Chemstry for Sustainable Development **22** (2014) 1–9

UDC 541.44+541.124

Mechanochemical Approaches to the Development of Materials for Hydrogen Accumulation on the Basis of Metal Hydrides*

I. G. KONSTANCHUK[1], K. B. GERASIMOV[1] and J.-L. BOBET[2]

[1]Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: irina@solid.nsc.ru

[2]Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS,
Université Bordeaux 1, 87 Av. Schweitzer, F-33608 Pessac (France)

Abstract

Various mechanochemical approaches to improving the sorption properties of metal materials accumulating hydrogen are discussed. Some experimental results illustrating the possibilities of each approach are presented. It is established that the sorption characteristics of known metal accumulators of hydrogen can be improved by affecting their structure, morphology and surface properties with the help of the mechanical activation and mechanical alloying with various kinds of additives. The possibility to search for new hydrogen-absorbing materials through the mechanochemical synthesis of metastable composites of components of various natures including thermodynamically immiscible components was demonstrated. These composites may possess a high reactivity with respect to hydrogen and serve as precursors for the synthesis of new phases. The synthesis of intermetallic compounds and hydride phases directly during the mechanochemical treatment also opens opportunities for the preparation of new materials promising for hydrogen storage.

Key words: mechanochemical treatment, mechanical alloying, metal hydrides, hydrogen storage

INTRODUCTION

At present, the development of efficient and safe methods to store and transport hydrogen is one of the most important problems; further outlooks of the progress of hydrogen power engineering is strongly dependent on the solution of this problem.

Hydrogen storage in the form of metal hydrides or intermetallic compounds (IMC) has some advantages, in comparison with other storage methods, such as high-pressure gas cylinders or cryogenic containers with liquid hydrogen, for which the provision of safe operation is a serious problem. The advantages of metal hydrides and IMC include a high density of accumulated energy, safe operation, high purity of hydrogen obtained by hydride decomposition, reversibility of hydrogenation-dehydrogenation processes. Due to the listed advantages, these compounds may be repeatedly used as hydrogen accumulators.

To solve applied tasks, hydrogen accumulators are to meet a number of requirements among which the most important ones are:

1) reversibility of hydrogenation;
2) hydrogen content;
3) "working" temperature and hydrogen pressure;
4) high rates of hydrogenation and dehydrogenation;
5) easy activation;
6) stability to admixtures present in hydrogen;
7) stability during cycling;
8) safety;
9) price.

As a rule, the key parameters are considered to be hydrogen capacity, working temperature and the rate of hydrogen absorption and evolution at the working temperature.

---

* Materials of the IV Int. Meeting "Fundamentals of Mechanochemical Technologies", June 25–28, 2013, Novosibirsk, Russia.

The major problem connected with hydrogen storage in metals, intermetallides and alloys based on them, which has not been solved yet, is the absence of a system possessing high hydrogen capacity at the temperature and pressure of hydrogen close to the normal conditions ($0 \le T$, °C ≤ 100, $1 \le P_{H_2}$, atm ≤ 10), which would help solve many practical problems [2]. The hydrogen capacity of hydrides able to evolve hydrogen with a high rate at a temperature close to the room temperature, as a rule, does not exceed 2 mass % H, while hydrides with high hydrogen capacity provide too low equilibrium hydrogen pressure at room temperature [3].

Two principal directions of research aimed at the improvement of sorption characteristics of hydrogen accumulators may be distinguished. The first one is the development of methods that allow optimizing the kinetic parameters of hydrogenation and dehydrogenation of already known metal phases absorbing hydrogen reversibly. The second direction involves changes of the thermodynamic characteristics of metal–hydrogen systems for the purpose of bringing the parameters of the diagrams of "pressure–temperature–composition of hydride phase" (*P–T–C* diagrams) to desirable values. The most decisive route in this direction is the search for new compounds able to absorb and evolve hydrogen in large amounts at rather low temperatures.

As the many years experience of research has shown, mechanochemical methods are very efficient for the development of both these directions [4–7]. In the present work, the major mechanochemical approaches to the development of materials for hydrogen storage are considered mainly with the example of magnesium systems which are promising from the viewpoint of their hydrogen capacity but have a number of essential limitations for practical use.

The theoretic hydrogen content in magnesium hydride is one of the highest ones (7.6 mass %); at the same time, this compound is characterized by relatively high thermal stability (equilibrium pressure of hydrogen, equal to 0.1 MPa, is achieved at a temperature of ~550 K), insufficiently high hydrogenation and dehydrogenation rates, long activation process, as well as incomplete transformation of magnesium into hydride, which causes a substantial decrease in actual hydrogen content. Attempts to improve these characteristics were made by many researchers.

IMPROVEMENT OF THE KINETIC PARAMETERS OF MAGNESIUM INTERACTION WITH HYDROGEN

Features of the interaction of magnesium with hydrogen

It has been established by present that the limiting stage of absorption (evolution) of hydrogen by magnesium is dissociative adsorption (recombination and desorption) of hydrogen on metal surface [8]. This explains long induction periods for the first-time hydrogenation of magnesium; its surface is coated with oxide layer on which the dissociative adsorption of hydrogen does not occur. The kinetics of the first hydrogenation is determined by the dynamics of oxide film destruction [9]. As a rule, in order to achieve the highest rates of hydrogen absorption and evolution, it is necessary to carry out so-called activation – several cycles of hydrogenation–dehydrogenation within which the microstructure of magnesium is formed.

The nuclei of magnesium hydride are formed on magnesium surface; while they grow, magnesium particles get coated with a dense layer of hydride, which prevents further hydrogen absorption. As a consequence, complete transformation of magnesium into hydride cannot be achieved; usually the transformation degree in the first hydrogenation cycle does not exceed 0.9, while in further cycles it is 0.6–0.7 [10].

To increase the rates of hydrogenation and dehydrogenation, it is necessary to use a catalyst to accelerate the dissociative adsorption of hydrogen. On the other hand, the introduction of a catalyst causes a decrease in hydrogen capacity, not only due to the additional catalyst mass but also due to the earlier formation of the dense hydride layer. This problem may be solved by a decrease in magnesium particle size and by the modification of their surface with the help of catalytic additives or other reagents affecting the nucleation of magnesium hydride and its morphology. Besides, it is desirable for the interlayer to be present between magnesium particles to prevent caking the particles at dehydrogenation.

Development of these microstructures is a non-trivial task; in the case of magnesium it is even more complicated by the fact that magnesium does not form alloys with many elements of the Periodic Table.

In this connection, mechanochemical methods turned out to be the most efficient ones (and in some cases even sole possible) for the development of materials for hydrogen accumulation, both based on magnesium and involving other metal systems.

Mechanical alloying in the inert atmosphere

The methods of mechanical alloying for the development of hydrogen-accumulating materials were used by the authors of [4, 5, 11, 12]. It was demonstrated that even at the initial stage of the treatment of a mixture of metal powders (within almost 5 min) in centrifugal planetary mills the formed composites are characterized by a substantial interface (Fig. 1) and increased reactivity with respect to hydrogen, in comparison with magnesium (Fig. 2). One can see that, unlike for pure magnesium and its alloys obtained using traditional methods, hydrogenation of mechanical alloys is almost free from the problem of their activation: as a rule, hydrogenation even in the first cycle starts at the maximal rate. This means that the catalyst surface in mechanical alloys is accessible for hydrogen, unlike for traditional alloys. This is explained by the specific structure of the surface of mechanical alloy, which is a disordered layer of surface oxides, “transparent to hydrogen”, while the clusters of catalyst metal are located beneath this layer [13].

Catalytic additives to magnesium were transition metals [4–6, 11–13], their oxides [14–18] or intermetallides [19, 20]. All these additives accelerated hydrogenation and dehydrogenation, however, the microstructure of these mechanical alloys was still rather coarse. As a consequence, the hydrogen capacity of these composites varied at a level of 4–5 mass % depending on the composition, time of mechanical treatment and other parameters.

To reduce the size of magnesium particles, we used surface-active additives preventing the agglomeration of magnesium particles during mechanical treatment. Some organic compounds or different modifications of carbon can be used as these additives [21–23].

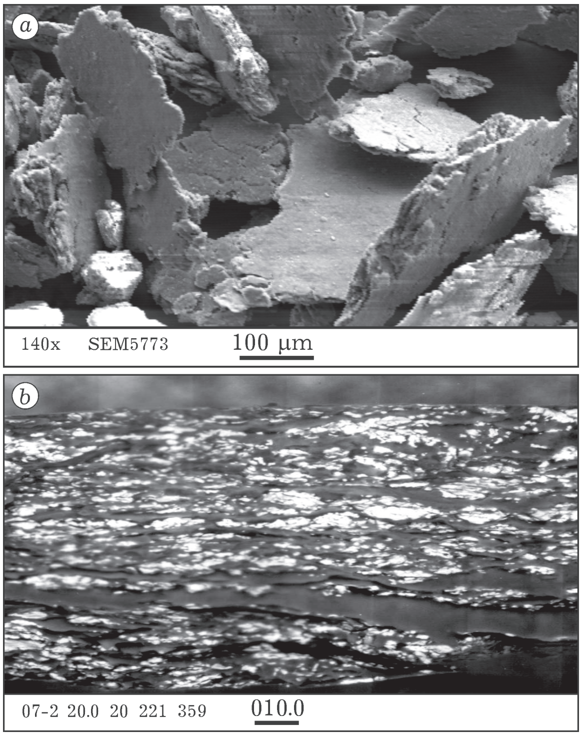

Fig. 1. Typical appearance (*a*) and layered microstructure (*b*) of mechanical alloys of magnesium with metal catalyst.

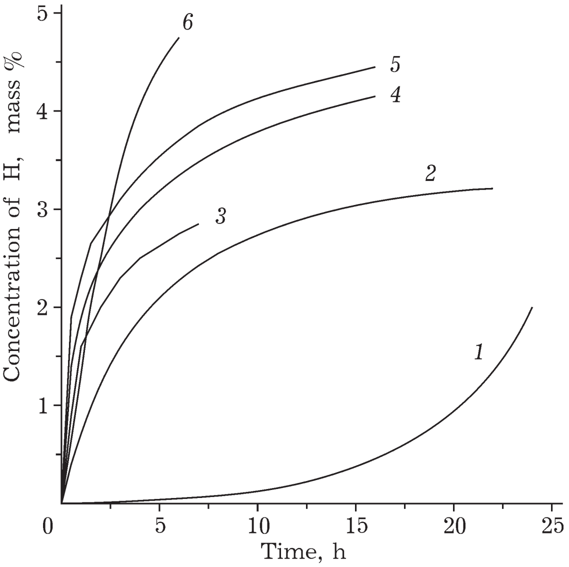

Fig. 2. First hydrogenation of the mechanical alloys of magnesium with catalytic additives (T = 615 K, P_{H_2} = 1.5 MPa): *1* – initial Mg; *2* – Mg–5 % Ti, *3* – Mg–10 % Fe_2O_3, *4* – Mg–5 % Fe, *5* – Mg–5 % Nb, *6* – Mg–5 % Co.

Interesting results were obtained when inorganic salts were used as additives [24–26]. On the one hand, they promoted magnesium grinding during mechanical treatment; on the other hand, they modified its surface, which affected the processes involved in the nucleation of magnesium hydride. A positive effect on the kinetics of hydrogenation and dehydrogenation is caused not only by the salts of transition metals which may exhibit catalytic activity as a result of partial or complete reduction but also by the salts of non-transition metals such as NaF, NaCl, MgF_2 for which the catalytic activity in the processes limited by the dissociative chemisorption of hydrogen is not typical. The hydrogen capacity of mechanical alloys of magnesium with salts reached almost 6 mass %.

It should be noted that mechanical alloys based on magnesium, obtained in the inert atmosphere, as a rule, are rather stable in the air. It is possible to work with them in the air without special precautions, which is convenient for practical use.

Mechanochemical treatment in the atmosphere of hydrogen

To obtain even more fine composites based on magnesium, it was proposed to carry out mechanochemical treatment in the atmosphere of hydrogen (so-called reactive mechanical alloying, or reactive mechanical grinding). In course of this mechanochemical treatment, magnesium is transformed into magnesium hydride [18, 27], or magnesium hydride is used as initial reagent [28–30].

Magnesium hydride is much more fragile than metal magnesium, so mechanochemical treatment causes it's grinding till the nanocrystalline state with the size of coherent scattering blocks about several ten nanometres. Nanocomposites having quite different compositions can be obtained by means of the joint mechanochemical treatment of magnesium hydride with various (mainly catalytic) additives [31, 32]. After preliminary dehydrogenation, these composites absorb hydrogen with a high rate even at a temperature of 373–473 K [28]; at a pressure below the atmospheric level they are able to evolve hydrogen at relatively low temperature (about 473 K) [28 – 30]. It is necessary to stress that the properties of these materials are conserved during more than 200 hydrogenation–dehydrogenation cycles [33, 34].

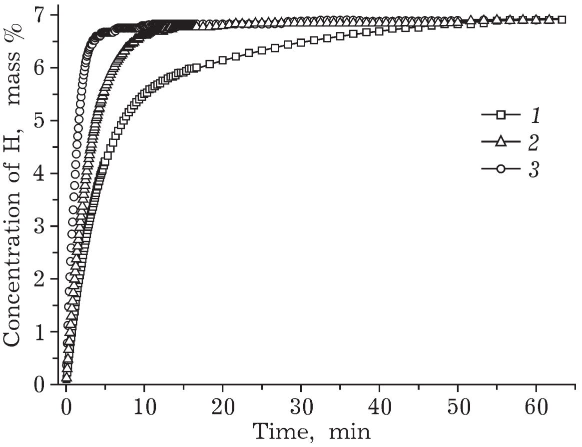

Fig. 3. Hydrogenation of MgH_2–2 mass % VH nanocomposite obtained as a result of reactive mechanical alloying (T = 623 K), P_{H_2}, MPa: 0.85 (*1*), 1.05 (*2*), 1.70 (*3*).

The highest rate of hydrogenation-dehydrogenation and high hydrogen capacity were achieved through mechanical alloying of magnesium hydride with the compounds of transition metals (oxides, hydrides or salts) [28, 31, 35, 36]. This is due to efficient grinding of these additives because of their higher fragility in comparison with metals, and due to the reduction of oxides or salts with the formation of metal clusters distributed uniformly over the particles of magnesium hydride. This kind of nanostructure provides the high rates of subsequent hydrogenation-dehydrogenation and allows one to achieve high hydrogen capacity (Fig. 3).

However, a complete transformation of magnesium into hydride does not occur in nanocomposites, especially at not very high temperature of experiment [28]. This is connected with another feature of magnesium, which manifests itself in hydrogenation of nanometre-sized particles. Due to very low solubility of hydrogen in magnesium [37] the formation of hydride nucleus in an isolated magnesium nanoparticle may be hindered, and not all the particles enter the reaction. As a result, total hydrogen capacity decreases [38]. With an increase in the concentration of dissolved hydrogen (for example, due to an increase in the pressure of gaseous hydrogen in the reactor), the probability of the formation of a nucleus in the particles of definite size increases. As a consequence, the number of particles entering the reaction increases, thus the hydrogen capacity increases (Fig. 4). Hindered nucleation of hy-

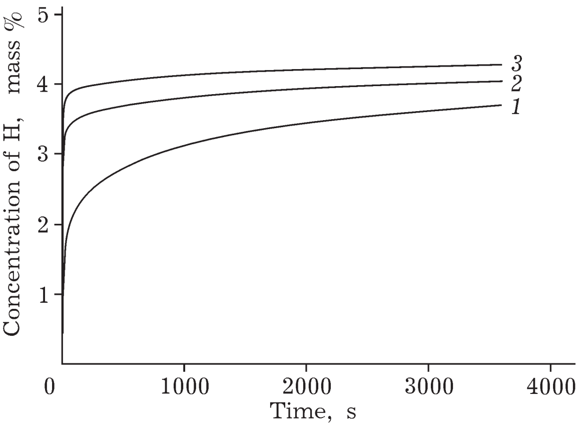

Fig. 4. Effect of pressure on hydrogen absorption by Mg–10 % TiH_2 nanocomposite at 373 K. P_{H_2}, MPa: 0.2 (*1*), 1.0 (*2*), 1.75 (*3*).

dride in magnesium nanoparticles is especially well pronounced under experimental conditions close to the equilibrium [39]. Hydrogenation rate becomes so low that some authors erroneously interpreted this fact as the hysteresis appearing in the region of equilibrium hydrogen pressure in hydrogenation and dehydrogenation of nanocrystalline magnesium, while hysteresis is not observed for magnesium with larger particle size. It was demonstrated in [38] that the contact between magnesium nanoparticles simplifies nucleation of magnesium hydride, likely due to hydrogen diffusion form one particle to another, and cooperative effects are also observed in the decomposition of magnesium hydride. It follows from these observations that composites with isolated magnesium nanoparticles should be avoided in the development of nanostructured materials for hydrogen storage. Additives used in the composites should not hinder hydrogen diffusion between magnesium particles, or they themselves should be the sources of hydrogen. These requirements are met, for example, by nonstoichiometric hydrides of transition metals, such as TiH_x, NbH_x, VH_x. Experimental results provide evidence that presently magnesium nanocomposites with exactly these additives possess the best sorption characteristics [28, 40].

INFLUENCE ON THERMODYNAMIC CHARACTERISTICS OF METAL–HYDROGEN SYSTEMS

As mentioned above, manufacture of very thin micro- and nanostructures is able to simplify the kinetic problems of hydrogenation of magnesium-based systems. However, much more complicated task is to change the thermodynamic properties of known metal–hydrogen systems for the purpose of obtaining higher hydrogen pressure at lower temperature.

The classical mechanical activation of intermetallides or hydrides may affect only the kinetic characteristics of reactions and, as a rule, does not lead to substantial and stable change of thermodynamic parameters [41] because defects formed during mechanical activation are annealed within several cycles of hydrogenation–dehydrogenation.

In principle, it is possible to decrease the enthalpy of hydride decomposition by mixing it with another component that forms intermetallic compound with the metal released in hydride decomposition [31, 42]. However, intermetallic compound formed during dehydrogenation is often stable and does not absorb hydrogen, which makes the process irreversible.

The equilibrium pressure of hydrogen can also be changed by partial replacing some elements in intermetallides with other ones (see, for example, [43, 44]). However, the influence of this replacement, as a rule, appears insignificant.

Search for new phases absorbing hydrogen

The most promising appears to be the search for new phases and compounds reversibly absorbing hydrogen in large amounts under mild conditions.

For example, unusual absorption properties may be exhibited by the phases with non-trivial crystal structure, as it was discovered for hydrogenation of the icosahedral phase obtained for the first time in the system Ti–Zr–Ni by means of spinning [45]. Later on, bulk samples [46] obtained by means of mechanical alloying allowed carrying out full-value kinetic and thermodynamic investigations of hydrogen absorption and evolution. It was demonstrated that hydrogen in the icosahedral phase with the composition $Ti_{45}Zr_{38}Ni_{17}$ occupies two unequal positions – inside Bergman clusters and between them. Correspondingly, hydrogen in these two positions possesses different bonding energies and gets evolved at substantially different temperatures.

An example of the successful use of mechanochemical alloying for the synthesis of new promising hydride phases may be the work by Canadian researchers carried out on the system Li–Be–H [47]. Those authors carried out mechanical alloying of LiH with Be and obtained a new hydride phase with very high hydrogen capacity (more than 8 mass %), able to absorb and evolve hydrogen at a temperature about 300 °C. This work was not developed further on, possibly because of the toxicity of lithium and beryllium, which holds back their practical application, especially on a large scale.

Among magnesium-based systems, a few intermetallic compounds are known that are able to absorb and evolve hydrogen without decomposition. Intermetallide Mg_2Ni only has always been considered for the practical application. This is mainly connected with the fact that magnesium is thermodynamically immiscible with a substantial number of the elements of the Periodic Table, especially with many transition metals. This circumstance limits but does not exclude the search for new magnesium-based systems for hydrogen storage. For example, hydride with the composition Mg_2FeH_6 [12, 48] was obtained through hydrogenation of a mixture of magnesium and iron which do not form intermetallides or solid solutions with each other (the mutual solubility of Mg and Fe in the solid state is negligibly small [49]). Hydrides Mg_2CoH_5 and $Mg_6Co_2H_{11}$ were discovered in the system Mg–Co–H_2 [50–52], in spite of the absence of intermetallic hydrogen-absorbing compounds from the Mg – Co phase diagram. These hydrides turned out to be thermodynamically more stable than MgH_2 but they possess a very high bulk hydrogen density (more than $7 \cdot 10^{22}$ H atoms/cm^3), which is important for the practical use [53].

The examples mentioned provide evidence of the principal possibility to find new hydride phases; the use of mechanochemical methods greatly simplifies the search for new promising systems for hydrogen storage. As mentioned above, mechanical alloying allows obtaining composites with the high level of mutual dispersing and mixing of the components including the components that do not form alloys when usual methods are used. These composites may be used as precursors for subsequent interaction with hydrogen and form new hydride phases.

Due to the fine microstructure of mechanical alloys, hydrides were successfully synthesized in the systems Mg–Fe–H_2 and Mg–Co–H_2 under soft conditions; it was established that the formation of ternary hydrides is possible both through the interaction of magnesium hydride with iron (cobalt) and in the direct interaction of magnesium, iron (cobalt) and hydrogen under the conditions when magnesium hydride is not formed [12, 51, 52, 54].

Combining mechanical alloying with the extrusion at increased temperatures and cold rolling, which are in fact the versions of mechanical treatment, the authors of [55] succeeded in obtaining mechanocomposites from magnesium and iron with nanometre-sized crystallites. In their interaction with hydrogen, almost 100 % yield of Mg_2FeH_6 was achieved, which was not achieved previously either by hydrogenation of preliminarily prepared mechanocomposites [54, 56] or by a direct synthesis in a mechanochemical reactor at an increased hydrogen pressure [7, 31, 57].

As a result of mechanical alloying of magnesium and titanium (also non-interacting with each other under usual conditions metals), homogeneous alloys with the body-centred cubic (BCC) structure were obtained [58]. Their interaction with hydrogen at 8 MPa and 423 K results in the formation of the hydride with the composition $Mg_{42}Ti_{58}H_{177}$ (4.7 mass % H) [59], while the joint mechanochemical treatment of MgH_2 and Ti resulted in the formation of hydrides $Mg_{40}Ti_{60}H_{177}$ and $Mg_{29}Ti_{71}H_{57}$ with hydrogen content 2.9 and 1.4 mass %, respectively [60].

Mechanochemical synthesis in the atmosphere of hydrogen

Hydride phases may be obtained also directly during mechanochemical treatment at increased hydrogen pressure. Very specific nonequilibrium processes can proceed under these conditions, in the mechanochemical reactor, in the course of which unusual metastable phases are formed. For example, the reaction that develops during mechanical alloying of magnesium and cobalt in energy-strain planetary mill AGO-2 at hydro-

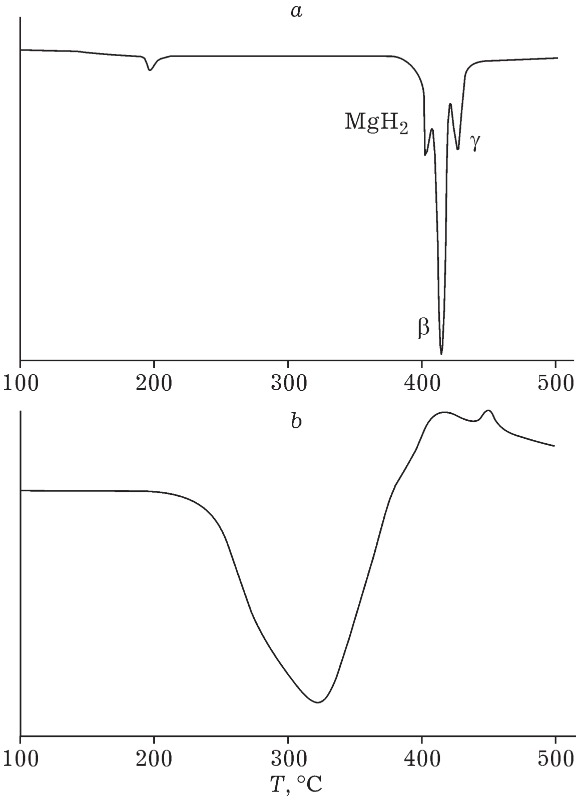

Fig. 5. DSC curves of the decomposition of: *a* – hydrogenated mechanical alloy 2Mg + Co obtained preliminarily in the inert atmosphere; *b* – 2Mg + Co sample obtained through reactive mechanical alloying in the atmosphere of hydrogen. β – Mg_2CoH_5, γ – $Mg_6Co_2H_{11}$.

gen pressure about 0.5 MPa is similar to self-propagating high-temperature synthesis [52].

At the initial stages, mutual grinding of metals and the formation of the large Mg/Co interface occur. Hydrogen gets adsorbed and distributed over the interface; when the Mg/Co interface and the concentration of adsorbed hydrogen reach definite values, the exothermal reaction of hydride formation starts. Heat evolving in this process causes "ignition" of the reaction and its very rapid propagation over the whole volume of the mechanochemical cylinder. As a result, a metastable amorphous phase containing hydrogen in different positions with different bond energies is formed. This is observed in DTA curves as a very broad peak starting to shape at much lower temperatures than the points of decomposition of magnesium hydrate or complex magnesium-cobalt hydrides (Fig. 5).

The further saturation of this phase with hydrogen during mechanical alloying or separate hydrogenation resulted in the formation of the complex hydride Mg_2CoH_5. Its decomposition gave an intermetallic compound of cubic structure absorbing hydrogen at room temperature with the formation of solid solutions and with the formation of complex hydrides magnesium with cobalt at increased temperatures.

As a rule, hydride phase obtained as a result of so-called "reactive mechanical alloying" are metastable by their nature and tend to turn into thermodynamically stable phases. The possibility of the formation of new thermodynamically stable phases cannot be excluded, as it was shown for Mg–Co system as an example. In addition, metastable phases in themselves can be interesting, especially when used under soft conditions.

CONCLUSION

1. Mechanochemical methods are efficient tools to improve sorption characteristics of known hydrogen accumulators based on hydrides, and to search and develop new materials for hydrogen storage.

2. The possibility to make very fine composites of various compositions and microstructures with the help of mechanochemical methods opens the outlooks for variations of the reactivity of these materials within a broad range and for the synthesis of new phases. High temperatures and long-term homogenizing annealing are not required for this purpose, which is especially important in the case of immiscible components or components strongly differing from each other in specific density.

3. Composites formed as a result of mechanical alloying possess increased reactivity with respect to hydrogen due to the destruction of oxide film on metal surface and the formation of hydrogen adsorption centres, as well as in view of the specific structure of the interface surface between the components comprising the composite, and the large value of this surface.

4. The mechanochemical treatment in the atmosphere of hydrogen allows one to obtain nanometre-sized composites with very high hydrogenation and dehydrogenation rates. However, when developing magnesium-based systems, it is necessary to take into account the features of its interaction with hydrogen in the

nanocrystalline state, in particular hindered hydride nucleation in nanometre-sized magnesium particles.

5. The use of mechanocomposites as precursors for the synthesis of hydrides and the synthesis of metastable intermetallic compounds or hydrides directly during mechanochemical treatment simplifies search for new phases promising for hydrogen storage.

6. As a rule, metal admixtures arising as a result of the mechanical treatment do not have a negative effect on hydrogenation and dehydrogenation, so mechanochemical methods are very convenient for the purpose of obtaining materials for hydrogen storage, unlike many other technologies in which the contamination of the substances under treatment by the material of reactors and milling bodies constitutes a substantial problem.

REFERENCES

1 Ziittel A., Borgschulte A., Schlapbach L., Hydrogen as a Future Energy Carrier, Wiley-VCH Verlag GmbH & Co, Weinheim, 2008.

2 Sandrock G., *J. Alloys Comp.*, 293–295 (1999) 877.

3 Bowman R. C., Jr., Fultz B., *MRS Bull.*, 27, 9 (2002) 688.

4 Ivanov E. Yu., Darriet B., Konstanchuk I. G., Stepanov A. A., Gerasimov K., Hagenmuller P., *Mater. Sci. Monogr.*, 28B (1985) 787.

5 Ivanov E. Yu., Konstanchuk I. G., Stepanov A. A., Boldyrev V. V., *Dokl. AN SSSR*, 286, 2 (1986) 385.

6 Konstanchuk I. G., Ivanov E. Yu., Boldyrev V. V., *Usp. Khim.*, 67, 1 (1998) 75.

7 Huot J., Ravnsbaek D. B., Zhang J., Cuevas F., Latroche M., Jensen T. R., *Progr. Mater. Sci.*, 58 (2013) 30.

8 Wiswall R., in: Hydrogen in Metals II, G. Alefeld and I. Völkl (Eds.), Springer-Verlag, Berlin, Ch. 5, 1978.

9 Gerasimov K. B., Goldberg E. L., Ivanov E. Yu., *Izv. SO AN SSSR. Ser. Khim. Nauk.*, 17(5) (1985) 66.

10 Stander C. M., *Z. Phys. Chem. N. F.*, 104 (1977) 238.

11 Ivanov E. Yu., Konstanchuk I. G., Stepanov A. A., Boldyrev V. V., *J. Less-Common Met.*, 131 (1987) 25.

12 Konstanchuk L. G., Ivanov E. Yu., Darriet B., Pezat M., Boldyrev V. V., Hagenmüller P., *J. Less Common Met.*, 131 (1987) 181.

13 Stepanov A. A., Voronin A. I., *Izv. SO AN SSSR. Ser. Khim. Nauk*, 5(2) (1986) 44.

14 Khrussanova M., Terzieva M., Peshev P., Ivanov E. Yu., *Mater. Res. Bull.*, 22 (1987) 405.

15 Khrussanova M., Terzieva M., Peshev P., Konstanchuk L. G., Ivanov E. Yu., *Mater. Res. Bull.*, 26 (1991) 561.

16 Bobet J.-L., Desmoulins-Krawiec S., Grigorova E., Cansell F., Chevalier B., *J. Alloys Compd.*, 351 (2003) 217.

17 Barkhordarian G., Klassen T., Bormann R., *J. Alloys Compd.*, 364 (2004) 242.

18 Castro F. J., Bobet J.-L., *J. Alloys Compd.*, 366 (2004) 303.

19 Terzieva M., Khrussanova M., Peshev P., *J. Alloys Compd.*, 267 (1998) 235.

20 Liang G., Wang E., Fang S., *J. Alloys Compd.*, 223 (1995) 111.

21 Imamura H., Sakasai N., Fujinaga T., *J. Alloys Compd.*, 253–254 (1997)34.

22 Bobet J.-L., Grigorova E., Khrussanova M., Khristov M., Stefanov P., Peshev P., Radev D., *J. Alloys Compd.*, 366 (2004) 298.

23 Reda M. R., *J. Alloys Compd.*, 480 (2009) 238.

24 Yu Z., Liu Z., Wang E., *J. Alloys Compd.*, 333 (2002) 207.

25 Ivanov E. Yu., Konstanchuk I. G., Bokhonov B. B., Boldyrev V. V., *J. Alloys Compd.*, 359 (2003) 320.

26 Konstanchuk I. G., Ivanov E. Yu., Boldyrev V. V., *Chem. Sustain. Dev.*,13, 2 (2005) 243.
URL: http://www.ru/en/journals/KhUR

27 Bobet J.-L., Chevalier B., Song M. Y., Darriet B., Etourneau J., *J. Alloys Compd.*, 336 (2002) 292.

28 Liang G., Huot J., Boily S., Van Neste A., Schulz R., *J. Alloys Compd.*, 292 (1999) 247.

29 Gennari F. C., Castro F. J., Urretavizcaya G., *J. Alloys Compd.*, 321 (2001) 46.

30 Malka I. E., Czujko T., Bystrzycki J., *J. Alloys Compd.*, 432 (2007) L1.

31 Varin R. A., Czujko T., Wronski Z. S., Nanomaterials for Solid State Hydrogen Storage, Springer, NY, 2009.

32 Andrievskiy P. A., *Usp. Khim.*, 80, 9 (2011) 890.

33 Dehouche Z., Djaozandry R., Huot J., Boily S., Goyette J., Bose T. K., Schulz R., *J. Alloys Compd.*, 305 (2000) 264.

34 Oelerich W., Goyette J., Bose T. K., Schulz R., *J. Alloys Compd.*, 347 (2002) 319.

35 Friedrichs O., Klassen T., Sánchez-López J. C., Bormann R., Fernández A., *Scripta Mater.*, 54 (2006) 1293.

36 Malka I. E., Czujko T., Bystrzycki J., *Int. J. Hydr. Energy*, 35 (2010) 1706.

37 Zeng K., Klassen T., Oelerich W., Bormann R., *Int J. Hydr. Energy.*, 24 (1999) 989.

38 Konstanchuk L. G., Gerasimov K. B., Bobet J.-L., *J. Alloys Compd.*, 509S (2011) S576.

39 Gerasimov K. B., Konstanchuk I. G., Chizhik S. A., Bobet J.-L., *Int. J. Hydr. Energy,* 34 (2009) 1916.

40 Konstanchuk I. G., Gerasimov K. B., in: Fundamental'nye Osnovy Mekhanicheskoy Aktivatsii, Mekhanosinteza i Mekhanokhimicheskikh Tekhnologiy, in E. G. Avvakumov (Ed.), Izd-vo SO RAN, Novosibirsk, 2009, p. 61.

41 Huot J., Liang G., Boily S., Van Neste A., Schulz R., *J. Alloys Compd.*, 295 (1999) 495.

42 Vajo J. J., Salguero T. T., Gross A. F., Skeith S. L., Olsen G. L., *J. Alloys Compd.*, 446–447 (2007) 409.

43 Tsushio Y., Enoki H., Akiba E., *J. Alloys Compd.*, 285 (1999) 298.

44 Couillaud S., Linsinger S., Duee C., Rougier A., Chevalier B., Pottgen R., Bobet J.-L., *Intermetallics,* 18, 6 (2010) 1115.

45 Viano A. M., Stroud R. M., Gibbons P. C., Mcdowell A. F., Conradi M. S., Kelton K. F., *Phys. Rev. B.,* 51 (1995) 2026.

46 Konstanchuk I. G., Ivanov E. Yu., Boldyrev V. V., Bokhonov B. B., *Zh. Fiz. Khim.*, 75, 10 (2001) 1880.

47 Zaluska A., Zaluski L., Strom-Olsen J. O., *J. Alloys Compd.*, 307 (2000) 157.

48 Didisheim J.-J., Zolliker P., Yvon K., Fisher P., Schefer J., Gubelman M., Williams A. F., *Inorg. Chem.,* 23 (1984) 1953.

49 Samsonov G. V., Perminov V. P., Magnidy, Nauk. dumka, Kiev, 1971.

50 Zolliker P., Yvon K., Schefer J., *Inorg. Chem.* 24 (1985) 4177.

51 Konstanchuk I. G., Ivanov E. Yu., Stepanov A. A., Samsonova T. I., *Izv. SO AN SSSR. Ser. Khim. Nauk*, 3 (1989) 93.

52 Konstanchuk I. G., Ivanov E. Yu., Boldyrev V. V., *Chem. Sustain. Dev.*, 15, 1–2 (2007) 73.
URL: http://www.ru/en/journals/KhUR

53 Bogdanovic B., Reiser A., Schlichte K., Spliethoff B., Tesche B., *J. Alloys Compd.*, 345 (2002) 77.

54 Konstanchuk I. G., Stepanov A. A., *Zh. Fiz. Khim.*, 63 (1989) 3123.

55 Lima G. F., Triques M. R. M., Kiminami C. S., Botta W. J., Jorge A. M. Jr., *J. Alloys Compd.*, 586 (2014) S409.

56 Polanski M., Witek K., Nielsen T. K., Jaroszewicz L., Bystrzycki J., *Int. J. Hydr. Energy*, 38 (2013) 2785.

57 Gennari F. C., Castro F. J., Andrade Gamboa J. J., *J. Alloys Compd.*, 339 (2002) 261.

58 Asano K., Enoki H., Akiba E., *J. Alloys Compd.*, 486 (2009) 115.

59 Asano K., Enoki H., Akiba E., *J. Alloys Compd.*, 478 (2009) 117.

60 Asano K., Enoki H., Akiba E., *J. Alloys Compd.*, 481 (2009) L8.