

**Zirconium Metal-Water Oxidation Kinetics
V. Oxidation of Zircaloy in
High Pressure Steam**

R. E. Pawel
J. V. Cathcart
J. J. Campbell
S. H. Jury

Prepared for the
U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Under Interagency Agreements DOE 40-551-75 and 40-552-75

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ZIRCONIUM METAL-WATER OXIDATION KINETICS
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FOREWORD

The following reports based on the results of the ZMWOK Program have been published.

1. J. V. Cathcart, *Quarterly Progress Report on the Zirconium Metal-Water Oxidation Kinetics Program Sponsored by the NRC Division of Reactor Safety Research for*
 - (a) April-June 1974, ORNL/TM-4655
 - (b) July-September 1974, ORNL/TM-4729
 - (c) October-December 1974, ORNL/TM-4805
 - (d) January-March 1975, ORNL/TM-4914
 - (e) April-June 1975, ORNL/TM-5021
 - (f) July-September 1975, ORNL/TM-5148
 - (g) October-December 1975, ORNL/TM-5248
 - (h) January-March 1976, ORNL/NUREG/TM-17
 - (i) April-June 1976, ORNL/NUREG/TM-41
 - (j) July-September 1976, ORNL/NUREG/TM-62
 - (k) October-December 1976, ORNL/NUREG/TM-87
 - (l) January-March 1977, ORNL/NUREG/TM-110
 - (m) April-June 1977, ORNL/NUREG/TM-132
 - (n) July-September 1977, ORNL/NUREG/TM-159
2. S. Malang, *SIMTRAN I - A Computer Code for the Simultaneous Calculation of Oxygen Distributions and Temperature Profiles in Zircaloy During Exposure to High-Temperature Oxidizing Environments*, ORNL-5083 (November 1975).
3. J. V. Cathcart, et al., *Zirconium Metal-Water Oxidation Kinetics I. Thermometry*, ORNL-5103 (February 1976).
4. R. A. Perkins, *Zirconium Metal-Water Oxidation Kinetics II. Oxygen-18 Diffusion in β -Zircaloy*, ORNL/NUREG/TM-19 (July 1976).
5. R. E. Pawel, *Zirconium Metal-Water Oxidation Kinetics III. Oxygen Diffusion in Oxide and Alpha Zircaloy Phases*, ORNL/NUREG-5 (October 1976).
6. J. V. Cathcart, R. E. Pawel, R. A. McKee, R. E. Drusche, G. J. Yurek, J. J. Campbell, and S. H. Jury, *Zirconium Metal-Water Oxidation Kinetics IV. Reaction Rate Studies*, ORNL/NUREG-17 (August 1977).
7. R. E. Pawel, J. V. Cathcart, J. J. Campbell, and S. H. Jury, *Zirconium Metal-Water Oxidation Kinetics V. Oxidation of Zircaloy in High Pressure Steam*, ORNL/NUREG-31 (November 1977).
8. G. J. Yurek, J. V. Cathcart, and R. E. Pawel, "Microstructures of the Scales Formed on Zircaloy-4 in Steam at Elevated Temperatures," *Oxidation of Metals* 10: 255 (1976).

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9. R. E. Pawel, R. A. Perkins, R. A. McKee, J. V. Cathcart, G. J. Yurek, and R. E. Druschel, *The Diffusion of Oxygen in Beta-Zircaloy and the High Temperature Zircaloy-Steam Reaction*, to be published in ASTM Symposium Book on "Zirconium in the Nuclear Industry," Quebec City, Canada, Aug. 19-22, 1976.
10. R. A. Perkins, "Oxygen Diffusion in β -Zircaloy," *J. Nucl. Mater.*, in press.
11. R. A. Perkins, "The Diffusion of Oxygen in Oxygen-Stabilized α -Zirconium and β -Zircaloy-4," *J. Nucl. Mater.*, in press.

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SUMMARY

A series of scoping tests to determine the influence of steam pressure on the isothermal oxidation kinetics of Zircaloy-4 PWR tubing was undertaken. The oxidation experiments were conducted in flowing steam at 3.45, 6.90, and 10.34 MPa (500, 1000, and 1500 psi) at 905°C (1661°F), and at 3.45 and 6.90 MPa at 1101°C (2014°F). A comparison of the results of these experiments with those obtained for oxidation in steam at atmospheric pressure under similar conditions indicated that measurable enhancement of the oxidation rate occurred with increasing pressure at 905°C, but not at 1100°C.

ZIRCONIUM METAL-WATER OXIDATION KINETICS
V. OXIDATION OF ZIRCALOY IN HIGH PRESSURE STEAM

ABSTRACT

Scoping tests of the effect of steam pressure on the oxidation rate of Zircaloy-4 PWR tubing were conducted at 905 and 1101°C (1161 and 2014°F). The majority of the tests were conducted in flowing steam at 3.45 MPa (500 psi); however, a few additional tests were performed at pressures of 6.9 MPa (1000 psi) and 10.34 MPa (1500 psi). Maximum exposure times were about 10 min at 1101°C and 45 min at 905°C.

The growth of the oxide and alpha layers during high pressure oxidation was compared to that obtained earlier for oxidation in steam at atmospheric pressure. At 1101°C, no differences in the growth behavior of the layers were evident. The data for high pressure oxidation at 905°C exhibited considerable scatter, particularly for oxide layer growth. The trend of these data, however, indicated that at this lower temperature a pressure effect on the kinetics of oxide layer growth does exist. In addition, metallographic examination of these oxide layers revealed a structural difference compared to those found for oxidation under similar conditions at atmospheric pressure.

The magnitude of the observed pressure effect on the oxide layer growth at 905°C is considered small for the reaction times studied and for pressures up to 6.9 MPa (1000 psi). For example, the maximum increase in oxide thickness observed at 6.9 MPa was less than 50 percent for times up to 30 min, and the kinetics continued to show negative deviations from ideal parabolic growth behavior. However, the few experiments at higher pressure yielded oxide layer thicknesses approximately twice as thick as those anticipated for oxidation at atmospheric pressure.

INTRODUCTION

This report summarizes the results of the high-pressure steam oxidation tests conducted as part of the Zirconium-Metal Water Oxidation Kinetics Program in the Metals and Ceramics Division at ORNL. The primary purpose of this program is to provide a reliable set of kinetic

measurements to describe the isothermal reaction of Zircaloy-4 PWR tubes with steam at elevated temperatures. Additionally, several scoping tests were conducted to examine the extent to which certain system parameters influence the reaction kinetics. With the exception of the work reported herein, these results have recently been published.¹

In certain types of postulated reactor accidents in pressurized Light Water Reactors, it is possible for the Zircaloy fuel cladding to reach relatively high temperatures at a time when the reactor core is still completely or partially pressurized. The objective of this part of the program was to perform scoping tests at 900 and 1100°C (1652 and 2012°F) in flowing steam at high pressures to determine whether or not steam pressure exerts a significant influence on the rate of isothermal oxidation of Zircaloy-4. Therefore, tests were conducted at pressures up to 10.34 MPa (1500 psi), and kinetic measurements were made and compared with the base data for oxidation at atmospheric pressure.

APPARATUS AND EXPERIMENTAL PROCEDURES

Methods

The apparatus constructed to accomplish the high pressure oxidation tests²⁻⁵ (called "SuperZWOK") consists basically of two interconnected, 5 in. diam stainless steel autoclaves as shown in Fig. 1. The lower one, 7 in. long, is a boiler that supplies pressurized steam generated by an internal resistance heater. The desired pressure of saturated steam is attained by controlling the boiler temperature in conjunction with appropriate settings of the pressure control valves.

The upper autoclave, 10 in. long, acts as the reaction chamber. The specimen is a length of PWR Zircaloy-4 tubing, the bottom end of which rests on but is not constrained by the specimen support tube attached to the bottom of the boiler. The upper end of the specimen is supported in the opening in the instrument head at the top of the autoclave. Steam entering the reaction chamber is confined by a 1 in. diam quartz tube to the annular region between the tube and the specimen.

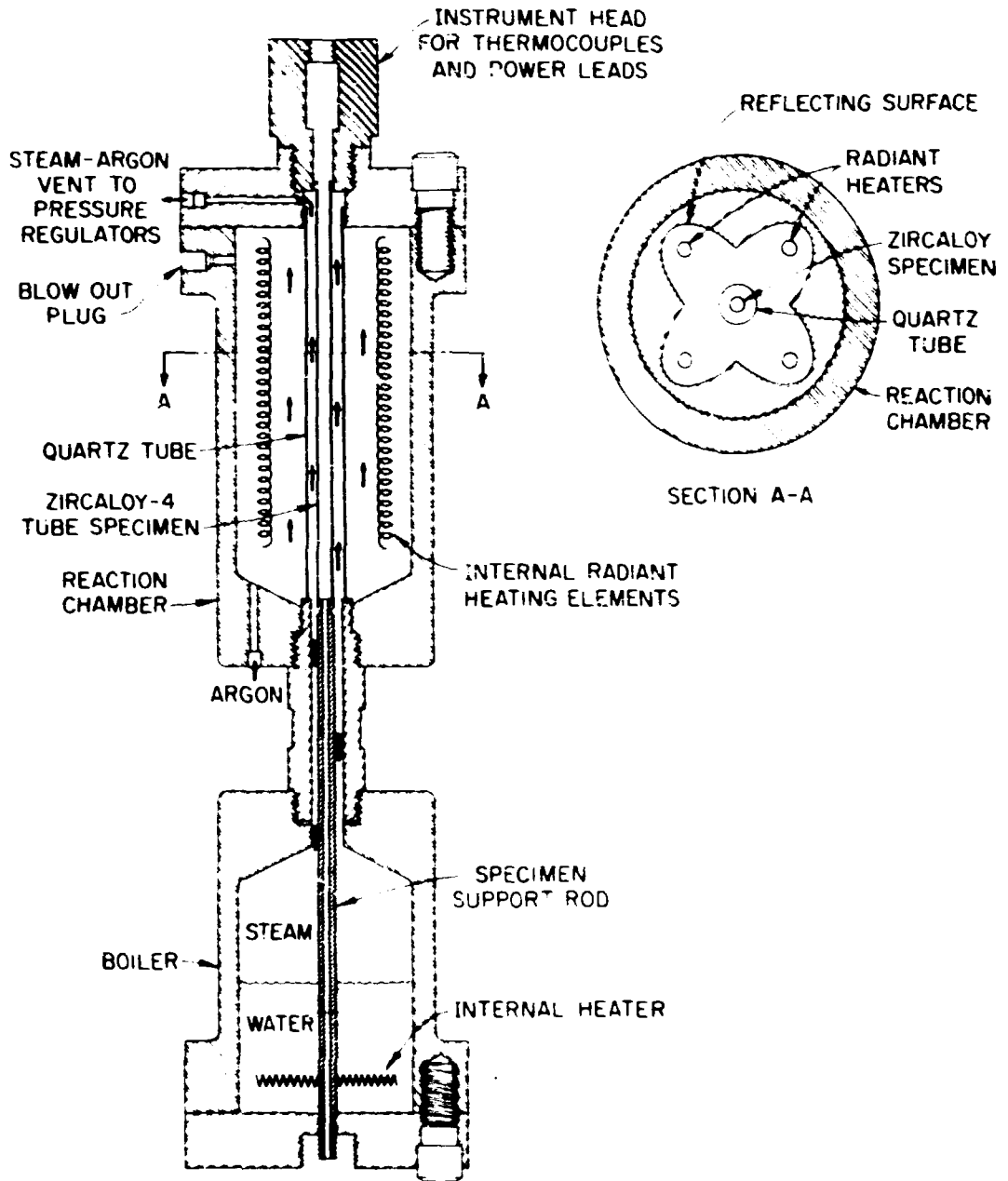


Fig. 1. Schematic Drawing of Autoclave for High-Pressure Steam Oxidation Studies.

Steam can also flow through the inside of the specimen, or the interior of the specimen can be filled with pressurized argon, which enters through the specimen support tube.

The specimen is heated to the desired reaction temperature by a specially constructed quad-elliptical radiant heating furnace that is contained within the reaction chamber. The reflector for the furnace is made of stainless steel, and the reflecting surfaces are gold-plated to ensure a high reflectivity.

The reflector for the furnace may be cooled by a flow of pressurized argon that enters through a port at the bottom of the reaction chamber. The argon exits through slots (not shown) in the upper closure of the autoclave just above the top of the quartz tube surrounding the specimen. There it mixes freely with steam from the boiler, and both gases then pass out of the system through a pressure regulating valve. Appropriate adjustments of the argon pressure and flow rate should prevent any serious mixing between argon and steam in the vicinity of the specimen. In any case, most experiments were accomplished without argon flow to the apparatus during oxidation, and a number of the tests were made in which argon was used only for the initial purge of the system.

A schematic diagram of the complete apparatus is shown in Fig. 2. The auxiliary equipment for specification of the pressure and flow conditions, as well as for temperature measurement and control, is illustrated. The manner in which the equipment was operated was changed somewhat during the course of the work in order to improve its performance. In a typical experiment, the reactor and boiler autoclaves were purged and pressurized with argon and then heated to a temperature at or above the boiling point of water at the desired pressure. At this point, the internal heater in the boiler autoclave was turned on to produce a flow of steam up through the reactor autoclave surrounding the specimen. When the steam flow had stabilized at the set pressure as evidenced by the discharge of steam and water from the relief valves, the specimen was heated through the required time-temperature cycle by the quad-elliptical infrared heating furnace. The argon flow through the interior of the specimen and about the reflecting surface of the quad-elliptical furnace

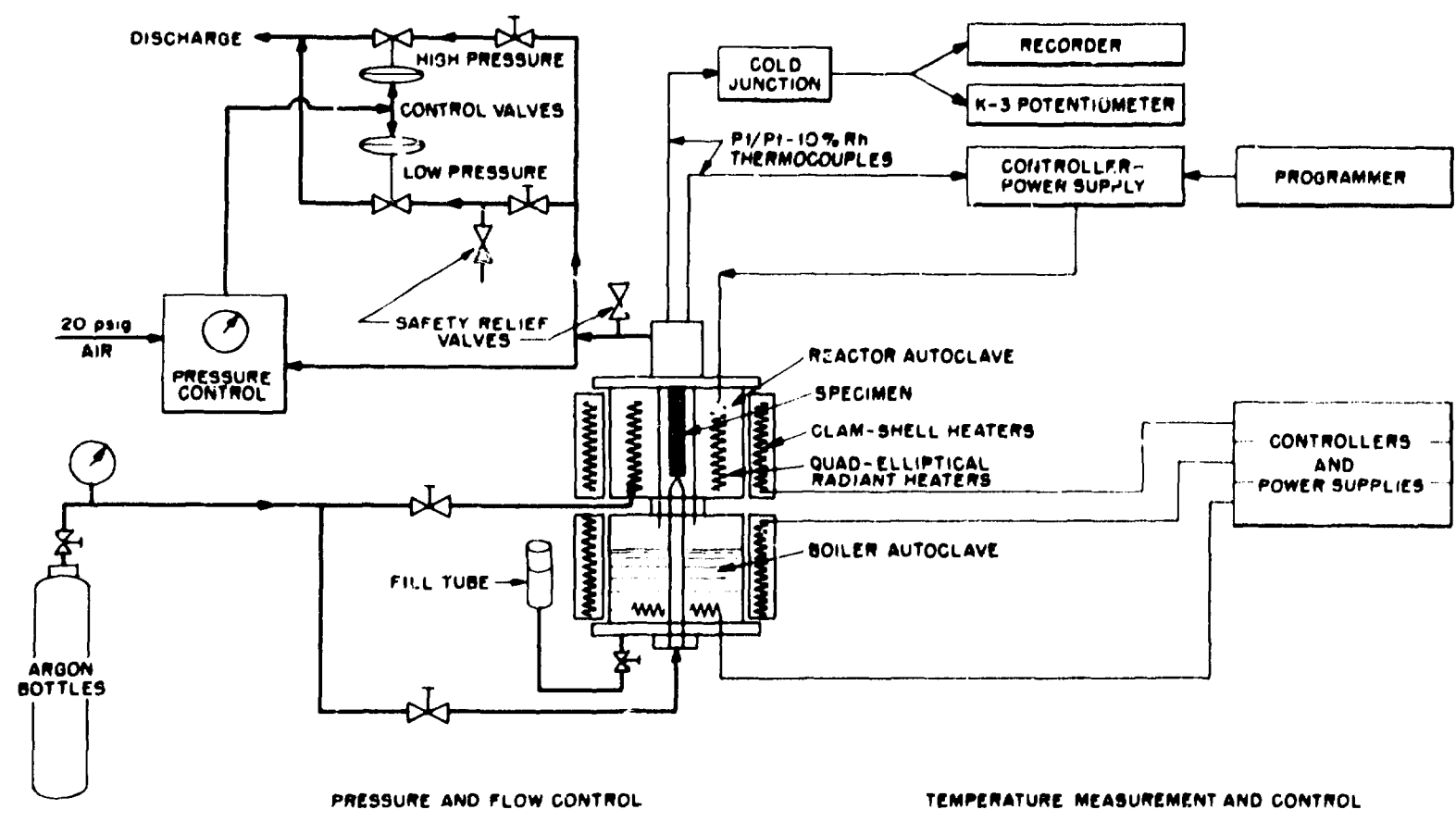


Fig. 2. Schematic Control Diagram of SuperZWOX High-Pressure Steam Oxidation Apparatus.

was stopped during a run to lessen thermocouple errors due to thermal shunting and to reduce the possibility of significant steam-argon mixing in the vicinity of the specimen.

The specimen consisted of a section of PWR* tubing about 40 cm (16 in.) long attached between a support at the top of the reactor autoclave and a spindle which extends from the boiler. Two Pt vs Pt-10% Rh thermocouples were welded to the inner wall of the tube at a position corresponding to the midpoint of the quad-elliptical furnace. This arrangement is shown in Fig. 3. One thermocouple was used to control the furnace temperature through the power supply/programmer unit; the other was connected to a recorder and potentiometer to provide the time-temperature record for the experiment. The thermocouple leads passed through the specimen support in a Conax feed-through. Tests of the potential thermocouple errors due to electrical shunting (by open-circuit resistance measurements) as well as a system fixed-point check (by observation of the alpha-beta transition temperature in a pure Zr specimen) indicated that no large thermocouple measurement errors were present.

The specimens were heated to the reaction temperature in approximately 30 s. Temperature control in this apparatus presented some difficulties at least partly because of the coupling between the stability of steam flow and the control of the specimen temperature. Cyclic operation of the pressure control valves to maintain a constant pressure under flow conditions often produced changes in steam flow that affected the temperature control. Apparently, convective heat losses to the flowing high pressure steam were large. The problem was more severe at the higher pressures of the investigation. Temperature control within $\pm 5-10^{\circ}\text{C}$ of the set point was achieved in most instances, with occasional larger variations due to erratic steam flow, and this is thought to be entirely satisfactory for these tests. The larger temperature variations were taken into account in determining the effective time of each "isothermal" experiment.

*Reactor Grade Zircaloy-4 PWR tubing from Sandvik Special Metals Corp. See References 1 and 6 for analyses and specifications.

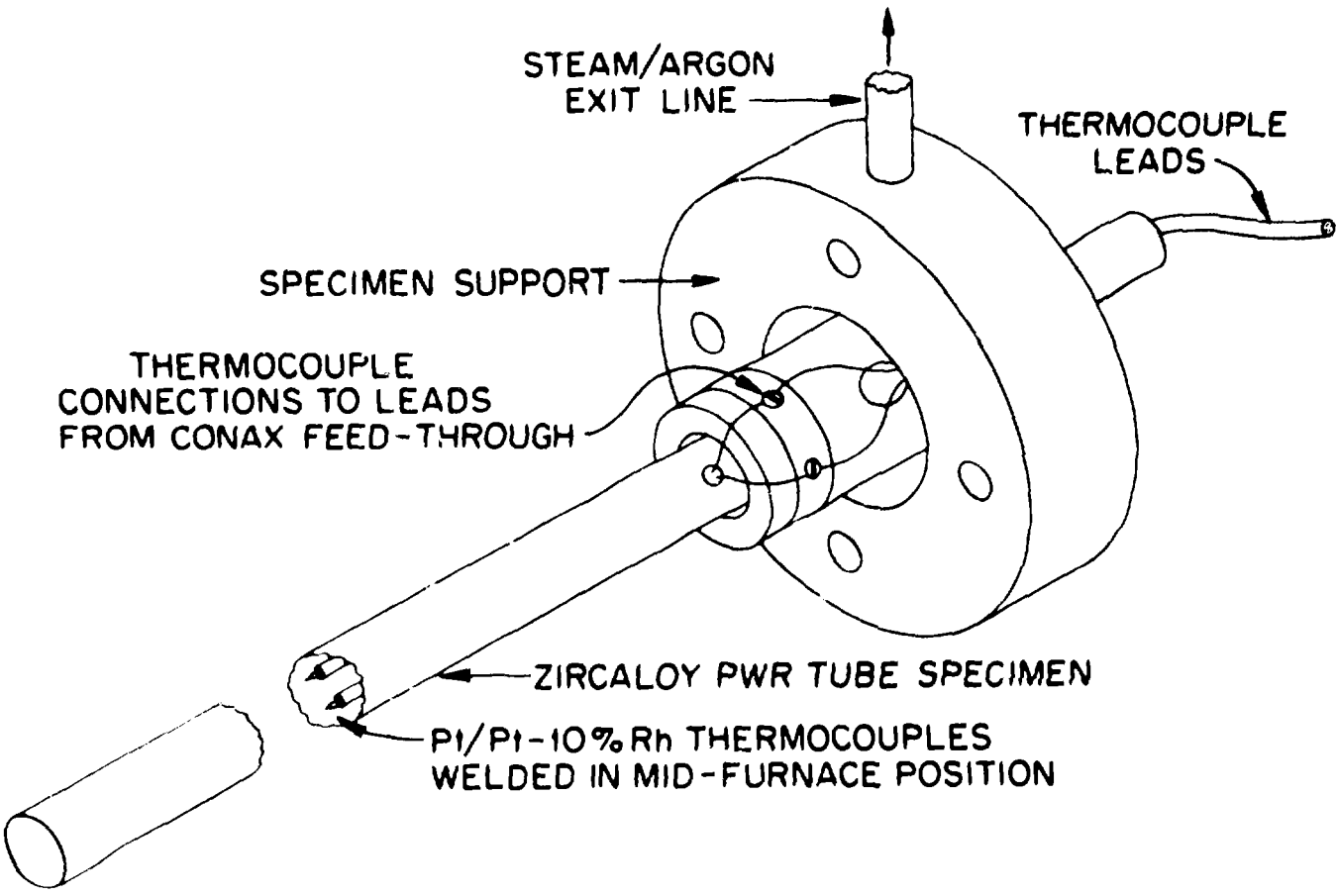


Fig. 3. Schematic Diagram of Specimen and Specimen Support.

Measurements

The methods for obtaining measurements of the oxide and oxygen-stabilized alpha layer thicknesses after oxidation experiments were essentially identical to those reported previously in conjunction with the earlier isothermal data sets.^{1,2} After oxidation, each specimen was sectioned at the elevation containing the thermocouple beads; the specimen was then mounted, polished, and prepared for metallographic examination by the etch-anodization procedure.^{1,2} Representative layer thickness measurements were obtained by averaging the results of 6-10 measurements made within ± 30 deg of the thermocouple positions. The measurements were obtained using a calibrated micrometer eyepiece on a small bench metallograph. On several specimens, measurements were made about the entire circumference in order to note the extent of the variation of oxide thickness with angular position. These measurements sometimes exhibited more variation than those observed from similar experiments in the MiniZWOK apparatus. This was particularly noticeable in some of the higher-pressure experiments where the oxide layers were comparatively thick. Typical results are shown in Figs. 4 and 5 for experiments at 905 and 1101°C (1661 and 2014°F) for oxidation at 3.45 MPa (500 psi) steam pressure. It is probable that small differences in the lamp efficiencies of the quadrilateral furnace are responsible for the systematic variations. While the variations are generally not large, we have nevertheless continued to make the phase thickness measurements in close proximity to the measuring thermocouple positions.

In order to compare the results of the high pressure steam oxidation experiments with the baseline data sets, the effective isothermal oxidation times for the individual experiments at nominally 900 and 1100°C (1652-2012°F) were normalized to 905 and 1101°C (1661-2014°F). The normalization procedure has also been discussed previously¹ and involves an integration of the entire time-temperature excursion from which the effective isothermal time is calculated.

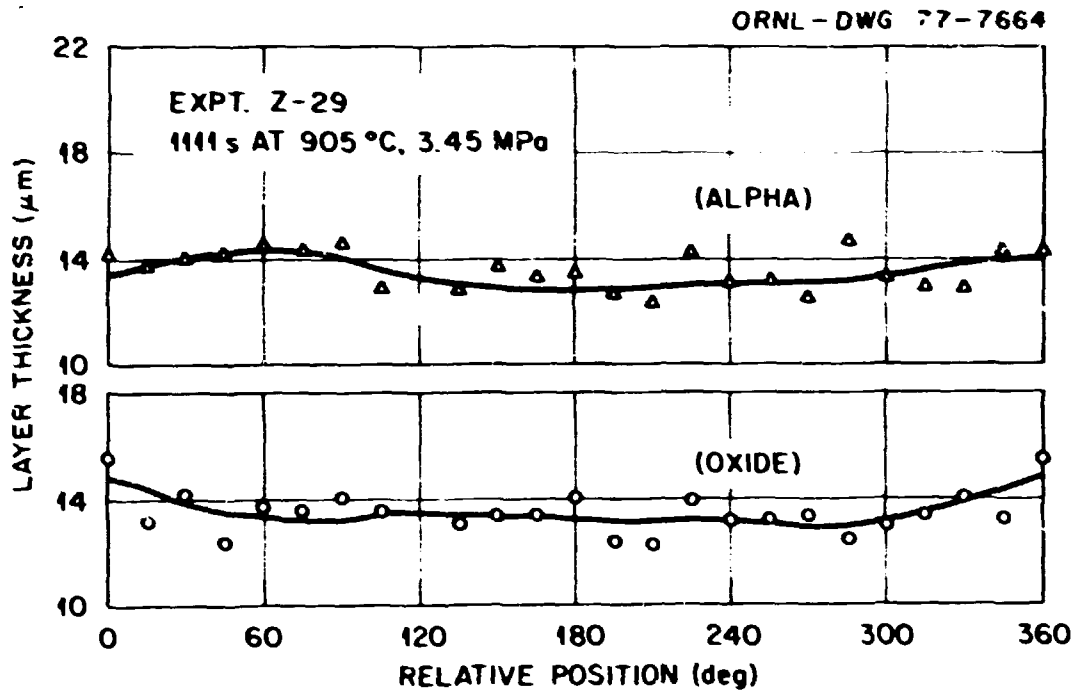


Fig. 4. Circumferential Variations in the Oxide and Alpha Layer Thicknesses on Specimen Z-29, Oxidized 1111 s at 905°C (1661°F), 3.45 MPa (500 psi).

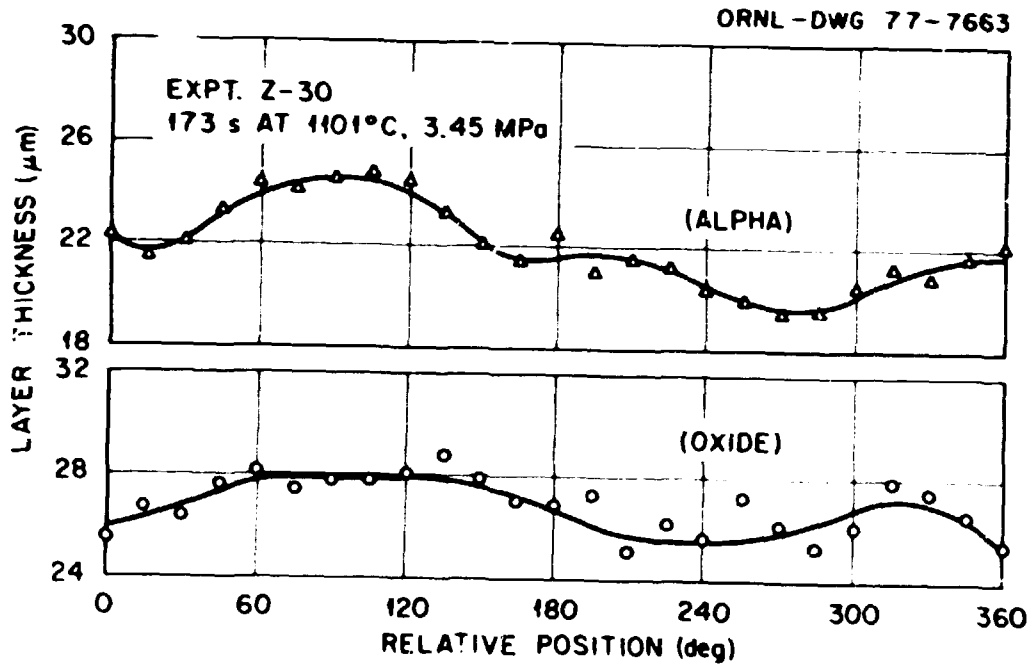


Fig. 5. Circumferential Variations in the Oxide and Alpha Layer Thicknesses on Specimen Z-30, Oxidized 173 s at 1101°C (2014°F), 3.45 MPa (500 psi).

RESULTS

Oxidation tests of Zircaloy-4 PWR fuel tube specimens were carried out in the SuperZWOK apparatus at 905 and 1101°C (1661 and 2014°F) in flowing high-pressure steam. Most experiments were conducted at a pressure of 3.45 MPa (500 psi); maximum oxidation times were about 2500 s for oxidation at 905°C, 500 s for oxidation at 1101°C. At each temperature, one experiment was done in which the system was maintained at a pressure only slightly above atmospheric in order to provide a direct low-pressure comparison. Because the data obtained for oxidation at steam at 3.45 MPa indicated that a small pressure effect existed at 905°C but not at 1101°C, several tests were conducted at these temperatures at 6.90 MPa (1000 psi). In addition, a few tests were made at 10.34 MPa (1500 psi) at 905°C.

Phase thickness measurements were obtained on all of the oxidized specimens. As in the case of the previous isothermal experiments, the total oxygen consumed by each specimen was calculated on the basis of the model which assumed that all the oxide was compact and stoichiometric, that a linear concentration-gradient existed in the alpha layer, and that a simplified diffusion calculation accounts for the amount of oxygen uptake in the beta phase.

The phase thickness measurements for all of the high pressure experiments are given in Tables 1-5. The kinetics of oxide and alpha growth for these sets of specimens are presented in Figs. 6 through 10 where they are compared with the values from the standard MiniZWOK data set obtained for steam oxidation at atmospheric pressure.¹

The comparison of the MiniZWOK (atmospheric pressure) and SuperZWOK (high pressure) data for oxidation at 1101°C (2014°F) given in Figs. 6 and 7 shows very good agreement in the phase layer thickness measurements for both oxide and alpha layers. Thus, at least for the time and pressure range encompassed by these tests, no measurable pressure effect is evident from the data for oxidation at this temperature.

At 905°C (1661°F), as presented in Figs. 8, 9, and 10, it is more difficult to judge unequivocally if an effect of pressure exists at the 3.45 MPa (500 psi) level. At least part of the problem is associated

Table 1. Steam Oxidation of Sandvik Zircaloy-4 PWR Tubing at 905°C (1661°F), 3.45 MPa (500 psi)

Expt. No.	Time (s)	Oxide Layer (μm)	Alpha Layer (μm)	Oxygen Consumed (mg/cm ²)
Z-12	430	10.9	8.3	1.851
Z-14	392	11.8	10	2.03
Z-16	530	12.2	10.7	2.107
Z-18	896	16.7	15.3	2.902
Z-19	103	6.5	5.6	1.12
Z-29	1111	13.8	13.6	2.422
Z-36	1435	17.2	17.7	3.039
Z-40	1254	20	14.6	3.38
Z-44	1069	18.5	13.6	3.129
Z-45	2235	15.5	20	2.842
Z-46	753	16.9	10.3	2.805
Z-48	2711	22.5	20.5	3.908
Z-50	1923	21.9	20.2	3.809
Z-64	1443	21.9	14.4	3.661
Z-17 ^a	410	11.3	12	2.005

^aExperiment conducted at .14 MPa (20 psi).

Table 2. Steam Oxidation of Sandvik Zircaloy-4 PWR Tubing at 1101°C (2014°F), 3.45 MPa (500 psi)

Expt. No.	Time (s)	Oxide Layer (μm)	Alpha Layer (μm)	Oxygen Consumed (mg/cm ²)
Z-23	121	22.7	23.2	4.43
Z-24	198	28.9	29.4	5.635
Z-30	173	26.4	21.1	4.994
Z-34	416	36.9	38.6	7.304
Z-35	532	45.5	45.2	8.87
Z-41	35	13.3	9.7	2.467
Z-42	344	38.8	34.5	7.413
Z-43	294	36.4	33.5	6.978
Z-22 ^a	386	39.9	42	7.827

^aExperiment conducted at .28 MPa (40 psi).

Table 3. Steam Oxidation of Sandvik Zircaloy-4 PWR Tubing at 905°C (1661°F), 6.90 MPa (1000 psi)

Expt. No.	Time (s)	Oxide Layer (μm)	Alpha Layer (μm)	Oxygen Consumed (mg/cm^2)
Z-52	161	11.5	5.7	1.875
Z-54	619	18.1	10.7	2.995
Z-55	249	11.1	8.2	1.879
Z-56	1829	23.2	16.5	3.911
Z-57	1169	21.2	13.4	3.53
Z-58	92	8.2	4.4	1.345

Table 4. Steam Oxidation of Sandvik Zircaloy-4 PWR Tubing at 1101°C (2014°F), 6.90 MPa (1000 psi)

Expt. No.	Time (s)	Oxide Layer (μm)	Alpha Layer (μm)	Oxygen Consumed (mg/cm^2)
Z-65	360	39.4	30.6	7.406
Z-66	153	26.8	19.9	4.994

Table 5. Steam Oxidation of Sandvik Zircaloy PWR Tubing at 905°C (1661°F), 10.34 MPa (1500 psi)

Expt. No.	Time (s)	Oxide Layer (μm)	Alpha Layer (μm)	Oxygen Consumed (mg/cm^2)
Z-62	416	22.0	6.0	3.462
Z-63	1290	39.0	15.7	6.267
Z-67	909	36.7	9.2	5.755

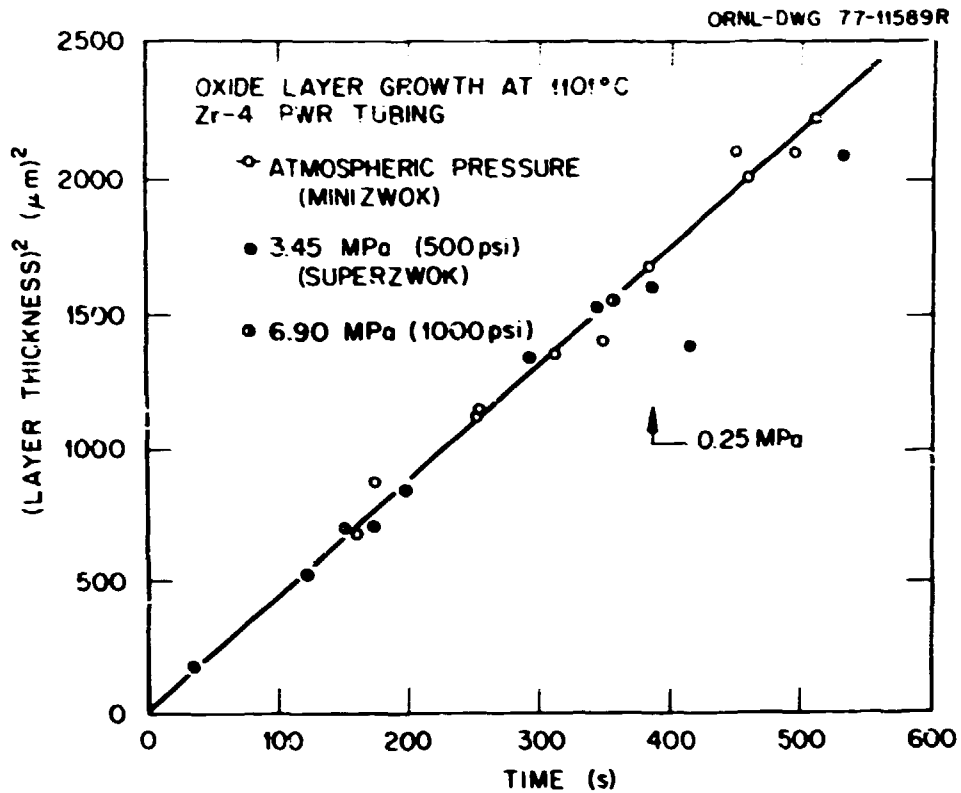


Fig. 6. Oxide Layer Growth During Oxidation of Sandvik Zircaloy-4 PWR Tubing at 1101°C (2014°F) in Steam at 3.45 MPa (500 psi), 6.90 MPa (1000 psi), and at Atmospheric Pressure. Solid line represents Minizwok data.

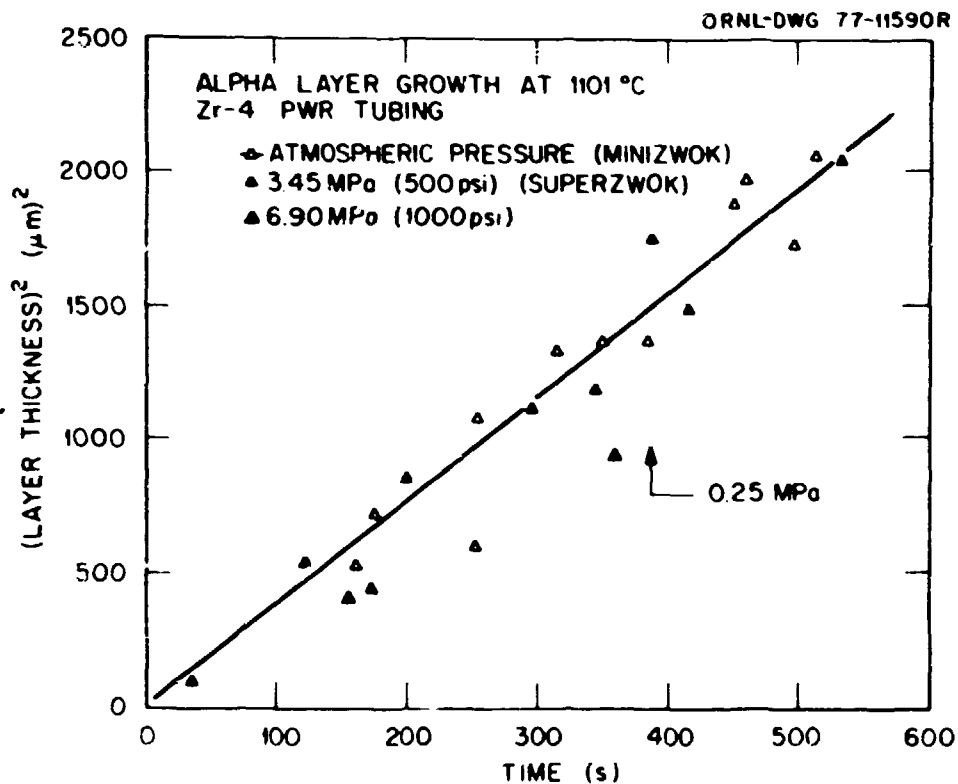


Fig. 7. Alpha Layer Growth During Oxidation of Sandvik Zircaloy-4 PWR Tubing at 1101°C (2014°F) in Steam at 3.45 MPa (500 psi), 6.90 MPa (1000 psi), and at Atmospheric Pressure. Solid line represents Minizwok data.

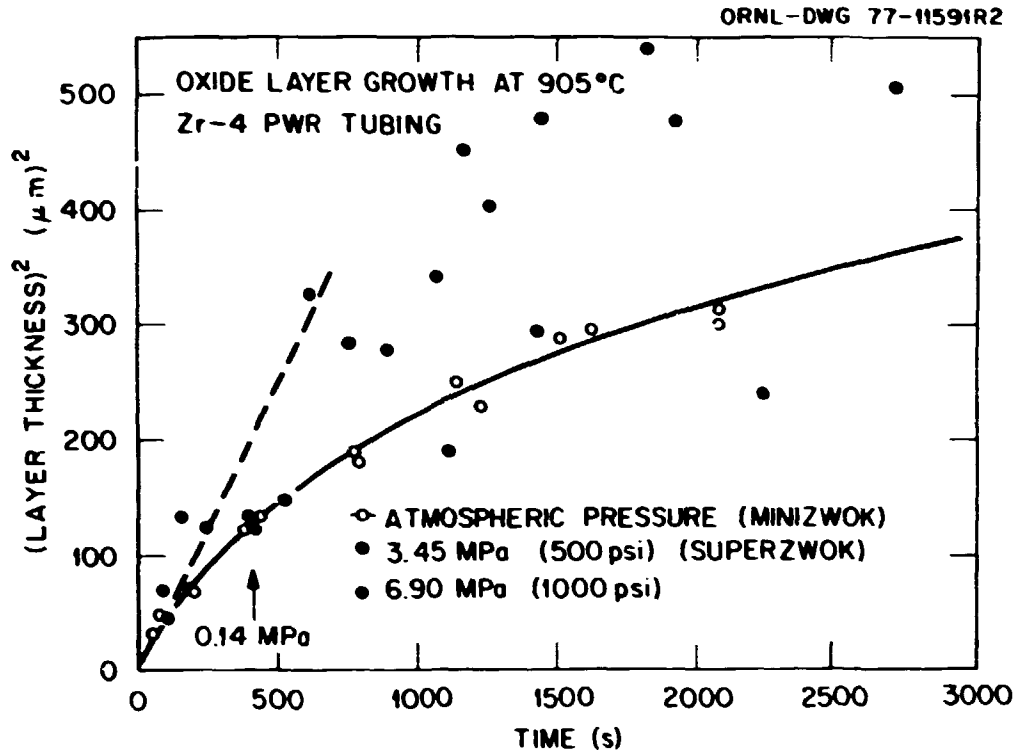


Fig. 8. Oxide Layer Growth During Oxidation of Sandvik Zircaloy-4 PWR Tubing at 905°C (1661°F) in Steam at High Pressures and at Atmospheric Pressure. Solid line represents MiniZWOK data; dashed line represents parabolic kinetics extrapolated from high-temperature MiniZWOK data.

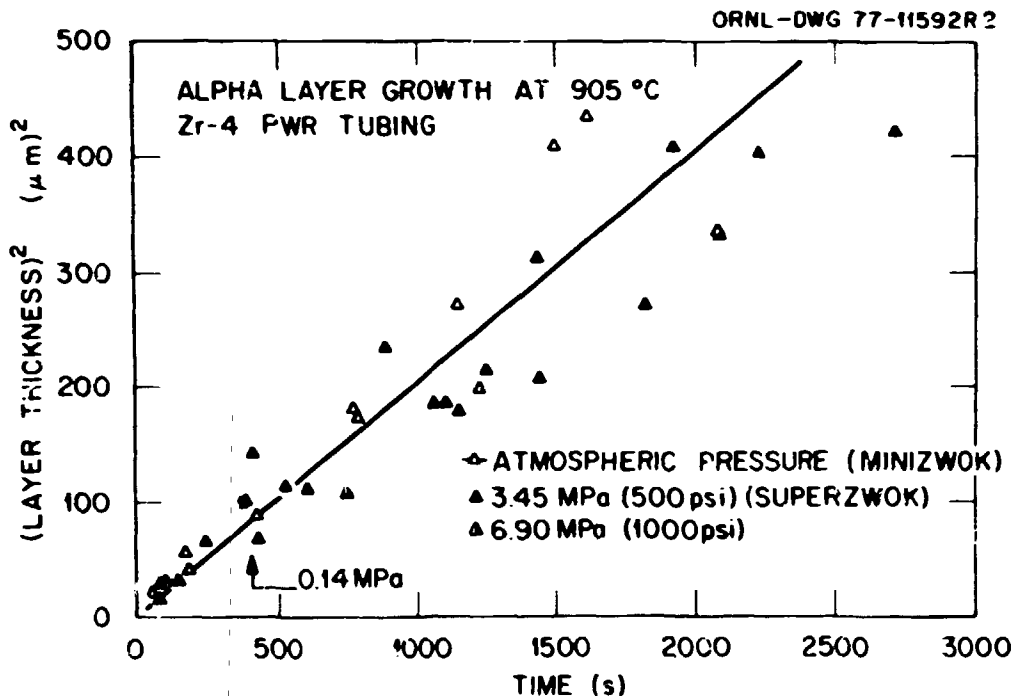


Fig. 9. Alpha Layer Growth During Oxidation of Sandvik Zircaloy-4 PWR Tubing at 905°C (1661°F) in Steam at High Pressures and at Atmospheric Pressure. Solid line represents MiniZWOK data.

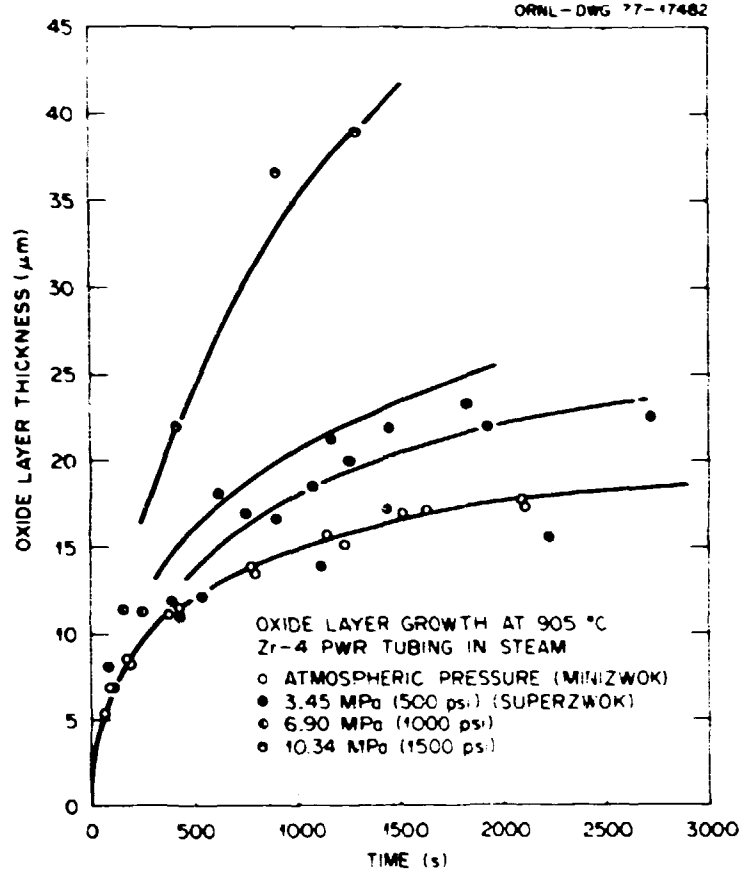


Fig. 10. Linear Plot of Oxide Layer Growth During Oxidation of Sandvik Zircaloy-4 PWR Tubing at 905°C (1661°F) in Steam at Various Pressures.

with the comparatively large scatter in oxide thickness measurements for these high-pressure experiments. While the short-time results and some of the long-time results compare well with the standard (atmospheric pressure) data, most of the long-time experiments yielded greater oxide thicknesses. Moreover, the oxide thicknesses obtained in the 6.90 MPa (1000 psi) experiments consistently lie above the values obtained at 3.45 MPa. While the behavior observed for pressures to at least 6.90 MPa suggests that the characteristic of protective (but non-parabolic) oxide growth observed for oxidation in steam at 905°C at atmospheric pressure is still present, insufficient data are available to determine positively if this behavior persists at still higher pressures. The few data for oxide growth at 10.34 MPa (1500 psi) at 905°C shown in Fig. 10 indicate that the effect of pressure has not yet saturated, although the rate

appears still to be decreasing with time. It should be noted here that the temperature control for the latter set of experiments was not as good as those conducted at lower pressures. No evidence presently exists that would indicate that a significant kinetic effect results from temperature cycles of the sort experienced in this case; however, the accuracy of these three data points may be somewhat lower than the other data.

For the oxidation of Zircaloy-4 in steam at 905°C, then, the data show a measurable, consistent effect of pressure on the kinetics of oxide layer growth. The rate of oxidation increases with increasing pressure, although the rate is a decreasing function of time and is less than parabolic at pressures at least as high as 6.9 MPa (1000 psi).

DISCUSSION

The observation of a pressure effect on the rate of oxide growth on Zircaloy at 905°C (1661°F) but not at 1101°C (2014°F) does not yet have a completely satisfactory explanation. Previous results concerning the effect of pressure (at lower temperatures) are somewhat ambiguous.⁷ At low pressures where reasonably uniform films were involved, variations in the oxygen partial pressure led to only minor kinetic effects. At higher pressures,⁸⁻¹⁰ larger influences on the kinetics have been observed. These effects seemed to be associated more with changes in the morphology of the oxide product induced by the high pressures rather than with a pure thermodynamic influence which might affect the rate through changes of the defect structure and the ionic diffusion rates in the oxide. For example, Cox¹⁰ suggested that porosity in the oxide film develops more rapidly at high pressures, leading to an enhancement of the oxidation rate. His results on the oxidation of Zircaloy-2 in stagnant steam indicate only minor effects of pressure on the post-transition rates for temperatures up to 450°C (840°F); however, from that temperature to 600°C (1110°F), significant enhancement was observed for pressures up to 34.5 MPa (5000 psi). For oxidation in the pre-transition region at 350°C (660°F), the enhancement was less dramatic, and the oxidation

rate curves exhibited characteristics similar to those shown in Fig. 10 for oxidation at 905°C.

In the present investigation we, too, have found evidence that physical changes in the oxide layer can be associated with oxidation in high pressure steam. In our experiments, standard optical microscopy revealed no profound difference in the appearance of the oxide between standard (atmospheric pressure) MiniZWOK and high-pressure SuperZWOK specimens under bright field illumination. In both dark field and under polarized light, however, a bright band of material was observed in the outer part of the oxide layers on specimens that exhibited a pressure effect. An example of this behavior is shown in Fig. 11, which is a cross section of a specimen oxidized in steam at 3.45 MPa (500 psi) at 905°C (1661°F) for 1069 s.

This band was absent on specimens oxidized at atmospheric pressure and also on those SuperZWOK specimens, oxidized at 905°C (1661°F) in steam at 3.45 MPa (500 psi), that showed no pressure effect (cf., for example, Fig. 8, the specimen oxidized 1435 s at 3.45 MPa). Likewise samples oxidized at high pressures at 1101°C (2014°F) did not exhibit this feature even though the oxide layers on some of these specimens were twice as thick as those formed at the lower temperatures.

Although the occurrence and the relative thickness of this bright oxide layer can be correlated with the formation of thicker than expected oxide layers, its cause and its influence, if any, on oxidation kinetics remains a matter of speculation. The optical effects observed, especially the response of the oxide to dark-field illumination, suggest strongly the existence of a rough reflecting surface. No such roughness in the physical surface of polished cross sections of samples could be detected either in bright field or by differential interference contrast techniques, and rough surfaces certainly did not exist on cross-sectioned standard MiniZWOK specimens, which were subjected to the same polishing procedures. However, even non-stoichiometric ZrO_2 is not completely opaque in thin sections, and all light is, therefore, not necessarily reflected from the polished surface of a cross-sectioned sample. Thus, if microcracks developed along grain boundaries in the outer portions of the oxide,

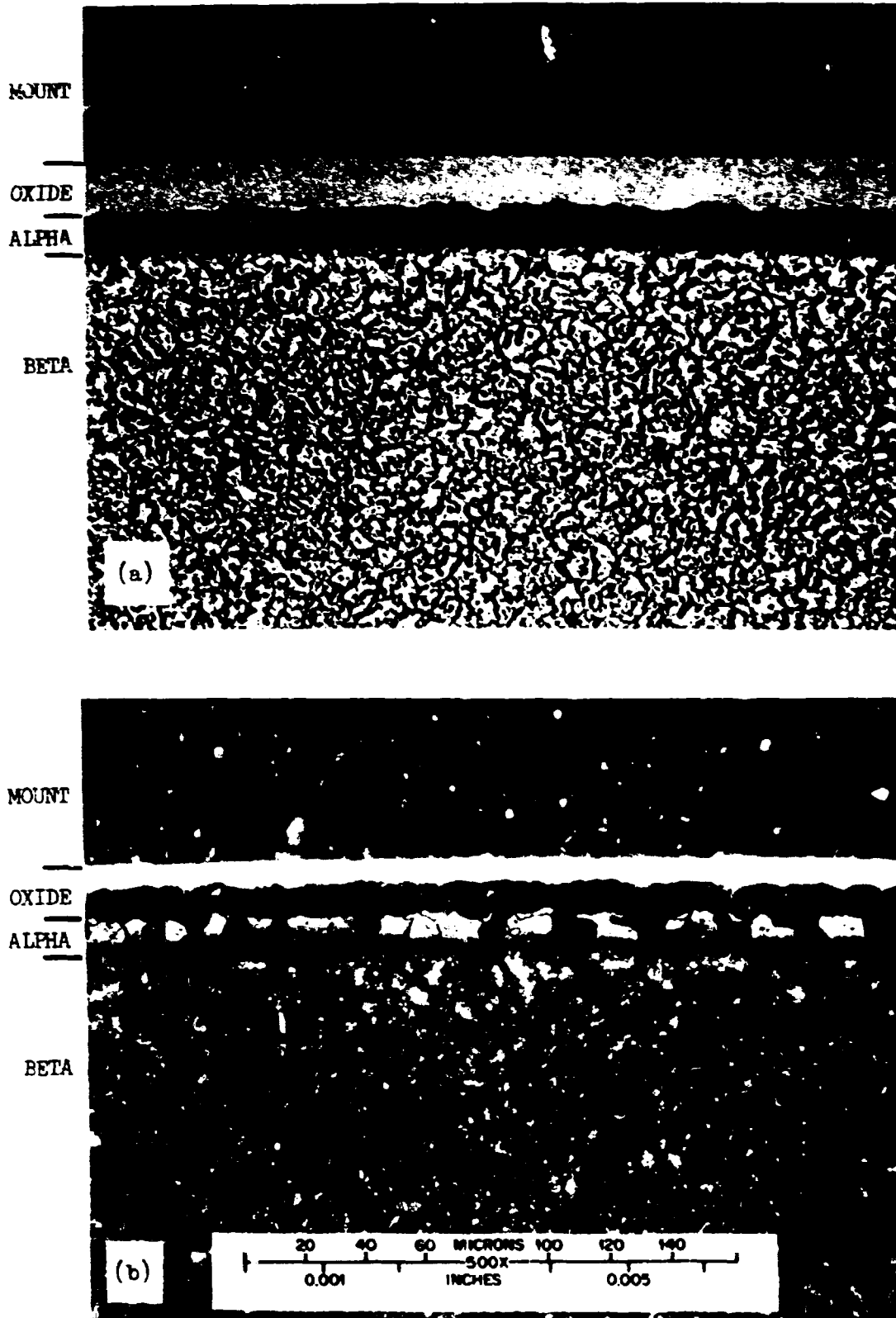


Fig. 11. Cross Section of Sandvik Zircaloy-4 PWR Tube Oxidized for 1069 s at 905°C (1661°F) in Steam at 3.45 MPa (500 psi) in SuperZWOK Apparatus. Expt. No. Z-44. 500×. (a) Bright-field illumination; (b) polarized light.

light reflected from such interfaces beneath the surface of the oxide could conceivably produce the optical effects observed. Certainly the presence of such cracks would lead to an increase in the rate of oxide growth.

Unfortunately for this hypothesis we were unable to detect the presence of a system of cracks in the outer regions when fractured oxide layers were examined in a scanning electron microscope. Both the standard specimens and those exhibiting a pressure effect appeared identical. This observation, of course, does not preclude the possibility that fine cracks, hidden within the features of the microstructure, did actually exist in the oxide, and we view the "crack hypothesis" as the most likely of the several we have considered.

For example, until the results at 900°C (1652°F) and 10.34 MPa (1500 psi) were obtained, we felt that the pressure-effect observations might be rationalized in terms of the differences in oxide structure that exist in the early stages of oxidation in this temperature range.¹ At temperatures above 1000°C (1832°F), predominately tetragonal oxide is formed on specimens heated rapidly to the desired temperature and subjected to isothermal oxidation. At lower temperatures, on the other hand, substantial quantities of the monoclinic oxide appear to form, and the transformation from the initial tetragonal to the monoclinic structure has been postulated as a cause of the decreased rate of oxidation (relative to that extrapolated from higher temperature data) and the departure from parabolic kinetics observed at 900 and 950°C (1652-1742°F) in steam at atmospheric pressure. Thus an increase in oxidation rate with increasing steam pressure would be expected at 900°C (1652°F) if the increased pressure somehow stabilized the tetragonal form of the oxide. This increase should stop once all the oxide is tetragonal, and the maximum oxidation rate should never exceed that predicted by an extrapolation of the high temperature data, which were obtained under conditions where all the oxide was tetragonal. As may be seen in Fig. 8, the initial data points obtained at 905°C (1661°F) and 6.9 MPa (1000 psi) do fall very close to the extrapolated rate curve (dashed line). The three data points at 10.34 MPa (1500 psi), however,

lie well above the extrapolation predictions, and one must conclude that the stabilization of the tetragonal form of the oxide cannot alone explain the observations. It also appears unlikely that steam pressure, in the thermodynamic sense, could substantially influence the diffusion flux through monoclinic oxide. Many previous investigators have failed to observe such an effect in short-time experiments at lower temperatures where the monoclinic oxide certainly forms.⁷

It is also possible that the observed pressure effect reflects some aspect of a "breakaway" oxidation process in which a growing, protective oxide layer suddenly becomes less protective because of cracking or other properties changes. The lack of reproducibility noted for oxidation at 3.45 MPa (500 psi) is characteristic of many such processes, but unlike "breakaway" oxidation, the observed rates of oxidation of Zircaloy are decreasing functions of time even at 10.34 MPa (1500 psi), and thus "classical" breakaway oxidation seems precluded. It is interesting to observe, however, that at high pressures the rate of growth of the "dark" inner oxide layer shows the same general behavior and is only slightly less than that observed for total oxide growth at atmospheric pressure. Thus, a breakaway process could be involved in which the thickness of the compact layer continues to increase with time.

Finally it is necessary to examine the possibility that the observed pressure effects represent an artifact of the experimental procedure. It is difficult to prove a negative, but we can find no evidence to support this idea. On the contrary, the data tend to confirm the validity of the results. For example, experiments in the SuperZWOK apparatus using steam pressures near atmospheric yielded results at both 900 and 1100°C (1652-2012°F) completely consistent with the standard MiniZWOK data set. Furthermore, at 3.45 and 6.90 MPa (500-1000 psi) and 1100°C (2012°F) no pressure effect was observed, again demonstrating that oxidation in the MiniZWOK and SuperZWOK apparatuses produces comparable results. Admittedly the quality of temperature control in the MiniZWOK apparatus was considerably better than in SuperZWOK, and one might argue that the resulting thermal cycling in SuperZWOK led to cracking of the oxide. However, a careful examination of the time-temperature records for

experiments at 905°C (1661°F) in steam at 3.45 MPa (500 psi) failed to show any correlation between relatively poor temperature control and an enhanced rate of oxidation. Additionally, an experiment was conducted at low pressure (~1 MPa) in which the specimen temperature was periodically perturbed by short-time (10 s) excursions of 75°C (135°F). The oxide thickness and appearance after this experiment were consistent with those produced for normal conditions at atmospheric pressure. This result is regarded as additional evidence that enhanced oxide growth is not a consequence of temperature cycling of reasonable frequency and magnitude.

Thus we believe that the pressure effects reported are real and cannot be attributed to an apparatus artifact. We are unable to specify a mechanism for the observed increase in oxidation rate with steam pressure at 905°C (1661°F), but we speculate that the rate increase is related to the formation of fine cracks in the outer portion of the oxide. Whatever the mechanism, its influence appears to disappear or diminish considerably when the oxidation temperature is increased to 1100°C (2012°F).

CONCLUSIONS

1. At 1101°C (2014°F), at the 3.45 MPa (500 psi) and 6.90 MPa (1000 psi) levels, no measurable effect was observed on the kinetics of oxide or alpha layer growth on Zircaloy-4 for times up to 530 s.

2. At 905°C (1661°F), oxide layer growth exhibited a modest effect of pressure at 3.45 MPa, 6.90 MPa, and 10.34 MPa (500, 1000 and 1500 psi) for times up to about 2500 s. The effect appears to be associated with some physical change in the oxide, possibly porosity or crack formation, rather than simply a thermodynamic influence of high pressure.

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