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Studies of Metallic Hydrides. I. Synthesis of Stoichiometric Hydrides of Group IVb Metals

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Formerly, hydrides of transition metals were generally treated as solid solutions or as hydrogen-occluding systems. It has been said that the elements in the IVb group of the periodic table, whose hydrides are typically metallic, do not form any stable hydride with a stoichiometric composition. The author intends to report the establishment of a process of synthesizing these hydrides, by which process the conditions necessary for the stoichiometric synthesis of IVb metal hydrides were determined.

Hydrides can be classified into three types according to their characteristics; (1) saline (salt-like) hydrides, (2) covalent hydrides, and (3) metallic hydrides. The covalent hydrides and the saline hydrides have been thoroughly studied. On the contrary, metallic hydrides have remained relatively uncultivated because of certain peculiarities and complexities in their experimental and theoretical treatment.

One of the anomalies of metallic hydrides is their indefinite hydrogen content over a wide range. Since Graham reported the occlusion of hydrogen by palladium,[1] many subsequent reporters have been inclined to treat a system of a transition metal and hydrogen as a solid solution. The idea that hydride forms in the matrix of metal[2] has also been considered. Recently uranium hydride with a stoichiometric composition has been prepared,[3] and the structure of various hydrides and the nature of their chemical bonding have been studied by neutron diffraction[4,5] and by nuclear magnetic resonance absorption.[6]

Concerning the hydrides of group IVb metals, in 1950 Gibb[7] denied the presence of a stable hydride with a stoichiometric composition on the basis of the observed unstability of $TiH_{2.00}$, whose composition was limiting.

Since this report by Gibb, stoichiometric hydrides (or deuterides) have not been produced: for example the samples used for neutron diffraction by Sidhu *et al.* in 1956 were $MD_{1.7-1.97}$[8] (M: metal), the samples used for X-ray diffraction by Yakel in 1958 were $TiH_{1.99}$, $TiD_{1.96}$, and $ZrD_{1.92}$,[9] and the samples used for nuclear magnetic resonance by Stalinski *et al.* in 1961 were $TiH_{1.969}$.[6]

Another anomaly involves the difficulties in understanding the chemical bond in metallic hydrides consistent with their physical properties, such as their electric conductivity and their brittleness. At present, the nature of the chemical bonding in the hydrides of transition elements, as well as that in borides, carbides, and nitrides, is still not clear. Also, in discussing this problem, it is necessary to synthesize stoichiometric compounds.

I am much interested in the fact that metallic hydrides have been less developed than ionic or covalent hydrides; I intend to establish a method of synthesizing stoichiometric metallic hydrides. First of all, the group IVb metals (Ti, Zr and Hf) which absorb a relatively large amount of hydrogen and whose hydrides are typical metallic ones with a metallic lustre, will be described in this paper.

Experimental

The change in the hydrogen content of a hydride with a change in the purity of the reactants, *viz.*, metals and hydrogen, was investigated in order to ascertain the limiting composition (x) in the hydrides of group IVb metals (MH_x), and in order to establish the necessary conditions for the reproducible preparation of hydrides of the limiting composition.

Materials. *Metals.* Several kinds of titanium, with purities slightly differing from one other, two kinks of zirconium, and one kind of hafnium were used. They are listed in Table 1. The analytical data for the metals are shown in Tables 2 and 3.

Hydrogen. Three grades of purified hydrogen (a,

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[4] R. E. Rundle, *ibid.*, **69**, 1719 (1947).

[5] R. E. Rundle, *ibid.*, **73**, 1751 (1951).

[6] B. Stalinski, C. K. Coogan and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 1191 (1961).

[7] T. R. P. Gibb, *J. Am. Chem. Soc.*, **72**, 5365 (1950).

[8] S. S. Sidhu, L. Heaton and D. P. Zauberis, *Acta Cryst.*, **9**, 607 (1956).

[9] H. L. Yakel, *Acta Cryst.*, **11**, 46 (1958).

Table 1. The purities and histories of sponge metals

		Purity (%)	Manufacture	Size	Treatment		
					Air-oxidized for 3 years	None	Packed♯1 with argon
Ti	(A)	99.75	Nihon Soda Co., Ltd.	Under 8 mesh		*	
	(B)	99.75	Nihon Soda Co., Ltd.	Under 8 mesh	*		
	(C)	99.8	Toho Titan Co., Ltd.	Under 10 mesh		*	
	(D)	99.8	Osaka Titan Co., Ltd.	Under 10 meth			*
	(E)	99.9	Osaka Titan Co., Ltd.	Under 10 mesh			*
	(F)	99.3	Osaka Titan Co., Ltd.	Under 10 mesh			*
Hf	(G)	97.3 (Zr+Hf =99.8)	Toyo Zirconium Co., Ltd.	Under 8 mesh		*	
	(H)	99.7	Toyo Zirconium Co., Ltd.	Under 8 mesh		*	
Zr	(I)	98.5 (Hf+Zr =99.8)	Toyo Zirconium Co., Ltd.	Under 8 mesh		*	

♯1 The metal was stored in an argon-filled container immediately after preparation to keep the surface uncontaminated.

Table 2. Analytical data of sponge titanium

Element	Kind of titanium				
	(A)	(C)	(D)	(E)	(F)
Ti	99.75	99.8	99.8	99.9	99.3
Fe	0.018	0.04	0.020	0.010	0.20
Cl	0.052	0.05	0.060	0.020	0.12
Mn	0.003	0.005	0.0027	0.0015	0.02
Mg	0.013	0.03	0.028	0.010	0.07
Si	0.012	0.03	0.014	0.007	0.05
N	0.005	0.005	0.005	0.008	0.028
C	0.013	0.008	0.008	0.010	0.05
H	0.0007		0.0020	0.005	0.005
O	0.052		0.030		0.15

Table 3. Analytical data of sponge Zr and Hf

Analyzed constituent	Zr-Sponge		Hf-Sponge
	Commercial grade (ppm)	Reactor grade (ppm)	Reactor grade (ppm)
Al	52	34	147
B	—	0.3	—
C	95	65	110
Cl	110	385	50
Cr	112	195	43
Co	5	5	—
Fe	622	1108	145
Mg	20	140	550
Mn	31	15	15
N	14	26	10
Ni	30	30	50
O	750	900	765
Pb	30	30	50
Si	45	30	50
Ti	30	30	50
V	20	20	100
Hf	2.5%	69	98.5%
Hf+Zr	99.8%	99.7%	99.8%
Brinell hardness	118	129	182

b, and c) were used to quantify, to some extent, the impurity effect on the composition of hydride. The methods of purification are shown in Table 4.

Apparatus. The apparatus for hydrogenation used in this research is schematically illustrated in Fig. 1.

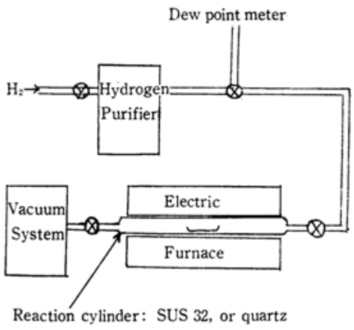

Fig. 1. Apparatus for hydrogenation.

The hydrogen purifiers utilized were the following two: *(1) Conventional Chemical Process:* This was a combination of the removal of carbon dioxide by a potassium hydroxide solution, deoxygenation by palladium asbestos at 375°C, and hydration by active alumina and phosphorus pentaoxide. Hydrogen of Grade a was obtained by using this method to purify electrolytic

TABLE 4. THE PURITY OF HYDROGEN

Starting material: Electrolytic hydrogen stored in a cylinder

	Purification processes	Purity
Grade (a)	KOH→Pd asbestos (375°C)→active alumina→P_2O_5	
Grade (b)	KOH→Pd asbestos (375°C)→active alumina→P_2O_5→TiH_x	Higher than 99.8%: Impurity-free based on gas chromatograph (sensitivity 200 ppm).
Grade (c)	A membrane of palladium alloy heated to an elevated temperature (450°C) was used as an "atomic sieve," through which only hydrogen atoms could diffuse.	Higher than 99.999% (dew point was lower than −60—−70°C).

hydrogen stored in a cylinder. In some experiments, denitrogenation by titanium hydride at 875°C was added; hydrogen of Grade b was thus obtained.

(2) Palladium Alloy Membrane. A hydrogen purifier made by the Japan Pure Hydrogen Manufacturing Co., Ltd. was employed.

This device was able to supply extremely pure hydrogen (Grade c) whose dew point was below −60—−70°C (purer than 99.9999%).

Procedure. *Initial Method.* Thirty grams of sponge titanium placed on a porcelain tray were inserted into a quartz reaction tube. The air within the cylinder has been expelled by passing purified hydrogen (a) through it at the rate of 400—500 cc/min for 30 min. The temperature of the reaction chamber was raised by an electric-tube furnace to about 400°C, whereupon an exothermic reaction was initiated and the sponge titanium became red hot. During this hydrogenation process, the rate of hydrogen flow increased to 800—900 cc/min. This red-hot condition lasted about 5 to 6 min. The reaction chamber was kept at a temperature of 400°C for 1 hr, and then gradually cooled by turning off the electric furnace while hydrogen was passed through at the rate of 400 cc/min.

Improved Method. In order to minimize the amount of gas adsorbed on the wall of the reaction chamber, *i. e.,* the amount of impurities, a reaction cylinder (30×1000 mm) made of stainless steel (SUS 32) and a stainless-steel tray were used instead of a quartz cylinder and a porcelain tray.

From three to ten grams of the metal placed on the stainless-steel tray were introduced into the reaction chamber, and the inner air was pumped out to attain a vacuum of 2×10^{-5} mmHg. After evacuation, the reaction chamber was baked at 800°C under a vacuum of 5×10^{-5} mmHg and then cooled to 400°C at which temperature a hydrogenation reaction occurred upon the introduction of hydrogen gas of three atmospheric pressures. After 10 min, the electric furnace was turned off, resulting in a gradual cooling.

Analysis. *Hydrogen Content.* Gravimetric analysis as well as gasometric analysis by a fusion method (JIS H 1619) was performed.

(i) Gravimetric Analysis. The weight difference between before and after hydrogenation was attributed to the hydrogen chemically combined.

(ii) Gas Analysis. The method prescribed in JIS H 1619 is a volumetric method based on the volumes of gases evolved. Since the amount of hydrogen occluded in these hydrides was very large, the weights of samples used for gas analysis were generally less than 10 mg.

The effect of gas impurities (the gases adsorbed on the wall of the reaction chamber) on the analytical data was negligible. The calculation was as follows:

Entire operating time………………… 1.0 hr
Result of pressurization test ………… 0.01 lμHg/sec
$0.01\times3600=36$ lμHg
$=36$ cc mmHg
$=0.048$ cc atm

Assuming that the gas is air, its weight must be 0.06 mg. This quantity could be overlooked in the results of gravimetric analysis.

Results and Discussion

The experimental results from 900 cases of hydrogenation are summarized in Table 5.

1) Composition. First, when the sponge titanium (A) with a purity of 99.75% and the hydrogen (a) purified by conventional chemical processes were used, titanium hydride, $TiH_{1.90}$, was formed. Its composition could not be regarded as stoichiometric (Experiment No. 1).

In Experiment No. 2, the purity of titanium was degraded by exposing the metal to air for three years, with the result that the hydrogen content decreased to 1.77.

A comparison of the results of Experiment No. 3 with those of Nos. 1 and 2 showed that the extremely pure hydrogen (c) was able to react with the deteriorated sponge titanium (B) to form the hydride, $TiH_{1.92}$ whose composition was even higher than that obtained in the case of the nondeteriorated metal (A) and the chemically-purified hydrogen (a).

In Experiment Nos. 3, 4, and 5, high-purity hydrogen, (c), and three kinds of titanium, (B), (C), and (D), were used. As the purity of the metal increased, the hydrogen content also increased, from 1.92 to 1.963, as is shown in Table 5.

In order to obtain higher hydrogen contents, the reaction system was improved by replacing the quartz cylinder with a stainless-steel (SUS 32) one; the pressurization (rate of pressure rise caused by outgasing) at 450°C was reduced to 0.01 lμHg/sec in and after Experiment No. 5. The resultant composition, obtained as the mean value of 20 runs, was $1.998_2\pm0.006_3$, which was the maximum hydrogen content attained. I have regarded the product as the stoichiometric hydride TiH_2.

TABLE 5. EXPERIMENTAL RESULTS

Exp. No.	Reactants								Products		
	Metal					Hydrogen					
	Kind	Purity (%)	History			(a)	(b)	(c)	Chemical composition x in MH_x	Lattice constant a (Å)	Remark
			Air-oxidized for 3 years	Packed with air	Packed with argon						
(1)	Ti (A)	99.75		*		*			1.90	4.43	Slightly colored $d=3.79$ (g/cm^3)
(2)	Ti (B)	99.75	*				*		1.77		
(3)	Ti (B)	99.75	*					*	1.92		
(4)	Ti (C)	99.8		*				*	1.963		Metallic lustre
(5)	Ti (D)	99.8			*			*	1.998_2 $\pm 0.006_8$	4.461	Complete metallic lustre $d=3.72$ (g/cm^3)
(6)	Ti (E)	99.9			*			*	1.998		Complete metallic lustre
(7)	Ti (F)	99.3			*			*	1.964		Complete metallic lustre
(8)	Zr (G)	97.3 (Zr+Hf =99.8)		*				*	1.944		Complete metallic lustre
(9)	Zr (H)	99.7		*				*	1.999 $\pm 0.001_1$		Complete metallic lustre
(10)	Hf (I)	98.5 (Hf+Zr =99.8)		*				*	2.016		Colored

When pressurization was greater than about 0.1 1μHg/sec, the composition obtained was lower than the maximum value.

This result was treaced by similar experiments on a large scale (Experiment No. 6), in which 100—150 g of sponge titanium was hydrogenated at a time; the same result, $x=1.998$, was reproducibly obtained.

In comparing the result of No. 7 with those of other experiments, particularly with that of No. 4, it is very interesting to note that the fresh surface of titanium preserved by argon could, to a certain extent, compensate for the low purity of the metal, although a stoichiometric composition could not be achieved by using only fresh surfaces; a high purity of the metal was also required.

Concerning ZrH_x and HfH_x, stoichiometric compositions were achieved with relative ease by applying the same experimental technique as that established in the preparation of stoichiometric TiH_2.

For zirconium hydride, the compositions obtained were $x=1.944$ for commercial zirconium (G) (Zr 97.3%+Hf 2.5%) and $x=1.999\pm0.001_1$ for reactor-grade zirconium (H) (Zr 99.7%); the latter stood for stoichiometry.

For hafnium hydride, the composition found was $x=2.016$, a little larger than stoichiometry; the difference could be attributed to contamination by impurities, as will be described later (2).

2) Appearance. When the hydride of titanium was almost free of contamination by impurities, it had the same lustrous appearance as the mother sponge metal, possessing a metallic lustre. A small amount of impurities rendered the surface of the hydrides gray-colored. Some impurities, such as oxygen and nitrogen, imparted blue or yellow surfaces to the hydrides; these surfaces might be attributable to the formation of suboxide and nitride. These impurities, of course, influenced the results of gravimetric analysis; therefore, tinted samples are omitted from Table 5.

One exception to the tinted samples omitted was $HfH_{2.016}$, which did not display a metallic lustre, which had a gray surface, and the composition of which higher than stoichiometry was attributed to contamination by impurities.

3) Density and Lattice Constant. The densities of the hydrides were measured by a method using a picnometer, while the lattice constants were examined by X-ray diffraction.

As the hydrogen content approached the stoichiometric composition, the density of the hydride decreased and the lattice constant increased.

The density and lattice parameters of titanium hydride with a stoichiometric composition were $d=3.72$ g/cm^3 and $a=4.461$ Å; the latter was larger than the values, $a=4.445$ Å by Chretién(10) and $a=4.454$ Å (315°K) given by Yakel.(9)

4) Stability. Gibb synthesized an unstable stoichiometric titanium hydride, about which he stated: "Two evanescent lines were found in the X-ray diffraction pattern of the stoichiometric

TABLE 6. CONDITIONS AND RESULTS BY SEVERAL INVESTIGATORS

Author	Purity of metal	Preservation and outgasssing of metal	Purification of hydrogen	Reaction chamber	Hydrogenation process	Resultant composition	Remarks
Gibb & others (1959, 1951) 7)	99.02% sponge Ti	Outgassed at 350°C. After reaching 0.1 1μHg, temp. was raised to 1000°C.	Passed over Pd, drierite a mixture of Ti sponge & Zr powder at 350°C.	A stainless steel cylinder	H_2 was introduced at 1000°C, then temp. was kept at 350°C over 9 hr and at 250°C over 16 hr.	3.99—4.00% of H	Samples for the study of dissociation pressure
Chretién & others (1954) 10)			Thermal decomposition of CaH_2		H_2 was introduced at 700—1000°C.	50—66.4 wt% of H a=4.445 Å	Samples for X-ray diffraction
Sidhu & others (1956) 8)	Rolled metal strip Ti & Hf	Dipped in an acid solution, rinsed in water and acetone, and air-dried.		A quarts cylinder	H_2 was introduced at 1000°C. Cycled several times between 500 and 1000°C. Hold for several hours at 500°C.	$MD_{1.7-1.97}$	Samples for neutron diffraction
Yakel (1958) 9)	High purity crystal bar Ti & Zr	Outgassed in a vacuum at 350°C and 1000°C.	Passed over uranium heated at at 700°C.	Mo tray	H_2 was introduced at 1000°C, then slowly cooled to 400°C and kept for several hours.	$TiD_{1.99}$ (a=4.54 Å at 315°K) $TiD_{1.96}$ $ZrD_{1.92}$	Samples for X-ray diffraction
Stalinski & others (1961) 6)	99.5% up Ti powder	Outgassed in a high vacuum for several hours at 820°C.	Thermal decomposition of TiH_2.		H_2 wat introduced at 450°C. Held for 20—40 hr at 250°C. Gradually cooled to room temp. Cycled for several times.	$TiH_{1.969}$	Samples for NMR 2.5—4 g
Present auther	99.8% up sponge Ti & Zr	Preserved in an argon-filled container. Outgassed at 10^{-5} mmHg at 800°C for 0.5 hr.	Passed through a Pd alloy membrane heated at 450°C.	A stainless steel cylinder. Pressurization was smaller than 0.1 1μHg/sec.	H_2 was introduced at 400°C for 100 min. Then temp. was reduced to room temp. for 2 hr.	$TiH_{1.998_2 \pm 0.006_8}$ 4.04 of H a=4.461 Å at 20°C $ZrH_{1.999 \pm 0.001_1}$	

hydride—There is thus evidence that an unstable compound of stoichiometric composition exists as a limiting composition."

On the contrary, with the product I obtained, no evanescent lines were found, and this stoichiometric hydride was stable in air.

Synthetic conditions and the results reported by several investigators are shown in Table 6 for the sake of comparison.

Summary

Stable and *stoichiometric* hydrides of group IVb metals were synthesized. The conditions necessary to obtain the stoichiometric hydrides have been reported to be as follows:

(1) The purity of the metal should be as great as possible, preferably exceeding 99.8%.

(2) The metal must be stored in an argon-filled container, or kept free from air immediately after preparation, in order to keep the surface uncontaminated by impurities.

(3) The hydrogen must be more than 99.9999% pure, or the dew point of the gas should be lower than -60°C.

(4) The rate of pressure rising due to outgasing must be kept under 0.1 1μHg/sec.

(5) The product must be cooled in the hydrogen described above.

When any one condition in the above requirements was not satisfied, the hydrogen content in the hydride did not exceed the value of 1.99, as is shown in Experiment Nos. 4, 7, and 8.

I wish to express my gratitude to Lecturer Nobuo Oshima for his long assistance in the experimental work. For their suggestions and advice, my thanks are also extended to Professor Emeritus Suketsugu Kimura, and Professor Emeritus Keizo Iwase of Kyoto University, and Professor Teruichiro Kubo of the Tokyo Institute of Technology. This research was partially financed by the Association of New Technological Research and Development to which I extend my appreciation.

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10) F. Chretién, *Compt. rend.*, **238**, 1423 (1954).