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Zirconium Hydride as a Storage Medium for Tritium

by
R. D. Scheele and L. L. Burger

July 1976

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SUMMARY

Conditions necessary for rapid production (approximately 20 minutes preparation time) have been determined for a 6-g sample of zirconium hydride with a composition of $ZrH_{1.5}$ to $ZrH_{1.9}$. Two alternate sets of conditions were found to produce a hydride of suitable physical integrity for tritium storage: the first condition involves isothermal absorption of H_2 at 760 torr and 600°C; the second involves addition of H_2 at 760 torr as the temperature is increased from 600°C until absorption ceases. The latter method appears to produce a hydride which is essentially crack-free. Small amounts of air in the hydrogen were found to have a very deleterious effect on the hydriding reaction.

The cost of zirconium is a disadvantage. However, the use of scrap metal may make the method more attractive and the possible use of irradiated Zircaloy cladding hulls would be even more economically favorable. Questions to be answered mainly concern the actinide and other residual activity remaining in the hulls after decladding. Zircaloy-2 tubing, cladding scrap, was studied and found to be very easily hydrided. Hydrides were produced from 0.25- and 0.50-in. diameter Zircaloy rod, 0.50-in. diameter Zircaloy tubing, and 0.25-in. diameter zirconium rod.

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INTRODUCTION

In the LWR fuel cycle, about 2.5 x 10^4 Ci/GWe-yr of tritium are produced, most of which enters the fuel reprocessing plant. Although present regulations permit environmental dispersal of the tritium, methods are being considered to prevent future releases. In these cases interim or permanent storage forms may be required.

Among the storage forms that appear attractive for use with concentrated tritium wastes are metal hydrides. The obvious advantages include high storage capacity (volume efficiency) and the easy recoverability of tritium. Several recent surveys describe tritium pathways in the fuel cycle, and discuss and evaluate removal and storage concepts.(1-6) This report describes preliminary work on the use of zirconium hydride as a tritium storage form.

To determine the feasibility of zirconium hydride as a fixation medium, an experimental program was designed to: 1) evaluate the experimental parameters for rapid production of massive hydrides with adequate physical integrity, 2) observe the physical stability of the hydrides, 3) prepare the tritiated hydride and examine the leach rate, 4) determine the effects of various physical forms of zirconium and Zircaloy, and compare other metals such as titanium, yttrium, and hafnium, 5) investigate the pyrophoricity of metal hydrides, and 6) consider and evaluate the application of metal hydride storage to reprocessing plant waste streams. Termination of the program before the end of the first year prevented many of these goals from being achieved. This report summarizes the first phase of the work which dealt largely with hydriding parameters using Zircaloy.

CANDIDATE METALS

Most metals form hydrides by direct combination with elemental hydrogen, and the metallic hydrides of zirconium, titanium, hafnium, yttrium, niobium, tantalum, and uranium have been used or proposed for hydrogen or tritium fixation and storage.(4) A good candidate hydride must be stable towards reaction with water and air, and must have a low dissociation pressure. These requirements leave zirconium, titanium, hafnium and yttrium as possible materials. Due to the relatively high costs of the metals, consideration may be further restricted to the more available zirconium and titanium. As a class the metal hydrides are reasonably well characterized and techniques for their production (with hydrogen) have received much attention.(7,8) The chemical and physical stability of these hydrides is found to be dependent to some extent on the hydrogen content and upon the method of preparation. Resistance to oxidation is a function of particle size, but zirconium and titanium hydride powders appear to be stable below about 300°C and, in massive form, can be heated to higher temperature. Other advantages of metal hydrides include the reversibility of the hydriding reaction, i.e., the tritium is recoverable, and the very high space economy; ZrH_2 for example has about twice the hydrogen density of liquid hydrogen.

Disadvantages of metal hydrides include the requirement that the tritium be in the elemental hydrogen form and that it be reasonably free from other reactive gases. Another disadvantage is the high cost of the metals which may be partially eliminated if scrap metal from the nuclear program (e.g., cladding hulls) can be utilized.

Based on the availability of zirconium as Zircaloy-2 and 4, it was chosen as the medium for tritium fixation. The properties of zirconium and the hydrides pertinent to this study are listed in Table 1 and in Figures 1 and 2. As can be seen from the phase diagram (Figure 1) hydrogen stabilizes the β phase by lowering the α-β transition from 862 to 550°C. However, some uncertainties exist about the exact limits of the δ and ε regions and a meta-stable γ phase (bct) which coexists with the α and δ phase at low temperatures. A δ+ε region not shown in Figure 1 exists below about

455°C.(10) The hydride densities listed are from X-ray data(11) which can be compared to a measured density for $ZrH_{1.92}$ of 5.47 reported by Trzeciak.(12)

TABLE 1. Properties of Zirconium and Zirconium Hydrides at 25°C

	α-Zr	β-Zr	δ-hydride	ε-hydride
Composition	-	-	61.4-62.5	62.5-66.7
Crystal Structure	hcp	bcc	fcc	fct
Density	6.50	-	5.64-5.65	5.61-5.64

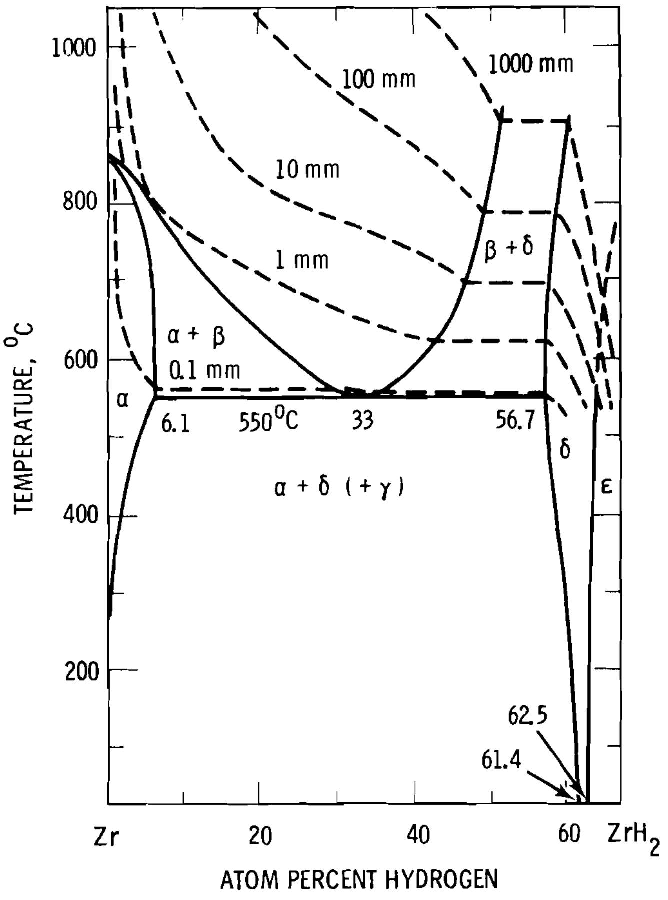

FIGURE 1. Zirconium-Hydrogen Phase Diagram(9)

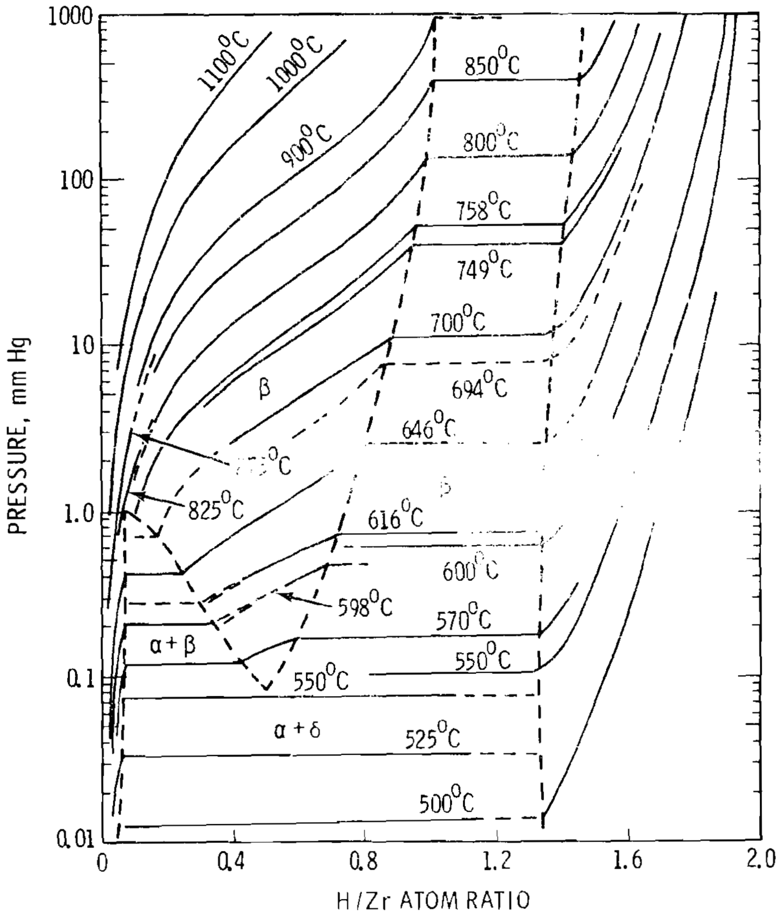

FIGURE 2. Pressure-Composition Isotherms (Composite Data)(9)

EXPERIMENTAL CONSIDERATIONS

We used a modified Sieverts apparatus similar to the one described by Blackledge(7) to prepare zirconium hydride. This system consisted of a copper vacuum manifold, a quartz reaction vessel, Bourdon and McLeod pressure gages, and a gas buret. Commercial 99.95% pure H_2 was supplied to the gas buret through copper tubing. The metal sample was placed in a basket made of stainless steel screen and inserted into the reaction tube where the temperature was measured using a chromel-alumel thermocouple. The system was later modified to provide pressure measurement with a capacitance manometer. Flashback arrestors were placed in key locations to prevent propagation of a hydrogen fire (explosion). The system was checked for leaks using a helium mass spectrometer leak detector.

The materials hydrided were 0.25-in. diameter Zircaloy-2 and 99.97% pure zirconium rod, 0.50-in. Zircaloy-4, and 0.50-in. Zircaloy-2 tubing (fuel cladding scrap); specifications for the Zircaloy rods are listed in Appendix A. Samples of irradiated Zircaloy cladding from Shippingport reactor fuel were prepared for hydriding but early termination of the program prevented completing the test. A goal composition of $\sim ZrH_{1.5}$ was selected on the basis that a single phase (δ) could exist over the entire temperature range of the experiments. Blackledge has listed a number of factors which influence hydride preparation:(7) impurities in the metal, surface condition of the metal (oxide, nitride films, etc.), impurities in hydrogen, form of the metal to be hydrided, pre- and post-heat treatment, as well as pressure-temperature relations. These factors are discussed in the following paragraphs.

The principal experimental difficulty encountered in the present work was air in-leakage into the hydrogen gas supply line. This allowed formation of the thermodynamically favored oxide and nitride (Table 2) which form protective films, preventing rapid hydrogen absorption. It is therefore important to eliminate air in-leakage.

The effect of surface conditioning was investigated by subjecting selected samples to the following treatment: the metal surface was first abraded with fine-grit silicon carbide paper then cleaned with reagent-grade acetone to remove any residual surface oils. The metal was then transferred to the reaction chamber with metal tweezers.

TABLE 2. Thermodynamic Data for Relevant Materials,(13) 298°K

	ΔH_f kcal/g-atom Zr	ΔG_f kcal/g-atom Zr	S° cal/deg-g-atom Zr	Cp cal/mol-deg
ZrO	-261.50	-247.75	12.12	13.40
ZrN	-87.30	-80.50	9.29	9.60
$ZrH_{1.5}$	-33.70(c)	(-25.70)(c)	(5.90)(c)	7.50(a)
ZrH_2	-38.90	-29.32(b)	8.38(b)	7.40(b)
ZrD_2	-40.22	-29.86(b)	9.16(b)	9.63(b)
Zr(α)	-	-	9.29	6.18

(a) For $ZrH_{1.58}$ from Tomasch, Reference 14.

(b) Calculated from the data of Reference 14 and entropy of elements.

(c) Calculated from H_2 pressure data and equations given by Gulbransen and Andrew.(15) ΔG_f data listed by Libowitz, -23.0, gives a negative entropy for $ZrH_{1.5}$. Actually, an increase in entropy over that for ZrH_2 would not be surprising.

The normal procedure was to evacuate the system to $<10^{-4}$ torr followed by increasing the temperature to the desired value before hydrogen was introduced and the reaction initiated. In other cases a preliminary degassing was incorporated by maintaining the sample at temperature and under vacuum for a period of time before the addition of hydrogen. Immediately following completion of the reaction, the hydride was normally allowed to cool in the presence of hydrogen. However, in some cases the effect of annealing was studied by maintaining the reaction temperature up to 1 hour after the reaction was completed. These and other exceptions to the normal operating procedure are noted in Table 3, which summarizes the experiments performed.

To study the effects of temperature and pressure, we used combinations of 400, 600, or 900°C and 200 or 760 torr; exceptions are again noted in Table 3.

TABLE 3. Experimental Data

Sample No.	Form$^{(a)}$	Mass of Metal, g	Degas Temp., °C	Hydriding Temp., °C	Hydriding Pressure, torr	H:Zr Atom Ratio by Mass Gain	Experiment Time, Hr.	95% Absorption Time, Hr.	Notes
1	0.25" rod	6.4719	600	600	200	0.1019$^{(b)}$	3.7		Dark gray to black color due to oxide and nitride formation; see Table 3.
2	0.25" rod	3.1711	800	800	200-250	0.1928$^{(b)}$	77.4		Same as #1.
3	0.25" rod	3.0950	800	(c)	(c)	0.6192$^{(b)}$	20.6		3/4 brown and 1/4 black color due to oxide and nitride formation; see Table 3; silver gray interior; heavily cracked.
4	0.25" rod	3.2204	800	(c)	(c)	0.0905$^{(b)}$	25.0		Same as #1; edges are splintered; degassed 15 hr.
5	0.25" rod	3.0003	450	(c)	(c)	0.0223$^{(b)}$	24.6		Same as #1.
6	0.25" rod	3.2556	800	(c)	(c)	0.2128$^{(b)}$	10.2		Same as #1.
7	0.50" tubing	6.3818	154	(c)	(c)	0.60 See Notes	21.9		Light gold with black spots; H:Zr ratio determined by volume H_2 absorbed.
8	0.25" rod	3.1110	25	500-800 3 cycles	10^{-4}	0.0000	3.0		No hydrogen introduced; preparation performed to determine mass gain in absence of hydrogen; sample washed and abraded; degassed at 25°C for 1 hr.
9	0.25" rod	3.0324	450	500-800 3 cycles	10^{-4}	0.0000	4.0		No hydrogen introduced; degassed 17 hr. 25°C and 1 hr 450°C; dull gray color.
10	0.25" rod	2.7874	919	919	200	0.713	4.25	1.75	Degassed 1 hr.; reddish with gray spots.
11	0.25" rod	3.1156	916	919	760	1.473	4.00	1.90	Reddish gray; few deep cracks; degassed 1 hr.; annealed 2 hr.; metal washed and abraded.
12	0.25" rod	3.5428		919-400-919	600	1.918	4.55	1.86	Brown with deep cracks; annealed 1.5 hr.; metal washed and abraded.
13	0.50" tubing	5.9134		918	760	1.917	0.77	0.64	Silver with tan edges; criss-crossed with microcracks; brittle; metal washed and abraded.
14	0.25" rod	3.1682	624	627	760	1.667	2.40	1.38	Silver gray with several cracks; metal washed and abraded; degassed 1 hr.
15	0.25" rod	3.3010		627	760	1.509	2.86	1.96	Silver with slight yellow tint; metal washed and abraded; a few deep cracks; see Table 3.
16	0.25" rod	3.1086		627	760	1.676	1.87	1.30	Silver with yellow tint.
17	0.25" rod	2.7442		23-626	760	1.808	3.50	2.13	Hydrogen added at 23°C; T was increased to 626°C; took 20 minutes once 626°C was reached for reaction to begin; hydride was dark gray to black. Bottom end more severely cracked than upper.
18	0.25" rod	2.5134		626	See Notes	1.532	4.20	3.64	Sufficient hydrogen to make $ZrH_{1.5}$ was added; pressure was allowed to drop as H_2 was absorbed; hydride was silver with yellow tint; see Table 3.
19	0.25" rod	2.3674		915	See Notes	1.314	3.00	1.60	Same as #18; only reddish silver with small cracks.
20	0.25" rod	3.3664		627	200	0.721	7.30	7.30	Silver with yellow tint; no cracks.

TABLE 3. (contd)

Sample No.	Form[a]	Mass of Metal, g	Degas Temp., °C	Hydriding Temp., °C	Hydriding Pressure, torr	H:Zr Atom Ratio by Mass Gain	Experiment Time, Hr.	95% Absorption Time, Hr.	Notes
21	0.50" tubing	5.1931		625	760	1.844	2.40	1.38	Silver; several deep cracks in bottom end; a few cracks in top end; brittle.
22	0.25" rod	3.3602		626	760	1.629	1.90	0.76	Silver; several deep cracks on the ends; shallow cracks on sides.
23	0.50" tubing	8.2188		418	760	0.488 See Notes	∿8.0	5.65	The sample was severely cracked and broken; therefore, the H:Zr was determined by volume H_2 absorbed. The hydride was black; not brittle.
24	0.50" tubing	6.1712	627	629	760	1.741	3.0	1.58	Silver with numerous deep cracks in bottom; four small cracks on top; flaking on bottom; degassed 1 hr.; brittle.
25	0.50" tubing	6.6457		626	636 See Notes	1.894	2.4	0.42	Silver; deep cracks on bottom; shallow in middle and top; H_2 absorption was very rapid; 760 torr was not reached before $ZrH_{1.5}$ was; brittle.
26	0.50" tubing	6.7366		921	760	1.741	∿3.0	0.70	Silver-gray; many microcracks on surface; brittle.
27	0.50" tubing	3.5543		622	630 See Notes	1.897	1.1	0.28	Silver; bottom is heavily cracked; top and middle have several small cracks; absorption was again too rapid to reach 760 torr; brittle.
28	0.50" tubing	3.2485		700-846 See Notes	760	1.799	2.6	0.48	Temperature was increased as H_2 added until absorption ceased. Hydride is silver and has no cracks. Not brittle.
29	0.50" tubing	4.3964		918	200-760 See Notes	1.940	5.5	4.95	Pressure was incrementally increased when absorption at previous pressure ceased. Hydride was principally brown with a gray top. Very small cracks; brittle.
30	0.50" tubing	4.9920	25	626	760	1.910	2.32	1.06	Sample degassed 15 hr.; hydride is silver with deep cracking on bottom. Surface has numerous small cracks; brittle, annealed 1 hr.
31	0.50" tubing	3.3800		625	626 See Notes	1.908	2.50	0.33	Same as #25; annealed for 1 hr.; brittle.
32	0.50" rod See Notes	10.7643		627	760	1.619	3.20	2.98	Zircaloy-4 rod used; hydride is silver with yellow tint; top is black; bottom more cracked than top.
33	0.50" tubing	4.9881		628	760	1.908	2.29	0.75	Silver with yellow tint; few large cracks; many small cracks; brittle.
34	0.50" tubing	5.5172		628-854 See Notes	760	1.858	2.70	0.81	Same procedure and results as #28; sample annealed 1 hr.; brittle.
35	0.50" tubing	5.1598		628	760	1.909	2.30	0.72	Silver; deep cracks on the end; and shallow on sides; brittle.
36	0.25" rod See Notes	2.1995		626	760	1.928	1.16	0.48	Pure zirconium starting material; hydride is silver with yellow tint and is heavily cracked.

(a) Zircaloy-2 except for #32 and 36.
(b) H:Zr ratio determined by fusion analysis.
(c) Temperature and pressure were varied in attempts to promote H-Zr reaction.

ANALYTICAL PROCEDURES

We used both weight gain and volume (STP) of H_2 absorbed to determine the final composition of the zirconium hydrides prepared. The former can be measured more accurately but includes a potential error due to reaction with impurity gases. However, except as noted for the first seven samples (discussed below) this error is believed to be small and the composition determined by weight gain is listed in Table 3. It is worth noting that the two values differ by no more than 5% for any of the hydrides. Hydrogen, oxygen, nitrogen, and carbon concentrations were determined by fusion analysis in selected samples (Table 4).

The volume (STP) of the hydriding system was calculated, assuming ideality, using the pressure change caused by addition of a known volume of H_2. The "apparent" volume of the system is a function of the reaction vessel equilibrium temperature and was determined at two points: 25 and 915°C. A linear relationship between "apparent" volume and temperature was assumed and used to calculate hydrogen absorption at a particular temperature.

TABLE 4. Carbon, Oxygen, Nitrogen, and Hydrogen Analyses of Selected Hydride Samples

Sample	Oxygen, wt ppm	Hydrogen, wt ppm	Carbon, wt ppm	Nitrogen, wt ppm
1	2,351	1,113	77.5	833
2	4,088	2,100	110.0	586
3	3,816	6,716	73.0	342
4	4,692	986	125.0	593
5	3,704	2,204	114.0	832
6	1,737	2,323	56.0	623
15	1,050	21,313	<70.0	54
18 (outer)	-	18,643	<70.0	<10
18 (inner)	340	18,263	<70.0	<10

RESULTS AND DISCUSSION

The conditions of preparation and the physical characteristics of the product hydrides are included in Table 3. Samples 1-7 were prepared prior to complete elimination of air inleakage into the hydrogen supply line. They are examples of the inhibiting properties of the nitride and oxide films formed by absorption of N_2 and O_2 impurities in H_2. With this inhibition present, variations in temperature, pressure, and pretreatment were equally ineffective in speeding up the desired reaction. The nitrides and oxides of zirconium are exceptionally stable compounds (see Table 2) and form a barrier to the hydrogen reaction apparently even at temperatures above where the oxide should dissolve or migrate into the metal.

Neither pretreatment (degassing or surface conditioning by washing and abrading) nor post-reaction treatment (annealing at the reaction temperature) had detectable effects on either formation rate or physical characteristics of the hydride: for degassing effects, see Samples 10, 11, 14, 24, for surface conditioning see Samples 8-15, and for annealing effects, see Samples 11, 12, 31, and 34.

The starting form of the metal was important in determining the rate of reaction and the physical state of the hydride. Samples 22, 31, and 32 shown in Figures 3 and 4, show the difference between the 0.25 in., 0.50 in. diameter rod and the 0.50 in. tubing forms. Because of its larger surface-to-volume ratio the tubing accepted hydrogen more rapidly and with less destruction of physical integrity. Sample 32 shows the effect of decreasing the surface-to-volume ratio. Comparison of 36 and 22 in Figures 3 and 4 suggests an increased reaction rate for pure zirconium relative to Zircaloy-2. The addition of the alloying components in Zircaloy possibly inhibits the rate of reaction slightly. However, the pure zirconium is more severely cracked than its Zircaloy-2 counterpart. A single 0.50-in. Zircaloy-4 rod was hydrided, but no Zircaloy-2 nor zirconium of comparable size were hydrided. Thus, a comparison cannot be made. It must be emphasized that the small number of samples examined makes the above comments very tentative. Likewise, the effects of other alloying materials originally scheduled were not determined.

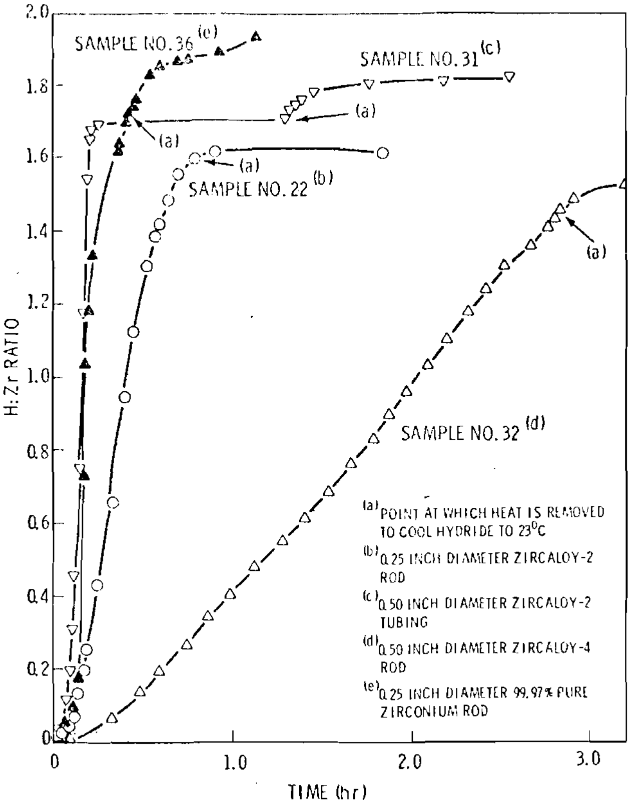

FIGURE 3. Effect of Starting Form of Zirconium on Reaction Rates at ∿630°C and 760 Torr Hydrogen Pressure

The effect of H_2 pressure on the reaction rates was greater than expected, the rate at 200 torr being much slower than at higher pressures (see for example Experiments 10, 11, 12, 18, and 22). The data are inadequate to permit quantitative interpretation. Experiments performed at Brookhaven National Laboratory (BNL) also showed considerable variation in reaction times with pressure.$^{(16)}$ For preparation of tritiated hydrides, the BNL workers chose the slower reaction at pressures <100 torr to avoid hydride cracking.

It would be expected that somewhat higher equilibrium pressure would exist over the Zircaloy as compared to pure zirconium, and therefore a lower terminal hydrogen-to-zirconium (H/Zr) ratio would be reached for Zircaloy under similar conditions. Information is lacking for Zircaloys. However, the assumption is supported by the measurements of Trzeciak, who found a

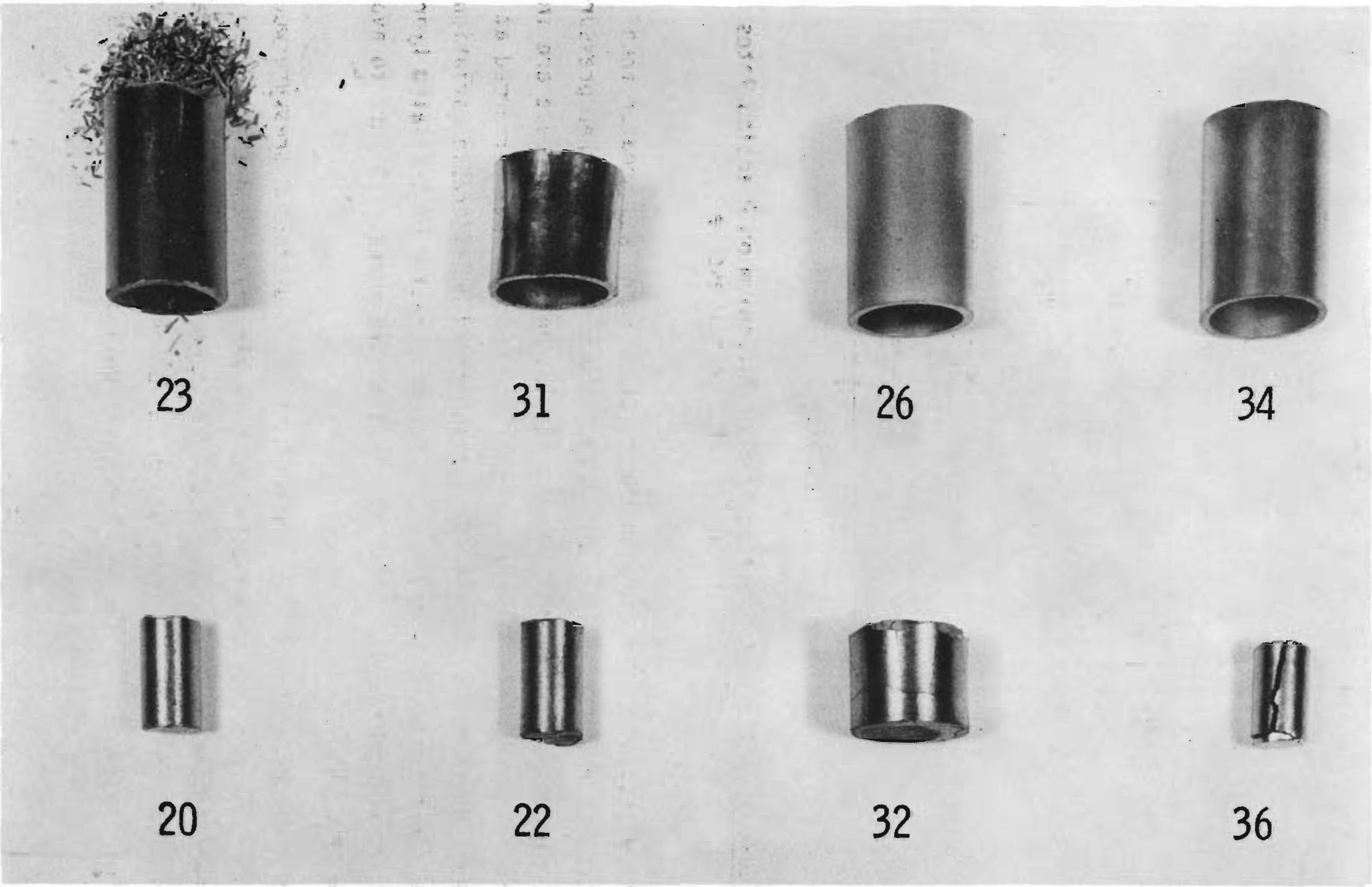

FIGURE 4. Representative Zirconium-Hydride Samples for Various Conditions of Preparation

maximum H/Zr ratio of 1.78 for a 4 at.% Sn alloy.(12) For a 5 at.% Sn alloy, Beck observed a considerably higher plateau pressure for the $\beta + \delta$ system at 800°C, 225 torr versus 134 torr for Zr.(11)

The maximum attainable hydride composition (H/Zr ratio) is limited by the partial pressure of hydrogen at a particular temperature, thus from Figure 2, higher pressures than those used were necessary to obtain a comparable final composition at 900°C to that at 600°C. Thus, the effect of temperature on reaction rates is best compared at a lower hydrogen content. At the point where the composition is $ZrH_{0.8}$ the average reaction times were (Figures 3, 5 and 6):

- Rod at 915°C, 0.71 hr.
  625°C, 0.75 hr.
- Tubing at 915°C, 0.22 hr.
  T increased from 600°C, 0.08 hr.
  625°C, 0.42 hr.
  400°C, >15 hr.

The very slow reaction found at 400°C, Sample 23 (Figure 5) is in agreement with work of LaGrange et al., who found the H_2-Zr reaction to proceed very slowly below 550°C.(17) The long reaction times observed below about 600°C may be due more to lack of mobility of the protective films of oxides, nitrides, etc., rather than the effect of temperature on the H_2-Zr reaction itself. The hydriding reaction is probably diffusion controlled over the temperature range of the present experiments.

The effect of temperature on the integrity of samples with high hydrogen content is significant. Higher temperatures apparently allow the metal to stress relieve itself as the hydrogen is absorbed. Samples prepared by H_2 addition while the temperature was being increased from 600 to about 900°C showed no cracks under a magnification of 215X. It might be anticipated that temperature changes which carry the sample through phase changes during hydriding might lead to more physical deterioration. Huffine, for example, observed that temperature variation and fluctuation caused increased cracking.(18) However, this was not evident from the present work.

Uniformity of hydriding was examined in Sample 18. Samples from the interior and exterior of the rod showed the same hydrogen content.

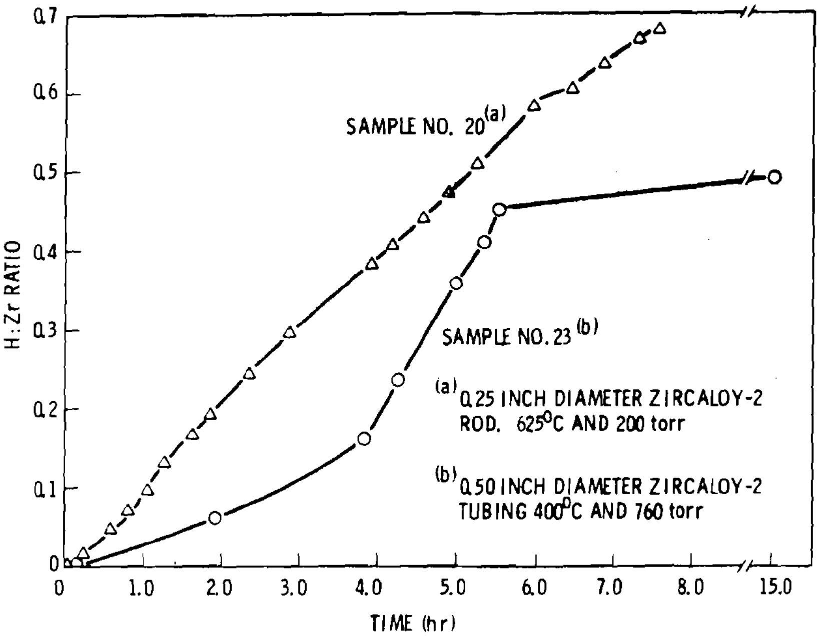

FIGURE 5. Effect of Low Pressure and Low Temperature on Zirconium-Hydride Formation

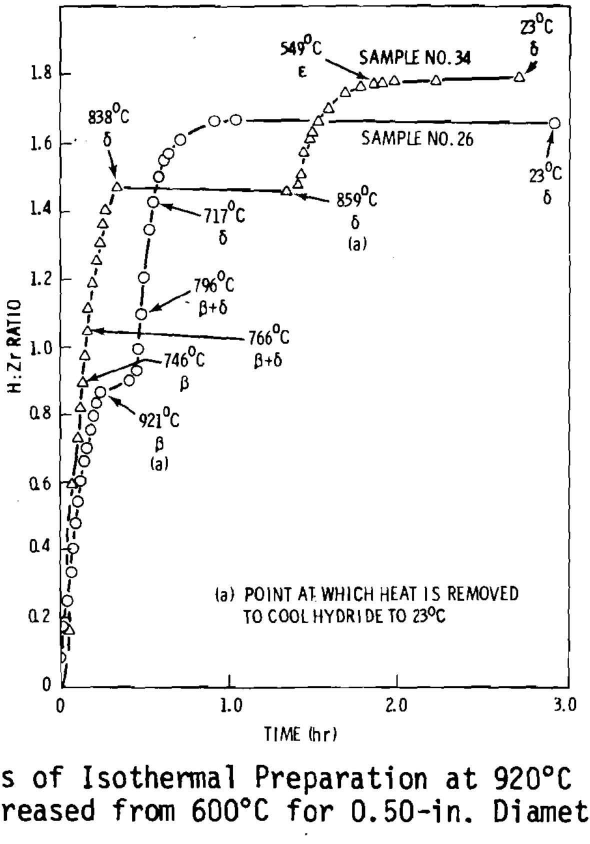

FIGURE 6. Effects of Isothermal Preparation at 920°C and as Temperature is Increased from 600°C for 0.50-in. Diameter Zircaloy Tubing

Figure 7 compares a hydrided Zircaloy-2 sample with the starting material. Note the intricate cracking and expansion of the hydrided tubing.

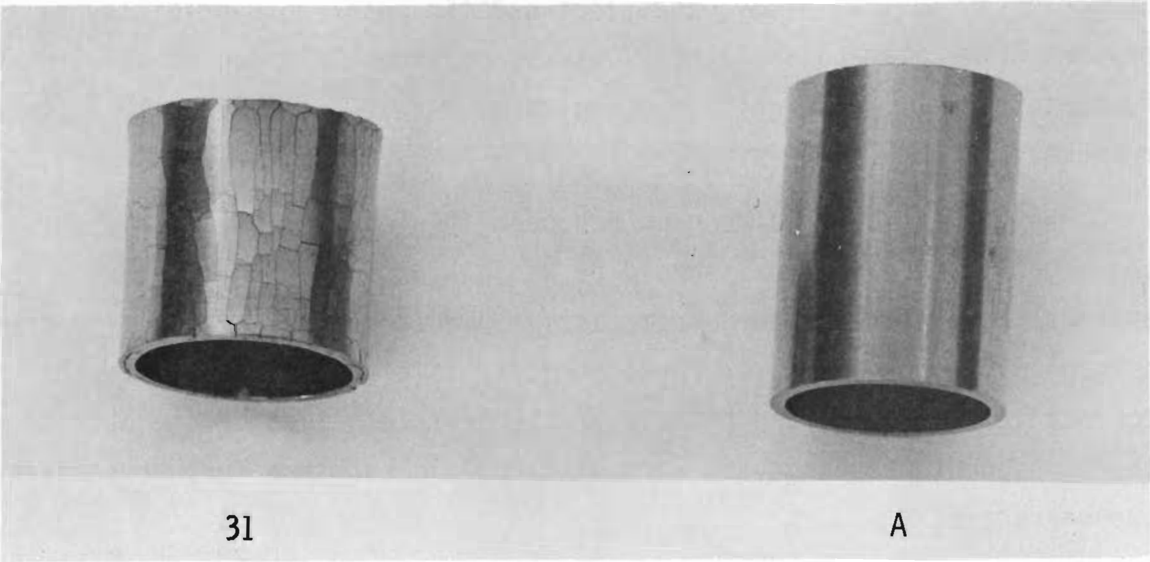

FIGURE 7. Zirconium-Hydride Sample Showing Intricate Cracking and Unhydrided Zircaloy-2 Sample

The appearance of the hydrided samples compared to the starting material may be examined in Figures 4 and 6. An expansion of about 8% was observed. The hydride samples are much more brittle than zirconium metal. The brittleness of the hydrides seem to correspond roughly to the degree of cracking; Sample 28, which was produced by the increasing temperature method, is relatively strong compared to other samples of similar hydrogen content.

The question of pyrophoricity of zirconium hydride is often raised due in part to experience with finely divided zirconium metal and to the pyrophoric nature of some other hydrides. Blackledge states that the hydride is generally more stable than the parent metal.(7) We attempted to ignite small fragments of both the zirconium and its hydride and tend to agree with that observation. Tesla coil sparks had no effect on fines removed from the samples. Pieces about 0.75 mm by about 1.5 mm square could not be ignited with a propane-oxygen torch. Smaller pieces, about 0.3 mm by 1 mm would ignite with the torch when held with a pair of forceps. These conclusions are supported by work carried out for BNL at the University of Denver.(19) In that study, the electrostatic spark susceptibility of the powders of metals and their hydrides was measured. Zirconium and ZrH_2 were found to have minimum ignition energies of 6×10^{-6} and 3.2×10^{-4} joules, respectively.

The combustion of zirconium has been studied in considerable detail and established guidelines should be useful for work with hydrides. There appears to be little hazard from massive pieces of either zirconium or zirconium hydride. However, pyrophoricity is directly related to the surface/volume ratio, and because of the brittle nature of the hydride and the consequent propensity to form small particles, some further studies are warranted.

As previously mentioned, the experimental program was not completed; thus no information was obtained on the stability of the tritiated hydride, i.e., the leachability of tritium from the solid. However, preliminary leach tests were carried out at BNL and very low losses were observed.(20)

Likewise, the experiments with cladding hulls were not completed. Pieces of Shippingport fuel cladding were washed with 6$\underline{M}$ HNO_3 and 0.1$\underline{M}$ Ce(IV) in 4$\underline{M}$ HNO_3. The radiation was low enough that they could be handled in the regular apparatus. Questions concerning the kinetic behavior of the irradiated versus unirradiated samples of Zircaloy and the physical behavior of the products have not been answered.

RECOMMENDATIONS

The brief study described here indicates that zirconium hydride should be an acceptable storage form for tritium and that scrap Zircaloy can be employed in place of zirconium. Used (irradiated) Zircaloy cladding hulls can probably be used, but this has not been demonstrated.[a]

Thus, although the feasibility is demonstrated, a number of problems need clarification:

- Elemental tritium is required. This can be achieved by electrolysis or by decomposition of the tritiated water with heated metal. Zirconium scrap may be ideal for this purpose, but the process has not been demonstrated.
- Impurities in the tritiated hydrogen may severely inhibit the hydriding rate. The obvious method of removing these is to pass the gas over a bed of Zircaloy scrap heated at a temperature above which the hydride is stable, about 1000 to 1200°C. Preparation of the hydrogen using heated metal as suggested above should simultaneously solve this problem. The possibility of using a flow system, i.e., placing the zirconium to be hydrided downstream from the purification bed, as opposed to the batch-vacuum technique used here should be investigated.
- Further information on the importance of the presence or absence of oxide (or other) films on the zirconium is needed.
- Further study of the effects of small amounts of alloying metals such as present in Zircaloy may be desirable.
- Studies with irradiated cladding hulls should be carried out to examine both the kinetics and the physical stability of the resulting hydride. Consideration of storage as related to residual radioactivity in these hulls is also required.
- Further leach testing under a variety of conditions, acidity, temperature, etc., should be done.
- Selected pyrophoricity studies with particle size and the Zr/H ratio as parameters should be carried out.

(a) Workers at Battelle-Northwest have shown that re-cast Zircaloy can be used to absorb the small quantities of hydrogen liberated when other hulls are melted.(21)

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APPENDIX A

COMPOSITIONS OF ZIRCALOYS

COMPOSITION[a] OF ZIRCALOY-2

Element	Top	Bottom
Composition in Percent		
Sn	1.56	1.41
Fe	0.14	0.16
Cr	0.11	0.11
Ni	0.06	0.06
Fe+Cr+Ni	0.31	0.33
Impurities in ppm		
Al	51	58
B	<0.2	<0.2
Cd	<0.2	<0.2
C	150	140
Co	<10	<10
Cu	13	13
Hf	58	66
H	9	6
Mn	<25	<25
N	28	27
Si	<50	<50
Ti	<25	<25
W	<25	<25
U	0.9	<0.5

(a) Analysis provided by Teledyne Wah Chang Albany

COMPOSITION[(a)] OF ZIRCALOY-4

Element	Top	Bottom
	Composition in Percent	
Sn	1.31	1.51
Fe	0.20	0.19
Cr	0.11	0.11
	Impurities in ppm	
Al	50	53
B	0.2	0.2
Cd	<0.2	<0.2
C	90	80
Co	<10	<10
Cu	28	31
Hf	74	77
H	11	7
Mn	<25	<25
Ni	<35	<35
N	33	32
Ti	<25	<25
W	<25	<25
U	<0.5	0.7
Cl	<5	<5
Pb	<25	<25
Ca	<10	<10
V	<25	<25
Mg	<10	<10
Si	95	88
Mn	<25	<25
Cb	<50	<50
O	1420	1420
Mo	<10	<10
Ta	<100	<100

(a) Analysis provided by Teledyne Wah Chang Albany

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