
Hydrogen Sorption Properties, Thermal Stability and Kinetics of Hydrogen Desorption From the Hydride Phase of The MgH$_2$ of a Mechanical Alloys of Magnesium with Ti, Ni and Y

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The mechanical alloys-composite MAs (Mg +10 % wt.Ti + 5 % wt.Y and Mg +10 % wt.Ni + 5 % wt.Y) were synthesized. The phase content, microstructure, the thermal stability, kinetics of hydrogen desorption from the MgH$_2$ hydride phase of the obtained MAs were studied by using XRD, SEM, TDS methods. It has been established that the addition of Ti + Y and Ni + Y to magnesium leads to significant improvement in the kinetics of hydrogen desorption from the MgH$_2$ hydride phase, which is evidenced by a significant reduction (in 6 and 15 times) in the time of release of all hydrogen from MA1 and MA2, respectively. Due to, Ti, Ni,Y alloying, the decrease in the thermodynamic stability of MgH$_2$ is not found.

Keywords: mechanical alloy; hydride MgH$_2$; thermodesorption spectroscopy; hydrogen-sorption properties; thermal stability; kinetics of hydrogen desorption.

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Introduction

The development of molecular hydrogen storage systems and technologies requires the creation of new hydrogen absorption materials. Safe and compact storage of hydrogen in the solid state is the most acceptable from the point of view of the needs of the hydrogen economy in relation to mobile and stationary applications. The properties of a large number of metal-hydrogen systems are well known. However, the widespread use of metal hydrides and alloys for the storage of hydrogen is constrained by the fact that most of them do not fully or partially satisfy the requirements that practice has for hydrogen sorbent materials. It is known that to use the material in hydrogen storage systems on board an automobile, a hydrogen capacity of 5 – 6 % wt. is required, and the temperature of decomposition of the hydride phase is not higher than 150 – 200 °C. Some magnesium alloys, composites based on it turned out to be the most promising from the point of view of the optimal combination of such properties as high hydrogen capacity, high kinetic characteristics, reasonable cost.

Despite the great attention of scientists, which in recent years has been given to magnesium dihydride, methods for its preparation and research of properties, it still does not find wide practical application as a hydrogen storage material due to difficulties in eliminating two significant drawbacks: high temperature (≥ 300 °C at 1 bar H$_2$) and slow dissociation kinetics. The main difficulty lies in the fact that, together with a decrease in the decomposition temperature, it is necessary to increase the decomposition rate while maintaining a high hydrogen capacity and the cyclic stability of the hydride phase MgH$_2$ of the obtained mechanical alloys-composites. That is, it is necessary to provide a whole range of characteristics that today constitute the problem. Most often, they most often try to solve this difficult task of forming several characteristics in MgH$_2$ by mechanically dispersing commercial MgH$_2$ in the presence of various kinds of catalytic additives (transition 3d, 4d metals, their oxides, fluorides, intermetallic compounds, additives of transition metals Al, Cu, Zn, In, Sn, graphite, etc.) or by grinding a metal Mg powder with the indicated additives in a hydrogen atmosphere (that is, reactive grinding) or in an inert gas atmosphere followed by its direct
hydrogenation from the gas phase [1-31]. One of the ways to reduce the thermodynamic stability of MgH2 is to use mechanical alloys, which are solid solutions in magnesium of one or several metals, which can reduce the enthalpy of formation / decomposition of Mg (Me) H2 [32-42]. According to the theoretical forecast [4], the hydride of a solid solution of Al, Ti, Fe, Ni, Cu, Nb in Mg should have a lower enthalpy of formation and decompose at a lower temperature compared to pure MgH2. Experimental studies show that the thermodynamic stability of such a solid solution hydride depends on the method and conditions for its preparation [32-36]. In [35], the decomposition of the hydride phase Mg (In) H2 of a mechanical alloy obtained by high-energy grinding of MgH2 powder with 10% at. in at a hydrogen pressure of 150 bar, starts at 262.3 °C and a hydrogen pressure in the reactor of 1 bar. At the same time, as follows from the analysis of the P – C – T curves [35], the hydride of a solid solution of aluminum in magnesium obtained by grinding a mixture of 90% at. MgH2 and 10% at. Al in a hydrogen atmosphere at a pressure of 150 bar, the effect of destabilization of the hydride phase of Mg (Al) H2 was not found. The authors of [19, 20] report observing the effect of lowering the decomposition temperature of MgH2 from 288 to 210 °C due to the complex doping of magnesium Al, Ni, Ti (Mn) during the synthesis.

In [43-46], Y was used to reduce thermal stability and improve the hydrogenation kinetics of Mg-based binary alloys. The authors of [43, 44] established the formation of one-dimensional MgH2 nanostructures (whiskers) as a result of the disproportionation of Mg23Y5 intermetallic compounds during its hydrogenation. This nanostructured MgH2, when heated in a vacuum, decomposes at a lower temperature and at a faster rate than commercial MgH2. The effect of cyclic hydrogenation / dehydrogenation on the hydrogen capacity of the material has also been investigated. It was established [43] that the presence of yttrium improves the diffusion of hydrogen. As studies of binary Mg23YX alloys (x = 1 - 5) have shown [45], an increase in the yttrium content, which acts as a modifier, leads to a significant difference in the microstructures of the studied alloys and, as a result, to an increase in the kinetics of hydrogen absorption due to the formation of YH2 nanoparticles that are dispersed throughout the MgH2 matrix. However, as noted by the authors of [45], an increase in the yttrium content inevitably leads to a decrease in the ability to absorb hydrogen back. A study of the hydrogenation of Mg-13Y alloy by the authors of [46] showed that the experimentally determined enthalpy of hydride formation of this alloy (42 kJ/mol H2) is significantly lower than the enthalpy of hydride formation of pure Mg (74.7 kJ/mol H2). This difference in thermodynamic data indicates that the hydrogenation process of the Mg-13Y alloy is very different from the hydrogenation of pure Mg. The dehydrogenation enthalpy of Mg-13Y powder is quite close to that for MgH2, which indirectly indicates the decomposition of only the hydride phase of MgH2 during the dehydrogenation process (and the decomposition of the YH2 phase does not occur).

The catalytic effect of titanium and yttrium on the hydrogen absorption properties of Mg + 14.5% at. Ti + 0.5% at. Y was studied in [47]. XRD analysis showed that the alloy consists of the main phase of Mg23Y5, a small amount of solid solution of Y in Mg and Ti clusters randomly dispersed in the sample. It was found that Mg23Y5 irreversibly reacts with hydrogen in two stages. In the first stage (at a hydrogen pressure of 50 kPa), YH2 and Mg are formed. The second stage (at higher hydrogen pressures) ends with the formation of YH3 and MgH2. So, hydrogen desorption consists of two desorption reactions: the transition of MgH2 to Mg and the transition of YH3 to YH2. It was found that the presence of both Y and Ti in this Mg-based alloy did not lead to any significant thermodynamic or kinetic improvement with respect to the sorption properties of pure magnesium hydride.

The influence of Y and Ni on the hydrogen absorption kinetics during the hydrogenation of Mg-20% wt. Ni-Y alloy, Mg60Ni3Y5 and Mg60Ni10Y10 alloys, and Mg11Y2Ni2 alloy were studied in [48–50]. It has been established that both the catalytic effect of the Mg2Ni and YH2 phases and the crystal lattice defects formed during mechanical activation are responsible for improving the hydrogen sorption kinetics in all of the above alloys during their hydrogenation. It was shown that ultrafine particles of yttrium hydride, which are formed during the hydrogenation of these alloys, contribute to the stabilization of the nanostructure during cycling and improve the kinetics of hydrogen sorption of magnesium.

Earlier, we investigated the role of each of the alloying elements Al, Ti, Mn, Fe, Ni separately in lowering the decomposition temperature of stoichiometric MgH2 hydride obtained by reactive mechanical alloying (RMA) [25, 27, 29, 31], as well as the role of the pair doping with Al + Ti, Al + Fe, Al + Ni [51-54]. This study, namely: the study of the possibility of complex doping of magnesium hydride MgH2 with both Ti and Y in order to lower the temperature and improve the kinetics of its dissociation, is a logical continuation of our previous studies, as well as [40, 41]. In this paper, the task was to obtain a mechanical alloys (MAs) of the composition Mg + 10 % wt. Ti + 5 % wt. Y and Mg + 10 % wt. Ni + 5 % wt. Y by RMA. To study the processes of hydrogen desorption from the MgH2 hydride phase at a hydrogen pressure of 0.1 MPa, to determine hydrogen sorption properties, thermal stability of the obtained MAs using thermal desorption spectroscopy (TDS). The task was also set to establish whether, due to the selected composition of alloying elements and the method of obtaining MA, the enthalpy of formation of the hydride phase of MgH2 decreases and, as a consequence, the equilibrium temperature of its decomposition. On the MAs samples, after their cyclic hydrogenation / dehydrogenation, trace how the microstructure and phase composition of the MAs change; how the effect of the addition of Ti, Ni and Y on the thermal stability and decomposition temperature of the MgH2 hydride phase as a result of cyclic hydrogenation changes. It was expected that the results of these studies will help determine the composition of alloying elements and the conditions for obtaining a mechanical alloy, which can provide the lowest possible thermal stability and decomposition temperature of the
MgH₂ hydride phase with a simultaneous improvement in the kinetics of hydrogen sorption / desorption from it.

I. Materials and methods

The mechanical alloys-composites has been synthesized by reactive grinding in hydrogen of powders: Mg + 10 % wt. Ti + 5 % wt. Y (MA1) and Mg + 10 % wt. Ni + 5 % wt. Y (MA2). For comparison, we synthesized an additional composite alloy Mg without any additives (MA3) and alloys-composites Mg + 10 % wt. Ti (MA4), Mg + 10 % wt. Ni (MA5). The commercial powders of Mg, Ti, Ni, Y with a purity of 99.98 % and particles sizes of 100; 6,7; 3; 200 μm, respectively, have been used as raw materials. The mechanical fusion by reactive grinding of the mixture of powders of MA1-MA5 composition, was realized in a RETCH100 ball mill with steel balls in a hydrogen atmosphere (under a hydrogen pressure of 1 MPa, for a velocity of rotation of 450 rot/min and a duration of grinding of 20 h). The ratio of the metallic balls mass to the treated mixture of powders was 20:1. Milling was interrupted every 60 min to allow the milling to cool down to room temperature allowed by the monitoring of the current state of hydrogen absorption. We use one and the same conditions of synthesis for all MAs under consideration that allows making a proper comparison of different alloying elements effect on temperature and the kinetics of MgH₂ hydride phase decomposition of synthesized MAs. Conditions of synthesis of all MAs derived by direct hydrogenation from the gas phase were also the same. After the MA synthesis and obtaining the first hydrogen desorption curve, the sample was not removed from the reactor. At temperature of 400 °C the reactor was filled with hydrogen until hydrogen pressure was 3 MPa and during the sample cooling together with the furnace its first (and subsequent) hydrogenation from the gas phase took place.

For the X-ray phase diffraction analysis of specimens, we used a DRON-3M diffractometer. The X-Ray patterns were obtained employing CuKa α-radiation with a graphite monochromator. The profiles of diffraction lines were plotted with scanning steps of 0.1⁰ and with exposure at each point of the spectrum over 15 sec. The diffraction patterns were analyzed using fullprof software Powder Cell 2.4 (https://powdercell-for-windows. software. informer. com /2.4/). The size changes of the powder particles upon mechanical milling were studied by a Super-Probe 733 scanning electron microscopy.

By the method of thermal desorption spectroscopy with a computerized automatic installation, we studied the influence of alloying elements on the hydrogen sorption properties, thermal resistance, the kinetics of hydrogen desorption from the MgH₂ hydride phase. This installation allows to plot the isobars of desorption-resorption of hydrogen under various pressures (from 0.1 to 1.0 MPa) in the reactor and to perform the hydrogenation/dehydrogenation of specimens under pressures up to 10 MPa and temperatures being in the range from room temperature to 1200 °C [29].

II. Results and Discussion

2.1 X-ray phase and microstructural analyzes of the samples.

Fig. 1 shows XRD pattern of the MA1, MA2 samples derived by reactive mechanical alloying (RMA) and Fig. 2 - after the gas phase hydrogenation (GPH) mechanical alloys. The information on the phase composition of the MAs specimens obtained by RMA and after GPH is presented in Table 1. Table 1 also shows the average particle size of mechanical alloys powders (after RMA). The lattice parameters and volume of unit cells for β-MgH₂ hydride phase of MA1-MA3 (Table 2) have been determined by the full-profile Rietveld method using Powder Cell2.4 program.

As Table 1 shows, both MAs (MA1,MA2) are composites, as are result of reactive mechanical alloying. In addition to MgH₂ with tetragonal structure, they contain a small amount of other hydride phases: γ-MgH₂,TiH₂, YH₃, YH₂ when MA1 and γ-MgH₂, YH₂, Mg₂NiH₆ when MA2. After the first hydrogenation / dehydrogenation cycles from the gas phase, all MAs showed the absence of changes in their phase composition. Based on our experimental data, the average particle size (which in turn consists of nanograin) in MA1, MA2, MA3 is 0.25, 0.2, 0.7 μm respectively. After repeated hydrogenation / dehydrogenation of powders from the gas phase, as shown by the study of their microstructure, the average particle size decreases and the average grain size increases due to cyclic heating / cooling.

2.2 Thermal behavior of the mechanical alloys-composites.

To evaluate the influence of complex alloying by Ti + Y and Ni + Y on decomposition temperature and thermal stability of MgH₂ phase hydrogen desorption from MA1-MA3 have been studied. All isobars were obtained at constant pressure of hydrogen in the reactor 0.1 MPa and sample heating rate of 3 °C/min. Hydrogen desorption isobars obtained at the first heating after RMA synthesis of MA1-MA3 samples are shown in Fig. 3, and after the first hydrogenation from the gas phase of MA1, MA2 are in Fig. 4. The isobars shown in Figs. 3 and 4 were used to determine both the hydrogen capacities and the hydrogen desorption beginning temperature (T_beg) from hydride phase MgH₂ of MA1-MA3 in the course of its first heating after mechanochemical synthesis and of its gas phase hydrogenation (GPH). The obtained data are shown in Table 3. From Figs. 3 and 4, Table 3, it is obvious that the temperature of the beginning of hydrogen release from the MgH₂ hydride phase of MA1, MA2, MA3 composites after RMA was 295, 295, 288 °C, respectively. After their first hydrogenation from the gas phase, the temperature was 288, 288, 320 °C, respectively. If one compares T_beg of the release of hydrogen from the unalloyed MgH₂ phase of MA3 (288 °C) with the same temperature for MA1, MA2, one can states that the addition of Ti+Y and Ni+Y to magnesium practically does not reduce the thermodynamic stability of hydride phase MgH₂ of MA1,MA2 and, consequently, does not reduce the
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temperature of the beginning of hydrogen desorption. In our opinion, the explanation of this can be the fact that in the conditions of our method of obtaining of MAs does not form a solid solution in magnesium Ti, Ni, Y, whose hydride is Mg(Ti,Y)H\(_2\) or Mg(Ni,Y)H\(_2\), according to [4], should have a lower formation enthalpy and a lower thermodynamic stability and decomposition temperature of MgH\(_2\). The evidence of the fact that Mg(Ti, Y)H\(_2\) or Mg(Ni, Y)H\(_2\) hydride was not derived (or its quantity is rather minor) can be, in accordance with the XRD data (Table 1), the presence in the composite MA1 of TiH\(_2\), YH\(_3\), YH\(_2\) phases and in the composite MA2 of Mg\(_2\)NiH\(_4\), YH\(_3\) phases (the latter phases are formed due to substantial amounts of the alloying elements Ti, Ni and Y). As can be seen from Table 2, the absence of the expected decrease in volume of the unit cell of MgH\(_2\) hydride phase of the composites MA1, MA2 compared with that of the same hydride phase of the composite MA3 can also be an indication of the absence of formation in our synthesis conditions of Mg(Ti, Y)H\(_2\) or Mg(Ni,Y)H\(_2\) hydride. From data listed in Table 3, it is worth noting a decrease of hydrogen capacity and \(T_{\text{beg}}\) of hydrogen desorption from 295 \(^\circ\)C to 288 \(^\circ\)C in the case of the composites MA1 and MA2 after their hydrogenation from the gas phase. In our opinion, the main role in this decrease in \(T_{\text{beg}}\) was played by Y. As is known [48-50],
It is able to inhibit the growth of grain size (crystallites) of mechanical alloys during their cyclic hydrogenation/dehydrogenation at elevated temperatures. It should be noted that as a result of 4-10 cycles of hydrogenation /dehydrogenation of the composites MA1, MA2 from the gas phase, we did not observe significant changes in the nature of the desorption curves and their position in the temperature scale. This may indicate reversibility of the process of cyclic hydrogenation / dehydrogenation of the obtained MAs and the absence of significant degradation of their hydrogen adsorption.

Table 2

<table>
<thead>
<tr>
<th>Mechanical alloy</th>
<th>Unit cell parameters: a, Å; c, Å; V, Å³</th>
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<tbody>
<tr>
<td></td>
<td>after RMA</td>
</tr>
<tr>
<td></td>
<td>after GPH</td>
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<tr>
<td>MA1</td>
<td></td>
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<td>MA2</td>
<td></td>
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<td>MA3</td>
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Table 3

<table>
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<th>Mechanical alloy</th>
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<th>C_{H₂}, %wt.</th>
<th>T_{beg.}, °C</th>
<th>C_{H₂}, %wt.</th>
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<tbody>
<tr>
<td>MA1</td>
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<td>6.0</td>
<td>288</td>
<td>5.7</td>
</tr>
<tr>
<td>MA2</td>
<td>295</td>
<td>5.9</td>
<td>288</td>
<td>5.5</td>
</tr>
<tr>
<td>MA3</td>
<td>288</td>
<td>5.1</td>
<td>320</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Fig. 3. Isobars of hydrogen desorption from the MgH₂ hydride phase of the mechanical alloys: (a) MA1, (b) MA2, (c) MA3, derived after synthesis RMA.

Fig. 4. Isobars of hydrogen desorption from the MgH₂ hydride phase of the mechanical alloys: (a) MA1, (b) MA2, derived after its first hydrogenation from the gaseous phase.
2.3 Mechanical alloys hydrogen desorption kinetics process.

Hydrogen desorption kinetics from the MgH₂ hydride phase of all MAs synthesized by us after their hydrogenation from the gas phase under the same conditions has been investigated at the temperatures 310, 330 °C and at a constant hydrogen pressure of 0.1 MPa in the reactor. Hydrogen desorption kinetic curves for MA1, MA2, MA3 are presented in Fig. 5 and for MA4, MA5 - in Fig. 6. The data of hydrogen time release of half of hydrogen quantity (τ₁/₂) and total hydrogen quantity release (τₖ) for all MAs are shown in Table 4. The analysis of the experimental data given in Table 4 allows us to conclude that the addition of magnesium at the same time Ti + Y and Ni + Y leads in both cases to a significant improvement in the kinetics of hydrogen desorption from the MgH₂ hydride phase obtained by MA1 and MA2. This is evidenced by the experimentally recorded reduction by 6 and 15 times of the time it takes to release half and all the desorbed hydrogen in the case of MA1 and MA2, respectively, compared to MA3. In our opinion, Ti and Ni play the main role in improving the kinetics of hydrogen desorption in the composites MA1 and MA2. They possess high catalytic properties and favor recombination of hydrogen on the particle surface of the hydride phase, and, consequently, reduce its thermal stability. It can be seen from table 4, that a greater improvement in the kinetics of hydrogen desorption from the hydride phase of MgH₂ is observed in the case of its doping with Ni, and less in the case of doping of Ti. A reasonable explanation can be given to this observation if we use the results of a study [56] on the effect of these transition metals as alloying elements on the physicochemical state of the surface of metal

<table>
<thead>
<tr>
<th>Mechanical alloy</th>
<th>τ₁/₂</th>
<th>τₖ</th>
<th>τ₁/₂</th>
<th>τₖ</th>
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</thead>
<tbody>
<tr>
<td>MA1 (Mg + 10wt.% Ti +5wt.Y)</td>
<td>6,5</td>
<td>18</td>
<td>5</td>
<td>14</td>
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<tr>
<td>MA2 (Mg + 10wt.% Ni +5wt.Y)</td>
<td>2,73</td>
<td>9</td>
<td>2,1</td>
<td>5</td>
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<tr>
<td>MA3 (Mg without Ti, N, Y)</td>
<td>88</td>
<td>130</td>
<td>30</td>
<td>80</td>
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<tr>
<td>MA4 (Mg + 10 wt.% Ti)</td>
<td>8,5</td>
<td>25</td>
<td>5,5</td>
<td>14</td>
</tr>
<tr>
<td>MA5 (Mg + 10 wt.% Ni)</td>
<td>2,2</td>
<td>7</td>
<td>1,6</td>
<td>5</td>
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</table>
Hydrogen Sorption Properties, Thermal Stability and Kinetics of Hydrogen Desorption from MgH₂

The addition of Ti + Y and Ni + Y to magnesium leads to a significant improvement in the kinetics of hydrogen desorption from the MgH₂ hydride phase of the obtained MAs, as evidenced by the experimentally recorded significant reduction in time of the half and total quantity of desorbed hydrogen. The reduction of the thermodynamic stability of MgH₂ hydride due to its doping by Ti, Ni, Y was not detected. Results of the present study can be used in the development of new hydrogen sorbent materials for hydrogen energy.

Conclusion

The new alloys-composites with reduced thermal stability and improved kinetics of the decomposition of their hydride phase MgH₂ were synthesized by the reactive grinding in the hydrogen atmosphere of a mixture of Mg powder with different content of additives Ti, Ni and Y. The influence of alloying elements Ti, Ni, Y on the hydrogen sorption properties, thermal stability and kinetics of the hydrogen desorption process from the hydride phase MgH₂ of the obtained MAs has been studied. It was established that the addition of Ti + Y and Ni + Y to magnesium leads to a significant improvement in the kinetics of hydrogen desorption from the MgH₂ hydride phase of the obtained MAs, as evidenced by the experimentally recorded significant reduction in time of the half and total quantity of desorbed hydrogen. The reduction of the thermodynamic stability of MgH₂ hydride due to its doping by Ti, Ni, Y was not detected. Results of the present study can be used in the development of new hydrogen sorbent materials for hydrogen energy.

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Воденьсорбційні властивості, термостабільність та кінетика десорбції водню з гідридної фази MgH₂ механічних сплавів на основі Mg з Ti, Ni та Y

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Були синтезовані механічні сплави - композити (МС) Mg + 10 % ваг. Ti + 5 % ваг. Y та Mg + 10 % ваг. Ni + 5 % ваг. Y. Фазовий склад, мікроструктура, термічна стабільність, кінетика десорбції водню з гідридної фази MgH₂ з отриманих МС були вивчені з використанням XRD, SEM, термодесорбційної спектроскопії (ТДС). Встановлено, що додавання Ti + Y та Ni + Y до магнію призводить до значного поліпшення кінетики десорбції водню з гідридної фази MgH₂, про що свідчить скорочення в 6 і 15 разів часу виділення всього водню з МС1 і МС2, відповідно при їхньому тиску в реакторі 0.1МПа. Внаслідок цього легування зниження термодинамичної стабільністі MgH₂ не встановлено.

Ключові слова: механічний сплав, гідрид MgH₂, воденьсорбційні властивості, термічна стійкість, кінетика десорбції водню.