressure welding of a thin foil.⁽³⁵⁾ The last, of course, is not suitable for single crystals. In the first two methods, the oxide film on the sample is first cleaned off by cathodic sputtering, after which the tracer is sputtered or evaporated onto the sample surface. The sample is not removed from the vacuum chamber until after the layer is deposited. Deposition of the isotope on an unsputtered uranium surface, although apparently successful once,⁽³³⁾ is not recommended by this reviewer.

The thin-layer-sectioning method is also applicable to the study of the diffusion of metallic elements in nonmetallic materials, e.g., the diffusion of U in UO_2 .⁽³⁶⁾ If the material in question is brittle, it has to be sectioned by grinding,⁽³⁷⁾ or by an electrochemical method. The various absorption methods of analysis are also applicable to nonmetallic materials.

2. Annealing

Uranium-containing diffusion couples must be protected from oxidation during the diffusion anneal. This is done by enclosing the U in an oxidation-resistant medium such as a stainless steel tube,⁽¹⁸⁾ or a bath of molten aluminum,⁽³⁸⁾ lead, or salt, or by sealing the couple off in Vycor or quartz under vacuum or in a noble gas atmosphere. The reviewer prefers a vacuum well under 10^{-5} mm Hg. If the annealing temperature is above 600°C , the sample should be wrapped in Ta⁽³⁹⁾ or Mo⁽⁴⁰⁾ foil to prevent reaction with the quartz. The use of a getter is also recommended.

Furnaces and furnace controls for encapsulated samples are described in Ref. 14. Nevertheless, it does not hurt to put in a reminder that, since diffusion coefficients vary exponentially with temperature, temperatures must be controlled and measured carefully.

A schematic of the control circuit for the in-pile sample mentioned above is shown in Fig. 8.⁽¹⁸⁾ The currents are set manually by variable transformers 1 and 4, and the temperatures are kept constant by motor-driven variable transformers 3 and 5, which are actuated by proportionating controllers. The motor drive of variable transformer 2 is operated by limit switches at the ends of the voltage range of No. 3.

Fig. 8. Schematic diagram of temperature control for in-pile diffusion couple. (18)

stant, the problem is to determine $C(x)$, the concentration-penetration curve.

The classical method for this is to cut the sample into slices perpendicular to the diffusion direction and to analyze them chemically or by counting. Details of the technique are given in Ref. 14. Other designs of precision chucks for aligning the diffusion sample exactly are given in Ref. 26 and 41.

The concentration-penetration curve in a chemical diffusion couple can be determined without sectioning by the use of an electron microanalyzer, or probe. (42-44) This apparatus fires a beam of electrons, ca. 1 micron² in cross section, at a definite spot on the sample and measures the intensity of the characteristic X-ray of the element in question. This is proportional to the concentration. To determine $C(x)$, the sample is sectioned parallel to the diffusion direction and polished metallographically, taking care to remove flowed metal. The electron beam is then moved along the sample, and the concentrations are measured. This method is both fast and accurate.

Any property that varies reproducibly with concentration can be used for analysis. Microhardness is often used. (45, 46) The sample is sectioned parallel to the diffusion direction, and a

The resetting action is needed because the range of transformer No. 3 is only a few volts. Using this control, the temperatures of specimens containing normal U were kept constant to $\pm 3^\circ\text{C}$ over 4 days in the worst case; the temperature of specimens containing 93% U^{235} dropped 10-15°C when the pile was scrambled.

3. Analysis

The interdiffusion of two metals is commonly studied by means of unidirectional diffusion, i.e., $C = C(x, t)$, where x is the coordinate in the diffusion direction. The value of D is determined by fitting the experimentally determined $C(x, t)$ to the appropriate solution of the diffusion equation. Since for a given sample t is con-

microhardness traverse is made. Concentrations can then be calculated from a calibration curve made with results from alloys of known composition. Penetration curves obtained by this method are in good agreement with ones obtained with a probe.⁽¹⁵⁾

The concentration $C(x)$ for a radioactive isotope can be determined by the sectioning and counting method, the absorption or surface-counting method,^(14,47) or by autoradiography.⁽⁴⁸⁾ The last two methods are not as reliable as the first.⁽¹⁴⁾ A comparison of the surface-counting method with the sectioning method shows the latter to be more reproducible.⁽⁴⁹⁾ Autoradiographic results are also in general not as reliable as the ones obtained by the sectioning technique.⁽¹⁴⁾ For instance, autoradiographically determined self-diffusion coefficients for gamma uranium⁽³³⁾ do not agree with the three sets of data measured by the sectioning method, which are in excellent agreement among themselves. On the other hand, the use of autoradiography and alpha-track counting (instead of measurement of optical density with a densitometer) has produced penetration curves for U-Zr couples in good agreement with ones obtained with a probe.⁽⁵⁰⁾ Here, again, calibration curves of track number vs. uranium concentration have to be constructed.⁽⁴⁰⁾

Uranium concentrations can be measured by alpha counting, autoradiography, and alpha-track counting, or by fission counting.^(51,52) The last can also be used to measure U^{235} or U^{233} concentrations in self-diffusion experiments. The distribution of U^{235} in a sample can be measured qualitatively by alpha-track autoradiography or by in-pile autoradiography, using a plate that is sensitive to fission tracks only,⁽⁵²⁾ such as Ilford K-2.

C. Diffusion in Pure Uranium

1. Alpha Phase

Since alpha uranium is orthorhombic, self-diffusion in it may be highly anisotropic. The magnitude of the anisotropy is of interest from a fundamental point of view as well as a proof or disproof of the diffusion theory of the growth of uranium under pile irradiation.⁽⁵³⁾

Measurements of self-diffusion in single crystals of alpha uranium made using a surface-counting technique,⁽⁵⁴⁾ gave

$$D_{[100]} = 1.8 \times 10^{-14} \text{ cm}^2/\text{sec}$$

$$D_{[010]} = 0.72 \times 10^{-14} \text{ cm}^2/\text{sec}$$

$$D_{[001]} = 0.66 \times 10^{-14} \text{ cm}^2/\text{sec}$$

at 640°C. Since these values may be in error by at least a factor of two, it

is hard to say how anisotropic diffusion in alpha uranium really is, although the absence of significant anisotropy is confirmed by the autoradiographic work of Adda. (55) Further, the surface-counting technique gives no information as to whether diffusion takes place predominantly in the grain volume or along imperfections; it is possible that volume diffusion is highly anisotropic, but is completely masked by isotropic diffusion along imperfections. It would be desirable to obtain more accurate data on self-diffusion in α -uranium single crystals, preferably by the sectioning method. Such small values of the diffusion coefficients require very precise sectioning methods, such as grinding or an electrochemical method; the experimental difficulties are great.

From an engineering standpoint, it can be said that diffusion in alpha uranium is quite slow. Other data (55-57) on self-diffusion and the diffusion of gold in alpha-uranium polycrystals at temperatures near the α - β transformation yield values of D from 10^{-14} to 10^{-12} cm^2/sec ; in particular, $10^{-12} \text{ cm}^2/\text{sec} > D_{650^\circ\text{C}} > 7 \times 10^{-13} \text{ cm}^2/\text{sec}$. (55)

2. Beta Phase

Self-diffusion in the beta phase is also slow, the values of D ranging from 2×10^{-12} to 3×10^{-11} cm^2/sec (see Fig. 9). (52, 58)

Fig. 9

Arrhenius plot for self-diffusion in gamma and beta uranium. (26, 31, 33, 52, 58)

Since there is some diffusion along grain boundaries, and diffusion in the grains appears to be anisotropic, it is difficult to assign any fundamental importance to these values of D , outside of pointing out that the great change in D on going from the gamma to the beta phase is undoubtedly due to the covalent bonding in the latter. (58)

3. Gamma Phase

a. Self-diffusion: Three sets of data, (26, 31, 33) in excellent agreement among themselves, indicate that volume diffusion predominates in self-diffusion in gamma uranium, and that self-diffusion in the gamma phase is very fast (see Fig. 9). The diffusion parameters $D_0 = 1.12 \times 10^{-3} \text{ cm}^2/\text{sec}$, and $Q = 26,500 \text{ cal/mol}$ (obtained from a least-squares fit of all three sets of data) are different enough from those expected from theoretical analyses based on the vacancy mechanism (59,60) as to suggest a different mechanism for self-diffusion in gamma uranium.

It has been suggested (31,61) that self-diffusion in γ uranium proceeds by a ring mechanism (62). The contradiction between this hypothesis and the Kirkendall effect found in chemical diffusion in γ -uranium alloy systems (15, 63, 64) is hard to eliminate, however, it is possible that the excess nonequilibrium vacancies introduced by the strains, high concentration gradient, etc., found in chemical diffusion couples, completely swamp the ring mechanism. The possibility of the interstitialcy mechanism can also not be eliminated; it is compatible with both the Kirkendall effect and the observed diffusion parameters, and the only evidence against is found in the calculations of Huntington and Seitz on copper. (65) On the other hand, the observed diffusion parameters would not be in disagreement with the theory based on the vacancy mechanism if the elastic constants of γ uranium and their temperature dependence would be anomalously low, in the neighborhood of 10^{10} dyn/cm^2 at $T = 0^\circ\text{K}$. There are unfortunately no data available on this point.

A critical experiment would be preferable to the above speculation. Two appear to be possible: the study of the effect of pressure on self-diffusion in γ uranium, and the measurement of the activation energy for the sintering of γ uranium. The first gives a volume of activation (66) which is different for each of the three mechanisms considered. The second experiment can distinguish between ring diffusion and a defect mechanism (if sintering takes place by volume diffusion), since sintering involves mass flow. Preliminary studies of sintering have been unsuccessful because of oxidation of the uranium. (67) Unfortunately, the phase transformations in uranium make quenching experiments and simultaneous dilatometry and lattice-parameter measurements impossible.

The above discussion points to one of the largest gaps in our understanding of diffusion in metals: the scarcity of fundamental diffusion data and supporting data on body-centered cubic (bcc) transition metals

b. Impurity diffusion: Data on the diffusion of several impurities in gamma uranium is shown in Table I. The diffusion parameters do not correlate with either the atomic radius⁽⁶⁹⁾ or the valence⁽⁷⁰⁾ of the diffusing atom. The only correlation found is a monotonic decrease of D with the Goldschmidt radius of the solute (see Fig. 10).⁽³⁰⁾ The values for self-diffusion and the diffusion of gold do not fit this correlation.

Table I

THE DIFFUSION OF IMPURITIES IN GAMMA URANIUM

Element	Fe	Cr	Si	Ni	Sr	La	Au	U
D_0 , cm ² /sec	1.3	0.7	20	2.5×10^2	2.38	1.17×10^2	4.86×10^{-3}	1.12×10^{-3}
Q , kcal/mol	32	34	45	46	47	55.7	30.4	26.5
Method	Two-phase method (sec. II-B-1)				Two-phase method (sec. II-B-1)		Tracer and sectioning	
Reference	30				28, 29		68	26, 31, 33

Fig. 10. Plot of D vs. Goldschmidt radius for diffusion of impurities in gamma uranium. (26, 30, 68)

The values of D for Fe, Cr, Si, and Ni are in every case higher by at least an order of magnitude than the values of D for self-diffusion or for the diffusion of gold. There does not seem to be any obvious reason for this difference, and the reviewer is inclined to withhold further discussion until the results with Fe, Cr, Si, Ni, Sr or La are duplicated by the tracer-sectioning technique (cf. Ref. 71).

D. Diffusion in Uranium Alloys

1. Chemical Diffusion in U-Mo, U-Ti and U-Zr Alloys

Chemical diffusion has been studied in the one-phase regions of the U-Zr,^(15,40,72) U-Ti,⁽⁶⁴⁾ and U-Mo⁽⁶³⁾ systems. The several sets of data on diffusion in the U-Zr system are in fair agreement.

The activation energy, D_0 , and D are strongly concentration dependent in all of these systems (see Figs. 11 - 13).

Fig. 11. Concentration dependence of the activation energy Q for chemical diffusion in one-phase gamma-uranium alloys. (15, 63, 64)

Fig. 12. Concentration dependence of D_0 for chemical diffusion in one-phase gamma-uranium alloys. (15, 63, 64)

Fig. 13. Concentration dependence of D at 1000°C for chemical diffusion in one-phase gamma-uranium alloys. (15, 63, 64)

The value of D increases strongly with the concentration of uranium at high uranium concentrations. There is also a marked Kirkendall effect in these systems, with the markers moving toward the uranium, and the formation of porosity in the uranium. This indicates that chemical diffusion in γ uranium takes place by a defect mechanism.

2. Kirkendall Effect in the U-Zr System

In the experiments with U-Zr, U-Mo, and U-Ti systems, the markers always move toward the uranium, indicating that the intrinsic diffusion coefficient of uranium at the marker composition is greater than that of its partner. However, in a careful study of marker movement as a function of concentration in U-Zr alloys, using markers in the uranium and in the zirconium, as well as at the interface, Adda, Mairy and Andreu⁽³⁵⁾ found that the direction of marker movement reverses in the region around 5 at% U, indicating that in alloys of this composition, the intrinsic diffusion coefficient of zirconium is greater than that of uranium. Experiments on the diffusion of U and Zr tracers in homogeneous alloys of this composition show that the ratio D_U^*/D_{Zr}^* is less than one, and equal to D_U/D_{Zr} . The variation of D_U^*/D_{Zr}^* with concentration is as yet unexplained.

Diffusion in γ -uranium alloys is superficially similar to the much more thoroughly studied diffusion in α -Cu alloys, although there are some important differences. The diffusion of uranium and, say, zirconium, tracers should now be studied as a function of concentration in homogeneous U-Zr alloys, and the thermodynamic properties of these alloys should be determined. Such studies would be more profitable than further studies of chemical diffusion in one-phase γ -uranium systems.

III. Diffusion in Multiphase Uranium Alloys

In a diffusion couple made up of metals that are not completely mutually soluble at the diffusion temperature, there is more than one phase present in the diffusion zone. Such systems are of great interest to the nuclear metallurgist, since many of the important uranium-cladding alloy systems contain intermetallic compounds, and chemical diffusion in many such systems consists essentially of the growth of the intermetallic compounds, since the terminal solid solubilities are small. The diffusion problems in such multiphase systems are: which phases appear, how fast they grow, and what is the concentration distribution.

The experimental techniques for preparing and annealing multiphase diffusion couples are given in Sections II, B, 1 and 2. The analysis consists of sectioning the couple parallel to the direction of diffusion and measuring the thickness of the intermetallic compound layer microscopically. The concentration gradients in the different phases, and the compositions at the phase boundaries, can be measured with a probe,^(24,73) or by autoradiography and track counting.⁽⁴⁰⁾ The study of multiphase regions with a probe is an ingenious way to determine the phase diagram.⁽⁷⁴⁾

A. Kinetics of Layer Growth

1. Qualitative Considerations⁽⁷⁵⁾

Considerations of thermodynamic equilibrium indicate that, in a two-component system, the diffusion zone should be made up of a series of single-phase layers, one for each phase stable at the diffusion temperature. Of course, a phase may decompose into two phases on cooling. The compositions at the boundaries between the phases should be the limiting compositions of the phases at the diffusion temperature (see Fig. 14). In a three-component system, two-phase layers can also appear,^(76,77) and there is no way of predicting which phases will be present. The discussion below applies to two-component systems.

Notwithstanding the thermodynamics, some phases are occasionally absent from the diffusion zone.^(78,79) This is presumed to be due to a difficulty in nucleation, or to a very low growth rate, the latter possibly due to a very low diffusion coefficient (high melting point) in the phase.⁽⁷⁵⁾ The absence of a phase can also be caused by particular combinations of the limiting concentrations and the diffusion coefficients.^(79a) It is also possible that the phase does form, but is too thin to be detected. On the other hand, diffusion studies may indicate the presence of a phase not discovered in conventional phase-diagram work.⁽²⁴⁾

Fig. 14

Relation of the phase diagram to the multiphase diffusion couple:

- a. Phase diagram;
- b. Concentration distribution in multiphase diffusion couple after diffusion.

Qualitative rules of thumb for layer growth are given by Seith (see Ref. 2, p. 162). He finds that a layer will grow more rapidly:

1. the more its diffusion coefficient exceeds that of the neighboring phase,
2. the narrower the neighboring two-phase region, and
3. the steeper the concentration gradient in the phase (the wider its homogeneity range).

Recent experimental data⁽¹⁹⁾ do not verify these rules.

2. Quantitative Treatment^(6,75,80-83)

a. The power law of layer growth: The movement of a phase boundary, which is a surface of fixed concentration, is proportional to the square root of the time if volume diffusion is the rate-controlling step.^(11,82) In other words, $x^2 = Kt$, where x is the distance the boundary moved (or the layer grew) in time t , and K is a temperature-dependent rate constant. On the basis of their experimental results, Lustman and Mehl⁽⁷⁸⁾ suggest a general parabolic law, $x^n = Kt$, where both n and K can

be temperature dependent. Evidently, $1 \leq n < 2$ if an interface reaction is rate controlling, or diffusion through an oxide film hinders layer formation, and $2 < n < 4$ if diffusion along grain boundaries contributes significantly.⁽⁷⁵⁾ Experimentally, n is usually found to be close to 2; whether or not it is equal to 2 should be decided from a log log plot of x vs. t rather than a plot of x^2 vs. t .⁽⁷⁸⁾

If $n = 2$, the dimensions of K are $(\text{length})^2/\text{time}$, that is, the same as a diffusion coefficient. One can thus write $x^2 = K'Dt$, and, using the well-known expression for the temperature dependence of D ,

$$x^2/t = K'D_0 \exp(-Q/RT) \quad , \quad (8)$$

where Q is the activation energy for diffusion and the other terms have their usual meaning. (In this review, activation energies for layer formation will always be given for x^2/t .) For $n \neq 2$, but independent of t , an activation energy can again be calculated as above. If n is temperature dependent, a complex analysis has to be used. In one such case taking the temperature dependence of n into account changes the activation energy from 11.06 to 20.7 kcal/mol.⁽⁸⁴⁾

b. Parabolic layer growth - 2 phases: Mathematical treatments of this case are given in Ref. 6, 81, 83, and 84. In these treatments the diffusion coefficient is assumed to be independent of concentration. Since this is generally a poor assumption, it is better to calculate the concentration-dependent diffusion coefficient by the Matano method,^(10,13) which should be valid at some distance from the phase boundary.^(85,86)

c. Parabolic layer growth - 3 phases: The case of one intermetallic compound between two terminal solid solutions is treated in Refs. 75 and 81. If solid solubilities in the terminal solid solutions can be neglected (and this is the case in many uranium systems), equating the growth of the layer, dx , in time dt with the diffusion flux across the compound, and neglecting volume changes, Kirkendall effect, and the concentration dependence of D , one obtains

$$x^2/t = 2D\Delta C/C \quad , \quad (9)$$

where x is the layer thickness, t the time of diffusion, ΔC the concentration difference across the compound (in mole fractions), C the average composition of the compound, and D the chemical diffusion coefficient in the compound. A similar derivation that avoids the often unknown concentration gradient across the compound, and has a sounder base in the thermodynamics of diffusion, is given for the U-Be system by Baird.⁽⁷⁵⁾ Noting that only Be diffuses,⁽¹⁷⁾ he obtains

$$x^2/t = 2D(-\Delta G/RT) \quad , \quad (10)$$

where ΔG is the free energy of formation of one mole of the compound, and D is the diffusion coefficient of Be in the compound.

The formulas of Vasileff and Smoluchowski are rather more complicated. Applying them to a case analogous to the above, Castleman obtained⁽⁸⁷⁾

$$\frac{x}{2\sqrt{Dt}} \exp\left(\frac{x^2}{4Dt}\right) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{(C_1 - C_2)}{2\sqrt{\pi}C_2} \quad (11)$$

where C_1 and C_2 are the concentrations at the ends of the layer. Equations 9 and 11 are in approximate agreement for $x/\sqrt{Dt} \approx \frac{1}{2}$. For $x/\sqrt{Dt} = 0.05$ or 3, they differ by a factor of 20. Both equations contain assumptions usually not fulfilled in diffusion couples, such as constant cross section, concentration-independent diffusion coefficient, and no change of volume.

3. Concentration Distribution in Multiphase Diffusion Couples

Solutions for the diffusion equation, using restrictive assumptions, are given in Ref. 81. Until recently, there were very few determinations of the concentration distribution in intermetallic compound layers, perhaps due to the experimental difficulties. The development of the electron microprobe (Section II, B, 3) has furnished a rapid and accurate method of such analysis, and application of the probe to some U systems has already lead to very interesting results. The investigation of phase equilibria and growth kinetics by this method is another interesting field in need of cultivation.

The diffusion coefficients for intermetallic compounds can be calculated by fitting such concentration-penetration data to the formulae of Vasileff and Smoluchowski. These formulae seem to be most useful for compounds with fairly small ranges of homogeneity, such as UCu_5 ; the Matano solution is preferred for intermediate solid solutions such as the γ phase in the U-Zr system. Using Eqs. (9) and (11), one obtains $D = 4 \times 10^{-9}$ and $4 \times 10^{-7} \text{ cm}^2/\text{sec}$ for UCu_5 at 700°C .

B. Systems with Slight Solid Solubility (Line Compounds)

A preliminary study of layer formation in a large number of uranium alloy systems was made by Kittel.⁽¹⁷⁾ More complete studies have been made of all the systems he worked on, except U-Fe, for which he gives

$$x^{2.6} = 6 \times 10^{-17} t \quad (12)$$

at 600°C . Here x is in cm and t in seconds. Other systems are discussed in greater detail below.

1. U-Be

One intermetallic layer, in agreement with the phase diagram,⁽⁸⁸⁾ has been observed in the U-Be system.^(17,75) The layer grows only on the uranium side of the interface, and does not become thicker than 0.0015 cm, due to severe cracking in the Be near the interface, according to Kittel. Baird calculates $10^{-13} < D < 10^{-12}$ cm²/sec at 600°C, assuming that volume diffusion predominates. However, he believes that grain boundary diffusion will predominate because of the comparatively low diffusion temperature ($0.43 T_m$) and small grain size of the compound (10^{-4} cm), and that this may cause the very slow growth at long times observed by Kittel, since predominant grain boundary diffusion implies $n = 4$. This disagrees with Kittel's finding that $n = 2$, which, however, is based on only two points. The data are too sparse for further comment.

2. U-Cu

Interdiffusion of uranium and copper^(19,89,90) results in the formation of one intermetallic compound, in agreement with the phase diagram.⁽⁹¹⁾ The existence of the second phase suggested by Bear and LeClaire⁽⁸⁹⁾ is uncertain. The results are shown in Fig. 15.

Fig. 15

Arrhenius plot for the thickness of the layer formed in the interdiffusion of uranium and copper for 2 and 4 days.

The layer thicknesses for equivalent treatments are in excellent agreement at low temperatures and times. The divergence at higher temperatures and times may be due to the fact that Weil measured maximum thickness and Bear and LeClaire measured average thickness; further, the latter report difficulty with measurements on the uranium side due to oxidation. The difference in activation energy (Bear and LeClaire: 21.6 kcal/mol; Weil: 23.5 kcal/mol) is a direct result of this discrepancy. The value of n [2.34⁽⁸⁹⁾, 2.5⁽¹⁹⁾] is somewhat greater than 2.

Bear and LeClaire find that 62% of the growth takes place into the copper, indicating that uranium diffuses faster in the compound than does copper.

The microprobe measurements of Adda *et al.* have shown that the composition of UCu_5 changes almost linearly across the compound, from $\text{UCu}_{4.70}$ to $\text{UCu}_{5.25}$, if there is no pressure on the diffusion couple (see Fig. 16).

Fig. 16

Schematic plots of concentration distribution in UCu_5 (after Ref. 19).

The application of pressure changes the penetration curve as shown in Fig. 16, i.e., it decreases its homogeneity range. Although according to Seith this should decrease the rate of layer growth, Adda *et al.* find the opposite; the growth rate is increased slightly by pressure (Section III, C, 8).

The lattice parameter of the U-Cu compound is a minimum at the stoichiometric composition, and rises linearly in both directions from there.⁽¹⁹⁾ Adda *et al.* consider that this is due to the dissolution of excess uranium or copper atoms in the compound. This may also explain the two hardness peaks in this compound found by Bear and LeClaire; on the other hand, the concentration curves of Adda *et al.* for zero applied pressure and 1000 kg/cm^2 each have one point on the high copper side that could represent a second phase. There are faint indications of a second phase in the micrographs of Adda *et al.*, but none in Weil's.

3. U-Al

a. General remarks: Since aluminum is the most commonly used cladding material for fuel elements in water-cooled reactors, the interdiffusion of uranium and aluminum is of great technical importance. The first mention of the interdiffusion of uranium and aluminum in relation to the failure of Al-clad fuel elements dates back to 1943.⁽⁹²⁾ There have been many studies of diffusion in the U-Al system since then.^(19,20,22,38,79,93-97)

b. Experimental work: Many different experimental techniques have been used in the different diffusion studies of the U-Al system. Since the uranium and aluminum tend to separate during the anneal, the couples are usually kept under uniaxial pressure while they are being annealed in vacuum. The total pressure is due to differences in thermal expansion and expansion due to layer growth as well as to externally applied pressure.

c. Structure of the diffusion zone: There are three intermetallic compounds in the U-Al system: UAl_2 , UAl_3 , and UAl_4 .^(98,99) The main phase in the diffusion zone at all investigated temperatures is UAl_3 . [Kiessling⁽⁹⁷⁾ reports that UAl_2 is the major phase at 250-350°C. The discrepancy may be due to the stresses in his particular geometry, an aluminum pin pressed into a hole in a uranium plate. He identifies UAl_2 by X-ray diffraction, although judging from his micrographs, he has UAl_3 .] UAl_2 is found in small amounts by some authors^(20,38,79,96,97) and not by others.^(22,94) UAl_4 is also not found in some studies^(79,94); others find it as a thin layer of gray⁽²⁰⁾ or black⁽⁹⁶⁾ friable material, which is sometimes found only by pulling the couple apart. The couple usually fractures at the UAl_3 -Al interface,^(22,94) and X-ray study of the fracture surface shows the presence of UAl_4 .⁽⁹⁶⁾

The complete or almost complete absence of UAl_4 is due to the low diffusion coefficient in that phase. Diffusion studies of UAl_3 -Al couples show that the diffusion coefficient in UAl_4 is lower by three orders of magnitude than in UAl_3 .⁽⁷⁹⁾ The reasons for the absence or thinness of UAl_2 are not clear; attempts to study its growth in U- UAl_3 couples were unsuccessful.⁽⁷⁹⁾

The microstructure of the U-Al diffusion zones is interesting and complex. The UAl_3 -Al boundary is usually quite regular, whereas the U- UAl_3 boundary is frequently very irregular.^(20,38) Stringers of U are sometimes trapped in the rapidly growing UAl_3 .⁽⁷⁹⁾ UAl_2 forms at the edges of the stringers and is finally converted to UAl_3 .⁽⁷⁹⁾

Large voids are found in the U-Al diffusion zone. It seems likely that these are Kirkendall pores, although the presence of gases in the voids has also been suggested.⁽⁹³⁾ High annealing temperatures are found to increase^(20,79) or decrease⁽⁹⁶⁾ the soundness of the diffusion zone. Increased pressure decreases the extent of void formation. The voids, as a rule, stay near the UAl_3 -Al interface,⁽⁷⁹⁾ although they are sometimes found distributed evenly throughout the diffusion zone.⁽⁷⁹⁾ There are also many cracks in the diffusion zones, at least some of which are due to post-diffusion treatment.

d. Kinetics of layer growth: The growth of the diffusion layer in the U-Al system follows a parabolic law in most cases. The growth rate is very fast; a 2-mm-thick layer grows in only 3 hr at 600°C.⁽⁷⁹⁾ Such

very rapid growth can lead to severe nonequilibrium effects, such as the entrapped U stringers mentioned above.

The growth rate also increases with the pressure up to a pressure between 700 and 1400 kg/cm². Since the pressure at a particular spot depends on other factors in addition to the applied pressure, such as the grain orientation (due to the anisotropic thermal expansion of uranium), the pressure effect is complicated even if the applied pressure is controlled.

The above considerations make it easy to understand the large scatter of values given in Fig. 17 (adapted from Ref. 96). Because of the large number of unknown variables, no attempt is made to reconcile the data of different authors. Fuel element designers are devised to choose the maximum values, which come from the careful and recent paper of Castleman,⁽⁷⁹⁾ and are in fair agreement with the thorough work of LeClaire and Bear.⁽²⁰⁾ Since Castleman obtains a layer thickness of 0.43 cm and Bierlein and Green obtain only 0.0686 cm in 110 hours at 390°C (notwithstanding the fact that the latter clean their surfaces by cathodic sputtering), an extrapolation of data from Ref. 79 is preferred over the actual data of Ref. 22.

Fig. 17. Arrhenius plot for the penetration coefficient for the interdiffusion of uranium and aluminum (after Ref. 96).

Unusual growth kinetics for UAl_4 can be deduced from the transformation of UAl_3 crystals to UAl_4 in U-Al alloys containing 7.05 a/o uranium, quenched from the liquid plus UAl_3 region.⁽¹⁰⁰⁾ A UAl_3 crystal, ca. 0.02 cm in cross section, which grows a UAl_4 border only 0.0013 cm thick in $\frac{1}{2}$ hour, is completely transformed to UAl_4 in one hour at 600°C. This indicates that there is either an incubation time, or that the kinetics change during the process. Nevertheless, the average of the two rates is of the same order as found by Castleman.⁽⁷⁹⁾

e. Discussion: There are two notable anomalies in this system: the "negative activation energy effect" (see Fig. 18),^(20,79) and the increase of the growth rate with pressure.^(20,79) Castleman⁽⁷⁹⁾ questions the significance of the first, since "small variations in the thicknesses of the multi-phase region or in the distribution and kind of the macroscopic defects would be sufficient to account for the phenomenon." Since the effect is reproducible, the reviewer is inclined to consider it real, although he cannot explain it.

Fig. 18. "Negative activation energy" in the interdiffusion of uranium and aluminum under 1400 kg/cm² pressure. ^(20,79)

The increase of the growth rate with pressure is explained by Castleman on a mechanical basis. Since pressure usually decreases D ,⁽⁶⁶⁾ and can be shown not to cause great enough a change in the solubility limits of the phases in this case,⁽⁸⁷⁾ Castleman attributes the pressure effect to the closing up of macroscopic defects and the improvement of contact at interfaces and within the diffusion zone. It should be noted that conventional Kirkendall pores also do not form under pressure.⁽¹⁰¹⁾

Both the rapidity of the diffusion and the pressure effect can be explained by the interstitial diffusion of aluminum atoms or ions in UAl_3 . In this mechanism, aluminum vacancy-interstitial pairs form in

the UAl_3 near the Al- UAl_3 boundary, and the interstitials diffuse away by the interstitialcy mechanism. The vacancies can coagulate to form the observed pores, as suggested by Bückle for the U-Zr system.⁽¹⁰²⁾

4. U-AlSi

The eutectic alloy of the Al-Si system is often used as a bonding agent and diffusion barrier between uranium slugs and aluminum cladding, since the rate of layer formation is three to five times slower in U-AlSi than in U-Al.^(96,103) There are two intermetallic layers formed, UAl_3 and USi_3 , or solutions between them (the two compounds have the same structure and are mutually soluble).⁽¹⁰⁴⁾ The USi_3 layer may act as the diffusion barrier. The diffusion zones are irregular and contain voids. Layer growth is again accelerated by pressure, increasing by a factor of three when the pressure is increased from zero to 140 kg/cm^2 .

Layer growth in U-AlSi is roughly parabolic if pressure is applied to the couple.⁽⁹⁶⁾ The temperature dependence of the rate constants is shown in Fig. 19. The layer thicknesses are determined conventionally in Ref. 96; in Ref. 103 the results of a large number of measurements are reported and the maximum thickness is calculated statistically from the distribution. Since these studies were carried out under different conditions (different pressures, different methods of calculating thickness, etc.), no attempt is made to reconcile them. Each set of data is scattered enough to make extrapolation unadvisable.

Fig. 19. Arrhenius plot of the penetration coefficient for the interdiffusion of uranium and AlSi.⁽⁹⁶⁾

The addition of silicon also slows down or stops entirely the transformation of UAl_3 to UAl_4 .⁽¹⁰⁰⁾

5. U-Ni

Nickel is also used as a diffusion barrier between aluminum and uranium, since the intermetallic compounds in the U-Ni system (there are seven of them⁽¹⁰⁵⁾) grow much more slowly than UAl_3 . Müller,⁽⁴⁰⁾ using autoradiography and alpha-track counting to establish the concentration penetration curve, finds that:

- i. six of the compounds appear on annealing for 1500 hours at 647°C.
- ii. each phase and the entire diffusion zone grow according to a parabolic law, and
- iii. the growth of the diffusion zone for $T < 530^\circ\text{C}$ is described by

$$K = 6 \times 10^{-3} \exp(-34,000/RT) \text{ cm}^2/\text{sec} \quad (13)$$

Above 530°C the activation plots curve downward, and in the case of UNi_5 there is a "negative activation energy" similar to that found in UAl_3 . This effect is not observed by Kittel,⁽¹⁷⁾ whose values for layer thickness and activation energy for $600^\circ\text{C} < T < 700^\circ\text{C}$ are in good agreement with Müller's. The values of Aas and Steinegger for the layer thickness⁽¹⁰⁶⁾ are far lower than these, possibly due to poor contact between the uranium and the nickel.

The effect of pressure on layer formation in this system has been studied by Adda *et al.*⁽¹⁹⁾ Since the annealing times are comparatively short, not all the phases appear in the diffusion zone. A finite homogeneity range in UNi_5 , which is isostructural with UCu_5 , is found in couples annealed without pressure and not in couples annealed under pressure. Pressure also increases the rate of layer formation, and increases the ratio [thickness $U_6Ni(\Delta V \text{ of formation} = 2\%)$]/[thickness $UNi_5(\Delta V \text{ of formation} = 3.7\%)$].

6. U-Stainless Steel

Notwithstanding the importance of stainless steel as a cladding material for fast reactors, only one thorough study of the interdiffusion of uranium and stainless steel (type 347) has been carried out.⁽¹⁸⁾ Two unidentified intermetallic compounds were found in the diffusion zone. The uranium-rich one is 4 to 12 times as thick as the other. It forms according to a parabolic law, with

$$K = 8.3 \exp(-45,620/RT) \text{ cm}^2/\text{sec} \quad (14)$$

Data for the iron-rich phase are given only for 4-day anneals; assuming a parabolic law, one calculates

$$K = 9.8 \times 10^3 \exp(-67,200/RT) \text{ cm}^2/\text{sec} \quad (15)$$

These data are in good agreement with Kittel's preliminary studies.⁽¹⁷⁾

7. The Effect of Irradiation on Layer Formation

Although many authors have commented on the desirability of studying the effect of neutron irradiation on the interdiffusion of uranium and cladding material, the only work done on this subject is that of Weil and Paine⁽¹⁸⁾ on U-stainless steel couples. They find that irradiation either decreases or does not effect the interdiffusion of uranium and stainless steel (see Fig. 20). A theoretical analysis, showing why radiation should not affect diffusion, is given by Lomer.⁽¹⁰⁷⁾

Fig. 20

Arrhenius plot of the thickness of the uranium-rich layer formed in the interdiffusion of uranium and stainless steel for 48 hours, with and without irradiation.⁽¹⁸⁾

8. The Effect of Pressure on Layer Formation

Experiments on self-diffusion in sodium,⁽⁶⁶⁾ phosphorus,⁽¹⁰⁸⁾ and lead⁽¹⁰⁹⁾ have shown that application of pressure decreases the diffusion coefficient. This is quite easy to explain in terms of the vacancy mechanism, since the volume of the crystal increases each time a vacancy is formed. Contrary to this, the rates of layer formation in the U-Al, U-Cu, and U-Ni systems increase with pressure. This could indicate that diffusion in these intermetallics takes place by an interstitialcy mechanism, since the volume of a crystal decreases when an interstitial is formed. There are, however, other factors to be considered.

The self-diffusion experiments^(66,108,109) are carried out under hydrostatic pressures up to 12,000 kg/cm². Most of the results in Ref. 19 are from measurements carried out under uniaxial pressures up to 1,200 kg/cm²; the few measurements carried out under hydrostatic pressure agree fairly well with them, and there appears to have been no creep in the diffusion zone. Nonetheless, it seems desirable to continue these measurements, using higher hydrostatic pressures.

Castleman's hypothesis that the effect of pressure is largely due to the improvement of contact⁽⁷⁹⁾ (Section III, C, 3, e) does not explain some of the results reported in Ref. 19. There does not seem to be as much room for improvement of the contact in U-Cu as there is in U-Al. Further, the explanation of improved mechanical contact does not explain the changes in the penetration curves found by Adda *et al.*⁽¹⁹⁾ These initial studies on the effect of pressure on layer formation have opened another interesting field.

C. Systems with Extended Solid Solubility⁽⁷³⁾

1. General Remarks

A region of extended solid solubility, the U-rich gamma phase, is present in the polyphase region of the U-Mo, U-Nb, U-Ti, and U-Zr phase diagrams. Below the gamma phase, the solubilities of the second element and the uranium in each other are small. Diffusion in the gamma phase of all these systems can be discussed together.

The diffusion coefficient in all these systems is concentration dependent. If the penetration plot (see Fig 21) is replotted on probability paper, the part corresponding to the gamma phase consists of one straight line or two straight lines joined by a curved portion (see Fig. 22), similar to what is found for single-phase systems.⁽¹³⁾

Fig. 21

Penetration plot for the interdiffusion of uranium and zirconium at 752°C for 89 hours.⁽⁷³⁾ (Reproduced by the permission of Presses Universitaires de France.)

Fig. 22

Penetration plot for the interdiffusion of uranium and zirconium at 752°C for 89 hours, re-plotted on probability paper. (73) (Reproduced by permission of Presses Universitaires de France.)

Diffusion in the gamma phase in the polyphase region is thus similar to diffusion in single-phase gamma alloys. The diffusion coefficient for the high uranium concentrations is almost the same for U-Mo (two-phase) and U-(U-30 a/o Mo) (one-phase) couples. The diffusion coefficient in both types of couples can be calculated by the Hall modification⁽¹³⁾ of the Matano method.⁽¹⁰⁾ A Kirkendall effect is observed during diffusion in the polyphase regions of these alloy systems, with the markers moving towards the uranium because of its greater mobility. The effect is always greater in the polyphase region than would be expected from results in the single phase.⁽⁷³⁾ This, as well as some anomalies in the diffusion coefficient (vide infra) are explained by the generation of excess vacancies at the phase boundaries.⁽⁷³⁾

On cooling to room temperature, the gamma phase decomposes. Since the structures of the decomposition products are strongly concentration dependent, the diffusion zone is divided into a number of layers with different structures. The boundaries between these layers, although not phase boundaries at the diffusion temperature, are planes of constant composition, and therefore move proportionally to $\sqrt{t}$.

2. U-Zr

Because of its great technical importance, many studies have been made on the U-Zr system. The work on one phase diffusion is in Section III, D; the work on polyphase diffusion is summarized in Table II.

Table II
DIFFUSION IN POLYPHASE U-Zr ALLOYS

	Adda et al. ⁽⁷³⁾	Mash and Disselhorst ⁽⁷²⁾	Müller ⁽⁴⁰⁾
Sample Preparation	As before.	Picture frame technique: 0.025 cm Zr on U core.	Zr-87 a/o U alloy cast into hollow cylinder of pure Zr.
Anneal	As before.	Vacuum, 10^{-5} mm Hg, with Zr getter, control to $\pm 4^\circ\text{C}$.	Vacuum, 10^{-4} mm Hg after flushing with purified argon, control to $\pm 3^\circ\text{C}$.
Measurement	Determined C-x curve with probe and microhardness measurement. Calculated D by Matano method. Measured Kirkendall effect.	Observed displacement of ϵ -Zr boundary metallographically. Measured Kirkendall effect.	Determined C-x curve by autoradiography and track counting. Calculated D by Matano method.
Results	Grain boundary diffusion into U at 600 and 650°C. D shown in Fig. 23. Kirkendall effect definitely present.	Grain boundary diffusion into Zr at 900°C. Motion of ϵ -Zr boundary proportional to $t^{1/2}$. Activation plot for K in Fig. 24. Found no Kirkendall effect.	Values of D shown in Fig. 23.

The number of phases on the concentration-penetration curves of Adda *et al.* agrees with the proposed phase diagram⁽¹¹⁰⁾ (3 phases at 651°C and 752°C, four phases at 700°C). One gamma phase does not appear in Müller's curve for diffusion at 679°C; in view of the closeness of this temperature to the decomposition temperature (ca. 670°C) of this phase, this is not a serious discrepancy.

The D values for the gamma phase found by Adda *et al.* and by Müller are in agreement (see Fig. 23). A diffusion coefficient calculated from the data of Mash and Disselhorst, using Eq. 9 (admittedly a very rough approximation), is also close to these. The variation of the diffusion coefficient with concentration in the restricted phase (see Fig. 23) is different from that in the range of complete solid solubility (see Fig. 13). The diffusion coefficient displays some further singularities near the phase boundaries; here D for 650°C is actually greater than D for 700°C.

Fig. 23

Plot of D vs. concentration for the interdiffusion of uranium and zirconium in the polyphase range.^(40, 73) (Reproduced by permission of Presses Universitaires de France.)

Mash's and Disselhorst's activation plot (see Fig. 24) shows a distinct break at a temperature between 740°C and 600°C. Their explanation of this is that below 600°C diffusion through the epsilon phase is rate controlling, and that, although this process has a lower activation energy, its D_0 is low enough to cause a discontinuity in the curve. This discontinuity cannot be explained by grain boundary diffusion⁽¹⁰²⁾ since several points on the lower curve lie below the extrapolated upper curve. The rate-limiting step for the upper curve must be diffusion through the gamma phase, the only one common to all three regions above 740°C.

There are some points of disagreement between the data of Ref. 72 and of Ref. 73. The authors of the former found no Kirkendall effect in experiments of a preliminary nature; the latter authors found a distinct Kirkendall effect. In view of the evidence for Kirkendall effect in similar systems, its presence in the U-Zr system is very likely.

Fig. 24

Arrhenius plot for the penetration coefficient for the interdiffusion of uranium and zirconium.⁽⁷²⁾

Since Mash and Disselhorst measured the distance of the epsilon-Zr interface from the marker interface and neglected the Kirkendall effect, their K and Q values are in error. Mash's and Disselhorst's contention that there is grain boundary diffusion into the Zr at temperatures as high as $900^\circ C$ is supported by work on self-diffusion in Zr.⁽¹¹¹⁾ Grain boundary diffusion is also present in self-diffusion in β U.⁽⁵²⁾ The parabolic layer-growth curves indicate that there is no grain boundary diffusion in the intermediate phases; this is compatible with grain boundary diffusion into the terminal phases.

As a matter of engineering interest, Mash and Disselhorst found that hardly any U penetrates the Zr until the epsilon-Zr interface is adjacent to the Zr surface. They also calculated the length of time required for U to penetrate 0.025 cm of Zr cladding at various temperatures (see Table III).

Table III

TIME FOR THE PENETRATION OF 0.025 cm OF ZIRCONIUM
CLADDING BY URANIUM DIFFUSION⁽⁷²⁾

Temperature, $^\circ C$	Time	Temperature, $^\circ C$	Time
1050	6.4 hr	600	17.2 yr
1000	12.5 hr	500	32.7 yr
900	54.3 hr	400	78.1 yr
850	126. hr	300	243. yr
740	1070. hr		

3. U-Ti⁽¹¹³⁾

Uranium and titanium are completely mutually soluble above 900°C.⁽¹¹²⁾ Below this temperature three, four, or five phases should appear in a diffusion couple. The total diffusion zone grows according to a parabolic law.⁽¹¹³⁾ The plot of $\log K$ vs. $1/T$ has 2 breaks, a change in slope between 850 and 900°C, and a discontinuity between 700 and 750°C (see Fig. 25), similar to that in Fig. 24. The first is due to the change from polyphase to single-phase diffusion. The discontinuity is probably due to the appearance of the uranium-rich gamma phase, which usually has a very high diffusion coefficient and therefore can grow very fast.

Fig. 25

Arrhenius plot for the penetration coefficient for the inter-diffusion of uranium and titanium.⁽¹¹³⁾

4. U-Mo⁽¹¹⁴⁾

The U-Mo system above 775°C consists of 2 bcc solid solutions, uranium-rich (65-100 a/o uranium) and molybdenum-rich (0-2 a/o uranium). The diffusion zone moves into the molybdenum because the uranium is the more mobile component. After cooling, the diffusion zone consists of four distinct zones (see Fig. 26). Comparison with the

phase diagram shows that zone "C" is the uranium-rich solid solution, the large crystals are the transformation product of material that goes through the beta-uranium zone, and the acicular crystals are martensite formed on cooling. The same zones form in cooled, one-phase U-(U-30 a/o Mo) diffusion couples, but the diffusion kinetics are different.

Fig. 26. Structure of the diffusion zone in uranium-molybdenum alloys.⁽¹¹³⁾

5. U-Nb

The U-Nb system above 770°C consists of two bcc solid solutions, uranium-rich and niobium-rich, separated by a miscibility gap. Diffusion studies have shown the existence of a third phase.⁽²⁴⁾ They also show parabolic growth of the diffusion zone^(24,114) and the delta

phase, and parabolic motion of the Kirkendall markers.⁽²⁴⁾ The activation energy for growth of the diffusion zone below 1000°C⁽¹¹⁴⁾ is in agreement with the activation energy for chemical diffusion at high uranium concentrations.⁽²⁴⁾ Since the intrinsic diffusion coefficient of uranium can be expected to be much higher than D_{Nb} (this is the case at high uranium concentrations),⁽²⁴⁾ the delta phase grows mostly into the niobium, and the penetration into niobium is equal to the growth of the delta phase. Data on this are given⁽²⁴⁾ only for $T \geq 800^\circ\text{C}$, and extrapolation to lower temperatures is impossible because the boundary of the delta phase is not known exactly.

IV. The Diffusion of Gases in Uranium

Both hydrogen (introduced during heat treatment) and fission gases (formed during irradiation) affect the properties of uranium. Hydrogen has a deleterious effect on various mechanical properties, (115-117) and the fission gases are supposed to cause the spectacular swelling of fuel elements above 500°C, (118,118a) both problems of technical importance.

A. Mathematical Treatment

Instead of analysis by sectioning, the diffusion coefficient of a gas in a solid is most often determined from the time variation of the amount of gas diffusing in or out. Steady-state and dynamic methods can both be used; the latter are more common. The commonest initial and boundary conditions are:

$$C = C_0 \text{ (all sample volume, } t = 0 \text{)}$$

$$C = 0 \text{ (all sample surface, } t > 0 \text{),}$$

i.e., the concentration of gas throughout the sample volume is uniform before diffusion starts, and the surface concentration drops to zero instantaneously the moment that diffusion starts. In the reviewer's opinion, the latter condition should not be used without experimental proof.

The solution to the diffusion equation for the above initial and boundary conditions in the case of a sphere of radius a , is (see Ref. 6 p. 86)

$$C = \frac{2aC_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin \frac{n\pi r}{a} \exp\left(-\frac{Dn^2\pi^2 t}{a^2}\right) . \quad (16)$$

Integrating over the volume of the sphere, one obtains

$$\frac{M_t}{M_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{a^2}\right) . \quad (17)$$

For short times ($t \ll a^2/\pi^2 D$),

$$\frac{M_t}{M_0} = \frac{6}{a} \sqrt{\frac{Dt}{\pi}} , \quad (18)$$

and for long times ($t \gg a^2/\pi^2 D$),

$$\frac{M_t}{M_0} = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{a^2}\right) . \quad (19)$$

Here M_t is the total amount of gas remaining in the sphere at time t , and $M_0 = (4/3)\pi a^3 C_0$ is the total amount of gas in the sphere at $t = 0$. Solutions for other geometries are given by Crank⁽⁶⁾ and by Inthoff and Zimen.⁽¹¹⁹⁾ For powders, an average spherical radius can be calculated from a knowledge of the density and surface area.^(120,121)

Another geometry is the sandwich with a thin layer of gas in the middle. The solution of the diffusion equation for this geometry is⁽¹²²⁾

$$\frac{M_t}{M_0} = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{2n-1} \exp \left[- \left(\frac{2n-1}{h} \pi \right)^2 Dt \right] , \quad (20)$$

where h is the half-thickness of the sandwich.

B. Experimental Techniques

1. Sample Preparation

In experiments on gas-solid couples, the total amount of gas diffusing into or out of the solid is measured as a function of time. Massive samples are used in gas-solid experiments on metals. Although they could also be used in the case of ionic crystals, such as UO_2 , powders are more commonly used, since the preparation of massive UO_2 samples of high theoretical density and a definite U/O ratio is difficult. On the other hand, the powders have the disadvantage that their surface area can change due to sintering during the diffusion anneal.

Sample preparation consists of charging the solid with the gas in question. The rare gases can be introduced by irradiating a solid containing fissionable material, which leads to a nearly homogenous distribution of gas. A metal-rare gas diffusion couple can also be made by making the metal the cathode in a glow discharge, cutting out two pieces, and rolling them together with their charged faces towards each other.⁽¹²²⁾ This gives a "sandwich" with a very thin layer of gas in the middle. Hydrogen, which diffuses much more rapidly than the rare gases, can be introduced by holding the sample in a hydrogen atmosphere until equilibrium is reached.

2. Measurement

The quantity of interest, the amount of gas that has diffused out of the sample up to time t , can be measured in several ways. The amount of hydrogen diffusing out can be measured by measuring the pressure rise.⁽¹²³⁾ Radioactive rare gases that diffuse out are removed either by pumping them off or by "sweeping" them away with another inert gas, and then are assayed by counting. Nonactive noble gases can be determined by irradiation and counting,⁽¹²⁴⁾ spectroscopy, or mass spectroscopy.⁽¹²²⁾

Oxidation is a problem in experiments on fission gas release from uranium. A comparison of the data of several investigators⁽¹²⁵⁾ shows that studies in which the radioactive noble gases are swept away from a uranium sample by argon or helium invariably produce higher D values than do studies in which the effusing gas is pumped away. Calculations show that this could very easily be due to the oxidation of the uranium by traces of O₂ in the sweeping gas. On the other hand, an oxide layer retards the diffusion of H out of U.^(117,123) These observations are not contradictory, since the emission of rare gases in all likelihood does not take place by diffusion, and that of hydrogen does.

Rare gas fission fragments can also leave the solid by recoil, and this should be taken account of in the calculation.⁽¹²⁶⁾

C. The Diffusion of Hydrogen in Uranium

Diffusion of hydrogen in uranium has been studied by a steady-state method⁽¹¹⁷⁾ and a dynamic method.^(117,123) In the first, the rate of diffusion through a uranium membrane is measured after the pressures on both sides of the membrane come to equilibrium. In the second, the rate of gas release from a sample charged with hydrogen is measured as a function of time. The experiments are fairly straightforward, although care has to be taken that the surface of the U is clean. This is best done by reacting the U with hydrogen at 300°C for a few minutes. Davis⁽¹¹⁷⁾ found that the surface concentration (contrary to the boundary condition) did not drop to zero but only to about 0.036 cc H/cc U, in the alpha phase. The results are shown in Fig. 27. The presence of impurities apparently lowers the diffusion coefficient somewhat; the reviewer is not certain that the differences (ca. 25%) are significant.

D. The Diffusion of Rare Gases

Four and one-half cc at NTP of the rare gases krypton and xenon are formed in 1 cc of uranium for each 1% burnup, and the pressure of this gas, when collected into bubbles, is supposed to cause the swelling of uranium fuel elements. Since the general question of swelling is covered elsewhere,^(118,118a) it is discussed here only as it bears on the diffusion of rare gases in uranium. Further, since the diffusion of rare gases in irradiated uranium is a very complex problem, it is better to discuss, first, some related experiments on the diffusion of rare gases in silver.

1. The Diffusion of Rare Gases in Silver

Ordinary diffusion experiments have shown that metals are, in general impermeable to the rare gases.⁽¹²⁷⁾ This is more probably due to the gases not dissolving in the metal than to their not diffusing once they are dissolved. The first problem in a study of the diffusion of rare gases is, then, the introduction of the rare gases into the metal.

Fig. 27. Arrhenius plot for the diffusion of hydrogen in uranium. (117, 123)

An elegant method for this was employed by LeClaire and Rowe, who introduced argon into silver in a hollow cathode discharge.⁽¹²²⁾ Two pieces of silver foil with the rare gas in solution in a thin layer on one side (probably trapped under sputtered silver) were roll-bonded with their gas-loaded faces against each other to make a sandwich. The value of D was calculated from the fraction of gas diffusing out of the metal as a function of time. Experiments of this type on the diffusion of argon,⁽¹²²⁾ krypton,⁽¹²⁴⁾ and xenon⁽¹²⁸⁾ in silver show that:

- i. the rare gas atoms do diffuse in silver in a manner similar to other impurities;
- ii. the diffusion coefficient for rare gas diffusion is two (for argon and xenon) or three (for krypton) orders of magnitude higher than for self-diffusion;
- iii. the activation energy for the diffusion of rare gases is close to that expected from the Lazarus theory;⁽⁷⁰⁾ and
- iv. the rare gases diffuse as singly charged positive ions.

2. The Diffusion of Rare Gases in Uranium⁽¹²⁵⁾

Experiments similar to the above are much harder to carry out on uranium, which cannot be bonded by cold rolling.⁽¹²⁹⁾ Experiments on rare gas diffusion in uranium are therefore carried out by irradiating the uranium to introduce the rare gases, and then measuring their release as a function of time, either during irradiation or during postirradiation annealing. If the gas release is due to a diffusion process, the total amount of gas released up to time t should be proportional to $t^{1/2}$, as given by (Eq. 18), a relation found experimentally only by Zimen and Dahl.⁽¹³⁰⁾ Although all other workers⁽¹³¹⁻¹³⁶⁾ found an irregular release of gas with time, indicating that gas release does not take place by diffusion, they nevertheless calculated diffusion coefficients (see Fig. 28).⁽¹²⁵⁾

Fig. 28. Arrhenius plot for the "diffusion" of rare gases in uranium⁽¹²⁵⁾

The data shown in Fig. 28 refer to the period before gross swelling takes place. The fraction of gas released in this time is very small, of the order of 1%. The gas evolution rate is markedly increased when gross dimensional changes occur, and the release during swelling is even more erratic and less amenable to quantitative treatment than before.

Since the $t^{1/2}$ law is not followed and the gas release is very irregular, one may conclude that the measured release of fission gases from irradiated uranium does not take place by classical volume diffusion. It appears more likely that the mechanism is flow along cracks (micro and macro) and along interconnected pores. Whatever diffusion does take place must be slower than this flow, i.e., $D_{\text{true}} < 10^{-15} \text{ cm}^2/\text{sec}$ at 600°C . A reasonable qualitative hypothesis is that the small bubbles

observed in samples that do not swell badly are due largely to the precipitation of vacancies caused by fission damage,⁽¹³⁷⁾ and that swelling and heavy gas release take place only when the uranium has been weakened either by thermal cycling or by holding in the gamma phase (for more detailed calculations, see Ref. 137). This view is confirmed by an experiment showing that helium introduced into uranium by alpha-particle bombardment⁽¹³⁸⁾ is not evolved until the sample breaks, although helium evolves from thorium under similar conditions, in agreement with a

diffusion mechanism.⁽¹³⁸⁾ It is difficult to explain why rare gases appear not to diffuse in gamma uranium, since diffusion of everything else in that material is very rapid.

A study⁽¹³⁹⁾ of the release of fission gases from a U-Al alloy ($\text{UAl}_4 + \text{Al}$) shows that no gases are released from the alloy at temperatures below the solidus. Above the solidus, gas release is initially rapid. The total gas given off is proportional to the fraction of UAl_4 dissolved in the melt. This indicates that rare gas atoms cross the UAl_4 -Al interface only with difficulty, or that they do not diffuse in aluminum.

Xenon diffuses out of a 5% U-95% Zr alloy⁽¹²⁶⁾ in negligible quantities at $T < 600^\circ\text{C}$. Above 600°C , a diffusion coefficient is measurable, ranging from $2.5 \times 10^{-12} \text{ cm}^2/\text{sec}$ at 700°C to $2 \times 10^{-11} \text{ cm}^2/\text{sec}$ at 900°C . The data are not complete enough to allow one to decide whether grain boundary diffusion, volume diffusion, or some nondiffusional process is responsible.

The present state of knowledge on the diffusion of rare gases in uranium can be summarized briefly by saying that, although irradiated uranium fuel elements swell due to the accumulation of fission gases, the gases do not accumulate by a classical diffusion process, and that the true diffusion of rare gases in uranium has not yet been measured.

V. Diffusion in UO_2

A. Self-diffusion

1. Introduction

Self-diffusion in ionic crystals is more complicated than self-diffusion in metals because the diffusing particles in the former are charged. This necessitates the simultaneous movement of other charged particles in order to maintain electrical neutrality. On the other hand, this property provides one with more tools to make measurements relevant to diffusion, such as measurements of the electrical conductivity or measurements on samples doped with anions or cations of different valence. A variety of such measurements on alkali and silver halides have led to a nearly complete understanding of transport processes and defect structures in these crystals.⁽¹⁴⁰⁾ The information on oxides is much less complete; thorough studies have not been carried out on any system yet.⁽¹⁴¹⁾ This interesting field of work is at present wide open; the greatest need is for concentrated studies of diffusion, electrical conductivity, etc., on one oxide, rather than a scattered survey of diffusion in a large number of systems.⁽¹⁴¹⁾

2. Mathematical Treatment

The appropriate geometries for the study of self-diffusion of uranium in UO_2 are the same as used for self-diffusion studies in metals (Section III, A). The thin layer geometry is recommended. Self-diffusion of oxygen in oxide crystals, on the other hand, is studied by an isotopic exchange method in which the oxygen from the crystal, which is enriched in O^{18} , exchanges with the oxygen of the furnace atmosphere (CO_2). The value of D is calculated by fitting the experimental measurements of the fraction exchanged as a function of time to the solution of the diffusion equation for the case of diffusion into a solid from a well-stirred solution of finite volume. For a spherical solid, this is (see Ref. 6, p. 88)

$$1 - \frac{M_t}{M_0} = \sum_{n=1}^{\infty} \frac{6\lambda(1+\lambda)}{9(1+\lambda) + \lambda^2 q_n^2} \exp\left(-\frac{q_n^2 Dt}{a^2}\right) \quad (21)$$

Here M_t is the total amount exchanged in time t , M_0 is the total amount exchanged in infinite time, λ is the ratio of the number of moles of exchanging specie in the gas to the number of moles of exchanging specie in the solid, a is the sphere radius, and the q_n are the nonzero positive roots of

$$\tan q = \frac{3q}{3 + \lambda q^2} \quad (22)$$

The same equation holds if the atmosphere instead of the crystal is enriched in O^{18} . Equations for cylindrical and plane geometries are also given by Crank (see Ref. 6, p. 53, 70). For long times ($q_n^2 Dt \gg a^2$), the above series can be cut off after the first term. For short times (142, 143)

$$1 - \frac{M_t}{M_0} = (1 + \lambda) \left[\frac{\gamma_1}{\gamma_1 + \gamma_2} e \operatorname{erfc} \left(\frac{3\gamma_1}{\lambda} \sqrt{\frac{Dt}{a^2}} \right) + \frac{\gamma_2}{\gamma_1 + \gamma_2} e \operatorname{erfc} \left(-\frac{3\gamma_2}{\lambda} \sqrt{\frac{Dt}{a^2}} \right) \right] - \lambda, \quad (23)$$

where

$$e \operatorname{erfc} Z = \exp(Z^2) \int_Z^{\infty} \exp(-b^2) db, \quad (24)$$

$$\gamma_1 = \frac{1}{2} \left[\left(1 + \frac{4\lambda}{3} \right)^{1/2} + 1 \right],$$

$$\gamma_2 = \gamma_1 - 1.$$

In an actual experiment, powders are used instead of crystals. It is assumed that the powder particles are spherical, and an average radius is calculated from measurements of the weight and surface area. Curves of Dt/a^2 vs. M_t/M_0 are prepared from the above equations, and values of Dt/a^2 for different times are determined from the measured values of M_t/M_0 . The value of D is determined from a plot of Dt/a^2 vs. t .

Although the use of powders is at first glance unappealing to those accustomed to dealing with massive diffusion samples, it can be shown that if the assumption of spherical powders is made, and the radius is calculated from the ratio of the measured volume to the measured surface area, the measured diffusion coefficient should be within a factor of two of the true diffusion coefficient.^(120,121) This sets the limit of precision of the diffusion coefficient, and further errors due to the change of surface area during the diffusion anneal are possible. Nevertheless, this seems to be the best method available for such measurements.

Booth and Rymer^(143a) obtained much better Dt/a^2 vs. t plots from powder prepared by crushing fused UO_2 than from common UO_2 powder, undoubtedly due to the absence of porosity from the fused powders.

3. Experimental Techniques

a. Uranium self-diffusion: These are the same as for self-diffusion in metallic uranium, except that the sectioning must be carried out by grinding.

b. Oxygen self-diffusion:^(142,143) Apparatus suitable for such measurements has been described by Cameron et al.⁽¹⁴⁴⁾ and by Kingery and coworkers.⁽¹⁴⁵⁾ The sample is held in a container, with which it does not react, in a closed vessel which contains the CO_2 atmosphere. Aliquots of the furnace atmosphere, small in comparison with the total volume, are drawn off from time to time and analyzed for O^{18} by means of a mass spectrometer. Better accuracy is obtained if the solid instead of the gas is charged with the enriched oxygen, since the diffusion coefficient is small. The vessel should be kept cool so that oxygen does not exchange with its walls, and the furnace atmosphere should be circulated. Since the diffusion coefficient may depend very strongly on the nonstoichiometry of the UO_2 , this should be carefully controlled.

4. Experimental Results

a. Uranium diffusion:⁽¹⁴⁶⁾ A few diffusion coefficients have been determined by the sectioning technique, using U^{235} as the tracer. The results should be considered preliminary; the penetration curve given

has a large grain-boundary tail, and only three points in the linear log C vs. X^2 region. The D values given are 10^{-13} cm²/sec at 1410°C and 4.3×10^{-12} cm²/sec at 1750°C. The activation energy is between 90 and 125 kcal/mol. The experiment is made especially difficult by the very small diffusion coefficient and the presence of some U^{235} in the basis material.

b. Oxygen diffusion:(142,143) The data of Belle and Auskern are shown in Fig. 29. Two of their plots of Dt/a^2 vs. t are shown in Fig. 30; it should be noted that they do not pass through the origin. The authors ascribe this to the nonsphericity of the particles, as do Kingery *et al.*;(147) it may also be due to a change of surface area due to sintering during the anneal. Plot B in Fig. 30, which fits a straight line better than does plot A, was obtained in an apparatus with provision for circulating the gas.

Fig. 29. Arrhenius plot for the self-diffusion of oxygen in UO_2 .(142) (Reproduced by permission of Technology Press.)

Fig. 30. Plot of Dt/a^2 vs. t for self-diffusion of oxygen in UO_2 .(142) (Reproduced by permission of Technology Press.)

The activation energy, 29.7 kcal/mol, appears to be independent of the O/U ratio. The D_0 values were 2.6×10^{-5} cm²/sec for $UO_{2.004}$ and 4.0×10^{-4} cm²/sec for $UO_{2.064}$. Belle and Auskern interpreted these results in terms of the diffusion of interstitial oxygen ions, and found that D_0^i , the D_0 for the diffusion of interstitials [$D_0 = (n/N) D_0^i$, where n is the number of excess (mobile) interstitial oxygen ions, and N the total number of oxygen ions], was 0.013 cm²/sec for both O/U ratios. This is in agreement with (i.e., only a factor of two greater than) the D_0 deduced for interstitial diffusion from measurements of the oxidation of UO_2 ,⁽¹⁴⁸⁾ which is considered to be limited by the diffusion of oxygen ions in UO_2 . The last is disputed by Blackburn, Weissbart and Gulbransen,⁽¹⁴⁹⁾ who found that U_3O_7 is formed near the beginning of the oxidation process, and that the rate-limiting process is diffusion through it, not through UO_2 .

The agreement with diffusion coefficients calculated from the rate of oxidation of uranium is poor; but, then, such disagreements are frequent,⁽¹⁵⁰⁾ and, further, the oxidation of uranium metal may not be diffusion controlled.⁽¹⁵¹⁾

Work on the sintering of UO_2 does not shed any light on the diffusion processes in UO_2 . It seems unlikely that UO_2 sinters by a diffusion process, since the diffusion coefficient of uranium in UO_2 is far too small to account for the sintering rates observed.

Although a fair start has been made, the problem of self-diffusion in UO_2 is far from finished. The reviewer would like to suggest that the measurements of diffusion of oxygen be extended to higher temperatures, using massive samples or fused powders, that similar experiments be carried out with "doped" UO_2 , and that new experiments be made on the diffusion of uranium ions in UO_2 . Recent correspondence^(151a,b) indicates that the results of such experiments will be published shortly.

B. The Diffusion of Rare Gases

The diffusion of rare gases in UO_2 and other uranium compounds is important because of its bearing on the retention of fission products in fuel elements. A large amount of work has been done on this subject. Experiments are carried out by irradiating the UO_2 and measuring fission gas release, either during irradiation or during postirradiation heating,⁽¹⁵²⁻¹⁵⁵⁾ by holding UO_2 at high temperature in a rare gas atmosphere until it is saturated,⁽¹⁵²⁾ and by including Ra^{226} in the oxide and measuring the rate of emanation of Rn^{222} .⁽¹⁵⁵⁾

The data on the diffusion of rare gases in UO_2 is about as scattered as that on the diffusion of rare gases in uranium.⁽¹⁵⁶⁾ Some of the workers⁽¹⁵²⁾ have not shown to this reviewer's satisfaction that the rate of fission gas release is indeed diffusion controlled. Another objection to the in-pile release experiments is that the temperature of the UO_2 is uneven, and known only from heat-transfer calculations.

The most reliable work on the straightforward ex-pile diffusion of rare gases in UO_2 appears to be that of Booth and Rymer^(143a) and of Lindner and Matzke.⁽¹⁵³⁻¹⁵⁵⁾ The use of crushed fused UO_2 gave results^(143a) consistent with a diffusion mechanism: a straight-line relationship between M_t/M_0 and $\sqrt{t}$ (see Eq. 18) and between M_t/M_0 and $1/a$ (see Eq. 18), the former straight line missing the origin by an amount that can be explained by nonsphericity of the powder. The scatter about the Arrhenius plot is also relatively small. On the other hand, the stoichiometry of this material is apparently not known, and the average particle radius is taken from sieve analyses instead of the surface area/volume ratio.^(120,121)

The results given in Ref. 143a on sintered powders are not so consistent, and, since no surface area measurements on the material used are given, no diffusion coefficient can be calculated.

Lindner and Matzke⁽¹⁵³⁻¹⁵⁵⁾ have studied the diffusion of various rare gases in UO_2 as a function of O/U ratio (see Fig. 31), in U_3O_8 (see Fig. 32), and in UC (see Fig. 33). Their plots of M_t/M_0 vs. $\sqrt{t}$ are straight lines.

Fig. 31. Arrhenius plots for the diffusion of xenon in UO_2 .⁽¹⁵³⁾ (Reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

Fig. 32. Arrhenius plots for the diffusion of krypton, xenon, and radon in U_3O_8 .⁽¹⁵⁴⁾ (Reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

Fig. 33. Arrhenius plot for the diffusion of xenon in UC.⁽¹⁵⁵⁾ (Reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

The agreement with Booth's results is good. The following conclusions may be drawn:

- i. The diffusion coefficient of krypton does not differ appreciably from that of xenon in either UO_2 or U_3O_8 , although the diffusion coefficient of radon in U_3O_8 is substantially lower (see Fig. 32).

- ii. The diffusion coefficient in UO_2 increases with increasing O/U ratio (see Fig. 31), although the activation energy does not change, in a manner similar to the self-diffusion of oxygen in UO_2 .⁽¹⁴²⁾ It should be noted that the last place in the stoichiometry is uncertain; $\text{UO}_{2.00}$ may be $\text{UO}_{2.01}$.^(151a)
- iii. The preliminary annealing of UC increases the diffusion coefficient, perhaps due to oxidation or the replacement of carbon by oxygen in the compound.

The mechanism of diffusion of the rare gases in UO_2 is not clear. The activation energy (ca. 49.3⁽¹⁵⁴⁾ or 46^(143a) kcal) and D_0 (ca. 2×10^{-8} cm²/sec) are very different from these for either oxygen diffusion⁽¹⁴²⁾ or uranium ion diffusion⁽¹⁴⁶⁾ in UO_2 , although the variation of the diffusion coefficient with O/U ratio is the same as that for the diffusion of oxygen.

The in-pile measurements of fission gas release are much more difficult to discuss. For one, knock-out and knock-in processes⁽¹⁵⁶⁾ play a considerable part. For another, the temperature distribution in the fuel pellet is unknown. These may account for the large scatter of the in-pile data.⁽¹⁵⁶⁾

VI. Conclusions

This section sums up the state of knowledge on diffusion in uranium.

- i. Self-diffusion in uranium metal: Self-diffusion in gamma and beta uranium are known. Data are needed on the anisotropy of self-diffusion in alpha uranium, and on the effect of pressure on self-diffusion in gamma uranium.
- ii. Diffusion in gamma uranium alloys: Chemical diffusion has been studied enough; attention should now be turned to the variation of self-diffusion with composition in homogenous alloys.
- iii. Layer formation in uranium alloys: The kinetics of layer formation in important uranium-cladding systems are known well enough for design purposes. The fundamentals of layer formation, especially the effect of pressure, need study.
- iv. The diffusion of gases in uranium: The diffusion of hydrogen is known. Information is needed on the "true" diffusion of rare gases in uranium.
- v. Diffusion in UO_2 : Until the new papers^(151a,b) on self-diffusion are out, comment is withheld. Rare gas diffusion is fairly well known.

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