

## Characteristics of $TiH_2$ under High Pressure\*

고압하에서  $TiH_2$ 의 특성화 연구

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**ABSTRACT:** The Earth outer core accomodates moderately considerable amount of lighter elements than pure iron itself. Hydrogen is one of the possible candidates of minor constituents in the outer core. It would be worth while to extend for the pressure effect on the solubility of hydrogen in the metal-hydrides including iron hydride. In view of hydrogen being one of the potential substitutes for petroleum, searching a more efficient way for storing hydrogen in the form of hydrides is of considerable value. For two purposes,  $TiH_2$  was selected among lot of hydrides for its characteristics under pressure and temperature.

There have been two kinds of experiment carried out on  $TiH_2$  under different experimental conditions. As one of these attempts, polycrystalline  $TiH_2$  was loaded up to 15 GPa stepwise at the constant temperature of 500°C using a piston-cylinder diamond anvil cell equipped with a miniature furnace of an electric power supply. The X-ray diffraction technique was employed on the quenched samples after the simultaneous high pressure and temperature treatments.

During these high pressure-temperature runs, an irreversible phase of  $TiH_2$  has been observed at the pressures higher than 11.3 GPa, which would be assigned to the orthorhombic crystal system as one of the new phase(s) of  $TiH_2$ . Molar volume change on this phase transition is ~10%.

**요약 :** 지구외핵은 순수한 철원소 이외에, 철보다 원자량이 낮은 원소가 상당량 포함되어 있다. 수소도 외핵내에 존재할 가능성이 있는 성분 중의 하나로 인식되고 있다. 따라서, 철수화물에 대한 압력에 따른 수소의 용해도에 대한 연구와 병행하여, 기타 금속수화물에 대한 연구의 확대 또한 중요하다. 수소는 또한 석유의 대체물질로써 그 가능성이 매우 높으며, 금속수화물상태로 수소를 보다 효율적으로 저장할 수 있는 결정구조에 대한 연구 역시 요구된다. 이러한 두가지 이유로,  $TiH_2$ 를 철수화물의 결정구조적 유사물로 선택하여, 고온-고압하에서 특성화 현상을 연구하였다.

결정질  $TiH_2$ 분말시료에 대하여 두가지 다른 온도-압력 조건하에서 고온-고압실험이 시행되었다. 이러한 실험 중 하나는 소형 고온 발생장치가 부착된 피스톤-실린더 다이아몬드 앤빌기기를 이용하여 압력은 최고 15 GPa 까지, 온도는 500°C에 고정시킨 상태에서 처리한 시료를 상온-상압상태로 변환시켜 X-선 회절실험을 하였다.

이러한 실험에서, 11.3 GPa 압력 이상에서 고온-고압처리한 시료로부터 사방정계 결정구조를 보이는 비가역성의 새로운 광물상을 발견하였는데 이는 Ti 수화물이 고압하에서 안정한 결정 격자구조를 보이는 새로운 것이다. 이 상변이에 따른 몰부피의 변화는 약 10%이다.

### INTRODUCTION

Hydrogen has been drawn Earth scientists' attention for its most abundances in the solar

system. Geophysically, the density of Earth's outer core is less than that of pure iron by 6 to 10% (Brett, 1976), and the mean atomic number of outer core is estimated to be 23, which is significantly

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lower than that of iron, where the mean atomic number is defined to the division of summed atomic weight by number of atoms present (Birch, 1972). These facts indicate that the Earth's outer core is not consisted of pure iron, and contains moderately consequential amount of lighter elements than iron itself. Among lots of lighter elements proposed as candidates, hydrogen is one of the possibilities, and only about 1 wt% content of hydrogen is enough to explain the density of the Earth's core (Stevenson, 1977). It would be of value to extend for the pressure effect on the solubility of hydrogen in the metal-hydride phases including iron hydride (Fukizawa, 1982; Ming et al., 1986).

Recently, the role of hydrogen has been extended to the low velocity zone in the asthenosphere based on its solubility and diffusivity experiments in a small amount of hydrogen is present at the low velocity layer on a global scale.

Metal hydrides are one of the possible as well as promising ways for storing hydrogen (Cohen and Wernick, 1981). A full knowledge of its physical, chemical, thermodynamical and crystal structure properties is necessary for its proper use in various applications. Systematic studies of enthalpy and entropy on many metal hydrides have been carried out at ambient conditions (i. e., at room temperature and atmospheric pressure) (Wiswall, 1978; Cohen and Wernick, 1981). However, it is deficient of experimental data on hydride phases under the extended high pressure and high temperature conditions.

High pressure research on solid phases has revealed that almost all solids have pressure-induced phase transition(s) with volume decrease from 0% (i. e., second-order transition) to ~64% (e. g., SiO<sub>2</sub> quartz → SiO<sub>2</sub> stishovite) with some exceptions of metals and their alloys (Pistorius, 1976). It is known that the phase transition would also occur under static high pressure with/without high temperature conditions for metal hydrides. Since it is so, separate experiments on hydride phases are necessary according to the high pressure-high temperature conditions. From this sort of approaches, if any high pressure phases of metal hydrides can be synthesized successfully, they would be one of the useful alternatives

for the hydrogen storage not only because it will contain more hydrogen per unit volume but also because it will be convenient way to handle as well.

On the basis of these views, TiH<sub>2</sub> was selected as one of the structural analogs to iron hydride as well as for hydrogen solubility into this phase at the extended pressure and/or temperature region. Therefore, the main purposes of this research on TiH<sub>2</sub> under high pressure and temperature conditions are the followings: (1) pressure effect at room temperature, (2) pressure effect at the high temperature of 500°C, on TiH<sub>2</sub>.

## EXPERIMENTAL METHODS

Polycrystalline TiH<sub>2</sub> was purchased from the Hawaii Chemicals. The starting sample was prepared in the very fine grained-size using agate mortar. This powder was mixed with NaCl fine powder together at the same ratio in volume. The mixed specimen was examined by X-ray diffraction (XRD) technique using a Debye-Scherrer camera. NaCl was used for geometrical correction of the XRD camera using its well established d-spacings of each XRD line at ambient conditions.

In the present studies, two experimental methods have been applied on the prepared as well as the starting specimens depending on the attempted approaches on high pressure and high pressure-temperature conditions. Both of two methods are described as follows:

**High pressure experiment at room temperature:** Polycrystalline TiH<sub>2</sub> was loaded into the gasketed sample chamber with a tiny ruby chip in the Bassett-type diamond anvil cell (DAC). The gasket used was 718 Inconel with a hole of 0.25mm in diameter and 0.125mm in thickness. A ruby of 30 μm in diameter was used for the pressure monitoring. Sample pressure at each run was determined both before and after X-radiation with the ruby fluorescence technique (Piermarini et al., 1975; Ming and Manghnani, 1978). The pressure uncertainty thus determined for each run was about ±0.06 GPa. The schematic section of the Bassett-type DAC and sample assemblage in the DAC were given elsewhere

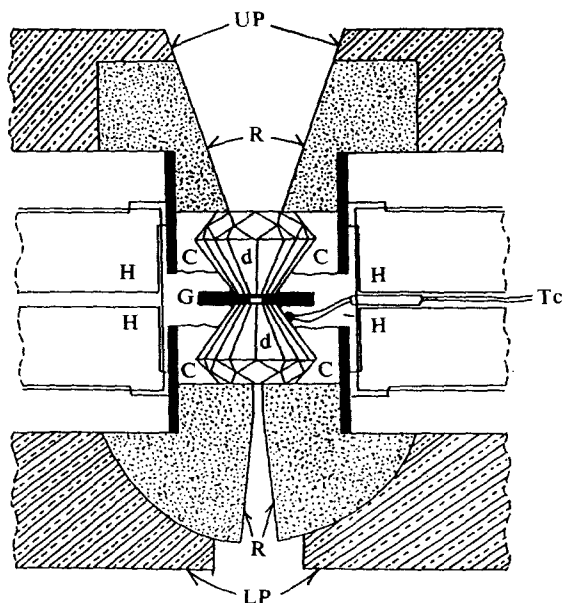


Fig. 1. Schematic cross section of the piston-cylinder parts in the diamond anvil cell: UP; upper plate, LP; lower plate, R; rocker, H; heater, C; high temperature cement, d; diamond, G; gasket and T<sub>c</sub>; thermocouple. Space shown in gasket between two diamonds is the sample chamber.

(see Figs. 1 & 2 of Kim, 1988).

The sample was squeezed up to 21.6 GPa by the rotation of the wrench manually. At each increment of pressure, the compressed sample in DAC was X-rayed in-situ using the Zr-filtered microfocused Mo-K $\alpha$  radiation ( $0.1 \times 1.0 \text{ mm}^2$ ) at 50 KV and 5 mA. The exposure time to X-radiation increases with pressure by virtue of the getting sample mass thinned, and the average time was about 72 hours.

**High pressure and temperature experiment:** Polycrystalline TiH<sub>2</sub> was loaded in the gasketed sample chamber with the small chip of ruby for pressure monitoring in the piston-cylinder diamond anvil cell (P-C DAC) (Fig. 1). The gasket used was 718 Inconel metal alloy with a hole of 0.30 mm in diameter and 0.25 mm in thickness. Therefore, the amount of sample increases in this gasket chamber compared with that in Bassett-type DAC. The pressure determination procedure is same as the described above in Bassett-type DAC. In this case, pressure uncer-

tainty was determined to be about  $\pm 0.05 \text{ GPa}$  from the measurements at both before and after heating. At each high pressure, the constant high temperature of 500°C has been sustained for an hour (60 minutes) for the complete reaction of the constituents under high P-T conditions simultaneously. The reason of constant temperature of 500°C is that this temperature is the maximum reached with P-C DAC because of the defrosting of diamond by oxidation in the air. Sample temperature was measured by a precalibrated Pt-Pt10%Rh thermocouple placed next to the sample (Fig. 1). The uncertainty of temperature thus determined is to be  $\pm 5^\circ\text{C}$ .

The quenched specimen was recovered from P-C DAC after each high P-T treatment. The compressed mass of starting powder was almost circular in shape and flat in thickness whenever produced in the gasket chamber of this DAC. This tiny mass was prepared for the XRD analysis using thin glassy film of the DUCO cement. Sandwiched specimen by cement was loaded in the Debye-Scherrer camera and X-rayed using the Ni-filtered microfocused Cu-K $\alpha$  radiation ( $0.1 \times 1.0 \text{ mm}^2$ ) at 40 KV and 4 mA. The exposure time to X-radiation for obtaining a good quality XRD film is about 100 hours.

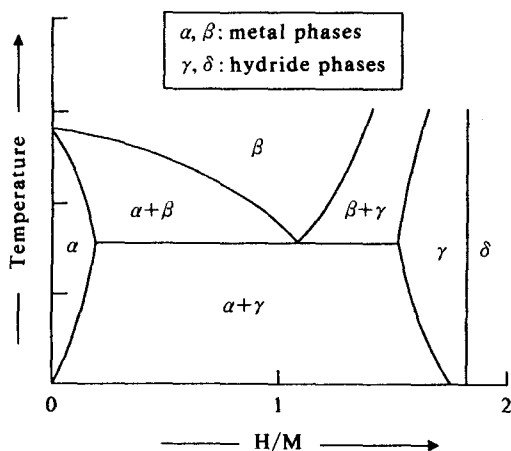
Photographic films exposed by X-radiation in both experiments were read on the film-measuring device. Detailed experimental methods described above are found elsewhere (Kim, 1989).

## RESULTS AND DISCUSSIONS

### TiH<sub>2</sub> Lattice Structure at Ambient Conditions

**Relationship of Ti and TiH<sub>2</sub>:** Hydrogen penetrates into metallic phase at the appropriate pressure and temperature conditions. The solubilities of hydrogen in the metals belonging the first long period of the periodic table are well established and the syntheses of other metals' hydrides were performed extensively (McLellan and Oates, 1973).

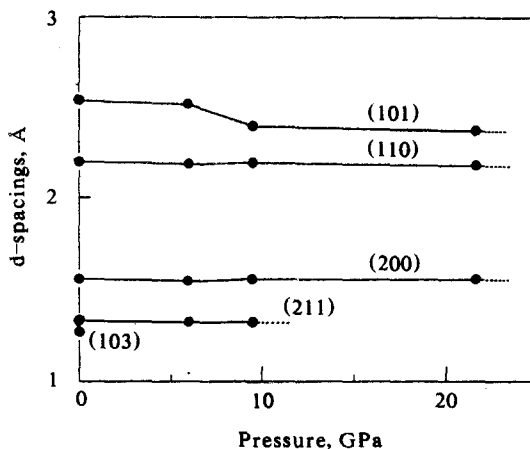
Not only the ratio of the hydrogen to metal phases Ti, Zr and Hf with respect to temperature, but its own crystal structures are shown in Fig. 2



**Fig. 2.** Relationship between temperature and ratio of hydrogen to metal(H/M) of several transition metals and their hydrides.  $\alpha$  phase of Ti, Zr and Hf: hcp,  $\beta$  phase of Ti, Zr and Hf: bcc,  $\gamma$  phase of Ti, Zr and Hf: fcc,  $\delta$  phase of Ti: fcc and  $\delta$  phase of Zr and Hf: fct (redrawn from Beavis, 1963).

(Beavis, 1969). Ti becomes hydride with hydrogen/metal (H/M) increases up to 1.6 as temperature does. Ti is in the hexagonal closed packing (hcp) structure with lattice parameter of  $a=2.950$  Å, and  $c=4.686$  Å at ambient conditions. Ti particles transform to  $\text{TiH}_2$  particles with a dodecahedral structure in the body-centered tetragonal crystal system initially and then face centered cubic (fcc) system martensitically when heated at  $250^\circ\text{C}$  for 5 minutes by absorption of  $\text{H}_2$  gas (Yanagida et al., 1986). This transformation is due to a slight modification of the dodecahedron in the crystal structure.

**$\text{TiH}_2$  structure of this study:** All XRD lines of  $\text{TiH}_2$  can be indexed into tetragonal crystal system ( $a=3.114$  Å,  $c=4.157$  Å;  $Z=2$ ). The XRD lines used in this study are indicated with d-spacings in Fig. 4. As expected from above considerations, all XRD lines can be indexed into fcc structure either. Indexing of the body-centered tetragonal system, however, could be used adequately through this study from a point of view of the purposes of the present study, thereby fcc indexing was discarded.



**Fig. 3.** The d-spacings of (101), (110), (200) and (211) XRD lines with high pressures of  $\text{TiH}_2$ . The (103) line is observable at zero-pressure, but not appeared at further high pressures. Notice the dramatic decrease of (101) line at 9.6 GPa.

**Table 1.** The lattice parameters, molar volume and volume ratio of  $\text{TiH}_2$  at ambient conditions and high pressures

Pressure (GPa)	Lattice parameters			$V_m$ cm <sup>3</sup> /mole	$V/V_0$
	a, (Å)	c, (Å)	c/a		
0.0001	3.114	4.157	1.335	12.137	1.0
6.1	3.098	4.311	1.392	41.362	0.9769
9.5	3.094	4.210	1.361	40.295	0.9514
21.6	3.093	4.084	1.320	39.077	0.9227

## Experimental Results and Discussions

**At high pressure and room temperature conditions:** When Bassett-type DAC was used to compress the starting specimen, there was not observed any phase change up to 21.6 GPa at room temperature (Fig. 3). Lattice parameters at high pressures of 6.1 GPa, 9.5 GPa and 21.6 GPa with those of 0.0001 GPa (i. e., 1 bar) are listed in Table 1. These parameters were determined by three diffraction lines of (101), (200) and (211).

In Fig. 3, (101) diffraction line shows the dramatic decrease of interplanar distance from 2.512 Å at 6.1 GPa to 2.493 Å at 9.8 GPa. This abnormal behavior at approximately 10 GPa area appears on the additional attempts repeatedly. At this mo-

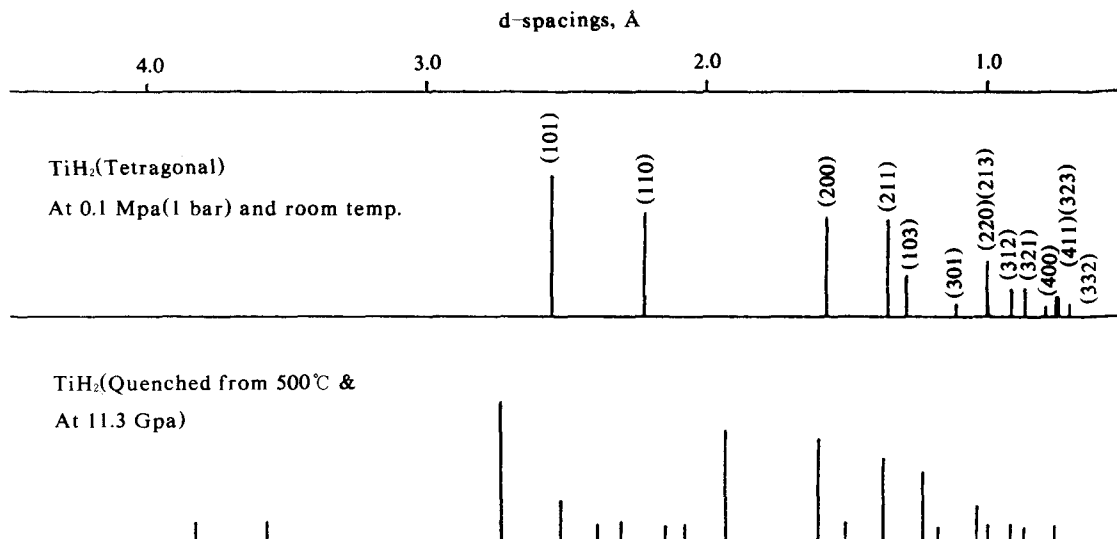


Fig. 4. X-ray diffraction patterns of the quenched TiH<sub>2</sub> phase from 500°C and 11.3 GPa and the starting phase in tetragonal system.

ment, this phenomenon would be explained due to the electronic transition typical to hydride structure with lesser confirmation. Besides of this line, the rest of diffraction lines show the normal compression behavior upon the extended pressures. The (211) diffraction line becomes pale on film above the 10 GPa and not observed to the high pressure range. However, this doesn't mean the disappearance of this XRD line itself completely.

As a result of this observation, it is concluded that the pressure effect at room temperature would be negligible on the stability of tetragonal TiH<sub>2</sub> crystal structure.

**At high pressure-temperature conditions:** Five quenched specimens were produced at high pressures of 3 GPa, 5.5 GPa, 7.6 GPa, 11.3 GPa and 15 GPa, respectively. Constant temperature of 500°C was sustained at each high pressure simultaneously. The XRD patterns at both 3 GPa and 5.5 GPa show no differences from those of the starting phase. This indicates that the starting tetragonal structure is stable up to these P-T regions. At 7.6 GPa, however, one new XRD line was appeared, which persists to higher pressures, and could be coincided with (111) line of

the new phase. Quenched product from 11.3 GPa at 500°C, which is irreversible, shows a quite different XRD pattern from those of the lower pressure products. This pattern is designated and compared with the starting phase in Fig. 4. The simple comparison of the XRD pattern is very convenient to distinguish any phase transition(s) from the starting phase. The similar XRD pattern was identified on the quenched sample from ~15 GPa at the temperature of ~500°C.

This new phase has been interpreted as follows: The d-spacings of quenched phase are marked in the strip and this was searched and correlated on the Hull-Davey charts for the appropriate match(es) of the XRD lines on the various crystal systems. Similar patterns or matches as much as can be chosen were assigned the closest indices, then the d-spacings at each system were calculated. These values were finally correlated with the quenched phase for completion of their match each other.

The most proper one was the orthorhombic structure as a new phase with lattice parameters of  $a=8.562\text{Å}$ ,  $b=3.903\text{Å}$ ,  $c=4.342\text{Å}$  (Table 2). The molar volume change following this phase transition (i. e., from  $12.137\text{cm}^3/\text{mole}$  to  $10.922\text{cm}^3/\text{mole}$ )

**Table 2.** X-ray diffraction data of TiH<sub>2</sub> at ambient conditions and unloaded from ~11.3 GPa and quenched from ~500°C

Tetragonal phase at ambient conditions				Orthorhombic phase after P-T treatments			
I/I <sub>0</sub> *	d(obs.)	d(calc.)	(hkl)	I/I <sub>0</sub> *	d(obs.)	d(calc.)	(hkl)
100	2.564	2.545	(101)	15	3.827	3.852	(101)
75	2.237	2.236	(110)	15	3.573	3.558	(110)
70	1.575	1.581	(200)	100	2.742	2.745	(111)
70	1.349	1.341	(211)	30	2.538	2.602/2.490	(300)/(310)
30	1.289	1.289	(103)	15	2.400	2.403	(221)
10	1.025	1.023	(301)	15	2.318	2.304	(230)
40	1.114	1.118	(220)	12	2.157	2.140	(040)
30	0.998	0.999	(213)	12	2.079	2.091/2.064	(102)/(104)
20	0.912	0.904	(312)	80	1.932	1.936	(022)
20	0.860	0.859	(321)	75	1.603	1.611	(430)
10	0.789	0.791	(400)	15	1.513	1.510	(431)
15	0.752	0.755	(411)	60	1.376	1.374	(422)
15	0.745	0.745	(323)	50	1.232	1.251/1.226	(313)/(233)
10	0.703	0.703	(332)	10	1.118	1.121	(423)
				25	1.041	1.042	(124)
				12	1.003	1.006/1.001	(134)/(304)
				12	0.920	0.926	(424)
				10	0.870	0.867	(444)

\* Intensity were measured visually, then compared with the strongest one(100%).

a = 3.114 Å, c = 4.157 Å, V<sub>m</sub> = 12.137 cm<sup>3</sup>/mole

a = 8.562 Å, b = 3.903 Å, c = 4.342 Å, V<sub>m</sub> = 10.922 cm<sup>3</sup>/mole

was calculated approx. 10%. This means that the new phase discovered from this study contains more hydrogen per unit volume at the rate of 10%.

The phase boundary at the temperature of 500°C is not certain at this moment. However, from the observation of the new line at 7.6 GPa, it is now possible to refer that phase boundary would exist between approx. 7.6 GPa and 11.3 GPa. At room temperature, there was no phase transition observed up to 21.6 GPa. Therefore, it is anticipated, if phase changes occur, that the slope of phase boundary would be a negative. In order to confirm this consideration, it is needed more work at different constant temperature values (e. g. 200, 300°C etc) at the same experimental set-up. It is hardly to mention the mechanism of phase transition from body-centered tetragonal to orthorhombic system at this time. This area should be added on the future studies.

## SUMMARY

The experimental results on TiH<sub>2</sub> are summa-

rized as follows:

(1) The effect of pressure at room temperature as well as high temperature on TiH<sub>2</sub> has been surveyed at different experimental conditions.

(2) The effect of pressure at room temperature turns out negligible on the stability of the tetragonal TiH<sub>2</sub> structure within present pressure range of 21.6 GPa.

(3) Being quenched from 11.3 GPa at 500°C, an irreversible new phase was discovered and this phase was assigned into the orthorhombic crystal system.

(4) The volume shrinkage by this phase transition is approximately 10%, and phase boundary would exist between 7.6 and 11.3 GPa in negative slope.

More experiments will be needed in the fields of the phase boundary determination as well as the mechanism of phase transition on TiH<sub>2</sub> in the future.

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