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TRITIUM STORAGE DEVELOPMENT

PROGRESS REPORT NO. 15
JANUARY - MARCH 1978

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DEPARTMENT OF NUCLEAR ENERGY

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P. Colombo and R. Johnson

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Summary

Two hydriding-dehydriding runs were made with zirconium sponge on an engineering scale for application to retrievable tritium storage systems. The dehydriding rates were low in comparison to hydriding rates. An overall hydrogen recovery of 35% was achieved after 16 hours at 500°C. At 600°C, the overall hydrogen recovery was 66% after 48 hours.

Hydriding rates were obtained for titanium rod at 450 and 525°C. The maximum reaction rates for an initial system pressure of 705-709 torr were 0.026 and 0.40 cm³ of H₂ at STP/cm²-min at 450 and 525°C, respectively. Increasing the initial system pressure to 1863 torr increased the maximum reaction rate to 1.04 cm³ of H₂ at STP/cm²-min at 525°C. In general, these rates are comparable to the rates obtained with zirconium sheet.

I. TRITIUM STORAGE IN METAL HYDRIDE

A program has been initiated to demonstrate a safe and economical process for the fixation of tritium as a tritide in a metal hydride. For tritium absorption and retention purposes, zirconium appears to be most desirable although alternatives such as Ti, Hf, V, Nb and certain alloys of these can also be used. The choice of zirconium as the leading candidate metal for this study is based on the known chemical and physical properties of the metal and its hydride. The process can be reversed, if desired, by heating the hydride above its decomposition temperature (defined as the temperature at which the hydride dissociation pressure is above 1 atm) and collecting the evolved gas. While the fixation process will be developed for long term storage or disposal by burial, retrievability of the tritium will be considered for future needs such as for use in controlled thermonuclear reactors.

A. Engineering Scale Equipment

In the engineering scale flowsheet (see Figure 1), a feed stream of H_2 or HT is regulated by a flow rate controller provided with a flow integrator. The pressure is monitored by gauges and pressure transducers (maximum design pressure: 100 psig). A vacuum system consisting of a cold trap, diffusion pump, and mechanical pump capable of producing a vacuum of 10^{-4} to 10^{-5} torr is provided for outgassing the reaction metal and removal of trace quantities of oxygen, nitrogen, etc., which have an inhibiting effect on the tritide-hydride reaction. The reaction vessel (see Figure 2) is approximately 3 inches in diameter and 19 inches high and is provided with a porous metal filter to prevent discharge of reaction product fines. An electric heater clamped externally to the vessel is used to provide an operating temperature up to $600^{\circ}C$. Temperatures in the reactor are monitored externally and also internally with a centerline thermowell. The reaction metal is placed in a wire mesh basket inside the reactor to permit optimum positioning for temperature control and measurement, and also to avoid expansion problems that can result from hydride formation.

B. Hydriding-Dehydriding of Zirconium Sponge

Two hydriding-dehydriding runs were made in the engineering scale equipment with commercial grade zirconium sponge and ultra-high purity hydrogen (99.999% minimum). The general hydriding procedure was described in previous reports. (1), (2)

In run R-1, two pieces of zirconium sponge weighing 10.7151 and 19.3537g were hydrided at approximately 500°C at a hydrogen flow rate of 2.87 cm³ at STP/g Zr-min over a 60 min period. The average H/Zr atom ratio of the two specimens at the termination of the hydriding step was 1.4 based on the hydrogen material balance. The specimens were maintained in the sealed system at 500°C and evacuated for 16 hours to a final vacuum of approximately 10⁻² torr. On a net weight gain basis, the final H/Zr atom ratios of the small and large sponge specimens were 0.58 and 1.09, respectively. These final H/Zr atom ratios represent hydrogen recoveries of 59% and 22%, or a combined overall recovery of 35%. Both specimens remained intact, but were friable as evidenced by some chip formation during handling.

In run R-2, two sponge specimens weighing 8.3678 and 18.1840g were hydrided at approximately 400°C at a hydrogen flow rate of 3.746 cm³ at STP/g Zr-min over a 63 min period to an average H/Zr atom ratio of 1.93. The specimens were evacuated at 600°C for 48 hours to a final vacuum of 10⁻² torr. Both specimens were completely broken apart. The average final H/Zr atom ratio was 0.65 on the basis of total combined net weight gain; this represents an overall hydrogen recovery of 66%.

The low hydrogen recovery for both runs indicates that the dehydriding rate is very slow in comparison with the rates obtained for hydriding. Zirconium hydride thus appears to have a modicum of stability even at 500-600°C, which, of course, is desirable from the standpoint of safety for tritium storage. The significant difference in the final H/Zr atom ratios for the small and large specimens from run R-1 (0.58 vs. 1.09) indicates that diffusion is rate controlling for those conditions. The concentration gradient or driving force for diffusion is therefore determined by the dissociation pressure (or equilibrium hydrogen pressure) of the metal hydride, which, in turn, is dependent on the H/Zr atom ratio.

The phase diagram and pressure-temperature-composition data for the zirconium-hydrogen system have been reported by Beck and Mueller⁽³⁾ (see Figure 3). The equilibrium hydrogen pressure at 600°C drops rapidly to about 0.6 torr during the dehydriding step as the H/Zr atom ratio falls between 1.3 and 1.4; another sharp drop occurs at a H/Zr atom ratio of about 0.1. At 500°C the equilibrium hydrogen pressure is considerably less and falls to less than 0.02 torr at a H/Zr atom ratio between 1.3 and 1.4. These hydrogen pressures are low compared to the hydrogen pressure used for hydriding sponge (see runs 1-10, references 1 and 2) and would account for the low dehydriding rates in runs R-1 and R-2. Also, there could be more buildup of a diffusion barrier of oxide, nitride, etc., on the metal surface from the longer exposure time to contaminants in the system during the dehydriding step.

A higher temperature would, of course, increase the equilibrium hydrogen pressure and dehydriding rate. At most of the H/Zr atom ratio range there is an order of magnitude difference in hydrogen pressure approximately every 100°C. The diffusivity would also be increased by an increase in temperature.

C. Hydriding of Titanium Rod

Four runs were made with 1/4 inch (6.4 mm) diameter commercial grade titanium rod* and ultra-high purity hydrogen (99.999% minimum) in the engineering scale equipment. For each run, a titanium specimen approximately three inches (7.6 cm) long was abraded with fine-grit paper and then degreased with acetone prior to placement in the wire mesh basket in the reaction vessel. The reaction system containing the specimen was outgassed at room temperature and during heating to operating temperature to a vacuum of 1×10^{-4} torr for run T-1 and to 2 to 4×10^{-5} torr for runs T-2 to T-4. The hydrogen was fed into the system rapidly until a final system pressure of approximately 1 atm absolute (2.5 atm for run T-4) was reached. The feed valve was then shut off and the system pressure was monitored under static (no-flow) and essentially isothermal conditions.

Run T-1 was made at 400°C for 24 hours. No significant change took place in the system pressure or the weight of the specimen during the run. The specimen had darkened slightly but otherwise remained unchanged.

The subsequent runs were made at higher temperatures (525°C for runs T-2 and T-4, and 450°C for run T-3). In Figures 4 and 5, the system hydrogen pressure for these runs is plotted against time on a semilog scale. Reaction rates and average H/Ti atom ratios (see Tables 1-3) were calculated from the PVT relationship by using the "apparent" system volume.

The semilog plots and tables for runs T-2 to T-4 show an initial induction period which was especially pronounced in run T-3 made at the lower temperature of 450°C . Runs T-2 and T-4 made at 525°C show a "tapering off" effect at the end of the run, which is probably due to the equilibrium hydrogen pressure of the titanium hydride. The pressure-temperature-composition data reported by Mueller⁽⁴⁾ and Beck⁽⁵⁾ (see Figure 6) indicate equilibrium hydrogen pressures of approximately 2.5 and 30 torr for the Ti/H atom ratios of 0.6 and 1.5, obtained at the end of runs T-2 and T-4, respectively. These pressures are in approximate agreement with the asymptotic values on the semilog plots.

*99.7% pure, grade M2N7, supplied by Alfa Products, Danvers, Massachusetts.

Comparison of the reaction rate for runs T-2 and T-3 (Tables 1 and 2) made at the same pressure range but different temperatures (525 and 450°C, respectively) shows maximum reaction rates of 0.40 and 0.026 cm³ of H₂ at STP/cm² of surface area per minute for the two respective runs. In each case the maximum reaction rate occurred at approximately 300 torr. These values indicate a fifteen-fold increase in rate at the higher temperature for the same pressure range. The effect of pressure can be observed by comparing runs T-2 and T-4, where both runs were made at the same temperature (525°C) but at different initial pressures (705 and 1863 torr for runs T-2 and T-4, respectively). The maximum reaction rate of 1.04 cm³ of H₂ at STP/cm²-min at approximately 1000 torr for run T-4 is 2.6 times greater. In general, these rates are comparable to those obtained with zirconium sheet (Cf. run F-7, reference 2: maximum rate of 1.34 cm²-min at 415-465°C at approximately 1000 torr for 0.065 inch zirconium sheet).

The specimens from runs T-2 and T-3 remained intact but turned blue and brown in color and also became slightly bent. The specimen from run T-4 cracked at one end (see Figure 7), apparently because of the higher H/Ti atom ratio attained in that run.

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- (4) W. M. Mueller, "Titanium Hydrides," in Metal Hydrides, edited by W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, Academic Press, pp 336-382, 1968.
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TABLE 1

Hydrogen Reaction Rate with Titanium Rod - Run T-2

<u>Time (min)</u>	<u>Pressure (torr)</u>	<u>H/Ti atom ratio</u>	<u>Reaction rate (cm³ at STP/cm²-min)</u>
0	705	0.00	0.26
50	610	0.08	0.30
100	486	0.18	0.36
150	343	0.30	0.40
200	217	0.41	0.29
250	127	0.48	0.18
300	73	0.53	0.12
350	39.8	0.55	0.07
400	20.9	0.58	0.04
450	12.0	0.58	0.02
500	7.7	0.58	0.01
700	7.5	0.58	0.0001
900	5.6	0.58	0.0000

Temperature: 525°C

Apparent system volume: 4.785 liters

Sample size: 1/4 inch diam. x 3 inches long

area: 15.96 cm²

weight: 11.1607g

TABLE 2

Hydrogen Reaction Rate with Titanium Rod - Run T-3

<u>Time</u> <u>(min)</u>	<u>Pressure</u> <u>(torr)</u>	<u>H/Ti atom</u> <u>ratio</u>	<u>Reaction rate</u> <u>(cm³ at STP/cm²-min)</u>
0	709	0.00	0.015
500	658	0.04	0.009
1000	621	0.07	0.011
1500	563	0.11	0.016
2000	491	0.17	0.019
2500	408	0.23	0.022
3000	317	0.30	0.026
3500	230	0.37	0.025
4000	117	0.46	0.021
4500	51	0.51	0.011
5000	19.5	0.53	0.004
5500	7.7	0.54	0.002
5800	4.3	0.55	0.001

Temperature: 450°C

Apparent system volume: 4.106 liters

Sample size: 1/4 inch diam. x 3 inches long

area: 15.96 cm²

weight: 11.1607g

TABLE 3

Hydrogen Reaction Rate with Titanium Rod - Run T-4

<u>Time (min)</u>	<u>Pressure (torr)</u>	<u>H/Ti atom ratio</u>	<u>Reaction rate (cm³ at STP/cm²-min)</u>
0	1863	0.00	0.13
50	1815	0.04	0.14
100	1750	0.09	0.14
150	1660	0.17	0.26
200	1560	0.25	0.36
250	1380	0.40	0.69
300	1040	0.68	1.04
350	670	0.99	1.03
400	365	1.24	0.68
450	188	1.39	0.39
500	93	1.47	0.20
600	36	1.51	0.02
700	29	1.52	0.005
900	25	1.52	0.000

Temperature: 525°C

Apparent system volume: 4.785 liters

Sample size: 1/4 inch diam. x 3 inches long

area: 15.96 cm³

weight: 11.1520g

Figure 1. Tritium Storage in Metal Hydride Engineering Scale Flowsheet

Figure 2. Metal Hydride Reaction Vessel

Figure 3. Phase Diagram and Pressure-Composition Isotherms for the Zirconium-Hydrogen System⁽³⁾

Figure 4. Hydrogen Pressure vs. Reaction Time for Titanium Rod - Runs T-2 and T-4.

Figure 5. Hydrogen Pressure vs. Reaction Time for Titanium Rod - Run T-3.

Figure 6. Pressure-Composition Isotherms for the Titanium-Hydrogen System^{(4), (5)}

Figure 7. Hydrided 1/4 Inch Diameter Titanium Specimen
from Run T-4

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