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# Influence of TiB<sub>2</sub> addition upon thermal stability and decomposition temperature of the MgH<sub>2</sub> hydride of a Mg-based mechanical alloy

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### Abstract

Intensive mechanical milling was used to synthesize a  $MgH_2$  (50 wt.%) +  $TiB_2$  (50 wt.%) composite. Thermal stability of the composite versus H-desorption was studied employing the thermodesorption spectroscopy (TDS) method. The TDS data have revealed that  $TiB_2$  addition decreases the dissociation temperature of the  $MgH_2$  hydride by about 50 °C. An X-ray photoelectron spectroscopy analysis has shown that  $TiB_2$  addition does not alter the surface chemical state of particles of the  $MgH_2$  hydride, a component of the composite under consideration. The effect of decreasing decomposition temperature of  $MgH_2$  due to addition of  $TiB_2$  has been attributed to catalytic influence of a  $TiB_2$  particle surface on processes of associative hydrogen desorption taking place on the surface of  $MgH_2$  particles, as well as to a higher degree of dispersion of magnesium dihydride provided by the presence of  $TiB_2$ .

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## 1. Introduction

Analysis of recent publications shows that, a number of researches have improved significantly hydrogen absorptiondesorption kinetics of Mg-based alloys. At the same time, thermodynamic stability and decomposition temperature of Mgbased hydrides are still too high for their practical utilization as hydrogen accumulators. Therefore, scientists still continue their attempts towards decreasing thermal stability of the MgH<sub>2</sub> hydride due to its mechanical dispersion (i.e. decreasing particle sizes) [1–3] and due to addition of transition metals [4–6] and their compounds with the VI and VII Group elements of the Periodic Table [7-14]. The authors [1-3] have revealed that the mechanical alloying of MgH<sub>2</sub> (without addition of any transition metals and their compounds) leads to improvement of hydrogen sorption/desorption kinetics because of the introduction of the internal structure defects. However, pressure concentration isotherms presented in Refs. [1-3] indicate that high-energy

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The combination of the mechanically induced disordered MgH<sub>2</sub> structure with transition metal catalysts increases synergetic effects and excellent absorption/desorption properties [4]. The 3d-metal additions could reduce significantly the activation energy of hydrogen desorption [4]. Deledda et al. [7] have showed that fluorine additions with Fe (and Ni) catalyst decrease effectively the desorption temperature of MgH<sub>2</sub> to about 227 °C. In a series of works [8–14] the catalyst effect of cheap metal oxides on hydrogen desorption properties of MgH<sub>2</sub> has been reported. Aguey-Zinsou et al. [15] have revealed that co-milling MgH<sub>2</sub> and MgO does not modify structural or thermodynamic properties of the MgH<sub>2</sub> hydride, but leads to a decrease of its particle size and therefore improved hydrogen kinetics. However, the role of metal oxide catalyst on hydrogen desorption properties has not been established so far.

The influence of milling with  $TiB_2$  has already been observed in Ref. [16] for titanium dihydride and the maximum decreasing temperature of hydride decomposition was found to be 230 °C due to addition of 50 wt.% titanium diboride to  $TiH_{1.9}$ . In the present work, thermal stability of the mechanical alloy MgH<sub>2</sub>

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 $(50 \text{ wt.}\%) + \text{TiB}_2$  (50 wt.%) was studied employing the method of thermodesorption spectroscopy (TDS) and the surface state of the alloy was investigated using the X-ray photoelectron spectroscopy (XPS) method. The influence of TiB<sub>2</sub> upon decomposition temperature of the MgH<sub>2</sub> hydride of this alloy was studied as well. Microstructures of the initial powder mixture and the composite derived were studied by the scanning electron microscopy (SEM) method.

#### 2. Experimental details

In order to test the influence of TiB<sub>2</sub> upon thermal stability of MgH<sub>2</sub>, a powder mixture containing MgH<sub>2</sub> (50 wt.%) and TiB<sub>2</sub> (50 wt.%) was undergone by high-energy ball milling in a spherical planetary mill (20 min, argon atmosphere, rotation speed 1630 rpm). The ratio of steal balls weigh to initial burden's weight was equal to 20:1. The MgH<sub>2</sub> hydride, a component of the mixture treated, was derived by direct hydriding a magnesium powder (purity greater than 99.9%; an average particle size was found to be 4  $\mu$ m) in gaseous medium. The dihydride MgH<sub>2</sub> used in our investigation was synthesized from magnesium powder at pressure 3.0 MPa and temperature 400 °C in hydrogen atmosphere. In order to avoid air exposure of the MgH<sub>2</sub> hydride used in the present experiments, after its synthesis we reloaded MgH<sub>2</sub> into special vials in a glove-box filled with argon.

Microstructures of the initial powder mixture and the composite MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) derived were studied using a Super-Probe 733 scanning electron microscope. Chemical states of the above powder mixture and the composite were studied by recording XPS O 1s, Mg 2p and Mg 2s core-level spectra. The XPS measurements were carried out using an ES-2401 spectrometer equipped with an ion-pumped chamber having a base pressure less than  $5 \times 10^{-8}$  Pa. The XPS spectra were excited by Mg K $\alpha$  radiation (E = 1253.6 eV). The energy scale of the ES-2401 spectrometer was calibrated by setting the measured Au  $4f_{7/2}$  binding energy of pure gold to 84.0 eV with respect to the Fermi energy of a spectrometer energy analyzer. Energy drift due to charging effects was corrected by taking as a reference the XPS C 1s line of hydrocarbons (285.0 eV).

An X-ray diffraction (XRD) analysis of the MgH<sub>2</sub> (50 wt.%) and TiB<sub>2</sub> (50 wt.%) powder mixture treated for 20 min in argon atmosphere was carried out with a DRON-3M programming diffractometer employing X-ray Cu K $\alpha$  radiation and a graphite monochromator. The present XRD measurements were made with a step of 0.1° and accumulative time was 10 s in every point.

Thermal stability of the MgH2 phase, a component of the composite under consideration, was studied using the TDS method employing a digital device allowing to evaluate quantities of hydrogen desorbing from a specimen heated either in hydrogen or in argon atmosphere at normal pressure. For comparison, the method was employed to investigate thermal stability of MgH<sub>2</sub> (without the presence of TiB<sub>2</sub>) treated at the same conditions. The TDS spectra were measured using Siverts' method as follows. An autoclave with the sample (m = 0.2 g)was attached to a volumetric device equipped with a piston mechanism; displacements of the latter were measured using a sensor calibrated on changes of volume of gas in the system. The autoclave with the sample was placed into a quartz reactor equipped with a K-type thermocouple and heated by an electric furnace connected to a controller and providing uniform heating the samples with speed 5 °C/min in the present experiments. The thermocouple and the displacement sensor were connected to a data acquisition system. After loading the sample, the system was evacuated by a rotary pump. The system was filled with hydrogen or argon prior to starting desorption experiments during the heating. After the maximum temperature of TDS experiments was reached, the furnace was switched off, and the reactor was cooled to room temperature.

#### 3. Results and discussion

Fig. 1 shows that the XRD analysis of the mechanical alloy  $MgH_2$  (50 wt.%) + TiB<sub>2</sub> (50 wt.%) reveals the presence of three phases, namely  $MgH_2$ , TiB<sub>2</sub> and MgO. Microstructures and morphologies of particles of the initial mixture  $MgH_2$  (50 wt.%)



Fig. 1. X-ray diffraction pattern of the mechanical alloy  $MgH_2$  (50 wt.%) + TiB<sub>2</sub> (50 wt.%) prepared by mechanical milling for 20 min.

and TiB<sub>2</sub> (50 wt.%) and of the mechanical alloy obtained after mechanical alloying the mixture for 20 min in argon atmosphere are presented in Fig. 2. From the SEM patterns presented in Fig. 2(a) it is obvious that particles of magnesium dihydride derived by direct hydriding of magnesium in gaseous medium possess nonspherical shapes with friable surfaces and sharp angles while smoothed surface and round-off shapes are char-



Fig. 2. SEM images of the composite MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) material: (a) before ( $100 \times$ ) and (b) after mechanical dispertion ( $10,000 \times$ ).



Fig. 3. Curves (panels a and c) and spectra (panels b and d) of thermodesorption of hydrogen from the  $MgH_2$  hydride of the  $MgH_2$  (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite (panels a and b) and mechanically treated  $MgH_2$  hydride (panels c and d).

acteristic for TiB<sub>2</sub> particles. A morphology of MgH<sub>2</sub> particles was undergone to dramatic changes due to intensive dispersion in the high-speed planetary mill: there was a significant quantity of nano-size MgH<sub>2</sub> particles, with almost spherical shapes, covering TiB<sub>2</sub> particles (the latter particles did not change their morphology due to such a dispersion in the mill; see Fig. 2(b)). High-energy influence on the powder mixture containing MgH<sub>2</sub> (50 wt.%) and TiB<sub>2</sub> (50 wt.%) leads to increasing its specific surface from 0.7 up to 4.87 m<sup>2</sup>/g. Taking into account this value of the specific surface, an average size of powder particles for the composite synthesized was calculated to be 0.4 µm. The average particle size was calculated from the data of specific surface area (SSA) by following equation SSA =  $6/\rho d_p$ , where  $\rho$  is the density of the material and  $d_p$  is the average diameter of the particles, as suggested in Ref. [17].

Thermal stability of the MgH<sub>2</sub> phase in the composite MgH<sub>2</sub>  $(50 \text{ wt.}\%) + \text{TiB}_2 (50 \text{ wt.}\%)$  was studied using the TDS method. For comparison, the method was also employed to investigate thermal stability of MgH<sub>2</sub> treated at the same conditions and without alloying with TiB<sub>2</sub>. Results of these studies are presented in Fig. 3 as desorption curves (i.e. dependencies of the volume of hydrogen releasing from the specimen upon its temperature; panels a and c) and as desorption spectra (dV/dT dependencies; panels b and d) that were derived by heating the samples with the rate 5 °C/min in hydrogen atmosphere. The desorption spectra presented in Fig. 3 reveal that an intensive release of hydrogen begins in the composite MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) and in the as-milled MgH<sub>2</sub> at temperatures 350 and 410 °C, respectively. Additionally, from the desorption spectra shown in Fig. 3(b) and (d), it is apparent that a maximum release of hydrogen occurs at temperatures 395 °C for

the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite and at 445 °C for the as-milled MgH<sub>2</sub>. Several weak peaks on the desorption spectra presented in Fig. 3(b) and (d), in the temperature range from 50 to 300 °C are artefact of the measurements. Comparison of the desorption curves on the same temperature scale (Fig. 4) allows to conclude that addition of TiB<sub>2</sub> to MgH<sub>2</sub> during milling leads to decreasing the decomposition temperature of MgH<sub>2</sub> by 50 °C.

An analogous effect of decreasing the decomposition temperature of titanium dihydride was detected previously when milling the TiH<sub>1.9</sub> hydride for 20 min in argon atmosphere [16]. From comparison of the TDS curve of the mechanically treated TiH<sub>1.9</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) mixture with the curve of



Fig. 4. Curves of hydrogen desorption from the MgH<sub>2</sub>  $(50 \text{ wt.}\%) + \text{TiB}_2$  (50 wt.%) composite and the MgH<sub>2</sub> hydride matched on the same temperature scale.



Fig. 5. Curve (panel a) and spectrum (panel b) of thermodesorption of hydrogen from the  $MgH_2$  hydride of the  $MgH_2$  (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite during its heating in Ar atmosphere.

thermal desorption of the non-treated TiH<sub>1.9</sub> hydride presented in Ref. [16], one could see that mechanical alloying TiH<sub>1.9</sub> with TiB<sub>2</sub> decreased additionally the decomposition temperature of dispersed TiH<sub>1.9</sub> hydride by 120 °C. The maximum total effect of decreasing temperature of hydride decomposition corresponds to 230 °C if we conclude about decomposition temperature of TiH<sub>1.9</sub> taking into account peaks of speed of a hydrogen release on the desorption spectra [16].

Fig. 5 displays the curve (panel a) and spectrum (panel b) of thermal desorption of hydrogen from the MgH<sub>2</sub> hydride of the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite during its heating in argon atmosphere. On the above spectrum of hydrogen thermodesorption, as in the case of desorption in hydrogen atmosphere (Fig. 3), one can observe a strong peak at the same temperature (395 °C). An XRD pattern of the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite after hydrogen thermodesorption (the composite was heated in hydrogen atmosphere) reveals the presence of Mg, MgO and TiB<sub>2</sub> (Fig. 6).

The mechanism of influence of TiB<sub>2</sub> upon the temperature decomposition of the MgH<sub>2</sub> phase is not quite clear. The high-energy milling of the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite does not lead to formation of a new hydride phase. The decreasing thermal stability of MgH<sub>2</sub> cannot be associated with the influence of TiB<sub>2</sub> upon surface chemical states of particles of the MgH<sub>2</sub> hydride. The XPS Mg 2s, Mg 2p and O 1s core-level spectra of the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) com-



Fig. 6. X-ray diffraction pattern of the  $MgH_2$  (50 wt.%) + TiB<sub>2</sub> (50 wt.%) mechanical alloy after desorption in H<sub>2</sub>.

posite resemble those of mechanically treated  $MgH_2$  (Fig. 7). Therefore, in the above two samples under consideration, there are no differences in the chemical states of the MgH<sub>2</sub> particles. It is noteworthy to mention that, XPS results reveal almost complete absence of the Ti 2p and B 1s lines in the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite under study. The above observations can be explained by the fact that the MgH<sub>2</sub> hydride, which is more brittle and more dispersive as compared with TiB<sub>2</sub>, will possess higher dispersion during milling. Therefore, almost every TiB<sub>2</sub> particle is covered by very thin layer consisting of MgH<sub>2</sub> nanoparticles. Another explanation of the absence of Ti 2p and B 1s peaks in the XPS spectrum for TiB<sub>2</sub> milled with MgH<sub>2</sub> is the insertion of titanium diboride into magnesium dihydride, the effect similar to that observed earlier by Friedrichs et al. [18] for Nb<sub>2</sub>O<sub>5</sub> milled with MgH<sub>2</sub>. Taking into account the fact that TiB2 is dispersed in higher degree as compared with MgH<sub>2</sub>, therefore TiB<sub>2</sub> will promote higher degree of dispersion of MgH<sub>2</sub> in the composite decreasing its decomposition temperature [6,19]. In addition, decreasing decomposition temperature of MgH<sub>2</sub> can be attributed to catalytic properties of surfaces of TiB<sub>2</sub> particles with respect to processes of associative hydrogen desorption on surfaces of MgH<sub>2</sub> particles in the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite (as mentioned above, such MgH<sub>2</sub> particles come into contact with TiB<sub>2</sub> particles). In this case, both titanium and boron atoms, components of TiB<sub>2</sub>, can influence significantly on the mentioned process of associative hydrogen desorption, taking part in the near-surface layer, as the following. We assume that, high thermal stability of MgH<sub>2</sub> hydride is caused with the ionic component of the Mg-H bonds. It is well known (see e.g., Refs. [20,21]) that, the compounds formed by boron with magnesium or titanium posses mainly covalent component of the chemical bonding and boron can decrease the positive charge of magnesium atoms (and, consequently, the ionic component of the Mg-H bonds). This leads to decreasing thermal stability of the magnesium dihydride. The above mechanism of boron influence on thermal stability of the hydride phase follows the correlation between ionicity degree of the metal-hydrogen bonds in a hydride and its thermal stability observed earlier in Ref. [22].

For a number of hydride-forming alloys based on transition and rare-earth metals it has been established [23–25] that their XPS O 1s core-level spectra can be decomposed on two features (lines) positioned at about 530 and 532 eV. The feature



Fig. 7. XPS (a) O 1s, (b) Mg 2p and (c) Mg 2s core-level spectra of mechanically treated MgH<sub>2</sub> hydride (solid curve 1) and the MgH<sub>2</sub> (50 wt.%) + TiB<sub>2</sub> (50 wt.%) composite (dashed curve 2).

at 530 eV is attributed to oxygen atoms belonging to a surface oxide layer while that at 532 eV is ascribed to oxygen atoms belonging to oxygen-containing structures, catalytic toxic substances [23,25]. Such structures adsorbed on alloy surfaces can block catalytic active centers and can prevent the dissociation of molecular hydrogen. Therefore, when comparing the XPS O 1s core-level spectra on one and the same intensity of the O 1s signal coming from the surface oxide, Fig. 7(a) reveals that the addition of 50 wt.% TiB<sub>2</sub> to MgH<sub>2</sub> leads to significantly decreasing the quantity of oxygen-containing structures, catalytic poisons preventing dissociative hydrogen chemisorption, adsorbed on the particle surfaces. It is noteworthy to mention that Friedrichs et al. [26] have shown that the XPS O 1s core-level spectrum of MgH<sub>2</sub> prepared by high-energy ball milling can be deconvoluted into two peaks at ca. 531.4 and 533.2 eV for oxide and hydrox-ide/water adsorbed species, respectively. Taking into account energy drifts due to charging effects in the present work and in Ref. [26], the maximum at ca. 532 eV of the XPS O 1s spectrum in Fig. 7(a) can be attributed partly to amorphous hydroxide passivation layer on MgH<sub>2</sub> particles. From Fig. 7(a) it is obvious that the addition of 50 wt.% TiB<sub>2</sub> to MgH<sub>2</sub> decreases significantly the quantity of the amorphous hydroxide layer on the magnesium dihydride particles.

## 4. Conclusion

Ball milling techniques were used to produce a composite containing MgH<sub>2</sub> (50 wt.%) and TiB<sub>2</sub> (50 wt.%). The thermal stability and decomposition temperature of powders of the composite were evaluated by the TDS method. It has been established that, high-energy treatment of the mixture of MgH<sub>2</sub> synthesized by directly hydriding magnesium in gaseous medium and TiB<sub>2</sub> powders decreases the thermal stability of the MgH<sub>2</sub> hydride. The decomposition temperature of MgH<sub>2</sub> decreases by 50 °C in the case of the treatment of magnesium with TiB<sub>2</sub> addition as compared with the decomposition temperature of magnesium treated at the same condition but without TiB<sub>2</sub> addition. It has been made a supposition about the origin of influence of TiB<sub>2</sub> addition upon thermal stability of magnesium dihydride taking into account results of the XPS analysis of surface chemical state of dihydride particles.

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