70
JUL 19 1967

~~CONFIDENTIAL~~
UNCLASSIFIED

NAA-SR-11960

COPY
MASTER

33258

MEASUREMENT OF THERMAL PROPERTIES
OF
SNAP FUEL MATERIALS

(Title Unclassified)

AEC Research and Development Report

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

~~GROUP 1~~

~~Excluded from automatic downgrading and declassification~~

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

0 665 000
0 665 000

UNCLASSIFIED ~~CONFIDENTIAL~~

67 8702
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA

Price \$1.45

Available from the

U.S. Atomic Energy Commission,
Division of Technical Information Extension,
P. O. Box 62
Oak Ridge, Tennessee.

Please direct to the same address inquiries covering the procurement of other classified AEC reports.

03729030

UNCLASSIFIED

~~CONFIDENTIAL~~

NAA-SR-11960
NUCLEAR TECHNOLOGY-
AEROSPACE SAFETY

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MEASUREMENT OF THERMAL PROPERTIES OF SNAP FUEL MATERIALS

(Title Unclassified)

By:

J. B. VETRANO*
C. J. AMBROSE†
G. E. CULLEY
F. A. FINCH
M. M. NAKATA

H. W. DEEM
E. A. ELDRIDGE
E. L. FOSTER
J. F. LAGEDROST
J. MATOLICH
S. G. NELSON

Atomics International, A Division
of North American Aviation, Inc.

Battelle Memorial Institute

*Now with Battelle-Northwest, Richland, Washington

†Now with Donald W. Douglas Laboratories, Richland, Washington

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains restricted data relating to civilian applications of atomic energy.

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(04-3)-701
ISSUED: JUNE 20, 1967

UNCLASSIFIED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISTRIBUTION OF THIS DOCUMENT IS LIMITED TO GOVERNMENT AGENCIES AND THEIR CONTRACTORS

~~CONFIDENTIAL~~

DISTRIBUTION

NUCLEAR TECHNOLOGY-AEROSPACE SAFETY M-3679 (50th Ed.)

	No. of Copies		No. of Copies
AEC Albuquerque Operations Office	1	NASA Goddard Space Flight Center	1
AEC New York Operations Office	1	NASA Langley Research Center	1
AEC Oak Ridge Operations Office	1	NASA Lewis Research Center	2
AEC Patent Office	1	NASA Manned Spacecraft Center	1
Aerojet-General Corporation (NASA)	2	NASA Marshall Space Flight Center	1
Aerojet General Corporation, Sacramento	2	NASA, Washington	2
Aerojet-General Nucleonics (NASA)	1	National Reactor Testing Station (INC)	4
Aeronautical Systems Division	2	Navy Air Systems Command	1
Air Force Headquarters	1	Navy Missile Center	1
Air Force Lowry Air Force Base	1	Navy Office of the Chief of Naval Operations	1
Air Force Surgeon General	1	Navy Ordnance Systems Command	1
Air Force Weapons Laboratory	2	Navy Radiological Defense Laboratory	1
Air University Library	1	Navy Research Laboratory	2
AI Research Manufacturing Company, Los Angeles	1	Navy Ship Systems Command Headquarters	1
Allison Division-GMC	1	Navy Weapons Evaluation Facility	1
Argonne National Laboratory	1	NUS Corporation	1
Army Materials Research Agency	1	Pratt and Whitney Aircraft Division (NASA)	1
Army Nuclear Defense Laboratory	1	Radio Corporation of America	1
ARO, Inc.	1	Radio Corporation of America, Cranbury	1
Battelle Memorial Institute	1	Rand Corporation	2
Battelle-Northwest	3	Republic Aviation Division	1
Bendix Corporation (NASA)	1	Sandia Corporation	8
Brookhaven National Laboratory	1	Tracerlab, Richmond	1
Central Intelligence Agency	1	TRW Systems	1
Combustion Engineering, Inc.	1	Union Carbide Corporation (ORNL)	4
Director of Defense Research and Engineering	1	Union Carbide Corporation (Paducah Plant)	1
Douglas Aircraft Company, Inc. (MSSD)	2	University of California, Livermore	1
Du Pont Company, Aiken	2	Westinghouse Electric Corporation, Lima	1
EG&G, Inc., Goleta	1	Westinghouse Electric Corporation (NASA)	1
General Atomic Division	1	AEC Division of Technical Information Extension	10
General Dynamics/Fort Worth	1	AI Library (Includes 2 copies to CPAO, 3 copies to AEC, Washington, 2 copies to SFOO)	43
General Electric Company, Cincinnati	1		
General Electric Company (FPD)	1		
General Electric Company (MSVD)	1		
Grumman Aircraft Engineering C Corporation	1		
Institute for Defense Analyses	1		
Jet Propulsion Laboratory	1		
Johns Hopkins University (APL)	1		
Lockheed-Georgia Company	1		
Los Alamos Scientific Laboratory	1		
Martin Company	1		
Mound Laboratory	1		
MSA Research Corporation (COO-765)	1		

NAA-SR-11960

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

CONTENTS

	Page
Abstract	7
I. Introduction	9
II. Materials	11
A. Background	11
B. Preparation of Material	11
C. Characterization of Material	15
III. Specific Heat	19
A. Apparatus and Methods	19
B. Experimental Results	23
1. Unhydrided Specimen	23
2. Hydrided Specimens	25
C. Evaluation of Data	31
IV. Thermal Diffusivity	37
A. Apparatus and Methods	37
B. Experimental Results	39
1. Unhydrided Specimen	39
2. Hydrided Specimens	45
C. Evaluation of Data	55
V. Thermal Conductivity	59
A. Apparatus and Method	59
B. Experimental Results	61
C. Evaluation of Data	67
VI. Summary	69
Appendix	73
References	75

TABLES

1. Hydrogen Content of Hydrided Fuel Rods	12
2. Chemical Analysis Results	16
3. Observed and Calculated Enthalpy Values for the Unhydrided Material	26

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLES

	Page
4. Instantaneous Specific Heats for the Unhydrided Material	27
5. Electrical Resistivity of the Unhydrided Material.	28
6. Observed and Calculated Enthalpy Values for the Hydrided Material.	32
7. Instantaneous Specific Heat Values for the Hydrided Material.	32
8. Electrical Resistivity of Hydrided Specimens	35
9. Thermal Diffusivity of Unhydrided Materials.	38
10. Thermal Diffusivity, Unhydrided Specimen, Transverse.	43
11. Thermal Diffusivity, Unhydrided Specimen, Longitudinal	44
12. Interpolated Thermal Diffusivity Values for Unhydrided Specimens	45
13. Thermal Diffusivity of Hydrided Material in a Vacuum	46
14. Thermal Diffusivity of Hydrided Material, Balanced Hydrogen Pressure	48
15. Thermal Diffusivity, Hydrided Specimen No. 1, Transverse	49
16. Thermal Diffusivity, Hydrided Specimen No. 2, Transverse	50
17. Thermal Diffusivity, Hydrided Specimen No. 1, Longitudinal	51
18. Thermal Diffusivity, Hydrided Specimen No. 2, Longitudinal	52
19. Thermal Diffusivity, Hydrided Specimen No. 3, Longitudinal	53
20. Interpolated Thermal Diffusivity Values for Hydrided Specimens	55
21. Observed Thermal Conductivity of the Unhydrided Material, Specimen No. 1, Individual Points	60
22. Observed Thermal Conductivity of the Unhydrided Material, Specimen No. 2, Individual Points	62
23. Observed Thermal Conductivity of the Unhydrided Material, Specimen No. 1.	63
24. Observed Thermal Conductivity of the Unhydrided Material, Specimen No. 2	63
25. Interpolated Thermal Conductivity of the Unhydrided Specimen No. 1	64
26. Interpolated Thermal Conductivity of the Unhydrided Specimen No. 2	64

~~CONFIDENTIAL~~

TABLES

	Page
27. Measured Thermal Conductivity of Unhydrided Material	67
28. Best Values for Properties of Unhydrided Fuel	69
29. Best Values for Properties of Hydrided Fuel.	70

FIGURES

1. Material Flow for Heat 396	13
2. Material Flow for Heat 397	14
3. Typical Microstructures of Sample Materials	17
4. Dissociation Pressure of Hydrided Specimens	18
5. Stainless Steel Ice Calorimeter	20
6. View of Pulse Heating Apparatus.	22
7. Enthalpy vs Temperature for the Unhydrided Material	23
8. Specific Heat vs Temperature for the Unhydrided Material.	27
9. Electrical Resistivity of Unhydrided Material	29
10. Enthalpy vs Temperature for the Hydrided Material.	30
11. Specific Heat vs Temperature for the Hydrided Material.	33
12. Specific Heat of Three Different Pulsed Specimens of Hydride	33
13. Electrical Resistivity of Hydrided Material	34
14. Summary of Specific Heat Data.	36
15. Thermal Diffusivity of Unhydrided Materials	41
16. Thermal Diffusivity, Unhydrided Specimen, Transverse.	43
17. Thermal Diffusivity, Unhydrided Specimen, Longitudinal	44
18. Thermal Diffusivity of Hydrided Materials (Vacuum)	47
19. Thermal Diffusivity of Hydrided Material (Balanced Hydrogen Pressure)	48
20. Thermal Diffusivity, Hydrided Specimen No. 1, Transverse.	49
21. Thermal Diffusivity, Hydrided Specimen No. 2, Transverse.	50

~~CONFIDENTIAL~~

FIGURES

	Page
22. Thermal Diffusivity, Hydrided Specimen No. 1, Longitudinal	51
23. Thermal Diffusivity, Hydrided Specimen No. 2, Longitudinal	52
24. Thermal Diffusivity Hydrided Specimen No. 3, Longitudinal	53
25. Comparison of Data on Diffusivity of Unhydrided Material.	56
26. Comparison of Data on Diffusivity of Hydrided Material	58
27. Thermal Conductivity of Unhydrided Material (Steady-State Direct Measurement)	66
28. Thermal Conductivity of Unhydrided Material (Calculated vs Measured Data)	66
29. Summary of Specific Heat Measurements	68
30. Summary of Resistivity Data	70
31. Summary of Diffusivity Measurements	71
32. Summary of Conductivity Measurements	71
33. Phase Diagram of Zirconium-Uranium Binary System	73
34. Phase Diagram of Zirconium-Hydrogen Binary System	73

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

ABSTRACT

Because of the existing conflicting information on the thermo-physical properties of zirconium hydride, two laboratories worked in close cooperation to develop highly reliable data on the uranium-bearing zirconium hydride and on the unhydrided alloy.

Measurements of specific heat and thermal diffusivity were made on both hydrided and unhydrided compositions, and the thermal conductivity was calculated from the product of these quantities and the density of the material. Because of thermal gradients that cause hydrogen redistribution, only the unhydrided composition was subjected to a direct steady-state measurement of the thermal conductivity. Agreement between experimental and calculated values proved to be remarkably good.

The two laboratories were Atomics International Division of North American Aviation, Inc., and the Columbus Division of Battelle Memorial Institute. The work was performed for the SNAP (Systems for Nuclear Auxiliary Power) Aerospace Nuclear Safety Program.

~~CONFIDENTIAL~~

BLANK

DECLASSIFIED
~~CONFIDENTIAL~~

I. INTRODUCTION

The literature on the thermophysical properties of zirconium hydride contains an abundance of conflicting information. Hydrogen is very mobile in zirconium hydride; this property, coupled with the 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 in the Zr-H system is clearly illustrated, for example, by the work of Bickel.^{(1)*} He shows transport behavior ranging from primarily hole-conduction to primarily electronic-conduction and from a moderately good conductor to almost a superconductor, depending on the hydrogen content.

Most conventional elevated-temperature thermophysical property measurements have been carried out either in a vacuum or in an inert atmosphere. These techniques are completely inadequate for zirconium hydride, because of its reversible decomposition to the elements. Many hydride investigators have realized this problem and have tried to overcome it by using special null-void volume apparatuses, 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. These data are not always known as precisely as is necessary. Slight errors in balance or in time to balance can lead to an important error in the composition of the condensed phase; this in turn influences the property being measured.

A thermal gradient across a specimen is not ordinarily a serious source of experimental error in elevated-temperature property investigations. In the measurement of thermal conductivity, for example, one must establish a heat flux by imposing a temperature gradient. The conductivity is then measured at an "average" specimen temperature. When zirconium hydride is subjected to a thermal gradient, hydrogen redistribution occurs in the solid so that there is also a composition gradient from the cold to the hot region. Hence, not only

*Superscript numbers in parentheses are for References at back of this report.

DECLASSIFIED
~~CONFIDENTIAL~~

CONFIDENTIAL 0005087030

is an "average" temperature involved but so is an "average" composition, and the sources of uncertainty are compounded.

The work presented in this report represents a concentrated effort by two laboratories working in close cooperation to develop highly reliable data on one composition of uranium-bearing zirconium hydride and also on the unhydrided alloy. All starting materials in the program were prepared from the same ingot stock using identical procedures. After their preparation, the materials were inspected for compositional conformance, and representative rods were then selected by a random process for distribution to the two laboratories where measurements were conducted. Each laboratory used calibrated equipment. They both used the same table of values for dissociation pressure as a function of temperature in making measurements, so that, except for kinetic effects, precise duplication of condensed phase composition existed, regardless of the temperature level maintained or the apparatus being employed.

Measurements of specific heat and thermal diffusivity were made on both the hydrided and the unhydrided compositions, and the thermal conductivity was calculated from the product of these quantities and the density of the material. Because of the thermal-gradient problems previously mentioned, only the unhydrided composition was subjected to a direct steady-state measurement of thermal conductivity.

The laboratories taking part in the program were Atomics International, a Division of North American Aviation, Inc. and the Columbus Division of Battelle Memorial Institute. The work was performed for the SNAP (Systems for Nuclear Auxiliary Power) Aerospace Nuclear Safety Program.

CONFIDENTIAL 0005087030

II. MATERIALS

A. BACKGROUND

There were two basic considerations for the production of specimen material for this program. These were to: a) include material that conformed to SNAP 10A composition specifications; and b) provide, insofar as possible, both participating laboratories with identical material. These considerations were met by using the standard production procedures for the SNAP 10A flight system fuel,^(2, 3) in conjunction with an extensive chemical analysis program.⁽⁴⁾

SNAP fuel is a hydrided zirconium-uranium alloy. For SNAP 10A the uranium concentration is 10 wt % with 0.15 wt % carbon added to improve the grain structure. For the present program, normal uranium was used in place of the highly enriched uranium used for the reactor fuel. The hydrogen content for the "fully" hydrided material was set at 1.81 H/Zr (effective).*

The phase diagrams of the zirconium-uranium and zirconium-hydrogen binary systems are given in the Appendix. The zirconium-uranium diagram is that given by Rough and Bauer;⁽⁵⁾ the zirconium-hydrogen diagram is one that has been tentatively adopted at Atomics International as the most reliable. It should be noted, however, that there still are areas of disagreement among investigators in the phase diagram of both binaries, and that investigations are being conducted at AI to resolve some of these differences. One should also be cautioned that identical notations, viz., δ and ϵ , are used in the two-phase diagrams; it is hoped that the δ and ϵ phases in the zirconium-uranium binary will not be confused with those of the zirconium-hydrogen system.

B. PREPARATION OF MATERIAL

After considering the size of specimens needed and the volume of fuel required to extrude satisfactorily, it was decided to produce the material in two heats. Heat 396 was produced by the standard triple-arc-melt and double-extrusion process,⁽²⁾ with a 0.632-in. (SNAP 8) diameter final extrusion. The yield was 14 rods each approximately 16 in. long and two shorter rods. Eight

*Effective H/Zr is the ratio of hydrogen atoms to zirconium atoms excluding those zirconium atoms in the carbide form.

of these rods were hydrided and eight were not. Four hydrided and four unhydrided rods were chosen in a random manner for each laboratory. The specimens obtained from these rods were to be used for specific heat, thermal diffusivity, and electrical resistivity measurements.

Hydriding of the eight rods from Heat 396 was performed by standard SNAP 10A procedures.⁽³⁾ All eight were hydrided in the same retort at the same time to minimize rod-to-rod variations. The hydrogen content of each after hydriding was determined by the weight-gain method. The rods were weighed to ± 0.001 gram before and after hydriding, and the increase in weight was taken to be the amount of hydrogen contained in the hydrided rod. A small sample was also cut from the hydrided rod and analyzed for hydrogen by vacuum extraction as a verification for the weight-gain result. Table 1 lists the hydrogen content of each of the hydrided rods. The average hydrogen content of the eight hydrided rods was 1.736 wt % or an effective H/Zr ratio of 1.81.

TABLE 1
HYDROGEN CONTENT OF HYDRIDED FUEL RODS

Fuel Rod No.	Hydrogen Content (wt %)	Density (gm/cc)	N_H (atoms $H_2/cm^3 \times 10^{22}$)
396A-1	1.743	6.064	6.32
396A-3	1.726	6.070	6.26
396B-1	1.732	6.070	6.28
396B-3	1.737	6.073	6.30
396C-1*	1.736	6.069	6.30
396C-3	1.735	6.071	6.29
396D-1	1.740	6.068	6.31
396D-3	1.739	6.072	6.31

*Broken during final machining.

The second heat (397) was to be used as material for the direct thermal conductivity measurements. It was originally planned to make some of these measurements by a radial heat-flow method, and this would require 2-in. -diameter discs. Heat 397 was, therefore, divided after the first extrusion. One-fourth of the heat was remelted and extruded under the same conditions as Heat 396, resulting

DECLASSIFIED

~~CONFIDENTIAL~~

in 4 rods 0.623 in. in diameter and 17 in. long. The remaining three-fourths of this heat was extruded through a 2.125-in. die. Four specimens resulted, each 3 in. long. None of the material in Heat 397 was hydrided.

Figures 1 and 2 describe the flow of material for each heat.

1-20-67 UNC

7700-2541

Figure 1. Material Flow for Heat 396

NAA-SR-11960

DECLASSIFIED
~~CONFIDENTIAL~~

1-20-67 UNC

7700-2542

Figure 2. Material Flow for Heat 397

~~CONFIDENTIAL~~

C. CHARACTERIZATION OF MATERIAL

A sampling and chemical analysis program was conducted to verify the composition of the material.⁽⁴⁾ The sampling plan was similar to that normally used for SNAP fuel production with the exception that more samples were taken. Sampling for uranium content consisted of cutting wafers from the extrusions between the specimen rods and at each end. Samples for carbon content consisted of the machine turnings taken where the uranium samples were removed. One additional thin wafer was cut from each extrusion for the analysis of hydrogen and oxygen impurities. Turnings from the final cutting operations furnished samples for other impurities. Vacuum extraction, vacuum fusion, calorimetric, x-ray fluorescence, and conductometric and spectrographic techniques were used in the analyses of this fuel material. Table 2 is a list of the concentrations of the elements tested for in each of the heats.

It is noted that all of the material lies within SNAP 10A composition requirements with the exception of Billet 397B. The oxygen content of this portion of the heat was in excess of the allowable 1000 ppm. This portion of the heat received only two vacuum arc-melts instead of the normal three.

In addition to the chemical analyses performed on the sample material, a specimen of each rod was obtained for metallographic examination. Figure 3 shows the microstructures typical of the hydrided and unhydrided material. The microstructure has the expected characteristics, and the random distribution of the carbide particles indicates very good homogeneity.

The density of the unhydrided material was calculated from the length, diameter, and weight measurements. The calculated density is 6.95 gm/cc $\pm 0.5\%$.

While performing experiments on the hydrided material, it is necessary to operate at temperatures at which the dissociation pressure is appreciable. In order to maintain composition at these temperatures it is necessary to provide a hydrogen atmosphere of the correct pressure. The pressure-temperature relationship used for the hydrided material in this program is shown in Figure 4. The equation for this isochore is:

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 2
CHEMICAL ANALYSIS RESULTS (Unhydrided Fuel)

Element	Units	Billet Number					
		396A	396B	396C	396D	397A	397D
Al	ppm	50	50	50	50	50	50
B		0.5	0.5	0.5	0.5	0.5	0.5
Ba		5	5	5	5	5	5
Be		1	1	1	1	1	1
Bi		2	2	2	2	2	2
Ca		20	20	20	20	20	20
Cd		0.5	0.5	0.5	0.5	0.5	0.5
Co		2	2	2	2	2	2
Cr		100	100	100	100	100	100
Cu		20	20	20	50	20	20
Fe		375	375	375	375	375	200
Hf		200	200	200	200	200	200
Mg		5	5	5	5	5	5
Mn		15	15	15	20	20	10
Mo		5	5	5	5	5	5
Na		5	5	5	5	5	5
Ni		10	10	10	10	10	10
Pb		5	5	5	5	5	5
Si		50	50	50	50	50	50
Sn		2	2	2	2	2	2
Ti		50	50	50	50	50	50
V		10	10	10	10	10	10
Zn		25	25	25	25	25	25
O		630	985	920	1000	670	1290*
H		7	10	8	8	9	8
W		6	5	5	6	18	20
N	ppm	70	82	98	95	70	80
U	wt %	10.19	10.21	10.15	10.21	10.33	10.23
C	wt %	0.14	0.14	0.16	0.15	0.15	0.15

*Exceeds SNAP 10A composition specification requirements

NAA-SR-11960

16

~~CONFIDENTIAL~~

a. Hydrided Material (Rod 396B-1)

1-17-67 CRD (GP-1)

7700-2543

b. Unhydrided Material (Rod 396A-2)

Figure 3. Typical Microstructures of Sample Materials

~~CONFIDENTIAL~~

$$\ln P = 20.903 - 1.971 \frac{10^4}{T} \quad \dots(1)$$

where P is in atmospheres and T is in °K. This isochore is for an effective H/Zr ratio of 1.81 and the data used to construct it were obtained from Johnson.⁽⁶⁾

Figure 4. Dissociation Pressure
of Hydrided Specimens

~~CONFIDENTIAL~~

CONFIDENTIAL

III. SPECIFIC HEAT

A. APPARATUS AND METHODS

The specific heat was measured at Battelle using a Bunsen ice calorimeter as described by Ginnings and Corrucini,⁽⁷⁾ and at Atomics International using a pulse-heating transient method.⁽⁸⁾

In the ice calorimeter, heat from a specimen melts ice that is in equilibrium with water in a closed system. The resulting volume change of the ice water system is determined by weighing mercury (in contact with the water) displaced as the system expands and contracts. The ratio of heat input to the mass of mercury displaced is a constant for the apparatus. There is no temperature change in the calorimeter during specimen cooling because all heat transfer occurs at the ice point.

Figure 5 shows schematically the calorimeter used for this program and described by Deem and Lucks.⁽⁹⁾ As the previously heated encapsulated specimen (L) is dropped into the central chamber of a double-wall stainless steel vessel, it gives up heat to the ice-covered finned section (J) which is enclosed in water in equilibrium. The portion of heat given up by the specimen is determined by subtracting from the total that contribution made by the capsule only. This latter amount is evaluated by a separate drop of an empty capsule. As the ice melts, mercury from the reservoir (B) and, in turn, from an external accounting system enters the inner vessel through tube (C) to make up the volume difference of ice melting to water. The total volume of mercury displaced while the specimen cools from its drop temperature to the ice point is measured accurately by this system, and, by weight, related to heat quantity transferred. This relationship was measured by Ginnings et al^(10,11,12) and at Battelle to be 270.48 joules per gram of mercury. Frequent checks of calorimeter operation, with NBS-calibrated Al_2O_3 as the specimen standard, demonstrated that the error of enthalpy measurement is less than $\pm 1\%$.

The hydrided and unhydrided specimens, in the form of 7/16-in.-diam by 1-1/2-in.-long cylinders, were encapsulated in Type 316 stainless steel (0.040-in. wall) under one atmosphere absolute of helium. The permeation of hydrogen through the capsule walls from the hydrided specimen in 1/2 hr at 660°C was

CONFIDENTIAL

CONFIDENTIAL

1-20-67 UNC

7700-2545

Figure 5. Stainless Steel Ice Calorimeter

NAA-SR-11960

20

CONFIDENTIAL

CONFIDENTIAL

estimated to be 0.05% of the amount in the specimen, based on work by Webb.⁽¹³⁾ This relatively minor amount of hydrogen loss did not significantly influence the results of the measurements.

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 measured simultaneously as a function of time. These quantities were photographically recorded using a dual-beam oscilloscope and Polaroid camera.

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

$$c_p = \frac{1}{m} dQ/dT \quad \dots (2)$$

$$= \frac{1}{m} EI \frac{d\rho/dT}{d\rho/dt}$$

$$= \frac{4EI d\rho/dT}{J\pi D^2 L \delta d\rho/dt} \quad \dots (3)$$

where c_p is in cal/gm-°C, J is the mechanical equivalent of heat (4.186 watt-sec/cal), D is the diameter of the specimen in cm, δ is its density, L is the distance between voltage probes, and ρ is the electrical resistivity in ohm-cm. The product EI 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 3 requires prior knowledge of electrical resistivity as a function of temperature. These data were obtained in separate experiments.

Calculation of specific heat was simplified, and at the same time made more accurate, by the use of a computer program⁽¹⁴⁾ 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.

CONFIDENTIAL

~~CONFIDENTIAL~~

Because of the very short heating times (less than a second), 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 apparatus with the vacuum bell removed is shown in Figure 6. The specimen (A) is soldered to the contact pistons (B), which in turn are connected to the large copper block current feedthroughs. The three spring-loaded probes beneath the specimen are used for measuring the voltage drop. Sharpened knife edges press the probes against the specimen (this detail is not evident in the photograph). The three spring-loaded members on top are merely for preserving specimen alignment during the pulse.

Figure 6. View of Pulse Heating Apparatus
(Vacuum bell removed)

The electrical resistivity measurements were made in a standard four-probe apparatus. Generally four specimens were loaded at once, thermal equilibrium was established under a balanced overpressure of hydrogen, and the resistance data were recorded for each specimen. After the data were taken in the temperature range of interest, the specimens were slowly cooled in a continuously balanced pressure of hydrogen, and the same specimens were

~~CONFIDENTIAL~~

then used for the pulse-heating experiments. The ρ -vs- T of each specimen was used as the input data for Equation 3.

The electrical resistivity apparatus and the pulse-heating apparatus were checked using high purity Ta as a standard.

B. EXPERIMENTAL RESULTS

1. Unhydrided Specimen

Figure 7 shows smooth curves drawn through experimental enthalpy data points for the unhydrided specimen from 0 to 900°C as determined in the drop calorimeter. Two transformations occurred in this material, the transformation from $\delta + \epsilon$ to $\gamma + \epsilon^{(5)}$ at 595°C and the transformation of $\gamma + \epsilon$ to pure $\gamma^{(5)}$

Figure 7. Enthalpy vs Temperature for the Unhydrided Material

at about 800°C (see Appendix). Equations of the form $A + BT + CT^2 + \dots$ were used to fit smooth curves to the distinct groupings of data. The equations are as follows:

For 0 to 560°C:

$$H_T = 5.881 \times 10^{-2}T + 2.388 \times 10^{-5}T^2 - 3.476 \times 10^{-9}T^3 \quad \dots (4)$$

For 600 to 790° C:

$$H_T = -25.3 + 0.115T \quad \dots (5)$$

For 815 to 900° C:

$$H_T = -11.680 + 9.9 \times 10^{-2}T \quad \dots (6)$$

where:

H_T = enthalpy (cal/gm)

T = temperature (° C)

The relative proportions of the δ and ϵ phases change very little with temperature from 0 to 595°C (i. e., the phase boundaries are both nearly vertical) so the heat released to the ice calorimeter is almost entirely a specific heat with only a minor contribution from the $\delta \rightleftharpoons \epsilon$ transformation. Because of this circumstance, it is possible to differentiate Equation 4 with respect to temperature in order to estimate a specific heat. The result is given in Equation 7:

$$\frac{dH_T}{dT_{0-560^\circ C}} = c_p = 5.881 \times 10^{-2} + 4.776 \times 10^{-5}T - 1.043 \times 10^{-8}T^2 \quad \dots (7)$$

Between 595 and about 800° C in the two-phase $\epsilon + \gamma$ field, the relative proportions of the two components change rapidly with temperature. Consequently, the heat released to the calorimeter includes not only a specific heat term, but also an isothermal heat of transformation term. The value of this latter term is not known precisely, but it is probably close to that of the heat of transformation of ϵ phase to γ phase.* This is 920 cal/mole, or about 10 cal/gm. It constitutes a large enough correction to be significant.

Above 595° C one can differentiate the enthalpy curves to find the total heat evolved per degree of temperature change for one gram of material. This is a useful quantity, but it should not be confused with the classic definition of specific heat which does not include heats of transformation. This derivative can not be substituted for c_p in all thermodynamic expressions.

*Corresponds to α - Zr to β - Zr transformation in pure zirconium.

REF ID: A62113
~~CONFIDENTIAL~~

Differentiation of Equations 5 and 6 give:

$$\frac{dH_T}{dT_{600-790^\circ\text{C}}} = 0.115 \text{ cal/gm-}^\circ\text{C} \quad \dots(8)$$

$$\frac{dH_T}{dT_{815-900^\circ\text{C}}} = 0.099 \text{ cal/gm-}^\circ\text{C} \quad \dots(9)$$

Table 3 gives the experimentally determined enthalpy values at the temperatures measured and compares them with values calculated for the same temperature using Equations 4, 5, and 6 for curves fitted to the data. The close agreement indicates that the curves are well fitted. Table 4 gives instantaneous specific heats at several temperatures as calculated from Equation 7. Figure 8 is a plot of these values. For the ranges 600 to 790°C and 815 to 900°C the heats of transformation are included in Equations 8 and 9; the corresponding "specific heats" are 0.115 and 0.099 cal/gm-°C, respectively. The specific heat data for the unhydried fuel determined from the pulse heating experiments showed an anomalous behavior. The difficulties could not be resolved during the program, and since the data are not considered reliable they are not reported. The electrical resistivity of the unhydried fuel was determined for use with the pulse-heating experiments; the data are tabulated in Table 5 and plotted in Figure 9. The values can be expressed by the equation:

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

2. Hydried Specimens

Figure 10 is a plot of enthalpy-vs-temperature data for the hydried material in the temperature range 0 to 660°C as determined in the drop calorimeter. The equation fitted to the experimental enthalpy data is

$$H_T = 6.821 \times 10^{-2}T + 9.745 \times 10^{-5}T^2 - 1.069 \times 10^{-8}T^3 \quad \dots(11)$$

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 3
OBSERVED AND CALCULATED ENTHALPY VALUES
FOR THE UNHYDRIDED MATERIAL

Temperature, T (°C)	Enthalpy, H _T (cal/gm)		Equation Number	Difference, Observed Minus Calculated Percent
	Observed	Calculated		
0	0	0		0
96	6.0 ₂	5.86	4	2.7
96	5.9 ₄	5.86	4	1.3
182	11.3 ₆	11.47	4	-0.9
183	11.4 ₆	11.54	4	-0.7
299	19.5 ₄	19.63	4	-0.5
302	19.8 ₆	19.84	4	0.1
446	30.7 ₁	30.67	4	0.1
447	30.7 ₇	30.75	4	0.0
553	39.5 ₀	39.24	4	0.7
561	39.6 ₅	39.89	4	-0.6
595	-	43.13	4	-
595	-	43.13	5	-
601	43.8 ₂	43.82	5	0.0
653	50.1 ₆	49.80	5	0.7
656	50.2 ₉	50.14	5	0.3
694	54.2 ₄	54.51	5	-0.5
709	56.2 ₇	56.24	5	0.0
788	65.4 ₀	65.32	5	0.1
815	-	68.43	5	-
815	-	68.43	6	-
817	69.2 ₉	69.35	6	-0.1
855	73.1 ₇	73.12	6	0.0
899	77.4 ₆	77.48	6	-0.0

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 4
INSTANTANEOUS SPECIFIC HEATS
FOR THE UNHYDRIDED
MATERIAL

Tempera- ture, T (°C)	Specific Heat, c_p (cal/gm-°C)
0	0.059
100	0.063
200	0.068
300	0.072
400	0.076
500	0.080

1-19-67 UNC

7700-2547

Figure 8. Specific Heat vs Temperature
for the Unhydrated Material

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 5
ELECTRICAL RESISTIVITY OF THE UNHYDRIDED MATERIAL

Temperature, T (°C)	Resistivity, ρ ($\mu\Omega$ -cm)			
	Sample 1	Sample 2	Sample 3	Sample 4
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	100.10	98.82	98.63
160	90.49	92.94	91.68	91.40
20	71.92	73.73	72.63	72.62

Sample 1: 396B-4-BII
Sample 2: 396C-4-BII

Sample 3: 396C-4-AII
Sample 4: 396B-4-AII

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2548

Figure 9. Electrical Resistivity of Unhydrided Material
(Composite data from Table 5)

NAA-SR-11960

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2549

Figure 10. Enthalpy vs Temperature for the Hydrided Material

NAA-SR-11960

30

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

The corresponding relation for instantaneous specific heat is

$$\frac{dH_T}{dT} = c_p = 6.821 \times 10^{-2} + 1.949 \times 10^{-4}T - 3.207 \times 10^{-8}T^2 \quad \dots(12)$$

Table 6 gives the observed and computed enthalpy values for hydrided material; the close agreement again gives confidence to the fitted curve. Table 7 lists instantaneous specific heat values for several temperatures, and Figure 11 is a plot of these values.

The pulse-heating method of measuring specific heat was used on three different specimens of the hydrided fuel. Although the specimens were pulsed to about 800°C, the resistivity data were known only to about 550°C; no specific heat data were reported above this temperature. The computational method used gives a smoothed curve of final data from essentially continuous input data, so that there are no data points as such to tabulate. Figure 12 gives the computer plotted results of the three specimens measured. The average values of the specific heat data can be given by the equation:

$$c_p = 5.96 \times 10^{-2} + 1.85 \times 10^{-4}T \quad \dots(13)$$

in the range 150 to 500°C.

The electrical resistivity data for the hydrided specimens are given in Table 8 and plotted in Figure 13. The resistivity vs temperature curve in the 20 to 550°C range can be expressed by:

$$\rho = 53.032 + 9.726 \times 10^{-2}T + 2.543 \times 10^{-5}T^2 - 9.309 \times 10^{-9}T^3. (\mu\Omega\text{-cm}) \quad \dots(14)$$

C. EVALUATION OF DATA

Values of enthalpy measured in this program are believed to be accurate to within $\pm 1\%$. This estimate is based on apparatus calibrations and includes errors of specimen temperature measurements.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 6
OBSERVED AND CALCULATED ENTHALPY VALUES
FOR THE HYDRIDED MATERIAL

Temperature, T (°C)	Enthalpy, H_T (cal/gm)		Difference, Observed Minus Calculated, Percent
	Observed	Calculated	
0	0	0	0
96	7.3 ₅	7.44	-1.3
96	7.3 ₉	7.44	0.7
298	28.7 ₁	28.70	0.4
300	28.9 ₉	28.94	0.2
458	50.4 ₃	50.65	-0.4
462	51.5 ₂	51.26	0.5
599	73.2 ₁	73.53	-0.4
651	83.0 ₁	82.75	0.3
654	83.2 ₃	83.30	0.1

TABLE 7
INSTANTANEOUS SPECIFIC
HEAT VALUES FOR THE
HYDRIDED MATERIAL

Temperature, T (°C)	Specific Heat, c_p (cal/gm-°C)
0	0.068
100	0.087
200	0.106
300	0.124
400	0.141
500	0.158
600	0.174
660	0.183

NAA-SR-11960

32

~~CONFIDENTIAL~~

Figure 11. Specific Heat vs Temperature for the Hydrided Material

Figure 12. Specific Heat of Three Different Pulsed Specimens of Hydride

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2552

Figure 13. Electrical Resistivity of
Hydrided Material
(Composite data from Table 8)

NAA-SR-11960

34

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 8
ELECTRICAL RESISTIVITY OF HYDRIDED SPECIMENS

Temperature, T (°C)	Resistivity, ρ ($\mu\Omega$ -cm)			
	396C-3-BII	396C-3-CII	396B-3-BII	396B-3-CII
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

Power series equations seemed to give the most appropriate curve fits for the enthalpy data points. As is evident, however, the computed specific heat relationship with temperature from these equations undergoes two significant changes in the phase transformation region above 550°C for the unhydrided material. Since this occurs in the transition region, it is possible that the particular specimen heat treatment (quenched to the ice point after each heating) associated with this measurement technique contributed to the sharp changes indicated in specific heat.

When the specific heat of Ta was measured with the pulse-heating method, the data were found to agree within 3% of the accepted literature values. The hydride data obtained by the same method are believed accurate to $\pm 5\%$.

~~CONFIDENTIAL~~

The data for both hydrided and unhydrided specimens are plotted in Figure 14. The pulse-heating method gave lower results for specific heat than the calorimetric method. If 5%-error bands are put on the data, the two methods agree. The true value of the specific heat of the hydride should probably be biased toward the calorimetric measurement.

1-20-67 UNC

7700-2553

Figure 14. Summary of Specific Heat Data

IV. THERMAL DIFFUSIVITY

A. APPARATUS AND METHODS

For the thermal diffusivity determination both laboratories used the flash method originally developed by Parker et al⁽¹⁵⁾ and as modified by Deem and Wood⁽¹⁶⁾ to use a laser heat source in place of a xenon flash lamp. The technique consists of irradiating the front face of a thin specimen with a high-intensity short-duration pulse of light. The resulting temperature transient on the back face of the specimen is used to calculate the thermal diffusivity under the boundary conditions of the experiment. For the configurations used in this program,

$$\alpha = 1.37 a^2 / \pi^2 t_{1/2} \quad \dots (15)$$

where

α = thermal diffusivity (cm²/sec)

a = specimen thickness (cm)

$t_{1/2}$ = time (sec) required for the rear-face temperature to reach half-maximum.

The major difference in the apparatuses used by the two laboratories was in the method of measuring rear-face temperature. Atomics International used 0.003-in. thermocouple wires spot-welded to the back face. These were chromel-alumel thermocouples for the measurements on unhydrided material in vacuum and geminol-P, geminol-N thermocouples for the measurements made in hydrogen with the hydrided material. Battelle used a lead sulfide radiation receiver and optical system to measure rear-face temperature. An orifice was used so that the radiation receiver viewed only the central part of the back face where the heat flow was undisturbed by edge effects.

Both laboratories operated the equipment in essentially the same fashion. For the unhydrided specimens, a thermal equilibrium was established in a vacuum, and the specimen was then pulsed with a laser beam of about 0.5-1.5-msec duration. This resulted in a temperature rise on the rear face of about 5-10°C

~~CONFIDENTIAL~~

TABLE 9
THERMAL DIFFUSIVITY OF UNHYDRIDED MATERIALS
(Samples 396C-4 1-I and 396B-4 1-II)

Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)
Sample 396C-4 1-I							
28	0.0758	298	0.0753	601	0.0816	705	0.0956
28	0.0739	310	0.0785	600	0.0740	753	0.100
28	0.0739	317	0.0766	33	0.0727	765	0.101
28	0.0744	401	0.0780	32	0.0714	847	0.119
80	0.0749	406	0.0766	33	0.0723	850	0.117
76	0.0749	403	0.0775	195	0.0740	898	0.124
137	0.0753	507	0.0780	193	0.0757	902	0.128
143	0.0739	507	0.0759	441	0.0775	896	0.126
150	0.0757	507	0.0785	460	0.0780	903	0.126
154	0.0766	501	0.0766	461	0.0785	901	0.127
157	0.0753	499	0.0785	579	0.0746	931	0.128
220	0.0775	499	0.0766	580	0.0731	913	0.122
226	0.0780	596	0.0688	699	0.0932	630	0.0831
230	0.0771	596	0.0735				
Sample 396B-4 1-II							
26	0.0704	563	0.0771	547	0.0781	629	0.0888
27	0.0704	564	0.0763	447	0.0800	620	0.0894
28	0.0701	568	0.0762	325	0.0767	626	0.0894
28	0.0708	705	0.0952	319	0.0728	649	0.0899
28	0.0697	346	0.0763	203	0.0732	665	0.0919
28	0.0704	699	0.0912	183	0.0724	674	0.0925
57	0.0694	560	0.0800	45	0.0698	662	0.0876
64	0.0720	554	0.0810	29	0.0716	668	0.0919
68	0.0689	562	0.0776	30	0.0698	734	0.0967
156	0.0712	698	0.0929	27	0.0679	771	0.105
158	0.0716	756	0.102	28	0.0693	766	0.106
275	0.0724	753	0.0973	28	0.0700	804	0.111
276	0.0753	829	0.117	586	0.0767	802	0.111
278	0.0762	830	0.116	589	0.0776	960	0.131
339	0.0781	825	0.114	580	0.0785	960	0.132
346	0.0771	888	0.118	584	0.0762	968	0.131
486	0.0785	915	0.125	587	0.0781	976	0.129
495	0.0795	787	0.100	612	0.0900	970	0.133
494	0.0776	694	0.0956	602	0.0906	967	0.128
552	0.0774	693	0.0945	617	0.0888		

~~CONFIDENTIAL~~

REF ID: A66011
~~CONFIDENTIAL~~

in about 20-100 msec. The procedure for the hydrided specimens was the same except that the hydrogen overpressure was balanced at each thermal equilibrium to maintain a constant composition in the condensed phase. Heat losses due to gas conduction in the hydrogen atmosphere were negligibly small, under the conditions of temperatures and pressures employed.

B. EXPERIMENTAL RESULTS

1. Unhydrided Specimens

Two specimens of the unhydrided material were measured at Atomics International in the range of room temperature to about 1000°C. Both were so cut that the heat flux was in the direction of the extrusion of the billet (i. e., the specimen was cut from the transverse direction in the as-received rod). The data are given in Table 9 and also shown in Figure 15. The values in the 20 to 595°C interval can be represented by the equation:

$$\alpha = 7.017 \times 10^{-2} + 3.291 \times 10^{-5} T - 3.754 \times 10^{-8} T^2 \quad \dots (16)$$

Two phase transitions are apparent from Figure 15, one at about 595°C and the second at about 800°C. These transition temperatures agree well with the $\delta + \epsilon \leftrightarrow \gamma + \epsilon$ and the $\gamma + \epsilon \leftrightarrow \gamma$ transition temperatures reported in the literature^(15,17) (see Appendix) for the Zr-U system. Thermal cycling apparently does not affect the measurements, as shown by good agreement between the first and second heating values.

Two specimens of unhydrided material, cut from the transverse and longitudinal directions in the as-received rod, were measured at Battelle from 200-1000°C. Data for the transverse specimen are shown in Figure 16 and Table 10, and data for the longitudinal specimen are given in Figure 17 and Table 11. In the temperature range from 200 to 600°C, the transverse specimen appears to have a slightly higher diffusivity (less than 10% higher) than the longitudinal specimen. The phase changes at about 595 and 800°C are also evident in these data.

Most of the data points were taken during the heating part of the thermal cycle, but a few points were also taken on cooling.

~~CONFIDENTIAL~~

BLANK

DECLASSIFIED

DECLASSIFIED

CONFIDENTIAL

1-20-67 UNC

7700-2554

Figure 15. Thermal Diffusivity of Unhydrided Materials

NAA-SR-11960

41

DECLASSIFIED

DECLASSIFIED

CONFIDENTIAL

BLANK

Figure 16. Thermal Diffusivity, Unhydrated Specimen, Transverse (BMI Data)

TABLE 10
THERMAL DIFFUSIVITY, UNHYDRATED SPECIMEN, TRANSVERSE
(Specimen 396B-2) (BMI Data)

Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)
265	0.0830	560	0.0890	920	0.1264
265	0.0856	560	0.0856	920	0.1325
265	0.0824	604	0.0897	920	0.1312
345	0.0784	604	0.0923	844	0.1253
345	0.0843	604	0.0883	844	0.1199
345	0.0812	646	0.0951	772	0.1070
400	0.0951	646	0.1021	772	0.1030
400	0.0869	646	0.0943	480	0.0843
400	0.0849	710	0.0897	480	0.0897
484	0.0927	710	0.0993	342	0.0818
484	0.0943	784	0.1288	342	0.0795
484	0.0927	784	0.1247	243	0.0742
560	0.0890	784	0.1236	243	0.0752

~~CONFIDENTIAL~~

Figure 17. Thermal Diffusivity, Unhydrated Specimen, Longitudinal (BMI Data)

TABLE 11

THERMAL DIFFUSIVITY, UNHYDRATED SPECIMEN, LONGITUDINAL
(Specimen 396B-2) (BMI Data)

Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)
214	0.0693	508	0.0838	884	0.1303
214	0.0627	580	0.0832	996	0.1265
214	0.0712	580	0.0813	996	0.1316
332	0.0782	580	0.0846	996	0.1297
333	0.0782	676	0.1067	808	0.1107
333	0.0807	676	0.1053	808	0.1000
431	0.0819	676	0.1032	618	0.0974
431	0.0825	790	0.1195	618	0.0902
431	0.0822	790	0.1217	618	0.0875
508	0.0841	884	0.1284	618	0.0947
508	0.0817	884	0.1351		

~~CONFIDENTIAL~~

TABLE 12
INTERPOLATED THERMAL DIFFUSIVITY VALUES
FOR UNHYDRIDED SPECIMENS
(BMI Data)

Temperature, T (°C)	Diffusivity, α (cm ² /sec)	
	Transverse Section	Longitudinal Section
200	0.079	0.073
300	0.083	0.078
400	0.086	0.081
500	0.088	0.083
600	0.089	0.083
700	0.108	0.109
800	0.123	0.122
900	0.131	0.130
1000	0.132	0.131

Table 12 shows thermal diffusivity values interpolated from the data shown in Figures 16 and 17.

2. Hydrided Specimens

At Atomics International, the thermal diffusivity was measured on hydrided specimens from room temperature up to about 450°C in vacuum. The specimens were then taken up to about 680°C, equilibrated with the appropriate hydrogen overpressure, and cooled in a balanced pressure of hydrogen while measurements were made. This technique was used to ensure that the starting composition was correct for the pressure-temperature relationship used. Some measurements were then made on reheating in hydrogen.

The diffusivity results on two specimens measured in vacuum are given in Table 13 and plotted in Figure 18. The data for one specimen measured under

~~CONFIDENTIAL~~

TABLE 13
THERMAL DIFFUSIVITY OF HYDRIDED
MATERIAL IN A VACUUM

Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)
Sample 396B-3 2-I (As-Received)					
18	0.107	40	0.096	15	0.108
18	0.107	62	0.093	96	0.091
18	0.107	82	0.099	97	0.089
18	0.108	247	0.072	102	0.097
18	0.107	249	0.073	112	0.099
18	0.107	260	0.077	125	0.099
18	0.105	301	0.078	140	0.086
20	0.107	319	0.066	152	0.082
23	0.111	342	0.068	203	0.084
29	0.112	356	0.071	217	0.082
Sample 396C-3 2-I (As-Received)					
24	0.105	22	0.095	296	0.075
24	0.100	22	0.105	303	0.067
24	0.101	22	0.101	307	0.071
24	0.095	22	0.105	345	0.069
76	0.101	291	0.075	355	0.066
86	0.091	286	0.070	352	0.064
107	0.086	285	0.070	370	0.068
111	0.090	285	0.074	377	0.064
124	0.088	260	0.068	418	0.062
166	0.080	70	0.091	418	0.064
177	0.079	70	0.092	447	0.057
182	0.086	67	0.101	450	0.066

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

Figure 18. Thermal Diffusivity of Hydrided Materials
(Vacuum)

balanced hydrogen pressures is given in Table 14 and plotted in Figure 19. The curve represented by the equation:

$$\alpha = 0.1125 - 2.131 \times 10^{-4} T + 3.234 \times 10^{-7} T^2 - 1.919 \times 10^{-10} T^3 \quad (15^\circ < T < 550^\circ) \quad \dots (17)$$

was drawn through the data points for the balanced-hydrogen measurements.

The balancing of pressure was done in the low pressure range with a calibrated 0-50-mm Wallace and Tiernan gage, readable to 0.1 mm Hg. For higher pressures a 0-6000-mm gage, readable to about 10 mm, was used. Before the more sensitive gage was installed in the system there was considerable bias in the diffusivity data as a result of overhydriding the specimen during the cooling cycle. This trouble disappeared with the use of the more accurate gage.

Five disk specimens of hydrided material, two cut transverse to the as-received rod and three in the longitudinal direction, were measured at Battelle. Measurements were made from approximately 200 to 670°C and, except as noted below, with balanced hydrogen pressures in the specimen chamber. Figures 20 through 24 and Tables 15 through 19 show the experimental data points for

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 14
THERMAL DIFFUSIVITY OF HYDRIDED MATERIAL,
BALANCED HYDROGEN PRESSURE
(Sample 396C-3 2-I)

Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)	Tempera- ture, T (°C)	Diffu- sivity, α (cm ² /sec)
685	0.054	16	0.106	369	0.069
684	0.054	17	0.115	418	0.062
682	0.055	17	0.106	418	0.067
682	0.052	100	0.092	418	0.064
682	0.051	99	0.098	498	0.064
672	0.056	98	0.093	501	0.065
658	0.053	96	0.094	505	0.063
653	0.059	88	0.098	507	0.060
650	0.053	87	0.093	417	0.064
648	0.053	58	0.101	510	0.066
648	0.058	58	0.101	535	0.063
647	0.056	58	0.105	540	0.065
648	0.054	52	0.101	543	0.061
631	0.056	52	0.104	548	0.062
622	0.055	52	0.101	552	0.058
618	0.058	335	0.072	555	0.061
612	0.058	323	0.072	560	0.060
608	0.057	325	0.072	562	0.058
604	0.057	361	0.065	562	0.061
601	0.058	368	0.068	565	0.060
601	0.059	371	0.072	567	0.063

1-20-67 UNC

7700-2558

Figure 19. Thermal Diffusivity of Hydrided Material
(Balanced Hydrogen Pressure)

NAA-SR-11960

48

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2559

Figure 20. Thermal Diffusivity, Hydrided Specimen No. 1, Transverse (396A-1)

TABLE 15
THERMAL DIFFUSIVITY, HYDRIDED
SPECIMEN NO. 1, TRANSVERSE
(Specimen 396A-1) (BMI Data)

Temperature, T (°C)	Diffusivity, α (cm ² /sec)	Temperature, T (°C)	Diffusivity, α (cm ² /sec)	Temperature, T (°C)	Diffusivity, α (cm ² /sec)
215	0.0762	511	0.0652	669	0.0630
215	0.0783	511	0.0684	622	0.0630
268	0.0732	550	0.0641	622	0.0660
268	0.0773	551	0.0641	552	0.0709
320	0.0737	578	0.0648	552	0.0752
320	0.0742	578	0.0652	445	0.0806
404	0.0684	615	0.0630	445	0.0812
404	0.0692	615	0.0652	445	0.0823
459	0.0742	640	0.0645	318	0.0910
459	0.0688	640	0.0637	318	0.0902
459	0.0701	670	0.0613		

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2560

Figure 21. Thermal Diffusivity, Hydrided Specimen No. 2, Transverse (396A-1)

TABLE 16
THERMAL DIFFUSIVITY, HYDRIDED
SPECIMEN NO. 2, TRANSVERSE
(Specimen 396A-1) (BMI Data)

Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)
222	0.0756	460	0.0695	671	0.0574
222	0.0771	460	0.0687	649	0.0651
222	0.0766	500	0.0643	646	0.0590
285	0.0777	550	0.0622	594	0.0670
285	0.0787	554	0.0629	594	0.0655
285	0.0777	601	0.0622	475	0.0662
351	0.0682	601	0.0612	475	0.0704
351	0.0713	639	0.0580	286	0.0866
414	0.0695	639	0.0636	286	0.0873
414	0.0691	671	0.0526		

NAA-SR-11960

~~CONFIDENTIAL~~

Figure 22. Thermal Diffusivity, Hydrided Specimen No. 1, Longitudinal (396A-1)

TABLE 17
THERMAL DIFFUSIVITY, HYDRIDED
SPECIMEN NO. 1, LONGITUDINAL
(Specimen 396A-1) (BMI Data)

Temperature, T (°C)	Diffu- sivity, α (cm²/sec)	Temperature, T (°C)	Diffu- sivity, α (cm²/sec)	Temperature, T (°C)	Diffu- sivity, α (cm²/sec)
158	0.0793	400	0.0690	570	0.0636
158	0.0793	466	0.0636	570	0.0651
158	0.0736	466	0.0658	608	0.0674
210	0.0740	410	0.0690	608	0.0666
210	0.0815	410	0.0740	635	0.0651
210	0.0740	410	0.0736	636	0.0662
246	0.0760	294	0.0776	668	0.0612
246	0.0755	294	0.0782	668	0.0647
246	0.0760	294	0.0755	650	0.0674
299	0.0787	205	0.0760	650	0.0674
299	0.0731	205	0.0787	620	0.0678
299	0.0736	482	0.0636	620	0.0678
354	0.0703	482	0.0651	502	0.0731
354	0.0708	484	0.0670	504	0.0740
354	0.0708	520	0.0682	438	0.0798
400	0.0703	520	0.0674	438	0.0782
400	0.0695				

~~CONFIDENTIAL~~

Figure 23. Thermal Diffusivity, Hydrided
Specimen No. 2, Longitudinal
(396A-1)

TABLE 18
THERMAL DIFFUSIVITY, HYDRIDED
SPECIMEN NO. 2, LONGITUDINAL
(Specimen 396A-1) (BMI Data)

Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)	Temperature, T (°C)	Diffu- sivity, α (cm ² /sec)
170	0.0813	630	0.0673	244	0.0807
170	0.0831	668	0.0677	303	0.0825
232	0.0790	664	0.0665	303	0.0801
232	0.0779	666	0.0621	356	0.0801
302	0.0706	650	0.0661	356	0.0807
302	0.0653	650	0.0677	418	0.0730
340	0.0729	626	0.0661	419	0.0748
340	0.0769	626	0.0657	419	0.0730
386	0.0729	560	0.0657	461	0.0670
386	0.0743	560	0.0711	461	0.0650
442	0.0734	560	0.0734	508	0.0631
442	0.0702	456	0.0795	508	0.0620
490	0.0693	456	0.0691	560	0.0614
490	0.0685	285	0.0904	560	0.0604
548	0.0665	285	0.0926	596	0.0601
548	0.0661	208	0.0843	596	0.0590
603	0.0673	208	0.0819	663	0.0595
603	0.0653	244	0.0807	663	0.0693
630	0.0653	244	0.0801	663	0.0650

~~CONFIDENTIAL~~

Figure 24. Thermal Diffusivity, Hydrided Specimen No. 3, Longitudinal (396A-1)

TABLE 19
THERMAL DIFFUSIVITY, HYDRIDED SPECIMEN NO. 3, LONGITUDINAL (Specimen 396A-1) (BMI Data)

Temperature, T (°C)	Diffusivity, α (cm ² /sec)	Temperature, T (°C)	Diffusivity, α (cm ² /sec)	Temperature, T (°C)	Diffusivity, α (cm ² /sec)
214	0.0752	642	0.0667	412	0.0784
214	0.0758	522	0.0712	412	0.0784
316	0.0729	522	0.0712	500	0.0752
316	0.0707	522	0.0696	500	0.0758
460	0.0657	522	0.0702	501	0.0719
460	0.0667	406	0.0817	610	0.0672
536	0.0627	406	0.0811	610	0.0648
536	0.0676	196	0.0879	610	0.0640
599	0.0595	198	0.0879	658	0.0631
599	0.0619	194	0.0904	658	0.0627
666	0.0607	194	0.0921	658	0.0623
666	0.0591	194	0.0858	540	0.0691
666	0.0595	300	0.0816	540	0.0702
653	0.0662	300	0.0794	340	0.0847
653	0.0667	300	0.0847	340	0.0847
639	0.0672	300	0.0839	214	0.0913
639	0.0662	412	0.0804	214	0.0904
642	0.0675	412	0.0784		

~~CONFIDENTIAL~~

these specimens. In generating these data, the procedure was to proceed slowly from lower to higher temperatures, with care being taken to maintain the required hydrogen pressure in the chamber at all temperatures. Although several checks were made on the cooling part of the cycle, the precision of these latter values is not believed to be comparable to that of the heating points. This is due to the difficulty in maintaining the correct balancing hydrogen pressure on cooling. The decreasing furnace power and hydrogen pressure are mutually compensating as far as the specimen temperature is concerned. Thus, it is possible that in some instances the specimen composition (hydrogen content) was altered on cooling.

As indicated on Figures 22, 23, and 24, various procedures on heating and cooling the longitudinal hydrided specimens were investigated. The objective here was to observe the effects on thermal diffusivity of possible composition change owing to an improper hydrogen pressure balance. In the case of Specimen 1 (Figure 22), no significant composition change is indicated on heating to 465°C, cooling, reheating to 670°C, and then cooling to about 500°C. At this point, the specimen seems to have changed in composition, probably in the direction of increased hydrogen content. Conversely, Specimen 2 (Figure 23) gave some evidence of changing composition during first cooling, but on second heating gave data points very close to those on first heating. There is no obvious explanation for the change between first cooling and second heating, especially in the temperature range below 450°C, where all data were taken under vacuum. The data for Specimen 3, longitudinal (Figure 24), appear consistent in that values after the first heating are essentially repeatable. This is reasonable if it is assumed that a composition change occurred shortly after the first cooling began. The data points seem to confirm this.

In general, major reliability is assigned to the data taken on first heating of these hydrided specimens. This assignment reflects the greater confidence which can be placed in these data because of more favorable experimental conditions for maintaining precisely the balancing hydrogen pressure. It assumes that the starting composition was that to which the indicated pressure-temperature relation applies. Accordingly, Table 20 shows interpolated values for the five hydrided specimens obtained on first heating.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 20
INTERPOLATED THERMAL DIFFUSIVITY VALUES
FOR HYDRIDED SPECIMENS

Temperature, T (°C)	Diffusivity, α (cm ² /sec)				
	Transverse Sections		Longitudinal Sections		
	No. 1	No. 2	No. 1	No. 2	No. 3
200	0.078	0.081	0.077	0.081	0.077
250	0.076	0.078	0.075	0.078	0.074
300	0.074	0.075	0.073	0.076	0.072
350	0.072	0.073	0.071	0.074	0.070
400	0.070	0.070	0.069	0.072	0.068
450	0.068	0.068	0.068	0.070	0.066
500	0.066	0.066	0.067	0.068	0.064
550	0.065	0.063	0.066	0.067	0.063
600	0.064	0.061	0.064	0.066	0.061
650	0.063	0.060	0.063	0.066	0.060

There appears to be no clear distinction in thermal diffusivity between transverse and longitudinal sections. Two longitudinal sections and one transverse section appear to have slightly higher diffusivities at the higher temperatures, but the trend is not consistent.

C. EVALUATION OF DATA

Both laboratories used Armco iron as a standard for calibrating their apparatus, and found agreement within 3-5% of the accepted literature values for this material. Battelle also ran samples of AISI Type 347 stainless steel, molybdenum, and Type 7087 graphite to further check out the equipment. Agreement with accepted literature values was $\pm 5\%$ in all cases. Both AI and Battelle believe that the measurements reported in this program are accurate to $\pm 5\%$ of the true diffusivity of the specimens at the time of measurement. Any differences greater than this are probably traceable to specimen changes.

~~CONFIDENTIAL~~

Figure 25. Comparison of Data on Diffusivity of Unhydrated Material

~~CONFIDENTIAL~~

The diffusivity of the unhydrided specimens is summarized in Figure 25. The agreement is within the $\pm 5\%$ error band up to about 500°C . At this point the approaching phase transformation probably accounts for the increased divergence. Above 600°C the selection of the best fit to the BMI data points is probably a bit arbitrary. With more measurements in the transformed region, and longer equilibration times the $\gamma + \epsilon \leftrightarrow \gamma$ transformation may have become more noticeable. The measurements made on the AI apparatus should probably be weighted more than the others in determining a best average value because they display less scatter.

The measurements on the hydrided material are summarized in Figure 26. Agreement in this case is outstandingly good. There is some suggestion of a change in slope in the AI data at about 560°C . Similar behavior was noted in the resistivity measurement (see Figure 13). This may be the effect of a $\epsilon \leftrightarrow \delta + \epsilon$ transformation in zirconium hydride.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2565

Figure 26. Comparison of Data on Diffusivity of Hydrided Material

NAA-SR-11960

58

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

V. THERMAL CONDUCTIVITY

A. APPARATUS AND METHOD

A longitudinal steady-state comparison method was used at Battelle in making the thermal conductivity measurements. The method, in brief, consists of: (1) heating one end of a specimen; (2) measuring the temperature gradients along the specimen; and (3) determining the rate of heat flow through it by means of a metal reference material of known thermal conductivity attached to the cold end of the specimen. Radial heat flow, into or away from the specimen and reference material assembly, is minimized by thermal insulation and an encircling guard tube in which temperatures at corresponding levels are adjusted, as closely as possible, to match those in the specimen and reference material. The thermal insulation consists of bubbled alumina which fills the annular space between the specimen reference material assembly and the guard cylinder. The specimen is protected by a vacuum of approximately 2×10^{-5} torr during the measurements.

Six 32-gage (0.008 in. diam) Chromel-Alumel thermocouples of calibrated wire were wedged into holes spaced along the specimen, and three similar thermocouples were placed in the reference material. Two reference materials, one for each specimen, were used in the thermal conductivity measurements. They were Armco iron and Type 347 stainless steel. Both of these reference materials are used at Battelle routinely. They have been checked, directly or indirectly, against National Bureau of Standards thermal conductivity "standard" lead. Each part of the specimen between thermocouples was regarded as an independent small specimen. A thermal conductivity value was calculated for each section of the specimen bounded by two thermocouples, and was reported as the value for the mean temperature of that particular section of specimen. The thermocouple placement used here permitted the calculation of five thermal conductivity values, each at a different mean temperature, for each thermal equilibrium setting.

Generally, thermal conductivity measurements are made in steps from lower to higher temperatures, after which one or more equilibria are obtained at lower temperatures. This duplication of measurements is used as a check

~~CONFIDENTIAL~~

TABLE 21

OBSERVED THERMAL CONDUCTIVITY OF THE UNHYDRIDED
MATERIAL, SPECIMEN NO. 1, INDIVIDUAL POINTS
(BMI Data)

	TEMPERATURE, T (°C)	THERMAL CONDUCTIVITY, k (cal/sec-cm-°C)	EQUILIBRIUM NUMBER*	SECTION NUMBER†		TEMPERATURE, T (°C)	THERMAL CONDUCTIVITY, k (cal/sec-cm-°C)	EQUILIBRIUM NUMBER*	SECTION NUMBER†
DATA FOR SPECI- MEN WHICH WAS NEVER ABOVE 580°C	100	0.0342	2	5	RE- MAINDER OF HEAT- ING DATA	609	0.0463	6	4
	115	0.0037	1	5		620	0.0468	5	3
	116	0.0349	10	5		707	0.0490	5	2
	141	0.0351	2	4		754	0.0523	6	3
	156	0.0344	1	4		761	0.0520	5	1
	167	0.0351	3	5		853	0.0596	6	2
	181	0.0363	2	3		912	0.0614	6	1
	195	0.0358	1	3					
	210	0.0363	9	5					
	211	0.0368	2	2					
	224	0.0342	1	2	DATA OB- TAINED ON COOLING	171	0.0365	10	4
	229	0.0358	3	4		215	0.0389	10	2
	231	0.0368	2	1		232	0.0382	10	1
	239	0.0361	4	5		287	0.0394	9	4
	244	0.0353	1	1		361	0.0399	9	3
	290	0.0370	3	3		414	0.0446	9	2
	312	0.0377	8	5		430	0.0416	8	4
	332	0.0423	4	4		446	0.0441	9	1
	335	0.0363	3	2		539	0.0446	8	3
	357	0.0382	5	5		577	0.0466	7	4
	365	0.0372	3	1		614	0.0514	8	2
	420	0.0399	7	5		659	0.0518	8	1
	422	0.0389	4	3		713	0.0525	7	3
	443	0.0399	6	5		805	0.0600	7	2
	488	0.0399	4	2		870	0.0623	7	1
	495	0.0418	5	4					
	530	0.0411	4	1					

*IN CHRONOLOGICAL ORDER IN WHICH DATA WERE OBTAINED.

†DIVISION OF SPECIMEN ACCORDING TO THERMOCOUPLE PLACEMENT, NO. 1 BEING THE HOTTEST SECTION.

NAA-SR-11960

60

CONFIDENTIAL

on thermocouples and specimen changes which may have taken place during the measuring period. Sections of the specimen can undergo structural changes as a result of their individual heat treatments.

Thermocouples are made from previously calibrated wire. A continuous program of establishing the values for the conductivity of the reference materials is maintained.

Experience has established that the relative error between different measurements performed in the apparatus used for these determinations 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.

Thermal conductivity measurements were made on material in the as-received condition. The specimens were machined 0.61-in. diam by 7-in.-length right cylinders.

B. EXPERIMENTAL RESULTS

Tables 21 and 22 give observed thermal conductivities of the two specimens at the individual temperatures where equilibria were established. These tables also identify the longitudinal sections of the specimens as divided by the thermocouple placements (No. 1 Section being that nearest the heated end) and the chronological order in which equilibria were established at each of the sections. For convenience, the data are grouped at fairly uniform temperature intervals in Tables 23 and 24. This grouping is accomplished by translating the data near a desired temperature to that temperature; the translation is along slopes parallel to a best curve drawn through all the experimental points. The values in Tables 23 and 24 are averages of the several values at each of the selected temperatures. Failure of a thermocouple on Specimen No. 1 during Equilibrium No. 10 (Table 21) resulted in Sections 4 and 5 yielding only one instead of two thermal conductivity values.

Tables 25 and 26 give interpolated thermal conductivity values for the two specimens as determined from curves drawn through the points shown in Tables 23 and 24.

CONFIDENTIAL

~~CONFIDENTIAL~~

TABLE 22
OBSERVED THERMAL CONDUCTIVITY OF THE UNHYDRIDED
MATERIAL, SPECIMEN NO. 2, INDIVIDUAL POINTS (BMI DATA)

	TEMPERATURE, T (°C)	THERMAL CONDUCTIVITY, k (cal/sec-cm-°C)	EQUILIBRIUM NUMBER*	SECTION NUMBER†
DATA FOR SECTIONS WHICH WERE NOT ABOVE 590°C	87	0.0332	7	5
	93	0.0336	1	5
	123	0.0339	3	5
	146	0.0358	7	4
	153	0.0353	1	4
	164	0.0356	2	5
	202	0.0365	7	3
	207	0.0363	3	4
	210	0.0372	1	3
	247	0.0377	4	5
	248	0.0372	6	5
	252	0.0384	1	2
	278	0.0389	1	1
	281	0.0384	2	4
	287	0.0380	3	3
	325	0.0392	5	5
	345	0.0396	3	2
	382	0.0406	3	1
	390	0.0413	2	3
	430	0.0418	4	4
	431	0.0420	6	4
	467	0.0439	2	2
DATA FOR SECTIONS WHICH WERE ABOVE 590°C	515	0.0456	2	1
	544	0.0466	5	4
	590	0.0496	4	3
	591	0.0494	6	3
	696	0.0554	4	2
	698	0.0559	6	2
	726	0.0566	5	3
	759	0.0611	4	1
	759	0.0630	6	1
	843	0.0664	5	2
	910	0.0740	5	1

*IN CHRONOLOGICAL ORDER IN WHICH DATA WERE OBTAINED.

†DIVISION OF SPECIMEN ACCORDING TO THERMOCOUPLE PLACEMENT, NO. 1 BEING THE HOTTEST SECTION.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

TABLE 23
OBSERVED THERMAL CONDUCTIVITY OF THE
UNHYDRIDED MATERIAL SPECIMEN NO. 1
(BMI Data)

Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)		Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)	
	Initial	Cooling		Initial	Cooling
100	0.0341	-	550	0.0415	0.0454
175	0.0356	0.0365	600	0.0458	0.0509
250	0.0358	0.0389	675	0.0475	0.0525
325	0.0372	0.0391	750	0.0518	0.0540
400	0.0387	0.0425	850	0.0596	0.0613
475	0.0406	0.0449	900	0.0609	0.0633

TABLE 24
OBSERVED THERMAL CONDUCTIVITY OF THE
UNHYDRIDED MATERIAL SPECIMEN NO. 2
(BMI Data)

Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)		Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)	
	Initial	Cooling		Initial	Cooling
100	0.0337	-	550	0.0468	-
175	0.0360	-	600	0.0501	-
250	0.0377	0.0411	700	0.0556	-
325	0.0391	-	750	0.0616	-
400	0.0411	-	850	0.0666	-
475	0.0441	-	900	0.0737	-

~~CONFIDENTIAL~~

TABLE 25
INTERPOLATED THERMAL CONDUCTIVITY OF THE
UNHYDRIDED SPECIMEN NO. 1
(BMI Data)

Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)		Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)	
	Initial	Cooling*		Initial	Cooling*
100	0.0349	-	550	0.0420	0.0459
150	0.0351	0.0372	600	0.0456	0.0506
200	0.0356	0.0377	700	0.0494	0.0530
300	0.0370	0.0396	750	0.0514	0.0544
400	0.0389	0.0420	850	0.0596	0.0616
500	0.0411	0.0444	900	0.0609	0.0640

*Data obtained on cooling from temperatures above 575°C.

TABLE 26
INTERPOLATED THERMAL CONDUCTIVITY OF THE
UNHYDRIDED SPECIMEN NO. 2
(BMI Data)

Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)		Temper- ature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)	
	Initial	Cooling		Initial	Cooling
100	0.0339	0.0380*	550	0.0473	0.0520*
150	0.0351	0.0387*	600	0.0532	0.0580
200	0.0363	0.0392	700	0.0556	0.0604
300	0.0387	0.0422	750	0.0568	0.0616
400	0.0415	0.0459*	850	0.0669	0.0726
500	0.0449	0.0495*	900	0.0680	0.0738

*Estimated

~~CONFIDENTIAL~~

Several observations are evident from the thermal conductivity data for the unhydrided material; the most important are as follows:

- 1) The thermal conductivity-temperature relation undergoes significant changes as the material phase transformations occur. These are in the temperature regions 550 to 600°C and 750 to 850°C.
- 2) Under the time-temperature conditions of these experiments, the changes which occur during phase transformations are not reversible insofar as thermal conductivity is concerned. Specimens which have been heated to above 550°C have higher conductivities on cooling than on initial heating. For both specimens in this investigation, Section 5 was at no time above this temperature. The conductivity of this section on cooling agreed with initial values for the whole specimen. The remainder of the specimens, which had been above 550°C during the measurements, had roughly a 10% increase in conductivity. This increase is considered to be real.
- 3) There is a real difference between thermal conductivities of the two specimens examined. This suggests at least slight variations in composition or fabrication history, or both. The 95% confidence limit for the thermal conductivity apparatus is $\pm 5\%$; the differences between specimens are much larger.

Figure 27 shows the locations of points of grouped data as given in Table 23 and 24 for the two specimens. Also shown are curves which are believed to be most representative of the thermal-conductivity temperature relation of the unhydrided material, based on measurements made at Battelle. The following comments discuss the validity of these curves for the various temperature regions:

- 1) For the range up to 550°C, the curve location is influenced primarily by the data for cooling of the first specimen, heating of the second, and conductivities calculated from the specific heats, densities, and thermal diffusivities measured at Battelle. The reasonable agreement of all these data places considerable confidence in the location of this section of the curve.
- 2) The slope for the curve in the 600 to 750°C range is determined by the No. 1 Specimen data, which are more complete. Its location is

~~CONFIDENTIAL~~

Figure 27. Thermal Conductivity of Unhydrated Material
(Steady-State, Direct Measurement) (BMI Data)

Figure 28. Thermal Conductivity of Unhydrated Material
(Calculated vs Measured Data)

~~CONFIDENTIAL~~

influenced by consideration of the data points shown, plus calculated values which are in the range 0.067 to 0.086 cal/sec-cm-°C. In this instance, the calculated values are weighted less than those measured because the experimental procedures associated with enthalpy (specific heat) measurements are not comparable to those in conductivity and diffusivity measurements in regard to heat treatment.

3) In the 850 to 900°C range, the curve location again is influenced by calculated values (which are in the 0.083 to 0.089 cal/sec-cm-°C range). Again, these are weighted less than those measured for the same reason.

Table 27 gives interpolated values from the curves drawn in Figure 27, and thus is considered to be most representative of Battelle's information on thermal conductivities for the unhydrided material.

TABLE 27
MEASURED THERMAL CONDUCTIVITY
OF UNHYDRIDED MATERIAL
(BMI Data)

Temperature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)	Temperature, T (°C)	Thermal Conductivity, k (cal/sec-cm-°C)
0	-	550	0.0464
100	0.0351	600	0.0510
200	0.0370	700	0.0549
300	0.0392	750	0.0570
400	0.0416	850	0.0662
500	0.0450	900	0.0693

C. EVALUATION OF DATA

The thermal conductivity of the unhydrided material was also calculated from the product of the diffusivity, specific heat, and density, using "best average" values of measurements made at both laboratories for the various properties. The results are plotted in Figure 28, along with the directly measured data. The agreement between the experimental and calculated values is remarkably good.

~~CONFIDENTIAL~~

1-20-67 UNC

7700-2568

Figure 29. Summary of Specific Heat Measurements

REF ID: A66000
~~CONFIDENTIAL~~

VI. SUMMARY

A "best value" for each property measured was arrived at by weighting the results obtained at each laboratory, AI and Battelle, and on each piece of apparatus according to the probable reliability of the individual measurements. The factors used in the weighting were discussed in the previous sections on individual properties. The actual weight used was arbitrary, but an attempt was made to stay within the postulated limit of error for what was considered the most accurate set of data in each case. The values arrived at are given in Tables 28 and 29, and plotted in Figures 29, 30, 31, and 32.

TABLE 28
BEST VALUES FOR PROPERTIES OF UNHYDRIDED FUEL

Temperature, T (°C)	Specific Heat, c_p (cal/gm-°C)	Resistivity, ρ ($\mu\Omega$ -cm)	Diffusivity, α (cm ² /sec)	Thermal Conductivity, k (cal/sec-cm-°C)
0	0.059	71.0	0.0715	-
100	0.063	81.9	0.0745	0.0351
200	0.068	97.3	0.0770	0.0370
300	0.072	108.8	0.0790	0.0392
400	0.076	118.0	0.0810	0.0416
500	0.080	124.9	0.0820	0.0450
595	0.084	129.5	0.0825	0.0481
600	-	-	0.0875	0.0510
700	-	126.1	0.0985	0.0549
800	-	118.5	0.1095	0.0594
815	-	-	0.1155	0.0636
900	-	115.0	0.1270	0.0693
1000	-	-	0.1380	-

~~CONFIDENTIAL~~

TABLE 29
BEST VALUES FOR PROPERTIES OF HYDRIDED FUEL

Temperature, T (°C)	Specific Heat, c_p (cal/gm-°C)	Resistivity, ρ ($\mu\Omega$ -cm)	Diffusivity, α (cm ² /sec)	Thermal Conductivity, k^* (cal/sec-cm-°C)
0	0.065	53.0	0.111	0.0438
100	0.0845	63.7	0.0940	0.0483
200	0.103	74.0	0.0820	0.0513
300	0.121	85.0	0.0735	0.0541
400	0.138	95.5	0.0680	0.0573
500	0.155	106.4	0.0640	0.0604
550	0.163	112.2	0.0630	0.0624
560	0.163	113.0	0.0630	0.0624
600	0.170	119.0	0.0605	0.0626
650	0.178	127.0	0.0575	0.0623
700	-	-	0.0545	-

*Calculated from $k = \alpha c_p \rho$

1-20-67 UNC

7700-2569

Figure 30. Summary of Resistivity Data

1-20-67 UNC

7700-2570

Figure 31. Summary of Diffusivity Measurements

1-20-67 UNC

7700-2571

Figure 32. Summary of Conductivity Measurements

BLANK

~~CONFIDENTIAL~~

APPENDIX PHASE DIAGRAMS OF ZIRCONIUM-URANIUM AND ZIRCONIUM-HYDROGEN BINARY SYSTEMS

Figure 33. Phase Diagram of Zirconium-Uranium Binary System [Rough and Bauer(5)]

66-7695-127-143A

Figure 34. Phase Diagram of Zirconium-Hydrogen Binary System [Maki(18)]

NAA-SR-11960

~~CONFIDENTIAL~~

BLANK

~~CONFIDENTIAL~~

REFERENCES

1. P. W. Bickel, "Measurements and Interpretation of Electrical Properties of Zirconium Hydride for Hydrogen-to-Metal Ratios Between 1.5 and 2," NAA-SR-4173 (January 15, 1960)
2. "Uranium-Zirconium Alloy, Consumable Electrode, Arc Melting and Extruding of," AI Specification NA 0622-009
3. "Uranium-Zirconium Fuel Alloy, Hydriding of," AI Specification NA 0611-001
4. T. L. Iliff, "SNAP 10A Compositional Fuel Alloy for Thermophysical Properties Referee Program," NAA-SR-MEMO-11533 (July 22, 1965)
5. F. A. Rough and A. A. Bauer, "Constitutional Diagrams of Uranium and Thorium Alloys," Addison-Wesley Publishing Company (1958)
6. H. E. Johnson, "Hydrogen Dissociation Pressures of Modified SNAP Fuels," NAA-SR-9295 (March 15 1964)
7. D. C. Ginnings, and R. J. Corruccini, "An Improved Calorimeter - The Determination of Its Calibration Factor and Density of Ice at 0°C," J. Res. Nat. Bur. Stds., 38, 583-591 (1947)
8. R. A. Finch, "Rapid Pulse Heating of Modified Zirconium-Uranium Hydrides to Destruction," NAA-SR-10482
9. H. W. Deem and C. F. Lucks, "An Improved All-Metal Bunsen-Type Ice Calorimeter," Instr. Soc. A., PPT-4, 1-9 (1958)
10. D. C. Ginnings, T. B. Douglas, and A. F. Ball, "Heat Capacity of Sodium Between 0° and 900°C, The Triple Point and Heat of Fusion," Journal of Research of the National Bureau of Standards, Vol 45, (1950) pp 23-33, RP 2110
11. D. C. Ginnings and R. J. Corruccini, "Enthalpy, Specific Heat, and Entropy of Aluminum Oxide From 0° to 900°C," Journal of Research of the National Bureau of Standards, Vol 38 (1947) pp 593-600, RP 1797
12. D. C. Ginnings and G. T. Furukawa, "Heat Capacity Standards for the Range 14° to 1200°K," Journal of the American Chemical Society, Vol 75 (1953) p 525
13. R. W. Webb, "Hydrogen Permeation Through Metals," NAA-SR-9844 (April 27, 1964)
14. M. E. Nathan, "Fortran Program for Computation of Specific Heat From Data of Pulse Heating Experiments," NAA-SR-TDR-11230

NAA-SR-11960

~~CONFIDENTIAL~~

CONFIDENTIAL

15. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, "Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity," Journal of Applied Physics, 32 (1961) pp 1679-1684
16. H. W. Deem and W. D. Wood, "Flash Thermal-Diffusivity Measurements Using a Laser," Review of Scientific Instruments, 33 (1962) pp 1107-1109
17. C. R. Tipton, Jr., Editor, "Reactor Handbook, Vol I, Materials," Second Edition, Interscience Publishers, New York (1960)
18. Data compiled by L. M. Maki, Atomics International (1966)

NAA-SR-11960

76

CONFIDENTIAL