ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 4, pp. 712–720. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © S.N. Klyamkin, 2007, published in Russkii Khimicheskii Zhurnal, 2007, Vol. 50, No. 6, pp. 49–55.

Metal Hydride Compositions on the Basis of Magnesium as Materials for Hydrogen Accumulation

S. N. Klyamkin

Chemical Department, Moscow State University,
build. 3, Leninskie gory 1, Moscow, 119992 Russia
tel.: (495) 9394576
fax: (495) 9393316
e-mail: klyamkin@highp.chem.msu.ru

Received September 26, 2006

Abstract—Properties of magnesium hydride and multicomponent materials on its basis are considered in terms their use for reversible hydrogen storage. Special attention is given to methods of magnesium hydride production, including application of various catalysts and nonequilibrium high-energy processing. Principal advances in the optimization of magnesium hydride compositions for practical use are presented and possible lines of further works in this field are formulated.

DOI: 10.1134/S1070363207040330

INTRODUCTION

Magnesium hydride MgH_2 takes a unique place in the series of hydrogen metal compounds and intermetallides. At the hydrogen content more than 7.6 wt% and the volumetric density 1.5 that of liquid hydrogen (0.11 g cm^{-3}), magnesium hydride can be obtained by direct synthesis in even far from critical p–T conditions, and, therewith, the reaction with hydrogen is almost fully reversible and proceeds with a minimum hysteresis. Metallic magnesium is fairly accessible and low-cost material. The principle obstacles to the practical application of magnesium hydride in hydrogen storage systems are the high temperatures of the direct and reverse reaction and high energy expenses for compensation of the endothermic effect of the dehydrogenation reaction (about 75 kJ mol^{-1} H_2), that leads to a loss of an almost one-third of the energy capacity of hydrogen accumulated in the hydride. Over the past two decades various metallurgical, chemical, and mechanochemical methods for optimization of interactions in the magnesium–hydrogen system have been tested. The present work dwells on the major approaches to this problem and the most interesting results.

PROPERTIES OF MAGNESIUM HYDRIDES

Magnesium hydride differs radically, in the type of the M–H bond and crystal structure and properties, from hydrides of transition metals and intermetallic compounds and is close in these respects to ionic hydrides of alkali and alkaline-earth metals. MgH_2 is a strictly stoichiometric compound with the H/Mg atomic ratio of 0.99 ± 0.01 [1]. Dissolution of hydrogen in metallic magnesium is accompanied by heat absorption, the limiting hydrogen content of the solid solution phase increases with temperature and varies, according to different authors, from 10^{-2} to 1 at.% [1–4]. The state diagram of the Mg–H system, constructed in [5], is shown in Fig. 1.

The equilibrium modification of magnesium hydride under normal conditions, α-MgH_2, has a tetragonal crystal structure of the rutile type ($P4/mmm$, $a = 0.45168$ nm, $c = 0.30205$ nm, $z = 2$) with the X-ray density $r = 1.419$ g cm^{-3} [6, 7]. Under high pressures α-MgH_2 undergoes polymorphic transformations [8–10] to form two modifications: γ-MgH_2 and β-MgH_2, having an orthorhombic structure like that of α-PbO_2 ($a = 0.45051$, $b = 0.54197$, $c = 0.49168$ nm) [10] and a hexagonal (pseudo-cubic) structure of the fluorite type ($a = 0.453$ nm, $c = 1.099$ nm [9]). Therewith, the γ-MgH_2 phase under usual pressure is metastable and can be present in magnesium hydride mechanochemical activation products [11].

The thermodynamic properties of α-MgH_2 were considered in [1, 5, 6, 12–15]. Optimization of the experimental data in [14, 15] with account for the temperature dependence of the solubility of hydrogen in magnesium and the deviation of gaseous hydrogen from ideal behavior in experimental conditions, gives the following estimates for the standard enthalpy and entropy of formation of magnesium hydride: $\Delta_f H^0$ = –74.7 kJ mol^{-1} and $\Delta_f S^0$ = 132.3 J mol^{-1}, and the effect of the temperature on the equilibrium volatility f (pressure aequivalent for nonideal gas, bar) of hydrogen is described by the expression:

$$\ln f = -7477.09t^{-1} - 24.1781 + 6.57578\ln T - 7.0423\times10^{-3}T - 2.57404\times10^{-7}T^2 - 2.042794\times10^4T^{-2}.$$

However, at pressures of several tens of atmospheres, quite satisfactory results can be obtained using a simpler dependence [1] (f, atim):

$$\ln f = 7.056 - 3888/T.$$

The chemical properties of magnesium hydride are strongly dependent on its production method. Unlike that obtained by decomposition of organometallic compounds [16], MgH_2 synthesized from elements is rather stable in air, and its reaction with water takes several weeks to come to completion. An intermediate position in the reactivity series belongs to a mechanochemically prepared magnesium hydride. Most likely, the key factors here are dispersity, size, and state of surface.

PRODUCTION OF MAGNESIUM HYDRIDE

Magnesium hydride MgH_2 was first prepared by the pyrolysis of ethylmagnesium iodide in a vacuum at 448 K [16], but the direct synthesis of this compound from elements was performed as late as 1951 [17]. The process was carried out a hydrogen pressure of 20 MPa at 840 K in the presence of MgI_2 as a catalyst, but even in such severe conditions the yield of the products was as low as 68%. By combining the catalytic effect of iodine (0.5–1%) and mechanical grinding in a ball mill at 650–720 K and 10–20 MPa, Dymova and co-workers [18, 19] could obtain magnesium hydride of 97–98% purity. The referees suggest that the mechanical action destroys the dense hydride layer on the surface of metal particles, whose low hydrogen permeability prevents the reaction from coming to completion. Evidence for the efficiency of this approach was later provided by many researchers, and with the intensive development of the instrumentation for mechanochemical activation this method became principal for fast and full hydrogenation of magnesium. Mechanochemical synthesis will be considered in more detail in a separate section. Here it should only be mentioned that the hydrogenation of magnesium in a high-energy ball mill can occur at a room temperature at a minimum hydrogen pressure (up to 0.2–0.5 MPa) and requires no catalysts [20, 21].

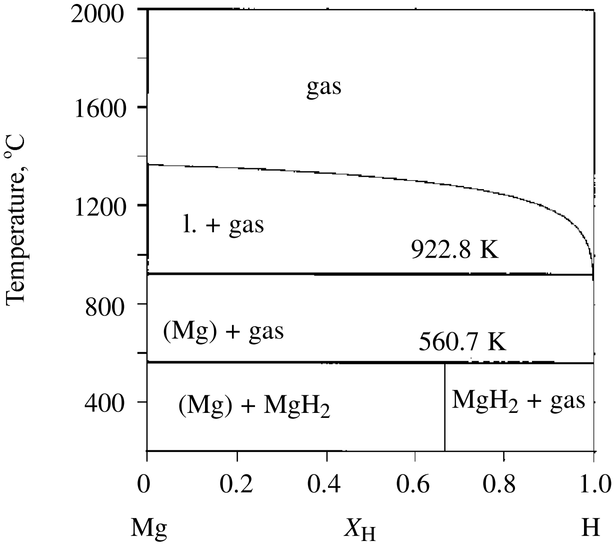

Fig. 1. State diagram of the magnesium–hydrogen system at atmospheric pressure [5].

The systematic research on the mechanism of phase transformations in the Mg–MgH_2–H_2 system [22–27] allow the following conclusions. Hydrogenation is preceded by an induction period necessary for destruction of the oxide film on the metal surface and dissociative chemisorption of molecular hydrogen [22]. The hydrogenation process as such proceeds in two stages. The first, faster stage involves formation on the surface of magnesium grains of discrete nonoriented nuclei of the hydride phase, whose growth and coalescence form a continuous surface layer [23]. Therewith, the reaction is sharply decelerated. This phenomenon explains the known fact that compact magnesium samples more than hundreds microns in size are impossible to hydrogenate completely. The degree of transformation, corresponding to the end of the initial stage, generally depends on the size ratio of initial magnesium particles and hydride nuclei. The latter factor, in its turn, is associated with the hydrogenation temperature and hydrogen pressure. Pederson and co-workers [24, 25] obtained experimental evidence to show that at 673 K ultradisperse magnesium (30–50 μm) can be completely hydrogenated starting from one nucleus to attain a 100% product yield. The referees note the importance of not only the size of particles but also their morphology: The powder obtained by mechanical grinding with a rough and defective particle surface much more actively reacts with hydrogen than the power of the same dispersity, but obtained by condensation from the gas phase, when particles have an almost ideal smooth spherical form. Increased hydrogen pressure first drives the reaction, but then, with hydrogenation progress, the reaction rate fast decreases to get almost zero values [26, 27].

This result is explained by the fact that at high hydrogen pressures (up to 100 MPa) the fast forming small nuclei coalesce to form a thin surface layer which prevents further reaction. Under optimum *p–T* conditions assuming a controllable nucleation process, no metallic magnesium is present in the reaction zone when coalescence is initiated [28]. Thus, the principal ways to a shorter induction period, high reaction rates, and maximum product yield in the synthesis of magnesium hydride are as follows:

(a) grinding of the starting metal to form a developed and highly defective surface;

(b) increasing of the synthesis temperature and decreasing of the hydrogen pressure (to values slightly higher than equilibrium for a given temperature);

(c) mechanical action on the material during hydrogenation for destruction of the oxide (at the initial stage) and hydride (at the diffusion-limited stage) film on magnesium particles;

(d) doping of magnesium with components capable of catalyzing hydrogen chemisorption and/or enhancing the diffusion permeability of magnesium hydride via changing the deficiency of its crystal structure and microstructure.

CATALYTIC SYNTHESIS OF MAGNESIUM HYDRIDE

An original procedure for the production of a highly active magnesium hydride by means of homogeneous catalysis was offered by Bogdanovic [29]. The synthetic scheme included two stages: (a) activation of metallic magnesium by its transition to a soluble (for example, in tetrahydrofuran) form in the form of a complex with anthracene; and (b) treatment of the solution with gaseous hydrogen in the presence of a catalyst ($CrCl_3$, $TiCl_4$) to form a suspension of magnesium hydride; and (c) separation of the solution and soluble admixtures and drying of the hydride. Optimization of the chemical composition of catalysts due to introduction in the solution during hydrogenation of additional components, in particular, magnesium or nickel chlorides, or organonickel or organopalladium compounds allowed the *p–T* parameters of the synthesis to be lowered to 0.1 MPa and 273–473 K [30]. Thus produced magnesium hydride possesses enhanced reactivity owing to, first of all, highly developed surface: up to 100–130 $m^2 g^{-1}$ (1–2 $m^2 g^{-1}$ at a standard solid-phase synthesis), which makes it a rather attractive reagent in synthetic chemistry. At the same time, this material is hardly suitable for hydrogen storage applications because of its extremely high sensitivity to traces of oxygen and moisture and the presence in hydrogen generated by its thermolysis of organic impurities. Moreover, the material is insufficiently stable: The temperature of the subsequent cyclic hydrogen desorption–absorption reaches 570–600 K and causes agglomeration (sintering) of the disperse powder, thus sharply decreasing its activity.

MECHANOCHEMICAL ACTIVATION

Mechanochemical treatment, i.e. milling in a controllable atmosphere in mills of various designs, is a fairly effective method of activation of solid-phase reactions. The essence of the mechanochemical treatment consists not only in grinding a material, thus creating a developed outer surface, but also in changing cardinally the microstructure of the substance (up to its amorphization) and forming a high concentration of defects and microstrains in the crystal lattice. Mechanochemical methods are also widely used to introduce into a material and uniformly distribute in it catalytically active components, to synthesize multicomponent compounds, including those unavailable by traditional methods.

Of tens of works on the application of mechanochemical activation in reactions in the magnesium–hydrogen system, the present review focuses on those which provided essentially new results in preliminar processing of metallic magnesium before hydrogenation, synthesis of magnesium hydride directly during grinding in hydrogen atmosphere, or mechanochemical synthesis of multicomponent materials on the basis of magnesium and its hydride.

Mechanochemical activation of metallic magnesium is strongly complicated by its plasticity and the tendency of the disperse powder for agglomeration. At short milling times (15 min), the oxide film is destroyed only partially, but the destruction degree is enough to shorten the induction period on the subsequent hydrogenation [31]. Longer mechanochemical treatment (up to some hours) substantially enhances its efficiency. The key factor here is not so much reduction of the powder particle size as reduction of the metal grain size inside each particle: As the grain size reduces from about 1 μm to 30–50 nm, the rate increases manyfold, and the conversion reaches 80% within 2 h at already 573 K (Fig. 2).

Zaluska et al. [32] believe that the forming nanocrystalline magnesium microstructure facilitates, due to the high concentration of defects and highly developed intergranular surfaces, hydrogen supply and hydride nucleation both on the outer surface of the metal and in particle bulk. One more important issue should be taken into account: Mechanochemical` activation is generally performed with the use of steel containers and balls, which entails the occurrence in the processed material of steel components, primarily iron. The "crop" of iron after many hours of treatment can reach 2–5 wt%, which is quite enough for the transition metal to exhibit catalytic activity in hydrogen dissociative chemisorption and hydride nucleation. Indirect evidence for this catalytic effect is provided by the fact that magnesium treated in ball mill is still highly active after several cycles hydrogenation-dehydrogenation cycles at temperatures of up to 600 K and obviously accompanied by recrystallization and partial defect bakeout.

The mechanochemical treatment of magnesium in a hydrogen atmosphere (so-called jet grinding) provides a lot of additional benefits [20, 21, 33, 34]. First, the heat effect from ball impact results in a significant local heating of the material and allows hydrogenation at room temperature without additional heating. Second, new nucleation centers are formed directly during hydrogenation. Third, the hydride phase does not form a continuous layer on particle surface under constant mechanical actions, thus lifting diffusion restrictions. Fourth, magnesium hydride is much less plastic than metallic magnesium, which favors a more efficient grinding at the micro and even nano level. And, finally, an important factor that defines the properties of magnesium hydride obtained by jet grinding is the metastable modification γ-MgH_2 that appears in the system upon prolong treatment. As a result, the temperature of the thermal decomposition of the hydride decreases, according to DSC data, by tens of degrees, and the reaction rate increases 100 times compared with that characteristic of the reaction with a mechanically activated magnesium. Gennari et al. [34] believe that the simultaneous presence in a system of the γ-MgH_2 and α-MgH_2 phases has a synergistic effect on hydrogen desorption, thereby affecting the reaction mechanism.

As far back as 1970s magnesium solid solutions with minimum contents of the second component (below 1 at% of Ag, Al, Cd, In, Pb, Y, and Zn [35] and Al, Ga, and In [36]) or mechanical mixtures of magnesium with hydride-forming metals and intermetallic compounds (Pd, V, $LaNi_5$, and TiFe [37]) were found to much faster react with individual magnesium than hydrogen. It is obvious that the use of mechanochemistry in this case can be rather productive, in view of the fact fact that the equilibrium solubility in magnesium of transitions metals potentially catalytically active in hydrogenation and dehydrogenation reactions (Pd, Ni, Fe, Co, Ti, V, etc.) is extremely low and mechanochemical synthesis allows not only preparation of metastable homogeneous solid solutions in a wide concentration range, but also simultaneous modification of the matrix microstructure. Konstanchuk et al. [38] conditionally divided all catalytic additives used in the mechanochemical treatment of magnesium into several groups.

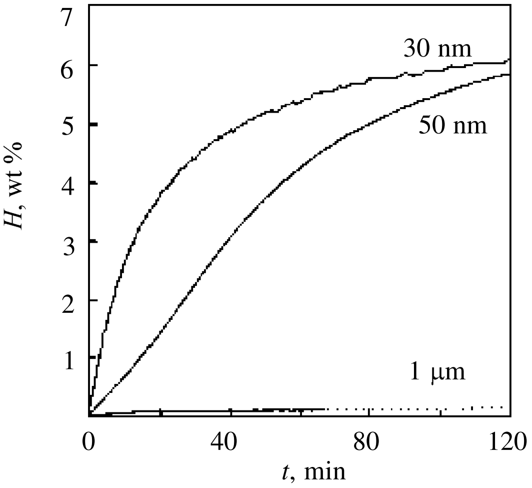

Fig. 2. Effect of magnesium grain size on hydrogen absorption at 573 K [32].

(1) Nickel is one of the most effective activating components [39]. It forms with magnesium the compound Mg_2Ni capable of reversibly absorbing hydrogen. Moreover, nickel clusters act as active centers of hydrogen chemisorption.

(2) Nb, Ti, and REMs form binary hydrides which, by changing stoichiometry, can serve as "hydrogen pumps" [40]. Palladium whose catalytic activity in hydrogenation is widely known can, too, be related to this group [32].

(3) $LnNi_5$ (Ln = La, Ce, Mm) and FeTi are intermetallides which absorb hydrogen in milder conditions than magnesium [41, 42].

(4) Fe, Co, and Cr are catalyst metals which do not form hydrides in the conditions studied [40, 43].

(5) Transition metal oxides (Cr_2O_3, V_2O_5, Nb_2O_5, etc.) [44–46] and salts (NaF, NaCl, MgF_2, $CrCl_3$), the information about which has appeared only last few years [47, 48]. The mechanism of the catalytic action of these substances is still not fully clear. Most authors suggest that the key factors in such systems are modification of the magnesium surface on mechanochemical treatment, destruction of the MgO layer, formation of active nucleation centers, and partial reduction of the oxides to form metal clusters (V, Nb). The effect is noticeably attenuated if oxides (salts) are used simultaneously with catalyst metals, such as nickel or cobalt [47–49].

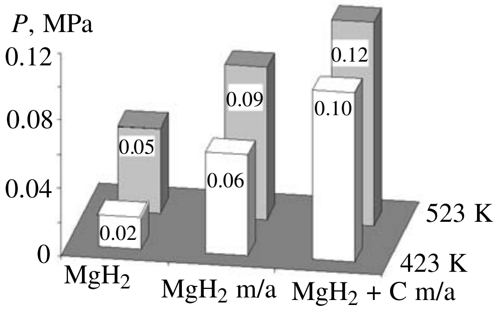

Fig. 3. Pressure of hydrogen desorbed by magnesium hydride and Mg–C composites [28]. (m/a) Mechanochemical activation.

(6) Si and C form with magnesium mostly covalent compounds. Unlike silicon, whose catalytic activity in reactions of magnesium with hydrogen is fairly low [50], introduction of carbon materials leads to rather essential and unexpected results. Imamura et al. [51–53] synthesized in the magnesium–graphite system obtained by grinding mixtures with organic additives (benzene, cyclohexane, tetrahydrofuran) composites that exhibit not only very high kinetic parameters in reactions with hydrogen, but also lower thermal stabilities compared with pure MgH_2 (Fig. 3). Thus, the thermal decomposition of these materials with hydrogen evolution occurred at pressures higher than equilibrium for pure MgH_2 at the given temperature [53]. Later it was shown that the similar effect can be reached without organic additives, when MgH_2 is used instead of metallic magnesium as the starting material in the mechanochemical modification [28, 54].

MAGNESIUM INTERMETALLIC COMPOUNDS AND ALLOYS

Melting of hydride-forming metals with components which do not react with hydrogen in normal conditions, aimed to reduce the thermal stability of their hydrogenation products and to reduce the hydrogen evolution temperature is a classical approach in hydride materials science. Reaction with hydrogen of binary and multicomponent intermetallic compounds of magnesium has been studied in detail in 1970–1980s (see, for example, reviews [55, 56]).

The majority of such compounds react with hydrogen at 550–650 K and decompose in the course of hydrogenation into magnesium hydride and pure second component or its compound. Some of such transformations are completely reversible [57, 58]:

$$Mg_2Al_3 + 2H_2 \rightleftarrows 2MgH_2 + 3Al,$$

$$Mg_2Cu + H_2 \rightleftarrows MgH_2 + MgCu_2.$$

The thermodynamic parameters of these reactions differ from those for pure magnesium hydride, and the equilibrium pressure of hydrogen at the same temperatures is higher, but the presence of a significant amount of the second component insusceptible to hydrogenation essentially reduces such a practically important parameter as the hydrogen content of the hydrogenation products.

Hydrogenation of the other group of intermetallic compounds containing rare-earth metals involves irreversible phase transformations in the first stage:

$$La_2Mg_{17} + 17H_2 \rightleftarrows 17MgH_2 + 2LaH_3.$$

The second, reversible stage is accompanied by decomposition of magnesium hydride and partial decomposition of the REM hydride [59]:

$$MgH_2 + LaH_3 \rightleftarrows Mg + H_2 + LaH_{3-x}.$$

Though the thermal stability of magnesium hydride here is the same as that of the individual compound, the presence of the REM hydride essentially improves the kinetics of hydrogen evolution and absorption. Combined mechanistic study of such reactions, involving kinetic measurements and electron microscopy, allowed the effect observed in the Mg–REM–N_2 systems, where REM is La, Ce, Pr, Nd, or Mm (michmetal), to be associated with the catalytic effect of the REM hydride. The decomposition of intermetallic compounds gives rise to a two-phase mixture with ultradisperse microstructure, and the LnH_{3-x} inclusion uniformly distributed in the magnesium matrix transfer the active dissociated hydrogen to the reaction surface and act as MgH_2 nucleation centers [60–62]. As a result, the Mg–REM binary alloys after primary activation reversibly absorb up to 5.5 wt% of hydrogen in milder conditions and at a much higher rate than pure magnesium.

Mg_2Ni and its multiphase magnesium-based alloys are the object of the most intensive research. Unlike the above intermetallic compounds, Mg_2Ni reversibly react with hydrogen at 470–500 K without disproportionation to form a ternary hydride Mg_2NiH_4 [63]:

$$Mg_2Ni + H_2 \rightleftarrows Mg_2NiH_4.$$

The standard enthalpy of this reaction is 65 kJ mol^{-1} H_2, and the equilibrium pressure is higher than 0.1 MPa already at 540 K. Nomura et al. [64] noted that the Mg_2Ni–H_2 system is characterized by an appreciable hysteresis, which results in different temperature dependences of the adsorption and desorption pressures [65]:

$$\log P_{\text{ads}}(\text{bar}) = -3.211/T + 6.2220,$$

$$\log P_{\text{des}}(\text{bar}) = -3.300/T + 6.2612.$$

In the hydrogen absorption and desorption kinetics Mg_2Ni compares with low-temperature metal hydride systems, and its hydrogen capacity reaches 3.7 wt%, which is much higher than those of classical intermetallic hydrides like $LaNi_5$ and TiFe, but half that of magnesium hydride.

Among magnesium-rich multiphase alloys, those obtained in the Mg–Ni and Mg–REM–Ni systems [66–70] deserve special attention. Double magnesium–nickel alloys with the weight contents of Ni of up to 50% are a combination of the Mg and Mg_2Ni phases whose hydrogenation gives the MgH_2 and Mg_2NiH_4 hydrides, respectively. Even small additives of nickel to magnesium sharply improve the kinetic parameters of hydrogenation, owing to the known catalytic activity of nickel in various processes involving hydrogen. Catalytic additives are the most efficient in the three-phase alloys Mg + 6–9% REM (Mm) + 19–21% Ni (eutectic composition in a ternary system) [70, 71]. The ultradisperse microstructure of these alloys ensures homogeneous distribution of components in the magnesium matrix. The synergistic effect the nickel–REM hydride nanoclusters formed during hydrogenation endow such compositions with the ability to fast absorb up to 5.4–5.8 wt% of hydrogen at 520–550 K and 1–1.5 MPa and to desorb it at 610–620 K and 0.15–0.20 MPa. Note that the kinetic parameters of the reaction with hydrogen of multiphase materials on the basis of the Mg–REM–Ni systems can be further improved by using for their preparation mechanochemical treatment with addition of hydride-forming intermetallides like $LaNi_5$ [71, 72].

TERNARY MAGNESIUM-CONTAINING HYDRIDES

This section focuses on multicomponent hydride magnesium compounds having no nonhydrogenous intermetallic analogs. One of the best studied compounds of this class is Mg_2FeH_6, which can be synthesized by prolong (2–10 days) sintering of a stoichiometric mixture od the metal powders at 723–793 K in a hydrogen atmosphere under a of pressure 2–12 MPa [73], as well as by mechanochemical synthesis from a mixture of iron and magnesium hydride with an excess of the latter [74] or under hydrogen [75]. The formation of Mg_2FeH_6 is reversible, and the significant hydrogen content (5.7 wt%) and, especially, its high weight density in the hydride phase (0.15 g cm^{-3}), which is one and half that of MgH_2, make it a fairly attractive material for hydrogen storage. The problem, however, is that this compound is too stabile thermally ($\Delta_f H^0$ = –77.4 kJ mol^{-1} H_2 [76]), and, consequently, should be heated (to 600–620 K) to evolve hydrogen.

Similar methods of synthesis were used for production of ternary complex magnesium–cobalt hydrides Mg_2CoH_5 [77], as well as ternary hydrides with more exotic components Ir, Ru and Re (Mg_3IrH_5, Mg_3RuH_6, Mg_3ReH_7) [78], which are obviously practically useless. Essential progress in the synthesis of new ternary hydrides on the basis of magnesium and transition metals was made by the application of quasi-hydrostatic high pressures of up to 8 GPa. The compounds Mg_3MnH_7 [79], Mg_3CrH_6 [80], Mg_7TiH ~16 [81], and Mg_6VH ~14, $Mg_{6.5}NbH$ ~14, and $MgNb_2H$ ~4 were synthesized [83], which, while featuring high hydrogen contents (and some of them, as, for example, the vanadium system, good kinetic characteristics of hydrogen desorption), irreversibly decompose on heating. Furthermore, their synthesis conditions are too rigid to allow wide application of such materials.

A separate group is formed by hydrogen magnesium compounds with alkali and alkaline-earth metals, including divalent Eu and Yb. At present 28 such compounds are already known, and their structure and synthesis are described in the review [84]. They have a close-to-ionic bond and evolve hydrogen at too high tempearatures (above 670 K). The authors suggest that four-component hydrides whose thermal stability might be reduced by varying the type and ratio of metal atoms at preservation of the high hydrogen content present interest, but such compounds have not yet been obtained.

HYDROGEN-SORBING COMPOSITE MATERIALS ON THE BASIS OF MAGNESIUM

Magnesium hydride materials should meet special requirements to be suitable for hydrogen storage. Such materials should possess satisfactory thermoconductivity and gas permeability to provide sufficient heat and hydrogen supply (and removal) to the reaction zone, thereby providing high hydrogenation–dehydrogenation rates. Furthermore, magnesium and its alloys tend for agglomeration and caking at elevated temperatures, which removes a certain part of the material from the operating cycle. Thus, one of the major problems solved on creation of special composite materials is to exclude local overheat and to ensure cyclic stability. Further technological requirement to such material is prevention of carry-over, with a stream of gas, of fine hydride particles, i.e. a combination of mechanical durability with the ability to compensate for significant volume effects (up to 20–

30%) associated with the formation and decomposition of hydride phases.

The basic approaches to development of hydrogen-sorbing composites are considered by Antonova [56, 85]. Materials consisting of an active hydride-forming component and a metal (Ni, Cu, or Al) frame work meet the entire set of technological requirements to the greatest degree. The referee also reports interesting results for pseudoalloys comprising components immiscible with each other, for example, Mg–Ti. Such composites with magnesium contents of 13–75% absorb hydrogen at temperatures below 600 K and atmospheric pressure up to the formation of the stoichiometric hydrides MgH_2 and TiH_2, were produced by powder metallurgy. In recent years mechanochemistry that provides nanocomposites exhibiting enhanced activity in reactions with hydrogen is considered as an alternative to powder metallurgy [86].

Huot et al. [87, 88] suggested to improve the hydrogen-sorption kinetics of mechanical magnesium alloys by etching. The approach consists in a grinding of nanocrystalline metastable alloys with addition of a component which is then etched by liquid- or gas-phase methods. After etching such composite acquires a nano- or nasoporous structure with a very high specific surface area. Experimental evidence was obtained to show that a series of Mg–Li, Mg–Al, and Mg–Ni materials evolve hydrogen 2–3 times faster than the initial alloys.

For simplification of the synthesis of magnesiun intermetallic hydrides (for example, Mg_2NiH_4) Saito et al. [89] offered the technique of self-propagating high-temperature synthesis (SHS). A homogeneous mixture of magnesium and nickel powders was heated to 873 K in a hydrogen atmosphere under a pressure of 4 MPa and then was cooled to room temperature. This procedure allows fast production of high-purity stoichiometric hydrides (including multicomponent structures [90]) without any activation process. The microstructure of the synthesized composites, controlled by the SHS conditions, endows them with hydrogen-accumulating properties surpassing the corresponding characteristics of hydrides of the same structure, but obtained by conventional methods.

CONCLUSION

The recent advances in the field of unconventional methods of synthesis and modification of metal hydrides, optimization of their chemical composition and crystal and microstructures have led to a considerable progress in the materials science of hydrides. Magnesium compounds and composites obtained by these technologies preserve the basic advantages of magnesium hydride and impart to it new properties principally important for practical application. The problem of kinetic restrictions in hydrogen absorption/desorption reactions can be considered to be solved completely due to the application of effective catalytic additives and formation of nanostructured materials. This allows magnesium hydride to be not only synthesized but also decomposed in a vacuum at 400–450 K at a satisfactory rate. At the same time, the thermodynamic stability of magnesium hydride phases still remains unacceptably high. Actually, magnesium–carbon composites are the only in which this parameter could be changed appreciably, but here, too, the nature of the destabilizing effect and ways to its preservation in cyclic hydrogen adsorption–desorption processes are still to be found out. Another promising line of research is synthesis of new hydrogen-containing multicomponent magnesium compounds, in particular, with various transition metals, whose thermostability could be reduced without essential losses in the sorption capacity.

REFERENCES

1. Stampfer, J.F., Holley, C.E., and Suttle, J.F., *J. Am. Chem. Soc.,* 1960, vol. 82, 7, p. 3504.
2. Popovic, Z.D. and Piercy, G.R., *Met. Trans.,* 1975, vol. 6A, 10, p. 1915.
3. Watanabe, T., Huang, Y.C., and Komatsu, R., *J. Jpn. Inst. Light Metals,* 1976, vol. 26, 2, p. 76.
4. Fromageau, R., Mairy, C., and Tzanetakis, P., *Scr. Met.,* 1980, vol. 14, 4, p. 395.
5. Zeng, K., Klassen, T., Oelerich, W., and Bormann, R., *Int. J. Hydrogen Energy,* 1999, vol. 24, p. 989.
6. Ellinger, F.G., Holley, C.E., McInter, B.B. et. al., *J. Am. Chem. Soc.,* 1955, vol. 77, no. 9, p. 2647.
7. Zachariasen, W.H., Holley, C.E., and Stampfer, J.F., *Acta Crystalallogr.,* 1963, vol. 16, no. 5, p. 352.
8. Semeneko, K.N., Verbetskij, V.N., Kalashnikov, A.N., et al., *Vestn. Mosk. Gos. Univ, Ser. 2: Chem.,* 1978, vol. 19, no. 6, p. 718.
9. Bastide, J.P., Bonnetot, B., Letoffe, J.M., and Claudy, P., *Mater. Res. Bull.,* 1980, vol. 15, no. 9, p. 1215.
10. Bortz, M., Bertheville, B., Bottger, G., and Yvon, K., *J. Alloys Comp.,* 1999, vol. 287, p. L4.
11. Gennari, F.C., Castro, F.J., and Urretavizcaya, G., *Ibid.,* 2001, vol. 321, p. 46.
12. Konneley, J.A., Varvig, J.M., and Mayers, H.M., *J. Phys. Chem.,* 1960, vol. 64, p. 703.
13. Bousquet, J., Blanchard, J.M., Bonnetot, B., and Claudy, P., *Bull. Soc. Chim. Fr.,* 1969, 6, p. 1841.

14. Bogdanovic, B., Bohmhammel, K, Christ, B., et. al., *J. Alloys Comp.,* 1999, vol. 282, p. 84.
15. Bohmhammel, K, Wolf, U., Wolf, G., and Konigsberger, E., *Thermochim. Acta,* 1999, vol. 337, p. 195.
16. Jolibois, P.C.R., *Acad. Sci.,* 1912, vol. 155, no. 5, p. 353.
17. Wiberg, E., Goelttzer, H., and Bauer, R., *Z. Naturforsch. B,* 1951, vol. 6, no. 7, p. 394.
18. Dymova, T.N., Sterlyadkina, Z.K., and Safronov, V.G., *Zh. Neorg. Khim.,* 1961, vol. 6, no. 4, p. 763.
19. Dymova, T.N., Sterlyadkina, Z.K., and Eliseeva, N.G., *Ibid.,* 1961, vol. 6, no. 4, p. 768.
20. Chen, Y. and Williams, J.S., *J. Alloys Comp.,* 1995, vol. 217, p. 181.
21. Huot, J., Akiba, E., and Takasa, T., *Ibid.,* 1995, vol. 231, p. 815.
22. Gerasimov, K.B., Gol'dberg, E.A., and Ivanov, E.Yu., *Izv. Sib. Otd. Akad. Naul SSSR, Ser. Khim. Nauk,* 1985, no. 17/6, p. 66.
23. Stander, C.M., *Z. Phys. Chem.,* 1977, vol. 104, nos. 4–6, p. 229.
24. Pederson, A.S., Kjoller, J., Larsen, B., and Vigeholm, B., in *Hydrogen Energy Progress V, Proc. 5th World Hydrogen Energy Conf.,* Toronto, Canada, July 15–20, 1985, vol. 3, p. 1269.
25. Vigeholm, B., Kjoller, J., Larsen, B., and Pederson, A.S., *Ibid.,* p. 1455.
26. Gerasimov, K.B. and Ivanov, E.Yu., *Mater. Letters,* 1985, vol. 3, no. 12, p. 497.
27. Gerasimov, K.B., *Cand. Sc. (Chem.) Dissertation,* Novosibirsk, 1986.
28. Lukashev, R.V., Klyamkin, S.N., and Tarasov, B.P., *Neorg. Mate.,* 2006, no. 7 (in press).
29. Bogdanovic, B., *Int. J. Hydrogen Energy,* 1984, vol. 9, no. 11, p. 937.
30. Bogdanovic, B. and Spliethoff, B., *Ibid.,* 1987, vol. 12, no. 12, p. 963.
31. Konstanchuk, I.G., Ivanov, E.Yu, Pezat, M., et. al., *J. Less-Common Met.,* 1987, vol. 131, p. 181.
32. Zaluska, A., Zaluski, L., and Strom–Olsen, J.O., *J. Alloys Comp.,* 1999, vol. 288, p. 217.
33. Huot, J., Liang, G., Boily, S., Van Neste, A., and Schulz, R., *Ibid.,* 1999, vols. 293–295, p. 495.
34. Gennari, F.C., Castro, F.J., and Urretavizcaya, G., *Ibid.,* 2001, vol. 321, p. 46.
35. Douglass, D.L., *Met. Trans.,* 1975, vol. A6, no. 12, p. 2179.
36. Mintz, M.H., Nalkiely, S., Gavra, Z., and Hadari, Z., *J. Inorg. Nucl. Chem.,* 1978, vol. 40, no. 11, p. 949.
37. Tanguy, B., Soubeyroux, J.L., Pezat, M., et. al., *Mater. Res. Bull.,* 1976, vol. 11, no. 11, p. 1441.
38. Konstanchuk, I.G., Ivanov, E.Yu., and Boldyrev, V.V., *Usp. Khim.,* 1998, vol. 67, no. 1, p. 75.
39. Song, M.Y., Ivanov, E., Darriet, M., et. al., *J. Less. Common Metals,* 1987, vol. 131, p. 71.
40. Ivanov, E., Konstanchuk, I., Stepanov, A., and Boldyrev, V., *Ibid.,* 1987, vol. 131, p. 25.
41. Terzieva, M., Khrussanova, M., and Peshev, P., *J. Alloys Comp.,* 1998, vol. 267, p. 235.
42. Liang, G., Wang, E., and Fang, S., *Ibid.,* 1995, vol. 223, p. 111.
43. Konstanchuk, I.G., Ivanov, E.Yu., Pezat, M., et. al., *Ibid.,* 1987, vol. 131, p. 181.
44. Khrussanova, M., Terzieva, M., Peshev, P., and Ivanov, E.Yu., *Mater. Res. Bull.,* 1987, vol. 22, p. 405.
45. Khrussanova, M., Terzieva, M., Peshev, P., et. al., *Ibid.,* 1991, vol. 26, p. 561.
46. Oelerich, W., Klassen, T., and Bormann, R., *J. Alloys Comp.,* 2001, vol. 315, p. 237.
47. Yu, Z., Liu, Z., and Wang, E., *Ibid.,* 2002, vol. 333, p. 207.
48. Ivanov, E., Konstanchuk, I., Bokhonov, B., and Boldyrev, V., *Ibid.,* 2003, vol. 359, p. 320.
49. Bobet, J.-L., Chevalier, B., Song, M.Y., et. al., *Ibid.,* 2002, vol. 336, p. 292.
50. Reule, H., Hirsher, M., Weshardt, A., and Kronmuller, H., *Ibid.,* 2000, vol. 305, p. 246.
51. Imamura, H. and Sakasai, N., *Ibid.,* 1995, vol. 231, p. 810.
52. Imamura, H., Sakasai, N., and Fijinaga, T., *Ibid.,* 1997, vols. 253–254, p. 34.
53. Imamura, H., Tabata, S., Shigetomi, N., et. al., *Ibid.,* 2002, vols. 330–332, p. 579.
54. Klyamkin, S.N., Tarasov, B.P., Straz, E.L., et. al., *Int. Sc. J. Altern. Energ. Ecol. (ISJAEE),* 2005, no. 1(21), p. 5.
55. Verbetsky, V.N. and Klyamkin, S.N., in *Hydrogen Energy Progress VII. Proc. 7th World Hydrogen Energy Conf.,* Moscow, September 25–29, 1988, New York: Pergamon, 1988, p. 1319.
56. Antonova, M.M., *Soedineniya vodoroda–akkumulyatory vodoroda* (Hydrogen Compounds–Hydrogen Accumulators), preprint of Powder Metallurgy Inst., Kiev, 1993.
57. Mintz, M.H., Gavra, Z., Kimmel, G., and Hadari, Z., *J. Less-Common Metals,* 1980, vol. 74, no. 2, p. 263.
58. Reilly, J.J. and Wiswall, R.H., *Inorg. Chem.,* 1967, vol. 6, no. 12, p. 2220.
59. Darriet, B., Pezat, M., Hbiko, A., and Hagenmuller, P., *Mater. Res. Bull.,* 1979, vol. 14, no. 3, p. 377.
60. Verbetskii, V.N., Semenenko, K.N., and Klyam-

kin, S.N., *Izv. Akad. Nauk SSSR, Neorg. Mater.,* 1984, vol. 20, no. 7, p. 1126.

61. Semenenko, K.N., Verbetskii, V.N., and Klyamkin, S.N., *Izv. Akad. Nauk SSSR, Metally,* 1987, no. 2, p. 220.
62. Verbetskii, V.N., Semenenko, K.N., and Klyamkin, S.N., *Izv. Akad. Nauk SSSR, Metally,* 1989, no. 2, p. 182.
63. Reilly, J.J. and Wiswall, R.H., *Inorg. Chem.,* 1968, vol. 7, no. 11, p. 2254.
64. Nomura, K., Akiba, E., and Ono, S., *Int. J. Hydrogen Energy,* 1981, vol. 6, no. 3, p. 295.
65. Song, M.Y. and Park, H.R., *J. Alloys Comp.,* 1998, vol. 270, p. 164.
66. Akiba, E., Nomura, K., Ono, S., and Mizuno, Y., *J. Less-Common Metals,* 1982, vol. 83, no. 2, p. L43.
67. Khrussanova, M., Pezat, M., Darriet, B., and Hagenmuller, P., *Ibid.,* 1982, vol. 86, no. 2, p. 153.
68. Karonik, V.V., Kazakov, D.N., Andrievskii, R.A., and Bogachkova, O.P., *Izv. Akad. Nauk SSSR, Neorg. Mater.,* 1984, vol. 20, no. 10, p. 339.
69. Semenenko, K.N., Verbetskii, V.N., Kuliev, S.I., et al., *Zh. Neorg. Khim.,* 1984, vol. 29, no. 9, p. 2192.
70. Kuliev, S.I., Klyamkin, S.N., Verbetskii, V.N., et al., *Izv. Akad. Nauk SSSR, Metally,* 1988, no. 1, p. 173.
71. Tarasov, B.P., Fokin, V.N., Borisov, D.N., et al., *J. Altern. Energ. Ecol. (ISJAEE),* 2004, no. 1, p. 58.
72. Gross, K.J., Spatz, P., Zuttel, A., and Schlapbach, L., *J. Alloys Comp.,* 1996, vol. 240, p. 206.
73. Didisheim, J.-J., Zolliker, P., Yvon, K., et. al., *Inorg. Chem.,* 1984, vol. 23, p. 1953.
74. Konstanchuk, I.G., Ivanov, E.Yu., Pezat, M., et. al., *J. Less-Common Metals,* 1987, vol. 131, p. 181.
75. Gennari, F.C., Castro, F.J., and Andrade Gamboa, J.J., *J. Alloys Comp.,* 2002, vol. 339, p. 261.
76. Bogdanovic, B., Reiser, A., Schlichte, K., et. al., *Ibid.,* 2002, vol. 345, p. 77.
77. Zoliker, P., Yvon, K., Fischer, P., and Schefer, J., *Inorg. Chem.,* 1985, vol. 24, p. 4177.
78. Yvon, K., *Encyclopedia of Inorganic Chemistry,* King, R.B., Ed., New York: Wiley, 1994, vol. 3, p. 1401.
79. Bortz, M., Bertheville, B., Yvon, K., et. al., *J. Alloys Comp.,* 1998, vol. 279, p. L8.
80. Kyoi, D., Ronnebro, E., Kitamura, N., et. al., *Ibid.,* 2003, vol. 361, p. 252.
81. Kyoi, D., Sato, T., Ronnebro, E., et. al., *Ibid.,* 2004, vol. 372, p. 213.
82. Kyoi, D., Sato, T., Ronnebro, E., et. al., *Ibid.,* 2004, vol. 375, p. 253.
83. Sato, T., Kyoi, D., Ronnebro, E., et. al., *Ibid.,* 2006 (in press).
84. Yvon, K. and Berthville, B., *Ibid.,* 2006 (in press).
85. Antonova, M.M., *Poroshk. Metallurg.,* 1989, no. 12, p. 50.
86. Zaluska, A., Zaluski, L., Strom–Olsen, J.O., *J. Appl. Phys.,* 2001, vol. A72, p. 157.
87. Huot, J., Bouaricha, S., Boily, S., et. al., *J. Alloys Comp.,* 1998, vol. 266, p. 307.
88. Huot, J., Liang, G., and Schulz, R., *J. Appl. Phys.,* 2001, vol. A72, p. 187.
89. Saita, I., Li, L., Saito, K., and Akiyama, T., *J. Alloys Comp.,* 2003, vols. 356–357, p. 490.
90. Qian, L., Qin, L., Lijun, J., et. al., *Ibid.,* 2003, vol. 359, p. 128.

Semen Nisonovich Klyamkin, Cand. Sc. (Chem.), Docent, Chair of Chemical Technology and New Materials, Chemical Department, Lomonosov Moscow State University. Scientific areas of focus: metal hydrides, hydrogen materials science, high pressures.