Zirconium Metal-Water Oxidation Kinetics III. Oxygen Diffusion in Oxide and Alpha Zircaloy Phases

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MASTER

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ZIRCONIUM METAL-WATER OXIDATION KINETICS
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M.A.S.

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ABSTRACT

The reaction of Zircaloy in steam at elevated temperature involves the growth of discrete layers of oxide and oxygen-rich alpha Zircaloy from the parent beta phase. The multiphase, moving boundary diffusion problem involved is encountered in a number of important reaction schemes in addition to that of Zircaloy-oxygen and can be completely (albeitly ideally) characterized through an appropriate model in terms of oxygen diffusion coefficients and equilibrium concentrations for the various phases. Conversely, kinetic data for phase growth and total oxygen consumption rates can be used to compute diffusion coefficients. In this paper, equations will be developed that express the oxygen diffusion coefficients in the oxide and alpha phases in terms of the reaction rate constants and equilibrium solubility values. These equations were applied to recent experimental kinetic data on the steam oxidation of Zircaloy-4 to determine the effective oxygen diffusion coefficients in these phases over the temperature range 1000-1500°C. Least-squares treatments of the data for diffusion in the tetragonal oxide phase and in the oxygen-stabilized alpha Zircaloy yielded the expressions:

$$D_{ox} = 0.1387 \exp[-34680/RT(^{\circ}K)] \text{ cm}^2/\text{s}$$

$$D_{\alpha} = 3.923 \exp[-51000/RT(^{\circ}K)] \text{ cm}^2/\text{s}$$

INTRODUCTION

The Zirconium Metal-Water Oxidation Kinetics (ZWOK) program presently in progress in the Metals and Ceramics Division of Oak Ridge National Laboratory has as one of its major goals the measurement of the appropriate kinetic parameters which describe the isothermal reaction of Zircaloy-4 with steam over the temperature range 900-1500°C.

In addition, as a part of this same program, direct measurements of the diffusivity of oxygen in β -Zircaloy have been made. It is anticipated that these data will serve as a basic data set whose prime function will be as input to a computer code designed to predict oxidation behavior of Zircaloy fuel tubes during transient temperature exposures using an idealized model. Details of the experimental program and preliminary results have been published in several quarterly and topical reports.¹⁻³

A computer code, SIMTRAN,³ has been written which solves (in cylindrical coordinates) the one-dimensional, multiphase, moving boundary, finite geometry transport problem for both heat and mass flow under transient temperature reaction conditions. The temperature excursion experienced by a Zircaloy specimen may be specified directly, or indirectly by supplying appropriate convective and radiative heat transfer coefficients. The code utilizes finite difference techniques and requires input data which includes physical, kinetic, and thermodynamic data as a function of temperature over the whole range of its use.

The mass-transport equations in SIMTRAN are solved using a model based on Fick's laws of diffusion and the premise that thermodynamic equilibrium is maintained at all interfaces at all times. The fundamental kinetic input to the code is in terms of the oxygen diffusion coefficients in the various phases rather than the phase incursion rates themselves. Literature data for diffusion coefficients in the oxide, alpha, and beta phases of the Zircaloy-oxygen system at elevated temperatures (1000-1500°C) are scarce and are of generally unknown accuracy. Thus, care must be exercised to insure that the predictions of the code which rely on this input agree with the experimental results for isothermal oxidation before comparisons are attempted for transient temperature reactions.

Two approaches are available by which appropriate diffusion coefficients can be determined from experimental isothermal kinetic data. First, the coefficients can be obtained via an "optimization" routine using SIMTRAN itself. Second, it is possible to use the experimental data to determine the coefficients directly. Several

procedures can be found in the literature for the latter method which vary in accuracy according to the approximations and assumptions invoked in each. The present paper describes a procedure by which the effective chemical diffusion coefficients for oxygen in Zircaloy oxide and in α -Zircaloy during steam oxidation may be obtained from the kinetic data by direct use of the parabolic rate constants.

THE MODEL

At temperatures above the α - β transition, the oxidation of Zircaloy involves the formation of layers of oxide (nominally ZrO_2) and oxygen-stabilized alpha as shown in the schematic diagram of Fig. 1. The growth of the compact oxide and alpha layers into the beta region is governed by diffusion processes. In the oxide, growth takes place most probably by an anion diffusion mechanism (bulk and/or short-circuit; vacancy and/or interstitial) whereby new oxide is formed at the oxide-alpha interface. As the volume of the oxide is greater than that of the metal from which it formed, the specimen will increase in thickness as it reacts. Care must therefore be exercised in the assignment of reference planes for diffusion calculations. Diffusion of oxygen in the alpha and beta phases occurs by an interstitial mechanism. The oxygen concentrations in the phases at the various interfaces are assumed to be maintained at the equilibrium values.

It should be noted that the following derivations are all carried out on the basis that single diffusion mechanism for oxygen is active in each phase and that the diffusion coefficient is independent of the oxygen concentration or position within each phase. These assumptions are thought to be entirely valid for the beta phase of the Zircaloy-oxygen system. However, the situation is not as clear for oxygen diffusion in the oxide or in α -Zircaloy. If anion vacancy diffusion is the principle mechanism of oxygen transport across the oxide film, the chemical diffusion coefficient for oxygen in the oxide would be expected to vary as the concentration of anion vacancies varies across the film. The extent of this variation would depend upon the precise nature of the defect structure and conceivably could be large or small.

Fig. 1. Schematic Diagram of Multiphase Diffusion Problem Pertinent to that which Occurs when Zirconium or Zircaloy Reacts with Oxygen at Elevated Temperatures.

If interstitial or grain boundary oxygen diffusion predominates in the oxide film, it is possible that no positional dependence would be observed. Thus, for purposes of diffusion calculations in the oxide phase, the simpler assumption was chosen. In α -Zircaloy, at the lower temperatures particularly, the large variation in oxygen concentration across this phase would make the existence of a concentration effect a distinct possibility, even for the case of an interstitial diffusion mechanism. However, there is some experimental evidence that the effect is, indeed, a small one over the range of concentration of real interest¹ and, therefore, the present method should yield accurate values for the oxygen diffusivity.

The problem is recognized as a classical multiphase, moving boundary diffusion problem for which solutions have been published.⁴⁻⁷ These analyses have been applied by a number of experimenters to interpret various oxidation rate data in terms of more fundamental parameters. The accuracy of these treatments has often been limited by the necessity of incorporating certain approximations that are difficult to achieve in practice. In addition, the complete analytical solution involves complex relationships between the many variables such that large discrepancies in a calculated parameter can be accumulated or generated by comparatively small errors in others. While the procedures utilized in the present paper do not eliminate these problems completely, the form of the equations derived makes efficient use of the experimentally determined quantities.

For purposes of the present discussion, it is assumed that the basic kinetic parameters for oxide growth, alpha layer growth, and total oxygen consumption can be reasonably well described by parabolic kinetics represented by equations of the form:

$$\frac{dK}{dt} = \frac{\delta^2 K}{2K} \quad (1)$$

where K = kinetic parameter (ϕ = oxide layer thickness, cm, α = alpha layer thickness, cm, and τ = total oxygen consumption, g/cm²,
 t = time, sec,

$\frac{\delta^2 K}{2}$ = parabolic rate constant for K .

Thus, for ideal isothermal behavior ($K = 0$ at $t = 0$):

$$K = \delta_K \sqrt{t} \quad (2)$$

Experimental data for the growth of the product phases during isothermal oxidation of Zircaloy in steam are being generated and, at least at temperatures above about 1000°C, appear to be represented satisfactorily in the early stages by the simple parabolic kinetics noted in Eqs. (1) and (2). The total oxygen consumed during such experiments can be calculated from the layer thickness measurements, knowledge of the various equilibrium solubility values, and the diffusivity of oxygen in the beta phase. While a model that involved several simplifying assumptions was used for this computation, the results agreed well with those generated by more sophisticated procedures and by experimental weight gain measurements. The kinetics of total oxygen consumption approximate those exhibited by the oxide layer thickness, since a large fraction of the total oxygen consumed resides there.

DETERMINATION OF OXYGEN DIFFUSION COEFFICIENTS

A. Oxide Layer: Employing simple one-dimensional Fickian terminology for the diffusion process and noting that all of the oxygen consumed by the specimen must enter through the gas-oxide interface, the total flux, J_T , can be expressed as:

$$J_T = \frac{d\tau}{dt} = -D_{ox} \left. \frac{\partial C_{ox}}{\partial x} \right|_{x'=0} \quad (3)$$

where $\frac{d\tau}{dt}$ = rate of total oxygen consumption, g/cm²-s,

D_{ox} = oxygen diffusion coefficient in oxide, cm²/s.

$\left. \frac{\partial C}{\partial x} \right|_{x'=0}$ = oxygen concentration gradient in the oxide at the gas-oxide interface.

It is evident that the diffusion coefficient in the oxide can be computed from the oxidation rate data if the oxygen concentration

gradient at the oxide-gas interface is known. Following C. Wagner's treatment as presented by Jost,⁷ it can be shown that the oxygen concentration in the oxide as a function of position and time is given by an expression of the form:

$$C_{ox} = C_{ox/gas} - B_{II} \operatorname{erf}\left(\frac{x'}{2\sqrt{D_{ox}t}}\right) \quad (4)$$

where, in this particular instance, x' is the distance measured from the oxide-gas interface rather than the original surface position as illustrated in Fig. 1. The concentration terms here and in succeeding expressions follow the nomenclature of Fig. 1. Noting that when $x' = \delta$, $C_{ox} = C_{ox/a}$, the constant B_{II} can be eliminated to yield:

$$C_{ox} = C_{ox/gas} - \frac{C_{ox/gas} - C_{ox/a}}{\operatorname{erf}\left(\frac{\delta}{2\sqrt{D_{ox}t}}\right)} \operatorname{erf}\left(\frac{x'}{2\sqrt{D_{ox}t}}\right) \quad (5)$$

It is convenient to express the oxygen concentration gradient in the oxide at the oxide-gas interface as a fraction of its limiting linear value, $(C_{ox/gas} - C_{ox/a})/\phi$. This expression can be obtained by differentiating Eq. (5) with respect to x , finding the value of the derivative at the interface, and rearranging:

$$\left[\frac{\partial C_{ox}}{\partial x}\right]_{x'=0} = - \left[\frac{C_{ox/gas} - C_{ox/a}}{\phi} \right] \left[\frac{\frac{\phi}{\sqrt{\pi D_{ox}t}}}{\operatorname{erf}\left(\frac{\phi}{2\sqrt{D_{ox}t}}\right)} \right] \quad (6)$$

Substituting for ϕ in the second term according to Eq. (2) gives:

$$\left[\frac{\partial C_{ox}}{\partial x}\right]_{x'=0} = - \left[\frac{C_{ox/gas} - C_{ox/a}}{\phi} \right] \left[\frac{\frac{\delta \phi}{\sqrt{\pi D_{ox}t}}}{\operatorname{erf}\left(\frac{\delta \phi}{2\sqrt{D_{ox}t}}\right)} \right] \quad (7a)$$

The factor by which the linear concentration gradient must be multiplied to give the actual concentration gradient at the gas/oxide interface comprises the second term on the right-hand side of Eq. (7a). Strictly speaking, an iterative procedure is necessary to solve for the factor, since D_{ox} is the prime unknown. When this is done, our experimental values of δ_ϕ lead to factors which vary from 1.0088 to 1.0098 over the temperature range of interest. Similarly, it can be shown that the oxygen concentration gradient in the oxide at the oxide-alpha interface is:

$$\left. \frac{\partial C_{ox}}{\partial x} \right]_{x'=\phi} = - \left[\frac{C_{ox/gas} - C_{ox/\alpha}}{\phi} \right] \left[\frac{\frac{\delta_\phi}{\sqrt{\pi D_{ox}}} \exp - \left(\frac{\delta_\phi}{2\sqrt{D_{ox}}} \right)^2}{\operatorname{erf} \left(\frac{\delta_\phi}{2\sqrt{D_{ox}}} \right)} \right]. \quad (7b)$$

The factor by which the linear gradient must be multiplied to give the actual gradient at this interface varied from .983 to .981 over the same temperature range. Thus, for the oxidation of Zircaloy subject to the conditions mentioned earlier, the gradient in the oxide must approximate very closely a linear gradient and, with an accuracy sufficient for most purposes, Eq. (3) can be rewritten:

$$\frac{d\tau}{dt} = D_{ox} \left[\frac{C_{ox/gas} - C_{ox/\alpha}}{\phi} \right]. \quad (8)$$

Substituting for the kinetic factors in terms of Eqs. (1) and (2), and solving for D_{ox} , we have finally the simple expression for the diffusion coefficient of oxygen in the oxide phase in terms of the experimentally available information:

$$D_{ox} = \frac{\delta_\tau \delta_\phi}{2(C_{ox/gas} - C_{ox/\alpha})} = \frac{\sqrt{\left(\frac{\delta_\tau^2}{2} \right) \left(\frac{\delta_\phi^2}{2} \right)}}{(C_{ox/gas} - C_{ox/\alpha})} \quad (9)$$

where, as indicated previously, $\frac{\delta_a^2}{2\tau}$ and $\frac{\delta_\phi^2}{2}$ are the parabolic rate constants [defined by Eq. (1)] for total oxygen consumption and oxide layer growth, respectively.

B. Alpha Layer: A similar approach is used for the determination of the oxygen diffusion coefficient in the alpha phase. The oxygen flux in the alpha phase at the alpha-beta boundary is equal to the flux necessary to move the boundary at its observed rate plus that which is dissolved into the beta phase in advance of the boundary. This total oxygen flux will be expressed analytically and then equated to the product of the diffusion coefficient and $C_{\alpha/\beta}$ concentration gradient at the boundary. Referring to Fig. 1,

$$J_{\alpha/\beta} = \left(\frac{d\xi}{dt} \right) (C_{\alpha/\beta} - C_{\beta/\alpha}) + (-D_\beta) \left. \frac{\partial C_\beta}{\partial x} \right|_{x=\xi} = -D_\alpha \left. \frac{\partial C_\alpha}{\partial x} \right|_{x=\xi} \quad (10)$$

where the concentration terms have their usual meanings, and:

$\frac{d\xi}{dt}$ = rate of movement of α - β interface, cm/s,

D_β = diffusion coefficient, oxygen in beta phase, cm^2/s ,

D_α = diffusion coefficient, oxygen in alpha phase, cm^2/s .

The velocity of the alpha-beta interface can be expressed in terms of the kinetics of individual layer growth if the oxide-metal volume ratio is known and the associated expansion is assumed to be limited to one direction. Thus

$$\frac{d\xi}{dt} = \frac{d\alpha}{dt} + \frac{1}{V} \frac{d\phi}{dt} \quad (11)$$

where V = volume of oxide/equivalent volume of metal; for ZrO_2 , $V = 1.50$. In terms of the parabolic rate constants defined in Eqs. (1) and (2), the oxygen flux necessary to move the boundary at this rate is given by:

$$J' = \left(\frac{\delta_a}{2\sqrt{t}} + \frac{1}{V} \frac{\delta_\phi}{2\sqrt{t}} \right) (C_{\alpha/\beta} - C_{\beta/\alpha}) \quad (12)$$

The concentration gradient in the beta phase at the alpha-beta boundary is found in a manner essentially identical in that used in the last section. Again following Wagner-Jost,⁷ the oxygen concentration in the beta phase as a function of position and time is given by:

$$C_{\beta} = C_0 + B_I \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{\beta}t}} \right) \right] \quad (13)$$

The elimination of the constant B_I by incorporating the boundary conditions $C_{\beta} = C_{\beta/\alpha}$ when $x = \xi$ yields

$$C_{\beta} = C_0 + \frac{(C_{\beta/\alpha} - C_0) \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{\beta}t}} \right) \right]}{\left[1 - \operatorname{erf} \left(\frac{\xi}{2\sqrt{D_{\beta}t}} \right) \right]} \quad (14)$$

Equation (14) is precise only for instances where the semi-infinite geometry criterion is satisfactorily met for the beta phase. While this criterion will not be met for long-time experiments on thin plate or tube specimens, the approximation is accurate in the early stages of these reactions and remains a satisfactory approximation until the beta phase begins to "fill-up" with oxygen. If the experimental rate constant data apply to the early stages of oxidation, the gradient at the interface determined by differentiation of Eq. (14) is similarly expected to be valid. This yields:

$$\left. \frac{\partial C_{\beta}}{\partial x} \right|_{x=\xi} = - \frac{(C_{\beta/\alpha} - C_0)}{\sqrt{\pi D_{\beta}t}} \frac{\left[\exp - \left(\frac{\xi}{2\sqrt{D_{\beta}t}} \right)^2 \right]}{\left[1 - \operatorname{erf} \left(\frac{\xi}{2\sqrt{D_{\beta}t}} \right) \right]} \quad (15)$$

Substituting for ξ according to Eqs. (2) and (11),

$$\left. \frac{\partial C_\beta}{\partial x} \right]_{x=\xi} = - \frac{(C_{\beta/\alpha} - C_0)}{\sqrt{\pi D_\beta t}} \frac{\left[\exp - \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\beta}} \right)^2 \right]}{\left[1 - \operatorname{erf} \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\beta}} \right) \right]} \quad (16)$$

Therefore, the oxygen flux into the beta phase at the alpha-beta boundary is:

$$J_{\beta/\alpha} = - D_\beta \left. \frac{\partial C_\beta}{\partial x} \right]_{x=\xi} = \frac{\sqrt{D_\beta} (C_{\beta/\alpha} - C_0)}{\sqrt{\pi t}} \frac{\left[\exp - \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\beta}} \right)^2 \right]}{\left[1 - \operatorname{erf} \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\beta}} \right) \right]} \quad (17)$$

Finally, in order to solve for D_α according to Eq. (16), the oxygen concentration gradient in the alpha at the alpha-beta interface needs to be known. Pemsler⁴ gives the expression for the concentration across the alpha layer as:

$$C_\alpha = C_{\alpha/\text{ox}} + \frac{(C_{\alpha/\text{ox}} - C_{\alpha/\beta}) \left[\operatorname{erf} \left(\frac{S}{2\sqrt{D_\alpha t}} \right) - \operatorname{erf} \left(\frac{x}{2\sqrt{D_\alpha t}} \right) \right]}{\left[\operatorname{erf} \left(\frac{\xi}{2\sqrt{D_\alpha t}} \right) - \operatorname{erf} \left(\frac{S}{2\sqrt{D_\alpha t}} \right) \right]} \quad (18)$$

In a manner identical to that used in determining the gradient in the oxide layer, we will express the oxygen concentration gradient in the alpha at the alpha-beta interface in terms of a factor, F , which is the fraction of the gradient's limiting value, $(C_{\alpha/\text{ox}} - C_{\alpha/\beta})/\alpha$. Thus, differentiating Eq. (18) and rearranging:

$$\left. \frac{\partial C_\alpha}{\partial x} \right]_{x=\xi} = - \left[\frac{C_{\alpha/\text{ox}} - C_{\alpha/\beta}}{\alpha} \right] \frac{\left[\frac{\alpha}{\sqrt{\pi D_\alpha t}} \exp - \left(\frac{\alpha + \frac{1}{V} \phi}{2\sqrt{D_\alpha t}} \right)^2 \right]}{\left[\text{erf} \left(\frac{\alpha + \frac{1}{V} \phi}{2\sqrt{D_\alpha t}} \right) - \text{erf} \left(\frac{\frac{1}{V} \phi}{2\sqrt{D_\alpha t}} \right) \right]} \quad (19)$$

or in terms of the kinetic parameters:

$$\left. \frac{\partial C_\alpha}{\partial x} \right]_{x=\xi} = - \left[\frac{C_{\alpha/\text{ox}} - C_{\alpha/\beta}}{\alpha} \right] \left\{ \frac{\left[\frac{\delta_\alpha}{\sqrt{\pi D_\alpha}} \exp - \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\alpha}} \right)^2 \right]}{\left[\text{erf} \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\alpha}} \right) - \text{erf} \left(\frac{\frac{1}{V} \delta_\phi}{2\sqrt{D_\alpha}} \right) \right]} \right\} \quad (20)$$

Substitution of available literature values of D_α in Eq. (20) suggests that the actual concentration gradient in the alpha phase will differ substantially from the linear approximation. Thus, the precise determination of D_α , as shown below, must involve an iterative procedure. It is evident, however, that the iteration involves only the slope factor. Thus, a quick convergence is anticipated, provided a reasonable starting value is chosen.

In order to write the final expression for D_α , the diffusion coefficient for oxygen in the alpha phase, in as simple and meaningful a manner as possible, we will make use of the F factor, where:

$$F = \frac{\frac{\delta_\alpha}{\sqrt{\pi D_\alpha}} \exp - \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\alpha}} \right)^2}{\text{erf} \left(\frac{\delta_\alpha + \frac{1}{V} \delta_\phi}{2\sqrt{D_\alpha}} \right) - \text{erf} \left(\frac{\frac{1}{V} \delta_\phi}{2\sqrt{D_\alpha}} \right)} = \frac{- \left. \frac{\partial C_\alpha}{\partial x} \right]_{x=\xi}}{\left[\frac{(C_{\alpha/\text{ox}} - C_{\alpha/\beta})}{\alpha} \right]} \quad (21)$$

Substituting the results of Eqs. (12), (17), and (21) into Eq. (10), we have after rearrangement:

$$D_{\alpha} = \frac{1}{F} \left\{ \left[\left(\frac{\delta_{\alpha}^2}{2} + \frac{1}{V} \frac{\delta_{\alpha} \delta_{\phi}}{2} \right) \frac{(C_{\alpha/\beta} - C_{\beta/\alpha})}{(C_{\alpha/ox} - C_{\alpha/\beta})} \right] + \left[\frac{\delta_{\alpha} \sqrt{D_{\beta}}}{\sqrt{\pi}} \frac{(C_{\beta/\alpha} - C_0)}{(C_{\alpha/ox} - C_{\alpha/\beta})} \right] \left[\frac{\exp - \left(\frac{\delta_{\alpha} + \frac{1}{V} \delta_{\phi}}{2\sqrt{D_{\beta}}} \right)^2}{1 - \operatorname{erf} \left(\frac{\delta_{\alpha} + \frac{1}{V} \delta_{\phi}}{2\sqrt{D_{\beta}}} \right)} \right] \right\} \quad (22)$$

While Eqs. (21) and (22) can be solved by hand, it is certainly more convenient to utilize machine computations. A program written for the ORNL PDP-10 (conversant) computer system was used to determine D_{α} from the experimental kinetic data. The iteration was continued until a convergence level better than 0.1 percent was reached. Values of the β -factor varied from about 0.55 to 0.78 over the experimental temperature range. (As a matter of interest, the slope factor for the gradient in the alpha at the oxide-alpha interface was calculated and was observed to vary from 1.4 to 1.2 over the same temperature range.)

Obviously, other expressions could have been derived for determining this diffusion coefficient from other variable combinations. However, it is felt that the type of approach used here, (as well as for the determination of the diffusion coefficient in the oxide phase) is particularly useful because of its direct use of the experimental kinetic data.

SUPPLEMENTARY DATA

In order to solve explicitly for D_{ox} and D_{α} from the equations derived above, it is necessary to have at hand, in addition to the experimental kinetic parameters, values of D_{β} and the equilibrium oxygen concentrations at the various interfaces. We have selected

the following expressions to represent these values for the Zircaloy-4-oxygen system over the temperature range 1273-1773°K.

$$D_{\beta} = (.0263) \exp(-28,200/RT[^\circ\text{K}]) \text{ cm}^2/\text{s} \quad (\text{Ref. 8})$$

$$C_{\text{ox/gas}} = 1.511 \text{ g/cm}^3 \quad (\text{Ref. 9})$$

$$C_{\text{ox}/\alpha} = 1.517 - 7.5 \times 10^{-5} T[^\circ\text{K}] \text{ g/cm}^3 \quad (\text{Ref. 10})$$

$$C_{\alpha/\text{ox}} = 0.4537 \text{ g/cm}^3 \quad (\text{Refs. 11 and 12})$$

$$C_{\alpha/\beta} = [-0.2263 + \frac{T[^\circ\text{K}]}{63.385} - 16.877]^{1/2} .0649 \text{ g/cm}^3 \quad (\text{Ref. 13})$$

(T > 1073°K)

$$C_{\beta/\alpha} = \left[\frac{T[^\circ\text{K}] - 1081.7}{491.159} \right] .0649 \text{ g/cm}^3 \quad (\text{Ref. 13})$$

$$(T > 1373^\circ\text{K})$$

$$C_{\beta/\alpha} = [-0.00428 + \frac{T[^\circ\text{K}]}{392.46} - 3.1417]^{1/2} .0649 \text{ g/cm}^3 \quad (\text{Ref. 13})$$

$$(1233^\circ\text{K} < T < 1373^\circ\text{K})$$

Experimental Oxidation Rate Data: As mentioned above, experimental measurements of the kinetic parameters describing the reaction of Zircaloy-4 with steam over the temperature range 900-1500°C have been made as part of this program. The reaction appears to be well-described by simple parabolic kinetics for oxidation temperatures above 1000°C. Below this temperature, more complicated behavior was observed, a fact thought to be more associated with the phase change in the oxide layer rather than the one in the metal. Because the model employed in this treatment is not applicable at temperatures below that required to create the beta phase in the alloy, and because parabolic growth behavior is required for the mathematical analysis, attention will be focused on the data for temperature above 1000°C. The experimental parabolic rate constants for oxide layer growth, alpha layer growth, and total oxygen consumption are given in Table 1. The details of the experimental and computational procedures leading to these results are being published separately.^{1,14} It should be mentioned that the rate constants for total oxygen consumption used here were computed from phase layer thickness measurements using the

Table 1. Parabolic Rate Constants Applicable to Kinetic Parameters During Steam Oxidation of Zircaloy-4

Temperature (°C)	Parabolic Rate Constants, $\frac{\delta^2}{2} = K \frac{dK}{dt}$		
	$\frac{\delta^2}{2}$, oxide layer cm ² /s	$\frac{\delta^2}{2}$, alpha layer cm ² /s	$\frac{\delta^2}{2}$, oxygen consumed (g/cm ²) ² /s
1001	7.072×10^{-9}	3.139×10^{-9}	2.081×10^{-9}
1050	1.399×10^{-8}	8.493×10^{-9}	4.488×10^{-8}
1101	2.171×10^{-8}	1.950×10^{-8}	7.665×10^{-8}
1153	3.631×10^{-8}	3.254×10^{-8}	1.317×10^{-7}
1203	5.389×10^{-8}	5.872×10^{-8}	2.073×10^{-7}
1253	7.663×10^{-8}	1.007×10^{-7}	3.130×10^{-7}
1304	1.141×10^{-7}	1.593×10^{-7}	4.811×10^{-7}
1352	1.651×10^{-7}	2.710×10^{-7}	7.285×10^{-7}
1404	2.351×10^{-7}	4.122×10^{-7}	1.070×10^{-6}
1454	3.366×10^{-7}	5.901×10^{-7}	1.550×10^{-6}
1504	4.525×10^{-7}	8.595×10^{-7}	2.152×10^{-6}

information presented in the previous section. For purposes of this particular calculation, linear oxygen concentration gradients were assumed to exist in both oxide and alpha phases, and a simplified diffusion calculation was used to determine the amount of oxygen in the beta phase.

RESULTS AND DISCUSSION

The calculated values of the diffusion coefficients for oxygen in the oxide and alpha phases obtained through the use of the derived equations are tabulated in Table 2. Values of D_β at the corresponding temperatures, calculated from Perkins' analytical expression, are also

Table 2. Oxygen Diffusion Coefficients in Oxide, Alpha, and Beta Phases of Zircaloy-4 During Steam Oxidation

Temperature (°C)	Oxygen Diffusion Coefficients		
	D_{ox} , cm ² /s	D_{α} , cm ² /s	D_{β} , cm ² /s
1001	1.355×10^{-7}	4.731×10^{-9}	3.819×10^{-7}
1050	2.688×10^{-7}	1.383×10^{-8}	5.769×10^{-7}
1101	4.204×10^{-7}	3.230×10^{-8}	8.591×10^{-7}
1153	6.849×10^{-7}	5.959×10^{-8}	1.252×10^{-6}
1203	1.009×10^{-6}	1.111×10^{-7}	1.754×10^{-6}
1252	1.428×10^{-6}	1.965×10^{-7}	2.404×10^{-6}
1304	2.087×10^{-6}	3.281×10^{-7}	3.247×10^{-6}
1352	2.993×10^{-6}	5.643×10^{-7}	4.236×10^{-6}
1404	4.188×10^{-6}	8.980×10^{-7}	5.554×10^{-6}
1454	5.848×10^{-6}	1.354×10^{-6}	7.096×10^{-6}
1504	7.753×10^{-6}	2.040×10^{-6}	8.941×10^{-6}

included. Figure 2 is an Arrhenius plot of the D_{ox} values in which we have compared the present results to those of Debuigne⁶ for oxygen diffusion in pure ZrO₂. The Debuigne results appear to be the only previous data for diffusion completely in the tetragonal phase of the oxide. The average values of the diffusion constants measured at each of the four temperatures investigated by Debuigne are also shown. The source of the discrepancy between the data points and the least-squares line given in the paper is not clear. The relatively small differences in Debuigne's results and the results of the present investigation may be associated with the effect of alloy additions or the different assumptions regarding the oxygen concentration values across the oxide film. A least squares representation of the data obtained in the present investigation (omitting the data point at 1001°C) yields:

$$D_{ox} = 0.1387 \left[\begin{matrix} +21\% \\ -18\% \end{matrix} \right] \exp(-34680(\pm 1.7\%)/RT) \text{ cm}^2/\text{s} \quad (23)$$

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Fig. 2. Arrhenius Plot Showing Temperature Dependence of Diffusion Coefficient for Oxygen in Zircaloy-4 Oxide from 1000 to 1500°C Determined in the Present Investigation. The data of Debuigne⁶ are included for comparison.

where $R = 1.987$ cal/mole-°K and T = temperature, °K. The bracketed terms refer to the *individual* 90% confidence range on the pre-exponential and activation energy terms. The *joint* confidence intervals, because the uncertainties on these terms are correlated, better describe the accuracy of the diffusion coefficient itself. From a construction of the joint confidence interval, the range of D_{ox} at the 90% level was shown to vary from about $\pm 3.6\%$ at 1000°C to $\pm 1.9\%$ at 1300°C to $\pm 3.2\%$ at 1500°C .

Figure 3 presents our values of the diffusion coefficients for oxygen in the alpha phase of Zircaloy-4. A comparison of these data with the results of several other investigators for Zircaloy and for pure Zr is also shown. Our data agree particularly well with the data of Debuigne⁶ and with the recent measurements of Chung, Garde, and Kassner¹⁵ which were determined by means of observations of boundary movements during homogenization of oxidized Zircaloy-4 specimens. The least squares representation of the present data set yields:

$$D_{\alpha} = 3.923 \begin{bmatrix} +27\% \\ -21\% \end{bmatrix} \exp(-51000[\pm 1.4\%]/RT) \text{ cm}^2/\text{sec} \quad (24)$$

where the terminology is the same as that used above. The confidence range of D_{α} at the 90% level varied from about $\pm 4.6\%$ at 1000°C to $\pm 2.4\%$ at 1300°C to $\pm 4.0\%$ at 1500°C .

An extrapolation of this Arrhenius expression shows good agreement with the data obtained by David¹⁸ and by Quataert¹⁹ in the 700 – 850°C temperature range. It should be mentioned here, however, that at temperatures below about 650°C , a tendency for deviations (positive) from a linear extrapolation of the high-temperature data has been observed.^{6,19}

CONCLUSIONS

Kinetic measurements obtained during the steam oxidation of Zircaloy-4 were used to calculate values for the diffusion coefficients of oxygen in Zircaloy oxide and alpha Zircaloy over the temperature

Fig. 3. Arrhenius Plot Showing Temperature Dependence of Diffusion Coefficient for Oxygen in Alpha Zircaloy-4 from 1000 to 1500°C Determined in the Present Investigation. Data from several previous investigations^{6,13,17} are included for comparison.

range 1000 to 1500°C. The diffusion coefficients were accurately defined by Arrhenius expressions with relatively narrow confidence intervals, and represent a significant contribution to the description of mass transport in this system at elevated temperatures.

An examination of the equations derived for the calculation of the diffusion coefficients revealed that, for the stipulations and reaction conditions under consideration, the oxygen concentration gradient in the oxide phase was virtually linear. For the alpha phase, however, a linear gradient was not a good approximation. For example, the gradient in the alpha phase at the alpha-beta interface was observed to range from 55 to 78% of the linear value. Of course, the behavior is a characteristic of the particular system, and the relative departure from a linear gradient will vary with temperature, but not with time.

While the equations derived in this paper refer specifically to the oxidation of zirconium and zirconium alloys, they are generally applicable or adaptable to other multiphase, moving boundary reaction/diffusion systems.

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APPENDIX

Stoichiometry Range in Zircaloy Oxide

Data are not presently available from which it would be possible to obtain accurate values for the extent of nonstoichiometry in Zircaloy oxide. Indeed, substantial disagreement exists in the literature concerning the construction of this portion of the pure Zr-O phase diagram. For example, Fig. A-1 shows in detail the diagram suggested by the data of the three oft-quoted papers in this subject area. Obviously, one disagreement concerns the extent of nonstoichiometry exhibited by the oxide phase.

Since our experiments concentrated on the temperature range where the tetragonal oxide is stable, we arbitrarily chose a simple analytical form to represent the equilibrium oxygen concentration in the oxide at the alpha boundary. A linear representation of the data of Ruh and Garrett¹⁰ was used. They report that $C_{\text{ox}/\alpha}$ increases from approximately 64.80 to 65.05 atom percent oxygen as the temperature decreases from 1400 to 1200°C. If oxygen ion vacancies are the principal defect, this corresponds to $\text{ZrO}_{1.84}$ and $\text{ZrO}_{1.86}$, respectively, and a straight-line representation over the applicable temperature range (about 1273 to 1763°K) can be derived (on the basis that the density of stoichiometric ZrO_2 is 5.82 g/cm³):

$$C_{\text{ox}/\alpha} = 1.517 - 7.5 \times 10^{-5} T \text{ (°K) g/cm}^3 \text{ .}$$

While the actual extent to which the alloy additions in Zircaloy-4 affect the stoichiometric range in the growing oxide is largely unknown, it is generally argued that it would be a small one. Such an effect, however, would have a direct influence on the diffusion coefficient in the oxide derived in the manner described in this report.