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Interaction of alloys and intermetallic compounds obtained by mechanochemical methods with hydrogen

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Abstract. Data on hydrogenation of mechanical alloys and intermetallic compounds formed in the course of mechanical alloying and mechanical milling are generalised. It is shown that mechanochemical methods make it possible to solve a number of problems arising in the hydrogenation of metals and alloys and to synthesise novel hydrides and nanocomposite materials. The mechanism of hydrogenation of mechanical alloys is discussed. The bibliography includes 98 references.

I. Introduction

The diversity of practical tasks associated with the accumulation of hydrogen and the use of metal hydrides and intermetallic compounds (IMC) in various technologies stimulate the development of research directed to the search for novel metal – hydrogen systems with definite structural, kinetic, and thermodynamical characteristics.

This type of research consists of the use of alloys and solid solutions based on the known hydride-forming metals, IMC and composite materials obtained from hydride-forming components containing binders that are inert with respect to hydrogen.[1] $LaNi_5$, TiFe, and magnesium and its alloys are considered to be the most promising from the viewpoint of the accumulation of hydrogen.[2,3] These materials are traditionally prepared by alloying and by the methods of powder metallurgy. One substantial problem is the activation of these materials which are usually covered by a layer of oxides and hydroxides, thus preventing the chemisorption of hydrogen at the surface and resulting in long induction periods and low reaction rates in the initial hydrogenation. To achieve the highest reaction rate it is necessary to perform several cycles of hydrogenation and dehydrogenation (cycling), which result in the dispersion of the alloy and the development of its microstructure. The microstructure plays a significant role in further cycling and affects considerably the reaction rate and the amount of absorbed hydrogen.

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In addition, traditional methods of preparation of alloys are mainly restricted by thermodynamically stable compounds and solid solutions.

Mechanochemical methods (mechanical alloying, mechanical milling, *etc.*) consist in mechanical treatment of metal powders in high-energy planetary ball mills. This treatment results mainly in plastic deformation of the material under conditions that fix its metastable state. These methods can be applied to the synthesis of metastable phases: amorphous phases,[4] supersaturated solid solutions, non-stoichiometric intermetallic compounds,[5] quasicrystals,[6,7] and composites with different microstructure and composition including those with non-interacting components.[8] These phases often exhibit unusual physicochemical properties and enhanced reactivity.[8,9] Mechanical alloying, as shown in the present review, can be a promising method for the preparation of materials with high reactivity with respect to hydrogen.

II. Magnesium systems

1. Problems arising in the hydrogenation of magnesium and its alloys

Magnesium and its alloys are promising materials for the accumulation of hydrogen. The stoichiometric hydrogen content in magnesium hydride is 7.6 mass % (Table 1), which exceeds its content in other known hydrides and also in gas cylinders.[10,11] However, the relatively high thermal stability of magnesium hydride (equilibrium hydrogen pressure of 0.1 MPa is achieved at ~ 560 K), insufficiently high rates of hydrogenation of magnesium and dehydrogenation of MgH_2, long-lasting activation, and incomplete conversion of magnesium into the hydride (which decreases the hydrogen content to 5 mass %) have stimulated the appearance of research projects aimed at the possibility of improving the above-mentioned characteristics.

It has been established to date that the formation of magnesium hydride is connected with the processes of formation and growth of MgH_2 nuclei. For the majority of metal – hydrogen systems, the first stage of the interaction of hydrogen with a metal is characterised by the formation of a solid solution of hydrogen in a metal, in which nuclei of the hydride phase are crystallised.[12] The formation of solid solutions of hydrogen is not typical of magnesium, or more precisely, their concentrations are low.[13–15] The hydride nuclei appear at the surface of magnesium particles; when the nuclei overlap, the reaction rate is controlled by diffusion processes. 'Diffusion retardation' then occurs, which prevents the complete conversion of magnesium into the hydride. In the first cycle of hydrogenation, the extent of conversion does

Table 1. Characteristics of hydrogen storage systems.[10,11]

Method of storage	Hydrogen content		Hydride density /g cm^{-3}	Accumulated energy		Hydrogenation rate
	(mass %)	/10^{22} at cm^{-3}		/kJ g^{-1}	/kJ cm^{-3}	
H_2, gas 20 MPa, 300 K	1.2[a]	0.9	–	142.7	2.13	–
H_2, liquid	$\leqslant$ 12[a]	4.2	–	142.7	9.96	–
$LaNi_5H_6$	1.4	5.5	6.2	2.0	13.04	High
$TiFeH_2$	1.9	6.3	5.5	2.7	14.93	"
MgH_2	7.6	6.6	1.5	10.8	15.64	Low
$MgNiH_4$	3.6	5.8	2.7	5.1	13.75	High
Gasoline	–	–	–	48	38	–

[a] With account of the mass of the storage system.

not usually exceed 0.9, in subsequent cycles it does not exceed 0.6–0.7.[16–18]

Kinetic characteristics of hydrogenation processes in the first cycle differ substantially from those in the later cycles. The surface layer of magnesium oxide, which is always present on the original metal particles before the first hydrogenation, inhibits the formation of magnesium hydride nuclei, because no dissociative adsorption of hydrogen on this layer occurs.[19] Therefore, the rate of hydrogenation of magnesium in the first cycle is determined by the processes of destruction of the oxide film and formation of a metallic surface with hydrogen chemisorption ability.[19–21] A model of the first cycle of hydrogenation of magnesium taking into account the dynamics of the destruction of the oxide film and kinetics of the nucleus growth has been proposed.[22]

During activation through cycling, exfoliation of the oxide film occurs. The initial reaction rate is determined by the dissociative chemisorption of hydrogen on a pure metal surface, and the nucleus growth occurs due to the surface diffusion within the layer of the chemisorbed hydrogen.[23] An increase in the number of nuclei with an increase of ΔP (the difference between the pressure in the reactor and the hydrogen equilibrium pressure for magnesium hydride at the temperature of the experiment), which is a driving force of the reaction, or the introduction of catalysts accelerates the initial stage of hydrogenation, leads to the faster formation of the continuous layer of the hydride, and to a change over to diffusion conditions at lower conversion rates.[24] It was shown by experiments on the movement of the Kirkendal mark that hydrogen atoms or ions are the diffusing species.[25]

The rate of decomposition of magnesium hydride depends on the dynamics of the formation and growth of nuclei of magnesium metal.[23] The desorption of hydrogen from the surface of the solid reaction product, metallic magnesium, is the limiting stage of the reaction; for this reason, the size of the Mg/MgH_2 interface plays a significant role.

Thus, the rate of magnesium hydrogenation in the first stage and the rate of decomposition of magnesium hydride are determined by the processes of adsorption (or desorption) of hydrogen on the metal surface (in the first hydrogenation, by the formation of the metal surface), by the rates of formation and growth of nuclei of the reaction product, and after the creation of the continuous layer of MgH_2 in the hydrogenation, by the rate of diffusion of hydrogen through the hydride. Hence, changes in the kinetics of hydrogenation and dehydrogenation can be achieved by controlling these stages.

In the majority of studies dealing with the improvement of kinetic and thermodynamic characteristics of magnesium in the interaction with hydrogen, its alloys with other metals have been used. However, it should be noted that in the case of magnesium, the choice of these metals is rather limited for the enthalpy of mixing of magnesium with many elements of the Periodic Table is positive.

To date, only two magnesium intermetallic compounds are known that absorb hydrogen reversibly, *viz*., Mg_2Ni and $Mg_{51}Zn_{20}$, and the corresponding hydrides, $MgNiH_4$ (Ref. 26) and $Mg_{51}Zn_{20}H_y$ ($y = 90-95$).[27] The hydride Mg_2NiH_4 is regarded as a promising one for the accumulation of hydrogen, because it interacts with hydrogen at a high rate at temperatures of about 473–573 K and $P_{H2} \simeq 0.5-1.0$ MPa,[28] although its hydrogen capacity is less than that of magnesium (see Table 1). At the first stage of hydrogenation of Mg_2Ni under the conditions ensuring fast heat removal and at rather high hydrogen pressures, chemisorption of hydrogen on the surface of IMC with an effective activation energy of 14.0±0.8 kJ mol^{-1} is the limiting stage.[29] However, due to high rates of hydrogenation and dehydrogenation, the processes of heat and mass transfer play a significant role and may become limiting, especially if this IMC is used on a technological scale. The creation of composite materials containing inert metallic fillers is the way to solve the problems of heat and mass transfer,[30] but this further decreases the hydrogen capacity of an accumulator.

The interaction of IMC of magnesium and of some other elements, such as rare earth metals, Cu, Al, Ca, with hydrogen leads to the decomposition of the intermetallic compound to form a mixture of two hydrides or a hydride and a metal (or another IMC). This process was termed hydrogenolysis,[31,32] in general it can be represented by the equation

$$A_xB_y + \frac{m}{2}H_2 \rightleftharpoons xAH_{m-n} + yBH_n,$$

where A, B are elements constituting the IMC; $n = 0$ if the second element does not give a hydride.

Hydrogenolysis can be reversible, as in the case of Mg_2Cu,[33] and irreversible, as for most IMC of magnesium with rare earth metals and Al.[11,32,34–40] The reversibility is determined by the relationship between the values of the heat of formation of the binary hydride and the initial IMC. The mechanism of hydrogenolysis has not been studied in detail. No complete separation of hydrides or a hydride and a metal (IMC) resulted from hydrogenolysis occurs. The material obtained is composed of particles with a developed interface between its constituents[35,36] which determines the reactivity of these particles in further hydrogenation–dehydrogenation cycles.

Of the systems that undergo hydrogenolysis, the main attention has been paid to IMC of magnesium with rare earth metals. Hydrogenolysis results in a non-stoichiometric hydride LnH_x, which plays the role of a 'hydrogen pump', which facilitates the delivery of hydrogen to the magnesium surface and thus accelerates hydrogenation.[35–37,41] However, no significant enhancement of the kinetics of dehydrogenation of these reaction mixtures occurs in comparison with pure MgH_2.[34–36,40] In order to accelerate dehydrogenation, it is necessary to introduce elements that facilitate the processes of hydrogen desorption and the formation of the metallic phase nuclei, for example, *d*-metals.[34,37,42–44] These additives form a separate phase as a result of cycling. After hydrogenolysis the material is a virtually multiphase system, its features being typical of those for multi-phase alloys.

Two- and multi-phase systems are alloys of magnesium with other elements, the composition of which does not correspond to the stoichiometric composition of intermetallic compounds. These can be alloys with Ni, Cu, rare earth, and some other metals.

Hydrogenation of alloys of magnesium with rare earth metals yields a mixture of binary hydrides, as in the case of hydrogenolysis of IMC. The compositions formed differ, first of all, in specific features of the microstructure and in the size of the magnesium/lanthanide hydride interface. In the decomposition of a non-stoichiometric alloy, the interface is, as a rule, smaller than that in hydrogenolysis of IMC, which results in a decrease in the rates of the interaction of these systems with hydrogen.

The alloys Mg–Ni and Mg–Cu are two-phase systems containing magnesium and IMC Mg_2Ni or Mg_2Cu. Hydrogenation of these alloys can be carried out in two versions: under conditions where both phases are hydrogenated and under conditions where only magnesium is hydrogenated and the intermetallic compound serves only as a catalyst. However, in both cases dissociative hydrogen adsorption takes place on clusters of the *d*-element resulting from segregation occurring in the course of hydrogenation–dehydrogenation.† Studies of the surface of alloys by ferromagnetic resonance,[45] X-ray photoelectron and Auger spectroscopy[46,47] gave reason to adopt a model of the structure of the surface of the alloy and the scheme of the initial stage of hydrogenation, which accounts for the catalytic activity of transition metals.[47–49] The essence of the model is as follows:

1. Activation of the material in hydrogenation–dehydrogenation cycles leads to dispersion of the sample, that is, to the formation of a new clean surface.

2. In the interaction with traces of oxygen and water, clusters of a *d*-element are formed on this surface (the so-called oxidative segregation).

3. Dissociative chemisorption of hydrogen takes place on the clusters of the *d*-element.

4. The hydrogen atoms formed diffuse into the bulk of the material along the metal/oxide interface .

The course of the reaction, as was mentioned above, depends largely on the size of the magnesium/catalyst interface and accordingly, on the size of magnesium particles in the alloy.

The size of magnesium crystallites determines the degree of its conversion into the hydride. The process of nucleation is accelerated under the action of catalytic additives, which leads to faster formation of a continuous layer of the hydride and to a change to the diffusion control of the reaction.[24] In the case of larger magnesium particles, these processes slow down and practically completely stop the reaction long before complete conversion. The portion of magnesium that does not enter the reaction decreases and the hydrogen content increases with a decrease in the size of particles in the alloy.

Hence, the main problems in the creation of two- and multicomponent materials for accumulation of hydrogen are, first, the choice of a catalyst and determination of its optimum concentration at which the maximum hydrogen content is achieved over a given time and second, the creation of the microstructure of the sample ensuring the maximum magnesium/catalyst interface.

In addition, the problem of activation exists for all the alloys. The rate of the first hydrogenation is determined by the rate of the rupture of the oxide film, by the rates of the formation and growth of magnesium hydride nuclei. The effect of additives reduces most commonly to a decrease in the induction period and to an increase in the rate of the first hydrogenation as compared to analogous characteristics for pure magnesium,[17,24,50,51] however, the duration of the first cycle remains too high.

† Segregation processes occur due to the presence of traces of oxygen and water in the hydrogen.

2. The interaction of mechanical alloys of magnesium with hydrogen

A new approach to the creation of two- and multi-component systems interacting with hydrogen has been proposed.[52–55] It is based on the use of mechanical alloying. In the initial stage of processing of a mixture of metal powders (in $\sim$5 min) in centrifugal planetary mills, composites are formed with a considerable interface similar to those resulting from hydrogenolysis of IMC, but the hydrogenolysis stage is excluded. These composites were termed mechanical alloys (MA). A typical (rather porous) structure of a particle of a mechanical alloy with uniformly distributed particles of a metal catalyst within the magnesium matrix is shown in Fig. 1.[55] Wide angle X-ray scattering (WAXS) of these materials did not reveal the formation of either intermetallic compounds or solid solutions.

The processes of hydrogenation and dehydrogenation have been studied for the systems Mg–Ce;[56] Mg–Fe, Mg–Co, Mg–Ti, Mg–V, Mg–Nb, Mg–Cr, Mg–C, Mg–Si;[52–54,57–59] Mg–Ni;[29,52,53,60–63] Mg–TiO_2;[64–66] Mg–V_2O_5, Mg–Cr_2O_3;[66] Mg–MnO_2; Mg–Fe_2O_3, Mg–NiO;[67] Mg–MmM'_5 (MM'_5 is IMC of the type $LaNi_5$, Mm is a mischmetall, M′ is Ni with admixtures of Al, Co, and Mn);[68,69] Mg–FeTi,[70] *etc*.

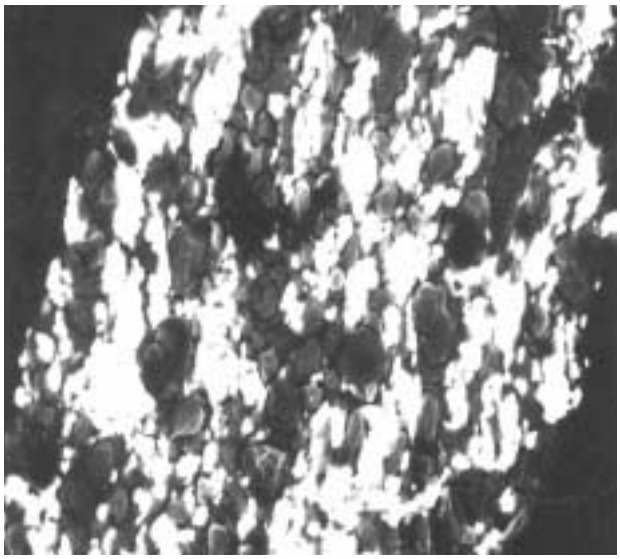


Figure 1. A particle of mechanical alloy Mg–Ni at a fracture; the image in the Ni K_α radiation.

Thus, mechanical alloying allows the considerable extension of the range of systems under study including mixtures that could not be alloyed by traditional methods, such as Mg–Fe, Mg–Ti, Mg–Nb, and Mg–Cr with positive enthalpy of mixing of the components, or mixtures of magnesium with oxides. It is also very difficult to prepare from the latter composites with homogeneous distribution of the components by traditional alloying methods.

The additives to magnesium used in mechanical alloys differ in their nature. Thus the above-mentioned additives can be divided into six groups.

1. Ni forms with magnesium the intermetallic compound Mg_2Ni, which can absorb and liberate hydrogen.

2. Ce, Nb, and Ti form hydrides CeH_3, NbH_2, and TiH_2, which can serve as 'hydrogen pumps' due to the change in stoichiometry.

3. MmM′ and FeTi are intermetallic compounds, which absorb hydrogen reversibly under milder conditions compared to magnesium.

4. Fe, Co, and Cr are metal catalysts, which do not form hydrides themselves under the conditions studied.

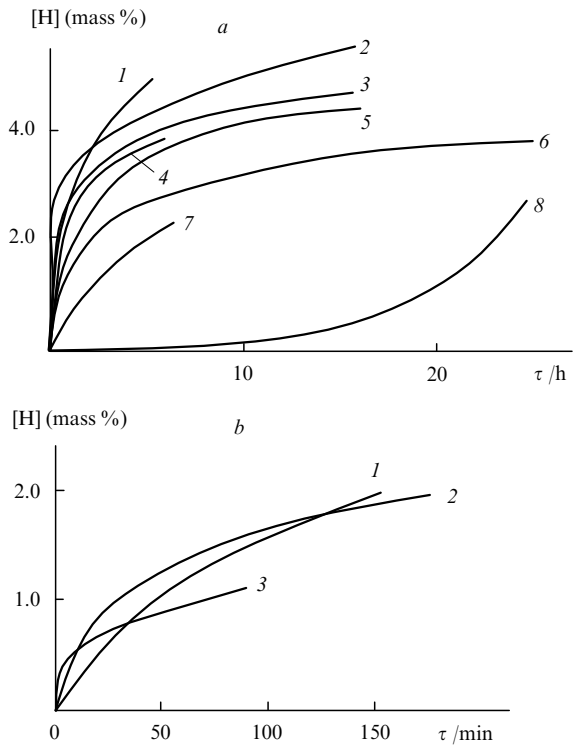


Figure 2. Kinetics of the first hydrogenation of magnesium and its mechanical alloys.
(*a*): $T = 625$ K and $P_{H_2} = 1.5$ MPa; (*1*) Mg + 5 mass % of Co; (*2*) Mg + 5 mass % of Nb; (*3*) Mg + 5 mass % of Fe; (*4*) Mg + 5 mass % of C; (*5*) Mg + 8 mass % of Ce; (*6*) Mg + 5 mass % of Ti; (*7*) Mg + 5 mass % of Si; (*8*) metallic magnesium, particle size is 20 μm;
(*b*): $T = 615$ K, $P_{H_2} = 1.5$ MPa; (*1*) Mg + 8 mass % of Fe; (*2*) Mg + 10 mass % of Fe_2O_3; (*3*) Mg + 10 mass % of NiO.

5. Si and C form with magnesium compounds with predominantly covalent bonds.

6. Metal oxides.

All the types of catalytic additives accelerate remarkably the first hydrogenation as compared to that of pure magnesium [52, 67] (Fig. 2). The character of the action of additives (except for Si and C) seems to be the same and consists in the acceleration of the stage of chemisorption of hydrogen on the surface of a catalyst. It is of note that mechanical alloys Mg – Ni are hydrogenated during the first cycle faster than the corresponding ordinary alloys Mg – Ni (Fig. 3).[61]

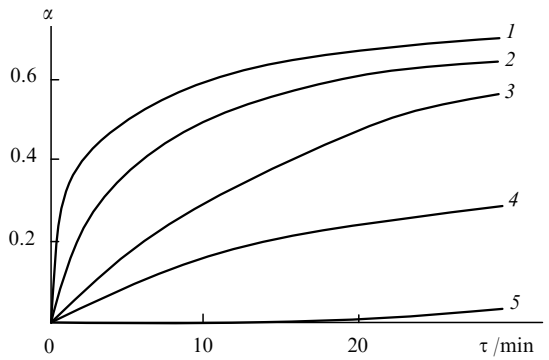


Figure 3. Kinetics of the first hydrogenation of mechanical alloys of magnesium with nickel.
[Ni] (mass %): (*1*) 60, (*2*) 53, (*3*) 35, (*4*) 1; (*1* – *4*) at $P_{H_2} = 1.8$ MPa, $T = 583 - 593$ K; (*5*) ordinary alloy of Mg with 25 mass % of Ni at $P_{H_2} = 2.1$ MPa, $T = 673$ K.

The rate of the first hydrogenation depends on the nature and concentration of the catalyst, but in almost all the systems examined, the reaction begins at the maximum rate (see Figs 2, 3). This means that the surface of the catalyst in mechanical alloys, unlike that in traditional alloys, is accessible to hydrogen.

X-ray photoelectron spectroscopic studies [29, 71] of the surface of MA have shown that it is covered with a layer of organic impurities and oxygen-containing magnesium compounds. The thickness of this layer is small, and it does not seem to affect the hydrogenation process. The profiles of concentration of the elements for magnesium MA containing 50 mass % Ni are shown in Fig. 4. The surface layer (3 – 5 nm) contained neither metallic magnesium, which appeared at a depth of 40 nm, nor nickel, which appeared at a depth of ~4 – 10 nm in the oxidised state and at a depth of 40 nm in the metallic state. The presence of oxygen throughout the entire layer provides evidence for the destruction of the surface MgO film and its dispersion in the matrix. Carbon-containing impurities also penetrate into the bulk upon mechanical alloying.

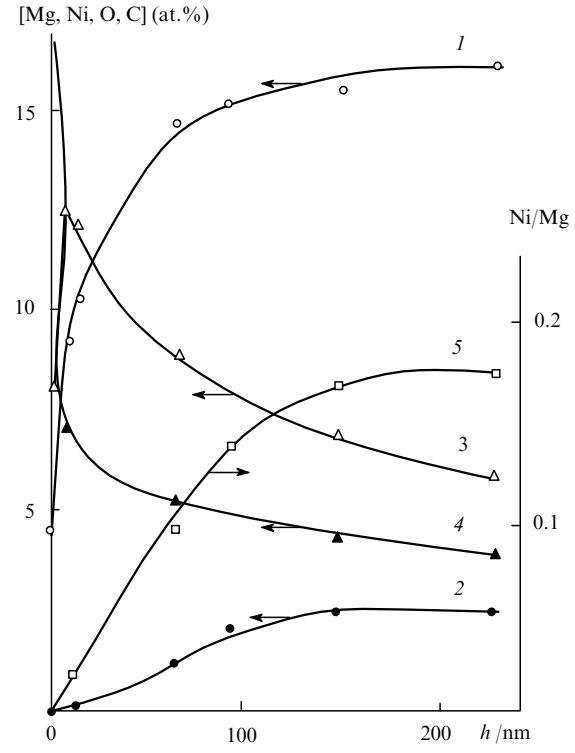


Figure 4. The dependence of the chemical composition on the etching depth (*h*) for a mechanical alloy of Mg with 50 mass % of Ni.
(*1*) Mg, (*2*) Ni, (*3*) O, (*4*) C, (*5*) Ni/Mg.

The chemical state of the elements in the near-surface layer of MA differs significantly from that in the original metals. The contour of the nickel $2p_{3/2}$ line at a depth of 40 nm corresponds to metallic nickel and to the nickel implanted into an inert matrix as isolated atoms. In addition, charge transfer from magnesium to non-bonding levels of the nickel atoms has been observed. In this case, a portion of magnesium is in the state to which the formal oxidation degree of +1 can be ascribed. The chemical state of oxygen also differs from that in the original metals and MgO, which might be due to defectiveness of the surface layer of MA.[29, 71] The nickel atoms resulting from the chemical interaction between Mg and Ni in the course of mechanical alloying bear an excessive electron density and are active catalysts of hydrogen dissociation. The nickel atoms are, probably, present not only in the surface layer, but also in the bulk of the sample forming a

supersaturated solid solution around the nickel particles upon dispersion of nickel within the matrix.

Other MA of magnesium with metals and IMC, even those having a positive enthalpy of mixing, seem to have a similar structure. This can be indirectly proved by the fact that the initial hydrogenation rate of mechanical alloys Mg–Fe and Mg–Ni depends linearly on the square of the concentration of the catalyst in MA.[59]

Hence, disordering of the surface layer, the rupture of the oxide film, and dispersion of the catalyst take place in mechanical alloys. Disordering of the surface layer makes the catalyst accessible to hydrogen, which is the main reason for the rapid first hydrogenation of MA as compared to that of alloys and mixtures of the same composition.[29, 71]

It should be noted that this surface structure is quite stable over a long period: the initial rate of hydrogenation of MA that have been stored in air for 9–12 months did not differ from that of freshly prepared samples.[29]

The high reactivity (with respect to hydrogen) of mechanical alloys of magnesium with transition metal oxides may also be accounted for by the presence of metallic particles and partially reduced metal oxides at the surface formed in the course of mechanical processing.[64–67] The efficiency of the action of metal oxides as catalysts depends on the ease of their reduction.[66]

For the majority of systems examined (except for Mg–Ce and, under special experimental conditions that will be considered below, Mg–Fe and Mg–Co), magnesium hydride (the second phase, catalyst) is the product of the first hydrogenation. The degree of conversion of magnesium into the hydride, as in two-phase systems, in these MA depends on their microstructures. A model of a microstructure reflecting qualitatively the initial stage of hydrogenation is presented in Fig. 5: MgH_2 is formed around the catalyst particles. It is difficult for hydrogen to penetrate through the layer of hydride; that is why the reaction slows down with an increase in the thickness of the layer. The thickness of the hydride layer, which depends on the distance between particles of the catalyst, decreases with an increase in the concentration of the catalyst, and the degree of conversion also increases. However, the hydrogen content (mass %) in the alloy decreases due to the large mass of catalyst. It has been found experimentally [59, 63] that the optimum catalyst content was in the range of 2 mass %–25 mass %.

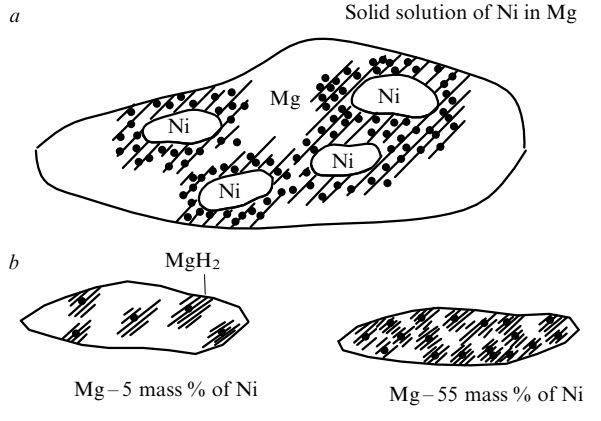


Figure 5. A model of the microstructure of mechanical alloy Mg–Ni (*a*) and the illustration of the effect of the Ni concentration on the degree of conversion (*b*).

In subsequent cycles, MA retain high rates of hydrogenation and dehydrogenation (Figs 6, 7) and rather high hydrogen capacity.[52]

In the case of the Mg–Ni mechanical alloy, the intermetallic compound Mg_2Ni is formed after 3–4 cycles of hydrogenation–dehydrogenation, mainly according to the equation [61]

$$2MgH_2 + Ni = Mg_2Ni + 2H_2.$$

Further, kinetic characteristics of the system do not differ from those of the ordinary two-phase system Mg–Ni or the intermetallic compound Mg_2Ni.[29, 63]

Kinetic characteristics of the mechanical alloy Mg–Ce in the cycling are also comparable with those of hydrogenation and dehydrogenation obtained in the hydrogenolysis of $Mg–CeH_x$ mixtures (Fig. 8).[56] This shows that the size of the interface in MA has the same order of magnitude as the interface in the mixtures obtained in the hydrogenolysis.

As for MA composed of thermodynamically immiscible components, one could expect rapid destruction of a sample in repeating hydrogenation–dehydrogenation cycles due to exfoliation of the system. However, these systems appeared to be rather stable in cycling. A mechanical alloy Mg–Fe retains its hydrogen capacity for ~70 cycles, and the rate of hydrogenation even

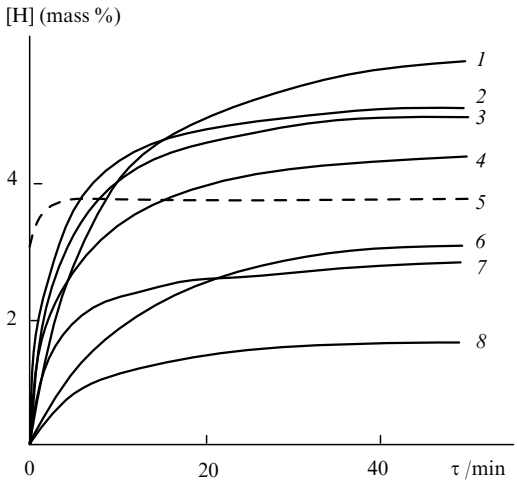


Figure 6. Kinetics of hydrogenation for the fifth cycle, P_{H_2} = 1.5 MPa, T = 625 K.
(*1*) Mg, particle size is 20 μm, mechanical alloy; (*2*) Mg + 5 mass % of Nb, (*3*) Mg + 5 mass % of Fe, Co or Ni, (*4*) Mg + 5 mass % of Ti, (*7*) Mg + 5 mass % of Si, (*8*) Mg + 50 mass % of C; (*5*) intermetallic compound Mg_2Ni; (*6*) Mg, particle size is equal to the size of particles of the mechanical alloy (P = 0.7 MPa, T = 583 K).

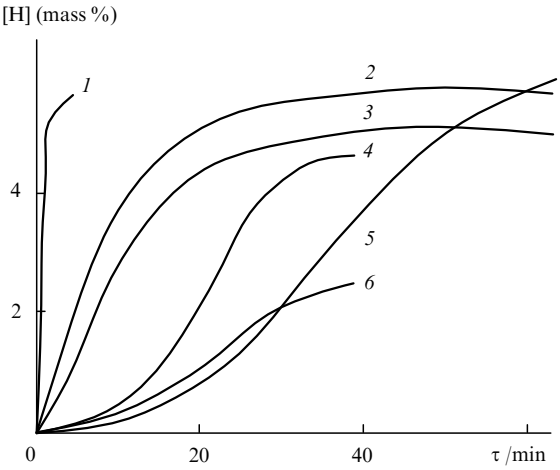


Figure 7. Kinetics of dehydrogenation, P = 0.1 MPa.
Mechanical alloy: (*1*) Mg + 5 mass % of Ni, T = 615 K; (*2*) Mg + 5 mass % of Fe, T = 625 K; (*3*) Mg + 5 mass % of Nb, T = 625 K; (*4*) Mg + 5 mass % of Ti, T = 625 K; (*6*) Mg + 5 mass % of Si, T = 621 K; (*5*) Mg, particle size is 20 μm, T = 625 K.

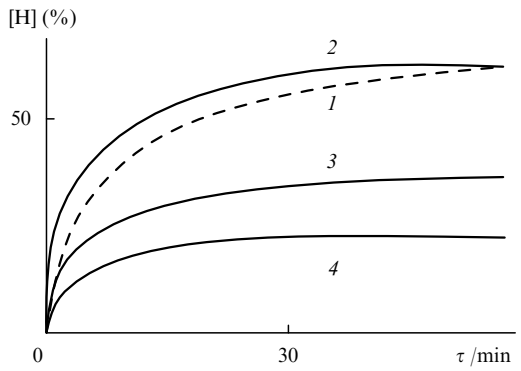


Figure 8. Kinetics of hydrogenation at $T = 603$ K and $P_{H_2} = 1.9$ MPa. (*1*) mechanical alloy Ce + 25Mg; (*2*) $CeMg_{12}$; mixture: (*3*) Mg + 10 mass % of $LaNi_5$; (*4*) Ce + 12Mg.

gradually increases;[59] a mechanical alloy $Mg-TiO_2$ retains its kinetic characteristics at least up to the 39th cycle [64] (there are no data on longer cycling).

It was shown [59, 72] that complex competing processes including sintering and dispersion of the sample occur in a Mg–Fe system in the hydrogenation–dehydrogenation. Hydrogen undergoes dissociation on iron and it further diffuses into the bulk of the sample along the interface and grain boundaries to form an Mg/Fe adsorption layer at the interface in which rather high mobility of both hydrogen and metals is observed. Some experiments on the annealing of a contact pair Mg/Fe using a microprobe analysis have shown that the principal possibility is for iron to diffuse along the surface of magnesium in a hydrogen atmosphere.[59, 72] This favours an increase in the Mg/Fe contact area and in the hydrogenation rate. When a definite hydrogen concentration in the adsorption layer at the interface Mg/Fe is achieved, a ternary hydride of the composition Mg_2FeH_6 crystallises at a noticeable rate, which was observed at $T \geqslant 615$ K. At hydrogen pressures exceeding the equilibrium pressure over MgH_2, catalytic hydrogenation of magnesium occurs in parallel, often at a higher rate; the synthesis of Mg_2FeH_6 can also occur according to the equation

$$2MgH_2 + Fe + H_2 \rightleftharpoons Mg_2FeH_6 .$$

However, since the equilibrium hydrogen pressure for Mg_2FeH_6 is lower than that for magnesium hydride [57] (Fig. 9), the synthesis of the latter was successfully accomplished directly from the elements. This reaction has been described in detail.[59, 72]

Analogous processes seem to occur in the hydrogenation of a mechanical alloy Mg–Co. This system does not belong to immiscible ones; however, for this system only one intermetallic compound $MgCo_2$ is known, which does not absorb hydrogen under ordinary hydrogenation conditions. In the hydrogenation of mechanical alloys in this system, two hydrides, *viz*., Mg_2CoH_x ($x = 4-5$) and Mg_3CoH_5, were detected [58, 59] which, like Mg_2FeH_6, can be synthesised from the elements (without the intermediate stage of formation of magnesium hydride). Decomposition of ternary magnesium–cobalt hydrides gave a previously unknown IMC with composition close to Mg_2Co and having a cubic structure. This compound interacts with hydrogen even at room temperature to form solid solutions and at elevated temperatures to form ternary hydrides (Table 2).

It should be noted that ternary magnesium–iron and magnesium–cobalt hydrides could not be detected for a long time due to the lack of hydride-forming IMC in the systems Mg–Fe and Mg–Co. Yvon *et al.*[73] considered the hydride Mg_2NiH_4 as a complex compound composed of the Mg^{2+} cation and the $[NiH_4]^{4-}$ anion. Assuming that the 18 electron rule, which determines the content of a ligand (H in this case), is valid for these complexes, they have predicted the possibility that hydrides Mg_2FeH_6 and Mg_2CoH_5 exist. Research by these authors in

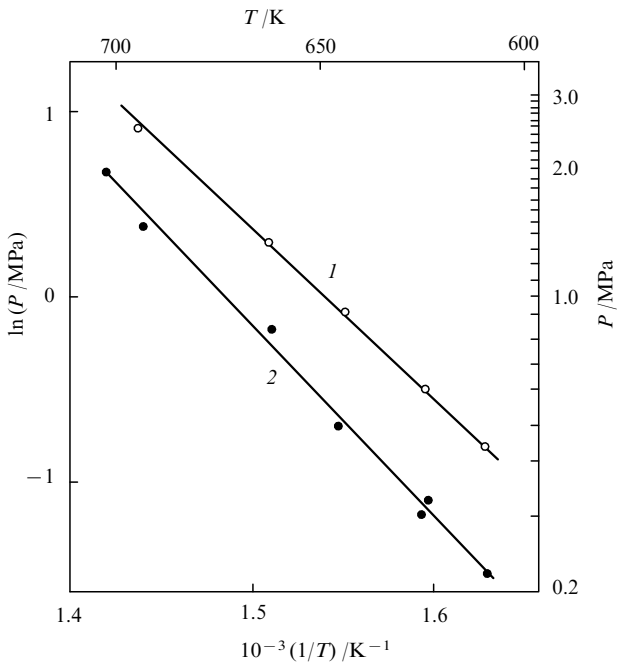


Figure 9. Temperature dependence of equilibrium pressures of hydrogen over the hydride phases MgH_2 (*1*) and Mg_2FeH_6 (*2*).

Table 2. Crystallographic data for novel ternary hydrides and intermetallic compounds.

Compound	Unit cell	Cell parameters /nm	Ref.
Mg_2FeH_6	Cubic,	$a = 0.6443$	74
	*Fm*3*m*	$a = 0.6442 \pm 0.0002$	59
Mg_2CoH_x,	Tetragonal	$a = 0.4477 \pm 0.0001$,	59
(low-temperature modification) [a]		$c = 0.6612 \pm 0.0001$, $a = 0.4480(2)$ $c = 0.6619(3)$	75
Mg_2CoH_x, (high-temperature modification)	Cubic	$a = 0.644$ at ~480 K	59
Mg_3CoH_5	Orthorhombic	$a = 0.4675 + 0.0002$, $b = 0.8073 + 0.0003$, $c = 1.0091 \pm 0.0003$, $Z = 4$	59
'Mg_2Co'	Cubic	$a = 1.143 + 0.001$	58, 59

[a] The temperature of a reversible phase transition of Mg_2CoH_x from the low-temperature modification to the high-temperature one is 470 K, ΔH for the phase transition is ~2 kJ mol^{-1}.[58, 59]

1984–1985 aimed at synthesising these hydrides was successful.[74, 75] At the same period, the hydrides were found in the hydrogenation of mechanical alloys.[76] The lack of a method for the preparation of a material with a large Mg/Fe and Mg/Co interface caused the authors [74, 75] to use a mixture of pressed metal powders. The reaction had to be conducted for weeks under drastic conditions, nevertheless, complete conversion of these mixtures into the hydrides was not achieved. Neither the second hydride Mg_3CoH_5 existing in the Mg–Co system nor the intermetallic compound Mg_2Co could be isolated and identified.

The magnesium–iron and magnesium–cobalt ternary hydrides were examined as catalysts for the hydrogenation of unsaturated hydrocarbons. These catalysts manifested catalytic activity comparable with that of catalysts based on platinum-group metals, and high selectivity in processes of partial reduction

Table 3. Catalytic characteristics of ternary hydrides and traditional catalysts.[59]

Catalyst	Degree of conversion (%)	Selectivity (%)
Compound to be hydrogenated is acetylene		
Mg_2CoH_x	44	100 (with respect to C_2H_4)
Pd/Al_2O_3	21	90
Compound to be hydrogenated is butadiene		
Mg_2FeH_6	51 – 55	99.2 – 99.7
$Pt-S/Al_2O_3$	23	100
$Pd-S/Al_2O_3$	36	72

of acetylene derivatives and compounds with several double bonds (Table 3).[59, 77]

Hydrogenation and dehydrogenation of MA containing, for example, two or more IMC can be more complicated. Depending on the composition of MA, cycling can result in the interaction between the components, their decomposition, and the formation of other phases, which can be both hydride-forming and hydride-non-forming. Thus a study of hydrogenation of a MA containing 66.6 mass % of La_2Mg_{17} and 33.3 mass % of $LaNi_5$ has shown [78] that several hydrogenation – dehydrogenation cycles result in their decomposition and the formation of Mg, Mg_2Ni, and LaH_x ($x = 2.00 - 2.99$). Then, depending on the temperature and hydrogen pressure used in hydrogenation, hydrogen is absorbed either by magnesium or by magnesium and Mg_2Ni, and LaH_x serves as a 'hydrogen pump'. After 20 cycles, the sample was a conglomerate of all the phases with a granule size of ~ 0.2 μm. Although these MA have lower hydrogen capacity as compared to that of pure La_5Mg_{17}, the rates of their hydrogenation and dehydrogenation are higher in the first cycles and depend, other conditions being the same, on the duration and intensity of mechanical processing. Thus MA obtained under the most drastic conditions (at an acceleration of 130 m s^{-2} for 25 min) absorbs 3.5 mass % of hydrogen (90% of full capacity) in less than 1 min at 523 K and liberates the same amount in 6 min, whereas under the same conditions it takes 2.5 h for pure La_5Mg_{17} to absorb 4.9 mass % of hydrogen (also 90% of its full capacity) and 3 h to desorb it.[78] This was explained [78] by the small size of MA particles (~ 10 μm), their multi-phase composition and catalytic activity of one or two components. It was thus concluded that a solution of the problem of improvement of the kinetic characteristics of hydrogenation and dehydrogenation lies in the creation of analogous composite materials.

3. Hydrogenation of Mg_2Ni obtained by mechanical alloying and mechanical milling

The intermetallic compound Mg_2Ni interacts with hydrogen at a high rate at 473 – 573 K and a hydrogen pressures of 0.5 – 1.0 MPa; however, a problem of activation exists. From 10 to 20 cycles of hydrogenation – dehydrogenation are necessary for activation [79] in the course of which dispersion of the material and the formation of a metallic surface occur. These difficulties can be avoided if Mg_2Ni is subjected to mechanical milling or is synthesised by mechanical alloying using the same procedure as for the synthesis of MA but increasing the duration of the treatment. It was shown [80, 81] that mechanical alloying of a mixture of Mg and Ni powders gives nanocrystalline Mg_2Ni with the size of crystallites of about 20 – 30 nm. This material interacts rapidly with hydrogen, and reproducible rates of hydrogenation are achieved even by the second cycle (Fig. 10). If a small amount of palladium (less than 1 mass %) is added to the reaction mixture during mechanical alloying, the thus modified Mg_2Ni absorbs hydrogen at room temperature (Fig. 11).[80–83] An analogous result was obtained without addition of palladium.[84] However, in this case

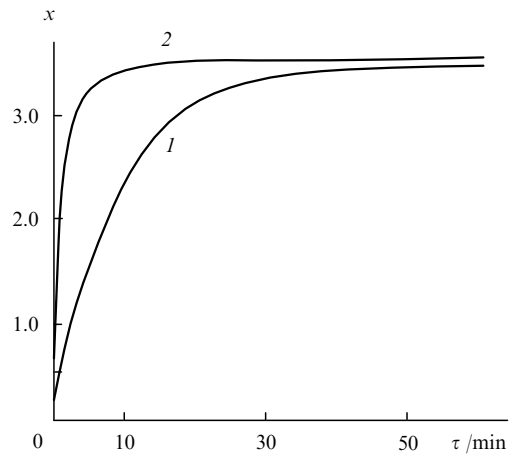


Figure 10. Kinetics of hydrogenation of nanocrystalline Mg_2Ni prepared by mechanical alloying at $T = 573$ K, $P_{H_2} = 1.16$ MPa; (*1*) the first cycle; (*2*) the second and subsequent cycles. The x values in the formula Mg_2NiH_x are shown in the y-axis.

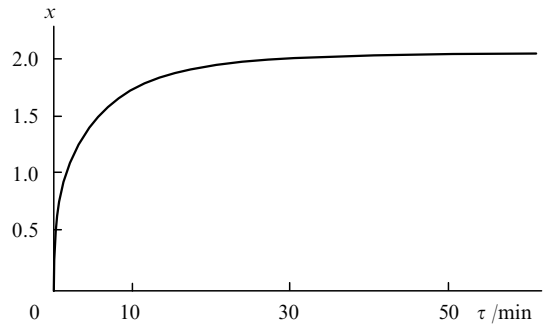


Figure 11. Kinetics of hydrogen sorption by nanocrystalline Mg_2Ni modified with palladium during mechanical alloying (room temperature, $P_{H_2} = 1.2$ MPa, without activation). The x values in the formula Mg_2NiH_x are shown in the y-axis.

hydrogenation of Mg_2Ni was performed immediately after its mechanical milling without exposure to air (Fig. 12). Mechanical milling implies practically the same procedure as mechanical alloying except that the initial material is not a mixture of metal powders but an intermetallic compound obtained by traditional alloying. As is shown by Fig. 12, the reaction rate and the amount of absorbed hydrogen increase as the duration of mechanical

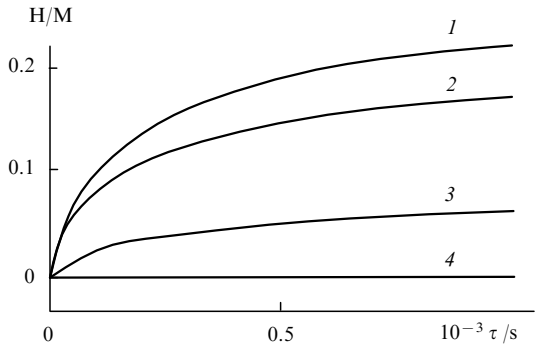


Figure 12. Kinetics of hydrogen sorption for Mg_2Ni (285 K, $P_{H_2} = 2$ MPa) after its mechanical milling in an argon atmosphere for 30 (*1*), 5 (*2*), 1 min (*3*), and without milling (*4*). The ratio of hydrogen atoms to metal atoms in Mg_2NiH_x is shown in the y-axis.

milling is increased, which can be due to gradual dispersion of the sample and the formation of pure metal surface during this milling. However, at room temperature hydrogenation does not go to completion; the hydrogen content corresponds to the formula Mg_2NiH_x ($x \approx 2$). This might be connected with the fact that as the temperature decreases, following the formation of a hydride layer on the surface of particles, the diffusion of hydrogen through this layer, the rate of which can be small at room temperature, becomes the limiting stage. The 'diffusion retardation' occurs similarly to that observed in the hydrogenation of magnesium. Moreover, at $T < 515$ K Mg_2NiH_4 exists as a low-temperature modification, the structure of which is the monoclinic distortion of a cubic high-temperature modification.[85] The latter normally results from hydrogenation at temperatures above the temperature of phase transition. The explanation of this fact calls for additional studies.

III. Hydrogenation of FeTi and $LaNi_5$ undergoing mechanical milling

As compared to magnesium systems, $LaNi_5$ and FeTi are low-temperature accumulators of hydrogen. They absorb hydrogen at room temperature. However, commercial polycrystalline samples covered with oxygen-containing compounds require, as a rule, preliminary activation. For instance, the procedure for activation of FeTi consists of heating the sample in a vacuum to 673 – 723 K and subsequent annealing in hydrogen at a pressure of ~ 0.7 MPa followed by cooling to room temperature and increase in the hydrogen pressure to 3.5 – 6.5 MPa.[86] This procedure is repeated several times so that hydrogenation is reproducible.

Activation of $LaNi_5$ proceeds much more easily than in the case of FeTi, but this is still required and consists of a prolonged exposure of the sample at high hydrogen pressure (about 5.0 MPa) at room[87] or elevated (~ 623 K) temperatures in vacuum.[88]

Mechanical milling of these intermetallic compounds in ball mills allows omission or simplification of the activation procedure. The kinetic curves of hydrogen sorption for mechanically milled FeTi are presented in Fig. 13.[84] After mechanical milling, contact of the sample with air was excluded. It is seen that in this case hydrogenation starts at the maximum rate, and the degree of conversion depends on the duration of the treatment. If the sample was exposed to air after mechanical milling and prior to hydrogenation, activation was necessary, but it occurred much more easily than for ordinary alloys: it is sufficient to heat the sample at 673 K in vacuum for 30 min.[89]

If FeTi is modified with a small amount of palladium, which is added during mechanical milling, neither annealing of the sample nor preliminary exposure of the sample to hydrogen are required.

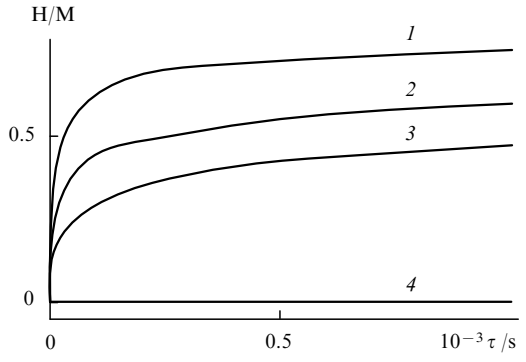


Figure 13. Kinetics of hydrogen sorption for FeTi (283 K, $P_{H_2} = 2$ MPa) after its mechanical processing in an argon atmosphere for 24 (*1*), 3 h (*2*), 30 min (*3*), and without processing (*4*).
The ratio of hydrogen atoms to metal atoms in $FeTiH_x$ is shown in the *y*-axis.

This sample immediately absorbs hydrogen at room temperature.[81, 83, 90]

Isotherms of 'pressure – composition' at room temperature without preliminary activation of samples were obtained[91] for amorphous and nanocrystalline FeTi formed upon mechanical alloying. It was shown that the shape of the isotherms is very 'sensitive' to the microstructure of the samples and changes significantly after their annealing. The relaxation of structural defects and mechanical strains upon annealing leads to a decrease in the solubility of hydrogen in both cases and to a change in the length and slope of the plateau in the isotherm of nanocrystalline FeTi. The shape of the adsorption isotherm of the initial nanocrystalline powder indicates the significant contribution of an amorphous component. This fact together with the electron microscopy and WAXS data allowed the authors[91] to draw the following conclusion: the microstructure of particles of nanocrystalline FeTi formed upon mechanical alloying is nanocrystallites with a highly disordered intercrystallite region; the portion of this structure in the bulk material is 20% – 30%. It should be emphasised that these data give direct evidence that the degree of disorder and mechanical strains affect the character of the hydrogen absorption in the sample. During preliminary activation, which is required for hydrogenation of intermetallic compounds not doped with palladium the relaxation processes have, as a rule, already occurred, which prevents the unambiguous interpretation of the results.

Analogous kinetic data have been obtained for $LaNi_5$.[81, 83] The kinetic curves for hydrogenation of mechanically milled samples of $LaNi_5$ — one of which was hydrogenated immediately after mechanical milling, another was kept in air for a long period, and the third was prepared with the addition of palladium — are presented in Fig. 14.

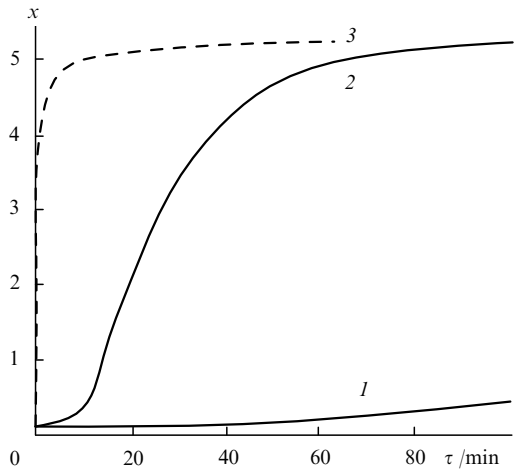


Figure 14. Kinetics of hydrogenation of $LaNi_5$ milled mechanically at $T = 313$ K and $P_{H_2} = 1.5$ MPa;
(*1*) the sample kept in air for several months; (*2*) the sample immediately after mechanical activation; (*3*) the sample modified with palladium.
The *x* values in the formula $LaNi_3H_x$ are shown in the *y*-axis.

Hence, mechanical milling of intermetallic compounds Mg_2Ni, FeTi, and $LaNi_5$ yields a metallic surface, on which dissociative adsorption of hydrogen occurs. However, upon contact of these samples with air the surface is rapidly oxidised and the kinetic characteristics of hydrogenation are impaired. Modification with palladium (one of the best catalysts for the dissociative adsorption of hydrogen) during mechanical milling of these intermetallic compounds allows hydrogenation to be carried out at room temperature without preliminary activation.

IV. The direct formation of hydrides during mechanical milling

The formation of metal hydrides is possible during mechanical milling.[92–96] To this end, mechanical milling is run in a hydrogen atmosphere at elevated pressure. In this way, binary hydrides of the compositions $TiH_{1.9}$, $ZrH_{1.66}$ and MgH_2 have been prepared and characterised by WAXS analysis, differential thermal analysis, and electron microscopy.[92–95] It is remarkable that magnesium usually absorbs hydrogen in noticeable amounts only at temperatures above 573 K, whereas hydrogenation concurrent with mechanical milling yields magnesium hydride without heating. To date it remains unclear which factor is determining in the formation of hydrides during mechanical milling in a hydrogen atmosphere. It might be crushing, plastic deformation, the formation of a fresh metal surface, local increase in temperature upon collision of grinding bodies, *etc*. Most likely, all these processes contribute to the formation of hydrides.

Mechanochemical processes are known to be non-equilibrium ones and often occur *via* metastable states. This is the case in the hydrogenation of ZrNi during its mechanical milling in a hydrogen atmosphere.[96] This process includes the stages differing from those in the traditional hydrogenation, namely, the consecutive formation of the hydride phases ZrNiH and/or $ZrNiH_3$ followed by their amorphisation, and then the decomposition of the amorphous phase to ZrH_2 and metastable hydride a-$Zr_{1-\delta}NiH_x$. As a result, composite particles composed of amorphous (a-$Zr_{1-\delta}NiH_x$) and crystalline (a-$ZrNiH_3$ and/or ZrH_2) hydride phases are formed according to the hydrogen pressure used, which varies from 0.1 to 1.0 MPa. Particles resulting from mechanical processing in a hydrogen atmosphere appeared to be much smaller in size (0.5–1.0 μm at a hydrogen pressure of 1.0 MPa) than those obtained under similar conditions in an argon atmosphere (50 μm) due to the higher fragility of the hydride phases as compared to that of ZrNi.

Taking this into account, it was concluded [96] that mechanical processing in a hydrogen atmosphere can be a promising method for the creation of hydrogen-accumulating materials with a very large interface between the amorphous and crystalline phases and for the creation of hard magnets with anisotropic nanosized grains, which can be obtained by consecutive hydrogenation, amorphisation, and dehydrogenation with simultaneous crystallisation.

When mechanical milling of Mg_2Ni was carried out in a hydrogen atmosphere at a pressure of 1.0 MPa in a 'Fritsch P7' ball planetary mill at a rotation rate of 400 rev min^{-1}, the sorption of hydrogen was also detected.[97] According to the WAXS data, the samples obtained corresponded to the α-phase, a solid solution of hydrogen in the intermetallic compound $Mg_2NiH_{0.3}$. The latter is usually formed in the initial stages of hydrogenation and at higher hydrogen concentrations, the formation of Mg_2NiH_4 begins.[98] However, upon hydrogenation during mechanical milling, the amount of hydrogen absorbed exceeded significantly that corresponding to the formula $Mg_2NiH_{0.3}$. For instance, after processing for 80 h this amount achieved 1.6 mass % ($Mg_2NiH_{1.8}$) without noticeable changes in X-ray patterns. In this case, a correlation between the value of specific surface of the sample and the hydrogen content in the sample was observed (Fig. 15). The authors [97] associate this fact not only with the disintegration of the sample, but also with the formation of a nanocrystalline composite material during mechanical milling composed of crystalline particles with this phase disordered at the grain interface where hydrogen can occupy more sites that in the crystalline phase. The thickness of this disordered phase might be only several nanometers and is not observed in X-ray patterns.

In our opinion, the data given in Ref. 97 do not rule out the principal possibility for the formation of the hydride Mg_2NiH_4 during mechanical milling since the investigations were performed in a low-energy 'Fritsch P7' apparatus. Under more drastic conditions (more powerful mills, higher hydrogen pressure), hydrogenation can occur to reach the stage of formation of the ternary hydride, which, probably, would be a metastable phase. In any case, the formation of a solid supersaturated solution of hydrogen in Mg_2Ni at the grain interface [97] indicates that the processes of traditional hydrogenation and hydrogenation during mechanical milling differ in the initial stages.

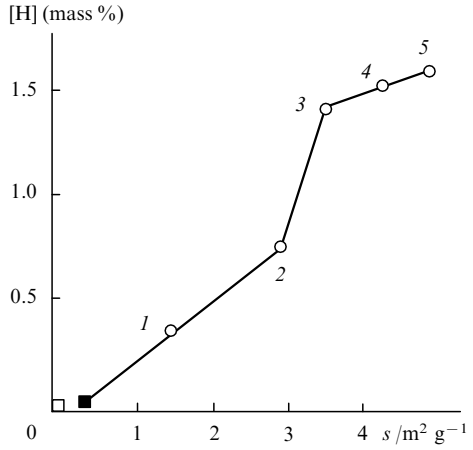


Figure 15. The correlation between the specific surface of the samples (s) prepared by hydrogenation of Mg_2Ni during mechanical milling and the hydrogen content in the samples.
τ /min: (*1*) 5, (*2*) 15, (*3*) 60, (*4*) 300, (*5*) 7800.

V. Conclusion

The above review of published data on the interaction between hydrogen and mechanical alloys and intermetallic compounds undergoing mechanical milling allows the following conclusions to be drawn.

Mechanical alloying is a promising method for the preparation of materials with high reactivity with respect to hydrogen.

As compared to traditional methods for the preparation of alloys and intermetallic compounds, mechanical alloying is substantially less time- and energy-consuming. There is no need for high temperatures. Depending on the apparatus design, the process of mechanical alloying takes from several minutes to several hours to yield homogeneous materials or composites with a sufficiently uniform phase distribution, while in the case of traditional alloying, as a rule, special prolonged homogenising annealing is necessary. This is especially important for obtaining alloys of metals differing considerably in their specific densities.

Mechanical alloys formed in the early stages of mechanical alloying are metastable systems with a large interface where the 'atomic' contact of metals occurs and their chemical interaction is possible. This interaction consists of both electron transfer from one element to another thus increasing the catalytic activity of the metal-catalyst and the reduction of oxides used as the second phase in magnesium systems thus creating centres of hydrogen adsorption.

A highly disordered specific structure of the MA surface with a catalyst dispersed in the form of atoms in the near-surface layer is responsible for the high hydrogenation rate in the first cycle. This structure is stable to oxygen and the operation with the sample in air does not require any special conditions.

The possibility to vary the microstructure during mechanical alloying allows the reaction rate and hydrogen capacity of MA to be varied.

The method of mechanical alloying provides a possibility to create composites from non-interacting components, which favours the synthesis of novel hydrides and IMC in the reaction of these MA with hydrogen.

Mechanochemical synthesis or mechanical processing of intermetallic compounds results in a material with nanosized particles and a pure metal surface, which excludes the necessity for its activation before hydrogenation. Despite the fact that this surface is prone to rapid oxidation, the activation of these materials after their contact with air still proceeds much more easily than that of ordinary IMC. If catalytic centres of hydrogen adsorption are created at the surface of IMC, for example, by the introduction of a small amount of palladium during mechanical alloying, high hydrogenation rates can be achieved at room temperature without preliminary activation, as in the case of Mg_2Ni, FeTi, and $LaNi_5$.

Some hydrides can be formed directly during mechanical processing in a hydrogen atmosphere. In this case, due to the non-equilibrium character of mechanochemical processes, metastable hydride phases and nanocomposites can be formed, which opens up new prospects for the synthesis of novel materials.

Of course, mechanical alloying does not solve all the problems associated with the hydrogenation of metals and alloys; all the potentialities of mechanical alloying have not been exhausted. The major part of the investigations dealt with magnesium systems for which mechanical alloying is the efficient method of preparation of materials with high reactivity towards hydrogen, and which has practically no alternative in the case of immiscible components. Examination of other systems has only just started, though for these systems the possibility of solving the problem of activation by means of mechanical processing has already been shown. Studies of the synthesis of nanocomposites that could possess high reactivity and high hydrogen capacity by mechanical processing seem to be promising. Unfortunately, it should be noticed that by now the problems concerning cycling of MA and IMC milled mechanically have not been sufficiently covered in the literature; little attention has been paid to processes of dehydrogenation, *etc*. We hope that these problems will find their researchers in the future.

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