



Mechanical alloys in the Ti–B–H system: Influence of dispersion and alloying by boron upon thermal stability of hydride phases

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ABSTRACT

Influence of dispersion and alloying by boron upon thermal stability and decomposition temperature of hydride phases of mechanical alloys of the Ti–B–H system that were derived in the conditions of high-energy ball milling either of (TiH_{1.9} + 9 wt.% B + 13 wt.% Ti) and (TiH_{1.9} + 50 wt.% TiB₂) mixtures (50 h milling, rotation speed 1000 rpm) or of (TiH_{1.9} + 40 wt.% B) and (TiH_{1.9} + 50 wt.% TiB₂) mixtures (20 milling, rotational speed 1630 rpm) has been studied employing scanning electron microscopy, X-ray diffraction analysis, and thermal desorption spectroscopy. It has been established that, dispersion and boron additives to the TiH_{1.9} powder followed by mechanical treatment influence thermal stability of the hydride. Mechanical milling the (TiH_{1.9} + 9 wt.% B + 13 wt.% Ti) mixture for 50 h in argon causes decreasing the decomposition temperature of a Ti(B,H)_x hydride phase by more than 300° compared with that of the initial TiH_{1.9} hydride. Mechanisms of influence of both dispersion and boron alloying upon thermal stability of the TiH_{1.9} hydride have been studied.

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1. Introduction

In recent years, a great attention is devoted to a synthesis of hydrides by methods that differ from the method of direct hydrogenation with molecular hydrogen. Among methods that are widely used for a synthesis of magnesium, transition metal and rare-earth metal hydrides, the method of mechanical alloying is rather famous and gives a good account of itself. However, literature data regarding an application of this method for deriving transition metal hydride derivatives, e.g., binary boron-containing hydrides, are scarce. Elaboration of new methods for a synthesis of such kinds of compounds (e.g., aluminum hydride-based materials) and studies of their physical and chemical properties allow to increase our knowledge regarding a nature of hydrides as well as interstitial alloys [1–3]. Titanium-boron hydride Ti(BH₄)₃ is known to be a rather prospective hydrogen capacitor (ca. 17 wt.%), however, it is unstable and decomposes at room temperature [4]. These disadvantages, as well as toxicity of products of its decomposition and irreversibility of the hydrogenation process, restrict the application of Ti(BH₄)₃ even in close systems of energy transformation and accumulation. Zhang and Kisi [5] have applied the thermogravimetric method for studies of thermal decomposition of nanocrystalline titanium dihydride derived by reactive mechanical alloying (RMA) in hydrogen atmosphere, and, for comparison, of standard (com-

mercial) TiH₂. It has been established that, nanocrystalline TiH₂ synthesized by the RMA method starts to decompose and completes its full decomposition at significantly lower temperatures compared with titanium dihydride obtained employing traditional methods. Additionally, the dehydrogenation process occurs in a narrower range in the case of TiH₂ synthesized by RMA in comparison with commercial titanium dihydride. Zhang and Kisi [5] attribute the dehydrogenation differences to extremely small particle sizes and high specific surface of TiH₂ powder obtained by the RMA method. Additionally, a great number of defects formed when milling titanium dihydride influences the above differences.

The influence of size upon dehydration of 40 μm commercial TiH₂, which has been undergone by high-energy mechanical treatment at irregular intervals in order to obtain hydride powder with different particle sizes, was studied in Ref. [6] employing methods of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) and adopting also X-ray diffraction and transmission electron microscopy. It has been established that, with increasing milling intervals (and, accordingly, with decreasing particle sizes of TiH₂ powder) the distance between two peaks on the DTA curve increases and the curve shifts towards lower temperatures. Like in Ref. [5], Bhosle et al. [6] explain a decrease of temperature of the TiH₂ → TiH_x phase transition by decreasing particle sizes of titanium hydride powder, increasing its specific surface and a quantity of defects caused by milling the powder.

The aim of the present work was to verify a possibility of synthesis of new hydride phases in the Ti–B–H system by mechanical alloying as well as to study the influence of boron and its

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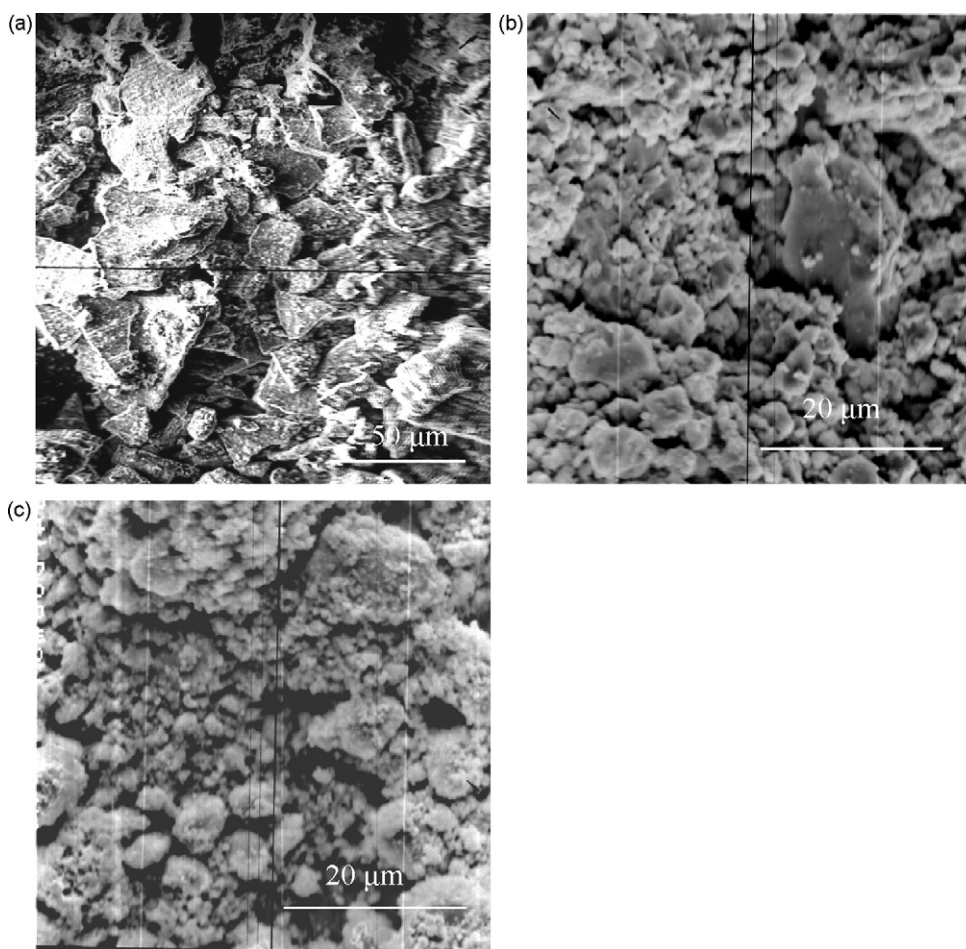


Fig. 1. SEM images of (a) the initial ($\text{TiH}_{1.9} + 9 \text{ wt.}\% \text{ B} + 13 \text{ wt.}\% \text{ Ti}$) mixture and the (b) MA1 and (c) MA2 mechanical alloys.

alloys with titanium upon thermal stability of TiH_2 decomposing at relatively high temperature. This dihydride is widely used when synthesizing different materials and in many applications the decreasing temperature of its decomposition plays an important role. With this aim, we have used possibilities of X-ray diffraction analysis, transmission electron microscopy and thermal desorption spectroscopy (TDS) methods to study hydride phases in the Ti–B–H system for mechanical alloys obtained using treatment of different mixture powders in a ball planetary mill and in Ar atmosphere.

2. Experimental

Mechanical alloys (MAs) that have been derived by treatment of ($\text{TiH}_{1.9} + 9 \text{ wt.}\% \text{ B} + 13 \text{ wt.}\% \text{ Ti}$) and ($\text{TiH}_{1.9} + 50 \text{ wt.}\% \text{ TiB}_2$) mixtures, for clarity, we shall refer to MA1 and MA2, respectively. These alloys were obtained by 50 h treatment of the mixtures in a spherical planetary mill (rotation speed 1000 rpm). The ratio of steel balls weight to initial burden's weight was equal to 20:1. Average grain sizes of initial $\text{TiH}_{1.9}$, Ti, B and TiB_2 powders were 12, 10, 2 and $10 \mu\text{m}$, respectively. MAs obtained by treatment of ($\text{TiH}_{1.9} + 40 \text{ wt.}\% \text{ B}$) and ($\text{TiH}_{1.9} + 50 \text{ wt.}\% \text{ TiB}_2$) mixtures we shall refer to MA3 and MA4, for clarity. The latter alloys were derived by 20 min treatment of the mentioned mixtures at rotation speed 1630 rpm. In this case, the ratio of steel balls weight to initial burden's weight was equal to 10:1. Titanium hydride $\text{TiH}_{1.9}$, a component of all the mixtures treated, was synthesized by direct hydrogenation of iodine titanium with molecular hydrogen.

Microstructures of MAs powders under consideration were studied using a CAMEBAX SX-50 scanning electron microscope-analyzer. An X-ray diffraction analysis of hydrides obtained was carried out using a computerized DRON-3M diffractometer equipped with $\text{CuK}\alpha$ source with a graphite monochromator on the diffracted beam. To determine the level of the hydride thermal stability and the decomposition temperature, thermal decomposition of hydrides was carried out using a computerized installation allowing measurements of a volume of hydrogen desorbed from the sample heated at a rate of $20^\circ/\text{min}$ in hydrogen atmosphere

under constant normal pressure (1 bar). TDS spectra of hydrides were obtained by measuring isobar–volumetric curves using the above-mentioned installation.

Changes of particle sizes of titanium hydride powder as a result of its mechanical dispersion were evaluated taking into account values of specific surfaces of initial and disperse 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

From a TEM image presented in Fig. 1a, it is evident that the presence of asymmetric particles is characteristic of the initial $\text{TiH}_{1.9} + 9 \text{ wt.}\% \text{ B} + 13 \text{ wt.}\% \text{ Ti}$ mixture. After its mechanical 50 h treatment, a disperse material MA1 was obtained (Fig. 1b). The similar microstructure is characteristic of the MA2 material, obtained by 50 h treatment of the initial $\text{TiH}_{1.9} + 50 \text{ wt.}\% \text{ TiB}_2$ mixture (Fig. 1c).

The XRD pattern of the MA1 sample reveals a broad line, which resembles a halo of an amorphous material, containing a number of rather broad and low-intensive reflexes (Fig. 2a, curve 2). The XRD pattern of the MA1 sample differs significantly from that of the initial mixture (Fig. 2a, curve 1) and represents a pattern typical for ultrafine powder that contains a great number of rather broad diffraction reflexes superposing each other. From Fig. 2a (curve 2), it is apparent that the MA1 sample is a multiphase material: high-energy treatment of Ti and B leads to the formation of TiB , TiB_2 , Ti_3B_4 , and Ti_2B_5 compounds. These compounds, due to the diffusive XRD pattern, were identified taking into account one or two diffraction lines corresponding to the above-mentioned

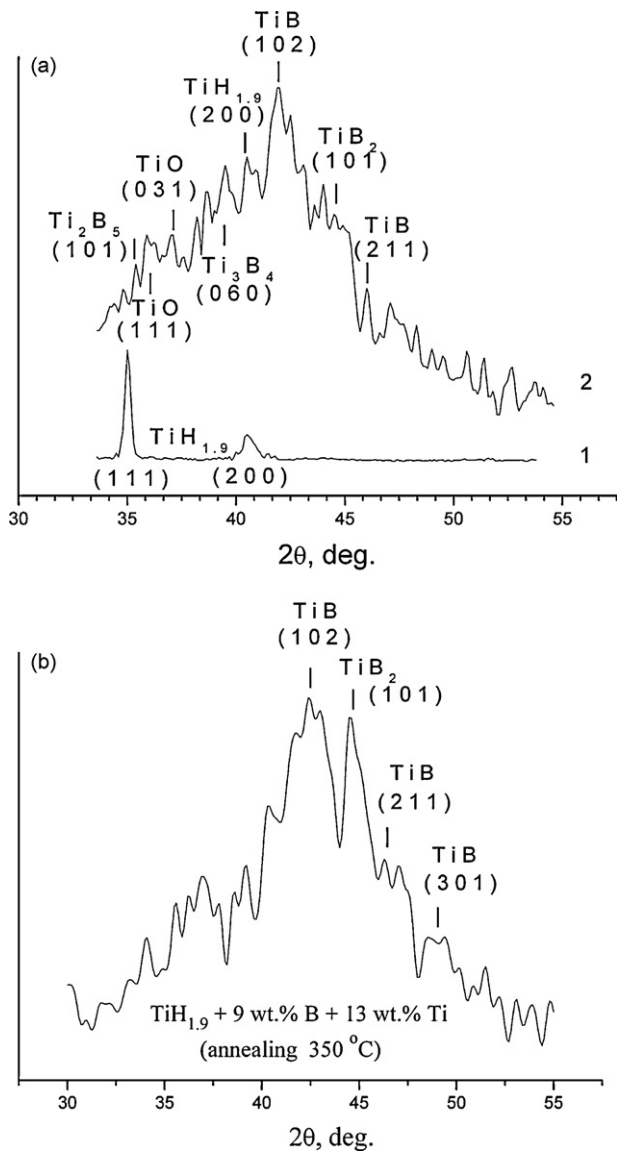


Fig. 2. X-ray diffraction patterns of (a) the initial ($\text{TiH}_{1.9} + 9 \text{ wt.}\% \text{ B} + 13 \text{ wt.}\% \text{ Ti}$) mixture (curve 1) and the MA1 sample (curve 2); (b) XRD pattern of MA1 annealed for 30 min at 350°C .

compounds. In addition, the XRD pattern of the MA1 sample contains several low-intensity lines, which can be attributed to cubic TiH_x and to monoclinic and cubic TiO . The XRD pattern presented in Fig. 2a (curve 2) does not allow to identify phases containing hydrogen (in addition to TiH_x). Further, from these data it is not possible to claim about the possible entering of boron into a content of titanium hydride. Additional information that can be obtained adopting other techniques is necessary for such a task [3]. It is worth to mention that, when heating the mechanical alloys under consideration from room temperature up to 1200°C , hydrogen was found to release only in the case of the MA1, MA3 and MA4 samples; in the case of the MA2 sample, a release of hydrogen has not been established. The XRD pattern of the MA2 sample is presented in Fig. 3a. From this figure, it is clear that reflexes belonging to titanium hydride TiH_x are absent in MA2: only two phases, namely TiB_2 and cubic TiO , are identified for this alloy.

The XRD pattern of the MA3 sample (Fig. 3b) reveals the presence of the diffraction lines of the phases detected for the initial mixture before its mechanical treatment, namely $\text{TiH}_{1.9}$ and boron; however, these diffraction lines are broaden significantly in MA3.

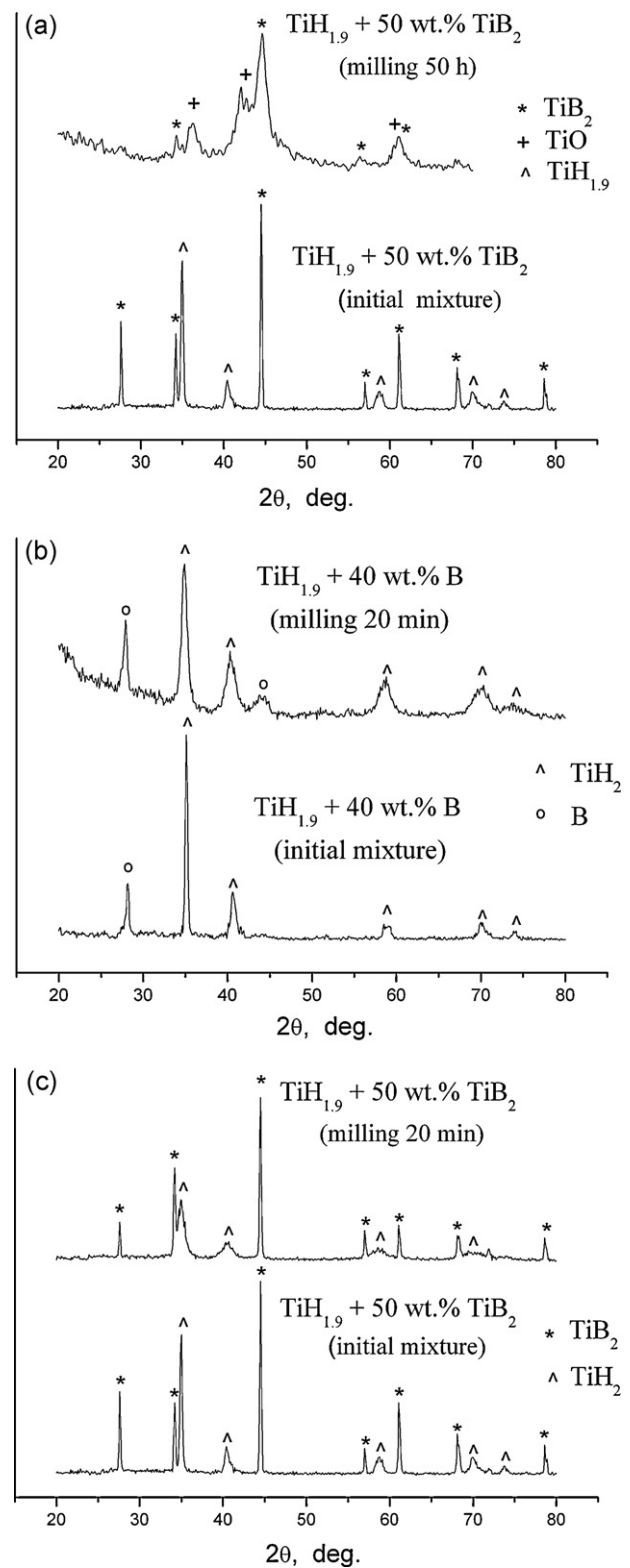


Fig. 3. X-ray diffraction patterns of the mechanical alloys under study: (a) MA2, (b) MA3, and (c) MA4.

The latter effect is a consequence of both mechanical dispersion of the particles and the appearance of a great amount of defects in them. Therefore, the XRD pattern presented in Fig. 3b permits to make a conclusion that 20 min mechanical treatment of the $\text{TiH}_{1.9} + 40 \text{ wt.}\% \text{ B}$ mixture does not induce changes of its phase content, i.e., decomposition and phase transformations of the ini-

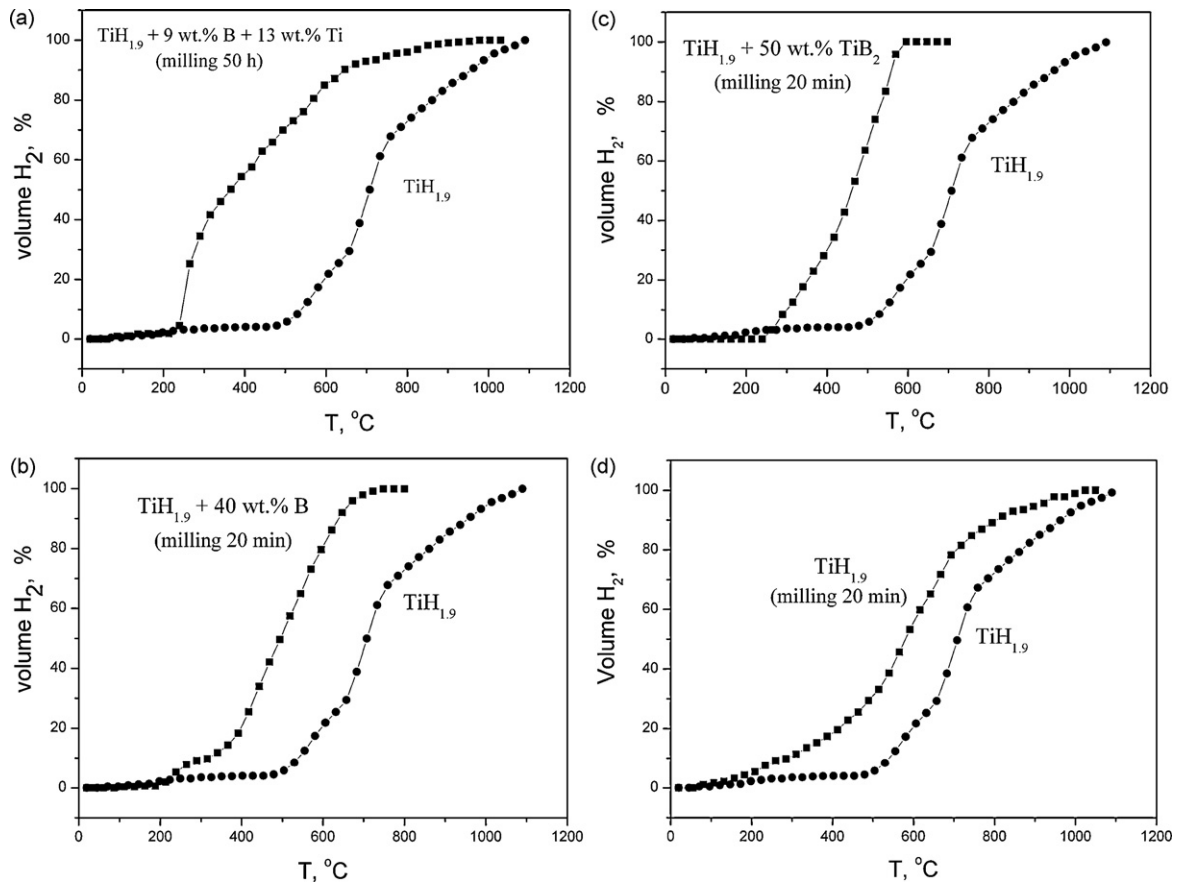


Fig. 4. Curves of thermodesorption of hydrogen (at $P=0.1$ MPa) from hydrides after their mechanical dispersion and alloying by boron: (a) MA1, (b) MA3, (c) MA4, and (d) $\text{TiH}_{1.9}$ (after its milling for 20 min as described in the text). Note: On every panel, the similar curve of untreated $\text{TiH}_{1.9}$ hydride is presented, for comparison.

tial mixture components do not occur in such a case. The above statements are true also in the case of the MA4 sample, which was derived at the same conditions as the MA3 sample. As Fig. 3c displays, only the reflexes belonging to TiH_x and TiB_2 phases are detected for the MA4 material under study.

Results of studies of thermodesorption of hydrogen of the mechanical alloys are presented in Fig. 4 (the $V(T)$ curves representing the dependence of the volume of hydrogen releasing from a sample upon its temperature we shall refer to the thermodesorption curves, for clarity). Curves representing derivatives $dV(T)/dT$ (Fig. 5) we shall refer to the thermodesorption spectra. For comparison, mechanically untreated $\text{TiH}_{1.9}$ hydride, a component of all the initial mixtures, was studied. The curve of thermodesorption of hydrogen in this hydride is also presented in Fig. 4. This allows comparing the thermal stability of hydrogen-containing phases of the alloys synthesized with that of initial (untreated) $\text{TiH}_{1.9}$. From Fig. 4a, it is apparent that, when heating the MA1 sample an intensive release of hydrogen starts at 230°C , whilst in the case of untreated $\text{TiH}_{1.9}$ a significant release of hydrogen occurs at 590°C . In the thermodesorption spectra, the maximum speed of releasing hydrogen occurs at 230 and 700°C in the case of the MA1 sample and the untreated $\text{TiH}_{1.9}$ hydride, respectively (Fig. 5a). It should be noted that when reaching temperature of 1000°C ($P=0.1$ MPa), the volume of hydrogen desorbed from the MA1 sample ($m=0.49$ g) was found to be 53 ml, i.e., 0.88% of the weight of the mechanical alloy. For comparison, hydrogen capacity of initial ($\text{TiH}_{1.9} + 9$ wt.% B + 13 wt.% Ti) mixture ($m=0.49$ g) equals 2.98 wt.%.

The above comparison permits to make a conclusion that a hydride phase (or phases) synthesized as a results of 50 h mechanical treatment in argon atmosphere of the $\text{TiH}_{1.9} + 9$ wt.% B + 13 wt.%

Ti mixture reveals significantly lower dissociation temperature compared with that of initial (untreated) $\text{TiH}_{1.9}$. Is the significant decreasing thermal stability of a hydride phase(s), a component(s) of the MA1 sample, has been happened due to either mechanical dispersion of the $\text{TiH}_{1.9}$ hydride or because of the mechanical alloying titanium hydride leading to a formation of a $\text{Ti}(\text{B,H})_x$ hydride phase? Probably, the both effects take place.

In order to answer the above questions, the following experiment has been carried out. A TiH_2 powder, a component of all the mechanical alloys derived, was undergone to 20 min dispersion in a spherical planetary mill at rotation speed 1630 rpm in argon atmosphere. After such a treatment, the hydride was decomposed thermally. The quantity of releasing hydrogen as a function of temperature in such a case and the spectrum of thermodesorption of hydrogen are presented in Figs. 4d and 5d, respectively. This experiment indicates that dissociation temperature of the dispersion titanium hydride (effective particle size was found to be about $0.18\ \mu\text{m}$) decreases by 150° compared with that of initial $\text{TiH}_{1.9}$. This means that dispersion of titanium dihydride particles due to high-energy influence balls of the planetary mill can cause a decreasing thermal stability of the dihydride. Therefore, remaining after 50 h treatment titanium dihydride (its diffraction line is presented on the XRD pattern of the MA1 sample; Fig. 2a) can reveal a decreasing thermal stability and this fact can explain more lower temperature of intensive releasing hydrogen when heating the MA1 sample. However, there are several facts which allow assuming that boron should be a component of the dispersive titanium hydride (i.e., most likely, a hydride $\text{Ti}(\text{B,H})_x$ phase was formed as a result of mechanical treatment of the $\text{TiH}_{1.9} + 9$ wt.% B + 13 wt.% Ti mixture). Since boron and titanium are the component of the above

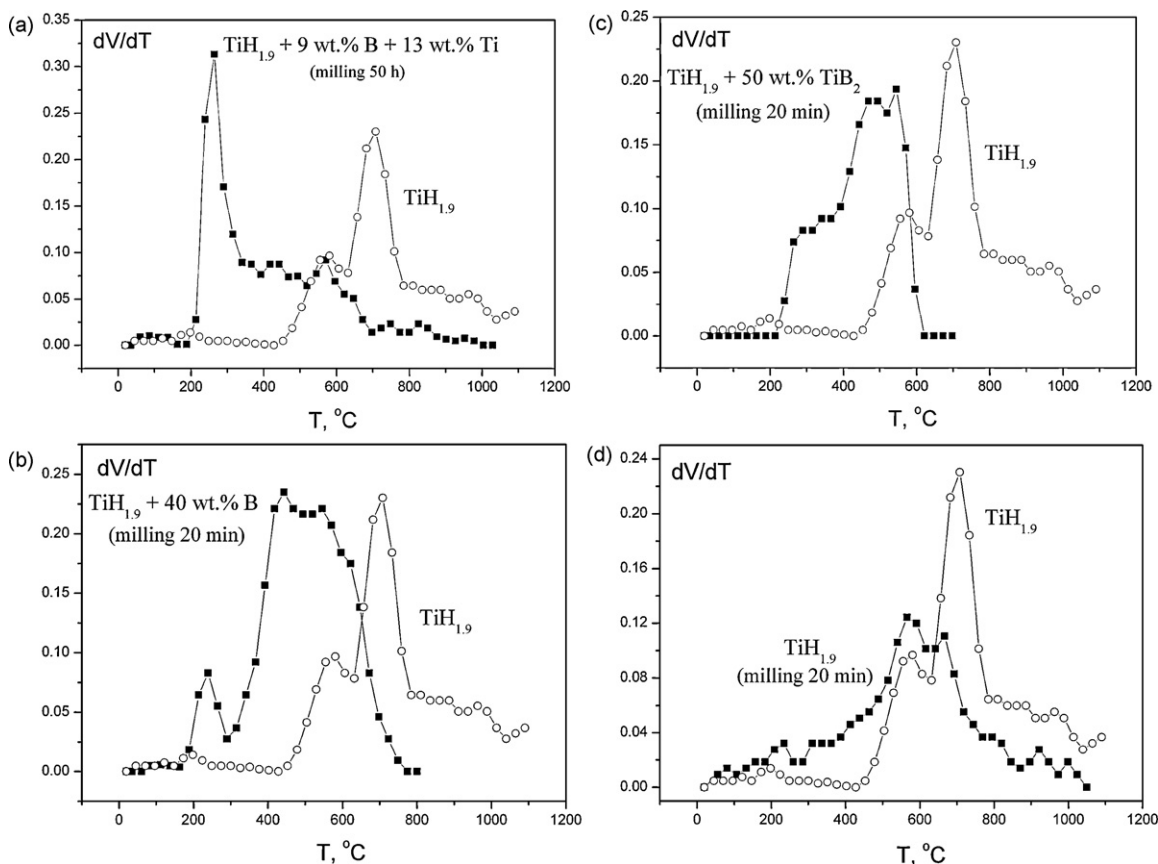


Fig. 5. The thermodesorption spectra ($P=0.1$ MPa) of hydrides after their mechanical dispersion and alloying by boron: (a) MA1, (b) MA3, (c) MA4, and (d) $\text{TiH}_{1.9}$ (after its milling for 20 min as described in the text). *Note:* On every panel, the thermodesorption spectrum of untreated $\text{TiH}_{1.9}$ hydride is presented, for comparison.

mixture (in addition to TiH_2), due to the intensive mechanical treatment titanium borides, namely TiB and TiB_2 , were synthesized. The presence of the above borides in the MA1 sample can be evidenced by the appearance of their peaks on the XRD pattern presented in Fig. 2a. Simultaneously with the formation of these borides and with local heating the initial $\text{TiH}_{1.9}$ hydride, its partial decomposition and a release of hydrogen take place. This hydrogen, as we suggest, can interact with boron and titanium leading to a formation of $\text{Ti}(\text{B},\text{H})_x$. One additional experimental fact can support a supposition about a possible formation of $\text{Ti}(\text{B},\text{H})_x$. Consistent interpretations of XRD data recorded for the MA1 sample after its 30 min heating at 350°C (Fig. 2b) can be made supposing that dissociation of the assuming $\text{Ti}(\text{B},\text{H})_x$ hydride occurs with the formation of TiB_2 and molecular hydrogen. The relative ratio of the (1 0 1) TiB_2 and (1 0 2) TiB lines on the XRD pattern of this sample is significantly higher compared with that of the unannealed (initial) MA1 sample (Fig. 2a). The above fact can indicate that after decomposition of the hydride phase when heating the MA1 sample up to 350°C , the amount of the TiB_2 phase increases.

Therefore, the whole set of experimental data concerning the MA1 material allow us to make a conclusion that, a decrease of thermal stability of the hydride phase of this multiphase mechanical alloy is caused mainly by dispersion of $\text{TiH}_{1.9}$ hydride, a component of the initial mixture used for obtaining MA1. In a planetary mill, during dispersion of titanium hydride particles, their elastic and plastic deformations occur and a formation of new surfaces and boundaries, extremely disordered areas, take place. As a result, a great quantity of different defects occurs mainly in near-surface and grain-boundary areas of dispersive particles. This causes an increase of free (Helmholtz) energy of titanium hydride particles [7] and, as a consequence, a decrease of decomposition temper-

ature of the hydride (i.e., a decrease of its thermal stability). The higher a degree of dispersion of particles of the hydride phase in the result of its mechanical treatment, the greater amount of extremely disordered areas where defects accumulate and, as a result, the higher energy accumulated in these areas [8,9]. The higher energy accumulated, the bigger amount of hydrogen atoms obtaining the energy of hydride lattice, will release the hydride during its heating and its decomposition at lower temperature. This means that dispersive hydride, which decomposes at lower temperature, is thermally less stable.

The present experimental data indicate that, boron plays an important role in decreasing thermal stability of the hydride phase of the MA1 sample. Small boron additives (9 wt.%) into the initial mixture as well as its dispersion favor decreasing thermal stability of titanium hydride due to insertion (alloying) boron, during milling the mixture, onto $\text{TiH}_{1.9}$ particle surface and into grain-boundary areas. The boron insertion causes weakening the Ti–H bonds in these areas [3,10]. In order to verify the role of boron and titanium borides (e.g., TiB_2) in decreasing thermal stability of $\text{TiH}_{1.9}$ hydride, the MA3 and MA4 materials have been derived. Their initial mixtures, namely ($\text{TiH}_{1.9} + 40$ wt.% B) and ($\text{TiH}_{1.9} + 50$ wt.% TiB_2) for MA3 and MA4, respectively, were 20 min treated in argon atmosphere (rotation speed 1630 rpm) at the same conditions as TiH_2 hydride, a component of the above initial mixtures. From comparison of the spectra of hydrogen thermodesorption of MA3 (Fig. 5b) and MA4 (Fig. 5c) with that of $\text{TiH}_{1.9}$ treated at the same conditions (Fig. 5d), one can see that the center of gravity of the TDS spectrum of treated $\text{TiH}_{1.9}$ is positioned at about 600°C , whilst the centers of gravity of the TDS spectra of the MA3 and MA4 specimens at about 500°C . Therefore, the above comparison of the TDS spectra reveals that mechanical treatment of $\text{TiH}_{1.9}$ with either

boron or TiB_2 additives leads to decreasing thermal stability of the hydride. We consider that the mechanism of decreasing thermal stability and decomposition temperature of $\text{TiH}_{1.9}$ in the case of its alloying by boron differs significantly from the mechanism of decreasing stability of $\text{TiH}_{1.9}$ during its dispersion. Boron inserting into the lattice of titanium hydride can influence the charge states of titanium and hydrogen and, consequently, the peculiarity of the chemical Ti–H bonds. As it has been established in Ref. [11], the Ti–H bonds in TiH_2 are mainly of a covalent (or covalent-metallic) type and an insignificant ionic component of the Ti–H bonds determines increasing thermal stability of titanium dihydride. Thermal stability of TiH_2 can be reduced by decreasing the positive effective charge on titanium atoms (estimations based on X-ray spectroscopy data have revealed the charge value of $+0.3e$, where e is the charge of electron [12]). We assume that boron can favor decreasing the positive effective charge on titanium atoms when inserting into the lattice of titanium dihydride (it is worth to mention that titanium-boron hydride, $\text{Ti}(\text{BH}_4)_3$, in contrast to TiH_2 , is unstable and it decomposes easily at room temperature).

4. Conclusions

A possibility of deriving new hydride phases in the Ti–B–H system using the method of mechanical alloying has been studied in the present work. The influence of mechanical treatment (dispersion) and additives of boron and its compounds with titanium upon thermal stability of titanium dihydride, $\text{TiH}_{1.9}$, has been

investigated. The mechanical 50 h treatment of the ($\text{TiH}_{1.9} + 9 \text{ wt.}\% \text{ B} + 13 \text{ wt.}\% \text{ Ti}$) mixture in argon atmosphere allows to decrease the temperature of dissociation of the hydride phase of the mechanical alloy by more than 300° compared with the temperature of dissociation of initial titanium hydride, $\text{TiH}_{1.9}$. Different mechanisms of influence of dispersion and alloying by boron upon thermal stability of titanium dihydride have been established.

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