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THERMOPHYSICAL PROPERTIES OF SNAP FUELS

(Title Unclassified)

By

R.E. TAYLOR
C.J. AMBROSE

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ABSTRACT

The specific heat, thermal diffusivity, thermal conductivity, electrical resistivity, and thermal expansion of various zirconium-uranium hydrides were measured. The coefficient of thermal expansion was found to be 6.89×10^{-6} per °F from room temperature to 1400°F, which agreed with previous results from this laboratory. The specific heat results, which increased from 0.102 cal/gm-°C at 400°K to 0.170 cal/gm-°C at 850°K for Zr - 10 wt % U alloy with an H/Zr ratio of 1.68, agreed within 8% of the results obtained using a simple theoretical model. Calculations of the specific heat based upon this model are within 8% of the experimental results obtained by numerous laboratories on a variety of compositions. Consequently, it is possible to calculate the specific heat as a function of composition and temperature, except near a phase change. The thermal conductivity of zirconium-uranium hydrides is markedly influenced by the composition but is nearly temperature independent. The formation of a hydrogen sublattice greatly increases the nonelectronic contribution to the thermal conductivity.

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I. INTRODUCTION

As a safety mechanism, it is desirable that a Systems for Nuclear Auxiliary Power (SNAP) reactor will disintegrate at the time of atmospheric reentry. If the reactor contains an inventory of fission products at the time of reentry, it is further desirable that the fuel elements be released at an altitude high enough that they can be melted and dispersed so finely that they will not present a measurable hazard at ground level. To insure that this will happen, the physical properties of the solid materials must be known to the melting point of the fuel.

This is an interim Aerospace Safety report on the physical properties of hydrided Zr - 10 U alloy of varying H/Zr ratios conducted primarily at lower temperatures. The fuel alloy has a melting point around 1800°C (3250°F). To be sure that the extrapolation of the physical behavior of the fuel is correct at high temperatures, it is necessary to understand its behavior at low temperatures. At temperatures of about 650°C (1200°F) hydrogen begins to dissociate at appreciable rates from the fuel, and the dissociation pressure increases exponentially with increasing temperature. Hydrogen fills the interstitial lattice of the alloy and temperature changes expand and contract the lattice by the sorption and desorption of hydrogen. Consequently, hydrogen dissociation from the alloy affects the physical properties.

Samples were prepared from the same fuel ingot, except for studies involving varying carbon concentrations, in which case the samples came from different ingots. Samples were hydrided utilizing the same system and procedures used for fuel element fabrication.¹ Each sample was machined to final dimensions by the same technique. Samples for the physical property measurements were analyzed chemically and metallographically, to define their structure and composition.

The following measurements were made on SNAP fuel alloy material:

- a) Electrical resistivity
- b) Specific heat
- c) Thermal diffusivity
- d) Density
- e) Thermal conductivity
- f) Thermal expansion.

The hydrogen dissociation pressure of the hydride above 650°C (1200°F) necessitated the fabrication or alteration of equipment to withstand the high pressures. The electrical resistivity and thermal diffusivity apparatus were equipped with high pressure valves and designed so a constant hydrogen composition was maintained in the sample for a given temperature by balancing the dissociation pressure with pressure from a hydrogen gas bottle. The thermal expansion apparatus was designed for an extremely small void volume, so hydrogen dissociation did not change the composition appreciably in the samples.

II. EXPERIMENTAL DATA AND RESULTS

A. SAMPLE PREPARATION

Since physical properties were to be measured on the same material as used in the SNAP reactors, samples were obtained from ingots produced in the identical fabrication facility. The aim of this program was reflected in the choice of samples, which included different hydrogen concentrations which may be present in the reactor during its operation. The influence of compositional changes must be investigated for a complete knowledge of the reactor's behavior.

The composition of the SNAP fuel alloy is 90 wt % Zr, 10 wt % U, and 0.15 wt % carbon. This material is hydrided to a H/Zr of 1.72 or 1.82, depending upon its application. The fuel alloy is melted and extruded three times to obtain homogeneous material. Carbon, in the form of ZrC, is added to the fuel alloy to prevent cracking during the hydriding process. Samples for this study were prepared with varying concentrations of hydrogen and carbon in order to assess the influence of these compositional variables upon behavior.

Hydrogen compositions were calculated from weight gains after hydriding. Experience has demonstrated that this method of determining hydrogen composition of the material is at least as reliable as chemical analysis, which may be biased by size, location, or local inhomogeneity of the sample. Although the possibility of a hydrogen gradient in the samples is not ruled out, these samples were small enough so that they should have been homogenized during the hydriding cycle.

Metallic impurities in the alloy did not exceed 0.25 wt % of the total metallic constituents.

Metallographic samples were taken from each rod. Figures 1 through 5 are representative microphotographs of the physical property samples. The microstructure of the alloy is, of course, affected drastically by the hydrogen content. There is a uniform dispersion of the uranium and carbide particles throughout the alloy. The samples were homogeneous and free of cracks.

B. ELECTRICAL RESISTIVITY

Electrical resistivity is used as the thermometer in the experimental specific heat measurements described in Section C. It is also useful in explaining heat conduction mechanisms as discussed in Section D.

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Figure 1. Microphotograph of SNAP Fuel Alloy H/Zr = 0

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Figure 2. Microphotograph of SNAP Fuel Alloy H/Zr = 0.50

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Figure 3. Microphotograph of SNAP Fuel Alloy H/Zr = 1.2

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Figure 4. Microphotograph of SNAP Fuel Alloy H/Zr = 1.57

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Figure 5. Microphotograph of SNAP Fuel Alloy H/Zr = 1.81

The electrical resistivity is determined by the dc potentiometric drop method in which the voltage drop caused by the passage of a dc current through the sample is compared to the voltage drop across a standard resistor. The current is then reversed and the process repeated in order to eliminate the effects of stray emfs. A closeup of the sample holder is shown in Figure 6. With this holder, the electrical resistivities of four samples can be measured at one time. The samples are 1/8-in. diameter rods, 3 in. long. Three of the mounted samples are visible at the left of Figure 6. The current can be switched into any one of the four samples and the resulting voltage drop compared to that across the standard resistor. Then the next sample can be substituted by appropriate switching, since all of the samples have one common terminal provided by the metal end plate shown at the extreme left of the figure. The holder is placed inside a stainless steel vacuum tube which in turn is placed inside a furnace. A view of the furnace, tube, and associated valving which permits control of the hydrogen environment is shown in Figure 7. Hydrogen pressure is adjusted to correspond to the appropriate dissociation pressure isochore for the hydride composition under test. The temperature is measured by the sheathed thermocouples shown in Figure 6. The data are accurate within $\pm 1\%$.

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Figure 6. Electrical Resistivity Sample Holder

The results shown in Figure 8 include data for zirconium metal² as well as for hydrided fuel alloy. This figure shows that the electrical resistivity of zirconium hydride is higher than that of zirconium metal at room temperature. As hydrogen is added to the zirconium-uranium alloy, the electrical resistivity decreases. For example, the electrical resistivity of the nonhydrided Zr - 10 U alloy is $79 \mu\Omega\text{-cm}$ at room temperature, while the resistivity of the alloy with an H/Zr of 0.5 is $70 \mu\Omega\text{-cm}$ and the resistivity of the alloy with an H/Zr of 1.2 is only $55 \mu\Omega\text{-cm}$. At higher H/Zr ratios, the alloy undergoes a phase change and the electrical resistivity of the delta and epsilon phases decreases with increasing hydrogen content; the resistivity of H/Zr = 1.81 material being less than that of material of H/Zr = 1.74.

Except for the 1.2 H/Zr material, the electrical resistivity increases almost linearly with temperature, which is the typical behavior for good electrical conductors. Of course, the effect of phase change is noted in the lower hydrides and in the nonhydrided material.

C. SPECIFIC HEAT

The specific heat of zirconium hydride and zirconium-uranium hydried has been the subject of numerous investigations in recent years. One of the best experimental programs on the $\alpha + \delta$ phase zirconium hydride was the work of Douglas

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Figure 7. Electrical Resistivity Apparatus

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Figure 8. Electrical Resistivity of Zirconium-Uranium-Hydrides Concentrations

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and Victor of the National Bureau of Standards,³ while Tomasch,⁴ Beck,⁵ Hedge and co-workers,⁶ Taylor,⁷ and Finch⁸ investigated the specific heats of the hydrides of zirconium or zirconium-uranium in the δ and ϵ phases.

In order to understand the specific heat of the various hydrides, the present effort was not limited to performing additional experimental measurements. Instead some effort was spent in explaining the specific heat of this material from a semitheoretical viewpoint. This effort has provided a semitheoretical knowledge of the effect of hydrogen on the specific heat. This allows one to predict the specific heat of any composition as a function of temperature, except near a phase change, and serves to limit the number of experimental measurements required to gain sufficient "understanding" of the effects of temperature and composition on the specific heat. No attempt was made to develop a precise mathematical model of the specific heat of zirconium hydride or to advance fundamental knowledge of the specific heat theory, as this is considered to fall outside the scope of the present work. However, it should be noted that progress on such a model is being made.⁹

Inelastic neutron scattering experiments have shown that the lattice vibration spectrum of zirconium hydride is nearly that of a linear diatomic lattice with very large mass ratios.¹⁰ An acoustical branch with a characteristic temperature of 230°K is observed along with a narrow optical branch with a characteristic temperature of 1500°K. Since the optical branch energy linewidth is quite narrow, these modes correspond to a single frequency. Consequently, it has been predicated that the hydrogen nuclei will make an independent Einstein contribution to the specific heat at constant volume, C_v , and that the thermal vibration contribution to C_v^* can be separated into two additive parts: one due to the gas nuclei $C_v(H)$, the other to the zirconium $C_v(Zr)$.³ The zirconium sublattice should make a typical Debye contribution ($\theta_D = 230^\circ K$) which will be saturated at the Dulong-Petit value above room temperature (i. e., $C_v Zr = 6$). Because of the high characteristic temperature associated with the gas nuclei, $C_v(H)$ will have a strong positive temperature coefficient causing $C_v(ZrH)$ to increase rapidly with increasing temperature since

$$C_v(ZrH) = C_v(Zr) + C_v(H) \quad \dots (1)$$

*Capital C refers to a per mole basis while small c refers to a per gram basis.

By comparing the specific heats of ZrH to ZrD, Tomasch was able to show the reasonableness of the above approach.³

In the present case Equation 1 was changed to

$$c_p(\text{ZrH}) = c_p(\text{Zr}) + c_v(\text{H}) \quad , \quad \dots (2)$$

where the specific heat at constant pressure c_p^* is substituted for C_v .

Equation 2 assumes that the specific heats at constant pressure are additive (Knoop's rule) and that $c_v(\text{H}) = c_p(\text{H})$. The second assumption should be fairly good below about two-thirds θ_E or 1000°K since c_p and c_v are nearly equal until one approaches the characteristic temperature. The first assumption is open to serious questioning from a fundamental viewpoint. However, it is possible to add specific heats at constant pressure at temperatures above the characteristic temperatures of all the components. Then:

$$c_p(\text{ABC}) = c_p(\text{A}) + c_p(\text{B}) + c_p(\text{C}) \quad . \quad \dots (3)$$

Since the characteristic temperatures of most components are less than room temperature, Equation 3 is generally useful. In fact, for many materials this equation can be used even at temperatures which are one-fourth the characteristic temperature, since materials which alloy in large proportions tend to have similar characteristic temperatures. For example, one may calculate the specific heats of Cu-Ni alloys at 50°K using Equation 3. In this regard, the hydride systems are unique in that a material with a high Debye temperature is "alloyed" with a material with a much lower characteristic temperature. However as the temperature approaches the Einstein temperature of the hydrogen nuclei, the error involved in adding the specific heats at constant pressure should become negligible. As indicated below, calculations of the specific heat of zirconium hydride indicates that the error is small at room temperature. Since the error caused by this assumption should be less at higher temperatures, the assumption is believed to be a reasonable one. It should be pointed out that the 1500°K Einstein temperature determined by inelastic neutron scattering is valid for α , δ , γ , and ϵ phases of zirconium hydride.⁴

*Capital C refers to a per mole basis while small c refers to a per gram basis.

By making the above assumptions and assigning an Einstein temperature of 1500°K to the optical branch mode of the hydrogen nuclei, it is possible to use Equation 3 to calculate the specific heat of any zirconium hydride or zirconium-uranium hydride. The procedure is as follows. Figure 9 is a plot of C_v vs θ_E/T obtained from the Einstein theory of specific heat.¹¹ With the aid of this curve, the specific heat of hydrogen can be obtained at any temperature T since θ_E equals 1500°K . Figure 10 shows the specific heats of zirconium¹¹ and uranium.¹¹ The specific heat of zirconium-uranium hydride is obtained by the following:

$$(c_p \text{ Zr})(\text{wt fraction Zr}) + (c_p \text{ U})(\text{wt fraction U}) + (c_p \text{ H})(\text{wt fraction H}) = c_p \text{ ZrUH.} \quad \dots (4)$$

A specific heat calculation is shown in the Appendix.

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Figure 9. Plot of C_v vs θ_E/T

In order to check the validity of this approach the specific heats of the various compositions which were measured by the Bureau of Standards³ were calculated. The results are compared to the experimental values in Figure 11. The

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Figure 10. Specific Heat of Zirconium and Uranium

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Figure 11. Comparison of Calculated and Experimental Specific Heats

results agree within a few percent below 350°C except for $\text{ZrH}_{0.701}$ at 250°C where the difference is 8%. Because of the effect of the phase change on the experimental specific heats, the results are not compared above 450°C.

The calculated specific heats of various compositions are compared in Figure 12. From Figure 12 it can be seen that the difference between the specific heat of the $\text{ZrH}_{1.56}$ and $\text{ZrH}_{1.74}$ is only 0.003 cal/gm-°C (3%) at 100°C and 0.015 cal/gm-°C (8%) at 700°C. Because of this it is possible to compare the results of various workers. This is done in Figure 13, where the experimental data (biased to ZrH_x if uranium was present) for various researchers are compared to that calculated for $\text{ZrH}_{1.74}$. In general the agreement is reasonably good and, except for the Armour Research Foundation data,⁶ have the same temperature dependency up to 800°K.

The present results were obtained by the pulse heating technique similar to that described previously.⁷ The apparatus is shown in Figure 14, and Figure 15 is a schematic of the electrical circuit. Following the electrical resistivity determination (see Section B), the sample was soft-soldered into pistons which served as high-current electrical contacts while permitting sample expansion. Platinum voltage probes were spring-loaded across the central centimeter of the sample. The pistons, sample, and voltage probes were enclosed in a vacuum chamber. Current to heat the specimens was supplied by a bank of heavy-duty 12-volt batteries. Heating rates were controlled by varying the value of the external resistor and by varying the number of batteries used. The duration of the pulse was controlled by a high-current relay, and could be controlled from 0.010 to 0.50 sec by means of a timing circuit. When the relay was closed, current flowed from the batteries through a standard resistor, sample, variable resistor, and back to the batteries. Heavy copper-lead wires or bus bar were used throughout the circuitry.

Photographic reproductions of traces obtained on a dual-beam oscilloscope were used for recording data input. The current flowing through the specimen was determined from the voltage drop across the standard resistor. The current through the specimen and the voltage drop across the central portion of the specimen were measured simultaneously and continuously, as a function of time, by the oscilloscope. The voltages and currents were measured on the photographic record at discrete-time intervals and the specific resistance at each time interval is calculated from the relationship

$$\rho = \frac{A E}{L I} , \quad \dots (5)$$

Figure 12. Calculated Specific Heats of Several Zirconium Hydride Compositions

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Figure 13. Specific Heat of Zirconium Hydride

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Figure 14. Pulse Heating Apparatus

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Figure 15. Schematic of Pulse Heating Apparatus

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where

A = cross-sectional area of the sample

L = distance between voltage probes

E = voltage, and

I = current.

The specific resistance as a function of time is then determined.

The specific heat at any temperature T is given by the expression

$$c_p = \frac{EI}{J} \frac{\left(\frac{d\rho}{dT}\right)}{\left(m\frac{d\rho}{dt}\right)}, \quad \dots (6)$$

where

J = 4.186 watts-sec/cal

m = mass of the sample between the voltage probes

$d\rho/dT$ = temperature coefficient of the resistivity at temperature T, and

$d\rho/dt$ = time rate of change of the resistivity at T.

The specific heat results are not affected by neglecting the influence of the thermal expansion on the resistivity. The experimental data obtained during the present work for 1.81 H/Zr material, which are shown in Figure 16, increase from 0.0905 cal/gm-°C at 100°C to 0.154 cal/gm-°C at 550°C.

The present results have been corrected to account for the uranium present, and these results are compared to those of other researchers and to the "theoretical" value in Figure 13. The results tend to be lower than that of other workers or the theoretical value. However, the difference between the present experimental values and the theoretical is only about 8%. In fact, virtually all the experimental values up to 800°K are within ±8% of the theoretical values. Consequently, it is felt that the theoretical values represent the true specific heats within ±8% from 300 to 800°K.

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Figure 16. Specific Heat of Zirconium-Uranium Hydride

D. THERMAL DIFFUSIVITY

The flash diffusivity method, which was originally described by Parker et al.,¹² was used for the thermal diffusivity measurements. In this method a pulse of energy is radiated to the front face of a disk-shaped sample, and the resulting temperature history of the rear face is used to determine a diffusivity value. The ambient temperature of the sample is controlled by a tantalum tube heater, and the pulse of energy raises the average sample temperature only a few degrees.

In the original description by Parker, et al., a xenon flash lamp was used as the energy source. The flash lamp is limited by the fact the emitting area is so large that optically focusing the energy on a small specimen is not very practical. Therefore, one must keep the flash lamp near the sample, which is not practical at high sample temperatures. On the other hand, a laser efficiently concentrates the flash lamp energy into a coherent light beam well suited for irradiating small samples which are enclosed within vacuum furnaces. Consequently, our laboratory uses a laser beam energy source for the flash diffusivity apparatus.

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Figure 17. Thermal Diffusivity Apparatus

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Figure 18. High Temperature Flash
Diffusivity Apparatus

The rear face temperature is measured with thermocouples. Each leg of the thermocouple is spot-welded separately onto the back face and the sample acts as the bead, thus decreasing the response time. The temperature response is recorded by photographing an oscilloscopic trace.

The sample holder and tantalum tube heater of the low temperature (i. e., no provisions for controlling hydrogen pressure) apparatus is shown in Figure 17. A vacuum chamber (not shown) fits over the tantalum tube heater and shield. The mounted sample, which is only 0.25 in. diameter by 0.10 in. thick, and radiation shields are shown near the heater. During a measurement the sample and holder are placed inside the tube heater. The laser is shown in the lower left hand corner of the photograph. The vacuum system is located underneath the table.

The second apparatus, which is quite similar to the low temperature apparatus except that it incorporates a hydrogen pressure system, is shown in Figure 18. This system is designed to balance the hydrogen dissociation pressure with bottled hydrogen and, thereby, keeping a constant composition for a hydrided fuel sample to temperatures approximating 800°C. Since the hydrogen dissociation pressure increases rapidly in this temperature range, there will be no attempt to keep hydrogen in the sample above these temperatures. This system uses a recording optical pyrometer to measure the sample's thermal history in the high temperature range. Data obtained on the two apparatus agree within 2%. However, the second system was completed late in the fiscal year. Consequently, most of the data were obtained with the low temperature system.

Figure 19 shows the thermal diffusivity of the SNAP fuel alloy hydride at different hydrogen concentrations. Usually, these samples were heated to temperatures below which appreciable hydrogen would be lost, so a nearly constant hydrogen composition could be maintained in the samples. As shown in Figure 19, the diffusivity of the samples increases with increasing hydrogen concentrations in the temperature range studied. Below $H/Zr = 1.5$, however, the diffusivity is not greatly affected by changes in hydrogen composition. The thermal diffusivity at 100°C for these hydrided samples is $0.13 \text{ cm}^2/\text{sec}$ for $H/Zr = 1.93$, $0.09 \text{ cm}^2/\text{sec}$ for $H/Zr = 1.71$, and $0.06 \text{ cm}^2/\text{sec}$ for $H/Zr = 0.05$; obviously, the diffusivity of the hydrided material is dependent upon

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Figure 19. Thermal Diffusivity of SNAP Fuel Alloy Hydride

hydrogen concentration, with greater dependency in the high H/Zr range. The diffusivity of 0.5 and 1.2 H/Zr material approach each other above 400°C and continue to gradually decrease. The data for the higher composition material does not seem to converge, but rather maintains a degree of separation. This shows that thermal diffusivity is dependent upon hydrogen concentration in the 1.5 to 1.9 H/Zr range.

Figure 20 shows the thermal diffusivity of a sample (H/Zr 1.93) that was heated to 950°C (1742°F). No attempt was made to keep a constant hydrogen composition in this sample; in fact, a dynamic vacuum was maintained throughout the experiment. The diffusivity of the material shows a definite decrease to a minimum around 575°C and then the diffusivity increases. This minimum has been observed¹³ before as a eutectoid temperature for zirconium hydrogen system. Undoubtedly, the sample was dehydrided during this experiment, and the second curve on the graph represents the data obtained on a nonhydrided sample. The samples had thermocouples spot welded to their back surface, and considerable electronic noise is picked up at high temperatures. It appears, therefore, that the data for the dehydrided and the nonhydrided material start to approach each other around 1100°C.

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Figure 20. Thermal Diffusivity of Hydrided and Nonhydrided SNAP Alloy

A gradual decrease in diffusivity of the hydrided samples was observed in repeated measurements on the same sample. In some of the cases a decrease in hydrogen concentration was observed, and the thermal diffusivity decreased also. In a few cases, however, there was no change in sample weight, and the diffusivity showed a decrease when the sample was measured again. This phenomenon is displayed by comparing the sample with $H/Zr = 1.93$ in Figures 19 and 20.

Thermal diffusivity is sometimes very sensitive to small material variations. The diffusivity of three different carbon concentrations (0.03, 0.08, and 0.12 wt % C) were measured to determine if it affected the measurements. Varying amounts of carbon had no effect upon the thermal diffusivity of the material.

Thermal diffusivity of SNAP fuel alloy hydride was also measured for different hydrogen concentrations. Particular emphasis was concentrated on H/Zr 1.6 to 1.9 material, since the reactor fuel elements will have this composition. Hydrogen redistribution due to thermal gradients within the fuel element will result in a hydrogen gradient in the element. Upon reentering the earth's atmosphere the elements will dehydride and pass through the lower hydrogen concentrations.

E. DENSITY

Densities of SNAP fuels were measured as a function of hydrogen content up to H/Zr ratios approaching the theoretical limit of 2.0. Measurements and techniques were straightforward, using precision balances and Archimedes' principle. Figure 21 shows the effect of various hydrogen concentrations on the densities of 90 Zr - 10 U fuel. An average fuel rod density was used for values in the figure, and the accuracy was within $\pm 3\%$. It will be noted that density decreases approximately linearly with hydrogen content up to H/Zr = 1.6; the density at H/Zr = 1.5, for example, being 6.2 gm/cc.

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Figure 21. Density of 90 Zr - 10 U Hydride

F. THERMAL CONDUCTIVITY

The thermal conductivity may be obtained by measuring the thermal diffusivity α , and calculating the conductivity from the relation

$$k = \alpha c_p d, \quad \dots (7)$$

where c_p is the specific heat (Section C) and d is the density (Section E). Thermal conductivity values obtained in this fashion are usually as reliable as those which are measured by a direct method and are more easily obtained. The sample size restrictions are less severe for thermal diffusivity measurements than for thermal conductivity measurements. In addition, the diffusivity measurements

are better suited for zirconium hydrides because of the tendency for the hydrogen composition to vary along the temperature gradient required for a conventional thermal conductivity measurement.

One can readily determine the thermal conductivity of the various samples for which specific heat values are available. In view of the success of Equation 2 in calculating specific heats of various composition, the specific heat was calculated in those cases where it was not measured.

Figure 22 shows the thermal conductivity values obtained. Diffusivity values have been obtained above 500°C only on material of H/Zr less than 1.5. Because of the eutectoid phase change at 550°C for $\alpha + \delta$ hydride, the specific heat of this material increases sharply near 550°C and is not well defined. Consequently, the thermal conductivity cannot be calculated above 500°C at this time.

Thermal conductivity of this material exhibits a definite pattern as seen in the figure, since increasing the hydrogen concentrations in the Zr-U-H_x system increases the thermal conductivity. The material's conductivity at 100°C is 0.084 cal/cm-°C-sec for H/Zr = 1.93, 0.054 cal/cm-°C-sec for H/Zr = 1.77, and 0.041 cal/cm-°C-sec for H/Zr = 1.20; the greatest influence of hydrogen is observed in the δ and ϵ phases. The thermal conductivity of the 1.93 H/Zr material appears to increase above 300°C.

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Figure 22. Thermal Conductivity of Zirconium-Uranium Hydride

Contemporary theory states that the heat conduction in electrically conducting materials is the sum of electronic k_e and phonon conduction k_p , i.e.,

$$k_t = k_e + k_p, \quad \dots(8)$$

where k_t is the total conductivity. The Wiedemann-Franz law can be expressed as

$$k_e = \frac{LT}{\rho}, \quad \dots(9)$$

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Figure 23. k_t and k_e Value for Three Hydride Compositions

where L is a constant, T is the absolute temperature, and ρ is the electrical resistivity. Although the phonon conduction should follow a $1/T$ law, there is ample evidence that it may not do this.¹⁴ In any event, the total conduction must be larger than the electronic conductivity alone and the ratio of electronic to phonon conduction can be established by measuring k_t and ρ .

The values for k_t and k_e are plotted for three compositions in Figure 23. From this figure it can be seen that the electronic conductivity accounts for all the heat conduction above room temperature in the 0.5 H/Zr alloy and accounts for 75% of the heat conduction in 1.2 H/Zr material at room temperature, increasing to 86% of the heat conduction at 500°C. However, the electronic contribution is only half the total conduction in 1.84 H/Zr fuel. Consequently, the major change in the heat conduction of this material caused by adding hydrogen is the increase in the phonon conduction. This is illustrated in Figure 24 which shows k_e , k_p , and k_t for each of these compositions. As additional thermal conductivity and electrical resistivity data become available, it should be possible to estimate the total thermal conductivity for any given composition of Zr - 10 U - H_x.

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Figure 24. Electron and Phonon Contribution to Thermal Conductivity of Zr - 10 U - H_x at 100°C

G. THERMAL EXPANSION

A schematic diagram of the thermal expansion apparatus is shown in Figure 25. A fused quartz system was used for these expansion measurements on the SNAP material. The furnace was controlled by a temperature program controller which provided a predetermined heating rate to the sample. A metal heat sink was placed inside the furnace to further restrict thermal surges. The recording thermocouple (chromel-alumel) was located between the heat sink and the quartz sample holder, while the controlling thermocouple was between the furnace and the heat sink. Hydrogen dissociation pressure was measured by a strain-gauge type pressure transducer and the output was recorded on a strip-chart recorder. Changes in sample dimensions were detected by movement of

Figure 25. Schematic of Thermal Expansion Apparatus

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Figure 26. Thermal Expansion Sample Chamber and Associated Parts

the core of the linear variable differential transformer. The resulting electrical signal from the output of the LVDT was transmitted to a recorder.

The sample chamber and its associated parts are shown in Figure 26. To avoid excessive loss of hydrogen at high temperatures, the apparatus was designed to give a null void volume system. The small amount of hydrogen which dissociated from the fuel at the higher temperatures would thus not significantly change the hydrogen concentration of the sample. The hydrided sample rested on the bottom of a quartz chamber with a quartz push-rod on top of the sample. The LVDT core was connected to the top of the rod and was positioned inside the LVDT coil.

Expansion, pressure, and temperature were measured during each experimental determination. A dual pen recorder, with two separate amplifiers and variable adjustments to standardize the chart, was used to record the data. Normally, expansion and pressure were recorded while the temperature was measured manually with a precision portable potentiometer.

Thermal expansion measurements are very susceptible to thermal surges using this apparatus. The apparatus was thoroughly insulated to eliminate air drafts. Heating rates were normally $3^{\circ}\text{F}/\text{min}$ to permit a sample to be heated to approximately 1100°F within a normal work day. The sample was soaked overnight and the following day the sample was heated to 1400°F . The contraction of the sample was also measured to room temperature, with cooling rates which were identical to the heating rates. Sample weight and dimensions were taken after each run to determine if there had been any loss of hydrogen.

Test specimens were taken parallel to the line of original billet extrusion and hydrided to desired composition. Thermal expansion samples were ground to a standard sized cylinder (0.25 in. by 2.0 in.).

Thermal expansion of the SNAP fuel alloy hydride was determined in the temperature range from room temperature to 1400°F . A series of different hydrogen concentrations from H/Zr 1.6 to 1.9 were studied. Three concentrations of carbon were also investigated.

Instantaneous thermal expansion can be obtained from Figure 27. This curve represents an average of samples examined in the ratio of H/Zr from 1.5 to 1.9. The three carbon concentrations (0.03 to 0.12 wt %) investigated had no detectable effect on thermal expansion. With the small void volume the slight change in H/Zr during testing did not significantly affect the thermal expansion of this material.

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Figure 27. Instantaneous Thermal Expansion Curve for
SNAP Fuel (H/Zr 1.5 to 1.9)

TABLE 1

COEFFICIENT OF LINEAR THERMAL EXPANSION
OF SNAP FUEL ALLOY HYDRIDE

Initial Composition Zr - U	H/Zr	Source	Room Temperature to Temperature (°F)	400	600	800	1000	1200	1400
90-10	1.5 to 1.9	AI	$\alpha \times 10^{-6}$ (in./in. - °F)	4.57	5.10	5.56	6.04	6.60	6.89
90-10	Avg. 1.8	ARF	$\alpha \times 10^{-6}$ (in./in. - °F)			5.79	6.78	7.05	7.38
93-7	1.8	AI	$\alpha \times 10^{-6}$ (in./in. - °F)				5.63	6.12	6.56

AI - Atomics International

ARF - Armour Research Foundation

Table I shows the linear thermal coefficient of expansion (α) for the hydrided SNAP fuel alloy in the delta and epsilon phases. The results in this table represent an average α for samples with varying hydrogen and carbon concentrations. The thermal expansion of this material was independent of hydrogen concentration for the compositions investigated. Calculation of these values were obtained by the following equation:

$$\alpha = \frac{\Delta L}{L_o \Delta T} , \quad \dots (10)$$

where:

α = coefficient of thermal expansion

L_o = original length of sample

ΔL = change in length of sample, and

ΔT = change in temperature.

The present values are slightly higher than values for 93 Zr - 7 U alloy hydride (H/Zr = 1.80) obtained previously by AI.¹⁵ Since the alloy expansion was measured basically with the same technique and apparatus, the increase in expansion was due to increasing the uranium content in the fuel alloy. Values reported by Armour Research Foundation⁶ are 10% higher than the present work within the temperature range. The estimated error in the present values are $\pm 5\%$.

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III. SUMMARY AND CONCLUSIONS

The electrical resistivity, specific heat, thermal diffusivity, density, thermal conductivity, and thermal expansion of the SNAP alloy hydride were determined as a function of temperature and composition. In general, the electrical resistivities of these alloys increases almost linearly with temperature from 55 to $70\mu\Omega$ -cm at room temperature (depending on composition) to 108 to $130\mu\Omega$ -cm at 500°C . The nonhydride material has the highest resistivity and up to a H/Zr ratio of 1.7 the resistivity decreases as hydrogen is added.

The specific heat results agreed within 8% of the results obtained using a simple theoretical model. Calculations of the specific heat based upon this model are within 8% of the experimental results obtained by numerous laboratories on a variety of compositions. Consequently, it is possible to calculate the specific heat as a function of composition and temperature except near a phase change.

The thermal conductivity of zirconium-uranium hydrides is markedly influenced by the composition. As hydrogen is first added to the alloy, the phonon contribution to the conductivity is negligible. However, as additional hydrogen is added, the phonon contribution of the hydrogen sublattice becomes appreciable and equals the electronic contribution at H/Zr = 1.8. In contrast to the effect of hydrogen on k_p , k_e is only changed slightly by compositional variations.

The thermal expansion values, which are accurate with $\pm 5\%$, agreed with previous results from this laboratory. However, the present values are 10% lower than the results reported by Armour Research Foundation.

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IV. RECOMMENDATIONS

Physical properties of the fuel must be determined in the temperature range from 800°C to the melting point. No attempt has been made to retain the hydrogen in the samples at dissociation pressures greater than 10 atm. Low hydrogen composition samples will, in the future, be pulse heated to their melting points in an attempt to obtain specific heat values. Thermal diffusivity measurements on the fuel alloy hydride are to be extended to 1500°F while maintaining the sample's hydrogen composition; the sample will be permitted to dehydride above this temperature. High temperature diffusivity measurements on the dehydrided and nonhydrided alloy will be made. Thermal expansion determinations on the dehydrided fuel alloy will be performed in the temperature range from 1400°F to the melting point, and expansion of cross axial hydrided samples will be measured in the temperature range from 70 to 1400°F to determine if the alloy is isotropic or anisotropic. Upon completion of these studies, the physical properties of the SNAP fuel alloy will be reported from room temperature up to its melting point.

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APPENDIX

Specific Heat of $\text{ZrH}_{1.74}$ at 373°K

$$\theta_E/T = \frac{1500}{373} = 4.021$$

$$C_v = 1.78 \text{ cal/mole}^\circ\text{K (Figure 9)}$$

$$C_v(\text{H}) = 1.78 \text{ cal/gm-}^\circ\text{C} = c_p(\text{H})$$

$$C_p(\text{Zr}) = 0.0705 \text{ cal/gm-}^\circ\text{C (Figure 10)}$$

$$\text{wt fraction Zr} = \frac{91.22}{91.22 + 1.74} = \frac{91.22}{92.96} = 0.9813$$

$$\text{wt fraction H} = \frac{1.74}{96.22 + 1.74} = \frac{1.74}{92.96} = 0.0187$$

$$C_p \text{ ZrH} = c_p(\text{Zr}) (\text{wt fraction Zr}) = c_p(\text{H}) (\text{wt fraction H})$$

$$= (0.0705)(0.9813) + (1.78)(0.0187) = 0.0692 + 0.0333 = 0.103$$

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