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Hydrogen-sorption and thermodynamic characteristics of mechanically grinded $TiH_{1.9}$ as studied using thermal desorption spectroscopy

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ABSTRACT

Isobaric thermal desorption spectroscopy and X-ray diffraction analysis were used to study the influence of mechanical dispersion during high-energy milling γ-$TiH_{1.9}$ hydride upon its hydrogen-sorption characteristics, temperature and enthalpy of the $\gamma \rightarrow \beta$ ($TiH_{1.9} \rightarrow Ti[H]_\beta$) phase transition at isobaric heating the sample under hydrogen atmosphere with speed 3°/min. Isobars of hydrogen thermal desorption in the regions of the γ and β phases of the Ti–H_2 system at pressures of 0.1, 0.25, 0.315 and 0.45 MPa of hydrogen in the reactor have been derived. Experimental data obtained for initial titanium hydride and mechanically grinded for 20 min in a planetary ball mill have been used for construction of Van't Hoff plots and for determination of enthalpy of formation of γ-hydride from solid solution of hydrogen in bcc titanium. Our experimental data reveal that 20 min high-energy influence on titanium hydride powder leads to increasing the specific surface of the samples from 0.13 to 8.58 m^2/g and to significant (more than 250°) decreasing the temperature of the beginning of hydrogen release when heating the sample (i.e., to a decrease of thermal stability of mechanically activated $TiH_{1.9}$). However, mechanical dispersion does not change the temperature of the $\gamma \rightarrow \beta$ phase transition. It has been established that high-energy milling $TiH_{1.9}$ powder causes the effect of a decrease of enthalpy of the formation of γ-hydride from 248 kJ/mole H_2 to 175 kJ/mole H_2.

1. Introduction

Processes taking place during mechanical treatment (significant dispersion and decreasing metallic powder particles, formation of new surfaces and accumulation of a great amount of different defects) can cause beginnings of excess energy and entropy and, as a consequent, a shift of phase equilibrium [1]. The influence of dispersion upon phase equilibrium has been studied in a great number of works; however studies of the influence of mechanical dispersion upon temperature of phase equilibrium in the Ti–H system, mainly upon temperature of decomposition and thermodynamic characteristics of TiH_2 hydride, in spite of wide practical applications of this hydride, are scarce. The necessity of studies of this influence is stressed in a number of works [2–8], where the mechanochemical method was adopted. In these works, it has been established that mechanical dispersion and alloying can change and increase hydrogen-sorption and kinetic characteristics of hydride phases, as well as can change and manage thermodynamic properties of mechanical alloys [9,10] varying treatment conditions and a chemical content of components of a mixture treated. The mechanochemical method allows to change thermal stability of a hydride phase, to decrease/increase temperature of its decomposition or a phase transition, to expand significantly a region of the α-solid solution or to constrict a two-phase region, to change equilibrium pressure, etc. [11–15].

Zhang and Kisi [16] have adopted the gravimetric method to study a thermal decomposition of nanocrystalline titanium dihydride synthesized by reactive mechanical alloying (RMA) under hydrogen atmosphere and, for comparison, of commercial TiH_2. The authors [16] have stressed different behavior of the above hydrides during their heating. Additionally, it has been established that nanocrystalline TiH_2 synthesized by the RMA method starts and completes to decompose at much more lower temperatures and dehydriding process occurs within significantly narrower temperature region as compared with TiH_2 synthesized by traditional methods [16]. Extremely small sizes of particles, high specific surface as well as a great number of defects arising during the milling of TiH_2 powder synthesized by the RMA method are considered to be responsible for different dehydriding behaviors of the two titanium dihydrides studied in Ref. [16].

The influence of powder sizes upon dehydriding 40 μm commercial TiH_2 undergone a high-energy mechanical treatment with different prolongation for obtaining titanium dihydride powder with different particle sizes has been studied in Ref. [17] employing

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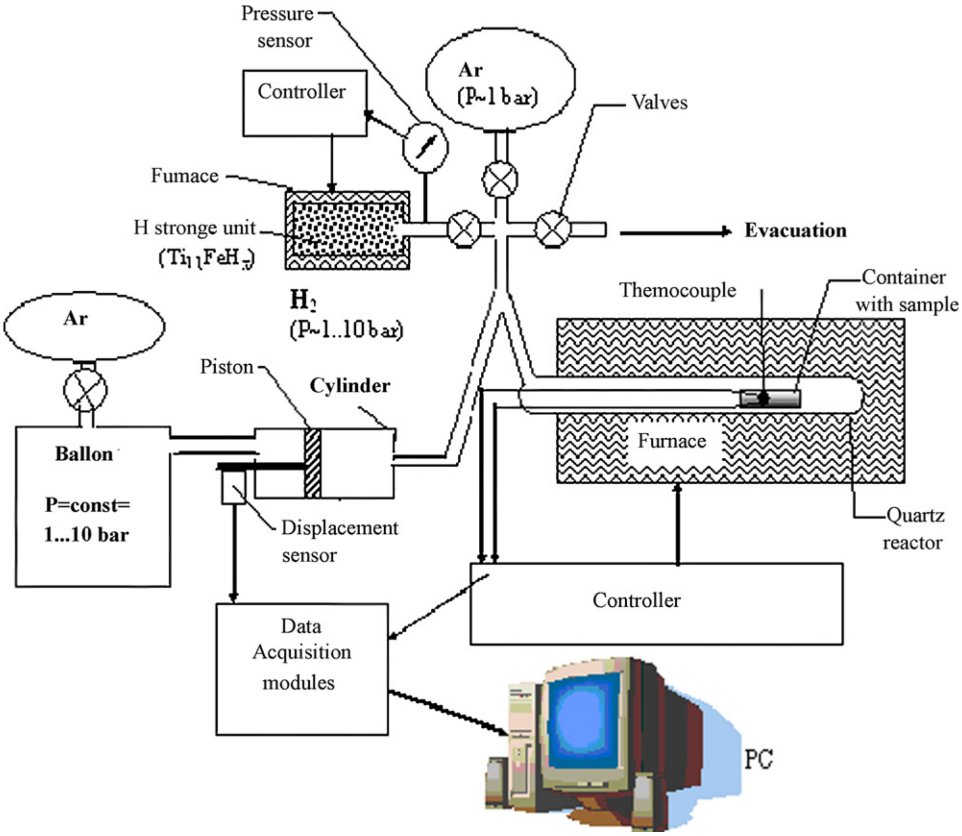

Fig. 1. Schematic drawing of the volumetric setup for studies of isobars during sorption/desorption of hydrogen by metals and alloys.

differential thermal analysis (DTA) and thermogravimetric analysis (TGA) methods as well as X-ray diffraction analysis and transmission electron microscopy (TEM). It has been shown in Ref. [17] that with an increase of milling time (and, as a result, with decreasing particle sizes of TiH_2 powder) the distance between two peaks on the DTA curve increases and the curve shifts towards lower temperatures. Bhosle et al. [17] have suggested to consider dehydriding TiH_2 as a two-stage process with two consecutive phase transitions $TiH_2 \rightarrow TiH_x$ and $TiH_x \rightarrow \alpha$-Ti. The authors [17] claim that the amount of hydrogen releasing at the first stage of the first phase transition increases (and at the second phase transition decreases) with increasing time of the milling of initial TiH_2. Like in Ref. [16], Bhosle et al. [17] have attributed a decrease of the temperature of the first phase transition to decreasing particle sizes of hydride powder, increasing its specific surface and amounts of defects accumulated during the milling of titanium dihydride. It should be mentioned that there are a number of investigations, where different techniques were employed to explore effects of ball milling and a nanocrystalline state of TiH_2, both pure and with different additives, upon some properties of the hydride (e.g., hydrogen mobility, thermal stability, sorption behavior, etc. [18–23]), however, to the best of our knowledge, the influence of the grinding of titanium dihydride on its thermodynamic characteristics has not been studied yet.

In the present work, methods of isobaric thermal desorption spectroscopy (TDS) and X-ray diffraction (XRD) analysis were used to investigate the influence of mechanical dispersion under the conditions of high-energy grinding $TiH_{1.9}$ hydride on its hydrogen sorption and thermodynamic characteristics (temperature and enthalpy of the $\gamma \rightarrow \beta$ ($TiH_{1.9} \rightarrow Ti[H]_\beta$) phase transition) employing the isobaric heating of specimens with the speed of 3°/min under hydrogen atmosphere at constant pressure in the reactor. We have modified our volumetric apparatus for isobaric studies of processes of hydrogen sorption/desorption by metals and alloys with the aim of measuring isobars of hydrogen thermal desorption in the region of the γ and β phases of the Ti–H system under different constant pressures of hydrogen in the reactor as following: 0.1, 0.25, 0.315, and 0.45 MPa. The experimental data derived employing the modified apparatus were used for construction of Van't Hoff plots and for evaluation of enthalpy of formation of the γ hydride from the solid solution of hydrogen in body-centered cubic (bcc) titanium in the case of initial titanium hydride as well as for the hydride grinded mechanically in a planetary ball mill.

2. Experimental

$TiH_{1.9}$ hydride powder, 99.5% pure with size ~12 μm, was used in this study. The hydride was grinded in a planetary ball mill under argon atmosphere employing the technique [24] with rotation speed 1630 rpm for 20 min. Ball-to-steel weight ratio was equal to 20:1 in the present experiments.

After unloading in a glove box filled with argon, the samples were taken for an XRD analysis and for series of TDS measurements under hydrogen atmosphere in temperature range from 20 to 900 °C.

Series of isobars of desorption/resorption of hydrogen from initial and grinded $TiH_{1.9}$ were measured with the modified Siverts apparatus at different pressures in the reactor, namely at 0.1 MPa, 0.25 MPa, 0.315 MPa, and 0.45 MPa. A schematic drawing of the apparatus is presented in Fig. 1. A quartz reactor with the sample ($m = 0.2$ g) was attached to a volumetric setup equipped with a piston mechanism; displacements of the latter were measured using a sensor calibrated on changes of a volume of gas in the system. The second outlet of the piston mechanism was attached to a 40 L argon-balloon to provide certain constant pressure in the mechanism during movement in the piston and to measure a volume of hydrogen desorbed. The reactor was equipped with a k-type thermocouple and was heated by an electric furnace connected to a controller providing linear heating (ramp rate 3°/min). The thermocouple and the displacement sensor were connected to a data acquisition system (based on ICP DAs Interface Modules). After loading the sample, the system was evacuated by a rotary pump, filled with hydrogen prior to starting the desorption experiments during the heating. After the maximum temperature of a TDS experiment was reached, the furnace was switched off, and the reactor was cooled to room temperature (in so doing, the logging of gas volume change and temperature were continued) followed by unloading the sample for an XRD analysis.

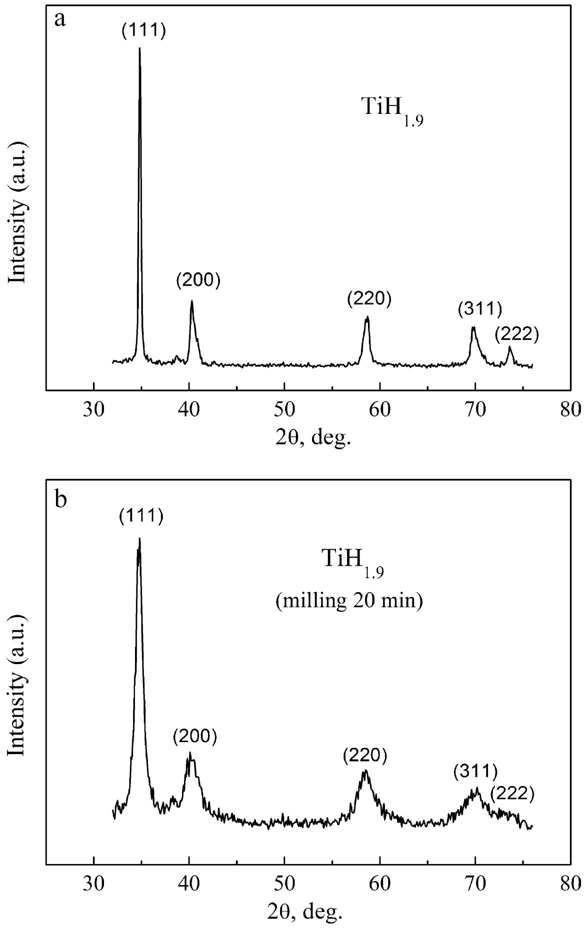

Fig. 2. XRD patterns of (a) initial and (b) mechanically grinded titanium dihydride $TiH_{1.9}$.

X-ray diffraction measurements of the hydrides under study were carried out using a computerized DRON-3M difractometer in copper radiation with a graphite monochromator mounted on the diffracted beam.

Changes of particle sizes of titanium hydride powder as a result of its mechanical grinding were evaluated taking into account values of specific surfaces of initial and grinded TiH_2. The specific surfaces were determined by measuring a quantity of nitrogen adsorbed on the particles (in a stream of nitrogen–helium mixture at the temperature of liquid nitrogen) and an amount of nitrogen desorbed with increasing temperature up to 20 °C. The calculations were made adopting the BET method.

3. Results and discussion

High-energy 20 min treatment of the initial titanium dihydride powder causes an increase of specific surface of the sample from 0.13 m^2/g to 8.58 m^2/g. An average size of $TiH_{1.9}$ powder particles (derived on the basis of the above data of specific surface measurements) decreases from 12 μm to 0.18 μm.

XRD patterns of initial titanium dihydride and the dihydride grinded due to treatments in the planetary ball mill are presented in Fig. 2. As one can see from Fig. 2, 20 min milling the titanium dihydride does not cause the appearance of new lines on the XRD pattern of the treated dihydride indicating a constant phase content in the both samples. However, the X-ray diffraction lines of cubic titanium dihydride broaden significantly after its treatment in the planetary ball mill. This means that the treatment of the dihydride changes sizes and causes a formation of a great number of defects and lattice distortion. The evaluation of contributions of microstresses and dispersions of mosaic blocks in broadening the (1 1 1) and (2 2 2) lines of titanium dihydride indicates that the main portion of the broadening is caused by a decrease of block sizes (~60–70%).

Table 1
Temperatures (°C) of the γ → β phase transition in initial and grinded $TiH_{1.9}$ that were derived using measurements of the hydrogen desorption and resorption isobars.

Pressure (MPa)	Initial $TiH_{1.9}$			Grinded $TiH_{1.9}$		
	$T_{desorption}$	$T_{sorption}$	$\langle T \rangle$	$T_{desorption}$	$T_{sorption}$	$\langle T \rangle$
0.1	932	895	913.5	928	865	896.5
0.25	963	916	939.5	959	906	932.5
0.315	971	923	947	966	918	942
0.45	986	929	957.5	981	935	958

Curves of thermal desorption of hydrogen from initial and grinded $TiH_{1.9}$ that were measured at pressures of 0.1, 0.25, 0.315 and 0.45 MPa in the reactor and with the speed of sample heating 3°/min are shown in Fig. 3. From the thermal desorption isobars derived at 0.1 MPa (see Fig. 3a) one can conclude that, intensive release of hydrogen from initial $TiH_{1.9}$ starts at 430 °C and from the hydride dispersed in the planetary ball mill at 180 °C. Therefore, 20 min mechanical dispersion of titanium dihydride causes a significant (more than 250°) decrease of temperature of the beginning of hydrogen release during the sample heating and leads to decreasing thermal stability of mechanically grinded (activated) $TiH_{1.9}$. This decrease of thermal stability indicates a significant redistribution of hydrogen on the places of its stable being in the lattice of grinded γ-titanium hydride as a result of increasing specific surface, big quantity of different kinds of defects and lattice distortions. From the thermal desorption isobars measured at pressures of 0.25, 0.315 and 0.45 MPa in the reactor (Fig. 3b–d), it is apparent that, like in the case of pressure of 0.1 MPa, significant decreasing temperature of the beginning of hydrogen desorption from grinded $TiH_{1.9}$ compared to that of initial titanium dihydride takes place. Nevertheless, in the result of mechanical grinding, the temperature of the γ → β phase transition in conditions of isobaric heating titanium dihydride under hydrogen atmosphere changes very little (only a few degrees towards lower temperatures). These changes (caused by powder dispersion) towards lower temperatures are evidenced as a shift of intervals of isobars corresponding to hydrogen desorption during the γ → β phase transition that are marked in Fig. 3a–d by letters A and B. Temperatures corresponding to the middle of the AB intervals for the all thermal desorption isobars under study are listed in Table 1. If one evaluate on the curves of hydrogen thermodesorption presented in Fig. 3 temperatures corresponding to the beginning of the γ → β phase transition (points A on the curves of hydrogen thermodesorption), one can see that mechanical dispersion almost does not change the temperature of the mentioned transition.

As can be concluded from isobars shown in Fig. 3, the higher pressure of hydrogen in the reactor in which the desorption takes place, the higher temperature of the γ → β phase transition for both the initial and mechanically grinded $TiH_{1.9}$ hydride (see Table 1).

In our experiments carried out at hydrogen pressure of 0.1 MPa in the reactor (Fig. 3a), when heating the initial $TiH_{1.9}$ hydride from room temperature up to 640 °C, it was evidenced that in this temperature region no phase transitions occur and both hydrogen desorption from γ-titanium hydride and a change of its content (in accordance with isobaric section of the Ti–H diagram at hydrogen pressure of 0.1 MPa [25]) take place. When heating the sample up to the temperature 644 °C (point A on the curve of hydrogen desorption from the initial $TiH_{1.9}$ hydride; Fig. 3a), hydrogen release increases abruptly (a sharp increase of the curve of hydrogen desorption in the AB intervals); this indicates the beginning of the γ → β ($TiH_2 \rightarrow TiH$) phase transition. It is necessary to point out that, strictly at this temperature (644 °C) Shilov and Padurets

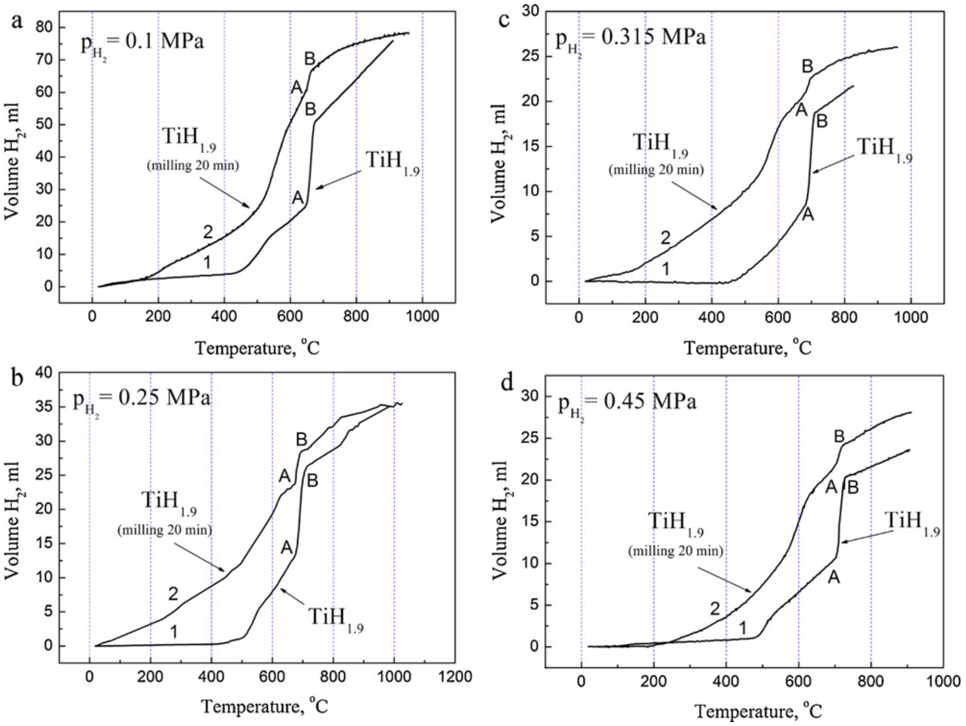

Fig. 3. Curves of thermal desorption of hydrogen from (1) initial and (2) grinded $TiH_{1.9}$ hydride measured at the following pressures of hydrogen in the reactor: (a) 0.1 MPa, (b) 0.25 MPa, (c) 0.315 MPa and (d) 0.45 MPa.

[26] have observed the beginning of the mentioned $\gamma \to \beta$ phase transition employing the DTA method in analogous experimental conditions, namely heating titanium dihydride at pressure of 0.1 MPa.

The fact of the occurrence of the phase transition in the AB interval of the curve of thermal desorption of hydrogen is confirmed in Fig. 4 by dependences "temperature of heating hydride vs. time" and "volume of hydrogen desorbed vs. time". From Fig. 4, it is obvious that when isothermal exposure of sample temperature was made at about 650 °C (at this temperature we kept the sample without further heating), hydrogen release from the sample persisted (with the same speed) at constant pressure in the reactor and at constant sample temperature in accordance wit Gibbs phase rule. Another behavior was detected in the case of isothermal exposure at temperature about 520 °C (Fig. 4): simultaneously with breaking of an increase of temperature, cessation of hydrogen release from the titanium dihydride sample occurs.

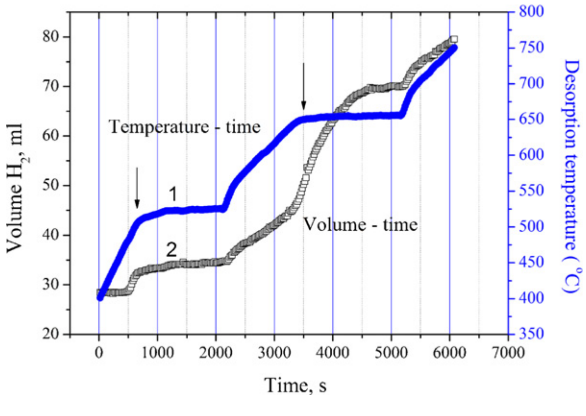

Fig. 4. (1) Curve of sample heating (temperature vs. time) and (2) curve of hydrogen desorption (volume vs. time) from $TiH_{1.9}$ hydride (P = 0.1 MPa).

During cooling the initial and grinded titanium dihydrides (after desorption of hydrogen from these samples), curves of resorption of hydrogen were recorded (Figs. 5 and 6). From Figs. 5 and 6 one can easily observe the existence of temperature hysteresis of the $\gamma \to \beta$ phase transition for the both initial and grinded titanium dihydride samples. For instance, as can be seen from Fig. 5a and data listed in Table 1, in the case of hydrogen pressure of 0.1 MPa in the reactor, temperature of the mentioned phase transition during desorption, that corresponds to the middle of the AB interval on the thermal desorption curve, equals 932 K (659 °C). This temperature does not correspond to that of the $\gamma \to \beta$ phase transition during sorption, namely 895 K (622 °C). Lack of coincidence of temperatures of the $\gamma \to \beta$ phase transition during desorption and sorption is detected also for other sets of hydrogen pressures in the reactor (see Fig. 5b–d). Temperatures of the $\gamma \to \beta$ phase transition for initial and grinded titanium hydrides determined experimentally using curves of desorption and resorption of hydrogen in dependence on constant pressure in the reactor are summarized in Table 1. In Table 1, we report also average temperatures of the mentioned phase transition ($\langle T \rangle$) that were used for construction of Van't Hoff plots.

Fig. 7 presents Van't Hoff plots based on data of temperature of the $\gamma \to \beta$ phase transition of initial and grinded $TiH_{1.9}$ hydrides (the data were derived using measurements of the desorption isobars; see Table 1). From Fig. 7 it is clear that the Van't Hoff plots possess the same slope. This result allows to make a conclusion that it is almost impossible to determine experimentally the influence of dispersion upon the slope of Van't Hoff plots (as well as on enthalpy of the formation of γ-titanium hydride in a solid solution of hydrogen in bcc titanium) if temperatures of the $\gamma \to \beta$ phase transition that correspond to different quasi-equal hydrogen pressures are determined taking into account isobars of initial and grinded titanium hydride and ignoring hysteresis of the temperatures. This fact (i.e., the existence of hysteresis and difficulties in determination of thermodynamic characteristics when using only data of hydrogen desorption in the first cycle of heating–cooling a hydride sample)

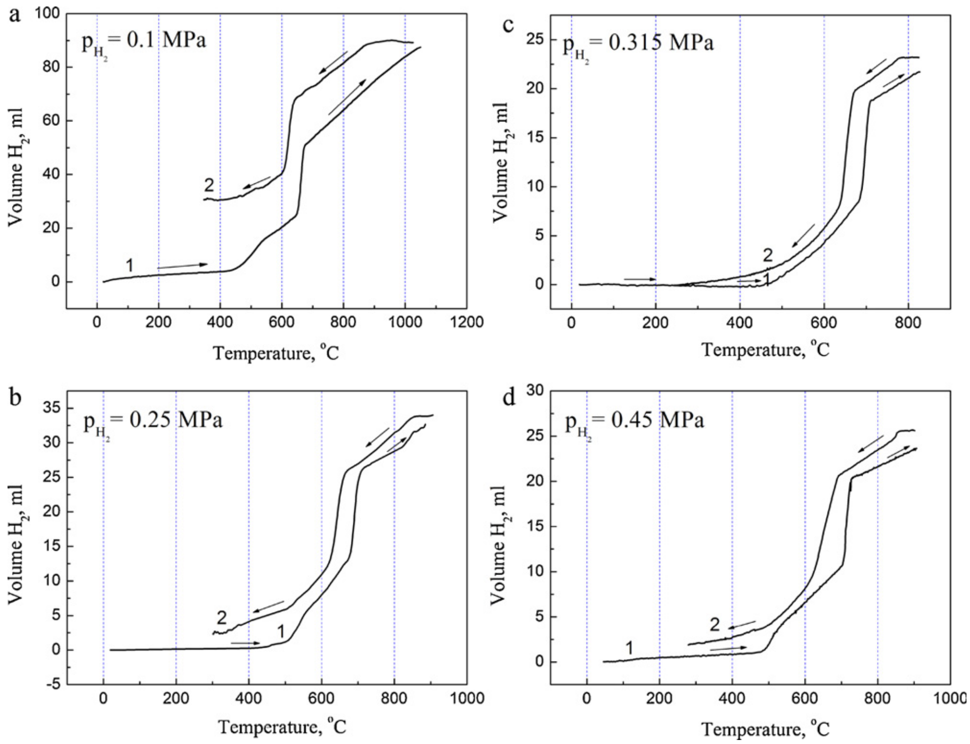

Fig. 5. Curves of (1) thermal desorption and (2) resorption of hydrogen from initial $TiH_{1.9}$ hydride recorded at the following pressures of hydrogen in the reactor: (a) 0.1 MPa, (b) 0.25 MPa, (c) 0.315 MPa and (d) 0.45 MPa.

was taken into account when constructing Van't Hoff plots presented in Fig. 8. In this figure, for temperatures of the $\gamma \to \beta$ phase transition we use the average value of temperatures determined adopting two curves (desorption and resorption of hydrogen) at every hydrogen pressure in the reactor, namely 0.1, 0.25, 0.315, and 0.45 MPa (see Table 1).

Enthalpy of the formation of initial $TiH_{1.9}$ γ-hydride from a solid solution of hydrogen in bcc titanium as determined from slopes of Van't Hoff plots equals 248 kJ/mole H_2, and enthalpy of grinded γ-titanium hydride 175 kJ/mole H_2. Therefore, one can conclude that our studies employing the isobaric method of thermal desorption spectroscopy reveal the effect of decreasing enthalpy of

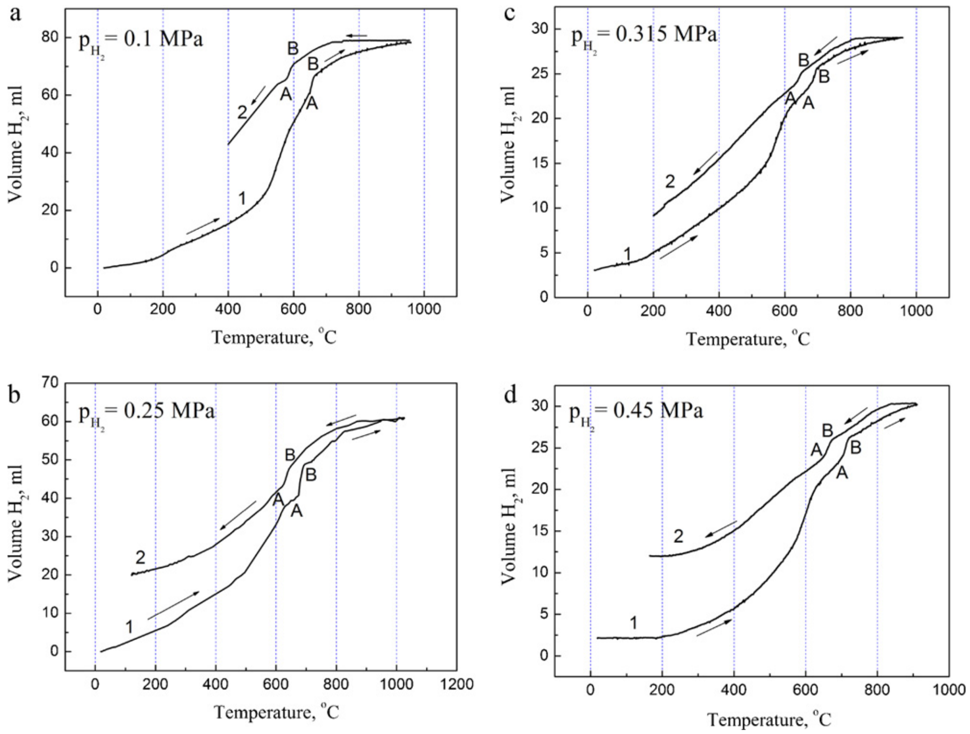

Fig. 6. Curves of (1) thermal desorption and (2) resorption of hydrogen from grinded $TiH_{1.9}$ hydride recorded at the following pressures of hydrogen in the reactor: (a) 0.1 MPa, (b) 0.25 MPa, (c) 0.315 MPa and (d) 0.45 MPa.

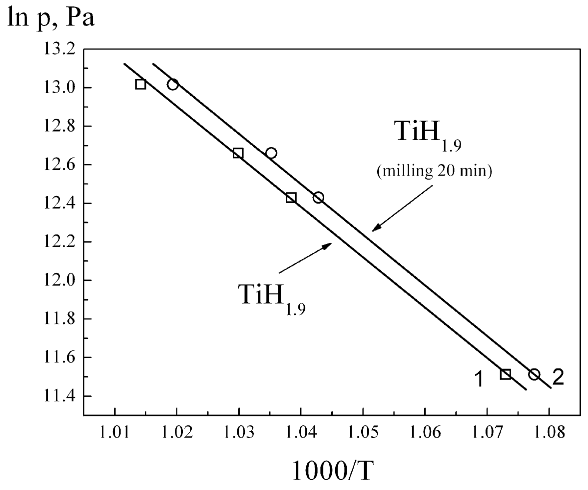

Fig. 7. Van't Hoff plots of (1) initial and (2) grinded $TiH_{1.9}$ that were constructed using temperatures of the $\gamma \rightarrow \beta$ phase transition (data of desorption isobars were used).

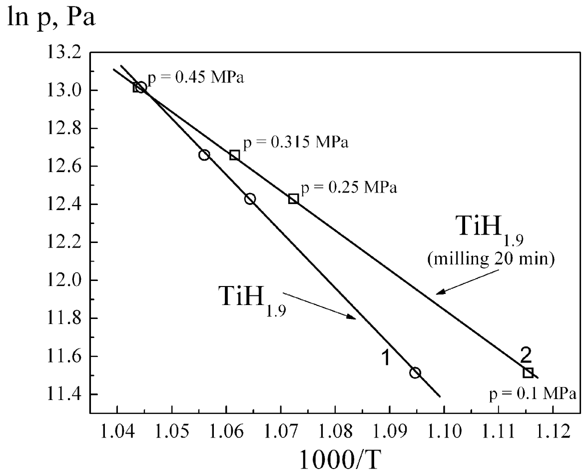

Fig. 8. Van't Hoff plots of (1) initial and (2) grinded $TiH_{1.9}$ that were constructed using average temperatures of the $\gamma \rightarrow \beta$ phase transition (data of hydrogen desorption and resorption isobars were used).

$TiH_{1.9}$ γ-hydride by 73 kJ/mole H_2 (from the value 248 kJ/mole H_2 to 175 kJ/mole H_2) due to 20 min grinding the hydride in a planetary ball mill with the speed 1630 rpm. These studies carried out employing the modified apparatus indicate that thermodynamic characteristics can be determined not only using experimental *p–c–T* curves (isotherms of desorption–sorption), but also using isobars of hydrogen sorption–resorption of hydride employing the isobaric TDS method at slow speed of sample heating.

4. Conclusions

In order to study the influence of dispersion upon thermodynamic characteristics of titanium dihydride, the isobaric TDS method was employed to reveal experimental data of temperature of the $\gamma \rightarrow \beta$ phase transition in initial and mechanically grinded $TiH_{1.9}$ at different constant pressures of hydrogen in the reactor. The data were used for construction of Van't Hoff plots and for determination of enthalpy of the formation of γ-titanium hydride from a solid solution of hydrogen in bcc titanium for both initial and grinded $TiH_{1.9}$. It has been established that 20 min mechanical grinding in a planetary ball mill with speed 1630 rpm causes significant decreasing thermal stability of titanium dihydride as well as enthalpy of formation of γ-titanium hydride from a solid solution of hydrogen in bcc titanium.

References

[1] V.I. Zubov, Zhurn. Mendeleev Vses. Khim. Obshchestva. 36 (2) (1991) 133–136 (in Russian).
[2] E.Yu. Ivanov, I.G. Konstanchuk, Dokl. AN SSSR 286 (2) (1986) 385–388 (in Russian).
[3] Y. Chen, J.S. Williams, J. Alloys Compd. 217 (1995) 181–184.
[4] J. Huot, G. Liang, R. Schulz, J. Appl. Phys. A 72 (2001) 187–195.
[5] V.D. Dobrovolsky, O.G. Radchenko, Y.M. Solonin, N.P. Gorbachuk, Powder Metall. Met. Ceram. 45 (2006) 381–386.
[6] O.G. Ershova, V.D. Dobrovolsky, Y.M. Solonin, R.A. Morozova, in: T.N. Veziroglu (Ed.), Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, Springer, Dordrecht, 2007, pp. 429–436.
[7] O.G. Ershova, V.D. Dobrovolsky, Y.M. Solonin, O.Yu. Khyzhun, in: B. Baranowski (Ed.), Carbon Nanomaterials in Clean Energy Hydrogen Systems, Springer Science + Business Media B.V., 2008, pp. 473–483.
[8] O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin, O.Yu. Khyzhun, A.Yu. Koval, J. Alloys Compd. 464 (2008) 212–218.
[9] P. Delchev, P. Solsona, B. Drenchev, N. Drenchev, T. Spassov, M.D. Baro, J. Alloys Compd. 388 (2005) 98–103.
[10] T. Spassov, V. Rangelova, P. Solsona, M.D. Baro, D. Zander, U. Köster, J. Alloys Compd. 398 (2005) 139–144.
[11] C. Moelle, H. Fecht, Nanostruct. Mater. 3 (1993) 93–99.
[12] L. Zaluski, P. Tessier, D.H. Ryan, J. Mater. Res. 8 (1993) 3059–3068.
[13] K. Aoki, T. Masumoto, J. Alloys Compd. 231 (1995) 20–28.
[14] H. Sakaguchi, T. Sugioka, G.-Y. Adachi, Chem. Lett. 7 (1995) 561–562.
[15] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Compd. 253–254 (1997) 70–79.
[16] H. Zhang, E. Kisi, J. Phys.: Condens. Matter 9 (1997) L185–L190.
[17] V. Bhosle, E.G. Baburaj, M. Miranova, K. Salama, Mater. Eng. A 356 (2003) 190–199.
[18] C. Borchers, O.S. Morozova, T.I. Khomenko, A.V. Leonov, E.Z. Kurmaev, A. Moewes, A. Pundt, Chem. Phys. Lett. 465 (2008) 82–85.
[19] C. Borchers, O.S. Morozova, T.I. Khomenko, A.V. Leonov, A.V. Postnikov, E.Z. Kurmaev, A. Moewes, A. Pundt, J. Phys. Chem. C 112 (2008) 5869–5879.
[20] O.S. Morozova, T.I. Khomenko, Ch. Borchers, A.V. Leonov, E.Z. Kurmaev, A. Moewes, J. Alloys Compd. 483 (2009) 309–312.
[21] E. Tal-Gutelmacher, R. Gemma, A. Pundt, R. Kirchheim, Acta Mater. 58 (8) (2010) 3042–3049.
[22] S. Garroni, C. Milanese, A. Girella, A. Marini, G. Mulas, E. Menéndez, C. Pistidda, M. Dornheim, S. Suriñach, M.D. Baró, Int. J. Hydrogen Energy 35 (11) (2010) 5434–5441.
[23] A.V. Soloninin, A.V. Skripov, O.A. Babanova, O.S. Morozova, A.V. Leonov, J. Phys. Chem. C 114 (2010) 646–651.
[24] V.D. Dobrovolsky, O.G. Ershova, Yu.M. Solonin, O.Yu. Khyzhun, V. Paul-Boncour, J. Alloys Compd. 465 (2008) 177–182.
[25] A.D. McQuillan, Proc. R. Soc. A 204 (1950) 309–323.
[26] A.L. Shilov, L.N. Padurets, Zhurn. Neorgan. Khim. 42 (8) (1997) 1258–1262 (in Russian).