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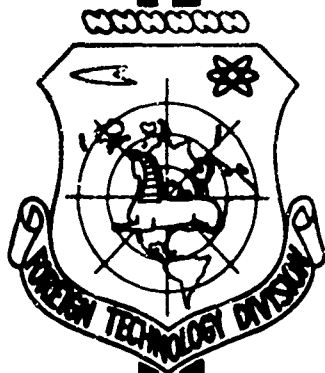
TITANIUM AND HYDROGEN

By

Yu. V. Baymakov and O. A. Lebedev

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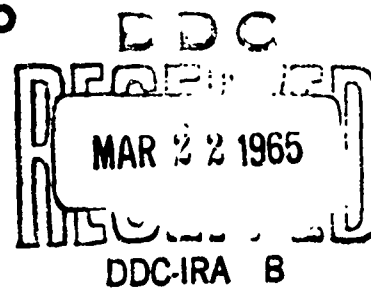
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BY: Yu. V. Baymakov and O. A. Lebedev

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TITANIUM AND HYDROGEN

Yu. V. Baymakov and O. A. Lebedev

Introduction

Titanium is in the fourth group of D. I. Mendeleev's periodic chart. Distribution of electrons in an atom of titanium is the following: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^2$, $4s^2$. Internal electron shells of titanium are similar in structure to electron shells of argon, and electrons $3d$ and $4s$ are located outside closed inner shells, due to which an atom of titanium is quite easily lost by them, forming ions Ti^{+2} , Ti^{+3} , Ti^{+4} .

Hydrogen is energetically absorbed by titanium; however, the salt-like hydrides characteristic for a number of metals of I and II groups will not form titanium with hydrogen. Interaction of titanium with hydrogen is the subject of many works [1-11]. Investigators have studied equilibrium pressures of hydrogen on titanium at different temperatures, structure of phases forming then [1-5,7], and also elasticity of dissociation of titanium hydride [6]. It was determined that by the method of saturation of purer titanium by pure hydrogen it is possible to attain a content of hydrogen in metal responding to the composition of TiH_2 ; however, doubt is expressed concerning the existence of a chemical compound of this composition.

Siewerts [2] on the basis of obtained dependency $C = K\sqrt{HP_1}$, makes the conclusion that in this case there will form a solid solution of atomic hydrogen in titanium. However, Morton K. Smith [11] indicates that titanium hydride TiH_2 has an ionic crystal lattice of the fluorite-body-centered lattice type, analogous to β -modification of titanium. In the bibliography assumptions are expressed on the existence of a gasiform hydride of the composition TiH_4 [4].

Wassilevsky and Jeel [8] studied diffusion rate of hydrogen in titanium and presented coefficients of diffusion for α - and β -titanium. Absorption of hydrogen by titanium after formation of hydride phase on surface of sample occurs with constant speed due to the fact that the hydride will form a porous layer on surface of sample.

A. D. McQuillan and M. K. McQuillan [9] present a composition diagram of titanium-hydrogen, built on the basis of a series of curves of dependency of isothermal pressure-concentration, on which sections of curves with slope correspond to single-phase regions, while those lying in parallel to the axis of concentrations of hydrogen-to two-phase regions. In the system titanium-hydrogen there exist α - and β - phases, stable at high temperatures, and γ -phase, stable at room temperature. A. D. McQuillan determined maximum content of hydrogen in γ -phase, corresponding to composition $TiH_{1.73}$, and in the γ -phase is already close to saturation; however, according to other data, given by A. D. McQuillan, γ -phase corresponds to the formula of TiH_2 .

Many experiments [10] are dedicated to the kinetics of interaction of titanium with hydrogen. A. V. Revyakin and V. A. Reznichenko studied the rate of absorption of hydrogen by titanium at different temperatures and pressures, determining the quantity of absorbed hydrogen at temperatures from 350 to 550°C by the volume method, and at higher temperatures by the weight method. They established that the presence of even thin oxide films on surface of titanium sharply lowers the absorption rate of hydrogen. The rate of absorption is determined by process of entry of hydrogen on the surface of titanium; therefore, the rate of the reaction depends on pressure of hydrogen in gas phase.

O. I. Vashkov and V. K. Gavrilov studied the process of hydrogenation of titanium sponge and compact titanium for the purpose of transformation of different forms of titanium waste and its alloys into powder or grit. They established that the highest rate of absorption of hydrogen for spongy titanium is observed at 500-600°C, and for compact metallic titanium, at 650-700°C. Forming on surface of sample, titanium hydride, having specific volume 15-16% more than volume of titanium, causes cracking of surface and promotes faster hydrogenation of compact titanium.

In the laboratory of electrometallurgy of ferrous metals of the Leningrad Polytechnical Institute experiments were undertaken on the study of interaction of titanium with hydrogen.

The results of these experiments are given below.

Absorption of Hydrogen by Titanium During Heating

The chemical composition of titanium, with which the investigations were conducted, is given in Table 1.

Table 1. Composition of Titanium

Samples	Composition, % (weight)						
	Ti	C	Fe	Mg	N	Cl	O and H
Powder obtained by magnesium-thermal reduction.....	98.4— 98.5	0.01— 0.07	0.06— 0.08	0.37— 0.4	0.027— 0.04	0.06— 0.14	No Data
Forged titanium obtained by reduction of titanium dioxide by calcium hydride.....	98.16— 99.9	0.045— 0.08	0.14— 0.24	0.024— 0.115	0.078— 0.081	—	Same

In a small nickel cylinder without a bottom, placed into a tubular furnace filled by hydrogen, into titanium powder a thermocouple joint was tapped. A

second thermocouple was placed in the working space of the tube and the temperature outside the cylinder was measured. Then the furnace was slowly heated during continuous supply to it of dried and purified hydrogen. Indications of the thermocouples are shown in Fig. 1.

Reaction between titanium and hydrogen starts at 332°C, continues for a rather short interval of time, and in the first minute there is observed intense absorption of gas and self-heating of the batch to 600°C.

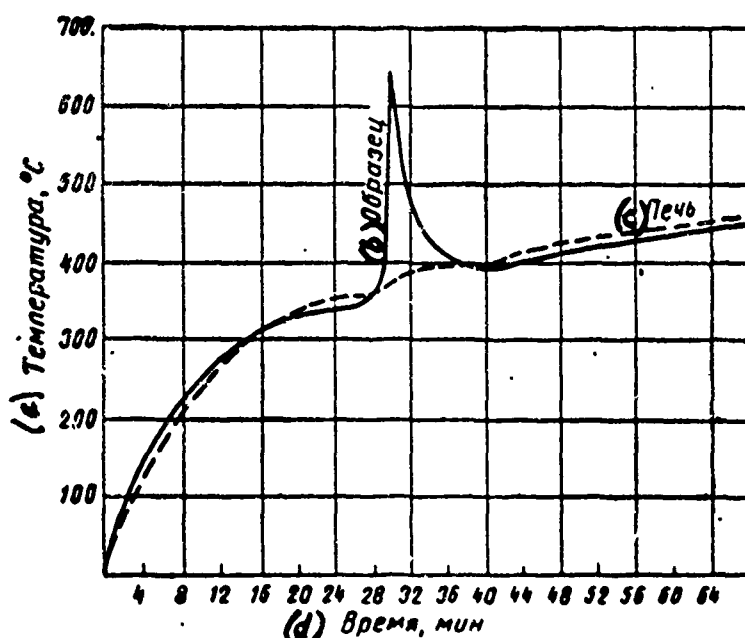


Fig. 1. Temperature-time curve during heating of batch of titanium powder in hydrogen.

KEY: (a) temperature, °C; (b) Sample; (c) Furnace; (d) Time, min.

Saturation of titanium by hydrogen at different temperatures was carried out in the following manner.

Into resistance furnace there was inserted a tube made from transparent quartz equipped at one end with a slide having a cock and a branch pipe for the thermocouple, and at the other end a branch pipe for entry of hydrogen (Fig. 2). By switching cocks 7, 8 and 13, it was possible to pass the hydrogen through the tube, heated to a definite temperature, and to either pump it through the rheometer recording the following data: drop-pressure-time and temperature. Into tube either

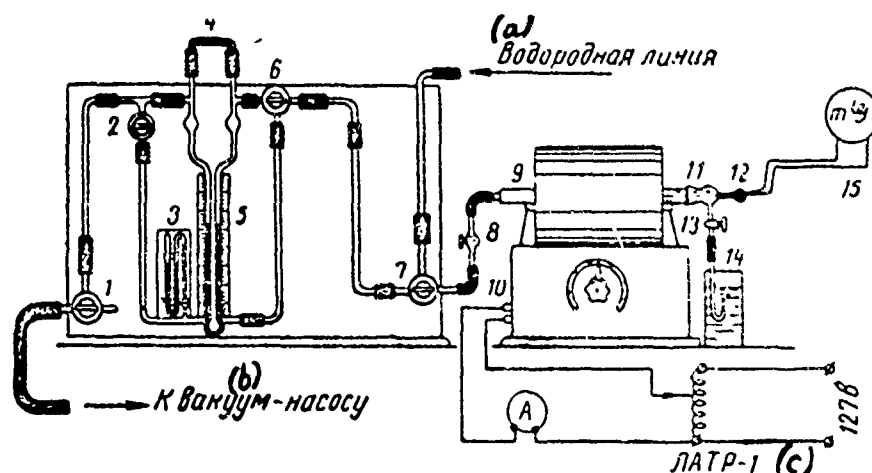


Fig. 2. Installation for study of saturation of titanium by hydrogen and kinetics of dissociation of hydride:

1-three-way cock; 2-cock for connection of manometer; 3-vacuum gage; 4-capillary of rheometer; 5-rheometer; 6-three-way cock for bypass of manometer; 7-three-way cock for switching on of hydrogen supply; 8-output cock of tube of furnace; 9-quartz tube; 10-resistance furnace; 11-quartz slide; 12-lead for thermocouple; 13-cock for washing of tube by hydrogen; 14-water lock; 15-galvanometer to thermocouple.

KEY: (a) Hydrogen line; (b) To vacuum-pump; (c) LATP-1.

pieces of titanium rods weighing about 2g are packed, preliminarily degreased, washed by alcohol, and dried, or boats with batch of titanium powder (9-10g). Before beginning of experiment the tube is washed for one hour by purified hydrogen, after which it is heated to a given temperature and hydrogen is passed through for 1-5 hours. After termination of experiment the inlet and outlet cocks are closed and tubes are removed from furnace for fast cooling. After cooling, compact samples are extracted and content of hydrogen in them is determined according to method presented in [12], including heating of analyzed sample to 1200° at residual pressure $1 \cdot 10^{-5}$ mm Hg with measurement of volume of liberated gas.

Determination of content hydrogen in powder was carried out on the same installation (see Fig. 2) and was based on determination of exhaust velocity of hydrogen during heating of batch in conditions of residual pressure 0.1 mm Hg and gradual increase of temperature [13]. Obtained data are shown in Fig. 3. Curves 1, 2, and 3 correspond to content of hydrogen in compact titanium. The biggest content of hydrogen in it is observed during exposure for 5 hours in a current of

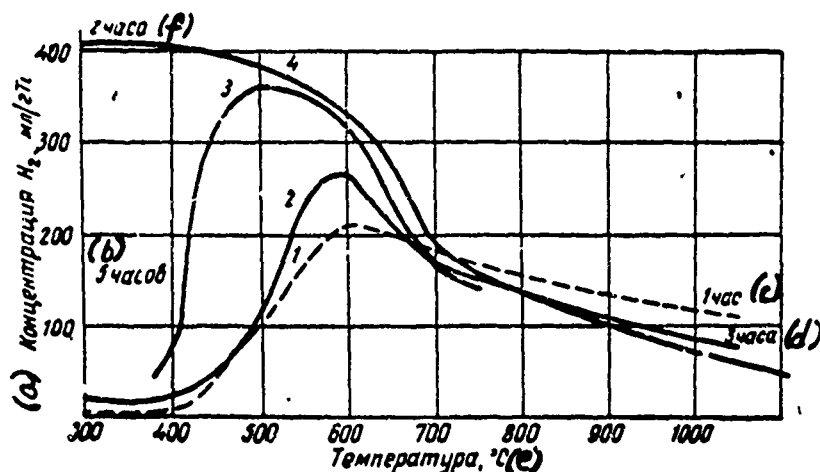


Fig. 3. Variation of content of hydrogen in powder and in titanium rods depending upon temperature and time of exposure:

1, 2, 3—moldings; 4—powder

KEY: (a) Concentration of H_2 , ml/g Ti;

(b) 5 hours; (c) 1 hour; (d) 3 hours;

(e) Temperature, °C; (f) 2 hours.

hydrogen at 500°C. Curve 4 corresponds to saturation of titanium powder. Maximum saturation of powder by hydrogen takes place at 350°C for the first few minutes and after further two-hour exposure and cooling in a current of hydrogen 42.96 $\frac{1}{100}$ of hydrogen is absorbed per 100 g of metal. Maximum content of hydrogen in compact titanium reached 38.14 $\frac{1}{100}$ g of metal.

From comparison of curves 1-4 it is clear that saturation of titanium powder by hydrogen occurs significantly faster than compact metal. For achievement of the same concentration of hydrogen in compact metal more than 5 hours are required. From consideration of curve 4 (Fig. 3) it is clear that the biggest saturation of powder is observed in interval of temperature 300-400°C and at high temperatures dissociation of hydride begins. At a temperature of 700°C, one hour is sufficient for saturation, but content of hydrogen will correspond to equilibrium. Obtained data basically agree with results of experiments described in [4, 6, 7, 9].

Saturation of Titanium Cathode by Hydrogen During Electrolysis In Solution of Sulfuric Acid with Lead Anode

Saturation was carried out in a solution of H_2SO_4 with concentration 10 g/l when $D_{H_2} = 1-2 \text{ a/}\partial\mu^2$, $t = 18^\circ\text{C}$. Duration of saturation was 48-96 hours. Content

of hydrogen in metal was determined according to the method described in [13].

Quantity of hydrogen did not exceed $0.073 \pm$ per 100 g of metal (quantity of hydrogen for compact metal was $38.14 \pm$ per 100 g), and for powder metal during heating, $42.96 \pm$ per 100 g.

Such a small content of hydrogen may be explained by the extremely low speed of reaction of formation of titanium hydride at 18–25°C and small diffusion rate of hydrogen in thickness of metal.

Kinetics of Decomposition of Titanium Hydride

Directly during determination of content of hydrogen in titanium by the earlier described methods we also carried out a study of kinetics of decomposition of titanium hydride.

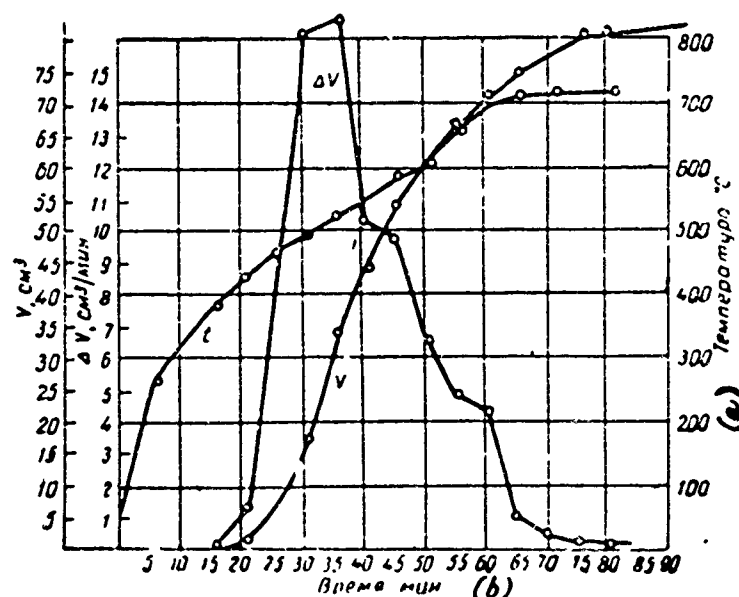


Fig. 4. Data on decomposition of titanium hydride during gradual increase of temperature.

KEY: (a) Temperature, °C; (b) Time, min.

The batch of hydride (0.2–0.35 g), obtained by saturation of compact titanium, was placed into the tube of the instrument of A. N. Morozov [12], which was evacuation to residual pressure of 10^{-5} mm Hg, and then is slowly heated. Volume of hydrogen then given off was periodically measured. Readings of temperature and

volume were produced every 5 minutes. Results of one of the experiments are shown in Fig. 4. Conditions of saturation in this case were the following: $t = 500^{\circ}\text{C}$, exposure 5 hours, slow cooling of hydrogen in atmosphere. Temperature of beginning of liberation of hydrogen during decomposition of titanium hydride was 388°C , temperature of maximum rate of liberation 520°C , temperature of end of liberation 900°C , and volume of liberated gas was $38.37 \text{ l}/100 \text{ g}$ of metal.

On the basis of experiments conducted with samples of compact metal, saturated under different conditions, one may assume that the temperature at the beginning of liberation of hydrogen is $344\text{--}388^{\circ}\text{C}$, maximum rate of liberation is observed at $485\text{--}560^{\circ}\text{C}$, and liberation terminates at $828\text{--}900^{\circ}\text{C}$.

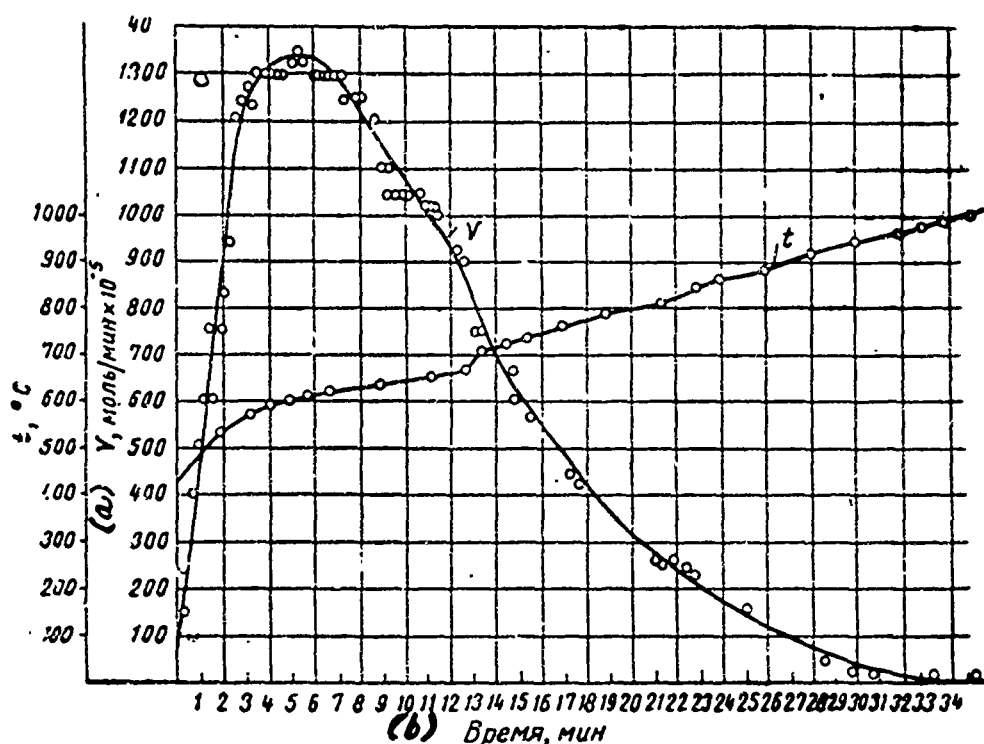


Fig. 5. Dependence of rate of decomposition V of titanium hydride on temperature. (according to experiment 3).
KEY: (a) V , $\text{mole}/\text{min} \cdot 10^{-5}$; (b) Time, minutes.

Kinetics of decomposition of titanium hydride was also studied on another installation (see Fig. 2). After establishment of constant vacuum (0.1 mm Hg), readings of rheometer were read, corresponding to idling of installation, then the tube was uniformly heated. Every 15-60 sec the temperature and readings

of the rheometer, countable subsequently by the quantity moles hydrogen per minute, were fixed. Results of one of the experiments are represented in Fig. 5. Data of some experiments are given in Table 2.

From given data it is clear that the temperature of the beginning of the reaction most exactly of all is fixed by experiments on thermal determination of beginning of reaction between titanium and hydrogen (see Fig. 1), and in this case the thermocouple junction is introduced directly into titanium.

In fulfillment of determinations according to method of A. N. Morozov, the beginning of liberation of gas is fixed with sufficient accuracy, but during measurement of temperature there may be an error (junction is placed at some distance from the suspension). During the study of kinetics by method of measurement of speed of liberation of hydrogen it is difficult to fix temperature of beginning of reaction since it is shielded by idling of instrument. But then the first method, at which readings are produced every 15-30 sec, is more sensitive with respect to fixation of temperatures to which corresponds the maximum rate of decomposition and end of reaction.

Table 2. Results of Experiments of Decomposition of Hydride
According to Method of Determination
Of Exhaust Velocity of Hydrogen

Experiment Number	Conditions of saturation	Temperature, °C		volume of gas l/100 g Ti	Note
		maximum speed of reaction	end of H ₂ liberation		
1	Heating to 600°C, exposure 1 hour, slow cooling in atmosphere of hydrogen....	652	836	42.18	Powder
2	the same	596	872	42.07	Powder
3	the same	572	988	37.95	Compact
4	the same	578	960	42.96	powder

Elasticity of Dissociation of Titanium

In reference [6] there is information about experiments by T. Gibb, who determined in 1951, the elasticity of dissociation of titanium hydride. Experiments were carried out in a steel cylinder heated to 800°C.

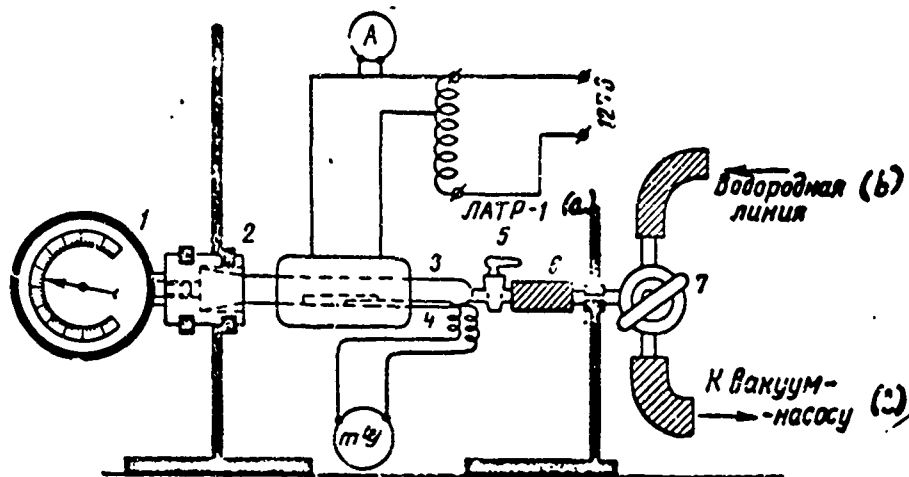


Fig. 6. Diagram of instrument for determination of elasticity of dissociation of titanium hydride: 1-manometer; 2-steel nut; 3-tube made from transparent quartz; 4-cap of thermocouple, placed on the outside and tightly adjoining wall of tube; 5-cock which cuts off tube I; 6-rubber connecting tube; 7-three-way cock.
KEY: (a) LATP-1; (b) Hydrogen line; (c) To vacuum pump.

Fig. 6 represents an instrument applied by us for determination of elasticity of dissociation of hydride. As the reaction space we used a tube made from transparent quartz with a cock on one end and a funnel-shaped expansion on the other. The expanded end of the tube was inserted into a steel bushing with threading on internal wall. The formed cavity was flooded by Mandelejev putty (filling by tin-lead alloys did not ensure airtightness in view of shrinkage). In bottom of steel bushing there was screwed a manometer with value of division 0.05 at. Junction of thermocouple was tightly pressed to external wall of pipe covered by sheet asbestos, around which was wound Nichrome wire. Difference of temperature of suspension and junction of thermocouple was removed by prolonged exposure.

Before the experiment air was pumped from the tube, after which it was filled by hydrogen, and then for every experiment the dependence of pressure on temperature was determined, which was equal to 0.35 atm(gage) at 300° and 0.5 atm(gage) at

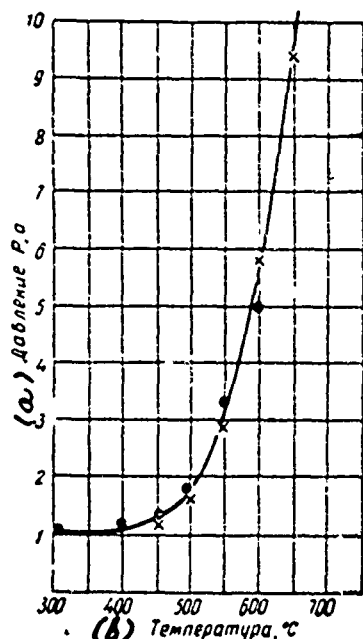


Fig. 7. Dependence of elasticity of dissociation of titanium hydride on temperature.

KEY: (a) Pressure P, a;
(b) Temperature, °C.

700°C. Later, these data were subtracted from readings of manometer. A suspension of 10 grams of titanium hydride powder in a nickel boat was introduced through a connecting hole for the manometer which was screwed on a lead lining. After ten-fold evacuation and filling by hydrogen the closing cock was covered. Measurements of pressure were produced at temperatures of 300, 450, 500, 650, and 700 °C, and at every temperature exposure was from 20 to 60 minutes.

In Table 3 are given data of one of the experiments, and in Fig. 7 the dependence of elasticity of dissociation on temperature is constructed.

Table 3. Data of Determination of Elasticity of Dissociation of TiH_2

Выдержка мин. (a)	Температура °C (b)	(c) Давление	
		атм (d)	lg P
20	300	1.35	0.021
20	400	1.10	0.042
60	450	1.20	0.105
60	500	1.60	0.23
30	550	2.90	0.504
30	600	5.83	0.755
20	650	9.4	0.994

KEY: (a) Exposure, minutes; (b) Temperature, °C; (c) Pressure; (d) atm (abs.).

[lg = log]

Table 4. Free Energy and Log K_p of Reaction at Different Temperatures

(a) Температура		Свободная энергия ккал/моль (b)	lg K_p
t, °C	t, °K		
500	773	-817	0.23
550	823	-1900	0.504
600	873	-3000	0.755
650	923	-4200	0.994
700	973	-5600	1.260
750	1023	-7100	1.510

KEY: (a) Temperature; (b) Free energy, cal/mole.

[lg = log]

Obtained results allowed us to calculate thermodynamic characteristics of titanium hydride:

$$\lg K_p = RT \lg \frac{P}{P_0}$$

where K_p is constant of dissociation;

P_0 is initial pressure.

Experiment was conducted at initial pressure of $P_0 = 1$ atm (abs.).

The constructed function $\lg K_p = f(t)$ reveals a linear dependency starting from 500°C. Below this temperature the dependence is expressed by a curve of second order. Consequently, decomposition of hydride correctly starts at a temperature of 500°C. At lower temperatures, beginning with 200°C, desorption of hydrogen takes place.

The values of free energy of formation of titanium hydride, calculated for 500-750°C, are given in Table 4.

Extrapolation of values of maximum work to lower temperatures gives magnitude of free energy at 25°C equal to +10,100 cal, and $\frac{dA}{dT} = -22 \frac{\text{cal}}{\text{deg}}$ (in interval 500-650°C). Hence the thermal effect of formation of titanium hydride at 25°C is equal to

$$Q_{298^\circ \text{K}} = A - T \frac{dA}{dT} = 10100 + 298 \cdot 22 = 16700 \text{ cal/mole H}_2.$$

Gibb [6] gives $\Delta H = 19,150$ cal/mole H_2 .

It is necessary to note our data obviously are less exact than Gibb's data, since during calculations we did not conduct extrapolation of value of maximum work of reaction from 500 to 25°C.

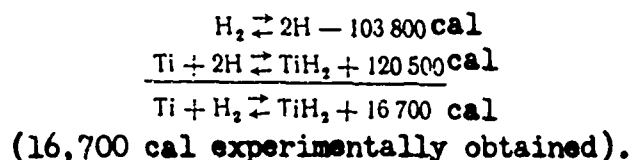
Discussion of Obtained Results and Conclusions

Maximum content of hydrogen, corresponding to the formula of hydride was not attained due to the presence of impurities in titanium which was applied for investigations. Reaction of the hydrogen compound with titanium starts at 330°C and continues at a high rate with liberation of a noticeable quantity of heat (Fig. 1). Such high speed of formation of hydride at comparatively low temperature

indicates that process of formation of hydride precedes adsorption of atomic hydrogen which is then being introduced into the α -lattice of titanium (hexagonal) with reconstruction of it into β -modification (body-centered).

The presence of a transitional stage of sorption of atomic hydrogen is indicated by the fact that speed of reaction of formation of TiH_2 is determined by state of surface of metal. Reaction of formation of hydride from compact metal is accomplished at a significantly lower speed than reaction of hydrogen with powder (see Fig. 3).

Our attention is attracted by the comparatively insignificant thermal effect of formation of titanium hydride and its dissociation at relatively low temperatures. However, one should not forget that process of formation of hydride is composed of two reactions:



As can be seen from given reactions, thermal effect of formation of titanium hydride is sufficiently large, but splitting of a molecule of hydrogen into atoms requires significant energy content. Kinetics of decomposition of titanium hydride was studied by two methods. Temperature of maximum of gas generation and end of decomposition of titanium hydride are established.

During heating of titanium hydride of sufficiently insignificant energy content in order to bring about the beginning of its dissociation with formation of atoms of hydrogen recombined into molecules, a significant energy content is liberated.

Data of experiments of decomposition of titanium hydride show that full decomposition takes place in interval of temperatures 800-1000°C. One should note, however, that at these temperatures, even in conditions of prolonged heating in a vacuum, in titanium there remains a certain quantity of hydrogen of the order

0.01-0.005%.

According to the work performed, the following conclusions can be made.

1. Maximum content of hydrogen in powder titanium is equal to 42.96 $\frac{1}{100}$ g, and in compact titanium, 38.14 $\frac{1}{100}$ g.
2. Temperature of beginning of reaction of hydrogen is equal to 330°C.
3. Maximum saturation of titanium by hydrogen is observed in interval 300-500°C. Speed of saturation by hydrogen of compact titanium is limited by diffusion.
4. During investigation of the kinetics of dissociation of titanium, decomposition of hydride starts at a temperature of 350-380°C, and maximum speed of dissociation in vacuum, depending upon conditions of experiment, was observed at 570-650°C.
5. On the basis of experiments of determination of elasticity of dissociation of titanium hydride in interval of temperatures 300-700°C, it is shown that from 300°C there starts desorption of hydrogen, and from 500°C -dissociation of hydride.
6. At a temperature of 25°C the free energy of formation and dissociation of titanium hydride on the basis of the obtained data is equal to +10,100 cal/mole, entropy 22 cal/deg. and thermal effect 16,700 cal/mole.

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