8. PHYSICO-CHEMICAL STUDIES OF CLAD UO_2 IN POTENTIAL MELTDOWN ENVIRONMENTS

(1175)

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The objective of this program is to study the behavior of zirconium-alloy-clad UO_2 fuel elements in steam and steam plus air from 1000°C to the melting point of UO_2 . This includes measurement, when necessary, of physical and mechanical properties of the cladding, the oxidized cladding, and UO_2 to their respective melting points.

During the period covered by this report, CY-67, the properties of stainless steel cladding material were also investigated. Since recent reactor designs have employed Zircaloy-4 exclusively for all claddings, spacers, and coolant channels, the effort on stainless steel property measurements is being phased out of the program.

The behavior of zirconium-alloy-clad and stainless-steel-clad UO_2 fuel elements during temperature excursions to the melted condition in the presence of steam or steam plus air has not been studied sufficiently to permit suitable hazard analyses when loss of coolant occurs. This program is being conducted to investigate the reactions that occur during meltdown in these atmospheres at heating rates which approximate those likely to be encountered in nuclear afterheat temperature excursions when the coolant has been lost. These investigations include the following studies:

1. Dynamic testing to determine the behavior of clad UO_2 when oxidized by steam, reactions between the various reactor core components, internal pressure effects, hydrogen release by the metal - steam reactions, and flow aspects of the molten constituents.
2. Measurements of the rates of metal - steam reactions, oxidation of UO_2 by steam, and reactions between core constituents.
3. Property measurements, including thermal properties of UO_2 , Zircaloy-4, and Type 304 stainless steel, and the mechanical properties of Zircaloy-4 and Type 304 stainless steel.

8.1 DYNAMIC TESTING OF ZIRCONIUM-BASE ALLOYS (K. M. Emmerich and E. F. Juenke)

INTERNAL PRESSURE EFFECTS

The effects of internal gas pressure and temperature on the deformation behavior of Zircaloy-4 cladding material during a thermal surge were investigated using the pressure test facility shown schematically in Figure 8.1. Figure 8.2c shows a typical tube sample prepared for testing. The composition and characterization of the Zircaloy-4 material used in these experiments meet LOFT specifications reported previously.¹ Details of the experimental procedure have been reported.²

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¹"Fifth Annual Report - High-Temperature Materials Program, Part A," GE-NMPO, GEMP-400A, February 28, 1966, p. 205.

²"AEC Fuels and Materials Development Program Progress Report No. 71," GE-NMPO, GEMP-1002, December 29, 1967, p. 123.

Fig. 8.1 — Schematic diagram of pressure test circuit

Fig. 8.2 — Typical pressure-test samples of Zircaloy-4 before and after testing at 1.11 kg/mm^2 . Sample length is 5.7 cm. (Neg. P67-11-1)
 a. Heated at 0.3°C per second to 668°C .
 b. Heated at 20°C per second to 753°C .
 c. Unheated.

In this series of tests, heating rates of 20°C and 0.3°C per second and internal helium pressures from 0.024 to 1.21 kg/mm^2 were used. The tubes were heated at a constant rate under fixed pressure in an argon atmosphere until 34 percent diametral expansion occurred, approximately the expansion which would result in major blockage of coolant channels in a typical reactor. Results for this series of tests are given in Table 8.1 which lists final internal pressure, surface (maximum) temperature when the sample had expanded 34 percent diametrically, tensile strength of the material at the maximum temperature, and calculated effective stress. Two typical samples tested at the same internal pressure ($\sim 1.11 \text{ kg/mm}^2$) are compared with an untested sample in Figure 8.2. The 34 percent diametral expansion was

reached at 668°C for sample A, heated at 0.3°C per second; and at 753°C for sample B, heated at 20°C per second.

Tensile tests at various constant-load levels were conducted on Zircaloy-4 for comparison with the internal pressure tests. In these experiments, sheet specimens cut parallel to the rolling direction were heated from room temperature to rupture temperature at rates of approximately 0.3°, 3°, and 20°C per second. Data are presented in Table 8.2.

In both the pressurized-tube tests and the constant-load tensile tests, the temperature attained at failure (34% expansion in the case of the pressurized tubes or rupture of the tensile specimens) showed heating rate dependence. At fixed pressures or load levels, higher maximum temperatures were obtained for the higher heating rates in all instances.

TABLE 8.1
EFFECTS OF INTERNAL PRESSURE ON ZIRCALOY-4 TUBING HEATED IN ARGON

Heating Rate, °C/sec	Internal Pressure (Gage), kg/mm ²	Maximum Temperature, °C	Calculated Effective Stress, ^a kg/mm ²	Tensile Strength, at Maximum Temperature, kg/mm ²
0.3	1.125	666	8.114	6.9
0.3	1.118	668	8.065	6.9
0.3	0.721	723	5.205	4.6
0.3	0.541	758	3.901	3.7
0.3	0.214	860	1.550	1.8
0.3	0.144	915	1.040	1.4
0.3	0.065	924	0.469	1.2
0.3	0.065	933	0.469	1.15
0.3	0.074	953	0.534	1.0
0.3	0.037	1020	0.267	0.68
0.3	0.036	1027	0.260	0.68
0.3	0.025	1187	0.181	0.38
23.1	1.209	737	8.727	4.0
22.8	1.055	753	7.615	3.8
20.9	0.703	820	5.074	2.5
22.0	0.352	881	2.541	1.6
21.9	0.352	886	2.541	1.6
20.4	0.141	955	1.031	0.99
21.5	0.141	1003	1.013	0.74
22.3	0.141	1024	1.013	0.68
22.6	0.037	1165	0.263	0.39
20.1	0.037	1282	0.266	0.29

^aBased on pre-test tube dimensions.

TABLE 8.2
CONSTANT LOAD CONTROLLED HEATING-RATE TEST
RESULTS FOR ZIRCALOY-4^a IN ARGON

Sample No.	Heating Rate, °C/sec	Initial Stress, kg/mm ²	Rupture Temperature, °C	Elongation, %	DPH Hardness (2-1/2 kg)	
					Before Test	After Test
22	0.3	1.195	945	68	209	245
18	3.0	6.327	765	48	220	215
19	3.0	12.654	665	28	225	206
17	3.0	3.164	900	54	224	218
15	3.0	1.195	1020	81	198	223.5
16	3.0	0.504	1120	102	221	206
21	20.0	1.195	1120	69	227	218
23	20.0	0.504	1235	102	215	200

^aSpecimens were 0.076 cm thick, 0.63 cm wide, with a gage length of 2.54 cm.

Data obtained in the two series of tests were analyzed to determine the inter-relationship of applied stress, rate of uniform heating, total strain, and maximum temperature. This was accomplished by examining the theoretical solutions for a uniaxial test under constant load and a linearly increasing temperature, and a test of a thin-walled tube with constant internal pressure and linearly increasing temperature under the following assumptions:

1. Deformations are primarily those due to second-stage creep.
2. Second-stage creep behavior can be represented by an equation of the form

$$\frac{d\epsilon}{dt} = A e^{-Q/RT} \sigma^n \quad (8.1)$$

where

ϵ = strain
 t = time
 T = absolute temperature
 R = gas constant
 Q = activation energy for creep
 σ = effective stress *
 A and n = material parameters.

3. Deformations are small.
4. For the case of the tube, the radial stress is negligible, i. e., $\sigma_r \cong 0$.

Under these assumptions, and letting $T = \beta t$, the governing equations are: for the uniaxial case,

$$d\epsilon_x = A e^{-Q/R\beta t} \sigma^n dt \quad (8.2)$$

and for the tube case,

$$d\epsilon_\theta = \frac{\sqrt{3}}{2} A e^{-Q/R\beta t} \sigma_e^n dt \quad (8.3)$$

where

$\sigma_e = \sqrt{3} \frac{P\rho}{h}$
 p = pressure
 ρ = inside radius
 h = wall thickness
 ϵ_θ = hoop (tangential) strain
 ϵ_x = axial strain

Letting $Q/RT = z$ and integrating these equations [(8.2) and (8.3)], gives the general result

$$\epsilon = \frac{a S^n Q}{\beta R} \left[-\frac{e^{-z}}{z} - \{-\text{Ei}(-z)\} \right]_{z=z_1}^{z=\infty} \quad (8.4)$$

where, for the uniaxial case and the tube case, $a = A$ and $\sqrt{3}/2 A$, $S = \sigma$ and σ_e , and $\epsilon = \epsilon_x$ and ϵ_θ , respectively.

*Based on the von Mises flow criterion, the effective stress for the multi-axial (tube) case is

$$\sigma_e = \frac{1}{\sqrt{2}} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]^{0.5},$$

where $\sigma_1, \sigma_2, \sigma_3$ are the principal stresses which, for the case of the tubes, are the radial (σ_r), hoop (σ_θ), and axial (σ_x) stresses.

The exponential integral function may be approximated for $z_1 > 10$ by

$$-Ei(-z) = e^{-z_1} \left\{ \frac{1}{z_1} - \frac{1}{z_1^2} + \frac{2!}{z_1^3} - \frac{3!}{z_1^4} + \dots \right\} \quad (8.5)$$

Since Q is the order of 40 T_m cal/mole, z_1 will always be much greater than 10. Therefore, neglecting all but the first two terms of the expansion, equation (8.4) becomes:

$$\epsilon \cong \frac{a S^n R T^2}{\beta Q} e^{-Q/RT} \quad (8.6)$$

Taking the logarithms of both sides and rearranging terms gives:

$$\ln S = \frac{1}{n} \left[\ln \epsilon - \log \frac{aR}{Q} + \ln \beta - 2 \ln T + \frac{Q}{RT} \right] \quad (8.7)$$

The exponent n for stress dependence and the activation energy Q are essentially constant for temperatures above about one half the absolute melting point (788°C for Zircaloy-4).

Logarithmic (true) strain, $\ln(1 + \epsilon)$, is more valid in this case than engineering strain because the expansion cannot be considered small. Accordingly, the combined data in Tables 8.1 and 8.2 for temperatures above 788°C were fitted to an equation of the form of (8.6), giving the final equation with a standard deviation of ± 40 percent:

$$S = 0.0113 k \exp \left(\frac{78,470 \pm 8900}{3.96 RT} \right) \left(\frac{r \epsilon_\ell}{T^2} \right)^{1/3.96} \quad (8.8)$$

where $k = 1$ for tensile tests and $(\sqrt{3}/2)^{1/3.96}$ for pressurized tube tests, and

S = stress, kg/mm²
 R = gas constant, 1.987 cal/mole-°K
 T = temperature, °K
 r = heating rate, °K/sec
 ϵ_ℓ = logarithmic strain = $\ln(1 + \epsilon)$.

The logarithm of stress versus $1/T$ for this equation is shown in Figures 8.3 and 8.4 for the several heating rates used in the tests described above. Experimental data for all temperatures are also plotted on these figures. A stress dependence (exponent n) of 3.96 and an activation energy (Q) of 78.5 kcal/mole for creep in Zircaloy-4 are indicated by this analysis. The value of n agrees well with the expected value of 4.0,³ and the value of the activation energy agrees with the estimated value of 81 kcal/mole for zirconium self-diffusion, using the approximation $Q = 38T_m$, where T_m is the melting point in °K.⁴

This analysis does not consider the effect of the α - β zirconium phase transformation which may occur in the temperature range of 900° to 1000°C in Zircaloy-4. Tensile data appear to show a difference in behavior above and below this range, but separate analyses of the two temperature regions are of dubious validity, due to the limited number of data points. The pressurized tube experiments showed no difference in behavior in the two temperature regions.

EFFECT OF OXIDATION ON TUBE DEFORMATION

The effects of oxidation on the deformation behavior of Zircaloy-4 tubing were studied under dynamic heating conditions. Initial tests were made with 0.3°C/sec heating rates and at various internal pressures of 0.040 to 0.141 kg/mm² to study the effect of steam

³J. M. Dorn, editor, The Mechanical Behavior of Materials at Elevated Temperatures, McGraw-Hill, 1961, p. 95.

⁴Ibid., p. 88.

Fig. 8.3 – Stress versus temperature for constant load tensile tests in argon

Fig. 8.4 – Effective stress versus temperature for constant pressure tube tests in argon + 3 vol % H₂

atmosphere. Results of these measurements are shown in Table 8.3 with the results of comparison tests in argon. These data show that in a steam atmosphere failure of partially oxidized Zircaloy-4 tubes due to internal pressure will occur at temperatures higher than predicted from the base metal strength data. Typical fracture failure for a tube heated in steam is compared in Figure 8.5 to a sample heated in argon.

TABLE 8.3
EFFECTS OF INTERNAL PRESSURE ON ZIRCALOY-4
TUBING HEATED AT 0.3°C PER SECOND

Atmosphere	Internal Gage Pressure, kg/mm ²	Maximum Temperature, °C	Diametral Expansion, %
Argon	0.040	1180	33
Steam	0.040	1475	12.5 ^a
Argon	0.057	1055	34
Steam	0.058	1460	11.4 ^a
Argon	0.078	970	34
Steam	0.077	1035	18.6 ^a
Argon	0.141	905	34
Steam	0.141	905	33

^aFailed by fracture.

Fig. 8.5 — Effect of atmosphere on the failure of Zircaloy-4 tubes heated at 0.3°C/sec with 0.040 kg/mm² internal pressure (Neg. 68-1-42)

The effects of atmosphere on the expansion rate of Zircaloy-4 tubes at constant temperature and constant internal pressure were studied in argon and in steam by measuring the rate of diametral expansion with a cathetometer. Test temperatures selected for a given pressure were about 50°C below the maximum temperature achieved in the argon atmosphere dynamic heating tests at 0.3°C per second. Two comparisons have been made between the behavior of Zircaloy-4 in argon and in steam. At 0.131 kg/mm^2 (195 psig), a Zircaloy-4 tube heated at 860°C required 260 minutes for 34 percent expansion in steam, but only 74 minutes in argon. At 995°C and 0.051 kg/mm^2 (72 psig), 34 percent expansion required 106 minutes in steam, compared to 20 minutes in argon. Figure 8.6 shows the post-test appearance of these latter two samples.

These tests show that (1) under the dynamic conditions of a thermal surge, oxidation permits the Zircaloy cladding to achieve higher temperatures before failure, and (2) at constant temperature and pressure, the rate of expansion is retarded by oxygen absorption in the Zircaloy. Figure 8.6 shows that the presence of steam results in a more uniform expansion of the tube. Steam oxidation, like strain hardening, results in more uniform expansion.

a. Heated in argon required 20 minutes for 34% expansion (Neg. P68-1-34A)

b. Heated in steam required 106 minutes for 34% expansion (Neg. P68-1-34B)

Fig. 8.6 — Zircaloy-4 tubes heated at 995°C with an internal pressure of 0.051 kg/mm^2

TESTING OF 50-cm-LONG ZIRCALOY-4-CLAD UO_2 FUEL ELEMENTS

A furnace capable of heating a 50-cm-long Zircaloy-4-clad UO_2 sample in steam was constructed for simulating the axial thermal gradient imposed upon a fuel element in a reactor loss-of-coolant accident. This equipment is being used to determine whether there are corrosion rate effects in Zircaloy-4 cladding due to a hydrogen boundary layer buildup, and to establish effects of internal pressure, conditions under which cladding rupture occurs with loss of internal pressure, and behavior under meltdown. Figure 8.7 is a schematic drawing of the furnace; construction and operation details were reported previously.⁵ Figure 8.8 shows a typical 50-cm-long Zircaloy-4-clad UO_2 sample assembled for test.

Fig. 8.7 — Schematic diagram of furnace for simulating reactor thermal and atmospheric environment during a loss-of-coolant accident

⁵"AEC Fuels and Materials Development Program Progress Report No. 69," GE-NMPO, GEMP-69, September 30, 1967, p. 139.

Fig. 8.8 — Typical 50-cm-long Zircaloy-4-clad UO_2 sample assembled for test (Neg. P67-7-24B)

Oxidation tests were run to study thickness of the oxide layers formed on 50-cm-long Zircaloy-4-clad UO_2 samples heated at rates of 0.3°C and 1.0°C per second in steam flowing at the rate of 3.4 standard liters (6×10^{-3} lb) per minute. The oxide thickness at the midpoint of the sample and at 7.6 cm from each end were determined metallographically and are summarized in Table 8.4. Circumferentially the thickness varied less than 50 percent. Longitudinally the oxide thickness at the midpoint, the hottest portion of the specimen, was from 1.5 to 2.5 times the thickness at the ends of the tube. For these tests, no difference was observed between the oxide thicknesses at the two ends. Consequently, assuming laminar flow under the test conditions, there was no evidence of a hydrogen-rich boundary layer at the metal - gas interface.

TABLE 8.4
VARIATION OF OXIDE THICKNESS ON 50-cm-LONG
ZIRCALOY-4-CLAD UO_2 ELEMENTS HEATED IN STEAM

Heating Rate, $^\circ\text{C}/\text{sec}$	Maximum Temperature, $^\circ\text{C}$			Oxide Thickness, microns ^a		
	Top	Middle	Bottom	Top ^b	Middle	Bottom
0.3	786	900	776	<13	13	<13
0.3	934	1098	922	19	32	16
0.3	c	1313	1222	25	86	60
0.3	c	1500	1430	117	200	102
1.0	c	1100	923	13	19	13
1.0	c	1300	1170	32	70	28
1.0	c	1510	1475	66	140	91
1.0	c	1510	1300	73	133	60

^aAverage of four circumferential measurements.

^bSteam entered furnace from the top.

^cTop thermocouple failed before maximum temperature was attained.

DYNAMIC TESTING OF IRRADIATED ZIRCALOY-2 AT CONSTANT INTERNAL PRESSURE

A test fixture for pressure testing irradiated Zircaloy-2 tubing at various heating rates is being constructed. Test pieces will be Zircaloy-2 and fuel rod cladding tubes from the spent fuel of an industrial reactor from which UO_2 has been removed. Tubes will be cleaned and cut to 8-inch lengths. The material is highly radioactive and must be handled remotely; equipment is being designed with the simplified assembly and disassembly features shown in Figure 8.9. The Zircaloy tube will be pressurized with helium from a line attached to the bottom of the fixture. The top and bottom of the tube will be made pressure tight with O-ring seals. The thermocouple will be attached in the form of a loop which is drawn against the sample by a constant weight. This permits about 1 cm of the thermocouple wire from the bead to contact the tubing, thus minimizing errors in temperature measurement arising from thermal losses due to heat transmission along the wires.

8.2 REACTION MECHANISMS AND KINETICS (J. T. Bittel and L. H. Sjodahl)

OXIDATION OF ZIRCONIUM ALLOYS BY STEAM OR AIR

Effects of the variation of steam flow rate and oxygen partial pressure on the oxidation kinetics of zirconium alloys were determined to 1585°C . Studies of Zircaloy-4 in steam were also extended to 1835°C .

Steam Oxidation

A thermogravimetric technique⁶ was used to determine the oxidation kinetics of Zircaloy-4 in steam at various flow rates. Parabolic rate constants determined from these tests are

⁶R. E. Latta, J. T. Bittel, and G. B. Hadesty, "Continuous Recording Strain Gauge Thermobalance," Rev. of Sci. Instr., Vol. 38, No. 11, November 1967, p. 1667.

Fig. 8.9 — Furnace assembly for internal pressure tests on irradiated Zircaloy-2 tubing

shown in Table 8.5 and plotted as log rate versus reciprocal temperature in Figure 8.10, along with the curve determined previously for steam oxidation of zirconium alloys.⁷ Results of the steam tests at various flow rates agree with previously reported corrosion data using lower flow rates; this indicates that the steam oxidation rate of Zircaloy-4 is independent of the steam flow rate in the range examined.

Although zirconium would not be expected to hydride appreciably at the temperatures of the steam corrosion tests, Lemmon⁸ reported that part of the hydrogen which formed as a result of the $\text{Zr-H}_2\text{O}$ reaction was found in tested Zircaloy-2 samples; 12.5 percent of the hydrogen formed in a 1600°C test and 6.8 percent in a 1000°C test. Hence hydrogen content of Zircaloy-4 samples tested in steam at 1200°C and at 1600°C was determined by hot extraction analysis. Two samples tested at 1200°C showed 40 and 332 ppm; the 1600°C test sample showed 98 ppm. The highest concentration of hydrogen found, 332 ppm or 1.3 percent of the hydrogen produced, is equivalent to less than 0.5-mg weight gain in this sample. This would have an insignificant effect (0.16%) on the total weight gain. The greater amounts of hydrogen reported by Lemmon may result from his testing in steam at a total pressure of 50 psi (0.035 kg/mm²) or from the fact that Zircaloy-2 absorbs hydrogen more readily than Zircaloy-4.

Tests on the steam oxidation of Zircaloy-4 were extended to 1835°C using solid cylindrical samples in an inductively heated furnace. Experimental details have been reported previously.⁹ A spectrographic analysis of the Zircaloy used in the present tests is given in Table 8.6.

⁷"Sixth Annual Report — High-Temperature Materials Program, Part A," GE-NMPO, GEMP-475A, March 31, 1967, pp. 240–245.

⁸A. W. Lemmon, "Studies Relating to the Reaction Between Zirconium and Water at High Temperatures," BMI-1154, 1957.

⁹GEMP-1002, p. 134.

Fig. 8.10 — Oxidation of zirconium alloys by steam and air

TABLE 8.5
RESULTS OF STEAM AND AIR CORROSION
OF ZIRCONIUM ALLOYS

Sample Material	Gas Composition	Gas Flow Rate, std. ml/min.	Temperature, °C	Parabolic Rate Constant, $(\text{mg O}_2)^2 / \text{cm}^4 \cdot \text{sec}$
Zr-4	Steam	300	1200	0.63
Zr-4	Steam	800	1500	5.96
Zr-4	Steam	2400	1500	8.3
Zr-4	Air ^a	300	1200	2.99
Zr-2	Air ^a	300	1200	3.17
Zr-2	Air ^a	300	1400	9.87
Zr-4	Air ^a	300	1500	12.2
Zr-4	Air ^a	300	1585	29.5
Zr ^b	O ₂	—	1100	0.158
Zr ^b	O ₂	—	1200	0.415
Zr ^b	O ₂	—	1290	0.800

^aDewpoint — 66°C.^bPemsler, gas flow rate unknown.

Test results from the steam oxidation of Zircaloy-4 in this high-temperature range are shown in Table 8.7 and Figure 8.11. Although these results fall nearly within the 95 percent confidence limits calculated from the lower-temperature data,¹⁰ they are about 36 to 70 percent higher than the extrapolated low-temperature Arrhenius curve. This indicates a possible change in controlling mechanism to one with higher activation energy for these higher temperatures. Fitting the $\ln W^2/t$ for the four data points above 1600°C, the previously measured data at 1600°C and 1615°C,¹⁰ and the datum point of Baker¹¹ for 1852°C to a linear equation by least squares, yields:

$$W^2/t = 1.5 \times 10^8 \exp \left(\frac{-60,600 \pm 5,400}{RT} \right) \quad (8.9)$$

where

W = weight gain per unit area, mg/cm^2

t = time, sec

R = gas constant, $\text{cal}/\text{mole} \cdot ^\circ\text{K}$

T = temperature, $^\circ\text{K}$

This can be compared to the expression derived for the least-squares fit to the data for temperatures between 1000° and 1600°C¹⁰:

$$W^2/t = 5.56 \times 10^5 \exp \left(\frac{-39,700 \pm 2300}{RT} \right) \quad (8.10)$$

TABLE 8.6

COMPOSITION OF ZIRCALOY-4^a
USED IN OXIDATION STUDIES

Element	Analysis	
	percent	ppm
Sn	1.45	-
Fe	0.186	-
Cr	0.108	-
Fe+Cr+Ni	0.294	-
Al	-	67.0
B	-	0.3
C	-	186.0
Cd	-	< 0.25
Co	-	< 5.0
Cu	-	< 20.0
Hf	-	60.0
Mg	-	< 10.0
Mn	-	< 20.0
Mo	-	< 20.0
Na	-	< 10.0
Ni	-	< 20.0
Pb	-	< 20.0
Si	-	31.0
Ti	-	20.0
V	-	< 20.0
W	-	< 20.0
U	-	< 0.2
Zr	-	Bal

^aIngot analysis provided by vendor.

TABLE 8.7

RESULTS OF STEAM CORROSION OF ZIRCALOY-4
BETWEEN 1500° and 1800°C

Temperature, °C	Time, min	Weight Gain, g	Area, cm ²	Parabolic Rate Constant
				(Kp), (mg O) ² /cm ⁴ -sec
1540	12	0.9827	11.09	10.9
1700	10	1.3687	10.83	26.6
1733	10	1.8820	11.19	47.2
1742	10	1.9041	10.92	50.0
1800	10	1.9437	10.77	54.3

¹⁰GEMP-475A, pp. 240-242.

¹¹L. Baker and L. C. Just, "Studies of Metal-Water Reactions at High Temperatures, III. Experimental and Theoretical Studies of the Zirconium-Water Reaction," ANL-6548, p. 1962.

Fig. 8.11 — Parabolic rate constant versus reciprocal temperature for oxidation of Zircaloy-4 by steam.

The oxidation of zirconium and Zircaloy proceeds by a combination of oxygen solution in the metal and growth of an oxide coating. Debuigne, et al.,¹² from investigation of zirconium in oxygen, concluded that diffusion of oxygen in the alpha metal was the rate-controlling step in the temperature range from 668° to 1200°C and that the process is parabolic but has exponents slightly greater than 2. Oxidation rates calculated from his data using an exponent of 2 agree with those of Pemsler¹³ for zirconium heated in oxygen. Although the crystal structure of the oxide films on zirconium are monoclinic at room temperature, the work of Ruh and Garrett on the system Zr-O¹⁴ predicts that the crystal

¹²J. Debuigne, J. P. Guerlet, and P. Lehr, "Aspects Fundementaux des Phenomenes D'oxydation du Zirconium sous Oxygene Pur," Etude Sur La Corrosion et la Protection Du Zirconium et de Ses Alliages, Presses Universitaires de France, Paris, 1966.

¹³J. P. Pemsler, "Studies on the Oxygen Gradients in Oxidizing Metals, V. The Oxidation of Oxygen Saturated Zirconium," J. Electrochem. Soc., 1966, pp. 1241-1244.

¹⁴R. Ruh and H. J. Garrett, "Nonstoichiometry of ZrO₂ and Its Relation to Tetragonal-Cubic Inversion in ZrO₂," J. Am. Ceram. Soc., Vol. 50, No. 5, May 1967, p. 257.

structure is tetragonal above about 1100°C and that it is cubic at temperatures as low as about 1500°C. Klepfer¹⁵ has suggested that since oxygen may diffuse at different rates through the different oxide crystallographic forms, the activation energies for the oxidation process may be different also. If so, the higher rates measured in this present work may be related to the change in crystallographic structures of the oxide film.

Air Oxidation

Corrosion tests in dry (-66°C dewpoint) air flowing at 300 std ml/min were conducted with Zircaloy-4 at 1200°, 1500°, and 1585°C and, for comparison, with Zircaloy-2 at 1200°C and 1400°C. Results of these tests are given in Tables 8.5 and 8.10. Also given, for comparison, are data on steam corrosion at 1200°C and 1500°C, and Pemsler's data on oxygen oxidation of unalloyed zirconium at 1100°, 1200°, and 1290°C. These data show that Zircaloy corrosion in air is more erratic and two to five times as rapid as in steam.

Figure 8.12 shows the microstructure of Zircaloy-4 corroded in air at 1200°C. A sample corroded in steam at the same temperature is shown in Figure 8.13. The coating on the air-tested sample varied greatly in thickness and density around the periphery of a cross section. Figure 8.12a and b show, respectively, the relatively thin, dense reacted layer and the thicker, more porous reacted layer which contains up to 10 percent crescent-shaped separations or large voids. Below the dense areas of coating on the air-tested samples is an oxygen-rich alpha zirconium zone similar to that seen in steam corrosion. Below the more porous oxide is a porous yellow phase identified by X-ray diffraction as zirconium nitride. The oxygen-stabilized alpha-phase metal layer beneath the yellow phase is very thin compared to that observed in the microstructure of steam-oxidized metal. Table 8.8 records measurements of the total sample diameter and of thicknesses of the coating and of the oxygen-stabilized, alpha-phase metal formed at 1200°C in both atmospheres.

TABLE 8.8
ZIRCALOY-4 OXIDIZED FOR 1 HOUR AT 1200°C
IN AIR AND IN STEAM

Atmosphere	Coating Thickness, microns	Alpha-Phase Metal Thickness, microns	Original Diameter, mm	Post-Test Diameter, mm
Air	356 to 1016	0 to 200	12.6	13.0
Steam	200	180	12.6	12.8

The higher rates for air corrosion relative to steam oxidation apparently result from the formation of zirconium nitride and its effect on the coating structure. Nelson¹⁶ reports that zirconium reacts more rapidly with air than with oxygen, producing a mixture of the nitride, oxide, and oxynitride of zirconium. Since Pemsler's results¹⁷ for zirconium in oxygen show even lower rates than those reported here for steam, the higher corrosion rates in air do not result from higher oxygen partial pressure in air, but rather from the presence of nitrogen.

¹⁵H. H. Klepfer, private communication.

¹⁶L. S. Nelson, "Combustion of Zirconium Droplets Ignited by Flash Heating," Western States Section, Combustion Institute, Paper WSS/CI 64-23, 1964.

¹⁷Pemsler, loc. cit.

Reaction layer
(ZrO_2)

α zone

Zr-4
metal

a. Dense area of reaction layer (Neg. 9029)

ZrO_2

Zr nitride
and ZrO_2

Zr-4
metal

b. Porous reaction layer (Neg. 8889)

Fig. 8.12 — Photomicrographs of Zircaloy-4 tested at 1200°C for 1 hour in air (As-polished, 100X)

Fig. 8.13 — Photomicrograph of Zircaloy-4 tested at 1200°C for 1 hour in steam (Neg. 8890, as-polished, 100X)

OXIDATION OF TYPE 304 STAINLESS STEEL IN STEAM OR AIR

Steam Oxidation

In the previous annual report,¹⁸ results of studies of the oxidation kinetics of Type 304 stainless steel in steam at temperatures between 1000° and 1350°C were presented. Scales which formed at 1200°C and above remained in place upon cooling although they cracked; those formed at lower temperatures tended to spall when cooled. The microstructure of the oxidized surface formed at the higher temperatures showed a multi-layer coating. The scales, formed on the surface of 304L stainless steel samples oxidized in steam at 1200°C and 1300°C, have been studied by microprobe analysis.

These microprobe analyses previously discussed¹⁹ in detail are summarized in Table 8.9. Both samples contain high-chromium oxide inner layers of a spinel structure, as revealed by X-ray diffraction analysis. Similar high concentrations of chromium as Fe-Cr spinel in the inner oxide layer have been observed by Fujii and Meussner²⁰ in studies of the oxidation of Fe-Cr alloys in argon plus steam at temperatures between 700° and 1100°C.

Previous studies of steam corrosion kinetics of 304 stainless steel at temperatures between 1000° and 1375°C showed that an initial linear oxidation rate (for 6 to 28 minutes) preceded the parabolic behavior.²¹ The parabolic rate was represented by the equation

$$W^2/t = 2.4 \times 10^{12} \exp \left(\frac{-84,300 \pm 2400}{RT} \right) \quad (8.11)$$

¹⁸GEMP-475A, pp. 246–251.

¹⁹GEMP-69, pp. 144–147.

²⁰C. T. Fujii and R. A. Meussner, "High Temperature Oxidation of Iron-Chromium Binary Alloys in Water Vapor, Part 1," U.S. Naval Research Laboratory, NRL Report 5506, September 21, 1960.

²¹GEMP-475A, p. 246.

TABLE 8.9
DESCRIPTION OF OXIDE LAYERS FORMED ON STAINLESS STEEL
DURING OXIDATION IN STEAM AT 1200°C AND 1300°C

Temperature, °C	Oxide Layer	Electron Probe Analyses, ^a wt %			Metallography of Oxide
		Fe	Cr	Ni	
1200	Outer Oxide	75	—	2	Two phases with large grains and large voids.
	Inner: Oxide	45	27	4	Small grains and voids
	Metal	47	10	43	plus metal.
1300	Outer: Oxide	77	—	— ^b	Two phases, large oxide grains,
	Metal	30	—	77 ^c	large voids, metallic inclusions.
	Inner: Oxide	47	22	7	Two phases, small grains and
	Metal	40	5	60 ^c	voids, metallic particle.

^aAverage values for weight percent metal at center of oxide layers.

^bApproximately 2% Mn concentrated near surface of oxide layer.

^cAlthough corrected for absorption and fluorescence, the calculated compositions totaled more than 100% in the metal phase. This does not affect the conclusions drawn in the text.

Recent analysis of the linear portion of the data yields a least-squares fit given by the equation

$$W/t = 1.1 \times 10^5 \exp \left(\frac{-44,350 \pm 2300}{RT} \right). \quad (8.12)$$

The linear rates for steam oxidation are plotted in Figure 8.14. The results of Higgins²² for steam oxidation of Type 321 stainless steel at 1260°C are included for comparison.

Air Oxidation

To compare the behavior of 304L stainless steel in air with its oxidation in steam, tests were run in flowing dry air (-66°C dewpoint) between 1100° and 1375°C using the thermogravimetric technique. Although weight gains in air at 1360°C and below were too small to accurately determine rate behavior, parabolic behavior is assumed because the low rates imply protective film formation. Parabolic rate constants, calculated for comparison with the parabolic and linear portions of the steam oxidation of 304L stainless steel, are included in Table 8.10.

The logarithms of parabolic rate constants in air are plotted in Figure 8.15 together with those for steam oxidation. The rate in air is less than that in steam by a factor of about 10³. Oxidation behavior of 304 stainless steel in air including the point at 1100°C may be represented by Hagel's²³ curve for chromium oxidation in air, which is included in Figure 8.15. Data of Caplan and Cohen²⁴ for 302 stainless steel in dry air, which show good agreement with the data of Hagel²³ for chromium, are also included in Figure 8.15. Oxidation rates determined by Hagel²³ and by Gulbransen²⁵ for chromium in oxygen are shown in this figure; they differ only slightly from the rates in air.

Tests of 304L stainless steel at 1375°C in air show oxidation rates comparable to those for steam at this temperature, much higher than the rates in air between 1100° and 1360°C.

²²H. M. Higgins, "A Study of the Reaction of Metals and Water," AECD-3664, April 15, 1955.

²³W. G. Hagel, "Factors Controlling the High Temperature Oxidation of Chromium," ASTM Trans., Vol. 56, 1960, p. 583.

²⁴D. Caplan and M. Cohen, "High Temperature Oxidation of Chromium-Nickel Steels," Corrosion, Vol. 15, 1959, p. 141t.

²⁵E. A. Gulbransen and K. F. Andrew, "Kinetics of the Oxidation of Chromium," J. Electrochem. Soc., Vol. 104, 1957, p. 334.

Fig. 8.14 — Linear rate constant versus temperature for steam oxidation of Type 304 stainless steel

TABLE 8.10

RESULTS OF OXIDATION OF 304L SS FROM 1000° TO 1375°C IN STEAM AND IN AIR^a

Atmosphere	Temperature, °C	Rate Constants ^b	
		Linear, mg/cm ² ·sec	Parabolic, mg ² /cm ⁴ ·sec
Steam	1000	0.0030	0.0095
	1050	0.0039	0.030
	1100	0.0087	0.095
	1150	0.016	0.18
	1150	0.017	—
	1200	0.033	0.75
	1200	0.034	0.80
	1250	0.038	2.1
	1300	—	4.4
	1350	0.11	13
	1375	Not observed	17
Air	1100	—	0.00025
	1200	—	0.00005
	1225	—	0.00012
	1350	—	0.0074
	1360	—	0.0079
	1375	—	21
	1375	—	25

^aDry air (−66°C dewpoint).

^bFor tests in steam, there was a change from linear to parabolic behavior after times ranging from 6 to 28 minutes.

The increased rate reflects the presence of a liquid phase, consistent with a temperature above the Fe-FeO solidus.²⁶ A sample after testing at this temperature is shown in Figure 8.16, where it is compared with an unoxidized sample and a sample oxidized at 1360°C in air. The scale formed at 1360°C is thin and uniform compared to that at 1375°C which is much thicker, very irregular, and shows evidence of melting. X-ray diffraction revealed the composition of the scale surface formed in air at 1360°C and below to be principally Fe₃O₄, with a minor amount of Fe₂O₃. The surface of the scale formed at 1375°C was Fe₃O₄. When the poorly adherent outer layer was removed from a sample tested at 1332°C,* however, a green oxide layer was exposed which was identified by X-ray diffraction as rhombohedral Cr₂O₃ with less than 20 percent Fe₂O₃.

Electron microprobe analysis of the sample oxidized in air at 1375°C showed a distribution of the iron, nickel, and chromium in both oxide and metallic phases which was very similar to that observed in the sample oxidized in steam at 1300°C. A sample oxidized at 1310°C in air, however, showed a very high chromium concentration (48%) and only 8 percent iron in the oxide layer attached to the metal substrate. This is consistent with the presence of a protective layer of Cr₂O₃ and agrees with the data of Yearian.²⁷

Scales formed in air at 1360°C and below generally spalled when the samples were cooled and removed from the furnace; this effect was not so noticeable on samples run in steam above 1200°C.

*These samples were not used in weight gain analysis because much of the oxide layer was lost by spallation.

²⁶L. S. Darkin and R. W. Gurry, "The System Iron - Oxygen, II: Equilibrium and Thermodynamics of Liquid Oxide and Other Phases," J. Am. Chem. Soc., Vol. 68, 1946, pp. 799-816.

²⁷H. J. Yearian, H. E. Boren, Jr., and R. E. Warr, "Structure of Oxide Scales on Nickel-Chromium Steels," Corrosion, Vol. 12, 1956, p. 561t.

Fig. 8.15 — Parabolic rate constant versus temperature for steam and air oxidation of Type 304L stainless steel

Fig. 8.16 — 304L stainless steel samples oxidized in air

A sample of mild steel was heated in air for 1 hour at 1280°C for comparison with the 304L stainless steel behavior. The parabolic rate constant was $1.26 \text{ mg}^2/\text{cm}^4\text{-sec}$ compared to about $0.001 \text{ mg}^2/\text{cm}^4\text{-sec}$ for 304L stainless steel under the same conditions.

The unusually low oxidation rate of stainless steel in air compared to that in steam at 1360°C and below is due to formation of a protective Cr_2O_3 layer which forms in air but not in steam. Seybolt²⁸ has shown that at 1300°C the oxide of an 0.8Fe – 0.2Cr alloy is rhombohedral $(\text{Cr, Fe})_2\text{O}_3$ only at oxygen partial pressures above 0.05 atmosphere, whereas spinel forms below 0.01 atmosphere. Since oxygen pressures in steam vary from about 2×10^{-4} to 8.8×10^{-6} atmospheres in the temperature range employed, the Fe-Cr spinel layer observed in the steam oxidation of 304L stainless steel is consistent with the results of Seybolt.²⁸ An increase of chromium in the oxide of alloys which have up to 0.85Cr, 0.15Fe, approximately the composition observed in the oxide formed on 304L stainless steel by air below 1360°C, stabilizes the rhombohedral phase down to 10^{-4} atmospheres oxygen, accounting for the Cr_2O_3 layer in the air-oxidized samples. Possibly because of reactions of Cr_2O_3 with liquid Fe-FeO, no Cr_2O_3 was observed at 1375°C in air, and protection was no greater than that in steam.

OXIDATION OF UO_2 BY STEAM

Oxidation Kinetics

The steam oxidation of UO_2 was investigated in the temperature range from 885° to 1835°C. Data for the range from 1100° to 1500°C were presented previously.²⁹ Recent oxidation studies at 885°C and 1000°C were conducted using the thermobalance apparatus described earlier.³⁰ Investigations from 1600° to 1835°C were carried out in an induction-heated furnace with a dense Al_2O_3 muffle to prevent oxidation of the molybdenum susceptor. Test specimens of $\text{UO}_{2.002}$ or $\text{UO}_{2.004}$ were right circular cylinders sintered to about 95 percent of theoretical density at 1700°C. The spectrographic analysis of a typical sample is given in Table 8.11. Sample dimensions were varied with oxidation temperature to compensate for the variation in oxidation rates. Details of the experimental procedures were given in earlier reports.^{31,32}

Exact dimensions of each sample, experimental data, calculated rate constants, and calculated oxygen diffusion coefficients for all UO_2 steam oxidation tests are listed in Table 8.12. The parabolic rate constants are plotted in Figure 8.17. The least-squares equation for these rates is:

$$w^2/t = 8.4 \times 10^4 \exp\left(\frac{-48,000 \pm 1900}{RT}\right) \quad (8.13)$$

Experiments using UO_2 of 98 percent theoretical density were run at 1390°C and 1520°C for comparison with the results of the tests using 95-percent-dense material. Data and results of these tests are included in Table 8.12 and Figure 8.17. The good agreement between these data and the data from 95-percent-dense samples is predictable using the data of Belle,³³ which show no open porosity in UO_2 for densities greater than 91 percent.

²⁸A. U. Seybolt, "Observations on the Fe-Cr-O System," J. Electrochem. Soc., Vol. 107, 1960, p. 147.

²⁹GEMP-475A, pp. 251–256.

³⁰Latta, Bittel, and Hadesty, loc. cit.

³¹"High-Temperature Materials Program Progress Report No. 63," GE-NMPO, GEMP-63, December 30, 1966, p. 120.

³²GEMP-1002, pp. 130–131.

³³J. Belle, "Uranium Dioxide: Properties and Nuclear Applications," Naval Reactors, Div. of Reactor Development, USAEC, 1961, p. 333.

TABLE 8.11

CHEMICAL ANALYSIS^a OF UO₂ USED
IN STEAM OXIDATION STUDIES

Element	ppm
C	68.5
N	65
S	40
F	1.5
P	6
Ag	<5
Al	<20
B	<0.2
Cd	<0.2
Co	<9
Cr	<10
Cu	<10
Fe	27
Mg	<10
Mn	<10
Mo	<10
Ni	17.5
Pb	<10
Si	11
Sn	<10
Ti	<10
Ca	<10
W	<10
O/U	2.002 ± 0.003

^aAverage of duplicate analyses

TABLE 8.12

RESULTS OF UO₂ OXIDATION BY STEAM

Temperature, °C	Test Time, sec	Sample Diameter, cm	Sample Height, cm	Original Weight, g	Weight Gain, g	Final Average O/U Ratio	Theoretical Equilibrium O/U Ratio	Parabolic Rate, mg ² /cm ⁴ -sec	Oxygen Diffusion Coefficient, cm ² /sec
1835	600	3.091	1.905	148.5231	0.6141	2.090 ^a	2.158	0.892 ^a	1.16 × 10 ^{-4a}
1795	600	3.089	1.911	148.9234	0.6828	2.074	2.162	0.691	8.10 × 10 ⁻⁵
1720	600	3.096	0.949	74.3928	0.4079	2.095	2.165	0.470	5.30 × 10 ⁻⁵
1715	600	3.086	1.921	148.9461	0.4703	2.055	2.166	0.327	3.20 × 10 ⁻⁵
1625	1200	3.109	0.948	74.3039	0.4001	2.093	2.170	0.223	2.37 × 10 ⁻⁵
1610	1200	3.086	1.908	148.6701	0.6365	2.074	2.171	0.302	3.00 × 10 ⁻⁵
1600	1800	3.084	1.903	148.5232	0.8587	2.100	2.171	0.368	4.21 × 10 ⁻⁵
1520 ^b	1200	2.731	0.8585	53.9598	0.2127	2.071	2.176	0.104	8.68 × 10 ⁻⁶
1500	1140	1.250	1.283	16.4467	0.0876	2.094	2.177	0.12	1.28 × 10 ⁻⁵
1500	2400	1.255	1.267	16.2287	0.1009	2.109	2.177	0.076	8.86 × 10 ⁻⁶
1500	4560	1.255	1.273	16.1417	0.1226	2.132	2.177	0.059	8.33 × 10 ⁻⁶
1410	3600	3.096	1.904	148.9666	0.6357	2.074	2.183	0.100	8.48 × 10 ⁻⁶
1400	5700	1.254	1.256	16.0962	0.1206	2.131	2.183	0.046	5.71 × 10 ⁻⁶
1400	6900	1.254	1.275	16.3291	0.1029	2.110	2.183	0.027	2.91 × 10 ⁻⁶
1390 ^b	2400	2.695	1.084	67.9490	0.2064	2.053	2.184	0.042	2.81 × 10 ⁻⁶
1200	7020	1.396	1.310	20.6454	0.0649	2.057	2.198	0.0077	5.23 × 10 ⁻⁷
1200	10800	1.403	1.272	20.5758	0.0735	2.064	2.198	0.0066	4.48 × 10 ⁻⁷
1100	10500	1.288	1.265	16.9978	0.0331	2.037	2.207	0.00175	1.02 × 10 ⁻⁷
1100	10860	1.263	1.275	16.5417	0.0187	2.023	2.207	0.00056	3.10 × 10 ⁻⁸
1000	24480	1.256	0.2525	15.0666 ^c	0.410	2.050	2.243 ^d	0.00023	1.04 × 10 ⁻⁸
885	17400	1.400	0.1259	9.8528 ^c	0.0210	2.039	2.262 ^d	0.00012	2.58 × 10 ⁻⁹

^aSome loss of UO₂ occurred in this test; consequently, the parabolic rate and oxygen diffusion are based on post-test chemical analysis. All others are based on weight gain.^bHigh-density sample, 98% theoretical density. All other samples approximately 95% theoretical density.^cThese two samples consisted of five pieces each.^dCalculated by equation of Aronson and Belle; others by equation of Anthony et al.

in equilibrium with steam at 1400°C. The entire sample of this test had a final average O/U ratio of 2.074 calculated from the weight gain.

Portions of this sample taken from the center and from the surface regions were analyzed chemically and O/U ratios of 2.072 in the interior and 2.084 toward the exterior were obtained, consistent with X-ray and weight gain analyses.

The O/U ratio for various portions of a sample heated 10 minutes at 1715°C showed 2.007 in the interior and 2.075 on the surface by X-ray analyses, and an overall average of 2.055 from the weight gain data; the O/U at equilibrium for this temperature is 2.166. Some redistribution of oxygen in the surface layer of the test sample occurs during the cooling cycle, but the discrepancy between the surface O/U and the equilibrium O/U value appears somewhat larger than can be explained on this basis.

Overall results indicate that the oxidation is primarily controlled by diffusion of oxygen, but the difference between the equilibrium O/U ratios and that measured for the exterior indicates that the surface reaction rate may be low enough to affect the results. If so, the true diffusion coefficients may be slightly higher than the values reported below.

Oxygen diffusion coefficients were calculated from the weight gain of the UO_2 tested in steam assuming a bulk diffusion mechanism and using the following equation derived by Jain³⁴ for right circular cylinders:

$$\bar{v} = 1 - \left[1 - 4 \left(\frac{\tau_H}{\pi} \right)^{1/2} \right] \left[1 - 4 \left(\frac{\tau_\rho}{\pi} \right)^{1/2} + \tau_\rho \right] \quad (8.14)$$

where

$\bar{v}$ = fractional completion of the oxidation

$\tau_x = Dt/x^2$

D = diffusion coefficient, cm/sec²

x = radius (ρ) or height (H), cm

t = time, seconds

Values of τ were obtained using $\bar{v}$ calculated from the weight gain and the UO_{2+x} composition in equilibrium with steam at test temperature. The latter was calculated from basic thermodynamic data and appropriate relationships between UO_{2+x} composition and equilibrium oxygen partial pressure. Data of Anthony, et al.,³⁵ were used for temperatures of 1100°C and above, and those of Aronson and Belle³⁶ were used for the lower temperatures.

Figure 8.18 shows the results of these calculations plotted as $\log D$ versus $10^4/T$. The least-squares equation for the curve fitted to those data and previously reported data³⁷ for the temperature range 1100° to 1600°C yields the following for the diffusion coefficient in cm²/sec.

$$D_{\text{chem}} = 151 \exp \left(\frac{-58,000 \pm 2000}{RT} \right) \quad (8.15)$$

³⁴S. C. Jain, "Simple Solutions of the Partial Differential Equation for Diffusion," Proc. Roy. Soc., A243, 1957, pp. 359–374.

³⁵A. M. Anthony, R. Kiyoura, and T. Sata, "Les Equilibres des Composés Oxygènes de l'Uranium entre 1500 et 2000°K," J. Nuc. Mat., Vol. 10, 1963, pp. 8–14.

³⁶S. Aronson and J. Belle, "Nonstoichiometry in Uranium Dioxide," J. Chem. Phys., Vol. 29, 1958, pp. 151–158.

³⁷"AEC Fuels and Materials Development Program Progress Report No. 67," GE-NMPO, GEMP-67, June 30, 1967, p. 160.

Theoretical – Thorn and Winslow³⁸ have derived the following theoretical relationship between oxygen self-diffusion coefficients in UO_{2+x} and the composition of UO_{2+x} :

$$D = \frac{Z}{4} \langle \ell^2 \rangle \nu \left\{ x + \left[x^2 + \frac{8q_i}{q_v} \exp \left(\frac{-(E_v - E_i)}{RT} \right) \right] \right\}^{1/2} \exp \left(\frac{-U_\ell}{RT} \right) \quad (8.16)$$

where

- D = self-diffusion coefficient for oxygen in UO_{2+x}
- Z = number of nearest neighbors
- $\langle \ell^2 \rangle$ = mean square of diffusional jump
- ν = mean vibrational frequency of lattice
- U_ℓ = energy composed of energies associated with correlation of the diffusing species vibrating out of phase with its shell of neighbors
- E_v = energy required to produce vacancies
- E_i = energy required to remove atoms from interstitial sites
- q_i = vibrational partition functions associated with interstitial sites
- q_v = vibrational partition functions associated with vacancy sites
- x = fractional deviation from stoichiometric (x in UO_{2+x})

They selected the following values for the parameters of the above equation:

$$\begin{aligned} \frac{Z}{2} \langle \ell^2 \rangle &= 22.4 \times 10^{-6} \text{ cm}^2 \\ \nu &= 18 \times 10^{12} \text{ sec}^{-1} \\ E_v &= 131.1 \text{ kcal/mole} \\ E_i &= 93.8 \text{ kcal/mole} \\ U_\ell &= 35.1 \text{ kcal/mole} \\ 8q_i/q_v &\cong 500 \end{aligned}$$

All the above values were derived from basic information except for the shell energy value which was derived from the experimental diffusion data of Auskern and Belle³⁹ for $\text{UO}_{2.002}$. In a later publication Thorn and Winslow⁴⁰ introduce new values for E_v and U_ℓ whereby the quantity $(E_v - E_i)$ becomes 40.9 kcal/mole and U_ℓ is 29.7 kcal/mole (the activation energy of Auskern and Belle for oxygen diffusion in UO_{2+x} having an O/U of 2.004 and 2.067 in the temperature range 300° to 600°C). Using either set of values for $(E_v - E_i)$ and U_ℓ in equation (8.16) gives correlation with the results of Auskern and Belle; the later set of values better explains their results for nearly stoichiometric material ($\text{UO}_{2.002}$).

Chemical diffusion coefficients for oxygen in UO_{2+x} (diffusion resulting from a chemical potential gradient) can be related to the coefficients for oxygen self diffusion (determined by tracer experiments) by the following equation:

$$D_{\text{chem}} = D_{\text{self}} \left(\frac{2+x}{2x} \right) \left(\frac{d \ln P_{\text{O}_2}}{d \ln x} \right) \quad (8.17)$$

where: P_{O_2} = oxygen partial pressure

Using Thorn and Winslow's equation (8.16) to calculate D_{self} values for $\text{UO}_{2.05}$ and converting these to D_{chem} by equation (8.17) gives good correlation between theory and

³⁸R. J. Thorn and G. H. Winslow, "Correlation of Thermodynamic Properties and Atomic Transport in the Uranium Dioxide Phase," *Thermodynamics: Proceedings of the Symposium on Thermodynamics*, Vol. 2, IAEA, 1966, p. 234.

³⁹A. B. Auskern and J. Belle, "Oxygen Ion Self Diffusion in Uranium Dioxide," *J. Nucl. Mat.*, No. 3, 1961, pp. 267-276.

⁴⁰R. J. Thorn and G. H. Winslow, "Oxygen Self-Diffusion in Uranium Dioxide," *J. Chem. Phys.*, Vol. 44, April 1966, p. 2822.

the experimental results of the present study, as shown in Figure 8.18. The dashed line is the theoretical curve and the solid line is the least-squares fit to the experimental data. The theoretical line in Figure 8.18 represents the composition $\text{UO}_{2.05}$, for which there is general agreement in the literature concerning the value of the thermodynamic function $\left(\frac{d \ln P_{\text{O}_2}}{d \ln x}\right)$. Furthermore, the composition $\text{UO}_{2.05}$ selected here is a reasonable first approximation to the composition of the test samples since the average O/U values changed from 2.003 to between 2.023 and 2.132 during the present experiments.

Fig. 8.18 — Oxygen diffusion coefficient versus reciprocal temperature for oxidation of UO_2 by steam compared to theoretical curve for oxygen diffusion coefficient in $\text{UO}_{2.05}$

Although good correlation is established between theoretical and experimental values, effort is continuing to determine the best theoretical values with which to compare experimental results. This includes selection of the best set of constants for the Thorn and Winslow equation (8.16) and of the most valid equation for determining the thermodynamic function to be used in the conversion from self- to chemical-diffusion coefficients in equation (8.17). It also remains to be determined which O/U value best represents experimental data obtained under oxidizing conditions in which the average O/U is constantly changing with time.

8.3 PHYSICAL AND MECHANICAL PROPERTIES (A. D. Feith, E. F. Juenke, and W. L. McCullough)

TENSILE STRENGTH OF TYPE 304 L STAINLESS STEEL

The tensile strength of annealed 304 L stainless steel sheet was measured from room temperature to 1375°C . The test specimens were fabricated from 0.076-cm-thick sheet and had a 2.54-cm gage length in the major rolling direction of the sheet. Table 8.13 shows the chemical analysis for this material.

TABLE 8.13

CHEMICAL ANALYSIS OF TYPE 304L
STAINLESS STEEL TENSILE SPECIMENS

Element	Percent
C	0.024
Co	0.05
Cr	18.00
Cu	0.28
Mn	1.69
Mo	0.16
Ni	10.95
P	0.024
Si	0.70
S	0.011

Measurements from room temperature to 800°C were performed in air, utilizing an extensometer to determine the 0.2-percent yield point and to control the strain rate at 0.005 cm per minute. The measurements from 800° to 1375°C were performed in argon at a crosshead speed of 0.15 cm per minute without using an extensometer. In all cases, the measurements were performed 0.6 hour after start of heat-up to temperature, allowing 0.3 hour to reach test temperature and 0.3 hour at temperature to attain constant temperature throughout the specimen. Ductility was measured as elongation at rupture, and the hardness (DPH) of each tested specimen was measured after test.

Strength, ductility, and hardness results are given in Table 8.14. The tensile strength data versus temperature are plotted in Figure 8.19. Strength data for 800°C measured in argon are somewhat higher than in air, possibly because of the effect of oxidation or because of a higher strain rate. Ductility and hardness data are plotted in Figure 8.20.

THERMAL CONDUCTIVITY OF 304 L STAINLESS STEEL

The thermal conductivity of Type 304 L stainless steel was measured in the 520° to 1340°C temperature range by the radial heat flow method described previously.^{41,42} Single Pt / Pt - 10Rh thermocouples were used to measure the temperatures at two radial locations of the test specimen over the entire temperature range studied. Although the thermal gradient was small (3° to 8°C), it was determined to a reasonable degree of precision (approximately ± 5%) by dividing the difference between the thermocouple outputs at the two radial locations by the sensitivity of the couple at the mean temperature value. This technique is widely employed when measuring small gradients, rather than using differential thermocouples.

The specimen was fabricated from a commercial grade 304L stainless steel of the composition listed in Table 8.15. Shown also in this table are the compositions of other 300 series stainless steels whose conductivities are compared with that of the tested material in Figure 8.21.

The thermal conductivity of this material increased with temperature; this appears to be typical of the stainless steels. The results of this study have been fit to the following linear equation with a standard deviation of 1.770×10^{-2} watt/cm-°C:

$$k = 8.924 \times 10^{-2} + 1.970 \times 10^{-4} T \quad (8.18)$$

⁴¹A. D. Feith, "A Radial Heat Flow Apparatus for High Temperature Thermal Conductivity Measurements," GE-NMPO, GEMP-296, August 1963.

⁴²A. D. Feith, "Measurements of the Thermal Conductivity and Electrical Resistivity of Molybdenum," GE-NMPO, GE-TM 65-10-1, October 1965.

TABLE 8.14
TENSILE TEST RESULTS FOR TYPE 304 STAINLESS STEEL SHEET

Specimen No. ^a	Atmosphere	Temperature, °C	0.2% Yield Strength, kg/mm ²	Tensile Strength, kg/mm ²	Elongation at rupture (in 2.54-cm gage length), percent	Hardness, DPH ^b
1	Air	25	27.3	65.4 ^c	65	174
10		25	28.5	66.5	64	174
2		200	22.4	46.4	36	203
11		200	22.9	47.2	38	227
3		400	20.0	44.9	32	266
12		400	20.3	44.8	31	254
4		600	16.1	33.2	23 ^d	218
13		600	15.9	33.9	34	218
5		800	8.1	10.4	44 ^e	173
14		800	8.0	10.0	46	164
6	Ar	800	—	13.0 ^f	53	164
15		800	—	13.0	52	170
7		1000	—	4.9	51	143
16		1000	—	5.0	44	145
8		1200	—	1.9	65	157
17		1200	—	2.1	53	127
9		1300	—	1.4	46	105
18		1300	—	1.3	48	110
19		1350	—	0.91	41	104
20		1375	—	0.86	43	107

^a0.076-cm-thick by 2.54-cm gage length, annealed condition.

^bAfter test; kg load.

^cStrain rate in air, 0.005/min.

^dFracture at extensometer knife edge.

^eFracture outside gage length.

^fLoading rate in argon, 0.15 cm/min. (cross-head speed).

Fig. 8.19 — Ultimate tensile strength of Type 304 stainless steel sheet

Fig. 8.20 — Ductility and hardness versus temperature as a result of tensile testing Type 304 stainless steel sheet

where

k = thermal conductivity, watt/cm-°C

T = temperature, °C

Values below 700°C are somewhat lower than other reported values, although the high-temperature data appear to agree well with values recommended by the TPRC data book.⁴³ The recommended values for Type 304 stainless steel were extrapolated above 900°K (627°C) and apparently maintain a uniform displacement above the values for Type 347 stainless steel. Values for Type 347 stainless steel above 1500°K (1227°C) were also extrapolated.

Thermal diffusivity data for this same 304L stainless steel have been obtained in the 300° to 1100°C temperature range and are reported under Task 1503. Enthalpy measurements are being made over the same temperature range and electrical resistivity measurements are planned. When these studies are complete, an adequate correlation

⁴³Thermal Physical Properties Research Center Data Book, Table 1089R, Vol. 1, June 1966.

TABLE 8.15
COMPOSITION OF STAINLESS STEELS USED IN
VARIOUS THERMAL CONDUCTIVITY TESTS

Element	This Study Type 304L	TPRC ^a Type 304	TPRC ^a Type 347	Silverman ^b Type 302	Lucks ^c Type 301 ^d	Powell ^e Type 18/8
C	0.024	0.053	0.06	0.116	0.15	0.08
Cu			0.09			
Mn	1.131	0.67	1.64		2.0	1.23
Si	0.70		0.58	0.13	1.0 Max.	0.62
P	0.014	0.025	0.013	0.021		
S	0.12		0.017	0.013		
Cr	18.37	18.51	17.65	18.4	16-18	18.68
Ni	9.89	9.09	10.94	9.6	6-8	8.85
Mo	0.09		0.02			
Nb						0.99
Ti						0.14

^aThermal Physical Properties Research Center Data Book, Vol. 1, June 1966, Table 1089R.

^bL. Silverman, "Thermal Conductivity Data Presented for Several Metals and Alloys Up to 900°C," J. Metals, Vol. 5 (1953) pp. 631-2.

^cC. F. Lucks and H. W. Deem, "Thermal Properties of Thirteen Metals," ASTM Special Tech. Pub. No. 227, 1958.

^dAnalysis not reported — values presented are typical for this material based on stainless steel catalogs.

^eR. W. Powell and R. P. Tye, "New Measurements on Thermal Conductivity Reference Materials," Proceedings of the Sixth Conference on Thermal Conductivity, Dayton, Ohio, 1966.

Fig. 8.21 — Thermal conductivity as a function of temperature for stainless steels

between the thermal conductivity and thermal diffusivity of this material can be made. This correlation will be used to ascertain the correct positioning of the low-temperature portion of the curve representing conductivity data presented above.

SPECTRAL AND TOTAL EMITTANCE MEASUREMENTS OF OXIDIZED ZIRCALLOY-4

Spectral and total hemispherical emittance measurements were carried out on both unoxidized and oxygen-saturated Zircaloy-4. The hole-in-tube method of measurement used in these studies is similar to that employed by Lemmon⁴⁴ for similar measurements on zirconium alloys and by Jain and Krishnan⁴⁵ in their studies on graphite. Figure 8.22

⁴⁴A. W. Lemmon, op. cit., p. A-1.

⁴⁵S. C. Jain and K. S. Krishnan, "The Distribution of Temperature Along a Thin Rod Electrically Heated in Vacuo. III: Experimental," Proc. Roy. Soc., Series A, Vol. 225, September 1954, p. 7.

Fig. 8.22 — Schematic diagram of furnace used for emittance measurements

is a schematic diagram of the sample and important features of the apparatus. The sample was a tube of Zircaloy-4 about 15.2 cm long and 0.71 cm in diameter with a wall thickness of 0.038 cm. A hole, 0.079 cm in diameter, was drilled through one wall of the tube near the center. Two 0.025-cm-diameter tungsten wire voltage probes were spot-welded to the tube approximately 1.27 cm above and below the hole. Electrical power was supplied to the sample through water-cooled copper electrodes. The sample was surrounded by a Vycor chamber; the system was capable of operating with atmospheres of argon, steam, or vacuum. The black-body temperature and the surface temperature adjacent to the hole were measured optically through a quartz window. A vacuum tube voltmeter was used to determine both the voltage between the voltage probes and the sample current, calculated from the voltage drop across a calibrated standard resistance in series with the sample. An oscilloscope across the standard shunt was used to ensure a pure sinusoidal wave form for the sample current.

The tube used in these experiments was long enough that the temperature at the middle of the tube in the region of the black-body hole was sensibly constant over a considerable length of the tube, approximately 5 cm. Under these conditions, the loss of heat from the region of the temperature measurement was due almost entirely to radiation from its surface, and little loss resulted from either thermal conduction toward the ends of the tube or from radiative transfer in the tube cavity.

The spectral emittance was determined using the relationship:

$$\ln E_2 = \frac{-C_2}{2} \frac{(T - S)}{TS} \quad (8.19)$$

where

E_λ = spectral emittance
 λ = observed wavelength
 C_2 = radiation constant, = 1.438 cm/°K
 S = surface temperature, °K
 T = black-body temperature, °K

The wavelength observed in these measurements was 0.65 microns.

Total hemispherical emittance was determined using the following equation:

$$E_T = \frac{IV}{2\pi r \ell \sigma T^4} \quad (8.20)$$

where

E_T = total hemispherical emittance
 I = sample current, amperes
 V = potential drop across measured section, volts
 r = radius of sample, cm
 ℓ = length of measured section, cm
 σ = Boltzman's constant = 5.673×10^{-12} watt/cm²-°K⁴
 T = black-body temperature, °K

Preliminary tests were run to compare spectral and total emittance values between 900° and 1300°C for unoxidized Zircaloy-4, oxygen-saturated Zircaloy-4, and Zircaloy-4 oxidized sufficiently to have a substantial ZrO₂ coating on the surface. The Zircaloy-4 tubes used in the experiments meet LOFT specifications and ASTM specifications B-353-645 Grade RA-2, and have a surface finish of 63 RMS or better inside and out. Table 8.16 gives the vendor's ingot analysis.

The measurements for unoxidized Zircaloy-4 were conducted on two samples heated in a vacuum ($<10^{-3}$ Torr). On initial heat-up of these samples the spectral emittance was in the range of 0.6 to 0.7 up to a temperature between 1100° and 1200°C, at which point it dropped to about 0.4. It is assumed that a change in surface condition, possibly oxidation or evaporation, accounts for this change in emittance behavior. The high emittance values are believed to result from oxidation of the metal by residual oxygen in the furnace during the initial heat-up. At high temperatures the oxygen dissolves rapidly in the metal and the emittance approaches that of the unoxidized metal. These initial experiments show that spectral emittance, E_λ , varies between 0.56 at 885°C and 0.43 at 1550°C. The value for 1100° to 1500°C is relatively constant, between 0.40 and 0.45. The total emittance, E_T , for the same temperature range lies between 0.20 and 0.28. These values are in fair agreement with the values obtained by Lemmon⁴⁴ for unoxidized Zircaloy-2 and Zircaloy-B in the same temperature ranges; E_λ = 0.43 to 0.44 and E_T = 0.22 to 0.26.

Application of an oxide layer by steam oxidation appreciably increased the spectral and total emittance. Several samples were oxidized for 30 minutes at temperatures between 950° and 1050°C. In each case both the spectral and total emittance increased to between 0.80 and 0.90 and remained thus through several thermal cycles. When steam oxidation was carried out for shorter periods of time, 5 to 10 minutes, the emittance reached high values as above. As heating continued, however, the oxygen of the scale dissolved in the metal and both spectral and total emittance values dropped, approaching the original values for the unoxidized metal.

These observations prove that in order to measure the effect of oxide layer thickness on the emittance of Zircaloy-4, it is necessary to saturate the metal with oxygen before

applying the oxide layers. Table 8.17 gives the calculated conditions for saturation of Zircaloy-4 tubes of the dimensions used in these experiments by steam oxidation at various temperatures. The time required to deposit enough oxygen to saturate the metal and the time required to homogenize the sample by diffusing oxygen into the metal have been calculated using equation (8.10):

$$W^2/t = 5.56 \times 10^5 \exp \left(\frac{-39,700 \pm 2300}{RT} \right)$$

developed in the reaction rate study described above and Lemmon's⁴⁴ equation for oxygen diffusion in alpha-zirconium, respectively. After saturation, oxide layers will be formed by additional oxidation in steam. Emittance values will then be determined and the oxide layer thickness will be measured metallographically.

8.4 SUMMARY AND CONCLUSIONS

Dynamic heating tests of Zircaloy-4 tubes with an internal pressure show that steam oxidation of the metal will result in lower deformation rates, less deformation, and higher failure temperatures. A model has been developed for expressing the tube failure by deformation when oxidation is negligible, as a function of tensile strength and rate of heating.

TABLE 8.16

CHEMICAL ANALYSIS OF ZIRCALOY-4
TUBING USED IN EMITTANCE MEASUREMENTS^a

Element	Ingot Analysis, wt %	
	Top	Bottom
Cr	0.09	0.09
Fe	0.19	0.20
Sn	1.45	1.40
Ni	<0.004	<0.004
Zr	Bal	Bal

Impurities	Ingot Impurities, ppm	
	Top	Bottom
C	<80	100
H	11	6
N	25	35
O	1400	1000
Al	<20	<20
B	<0.2	<0.2
Cd	<0.2	<0.2
Cl	<10	<10
Co	<10	<10
Cu	<20	40
Hf	<100	<100
Mg	<10	<10
Mn	<20	<20
Mo	<20	<20
Pb	<20	<20
Si	<30	30
Ti	<20	<20
V	<20	<20
W	<50	<50

^aAnalysis by vendor.

TABLE 8.17

CALCULATED TIMES FOR SATURATION
OF ZIRCALOY-4 TUBES^a BY STEAM OXIDATION

Temperature, °C	Oxidation	
	Time, ^b min	Solution Time, ^c min
1000	17	337
1050	10	183
1100	5	103
1150	3	61
1200	2	37
1250	1	23
1300	0.8	15
1350	0.6	10
1400	0.4	7
1450	0.3	5
1500	0.2	3

^aCalculations based on a sample dimension of 15.2-cm length, 0.71-cm diameter, 0.038-cm wall thickness.

^bCalculated from equation (8.10):

$$W^2/t = 5.56 \times 10^5 \exp \left(\frac{-39,700 \pm 2300}{RT} \right)$$

^cCalculated from $D_a = 0.196 \exp \left(\frac{-41,000 \pm 1500}{RT} \right)$

The oxidation of Zircaloy-4 and zirconium by steam shows a higher rate above about 1600°C which can be expressed as

$$W^2/\text{sec} = 1.5 \times 10^8 \exp \left(\frac{-60,600 \pm 5400}{RT} \right).$$

Oxidation of Zircaloy-4 in air is somewhat erratic and occurs at a greater rate than in steam; the difference is attributed to the reaction with nitrogen in the air.

The rate-controlling mechanism for oxidation of UO_2 by steam is considered to be diffusion of oxygen through the UO_{2+x} lattice. This proposed mechanism was verified by measuring an oxygen gradient in samples which had not reached equilibrium conditions.

The oxidation rate of 304 L stainless steel in air is about 10^3 times less than in steam up to 1370°C. This behavior is believed to be due to the presence of Cr_2O_3 as a protective film. During steam oxidation, however, formation of a film having the spinel structure provides less resistance to oxidation. The air oxidation rate becomes equal to or greater than that for steam at 1370°C and above, since molten Fe-FeO destroys the protective Cr_2O_3 film.

The tensile strength of annealed 304L stainless steel decreased from about 66 kg/mm² at room temperature to 0.86 kg/mm² at 1375°C.

The thermal conductivity of Type 304L stainless steel increased with temperature between 520° and 1340°C. The variation of thermal conductivity with temperature for this temperature range may be expressed as follows:

$$k = 8.924 \times 10^{-2} + 1.970 \times 10^{-4}T.$$

The spectral emittance of unoxidized Zircaloy-4, at a wave length of 0.65 microns, varied between 0.56 at 885°C and 0.43 at 1550°C. Total hemispherical emittance varied between 0.20 and 0.28 over the same range. The presence of an oxide layer increased the values for both spectral and total emittance to between 0.8 and 0.9. For thin oxide films, however, solution of the oxygen in the metal during prolonged heating caused both spectral and total emittance to approach original values for the unoxidized metal.

8.5 PLANS AND RECOMMENDATIONS

Spectral and total hemispherical emittance measurements will be continued on unoxidized, oxygen-saturated, and oxidized Zircaloy-4 to determine the effect of oxide layer thickness on the emittance of oxidized Zircaloy-4.

A thermal-arrest technique will be employed to study the solidus temperatures for the system Zr- UO_2 from the zirconium-rich end to compositions in the range likely to be encountered in a loss-of-coolant meltdown accident. Phases present in quenched samples will be examined to augment the lower-temperature, pseudo-binary information presently available.

Measurement of the effect of internal pressure on Zircaloy-4 tubing will continue with emphasis on the effect of oxide film thickness on the deformation and failure characteristics of this material.

Irradiated Zircaloy-2 from the spent fuel discharge of a power-producing reactor will be studied to determine the effect of radiation damage on the behavior of pressurized tubes under dynamic heating conditions.