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EFFECT OF VARIOUS ADDITIVES ON THE HYDROLYSIS PERFORMANCE OF NANOSTRUCTURED MgH_2 SYNTHESIZED BY HIGH-ENERGY BALL MILLING IN HYDROGEN

Magnesium hydride is a promising material for hydrogen generation via hydrolysis owing to high hydrogen storage capacity, mild reaction conditions, and low cost of magnesium metal. Unfortunately, the hydrolysis reaction of MgH_2 is rapidly hindered due to the formation of a passive $Mg(OH)_2$ layer. Various additives can be used to improve the efficiency of the reaction. The present study examines the influence of 5 wt.% EDTA and TiC–2TiB₂ additives on the hydrolysis of the nanostructured MgH_2 and compares it with the hydrolysis performance of pure MgH_2 and MgH_2 + 5 wt.% $AlCl_3$ for the first time. MgH_2 was synthesized by high-energy ball milling of Mg powder in hydrogen gas, while MgH_2 -based nanocomposites were prepared either by mixing the obtained MgH_2 with 5 wt.% of additives or by milling Mg with 5 wt.% of additive in hydrogen. The synthesized MgH_2 is nanosized, containing a mixture of β - MgH_2 and high-pressure γ -modification of MgH_2 . The hydrogen generation performance in terms of MgH_2 conversion rate and hydrogen yield was determined volumetrically. It was found that the MgH_2 + 5 wt.% EDTA composite displays the lowest reactivity among the tested materials, probably due to the interaction of MgH_2 with EDTA during the ball milling. Pure MgH_2 and MgH_2 + 5 wt.% (TiC–2TiB₂) composite demonstrate almost twice as better hydrolysis performance, which is, however, still quite far from application requirements. The maximum hydrogen yield of 557 mL/g MgH_2 and conversion rate of 30.3% was observed for MgH_2 + 5 wt.% $AlCl_3$ composition after 10 min of hydrolysis, which can be attributed to the destabilization of the $Mg(OH)_2$ layer by chlorine ions.

Keywords: magnesium hydride, hydrolysis, hydrogen generation, composites, high-energy ball milling.

Introduction

Hydrogen as a clean energy carrier is an ideal choice for future energy systems, contributing to the reduction of greenhouse gas emissions and improvement of the security of energy supply. In contrast to fossil fuels, hydrogen

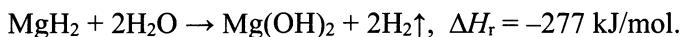
is a renewable and environmentally friendly alternative benefiting from its high energy density (120 MJ/kg) [1–5]. Although the majority of hydrogen today is produced through fossil-fuel reforming, it can also be produced by biological processes or electrolysis using electricity obtained from renewable energy sources.

The generated hydrogen can be used in fuel cells for electricity production to power electric vehicles and households. However, one of the biggest obstacles to use hydrogen in mobile applications is the lack of efficient storage methods. There are various hydrogen storage techniques, but storage as liquid and compressed gas are the most frequently used [2, 3]. Storage of hydrogen in metal hydrides is a promising solution to this problem as they can reversibly absorb/release hydrogen at controlled temperature and pressure conditions [1–5]. Among the metal hydrides, MgH_2 -based materials have attracted considerable attention due to the high natural abundance of magnesium, low cost, good reversibility of hydrogen desorption and absorption, light weight, and high hydrogen storage capacity (7.6 wt.%) [1–5]. However, major drawbacks of MgH_2 , including slow desorption kinetics and high thermal stability, impede its commercial applications. Based on the experimental and theoretical studies, appropriate doping, particle size control, and development of novel reactions are considered as the most promising options to overcome these limitations [1, 3–5]. Thus, a huge amount of studies has been performed on the nanosizing, nanoconfinement, alloying, and modifying with intermetallic compounds, metal oxides, halides, carbon materials, hydrides, borohydrides, their mixtures, etc. [1, 4–8]. The addition of catalysts resulted in a remarkable improvement of the hydrogen absorption/desorption kinetics of MgH_2 since catalysts decrease the activation energy of the hydrogenation process. Moreover, it has been found that transition metal halides exhibit a better catalytic effect than the corresponding metals or metal oxides due to a higher oxidation state in halides [9].

In recent years, significant attention has been paid to the hydrolysis process as a convenient hydrogen generation technology. Compared to the reversible hydrogen storage materials, hydrogen production by hydrolysis has the advantages of high hydrogen yield, fast hydrogen generation rate, and low operation temperature. Various metals (e.g., Al-based alloys, Mg [10, 11]) and metal hydrides (e.g., LiH, LiBH_4 , NaBH_4 , MgH_2 [12, 13]) have been tested as active materials subjected to the hydrolysis. However, Al- and Mg-based alloys frequently have poor hydrogen generation kinetics, while in contrast, LiBH_4 shows a too violent and highly exothermic reaction with water [10]. The hydrolysis of NaBH_4 is less exothermic but requires the presence of catalysis and needs an application of a high energy consumption process to regenerate the NaBH_4 from NaBO_2 [14].

In the search for advanced active materials for hydrolysis, considerable attention has been focused on MgH_2 owing to the high hydrogen yield (15.2 wt.% H_2 , when hydrolyzed), relatively low cost, and a formation of an environmental-friendly reaction product Mg(OH)_2 [13, 15].

Hydrogen can be released via the following reaction with water:



However, the hydrolysis of MgH_2 immediately terminates due to the formation of a passive Mg(OH)_2 layer on the MgH_2 surface. Magnesium hydroxide has poor solubility in water (1.22 mg/100 mL at 20 °C) [16], and the maximum reaction yield after 1 h does not exceed 30% [13]. Various approaches to sup-

press the formation of $\text{Mg}(\text{OH})_2$, e.g. nanostructuring, the addition of salts, acids, alkali metals, inert additives at ambient conditions or when under heating, ultrasonic irradiation, stirring, were tested to achieve higher hydrogen yield [11, 13, 15, 18, 19]. Among these, ball milling of Mg or MgH_2 with additives under hydrogen atmosphere is an efficient way to improve the hydrolysis performance [11, 15, 17]. However, there is a lack of comparative data on the efficiency of various additives on hydrolysis performance of MgH_2 [13, 15, 17–19].

Intending to address this fact, we investigated the effect of additives of different nature, namely AlCl_3 , ethylenediaminetetraacetic acid (EDTA), and $\text{TiC}-2\text{TiB}_2$, on hydrolysis of nanocomposites prepared by high-energy ball milling with MgH_2 in Ar atmosphere or reactive ball milling under pressurized hydrogen gas. The effect of EDTA and $\text{TiC}-2\text{TiB}_2$ additives on hydrogen generation after hydrolysis of MgH_2 -based nanocomposites was studied for the first time.

Materials and Experimental Procedure

Magnesium hydride (MgH_2) was synthesized by a reactive ball milling of Mg powder under hydrogen pressure. The milling was performed in a Fritsch Pulverisette 6 mill using a duplex steel vial ($V = 500$ mL) filled with hydrogen gas ($P = 24$ bar H_2) and 202 steel balls of 10 mm in diameter each ($m_{\text{balls}} = 817$ g), at a rotation speed of 400 rpm, with a ball-to-powder mass ratio of 40 : 1. Magnesium powder (Fluka, 99.8%, grit, 50–150 mesh), weighing 20.425 g, was used for the synthesis. The duration of each milling interval was 30 min while following the 390th min of milling, it was increased to 60 min. After every milling step, the vial was connected to a Sievert's-type apparatus, and the pressure drop was measured to monitor the hydrogen uptake. Afterwards, the vial was refilled with hydrogen gas (24 bar), and the milling continued. The total milling time comprised 570 min. The handling of samples was done in a glove box filled with purified argon gas.

MgH_2 -based nanocomposites were prepared either by mixing the obtained MgH_2 with 5 wt.% of additives, or synthesized simultaneously with hydrogenation of magnesium in the case of $\text{TiC}-2\text{TiB}_2$ additive. For the EDTA and AlCl_3 additives, the MgH_2 -based mixtures were milled in Ar at 500 rpm for 15 min using the Fritsch P6 mill, 80 mL steel vial, 32 steel balls of 10 mm, at the balls-to-powder ratio 80 : 1. Reactive ball milling of Mg and 5 wt.% ($\text{TiC}-2\text{TiB}_2$) for 300 min under a hydrogen pressure of 30 bar was conducted in the P6 mill with identical milling parameters except for the balls-to-powder ratio of 40 : 1.

The crystal structure of synthesized materials was characterized by X-ray diffraction (XRD) using a Panalytical X'Pert PRO diffractometer.

The morphology of the powders was examined with a scanning electron microscope (SEM) Zeiss Ultra Plus equipped with an energy dispersive X-ray (EDX) Bruker Quantax 400 system applied for elemental analysis.

The hydrogen generation during the hydrolysis reaction was monitored volumetrically by using a custom-made setup that consists of a reaction volume and gas collecting/measuring components. The reaction part is a 500 mL four-neck glass flask with openings for water addition, insertion of a thermometer, Ar purge gas, and H_2 removal, which is connected by a silicone tube to the collecting/measuring part—syringe—to measure the hydrogen yield.

The samples in a form of powders were placed into the flask with subsequent system sealing. After that, the apparatus was purged with argon gas for

5 min, and the flask was filled with distilled water from the pressure-equalizing funnel to start the hydrolysis reaction. The amount of hydrogen was quantified by syringe piston displacement after being recorded by a camera. All experiments were carried out at room temperature and atmospheric pressure.

The efficiency of the hydrogen generation or conversion yield (%) was defined as the ratio between the actual volume of the produced hydrogen and the theoretical volume that should be released, assuming completeness of the reaction of the hydride with water.

Results and Discussion

According to the XRD data shown in Fig. 1, reactive ball milling of Mg powder under hydrogen pressure leads to complete hydrogenation of magnesium and formation of 2 phases of MgH_2 , i.e. $\beta\text{-MgH}_2$ and a high-pressure modification $\gamma\text{-MgH}_2$. However, for the magnesium with 5 wt.% of TiC-2TiB_2 additive, ball-milled in hydrogen, the peaks of unreacted Mg were present in the XRD pattern (Fig. 2b) besides two forms of MgH_2 and strong diffraction lines of TiC-2TiB_2 (Fig. 2a). Obviously, the traces of magnesium are left as the duration of the milling was not sufficient to finish the process of hydride formation. SEM study demonstrated that nanostructuring of the final product occurs for TiC-2TiB_2 doped magnesium hydride obtained by reactive ball milling. It is evidenced on the SEM micrograph (Fig. 3), indicating a presence of nanocrystallites with a size below 20 nm.

Elemental mapping by EDX (see Fig. 4) showed a uniform distribution of Mg and Ti, which suggests that TiC-2TiB_2 particles are evenly distributed in the bulk of MgH_2 . It should be noted that the presence of Zr is observed possibly owing to the wear of the ceramic mold utilized for the preparation of the sample for the measurement.

Thermogravimetric analysis revealed a slight decrease (ca. 30 °C) in the onset temperature of hydrogen desorption as compared to the pure MgH_2 synthesized by the reactive ball milling, whereas total weight loss amounted to ca. 6.6 wt.% at 375 °C.

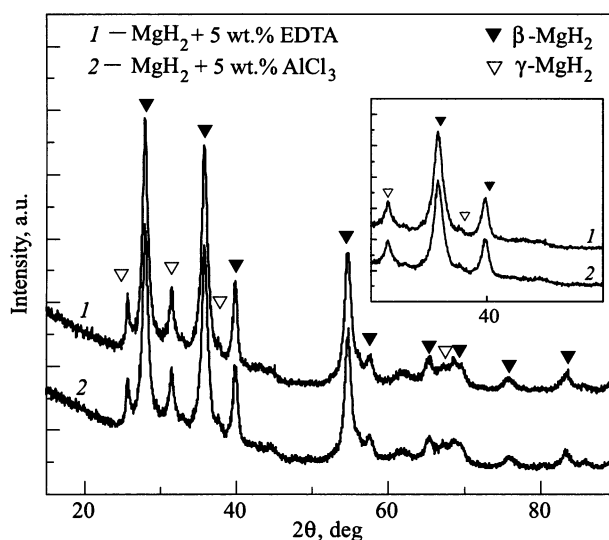


Fig. 1. XRD patterns of the MgH_2 -based composites; the insert – detailed picture in the narrow 2θ range of 30 to 50°

Fig. 2. XRD pattern of the $\text{MgH}_2 + 5 \text{ wt.}\% (\text{TiC}-2\text{TiB}_2)$ composite (a) and its XRD profile in the range 2θ of 30 to 50° (b)

Figure 5 shows the kinetics of hydrogen generation and conversion rate of MgH_2 , $\text{MgH}_2 + 5 \text{ wt.}\% \text{AlCl}_3$, $\text{MgH}_2 + 5 \text{ wt.}\% \text{EDTA}$, and $\text{MgH}_2 + 5 \text{ wt.}\% (\text{TiC}-2\text{TiB}_2)$ composites by the reaction with distilled water at room temperature for 10 min. The obtained curves are logarithmic in shape, indicating that the hydrogen production slows down with time.

As expected, the hydrolysis reaction of pristine MgH_2 significantly slowed down after 10 min due to the formation of passive $\text{Mg}(\text{OH})_2$ layer onto the Mg particles surface, resulting in only 316 mL/g of hydrogen yield and 17.2% of the conversion rate after 10 min (see Fig. 5). Since $\text{Mg}(\text{OH})_2$ has low solubility in water (1.22 mg/100 mL at 20°C) [16]), it remains solid and prevents further contact between the water and the hydride. The reason for the formation of $\text{Mg}(\text{OH})_2$ despite the low pH of the solution is the formation

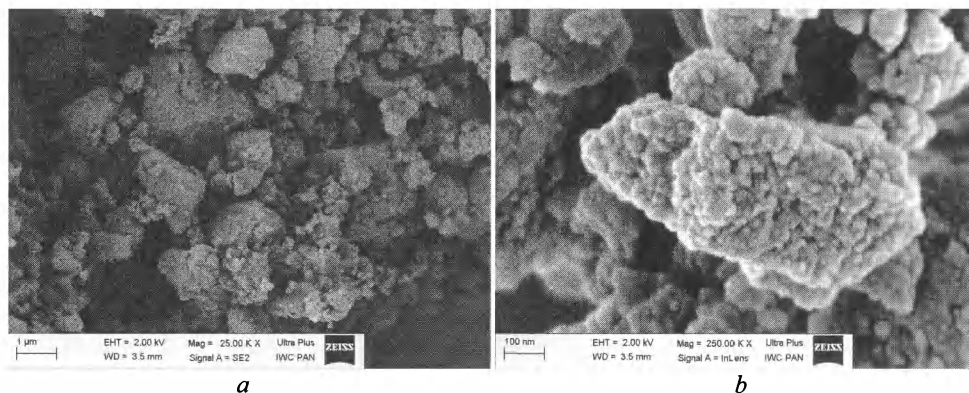
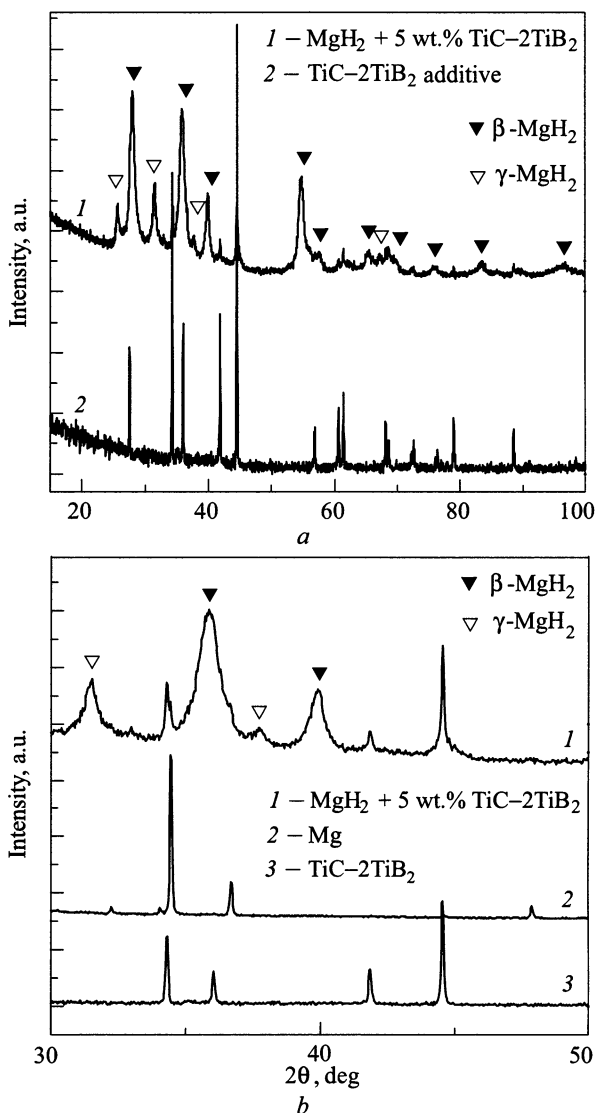


Fig. 3. SEM micrographs of the $\text{MgH}_2 + 5 \text{ wt.}\% (\text{TiC}-2\text{TiB}_2)$ nanocomposite

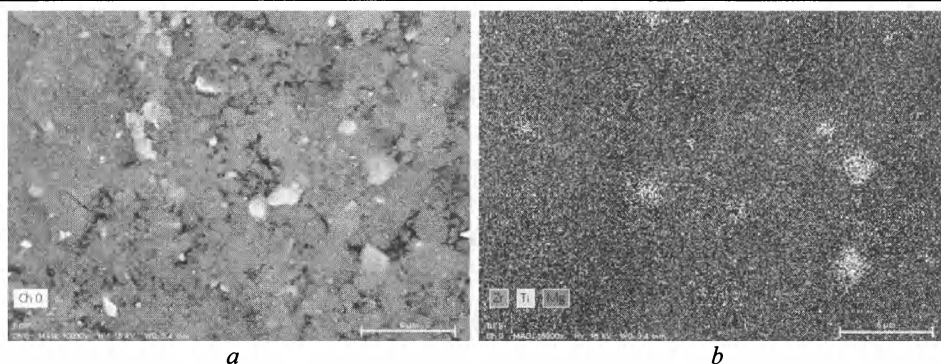


Fig. 4. Elemental distribution for the $\text{MgH}_2 + 5 \text{ wt.}\% (\text{TiC}-2\text{TiB}_2)$ nanocomposite

of hydroxide ions due to the hydrogen evolution reaction, which leads to an increased pH, exceeding 10 at the powder/solution interface that favors the appearance of $\text{Mg}(\text{OH})_2$ [20].

It is known that the hydrogen yield of MgH_2 can be increased by adding hard and brittle powdered materials that help to increase the specific surface area and the number of defects in hydrides during ball milling [8, 15, 21]. Considering this fact, we added 5 wt.% ($\text{TiC}-2\text{TiB}_2$) to MgH_2 . However, the result was opposite to the expected one since the sample showed slightly lower hydrogen yield (309 mL/g of hydrogen yield and 16.8% of the conversion rate after 10 min) as compared to a pure MgH_2 (see Fig. 5). Despite the expected favorable morphology, rather a poor hydrolysis performance could be associated with the agglomeration of Mg particles as a result of cold welding and non-optimized ball milling parameters. Moreover, the $\text{TiC}-2\text{TiB}_2$ additive does not participate in the hydrolysis reaction either as a raw material or as a part of a micro-galvanic cell. Thus, the overall hydrogen capacity of the MgH_2 mixture is reduced due to the added weight of the $\text{TiC}-2\text{TiB}_2$.

From Fig. 5a, it is revealed that $\text{MgH}_2 + 5 \text{ wt.}\% \text{ EDTA}$ demonstrates the lowest reactivity among the tested materials and produces only 176 mL/g of

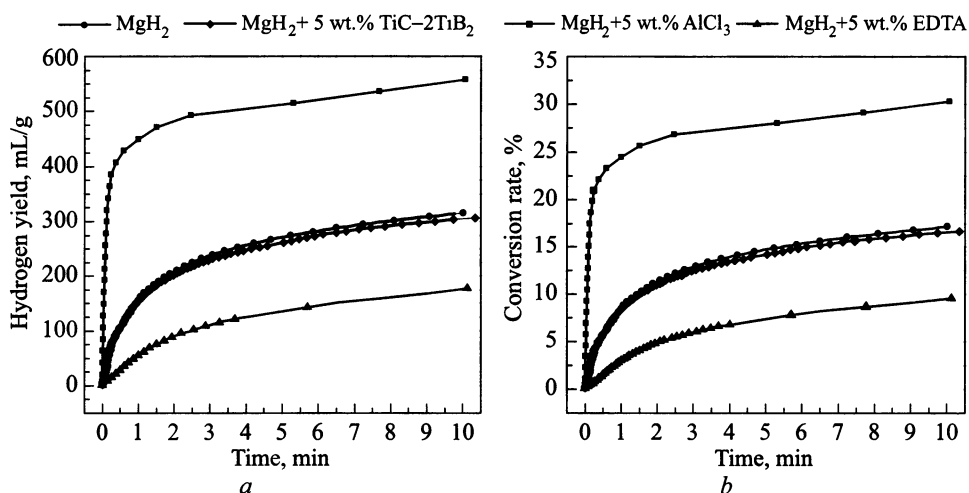


Fig. 5. Kinetics of hydrogen yield (a) and conversion rate (b) of the MgH_2 composites at the hydrolysis reaction

hydrogen in 10 min. Initially, the addition of EDTA to MgH_2 was expected to enhance the reaction kinetics via dissolution of Mg(OH)_2 passivation layer, which is present on the surface of the MgH_2 particles, and precipitation of Mg-EDTA complex. However, the reaction progress was limited to only 9.6% after 10 min of hydrolysis (Fig. 5b). The most probable reason for such a decreased efficiency is an interaction of MgH_2 with EDTA during the ball milling, which leads to the formation of magnesium salts and reduces the amount of highly active MgH_2 nanoparticles. As the result, only a small volume of MgH_2 can generate hydrogen during the hydrolysis, while the formed salts do not contribute to the hydrogen yield. Thus, the EDTA can be suggested to effectively accelerate MgH_2 hydrolysis when only present as an additive for the preparation of a hydrolysis solution [17].

The highest hydrogen yield of 557 mL/g and a conversion rate of 30.3% was observed for $\text{MgH}_2 + 5 \text{ wt.}\% \text{ AlCl}_3$ composition after 10 min of hydrolysis (Fig. 5). The significant improvement of the hydrolysis reaction efficiency is attributed to the destabilization of the Mg(OH)_2 layer by chloride ions. When aluminum chloride comes into a contact with water, it releases Cl^- ions, which substitute the OH^- ones to form more soluble MgCl_2 than Mg(OH)_2 [22], while OH^- ions are consumed in the formation of Al(OH)_3 . It causes the passive layer to dissolve and break down, creating fresh MgH_2 surfaces available to the water molecules, while the formation of a new Mg(OH)_2 layer is prevented by Cl^- ions.

Conclusions

The effect of different additives, such as AlCl_3 , EDTA, and TiC-2TiB_2 , on the hydrolysis performance of MgH_2 synthesized by high-energy ball milling, was studied for the first time. The synthesized MgH_2 contains a mixture of $\beta\text{-MgH}_2$ and a high-pressure modification $\gamma\text{-MgH}_2$, while the incomplete hydrogenation of Mg was observed for $\text{MgH}_2 + 5 \text{ wt.}\% (\text{TiC-2TiB}_2)$ composite. The SEM analysis confirmed the nanometric size range of the milled powders. When studying the hydrolysis of the obtained materials, pure MgH_2 and $\text{MgH}_2 + 5 \text{ wt.}\% (\text{TiC-2TiB}_2)$ were found to have similar poor hydrolysis kinetics and a low hydrogen yield, which can be explained by the formation of poorly soluble in water Mg(OH)_2 layer on the surface of the particles. Thus, the TiC-2TiB_2 additive is ineffective in destroying or preventing the formation of Mg(OH)_2 . At the same time, it was found that $\text{MgH}_2 + 5 \text{ wt.}\% \text{ EDTA}$ has the lowest reactivity (9.6% of the conversion rate after 10 min of hydrolysis) among the tested materials, probably due to the interaction between MgH_2 and EDTA during the high-energy ball milling. Therefore, we expect that EDTA can accelerate MgH_2 hydrolysis only as a component of the aqueous solution. The $\text{MgH}_2 + 5 \text{ wt.}\% \text{ AlCl}_3$ sample demonstrated the best hydrolysis performance (hydrogen yield of 557 mL/g and a conversion rate of 30.3% after 10 min of hydrolysis) among the examined samples and, thus, it can be recommended as an efficient material for hydrogen generation.

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ВПЛИВ РІЗНИХ ДОБАВОК НА ГІДРОЛІЗ MgH_2 , СИНТЕЗОВАНОГО МЕХАНІЧНИМ ВИСОКОЕНЕРГЕТИЧНИМ РОЗМЕЛЮВАННЯМ В СЕРЕДОВИЩІ ВОДНЮ

Гідрид магнію є перспективним матеріалом для отримання водню шляхом гідролізу, завдяки високому вмісту водню, м'яким умовам реакції і низькій вартості. Однак реакція гідролізу MgH_2 швидко сповільнюється через утворення пасивного шару Mg(OH)_2 . Для підвищення ефективності реакції використовують різні добавки. У даній роботі вперше досліджено вплив добавки 5 % (мас.) ЕДТА та TiC-2TiB_2 на гідроліз наноструктурного MgH_2 у порівнянні з чистим MgH_2 та $\text{MgH}_2 + 5\%$ (мас.) AlCl_3 . Гідрид магнію синтезований механічним високоенергетичним розмелюванням порошку Mg в середовищі водню під тиском, при цьому нанокомпозити на основі MgH_2 були одержані або змішуванням попередньо синтезованого MgH_2 з 5 % (мас.) добавки, або синтезовані одночасно з гідруванням магнію. Синтезований MgH_2 являє собою нанодисперсний порошок, що складається із двох фаз: $\beta\text{-MgH}_2$ та метастабільної модифікації $\gamma\text{-MgH}_2$. Ефективність отримання водню, з огляду на ступінь проходження реакції та вихід водню, визначали об'ємним методом. Встановлено, що композит $\text{MgH}_2 + 5\%$ (мас.) ЕДТА має найнижчу реакційну здатність серед випробуваних матеріалів, ймовірно, внаслідок взаємодії MgH_2 з ЕДТА при подрібненні в кульовому млині. Чистий MgH_2 і композит $\text{MgH}_2 + 5\%$ (мас.) (TiC-2TiB_2) володіють майже в два рази кращими характеристиками гідролізу, але все ще далекими від вимог для практичного застосування. Максимальний вихід водню 557 мл/г MgH_2 і ступінь перетворення 30,3% спостерігалися для $\text{MgH}_2 + 5\%$ (мас.) AlCl_3 після 10 хв гідролізу, що пояснюється дестабілізацією шару Mg(OH)_2 іонами хлору.

Ключові слова: гідрид магнію, гідроліз, отримання водню, композити, механічне високоенергетичне розмелювання.

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