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THE REACTION OF HYDROGEN WITH ZIRCONIUM-1 AND -25 w/o URANIUM ALLOYS

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THE REACTION OF HYDROGEN WITH ZIRCONIUM-1 AND -25 w/o URANIUM ALLOYS

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Hydrogen-absorption isotherms were measured over the range 535 to 835 C for zirconium-1 w/o and -25 w/o uranium alloys. X-ray diffraction studies were made over approximately the same temperature range for the zirconium-1, -25, and -50 w/o uranium alloys.

In general, the alloys resenble the zirconium-hydrogen system, modified by the presence of uranium. With 1 w/o uranium, the phase boundaries of the zirconium-hydrogen system are shifted to slightly lower hydrogen contents. With 25 w/o uranium, the first "two-phase" region shifts to a hydrogen content 20 a/o greater than in the zirconium-hydrogen system, while the second "two-phase" region is unchanged. The eutectoid temperature is increased from 547 to 601 C.

Heats of solution of hydrogen in the alloys were found to range from -25.9 to -47.9 kcal per mole for the 1 w/o alloy, and from -30.7 to -50.6 kcal per mole for the 25 w/o alloy.

The X-ray diffraction data support the interpretation that, as hydrogen is absorbed, the alloys break down to form uranium and zirconium, and the latter absorbs the hydrogen. The entire ternary isotherms could not be deduced from the data. However, three aspects appear certain: (1) the extent of the phase fields along the zirconium-hydrogen binary at 1 w/o uranium, (2) the existence of alpha zirconium, alpha uranium, and ZrH_x three-phase fields at low temperatures, and (3) the existence of fields containing beta uranium and ZrH_x at higher temperatures for both the 25 and 50 w/o alloys.

INTRODUCTION

This study has been concerned with the phase relationships in the ternary system zirconium-uranium-hydrogen. A high concentration of hydrogen atoms can be achieved by hydriding zirconium to compositions approaching ZrH_2. This property makes zirconium hydride a useful moderator for nuclear reactors, especially since the zirconium provides structural strength with low neutron cross section. A fueled moderator can be obtained by incorporating fissionable uranium in the zirconium hydride. With this concept of a fueled moderator in view, the absorption of hydrogen by two zirconium-uranium-alloy compositions was measured. The effect of a small amount of uranium on the zirconium-hydrogen system was determined with a 1 w/o uranium alloy. The effect of a relatively large uranium content was studied in the 25 w/o uranium alloy.

There is adequate information in the literature on the three binary systems involved. Libowitz, et al.,[1] has shown that uranium forms the single hydride, UH_3, at temperatures below 650 C. The zirconium-hydrogen system includes several hydride phases, of which the delta hydride, having a composition in the range $ZrH_{1.5}$ to

* References at end of text.

$ZrH_{1.7}$, is of the greatest interest for moderator purposes. The zirconium-hydrogen system has been described in numerous papers.[2-10] The uranium-zirconium system has also been studied in detail.[11] However, there has been only one reported study on the ternary system. Gulbransen and his associates[12,13] obtained data on the 50 w/o uranium alloy. Their chief concern was the possible corrosive effects of hydrogen on such alloys in a pressurized-water reactor.

In the present investigation, the hydrogen-absorption data have been supplemented by high-temperature X-ray diffraction. By this means the solid-state reactions indicated by the hydrogen-solubility data could be identified. Furthermore, X-ray examination of the samples at the absorption-isotherm temperature is desirable in a system where transformations can occur even on rapid cooling from elevated temperatures. The high diffusivity of hydrogen makes this system particularly susceptible to such changes, so quenching of samples was avoided in this work. Selected alloys with hydrogen contents near the terminal phases and the eutectoid composition were examined.

EXPERIMENTAL PROCEDURES

The hydrogen-absorption isotherms were measured over the temperature range 535 to 835 C for both the 1 w/o and 25 w/o uranium alloys. Nine alloy compositions were selected for X-ray study: zirconium-base alloys containing 1, 25, and 50 w/o uranium, each with 10, 30, and 50 a/o hydrogen. The atomic percentage of hydrogen was based on the zirconium portion alone in order that the results could be compared with the study of the zirconium-hydrogen system made by Vaughan and Bridge.[8] The 10 and the 50 a/o hydrogen contents correspond to positions near the terminal phases in the zirconium-hydrogen system, and the 30 a/o hydrogen addition approximates the eutectoid composition.

Materials and Fabrication Techniques

The zirconium used in this work was iodide metal and the uranium was center cut from biscuit stock. Both 1 w/o and the 50 w/o uranium alloy were double melted by consumable-electrode arc-melting, as part of large batches prepared for other studies. The 25 w/o uranium alloy was prepared by a tungsten-electrode arc-melting method. The alloys were hot rolled at 1500 F, cleaned, and cold rolled to a final thickness of 0.125 in.

Pure hydrogen for the isotherm determinations, and also for hydriding the alloys used in the X-ray study, was obtained by the thermal decomposition of uranium hydride. Tables 1 and 2 give the compositions of the alloys and the hydrides used in this program, as obtained by vacuum-fusion analysis and spectrographic analysis.

TABLE 1. COMPOSITION OF ZIRCONIUM-URANIUM ALLOYS PREPARED FOR THE STUDY

Constituent	Analyzed Impurity Content of Alloy Shown, ppm		
	Zirconium-1 w/o Uranium	Zirconium-25 w/o Uranium	Zirconium-50 w/o Uranium
Oxygen	360	443	311
Hydrogen	8	32	21
Nitrogen	10	20	30
Silicon	250	100	120
Iron	1500	400	600
Lead	10	2	2
Magnesium	5	30	3
Nickel	50	20	30
Aluminum	100	<10	10
Copper	100	60	80
Calcium	100	60	<2
Tungsten	N. d. (a)	<200	N. d.
Barium	10	<0. 2	3
Beryllium	5	<0. 2	<0. 2
Boron	1	10	0. 1
Phosphorus	N. d.	<200	N. d.
Manganese	30	2	5
Molybdenum	N. d.	10	N. d.
Vanadium	N. d.	<5	N. d.
Sodium	N. d.	<80	N. d.
Cobalt	500	<5	400
Cadmium	N. d.	<0. 2	N. d.
Chromium	20	10	10
Zinc	N. d.	40	N. d.
Tin	N. d.	50	N. d.

(a) N.d. indicates constituent not determined.

TABLE 2. HYDROGEN CONTENT OF HYDRIDED ALLOYS USED IN X-RAY DIFFRACTION STUDY

Uranium, w/o	Hydrogen Concentration, w/o	Hydrogen Concentration per Zirconium Atom, a/o
1	0. 127	10. 4
1	0. 505	31. 7
1	1. 05	49. 3
25	0. 10	10. 8
25	0. 38	31. 6
25	0. 77	48. 4
50	0. 061	10. 0
50	0. 285	34. 1
50	0. 515	48. 4

Apparatus

The hydrogen-absorption apparatus, shown in Figure 1, consisted of three self-contained units. The first unit provided a source of, and storage facilities for, pure hydrogen, which was obtained by the thermal decomposition of uranium hydride. The second unit provided precise metering of hydrogen at a known temperature, for delivery to the reaction system. The third unit was a constant-volume section in which the reaction of hydrogen with the zirconium-uranium alloy occurred at a controlled temperature (±3C). The equilibrium pressures of hydrogen were measured in this section also.

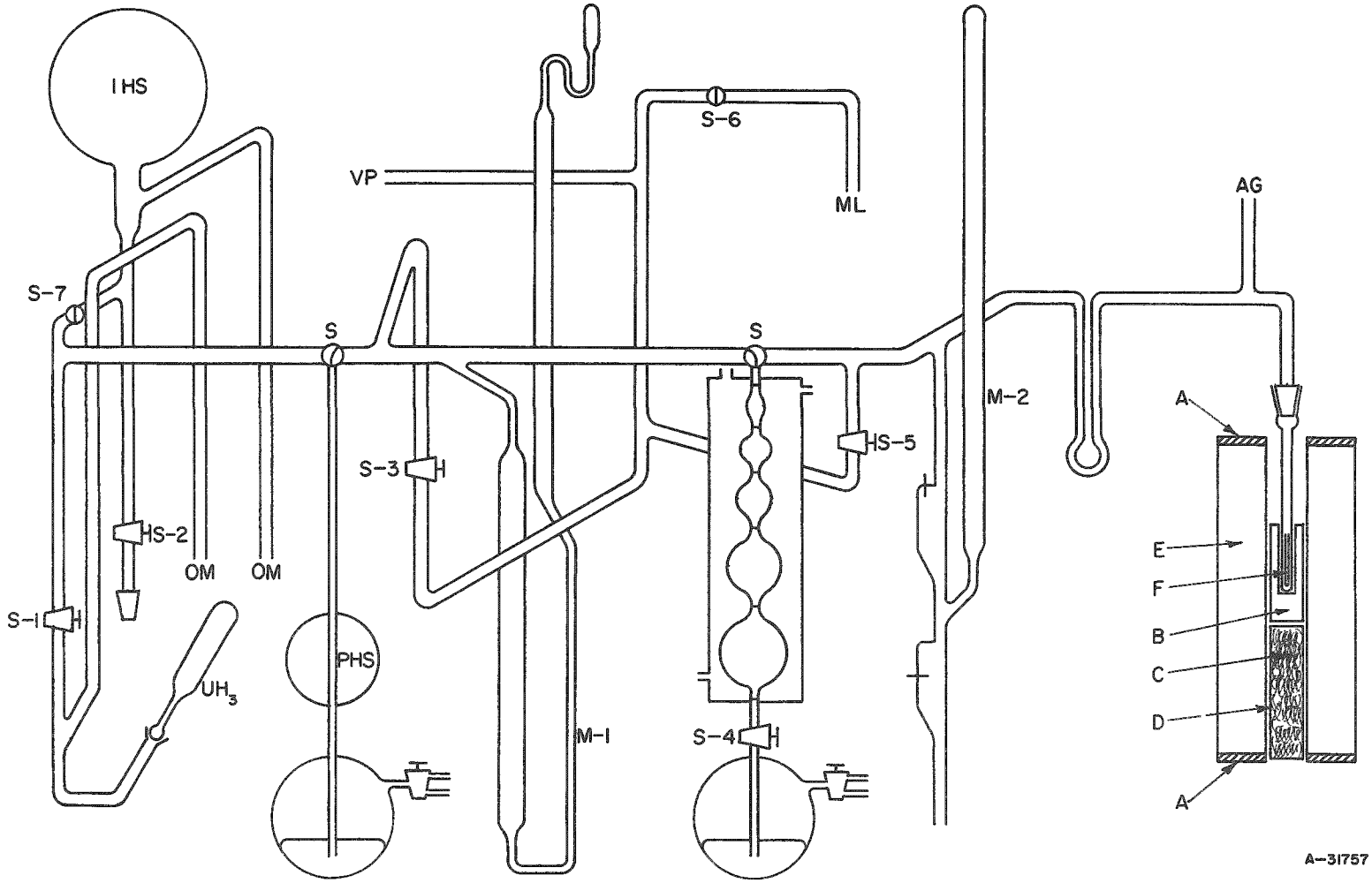
The X-ray studies were made with a high-temperature X-ray diffraction camera of Hume-Rothery design. This camera had a 9-cm diameter and employed the Straumanis film setting. A fine Chromel-Alumel thermocouple within the furnace cavity and adjacent to the sample served to measure and control temperature. The sample temperature was calibrated against the thermocouple emf through a series of lattice-constant measurements on pure silver.

Experimental Methods

The absorption of hydrogen by the zirconium-uranium alloys was measured isothermally, using the constant-volume section of the system. An Autovac gage was used to measure pressures below 2 mm, and a large-bore manometer was used for higher pressures. A cathetometer was employed for the manometer readings. Possible contaminants such as mercury and stopcock grease were excluded from the reaction vessel by means of a -78 C trap. The alloy samples were placed in an Inconel container to prevent possible reaction with the mullite tube in which the hydriding was effected.

At each temperature successive additions of hydrogen were made and the equilibrium pressures measured. Equilibrium was reached in minutes at temperatures above 700 C, but several hours were required at lower temperatures. Additions of hydrogen were continued until the amount of hydrogen absorbed per gram of zirconium approximated 60 a/o. The volume of hydrogen taken up by the sample was determined as the difference between that added and the volume remaining in the reaction system at equilibrium. Corrections were made for the differences in manifold temperatures encountered during the experiments.

For the X-ray work, "wire" samples were prepared by shearing 0.010-in. sheet of the desired uranium-zirconium-alloy composition, keeping the width as close to the thickness as possible. A small batch of these wires was then hydrided at 800 C to the desired hydrogen content along with a small block of the same alloy to bring the sample weight to a feasible value. The hydrided material of each composition was then sealed in an evacuated Vycor capsule and homogenized at 1000 C.



S-1 through S-7 - One-way stopcocks
PHS - Pure-hydrogen storage
IHS - Impure-hydrogen storage
M-1 and M-2 - Manometer

VP - To vacuum pumps
ML - To McLeod gage
AG - To Autovac gage
OM - Open-end manometer

Furnace Details
A - Transite ends
B - Stainless steel temperature-equalizing cylinder

C - Fiberfrax insulation
D - Alundum support tube
E - Insulation
F - Inconel capsule and specimen

FIGURE 1. HYDROGEN-ABSORPTION SYSTEM

Individual wire sections chosen for straightness and desirable cross-sectional shape were cut to desired length and etched in a nitric acid-hydrofluoric acid-water solution to remove the inevitable scale that occurs on closed heating. The bright sample was then rinsed in 1:1 nitric acid to remove any green deposit that might have formed during etching.

Each alloy was examined at temperature levels about 100 C apart, starting at either 400 or 500 C, and extending to 800 C. The 400 or 500 C level was preceded by room-temperature examination, and the sample was sometimes re-examined at room temperature after the elevated-temperature excursion. Each X-ray photogram was obtained by a 2-hr exposure to unfiltered nickel radiation.

The 800 C examination was seldom considered useful because of apparent reaction with the capillary wall. The diffraction photograms at that temperature level indicated the presence of uranium dioxide, cristobalite from devitrification of the silica capillary, and an unknown corrosion product. These effects were sometimes noted to a mild degree at 700 C also. In most cases of the 800 C examination, the silica capillary split open during exposure.

RESULTS AND DISCUSSION

The absorption-isotherm method provides a very useful approach to the study of a gas-solid system. Inflection points in the isotherms locate phase boundaries, and a plot of log P versus 1/T (Arrhenius plot) permits calculation of heats of solution and estimation of the eutectoid temperature. The shape of the isotherms depends only on those phases which affect the hydrogen absorption, rather than all phases present. Consequently, the isotherms in this study are treated with a view to the effect of uranium on the phase boundaries of the zirconium-hydrogen system. The actual phases present were then identified by high-temperature X-ray diffraction.

Zirconium-1 w/o Uranium Alloy

Isotherms for the 1 w/o uranium alloy were run at six temperatures, covering the range 534 to 802 C. The X-ray diffraction studies on this alloy were made at room temperature and from 500 to 800 C. The general effect of the addition of the uranium is to shift the phase boundaries of the zirconium-hydrogen system to slightly lower hydrogen percentages, as shown in Figure 2. The eutectoid temperature is also lowered from 547 to 541 C.

Hydrogen-Absorption Isotherms

The isotherms determined for the zirconium-1 w/o uranium alloy are shown in Figure 3. Solid solution of hydrogen in the alloy is represented by the initial portions

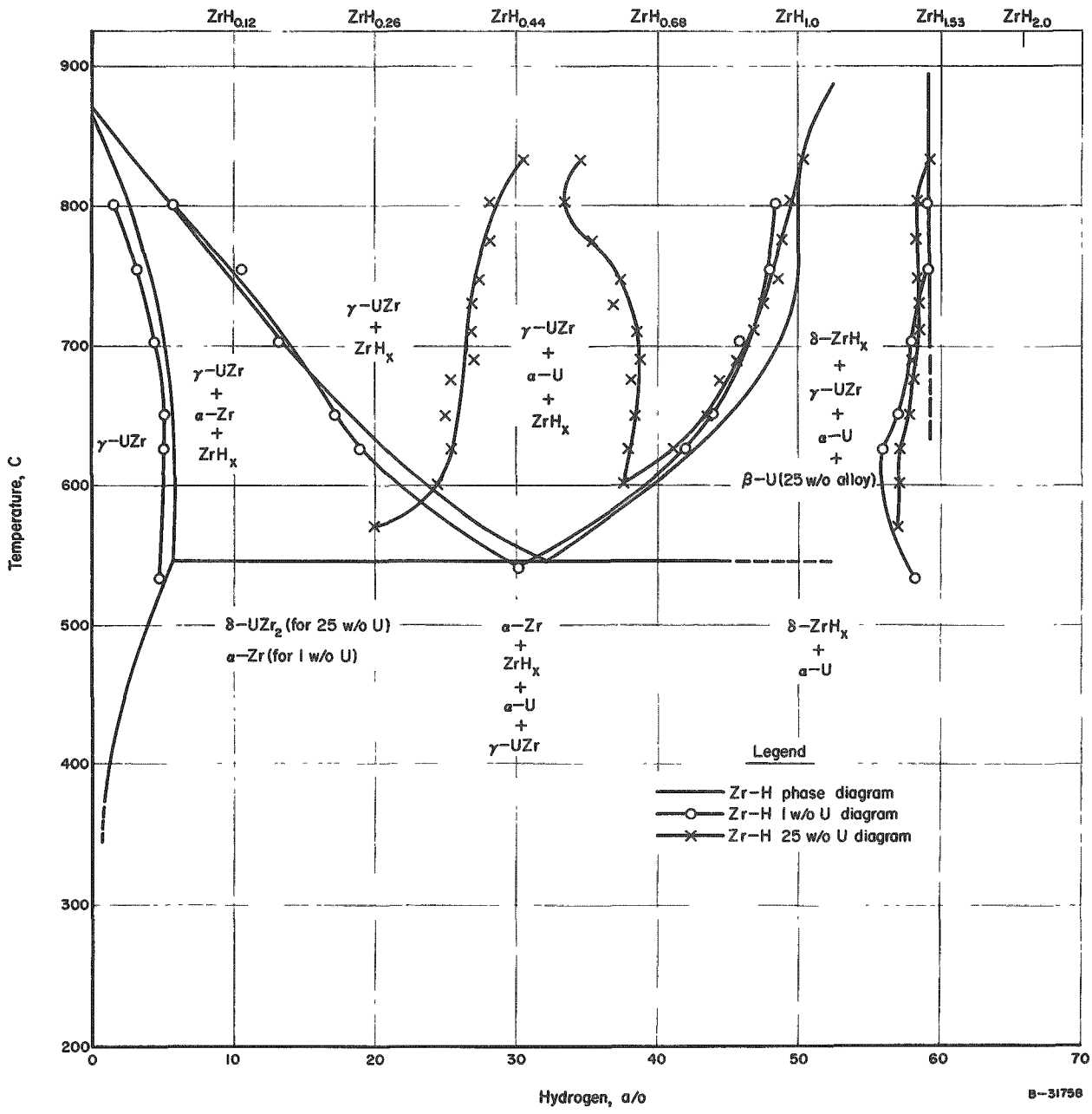


FIGURE 2. PHASE DIAGRAM OF THE ZIRCONIUM-HYDROGEN SYSTEM, WITH MODIFICATIONS PRODUCED BY THE SUBSTITUTION OF 1 w/o AND 25 w/o URANIUM

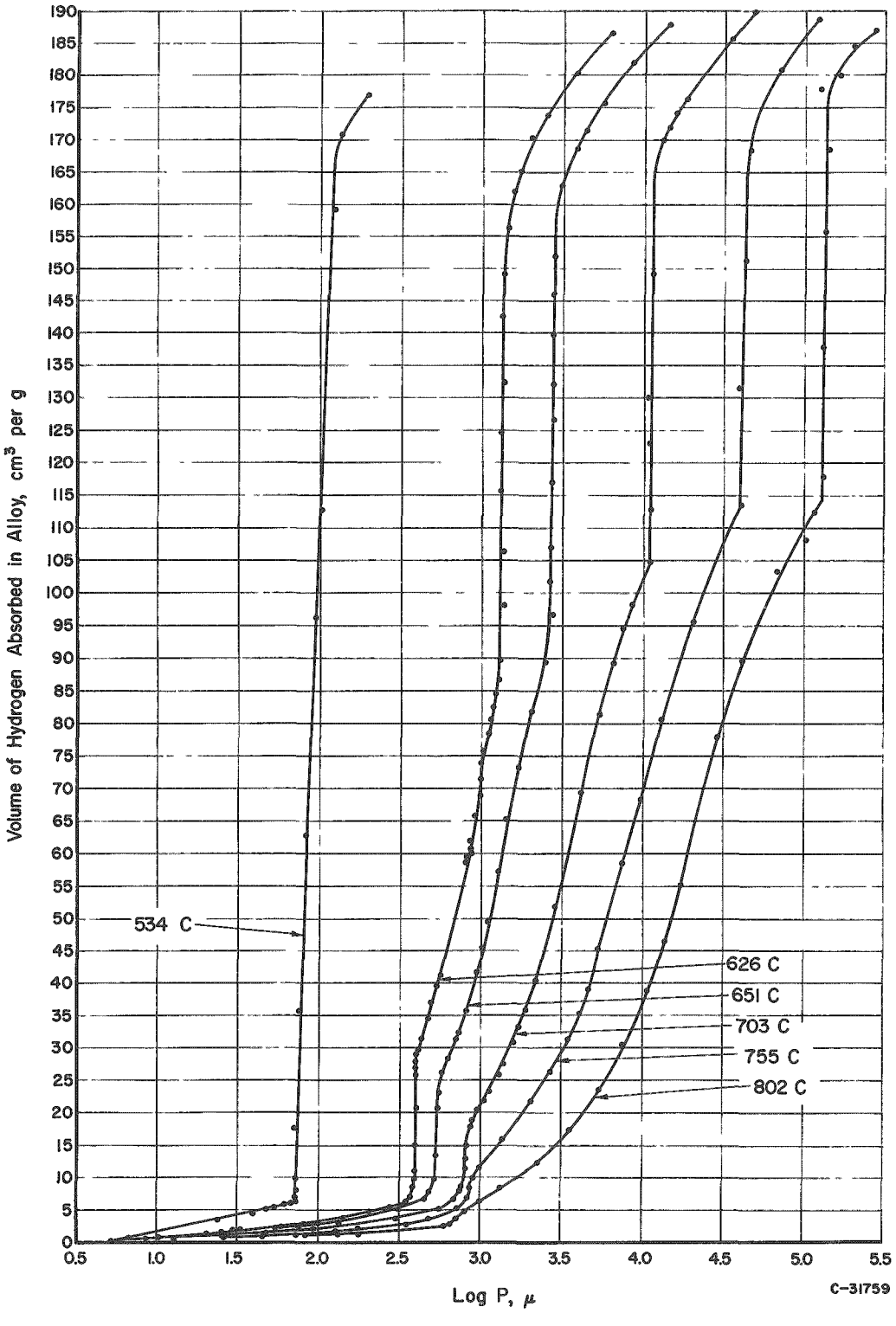


FIGURE 3. HYDROGEN-ABSORPTION ISOTHERMS FOR THE ZIRCONIUM-1 w/o URANIUM ALLOY

of all the curves, which show a rapid change of pressure with the volume of hydrogen absorbed. The inflection points of the curves represent phase boundaries, and the transition from alpha zirconium to a multiphase region is indicated by the first such point on each curve. The vertical portions of the curves, which indicate hydrogen uptake at constant pressure, show the extent of the multiphase regions as given in the phase diagram of Figure 2.

The isotherm at 534 C has a very sharp inflection, followed by an almost vertical portion, as the multiphase region is traversed. The slight change in pressure that does occur in the multiphase regions may be due to changes in lattice parameters of the zirconium and its hydrides, as noted by Vaughan and Bridge.[8] As these parameters change with hydrogen absorption, the dissociation pressure of the hydride phase will change also. The second inflection in the 534 C isotherm indicates the transition to the single hydrogen-absorbing phase, delta-zirconium hydride. Because this isotherm lies below the eutectoid temperature, only two phase boundaries are crossed.

The four isotherms at 626, 651, 703, and 755 C have similar shapes. After the pressure-sensitive initial portion, there is an inflection, followed by a short vertical portion. The multiphase region is delineated by the vertical section. The second inflection point is followed by another pressure-sensitive region, as hydrogen is taken up by a single phase. The second vertical portion represents another multiphase region, consisting of delta zirconium hydride, gamma UZr, and alpha uranium. The transition back to solid-solution formation is not as sharply defined as the other transitions. At the higher content of hydrogen, uranium precipitation from the alloy brings about changes in the alloy composition which affect the rate of hydrogen absorption.

The 802 C isotherm differs slightly from the others, in that the inflections at low hydrogen absorptions are not very pronounced. However, when the data are plotted on the phase diagram, a narrow multiphase region appears. Extrapolation indicates that above 840 C, this multiphase region would not exist. The remainder of the isotherm is the same as the others.

The phase boundaries which are indicated by these isotherms represent slight shifts from those of the zirconium-hydrogen system, and show that no unexpected change results from small uranium additions. The hydrogen-absorption data from which the phase boundaries were determined are summarized in Table 3.

X-Ray Diffraction Study

The X-ray examination of the 1 w/o alloy containing 10 a/o hydrogen showed that from room temperature to 600 C, alpha zirconium and traces of the cubic zirconium-hydride phase were present. The absence of the gamma solid solution of uranium and zirconium at 600 C was unexpected, since both the uranium-zirconium eutectoid at 593 C and the zirconium-hydrogen eutectoid at 547 C are below this temperature. This result was checked by a second X-ray examination and was found to be reproducible. However, at 700 C the sample did show the presence of the body-centered-cubic gamma solid solution. The value of a_o for this phase was found to be 3.62 A. The formation of the gamma solid solution between 600 and 700 C indicates that within this temperature range the solubility of hydrogen in alpha zirconium is exceeded. An unidentifiable phase, which has been designated as Unknown A, was detected in moderate intensity

TABLE 3. PHASE BOUNDARIES IN THE ZIRCONIUM-1 w/o URANIUM-ALLOY HYDRIDE SYSTEM

Phase Boundary	Hydrogen Absorption, cm^3 per g		Hydrogen, a/o in zirconium	Hydrogen Pressure, cm of mercury
	Alloy	Zirconium		
		802 C		
1	2.4	2.4	1.92	0.0614
2	7.6	7.6	5.82	0.132
3	114.0	115.0	48.35	13.3
4	176.6	178.4	59.21	14.8
		755 C		
1	4.5	4.6	3.61	0.078
2	14.5	14.6	10.62	0.116
3	112.5	113.6	48.04	4.0
4	176.9	178.7	59.26	4.65
		703 C		
1	5.9	5.9	4.58	0.075
2	18.6	18.8	13.27	0.086
3	103.4	104.4	45.94	1.12
4	168.5	170.2	58.08	1.19
		651 C		
1	6.7	6.8	5.24	0.053
2	25.6	25.8	17.35	0.057
3	95.9	96.8	44.07	0.285
4	162.0	163.6	57.11	0.285
		626 C		
1	6.7	6.8	5.24	0.0395
2	28.6	28.9	19.04	0.0405
3	88.6	89.5	42.15	0.137
4	156.0	157.6	56.19	0.140
		534 C(a)		
1	6.3	6.4	4.95	0.0073
2	--	--	--	--
3	--	--	--	--
4	170.8	172.5	58.4	0.0136

(a) Only two phase boundaries were detected at this temperature.

at 700 C. This same material was observed in several samples at 700 and 800 C, and is believed to be a surface contamination resulting from a reaction with the silica container. This unknown phase remains when the sample is cooled to room temperature.

With 30 a/o hydrogen, the alloy consists of alpha zirconium and the face-centered-cubic zirconium hydride (delta hydride) at room temperature and at 500 C. At 600 C the body-centered-cubic gamma solid solution appeared, as the result of reaction of alpha zirconium and hydride above the eutectoid temperature. Alpha zirconium was still detectable, indicating either incomplete reaction, or that the sample was below the solvus surface on the alpha-zirconium side of the ternary eutectoid. At 720 C the reaction was complete, only the gamma solid solution remaining in evidence. The lattice constant of the gamma phase increased from 3.62 A at 10 a/o hydrogen to 3.66 A at 30 a/o, indicating that hydrogen enters interstitially into the body-centered-cubic zirconium lattice.

Results for the 50 a/o hydrogen alloy also indicated that a eutectoid exists between 500 and 600 C. At 600 C three phases were observed: gamma solid solution, delta zirconium hydride, and alpha zirconium, the latter probably as the result of incomplete reaction. At 700 C the sample was above the solvus temperature in the single-phase gamma field. The lattice constant increased from 3.66 A at 30 a/o hydrogen to 3.698 A at 50 a/o hydrogen.

Table 4 shows the intensities of the phase patterns observed for the 1 w/o uranium alloy. The intensity is indicative of the quantity of a given phase that is present, but the amount present is not necessarily proportional to the intensity.

Heats of Solution

The heats of solution of hydrogen in the alloy were determined from the Arrhenius plots of the isotherm data (log P versus 1/T). Figure 4 shows such a plot for the 1 w/o alloy. The average ΔH values, calculated from the slopes of the isochores, range from -25.9 to -47.9 kcal per mole for the various regions of the phase diagram. Table 5 presents the data for the five regions that are delineated by the isotherms which are comparable to the following parts of the zirconium-hydrogen system: (1) alpha solid solution, (2) alpha-beta two-phase region, (3) beta solid solution, (4) beta-delta two-phase region, and (5) delta solid solution.

The eutectoid temperature as determined from the Arrhenius plot is 541 C, as compared to 547 C for the zirconium-hydrogen system.

Zirconium-25 w/o Uranium Alloy

Thirteen hydrogen-absorption isotherms covering the range 572 to 835 C were run on the 25 w/o uranium alloy. The X-ray diffraction patterns were taken at room temperature and at 500, 600, 700, and 800 C. The effect of the uranium on the zirconium-hydrogen system in this case is appreciable below 40 a/o hydrogen. The two-phase region of the zirconium-hydrogen system, which consists of alpha plus beta zirconium hydride, is shifted to much higher hydrogen contents, as shown in Figure 2. Similarly, the eutectoid shifts to a higher atomic percentage of hydrogen, and its temperature boundary rises from 547 to 601 C.

TABLE 4. PHASES DETECTED BY X-RAY DIFFRACTION EXAMINATION OF THE HYDRIDED ZIRCONIUM-1 w/o URANIUM ALLOY

Hydrogen Content, a/o in zirconium	Temperature, C	Intensities of Phase Patterns Observed[a]			
		α-Zr	γ-UZr	ZrH_x	Unknown A
10	26	S	0	VVF-VF	0
10	500	S	0	VVF-VF	0
10	600	S	0	VVF-VF	0
10	700	S	M	0	MF
10	800	0	0	0	S
30	27	S	0	M	0
30	500	VS	0	MS	0
30	600	MS	S	F	0
30	720	0	VS	0	0
30	815	0	VS	0	MF
50	28	M	0	MS	0
50	515	M	0	S	0
50	600	M	MF	M	0
50	700	0	VS	0	0
50	815	0	S	0	MF

(a) S = strong, M = medium, F = faint, V = very, 0 = absent.

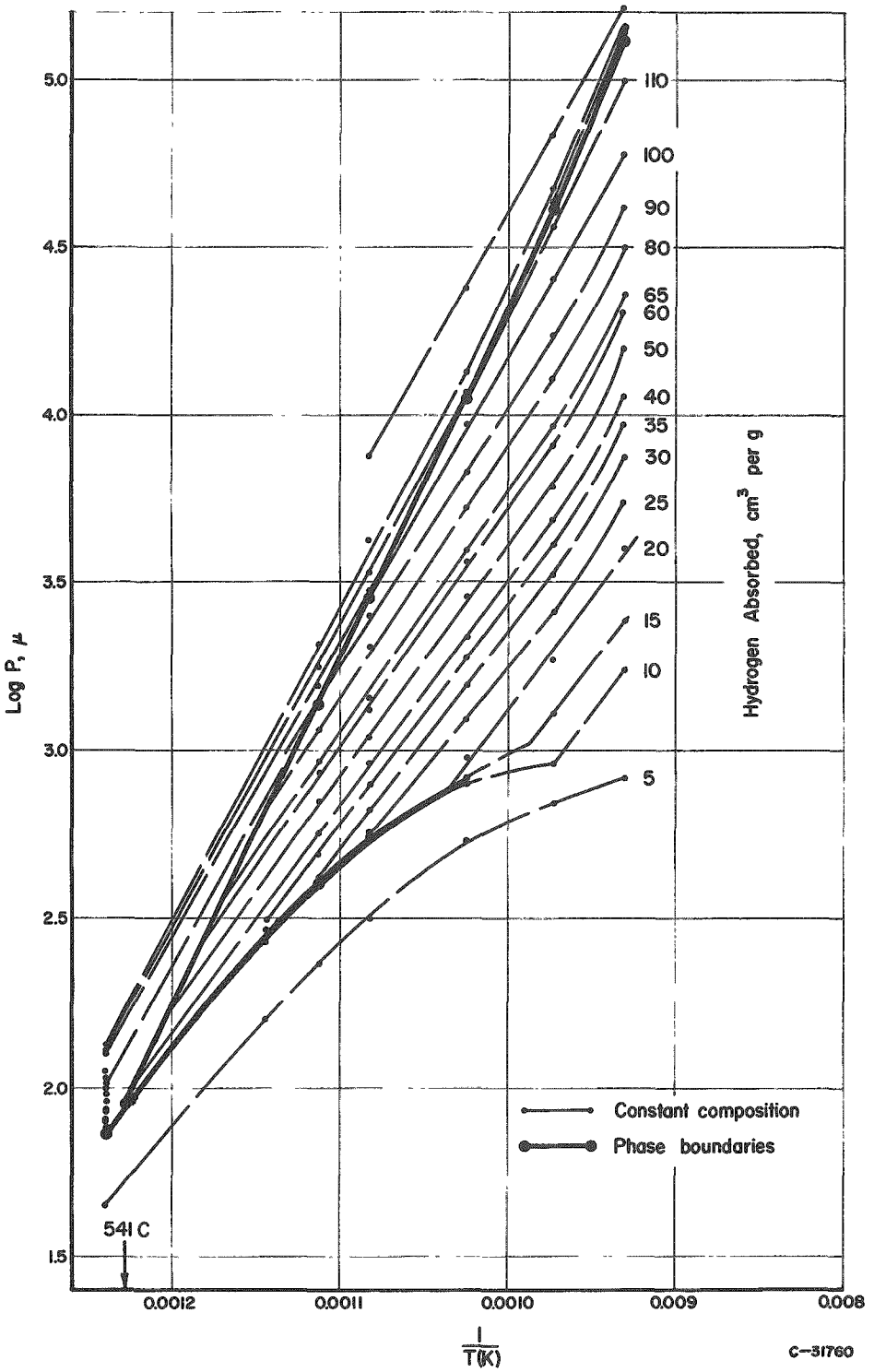


FIGURE 4. ARRHENIUS PLOT FOR THE ZIRCONIUM-1 w/o URANIUM ALLOY

TABLE 5. HEATS OF SOLUTION OF HYDROGEN IN THE ZIRCONIUM-1 w/o URANIUM ALLOY

Zirconium-Hydrogen Phase	Volume of Hydrogen Absorbed, cm^3 per g	$-\Delta H$, kcal per mole	Average $-\Delta H$, kcal per mole
Alpha solid solution	5	25.9	25.9
Alpha-beta two-phase region	10	30.5	29.5
	15	29.4	
	20	30.1	
	25	27.9	
Beta solid solution	30	29.6	33.4
	40	30.7	
	50	31.8	
	60	32.5	
	65	33.0	
	80	32.5	
	80	34.6	
	90	35.9	
	100	39.9	
Beta-delta two-phase region	110-140	47.9	47.9
Delta solid solution	170	42.4	41.2
	180	40.0	

Hydrogen-Absorption Isotherms

The isotherms for the 25 w/o uranium alloy constitute a family of curves closely resembling each other. Seven of the 13 isotherms which were measured are plotted in Figure 5. Isotherms intermediate between each adjacent pair were omitted to reduce the complexity of the plot. The isotherms at 572 C (not shown) and at 601 C are the only ones that do not cross four phase boundaries. The data for all the isotherms determined for the 25 w/o alloy are summarized in Table 6.

When the isotherms for the 25 w/o uranium alloy are compared with those for the 1 w/o alloy, significant differences are noted. The region of solid solution of hydrogen in alpha zirconium is much broader in the 25 w/o alloy. The multiphase region is much more clearly defined in the 25 w/o alloy. The first two inflection points are shifted to higher values of hydrogen content. This shift makes the area between the second and third phase boundaries decidedly narrower, because the third and fourth phase boundaries, encompassing the region in which delta zirconium hydride predominates, are practically unchanged from the 1 w/o alloy.

The vertical portions of the 25 w/o alloy isotherms, representing hydrogen uptake at constant pressure, show practically no variation of pressure, whereas there was a slight drift to higher pressure in the case of the 1 w/o alloy.

X-Ray Diffraction Study

The 25 w/o uranium alloys presented more experimental difficulties than the 1 w/o alloys, because large grain size in the alloys resulted in spotty diffraction patterns. Consequently, relative intensities were more difficult to estimate, and it became necessary to examine additional samples to be sure that the entire pattern was detected.

With 10 a/o hydrogen, at room temperature, gamma solid solution of uranium and zirconium was present. In addition, there was detected a phase which was either delta UZr_2 or an omega-type phase with the same structure. (Omega phase occurs as the single phase in quenched zirconium-molybdenum and zirconium-niobium alloys and in quenched zirconium-uranium alloys containing 10, 15, 25, or 75 w/o uranium. In zirconium-uranium alloys it decomposes into alpha zirconium and delta UZr_2 upon annealing. The standard diffraction patterns of omega and delta are almost identical.) The diffraction pattern observed for these samples indicated omega rather than delta, but an exact differentiation could not be made. At 500 C this phase was the only one observed, except for faint evidence of zirconium hydride. However, at 600 C, the omega phase had decomposed to alpha zirconium, alpha uranium, and gamma solid solution. At 700 C, only alpha zirconium and gamma solid solution were found. The phases detected in the 10 a/o hydrogen alloy were what would be expected from the uranium-zirconium phase diagram.

The 30 a/o hydrogen alloy at room temperature and at 515 C contained no omega or delta phase. Instead, alpha zirconium, alpha uranium, and zirconium hydride were found. At 620 C, these same three phases were present, plus the gamma phase. At 720 and 815 C, the gamma phase was split into two portions having the lattice constants 3.68 and 3.64 A, respectively. A new phase, which has been designated as Unknown B also appeared at 720 C. These results were verified in three different samples at the

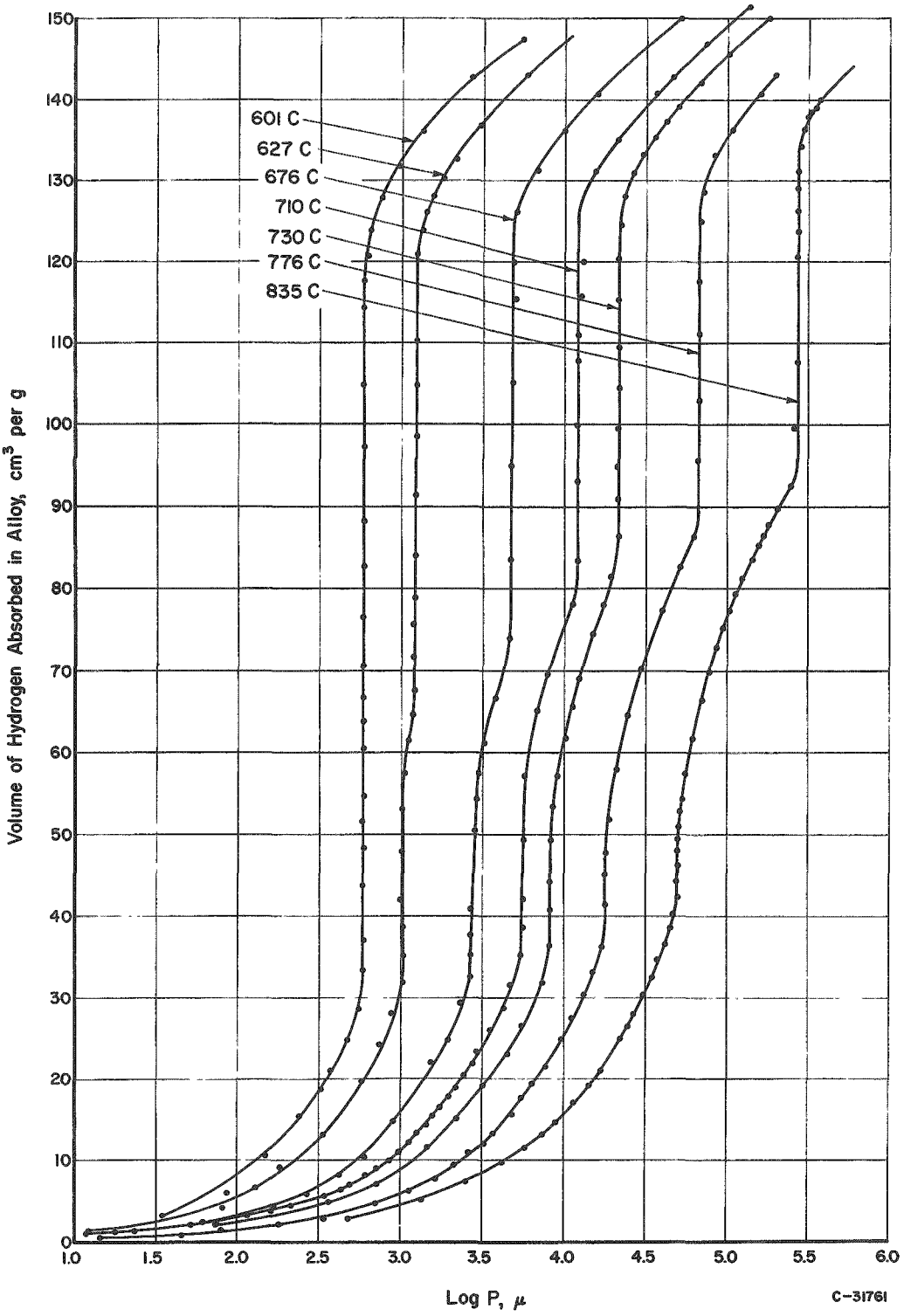


FIGURE 5. HYDROGEN-ABSORPTION ISOTHERMS FOR THE ZIRCONIUM-25 w/o URANIUM ALLOY

TABLE 6. PHASE BOUNDARIES IN THE ZIRCONIUM-25 w/o URANIUM-ALLOY HYDRIDE SYSTEM

Phase Boundary	Hydrogen Absorption, cm^3 per g		Hydrogen, a/o in zirconium	Hydrogen Pressure, cm of mercury
	Alloy	Zirconium		
		835 C		
1	40.6	54.2	30.59	5.00
2	48.8	65.0	34.61	5.00
3	93.8	125.1	50.44	26.85
4	136.1	181.5	59.63	28.30
		803 C		
1	36.5	48.6	28.35	2.90
2	46.9	62.5	33.73	2.90
3	89.9	119.8	49.37	12.90
4	130.2	173.6	58.55	13.25
		776 C		
1	36.2	48.3	28.20	1.84
2	50.8	67.7	35.53	1.84
3	88.3	117.7	48.93	6.70
4	129.8	173.1	58.48	6.75
		748 C		
1	35.2	46.9	27.64	1.06
2	55.8	74.4	37.71	1.19
3	87.2	116.2	48.61	3.36
4	130.0	173.3	58.51	3.50
		730 C		
1	33.9	45.2	26.90	0.84
2	54.0	72.0	36.95	0.84
3	84.3	112.4	47.78	2.19
4	129.6	172.9	58.45	2.26
		716 C		
1	34.3	45.3	26.93	0.634
2	56.1	74.8	37.84	0.634
3	84.5	112.7	47.84	1.484
4	129.6	172.8	58.44	1.520

TABLE 6. (Continued)

Phase Boundary	Hydrogen Absorption, cm^3 per g		Hydrogen, a/o in zirconium	Hydrogen Pressure, cm of mercury
	Alloy	Zirconium		
		710 C		
1	34.0	45.3	26.93	0.556
2	58.1	77.5	38.68	0.588
3	81.2	108.3	46.85	1.24
4	131.0	174.7	58.71	1.35
		690 C		
1	34.6	46.1	27.28	0.395
2	58.8	78.4	38.95	0.398
3	77.3	103.1	45.62	0.670
4	127.5	170.0	58.04	0.692
		676 C		
1	31.6	42.2	25.55	0.273
2	57.5	76.7	38.43	0.301
3	73.5	98.0	44.36	0.455
4	128.4	171.3	58.22	0.507
		650 C		
1	31.0	41.3	25.15	0.161
2	57.7	76.9	38.50	0.164
3	71.8	95.7	43.78	0.235
4	127.3	169.7	58.00	0.248
		627 C		
1	31.6	42.2	25.55	0.104
2	56.5	75.3	38.00	0.104
3	65.0	86.7	41.37	0.122
4	124.0	165.0	57.32	0.127
		601 C[a]		
1	30.0	40.0	24.56	0.059
2	--	--	--	--
3	--	--	--	--
4	123.2	164.2	57.21	0.059
		572 C[a]		
1	23.2	30.9	20.09	0.024
2	--	--	--	--
3	--	--	--	--
4	123.1	164.1	57.18	0.024

(a) Only two phase boundaries were detected at these temperatures.

700 C level. It is suspected that the two different gamma phases were of high hydrogen and low hydrogen contents, respectively. The high-hydrogen phase is probably the enlargement of the gamma field of the zirconium-hydrogen eutectoid, and the phase of low hydrogen content is probably a similar effect at the zirconium-uranium eutectoid. Unknown B may be a complex uranium-zirconium hydride.

The 50 a/o hydrogen alloy showed alpha uranium and zirconium hydride at room temperature and at 515 C. At 600 C, the gamma phase also appeared. At 700 C, weak patterns of beta uranium and zirconium hydride were observed, together with a strong gamma phase pattern.

The unidentified pattern designated as Unknown A in the 1 w/o uranium alloy also appeared at 815 C with the 25 w/o alloy. It is believed to be due to reaction of the sample with the quartz capsule. Some faint patterns of UO_2 were also observed, particularly with the 50 a/o hydrogen alloy. Slight surface contamination with oxygen would account for the UO_2. Table 7 shows the X-ray diffraction results in terms of phase-pattern intensities.

Heats of Solution

The heats of solution of hydrogen in the 25 w/o uranium alloy, as determined from an Arrhenius plot of the isotherm data, do not differ greatly from those found with the 1 w/o uranium alloy. Table 8 gives the ΔH values for the five regions of the isotherms, all of which have counterparts in the zirconium-hydrogen system. The values found for corresponding regions are a few kilocalories per mole higher for the 25 w/o uranium alloy. The range of values in this case is from -30.7 to -50.6 kcal per mole. The Arrhenius plot from which the values were obtained is presented as Figure 6. The eutectoid temperature determined from the plot is 601 C, as compared to 541 C for the 1 w/o uranium alloy, and 547 C for the zirconium-hydrogen system.

Zirconium-50 w/o Uranium Alloy

This system was examined by Gulbransen and his associates[12,13], but their X-ray studies were made on quenched samples, so there has been uncertainty as to the exact nature of the phases present at the higher temperatures. Consequently, X-ray diffraction patterns of the 50 w/o uranium alloy were taken over the range 500 to 800 C.

A 50 w/o uranium alloy free of interstitial impurities such as hydrogen would consist of the intermetallic compound UZr_2, designated as the delta phase. This was also found to be the case for the alloy with 10 a/o hydrogen at room temperature. However, at 500 C medium-faint patterns of alpha zirconium and alpha uranium appeared, although a large amount of the delta UZr_2 remained. At 600 C, the delta phase disappeared completely, and the alpha-zirconium and alpha-uranium phases were correspondingly increased in intensity. Despite the difficulty in distinguishing between small amounts of gamma and delta phase (the delta pattern resembles merely a superlattice pattern of the gamma), a minor amount of gamma phase was detected.

TABLE 7. PHASES DETECTED BY X-RAY DIFFRACTION EXAMINATION OF THE HYDRIDED ZIRCONIUM-25 w/o URANIUM ALLOY

Hydrogen Content, a/o in zirconium	Temperature, C	Intensities of Phase Patterns Observed[a]								Lattice Parameter of Cubic Gamma Phase, A
							Unknown			
		α-Zr	α-U	ω or δUZr_2	γ-UZr	ZrH_x	A	B	UO_2	
10	26	0	0	S	MS	0	0	VVF	VVF	3.56
10	500	VF	0	S	0	VF	0	VVF	0	--
10	600	MS	VF	0	S	0	0	VF	0	3.631
10	700	VF	0	0	S	0	0	VVF	0	3.639
10	815	0	0	0	S	0	M	MF	0	3.615
30	26	S	F	0	0	M	0	0	0	--
30	515	S	F	0	F	M	0	VVF	0	--
30	620	MS	M	0	MF	MS	0	F	0	3.68
30	720	0	F	0	S and M[b]	VVF	VF	M	0	3.68 and 3.64
30	815	0	0	0	S and M[b]	0	VS	0	0	3.68 and 3.64
50	26	0	F	0	0	S	0	VVF	0	--
50	515	0	F	0	0	S	0	0	VF	--
50	600	0	MF	0	M	MS	0	VVF	VVF	3.68
50	700	0	F[c]	0	S	MF	0	VVF	VF	3.712

(a) S = strong, M = medium, F = faint, V = very, 0 = absent.
(b) Duplex gamma phase observed.
(c) Beta uranium rather than alpha uranium.

TABLE 8. HEATS OF SOLUTION OF HYDROGEN IN THE ZIRCONIUM-25 w/o URANIUM ALLOY

Zirconium-Hydrogen Phase	Volume of Hydrogen Absorbed, cm^3 per g	$-\Delta H$, kcal per mole	Average $-\Delta H$, kcal per mole
Alpha solid solution	10	28.4	30.7
	15	30.6	
	20	31.3	
	30	32.5	
Alpha-beta two-phase region	40-50	35.2	35.2
Beta solid solution	60	37.9	39.1
	70	39.2	
	80	40.3	
Beta-delta two-phase region	100-120	47.6	50.6
		53.7	
Delta solid solution	130	45.6	47.2
	130	49.8	
	140	46.3	

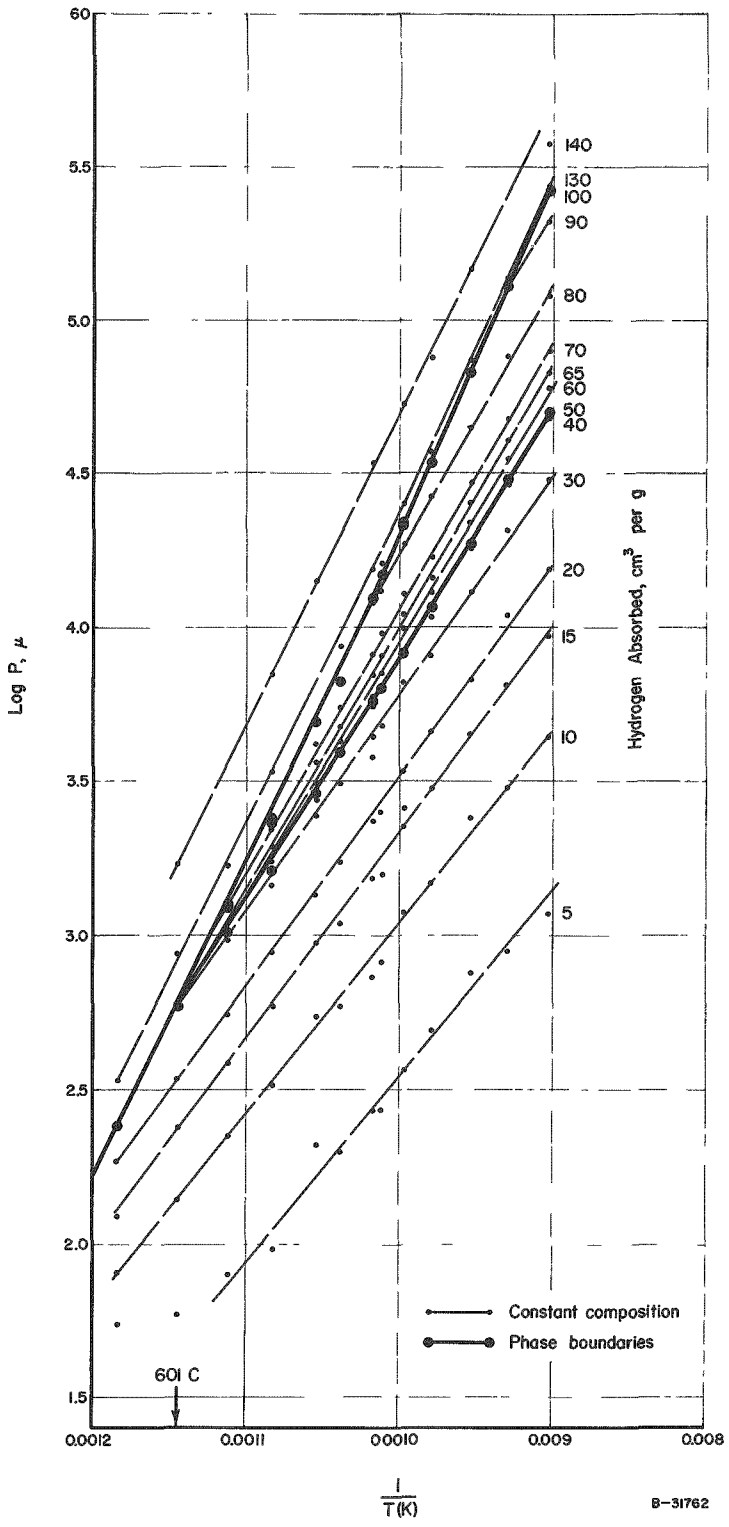


FIGURE 6. ARRHENIUS PLOT FOR THE ZIRCONIUM-25 w/o URANIUM ALLOY

At 700 C, the gamma phase predominated, but a considerable quantity of alpha zirconium was also present, with possibly a trace of alpha uranium. The results for this alloy show that hydrogen at a concentration of 10 a/o (based on the zirconium present) reduces the stability of the delta compound. At the higher hydrogen concentrations the delta phase was not observed at all. These facts are a verification of similar results obtained by Gulbransen and associates.[13] The effect of hydrogen on the stability of the delta phase is therefore comparable to the effect of oxygen and nitrogen on the uranium-zirconium system.[14] The delta phase is possibly a nonequilibrium structure produced by the transformation of the gamma phase.

At 30 a/o hydrogen the alpha zirconium intensity was reduced almost to zero, the alloy consisting essentially of alpha uranium and the face-centered-cubic zirconium hydride (delta hydride). These phases were present from room temperature to 620 C. The disappearance of the alpha zirconium phase indicates that the hydrogen combines with the zirconium in preference to uranium. At 720 C, the alpha uranium and most of the hydride had reacted to form the gamma solid solution, indicating a eutectoid between 600 and 700 C for this alloy.

With 50 a/o hydrogen, alpha uranium and the face-centered-cubic zirconium hydride (delta hydride) are the only phases present from room temperature through 620 C. The relative intensity of the hydride pattern was greater than in the 30 a/o hydrogen alloy. At 720 C, the alpha uranium apparently was replaced by beta uranium. The gamma solid solution was not observed in this alloy.

The unidentified phase, previously designated as Unknown A, appeared in the 50 w/o uranium alloy also. Unknown A again was noted at 720 and 800 C, while extremely faint evidence of other unknowns was seen at all temperatures. Some UO_2 was observed with the 30 and 50 a/o hydrogen samples. Table 9 gives the relative intensities of the phase patterns observed for the 50 w/o uranium alloy.

TABLE 9. PHASES DETECTED BY X-RAY DIFFRACTION EXAMINATION OF THE HYDRIDED ZIRCONIUM-50 w/o URANIUM ALLOY

Hydrogen Content, a/o in zirconium	Temperature, C	Intensities of Phase Patterns Observed[a]								Lattice Parameter of Cubic Gamma Phase, A
							Unknown			
		α-Zr	α-U	δ-UZr_2	γ-UZr	ZrH_x	A	Other	UO_2	
10	28	0	0	VS	0	0	0	VVF	0	--
10	500	MF	MF	S	0	VF	0	VVF	0	--
10	600	M	MS	0	MF	0	0	VVF	0	3.61
10	700	M	VF	0	S	0	M	VVF	0	3.608
30	28	0 to VF	MS	0	0	M	0	VVF	0	--
30	515	0 to VF	M	0	0	M	0	VVF	F	--
30	620	0 to VF	M	0	0	MS	0	VF	F	--
30	720	0	0	0	MS	F	VF	VF	F[b]	3.696
30	815	0	0	0	M	0	MS	VF	S	3.710
50	28	0	MF	0	0	MS	0	VF	0	--
50	515	0	M	0	0	S	0	0	VF	--
50	620	0	M	0	0	S	0	0	VVF	--
50	720	0	MF[c]	0	0	S	VF	VF	VF	--
50	800	0	0	0	0	S	S	VF	F	--

(a) S = strong, M = medium, F = faint, V = very, 0 = absent.

(b) Faint patterns for both UO and UO_2 were obtained.

(c) Beta uranium.

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