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THERMOPHYSICAL PROPERTIES
OF
SNAP FUEL MATERIALS

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AEC Research and Development Report

ATOMICS INTERNATIONAL

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THERMOPHYSICAL PROPERTIES
OF
SNAP FUEL MATERIALS

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ABSTRACT

Thermal diffusivity, heat capacity, thermal conductivity, and electrical resistivity measurements, made on SNAP fuel materials, are presented. Compositions investigated include the unhydrided zirconium - 10 wt % uranium alloy and the alloy hydrided to 0.50, 1.26, 1.58, 1.81, and 1.90 H/Zr atom ratios. Anomalies observed in the property vs temperature curves are discussed and related to the available phase diagrams.

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I. INTRODUCTION

The behavior of zirconium hydride, as functions of temperature and composition, is of interest to several SNAP reactor programs from the standpoint of moderator behavior during reactor operation and re-entry. A considerable number of investigations⁽¹⁻⁶⁾ have been carried out on the behavioral characteristics of SNAP fuel during severe temperature transients, such as those encountered during re-entry from space, and much useful information has been generated from these studies. There are other problems, however, the answers to which can best be obtained from systematic investigations of the thermal properties of the material. This report describes the experimental work conducted at Atomics International in a continuing program to obtain reliable thermophysical properties data on SNAP fuel materials.

The literature on the thermophysical properties of zirconium hydride contains an abundance of incorrect information. The problems that many investigators have encountered are traceable to treating a unique material by conventional methods. Hydrogen is quite mobile in zirconium hydride; and this, coupled with the quite sensitive dependence of the thermophysical properties on the hydrogen content, leads to most of the difficulties that have been experienced.

The effect of hydrogen content on transport properties is most clearly illustrated by the work of Bickel.⁽⁷⁾ He shows transport behavior, ranging from primarily hole conduction to primarily electronic conduction, and from a moderately good conductor to almost a superconductor, all depending on the hydrogen content. The initial first-order assumption of many investigations has been that zirconium hydride is like zirconium metal with a bit of hydrogen added. The truth is that, for most composition regions investigated, there are more hydrogen atoms present than metal atoms. Zirconium hydride is really more a sea of hydrogen, loosely bound by zirconium atoms, than it is a zirconium lattice with a little added hydrogen.

Most conventional elevated-temperature thermophysical properties work has been done in either a vacuum or inert atmosphere. Such techniques are completely inadequate for zirconium hydride, because of its reversible decomposition to its constituent elements. Many hydride investigators have realized this

problem, and have tried to overcome it by using special null-void volume apparatus, making transient measurements, or using balanced hydrogen overpressures. While sound in principle, these methods have been difficult to master in practice. The balanced-pressure method assumes a knowledge of the kinetics of equilibration, and a knowledge of the equilibrium pressures for pure and contaminated materials; and these data are not always known as precisely as is necessary. Slight errors in balance, or insufficient time to balance, can make for an important error in the composition of the condensed phase; and this, in turn, influences the property being studied.

A thermal gradient across a specimen is not usually too serious a source of experimental error in elevated-temperature properties investigations. In the measurement of thermal conductivity, for example, one must establish a heat flux by imposing a thermal gradient. The conductivity is then measured at an "average" specimen temperature. When zirconium hydride is subjected to a thermal gradient, the hydrogen redistributes itself, so that there is also a composition gradient from the cold to the hot region. One then is dealing not only with an "average" temperature, but also with an "average" composition, and the sources of error multiply.

The work presented in this report has been performed with considerable attention to details, in order to derive reliable thermophysical properties data on SNAP fuel materials. A portion of the work was conducted by the Columbus Division of Battelle Memorial Institute, in a joint effort with Atomics International, to produce data of increased reliability.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

A. GENERAL COMMENTS

Heat capacity, thermal diffusivity, electrical resistivity, and thermal conductivity measurements were made on the SNAP fuel alloy, zirconium - 10 wt % uranium, as well as on this alloy hydrided to H/Zr atom ratios of 0.50, 1.26, 1.58, 1.81, and 1.90. Of the above six compositions, the unhydrided alloy and the 1.81 H/Zr material were investigated jointly by Atomics International and Battelle Memorial Institute, under a specially controlled program, hereafter referred to as the referee program.⁽⁸⁾

In the referee program, the starting materials used were prepared from the same ingot stock, using identical procedures. After preparation, the materials were inspected for compositional conformance, and then selected by a random process for distribution to the two laboratories. Measurements were made by each of the two laboratories, using calibrated equipment. Each laboratory used the same table of values for dissociation pressure as a function of temperature; so that, except for kinetic effects, there was precise control of condensed-phase composition, regardless of the temperature level maintained or the apparatus employed. Details of the experimental program and the results of the referee program have been presented in a separate topical report.⁽⁸⁾ Therefore, only the final results on the unhydrided alloy and 1.81 H/Zr material are presented here.

The flash technique⁽⁹⁻¹¹⁾ was employed by both laboratories in measuring thermal diffusivity. The specific heat measurements at Atomics International were conducted, using an electrical pulse heating technique,^(6,12) while Battelle employed an ice drop calorimeter.⁽¹³⁾ Electrical resistivity measurements⁽¹⁴⁾ were also made at AI; since, in the pulse heating technique, electrical resistivity as a function of temperature is one of the inputs required in the solution of heat capacity. Thermal conductivity was calculated from the heat capacity, thermal diffusivity, and density of the materials, viz:

$$k = \alpha c_p d . \quad \dots (1)$$

Because of the thermal gradient problems previously mentioned, only the unhydrided composition was investigated for a direct measurement of thermal conductivity. Battelle used a steady-state longitudinal comparative method⁽¹⁵⁾ for this measurement. No direct thermal conductivity measurement was made at Atomics International.

The experimental techniques described in detail in this report are those employed at Atomics International. Techniques used at Battelle have been described in detail in the previous report,⁽⁸⁾ so that only pertinent remarks about their apparatus are made here.

The symbols and units of the various quantities employed in this report are given in Table 1, unless otherwise stated in the text.

TABLE 1
SYMBOLS AND UNITS

Quantity	Symbol	Unit
Thermal Diffusivity	α	cm^2/sec
Heat Capacity	c_p	$\text{cal/g-}^\circ\text{C}$
Electrical Resistivity	ρ	$\mu\Omega\text{-cm}$
Thermal Conductivity	k	$\text{cal/sec-cm-}^\circ\text{C}$
Density	d, δ	g/cc
Temperature	T	$^\circ\text{C}$
Length, Thickness	a, L	cm
Time	t	sec
Mass	m	g
Voltage	E	v
Current	I	amp
Area	A	cm^2

B. MATERIALS

1. Background

The materials investigated were the same as those used in the SNAP reactors. Several hydrogen compositions, however, were employed to study the effect of this variable in the thermal properties of the fuel. The hydrogen contents of the specimens are given as H/Zr atom ratios.*

2. Specimen Preparation

The materials were fabricated, employing the normal production processes for SNAP fuel element fabrication,^(16,17) except that natural isotopic uranium was used instead of enriched. The fuel alloy was triple arc melted and extruded to obtain homogeneous materials.

Hydrogen compositions were calculated from weight gain data.⁽¹⁸⁾ This method of determining the hydrogen content has been shown to be as reliable as chemical analysis. Photomicrographs of the hydrided samples also confirmed, qualitatively, the amount of hydrogen present in the samples, by indicating the phases present.

The extruded and hydrided fuel rods were then machined into specimen sizes appropriate for the various physical properties measurements. Table 2 gives the dimensions of the specimens used. The samples were machined so that the heat flux during the property measurements was in the direction of extrusion of the billet. Thermal diffusivity measurements were also made by BMI on a few samples, machined so that the heat flux was perpendicular to the direction of extrusion.

3. Material Characterization

The nominal composition of the SNAP fuel alloy is 90 wt % Zr and 10 wt % U. The alloy was hydrided to the various H/Zr levels desired, before machining into specimens. The hydrogen content of the specimens was maintained at constant level during the properties measurements by using hydrogen overpressures based on the hydrogen dissociation pressure isochore given by Johnson⁽¹⁹⁾ for modified SNAP fuels.

*Throughout this report, all H/Zr ratios are the effective H/Zr for the modified fuel, as discussed in Reference 8.

TABLE 2
SPECIMEN DIMENSIONS

Property	Form	Size (cm)		
		Diameter	Thickness	Length
Thermal Diffusivity	Disc	0.64	~0.25	
Thermal Diffusivity*	Disc	0.95	~0.15	
Electrical Resistivity	Rod	0.32		7.6
Heat Capacity (Pulse Method)	Rod	0.32		7.6
Heat Capacity* (Drop Calorimeter)	Rod	1.11		3.81
Thermal Conductivity* (Longitudinal)	Rod	1.55		17.8

*BMI Specimens

Figures 1a through 1f are typical photomicrographs of the specimens measured. The densities of the specimens were well within 1% of the values given in Figure 2.

C. THERMAL DIFFUSIVITY

1. Apparatus and Methods

The flash technique^(9,11) was used to measure the thermal diffusivity. In the flash technique, a pulse of energy is incident on one of two parallel faces of a sample. The subsequent temperature history of the opposite face is then related to the thermal diffusivity. The ambient temperature is controlled by a tube heater, while the pulse of energy raises the average sample temperature only a few degrees. When the heat pulse is of infinitesimal duration, compared to the characteristic rise time of the rear face temperature, the diffusivity is obtained from the transient response of the rear face temperature by

$$\alpha = 1.37 a^2 / \pi^2 t_{1/2} \quad \dots (2)$$

6-13-66 UNC

6339-5-1

a. Unhydried Material

6-13-66 UNC

5785-1-1

b. 0.50 H/Zr Material

6-13-66 UNC

5785-2-1

c. 1.26 H/Zr Material

6-13-66 UNC

6167-6-1

d. 1.58 H/Zr Material

6-13-66 UNC

6639-11-1

e. 1.81 H/Zr Material

6-13-66 UNC

6167-4-3

f. 1.90 H/Zr Material

Figure 1. Typical Microstructures of Specimens

6-13-66 UNC

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Figure 2. Room-Temperature Density vs H/Zr for SNAP Fuel Material

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In Equation 2, $t_{1/2}$ is the time required for the rear face temperature to reach half-maximum, and a is the sample thickness. The characteristic rise time is given by

$$t_c = a^2 / \pi^2 \alpha \quad \dots (3)$$

Detailed treatments of the theory of the method, as well as special cases involving the technique, can be found in various published reports. (9,20-22)

A schematic diagram of the apparatus is shown in Figure 3a. The essential components are the laser with its power supply, tube furnace, sample and thermocouple holder, photocell, and a dual-beam oscilloscope with its auxiliary components. Two thermal diffusivity systems, as shown in the photographs in Figures 3b and 3c, were employed. The high-temperature system, shown in Figure 3b, was used for some of the earlier measurements. This system uses a molybdenum tube furnace enclosed in a water-cooled chamber. Temperatures in excess of 2000°C can be readily attained in this furnace. However, when a hydrogen atmosphere is required in the system, the problem of gas convection becomes intolerable, especially at high gas pressures and/or high temperatures. Radiation and convection barriers, in the form of concentric molybdenum and stainless steel baffles, were used to eliminate most of the temperature fluctuations caused by gas convection; but, at high temperatures, the fluctuations remained quite troublesome. A second system, shown in Figure 3c, was therefore constructed to alleviate this problem. In the new system, the furnace chamber consists of a 3/4-in. ID by 7/32-in. wall by 12-in. long stainless steel tube which is heated uniformly over its center 5 in. by a tantalum tube heater. The tantalum tube heater is enclosed in a water-cooled vacuum jacket. Temperature fluctuations were completely eliminated in this system. Furthermore, since the furnace chamber volume was reduced by an order of magnitude compared to the first system, and was devoid of extraneous components, much better sensitivity of gas pressure and control of gas purity were obtainable. The operating temperature of the furnace is limited to ~ 1100°C when pressurized with a 10-atm pressure of hydrogen. Except for the differences mentioned previously, the two systems are essentially identical, so that the description which follows applies to both.

a. Schematic

6-13-66 UNC

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b. High-Temperature Apparatus

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c. Low-Temperature Apparatus

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Figure 3. Thermal Diffusivity Apparatus

The sample was supported by three pins, to minimize thermal contact with the holder. The tube heater was supported on water-cooled electrodes, and was heated by direct current from a set of motor generators. A Raytheon Model LH3 solid-state laser was used as the source of pulsed energy. The laser uses a 3/8-in. diameter ruby rod, and is operated at liquid nitrogen temperatures. The output of the laser is rated at 15 to 20 joules at this temperature, and the pulse duration is 1.5 msec. The sample temperature was measured, using a 3-mil Chromel-Alumel or Geminol P/Geminol N thermocouple which was spot welded to the center back face of the sample, with the two wires $\sim 1/16$ in. apart. The temperature-measuring instrumentation included a Rubicon Model 2745 potentiometer for measuring the steady-state temperature. By means of a manual knife switch, the thermocouple could be switched from the potentiometer to the dual-beam oscilloscope (Tektronix 502), for recording the transient which follows the pulse from the laser. A Dana amplifier, Model 2200, and an appropriate biasing circuit were employed to display the thermocouple output on the oscilloscope and to record the transient on Polaroid film. The photocell (lead sulfide cell) was used to intercept a small portion of the laser beam, and the output of the cell was displayed by the second beam of the oscilloscope, thus accurately establishing the zero time.

The systems can be evacuated to $< 5 \times 10^{-6}$ torr at room temperature, and can also be filled with hydrogen gas, up to a pressure of 10 atm. Ultra-pure hydrogen gas (99.99⁺ % purity) was used. The gas pressure in the system was indicated by a 0 to 50 mm Hg absolute Wallace & Tiernan gauge and a 0 to 6000 mm Hg absolute U.S. Gauge Co. pressure gauge. Both gauges were calibrated to standards traceable to the National Bureau of Standards. The accuracy of the gauges were ± 0.2 mm Hg and $\pm 1\%$ of full scale for the 0 to 50 mm and 0 to 6000 mm gauges, respectively.

The temperature of the unhydrided Zr-U alloy was measured in vacuum, using a Chromel-Alumel thermocouple. In general, the hydrided samples were initially heated to temperatures above 600°C (in the appropriate hydrogen over-pressure to assure the proper composition) before measurements were made. A few samples were measured as-received, and these are so indicated. Most of the measurements made in hydrogen atmospheres were obtained using Geminol P/Geminol N thermocouples, which are stable in a reducing

6-13-66 UNC

7611-4747

Figure 4. Thermal Diffusivity of Unhydrated Material

atmosphere. The 1.90 H/Zr samples were measured with Chromel-Alumel thermocouples, but calibrations indicated that the thermocouples were not affected at the temperatures and durations used.

Battelle Memorial Institute also employed the flash technique for measuring thermal diffusivity;^(9,10) but, instead of thermocouples, a lead sulfide photo-detector was used for measuring the temperature transient.

2. Accuracy

The thermal diffusivity systems were calibrated, using standard Armco iron samples. These samples were machined from an Armco iron rod received from the Battelle Memorial Institute. The rod is part of Battelle's round-robin thermal conductivity samples that have been well characterized and the thermal conductivity measured by several competent laboratories.⁽²³⁾ Measurements obtained have been within $\pm 2\%$ of the accepted literature values for Armco iron, so that the accuracy of the thermal diffusivity measurements are believed to be $< \pm 5\%$.

3. Results and Discussions

The results of measurements made on unhydrided zirconium-uranium alloy, and on alloys hydrided to 0.50, 1.58, 1.81, and 1.90 H/Zr atom ratios, are given in the following sections. The data in the tables were obtained in the order in which they are tabulated.

a. Unhydrided Material

Measurements were made, at Atomics International, on two samples in the range of room temperature to 975°C. The results are shown in Figure 4, and the data are given in Table 3. Two phase transformations are apparent from the graph, one at $595^\circ \pm 10^\circ\text{C}$ and the second at $795^\circ \pm 10^\circ\text{C}$. These phase changes are in good agreement with the $\delta + \epsilon \rightleftharpoons \gamma + \epsilon$ and the $\gamma + \epsilon \rightleftharpoons \gamma$ phase transitions reported in the literature⁽²⁴⁾ for Zr - 10 wt % U.*

The thermal diffusivity data for the unhydrided alloy in the range of 20 to 595°C can be represented by the equation

$$\alpha = 7.017 \times 10^{-2} + 3.291 \times 10^{-5}T - 3.754 \times 10^{-8}T^2 \quad \dots(4)$$

*The δ and ϵ hydride phases are not to be confused with the δ and ϵ phases of the unhydrided material (see References 8, 24, and 48 for phase diagrams).

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Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)
Sample 396 B-4 1-I (Cont'd)		Sample 396 B-4 1-I (Cont'd)		Sample 396 B-4 1-I (Cont'd)		Sample 396 C-4 1-I (Cont'd)	
26	0.0704	825	0.114	668	0.0919	507	0.0785
27	0.0704	888	0.118	734	0.0967	501	0.0766
28	0.0701	915	0.125	771	0.105	499	0.0785
28	0.0708	787	0.100	776	0.106	499	0.0766
28	0.0697	694	0.0956	804	0.111	596	0.0688
28	0.0704	693	0.0945	802	0.111	596	0.0735
57	0.0694	547	0.0781	960	0.131	601	0.0816
64	0.0720	447	0.0800	960	0.132	600	0.0740
68	0.0689	325	0.0767	968	0.131	33	0.0727
156	0.0712	319	0.0728	976	0.129	32	0.0714
158	0.0716	203	0.0732	970	0.133	333	0.0723
275	0.0724	183	0.0724	967	0.128	195	0.0740
276	0.0753	45	0.0698	Sample 396 C-4 1-I		193	0.0757
278	0.0762	29	0.0716	28	0.0758	441	0.0775
339	0.0781	30	0.0698	28	0.0739	460	0.0780
346	0.0771	27	0.0679	28	0.0739	461	0.0785
486	0.0785	28	0.0693	28	0.0744	579	0.0746
495	0.0795	28	0.0700	80	0.0749	580	0.0731
494	0.0776	586	0.0767	76	0.0749		
552	0.0774	589	0.0776	137	0.0753	699	0.0932
563	0.0771	580	0.0785	143	0.0739	705	0.0956
564	0.0763	584	0.0762	150	0.0757	753	0.100
568	0.0762	587	0.0781	154	0.0766	765	0.101
705	0.0952	612	0.0900	157	0.0753	847	0.119
346	0.0763	602	0.0906	220	0.0775	850	0.117
699	0.0912	617	0.0888	226	0.0780	898	0.124
560	0.0800	629	0.0888	230	0.0771	902	0.128
554	0.0810	620	0.0894	298	0.0753	896	0.126
562	0.0776	626	0.0894	310	0.0785	903	0.126
698	0.0929	649	0.0899	317	0.0766	901	0.127
756	0.102	665	0.0919	401	0.0780	931	0.128
753	0.0973	674	0.0925	406	0.0766	913	0.122
829	0.117	662	0.0876	403	0.0775	630	0.0831
830	0.116			507	0.0780		
				507	0.0759		

Table 3. Thermal Diffusivity of Unhydrided Material

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For comparison, the BMI data on two specimens are shown in Figure 4 by the dashed curves. The upper dashed curve represents the values obtained for the specimen cut from the transverse direction, and the lower dashed curve is for the specimen cut from the longitudinal direction.

The phase changes at about 595 and 800°C were also evident from this data, although the latter is not obvious from the curves shown. The data are tabulated in Table 4, but the data points were not plotted in Figure 4.

In arriving at the best value for the unhydrided material, the data have been weighted slightly in favor of the AI data, as discussed in the earlier topical report.⁽⁸⁾

b. 0.50 H/Zr Material

The results of measurements made on three samples, in the range of room temperature to 800°C, are given in Table 5 and Figure 5. The diffusivity diminishes nearly linearly from 0.059 cm²/sec at room temperature to 0.050 cm²/sec at ~390°C. Between 390 and 510°C, the values for diffusivity depart from an extension of the curve through the lower temperature data. Above 510°C, the data again become regular, but with a positive temperature coefficient. Sharp discontinuities in property data, such as those observed in the diffusivity at 390 and 510°C, often indicate a phase change in the material being studied. None of the three binary systems (Zr-H, U-H, or U-Zr) show phase changes at 390 or 510°C. The ternary U-Zr-H has only been studied in detail^(25,26) at temperatures above 600°C.

The data points in the 15 to 400°C range can be represented by the equation

$$\alpha = 5.838 \times 10^{-2} - 4.499 \times 10^{-6}T - 4.598 \times 10^{-8}T^2 \quad \dots(5)$$

Between 500 and 750°C, the data can be given by the equation

$$\alpha = 2.282 \times 10^{-2} + 7.027 \times 10^{-5}T \quad \dots(6)$$

c. 1.58 H/Zr Material

Three samples were measured in the range of room temperature to 500°C, and a few measurements were obtained at temperatures of about 880 and 930°C.

TABLE 4
THERMAL DIFFUSIVITY OF UNHYDRIDED MATERIAL
(BMI Data)

Transverse - Specimen 396-B2		Longitudinal - Specimen 396-B2	
Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)
265	0.0830	214	0.0693
265	0.0856	214	0.0627
265	0.0824	214	0.0712
345	0.0784	332	0.0782
345	0.0843	333	0.0782
345	0.0812	333	0.0807
400	0.0951	431	0.0819
400	0.0869	431	0.0825
400	0.0849	431	0.0822
484	0.0927	508	0.0841
484	0.0943	508	0.0817
484	0.0927	508	0.0838
560	0.0890	580	0.0832
560	0.0890	580	0.0813
560	0.0856	580	0.0846
604	0.0897	676	0.1067
604	0.0923	676	0.1053
604	0.0883	676	0.1032
646	0.0951	790	0.1195
646	0.1021	790	0.1217
646	0.0943	884	0.1284
710	0.0897	884	0.1351
710	0.0993	884	0.1303
784	0.1288	996	0.1265
784	0.1247	996	0.1316
784	0.1236	996	0.1297
920	0.1264	808	0.1107
920	0.1325	808	0.1000
920	0.1312	618	0.0974
844	0.1253	618	0.0902
844	0.1199	618	0.0875
772	0.1070	618	0.0947
772	0.1030		
480	0.0843		
480	0.0897		
342	0.0818		
342	0.0795		
243	0.0742		
243	0.0752		

TABLE 5
THERMAL DIFFUSIVITY OF 0.50 H/Zr MATERIAL

Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)
Sample 246-D10		Sample 246-D10 (Cont'd)		Sample 246-D10 (Cont'd)		Sample 246-D10 (Cont'd)	
28	0.056	168	0.053	647	0.070	523	0.055
26	0.058	679	0.069	642	0.067	514	0.058
27	0.058	680	0.070	625	0.067	15	0.054
27	0.057	680	0.076	553	0.061	15	0.062
26	0.056	680	0.072	550	0.064	15	0.061
205	0.054			548	0.066	17	0.058
204	0.055	680	0.070	548	0.059	498	0.043
197	0.057	680	0.069	519	0.058	498	0.042
188	0.055	735	0.073	509	0.055	500	0.043
128	0.057	740	0.076	13	0.054	503	0.043
		742	0.076	15	0.059	510	0.044
121	0.060	96	0.054	17	0.060	517	0.043
121	0.060	96	0.054	397	0.045	523	0.045
114	0.058	51	0.059	407	0.045		
114	0.057	48	0.057	418	0.043	Sample 248-D6-1	
48	0.061	45	0.056	427	0.042	25	0.065
48	0.058			431	0.042	131	0.053
252	0.056	42	0.056	433	0.041	332	0.053
252	0.057	40	0.056	440	0.042	386	0.051
252	0.054	40	0.059	447	0.040	524	0.045
330	0.052	26	0.056	453	0.040	623	0.063
		27	0.059	465	0.039	724	0.068
309	0.054	28	0.059	473	0.039		
308	0.053	28	0.057	478	0.039	Sample 248-D6-2	
411	0.047	262	0.052	482	0.038	25	0.069
408	0.046	260	0.053	487	0.041	96	0.060
390	0.050	257	0.053	583	0.065	240	0.061
393	0.051			585	0.065	330	0.054
392	0.049	395	0.046	568	0.061	333	0.054
388	0.050	406	0.045	566	0.067	436	0.043
27	0.058	412	0.044	562	0.064	565	0.066
27	0.057	425	0.043	557	0.061	655	0.067
		712	0.076	556	0.061	750	0.073
27	0.062	722	0.070	552	0.062		
27	0.059	725	0.071	550	0.065		
28	0.057			546	0.060		
28	0.054	730	0.080	537	0.059		
175	0.052	666	0.070				
		653	0.072

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Figure 5. Thermal Diffusivity of 0.50 H/Zr Material

The data are given in Table 6 and shown in Figure 6. At the time measurements were made on these samples, the 0 to 50 mm pressure gauge was not available. Accurate balancing of hydrogen pressure in the temperature range of 500 to 700°C (~45 mm Hg pressure at 700°C) was therefore difficult, using the 0 to 6000 mm pressure gauge. Rather than to risk obtaining erroneous data, therefore, measurements in the ~ 500 to 800°C range were omitted. After measurements were made at the higher temperatures, the sample was cooled as rapidly as possible, following the appropriate hydrogen pressures, and the system was evacuated when the sample reached ~ 500°C. Measurements were then made in dynamic vacuum, as the sample was gradually cooled to room temperature. The measurements made on two samples in this manner show some scatter in the data, but are in good agreement with the data obtained on the as-received sample, which was measured to ~500°C in vacuum.

The data in the 20 to 500°C range can be represented by the equation

$$\alpha = 7.702 \times 10^{-2} - 9.563 \times 10^{-5}T + 7.850 \times 10^{-8}T^2 \quad \dots (7)$$

d. 1.81 H/Zr Material

At Atomics International, one sample was measured as received; and a second sample was measured as received, followed by measurements with the appropriate hydrogen overpressure. The data are given in Table 7 and in Figure 7. The curve, represented by the equation,

$$\alpha = 0.1125 - 2.131 \times 10^{-4}T + 3.234 \times 10^{-7}T^2 - 1.919 \times 10^{-10}T^3 \quad (15 < T < 550) , \quad \dots (8)$$

was drawn through the data points for the balanced-hydrogen measurements. There is an inflection in the curve at ~ 550°C, indicating that perhaps the $\epsilon \pm \delta + \epsilon$ boundary exists near this temperature for the 1.81 H/Zr material. Chang⁽²⁷⁾ gives a phase diagram showing this boundary at ~550°C in $ZrH_{1.80}$.

The average of the data obtained by Battelle on five specimens is shown in Figure 7 as the dashed curve, and the values are given in Table 8. The agreement between the AI and BMI data are extremely good. The best values

TABLE 6
THERMAL DIFFUSIVITY OF 1.58 H/Zr MATERIAL

Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)
Sample 247-D1		Sample 246-D7 (Cont'd)	
873	0.0471	114	0.0662
878	0.0448	112	0.0630
496	0.0494	111	0.0594
495	0.0475	62	0.0655
494	0.0498	62	0.0734
392	0.0538	47	0.0708
393	0.0552	47	0.0727
395	0.0547	36	0.0822
292	0.0582	26	0.0690
290	0.0569	26	0.0704
243	0.0619	Sample 246-D6*	
239	0.0622	26	0.069
235	0.0616	26	0.076
102	0.0704	26	0.076
100	0.0712	26	0.071
98	0.0736	120	0.065
58	0.0827	120	0.069
57	0.0787	120	0.063
Sample 246-D7		211	0.058
929	0.0429	220	0.061
929	0.0444	222	0.055
930	0.0414	221	0.060
482	0.0466	223	0.066
499	0.0480	232	0.056
385	0.0490	302	0.056
392	0.0476	305	0.054
398	0.0457	404	0.051
292	0.0547	431	0.054
290	0.0494	498	0.055
288	0.0571	502	0.051
287	0.0534	505	0.044

*Composition was 1.58 H/Zr, as received.

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Figure 6. Thermal Diffusivity of 1.58 H/Zr Material

TABLE 7
THERMAL DIFFUSIVITY OF 1.81 H/Zr MATERIAL

Temperature (°C)	(cm ² /sec)	Temperature (°C)	(cm ² /sec)	Temperature (°C)	(cm ² /sec)
Sample 396-B3-2I (As Received)		Sample 396-C3-2I (As Received) (Cont'd)		Sample 396-C3-2I (Hydrogen Atmosphere (Cont'd))	
18	0.107	22	0.105	601	0.059
18	0.107	22	0.101	16	0.106
18	0.107	22	0.105	17	0.115
18	0.108	291	0.075	17	0.106
18	0.107	286	0.070	100	0.092
18	0.107	285	0.070	99	0.098
18	0.105	285	0.074	98	0.093
20	0.107	260	0.068	96	0.094
23	0.111	70	0.091	88	0.098
29	0.112	70	0.092	87	0.093
40	0.096	67	0.101	58	0.101
62	0.093	296	0.075	58	0.101
82	0.099	303	0.067	58	0.105
247	0.072	307	0.071	52	0.101
249	0.073	345	0.069	52	0.104
260	0.077	355	0.066	52	0.101
301	0.078	352	0.064	335	0.072
319	0.066	370	0.068	323	0.072
342	0.068	377	0.064	325	0.072
356	0.071	418	0.062	361	0.065
15	0.108	418	0.064	368	0.068
96	0.091	447	0.057	371	0.072
97	0.089	450	0.066	369	0.069
102	0.097	Sample 396-C3-2I (Hydrogen Atmosphere)		418	0.062
112	0.099	685	0.054	418	0.067
125	0.099	684	0.054	418	0.064
140	0.086	682	0.055	498	0.064
152	0.082	682	0.052	501	0.064
203	0.084	682	0.051	505	0.063
217	0.082	672	0.056	507	0.060
Sample 396-C3-2I (As Received)		658	0.053	417	0.064
24	0.105	653	0.059	510	0.066
24	0.100	650	0.053	535	0.063
24	0.101	648	0.053	540	0.065
24	0.095	648	0.058	543	0.061
76	0.101	647	0.056	548	0.062
86	0.091	648	0.054	552	0.058
107	0.086	631	0.056	555	0.061
111	0.090	622	0.055	560	0.060
124	0.088	618	0.058	562	0.058
166	0.080	612	0.058	562	0.061
177	0.079	608	0.057	565	0.060
182	0.086	604	0.057	567	0.063
22	0.095	601	0.058

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Figure 7. Thermal Diffusivity of 1.81 H/Zr Material

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Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)	Temperature (°C)	α (cm ² /sec)
Transverse; Specimen 396-A1, No. 1		Transverse; Specimen 396-A1, No. 2 (Cont'd)		Longitudinal; Specimen 396-A1, No. 1 (Cont'd)		Longitudinal; Specimen 396-A1, No. 1 (Cont'd)		Longitudinal; Specimen 396-A1, No. 2 (Cont'd)		Longitudinal; Specimen 396-A1, No. 3 (Cont'd)		Longitudinal; Specimen 396-A1, No. 3 (Cont'd)	
215	0.0762	222	0.0766	246	0.0755	620	0.0678	626	0.0661	316	0.0729	500	0.0752
215	0.0783	285	0.0777	246	0.0760	620	0.0678	626	0.0657	316	0.0707	500	0.0758
268	0.0732	285	0.0787	299	0.0787	502	0.0731	560	0.0657	460	0.0657	501	0.0719
268	0.0773	285	0.0777	299	0.0731	504	0.0740	560	0.0711	460	0.0667	610	0.0672
320	0.0737	351	0.0682	299	0.0736	438	0.0798	560	0.0734	536	0.0627	610	0.0648
320	0.0742	351	0.0713	354	0.0703	438	0.0782	456	0.0795	536	0.0676	610	0.0640
404	0.0684	414	0.0695	354	0.0708	Longitudinal; Specimen 396-A1, No. 2		456	0.0691	599	0.0595	658	0.0631
404	0.0692	414	0.0691	354	0.0708			285	0.0904	599	0.0619	658	0.0627
459	0.0742	460	0.0695	400	0.0703	170	0.0813	285	0.0926	666	0.0607	658	0.0623
459	0.0688	460	0.0687	400	0.0695	170	0.0831	208	0.0843	666	0.0591	540	0.0691
459	0.0701	500	0.0643	400	0.0690	232	0.0790	208	0.0819	666	0.0595	540	0.0702
511	0.0652	550	0.0622	466	0.0636	232	0.0779	244	0.0807	653	0.0662	340	0.0847
511	0.0684	554	0.0629	466	0.0658	302	0.0706	244	0.0801	653	0.0667	340	0.0847
550	0.0641	601	0.0622	410	0.0690	302	0.0653	244	0.0807	639	0.0672	214	0.0913
551	0.0641	601	0.0612	410	0.0740	340	0.0729	303	0.0825	639	0.0662	214	0.0904
578	0.0648	639	0.0580	410	0.0736	340	0.0769	303	0.0801	642	0.0675		
578	0.0652	639	0.0636	294	0.0776	386	0.0729	356	0.0801	642	0.0667		
615	0.0630	671	0.0526	294	0.0782	386	0.0743	356	0.0807	522	0.0712		
615	0.0652	671	0.0574	294	0.0755	442	0.0734	418	0.0730	522	0.0712		
640	0.0645	649	0.0651	205	0.0760	442	0.0702	419	0.0748	522	0.0696		
640	0.0637	646	0.0590	205	0.0787	490	0.0693	419	0.0730	522	0.0702		
670	0.0613	594	0.0670	482	0.0636	490	0.0685	461	0.0670	406	0.0817		
669	0.0630	594	0.0655	482	0.0651	490	0.0685	461	0.0650	406	0.0811		
622	0.0630	475	0.0662	484	0.0670	548	0.0665	508	0.0631	196	0.0879		
622	0.0660	475	0.0704	520	0.0682	548	0.0661	508	0.0620	198	0.0879		
552	0.0709	286	0.0866	520	0.0674	603	0.0673	560	0.0614	194	0.0904		
552	0.0752	286	0.0873	570	0.0636	603	0.0673	560	0.0604	194	0.0921		
445	0.0806	Longitudinal; Specimen 396-A1, No. 1		570	0.0651	603	0.0653	596	0.0601	194	0.0858		
445	0.0812			608	0.0674	630	0.0653	596	0.0590	300	0.0916		
445	0.0823	158	0.0793	608	0.0666	630	0.0673	663	0.0595	300	0.0794		
318	0.0910	158	0.0793	635	0.0651	668	0.0677	663	0.0693	300	0.0847		
318	0.0902	158	0.0736	636	0.0662	664	0.0665	663	0.0650	300	0.0839		
Transverse; Specimen 396-A1, No. 2		210	0.0740	668	0.0612	666	0.0620	Longitudinal; Specimen 396-A1, No. 3		412	0.0804		
		210	0.0815	668	0.0647	650	0.0661			412	0.0784		
222	0.0756	210	0.0740	650	0.0674	650	0.0677	214	0.0752	412	0.0784		
222	0.0771	246	0.0760	650	0.0674	650	0.0677	214	0.0758	412	0.0784		

Table 8. Thermal Diffusivity of
1.81 H/Zr Material (BMI Data)

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for the 1.81 H/Zr material, which were obtained by placing slightly more weight on the Al data,⁽⁸⁾ are shown later in Figure 9.

e. 1.90 H/Zr Material

The results of measurements made on three samples are shown in Figure 8 and the data are given in Table 9. There is no apparent anomalous indication in the range of room temperature to 680°C. The data are represented by the equation

$$\alpha = 0.1542 - 3.239 \times 10^{-4}T + 4.450 \times 10^{-7}T^2 - 2.350 \times 10^{-10}T^3 \dots (9)$$

4. Summary

The best thermal diffusivity values of the unhydrided alloy and the four hydride compositions, as functions of temperature, are shown in Figure 9. It can be seen that the thermal diffusivity goes through a minimum as the H/Zr ratio is increased from 0 to 1.90. This is more apparent in Figure 10, where the thermal diffusivity is plotted as a function of H/Zr atom ratio. The data points in Figure 10 were joined by straight lines, since more data would be required at different H/Zr ratios in order to draw smooth curves through the points (i. e., the lines are intended merely to aid the eyes in following the trend in the data points).

D. ELECTRICAL RESISTIVITY

1. Apparatus and Methods

The potentiometric method of measuring resistance was used. This consists of measuring the potential difference across a standard resistor and across the specimen, which is in series with the standard. Since the current is the same everywhere in the series circuit, the resistance of the specimen can be calculated from the equation,

$$R_{\text{specimen}} = R_{\text{standard}} \cdot \left(\frac{E_{\text{specimen}}}{E_{\text{standard}}} \right), \dots (10)$$

where

R = Resistance

E = Potential difference.

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Figure 8. Thermal Diffusivity of 1.90 H/Zr Material

TABLE 9
THERMAL DIFFUSIVITY OF 1.90 H/Zr MATERIAL

Temperature (°C)	(cm ² /sec)	Temperature (°C)	(cm ² /sec)	Temperature (°C)	(cm ² /sec)
Sample 246-D2		Sample 248-C3 (Cont'd)		Sample 248-C3 (Cont'd)	
661	0.0656	682	0.0662	92	0.136
661	0.0640	682	0.0668	90	0.139
663	0.0647	682	0.0665	87	0.132
682	0.0610	675	0.0662	86	0.136
682	0.0632	675	0.0693	44	0.143
670	0.0647	674	0.0662	43	0.146
652	0.0660	674	0.0668	41	0.153
612	0.0699	653	0.0697	27	0.154
605	0.0695	654	0.0670	27	0.153
595	0.0698	654	0.0668	Sample 247-D5	
589	0.0699	612	0.0716	611	0.070
588	0.0668	612	0.0670	611	0.069
525	0.0742	601	0.0730	612	0.070
525	0.0747	601	0.0693	611	0.070
525	0.0705	601	0.0690	611	0.068
347	0.0840	602	0.0700	611	0.069
349	0.0820	558	0.0735	14	0.147
354	0.0820	557	0.0735	16	0.147
198	0.103	553	0.0724	16	0.146
198	0.105	502	0.0777	114	0.116
194	0.111	503	0.0781	116	0.118
192	0.105	7	0.151	118	0.120
21	0.140	7	0.146	244	0.096
21	0.150	7	0.145	239	0.097
21	0.150	7	0.145	238	0.096
21	0.148	21	0.145	238	0.097
21	0.140	21	0.142	238	0.097
96	0.123	202	0.104	353	0.084
95	0.130	201	0.105	355	0.082
93	0.128	195	0.107	355	0.083
64	0.140	192	0.108	355	0.083
63	0.139	292	0.0906	355	0.085
62	0.128	294	0.0917	356	0.085
44	0.143	295	0.0917	427	0.080
43	0.145	295	0.0940	415	0.080
43	0.145	387	0.0816	414	0.078
43	0.142	391	0.0822	415	0.080
Sample 248-C3		394	0.0820	417	0.078
662	0.0675	612	0.0677	553	0.071
662	0.0670	620	0.0680	557	0.072
661	0.0670	624	0.0640	558	0.072
660	0.0650	514	0.0770	560	0.070
682	0.0662	510	0.0728

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Figure 9. Summary of Thermal Diffusivity Data

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Figure 10. Thermal Diffusivity vs H/Zr Atom Ratio

The current is reversed for each reading, to subtract out any errors caused by thermoelectric effects between the materials in the measuring system. Each pair of readings is averaged and called one observation. The resistivity (in Ω -cm) is calculated from the equation,

$$\rho = RA/L \quad , \quad \dots (11)$$

where

A = Cross-sectional area of the specimen

L = Length of the specimen between the potential probes

R = Resistance measured between the potential probes (Ω).

Photographs of the sample holder and the resistivity apparatus, as well as a schematic diagram of the electrical system, are shown in Figure 11. The sample holder is designed to accommodate various size samples with a minimum of modification. The holder has provisions for mounting four samples at any one time. Connections to samples were made by spot-welding Nichrome wires to the samples, since spring-loaded voltage probes were found to lose contact with the samples when the furnace temperature was cycled. After all connections to the samples are made, the length between the potential contacts is measured by means of a traveling micrometer.

Four thermocouples extend into the sample area, to monitor the sample temperature. Sheathed Pt - Pt 10% Rh thermocouples were used for the earlier measurements, but these were replaced with sheathed Geminol P/Geminol N thermocouples, because of the inherent stability of the latter in hydrogen atmosphere. Calibration of the Pt - Pt 10% Rh thermocouples after use, however, indicated that the outputs were the same as before use.

The systems can be evacuated to a dynamic vacuum of 2×10^{-5} torr. Provisions are also available for introducing ultra-pure hydrogen gas into the system, for measurements that require a hydrogen overpressure. As in the thermal diffusivity systems, a 0 to 50 mm Hg absolute (Wallace & Tiernan) gauge and a 0 to 6000 mm Hg absolute pressure gauge (U. S. Gauge) were used to monitor the hydrogen pressure in the system. The measurements on unhydrided fuel material and on the 0.50 and 1.26 H/Zr materials were made in

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a. Sample Holder

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b. Apparatus

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c. Schematic of
Electrical
System

Figure 11. Electrical Resistivity Apparatus

vacuum because, at the temperatures of measurements, the dissociation pressure was negligibly small. All other compositions were measured with a balanced hydrogen pressure.

2. Accuracy

Potential measurements were made with a Leeds and Northrup K-3 potentiometer with an accuracy of $\pm 0.05\%$. The Rubicon standard resistor is accurate to $\pm 0.005\%$. When these values are used in the formula

$$\rho = \frac{E_{\text{specimen}} R_{\text{standard}}}{E_{\text{standard}}} \times \frac{A}{L} , \quad \dots (12)$$

along with the errors associated with the A/L determinations, the error is $\leq 1\%$ of the quoted ρ values. The greatest uncertainty in the measurements, however, is probably in the composition of the material and in the ability to impose an accurate hydrogen balancing pressure. The total uncertainty is believed to be approximately $\pm 3\%$.

The apparatus was calibrated, using a tantalum sample ($99.9^+ \%$ purity) obtained from the Kawecki Chemical Co. The results, as shown in Table 10 and in Figure 12, are in excellent agreement with the data of Langmuir and Malter⁽²⁸⁾ and those obtained previously in this laboratory using a different technique,⁽¹²⁾ and can be represented by the equation,

$$\begin{aligned} \rho = & 12.68 + 4.729 \times 10^{-2} T - 5.766 \times 10^{-6} T^2 \\ & + 3.524 \times 10^{-10} T^3 \quad (20 < T < 1040^\circ\text{C}) \end{aligned} \quad \dots (13)$$

3. Results and Discussions

Electrical resistivity measurements were made on the unhydrided material, and on materials hydrided to 0.50, 1.26, 1.58, 1.81, and 1.90 H/Zr atom ratios. In determining the best values of electrical resistivity for each composition, the values obtained for all samples in each composition were averaged. In the pulse-heating runs, however, the resistivity values obtained for each particular sample were, in general, used.

TABLE 10
ELECTRICAL RESISTIVITY OF TANTALUM

T (°C)	ρ ($\mu\Omega\text{-cm}$)				
	Sample 1	Sample 2	Sample 3	Sample 4	Average
22	13.69	13.71	13.78	13.47	13.66
102	17.04	17.24	17.34	17.04	17.16
179	20.68	20.81	20.90	20.45	20.71
247	23.78	23.88	23.89	23.77	23.83
357	28.77	28.78	29.00	28.49	28.51
476	34.06	34.08	34.46	33.51	34.02
565	37.57	37.51	37.82	37.10	37.50
669	41.78	41.70	42.12	41.16	41.69
664	41.73	41.63	42.01	41.11	41.62
748	44.97	44.92	45.33	44.35	44.89
861	49.31	49.23	49.73	-	49.42
952	52.79	52.69	53.14	51.99	52.65
1038	56.18	56.09	56.57	55.33	56.04
778	46.32	46.19	46.65	45.47	46.16
530	36.51	36.34	36.62	35.88	36.34
526	36.34	36.14	36.68	35.75	36.23
229	23.49	23.51	23.77	23.63	23.60
25	14.18	14.13	14.29	13.98	14.14

Figure 12. Electrical Resistivity of Tantalum

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a. Unhydrided Material

Results of measurements made on four unhydrided samples are given in Table 11 and in Figure 13. The average electrical resistivity values for the four specimens can be expressed by the equation,

$$\rho = 70.96 + 0.1366T - 3.359 \times 10^{-6} T^2 - 1.038 \times 10^{-7} T^3 \quad \dots (14)$$

in the range of 20 to 590°C. The results are in excellent agreement with previous measurements.⁽²⁹⁾ The abrupt change in the ρ vs T curves at ~590°C (cf. $595 \pm 10^\circ\text{C}$ in thermal diffusivity measurements) indicates a phase transition, probably the $\delta + \epsilon \rightleftharpoons \gamma + \epsilon$ transition.

At ~800°C, the $\gamma + \epsilon \rightleftharpoons \gamma$ phase boundary is crossed, and above this temperature the equilibrium phase is pure γ . The electrical resistivity is not a smooth function of temperature above 590°C, because of the changing proportions of the γ and ϵ phases.

b. 0.50 H/Zr Material

The data are given in Table 12 and are shown also in Figure 14. The data are in excellent agreement with previous measurements made at this laboratory.⁽⁶⁾ At room temperature, the values are identical; and, at ~400°C, the values reported here are ~2.4% greater than the earlier data.

The data fall on a smooth curve represented by:

$$\rho = 64.68 + 0.1710 T - 1.671 \times 10^{-5} T^2 - 8.653 \times 10^{-8} T^3 \quad \dots (15)$$

up to some temperature between 480 and 545°C. One would expect a break in this region to be due to the eutectoid reaction in the Zr-H binary system.

c. 1.26 H/Zr Material

Two samples were measured, the results of which are given in Table 13 and in Figure 15. The data of the two samples show a disagreement of ~10% at room temperature and 7% at ~400°C. This is not altogether surprising, since this composition has shown anomalous behavior in several previous measurements.^(6,29)

TABLE 11

ELECTRICAL RESISTIVITY OF UNHYDRIDED MATERIAL

Temperature (°C)	ρ ($\mu\Omega\text{-cm}$)			
	Sample 1 396 B-4 B-II	Sample 2 396 C-4 B-II	Sample 3 396 C-4 A-II	Sample 4 396 B-4 A-II
22	75.30	73.90	75.34	73.78
128		88.39	89.90	88.06
230		101.46	103.05	100.94
284				107.36
22	74.33	74.39		73.63
19	72.95	74.25	74.11	73.84
179	94.22	95.72		94.17
268	104.63	106.29		104.62
343	112.32	114.05	113.61	112.52
419	118.81	120.31	120.24	119.06
485	123.93	125.49	125.34	124.15
550	127.10	128.51	128.54	127.26
587	127.96	130.01	129.53	128.40
599	123.26	124.98	124.67	123.45
646	124.39	126.25	125.90	124.53
705	124.95	127.55	126.53	124.98
787	120.17	122.36	122.62	120.68
811	117.18	119.60	119.77	117.63
843	113.85	117.37	117.07	114.47
945	113.32	116.61	116.35	113.97
855	112.92	116.50	116.43	113.70
762	121.37	124.71	124.58	121.99
752	122.01	125.52	125.33	122.17
678	124.39	127.96	127.67	124.98
712	123.97	127.73	127.46	124.70
532	125.88	129.49	129.43	126.26
425	118.63	122.16	122.33	120.75
744	122.09	126.13	125.99	123.05
778	119.82	123.78	123.51	120.53
802	117.68	121.55	121.18	118.38
879	112.15	116.04	115.67	112.91
908	112.16	115.89	115.65	112.80
586	126.55	130.40	130.39	127.60
718	122.41	127.24	125.95	123.96
732	122.44	127.00	126.30	123.45
450	119.89	123.34	123.76	121.10
468	121.10	124.48	125.08	122.58
389	115.21	118.29	119.03	116.37
301	107.23	111.02	110.56	108.24
214	97.46	110.10	98.82	98.63
160	90.49	92.94	91.68	91.40
20	71.92	73.73	72.63	72.62

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Figure 13. Electrical Resistivity of Unhydrated Material

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TABLE 12
ELECTRICAL RESISTIVITY OF 0.50 H/Zr MATERIAL

Sample	Temperature (°C)	ρ ($\mu\Omega\text{-cm}$)	Sample	Temperature (°C)	ρ ($\mu\Omega\text{-cm}$)
246 - D3 A	23.3	69.2	246 - D8 B	23.2	69.1
	102.8	82.7		104.0	82.3
	174.7	93.8		174.4	93.3
	241.0	105.2		241.6	104.6
	323.8	116.0		323.6	115.0
	396.0	125.0		396.4	123.9
	474.6	134.0	246 - D8 A	23.2	69.0
	545.6	127.7		103.7	82.0
247 - D3 A	611.0	129.8		174.5	93.3
	23.3	67.8		241.1	104.7
	103.4	80.6		323.8	115.5
	174.6	92.2		396.6	124.4
	241.0	103.4		475.4	133.2
	323.9	114.8		545.0	128.0
	396.4	122.7		610.8	129.2
	475.2	132.1		686.8	132.8
	545.7	127.7		869.0	125.8
	610.8	129.2		947.2	132.1

Figure 14.
Electrical
Resistivity
of 0.50
H/Zr
Material

TABLE 13
ELECTRICAL RESISTIVITY OF 1.26 H/Zr MATERIAL

Temperature (°C)	ρ ($\mu\Omega\text{-cm}$)	
	247 - D7 A	247 - D7 B
23	81.91	71.55
513	-	141.04
539	141.59	143.77
425	139.69	133.19
320	127.85	118.97
213	110.03	100.58
115	93.35	85.05
23	79.93	72.15

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Figure 15. Electrical Resistivity of
1.26 H/Zr Material

Figure 16.
Electrical
Resistivity
of 1.58 H/Zr
Material

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TABLE 14
ELECTRICAL RESISTIVITY OF 1.58 H/Zr MATERIAL

Temperature (°C)	ρ ($\mu\Omega$ -cm)		
	246 - D7 A	246 - D7 B	
866	159.42	-	
735	141.07	144.00	
586	125.73	127.87	
454	110.35	106.02	
326	96.75	97.48	
22	65.80	66.50	
	248 - C6	247 - D8	247 - D6
908	169.14	166.30	165.51
774	152.47	149.89	149.40
639	135.73	132.93	133.72
517	122.36	119.54	124.11
346	99.83	101.58	100.72
146	80.55	80.74	80.06
24	67.47	67.00	66.00

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A least squares equation that fits the data with an RMS deviation of 4.55 $\mu\text{ohm-cm}$ is given by

$$\rho = 73.85 + 0.1023 T + 3.298 \times 10^{-4} T^2 - 5.270 \times 10^{-7} T^3 \quad \dots (16)$$

in the range of 20 to 540°C.

d. 1.58 H/Zr Material

The results of measurements made on five specimens are shown in Figure 16, and the data are given in Table 14. All of the data points in the 20 to 900°C range were used to fit a least squares equation to the results. The equation is given by

$$\rho = 64.475 + 0.10081 T + 6.2542 \times 10^{-6} T^2 + 7.2810 \times 10^{-9} T^3 \quad \dots (17)$$

This expression is sufficiently accurate for estimating the electronic contribution to conductivity. In Figure 16, however, it can be seen that the resistivity as a function of temperature, in the 20 to 900°C range, can be given by three separate curves. The first break in this range appears in the interval of 450 to 515°C, and the second in the interval of 735 to 775°C.

It should be noted that the grouping of the data into the three temperature regions was somewhat arbitrary, and that it was influenced to a large degree by the appearance of similar discontinuities in the heat capacity data at approximately the same temperature intervals.

In the two upper regions, the data points for the individual specimens were connected with dashed lines. It can be observed that, with one exception, all of the dashed lines have nearly the same slopes, indicating identical temperature coefficients of resistivity. The absolute resistivity values deviate by as much as $\pm 2\%$ from the mean, which is shown by the solid line. The fact that the temperature coefficients of resistivity agree in the upper temperature regions, and that the resistivity values are much closer together in the low temperature region, suggest that perhaps some of the specimens contained microcracks.

e. 1.81 H/Zr Material

The results of measurements made on four samples are given in Table 15 and in Figure 17. The resistivity vs temperature curve in the 20 to 550°C range can be expressed by:

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Figure 17. Electrical Resistivity of 1.81 H/Zr Material

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TABLE 15
ELECTRICAL RESISTIVITY OF 1.81 H/Zr MATERIAL

Temperature (°C)	ρ ($\mu\Omega\text{-cm}$)			
	396-C3-B-II	396-C3-C-II	396-B3-B-II	396-B3-C-II
687	134.66	132.72	133.32	133.70
685	134.12	132.12	132.96	133.29
640	126.47	124.69	125.65	125.82
597	119.92	118.27	119.11	119.19
554	114.04	112.09	113.07	113.29
499	107.29	105.57	106.75	107.34
233	77.38	75.99	-	77.11
292	84.09	82.52	82.47	83.90
372	93.13	91.26	91.44	93.03
433	100.13	98.25	98.68	99.92
222	76.52	74.89	76.34	76.30
136	67.13	65.78	67.00	66.89
116	65.09	63.67	64.93	64.73
18	55.20	54.08	55.09	54.81

$$\rho = 53.032 + 9.726 \times 10^{-2} T + 2.543 \times 10^{-5} T^2 - 9.309 \times 10^{-9} T^3. \dots (18)$$

Comparison of the data with measurements made previously at this laboratory⁽⁶⁾ show excellent agreement over the entire temperature range. The break in the curve at 560°C may be due to the $\epsilon \rightleftharpoons \delta + \epsilon$ transition.

f. 1.90 H/Zr Material

The data are given in Table 16 and also shown in Figure 18. The resistivity can be expressed by:

$$\rho = 35.92 + 0.1146 T - 7.389 \times 10^{-5} T^2 + 1.352 \times 10^{-7} T^3 \dots (19)$$

in the range of 20 to 700°C. There is apparently no evidence of any phase change in this temperature range.

TABLE 16
ELECTRICAL RESISTIVITY OF 1.90 H/Zr MATERIAL

Sample	Temperature (°C)	ρ ($\mu\Omega$ -cm)	Sample	Temperature (°C)	ρ ($\mu\Omega$ -cm)	
247-D10 A	585	106.31	247-D2 B	608	107.31	
	645	117.81		531	94.18	
	675	123.38		435	81.54	
	696	126.32		348	71.53	
	600	110.67		18	37.68	
	515	93.78		643	113.27	
	398	78.92		18	39.89	
	25	38.54		248-C1 B	605	108.11
	18	37.89		699	123.97	
	135	49.25		603	108.77	
	643	118.05		501	94.71	
	695	128.20		389	80.61	
	247-D10 B	536		93.73	595	105.81
		594		108.44	546	96.84
592		107.72	454	83.11		
643		116.16	330	68.57		
695		126.44	25	36.50		
608		105.10	248-C1 A	605	107.86	
531		97.41	699	124.08		
247-D2 A	18	39.24	603	108.44		
	536	92.42	501	94.17		
	594	104.75	389	80.51		
	592	104.14	595	105.97		
	643	112.24	546	97.78		
	695	122.76	454	87.13

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Figure 18. Electrical Resistivity of 1.90 H/Zr Material

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Figure 19. Summary of Electrical Resistivity Data

4. Summary

The electrical resistivity measurements made on all compositions are shown in Figure 19, as functions of temperature; and, in Figure 20, as functions of H/Zr atom ratio. Figure 20 indicates systematic variation in electrical resistivity with H/Zr atom ratio and temperature. This is not necessarily a criterion for the reliability of data; however, the absence of random scatter is encouraging.

The electronic contribution to thermal conductivity, k_e , has been calculated for each fuel composition, and is discussed in the section on thermal conductivity measurements.

E. HEAT CAPACITY

1. Apparatus and Methods

Heat capacity measurements were made in this laboratory, using the pulse heating technique.^(6, 12) In the pulse heating measurements, a cylindrical specimen of known cross section and density was subjected to a rapid current pulse. The current (I) flowing through the sample, and the voltage drop (E) between two voltage probes, were simultaneously measured as a function of time (t). These were photographically recorded on a dual beam oscilloscope.

The specific heat (c_p) at any temperature (T) is calculated, using the following relationship:

$$c_p = \frac{1}{m} dQ/dT \quad \dots (20)$$

$$\begin{aligned} &= \frac{1}{m} EI \frac{d\rho/dT}{d\rho/dt} \\ &= \frac{4 EI d\rho/dT}{J\pi D^2 L \delta d\rho/dt} \quad \dots (21) \end{aligned}$$

where

c_p = Specific heat (cal/g-°C)

J = Mechanical equivalent of heat (w-sec/cal)

D = Diameter of the specimen (cm)

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Figure 20. Electrical Resistivity vs H/Zr Atom Ratio

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δ = Specimen density (g/cc)

L = Distance between voltage probes (cm)

ρ = Electrical resistivity (Ω -cm)

The product, $E \cdot I$, is the instantaneous power input. The values of E and I at selected time intervals were read directly from an enlargement of the photograph of the oscilloscope traces, using proportional dividers.

An evaluation of the two derivatives in Equation 21 required prior knowledge of electrical resistivity as a function of temperature. These data were obtained in separate experiments (Section II-D).

Calculation of specific heat was simplified by the use of a computer program,⁽³⁰⁾ written for the IBM 7094. The input data were E vs t , I vs t , and ρ vs T (all in tabular form), and specimen dimensions and density.

Because of the very short heating times (< 0.5 sec), the apparatus was operated in a vacuum instead of a balanced hydrogen overpressure. No hydrogen was evolved from the specimens under these conditions.

A photograph of the pulse heating apparatus, as well as of the test chamber with the vacuum bell removed, is shown in Figure 21. The specimen is soldered to the contact pistons, which in turn are connected to the large, copper block, current feed-throughs. The three spring-loaded probes beneath the specimen are used for measuring the voltage drop. A sharpened knife edge presses the probe against the specimen. The three spring-loaded members on top are merely for preserving specimen alignment during the pulse. Figure 21 also shows a schematic diagram of the pulse heating apparatus.

As stated previously, Battelle employed the ice drop calorimeter^(8,13) for measuring enthalpy, from which heat capacity was derived.

2. Accuracy

Because some of the values for the specific heat of SNAP fuels, measured by the pulse heating technique, were surprisingly high, a complete instrumentation and method standardization program was carried out, using tantalum metal as the reference material. Tantalum was chosen for the calibration standard, since:

a. Apparatus

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b. Test Chamber

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LEGEND:

I = SAMPLE CURRENT	P = SYSTEM PRESSURE
E_1 = VOLTAGE DROP ACROSS SAMPLE LENGTH, l_1	T_F = FINAL SAMPLE TEMPERATURE
E_2 = VOLTAGE DROP ACROSS SAMPLE LENGTH, l_2	T_G = EVOLVED GAS TEMPERATURE

c. Schematic

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Figure 21. Pulse Heating Apparatus

- 1) Tantalum does not undergo any phase transition
- 2) It is a relatively stable metal
- 3) Its properties are such that experimental parameters, comparable to those used for the hydrides, can be employed
- 4) An appreciable amount of reliable specific heat measurements on tantalum are available in the literature. (31-40)

A variety of heating rates were employed, and the oscilloscope gain factors were purposely varied. When the data were reduced, a large scatter was found in the calculated specific heats at various temperatures. A careful correlation was made between the experimental conditions employed in a given run and the degree of departure of the resulting data from the accepted literature values of the specific heat of tantalum.

The sensitive factor was found to be the readability of the slopes of the current and voltage oscilloscope traces. When the sum of the absolute values of the slopes of the voltage vs time traces and the current vs time traces was < 0.5 , agreement with the literature data was quite poor. Above this value, the agreement was good at all heating rates. This minimum slope of 0.5 has now been accepted as a necessary criterion to be met for all pulse heating work.

Figure 22 is a graph showing the specific heat data obtained on a tantalum sample, using the pulse heating technique, compared with specific heat data reported by other investigators. (31-40) The measured values, which can be represented by the equation

$$c_p = 3.128 \times 10^{-2} + 1.199 \times 10^{-5} T - 4.1096 \times 10^{-9} T^2 \quad (300 < T < 1300^\circ\text{C}) \dots (22)$$

agree, within 3%, with the average of the best values reported in the literature over the interval of 300 to 1300°C. The hydride data are believed accurate to $\pm 5\%$.

3. Results and Discussions

Specific heat data obtained from pulse heating measurements for the unhydrided alloy and for the 1.58, 1.81, and 1.90 H/Zr materials are given. The

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Figure 22. Specific Heat of Tantalum

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Figure 23. Specific Heat of Unhydrided Material

0.50 H/Zr material was measured previously, and the results have been given in an earlier report.⁽⁶⁾ The results of the measurements obtained for the unhydrided alloy and 1.81 H/Zr material by BMI in the referee program are also given.

The computational method employed in the pulse heating method gives a smoothed curve of final data from essentially continuous input data; so that there are no data points, as such, to tabulate for the specific heat.

a. Unhydrided Material

Measurements were made at Atomics International on one sample in the rather limited temperature range of 140 to 400°C, so that additional measurements are certainly needed to establish reliability. The results are shown in Figure 23 as the broken curve. It is believed that the data are good up to ~300°C; the downward bending above this temperature is not explainable at this time. The data obtained by Battelle Memorial Institute,⁽⁸⁾ using an ice drop calorimeter, are also shown in Figure 23 by the dashed lines. The data obtained by the two laboratories in the 150 to 300°C range show a disagreement of ~5%. Because of the limited pulse heating measurements and the apparent anomaly in the specific heat curve, the data by BMI are considered the more reliable, and have been used in calculating the thermal conductivity of this composition. The Battelle data can be represented by the following equations:

$$c_p = 5.881 \times 10^{-2} + 4.776 \times 10^{-5} T - 1.043 \times 10^{-8} T^2 \quad (0 < T < 560) \quad \dots (23)$$

$$c_p = 0.115 \quad (600 < T < 790) \quad \dots (24)$$

$$c_p = 0.099 \quad (815 < T < 900) \quad \dots (25)$$

Two transformations occurred in this material: the $\delta + \epsilon \rightleftharpoons \gamma + \epsilon$ transformation at ~595°C, and the $\gamma + \epsilon \rightleftharpoons \gamma$ transformation at ~800°C.

b. 0.50 H/Zr Material

The results of measurements made on this material were presented in an earlier report.⁽⁶⁾ Since the data were used, together with the thermal

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Figure 24. Specific Heat of 1.58 H/Zr Material

Figure 25. Specific Heat of 1.81 H/Zr Material

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diffusivity data, in calculating thermal conductivity, the equation for the heat capacity as a function of temperature is given below.

$$c_p = 4.312 \times 10^{-2} + 4.330 \times 10^{-4} T - 1.496 \times 10^{-6} T^2 + 2.038 \times 10^{-9} T^3 \quad (100 < T < 500^\circ\text{C}) \quad \dots(26)$$

c. 1.58 H/Zr Material

Two specimens were pulse heated to 1200°C to obtain specific heat data in the 200 to 1000°C range, and the results are shown in Figure 24. The data were limited to 1000°C because electrical resistivity data were available only to that temperature. The broken lines represent the experimental data; and the solid lines, the mean of the two curves. The voltage and current traces for both specimens showed discontinuities in the regions $490 \pm 20^\circ$, $775 \pm 30^\circ$, and $1150 \pm 40^\circ$. The last region, however, was not shown in Figure 24. Similar discontinuities were observed in the electrical resistivity data for this material.

d. 1.81 H/Zr Material

Three samples were pulse heated to $\sim 800^\circ\text{C}$. Heat capacity data could be obtained only to $\sim 500^\circ\text{C}$, however, since the electrical resistivity data could be used only to that temperature.* The results are shown in Figure 25 by the broken line. The heat capacity can be represented by the equation

$$c_p = 5.96 \times 10^{-2} + 1.85 \times 10^{-4} T \quad \dots(27)$$

in the range of 150 to 500°C. Discontinuity in the oscilloscope traces in the vicinity of 585°C was observed for all of the specimens. Similar discontinuities were observed in the electrical resistivity and thermal diffusivity measurements.

The data obtained by BMI⁽⁸⁾ are also shown in Figure 25 by the dashed curve. Battelle's c_p values are about 10% greater than those obtained by the pulse heating technique, and are given by the equation:

*Due to break in ρ vs T curve at $\sim 560^\circ\text{C}$ (see Figure 17)

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Figure 26. Specific Heat of 1.90 H/Zr Material

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Figure 27. Summary of Heat Capacity Data

$$c_p = \frac{dH_T}{dT} = 6.821 \times 10^{-2} + 1.949 \times 10^{-4} T - 3.207 \times 10^{-8} T^2 \quad \dots (28)$$

in the range of 0 to 660°C. There was no indication of a change in slope in the enthalpy vs temperature curve in the region of 550°C.

The solid line in Figure 25 represents a weighted average of the data obtained by the two laboratories, with the BMI data weighted slightly more than the AI data, as explained in the separate topical report. ⁽⁸⁾

e. 1.90 H/Zr Material

Two specimens were pulse heated to ~ 1200°C. The results are shown in Figure 26, where the experimental data are given by the broken lines and the mean of the two measurements by the solid line. The heat capacity values are given only to ~ 700°C, because the resistivity data are limited to 700°C. The average heat capacity values can be given by the equation

$$c_p = 9.5066 \times 10^{-2} - 1.6130 \times 10^{-4} T + 1.0322 \times 10^{-6} T^2 \\ - 7.4487 \times 10^{-10} T^3 \quad (200 < T < 700) \quad \dots (29)$$

4. Summary

The heat capacity data for the unhydrided alloy and the alloy hydrided to 1.58, 1.81, and 1.90 H/Zr atom ratios are summarized in Figure 27. The heat capacity data of the 0.50 H/Zr material ⁽⁶⁾ are also shown for comparison. It appears, from the graph, that heat capacity is relatively independent of hydrogen content near room temperature.

F. THERMAL CONDUCTIVITY

1. Apparatus and Methods

As stated earlier, direct measurements of the thermal conductivity of hydrided specimens, using steady-state techniques, are not feasible because of the temperature gradient required within the sample. The unhydrided specimen, however, can be measured by steady-state methods. Battelle Memorial

Institute employed a steady-state longitudinal comparison method in making thermal conductivity measurements of unhydrided samples in the referee program. ⁽⁸⁾

The thermal conductivity of the hydrided, as well as unhydrided specimens, was calculated from thermal diffusivity, heat capacity, and density of the materials, following Equation 1. For the unhydrided and 1.81 H/Zr material, the thermal diffusivity and heat capacity data obtained by both laboratories were carefully analyzed, and the values that were believed to be the most reliable were selected for calculating the thermal conductivity values.

The electronic contributions to thermal transport in these materials were also calculated, using the Wiedemann-Franz-Lorenz relationship. The ratio of the thermal conductivity due to electrons (k_e) and the electrical conductivity (σ) is given by:

$$\frac{k_e}{\sigma} = \frac{\pi^2}{3} \left(\frac{K}{e} \right)^2 T \quad , \quad \dots (30)$$

known as the Wiedemann-Franz ratio. In Equation 30, K is the Boltzmann constant, e is the electronic charge, and T is the absolute temperature. For metals, the product of the Wiedemann-Franz ratio and the reciprocal of the absolute temperature is nearly constant, i. e. ,

$$\frac{k_e}{\sigma T} = \frac{k_e \rho}{T} = \frac{\pi^2}{3} \left(\frac{K}{e} \right)^2 = L \quad , \quad \dots (31)$$

where ρ is the electrical resistivity and L is the Lorenz number, 5.84×10^{-9} cal- Ω /°C²-sec. The thermal conductivity due to electrons, therefore, is given by:

$$k_e = \frac{LT}{\rho} \quad . \quad \dots (32)$$

The lattice conductivity, k_L , was calculated by subtracting k_e from the total conductivity, k , i. e. ,

$$k = k_e + k_L \quad \dots (33)$$

2. Accuracy

The accuracy of the calculated thermal conductivity values depends on the combined uncertainties in the thermal diffusivity ($<\pm 5\%$), heat capacity ($\pm 5\%$), and density ($<\pm 1\%$) values, so that the uncertainty in the thermal conductivity is $<\pm 11\%$.

In the steady-state longitudinal comparative method, two reference materials, Armco iron and Type 347 stainless steel, were used. They have been checked against NBS thermal conductivity "standard" lead. Experience has established that the relative error between different measurements performed in the apparatus does not exceed $\pm 2\%$. This is considered to be the apparatus reproducibility, when using the same reference material. The absolute error of the thermal conductivity values is estimated not to exceed $\pm 5\%$, the chief uncertainty being the absolute thermal conductivity of the reference material.

3. Results and Discussions

The calculated thermal conductivity values, as well as the electronic conductivity values for the unhydrided and 0.50, 1.58, 1.81, and 1.90 H/Zr materials, are given; for the unhydrided alloy, the directly measured values obtained by BMI are also given. For the 1.26 H/Zr material, only the electronic conductivity is given, since no thermal diffusivity nor heat capacity measurements were made.

a. Unhydrided Material

Table 17 summarizes the data for the unhydrided alloy. The calculated thermal conductivity (k) is the product of the heat capacity, thermal diffusivity, and density of the material. The heat capacity values are those obtained by BMI in their drop calorimeter. The thermal diffusivity values represent the values considered best in the Referee Program (i. e., the AI-BMI data were weighted slightly in favor of the AI data). Values shown as k (best data) are the thermal conductivity values considered the most reliable, taking into account both the measured and calculated values. The best data given in the range up to 600°C are also those measured by BMI, using their steady-state method.

TABLE 17

THERMAL CONDUCTIVITY OF UNHYDRIDED MATERIAL

T (°C)	c_p (cal/g-°C)	α (cm ² /sec)	k (calculated) (cal/sec-cm-°C)	k (best data) (cal/sec-cm-°C)	k_e (cal/sec-cm-°C)
20	0.059	0.0720	0.0295	-	0.0232
100	0.063	0.0745	0.0326	0.0351	0.0258
200	0.068	0.0770	0.0364	0.0370	0.0284
300	0.072	0.0790	0.0395	0.0392	0.0307
400	0.076	0.0810	0.0428	0.0416	0.0333
500	0.080	0.0820	0.0456	0.0450	0.0360
595	0.084	0.0825	0.0482	0.0481	
600	0.115	0.0875	0.0699	0.0510	
700	0.115	0.0985	0.0787	0.0549	
750	0.115	-	-	0.0572	
800	0.115	0.1095	0.0875	0.0594	
815	0.099	0.1155	0.0795	0.0636	
850	0.099	-	-	0.0662	
900	0.099	0.1270	0.0874	0.0693	

Density = 6.95 g/cc

In this range, the measured and calculated values are in excellent agreement, as shown in Figure 28, lending considerable confidence to the data. In the 600 to 750°C and 850 to 900°C ranges, the best data were computed by weighting the measured values considerably more than the calculated values, since the heat capacity measurements were not considered so accurate as the thermal diffusivity and thermal conductivity measurements. The poor agreement between the measured data and calculated data in the upper temperature regions is probably due to overestimation in specific heat values at the phase changes, giving erroneously high thermal conductivity values. The electronic contribution to thermal conductivity is also given in Table 17, and is shown in Figure 28 as the dashed line. Up to 600°C, the electronic thermal conductivity accounts for ~75% of the total thermal conductivity. Figure 28 also shows the locations of the two phase transitions. The closed circle indicates data reported by Przybycien and Linde.⁽⁴¹⁾

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Figure 28. Thermal Conductivity of Unhydrated Material

TABLE 18
THERMAL CONDUCTIVITY OF
0.50 H/Zr MATERIAL

T (°C)	α (cm ² /sec)	c_p (cal/g-°C)	k (cal/sec-cm-°C)	k_e (cal/sec-cm-°C)
20	0.060	-	-	0.0251
100	0.0575	0.0735	0.0282	0.0267
200	0.0556	0.0862	0.0320	0.0283
300	0.0529	0.0934	0.0330	0.0298
400	0.0492	0.1074	0.0353	0.0315
420	0.043	0.1125	0.0323	
450	0.040	0.1225	0.0327	
475	0.039	0.130	0.0339	

Density = 6.68 g/cc

TABLE 19
ELECTRONIC THERMAL
CONDUCTIVITY OF 1.26
H/Zr MATERIAL

T (°C)	ρ ($\mu\Omega$ -cm)	k_e (cal/sec-cm-°C)
20	76.0	0.0225
100	87.5	0.0249
200	103.0	0.0268
300	119.7	0.0280
400	133.8	0.0294
500	141.0	0.0320

Figure 29.
Thermal Con-
ductivity of
0.50 H/Zr
Material

b. 0.50 H/Zr Material

The thermal conductivity of this material was calculated from the thermal diffusivity measurements and the heat capacity data previously reported.⁽⁶⁾ The electronic contribution to thermal conduction was also calculated, using the electrical resistivity data. The results are given in Table 18 and shown in Figure 29. The electronic thermal conduction for the 0.50 H/Zr material appears to be about 90% of the total thermal conductivity up to 400°C.

c. 1.26 H/Zr Material

Only the electrical resistivity measurements were obtained on this material. The calculated electronic thermal conductivity is given in Table 19.

d. 1.58 H/Zr Material

The calculated thermal conductivity values are shown in Figure 30, and the data are tabulated in Table 20. Since no thermal diffusivity data were obtained in the 500 to 850°C interval, the diffusivity values in this region were obtained by assuming a smooth curve over the entire room temperature to 900°C range. The thermal conductivities calculated for the regions above 500°C, therefore, are shown in broken lines, denoting some uncertainty in the data. The calculated thermal conductivity in the 200 to 400°C interval falls below the curve of the electronic thermal conductivity, indicating that the thermal conductivity values are too low. This discrepancy can probably be traced to the heat capacity data, since the extension of the two upper curves in Figure 24 appears to fall above that indicated in the low-temperature region. There is also some uncertainty in the thermal diffusivity data, since it was not possible to monitor the hydrogen overpressure below 700°C.

e. 1.81 H/Zr Material

The calculated thermal conductivity values are shown in Figure 31 and the data are tabulated in Table 21. Both the heat capacity and thermal diffusivity values used to calculate thermal conductivity represent the best values of the AI-BMI measurements. The thermal conductivity rises linearly between 100 and 550°C. At ~ 550°C, the temperature coefficient becomes slightly negative. According to Figure 31, the electronic contribution to thermal conduction is about 70% of the total thermal conductivity, over the entire temperature range investigated for the 1.81 H/Zr material.

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Figure 30. Thermal Conductivity of 1.58 H/Zr Material

TABLE 20

THERMAL CONDUCTIVITY OF 1.58 H/Zr MATERIAL

T (°C)	c_p (cal/g-°C)	α (cm ² /sec)	k (cal/sec-cm-°C)	k_e (cal/sec-cm-°C)
100	-	0.068	-	0.0292
200	0.076	0.061	0.0283	0.0326
250	0.080	0.058	0.0281	-
300	0.087	0.056	0.0292	0.0350
350	0.098	0.053	0.0317	-
400	0.116	0.051	0.0361	0.0370
450	0.145	0.050	0.0439	-
550	0.150	(0.0475)*	(0.0435)	-
600	0.189	(0.0465)	(0.0452)	0.0396
650	0.170	(0.046)	(0.0478)	-
700	0.185	(0.0455)	(0.0514)	0.0404
750	0.206	(0.045)	(0.0566)	-
800	0.210	(0.045)	(0.0577)	0.0410
850	0.227	0.0445	0.0617	-
900	0.244	0.044	0.0663	0.0414
950	0.267	0.044	0.0718	-

Density = 6.11 g/cc

*Values in parentheses were obtained by interpolation

6-13-66 UNC

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Figure 31. Thermal Conductivity of 1.81 H/Zr Material

TABLE 21

THERMAL CONDUCTIVITY OF 1.81 H/Zr MATERIAL

T ($^\circ\text{C}$)	c_p ($\text{cal/g-}^\circ\text{C}$)	α (cm^2/sec)	k ($\text{cal/sec-cm-}^\circ\text{C}$)	k_e ($\text{cal/sec-cm-}^\circ\text{C}$)
20	-	-	-	0.0311
100	0.0845	0.0940	0.0483	0.0346
200	0.103	0.0820	0.0513	0.0376
300	0.121	0.0735	0.0541	0.0397
400	0.138	0.0680	0.0573	0.0412
500	0.155	0.0640	0.0604	0.0422
550	0.163	0.0630	0.0624	0.0427
600	0.170	0.0605	0.0626	0.0426
650	0.178	0.0575	0.0623	0.0422

Density = 6.09 g/cc

TABLE 22

THERMAL CONDUCTIVITY OF 1.90 H/Zr MATERIAL

T (°C)	c_p (cal/g-°C)	α (cm ² /sec)	k (cal/sec-cm-°C)	k_e (cal/sec-cm-°C)
20	-	0.147	-	0.0448
100	-	0.126	-	0.0466
200	0.096	0.106	0.0619	0.0485
300	0.121	0.090	0.0662	0.0497
400	0.147	0.081	0.0724	0.0500
500	0.179	0.074	0.0805	0.0493
600	0.208	0.069	0.0873	0.0475
700	0.230	0.065	0.0909	0.0450

Density = 6.08 g/cc

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Figure 32. Thermal Conductivity of 1.90 H/Zr Material

f. 1.90 H/Zr Material

The thermal conductivity values calculated for this material are tabulated in Table 22 and are shown in Figure 32. According to Figure 32, k_e accounts for about 80% of the total conductivity at 200°C. At 700°C, however, the lattice conductivity is about equal to k_e . The S-shaped characteristic is a carry over from the specific heat curve for this material.

4. Summary

The thermal conductivities of the various materials are summarized in Figure 33, and the electronic thermal conductivities are summarized in Figure 34, both as functions of temperature.

One can observe from the figures that the thermal conductivities of the materials increase with temperature, at least over most of the temperature range covered. This is contrary to the results obtained by Beck⁽⁴²⁾ on the zirconium hydrides, of compositions $ZrH_{1.5}$, $ZrH_{1.3}$, and $ZrH_{0.83}$, and containing no uranium. Beck shows that the temperature coefficients of thermal conductivity for $ZrH_{1.5}$ and $ZrH_{0.83}$ are negative, and that the conductivity of $ZrH_{1.3}$ is nearly temperature independent in the range of ~ 200 to 500°C.

The difference in the temperature coefficients between the materials, with and without uranium, can perhaps be appreciated if one looks at the thermal conductivities of the various materials and the components involved. Figure 35 shows the thermal conductivities of uranium⁽⁴³⁾ and zirconium⁽⁴³⁾ metals, Beck's⁽⁴²⁾ $ZrH_{1.5}$ data, Przybycien and Linde's⁽⁴¹⁾ Zr - 10 wt % U data, and the present thermal conductivity data on Zr - 10 wt % U alloy. In the room temperature to ~700°C range, uranium has a positive temperature coefficient of conductivity, whereas zirconium has a slightly negative temperature coefficient. The effect of adding 10% by weight of uranium to zirconium is to reduce the room temperature value of the thermal conductivity of zirconium by ~ 50%. The temperature coefficients of thermal conductivity for the Zr - 10 wt % U alloy, as well as for its hydrides, are all positive. The slopes of the thermal conductivity vs temperature curves for the Zr-U alloys have been shown to increase with increasing uranium content.^(41,43)

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Figure 33. Summary of Thermal Conductivity Data

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Figure 34. Summary of Electronic Thermal Conductivity Data

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Figure 35. Thermal Conductivity of Zr-U-H System

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Figure 36. Relative Contributions of Electronic and Lattice Conductivities

The effect of a small amount of uranium in zirconium (i. e., in 23:1 atom ratio of zirconium to uranium) therefore can be seen to have a pronounced effect on the magnitude and mode of thermal conductivity. The investigation of the thermal transport mechanisms in the Zr-U-H system should be very interesting; however, it is outside the scope of the present work.

Figure 36 shows the relative contributions of the electronic and lattice conductivities to the total thermal conductivity of the various compositions, at 100, 200, 300, and 400°C. The electronic contribution was estimated from Equation 32, and the lattice conduction represents the difference between the total and the electronic conductions. For 1.26 and 1.58 H/Zr, only the electronic contribution is shown. Table 23 shows the ratio of the electronic thermal conduction to the total conduction for several material compositions.

TABLE 23
RATIO OF ELECTRONIC TO TOTAL
CONDUCTIVITIES

T (°C)	k_e/k			
	0.00	0.50	1.81	1.90
100	0.74	0.95	0.74	-
200	0.77	0.88	0.75	0.78
300	0.78	0.90	0.74	0.75
400	0.80	0.89	0.73	0.69
500	0.80	-	0.71	0.61
600	-	-	0.71	0.54
700	-	-	-	0.50

G. PHASE RELATIONSHIPS

The proper interpretation and evaluation of the thermophysical properties data of the hydrides depend on a reasonably sound knowledge of their phase relationships and on the kinetics associated with phase transformation and hydrogen migration. The zirconium-hydrogen system has received considerable attention⁽⁴⁴⁻⁵⁰⁾ in the past few years; and its phase diagram has been fairly well established, although there still are areas where general agreement does

TABLE 24
DISCONTINUITIES OR INFLECTIONS IN PROPERTY vs
TEMPERATURE CURVES

H/Zr	Property	Temperature (°C)	Phase Transition
0.00	ρ	585-600	} $\delta + \epsilon \rightleftharpoons \gamma + \epsilon$
	α	595 $\pm$ 10	
	c_p	560-600*	
	ρ	~800	} $\gamma + \epsilon \rightleftharpoons \gamma$
	α	795-800	
	c_p	790-815*	
0.50	ρ	>475?	} $(\alpha + \delta \rightleftharpoons \alpha + \beta)$ and $(\alpha + \beta \rightleftharpoons \beta)$
	α	390-510	
	c_p	~400	
1.58	ρ	460-515	
	c_p	475-515	
	ρ	720-780	
	c_p	750-800	
	c_p	1150 $\pm$ 50	
1.81	ρ	560 $\pm$ 10	} $(\epsilon \rightleftharpoons \delta + \epsilon)$
	α	550 $\pm$ 10	
	c_p	~585	
1.90	c_p	850 $\pm$ 50	$(\epsilon \rightleftharpoons \delta + \epsilon)$

*BMI data
() Probable phase transformation

not exist. The Zr-U-H system has also been investigated by several workers,^(25,26) but the investigations have been limited to selected temperature regions.

The present work had as its primary aim the measurement of the thermo-physical properties of Zr-U-H compositions. It was not the intent to deduce the phase relationship from the measurements obtained. Many of the data, however, when plotted as functions of temperature, showed either discontinuities or inflections in the curves. Such behaviors are usually encountered when phase boundaries are crossed. None of the binary systems, Zr-H, U-H, or Zr-U, show phase changes at the temperatures where some of the discontinuities were observed; and, since no information was available in the literature on the ternary Zr-U-H in the temperature regions where these discontinuities were observed, no immediate conclusion could be reached as to the significance of these behaviors. Structural studies (e.g., high-temperature x-ray diffraction techniques) would be necessary to establish the phases present. However, the observations made in the present work, though qualitative, are summarized in Table 24. They should be of value in further investigations on the Zr-U-H phase diagram, by allowing one to select some of the more interesting areas for detailed studies.

For the unhydrided alloy, the $\delta + \epsilon \rightleftharpoons \gamma + \epsilon$ and the $\gamma + \epsilon \rightleftharpoons \gamma$ phase transitions agree well with the literature data,⁽²⁴⁾ which give 593 and $800 \pm 20^\circ\text{C}$ for the temperatures of the two transitions, respectively. A typical oscilloscope film obtained in the pulse heating experiment is shown in Figure 37. The two inflections in the E and I traces indicate the phase transitions.

Although the discontinuity in the electrical resistivity curve for the 0.50 H/Zr material apparently occurs above 475°C (see Figure 12), it is conceivable that the break actually occurs below this temperature. If one can draw an analogy from the thermal diffusivity data, it is possible that the break actually occurs closer to 400°C (i.e., the thermal diffusivity data points at $\sim 500^\circ\text{C}$ fall on the curve extrapolated from the lower temperature region, although the data points between 400 and 500°C fall below the curve). Unfortunately, no electrical resistivity data were obtained in the interval of 395 to 475° . The heat capacity curve shows an inflection at $\sim 400^\circ\text{C}$ also.

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a. Unhydrided Material

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b. 1.58 H/Zr Material

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c. 1.81 H/Zr Material

6-13-66 UNC

7611-4781

d. 1.90 H/Zr Material

Figure 37. Oscilloscope Traces in Pulse Heating Experiment

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The inflection in the electrical resistivity curve at $\sim 400^\circ\text{C}$ for the 1.26 H/Zr material, coupled with the inflection at about the same temperature in the heat capacity curve reported previously⁽⁶⁾ for the 1.20 H/Zr material, causes one to suspect that something is taking place at this temperature. Probably the most plausible explanation is that these inflections are due to the $\alpha + \delta \rightleftharpoons \beta + \delta$ transition in the Zr-H system. This transition in the Zr-H system is at 547°C , but it may be that the eutectoid temperature is lowered considerably by the presence of uranium. The fact that the inflections in the 0.50 H/Zr curves also occur at $\sim 400^\circ\text{C}$ seems to support this. Krause et al.⁽²⁵⁾ found that the addition of 1 wt % U lowered the eutectoid temperature from 547 to 541°C , whereas the addition of 25 wt % U raised the boundary from 547 to 601°C .

Apparent departures from smoothed curves were observed in the electrical resistivity and heat capacity data in the 460 to 515°C and 720 to 800°C regions for the 1.58 H/Zr material. A third inflection was also observed in the pulse heating curves at $1150 \pm 50^\circ\text{C}$. Two of the inflections can be seen in Figure 37b, which is a typical oscilloscope trace obtained for this material in the pulse heating experiment. The third inflection is difficult to discern in Figure 37b, but is brought out clearly when the gain in the oscilloscope is increased.

The inflection in the curves for the thermal diffusivity and electrical resistivity data for the 1.81 H/Zr material at $\sim 550^\circ\text{C}$ are believed to be due to the $\epsilon \rightleftharpoons \delta + \epsilon$ phase transition in the Zr-H binary. Libowitz⁽⁴⁸⁾ proposes that the $\delta + \epsilon$ region curves towards the hydrogen-rich end of the Zr-H phase diagram at higher temperatures, but shows the transition boundary for 1.81 H/Zr to be greater than 700°C . Figure 37c shows the oscilloscope traces obtained in the pulse heating experiment for the 1.81 H/Zr material. The enthalpy vs temperature curve obtained by Battelle did not show evidence of an inflection, but this may be due to insufficient sensitivity of the drop calorimetric technique for this particular transition.

The 1.90 H/Zr specimens were pulse heated to $\sim 1200^\circ\text{C}$. Although heat capacity calculations were limited to $\sim 700^\circ\text{C}$, the oscilloscope traces indicated an apparent phase transformation at $\sim 850^\circ\text{C}$, as shown in Figure 37d.

In the absence of the ternary Zr-U-H diagrams in the temperatures of interest, the probable phase transformations in Table 24 have been obtained by reference to the Zr-H binary, and will no doubt require refinement or revision when additional phase information becomes available.

III. SUMMARY AND CONCLUSIONS

The values of highest confidence, representing the measurements made on the various SNAP materials, have been summarized in Figure 9 for thermal diffusivity, Figure 19 for electrical resistivity, Figure 27 for heat capacity, and Figure 33 for thermal conductivity, where the properties are plotted as functions of temperature. Thermal diffusivity, electrical resistivity, and thermal conductivity, as functions of H/Zr atom ratio, have also been illustrated in Figures 10, 20, and 36, respectively.

The thermal conductivity curves for the SNAP fuel materials all show positive temperature coefficients over the temperature range covered in this investigation. The 1.81 H/Zr material shows a negative temperature coefficient, but only above $\sim 550^{\circ}\text{C}$. This shows the influence of the small amount of uranium in the alloy, since zirconium hydrides, without uranium, have been shown to have negative temperature coefficients of thermal conductivity.

The electronic contribution to thermal conductivity has been estimated for each of the materials, using the Wiedermann-Franz-Lorenz relationship. The only anomaly appears to be in the 1.58 H/Zr material data, where the total conductivity values in the 200 to 400°C range are less than the electronic conductivity values. The heat capacity data are suspect in this case, and confirmatory measurements should be made.

The discontinuities and/or inflections observed in the thermal diffusivity, electrical resistivity, and pulse heating measurements have been noted; and their probable implications, as related to the phase relationship of the materials, have been discussed.

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