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POSTIRRADIATION METALLURGICAL TECHNIQUES
TO ESTIMATE LOFT PEAK CLADDING TEMPERATURES

C. S. Olsen

THIS REVISION COMPLETELY SUPERSEDES ALL PREVIOUS ISSUES OF LTR 1111-54.

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ABSTRACT

A comprehensive review of the zircaloy microstructure and oxidation characteristics was performed to establish the state-of-the-art capability for estimating peak cladding temperatures for LOCE's by postirradiation examination techniques. Cladding oxidation characteristics were compared with microstructure characteristics to determine the best approach.

Deficiencies were identified in the low-temperature oxidation characteristics required for LOCE's, and an experimental plan is proposed to obtain low-temperature oxidation data which will expand the current data base and confirm the feasibility of estimating zircaloy cladding temperatures for transient conditions.

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SUMMARY

This report presents a comprehensive review of zircaloy microstructure and oxidation characteristics. This information will be used to estimate LOFT peak cladding temperatures by metallographic analysis. Cladding temperatures expected for the LOFT L2-3 and L2-4 tests will be between 1050 and 1400 K and their estimations present unique problems in using current metallographic data and techniques.

Cladding microstructure characteristics can, in principle, permit determination of whether peak cladding temperatures achieved during the LOFT tests are within the α -phase (< 1100 K), α plus β -phase (1100 to 1240 K), or β -phase (> 1240 K). Determination of the actual temperatures with published microstructure data alone is not possible. At temperatures below 1240 K, even determining the transition temperature through identification of the allotropic phases from microstructures is imprecise because of uncertainties associated with the multiple transient history of the LOFT fuel and effects of cooling rate upon the zircaloy microstructures. For temperatures above 1240 K, the β -phase can be identified from the microstructure for different cooling rates expected during a LOCE.

Cladding oxidation characteristics offer a more promising approach to accurate estimation of peak cladding temperatures. High temperature (> 1270 K) oxidation is well characterized as a function of temperature and time-at-temperature and with existing data and experience gained

from PIE (Post Irradiation Examination) of PBF (Power Burst Facility) fuel rods, peak cladding temperatures between 1270 and 1770 K can be inferred within an estimated uncertainty of ± 30 to 70 K (95% confidence level) respectively. However, current estimates of peak cladding temperatures for the center L2-3 and L2-4 peripheral fuel modules indicate that cladding temperatures lie below the range of well characterized high-temperature data.

For peak cladding temperatures below 1243 K, the limited oxidation data which exist suggests that peak cladding temperatures in the high α and in the α plus β region (970 to 1243 K) may be estimated by evaluating the extent of zircaloy oxidation. The current data in this temperature range are limited because (1) only one source of experimental data currently exists, and evaluation of potential systematic errors is not possible, (2) the data are not in a form which can be directly used for posttest metallographic analysis, and (3) the effect of multiple transients on oxidation characteristics has not yet been evaluated. Additional tests in this lower temperature range are planned at AECL to study the effect of oxidation upon the α to β transformation, and if oxide thicknesses are obtained, these data will still not be sufficient because of items (1) and (3) above. An experimental plan is presented to obtain additional low-temperature oxidation data, to expand the current data base, and to confirm the feasibility of estimating zircaloy temperatures from low-temperature oxidation characteristics. Without these additional data, peak cladding temperature estimates by metallographic techniques will be seriously impaired because of assumptions required to replace the experimental data.

CONTENTS

SUMMARY	ii
I. INTRODUCTION	1
II. CALCULATED PEAK CLADDING TEMPERATURES FOR LOFT L2 TESTS	4
III. METALLURGICAL TECHNIQUES FOR EVALUATING CLADDING TEMPERATURES FOR THE L2 TEST SERIES	7
1. Zircaloy Microstructures	7
2. Zircaloy Oxidation	10
2.1 High Temperature Oxidation Data	10
2.2 Low Temperature Oxidation Data	12
2.3 Discussion	14
IV. PROPOSED TEST PLAN	17
V. REFERENCES	25
APPENDIX A. TEMPERATURE ESTIMATES FROM ZIRCALOY MICROSTRUCTURES	28
APPENDIX B. ZIRCALOY OXIDATION	51
APPENDIX C. ANALYSIS OF TEMPERATURE ERRORS FROM OXIDATION KINETICS	65

FIGURES

1. Idealized multiple transient temperature- time profile	19
2. Conceptual diagram for apparatus for oxidation and microstructure studies	22
3. Schedule for oxidation and microstructure tests and its relation to PIE for PBF/LOFT lead rod tests and for L2-3 center module.	24

FIGURES (APPENDICES)

A-1 Hardness results for all transient tests	33
A-2 Microstructure of as-received, uncrystallized zircaloy	34
A-3 Microstructure of unrecrystallized zircaloy after heating at 811K for 135 seconds	34

A-4	Microstructure of partially recrystallized zircaloy after heating at 866K for 5 seconds	34
A-5	Microstructure of recrystallized zircaloy after heating at 866K for 15 seconds	34
A-6	Microstructure of unirradiated zircaloy heated at 1072K (α -phase) for 300 seconds and slowly cooled	36
A-7	Microstructure of irradiated zircaloy heated at 1072K (α -phase) for 300 seconds and slowly cooled	36
A-8	Microstructure of cracked oxygen-rich layer and underlying hydride needles after heated in steam at 948K for 360 hours	38
A-9	Microstructures of the two phase, α plus β , region for different proportions of β after heating for 1½ hours at 805K	40
A-10	Microstructure of irradiated zircaloy heated at 1115K (α plus β) for 300 seconds and slowly cooled	41
A-11	Microstructure of irradiated zircaloy heated at 1234K (α plus β) for 300 seconds and slowly cooled	41
A-12	Cross-Section of zircaloy-4 tube oxidized in steam at 1473K (β -phase)	44
A-13	Microstructure of unirradiated zircaloy heated at 1254K (β -phase) for 300 seconds and slowly cooled	44
A-14	Effect of cooling rate on the microstructure of Zr-1 w/o Cr-0.1 w/o Fe alloy cooled from 1323K (β -phase)	45
B-1	Summary of oxidation kinetics for high and intermediate temperatures	62

TABLES

I.	Estimated Cladding Temperatures And Expected Fuel Cycling And PIE for LOFT L2 Test Series	5
II.	Cladding Temperature Ranges For Zircaloy Crystallographic Phase Transitions	8
III.	Temperature-Time Parameters For Multiple Transient Tests	20

TABLES (APPENDICES)

B-I	Exponents on Time Derived From Leistikow and ORNL Data	58
C-I	Temperature Errors And Relative Contribution for Oxide Plus Alpha Thickness (Equation (C-3))	68
C-II	Temperature Errors and Relative Contribution for Total Oxygen Absorption (Equation (C-4))	69
C-III	Temperature Errors and Relative Contribution for Oxygen Absorption at Intermediate Temperatures (Equation (C-5))	71

I. INTRODUCTION

Cladding temperatures during the LOFT L2 Test Series are the primary means for determining the effectiveness of ECC and to insure that the core will remain amenable to cooling. Two ECCS criteria⁽¹⁾ for light-water-cooled nuclear power reactors were established in December, 1973, to ensure the integrity of the cladding during a LOCA (Loss-of-Coolant-Accident). One criterion stated that the maximum cladding temperature shall not exceed 2200°F (1478 K). Associated with the first criterion, the second criterion limits the total oxidation of the cladding (in the form of ZrO_2) to 0.17 times the original cladding thickness. The first criterion is based upon temperature alone, but the latter incorporates, through cladding oxidation, time at temperature in addition to temperature. These criteria establish the importance of reliably determining cladding temperatures during the LOFT L2 Test Series.

Cladding temperatures are also the most important single measurement for evaluating fuel rod models that predict the thermal-mechanical response of the cladding and for estimating the fuel rod-to-coolant heat transfer which is required to evaluate the analytical models that predict subchannel thermal-hydraulic response. The cladding surface temperature of the LOFT core will be measured by thermocouples attached to the cladding surface at 185 locations. The measured cladding surface temperature, however, can be different from the true cladding surface temperature as a result of perturbations in the cladding surface geometry and

potential selective cooling of the thermocouple as a result of its protrusion into the coolant steam. Biederman⁽²⁾ indicated that for steady state power and flowing steam, measured cladding temperatures were 100 K lower than true temperatures. During PBF (Power Burst Facility) tests⁽³⁻⁸⁾ characterized by high steady state heat fluxes (492 to 656 W/cm) in film boiling conditions, measured cladding temperatures have been lower than the true temperatures (estimated from posttest metallurgical evaluations) by as much as 100 to 300 K. Although these temperature perturbations may not be typical for the LOFT transient (low-heat flux conditions for a LOCE), these results suggest some perturbation of the true cladding temperature as a result of attaching surface thermocouples.

Postirradiation Examinations (PIE) which include metallographic analysis of the cladding microstructure and oxidation characteristics offer a means to determine peak cladding temperature which is independent of the thermocouple measurements, and therefore, peak cladding temperatures of uninstrumented core fuel rods can be determined. Thus PIE techniques provide a means to (1) verify cladding thermocouple measurements, (2) evaluate uninstrumented fuel rod response, and (3) quantitatively determine the effect of core instrumentation (cladding thermocouples) on the rod response by comparing cladding temperatures of instrumented rods with that of uninstrumented rods.

This report reviews and summarizes present state-of-the-art capability to determine peak cladding temperatures from posttest metallographic analysis of zircaloy microstructure and oxidation characteristics.

Section II presents a summary of the expected cladding temperatures for the L2 tests. This information is required as a basis for evaluating the metallographic methods discussed in the remainder of the report. Section III presents the results of a comprehensive literature search to evaluate the adequacy of available zircaloy microstructures and oxidation data for accurately estimating expected LOFT peak cladding temperatures. Section IV summarizes additional work proposed to further evaluate and characterize low-temperature zircaloy oxidation for posttest metallographic applications.

II. CALCULATED PEAK CLADDING TEMPERATURES FOR LOFT L2 TESTS

To assess the adequacy of the different posttest metallographic techniques to predict cladding temperatures, current predictions of peak cladding temperatures for the LOFT L2 Test Series are summarized here. Knowledge of the cladding temperature history will permit better evaluation of the ability of the metallographic techniques to accurately estimate peak cladding temperatures. Also, since these metallographic techniques may partly depend upon the number of transients, a schedule for removal of core fuel modules is presented.

Table I presents a summary of the tests in the L2 Test Series and the calculated peak cladding temperatures for both the central and peripheral fuel modules. These estimates are based upon FRAP-T calculations⁽⁹⁾ which do not include radiation heat transfer, but preliminary calculations with MOXY/SCORE code⁽¹⁰⁾ indicate that radiation heat transfer may decrease the temperature for L2-4 test by as much as 100 K. These latter calculations are still being evaluated.

Cladding temperatures for the center modules are expected to range from 960 K in L2-3 to 1390 K in L2-4 (not accounting for radiation heat transfer). Temperatures for L2-5 and L2-6 will also be in this range. Because the center modules will be removed after each of the tests from L2-3 through L2-6, PIE temperature estimates can be made after each test. The peripheral modules will not be removed until after L2-4 and not again until after L2-6. Therefore the first peripheral modules will experience peak temperatures between 600 and 1150 K, and the second peripheral modules will experience temperatures between 600 and 1030 K.

TABLE I
ESTIMATED CLADDING TEMPERATURES
AND EXPECTED FUEL CYCLING AND PIE FOR LOFT L2 TEST SERIES

TEST NO.	CENTRAL FUEL MODULES				PERIPHERAL FUEL MODULES			
	PEAK POWER (kW/m)	FRAP-T3 CALCULATED PEAK CLADDING TEMP (K)	EXPECTED FUEL REMOVAL [1]	PIE TEMP RANGE [2] (K)	PEAK POWER (kW/m)	PEAK CLADDING TEMP (K)	EXPECTED FUEL REMOVAL [1]	PIE TEMP RANGE [3] (K)
L2-2	26.3	990	NO	--	23.3	870 ⁽⁴⁾	NO	--
L2-3 ^[5]	39.4	1210	YES	960-1210	35.1	1030	NO	600
L2-4 ^[6]	52.5	1390	YES	1100-1390	46.6	1150	YES	600-1150
L2-5	39.4	1230	YES	970-1230	35.1	1030	NO	--
L2-6	39.4	1240	YES	980-1240	35.1	1030	YES	600-1030

- [1] Expected fuel removal after the designated test is based on fuel behavior calculations and will depend on cladding mechanical degradation at higher temperature.
- [2] Estimated by scaling the central module peak temperature prediction by ratio of min/max power in central module.
- [3] Lower limit based on steady state coolant temperature.
- [4] Estimated by scaling the central module peak temperature prediction by ratio of power in peripheral/central fuel module.
- [5] Radiation heat transfer to surrounding fuel and guide tubes will decrease FRAP-T3 temperature (estimated 25-50 K)
- [6] Radiation heat transfer to surrounding fuel and guide tubes will decrease FRAP-T3 temperatures (estimated 100-150 K).

The nominal peak cladding temperatures and the temperature ranges listed in Table I show that for most of the L2 tests, the metallurgical techniques to estimate cladding temperatures must be applied below 1270 K, a temperature above which most of the cladding temperature evaluations for the PBF Program were performed. Only for the L2-4 central module may the peak cladding temperatures be above 1270 K and this will occur only if radiation heat transfer during the test is small.

The fuel module removal schedule is based upon the assumed occurrence of cladding waisting (or ballooning of pressurized rods in L2-6⁽¹¹⁾), which, in turn, is based upon thermal behavior predictions⁽⁹⁾ and out-of-pile waisting experiments⁽¹²⁾.

III. METALLURGICAL TECHNIQUES FOR EVALUATING CLADDING TEMPERATURES FOR THE L2 TEST SERIES

Zircaloy microstructures are sufficiently different among the allotropic phase (α , α plus β , and β) to permit microstructures to be correlated with temperatures. Evaluation of microstructures is primarily useful for establishing peak cladding temperature ranges rather than specific temperatures. Measurement of the extent of oxidation (oxide layer thickness or weight gain) allows a more exact evaluation of cladding temperatures compared with a broad temperature range from microstructure evaluations. State-of-the-art techniques for using both zircaloy microstructures and oxidation to determine peak cladding temperatures in LOFT are summarized in the following sections.

1. ZIRCALOY MICROSTRUCTURES

Since the zircaloy phase transformation is dependent upon the solutes (Ni, Cr, Fe, Sn, O, and H), the transition from the α -phase to β -phase occurs over a temperature range rather than at a single temperature⁽¹¹⁻¹³⁾. Experimental data for hydrogen-free zircaloy show the temperature range for transformation from α to β zircaloy is 1103 to 1243 K⁽¹³⁾. In principle, the grain structures of each phase can be differentiated and used to determine peak cladding temperatures by metallographic techniques during PIE. In addition zircaloy recrystallization has been shown to initiate at 866 K. The resulting grain structure is readily distinguishable from the cold-worked microstructure⁽¹⁴⁾. These zircaloy microstructure characteristics can be correlated with peak cladding temperature ranges as shown in Table II.

TABLE II

CLADDING TEMPERATURE RANGES
FOR ZIRCALOY CRYSTALLOGRAPHIC PHASE TRANSITIONS

<u>TRANSITION</u>	<u>TRANSITION TEMPERATURE (K)</u>	<u>IDENTIFIED PHASE</u>	<u>TEMPERATURE RANGE (K)</u>
Recrystallization	866	Cold Worked	>866
α to α plus β	1103	Annealed	866 to 1103
α plus β to β	1243	α plus β	1103 to 1243
		β	1243

Identification of the cold-worked vs annealed microstructure entails no problem, and the β -phase microstructures can be readily identified for cooling rates above 2 K/s since they exhibit a readily identifiable acicular (needle-like) or platelet grain shape⁽¹⁷⁻²⁰⁾. The α - and the α plus β -phases have a more equiaxed grain shape than the β -phase grain.

Certain problems exist in distinguishing the two-phase, α plus β zircaloy from the single-phase α -zircaloy and consequently the onset of the α to α plus β transition. For cooling rates between 1 and 20 K/s, both the α and α plus β phases exhibit nearly identical equiaxed grain structures (Appendix B) and the microstructures change markedly with different cooling rates^(12, 21-25). Since cooling rates for the LOFT tests may be in this range, peak cladding temperatures can not be established below the α -plus- β to β transus.

Identification of the β -phase has been used in tests conducted to date in the PBF program to establish peak cladding temperatures over 1243 K, but the need to rely upon the lower temperature microstructures did not exist for these tests⁽³⁻⁸⁾. For the LOCA-11⁽²⁶⁾ and LOFT Lead Rod Tests⁽²⁷⁾ in PBF, cladding temperatures are expected to be below 1243 K, and the use of metallurgical techniques, not previously tried, to estimate these lower temperatures will be required.

Although the presently available published microstructure data applicable to LOCE transients do not substantiate the use of microstructures to pinpoint temperatures within each phase region, these data do

not preclude the possibility that new microstructure data, reflecting cooling rate effects, etc. could pinpoint temperatures within ± 20 to ± 30 K⁽²⁸⁾. Because of the fine temperature resolution that zircaloy oxidation offers and zircaloy microstructure characteristics presently do not, zircaloy oxidation techniques will be emphasized. Microstructure characteristics will be examined further, but with a lower priority than zircaloy oxidation.

2. ZIRCALOY OXIDATION

Zircaloy reacts with steam to form ZrO_2 , and part of this oxide dissolves in zircaloy at high temperatures to form different reaction layers⁽¹³⁾. Experimental data were obtained to characterize the extent of oxidation as a function of temperature and reaction time (time-at-temperature) for temperatures above 973 K^(20, 29-39). The extent of oxidation is determined by either weight gain or reaction layer thicknesses. The experimental data are categorized as to high temperature oxidation (> 1270 K) and low-temperature oxidation (< 1270 K) in the following discussions.

2.1 High Temperature Oxidation Data

Zircaloy oxidation rates have been investigated for isothermal conditions above 1270 K^(20, 29-34) from which the Cathcart data⁽²⁰⁾ are accepted as the most comprehensive and reliable data. Extreme care was taken to calibrate thermocouple response in-situ and correlate

oxidation extents with precise locations of the verified thermocouple measurements. The oxidation extents were characterized for times up to 2000 seconds by total weight gain and by three separate expressions for reaction layer thicknesses.

Analytical models were developed to correlate this isothermal data with temperature and the square root of time for subsequent application to transient temperature conditions⁽²⁰⁾. The details of the four correlations are given in Appendix B. The correlation based upon the thickness of the oxide plus oxygen-stabilized α -zircaloy layers, which is directly applicable to PIE, results in errors in estimated temperatures between 40 and 70 K (95% confidence level) (see Appendix C for details). This correlation has been extensively applied to evaluate peak cladding temperatures during PBF tests in which cladding temperatures exceeded 1273 K⁽³⁻⁸⁾.

The extent of oxidation measured after temperature transients was first shown, by Biederman⁽²⁹⁾ and substantiated afterwards by Cathcart⁽²⁰⁾, to be substantially less than that predicted by models derived from isothermal data. From limited data between 1323 K and 1673 K, this transient effect was found to predominate between 1323 and 1473 K, but the data are not sufficient to determine the cause of the anomalous behavior or to develop a transient correlation in this temperature range (Appendix B). The application of isothermal data to transient problems is often done,⁽⁴⁰⁾ but care has to be taken to ensure no unexpected behavior during integration over the transient. Additional effort will

be required in the form of more transient data and further evaluation to develop the application of isothermal data to transient conditions.

Other data have been published⁽²⁹⁻³²⁾ but show significant differences from Cathcart's data. The extrapolation of Baker-Just correlation⁽³⁰⁻³²⁾, based upon a few data points and verified by SPERT tests⁽⁴¹⁾ at the zircaloy melting point, to lower temperatures is about a factor of two higher than Cathcart's correlation. Extrapolation of the Baker-Just correlation to temperatures below the zircaloy melting point is not justified. Biederman's reaction layer thicknesses⁽²⁹⁾ are a factor of two less than Cathcart's reaction layer thicknesses⁽²⁰⁾ and the differences are attributed to poor temperature measurements. The discrepancy between Biederman's and Cathcart's data emphasizes the importance of accurate experiment characterization for all temperatures.

2.2 Low-Temperature Oxidation Data

Isothermal oxidation data between 973 and 1273 K and at atmospheric pressure were obtained from Leistikow⁽³⁵⁾ and limited data in this temperature range for pressures up to 10.34 MPa were obtained from Pawel⁽³⁶⁾. Leistikow determined the oxidation extent gravimetrically so that the total oxygen weight gain (mg/cm^2) is correlated with temperature and time. The data from Oak Ridge were based upon thickness measurements with oxygen weight gain derived from the thickness measurements by the use of computer codes.

An analytical model was developed from these data for application to isothermal as well as transient conditions (Appendix B). The estimated uncertainty in the isothermal correlation based upon oxygen weight gain correlations is between 60 and 80 K for a 95% confidence level (Appendix C). To evaluate the application of this isothermal model to transient conditions, transient data below 1273 K are needed since the anomolous high temperature behavior was not examined below 1323 K.

The correlation for intermediate temperatures was based primarily upon data from Karlsruhe, West Germany, except for only three data points from Oak Ridge National Laboratory. This data base is tantamount to a single source, and is subject to systematic errors as observed with the high temperature Biederman⁽²⁹⁾ and Baker-Just data⁽³⁰⁻³²⁾. Data from different sources will be required to evaluate systematic errors in this intermediate temperature range. Gravimetric tests are tentatively planned to begin in May or June, 1978 at Chalk River Nuclear Laboratory, with the emphasis on studying the effect of oxidation upon the α -zircaloy to β -zircaloy phase transformation^(42,43). Oxide thickness measurements are planned and will provide a correlation based upon reaction layers, which is a requirement for PIE. Evaluation of the systematic errors in thickness measurements can be performed through comparisons of weight gain measurements from the Karlsruhe data and from these data, but both sets of data will not be sufficient for this evaluation.

Oxidation at temperatures below 1273 K will result in small oxide thicknesses and, as a result, correlating temperature and reaction time

with oxide thicknesses may be difficult. The weight gain model could be applied to reaction layer thicknesses, but this application would require assumed oxide densities and unproven oxygen diffusion models. Zircaloy-clad heater rods obtained from the blowdown facility⁽⁴⁴⁾ and subjected to multiple transients, and fuel rods from PBF LOCA-11 tests are being examined to estimate cladding temperatures from zircaloy microstructures and low temperature oxidation kinetics. These estimated temperatures will be compared with measured temperatures to evaluate the ability to measure oxide thicknesses, the effects of multiple transients, and the low temperature oxidation correlation in its present form of weight gain.

From current temperature predictions presented in Section II, all peak cladding temperatures in the L2 Test Series except the center fuel module temperatures for L2-4 will be in the low oxidation temperature range. Thus, the use of low-temperature oxidation characteristics offers the only way to evaluate cladding temperatures by PIE for nearly all fuel rods.

2.3 Discussion

Metallurgical examinations of zircaloy cladding during PIE offer two independent techniques to estimate cladding temperatures. The first technique based upon zircaloy microstructures permits determination of only a temperature range through identification of allotropic phases and knowledge of the transition temperatures. Problems do exist in distinguishing the α - and α plus β -phases at different cooling rates. For cooling

rates above 2 K/s, expected during LOCE's, the β -phase can be readily identified. The second technique, based upon measurement of reaction layer thicknesses and correlations for oxidation kinetic rates will be used to pin-point cladding temperatures much more closely than can be done from microstructures alone. Since a second order correlation is required to represent the zircaloy oxidation kinetics between 1243 and 1773 K, and a third order correlation is required between 973 and 1243 K, the absence of the β -phase is required to select the appropriate third order kinetic equation for the low temperature LOCE's in the LOFT facility.

The isothermal oxidation data above 1273 K are well characterized and provide a means for determining peak cladding temperatures within ± 60 K (95% confidence level) using Cathcart's model to evaluate oxide layer thicknesses. Limited transient data between 1323 and 1473 K suggest that a problem exists in extrapolating isothermal oxidation data to transient conditions. Additional transient data and further evaluations will be required to resolve this problem.

Low-temperature oxidation data based upon weight gain are available only from a single source and are not directly applicable to PIE. The uncertainties in temperature measurements based upon weight gain are slightly larger than those for high temperature reaction layer thicknesses. Well characterized oxidation data in the form of reaction layer thicknesses will be required over the temperature interval 973 to 1273 K in order to evaluate cladding temperatures from the LOFT L2 Test Series. Transient data will also be required within this temperature range to evaluate the applicability of isothermal data to transient conditions.

A test plan for obtaining the additional data required to improve the capability to estimate cladding temperatures from PIE is presented in the next section of this document.

IV. PROPOSED TEST PLAN

From the review of the available literature presented in the appendices and summarized in the previous sections, the following primary objectives have been established for obtaining additional data.

1. Isothermal oxidation data between 970 K and 1270 K are required to obtain reaction layer thicknesses in addition to weight gain measurements. Although the actual need is to correlate reaction layer thicknesses with temperature and time, the measurement of oxygen uptake by gravimetric techniques permits comparison of weight gain measurements with other data to evaluate systematic differences.
2. Multiple and single transient oxidation data are required to evaluate the applicability of isothermal oxidation data to multiple transient tests in the temperature range from 970 K to 1270 K for low temperature oxidation and from 1270 K to 1470 K for high temperature oxidation.

Forty-two isothermal oxidation tests are planned for seven temperatures (970, 1020, 1070, 1115, 1165, 1215, and 1270 K) and for six time durations for each temperature (60, 120, 300, 420, 600, and 900 seconds). A zircaloy sample will be rapidly heated in steam to a specified temperature, held at temperature for the required time, and then rapidly cooled (>100 K/s) through the α to β transition. Each sample will be metallographically

examined after each time exposure to determine reaction layer thicknesses and to record the microstructure. Duplicate samples will be oxidized at selected temperatures to determine reproducibility.

The idealized temperature-time profile for the multiple oxidation tests is shown in Figure 1 with the specific parameters listed in Table III for the different transients. Two consecutive thermal transients are proposed representing multiple LOFT tests. The first transient will be initiated from 616 K, in which the sample will be rapidly heated to the desired temperature, held at temperature for the specified time, and then rapidly cooled to 616 K. The second transient will be conducted in a similar manner, except that the temperatures will be different from those of the first transient. Table III lists the specific temperatures and time durations for the different tests. Tests 1, 5 and 7 are the nominal cases derived from Table I (Section 2) for the hot pins in the center and peripheral modules. In the remaining tests, the test parameters will be varied in order to scope the effects of temperature and time upon the extent of oxidation during the second transient. Test 2 will determine the effect of a longer time during the first transient upon the oxidation resulting during the second transient. Tests 3 and 4 will scope the effect of different peak temperatures for rods in the center module during the second transient. Tests 6 and 8 will scope the effect of different cladding temperatures for the peripheral rods.

A few single LOCE type transient tests will be performed for temperature-time histories representing L2-4, L2-5, and L2-6 center fuel modules. Peak cladding temperatures are currently expected to be 1390 K for L2-4 and

INEL-A-8658

Fig. 1 Idealized multiple transient temperature-time profile.

TABLE III

TEMPERATURE-TIME PARAMETERS FOR MULTIPLE TRANSIENT TESTS

Test No.	First Transient		Second Transient		LOFT Condition	Comments
	B (K)	A (s)	D (K)	C (s)		
1	993	90	1213	170	L2-2 and L2-3 center module	This test is nominal case. Time is varied in L2-2.
2	993	170	1213	170		Temperature is varied during L2-3
3	993	90	1113	170		
4	993	90	1313	170		
5	873	90	1033	170	L2-2 and L2-3 peripheral module	This test is nominal case
6	873	90	1133	170		Temperature is varied
7	1033	170	1033	170	L2-5 and L2-6 peripheral module	This test is nominal Temperature of L2-6 is changed.
8	1033	170	1133	170		

between 1230 and 1240 K for L2-5 and L2-6, respectively. These tests will be performed with typical heating and cooling rates expected for the LOCE tests which are still being determined.

A schematic of the test apparatus is shown in Figure 2. The apparatus consists of a steam generator, a steam condenser, a tube furnace and a gravimetric balance. The steam generator will provide up to 25 grams of steam per minute, which will be condensed after passage through the furnace. The tube furnace will provide uniform circumferential temperatures and can be moved to achieve rapid heating and cooling rates in the sample. The gravimetric balance consisting of a cathetometer and quartz spring will have a sensitivity of 0.1 mg/mm with a capacity of 5 grams.

The results from these out-of-file tests will expand the current data base and confirm the feasibility of estimating zircaloy temperatures from oxidation characteristics. The isothermal oxidation data will provide reaction layer thickness measurements at intermediate temperatures which in conjunction with those expected from AECL will be used to derive a correlation of reaction layer thicknesses as a function of time and temperature. This correlation will be verified as a multiple source correlation through comparisons of oxygen weight gain measurements with those from Karlsruhe, West Germany⁽³⁵⁾ and Chalk River, Ontario⁽⁴²⁻⁴³⁾. The single and multiple transient tests will confirm the application of isothermal data to transient conditions.

INEL-A-8656

Fig. 2 Conceptual diagram for apparatus for oxidation and microstructure studies.

This test program emphasizes the oxidation characteristics of zircaloy rather than microstructures because, based upon the published data, oxidation characteristics offer a finer temperature resolution than microstructures.

A schedule and costs for the proposed oxidation tests is shown in Figure 3. The tests will start in FY-79 and continue through the fiscal year. The oxidation results will be completed in time for the PIE examination of the LOFT lead rod tests and the subsequent PIE examination of the LOFT core modules. However the evaluation of the thermal response of the PBF LOCA-11 fuel rod will have to be done with the existing data. This schedule includes the separate costs for the isothermal tests and multiple transient tests.

Fig. 3 Schedule for oxidation and microstructure tests and its relation to PIE for PBF/LOFT lead rod tests and for L2-3 center module.

V. REFERENCES

1. Acceptance Criteria for Emergency Core Cooling Systems for Light Water Cooled Nuclear Power Reactors, Docket No. RM-50-1, December 28, 1973.
2. R. G. Ballinger, W. G. Dobson and R. R. Biederman, "Oxidation Reaction Kinetics of Zircaloy-4 in Unlimited Steam Environment," J. Nucl. Mat. 62 (1976) 213-220.
3. S. L. Seiffert and G. R. Smolik, Post Irradiation Examinations Results for the Power-Cooling-Mismatch Test 2A, TREE-NUREG-1029 (February, 1977).
4. S. L. Seiffert, Power Cooling-Mismatch Test Series PCM-2 Post Irradiation Examination, TREE-NUREG-1069 (March 1977).
5. S. Ploger et al., Post Irradiation Examination Results for the Irradiation Effects Test 2, TREE-NUREG-1195 (January 1978).
6. D. W. Croucher et al., Irradiation Effects Test Series Test IE-5 Test Results Report, TREE-NUREG-1130 (January 1978).
7. S. Ploger et al., Post Irradiation Examination Results for the Irradiation Effects Test IE-3, TREE-NUREG-1299 (March 1978).
8. T. F. Cook et al., Post Irradiation Examination Results for the Irradiation Effects Test IE-5, TREE-NUREG-1201 (March 1978).
9. D. Niebrugge, Preliminary Fuel Behavior Analysis for LOFT L2 Test Series, LTR-20-83, to be published.
10. S. C. Chang, Potential Influence of Crossflow and Radiation Heat Transfer on LOFT LOCA Behavior, LTR-1111-53, to be published.
11. R. D. Waddell, Jr. and P. L. Rittenhouse, High-Temperature Burst Strength and Ductility of Zircaloy Tubing, ORNL-TM-3289 (March 1971).
12. C. S. Olsen, Zircaloy Cladding Collapse under Off-Normal Temperature and Pressure Conditions, TREE-NUREG-1239 (April 1978).
13. E. Gebhardt, et al, "Untersuchungen in System Zirkonium-Sauerstoff, Teil 2, "Untersuchungen zur Kinetik der Reaction Zwischen Zirkonium und Sauerstoff, sowie uber die Konstitution des Systems Zirkonium-Sauerstoff", J. Nucl. Mat. 4 (1961) 255.
14. R. L. Beck, "Zirconium-Hydrogen Phase System," Trans ASM 55 (1962), 542.
15. M. L. Picklesimer, "Method of Annealing and Rolling Zirconium Base Alloy", U.S. Patent 2,894,866 (July 14, 1959).

16. D. O. Hobson, The Effect of Thermal Transients on the Hardness of Zircaloy Fuel Cladding, ORNL-NUREG-TM-26 (June 1976).
17. C. S. Olsen, Effects of Irradiation Upon Zircaloy Microstructures and Transformation Temperatures, RE-M-77-010 Fuel and Materials Division, September 30, 1977.
18. H. M. Chung et al., "Mechanical Properties of Zircaloy Containing Oxygen," in Light-Water-Reactor-Safety Research Program Quarterly Progress Report, January-March 1976, ANL-76-49 (1976) p 37.
19. W. M. Rumball, The "Hardenability" of Zr-1.2 wt% Cr-0.1 wt% Fe, AECL 3050 (1968).
20. J. V. Cathcart, et al., Zirconium Metal-Water Oxidation Kinetics-IV Reaction Rate Studies, ORNL-NUREG-17 (August 1977).
21. J. J. Kearns et al., "Effect of Alpha/Beta Phase Constituent on Superplasticity and Strength of Zircaloy-4," J. Nucl. Mat. 61, 169-184 (1976).
22. J. C. Greenbank and S. Harper, "Solute Distribution in Oxidized Zirconium Alloys," Electrochem Tech 4 pg 142 (1966).
23. Private Communication from G. Schanz, Karlsruhe, West Germany to C. S. Olsen, INEL, March 21, 1978.
24. B. Nath et al., "Effect of Hydrogen Concentration and Cooling Rate on Hydride Precipitation in α -Zirconium," J. Nucl. Mat. 58 (1975) pg 153-162.
25. Private Communication from R. Biederman, Worcester Polytechnic Institute, to C. S. Olsen, INEL, March 16, 1978.
26. J. M. Broughton et al., PBF-LOCA Test Series Test LOC-11C Experiment Test Prediction, TFBP-TR-259 (February 1978).
27. Letter from P. E. MacDonald to L. P. Leach, "Transmittal of Revised Costs and Schedule for the PBF/LOFT Lead Rod Test Program," MacD-32-78, February 28, 1978.
28. Private Communication from J. A. Christensen, BNWL, to C. S. Olsen, INEL, April 6, 1978.
29. R. Biederman et al., A Study of Zircaloy-4-Steam Oxidation Reaction Kinetics, EPRI NP-225 (PB 260 693) (September 1976).

30. L. Baker Jr. and L. C. Just, Studies of Metal-Water Reactions at High Temperatures III Experimental and Theoretical Studies of the Zirconium-Water Reactions, ANL-6548 (May 1962).
31. W. A. Bostrom, The High Temperature Oxidation of Zircaloy in Water, WAPD-104 (March 19, 1954).
32. A. W. Lemmon Jr., Studies Relating to the Reaction Between Zirconium and Water at High Temperature, BMI-1154 (January 8, 1957).
33. J. P. Pemsler, "Studies on the Oxygen Gradients in Oxidizing Metals," J. Electro. Chem. Soc. 112 (1965), 477.
34. C. J. Rosa and W. W. Smeltzer, "The Parabolic Oxidation Kinetics of Beta-Zirconium," Acta Met Vol. 13 (1955) 55.
35. Private Communication from Dr. Leistikow during a Zircaloy Oxidation Workshop at a Zircaloy Review Meeting at the INEL, May 18, 1977.
36. R. E. Pawel, et al., Zirconium Metal-Water Oxidation Kinetics V. Oxidation of Zircaloy in High Pressure Steam, ORNL-NUREG-31 (December 1977).
37. R. J. Hussey and W. W. Smeltzer, "The Mechanism of Oxidation of Zirconium in the Temperature Range 400-850°C," J. Electro. Chem. Soc. 111 (1964) 1221.
38. G. R. Wallwork et al., "The Parabolic Oxidation Kinetics of Alpha Zirconium at 850°C," Acta. Met. 12 (1964), 409.
39. M. Leclercq, Contribution a L'Etude du Mecanisme D'Oxydation du Zirconium Pur ou Allie par L'Oxygene et La Vapeur D'Eau, EUR 4507 (1970).
40. S. Malang, SIMTRAN 1 - 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).
41. Z. R. Martinson, Behavior of 5-in. Long, 1/4-inch OD, Zircaloy-2 Clad Oxide Fuel Rods Subjected to High Energy Power Bursts, IN-ITR-107 (August 1969).
42. Private Communication from Dr. V. Urbanic, Chalk River, Canada to C. S. Olsen, INEL, March 6, 1978.
43. Private Communication from R. Herring, Chalk River, Canada to C. S. Olsen, INEL, May 25, 1978.
44. "High Power Zircaloy Clad Heater Rod Test Requirements," Letter from E. L. Tolman to C. W. Solbrig, Tol-2-78, March 31, 1978.

APPENDIX A

Temperature Estimates from Zircaloy Microstructures

INTRODUCTION

The role of zircaloy microstructures in estimating temperatures will be presented with identification of important parameters and the data base that is presently available. First, the transus temperatures and the use of microstructures to deduce the transus temperatures will be presented, second, the zircaloy microstructures for identifying the phases will be discussed, and finally, the discrepancies in the data will be summarized.

1. TRANSUS TEMPERATURES FOR α/β TRANSFORMATION

Zircaloy microstructures have been used to estimate peak cladding temperatures from the presence of alpha or beta phases during thermal transients^(A-1). The alloying elements, tin, iron, chromium, and in zircaloy-2, nickel, expand the instantaneous (diffusionless) alpha/beta transformation in pure zirconium from a single temperature (1135 K) to a temperature range (1103 to 1243 K). These solutes, normally considered to be in solid solution, precipitate during temperature excursions. The formation of three phase regions (α , $\alpha + \beta$, and β) and the distribution of the precipitates form a basis to identify cladding

temperatures from zircaloy microstructures. Also, the microstructure change from cold-worked to annealed cladding can be used to identify a cladding temperature in the high α phase region.

The temperature estimates are derived from the transus temperatures of the zircaloy phase changes^(A-2), once the phases are identified from the zircaloy microstructures. The α to $\alpha + \beta$ transus establishes a temperature of 1103 K^(A-2) and the $\alpha + \beta$ to β transus establishes the temperature of 1243 K^(A-2). For a particular location on the cladding, if the microstructure is identified as β -phase then the cladding temperature would be greater than 1243 K, or if the $\alpha + \beta$ phase were identified, then the cladding temperature would be between 1103 and 1243 K. And if only the α -phase is present, then the cladding temperature would be less than 1103 K. An instantaneous annealing temperature of 866 K occurring in the high α -region but below the α to $\alpha + \beta$ transus is another point to bracket a temperature range in the high α -phase region.

The above transus temperatures are based upon the normal alloy content of zircaloy-2 or -4 (1.5% Sn, 0.1% Cr 0.2% Fe with Fe + Cr = 0.28%). During LOCE conditions, hydrogen and oxygen may dissolve into the cladding. Oxygen is an α -stabilizer and raises the α/α plus β transus temperatures^(A-3) whereas, on the other hand, hydrogen is a β -stabilizer and lowers the α plus β/β transus temperatures^(A-4). If both are simultaneously dissolved and do not interreact with each other, their separate effects will not be compensated. Oxygen and hydrogen contents in conjunction with phase equilibria must be taken into account to assess the transformation temperatures^(A-3, A-4).

2. ZIRCALOY MICROSTRUCTURES

To estimate cladding temperature ranges from microstructures, a correlation between microstructure and the α , $\alpha + \beta$, and β phases are required under LOCE-type conditions. Microstructures obtained under other types of conditions may be different, and consequently incorrect interpretation of the microstructures may arise.

Zircaloy microstructures are characterized by grain size and shape, chemical composition, size and distribution of alloying precipitates, and the chemical composition and distribution of reaction products formed from chemical reaction of zircaloy and surrounding materials. These characteristics will be used to identify the phases and hence the temperature changes.

Microstructures obtained for conditions similar to those during a LOCE for the change from cold worked to annealed cladding and (recrystallization) for the three phase fields, α , $\alpha + \beta$, and β will be presented next. These microstructures typify the catalogue of microstructures presently available.

2.1 CHANGE FROM COLD-WORKED TO RECRYSTALLIZED ZIRCALOY

Because of the rapid heat-up during a LOCE, an instantaneous annealing temperature for a complete change from cold-worked to annealed cladding can be used to estimate cladding temperature rather than the traditional

recrystallization temperature, based upon 50% recrystallization in one hour. The recrystallization of cold-worked LOFT cladding and an instantaneous recrystallization temperature were determined from both hardness measurements and zircaloy microstructures (A-5).

Zircaloy samples were heated from 589 K at about 110 K/sec to the desired temperature, held at temperature for a specified time, and then rapidly cooled to room temperature. To determine the effect of multiple transients, samples were also heated for three successive transients similar to the single-cycle transient, but with the samples reheated after the first two cycles when the temperature dropped below 589 K. The total time at temperature for a particular triple-cycle specimen was equal to the total time at temperature for a corresponding single-cycle specimen.

Hardness measurements performed with a diamond-pyramid indenter with a 1-kg load and metallography were used to determine the annealing temperature. Initially, four midwall readings were taken from each ring, with the impressions spaced every 90° from the thermocouple attachment position. During the measurements, the short-time tests produced specimens with varying hardness in the circumferential direction due to uneven heating rates that created temperature differences around the specimen. Hardness readings for these specimens were repeated and concentrated near the thermocouple position - the position of maximum confidence in temperature.

The results of the hardness measurements demonstrate that significant annealing of the zircaloy tubes can occur in relatively short times at temperatures of 922 K and above. Figure A-1 shows the hardness results as a function of maximum nominal test temperature. The average hardness of the as-received material was measured to be 237 DPH (Diamond Pyramid Hardness). All tests conducted at a 811 K maximum temperature were found to have average hardness only slightly less than the as-received material (230-235 DPH). The 866K maximum-temperature tests clearly showed typical annealing behavior with the shorter test times producing little hardness drop (230-237 DPH) and the longer times producing almost fully softened material (182-192 DPH). Tests cycled to maximum temperatures of 977 and 1033 K were completely softened even after the minimum test times.

As shown in Figure A-1, the annealing behavior of the LOFT cladding subjected to a triple transient at any particular maximum temperature does not correlate with the corresponding single transient with the same time. This behavior resulted probably from the very rapid heat-up and cool-down rates employed in these tests. If slower rates had been used, the integrated time-temperature effect would probably have been more pronounced, and a triple-cycle transient would have resulted in a lower hardness than the equivalent single cycle.

Zircaloy microstructures of LOFT zircaloy tubing at different temperature and time exposures are shown in Figures A-2 to A-5. Figure A-2 is typical of the as-received cladding, and Figure A-3 shows the microstructure after heating at 811 K for 135 seconds. Both microstructures

Fig. A-1 Hardness results for all transient tests.

Fig. A-2 Microstructure of as-received, uncrystallized zircaloy.

Fig. A-3 Microstructure of unrecrystallized zircaloy after heating at 811K for 135 seconds.

Fig. A-4 Microstructure of partially recrystallized zircaloy after heating at 866K for 5 seconds.

Fig. A-5 Microstructure of recrystallized zircaloy after heating at 866K for 15 seconds.

are characteristic of the cold-worked zircaloy with no distinct development of the grain structure.

Figures A-4 and A-5 show the microstructures of samples heated at 866 K for 5 and 15 seconds, respectively. At 5 seconds, the structure is partially annealed. Some fine, equiaxed, recrystallized grains have formed, but some are still unresolved and give a blurry appearance to the structure. In contrast, Figure A-5 indicates a completely recrystallized structure with all the grains clearly developed after a 15 second temperature exposure. At 922 K and for times of 5 and 15 seconds, microstructures similar to those in Figures A-4 and A-5 were obtained respectively so that as far as a microstructural measurement, recrystallization starts at 866 K rather than 922 K as derived from hardness measurements. This temperature may be reduced by longer annealing times than 15 seconds but even for times as long as 135 seconds (the longest time used) at 811 K, no recrystallization took place. For times at temperature expected for LOCE's, 866 K is an appropriate value for the recrystallization temperature.

2.2 ALPHA PHASE MICROSTRUCTURE

Figure A-5 shows the microstructure of a completely recrystallized α -phase heated at 866 K and rapidly cooled. Only a few precipitates are visible. Upon heating to a higher temperature (1072 K for 300 seconds) in the α phase region (Figure A-6)^(A-6), the grain structure remains essentially the same except that the number of precipitates is substantially increased, probably because of the slower cooling rate (< 2 K/s),

Fig. A-6 Microstructure of unirradiated zircaloy heated at 1072K (α -phase) for 300 seconds and slowly cooled.

Fig. A-7 Microstructure of irradiated zircaloy heated at 1072K (α -phase) for 300 seconds and slowly cooled.

rather than the higher temperature. The microstructure shown in Figure A-5 was obtained after rapid cooling at an unspecified rate from 866 K^(A-5). Because of the higher temperature and longer heating time, the grain size shown in Figure A-6 is larger than that shown in Figure A-5.

Figure A-7 shows the microstructure of irradiated zircaloy cladding after being heated to 1072 K and cooled at less than 2 K/s in vacuum. In addition to the intermetallic precipitates, hydrides are also found within the grains. Hydrides may not always precipitate within the grains, but may extend through several grains or be distributed on the grain boundaries^(A-7). The morphology of hydride precipitation has been shown to be effected by cooling rate^(A-7).

The hydrides shown in Figure A-7 formed as a result of a 2-3 year irradiation exposure at operating temperature in the Saxton Reactor^(A-8).

The present LOFT core is BOL (Beginning of Life) and for the planned operating exposure, the cladding may not have the hydrogen distributed as the Saxton cladding has. However hydrogen pick-up from zircaloy/steam reaction could be substantial for the temperatures expected for the LOCE. The hydride may form underneath an oxygen-rich α -zircaloy layer as depicted in Figure A-8^(A-9). The outer layer consisting of coarse, equiaxed, α -zircaloy grains with an inner layer of α -zircaloy grains with copious amounts of the acicular precipitate of zirconium hydride. The effect of hydrogen pick-up during LOCE's upon the zircaloy microstructures can not be precluded from the microstructures.

Fig. A-8 Microstructure of cracked oxygen-rich layer and underlying hydride needles after heated in steam at 948K for 360 hours.

2.3 ALPHA PLUS BETA-PHASE MICROSTRUCTURES

The zircaloy microstructures shown in Figure A-9, show different proportions of β -phase in the two phase α plus β region^(A-10). These microstructures were obtained from zircaloy samples loaded with hydrogen from 700 to 2700 ppm and heated in an inert atmosphere so that different proportions of prior β -phase are formed by quenching from 1005 K. In Figure A-9 α and β , β -phase forms at the α -grain boundaries and isolate the α -grains from other α -grains as the proportion of β -phase increases. Although hydrogen was introduced only to vary the proportions of the β -phase, the hydride has still left its mark on the microstructure through the appearance of platelets within the grains. Also the β -grains in an $\alpha + \beta$ two-phase region may resemble the microstructure shown in Figure A-9c for 100% β -phase with rapid rates of cooling. This microstructure is not apparent in Figure A-9a and b, possibly because of the hydride introduced into the samples.

Figures A-10 and A-11 show two $\alpha + \beta$ microstructures, one unirradiated and heated in vacuum to 1115 K and the other irradiated and heated in vacuum to 1234 K, respectively^(A-6). Both microstructures resulted from slow cooling (< 2 K/sec) from temperature, and are distinctly different than those depicted in Figure A-8. In Figure A-10, the equiaxed grain shape is not significantly different from the α -structure (Figures A-5 to A-7), but the intermetallic precipitates were redistributed from within the grains to the grain boundaries. With faster cooling rates, the amount of precipitation may be about the same magnitude as indicated

(a) 700 ppm H 12% β

(b) 1100 ppm H 47% β

(c) 2700 ppm H 100% β

Fig. A-9 Microstructures of the two phase, α plus β , region for different proportions of β after heating for $1\frac{1}{2}$ hours at 805K.

Fig. A-10 Microstructure of irradiated zircaloy heated at 1115K (α plus β) for 300 seconds and slowly cooled.

Fig. A-11 Microstructure of irradiated zircaloy heated at 1234K (α plus β) for 300 seconds and slowly cooled.

in Figure A-5. With irradiated cladding shown in Figure A-11, the additional hydride precipitates are still associated within the grains rather than at the grain boundaries as with the intermetallic precipitates. Increasing the cooling rate will modify these microstructures, but to what extent is not known.

Upon heating zircaloy samples to temperatures in the two phase, α plus β region in air, the zircaloy microstructure progressively changed for several minutes (A-11). This transition in microstructure was attributed to be a retardation of the α to α plus β transformation. This time effect is not consistent with the instantaneous transformation in pure zirconium, but was speculated by Dr. Hofmann to arise from the slow rate of segregation of alloying elements at the grain boundaries which normally enhances the transformation. Microstructures obtained from samples heated in a vacuum exhibited different microstructure than that obtained in air indicating that if the time effect were real, the presence of oxygen would be important in distinguishing the progress of the alpha to alpha plus beta transformation with time. However, from oxidation tests in the intermediate temperature range, this retardation in the α to α plus β transformation has not been confirmed (A-12) so that these results from Dr. Hofmann apparently reflect the role of the environment upon the zircaloy microstructure. Shanz^(A-12) also noted that zircaloy microstructures are very sensitive to cooling rate in the two phase, α plus β , region. This effect may also be a factor in the anomalous time effect.

2.4 BETA-PHASE MICROSTRUCTURE

The β -phase microstructures are very distinct from either the α or $\alpha + \beta$ phase microstructures so that the β -phase can generally be separated from either the α or $\alpha + \beta$ phases whereas the α and $\alpha + \beta$ phases may not always be separated. Figure A-12 shows the microstructure of cladding heated to 1473 K in steam with an unspecified rapid cooling rate to ambient temperature^(A-13). A very sharp circular (almost basket-weave) structure is formed. With slower cooling rates (< 2 K/s), a platelet type structure is formed (Figure A-13)^(A-6). Biederman^(A-14) has suggested that the zircaloy microstructure is more dependent upon the temperature from which quench is initiated rather than cooling rate. The cooling rate affects the separation between plates. The differences between the microstructures in Figures A-12 and A-13, may be attributed to differences in cooling rate causing different platelet thicknesses. A change in the beta microstructure from a platelet to basket-weave structure was also noted in increasing the cooling rate from 55 K/min. to 180 K/min.^(A-15). Figures A-12 and A-13 represent extremes in the beta microstructures for wide differences in cooling rates. Only the precipitation of intermetallics in the grain boundaries outline the platelet structure, and with more rapid cooling, the platelets may not be distinguished because of less intermetallic precipitation. Figure A-14 illustrates the effects of even faster cooling rates for a 7r-1.2% Cr-0.1% Fe alloy cooled from 1323 K^(A-11). For cooling rates between 20 and 2000 K/s, the Widmanstatten structure is formed, but for cooling rates 2000 K/s and greater, a martensitic structure is formed which has fine, acicular grains which

Fig. A-12 Cross-section of zircaloy-4 tube oxidized in steam at 1473K (β -phase).

Fig. A-13 Microstructure of unirradiated zircaloy heated at 1254K (β -phase) for 300 seconds and slowly cooled.

(a) Cooling rate ≈ 20 K/s

(b) Cooling rate ~ 1000 K/s

(c) Cooling rate ~ 2000 K/s

(d) Cooling rate ~ 4200 K/s

Fig. A-14 Effect of cooling rate on the microstructure of Zr-1 w/o Cr-0.1 w/o Fe alloy cooled from 1323K (β -phase).

are largely unresolvable under the optical microscope. Although this alloy with its high chromium content is atypical of the zircalloy alloy used for LOFT cladding, the microstructures represent the different microstructures for the β -phase. Microstructures of the β -phase would be needed with cooling rates less than 1 K/s to ensure that the β -microstructure can always be identified, if the actual LOCE cooling rates were less than 2 K/s predicted.

Besides the basic microstructure of the beta-phase, another characteristic of the β -microstructure after being heated in steam, is the formation of a layer of oxygen-stabilized α -zirconium (Figure A-12). The dissolution of oxygen in beta zircaloy raises the transus temperatures to sufficiently high value so that α -zirconium is stabilized in a temperature range in which oxygen-free beta zircaloy is normally stable. However, upon cooling to room temperature, the decrease in oxygen solubility causes α -zircaloy to precipitate in the beta phase adjacent to the oxygen stabilized α -layer and a displacement of the stabilized α -layer towards the beta region^(A-17). This two-phase (α plus β) layer cannot be distinguished from β at high temperatures because of the α -phase precipitated in the β -region. However, this precipitation only occurs in a narrow region adjacent to the oxygen-stabilized α -layer. The remaining metal layer should be characteristic of β -zircaloy.

3. SUMMARY

Zircaloy microstructures and the known transus temperatures in principle provide an excellent independent means to bracket cladding temperatures from PIE (Post Irradiation Examination). Although the present data base is not capable to determine exact temperatures within each phase region, this data base does not preclude that new microstructure data can be used to resolve temperatures in the two phase, α plus β , region within ± 30 K^(A-18). Because of the potential benefits, the latter proposition needs to be explored further.

Besides the normal zircaloy alloying elements, tin, iron, chromium, and nickel, oxygen and hydrogen which can be introduced during a LOCE also affect the zircaloy phase transformation and microstructures. Dissolved oxygen tends to stabilize the alpha phase and raises the transus temperature for the alpha to beta transformation, whereas dissolved hydrogen is a beta phase stabilizer and lowers the transus temperatures. The change in transus temperatures arising from the dissolved hydrogen and oxygen must be taken into account when microstructures are used to estimate temperatures.

The platelet or basket-weave microstructure is sufficient to identify the high temperature, single-phase beta-phase and the upper transus temperature, but sufficient β -microstructures for low cooling rates (< 1 K/s) are not available to ensure that the β -phase can always be identified from either platelet or basket-weave structures. Also the

β -phase in the two-phase (α plus β) region cannot always be identified to separate the single α -phase from the two-phase $\alpha + \beta$ region. These two regions cannot be distinguished with slow cooling except by the redistribution of precipitates which is also affected by cooling rate. The β -phase morphology in the two-phase, α plus β , region and the beta-phase region as well as the distribution of precipitates in each region needs to be correlated with cooling rates (for LOCE conditions between 1 and 20 K/s) to adequately characterize zircaloy microstructures in a steam atmosphere.

The transition from cold-worked to annealed zircaloy establishes a temperature in the high α -phase region which can be used to estimate cladding temperatures. The transition temperature determined from microstructures is 866 K, slightly lower than 922 K determined from microhardness measurements.

4. REFERENCES

- A-1. S. L. Seiffert and G. R. Smolik, Post Irradiation Examinations Results for the Power-Cooling-Mismatch Test 2A, TREE-NUREG-1029 (February 1977).
- A-2. M. L. Picklesimer, "Method of Annealing and Rolling Zirconium Base Alloys," U. S. Patent 2,894,866 (July 14, 1959).
- A-3. E. Gebhardt, et al, "Untersuchungen in System Zirkonium-Sauerstoff, Teil 2, "Untersuchungen zur Kinetik der Reaktion Zwischen Zirkonium und Sauerstoff, sowie über die Konstitution des Systems Zirkonium- Sauerstoff," J. Nucl. Mat. 4 (1961) 255.
- A-4. R. L. Beck, "Zirconium-Hydrogen Phase System," Trans ASM 55 (1962), 542.
- A-5. D. O. Hobson, The Effect of Thermal Transients on The Hardness of Zircaloy Fuel Cladding, ORNL-NUREG-TM-26 (June 1976).
- A-6. C. S. Olsen, Effects of Irradiation Upon Zircaloy Microstructures and Transformation Temperatures, RE-M-77-010 Fuel and Materials Division (September 30, 1977).
- A-7. B. Nath et al., "Effect of Hydrogen Concentration and Cooling Rate on Hydride Precipitation in α -Zirconium," J. Nucl Mat. 58 (1975) P153-162.
- A-8. G.W. Gibson et al, Characteristics of UO₂-Zircaloy Fuel Rod Materials from the Saxton Reactor for Use in the Power Burst Facility, ANCR-NUREG-1321 (September 1976).
- A-9. J.C. Greenbank and S. Harper, "Solute Distribution in Oxidized Zirconium Alloys," Electrochem Tech. 4 Pg. 142 (1966).
- A-10. J.J. Kearns et al, "Effect of Alpha/Beta Phase Constituents or Superplasticity and Strength of Zircaloy-4," J. Nucl Mat. 61 169-184 (1976).
- A-11. Private Communication from P. Hofmann, Karlsruhe, West Germany to C.S. Olsen, INEL, August 5, 1977.
- A-12. Private Communication from G. Schanz, Karlsruhe, West Germany to C.S. Olsen, INEL, March 21, 1978.
- A-13. J.V. Cathcart, et al, Zirconium Metal-Water Oxidation Kinetics-IV Reaction Rate Studies, ORNL-NUREG-17 (August 1977).

- A-14 Private Communication from R. Biederman, Worcester Polytechnic Institute to C.S. Olsen, INEL, March 16, 1978.
- A-15 H.M. Chung et al, "Mechanical Properties of Zircaloy Containing Oxygen", in Light-Water-Reactor-Safety Research Program Quarterly Progress Report, January-March 1976, ANL-76-49 (1976) Pg. 37.
- A-16 W.M. Rumball, The "Hardenability" of Zr-1.2 wt% Cr-0.1 wt % Fe, AECL 3050 (1968).
- A-17 A. Sawatzky et al, "Oxidation of Zirconium During a High Temperature Transient," in Zirconium in the Nuclear Industry , ASTM STP 633, American Society for Testing and Materials (1977).
- A-18 Personal Communications from J.A. Christensen, BNWL, to C.S. Olsen, INEL, April 6, 1978.

APPENDIX B

ZIRCALOY OXIDATION

Cladding temperatures can be derived from an oxidation kinetic rate and an oxygen uptake or layer thickness. Oxidation kinetics usually follow an expression of the form:

$$W = k e^{-Q/RT} t^n \quad (B-1)$$

where

W is weight gain or oxide thickness, ect.

k is a constant

Q is the activation energy

R is the gas constant

T is the temperature

t is the exposure time, and

n is a constant dependent upon the rate law ($n = 1/3$ for cubic and $1/2$ for parabolic kinetics).

The values k, Q and n will be known from previous kinetic measurements with well established temperatures and times. The layer thickness, but not the weight gain, W, is measured during PIE after a fuel rod is

removed from the reactor. The time at temperature is a little more nebulous quantity since it may involve a single transient or multiple transients with the same fuel rod.

The general procedure is to use the temperature time profile derived from a thermocouple measurement as a measurement of time at temperature, but the temperature is assumed not to be known. Using the time at temperature and the appropriate oxidation kinetics, a multiplication factor for temperature is determined through iteration until the calculated extent of oxidation agrees with the measured value. As will be shown, the error in time is not significant because of the exponential relationship with temperature.

Temperatures predicted for the LOFT L2 test series are between 600 and 1390K (Section II) for times up to 400 seconds. These temperatures and times are in the range in which oxide thicknesses can be used to derive cladding temperatures^(B-1). Oxidation data for zircaloy were sought for these temperatures and times to derive kinetic rates. For convenience, oxidation data will be categorized according to the temperature ranges: between 973 and 1273K and between 1273 and 1773K. Temperature errors from oxidation rates are presented in Appendix C for each temperature range.

1. TEMPERATURE BETWEEN 1273 AND 1773 K

Cathcart^(B-2) determined the oxidation kinetics of zircaloy between 1273K and 1773K in steam. From metallographic examinations of the oxidized samples, he measured the thicknesses of the oxide, alpha, and oxide plus alpha layers. The total oxygen uptake was evaluated from these thicknesses using a computer program that calculates the oxygen distribution. In these experiments, particular care was taken to obtain very precise temperature measurements at the points where the thickness measurements were made. The layer thicknesses and oxygen uptake followed the parabolic (second order) oxidation kinetics given by Equation (B-2):

$$\frac{dW}{dt} = \delta^2/2W \quad (B-2)$$

where W represents the oxide, alpha, or oxide plus alpha thicknesses or the oxygen uptake. The term $\delta^2/2$ represents the parabolic reaction rate constant which is given respectively for oxide, alpha, oxide plus alpha layers and oxygen pickup by the next four equations:

$$\frac{\delta_{\phi}^2}{2} = .01126 \left[\begin{smallmatrix} +30\% \\ -23\% \end{smallmatrix} \right] \exp(-35890[+2.2\%]/RT) \text{ cm}^2/\text{s} \quad (B-3)$$

$$\frac{\delta_{\alpha}^2}{2} = .7615 \left[\begin{smallmatrix} +54\% \\ -35\% \end{smallmatrix} \right] \exp(-48140[+2.6\%]/RT) \text{ cm}^2/\text{s} \quad (B-4)$$

$$\frac{\delta_{\xi}^2}{2} = .3412 \left[\begin{smallmatrix} +17\% \\ -15\% \end{smallmatrix} \right] \exp(-41700[\pm 1.2\%]/RT) \text{ cm}^2/\text{s} \quad (\text{B-5})$$

$$\frac{\delta_{\tau}^2}{2} = .1811 \left[\begin{smallmatrix} +20\% \\ -16\% \end{smallmatrix} \right] \exp(-39940[\pm 1.4\%]/RT) (\text{g/cm}^2)^2/\text{s} \quad (\text{B-6})$$

The quantities in the brackets refer to the individual 90% confidence limits on the pre-exponential and activation energy terms.

These equations were derived from data obtained in the temperature range from 1273 to 1773K which followed the parabolic kinetics. To be shown, oxidation data below 1273K do not follow parabolic kinetics. Therefore, Equations (B-3) to (B-6) should never be extrapolated to temperatures below 1273K.

Biederman et al^(B-3) has also measured oxidation kinetics between 1255 and 1755K in atmospheric steam, and used metallography as the principal tool to determine reaction layer thicknesses. For the thickness of the oxide and oxygen-stabilized alpha layer, the following expression was obtained by Biederman^(B-3):

$$\frac{\delta_{\epsilon}^2}{2} = 0.02244 \exp(-33,620/RT) \quad (\text{B-7})$$

and for total oxygen uptake:

$$\frac{\delta^2}{2} = 0.01907 \exp(-33,370/RT) (\text{mg/cm}^2)^2 / \text{sec} \quad (\text{B-8})$$

Biederman's Equations result in oxidation rates about a factor 2 less than that of Cathcart's at 1773K.

There is some question as to the accuracy of the temperature measurements during Biederman's experiments and because of the discrepancy between Biederman and Cathcart, who had better temperature control, Cathcart's data appears to be better.

During transient heating for a double-peak blowdown temperature-time curve, oxidation during the first peak was found to reduce the amount of oxidation during subsequent heating during reflood^(B-3). Similar behavior was found by Cathcart^(B-2). For example, one sample was heated first to a maximum temperature of 1323K, then cooled to 923K, and then reheated to a second peak temperature of 1323K. For this transient, the observed oxide thickness was 12.2 μm compared with a calculated value of 25.2 μm , a discrepancy of 107%. The monoclinic to tetragonal phase transformation in the zirconium dioxide was thought to be the cause for this discrepancy.

The anomalous oxidation behavior was observed for temperatures less than 1473K, the temperature range expected for the LOFT L2 transients. Although these measurements were derived from a double-peak LOCE transient, the results would be applicable to multiple transients. The 100% reduction in oxidation is tantamount to a systematic 100% error in oxide thickness.

and would result in a lower temperature of 120K for an initial peak of 1323K followed by a second peak of 1323K for 210 second duration. Transient oxidation data is not available for initial peak temperatures less than 1323K, a temperature much higher than that expected for L2-2. Whether this anomolous oxidation behavior occurs for low initial temperatures is not known. Multiple oxidation transients simulating the power ascension series would verify any anomolous behavior during the L2 power ascension series.

Baker-Just^(B-4) had one data point, took data from Bostrom^(B-5) and Lemmon^(B-6) and derived the following equation from this data at the zircaloy melting point:

$$W^2 = 3.36 \times 10^7 e^{-45,500/RT_t} \quad (B-9)$$

where

W is the weight of zirconium reacted (g/cm^2), and other terms have been defined above.

The data base for this correlation is based on the reaction of molten zircaloy with steam, and results in oxidation rates about a factor 2 higher than that from Cathcart's equations. Oxidation extents determined from hydrogen release from SPERT tests with molten zircaloy agree within $\pm 10\%$ of values predicted from the Baker-Just Equation. The data base for the Baker-Just equation and the agreement of the equation with the SPERT data show that this equation is only applicable for molten zircaloy and has not been proved at low temperatures.

2. OXIDATION BETWEEN 973 AND 1273 K

Leistikow^(B-7) measured the oxygen absorption at atmospheric pressure and Pawel^(B-8) determined the oxidation kinetics at higher pressures from 973 to 1273K. The time exponents derived from this data are listed in Table B-I for different steam pressures. The exponents for Leistikow's data vary from 0.32 to 0.35 (3-values) and between 0.38 and 0.39 (three values) and at the highest temperature employed, the time exponent was 0.45. For temperatures at 1229K and lower and pressures between atmospheric and 6.90 MPa, the time exponents indicate that the zircaloy oxidation kinetics are cubic. A change to parabolic kinetics was indicated at 10.34 MPa and 1178K. The kinetics change from cubic to parabolic between 1229 and 1273K. This temperature range also includes the α plus β to β -zircaloy phase transition (1243K). Because of the similarity between the transition in oxidation kinetics and the zircaloy phase transition, the transition from cubic to parabolic kinetics is assumed to occur at 1243K.

The oxidation rates obtained at atmospheric pressure were fit to a cubic law (third order) by least squares regression techniques (Equation (B-10)):

$$W = 2.8832 \left[\begin{smallmatrix} +23\% \\ -19\% \end{smallmatrix} \right] \exp\left(\frac{-21,722(+1.1\%)}{RT}\right) t^{1/3} \quad (B-10)$$

TABLE B-I

EXPONENTS ON TIME DERIVED FROM LEISTIKOW^(B-7)
AND ORNL DATA^(B-8)

<u>Temperature (K)</u>	<u>Pressure (MPa)</u>	<u>Exponent</u>	<u>Reference</u>
973	0.1	0.343	B-7
1023	0.1	0.391	B-7
1073	0.1	0.316	B-7
1123	0.1	0.382	B-7
1173	0.1	0.353	B-7
1178	0.1	0.295	B-8
1178	3.45	0.365	B-8
1178	6.90	0.356	B-8
1178	10.34	0.545	B-8
1223	0.1	0.399	B-7
1229	0.1	0.309	B-8
1273	0.1	0.446	B-7
1278	0.1	0.461	B-7

where

W is weight gain mg/cm^2

R is 1.987 cal/mole-K, and

t is time in seconds.

The errors listed with Equation (B-10) are 1-sigma values.

The correlation for intermediate temperatures was based primarily upon data from Karlsruhe, West Germany, except for only three data points from Oak Ridge National Laboratory. This data base is tantamount to a single source, and is subject to systematic errors as observed with the high temperature Biederman (B-3) and Baker-Just data (B-4 to B-6). Data from different sources are required to evaluate systematic errors. Gravimetric tests are tentatively planned to begin in May or June, 1978 at Chalk River, Canada (B-9), to examine the effect of oxidation upon the α -zircaloy to β -zircaloy phase transition. Oxide thickness measurements are planned and can establish a correlation based upon reaction layers which is required for PIE. Evaluation of the systematic errors is thickness measurements can be performed through comparison's of weight gain measurements of the Karlsruhe data and this data, but both sets of data will not be sufficient for this evaluation.

Equation (B-10) was derived solely from oxygen uptake data and is not directly applicable to PIE results which do not measure the oxide dissolved into the base metal (B-10, B-11). The use of Equation (B-10)

with appropriate assumptions as to oxide densities, dissolved oxygen etc. results in systematic errors not properly accounted for during PIE. An equation similar to high-temperature Equations (B-3) or (B-5) based upon oxide or oxide plus oxygen-stabilized alpha layers will be required for the LOFT PIE.

Other oxidation data have been reported in this temperature range^(B-11 to B-15), with subatmospheric oxygen or steam. Under these conditions, the reaction kinetics were parabolic rather than cubic, but because of the extremely low pressures not representative of LOFT, these kinetic measurements are not applicable and will not be considered here.

3. SUMMARY

The rate constants for parabolic and cubic reactions are summarized in Figure B-1 for the high and intermediate temperatures, respectively. A psuedo-parabolic reaction rate is also shown for the intermediate temperatures for comparison with ORNL high temperature parabolic rate and the Leistikow and ORNL cubic rates. The one parabolic value at 10.34 MPa and 1178K is shown to be much higher than the corresponding value extrapolated to 1178K with the ORNL high temperature equation. This difference must be due to an accelerated reaction rate by high pressure steam at the low temperature. The cubic rate is applicable for steam pressures between 0.1 and 6.9 MPa.

The oxidation kinetics may be conveniently divided into two temperature regimes corresponding to the zircaloy phase regions: An intermediate temperature range in which α or α plus β phases exist and the high temperature range in which only β -phase exists. The appropriate oxidation equations will be selected from the temperature range determined from the zircaloy microstructure. The high temperature kinetics result in a random temperature error between ± 38 and ± 69 K for 95% confidence level and the intermediate temperature kinetics result in an accuracy not quite as good, between ± 57 and ± 81 K (Appendix C) with most of the error associated with the rate equation. Measurements of the oxidation kinetics in the intermediate temperature range need to be improved to reduce the uncertainty and to insure no systematic error exists, and particularly

Fig. B-1 Summary of oxidation kinetics for high and intermediate temperatures.

measurements of the reaction layers (in conjunction with the weight gain measurements) need to be made for LOFT PIE.

For multiple transients, a systematic error may occur from heating, cooling and then reheating, but further multiple oxidation transients are required to evaluate possible anomolous behavior during the LOFT L2 power ascension test series. This anomolous behavior needs to be evaluated for temperatures below 1270K for the intermediate temperature kinetics and between 1270K and 1390K for the high temperature oxidation kinetics.

4. REFERENCES

- B-1 D. A. Niebrugge, Fuel Behavior Predictions for LOFT L2 Test Series, to be published (December 1977).
- B-2 J. V. Cathcart, et al, Zirconium Metal-Water Oxidation Kinetics-IV Reaction Rate Studies, ORNL-NUREG-17 (August 1977).
- B-3 R. Biederman et al., A Study of Zircaloy-4-Steam Oxidation Reaction Kinetics, EPRI NP-225 (PB 260 693) (September 1976).
- B-4 L. Baker Jr. and L. C. Just, Studies of Metal-Water Reactions at High Temperatures III Experimental and Theoretical Studies of the Zirconium-Water Reactions, ANL-6548 (May 1962).
- B-5 W. A. Bostrom, The High Temperature Oxidation of Zircaloy in Water, WAPD-104 (March 19, 1954).
- B-6 A. W. Lemmon Jr., Studies Relating to the Reaction between Zirconium and Water at High Temperature, BMI-1154 (January 8, 1957).
- B-7 Private Communication from Dr. Leistikow during a Zircaloy Oxidation Workshop at a Zircaloy Review Meeting at the INEL, May 18, 1977.
- B-8 R. E. Pawel, et al, Zirconium Metal-Water Oxidation Kinetics V. Oxidation of Zircaloy in High Pressure Steam, ORNL-NUREG-31 (December 1977).
- B-9 Private communication from V. Urbanic, Chalk River, Canada, to C. S. Olsen, INEL, March 1978.
- B-10 Private communication from R. Herring, Chalk River, to C. S. Olsen, INEL, May 25, 1978.
- B-11 R. J. Hussey and W. W. Smeltzer, "The Mechanism of Oxidation of Zirconium in the Temperature Range 400-850°C", J. Electro. Chem. Soc. 111 (1964) 1221.
- B-12 G. R. Wallwork et al, "The Parabolic Oxidation Kinetics of Alpha-Zirconium at 850°C", Acta. Met. 12 (1964), 409.
- B-13 J. P. Pemsler, "Studies on the Oxygen Gradients in Oxidizing Metals", J. Electro. Chem. Soc. 112 (1965), 477.
- B-14 C. J. Rosa and W. W. Smeltzer, "The Parabolic Oxidation Kinetics of Beta-Zirconium", Acta Met 13 (1955) 55.
- B-15 M. Leclercq, Contribution a L'Etude du Mecanism D'Oxydation du Zirconium Par ou Allie par L'Oxygene et La Vapeur D'Eau, EUR 4507 (1970).

APPENDIX C

ANALYSIS OF TEMPERATURE ERRORS
FROM OXIDATION KINETICS

Linear error propagation techniques were used to evaluate the errors in temperatures derived from measurements of oxide thickness, time at temperature, and an analytical expression for the oxidation kinetics. The basic procedure is to perturbate each parameter and calculate the change in temperature for each parametric perturbation. The overall error in temperature is determined from the following equation:

$$\Delta T = \sum_{i=1}^n \left(\frac{\partial T}{\partial P_i} \right)^2 \sigma_i^2 \quad (C-1)$$

w

where

n is the number of parameters,

σ_i is the standard deviation in the i^{th} parameter

∂T is the change in temperature

∂P_i is the perturbation in the i^{th} parameter.

The relative contribution from each parameter is determined from the following equation:

$$CON_i = \frac{\left(\frac{\partial T}{\partial P_i}\right)^2 \sigma_i^2}{\sum_{i=1}^n \left(\frac{\partial T}{\partial P_i}\right)^2 \sigma_i^2} \quad (C-2)$$

where

CON_i is the contribution from the i^{th} parameter and other terms are defined above.

1. ERRORS FROM HIGH TEMPERATURE KINETICS

Equations (C-3) and (C-4) from Cathcart were used to evaluate errors in isothermal temperature estimates from measurements of thickness measurements of the oxide plus alpha layer and oxygen uptake using linear error propagation techniques. The errors in Equations (C-3) and (C-4) were reduced to 1-sigma values and the error (1-sigma) in the oxide plus alpha layer thickness or oxygen uptake was assumed to be 10%, and the error in the time at temperature was assumed to be $\pm 5\%$ (1-sigma). With linear error propagation, the relative contribution from each parameter to the total error was also determined.

$$x^2 = .3412 \left[\begin{smallmatrix} +17\% \\ -15\% \end{smallmatrix} \right] \exp (41700[\pm 1.2\%]/RT) t \quad (C-3)$$

$$w^2 = .1811 \left[\begin{smallmatrix} +20\% \\ -16\% \end{smallmatrix} \right] \exp (39940[\pm 1.4\%]/RT)t \quad (C-4)$$

where

T is the temperature (K)

R is 1.987 (cal/mole-K),

X is the thickness of the oxide plus alpha layer (cm), and

W is the total oxygen weight gain (g/cm²)

The quantities in the brackets refer to the individual 90% confidence limits on the pre-exponential and activation energy terms.

The results of these calculations are summarized in Tables C-I and C-II for Equations (C-3) and (C-4), respectively. For either Equation (C-3) or (C-4), the error (based upon 1-sigma) varies from about 20K at 1273K to about 40K at 1773K. The percentage error does not vary as much as the absolute error and has an average of 1.75% for Equation (C-3) and an average of 1.91% for Equation (C-4). Assuming a 95% confidence level for the error in cladding temperature, Equation (C-3) results in a error of ± 38 K at 1273 K and an error of ± 69 K at 1773 K, and Equation (C-4) results in a error of ± 41 K at 1273 K and ± 75 K at 1773 K. For PIE of LOFT fuel rods, since oxide plus alpha layer thicknesses will be measured, the applicable random error is between ± 38 and ± 69 K for temperatures above 1273K.

The relative error from the parameters show that errors in time are not significant and the errors in thickness measurement are about the same as that from the combined errors of energy term and pre-exponential constant. The last two terms were determined about as close as one can

TABLE C-I

TEMPERATURE ERRORS AND RELATIVE CONTRIBUTION FOR
OXIDE PLUS ALPHA THICKNESSES (EQUATION (C-3))

Temperature (K)	Error (1-sigma) Deg.K	Percent	Relative Contribution (Fraction)			
			Energy	Pre-Exponential Constant	Time	Thickness
1273	19.3	1.52	.2320	.1343	.0379	.5959
1373	22.1	1.61	.2059	.1385	.0391	.6164
1473	25.1	1.70	.1837	.1420	.0402	.6341
1573	28.3	1.80	.1647	.1450	.0410	.6449
1673	31.7	1.89	.1483	.1474	.0418	.6626
1773	35.0	1.97	.1341	.1495	.0424	.6741

TABLE C-II

TEMPERATURE ERRORS AND RELATIVE CONTRIBUTION FOR
TOTAL OXYGEN ABSORPTION (EQUATION (C-4))

<u>Temperature (K)</u>	<u>Error (1-sigma) Deg. K Percent</u>		<u>Relative Contribution (Fraction)</u>			
			<u>Energy</u>	<u>Pre-Exponential Component</u>	<u>Time</u>	<u>Thickness</u>
1273	21.1	1.66	.2619	.1622	0.0344	.5414
1373	24.2	1.76	.2336	.1680	0.0357	.5628
1473	27.4	1.86	.2092	.1729	0.0368	.5812
1573	30.8	1.96	.1881	.1770	0.0377	.5972
1673	34.5	2.06	.1699	.1805	0.0385	.6112
1773	38.4	2.17	.1540	.1834	0.0391	.6235

measure kinetic data so that the only feasible improvement is the measurement of the layer thickness. The 10% error assumed here probably represents a value expected with the use of photomicrographs. This error should be examined more closely to see whether the technique can be improved, and the error reduced.

2. ERRORS FROM INTERMEDIATE TEMPERATURE KINETICS

The temperature errors from Equation (C-5) were evaluated using the 1-sigma errors listed in Equation (C-5) and assuming a 10% error in weight gain measurements and a 5% error in time. The results of these calculations are summarized in Table C-III. The estimated errors in temperature using weight gain measurements vary from $\pm 29.3\text{K}$ (2.86%) at 1023K to $\pm 41.1\text{K}$ (3.36%) at 1223K. The average percentage error is 3.1%, about 1-1/2 times greater than the error using similar techniques at high temperature. The corresponding 95% confidence level is $\pm 57\text{ K}$ at 1023 K and $\pm 81\text{ K}$ at 1223 K. Between 89 and 90% of the temperature error originates with the uncertainties in the constants in Equation (C-5) compared with about 40% using the high temperature Equation (C-4).

$$W = 2.8832 \left[\begin{smallmatrix} +23\% \\ -19\% \end{smallmatrix} \right] \exp\left(\frac{21,722(+1.1\%)}{RT}\right) t^{1/3} \quad (\text{C-5})$$

where

W is weight gain (mg/cm^2)

T is the temperature (K),

R is 1,987 (cal/mole-K).

TABLE C-III

TEMPERATURE ERRORS AND RELATIVE CONTRIBUTION FOR
OXYGEN ABSORPTION AT INTERMEDIATE TEMPERATURES
(EQUATION (C-5))

<u>Temperature (K)</u>	<u>Error (1-sigma) Deg. K Percent</u>		<u>Relative Contribution (Fraction)</u>			
			<u>Energy</u>	<u>Pre-Exponential Constant</u>	<u>Time</u>	<u>Thickness</u>
1023	29.3	2.86	0.1458	0.7512	0.0026	.1005
1073	32.0	2.98	0.1340	0.7618	0.0026	.1016
1123	34.9	3.11	0.1235	0.7713	0.0027	.1026
1173	37.8	3.22	0.1142	0.7797	0.0027	.1035
1223	41.1	3.36	0.1058	0.7873	0.0027	.1042

The data obtained in this intermediate temperature range are comprised solely of oxygen uptake except for the limited ORNL data⁽¹³⁾. Pawel⁽¹³⁾ did measure the oxide and alpha layer thicknesses, but the number of values is not sufficient to derive an analytical equation with its uncertainties. Since in PIE examinations the temperature estimates will be derived only from measurements of layer thicknesses and not from total oxygen absorption, kinetic equations based upon layer thicknesses are needed in addition to the total oxygen absorption. Errors in temperature estimates from correlations derived from reaction layers will also have to be evaluated.

3. SUMMARY

The temperature errors resulting from the high temperature oxidations kinetics of Cathcart and the measurement of the thickness of oxide plus oxygen-stabilized alpha-layer results in a random error between 38 and 69 K based upon a 95% confidence level. Most of the error is attributed to the measurement of the reaction layers. The Cathcart equation needs no further improvement and offers the best representation for deducing temperatures from measurements of reaction layers. The only improvement that may be required is in the measurement of thicknesses.

However, for intermediate temperatures between 973 and 1273K, the oxidation kinetics are not quite as good as the high temperature oxidation kinetics. The uncertainty in the temperature estimates are between ± 57

and 81 K with most of the error involving the constants in the equation for the reaction kinetics. Although additional data is needed to improve the uncertainties in the constants, this new data should be obtained for measurements of oxide and oxygen-stabilized alpha layer thicknesses and errors in temperature estimates re-evaluated for the correlations derived from reaction layers.