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# High-Temperature Oxidation of Zircaloy-4 in Steam and Steam-Hydrogen Environments

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Operated by  
Battelle Memorial Institute

Prepared for  
U.S. Nuclear Regulatory  
Commission

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## ABSTRACT

The oxidation kinetics of Zircaloy-4 in steam have been extended to 2400°C. The  $ZrO_2$  and  $\alpha$ -Zr layers display parabolic growth behavior over the entire temperature range studied. A discontinuity in the oxidation kinetics at 1510°C causes rates to increase above those previously established by the Baker-Just relationship. This increase coincides with the tetragonal-to-cubic phase transformation in  $ZrO_{2-x}$ . No additional discontinuity in the oxide growth rate was observed when the metal phase melted. The effects of temperature gradients were taken into account, and corrected values representative of near-isothermal conditions were computed. Oxide growth was also measured in various steam-hydrogen mixtures at 1565°C and 1815°C. Hydrogen concentrations up to 90 mol% had no effect on oxidation kinetics. The rate-controlling factor appears to be diffusion through the oxide layer.

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## SUMMARY

The high-temperature reaction rate of Zircaloy-4 in a steam environment was measured as part of a program to determine the important physical properties of light-water reactor materials that are relevant to loss-of-coolant accidents. Isothermal oxidation rates were measured from 1300 to 2400°C in flowing steam and steam-hydrogen environments at 1 atmosphere.

Metallographic sectioning of the samples indicated that the growth kinetics of the oxide layer were parabolic. The study confirmed the previous findings of Urbanic that identified a discontinuity in the oxide growth rate above 1500°C coinciding with the tetragonal-to-cubic phase transformation in  $ZrO_{2-x}$ . Above 1500°C, the parabolic growth rate constants for the  $ZrO_2$  layer ( $\phi$ ) and the combined  $ZrO_2$  and  $\delta$ -Zr(O) layer ( $\xi$ ) thicknesses were:

$$\delta_{\phi} = 5.46 \exp \frac{-14,210}{T(K)} (\pm 35\%) \text{ cm-s}^{-1/2} \quad (T = 1510 \text{ to } 2400^{\circ}\text{C})$$

$$\delta_{\xi} = 2.05 \exp \frac{-11,550}{T(K)} (\pm 42\%) \text{ cm-s}^{-1/2} \quad (T = 1510 \text{ to } 1900^{\circ}\text{C})$$

The oxidation kinetics were independent of steam pressure, flow rate, and hydrogen content, as long as sufficient steam was available to satisfy the requirements of the oxidation reaction. Particularly, oxidation experiments conducted in steam-hydrogen mixtures at 1565°C and 1815°C revealed that concentrations of hydrogen up to 90 mol% had no effect on the oxidation kinetics.



## INTRODUCTION

The results of a research program investigating the oxidation behavior of Zircaloy-4 in pure steam and steam-hydrogen gas mixtures are reported as part of the Severe Core Damage Materials Property Tests Program. The objective of the program is to perform high-temperature materials property tests to assist the U.S. Nuclear Regulatory Commission (NRC) in evaluating the damage that a nuclear reactor core and fuel assemblies might sustain during a loss-of-coolant accident (LOCA). The experimental work presented in this report was performed by Pacific Northwest Laboratory (PNL)<sup>(a)</sup> for the NRC Division of Accident Evaluation.

The high-temperature oxidation of zirconium alloys in steam is of great interest because of its importance to nuclear reactor safety. The oxidation behavior of Zircaloy at temperatures above 1300°C must be known to estimate peak cladding temperatures and hydrogen production rates that could result during a reactor LOCA. In cases where a small breach occurs in the coolant system of a pressurized-water reactor, severe core damage can result, as appears to have resulted at Three Mile Island Unit-2 (TMI-2). In this type of accident, the top portion of the core is uncovered; but a reservoir of water remains in the lower portion of the reactor, allowing cladding oxidation to continue. While loss of the moderator automatically shuts down the nuclear reaction, fission product decay heat in the fuel combined with the heat released by the highly exothermic oxidation of the uncovered Zircaloy cladding can drive fuel rod temperatures in the uncovered section of the fuel assemblies well above the melting point of Zircaloy. The severity of the LOCA is extremely dependent on the size of the breach and on the elapsed time before the emergency core cooling system refloods the core and begins to reverse the temperature rise.

Experimental data on the behavior of a full-size reactor core under these accident conditions do not exist. Instead, the NRC is developing computer codes to provide best-estimate calculations of the core behavior. Small-scale in-reactor tests are also being conducted to provide partial verification of the codes.

The success of these computer codes depends on the incorporation of good materials property data. The oxidation kinetics of Zircaloy is among the most critical because it is required to calculate the rate of energy release and the extent of cladding oxidation and hydrogen generation during the accident transient. Current U.S. power plant licensing criteria established in 10 CFR 50 (U.S. Code of Federal Regulations 1981) require the use of the Baker-Just

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(a) Operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

(1962) isothermal oxidation kinetics rates in all computer codes used to characterize cladding oxidation behavior during the transient. The Baker-Just rates were adopted because they provided a conservative estimate of oxidation-induced cladding embrittlement (overestimated cladding oxidation and thus embrittlement) during a large-break LOCA. Baker-Just rates provided for establishment of criteria that would avoid fuel fragmentation during core reflood. In a small-break LOCA, thermal excursions reach much higher temperatures. In this type of accident, the oxidation rates establish not only the extent of oxidation but also the rate of temperature rise and extent of cladding melting and fuel redistribution. Thus, it is extremely important that realistic rates be established and that any limitations on the accuracy and use of the oxidation kinetics be understood.

Considerable oxidation data now exist in the temperature range from 1000 to 1500°C.<sup>(a)</sup> However, there is only limited data reported on the oxidation kinetics of Zircaloy above the tetragonal-to-cubic phase transformation in  $ZrO_{2-x}$  at approximately 1500°C.<sup>(b)</sup> This phase transition results in a discontinuous increase in the oxide growth rate (Urbanic and Heidrick 1978). The effect that large quantities of hydrogen, evolving during a LOCA, have on Zircaloy oxidation kinetics is also a concern. Previous studies suggest that hydrogen may have a significant effect at concentrations over 50 mol% hydrogen (Chung and Thomas 1981). More recent work has raised the concentration limit to 70 mol% hydrogen (Chung and Thomas 1983).

In this study, isothermal oxidation rates of Zircaloy-4 from 1300°C to 2400°C in steam were determined and the influence of hydrogen on rate kinetics was investigated.

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(a) Cathcart and Pawel 1977; Hobson and Rittenhouse 1972; Suzuki, Kawasaki, and Furuta 1977; Ikeda, Ito, and Ohashi 1975; Leistikow, Shanz, and Berg 1978; Biederman et al. 1976; Sawatsky, Ledoux, and Jones 1977.

(b) Baker and Just 1962; Bostrum 1954; Lemmon 1957; Urbanic and Heidrick 1978.

## EXPERIMENTAL PROCEDURE

To measure the high-temperature oxidation kinetics of Zircaloy, an apparatus with low thermal inertia was required. A system was devised that employed laser energy to heat the sample. Oxidation kinetics were established by exposing samples to flowing steam for varying times at the same nominal temperature and then metallographically examining each sample to determine the growth behavior of the oxide layers.

A schematic of the oxidation apparatus is presented in Figure 1. Experiments were performed on disk specimens (3.8 mm diameter x 0.9 mm thick) that had been machined from reactor-grade Zircaloy-4 bar stock obtained from Teledyne Wah Chang. The nominal alloy composition was 1.5 wt% Sn, 0.20 wt% Fe, 0.11 wt% Cr, 0.125 wt% O, 0.016 wt% C, 0.004 wt% N, and 0.001 wt% H. Prior to oxidation testing, the disks were mechanically polished with 15- $\mu$ m SiC powder and then ultrasonically rinsed in isopropyl alcohol, acetone, and methanol.

A defocused CO<sub>2</sub> laser beam ( $\lambda = 10.6 \mu\text{m}$ ) with a maximum power output of 400 W was used to heat the samples from one side. The surface temperature of the sample was measured using a two-color pyrometer ( $\lambda = 0.95$  and  $1.06 \mu\text{m}$ ) calibrated regularly against an internal radiation source and initially standardized to the melting point of alumina. Temperature measurements were considered accurate to within  $\pm 15^\circ\text{C}$ . The experimental configuration permitted placement of the pyrometer to view either the heated or the nonheated side of the sample. A computer was coupled to both the pyrometer output and the power control circuit of the CO<sub>2</sub> laser, permitting rapid and reproducible temperature control to a preprogrammed time sequence. Real-time temperature profiles were also recorded.

### ISOTHERMAL OXIDATION

Isothermal oxidation experiments were performed between 1300°C and 2400°C. The specimens were first heated to a predetermined temperature in argon. Preheated 600°C steam was then introduced through a fast-acting valve at a rate of 3 g/min. The ensuing oxidation resulted in a rapid rise to the desired temperature, which was then held at a constant level by controlling the laser heat input. Each test was terminated after the desired time increment by closing the shutter on the laser, which resulted in a rapid quench of the sample at an initial rate of 500°C/s. Standard deviations for the isothermal temperatures were  $\pm 7^\circ\text{C}$  at 1600°C,  $\pm 10^\circ\text{C}$  at 1700°C,  $\pm 18^\circ\text{C}$  at 1780°C, and  $\pm 25^\circ\text{C}$  at 1800°C and above. An example of a 2300°C test is shown in Figure 2.

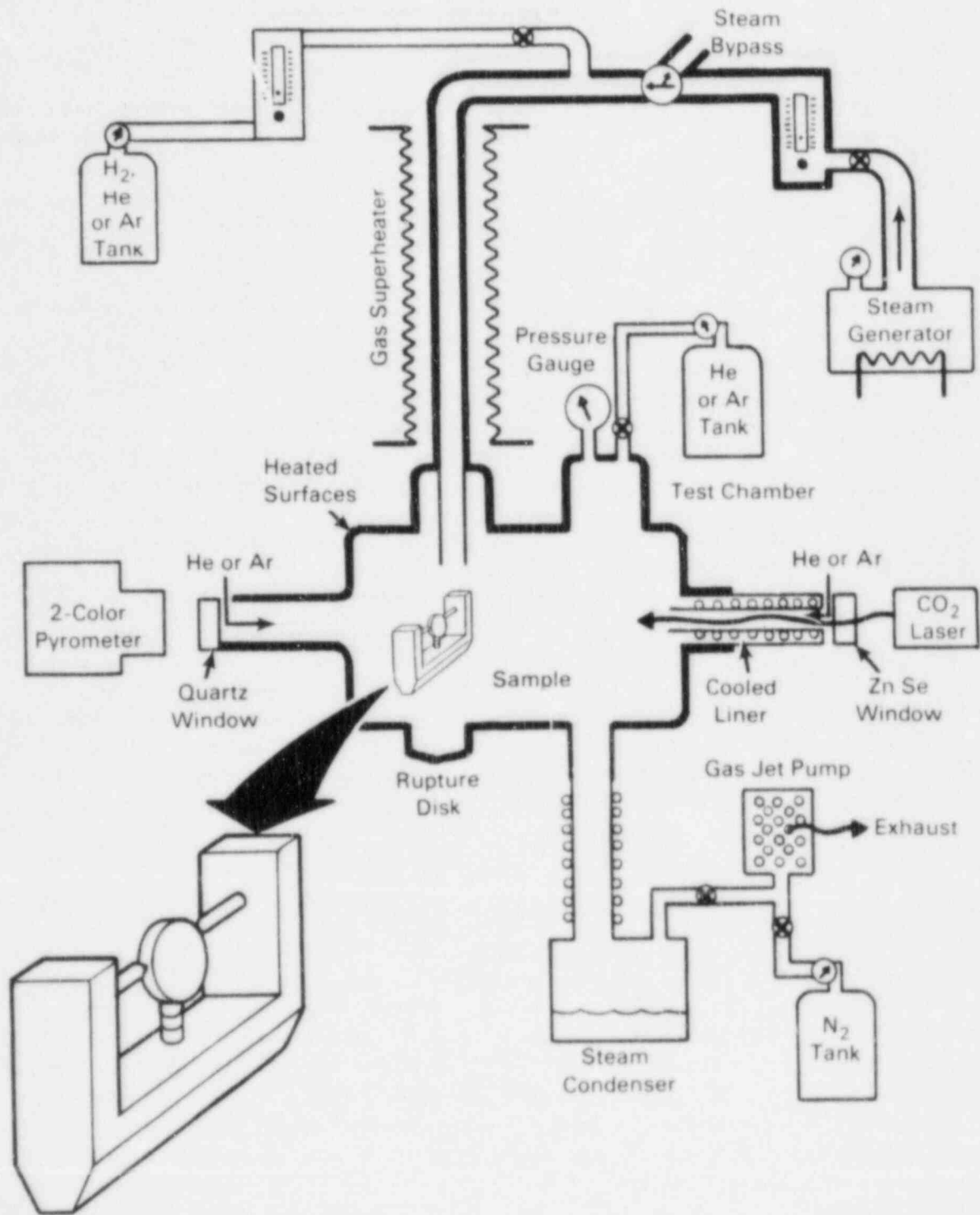


FIGURE 1. Apparatus Used to Measure High-Temperature Oxidation of Zircaloy

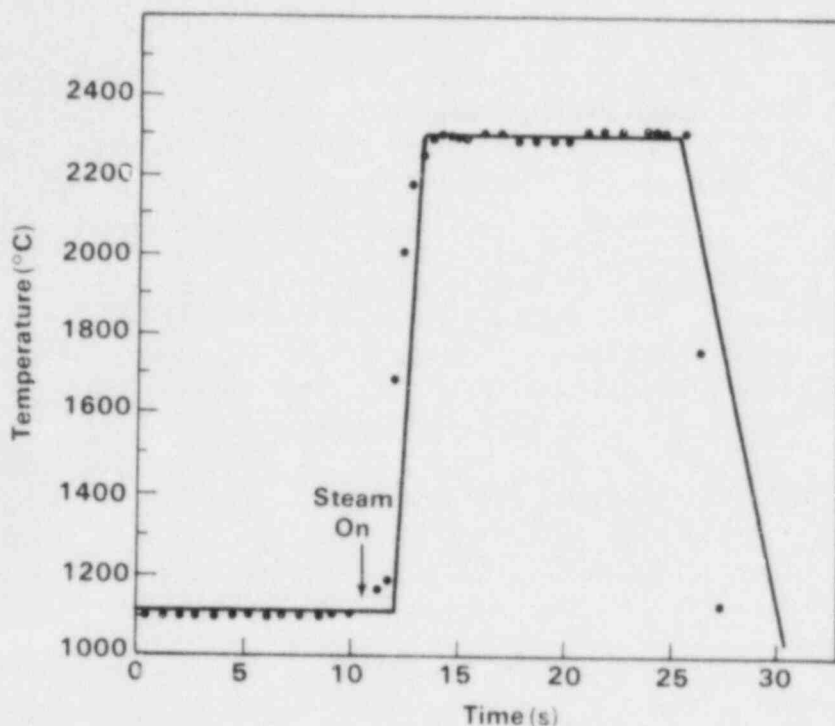


FIGURE 2. Temperature-Time Excursion for Isothermal Oxidation Experiment at 2300°C as Recorded by Computer. Actual data points are plotted along with the preprogrammed curve.

Oxidation kinetics were determined by metallographically sectioning each sample and measuring the thicknesses of the  $ZrO_2$  and  $\alpha$ -Zr layers that formed. A minimum of five specimens comprised the data set at each temperature. The small amount of oxidation that occurred during the initial exothermic reaction to temperature was measured independently and used to correct for  $t = 0$ .

Oxidation occurred from both sides of the sample. Thus, the oxygen concentration fluxes from the two sides of the sample overlapped at longer exposures. There was initial concern that the lack of an infinite  $\beta$ -Zr oxygen sink would accelerate the growth rates of the reaction layers, but the effect seemed to be small. This was confirmed by two observations: 1) both  $ZrO_2$  and  $\alpha$ -Zr displayed parabolic growth behavior up to the time of nearly complete overlap of the respective layers and 2) selected experiments with thicker samples (1.4 and 1.9 mm thick) displayed the same oxide growth kinetics as the standard (0.9-mm thick) samples.

#### TEMPERATURE GRADIENTS

The heating technique used in this study allowed the effect of temperature gradients across the thickness of the sample to be established. Gradients

arise from the insulating effect of the developing oxide. The exact profile of the temperature gradient across the sample could not be determined because the distribution of the heat from the oxidation was not known. However, the temperatures on the two faces could be measured. Thus, it was found that the temperature across the sample varied in proportion to the oxide thickness. Each 100  $\mu\text{m}$  of oxide thickness produced an additional temperature drop of about 50°C across the sample.

Two experiments were performed to establish the effect of the temperature gradient on oxidation kinetics. Oxide layer growth was measured on both the laser-heated side and the opposite side of the sample. For these two experimental configurations, the temperature gradients produced by the laser heating decreased or increased, respectively, away from the isothermally controlled surface temperature. The two data sets were expected to bracket the relationship that would be derived under "true" isothermal heating conditions and thereby provide a measure of the effect that the temperature gradient had on oxidation kinetics.

Metallographic examination of the samples revealed that there were also surface gradients that decreased from the center of the laser spot towards the outer circumference (Figure 3). In the area monitored by the pyrometer (the center two-thirds of the sample), oxide thickness variations around the mean did not exceed  $\pm 17\%$  on the laser-heated side or  $\pm 3\%$  on the nonheated side of the sample. For the worst case, this variation corresponded to a temperature drop of 90°C across the face of the sample; the typical decrease was about 15°C.

Average oxide layer thicknesses were calculated in a way that approximated the temperature averaging performed by the pyrometer. The samples were initially sectioned through the center of the laser-heated zone, and thicknesses were measured at five equally spaced locations that bounded the center two-thirds of the sample. These five values were then averaged giving full weight to the point in the center and half weight to the other four thickness measurements.

#### STEAM DILUTION IN HYDROGEN

Transient tests were performed in steam-hydrogen mixtures varying from 0 to 100% steam. In one test, samples were heated to 1450°C in helium before preheated steam-hydrogen mixtures were introduced directly over the surface. The temperature on the nonlaser-heated face was then stabilized and raised to 1565°C in 3 s where it was maintained for 25 s before quenching. Thickness measurements were made on the nonheated face. For testing at higher temperatures, it was necessary to control the temperature on the laser-heated side of the sample because there was insufficient energy capacity to raise the

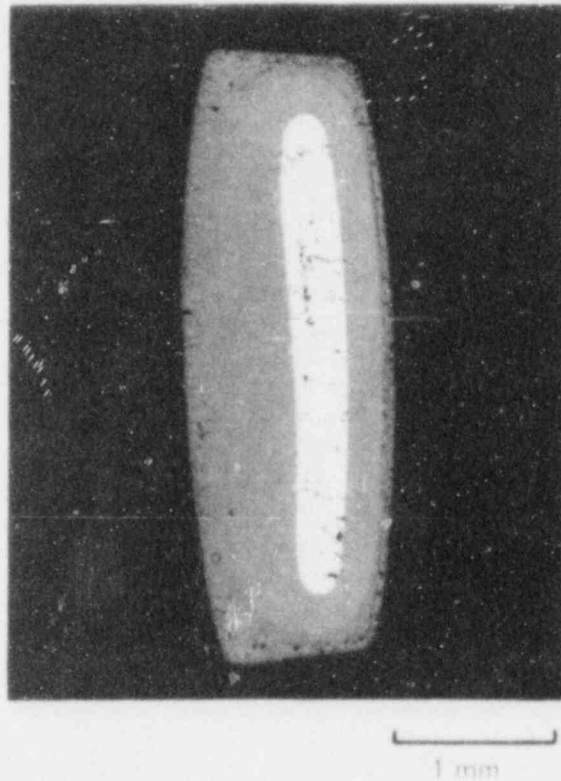


FIGURE 3. Micrograph of Zircaloy-4 Sample Oxidized in Steam for 54 s at 2020°C

nonheated side in the presence of hydrogen. First, the sample was heated to 1500°C in helium, the steam-hydrogen mixture was introduced, and then the temperature was raised at 10°C/s to 1815°C and maintained for 40 s.

The introduction of hydrogen (high thermal conductivity) had a decided cooling effect on the sample, as indicated by a cooling spike in the temperature-time plots. Steam had the opposite effect, causing sample temperatures to rise. Despite these perturbations, temperature control at the set point was maintained at  $\pm 35^\circ\text{C}$  and the average plateau temperature from run to run reproduced within  $\pm 12^\circ\text{C}$  at 1565°C and within  $\pm 8^\circ\text{C}$  at 1815°C.

For these experiments, a constant steam flow rate was maintained at 3 g/min and the hydrogen flow was varied to provide the desired  $\text{H}_2/\text{H}_2\text{O}$  ratio. This procedure helped assure that the supply of steam to the sample was maintained at an adequate level to support oxidation requirements; i.e., that steam starvation was not inadvertently induced as a result of the gas mixing and then mistakenly identified as a hydrogen effect.

## RESULTS AND DISCUSSION

Isothermal oxidation kinetics, metallography, and steam dilution results are presented in this section.

### ISOTHERMAL OXIDATION KINETICS

Oxide and alpha layer thicknesses were measured at 100°C intervals for temperatures between 1300°C and 2400°C. An example of the growth rates of the oxide, alpha, and combined layer growth at 1780°C is presented in Figure 4. An excellent correlation of layer thickness measurements with ideal parabolic behavior and the high degree of self-consistency are evident. Parabolic growth kinetics apply over the entire temperature range studied and can be described by the expression:

$$k = \delta_k t^{1/2}$$

where  $k$  = a kinetic parameter (oxide thickness,  $\phi$ ; alpha layer thickness,  $\alpha$ ; or combined oxide and alpha layer thickness,  $\xi$ )  
 $\delta_k$  = parabolic rate constant  
 $t$  = reaction time.

The linear relationship between the thickening of the reaction layers versus the square root of time (Figure 4) confirmed that the Zircaloy-steam reaction obeys parabolic kinetics, indicating that the reaction was probably controlled by anion diffusion through the oxide. To further test this conclusion, experiments were performed where the oxidation kinetics were compared among samples exposed to different steam flow rates (from 3 to 18 g/min) and to steam pressures of 0.1 and 0.5 MPa (1 and 5 atm absolute). No change in oxide growth rates was observed, indicating that the reaction was not gas phase diffusion limited.

The temperature dependence of the growth constants for the  $ZrO_2$  and the combined layer thicknesses are presented in Figure 5. The data measured on the heated and nonheated surfaces produced two distinct curves with approximately the same slope and activation energies. The two curves are offset along the temperature axis by an amount representing the difference between the actual measured temperature at the oxide surface and the effective temperature that characterizes (averages) the diffusional process across the entire oxide layer. The best estimate for the "true" isothermal oxidation rate, where no temperature gradient exists across the oxide layer, is the bisector of the two data curves.

The discontinuity in the growth rate observed around 1510°C was associated with the development of the cubic high-temperature oxide phase. No other



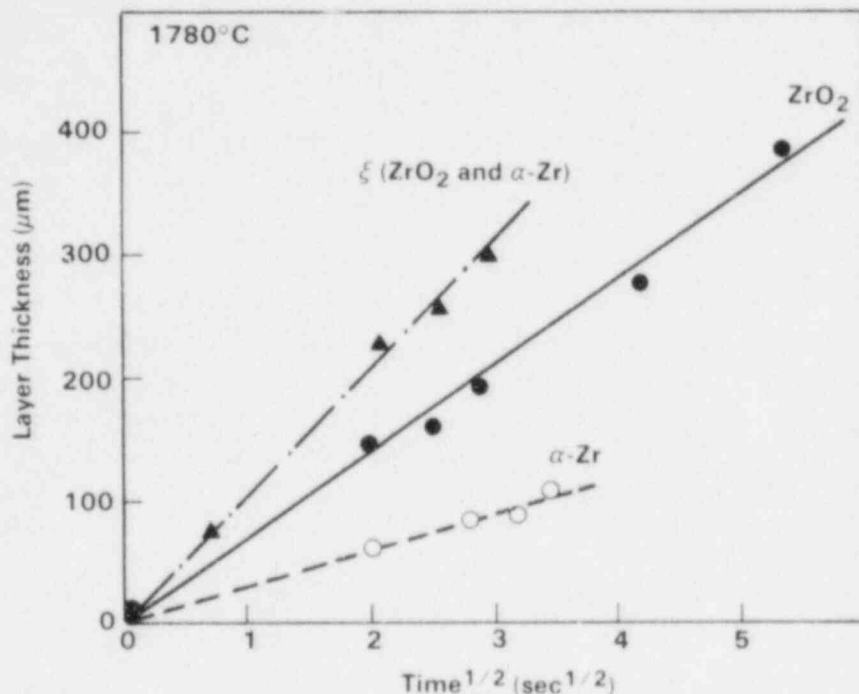


FIGURE 4. Growth of Oxide and  $\alpha$ -Zr Layers on Zircaloy-4 in Steam at 1780°C

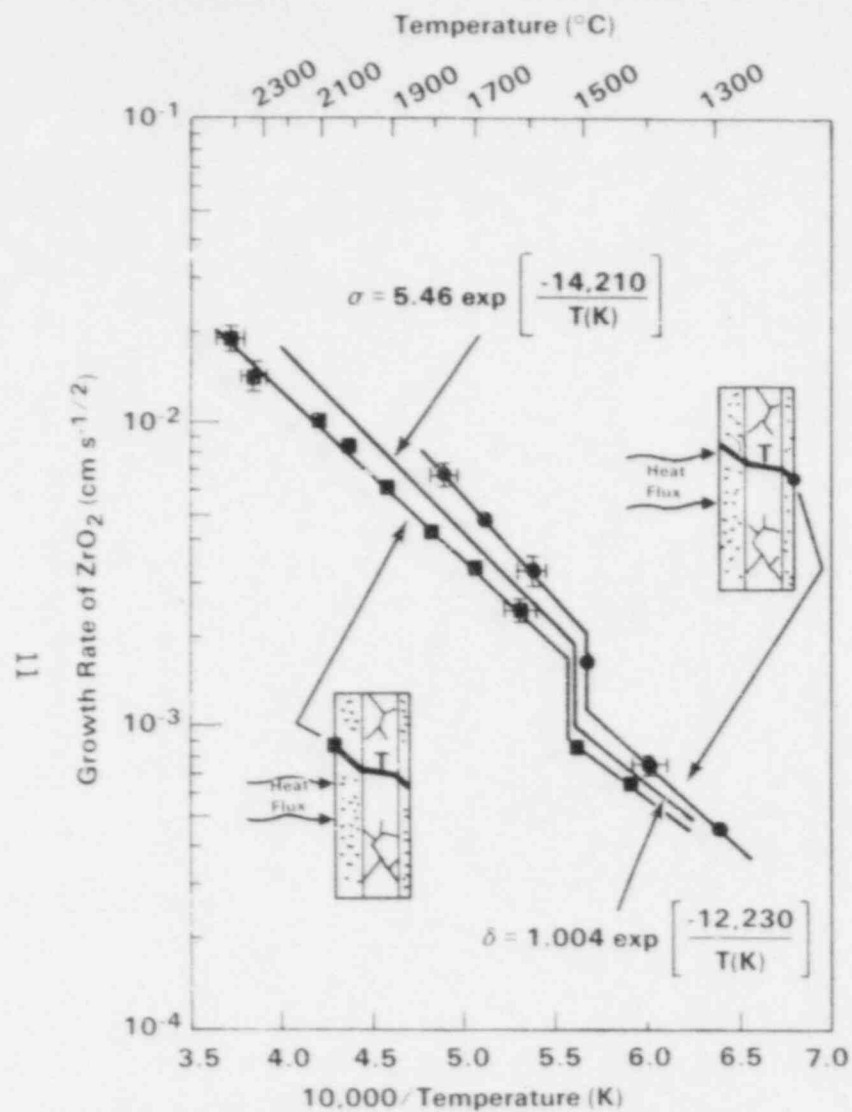
discontinuity in growth rate was observed, neither upon melting of the underlying metal at 1980°C nor upon transformation of the duplex (tetragonal-cubic)  $ZrO_2$  layer to a single-phase cubic oxide at 2285°C (Levin and McMurdie 1975). The temperature dependence of the isothermal growth constants above 1510°C for the  $ZrO_2$  layer ( $\delta_\phi$ ) and the combined layer ( $\delta_\xi$ ) can be described by the following equations:<sup>(a)</sup>

$$\delta_\phi = 5.46 \exp\left(\frac{-14,210}{T(K)}\right) (\pm 35\%) \text{ cm}\cdot\text{s}^{-1/2} \quad (T = 1510 \text{ to } 2400^\circ\text{C})$$

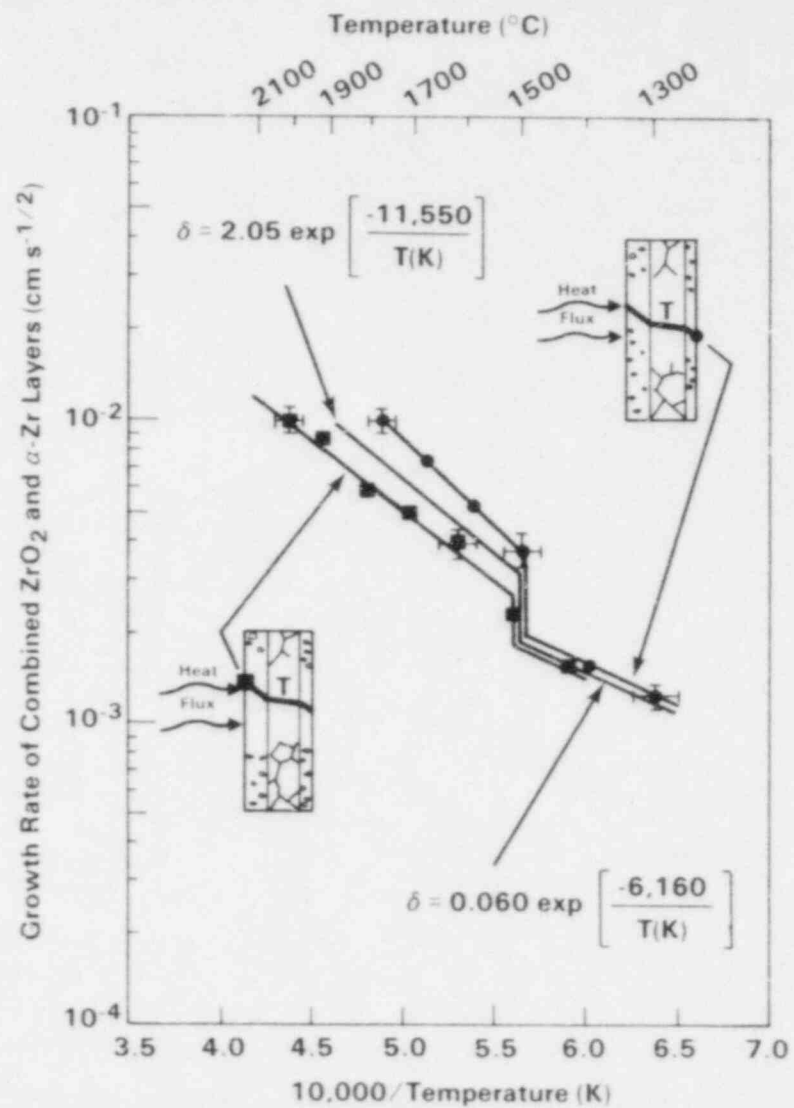
$$\delta_\xi = 2.05 \exp\left(\frac{-11,550}{T(K)}\right) (\pm 42\%) \text{ cm}\cdot\text{s}^{-1/2} \quad (T = 1510 \text{ to } 1900^\circ\text{C})$$

$ZrO_2$  growth rates determined in this work are compared with those of Cathcart-Pawel (1977), Urbanic-Heidrick (1978), and Baker-Just (1962) in Figure 6. For temperatures below 1500°C, the Cathcart-Pawel curve correlates with

(a) The uncertainties in the rate constants ( $\pm 35\%$  and  $\pm 42\%$ ) were determined by establishing 95% confidence limits for the data shown in Figure 5 and then determining the uncertainty in the bisector as extreme values of the experimental curves were taken.



a) ZrO<sub>2</sub> Layer



b) Combined ZrO<sub>2</sub> and  $\delta$ -Zr Layer

FIGURE 5. Parabolic Rate Constants for Oxide Layer Growth. Two sets of data, corresponding to the two experimental test configurations described in the text, are shown. The intermediate curve represents the best estimate of the growth constants for "true" isothermal conditions.

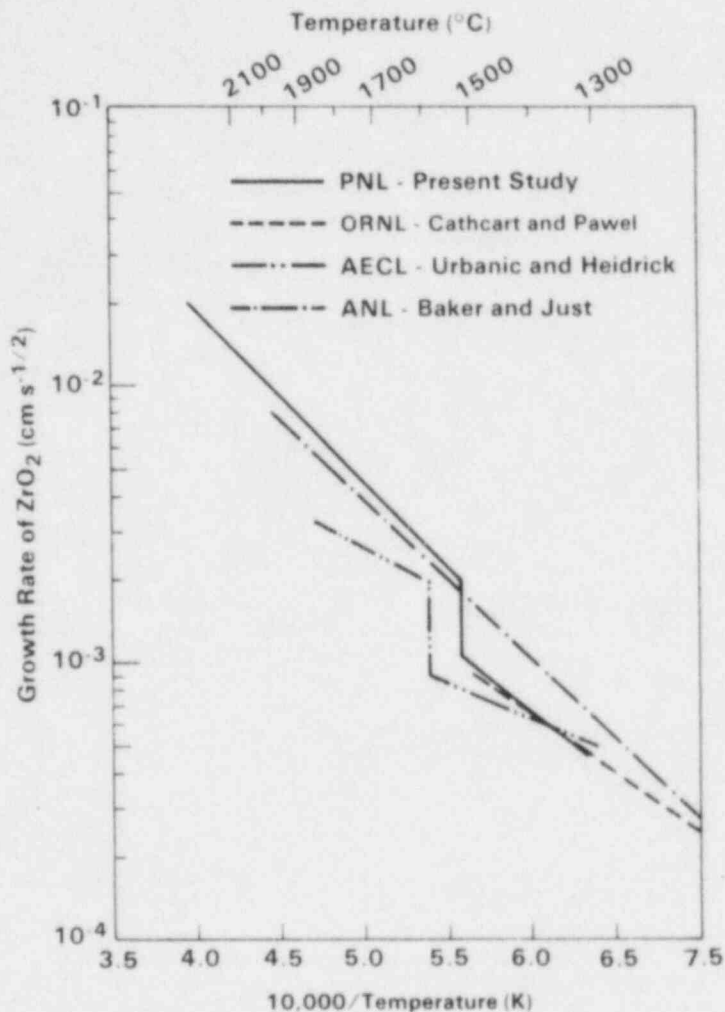


FIGURE 6. Comparison of Parabolic Rate Constants for Oxide Layer Growth

at least six other studies.<sup>(a)</sup> The agreement between the  $ZrO_2$  curves for Cathcart-Pawel and those from this study is very close, which lends confidence to the results obtained at higher temperatures. Above  $1510^\circ C$ , the kinetics increase to rates slightly above those reported by Baker-Just. The discontinuity in kinetics at  $1510^\circ C$  coincides well with the transformation temperature of  $1490^\circ C$  where cubic  $ZrO_2$  becomes stable (Ruh and Garrett 1967). The discrepancy between the data from this study and those of Urbanic-Heidrick, both for the rate curves above  $1500^\circ C$  and the temperature at which the discontinuity in

(a) Cathcart and Pawel 1977; Hobson and Rittenhouse 1972; Suzuki, Kawasaki, and Furuta 1977; Ikeda, Ito, and Ohashi 1975; Leistikow, Shanz, and Berg 1978; Biederman et al. 1976; Sawatsky, Ledoux, and Jones 1977.

the growth kinetics occurs, cannot be easily explained except by attributing them to uncertainties in the temperature measurements.

In applying the rate equations to the modeling of a fuel rod during a LOCA, consideration should be given to the heat flux within the rod. For example, actual oxidation rates might be better approximated by biasing the rates towards the experimental curve derived from samples with the temperature gradient similar to that of the fuel rod being modeled. A detailed heat balance within the cladding cannot be performed because the distribution of heat generated by the oxidation reaction is not known. However, for a first approximation, it may be reasonable to disregard this component because it is intrinsically contained within the experimental data. By doing this, the major consideration becomes one of calculating the relative contributions from the supplemental heat sources, i.e., from the fission product decay heat of the fuel and the heat being radiated from neighboring rods. When internal heating dominates, the rates will approach those of the upper curve. This is certainly the case at the start of an accident when the decay heat of the fuel is the major source of heat. Later, as rod-to-rod radiation becomes a major contributor, rates should be closer to the lower curve.

#### METALLOGRAPHY

Metallography from the three major temperature regimes are presented in Figures 7, 8, and 9. The structures are consistent with the Zr-O phase diagram (Levin and McMurdie 1975). Below 1510°C, the  $\beta$ -Zr reacts with oxygen to form a layer of tetragonal  $ZrO_2$  and a layer of oxygen-stabilized  $\alpha$ -Zr (Figure 7). Above 1510°C, a duplex oxide layer forms consisting of an outer layer of tetragonal zirconia and an inner layer of cubic zirconia (Figure 8). Depending on the oxygen content of the metal,  $\beta$ -Zr melts at 1850 to 1940°C and  $\alpha$ -Zr melts at 1900 to 1975°C. Thus, above 1980°C, the metal phase exists as a single molten phase and the only reaction product that forms is the duplex oxide (Figure 9). Although not as easily distinguished, the tetragonal oxide converts to the cubic phase above 2300°C, resulting in a single cubic oxide layer.

The presence of the light  $\alpha$ -Zr metal stringers in the oxide are a product of the eutectoid decomposition that the substoichiometric cubic oxide undergoes upon cooling to 1490°C to form  $\alpha$ -Zr (about 10 vol%) and tetragonal  $ZrO_2$ . To a lesser extent, a second eutectoid decomposition occurs in tetragonal  $ZrO_2$  upon cooling to 1000°C, producing stable monoclinic  $ZrO_2$  and  $\alpha$ -Zr. The latter phase is about 1 to 2 vol% and is visible only at higher magnifications.

The discontinuity in the oxidation kinetics is associated with the tetragonal-to-cubic phase transformation in the oxide (Urbanic and Heidrick

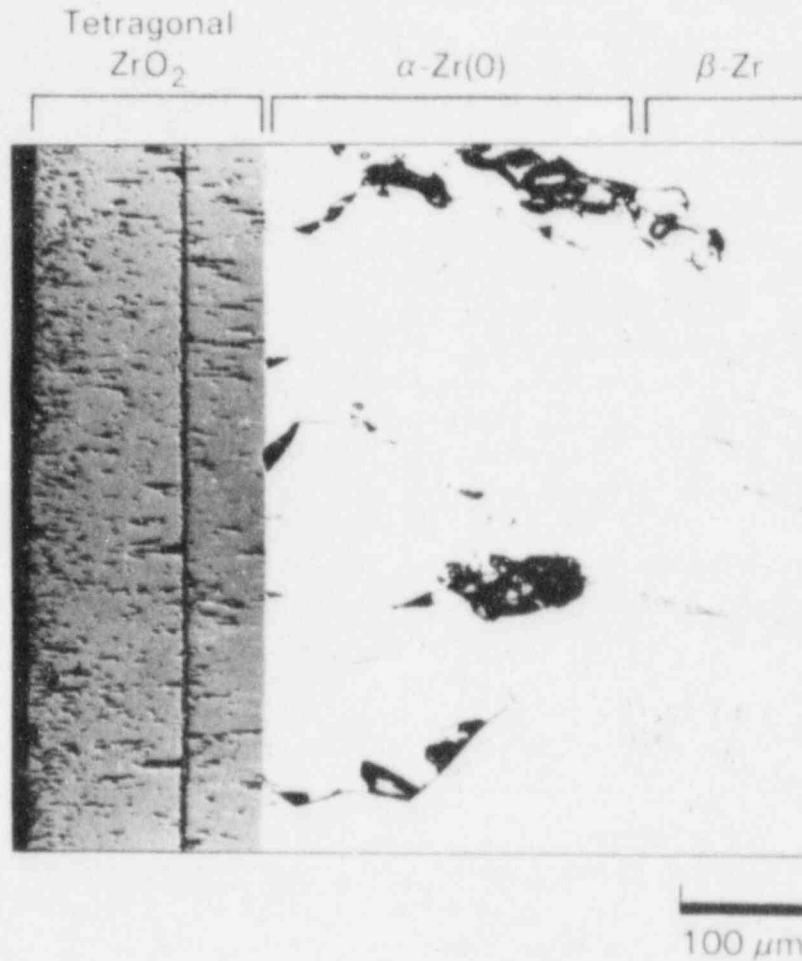


FIGURE 7. Micrograph of Zircaloy-4 Oxidized in Steam for 300 s at 1400°C

1978). Examination of the metallography for samples oxidized above 1510°C revealed that the direction of the temperature gradient across the oxide changed the ratio of the tetragonal/cubic oxide present. When the temperature increased toward the interior of the oxide layer, the tetragonal layer was relatively thin (approximately 25% of the total oxide thickness). In contrast, the tetragonal oxide that formed on the heated side, where the temperature decreased toward the interior of the sample, was thicker (approximately 35% of the total oxide layer thickness). This phenomena affects the oxidation kinetics since a relatively thick tetragonal phase is a better diffusion barrier, as evidenced by the decrease in the oxidation rates below 1510°C (Figure 5). Since oxygen diffusion in the cubic phase is faster than in the tetragonal

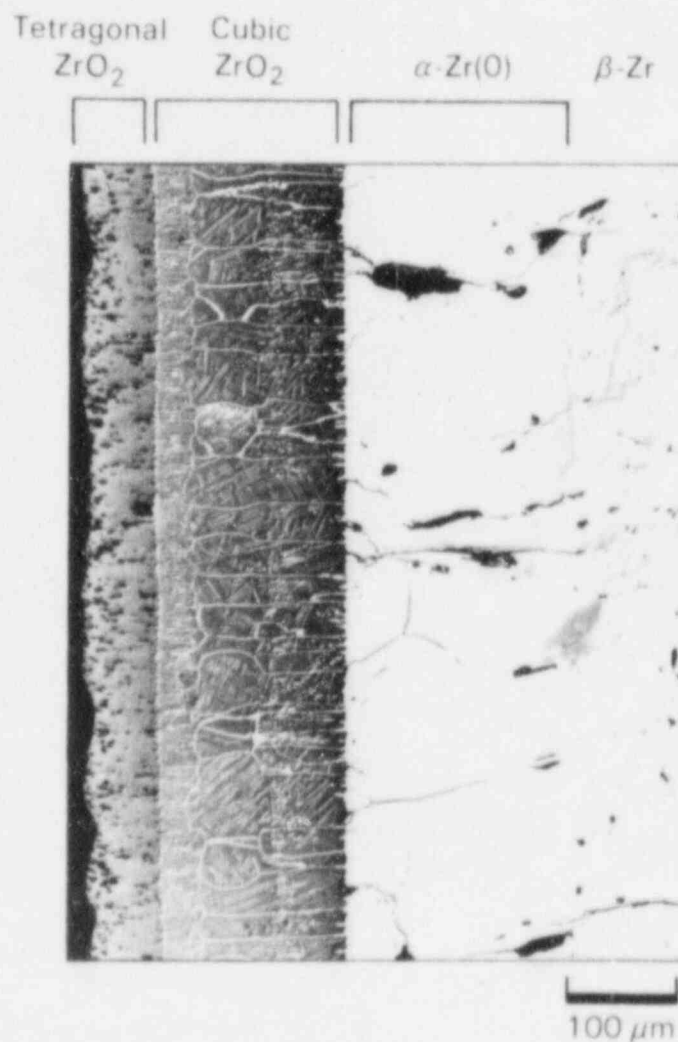


FIGURE 8. Micrograph of Zircaloy-4 Oxidized in Steam for 40 s at 1595°C

phase, further increases in oxidation kinetics might be expected above 2285°C where no tetragonal oxide exists. However, no discontinuous change in growth rate was observed.

The microstructure of molten Zircaloy is denoted by the presence of ZrO<sub>2</sub> precipitates that formed when liquid containing oxygen in excess of the

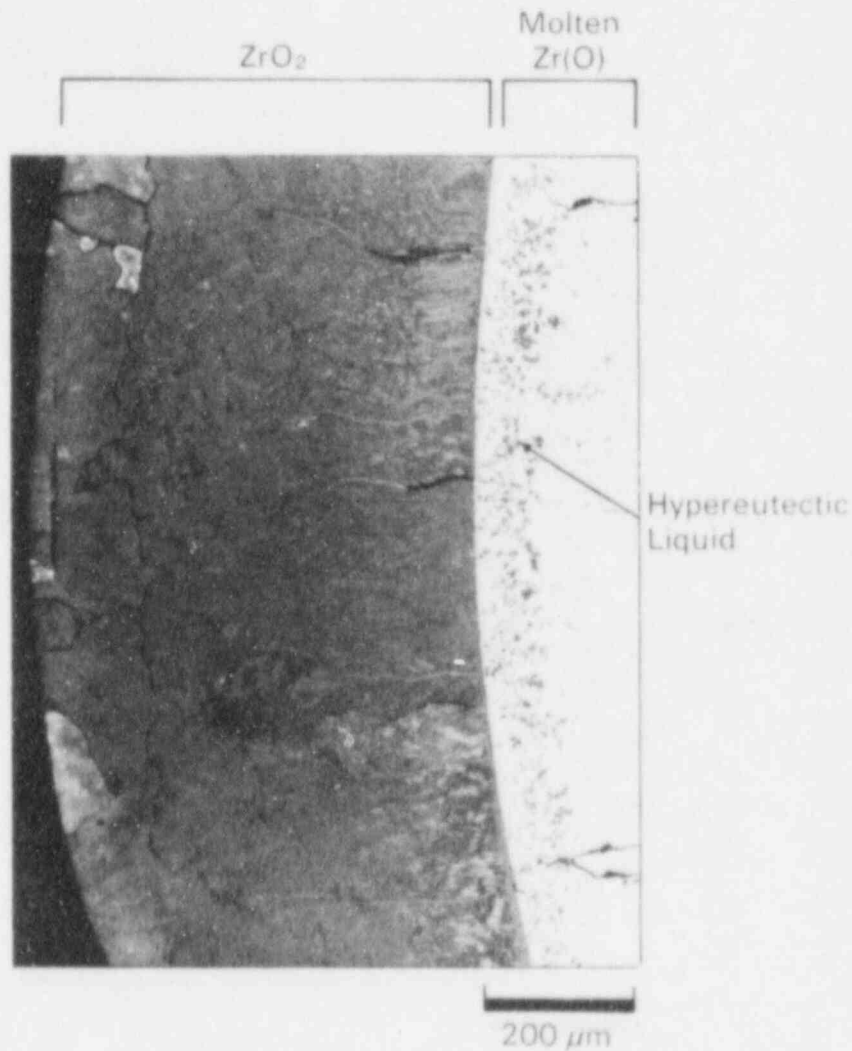


FIGURE 9. Micrograph of Zircaloy-4 Oxidized in Steam for 8.4 s at 2335°C

$\alpha$ - $Zr(O)$ - $ZrO_2$  eutectic composition cooled to below the eutectic temperature at 1900°C. Micrographs of samples oxidized above the melting point of the metallic phases reveal only a thin layer of hypereutectic liquid (Figure 9), suggesting that a steep oxygen gradient existed in the metallic phase, even though it was molten. The oxidation rates observed in this study should represent the oxidation behavior of nonturbulent molten zirconium metal. In a turbulent melt, the oxygen would be more homogeneously distributed and the oxide

layer growth would be retarded, although perhaps only slightly, since the metal phase would then represent a larger sink for oxygen. The continuity of rates through the melting point of the metal further supports the hypothesis that diffusion through the oxide layer represents the rate-controlling factor in the oxidation process over the temperature regime studied.

#### STEAM DILUTION EXPERIMENT

Oxide thickness measurements for a series of samples exposed to different steam-hydrogen mixtures under equivalent temperature transient conditions are compared in Figure 10. At 1565°C, no significant change in oxide thickness was observed for any of the steam-hydrogen mixtures (5 to 100 mol% steam). Oxide growth was inhibited only in pure hydrogen. The small rise in the curve at higher hydrogen contents was a result of sample cooling by the hydrogen gas. This cooling steepened the temperature gradient across the sample and increased the oxidation rate slightly on the nonheated side of the samples.

At 1815°C, the oxidation kinetics dropped sharply as the steam concentration decreased below 8% steam. However, a mixture of 9% H<sub>2</sub>O and 91% He exhibited a similar decrease in kinetics, suggesting that the supply of steam to the sample surface (gaseous transport) may have been limiting the kinetics. Mass transfer coefficients in the gas phase are flow rate dependent (Bennett and Meyers 1962). At the higher gas flow rates used to obtain the more dilute steam mixtures, steam supply to the sample surface may have been insufficient to satisfy full rate oxidation and thereby caused a decrease in the oxide thickness. Thus, the rapid decrease in oxidation does not appear to be uniquely caused by hydrogen but rather resulted from a more general gas dilution effect.

As the hydrogen concentration was increased, the cooling effect of the hydrogen-rich gas mixtures again increased the temperature gradient across the sample. However, because the 1815°C experiments were performed on the laser-heated side of the sample, the oxidation rate decreased slightly as the gas composition was varied from 0 to 90% hydrogen.

To obtain some indication of the hydrogen uptake by the samples, selected specimens were furnace annealed at 600°C and slow cooled (50°C/h) to promote the formation of hydrides in the metal phase. Metallographic sectioning and etching revealed hydrides only in those samples originally exposed to the pure hydrogen environment. No hydrides were observed in samples on which an oxide layer had formed. No quantitative analysis of the samples has yet been completed.



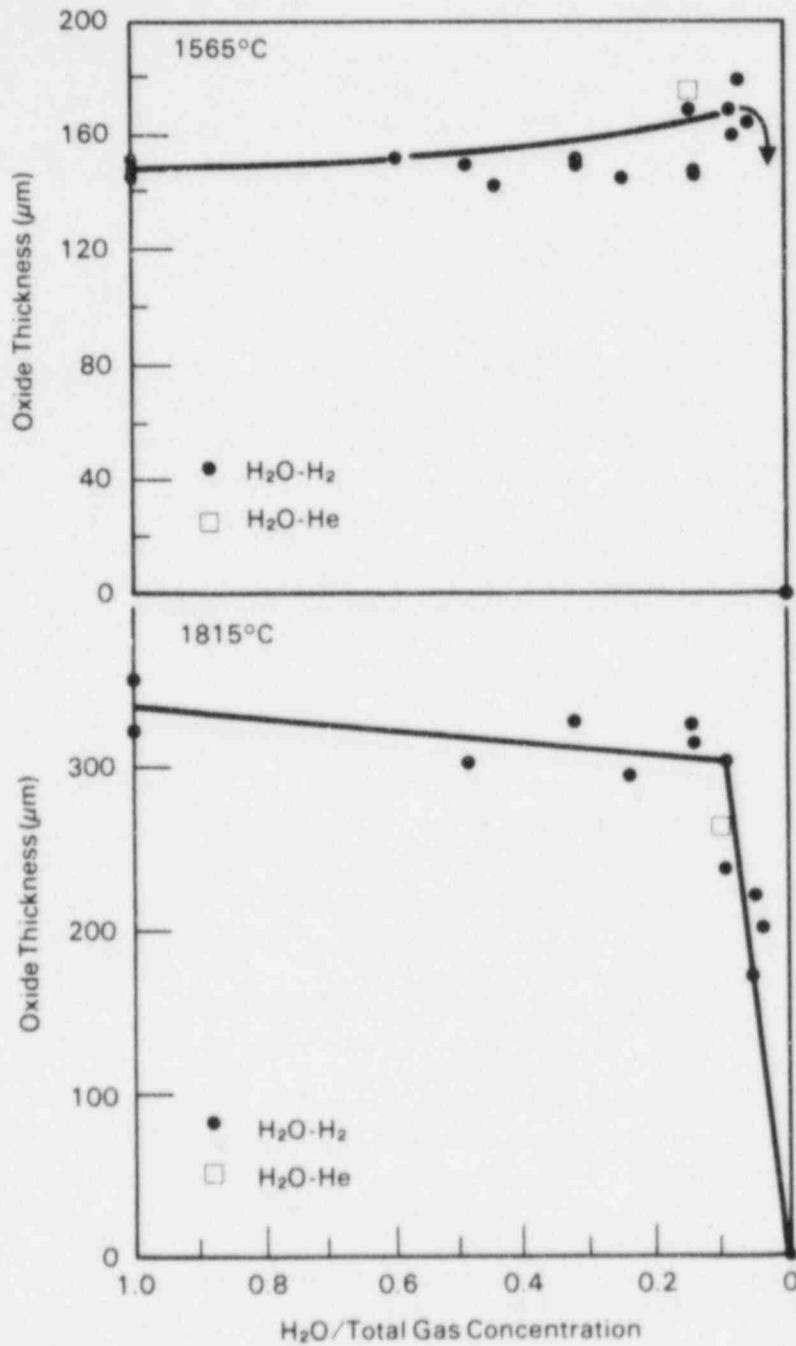


FIGURE 10. Effect of Hydrogen on Oxidation Kinetics. Zircaloy was oxidized at 1565°C for 25 s and at 1815°C for 40 s in various  $\text{H}_2\text{O}-\text{H}_2$  gas mixtures and the thicknesses of the resultant oxide layers were measured.

## CONCLUSIONS

The following conclusions are based on the work reported in this document:

- Oxidation rates for Zircaloy-4 in steam above 1500°C are greater than those previously reported by Baker-Just and Urbanic-Heidrick.
- A discontinuity in the growth rate constants of the reaction layers at 1510°C is a result of the change in oxide crystal structure from a tetragonal to a duplex tetragonal-cubic layer.
- No discontinuity in oxide growth rate occurs when the metal phase melts (at least if it remains nonturbulent) or when the oxide becomes a single cubic phase at about 2285°C.
- Large temperature gradients across the oxide thickness alter the cubic/tetragonal thickness ratio above 1510°C and, therefore, may also affect the oxidation kinetics.
- The presence of large amounts of hydrogen (up to 90 mol%) mixed with steam does not affect oxidation rates. The rate-controlling factor appears to be diffusion through the oxide layer.
- As long as the steam supply to the sample surface is sufficient to satisfy the oxidation requirements (steam starvation is not occurring), changes in the gas flow rate, pressure, or composition do not affect the oxidation kinetics.

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The oxidation kinetics of Zircaloy-4 in steam have been extended to 2400°C. The ZrO<sub>2</sub> and α-Zr layers display parabolic growth behavior over the entire temperature range studied. A discontinuity in the oxidation kinetics at 1510°C causes rates to increase above those previously established by the Baker-Just relationship. This increase coincides with the tetragonal-to-cubic phase transformation in ZrO<sub>2-x</sub>. No additional discontinuity in the oxide growth rate was observed when the metal phase melted. The effects of temperature gradients were taken into account, and corrected values representative of near-isothermal conditions were computed. Oxide growth was also measured in various steam-hydrogen mixtures at 1565°C and 1815°C. Hydrogen concentrations up to 90 mol% had no effect on oxidation kinetics. The rate-controlling factor appears to be diffusion through the oxide layer.

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