100-100000-1

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A Comparison of the High Temperature Oxidation Behavior of Zircaloy-4 and Pure Zirconium*

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ABSTRACT

Oxidation rate data for Zircaloy-4 in steam under isothermal conditions in the temperature range 1000–1500°C indicate that the kinetics of layer growth and oxygen consumption can be described by virtually ideal parabolic behavior. Thus, the growth of the two product phases, oxide and oxygen-stabilized alpha, is presumed to be controlled by diffusion processes leading to uniform layer thickening. We have measured the oxidation rate of pure, arc-melted, crystal-bar zirconium under similar conditions and have found differences in the reaction characteristics compared to Zircaloy-4. At temperatures from 1098 to 1416°C, while parabolic kinetics are still observed, the growth rates for both phases are measurably different. Our analysis of these data in terms of a multi-layer diffusion model suggests that the effective chemical diffusion coefficient for oxygen in the oxide phase has been altered. However, despite the kinetic differences, the analysis also concludes that the diffusion coefficient of oxygen in the alpha layers is identical, a finding consistent with the results of independent measurements.

In addition to the decreased oxygen diffusivity in the oxide phase on pure zirconium compared to that on Zircaloy-4, a higher activation energy was also observed, implying that some mechanistic differences exist. Without additional information, it is not possible to attribute these differences to

*Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

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changes in the oxide defect structure resulting from alloying. However, significant morphological and grain size differences exist in the columnar oxide growing on the two materials, and it is possible that the relative contributions to oxide growth from short-circuit diffusion differ in the two oxides.

Key Words: Zirconium, ⁶⁰Ni alloy, oxidation, oxygen diffusion, kinetics, diffusion modeling

INTRODUCTION

In the past several years, there have been several systematic investigations of the reaction between Zircaloy and steam at elevated temperatures.¹⁻⁹ Of particular interest in these studies has been a detailed kinetic analysis of this reaction at temperatures above the alpha-beta transition. Much of this work was undertaken in order to provide a basis for assessing the behavior of PWR fuel tubes during hypothetical accident conditions in which an excursion to high temperatures might be anticipated. For example, we have recently reported the oxidation kinetics of Zircaloy-4* in steam at temperature from 900 to 1500°C.² Regardless of the fact that the oxide layer forming under these conditions exhibits a rather complicated microstructure, at least in part brought about by the partitioning of tin, the growth of the product oxide and oxygen-stabilized alpha layers into the host beta phase is surprisingly uniform and, therefore, amenable to diffusion modeling in terms of a simple, moving boundary, diffusion analysis. Such observations have led to the development of computer codes^{4,10-12} based principally on diffusion or simplified growth kinetics models that permitted calculations to be made describing the progress of oxidation under transient temperature conditions.

While a great deal of new information is available on the high temperature oxidation of Zircaloy and a few other dilute zirconium alloys, only limited data are found for pure zirconium at temperatures in excess of 1100-1200°C. An excellent contribution to the understanding of the oxidation behavior of zirconium was given by Debuigne¹³ who described various important aspects

*Reactor Grade Zircaloy-4 PWR Tubing. Sandvik Special Metals Corporation. Nominal composition (weight percent): 1.60 Sn, 0.25 Fe, 0.12 Cr, 0.12 O, 0.009 C, 0.003 N, and 0.0025 H.

of the oxidation process in some detail and included experimental data at temperatures up to 1200°C. Pensler¹⁴ presented experimental data to about 1300°C and appeared to be the first investigator to recognize the importance of the nature of the monoclinic-tetragonal transformation in the oxide on the kinetic processes. Many pertinent observations and discussions are found in the review articles of Cox,¹⁵ Rosa,¹⁶ and Douglass,¹⁷ although the emphasis in these papers is on the lower temperature results.

In our present work, we are studying the oxidation of pure Zirconium* over essentially the same temperature range in order to examine the influence of minor alloying additions on the parameters critical to the oxidation behavior. While the basic oxidation processes for zirconium and Zircaloy-4 are identical, significant differences in the kinetics, oxygen diffusivities, and morphology have been found. In this paper we will present comparisons of these quantities and point out the principle manner in which the alloy additions in Zircaloy influence high temperature oxidation.

EXPERIMENTAL TECHNIQUE

Oxidation studies at temperatures above 1000°C have seldom been performed with an accuracy sufficient to test in a critical manner mechanistic arguments concerning the influence of small alloy additions on oxidation kinetics. Our apparatus and techniques were developed over an extended period of time and are capable of producing kinetic measurements for the oxidation of zirconium with a high degree of accuracy and reproducibility. The procedures have been discussed in detail previously for Zircaloy-4 oxidation and are essentially identical for zirconium specimens. The basic measurements for the isothermal reaction rate studies are metallographic determinations of

*Arc Melted, Crystal-Bar Zirconium: Interstitial impurities — (O, C, H, N) 0 to 30 ppm by wt; metallic impurities — 30 ppm Hf, other metals 0-10 ppm by wt.

oxide and alpha layer thicknesses on a series of specimens each oxidized for a given period under well documented conditions of time and temperature.

The apparatus is based on a low thermal inertia, radiant heating system in which a short length of cylindrical tube specimen is exposed to flowing steam or other oxidant on its outer surface only while being heated according to a programmed temperature cycle. Specimens of zirconium were machined from arc melted crystal-bar stock in the form of cylindrical tubes 3 cm long, 1.1 cm diam, with a wall thickness of .075 cm. The outer surfaces were mechanically abraded through 4/0 metallurgical papers and then chemically polished to remove the cold-worked surface regions. Three Pt vs Pt-10% Rh thermocouples monitor temperatures on the inner surface of the specimen, and a computer-operated data acquisition system furnishes the detailed description of the time-temperature excursion so that an effective isothermal reaction time can be calculated for each specimen at the nominal oxidation temperature of the entire set. Heating rates in excess of 100 K/s insure that for most experiments virtually all of the reaction takes place at the assigned temperature.

Measurements of the product layer thicknesses are made with a digital micrometer eyepiece from a suitably polished and etched specimen cross-section. If desired, reasonable estimates of the total oxygen consumed (i.e., weight gain) can be calculated from these measurements; however, values based on a complete modeling analysis are likely to be more accurate in that the latter accounts in detail for the oxygen in each of the three phases. Modeling analyses also point out the sensitivity of the parabolic kinetics of layer growth to other experimental or specimen variables.¹⁸ For example, a "thin" specimen of either Zircaloy or zirconium that tends

to saturate with oxygen during the reaction time will exhibit layer growth kinetics that change appreciably with time, complicating the analysis unless the source of these changes is recognized. The effect is most pronounced for growth of the alpha phase, and increases in the apparent parabolic rate constant of more than one hundred percent may be observed. In the results reported here, care was taken to restrict the data to times sufficiently short so that such "geometrical" effects were negligible.

RESULTS, COMPARISONS, AND DISCUSSION

In order to compare the oxidation characteristics of pure arc melted crystal-bar zirconium with those recently measured for the steam oxidation of Zircaloy-4 from 1000 to 1500°C, similar sets of experiments and analyses were conducted on the pure material at 1000, 1098, 1200, and 1416°C.

Zirconium, like Zircaloy-4, formed uniform layers of oxide and oxygen-stabilized alpha phase during high temperature isothermal oxidation in flowing steam. Parabolic kinetics were observed for the growth of both layers in the early stages of the reaction with the possible exception of the data set at 1000°C. At this temperature, very complicated kinetic behavior was observed for times from a few hundred to a few thousand seconds, particularly for oxide growth, most probably as a consequence of a conversion from the tetragonal to the monoclinic form of the oxide. These results will be described in detail in a subsequent paper, and in our present treatments (to follow), the temperature dependence of the oxidation and diffusion kinetics will be based on the three higher temperature data sets where only the tetragonal form of the oxide is presumed to form.

Oxidation Product Morphology — A characterization of the microstructures of oxidized Zircaloy-4 specimens has been presented and discussed previously.^{4,18-20} In the early stages of the reaction, before the beta phase in a thin specimen approaches saturation with oxygen, the oxide and alpha layers are uniform in thickness and are easily distinguished by ordinary metallographic preparation of specimen cross sections. The dominant features of the oxide formed on Zircaloy-4 are a line of tin-rich metallic particles lying parallel to the interface and stringers or thin sheets of tin-rich material co-existing with the fine columnar grains of oxide between the "particle line" and the oxide-alpha interface. The outermost oxide, from the particle-line to the oxide-gas interface, contains little tin. We have located the particle line in specimens oxidized at temperatures as low as 1000°C, but it is more easily found in the oxide after oxidation above about 1100°C. The relative position of the particle line is independent of time for isothermal reaction, but dependent upon the reaction temperature. At the higher temperatures, the particle line is more pronounced and, for thicker oxide layers, there is a tendency for separation of the oxide at the particle line during cooling or subsequent handling.

A micrograph typical of the cross-section of a Zircaloy-4 fuel tube oxidized at temperatures in this range is shown in Fig. 1. The nominal oxidation conditions were 600 s at 1200°C. The particle line is visible near the midplane of the oxide layer, which is otherwise essentially featureless at this magnification. Specimens fractured and viewed in the SEM show that this oxide is comprised mainly of thin, columnar grains resembling tightly packed broomstraws. The grain thicknesses vary slightly in a given specimen and with temperature, ranging from about 1 μm at 1000°C to about

2 μm at 1300°C. The alpha layer is seen to contain large columnar grains, many extending completely across the layer. Cracks in the alpha layer occur for the most part during cooling and specimen preparation and indicate the brittle nature of this high-oxygen phase. At the stage of oxidation depicted in the figure, the (prior) beta phase is at about 70 percent relative saturation, and the alpha-beta interface is relatively uniform and free of "incursions," or protrusions of alpha into the beta.

At low magnifications, the microstructure of a zirconium specimen oxidized in a comparable manner is quite similar to that of the alloy. Figure 2 illustrates the layers on a pure zirconium specimen after oxidation in steam for about 720 s at 1200°C. Of course there is no particle line in the oxide on the high-purity metal, and the apparent porosity here is largely a polishing artifact that can be avoided only by very careful specimen preparation. Examination of the oxide in the SEM shows large columnar grains (about 5–20 μm thick at 1200–1400°C) extending on the average through a significant fraction of the total oxide layer thickness. The oxygen-stabilized alpha layer is again comprised of large, brittle, columnar grains. The larger apparent grain size of the (prior) beta region of this specimen is characteristic of the arc-melted crystal-bar material.

In Zircaloy-4, a characteristic feature in specimens oxidized for extended periods of time is the appearance of irregular growths of alpha at the alpha-beta interface resulting in an ill-defined zone of oxygen-rich metal. In quenched specimens, incursions appear to be initiated at such a time when the oxygen concentration gradient in the beta phase becomes flat (as the beta becomes saturated).^{10,18,21} While slow cooling from the reaction temperature promotes incursion formation,^{18,20} it appears that

a high degree of saturation of the beta phase is still a necessary condition.¹⁸ An example of incursion formation is given in Fig. 3, which is the cross-section of a Zircaloy-4 specimen oxidized 950 s at 1300°C and quenched into flowing steam. Calculations based on an ideal diffusion modeling analysis indicate that the average oxygen concentration in the beta phase was 98 percent of its saturation value at the oxidation temperature.

In contrast, prolonged oxidation of similar specimens of pure zirconium does not lead to incursion formation. The alpha-beta boundary remains uniform and well-defined even as a fully saturated beta phase is being completely consumed by the advancing alpha. Figure 4 is from a specimen of pure zirconium oxidized for 500 s at 1416°C, approximately the same extent of oxidation and beta saturation as the Zircaloy-4 specimen in Fig. 3. In this instance, the continued uniform growth of both the oxide and alpha layers is evident, and no incursions are observed. The mechanism by which incursion formation occurs is not known; however, it must involve the alloying elements and be associated in some way with the oxygen content in the beta phase. For example, in Zircaloy-4 a segregation of the small amounts of Fe and Cr to the beta phase immediately behind the alpha-beta boundary has been reported.¹⁹ Such a partitioning may influence oxygen diffusion or disturb the local interface movement leading to an erratic or distorted interface. Additional information is necessary before a quantitative mechanism can be proposed.

Oxidation Kinetics — The rates of growth of the oxide and oxygen-stabilized alpha layers on zirconium in flowing steam at 1098, 1200, and 1416°C were described accurately in the early stages of reaction by parabolic kinetics. The applicable rate expression is

$$\frac{dk}{dt} = \frac{1}{k} \frac{\delta_k^2}{2} \quad (1)$$

where k is any kinetic parameter (oxide layer thickness, ϕ ; alpha layer thickness, α ; oxygen consumed, τ) and $\frac{\delta_k^2}{2}$ is the parabolic rate constant for the kinetic parameter. Thus, a plot of the square of the kinetic parameter versus time is linear with a slope of δ_k^2 .

Data typical of the kinetics of oxide and alpha growth on zirconium in the temperature range of interest are presented in Fig. 5 for oxidation at 1200°C. Ideal parabolic growth was found at this temperature for at least 500 s. At longer times, increased rates were observed, particularly for the alpha layer, as a consequence of the increasing oxygen levels in the beta phase. The time at which such deviations from parabolic behavior are observed depends upon the temperature, the specimen thickness, and whether a one- or two-side experiment is conducted.¹⁸

Figure 5 also illustrates the typical differences in growth kinetics for zirconium compared to Zircaloy-4. The parabolic rate constant for oxide growth on pure zirconium is substantially less than that on Zircaloy-4, while growth of the alpha layer is slightly higher. Similar comparisons were found at all three temperatures of our investigation. A summary of the kinetic data at the three temperatures chosen for comparison is given in Table I. Included here are the parabolic rate constants for total oxygen consumption (weight gain) computed by means of a modeling analysis that accounts for the oxygen gradients in each phase and calculates the amount of oxygen accordingly. Significant differences in the kinetics of zirconium and Zircaloy-4 oxidation are observed at each temperature, and the differences are larger at the lower temperatures. The kinetic data are plotted in

Arrhenius fashion in Fig. 6, the solid lines representing the data for zirconium, the dashed lines representing the data for Zircaloy-4.

The least-squares Arrhenius expressions for the parabolic rate constants for the oxidation of zirconium in steam are

$$\frac{\delta_{\phi}^2}{2} = 0.04361 \left[\begin{smallmatrix} +35\% \\ -26\% \end{smallmatrix} \right] \exp(-176500[\pm 2.1\%]/RT) \text{ cm}^2/\text{s}. \quad (2)$$

$$\frac{\delta_{\alpha}^2}{2} = 0.2693 \left[\begin{smallmatrix} +1350\% \\ -13\% \end{smallmatrix} \right] \exp(-185400[\pm 18\%]/RT) \text{ cm}^2/\text{s}. \quad (3)$$

$$\frac{\delta_{\tau}^2}{2} = 0.4948 \exp(-187300/RT) (\text{g}/\text{cm}^2)^2/\text{s} \quad (4)$$

where the subscripts ϕ , α , and τ refer to the parameters of oxide and alpha growth and of oxygen consumption, respectively. The activation energy values are expressed in units of joules/mole, and R is $8.314 \text{ J/g-mol}\cdot\text{K}$. The quantities in brackets are the individual 90 percent confidence intervals on each term. Their significance has been discussed previously,² and they are larger than the corresponding values for Zircaloy-4 (see below) mainly because of the small number of data points used. The joint confidence intervals, which reflect the statistical uncertainty on the rate constants themselves, are about ± 3 percent for oxide growth and about ± 25 percent for alpha growth measured at the mean of the reciprocal temperatures covered. No statistics are reported in Eq. (4) because these values for oxygen consumed were computed from the smoothed data sets utilized in modeling rather than directly from experimental data.

The corresponding rate constants for Zircaloy-4 oxidation in steam are (p. 12)

$$\frac{\delta_{\phi}^2}{2} = 0.01126 \left[\begin{smallmatrix} +29\% \\ -22\% \end{smallmatrix} \right] \exp(-150200[\pm 2.1\%]/RT) \text{ cm}^2/\text{s} \quad (5)$$

$$\frac{\delta_{\alpha}^2}{2} = 0.7615 \left[\begin{smallmatrix} +54\% \\ -35\% \end{smallmatrix} \right] \exp(-201400[\pm 2.6\%]/RT) \text{ cm}^2/\text{s} \quad (6)$$

$$\frac{\delta_{\tau}^2}{2} = 0.1389 \exp(-165200/RT) \quad (g/cm^2)^2/s \quad (7)$$

where the nomenclature is the same as that above. The midspan joint confidence intervals in these cases are ± 2.5 percent for oxide growth and ± 6 percent for alpha growth.

The above analytical expressions accurately describe the temperature dependence of the parabolic rate constants appropriate to the oxidation of these materials. It should be mentioned, however, that there is no *a priori* reason that the temperature dependence of these rate constants should be represented by Arrhenius expressions with a unique activation energy. Each rate constant is dependent upon rate behavior in more than one phase and thus may depend upon several "pure" processes (diffusivity, for example) each having different activation energies. In fact, however, the experimental results can be reasonably approximated by a single Arrhenius relationship, and the above expressions are useful, particularly for computational purposes.

Oxygen Diffusion — The oxidation of Zircaloy-4 has been shown to be modeled accurately as a multiphase, moving boundary, diffusion problem utilizing available phase diagram information and derived values for the diffusion coefficients for oxygen in each of the phases. Both computer modeling^{4,11,18} and analytical solutions^{8,14,16,22} have been employed.

Based on the ideal diffusion model, analytical expressions that relate the effective chemical diffusion coefficients in the growing oxide and alpha phases to the measured parabolic rate constants for growth of these phases

have been published and applied to the Zircaloy-4 system.²² In an identical fashion, it is possible to apply these equations, with suitably altered phase equilibria, to the kinetic data for pure zirconium to arrive at diffusion coefficients applicable to this system.

In addition to the parabolic rate constants for oxide and alpha layer growth on pure zirconium presented in Table I, it is necessary to have values for the diffusivity of oxygen in beta zirconium and the equilibrium oxygen concentrations at the various interfaces in the zirconium-oxygen system. Only the concentrations at the alpha-beta interface are assumed to be different for zirconium as compared to Zircaloy and, employing the terminology $C_{A/B}$ to represent the oxygen concentration in phase A in contact with phase B, the following expressions were used:

$$C_{\phi/\text{gas}} = 1.511 \text{ g/cm}^3 \text{ (ref. 23)}$$

$$C_{\psi/\alpha} = 1.517 - 7.5 \times 10^{-5} T(K) \text{ g/cm}^3 \text{ (ref. 24)}$$

$$C_{\alpha/\phi} = 0.4537 \text{ g/cm}^3 \text{ (refs. 25,26)}$$

$$C_{\alpha/\beta} = -2.906 + 5.322 \times 10^{-3} T(K) - 3.170 \times 10^{-6} T^2(K) \\ + 6.519 \times 10^{-10} T^3(K) \text{ g/cm}^3 \text{ (refs. 25,26)}$$

$$C_{\beta/\alpha} = -0.11136 + 7.109 \times 10^{-5} T(K) \\ + 2.271 \times 10^{-8} T^2(K) \text{ g/cm}^3 \text{ (refs. 25,26,27)}$$

$$D_{\beta} = 0.0263 \exp(-118000/RT) \text{ cm}^2/\text{s} \text{ (ref. 28)}$$

A computer program was used with the above data to solve Eqs. (11) and (18) of reference 22. The oxygen diffusion coefficients are presented in Table II where they are compared with the corresponding values for Zircaloy-4. A large difference in the effective diffusion coefficient for oxygen in the oxide phase growing on zirconium and Zircaloy-4 is observed. On the other hand, the difference in the diffusion coefficients for oxygen in the alpha layers is very small and cannot really be distinguished from zero on the basis of these data. In fact, the least squares Arrhenius expression is statistically indistinguishable at the 90% confidence level from that for diffusion in the alpha phase for Zircaloy-4. Thus, we conclude, in accord with the results of other investigators,²⁸ that the minor alloy additions in Zircaloy-4 do not measurably affect diffusion in the metallic alpha phase. This consistency and the excellent quantitative agreement of our values of D_α with those obtained by other means is evidence that the general technique is valid and that the corresponding values of D_ϕ are similarly accurate.

The calculated oxygen diffusion coefficients in the oxide on zirconium and on Zircaloy-4 are compared in Fig. 7. Values determined by Deguigne¹³ for zirconium are also included. The least squares Arrhenius expressions for the two data sets are as follows:

For pure Zr:

$$D_\phi = 0.4684 \left[\begin{smallmatrix} +43\% \\ -30\% \end{smallmatrix} \right] \exp(-168500 [\pm 2.6\%]/RT) \text{ cm}^2/\text{s}; \quad (8)$$

and for Zircaloy-4:

$$D_\phi = 0.1270 \left[\begin{smallmatrix} +21\% \\ -17\% \end{smallmatrix} \right] \exp(-144400 [\pm 1.6\%]/RT) \text{ cm}^2/\text{s}; \quad (9)$$

for both zirconium and Zircaloy-4, based on the extensive data set available for Zircaloy-4:²²

$$D_{\alpha} = 3.920 \left[\begin{smallmatrix} +27\% \\ -21\% \end{smallmatrix} \right] \exp(-213400 [\pm 1.4\%]/RT) \text{ cm}^2/\text{s} \quad (10)$$

As before, the brackets refer to the 90 percent individual confidence intervals. The midspan joint confidence intervals are approximately ± 3.5 , ± 2 , and ± 2.5 percent, respectively. These parameters are, like the rate constants, expected to be valid over the temperature range 1098 to 1416°C.

The above data indicate that not only is there a difference in diffusion rates for oxygen in the oxide growing on the two materials, but that a higher activation energy applies for diffusion in the oxide on zirconium. At these temperatures, the oxide appears to grow predominantly by anion vacancy diffusion in both cases, and the mechanism by which these differences arise is not clear. One possibility is that the morphological and grain size differences discussed earlier may lead to different relative contributions of short-circuit diffusion to the growth processes.

Regardless of the precision of the kinetic data, the absolute accuracy of the calculated diffusion coefficients is related to the accuracy of the phase diagrams available for each system. While large discrepancies are not expected in the region of the metallic phases, the phase boundaries for tetragonal ZrO_2 are not well defined. The assumption that stoichiometric ZrO_2 exists at the oxide-steam interface is a matter that also needs further examination. However, despite the approximations inherent in stipulating the equilibrium concentrations, the calculated diffusivities presented in this paper comprise a highly self-consistent set of values, in good agreement

with independent measurements (where comparisons are possible), and are capable of serving as input to modeling codes in order to predict oxidation behavior for a variety of experimental conditions.

CONCLUSIONS

1. During oxidation at temperatures above about 1100°C, zirconium and Zircaloy-4 exhibit, for at least at short reaction times, ideal parabolic kinetics for the growth of both oxide and alpha layers into the host beta phase.

2. The parabolic rate constants for growth of the oxide and alpha phases are different for the alloy as compared to the pure metal. From 1098 to 1416°C, the difference in these constants varies from $\pm 159\%$ to $+68\%$ for oxide growth, -36% to -14% for alpha layer growth, and $+97\%$ to $+37\%$ for total oxygen consumption or weight gain.

3. At longer oxidation times, the uniform growth of the alpha layer for Zircaloy-4 specimens is perturbed by the tendency to form "alpha incursions," irregular protrusions of oxygen-rich material into the beta phase. The initiation of this event is tied closely to the time at which the remaining beta phase approaches saturation with oxygen and, thus, is dependent upon the specimen thickness and other experimental conditions. Conversely, for isothermal oxidation under similar conditions, the development of incursions was not observed for pure zirconium.

4. While significant differences in the parabolic rate constants for both oxide and alpha layer growth were observed for zirconium as compared to Zircaloy-4; the modeling analysis concludes that this response is consistent with a difference in the effective diffusion coefficient of oxygen in the oxide layers alone. A different activation energy was also

observed. The different morphologies of the oxide layers on the two materials may be responsible.

5. Unlike Zircaloy-4, the observation of complex oxidation kinetics at 1000°C for zirconium suggests that the effects of the monoclinic-tetragonal transition in the oxide may be felt at higher temperatures in the pure metal for isothermal oxidation.

6. Despite the complexity of the oxidation process for these materials, the ideal nature of the layer growth permits comparisons to be made and mechanistic information to be extracted on the basis of diffusion modeling. In many instances, modeling is a useful and accurate tool to predict the oxidation response for a variety of conditions.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the aid and continuing discussions with J. V. Cathcart during the course of this work and in the preparation of the manuscript. Mrs. Kaye Russell assisted with the specimen preparation and metallography. Thanks are extended to D. O. Hubson for his suggestions and for a critical review of the manuscript.

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Fig. 1. Cross-section of Zircaloy-4 PWR fuel tube oxidized in steam for 600 s at 1200°C. The relative oxygen saturation of the beta phase was calculated to be about 70 percent. The specimen was etched in a diluted Kroll's reagent and anodized to 20 v in 1% KOH. Bright-field micrograph.

Fig. 2. Cross-section of pure zirconium specimen oxidized in steam for 720 s at 1200°C. The relative oxygen saturation of the beta phase was also calculated to be about 70 percent.

Fig. 3. Cross-section of Zircaloy-4 specimen oxidized in steam for 950 s at 1300°C. The relative oxygen saturation of the beta phase was calculated to be about 98 percent. Note this irregular alpha-beta interface, and "incursions" of alpha into the prior beta region. A slight separation of the oxide layer along the particle line is also observed in this specimen.

Fig. 4. Cross-section of pure zirconium specimen oxidized in steam for 500 s at 1416°C. The relative oxygen saturation of the beta phase is about 95 percent and no incursions or irregular growths are observed at the alpha-beta interface. The large columnar grains in the oxide, some of which have fallen out during polishing, are visible.

Fig. 5. Growth of the oxide and alpha layers on pure zirconium and Zircaloy-4 during oxidation in steam at 1200°C. While longer-time experiments are not included in this figure, oxygen build-up in the beta phase is beginning to affect the kinetics of alpha growth as indicated.

Fig. 6. Parabolic rate constants for oxide layer growth, alpha layer growth, and oxygen consumption for the reaction of zirconium (solid lines) and Zircaloy-4 (dashed lines, from ref. 2) with steam. The rate constants for oxygen consumed (weight gain) were determined from modeling analyses.

Fig. 7. Diffusion coefficients for oxygen in the growing oxide on zirconium and Zircaloy-4 during isothermal reaction in steam. The data of Debuigne¹³ for zirconium are included for comparison. The data point for zirconium at 1000°C is suspect because an accurate measurement of the kinetics for tetragonal oxide growth at this temperature could not be obtained.

Table I. Parabolic Rate Constants for Oxidation of Zirconium and Zircaloy-4 in Steam

Temperature (°C)	Parabolic Rate Constants								
	Oxide, $\frac{\delta^2}{2}$, cm ² /s			Alpha, $\frac{\delta^2}{2}$, cm ² /s			Ox. Cons. $\frac{\delta^2}{2}$, (g/cm ²) ² /s (a)		
	Zr	Zr-4	Diff. % (b)	Zr	Zr-4	Diff. % (b)	Zr	Zr-4	Diff. % (b)
1098	8.27×10^{-9}	2.14×10^{-8}	+159	2.50×10^{-8}	1.61×10^{-8}	-36	3.60×10^{-8}	7.10×10^{-8}	+97
1200	2.37×10^{-8}	5.33×10^{-8}	+125	6.46×10^{-8}	5.48×10^{-8}	-15	1.13×10^{-7}	1.93×10^{-7}	+71
1416	1.52×10^{-7}	2.56×10^{-7}	+68	4.49×10^{-7}	4.49×10^{-7}	-14	7.95×10^{-7}	1.09×10^{-6}	+37

(a) Based on modeling calculation.

(b) Percent change compared to pure Zr.

Table 11. Oxygen Diffusion Coefficients in Oxide and Alpha Phases of Zirconium and Zircaloy-4 During Steam Oxidation

Temperature (°C)	Oxygen Diffusion Coefficients					
	Oxide, D_{ϕ} , cm ² /s			Alpha, D_{α} , cm ² /s		
	Zr	Zr-4	Diff. % (a)	Zr	Zr-4	Diff. % (a)
1098	1.80×10^{-7}	4.01×10^{-7}	+123	3.10×10^{-8}	2.91×10^{-8}	-6.1
1200	4.90×10^{-7}	9.64×10^{-7}	+97	1.01×10^{-7}	1.06×10^{-7}	+5.0
1416	2.90×10^{-6}	4.35×10^{-6}	+50	1.01×10^{-8}	9.87×10^{-7}	-2.6

(a) Percent change compared to pure Zr.

Fig. 1. Cross-section of Zircaloy-4 PWR fuel tube oxidized in steam for 600 s at 1200°C. The relative oxygen saturation of the beta phase was calculated to be about 70 percent. The specimen was etched in a diluted Kroll's reagent and anodized to 20 v in 1% KOH. Bright-field micrograph.

Fig. 2. Cross-section of pure zirconium specimen oxidized in steam for 720 s at 1200°C. The relative oxygen saturation of the beta phase was also calculated to be about 70 percent.

Fig. 3. Cross-section of Zircaloy-4 specimen oxidized in steam for 950 s at 1300°C. The relative oxygen saturation of the beta phase was calculated to be about 98 percent. Note the irregular alpha-beta interface, and "incursions" of alpha into the prior beta region. A slight separation of the oxide layer along the particle line is also observed in this specimen.

Fig. 4. Cross-section of pure zirconium specimen oxidized in steam for 500 s at 1416°C. The relative oxygen saturation of the beta phase is about 95 percent and no incursions or irregular growths are observed at the alpha-beta interface. The large columnar grains in the oxide, some of which have fallen out during polishing, are visible.

Fig. 5. Growth of the oxide and alpha layers on pure zirconium and Zircaloy-4 during oxidation in steam at 1200°C. While longer-time experiments are not included in this figure, oxygen build-up in the beta phase is beginning to affect the kinetics of alpha growth as indicated.

Fig. 6. Parabolic rate constants for oxide layer growth, alpha layer growth, and oxygen consumption for the reaction of zirconium (solid lines) and Zircaloy-4 (dashed lines, from ref. 2) with steam. The rate constants for oxygen consumed (weight gain) were determined from modeling analyses.

Fig. 7. Diffusion coefficients for oxygen in the growing oxide on zirconium and Zircaloy-4 during isothermal reaction in steam. The data of Debuigne¹³ for zirconium are included for comparison. The data point for zirconium at 1000°C is suspect because an accurate measurement of the kinetics for tetragonal oxide growth at this temperature could not be obtained.