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► **To cite this version:**

Irina Konstanchuk, Konstantin Gerasimov, Jean-Louis Bobet. Mechanochemically prepared magnesium-based materials for hydrogen storage. *International Scientific Journal for Alternative Energy and Ecology*, 2010, 5, pp.21-30. hal-00530059

HAL Id: hal-00530059

<https://hal.science/hal-00530059>

Submitted on 7 Mar 2024

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МЕХАНОХИМИЧЕСКИ ПРИГОТОВЛЕННЫЕ МАТЕРИАЛЫ НА ОСНОВЕ МАГНИЯ ДЛЯ ХРАНЕНИЯ ВОДОРОДА

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Заключение совета рецензентов: 17.05.10 Заключение совета экспертов: 22.05.10 Принято к публикации: 25.05.10

Обсуждаются различные механохимические подходы к усовершенствованию сорбционных свойств аккумулирующих водород материалов на основе магния, и некоторые экспериментальные результаты иллюстрируют возможности каждого подхода. Демонстрируется, что механохимические методы эффективны как для улучшения сорбционных характеристик известных водород-адсорбирующих фаз, так и для создания новых материалов для хранения водорода.

Ключевые слова: хранение водорода, механохимические подходы, сорбционные свойства, водород-адсорбирующие фазы.

MECHANOCHEMICALLY PREPARED MAGNESIUM-BASED MATERIALS FOR HYDROGEN STORAGE

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Referred: 17.05.10 Expertise: 22.05.10 Accepted: 25.05.10

Various mechanochemical approaches to improvement of hydrogen storage properties of Mg-based materials are discussed and some experimental results illustrate the possibility of each approach. It is demonstrated that mechanochemical methods are effective both for improving hydriding characteristics of known hydrogen absorbing phases and for search for new materials for hydrogen storage.

Keywords: hydrogen storage, mechanochemical approaches, hydrogen absorbing phases.

Introduction

One of the main problems in development of "hydrogen economy" is a problem of effective and safe storage and transportation of hydrogen.

In comparison to other methods, hydrogen storage in metal hydrides has a number of advantages such as high density of stored energy, high purity of evolved

hydrogen, relatively safety of operating and so on. The materials for hydrogen storage have to satisfy a set of criteria. The most important of them are reversible hydrogen capacity, operating pressure/temperature range, reaction kinetics, minimal degradation after cycling of repeated hydriding and dehydriding and cost. The material that would excellently meet all these requirements is not found so far.

Magnesium and magnesium-based alloys are very attractive from hydrogen capacity point of view (the theoretical hydrogen capacity of MgH_2 is 7.6 wt.%), but MgH_2 is relatively stable (the equilibrium hydrogen pressure of 0.1 MPa is achieved at temperature ~ 550 K), magnesium requires long activation, the kinetics of hydrogen absorption by magnesium and decomposition of MgH_2 are not sufficiently fast even at temperatures as high as 573–623 K. Moreover, the theoretical hydrogen capacity practically is never achieved.

A large number of researches are directed at the search for opportunities to improve these characteristics.

Mechanochemical methods are very promising techniques for fabrication of hydrogen storage materials possessing good hydriding properties. The fine materials with various microstructure, composition and components content may be obtained by means of mechanochemical treatment. The use of mechanochemical methods permits to solve a problem of activation of the hydrogen absorbing material before hydriding, to accelerate hydriding and dehydriding reactions and to increase the hydrogen capacity. They are almost unique methods for fabrication of composites from immiscible components. This is especially important for magnesium-based materials because Mg is thermodynamically immiscible with a large number of elements of Periodic table.

Two principal approaches may be developed on the basis of these methods: (1) improving the hydrogen storage properties of known hydrogen absorbing materials by affecting their structure, morphology, surface properties and so on, using mechanical activation and mechanical alloying with various types of additives and (2) searching for new hydrogen absorbing materials with good hydriding properties. The mechanochemical methods are especially important for the second approach due to the possibility of preparation of metastable composites of components very different in nature, including thermodynamically immiscible ones. These composites may possess very interesting hydrogen storage properties and serve as precursors for synthesis of the new phases promising for hydrogen storage.

In this work, some experimental results on hydrogen storage properties of mechanochemically prepared magnesium-based materials illustrate possibilities of various approaches developed on the basis of mechanochemical methods for fabrication of materials for hydrogen storage.

Improvement of hydrogen storage properties of magnesium by mechanochemical treatment with various additives

One of the main drawbacks of magnesium as hydrogen storage material is slow rate of hydrogen absorption and desorption under the conditions appropriate to wide practical use. The investigations directed at improvement of kinetics of these reactions are now being developed very intensively.

Some peculiarities have been shown to be inherent in the magnesium-hydrogen interaction. Kinetics of hydriding at the first and subsequent cycles differ very much from each other. A compact oxide layer usually covers the magnesium particles and prohibits hydrogen chemisorption on their surface. According to one of the most reliable models proposed in [1], the overall kinetics of first hydriding of magnesium is determined by the statistical cracking of an oxide layer (owing to different coefficients of thermal expansion of Mg and MgO) and hydride nucleation on the metal sites formed. This leads to a long induction period and sigmoid shape of the kinetic curve. As a rule several hydriding-dehydriding processes are required for achieving the highest reaction rate (the so-called activation procedure).

The fragmentation of the material along with the formation of an oxide-free magnesium surface is the result of hydriding and dehydriding at the first cycle. According to the present day concept the rate of magnesium hydriding at the initial stages of second and subsequent cycles and the rate of decomposition of MgH_2 are limited by the dissociative adsorption (recombination and desorption) of hydrogen on the metal surface. This is quite a common feature for interaction between metals and hydrogen [2]. The nuclei of magnesium hydride are formed on the metal surface, with the interface propagating along the metal surface [3]. The overlap of nuclei leads to formation of a "surface shell" of magnesium hydride which blocks further hydrogen absorption.

Catalyst addition accelerates the hydride formation but decreases the hydrogen capacity not only because of additional weight of the catalyst phase but also due to the earlier formation of a hydride layer.

A possible way of overcoming this problem may be found by decreasing the particle size of magnesium and magnesium-based alloys, by modifying their surface with catalytic additives and/or other chemical reagents which can change the nucleation conditions of the magnesium hydride, the morphology of the hydride layer and the hydrogen permeation through it.

The use of mechanochemical methods appreciably promotes a solution of this problem.

Mechanical alloying under inert gas atmosphere

Mechanical alloying (mechanochemical treatment of powdery mixture of two or several components) have been applied for the first time for the fabrication of hydrogen storage materials in the works [4–7]. Mechanical alloying of magnesium powder with addition of transition metal (Ni, Fe, Co and other) was carried out under argon atmosphere. It has been shown that the composites with a large interface between components (mechanical alloys) are formed already at the first stages of mechanical alloying. Typical appearance and lamellar microstructure of mechanical alloys are shown in Fig. 1.

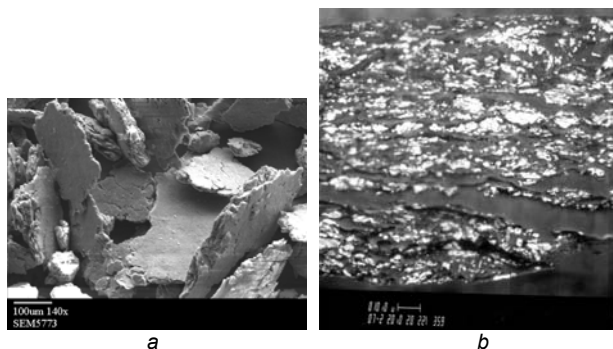


Рис. 1. Типичный вид (а) и слоистая микроструктура (b) механических сплавов магния с металлом-катализатором
Fig. 1. Typical appearance (a) and lamellar microstructure (b) of magnesium mechanical alloy with metal-catalyst

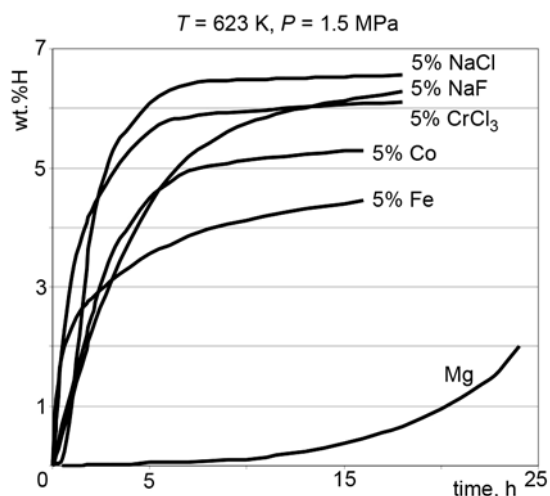


Рис. 2. Первое гидрирование механических сплавов магния с добавками солей или металлов
Fig. 2. First hydriding of magnesium mechanical alloys with additives of salts or metals

These mechanical alloys have been revealed to possess enhanced reactivity towards hydrogen in comparison with conventional alloys. As a rule, the first hydriding of mechanical alloys starts at a maximal rate without any induction period (Fig. 2). It considerably facilitates the activation process. This phenomenon may be explained by specific structure of the surface of mechanical alloy. The oxide layer covering the particles of mechanical alloy is disordered and “transparent for hydrogen”. Therefore metal-catalyst clusters located under this layer are accessible to hydrogen [8].

Mechanical alloying with transition metals [4–10], intermetallic compounds [10–18] and oxides of transition metals [10, 19–24] usually improved hydriding properties of magnesium. However the microstructure of these mechanical alloys was still rough; hydrogen capacity was varying at a level of 4–5 wt.% depending on composition, duration of mechanical alloying and other parameters.

As it has been mentioned above, the further progress in improving hydrogen storage properties of magnesium-based mechanical alloys can be reached by decreasing particle size of both magnesium and catalyst [25–26].

Magnesium, being very soft and ductile, is quite difficult to be disintegrated by mechanical milling. The special surface-active additives capable of impeding aggregation processes are desired for obtaining fine magnesium powder. Some organic compounds and graphite have been used for this purpose [18, 27–35].

Interesting results have been obtained when inorganic salts were used as additives to magnesium in the course of mechanical alloying [36–38]. Salts have been shown to promote comminution of metal during mechanical alloying. Surprisingly even salts containing non-transition metals (NaF, NaCl and MgF₂, which hardly can show catalytic activity in the hydrogen chemisorption processes) have a positive influence on the hydriding properties of magnesium due to modification of surface of metal particle [37, 38]. The acceleration of hydriding and dehydriding reactions at first and subsequent cycles has been observed and quite high hydrogen capacity (about 5.5–6 wt.%) has been reached for these mechanical alloys (Fig. 2 and Fig. 3).

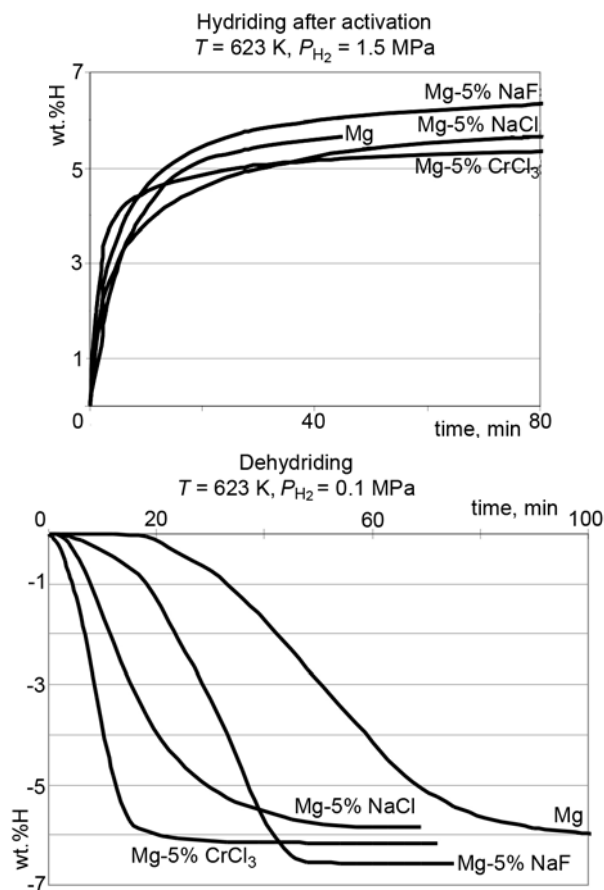


Рис. 3. Гидрирование и дегидрирование механических сплавов магния с солями
Fig. 3. Hydriding and dehydriding of magnesium-salt mechanical alloys after activation

It has to be noted that magnesium-based mechanical alloys fabricated under inert gas atmosphere usually are quite stable in air. It is possible to operate with samples in air without any precautions. This is very convenient from practical point of view.

Mechanochemical treatment under hydrogen atmosphere

Another very successful method of obtaining fine composites consists in mechanochemical treatment under hydrogen atmosphere (so-called “reactive mechanical alloying, RMA, or “reactive mechanical milling”, RMM), with magnesium hydride forming in the course of treatment [39–45] or being used as original reactant instead of magnesium [46–53].

Mechanical alloying of magnesium hydride which is more brittle than metal magnesium leads to formation of nanocrystalline composites of MgH_2 with additives. These composites after preliminary dehydriding very easily react with hydrogen even at temperature as low as 373–473 K [47]. Hydrogen desorption also can occur at relatively low temperature (~473 K), but in this case hydrogen pressure in a reactor must be lower than 0.1 MPa [47, 50–52]. The good hydriding properties of such materials were being preserved during long cycling (more than 200 cycles [53, 54]).

From kinetic and hydrogen capacity point of view, the best results have been obtained by mechanical alloying of MgH_2 with additives of compounds of transition metals (oxides, hydrides or salts) [47, 55–64]. It can be explained by relatively high brittleness of compounds and by the formation of nanosized clusters of transition metals as a result of reduction of salts and oxides during mechanical alloying. This leads to uniform distribution of metal clusters over particles of magnesium hydride and increase of both reaction rate and hydrogen capacity (Fig. 4).

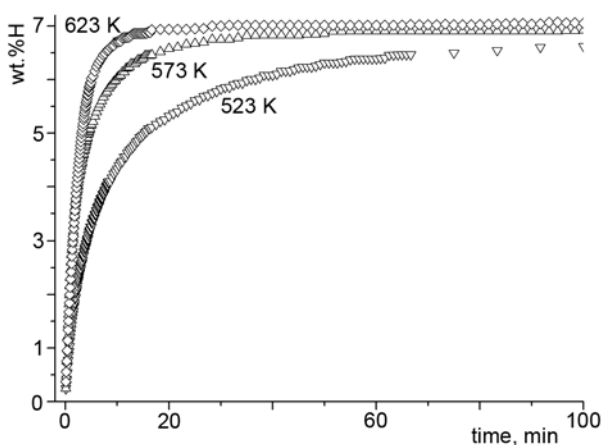


Рис. 4. Гидрирование MgH_2 -2 wt.% VH нанокompозита, полученного в результате РМС: $P = 1,0$ МПа

Fig. 4. Hydriding of MgH_2 -2 wt.% VH nano-composite obtained in the result of RMA: $P = 1.0$ MPa

Unfortunately and contrary to expectation the full transformation of magnesium into hydride was not achieved in nanocrystalline composites. The shape of kinetic curves of hydriding of nanocrystalline magnesium especially at low temperatures differs from the shape of hydriding curves of ordinary magnesium. The reaction rate quickly decreases after achievement of the certain

degree of transformation. This leads to incomplete transformation of magnesium into hydride (Fig. 5).

Moreover some other peculiarities have been revealed in hydriding properties of nanocrystalline magnesium. Several authors reported about “hysteresis” phenomenon observed for nanocrystalline Mg-based systems [47, 53, 65–68], which is not observed for magnesium powders with an ordinary particle size (more than 1 μm). A stronger dependence of reaction rate on hydrogen pressure was observed for hydriding of nanocrystalline magnesium in comparison with coarse-grained magnesium.

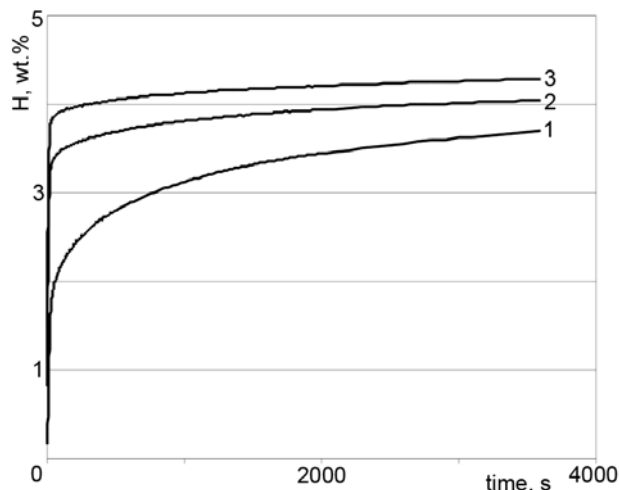


Рис. 5. Влияние давления на поглощение водорода нанокompозитом Mg -10% TiH_2 при 373K:
1 – $P = 2$ бар; 2 – $P = 10$ бар; 3 – $P = 17,5$ бар

Fig. 5. Influence of pressure on hydrogen absorption by Mg -10% TiH_2 nano-composite at 373 K: 1 – $P = 2$ bar; 2 – $P = 10$ bar; 3 – $P = 17.5$ bar

These peculiarities can be explained on the basis of role of nucleation processes in hydriding of nanocrystalline magnesium. Due to very low solubility of hydrogen in magnesium, the nucleation processes play even a more important role in hydriding of nano-sized Mg than in hydriding of coarse-grained Mg. The number of hydrogen atoms dissolved in nano-sized particle of magnesium may be not enough for formation and growth of a critical hydride’s nucleus.

It may explain the «hysteresis» phenomenon. Actually, there is no hysteresis in the interaction of Mg with hydrogen. The apparent «hysteresis» is caused by a hampered nucleation of MgH_2 at a hydrogen pressure close to equilibrium pressure [69]. Initiation of nucleation by short-time increase of hydrogen pressure leads to approaching the equilibrium pressure which is the same as obtained in dehydriding process. Equilibrium pressure for nano-sized Mg turns out to be lower, than for coarse-grained Mg. The most possible reason of this is the lesser surface energy of MgH_2 than Mg.

The hampered hydride nucleation in nano-sized particles may lead to decrease of total hydrogen capacity

especially at not very high temperatures because some particles remain unreacted.

Increase of solubility of hydrogen in magnesium (for example, by means of enhancement of hydrogen pressure) should increase the number of particles involved in reaction and consequently increase total hydrogen capacity (see Fig. 5).

Thus, mechanical alloying of magnesium (or better, magnesium hydride) with catalytic additives and/or additives modifying particle surface considerably improves the reaction rate of hydriding and dehydriding. It becomes possible to carry out the hydriding at a reasonable rate at a temperature of about 373–473 K. The hydrogen capacity close to 7 wt.% can be achieved at elevated temperature (623 K) (Fig. 4), but at mild conditions (temperature of about 373 K) the hydrogen content in the composites did not exceed very much 4 wt%. Moreover the reasonable rates of dehydriding at hydrogen pressures higher than 0.1 MPa can be achieved only at elevated temperatures and it is connected with thermodynamic properties of magnesium hydride.

Searching for new hydrogen absorbing phases

Very significant drawback hampering wide use of magnesium-based materials for hydrogen storage is relatively high thermal stability of magnesium hydride (equilibrium hydrogen pressure 0.1 MPa is achieved at a temperature ~ 550 K). This disadvantage is very difficult to overcome. The thermodynamic characteristics of metal hydrogen system have to be changed with the aim to bring the parameters of P-T-C (pressure-temperature-composition) diagram to desirable values.

The classical mechanical activation of magnesium and magnesium hydride [70] does not lead to a great success because its influence disappears after several hydriding-dehydriding cycles due to relaxation processes which develop very intensively at elevated temperatures.

It is possible to destabilize a thermally stable hydride by mechanical alloying with second constituent, which can react with the stable hydride during dehydriding with the formation of intermetallic compound, lowering the enthalpy change [71–73]. But the intermetallic compound formed in the course of dehydriding as a rule is stable and can't absorb hydrogen. This excludes subsequent hydriding – the process become irreversible.

The destabilization of magnesium hydride has been reported to be possible by mechanochemical treatment with carbon [18, 34, 35] or by “nano-compositing” with other hydride having lower temperature of hydrogen desorption [73]. These effects are very interesting and require the further investigation because their nature is not clear so far. Although the reported results have been obtained directly after mechanochemical

treatment and there is no confidence that destabilizing action will be preserved during the subsequent hydriding-dehydriding cycles.

In principle, the change of thermodynamic parameters can be achieved by partial substitution of one element by another in the intermetallic compounds as it was shown, for example, in works [74–79]. But usually the influence of such substitution is not very considerable.

The more promising way seems to be search for new phases and compounds capable of reversibly absorb a large quantity of hydrogen under mild conditions.

There are very few intermetallic compounds absorbing hydrogen reversibly without decomposition in Mg-based systems. As a rule, only Mg₂Ni was regarded as a candidate for practical application. One of the possible explanations of this fact may be immiscibility of magnesium with a large number of elements of Periodic system, in particular with many transition metals. It makes difficult but not impossible search for new magnesium-based systems for hydrogen storage. For example, it was shown that hydriding (at definite experimental conditions) of mixture of immiscible Mg and Fe led to the formation of ternary hydride Mg₂FeH₆ [7, 80]. Two ternary hydrides (Mg₂CoH₅ and Mg₆Co₂H₁₁) and one intermetallic compound were found in the case of Mg and Co [81–84] in spite of the absence of hydride forming intermetallic compound in magnesium-cobalt equilibrium phase diagram. These ternary hydrides proved to be thermally more stable than MgH₂, but they possess higher hydrogen capacity than Mg₂NiH₄ and very high hydrogen density by volume (more than 7·10²² atoms H/cm³).

These examples show a principle possibility of finding new hydrogen storage systems. It should be noted that new cubic intermetallic compound formed in the result of decomposition of magnesium-cobalt ternary hydrides or of prolonged mechanical alloying can absorb hydrogen at room temperature and it is reasonable to pay attention to a more detailed investigation of its properties.

The search for new hydride phases can be significantly facilitated by using the methods of mechanical alloying which allow to produce very fine composites consisting of two, three and more components including immiscible ones. These methods were successfully applied to the synthesis of ternary hydrides in Mg-Fe and Mg-Co systems both for formation of precursors (mechanical alloys) of subsequent hydrogenation [7, 82, 85, 86] and for direct synthesis of hydride phases in the course of mechanical alloying under hydrogen pressure [87–90].

The fine morphology of mechanical alloys allowed to reveal that ternary hydride can be formed directly from magnesium, iron (cobalt) and hydrogen under conditions when MgH₂ is not formed [7, 82, 91, 92] (Fig. 6).

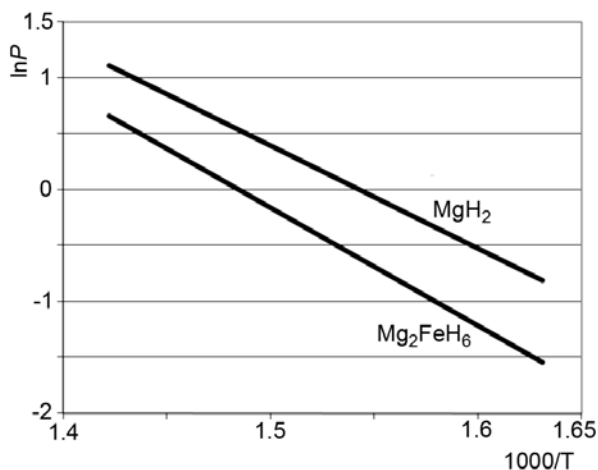


Рис. 6. Температурная зависимость равновесного давления для фаз MgH_2 и Mg_2FeH_6 . Прямой синтез тройного гидроксида по реакции $2Mg+Fe+3H_2 = Mg_2FeH_6$ возможен в области между этими двумя линиями

Fig. 6. Temperature dependence of equilibrium hydrogen pressure for MgH_2 and Mg_2FeH_6 phases. The direct synthesis of ternary hydride from Mg, Fe and H_2 according to reaction $2Mg+Fe+3H_2 = Mg_2FeH_6$ is possible in the region between these two lines

Reactive mechanical alloying

Mechanical alloying under hydrogen atmosphere (reactive mechanical alloying) usually is carried out at hydrogen pressures of several atmospheres. Very specific nonequilibrium processes can develop under these conditions during mechanical alloying. For example, the process similar to self-propagating high-temperature synthesis (SHS) has been shown to occur in the course of mechanical alloying of Mg and Co under hydrogen pressure of about 0.5 MPa [92].

The mechanical alloying of magnesium and cobalt powders under hydrogen atmosphere leads to mutual comminution of metals, creation of large Mg/Co interface and hydrogen adsorption on this interface. When the magnitude of interface and the concentration of adsorbed hydrogen reach the definite values the exothermic reaction begins. The heat being evolved leads to “ignition” of rapid self-sustaining reaction in all volume of composite.

The product formed as a result of SHS-like process contains hydrogen and seems not to be a mixture of phases. Only one rather broad peak can be observed in DTA curve at decomposition of this product (Fig. 7).

More probably this product is an amorphous phase containing hydrogen in various positions with different bonding energy.

Subsequent absorption of hydrogen by this phase either in the course of mechanical alloying or in separate hydriding leads to the formation of Mg_2CoH_5 hydride.

It should be noted that this intermediate phase begins to desorb hydrogen at lower temperature (about 500 K) than the temperature of MgH_2 or Mg_2CoH_5 decomposition. The cubic intermetallic compound is crystallised in the result of the decomposition. This

compound is able to reabsorb hydrogen at room temperature with the formation of solid solutions and at elevated temperatures with the formation of magnesium-cobalt ternary hydrides.

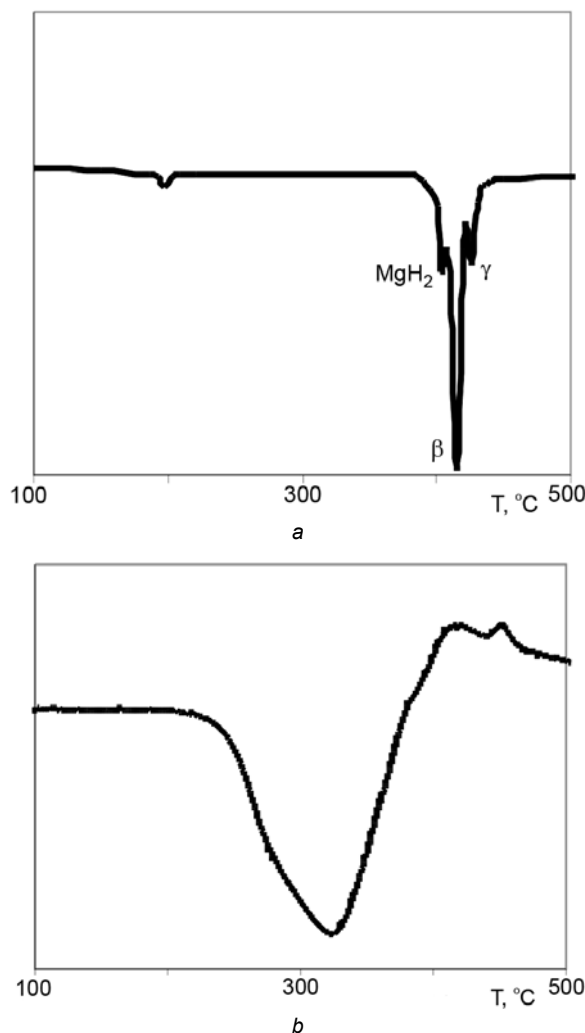


Рис. 7. Кривые DSC, полученные при разложении (а) прогидрированного механического сплава $2Mg+Co$, предварительно полученного в инертной атмосфере, и (б) образца $2Mg+Co$, полученного реактивным механическим сплавлением в атмосфере водорода, $\beta - Mg_2CoH_5$, $\gamma - Mg_6Co_2H_{11}$

Fig. 7. DSC curves obtained at decomposition (a) of separately hydrided $2Mg+Co$ mechanical alloy obtained under inert atmosphere and (b) of $2Mg+Co$ sample mechanically alloyed under hydrogen atmosphere, $\beta - Mg_2CoH_5$, $\gamma - Mg_6Co_2H_{11}$

The hydrided phases formed in the result of reactive mechanical alloying as a rule are metastable in their nature. They tend to be transformed into thermodynamically stable phases in particular at elevated temperature. But the formation in the result of such transformation of new thermodynamically stable phases (as it was in Mg-Co system) can not be excluded. And the hope that these phases will possess good hydriding properties also exists.

Conclusions

1. Improvement of hydrogen storage properties of known Mg-based hydrogen absorbing materials has been demonstrated to be possible by mechanical activation and mechanical alloying with various types of catalytic and surface modifying additives.

2. The composites with homogeneous distribution of phases and high interface area (so called “mechanical alloys”) possessing improved reactivity towards hydrogen are formed at the initial stages of mechanical alloying of metal powder mixture or mixture of metal with other additives. The high temperature and long homogenizing annealing are not required. It is especially important in the case of components with very different specific gravity. Mechanical alloying is almost unique method of fabrication of composites from immiscible components.

3. Metastable composites formed in the result of mechanical alloying may possess very interesting hydrogen storage properties and also serve as precursors for the synthesis of new phases which may be promising for hydrogen storage.

4. Direct synthesis of metastable intermetallic compounds or hydrided phases in the course of mechanical alloying also opens opportunities for obtaining of materials perspective for hydrogen storage.

5. The nanocrystalline magnesium-catalyst composites can be obtained in the result of reactive mechanical alloying of magnesium or magnesium hydride with specific additives (hydrides, salts, oxides etc.). As a rule, these composites possess excellent kinetic characteristics of hydriding and dehydriding reactions. But some peculiarities (such as apparent “hysteresis” phenomenon, unusual shape of kinetic curves at hydriding, very strong dependence of reaction rate on hydrogen pressure and incomplete transformation into hydride) have been revealed in interaction between nanocrystalline magnesium and hydrogen. These peculiarities are explained on the basis of role of nucleation processes in hydriding of nanocrystalline magnesium and should be taken into consideration at investigation and development of nanocrystalline hydrogen storage materials.

Acknowledgements

This work was performed in the framework of INTAS project (reference number INTAS 05–1000005–7669) and PICS program (the RFFI project 07-08-92168).

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