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LABORATORY METHOD FOR ADJUSTING HYDROGEN CONTENT OF ZIRCONIUM

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LABORATORY METHOD FOR ADJUSTING HYDROGEN CONTENT OF ZIRCONIUM

by

John J. Kearns

May 26, 1958

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ABSTRACT

A new method of introducing predetermined quantities of hydrogen into zirconium has been developed and evaluated. The procedure is simple, effective, and inherently good in preventing oxygen and nitrogen contamination. Zirconium samples containing four levels of dissolved oxygen, in the range 160 to 1380 parts per million, were hydrogenated to 100, 300, 3500, and 7700 parts per million hydrogen. Dissolved oxygen was found to decrease hydrogen absorption in both the alpha and beta modifications of zirconium. The effect of hydrogen on density, hardness, and microstructure was determined. X-ray diffraction measurements were also obtained.

ACKNOWLEDGMENTS

The investigation described in this report was a thesis project conducted in partial fulfillment for the Degree of Master of Science in Metallurgical Engineering at the University of Pittsburgh. The author wishes to thank Dr. J. Alfred Berger, thesis advisor and head of the Metallurgical Engineering Department, and Dr. Richard Mateer, thesis advisor, for their helpful suggestions and for their permission to publish this document. Thanks is also due the United States Atomic Energy Commission and the Westinghouse Electric Corporation for permission to use materials and facilities at the Bettis Plant for the experimental work.

LABORATORY METHOD FOR ADJUSTING HYDROGEN CONTENT OF ZIRCONIUM

I. INTRODUCTION

In the course of a study on the effect of hydrogen on the fatigue of zirconium, one of the first and most important problems encountered was that of adding hydrogen to zirconium samples without permitting any contamination with oxygen or nitrogen. Zirconium has a strong affinity for these gases and will dissolve appreciable amounts. Pickup of even very minor quantities of these elements hardens zirconium and consequently cannot be tolerated in any study aimed at evaluating the influence of some variable on strength. Increasing oxygen by 0.03 w/o increases the hardness of zirconium about 10 DPH* units; in high purity zirconium this represents more than a 10% increase in hardness. Such an increase would certainly be reflected in fatigue strength. Hydrogenating zirconium to a level of 300 ppm was first attempted by a conventional technique of adding pure hydrogen obtained from the decomposition of UH_3 to an evacuated chamber containing zirconium samples. The result was an increase in hardness ranging from 10 to 25 DPH units, an amount indicating contamination with oxygen or nitrogen. It became necessary therefore to either construct a more elaborate vacuum system or to use a different approach to the hydrogenating problem. A simple experiment was conducted to check another possible method of hydrogenation, and this preliminary experiment proved quite successful.

In gas-metal solid solutions the amount of the diatomic gaseous element dissolved in the metal at a given temperature depends upon the partial pressure of the gas phase over the metal; according to Sieverts' law, $c = kp^{1/2}$, where c is concentration in metal, p is the partial pressure, and k is a constant. Figure 1 is a schematic of the Zr-H phase diagram and a plot of partial pressure (equilibrium pressure) versus composition at temperature T_1 . If a sample of zirconium of zero hydrogen concentration, point A, and a sample of zirconium hydride, point C₂, were placed in an evacuated container and heated to temperature T_1 , the initial hydrogen pressure in the container would correspond to point F. Since the hydrogen pressure would be above the equilibrium pressure for zero dissolved hydrogen, the zirconium sample at A would dissolve hydrogen and move from A toward B and the hydride would move down the curve from F. If the ratio of the weights of the two samples were chosen so that the total hydrogen concentration in the container would be at C₁, then after attaining equilibrium, C₁ would be the concentration of hydrogen in both the zirconium sample and the original hydride.

To determine if such equilibration of hydrogen would actually occur experimentally, a preliminary experiment was conducted. Details of the preliminary experiment are given in Appendix A. Briefly, the basic experiment was as follows: Samples of zirconium containing about 20 ppm of hydrogen were sealed within an evacuated Vycor bulb along with some zirconium hydride powder containing about 21,200 ppm hydrogen. The weights of the zirconium and the hydride were such as to result in a 300 ppm increase in the zirconium sample if equilibrium were attained. Measurement of hydrogen content of the zirconium samples following an equilibration heat treatment showed that a pickup of about 300 ppm did occur, indicating attainment of equilibrium. In addition, hardness changes were minor,

*DPH refers to Vickers Diamond Pyramid Hardness.

Fig. 1 Schematic Diagram of Zr-H System
and Absorption Isotherm
(Neg 24045-1)

indicating very little contamination by oxygen or nitrogen. These results were very encouraging, and the equilibration technique was adopted as a method for hydrogenation. It has the advantage of being easily conducted without elaborate apparatus, is relatively accurate for predetermined levels of hydrogen, and, most important, has inherent superiority over conventional techniques in prevention of contamination. After a tube is evacuated and sealed off, zirconium chips in the bulb can be heated by torch without the samples becoming even warm. This technique getters residual oxygen and nitrogen, and thereafter there is no source of contamination within the sealed tube. Conventional techniques require that samples be isolated from the vacuum pumps during hydrogenation, and if minor leaks are present, contamination results.

It was felt desirable to further evaluate the equilibration method to determine if large quantities of hydrogen could be added. Also, since the quantity of hydrogen absorbed by zirconium for any given partial pressure was reported to be influenced by dissolved oxygen, the effect of dissolved oxygen on hydrogen absorption was of interest. Details are given in the next section, but briefly the experiment to be described in the body of this report involved hydrogenation of zirconium containing four levels of dissolved oxygen to hydrogen concentrations of 100, 300, 3500, and 7700 ppm. The effect of oxygen was determined by sealing four samples in the same bulb, each containing a different level of dissolved oxygen. In this way all four samples were in equilibrium with the same partial pressure of hydrogen. Since four bulbs were involved, one for each level of hydrogen, the effect of oxygen on hydrogen absorption was obtained at four pressures of hydrogen. The four oxygen levels were 160, 360, 325, and 1380 ppm. It is important to recognize that these represent rather small concentrations on the a/o basis in relation to the concentrations of hydrogen involved. On the a/o scale, the oxygen contents studied were 0.09, 0.20, 0.18, and 0.78%, while the levels of hydrogen studied were 0.9, 2.7, 25, and 41 a/o. Appendix B contains further information in this connection.

Physical property data were also obtained during the investigation by hardness and density measurements. In addition, microscopic and X-ray diffraction examinations were conducted and contributed some information on the Zr-H phase diagram.

II. LITERATURE SURVEY

Vaughn and Bridge (Ref 1) recently determined the features of the Zr-H phase diagram by a high temperature X-ray diffraction study. The diagram is shown in Fig. 2. It is the same type of system as the Ti-H which was determined by McQuillan (Ref 2) in an equilibrium pressure-concentration study. The limited solubility of hydrogen in alpha zirconium was determined by a diffusion couple experiment by Schwartz and Mallett (Ref 3), and also by an equilibrium pressure study by Gulbransen and Andrew (Ref 4).

The existence of more than one hydride phase has been reported by several investigators (Refs 3 and 5). *The work by Vaughn and Bridge however revealed only one hydride phase which has a homogeneity range from about 58 to 67 a/o hydrogen. The phase is face-centered tetragonal and the c/a ratio varies with composition from values greater than 1.0 below 60 a/o hydrogen to values less than 1.0 above 60%. Vaughn and Bridge point out that the structure is cubic at 60% hydrogen and suggest that this is the reason for the earlier belief that two separate hydrides existed above 60%, one cubic and the other tetragonal.

*Also by K. H. Jack in unpublished work (see Ref 7)

Fig. 2 The Zirconium-Hydrogen System

(Neg 25322-6.)

The tetragonal phase, which has been observed to form at low temperatures and at concentrations below 60% hydrogen, is reported by Vaughn and Bridge to be stable only at temperatures above the eutectoid but can exist as a metastable phase at lower temperatures.

Equilibrium pressure studies have been conducted on Zr-H alloys by many investigators (Refs 4, 6, 7, 8, 9, and 10). Hall, Martin, and Reese determined hydrogen absorption at partial pressures of 1 to 760 mm Hg and from room temperature to 1050°C. In this work the effect of dissolved oxygen on hydrogen absorption was studied with alloys containing 0.4 to 11.7 w/o oxygen. Dissolved oxygen reduced the amount of hydrogen absorbed for any given pressure. Edwards, Levesque, and Cubicciotti obtained equilibrium pressure data from 600 to 900°C and deduced a Zr-H phase diagram. Edwards and Levesque extended the study to include alloys with up to 25 a/o oxygen. From these data a provisional Zr-H-O ternary section was drawn. Both of these extensive investigations by Edwards, et al., unfortunately were handicapped since pressure measurements were not conducted below a hydrogen pressure of about 1 mm Hg. Significant changes occur below this pressure. The data were therefore incorrectly interpreted to show large solubility of hydrogen (about 50 a/o) in the alpha phase of zirconium.

The absorption of hydrogen at low pressures, around 0.001 mm Hg, has been studied by Gulbransen and Andrew and most recently by Mallett and Albrecht. The latter work illustrated the effect of 0.03, 0.14 and 0.43 w/o dissolved oxygen on the absorption of hydrogen by alpha and beta zirconium at pressures below 0.004 mm Hg. For a given pressure, oxygen was found to slightly increase absorption by the alpha phase, and to slightly decrease absorption by the beta phase.

III. EXPERIMENTAL PROCEDURE

A. Materials and Specimen Preparation

Four zirconium ingots, differing mainly in oxygen content, were selected for study. They have been identified as ingots A, B, C, and D and the analysis of each is given in Table I. Ingots A and B were made by arc-melting Westinghouse Grade A crystal bar* zirconium, while ingot C was arc-melted from Foote Grade A crystal bar. Ingot D was arc-melted from Bureau of Mines sponge** zirconium. Ingots A, B, and C were forged at 950°C and hot-rolled to 1/2-in. thick plate at 800°C. Bars about 1/2-in. wide were cut longitudinally and were cold-rolled 25%. Material from ingot D was not forged or hot-rolled but did receive 25% cold reduction. Each bar was then machined and degreased by successive cleaning with trichloroethylene, acetone, and alcohol. The bars were wrapped in zirconium foil and were then heated at 825°C for 24 hr in a dynamic vacuum of about 10^{-6} mm Hg. This treatment annealed the material and also lowered the hydrogen to about 20 ppm, as shown in Table I. A thin longitudinal section was removed from each bar for metallographic examination. Each bar was then cut transversely into nearly cubical samples about 3/8-in. on a side and weighing about 10 g.

*Crystal bar refers to zirconium obtained in the iodide decomposition process of van Arkel-de Boer.

**Sponge refers to zirconium made by the Kroll reduction process.

TABLE I
CHEMICAL ANALYSIS OF ZIRCONIUM INGOTS*
(values in ppm)

Element	Ingot I			
	A	B	C	D
Zr	Major	Major	Major	Major
Sn	< 10	< 10	< 10	< 10
Si	< 20	< 20	< 20	40
Fe	200	30	150	200
Al	< 35	< 35	< 30	< 35
Hf	75	75	160	105
Cu	< 25	60	< 5	< 25
Ti	< 25	< 25	< 10	< 25
Ca	< 10	< 10	50	< 10
Mn	< 25	< 25	< 10	< 25
Pb	< 20	< 20	< 30	< 20
Ni	< 20	< 20	< 10	< 20
Cr	< 20	< 20	< 10	< 20
W	34	71	< 10	< 20
C	24	26	90	24
H	21	16	17	20
N	10	10	10	50
O	{ 80 150 160 240	{ 330 390	{ 270 380	{ 1340 1410

*Analysis was determined on samples from the hot-rolled strip except for H, N, and O which were determined after vacuum degassing. Methods for analysis of H and O are discussed in Appendix C. Values for Si, Fe, W, C, and N were obtained by wet chemical methods. The remaining elements were obtained by spectrochemical methods.

B. Hydrogenation

Because of its uniqueness, the feature of the experimental procedure that is most important is the method of hydrogenation. Hydrogenation was performed in the following manner:

Sixteen samples, four from each ingot, were degreased and weighed on a Gram-atic balance accurate to ± 0.00002 g, which is equivalent to ± 2 ppm in a 10-g sample. Also prepared were four groups of vacuum-annealed zirconium chips each weighing about 2 g. The zirconium samples were separated into four groups, each group consisting of one sample from each ingot. Each group of samples was loaded into a separate Vycor glass bulb along with a group of chips. The arrangement is shown schematically in Fig. 3. The large end of the bulb was sealed with a hydrogen-oxygen torch. Zirconium hydride powder, 160 mesh, was then dropped through the constriction at the small end of the bulb. The bulbs

Fig. 3 Schematic Vycor Encapsulation

(Neg 24045-13)

were evacuated to 10^{-5} mm Hg, flushed with argon, re-evacuated, and sealed off at the constriction. The chips were brought to a red heat by a torch in order to getter residual oxygen and nitrogen.

The hydride powder was prepared prior to this investigation by reacting purified hydrogen with crystal bar zirconium at 700°C and slowly cooling it in an atmosphere of hydrogen. The hydride was taken to be $\text{Zr-H}_{1.96}$ which is equivalent to 21,200 ppm of hydrogen. Gulbransen and Andrew (Ref 7) reported $\text{Zr-H}_{1.96}$ to be the highest hydride obtained under these conditions. The quantity of hydride added to each bulb was determined by assuming that an equal distribution of hydrogen would be obtained in all the zirconium contained in the bulb; that is, the samples, the chips, and the zirconium in the hydride.

The following relation was used in making calculations:

$$\text{ppm H} = \frac{\text{wt of H} \cdot 10^6}{\text{Total wt of H and Zr}} = \frac{(21,200) (\text{wt of Zr-H}_{1.96})}{\text{wt of Zr-H}_{1.96} + \text{wt of Zr sample}} \quad (1)$$

which simplifies to

$$\text{wt of Zr-H}_{1.96} = \frac{(\text{wt of Zr sample}) (\text{ppm H desired})}{(21,200) - (\text{ppm H desired})} \quad (2)$$

The hydride powder was weighed on a torsion balance accurate to ± 0.005 g which was, respectively, $\pm 2.5\%$, $\pm 1.0\%$, $\pm 0.07\%$, and $\pm 0.02\%$ of the hydride weight used for the 100, 300, 3500, and 7700 ppm levels of hydrogen.

The heat treatment chosen for hydrogen equilibration was 700°C for 24 hr followed by a quench into ice water for 10 sec and then into liquid nitrogen to promote rapid cooling. The samples remained sealed in the bulbs throughout the quench. Following removal from the bulbs, the samples were again weighed to determine hydrogen absorption. Justification for the use of the weight changes is discussed later. A cross section was removed from the middle of each sample for hydrogen analysis, which was done by the hot-vacuum-extraction method. Also, a section was removed from each of the four "A" samples for oxygen analysis and from each of the four "B" samples for nitrogen analysis. This was done to check on contamination. A section from each sample was also prepared for metallographic and X-ray examination. The remaining portions of the samples were re-encapsulated in four bulbs just as before and were given a treatment consisting of 1 hr at 700°C , a slow cool to 400°C , and a hold at 400°C for 1 week. The bulbs were air-cooled from 400°C . This treatment was conducted to obtain microstructures presumed to represent equilibrium.

C. Physical Property and Structural Data

Hardness, density, and structural data were obtained after each heat treatment; that is, after the vacuum degassing, hydrogenation, and the treatment at 400°C . A Vickers diamond pyramid hardness machine with a load of 20 kg was used for hardness measurement. At least three, and usually five, impressions were obtained for each hardness determination.

Densities were measured by the displacement method, using carbon tetrachloride and an A B C Quik Chex balance accurate to ± 0.0002 g. The accuracy

in density depended on the size of the sample and was, in the worst case, ± 0.005 g/cc. For the purpose of calculating this number the accuracy was assumed to be limited only by the sensitivity of the balance. Duplicate density determinations on several samples indicated this number to be realistic.

Samples were prepared for microstructural examination by employing conventional polishing techniques and an etchant consisting of 60 cc of hydrogen peroxide, 40 cc concentrated nitric acid, and 5 drops of concentrated hydrofluoric acid.

X-ray diffraction data were obtained with a Norelco X-ray spectrometer. Cu K alpha radiation was used, and the spectrometer was calibrated with a standard silicon sample supplied with the equipment.

IV. RESULTS

A. Hydrogen Absorption

The weight gains exhibited by each sample following the equilibration treatment at 700°C are listed in the second column of Table II.

TABLE II

WEIGHT GAIN AND HYDROGEN ANALYSIS FOLLOWING EQUILIBRATION AT 700°C
(values in ppm)

<u>Sample No.</u>	<u>Weight Gain</u>	<u>H by Weight</u>	<u>H by Vac. Extraction</u>
A-1	148	139	113
B-1	148	134	110
C-1	125	112	109
D-1	<u>105</u>	<u>95</u>	<u>106</u>
Average	130	120	110
A-2	325	330	304
B-2	326	326	297
C-2	314	315	300
D-2	<u>293</u>	<u>297</u>	<u>291</u>
Average	316	317	298
A-3	3908	3679	3200
B-3	3897	3663	2410
C-3	3650	3417	2840
D-3	<u>3523</u>	<u>3293</u>	<u>2710</u>
Average	3750	3510	2790
A-4	8177	8069	7775
B-4	8045	7932	8130
C-4	7847	7735	6350
D-4	<u>7337</u>	<u>7228</u>	<u>6390</u>
Average	7829	7741	7161

The results show that the equilibration method was generally successful, but the total weight gain of the four samples in each group (or bulb) was greater than the nominal amount of hydrogen added. The excess weight gain was 30, 16, 250, and 129 ppm, respectively, for additions of 100, 300, 3500, and 7700 ppm hydrogen. It was suspected that these excess gains were due to oxygen or nitrogen contamination originating probably from gases mechanically trapped in the fine hydride powder. Nitrogen analysis before and after hydrogenation failed to reveal any change. However, the oxygen analysis did indicate contamination. While oxygen determination is reported to be accurate to only ± 200 ppm, the values determined on the "A" sample from each bulb show a definite correspondence to the excess weight gains. Table III illustrates that as the excess weight gain increased, the oxygen (pickup) increased.

TABLE III

EXCESS WEIGHT GAINS AND OXYGEN PICKUP FOR INGOT "A" SAMPLES
(values in ppm)

<u>Nominal H Added</u>	<u>Excess Weight Gain</u>	<u>Oxygen Analysis</u>
300	16	170
100	30	210
7700	129	370
3500	250	410

In view of this evidence, it was assumed that the excess weight gains represented oxygen contamination, and further, that the level of contamination was equal among the four samples within any one bulb. To determine the hydrogen concentration in each sample, the weight gain was reduced by the average excess weight gain and then this value was added to the original hydrogen concentration of the sample before the equilibration treatment. These numbers are listed in the third column of Table II. Analysis for hydrogen by hot extraction yielded the values shown in the fourth column. Concentration of hydrogen by weight changes is greater with a few exceptions than that by hot extraction. At each nominal level of hydrogen, weight changes show a consistent decrease in hydrogen content with increase in dissolved oxygen. The values by hot extraction also reveal this trend, but it is not so consistent. The consistency of the values by weight would be some justification for assuming them to be more reliable than values by hot extraction. Much stronger evidence is shown later, however, where density is related to hydrogen concentration. In this report all subsequent reference to hydrogen concentration, unless otherwise stated, implies the values determined by weight measurements.

The effect of dissolved oxygen on hydrogen absorption is illustrated in Figs. 4 and 5, which are plots of the average hydrogen concentration in each bulb versus the actual hydrogen in each sample. It can be seen that oxygen decreases hydrogen absorption and the magnitude is proportional to the hydrogen concentration.

Fig. 4 Effect of Dissolved Oxygen on Hydrogen Absorption

(Neg 25322-3)

Fig. 5 Enlarged Section of Fig. 4
(Neg 25322-5)

Reheating to 700°C, cooling slowly to 400°C, and holding 1 week modified the effect of oxygen on hydrogen absorption. Table IV reveals the changes which occurred during this second treatment.

TABLE IV
WEIGHT CHANGES DURING 400°C TREATMENT
(values in ppm)

Sample No.	Weight Change	Adjusted H Concentration
A-1	Negligible*	139
B-1	Negligible*	134
C-1	Negligible*	112
D-1	Negligible*	<u>95</u>
	Average	120
A-2	+ 40	370
B-2	Negligible*	326
C-2	+ 16	331
D-2	Negligible*	<u>297</u>
	Average	331
A-3	-318	3361
B-3	-406	3257
C-3	-345	3072
D-3	-176	<u>3117</u>
	Average	3202
A-4	-600	7469
B-4	-608	7324
C-4	-239	7496
D-4	+ 28	<u>7256</u>
	Average	7386

*Negligible implies less than 10 ppm. The accuracy for these weights is only ± 10 ppm since the samples weighed from 2 to 4 g.

The purpose of this second treatment was to obtain a microstructure representing equilibrium. Small samples were used, and for this reason the accuracy in weights was no better than ± 10 ppm. The values in Table IV are erratic but do show significant changes for the two higher levels of hydrogen. A smaller spread in hydrogen content is observed between the samples containing the lowest and highest oxygen. It is not known, however, whether or not equilibrium was attained at 400°C. More work is needed at this temperature.

Another feature to be noted about the data for the two higher levels of hydrogen is that an average of about 300 ppm of hydrogen, equaling 10^{-3} g, was lost. How the hydrogen was lost has not been determined. The quantity of hydrogen in the residual gas phase within the Vycor bulbs was negligible, being

less than 10^{-5} g. Also, with permeability constants of 3.9×10^{-9} and 0.5×10^{-9} cc · mm/sec/cm²/cmHg at 700 and 400°C, taken from Barrer (Ref 11), the loss by permeation through the Vycor walls was calculated and found to be negligible, on the order of 10^{-7} g.

B. Physical Properties

1. Density

The density of zirconium, as determined by the displacement method, is decreased by the addition of hydrogen. Table V and Fig. 6 contain density values after both the 700°C and the 400°C treatments.

TABLE V
DENSITY OF ZIRCONIUM SAMPLES AFTER HYDROGENATION
(values in g/cc)

Sample No.	700°C Treatment		700 + 400°C Treatment	
	Measured	Corrected for O	Measured	Corrected for O
A-1	6.509	6.508	x	x
B-1	6.499	6.496	x	x
C-1	6.499	6.493	x	x
D-1	6.502	6.491	x	x
A-2	6.488	6.487	x	x
B-2	6.489	6.486	x	x
C-2	6.478	6.473	x	x
D-2	6.490	6.479	x	x
A-3	6.348	6.345	6.323	6.320
B-3	6.302	6.297	6.334	6.329
C-3	6.306	6.299	6.339	6.332
D-3	6.325	6.312	6.345	6.332
A-4	6.057	6.055	6.099	6.097
B-4	6.065	6.061	6.081	6.077
C-4	6.080	6.073	6.107	6.100
D-4	6.151	6.139	6.116	6.104

Note: x indicates values not determined.

A straight line can be drawn through the average of the four groups of points in Fig. 6. Interestingly, displaced but parallel straight lines can be drawn through the points within each group, suggesting that the variation in oxygen within each group is affecting the density. Each density value was therefore corrected to zero oxygen using a value of minus 8.0×10^{-6} g/cc/ppm oxygen taken from data by Treco (Ref 12). The corrected values of density are replotted in Fig. 7; points are also shown which correspond to hydrogen values determined by hot extraction.

Fig. 6 Effect of Hydrogen on the Density of Zirconium
(Neg 24045-12)

Fig. 7 Effect of Hydrogen on the Density of Zirconium
(Neg 25322-4)

2. Hardness

The hardness values after the 700°C and the 400°C treatments are shown in Table VI and are plotted in Figs. 8 and 9.

TABLE VI
VICKERS DIAMOND PYRAMID HARDNESS*

Sample No.	700°C Treatment**	700°C + 400°C Treatment†
A-1	67	66
B-1	87	75
C-1	87	85
D-1	157	147
A-2	72	60
B-2	91	78
C-2	90	89
D-2	162	156
A-3	112	96
B-3	139	121
C-3	130	115
D-3	177	168
A-4	173	164
B-4	192	164
C-4	164	161
D-4	220	205

*Average DPH for vacuum-annealed material:
A=63, B=76, C=88, D=160

**Hardness on longitudinal cross section

†Hardness on transverse cross section

3. X-ray Diffraction

Table VII is a listing of the X-ray diffraction data obtained at room temperature after the 400°C treatment. The patterns were obtained from the A and D ingot samples containing the highest quantity of hydrogen. Little difference exists between the two patterns. Both reveal the presence of not two, but three phases: alpha zirconium, hexagonal close packed; a face-centered cubic phase, presumably gamma hydride; and a face-centered tetragonal phase with $c/a = 1.08$. The tetragonal phase is designated in Table VII as gamma prime. The lattice parameter, a_0 , for the cubic hydride is 4.780 Å. The calculated density corresponding to this parameter and a composition of 58 a/o hydrogen is 5.598 g/cc.

Fig. 8 Effect of Hydrogen on the Hardness of Zirconium
(Neg 24045-6)

Fig. 9 Effect of Hydrogen on the Hardness of Zirconium
(Neg 24045-8)

TABLE VII

X-RAY SPECTROMETER DATA AFTER 400°C TREATMENT*

Line No.	Sample D-4 (7256 ppm H)				hkl α Zr	hkl γ	hkl γ^1	Sample A-4 (7469 ppm H)			
	R.I.	2 θ	d, Å	$\gamma_{a_o}, \text{\AA}$				R.I.	2 θ	d, Å	$\gamma_{a_o}, \text{\AA}$
1	M	31.92	2.804	-	(100)	-	-	W	31.79	2.814	-
2	S	32.4	2.764	4.787	-	(111)	-	VS	32.31	2.771	4.799
3	MS	32.9	2.723	-	-	-	(111)	S	32.78	2.733	-
4	M	34.8	2.578	-	(002)	-	-	W	34.72	2.584	-
5	VS	36.45	2.465	-	(101)	-	-	M	36.38	2.457	-
6	M	37.57	2.394	4.788	-	(200)	-	W	37.47	2.400	4.800
7	W	39.11	2.303	-	-	-	(200)	-	-	-	-
8	M	47.92	1.899	-	(102)	-	-	W	47.87	1.900	-
9	M	54.08	1.696	4.796	-	(220)	-	W	54.23	1.691	4.782
10	M	56.9	1.618	-	(110)	-	-	W	56.87	1.619	-
11	W	62.92	1.477	-	-	-	(113)	W	62.87	1.478	-
12	M	63.5	1.465	-	(103)	-	-	W	63.49	1.465	-
13	M	64.6	1.443	4.786	-	(311)	-	W	64.53	1.445	4.793
14	W	66.9	1.399	-	(200)	-	-	VW	66.90	1.399	-
15	W	67.9	1.381	4.784	-	(222)	-	W	67.77	1.383	4.791
16	M	68.5	1.370	-	(112)	-	-	VW	68.7	1.366	-
17	M	69.5	1.352	-	(201)	-	-	W	69.5	1.352	-
18	W	89.4	1.096	4.777	-	(331)	-	W	89.20	1.097	4.781
19	VW	90.6	1.085	-	(203)	-	-	-	-	-	-
20	VW	92.3	1.069	4.781	-	(420)	-	VW	92.10	1.070	4.785
21	VW	93.7	1.057	-	-	-	(124)	-	-	-	-

TABLE VII (Cont)

Line No.	Sample D-4 (7256 ppm H)				hkl α Zr	hkl γ	hkl γ^1	Sample A-4 (7469 ppm H)			
	R.I.	2 θ	d, Å	γa_o , Å				R.I.	2 θ	d, Å	γa_o , Å
22	W	95.9 α_1	1.037	-	(121)	-	-	VW	95.90	1.039	-
23	W	99.75 α_1	1.007	-	(11 $\bar{1}$ 4)	-	-	VW	99.90	1.007	-
24	W	104.3	0.976	-	(1 $\bar{2}$ 2)	-	-	W	104.25	0.977	-
25	W	113.71 α_1	0.920	4.780	(333)	(511)	-	W	113.64	0.920	4.780
26	W	117.8	0.900	-	(1 $\bar{2}$ 3)	-	-	W	-	-	-
27	W	122.8	0.878	-	(3 $\bar{0}$ 2)	-	-	-	-	-	-
28	M	144.7 α_1	0.808	4.780	-	(531)	-	M	144.70	0.808	4.780
29	W	150.4 α_1	0.7967	4.780	-	600-442	-	-	-	-	-

*The symbols shown in the table have the following meanings:

γ - F.C.C. hydride; γ^1 - F.C.T. hydride; α Zr - H.C.P. Zr;

R.I. - relative intensity; VS - very strong; S - strong;

MS - medium strong; M - medium; W - weak;

VW - very weak; 2 θ - two times the Bragg angle;

d - interplanar spacing; hkl - Miller indices;

a_o - lattice parameter of F.C.C. γ phase;

α_1 - line from Cu $K\alpha_1$ radiation.

4. Microstructure

Figures 10 through 14 are photomicrographs illustrating the structures after the vacuum-degassing treatment and the 700°C hydrogenation treatment. The effect of reheating and slowly cooling to 400°C is shown in Figs. 15 through 19. In the photomicrographs the darker etching phase is the hydride, the white phase is alpha zirconium. The grain size is different for each ingot, presumably because of the variation in impurity level. Also, each material, with the exception of ingot C, exhibits a duplex grain structure. The variation in grain size has a major effect on the over-all appearance of the hydrided structures. For example, at high hydrogen concentration the hydrides in the larger-grained material are much more massive. Particularly large hydride masses are evident at high hydrogen content following the 400°C treatment.

V. DISCUSSION

A. Equilibration as a Method of Hydrogenation

The results of the study presented here indicate that the equilibration method of adding predetermined amounts of hydrogen to zirconium is both successful and attractive. However, one of the prime requisites of an acceptable method of hydrogenation, that of low contamination, was not met as well as expected. Samples picked up oxygen. The amount was small, but it would be desirable to have essentially zero contamination. The equilibration method would probably meet this requirement if the source of hydrogen were a solid block of zirconium containing high hydrogen rather than the powdered hydride, for it is suspected that oxygen mechanically trapped in the powder was responsible for the contamination. This difficulty could be circumvented by charging a large solid block of zirconium with hydrogen by means of equilibration with hydride powder and then using sections of this block for subsequent equilibration treatments. In addition to eliminating the source of contamination, a solid sample has a second advantage in that it could be weighed before and after equilibration and the weight loss could be a measure of the hydrogen liberated, since oxygen and nitrogen are not volatile at the temperatures used for hydrogen equilibration. This method of equilibration was actually performed during part of the preliminary experiments discussed in the introductory remarks and in the appendix. Preliminary experiments did not reveal the need for this refinement, therefore it was not used for the systematic study. The hydride powder had worked satisfactorily.

The phase relations in the Zr-H system impose certain limitations on the equilibration technique. Transfer of hydrogen via the gaseous phase from a solid of high hydrogen concentration to a solid of low concentration will theoretically cease, not when the hydrogen concentration in each solid is equal, but rather when the hydrogen pressure associated with the solid phase (s) in each sample is equal. This is best understood by considering the schematic pressure-concentration curve shown in Fig. 1. Suppose that the curve represents the 700°C absorption isotherm in the Zr-H system. If the total hydrogen concentration of both the high and the low hydrogen samples is in the single-phase regions between A and B, C and D, or E and F, then equilibration would result in equal hydrogen concentration in each sample, since this is the only way the partial hydrogen pressures for each sample could balance. If, on the other hand, the total hydrogen concentration were within either of the two-phase

Ingot A

Ingot B

Ingot C

Ingot D

Fig. 10 Microstructures after Vacuum Degassing. 100X
Variation in grain size is illustrated.

(Neg 24045-18)

Fig. 11 Microstructures of Ingot A after Hydrogenation at 700°C. 100X
ppm H: (a) 139; (b) 330; (c) 3679; (d) 8069
Massive hydride phase outlines prior beta grains in (d).

(Neg 24045-19)

Fig. 12 Microstructures of Ingot B after Hydrogenation at 700°C. 100X
ppm H: (a) 134; (b) 326; (c) 3663; (d) 7932
Structures are similar to those for Ingot A in Fig. 11.

(Neg 24045-20)

Fig. 13 Microstructures of Ingot C after Hydrogenation at 700°C. 100X
ppm H: (a) 112; (b) 315; (c) 3417; (d) 7735
Structures show same characteristics as those for Ingots A and
B but are finer due to smaller grain size.

(Neg 24045-21)

(a)

(b)

(c)

(d)

Fig. 14 Microstructures of Ingot D after Hydrogenation at 700°C. 100X
ppm H: (a) 95; (b) 297; (c) 3293; (d) 7228
Structures are similar to those for Ingot C in Fig. 13.

(Neg 24045-22)

Fig. 15 Microstructures of Ingot A after 400°C Treatment. 100X
ppm H: (a) 3361; (b) 7469

Hydride phase is much more massive, especially in (b),
than it was after the hydrogenation treatment at 700°C.

(Neg 24045-17)

Fig. 16 Microstructure at Higher Magnification of Sample shown in Fig. 15, (b). 500X
A Widmanstätten precipitate, presumably γ^1 , is shown within massive hydride area. The phase along grain boundary at right is α Zr.

(Neg 24045-23)

Fig. 17 Microstructures of Ingot B after 400°C Treatment. 100X
ppm H: (a) 3257; (b) 7324
Structures are coarser than those after the 700°C
hydrogenation treatment.

(Neg 24045-16)

Fig. 18 Microstructures of Ingot C after 400°C Treatment. 100X
ppm H: (a) 3072; (b) 7496
Structures are similar to those in Fig. 17 for Ingot B
but are less coarse.

(Neg 24045-15)

Fig. 19 Microstructures of Ingot D after 400°C Treatment. 100X
ppm H: (a) 3117; (b) 7256

Structures are similar to those for Ingot C in Fig. 18.

(Neg 24045-14)

regions, then transfer of hydrogen would cease when the partial pressures for both samples reached the value corresponding to the two phases in equilibrium. In such a case, the hydrogen concentration in the two samples would not be equal. One sample would be single-phase with a concentration at the extremity of the two-phase field; i.e., the phase boundary, while the other sample would consist of both phases. Which sample would be two-phase and which single-phase would depend on which sample reached the two-phase region first. This in turn would depend on the initial hydrogen concentration and the relative weights of the two samples before equilibration. Such considerations suggest a method of determining the phase boundaries of the Zr-H system. Pre- and post-equilibration weight measurements on a series of samples of properly selected weights and hydrogen contents would yield the solubility limits for each phase in the system. These considerations are based on ideal behavior. To know whether or not boundaries could, in fact, be determined this way would require trial experiments.

In connection with the preceding discussion, it is surprising that hydrogenation to the 3500-ppm level, which is in the middle of the alpha-plus-beta field, was successful. If the original hydride stopped liberating hydrogen when it reached the alpha-plus-beta to beta-phase boundary, the zirconium samples would have picked up roughly 3000 ppm rather than 3500 ppm. Perhaps the hydride contained considerably more dissolved oxygen than did the zirconium samples and this altered the equilibrium pressure relationships enough to permit the observed transfer of hydrogen. Another interesting feature of the equilibration to 3500 ppm is that at 700°C the samples, as revealed by the microstructures, consisted of a homogeneous mixture of the alpha and beta phases. One might expect that at 700°C the samples would consist of a single alpha-phase at the center covered by a single-phase beta layer. In other words, if hydrogenation is viewed as a diffusion couple between zirconium and hydrogen, then two-phase regions should not form during diffusion. The fact that a layered structure was not observed apparently stems from the extremely rapid diffusion of hydrogen through zirconium (Refs 3, 10). Mallett and Albrecht point out that surface phenomena appear to be the rate-controlling factors in absorption of hydrogen by zirconium. At 700°C the hydrogen apparently diffused into the center of the samples rapidly, and the rate of hydrogen absorption at the surface was too low to permit the establishment of a hydrogen gradient. Or alternatively, the hydrogen was absorbed and homogeneously distributed just as rapidly as it could be liberated from the zirconium hydride source. In either case the entire sample could have become super-saturated throughout, thus permitting uniform nucleation of beta.

B. Effect of Oxygen on Hydrogen Absorption

Probably the most significant aspect of the experimental results is the pronounced effect of dissolved oxygen on hydrogen absorption. This influence is illustrated in Figs. 4 and 5, in which the actual hydrogen in each sample is plotted as a function of the average hydrogen in each group of samples. With the exception of the group at 100 ppm, the points define straight lines, one line for each level of dissolved oxygen. This method of plotting is convenient, therefore, because the slopes of the curves can be used as parameters relating dissolved oxygen with hydrogen absorption between zero and 7700 ppm of hydrogen at a temperature of 700°C. Figure 20 is a plot of the slope from Fig. 4 as a function of dissolved oxygen. According to this figure, absorption decreases

Fig. 20 Effect of Dissolved Oxygen on Slope of Curves in Fig. 4
(Neg 24045-7)

linearly with increasing oxygen in the range studied. The point for ingot C, however, falls well off the curve. Material from ingot C is anomalous in another respect as well. Ingot C is the only one of the three crystal bar ingots which does not have a hardness commensurate with its oxygen content. Figure 21 is a plot of hardness versus oxygen obtained by converting R_a hardness data reported by Treco (Ref 13) to the DPH scale. The DPH- R_a conversion was from work by Mudge.* From hardness alone, ingot C would be expected to contain around 670 ppm oxygen. If this value for oxygen were used for ingot C in Fig. 20, the point would fall nearly on the straight line. Of course the oxygen is not this high, but the quantity of some other element or combination of elements is higher, or lower, in ingot C and this appears to affect both hardness and hydrogen absorption.

While the curve in Fig. 20 reflects the influence of oxygen, it has limited usefulness since the values of the slopes pertain only to the actual experiment conducted. That is, if more or less than four different oxygen levels were used, or if any one of the oxygen levels were changed, all slopes would be altered. The values which are independent of the experimental conditions are the ratios of the slopes. These values are equivalent to the ratios of Seivert's constant. For example, slope A:slope B = concentration A:concentration B = $k_A \sqrt{P} : k_B \sqrt{P} = k_A : k_B$. Hydrogen absorbed by a sample of some known oxygen level can therefore be referred to as a percent of that absorbed by a sample of some other oxygen level. Since the curve of Fig. 20 can be extrapolated to zero oxygen, hydrogen absorption can be expressed as the percent of the hydrogen absorbed by zirconium containing zero dissolved oxygen. With the value for zero oxygen being 100%, the values for ingots A, B, C, and D are 98.7%, 97.0%, 94.1%, and 88.6%, respectively. The percent reduction in absorption represented by these values is plotted in Fig. 22.

The linearity of the curves in Fig. 4 was not expected, since the hydrogen range involves both the alpha and beta phases. The 100- and 300-ppm levels are in the single-phase alpha region of the phase diagram, the 3500 in the alpha-plus-beta region, and the 7700 in the single-phase beta region. It must therefore be concluded that dissolved oxygen is just as effective in decreasing hydrogen absorption in the alpha phase as it is in the beta phase. This finding is an apparent disagreement with the results reported by Mallett and Albrecht, who found oxygen to increase hydrogen absorption in the alpha phase. These workers, however, studied hydrogen absorption up to 46 ppm, in comparison with the 100- to 300-ppm level studied in this investigation. Perhaps a reversal in the effect of oxygen on hydrogen absorption occurs between 46 ppm and 100 ppm hydrogen. The data at both of these levels appear consistent within themselves. The only point of doubt concerning the work of Mallett and Albrecht is that the difference in hydrogen absorption caused by oxygen is quite small. For example, the difference between 40 ppm hydrogen for a 300 ppm oxygen sample and 46 ppm hydrogen for a 4300 ppm oxygen sample was the largest effect observed. The analysis for hydrogen was done by the vacuum-fusion method which involves the measurement of gases liberated when the sample is melted under high vacuum. Analyzing two samples of zirconium containing 300 and 4300 ppm oxygen for a difference of 6 ppm hydrogen requires extreme accuracy in separation of the oxygen and hydrogen liberated. If the analysis were in fact accurate, and no reversal in trend of hydrogen absorption between 46 and 100 ppm occurs, then there must be a subtle factor not recognized in either the work by Mallett and Albrecht or the work reported here.

*W. L. Mudge, Jr., Bettis Plant, unpublished research

Fig. 21 Hardness of Zirconium as a Function of Dissolved Oxygen
(Neg 24045-9)

Fig. 22 Effect of Oxygen on Hydrogen Absorption at 700°C
(Neg 25322-7)

C. Structure and Physical Properties1. Density

The density data are of particular interest for two reasons. First, the density of zirconium is lowered appreciably by relatively small weight additions of hydrogen; the data in Fig. 7 indicate a decrease of about 6.6% (6.51 to 6.08 g/cc) for an addition of 0.75 w/o (7500 ppm) of hydrogen. Of possibly more importance to the work reported here, the behavior of the density data affords a justification for the use of weight changes rather than hot vacuum extraction as a measure of hydrogen content. When the density values are plotted as a function of hydrogen determined by weight measurements, as in Fig. 7, a rather consistent decrease in density is noted within each group of samples. If, on the other hand, values for hydrogen determined by hot extraction are plotted, they show erratic behavior within each group. Also, if the average density is plotted as a function of the average hydrogen within each group, as in Fig. 23, the values by weight measurements fall on a straight line, while the values by hot extraction do not. This point, however, needs some elaboration since linearity of density with w/o hydrogen should not be expected. According to the Zr-H phase diagram, the samples being considered consist of a mixture of alpha-plus-gamma. The density, D , of a mixture is proportional to the volume %, designated as v/o, and the density of the constituents according to the linear relation,

$$D_{\alpha + \gamma} = \left[\frac{v/o \gamma}{100} D_{\gamma} + \left(\frac{100 - v/o \gamma}{100} \right) D_{\alpha} \right] / 100 \quad (3)$$

Thus, density would not be a linear function of w/o hydrogen (w/o H) unless v/o γ varies linearly with w/o H. The relation between v/o γ and w/o H has been calculated using 58 a/o (1.51 w/o) hydrogen as the composition of the gamma (γ) hydride. The following equations were used:

$$w/o \gamma = \frac{(100) (w/o H)}{1.51} = (66.2) (w/o H) \quad (4)$$

$$\text{Volume} = \text{weight/density} \quad (5)$$

$$v/o \gamma = \frac{\frac{w/o \gamma}{D_{\gamma}}}{\frac{w/o \gamma}{D_{\gamma}} + \frac{(100 - w/o \gamma)}{D_{\alpha}}} \times 100 \quad (6)$$

D_{α} was taken as 6.51 g/cc from the measured values, and the value of 5.60 g/cc calculated from the X-ray data was used for D_{γ} . The results of the calculations are shown in Fig. 24, which is a plot of v/o γ as a function of w/o H and also of a/o hydrogen. The v/o versus w/o curve deviates so slightly from a straight line that the linear appearance of the density curve in Fig. 7, drawn on the basis of hydrogen determined by weight measurements, is understandable. The deviation from linearity of the points based on hot extraction is too great, however, to be accounted for by the slight deviation of the v/o γ versus w/o H curve.

Fig. 23 Average Density for Each Group of Sample vs Average Hydrogen for Each Group
(Neg 24045-11)

Fig. 24 Calculated Volume Percent Gamma Phase vs Percent Hydrogen
(Neg 25322-2)

2. Hardness

The hardness data shown in Figs. 8 and 9 are erratic but appear to be best represented by straight lines. Since the samples consist of a mixture of the alpha and gamma phases, the hardness might be expected to be nearly proportional to the v/o and the hardness of these two phases.* On this basis, the slopes of the hardness curves would be expected to decrease, as they do, with an increase in the original hardness of the alpha phase.

3. Microstructure and X-ray Diffraction

One of the more interesting and significant features of the structural data is the evidence of three phases in the samples containing the two higher levels of hydrogen. The X-ray diffraction results revealed, as expected, the presence of alpha zirconium and the cubic gamma hydride. In addition, a tetragonal phase was present which was designated as gamma prime. Substantiation of the diffraction data is provided by the appearance of the microstructures of these samples. The microstructures reveal a third phase which has a Widmanstätten structure. This phase is most clearly revealed (in Fig. 16) as a precipitate within the massive hydride area. Examination with polarized light indicated the platelets to be anisotropic since they were optically active. The massive hydride was not optically active and must therefore be the cubic gamma hydride. The gamma prime phase has been observed previously in X-ray diffraction studies (see Sec. II, Literature Survey); the fact that the microstructures indicate that the gamma prime phase precipitated from the massive hydride areas is significant in that it supports Jack's supposition that the phase is a metastable transition phase between the cubic gamma hydride and the hexagonal alpha zirconium. According to the phase diagram, the hydride phase which forms at the eutectoid would precipitate alpha zirconium upon cooling. Evidently gamma prime forms in preference to the alpha zirconium. Another possible explanation for the gamma prime phase is that the phase is a stable one existing in the Zr-H-O ternary system and is present in the samples studied due to the oxygen content. This explanation appears less likely than the one discussed above since the oxygen concentrations are so low and the quantity of the gamma prime phase did not appear any greater in the samples containing 1380 ppm oxygen than in those containing 160 ppm oxygen.

VI. CONCLUSIONS

The following conclusions can be drawn from the work presented in the preceding sections:

1. The original purpose, to develop a satisfactory method of adding hydrogen to zirconium, was accomplished. Hydrogen can be added to zirconium by gaseous equilibration with zirconium of an initially higher hydrogen concentration. A low level of contamination is assured, and no elaborate apparatus is required.
2. Dissolved oxygen, in the range from 160 to 1400 ppm, reduces hydrogen absorption in both the alpha and beta modifications of zirconium. The magnitude of this effect is proportional to the oxygen content and to the hydrogen content.

* A value of 230 DPH was obtained for the gamma phase with a load of 2-1/2 kg

3. The change in weight can be used satisfactorily as a measure of the change in hydrogen concentration.
4. Addition of hydrogen decreases the density, or increases the volume, of zirconium.
5. Hardness of zirconium increases linearly with w/o hydrogen in the range studied. The rate of increase depends upon the original hardness, being lower for samples of higher hardness.

VII. RECOMMENDATIONS

Several features of the experimental results indicate a need for further study. For example, from the metallographic work it was possible to explain logically the origin of the controversial gamma prime phase, a third phase which appears in binary alloys of zirconium and hydrogen. Of the several explanations found in the literature for the origin of this phase, the metallographic work supports that of Jack, who suggested that gamma prime formed as a transition phase between gamma hydride and alpha zirconium. Microstructures exhibited in this report revealed that the gamma prime phase precipitated from the gamma hydride phase. This fact, along with the phase diagram by Vaughn and Bridge which indicates that the gamma hydride should precipitate alpha zirconium on cooling, validates the transition theory of Jack. It is recommended, however, that further study be conducted on the phase diagram at the hydride end in order to determine whether or not the gamma prime phase is formed by some other solid-state reaction not shown in the diagram by Vaughn and Bridge.

Another aspect which needs clarification is the effect of oxygen on hydrogen absorption by the alpha phase of zirconium. The results reported here show an effect that is in opposition to published results. This point should be studied further, possibly by both the equilibration method described in this report and a more conventional method. A way in which the equilibration method might be used for phase boundary determination in the zirconium-hydrogen system was described in the body of the report. It is recommended that a few experiments be conducted to check the feasibility of such an application of the principles governing equilibration.

APPENDIX A

The following remarks are an account of the preliminary experiments which led to the adoption of the equilibration method as a means of adding hydrogen to zirconium, and which also led to the systematic study described in the body of this report.

A group of arc-melted, crystal bar zirconium samples was given a degassing heat treatment at 825° C for 24 hr in a vacuum of 10^{-6} mm Hg. This treatment reduced the hydrogen level to 10-20 ppm. Three of these samples were then sealed in an evacuated Vycor tube along with zirconium chips (for gettering) and a sample of $ZrH_{1.96}$ weighing enough to result in 300 ppm total hydrogen concentration. A second Vycor tube was prepared in the same manner but with only one zirconium sample rather than three. A third tube was prepared as a control and contained chips and one sample but no hydride. The three tubes were heated to 700°C for 6 hr. Weight measurements accurate to ± 1 ppm were obtained before and after treatment as a measure of the change in hydrogen content. Changes in weight and hardness are listed in Table VIII. The weight changes illustrated the effectiveness of the method for obtaining desired levels of hydrogen, and the minor changes in hardness indicated there was very little contamination.

A second experiment was conducted which demonstrated more conclusively the effect of hydrogen on hardness and also the usefulness of equilibration method of hydrogenation. Table IX shows the results obtained when samples No. 4 and 5, containing approximately 300 and 20 ppm, respectively, were placed in the same tube and given a second 6-hr treatment at 700°C.

TABLE VIII
CHANGES IN HARDNESS AND WEIGHT OF ZIRCONIUM
SAMPLES HEATED AT 700°C

Sample No.	Weight Gain ppm	Hardness, DPH		
		Before	After	Change
1 (Tube No. 1)	+304	72	76	+4
2 (Tube No. 1)	+286	76	82	+6
3 (Tube No. 1)	+286	77	79	+2
4 (Tube No. 2)	+319	75	82	+7
5 (Tube No. 3)	- 5	75	75	0

The weight lost by the high hydrogen sample essentially equalled the weight gained by the low hydrogen sample. Hardness behaved similarly. Within the $\pm 5\%$ error of the hot extraction method, the hydrogen analysis indicated that equilibrium had been essentially achieved.

TABLE IX

RESULTS OF SECOND TREATMENT AT 700°C

Sample No.	Weight Change		Hydrogen Analysis (ppm) (by Hot Extraction)	Hardness, DPH		
	Grams	ppm		Before	After	Change
4	-0.00511	-143	153	82	77	-5
5	+0.00500	+141	142	75	80	+5

APPENDIX B

Concentrations of hydrogen and oxygen referred to in the body of this report usually were in units of ppm; that is, in parts per million by weight. A better understanding of the effective concentrations of hydrogen and oxygen in zirconium is given by a/o units. Table X contains conversions from w/o to a/o for the levels of hydrogen and oxygen studied in this work.

TABLE X
CONVERSION OF % UNITS FOR HYDROGEN
AND OXYGEN IN ZIRCONIUM

<u>Hydrogen</u>			
<u>ppm</u>	<u>w/o</u>	<u>a/o</u>	<u>v/o γ</u>
100	0.01	0.91	1
300	0.03	2.69	2.3
3500	0.35	24.6	26
7700	0.77	40.8	55
<u>Oxygen</u>			
<u>ppm</u>	<u>w/o</u>	<u>a/o</u>	
160	0.0160	0.09	
360	0.0360	0.20	
325	0.0325	0.18	
1380	0.1380	0.78	

The values in Table X illustrate that the alloys studied were dilute with respect to oxygen but involved some high hydrogen alloys.

Also included in Table X are values for v/o of the gamma hydride that is present for each level of hydrogen. The v/o numbers were taken from Fig. 24. In addition to giving v/o values, the curves in Fig. 24 can be used to convert between the w/o and a/o scales. The curves from Fig. 24 are shown in Fig. 25 along with a dotted line illustrating a conversion between 0.77 w/o hydrogen and 40.8 a/o hydrogen.

Fig. 25 Illustration of Conversion Between Atomic Percent and Weight Percent
(Neg 25322-1)

APPENDIX C

Methods for Analysis of Gaseous Elements in Zirconium

The values for oxygen listed in Table I were obtained by a method in which hydrogen chloride vapor is reacted with the zirconium sample. Zirconium tetrachloride gas is driven off, and the residue is taken to be zirconium dioxide from which the oxygen analysis of the sample is calculated. This method is reported to be accurate to about ± 200 ppm. Since one of the aims of this report was to evaluate the influence of dissolved oxygen, a more precise method would have been desirable. Another common method for oxygen determination in zirconium is the vacuum-fusion method. While this method can give more accurate values than the hydrogen chloride method, it is often erratic because the technique is difficult. In this method, the zirconium sample is melted in a platinum metal bath under a high vacuum. The gaseous elements, oxygen, nitrogen, and hydrogen, are driven off and separated. Quantities are determined by pressure measurements in standard volumes.

Values for hydrogen in Table I and in later tables were determined by the hot vacuum extraction method in which the hydrogen is extracted from the zirconium sample by a high vacuum at 1200°C . Pressure measurements in a standard volume yields the analysis. The accuracy is about $\pm 5\%$ of the hydrogen present. As mentioned, hydrogen can also be determined by the vacuum-fusion method. Vacuum fusion is less accurate than hot extraction for the hydrogen levels involved in this report.

Nitrogen values are very low for the materials studied. They were determined by a wet chemical method referred to as the Micro-Kjeldahl method which is accurate to $\pm 10\%$ of the amount present.

APPENDIX D

Actual measured weights of the samples used in this research work are recorded in Table XI.

TABLE XI
WEIGHTS OF ZIRCONIUM SAMPLES, CHIPS, AND HYDRIDE
FOR EACH NOMINAL LEVEL OF DESIRED HYDROGEN
(values in g)

Sample	700°C Hydrogenation Treatment		400°C Reheat Treatment	
	Before	After	Before	After
<u>100 ppm H Level</u>				
A-1	7.70391	7.70505	2.13187	2.13189
B-1	10.23839	10.23991	3.96710	3.96711
C-1	10.45217	10.45348	5.73768	5.73768
D-1	11.73614	11.73737	7.11486	7.11493
Chips	2.08401	*	**	**
Hydride	0.201	*	**	**
<u>300 ppm H Level</u>				
A-2	7.30336	7.30573	1.90705	1.90713
B-2	9.62940	9.63254	3.92943	3.92939
C-2	8.58529	8.58799	4.46116	4.46123
D-2	6.51560	6.51751	2.34731	2.34734
Chips	2.12120	*	**	**
Hydride	0.490	*	**	**
<u>3500 ppm H Level</u>				
A-3	7.15774	7.18571	1.66806	1.66753
B-3	9.34849	9.38492	4.09494	4.09328
C-3	9.56765	9.60265	4.47224	4.47070
D-3	7.15810	7.18332	3.11541	3.11486
Chips	2.20114	*	**	**
Hydride	7.007	*	**	**
<u>7700 ppm H Level</u>				
A-4	7.52995	7.59152	2.41774	2.41629
B-4	10.22285	10.30509	3.90010	3.89773
C-4	9.06900	9.14016	3.05118	3.05045
D-4	10.12395	10.19823	3.35416	3.35431
Chips	1.97930	*	**	**
Hydride	22.202	*	**	**

*Not determined

**Hydride was not included for 400°C treatment. The chips used for the 700°C were used again for the 400°C treatment.

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