

Temperative Estimates from the Zircaloy Oxidation Kinetics in the α plus β Phase Region

C.S. Olsen

*EG & G Idaho, Inc., P.O. Box 1625,
Idaho Falls, Idaho 83401, U.S.A.*

SUMMARY

Oxidation rates of zircaloy in steam were measured at temperatures between 961 and 1264 K and for durations between 25 and 1900 s in order to calculate, in conjunction with measurements from postirradiation metallographic examinations, the prior peak temperatures of zircaloy fuel rod cladding. These temperature estimates will be used in light water reactor research programs to assess (a) the accuracy of measurements of fuel rod cladding peak temperatures from thermocouples attached to the surface during loss-of-coolant experiments (LOCEs), (b) the perturbation of the fuel rod cladding LOCE temperature history caused by the presence of thermocouples, and (c) the measurements of cladding azimuthal temperature gradients near thermocouple locations.

Zircaloy-4 samples about 2.3 cm long were cut from unirradiated tubing (1.07-cm outside diameter by 0.0601 cm thick), fabricated according to commercial specifications used for the Loss-of-Fluid Test (LOFT) fuel rods. The samples were heated in a tube furnace with a steam flow of 20 g/min. A Chromel-Alumel thermocouple placed inside the tube sample was used to record the sample temperature as a function of time. Effective oxidation times at temperature were calculated from temperature-time plots. Weight gain measurements were obtained from deflections of a quartz spring and from pre- and posttest weight measurements. Oxide and oxide plus oxygen-rich alpha thicknesses were obtained from metallographic measurements.

Zircaloy oxidation rates were applied to a zircaloy-clad electrical heater rod that had been subjected to four LOCEs, and to three nuclear fuel rods that had been subjected to four, three, and one transients, respectively. The calculated temperatures near two surface thermocouples and one embedded thermocouple of the electrical heater rod were higher than the measured values by 34, 19, and 16 K, respectively. Measurements of the oxide thickness indicated the peak temperature of 1191 K occurred between the two surface attached thermocouples. The error in the measurements derived from the four rods is about 25 K.

The results presented here extend the kinetics of zircaloy oxidation to reaction layer thicknesses in the two-phase alpha plus beta temperature region and establish parabolic temperature kinetics in this temperature region. These oxidation kinetics and measurements from postirradiation metallographic examinations can be used to estimate prior cladding peak temperatures and temperature gradients achieved during LOCEs.

1. INTRODUCTION

A technique to determine prior cladding peak temperature is to use the oxidation rates of zircaloy in steam in conjunction with measurements of oxide layer growths from postirradiation examinations (PIE). This technique will be used to assess (a) the accuracy of temperature measurements of fuel rod peak cladding temperatures from thermocouples attached to the surface during LOCEs, (b) the perturbation of the fuel rod cladding LOCE temperature history caused by the presence of thermocouples, and (c) the measurements of cladding azimuthal temperature gradients near the thermocouple locations. Layer thicknesses rather than weight gain are normally the cladding parameter measured during PIE. Weight gain cannot usually be determined directly from the cladding of a fuel rod, but must be calculated from diffusion coefficients, which requires knowledge of the temperature and layer thicknesses. This technique of using layer thicknesses has been used at the INEL to estimate cladding peak temperatures above the α plus β/β transition (1243 K) using various correlations from Cathcart [1]. Experimental data for layer thicknesses and verified correlations are required in the α plus β two-phase temperature region to verify an oxidation technique for estimating prior cladding peak temperatures.

Oxidation kinetics of the oxide layer growth and oxygen uptake is reported in Section 2 and the application of this data to estimate prior cladding peak temperatures from different LOCEs is described in Section 3.

2. OXIDATION KINETICS IN THE ALPHA PLUS BETA TWO-PHASE TEMPERATURE REGION

The experimental procedure used to determine the extent of the zircaloy/steam reaction is described, and a discussion of the results is presented in the following sections.

2.1 Experimental Procedure

Zircaloy-4 nuclear grade tubing was manufactured by Sandvik Special Metal Corporation according to commercial specifications used for the LOFT fuel rods. As part of the commercial specification, the tubes were pickled to remove about 0.038 mm of material from the outside surface. The tubing has an outside diameter of 10.72 mm, a thickness of 0.601 mm, and a length of approximately 180 cm.

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Oxidation samples about 2.3 cm long were cut from the tubes. No further etching or other surface treatment was done so that oxidation results would be representative of beginning-of-life tubing and tubing manufactured to current commercial practice. The length of the samples was measured, and the samples were degreased and weighed immediately prior to use. Certified tubing chemical analyses of major elements in this alloy were given as 1.60% Sn, 0.21% Fe, 0.11% Cr, 47 ppm Ni, 1210 ppm O, and 45 ppm N.

The test facility used to oxidize the zircaloy-4 samples in steam consisted of a steam generator and superheater, a condensing system, a reaction chamber, and a furnace. In addition to the pre- and posttest weight measurements, in-situ weight measurements were performed in the reaction chamber using a quartz spring and cathetometer. The quartz spring was contained in a water cooled chamber, with access to the chamber restricted to a diameter a little larger than the diameter of the quartz fiber holding the sample in order to minimize the entry of steam into the chamber.

Saturated steam, which is produced from demineralized water in a three-necked flask that is heated with a Glas-Col heater, is superheated to the desired temperature and passed through the reaction chamber and finally to a condenser. A flow of 20 g/min steam is regulated by the power to the Glas-Col heater.

An in-situ calibration was performed to determine the axial temperature profile in the furnace in order to establish the location and length of the hot zone. A "chimney" effect in the furnace moved the hot zone above the midpoint of the furnace, but the flow of steam down through the furnace slightly shifted the hot zone toward the center. The furnace is moved vertically to position the sample in the hot zone after the steam flow is established to start the reaction, and removed from around the sample to quench the sample in steam.

Sample temperature was measured using a 1.59-mm-outer-diameter, stainless steel sheathed, Chromel-Alumel thermocouple. The thermocouple was positioned in the center of the sample but not attached to it because of the in-situ weight measurements. Sufficient clearance was provided to allow the passage of steam through and around the sample. A few tests were performed with a thermocouple spot welded to the inside of the cladding to measure heating and cooling rates and to determine any effects on peak temperature. The heating and cooling rates were about 10 K/s faster than the 3 K/s of the unattached thermocouple, but no differences in peak temperature were noted.

After oxidation, each specimen was weighed and sectioned in the transverse plane, mounted, polished, and etched for metallographic examination. The oxide layer forms on the surface, with a layer of oxygen-rich zirconium adjacent to the oxide layer caused by the oxygen diffusion into the base metal. The total thickness of the layers was measured, and the weight gain was determined from the difference between pre- and posttest weight measurements. The weight gain per unit area was calculated from the total area inside and outside the cladding.

A total of 108 samples was used in the temperature range from 961 to 1263 K and for effective times ranging from 1 to 30 min. Effective times were calculated from the average isothermal temperature and the exponential Arrhenius equation to compensate for heating and cooling times.

2.2 Results and Discussion

Results of the oxygen uptake measurements and a comparison with other data, as well as those of the oxide plus oxygen-rich alpha layers, are presented in the following subsections.

2.2.1 Oxygen Uptake

The oxygen uptake data were compared with other data in the literature to establish the validity of the procedure and equipment, since weight gain measurements are normally more precise than layer thickness measurements. If good agreement is obtained with oxygen uptake data, then the only other uncertainty is in the measurements of layer thicknesses, since the same samples are used for both oxygen uptake and layer thickness measurements.

The weight gain measurements are shown in Figure 1 as a function of time for different temperatures. The oxygen uptake at atmospheric pressure varies with the square root of time in this temperature region.

Measurements by Pawel [2] indicate that for pressures between atmospheric and 3.45 MPa, the oxidation kinetics is parabolic. For higher pressures or extremely low pressure [3], the kinetics in the two-phase temperature region follows the cubic rate law.

The temperature dependence of the parabolic rate constant for oxygen uptake is shown in Figure 2 for the temperature range between 1000 and 1250 K. This temperature dependence is represented by eq. (1), and the errors in the constants represent one standard deviation.

$$k_w = 479.02 \left(\begin{matrix} +23.3\% \\ -28.9\% \end{matrix} \right) \exp \left[-20400 \left(\pm 2.3\% \right) / RT \right] \quad (1)$$

where

k_w = parabolic constant for weight gain ($\text{Mg O/cm}^2 \cdot \text{s}^{1/2}$)

R = 1.987 cal/mole·K

T = temperature (K).

The data are compared with results from Leistikow [4], Cathcart [1,2], and unpublished results from Urbanic in Figure 2. Urbanic chose to differentiate the kinetics between the single α -phase temperature region and the two-phase α plus β temperature region. The

data agree well with Urbanic's and Cathcart's data; Leistikow's data are higher than both sets. Leistikow combined data from the β phase temperature region and the two-phase temperature region, but his low temperature data exhibited increasing cubic kinetics with decreasing temperature.

2.2.2 Oxide Layer Thickness

Oxide layer thickness measurements in the α plus β two-phase temperature region include an oxygen-rich layer adjacent to the oxide layer so that most of the oxygen can be accounted for in the oxide thickness measurement. The oxide thicknesses from the outside and inside surfaces were combined in deriving the parabolic rate constants for different temperatures.

The oxide thickness measurements are shown in Figure 3 as a function of time for different temperatures. The growth of the oxide layer, as with oxygen uptake, follows the parabolic oxidation rate law.

The temperature dependence of the parabolic rate constants for oxide layer growth is shown in Figure 4 and can be represented by eq. (2). The errors represent one standard deviation.

$$k_o = 2.526 \times 10^4 \left(\begin{array}{l} +38.5\% \\ -27.8\% \end{array} \right) \exp [-23\ 920(+3.1\%)/RT] \quad (2)$$

where

$$k_o = \text{oxide layer parabolic rate constant} \\ (\mu\text{m}/\text{cm}^2 \cdot \text{s})^{1/2}.$$

The data are compared with results from Leistikow [4], Cathcart [1], Pawel [2], and Biederman [5] in Figure 4. Leistikow's data, as with the oxygen uptake data and Biederman's data, are above those of the INEL and Cathcart. Biederman separated his data into two temperature intervals from 922 to 1144 K and from 1172 to 1227 K, intervals approximating the α and α plus β phase temperature regions, as with Urbanic's oxygen uptake data. The oxygen uptake and oxide layer data do not substantiate different oxidation rates in this temperature interval.

3. ESTIMATING PRIOR CLADDING PEAK TEMPERATURES FROM OXIDATION KINETICS

An electrical heater rod and three nuclear fuel rods [6] that were subjected to a series of LOCEs were used to evaluate the technique of using oxidation kinetics to determine the prior cladding peak temperature. The electrical heater rod was subjected to four LOCE transients during which a peak temperature of 1125 K was measured. The first nuclear rod was subjected to three LOCEs, and a peak temperature of 1070 K was measured;

the second nuclear rod was subjected to only one LOCE, during which a temperature of 1200 K was measured; and the third nuclear rod was subjected to four LOCEs, during which a peak temperature of 1125 K was measured.

The temperature estimates for the prior cladding peak temperatures were obtained from the measured oxide layer thickness and by using measured temperatures as a basis for calculating oxide thickness from eq. (2). The measured temperatures are multiplied by a correction factor to obtain a corrected temperature profile, from which the calculated oxide thickness is compared with the measured value. This multiplication factor is changed incrementally, and the oxide thickness calculated for each change. The estimated cladding temperature is selected when the calculated oxide thickness is the same as the measured oxide thickness. This approach inherently assumes that the estimated temperatures are proportional to the measured temperature-time profiles.

Linear error propagation theory was used to estimate the accuracy of the oxidation method using the errors listed in eq. (2) and assuming errors of 5% in time and 10% in oxide thickness measurements. The maximum estimated error varies from 40 at 973 K to 56 at 1223 K. The contribution to the total error arises mainly from the errors in the constants in eq. (2). For example, 40% of the 40-K error can be attributed to the preexponential constant, and 57% from the error in activation energy. The error in time contributes the smallest error of about 0.2%; therefore, prior cladding peak temperatures may be estimated from fuel rods without measured thermal histories because gross errors in assumed time may be tolerated. However, to evaluate prior cladding peak temperatures of uninstrumented fuel rods in LOFT, temperature-time profiles will be selected from symmetrically located, instrumented fuel rods.

Temperature estimates from the oxidation kinetics in the electrical heater rod and the relative location of these estimates are shown in Figure 5, with the cross section of the electrical heater rod at the junction of the thermocouples. On the basis of the oxidation kinetics, the cladding peak temperature was 1191 K, occurring opposite the two surface thermocouples. The temperatures near the two surface thermocouples were 1149 and 1145 K. For the different oxide thicknesses, the temperature varied from 1141 to 1191 K, resulting in a 50-K variation around the circumference of the zircaloy cladding.

The temperature estimates for the nuclear fuel rods were: 1076 K compared with 1070 K measured value for the first rod, 1186 K compared with 1200 K measured for the second rod, and 1145 K compared with 1125 K measured for the third rod. Three of the four rods exhibited temperatures higher than the measured temperatures, which would be expected from thermocouple effects on cladding temperature. The low estimated temperatures for the second nuclear rod may be due to sloughed oxide or the lack of any thermocouple effect. The standard deviation for the four measurements is 26 K. Estimated errors from 40 to 55 K appear to be conservatively high when compared with the measured value of 26 K based on the four measurements and assuming no thermocouple effects. The error may be less than 26 K, because the trend in the data does indicate reduced cladding temperatures because of the presence of the thermocouples.

4. CONCLUSIONS

The kinetics of the zircaloy oxidation in steam was extended to reaction layer thicknesses at the intermediate temperatures in the two-phase α plus β temperature region. Parabolic kinetics was established for steam pressure between atmospheric and 10.3 MPa. The validity of the layer thickness measurements was established by the good agreement for oxygen uptake with other investigators.

Use of the oxidation kinetics in conjunction with measurements of oxide layer thicknesses is a valid technique to estimate prior cladding peak temperatures and circumferential temperature gradients. Assuming that the measured temperatures during LOCEs are correct, the experimental error in this technique is about 25 K, compared with an estimated error of between 40 and 55 K. The selection of the appropriate oxidation equation for the β -phase or α -plus- β -phase temperature regions can be determined from the zircaloy microstructure.

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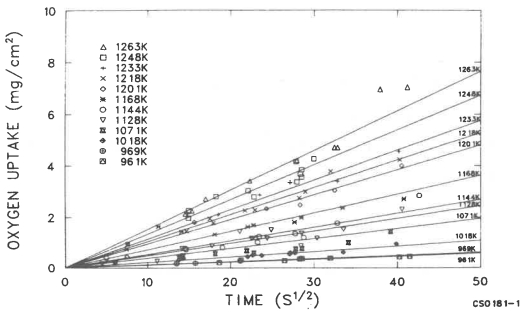


Figure 1. Oxygen uptake as a function of time for different temperatures.

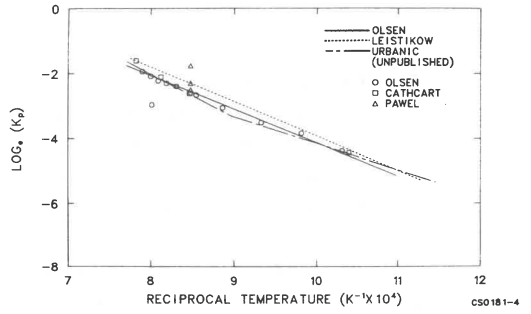


Figure 2. Temperature dependence of parabolic rate constant for oxygen uptake.

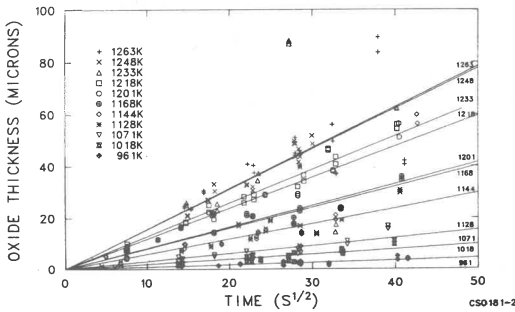


Figure 3. Oxide layer growth as a function of time for different temperatures.

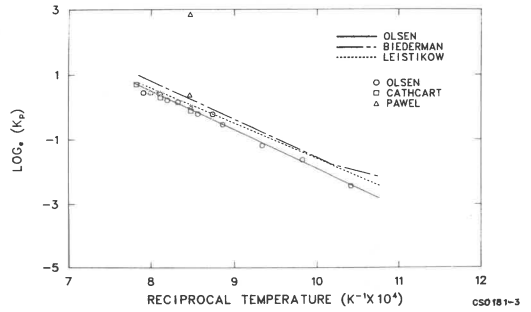


Figure 4. Temperature dependence of parabolic rate constant for growth of oxide plus oxygen-rich layers.

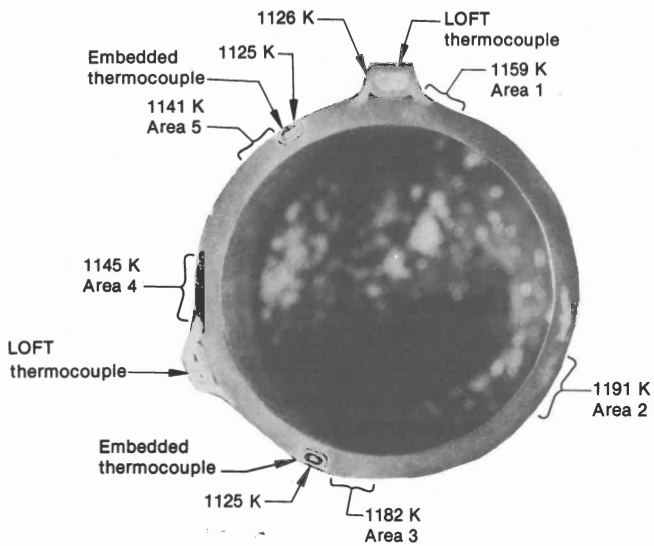


Figure 5. Estimated cladding temperatures at thermocouple locations.

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