NF-810801--61

CONF-810801--61

DE82 005952

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TEMPERATURE ESTIMATES FROM THE ZIRCALOY OXIDATION KINETICS IN THE α PLUS β PHASE REGION

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Work supported by the U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Research under DOE Contract No. DE-AC07-76ID01570.

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SUMMARY

Oxidation rates of zircaloy in steam were measured at temperatures between 961 and 1264 K and for duration times between 25 and 1900 seconds in order to calculate, in conjunction with measurements from postirradiation metallographic examination, 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 temperature 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 per minute. 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.

The growth of the oxide plus oxygen-rich layer followed parabolic kinetics and is given by:

$$X = 2.52611\times10^{4} \left(\begin{smallmatrix}+38.5\% \\ -27.8\%\end{smallmatrix}\right) \exp\left(-23{,}920\ (\pm 3.1\%)/RT\right)\ t^{1/2}$$

where

X = the thickness (micrometers)

R = 1.987 cal/mole-K

T = temperature (K)

t = time (s).

Zircaloy oxidation rates from the above equation were applied to a zircaloy cladded electrical heater rod which had been subjected to four LOCEs and three nuclear fuel rods which had been subjected to four, three and one transients, respectively. The calculated temperatures near two surface-attached thermocouples and one embedded thermocouple of the electrical heater rod were 34, 19, and 16 K, respectively, higher than the values determined by thermocouples. These differences are within the 4% uncertainty (50 K) estimated by linear error propagation techniques. Measurements of the oxide thickness indicated the peak temperature of 1191 K occurred between the two surface attached thermocouples. The error in the four 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 can be used to estimate prior cladding peak temperatures achieved during LOCEs from postirradiation metallographic examinations.

TEMPERATURE ESTIMATES FROM THE ZIRCALOY OXIDATION KINETICS IN THE α PLUS β PHASE REGION

1. INTRODUCTION

Temperature measurements performed in the Loss-of-Fluid Test (LOFT) facility located at the Idaho National Engineering Laboratory (INEL) have been questioned because of a "fin" effect caused by increased heat transfer through a surface attached thermocouple and the resulting lower cladding temperatures during a loss-of-coolant experiment (LOCE), and because of the concern that the surface attached thermocouples may cause premature rewetting and quenching of the fuel rods. Independent techniques are required to determine cladding temperature without perturbing the temperature. These techniques will be used to assess (1) the accuracy of temperature measurements of fuel rod peak cladding temperatures from thermocouples attached to the surface during LOCEs, (2) the perturbation of the fuel rod cladding LOCE temperature history caused by the presence of thermocouples, and (3) the measurements of cladding azimuthal temperature gradients near the thermocouple locations.

A technique to determine cladding temperature is to use the oxidation rates of zircaloy in steam in conjunction with measurements of oxide layer growths from post irradiation examinations (PIE) in order to calculate the prior peak cladding temperatures. Layer thicknesses rather than oxygen uptake are normally the cladding parameter measured during PIE. Oxygen uptake cannot usually be determined directly from the cladding of a fuel rod but has to be calculated from diffusion coefficients which requires knowledge of the temperature and layer thicknesses. This technique of using layer thicknesses has been used at INEL to estimate peak cladding 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 peak cladding temperatures.

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

2. OXIDATION KINETICS IN THE α PLUS β TWO-PHASE TEMPERATURE REGION

The experimental procedure used to determine the extent of the zircaloy/steam reaction is described in Section 2.1, and the results with a discussion of the results is presented in Section 2.2.

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 is 10.72 mm OD by 0.601 mm thick and approximately 180 cm long.

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 representive 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 was 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 additiion to the pre- and post-test 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 the access to the chamber restricted to a diameter a little longer 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 heated with a Glas-Col heater is superheated to the desired temperature and passed through the reaction chamber and finally to a condensor. 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 towards the center of the furnace. 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 OD 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 passage of the steam through the sample and around it. A few tests were performed with a thermocouple spot welded to the inside of the cladding in order to measure heating and cooling rates and determine any differences on peak temperature. The heating and cooling rates were about 10 K/s faster than the 3 K/s of the unattached thermocouple, and no differences were observed in peak temperature.

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 post-test 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 K to 1263 K and for effective times ranging from 1 to 30 minutes. 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

The results of the oxygen uptake measurements with a comparison with other data are presented in Section 2.2.1 and those of the oxide plus oxygen-rich alpha layers are presented in Section 2.2.2.

2.2.1 Oxygen Uptake

The oxygen uptake data was 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, 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 pressure and 3.45 MPa, the oxidation kinetics are parabolic. For higher pressures or extremely low pressure,[3] the kinetics in the two-phase temperature region follow 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 Equation 1, and the errors in the constants represent one standard deviation.

$$k_w = 479.02 \begin{pmatrix} +23.3\% \\ -28.9\% \end{pmatrix} \exp\left(-20{,}400(\pm\ 2.3\%)/RT\right) \tag{1}$$

where

k_w = parabolic constant for weight gain (Mg 0/cm^2-sec$^{1/2}$)

R = $1.987 \frac{\text{cal}}{\text{mole-K}}$ (1,3)

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 of data. Leistikow combined data from the β phase temperature region and the two-phase temperature region, but the Leistikow's low temperature data exhibited increasing cubic kinetics with decreasing temperature.

2.2.2 Oxide Layer Thickness

Oxide layer thickness measurements, in this 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 thickness from the outside surface and inside surface were combined in deriving the parabolic rate constants for different temperatures.

The weight gain 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 Equation 2. The errors represent one standard deviation.

$$k_o = 2.526 \times 10^4 \begin{pmatrix} +38.5\% \\ -27.8\% \end{pmatrix} \exp\left(-23920(\pm 3.1\%)/RT\right) \tag{2}$$

where

k_o = oxide layer parabolic rate constant (micrometers/cm^2-sec$^{1/2}$).

The data are compared with results from Leistikow,[4] Cathcart[1] and Biederman[5] in Figure 4. Leistikow's data, as with the oxygen uptake data and also Biederman's data, are above the INEL and Cathcart data. 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 Urbanics oxygen uptake data. The oxygen uptake and oxide layer data do not substantiate different oxidation rates in this temperature interval.

3. ESTIMATING PRIOR PEAK CLADDING TEMPERATURES FROM OXIDATION KINETICS

An electrical heater rod and three nuclear fuel rods[6] which were subjected to a series of LOCEs were used to evaluate the technique of using oxidation kinetics to determine the prior peak cladding temperature. The electrical heater rod was subjected to 4 LOCE transients in which a peak temperature of 1125 K was measured. The first nuclear rod was subjected to three LOCEs, and the peak temperature of 1070 K was measured. The second nuclear rod was subjected to only one LOCE in which a temperature of 1200 K was measured. The third nuclear rod was subjected to four LOCEs in which a peak temperature of 1125 K was measured.

The temperature estimates for the prior peak cladding temperatures were obtained from the measured oxide layer thickness and using measured temperatures as a basis for calculating oxide thickness from Equation 2. The measured temperatures are multiplied by a correction factor, in order 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 Equation 2 and assumed errors of 5% in time and 10% in oxide thickness measurements. The estimated error varies from 40 K at 973 K to 56 K at 1223 K. The contribution to the total error arises mainly from the errors in the constants in Equation 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 peak cladding temperatures may be estimated from fuel rods without measured thermal histories because gross errors in assumed time may be tolerated. However for evaluation of prior peak cladding 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 temperature estimates are shown in Figure 5 with the cross-section of the electrical heater rod at the junction of the thermocouples. Based upon the oxidation kinetics, the peak cladding 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 measured 1125 K 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 sluffed oxide or the lack of any thermocouple effect. Since the differences between the estimated and measured temperatures are less than the estimated error of 40 K for this method, the cooling effects of cladding thermocouples upon cladding temperature cannot be concluded. The standard deviation for the four measurements is 26 K. Estimated errors from 40 to 55 K appear to be conservatively high compared with the measured value of 26 K based upon the four measurements.

4. CONCLUSIONS

The kinetics of the zircaloy oxidation in steam was extended to reaction layer thicknesses in the intermediate temperatures in the two-phase α plus β temperature region. Parabolic kinetics was established for steam pressure between atmospheric pressure and 10.3 MPa. The validity of the layer thickness measurements were 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 peak cladding 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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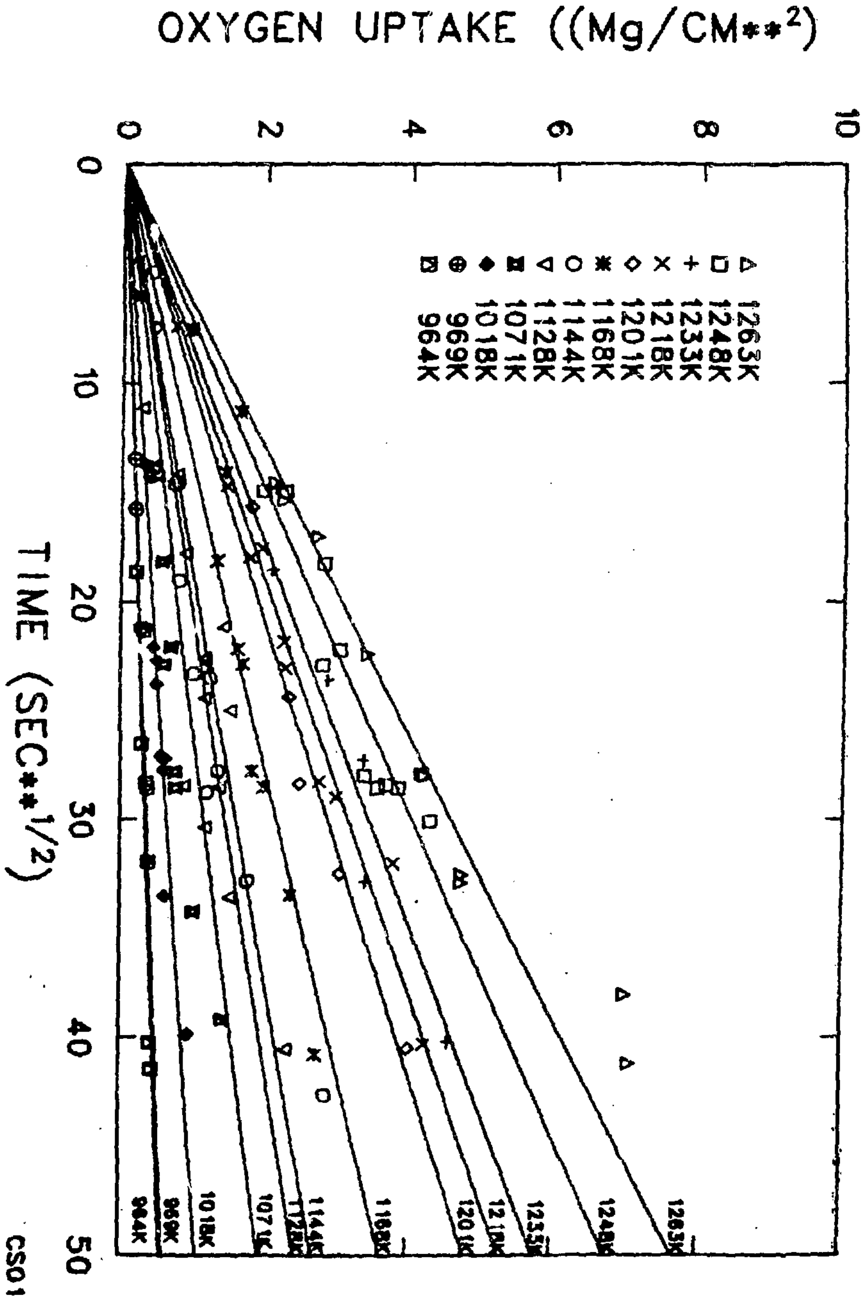
OXYGEN UPTAKE ((Mg/CM**2)
0
2
4
6
8
10
TIME (SEC**1/2)
0
10
20
30
40
50
△ 1263K
□ 1248K
+ 1233K
× 1218K
◇ 1201K
✱ 1168K
○ 1144K
▽ 1128K
⧗ 1071K
◆ 1018K
⊕ 969K
⊠ 964K
1263K
1248K
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1201K
1168K
1144K
1128K
1071K
1018K
969K
964K

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FIGURE 2. TEMPERATURE DEPENDENCE OF PARABOLIC RATE FOR OXYGEN UPTAKE

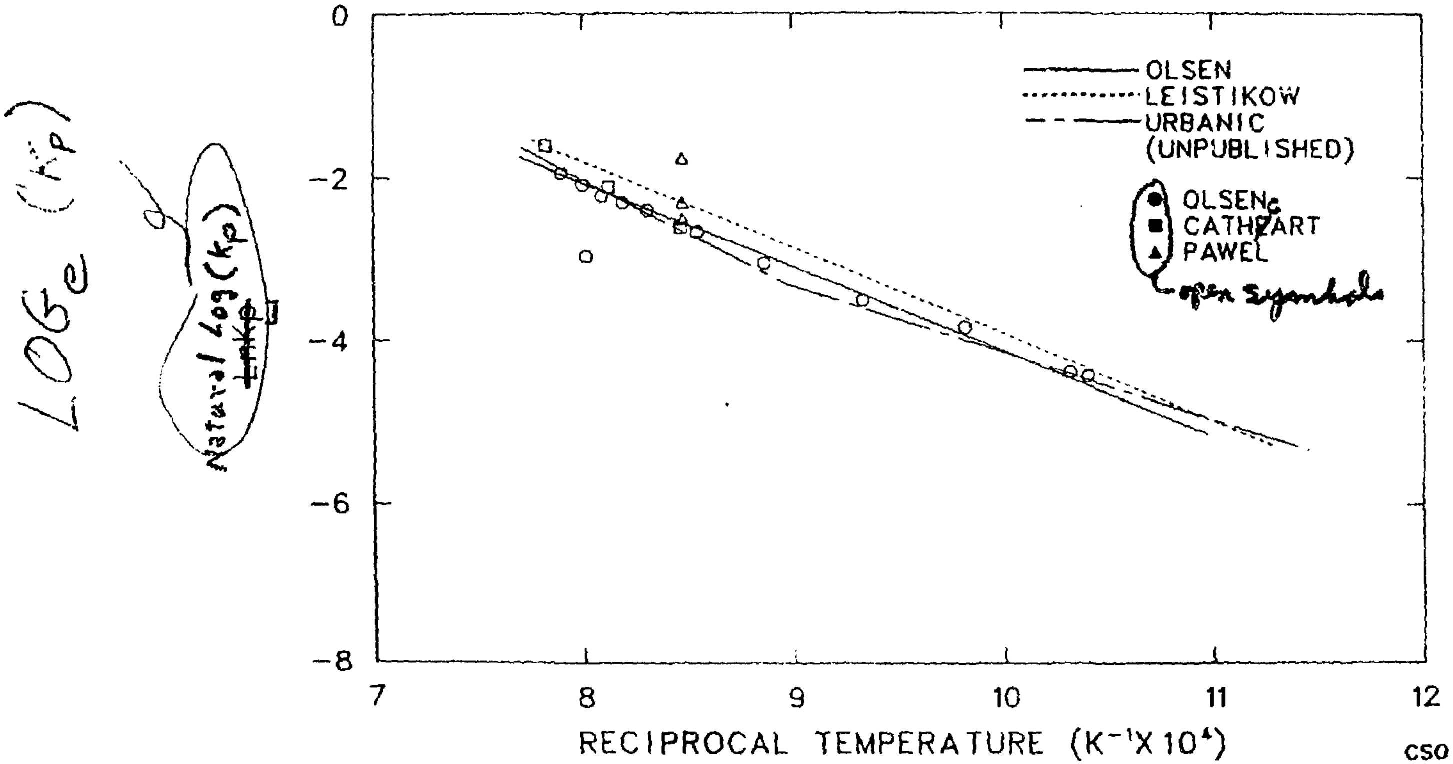

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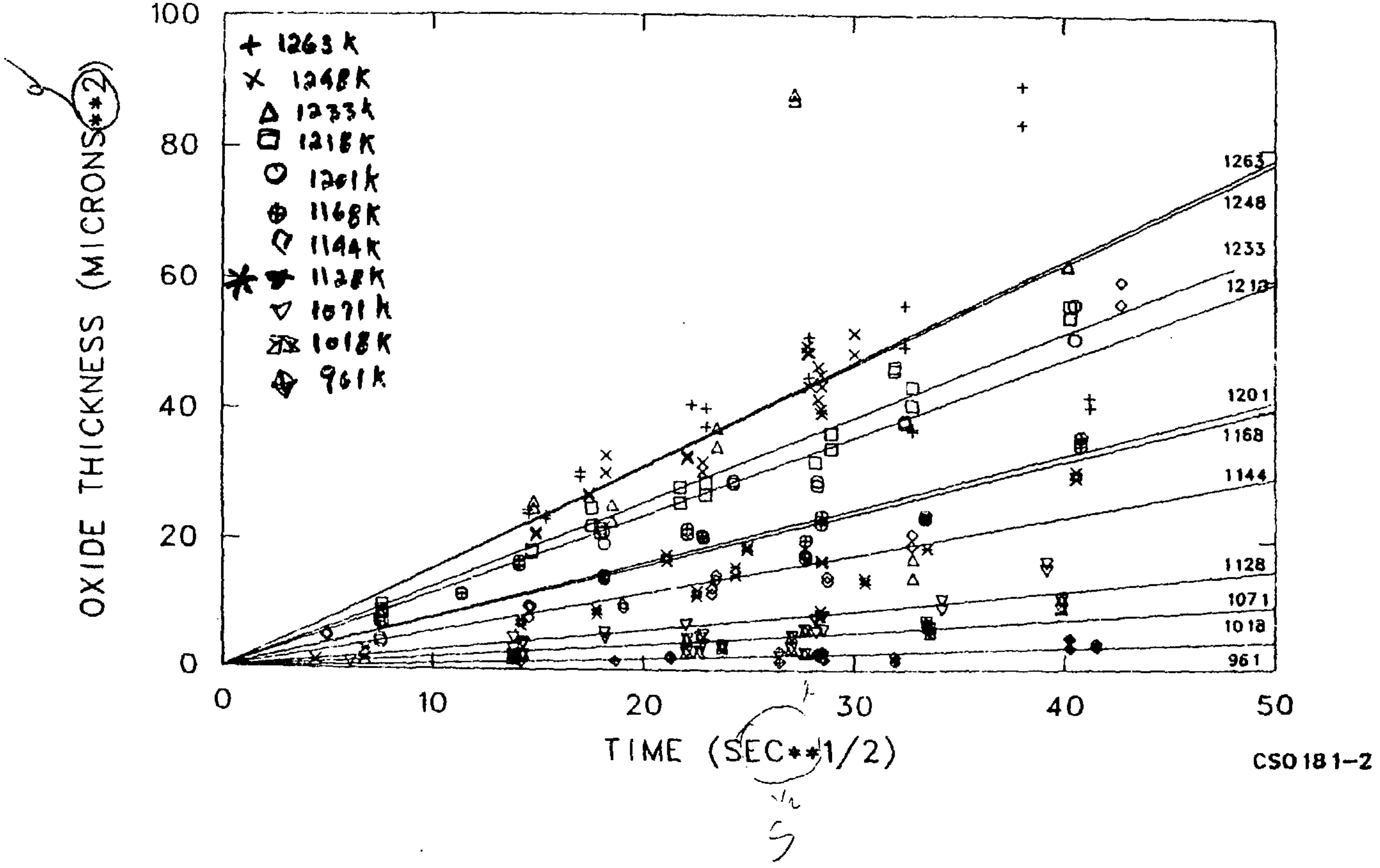
FIGURE 3. OXIDE LAYER GROWTH AS A FUNCTION OF TIME FOR DIFFERENT TEMPERATURES



$(S^{1/2})$

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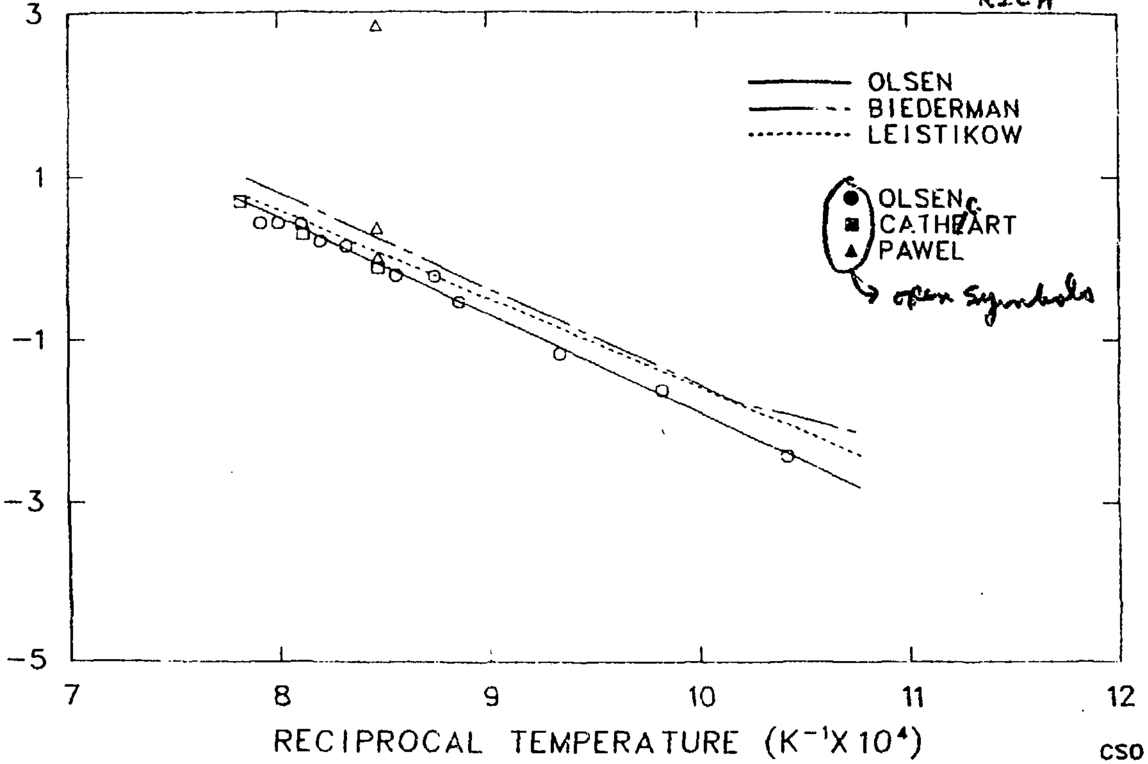
FIGURE ~~7~~ 4 TEMPERATURE DEPENDENCE OF PARABOLIC RATE CONSTANT FOR GROWTH OF OXIDE PLUS OXYGEN-~~RED~~ RICH LAYERS



LOGe (Kp)

Natural Log (Kp)

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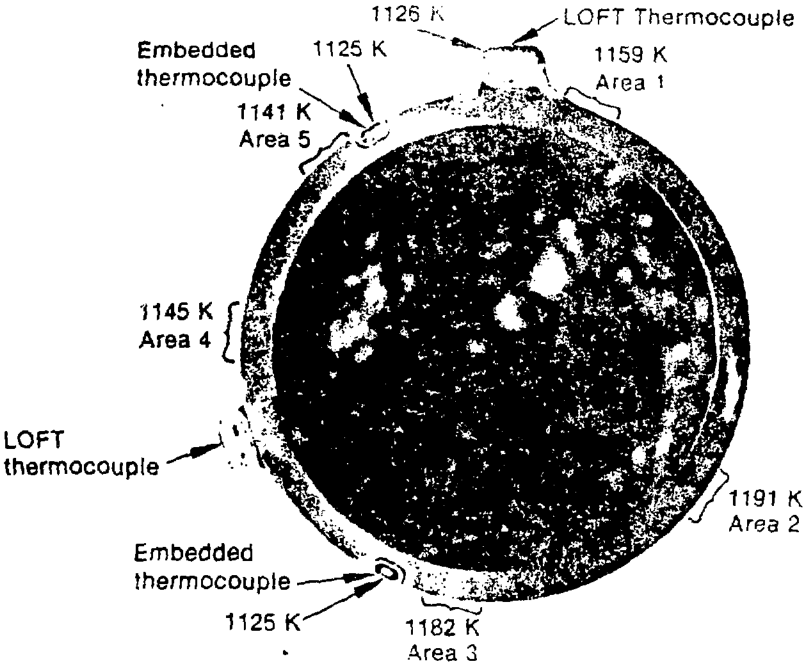

Figure ~~28~~ 5. Estimated Cladding Temperatures at Thermocouple Location.