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ON SNAP FUELS

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OXIDATION KINETIC STUDIES

ON SNAP FUELS

(Title Unclassified)

By

W. A. YOUNG

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ABSTRACT

Isothermal rate constants were obtained for the oxidation of nonhydrided SNAP fuel for the range of 570 to 1190°C. In addition, a study was made of the behavior of hydrided and of nonhydrided SNAP fuel alloy subjected to air oxidation under a temperature transient typical of that to be expected upon atmospheric reentry. The temperatures attained during this latter study approached 1700°C. These studies were conducted as a portion of the overall Aerospace Nuclear Safety Program at Atomics International.

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SUMMARY

Isothermal rate constants were obtained for the oxidation of nonhydrided SNAP fuel for the range of 570 to 1190°C. These studies yield the following expressions for the rate constants:

$$\text{Log } K(\text{mg}^3/\text{cm}^6\text{-sec}) = 3.63 \pm 0.20 - \frac{(29.4 \pm 0.9) 10^3}{4.576 T} \quad (570 \text{ to } 933^\circ\text{C}).$$

$$\text{Log } K(\text{mg}^2/\text{cm}^4\text{-sec}) = 9.31 \pm 1.24 - \frac{(60.5 \pm 7.5) 10^3}{4.576 T} \quad (950 \text{ to } 1190^\circ\text{C}).$$

The small amount of carbon (0.15 wt %) in the alloy does not affect the oxidation rate. Within experimental accuracy, the presence of nitrogen does not appear to affect the rate; however, there is some indication that the activation energy for air oxidation is somewhat lower than for oxidation in pure oxygen. The addition of uranium to zirconium appears to increase the activation energy required for diffusion of oxygen in the metal and to reduce slightly the temperature range over which a cubic rate law is valid. Spallation was observed only in the range of 650 to 900°C and at exposure times greater than 30 min. Metallographic examination and chemical analysis yielded no evidence of nitriding.

A study was made of the behavior of hydrided and of nonhydrided SNAP fuel alloy subjected to air oxidation under a temperature transient typical of that to be expected upon atmospheric reentry. The temperatures attained during this study approached 1700°C. For the nonhydrided alloy, the results obtained are in agreement with the isothermal work, with the exception that a considerable amount of nitriding occurred, particularly at the higher temperatures. No spallation or cracking was observed even at magnifications of 500X. In the case of hydrided fuel, extremely rapid evolution of hydrogen occurs for the first 40 to 50 sec which reduces the total hydrogen content of the alloy by a factor of two and causes extensive cracking of the material. The extent of oxidation was less than in the case of the nonhydrided alloy, probably due to shielding of the sample by the rapidly evolved hydrogen. Metallographic examination indicates that hydrogen is evolved from all surfaces including those of microcracks which

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extend to the exterior of the material. For both the hydrided and nonhydrided alloy, four distinct regions were observed upon metallographic examination: (1) a porous outer layer, undoubtedly oxide (with some nitride); (2) a columnar-grained phase which is depleted in uranium and may be a Zr-ZrO₂ eutectoid; (3) a thin interfacial phase, shown to be rich in uranium and devoid of zirconium; and (4) the alloy.

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I. INTRODUCTION

The proposed use of SNAP nuclear reactors for auxiliary power in space exploration has given rise to questions concerning the behavior of the fuel, a hydrided zirconium-uranium alloy (90 wt % Zr), upon reentry into the atmosphere. In order to construct a model which will predict the behavior of the fuel for any set of reentry conditions, a basic understanding of all competing phenomena must be obtained. One of the most critical interactions is that between hydrogen evolution and fuel oxidation. Hydrogen evolution would be expected to be inhibited by the tendency of the alloy to form an adherent oxide envelope. At the same time, oxidation characteristics would be changed by fragmentation of the oxide layer and cracking of the alloy due to hydrogen evolution. The relative importance of these two processes could well dictate the behavior of SNAP fuel elements during atmospheric reentry.

To predict the effects of these processes, they must first be understood separately in terms of material constants and then studied together over a temperature transient typical of those to be expected for atmospheric reentry. Hydrogen evolution is dependent upon the dissociation pressures and diffusion coefficients of hydrogen in the fuel; these parameters have been previously determined.^(1,2,3) The oxidation characteristics of the nonhydrided fuel alloy have been experimentally determined in this work and are discussed in Section II. The behavior of fuel subjected to the temperature transient has also been investigated in this work and is discussed in Section III.

*Superscripts refer to the References listed in Section V of this report.

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II. ISOTHERMAL OXIDATION OF FUEL ALLOY

A. THEORETICAL CONSIDERATIONS

Since fuel oxidation is highly exothermic, it is important to know the rate of oxidation and, thus, the rate of energy input due to oxidation. Several different oxidation rate laws have attained 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 were seen to fit two of these forms; the parabolic,

$$W^2 = Kt + C, \quad \dots (1)$$

where

W = weight of oxygen gained,

K = rate constant,

t = time, and

C = constant;

and the cubic,

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

Pilling and Bedford⁽⁴⁾ set down the original theoretical basis for the parabolic law, while Wagner and Grunewald⁽⁵⁾ and Mott⁽⁶⁾ have recently derived it in more precise terms.

The cubic rate law has resisted an accepted theoretical explanation; though recently, Smith^(7,8) has derived this law by including a concentration effect on interstitial diffusion.

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:

$$K = K_0 \exp\left(-\frac{\Delta H}{kT}\right), \quad \dots (3)$$

where ΔH is energy of activation (cal/atom), k is Boltzmann constant, and T is 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 reaction 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.

B. EXPERIMENTAL

1. 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 carbon-modified alloy. Nonmodified fuel alloy (no carbon additions) was used to separate 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		Trace Elements (continued)	
Element	wt %	Element	ppm
U	9.95	Fe	325
C	0.14	Hf	<200
Trace Elements		Li	<1
Element	ppm	Mg	<5
Ag	-	Mn	<10
Al	60	Mo	<50
B	<0.5	N	30
Ba	<5	Na	<50
Be	<0.5	O	1145
Bi	<2	Pb	<5
Ca	<25	Si	75
Cd	5	Ti	<25
Co	<5	V	<10
Cr	35	W	18
Cu	300	Zn	<20

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TABLE 1
OXIDATION RATE CONSTANTS FOR 90-10 ZIRCONIUM-URANIUM ALLOY

Material	Atmosphere	Temperature (°C)	Rate Constant (mg/cm ² -sec) ⁿ	Exponent	Breakaway (min)
Modified	Air (1 atm)	570	1.49×10^{-4}	3.51	-
Unmodified	Air (1 atm)	600	1.62×10^{-4}	2.48	-
Modified	O ₂ (150 mm Hg)	600	2.15×10^{-4}	2.34	-
Modified	Air (1 atm)	629	3.78×10^{-4}	2.58	-
Modified	O ₂ (150 mm Hg)	650	3.79×10^{-4}	2.51	-
Modified	Air (1 atm)	657	6.21×10^{-4}	2.83	88
Modified	Air (1 atm)	715	8.86×10^{-4}	2.28	75
Modified	Air (1 atm)	737	1.89×10^{-3}	2.99	65
Modified	O ₂ (150 mm Hg)	747	1.41×10^{-3}	2.62	58
Modified	Air (1 atm)	755	2.66×10^{-3}	2.70	31
Modified	Air (1 atm)	762	1.77×10^{-3}	2.96	72
Modified	Air (1 atm)	769	1.89×10^{-3}	2.99	50
Modified	Air (1 atm)	771	2.29×10^{-3}	2.88	51
Modified	Air (1 atm)	800	3.12×10^{-3}	2.90	65
Modified	Air (1 atm)	800	3.50×10^{-3}	3.09	57
Modified	O ₂ (150 mm Hg)	800	3.57×10^{-3}	2.62	95
Modified	O ₂ (150 mm Hg)	828	5.03×10^{-3}	2.66	-
Modified	Air (1 atm)	829	8.78×10^{-3}	2.82	55
Modified	Air (1 atm)	850	9.39×10^{-3}	2.64	35
Modified	Air (1 atm)	900	1.56×10^{-2}	2.56	55
Modified	O ₂ (150 mm Hg)	900	1.43×10^{-2}	2.68	-
Modified	O ₂ (150 mm Hg)	933	4.28×10^{-2}	2.68	-
Modified	O ₂ (150 mm Hg)	950	5.00×10^{-2}	2.17	-
Modified	Air (1 atm)	950	7.25×10^{-2}	2.19	-
Modified	Air (1 atm)	1000	4.02×10^{-2}	1.70	-
Modified	O ₂ (150 mm Hg)	1000	3.40×10^{-2}	1.95	-
Unmodified	Air (1 atm)	1005	9.71×10^{-2}	2.07	-
Modified	Air (1 atm)	1080	1.93×10^{-1}	1.62	-
Modified	O ₂ (150 mm Hg)	1080	2.45×10^{-1}	2.00	-
Modified	Air (1 atm)	1140	4.13	2.40	-
Modified	Air (1 atm)	1160	1.69	2.00	-
Modified	Air (1 atm)	1190	1.01	1.85	-

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2. 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 polished spherical sample on platinum wire 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 gm. Balance sensitivity is ± 0.5 mg.
- 2) Sample Furnace — Sample heating was accomplished by means of 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. This design demanded a Kovar glass-to-metal seal. The thermocouples used were 20-mil Geminol with a precision of $\pm 1^{\circ}\text{C}$.

The rate constants at each temperature were determined from weight gain as a function of time using a least-squares computer program which also yielded values for the exponent of the weight change in the expression, $W^n = Kt$, where K = rate constant and t = time.

C. RESULTS AND DISCUSSION

The oxidation rates were found to obey an approximately cubic law from 570 to 933°C and an approximately parabolic law above this range. The data are given in Table 1 and shown graphically in Figure 1. Least-squares treatment of the data yields the following kinetic rate expressions which are represented by the lines in Figure 1:

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Figure 1. Oxidation Rate Constant vs Reciprocal Temperature for SNAP Fuel Alloy

$$\text{Log } K(\text{mg}^3/\text{cm}^6\text{-sec}) = (3.63 \pm 0.20) - \frac{(29.4 \pm 0.9)10^3}{4.576T} \quad (527 \text{ to } 933^\circ\text{C}) \quad \dots(4)$$

$$\text{Log } K(\text{mg}^2/\text{cm}^4\text{-sec}) = (9.31 \pm 1.24) - \frac{(60.5 \pm 7.5)10^3}{4.576T} \quad (950 \text{ to } 1190^\circ\text{C}) \quad \dots(5)$$

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 29.4 and 60.5 kcal/g-mol, respectively, for the lower and higher temperatures. These values compare favorably with values of 28.1 to 33.4 kcal reported by other authors⁽⁸⁻¹²⁾ for the activation energy of diffusion of oxygen through zirconium oxide, and with 51.8 to 59.7 kcal reported^(13,14,15) for the activation energy of diffusion of oxygen in the metal. 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

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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 5 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 2 through 8. The times for breakaway initiation, tabulated in Table 1, apparently can not be expressed in terms of any simple function of temperature. It should be noted that spallation occurred only in the case of the alloy and only in the range of 650 to 900°C. The intermediate temperature character of 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 are commonly encountered in pure zirconium, though at lower temperatures and longer times than observed for the fuel alloy.⁽¹⁶⁾ 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. Up to 605°C, the equilibrium phase of the zirconium-uranium system is essentially α zirconium, a hexagonal close-packed structure. At these temperatures, as can be seen from Equation 4, 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 2. The microstructure of the sample, pictured in Figure 2b, shows the adherent oxide film surrounding an extruded structure typical of the original material.

For the temperature range of 600 to 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 stabilizes the beta phase. As oxygen dissolves into

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a. SPHERE

250X

b. CROSS-SECTIONAL MICROSTRUCTURE

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Figure 2. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 575°C, Time = 80 min)

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a. SPHERE

b. CROSS-SECTIONAL MICROSTRUCTURE

250X

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Figure 3. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 657°C, Time = 170 min)

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Figure 4. One-Inch Sphere of Modified Alloy
Oxidized in Oxygen at 150 mm Hg
(Temperature = 747°C, Time = 780 min)

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Figure 5. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 762°C, Time = 300 min)

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a. SPHERE

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Figure 6. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 850°C, Time = 480 min)
(Sheet 1 of 2)

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b. CROSS-SECTION THROUGH OXIDIZED SURFACE

250X

c. SUBSURFACE STRUCTURE

500X

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Figure 6. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 850°C, Time = 480 min)
(Sheet 2 of 2)

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a. SPHERE

b. CROSS-SECTIONAL MICROSTRUCTURE

100X

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Figure 7. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 950°C, Time = 225 min)

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a. SPHERE

b. CROSS-SECTIONAL MICROSTRUCTURE SHOWING
BRITTLE FRACTURE OF OXIDE FILM

100X

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Figure 8. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature = 1080°C, Time = 95 min)
(Sheet 1 of 2)

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500X

c. CROSS-SECTION OF OXIDIZED SURFACE

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Figure 8. One-Inch Sphere of Modified Alloy
Oxidized in Air at 1 atm
(Temperature - 1080°C, Time = 95 min)
(Sheet 2 of 2)

the metal lattice, it causes the alpha phase to transform to beta, thereby creating a strained matrix. The material must eventually relieve these internal stresses by expansion at the expense of the brittle oxide envelope. The result of this can be seen in Figures 3 through 6. The transformed alpha, responsible for the induced stresses, can be seen in the photomicrographs presented in Figure 6b 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 7 and 8. The brittle fracture form of the oxide is seen in Figure 8b.

Several nonmodified fuel samples were run with no observable effect on the rate constants. Thus, the addition of a small amount of carbon (0.15 wt %) to the basic 90-10 alloy has no appreciable effect on oxidation behavior.

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As seen in Table 1, oxidation kinetics were studied both in atmospheres of oxygen and of air. The kinetic constant results were the same within experimental error. Chemical analyses from runs at similar temperatures in the two atmospheres showed negligible differences in nitrogen content; in addition, metallographic examination of the samples indicated no evidence of nitriding. Thus, within experimental error, the presence of nitrogen appears to have no significant effect on the oxidation kinetics within the temperature range used in these isothermal studies. However, it may be that the activation energy for air oxidation is somewhat lower than for oxidation in pure oxygen. If only the data from air oxidation are considered, the activation energy is reduced to 28.0 ± 1.0 kcal/g-mol from 29.4 ± 0.9 kcal/g-mol obtained when all data are used. In addition, the activation energy given below for air oxidation of pure zirconium is slightly lower than the activation energy observed in earlier work^(13,14,15) for diffusion of oxygen in zirconium. It should be noted, in this connection, that the rate of reaction of zirconium with nitrogen has been found^(17,18) to be parabolic with an activation energy of approximately 50 kcal/g-mol over the range of 860 to 1640°C.

A limited study of the air oxidation of pure zirconium was undertaken to determine the effect of the addition of uranium. The results, given in Table 2 and in Figure 9, fit a cubic rate law and yield the expression,

$$\text{Log } K(\text{mg}^3/\text{cm}^6\text{-sec}) = 7.73 \pm 0.27 - \frac{(49.6 \pm 1.3)10^3}{4.576T} \quad (625 \text{ to } 1025^\circ\text{C}) \quad \dots (6)$$

The activation energy, though lower than that reported for diffusion of oxygen in zirconium, compares favorably with the value, 47.2 kcal/g-mol, reported by Belle and Mallet.⁽¹⁹⁾

Since the activation energies obtained for air oxidation of zirconium and of the alloy in the higher temperature range are of the same order of magnitude as the activation energies obtained by other authors for diffusion of oxygen in zirconium, it is reasonable to assume that such diffusion is the rate controlling factor for oxidation in these cases. If this is true, then the addition of uranium

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appears to increase the energy required for oxygen diffusion in the metal. It is apparent from the temperature ranges over which a cubic rate law is obeyed for the two materials that uranium reduces the range over which such a law is valid.

TABLE 2
OXIDATION RATE CONSTANTS
FOR PURE ZIRCONIUM
(Air at 1 atm)

Temperature (°C)	Rate Constant (mg ³ /cm ⁶ -sec)
625	6.63×10^{-5}
640	8.65×10^{-5}
650	6.47×10^{-5}
700	4.84×10^{-4}
850	8.88×10^{-3}
850	8.90×10^{-3}
901	2.79×10^{-2}
1000	3.09×10^{-1}
1025	2.28×10^{-1}

Figure 9. Cubic Oxidation
Rate Constant vs Recip-
rocal Temperature
for Zirconium

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Figure 10. Experimental Equipment

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III. TEMPERATURE TRANSIENT STUDIES

A. EXPERIMENTAL

1. Materials

Two materials were used in these studies: nonhydrided SNAP fuel alloy and hydrided alloy. Except for the elements listed below, the concentrations of trace constituents of the alloy and of the hydride were not greater than those given for the material used in the isothermal work.

<u>Nonhydrided Alloy</u>	<u>Element</u>	<u>Hydrided Alloy</u>
10.1 wt %	U	10.24 wt %
0.22 wt %	C	0.13 wt %
570 ppm	O	650 ppm
95 ppm	N	90 ppm
-	H	1.749 - 1.758 wt %

Each run required two right-cylindrical samples, nominally 0.625 in. in diameter and 0.625 in. long. In each case, one of the samples used for temperature measurement as described below contained, in one end, a conical hole of 15 degrees included angle with a base of approximately 0.160 in. The length of this sample was slightly greater than that of the other so that the masses of the two would be nearly identical; the observed variation in the weights of the two samples never exceeded 0.5%. The maximum variation in the diameters of the two samples was 0.0004 in. Except for cleaning, the samples were used as machined with an rms surface finish of approximately 150 μ in.

2. Equipment and Calibration

The experimental arrangement is depicted in Figure 10. The components of the system are described in the following paragraphs.

a. Balance

The Ainsworth Automatic Recording Balance used in the isothermal work was used in these studies. However, continuous weighings could not be made due to magnetic forces exerted on the sample by the induction field used for heating.

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Instead, the weight at the end of each run was determined by lowering the balance beam at approximately the same instant that the induction unit was shut down.

b. Temperature Measurement

Since temperatures to be used in these studies exceed the eutectic temperatures of zirconium-noble metal systems and since an oxidizing atmosphere was used, the use of thermocouples was excluded and optical pyrometry was required. It was necessary to provide a black-body hole in the sample to permit reliable temperature measurement because the emittance of the materials used is not known as a function of temperature and oxidation level. The pyrometer was a small-spot Infrascopes (Huggins Laboratories) which is an infrared instrument with a band pass of 1.8 to 2.5 microns. It is a double range, direct-reading pyrometer with the high range (750 to 5650°F) having a linear output of 0 to 100 mv. The optical system, including the pyrometer, mirror, and window (described below), was calibrated using a 3000°K black-body source (emissivity = 0.98) manufactured by the Rocketdyne Division of North American Aviation; the statistical error in the calibration was 9°C.

Simultaneous temperature measurements to 1200°C of an alloy sample with the pyrometer and a Pt/Pt-Rh thermocouple indicated that the conical black-body hole had an emissivity in the range of the pyrometer of 0.98. This value was assumed to be valid over the entire temperature transient used and for all levels of oxidation.

Since the pyrometer was focussed on only one of the two samples used in each run, it was necessary to obtain assurance that the measured temperature was applicable to both samples. Experiments were performed using nonhydrided alloy samples in vacuum, in helium, and in air to obtain this assurance. In these experiments, the temperature of the lower (black-body) sample was maintained constant, as indicated by the recorder tracing, while the apparent temperature of the curved surface of each sample was determined using a "Pyro" hand pyrometer. The positions of the two samples within the induction coil were then adjusted until their apparent temperatures differed by not more than 10°C. The procedure was then repeated at successively higher temperatures to obtain the optimum positions of the samples. In the final experiments, conducted with

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an air flow corresponding to that used in the study, the maximum temperature difference detected using the "Pyro" was 4°C over the range of 900 to 1700°C. In the case of hydrided material, impingement of a hydrogen-air flame at the bottom of the lower sample resulted in excessive heating of that sample. To obtain the proper positions for these samples, motion pictures were taken of preliminary runs. The brightness of the images of the two samples were compared after each run and the position of the samples were adjusted until no difference was visually detected.

c. Heating and Temperature Control

The samples were heated inductively using a 10-kc, 15-kva "TOCCO" motor-generator induction unit. The power output of the unit is controlled by varying the power supplied to the generator field coils. This power could be varied manually by means of a variable transformer or automatically by the controller.

The controller used was a Model 5052 "PREKORDER" programmer-recorder-controller (Research, Incorporated) having a 0- to 100-mv input.

d. Sample Support and Containment

Since weight change data obtained using samples containing a black-body hole could lead to erroneous conclusions when applied to solid cylindrical fuel elements, it was necessary to use two samples for each run. The upper sample, used to obtain weight data, was a solid cylinder. It was contained in an open support fabricated from high-density alumina (see Figure 11), and was supported on the apices of three alumina cones. Lateral motion within the support was prevented by three points loosely attached to the vertical support rods. These rods were held in place at the top by platinum wire and an alumina ring with an ID of approximately 3/4 in.; they were contained at the bottom by an alumina disc with recessed slots. The entire assembly was suspended from the balance on platinum wire.

The lower sample, containing the black-body hole, was supported on a high-density alumina tube (5/8-in. OD by 1/2-in. ID) the top of which was ground so that the sample rested on four knife edges. Lateral motion was prevented by three alumina rods which were ground so that only point contact was made with the sample; these rods fit into holes in an alumina ring fitted to the top of the supporting tube.

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Figure 11. Sample Supports

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Alumina was used for the support for several reasons: (1) it is readily available, (2) it is not appreciably attacked by zirconium at elevated temperatures, (3) it is nonconducting at the temperatures used in these studies, (4) it has a low thermal conductivity, and (5) it has a low coefficient of expansion. Point contact of the samples with the supports was desired to reduce the heat-sink effects which would be present with a large support area. The open structure of the supports minimized unwanted heating of the samples by re-radiation from the support, maximized the cooling rates, and maximized the flow of air at the sample surfaces.

The samples and their supports were contained in a quartz retort (48-mm OD) attached to the bottom plate of the balance. The retort was constricted at the lower end to support the 5/8-in. alumina tube in a centered vertical position above an infrasil window fused to the quartz retort; a small ground joint just above the window permitted gas flow through the retort.

e. Gas and Vacuum Control

An oil diffusion pump and high-capacity (300 ft³/hr) mechanical pump were used for evacuation of the system. To obtain the air flow used in these studies, air was pumped through the retort using only the mechanical pump. For several runs on the nonhydrided alloy the flow was restricted to approximately 54 ft³/hr by capillary tubing attached to the ball joint of the retort. Pressures were measured by an absolute pressure gage (0 to 1000 mm) and vacuum was measured by thermocouple and ion gages.

3. Experimental Procedure

For each run, two samples were selected which were adjacent cuts from the same fuel rod. They were rinsed a minimum of three times with petroleum ether to remove surface oil and grease, and were weighed separately using the recording balance. The lower sample was then lowered into the retort and centered on its support with the black-body hole down. The upper sample was placed in its support; the sample and support were suspended from the balance and weighed. The pyrometer was focussed, by means of a front-surfaced mirror, on the black-body hole, near its edge. Air, dried to reduce variation in its composition between successive runs, was pumped downward through the balance and retort. The upper sample and its support were re-weighed in

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flowing air. The balance beam was arrested and the chart drive of its recorder was turned off. The controller was allowed to warm up in a noncontrol mode and the induction unit was turned on with no power supplied to the field coils of the generator.

To start the run, the chart drive of the balance recorder and the chart drive and control mode of the controller were simultaneously switched on. At the end of the run, the induction unit was shut down at its main power switch and, essentially simultaneously, the balance beam was lowered to record weight change. Air flow was continued for 10 to 15 sec to permit back extrapolation of the balance recorder tracing to the end of the run. By means of two solenoid valves, controlled by a single switch, air flow was cut off and, simultaneously, evacuation was begun through the top of the retort and the balance (larger tubing). Approximately 1 min was required to reduce the pressure in the system to 25 microns, at which time the valve to the diffusion pump was opened. After evacuation to approximately 1 micron, helium was admitted to increase the cooling rate of the samples; after cooling, helium was pumped out and the system was filled with air. The upper sample and support were again weighed and the samples were removed from their supports and re-weighed.

For the nonhydrided alloy, duplicate runs were made in most cases. For the hydride, triplicate runs were made in all cases. The samples from two of these runs were dehydrided to determine the amount of hydrogen evolved during the run; the samples from the third run were used for metallographic examination. Dehydriding was accomplished by replacing the samples in the retort, which was evacuated to a pressure not greater than 10^{-5} mm Hg, and heating at approximately 1200°C for 15 to 20 min. Evacuation and heating were continued until the pressure returned to its initial value and no observable weight change occurred over a period of 3 to 5 min. The samples were allowed to cool in vacuum and then were re-weighed. The difference in weight represented the amount of hydrogen which remained in the sample after oxidation. Since the initial weight of hydrogen in the sample was known, the hydrogen evolved during oxidation could be calculated. The oxides and nitrides of zirconium and uranium are thermodynamically more stable than water or ammonia under the conditions used in this study; it is therefore not possible that hydrogen reduction of oxides or nitrides could occur during dehydriding. That only hydrogen was evolved

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during dehydrating is evident from these thermodynamic considerations and from the fact that no change in weight was observed upon subjecting a heavily oxidized sample of nonhydrated alloy to the dehydrating conditions.

B. DATA REDUCTION

It was necessary to obtain the data in a step-wise manner because continuous recording of the weight change was not possible due to the strong induction field. For each run, fresh samples were selected and the run was conducted as described earlier for a given length of time. In most cases, at least two runs were obtained for each period of time.

In the case of those runs using nonhydrated alloy with an air flow of $\sim 54 \text{ ft}^3/\text{hr}$, the recorder tracing obtained for the time between the end of the run and the start of evacuation was extrapolated to the end of the run to obtain the weight gain during the run. With the higher flow rate, this procedure could not be used with any confidence due to erratic fluctuations in the trace caused by the air flow (velocity $\sim 5 \text{ ft/sec}$) in the region of the sample. To obtain the oxidation values for these runs, a computer program was written to calculate the weight changes based on the isothermal rate constants given by Equations 4 and 5.

This program is based on the following considerations:

If

$$m^n = Kt \quad , \quad \dots (7)$$

then

$$\frac{d}{dt} (m^n) = K \quad . \quad \dots (8)$$

But

$$K = K_{\infty} e^{-\frac{\Delta H}{RT}} = K_{\infty} e^{-\frac{Q}{T}} \quad ; \quad \dots (9)$$

then for regions where

$$T = a + bt \quad , \quad \dots (10)$$

$$m^n = K_{\infty} \int e^{-\frac{Q}{a+bt}} dt \quad . \quad \dots (11)$$

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Then for the region from t_1 to t_2 ,

$$m_{t_1 \rightarrow t_2}^n = \frac{K_\infty}{Qb} \left[T_2^2 e^{-\frac{Q}{T_2}(1+S_2)} - T_1^2 e^{-\frac{Q}{T_1}(1+S_1)} \right], \quad \dots(12)$$

where

$$S_i = \sum_{k=1}^{\infty} \frac{(-1)^k T_i^k (k+1)!}{Q^k}. \quad \dots(13)$$

But since

$$b = \frac{T_1 - T_2}{t_1 - t_2}, \quad \dots(14)$$

$$m_{t_1 \rightarrow t_2}^n = \frac{(t_1 - t_2) K_\infty}{(T_1 - T_2) Q} \left[T_2^2 e^{-\frac{Q}{T_2}(1+S_2)} - T_1^2 e^{-\frac{Q}{T_1}(1+S_1)} \right]. \quad \dots(15)$$

In these expressions, t = time and T = absolute temperature.

Thus, the theoretical weight gain is obtained from the experimental temperature-time recording by breaking this trace into successive linear sections and adding the contribution of all sections; it is necessary, of course, that the change in the values of K_∞ and ΔH at 950°C be included in the calculation. For the calculation, the average value of the exponent, n , for each of the two temperature ranges was used.

Although the average values of the rate constants given by Equations 4 and 5 did not agree precisely with the results observed for the low flow rate, these results were "bracketed" by calculated values obtained using values for K_∞ and ΔH within the indicated uncertainties for these quantities. For each run, two computer results were used to obtain values of m_{calc} ,

$$m_{\text{calc}} = W_o m_c / W_c, \quad \dots(16)$$

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where W_o = observed total weight change, W_c = computer value of total weight change, and m_c = computer value of weight gain per unit area during the run. In each case, the values of m_{calc} obtained from the two computer calculations differed by not more than 4% and in most cases, the differences were less than 1%. For the lower flow rate the values thus obtained agreed, in every case, with the observed weight changes.

For the nonhydrided alloy using the higher flow, the oxidation values were calculated as described above, using the total weight change observed in these runs. The differences between the values of m_{calc} obtained from two computer calculations again were less than 1% in most cases and always less than 4%.

For the hydrided fuel, the total weight, W_o , used in Equation 16 was the difference between the observed weight change and the amount of hydrogen lost as determined from dehydriding of the samples after the runs. The assumption was made that no hydrogen was evolved after the induction heating coil was shut off. This assumption is considered reasonable since, in every run, the hydrogen-air flame collapsed almost instantaneously with collapse of the induction field. The values obtained for the oxidation levels are based on the initial areas of the samples (11.791 to 11.934 cm²) and do not consider the area added by cracking.

C. RESULTS

1. Nonhydrided Alloy

The nonhydrided alloy was first studied at a low air flow rate (~ 54 ft³/hr) using the temperature-time transient given in Figure 12. The results obtained from this study are given in Table 3 and in Figure 13. A typical observed temperature-time curve is given in Figure 14. No cracking of the samples was apparent at magnifications as high as 500X.

In order to reduce the probability of oxygen starvation, the remainder of this work was conducted at the maximum flow rate (~ 300 ft³/hr) obtainable with available equipment. It is fortunate that the behavior of hydrided fuel was investigated at this flow rate before the nonhydrided alloy, because the desired temperature transient could not be attained for the hydride due to rapid evolution of hydrogen. The results obtained for the nonhydrided alloy are given in

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Figure 12. Desired Temperature-Time Transient with Hydrogen Content Predicted for Fuel Samples

Figure 13. Weight Gain and Temperature vs Time for Nonhydrided Alloy at 54 ft³/hr

Figure 14. Typical Observed Temperature-Time Transient for Nonhydrided Alloy at 54 ft³/hr

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TABLE 3
AIR OXIDATION OF NONHYDRIDED FUEL ALLOY
($\sim 54 \text{ ft}^3/\text{hr}$)*

Alloy Rod Identification	Run Duration (sec)	Maximum Temperature ($^{\circ}\text{C}$)	Weight Gain (mg/cm^2)
348-6	40.8	1162	3.4 ± 0.2
348-6	42.6	1163	3.7 ± 0.4
348-2	57.5	1162	4.8 ± 0.3
348-2	75.7	1158	5.7 ± 0.4
348-2	76.8	1157	5.4 ± 0.4
348-2	92.8	1186	6.7 ± 0.2
348-2	105.0	1231	7.0 ± 0.3
348-2	105.4	1236	7.7 ± 0.2
348-2	120.2	1418	9.7 ± 0.4
348-2	121.2	1433	9.7 ± 0.3
348-5	130.4	1629	16.2 ± 1.2
348-5	131.4	1654	13.8 ± 0.9
348-5	144.8	1694	22.3 ± 0.4
348-5	141.4	1694	24.3 ± 1.8

*Transient used was that depicted in Figure 13.

Table 4 and in Figure 15 which also shows the transient observed for hydrided fuel and used for both materials at the higher flow rate. A typical observed temperature-time curve is given in Figure 16. Again no cracking of the alloy was observed, although minor cracks do appear in the oxide layer. A considerable amount of nitride was found in those samples subjected to the entire transient (see Figure 17), particularly on the bottom (downstream) surface. The fact that the weight gains for the shorter runs ($<100 \text{ sec}$) were less than those found for the lower flow is attributed to the higher temperatures experienced at the lower flow.

Metallographic examination revealed four distinct regions (see Figure 18): a porous outer layer, a columnar-grained phase, a thin region separating this

TABLE 4
AIR OXIDATION OF NONHYDRIDED FUEL ALLOY
($\sim 300 \text{ ft}^3/\text{hr}$)*

Alloy Rod Identification	Run Duration (sec)	Maximum Temperature ($^{\circ}\text{C}$)	Weight Gain (mg/cm^2) $\pm 5\%$
348-6	32.9	1033	1.01
348-6	33.2	1038	0.86
348-5	37.3	1027	1.25
348-6	38.3	1077	1.76
348-3	50.2	1065	2.48
348-4	50.6	1051	2.34
348-4	65.1	1126	3.87
348-5	65.8	1131	4.04
348-3	106.0	1269	7.8
348-3	105.4	1258	8.7
348-3	120.9	1402	10.7
348-3	141.0	1733	25.6
348-3	141.4	1741	24.5

*Transient used was that depicted in Figure 15.

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Figure 15. Weight Gain and Temperature vs Time for Nonhydrated Alloy at $300 \text{ ft}^3/\text{hr}$

Figure 16. Typical Observed Temperature-Time Transient for Nonhydrated Alloy at $300 \text{ ft}^3/\text{hr}$

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Figure 17. Nonhydrided Alloy
Oxidized in Air for 140 sec
(Center longitudinal sec-
tion at bottom of sample)

MAXIMUM TEMPERATURE = 1733°C 250X

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Figure 18. Nonhydrided
Alloy Oxidized in Air
for 140 sec (Center
longitudinal section
at top of sample)

MAXIMUM TEMP = 1733°C 500X (ELECTRO-ETCHED)

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a. SURFACE CURRENT 200X

b. BACK-SCATTERED ELECTRONS 200X

MAXIMUM TEMPERATURE = 1733°C

CENTER LONGITUDINAL SECTION AT TOP OF SAMPLE

c. URANIUM L_{α} X-RAY 800X

d. ZIRCONIUM L_{α} X-RAY 800X

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Figure 19. Electron Microprobe Photographs of
Nonhydrided Alloy Oxidized in Air for 140 sec

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phase from the next, and, finally, a structure typical of alpha zirconium-uranium alloys. This photomicrograph is almost identical to one obtained in earlier arc-jet studies of SNAP fuel.⁽²⁰⁾ The outer layer is undoubtedly oxide with some nitride. From electron microprobe analysis, the columnar-grained phase appears to be slightly depleted in uranium (see Figure 19a through d) and has been postulated⁽²⁰⁾ to be primarily a Zr-ZrO₂ eutectoid. The thin phase separating this eutectoid from the alloy is essentially devoid of zirconium (see Figure 19d) and very rich in uranium (see Figure 19c). It is reasonable to conclude that it is uranium (possibly uranium oxide) formed by precipitation from the columnar-grained eutectoid. This conclusion is supported (see Figure 19c) by the apparent increase in uranium concentration near grain boundaries in the alpha zirconium-uranium region adjacent to the uranium-rich phase. That the eutectoid and uranium-rich phases are formed well below the melting point of the alloy is demonstrated (see Figure 20) by the fact that they are present in a sample which did not exceed 1300°C.

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Figure 20. Nonhydrided Alloy Oxidized in Air
for 106 sec
(Center longitudinal section
at top of sample)

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TABLE 5
AIR OXIDATION OF HYDRIDED SNAP FUEL
($\sim 300 \text{ ft}^3/\text{hr}$)^{*}

Fuel Rod Identification	Duration of Run (sec)	Maximum Temperature (°C)	Hydrogen Content				Hydrogen Evolved (%)	Weight Gain (mg/cm ²) ± 10%
			N _H		Total H/Zr			
			Initial	Final	Initial	Final		
340-1	35.8	918	6.37	4.67	1.811	1.332	26.45	2.5
340-1	33.6	927	6.37	4.59	1.811	1.309	27.70	2.6
336-4	35.8	973	6.35	4.80	1.808	1.366	24.45	1.5
336-4	38.5	970	6.35	4.57	1.808	1.301	28.03	1.7
337-6	38.4	976	6.33	4.62	1.800	1.315	26.95	2.0
337-6	48.4	1003	6.33	3.51	1.800	1.000	44.47	2.8
337-6	50.8	962	6.33	2.98	1.800	0.848	52.91	3.8
337-6	51.0	969	6.33	2.94	1.800	0.838	53.41	3.8
337-6	66.0	1146	6.33	1.77	1.800	0.505	71.96	6.7
337-6	65.4	1169	6.33	1.42	1.800	0.404	77.52	5.9
340-1	100.1	1230	6.37	1.01	1.811	0.287	84.17	12.7
340-1	100.3	1204	6.37	1.21	1.811	0.346	80.92	12.5
336-4	142.5	1634	6.35	0.20	1.808	0.057	96.83	24.1
336-4	142.0	1674	6.35	0.30	1.808	0.085	95.30	22.3

^{*}Transient used was that depicted in Figure 24. Oxidation values do not include increase in surface due to cracking.

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2. Hydrided Fuel

The results obtained for hydrided fuel are given in Table 5 and in Figure 21. The transient used is that given in Figure 15. A typical observed temperature-time curve is given in Figure 22. The oxidation levels given in Table 5 do not include any increase in the areas of the samples due to cracking. Because of the extensive cracking (see Figures 23 and 24), the actual surface is conservatively estimated to be twice that used in the calculations, although a five- or ten-fold increase may be more realistic. If only a two-fold increase is assumed, it is apparent that the amount of oxidation (and nitridation) per unit area is less than for the nonhydrided alloy. This decrease is probably due to a shielding effect produced by the rapidly evolved hydrogen which reduces the oxygen concentration at the sample surface by reaction to form water and by a tendency to "drag" the surrounding atmosphere with it away from the sample. This hypothesis is supported by the experimental observation that the flame surrounding the sample did not appear to contact it but rather formed a halo around it. In addition, the amount of nitride present in the oxide layer was observed to be greater for the hydride than for the alloy.

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Figure 21. Hydrogen Content, Oxidation Weight Gain, and Temperature vs Time for Hydrided Fuel

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Figure 22. Typical Observed Temperature-Time Transient for Hydrided Fuel at 300 ft³/hr

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DIRECTION
OF
AIR FLOW

MAXIMUM TEMPERATURE = 969°C
CENTER LONGITUDINAL SECTION

7611-01275
(5X)

Figure 23. Hydrided SNAP Fuel Oxidized in Air for 51 sec

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DIRECTION
OF
AIR FLOW

MAXIMUM TEMPERATURE = 1569°C
CENTER LONGITUDINAL SECTION

7611-01276
(5X)

Figure 24. Hydrided SNAP Fuel Oxidized in Air for 140 sec

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The temperatures obtained for the first 35 sec differed for each of the three rods used in the study (see Figure 25). The reason for the difference is not clear. It may be related to the concentration of modifier which was different for each rod: 0.13, 0.11, and 0.14% carbon for rods 336-4, 337-6, and 340-1, respectively; the magnitude of the dip does increase with an increase in modifier concentration. Metallographic examination did not reveal any differences in structure or in the distribution of modifier that could account for the differences in behavior of the three rods.

Metallographic examination revealed the same four phases near the surface as were observed for the nonhydrided alloy. The fact that hydrogen is evolved from the interior of the samples by means of microcracks which extend to the surface is well illustrated by Figure 26. This photomicrograph was obtained from a sample of rod 340-1 subjected to only 33 sec of the transient and a maximum temperature of 921°C.

Figure 25. Typical Observed Temperatures for Three Hydrided Fuel Rods

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Figure 26. Hydrided SNAP Fuel Oxidized in Air for 33 sec

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IV. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

On the basis of the results reported in this study, it is possible to form the following conclusions:

- 1) In this work, samples were internally heated (approximately 90% of the volumes was within the depth of penetration of the induction field) so that the rate of hydrogen evolution obtained was much greater than that observed in arc-jet studies or to be expected upon reentry. Cracking was observed but not disintegration or spallation. It is expected that hydrogen evolution of the fuel will not, within itself, lead to disintegration of SNAP fuel elements upon atmospheric reentry.
- 2) The concentration of modifier may have a pronounced effect on the rate of hydrogen evolution during the first 30 to 40 sec of reentry.
- 3) Hydrogen evolution reduces the extent of oxidation per unit area, but the extensive cracking of the fuel increases the total area to such an extent that the total amount of oxidation is greater than for nonhydrided alloy.
- 4) Hydrogen evolution occurs so rapidly during the first 50 sec that the temperatures experienced by the fuel are significantly less ($\sim 150^{\circ}\text{C}$) than were predicted. This discrepancy, however, may be due to the method of heating and would be expected to be smaller with surface heating only.
- 5) Combustion of hydrogen with air occurs simultaneously with incandescence of the fuel.
- 6) Hydrogen evolution proceeds from all surfaces, including those of microcracks which extend to the surface.
- 7) The isothermal rate constants obtained in this work are applicable to temperatures near the melting point of SNAP fuel alloy.
- 8) Uranium migrates inward from the surface of oxidizing fuel and precipitates at the interface between the Zr-ZrO_2 eutectoid and the alpha alloy.

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9) Considerable nitriding occurs with both hydrided and nonhydrided fuel, especially at the higher temperatures reached near the end of the temperature transient.

B. RECOMMENDATIONS

In view of the observed formation of nitrides, it is desirable to obtain rate data for nitriding. Indeed, it may be advisable to obtain rate data for both pure nitrogen and for pure oxygen at temperatures from 900°C to near the melting point, so that a more accurate model may be constructed for predicting reentry conditions. Theoretical work by H. S. Levine⁽²¹⁾ suggests that presence of nitrogen in air may have pronounced effects on oxidation behavior at high temperatures due to changes in the boundary conditions.

The observed differences in the behavior of the three fuel rods used in this study suggest that further work is required to delineate the effects on hydrogen evolution of variation in the microstructure of the fuel and of variations in the modifier concentration.

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