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THE PARTITIONING OF OXYGEN BETWEEN ZIRCONIUM AND LIQUID POTASSIUM

A. P. Litman
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THE PARTITIONING OF OXYGEN BETWEEN ZIRCONIUM AND LIQUID POTASSIUM*

A. P. Litman and J. W. Prados

APRIL 1965

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THE PARTITIONING OF OXYGEN BETWEEN ZIRCONIUM AND LIQUID POTASSIUM

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ABSTRACT

A study of the distribution of oxygen between zirconium and liquid potassium at 815°C is reported. The rate of oxygen uptake by zirconium samples exposed to a dilute solution of oxygen in liquid potassium is correlated with a diffusion model for oxygen movement through the solid. Mass transfer calculations based on literature values for the diffusion coefficient of oxygen in zirconium are in reasonable agreement with experimental rates of oxygen uptake; however, the equilibrium distribution coefficient for oxygen in this system appears to be far smaller than that predicted from thermodynamic considerations.

The distribution ratio for oxygen between zirconium and potassium is sufficiently reproducible at 815°C to afford a useful analytical procedure for the determination of oxygen in potassium. This procedure, termed the gettering-vacuum fusion technique, gives complete recovery of oxygen from doped potassium samples at oxygen levels of less than one hundred to several thousand parts per million. Recoveries are not influenced by the prior thermal history of the alkali metal.

INTRODUCTION

The alkali metals have properties that make them useful as coolants and working fluids in nuclear reactors. The pressure-volume-temperature relationship of potassium is especially conducive to the transfer of heat in compact reactors being developed for space exploration (1,2). Numerous investigations have indicated that potassium is best contained at elevated temperatures by the transition metals in groups IV, V, and VI of the periodic table (3,4). In addition to corrosion resistance, these metals afford physical and metallurgical properties required for proposed high-temperature service conditions.

Many of the transition metals are chemically active and tend to interact with impurities such as oxygen, hydrogen, nitrogen, and carbon in alkali metals (3–6). The effects of such impurities are often deleterious to mechanical properties (7) and corrosion resistance (8). To minimize impurity effects, potassium is conventionally purified before and during service by reaction with one of the more highly active transition metals, zirconium. Control of oxygen by this method is hampered, however, by uncertainties as to the nature of the oxygen partitioning between zirconium and potassium and by difficulties in detecting small oxygen concentrations in potassium. Accordingly, the present study was undertaken to investigate the oxygen partitioning characteristics of the zirconium-potassium system at 815°C. It was hoped that the results would give guidance in the design of zirconium oxide traps and, equally important, would open the way to a reliable method for analyzing oxygen in potassium.

MATERIALS

The zirconium specimens used in most of the experiments were prepared from iodide-process bar stock. The surfaces of the as-received bar were mechanically abraded, and the stock was cold rolled into strips varying from 0.010 to 0.065 in. in thickness. Coupons measuring 1/2 × 1 in. were sheared from the strips, acetone washed, and annealed for 1 hr in vacuum at 850°C. Prior to being placed in test, the coupons were chemically polished in an HNO_3-HF-H_2O solution. The oxygen concentration in the specimens varied from approximately 30 to 85 ppm, as determined by vacuum fusion analysis, while the hydrogen, nitrogen, and carbon contents were 50, 10, and < 20 ppm, respectively. Other impurities totaled 500 ppm, approximately one-half of which was iron.

The potassium used in this investigation was a slagged and filtered grade supplied by MSA Research Corporation. It was further purified at ORNL as follows:

1. filtered at 200°C through a 10-μ stainless steel filter to reduce gross amounts of oxygen contamination and to remove any foreign solids,
2. gettered with zirconium foil at 760°C to reduce the oxygen concentration to approximately 200 ppm,
3. gettered a second time with zirconium foil at 800 to 840°C to further reduce the oxygen concentration[1] to 50 to 135 ppm depending on the specific purification cycle.

Many experiments were performed using higher concentrations of oxygen in the potassium. For these tests, measured amounts of pure K_2O (ref. 9) were added to the alkali metal under a protective argon atmosphere.

---

[1]Oxygen concentrations in potassium were determined by the gettering-vacuum fusion procedure described in a later section.

EXPERIMENTAL PROCEDURE

The distribution of oxygen between dilute K(O) liquid and Zr(O) solid solutions was studied at 815°C. The test system, shown in Fig. 1, consisted of zirconium coupons suspended in approximately 8 g of potassium contained in a molybdenum capsule. To protect the molybdenum from oxidation during test, it was wrapped with tantalum foil and enclosed in a stainless steel capsule. All loading and unloading operations involving the potassium were carried out in a vacuum inert-gas atmosphere chamber. Both the molybdenum and stainless steel capsules were sealed in this chamber under an argon atmosphere of 99.995%, or greater, purity.

The ratio of the surface area of the zirconium specimens in square inches to the volume of potassium in cubic inches was kept constant at 0.5, while the weight ratio $\left(\frac{w_{Zr}}{w_K}\right)$ was varied from 0.5 to 0.06. Tests were begun by heating the capsules approximately 1 hr in a position inverted to that shown in Fig. 1 until the system was isothermal and then inverting the container so that the zirconium was surrounded by the potassium. After 100 hr in the latter position, the system was removed from the furnace, reinverted, and quenched in cold oil. The container was opened, the specimen removed, and the thin layer of potassium clinging to the specimen was dissolved by a cold isopropyl alcohol-warm water-acetone stripping sequence.

RESULTS AND DISCUSSION

Partition of Oxygen Between Zirconium and Potassium

In all experiments, the weight of the zirconium specimens increased during exposure to potassium. Chemical analysis of the system components

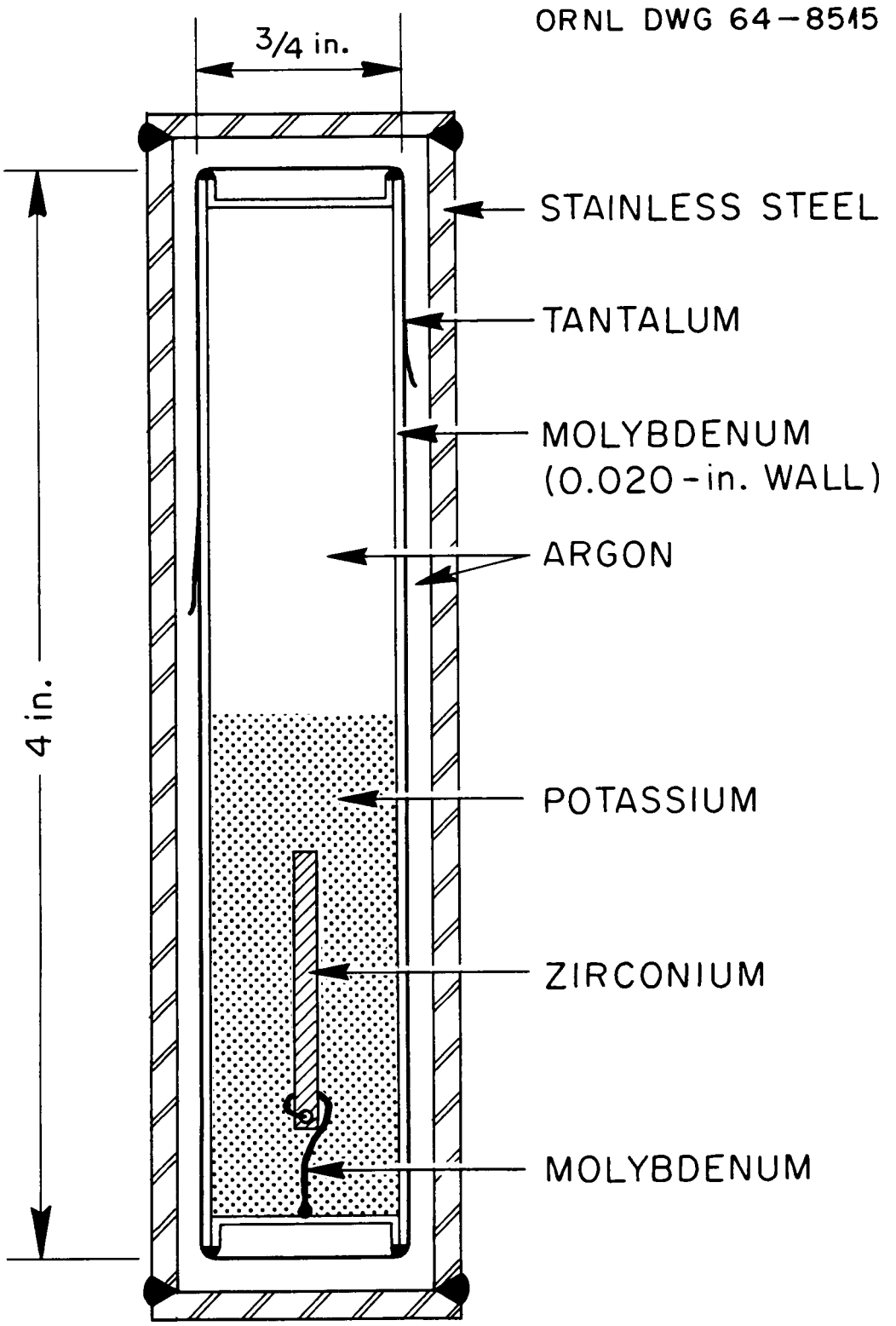

Fig. 1. Zirconium-Oxygen-Potassium Test System.

indicated that essentially all of the weight gain was due to oxygen gettered from the potassium by the zirconium. Spectrochemical analysis of the potassium further showed that there was negligible uptake of molybdenum and zirconium by the liquid metal. Accordingly, the primary mass transfer process operative under the experimental conditions appeared to be the oxygen exchange reaction represented symbolically by Eq. (1).

$$K(\underline{O})_{\ell} + Zr(\underline{O})^{*}_{s} \rightarrow K(\underline{O})^{*}_{\ell} + Zr(\underline{O})_{s} \qquad (1)$$

where * represents a relatively small weight fraction of oxygen in zirconium or potassium.

To study the kinetics of the oxygen exchange between zirconium and potassium, a series of zirconium coupons with thicknesses ranging from 0.010 to 0.065 in. were reacted with oxygen in potassium at 815°C for 100 hr. An additional 500-hr test was completed on the 0.010-in.-thick specimen.

The effect of specimen thickness on the average oxygen weight fraction in zirconium is shown in Fig. 2. The specimens described in this figure were exposed to potassium containing the same initial oxygen level, 135 ppm. It can be seen that the change in oxygen content of the zirconium, as determined by vacuum fusion analysis,[2] correlates closely with the total weight change found for the specimens. A comparison of the oxygen content of the potassium before and after test (Fig. 2) shows a reduction in oxygen that was independent of zirconium thickness. Further, the amount of oxygen lost from potassium closely matched the

[2]Independent studies at ORNL have shown that oxygen in zirconium can be determined by a platinum bath, vacuum fusion technique to an accuracy of ±10% at oxygen levels of 100 to 5000 ppm.

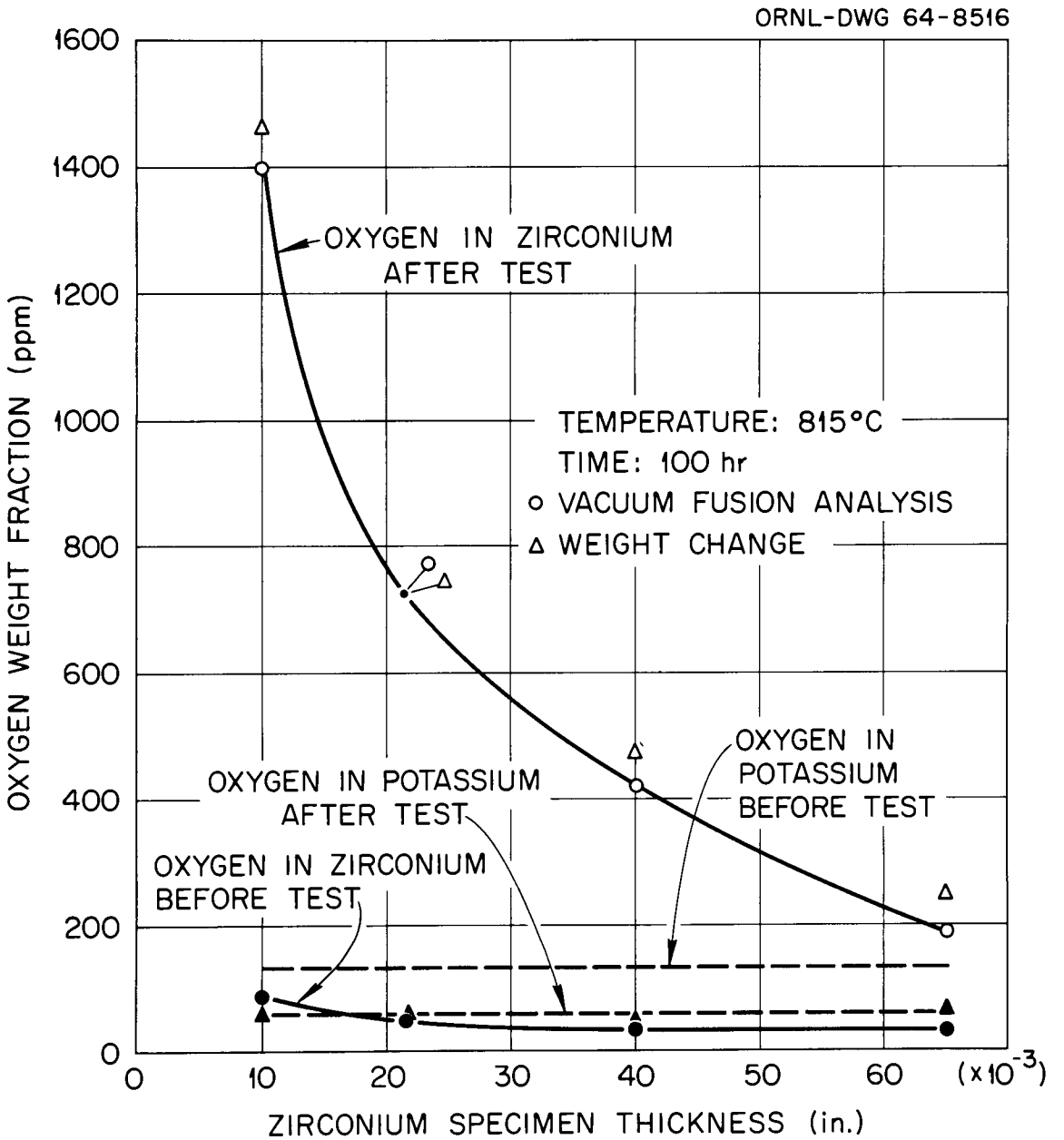

Fig. 2. Oxygen Transfer in the Zr-O-K System.

oxygen picked up by the zirconium. It is significant that the zirconium specimen removed from these tests gave no visual indication of oxide film.

Additional exposures of zirconium coupons were conducted with variable specimen thicknesses in potassium containing up to 2000 ppm of oxygen. The ratio of the final weight fraction of oxygen in zirconium to oxygen in potassium was found to be a reproducible function of the zirconium specimen thickness and to depend very little on the initial oxygen in potassium. These weight fraction ratios are compared in Fig. 3. The ratio for an 0.010-in. specimen was approximately 25 after 100 hr and approximately 30 after 500 hr. The relatively small change in this ratio as a function of test time suggests that the 500-hr ratio is approaching the equilibrium distribution ratio (coefficient), κ^0, for the system. Curves in Fig. 3 have been extrapolated to smaller specimen thicknesses on the basis that the ratios for these specimens would reach the same terminal value, 30, as the 0.010-in. specimen within the test times employed.

Further evidence that the 0.010-in. specimens had effectively attained equilibrium with respect to oxygen was afforded by microhardness measurements and chemical analyses of sections near the center and surface of the specimens. A relatively flat oxygen profile was found in examining the 0.010-in. specimens, while the thicker specimens showed a marked oxygen gradient.

Using several basic assumptions regarding the oxygen activities in zirconium and potassium, one can derive thermodynamically the equilibrium oxygen distribution coefficient in the Zr-O-K system. The derivation is based on the necessary condition that the chemical potential of any substance be the same in two phases in equilibrium. The assumption that oxygen forms a dilute solution, obeying Henry's Law, in the mutually

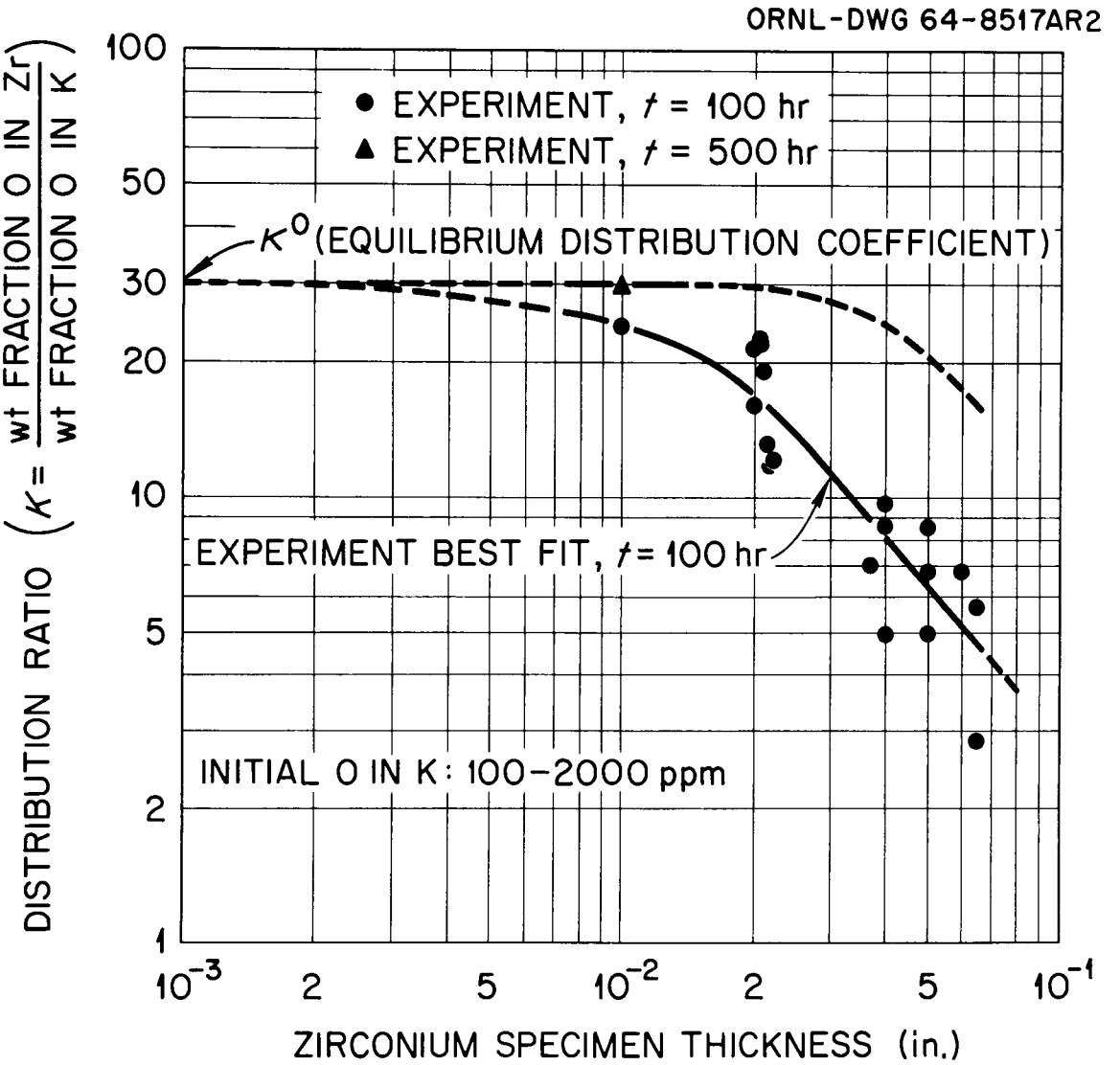

Fig. 3. Distribution Ratio for Oxygen Between Zirconium and Potassium at 815°C.

immiscible solvents potassium and zirconium and that the terminal oxides in the system are simply ZrO_2 and K_2O leads to the expression for the equilibrium distribution coefficient given by Eq. (2).

$$\kappa_T^0 = \frac{y_{Zr}}{y_K} = \exp\left[\frac{\Delta F_f^0(K_2O) - \Delta F_f^0(ZrO_2)}{RT}\right] \frac{(y_{Zr})_S}{(y_K)_S} \qquad (2)$$

where

y_{Zr} or y_K = weight fraction oxygen in zirconium or potassium,

$\Delta F_f^0(K_2O)$ = standard free energy of formation of the alkali metal oxide in equilibrium with saturated solution of oxygen in the alkali metal,

$\Delta F_f^0(ZrO_2)$ = standard free energy of formation of the zirconium oxide in equilibrium with saturated solution of oxygen in the refractory metal,

$(y_{Zr})_S$ or $(y_K)_S$ = solubility limit of oxygen in zirconium or potassium at T(°K),

$\kappa^0_{815°C}$ = 1×10^{12}, based on extrapolated values for standard free energies of formation and solubility limits.

This approach to calculating distribution coefficients has been discussed by Weeks (10) and DiStefano (11) in describing corrosion phenomena in solid-liquid systems.

For the Zr-O-K system at 815°C, $\kappa^0_{calcd} = 1 \times 10^{12}$. Several reasons can be advanced to account for the poor agreement between the calculated value and the value 30 suggested by our experiments. These have been discussed in detail by DiStefano (12) and include:

1. errors in the reported free energies of formation of the terminal oxides, in the solubility data, and in the extrapolations of both,
2. the presence of other oxygen-containing species, such as mixed metal oxides, soluble in the potassium.

Correlation of Oxygen Transfer Rates with Diffusion in Zirconium

The preceding findings suggest that the rate of oxygen uptake under the experimental conditions is controlled by the rate at which oxygen diffuses into the zirconium. The diffusion equation and boundary conditions applicable to the experiments are given in Eqs. (3–5).

In the solid:

$$\frac{\partial y}{\partial t} = D \frac{\partial^2 y}{\partial x^2} \qquad \begin{array}{r} t > 0 \\ 0 < x < \ell \end{array}$$

$$y(x,0) = y_0 \qquad t = 0,\ x > 0 \tag{3}$$

$$\left.\frac{\partial y}{\partial x}\right|_{x = \ell} = 0 \qquad t > 0,\ x = \ell$$

In the liquid:

$$\frac{1}{2} w_K \frac{\partial y_\ell}{\partial t} = \frac{1}{2} \frac{w_{Zr}}{\ell} D \left.\frac{\partial y}{\partial x}\right|_{x = 0} \qquad t > 0 \tag{4}$$

$$y_\ell(0) = y_{\ell_0} \qquad t = 0$$

At interface:

$$y(0,t) = \kappa^0 y_\ell(t) \qquad t > 0,\ x = 0 \tag{5}$$

where

$y(x,t)$ = weight fraction of oxygen in the solid,

$y_\ell(t)$ = weight fraction of oxygen in the liquid,

x = distance from solid surface; t = time,

y_0, y_{ℓ_0} = initial weight fractions of oxygen in solid and liquid, respectively,

w_{Zr}, w_K = weights of solid and liquid, respectively,

D = diffusivity of oxygen in solid,

ℓ = half thickness of solid,

κ^0 = equilibrium distribution coefficient.

Because the contribution of the edges to the total surface area of the specimens is small, a flat plate geometry has been assumed. The solution to this system of equations, shown in Eq. (6) and taken from Carslaw and Jaeger (13), gives the oxygen composition of the solid as a function of time and distance from the surface. Oxygen profiles for several specimen thicknesses were calculated using an assumed diffusivity of 4.7×10^{-10} cm^2/sec for oxygen in zirconium, based on the data of Pemsler (14). The results predict that the ratio of the weight fraction of oxygen at the surface of the 0.010-in. specimen to that in the center should be approximately 1 after 500 hr. Other surface-to-center calculations for oxygen in thicker zirconium specimens were also in reasonable agreement with experimental findings.

$$y(x,t) = y_0 + (\kappa^0 y_{\ell_0} - y_0)\left[\frac{1}{1+k} + 2k\sum_{n=1}^{\infty}\frac{\cos\,[\alpha_n(1 - x/\ell)]e^{-\alpha_n^2 Dt/\ell^2}}{[\alpha_n^2 + k^2 + k]\cos\alpha_n}\right] \quad (6)$$

where

$k = \kappa^0(w_{Zr}/w_K)$, a capacity ratio,

α_n = the roots of $\alpha_n \operatorname{ctn} \alpha_n + k = 0$.

Equation 6 was further applied to a determination of equilibration times for oxygen in zirconium as a function of specimen thickness. Equilibration times were arbitrarily taken as the time at which the first (and largest) term of Eq. (6) had decayed below 1% of its initial value. The results are shown in Fig. 4. It can be seen that the 0.010-in. specimen should have reached equilibrium in approximately 200 hr, while approximately 5500 hr would be required for the 0.065-in. specimen. These results are also in general agreement with experimental findings.

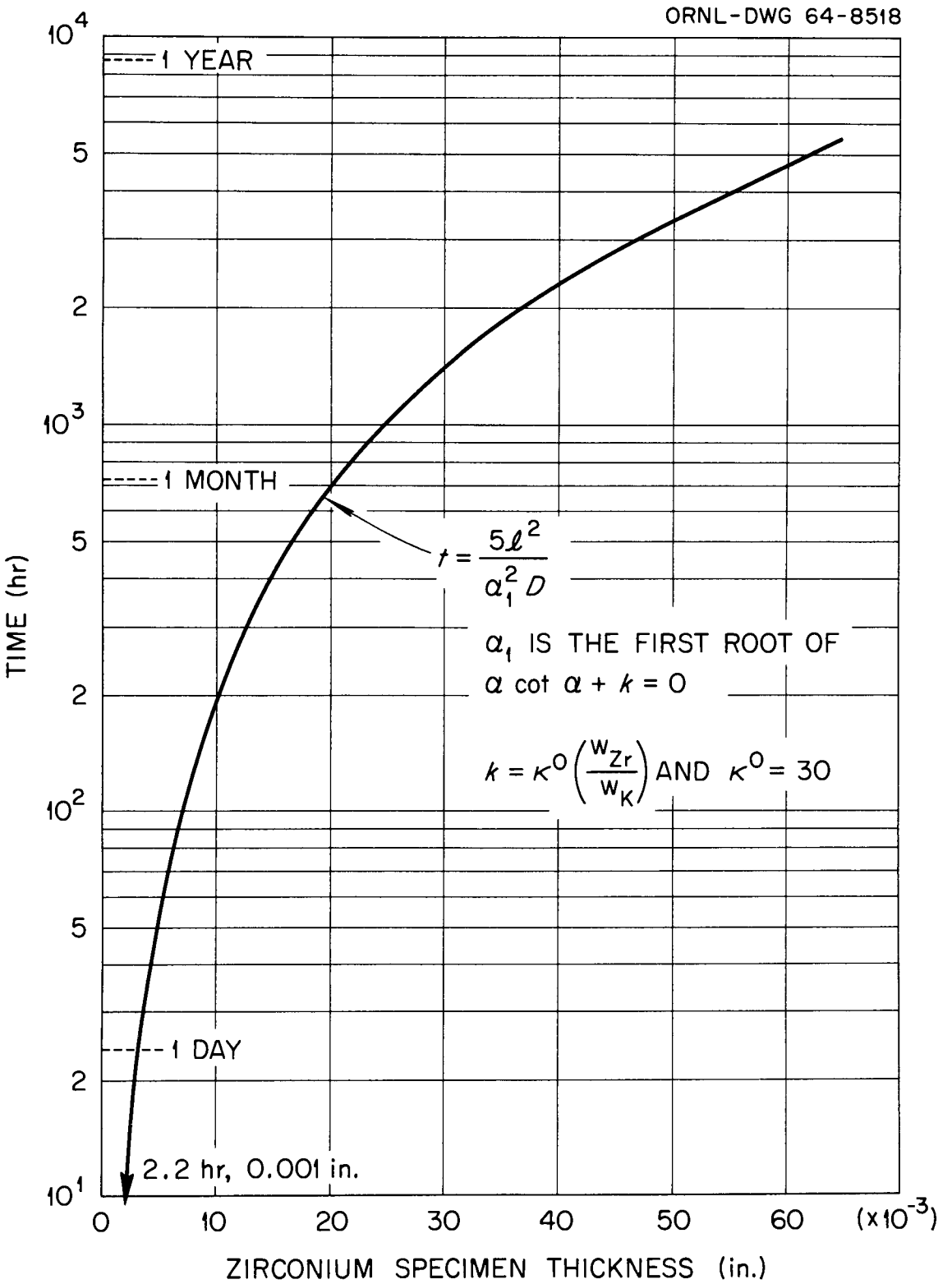

Fig. 4. Calculated Equilibrium Time for Oxygen Partitioning in the Zr-O-K System at 815°C.

Integrating Eq. (6) across the specimen thickness leads to a value for the overall weight fraction of oxygen in the specimen. Knowing the initial oxygen in potassium, this fraction and the oxygen material balance for the system yield the final weight fraction of oxygen in potassium. Thus, it is possible to calculate oxygen distribution ratios for various times and specimen thicknesses:

$$\kappa \equiv \frac{y_{Zr}}{y_K} = \kappa^0 \left\{ \frac{1 - 2S(1 + k) + \frac{y_0}{\kappa^0 y_{\ell_0}} [k + 2S(1 + k)]}{1 + 2Sk(1 + k) + \frac{y_0}{\kappa^0 y_{\ell_0}} [k - 2S(1 + k)]} \right\} \tag{7}$$

where

$$y_{Zr} = \left(\frac{2}{\ell}\right) \int_0^{\ell/2} y(x,t)dx$$

$$S = \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 Dt/\ell^2}}{\alpha_n^2 + k^2 + k}$$

Recall that κ and α_n are functions of the ratio of the mass of solid to that of liquid. From Eq. (7) it is seen that the distribution ratio, κ, should depend on this mass ratio as well as on the initial composition of each phase, the specimen thickness, ℓ, the test time, t, and the temperature, since κ^0 and D would be expected to be temperature dependent. However, if high-purity zirconium is used, $y_0 \ll \kappa^0 y_{\ell_0}$, and Eq. (7) simplifies to:

$$\frac{y_{Zr}}{y_K} = \kappa^0 \left[\frac{1 - 2S(1 + k)}{1 + 2Sk(1 + k)}\right], \tag{7a}$$

eliminating the dependence of κ on both initial compositions. In the present experiments, the ratio $y_0/\kappa^0 y_{\ell_0}$ was always < 0.025, and in addition, the relative masses of solid and liquid were always the same

for a given specimen thickness. Hence, the experimental distribution ratio should be, for these conditions, a function only of temperature, time, and specimen thickness, or $\kappa(T, t, \ell)$.

The ratio of average weight fraction of oxygen in the solid to that in the liquid as a function of time was calculated from Eq. (7) assuming $\kappa^0 = 30$. It can be seen in Fig. 5 that the experimental results fall between two curves for which the diffusivities differ only by a factor of 4 (i.e., $D = 1 \times 10^{-10}$ cm^2/sec and $D = 4 \times 10^{-10}$ cm^2/sec). The best fit curve through the experimental points in Fig. 5 suggests $D = 3 \times 10^{-10}$ cm^2/sec, which is in good agreement with the value of 4.7×10^{-10} cm^2/sec (ref. 14).

Determination of Oxygen in Potassium

Conventional techniques for the analysis of oxygen in potassium currently have narrowed to the amalgamation (15) and vacuum distillation (16) procedures. Experimentally, both techniques appear effective in separating oxides from potassium. In each, however, the extracted species is indeterminate, and in the case of potassium, is tacitly assumed to be pure K_2O. Studies at ORNL have indicated that this assumption is usually not valid once the potassium has been exposed to transition metals above approximately 400°C (6). Accordingly, there is need for an analytical technique that is less dependent on the exact knowledge of the chemistry of the oxides in potassium.

The procedure of using an active metal to getter oxygen from an alkali metal and of relating the uptake to the initial oxygen concentration in the alkali metal was originally reported by Goble, Albrecht, and Mallett (17). Using titanium as a getter, they attempted to analyze

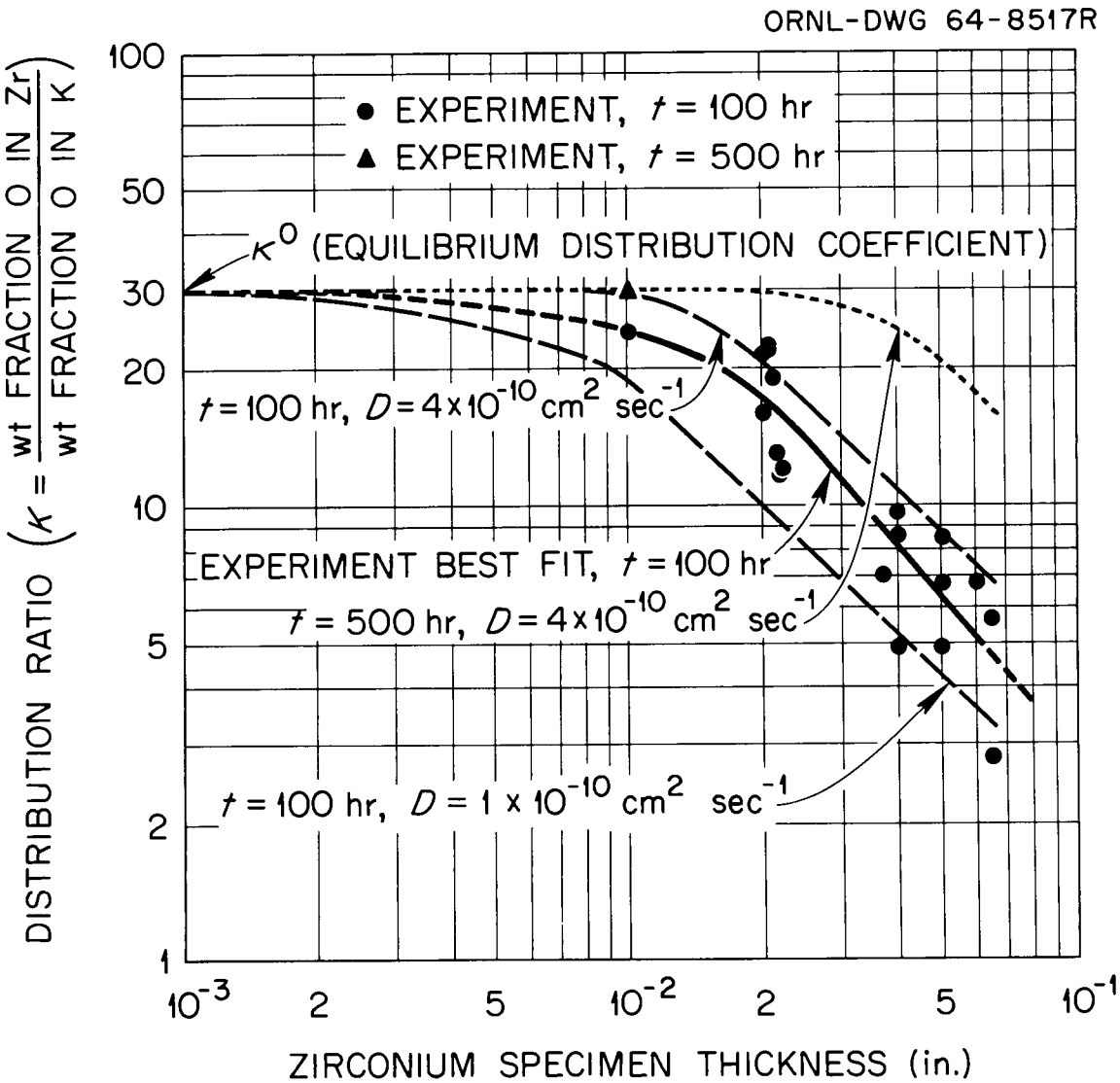

Fig. 5. Distribution Ratio for Oxygen in the Zr-O-K System at 815°C.

low levels of oxygen in sodium. Their results were not very precise, perhaps due to the short gettering times of 2 to 4 hr. In order to use the exchange of oxygen between zirconium and potassium as an analytical tool, it must be demonstrated that the ratio of the oxygen level finally achieved in the zirconium to that achieved in the potassium is a reproducible function of the time and temperature at which the exchange takes place. The results discussed in the preceding sections were quite encouraging with respect to this requirement. However, to afford a more rigorous evaluation of the accuracy of the method, it was tested against known potassium standards.

Standards were provided by spiking purified potassium with measured oxygen additions. Oxygen analyses of the as-purified potassium, using the amalgamation technique, showed levels below 20 ppm. Later analyses based on the reaction of the same potassium with zirconium indicated slightly higher oxygen levels, although by either method the initial oxygen concentration usually made a negligible contribution to the total oxygen of the spiked standard. The standards were prepared by the addition of oxygen by two methods: (1) the direct addition of K_2O in an argon-filled atmosphere chamber and (2) the reaction of the potassium with oxygen-containing niobium. In the first method, the amount of added oxygen was determined simply by weighing the K_2O addition, and in the second by analyzing the niobium for oxygen before and after contact with potassium. In some cases the oxygenated potassium was then exposed to nickel or molybdenum containers for various times at several temperatures to simulate service environments that the potassium must ultimately experience. Finally, the potassium was transferred to a molybdenum

capsule containing a zirconium tab of relatively high purity (< 100 ppm O), and the gettering analysis was performed. The containment materials used in each step of the process were carefully analyzed for any changes in oxygen and the changes factored into the standard analyses.

The final gettering step, from which the oxygen analysis was determined, was conducted for 100 hr at 815°C. Upon determining the initial and final oxygen content of the zirconium, the initial oxygen content of the potassium was deduced from the material balance for oxygen given in Eq. (8).

$$\kappa(\ell) = \frac{y_i(\text{O in Zr}) + \Delta y(\text{O in Zr})}{y_i(\text{O in K}) - \Delta y(\text{O in Zr})\,(w_{Zr}/w_K)} \tag{8}$$

where

y_i = initial weight fraction,

Δy = change in weight fractions,

w = mass of zirconium or potassium,

$\Delta y(\text{O in Zr})\,(w_{Zr}/w_K) = \Delta y(\text{O in K})$.

The equation is based on the assumptions that oxygen exchange is restricted to potassium and zirconium and that the weight fraction ratio, κ, is a function of zirconium thickness for a given test time and temperature and is independent of the initial oxygen content of the potassium.

With these assumptions, if a sample of potassium is gettered twice for the same time and temperature but with two different zirconium specimens of the same thickness, two independent equations for κ, based on Eq. (8), can be developed. By equating these expressions, the initial concentration of oxygen in potassium can be calculated without directly determining κ. This latter procedure, that is, double gettering, is

particularly useful for bench-scale corrosion experiments, since κ need not be determined beforehand. However, for these standard sample analyses, the appropriate κ was selected from Fig. 3. It is emphasized that the analytical technique requires that κ be a reproducible function of temperature, time, and thickness. The diffusion model predicts that this will be observed if high-purity zirconium is employed and if the relative masses of solid and liquid are the same for each specimen thickness.

The oxygen analyses obtained by this method are shown in Table 1. The data indicate that the analytical procedure permitted an oxygen accountability within ±10% for weight fractions of oxygen in potassium from approximately 100 to 3000 ppm. These complete recoveries showed that the gettering-vacuum fusion procedure will accurately indicate oxygen in potassium despite variations in the prior thermal history or environment seen by the potassium. Furthermore, the method does not require that oxygen attain complete equilibrium between the potassium and zirconium; it requires only that the total oxygen concentration of the zirconium be a known and reproducible function of the potassium-oxygen concentration, in which case a reasonable kinetic model can be applied to calculating the oxygen level of the potassium.

SUMMARY AND CONCLUSIONS

The distribution of oxygen between dilute K(<u>O</u>) liquid and Zr(<u>O</u>) solid solutions was investigated at 815°C for times of 100 and 500 hr. Where no oxide scale was visible on the specimens after test, the final weight fraction of oxygen in the zirconium varied from 3 to 30 times that in the potassium. For a specific zirconium thickness, the ratio of the

Table 1. Oxygen Recovered from Potassium by Gettering-Vacuum Fusion Analysis[a]

Oxygen Added[b] (ppm)	Total Oxygen (ppm)	Temperature[c] (°C)	Oxygen Found (ppm)	Oxygen Recovery (%)
905[d]	955	200	960	102
1045[d]	1095	200	1135	104
15[d]	65	600	60	92
155	205	600	225	110
340	390	800	355	91
1100	1225	800	1210	99
1375	1500	800	1650	110
2780	2905	800	2820	97
250[d]	300	815	275	92
610[d]	745	815	740	99
1380[d]	1430	815	1565	109

[a]Zirconium specimen thickness, 0.020 to 0.065 in.; temperature, 815°C; and time, 100 hr.

[b]Oxygen added as K_2O.

[c]Heated in molybdenum, nickel, or niobium containers for times varying from 1 to 100 hr before analysis.

[d]Oxygen added as Nb(O).

weight fractions increased with time; whereas, at a constant time, the ratio decreased with increasing specimen thickness. The equilibrium distribution coefficient for oxygen in the Zr-O-K system, as determined in these studies, was far smaller than that predicted from rudimentary thermodynamic calculations. The rate of oxygen uptake by the zirconium appeared to be controlled by diffusion of oxygen through the zirconium. Also, the oxygen profiles in the zirconium were in accord with those predicted using extrapolated literature values of the oxygen diffusivity in zirconium.

The experimentally determined distribution ratios between zirconium and potassium and an oxygen mass balance were applied in independent experiments to the analysis for oxygen in the potassium. Determinations of oxygen in doped potassium samples at oxygen levels of < 100 to 2900 ppm were shown to be accurate even after the potassium had been subjected to a wide variety of elevated temperature exposures in transition-metal containers. Similar exposures confounded the results of amalgamation and vacuum distillation analyses.

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