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THE REACTION OF HYDROGEN WITH A 50 WEIGHT
PERCENT ALLOY OF URANIUM AND ZIRCONIUM BETWEEN
542°C and 798°C

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ABSTRACT

Hydrogen sorption isotherms have been measured between 542°C and 798°C at pressures of 0.001 to 70cm of Hg. The isotherms give the terminal solubility of hydrogen in the initial alloy phases and the limiting compositions of new phases containing hydrogen. Values for the heat of solution of hydrogen at all hydrogen concentrations are presented. A comparison of the data with that of the hydrogen-zirconium system indicates that, above a minimum hydrogen concentration, the alloy breaks down to give uranium and zirconium. The alloy then behaves, to some extent, as the hydrogen-zirconium system modified by the presence of uranium. X-ray diffraction studies give support to this interpretation.

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INTRODUCTION

Uranium-zirconium alloys are of importance in the construction of nuclear power reactors. In a pressurized water reactor the alloys may be subject to corrosion in the presence of hydrogen.

This paper will consider the nature of the reaction with hydrogen over the temperature range of 542°C to 798°C and for pressures of 10^{-2} mm of Hg to 1 atm. of hydrogen. Another paper from this laboratory¹ will consider the reaction at temperatures of 300°C to 600°C and for low pressures of hydrogen.

The phase diagram of the uranium-zirconium system is not completely defined in the region of the 50 weight percent alloy. At high temperatures the alloy exists in a body centered cubic gamma phase. At low temperatures a stable epsilon phase is obtained, of uncertain structure, in the composition region of approximately 62-78 atom percent zirconium.²⁻⁶ The lower limit varies with the oxygen content.⁷ The temperature and composition ranges of the two-phase $\gamma + \epsilon$ region is not accurately known.^{7,8} It is stated to be about 590 to 600°C⁷ although it may be appreciably lower.⁸

The reactions of uranium and zirconium with hydrogen have been studied. Uranium forms one hydride, UH_3 , at temperatures below

650°C.⁹ The zirconium-hydrogen system is rather complex with several hydride phases being formed.¹⁰⁻¹⁵

EXPERIMENTAL PROCEDURE*

A. Adsorption System

The uptake of hydrogen by the alloy samples was measured, isothermally, using a conventional constant-volume adsorption system. A large-bore manometer was used for high pressure measurements and a Pirani gauge below 1mm pressure. The alloy sample was placed in a Nichrome** container to avoid contamination by silica from the mullite furnace tube. Mercury and stopcock grease were excluded from the furnace by a trap cooled to -78°C.

At each sample temperature successive, accurately known, hydrogen volumes were admitted to the sorption system and the equilibrium pressures were measured. Less than 5 minutes was necessary for equilibration above 650°C, but at lower temperatures several hours were required. The "dead space" volume of the sorption system was measured at each isotherm temperature using helium gas. The volume of gas sorbed by the sample was obtained by subtracting that in the gas phase from the total volume added to the system. The volume in the gas phase was appreciable at all pressures above 10^{-1} cm.

B. X-ray Samples

In order to remove samples for X-ray analysis, the sampling device, shown in Figure 1, was used. The main alloy sample was

* A detailed account is contained in an appendix.

** Registered trade mark of Driver-Harris Company, Harrison, N. J.

wrapped in Nichrome foil and placed in the furnace zone. A small sliver of alloy, approximately $2 \times 0.02 \times 0.02$ cm., was fastened to one end of a 28 B & S Gauge, Nichrome wire, using fine platinum wire. Two slivers were normally inserted with the main specimen. The isotherm was measured and at each composition of interest a sliver was raised magnetically to the cold zone, giving a quench to -78°C in less than a second.

For X-ray diffraction analysis iron radiation was used together with a Unicam 9cm. camera. Specimens for examination in a high temperature X-ray camera were sealed in silica capillaries under high vacuum.

C. Uranium-Zirconium Alloy Samples

The alloy was supplied by Westinghouse Atomic Power Division. It contained $49.7 \pm 0.15\%$ uranium and $50.1 \pm 0.15\%$ zirconium (weight percent). Spectroscopic analysis gave the following impurities in weight percent.

$$\text{Si} < 0.07 : \text{Mn} < 0.03 : \text{Fe} < 0.01$$

The hafnium content was less than 0.005% and oxygen 0.05 - 0.075%, based on the analyses of the constituent metals.

Specimens were cut from 5 mil sheet and abraded with polishing papers from grade 1/0 through 4/0 under purified kerosene. The specimens were cleaned with petroleum ether and absolute alcohol, evacuated to better than 10^{-7} cm* and carefully outgassed at 800°C . Each specimen was used for a number of isotherm measurements being heated to 800°C in vacuo for at least 3 hours between experiments. The specimens were cooled from 800°C and held at the isotherm temperature for several hours before admitting hydrogen.

* Pressures are quoted in centimeters of mercury throughout the paper.

D. Accuracy

Isotherms were usually repeated using different specimens. Reproducibility was within the experimental error. Desorption points, at high temperatures, reproduced the sorption isotherms, provided sufficient time was allowed for equilibration. At temperatures below 600°C the equilibrium gas pressures were too low to permit desorption in a reasonable time. The estimated errors are as follows:

Temperature	0.25°C variation in a run	± 5°C absolute value
Volume sorbed	± 0.5%	
Pressure	0.01 - 76 cm.	+0.01 cm. with manometer
	1 x 10 ⁻³ - 1 x 10 ⁻² cm.	+5%, with Pirani gauge
	1 x 10 ⁻² - 1 x 10 ⁻¹ cm.	+10%, with Pirani gauge

RESULTS

A. Sorption Isotherms

1. 542 and 562°C Isotherms

Figure 2 shows isotherms for hydrogen sorption in the alloy. The sorption is plotted in units of ml./g. as a function of pressure in cm. of Hg. A value of 83.9 ml./g. on the figure corresponds to the formula $U_{0.28} Zr_{0.72} H_{1.00}$, i.e., 1 gram atom of oxygen per gram atom of uranium plus zirconium.

The initial pressure sensitive part of the isotherms is for the process of solid solution of hydrogen in the alloy. Figure 3 shows a Sieverts' plot of the square of the concentration versus pressure for the 562°C isotherm. A linear relation is observed which confirms Sieverts' law for solid solution of hydrogen in the alloy. The vertical portion in Figure 3 corresponds to hydrogen uptake at constant equilibrium pressure and is identical to that at the same pressure, in the 562°C isotherm of Figure 2. The function $N_N/2 - N_H$ is used for plotting the concentration of hydrogen. Here N_H is the number of gram atoms of hydrogen per gram atom of uranium plus zirconium. The value 2 results from the assumption of two interstitial sites for hydrogen, per metal atom.

A terminal solubility of 3.2 atom percent of hydrogen at 562°C is found from Figure 3. This is in reasonable agreement with the results observed by Gulbransen, Andrew, and Ruka¹ using a different method.

The shape of the isotherms is not dependent on the total number of phases present, but only on those phases which directly affect the hydrogen sorption. Therefore, in the following discussion we shall refer to the solid phases only, and specifically to those sorbing hydrogen. For example, a "two-phase" region will exhibit a constant hydrogen pressure, at constant temperature.

The isotherms in Figure 2 have "two-phase" regions, but the pressure increases slightly with the volume of gas sorbed. Clearly the system is not as simple as was assumed in the above discussion. This pressure variation may be caused by the presence of impurities, by additional phases which absorb only a small volume of hydrogen or by changes in composition of the principal phases. The question is fully discussed in a later section of this report.

Above the "two-phase" region the pressure increases rapidly to 60-70cm., on both isotherms, with no apparent deviation from a smooth curve, in a similar way to the curves in Figure 9. It is important to emphasize that, at high pressure, the greater fraction of each additional dose remains in the gas phase; small changes in the sorbed volume cannot be accurately measured. Therefore, discontinuities in the isotherms, produced by phase changes, might not be observed.

2. Isotherms at 580 and 594°C

The initial portions of the curves shown in Figure 4 are very similar to those in Figure 1, for lower temperatures, indicating that the first hydrogen sorption is again by solid solution.

The small step at 1.1×10^{-2} cm. pressure, on the 580°C isotherm, was observed in the accurate isotherm measurements and was

reproducible. In other experiments, used in obtaining samples for X-ray analysis, the step only developed after 12-24 hours. On these latter specimens, points taken at 2 hour intervals followed a smooth curve up to the "two-phase" region. The development of the step appears to be the production of a new phase and is a slow process, possibly depending on the presence of sufficient nuclei. Following this step, sorption occurs smoothly to a "two-phase" region. This intermediate sorption does not obey Sieverts' law and is therefore unlikely to be a simple solid solution process.

The 594°C isotherm also contains a large section, between the initial solid solution region and the pronounced "two-phase" region, in which the mechanism of sorption is not clear. A discontinuity at about 3.5×10^{-2} cm. pressure may indicate a small "two-phase" region.

The "two-phase" and higher pressure regions of the isotherms at 580 and 594°C are closely comparable with those in Figure 1 at lower temperatures.

3. Isotherms from 622.5 to 798°C

The curves shown in Figure 5, 6 and 7 have a common form and will be discussed as a group. With the exception of the curve at 622.5°C, the initial part of each isotherm obeys Sieverts' law. Two examples are given in the lower part of Figure 8. The hydrogen is therefore present in solid solution. The heat of solution is obtained from Arrhenius plots, at constant hydrogen content. From five different hydrogen concentrations an average value of -32.7 ± 1.7 Kcal./mol. is calculated. The terminal solubility of hydrogen in the phase is almost constant, at 11.6 atomic percent over the temperature range studied.

The lowest part of the curve at 622.5°C does not obey Sieverts' law and there is no well defined "two-phase" region below 0.1 cm. pressure. A comparison of the isotherms at 580, 594 and

622.5°C suggests that they occupy a transition region between the two isotherms at 542 and 562°C and the series from 649 to 798°C.

At 649°C and above, the solid solution phase is followed by a "two-phase" region. At temperatures close to 649°C the sorption in this region occurs at almost constant pressure, but at the higher isotherm temperatures this is no longer the case. Thus, for the 798°C isotherm the pressure increases continuously, in the "two-phase" region and it is impossible to distinguish a junction between this region and the following "single-phase" region, which is assumed to be present, by analogy with the 649°C isotherm.

Assuming that the first "two-phase" region is of identical composition between 649°C and 798°C, the decomposition pressure of the new phase will be established at the junction between the solid solution and first "two-phase" region at each temperature. An Arrhenius plot of these pressures is shown in Figure 10. The heat of solution of hydrogen in the first "two-phase" region is -36.4 Kcal./mol.

The production of a second "two-phase" region is sharply marked in all isotherms from 622.5 to 798°C. A heat of solution of hydrogen, in the second "two-phase" region, of -53.9 Kcal./mol. is obtained from the Arrhenius plot shown in Figure 10. It is significant to note that the corresponding decomposition pressures, from the single "two-phase" region obtained in isotherms below 600°C, fall on the same curve as the higher temperature data from the second "two-phase" region. This indicates that this "two-phase" region is identical throughout the temperature range investigated.

To examine the "single-phase" region which must exist between the "two-phase" regions, Sieverts' plots of the isotherms at 693.5 and 742°C are shown in Figure 8. The lower part shows the low pressure sorption on large scale. The upper part includes data from the first "two-phase" region and pressures. Following the uptake of hydrogen at constant pressure in the first "two-phase" region, a distinctly non-linear portion occurs. At 693.5°C this gives way to an

approximately linear approach to the second "two-phase" region. At 742°C even this cannot be distinguished. Thus, as the temperature is increased, the identities of the "single-phase" and "two-phase" regions appear to merge.

The upper regions of all the isotherms were obtained to 60-70cm. pressure. The results shown in Figure 9 are typical.

4. Sorption of Hydrogen by Zirconium

The sorption of hydrogen on pure zirconium was studied at 798°C. To facilitate direct comparison with the uranium-zirconium alloy at this temperature, the two plots, shown in Figure 7, are based on equal weights of zirconium.

At low pressure region of the zirconium-hydrogen isotherm is shown in the inset. The solubility of hydrogen in the initial phase is very low and is followed by a small discontinuity. This may be interpreted as a two-phase region. With further uptake of hydrogen a steady pressure increase occurs which cannot be identified as either a two-phase region or solid solution. At approximately 60 ml. of hydrogen/g. a two-phase region is observed, followed by a smooth pressure increase to 70cm. The curve is similar to data published by previous workers^{12,13} except that the data of Hall et.al.¹² is approximately 10% to low at high pressures.¹³

B. Phase Diagram For The Uranium-Zirconium-Hydrogen System

The isotherm data may be used to obtain a tentative phase diagram for the UZr alloy/hydrogen system. In obtaining the upper limits of the "two-phase" regions, for the 622.5 to 798°C isotherms, it is particularly advantageous to examine the Arrhenius plots, obtained at constant hydrogen sorption, across the complete series of isotherms. The temperature limits of the linearity of each plot indicate the limits of "single" and "two-phase" regions. In addition the variation of the heats of solution for the appropriate phases is

obtained as a function of volume of hydrogen sorbed. The data is collected in Table 1. It is significant to note that the values obtained for the solid solution in each single phase are constant with variation of the volume sorbed. In the "two-phase" regions the ΔH values increase continuously with the volume sorbed; only the limiting values are tabulated. This suggests that the nature of the "two-phase" regions changes, as reflected by the rise in equilibrium gas pressure with increasing sorption.

The phase diagram is shown in Figure 11. The uncertainty of each phase boundary is shown by the length of the lines. The composition of each phase, as obtained by X-ray analysis of quenched specimens, is shown. It is obvious that the diagram is incomplete being plotted only on the basis of the reaction of hydrogen with the alloy. The quantity of the uranium phase, for example, is undetermined.

C. X-ray Analysis of the Alloy

The evidence for the identity of the phases is obtained by analysis of quenched specimens. The validity of the analysis, therefore rests on the assumption that the high temperature structure is retained on cooling. In order to test the method, a specimen of uranium-zirconium was quenched from 800°C, using a low helium pressure to give good thermal conduction between the specimen and the walls of its container. The X-ray diffraction pattern gave the results shown in Tables 2 and 3. The principal lines are those of the δ -phase of the uranium-zirconium alloy and no trace is found of the ϵ -phase, which is stable at temperatures below 600°C. Some trace lines are detected which possibly result from the quenching procedure. The method is evidently satisfactory for this rather difficult quench.

In a further attempt to confirm the analysis, obtained on quenched specimens, X-ray diffraction patterns were measured in a

Table 1

 ΔH VALUES FOR HYDROGEN SORPTION BETWEEN 622.5 AND 798°C

<u>Volume of Hydrogen (ml./g.)</u>	<u>Phase</u>	<u>$-\Delta H$ (Kcal./mol.)</u>	<u>Average $-\Delta H$ (Kcal./mol.)</u>
2		32.6	
4		31.9	
6	Solid Solution	33.0	32.7
8		31.6	
10		32.7	
12.5	1st two-phase	35.0	
30.0		38.5	
35		40.5	
38		40.0	
40	Solid Solution	39.1	40.0
42		40.3	
45		40.0	
46		40.3	
55	2nd two-phase	52.4	
80		55.0	
85		51.7	
86	Solid Solution	45.6	47.3
90		44.6	

high temperature camera.* A specimen, containing hydrogen, was examined at 800°C. The diffraction pattern was considerably different from that previously obtained at room temperature, by quenching the same specimen. Some evidence was obtained which indicates that the difference between these patterns arises from a secondary effect, the contamination of the specimen on heating at 800°C in contact with silica. Thus the high temperature X-ray diffraction pattern was almost identical with that of several quenched specimens, obtained in experiments at 798°C, from samples showing abnormally low hydrogen sorption. These specimens, which had accidentally been in contact with glass fragments during the measurements, were powdered and re-examined. The powder analysis corresponded to that of specimens showing normal hydrogen sorption, at the same equilibrium pressure. It seems certain that contamination, originating at the surface, decreased the total hydrogen sorption. The X-ray diffraction analysis of the sliver is characteristic of the surface atomic layers, while the powdered specimen includes a major contribution from the uncontaminated bulk sample.

As it was not possible to obtain X-ray patterns at high temperatures we cannot be sure that all the phases reported in the alloy are retained from the isotherm temperature. For example, no β -zirconium has been observed in the alloy or in pure zirconium quenches; the low temperature α -zirconium was always identified. The identity of the phases reported is subject to confirmation with high temperature studies.

To determine that the quenched material was homogeneous, several slivers were powdered, after X-ray diffraction examination,

* We are indebted to R. M. Jones and A. Taylor of the Technology Dept., Research Laboratories, for obtaining the high temperature X-ray diffraction patterns.

Table 2

QUENCH OF UZr ALLOY IN HELIUM

Temperature (°C)	ϵ - UZr	Phases δ - UZr	α - Zr	X ^a
571	S		W	W
599	S		S	M
625	S		S	M
645	(S) ^b	(S) ^b	W	W
799		S	W	VW

Note: S, M and W are relative intensities: V - Very

(a) X is a cubic phase, $a_0 \approx 4.665$

(b) Some lines of ϵ -phase, but δ -phase probably predominant.

Table 3

X-RAY DIFFRACTION PATTERN OF 50 WEIGHT % UZr,
QUENCHED FROM 800°C IN 1mm PRESSURE OF HELIUM

α -Zr ^a	$\frac{d_{hkl}}{\gamma$ -UZr ^b	x^c	I/I max. (Visual)
2.818			1
		2.693	tr
2.591			tr
	2.521		10
2.476			2
		2.333	tr
	1.783		7
		1.649	tr
1.627			tr
1.473			tr
	1.456		9
		1.407	tr
1.378			tr
1.360			tr
		1.347	tr
	1.261		5
	1.1276		6
1.043		1.043	3 - diffuse
	1.0294		6

- a. Hexagonal phase with a_o and c_o parameters about 0.67% higher than pure α -Zr^o ($a_o = 3.254$, $c_o = 5.181$)
- b. γ -UZr B.C. Cubic phase, $a_o \approx 3.566$
- c. Identified only as a F.C. Cubic phase with $a_o \approx 4.665$

and a second pattern obtained. The patterns were identical, with slight intensity variations, with one exception which is noted in the text.

X-ray analysis of quench specimens of the pure alloy are shown in Table 2. Due to the overlap of many lines, positive identification is not always possible. For example, the pattern of ϵ -UZr is nearly identical to γ -UZr, of the same composition, but has additional lines. Therefore, γ -phase may be undetected in the presence of ϵ -phase. At 644°C, the relative intensities of the specific ϵ -phase lines indicate that this is a minor phase compared to the γ -phase. Weak lines of a cubic phase, X, appear frequently in many patterns, independent of the presence of hydrogen; the phase has not been identified.

From the data we conclude that above 644°C, the γ -phase is predominant. In a range including 624 and 600°C both ϵ -UZr and α -Zr are present and at 574°C, the principal phase is ϵ -UZr.

2. X-ray Analysis of Alloy Specimens Containing Sorbed Hydrogen

X-ray specimens were obtained from the initial portions of the isotherms. At 562 and 580°C, X-ray patterns of samples 1 and 5 are indistinguishable.* The principal phase is ϵ -UZr with minor traces of α -Zr and the cubic phase, X. This agrees well with the X-ray pattern of the pure alloy at 571°C (Table 2) and gives confirmation that this part of the curves involves the solid solution of hydrogen in the ϵ -UZr phase.

A sample (No. 17, Table 4) from the initial part of the 798°C isotherm gave an X-ray pattern of γ -UZr and traces of the cubic phase, X. This indicates the presence of a solid solution phase. Good

* Analyses of all hydrogen/UZr specimens are assembled in Table 4.

Table 4

X-RAY ANALYSES OF UZr ALLOY CONTAINING HYDROGEN

Sample	Composition Atom % H	Temperature (°C)	ϵ -UZr	δ -UZr	α -U	α -Zr	δ -ZrH _x	ϵ -ZrH _x	X
1	2	562	S			W			W
2	24	562		S	S	M	S		
3	39	562		S	S	M	S		
4	54	562			S		S, δ - or ϵ -		
5	2	580	S			M			W
6	4	580		?	M	S			M
7	7	580		S	M	S			W
8	11	580		?	M	S			W
9	19	594			M	S			VW
10	21	594		S	M	M			VW
11	38	580		S	S	?	S		
12	35	594		S	S	?	M		
13	10	622.5		S	M	S			VW
14	37	622.5		M	S	M	M		
15	50	622.5		M	S	M	S		W
16	56	622.5		M	M			S	W
17	5	798		S	?				VW
18	15	798		S	S			M	
19	28	798		S	S			S	
20	32	798		M	S			S	
21	38	798		M	S			S	
22	46	798		M	S		S		
23	52	798			S			S	VW

Note: 1. Symbols are as in Table 2
 2. The α -Zr phase may contain up to 2% U in solid solution

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Arrhenius plots are obtained for this phase between 649 and 798°C, from which we conclude that δ -phase solid solution must predominate. The ϵ -UZr detected in a quench of the pure alloy from 645°C (Table 2) is probably a minor trace formed during quenching.

The main "two-phase" region below 594°C and the upper "two-phase" region above that temperature are shown to be identical on the basis of an Arrhenius plot (Figure 1). This conclusion is confirmed by X-ray analyses on specimens 2,3 (562°C, Figure 2), 11,12 (580°C, and 594°C, Figure 4), 14 (622.5°C, Figure 5) and 22 (798°C, Figure 7). All specimens contain δ -UZr, α -U and the cubic δ -zirconium hydride.¹⁰ One minor discrepancy is noted in the analysis of specimen 11, at 580°C. An X-ray pattern from the sliver does not contain lines of the δ -hydride. However, a pattern from the powdered specimen shows the hydride, in agreement with the samples at other temperatures. The discrepancy between bulk and surface material is not readily explained.

A detailed consideration of the "two-phase" region indicates some important questions which require further X-ray studies, at isotherm temperature. First, at 562°C, the ϵ -UZr phase initially present is completely replaced by the δ -UZr phase at the beginning of the "two-phase" region. The addition of hydrogen above the terminal solubility may render the ϵ -UZr phase unstable in favor of the δ -UZr phase. Second, at temperatures above 654°C, two distinct "two-phase" regions appear. In the detailed X-ray diffraction study at 798°C the δ -UZr phase was detected, as a major component, in both "two-phase" regions. This discrepancy may be due to either inadequate quenching, or to the extreme complexity of the X-ray diffraction patterns making positive identification difficult.

To identify the phases present above the second "two-phase" region samples were examined at several temperatures. X-ray diffraction studies showed that all the specimens contain α -U and either δ - or ϵ -zirconium hydride. It appears that a transformation occurs from δ - to ϵ -hydride, as the pressure of hydrogen is increased, the

critical concentration depending on the temperature. This phenomenon has been observed in the zirconium-hydrogen system.¹⁰ Thus at 622.5°C, sample 15 (82.2 ml. H₂/g., 0.3 cm. pressure) contains δ -zirconium hydride, and sample 16 (107.3 ml. H₂/g., 14.3 cm. pressure) contains ϵ -zirconium hydride. Sample 23 (89.3 ml. H₂/g., 24.9 cm. pressure) extracted at 798°C and lying well above the "two-phase" region contains ϵ -zirconium hydride. At 564°C, sample 4 (98.2 ml. H₂/g., 1.1 cm. pressure) is again well above the "two-phase" region, but contains both ϵ - and δ -zirconium hydride phases.

To summarize, the transformation from δ - to ϵ - phase occurs near ZrH_{1.6} at 564°C, between ZrH_{1.35} and ZrH_{1.75} at 622.5°C and below ZrH_{1.45} at 798°C.

An X-ray diffraction analysis of the pure alloy quenched at 599 and 625°C (Table 2) suggests the presence of a transition region between ϵ - and γ -UZr. This is in agreement with the complex isotherms found between 580 and 622.5°C. At 580°C (Figure 4) specimens were obtained in the region of the minor discontinuity. Sample 6 was obtained 2 hours after admitting a gas dose and was not at equilibrium. The sample has an X-ray pattern identical with No. 8, obtained at equilibrium above the discontinuity, and contains α -Zr, and α -U. Specimen 7 was also at equilibrium and contains α -Zr, a minor amount of α -U and strong lines of γ -UZr.

These results, at 580°C, may be tentatively interpreted in the following way. Above the terminal solubility of hydrogen, in the ϵ -phase, the alloy is split into the components, α -U and α -Zr. At certain concentrations near the terminal solubility it is possible to reprecipitate the alloy in a γ -UZr-phase, but this process can be slow, possibly due to the absence of nuclei. At slightly higher concentrations α -Zr and α -U are the stable phases.

The 594°C isotherm shows some similarities to that at 580°C. Above the ϵ -solid solution phase, the alloy splits into α -Zr and α -U (specimen 9). γ -UZr is apparently obtained (specimen 10) above the

discontinuity.

From the 622.5°C isotherm only one analysis is available at low hydrogen concentration. Specimen 13 contains γ -UZr, and α -Zr and α -U. The analysis is similar to that of the pure alloy at 625°C (Table 2). Further X-ray studies are necessary for detailed consideration of the isotherm.

The first "two-phase" region at 798°C (Figure 7) was examined using specimens 18 to 21. The X-ray patterns are complex and phase identification is particularly uncertain. The samples all indicate the presence of α -U, γ -UZr and the ϵ -zirconium hydride. It is not possible to draw any conclusions regarding the changes in concentration of these phases. The fact that γ -UZr is still a major component in sample 21, where the "two-phase" region is presumably complete, cannot be explained. Similarly, the identification of the ϵ -zirconium hydride is in great doubt at low hydrogen concentrations. It must be concluded that further high temperature X-ray diffraction studies are necessary.

3. X-ray Analysis of Zirconium

A number of samples were obtained from pure zirconium at 798°C. The analysis are presented in Table 5. Specimen 24 contains

Table 5

X-RAY ANALYSES OF ZIRCONIUM CONTAINING HYDROGEN AT 798°C

Sample	Composition Atom %H	α -Zr	Phases δ -Zr H _x	ϵ -Zr H _x
24	37	S	S	
25	46		S	
26	50	S		S
27	56	S		S

Note 1. Symbols are as in Table 2.

2. The α -Zr phase may contain up to 2% uranium

α -Zr and the cubic δ -Zirconium hydride, while specimen 25 is pure δ -hydride. Sample 26 and 27, from the two phase region, are α -Zr, and the tetragonal ϵ -hydride. These analyses do not coincide with the results of Vaughan and Bridge¹¹ for comparable concentrations, although we obtain similar X-ray patterns. The main points of interest are that sample 25 is identified as a single phase region while 24 is definitely two-phase. In addition, the δ -zirconium hydride phase disappears at the upper two-phase region, (specimens 26 and 27) being replaced by a phase of similar structure to α -Zr. It is significant to note that in obtaining the isotherm, the rate of establishment of equilibrium for this two-phase region was extremely slow compared with all other parts of the curve. Possibly the transformation of δ -hydride to α -Zr is responsible for the slow rate of reaction.

Due to the fact that transformations may occur, even in a rapid quench, it is doubtful if the X-ray diffraction results discussed here are those existing at 798°C. The interpretation of the equilibrium data is therefore uncertain. According to Vaughan and Bridge,¹¹ working with a high temperature camera, β -Zr should have been detected in all our specimens.

DISCUSSION

The isotherms for hydrogen sorption facilitate the detection of phases occurring in the alloy-hydrogen system. The phase boundaries are sharply defined at each point where addition of hydrogen produces a second phase. However, the phase boundary occurring at the termination of a "two-phase" region, to a "single-phase" region formed as a result of further hydrogen sorption, is not so well defined. This may be due, in part, to the complexity of the system. For example, the precipitation of uranium from the alloy changes the composition of the alloy phase and thus influences the hydrogen uptake.

Before discussing the hydrogen sorption by the alloy, it is useful to examine the effect of hydrogen on the pure component metals. The sorption of hydrogen by uranium is negligible under the conditions of temperature and pressure used in this investigation.⁹ Thus, precipitation of uranium from the alloy should result in an inert phase, in so far as direct sorption by the uranium is concerned.

In contrast the sorption of hydrogen by pure zirconium is considerable. The isotherm at 798°C, shown in Figure 7, exhibits a steady increase in pressure, with sorption, up to the two-phase region at 11 cm. pressure. This region has been interpreted^{11,13,15} in terms of the phase changes:

The position of the phase boundaries, suggested by previous workers, varies considerably. Ells and McQuillan¹⁵ locate a two-phase region between approximately $\text{ZrH}_{0.03}$ and $\text{ZrH}_{0.06}$. From the insert in Figure 7, it can be seen that a change of slope occurs at $\text{ZrH}_{0.04}$ (2.5ml H_2 /0.5g with a possibility of a second boundary at $\text{ZrH}_{0.08}$. Ells and McQuillan¹⁵ suggest that the lack of definition of this boundary is caused by the presence of oxygen and identify the region above this boundary as solid solution of hydrogen in $\beta\text{-Zr}$. It is to be noted that this interpretation is based on sorption measurements only. However, the data in this region do not obey Sieverts' law and high temperature X-ray studies¹¹ place the upper boundary of the two phase, $\alpha + \beta$ region, much higher, at about $\text{ZrH}_{0.33}$, for a temperature of 800°C. It is unfortunate that these later studies were not extended into the low hydrogen concentration region at high temperatures.

In view of the conflicting evidence noted above, and that found in the comparison of the phase diagrams obtained by X-ray analysis¹¹ and sorption measurements^{13,15} at other compositions and temperatures, it is clear that further work is necessary on this subject. In particular it is desirable to determine the phase changes

occurring between $\text{ZrH}_{0.06}$ and ZrH (4.5 and 60.7 ml. $\text{H}_2/0.5\text{g}$ respectively) to determine if a true two-phase region is present.

The two quenched specimens (24,25, Figure 7, Table 4) which we have obtained, on the 798°C zirconium-hydrogen experiment show the boundary of a two-phase and single-phase region to lie between $\text{ZrH}_{0.59}$ and $\text{ZrH}_{0.86}$ (37 - 46 atomic %). The identification of the phases is not certain, especially as no trace of β -Zr was detected but the results indicate that the phase diagram is more complex than the present published data suggest.

The upper two-phase region of the zirconium-hydrogen system is better defined, but again exhibits considerable pressure change during sorption through the composition region. This type of behavior is also observed in the uranium-hydrogen system. At low temperatures a well defined two-phase region, $\text{U} + \text{UH}_3$, is observed,¹⁷ having a constant pressure over its range of existence. As the temperature is raised, the same region shown an increase in hydrogen pressure, with volume sorbed.⁹ Preliminary X-ray work at the higher temperature, at this temperature, suggests that the "two-phase" region is actually a single phase, involving the solid solution of hydrogen in α -U.¹⁸

In the zirconium-hydrogen system, for the upper "two-phase" region, shown in the 798°C isotherm (Figure 7), the presence of β -Zr and δ -zirconium hydride has been confirmed by X-ray analysis.¹¹ Therefore, the explanation invoked above, for the uranium-hydrogen system is not applicable. However, Vaughan and Bridge¹¹ give evidence that the parameter of the δ -phase zirconium hydride changes continuously with the sorption of hydrogen. Since the parameter change is presumably reflected in a variation of the hydrogen decomposition pressures of the phase, it may account for the pressure change occurring in the "two-phase" region. A similar mechanism may also explain the variation in pressure found in the first two phase region of the zirconium-hydrogen isotherm at 798°C .

As the detailed behavior of the zirconium-hydrogen system is

not completely understood, it is impossible to make a complete interpretation of the uranium-zirconium-hydrogen system, in that this latter system involves the zirconium-hydrogen reaction. However, certain conclusions can be drawn from the data. The addition of hydrogen to the alloy produces precipitation of uranium at all concentrations above the terminal solubility of hydrogen in the ϵ - and γ -UZr phases (Table 4). It is possible that we observe this precipitation as a result of the quenching process, but the appearance of zirconium hydrides is strong evidence for decomposition of the alloy.

The phase diagram for uranium-zirconium alloys² shows that at 800°C uranium and zirconium form a continuous solid solution, the γ -phase, to over 90 atomic percent zirconium. At this temperature, formation of a zirconium hydride could occur without precipitation of uranium, the removal of zirconium causing a composition change in the γ -phase. The experimental observation, that uranium is precipitated shows that the concentration limits of the γ -phase in the phase diagram are modified by the presence of hydrogen. This interpretation does not rule out some composition change in the γ -phase. Excess uranium could also form a solid solution in the hydride phase. Only an extensive x-ray diffraction study could provide a definite answer to these questions.

The precipitation of uranium, may account for the pressure change in the "two-phase" uptake of hydrogen by the alloy. But since very similar isotherms are obtained in the zirconium-hydrogen system definite conclusions on this point are not warranted. The upper "two-phase" region for zirconium and zirconium-uranium alloy (Figure 7) have almost identical pressure dependence and similar hydrogen sorption limits. The heat of solution of hydrogen in the two phase change is 53.9 Kcal./mol., for the alloy (Figure 10) and 45.8 Kcal./mol. for pure zirconium.¹⁴ The differences observed are remarkably small considering the large uranium content of the alloy and could be explained

simply on terms of the dilution of zirconium with non-reacting uranium.

The effect of hydrogen on the uranium-zirconium alloy is complex. The evidence obtained gives strong indications that, after initial solid solution of hydrogen in the ϵ - or γ -UZr, further gas causes the alloy to split into its components. Above 650°C this occurs at approximately 1000 ppm. and at 550°C, at 400 ppm. of hydrogen. Between these temperatures some α -Zr seems to precipitate from the alloy, even in the absence of hydrogen.

It is evident that the measurement of isotherms for hydrogen sorption is a sensitive technique for the detection of phase changes. However, in a complex system such as we have examined, or even in the simpler zirconium-hydrogen system, the method cannot give positive identification of the phases involved. Supplementary X-ray analyses are of great importance but they must necessarily be obtained at the equilibrium temperature under investigation. To this end careful experimental techniques are required to avoid contamination and also to maintain a known hydrogen concentration in the sample.

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APPENDIX

Detailed Experimental Procedure

Vacuum System

The system was constructed of pyrex, using stopcocks lubricated with Apiezon N Grease. It was evacuated by two mercury pumps, placed in series, and a two stage mechanical pump. A vacuum of 10^{-7} cm or better was readily obtained, after baking the glass with a hand torch. A large (500ml.) McLeod gauge was included in order to calibrate a pirani gauge for hydrogen pressure measurements.

Gas Purification

Tank hydrogen was passed over platinized asbestos, at 350°C and through a cold trap (-195°C) to remove oxygen and condensable gases and further purified by diffusion through a palladium tube at $400-500^{\circ}\text{C}$. The gas was stored in a 2L. bulb.

Tank helium was passed through a trap at (-195°C) and stored in a 1L. bulb.

Gas Transfer System

The apparatus is shown diagrammatically in Figure 12. Hydrogen and helium were removed from the storage bulbs by means of a 300ml. Toepler pump, A. The gas could be adjusted to any desired pressure in the pump and admitted to a gas burette, B. This consisted of three bulbs of accurately measured volume. During the assembly of the burette, the volume from the upper stopcock to etch marks between each bulb was measured by filling with mercury and weighing. The capacity was approximately 0.7, 5 and 16 ml. The burette was controlled at $30 \pm 0.1^{\circ}\text{C}$ by water circulated from a thermostat bath. A measured volume of gas could be completely displaced from the burette, to the sorption system, by mercury.

A U-Tube manometer, C, was used to measure the pressure of gas in the burette. It was made with precision bore tubing, 15 mm. i.d. Triply distilled mercury was used. An accurate cathetometer was used to read the mercury level in this and the constant-volume manometer described below, to an accuracy of ± 0.005 cm.

Sorption System

The system was made with the smallest volume consistent with efficient evacuation of the specimen at low pressures. This was necessary in order to reduce contamination of the specimen because of their extreme reactivity at high temperatures.

The specimen was heated in a mullite tube, G, sealed directly to pyrex tube of 8mm. i.d. The U-Tube, E, was cooled to -78°C to protect the specimen from stopcock grease and mercury vapor. A "Constant-volume manometer" D was used for pressure measurements from 0.01 to 76 cm. The leg of the manometer connected to the sorption system was short, wide bore, and contained a tungsten point contact, H. In all pressure measurements the mercury level was adjusted, by means of the reservoir I, to make contact with the tungsten. A neon lamp was used as an indicator and constant level could be maintained within 0.005 cm. The pressure in the system was read by observing the mercury level in the evacuated limb, J. Therefore, at all pressures, the volume of the sorption system was constant while accurate measurements were facilitated by the use of a wide bore (15 mm.) manometer tube.

Low pressure measurements from 10^{-4} to 10^{-7} cm. were made with a sensitive Pirani gauge, F. The gauge was made by placing a tungsten coil (15w 115v. lamp filament) in a 120mm x 4mm i.d. tube. The tube was placed in an oil thermostat and controlled at approximately 30°C constant to $\pm 0.01^{\circ}\text{C}$. The filament was made one arm of a Wheatstone bridge circuit, balanced with an applied potential of about 0.4v, with the gauge evacuated to 10^{-7} cm. The applied potential was accurately

measured to ± 0.00005 v. At pressures above 10^{-7} cm. the voltage applied was increased in order to balance the Wheatstone bridge. A calibration curve, a function of the applied voltage against pressure of hydrogen, was made using the McLeod gauge.

Alloy Specimen

The uranium-zirconium alloy specimen was cut from 10 mil. sheet. The material was cleaned by abrading with 1/0 through 4/0 polishing papers, using purified kerosene. The polished sample was then thoroughly cleaned with petroleum ether and absolute alcohol. Approximately 0.5g of material was placed in a Nichrome* bucket, fitted with a loose lid. This protected the alloy from contact with the mullite tube, reducing the danger of contamination by silica.

Extraction of Samples for X-ray Analysis

In order to remove samples, the normal furnace tube was replaced by that shown in Figure 1. The dewar was cooled to -78°C to provide a rapid quench for samples drawn from the furnace. An alloy sample of about 0.5g was wrapped in Nichrome sheet to prevent contamination from the furnace tube and left in position. The removable portions of the sample were 10 mil. square and 1 inch long. Each sliver was bound to the end of a straight length 29 B & S gauge Nichrome wire by two short lengths of pure platinum wire. The other end of the Nichrome carried a small slug of pure iron. When the Nichrome wire was lowered into the furnace so that the alloy sample was in the heated zone, with the bulk of the alloy, the iron slug projected above the level of the quenching dewar. By means of a small permanent magnet the alloy sliver could be removed from the furnace and quenched to -78°C in about one second. Two such samples

* Registered trade mark of the Driver-Harris Company, Harrison, N. J.

could be withdrawn in the course of one experiment.

Furnace

The furnace used for heating the specimens was made from a cylinder of stainless steel approximately 6 inches long by 2 1/2 inches in diameter. This was drilled axially to form a well into which the mullite furnace tube was placed, with the specimen area in the furnace center. A chromel-alumel thermocouple was fastened to the mullite tube close to the specimen zone. This was used to determine the specimen temperature. A heating element, of Nichrome tape, was wound on the outside surface of the stainless steel block, insulated by asbestos paper and held in place by alundum cement. A second, control, chromel-alumel thermocouple was placed very close to the heater windings, at the middle of the block. The block was surrounded by about 2 inches of insulation.

A Leeds and Northrup P.A.T. Control was used to maintain furnace temperature. This essentially controlled the heater winding to $\pm 1^\circ\text{C}$, giving $\pm 0.25^\circ\text{C}$ or better, in the specimen zone. The temperature gradient through the specimen zone was less than 1°C .

Experimental Procedure

The sorption system was carefully outgassed by heating and evacuation before inserting the alloy. Each specimen was used for several isotherms, being heated to 800°C at 10^{-7} cm. pressure for several hours, after each run. It was cooled to the temperature of the next experiment and left in vacuo for several hours before carrying out the isotherms determination. Each isotherm was measured and duplicated using a different specimen.

For the preparation of X-ray specimens, it was not practical to renew the main specimen for each experiment and to reduce contamination problems the system was cooled to room temperature in the

presence of hydrogen before opening to the atmosphere to remove the sliver specimens. Thus, in the subsequent outgassing involving raising the specimen and 800°C, a stream of hydrogen was removed from the alloy, tending to sweep traces of gases away from the specimen.

The "dead space" of the sorption system was determined at the temperature of each run, by expansion of known volumes of helium from the burette and observing the pressure in the system. It was essential throughout the whole run to maintain constant temperature in all parts of the sorption system. The cold trap was filled to a constant level; the parts of the system other than the trap and furnace were at room temperature which was constant to better than 1°C. The dead space calibration was responsible to $\pm 0.5\%$.

To determine a sorption isotherm, successive volumes of hydrogen were introduced to the specimen and the equilibrium pressures measured. In most cases the system came to equilibrium in 5-10 minutes, although at lower temperature several hours were sometimes required, particularly where the sample was in a "two-phase" region.

Fig. 1 - Apparatus for removal of X-ray specimens.

Fig. 2 - Sorption isotherms on uranium-zirconium alloy

034 032

Fig.3 - Sieverts plot for solid solution in ξ -UZr

Fig. 4 - Sorption isotherms on uranium-zirconium alloy.

Fig. 5 — The sorption of hydrogen by uranium-zirconium alloy.

Fig. 6 — The sorption of hydrogen by uranium-zirconium alloy

Fig. 7 - The sorption of hydrogen by zirconium & uranium-zirconium alloy at 798°C.

Fig.8 — Sieverts plots for hydrogen sorption on uranium - zirconium alloy.

038 734

Hydrogen sorption isotherms for Zirconium-Uranium alloy
Fig. 9

Fig.10-Log p - $1/T$ curves for the "two-phase" regions in Uranium - Zirconium-Hydrogen System

Fig. II—Phase diagram for hydrogen sorption on uranium-zirconium alloy.

Fig. 12 — Schematic diagram of apparatus.

References

1. E. A. Gulbransen, K. F. Andrew, and R. Ruka, Westinghouse Research Paper 100FF1010-P1.
2. D. Summers-Smith, J. Inst. Metals, 83, 277 (1955).
3. B. Lustman and F. Kerze, Jr., ed., "The Metallurgy of Zirconium", p. 477, McGraw-Hill Book Co., Inc., N. Y. (1955).
4. A. G. Knapton, Discussion in J. Inst. Metals, 83, 598 (1955).
5. A. N. Holden and W. E. Seymour, Preprint No. 101, A.I.M.M.E. Nuclear Engineering and Science Congress, Cleveland, Dec. 1955.
6. R. P. Larsen et al., Argonne Natl. Lab. Report ANL-5135, July, 1954.
7. Private Communication, Westinghouse Atomic Power Division.
8. Private Communication, Dr. Pfeill, Harwell, England.
9. G. G. Libowitz, Progress Report, NYO-3919, Contract AT (30-1) 1355, Tufts College, 3/17/55.
10. G. Hagg, Z. physick, Chem., 11, 439 (1930).
11. D. A. Vaughan and J. R. Bridge, J. Metals, 528, 8, (1956).
12. M. N. A. Hall, S. L. H. Martin and A. L. G. Rees, Trans. Faraday Soc., 41, 306 (1945).
13. R. K. Edwards, P. Levesque and D. Cubicciotti, J. Amer. Chem. Soc., 77, 1307 (1955).
14. E. A. Gulbransen and K. F. Andrew, Trans. AIME, 203, 136 (1955).
15. C. E. Ells and A. D. McQuillan, Private Communication; to be published.
16. Reference 2, p. 566.
17. F. H. Speeding, A. S. Newton, J. C. Ward, O. Johnson, R. W. Nortorf, J. B. Johns and A. H. Doane, Nucleonics 4, 4 (1949)
18. E. I. Goon, Progress Report NYO-3919, Contract AT (30-1) 1355, Tufts College, 3/17/55.

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