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METAL HYDRIDES INCORPORATED
CHEMICAL RESEARCH LABORATORY

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Prepared By: E.P. Gibb Jr.

CHEMICAL RESEARCH STAFF FOR NEPA

Peter P. Alexander, President and General Manager

Robert W. Bragdon

Thomas R. P. Gibb, Jr.

Henry W. Kruschwitz, Jr.

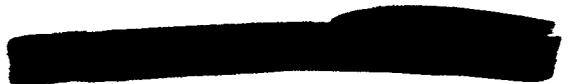
James J. McSharry



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Contents

General Summary	p 1
Report of Conference with Chemistry Section	p 2
Calculation of ΔH_0 and ΔF for TiH_2	p 3
Dissociation Apparatus and Discussion	p 4
Preparation of TiH_2	p 5
X-Ray Studies of TiH_2 , ZrH_2	p 6
Hydrogen Diffusion Studies	p 7
Photosnell Fabrication	p 7
Appendix	p 9

UNCLASSIFIED

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-1-

Metal Hydrides - Report No. 9

General Summary

It was hoped that work on photoshell fabrication and titanium hydride synthesis would be completed during May. Unfortunately the good fortune which had attended the photoshell fabrication program from the first appears to have run out. The die used to compress hydride wafers was spoiled by trials at 300 tons (Merriman Company) and has had to be partially rebuilt. It is now finished and will be tested shortly. The particular batch of stainless steel alloy 347 bar stock from which covers for photoshells of design (2) were made has been found defective in that it develops microporosity on welding. All current photoshells of this alloy, including the last one sent to NEPA, are therefore not up to standard and should not be used for test purposes. Not only was a considerable amount of time lost because of this unforeseeable difficulty, but also a quantity of titanium hydride. This loss, together with requests for additional filled photoshells, has made it necessary to make more hydride. For reasons presented in a later section, additional studies on titanium hydride synthesis appear warranted.

During the month a study has been commenced of certain details of the manufacture of titanium hydride via calcium hydride reduction of titanium dioxide. Encouraging results have been obtained. It is expected that the physical properties of hydride so prepared, together with the absence of magnesium (which is present in titanium from other sources), will have an effect on the dissociation pressure. Extra heavy-wall photoshells and a high-pressure assembly are now available for high-temperature dissociation studies. Considerable effort has been put into the design and construction of this equipment. There is new evidence that the presence of nitrogen in titanium (order of 0.1 - 0.3%) considerably inhibits complete reaction with hydrogen. This effect and that of oxygen are now under investigation. X-ray diffraction data are presented in a later section of this report.

The dissociation apparatus is now in operation and is yielding useful information, although the rate of reaction of metals with hydrogen at the moderate temperatures employed is slower than expected which, of course, delays the final result.

Work on hydrogen permeability is nearly complete. On request of NEPA we are trying to obtain suitable samples of 2S aluminum for permeability tests. (The low melting point of aluminum and its poor mechanical properties rule it out for 650° C use).

Several extra-long photoshells of various wall thicknesses (unfilled) have been made of 316 stainless steel rather than 347 in view of the procurement problem for 347 tubing. Two of these extra long shells will be tested for diffusion loss, and both a welded and an unwelded (empty) shell will be sent to NEPA shortly. Additional shells of 347 alloy will be available in a week and will be filled, welded, and sent to NEPA as per request (provided the die used to compress the filling is not again ruined by the high-pressure employed).

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Metal Hydrides - Report No. 9

Report of Conference with Chemistry Section

The author spent the period April 27 - May 3 inclusive away from the laboratory in conference with NEPA personnel at Oak Ridge. Work on hydrides by both NEPA and Metal Hydrides Incorporated laboratories was reviewed and plans for next year were tentatively formulated. Discrepancies in dissociation pressure measurements were attributed to diffusion of gases through the quartz and Vycor tubes employed by the NEPA group.

It may be shown qualitatively that rapid diffusion of hydrogen outward and slow diffusion of nitrogen and/or oxygen inward through the container walls can account for the variations in pressure observed in the NEPA laboratory. Of probable equal importance, especially if the amount of hydride is small, is its reaction with silica and vycor at high temperatures. Any slight pick up of oxygen (moisture) or especially nitrogen appears to "poison" titanium so that it will not react quantitatively with hydrogen.

The pertinent reactions are:

1. $TiH_2 \longrightarrow Ti + H_2$ promoted by N_2 , O_2 , Hg, volatile metals.
2. $Ti + H_2 \longrightarrow TiH_2$ poisoned by N_2 , O_2 .
3. $TiH_2 + \frac{n}{2}N_2 \longrightarrow TiN_n + H_2$ irreversible at moderate temperatures. n probably equals unity.
4. $TiH_2 + \frac{n}{2}O_2 \longrightarrow TiO_n + H_2$ possibly somewhat reversible when n is small and temperature $\sim 1000^\circ C$.
5. $TiH_2 + SiO_2 \longrightarrow SiO + TiO + H_2$ coefficients unknown
6. $TiH_2 + H_2O \longrightarrow TiO + 2H_2$ eventually gives TiO_2 .

Titanium may pick up considerable quantities of oxygen or nitrogen without forming a compound and without significant change of appearance or lattice dimensions. The hydrogen equilibrium, equation 1., however, is displaced to the right.

The lower dissociation pressures of titanium hydride reported by NEPA are undoubtedly due to the size sample taken relative to the volume of the system. The latter must be small compared to the volume occupied by the hydride. The effect of metal turnings in the system used by NEPA is probably ascribable to adsorbed gases or moisture reacting in accordance with equations 3., 4., and 6. above.

Some of the above phenomena have recently been noted by the Metal Hydrides group in connection with the low-pressure dissociation equipment which employs a silica tube. Part of the difficulty has been eliminated by employing a stainless steel crucible within the tube, thus avoiding not only contact of hydride with silica but also reducing contact with air diffusing through the hot silica walls.

Metal Hydrides - Report No. 9

In keeping with the tentative program for future work, this laboratory is procuring raw materials and setting up equipment for studies on tungsten and tantalum hydrides. Work on titanium hydride preparation will be concluded shortly. Further work on titanium hydride and zirconium hydride dissociation are earnestly recommended, not only because of the probable value to NEPA, but since such studies will furnish a set of reference data to which subsequent work on other hydrides may be compared.

Calculation of H_0 and F of Titanium Hydride (R.F.B.)

The general free energy equation relating ΔF , ΔH , and ΔC_p has the form

$$\Delta F = \Delta H_0 - \Delta \Gamma_0 \ln T - 1/2 \Delta \Gamma_1 T^2 - 1/6 \Delta \Gamma_2 T^3 \dots + IT$$

where $\Delta H_0 = \Delta H - \int C_p dT$, and is a hypothetical heat of reaction at absolute zero assuming the heat capacity relations determined experimentally hold down to absolute zero.

ΔC_p of the reaction:



can be estimated from Kopp's rule. The contribution of titanium is assumed to be the same, both free and combined, while a value of 2.3 is assigned to each atom of combined hydrogen. The value of C_p for hydrogen gas at room temperature is 6.8, and thus we find

$$\Delta C_p = 6.8 - 2 \times 2.3 = 2.2 \text{ cal/mol-deg.}$$

Actually on applying this to the existing data, the value of 2.2 cal/mol-deg. has been found to be unsatisfactory and a value of 1.0 to give more accurate results. A figure of 1.0 has also been observed in the thermodynamic interpretation of calcium hydride dissociation. This is attributed by Lewis and Randall to the rapid rise in the heat capacity of the hydride with temperature, and in fact ΔC_p may approach zero at high temperatures.

ΔH at 573° K for the dissociation of titanium hydride was calculated as + 7530 cal/mol from the slope of curve I, Figure 3 in Report No. 8. Then:

$$\Delta H_0 = +7530 - 1.0(573) = 6957 \text{ cal/mol}$$

The general free energy equation would then be:

$$\Delta F = 6957 - 1.0T \ln T + IT$$

where I is an integration constant that can be evaluated from the data of Report No. 8.

Metal Hydrides - Report No. 9

Table I

Calculation of I from Dissociation Data

<u>T°K</u>	<u>log T</u>	<u>Kp (atmos)</u>	<u>log Kp</u>	<u>-RTlnKp</u>	<u>1.0TlnT</u>	<u>I</u>
548	2.7388	5.65	0.7520	-1880	1368	-13.63
573	2.7582	7.83	0.8938	-2340	1582	-13.48
598	2.7767	10.41	1.0174	-2780	1663	-13.50
623	2.7945	13.95	1.1446	-3270	1738	-13.61

Substituting the average value of -13.55 for I as obtained in Table I into the general free energy equation, we obtain

$$\Delta F = 6957 - 1.0T \ln T - 13.55 T$$

This relationship probably holds fairly well over the range from room temperature to 400 to 500° C. At higher temperatures the rapid drop of ΔC_p suspected could cause large errors. The straight line plot obtained for log P vs. 1/T in Report No. 8 would seem to indicate that the experimental data used are fairly reliable. However, it should be borne in mind that the data are meant only as a guide to more exacting investigations. It should also be noted that the calculated ΔF and ΔH values are for a negligible dissociation and as such would not necessarily agree with values from calorimetric data. This is a result of the peculiar effect of the presence of solid solutions.

Dissociation Apparatus (H.W.K.)

The remaining portions of the system were calibrated and the final determinations are included. (See Fig. 4, Report No. 5).

ABCFD	419.5 cc
BCDF	349.7
DCF	291.9
D	251.0
CF	40.9
BCF	98.7
B empty	57.8
B with steel tube	51.7
E	2149.4

The two Brown gauges were calibrated for volume difference at various pressures and a correction graph prepared. Since one of the gauges (1-100 mm Hg) requires an added correction to be considered, it

UNCLASSIFIED

-5-

Metal Hydrides - Report No. 9

has been decided (at least for the present) to operate the system without them. The first silica reaction tube was broken during the reduction of the first steel tube. The casualty was due to expansion of the stainless steel crucible-tube, the diameter of the silica tube not being sufficient to allow for it. The second tube is of larger inside diameter, and no further trouble has resulted. Upon treatment with hydrogen, the steel tube was found to take up 1.8 cc.

One of the first problems encountered during the first trial run was the determination of the initial H_2 pressure over the sample. During the procedure the hydrogen is allowed to fill the system completely except for segment "B" which has been evacuated to .03-.04 microns. The pressure can be accurately determined from the manometer, but as soon as the hydrogen is allowed to expand into "B," the sample begins to dissociate. Therefore, it is necessary to determine the pressure change due to the expansion into "B" at several different initial pressures and plot a graph of the results. The plot is a straight line and, therefore, any initial pressure may be multiplied by a factor to give the correct pressure for the whole system including "B."

The results of the second trial run were poor. The sample took up less than half the H_2 it theoretically should have. Upon examination the product indicated contamination by oxygen and nitrogen. To remedy this an all stainless steel tube has been designed which will incorporate a water-cooled jacket to protect the joint. (Fig 1.).

A further possible source of contamination could have been from the gas purification trains. Since they have no pyrometers, it was not possible to determine how long they should be heated to enable them to operate efficiently. Using a chromel-alumel thermocouple with a zero bath and potentiometer, it was found that the helium train required 80 min. to reach $725^\circ C$ and 2 hrs. for a temperature of $760^\circ C$. The hydrogen train reached $600^\circ C$ after 1 hr. and 650° after 2 hrs.

A second problem encountered in the trial runs has been the inability to pull a vacuum of less than 0.2 of a micron in degassing. When the dry ice bath on the main trap was replaced by liquid nitrogen, the pressure very quickly dropped to .01 of a micron.

Preparation of TiH_2

Three reactions have been carried out in the investigation of the Hydrimet process as a source of large amounts of pure titanium hydride. The procedure was as follows: Calcined titanium oxide (grade 2) was mixed in a mortar with 100% molar excess of powdered calcium hydride. The charge was heated in an atmosphere of pure hydrogen to $950^\circ C$ for 90 to 150 minutes and cooled slowly to room temperature. The furnace product was leached in aqueous hydrochloric acid, washed with water, and dried with alcohol and ether. The analyses appear in Table II.

UNCLASSIFIED

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-6-

Metal Hydrides - Report No. 9

Table II

Analyses of Hydrimet TiH₂

<u>Sample</u>	<u>% Ti</u>	<u>% H₂</u>	<u>% N₂</u>	<u>% Acid Insol.</u>
3B100	94.6	3.94	0.18	0.72
3B101	94.5	3.81	0.15	0.46
3B103	94.2	3.94	0.20	0.65

These hydrides were then degassed for three hours @ 1000° C. The sintered malleable products were again analyzed.

Table III

Analyses of Hydrimet Ti

<u>Sample</u>	<u>% Ti</u>	<u>% H₂</u>	<u>% N₂</u>	<u>% Acid Insol.</u>
3B100	96.8		0.20	0.33
3B101	97.2*	.1	0.16	0.62
3B103	97.2	.1	0.22	0.49

The increase in titanium content on degassing does not correspond to that expected from the hydrogen lost. Also there is upwards of 1% unaccounted for. Advance reports from the Analytical Laboratory indicate that a small portion (about 0.4%) of this may be due to silica. The balance of the discrepancy is possibly due to oxygen.

The leaching experiments mentioned in Report No. 8 are completed but cannot be reported until the calcium analyses have been completed. A sample of titanium metal (submitted by Harold Brown for hydriding) took up 3.74% H₂. The original titanium analysis was 98.3%, together with about 0.3% N₂. It seems possible that the nitrogen is poisoning the ability of apparently otherwise pure metal to absorb hydrogen.

X-Ray Studies on Titanium and Zirconium Hydrides

An error in Hagg's data as reported by H. T. Evans was discovered by one of us (R.F.B.). On p 10 of Report No. 8, the second entry in tabular column 2 should be 52.4 instead of 62.4. Hagg evidently believed he had prepared titanium hydride containing slightly more hydride than TiH₂. This is dubious in view of the actual lattice constants he reports which do not follow Vegard's law.

Debye-Scherrer patterns have been made of a second sample of titanium hydride containing 4.0% hydrogen. The pattern is identical with that from material prepared by us via the Hydrimet process and

UNCLASSIFIED

Metal Hydrides - Report No. 9

shows no extraneous lines from impurities. Neither does it show the 2.076 or 1.801 Å lines noted for the first time in another sample of 4.0% hydrogen content and cited on p 10 of Report No. 8. This tends to confirm the suspicion that the lines arise from a novel hydride phase.

Hydrogen Diffusion Studies

The low-pressure diffusion apparatus has been under repair and no measurements have been obtained. No results are reported for high-pressure diffusion rates on 316 welded photoshells at 650° C because the equipment has been set up for equilibration work. The latter has been delayed by the difficulties encountered with porous welds in the 347 bar stock. The latter is perfectly sound in appearance and welds easily; however, the weld shows micro cracks or porosity at the outer edges of the heated area. Also for this reason no diffusion rate studies have been carried out on 347 photoshells.

A permanent assembly has been set up for determining the volume of photoshell systems and a new 1000 psi recording pressure gage has been ordered.

Planned for next month are completion of studies on the diffusion rate for 316 photoshells. It is proposed to use the new design no. 3 photoshells which are considerably longer than the previous designs. As soon as 347 shells may be fabricated with covers made from sheet stock rather than bar stock, their permeability will be measured. At NEPA request we will investigate the permeability of 2S aluminum at temperatures somewhat below 650° C. This tubing has been on order for two weeks.

In connection with the dissociation tests at high pressures, we propose to measure diffusion through one of the very thick-wall photoshells in order to make necessary pressure drop corrections.

Photoshell Fabrication

As noted above the tendency of 347 bar stock to show micro cracks or porosity in the weld area constitutes a serious hindrance. Our machine shop (Gurnard Manufacturing Company) is designing a jig for precision machining of discs from sheet stock, and will make new photoshells of (thin wall) design no. 2 from 347 stainless steel. We have had made six design no. 3 photoshells of the following description from 316 stainless steel:

wall thickness	.028" (.071 cm)	(3 each)
wall thickness	.041" (.104 cm)	(3 each)
cover thickness	0.125" (.318 cm)	
I.D.	1.840" (4.68 cm)	
length overall	10.5" (26.7 cm)	
capacity	447 ^{0.3}	

Metal Hydrides - Report No. 9

ext. volume	(.028" wall)	487 cm ³
ext. volume	(.041" wall)	501 cm ³
area cyl. walls	(.028" wall)	395 cm ²
area cyl. walls	(.041" wall)	400 cm ²
area top + bottom	(.028" wall)	36.5 cm ²
area top + bottom	(.041" wall)	37.6 cm ²

These photoshells are made by machining 2" O.D. 1.830" I.D. 316 tubing to dimensions. A 0.001" shoulder is machined inside one end to receive the beveled cover. The bevel is provided to ensure weld penetration. To facilitate capping a slight lead is machined on the cap, and a band 1/16" wide is left to give good contact with the machined shoulder. By making the cap 0.003" larger in diameter than the shoulder, an hermetical friction fit is obtained. The other end is capped with a rough fit only, since it is welded prior to filling the photoshell.

A number of extra-thick-wall photoshells have been constructed for high-pressure dissociation studies. These are fabricated from 347 stainless steel with the following dimensions. Suitable lips and shoulders are machined to provide 100% weld penetration:

wall thickness	0.37 cm
end thickness	1.52 cm
length over all	10.64 cm
O.D.	4.82 cm
volume	99.3 cm

A stem of 1/4" tubing is welded in one cover. The shells will be filled with powdered hydride or metal through the stem. This avoids possible decomposition through welding the filled shell.

UNCLASSIFIED

Metal Hydrides - Report No. 9

Appendix

Description of Thin-Wall Photoshell No. T347-2

Alloy - stainless steel No. 347

Welds - atomic hydrogen (Middlesex Welding Co.)

Dimensions (See Report No. 8)

O.D.	4.80 cm.
I.D.	4.64 cm.
Length overall	7.51 cm.
Inside length	6.87 cm.
Volume internal	116 cc.
Volume external	136 cc.
Wall plus end volume	20 cc. = 14.7% total volume
Original weight hydride	355 g.
Original H content	13.85 g.
Equilibration conditions	650° C, 200 psi (2 hrs.)
Hydrogen removed	12.6 L (S.T.P.) or 1.125 g. or 8.12% orig.
% Hydrogen in equilibrated shell (theor. 4.0%)	3.59% ± 89.7% pure
Actual density 89.7% hydride in shell	3.04 g/cc
N _H of 89.7% hydride	6.64
N _H of complete photoshell	5.65

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