

**MECHANICALLY ALLOYED MAGNESIUM-BASED MATERIALS
FOR HYDROGEN STORAGE**I. Konstanchuk^{1,§}, K. Gerasimov¹, J.-L. Bobet²¹Institute of the Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia²Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS, Université Bordeaux, Pessac, France

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Abstract

Mechanical alloying is very promising technique for fabrication of hydrogen storage materials possessing good hydriding properties.

Magnesium and magnesium-based alloys are attractive from hydrogen capacity point of view, but the kinetics of hydriding-dehydriding of magnesium are not sufficiently fast even at elevated temperature. Moreover, the theoretical hydrogen capacity is never achieved in practice.

In this work, various approaches to improving hydrogen storage properties of magnesium-based materials with the help of mechanical alloying are discussed and some experimental results illustrate the possibility of each approach. It is demonstrated that improving the hydrogen storage properties of known hydrogen absorbing materials is possible by affecting their structure, morphology, surface properties and so on, using mechanical activation and mechanical alloying with various types of additives. It is possible to search for new hydrogen absorbing materials by means of mechanochemical fabrication 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 the synthesis of new phases. Direct synthesis of metastable intermetallic compounds or hydrided phases in the course of mechanical alloying also opens opportunities to obtain materials promising for hydrogen storage.

Introduction

One of the main problems in development of "hydrogen economy" is the 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, minimum degradation after cycling (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 MgH₂ is 7.6 wt.%), but the kinetics of hydrogen absorption by magnesium and decomposition of MgH₂ are not sufficiently fast even at temperatures as high as 573-623K. Moreover, the theoretical hydrogen capacity practically is never achieved, usually being at a level lower than 6 wt.%.

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

Mechanical alloying is one of the most promising methods for preparing fine materials with various microstructure, composition and components content. The use of mechanical alloying permits solution of the problem of activating of the hydrogen absorbing material before hydriding, accelerating the hydriding and dehydriding reactions and increasing the hydrogen capacity. Two principal approaches may be developed on the basis of this method: (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 method of mechanical alloying is especially important for the second approach due to the possibility of preparing 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 mechanically alloyed magnesium-based materials will illustrate possibilities of various approaches developed on the basis of mechanochemical methods for fabrication of materials for hydrogen storage.

Improving the Hydrogen Storage Properties of Magnesium by Mechanical Alloying with Various Additives

One of the main disadvantages 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 interaction of magnesium with hydrogen. The 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.

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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 MgH₂ are limited by the dissociative adsorption (recombination and desorption) of hydrogen on the metal surface. This is quite a common feature for hydrogen interaction with metals [2]. The nuclei of magnesium hydride are formed on the metal surface, with an 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 mechanical alloying appreciably promotes a solution of this problem.

Mechanical Alloying under Inert Gas Atmosphere

For the first time the methods of mechanical alloying were applied 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 (characteristic time is equal to a few minutes of treatment in AGO-2 mills designed at ISSChM, Novosibirsk). Typical appearance and lamellar microstructure of mechanical alloys are shown in Fig. 1.

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].

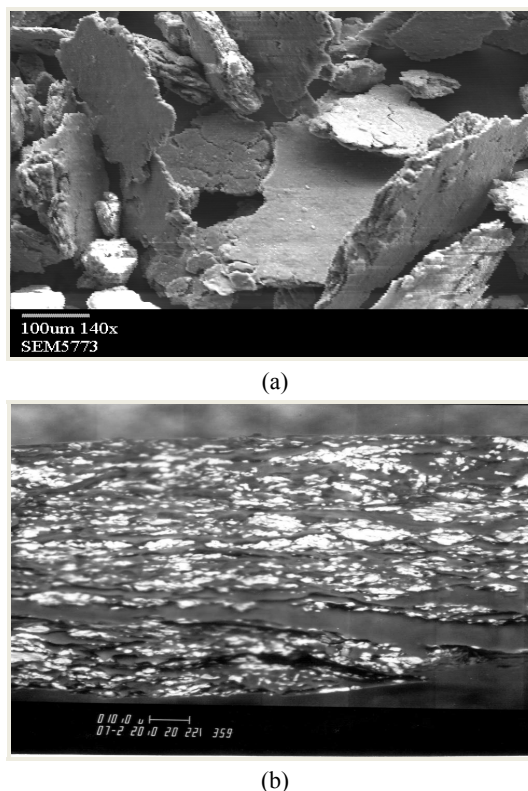


Figure 1. Typical appearance (a) and lamellar microstructure (b) of magnesium mechanical alloy with metal-catalyst

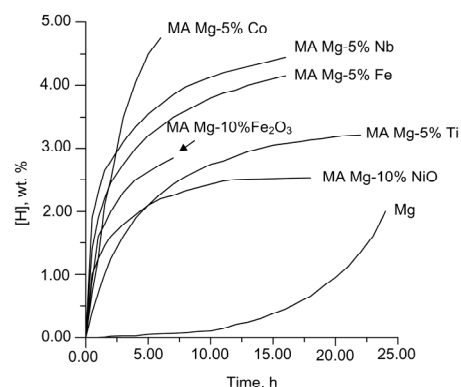


Figure 2. First hydriding of mechanical alloys with various additives, T=623 K, P_{H₂}= 1.5 MPa

Mechanical alloying of magnesium with other metals (such as Ce [9], Fe, Co, Ti, V, Nb, Cr, Ni [4-8]), intermetallic compounds [10-17] and oxides of transition metals [18-29] usually improved hydriding properties of materials obtained in such a way. 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.

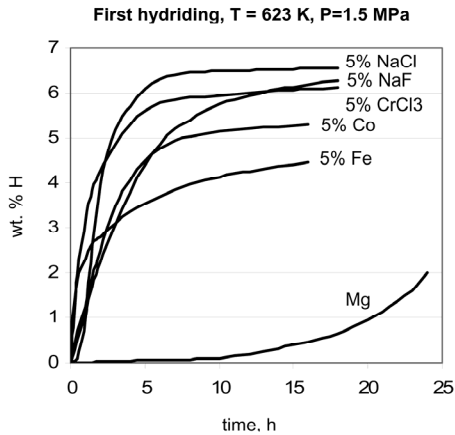


Figure 3. First hydriding of mechanical alloys with salt and metal Co and Fe additives, $T=623\text{ K}$, $P_{H_2}=1.5\text{ MPa}$

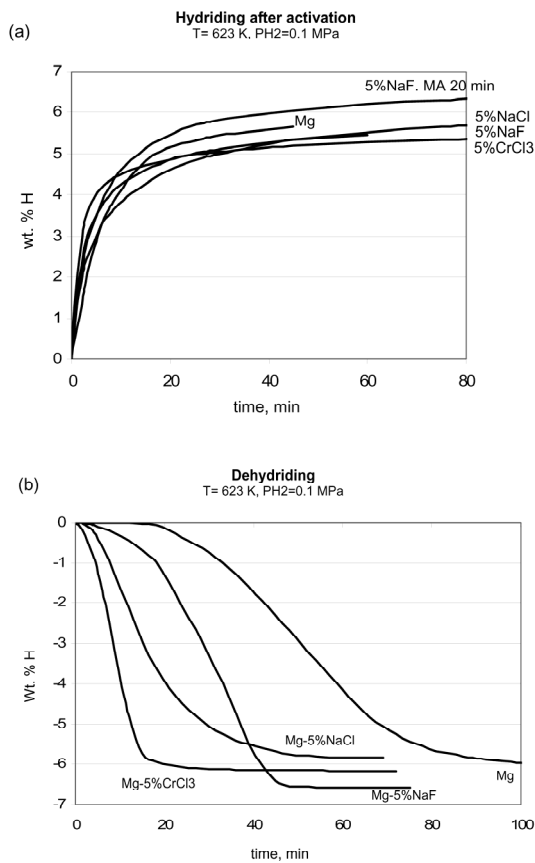


Figure 4. Hydriding (a) and dehydriding (b) after activation of magnesium-salt mechanical alloys

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.

Magnesium, being very soft and ductile, is quite difficult to be disintegrated by mechanical alloying. The special surface-active additions capable of impeding aggregation processes are desired for obtaining fine magnesium powder. Some organic compounds and graphite have been used for this purpose [30-38].

Interesting results have been obtained when inorganic salts were used as additives to magnesium in the course of mechanical alloying [39-41]. Salts have been shown to promote comminution of metal during mechanical alloying. Surprisingly even salts containing non-transition metals (NaF, NaCl and MgF_2 , 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 [40,41]. 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. 3 and Fig. 4).

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 and this is very convenient from practical point of view.

Mechanical Alloying under Hydrogen Atmosphere

Another very successful method of obtaining fine composites consists in mechanical alloying under hydrogen atmosphere (so-called “reactive mechanical alloying” or “reactive mechanical milling”) [42,43], with magnesium hydride being used as original reactant instead of magnesium [44-56]. Mechanical alloying of magnesium hydride which is more brittle than metal magnesium leads to formation of nanostructured composites of MgH_2 with additives. These composites after preliminary dehydriding very easy react with hydrogen even at temperature as low as 373-473 K (Fig.5) [45]. Hydrogen desorption also can occur at relatively low temperature ($\sim 473\text{ K}$), but in this case hydrogen pressure in a reactor must be lower than 0.1 MPa (Fig. 6) [45]. The good hydriding properties of such materials were being preserved during long cycling (more than 200 cycles [49]).

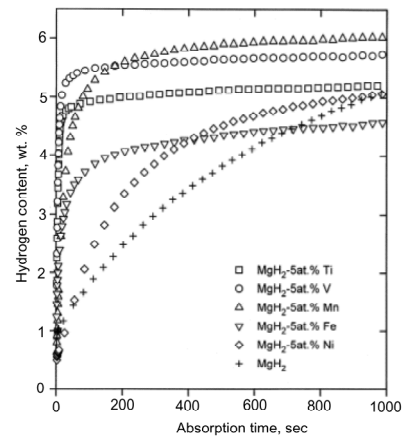


Figure 5. Hydriding of nanostructured composites formed in a result of mechanical alloying of MgH_2 with transition metal additives, $T=473\text{ K}$, $P_{H_2}=1.0\text{ MPa}$ [45]

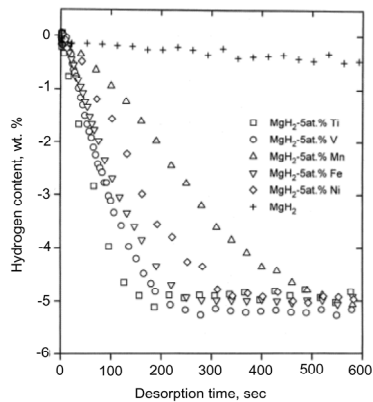


Figure 6. Dehydrogenating of nanostructured composites formed in a result of mechanical alloying of MgH₂ with transition metal additives, T=573 K, P_{H₂}=0.015 MPa [45]

From kinetic and hydrogen capacity point of view, the best results have been obtained by mechanical alloying of MgH₂ with additives of compounds of transition metals (oxides, hydrides or salts) [45, 56, 57-64]. It can be explained by relatively high brittleness of compounds and by the formation of nanosized clusters of metals as a result of reduction of salts and oxides during mechanical alloying. This leads to uniform distribution of clusters over particles of magnesium hydride (Fig. 7) and increase of both reaction rate and hydrogen capacity (Fig. 5 and Fig. 8, for example).

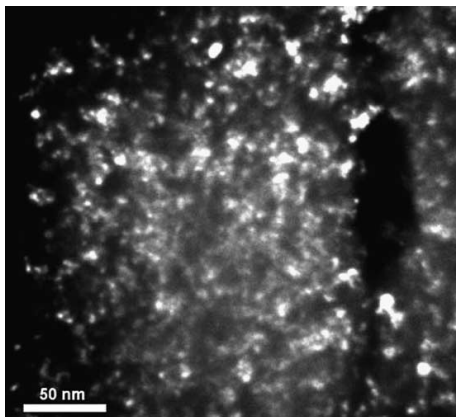


Figure 7. TEM image of nanostructural composite MgH₂+3%FeF₃ formed as the result of mechanical alloying [61]

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. 8), but at mild conditions (temperature of about 373 K) the hydrogen content in the composites did not exceed very much 4 wt/%. We explain this phenomenon by hampered nucleation of magnesium hydride in

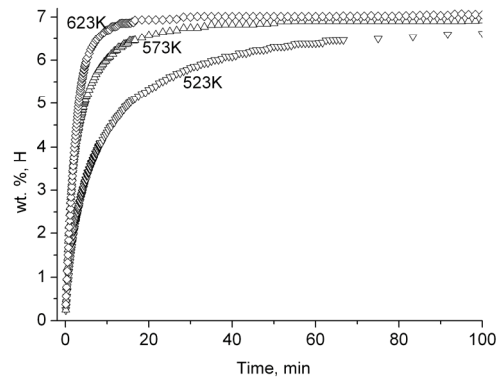


Figure 8. Hydriding of nanostructural composite obtained in the result of mechanical alloying of MgH₂ with the addition of 2 wt.% VH, P=1.0 MPa

nano-sized particles of magnesium at mild conditions. 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

The other significant disadvantage 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 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.

In principle, the change the 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 [65-68]. 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 Mg_2FeH_6 [7,69]. Two ternary hydrides (Mg_2CoH_5 and $Mg_6Co_2H_{11}$) and one intermetallic compound were found in the case of Mg and Co [70-72] 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 MgH_2 , but they possess higher hydrogen capacity than Mg_2NiH_4 and very high hydrogen density by volume (more than $7 \cdot 10^{22}$ atoms H/cm^3).

These examples show a principle possibility of finding new hydrogen storage systems. It should be noted that new intermetallic compound Mg_2Co 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 [7,71,73,74] and for direct synthesis of hydride phases in the course of mechanical alloying under hydrogen pressure [75-78].

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 MgH_2 is not formed [7,71,79,80] (Fig. 9).

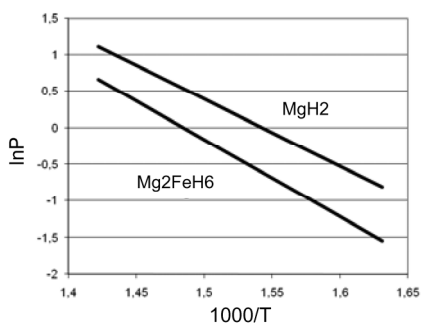


Figure 9. Temperature dependence of equilibrium hydrogen pressure for MgH_2 and Mg_2FeH_6 phases. The direct synthesis of ternary hydride from Mg, Fe and H_2 according to reaction $2Mg+Fe+3H_2 = Mg_2FeH_6$ is possible in the region between these two lines

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 [80].

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

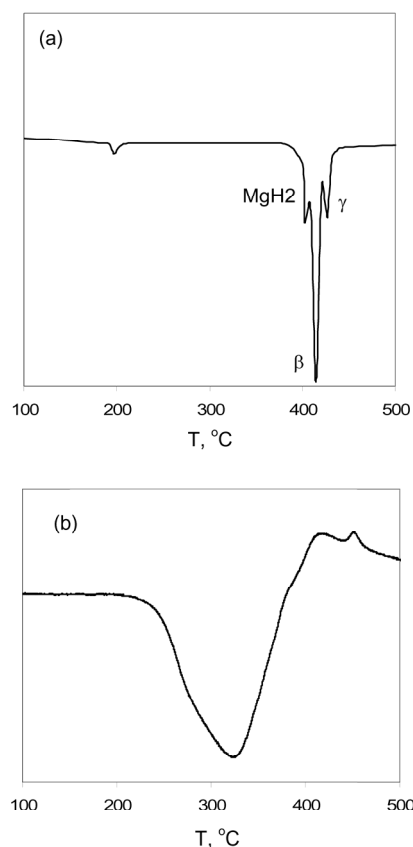


Figure 10. DSC curves obtained at decomposition (a) of separately hydrided $2Mg+Co$ mechanical alloy obtained under inert atmosphere and (b) of $2Mg+Co$ sample mechanically alloyed in hydrogen atmosphere at acceleration 40g for 50 min. β - Mg_2CoH_5 , γ - $Mg_6Co_2H_{11}$

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 intermetallic compound Mg_2Co is crystallised in the result of the decomposition. Mg_2Co 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.

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. The composites with homogeneous phase distribution 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. It takes a few minutes and sufficiently decreases time and energy consumption for material fabrication. 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.
2. The first hydriding of mechanical alloys starts at maximal rate without any induction period. This sufficiently facilitates the activation process.
3. The specific structure of the surface of mechanical alloy makes catalytic additives accessible to hydrogen, but it is proof against oxygen. It is possible to operate with samples in air without any precautions.
4. The rates of hydriding and dehydriding at second and subsequent cycles depend on the nature of catalyst but always exceed reaction rate of pure magnesium.
5. Surface-active additives to magnesium promote pulverization of metal and increase of hydrogen capacity.
6. The comminution of the material and modification of its surface take place simultaneously in the course of the mechanical alloying with salt addition. The salts of transition metals as well as salts containing non-transition metal can positively affect hydrogen storage properties of magnesium and magnesium-based alloys.
7. Mechanical alloying of magnesium hydride which is more brittle than metal magnesium leads to formation of nanostructural composites of MgH_2 with additives. These composites after preliminary dehydriding very easy react with hydrogen even at temperature as low as 373-473 K.
8. It is possible to achieve hydrogen capacity higher than 4 wt.% at a temperature of 373 K and close to 7 wt.% at 623 K in nano-composites obtained by mechanical alloying of magnesium hydride with hydride of transition metal under hydrogen pressure.
9. The possibility of synthesis of new ternary hydrides by means of hydriding of mechanical alloys of immiscible metals (Mg-Fe) has been demonstrated.

10. The carrying out mechanochemical processes under hydrogen atmosphere at definite conditions may lead to the formation of hydrides directly in the course of mechanical alloying (the so-called "reactive mechanical alloying"). As a rule the phases formed in such a way are metastable in their nature and possess properties interesting and different from conventional phases.

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