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**Zirconium Metal-Water Oxidation
Kinetics II. Oxygen-18 Diffusion
in β -Zircaloy**

R. A. Perkins

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METALS AND CERAMICS DIVISION

ZIRCONIUM METAL-WATER OXIDATION KINETICS II.
OXYGEN-18 DIFFUSION IN β -ZIRCALOY

R. A. Perkins

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ABSTRACT

At the end of a hypothetical loss-of-coolant-accident in a Light Water Reactor the mechanical properties of the "prior" beta region of the Zircaloy fuel clad will be determined to a large extent by its oxygen content. For this reason the diffusion of oxygen-18 in β -Zircaloy-4 has been measured from 900 to 1500°C (1652-2732°F), and survey measurements have been made for β -zirconium and β -Zircaloy-2. The tracer diffusivity was measured over the entire temperature range and the chemical diffusivity from 1100 to 1500°C (2012-2732°F). The experiments were performed by using oxygen-18 as the tracer and activating it by proton bombardment. Some complementary measurements were made using Auger Electron Spectroscopy. The results indicated that the tracer and chemical diffusivity of oxygen in β -Zircaloy-4 are statistically identical, and there is no oxygen concentration dependence over the oxygen concentration range studied, 0.1 to 0.6 wt %. The temperature dependence of the diffusivity from 1000 to 1500°C (1832-2732°F) is

$$D = 2.48 \times 10^{-2} \exp(-28200/RT) \text{ cm}^2/\text{s} .$$

Below 1000°C (1832°F) the diffusivity dropped sharply because a two phase $\alpha + \beta$ mixture was present. The results for the β -Zircaloy-2 and β -zirconium indicated that the alloying additions have no influence upon the oxygen diffusivity. The combination of three sets of boundary conditions (thin film tracer diffusion, single-phase chemical diffusion couple and phase-boundary-movement chemical diffusion couple) and two methods of oxygen profiling (oxygen-18 radioactivation and Auger Electron Spectroscopy) were used to increase the confidence in the results. The current results are about 50% lower than the previous results of Mallett, Albrecht, and Wilson. The diffusivity of oxygen-16 is expected to be 6% greater than that for oxygen-18.

INTRODUCTION

A series of zirconium-based alloys, known as Zircalloys, has been developed for use as the fuel cladding in light water nuclear reactors. The fourth alloy in the series, i.e., Zircaloy-4, is currently the most generally used alloy of the series. The oxidation of and oxygen diffusion in these alloys are important in determining safety criteria for light water reactors.

In the event of a hypothetical Loss of Coolant Accident (LOCA) in which the coolant is drained from the reactor core, the residual and fission product decay heat from the nuclear fuel and the heat generated by the highly exothermic Zircaloy-steam reaction will cause the temperature of the cladding to increase as the core is refilled with coolant by an Emergency Core Cooling System (ECCS). One of the current safety criteria states that the peak fuel cladding temperature shall not exceed 1204°C (2200°F) during a LOCA. When the core is refilled with coolant (borated water), steam will be produced, and the kinetics of the steam-Zircaloy reaction will in part determine the ability of the Zircaloy cladding to maintain its integrity and confine the fuel in a geometry amenable to cooling.

A portion of the zirconium rich region of the Zr-O phase diagram is shown in Fig. 1. At about 860°C (1580°F), pure zirconium transforms from the low temperature, hexagonal close packed (hcp) alpha phase to the high temperature, body centered cubic (bcc) beta phase. The alpha phase is stabilized by the presence of oxygen. Therefore, at higher oxygen concentrations, the alpha phase is stable at higher temperatures. The maximum solubility of oxygen in the alpha phase is about 29 at. % and is nearly independent of temperature. Figure 2 shows a portion of the equilibrium diagram that has been determined for Zircaloy-2 and Zircaloy-4¹ and provides a comparison to pure zirconium. The results indicate that at low oxygen concentrations the transformation from 100% alpha to 100% beta occurs over a much wider temperature interval for Zircaloy-2 and Zircaloy-4. Therefore, at low oxygen concentrations (about 0.11 wt % is common for fuel cladding applications) Zircaloy-4 will exist as the

Fig. 1. Phase diagram for the zirconium-oxygen system.

Fig. 2. Phase diagram for the Zircaloy-oxygen system. After Chung et al.¹

bcc β phase above about 950°C (1742°F); between about 800°C (1472°F) and 950°C (1742°F) the two phase $\alpha + \beta$ Zircaloy is present.

Thus during oxidation at temperatures above the transition, a scale consisting of an external oxide layer (tetragonal or monoclinic ZrO_2) and an inner α layer will be formed. The mechanical strength of the cladding will depend largely upon the portion of the cladding existing in the β phase because the oxide and α phase will be very brittle. As the Zircaloy oxidizes, the migration of oxygen will extend well ahead of the α/β interface, and the amount of oxygen in the β phase will be appreciable. The mechanical properties of the β phase are dependent upon the oxygen concentration with the ductility decreasing as the oxygen content increases. Therefore, the oxygen distribution in the remaining β phase region of the fuel cladding is critical in assessing the mechanical stability of the cladding. The diffusion coefficient of oxygen in the β phase must be determined in order to obtain the oxygen distribution in the β phase during oxidation.

Several studies of oxygen diffusion in β -zirconium and Zircaloy have been conducted. The results, which are shown in Fig. 3, indicate large differences. The data of Mallett et al.² were obtained by oxidizing Zircaloy-2 and Zircaloy-3 under conditions for which a very thin oxide was maintained on the specimen. The oxygen concentration profile in the β phase was obtained using vacuum fusion analysis. The oxygen diffusivity was then calculated from the concentration profile. Diffusivity measurements often can be expressed empirically by the Arrhenius-type equation:

$$D = D_0 \exp[-Q/RT] \quad (1)$$

where

D_0 is a constant independent of temperature

Q is the activation energy, and

R and T are the gas constant and absolute temperature, respectively.

The results of Mallett et al. yield

$$D = 0.0453 \exp[-(28200 \pm 2400)/R1] \text{ cm}^2/\text{s} \quad (2)$$

Fig. 3. Arrhenius plot of data from previous studies of oxygen diffusion in zirconium and Zircaloy.

The confidence level for the error limits on Q is not reported. Debuigne³ determined the diffusivity of oxygen in β -zirconium by oxidizing β -zirconium and measuring the thickness of the oxide + alpha scale after a given time and temperature of oxidation. The oxygen diffusivity in the β was obtained graphically from an equation defining the conservation of mass of oxygen at the α/β interface. His results can be expressed by

$$D = 0.977 \exp(-41,000/RT) \text{ cm}^2/\text{s} . \quad (3)$$

Schmidt et al.⁴ made a diffusion couple consisting of two zirconium rods of differing oxygen concentrations (125 and 750 ppm O). The rods were butt-welded together and annealed in an electric field to obtain simultaneously electrotransport data. After the anneal the oxygen concentration profile was obtained by vacuum fusion analysis, and the oxygen diffusivity was calculated from the profile using the Grube method. Only three data points were obtained so no temperature dependence was calculated. DeChamps⁵ obtained a value for the oxygen diffusivity in β -zirconium at 1100°C (2012°F) by measuring the weight gain during oxidation of a β -zirconium specimen. The oxygen diffusivity was calculated from an equation that related the portion of the weight gain attributed to oxygen pickup in the β phase in the presence of oxide and α layers to the oxygen diffusivity in the β phase. Because of the variety of experimental and analytical methods employed, the disparity between the results is not too surprising. The data of Mallett et al. and Debuigne obviously are in conflict, but the results of Schmidt et al. are compatible with either data set. The data point of DeChamps, which was obtained very indirectly, supports the results of Mallett et al. The compositional differences in the materials in these studies are not likely to account for the differences obtained for the oxygen diffusivity. Therefore, additional measurements of the oxygen diffusivity in the oxygen-zirconium and Zircaloy systems were deemed necessary.

The goals of this investigation were to 1) determine the diffusivity of oxygen-18 in β -Zircaloy-4 between 900 and 1500°C (1652-2732°F); 2) compare the oxygen diffusivity in pure zirconium, Zircaloy-2 and Zircaloy-4; 3) compare the tracer diffusivity and chemical diffusivity of oxygen in Zircaloy-4; and 4) obtain an expression for the diffusivity of oxygen-16.

In addition to the above goals, this study would provide information concerning the mechanism by which oxygen diffuses in β -zirconium. Data for the diffusion of interstitial impurities in bcc metals have been compiled in a recent review.⁶ The majority of the investigations involved internal friction measurements at low temperatures; however, mass flow measurements are becoming more numerous. Of the three systems (vanadium, niobium, and tantalum) in which the oxygen diffusivity has been fairly well determined, two seem to be anomalous in comparison with the diffusion of other interstitial impurities in bcc metals. It was hypothesized that Snoek's model, which assumes that the interstitials occupy octahedral sites and jump from one octahedral site to an adjacent one, may not apply for these systems. Because low temperature internal friction studies are not possible in β -zirconium, a comprehensive mass flow study is required to gain insight into the atomistics of oxygen in this system.

EXPERIMENT PROCEDURES

Oxygen diffusivities were determined primarily in Zircaloy-4 with survey measurements also being made in pure zirconium and Zircaloy-2. Both tracer and chemical diffusivities were determined for Zircaloy-4, while only tracer measurements were made on Zircaloy-2 and zirconium. The ¹⁸O radioactivation technique was used in all the tracer studies but was supplemented in the chemical diffusion work with boundary-movement and Auger Electron Spectroscopy (AES) measurements. In this section the various procedures used in specimen preparation, temperature measurements, the diffusion anneals, and the determination of oxygen profiles and diffusivities are discussed for each method used.

Specimen Preparation

The Zircaloy alloys were obtained from Teledyne, Wah Chang Albany as rods approximately 13 mm in diameter. The average ingot analysis for each alloy is given in Table 1. The zirconium was reactor-grade 1 in the form of a crystal-bar ingot of 99.94% minimum purity. The ingot was arc-melted, forged to a 37 mm diameter bar and swaged to an 18 mm diameter rod. The impurity content of the zirconium is also given in Table 1. The rods were machined down to 11 mm diameter and cut into disks approximately 4 mm thick. The disks were then wrapped in tantalum, encapsulated in an evacuated quartz ampoule and preannealed 6 h at 1300°C (2372°F).

Table 1. Alloy Content and Impurities in the Zircaloy-2, Zircaloy-4 and Zirconium.^a

	Zircaloy-2	Zircaloy-4	Zirconium
Ni	0.06	<35 ^b	24 ^b
Sn	1.63	1.59	
Fe	0.15	0.21	242 ^b
Cr	0.12	0.11	
Al	54	57	
B	0.2	0.2	
C	115	140	50
Cu	14	22	25
Hf	37	39	135
H	10	6	53
N	43	43	10
Si	50	87	22
U	0.8	0.7	
O	1250	1180	19

^aThe Ni, Sn, Fe and Cr are given in weight percent and the others are in ppm.

^bGiven in ppm.

After the preanneal the disks to be used for the tracer diffusion experiments were polished on both faces through 600 grit SiC paper. The specimens were then oxidized with oxygen-18 in the apparatus shown in Fig. 4. Approximately 1.2 microliters of $D_2^{18}O$ (90% ^{18}O) per specimen were placed in the arm as shown and frozen in liquid nitrogen. The quartz tube containing the specimens was evacuated to about 1.3×10^{-3} Pa (10^{-5} torr) and the specimens were then heated to 800°C (1472°F). When the furnace reached 800°C (1472°F), the valve to the vacuum system was closed, and the liquid nitrogen was removed to allow the $D_2^{18}O$ to evaporate. After the specimens had oxidized for 15 min, the furnace was opened to cool the specimens rapidly. The weight gain per specimen was equivalent to the formation of a $3\text{ }\mu\text{m}$ thick ZrO_2 scale. At 800°C (1472°F) approximately 50% of the oxygen-18 will be dissolved in the specimen.⁷ The maximum penetration of oxygen-18 into the specimen during the oxidation procedure was about 2×10^{-2} mm. The oxygen-18 was removed from the circumference and one face of the specimens by polishing on SiC paper.

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Fig. 4. Apparatus for oxidizing the tracer diffusion specimens with oxygen-18.

The chemical diffusion couple consisted of two disks, one containing the original 0.12 wt % oxygen and the other enriched to approximately 0.6 wt % oxygen using 90% enriched oxygen-18 gas. The oxygen-18 enrichment was performed in the same apparatus shown in Fig. 4 except that the arm was connected to a break-seal ampoule containing the oxygen-18. After the quartz tube was evacuated to approximately 1.33×10^{-3} Pa (10^{-5} torr), the specimens were heated to 950°C (1742°F). The break-seal was opened and the specimens oxidized for 30 minutes. After the oxidation the specimens were wrapped in tantalum foil, encapsulated in quartz ampoules and annealed 7 hours at 1300°C (2372°F) to homogenize the oxygen. One face of each oxidized specimen was polished and lapped on a Meehanite disk using 1 μ m diamond paste. The surface was flat to within one part per million. One face of a disk of the preannealed material was similarly prepared. The lapped surfaces were placed in contact, and pressure was applied by the apparatus shown in Fig. 5. The couple was then welded for 15 min at 1000°C (1832°F) under a load of 800 grams. A good weld was obtained without causing significant oxygen diffusion between the two disks.

Temperature Measurement and Annealing Procedures

After a specimen was prepared for the diffusion anneal, three tantalum tabs (1 $\times$ 1.5 mm) were spot welded onto the side of the specimen at 45° intervals. Tantalum tabs were necessary because platinum thermocouples could not be attached directly to the specimens. A Pt vs Pt-10% Rh thermocouple was spot welded onto the center tab, and Pt-6% Rh vs Pt-30% Rh thermocouples were welded onto the outside tabs. In addition, a black-body made of crystal-bar zirconium was placed next to the specimen, as shown in Fig. 6, so that optical pyrometer measurements could also be taken during the anneal. The calibration of the optical pyrometer and thermocouple wire, temperature control and recording systems, and the various errors involved in temperature measurement have been previously reported.⁸ The probable accuracy

Fig. 5. Apparatus for welding the chemical diffusion couples.

Fig. 6. Specimen arrangement for the diffusion anneal.

of the temperature measurements varied from $\pm 1^\circ\text{C}$ (1.8°F) at 900°C (1652°F) to $\pm 2^\circ\text{C}$ (3.6°F) at 1500°C (2372°F). Furthermore, the temperature variations during an anneal were within $\pm 1^\circ\text{C}$ (1.8°F).

A tantalum split-shield furnace was used for the diffusion anneals. The furnace was located inside a metal bell jar which was evacuated to about 4×10^{-4} Pa (3×10^{-6} torr) prior to the anneal. A schematic illustration of the heating element, heat shields and specimen placement is shown in Fig. 6. The low thermal inertia of the system allowed the heating and cooling portions of the annealing cycle to be fairly short. A typical time-temperature cycle is shown in Fig. 7. The effective anneal time was calculated from³

$$t_e = \frac{\int_0^{t_t} \frac{\exp[-Q/RT(t)]}{\exp(-Q/RT_d)} dt}{\exp(-Q/RT_d)} \quad (4)$$

Fig. 7. Temperature versus time profile for the diffusion anneal of specimen 4-T-16.

where

- t_e is the equivalent time at the diffusion temperature T_d .
- $T(t)$ is the measured temperature as a function of time,
- Q is the activation energy for diffusion and
- t_t is the total anneal time.

The effective contribution of the heating and cooling transients to the diffusion time was about 6 min at all temperatures. The error in the time of anneal is estimated to be approximately ± 40 s, which leads to an error of about $\pm 3.9\%$ at 1500°C (2732°F) and becomes negligible below 1300°C (2372°F).

After the diffusion anneal, the specimens were cut parallel to the diffusion direction, and the cross-section was then polished through 600 grit SiC paper, lapped on Meehanite disks with 6 μm diamond paste, and finally polished with 6 μm diamond paste. The oxygen profile across the surface was then determined using either proton bombardment radio-activation of the oxygen-18 or Auger Electron Spectroscopy (AES) measurements.

Determination of Penetration Profiles and Diffusivities

The nuclear reaction $^{18}\text{O}(\text{p},\text{n})^{18}\text{F}$ occurs when oxygen-18 is bombarded with protons. The reaction has a sharp resonance peak at a proton energy of 2.643 MeV.¹⁰ The resultant fluorine-18 emits a 0.6 MeV positron and has a half-life of 112 minutes. Therefore, the diffusion of oxygen in a material can be studied by using oxygen-18 as the diffusing species, bombarding the specimen with protons, and determining the oxygen profile by measuring the positron emission from fluorine-18.¹¹ A proton bombardment energy of 2.7 MeV was used so that the activated region was limited to within about 5 μm of the surface. The bombardment was performed on the ORNL Tandem Van de Graaff. The proton beam was shaped into a horizontal line and passed through a narrow slit (1 mm $\times$ 7 mm) as shown in Fig. 8. The beam then passed through a slit (5 mm $\times$ 5 mm) which defined the portion of the specimen which was bombarded. The specimen holder was cycled so that the specimen oscillated through the beam parallel to the diffusion direction. The beam current striking the specimen was integrated so that the total bombardment of the specimen was measured. The tracer diffusion specimens (4 mm wide) received a bombardment of approximately 1.5×10^{-3} coul, and the chemical diffusion specimens (7 mm wide) received approximately 1.8×10^{-3} coul. A specimen was bombarded, and the radioactivity emitted was counted using a silicon surface barrier detector. The activity as a function of time was obtained using a multichannel analyzer. The results, shown in Fig. 9, indicate that the isotope measured had a half-life of approximately 112 minutes which corresponds to the half-life of fluorine-18. After bombardment, the surface of the specimen was placed in contact with Kodak AA 54 X-ray film. Two exposures, the first for two h and the second for about 12 h, were made for each specimen. After developing the film, the percent transmission of light through the autoradiographs was measured using an Anco Microphotometer. The percent transmission was recorded on a strip chart while a measuring slit (10 μm wide and 1200 μm long) passed across the autoradiograph. Because the activated region of the specimen was 5 mm wide, four independent microphotometer traces were averaged for each specimen.

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Fig. 8. Specimen arrangement for the proton bombardment.

Fig. 9. Radioactivity emitted from a specimen as a function of time after the proton bombardment.

To relate the percent transmission of incident light measured by the microphotometer from the autoradiograph to the concentration of fluorine-18 in the specimen, a series of exposures using thallium-204 was made. Thallium emits a 0.76 MeV electron and has a 3.8 year half-life. The Lambert-Beer law was used to correct the data as shown in Table 2. The Lambert-Beer law for an absorber states that

$$\log \frac{I_0}{I} = A_s = a_s bc \quad (5)$$

where

- I_0 is the incident intensity,
- I is the transmitted intensity,
- A_s is the optical density (O.D.) of the absorber,
- a_s is the extinction coefficient of the absorber,
- b is the sample thickness and
- c is the concentration of absorbing particles.

Because a_s and b are constant, the optical density is proportional to c , which is a measure of the concentration of fluorine-18 in the specimen. The correspondence between the normalized time of exposure of the film to the thallium-204 source and the normalized logarithm of the light intensity transmitted through the film on the microphotometer (last two columns of Table 2) verifies the Lambert-Beer law correction for the film.

Another problem, referred to as "broadening," can affect the optical density measurements because of the finite width of the microphotometer slit and the range of the positrons emitted by the fluorine-18 in the specimen.^{12,13} To measure the broadening for the current experimental procedures, a Zircaloy-4 specimen was lapped and anodized in $H_2^{18}O + 12\% KOH$ at 15 volts, which created a $Zr^{18}O_2$ layer approximately 300 Å thick. The specimen was cut perpendicular to the anodized surface, and the lapped faces were placed together and mounted in a sample holder. The cross-section thus created was polished and then bombarded with protons. Autoradiographs of this "thin film" source were measured on the microphotometer to obtain the broadening profile as shown in Fig. 10. The results

Table 2. Calibration of Kodak AA54 Film with ^{204}Tl to Verify the Applicability of the Lambert-Beer Law

Exposure Time(t) (min)	Z Transmission ($100 \times I$)		$-\log I$	$-\log I / -\log I_f$	t/t_f
	ave	σ			
1	95.7	± 1.06	.019	.025	.033
1.5	92.5	± 0.59	.034	.045	.050
2	90.2	± 0.59	.045	.059	.067
2.5	86.8	± 0.68	.061	.081	.083
5	75.6	± 0.64	.121	.160	.166
10	55.8	± 0.53	.253	.334	.332
15	41.9	± 0.50	.378	.499	.500
30	17.5	± 0.63	.757	1	1

Fig. 1G. The broadening profile obtained from a line source of oxygen-18 after a proton bombardment.

are from three autoradiographs of differing optical densities. As demonstrated in the section on Error Analysis, the broadening had a negligible influence upon the diffusivity values obtained from the oxygen profiles, which were about 3.5 mm wide.

Figure 11 shows the output of the microphotometer as a function of distance for a tracer diffusion specimen and a chemical diffusion specimen. A smooth curve was fit to the results, and the four curves for each specimen were averaged after the background was subtracted. The resultant curve was then analyzed to obtain the diffusion coefficient.

The thin film solution to Fick's second law of diffusion was appropriate for analyzing the tracer diffusion specimens. This solution states:

$$A(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp - \frac{x^2}{4Dt}, \quad (6)$$

where

- $A(x,t)$ is the tracer concentration at a distance x from the surface after an anneal of time t ,
- M is the quantity of diffusant per unit area initially on the surface, and
- D is the diffusion coefficient.

The diffusion coefficient was obtained from the slope of the least squares fit of the log of the optical density versus the penetration distance squared.

Two sets of boundary conditions were used in the chemical diffusion experiments; at high temperatures [$\geq 1200^\circ\text{C}$ (2192°F)] both portions of the diffusion couple existed as δ -Zircaloy, but at lower temperatures the high oxygen side of the couple was an $\alpha + \delta$ mixture while the low oxygen side was δ . For the first set of boundary conditions, the Matano-Boltzmann analysis was initially employed to calculate the oxygen diffusivity as a function of oxygen concentration. However, because no

Fig. 11a. Microphotometer profiles for a) a tracer diffusion specimen and b) a chemical diffusion specimen.

Fig. 11b.

concentration dependence was observed, the Grube analysis,¹⁴ which assumes no concentration dependence, was used in subsequent analyses. For a diffusion couple with two sides, each of uniform composition, Fick's second law yields

$$c(x,t) - c_0 = \frac{c' - c_0}{2} [1 - \operatorname{erf}(x/2 \sqrt{Dt})] \quad (7)$$

where

$c(x,t)$ is the concentration at a distance x from the interface after an anneal of time t

c_0 and c' are the initial oxygen-18 concentrations on the low and high oxygen sides of the couple, respectively, and

D is the diffusion coefficient.

Equation (7) may be simplified by noting that c_0 is essentially zero and that c' may be normalized to unity since only relative concentration values are required. Thus Eq. (7) becomes

$$2c(x,t) - 1 = -\operatorname{erf}(x/2 \sqrt{Dt}) = \operatorname{erf}(-x/2 \sqrt{Dt}) \quad (8a)$$

$$\operatorname{erf}^{-1} [2c(x,t) - 1] = -x/2 \sqrt{Dt} \quad (8b)$$

Keeping in mind that the normalized concentration, $c(x,t)$, is equal to the normalized optical density (O.D.) values obtained from the autoradiographs, using Eq. (8b), D can be calculated from the slope of a least squares fit to a plot of the inverse error function, $\operatorname{erf}^{-1} (2 \text{ O.D.} - 1)$, versus the diffusion distance. The slope of interest is, of course, that of the straight line portion of the plot centered on the midpoint of the ^{18}O concentration range (see Fig. 15).

For the second set of boundary conditions, the solution developed by Wagner for diffusion in a two-phase system was used.¹⁵ The

solution to Fick's second law in the single phase portion of the couple is given by:

$$\frac{c_{\beta,0} - c_{\beta,1}}{c_{\beta,1} - c_{\alpha+\beta,0}} = \sqrt{\pi} \gamma \exp(\gamma^2) [1 + \operatorname{erf}(\gamma)] \quad (9)$$

and

$$\xi = 2\gamma \sqrt{Dt} \quad (10)$$

where

$c_{\beta,0}$, $c_{\beta,1}$, and $c_{\alpha+\beta,0}$ are the oxygen-18 concentrations in the β initially, in the β at the $\beta/\alpha + \beta$ interface at equilibrium and in the $\alpha + \beta$ initially, respectively;

ξ is the distance the $\beta/\alpha + \beta$ interface moved during an anneal of time t ;

D is the diffusion coefficient; and

γ is a dimensionless parameter.

From the optical density curve, the necessary relative concentrations were obtained and put in Eq. (9) to obtain γ graphically. The initial $\beta/\alpha + \beta$ interface was at the weld, and the final interface position was measured from the autoradiographs. With ξ and γ determined, the diffusivity was calculated from Eq. (10). This solution assumes that no diffusion occurs in the two-phase mixture and that the mass of oxygen crossing the interface is compensated only by the migration of the interface. In some specimens diffusion in the $\alpha + \beta$ mixture was evident but was taken into account, by graphically integrating the mass of oxygen which diffused out of the two phase mixture, when determining the interface movement.

To verify the results obtained from the oxygen-18 radioactivation technique, several oxygen profiles for single-phase, chemical diffusion couples were also determined by AES. The cross-section of the specimen was prepared as previously with a final etch in 5 parts 70% HNO_3 , 5 parts 85% lactic acid, 2 parts H_2O and 1 part 48% HF. The specimen was placed in the AES system which operated at a pressure of $7 - 13 \times 10^{-10}$ Pa ($0.5 - 1 \times 10^{-11}$ torr). The surface was sputtered for several hours

to remove the oxide layer. An analyzing beam about 10 μm in diameter was moved across the specimen parallel to the diffusion direction and rastered to obtain an analyzing path about 100 μm wide. A sputtering beam simultaneously cleaned the surface to prevent the adsorption of oxygen. Measurements were made until two consecutive profiles were identical, which indicated that the results were not being affected by adsorbed oxygen. When these procedures are followed, the intensity of the oxygen Auger signal has been shown to be proportional to the oxygen concentration, Fig. 12. The relative intensity of the Auger signal was plotted versus the distance and analyzed using the Grube technique previously described. This procedure allowed the oxygen profile to be determined by two independent methods on the same diffusion specimens.

The use of three different sets of boundary conditions and two independent oxygen profiling techniques allowed a greater degree of confidence to be ascribed to the results which were obtained. The section on Error Analysis will investigate more deeply some areas of the experimental procedures.

Fig. 12. Calibration curve for the Auger signal intensity as a function of dissolved oxygen content in zirconium.

RESULTS

The tracer diffusivity of oxygen-18 in Zircaloy-4 was measured at 50°C (90°F) intervals from 950 to 1500°C (1742–2732°F) with at least two specimens run at each temperature. In addition single measurements were made at 900 and 930°C (1652–1706°F). Plots of the logarithm of the average optical density of the autoradiograph versus penetration distance squared are shown for five representative specimens in Fig. 13. Two types of near surface effects were observed. At 1000°C (1832°F) and above a depletion of oxygen-18 at the surface was observed, which was likely due to the release of oxygen-18 or exchange with oxygen-16 in the atmosphere during the anneal. Below 1000°C (1832°F) there was an enhancement of oxygen-18 at the surface due to the tie up of the oxygen-18 as ZrO_2 .

Fig. 13. Log (optical density) versus x^2 profiles for several tracer diffusion specimens.

Therefore, the data points within about 0.4 mm of the initial surface were not used in determining the slope of the oxygen profile.

The tracer diffusivity results are listed in Table 3. A plot of the logarithm of the diffusivity versus reciprocal temperature is linear above 1000°C (1862°F) so that the Arrhenius-type equation, Eq. (1), is applicable. These data are shown in Fig. 14 along with the least-squares fit and 90% confidence interval. The technique for calculating the confidence interval has been previously described¹⁶ and is considered further in Appendix B. The temperature dependence of the tracer diffusivity is

$$D^* = 3.01 \times 10^{-7} \exp(-28800/RT) \text{ cm}^2/\text{s} . \quad (11)$$

The confidence limits for the activation energy and pre-exponential are calculated in Appendix B. As is discussed more fully below (see Fig. 23) the observed diffusivity values drop sharply at temperature below 1000°C (1832°F). The reason for this behavior may be seen in the Zircaloy-oxygen phase diagram (see Fig. 2) where between about 800 and 975°C (1472-1787°F), at an oxygen concentration of 0.12 wt %, a two phase $\alpha + \beta$ mixture is present. Therefore, the diffusivity measured below 975°C (1787°F) is characteristic of an $\alpha + \beta$ mixture, and because the diffusivity of oxygen in α is much smaller than in β , the diffusivity drops sharply. The ratio of $\beta:\alpha$ in the mixture will decrease with temperature, which will cause an additional decrease in the diffusivity over and above the decrease expected on the basis of the diffusivity temperature dependence alone. The measured diffusivity is an "apparent" diffusivity which will vary with the oxygen concentration because of its effect on the $\alpha:\beta$ ratio. The current results are for an alloy with about 0.12 wt % oxygen.

Chemical diffusion measurements were made at 50°C (90°F) intervals from 1100 to 1450°C (2012 to 2642°F) with duplicate specimens at each temperature. Four specimens were run at 1200°C (2192°F) where the Grube technique used at the higher temperatures and the phase boundary movement technique used at the lower temperatures overlap. The oxygen concentration (optical density) profiles for three specimens analyzed using the Grube

Table 3. Tracer Diffusivity Data in β -Zircaloy-4

Specimen	Temperature (°C)	Time (sec) $\times 10^{-3}$	Diffusivity (cm^2/sec) $\times 10^7$
4-T-30	905	111.	0.254
4-T-42	930	71.6	0.674
4-T-41	955	53.3	1.96
4-T-28	952	50.1	1.50
4-T-31	1001	30.2	3.01
4-T-17	1005	31.7	3.76
4-T-22	1048	19.2	5.90
4-T-34	1049	20.6	5.95
4-T-21	1102	11.5	6.40
4-T-14	1105	16.6	7.53
4-T-33	1150	9.12	12.8
4-T-26	1153	8.49	10.1
4-T-39	1196	4.56	19.1
4-T-38	1198	4.02	16.4
4-T-15	1199	6.43	13.6
4-T-27	1200	6.32	14.4
4-T-32	1248	4.14	26.0
4-T-19	1250	4.89	25.2
4-T-29	1300	4.18	21.2
4-T-13	1309	3.83	30.1
4-T-24	1346	2.95	35.5
4-T-18	1347	2.96	50.0
4-T-35	1397	1.87	47.7
4-T-16	1398	2.05	58.8
4-T-23	1445	1.38	66.9
4-T-36	1450	1.50	73.0
4-T-37	1500	1.14	92.0
4-T-25	1504	1.03	71.4
4-T-40	1502	1.20	81.3

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Fig. 14. Arrhenius plot of the tracer diffusion data with the 90% confidence interval.

technique are shown in Fig. 15a-c. The optical density is plotted versus the penetration distance on probability paper, which will yield a straight line if the diffusivity is constant and Eq. (8) is the appropriate solution to Fick's second law. Therefore, the central straight line portion of the plot was used to calculate the diffusivity. The "tails" of the plots at the high and low O.D. values occur because the scale is greatly extended at the ends, and there is no increase in the accuracy of measuring the O.D. values in these regions where the slope of the oxygen profile is changing very slowly and, thus, cannot be detected. The percent transmission profiles for three specimens analyzed using the phase boundary technique are shown in Fig. 16a-c. For the specimens in which there was some oxygen transport out of the $\alpha + \beta$ mixture, the final position of the interface was adjusted by graphical integration.

The chemical diffusivity that is measured is the interdiffusion coefficient

$$\tilde{D} = N_O D_{Zr} + N_{Zr} D_O \quad (12)$$

Because the oxygen concentration is very small ($N_O \ll 0.025$) and the self-diffusivity of zirconium is about three orders of magnitude lower than the oxygen diffusivity,¹⁷ Eq. (12) becomes $\tilde{D} = N_{Zr} D_O$. A 3% variation of N_{Zr} occurs across the specimen, and the techniques for measuring $\tilde{D}$ are insensitive to this variation. Therefore, the constant interdiffusion coefficient obtained is assumed equal to the chemical diffusivity of oxygen, D_O .

The chemical diffusion data obtained from the two sets of boundary conditions and two oxygen measurement techniques are given in Table 4. The three data sets have been shown statistically to be from the same data population (see Appendix A) and are, therefore, plotted together in Fig. 17. The least squares fit and 90% confidence interval are also shown. The temperature dependence of the chemical diffusion data is

$$D_O = 1.32 \times 10^{-2} \exp(-26200/RT) \text{ cm}^2/\text{s} . \quad (13)$$

Fig. 15. Probability plots for the optical density versus distance for three chemical diffusion specimens: a) 4-C-8, b) 4-C-2, and c) 4-C-7.

a

b

c

Fig. 16. Percent transmission versus distance profiles for three specimens analyzed using the phase boundary movement technique a) 4-C-21, b) 4-C-19 and c) 4-C-17.

Table 4. Chemical Diffusivity Data in β -Zircaloy-4

Specimen	Temperature (°C)	Time (sec) $\times 10^{-3}$	Diffusivity (cm^2/sec)	
			Radioactivation $\times 10^6$	AES $\times 10^6$
4-C-21*	1059	12.5	0.935	
4-C-20*	1102	11.8	0.801	
4-C-19*	1149	6.66	1.21	
4-C-18*	1152	7.56	1.04	
4-C-13*	1199	2.76	1.93	
4-C-3+	1200	5.46	2.02	
4-C-12*	1201	3.96	1.65	
4-C-17*	1205	3.54	1.83	
4-C-10+	1249	4.20	2.28	2.65
4-C-3+	1250	3.94	2.23	
4-C-2+	1296	3.76	3.00	
4-C-14+	1301	3.96	2.94	
4-C-11+	1347	2.76	4.06	4.06
4-C-6+	1348	2.70	3.61	
4-C-7+	1398	1.80	4.81	4.76
4-C-15+	1401	1.86	5.10	
4-C-9+	1446	1.44	6.06	5.65
4-C-16+	1449	1.38	5.80	

*Phase boundary movement determinations.

+Grube analysis.

Fig. 17. Arrhenius plot of the chemical diffusion data with the 90% confidence interval.

The confidence limits for D_0 and Q are given in Appendix B. The chemical diffusivity values obtained by AES were not included in the data to obtain Eq. (13) because of the larger error in the measured diffusivities. The results obtained from the AES technique, however, agree with the other data within the experimental error.

In Fig. 18 the chemical diffusion data are plotted with the least-squares fit and confidence interval of the tracer data (see Appendix A). The tracer and chemical diffusion results belong to the same data set statistically and, therefore, have been combined to obtain a comprehensive value for oxygen diffusion in β -Zircaloy-4

$$D = 2.48 \times 10^{-2} \exp(-28200/RT) \text{ cm}^2/\text{s} . \quad (14)$$

The confidence limits for D_0 and Q are given in Appendix B. The uncertainty in D based on the 90% confidence interval for the combined data varies from $\pm 4\%$ at 1250°C (2283°F) to $\pm 9\%$ at 1000°C (1832°F) and $\pm 7\%$ at 1500°C (2732°F).

In the autoradiograph of the chemical diffusion specimens, segregation of oxygen was evident as can be seen in Fig. 19 a-c. The segregation is easily related to phase structure seen in the cross-section of the specimen. The specimens were heavily etched so that portions of the weld position are visible. The segregation, which occurred during the β to α transformation upon cooling from the diffusion temperature did not affect the microphotometer measurements because the microphotometer slit was 1.2 mm wide, which is much larger than the microstructural variations, and traces were averaged over the 5 mm width of the activated area of the specimen. The AES measurements had more scatter which may partially be caused by the segregation because a relatively narrow path (100 μm wide) was analyzed.

The tracer diffusivity of oxygen-18 in pure zirconium and Zircaloy-2 was measured at 1000, 1200, and 1400°C (1832 , 2192 , and 2552°F). The results are listed in Table 5 and plotted in Fig. 20 with the least-squares fit to the tracer data for Zircaloy-4. The oxygen diffusivity is statistically identical in the three materials.

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Fig. 18. Comparison of the chemical diffusion data to the tracer diffusion results.

a

Fig. 19. Comparison of the segregation in the autoradiographs of the chemical diffusion specimens to the microstructure for a) 4-C-12, b) 4-C-16, and c) 4-C-3.

Y-135292

Y-135290

Fig. 19b

Fig. 19c

Table 5. Tracer Diffusivity Data in β -Zircaloy-2 and β -Zirconium

Specimen	Temperature (°C)	Time (sec) $\times 10^{-3}$	Diffusivity (cm^2/sec) $\times 10^7$
Z-T-2	1004	30.8	0.400
Z-T-6	1006	33.7	0.361
Z-T-1	1198	6.21	1.79
Z-T-3	1198	5.61	1.65
Z-T-4	1395	2.64	3.97
Z-T-5	1401	2.42	4.05
2-T-1	998	28.4	0.345
2-T-3	1000	30.7	0.403
2-T-2	1197	5.76	1.39
2-T-6	1198	6.02	2.02
2-T-4	1393	2.36	4.91
2-T-5	1397	2.46	4.56

Fig. 20. Comparison of the tracer diffusion of oxygen-18 in β -Zircaloy-4, β -Zircaloy-2 and pure zirconium.

ERROR ANALYSIS

To determine the uncertainty in the results of the diffusion measurements both a statistical analysis of the data and an error analysis of the steps of the experimental program can be used. The statistical analysis is a measure of the reproducibility of the diffusion measurements, and the error analysis gives an indication of the maximum error that may be present in a given diffusivity measurement.

The statistical treatment indicated that the most useful measure of the uncertainty in the results is the calculation of the confidence limits about the best fit to the data. The method of treatment of the data is given in Appendix B. The confidence intervals for the chemical diffusivity results, the tracer diffusivity results, and the combined data set are given in Table 6 at the mean and extremes of the temperature observations for each data set. Thus, the uncertainty in the expected value of the diffusivity from the combined data set is less than $\pm 10\%$ over the entire temperature range.

The error analysis is used to determine an uncertainty in the resultant diffusivity arising from each step of the experimental procedure, and by assuming that these uncertainties are additive, the maximum

Table 6. 90% Confidence Intervals for the Diffusivity Values
(Percent deviation from the expected value)

	Upper Limit	Midpoint	Lower Limit
Tracer Diffusivity	1500°C +11.6, -10.5	1250°C +6.5, -6.1	1000°C +14.0, -12.2
Chemical Diffusivity	1450°C +8.3, -7.7	1300°C +4.6, -4.4	1100°C +8.5, -8.0
Combined Data	1500°C +10.0, -9.1	1250°C +4.2, -3.9	1000°C +7.8, -7.2

uncertainty is obtained for the measured value. This method can only account for determinant errors; indeterminant errors, which by definition are undefined and indeterminable, may also be present. The results of the error analysis indicate an uncertainty of from $\pm 13\%$ at 900°C (1652°F) to $\pm 17\%$ at 1500°C (2732°F). The indeterminant errors could contribute an uncertainty of up to twice that magnitude. The error analysis is outlined in Appendix C.

DISCUSSION

Chemical Diffusion

The results from the chemical diffusion specimens have shown that the chemical diffusivity of oxygen in β -Zircaloy-4 is independent of the oxygen concentration from 0.1 to 0.6 wt % oxygen. The chemical diffusion coefficient can be described by

$$D_0 = B_0 RT(1 + d \ln \gamma_0 / d \ln N_0) , \quad (15)$$

where B_0 is the oxygen mobility in the Zircaloy-4 lattice, N_0 is the atomic fraction of oxygen present, and γ_0 is the activity coefficient which relates the oxygen activity to the oxygen concentration. The effect of the oxygen concentration gradient upon the diffusivity is contained in the term relating the activity coefficient to the oxygen concentration. Because D_0 is independent of N_0 , γ_0 must also be constant, which indicates that Henry's Law is obeyed in the range of relatively dilute oxygen concentrations studied in this investigation. Therefore, the oxygen interstitial atoms must be sufficiently separated so that they do not interact. In such a case the expression for the chemical diffusivity reduces to $D_0 = B_0 RT$. Because the oxygen interstitial mobility should be equivalent in a chemical diffusion experiment and a tracer diffusion experiment, the tracer diffusivity, which is defined as $D_0^* = B_0^* RT$, should be the same as the chemical diffusivity. The experimental results, Fig. 18, indicate that the chemical and tracer diffusivities are, indeed, equivalent.

Therefore, the two sets of data were combined to obtain the temperature dependence of the oxygen diffusivity as given in Eq. (14).

Diffusion in the $\alpha + \beta$ Region

Below 1000°C (1832°F) the tracer diffusivity dropped sharply with decreasing temperature in the two phase $\alpha + \beta$ mixture. In Fig. 21 the diffusivity of oxygen in the α and β phases are shown along with the diffusivities obtained in the the $\alpha + \beta$ mixture. A linear extrapolation of the data for the $\alpha + \beta$ mixture intercepts the curve for β at 990°C (1814°F) and the curve for α at 815°C (1499°F). Because the dominate effect on the oxygen diffusivity in the mixture will be the $\alpha:\beta$ ratio, the extrapolation should intersect the α and β curves at the $\alpha \rightleftharpoons \alpha + \beta$ and $\alpha + \beta \rightleftharpoons \beta$ equilibrium temperatures, respectively. The oxygen content of the specimens was 0.12 wt %; therefore, the data agree well with the phase diagram, Fig. 2. The results for the $\alpha + \beta$ mixture will be dependent upon the oxygen content of the Zircaloy.

Fig. 21. Arrhenius plot of the diffusivity of oxygen in α and β zirconium and the $\alpha + \beta$ mixture.

Oxygen Segregation

The segregation of oxygen in the Zircaloy-4 chemical diffusion specimens (see Fig. 19) occurs because the cooling rate through the transformation region, 990 to 815°C (1814–1499°F), is approximately 40°C/min (72°F/min) (see Fig. 7). Ostberg¹⁸ has generated an isothermal transformation diagram for Zircaloy-2 (Fig. 22) which should closely approximate that for Zircaloy-4. Obviously the cooling rate after an anneal is too slow for the beta to transform to alpha martensitically. Rather, while the specimen is in the $\alpha + \beta$ region, transformation occurs by a nucleation and growth mechanism, and time is available for the oxygen to segregate between the α and β phases during cooling. The specimen may be in the two-phase region for times up to three minutes. The duplex structure that is formed consists of relatively coarse α platelets, which preferentially absorb oxygen from the remaining β as they grow. Significant oxygen enrichment of the alpha platelets is possible because of the high diffusivity of oxygen in the beta phase. At 900°C (1652°F) D is 2.5×10^{-8} cm²/s, and the diffusion distance for oxygen in a three minute period is estimated to be about 4.3×10^{-3} cm. This result is consistent with the thickness and spacing of the α platelets (5×10^{-3} cm).

Fig. 22. Isothermal transformation diagram (TTT curve) for Zircaloy-2. After Ostberg¹⁸

Diffusion Mechanism

For many years Snoek's¹⁹ model has been used to describe the diffusion mechanism of interstitial solutes in body-centered-cubic metals. Snoek's model assumes that the interstitial atom occupies octahedral sites in the lattice and jumps from one octahedral site to an adjacent one (0-0). This model has been shown to be a correct representation of the diffusion mechanism for interstitials in many bcc metals.⁶ A model developed by Wert and Zener for interstitial diffusion²⁰ can be used to calculate the activation entropy for the diffusion process from D_0 . This model is based on a kinetics approach to the diffusion process. Assuming that Snoek's model is applicable, the activation entropy for the atom jump is

$$S_m^k = k \ln \left(\frac{3}{2} \frac{D_0}{\gamma \alpha^2} \right), \quad (16)$$

where

γ is the frequency of vibration of a solute atom in an octahedral interstitial position,

α is the distance between octahedral sites,

k is Boltzmann's constant, and

D_0 is the pre-exponential term of the diffusion equation.

The vibration frequency is approximately

$$\gamma = \left[\frac{Q}{2m \alpha^2} \right]^{1/2}, \quad (17)$$

where m is the mass of the diffusing species. From our values for D_0 and Q , the vibration frequency for an interstitial oxygen atom in β -zirconium is approximately $8.6 \times 10^{12} \text{sec}^{-1}$, and $\Delta S_m^k/k$ is approximately 2.59. The uncertainty in D_0 causes an uncertainty of $\pm 10\%$ in ΔS_m^k .

An alternate thermodynamical approach for calculating the activation entropy has been developed by Zener based on a strain energy argument.²¹ In this approach the activation entropy is given by

$$\Delta S_m^t \approx \beta \frac{Q}{T_m}, \quad (18)$$

where T_m is the solvent melting point and

$$\beta \equiv \frac{T_m}{\mu} \frac{d\mu}{dT}, \quad (19)$$

where μ is an appropriate elastic constant, although which one "is appropriate is uncertain."⁶ The values of β obtained for several bcc metals indicate that an average value of 0.4 might be used for β -zirconium.⁶ From Eq. (18) $\Delta S_m^t/k$ is then approximately 2.68.

In order to determine the applicability of Snoek's model, the ratio

$$\lambda = \Delta S_m^k / \Delta S_m^t \quad (20)$$

has been obtained for several systems involving the diffusion of interstitial atoms in bcc metals.⁶ In those systems for which Snoek's model seems applicable, λ was found empirically to fall in the range of 0.55 ± 0.20 . For oxygen diffusion in β -zirconium λ is 0.97 ± 0.10 . Although the value assumed for β is rather uncertain, it may be tentatively concluded that the diffusion mechanism in this system may not be described by Snoek's model. This is in accord with the results for oxygen diffusion in vanadium and niobium. The oxygen atoms may occupy tetrahedral sites in β -zirconium as has been suggested for oxygen in vanadium and niobium.²² Also the jump processes may vary if the tetrahedral sites are involved significantly because octahedral-tetrahedral-octahedral (O-T-O) and octahedral-tetrahedral-tetrahedral-octahedral (O-T-T-O) jumps paths may occur. Either of these possibilities would change the results obtained for ΔS_m^k ; thus affecting λ .

Comparisons with Other Data

As was pointed out in the Introduction, previous determinations of the diffusivity of oxygen in β -Zircaloy or β -zirconium were made by Mallett, et al.,² Debuigne,² Schmidt, et al.,⁴ and Dechamps, et al.⁵ These data are shown in Fig. 23 along with the best estimate line for our tracer data, the latter being statistically indistinguishable from our combined tracer and chemical diffusion data set.

The Schmidt results consist of three data points at temperatures outside the range of our measurements, and Dechamps reported but a single diffusivity value. Thus for purposes of comparison, only the data of Mallett and of Debuigne need be considered, although the Schmidt data are reasonably consistent with an extrapolation of both our results and those of Mallett and Debuigne as well.

As may be seen, the activation energy calculated from our data agrees almost exactly with that from Mallett's data, although the pre-exponential terms differ by a factor of two. The Debuigne results exhibit a higher activation energy but a still smaller pre-exponential term, yielding diffusivity values 2 to 4 times smaller than ours in the temperature range of Debuigne's determinations. We have shown previously¹⁶ on the basis of F tests that these three data sets are significantly different at the 5% significance level.

We do not know the source of this disagreement. Rather different techniques were used in each of the three investigations, but there is no *a priori* reason to consider any of the methods suspect. Different materials were used in each study: Zircaloy 2 and 3 by Mallett, pure zirconium by Debuigne, and Zircaloy-4 by us. However, the good agreement we obtained among diffusivity values in pure zirconium, β -Zircaloy-2, and Zircaloy-4 (see Fig. 20) and the corresponding agreement in Mallett's results for Zircaloy-2 and 3 (see Fig. 3) indicate that small alloying additions do not influence the diffusion of oxygen in zirconium. Thus one is led to the conclusion that systematic errors of some sort exist in at least two of the three sets of measurements.

Fig. 23. Comparison of the results of the present investigation to the previous studies.

Systematic, indeterminant errors, by their very nature, are generally impossible to detect in data gathered by a single technique; however, the existence of such errors can be demonstrated through a comparison of similar data sets obtained by two or more independent methods. It was for this purpose that we supplemented the results of the ^{18}O radioactivation technique with diffusivity determinations obtained by Auger Electron Spectroscopy and by boundary movement measurements. As already discussed (see Fig. 17), chemical diffusion data gathered by all three techniques agree well, and the three data sets are statistically indistinguishable at the 5% significance level as demonstrated by F tests. Similar agreement was observed among our data obtained under three different sets of boundary conditions (tracer, chemical, and boundary movement measurements). These results give us confidence that our experimental procedures do not contain large systematic errors and that our estimates of the diffusivity values are correct within the error limits stipulated in the Error Analysis Section (see Table 6, p. 39).

Relationship to Other Light Water Reactor Safety Programs

This study of the diffusivity of oxygen in beta-Zircaloy is a part of the Separate Effects Program sponsored by the Division of Reactor Safety Research of NRC, and, as such, our results will contribute to the final integrated analysis of the data obtained from all the different research projects that make up this program. Our measurements are significant because the diffusivity of oxygen in beta Zircaloy influences the distribution of oxygen in the fuel cladding during a hypothetical LOCA. More importantly, the diffusivity determines the flux of oxygen into the beta region, thus bearing on the problem of the loss of ductility and the embrittlement of the beta occasioned by increases in its oxygen content. It should be borne in mind that the properties of the beta region can also be influenced by other factors, e.g., the existence of alpha incursions into the beta, that may be even more important than the total oxygen content itself. Nevertheless, these new results show that the diffusivity of oxygen in beta-Zircaloy is only half of the currently accepted value obtained from the Mallett data.² Thus, all other things being equal, using the new data rather than those of Mallett, one would calculate a smaller oxygen concentration in the beta after a postulated reactor accident.

Diffusivity of Oxygen-16

Because oxygen-16 is the most abundant isotope of oxygen in the atmosphere (>99%), it is desirable to obtain the diffusivity of that isotope also. To relate the diffusivities of different isotopes of the same element, the activation energy for migration is assumed to be independent of the isotopic mass. If the vibrational frequencies of the two species follow the classical relationship given in Eq. (17), the mass dependence of the diffusion coefficients of the two species is

$$\frac{D_1}{D_2} = \frac{\gamma_1}{\gamma_2} = \left(\frac{m_2}{m_1} \right)^{1/2} . \quad (21)$$

Therefore, the diffusivity of oxygen-16 will be approximately 6% greater than the diffusivity of oxygen-18. This increase will be contained in the pre-exponential portion of the Arrhenius expression (Eq. 1) for the diffusivity. Thus, the diffusivity of oxygen-16 based on the combined data set is given by

$$D = 2.63 \times 10^{-2} \exp(-28200/RT) \text{ cm}^2/\text{s} . \quad (22)$$

This will not significantly effect the comparison of the current data set to the results of previous investigators.

CONCLUSIONS

- 1) The chemical diffusivity of oxygen in β -Zircaloy-4 is independent of the oxygen concentration.
- 2) The tracer and chemical diffusivity of oxygen in β -Zircaloy-4 are equivalent, and the temperature dependence of the diffusivity is

$$D = 2.43 \times 10^{-2} \exp[-28200/RT] \text{ cm}^2/\text{s} \text{ for oxygen-18 and}$$

$$D = 2.63 \times 10^{-2} \exp[-28200/RT] \text{ cm}^2/\text{s} \text{ for oxygen-16.}$$

3) The diffusivity of oxygen is the same in β -Zircaloy-4, β -Zircaloy-7, and pure zirconium.

4) Between 900 and 815°C (1652–1499°F) the apparent diffusivity of oxygen decreases sharply because at these temperatures Zircaloy-4 containing 0.11 wt % oxygen exists as a two-phase $\alpha + \beta$ mixture.

5) Between 1000 and 1500°C (1832–2732°F) the diffusivities measured in the present study are approximately half the currently accepted values derived from the data of Mallett, et al.²

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APPENDIX A

COMPARISON OF DATA SETS

Three techniques were used to obtain the chemical diffusivity values listed in Table 4. In order to test if the data from each method represents the same data population, the linear diffusion rate model

$$\ln D = \ln D_0 - (Q/R) \cdot 1/T \quad (A-1)$$

was fit to each data set and to the combined data set. By calculating the sum of squares of errors, $SSE = \sum_{i=1}^N (\text{observed-predicted})^2$ for the N data points in each set and the combined set, the hypothesis that the slope and intercept for each set are equivalent can be tested by the F-statistic. The F-statistic is

$$F = \frac{(SSE_C - SSE_{PBM} - SSE_A - SSE_G)/(dF_C - dF_{PBM} - dF_A - dF_G)}{SSE_C/dF_C} \quad (A-2)$$

where

SSE is the sum of squares of error for the least squares fit of a linear fit to the data set on an Arrhenius plot;

dF is the degrees of freedom for the data set; and

PBM, A and G refer to the phase-boundary-movement, Auger Electron Spectroscopy, and Grube analysis methods, respectively, with C referring to the combined data set.

The necessary values for Eq. (A-2) are given in Table A-1. The F-statistic is 1.85, which is not larger than the critical F-value, $F(4,20) = 4.35$ with four and twenty degrees of freedom at the 5% significance level. This indicates that the three data sets can be considered as one data set to estimate $\ln D_0$ and (Q/R) .

Table A-1. Sums of Squares for Error and Degrees of Freedom for the Sets

Data Set	Degrees of Freedom (df)	Sum of Squares for Error (SSE)
Tracer	23	0.5357
Chemical		
Auger Measurement	2	0.0007
Grube Analysis	9	0.0300
Phase Boundary Movement	5	0.0643
Combined	20	0.1505
Total Combined	41	0.7110

The tracer diffusivity and chemical diffusivity data were also tested to determine if they could be considered as part of the same data set. The F-statistic for this case is

$$F = \frac{(SSE_C - SSE_{CH} - SSE_{TR}) / (df_C - df_{CH} - df_{TR})}{SSE_C / df_C} \quad (A-3)$$

where CH, TR, and C refer to the chemical diffusivity, tracer diffusivity, and combined data sets, respectively.

Since the F-statistic, $F = 1.69$, calculated using the values in Table A-1, is not larger than the critical F-value, $F(2,39) = 3.24$, with 2 and 39 degrees of freedom at the 5% significance level, the hypothesis that the combined data set can be used to estimate $\ln D_0$ and (Q/R) was accepted.

APPENDIX B

STATISTICAL TREATMENT OF THE DIFFUSION DATA

INTRODUCTION

The immediate goal of this study was to provide a reliable means for calculating the diffusion coefficient of oxygen in β -Zircaloy-4 as a function of temperature. Implicit in this aim is the need to specify uncertainty limits on predicted diffusivities. One approach to this problem is to perform a statistical analysis of the data, which results in a probability statement of the uncertainty based on the actual scatter of the experimental data about best estimate values.

It should be borne in mind, however, that in providing a "best estimate" and uncertainty limits for the quantity being measured, statistics provides no information regarding the "real" value of that quantity. Statistical results simply reflect the character of the data. If, on the other hand, one can assure himself by independent checks as we have done that a given data set contains no significant systematic errors, statistical methods are particularly powerful in establishing realistic and objective limits for a set of experimental data.

The procedures used in the statistical treatment of the data of this study are described in this Appendix. A different approach to error analysis is considered in Appendix C.

DATA TREATMENT

The experimental diffusivity values were fitted to the standard Arrhenius equation for diffusion

$$D = D_0 \exp(-Q/RT) \quad (B-1)$$

where

- D is the diffusion coefficient,
- R is the gas constant (1.987 cal/mole/°K), and
- T is the absolute temperature.

This equation was linearized to obtain

$$\ln D = \ln D_0 - (Q/RT) , \quad (B-2)$$

and the two constants, D_0 and Q , were estimated on the basis of standard least squares methods. Under the assumption that the logarithms of the observations, $\ln D_i$, are normally distributed, confidence intervals for the predicted values and the estimators were calculated. The validity of the normal assumption was checked by examining the residuals ($\epsilon_i = \text{observed value} - \text{predicted value}$) from the linearized diffusion rate model, Eq. (B-2).

Data

As described in the body of the report, the diffusivity data consisted of two types, tracer (4-T) and chemical (18-C); both are tabulated in Table B-1. For the reasons given previously, diffusivity values obtained below 1000°C (1832°F) are omitted from the tracer data set, and in the final calculations the AES measurements were also deleted because of the relatively large error limits assigned them. Thus there are 25 tracer diffusivity measurements, $3.01 \times 10^{-7} \leq D \leq 9.20 \times 10^{-6}$, made over a temperature range of 1001 to 1504°C (1834–2739°F). The 18 chemical diffusion measurements, $8.01 \times 10^{-7} \leq D \leq 6.06 \times 10^{-6}$ were made between 1099 and 1449°C (2010–2640°F). Furthermore, as discussed in Appendix A, the chemical and tracer measurements are statistically indistinguishable from each other at the 5% significance level, thus making it possible to consider a combined data set consisting of a total of 43 observations.

Prediction Equations

In treating the data, an actual experimental observation, $\ln D_i$, $i = 1, 2, \dots, N$, is assumed to deviate from the predictions of the linearized diffusion rate model by an experimental random error, ϵ_i . Thus $\ln D_i = \ln D_0 - (Q/RT) + \epsilon_i$. The prediction model, $\ln \hat{D}_i$, is found by estimating $\ln D_0$ by $\ln \hat{D}_0$ and Q/R by Q/R to minimize the sum of the squares of the errors, $\sum_{i=1}^N \epsilon_i^2$. This procedure is, of course, simply the least squares estimation method, and the resulting prediction equation for the combined data set, $1001 \leq T \leq 1504^\circ\text{C}$ ($1834 \leq T \leq 2739^\circ\text{F}$) is

$$\ln \hat{D} = -3.69674 - 14191.03/T, \quad (\text{B-3})$$

or

$$\hat{D} = 0.0248 \exp(-28198/RT). \quad (\text{B-4})$$

Confidence Intervals

To place confidence intervals about the coefficients and the expected values of the linearized diffusion rate model, the assumption is made that the random error variables, ϵ_i , are independent and identically distributed as a normal distribution with zero mean and constant variance, σ^2 . The variance can be estimated by

$$\hat{\sigma}^2 = \frac{1}{N} \sum_{i=1}^N (\text{Residuals})^2 / (N - 2), \quad (\text{B-5})$$

which for the combined data set becomes

$$\hat{\sigma}^2 = \frac{1}{43} \sum_{i=1}^{43} (\ln D_i - \ln \hat{D}_i)^2 / 41. \quad (\text{B-6})$$

The validity of the independent and random assumptions was checked by plotting the residuals versus $\ln \hat{D}_i$ and versus $(1/T)_i$. The graphs should be symmetrical about zero and have a random scatter. From a visual examination of the plots, no trends or outliers could be discerned.

The normal distribution assumption was tested by calculating the skewness, $\sqrt{b_1}$, and the kurtosis, b_2 , statistics for the residuals. For 43 observations (combined data set), the expected value of $\sqrt{b_1}$ and b_2 for the normal distribution are $E[\sqrt{b_1}] = 0$ and $E[b_2] = 2.86$, respectively. The calculated residual values were $\sqrt{b_1} = -0.30$ and $b_2 = 2.83$, which are not significantly different from the normal values at the 10% significance level.¹

The confidence intervals for the expected values of the different estimators may be calculated using the following estimated variances

$$\hat{\text{Var}} [\ln \hat{D}] = \hat{\sigma}^2 = 0.01734 \quad (\text{B-7})$$

$$\hat{\text{Var}} [\ln \hat{D}_0] = a_{11} \hat{\sigma}^2 = 0.04875 \quad (\text{B-8})$$

$$\hat{\text{Var}} [\hat{Q}/R] = a_{22} \hat{\sigma}^2 = 111831.77 \quad (\text{B-9})$$

and the covariance

$$\hat{\text{Cov}} [\ln \hat{D}_0, \hat{Q}/R] = a_{12} \hat{\sigma}^2 = 73.53, \quad (\text{B-10})$$

where

$$\begin{aligned} a_{11} &= 2.81157, \\ a_{22} &= 6449352.12, \text{ and} \\ a_{12} &= 4240.61. \end{aligned}$$

The $a_{ik} \hat{\sigma}^2$ are the coefficients of the variance-covariance matrix. The numerical values listed for the various quantities are for the combined data set, the a_{ik} 's being calculated from the expressions

$$a_{11} = \frac{\sum_{i=1}^{43} (1/T)_i^2}{43 \sum_{i=1}^{43} [(1/T)_i - (1/\bar{T})]^2} \quad (\text{B-11})$$

$$a_{22} = \frac{1}{\sum_{i=1}^{43} [(1/T)_i - (\bar{1/T})]^2} \quad (B-12)$$

$$a_{12} = \frac{(\bar{1/T})}{\sum_{i=1}^{43} [(1/T)_i - (\bar{1/T})]^2}, \quad (B-13)$$

where

$$\begin{aligned} (1/T)_i \text{'s} &= \text{the observed reciprocal temperature values and} \\ (\bar{1/T}) &= (1/43) \sum_{i=1}^{43} (1/T)_i. \end{aligned}$$

The estimated variance of a predicted value of $\ln D$ at a selected reciprocal temperature, $(1/T)_k$ is

$$\begin{aligned} \text{Var} [\ln D_k] &= \text{Var} [\ln D_o] + (1/T)_k^2 \text{Var} [Q/R] \\ &\quad - 2(1/T)_k \text{Cov} [\ln D_o, (Q/R)]. \end{aligned} \quad (B-14)$$

With these variance estimates, the confidence intervals for $\ln D_o$, (Q/R) , and $\ln D$ may be found. The general formula for a $(1 - \alpha)\%$ confidence interval for the expected value, ξ , of the estimator, $\hat{\xi}$, takes the form of a probability statement:

$$\Pr \{ \hat{\xi} - t_{\alpha/2} \sqrt{\text{Var}(\hat{\xi})} < \xi < \hat{\xi} + t_{\alpha/2} \sqrt{\text{Var}(\hat{\xi})} \} = 1 - \alpha, \quad (B-15)$$

where $t_{\alpha/2}$ is the $\alpha/2$ percentage point of the t-distribution with $N-2$ degrees of freedom.

Individual Confidence Limits

If a diffusivity data set is determined with the object of obtaining values of D_0 and Q because of interest in the relationship of these quantities to the jump frequency and activation energy for diffusion, then individual confidence intervals on the intercept and slope of the Arrhenius plot are appropriate for specifying uncertainty ranges for the individual estimators, $\ln D_0$ and $\hat{Q}$, irrespective of the other estimator. In such a case the quantity $\hat{V}ar(\hat{\xi})$ in Eq. (B-15) is replaced by $\hat{V}ar[\ln D_0]$ or $\hat{V}ar[\hat{Q}/R]$ from Eq. (B-8) or Eq. (B-9). Individual confidence intervals for the data from the current study are given in Table B-2. Assuming that $\hat{D} = \exp(\ln D)$ and that the estimated values of D_0 and Q may be obtained directly from $\ln D_0$ and (Q/R) , one may express the results in Table B-2 as percentage uncertainties on D_0 and Q . The following results were obtained from the results of this study:

Tracer diffusivity:

$$D = 3.01 \left(\begin{smallmatrix} +66\% \\ -40\% \end{smallmatrix} \right) \times 10^{-2} \exp[-(28809 \pm 5\%)/RT] \text{ cm}^2/\text{s} . \quad (\text{B-16})$$

Chemical diffusivity:

$$D = 1.32 \left(\begin{smallmatrix} +65\% \\ -40\% \end{smallmatrix} \right) \times 10^{-2} \exp[-(26220 \pm 6\%)/RT] \text{ cm}^2/\text{s} . \quad (\text{B-17})$$

Combined data set:

$$D = 2.48 \left(\begin{smallmatrix} +45\% \\ -31\% \end{smallmatrix} \right) \times 10^{-2} \exp[-(28198 \pm 4\%)/RT] \text{ cm}^2/\text{s} . \quad (\text{B-18})$$

Table B-2. Expected Values and 90% Confidence Intervals for the Estimators $\ln D_0$ and (Q/R)

		Lower Limit	Estimated Value	Upper Limit
Tracer	$\ln D_0$	-4.0147	-3.5048	-2.9948
Diffusivity	(Q/R)	13731	14499	15267
Chemical	$\ln D_0$	-4.8331	-4.3302	-3.8273
Diffusivity	(Q/R)	12438	13196	13965
Combined	$\ln D_0$	-4.0686	-3.6967	-3.3249
Data	(Q/R)	13628	14191	14754

Joint Confidence Intervals

If, as in the case of the present study, one's interest lies primarily in the predicted values for the diffusion coefficient itself rather than in those for D_0 and Q , Eqs. (B-16)–(B-18) are of no value because uncertainties on D_0 are Q correlated. The calculation of meaningful uncertainties on D (or $\ln D$) requires the use of Eq. (B-15) together with the estimated variance of the estimator of $\ln D$ at the particular inverse temperature, $(1/T)_k$, used. The results for the joint confidence intervals on the combined data set are given in Table B-1 and are summarized in percentage form for the extremes and mean of the temperature observations, $(1/T)_k$, in Table B-3. This and similar joint confidence intervals are shown graphically on several Arrhenius plots in the Results Section.

Table B-3. 90% Confidence Intervals for the Diffusivity Values
(Percent deviation from the expected value)

	Upper Limit	Midpoint	Lower Limit
Tracer	1500°C	1250°C	1000°C
Diffusivity	+11.6, -10.5	+6.5, -6.1	+14.0, -12.2
Chemical	1450°C	1300°C	1100°C
Diffusivity	+8.3, -7.7	+4.6, -4.4	+8.5, -8.0
Combined	1500°C	1250°C	1000°C
Data	+10.0, -9.1	+4.2, -3.9	+7.8, -7.2

It is worthwhile discussing the concept of a joint confidence interval further because many experimenters make the mistake of interpreting individual confidence limits simultaneously. Consider two experimentally determined coefficients, β_1 and β_2 (equivalent to $\ln D_0$ and Q/R , respectively), in a linear equation of the form $Y = \beta_1 + \beta_2 X$, that are correlated and for which individual confidence limits have been established. If the individual limits are applied simultaneously, it might be thought that the uncertainty on the total measured quantity ($\ln D$, in our case) would be represented by the rectangle defined by the dashed lines in

Fig. B-1. Such a representation is incorrect, however, because it fails to take into account the correlation between the estimators, b_1 and b_2 , of β_1 and β_2 .

Fig. B-1. Joint confidence interval for the parameters β_1 and β_2 . The estimators of β_1 and β_2 are b_1 and b_2 , respectively, and the individual confidence limits on b_1 and b_2 are indicated by the sets of perpendicular and horizontal dashed lines. After Draper and Smith.²

The correct joint confidence region on β_1 and β_2 is an elliptically shaped region (See Fig. B-1) defined by the equation

$$n(\beta_1 - b_1)^2 + 2 \sum_{i=1}^n X_i (\beta_1 - b_1)(\beta_2 - b_2) + \sum_{i=1}^n X_i^2 (\beta_2 - b_2)^2 \leq 2\hat{\sigma}^2 F(2, n-2, 1-\alpha), \quad (B-19)$$

where

X_i is the independent variable (equivalent to $1/T$),
 $F(2, n-2, 1-\alpha)$ is the α percentile point of the F-distribution with 2 and $n-2$ degrees of freedom.

This region has a $(1-\alpha)\%$ chance of containing the joint values of the intercept, β_1 , and the slope, β_2 , if the experimenter repeats his

experiment many times under identical conditions. The boundary of the region is found by equating the right and left hand sides of Eq. (B-19). (Another way of describing this ellipse is to identify it with the locus of the curve defined by the slopes and intercepts of all straight lines tangent to the confidence interval limits on an Arrhenius plot.) Note that the point E in Fig. B-1 could be erroneously regarded as a possible joint value of the intercept and slope if individual confidence limits are used to define the joint confidence region.

The joint confidence region for $\ln D_0$ and Q/R for our combined data set is shown in Fig. B-2. Only those combinations of $\ln D_0$ and Q/R values that define points inside or on the ellipse are consistent with this data set.

Fig. B-2. Joint confidence interval for $\ln D_0$ and Q/R for the combined diffusion data set.

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APPENDIX C

ERROR ANALYSIS BASED ON MAXIMUM ABSOLUTE ERROR
OF EXPERIMENTAL PROCEDURES

INTRODUCTION

As noted in Appendix B, a statistical treatment of a data set is helpful in obtaining best estimate values for parameters of interest and for establishing uncertainty limits for these estimates. Statistics, however, provides no information regarding the absolute values for these parameters. For this reason we have analyzed the various steps in the experimental procedures used in this study in order to arrive at estimates of the determinant errors inherent in each step. The maximum possible total determinant error was calculated under the assumption that errors related to individual steps of a given procedure are additive. We also give a rough value for the indeterminant errors in our measurements; this estimate is based on the actual scatter observed in the data, taking into account the important finding (see below) that no significant systematic errors exist in our data.

It should be emphasized that this form of error analysis does *not* provide realistic uncertainty limits for the best estimate values of the diffusion measurements. Rather it delineates a scatter band within which, to a very high level of confidence, all future measurements made by the identical procedures would be expected to fall.

DETERMINANT ERRORS

Determinant errors in the following areas were considered: 1) measurement of the diffusion anneal temperature, 2) determination of the time of the diffusion anneal, 3) bisection of the specimen, 4) obtaining the optical density from the microphotometer trace, 5) correction for the "broadening" effect, 6) measurement of the penetration distance and 7) uncertainty of the least squares fit to the oxygen profile. The four types of analysis which have been used will be examined.

Temperature Errors

The various errors involved with the temperature measurements have been examined, and the probable accuracy has been assessed to range from $\pm 1^\circ\text{C}$ (1.8°F) at 900°C (1652°F) to $\pm 2^\circ\text{C}$ (3.6°F) at 1500°C (2732°F).¹ Because the diffusivity can be described by the Arrhenius-type equation, Eq. (1), the uncertainty in the diffusivity value caused by the uncertainty in the measured temperature, assuming an activation energy of 28,200 cal/mole, can be calculated and is plotted in Fig. C-1. The uncertainty in the diffusivity values resulting from the inaccuracy of the temperature measurement decreases from 1.1% at 900°C (1652°F) to 0.9% at 1500°C (2732°F).

Fig. C-1. Effect of the uncertainty in the diffusion anneal temperature upon the diffusivity.

Time Determination Errors

The heating and cooling transients of the diffusion anneal cycle were evaluated using Eq. (4). The effective time at the anneal temperature arising from the heating and cooling transients for several specimens are listed in Table C-1. At least one correction was calculated for each annealing temperature. The average correction was 5.81 minutes with a standard deviation of 0.59 minutes. For the other anneals a standard time correction of 6 minutes was used, and the uncertainty in the time measurement was estimated to be ± 0.7 minute. This will cause an uncertainty in the total time of approximately $\pm 4.1\%$ at 1500°C (2732°F), $\pm 1.0\%$ at 1300°C (2372°F), $\pm 0.4\%$ at 1100°C (2012°F) and $\pm 0.04\%$ at 900°C (1652°F). As expected, the uncertainty associated with the time of the anneal becomes larger as the temperature increased with a corresponding decrease in the anneal time.

Table C-1. Anneal Time Corrections for the Heating and Cooling Transients of the Anneal Cycle

Anneal Temperature $^{\circ}\text{C}$	Anneal Time (min)	Heating Time (min)	Cooling Time (min)	Total Adjustment (min)
952	829	6.13	0.54	6.67
1001	522	4.10	1.39	5.49
1049	313	5.64	0.83	6.47
1098	186	4.87	0.76	5.63
1105	151	4.30	1.10	5.40
1149	137	5.65	0.90	6.55
1153	135	5.88	0.65	6.53
1198	102	4.36	0.88	5.24
1200	99	5.55	0.60	6.25
1249	60	4.80	0.87	5.67
1250	76	4.60	0.90	5.50
1296	57	4.88	0.81	5.67
1300	63	6.13	0.54	6.67
1309	59	4.17	0.63	4.80
1346	43	5.65	0.55	6.20
1347	44	4.52	0.82	5.34
1398	28	5.48	0.75	6.23
1445	18	4.54	0.50	5.04
1504	11	5.60	0.47	6.07

An additional uncertainty in the effective diffusion time arises from the oxygen-18 oxidation procedure for the tracer diffusion specimens and the welding procedure for the chemical diffusion specimens. The maximum effective time at temperature for the diffusion anneal resulting from the oxidation procedure of 15 minutes at 800°C (1472°F) would be approximately 5 min (+0.3%) at 900°C (1652°F), 51 s (+0.3%) at 1100°C (2012°F), 14 s (+0.4%) at 1300°C (2372°F), and 5 s (+0.4%) at 1500°C (2732°F). The welding procedure for the chemical diffusion specimens, 10 min at 1000°C (1832°F), would result in an effective time at the diffusion temperature of up to approximately 4.4 min (+2.2%) at 1100°C (2012°F), 1.2 min (+2.4%) at 1300°C (2372°F) and 0.4 min (+2.5%) at 1500°C (2732°F). Because the exact time of welding is not known, the calculated uncertainty represents the maximum contribution.

The tracer diffusivity is calculated from the slopes of plots of $\ln O.D.$ versus x^2 such as those shown in Fig. 13 using the expression

$$D = \left[4 \left(\frac{\partial \ln O.D.}{\partial x^2} \right) t \right]^{-1} \quad (C-1)$$

In the Grube analysis and the phase boundary movement technique the product of Dt is obtained as shown in Eq. (8) and Eq. (10), respectively. Therefore, the uncertainty in the time measurement will yield an uncertainty of similar magnitude in the diffusivity for each technique. Because the diffusivity is inversely proportional to the time, the uncertainty in the time cannot be directly applied to the diffusivity, but, as shown in Appendix D, it is an adequate approximation.

Penetration Distance Errors

Before the specimens can be bombarded with protons or analyzed with AES, they must be bisected parallel to the diffusion direction to obtain the surface on which the oxygen profile is measured. If the specimen is not cut exactly perpendicular to the surface, an error in

the penetration distance measurement will result. The maximum amount of nonperpendicularity is estimated to be three degrees, which would cause an uncertainty of up to +0.15% in the distance measurements. This would result in an uncertainty of up to +0.3% for the tracer diffusivities and an uncertainty of up to +0.3% for the chemical diffusivities calculated using the Grube analysis. The maximum uncertainty resulting from the phase boundary movement technique would be -0.3%.

Another source of error in measuring the penetration distance is associated with aligning the microphotometer or AES path parallel with the diffusion direction. The alignment was within $\pm 2^\circ$ of the diffusion direction, which would cause an uncertainty of up to +0.11% in the distance measurement. This would cause an uncertainty of up to +0.2% in the tracer diffusivity and +0.6% for the chemical diffusivity using the Grube analysis. The position relative to the end of the specimen must be determined for the tracer diffusion measurements. This can be determined to within about ± 0.025 mm which would cause an uncertainty of about $\pm 0.2\%$ in the diffusivity. The accuracy of the distance scale on the microphotometer was checked against a calibrated reticle and was found to be correct to ± 0.005 mm. Therefore; no additional uncertainty beyond that attributable to the bisection and alignment procedures was assigned.

Optical Density Measurement Errors

A typical microphotometer trace for a tracer diffusion specimen is shown in Fig. 11a (see p. 19). Because of the "noise" in the trace, the determination of the background level will have some uncertainty. The background for the profile in Fig. 11a is indicated by the horizontal line; the average percent transmission in this region is 74.6% with a standard deviation of $\pm 0.78\%$. The background is fairly well defined because care was taken to insure that a fairly wide background region was present for each specimen. The uncertainty in the optical density of the background was about $\pm 2.5\%$, which was shown graphically to result in an uncertainty of about $\pm 7.0\%$ in the diffusivity value. Because

four profiles are averaged for each specimen, a maximum uncertainty of about $\pm 4.0\%$ in the diffusivity is more appropriate.

For the phase boundary movement technique the dimensionless parameter γ is calculated from the concentration ratio in Eq. (9). A $\pm 2.5\%$ uncertainty in the background would cause a $\pm 3.6\%$ uncertainty in the value of γ ; however, because the results of four profiles are averaged, the maximum uncertainty in the diffusivity would be about $\pm 2.0\%$. An uncertainty of about $\pm 5.5\%$ in the diffusivity calculated using the Grube technique will result from a $\pm 2.5\%$ uncertainty in the background. Again, because four profiles are averaged, the maximum uncertainty in the diffusivity would be about $\pm 3.0\%$. For the Auger analysis the background uncertainty was about $\pm 4.0\%$, which caused an uncertainty of about $\pm 8.8\%$ in the diffusivity values.

The cause of the "broadening" effect and the broadening profile, Fig. 10, were discussed in the experimental section. In order to determine if the broadening effect was significant, a matrix inversion technique was used to correct the optical density curve. The results, Table C-2, indicate that the slope $\partial \ln c / \partial x^2$, increased an average of 0.5% for the tracer diffusion profile. The standard deviation was 0.68% . The

Table C-2. Effect of the "Broadening" Correction Upon the Optical Density Profile for Tracer Diffusion Specimens

Specimen	$\frac{\partial \ln \text{O.D.}}{\partial x^2}$ (original)	$\frac{\partial \ln \text{O.D.}}{\partial x^2}$ (corrected)	$\frac{\text{Original-Corrected} \times 100}{\text{original}}$
4-T-21	-33.963	-34.514	-1.62
4-T-23	-28.814	-28.641	0.60
4-T-25	-34.129	-34.165	-0.11
4-T-26	-30.465	-30.310	-0.51
4-T-27	-27.807	-27.937	-0.47
4-T-28	-33.418	-33.587	-0.51
4-T-29	-28.862	-29.117	-0.88

slope should actually be smaller after a broadening correction is made,² so it was concluded that the correction was insignificant. A similar inversion of the chemical diffusion profiles indicated negligible change in the center portion of the profile that was used to calculate the diffusivity. A similar adjustment for the AES measurements might have been necessary if a large electron beam had been used, but no correction was necessary for the small beam (10 μm).

Least-Squares Fit to the Data

The slope from which the diffusivity is calculated for the tracer diffusivity and Grube analysis is obtained from a least squares fit to the data. In Table C-3 the slopes for several tracer diffusion specimens

Table C-3. Confidence Limits for $d \ln \text{O.D.} / d x^2$ from the Least-Square Fits to the Tracer Diffusion Profiles

	$\frac{d \ln \text{O.D.}}{d x^2 (\text{cm}^{-2})}$	95% Confidence Limit	Z
4-T-13	21.529	± 0.450	2.1
4-T-14	19.757	± 1.024	5.2
4-T-15	26.783	± 1.356	5.1
4-T-16	24.894	± 1.598	6.4
4-T-17	20.791	± 0.617	3.0
4-T-18	19.708	± 0.849	4.3
4-T-19	19.743	± 0.757	3.8
4-T-21	33.963	± 0.925	2.7
4-T-22	22.569	± 0.880	3.9
4-T-23	28.814	± 0.676	2.3
4-T-24	22.476	± 1.235	5.5
4-T-25	34.129	± 1.055	3.1
4-T-26	30.465	± 1.366	4.5
4-T-27	27.807	± 1.769	6.4
4-T-28	33.418	± 0.680	2.0
4-T-29	28.862	± 0.659	2.3
4-T-31	27.596	± 0.511	1.9
4-T-38	37.838	± 1.068	2.8
4-T-39	28.727	± 1.820	6.3
4-T-40	25.616	± 0.456	1.8

are listed along with the 95% confidence limits. The confidence limits were calculated assuming that the points are randomly distributed. While it is evident from Fig. 13 that this condition is not strictly met and that, therefore, the calculation is only an approximate one, the use of confidence limits to estimate the slope errors appears reasonable. The average confidence limit for the slopes of all of the penetration profiles listed in Table C-3 is $\pm 3.8\%$ with a standard deviation, σ , of 1.6% . Therefore, the maximum average uncertainty in the diffusivity arising from the uncertainty in the slope is approximately $\pm(3.8 + 2\sigma)\%$ or $\pm 7.0\%$. The uncertainty in the least squares fit to the optical density data for the Grube analysis using Eq. (8) is shown in Table C-4. The average uncertainty for the 95% confidence limit of the slope is $\pm 1.7\%$

Table C-4. Confidence Limits for $d \operatorname{erf}^{-1}(2c - 1)/dx$ from the Least-Square Fits to the Chemical Diffusion Profiles

Specimen	$\frac{d \operatorname{erf}^{-1}(2c - 1)}{dx}$ (cm^{-1})	95% Confidence Limit	%
18-C-2	-4.707	± 0.034	0.72
18-C-3	-5.333	± 0.087	1.63
18-C-6	-5.067	± 0.123	2.42
18-C-7	-5.372	± 0.064	1.20
18-C-8	-4.741	± 0.076	1.60
18-C-9	-5.354	± 0.085	1.59
18-C-10	-5.106	± 0.092	1.80
18-C-11	-4.811	± 0.064	1.33
18-C-14	-4.633	± 0.048	1.04
18-C-15	-5.133	± 0.132	2.57
18-C-16	-5.589	± 0.125	2.21

with a standard deviation of $\pm 0.68\%$. This would result in a maximum uncertainty of $\pm 5.8\%$ in the diffusivity. Table C-5 contains the 95% confidence limits for the Auger results. The scatter in the data as shown in Fig. C-2 is random and could be partially caused by the segregation of oxygen in the specimen. Because of the limited number

Table C-5. Confidence Limits for $d \operatorname{erf}^{-1}(2c - 1)/dx$ from the Least-Squares Fits to the Chemical Diffusion Profiles Obtained by AES for the Grube Analysis

Specimen	$\frac{d \operatorname{erf}^{-1}(2c - 1)}{dx}$ (cm^{-1})	95% Confidence Limit	Uncertainty in slope %	Uncertainty in D %
18-C-7	-5.434	± 0.188	3.46	± 7.0
18-C-9	-5.546	± 0.808	14.57	± 29.2
18-C-10	-4.758	± 0.239	5.02	± 10.0
18-C-11	-4.018	± 0.353	8.78	± 17.6

Fig. C-2. The oxygen concentration profile for specimen 4-C-7 measured by Auger Electron Spectroscopy.

of Auger measurements, no average uncertainty was determined; however, it is obvious that the Auger results have a greater uncertainty than the radioactivation results. The uncertainty for the diffusivity for each specimen is given in Table C-5. In Table C-6, $\pm 10\%$ is listed as a rough indication of the uncertainty present.

Measurement of Phase Boundary Position

An additional source of error in the phase boundary movement technique involves the location of the original $\alpha + \beta/\beta$ interface, which was the weld interface. This could be determined to within ± 0.025 mm, which would cause an uncertainty of about $\pm 3.1\%$ in the diffusivity value. An uncertainty of about ± 0.025 mm was also present in measuring the width of the $\alpha + \beta$ region from the autoradiograph after the anneal. This causes an additional uncertainty of 3.1%.

Maximum Total Determinant Error

The determinant error limits for each step in the various procedures used are listed in Table C-6, and the maximum total determinant error for each technique was computed on the assumption that all errors are additive. The maximum uncertainties range from $\pm 13\%$ to $\pm 17\%$ between 900 and 1500°C (1652–2732°F) for the ^{18}O radioactivation method and $\pm 12\%$ in the more limited temperature regime of the boundary movement measurements. The AES method had a greater uncertainty ($\pm 25\%$) because of the greater scatter in the oxygen profile.

It should be emphasized that the error limits given in Table C-6 are for determinant errors only, and it is likely that indeterminant errors, i.e., errors of unknown magnitude and unidentifiable sources, also exist in the experimental techniques used. In fact, a close examination of the experimental data will reveal that approximately 10% of the experimental data points differ from the best estimate values by more than the error limits given in Table C-6. It is, of course, possible that the ranges cited for the determinant errors are too small, but the error limits in Table C-6 represent our best estimates, and we are, therefore, inclined to feel that the additional uncertainty in the data is indeterminant in nature.

Table C-6. Summary of the Uncertainties in the Diffusion Coefficients from the Determinant Errors in the Experimental Procedures

Measurement	Chemical Diffusivity									
	Tracer Diffusivity				Grube		Phase Boundary		Auger	
	900°C	1100°C	1300°C	1500°C	1300°C	1500°C	1100°C	1300°C	1300°C	1500°C
Temperature	±1.1%	±1.0%	±1.0%	±0.9%	±1.0%	±0.9%	±1.0%	±1.0%	±1.0%	±0.9%
Time										
Anneal	±0.04	±0.4	±1.0	±4.1	±1.0	±4.1	±0.4	±1.0	±1.0	±4.1
Welding					±2.4	±2.5	±2.2	±2.4	±2.4	±2.5
Oxidation	±0.3	±0.3	±0.4	±0.4						
Bisection	±0.3	±0.3	±0.3	±0.3	±0.3	±0.3	±0.6	±0.6	±0.3	±0.3
Background	±4.0	±4.0	±4.0	±4.0	±3.0	±3.0	±2.0	±2.0	±8.8	±8.8
Alignment	±0.2	±0.2	±0.2	±0.2	±0.6	±0.6			±0.6	±0.6
Position of Edge	±0.2	±0.2	±0.2	±0.2						
Slope	±7.0	±7.0	±7.0	±7.0	±5.8	±5.8			±10.0	±10.0
Position of Weld							±3.1	±3.1		
Position of Interface							±3.1	±3.1		
Total	±13.1 -12.3	±13.4 -12.6	±14.1 -13.2	±17.1 -16.2	±13.9 -10.8	±17.2 -13.8	±11.8 -10.2	±12.6 -10.8	±24.1 -20.8	±27.0 -23.6

INDETERMINANT ERRORS

Before discussing such error sources further it is useful to point out two characteristics of the experimental data.

1. Careful statistical tests (see Appendix B) demonstrated that the individual data points are distributed normally in $\ln D$ vs $1/T$ space about the best estimate line on an Arrhenius plot.
2. Diffusivity values were obtained by three independent techniques and under two sets of boundary conditions, all of which yielded statistically indistinguishable data sets.

The latter result demonstrates that none of the techniques used was subject to *large, systematic indeterminant errors*. This conclusion along with the normal distribution exhibited by the experimental data allows one to assert that experimental errors of all kinds influenced the diffusion measurements in a random fashion. In other words, both the determinant and indeterminant errors were random.

We have no way of making an independent estimate of the magnitude of the indeterminant errors. The fact that these errors are random, however, means that they should be reflected in the scatter of the data about the estimate line. Since the maximum deviation from the best estimate line for any single data point was ~30% [Cf., the lowest 1300°C (2372°F) point in Fig. 14], it is evident that the maximum indeterminant error is probably no more than twice the determinant error limit. In any event, an error band of ± 30 to $\pm 40\%$ is more than sufficient to encompass all the experimental points. This reasoning allows us to set an upper limit for the *maximum possible total error on the assumption that all errors are additive*.

Obviously, however, if all the errors are random, the probability is small that they will all be additive for a given determination of the diffusivity, and, in general, as we have observed, the deviation of a single point from the best estimate line is much less than that indicated by the maximum possible error. In fact, as discussed in detail in Appendix B, if one takes into account the correlation of the uncertainties on the pre-exponential term, D_0 , and on the activation energy,

Q, the uncertainty on the diffusion coefficient itself at the 90% confidence level for the combined chemical and tracer diffusion data is $\pm 9\%$ at 1000°C (1832°F), $\pm 4\%$ at 1250°C (2282°F), and $\pm 7\%$ at 1500°C (2732°F).

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APPENDIX D

DETERMINATION OF THE UNCERTAINTY ARISING FROM
A RECIPROCAL RELATIONSHIP

To determine the uncertainty in a result arising from the uncertainty in a value to which it is inversely proportional, the variance of the reciprocal of the value must be determined. A Taylor series expansion for the reciprocal of T about its expected value, $E[T]$, yields

$$\frac{1}{T} \approx \frac{1}{E[T]} + (T - E[T]) \left. \frac{\partial (1/T)}{\partial T} \right|_{T = E[T]}, \quad (D-1)$$

or

$$\frac{1}{T} \approx \frac{1}{E[T]} + (T - E[T]) (-1/E[T]^2). \quad (D-2)$$

Rearrangement of Eq. (D-2) yields

$$\frac{1}{T} - \frac{1}{E[T]} \approx (T - E[T]) \left(\frac{-1}{E[T]^2} \right). \quad (D-3)$$

The variance of T is defined as the expected value of the square of the difference between the value of T and its expected value

$$\text{var}(T) = E[(T - E[T])^2]. \quad (D-4)$$

From Eq. (D-3),

$$E\left[\left(\frac{1}{T} - \frac{1}{E[T]}\right)^2\right] \approx E[(T - E[T])^2] \left(\frac{1}{E[T]^4}\right); \quad (D-5)$$

therefore,

$$\text{var}(1/T) \approx \text{var}(T)/E[T]^4. \quad (D-6)$$

The variance of the reciprocal of T is approximately equal to the variance of T divided by the expected value of T raised to the fourth power.

Assume an anneal of 20 minutes total time had an uncertainty of $\pm 5\%$, or one minute. The variance of the time is proportional to the square of the uncertainty. Therefore, $\text{var}(t) \approx \sigma^2 \approx (1 \text{ min})^2$, and

$$\text{var} \left(\frac{1}{t} \right) = \frac{\text{var}(t)}{t^4} = 6.25 \times 10^{-6} . \quad (\text{D-7})$$

The uncertainty of $(1/t)$ is approximately $[\text{var}(1/t)]^{1/2}$ or 2.5×10^{-3} . Dividing the uncertainty of $(1/t)$ by $(1/t)$ yields 5% uncertainty. Thus, in the current error analysis, the uncertainty of the reciprocal of a number is well approximated by the uncertainty of the number.