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REPORT TITLE **The Oxidation Kinetics of SNAP Fuel Alloy,
Modified 90-10 Zirconium-Uranium**

AUTHOR **S.D. Harkness**

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ATOMICS INTERNATIONAL A Division of North American Aviation, Inc.		NAA-SR-MEMO- TDR NO. 10914	APPROVALS <i>William R. Young</i> <i>D. F. Atkins</i>
TECHNICAL DATA RECORD		PAGE 1 OF 33	
AUTHOR S. D. Harkness		DEPT. & GROUP NO. 735-52	DATE 1-18-65
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STATEMENT OF PROBLEM			
To determine the kinetic rate constants for oxidation of non-hydrated SNAP fuel alloy.			
ABSTRACT:			
Oxidation kinetic rate constants for 90-10 modified zirconium-uranium alloy are presented for the temperature range 575° - 1190°C. These studies resulted in the following expressions for the rate constants:			
$\text{Log } K(\text{mg}^2/\text{cm}^4 \text{ sec}) = 1.01 \pm 0.84 - \frac{(1.93 \pm 0.34)10^4}{4.576 T} \quad (843^\circ - 1113^\circ \text{K})$			
$\text{Log } K(\text{mg}^3/\text{cm}^6 \text{ sec}) = 2.87 \pm 0.63 - \frac{(2.60 \pm 0.29)10^4}{4.576 T} \quad (893^\circ - 1043^\circ \text{K})$			
$\text{Log } K(\text{mg}^2/\text{cm}^4 \text{ sec}) = 10.2 \pm 0.7 - \frac{(6.60 \pm 0.42)10^4}{4.576 T} \quad (1113^\circ - 1463^\circ \text{K})$			
The last expression is expected to be valid to the melting point.			
The small amount (0.15 w/o) of carbon in the samples and the presence of nitrogen in the atmosphere do not significantly affect oxidation rates. The addition of uranium to zirconium, however, appears to increase the activation energy of the process and to reduce the temperature range over which a cubic fit is obtained.			
Spalling of the samples appeared to occur for the modified 90-10 zirconium-uranium alloy only from 650°C to 900°C, at times greater than 30 minutes.			
Metallographic studies, experimental apparatus and procedures are presented.			
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I. INTRODUCTION

At present there is great concern over whether SNAP fuel material, modified 90-10 zirconium uranium hydride, will burn up upon re-entry into the atmosphere. In order to construct a model which will predict burnup behavior for any set of re-entry conditions, a broad basic understanding of all competing phenomena must be gained. One of the most critical interactions is that between hydrogen evolution and fuel alloy oxidation. Hydrogen evolution will be inhibited by the tendency to form an adherent oxide envelope around the fuel element. Conversely, oxidation characteristics will be changed by fragmentation of the adherent oxide layer by internal hydrogen pressure. The balance between these two processes could well decide the ultimate fate of the SNAP fuel elements.

To analytically predict this balance, hydrogen evolution and fuel oxidation must be studied separately and understood in terms of material constants. After this is completed, the phenomena must be studied together over temperature transients typical of atmospheric re-entry. From these experimental results, and the material constants gained earlier, an analytical model should be possible that will allow prediction of hydrogen evolution and fuel oxidation interaction for re-entry conditions.

It is the purpose of this work to study the oxidation characteristics of SNAP fuel alloy.

Two areas are of utmost importance in determining the effect of fuel oxidation on burnup.

First, since fuel oxidation is highly exothermic, it is important to know the rate of oxidation and, in turn, the rate of energy input from the oxidation reaction. Rate constants for the SNAP fuel material have been experimentally determined as a function of temperatures toward this end.

Second, the adherence of the oxide film must be known to enable accurate heat transfer calculations. Oxide film adherence were examined for a wide range of temperatures. An attempt was made to gain a qualitative understanding of this phenomena.

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II. THEORETICAL CONSIDERATIONS

Several different oxidation rate laws have found experimental agreement, though only the parabolic has a solid basis in theory. The linear, logarithmic, and cubic laws have all been used, however, when they most closely fit experimental data.

In this work, data was seen to fit three of these forms; the parabolic, $W^2 = Kt + C$ (1)

where W = weight of oxygen gained

K = rate constant

t = time

C = constant

the cubic,

$$W^3 = Kt + C \quad (2)$$

and the linear

$$W = Kt + C \quad (3)$$

Pilling and Bedford⁽¹⁾ set down the original theoretical basis for the parabolic law while Wagner and Grunewald⁽²⁾ and Mott⁽³⁾ have derived it in more precise terms recently.

The cubic rate law has resisted an accepted theoretical explanation, though recently Smith^(4,5) has derived this law by including a concentration effect on interstitial diffusion.

A linear rate relation indicates an independence of film thickness with the possibility of nucleation reactions at the metal-oxide interface being rate controlling.

The temperature dependence of rate constants is an important function to evaluate. If the rate process is an activated one, it may be represented by an equation of the form:

$$K = K_0 \exp \left(\frac{-\Delta H}{kT} \right) \quad (4)$$

where

ΔH = energy of activation (cal/atom)

k = Boltzmann constant

T = temperature

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This form was first derived by Maxwell to describe the fraction of atoms which will have the energy ΔH to make a jump between states when the average atom energy is kT . As long as the mode of transfer between states remains the same ΔH will not change. Thus, change in activation energy reflects change in rate mechanism. Since activation energy is obtainable from the slope of a plot of $\log K$ vs $1/T$, changes in the mechanism are readily detected.

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NO. NAA-SR-MEMO-10914DATE 1-18-65PAGE 5 OF 33**III. EXPERIMENTAL****A. Materials**

Three basic materials were used in these experiments to delineate the role of various elements. The primary material was SNAP fuel, 90-10 Zr-U modified alloy. Nonmodified fuel alloy was used to study the effect of the carbon modifier. Pure zirconium was used to isolate the effect of uranium on the oxidation kinetics. Typical analysis of the fuel alloy is as follows:

Major Constituents

<u>Element</u>	<u>Wt. %</u>
U	9.95
C	0.14

Trace Elements

<u>Element</u>	<u>PPM</u>
Ag	----
Al	60
B	< 0.5
Ba	< 5
Be	< 0.5
Bi	< 2
Ca	< 25
Cd	5
Co	< 5
Cr	35
Cu	300
Fe	325
Hf	< 200
Li	< 1
Mg	< 5
Mn	< 10
Mo	< 50
N	30
Na	< 50
O	1145
Pb	< 5
Si	75
Ti	< 25
V	< 10
W	18
Zn	< 20

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B. Experimental Technique

The experimental work was aimed at obtaining isothermally and isobarically the oxygen content as a function of time for modified 90-10 zirconium uranium alloy. This was accomplished by suspending a spherical sample from a gravimetric balance into a furnace and introducing a specified pressure of oxygen or air. Samples were degreased with chemically pure ethyl alcohol and then vacuum outgassed prior to the experimental run. The major components of the resulting kinetic system were as follows:

1. Balance:

An Ainsworth Vacuum Semi-Micro Automatic Recording Balance Type A-K was used because it allowed a continuous plot of weight change versus time. Weight changes are detected by a transducer device which electronically transmits them to a strip-chart recorder. The maximum weight change that can be recorded is 3.9 grams. Balance sensitivity is $\pm .5$ milligrams.

2. Sample Furnace:

Sample heating was accomplished by a 3 zone, clam shell Marshall furnace with a maximum temperature rating of 1100°C. A Wheelco 402 Controller was used to regulate temperature to $\pm 3^\circ\text{C}$.

3. Temperature Measurement:

Exact temperature measurements were periodically taken via a system of thermocouples inserted from the bottom of the Vycor retort (See Figure 23). This design demanded a Kovar glass to metal seal. The thermocouples used were 20 mil Geminol with a precision of $\pm 1^\circ\text{C}$.

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IV. RESULTS AND DISCUSSION

Oxidation rates of the fuel alloy, modified 90-10 zirconium - uranium, were found to obey principally a parabolic law, $W^2 = Kt + c$, though for a limited range a cubic fit, $W^3 = Kt + c$, was also found. Since both expressions were found, it is possible, perhaps probable, that the rates may better be expressed by an intermediate fit; an attempt to determine such an intermediate law will be performed at a later date.

The data are given in Table I and graphically in Figure 1. Least squares treatment of the data yields the following kinetic rate equations which are represented by the lines in Figure 1.

$$\text{Log } K(\text{mg}^2/\text{cm}^4 \text{ sec}) = 1.01 \pm 0.84 - \frac{(1.93 \pm 0.34)10^4}{4.576 T} \quad (843^\circ - 1113^\circ \text{K}) \quad (5)$$

$$\text{Log } K(\text{mg}^3/\text{cm}^6 \text{ sec}) = 2.87 \pm 0.63 - \frac{(2.60 \pm 0.29)10^4}{4.576 T} \quad (893^\circ - 1043^\circ \text{K}) \quad (6)$$

$$\text{Log } K(\text{mg}^2/\text{cm}^4 \text{ sec}) = 10.2 \pm 0.7 - \frac{(6.60 \pm 0.42)10^4}{4.576 T} \quad (1113^\circ - 1463^\circ \text{K}) \quad (7)$$

In light of the discussion presented in the theoretical section, it is evident that different mechanisms predominate at lower and higher temperatures. When two competing processes can occur, that which has the lower activation energy will be the governing process at lower temperatures and that which has the higher activation energy will govern at higher temperatures; at intermediate temperatures, both processes may be expected to occur. The activation energies obtained in this work are 19,300 cal/g mole and 66,000 cal/g mole, respectively for the parabolic fit at the lower and higher temperatures. These values compare favorably with 18,000 cal/g mole reported by Gulbransen and Andrews⁽⁶⁾ for the activation energy of diffusion of oxygen through zirconium oxide and with 66,000 cal/g mole observed by Debuigne and Lehr⁽⁷⁾ for the activation energy of diffusion of oxygen in the metal

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lattice. Thus, it is reasonable to conclude that for the oxidation of the fuel in the lower temperature range, the rate controlling mechanism is diffusion of oxygen through the oxide layer formed at the sample surface and that in the higher range, the controlling mechanism is diffusion through the metal. Since no phase changes occur between the last experimental point (1190°C) and the melting point, the rate constants given by equation (7) may be expected to be valid to the melting point of the alloy.

The phenomenon of breakaway, the spalling of oxides with accompanying rate change, was observed and studied. Photographs of macro and micro samples for the whole temperature range are presented in Figures 3 through 21. The times for breakaway initiation, tabulated in Table 1, were plotted versus temperature in an attempt to determine a time-temperature relationship. No such relationship was apparent. A linear rate form was found to govern after breakaway. The intermediate temperature character of this breakaway is explained in the following manner.

First, it should be noted that as oxidation proceeds a brittle ZrO_2 layer is built up on the curved sample surface. It would be expected that at some time this layer would become sufficiently thick to crack due to self-induced stresses. Indeed, breakaway phenomena is commonly encountered in pure zirconium, though at lower temperatures and longer times than observed for the fuel alloy.⁽⁶⁾ This suggests that another stress inducing mechanism is aiding breakaway in the fuel alloy. An examination of the metallurgical structure of the alloy reveals the answer. The uranium-zirconium phase diagram (Figure 22) shows that up to 605°C the equilibrium phase is essentially α zirconium, a hexagonal close packed structure. At these temperatures, as can be seen from Figure 1, the rate of oxidation is limited by diffusion through the oxide layer; hence, nearly all oxygen occluded by the sample will be contained in the oxide layer. The result is that an adherent oxide is formed so that no stresses are induced within the sample due to phase changes caused by oxygen solid solution. This is well exhibited in Figure 3, a and b. The microstructure of the sample, pictured in Figure 3 b, shows the adherent oxide film surrounding an extruded structure typical of the original material. Pictures of

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samples oxidized in air and oxygen for varying times are presented in Figures 4 and 5. No obvious difference is seen between the form of the two oxides.

For the temperature range 600 - 875°C, there are initially two phases in equilibrium, body centered cubic, β , and hexagonal close packed, α . This is also the temperature range in which diffusion in the metal and in the oxide become comparable. The combination of these two factors leads to induced stresses because oxygen is an alpha stabilizer (See Figure 24). As oxygen dissolves into the metal lattice, it causes the beta phase to transform to alpha, thereby creating a strained matrix. The material must eventually relieve these internal stresses by expansion or contraction at the expense of the brittle oxide envelope. The result of this can be seen in Figures 6 through 15. The transformed beta, responsible for the induced stresses, can be seen in the photomicrographs presented in Figure 13 b, c and d. The original alpha needles are seen among the transformed grains. Cracks due to the induced stresses can be seen in Figure 13, b and c.

Above 875°C, the initial structure is single phase, body centered cubic, β . For this temperature range, diffusion conditions are such that oxygen diffusion through the metal is greater than through the oxide layer. These two factors result in lower induced stresses and relatively thin oxide films.

The adherence of the high temperature oxide may be seen in Figures 16 through 21. That microcracks do occur in the matrix can be seen in Figure 21 c. The brittle fracture form of the oxide is seen in Figure 21 b.

As a concluding point, it should be noted that breakaway is not directly important for re-entry conditions, since the shortest time experienced for the phenomenon was 30 minutes.

Several unmodified fuel samples were run with no deviation seen from carbon modified results. It was concluded from this that carbon has a negligible effect on oxidation kinetics.

As seen in Table I, oxidation kinetics were studied both in atmospheres of oxygen and air. Activation energies for both processes were identical. The kinetic constant results for both were within

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experimental error of the techniques employed. Chemical analysis from runs at similar temperatures in the two atmospheres revealed negligible differences in nitrogen content. It was, therefore, concluded that the presence of nitrogen has a negligible effect on the oxidation kinetics of the fuel alloy.

Several runs were made in which the air stream was passed through a desiccant in order to determine the effect of water vapor. No effect was noted.

A study of pure zirconium was undertaken to establish the effect of uranium. The results from this study are presented in Table II and plotted in Figure 2. It is seen that a cubic rate law is followed for a large temperature range 600 - 1025°C. Parabolic fits were obtained above and below this range, again indicating the intermediate nature of the cubic rate law. Least square treatment of the data yield the expression:

$$\text{Log } K(\text{mg}^3/\text{cm}^6 \text{ sec}) = 7.52 \pm 0.73 - \frac{(4.84 \pm 0.34) 10^4}{4.576 T} \quad (8)$$

The activation energy, 48,400 cal/g mole, compares favorably with 47,200 cal/g mole reported by Belle and Mallet.⁽⁸⁾

It appears that the presence of uranium serves to limit the temperature range in which a cubic rate law is obeyed as well as to increase the activation energy required for diffusion through the metal.

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The efforts of Mr. R. J. Asher toward data collection were highly appreciated. Mr. C. Davids was responsible for most of the metallographic work.

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TABLE I

OXIDATION RATE CONSTANTS FOR 90-10 ZIRCONIUM URANIUM ALLOY

SAMPLE	ATMOSPHERE	TEMPERATURE °C	BREAKAWAY TIME (Minutes)	K PARABOLIC (mg ² /cm ⁴ .sec)	K CUBIC (mg ³ /cm ⁶ .sec)
90-10 Zr-U Mod.	760 torrs Air	570	--	8.68 x 10 ⁻⁵	--
90-10 Zr-U Unmod.	"	600	--	1.47 x 10 ⁻⁴	--
90-10 Zr-U Mod.	150 torrs O ₂	600	--	1.72 x 10 ⁻⁴	--
"	760 torrs Air	629	--	2.52 x 10 ⁻⁴	3.74 x 10 ⁻⁴
"	150 torrs O ₂	650	--	2.77 x 10 ⁻⁴	4.02 x 10 ⁻⁴
"	760 torrs Air	657	88	2.435 x 10 ⁻⁴	6.89 x 10 ⁻⁴
"	"	715	80	--	1.30 x 10 ⁻³
"	"	737	65	8.45 x 10 ⁻⁴	2.09 x 10 ⁻³
"	150 torrs O ₂	747	65	--	2.03 x 10 ⁻³
"	760 torrs Air	755	30	--	3.76 x 10 ⁻³
"	"	762	72	--	1.75 x 10 ⁻³
"	"	769	68	9.95 x 10 ⁻⁴	--
"	"	771	55	--	2.47 x 10 ⁻³
"	"	800	67	8.42 x 10 ⁻⁴	--
"	"	800	58	--	3.21 x 10 ⁻³
"	150 torrs O ₂	800	90	1.425 x 10 ⁻³	--
"	"	828	--	1.48 x 10 ⁻³	--
"	760 torrs Air	829	35	2.86 x 10 ⁻³	--
"	"	850	35	4.58 x 10 ⁻³	--
"	"	900	85	6.90 x 10 ⁻³	--
"	150 torrs O ₂	900	--	3.62 x 10 ⁻³	--
"	"	933	--	1.08 x 10 ⁻²	--
"	"	950	--	2.70 x 10 ⁻²	--
"	760 torrs Air	950	--	4.60 x 10 ⁻²	--
"	"	1000	--	9.36 x 10 ⁻²	--
"	150 torrs O ₂	1000	--	4.08 x 10 ⁻²	--
90-10 Zr-U Unmod.	760 torrs Air	1005	--	8.17 x 10 ⁻²	--
90-10 Zr-U Mod.	"	1080	--	6.83 x 10 ⁻¹	--
"	150 torrs O ₂	1080	--	2.71 x 10 ⁻¹	--
"	760 torrs Air	1140	--	1.235	--
"	"	1160	--	1.29	--
"	"	1190	--	1.72	--

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FIGURE 1

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OXIDATION RATE CONSTANT VS. RECIPROCAL TEMPERATURE

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Page 15 of 33~~CONFIDENTIAL~~TABLE IIOXIDATION RATE CONSTANTS FOR PURE ZIRCONIUM

<u>SAMPLE</u>	<u>ATMOSPHERE</u>	<u>TEMPERATURE</u> °C	K PARABOLIC (mg ² /cm ⁴ ·sec)	K CUBIC (mg ³ /cm ⁶ ·sec)
Pure Zirconium	760 torrs Air	609	5.16×10^{-6}	---
" "	"	625	---	8.58×10^{-5}
" "	"	640	---	1.08×10^{-4}
" "	"	650	---	1.08×10^{-4}
" "	"	700	---	5.34×10^{-4}
" "	"	850	---	5.38×10^{-3}
" "	"	850	---	5.50×10^{-3}
" "	"	901	---	1.96×10^{-2}
" "	"	1000	---	2.75×10^{-1}
" "	"	1025	---	6.20×10^{-1}
" "	"	1074	2.64×10^{-1}	---

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FIGURE 2

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OXIDATION RATE CONSTANT
VS.
RECIPROCAL TEMPERATURE
for
ZIRCONIUM

APPENDIX I

Error Analysis

Data reduction is accomplished by fitting experimental data to a parabolic or cubic rate law. Error sources which must be considered are slope measurement, temperature fluctuations, pressure changes and sample expansion.

Slope measurement will be the most serious source of error since experimental fits are rarely exact. This error was evaluated by drawing the extreme lines through data points. A $\pm 3\%$ deviation is representative.

Temperature fluctuations during a run are essentially non-existent along the length of the center zone of the Marshall furnace. However, the 402 Wheelco controller used with the furnace allows a $\pm 3^\circ\text{C}$ temperature confidence, which corresponds to an error in the rate constant of 1% for the lower activation energy and 3% for the higher activation energy process.

Pressure fluctuations are very small during experimental run. Gulbransen and Andrews⁽⁶⁾ have shown that order of magnitude changes in oxygen pressure have a small effect on the rate constant. For this reason, error contribution due to pressure fluctuations is assumed to be nil.

Sample expansion will be a function of the amount of oxygen absorbed which, in turn, is a function of time and temperature of run. A $\pm 1\%$ error was found to be representative for this contribution.

A summation of errors results in an expected experimental data precision of $\pm 5\%$ for the lower temperature work and $\pm 7\%$ for the high temperature study.

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APPENDIX II

PHOTOGRAPHS AND PHOTOMICROGRAPHS

3-a 1" Sphere, Mod. 90-10 Zirconium Uranium
 T = 575°C, Atm = 760 mm Hg Air
 t = 80 minutes

Bakelite

ZrO₂ Layer

3-b
 FIGURE 3.

250X

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1" Sphere, Modified 90-10 Zirconium Uranium;
T = 600°C, P = 150 mm O₂, time = 60 min.
FIGURE 4.

90-10 Zr-U Unmodified, T = 600°C, P = 760 mm Hg Air,
time = 260 min.
FIGURE 5.

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6-a 1" Diam. Sphere, Modified 90-10 Zirconium-Uranium Alloy, $T = 657^{\circ}\text{C}$, $P = 760 \text{ mm Hg Air}$,
time = 170 minutes.

6-b Surface Microstructure

250X

FIGURE 6.

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1" Sphere, Modified 90-10 Zirconium-Uranium Alloy,
T = 650°C, P = 150 mm O₂, time = 120 min.
FIGURE 7.

1" Sphere, 90-10 Zirconium-Uranium Alloy,
T = 715°C, P = 150 mm O₂, time = 960 minutes.
FIGURE 8.

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1" Sphere, Modified 90-10 Zr-U Alloy, $T = 725^{\circ}\text{C}$,
 $P = 760$ mm Hg Air, time = 1020
FIGURE 9.

1" Sphere, 90-10 Modified Zr-U Alloy, $T = 750^{\circ}\text{C}$,
 $P = 760$ mm Hg Air, time = 180.
FIGURE 10.

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1" Sphere Modified 90-10 Zr-U Alloy, T = 747,
P = 150 mm O₂, time = 780 minutes.
FIGURE 11.

1" Sphere Modified 90-10 Zr-U Alloy, T = 762,
P = 760 mm Hg Air, time = 300 minutes.
FIGURE 12.

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13-a 1" Sphere Modified 90-10 Zr-U Alloy, $T = 850^{\circ}\text{C}$,
 $P = 760 \text{ mm Hg Air}$, time = 480 minutes.

13-b Surface Structure

100X

FIGURE 13.

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13-c Surface Structure

250X

13-d Structure Just in From Surface
FIGURE 13.

500X

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14-a 1" Sphere, Modified 90-10 Zr-U Alloy,
T = 900°C, P = 150 mm O₂, time = 1020 minutes.

14-b Note Eruption of Originally Adherent Film.
FIGURE 14.

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1" Sphere, Modified 90-10 Zr-U Alloy, $T = 900^{\circ}\text{C}$,
 $P = 760 \text{ mm Hg Air}$, time = 145 minutes.

FIGURE 15.

1" Sphere, Modified 90-10 Zr-U Alloy, $T = 933^{\circ}\text{C}$,
 $P = 150 \text{ mm O}_2$, time = 320 minutes.

FIGURE 16.

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17-a 1" Sphere Modified 90-10 Zr-U Alloy, $T = 950^{\circ}\text{C}$,
 $P = 760 \text{ mm Hg Air}$, time = 225 minutes.

17-b Surface Structure
FIGURE 17.

100X

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17-c Surface Structure

500X

17-d Interior Structure

500X

FIGURE 17.

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90-10 Zr-U Unmodified, $T = 1005^{\circ}\text{C}$, $P = 760 \text{ mm Hg Air}$,
Time = 1020 minutes.
FIGURE 18.

1" Sphere Modified 90-10 Zr-U Alloy, $T = 1000^{\circ}\text{C}$,
 $P = 150 \text{ mm O}_2$, Time = 260 minutes.
FIGURE 19.

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20-a 1" Sphere Modified 90-10 Zr-U Alloy, $T = 1000^{\circ}\text{C}$,
 $P = 760 \text{ mm Hg Air}$, time = 240 minutes.

20-b Surface Structure

100X

FIGURE 20.

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21-a 1" Sphere Modified 90-10 Zr-U Alloy, $T = 1080^{\circ}\text{C}$,
 $P = 760 \text{ mm Hg Air}$, time = 95 minutes.

21-b Surface Structure Showing Brittle Fracture of
Oxide Film. 100 X

FIGURE 21.

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21-c Typical Surface Structure

100X

21-d Typical Surface Structure

500X

FIGURE 21.

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