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A Calorimetric Investigation of Zirconium, Titanium, and Zirconium Alloys from 60 to 960°C

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I am submitting herewith a thesis written by James L. Scott entitled "A Calorimetric Investigation of Zirconium, Titanium, and Zirconium Alloys from 60 to 960°C." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in .

E.E. Stansbury, Major Professor

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Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

May 24, 1957

To the Graduate Council:

I am submitting herewith a thesis written by James L. Scott entitled "A Calorimetric Investigation of Zirconium, Titanium, and Zirconium Alloys from 60 to 960°C." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgy.

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Major Professor

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Dean of the Graduate School

A CALORIMETRIC INVESTIGATION OF ZIRCONIUM, TITANIUM,
AND ZIRCONIUM ALLOYS FROM 60 to 960°C

A THESIS

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the degree of
Doctor of Philosophy

by
James L. Scott

June 1957

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CHAPTER I

SUMMARY

The favorable nuclear properties of zirconium make it a very attractive construction material for nuclear reactors. Full benefit of the material, however, can only be gained by the addition of alloys which increase the high-temperature strength. Consequently, a fundamental knowledge of the alloying behavior of zirconium is desirable. A better insight to this behavior may be secured by studying the similarities and differences between alloys of zirconium, titanium, and hafnium since these elements appear to be quite similar in the metallic state.

One approach to the study of the alloying behavior of a metal is the determination of the changes of the thermodynamic functions with the addition of a given solute. For such a determination, a knowledge of the specific heats and heats of transformation of the alloys of interest is required. Consequently, the measurement of the specific heats and heats of transformation of a series of alloys of zirconium as well as titanium was undertaken.

The pure metals and alloys studied were iodide zirconium, iodide titanium, and alloys of zirconium with 0.881 and 5.37 weight per cent silver, 7.77 weight per cent indium, 17.5 weight per cent niobium, 34.4 weight per cent titanium, and 300 parts per million of hydrogen. Measurements were made over the temperature range of 60 to 960°C through the use of a high-temperature-adiabatic calorimeter. The results are presented graphically in the text.

The conclusions which were drawn from this investigation are:

1. The specific heat of beta zirconium is lower than that of alpha at the transformation temperature of $870 \pm 2^\circ\text{C}$. Analogously the specific heat of beta titanium is lower than that of alpha at the transformation temperature of $883 \pm 2^\circ\text{C}$. For a zirconium - 17.5 weight per cent niobium alloy, which should correspond quite well to pure zirconium, the specific heat of the beta phase has the constant value 0.069 ± 0.002 calories/gram- $^\circ\text{C}$ from room temperature to 800°C . Within the limits of error the addition of 0.746 atomic per cent of silver or 6.27 atomic per cent of indium does not affect the specific heat of either the alpha or beta phase over their ranges of stability above room temperature. An alloy of higher silver content (4.58 atomic per cent) does have a slightly higher specific heat in the alpha region, presumably because of the higher specific heat of the intermetallic compound Zr_2Ag .

2. The heat of transformation of zirconium is 993 ± 25 calories per gram atom at 870°C , and the heat of transformation of titanium is 978 ± 25 calories per gram atom at 883°C . Within the limits of experimental error the heats of transformation of zirconium and titanium would have the same value if the transformations occurred at the same temperature. Although the transformation from the alpha to the beta phase in a 0.746 atomic per cent silver alloy occurs over the temperature range $830 - 865^\circ\text{C}$, the heat of transformation at an arbitrary intermediate temperature is the same as the value zirconium would have if it transformed at the same temperature within the limits of error. This is also true for an alloy of zirconium with 6.27 atomic per cent of indium,

which transforms over the range of 910 - 940°C. The temperature of the eutectoid transformation in the zirconium silver system is $825 \pm 2^\circ\text{C}$ and the heat of transformation of the eutectoid (3.73 atomic per cent silver) is 1240 ± 25 calories per gram atom.

3. The changes in the thermodynamic functions ΔH_0^x and

$$\int_0^T \frac{dT}{T} \int_0^T \Delta C^x d \ln T$$

are quite small, so that the precision of the calorimeter used was not sufficient to permit their evaluation.

4. The heat due to the solution of ZrH_2 in alpha zirconium may be detected calorimetrically even when the hydrogen content is as low as 28.5 ppm. The heat of solution is approximately 11,000 calories per mole of hydrogen.

5. There exists a metastable transition in a zirconium - 17.5 weight per cent niobium alloy below 520°C which has decided effects on the specific heat curves and on the hardness but cannot be identified by metallographic or x-ray investigations. This transformation is tentatively called the omega transition. A second metastable phase which occurs at lower temperature can be identified metallographically and with x-rays, but has little effect on the hardness or the specific heat.

6. An alloy containing 50 atomic per cent titanium with zirconium shows the expected specific heat behavior in the alpha phase, but the specific heat of the beta phase is definitely abnormal. The beta specific heat decreases linearly from 650°C to 800°C . This effect may be

interpreted as a disordering of the beta phase. The transformation occurred over the range 550 - 640°C on heating and 558.5 - 560.5°C during cooling. The heat of transformation of 740 ± 20 calories per gram atom at 600°C is abnormally low.

CHAPTER II

INTRODUCTION

Structural materials for nuclear reactors must meet three stringent conditions: they must have adequate mechanical properties at the operating temperature, they must be corrosion resistant to the heat transfer medium (air, water, or alkali metals), and they must not absorb neutrons excessively. This last requirement is a particularly stringent one, for it is met by only four accessible metals: aluminum, magnesium, beryllium, and zirconium, as Table I shows.

For reactors which operate at low temperatures, aluminum serves as an excellent constructional material, but it cannot be used for more efficient high-temperature reactors, because of its low elevated temperature strength associated with its low melting point of 660°C . Although magnesium has a lower absorption cross section than aluminum, it has a lower melting point (650°C) and poorer corrosion resistance, thus offering no particular advantages over aluminum. The use of beryllium is impractical except for very special applications, because of its extreme brittleness and the relative scarcity of its ores. In contrast, zirconium ores are abundant; the metal is fairly easily produced; it has satisfactory mechanical properties and excellent corrosion resistance at temperatures above the practical operating range for aluminum; and techniques of fabrication are now well developed. Thus zirconium comes at once to the foreground as a structural material for the construction of nuclear reactors.

TABLE I

MICROSCOPIC THERMAL-NEUTRON CROSS SECTIONS
OF WHOLE ELEMENTS (1)

Element	Atomic Weight	Absorption (barns)	Scattering (barns)
Beryllium	9.01	0.009	7.0
Magnesium	24.32	0.060	3.6
Aluminum	26.98	0.21	1.4
Titanium	47.90	5.6	4.0
Chromium	52.01	2.9	3.0
Iron	55.85	2.4	11.0
Nickel	58.69	4.5	17.5
Copper	63.54	3.6	7.2
Zirconium	91.22	0.18	8.0
Niobium	92.91	1.1	5.0
Molybdenum	95.95	2.4	7.0
Silver	107.88	60.0	6.0
Hafnium	178.6	115.0	

No one element can ever meet the insatiable demands of the design engineer, who is ever striving for operation at higher and higher temperatures, and zirconium is no exception. With respect to mechanical properties zirconium behaves as a low melting point element instead of the high melting metal it is, and its strength drops rapidly with increasing temperature such that it is no longer useful above about 350°C. By the addition of alloying elements the operating temperature may be increased to 500°C or possibly higher; hence an understanding of the alloying behavior of zirconium is absolutely essential to its projected use in a reactor system.

Zirconium is one of the Group IV transition elements. Other members of this group are titanium, which has a high strength to weight ratio, a property much valued for aircraft construction; and hafnium, whose high absorption cross section for neutrons makes it a useful reactor control rod construction material. From its position in the Periodic Table thorium would also be included in this group. In reality, however, the properties of this element are more closely related to those of the other members of the actinide series than to those of the Group IV transition metals.

The chemical similarity of the Group IV transition metals is surprising. All three metals form tetravalent compounds. Their oxides (TiO_2 , ZrO_2 , and HfO_2), for instance, are among the most refractory materials. This chemical similarity between zirconium and hafnium is one of the deterrents to the use of zirconium in reactors, since its ores generally contain from one to three per cent hafnium. If a good

neutron economy in a reactor is to be secured, the high cross section hafnium must be separated from the zirconium. Although this separation is difficult, low hafnium zirconium is now being produced. That this similarity persists in the metallic state is intriguing to theoretical metallurgists and presents an opportunity to study the similarities and differences between alloys of various solutes in zirconium, hafnium, and titanium. Such studies should lead to a better understanding of alloy formation in general and specifically the importance of the Hume-Rothery factors: atom size, valence electron-atom ratios, and electronegative valency effect on the alloying behavior of the transition elements.

The physical metallurgy of zirconium and titanium is now well established. Less is known about hafnium. All three metals transform from a closed-packed hexagonal structure which is stable at low temperatures to a body-centered-cubic structure which is stable at higher temperatures. The former structure, according to the usual terminology, is called alpha, whereas the latter structure is denoted as beta. The lattice parameter of these phases for zirconium, titanium, and hafnium together with the transition temperatures and other physical constants are shown in Table II.

The existence of an allotropic transition in a pure metal with rising temperature may be understood in terms of the free energies of the allotropic forms, the criterion for stability being that at constant temperature and pressure the phase is stable which has the lowest free energy. For a given phase, say alpha, the free energy F at a temperature T may be expressed by the equation

TABLE II

PROPERTIES OF HAFNIUM, ZIRCONIUM, AND TITANIUM (2)

Property	Titanium	Zirconium	Hafnium
Crystal Structure:			
Alpha phase, c.p.h., A (25°C)			
a_o	2.950	3.232	3.186
c_o	4.683	5.147	5.037
c_o/a_o	1.587	1.593	1.581
Beta phase (b.c.c.) A			
a_o (900°)	3.306	3.61	-
Transition temperature	882	870	~1310
Melting point, °C	1795	1845	1975
Specific resistivity (25°C) ohm-cm x 10 ⁶	45	40	32
Young's modulus lb/in. ² x 10 ⁻⁶	16	13.7	20

$$F_{\alpha} = H_{0\alpha}^{\circ} - \int_0^T dT \int_0^T \frac{C_{p\alpha}}{T} dT \quad (1)$$

where $H_{0\alpha}^{\circ}$ is the enthalpy of the alpha phase at absolute zero and $C_{p\alpha}$ is the specific heat at constant pressure. In the same manner the free energy of the beta phase may be expressed as

$$F_{\beta} = H_{0\beta}^{\circ} - \int_0^T dT \int_0^T \frac{C_{p\beta}}{T} dT. \quad (2)$$

The fact that beta becomes stable at an elevated temperature means that

$$\left/ \int_0^T dT \int_0^T \frac{C_{p\beta}}{T} dT \right/$$

increases more rapidly as the temperature increases than

$$\left/ \int_0^T dT \int_0^T \frac{C_{p\alpha}}{T} dT \right/.$$

This observation is shown more clearly by Figure 1, which gives a plot of the alpha and beta phases as a function of the absolute temperature.

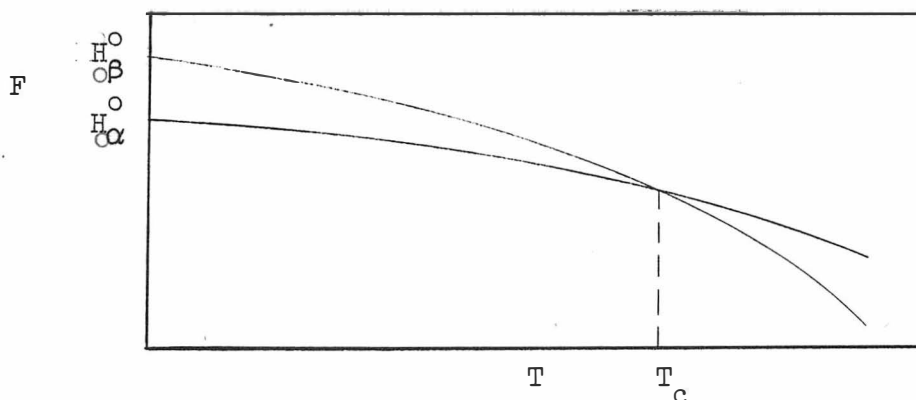


Figure 1. Hypothetical plot of the free energy of the α and β phases of zirconium as a function of temperature.

Thus at absolute zero $H_{\beta}^{\circ} > H_{\alpha}^{\circ}$ makes alpha the stable phase, but as the temperature increases F_{β} decreases more rapidly than F_{α} until at T_c , $F_{\beta} = F_{\alpha}$. At temperatures greater than T_c , $F_{\beta} < F_{\alpha}$ makes beta the stable phase. This more rapid decrease of the free energy of beta with increasing temperature may be due to a higher heat capacity of the beta phase or a higher Debye temperature for the alpha phase. If the alpha to beta transitions in pure titanium, zirconium and hafnium are to be understood, then accurate thermodynamic data on both the alpha and beta phases must be secured.

The earliest determinations of the specific heats of both titanium and zirconium were made by Jaeger and his associates (3) (4) using a dropping calorimeter with materials purified by the decomposition of zirconium and titanium iodide, a process which was developed by van Arkel and de Boer. The samples were sealed in platinum capsules and dropped into a copper block after they had reached equilibrium in a furnace at a predetermined temperature. The measured-temperature rise in the copper block was compared to the rise produced by known quantities of heat. The heat effect of the platinum was subtracted to give the enthalpy of zirconium and titanium as a function of temperature. The temperature derivative of this function is the specific heat. More recently Skinner (5) and Coughlin and King (6) have determined the specific heat and the heat of transformation of zirconium using the same method. Redmond and Lones (7) have also measured the specific heat of zirconium using an ice calorimeter. In an ice calorimeter the enthalpy decrease of the sample corresponds to a certain volume of ice which is

melted by dropping the sample into the receiving tube which is compared to the volume change produced by known quantities of heat. The specific heat and heat of transformation of titanium has been measured by Skinner, Johnston, and Beckett (8) using the same apparatus Skinner used for zirconium. The specific heats for zirconium, which have been reported by the above investigators are shown in Figure 2 together with the results of the present investigation. The temperatures and heats of transformation for zirconium, which were reported, are compared in Table III.

In the same fashion values for the specific heat and the heat of transformation of titanium are shown in Figure 3 and Table IV.

The wide variations in these results are due partly to impurity effects of oxygen, nitrogen, and hydrogen, and partly to inherent difficulties in making high temperature calorimetric measurements. All investigations show that the beta specific heats of both titanium and zirconium are lower than those of the alpha phase at the transition temperature, suggesting that a lower Debye temperature of the beta phase is responsible for greater decrease of the free energy of beta as the temperature is increased. The measurements of the heats of transformation of zirconium and titanium were integral parts of the measurements of the specific heats except for the value for titanium reported by Schofield (9). This value was calculated from measurements of the change in the time for the transformation at different cooling rates. The method used by Backhurst (10) for the determination of the heat of transformation of titanium has not been published.

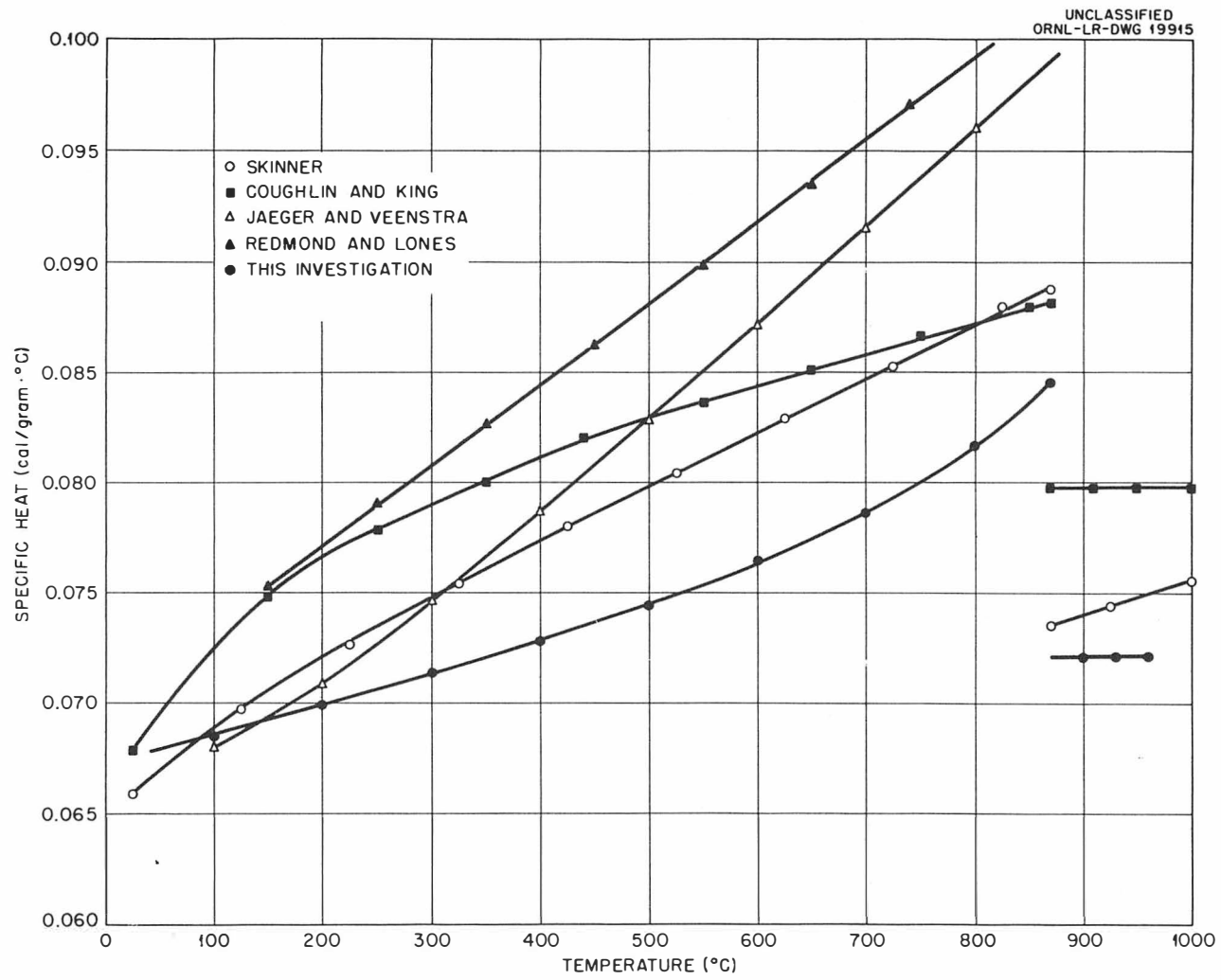


Figure 2. The reported values of the specific heat of zirconium.

TABLE III

REPORTED VALUES OF THE HEAT OF TRANSFORMATION
OF ZIRCONIUM

Investigator	Heat of Transformation: cal/gram atom	Temperature of Transformation °C
Skinner (5)	1040	870
Coughlin and King (6)	920	837 - 917
This investigation	993 ± 25	870 ± 2

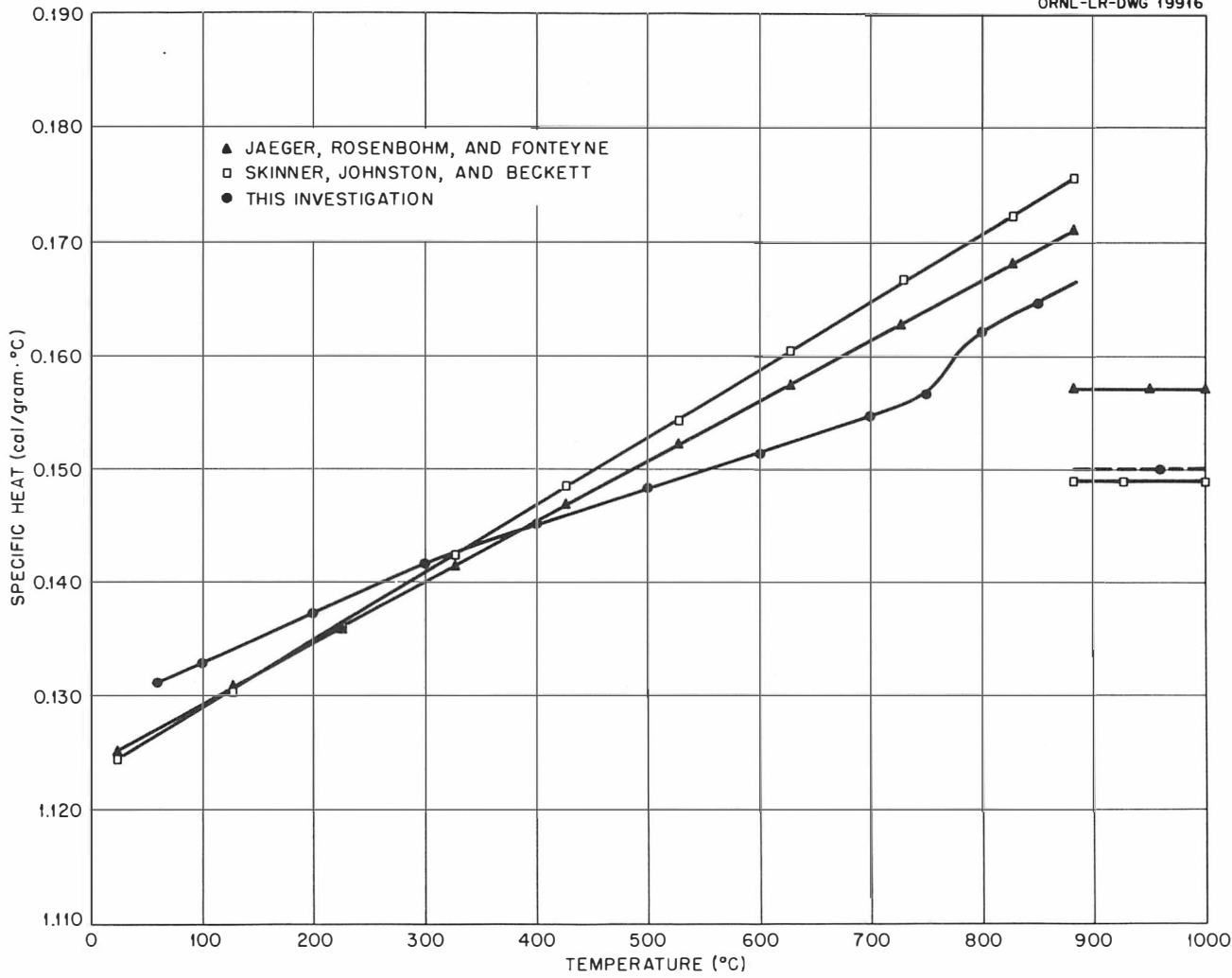


Figure 3. The reported values of the specific heat of titanium.

TABLE IV

REPORTED VALUES OF THE HEAT OF TRANSFORMATION OF TITANIUM

Investigator	Heat of Transformation cal/gram/atom	Temperature of Transformation °C
Jaeger, Rosenbohm, and Fonteyne (4)	950	882
Skinner, Johnson, and Beckett (8)	943	883
Schofield (9)	813 ± 80	885 ± 2.5
Backhurst (10)	880 ± 44	-
This investigation	978 ± 25	883 ± 2

The alpha to beta transition in zirconium and titanium is of considerable practical interest. For example, certain alloy additions tend to stabilize the low-temperature form to higher temperatures thereby avoiding stress and dimensional changes produced by the transformation during fabrication or use. In other instances solutes may be added which will stabilize the high-temperature form at lower temperatures. These additions may also permit metastable phases or precipitation hardening to occur which lead to more favorable physical properties, as in the heat treatment of steel or aluminum alloys.

Because of the possible improvement of engineering properties of zirconium by the addition of alloys and its unique role in reactor design, an intensive research program has been carried out since 1950 under the auspices of the Atomic Energy Commission to determine the phase diagrams of various binary systems with zirconium. Compilations of this research have shown that zirconium-binary-alloy systems may be catalogued into five types (11):

1. Peritectic and Peritectoid (raising of the alpha-beta transition): Zr-Al, Zr-O, Zr-Sn, Zr-N, Zr-In.
2. Extended beta (depression of the alpha-beta transition): Zr-Nb, Zr-Ta, Zr-Th, Zr-U.
3. Eutectic and Eutectoid: Zr-Ag, Zr-Be, Zr-Co, Zr-Cr, Zr-Cu, Zr-Fe, Zr-Mn, Zr-Mo, Zr-Ni, Zr-V, Zr-W, and Zr-H.
4. Miscellaneous (including types 1, 2, and 3): Zr-C, Zr-Ge, Zr-Si.

5. Complete solid solubility: Zr-Hf, Zr-Ti.

These results indicate that in general the alpha-beta boundaries of zirconium alloys vary regularly with the position of the solute in the Periodic Table. Thus when zirconium is alloyed with transition element solutes to the right in the Periodic Table and including the elements of Group IB, the alpha-beta boundaries are depressed; whereas when the solute is a member of Groups IIIB, IVB, or VB, the alpha-beta boundaries are elevated.

Betterton and Frye (12) have expressed these systematic alloying effects in terms of the valency rule, and have shown that such a rule does apply for zirconium. The valency rule states that for those solutes which depress the alpha to beta transition the degree of lowering the transition temperature should be a linear function of the difference in valency between the solute and the solvent; and for those solutes which raise the transformation temperature the degree of raising of the transition temperature should also be a linear function of the difference in valency between the solute and the solvent. In addition positive valency differences should have an opposite effect to negative valency differences. Silver, for instance, which is usually considered to be monovalent, lowers the transformation temperature of zirconium, whereas indium, which is ordinarily given a valence of three, raises the transformation temperature. If it is assumed that these valences are correct, zirconium, according to the valency rule, must have a valence of two, and those elements with lower valency would produce eutectoids while those elements with a higher valence would form peritectoids. Dilute

solutions of divalent solutes would be expected to have little effect on the transition temperature unless size effects or electronegativity effects come into importance. The transition elements, chromium, iron, cobalt, and nickel would be assigned their usual valence of zero to agree with this scheme.

The sign of the valency difference is reversed, but the theory otherwise holds, if the valences for metals which have been derived by Pauling (13) are applied. Pauling states that the valence of silver is 5.56, indium is 3.56, and zirconium is 4. According to this valency theory those elements with a higher valence than zirconium form eutectoids and those elements which have a lower valence form peritectoids. The valence of six is assigned to the elements chromium, iron, cobalt, and nickel by Pauling. This valence gives agreement to the valency rule for these elements. Betterton and Frye have shown that with either set of valencies which one wishes to adopt, titanium alloys follow the same valency rule as zirconium if the difference in size between the zirconium and titanium atoms is taken into account, the titanium atom being roughly nine per cent smaller than that of zirconium.

It is possible to express the effects of solutes of different valences on the transformation temperature in terms of changes in the thermodynamic parameters of the alpha and beta phases. If one assumes that a given solute forms a regular solution in both the alpha and beta phases, he may write the free energies of the alpha and beta solutions, which have a solute mole fraction of X, as follows:

$$F_{\alpha} = H_{\alpha}^{\circ}(X) - \int_0^T dt \int_0^T C_{p_{\alpha}}(X) d \ln T + KT[X \ln X - (1-X)\ln(1-X)] \quad (3)$$

and

$$F_{\beta} = H_{\beta}^{\circ}(X) - \int_0^T D T \int_0^T C_{p\beta}(X) d \ln T + K T [X \ln X + (1-X) \ln (1-X)] \quad (4)$$

A change in the mole fraction of a solute with a given valency would be expected to shift the enthalpies at absolute zero, $H_{\alpha}^{\circ}(X)$ and $H_{\beta}^{\circ}(X)$, and the integrated specific heat terms

$$\int_0^T dT \int_0^T C_{p\alpha}(X) d \ln T$$

and

$$\int_0^T dT \int_0^T C_{p\beta}(X) d \ln T.$$

A change in one or both of these parameters for the alpha phase produced by a change in X would be expected to be different from the change in the beta phase. In addition higher valence solutes would be expected to shift these parameters in an opposite direction to those produced by lower valence solutes. Using the above expressions for the free energies of the alpha and beta phases, respectively, and the usual conditions of equilibrium, i.e.,

$$\frac{\partial F_{\alpha}}{\partial X_{\alpha}} = \frac{\partial F_{\beta}}{\partial X_{\beta}} = \frac{F_{\alpha} - F_{\beta}}{X_{\alpha} - X_{\beta}} \quad (5)$$

Betterton and Frye (12) derived the following expressions for the compositions of the phase boundaries, X_{α} and X_{β} , at a given temperature T:

$$X_{\alpha} = \frac{-e^{-\frac{L}{KT}} + 1}{-e^{-\frac{N}{KT}} + 1} \quad (6)$$

and

$$X_{\beta} = \frac{e^{+\frac{L}{KT}} - 1}{e^{+\frac{N}{KT}} - 1} \quad (7)$$

where

$$L = \Sigma_{\alpha} - \Sigma_{\beta} - X_{\alpha} \dot{\Sigma}_{\alpha} + X_{\beta} \dot{\Sigma}_{\beta} \quad (8)$$

and

$$N = \dot{\Sigma}_{\beta} - \dot{\Sigma}_{\alpha} \quad (9)$$

In these expressions

$$\Sigma_{\alpha} \equiv H_{\alpha}^{\circ}(X_{\alpha}) - \int_0^T dT \int_0^T C_{\alpha}(X_{\alpha}) d \ln T, \quad (10)$$

$$\Sigma_{\beta} \equiv H_{\beta}^{\circ}(X_{\beta}) - \int_0^T dT \int_0^T C_{\beta}(X_{\beta}) d \ln T, \quad (11)$$

$$\dot{\Sigma}_{\alpha} \equiv \frac{\partial \Sigma_{\alpha}}{\partial X_{\alpha}}, \quad (12)$$

and

$$\dot{\Sigma}_{\beta} \equiv \frac{\partial \Sigma_{\beta}}{\partial X_{\beta}}, \quad (13)$$

Because of a lack of thermodynamic data Betterton and Frye assumed that

$$L = \Delta F_0 \quad (14)$$

and

$$N = K_1 \Delta V - K_2 S. \quad (15)$$

In the above equations ΔF_0 is the free energy change for the pure solvent, ΔV is the difference in valence between the solute and the solvent, and S is the square of the difference between the solute and solvent atom diameters divided by the square of the diameter of the solvent atom. They then calculated values for N for different solutes from their phase diagrams and solved the constants for K_1 and K_2 by

least squares. Using these values of K_1 and K_2 they recomputed the phase boundaries for the various solutes in zirconium and titanium and found a good correlation between the calculated and experimental $\alpha/\alpha + \beta$ and $\alpha + \beta/\beta$ boundaries. In addition the values of the constants K_1 and K_2 for titanium were found to be approximately the same as those for zirconium. Betterton and Frye suggested that a better correlation could be obtained if accurate thermodynamic data for the various alloys were available.

Because of this need for calorimetric data on zirconium and its alloys, and because of the wide scatter in the reported values of the thermodynamic functions of zirconium, the measurement of the specific heat and heats of transformation of zirconium and alloys of zirconium with silver, indium, hydrogen, niobium, and titanium was undertaken by the author at the University of Tennessee in January, 1956. As a corollary study, the measurement of the specific heat and heats of transformation of titanium was also undertaken. The zirconium-silver and zirconium-indium systems were selected for study because the phase diagrams have been very carefully worked out by Betterton et al (14) (15), and because they serve as typical representatives of lower and higher valence solutes in zirconium with corresponding reversed effects on the stability of the alpha and beta phases. Zirconium-hydrogen alloys were studied to explain anomalous peaks in the specific heat curve for zirconium which were observed during the course of the investigation. Alloys of zirconium with titanium and niobium were studied because in these systems the beta phase is suppressed to temperatures much lower

than 870°C and thus information can be obtained on the beta phase over a wider range of temperatures. All measurements were made in the University of Tennessee high-temperature adiabatic calorimeter developed by G. E. Elder (16), M. L. Picklesimer (17) and D. L. McElroy (18).

There are characteristic features of each alloy system studied, and the results of this investigation will be presented in eight sections. These are:

- Section I. General Information
- Section II. Zirconium
- Section III. Zirconium-Silver
- Section IV. Zirconium-Indium
- Section V. Zirconium-Hydrogen
- Section VI. Zirconium-Niobium
- Section VII. Titanium
- Section VIII. Zirconium-Titanium

Because the University of Tennessee calorimeter operates only above room temperature, these results will serve only as a partial thermodynamic analysis of the systems, and are not intended to be complete. For a complete analysis one needs calorimetric data down to absolute zero on both the basic components and the alloys, and data on the difference of free energies of alloys and their pure constituents such as those one obtains from vapor pressure or electromotive-force-cell measurements. These data should, however, be of much value to future studies on zirconium alloys and will illustrate the usefulness of calorimetric measurements on the study of alloy systems.

CHAPTER III

THE PREPARATION OF THE ALLOYS

It is difficult to prepare a homogeneous alloy of zirconium containing insufficient oxygen, nitrogen, or hydrogen to affect seriously its mechanical properties. For this reason the methods of preparing the alloys used in this research will be described in detail.

To prepare a high-purity alloy one must start with pure zirconium, which is itself a difficult material to produce since it is among the most reactive of metals at elevated temperatures, a property illustrated by its use as a getter in electronic tubes. Not only does zirconium react with oxygen, hydrogen, and nitrogen, but it also dissolves the reaction products rapidly above the following temperatures: oxygen - 700°C, hydrogen - 300°C, and nitrogen - 1000°C (19). The resulting solutions may be quite brittle and fabricated only with difficulty. For this reason zirconium must always be melted and heat treated in extremely inert atmospheres.

Zirconium of sufficient purity for most processes is produced by the Kroll process (20). In this process zirconium oxide (ZrO_2), which has been highly purified, is reacted with carbon to produce zirconium carbide. This carbide is chlorinated to produce zirconium tetrachloride ($ZrCl_4$) which is then reacted with molten magnesium under an inert atmosphere to produce metallic zirconium and magnesium chloride. The chloride is removed by washing and any excess magnesium is recovered by a distillation process. The resulting zirconium is a porous-spongy

mass which is then remelted in suitable furnaces into a useful form. The current price of low hafnium sponge zirconium is about \$15 per pound.

For reactor applications the stipulation of low hafnium is made because the normal hafnium content in zirconium ores, if allowed to remain, would make the neutron absorption cross section of the final sponge prohibitive. Because the chemical properties of zirconium and hafnium are almost identical, the removal of the one to three per cent hafnium is quite difficult. The separation is permitted, however, by the slightly different solubilities of hafnium and zirconium salts such as $(\text{NH}_4)_2\text{HfF}_6$ and $(\text{NH}_4)_2\text{ZrF}_6$ in dilute hydrofluoric acid solutions. By a continuous fractional crystallization process with about 10 stages, a salt with a hafnium-zirconium ratio of less than 0.001 may be produced (21).

If a product of greater purity than sponge is required, as in fundamental research, zirconium (or hafnium or titanium) may be purified by the van Arkel and de Boer iodide decomposition process (22). In this process the zirconium sponge is reacted with iodine at 450°C to produce zirconium iodide (ZrI_4) vapor. This compound is then decomposed by and deposited on a filament of zirconium at a temperature of 1200°C . The resulting zirconium is in the form of a dense rod which is low in total impurities and is ready to fabricate.

The high reactivity of zirconium at high temperatures also makes its fabrication difficult. Melting and casting, especially, are difficult processes to carry out without contaminating the metal. There

is no crucible material which is inert to liquid zirconium, for it readily reduces oxides, etc., and dissolves up to 0.4 per cent carbon from graphite. Carbon, like oxygen, embrittles the zirconium. Arc melting of zirconium in a water-cooled copper crucible has proved to be the most satisfactory method. The conductivity of copper is so much higher than that of zirconium that the first layer of zirconium to solidify on the copper surface acts as a layer of insulation to the metal adjacent to it, so that zirconium is actually melted in a zirconium crucible. In order to have molten zirconium (melting point 1845°C) in contact with solid copper a method of generating a large quantity of heat in a confined area is essential. This is done by utilizing an electric arc either from an inert tungsten electrode or a consumable electrode of zirconium itself. Alloys are made by melting the alloy and the zirconium in the arc at the same time.

The materials used in this research were iodide zirconium obtained from the Westinghouse Atomic Power Laboratory and iodide titanium purchased from the Foote Mineral Company. The compositions of the alloys produced from them are shown in Table V. The iodide zirconium had been deposited in the form of a one-inch diameter rod, and the calorimetric specimens of dimensions two inches long and seven-eighths inch diameter were machined directly from the deposited material. Since the as deposited titanium was only a half inch spiny rod, it required remelting to produce an ingot large enough for a calorimeter specimen. The melting of the titanium was effected by the author at the Oak Ridge National Laboratory in a consumable electrode arc furnace.

TABLE V

COMPOSITIONS AND HARDNESSES OF METALS AND ALLOYS

Property	Iodide Zirconium		Zr + 0.881 w/o Ag		Zr + 5.37 w/o Ag		Zr + 7.77 w/o In		Iodide Titanium		Zr + 17.5 w/o Nb	Zr + 34.4 w/o Ti
DPH Hardness ^{1,2}	66.5		95.7		162		147		79.2		194	366
Solute Content	Wet	Activation	Ingot Top	Ingot Bottom	Ingot Top	Ingot Bottom	Ingot Top	Ingot Bottom	Wet	Spectro-graphic		
Al ppm	4	1								30		
Ag w/o			0.879	0.883	5.44	5.30						
Ca ppm	6									trace		
Co ppm	1	0.5										
Cr ppm	7	23								trace		
Cu ppm	14	12.9										
Fe ppm	130	186	360	330	280	300	210		300	50		
Hf ppm	70	162										
In w/o							7.77					
K ppm	40											
Mg ppm	5									100		
Mo ppm	3.5	1.9										
Na ppm	30											
Ni ppm	30	49								trace	Nb - 17.5 w/o	
Pb ppm	5											
Si ppm	18	6								500		
Sn ppm	4											
Ti ppm	2											34.4 w/o
W ppm	18	2.4								Remainder		
C ppm ³	220		140	100	130	320	67		320			
H ppm ⁴	35		4.4	4.0	11	67	5.1		67			
N ppm ⁴	75		8.6	4.6	4.9	7.7	30		7.7			
O ppm ⁴	150		150	180	220	110	160		110			

1. 10 Kg load
2. All specimens furnace cooled
3. Direct combustion
4. Vacuum fusion

To prepare the silver-zirconium and the indium-zirconium alloys, plates of iodide zirconium, again obtained from Westinghouse Atomic Power Division, were pressed and swaged into tubes. After a thorough cleaning with hydrofluoric acid, water, and alcohol, three short lengths of tube were welded together in a dry box to form a pipe of sufficient length for use in the consumable-electrode arc furnace. Wires of 99.999 per cent indium or silver of the proper diameter to produce the desired composition were then inserted inside the tube along its full length. The tubes were then consumably melted to produce the desired alloy. Although the original intention was to remelt the resulting ingots, results of hardness measurements, metallographic and chemical analyses indicated that the alloys were homogeneous after a single pass. Finally the alloys were homogenized in a vacuum of 10^{-6} mm of mercury for two weeks at 1300°C . Since the hardness is a good measure of the quality of the zirconium alloy, the hardness values of the pure metals and the alloys are also shown in Table V.

Because of the fact that only a small quantity of 99.9 per cent niobium was available, the zirconium-niobium alloy used in this investigation was made in a slightly different way. Enough zirconium and niobium were weighed out quantitatively to produce 200 grams of a 17.5 weight per cent niobium alloy. These ingredients were then placed in a copper hearth, tungsten electrode arc furnace and melted by J. B. Flynn at Oak Ridge National Laboratory. The resulting ingot was removed from the furnace, cut into small pieces and remelted twice. This care was taken to improve the homogeneity of the final alloy. Due to the limited size

of this "button" melting assembly, the final calorimeter specimen after being swaged to a round cross section was about a half inch in diameter. This, however, was of sufficient size to make an adequate calorimeter specimen. Since neither component of this alloy is volatile the final composition was assumed to be the same as the initial charge. An alloy of zirconium with 34.4 weight per cent titanium was produced in the same way from the iodide materials.

The other specimen used in this investigation, the zirconium-hydrogen alloy, was produced by heating a zirconium calorimeter specimen in a rarefied atmosphere of hydrogen. The actual pressure of the system was uncertain and unfortunately no chemical analyses were made so that the actual hydrogen content was unknown. There are indications which are discussed later that the final hydrogen content was about 300 ppm.

The chemical analyses of the alloys produced for this investigation were made by the Analytical Chemistry Division of Oak Ridge National Laboratory. These methods included vacuum fusion for hydrogen, oxygen, and nitrogen, direct combustion for carbon, flame spectrophotometry for indium, and the chloride precipitation of silver. Other analyses on the original zirconium and titanium were supplied by Westinghouse Atomic Power Division and the Foote Mineral Company. A complete resumé on the analytical methods used by Westinghouse Atomic Power Division has been given by Read (23).

CHAPTER IV

DESCRIPTION OF THE CALORIMETER

The calorimeter used in this investigation was a high-temperature-adiabatic unit designed and described in detail by D. L. McElroy (18). McElroy's design incorporated improvements over previous calorimeters built at the University of Tennessee by M. L. Picklesimer (17) and G. E. Elder (16) under the guidance of E. E. Stansbury.

The original objective of the calorimeter program at the University of Tennessee was to utilize modern high-precision controllers such as the Leeds and Northrup Speedomax G and DAT 50 unit as the control mechanisms for a high-temperature adiabatic calorimeter which would operate continuously from room temperature to 1000°C. The underlying principle for such a calorimeter had been proposed previously by Quinney and Taylor (24) and Sykes and Jones (25). This principle is to install a heater inside the specimen to be studied in such a way that all the power dissipated by the heater will be absorbed by the specimen. The specimen with its heater is then placed in a furnace of special design which serves as an adiabatic shield and whose heating circuit is fed by an independent power supply. The power input to the shield is controlled by a differential thermocouple between the specimen and the shield so that no temperature difference between the two will exist. With this arrangement one measures the electrical energy dissipated in the specimen heater when the temperature of a specimen of known mass is raised a certain number of degrees. The heat capacity is then computed from the

following equation:

$$C_p = \frac{EI\Delta t \cdot f}{m\Delta T} . \quad (16)$$

In this expression C_p is the heat capacity, E is the voltage across the specimen heater, I is the heater current, Δt is the time required for the specimen to rise ΔT degrees, m is the mass of the specimen, and f is a factor which converts electrical units to heat units. The heat capacity thus computed is the average heat capacity over the temperature range included in ΔT .

The primary application of this type of calorimeter is to measure the specific heats of materials at elevated temperatures. It may, however, also be used to measure the heat of transformation of a substance from one allotropic form to another, the heat of fusion, the heat involved in an order-disorder reaction, or the heat associated with the demagnetization of a ferromagnetic material. By the addition of separate thermocouples to the specimen and to the adiabatic shield, the temperature of the shield may be held constant while one varies the temperature of the specimen. Such an arrangement permits the use of the instrument as an isothermal calorimeter, to measure the heat released during the isothermal transformation of an alloy below the critical temperature. Finally, by controlling the power to the shield in such a manner that a given deflection of the galvanometer is maintained, one can induce in a specimen any cooling rate which is desired below the maximum rate obtained by turning the power off and thus operate the calorimeter as a precise thermal analysis unit. Thus, an adiabatic

calorimeter appears to be a simple instrument with a variety of quite useful applications.

Unfortunately the design and operation of a high-precision, high-temperature adiabatic calorimeter entails a number of discouraging problems. These problems may be listed as follows:

1. The design of a truly adiabatic shield.
2. The response of the adiabatic shield.
3. The inaccuracies of thermocouples.
4. The instability of thermocouples.
5. The conduction of ceramics at elevated temperatures.
6. The vaporization of metals at elevated temperatures.
7. The emission of electrons from heaters at elevated temperatures.
8. The low thermal conductivity of high strength elevated temperature materials.
9. The corrosion of materials at elevated temperatures.
10. The thermal stresses.

Each of these difficulties places a separate requirement on the design and the simultaneous fulfillment of all the requirements changes the calorimeter from a simple device in principle to an intricate network of wires, pipes, pumps, and electronic apparatus.

The calorimeter which McElroy designed to optimize these diverse requirements is shown schematically in Figure 4. A smaller, but otherwise identical calorimeter designed to operate over a smaller temperature

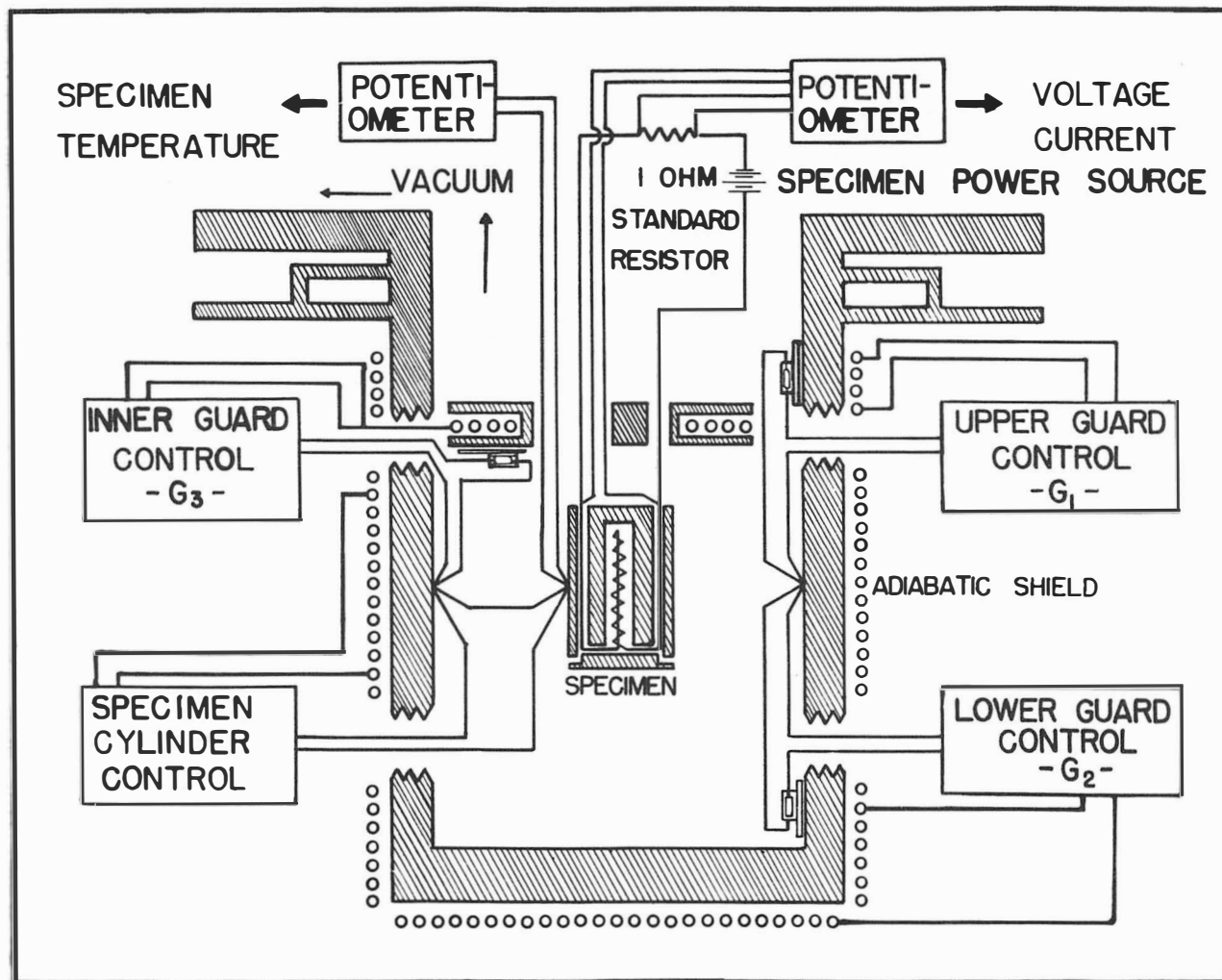


Figure 4. Schematic representation of the calorimeter system.

range utilizing the same control system as the McElroy calorimeter has been described in detail by Pawel (26). Since the wiring diagrams for the control and detecting circuitry have been thus described, only a general description to explain the schematic will be given here.

The material for the adiabatic shield consisted of a tube of monel with a one and one-half inch internal diameter which was thirty-eight inches long. Monel was selected because of its relatively high thermal conductivity and freedom from heat capacity anomalies. The long tube length was used because it was felt that a very long tube evenly wound with a resistance wire would result in a longer constant temperature section than would a shorter tube. To reduce heat transfer between the specimen and the wall a vacuum of approximately 0.01 micron of Hg was maintained on the inside of the tube. A helium atmosphere was maintained on the outside of the tube to prevent oxidation of the monel and to even out temperature gradients along the tube. On the outside of the helium chamber was a layer of insulation to reduce the power requirements for the system. The heating elements of the shield consisted of nichrome and were insulated with high purity Alundum beads. Semicircular-spiral grooves of the same diameter as the beads were machined into the outer diameter of the tube to hold the heating elements in place and to reduce the mass of the shield for more rapid response.

Four separate control circuits were utilized to reduce temperature gradients in the shield. These control units were the specimen cylinder control, the upper guard control G_1 , the lower guard control G_2 , and the inner guard control G_3 . The specimen cylinder control

maintained the surface of the inner wall of the tube adjacent to the specimen at the same temperature as that of the center of the outer surface of the specimen. G_1 and G_2 kept the temperature of the upper and lower ends, respectively, of the inner surface of the tube the same as that of the center of the inner surface of the tube. G_3 prevented the top surface of the specimen from radiating heat to the cover of the calorimeter through the end of the tube.

The control units for these systems were all null balance Speedomax G's with DAT 50 (pulse type proportioning control) except for the G_3 which was controlled by a Liston Becker unit. The sensitivity of the Speedomax units was increased through the use of a Leeds and Northrup D. C. Microvolt Amplifier on each circuit. The resulting sensitivity was such that one small division on the Speedomax G chart represented 0.1 microvolt. Except at high temperatures control deviations were no greater than one-tenth of one small division even when heating rates in the calorimeter were as high as 7 degrees a minute.

The thermocouples used for the control circuitry were platinum/platinum-13 per cent rhodium which had been tested for thermals in a special temperature gradient furnace described by McElroy (18). These thermocouples, which were selected for their high stability at the expense of a high emf, were carefully installed to insure a minimum of cold working. Rubber gloves were worn by those who installed thermocouples to prevent contamination of the thermocouple wires or the high-purity Alundum insulation. The thermocouples were attached to the specimen and to the cylinder by spot welding the thermocouples to tabs

of platinum or nichrome for the cylinder and titanium or zirconium for the specimen and then spot welding the tabs to the respective components. The necessity for special care with thermocouples and the fabrication of the special tabs that gave good thermal contact and no electrical contact required for the control of the auxiliary heating circuits has been described by Pawel.

The specimens, which were suspended in the tube by the heater leads for a minimum contact between the specimen and the surroundings, were cylinders two inches long and seven-eighths inch in diameter which were machined to receive a special heater of nichrome insulated with high-purity Alundum. A standard zirconium specimen and heater are shown in Figure 5, together with the smaller zirconium-niobium specimen which was cast in the button-type arc furnace. Attached to the heater directly at the top of the specimen are leads for measuring the voltage drop across the heater. Also in the heater circuit is a standard one ohm resistance which, by measurement of the voltage drop across it, permits determination of the heater current.

Since a very uniform rate of temperature increase is required for energy input measurement and successful controller performance, the power source to the heater circuit must be very stable. This stability was obtained in the present calorimeter by using a heavy duty 12 volt automobile storage battery as the source of power. By varying the voltage applied to the specimen circuit by the two volt intervals which were available directly from the battery, different heating rates for a given specimen were obtainable.

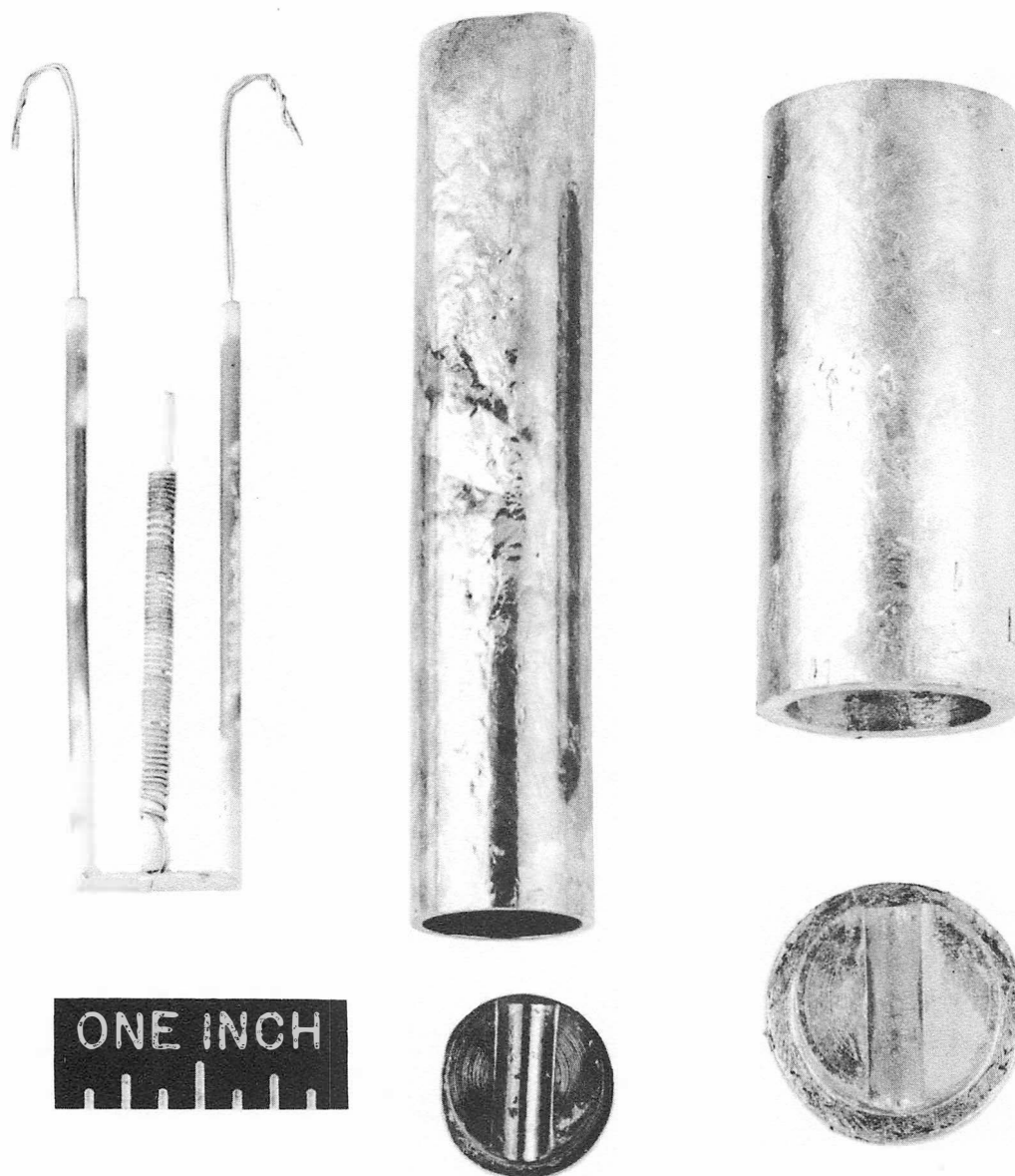


Figure 5. Typical calorimeter specimens and a specimen heater. Note particularly the metal deposit on the ceramic of the specimen heater. The white areas were covered with powdered alumina. The surface roughness produced by several cycles through the alpha-beta transition may be seen on the iodide-zirconium specimen on the right. The roughness of the surface of the zirconium-niobium sample in the center is due primarily to the swaging operation which produced a circular cross section.

The specimen heater circuit represents one of the critical problems limiting the precision of the data. Two contradictory requirements must be met by the specimen heater, good thermal contact to facilitate the heat transfer from the heater to the specimen, and poor electrical contact so that no current can flow from the heater circuit to ground through the differential thermocouple between the specimen and the shield. A secondary requirement is that the mass of the heater should be a minimum because a correction must be made for the specific heat of the heater. Difficulties arise due to decrease in the electrical resistance of ceramics at high temperatures and surface conduction due to the deposition of vaporized metal atoms onto the ceramics. This deposition was found to be particularly high with zirconium. For this reason, powdered Al_2O_3 was pressed into the cavity between the heater and the specimen. High-purity aluminum oxide has been found to be the best available ceramic for high-temperature heater insulation.

Another problem associated with the specimen heater is the emission of electrons from the very hot heater filament. These electrons collect on the specimen and flow to ground through the differential thermocouple in the same way as leakage current mentioned above. Such a current flow produces an emf between the junctions of the differential thermocouple and affects the control system the same way as a temperature difference. Since the control system reacts to induce zero potential between the specimen and the shield, a temperature difference equal electrically and opposite to the leakage current results. If this

effect is not compensated for, the measured heat capacity progressively deviates from the true value as the temperature increases. Compensation for this effect, which generally first appears at about 600°C, is made by the thermal compensation circuit described by Pawel, which is essentially a system for placing a biasing voltage between heater circuit and ground. The error potential across the platinum-13 per cent rhodium leads from the specimen and the shield thermocouple was monitored continually during the course of a run and the bias was adjusted to maintain zero potential. This essential part of the specimen heater circuit was omitted from the schematic diagram for the sake of simplicity.

The operation of the calorimeter was carried out by bringing each component of the calorimeter into thermal equilibrium with the specimen and then applying a d.c. voltage to the specimen. The drive mechanism for each circuit was adjusted and the unit allowed again to attain dynamic equilibrium. Ordinarily the temperature of the specimen had reached 60 degrees Celsius by the time the dynamic equilibrium was established. A potential corresponding to a given temperature was set on a Rubicon B potentiometer used to read the specimen thermocouple. The instant the deflection of the galvanometer was zero, one of a pair of precision chronographs was started. The Rubicon B potentiometer was then set at an emf corresponding to a higher temperature. When the galvanometer was again zero, the first chronograph was stopped and the second was started. Immediately after starting a chronograph the voltage and current to the specimen was read with the same potentiometer. The measurements consisted of the time Δt required for the specimen of mass

m to rise ΔT degrees when the power applied to the heater was the EI product. The heat capacity was then computed from Equation 16.

Between readings the four separate control systems were checked and the bias to the heater circuit was adjusted. The temperature intervals were selected so that one set of data was taken approximately every five minutes. The duration of a run from room temperature to 950°C required from four to ten hours. Temperatures were taken from the tables of emf versus temperature for platinum/platinum-13 per cent rhodium derived by Picklesimer (17), which are smoothed values of the table published by the Bureau of Standards (NBS Bulletin No. 508 or 561).

As one would expect, certain operational troubles are sure to arise during the operation of a device as complicated as this calorimeter, especially at high temperatures. A few of the more serious problems encountered are listed as follows:

1. Burn out of a shield heater circuit.
2. Power failures.
3. Breaking of thermocouples inside the calorimeter due to thermal stress.
4. Controller drifts or failure.
5. Failure of the specimen heater.
6. Loose connections.
7. Failure of variac drive mechanisms.

One or a combination of these troubles resulted in approximately half of the total number of the runs made being discarded. The first twelve runs were discarded because of the inability of an inexperienced operator to get good control at the higher temperatures where emf pickup occurred.

CHAPTER V

EXPERIMENTAL DATA AND RESULTS

1. General Information

In the course of the present investigation ten specimens were studied. These specimens consisted of two iodide-zirconium samples, two alloys of zirconium-0.881 weight per cent silver, a sample of zirconium-5.37 weight per cent silver, a sample of zirconium-7.77 weight per cent titanium, a sample of zirconium-300 ppm hydrogen, and a sample of iodide titanium. Details on the weights of these specimens and their heaters together with information on the successful runs made with each specimen are given in Table VI.

The ratio of the heater weight to the specimen weight is a very important quantity in the determination of the specific heat of the material, for in addition to supplying the heat to raise the temperature of the specimen, the heater must also supply the energy required to heat itself and whatever insulation it is mounted on. If one defines the total specific heat of a specimen and its heater to be C_T , the specific heat of the specimen alone to be C_S and the specific heat of the heater alone to be C_H , and assumes that the temperature of the heater is the same as that of the specimen at all times, then a simple heat balance will yield the relation

$$C_S = C_T + \frac{W_H}{W_S} (C_T - C_H) \quad (17)$$

where W_H/W_S is the ratio of the heater weight to that of the specimen.

TABLE VI

DESCRIPTION OF CALORIMETER SPECIMENS

Specimen	Atomic Per Cent Solute	Mean Atomic Weight	Specimen Weight - Grams	Heater Weight - Grams	Total Weight - Grams	Runs Used
Iodide Zirconium A	0.00	91.22	120.5731	2.4777	123.0508	17,18,24,26,28
Iodide Zirconium B	0.00	91.22	112.3564	3.2612	115.6176	60,62,63,64
Zirconium-0.881 w/o Silver A	0.746 Ag	91.34	122.0947	2.5221	124.6168	13,14,15
Zirconium-0.881 w/o Silver B	0.746 Ag	92.34	118.6492	2.6761	121.3253	50
Zirconium-5.37 w/o Silver	4.58 Ag	92.11	122.6848	2.4728	125.1576	32,33,36,37
Zirconium-7.77 w/o Indium	6.27 In	93.05	122.1519	3.4750	125.6269	54,55,56,58,59
Zirconium-17.5 w/o Niobium	17.24 Nb	91.50	81.6971	3.8345	85.5316	67,68,69,70,77,78
Zirconium-34.4 w/o Titanium	50.00 Ti	69.56	98.1422	3.2193	101.3615	43,45,46,47,48,49,79
Zirconium-0.03 w/o Hydrogen	2.75 H	88.74	109.5424	3.5232	113.0656	71,72,73,74,75
Iodide Titanium	0.00	47.90	82.6217	2.2572	84.8789	38,39,40,41,42

Since a larger fraction of the total weight of the heater is Alundum (Al_2O_3), whose specific heat is approximately 0.27 cal/gram °C, and the specific heat of the metals being studied are in the range of 0.06 - 0.16 cal/gram °C, the difference ($C_S - C_H$) is not a negligible quantity. Thus the smaller is the ratio W_H/W_S , the lower is the heater correction. Actually the temperature of the heater must be much higher than that of the specimen to produce the experimental heating rates so that equation (17) does not apply. By assuming that only radiant heat transfer from the heater to the specimen occurred, and that the heat transferred was independent of temperature, Pawel derived the expression:

$$C_S = C_T + \frac{W_H}{W_S} (C_T - 0.55 C_H) . \quad (18).$$

The heater correction is reduced somewhat in the expression. In the present case the alumina, which was packed around the heater to prevent the deposition of zirconium on the surface of the heater ceramic, probably acted somewhat as an insulation, making the temperature of the heater even higher. Since, however, the alumina also inhibited radiant heat transfer to some extent, the heat transfer process is difficult to describe quantitatively and a simple analytic expression for the correction could not be derived. If the temperature of the heater were higher than when the heat transfer was by a radiant mechanism, the heater correction would probably be smaller than Pawel's estimate. For lack of a better value, Pawel's expression was assumed to apply, and although the relative weights of heater wire and Alundum varied from specimen to specimen, it was assumed that seventy-five

per cent of the weight of the heater was Alundum. This assumption greatly simplified the heater correction calculations and introduced less than 0.25 per cent error in the final specific heat.

The fact that the temperature of the heater is higher than that of the specimen introduces another important consideration. This is that in an adiabatic calorimeter which utilizes an internally heated specimen, heat flows into the specimen, but not out of it. The heat flow can only occur if there is a temperature gradient so that there must be a temperature gradient in the specimen. That this temperature gradient exists makes any heat capacity measurement an average value rather than an absolute one. This is relatively unimportant in the present work since data were taken over twenty or forty degree intervals and an average value was computed. The temperature gradient, however, also causes the inside of the specimen to reach a transformation temperature before the outside. For this reason one would expect a transformation to appear to occur over a range of temperatures even when it would otherwise occur at a single point.

The temperature gradient may be estimated, if one assumes that the specimen consists of an infinite tube of outer radius a and inner radius b . If every point in the specimen is rising in temperature at the same rate, and this rate is constant, the solution to the Fourier conduction equation for adiabatic conditions has been shown by Awberry and Snow (27) to be

$$\theta_b - \theta_a = \frac{bQ}{K(a^2 - b^2)} \left[a^2 \ln \frac{a}{b} - \frac{a^2 - b^2}{2} \right] \quad (19)$$

where Q is the heat input to the specimen per unit area of inner surface, K is the thermal conductivity of the specimen and θ is the temperature at a given radius. The rate of temperature rise n of any point in the specimen is

$$n = \frac{2h^2 bQ}{K (a^2 - b^2)} \quad (20)$$

where $h = K/C\rho$ is the thermal diffusivity of the specimen, $C\rho$ is the specific heat of the specimen, and ρ is the density. If one uses the data of Bing et al (28) for the thermal conductivity of zirconium (0.187 watts/cm deg C at 300°C), measures a (1.1 cm) and b (0.3 cm) and assumes 5 watts are dissipated over a length of 5.3 centimeters, the temperature difference across the sample is calculated to be approximately one degree. The corresponding rate of heating is 41 degrees in five minutes, a value that is close to the observed heating rate for this power input. Since most specimens were run with lower power, one degree represents a maximum temperature gradient. The lower thermal conductivity of the alloys would raise this temperature gradient perhaps to as high as three degrees. For the button-type specimens (Zr-Nb and Zr-Ti), however, the decreased value of the outer radius would result in a smaller temperature gradient.

In the above discussion it was assumed that the heat transfer at the outer surface of the specimen was zero. This would only be true if the shield were ideally adiabatic, a condition that is most difficult if not impossible to obtain except over a very limited temperature range. If there are any temperature gradients along the surface of the tube which serves as a shield, these will result in a heat loss

or gain to the specimen and introduce an error in the measurement of the specific heat. In order to determine how near to the ideal adiabatic condition he is operating at a given temperature one may turn off the specimen power and observe how the temperature of the specimen changes or "drifts" as a function of time. Another way one may determine the adiabaticity is to measure the specific heat of a material at a series of different heating rates and compare the resulting values. Only if the calorimeter is truly adiabatic will the curves superimpose. Otherwise the heat capacity will be higher the slower the heating rate if the specimen is losing heat and lower the slower the heating rate if the specimen is absorbing heat from the surroundings. Pawel (26) showed that two ways of determining the nonadiabaticity were comparable, so that only the easier of the two measurements, the drift rate, need be made to correct for nonadiabatic conditions.

When drift rates are measured in the McElroy calorimeter, a very odd effect is found. If the measurements are made on a given specimen at a given temperature after successive runs, they are quite reproducible.. If, on the other hand, the specimen is removed, and then returned to the calorimeter, one finds that he can no longer duplicate the drift measurement. If the control thermocouples are moved and rewelded, again the drift rates are not reproducible with previously determined values. These observations indicate that the relative adiabaticity of a given specimen in the calorimeter is very strongly dependent on its exact position in the tube and the exact position of each controlling thermocouple. If one is very careful to

insure that the precise position is repeated each time a specimen is replaced in the calorimeter, this effect is lessened. When a drift rate is measured in the calorimeter, one has three choices. The first, a rather impractical one, is to disassemble the calorimeter and redesign it. The second is to offset one or more of the control units to the calorimeter so that the drift will be decreased. The third and usual choice is to allow the shield to be nonadiabatic and then correct the data by measuring the drift rates of the individual specimen at a series of temperatures. Unfortunately it takes an hour or so for the calorimeter to reach its equilibrium drift rate once the specimen power is turned off, so that the measurement of the drift rate is a time consuming task. In the present work the upper guard heater was offset to reduce the drift so that a smaller correction would be needed, but otherwise method three was utilized.

During the course of the investigation certain accidents such as breaking of thermocouple welds caused the adiabaticity in the calorimeter to change, so that different drift rates were found for different sets of runs. These drift rates even went from large positive values to large negative ones. The drift rates which were used to correct the data are shown in Figure 6.

The drift rate correction is found by a simple heat balance to be

$$C_{pT} = \frac{C_{pA}}{1 - \frac{\Delta t}{\Delta T} \frac{R(T)}{3600}} \quad (21)$$

where C_{pA} is the apparent total specific heat $(EI\Delta t'f / (m_s + m_H) \Delta T)$,

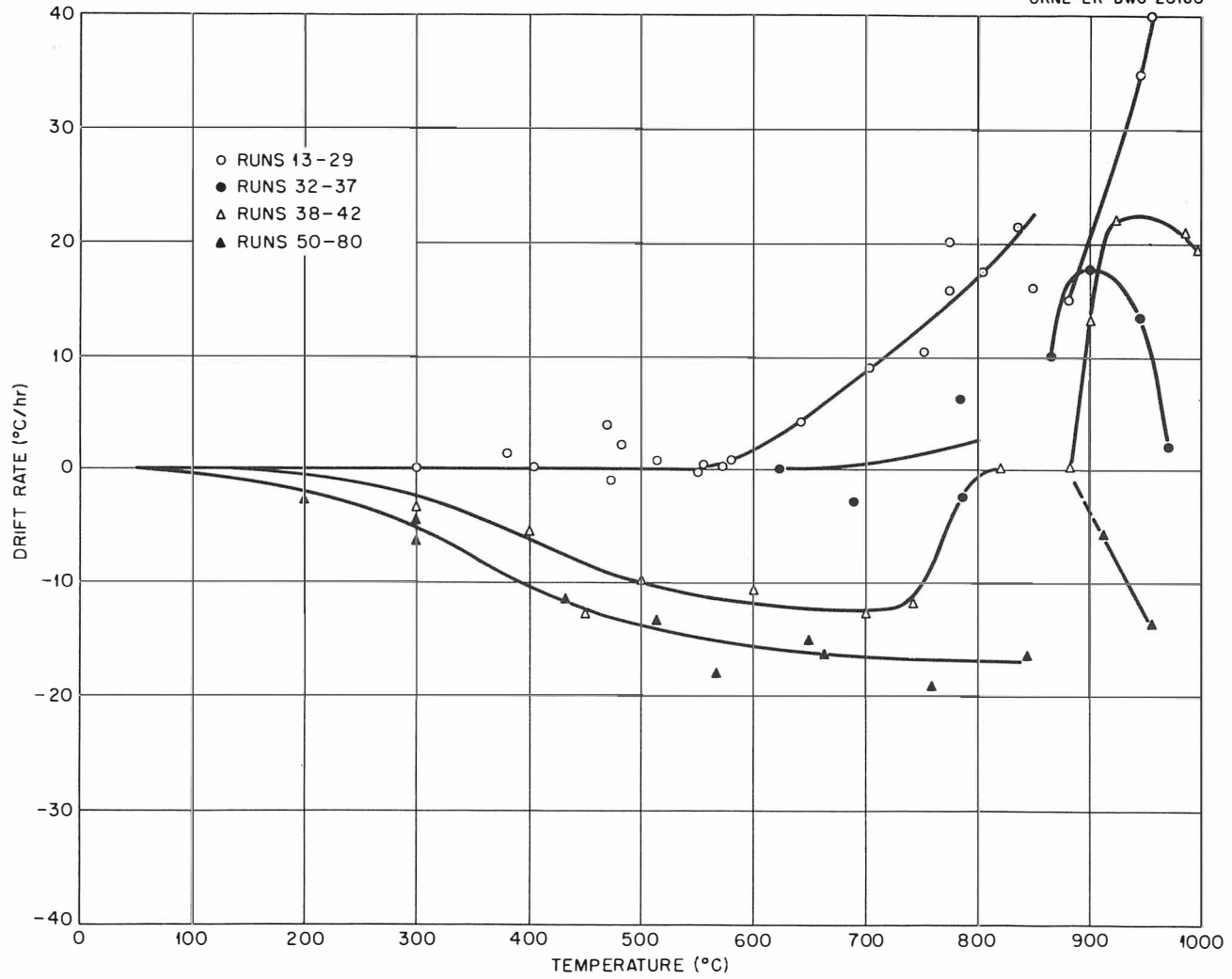


Figure 6. Values of the measured drift rates.

C_{p_T} is the total corrected specific heat (specimen plus heater), $\Delta t/\Delta T$ is the reciprocal of the heating rate sec/deg., and $R(T)$ is the drift rate with no power input, deg./hr. The S and H refer to the specimen and heater, respectively. The actual correction factor is the dimensionless term $\frac{\Delta t}{\Delta T} \frac{R(T)}{3600}$ which will subsequently be called ϵ . This correction is smaller—the greater one makes the reciprocal heating rate $\Delta t/\Delta T$, so that for a minimal correction one would use a large power input to the specimen. Sample calculations illustrating the drift and heater corrections are given in Table VIII of the Appendix.

Such a large power input, while decreasing ϵ , has inherent disadvantages. The first is that the specimen is always further from equilibrium at high heating rates. For if a transformation occurs, it would tend to occur at a higher temperature at a higher heating rate. A second disadvantage is the increased difficulty in attaining precision control on the adiabatic shield. Since the temperature of the specimen is changing more rapidly at the high heating rates, it becomes more difficult for the control system to respond and maintain control to within 0.01°C . When the specimen temperature levels out due to a transformation, there is a much greater tendency for the control system to overshoot. This requires that at high temperatures the operator must anticipate a transformation and assist the control system by reducing the power to the shield windings when a transformation occurs. In an analogous fashion the operator must sense the end of a transformation and increase the power as the specimen begins a more rapid temperature increase. One must balance the opposing desires for a low

ϵ and high precision control by selecting an optimum range of power input levels for each specimen.

In the plot of the drift rate as a function of temperature it may be observed that the data are given in terms of a set of runs and not in terms of data on each specimen. It is possible to correlate drift data for different specimens, if they are carefully placed in exactly the same depth in the calorimeter and if it is assumed that the function $MCpR(T)$ is a constant. For specimens with different outer diameters the function which is constant is $\frac{M C_p R(T)}{A}$, where A is the external surface area of the specimen.

The use of the drift rate correction is very restricted in the temperature range where a transformation occurs, because the drift is immeasurably small during a transformation. In order to correct the measured enthalpy data taken during a transformation, one must rely on some type of extrapolation from the drift in the all-alpha or all-beta regions. In this work the corrections on the transformation data were made by assuming that ϵ varied linearly over the range of transformation temperatures. The value of the enthalpy over a given temperature range in a region of transformation is computed from the equation

$$\Delta H = \frac{\Delta H \text{ measured}}{1 - \bar{\epsilon}} \quad (22)$$

where $\bar{\epsilon}$ is the average value of ϵ over the temperature range associated with ΔH . The heats of transformation are then determined graphically by measuring the height of the discontinuous jump in ΔH . The use of the assumption of linearity of ϵ causes no greater scatter in the heat

of transformation data than one finds in the specific heat data where $R(T)$ is known.

The fact that there is scatter in the specific heat data amounting to two per cent at low temperatures and three to five per cent at high temperatures indicates that the heat loss is a function of the heating rate as well as the time interval. A method of measuring the effect of the heating rate on the nonadiabaticity has not yet been developed. The scatter that is produced in the data is much higher than one would expect from errors in reading Δt , ΔT , E or I as discussed by Pawel. Thus the scatter appears to be due to loss of precise control at high temperatures and spurious emfs resulting from contaminated thermocouple protection tubes. As a specimen was rerun more and more, the ability to maintain precise control became progressively more difficult. Another effect of the progressive contamination was the loss of precision at low temperatures. Thus if the calorimeter had never been operated above 600°C a precision of about 0.5 per cent could be expected from the results of Pawel. After a few runs to 900 degrees with zirconium alloys the precision at low temperatures was decreased to about 2 per cent. Since the characteristics of the calorimeter change completely when the thermocouples are replaced, and the calibration runs would serve to contaminate the system, one is forced to accept the lowered precision until some type of specimen shielding to prevent its seeing the control thermocouples can be devised. Although the absolute errors are difficult to estimate, it is believed that the absolute accuracy is within the 2-5 per cent spread of the calculated values.

2. Iodide Zirconium

The corrected values of the specific heat of iodide zirconium for nine successful runs are shown in Figure 7. The data are also given in tabular form in Table IX of the Appendix. Included in the data are runs with high and low heating rates for runs with both high positive drift rates (Runs 17, 18, 24, 26, 28) and high negative ones (60, 62, 63, 64); thus any consistent errors in the first set would be expected to be opposite to those of the latter. Although even in the alpha region the spread in the data is high, several runs agreed within one per cent in the alpha region. The curve which is believed to be the best value was the set of mean points between these closely agreeing curves.

In the beta region the spread of the data is such that it is difficult to assign a best value with any confidence. For this reason an approximate mean value was adopted. Although the specific heat seems to increase with increasing temperature in the beta region, a constant value was assumed to apply for the specific heat over the range studied. That this value should be constant is indicated by the results on the zirconium - 17.5 weight per cent niobium alloy discussed in Section V. In any case, the specific heat of the beta phase is considerably lower than that of the alpha at the transformation temperature. This result agrees with the findings of Coughlin and King (6) and Skinner (5) as shown in Figure 2.

Although the specific heat values for alpha zirconium are somewhat lower than those reported by the previous investigations, they do

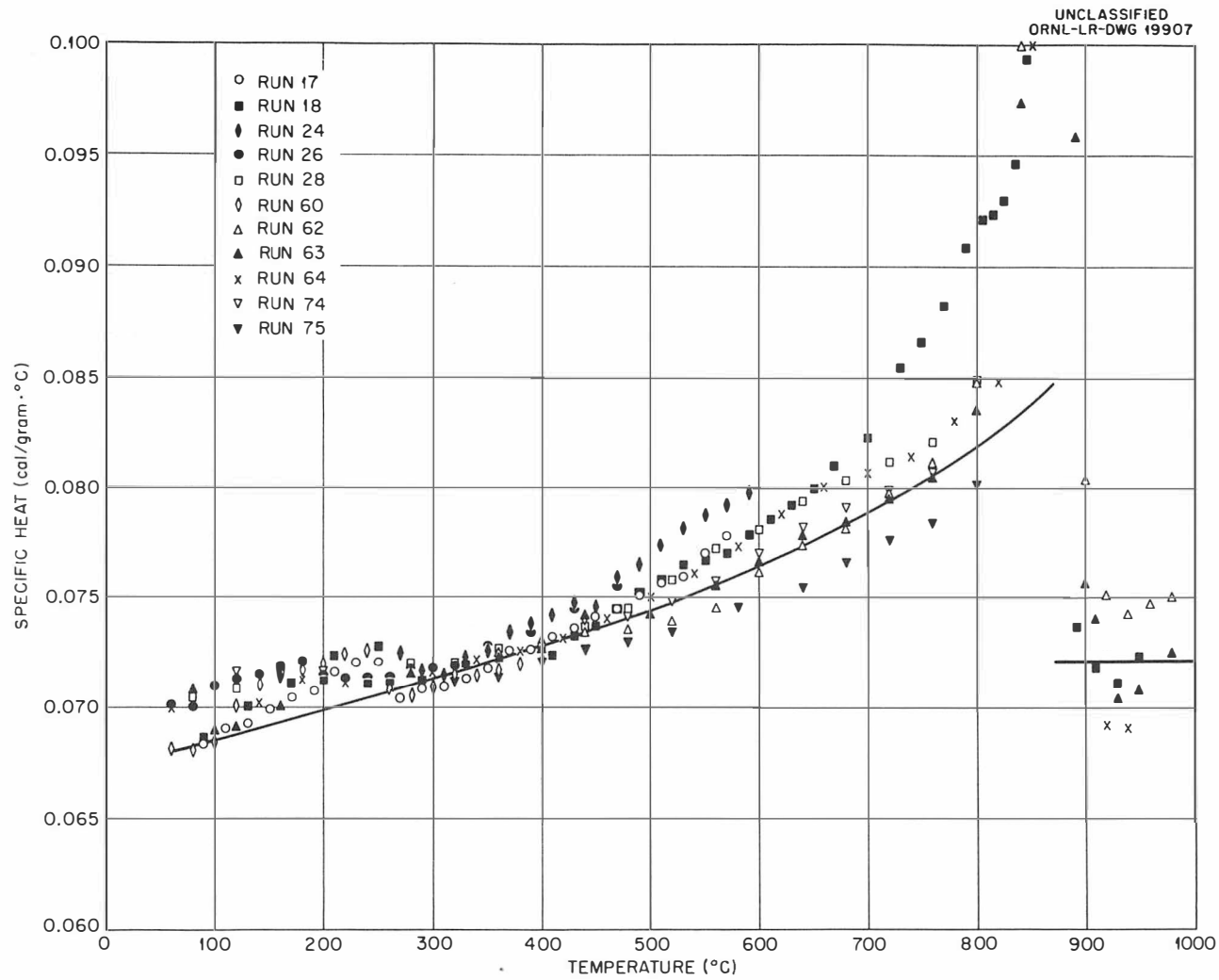


Figure 7. The measured values of the specific heat of zirconium.

indicate an abnormal rise in the specific heat with increasing temperature as previously reported.

The peak in the alpha specific heat curve in the neighborhood of 240°C will be shown to be due to the solution of zirconium hydride in the alpha zirconium in Section VII.

The plot of the measured enthalpies of zirconium above 800°C is shown in Figure 8. These data are also given in Table XVII of the Appendix. For comparison the enthalpy values of zirconium-silver alloys, a zirconium-indium alloy, and titanium are included in the same figure. The zirconium data indicate that the transformation of iodide zirconium is $870 \pm 2^\circ\text{C}$ and that the heat of transformation of zirconium is 993 ± 25 calories per gram atom. This value is compared to previously reported results in Table III.

It should be noted that there is an abnormal rise in the enthalpy curve for zirconium above 850°C. This rise is believed to be due to the iron contamination of approximately 150 parts per million. Betterton (13) showed that the purest obtainable iodide zirconium has two phases in this range of temperatures.

13. Zirconium-Silver Alloys

The zirconium-silver phase diagram has been thoroughly studied by Betterton and co-workers (14). The resulting diagram, which is shown in Figure 9, shows that silver lowers the temperature at which the beta phase is stable to 821°C, the eutectoid composition being 3.76 atomic

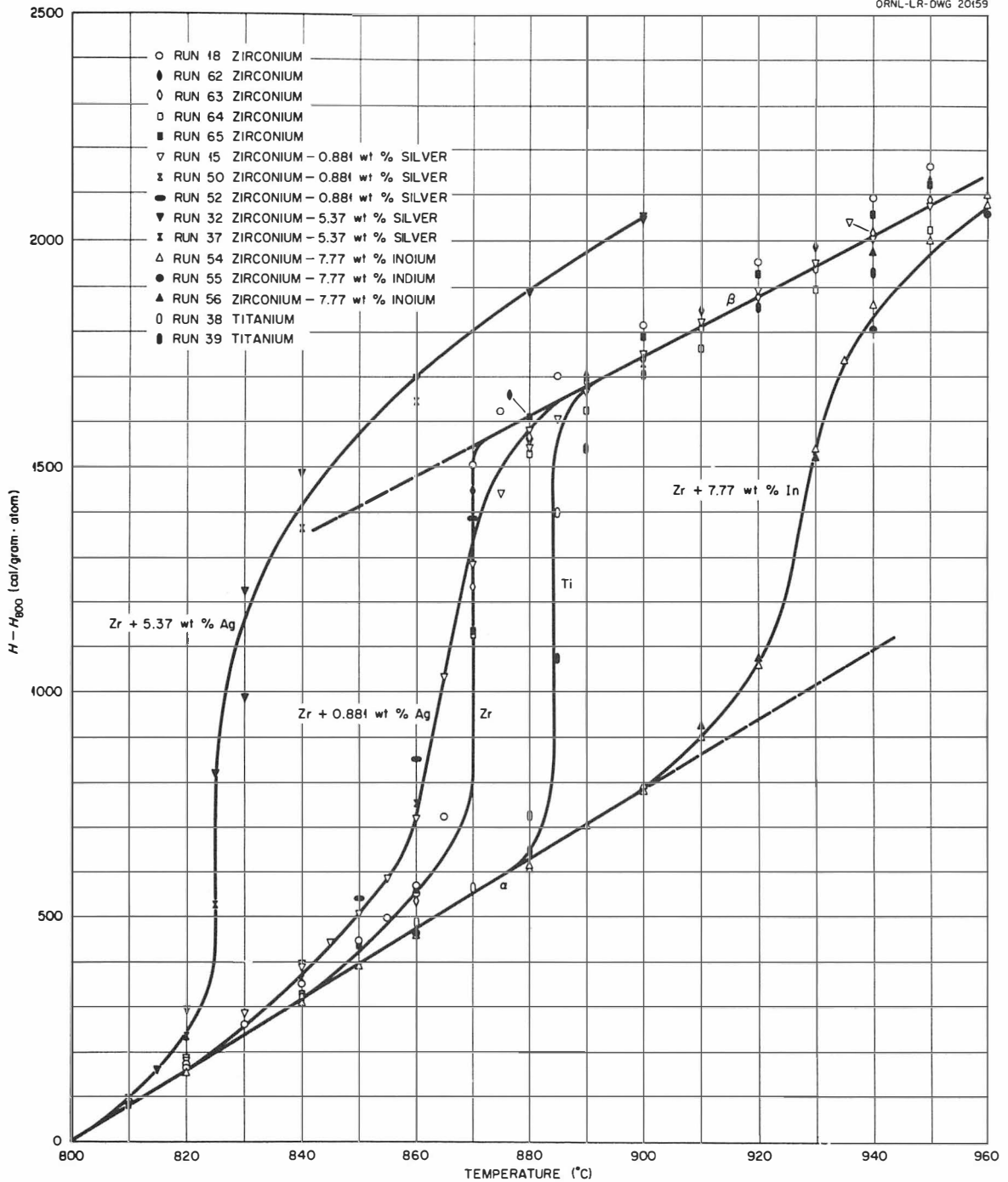


Figure 8. The measured values of the transformation enthalpies of zirconium, titanium, and alloys of zirconium with silver and indium.

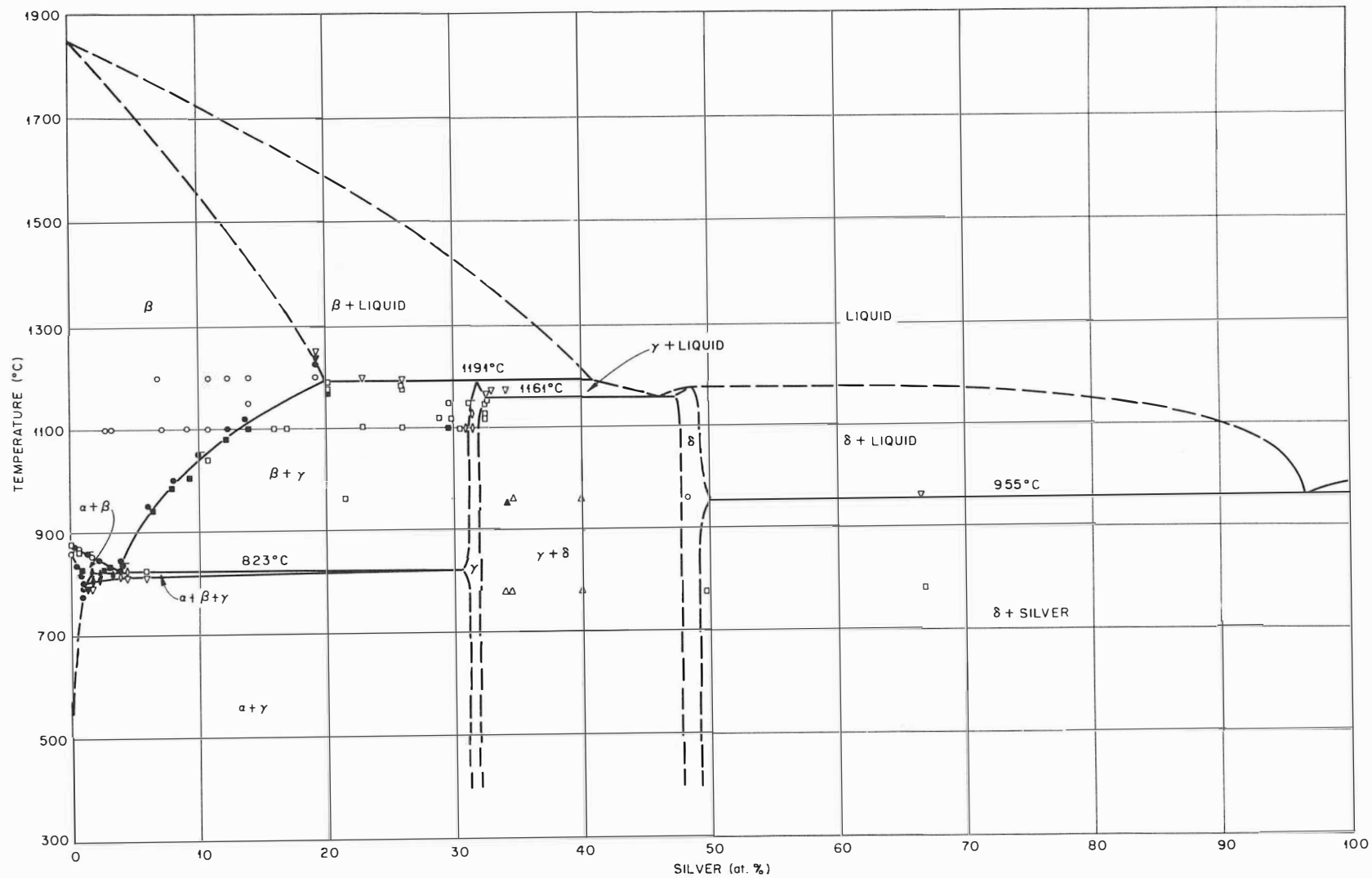


Figure 9. The silver-zirconium phase diagram.

per cent silver. The maximum solubility of silver in the alpha phase is 1.10 atomic per cent. Two intermetallic compounds are formed in this system, Zr_2Ag and $ZrAg$.

In order to determine the thermodynamic characteristics of the eutectoid decomposition, two alloys of silver and zirconium were studied, an alloy in the alpha solid solution range containing 0.748 atomic per cent silver and a hypereutectoid alloy containing 4.58 atomic per cent silver. More difficulty was experienced in maintaining control with the silver alloys than with zirconium, because of the high volatility of silver even in the dilute solutions.

The specific heat data for the zirconium - 0.746 atomic per cent silver alloy is shown in Figure 10. The data are also tabulated in Table X of the Appendix. The data indicate that the specific heat of the alpha-solid solution is about two per cent higher than the specific heat of the alpha phase in pure zirconium, the difference increasing at the higher temperatures. The data also indicate that there is only a small solution heat effect from the solution of Zr_2Ag in alpha zirconium. The scatter in the data is such that it is impossible to tell if the slightly high specific heats in run 14 and 15 in the neighborhood of 700°C are due to impurity effects or experimental errors. That the measured heat of solution should be small is in agreement with the data of Betterton which show that the change in the terminal solubility of silver in alpha with decreasing temperature is small. No explanation can be given for the higher specific heat at low temperatures found in Run 50, but the effect is probably due to hydrogen. The peak at 160°C

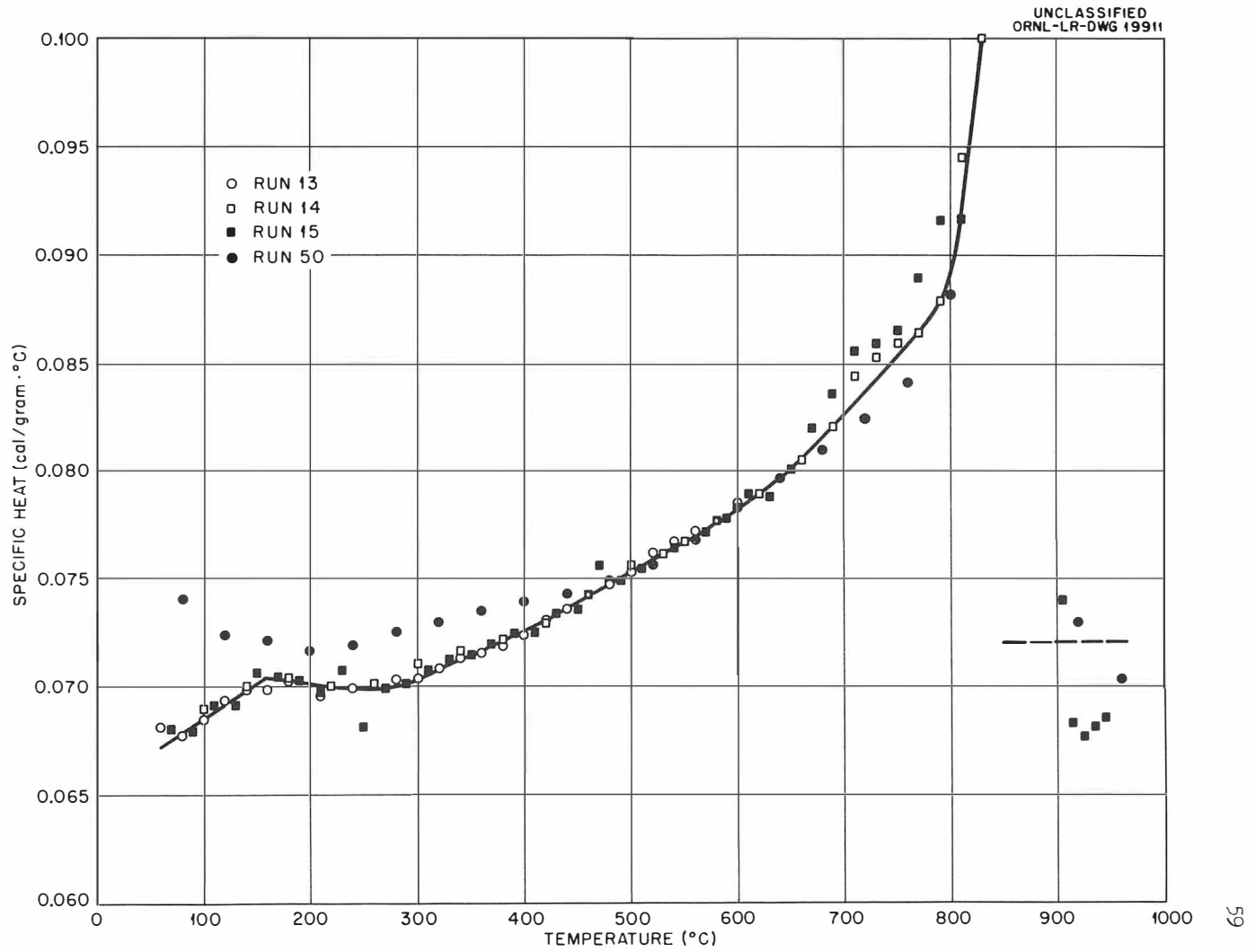


Figure 10. The measured specific heat values for a zirconium - 0.746 atomic per cent silver alloy.

is definitely due to hydrogen. The sharp drop in the specific heat values in the first few measurements of Run 50 is due to the fact that a higher rate of heating was used in Run 50 than in Runs 13, 14, and 15. This drop in the first few specific heat values for the higher heating rates was observed in several of the runs.

The specific heat data for the 4.58 atomic per cent silver alloy are shown in Figure 11 and are given in Table XI. In the alpha range these data are about four per cent higher than the specific heat values for the 0.746 atomic per cent silver alloy. Such a behavior would be expected since the specific heat of the intermetallic compound Zr_2Ag would be expected to be high. Due to the uncertainties of the measured curves, it was not believed to be worthwhile to calculate the specific heat of the compound on the basis of this information.

There is a rather rapid rise in the specific heat of the zirconium - 4.58 atomic per cent silver alloy above $600^{\circ}C$. This rise is believed to be due to an increased solubility of zirconium in the compound Zr_2Ag with increasing temperature, since the change in the alpha solubility was found to be small. The total heat of solution was found to be approximately 100 calories per mole by extrapolating the specific heat data of the alloy to $825^{\circ}C$, subtracting the specific heat of pure zirconium, and integrating from 600 to $825^{\circ}C$. Such a calculation is only an approximation since it is not known how much heat due to this reaction is included in the heat of transformation. Within the limits of error the specific heat of the beta phase was unchanged by the addition of silver.

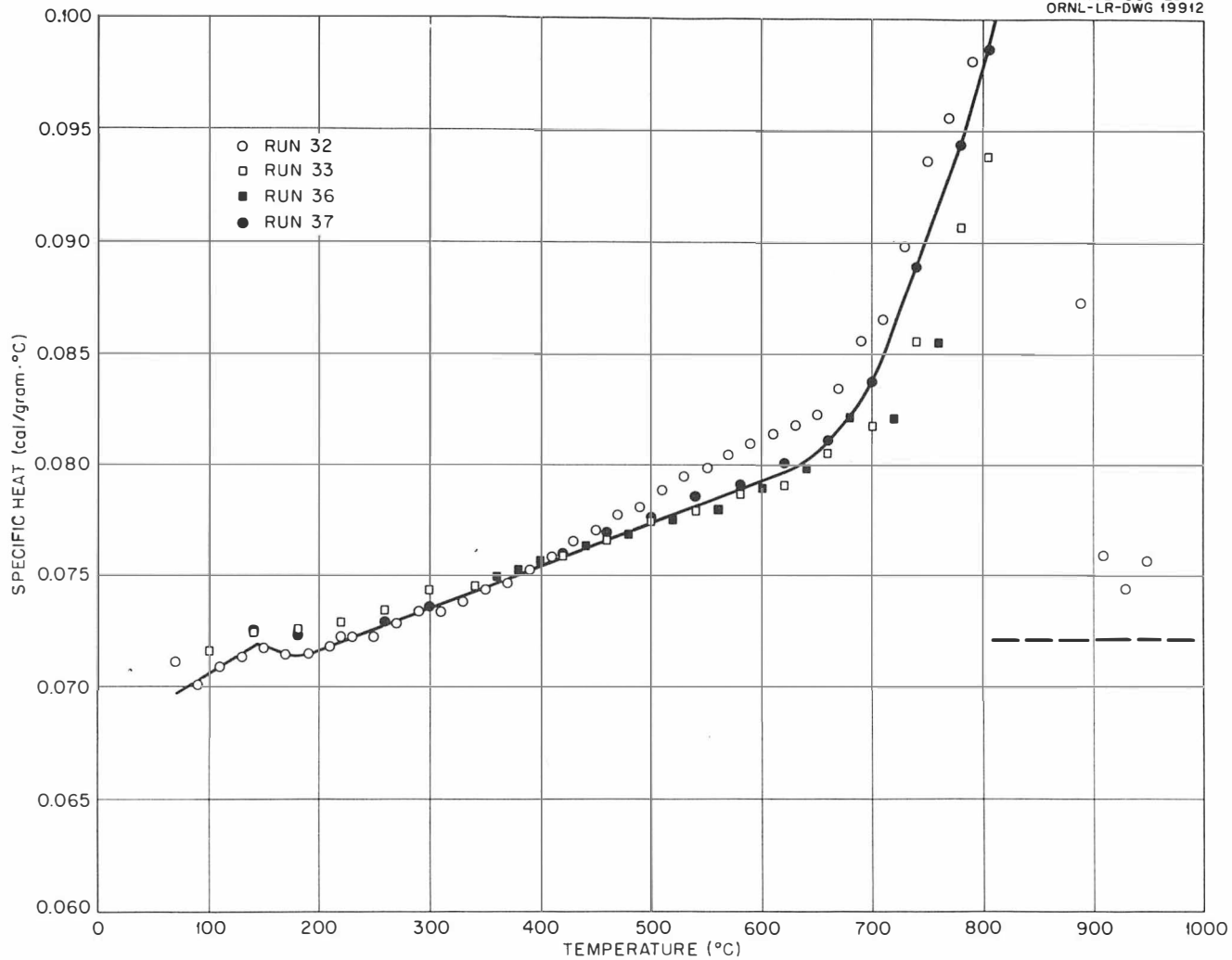


Figure 11. The measured specific heat values for a zirconium - 4.58 atomic per cent silver alloy.

The heats of transformation and temperatures of transformation for the 0.746 atomic per cent silver alloy were determined from the enthalpy-temperature plot shown previously (Figure 8). These enthalpy data are also tabulated in Table XVIII of the Appendix. The temperature of the start of the alpha-beta transition in the zirconium - 0.746 atomic per cent silver was found to be about 830°C in agreement with the work of Betterton. The completion of the transformation, disregarding hysteresis effects, would be 870° for the alloy studied. This is about five degrees higher than the temperature reported by Betterton. This increase in the transformation temperature would be expected if the oxygen content were high. Since the alloy was melted in a consumable-electrode arc furnace whereas the pure zirconium was not remelted, more oxygen would be expected to be found in the alloy. The chemical analyses did not show any significant pickup of oxygen on melting, but such an analysis is not only difficult, but also relatively inaccurate.

The enthalpy data for the zirconium - 4.58 atomic per cent silver alloy which are shown in Figure 8 and tabulated in Table XIX of the Appendix indicate that the eutectoid temperature is 825°C, and that both the heat of solution of some phase in the three phase region and the heat of solution of Zr_2Ag in beta significantly affect the enthalpy of the alloy and broaden the apparent transformation range.

By extrapolating the alpha and beta specific heats and measuring graphically the enthalpy change during the transformation at an arbitrary intermediate temperature, the heat of transformation of the zirconium - 0.746 atomic per cent silver alloy was found to be

995 \pm 25 calories per gram atom at 865°C. This heat of transformation is the same as that for zirconium at the same temperature. The heat of transformation of the zirconium - 4.58 atomic per cent silver alloy was found to be 1360 \pm 25 calories per gram atom at 825°C. This is 310 calories per mole higher than the heat of transformation of zirconium at the same temperature. The heat of transformation of the eutectoid (3.73 atomic per cent silver) may be estimated by subtracting out the contribution of the reaction; excess Zr_2Ag above 3.73 atomic per cent silver goes into solution in the beta. Betterton (14) has reported the heat of solution of Zr_2Ag in beta to be 14,400 calories per gram atom of silver. The excess silver for the alloy studied is 0.0085 gram atoms per gram atom of alloy. The heat of solution of the amount of silver would be 120 calories per mole. The heat of transformation of the eutectoid, then, is 1240 \pm 25 calories per gram atom.

Zirconium-Indium Alloys

Indium has an opposite effect on the alpha-beta transformation to that of silver. This has been shown by Betterton (15) who developed the phase diagram presented in Figure 12. This diagram shows that indium raises the maximum temperature of alpha stability to a temperature of 995°C, the peritectoid composition being 10 atomic per cent indium. The gamma phase is an intermetallic compound with the approximate composition Zr_3In .

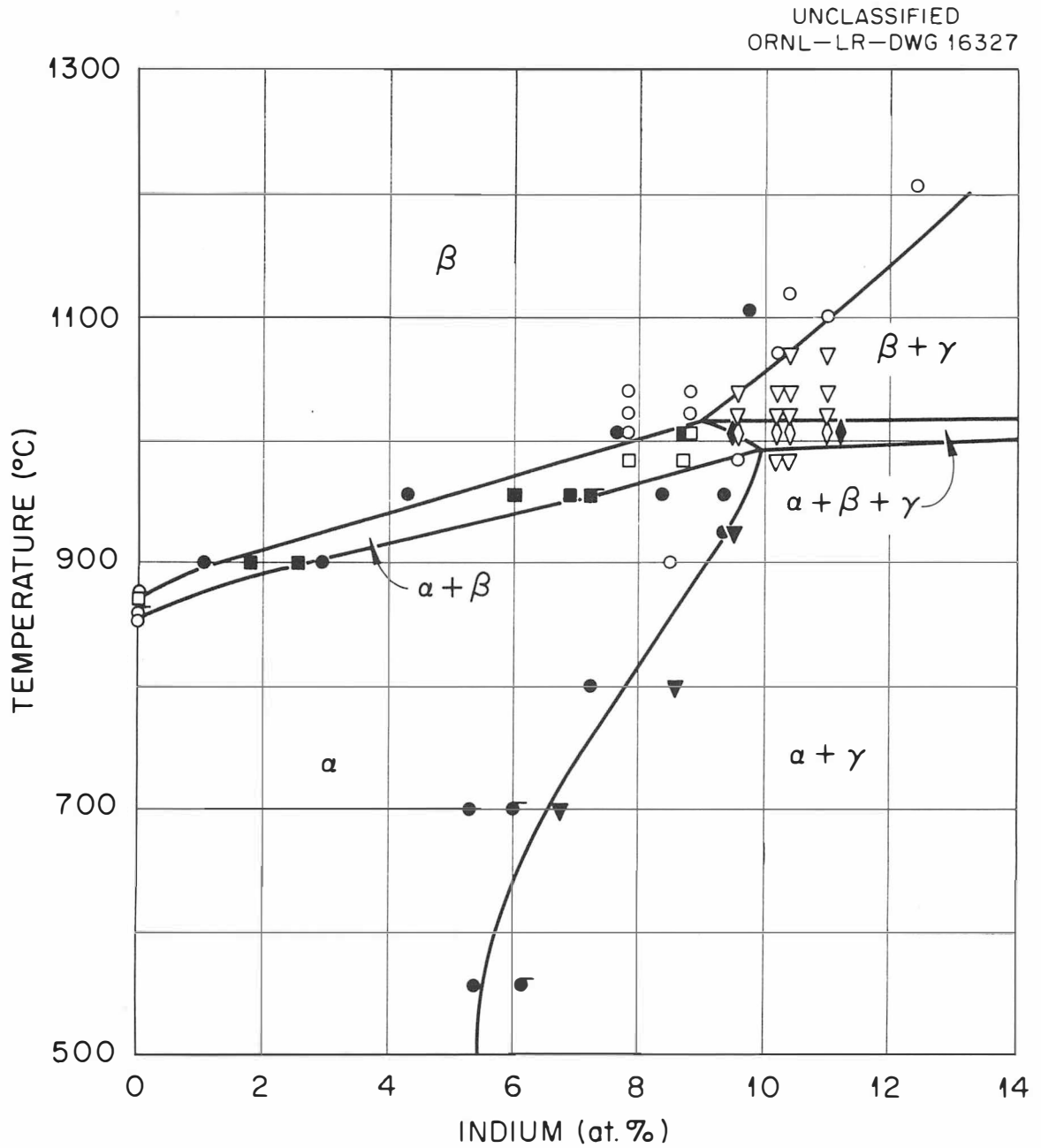


Figure 12. The indium-zirconium phase diagram to 14 atomic per cent indium.

The specific heat curves of an alloy containing 6.27 atomic per cent indium are shown in Figure 13. The data, which are also given in Table XII, show that within the limits of experimental accuracy the specific heat of this indium alloy is the same as that of pure zirconium. Two chemical effects due to the solution of the gamma phase were found. This alloy is so near to the saturation limit of indium in the alpha phase, that no effect from the solution of Zr_3In would be expected.

The data on the enthalpy of transformation are shown in Figure 8 and are tabulated in Table XX of the Appendix. These data indicate that the alpha to beta transition starts at 915° and is complete at about $960^\circ C$. This is a wider spread than Betterton has shown, and also is at a somewhat lower temperature for the given composition. The increased spread is probably due to oxygen absorbed during the casting operation. The iron content may also be affecting a shift in the reaction temperature.

The heat of transformation of the zirconium - 6.27 indium alloy was found to be 930 ± 25 calories per gram atom at $930^\circ C$ by the same method used previously for silver alloys. This is the same value that the heat of transformation of pure zirconium would have if it transformed at the same temperature within experimental error.

The fact that the heats of transformation of solid-solution alloys of silver and indium in zirconium are the same as the values zirconium would have if it transformed at the same temperatures places certain restrictions on the thermodynamic properties. This may be shown by equating the free energy change, $\Delta F_{T_c}^0$, for the transformation of pure

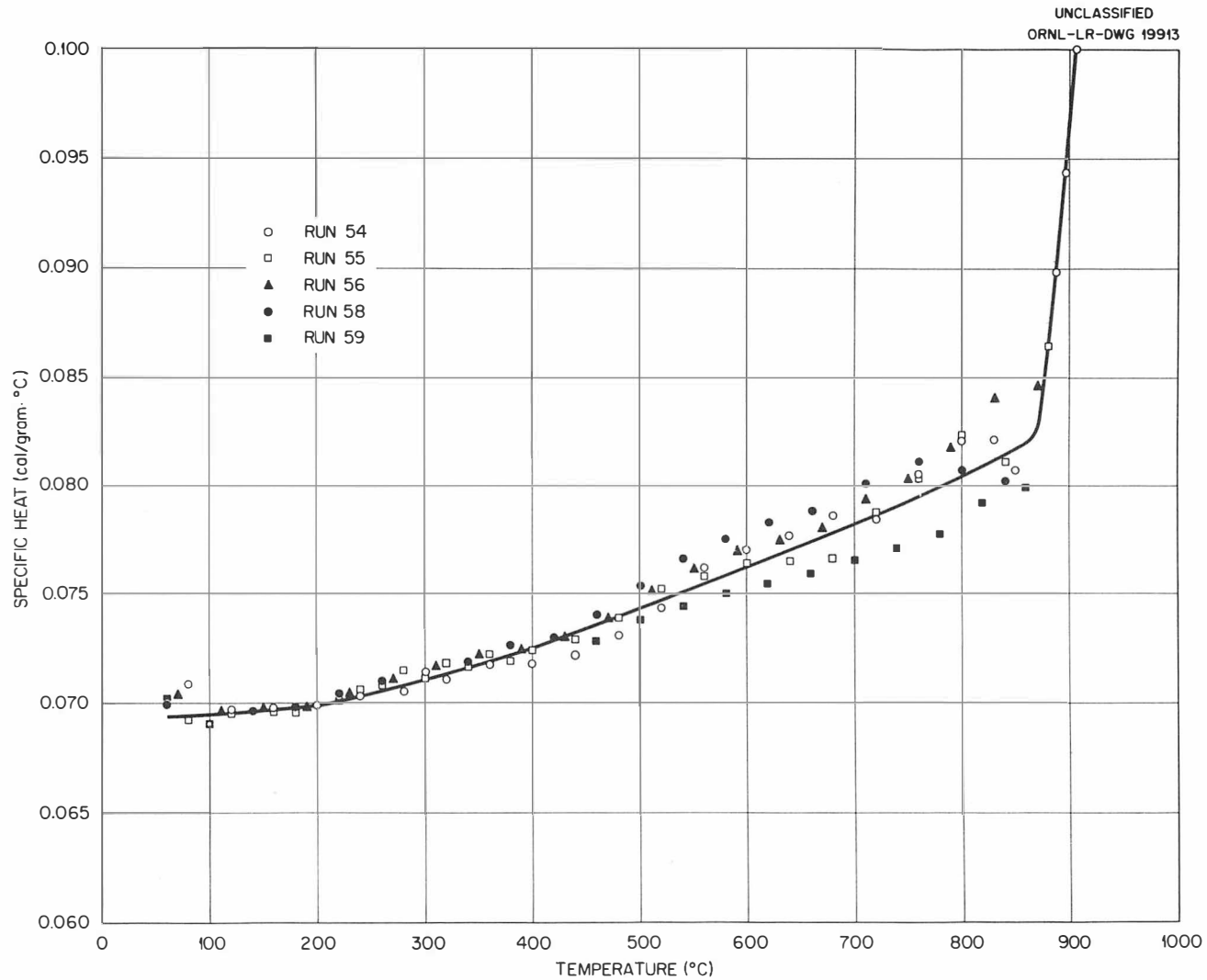


Figure 13. The measured specific heat values for a zirconium-6.27 atomic per cent indium alloy.

alpha zirconium to pure beta at the equilibrium transformation temperature, T_c , with the free energy change, ΔF_T^x , for the hypothetical reaction alpha of composition x to beta of the same composition for a binary alloy of zirconium at a temperature T in the alpha plus beta region. If x is the composition of an alloy for which the enthalpy change has been measured, T will be taken to be the temperature at which $F_\alpha = F_\beta$ for this composition. It will also be assumed that

$$\Delta H_o = \Delta H_o^o + \Delta H_o^x \quad (23)$$

and

$$\Delta C = \Delta C^o + \Delta C^x. \quad (24)$$

In these equations ΔH_o^o and ΔC^o refer to the enthalpy difference at absolute zero, $H_{o\beta}^o - H_{o\alpha}^o$, and the difference in the specific heats, $C_\beta^o - C_\alpha^o$, for pure zirconium. ΔH_o^x and ΔC^x are the enthalpy differences due to alloying at absolute zero and the specific heat differences due to alloying in the sense beta minus alpha for the alloy of composition x . Hence, ΔH_o and ΔC are the total enthalpy at absolute zero and specific heat differences between the beta and alpha phases of the alloy.

From equations (1) and (2),

$$\Delta F_T^x = \Delta H_o^o + \Delta H_o^x - \int_0^T dT \int_0^T (\Delta C^o + \Delta C^x) d \ln T = 0. \quad (25)$$

Likewise for the pure zirconium at the transformation temperature,

$$\Delta F_{T_c}^o = \Delta H_o^o - \int_0^{T_c} dT \int_0^T \Delta C^o d \ln T = 0. \quad (26)$$

If equation 26 is subtracted from equation 25, the result is

$$\Delta H_{\text{O}}^{\text{X}} + \int_{\text{T}_c}^{\text{T}} \Delta C^{\text{O}} dT - (T - \text{T}_c) \int_{\text{O}}^{\text{T}_c} \Delta C^{\text{O}} d \ln T - T \int_{\text{T}_c}^{\text{T}} \Delta C^{\text{O}} d \ln T + \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} dT - T \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} d \ln T = 0 \quad (27)$$

Since the enthalpy for the transformation of the pure zirconium, λ_c , is equal to $\Delta S^{\text{O}} \cdot \text{T}_c$, where ΔS^{O} is the entropy change associated with the transformation and

$$\Delta S^{\text{O}} = \int_{\text{O}}^{\text{T}_c} \Delta C^{\text{O}} d \ln T,$$

certain simplifications of equation 27 may be made. If it is further observed that $\Delta C^{\text{O}} \approx -1$ for zirconium in the neighborhood of T_c and

$\ln \frac{\text{T}}{\text{T}_c} \approx \frac{\text{T}}{\text{T}_c} - 1$, equation 27 may be written as follows:

$$\Delta H_{\text{O}}^{\text{X}} - (T - \text{T}_c) - \frac{(T - \text{T}_c)}{\text{T}_c} \lambda_c + \frac{(T - \text{T}_c)}{\text{T}_c} T + \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} dT - T \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} d \ln T \approx 0 \quad (28)$$

Since $\lambda_c \approx T$ for zirconium in the neighborhood of T_c ,

$$\Delta H_{\text{O}}^{\text{X}} + \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} dT - T \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} d \ln T \approx T - \text{T}_c \quad (29)$$

Next consider the enthalpy difference $\Delta H_{\text{T}}^{\text{X}}$ at temperature T and composition x , which can be measured. This quantity may be written

$$\Delta H_{\text{T}}^{\text{X}} = \Delta H_{\text{O}}^{\text{O}} + \int_{\text{O}}^{\text{T}_c} \Delta C^{\text{O}} dT + \int_{\text{T}_c}^{\text{T}} \Delta C^{\text{O}} dT + \Delta H_{\text{O}}^{\text{X}} + \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} dT, \quad (30)$$

or

$$\Delta H_{\text{T}}^{\text{X}} = \lambda_c + \int_{\text{T}_c}^{\text{T}} \Delta C^{\text{O}} dT + \Delta H_{\text{O}}^{\text{X}} + \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} dT \quad (31)$$

The experimental data indicate

$$\Delta H_{\text{T}}^{\text{X}} = \lambda_c + \int_{\text{T}_c}^{\text{T}} \Delta C^{\text{O}} dT \pm 25 \text{ cal/g atom}, \quad (32)$$

so that

$$\Delta H_{\text{O}}^{\text{X}} + \int_{\text{O}}^{\text{T}} \Delta C^{\text{X}} dT = \pm 25 \text{ cal/g atom} \quad (33)$$

Substitution of equation 33 into equation 29 yields the result

$$\int_0^T \Delta C^x d \ln T = - \frac{T - T_c}{T} \pm 25 \text{ cal/g atom.} \quad (34)$$

If in equation 32,

$$\Delta H_T^x = \lambda_c + \int_{T_c}^T \Delta C^o dT,$$

equation 34 shows that ΔC^x could not be zero at all temperatures, but the scatter of the data is such that one cannot separate the effects of ΔC^x and ΔH_o^x . In any event equation 34 indicates that ΔC^x is quite small. If this is the case equation 29 indicates that ΔH_o^x is also quite small. It is doubtful that an adiabatic calorimeter with the precision to separate these terms could ever be developed except for systems where very anomalous results are found.

5. Zirconium-Hydrogen Alloys

In the study of the specific heat of pure zirconium an anomalous, but reproducible, peak always appeared in the first runs made on a given specimen. As the specimen was recycled to high temperatures in the high vacuum maintained within the calorimeter, the magnitude of this peak decreased. Because of this decrease in effect after vacuum annealing, it was suspected that the peak was due to hydrogen. To prove the validity of this supposition a specimen of iodide zirconium was purposely heated in an atmosphere of rarified hydrogen. The pressure of hydrogen was adjusted so that the equilibrium content of hydrogen in the zirconium would be 250 ppm at the temperature of the

absorption. The equilibrium-pressure-temperature data of Gulbransen and Andrew (29) was used to select the proper pressure. The resulting specific heat curve of the hydrogenated zirconium, together with low temperature data on the iodide zirconium runs are presented in Figure 14 and in Table XIII of the Appendix. The data show that a decided peak in the specific heat curve of zirconium is produced by the addition of hydrogen.

The peak is undoubtedly due to the solution of the hydride ZrH_2 in alpha phase as the temperature increased. When all the hydrogen from the hydride had gone into solution, the specific heat of the zirconium-hydrogen alloy was identical to that of pure zirconium. A study of the specific heat curve under different heating rates showed that within the available range of heating rates the curve is independent of the heating rate. This would imply that the rate of reaction is quite high.

The phase diagram for the hydrogen-zirconium system has been studied by Edwards, Levesque, and Cubicciotti (30), Vaughan and Bridge (31), Schwartz and Mallett (33), Gulbransen and Andrew (29) and Ells and McQuillan (33). The constitutional diagram determined by these investigators is shown in Figure 15. A better description of the alpha-terminal solubility is given in Figure 16 which shows the logarithm of the terminal solubility in atomic per cent as a function of the reciprocal of the absolute temperature.

If one assumes that equilibrium was essentially maintained in the hydrogen-zirconium system under the conditions of operation of the calorimeter, a correlation between the terminal-solubility curve and

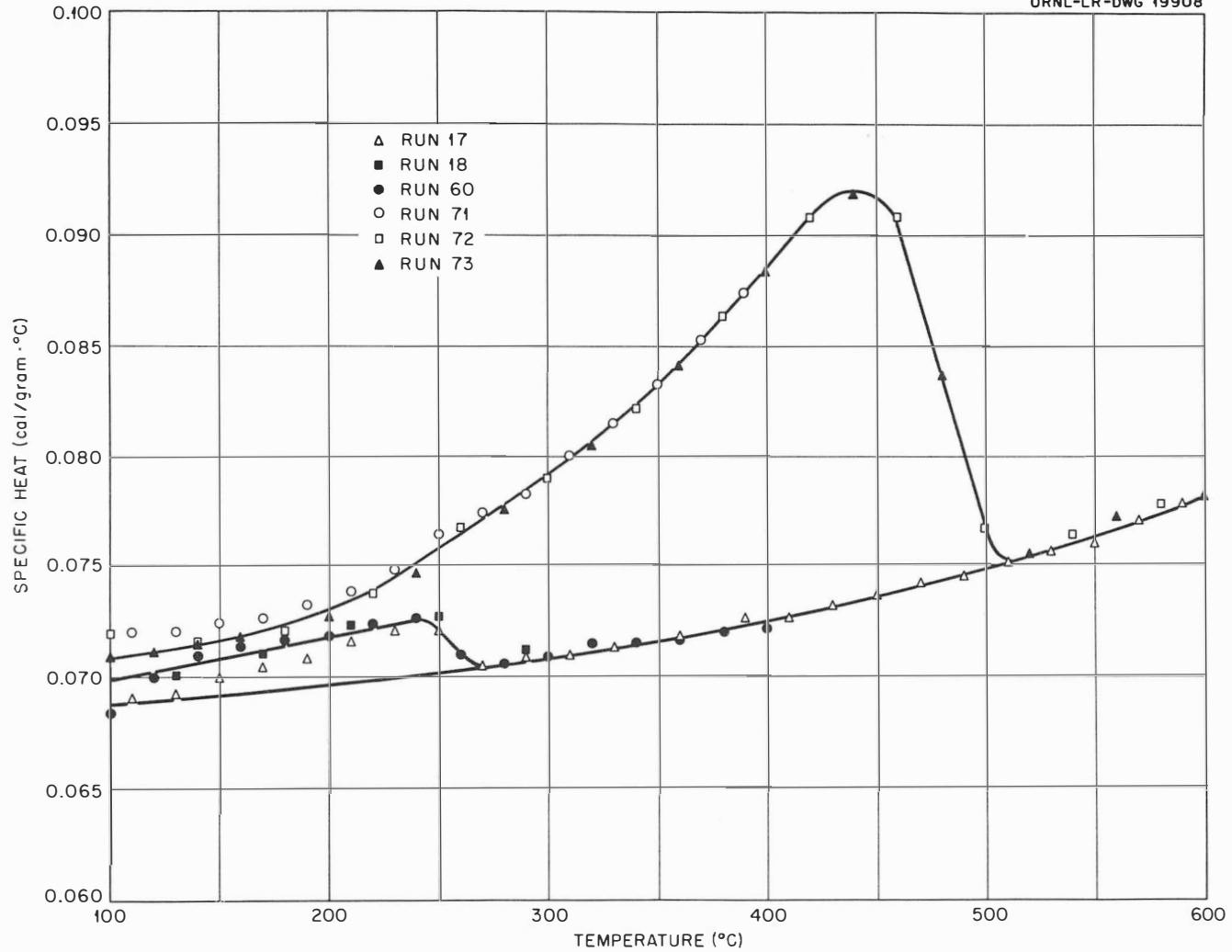


Figure 14. The measured specific heat values for alloys of zirconium with 0.26 and 2.75 atomic per cent hydrogen.

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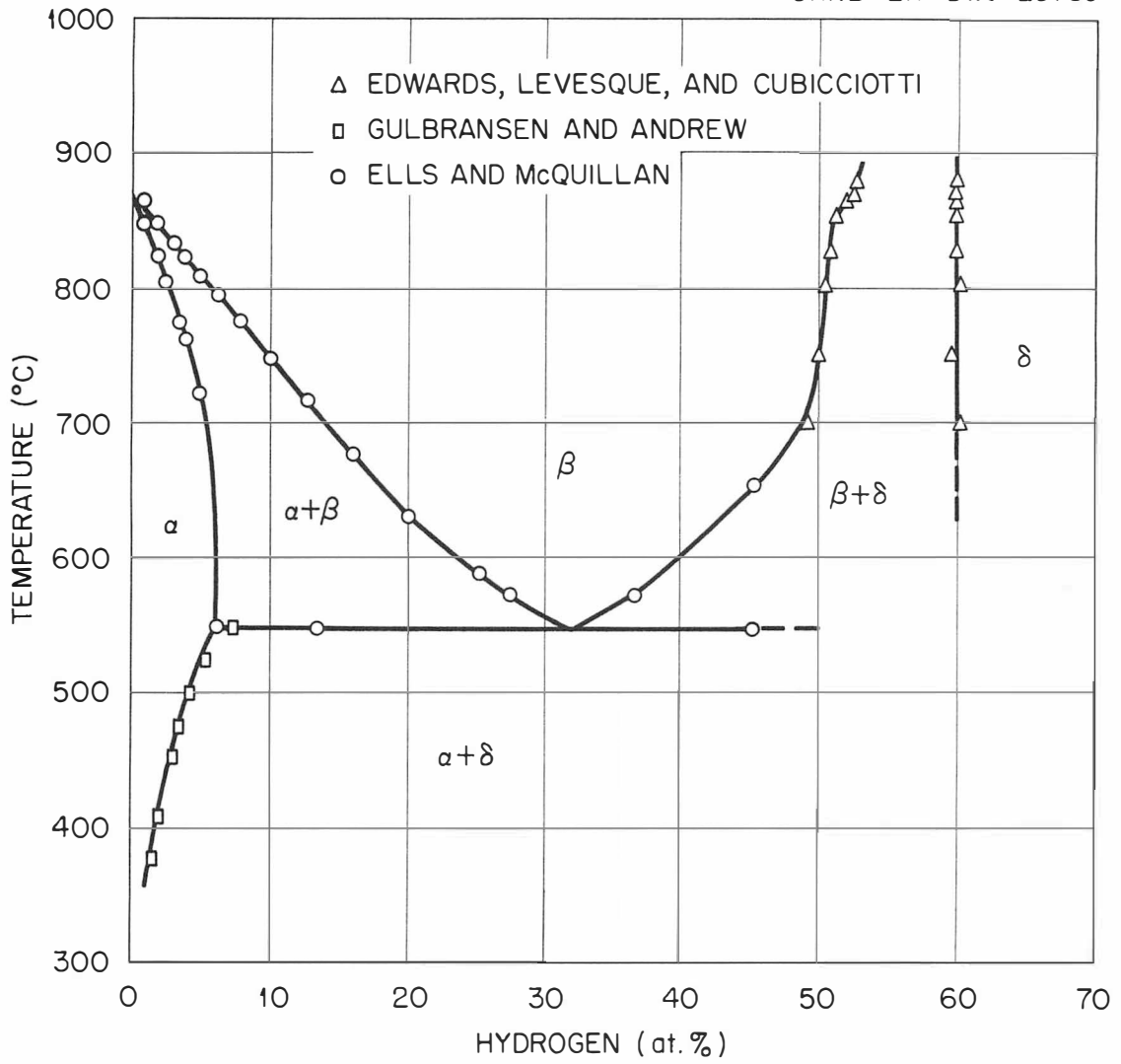


Figure 15. The hydrogen-zirconium phase diagram.

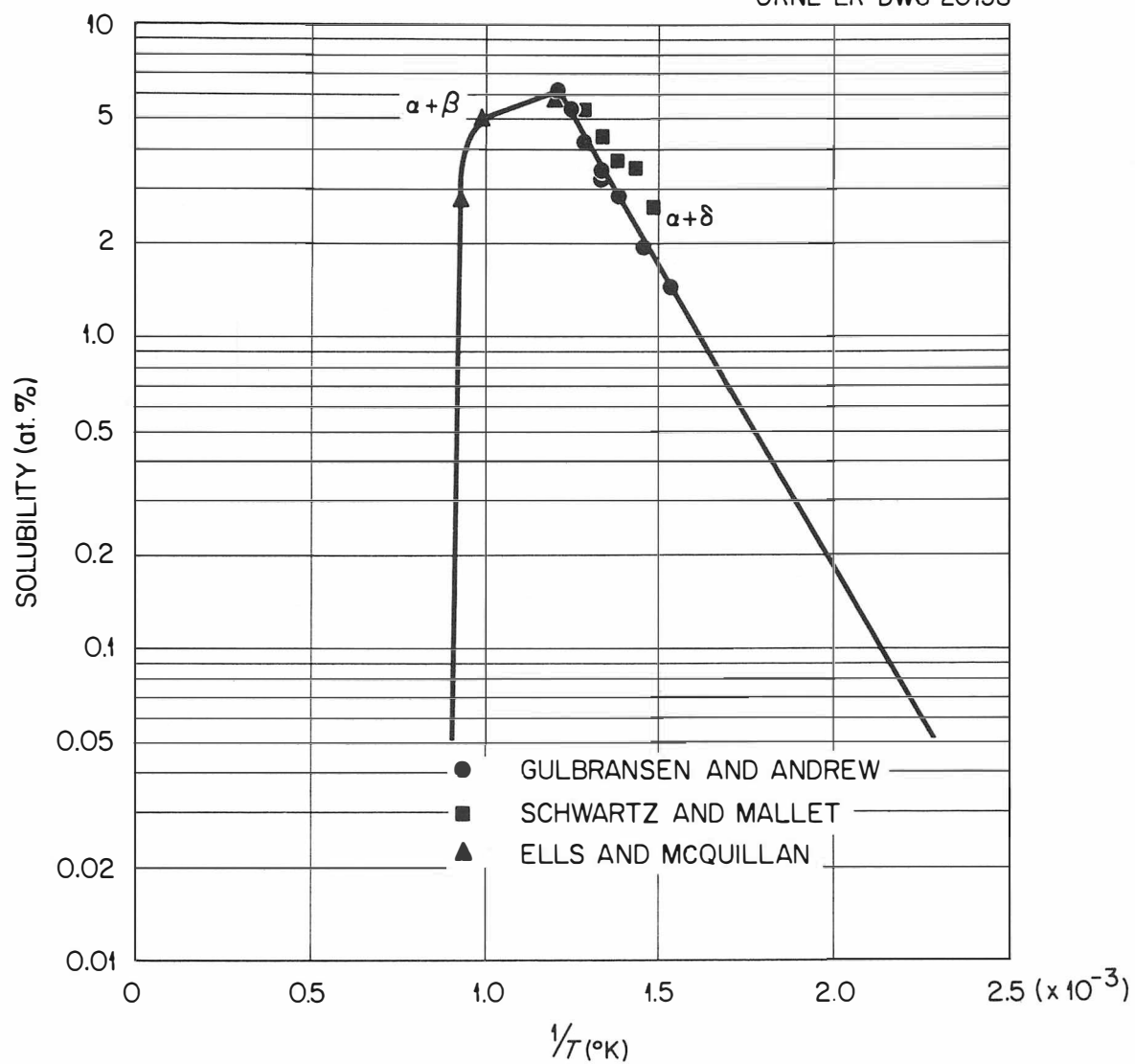
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Figure 16. Log of the terminal solubility of hydrogen in zirconium versus $1/T$.

the specific heat curve can be made. For if equilibrium were attained, the peak in the specific heat curve would indicate the temperature at which one crossed the terminal-solubility boundary. This temperature then corresponds to a certain hydrogen content. For the iodide zirconium the peak, which occurred at 242°C, corresponds to 28.5 parts per million of hydrogen in good agreement with the value of 35 parts per million obtained by vacuum fusion analysis. The hydrogenated-zirconium peak occurred at 450°C which corresponds to 300 parts per million of hydrogen. Unfortunately a direct analysis of the specimen was not made before the run and the hydrogen was removed by the vacuum anneal associated with the specific heat measurements. The heat associated with the solution process in both the iodide specimen and the hydrogenated specimen were measured by integrating the area under each peak numerically. The results are shown in Table VII.

The agreement is surprisingly good considering the long extrapolation in the solubility curve. The heat of solution may also be computed by the approximate equation:

$$S = S_0 e^{-\frac{\Delta H}{RT}}$$

From the slope of the curve of $\log S$ versus $1/T$ the heat of solution was calculated to be 8,616 calories per gram atom of hydrogen using the data of Gulbransen. This is also in fair agreement with the measured heats of solution. Thus the calorimetric data substantiate the reported terminal solubility which had been previously reported. The

TABLE VII

COMPUTED HEAT OF SOLUTION OF ZrH_2 IN ALPHA ZIRCONIUM

Specimen	Gram Atoms of Hydrogen	Heat of Solution	Heat of Solution
	Gram Atoms of Specimen	Calories Gram Atom of Spec.	Calories Gram Atom of Hydrogen
Zr + 28.5 ppm H	0.0026	0.2999	10,500
Zr + 300 ppm H	0.0275	3.4678	11,500

data also show that an adiabatic calorimeter would be an excellent instrument for studying the zirconium-hydrogen phase diagram and transformation kinetics.

6. Zirconium-Niobium Alloys

The small range of temperatures between the transformation temperature of zirconium (870°C) and the maximum operating temperature of the calorimeter (960°C) made the determination of the specific heat of the beta phase and the effect of temperature on this quantity very difficult. For this reason an alloy was prepared in which the beta stability was lowered to 610 degrees Celsius and in which the solute, niobium, was known to have the same structure and almost the same mass as the beta phase of zirconium. A similarity of these properties is desirable, because the specific heat would be less affected by the addition of such a solute. The composition of the zirconium-niobium alloy which was run in the adiabatic calorimeter was 17.5 weight per cent niobium.

The phase diagram for the zirconium-niobium system, which was developed by Rodgers and Atkins (34), is shown in Figure 17. This diagram shows the beta phase to be stable as low as 610°C at a composition of 17.5 weight per cent niobium. Rodgers and Atkins reported that the decomposition of the beta phase is quite sluggish so that the beta phase may be retained to room temperature if the niobium content is greater than 5 weight per cent. It was hoped that such a retention of the beta phase would permit the determination of its specific heat over the range of 100 - 900°C .

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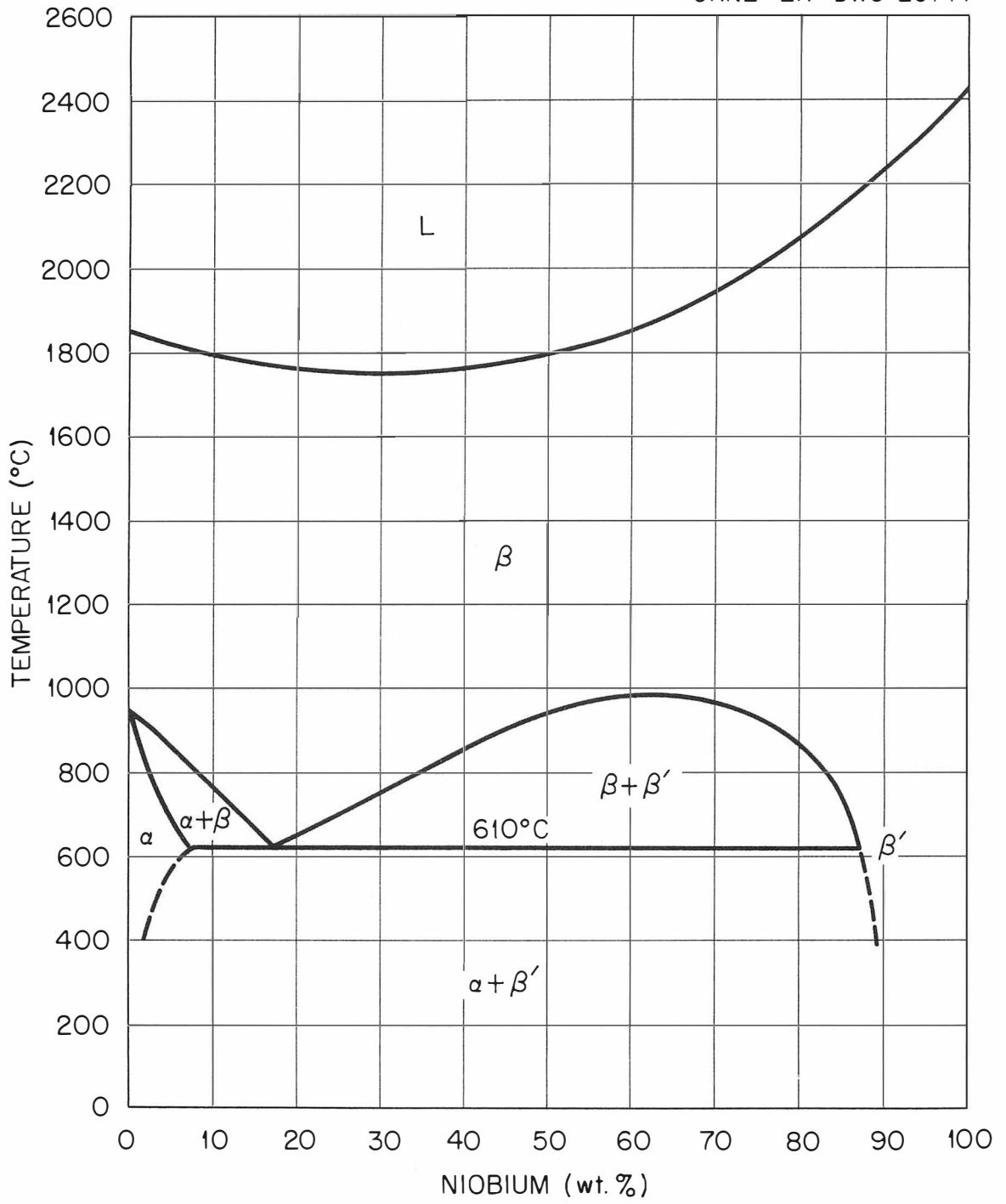


Figure 17. The niobium-zirconium phase diagram.

The measured specific heat curves for the zirconium-17.5 weight per cent niobium alloy are shown in Figure 18 and are given in Table XIV of the Appendix. The first two runs (67 and 68) were made only up to a temperature of three hundred degrees to prevent any transformation from obscuring the specific heat of the beta phase in the vicinity of room temperature. On the third run (No. 69) which was carried to higher temperatures, a slight peak was observed at 320°C. Then there was a large dip at approximately 400°, and finally a decided peak was again observed at 480°. From 520° to 800° the specific heat of the alloy was constant within experimental error. The heating rate of this run was seven degrees a minute at 200 degrees. Thus the reaction consisting of a precipitation and resolution of a new phase, which undoubtedly occurred, was exceedingly rapid.

After the specimen had cooled in the calorimeter to room temperature the specific heat curve was redetermined. The same result was found except that the dip at 400°C was more severe. This indicated that even with the relatively slow cooling rates associated with the cooling of the specimen in a vacuum, some nuclei for the precipitation might have formed, but the reaction by no means had gone to completion. When the temperature reached 460° the power to the specimen was turned off, and the specimen was allowed to drift for two hours to determine if further precipitation would occur isothermally. The higher peak on resolution (Run 70) indicated that there was indeed additional precipitation. Again above 520° specific heat was essentially constant which indicated that the structure was all beta.

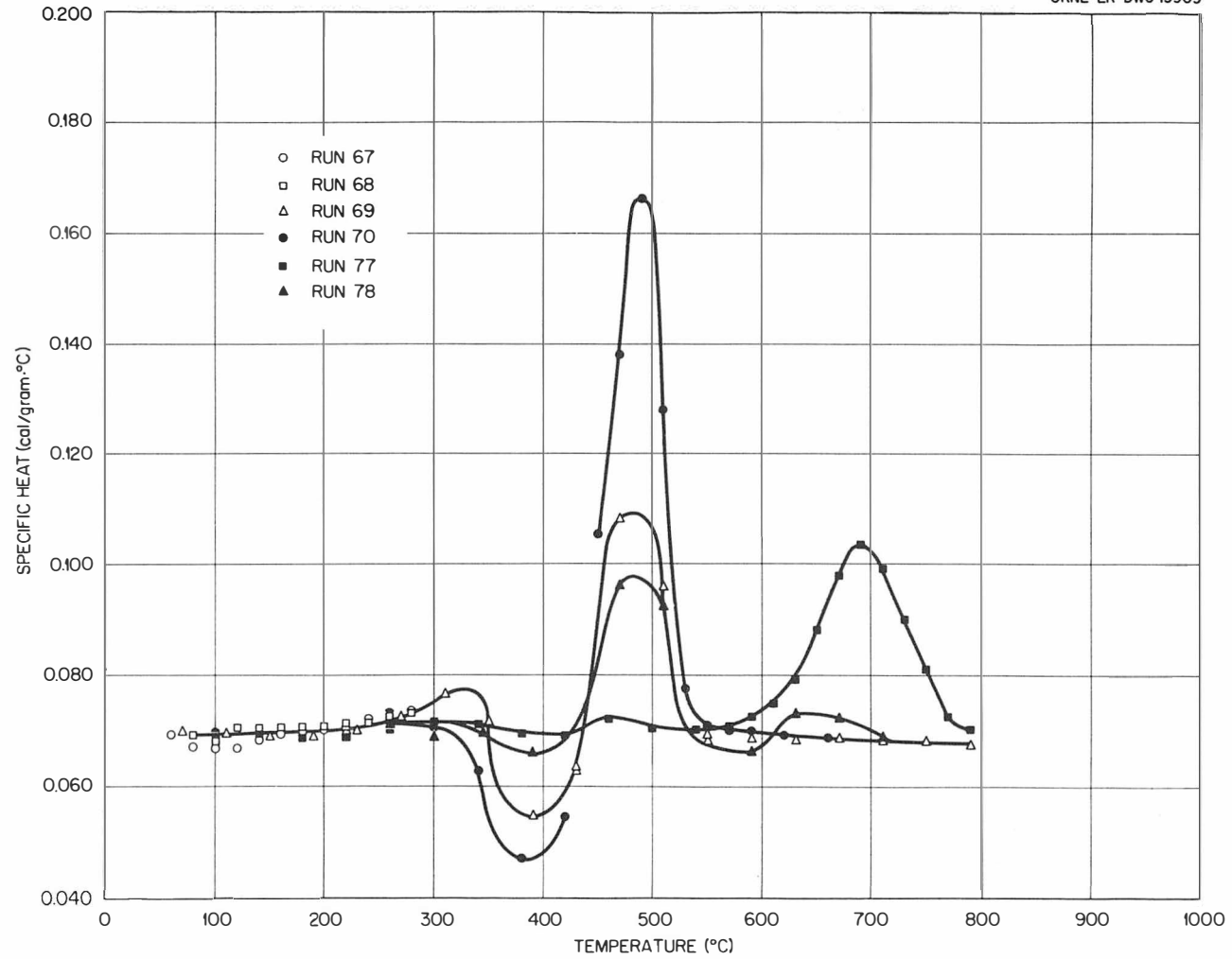


Figure 18. The measured specific heat values for a zirconium-17.5 weight per cent niobium alloy.

The results of these initial runs had little correlation with the phase diagram which had been reported. It was suspected that this lack of correlation was due to the rapid precipitation and resolution of a nonequilibrium structure, omega, which will be discussed later, and the sluggishness of the equilibrium reaction. To check this hypothesis the specimen was removed from the calorimeter, sealed in a quartz tube with rarefied argon, and annealed for two weeks at 600°C , ten degrees below the reported equilibrium transformation temperature. It was hoped that a two-week anneal at this temperature would produce the equilibrium structure in the alloy. After the heat treatment, the specimen was returned to the calorimeter and Run 77 was made. The pronounced peaks and dips observed in Runs 69 and 70 were now almost completely removed, but traces were still evident. Above 600° the specific heat rose sharply indicative of a transformation. The fact that the specific heat remained abnormally high up to 800° showed that this transformation was quite sluggish. An integration of the specific heat-temperature curve gave a heat of transformation of only 332 calories per gram atom. At the peak temperature of 700° the heat of transformation of pure zirconium would be approximately 1270 calories per gram atom.

After the specimen cooled to room temperature, a final run (Run 78) was made. This run showed essentially the same characteristics as the run made on the beta-quenched specimen (Run 69).

Additional information on the reactions occurring during the calorimetric runs was obtained by sectioning samples from the original specimen and giving them heat treatments which corresponded approximately

to the thermal history received in the calorimeter. These samples were then analyzed metallographically, with hardness measurements, and with x-rays. The x-ray technique used was the analysis of the patterns obtained from filings in a standard Debye-Sherrer camera. The x-ray study was done by R. M. Steele of the Metallurgy Division of the Oak Ridge National Laboratory.

The sample which had been held for two weeks at 600°C will be discussed first. This sample consisted of two phases which were identified as alpha and beta ($a = 3.526\text{\AA}$). No niobium-rich beta prime (β' , $a \approx 3.35$) was detected. A visual examination of the relative intensities of the x-ray lines indicated that the structure was approximately 30 per cent alpha. A lineal analysis of the microstructure indicated that the amount of alpha was 17.5 per cent; however, due to the difficulties in etching zirconium-niobium alloys, microscopic interpretations are only qualitative. If the latter figure is assumed to be correct, the heat of transformation of the alpha to beta in this alloy at 700° is approximately 1840 calories per mole. That this is higher than the heat of transformation of zirconium at the same temperature (1270 cal/mole) would indicate that there is also beta prime in the structure which is not resolvable metallographically or with x-rays. Additional heat would be released if this were the case corresponding to the heat of resolution of beta prime in beta. If, on the other hand, no beta prime is present, the alpha would indicate that there was metastable equilibrium between the alpha and beta. The amount would correspond to the calculated value obtained by applying the lever

rule to the extrapolated alpha-alpha plus beta, and beta-alpha plus beta boundary if the eutectoid temperature is raised to 620°C . At 610° this calculation would predict seven per cent of alpha. Thus the nature of the structure obtained by annealing a 17.5 weight per cent niobium alloy for two weeks at 600° is uncertain other than that it is definite that equilibrium was not attained. The hardness of this specimen was 173 DPH.

A second sample was annealed for two hours at 800°C and then water quenched. The hardness of this specimen was 179 DPH and the metallographic study showed that there was a needlelike phase comprising two per cent of the structure. This phase was not detected by x-rays.

A phase of similar appearance was observed in a sample cooled from 800° in the calorimeter. In this instance the matrix adjoining the phase was depleted in one of the constituents so that the specimen looked like a cored casting. The hardness of the calorimeter sample was 194 DPH, fifteen points harder than the quenched sample. When this specimen was reheated to 450° for two hours the hardness rose to 251 DPH. A decrease in the amount of the metallographically observable second phase indicated that this phase was going back into solution. X-ray data indicated the phase in the calorimeter cooled specimen had a face-centered cubic structure with a lattice constant 5.61A. After the two-hour anneal at 450° , insufficient second phase for x-ray detection remained. Thus x-ray and metallographic examination indicated a low-temperature phase but failed to show a structure which could account for the high hardness after a two-hour anneal at 450° and the

anomalous dips and peaks in the specific heat curves below 520° . Little hardening is associated with the low-temperature phase.

Although it cannot be detected except by hardness and calorimetric measurements, the transition which causes the pronounced dip and rise in the specific heat is believed to be the beta-omega transition which has been reported previously in the zirconium-niobium system (35). This transition, which was first reported in titanium alloys with beta stabilizers, is not yet fully understood, although the increased hardness associated with it is of considerable practical significance. Omega is known to be a metastable phase, which ultimately decomposes to equilibrium constituents after prolonged ageing treatments. The metastable phase forms because of its ability to form much more rapidly than the equilibrium constituents, particularly during a quench and reheat treatment (36). Although x-ray data have been reported for the omega structure in zirconium-molybdenum (35) and in titanium alloys (37), it has not been observed metallographically at the present time.

The calorimetric data indicate the omega phase retrogresses to beta above a temperature of 520°C , about one hundred degrees below the equilibrium transformation. The data also indicate that the amount of omega increases with time at a temperature of 450°C . Prolonged heating at 600° greatly decreases the tendency for beta to form omega, possibly because of the formation of alpha in favorable nucleation sites. Although further work is needed to rationalize the omega transition in the zirconium system, these data indicate the usefulness of the adiabatic calorimeter in the study of the kinetics of phase transformations.

If one ignores the beta-omega transition, he will find that the specific heat of the beta phase in this alloy is essentially constant from room temperature to 800°C. It is for this reason that the specific heat of beta zirconium was assumed to be constant from 870° to 950°C in Figure 18.

7. Iodide Titanium

The corrected specific heat data for iodide titanium are given in Figure 19 and Table XV of the Appendix. The data are compared with values determined by previous investigators in Figure 3. The values given in the present determination are lower than those of Jaeger, Rosenbohm, and Fonteyne (4) and Skinner, Johnston, and Beckett (8). It will be remembered that the data given for the specific heat of zirconium were also lower than the results previously reported. As reported by previous investigators, there is an abnormal increase in the specific heat of the alpha phase in comparison to other metals and the specific heat of the beta phase is lower than that of the alpha phase at the transformation temperature.

The enthalpy of titanium above 800°C is given in Figure 8, and in Table XXI of the Appendix. These data indicate that the transformation temperature of titanium is $883 \pm 2^\circ\text{C}$ and the heat of transformation of titanium is the same as the value zirconium would have if it transformed at the same temperature. In addition the gram-atomic

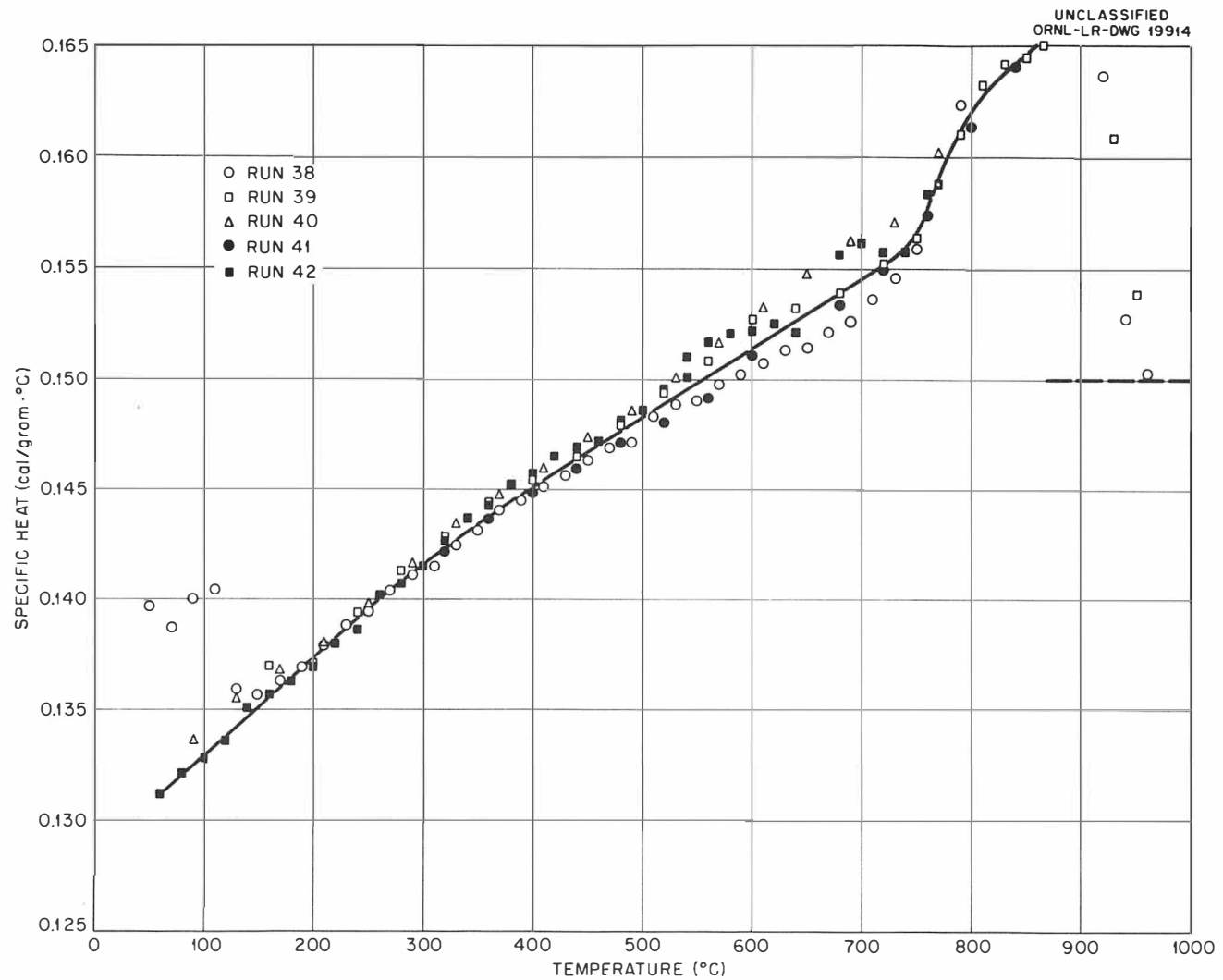


Figure 19. The measured specific heat values for titanium.

specific heat of titanium and zirconium are the same within experimental error. These observations emphasize the similarity between zirconium and titanium.

7. Zirconium-Titanium Alloys

The phase diagram for the zirconium-titanium system, which was determined by Fast (36) and Hayes et al (37) is shown in Figure 20. This diagram is surprising in that the beta phase is stable down to a temperature of approximately 550°C at a composition of 34.4 weight per cent titanium (50 atomic per cent). Smoluchowski (38) has rationalized this decrease in the transformation temperature by the argument that preferential ordering in the beta phase, because of the greater importance of the size effect in body-centered cubic alloys, leads to a lowering of the free energy of the beta phase so that it is stable at lower temperatures. It was felt by the author that such an effect would be indicated by calorimetric data if it were indeed true. Thus an alloy of 50 atomic per cent titanium and zirconium was studied.

The results of the calorimetric studies are given in Figure 21 and Table XVI of the Appendix. These data indicate that the specific heat of the alpha phase on a gram-atomic basis is the same as that of zirconium up to 550°C . From 550 to 640° a sluggish transformation from alpha to the beta phase occurs with a heat of transformation of 740 ± 20 calories per gram atom of the alloy at 600°C . On slow cooling the transformation begins at 558.5°C and the temperature rises to a maximum temperature

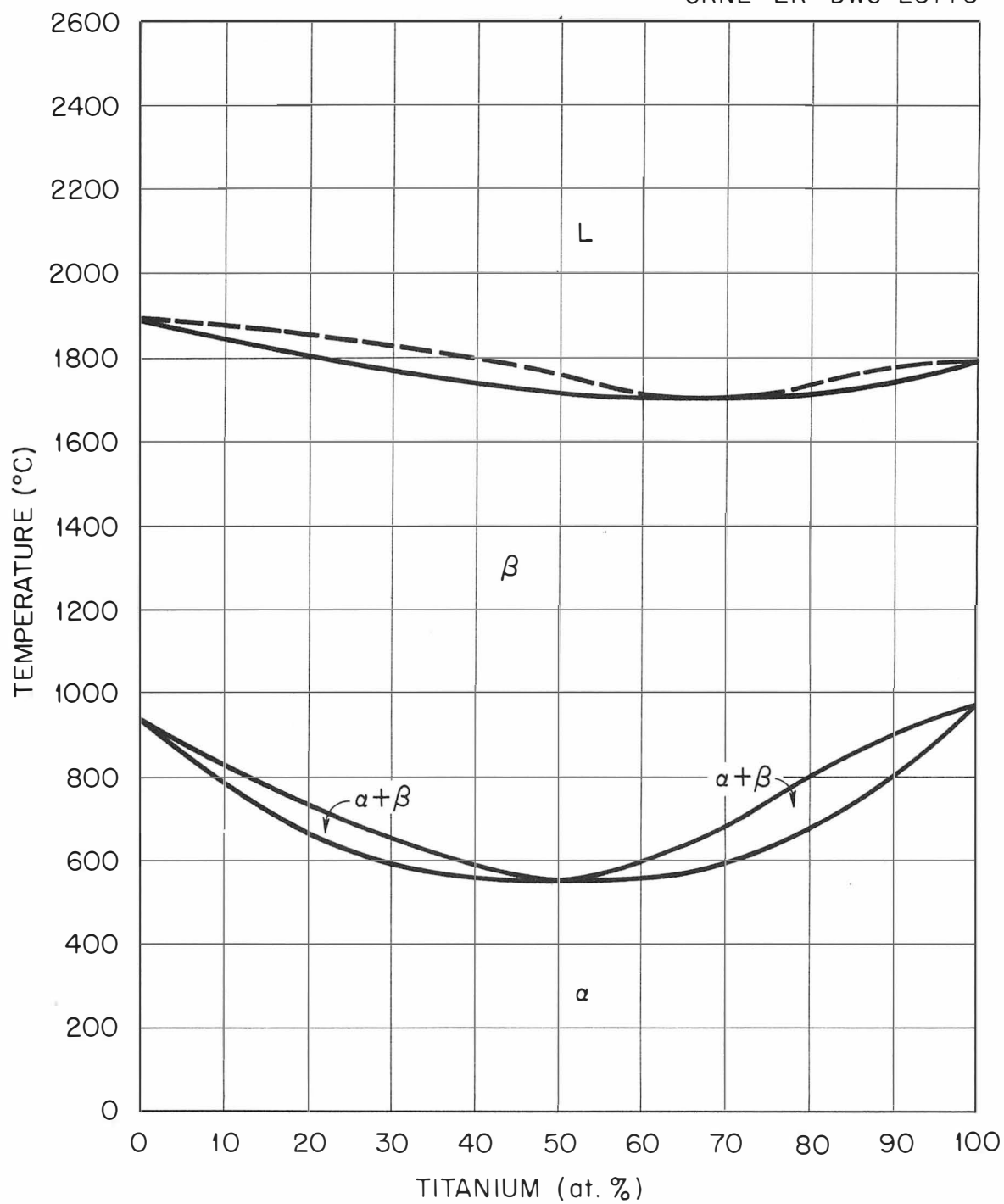
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Figure 20. The titanium-zirconium phase diagram.

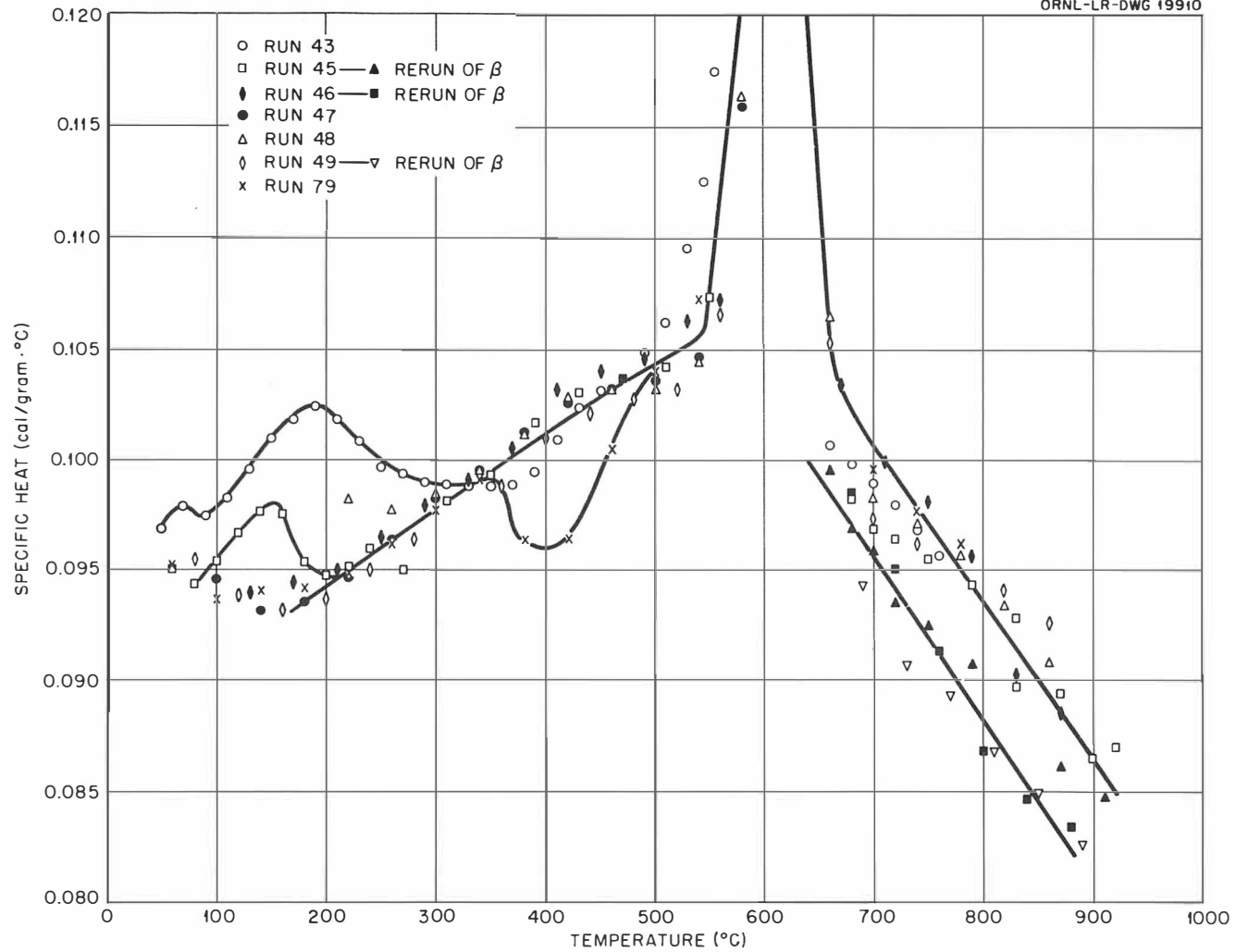


Figure 21. The measured specific heat values for a zirconium-50 atomic per cent titanium alloy.

of 560.5°C . Above 640 degrees the specific heat of the beta phase decreases linearly up to a temperature of 900°C , the highest temperature studied. That this decrease is reversible is shown by the fact that when the specimen was cooled to 650° and rerun to a temperature of 900° the linear decrease was again observed. In an attempt to obtain data on the beta phase at lower temperatures, the calorimeter specimen was homogenized at 800°C for two hours and water quenched. After the sample was returned to the calorimeter Run 79 was obtained. This run showed a dip in the alpha specific heat between 320° and 480°C which can be interpreted by assuming that 4.7 per cent of the beta was retained on quenching. Thus data for the beta phase at temperatures below 640° were not obtainable.

The linear decrease in the specific heat of the beta phase can be interpreted as being due to disordering of an ordered beta structure in agreement with the hypothesis of Smoluchowski. The fact that at 900 degrees these data fall to the value $3R$, the classical value of the specific heat, cannot be explained.

The peaks at 190°C in Run 43 and 150°C in Run 45 are undoubtedly due to hydrogen. The effect of hydrogen on the specific heat disappeared, because the hydrogen was removed by the vacuum anneal associated with these runs.

CHAPTER VI

CONCLUSIONS

The following conclusions may be drawn from the results of this investigation:

1. The specific heat of beta zirconium is lower than that of alpha at the transformation temperature of $870 \pm 2^\circ\text{C}$. Analogously the specific heat of beta titanium is lower than that of alpha at the transformation temperature of $883 \pm 2^\circ\text{C}$. For a zirconium-17.5 weight per cent niobium alloy, which should correspond quite well to pure zirconium, the specific heat of the beta phase has the constant value 0.069 ± 0.002 calories/gram- $^\circ\text{C}$ from room temperature to 800°C . Within the limits of error the addition of 0.746 atomic per cent of silver or 6.27 atomic per cent of indium does not affect the specific heat of either the alpha or beta phase over their ranges of stability above room temperature. An alloy of higher silver content (4.58 atomic per cent) does have a slightly higher specific heat in the alpha region, presumably because of the higher specific heat of the intermetallic compound Zr_2Ag .

2. The heat of transformation of zirconium is 993 ± 25 calories per gram atom at 870°C , and the heat of transformation of titanium is 978 ± 25 calories per gram atom at 883°C . Within the limits of experimental error the heats of transformation of zirconium and titanium would have the same value if the transformations occurred at the same temperature. Although the transformation from the alpha to the beta

phase in a 0.746 atomic per cent silver alloy occurs over the temperature range 830 - 854°C, the heat of transformation at an arbitrary intermediate temperature is the same as the value zirconium would have if it transformed at the same temperature within the limits of error. This is also true for an alloy of zirconium with 6.27 atomic per cent of indium, which transforms over the range of 910 - 940°C. The temperature of the eutectoid transformation in the zirconium-silver system is $825 \pm 2^\circ\text{C}$ and the heat of transformation of the eutectoid (3.73 atomic per cent silver) is 1240 ± 25 calories per gram atom.

3. The changes in the thermodynamic functions ΔH_o^x and

$$\int_0^T dT \int_0^T \Delta C^x d \ln T$$

are quite small, so that the precision of the calorimeter used was not sufficient to permit their evaluation.

4. The heat due to the solution of ZrH_2 in alpha zirconium may be detected calorimetrically even when the hydrogen content is as low as 28.5 ppm. The heat of solution is approximately 11,000 calories per mole of hydrogen.

5. There exists a metastable transition in a zirconium-17.5 weight per cent niobium alloy below 520°C which has decided effects on the specific heat curves and on the hardness but cannot be identified by metallographic or x-ray investigations. This transformation is tentatively called the omega transition. A second metastable phase which occurs at lower temperature can be identified metallographically and with x-rays, but has little effect on the hardness or the specific heat.

6. An alloy containing 50 atomic per cent titanium with zirconium shows the expected specific heat behavior in the alpha phase, but the specific heat of the beta phase is definitely abnormal. The beta specific heat decreases linearly from 650°C to 800°C. This effect may be interpreted as a disordering of the beta phase. The transformation occurred over the range 550 - 640°C on heating and 558.5 - 560.5°C during cooling. The heat of transformation of 740 ± 20 calories per gram atom at 600°C is abnormally low.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Glasstone, S., Principles of Nuclear Reactor Engineering, Van Nostrand (1955) 841
2. Kaufmann, A. R. and Magel, T. T., "Physical Metallurgy of Zirconium and Its Alloys" Metallurgy of Zirconium B. Lustman and F. Kerze editors, McGraw Hill (1955) 349
3. Jaeger, F. M. and Veenstra, W. A., "The Exact Measurement of the Specific Heats of Solid Substances at High Temperatures VII. The Calorimetric Behavior of Zirconium" Rec. trav. chim. 53 (1934) 917
4. Jaeger, F. M., Rosenbohm, E., and Fonteyne, R., "The Exact Measurement of the Specific Heats of Metals at High Temperatures XXIII. The Calorimetric, Electrical, and Thermoelectrical Behavior of Ductile Titanium" Rec. trav. chim. 55 (1936) 615
5. Skinner, G. B., "Thermodynamic and Structural Properties of Zirconium," Ohio State University Thesis (Ph.D.) 1951
6. Coughlin, J. P. and King, E. G., "High Temperature Heat Contents of Some Zirconium-containing Substances" J. Am. Chem. Soc. 72 (1950) 2262
7. Redmond, R. F. and Lones, J., "Enthalpies and Heat Capacities of Stainless Steel (316), Zirconium and Lithium at Elevated Temperatures" U.S. A.E.C. Publ. ORNL-1342 (1952)
8. Skinner, G., Johnston, H. L., and Beckett, C., Titanium and Its Compounds H. L. Johnston Enterprises (1954) 95
9. Schofield, T. H., "Some Experiments on the Determination of the Latent Heats of Transition of Titanium and Iron" J. Inst. Metals 24 Part 2 (1956) 68
10. Backhurst, I., Unpublished Research
11. Finley, J. A., "Methods of Study of Zirconium Alloy Systems" Metallurgy of Zirconium B. Lustman and F. Kerze editors, McGraw Hill (1955) 439
12. Betterton, J. O., Jr. and Frye, J. H., Jr., Article submitted to Acta Metallurgica, May 1, 1957

13. Pauling, L., "The Electronic Structure of Metals and Alloys" Theory of Alloy Phases, A.S.M. Seminar, Oct. 15, 1955, p. 220
14. (a) Betterton, J. O., Jr. and Easton, D. S., "Fundamental Studies of Zirconium Alloys, the Silver-Zirconium System" ORNL Metallurgy Division Semiannual Progress Report, Oct. 10, 1956, ORNL-2217, p. 215
- (b) Betterton, J. O., Jr., Easton, D. S., and Cunningham, C. W., "The Silver-Zirconium System" ORNL Metallurgy Division Semiannual Progress Report, April 10, 1954, ORNL-1727, p. 120
- (c) Betterton, J. O., Jr., and Easton, D. S., "The Silver-Zirconium System" ORNL Metallurgy Division Semiannual Progress Report, April 10, 1956, ORNL-2080, p. 218
- (d) Betterton, J. O., Jr. and Easton, D. S., "The Silver-Zirconium System" ORNL Metallurgy Division Semiannual Progress Report, April 10, 1956, ORNL-2080, p. 218
15. (a) Betterton, J. O., Jr. and Noyce, W. K., "Fundamental Studies of Zirconium Alloys, the Indium-Zirconium System" ORNL Metallurgy Division Semiannual Progress Report, Oct. 10, 1956, ORNL-2217, p. 216
- (b) Betterton, J. O., Jr., Boyd, G. W., and Noyce, W. K., "The Indium-Zirconium System" ORNL Metallurgy Division Quarterly Progress Report, August 28, 1952, Report ORNL-1267
16. Elder, G. E., "The Design and Development of a High Temperature Calorimeter," University of Tennessee Thesis (M.S.) 1952
17. Picklesimer, M. L., "Calorimetric Measurements on High Purity Iron and Eutectoid Steels," University of Tennessee Thesis (Ph.D.) 1954
18. McElroy, D. L., "Calorimetry of High Purity Irons and Steels," University of Tennessee Thesis (Ph.D.) to be published
19. Fast, J. D., "Zirconium as a Getter" Footprints 13(1):22 (1940)
20. Kroll, W. J., "Production of Ductile Titanium" Trans. Electrochem. Soc. 78 (1940) 35
21. Beaver, W. W., Report BBC-54, August 1950
22. Van Arkel, A. E. and deBoer, J. H., Z. anorg. u. allgem. chem. 148 (1925) 345

23. Reed, E. B., "Analytical Chemistry of Zirconium" Metallurgy of Zirconium B. Lustman and F. Kerze editors, McGraw-Hill (1955) p. 687
24. Quinney, H. and Taylor, G. I., "The Emission of the Latent Energy Due to Previous Cold Working When a Metal is Heated" Proc. Roy. Soc. A163 (1937) 157
25. Sykes, C. and Jones, F. W., "Methods for the Examination of Thermal Effects Due to Order-Disorder Transformations" J. Inst. Metals 59 (1936) 257
26. Pawel, R. E., "The Application of Dynamic Calorimetry to the Copper-Nickel System from 50 to 620°C," University of Tennessee Thesis (Ph.D.) 1956
27. Awberry, J. H. and Snow, A., "Total Heat of Iron at Various Temperatures up to 950°C" Second Report of the Alloy Steel Research Committee Report Section IX (3), 216
28. Bing, G., Fink, F. W., and Thompson, H. B., "The Thermal and Electrical Conductivities of Zirconium and its Alloys" Report BMI-65 April 16, 1951
29. Gulbransen, E. A. and Andrew, K. F., "Solubility and Decomposition Pressures of Hydrogen in Alpha Zirconium" Trans. A.I.M.E. 203 (1955) 136
30. Edwards, R. K., Levesque, P., and Cubicciotti, D., "Solid Solution Equilibria in the Zirconium Hydrogen System" J. Am. Chem. Soc. 77 (1955) 1312
31. Vaughan, D. A. and Bridge, J. R., "High Temperature X-Ray Diffraction Investigation of the Zirconium-Hydrogen System" Trans. A.I.M.E. 206 (1956) 528
32. Schwartz, C. M. and Mallett, M. W., "Observations on the Behavior of Hydrogen in Zirconium" Trans. A.S.M. 46 (1954) 640
33. Ells, C. E. and McQuillan, A. D., "A Study of the Hydrogen-Pressure Relationships in the Zirconium-Hydrogen System" J. Inst. of Metals 24 Part 3 (1956) p. 89
34. Rodgers, B. A. and Atkins, D. F., "Zirconium-Columbium Diagram" Trans. A.I.M.E. 203 (1955) 1034
35. Robinson, H. A., Doig, J. R., Mote, M. W., Schwartz, C. M., and Frost, P. D., "Beta-Omega Age Hardening Means Stronger Zirconium Alloys" J. of Metals 8 (1956) 1544

36. Picklesimer, M. L., Private Communication
37. Brotzen, Franz R., Harmon, E. L., Jr., and Troiano, A. R.,
"Decomposition of Beta Titanium" Trans. A.I.M.E. 203 (1955) 413
38. Fast, J. D., "The Transition Point Diagram of the Zirconium-Titanium System" Rec. trav. chim., 58 (1939) 973
39. Hayes, E. T., Roberson, A. H., and Paasche, O. G., "Zirconium-Titanium System: Constitutional Diagram and Properties" Bureau of Mines Report. Invest. 4826 November, 1951
40. Smoluchowski, R., "Zirconium Alloy Systems-Theoretical Survey" Metallurgy of Zirconium B. Lustman and F. Kerze editors, McGraw-Hill (1955) p. 432

APPENDIX

TABLE VIII

SAMPLE CALCULATIONS

Zirconium - 0.03 Weight Per Cent Hydrogen, Run 74																
T (°C)	Δt sec.	T (μv)	E (volts)	\bar{E} (volts)	I (amps)	\bar{I} (amps)	$\bar{E} \bar{I} \Delta t$ (watt-sec.)	C_{pA} cal/g °C	$\frac{\Delta t}{\Delta T}$ (sec/°C)	R(T) (°C/hr)	$1 - \frac{\Delta t}{\Delta T} \frac{R(T)}{3600}$ (dimensionless)	C_{pT} cal/g °C	$C_{pT} - .55C_H$ cal/g °C	$\frac{WH}{W_S} (C_{pT} - .55C_H)$ cal/g °C	C_S cal/g °C	\bar{T} (°C)
100	0	645.5	5.3935		0.74418											
140	347.1	957.0	5.3928	5.3931	0.74392	0.74405	1392.82	0.07359	8.68	0.90	1.0022	0.07343	0.0607	0.00195	0.07148	120
180	349.2	1251.0	5.3894	5.3911	0.74321	0.74356	1395.81	0.07399	8.73	1.67	1.0041	0.07369	0.0604	0.00194	0.07175	160
220	350.8	1643.7	5.3860	5.3877	0.74276	0.74298	1404.24	0.07419	8.77	2.80	1.0068	0.07369	0.0604	0.00194	0.07175	200
260	348.4	2012.6	5.3826	5.3843	0.74206	0.74241	1396.68	0.07379	8.74	4.16	1.0101	0.07305	0.0610	0.00196	0.07109	240
300	354.4	2395.6	5.3794	5.3810	0.74132	0.74169	1414.42	0.07473	8.86	5.53	1.0136	0.07372	0.0604	0.00194	0.07178	280
340	359.5	2750.4	5.3759	5.3777	0.74060	0.74096	1432.45	0.07569	8.99	6.91	1.0173	0.07440	0.0597	0.00192	0.07248	320
380	362.0	3195.1	5.3735	5.3747	0.73995	0.74027	1440.30	0.07610	9.05	8.20	1.0206	0.07456	0.0595	0.00191	0.07265	360
420	365.5	3508.4	5.3706	5.3720	0.73923	0.73959	1452.16	0.07672	9.14	9.61	1.0244	0.07489	0.0592	0.00190	0.07299	400
460	370.7	4029.9	5.3679	5.3692	0.73851	0.73887	1470.62	0.07770	9.27	10.90	1.0281	0.07558	0.0585	0.00188	0.07370	440
500	374.6	4459.4	5.3691	5.3685	0.73830	0.73840	1484.95	0.07845	9.37	12.81	1.0333	0.07593	0.0582	0.00187	0.07406	480
540	378.9	4896.6	5.3752	5.3711	0.73876	0.73853	1502.99	0.07941	9.47	13.49	1.0355	0.07669	0.0574	0.00185	0.07484	520
580	383.7	5341.5	5.3801	5.3776	0.73861	0.73878	1524.39	0.08054	9.59	14.50	1.0386	0.07755	0.0565	0.00182	0.07573	560
620	390.9	5794.1	5.3843	5.3822	0.73855	0.73866	1554.11	0.08211	9.77	15.38	1.0423	0.07878	0.0553	0.00178	0.07700	600
660	398.1	6254.4	5.3829	5.3836	0.73801	0.73828	1582.29	0.08360	9.95	16.50	1.0456	0.07955	0.0541	0.00174	0.07821	640
700	405.8	6722.3	5.3919	5.3874	0.73736	0.73768	1604.77	0.08479	10.15	17.40	1.0491	0.08082	0.0533	0.00171	0.07911	680
740	408.5	7197.9	5.3903	5.3911	0.73586	0.73661	1622.21	0.08571	10.21	18.28	1.0518	0.08149	0.0526	0.00169	0.07980	720
780	416.1	7681.0	5.3940	5.3921	0.73506	0.73546	1650.12	0.08718	10.40	19.10	1.0552	0.08262	0.0515	0.00165	0.08096	760

TABLE IX

TRUE SPECIFIC HEAT VALUES OF IODIDE ZIRCONIUM

Run 17		Run 18		Run 18	
EI = 2.410 watts		EI = 2.546 watts		EI = 2.546 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$
90	0.06838	90	0.06849	845	0.09938
110	0.06903	130	0.07009		
130	0.06926	170	0.07106	TRANSFORMATION	
150	0.06992	210	0.07232		
170	0.07041	250	0.07276	892.5	0.07361
				910	0.07179
190	0.07079	290	0.07124	930	0.07102
210	0.07160	330	0.07195	950	0.07224
230	0.07201	410	0.07237		
250	0.07201	430	0.07325	Run 24	
270	0.07042	450	0.07366	EI = 1.402 watts	
				T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$
290	0.07081	470	0.07448	270	0.07243
310	0.07091	490	0.07512	290	0.07161
330	0.07126	510	0.07563	310	0.07149
360	0.07173	530	0.07646	330	0.07209
390	0.07257	550	0.07668	350	0.07257
				370	0.07349
410	0.07256	570	0.07699	390	0.07371
430	0.07317	590	0.07783	410	0.07419
450	0.07359	610	0.07857	430	0.07454
470	0.07410	630	0.07914	450	0.07450
490	0.07445	650	0.07991		
				470	0.07584
510	0.07506	670	0.08094	490	0.07646
530	0.07560	700	0.08223	510	0.07736
550	0.07590	730	0.08543	530	0.07814
570	0.07696	750	0.08660	550	0.07873
590	0.07779	770	0.08820		
				570	0.07919
610	0.07826	790	0.09086	590	0.07973
		805	0.09212		
		815	0.09235		
		825	0.09296		
		835	0.09464		

TABLE IX(Continued)

TRUE SPECIFIC HEAT VALUES OF IODIDE ZIRCONIUM

Run 26		Run 28		Run 60	
EI = 2.454 watts		EI = 3.780 watts		EI = 1.441 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
60	0.07012	280	0.07196	260	0.07099
80	0.07004	320	0.07232	280	0.07051
100	0.07095	360	0.07266	300	0.07092
120	0.07122	400	0.07289	320	0.07146
140	0.07145	440	0.07362	340	0.07143
160	0.07180	480	0.07448	360	0.07163
180	0.07202	520	0.07578	380	0.07191
200	0.07146	560	0.07718	400	0.07216
220	0.07122	600	0.07801	Run 62	
240	0.07130	640	0.07937	EI = 3.928 watts	
260	0.07136	680	0.08035	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
280	0.07170	720	0.08113	320	0.07231
300	0.07178	760	0.08201	360	0.07268
320	0.07187	800	0.08483	400	0.07301
350	0.07257	Run 60		440	0.07339
390	0.07335	EI = 1.441 watts		480	0.07341
430	0.07441	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	520	0.07263
470	0.07543	60	0.06816	560	0.07477
Run 28		80	0.06809	600	0.07600
EI = 3.780		100	0.06840	640	0.07726
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	120	0.07007	680	0.07814
80	0.07045	140	0.07100	720	0.07970
120	0.07081	160	0.07138	760	0.08107
160	0.07152	180	0.07166	800	0.08493
200	0.07135	200	0.07183	840	0.10069
240	0.07118	220	0.07233	TRANSFORMATION	
		240	0.07260	900	0.08030
				920	0.07504
				940	0.07418
				960	0.07462
				980	0.07497

TABLE IX (Continued)

TRUE SPECIFIC HEAT VALUES OF IODIDE ZIRCONIUM

Run 64		Run 74		Run 75 cont.	
EI = 2.540 watts		EI = 3.968 watts		EI = 3.986 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{grams}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
60	0.07008	120	0.07148	340	0.07269
100	0.06891	160	0.07175	380	0.07291
140	0.07026	200	0.07175	420	0.07342
180	0.07127	240	0.07109	480	0.07465
220	0.07112	280	0.07178	540	0.07553
260	0.07110	320	0.07248	580	0.07657
300	0.07169	360	0.07265	620	0.07768
340	0.07213	400	0.07299	660	0.07834
380	0.07258	440	0.07370	700	0.08016
420	0.07310	480	0.07406		
460	0.07403	520	0.07484		
500	0.07506	560	0.07573		
540	0.07604	600	0.07700		
580	0.07726	640	0.07821		
620	0.07877	680	0.07911		
660	0.07996	720	0.07980		
700	0.08065	760	0.08096		
740	0.08131				
780	0.08309	Run 75			
820	0.08472	EI = 3.986 watts			
850	0.10497	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$		
TRANSFORMATION					
900	0.07553	140	0.07104		
920	0.06918	180	0.07161		
940	0.06901	220	0.07122		
		260	0.07157		
		300	0.07210		

TABLE X

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 0.881
WEIGHT PER CENT SILVER ALLOY

Run 13		Run 14		Run 15	
EI = 2.511 watts		EI = 2.590 watts		EI = 2.500 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
60	0.06814	100	0.06894	70	0.06802
90	0.06764	140	0.07000	90	0.06795
100	0.06847	180	0.07038	110	0.06918
120	0.06932	220	0.07005	130	0.06911
140	0.06985	260	0.07014	150	0.07068
160	0.06989	300	0.07102	170	0.07043
180	0.07025	340	0.07161	190	0.07028
210	0.06960	380	0.07218	210	0.06972
240	0.06996	420	0.07295	230	0.07079
260	0.06994	460	0.07422	250	0.06819
280	0.07031	500	0.07558	270	0.06996
300	0.07039	540	0.07638	290	0.07015
320	0.07082	580	0.07764	310	0.07072
340	0.07131	620	0.07885	330	0.07121
360	0.07153	660	0.08044	350	0.07146
380	0.07186	690	0.08201	370	0.07197
400	0.07232	710	0.08436	390	0.07242
420	0.07302	730	0.08521	410	0.07242
440	0.07351	750	0.08590	430	0.07332
460	0.07420	770	0.08632	450	0.07353
480	0.07467	790	0.08782	470	0.07554
500	0.07527	810	0.09477	490	0.07488
520	0.07612	830	0.10544	510	0.07541
540	0.07664			530	0.07609
560	0.07719			550	0.07666
580	0.07766			570	0.07710
600	0.07843			590	0.07779
				610	0.07885
				630	0.07875
				650	0.08008

TABLE X(Continued)

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 0.881
WEIGHT PER CENT SILVER ALLOY

Run 15 cont.		Run 50	
EI = 2.500 watts		EI = 3.821 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
670	0.08196	80	0.07405
690	0.08357	120	0.07237
710	0.08555	160	0.07212
730	0.08588	200	0.07165
750	0.08649	240	0.07192
770	0.08891	280	0.07254
790	0.09153	320	0.07299
810	0.09160	360	0.07349
TRANSFORMATION		400	0.07390
		440	0.07427
905	0.07397	480	0.07488
915	0.06833	520	0.07555
925	0.06772	560	0.07677
935	0.06819	600	0.07828
945	0.06857	640	0.07966
		680	0.08093
		720	0.08238
		760	0.08403
		800	0.08811
		TRANSFORMATION	
		920	0.07290
		960	0.07030

TABLE XI

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 5.37
WEIGHT PER CENT SILVER ALLOY

Run 32		Run 32 cont..		Run 33 cont.	
EI = 2.361 watts		EI = 2.361 watts		EI = 3.649 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \cdot ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \cdot ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \cdot ^\circ\text{C}$
70	0.07111	670	0.08343	500	0.07743
90	0.07010	690	0.08560	540	0.07791
110	0.07088	710	0.08650	580	0.07863
130	0.07135	730	0.08975	620	0.07907
150	0.07173	750	0.09359	660	0.08057
170	0.07140	770	0.09552	700	0.08171
190	0.07148	790	0.09802	740	0.08554
210	0.07183	805	0.10276	780	0.09061
230	0.07226			805	0.09386
250	0.07223	850	0.10586		
270	0.07286	870	0.10045	Run 36	
290	0.07338	890	0.08728	EI = 3.649 watts	
310	0.07337	910	0.07588	T°C	
330	0.07390	930	0.07436	Cp $\frac{\text{cal}}{\text{gram}} \cdot ^\circ\text{C}$	
350	0.07434	950	0.07561		
370	0.07461	Run 33		360	0.07490
390	0.07523	EI = 3.649 watts		400	0.07566
410	0.07585	T°C		440	0.07638
430	0.07653	Cp $\frac{\text{cal}}{\text{gram}} \cdot ^\circ\text{C}$		480	0.07689
450	0.07701	110	0.07163	520	0.07750
470	0.07773	140	0.07244	560	0.07796
490	0.07808	180	0.07261	600	0.07894
510	0.07888	220	0.07295	640	0.07981
530	0.07946	260	0.07346	680	0.08216
550	0.07982	300	0.07440	720	0.08711
570	0.08048	340	0.07453	760	0.09049
590	0.08092	380	0.07526		
610	0.08137	420	0.07587		
630	0.08174	460	0.07661		
650	0.08224				

TABLE XI (Continued)

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 5.37
WEIGHT PER CENT SILVER ALLOY

Run 37

EI = 3.810 watts

T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$
100	0.07414
140	0.07251
180	0.07234
220	0.07229
260	0.07291
300	0.07364
340	0.07451
380	0.07527
420	0.07595
460	0.07692
500	0.07756
540	0.07855
580	0.07910
620	0.08006
660	0.08110
700	0.08373
740	0.08887
780	0.09432
805	0.09862
815	0.16941
TRANSFORMATION	
850	0.14361
880	0.10803

TABLE XII

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 7.77
WEIGHT PER CENT INDIUM ALLOY

Run 54		Run 55		Run 56 cont.	
EI = 2.485 watts		EI = 3.866 watts		EI = 3.884 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
80	0.07082	80	0.06924	270	0.07109
120	0.06970	120	0.06960	310	0.07168
160	0.06980	160	0.06969	350	0.07220
200	0.06991	200	0.06991	390	0.07244
240	0.07032	240	0.07065	430	0.07300
280	0.07052	280	0.07153	470	0.07381
320	0.07109	320	0.07185	510	0.07503
360	0.07175	360	0.07227	550	0.07611
400	0.07184	400	0.07247	590	0.07692
440	0.07215	440	0.07296	630	0.07748
480	0.07310	480	0.07397	670	0.07802
520	0.07438	520	0.07529	710	0.07938
560	0.07626	560	0.07582	750	0.08024
600	0.07705	600	0.07642	790	0.08175
640	0.07772	640	0.07653	830	0.08403
680	0.07863	680	0.07668	870	0.08465
720	0.07845	720	0.07880	900	0.11912
760	0.08053	760	0.08039		
800	0.08209	800	0.08024		
830	0.08211	840	0.08113		
850	0.08071	880	0.08643		
870	0.08465				
885	0.08982				
895	0.09436				
905	0.10867				
		Run 56		Run 58	
		EI = 3.884 watts		EI = 2.492 watts	
		T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
		70	0.07034	60	0.06999
		110	0.06965	100	0.06903
		150	0.06976	140	0.06964
		190	0.06980	180	0.06986
		230	0.07041	220	0.07044

TABLE XII (Continued)

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM
- 7.77 WEIGHT PER CENT INDIUM ALLÖY

Run 58 cont.		Run 59	
EI = 2.492 watts		EI = 3.914 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$
260	0.07103	60	0.07017
300	0.07142	100	0.06916
340	0.07197	140	0.06964
380	0.07261	180	0.06959
420	0.07303	220	0.07015
460	0.07409	260	0.07081
500	0.07540	300	0.07116
540	0.07669	340	0.07169
580	0.07758	380	0.07199
620	0.07837	420	0.07226
660	0.07886	460	0.07285
710	0.08011	500	0.07384
760	0.08111	540	0.07444
800	0.08074	580	0.07501
840	0.08028	620	0.07538
		660	0.07591
		700	0.07659
		740	0.07712
		780	0.07773
		820	0.07922
		860	0.07992

TABLE XIII

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM
- 300 PPM HYDROGEN ALLOY

Run 71		Run 72		Run 73	
EI = 2.556 watts		EI = 3.927 watts		EI = 3.918 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram} \cdot ^\circ\text{C}}$
50	0.07175	60	0.07306	80	0.07118
70	0.07316	100	0.07201	120	0.07117
90	0.07215	140	0.07154	160	0.07173
110	0.07205	180	0.07209	200	0.07271
130	0.07208	220	0.07378	240	0.07463
150	0.07242	260	0.07673	280	0.07749
170	0.07267	300	0.07892	320	0.08039
190	0.07327	340	0.08219	360	0.08405
210	0.07387	380	0.08637	400	0.08825
230	0.07487	420	0.09077	440	0.09178
250	0.07645	460	0.09077	480	0.08355
270	0.07740	500	0.07661	520	0.07546
290	0.07823	540	0.07638	560	0.07717
310	0.07995	580	0.0774	600	0.07806
330	0.08144			640	0.07917
350	0.08322			680	0.07962
370	0.08526			710	0.08185
390	0.08735			730	0.08706
				750	0.09765
				770	0.09795
				790	0.11249

TABLE XIV

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 17.5
WEIGHT PER CENT NIOBIUM ALLOY

Run 67		Run 69		Run 70 cont.	
EI = 1.380 watts		EI = 3.850 watts		EI = 2.455 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$
60	0.06948	70	0.06987	300	0.07073
80	0.06713	110	0.06943	340	0.06304
100	0.06671	150	0.06896	380	0.04733
120	0.06714	190	0.06888	420	0.05463
140	0.06813	230	0.07008	Specimen held 2 hr	
160	0.06932	270	0.07253	450	0.10552
180	0.06990	310	0.07672	470	0.13819
200	0.07029	350	0.07180	490	0.16627
220	0.07136	390	0.05491	510	0.12829
240	0.07228	430	0.06347	530	0.07760
260	0.07308	470	0.10815	550	0.07134
280	0.07369	510	0.09580	570	0.07038
		550	0.06921	590	0.07001
Run 68		590	0.06854	620	0.06949
EI = 1.402 watts		630	0.06829	660	0.06894
T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	670	0.06847	Run 77	
60	0.06940	710	0.06897	EI = 2.396 watts	
80	0.06940	750	0.06800	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$
100	0.06830	790	0.06729	60	0.06960
120	0.07058	Run 70		100	0.06956
140	0.07047	EI = 2.455 watts		140	0.06979
160	0.07052	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	180	0.06869
180	0.07069	100	0.06998	220	0.06890
200	0.07075	140	0.06991	260	0.07039
220	0.07136	180	0.06991	300	0.07156
240	0.07160	220	0.07113	340	0.07110
260	0.07264	260	0.07269	380	0.06968
280	0.07363			420	0.06938

TABLE XIV (Continued)

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 17.5
WEIGHT PER CENT NIOBIUM ALLOY

Run 77 cont.		Run 79	
EI = 2.396 watts		EI = 2.394 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$
460	0.07213	100	0.06913
500	0.07041	140	0.06892
540	0.07036	180	0.06905
570	0.07070	220	0.07020
590	0.07259	260	0.07073
610	0.07513	300	0.06868
630	0.07929	345	0.06973
650	0.08820	390	0.06589
670	0.09802	430	0.06340
690	0.10367	470	0.09606
710	0.09923	510	0.09220
730	0.09015	550	0.06806
750	0.08110	590	0.06620
770	0.07255	630	0.07337
790	0.07041	670	0.07235
		710	0.06855

TABLE XV

TRUE SPECIFIC HEAT VALUES OF IODIDE TITANIUM

Run 38		Run 38 cont.		Run 39 cont.	
EI = 2.338 watts		EI = 2.338 watts		EI = 3.705 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
50	0.1397	650	0.1514	560	0.1508
70	0.1387	670	0.1521	600	0.1527
90	0.1400	690	0.1526	640	0.1532
110	0.1404	710	0.1536	680	0.1539
130	0.1359	730	0.1545	720	0.1552
150	0.1357	750	0.1558	750	0.1563
170	0.1363	770	0.1588	770	0.1588
190	0.1369	790	0.1623	790	0.1610
210	0.1379	810	0.1652	810	0.1632
230	0.1388	830	0.1665	830	0.1641
250	0.1394	TRANSFORMATION		850	0.1644
270	0.1404			865	0.1656
290	0.1411	900	0.1841	875	0.1830
310	0.1415	920	0.1636		
330	0.1424	940	0.1527	TRANSFORMATION	
350	0.1431	960	0.1502		
370	0.1440	Run 39		910	0.1709
390	0.1447			930	0.1608
410	0.1451	EI = 3.705 watts		950	0.1538
430	0.1456			Run 40	
450	0.1463	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	EI = 3.674 watts	
470	0.1469				
490	0.1471	160	0.1370	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
510	0.1483	200	0.1371		
530	0.1488	240	0.1394	90	0.1336
550	0.1490	280	0.1413	130	0.1355
570	0.1497	320	0.1428	170	0.1368
590	0.1502	360	0.1444	210	0.1380
610	0.1507	400	0.1454	250	0.1397
630	0.1513	440	0.1465		
		480	0.1479		
		520	0.1494		

TABLE XV (Continued)

TRUE SPECIFIC HEAT VALUES OF IODIDE TITANIUM

Run 40 cont.		Run 42		Run 42 cont.	
EI = 3.674 watts		EI = 2.307 watts		EI = 2.307 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$
290	0.1416	60	0.1312	660	0.1521
330	0.1434	80	0.1321	680	0.1556
370	0.1447	100	0.1328	700	0.1561
410	0.1459	120	0.1336	720	0.1557
450	0.1473	140	0.1351	740	0.1557
490	0.1485	160	0.1357	760	0.1583
530	0.1500	180	0.1363		
570	0.1516	200	0.1370		
610	0.1532	220	0.1380		
650	0.1547	240	0.1386		
690	0.1562	260	0.1402		
730	0.1570	280	0.1407		
770	0.1601	300	0.1415		
Run 41		320	0.1427		
		340	0.1437		
		360	0.1443		
		380	0.1452		
		400	0.1457		
		420	0.1465		
		440	0.1469		
		460	0.1472		
		480	0.1480		
		500	0.1486		
		520	0.1495		
		540	0.1501		
		560	0.1510		
		580	0.1517		
		600	0.1521		
		620	0.1522		
		640	0.1525		
720	0.1549				
760	0.1573				
800	0.1613				
840	0.1640				

TABLE XVI

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 34.4
WEIGHT PER CENT TITANIUM ALLOY

Run 43		Run 43 cont.		Run 45 cont.	
EI = 3.120 watts		EI = 3.120 watts		EI = 3.110 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
50	0.09685	592.5	0.21651	270	0.09498
70	0.09787	597.5	0.30203	310	0.09810
90	0.09741	602.5	0.44915	350	0.09929
110	0.09826	607.5	0.63227	390	0.10169
130	0.09952	612.5	0.41325	430	0.10304
150	0.10099	617.5	0.19066	470	0.10374
170	0.10186	635	0.21250	510	0.10420
190	0.10243	660	0.10063	550	0.10737
210	0.10182	680	0.09974	580	0.12580
230	0.10084	700	0.09885	595	0.13778
250	0.09966	720	0.09789	TRANSFORMATION	
270	0.09938	740	0.09671	640	0.12261
290	0.09893	760	0.09554	660	0.09948
310	0.09889	780	0.09557	680	0.09816
330	0.09972	Run 45		700	0.09680
350	0.09877	EI = 3.110 watts		720	0.09634
370	0.09882	T°C		750	0.09541
390	0.09942	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$		790	0.09427
410	0.10088	60	0.09502	830	0.09274
430	0.10230	80	0.09434	870	0.08932
450	0.10314	100	0.09532	900	0.08640
470	0.10369	120	0.09669	920	0.08695
490	0.10475	140	0.09762	Rerun of the β region	
510	0.10620	160	0.09754	680	0.09682
530	0.10957	180	0.09523	700	0.09573
545	0.11257	200	0.09471	720	0.09340
555	0.11741	220	0.09516		
565	0.12112	240	0.09597		
575	0.13263				
585	0.16226				

TABLE XVI (Continued)

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 34.4
WEIGHT PER CENT TITANIUM ALLOY

Run 45 cont.		Run 46 cont.		Run 48	
EI = 3.110 watts		EI = 3.094 watts		EI = 4.398 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
750	0.09236	830	0.09011	220	0.09812
790	0.09067	870	0.08844	260	0.09769
830	0.08961	Rerun of β region		300	0.09839
870	0.08605			340	0.09940
910	0.08464	680	0.09841	380	0.10131
		720	0.09501		
Run 46		760	0.09128	420	0.10270
		800	0.08679	460	0.10320
EI = 3.094 watts				500	0.10329
		840	0.08456	540	0.10442
T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	880	0.08338	580	0.11632
130	0.09399	Run 47		TRANSFORMATION	
170	0.09443	EI = 4.415 watts		660	0.10646
210	0.09493	T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$	700	0.09817
250	0.09644			740	0.09697
290	0.09794			780	0.09548
		100	0.09456	820	0.09325
330	0.09905	140	0.09317	860	0.09069
370	0.10052	180	0.09354		
410	0.10313	220	0.09469	Run 49	
450	0.10396	260	0.09634	EI = 4.398 watts	
490	0.10459			T°C	Cp $\frac{\text{cal}}{\text{gram}} \text{ } ^\circ\text{C}$
		300	0.09820		
530	0.10628	340	0.09941	80	0.09547
560	0.10728	380	0.10121	120	0.09380
590	0.12245	420	0.10251	160	0.09319
595	0.12838	460	0.10313	200	0.09365
TRANSFORMATION				240	0.09496
640	0.15559	500	0.10351		
670	0.10334	540	0.10466	280	0.09639
710	0.09983	580	0.11581	320	0.09748
750	0.09803			360	0.09872
790	0.09560			400	0.10099
				440	0.10206

TABLE XVI (Continued)

TRUE SPECIFIC HEAT VALUES OF A ZIRCONIUM - 34.4
WEIGHT PER CENT TITANIUM ALLOY

Run 49 cont.		Run 79	
EI = 4.372 watts		EI = 3.495 watts	
T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$	T°C	Cp $\frac{\text{cal}}{\text{gram } ^\circ\text{C}}$
480	0.10273	60	0.09515
520	0.10314	100	0.09362
560	0.10659	140	0.09401
		180	0.09416
		220	0.09479
TRANSFORMATION			
660	0.10528	260	0.09615
		300	0.08764
700	0.09720	340	0.09807
740	0.09610	380	0.09635
780	0.09568	420	0.09635
820	0.09400		
860	0.09248	460	0.10049
Rerun of β region		500	0.10398
690	0.09421	540	0.10728
730	0.09064	580	0.12285
770	0.08922	620	0.31808
810	0.08675		
		660	0.10640
850	0.08488	700	0.09950
890	0.08253	740	0.09756
		780	0.09613

TABLE XVII

TRANSFORMATION ENTHALPY DATA FOR IODIDE ZIRCONIUM

Run 18		Run 63		Run 65	
T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$
800	0.00	800	0.00	800	0.00
810	86.71	820	161.49	810	83.49
820	173.88	860	536.44	850	436.42
830	261.93	870	1238.23	860	558.40
840	351.81	880	1569.72	870	1130.42
850	446.15	900	1745.53	880	1607.66
855	498.73	920	1884.11	900	1788.59
860	565.57	940	2017.35	920	1926.97
865	724.44	950	2085.28	940	2058.82
870	1504.86			950	2127.02
875	1621.68				
885	1701.87	Run 64			
900	1811.99	T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$		
920	1954.28				
940	2093.17	800	0.00		
950	2161.52	840	327.16		
		860	533.94		
Run 62		870	1126.24		
T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	880	1529.39		
800	0.00	890	1622.71		
820	160.29	910	1760.80		
860	552.93	930	1891.98		
970	1444.61	950	2021.98		
890	1698.52				
910	1847.60				
930	1989.04				
950	2130.79				

TABLE XVIII

TRANSFORMATION ENTHALPY DATA FOR A ZIRCONIUM
- 0.881 WEIGHT PER CENT SILVER ALLQY

Run 15		Run 50		Run 52	
T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T °C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$
800	0.00	800	0.00	800	0.00
820	190.23	820	173.79	820	184.50
830	289.26	840	382.23	830	289.20
840	390.17	860	759.05	840	399.40
845	445.55	880	1568.12	850	540.34
850	507.61	900	1730.60	860	858.21
855	587.65	940	2009.57	870	1385.76
860	720.97	950	2078.28	880	1582.97
865	1035.80			900	1749.13
870	1285.44			920	1885.47
875	1443.67			940	2016.00
880	1541.93			950	2082.26
885	1609.79				
890	1666.83				
900	1750.80				
910	1822.66				
920	1889.07				
930	1954.35				
940	2019.31				
950	2082.54				

TABLE XIX

TRANSFORMATION ENTHALPY DATA FOR A ZIRCONIUM
- 5.37 WEIGHT PER CENT SILVER ALLOY

Run 32		Run 37	
T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$
800	0.00	800	0.00
810	98.36	810	93.81
815	164.17	820	234.06
820	295.12	825	525.41
825	824.63	830	989.63
830	1225.71	840	1361.70
840	1488.64	860	1643.28
860	1700.44	900	2051.28
880	1889.99		
900	2055.05		

TABLE XX

TRANSFORMATION ENTHALPY DATA FOR A ZIRCONIUM
-7.77 WEIGHT PER CENT INDIUM ALLOY

Run 54		Run 55		Run 56	
T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$
800	0.00	800	0.00	800	0.00
820	152.74	820	149.32	810	76.07
840	305.53	860	451.29	850	388.83
860	455.71	880	612.13	880	625.13
880	613.24	900	780.05	890	707.41
890	700.36	920	1056.83	910	942.32
900	792.20	940	1801.99	930	1520.73
910	899.37	960	2058.44	950	1975.99
920	1071.94			960	2073.75
930	1536.34				
935	1733.23				
940	1858.87				
950	1998.68				
960	2095.95				

TABLE XXI

TRANSFORMATION ENTHALPY DATA FOR IODIDE TITANIUM

Run 38		Run 39	
T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$	T°C	H-H ₈₀₀ $\frac{\text{cal}}{\text{g atom}}$
800	0.00	800	0.00
820	162.70	820	160.69
840	323.50	840	320.31
860	483.95	860	480.22
870	564.60	870	560.78
880	724.71	880	649.78
885	1398.99	885	1074.35
890	1647.04	890	1540.48
910	1808.36	900	1703.29
930	1945.90	920	1855.64
		930	1927.21

TABLE XXII

TRANSFORMATION ENTHALPY DATA FOR A ZIRCONIUM
- 34.4 WEIGHT PER CENT TITANIUM ALLOY

Run 43		Run 45		Run 46	
T°C	H-H ₅₀₀ $\frac{\text{cal}}{\text{g atom}}$	T°C	H-H ₅₀₀ $\frac{\text{cal}}{\text{g atom}}$	T°C	H-H ₅₀₀ $\frac{\text{cal}}{\text{g atom}}$
500	0.00	500	0.00	500	0.00
520	154.11	530	227.02	510	75.92
540	312.87	570	538.47	550	383.36
550	394.32	590	719.68	570	541.02
560	479.13	600	818.66	590	718.78
570	566.50	610	955.63	600	811.16
580	661.78	620	1326.10	610	918.24
590	778.34	630	1641.73	620	1105.66
595	856.11	650	1818.52	630	1621.67
600	964.59	670	1963.34	650	1846.74
605	1125.92	690	2106.34	690	2147.06
610	1353.03	700	2176.90	700	2219.71
615	1501.46				
620	1569.94				
650	1798.92				
670	1945.35				
690	2090.53				
700	2162.50				