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Self-Diffusion Studies of Gamma Plutonium

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1. Introduction

The diffusion behavior of plutonium has been investigated at Los Alamos for a number of years. This paper covers the most recent work to be completed, a study of self-diffusion in the face-centered orthorhombic gamma phase (190° to 310°C). The experimental technique used, which was determined in part by the equipment available for handling this reactive, toxic and intensely α -active metal, included roll-bonding of the diffusion couples, lathe-sectioning of the annealed couples and pulse-height analysis of the alpha activity from representative sections to determine the distribution of the Pu²³⁸ tracer as a function of time at various annealing temperatures. This technique had been used previously to study self-diffusion in the delta phase [1] and some modifications in detail were incorporated to improve the technique.

2. Experimental Procedure2.1 Couple Preparation

Two special stocks of plutonium, one of which had been enriched in Pu²³⁸ as shown in the isotopic analyses listed in Table I, were cast and then machined to small pieces 0.18 in. by 0.39 in. by 1.00 in. The plutonium pieces and all materials necessary for couple assembly were placed in an inert-atmosphere glove box. The box was prepared for work by being evacuated overnight and then backfilled with high-purity argon. During couple assembly the box atmosphere was recirculated over magnesium perchlorate to remove traces of water. One large face of a plutonium piece of each analysis was abraded in the inert atmosphere, first on 400-grit, then on 600-grit silicon carbide papers. The object of this operation

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was to expose a fresh, unreacted, flat surface. Two plutonium pieces were placed with fresh surfaces face-to-face in a jacket of square-cross section which had been made from 5 inches of 0.065-in.-wall aluminum tubing. The jacket had inside dimensions of 0.425 in. by 0.425 in. One end had been sealed by being flattened in a press and fusion welded. Thin Z-shaped aluminum spacers were used to prevent the plutonium from shifting longitudinally. After the plutonium was inserted, the open end of the jacket was sealed by cold welding, the tube being flattened and severely deformed with a fixture mounted in a hydraulic press.

The assembly was transferred to a glove box with an air atmosphere where it was heated for 30 minutes in a furnace at 250°C and reduced in thickness by being passed through a rolling mill with rolls heated to 200°C. The rolling schedule (4 passes of 100 mils each with a 10-minute reheat after two passes) reduced the thickness of the assembly to 100 mils. The rolled assembly was allowed to cool normally in air and the four edges were sheared. The aluminum was peeled from the laminated plutonium sheet, which was about 55 mils thick. Metallographic examination of the samples cut from the ends and center of the sheet showed that it was usually well bonded and had very few regions where oxide particles marked the interface. It appears that the inert-atmosphere method of couple preparation is preferable to the less reliable vacuum method used previously in studying delta plutonium self-diffusion [1]. Disks 0.382 in. in diameter were punched from the sheet after it had been heated on a hot plate to the ductile low beta range (140°C as measured by temperature-indicating pellets).

2.2 Diffusion Anneal

Each disk to be diffusion annealed was wrapped in 1-mil-thick tantalum foil and sealed in a Pyrex capsule evacuated to 3×10^{-5} torr or better. This capsule was then sealed within a second Pyrex capsule under a similar vacuum.

The diffusion anneals were carried out at temperatures between 215° and 310°C in Marshall furnaces which had been adjusted to have a temperature gradient no greater than $\pm 1/2^\circ\text{C}$ over a 5-in. length. Heavy-wall nickel tubes were used as furnace liners to further smooth the gradient. The liners were divided into three longitudinal cavities by a septum of nickel sheet to which two calibrated Chromel-Alumel thermocouples were attached. One thermocouple was used for controlling the furnace temperature with a Brown Pyrovane controller equipped with a Capaciline anticipation circuit; the second thermocouple was monitored daily with a Leeds and Northrup K-2 precision potentiometer.

To determine reasonable annealing times and temperatures, capsulated disks were annealed at 219° and 299°C for 43 days, then analyzed. With the magnitude of the gamma self-diffusion coefficient thus established, two capsulated disks were

placed in each of three furnaces set respectively at 219°, 250°, and 280°C; each capsule in a separate longitudinal cavity, and one capsulated disk was placed in a furnace at 307°C. Capsules were withdrawn from the furnace at intervals of three to five months and allowed to cool normally in air. Since the minimum annealing time was 43 days, the time for the couple to reach the furnace temperature and to cool to room temperature was considered to be insignificant.

2.3 Sampling Method

After the diffusion anneal, the disks were found to be distorted as a result of the dimensional changes that occurred during heating and cooling the plutonium through its alpha $\rightleftharpoons$ beta and beta $\rightleftharpoons$ gamma phase transformations. Since nonplanar specimens would give erroneous results, the specimens were flattened by being pressed in the low beta range in much the same manner as they were punched. Resulting changes in thickness (approximately 3 mils) were measured with a micrometer caliper. This dimensional change was treated as thermal contraction; the distance measurements of the sample layers from the reference plane were multiplied by the ratio of the original thickness of the disk to its final thickness.

Each flattened disk was carefully cemented to the end of a 3/8-in.-diameter by 1-in. long Duralumin spindle with epoxy cement. Initially, cement alone was used, but later the reliability of the joint was greatly increased by drilling two 0.052-in.-diameter holes on a diameter of the couple and using 0.046-in.-diameter steel dowel pins and epoxy cement to join the couple to the spindle. The steel contamination of the samples did not interfere with subsequent radiochemical analysis. Disks were mounted with the side rich in Pu^{238} exposed; the increase in the L series X-ray activity from the side of the couple rich in Pu^{238} was clearly distinguishable with a radiation survey instrument.

The spindle was chucked in the lathe collet and the specimen surface was checked to see that its plane was perpendicular to the lathe axis within 0.001 in. ($\sim 0.20^\circ$). Samples were turned with a carbide-tipped tool in an atmosphere of 98 percent helium. First the diameter of the specimen was turned to ~ 0.3 in. to eliminate possible edge effects. Then layers 0.001 in. thick were removed consecutively from the specimen. The turnings from each layer were collected on a fresh sheet of aluminum foil and transferred to a numbered vial. The lathe tool was cleaned with a fresh wooden dowel between cuts to eliminate the possibility of cross contamination. The positions which the machined layers had occupied in the disk were determined by using a dial indicator having a least count of 0.0001 in. to locate the successive positions of the lathe carriage and tool. The position where the lathe tool first touched the specimen disk was considered the reference plane and distances were measured relative to this plane.

Samples for the determination of the Pu^{238} content were taken at 0.002-in.

intervals--in one case at each 0.001 in.--near the couple interface and at intervals of 0.006 in. at some distance from the interface. As many as 20 layers were analyzed from a specimen.

The dimensional measurements were made near room temperature ($\sim 25^\circ\text{C}$). For calculation, it is desirable to convert these dimensions to the dimensions that existed at the temperature of the diffusion anneal. The change in linear dimension between 20°C and 235°C (disregarding anisotropic expansion) may be approximated from the density at 25°C ($\rho_{25} = 19.84$ g per cu cm) [2] and at 235°C ($\rho_{235} = 17.14$ g per cu cm) [2] by the following expression:

$$\frac{l_{235}}{l_{25}} = \left(\frac{\rho_{25}}{\rho_{235}} \right)^{1/3} = 1.050 \quad (1)$$

Combined with the expansion coefficient of the gamma phase (34.6×10^{-6}) [2] a dimension measured at room temperature l_{25} can be converted to a dimension l_t at a temperature $t^\circ\text{C}$ in the gamma phase by the relation

$$l_t = 1.050l_{25} + 1.050l_{25}(34.6 \times 10^{-6})(t - 235) \quad (2)$$

2.4 Tracer Analysis

The Pu^{238} content in the various layers from each disk was determined by radiochemical methods. The interfering americium was separated by a solvent-extraction procedure in which Pu^{4+} ion is extracted by 2-thenoyl-trifluoroacetone, and the percent of the total α activity due to Pu^{238} was determined by pulse-height analysis.

The specific activity S (disintegrations per minute per gram) of each isotope may be computed from the half-life $t_{1/2}$:

$$S = -\frac{dN}{dt} = \frac{\ln 2}{t_{1/2}} N \quad (3)$$

where N is the number of atoms of the isotope.

For Pu^{238} where $t_{1/2}$ is 90 years, [3] and using 6.02×10^{23} as Avogadro's number,

$$S_{238} = -\frac{dN}{dt} = \left[\frac{\ln 2}{90 \cdot 365 \cdot 24 \cdot 60} \right] \left[\frac{1}{238} \cdot 6.02 \times 10^{23} \right] = 3.71 \times 10^{13}$$

For Pu^{239} $t_{1/2}$ is 24,360 years [3] and for Pu^{240} $t_{1/2}$ is 6580 years [3]. The α emission from Pu^{242} with its 3.7×10^5 -year half-life [3] is insignificant and Pu^{241} is a β emitter.

If γ_1 is the number of counts assignable to Pu^{238} , and γ_2 is the number of counts assignable to Pu^{239} and Pu^{240} , then the relation between the percent of

Pu^{238} α disintegrations and the weight percent (wt pct) Pu^{238} is

$$\text{pct Pu}^{238} \alpha's = \frac{100 \gamma_1}{\gamma_1 + \gamma_2} \quad (4)$$

$$= \frac{100 (\text{wt pct Pu}^{238})(S_{238})}{(\text{wt pct Pu}^{238})(S_{238}) + (\text{wt pct Pu}^{239})(S_{239}) + (\text{wt pct Pu}^{240})(S_{240})} \quad (4a)$$

The isotopic compositions of the plutonium stocks used in the experiment are shown in Table I. A concentration-penetration curve obtained from an unannealed disk showed the expected step function. Concentration of Pu^{238} was uniform throughout the enriched half, dropped immediately at the interface to the Pu^{238} concentration of the unenriched material, and remained at that level throughout the unenriched half.

2.5 Autoradiography

To investigate the possibility that the predominate mode of diffusion was grain boundary diffusion, autoradiographs were made from disks that had been annealed at 219° and 250°C. The disks were set on edge and a cylinder of polymerizing plastic was cast around them. The cylindrical mounts were then faced off on a lathe, ~ 0.040 in. being removed from the edge of the diffusion couple. The exposed surface was then polished as for metallographic examination. The samples were wrapped with a layer of 0.25-mil-thick rubber hydrochloride film to prevent α contamination of the photographic emulsion and placed in contact with Kodak NTA or Ilford N-40 plates for 15 or 20 seconds. After development of the plates, the areas corresponding to those rich in Pu^{238} were clearly visible. A sharp demarcation line separated the two sides of an unannealed couple and there was a gradual change in the photographic density for the annealed couples. No indication of diffusion along preferential paths (such as grain boundaries) was observed by examining the autoradiographs under a microscope at 100 diameters magnification.

3. Results

The appropriate solution [4] of Fick's equation for the semi-infinite diffusion-couple geometry and boundary conditions¹ used is

$$\frac{C - c_1}{C_0 - c_1} = \frac{1}{2} \left[1 - \frac{2}{\pi} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\lambda^2} d\lambda \right] \quad (5)$$

where C is the concentration of Pu^{238} at a distance x from the couple interface,

¹ $C = C_0$ for $x < 0$, and $C = c_1$ for $x > 0$ when $t = 0$.

c_1 the initial concentration of Pu^{238} on the side of low concentration, C_0 the initial concentration of Pu^{238} on the side of high concentration, and t the time of the diffusion anneal. D is the diffusion coefficient defined by Fick's equation and λ is an integration variable. Data which satisfy this equation will determine a straight line when plotted on arithmetic-probability paper [5].

A typical set of data, the concentration-penetration points obtained for the diffusion of Pu^{238} at 307°C , is shown in Figure 1. These same data plotted on arithmetic-probability coordinates, Figure 2, show the agreement with a straight line fit. It can be shown that the diffusion coefficient D equals the square of the distance along the linear axis between the intersections of the straight line at the 50th and 84th percentile points divided by twice the annealing time [1]. Initial estimates of D for each annealed diffusion couple were derived from plots of this kind.

Values of D were refined by a computer least-squares technique previously developed by Goldman for analyzing the self-diffusion in delta plutonium [1]. In this technique the data points are weighted as a function of the number of α counts observed in determining the Pu^{238} concentration. The annealing temperatures, times, and values of D obtained for the nine couples used are given in Table II.

The nine sets of data were fitted by a computer least-squares technique [1] to the Arrhenius-type equation to give the relationship

$$D = 2.1 \times 10^{-5} \exp \left[\frac{-16,700}{RT} \right] \text{ cm}^2/\text{sec} \quad (6)$$

which is shown in Figure 3. The apparent reproducibility of the points at the intermediate temperatures is thought to be fortuitous.

4. Discussion

The values of the frequency factor D_0 and activation energy Q for face-centered orthorhombic gamma plutonium are significantly lower than might be expected from currently accepted theories of diffusion mechanism. Low D_0 and Q values are usually attributed to short-circuiting diffusion paths. However, autoradiographic experiments with plutonium indicate that grain boundary diffusion is unlikely. Anomalous behavior of this metal has almost become accepted by plutonium metallurgists as the rule rather than the exception. Recently solid state band theory and computation have been applied to some plutonium problems, i.e. negative thermal expansion and alloying behavior of delta plutonium, by Kmetko [6,7] and it is planned to apply similar ideas to plutonium diffusion behavior.

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Table I
Isotopic Composition of Special Plutonium Stocks
Used for Self-Diffusion Experiments

Isotope	Pu ²³⁸	Pu ²³⁹	Pu ²⁴⁰	Pu ²⁴¹	Pu ²⁴²
Enriched, percent	0.516	94.29	4.91	.25	.013
Unenriched, percent	0.009	94.49	5.18	.30	.013

Table II
Summary of Data for Self-Diffusion in Gamma Plutonium

Couple No.	Temperature °C	Time hours	Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^{12}$
III-a	307	3285	10.02
II-a	299	1030	10.92
III-c	280	2277	6.03
III-b	280	3285	5.85
III-e	250	2277	2.15
III-d	250	3813	2.01
II-b	219	1030	1.23
III-g	220	3645	.70
III-f	220	3813	.98

Fig. 1. Concentration-penetration data for couple III-a annealed for 3285 hours at 307°C.

Fig. 2. Probability plot for couple III-a annealed for 3285 hours at 307°C.

$$\frac{C - c_1}{C_0 - c_1}$$

.99

.95

.80

.60

.40

.20

.05

.01

0 .02 .04 .06 .08 .10 .12 .14
CM AT 307° C

Fig. 3. Arrhenius plot for self-diffusion in gamma plutonium.

Figure Captions

- Fig. 1 Concentration-penetration data for couple III-a annealed for 3285 hours at 307°C
- Fig. 2 Probability plot of data for couple III-a annealed for 3285 hours at 307°C
- Fig. 3 Arrhenius plot for self-diffusion in gamma plutonium

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